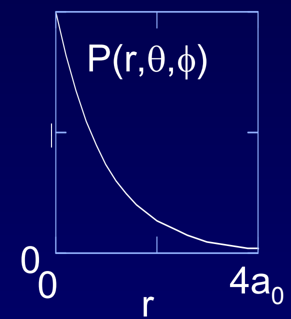
Supplement: Why Radial Probability Isn't the Same as Volume Probability

Let's look at the n=1, l=0 state (the "1s" state): $\psi(r,\theta,\phi) \propto R_{10}(r) \propto e^{-r/a_0}$.

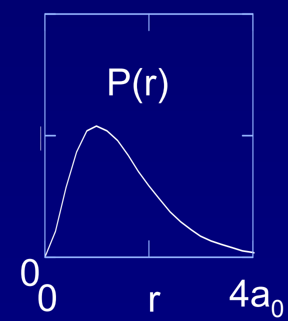
So, $P(r,\theta,\phi) = \psi^2 \propto e^{-2r/a_0}$.
This is the volume probability density.



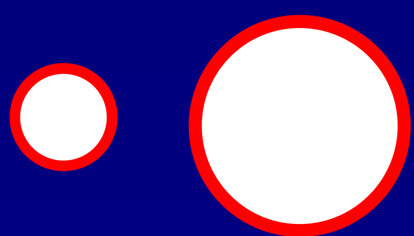
If we want the radial probability density, we must remember that:

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

We're not interested in the angular distribution, so to calculate P(r) we must integrate over θ and ϕ. The s-state has no angular dependence, so the integral is just 4π. Therefore, $P(r) \propto r^2 e^{-2r/a_0}$.



The factor of r^2 is due to the fact that there is more volume at large r. A spherical shell at large r has more volume than one at small r:



Compare the volume of the two shells of the same thickness, dr.