Problem 4.15

(a) Find $\langle r \rangle$ and $\langle r^2 \rangle$ for an electron in the ground state of hydrogen. Express your answers in terms of the Bohr radius.

(b) Find $\langle x \rangle$ and $\langle x^2 \rangle$ for an electron in the ground state of hydrogen. *Hint*: This requires no new integration—note that $r^2 = x^2 + y^2 + z^2$, and exploit the symmetry of the ground state.

(c) Find $\langle x^2 \rangle$ in the state $n = 2$, $\ell = 1$, $m = 1$. *Hint*: this state is *not* symmetrical in x, y, z. Use $x = r \sin\theta \cos\phi$.

Solution

The wave function of an electron in the ground state of hydrogen is

$$\begin{aligned}\Psi_{100}(r,\theta,\phi,t) &= R_{10}(r)Y_0^0(\theta,\phi)T_1(t) \\ &= \left(\sqrt{\frac{4}{a_0^3}}\,e^{-r/a_0}\right)\left(\sqrt{\frac{1}{4\pi}}\right)e^{-iE_1t/\hbar} \\ &= \frac{1}{\sqrt{\pi a_0^3}}\,e^{-r/a_0}e^{-iE_1t/\hbar},\end{aligned}$$

and the wave function of an electron in the $n = 2$, $\ell = 1$, $m = 1$ state of hydrogen is

$$\begin{aligned}\Psi_{211}(r,\theta,\phi,t) &= R_{21}(r)Y_1^1(\theta,\phi)T_2(t) \\ &= \left[\frac{1}{2\sqrt{6a_0^3}}\left(\frac{r}{a_0}\right)e^{-r/(2a_0)}\right]\left(-\sqrt{\frac{3}{8\pi}}\sin\theta\,e^{i\phi}\right)e^{-iE_2t/\hbar} \\ &= -\frac{1}{8\sqrt{\pi a_0^5}}re^{-r/(2a_0)}\sin\theta\,e^{i\phi}e^{-iE_2t/\hbar}.\end{aligned}$$

Part (a)

Calculate the expectation value of r at time t for an electron in the ground state of hydrogen.

$$\begin{aligned}\langle r \rangle &= \langle \Psi_{100} \,|\, r \,|\, \Psi_{100} \rangle \\ &= \iiint\limits_{\text{all space}} \Psi_{100}^*(r,\theta,\phi,t)\, r\, \Psi_{100}(r,\theta,\phi,t)\, d\mathcal{V} \\ &= \int_0^\pi \int_0^{2\pi} \int_0^\infty \left(\frac{1}{\sqrt{\pi a_0^3}}\,e^{-r/a_0}e^{iE_1t/\hbar}\right) r \left(\frac{1}{\sqrt{\pi a_0^3}}\,e^{-r/a_0}e^{-iE_1t/\hbar}\right)(r^2\sin\theta\,dr\,d\phi\,d\theta) \\ &= \frac{1}{\pi a_0^3}\left(\int_0^\pi \sin\theta\,d\theta\right)\left(\int_0^{2\pi} d\phi\right)\left(\int_0^\infty r^3e^{-2r/a_0}\,dr\right) \\ &= \frac{1}{\pi a_0^3}(2)(2\pi)\int_0^\infty \frac{\partial^3}{\partial u^3}(-e^{-ur})\bigg|_{u=2/a_0}\,dr\end{aligned}$$

Pull the derivative in front of the integral and simplify.

$$\begin{aligned}
\langle r\rangle &= -\frac{4}{a_0^3}\frac{d^3}{du^3}\left(\int_0^\infty e^{-ur}\,dr\right)\bigg|_{u=2/a_0} \\
&= -\frac{4}{a_0^3}\frac{d^3}{du^3}\left(-\frac{1}{u}e^{-ur}\bigg|_0^\infty\right)\bigg|_{u=2/a_0} \\
&= -\frac{4}{a_0^3}\frac{d^3}{du^3}\left(\frac{1}{u}\right)\bigg|_{u=2/a_0} \\
&= -\frac{4}{a_0^3}\frac{d^2}{du^2}\left(-\frac{1}{u^2}\right)\bigg|_{u=2/a_0} \\
&= -\frac{4}{a_0^3}\frac{d}{du}\left(\frac{2}{u^3}\right)\bigg|_{u=2/a_0} \\
&= -\frac{4}{a_0^3}\left(-\frac{6}{u^4}\right)\bigg|_{u=2/a_0} \\
&= -\frac{4}{a_0^3}\left(-\frac{6a_0^4}{16}\right) \\
&= \frac{3}{2}a_0
\end{aligned}$$

Calculate the expectation value of r^2 at time t for an electron in the ground state of hydrogen.

$$\begin{aligned}
\langle r^2\rangle &= \langle \Psi_{100}\,|\,r^2\,|\,\Psi_{100}\rangle \\
&= \iiint\limits_{\text{all space}} \Psi_{100}^*(r,\theta,\phi,t)\,r^2\,\Psi_{100}(r,\theta,\phi,t)\,d\mathcal{V} \\
&= \int_0^\pi\int_0^{2\pi}\int_0^\infty \left(\frac{1}{\sqrt{\pi a_0^3}}\,e^{-r/a_0}e^{iE_1t/\hbar}\right) r^2 \left(\frac{1}{\sqrt{\pi a_0^3}}\,e^{-r/a_0}e^{-iE_1t/\hbar}\right)(r^2\sin\theta\,dr\,d\phi\,d\theta) \\
&= \frac{1}{\pi a_0^3}\left(\int_0^\pi \sin\theta\,d\theta\right)\left(\int_0^{2\pi} d\phi\right)\left(\int_0^\infty r^4 e^{-2r/a_0}\,dr\right) \\
&= \frac{1}{\pi a_0^3}(2)(2\pi)\int_0^\infty \frac{\partial^4}{\partial u^4}(e^{-ur})\bigg|_{u=2/a_0}\,dr \\
&= \frac{4}{a_0^3}\frac{d^4}{du^4}\left(\int_0^\infty e^{-ur}\,dr\right)\bigg|_{u=2/a_0} \\
&= \frac{4}{a_0^3}\frac{d^4}{du^4}\left(-\frac{1}{u}e^{-ur}\bigg|_0^\infty\right)\bigg|_{u=2/a_0} \\
&= \frac{4}{a_0^3}\frac{d^4}{du^4}\left(\frac{1}{u}\right)\bigg|_{u=2/a_0}
\end{aligned}$$

Evaluate the derivatives and then set $u = 2/a_0$.

$$\begin{aligned}
\langle r^2 \rangle &= \frac{4}{a_0^3}\frac{d^3}{du^3}\left(-\frac{1}{u^2}\right)\bigg|_{u=2/a_0} \\
&= \frac{4}{a_0^3}\frac{d^2}{du^2}\left(\frac{2}{u^3}\right)\bigg|_{u=2/a_0} \\
&= \frac{4}{a_0^3}\frac{d}{du}\left(-\frac{6}{u^4}\right)\bigg|_{u=2/a_0} \\
&= \frac{4}{a_0^3}\left(\frac{24}{u^5}\right)\bigg|_{u=2/a_0} \\
&= \frac{4}{a_0^3}\left(\frac{24a_0^5}{32}\right) \\
&= 3a_0^2
\end{aligned}$$

Part (b)

Calculate the expectation value of x at time t for an electron in the ground state of hydrogen.

$$\begin{aligned}
\langle x \rangle &= \langle \Psi_{100} \,|\, x \,|\, \Psi_{100} \rangle \\
&= \iiint\limits_{\text{all space}} \Psi_{100}^*(r,\theta,\phi,t)\, x\, \Psi_{100}(r,\theta,\phi,t)\, d\mathcal{V} \\
&= \int_0^\pi \int_0^{2\pi} \int_0^\infty \left(\frac{1}{\sqrt{\pi a_0^3}}\, e^{-r/a_0} e^{iE_1 t/\hbar}\right)(r\sin\theta\cos\phi)\left(\frac{1}{\sqrt{\pi a_0^3}}\, e^{-r/a_0} e^{-iE_1 t/\hbar}\right)(r^2 \sin\theta\, dr\, d\phi\, d\theta) \\
&= \frac{1}{\pi a_0^3}\left(\int_0^\pi \sin^2\theta\, d\theta\right)\left(\int_0^{2\pi} \cos\phi\, d\phi\right)\left(\int_0^\infty r^3 e^{-2r/a_0}\, dr\right) \\
&= \frac{1}{\pi a_0^3}\left(\int_0^\pi \sin^2\theta\, d\theta\right)(0)\left(\int_0^\infty r^3 e^{-2r/a_0}\, dr\right) \\
&= 0
\end{aligned}$$

Calculate the expectation value of x^2 at time t for an electron in the ground state of hydrogen.

$$\langle x^2 \rangle = \langle \Psi_{100} \,|\, x^2 \,|\, \Psi_{100} \rangle$$

$$= \iiint\limits_{\text{all space}} \Psi_{100}^*(r,\theta,\phi,t)\, x^2\, \Psi_{100}(r,\theta,\phi,t)\, d\mathcal{V}$$

$$= \int_0^\pi \int_0^{2\pi} \int_0^\infty \left(\frac{1}{\sqrt{\pi a_0^3}}\, e^{-r/a_0} e^{iE_1 t/\hbar} \right) (r \sin\theta \cos\phi)^2 \left(\frac{1}{\sqrt{\pi a_0^3}}\, e^{-r/a_0} e^{-iE_1 t/\hbar} \right) (r^2 \sin\theta\, dr\, d\phi\, d\theta)$$

$$= \int_0^\pi \int_0^{2\pi} \int_0^\infty \left(\frac{1}{\sqrt{\pi a_0^3}}\, e^{-r/a_0} e^{iE_1 t/\hbar} \right) (r^2 \sin^2\theta \cos^2\phi) \left(\frac{1}{\sqrt{\pi a_0^3}}\, e^{-r/a_0} e^{-iE_1 t/\hbar} \right) (r^2 \sin\theta\, dr\, d\phi\, d\theta)$$

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

$$= \frac{1}{\pi a_0^3} \left[\int_0^\pi (1 - \cos^2\theta) \sin\theta\, d\theta \right] \left[\int_0^{2\pi} \frac{1}{2}(1 + \cos 2\phi)\, d\phi \right] \left(\frac{24 a_0^5}{32} \right)$$

Make the following substitution in the first integral.

$$w = \cos\theta$$

$$dw = -\sin\theta\, d\theta \quad \rightarrow \quad -dw = \sin\theta\, d\theta$$

Therefore, since the first integrand is even,

$$\langle x^2 \rangle = \frac{1}{\pi a_0^3} \left[\int_{\cos 0}^{\cos\pi} (1 - w^2)(-dw) \right] \left[\frac{1}{2} \int_0^{2\pi} (1 + \cos 2\phi)\, d\phi \right] \left(\frac{24 a_0^5}{32} \right)$$

$$= \frac{1}{2\pi a_0^3} \left[-\int_1^{-1} (1 - w^2)\, dw \right] \left[\left(\phi + \frac{1}{2} \sin 2\phi \right) \Big|_0^{2\pi} \right] \left(\frac{24 a_0^5}{32} \right)$$

$$= \frac{1}{2\pi a_0^3} \left[\int_{-1}^1 (1 - w^2)\, dw \right] (2\pi) \left(\frac{24 a_0^5}{32} \right)$$

$$= \frac{1}{a_0^3} \left[2 \int_0^1 (1 - w^2)\, dw \right] \left(\frac{24 a_0^5}{32} \right)$$

$$= \frac{1}{a_0^3} \left[2 \left(w - \frac{w^3}{3} \right) \Big|_0^1 \right] \left(\frac{24 a_0^5}{32} \right)$$

$$= \frac{1}{a_0^3} \left[2 \left(1 - \frac{1^3}{3} \right) \right] \left(\frac{24 a_0^5}{32} \right)$$

$$= \frac{1}{a_0^3} \left(\frac{4}{3} \right) \left(\frac{3 a_0^5}{4} \right)$$

$$= a_0^2.$$

Part (c)

Calculate the expectation value of x^2 at time t for an electron in the $n = 2$, $\ell = 1$, $m = 1$ state of hydrogen.

$$\begin{aligned}
\langle x^2\rangle &= \langle \Psi_{211} \,|\, x^2 \,|\, \Psi_{211}\rangle \\
&= \iiint_{\text{all space}} \Psi^*_{211}(r,\theta,\phi,t)\, x^2\, \Psi_{211}(r,\theta,\phi,t)\, d\mathcal{V} \\
&= \int_0^\pi \int_0^{2\pi} \int_0^\infty \left[-\frac{1}{8\sqrt{\pi a_0^5}} r e^{-r/(2a_0)} \sin\theta\, e^{-i\phi} e^{iE_2t/\hbar}\right] (r\sin\theta\cos\phi)^2 \left[-\frac{1}{8\sqrt{\pi a_0^5}} r e^{-r/(2a_0)} \sin\theta\, e^{i\phi} e^{-iE_2t/\hbar}\right] (r^2 \sin\theta\, dr\, d\phi\, d\theta) \\
&= \int_0^\pi \int_0^{2\pi} \int_0^\infty \left[-\frac{1}{8\sqrt{\pi a_0^5}} r e^{-r/(2a_0)} \sin\theta\, e^{-i\phi} e^{iE_2t/\hbar}\right] (r^2\sin^2\theta\cos^2\phi) \left[-\frac{1}{8\sqrt{\pi a_0^5}} r e^{-r/(2a_0)} \sin\theta\, e^{i\phi} e^{-iE_2t/\hbar}\right] (r^2 \sin\theta\, dr\, d\phi\, d\theta) \\
&= \frac{1}{64\pi a_0^5}\left(\int_0^\pi \sin^5\theta\, d\theta\right)\left(\int_0^{2\pi} \cos^2\phi\, d\phi\right)\left(\int_0^\infty r^6 e^{-r/a_0}\, dr\right) \\
&= \frac{1}{64\pi a_0^5}\left[\int_0^\pi (1-\cos^2\theta)^2 \sin\theta\, d\theta\right](\pi)\left[\int_0^\infty \frac{\partial^6}{\partial u^6}(e^{-ur})\bigg|_{u=1/a_0} dr\right] \\
&= \frac{1}{64 a_0^5}\left[\int_{\cos 0}^{\cos\pi} (1-w^2)^2(-dw)\right] \frac{d^6}{du^6}\left(\int_0^\infty e^{-ur}\, dr\right)\bigg|_{u=1/a_0} \\
&= \frac{1}{64 a_0^5}\left[\int_{-1}^{1} (1-w^2)^2\, dw\right] \frac{d^6}{du^6}\left(\frac{1}{u}\right)\bigg|_{u=1/a_0} \\
&= \frac{1}{64 a_0^5}\left[2\int_0^1 (1-2w^2+w^4)\, dw\right] \frac{d^5}{du^5}\left(-\frac{1}{u^2}\right)\bigg|_{u=1/a_0} \\
&= \frac{1}{32 a_0^5}\left(w - \frac{2}{3}w^3 + \frac{1}{5}w^5\right)\bigg|_0^1 \frac{d^4}{du^4}\left(\frac{2}{u^3}\right)\bigg|_{u=1/a_0}
\end{aligned}$$

Therefore,

$$\begin{aligned}
\langle x^2 \rangle &= \frac{1}{32a_0^5}\left(1 - \frac{2}{3} + \frac{1}{5}\right)\frac{d^3}{du^3}\left(-\frac{6}{u^4}\right)\bigg|_{u=1/a_0} \\
&= \frac{1}{32a_0^5}\left(\frac{8}{15}\right)\frac{d^2}{du^2}\left(\frac{24}{u^5}\right)\bigg|_{u=1/a_0} \\
&= \frac{1}{60a_0^5}\frac{d}{du}\left(-\frac{120}{u^6}\right)\bigg|_{u=1/a_0} \\
&= \frac{1}{60a_0^5}\left(\frac{720}{u^7}\right)\bigg|_{u=1/a_0} \\
&= \frac{1}{60a_0^5}(720a_0^7) \\
&= 12a_0^2.
\end{aligned}$$