# HOMEWORK 3

1. Here are the 5 spherical harmonics for $\ell = 2$:

$$Y_2^{\pm 2}(\theta,\varphi) = \frac{1}{2}\sqrt{\frac{15}{2\pi}}\sin^2\theta e^{\pm 2i\varphi}$$
$$Y_2^{1}(\theta,\varphi) = -\frac{1}{2}\sqrt{\frac{15}{2\pi}}\sin\theta\cos\theta e^{\pm i\varphi}$$
$$Y_2^{-1}(\theta,\varphi) = \frac{1}{2}\sqrt{\frac{15}{2\pi}}\sin\theta\cos\theta e^{\pm - i\varphi}$$
$$Y_2^{0}(\theta,\varphi) = \frac{1}{4}\sqrt{\frac{5}{\pi}}\left(3\cos^2\theta - 1\right)$$

Thus, their sum:

$$\begin{aligned}
\sum_{m=-2}^{2} Y_2^m * Y_2^m &= 2\left(\frac{15}{32\pi}\sin^2\theta\right) + 2\left(\frac{15}{8\pi}\sin^2\theta\cos^2\theta\right) + \frac{5}{16\pi}\left(3\cos^2\theta - 1\right)^2 \\
&= \frac{5}{16\pi}\left(3\sin^2\theta + 12\sin^2\theta\cos^2\theta + 9\cos^4\theta - 6\cos^2\theta + 1\right) \\
&= \frac{5}{16\pi}\left[3\sin^2\theta\left(1-\cos^2\theta\right)12\sin^2\theta\cos^2\theta + 9\cos^2\theta\left(1-\sin^2\theta\right) - 6\cos^2\theta + 1\right] \\
&= \frac{5}{16\pi}\left(3\sin^2\theta + 3\cos^2\theta + 1\right) \\
&= \frac{5}{4\pi} = \frac{2\ell+1}{4\pi}
\end{aligned}$$

Hence, we have verified Unsöld's theorem for $\ell = 2$, and shown that the completely closed atomic subshell is independent of $\theta$ and $\varphi$.

2. (a)

$$\begin{aligned}
\langle r\rangle &= \int_0^\infty r\mathcal{P}_{n,n-1}dr \\
&= \int_0^\infty r^3 R_{n,n-1}^2 dr \\
&= \int_0^\infty \left[r^3\left(\frac{2}{na_0}\right)^3\frac{1}{(2n)!}\left(\frac{2r}{na_0}\right)^{2(n-1)}e^{-2r/na_0}\right]dr \\
&= \frac{1}{(2n)!}\int_0^\infty\left(\frac{2r}{na_0}\right)^{2n+1}e^{-2r/na_0}dr \\
&= \frac{na_0}{2}\frac{1}{(2n)!}\int_0^\infty u^{2n+1}e^{-u}du \qquad\qquad u = \frac{2r}{na_0} \quad du = \frac{2}{na_0}dr \\
&= \frac{na_0}{2}\frac{1}{(2n)!}(2n+1)! \\
&= \frac{na_0}{2}\frac{1}{(2n)!}(2n)!\,(2n+1) \\
&= (2n+1)\frac{na_0}{2}
\end{aligned}$$

(b) We have:

$$\langle r^2\rangle = \int_0^\infty r^2 \mathcal{P}_{n.n-1} dr$$

I am only repeating all of the math from the previous part because I can copy/paste (finally a Latex win!!). Note that it is pretty much identical to before:

$$\begin{aligned}
\langle r^2\rangle &= \int_0^\infty r^2 \mathcal{P}_{n,n-1} dr \\
&= \int_0^\infty r^4 R_{n,n-1}^2 dr \\
&= \int_0^\infty \left[ r^4 \left(\frac{2}{na_0}\right)^3 \frac{1}{(2n)!} \left(\frac{2r}{na_0}\right)^{2(n-1)} e^{-2r/na_0}\right] dr \\
&= \frac{na_0}{2}\frac{1}{(2n)!}\int_0^\infty \left(\frac{2r}{na_0}\right)^{2n+2} e^{-2r/na_0} dr \\
&= \left(\frac{na_0}{2}\right)^2 \frac{1}{(2n)!}\int_0^\infty u^{2n+2}e^{-u}du \qquad\qquad u = \frac{2r}{na_0} \quad du = \frac{2}{na_0}dr \\
&= \left(\frac{na_0}{2}\right)^2 \frac{1}{(2n)!}(2n+2)! \\
&= \left(\frac{na_0}{2}\right)^2 \frac{1}{(2n)!}(2n)!\,(2n+1)\,(2n+2) \\
&= (2n+1)\,(2n+2)\left(\frac{na_0}{2}\right)^2
\end{aligned}$$

(c)

$$\begin{aligned}
(\Delta r)^2 &= \langle r^2\rangle - (\langle r\rangle)^2 \\
&= (2n+2)\,(2n+1)\left(\frac{na_0}{2}\right)^2 - \left[(2n+1)\,\frac{na_0}{2}\right]^2 \\
&= (2n+2)\,(2n+1)\left(\frac{na_0}{2}\right)^2 - (2n+1)^2\left(\frac{na_0}{2}\right)^2 \\
&= \left[(2n+2)\,(2n+1) - (2n+1)^2\right]\left(\frac{na_0}{2}\right)^2 \\
&= \left[3n^2+6n+2-4n^2-4n-1\right]\left(\frac{na_0}{2}\right)^2 \\
&= (2n+1)\left(\frac{na_0}{2}\right)^2
\end{aligned}$$

Thus,

$$\Delta r = \sqrt{2n+1}\frac{na_0}{2}$$

And,

$$\frac{\Delta r}{\langle r\rangle} = \frac{1}{\sqrt{2n+1}}$$

For large values of $n$, we see that the *relative* uncertainty in $r$ goes to zero. Physically, this means that we can expect a near circular orbit for large values of $n$. This makes sense with our classical idea of an orbit.

3.

$$
\begin{aligned}
R_{10} &= 2a_0^{-3/2}e^{-r/a_0} \\
R_{20} &= \frac{1}{\sqrt{2}}a_0^{-3/2}\left(1-\frac{1}{2}\frac{r}{a_0}\right)e^{-r/2a_0} \\
R_{21} &= \frac{1}{2\sqrt{6}}a_0^{-3/2}\left(\frac{r}{a_0}\right)e^{-r/2a_0}
\end{aligned}
$$

Since $R_{10}$ and $R_{21}$ match the form $R_{n,n-1}$, we can apply the formula from the last question to get the expectation values:

$$
\begin{aligned}
\langle r_{n,n-1}\rangle &= (2n+1)\frac{na_0}{2} \\
\langle r_{10}\rangle &= \frac{3a_0}{2} \\
\langle r_{21}\rangle &= 5a_0
\end{aligned}
$$

For $R_{20}$ we have to a bit more work:

$$
\begin{aligned}
\langle r_{20}\rangle &= \int_0^\infty r\mathcal{P}_{20}(r)\,dr \\
&= \int_0^\infty r^3 R_{20}^2 \\
&= \int_0^\infty r^3\frac{1}{2a_0^3}\left(1-\frac{1}{2}\frac{r}{a_0}\right)^2 e^{-r/a_0} \\
&= \int_0^\infty \left(\frac{r^3}{2a_0^3}-\frac{r^4}{2a_0^4}+\frac{r^5}{8a_0^5}\right)e^{-r/a_0}
\end{aligned}
$$

Distributing we have three integrals, all fitting the form of $\int_0^\infty u^n e^{-u}du$

$$
\begin{aligned}
&= \frac{3!}{2}a_0-\frac{4!}{2}a_0+\frac{5!}{8}a_0 \\
&= 6a_0
\end{aligned}
$$

In E&R, we have the equation (7-29):

$$
\overline{r_{nl}} = \frac{n^2a_0}{Z}\left\{1+\frac{1}{2}\left[1-\frac{l(l+1)}{n^2}\right]\right\}
$$

By plugging in $Z=1$, we see that:

$$
\begin{aligned}
\overline{r_{10}} &= a_0+\frac{1}{2}a_0 = \frac{3}{2}a_0 \\
\overline{r_{20}} &= 4a_0+2a_0 = 6a_0 \\
\overline{r_{21}} &= 4a_0+1a_0 = 5a_0
\end{aligned}
$$

Hence, our expected values, $\langle r_{nl}\rangle$, match those found using (7-29) in E&R.

By comparing $\langle r_{10} \rangle$ and $\langle r_{20} \rangle$, we note that their difference is large ($\frac{7}{2}a_0$). This large difference makes sense as the two states are in different shells. However, the relative difference between $r_{20}$ and $r_{21}$ is relatively small ($a_0$), which makes sense because they are two subshells of the same shell ($n = 2$). The surprising discovery is that the *2p* subshell is closer to the nucleus than the *2s* subshell.

4.

$$\begin{aligned}
P_{10} &= \int_0^{a_0} r^2 R_{10}^2 dr \\
&= \int_0^{a_0} \frac{r^2}{2}\left(\frac{2}{a_0}\right)^3 e^{-2r/a_0} \\
&= \int_0^{a_0} \frac{4}{a_0^3} r^2 e^{-2r/a_0} \\
&= \int_0^{a_0} \frac{4}{a_0^3} r^2 e^{-2r/a_0} && u = -\frac{r}{a_0} \quad du = -\frac{1}{a_0} dr \\
&= -4 \int_0^{a_0} u^2 e^{2u} du && \text{integrate by parts: } f = u^2,\ g' = e^{2u} \\
&= -4\left[\frac{u^2 e^{2u}}{2} - \int_0^{a_0} u e^{2u} du\right] && \text{integrate by parts again: } f = u,\ g' = e^{2u} \\
&= -4\left[\frac{u^2 e^{2u}}{2} - \frac{u e^{2u}}{2} + \int_0^{a_0} \frac{e^{2u}}{2} du\right] \\
&= -4\left[\frac{u^2 e^{2u}}{2} - \frac{u e^{2u}}{2} + \frac{e^{2u}}{4}\right] \\
&= -4\left[\left(\frac{r^2/a_0^2}{2} + \frac{r/a_0}{2} + \frac{1}{4}\right) e^{-2r/a_0}\right]_0^{a_0} \\
&= -4\left(\frac{5}{4}e^{-2} - \frac{1}{4}\right) \\
&= 1 - \frac{5}{e^2} \approx .323
\end{aligned}$$

$$\begin{aligned}
P_{21} &= \int_0^{a_0} r^2 R_{21}^2 dr \\
&= \int_0^{a_0} r^4 \frac{1}{24 a_0^4} e^{-r/a_0} dr \\
&= \frac{1}{24 a_0^4} \int_0^{a_0} r^4 e^{-r/a_0} dr && u = \frac{r}{a_0} \quad du = \frac{1}{a_0} dr \\
&= \frac{1}{24} \int_0^1 u^4 e^{-u} du \\
&= \frac{1}{24}\left[-\left(u^4 + 4u^3 + 12u^2 + 24u + 24\right) e^{-u}\right]_0^1 \\
&= 1 - \frac{65}{24e} \approx 0.004
\end{aligned}$$

We see that when $\ell$ is non-zero, there is a very low probability of the electron being within one Bohr radius of the origin. Furthermore, since $P_{10}$ has a smaller $n$ value, it makes sense that the probability of electron being closer to the nucleus is higher since it lies in the innermost shell. Conversely, for the higher $n = 2$ shell, it would make sense for the electron to be further from the nucleus.