Assignment 4

Physics 250
September 29th, 2008
Erik Born
SID#: 1072989

Question 1: Calculate the average potential and kinetic energies for the electron in the ground state of hydrogen.

The formula for the average value of any function $f(r)$ is: $\langle r \rangle = \displaystyle\int_0^\infty f(r) P_{n,l}(r) dr$

For the total kinetic energy of the electron, $KE_{orb} + KE_{rad}$:

$$KE(r) = \frac{-\hbar^2}{2m}\left[\frac{d^2}{dr^2} + \left(\frac{2}{r}\right)\frac{d}{dr}\right]\psi(\mathbf{r}) + \frac{l(l+1)\hbar^2}{2mr^2}\psi(\mathbf{r}) = (E - U(r))\psi(\mathbf{r})$$

For $\psi(\mathbf{r})$ in the ground state $\psi(\mathbf{r}) = Y_0^0(\theta,\phi)R_{1,0}(r) = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$

Using this $KE(r)$ becomes:

$$KE(r) = \frac{-\hbar^2}{2m}\left[\frac{d^2}{dr^2} + \left(\frac{2}{r}\right)\frac{d}{dr}\right]\frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0} + \frac{0(0+1)\hbar^2}{2mr^2}\frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$$

$$= \frac{-\hbar^2}{2m}\frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left[\frac{d^2}{dr^2}e^{-r/a_0} + \left(\frac{2}{r}\right)\frac{d}{dr}e^{-r/a_0}\right]$$

Since $\frac{d}{dr}e^{-r/a_0} = -\left(\frac{1}{a_0}\right)e^{-r/a_0}$; and $\frac{d^2}{dr^2}e^{-r/a_0} = \left(\frac{1}{a_0}\right)^2 e^{-r/a_0}$, this becomes:

$$KE(r) = \frac{-\hbar^2}{2m}\frac{1}{\sqrt{\pi}}\left[\left(\frac{1}{a_0}\right)^2 e^{-r/a_0} + \left(\frac{2}{r}\right)\left(\frac{-1}{a_0}\right)e^{-r/a_0}\right]$$

Substituting this into the formula for the average KE as above, and using $P_{1,0} = r^2|R_{1,0}(r)|^2$ we get:

$$\begin{aligned}
\langle r \rangle &= \textstyle\int_0^\infty \frac{-\hbar^2}{2m_e}\frac{1}{\sqrt{\pi}}\left[\left(\frac{1}{a_0}\right)^2 e^{-r/a_0} + \left(\frac{2}{r}\right)\left(\frac{-1}{a_0}\right)e^{-r/a_0}\right]\left[\frac{4}{a_0^3}r^2 e^{-2r/a_0}\right] dr \\
&= \textstyle\int_0^\infty \frac{-\hbar^2}{2m_e}\frac{4}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^4\left[\left(\frac{r^2}{a_0}\right)e^{-3r/a_0} + -2re^{-3r/a_0}\right] dr \\
&= \textstyle\frac{-\hbar^2}{2m_e}\frac{4}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^4\left[\int_0^\infty \left(\frac{r^2}{a_0}\right)e^{-3r/a_0}dr - \int_0^\infty 2re^{-3r/a_0}dr\right]
\end{aligned}$$

Using integration by parts, with $u = \frac{r^2}{2a_0}, dv = e^{-3r/a_0}, du = \frac{du}{2a_0}, v = \frac{-a_0}{3}e^{-3r/a_0}$:

$$\begin{aligned}
&= \textstyle\frac{-\hbar^2}{2m_e}\frac{4}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^4\left[\frac{-r^2}{3}e^{-3r/a_0}\Big|_0^\infty + \frac{2}{3}\int_0^\infty re^{-3r/a_0}dr - \int_0^\infty 2re^{-3r/a_0}dr\right], \text{since } \frac{-r^2}{3}e^{-3r/a_0}\Big|_0^\infty = 0, \\
&= \textstyle\frac{-\hbar^2}{2m_e}\frac{4}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^4\left[-\frac{4}{3}\left[\frac{-ra_0}{3}e^{-3r/a_0}\right]_0^\infty - 4\int_0^\infty \frac{-a_0}{3}e^{-3r/a_0}dr\right] \{\text{integration by parts again}\} \\
&= \textstyle\frac{\hbar^2}{2m_e}\frac{4}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^4 \frac{4a_0^2}{9}e^{-3r/a_0}\Big|_0^\infty = \frac{8\hbar^2}{9m_e\sqrt{\pi}}\left(\frac{1}{a_0}\right)^2 = \frac{8(6.58\text{E}-16eV\cdot s)^2(3\text{E}8\frac{m}{s})^2}{.511\text{E}6eV)\sqrt{\pi}(.529\text{E}-10m)^2} = 1.708eV
\end{aligned}$$

The total energy of the ground state, $E = -13.6eV$ is the sum of the average kinetic and average potential energies, therefore,

$$\langle U(r) \rangle = -13.6eV - \langle KE(r) \rangle = -13.6eV - 1.708eV = 11.89eV$$

Question 2:

Part (a) The most probable distance of the electron from the nucleus for the hydrogen $2s$ state is given by the maximum of $P_{2,0}(r)$, to find this, get the zeros of the derivative:

$$\frac{d}{dr}\left[r^2\left|R_{2,0}\right|^2\right] = \frac{d}{dr}\left[r^2\left(\frac{Z}{2a_0}\right)^3\left(2-\frac{Zr}{a_0}\right)^2 e^{-Zr/a_0}\right] = \frac{d}{dr}\left[r^2\left(\frac{1}{2a_0}\right)^3\left(4-\frac{4r}{a_0}+\frac{r^2}{a_0^2}\right)e^{-r/a_0}\right]$$

$$= \frac{d}{dr}\left[\left(\frac{r^2}{8a_0^3}-\frac{4r^3}{8a_0^4}+\frac{r^4}{8a_0^5}\right)e^{-r/a_0}\right]$$

$$= \left(\frac{2r}{8a_0^3}-\frac{12r^2}{8a_0^4}+\frac{4r^3}{8a_0^5}\right)e^{-r/a_0}+\left(\frac{r^2}{8a_0^3}-\frac{4r^3}{8a_0^4}+\frac{r^4}{8a_0^5}\right)\frac{-1}{a_0}e^{-r/a_0}$$

$$= e^{-r/a_0}\left[\left(\frac{2r}{8a_0^3}-\frac{12r^2}{8a_0^4}+\frac{4r^3}{8a_0^5}\right)-\left(\frac{r^2}{8a_0^4}-\frac{4r^3}{8a_0^5}+\frac{r^4}{8a_0^6}\right)\right]$$

$$= \frac{e^{-r/a_0}}{8}\left(\frac{2r}{a_0^3}-\frac{13r^2}{a_0^4}+\frac{8r^3}{a_0^5}-\frac{r^4}{a_0^6}\right) = \frac{re^{-r/a_0}}{8a_0^3}\left(2-\frac{13r}{a_0}+\frac{8r^2}{a_0^2}-\frac{r^3}{a_0^3}\right)$$

Plotting this function for the derivative gives the figure below.

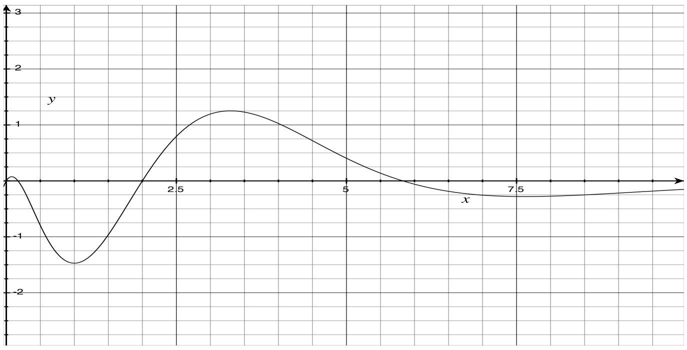

FIGURE 1. Plot of $\frac{dP_{2,0}(r)}{dr}$, x-axis in units of a_0.

From this figure we can tell that there are two maximum points, one at about $.1715a_0$ and one at about $5.8283a_0$. The other zeros are not maximum because maximum values can only occur where the derivative changes from positive to negative. Plugging these values into the initial function for $P_{2,0}(r)$ gives:

$$P_{2,0}(.1715) = \left[.1715^2\left(\frac{1}{2}\right)^3(2-.1715)^2 e^{-.1715}\right] = .0104a_0$$

$$P_{2,0}(5.8283) = \left[5.8283^2\left(\frac{1}{2}\right)^3(2-5.8283)^2 e^{-5.8283}\right] = .1832a_0$$

Therefore the most probable position for an electron in the $2s$ state for hydrogen is about $5.8a_0$.

Part (b) Since $R_{n,n-1} = Kr^{n-1}\exp(-r/na_0)$, for some proportionality constant K, for states of maximum orbital angular momentum, $l = n-1$, the most probable distance of the electron from the nucleus is given by the maximum of:

$$\frac{d}{dr}\left[r^2\left|R_{n,n-1}\right|^2\right] = \frac{d}{dr}\left[r^2K^2r^{2n-2}\exp(-2r/na_0)\right] = \frac{d}{dr}\left[K^2r^{2n}\exp(-2r/na_0)\right]$$

$$= K^2\left[2nr^{2n-1}e^{-2r/na_0} - r^{2n}\frac{2}{na_0}e^{-2r/na_0}\right] = 2K^2r^{2n-1}e^{-2r/na_0}\left[n-\frac{r}{na_0}\right]$$

From this it is easy to see that the maximum will occur at $r = n^2a_0$, it is known to be a maximum because $\lim_{r\to n^2a_0^-} P_{n,n-1}$ is positive and $\lim_{r\to n^2a_0^+} P_{n,n-1}$ is negative.

Part(c) The probability for finding an electron in the region within an angle of ±30° from the $x-y$ plane for the states:

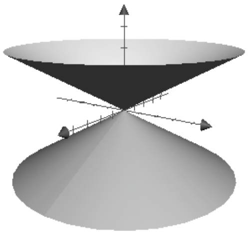

FIGURE 2. Region $\pi/3 \leq \theta \leq 2\pi/3$

(i) With $\psi_{2,0,0}(r,\theta,\phi) = \frac{1}{2\sqrt{\pi}}\left(\frac{Z}{2a_0}\right)^{3/2}\left(2-\frac{Zr}{a_0}\right)e^{-Zr/2a_0}$ the probability of finding an electron in the given region is:

$$\begin{aligned}
P(r,\theta,\phi) \quad &= \int_0^\infty \int_0^{2\pi} \int_{\pi/3}^{2\pi/3} \left| \frac{1}{2\sqrt{\pi}}\left(\frac{Z}{2a_0}\right)^{3/2}\left(2-\frac{Zr}{a_0}\right)e^{-Zr/2a_0}\right|^2 r^2 \sin\theta d\phi dr \\
&= \int_0^\infty \int_0^{2\pi} \int_{\pi/3}^{2\pi/3} \frac{r^2}{4\pi}\left(\frac{1}{2a_0}\right)^3\left(2-\frac{r}{a_0}\right)^2 e^{-r/a_0}\sin\theta d\theta d\phi dr \\
&= \int_0^\infty \int_0^{2\pi} \frac{r^2}{4\pi}\left(\frac{1}{2a_0}\right)^3\left(2-\frac{r}{a_0}\right)^2 e^{-r/a_0}\cos\theta\Bigg|_{\theta=\pi/3}^{\theta=2\pi/3} d\phi dr \\
&= \int_0^\infty \int_0^{2\pi} \frac{r^2}{4\pi}\left(\frac{1}{2a_0}\right)^3\left(2-\frac{r}{a_0}\right)^2 e^{-r/a_0}\, d\phi dr \\
&= \int_0^\infty \frac{\phi r^2}{4\pi}\left(\frac{1}{2a_0}\right)^3\left(2-\frac{r}{a_0}\right)^2 e^{-r/a_0}\Bigg|_{\phi=0}^{\phi=2\pi} dr \\
&= \int_0^\infty \frac{r^2}{2}\left(\frac{1}{2a_0}\right)^3\left(2-\frac{r}{a_0}\right)^2 e^{-r/a_0}dr \\
&= \int_0^\infty \frac{r^2}{2}\left(\frac{1}{2a_0}\right)^3\left(4-\frac{4r}{a_0}+\frac{r^2}{a_0^2}\right) e^{-r/a_0}dr \\
&= \int_0^\infty \left[\frac{r^2}{4a_0^3}-\frac{r^3}{4a_0^3}+\frac{r^4}{16a_0^5}\right] e^{-r/a_0}dr
\end{aligned}$$

This gives: $\int_0^\infty \frac{r^2}{4a_0^3}e^{-r/a_0}dr - \int_0^\infty \frac{r^3}{4a_0^4}e^{-r/a_0}dr + \int_0^\infty \frac{r^4}{16a_0^5}e^{-r/a_0}dr.$

By using the fact that $\int_0^\infty r^n e^{-ax} = \frac{n!}{a^{n+1}}$ for integral values of n:

$$\frac{1}{4a_0^3}\frac{2!}{a_0^{-3}} - \frac{1}{4a_0^4}\frac{3!}{a_0^{-4}} + \frac{1}{16a_0^5}\frac{4!}{a_0^{-5}} = \frac{1}{2} - \frac{3}{2} + \frac{24}{16} = \boxed{\frac{1}{2}}$$

(ii) With $\psi_{2,1,0}(r,\theta,\phi)=\frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta\left(\frac{Z}{2a_0}\right)^{3/2}\left(2-\frac{Zr}{a_0}\right)e^{-Zr/2a_0}$

$$\begin{aligned}
P_{2,1,0}(r,\theta,\phi) &= \int_0^\infty\int_0^{2\pi}\int_{\pi/3}^{2\pi/3}\left|\frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta\left(\frac{Z}{2a_0}\right)^{3/2}\left(2-\frac{Zr}{a_0}\right)e^{-Zr/2a_0}\right|^2 r^2\sin\theta d\theta d\phi dr \\
&= \int_0^\infty\int_0^{2\pi}\int_{\pi/3}^{2\pi/3}\frac{3}{4\pi}\cos^2\theta\sin\theta\left(\frac{1}{2a_0}\right)^3\left(2-\frac{r}{a_0}\right)^2 e^{-r/a_0}r^2 d\theta d\phi dr \\
&= \int_0^\infty\int_0^{2\pi}\frac{3}{4\pi}\left\{\frac{-1}{3}\cos^3\theta\Big|_{\pi/3}^{2\pi/3}\right\}\left(\frac{1}{2a_0}\right)^3\left(2-\frac{r}{a_0}\right)^2 e^{-r/a_0}r^2 d\phi dr \\
&= \int_0^\infty\int_0^{2\pi}\frac{3}{4\pi}\left\{\frac{1}{3}\left(\cos^3(2\pi/3)-\cos^3(\pi/3)\right)\right\}\left(\frac{1}{2a_0}\right)^3\left(2-\frac{r}{a_0}\right)^2 e^{-r/a_0}r^2 d\phi dr \\
&= \int_0^\infty\int_0^{2\pi}\frac{3}{4\pi}\left\{\frac{-1}{3}\left(\frac{1}{8}+\frac{1}{8}\right)\right\}\left(\frac{1}{2a_0}\right)^3\left(2-\frac{r}{a_0}\right)^2 e^{-r/a_0}r^2 d\phi dr \\
&= \int_0^\infty\int_0^{2\pi}\frac{3}{4\pi}\{1/12\}\left(\frac{1}{2a_0}\right)^3\left(2-\frac{r}{a_0}\right)^2 e^{-r/a_0}r^2 d\phi dr \\
&= \int_0^\infty\{\phi|_0^{2\pi}\}\frac{1}{16\pi}\left(\frac{1}{2a_0}\right)^3\left(2-\frac{r}{a_0}\right)^2 e^{-r/a_0}r^2 dr \\
&= \int_0^\infty\{2\pi\}\frac{1}{16\pi}\left(\frac{1}{2a_0}\right)^3\left(2-\frac{r}{a_0}\right)^2 e^{-r/a_0}r^2 dr \\
&= \int_0^\infty\left(\frac{1}{64a_0^3}\right)\left(4-\frac{4r}{a_0}+\frac{r^2}{a_0^2}\right)e^{-r/a_0}r^2 dr \\
&= \int_0^\infty\left(\frac{r^2}{16a_0^3}-\frac{r^3}{16a_0^4}+\frac{r^4}{64a_0^5}\right)e^{-r/a_0}dr \\
&= \int_0^\infty\frac{r^2}{16a_0^3}e^{-r/a_0}dr-\int_0^\infty\frac{r^3}{16a_0^4}e^{-r/a_0}dr+\int_0^\infty\frac{r^4}{64a_0^5}e^{-r/a_0}dr \\
&= \text{(As above) }\frac{2!}{16}-\frac{3!}{16}+\frac{4!}{64}=\frac{1}{8}-\frac{3}{8}+\frac{24}{64}=\boxed{\frac{1}{8}}
\end{aligned}$$

(iii) With $\psi_{2,1,\pm1}(r,\theta,\phi) = \mp\frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta e^{\pm i\theta}\left(\frac{Z}{2a_0}\right)^{3/2}\left(2-\frac{Zr}{a_0}\right)e^{-Zr/2a_0}$

$$\begin{aligned}
P_{2,1,\pm1}(r,\theta,\phi) &= \int_0^\infty\int_0^{2\pi}\int_{\pi/3}^{2\pi/3}\left|\mp\frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta e^{\pm i\theta}\left(\frac{Z}{2a_0}\right)^{3/2}\left(2-\frac{Zr}{a_0}\right)e^{-Zr/2a_0}\right|^2 r^2\sin\theta d\theta d\phi dr \\
&= \int_0^\infty\int_0^{2\pi}\int_{\pi/3}^{2\pi/3}\frac{3}{8\pi}\sin^2\theta\left(\frac{1}{8a_0^3}\right)\left(4-\frac{4r}{a_0}+\frac{r^2}{a_0^2}\right)e^{-r/a_0}r^2\sin\theta d\theta d\phi dr \\
&= \frac{3}{64\pi}\int_0^\infty\int_0^{2\pi}\left\{\int_{\pi/3}^{2\pi/3}\sin^3\theta d\theta\right\}\left(\frac{4^2}{a_0^3}-\frac{4r^3}{a_0^5}+\frac{r^4}{a_0^5}\right)e^{-r/a_0}d\phi dr \\
&= \frac{3}{64\pi}\int_0^\infty\int_0^{2\pi}\left\{\int_{\pi/3}^{2\pi/3}\sin\theta\left(1-\cos^2\theta\right)d\theta\right\}\left(\frac{4r^2}{a_0^3}-\frac{4r^3}{a_0^5}+\frac{r^4}{a_0^5}\right)e^{-r/a_0}d\phi dr \\
&= \frac{3}{64\pi}\int_0^\infty\int_0^{2\pi}\left\{\int_{\pi/3}^{2\pi/3}\left(\sin\theta-\cos^2\theta\sin\theta\right)d\theta\right\}\left(\frac{4r^2}{a_0^3}-\frac{4r^3}{a_0^5}+\frac{r^4}{a_0^5}\right)e^{-r/a_0}d\phi dr \\
&= \frac{3}{64\pi}\int_0^\infty\int_0^{2\pi}\left\{\left(-\cos\theta+\frac{1}{3}\cos^3\theta\right)_{\theta=\pi/3}^{\theta=2\pi/3}\right\}\left(\frac{4r^2}{a_0^3}-\frac{4r^3}{a_0^5}+\frac{r^4}{a_0^5}\right)e^{-r/a_0}d\phi dr \\
&= \frac{3}{64\pi}\int_0^\infty(\phi)_{\phi=0}^{\phi=2\pi}\left\{1-\frac{1}{12}\right\}\left(\frac{4r^2}{a_0^3}-\frac{4r^3}{a_0^5}+\frac{r^4}{a_0^5}\right)e^{-r/a_0}dr \\
&= \frac{3}{32}\int_0^\infty\left\{\frac{11}{12}\right\}\left(\frac{4r^2}{a_0^3}-\frac{4r^3}{a_0^5}+\frac{r^4}{a_0^5}\right)e^{-r/a_0}dr \\
&= \frac{33}{32\cdot12}\left[\int_0^\infty\frac{4r^2}{a_0^3}e^{-r/a_0}dr-\int_0^\infty\frac{4r^3}{a_0^5}e^{-r/a_0}dr+\int_0^\infty\frac{r^4}{a_0^5}e^{-r/a_0}dr\right] \\
&= \text{As above this simplifies to: } \tfrac{33}{32\cdot12}\left[4\cdot2!-4\cdot3!+4!\right]=\boxed{\frac{11}{16}}
\end{aligned}$$

As expected from a spherically symmetric distribution, $\psi_{2,0,0}$ had a 50% chance of being in a region that was 1/2 the total space. The other two states showed spherically asymmetric distributions, with $\psi_{2,1,0}$ tending to lie along the z axis, and $\psi_{2,1,\pm1}$ tending to be nearer to the $x-y$ plane. This is what we would expect from what we have seen so far of s and p orbitals.

Question 3:

Using the fact that:

$$\langle r\rangle_{n,l} = \int_0^\infty rP_{n,l}(r)dr = \frac{1}{2}a_0\left[3n^2-l(l+1)\right]$$

$$\text{and } \langle r^2\rangle_{n,l} = \int_0^\infty r^2P_{n,l}(r)dr = \frac{1}{2}n^2a_0^2\left[5n^2+1-3l(l+1)\right]$$

The expression $\dfrac{(\Delta r)_{n,l=n-1}}{\langle r\rangle_{n,l=n-1}} = \dfrac{\sqrt{\langle r^2\rangle_{n,l=n-1}-\langle r\rangle_{n,l=n-1}^2}}{\langle r\rangle_{n,l=n-1}}$ becomes:

$$\begin{aligned}
\frac{(\Delta r)_{n,l=n-1}}{\langle r\rangle_{n,l=n-1}} &= \frac{\sqrt{\frac{1}{2}n^2a_0^2\left[5n^2+1-3l(l+1)\right]-\left(\frac{1}{2}a_0\left[3n^2-l(l+1)\right]\right)^2}}{\frac{1}{2}a_0\left[3n^2-l(l+1)\right]} \\
&= \frac{\sqrt{\frac{1}{2}n^2a_0^2\left[5n^2+1-3l(l+1)\right]-\frac{1}{4}a_0^2\left[9n^4-6l(n^2)(l+1)+l^2(l+1)^2\right]}}{\frac{1}{2}a_0\left[3n^2-l(l+1)\right]}
\end{aligned}$$

$$\begin{aligned}
\frac{(\Delta r)_{n,l=n-1}}{\langle r\rangle_{n,l=n-1}} &= \frac{\sqrt{2n^2\left[5n^2+1-3l(l+1)\right]-\left[9n^4-6l(n^2)(l+1)+l^2(l+1)^2\right]}}{\left[3n^2-l(l+1)\right]} \\
&= \frac{\sqrt{\left[10n^4+2n^2-6n^2l(l+1)\right]-\left[9n^4-6l(n^2)(l+1)+l^2(l+1)^2\right]}}{\left[3n^2-l(l+1)\right]} \\
&= \frac{\sqrt{10n^4-9n^4+2n^2-6n^2l(l+1)+6n^2l(l+1)-l^2(l+1)^2}}{\left[3n^2-l(l+1)\right]} \\
&= \frac{\sqrt{n^4+2n^2-l^2(l+1)^2}}{\left[3n^2-l(l+1)\right]}\ (\text{with } l=n-1) = \frac{\sqrt{n^4+2n^2-(n-1)^2n^2}}{\left[3n^2-n-1(n)\right]} \\
&= \frac{\sqrt{n^4+2n^2-(n^2-2n+1)n^2}}{3n^2-n^2+n} = \frac{\sqrt{n^4+2n^2-(n^4-2n^3+n^2)}}{2n^2+n} \\
&= \frac{\sqrt{2n^3+n^2}}{2n^2+n} = \frac{\sqrt{\frac{1}{n}+\frac{1}{n^2}}}{2+\frac{1}{n}} \ \therefore\ \lim_{n\to\infty}\frac{(\Delta r)_{n,l=n-1}}{\langle r\rangle_{n,l=n-1}} = \lim_{n\to\infty}\frac{\sqrt{\frac{1}{n}+\frac{1}{n^2}}}{2+\frac{1}{n}} = 0
\end{aligned}$$

This result implies that the higher the orbital quantum number the lower the uncertainty in the mean distance. This means that for electrons in higher energy states their position can be known more accurately