Problem 4.53

(a) Construct the wave function for hydrogen in the state $n = 4$, $\ell = 3$, $m = 3$. Express your answer as a function of the spherical coordinates r, θ, and ϕ.

(b) Find the expectation value of r in this state. (As always, look up any nontrivial integrals.)

(c) If you could somehow measure the observable $L_x^2 + L_y^2$ on an atom in this state, what value (or values) could you get, and what is the probability of each?

Solution

Part (a)

Using separation of variables to solve the Schrödinger equation for hydrogen results in product solutions for the wave function.

$$\Psi(r,\theta,\phi,t) = R(r)\Theta(\theta)P(\phi)T(t)$$

$$\Psi_{n\ell m}(r,\theta,\phi,t) = R_{n\ell}(r)Y_\ell^m(\theta,\phi)e^{-iE_nt/\hbar}$$

$R_{n\ell}(r)$ and $Y_\ell^m(\theta,\phi)$ are the radial wave functions and spherical harmonics, respectively, and they're listed on page 151 and page 137. The wave function for the state with $n = 4$, $\ell = 3$, and $m = 3$ is

$$\begin{aligned}
\Psi_{433}(r,\theta,\phi,t) &= R_{43}(r)Y_3^3(\theta,\phi)e^{-iE_4t/\hbar} \\
&= \left[\frac{1}{768\sqrt{35a_0^3}}\left(\frac{r}{a_0}\right)^3 \exp\left(-\frac{r}{4a_0}\right)\right]\left(-\sqrt{\frac{35}{64\pi}}\sin^3\theta\, e^{3i\phi}\right)e^{-iE_4t/\hbar} \\
&= -\frac{1}{768\sqrt{64\pi a_0^3}}\frac{r^3}{a_0^3}\exp\left(-\frac{r}{4a_0}\right)\sin^3\theta\, e^{3i\phi}e^{-iE_4t/\hbar} \\
&= -\frac{1}{6144\sqrt{\pi a_0^9}}r^3\exp\left(-\frac{r}{4a_0}\right)\sin^3\theta\, e^{3i\phi}e^{-iE_4t/\hbar},
\end{aligned}$$

where

$$E_4 = -\left[\frac{m_e}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]\frac{1}{4^2}.$$

Part (b)

The expectation value of r in the state with $n = 4$, $\ell = 3$, and $m = 3$ is

$$\begin{aligned}
\langle r \rangle &= \frac{\langle \Psi_{433} \,|\, r \,|\, \Psi_{433} \rangle}{\langle \Psi_{433} \,|\, \Psi_{433} \rangle} \\
&= \frac{\displaystyle\iiint\limits_{\text{all space}} \Psi_{433}^* r \Psi_{433} \, d\mathcal{V}}{\displaystyle\iiint\limits_{\text{all space}} \Psi_{433}^* \Psi_{433} \, d\mathcal{V}} \\
&= \frac{\displaystyle\iiint\limits_{\text{all space}} r |\Psi_{433}|^2 \, d\mathcal{V}}{1} \\
&= \int_0^\pi \int_0^{2\pi} \int_0^\infty r \left| R_{43}(r) Y_3^3(\theta, \phi) e^{-iE_4 t/\hbar} \right|^2 (r^2 \sin\theta \, dr \, d\phi \, d\theta) \\
&= \int_0^\pi \int_0^{2\pi} \int_0^\infty r \left| -\frac{1}{6144\sqrt{\pi a_0^9}} r^3 \exp\left(-\frac{r}{4a_0}\right) \sin^3\theta \, e^{3i\phi} e^{-iE_4 t/\hbar} \right|^2 (r^2 \sin\theta \, dr \, d\phi \, d\theta) \\
&= \int_0^\pi \int_0^{2\pi} \int_0^\infty r \frac{1}{6144^2 \pi a_0^9} r^6 \exp\left(-\frac{2r}{4a_0}\right) \sin^6\theta \, (r^2 \sin\theta \, dr \, d\phi \, d\theta) \\
&= \frac{1}{6144^2 \pi a_0^9} \left(\int_0^\pi \sin^6\theta \sin\theta \, d\theta \right) \left(\int_0^{2\pi} d\phi \right) \int_0^\infty r^9 e^{-r/(2a_0)} \, dr \\
&= \frac{1}{6144^2 \pi a_0^9} \left[\int_0^\pi (\sin^2\theta)^3 \sin\theta \, d\theta \right] (2\pi) \int_0^\infty \frac{\partial^9}{\partial k^9} \left(-e^{-kr} \right) \Big|_{k=1/(2a_0)} dr \\
&= \frac{2}{6144^2 a_0^9} \left[-\int_0^\pi (1 - \cos^2\theta)^3 \sin\theta \, d\theta \right] \frac{d^9}{dk^9} \left(\int_0^\infty e^{-kr} \, dr \right) \Big|_{k=1/(2a_0)} \\
&= \frac{2}{6144^2 a_0^9} \left[-\int_{\cos 0}^{\cos\pi} (1 - u^2)^3 (-du) \right] \frac{d^9}{dk^9} \left(-\frac{1}{k} e^{-kr} \Big|_0^\infty \right) \Big|_{k=1/(2a_0)} \\
&= \frac{2}{6144^2 a_0^9} \left[-\int_1^{-1} (u^2 - 1)^3 \, du \right] \frac{d^9}{dk^9} \left(\frac{1}{k} \right) \Big|_{k=1/(2a_0)} \\
&= \frac{2}{6144^2 a_0^9} \left[\int_{-1}^1 (u^2 - 1)^3 \, du \right] \left[\frac{(-1)^9 9!}{k^{1+9}} \right] \Big|_{k=1/(2a_0)}.
\end{aligned}$$

Since the first integrand is even, the interval of integration can go from 0 to 1 by placing a factor of 2 in front.

$$\begin{aligned}\langle r\rangle &= \frac{2}{6144^2 a_0^9}\left[2\int_0^1 (u^2-1)^3\,du\right]\left[-\frac{9!}{k^{10}}\right]\bigg|_{k=1/(2a_0)} \\ &= -\frac{4}{6144^2 a_0^9}\left[\int_0^1 (u^6-3u^4+3u^2-1)\,du\right]9!(2^{10}a_0^{10}) \\ &= -\frac{4}{6144^2 a_0^9}\left(\frac{1}{7}-\frac{3}{5}+1-1\right)9!(2^{10}a_0^{10}) \\ &= 18a_0\end{aligned}$$

Part (c)

The eigenvalues of $L_x^2 + L_y^2$ are the possible measurements. Write this operator in terms of L^2 and L_z, two operators that have known eigenvalues (given in Equation 4.118 on page 160).

$$\begin{cases} L^2 f_\ell^m = \hbar^2 \ell(\ell+1) f_\ell^m \\ L_z f_\ell^m = \hbar m f_\ell^m \end{cases} \tag{4.118}$$

Use the fact that $L^2 = L_x^2 + L_y^2 + L_z^2$.

$$\begin{aligned}(L_x^2+L_y^2)\Psi_{433} &= (L^2 - L_z^2)\Psi_{433} \\ &= L^2\Psi_{433} - L_z^2\Psi_{433} \\ &= \hbar^2 3(3+1)\Psi_{433} - L_z(\hbar\cdot 3)\Psi_{433} \\ &= 12\hbar^2\Psi_{433} - 3\hbar L_z\Psi_{433} \\ &= 12\hbar^2\Psi_{433} - 3\hbar(\hbar\cdot 3)\Psi_{433} \\ &= 12\hbar^2\Psi_{433} - 9\hbar^2\Psi_{433} \\ &= 3\hbar^2\Psi_{433}\end{aligned}$$

Therefore, if one measured $L_x^2 + L_y^2$ on a hydrogen atom in the state with $n = 4$, $\ell = 3$, and $m = 3$, the value obtained would be $3\hbar^2$ with a probability of 1.