

PHY140Y

27 Properties of Hydrogen Atom Wave Functions

27.1 Overview

- Solutions to Schrödinger's Equation
- Normalization
- Probability Calculations

27.2 Solutions to Schrödinger's Equation

In the previous lecture, had shown that the ground state solution for the wave function of the hydrogen atom is

$$\psi_1(r) = A_1 e^{-r/a_0}, \text{ where} \quad (1)$$

$$a_0 = \frac{\hbar^2}{kme^2} = 5.29 \times 10^{-11} \text{ m} \quad \text{and} \quad E_1 = -\frac{\hbar^2}{2ma_0^2} = -13.6 \text{ eV}. \quad (2)$$

There are an infinite number of additional solutions to Schrödinger's equation that only depend on the radius, and these can be characterized by the principal quantum number n and have

$$\psi_n(r) = (\text{polynomial in } r) e^{-r/na_0}, \text{ with} \quad (3)$$

$$E_n = -\frac{\hbar^2}{2ma_0^2} \frac{1}{n^2}. \quad (4)$$

The wave function $\psi_n(r)$ has $n - 1$ "nodes," ie. places where it is zero, and increases in spatial extent as n increases. Thus, the higher the excited state, the larger the electron's orbital radius.

27.3 Normalization

Recall that in the 1-dimensional case, the probability of finding the particle in an interval $(x, x + dx)$ was given by the expression

$$P(x)dx = |\psi(x)|^2 dx, \quad (5)$$

where we called the function $P(x)$ the probability density. In 3-dimensions, we have to replace the infinitesimal dx with its 3-dimensional analogue

$$dV = dx dy dz, \quad (6)$$

which is just a microscopic cube. This is easy to visualize in Cartesian coordinates, but the analogous expression in spherical-polar coordinates looks more complicated:

$$dV = r^2 \sin \theta dr d\theta d\phi. \quad (7)$$

This can be seen to just be the volume of the object defined by the intervals $(r, r + dr)$, $(\theta, \theta + d\theta)$ and $(\phi, \phi + d\phi)$.

With this definition, we can define for a hydrogen atom in its ground state the overall probability of finding an electron anywhere around the hydrogen nucleus to be

$$1 = \int_0^\infty \int_0^\pi \int_0^{2\pi} A_1^2 e^{-2r/a_0} r^2 \sin \theta dr d\theta d\phi \quad (8)$$

We can rearrange this to do the integrations in ϕ and θ first since they are easy:

$$1 = A_1^2 \int_0^\infty r^2 e^{-2r/a_0} dr \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi \quad (9)$$

$$= A_1^2 \int_0^\infty r^2 e^{-2r/a_0} dr (2) (2\pi). \quad (10)$$

The integral in r requires a little more work. We can integrate it by parts to obtain

$$\int_0^\infty r^2 e^{-2r/a_0} dr = -\frac{r^2 a_0}{2} e^{-2r/a_0} \Big|_0^\infty + \frac{a_0}{2} \int_0^\infty 2r e^{-2r/a_0} dr \quad (11)$$

$$= a_0 \int_0^\infty r e^{-2r/a_0} dr. \quad (12)$$

We can repeat this integration by parts to yield the final result:

$$a_0 \int_0^\infty r e^{-2r/a_0} dr = -\frac{a_0^2}{2} r e^{-2r/a_0} \Big|_0^\infty + \frac{a_0^2}{2} \int_0^\infty e^{-2r/a_0} dr \quad (13)$$

$$= \frac{a_0^2}{2} \int_0^\infty e^{-2r/a_0} dr \quad (14)$$

$$= \frac{a_0^3}{4}. \quad (15)$$

Hence, the normalization of the ground state is defined by

$$1 = A_1^2 4\pi \frac{a_0^3}{4} \quad (16)$$

$$= A_1^2 \pi a_0^3 \quad (17)$$

$$\Rightarrow A_1 = \frac{1}{\sqrt{\pi a_0^3}} = 1.46 \times 10^{15} \text{ m}^{-3/2}. \quad (18)$$

27.4 Probability Calculations

With this result, we can now use the wave function to calculate specific probabilities for the behaviour of the electron in the hydrogen atom.

As a specific example, how often would we expect the electron to be within one Bohr radius of the proton? This is

$$P_{(r < a_0)} = \int_0^{a_0} |\psi|^2 dV \quad (19)$$

$$= \frac{1}{\pi a_0^3} (4\pi) \int_0^{a_0} r^2 e^{-2r/a_0} dr \quad (20)$$

$$= 0.323. \quad (21)$$

The factor of (4π) comes from performing the angular integrations first. Verify the final result by doing the integration by parts!

We see that the electron is far more likely to be found outside the Bohr radius than in it when it is in the ground state. From the radial dependence of the excited states, one finds this to be increasingly the case, again reflecting the general tendency for the atom to grow as the level of excitation of the atom increases.