Statistics for hydrogen atom

Start with the ground state wave function ψ_{100}.

$$\psi_{100}(r, \theta, \phi) = \frac{1}{\sqrt{\pi a_0^3}} \exp\left(-\frac{r}{a_0}\right)$$

The cumulative distribution function $\Pr(r < a)$ is obtained by integrating $|\psi_{100}|^2$ over the volume element $r^2 \sin\theta \, dr \, d\theta \, d\phi$.

$$\Pr(r < a) = \frac{1}{\pi a_0^3} \int_0^a \int_0^\pi \int_0^{2\pi} \exp\left(-\frac{2r}{a_0}\right) r^2 \sin\theta \, dr \, d\theta \, d\phi$$

Integrate over ϕ (multiply by 2π).

$$\Pr(r < a) = \frac{2}{a_0^3} \int_0^a \int_0^\pi \exp\left(-\frac{2r}{a_0}\right) r^2 \sin\theta \, dr \, d\theta$$

Transform the integral over θ to an integral over y where $y = \cos\theta$ and $dy = -\sin\theta \, d\theta$. The minus sign in dy is canceled by interchanging integration limits $\cos 0 = 1$ and $\cos\pi = -1$.

$$\Pr(r < a) = \frac{2}{a_0^3} \int_0^a \int_{-1}^1 \exp\left(-\frac{2r}{a_0}\right) r^2 \, dr \, dy$$

Integrate over y (multiply by 2).

$$\Pr(r < a) = \frac{4}{a_0^3} \int_0^a \exp\left(-\frac{2r}{a_0}\right) r^2 \, dr$$

Solve the integral over r.

$$\Pr(r < a) = 1 - \left(\frac{2a^2}{a_0^2} + \frac{2a}{a_0} + 1\right) \exp\left(-\frac{2a}{a_0}\right) \tag{1}$$

For $a = a_0$ we have

$$\Pr(r < a_0) = 0.32$$

Hence the probability that the electron is inside the Bohr radius is 32%.

Another form of the cumulative distribution function is $F(r)$ where

$$F(r) = \frac{4}{a_0^3} \int \exp\left(-\frac{2r}{a_0}\right) r^2 \, dr = -\left(\frac{2r^2}{a_0^2} + \frac{2r}{a_0} + 1\right) \exp\left(-\frac{2r}{a_0}\right) \tag{2}$$

Then

$$\Pr(a < r < b) = F(b) - F(a)$$

and

$$\Pr(r < a) = F(a) - F(0)$$

The probability density function $f(r)$ is the derivative of $F(r)$.

$$f(r) = \frac{dF(r)}{dr} = \frac{4r^2}{a_0^3} \exp\left(-\frac{2r}{a_0}\right)$$ (3)

Use $f(r)$ to compute expectation values.

$$\langle r \rangle = \int_0^\infty r f(r)\, dr = \tfrac{3}{2} a_0$$

$$\langle r^2 \rangle = \int_0^\infty r^2 f(r)\, dr = 3 a_0^2$$

Hence

$$\mathrm{Var}(r) = \langle r^2 \rangle - \langle r \rangle^2 = \tfrac{3}{4} a_0^2$$