Question
Let

$$\Psi_{1s} = \frac{1}{\sqrt{\pi a_0^3}} e^{\frac{-r}{a_0}}, \quad \Psi_{2s} = \frac{1}{4\sqrt{2\pi a_0^3}} \left(2 - \frac{r}{a_0}\right) e^{\frac{-r}{2a_0}},$$

and

$$\Psi_{2p_z} = \frac{1}{4\sqrt{2\pi a_0^5}} r e^{\frac{-r}{a_0}} \cos(\theta).$$

Show that each of Ψ_{1s}, Ψ_{2s} and Ψ_{2p_z} is *normalised*, i.e. that

$$\iiint \Psi^2 \, dV = 1$$

where the integration is taken over all of space. Show also that

$$\iiint \Psi_{1s}\Psi_{2s} \, dV = \iiint \Psi_{1s}\Psi_{2p_s} \, dV = 0.$$

Answer
In the spherical polar coordinates a volume element is

$$dv = r^2 \sin\theta dr \, d\theta \, d\phi$$

Integrating over all of space means that $\left.\begin{array}{ccccc} 0 & \leq & \phi & \leq & 2\pi \\ 0 & \leq & \theta & \leq & \pi \\ 0 & \leq & r & & \end{array}\right\}$ We will require the following integrals:

$\displaystyle\int_0^\pi sin\theta \, d\theta = 2,$

$\displaystyle\int_0^{2\pi} d\phi = 2\pi$

$\displaystyle\int_0^\pi \sin\theta\cos\theta \, d\theta = \int_0^\pi \frac{1}{2}\sin 2\theta \, d\theta = \left[-\frac{1}{4}\cos 2\theta\right]_0^\pi = -\frac{1}{4} + \frac{1}{4} = 0$

Note that $\displaystyle\frac{d}{d\theta}\left(-\frac{1}{3}cos^3\theta\right) = \cos^2\theta\sin\theta$ so that $\displaystyle\int_0^\pi \cos^2\theta\sin\theta \, d\theta = \left[-\frac{1}{3}\cos^3\theta\right]_0^\pi = \frac{1}{3} + \frac{1}{3} = \frac{2}{3}$

Also note we have $\displaystyle\int_0^\infty r^n e^{-\lambda r} \, dr = \frac{n!}{\lambda^{n+1}}$

To see this let $\displaystyle I_n = \int_0^\infty r^n e^{-\lambda r} \, dr$ (n a positive integer)

As a special case we have

$$
\begin{aligned}
I_0 &= \int_0^{\infty} e^{-\lambda r} dr \\
&= \left[-\frac{1}{\lambda} e^{-\lambda r} \right]_0^{\infty} \\
&= \left(0 + \frac{1}{\lambda} \right) \\
&= \frac{1}{\lambda}
\end{aligned}
$$

In general

$$
\begin{aligned}
I_n &= \int_0^{\infty} r^n e^{-\lambda r} dr \\
&= \left[\frac{r^n}{-\lambda} e^{-\lambda r} \right]_0^{\infty} + \int_0^{\infty} \frac{n r^{n-1}}{\lambda} e^{-\lambda r} dr \\
&= 0 + \frac{n}{\lambda} \int_0^{\infty} r^{n-1} e^{-\lambda r} dr \\
&= \frac{n}{\lambda} I_{n-1}
\end{aligned}
$$

So $I_n = \dfrac{n}{\lambda} I_{n-1}$. We find that:

$$
\begin{aligned}
I_n &= \left(\frac{n}{\lambda} \right) I_{n-1} \\
&= \left(\frac{n}{\lambda} \right) \left(\frac{n-1}{\lambda} \right) I_{n-2} \\
&= \left(\frac{n}{\lambda} \right) \left(\frac{n-1}{\lambda} \right) \left(\frac{n-2}{\lambda} \right) I_{n-3} \\
&\quad \ldots\ldots \\
&= \left(\frac{n}{\lambda} \right) \left(\frac{n-1}{\lambda} \right) \left(\frac{n-2}{\lambda} \right) \ldots . \left(\frac{1}{\lambda} \right) I_0 \\
&= \frac{n!}{\lambda^n} I_0 \\
&= \left(\frac{n!}{\lambda^n} \right) \left(\frac{1}{\lambda} \right) \\
&= \frac{n!}{\lambda^{n+1}}
\end{aligned}
$$

[QED]

$$\begin{aligned}\iiint \Psi_{1s}^2 dv &= \frac{1}{\pi a_0^3}\int_0^\infty r^2 e^{-\frac{2r}{a_0}} dr \int_0^\pi sin\theta d\theta \int_0^{2\pi} d\phi \\ &= \frac{4}{a_0^3}\int_0^\infty r^2 e^{-\frac{2r}{a_0}} dr \\ &= \left(\frac{4}{a_0^3}\right)\left(\frac{2!}{\left(\frac{2}{a_0}\right)^3}\right) \\ &= \frac{8a_0^3}{8a_0^3} \\ &= 1\end{aligned}$$

$$\begin{aligned}\iiint \Psi_{2s}^2 dv &= \frac{1}{32\pi a_0^3}\int_0^\infty r^2 \left(2-\frac{r}{a_0}\right)^2 e^{-\frac{r}{a_0}} dr \int_0^\pi sin\theta d\theta \int_0^{2\pi} d\phi \\ &= \frac{1}{8a_0^3}\int_0^\infty \left(4r^2 - \frac{4r^3}{a_0} + \frac{r^4}{a_0^2}\right) e^{-\frac{r}{a_0}} dr \\ &= \frac{1}{8a_0^3}\left\{4\left(\frac{2!}{\left(\frac{1}{a_0}\right)^3}\right) - \frac{4}{a_0}\left(\frac{3!}{\left(\frac{1}{a_0}\right)^4}\right) + \left(\frac{1}{a_0^2}\right)\left(\frac{4!}{\left(\frac{2}{a_0}\right)^5}\right)\right\} \\ &= \frac{1}{8a_0^3}\left\{8a_0^3 - 24a_0^3 + 24a_0^3\right\} \\ &= \frac{8a_0^3}{8a_0^3} \\ &= 1\end{aligned}$$

$$\begin{aligned}\iiint \Psi_{2p_z}^2 dv &= \frac{1}{23\pi a_0^5}\int_0^\infty r^4 e^{-\frac{r}{a_0}} dr \int_0^\pi sin\theta \cos^2\theta d\theta \int_0^{2\pi} d\phi \\ &= \frac{\frac{4\pi}{3}}{32\pi a_0^5}\int_0^\infty r^4 e^{-\frac{r}{a_0}} dr \\ &= \frac{1}{24a_0^5}(4!a_0^5) \\ &= 1\end{aligned}$$

$$\begin{aligned}\iiint \Psi_{1s}\Psi_{2s} dv &= \frac{1}{4\pi a_0^3\sqrt{2}}\int_0^\infty r^2\left(2-\frac{r}{a_0}\right) e^{-\frac{r}{a_0}} e^{-\frac{r}{2a_0}} dr \int_0^\pi sin\theta d\theta \int_0^{2\pi} d\phi \\ &= \frac{1}{a_0^3\sqrt{2}}\int_0^\infty \left(2r^2 e^{-\frac{3r}{2a_0}} - \frac{r^3}{a_0} e^{-\frac{3r}{2a_0}}\right) dr \\ &= \frac{1}{a_0^3\sqrt{2}}\left\{2\left(\frac{2!}{\left(\frac{3}{2a_0}\right)^3}\right) - \frac{1}{a_0}\left(\frac{3!}{\left(\frac{3}{2a_0}\right)^4}\right)\right\}\end{aligned}$$

$$\begin{aligned} &= \frac{1}{a_0^3\sqrt{2}}\left\{\frac{2^5 a_0^3}{3^3} - \left(\frac{1}{a_0}\right)\left(\frac{2^5 a_0^4}{3^3}\right)\right\} \\ &= 0 \end{aligned}$$

$$\begin{aligned} \iiint \Psi_{1s}\Psi_{2P_z} dv &= \frac{1}{4\pi a_0^4\sqrt{2}}\int_0^\infty r^3 e^{-\frac{3r}{2a_0}} dr \int_0^\pi sin\theta \cos\theta d\theta \int_0^{2\pi} d\phi \\ &= 0 \end{aligned}$$

Since $\int_0^\infty \sin\theta\cos\theta d\theta = 0$ by above.