Problem 1

> *An electron is in an (orbital) angular momentum state with $l = 3$.*
> *(a) What is the length of this electron's angular momentum vector?*
> *(b) How many different possible z components can the angular momentum vector have and what are these possible z components?*
> *(c) What are the values of the angle that the angular momentum vector makes with the z axis (this is the angle θ from class)?*

A)
$L = \sqrt{l(l+1)}\bar{h} = 2\sqrt{3}\bar{h}$

B and C)
$cos\theta_m = \frac{m_l \bar{h}}{L}$

m_l	L_z	$cos\theta_m$	θ(r)
3	$3\bar{h}$	$\sqrt{3}/2$	$\pi/6$
2	$2\bar{h}$	$1/\sqrt{3}$	0.955
1	$1\bar{h}$	$1/(2\sqrt{3})$	1.277
0	0	0	$\pi/2$
-1	$-1\bar{h}$	$-1/(2\sqrt{3})$	1.864
-2	$-2\bar{h}$	$-1/\sqrt{3}$	2.186
-3	$-3\bar{h}$	$-\sqrt{3}/2$	$5\pi/6$

Problem 2

> *Show that the (n, l, m_l) = (1, 0, 0) and (2, 0, 0) hydrogen atom wave functions (listed in Table 7.1 in the textbook) are indeed properly normalized.*

$$P(r)dr = |R(r)|^2 r^2\ dr\ \int_0^{\pi} |\Theta(\theta)|^2\ sin(\theta)\ d\theta\ \int_0^{2\pi} |\Phi(\phi)|^2\ d\phi$$

$$1 = \int_0^{\infty} |R(r)|^2 r^2\ dr\ \int_0^{\pi} |\Theta(\theta)|^2\ sin(\theta)\ d\theta\ \int_0^{2\pi} |\Phi(\phi)|^2\ d\phi$$

For (1, 0, 0):

$$\int_0^{\pi} |\Theta(\theta)|^2 sin(\theta)dr = \int_0^{\pi} \left|\frac{1}{\sqrt{2}}\right|^2 sin(\theta)dr$$

$$= \frac{1}{2}(-cos(\pi) - -cos(0)) = 1/2 \cdot (-(-1) - (-1)) = 1$$

$$\int_0^{2\pi} |\Phi(\phi)|^2\ \ d\phi = \int_0^{2\pi} \left|\frac{1}{\sqrt{2\pi}}\right|^2\ d\phi = \frac{1}{2\pi}(2\pi - 0) = 1$$

$$1 = \int_0^{\infty} |R(r)|^2 r^2\ dr$$

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

$$1 = \frac{4}{a_0^3} \int_0^{\infty} e^{-2r/a_0} r^2\ dr$$

$$= \frac{4}{a_0^3} \left(-e^{-2/a_0 \cdot r} \frac{(2/a_0)^2 r^2 + 2(2/a_0)r + 2}{(2/a_0)^3}\right)_0^{\infty}$$

$$= \left(-e^{-2/a_0 \cdot r} \frac{4/a_0^2 r^2 + 4/a_0 r + 2}{2}\right)_0^{\infty}$$

The exponential grows faster than the numerator, so the evaluation of the limit as r approaches infinity is 0.

$$1 = e^{-2/a_0 \cdot r} \frac{4/a_0^2 r^2 + 4/a_0 r + 2}{2}\ where\ r = 0$$

$$1 = 1 \cdot \frac{0 + 0 + 2}{2}$$

The probability density equation is normalized properly.

For (2, 0, 0):
The equations for Θ and Φ are both the same, which means they end up being 1 again after integrating.

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

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

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

$$1 = \frac{1}{8a_0^3} \left[\int_0^\infty 4r^2 e^{-r/a_0} dr - \int_0^\infty 4\frac{r^3}{a_0} e^{-r/a_0} dr + \int_0^\infty \frac{r^4}{a_0^2} e^{-r/a_0} dr \right]$$

We can remember that the laplace transform of $r^n e^{-r} = \frac{n!}{c^6}$.

$$1 = \frac{1}{8a_0^3} \left[4 \cdot 2! \cdot a_0^3 - \frac{4}{a_0} \cdot 3! \cdot a_0^4 + \frac{1}{a_0^2} 4! \cdot a_0^5 \right]$$

$$1 = \frac{1}{8a_0^3} \left[8 \cdot a_0^3 - 24 \cdot a_0^3 + 24 \cdot a_0^3 \right]$$

$$1 = \frac{1}{8} \left[8 - 24 + 24 \right]$$

This function is also normalized properly.

Problem 3

> *Consider the radial probability density for the hydrogen atom wave functions. If $n = 2$ and $l = 0$, for what value of the radius (r) does the radial probability density have its maximum values?*

$$P(r) = |R(r)|^2 r^2 \ dr$$

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

From the previous problem. We'll just trim off the constants since they won't matter here.

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

$$P(r) = \left(4r^2 - 4\frac{r^3}{a_0} + \frac{r^4}{a_0^2}\right) e^{-r/a_0}$$

$$\frac{dP}{dr} = e^{-r/a_0}(4r^2)(-1/a_0) + (8r)e^{-r/a_0} - e^{-r/a_0}(4r^3/a_0)(-1/a_0) + (-12r^2/a_0)e^{-r/a_0} + e^{-r/a_0}(r^4/a_0^2)(-1/a_0) + (4r^3/a_0^2)e^{-r/a_0}$$

$$\frac{dP}{dr} = e^{-r/a_0}\left((-4r^2/a_0) + (8r) + (4r^3/a_0^2) + (-12r^2/a_0) + (-r^4/a_0^3) + (4r^3/a_0^2)\right)$$

$$\frac{dP}{dr} = e^{-r/a_0} r \left(8 + -16/a_0 r + 8/a_0^2 r^2 - 1/a_0^3 r^3\right)$$

We did the derivative by hand, but we'll need to use wolfram to solve the 4th order polynomial equation for the max that we're looking for. We end up getting $\sqrt{5}a_0 + 3a_0$.

Problem 4

> *Now instead consider the angular probability density for the hydrogen atom wave functions. Find the directions in space where the angular probability density for the $l = 2$, $m = 0$ electron in hydrogen has its maxima and minima? Hint: Consider $dP/d\theta$ as in example 7.7 in the textbook.*

$$P(\theta,\phi) = |\Theta(\theta)\Phi(\phi)|^2 = \left|\sqrt{\frac{5}{8}}(3cos^2\theta - 1)\frac{1}{\sqrt{2\pi}}\right|^2$$

$$P(\theta,\phi) = \frac{5}{8}(3cos^2\theta - 1)^2\frac{1}{2\pi}$$

$$P(\theta,\phi) = \frac{5}{15\pi}\left(\frac{3}{2}(1 + cos2\theta) - 1\right)^2$$

$$P(\theta,\phi) = \frac{5}{16\pi}\left(\frac{3}{2}cos2\theta + 1/2\right)^2$$

$$\frac{dP}{d\theta} = \frac{5}{8\pi}\left(\frac{3}{2}cos2\theta + 1/2\right)(-3sin2\theta)$$

$$\frac{dP}{d\theta} = \frac{5}{8\pi}\left(\frac{3}{2}cos2\theta + 1/2\right)(-3sin2\theta)$$

Zeroes occur where

$$\frac{3}{2}cos2\theta = -1/2$$

$$cos2\theta = -1/3$$

Theta = 0.955
And

$$sin2\theta = 0$$

Theta = 0.

We can look at the second derivative to determine which is maxima/minima.

$$\frac{d^2P}{d\theta^2} = \frac{5}{8\pi}\left(\frac{3}{2}cos2\theta(-6cos2\theta) + (-3sin2\theta)(3/2cos2\theta) + 1/2(-6cos2\theta)\right)$$

We can tell from a cursory glance that the function is concave up at $\theta = 0.955$ and concave down at $\theta = 0$, meaning the former is the min and the latter is the max. Just kidding, I plugged it into wolfram after doing the second derivative by hand.

Problem 5

> *For a hydrogen atom in the (3, 2, 0) state:*
> *(a) Show that the wave function from Table 7.1 is properly normalized.*
> *(b) What is the most likely radius of the electron? How does the result compare with what the Bohr' model predicts?*
> *(c) Calculate the average value of the electron's potential energy. How does it compare with the corresponding result from the Bohr model?*

A)

$$P(r)dr = |R(r)|^2 r^2 \ dr \ \int_0^{\pi} |\Theta(\theta)|^2 \ sin(\theta) \ d\theta \ \int_0^{2\pi} |\Phi(\phi)|^2 \ d\phi$$

$$1 = \int_0^{\infty} \left| \frac{4}{27\sqrt{10}(3a_0)^{3/2}} \frac{r^2}{a_0^2} e^{-r/(3a_0)} \right|^2 r^2 \ dr \ \cdot \int_0^{\pi} \left| \sqrt{\frac{5}{8}}(3cos^2\theta - 1) \right|^2 \ sin(\theta) \ d\theta \ \cdot \int_0^{2\pi} \left| \frac{1}{\sqrt{2\pi}} \right|^2 \ d\phi$$

We already know the Phi term is normalized. Looking at the theta term first:

$$\int_0^{\pi} \left| \sqrt{\frac{5}{8}}(3cos^2\theta - 1) \right|^2 \ sin(\theta) \ d\theta$$

$$\frac{5}{8} \int_0^{\pi} \left(3cos^2\theta - 1\right)^2 \ sin(\theta) \ d\theta$$

Where $u = \sqrt{3}cos\theta$, $\frac{du}{-\sqrt{3}} = sin\theta \ d\theta$
And $\sqrt{3} = \sqrt{3}cos(0), -\sqrt{3} = \sqrt{3}cos(\pi)$

$$\frac{5}{8\sqrt{3}} \int_{-\sqrt{3}}^{\sqrt{3}} \left(u^4 - 2u^2 + 1\right) du$$

$$\frac{5}{8\sqrt{3}} \left(1/5u^5 - 2/3u^3 + u\right)_{-\sqrt{3}}^{\sqrt{3}}$$

Function is even

$$\frac{10}{8\sqrt{3}} \left((1/5)9\sqrt{3} - (2/3)3\sqrt{3} + \sqrt{3}\right)$$

$$\frac{5}{4} (9/5 - 2 + 1)$$

$$\frac{5}{4} (9/5 - 5/5)$$

The theta one is equal to 1.

$$1 = \int_0^{\infty} \left| \frac{4}{27\sqrt{10}(3a_0)^{3/2}} \frac{r^2}{a_0^2} e^{-r/(3a_0)} \right|^2 r^2 \ dr$$

$$\frac{16}{27^2 \cdot 10(3a_0)^3} \int_0^{\infty} \left| e^{-r/(3a_0)} \right|^2 \frac{r^4}{a_0^4} r^2 \ dr$$

$3^3 = 27$

$$\frac{16}{27^3 \cdot 10(a_0)^7} \int_0^{\infty} e^{-r\frac{2}{3a_0}} r^6 \ dr$$

$c = \frac{2}{3a_0}, c^7 = \frac{2^7}{3^7 a_0^7}$

$$\frac{16}{27^3 \cdot 10(a_0)^7} \left[\frac{e^{-rc}}{c} \left(\frac{c^6 r^6 + 6c^5 r^5 + 30c^4 r^4 + 120c^3 r^3 + 360c^2 r^2 + 720cr + 720}{c^6} \right) \right]_0^\infty$$

$27^3 = 3^7 3^2,\ 16 = 2^4$

$$\frac{1}{3^2 2^4 \cdot 5} \left[e^{-rc} \left(c^6 r^6 + 6c^5 r^5 + 30c^4 r^4 + 120c^3 r^3 + 360c^2 r^2 + 720cr + 720 \right) \right]_0^\infty$$

At r = infinity, the integral evaluates to zero as the exponent rises faster than any polynomial.
At r = 0, the exponent evaluates to 1 and every r term evaluates to zero. This leaves, after simplyfing the fraction at the beginning of the expression:

$$\frac{1}{720} [720] = 1$$

B)
We already verified that the integrals across Theta and Phi are 1.

$$P(r) = \left| \frac{4}{27\sqrt{10}(3a_0)^{3/2}} \frac{r^2}{a_0^2} e^{-r/(3a_0)} \right|^2 r^2 \ dr$$

$$P(r) = \frac{16}{27^3 \cdot 10(a_0)^7} e^{-r\frac{2}{3a_0}} r^6 \ dr$$

$$\frac{dP}{dr} = \frac{16}{27^3 \cdot 10(a_0)^7} \left(\frac{-2}{3a_0} e^{-r\frac{2}{3a_0}} r^6 \ dr \ + \frac{-2}{3a_0} e^{-r\frac{2}{3a_0}} r^6 \ dr \right)$$

$$\frac{dP}{dr} = \frac{16}{27^3 \cdot 10(a_0)^7} \cdot r^5 \cdot e^{-r\frac{2}{3a_0}} \left(\frac{-2}{3a_0} r + 6 \right)$$

We can see that there are zeros at infinity, 0, and $r = 9a_0$. This matches Bohr's prediction of $n^2 a_0$.
C)

$$U(r) = -\frac{e^2}{4\pi\epsilon_0} \cdot \frac{1}{r}$$

$$P(r) = \frac{16}{27^3 \cdot 10(a_0)^7} e^{-r\frac{2}{3a_0}} r^6 \ dr$$

$$< U >= \int_0^\infty U(r)P(r)dr = \int_0^\infty -\frac{e^2}{4\pi\epsilon_0} \cdot \frac{1}{r} \frac{16}{27^3 \cdot 10(a_0)^7} e^{-r\frac{2}{3a_0}} r^6 \ dr$$

$$< U >= \frac{2^4}{3^9 \cdot 10(a_0)^7} \frac{-e^2}{4\pi\epsilon_0} \int_0^\infty e^{-r\frac{2}{3a_0}} r^5 \ dr$$

$$c = \frac{2}{3a_0}$$

$$< U >= \frac{c^7}{8} \frac{1}{90} \frac{-e^2}{4\pi\epsilon_0} \int_0^\infty e^{-rc} r^5 \ dr$$

$$< U >= \frac{c^7}{8} \frac{-e^2}{360\pi\epsilon_0} \left[e^{-rc} \left(\frac{c^5 r^5 + 5c^4 r^4 + 20c^3 r^3 + 60c^2 r^2 + 120cr + 120}{c^6} \right) \right]_0^\infty$$

The integral is zero at infinity, and each r term is zero at zero.

$$< U >= \frac{c^7}{8} \frac{-e^2}{360\pi\epsilon_0} \frac{120}{c^6}$$

$$< U >= \frac{c}{8} \frac{-e^2}{3\pi\epsilon_0}$$

$$< U >= \frac{1}{36a_0} \frac{-e^2}{\pi\epsilon_0}$$

This matches the classical prediction of $U = \frac{-e^2}{4\pi\epsilon_0(9a_0)}$

Problem 6

> *Explain why each of the following sets of quantum numbers (n, l, m_l, m_s) is not permitted for hydrogen:*
> *(a) (2, 2, -1, +1/2)*
> *(b) (3, 1, +2, -1/2)*
> *(c) (4, 1, +1, -3/2)*
> *(d) (2, -1, +1, +1/2)*

A The maximum absolute value of l is $n - 1$

B The maximum absolute value of m_l is l

C Electrons cannot have 3/2 spin

D There's no such thing as negative l values

Problem 7

> *(a) A hydrogen atom is in an excited 5g state, from which it makes a series of transitions by emitting photons, ending in the 1s state. Show, on a diagram similar to Figure 7.19 from the textbook, the sequence of transitions that can occur?*
> *(b) Repeat part (a) if the atom instead begins in the 5d state?*

A)

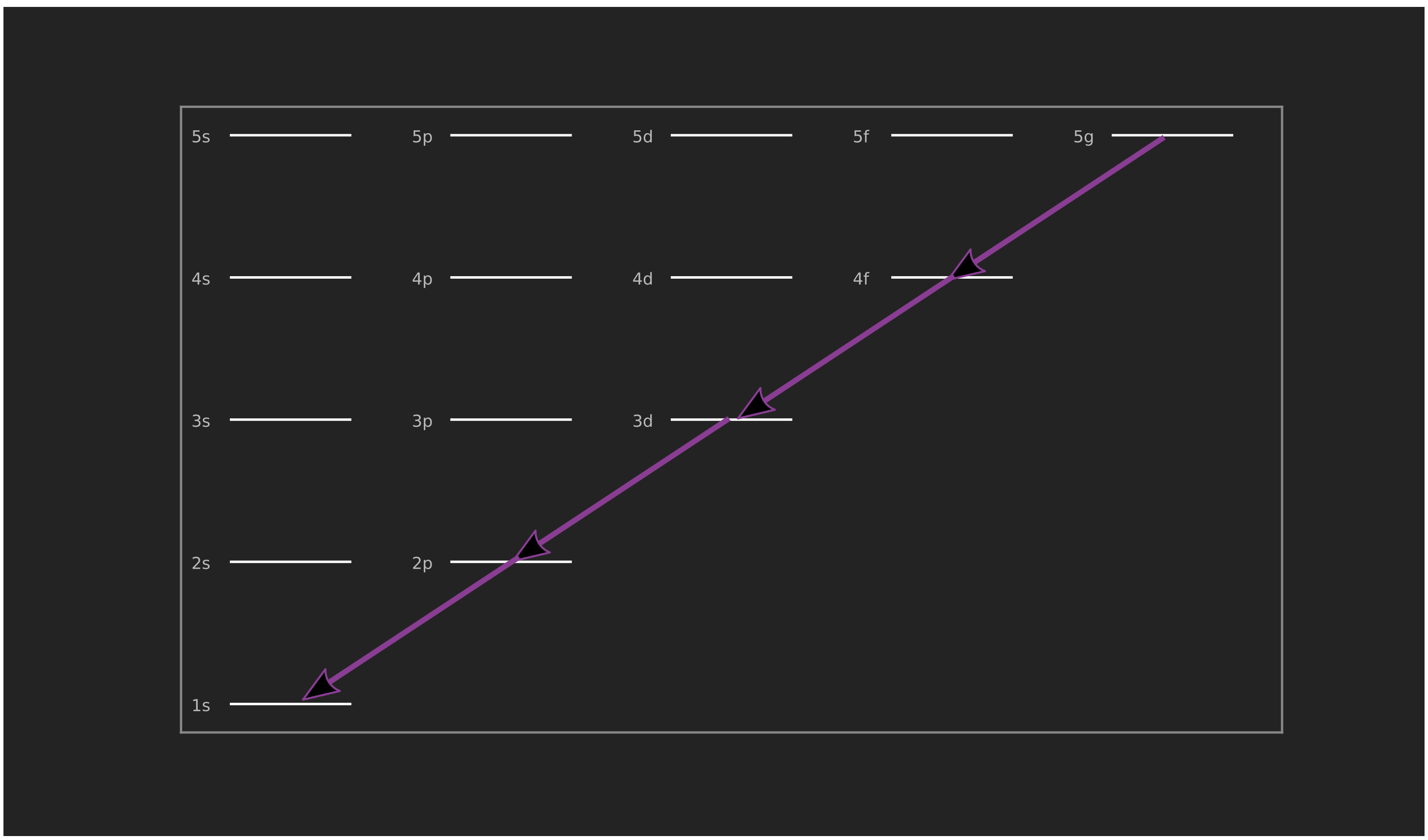

Figure 1:

B)

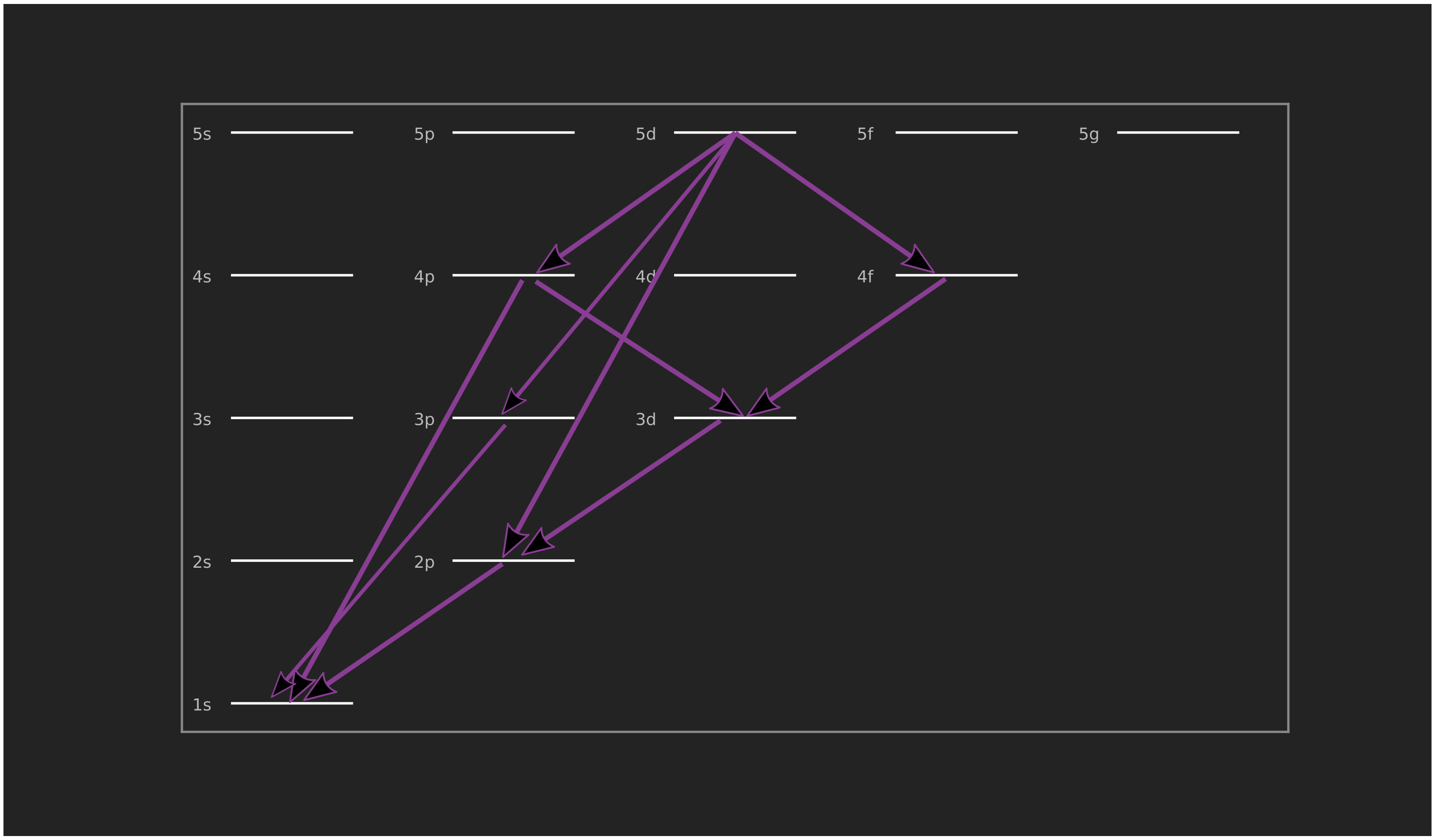

Figure 2: