Question

Electron Probability Density: **Unsöld's theorem** states that for any value of the orbital quantum number l, the probability densities summed over all possible states from $m_l = -l$ to $m_l = +l$ yield a constant independent of angles θ or ϕ; that is

$$\sum_{m_l=-l}^{+l} |\Theta|^2|\Phi|^2 = \text{constant}$$

Every closed subshell atom or ion has a spherically symmetric distribution of electric charge. Verify Unsöld's theorem for $l = 0$, $l = 2$, and $l = 3$.

Solution

For a H atom $\psi = R_{nl}\Theta_{lm_l}\Phi_{m_l}$. (The *normalized* wave functions R, Θ, Φ are shown on Table 6.1 in the text.)

For $l = 0$ (s subshell)

$m_l = 0$

$$\Theta(\theta) = \frac{1}{\sqrt{2}} \qquad \Phi(\phi) = \frac{1}{\sqrt{2\pi}}$$

$$\sum_{m_l=-l}^{+l} |\Theta|^2|\Phi|^2 = \frac{1}{4\pi}$$

$l = 1$ (p subshell)

$m_l = 0$

$$\Theta(\theta) = \frac{\sqrt{6}}{2}\,cos\theta \qquad \Phi(\phi) = \frac{1}{\sqrt{2\pi}}$$

$m_l = \pm 1$

$$\Theta(\theta) = \frac{\sqrt{3}}{2}\,sin\theta \qquad \Phi(\phi) = \frac{1}{\sqrt{2\pi}}\,e^{\pm i\phi}$$

$$\sum_{m_l=-l}^{+l} |\Theta|^2|\Phi|^2 = \frac{3}{8\pi}\,sin^2\theta + \frac{6}{8\pi}\,cos^2\theta + \frac{3}{8\pi}\,sin^2\theta = \frac{3}{4\pi}$$

For $l = 2$ (d subshell)

$m_l = 0$

$$\Theta(\theta) = \frac{\sqrt{10}}{4}(3cos^2\theta - 1) \qquad \Phi(\phi) = \frac{1}{\sqrt{2\pi}}$$

$m_l = \pm 1$

$$\Theta(\theta) = \frac{\sqrt{15}}{2}\,sin\theta cos\theta \qquad \Phi(\phi) = \frac{1}{\sqrt{2\pi}}\,e^{\pm i\phi}$$

$m_l = \pm 2$

$$\Theta(\theta) = \frac{\sqrt{15}}{4}\,sin^2\theta \qquad \Phi(\phi) = \frac{1}{\sqrt{2\pi}}\,e^{\pm 2i\phi}$$

$$\begin{aligned}\sum_{m_l=-l}^{+l} |\Theta|^2|\Phi|^2 &= 2\left(\frac{15}{32\pi}\, sin^4\theta\right) + 2\left(\frac{15}{8\pi}\, sin^2\theta cos^2\theta\right) + \frac{10}{32\pi}(3cos^2\theta - 1)^2 \\ &= \frac{10}{32\pi}\Big(3sin^4\theta + 12sin^2\theta cos^2\theta + 9cos^4\theta - 6cos^2\theta + 1\Big) \\ &= \frac{10}{32\pi}\Big(3sin^2\theta(1 - cos^2\theta) + 12sin^2\theta cos^2\theta + 9cos^2\theta(1 - sin^2\theta) - 6cos^2\theta + 1\Big) \\ &= \frac{10}{32\pi}\Big(3sin^2\theta + 3cos^2\theta + 1\Big) \\ &= \frac{5}{4\pi}\end{aligned}$$

In each case the sum of probability densities is a constant, independent of either θ or ϕ and the theorem is verified for these values of l.
