Assignment 5

Solution Key

① a$_1$)
$$\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty}\psi^*_{n'\ell'm'}\psi_{n\ell m}\, r^2\sin\theta\, dr\, d\theta\, d\phi = \delta^n_{n'}\delta^\ell_{\ell'}\delta^m_{m'}$$

i) $$\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty}\psi^*_{100}\psi_{200}\, r^2\sin\theta\, dr\, d\theta\, d\phi$$

$$= \frac{1}{4\sqrt{2}\,\pi}\left(\frac{Z}{a_0}\right)^3\int_0^{\infty} r^2\left(2-\frac{Zr}{a_0}\right)e^{-3Zr/2a_0}\,dr$$

$$\times \int_0^{\pi}\sin\theta\, d\theta \int_0^{2\pi} d\phi$$

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

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

$$= \frac{1}{\sqrt{2}}\left(\frac{Z}{a_0}\right)^3\left[2\left(\frac{2}{(3Z)^3}(2a_0)^3\right) - \frac{Z}{a_0}\left(\frac{2\cdot 3}{(3Z)^4}(2a_0)^4\right)\right]$$

$$= \frac{1}{\sqrt{2}}\left(\frac{Z}{a_0}\right)^3\left[\frac{32}{27}\frac{a_0^3}{Z^3} - \frac{32\, a_0^3}{27\, Z^3}\right]$$

$$= \varnothing.$$

ii) $$\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} \psi_{200}^{*}\,\psi_{210}\, r^2 \sin\theta \, dr\, d\theta\, d\phi$$

$$\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} \frac{1}{32\pi}\left(\frac{Z}{a_0}\right)^3\left(2-\frac{Zr}{a_0}\right)\frac{Zr}{a_0}\, e^{-Zr/a_0}\, r^2 \cos\theta \sin\theta \, dr\, d\theta\, d\phi$$

$$\frac{1}{32\pi}\left(\frac{Z}{a_0}\right)^4 \int_0^{\infty}\left(2-\frac{Zr}{a_0}\right) r^3 e^{-Zr/a_0}\, dr \int_0^{\pi} \cos\theta \sin\theta \, d\theta \int_0^{2\pi} d\phi$$

$$\int_0^{\pi} \cos\theta \sin\theta \, d\theta = \emptyset$$

$= \emptyset$.

iii) $$\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} \frac{1}{32\pi\sqrt{2}}\left(\frac{Z}{a_0}\right)^5 r^4 e^{-Zr/a_0} \cos\theta \sin^2\theta \, dr\, d\theta\, d\phi$$

$$= \frac{1}{32\pi\sqrt{2}}\left(\frac{Z}{a_0}\right)^5 \int_0^{\infty} r^4 e^{-Zr/a_0}\, dr \int_0^{\pi} \cos\theta \sin^2\theta \, d\theta \int_0^{2\pi} d\phi$$

$$\int_0^{\pi} \cos\theta \sin^2\theta \, d\theta = \emptyset.$$

$= \emptyset$.

b.) $\Psi_2 = \frac{1}{2}\left(\psi_{200} + \psi_{210} + \psi_{211} + \psi_{21-1}\right)$

$$P_2 = \frac{1}{4}\left(\psi_{200}^*\psi_{200} + \psi_{210}^*\psi_{210} + \psi_{211}^*\psi_{211} + \psi_{21-1}^*\psi_{21-1}\right)$$

$$\psi_{200}^*\psi_{200} = \frac{1}{32\pi}\left(\frac{Z}{a_0}\right)^3\left(2 - \frac{Zr}{a_0}\right)^2 e^{-Zr/a_0}$$

$$\psi_{210}^*\psi_{210} = \frac{1}{32\pi}\left(\frac{Z}{a_0}\right)^5 r^2 e^{-Zr/a_0}\cos^2\theta$$

$$\psi_{21\pm1}^*\psi_{21\pm1} = \frac{1}{64\pi}\left(\frac{Z}{a_0}\right)^5 r^2 e^{-Zr/a_0}\sin^2\theta$$

$$P_2 = \frac{1}{4}\left(\frac{1}{32\pi}\left(\frac{Z}{a_0}\right)^3 e^{-Zr/a_0}\left[\left(2-\frac{Zr}{a_0}\right)^2 + \left(\frac{Z}{a_0}\right)^2\left(\cos^2\theta + \frac{1}{2}\sin^2\theta + \frac{1}{2}\sin^2\theta\right)\right]\right)$$

$$= \frac{1}{4}\left(\frac{1}{32\pi}\left(\frac{Z}{a_0}\right)^3 e^{-Zr/a_0}\left[\left(2-\frac{Zr}{a_0}\right)^2 + \left(\frac{Z}{a_0}\right)^2\right]\right)$$

$$P_2 = \frac{1}{128\pi}\left(\frac{Z}{a_0}\right)^3 e^{-Zr/a_0}\left[\left(2-\frac{Zr}{a_0}\right)^2 + \left(\frac{Z}{a_0}\right)^2\right].$$

6.) There are 9 states that are in superposition.

$$\Psi = \frac{1}{3}\left(\psi_{300} + \psi_{310} + \psi_{311} + \psi_{31-1} + \psi_{320} + \psi_{321} + \psi_{32-1} + \psi_{322} + \psi_{32-2}\right)$$

$$P_3 = \frac{1}{9}\Big(\psi_{300}^*\psi_{300} + \psi_{310}^*\psi_{310} + \psi_{311}^*\psi_{311} + \psi_{31-1}^*\psi_{31-1} + \psi_{321}^*\psi_{321} + \psi_{32-1}^*\psi_{32-1}$$
$$\psi_{320}^*\psi_{320} + \psi_{32-2}^*\psi_{32-2} + \psi_{322}^*\psi_{322}\Big)$$

$$P_{300} = \psi_{300}^*\psi_{300} = \frac{1}{81^2(\pi)}\frac{Z^3}{a_0^3}\left(27 - 18\frac{Zr}{a_0} + 2\frac{Z^2r^2}{a_0^2}\right)^2 e^{-2Zr/3a_0}$$

$$P_{310} = \psi_{310}^*\psi_{310} = \frac{2}{81^2(\pi)}\left(\frac{Z}{a_0}\right)^5\left(6 - \frac{Zr}{a_0}\right)^2 r^2 e^{-2Zr/3a_0}\cos^2\theta$$

Define $R_{31} = \frac{1}{81^2\pi}\left(\frac{Z}{a_0}\right)^5\left(6 - \frac{Zr}{a_0}\right)^2 r^2 e^{-2Zr/3a_0}$

Such that $P_{310} = 2R_{31}\cos^2\theta$.

$$P_{31\pm1} = \psi_{31\pm1}^*\psi_{31\pm1} = \frac{1}{81^2\pi}\left(\frac{Z}{a_0}\right)^5\left(6 - \frac{Zr}{a_0}\right)r^2e^{-2Zr/a_0}\sin^2\theta$$

$$= R_{31}\sin^2\theta.$$

$$P_{320} = \psi_{320}^*\psi_{320} = \frac{1}{6\cdot 81^2\pi}\left(\frac{Z}{a_0}\right)^3\frac{Z^4}{a_0^4}r^4e^{-2Zr/3a_0}(3\cos^2\theta - 1)^2$$

Define $R_{32} = \frac{1}{81^2\pi}\left(\frac{Z}{a_0}\right)^7 r^4 e^{-2Zr/3a_0}$

$$P_{320} = \frac{1}{6}R_{32}(3\cos^2\theta - 1)^2$$

$$P_{32\pm1} = \psi^*_{32\pm1}\psi_{32\pm1} = R_{32}\sin^2\theta\cos^2\theta$$

$$P_{32\pm2} = \psi^*_{32\pm2}\psi_{32\pm2} = \frac{1}{4}R_{32}\sin^4\theta$$

Put it all together:

$$P_3 = \frac{1}{9}\Big(P_{300} + 2R_{31}\cos^2\theta + 2R_{31}\sin^2\theta + \frac{1}{6}R_{32}(3\cos^2\theta-1)^2 + 2R_{32}\sin^2\theta\cos^2\theta + 2\cdot\frac{R_{32}}{4}\sin^4\theta\Big)$$

$$P_3 = \frac{1}{9}\Big(P_{300} + 2R_{31} + \frac{R_{32}}{6}\underbrace{\Big[(3\cos^2\theta-1)^2 + 12\sin^2\theta\cos^2\theta + 3\sin^4\theta\Big]}_{\text{eqn } A}$$

$$A = (3\cos^2\theta-1)^2 + 12\sin^2\theta\cos^2\theta + 3\sin^4\theta$$

$$= 9\cos^4\theta - 6\cos^2\theta + 1 + 12\sin^2\theta\cos^2\theta + 3\sin^4\theta$$

$$1 = (\cos^2\theta + \sin^2\theta)^2 = \cos^4\theta + \sin^4\theta + 2\sin^2\theta\cos^2\theta$$

$$3 = 3\cos^4\theta + 3\sin^4\theta + 6\sin^2\theta\cos^2\theta$$

$$A = 6\cos^4\theta - 6\cos^2\theta + 1 + 3 + 6\underset{\substack{\downarrow \\ 1-\cos^2\theta}}{\sin^2\theta}\cos^2\theta$$

$$= 6\cos^4\theta - 6\cos^2\theta + 4 + 6\cos^2\theta - 6\cos^4\theta$$

$$= 4$$

so $$P_3 = \frac{1}{9}\Big(P_{300} + 2R_{31} + \frac{4R_{32}}{6}\Big)$$

② a.) For $n=2$, $l=1$, all wavefcns have the same radial part regardless of m.

$$P_{21}(r) = r^2 R_{nl}^*(r) R_{nl}(r)$$

$$R_{nl}(r) = C r e^{-Zr/2a_0} \qquad C = \text{constant.}$$

$$P_{21}(r) = C r^4 e^{-Zr/a_0}$$

At maximum $\frac{dP_{21}}{dr} = \emptyset$

$$C\left[4r^3 e^{-Zr/a_0} - \left(\frac{Z}{a_0}\right) r^4 e^{-Zr/a_0}\right]_{r=r_m} = \emptyset$$

2 solutions: $r_m = \emptyset$ is a solution but this is a minimum.
Aside from this trivial solution we also have

$$4 - \left(\frac{Z}{a_0}\right) r_m = \emptyset$$

$$r_m = \frac{4a_0}{Z} = 4a_0 \text{ if } Z = 1.$$

b.) For the full expectation value of r, we have to consider the results for all 3 eigenfcns associated with m, namely $m = -1, 0, +1$

In each case we have

$$\langle r \rangle = \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} \left(R_{n\ell}^*(r)\, r\, R_{n\ell}(r)\right) r^2 dr \left(\Theta_{\ell m}^* \Theta_{\ell m} \sin\theta\right) d\theta$$

$$\times \left(\Phi_m^* \Phi_m\right) d\phi$$

$\int_0^{2\pi} \Phi_m^* \Phi_m \, d\phi = 2\pi$ always, regardless of m.

For $\ell = 1$, $m = 0$: $\int_0^{\pi} \Theta_{\ell m}^* \Theta_{\ell m} \sin\theta \, d\theta = \int_0^{\pi} \cos^2\theta \sin\theta \, d\theta$

$$= -\frac{1}{3}\cos^3\theta \Big|_0^{\pi} = \frac{2}{3}$$

For $\ell = 1$, $m = \pm 1$: $\int_0^{\pi} \Theta_{\ell m}^* \Theta_{\ell m} \sin\theta \, d\theta = \int_0^{\pi} \sin^3\theta \, d\theta = -\frac{1}{3}\cos\theta\left(\sin^2\theta + 2\right)$

$$= -\frac{1}{3}\left[\cos\theta \sin^2\theta + 2\cos\theta\right]_0^{\pi}$$

$$= \frac{4}{3}$$

The radial parts of the wavefcn have different normalization and differ a bit for each m.

For $n=2,\ l=1,\ m=0$:

$$\int_0^\infty \left(\frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \left(\frac{Zr}{a_0}\right) e^{-Zr/2a_0} \right)^2 r^3\, dr$$

$$= \frac{1}{16(2\pi)} \left(\frac{Z}{a_0}\right)^5 \underbrace{\int_0^\infty r^5 e^{-Zr/a_0}\, dr}_{\frac{5!}{\left(\frac{Z}{a_0}\right)^6} = \frac{5!\, a_0^6}{Z^6}}$$

$$= \frac{1}{32\pi} \left(\frac{Z}{a_0}\right)^5 \left(\frac{a_0}{Z}\right)^6 5!$$

$$= \frac{1}{32\pi} \frac{a_0}{Z} 5!$$

$n=2,\ l=1\ \ m=\pm 1$:

$$\int_0^\infty \left(\frac{1}{8\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \left(\frac{Zr}{a_0}\right) e^{-Zr/2a_0} \right)^2 r^3\, dr$$

$$= \frac{1}{64\pi} \left(\frac{Z}{a_0}\right)^3 \int_0^\infty \left(\frac{Zr}{a_0}\right)^2 e^{-Zr/a_0}\, r^3\, dr$$

$$= \frac{1}{64\pi} \left(\frac{Z}{a_0}\right)^5 \int_0^\infty r^5 e^{-Zr/a_0}\, dr = \frac{1}{64\pi} \left(\frac{Z}{a_0}\right)^5 \frac{5!\, a_0^6}{Z^6}$$

$$= \frac{1}{64\pi} \frac{a_0}{Z} 5!$$

Combine these results:

$$\langle r_{210} \rangle = \underbrace{\frac{1}{32\pi} \frac{a_0}{Z} 5!}_{\text{radial}} \cdot \underset{\uparrow \atop \theta\,\text{part}}{\frac{2}{3}} \cdot \underset{\uparrow \atop \phi\,\text{part}}{2\pi}$$

$$= \frac{5a_0}{Z}$$

$$\langle r_{21\pm1} \rangle = \frac{1}{64\pi} \frac{a_0}{Z} 5! \cdot \frac{4}{3} \cdot 2\pi$$

$$= \frac{5a_0}{Z}$$

c.) So why does $\langle r_{210} \rangle = \langle r_{21\pm1} \rangle \neq r_m$?

The probability distribution given by the Schrödinger equation has a long tail. This skews the values of $\langle r \rangle$ to higher radii on average.

③ a.) We want $\langle V \rangle$ for ψ_{200}, ie $n=2$, $l=0$, $m=0$
In this state we only need to consider one eigenfunction ψ_{200}.

$$\psi_{200} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2-\frac{Zr}{a_0}\right)e^{-Zr/2a_0}$$

$$\langle V \rangle = \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty}\left[\frac{1}{32\pi}\left(\frac{Z}{a_0}\right)^3\left(2-\frac{Zr}{a_0}\right)^2 e^{-Zr/a_0}\right]\left(\frac{-Ze^2}{4\pi\varepsilon_0 r}\right)r^2\sin\theta\, dr\ldots$$

$$= \frac{1}{32\pi}\left(\frac{Z}{a_0}\right)^3\int_0^{\infty}\left(2-\frac{Zr}{a_0}\right)^2 e^{-Zr/a_0}\, r\,dr\int_0^{\pi}\sin\theta\, d\theta\int_0^{2\pi}d\phi$$

$$= \frac{1}{32\pi}\left(\frac{Z}{a_0}\right)^3\left(\frac{-Ze^2}{4\pi\varepsilon_0}\right)\cdot 4\pi\cdot\left[\int_0^{\infty}\left(4-4\frac{Zr}{a_0}+\frac{Z^2r^2}{a_0^2}\right)r\, e^{-Zr/a_0}dr\right]$$

$$= \frac{1}{8}\left(\frac{Z}{a_0}\right)^3\left(\frac{-Ze^2}{4\pi\varepsilon_0}\right)\left[4\int_0^{\infty}r e^{-Zr/a_0}dr - \frac{4Z}{a_0}\int_0^{\infty}r^2 e^{-Zr/a_0}dr + \frac{Z^2}{a_0^2}\int_0^{\infty}r^3 e^{-Zr/a_0}dr\right]$$

$$= \frac{1}{8}\left(\frac{Z}{a_0}\right)^3\left(\frac{-Ze^2}{4\pi\varepsilon_0}\right)\left[4\cdot\frac{a_0^2}{Z^2} - \frac{4Z}{a_0}\left(2\frac{a_0^3}{Z^3}\right) + \frac{Z^2}{a_0^2}\left(\frac{6a_0^4}{Z^4}\right)\right]$$

$$= \frac{1}{8}\left(\frac{Z}{a_0}\right)^3\left(\frac{-Ze^2}{4\pi\varepsilon_0}\right)\left[\frac{4a_0^2}{Z^2} - 8\frac{a_0^2}{Z^2} + 6\frac{a_0^2}{Z^2}\right]$$

$$= \frac{1}{8}\left(\frac{Z}{a_0}\right)^3\left(\frac{a_0}{Z}\right)^2\left(\frac{-Ze^2}{4\pi\varepsilon_0}\right)\left[4-8+6\right] = \frac{1}{4}\left(\frac{-Z^2e^2}{4\pi\varepsilon_0 a_0}\right)$$

$a_0 = \dfrac{4\pi\varepsilon_0\hbar^2}{\mu e^2}$ so $\langle V \rangle = -\dfrac{\mu Z^2 e^4}{4(4\pi\varepsilon_0)^2\hbar^2} = 2E_2$

b.) In the $n=2$, $l=1$ state m can take on the values $m=-1, 0, 1$. We will consider all 3 of these cases.

For $m=0$:

$$\langle V \rangle = \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} \frac{1}{32\pi}\left(\frac{Z}{a_0}\right)^5 \left(\frac{-Ze^2}{4\pi\varepsilon_0}\right) r^3 e^{-Zr/a_0} \cos^2\theta \sin\theta \, dr\, d\theta\, d\phi$$

$$= \frac{1}{32\pi}\left(\frac{Z}{a_0}\right)^5\left(\frac{-Ze^2}{4\pi\varepsilon_0}\right) \underbrace{\int_0^{\infty} r^3 e^{-Zr/a_0}\,dr}_{\frac{3!}{(Z/a_0)^4}} \underbrace{\int_0^{\pi}\cos^2\theta\sin\theta\,d\theta}_{=2/3} \underbrace{\int_0^{2\pi} d\phi}_{2\pi}$$

$$= \frac{1}{32\pi}\left(\frac{Z}{a_0}\right)^5\left(\frac{-Ze^2}{4\pi\varepsilon_0}\right)\frac{6}{Z^4}a_0^4 \cdot \frac{2}{3}\cdot 2\pi$$

$$= \frac{1}{4}\left(\frac{Z}{a_0}\right)\left(\frac{-Ze^2}{4\pi\varepsilon_0}\right)$$

$$= \frac{-Z^2e^2}{4(4\pi\varepsilon_0)a_0} = \frac{-Z^2e^4}{4(4\pi\varepsilon_0)^2\hbar^2}$$

$$= 2E_2$$

For $n=2,\ \ell=1,\ m=\pm 1$

$$\langle V\rangle = \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} \frac{1}{64\pi}\left(\frac{Z}{a_0}\right)^5 r^2 e^{-Zr/a_0}\sin^2\theta\left(\frac{-Ze^2}{4\pi\varepsilon_0 r}\right) r^2\sin\theta\, dr\, d\theta\, d\phi$$

$$= \frac{1}{64\pi}\left(\frac{Z}{a_0}\right)^5\left(\frac{-Ze^2}{4\pi\varepsilon_0}\right)\underbrace{\int_0^{\infty} r^3 e^{-Zr/a_0}\,dr}_{\frac{3!}{(Z/a_0)^4}}\ \underbrace{\int_0^{\pi}\sin^3\theta\, d\theta}_{\frac{4}{3}}\ \underbrace{\int_0^{2\pi} d\phi}_{2\pi}$$

$$= \frac{1}{64\pi}\left(\frac{Z}{a_0}\right)^5\frac{a_0^4}{Z^4}\left(\frac{-Ze^2}{4\pi\varepsilon_0}\right) 6\cdot\frac{4}{3}\cdot 2\pi$$

$$= \frac{1}{4}\,\frac{Z}{a_0}\left(\frac{-Ze^2}{4\pi\varepsilon_0}\right)$$

$$= -\frac{\mu Z^2 e^4}{4(4\pi\varepsilon_0)^2\hbar^2}$$

$$\langle V\rangle = 2E_2$$

c.) In all these cases the Virial theorem is satisfied.

Due to degeneracy all E_n values are the same for a given n! So all Expectation value calculations for such a state must also be consistent which we observe,

$$\langle V\rangle = 2E_2.$$