Problem 4.18

A hydrogen atom starts out in the following linear combination of the stationary states $n = 2$, $\ell = 1$, $m = 1$ and $n = 2$, $\ell = 1$, $m = -1$:

$$\Psi(\mathbf{r}, 0) = \frac{1}{\sqrt{2}}(\psi_{211} + \psi_{21-1}).$$

(a) Construct $\Psi(\mathbf{r}, t)$. Simplify it as much as you can.

(b) Find the expectation value of the potential energy, $\langle V \rangle$. (Does it depend on t?) Give both the formula and the actual number, in electron volts.

Solution

Part (a)

The behavior of the wave function for $t > 0$ is determined by tacking on the usual wiggle factor $e^{-iE_n t/\hbar}$ to each of the stationary states. Both of the states have $n = 2$, so

$$\begin{aligned}
\Psi(r, \theta, \phi, t) &= \frac{1}{\sqrt{2}}\left(\psi_{211}e^{-iE_2 t/\hbar} + \psi_{21-1}e^{-iE_2 t/\hbar}\right) \\
&= \frac{1}{\sqrt{2}}\left[R_{21}(r)Y_1^1(\theta, \phi)e^{-iE_2 t/\hbar} + R_{21}(r)Y_1^{-1}(\theta, \phi)e^{-iE_2 t/\hbar}\right] \\
&= \frac{1}{\sqrt{2}}R_{21}(r)\left[Y_1^1(\theta, \phi) + Y_1^{-1}(\theta, \phi)\right]e^{-iE_2 t/\hbar} \\
&= \frac{1}{\sqrt{2}}\left[\frac{1}{2\sqrt{6a_0^3}}\left(\frac{r}{a_0}\right)e^{-r/(2a_0)}\right]\left(-\sqrt{\frac{3}{8\pi}}\sin\theta\, e^{i\phi} + \sqrt{\frac{3}{8\pi}}\sin\theta\, e^{-i\phi}\right)e^{-iE_2 t/\hbar} \\
&= \frac{1}{\sqrt{2}}\frac{1}{2\sqrt{6a_0^3}}\left(-\sqrt{\frac{3}{8\pi}}\right)\left(\frac{r}{a_0}\right)e^{-r/(2a_0)}\sin\theta\,(e^{i\phi} - e^{-i\phi})e^{-iE_2 t/\hbar} \\
&= -\frac{1}{2}\sqrt{\frac{1}{32\pi a_0^5}}\,re^{-r/(2a_0)}\sin\theta\,(2i\sin\phi)e^{-iE_2 t/\hbar} \\
&= -\frac{i}{\sqrt{32\pi a_0^5}}(r\sin\theta\sin\phi)\,e^{-r/(2a_0)}\,e^{-iE_2 t/\hbar}.
\end{aligned}$$

Therefore,

$$\Psi(x, y, z, t) = -\frac{i}{\sqrt{32\pi a_0^5}}\,y\exp\left(-\frac{1}{2a_0}\sqrt{x^2 + y^2 + z^2}\right)e^{-iE_2 t/\hbar},$$

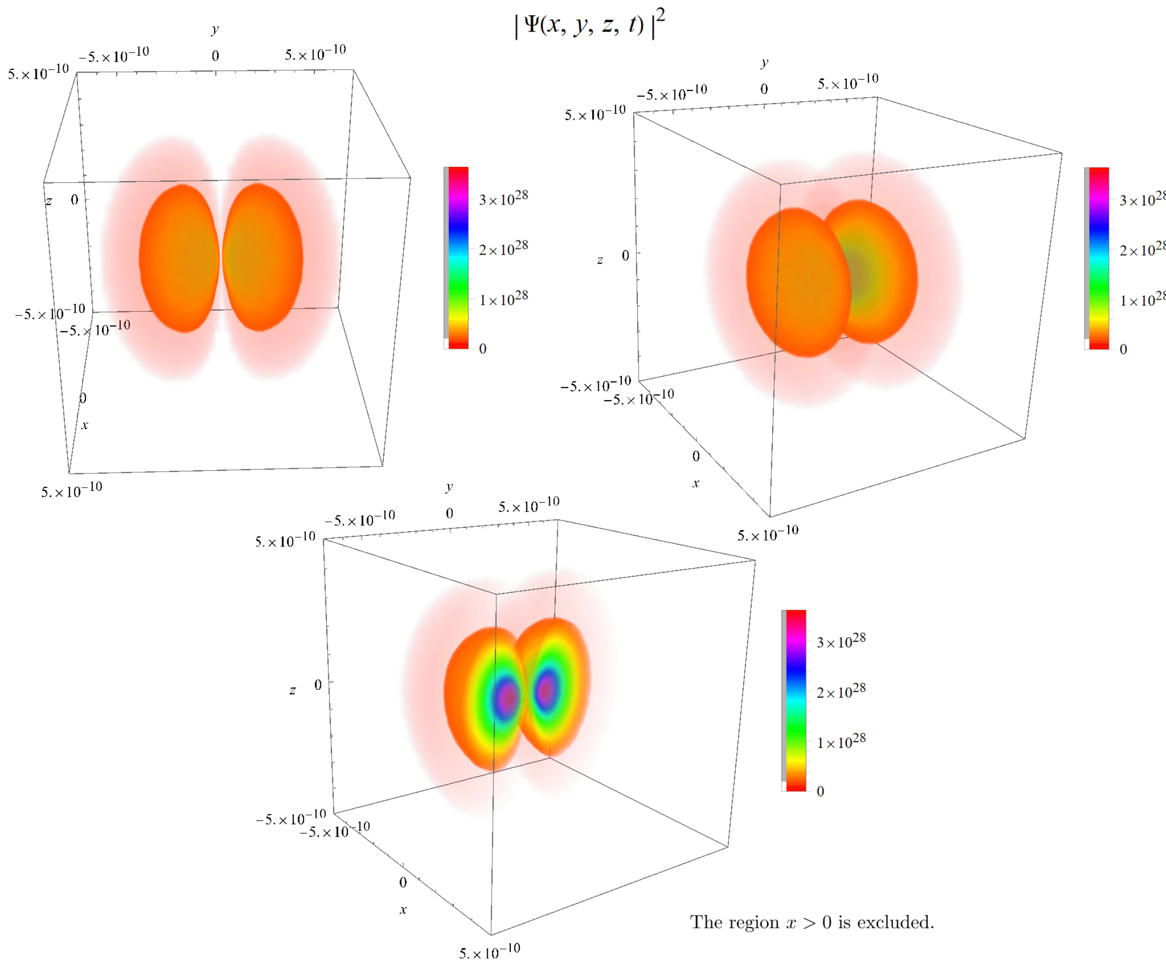
where

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} \approx 0.529 \times 10^{-10}\text{ m} \quad \text{and} \quad E_n = -\left[\frac{m_e}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]\frac{1}{n^2} \approx -\frac{2.18 \times 10^{-18}\text{ J}}{n^2}.$$

The probability density of the electron's position is then

$$|\Psi(x,y,z,t)|^2 = \frac{1}{32\pi a_0^5}\, y^2 \exp\left(-\frac{1}{a_0}\sqrt{x^2+y^2+z^2}\right)$$

and visualized below in SI units.



Part (b)

Calculate the expectation value of the potential energy at time t.

$$
\begin{aligned}
\langle V \rangle &= \langle \Psi \,|\, V \,|\, \Psi \rangle \\
&= \iiint\limits_{\text{all space}} \Psi^*(r,\theta,\phi,t) V(r) \Psi(r,\theta,\phi,t)\, d\mathcal{V} \\
&= \int_0^{\pi} \int_0^{2\pi} \int_0^{\infty} \left[+ \frac{i}{\sqrt{32\pi a_0^5}} \,(r\sin\theta\sin\phi)\, e^{-r/(2a_0)}\, e^{iE_2 t/\hbar} \right] \left(-\frac{e^2}{4\pi\epsilon_0 r} \right) \left[- \frac{i}{\sqrt{32\pi a_0^5}} \,(r\sin\theta\sin\phi)\, e^{-r/(2a_0)}\, e^{-iE_2 t/\hbar} \right] (r^2 \sin\theta \, dr\, d\phi\, d\theta) \\
&= -\frac{e^2}{4\pi\epsilon_0 (32\pi a_0^5)} \left(\int_0^{\pi} \sin^3\theta \, d\theta \right) \left(\int_0^{2\pi} \sin^2\phi \, d\phi \right) \left(\int_0^{\infty} r^3 e^{-r/a_0} \, dr \right) \\
&= -\frac{e^2}{128\pi^2 \epsilon_0 a_0^5} \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[\int_0^{\infty} \frac{\partial^3}{\partial u^3} (-e^{-ur}) \bigg|_{u=1/a_0} dr \right] \\
&= \frac{e^2}{128\pi^2 \epsilon_0 a_0^5} \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] \frac{d^3}{du^3} \left(\int_0^{\infty} e^{-ur} \, dr \right) \bigg|_{u=1/a_0} \\
&= \frac{e^2}{128\pi^2 \epsilon_0 a_0^5} \left[\int_{-1}^{1} (1 - w^2)\, dw \right] \left[\frac{1}{2} \left(\phi - \frac{1}{2} \sin 2\phi \right) \bigg|_0^{2\pi} \right] \frac{d^3}{du^3} \left(\frac{1}{u} \right) \bigg|_{u=1/a_0} \\
&= \frac{e^2}{128\pi^2 \epsilon_0 a_0^5} \left[2 \int_0^1 (1 - w^2)\, dw \right] \left[\frac{1}{2} (2\pi) \right] \left(-\frac{6}{u^4} \right) \bigg|_{u=1/a_0} \\
&= \frac{e^2}{128\pi^2 \epsilon_0 a_0^5} \left(\frac{4}{3} \right) (\pi)(-6a_0^4) \\
&= -\frac{e^2}{16\pi\epsilon_0 a_0} \approx -\frac{(1.60 \times 10^{-19}\ \text{C})^2}{16(3.14)\left(8.85 \times 10^{-12}\ \frac{\text{C}^2}{\text{J}\cdot\text{m}}\right)(0.529 \times 10^{-10}\ \text{m})} \approx -1.09 \times 10^{-18}\ \text{J} \approx -6.80\ \text{eV}
\end{aligned}
$$

It does not depend on time.