Problem 4.17

Calculate $\left\langle z\hat{H}z\right\rangle$, in the ground state of hydrogen. *Hint:* This takes two pages and six integrals, or four lines and no integrals, depending on how you set it up. To do it the quick way, start by noting that $[z,[H,z]] = 2zHz - Hz^2 - z^2H$.[25]

[TYPO: Actually, seven integrals need to be evaluated.]

Solution

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

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

Calculate $\left\langle \hat{z}\hat{H}\hat{z}\right\rangle$ at time t in the ground state of hydrogen, noting that $\hat{H}$ is the Hamiltonian operator, the sum of the operators for kinetic and potential energy.

$$\begin{aligned}\left\langle \hat{z}\hat{H}\hat{z}\right\rangle &= \left\langle \Psi_{100}\,\middle|\,\hat{z}\hat{H}\hat{z}\,\middle|\,\Psi_{100}\right\rangle\\ &= \iiint_{\text{all space}} \Psi_{100}^*(r,\theta,\phi,t)\,\hat{z}\hat{H}\hat{z}\,\Psi_{100}(r,\theta,\phi,t)\,d\mathcal{V}\\ &= \iiint_{\text{all space}} \Psi_{100}^*(r,\theta,\phi,t)\,z\left(\frac{\hat{p}^2}{2m_e}+V\right)z\,\Psi_{100}(r,\theta,\phi,t)\,d\mathcal{V}\\ &= \iiint_{\text{all space}} \Psi_{100}^*(r,\theta,\phi,t)\,z\left(-\frac{\hbar^2}{2m_e}\nabla^2-\frac{e^2}{4\pi\epsilon_0 r}\right)z\,\Psi_{100}(r,\theta,\phi,t)\,d\mathcal{V}\\ &= -\frac{\hbar^2}{2m_e}\iiint_{\text{all space}} \Psi_{100}^*(r,\theta,\phi,t)\,z\nabla^2[z\,\Psi_{100}(r,\theta,\phi,t)]\,d\mathcal{V}\\ &\qquad -\frac{e^2}{4\pi\epsilon_0}\iiint_{\text{all space}} \Psi_{100}^*(r,\theta,\phi,t)\,z\left(\frac{1}{r}\right)z\,\Psi_{100}(r,\theta,\phi,t)\,d\mathcal{V}\end{aligned}$$

[25]The idea is to reorder the operators in such a way that $\hat{H}$ appears either to the left or to the right, because we know (of course) what $\hat{H}\psi_{100}$ is.

Substitute the formula for Ψ_{100} and expand the integrals in spherical coordinates.

$$\begin{aligned}
\left\langle \hat{z}\hat{H}\hat{z}\right\rangle &= -\frac{\hbar^2}{2m_e}\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\cos\theta)\nabla^2\left[(r\cos\theta)\left(\frac{1}{\sqrt{\pi a_0^3}}\,e^{-r/a_0}e^{-iE_1 t/\hbar}\right)\right](r^2\sin\theta\,dr\,d\phi\,d\theta) \\
&\quad - \frac{e^2}{4\pi\epsilon_0}\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\cos\theta)\left(\frac{1}{r}\right)(r\cos\theta)\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{\hbar^2}{2\pi m_e a_0^3}\int_0^\pi \int_0^{2\pi}\int_0^\infty (r^3 e^{-r/a_0}\sin\theta\cos\theta)\nabla^2(re^{-r/a_0}\cos\theta)\,dr\,d\phi\,d\theta \\
&\quad - \frac{e^2}{4\pi^2\epsilon_0 a_0^3}\left(\int_0^\pi \cos^2\theta\sin\theta\,d\theta\right)\left(\int_0^{2\pi} d\phi\right)\left(\int_0^\infty r^3 e^{-2r/a_0}\,dr\right) \\
&= -\frac{\hbar^2}{2\pi m_e a_0^3}\int_0^\pi \int_0^{2\pi}\int_0^\infty (r^3 e^{-r/a_0}\sin\theta\cos\theta)\left(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}+\frac{1}{r^2}\frac{\partial^2}{\partial\theta^2}+\frac{\cot\theta}{r^2}\frac{\partial}{\partial\theta}+\frac{\csc^2\theta}{r^2}\frac{\partial^2}{\partial\phi^2}\right)(re^{-r/a_0}\cos\theta)\,dr\,d\phi\,d\theta \\
&\quad - \frac{e^2}{4\pi^2\epsilon_0 a_0^3}\left[\int_{\cos 0}^{\cos\pi} w^2(-dw)\right](2\pi)\left[\int_0^\infty \frac{\partial^3}{\partial u^3}(-e^{-ur})\bigg|_{u=2/a_0}\,dr\right] \\
&= -\frac{\hbar^2}{2\pi m_e a_0^3}\int_0^\pi \int_0^{2\pi}\int_0^\infty (r^3 e^{-r/a_0}\sin\theta\cos\theta)\left[\frac{\partial^2}{\partial r^2}(re^{-r/a_0}\cos\theta)+\frac{2}{r}\frac{\partial}{\partial r}(re^{-r/a_0}\cos\theta)+\frac{1}{r^2}\frac{\partial^2}{\partial\theta^2}(re^{-r/a_0}\cos\theta)+\frac{\cot\theta}{r^2}\frac{\partial}{\partial\theta}(re^{-r/a_0}\cos\theta)\right]dr\,d\phi\,d\theta \\
&\quad + \frac{e^2}{2\pi\epsilon_0 a_0^3}\left(\int_{-1}^1 w^2\,dw\right)\frac{d^3}{du^3}\left(\int_0^\infty e^{-ur}\,dr\right)\bigg|_{u=2/a_0} \\
&= -\frac{\hbar^2}{2\pi m_e a_0^3}\int_0^\pi \int_0^{2\pi}\int_0^\infty (r^3 e^{-r/a_0}\sin\theta\cos\theta)\left[\frac{1}{a_0^2}(r-4a_0)e^{-r/a_0}\cos\theta\right]dr\,d\phi\,d\theta + \frac{e^2}{2\pi\epsilon_0 a_0^3}\left(\frac{2}{3}\right)\frac{d^3}{du^3}\left(\frac{1}{u}\right)\bigg|_{u=2/a_0} \\
&= -\frac{\hbar^2}{2\pi m_e a_0^5}\left(\int_0^\pi \cos^2\theta\sin\theta\,d\theta\right)\left(\int_0^{2\pi} d\phi\right)\left[\int_0^\infty r^3(r-4a_0)e^{-2r/a_0}\,dr\right] + \frac{e^2}{3\pi\epsilon_0 a_0^3}\left(-\frac{6}{u^4}\right)\bigg|_{u=2/a_0}
\end{aligned}$$

Therefore,

$$
\begin{aligned}
\left\langle \hat{z}\hat{H}\hat{z} \right\rangle &= -\frac{\hbar^2}{2\pi m_e a_0^5}\left(\frac{2}{3}\right)(2\pi)\left(\int_0^\infty r^4 e^{-2r/a_0}\,dr - 4a_0\int_0^\infty r^3 e^{-2r/a_0}\,dr\right) + \frac{e^2}{3\pi\epsilon_0 a_0^3}\left(-\frac{6a_0^4}{16}\right) \\
&= -\frac{2\hbar^2}{3m_e a_0^5}\left[\int_0^\infty \frac{\partial^4}{\partial u^4}(e^{-ur})\bigg|_{u=2/a_0} dr - 4a_0\int_0^\infty \frac{\partial^3}{\partial u^3}(-e^{-ur})\bigg|_{u=2/a_0} dr\right] - \frac{e^2 a_0}{8\pi\epsilon_0} \\
&= -\frac{2\hbar^2}{3m_e a_0^5}\left[\frac{d^4}{du^4}\left(\int_0^\infty e^{-ur}\,dr\right)\bigg|_{u=2/a_0} + 4a_0\frac{d^3}{du^3}\left(\int_0^\infty e^{-ur}\,dr\right)\bigg|_{u=2/a_0}\right] - \frac{e^2 a_0}{8\pi\epsilon_0} \\
&= -\frac{2\hbar^2}{3m_e a_0^5}\left[\frac{d^4}{du^4}\left(\frac{1}{u}\right)\bigg|_{u=2/a_0} + 4a_0\frac{d^3}{du^3}\left(\frac{1}{u}\right)\bigg|_{u=2/a_0}\right] - \frac{e^2 a_0}{8\pi\epsilon_0} \\
&= -\frac{2\hbar^2}{3m_e a_0^5}\left[\left(\frac{24}{u^5}\right)\bigg|_{u=2/a_0} + 4a_0\left(-\frac{6}{u^4}\right)\bigg|_{u=2/a_0}\right] - \frac{e^2 a_0}{8\pi\epsilon_0} \\
&= -\frac{2\hbar^2}{3m_e a_0^5}\left[\left(\frac{24a_0^5}{32}\right) + 4a_0\left(-\frac{6a_0^4}{16}\right)\right] - \frac{e^2 a_0}{8\pi\epsilon_0} \\
&= -\frac{2\hbar^2}{3m_e a_0^5}\left(-\frac{3}{4}a_0^5\right) - \frac{e^2 a_0}{8\pi\epsilon_0} \\
&= \frac{\hbar^2}{2m_e} - \frac{e^2 a_0}{8\pi\epsilon_0} \\
&= \frac{\hbar^2}{2m_e} - \frac{e^2}{8\pi\epsilon_0}\left(\frac{4\pi\epsilon_0\hbar^2}{m_e e^2}\right) \\
&= \frac{\hbar^2}{2m_e} - \frac{\hbar^2}{2m_e} \\
&= 0.
\end{aligned}
$$