Homework 8 Key

1. (a) *Proof.* $[L_y, L_z] = i\hbar L_x$ The p7 slide 4 $\square$

   (b) *Proof.* $[L_z, L_x] = i\hbar L_y$ The p7 slide 4 $\square$

   (c) *Proof.* $[L^2, L_x] = [L^2, L_y] = 0$ The p7 slide 5 $\square$

2. Calculate and Simplify

   (a) $[L_+^2, L_z]$; Recall $[L_z, L_+] = \hbar L_+$

   $= L_+^2 L_z - L_z L_+^2$

   $= L_+^2 L_z - L_z L_+^2 - L_+ L_z L_+ + L_+ L_z L_+$

   $= L_+[L_+, L_z] + [L_+, L_z]L_+$

   $= -\hbar L_+^2 + (-\hbar L_+^2)$

   $= -2\hbar L_+^2$

   (b) $[L_+^2, L_-^2]$; Recall $[L_+, L_-] = 2\hbar L_z$

   use the commutator property $[AB, CD] = [AB, C]D + C[AB, D]$

   $= A[B, C]D + [A, C]BD + CA[B, D] + C[A, D]B$

   $= L_+[L_+, L_-]L_- + [L_+, L_-]L_+L_- + L_-L_+[L_+L_-] + L_-[L_+, L_-]L_+$

   $= L_+(2\hbar L_z)L_- + (2\hbar L_z)L_+L_- + L_-L_+(2\hbar L_z) + L_-(2\hbar L_z)L_+$

   $= 2\hbar L_z(L_+L_zL_- + L_zL_+L_- + L_-L_+ + L_-L_zL_+)$

   (c) $[L^2, L_+^2 + L_-^2 + L_z^2]$

   $= L^2L_+^2 + L^2L_-^2 + L^2L_z^2 - L_+^2L^2 - L_-^2L^2 - L_z^2L^2$

   L^2 commute with L_+, L_-, L_z it commutes with the squares because the commutator property $[A, BC] = [A, B]C + B[A, C]$

3. Is it possible to linearly combine wavefunctions for 3rd and 4th excited state of a particle on a sphere:

   (a) L_z has precise value of $-2\hbar$

   $L_z\psi(x) = m\hbar\psi(x)$

n	m
4	-3,-2,-1,0,1,2,3
5	-4,-3,-2,-1,0,1,2,3,4

Table 1: 3rd and 4th excited state correspond to n=4 and n=5. The table lists all the possible values of possible l, m_l.

$\psi_{4,3,-2}$ has an L_z eigenvalue of -2.

(b) L_z has average value of $7\hbar$

The largest m go up to 4 and you need numbers above 7 to get an average of $7\hbar$.

(c) L_z has average value of $1.4\hbar$

Because the average is 1.4, it will consist of $m = 1, 2$, and we will find the probability of the wavefunctions at those states.

$p_1(\hbar) + p_2(2\hbar) = 1.4\hbar$; p is probability

We will try out some numbers of p_1, p_2 to get 1.4 and voila, the solutions are $p_1 = 3/5, p_2 = 2/5$. This is not super elegant but it works.

$p_1 = \frac{c_1^2}{c_1^2+c_2^2} = 3/5$ and $p_2 = \frac{c_2^2}{c_1^2+c_2^2} = 2/5$; Postulates of quantum mechanics.

$\frac{p_1}{p_2} = \frac{3}{2} = \frac{c_1^2}{c_2^2}$

$c_1 = \sqrt{3}$ and $c_2 = \sqrt{2}$

$\psi = \sqrt{3}\psi_{4,3,1} + \sqrt{2}\psi_{4,3,2}$; for simplicity, the two ψ are ψ_1, ψ_2

To normalize: $\psi = N\left(\sqrt{3}\psi_1 + \sqrt{2}\psi_2\right)$

$\langle\psi|\psi\rangle = 1$

$N^2\left\langle\sqrt{3}\psi_1+\sqrt{2}\psi_2\middle|\sqrt{3}\psi_1+\sqrt{2}\psi_2\right\rangle = 1$ and $\langle\psi_1|\psi_1\rangle = 1$ and $\langle\psi_1|\psi_2\rangle = 0$ because they are orthogonal.

$N^2(3+2) = 1$

$N = \frac{1}{\sqrt{5}}$

Finally, $\psi = \frac{1}{\sqrt{5}}\left(\sqrt{3}\psi_{4,3,1} + \sqrt{2}\psi_{4,3,2}\right)$ is the normalized form.

4. *Proof.* $2p_x, 2p_y$ are mutually orthogonal.

   The integral $\int_0^{2\pi} 2p_x * 2p_y d\tau$ has the factor $\int_0^{2\pi} \cos\phi \sin\phi d\phi = \frac{1}{2}\sin^2\phi\Big|_0^{2\pi} = 0$. $\square$

5. Derive an equation that yields probability of finding electron within distance "d" from nucleus:

   $P(r) = \int_0^d dr \int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\phi r^2 \psi^*_{n,l,m_l}(r,\theta,\phi)\psi_{n,l,m_l}(r,\theta,\phi)$
   $P(r) = \int_0^d dr \int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\phi r^2 R^*_{n,l}(r) Y^*_{l,m_l}(\theta,\phi) R_{n,l}(r) Y_{l,m_l}(\theta,\phi)$
   $\int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\phi Y^*_{l_1,m_{l1}}(\theta,\phi) Y_{l_2,m_{l2}}(\theta,\phi) = \delta_{l_1 l_2}\delta_{m_{l1} m_{l2}}$
   $P(r) = \int_0^d R^2_{n,l}(r') r'^2 dr'$

6. Calculate $\langle r\rangle$ for an electron in 2s. Compare with radial probability.

   $\psi_{2s} = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(2 - \frac{r}{a_0} e^{\frac{-r}{a_0}}\right)$
   $\langle r\rangle = \int\int\int \psi^* * r * \psi \; dxdydz$
   $\langle r\rangle = \int_0^{2\pi}\int_0^\pi\int_0^\infty \psi^* * r * \psi * r^2 dr \sin\theta d\theta d\phi$
   $\langle r\rangle = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^3 \frac{1}{4\sqrt{2\pi}} \int_0^{2\pi}\int_0^\pi\int_0^\infty [(2 - \frac{r}{a_0})e^{\frac{-r}{a_0}}]^2 r^3 dr$
   $= \frac{1}{32\pi}\left(\frac{1}{a_0}\right)^3 \int_0^{2\pi}\int_0^\pi\int_0^\infty \left(4e^{\frac{-r}{a_0}} - \frac{4r}{a_0}e^{\frac{-r}{a_0}} + \left(\frac{r}{a_0}\right)^2 e^{\frac{-r}{a_0}}\right) r^3 dr \sin\theta d\theta d\phi$
   $\int_0^{2\pi}\int_0^\pi \sin\theta d\theta d\phi = 4\pi$
   $= \frac{4\pi}{32\pi}\left(\frac{1}{a_0}\right)^3 \int_0^\infty \left(4e^{\frac{-r}{a_0}} - \frac{4r}{a_0}e^{\frac{-r}{a_0}} + \left(\frac{r}{a_0}\right)^2 e^{\frac{-r}{a_0}}\right) r^3 dr$

   The rest is just integration by parts so I resorted to Wolfram.

   $r = 6a_0$

   For maximum of radial probability, set derivative of probability density to equal 0.

   $\frac{d}{dr}\int R^2_{2,0}(r)^2 dr = 0$;ignore all constants
   $\frac{d}{dr} r^2 e^{\frac{-r}{a_0}} = 0$
   $2re^{\frac{-r}{a_0}} - \frac{r^2}{a_0}e^{\frac{-r}{a_0}} = 0$
   $e^{\frac{-r}{a_0}}(2r - \frac{r^2}{a_0}) = 0$
   $r = 2a_0$ expectation value 3x max radial probability.

7. An electron is more likely to be 2Å if it is in 1s or 2s orbital?

$\langle\psi_{1s}|\psi_{1s}\rangle = \frac{1}{\pi}\left(\frac{1}{a_0}\right)^3 e^{\frac{-2r}{a_0}}$

$\langle\psi_{1s}|\psi_{1s}\rangle = \frac{1}{\pi}\left(\frac{1}{a_0}\right)^3 e^{\frac{-2(2*10^{-10})}{52.9*10^{-12}}}$

$\langle\psi_{2s}|\psi_{2s}\rangle = \frac{1}{32\pi}\left(\frac{1}{a_0}\right)^3 (2-\frac{r}{a_0})^2 e^{\frac{-2r}{a_0}}$

The probability of $2s > 1s$, also because 2s radius is greater than 1s and closer to 2Å.