Problem 4.52

(a) Construct the spatial wave function (ψ) for hydrogen in the state $n = 3$, $\ell = 2$, $m = 1$. Express your answer as a function of r, θ, ϕ, and a (the Bohr radius) *only*—no other variables (ρ, z, etc.) or functions (Y, v, etc.), or constants (A, c_0, etc.), or derivatives, allowed (π is okay, and e, and 2, etc.).

(b) Check that this wave function is properly normalized, by carrying out the appropriate integrals over r, θ, and ϕ.

(c) Find the expectation value of r^s in this state. For what range of s (positive and negative) is the result finite?

Solution

Part (a)

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

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

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

The part of it that doesn't depend on time is the spatial wave function.

$$\psi_{n\ell m}(r,\theta,\phi) = R_{n\ell}(r)Y_\ell^m(\theta,\phi)$$

$R_{n\ell}(r)$ 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 spatial wave function for the state with $n = 3$, $\ell = 2$, and $m = 1$ is

$$\begin{aligned}
\psi_{321}(r,\theta,\phi) &= R_{32}(r)Y_2^1(\theta,\phi) \\
&= \left[\frac{4}{81\sqrt{30a_0^3}}\left(\frac{r}{a_0}\right)^2\exp\left(-\frac{r}{3a_0}\right)\right]\left(-\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta\, e^{i\phi}\right) \\
&= -\frac{4}{81\sqrt{2(8\pi)a_0^3}}\frac{r^2}{a_0^2}\exp\left(-\frac{r}{3a_0}\right)\sin\theta\cos\theta\, e^{i\phi} \\
&= -\frac{1}{81\sqrt{\pi a_0^7}}r^2\exp\left(-\frac{r}{3a_0}\right)\sin\theta\cos\theta\, e^{i\phi}.
\end{aligned}$$

Part (b)

Check to see that the state with $n = 3$, $\ell = 2$, and $m = 1$ is normalized.

$$\iiint_{\text{all space}} |\Psi_{321}|^2 \, d\mathcal{V} = \int_0^\pi \int_0^{2\pi} \int_0^\infty \left| \psi_{321}(r,\theta,\phi) e^{-iE_3 t/\hbar} \right|^2 (r^2 \sin\theta \, dr \, d\phi \, d\theta)$$

$$= \int_0^\pi \int_0^{2\pi} \int_0^\infty \left| -\frac{1}{81\sqrt{\pi a_0^7}} r^2 \exp\left(-\frac{r}{3a_0}\right) \sin\theta \cos\theta \, e^{i\phi} e^{-iE_3 t/\hbar} \right|^2 (r^2 \sin\theta \, dr \, d\phi \, d\theta)$$

$$= \int_0^\pi \int_0^{2\pi} \int_0^\infty \frac{1}{81^2 \pi a_0^7} r^4 \exp\left(-\frac{2r}{3a_0}\right) \sin^2\theta \cos^2\theta \, (r^2 \sin\theta \, dr \, d\phi \, d\theta)$$

$$= \frac{1}{6561\pi a_0^7} \left(\int_0^\pi \sin^2\theta \cos^2\theta \sin\theta \, d\theta \right) \left(\int_0^{2\pi} d\phi \right) \int_0^\infty r^6 e^{-2r/(3a_0)} \, dr$$

$$= \frac{1}{6561\pi a_0^7} \left[\int_0^\pi (1 - \cos^2\theta) \cos^2\theta \sin\theta \, d\theta \right] (2\pi) \int_0^\infty \frac{\partial^6}{\partial k^6} \left(e^{-kr} \right) \Big|_{k=2/(3a_0)} dr$$

$$= \frac{2}{6561 a_0^7} \left[\int_{\cos 0}^{\cos\pi} (1 - u^2) u^2 (-du) \right] \frac{d^6}{dk^6} \left(\int_0^\infty e^{-kr} \, dr \right) \Big|_{k=2/(3a_0)}$$

$$= \frac{2}{6561 a_0^7} \left[\int_{-1}^1 (1 - u^2) u^2 \, du \right] \frac{d^6}{dk^6} \left(-\frac{1}{k} e^{-kr} \Big|_0^\infty \right) \Big|_{k=2/(3a_0)}$$

$$= \frac{2}{6561 a_0^7} \left[2 \int_0^1 (u^2 - u^4) \, du \right] \frac{d^6}{dk^6} \left(\frac{1}{k} \right) \Big|_{k=2/(3a_0)}$$

$$= \frac{2}{6561 a_0^7} \left[2 \left(\frac{1}{3} - \frac{1}{5} \right) \right] \left[\frac{(-1)^6 6!}{k^{1+6}} \right] \Big|_{k=2/(3a_0)}$$

$$= \frac{2}{6561 a_0^7} \left(\frac{4}{15} \right) \left(\frac{720}{k^7} \right) \Big|_{k=2/(3a_0)}$$

$$= \frac{2}{6561 a_0^7} \left(\frac{4}{15} \right) \left(\frac{720}{2^7} \right) 3^7 a_0^7$$

$$= 1$$

It is indeed.

Part (c)

The expectation value of r^s in the state with $n = 3$, $\ell = 2$, and $m = 1$ is

$$\begin{aligned}
\langle r^s\rangle &= \frac{\langle \Psi_{321} \,|\, r^s \,|\, \Psi_{321}\rangle}{\langle \Psi_{321} \,|\, \Psi_{321}\rangle} \\
&= \frac{\displaystyle\iiint_{\text{all space}} \Psi_{321}^* r^s \Psi_{321}\, d\mathcal{V}}{\displaystyle\iiint_{\text{all space}} \Psi_{321}^* \Psi_{321}\, d\mathcal{V}} \\
&= \frac{\displaystyle\iiint_{\text{all space}} r^s |\Psi_{321}|^2\, d\mathcal{V}}{1} \\
&= \int_0^\pi \int_0^{2\pi} \int_0^\infty r^s \left|\psi_{321}(r,\theta,\phi)e^{-iE_3t/\hbar}\right|^2 (r^2 \sin\theta\, dr\, d\phi\, d\theta) \\
&= \int_0^\pi \int_0^{2\pi} \int_0^\infty r^s \left|-\frac{1}{81\sqrt{\pi a_0^7}} r^2 \exp\left(-\frac{r}{3a_0}\right) \sin\theta\cos\theta\, e^{i\phi} e^{-iE_3t/\hbar}\right|^2 (r^2 \sin\theta\, dr\, d\phi\, d\theta) \\
&= \int_0^\pi \int_0^{2\pi} \int_0^\infty r^s \frac{1}{81^2 \pi a_0^7} r^4 \exp\left(-\frac{2r}{3a_0}\right) \sin^2\theta\cos^2\theta\, (r^2 \sin\theta\, dr\, d\phi\, d\theta) \\
&= \frac{1}{6561\pi a_0^7} \left(\int_0^\pi \sin^2\theta\cos^2\theta\sin\theta\, d\theta\right)\left(\int_0^{2\pi} d\phi\right)\int_0^\infty r^{s+6} e^{-2r/(3a_0)}\, dr \\
&= \frac{1}{6561\pi a_0^7}\left(\frac{4}{15}\right)(2\pi)\int_0^\infty r^{s+6} e^{-2r/(3a_0)}\, dr \\
&= \frac{8}{98\,415 a_0^7}\int_0^\infty r^{s+6} e^{-2r/(3a_0)}\, dr.
\end{aligned}$$

Make the following substitution.

$$v = \frac{2r}{3a_0} \quad\rightarrow\quad \frac{3a_0 v}{2} = r$$

$$dv = \frac{2}{3a_0}\, dr \quad\rightarrow\quad \frac{3a_0}{2}\, dv = dr$$

As a result,

$$\begin{aligned}
\langle r^s \rangle &= \frac{8}{98\,415 a_0^7} \int_0^\infty \left(\frac{3a_0 v}{2}\right)^{s+6} e^{-v} \left(\frac{3a_0}{2}\,dv\right) \\
&= \frac{8}{98\,415 a_0^7} \left(\frac{3a_0}{2}\right)^{s+7} \int_0^\infty v^{s+6} e^{-v}\,dv \\
&= \frac{8}{98\,415 a_0^7} \left(\frac{3a_0}{2}\right)^{7} \left(\frac{3a_0}{2}\right)^{s} \int_0^\infty v^{(s+7)-1} e^{-v}\,dv \\
&= \frac{1}{720} \left(\frac{3a_0}{2}\right)^{s} \Gamma(s+7).
\end{aligned}$$

The condition that needs to be satisfied for the gamma function to converge is $s + 7 > 0$. The range of s for which $\langle r^s \rangle$ is finite is therefore $s > -7$.