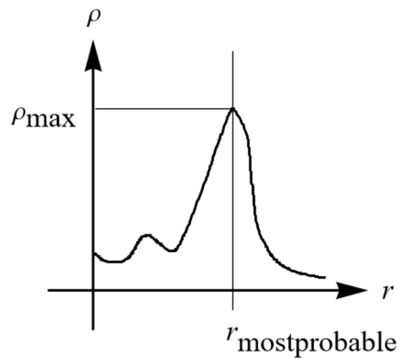
Problem 4.16

What is the *most probable* value of r, in the ground state of hydrogen? (The answer is *not* zero!) *Hint:* First you must figure out the probability that the electron would be found between r and $r + dr$.

Solution

If a continuous probability distribution $\rho = \rho(r)$ is known, the most probable value of r is the value of r at the absolute maximum.



The wave function of an electron in the ground state of hydrogen is

$$\begin{aligned}\Psi_{100}(r,\theta,\phi,t) &= R_{10}(r)Y_0^0(\theta,\phi)T_1(t)\\ &= \left(\sqrt{\frac{4}{a_0^3}}\,e^{-r/a_0}\right)\left(\sqrt{\frac{1}{4\pi}}\right)e^{-iE_1t/\hbar}\\ &= \frac{1}{\sqrt{\pi a_0^3}}\,e^{-r/a_0}e^{-iE_1t/\hbar}.\end{aligned}$$

According to Born's statistical interpretation, $|\Psi_{100}(r,\theta,\phi,t)|^2$ is the probability distribution for the electron's position in the ground state of hydrogen, and the probability of finding this electron within an infinitesimal volume $d\mathcal{V}$ is

$$\begin{aligned}dP &= |\Psi_{100}(r,\theta,\phi,t)|^2\,d\mathcal{V}\\ &= \Psi_{100}^*(r,\theta,\phi,t)\Psi_{100}(r,\theta,\phi,t)\,d\mathcal{V}\\ &= \left(\frac{1}{\sqrt{\pi a_0^3}}\,e^{-r/a_0}e^{iE_1t/\hbar}\right)\left(\frac{1}{\sqrt{\pi a_0^3}}\,e^{-r/a_0}e^{-iE_1t/\hbar}\right)d\mathcal{V}\\ &= \frac{1}{\pi a_0^3}e^{-2r/a_0}\,d\mathcal{V}.\end{aligned}$$

Write $d\mathcal{V}$ in terms of dr by using a spherical volume element in particular.

$$dP = \frac{1}{\pi a_0^3}e^{-2r/a_0}(r^2\sin\theta\,dr\,d\phi\,d\theta)$$

Integrate both sides with respect to ϕ from 0 to 2π.

$$\begin{aligned}\int dP &= \int_0^{2\pi} \frac{1}{\pi a_0^3} e^{-2r/a_0} (r^2 \sin\theta \, dr \, d\phi \, d\theta) \\ &= \left(\int_0^{2\pi} d\phi\right) \frac{1}{\pi a_0^3} e^{-2r/a_0} (r^2 \sin\theta \, dr \, d\theta) \\ &= (2\pi) \frac{1}{\pi a_0^3} e^{-2r/a_0} (r^2 \sin\theta \, dr \, d\theta) \\ &= \frac{2}{a_0^3} e^{-2r/a_0} (r^2 \sin\theta \, dr \, d\theta)\end{aligned}$$

Integrate both sides with respect to θ from 0 to π.

$$\begin{aligned}\iint dP &= \int_0^{\pi} \frac{2}{a_0^3} e^{-2r/a_0} (r^2 \sin\theta \, dr \, d\theta) \\ &= \left(\int_0^{\pi} \sin\theta \, d\theta\right) \frac{2}{a_0^3} e^{-2r/a_0} (r^2 \, dr) \\ &= (2) \frac{2}{a_0^3} e^{-2r/a_0} (r^2 \, dr) \\ &= \frac{4}{a_0^3} r^2 e^{-2r/a_0} \, dr \\ &= \rho(r) \, dr\end{aligned}$$

This double integral represents the probability of finding the electron between r and $r + dr$ (see Equation 1.14 on page 12). Integrating both sides with respect to r from a to b, for example, would give the probability of finding the electron between $r = a$ and $r = b$.

$$P(a < r < b) = \iiint dP = \int_a^b \rho(r) \, dr$$

Take the derivative of $\rho(r)$

$$\begin{aligned}\frac{d}{dr}\rho(r) &= \frac{d}{dr}\left(\frac{4}{a_0^3} r^2 e^{-2r/a_0}\right) \\ &= \frac{4}{a_0^3}\left[2re^{-2r/a_0} + r^2 e^{-2r/a_0}\left(-\frac{2}{a_0}\right)\right] \\ &= \frac{8}{a_0^3} r \left(1 - \frac{r}{a_0}\right) e^{-2r/a_0}\end{aligned}$$

and set it equal to zero to find the values of r at which there are extrema.

$$\frac{8}{a_0^3} r \left(1 - \frac{r}{a_0}\right) e^{-2r/a_0} = 0$$

$$r = \{0, a_0\}$$

Take the second derivative of $\rho(r)$.

$$\begin{aligned}\frac{d^2\rho}{dr^2} &= \frac{d}{dr}\left[\frac{8}{a_0^3}r\left(1-\frac{r}{a_0}\right)e^{-2r/a_0}\right]\\ &= \frac{8}{a_0^3}\left[\left(1-\frac{r}{a_0}\right)e^{-2r/a_0}+r\left(-\frac{1}{a_0}\right)e^{-2r/a_0}+r\left(1-\frac{r}{a_0}\right)e^{-2r/a_0}\left(-\frac{2}{a_0}\right)\right]\\ &= \frac{8}{a_0^3}\left(1-\frac{4r}{a_0}+\frac{2r^2}{a_0^2}\right)e^{-2r/a_0}\end{aligned}$$

Plug in $r = 0$ and $r = a_0$.

$$r = 0: \qquad \frac{d^2\rho}{dr^2}(0) = \frac{8}{a_0^3}(1-0+0)e^0 = \frac{8}{a_0^3}$$

$$r = a_0: \qquad \frac{d^2\rho}{dr^2}(a_0) = \frac{8}{a_0^3}(1-4+2)e^{-2} = -\frac{8}{a_0^3}e^{-2}$$

Since

$$\frac{d^2\rho}{dr^2}(0) > 0 \quad \text{and} \quad \frac{d^2\rho}{dr^2}(a_0) < 0,$$

there's a minimum at $r = 0$ and a maximum at $r = a_0$ by the Second Derivative Test. Therefore, the most probable value of r for the electron in the ground state of hydrogen is

$$r = a_0,$$

the Bohr radius. The graph of $a_0\rho(r)$ versus r/a_0 below confirms this.