8.1 The radial wave function is

$$R_{10}(r) = c_0 e^{-Zr/a_0}$$

The normalization condition on the radial wave function is

$$1 = \int_0^\infty r^2 \left|R_{n\ell}\left(r\right)\right|^2 dr$$

giving

$$1 = \int_0^\infty r^2 \left|c_0 e^{-Zr/a_0}\right|^2 dr = \left|c_0\right|^2 \int_0^\infty r^2 e^{-2Zr/a_0} dr = \left|c_0\right|^2 \left(\frac{a_0}{2Z}\right)^3 2$$

The normalized wave function is thus

$$R_{10}(r) = 2\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$$

as in Table 8.1.

8.2 The recurrence relation in Eq. (8.25), with the value $\gamma = 1/n$ from Eq. (8.33), is

$$c_{j+1} = \frac{2\left(1+j+\ell\right)/n - 2}{(j+1)(j+2\ell+2)} c_j$$

The polynomial terminates at the value $j_{max} = n - \ell - 1$. For the principal quantum number $n = 3$, the allowed angular momentum quantum numbers are $\ell = 0,1,2$. For the 3*s* state ($\ell = 0$), the polynomial terminates at $j_{max} = 2$. The polynomial is therefore $H(Zr/a_0) = c_0 + c_1\left(Zr/a_0\right) + c_2\left(Zr/a_0\right)^2$. The coefficients are related by the recurrence relation, giving

$$c_1 = -\frac{2}{3}c_0 \quad , \quad c_2 = -\frac{1}{9}c_1 = \frac{2}{27}c_0$$

The resulting radial wave function (using $R_{n\ell}\left(r\right) = \left(Zr/a_0\right)^\ell \ e^{-Zr/na_0} \ H\left(Zr/a_0\right)$) is

$$R_{30}(r) = c_0\left(1 - \frac{2}{3}\left(\frac{Zr}{a_0}\right) + \frac{2}{27}\left(\frac{Zr}{a_0}\right)^2\right) e^{-Zr/3a_0}$$

For the 3*p* state ($\ell = 1$), the polynomial terminates at $j_{max} = 1$. The polynomial is therefore $H(Zr/a_0) = c_0 + c_1\left(Zr/a_0\right)$. The coefficient relation is

$$c_1 = -\frac{1}{6}c_0$$

The resulting radial wave function is

$$R_{31}(r) = c_0\left(\frac{Zr}{a_0}\right)\left(1-\frac{1}{6}\left(\frac{Zr}{a_0}\right)\right)e^{-Zr/3a_0}$$

For the 3*d* state ($\ell = 2$), the polynomial terminates at $j_{max} = 0$. The polynomial is therefore $H(Zr/a_0) = c_0$. The resulting radial wave function is

$$R_{32}(r) = c_0\left(\frac{Zr}{a_0}\right)^2 e^{-Zr/3a_0}$$

Normalizing this gives

$$1 = \int_0^\infty r^2\left|c_0\left(\frac{Zr}{a_0}\right)^2 e^{-Zr/3a_0}\right|^2 dr = \left|c_0\right|^2\left(\frac{Z}{a_0}\right)^4\int_0^\infty r^6 e^{-2Zr/3a_0}\,dr = \left|c_0\right|^2\left(\frac{Z}{a_0}\right)^4\left(\frac{3a_0}{2Z}\right)^7 6!$$

The normalized wave function is thus

$$R_{32}(r) = \frac{2\sqrt{2}}{27\sqrt{5}}\left(\frac{Z}{3a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)^2 e^{-Zr/3a_0}$$

as in Table 8.1.

8.3 Using Eq. (8.67), with $n = 4$ and $\ell = 2$ we get

$$R_{42}(r) = -\left\{\left(\frac{Z}{2a_0}\right)^3\frac{1}{8[6!]^3}\right\}^{1/2} e^{-Zr/4a_0}\left(\frac{Zr}{2a_0}\right)^2 L_6^5(Zr/2a_0)$$

The definitions of the Laguerre polynomials are

$$L_q^p(x) = \frac{d^p}{dx^p}L_q(x)\,, \quad L_q(x) = e^x\frac{d^q}{dx^q}\left(x^q e^{-x}\right)$$

So we get

$$L_6(x) = e^x\frac{d^6}{dx^6}\left(x^6 e^{-x}\right) = x^6 - 36x^5 + 450x^4 - 2400x^3 + 5400x^2 - 4320x + 7200$$

$$L_6^5(x) = \frac{d^5}{dx^5}L_6(x) = 720x - 4320$$

The radial function is thus

$$R_{42}(r) = -\left\{\left(\frac{Z}{2a_0}\right)^3 \frac{1}{8[6!]^3}\right\}^{1/2} e^{-Zr/4a_0}\left(\frac{Zr}{2a_0}\right)^2\left(720\frac{Zr}{2a_0} - 4320\right)$$
$$= \frac{1}{64\sqrt{5}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/4a_0}\left(\frac{Zr}{a_0}\right)^2\left(1 - \frac{Zr}{12a_0}\right)$$

8.4 The wave functions are

$$\psi_{100}(r,\theta,\phi) = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$$
$$\psi_{210}(r,\theta,\phi) = \frac{1}{2\sqrt{\pi}}\left(\frac{Z}{2a_0}\right)^{3/2} \frac{Zr}{a_0} e^{-Zr/2a_0}\cos\theta$$

The inner product of the two states is

$$\langle 100|210\rangle = \int \psi^*_{100}(r,\theta,\phi)\psi_{210}(r,\theta,\phi)\,dV$$
$$= \int_0^\infty\int_0^{2\pi}\int_0^\pi \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0} r^2 \frac{1}{2\sqrt{\pi}}\left(\frac{Z}{2a_0}\right)^{3/2}\frac{Zr}{a_0} e^{-Zr/2a_0}\cos\theta\sin\theta\, d\theta\, d\phi\, dr$$
$$= \frac{1}{2\pi}\left(\frac{Z}{a_0}\right)^4\left\{\left(\int_0^\infty r^3 e^{-3Zr/2a_0}\,dr\right)\left(\int_0^\pi \cos\theta\sin\theta\, d\theta\right)\left(\int_0^{2\pi} d\phi\right)\right\}$$

The polar angle integral is the one that ensures orthogonality:

$$\int_0^\pi \cos\theta\sin\theta\, d\theta = \frac{1}{2}\left[\sin^2\theta\right]_0^\pi = \frac{1}{2}\left[0-0\right] = 0$$

8.5 The wave function is

$$\psi_{321}(r,\theta,\phi) = -\frac{\sqrt{3}}{27\sqrt{\pi}}\left(\frac{Z}{3a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)^2 e^{-Zr/3a_0}\sin\theta\cos\theta e^{+i\phi}$$

The L_z operator acting on the wave function gives

$$
\begin{aligned}
L_z\psi_{321}(r,\theta,\phi) &= -i\hbar\frac{\partial}{\partial\phi}\left(-\frac{\sqrt{3}}{27\sqrt{\pi}}\left(\frac{Z}{3a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)^2 e^{-Zr/3a_0}\sin\theta\cos\theta e^{+i\phi}\right)\\
&= -i\hbar(i)\left(-\frac{\sqrt{3}}{27\sqrt{\pi}}\left(\frac{Z}{3a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)^2 e^{-Zr/3a_0}\sin\theta\cos\theta e^{+i\phi}\right)\\
&= \hbar\psi_{321}(r,\theta,\phi)
\end{aligned}
$$

Hence the eigenvalue is $\hbar$, as expected for $m=1$. The $\mathbf{L}^2$ operator acting on the wave function gives

$$
\begin{aligned}
\mathbf{L}^2\psi_{321} &= -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\left(-\frac{\sqrt{3}}{27\sqrt{\pi}}\left(\frac{Z}{3a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)^2 e^{-Zr/3a_0}\sin\theta\cos\theta e^{+i\phi}\right)\\
&= -\hbar^2\left(-\frac{\sqrt{3}}{27\sqrt{\pi}}\left(\frac{Z}{3a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)^2 e^{-Zr/3a_0}e^{+i\phi}\right)\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\left(1-2\sin^2\theta\right)\right)+\frac{\sin\theta\cos\theta}{\sin^2\theta}i^2\right]\\
&= -\hbar^2\left(-\frac{\sqrt{3}}{27\sqrt{\pi}}\left(\frac{Z}{3a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)^2 e^{-Zr/3a_0}e^{+i\phi}\right)\left[\frac{1}{\sin\theta}\left(\cos\theta-6\sin^2\theta\cos\theta\right)-\frac{\cos\theta}{\sin\theta}\right]\\
&= -\hbar^2\left(-\frac{\sqrt{3}}{27\sqrt{\pi}}\left(\frac{Z}{3a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)^2 e^{-Zr/3a_0}e^{+i\phi}\right)\left[-6\sin\theta\cos\theta\right]\\
&= 6\hbar^2\psi_{321} = 2(2+1)\hbar^2\psi_{321}
\end{aligned}
$$

Hence the eigenvalue is $6\hbar^2$, as expected for $\ell=2$. The Hamiltonian is

$$
\begin{aligned}
H &\doteq -\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]+V(r)\\
&\doteq -\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)-\frac{\mathbf{L}^2}{r^2\hbar^2}\right]-\frac{Ze^2}{4\pi\varepsilon_0 r}
\end{aligned}
$$

Acting on the wave function gives (use the electron mass as we did to define the Bohr radius)

$$H\psi_{321} = -\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{\mathbf{L}^2}{r^2\hbar^2} + \frac{2mZe^2}{4\pi\varepsilon_0\hbar^2 r}\right]\left(-\frac{\sqrt{3}}{27\sqrt{\pi}}\left(\frac{Z}{3a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)^2 e^{-Zr/3a_0}\sin\theta\cos\theta e^{+i\phi}\right)$$

$$= \frac{\hbar^2}{2m}\left(\frac{9\sqrt{3}}{27\sqrt{\pi}}\left(\frac{Z}{3a_0}\right)^{7/2}\right)\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(2r^3 - \frac{Zr^4}{3a_0}\right) - \left(\frac{6\hbar^2}{r^2\hbar^2} - \frac{2mZe^2}{4\pi\varepsilon_0\hbar^2 r}\right)r^2\right]e^{-Zr/3a_0}\sin\theta\cos\theta e^{+i\phi}$$

$$= \frac{\hbar^2}{2m}\left(\frac{9\sqrt{3}}{27\sqrt{\pi}}\left(\frac{Z}{3a_0}\right)^{7/2}\right)\left[\left(6 - \frac{2Zr}{a_0} + \frac{Z^2r^2}{9a_0^2}\right) - \left(\frac{6}{r^2} - \frac{2mZe^2}{4\pi\varepsilon_0\hbar^2 r}\right)r^2\right]e^{-Zr/3a_0}\sin\theta\cos\theta e^{+i\phi}$$

$$= \frac{\hbar^2}{2m}\left(\frac{9\sqrt{3}}{27\sqrt{\pi}}\left(\frac{Z}{3a_0}\right)^{7/2}\right)\left[\frac{Z^2r^2}{9a_0^2} - \left(\frac{2Z}{a_0} - \frac{2Z}{a_0}\right)r\right]e^{-Zr/3a_0}\sin\theta\cos\theta e^{+i\phi}$$

$$= -\frac{1}{9}\frac{\hbar^2Z^2}{2ma_0^2}\psi_{321} = -\frac{1}{9}\frac{\hbar^2Z^2}{2ma_0}\frac{me^2}{4\pi\varepsilon_0\hbar^2}\psi_{321} = -\frac{1}{9}\frac{Z^2e^2}{8\pi\varepsilon_0 a_0}\psi_{321}$$

$$= -\frac{1}{9}Z^2 Ryd\ \psi_{321}$$

So the energy eigenvalue is $-Z^2Ryd/9$ as we expect for $n = 3$.

8.6 The probability is the integral over a sphere of radius a_0:

$$\mathcal{P}_{r\le a_0} = \int_{sphere\ r\le a_0} \mathcal{P}(r,\theta,\phi)\,dV = \int_0^{a_0}\int_0^{2\pi}\int_0^{\pi}\left|R_{n\ell}(r)Y_\ell^m(\theta,\phi)\right|^2 r^2\sin\theta\,d\theta\,d\phi\,dr$$

The angular integral is unity, leaving just the radial integral. For the 2*s* state we get

$$\mathcal{P}_{r\le a_0} = \int_0^{a_0} r^2\left|R_{n\ell}(r)\right|^2 dr = \int_0^{a_0} r^2\left|2\left(\frac{1}{2a_0}\right)^{3/2}\left[1 - \frac{r}{2a_0}\right]e^{-r/2a_0}\right|^2 dr$$

$$= 4\left(\frac{1}{2a_0}\right)^3\int_0^{a_0} r^2\left[1 - \frac{r}{a_0} + \frac{r^2}{4a_0^2}\right]e^{-r/a_0}\,dr = \frac{1}{2}\int_0^1 x^2\left[1 - x + \frac{x^2}{4}\right]e^{-x}\,dx$$

$$= 1 - \frac{21}{8e} \cong 0.0343$$

For the 2*p* state we get

$$\mathcal{P}_{r\le a_0} = \int_0^{a_0} r^2 \left| \frac{1}{\sqrt{3}} \left(\frac{1}{2a_0} \right)^{3/2} \frac{r}{a_0} e^{-r/2a_0} \right|^2 dr$$

$$= \frac{1}{3} \left(\frac{1}{2a_0} \right)^3 \int_0^{a_0} r^2 \left[\frac{r^2}{a_0^2} \right] e^{-r/a_0} \, dr = \frac{1}{24} \int_0^1 x^4 e^{-x} \, dx = 1 - \frac{65}{24e} \cong 0.00366$$

The $2p$ state is pushed farther from the origin by the centrifugal barrier (see Fig. 8.4). Only s states have a nonzero probability of being found at the origin.

8.7 The classically forbidden region is defined by the classical turning points beyond which the kinetic energy is negative. For the three-dimensional hydrogen atom, we use the effective potential energy, and set that equal to the total energy. Hence the radial turning points are defined by

$$V_{eff} = E_n$$

$$\frac{-e^2}{4\pi\varepsilon_0 r} + \frac{\hbar^2 \ell(\ell+1)}{2mr^2} = -\frac{1}{2n^2} \left(\frac{e^2}{4\pi\varepsilon_0 a_0} \right)$$

which simplifies to

$$r^2 - 2n^2 a_0 r + n^2 \ell(\ell+1) a_0^2 = 0$$

with solutions

$$r = na_0 \left(n \pm \sqrt{n^2 - \ell(\ell+1)} \right)$$

For the $n = 2$ states, the solutions are

$$2s: \quad r_1 = 0, \;\; r_2 = 8a_0$$

$$2p: \quad r_1 = 2a_0 \left(2 - \sqrt{2} \right), \;\; r_2 = 2a_0 \left(2 + \sqrt{2} \right)$$

The probability that the electron is measured to be in the forbidden region is

$$\mathcal{P}_{r<r_1} + \mathcal{P}_{r>r_2} = 1 - \mathcal{P}_{r_1<r<r_2} = 1 - \int_{r_1}^{r_2} r^2 \left| R_{n\ell}(r) \right|^2 dr$$

For the $2s$ state we find

$$
\begin{aligned}
\mathcal{P}_{forb,2s} &= 1-\int_0^{8a_0} r^2 \left|R_{2s}\left(r\right)\right|^2 dr \\
&= 1-\int_0^{8a_0} r^2 \tfrac{1}{2a_0^3}\left(1-\tfrac{r}{2a_0}\right)^2 e^{-r/a_0}\, dr \\
&= 1-\tfrac{1}{2}\int_0^8\left(x^2-x^3+\tfrac{x^4}{4}\right)e^{-x}\, dx \\
&= 1-\tfrac{1}{2}\left[\left(-2-2x-x^2-\tfrac{x^4}{4}\right)e^{-x}\right]_0^8 \\
&= 553e^{-8} = 0.19
\end{aligned}
$$

For the $2p$ state we find

$$
\begin{aligned}
\mathcal{P}_{forb,2p} &= 1-\int_{\left(2-\sqrt{2}\right)a_0}^{\left(2+\sqrt{2}\right)a_0} r^2 \left|R_{2p}\left(r\right)\right|^2 dr \\
&= 1-\int_{\left(2-\sqrt{2}\right)a_0}^{\left(2+\sqrt{2}\right)a_0} r^2 \tfrac{1}{24a_0^3}\tfrac{r^2}{a_0^2} e^{-r/a_0}\, dr \\
&= 1-\tfrac{1}{24}\int_{\left(2-\sqrt{2}\right)}^{\left(2+\sqrt{2}\right)} x^4 e^{-x}\, dx \\
&= 1-\tfrac{1}{24}\left[\left(-24-24x-12x^2-4x^3-x^4\right)e^{-x}\right]_{\left(2-\sqrt{2}\right)}^{\left(2+\sqrt{2}\right)} \\
&= 1-\frac{e^{-4}}{3}\left(534\sinh\left(2\sqrt{2}\right)-364\sqrt{2}\cosh\left(2\sqrt{2}\right)\right) = 0.20
\end{aligned}
$$

The probabilities are comparable for the two states.

8.8 The expectation value of r^2 is

$$
\begin{aligned}
\left\langle r^2\right\rangle &= \langle 100|r^2|100\rangle = \int_0^\infty r^2\left|R_{10}(r)\right|^2 r^2\, dr = \int_0^\infty r^4 \frac{4}{a_0^3} e^{-2r/a_0}\, dr \\
&= \frac{4}{a_0^3}4!\left(\frac{a_0}{2}\right)^5 = 3a_0^2
\end{aligned}
$$

This agrees with Eq. (8.89). The expectation value of $1/r$ is

$$
\begin{aligned}
\left\langle \frac{1}{r}\right\rangle &= \langle 100|\frac{1}{r}|100\rangle = \int_0^\infty \frac{1}{r}\left|R_{10}(r)\right|^2 r^2\, dr = \int_0^\infty r \frac{4}{a_0^3} e^{-2r/a_0}\, dr \\
&= \frac{4}{a_0^3}1!\left(\frac{a_0}{2}\right)^2 = \frac{1}{a_0}
\end{aligned}
$$

Again, this agrees with Eq. (8.89). Because $\langle r\rangle = 3a_0/2$, we see that $\langle 1/r\rangle \neq 1/\langle r\rangle$. This is expected because the radial probability distribution is not symmetric about its center. The expectation value of the kinetic energy is

$$\langle T\rangle=\langle H-V\rangle=\langle H\rangle-\langle V\rangle=E-\left\langle-\frac{e^2}{4\pi\varepsilon_0 r}\right\rangle=E+\frac{e^2}{4\pi\varepsilon_0}\left\langle\frac{1}{r}\right\rangle$$
$$=-\frac{1}{2}\frac{e^2}{4\pi\varepsilon_0 a_0}+\frac{e^2}{4\pi\varepsilon_0}\frac{1}{a_0}=+\frac{1}{2}\frac{e^2}{4\pi\varepsilon_0 a_0}=+\ 13.6\ eV$$

This must mean that the expectation value of the potential energy is $-27.2\ eV$. The ratio of 2 between the magnitudes of the kinetic and potential energies is a manifestation of the virial theorem.

8.9 The expectation value of r is

$$\langle r\rangle=\langle n\ell m|r|n\ell m\rangle=\int_0^\infty r\left|R_{n\ell}(r)\right|^2 r^2\,dr=\int_0^\infty r^3\left|R_{n\ell}(r)\right|^2 dr$$

It is independent of *m*, so we must do 3 integrals. For the 3*s* state, we get

$$\langle r\rangle_{3s}=\int_0^\infty r^3\left|R_{3s}(r)\right|^2 dr=4\left(\frac{1}{3a_0}\right)^3\int_0^\infty r^3\left[1-\frac{2r}{3a_0}+\frac{2}{27}\left(\frac{r}{a_0}\right)^2\right]^2 e^{-2r/3a_0}\,dr$$
$$=4\left(\frac{1}{3a_0}\right)^3\int_0^\infty\left[r^3-\frac{4r^4}{3a_0}+\frac{16r^5}{27a_0^2}-\frac{8r^6}{81a_0^3}+\frac{4r^7}{729a_0^4}\right]e^{-2r/3a_0}\,dr$$
$$=4\left(\frac{1}{3a_0}\right)^3\left[\begin{array}{l}3!\left(\frac{3a_0}{2}\right)^4-\frac{4}{3a_0}4!\left(\frac{3a_0}{2}\right)^5+\frac{16}{27a_0^2}5!\left(\frac{3a_0}{2}\right)^6\\-\frac{8}{81a_0^3}6!\left(\frac{3a_0}{2}\right)^7+\frac{4}{729a_0^4}7!\left(\frac{3a_0}{2}\right)^8\end{array}\right]$$
$$=\frac{27}{2}a_0$$

For the 3*p* state, we get

$$\langle r\rangle_{3p}=\int_0^\infty r^3\left|R_{3p}(r)\right|^2 dr=\frac{32}{81}\left(\frac{1}{3a_0}\right)^3\int_0^\infty r^3\left[\frac{r}{a_0}\left(1-\frac{r}{6a_0}\right)\right]^2 e^{-2r/3a_0}\,dr$$
$$=\frac{32}{81}\left(\frac{1}{3a_0}\right)^3\int_0^\infty\left[\frac{r^5}{a_0^2}-\frac{r^6}{3a_0^3}+\frac{r^7}{36a_0^4}\right]e^{-2r/3a_0}\,dr$$
$$=\frac{32}{81}\left(\frac{1}{3a_0}\right)^3\left[\frac{1}{a_0^2}5!\left(\frac{3a_0}{2}\right)^6-\frac{1}{3a_0^3}6!\left(\frac{3a_0}{2}\right)^7+\frac{1}{36a_0^4}7!\left(\frac{3a_0}{2}\right)^8\right]$$
$$=\frac{25}{2}a_0$$

For the 3*d* state, we get

$$\begin{aligned}
\langle r\rangle_{3d} &= \int_0^\infty r^3 \left|R_{3d}(r)\right|^2 dr = \frac{8}{3645}\left(\frac{1}{3a_0}\right)^3 \int_0^\infty r^3 \left[\left(\frac{r}{a_0}\right)^2\right]^2 e^{-2r/3a_0}\,dr \\
&= \frac{8}{3645}\left(\frac{1}{3a_0}\right)^3 \int_0^\infty \left[\frac{r^7}{a_0^4}\right] e^{-2r/3a_0}\,dr \\
&= \frac{8}{3645}\left(\frac{1}{3a_0}\right)^3 \left[\frac{1}{a_0^4} 7!\left(\frac{3a_0}{2}\right)^8\right] \\
&= \frac{21}{2} a_0
\end{aligned}$$

All the results agree with Eq. (8.89). The average radius decreases as the angular momentum increases.

8.10 The probability that the electron resides within the nucleus is

$$\mathcal{P}_{inside} = \int_{nucleus} \mathcal{P}(r,\theta,\phi)\,dV = \int_0^r \int_0^{2\pi} \int_0^{\pi} \left|R_{n\ell}(r) Y_\ell^m(\theta,\phi)\right|^2 r^2 \sin\theta\, d\theta\, d\phi\, dr$$

The angular integral is unity, leaving just the radial integral. For the 1*s* state we get

$$\begin{aligned}
\mathcal{P}_{inside} &= \int_0^r r^2 \left|R_{10}(r)\right|^2 dr = 4\left(\frac{Z}{a_0}\right)^3 \int_0^r r^2 e^{-2Zr/a_0}\,dr = 4\left(\frac{Z}{a_0}\right)^3 \left(\frac{a_0}{2Z}\right)^3 \int_0^{2Zr/a_0} x^2 e^{-x}\,dx \\
&= 4\left(\frac{Z}{a_0}\right)^3 \left(\frac{a_0}{2Z}\right)^3 \left[-x^2 e^{-x} - 2xe^{-x} - 2e^{-x}\right]_0^{2Zr/a_0} \\
&= \frac{1}{2}\left[-\left(\frac{2Zr}{a_0}\right)^2 e^{-2Zr/a_0} - 2\left(\frac{2Zr}{a_0}\right) e^{-2Zr/a_0} - 2e^{-2Zr/a_0} + 2\right] \\
&= 1 - e^{-\beta} - \beta e^{-\beta} - \tfrac{1}{2}\beta^2 e^{-\beta}
\end{aligned}$$

where we have defined $\beta = 2Zr/a_0$. The nuclear radius is approximately $r = A^{1/3}\ 1.2\times10^{-15}\ \text{m}$, giving $\beta = 2ZA^{1/3}\ 1.2\times10^{-15}\ \text{m}/a_0 = 4.54\times10^{-5} ZA^{1/3}$. For hydrogen, $A = Z = 1$, giving $\beta = 4.54\times10^{-5}$ and a probability

$$\mathcal{P}_{inside\ H} \simeq 1.6\times10^{-14}$$

For uranium, $Z = 92$ and $A = 238$, giving $\beta = 2.59\times10^{-2}$ and a probability

$$\mathcal{P}_{inside\ H} \simeq 2.8\times10^{-6}$$

Still small, but 8 orders of magnitude larger than for hydrogen.

8.11 The ground state of tritium is ($Z = 1$)

$$\psi_{T100}(r,\theta,\phi) = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$$

The ground state of helium 3 is ($Z = 2$)

$$\psi_{He100}(r,\theta,\phi) = \frac{\sqrt{8}}{\sqrt{\pi a_0^3}} e^{-2r/a_0}$$

The wave function is unchanged in the decay, so the probability is found from the inner product of the two states:

$$\mathcal{P}_{T \to He} = \left| \langle \psi_{He100} | \psi_{T100} \rangle \right|^2$$

The inner product is

$$\begin{aligned}
\langle \psi_{He100} | \psi_{T100} \rangle &= \int \psi^*_{He100}(r,\theta,\phi) \psi_{T100}(r,\theta,\phi)\, dV \\
&= \int_0^\infty \int_0^{2\pi} \int_0^\pi \frac{\sqrt{8}}{\sqrt{\pi a_0^3}} e^{-2r/a_0} \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0} r^2 \sin\theta\, d\theta\, d\phi\, dr \\
&= \frac{\sqrt{8}}{\pi a_0^3} \left\{ \left(\int_0^\infty r^2 e^{-3r/a_0}\, dr \right) \left(\int_0^\pi \sin\theta\, d\theta \right) \left(\int_0^{2\pi} d\phi \right) \right\} \\
&= \frac{\sqrt{8}}{\pi a_0^3} \left(\frac{2a_0^3}{27} \right) (2)(2\pi) = \frac{8\sqrt{8}}{27}
\end{aligned}$$

giving a probability

$$\mathcal{P}_{T \to He} = \left| \tfrac{8\sqrt{8}}{27} \right|^2 = \tfrac{512}{729} \cong 0.702$$

8.12 The ground state energy is

$$E_1 = -\frac{1}{2} \left(\frac{Ze^2}{4\pi\varepsilon_0} \right)^2 \frac{\mu}{\hbar^2} = -\frac{1}{2} Z^2 \alpha^2 \mu c^2 .$$

The effective Bohr radius is

$$a = \frac{4\pi\varepsilon_0 \hbar^2}{\mu Z e^2} = a_0 \frac{m_e}{\mu Z} .$$

The Lyman alpha wavelength is

$$\lambda_{L_\alpha} = \frac{hc}{E_2 - E_1} = \frac{hc}{-\frac{3}{4} E_1} = \frac{2hc}{3Z^2 \alpha^2 \mu c^2} .$$

The reduced mass is

$$\mu = \frac{m_1 m_2}{m_1 + m_2}\,.$$

For hydrogen, we get

$$\begin{aligned}
\mu &= \frac{0.511\times 938.27}{0.511+938.27}\,MeV/c^2 = 510.72\ keV/c^2 \\
E_1 &= -\frac{1}{2}1^2\left(\tfrac{1}{137.036}\right)^2 510720eV = 13.598\ eV \\
a &= 0.52918nm\frac{511.0\,keV/c^2}{510.72\,keV/c^2} = 0.5295\ nm \\
\lambda_{L_\alpha} &= \frac{1239.84eVnm}{\frac{3}{4}\times 13.598eV} = 121.57\ nm
\end{aligned}\,.$$

a) Deuterium: $m_1 = m_e$, $m_2 \cong m_p + m_n \cong 2m_p$, and $Z = 1$:

$$\begin{aligned}
\mu &= 510.86\ keV/c^2 \\
E_1 &= 13.602\ eV \\
a &= 0.5293\ nm \\
\lambda_{L_\alpha} &= 121.54\ nm
\end{aligned}\,.$$

b) Helium ion: $m_1 = m_e$, $m_2 \cong 4m_p$, and $Z = 2$:

$$\begin{aligned}
\mu &= 510.93\ keV/c^2 \\
E_1 &= 54.42\ eV \\
a &= 0.2646\ nm \\
\lambda_{L_\alpha} &= 30.38\ nm
\end{aligned}\,.$$

c) Positronium: $m_1 = m_e$, $m_2 = m_e$, and $Z = 1$:

$$\begin{aligned}
\mu &= 255.5\ keV/c^2 \\
E_1 &= 6.803\ eV \\
a &= 1.508\ nm \\
\lambda_{L_\alpha} &= 243.0\ nm
\end{aligned}\,.$$

d) Muonium: $m_1 = m_e$, $m_2 \cong 207m_e$, and $Z = 1$:

$$\begin{aligned}
\mu &= 508.54\ keV/c^2 \\
E_1 &= 13.540\ eV \\
a &= 0.5317\ nm \\
\lambda_{L_\alpha} &= 122.09\ nm
\end{aligned}\,.$$

e) Muonic hydrogen: $m_1 \cong 207 m_e$, $m_2 = m_p$, and $Z = 1$:

$$\begin{aligned} \mu &= 95.06\ \ MeV/c^2 \\ E_1 &= 2531.04\ eV \\ a &= 0.00284\ nm \\ \lambda_{L_\alpha} &= 0.6531\ nm \end{aligned}.$$

f) Uranium ion: $m_1 = m_e$, $m_2 \cong 235 m_p$, and $Z = 92$:

$$\begin{aligned} \mu &= 511.0\ keV/c^2 \\ E_1 &= 115.16\ keV \\ a &= 0.00575\ nm \\ \lambda_{L_\alpha} &= 0.144\ nm \end{aligned}.$$

8.13 For the superposition state $|\psi_1\rangle = \left(|100\rangle + |210\rangle\right)/\sqrt{2}$, the wave function is [Eq. (8.95)].

$$\psi_1(r,\theta,\phi,t) = \frac{1}{\sqrt{2\pi a_0^3}} e^{-iE_1 t/\hbar}\left(e^{-r/a_0} + \frac{z}{4\sqrt{2}a_0} e^{-r/2a_0} e^{-i\omega_{21}t} \right)$$

Calculate the one-dimensional probability density $\mathcal{P}(z)$ along the *z*-axis by integrating over a plane perpendicular to the *z*-axis:

$$\mathcal{P}_1(z) = \int_0^{2\pi}\int_0^{\infty} \left|\psi_1(\rho,\phi,z)\right|^2 \rho\, d\rho\, d\phi$$

The wave function written in cylindrical coordinates is

$$\psi_1(\rho,\phi,z,t) = \frac{1}{\sqrt{2\pi a_0^3}} e^{-iE_1 t/\hbar}\left(e^{-\sqrt{\rho^2+z^2}/a_0} + \frac{z}{4\sqrt{2}a_0} e^{-\sqrt{\rho^2+z^2}/2a_0} e^{-i\omega_{21}t} \right)$$

Now do the integral

$$\begin{aligned} \mathcal{P}_1(z) &= \frac{1}{2\pi a_0^3}\int_0^{2\pi}\int_0^{\infty} \left| e^{-\sqrt{\rho^2+z^2}/a_0} + \frac{z}{4\sqrt{2}a_0} e^{-\sqrt{\rho^2+z^2}/2a_0} e^{-i\omega_{21}t} \right|^2 \rho\, d\rho\, d\phi \\ &= \frac{1}{2\pi a_0^3}\int_0^{2\pi}\int_0^{\infty} \left[e^{-2\sqrt{\rho^2+z^2}/a_0} + \frac{z^2}{32a_0^2} e^{-\sqrt{\rho^2+z^2}/a_0} + \frac{z}{2\sqrt{2}a_0} e^{-3\sqrt{\rho^2+z^2}/2a_0} \cos\omega_{21}t \right] \rho\, d\rho\, d\phi \end{aligned}$$

The integral we need is (to show this use Eq. (F.17) with $x = \alpha\sqrt{\rho^2+z^2}/a_0$):

$$\int_0^{\infty} e^{-\alpha\sqrt{\rho^2+z^2}/a_0} \rho\, d\rho = \frac{a_0}{\alpha^2}\left(a_0 + \alpha\sqrt{z^2}\right) e^{-\alpha\sqrt{z^2}/a_0}$$

The result is

$$\mathcal{P}_1(z) = \frac{1}{2\pi a_0^3} 2\pi \left[\begin{array}{l} \frac{a_0}{4}\left(a_0 + 2\sqrt{z^2}\right)e^{-2\sqrt{z^2}/a_0} + \frac{z^2}{32a_0^2} a_0\left(a_0 + \sqrt{z^2}\right)e^{-\sqrt{z^2}/a_0} \\ + \frac{z}{2\sqrt{2}a_0}\frac{4a_0}{9}\left(a_0 + \frac{3}{2}\sqrt{z^2}\right)e^{-3\sqrt{z^2}/2a_0}\cos\omega_{21}t \end{array} \right]$$

$$= \frac{1}{a_0}\left[\begin{array}{l} \frac{1}{4}\left(1 + 2\frac{\sqrt{z^2}}{a_0}\right)e^{-2\sqrt{z^2}/a_0} + \frac{z^2}{32a_0^2}\left(1 + \frac{\sqrt{z^2}}{a_0}\right)e^{-\sqrt{z^2}/a_0} \\ + \frac{\sqrt{2}z}{9a_0}\left(1 + \frac{3}{2}\frac{\sqrt{z^2}}{a_0}\right)e^{-3\sqrt{z^2}/2a_0}\cos\omega_{21}t \end{array} \right]$$

For the superposition state $|\psi_2\rangle = \left(|200\rangle + |210\rangle\right)/\sqrt{2}$, the wave function is (Eq. (8.97) with typos in book corrected).

$$\psi_2(r,\theta,\phi,t) = \frac{1}{4\sqrt{\pi a_0^3}} e^{-iE_2t/\hbar}\left(\left(1 - \frac{r}{2a_0}\right)e^{-r/2a_0} + \frac{z}{2a_0}e^{-r/2a_0}\right)$$

The wave function written in cylindrical coordinates is

$$\psi_2(\rho,\phi,z,t) = \frac{1}{4\sqrt{\pi a_0^3}} e^{-iE_2t/\hbar}\left(\left(1 - \frac{\sqrt{\rho^2+z^2}}{2a_0}\right)e^{-\sqrt{\rho^2+z^2}/2a_0} + \frac{z}{2a_0}e^{-\sqrt{\rho^2+z^2}/2a_0}\right)$$

Now do the integral:

$$\mathcal{P}_2(z) = \frac{1}{16\pi a_0^3}\int_0^{2\pi}\int_0^{\infty}\left|\left(1 - \frac{\sqrt{\rho^2+z^2}}{2a_0}\right)e^{-\sqrt{\rho^2+z^2}/2a_0} + \frac{z}{2a_0}e^{-\sqrt{\rho^2+z^2}/2a_0}\right|^2 \rho\, d\rho\, d\phi$$

$$= \frac{1}{16\pi a_0^3}\int_0^{2\pi}\int_0^{\infty}\left(1 - \frac{\sqrt{\rho^2+z^2}}{2a_0} + \frac{z}{2a_0}\right)^2 e^{-\sqrt{\rho^2+z^2}/a_0}\rho\, d\rho\, d\phi$$

$$= \frac{1}{16\pi a_0^3}\int_0^{2\pi}\int_0^{\infty}\left[\begin{array}{l} 1 + \frac{\rho^2+z^2}{4a_0^2} + \frac{z^2}{4a_0^2} - \frac{\sqrt{\rho^2+z^2}}{a_0} \\ + \frac{z}{a_0} - \frac{z\sqrt{\rho^2+z^2}}{2a_0^2} \end{array} \right] e^{-\sqrt{\rho^2+z^2}/a_0}\rho\, d\rho\, d\phi$$

Other integrals we need are [see Eqs. (F.18) and (F.19)]:

$$\int_0^\infty \sqrt{\rho^2+z^2}\, e^{-\alpha\sqrt{\rho^2+z^2}/a_0} \rho\, d\rho = \frac{a_0}{\alpha^3}\left(\alpha^2 z^2 + 2a_0^2 + 2\alpha a_0 \sqrt{z^2}\right) e^{-\alpha\sqrt{z^2}/a_0}$$

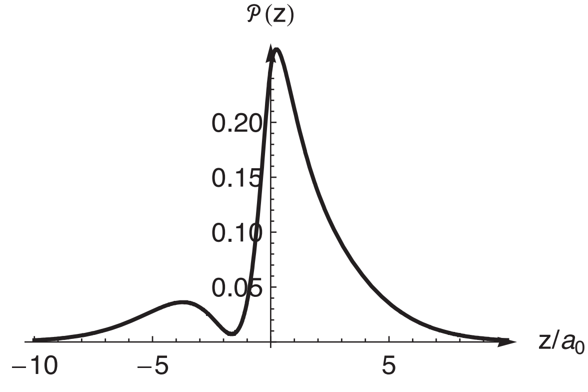
$$\int_0^\infty \left(\rho^2+z^2\right) e^{-\alpha\sqrt{\rho^2+z^2}/a_0} \rho\, d\rho = \frac{a_0}{\alpha^4}\left(3\alpha^2 a_0 z^2 + 6a_0^3 + 6\alpha a_0^2\sqrt{z^2} + \alpha^3 z^2\sqrt{z^2}\right) e^{-\alpha\sqrt{z^2}/a_0}$$

The result is

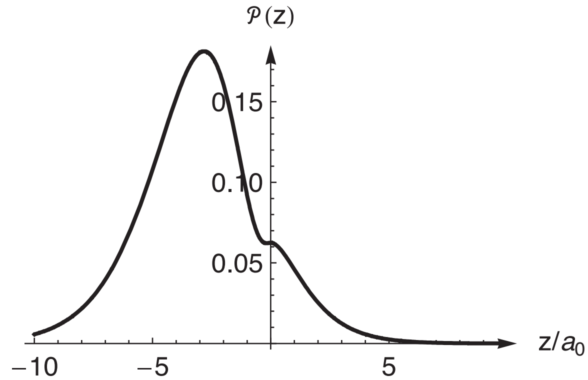
$$\begin{aligned}
\mathcal{P}_2(z) &= \frac{1}{8a_0^3} e^{-\sqrt{z^2}/a_0} \begin{bmatrix} a_0\left(a_0+\sqrt{z^2}\right)\left(1+\frac{z}{a_0}+\frac{z^2}{4a_0^2}\right) \\ +\frac{a_0}{4a_0^2}\left(3a_0 z^2 + 6a_0^3 + 6a_0^2\sqrt{z^2} + z^2\sqrt{z^2}\right) \\ -\left(1+\frac{z}{2a_0}\right)\left(z^2 + 2a_0^2 + 2a_0\sqrt{z^2}\right) \end{bmatrix} \\
&= \frac{1}{8a_0} e^{-\sqrt{z^2}/a_0} \begin{bmatrix} \left(1+\frac{\sqrt{z^2}}{a_0}\right)\left(1+\frac{z}{a_0}+\frac{z^2}{4a_0^2}\right) \\ +\frac{1}{4}\left(\frac{3z^2}{a_0^2} + 6 + 6\frac{\sqrt{z^2}}{a_0} + \frac{z^2}{a_0^2}\frac{\sqrt{z^2}}{a_0}\right) \\ -\left(1+\frac{z}{2a_0}\right)\left(\frac{z^2}{a_0^2} + 2 + 2a_0\frac{\sqrt{z^2}}{a_0}\right) \end{bmatrix} \\
&= \frac{1}{16a_0} e^{-\sqrt{z^2}/a_0}\left(1+\frac{\sqrt{z^2}}{a_0}+\frac{z^2}{a_0^2}\frac{\sqrt{z^2}}{a_0}-\frac{z^3}{a_0^3}\right)
\end{aligned}$$

The plots below show that the charge density is predominantly above the $z=0$ plane for $|\psi_1\rangle$ and predominantly below the $z=0$ plane for $|\psi_2\rangle$.

$\mathcal{P}_1(z)$ plot:



$\mathcal{P}_2(z)$ plot:



We can quantify this with the expectation value of the electric dipole moment $\mathbf{d} = q\mathbf{r}$:

$$\begin{aligned}\langle \mathbf{d} \rangle &= \langle \psi | -e\mathbf{r} | \psi \rangle = -e\langle \psi | \mathbf{r} | \psi \rangle \\ &= -e\langle \psi | x\hat{\mathbf{i}} + y\hat{\mathbf{j}} + z\hat{\mathbf{k}} | \psi \rangle\end{aligned}$$

Both $\psi_1(r,\theta,\phi)$ and $\psi_2(r,\theta,\phi)$ are even functions with respect to *x* and *y*, so the integrals over the odd functions *x* and *y* are zero, leaving

$$\begin{aligned}\langle \mathbf{d} \rangle &= -e\langle \psi | z\hat{\mathbf{k}} | \psi \rangle = -e\hat{\mathbf{k}}\langle \psi | z | \psi \rangle \\ &= -e\hat{\mathbf{k}}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \psi^*(x,y,z)\; z\; \psi(x,y,z)\,dx\,dy\,dz \\ &= -e\hat{\mathbf{k}}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} z\,|\psi(x,y,z)|^2\,dx\,dy\,dz \\ &= -e\hat{\mathbf{k}}\int_{-\infty}^{\infty} z\left[\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} |\psi(x,y,z)|^2\,dx\,dy\right]dz \\ &= -e\hat{\mathbf{k}}\int_{-\infty}^{\infty} z\;\mathcal{P}(z)\;dz\end{aligned}$$

Doing this integral yields

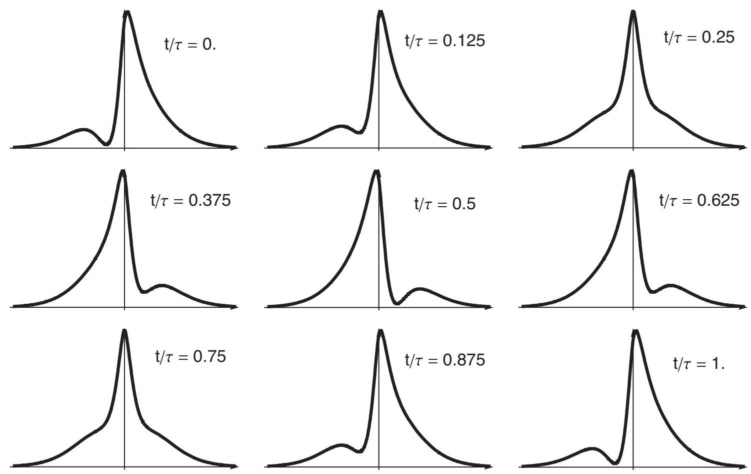
$$
\begin{aligned}
\langle \mathbf{d}_1 \rangle &= -e\hat{\mathbf{k}} \int_{-\infty}^{\infty} z\ \mathcal{P}(z)\ dz \\
&= -e\hat{\mathbf{k}} \int_{-\infty}^{\infty} \frac{z}{a_0} \begin{bmatrix} \frac{1}{4}\left(1+2\frac{\sqrt{z^2}}{a_0}\right) e^{-2\sqrt{z^2}/a_0} + \frac{z^2}{32a_0^2}\left(1+\frac{\sqrt{z^2}}{a_0}\right) e^{-\sqrt{z^2}/a_0} \\ + \frac{\sqrt{2}z}{9a_0}\left(1+\frac{3}{2}\frac{\sqrt{z^2}}{a_0}\right) e^{-3\sqrt{z^2}/2a_0} \cos\omega_{21}t \end{bmatrix} dz \\
&= \frac{-e\hat{\mathbf{k}}}{a_0} \int_{-\infty}^{\infty} \begin{bmatrix} \frac{1}{4}\left(z+2\frac{z\sqrt{z^2}}{a_0}\right) e^{-2\sqrt{z^2}/a_0} + \frac{1}{32a_0^2}\left(z^3+\frac{z^3\sqrt{z^2}}{a_0}\right) e^{-\sqrt{z^2}/a_0} \\ + \frac{\sqrt{2}}{9a_0}\left(z^2+\frac{3}{2}\frac{z^2\sqrt{z^2}}{a_0}\right) e^{-3\sqrt{z^2}/2a_0} \cos\omega_{21}t \end{bmatrix} dz \\
&= \frac{-e2\sqrt{2}\hat{\mathbf{k}}}{9a_0^2} \cos\omega_{21}t \int_0^{\infty} \left(z^2+\frac{3}{2}\frac{z^2\sqrt{z^2}}{a_0}\right) e^{-3z/2a_0}\ dz = \frac{-e2\sqrt{2}\hat{\mathbf{k}}}{9a_0^2} \cos\omega_{21}t \left[\frac{64}{27}a_0^2\right] \\
&= \frac{-128\sqrt{2}}{243} ea_0\hat{\mathbf{k}} \cos\omega_{21}t
\end{aligned}
$$

for state 1 and

$$
\begin{aligned}
\langle \mathbf{d}_2 \rangle &= -e\hat{\mathbf{k}} \int_{-\infty}^{\infty} z\ \mathcal{P}(z)\ dz \\
&= -e\hat{\mathbf{k}} \int_{-\infty}^{\infty} \frac{z}{16a_0} \left[e^{-\sqrt{z^2}/a_0} \left(1+\frac{\sqrt{z^2}}{a_0}+\frac{z^2}{a_0^2}\frac{\sqrt{z^2}}{a_0}-\frac{z^3}{a_0^3}\right)\right] dz \\
&= \frac{-e\hat{\mathbf{k}}}{16a_0} \int_{-\infty}^{\infty} \left(z+\frac{z\sqrt{z^2}}{a_0}+\frac{z^3}{a_0^2}\frac{\sqrt{z^2}}{a_0}-\frac{z^4}{a_0^3}\right) e^{-\sqrt{z^2}/a_0}\ dz \\
&= \frac{e\hat{\mathbf{k}}}{8a_0^4} \int_0^{\infty} z^4 e^{-z/a_0}\ dz = \frac{e\hat{\mathbf{k}}}{8a_0^4}\left(24a_0^5\right) \\
&= 3ea_0\hat{\mathbf{k}}
\end{aligned}
$$

for state 2.

State 2 is stationary as expected, while state 1 oscillates at the Bohr frequency, as shown below, where τ is the oscillation period



8.14 a) For this state, the possible energies are E_2, E_3, and E_4. The energy values are

$$E_n = -\frac{13.6\ eV}{n^2}$$

The probabilities are

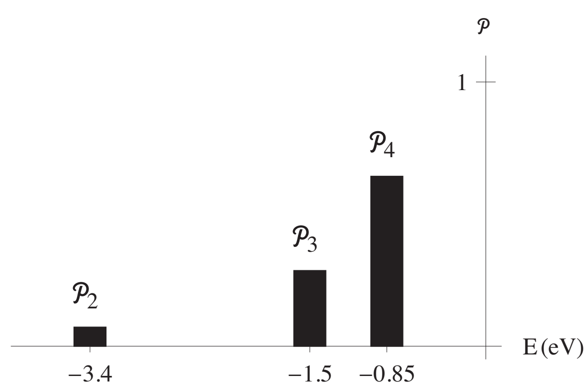
$$\mathcal{P}_{E_n} = \sum_{\ell=0}^{n-1}\sum_{m=-\ell}^{\ell}\left|\langle n\ell m|\psi\rangle\right|^2 = \sum_{\ell=0}^{n-1}\sum_{m=-\ell}^{\ell}\left|\langle n\ell m|\left(\tfrac{1}{\sqrt{14}}|211\rangle - \tfrac{2}{\sqrt{14}}|32,-1\rangle + i\tfrac{3}{\sqrt{14}}|422\rangle\right)\right|^2$$

$$\mathcal{P}_{E_2} = \sum_{\ell=0}^{1}\sum_{m=-\ell}^{\ell}\left|\langle 2\ell m|\left(\tfrac{1}{\sqrt{14}}|211\rangle - \tfrac{2}{\sqrt{14}}|32,-1\rangle + i\tfrac{3}{\sqrt{14}}|422\rangle\right)\right|^2 = \tfrac{1}{14}$$

$$\mathcal{P}_{E_3} = \sum_{\ell=0}^{2}\sum_{m=-\ell}^{\ell}\left|\langle 3\ell m|\left(\tfrac{1}{\sqrt{14}}|211\rangle - \tfrac{2}{\sqrt{14}}|32,-1\rangle + i\tfrac{3}{\sqrt{14}}|422\rangle\right)\right|^2 = \tfrac{4}{14}$$

$$\mathcal{P}_{E_4} = \sum_{\ell=0}^{3}\sum_{m=-\ell}^{\ell}\left|\langle 4\ell m|\left(\tfrac{1}{\sqrt{14}}|211\rangle - \tfrac{2}{\sqrt{14}}|32,-1\rangle + i\tfrac{3}{\sqrt{14}}|422\rangle\right)\right|^2 = \tfrac{9}{14}$$

Histogram:



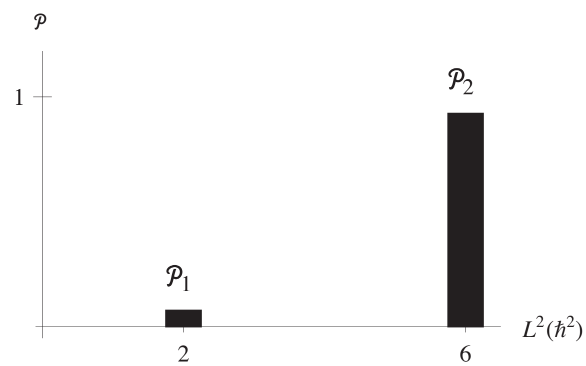
The expectation value of the energy is

$$\langle E\rangle = \langle\psi|H|\psi\rangle = \sum_{n=1}^{\infty} E_n \mathcal{P}_{E_n} = -13.6\ eV \sum_{n=1}^{\infty} \frac{1}{n^2}\mathcal{P}_{E_n}$$
$$= -13.6\ eV\left(\tfrac{1}{4}\mathcal{P}_{E_2} + \tfrac{1}{9}\mathcal{P}_{E_3} + \tfrac{1}{16}\mathcal{P}_{E_4}\right) = -13.6\ eV\left(\tfrac{1}{4}\tfrac{1}{14} + \tfrac{1}{9}\tfrac{4}{14} + \tfrac{1}{16}\tfrac{9}{14}\right)$$
$$= -13.6\ eV\left(\tfrac{181}{2016}\right) = -1.221\ eV$$

b) The allowed values of $\mathbf{L}^2$ are $\ell(\ell+1)\hbar^2$. The probabilities of an $\mathbf{L}^2$ measurement are

$$\mathcal{P}_\ell = \sum_{n=\ell+1}^{\infty}\sum_{m=-\ell}^{\ell}\left|\langle n\ell m|\psi\rangle\right|^2 = \sum_{n=1}^{\ell+1}\sum_{m=-\ell}^{\ell}\left|\langle n\ell m|\left(\tfrac{1}{\sqrt{14}}|211\rangle - \tfrac{2}{\sqrt{14}}|32,-1\rangle + i\tfrac{3}{\sqrt{14}}|422\rangle\right)\right|^2$$
$$\mathcal{P}_1 = \sum_{n=2}^{\infty}\sum_{m=-1}^{1}\left|\langle n1m|\left(\tfrac{1}{\sqrt{14}}|211\rangle - \tfrac{2}{\sqrt{14}}|32,-1\rangle + i\tfrac{3}{\sqrt{14}}|422\rangle\right)\right|^2 = \tfrac{1}{14}$$
$$\mathcal{P}_2 = \sum_{n=3}^{\infty}\sum_{m=-2}^{2}\left|\langle n2m|\left(\tfrac{1}{\sqrt{14}}|211\rangle - \tfrac{2}{\sqrt{14}}|32,-1\rangle + i\tfrac{3}{\sqrt{14}}|422\rangle\right)\right|^2 = \tfrac{4}{14} + \tfrac{9}{14} = \tfrac{13}{14}$$

Histogram:



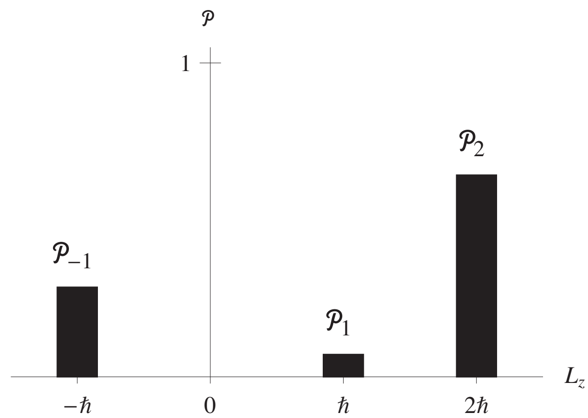
The expectation value of $\mathbf{L}^2$ is

$$\langle\mathbf{L}^2\rangle = \langle\psi|\mathbf{L}^2|\psi\rangle = \sum_{\ell=0}^{\infty}\ell(\ell+1)\hbar^2\,\mathcal{P}_\ell = \hbar^2\left(2\mathcal{P}_1 + 6\mathcal{P}_2\right) = \hbar^2\left(2\tfrac{1}{14} + 6\tfrac{13}{14}\right) = \tfrac{40}{7}\hbar^2$$

c) The allowed values of L_z are $m\hbar$. The probabilities of an L_z measurement are

$$\mathcal{P}_{L_z=m\hbar} = \sum_{n=|m|+1}^{\infty}\sum_{\ell=|m|}^{n-1}\left|\langle n\ell m|\psi\rangle\right|^2 = \sum_{n=1}^{\infty}\sum_{\ell=|m|}^{n-1}\left|\langle n\ell m|\left(\tfrac{1}{\sqrt{14}}|211\rangle - \tfrac{2}{\sqrt{14}}|32,-1\rangle + i\tfrac{3}{\sqrt{14}}|422\rangle\right)\right|^2$$
$$\mathcal{P}_{-1} = \sum_{n=2}^{\infty}\sum_{\ell=1}^{n-1}\left|\langle n\ell,-1|\left(\tfrac{1}{\sqrt{14}}|211\rangle - \tfrac{2}{\sqrt{14}}|32,-1\rangle + i\tfrac{3}{\sqrt{14}}|422\rangle\right)\right|^2 = \tfrac{4}{14}$$
$$\mathcal{P}_1 = \sum_{n=2}^{\infty}\sum_{\ell=1}^{n-1}\left|\langle n\ell 1|\left(\tfrac{1}{\sqrt{14}}|211\rangle - \tfrac{2}{\sqrt{14}}|32,-1\rangle + i\tfrac{3}{\sqrt{14}}|422\rangle\right)\right|^2 = \tfrac{1}{14}$$
$$\mathcal{P}_2 = \sum_{n=3}^{\infty}\sum_{\ell=2}^{n-1}\left|\langle n\ell 2|\left(\tfrac{1}{\sqrt{14}}|211\rangle - \tfrac{2}{\sqrt{14}}|32,-1\rangle + i\tfrac{3}{\sqrt{14}}|422\rangle\right)\right|^2 = \tfrac{9}{14}$$

Histogram:



The expectation value of L_z is

$$\langle L_z\rangle = \langle\psi|L_z|\psi\rangle = \sum_{m=-\infty}^{\infty} m\hbar\,\mathcal{P}_{L_z=mh} = (-1\hbar)\mathcal{P}_{L_z=-1h} + 1\hbar\mathcal{P}_{L_z=1h} + 2\hbar\mathcal{P}_{L_z=2h}$$

$$= (-1\hbar)\tfrac{4}{14} + 1\hbar\tfrac{1}{14} + 2\hbar\tfrac{9}{14} = \tfrac{15}{14}\hbar$$

d) The answers to (a), (b), and (c) are time independent because the operators all commute with the Hamiltonian. This is evident in the calculations because the time dependent state vector is

$$|\psi(t)\rangle = \tfrac{1}{\sqrt{14}}e^{-iE_2t/\hbar}|211\rangle - \tfrac{2}{\sqrt{14}}e^{-iE_3t/\hbar}|32,-1\rangle + i\tfrac{3}{\sqrt{14}}e^{-iE_4t/\hbar}|422\rangle$$

and in each of the probability calculations, the time dependence drops out in the complex square step.

8.15 The energy eigenvalue equation for a particle of mass *m* in a potential $V(x,y,z)$ is

$$\left[\frac{\mathbf{p}^2}{2m} + V(x,y,z)\right]|E\rangle = E|E\rangle$$

In the position representation, this is

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(x,y,z)\right]\psi(x,y,z) = E\psi(x,y,z)$$

$$\left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V(x,y,z)\right]\psi(x,y,z) = E\psi(x,y,z)$$

Outside the box, the potential is infinite and the wave function must be zero. So we are left to find the solutions inside the box where the potential is zero, give the differential equation

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi(x,y,z)=E\psi(x,y,z)$$

Now follow the separation of variables procedure from Appendix E.
Step 1: Write the partial differential equation in the appropriate coordinate system:

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi(x,y,z)=E\psi(x,y,z)$$

Step 2: *Assume* that the solution can be written as the product of functions, at least one of which depends on only one variable, in this case we separate all three coordinates:

$$\psi(x,y,z)=f(x)g(y)h(z)$$

Plug this assumed solution into the partial differential equation from step 1. Because of the special form of ψ, the derivatives each act on only one of the functions. Any partial derivatives that act only on a function of a single variable may be rewritten as total derivatives, yielding

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)f(x)g(y)h(z)=Ef(x)g(y)h(z)$$

$$-\frac{\hbar^2}{2m}\left(g(y)h(z)\frac{d^2}{dx^2}f(x)+f(x)h(z)\frac{d^2}{dy^2}g(y)+f(x)g(y)\frac{d^2}{dz^2}h(z)\right)=Ef(x)g(y)h(z)$$

Step 3: Divide both sides of the equation by the full function:

$$-\frac{\hbar^2}{2m}\left(\frac{1}{f(x)}\frac{d^2}{dx^2}f(x)+\frac{1}{g(y)}\frac{d^2}{dy^2}g(y)+\frac{1}{h(z)}\frac{d^2}{dz^2}h(z)\right)=E$$

Step 4: Isolate *all* of the dependence on one coordinate on one side of the equation:

$$-\frac{\hbar^2}{2m}\frac{1}{f(x)}\frac{d^2}{dx^2}f(x)=E+\frac{\hbar^2}{2m}\left(\frac{1}{g(y)}\frac{d^2}{dy^2}g(y)+\frac{1}{h(z)}\frac{d^2}{dz^2}h(z)\right)$$

Step 5: Now imagine changing the isolated variable x by a small amount. In principle, the left-hand side of the equation could change, but nothing on the right-hand side would. Therefore, if the equation is to be true for all values of x, the particular combination of x dependences on the left-hand side must result in no overall dependence on x —*the left-hand side must be a constant*. We thus define a **separation constant**, which we call E_X in this case

$$-\frac{\hbar^2}{2m}\frac{1}{f(x)}\frac{d^2}{dx^2}f(x)=E+\frac{\hbar^2}{2m}\left(\frac{1}{g(y)}\frac{d^2}{dy^2}g(y)+\frac{1}{h(z)}\frac{d^2}{dz^2}h(z)\right)\equiv E_x$$

Apply the same reasoning to the two parts of the right hand side to get:

$$-\frac{\hbar^2}{2m}\frac{1}{g(y)}\frac{d^2}{dy^2}g(y)\equiv E_y$$
$$-\frac{\hbar^2}{2m}\frac{1}{h(z)}\frac{d^2}{dz^2}h(z)\equiv E_z$$

where

$$E = E_x + E_y + E_z$$

Step 6: Write each equation in standard form by multiplying each equation by its unknown function to clear it from the denominator. Rearranging slightly, we obtain

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}f(x)=E_x f(x)$$
$$-\frac{\hbar^2}{2m}\frac{d^2}{dy^2}g(y)=E_y g(y)$$
$$-\frac{\hbar^2}{2m}\frac{d^2}{dz^2}h(z)=E_z h(z)$$

We thus have three separated equations. The three equations are identical, so their solutions will be of the same form. Starting with the first equation, we write is as

$$\frac{d^2}{dx^2}f(x)=-\frac{2m}{\hbar^2}E_x f(x)=-k_x^2 f(x)$$

and see that it is the same equation (5.51) we used to solve the one-dimensional infinite square well problem. The solutions are [see Eqs. (5.62) and (5.66)]

$$f(x)=\sqrt{\frac{2}{L}}\sin\frac{n_x\pi x}{L}$$
$$E_{x,n_x}=\frac{n_x^2\pi^2\hbar^2}{2mL^2}$$

for $n_x = 1,2,3,...$ Likewise the solutions for the other two equations are

$$g(y)=\sqrt{\frac{2}{L}}\sin\frac{n_y\pi y}{L} \qquad h(z)=\sqrt{\frac{2}{L}}\sin\frac{n_z\pi z}{L}$$
$$E_{y,n_y}=\frac{n_y^2\pi^2\hbar^2}{2mL^2} \qquad E_{z,n_z}=\frac{n_z^2\pi^2\hbar^2}{2mL^2}$$

The full solution is thus

$$\psi(x,y,z)=f(x)g(y)h(z)=\left(\frac{2}{L}\right)^{3/2}\sin\frac{n_x\pi x}{L}\sin\frac{n_y\pi y}{L}\sin\frac{n_z\pi z}{L}$$
$$E_{n_xn_yn_z}=E_{x,n_x}+E_{y,n_y}+E_{z,n_z}=\frac{\pi^2\hbar^2}{2mL^2}\left(n_x^2+n_y^2+n_z^2\right)$$

The first 6 energy levels and the degeneracies are

n_x	n_y	n_z	$n_x^2+n_y^2+n_z^2$
1	1	1	3
1	1	2	6
1	2	1	6
2	1	1	6
1	2	2	9
2	1	2	9
2	2	1	9
1	1	3	11
1	3	1	11
3	1	1	11
2	2	2	12
1	2	3	14
1	3	2	14
2	1	3	14
2	3	1	14
3	1	2	14
3	2	1	14

Energy	degeneracy
$3\dfrac{\pi^2\hbar^2}{2mL^2}$	1
$6\dfrac{\pi^2\hbar^2}{2mL^2}$	3
$9\dfrac{\pi^2\hbar^2}{2mL^2}$	3
$11\dfrac{\pi^2\hbar^2}{2mL^2}$	3
$12\dfrac{\pi^2\hbar^2}{2mL^2}$	1
$14\dfrac{\pi^2\hbar^2}{2mL^2}$	6