Model of the Hydrogen Atom

Partial Differential Equations

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Objectives

In this lesson we will:

- model the simplest atom,
- solve the Schrödinger equation for the hydrogen atom, and
- discuss some of the properties of the solution.

Hydrogen Atom

- Mass of a proton $m_p = 1.67262 \times 10^{-27}$ kg.
- Mass of an electron is $m_e = 9.10938 \times 10^{-31}$ kg.
- The proton's mass is about 1836 times that of the electron, thus the center of mass of a hydrogen atom is located nearly at the position of the proton in the nucleus.
- The proton and electron possess charges of $e_0 = 1.60218 \times 10^{-19}$ Coulomb and $-e_0$ respectively.
- The potential for this attractive force between electron and proton is $V(\rho) = -e_0^2/(4\pi\epsilon_0\rho)$ where ρ is the distance separating the proton and electron.
- ϵ_0 is known as the permittivity of free space and has value 8.854×10^{-12} Farad/meter.

Schrödinger Equation

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2\mu}\Delta\Psi - \frac{e_0^2}{4\pi\epsilon_0\rho}\Psi.$$

The origin of the spherical coordinate system is assumed to lie at the center of the proton.

μ represents the reduced mass of the electron,

$$\mu = \frac{m_e m_p}{m_e + m_p} \approx m_e.$$

The expression $\Psi(\rho, \varphi, \theta, t)$ is the wave function of the electron. Solutions should have the property that

$$\int_0^\infty \int_0^\pi \int_{-\pi}^\pi \Psi(\rho, \varphi, \theta, t)\overline{\Psi(\rho, \varphi, \theta, t)}\rho^2 \sin\varphi \, d\theta \, d\varphi \, d\rho = 1.$$

This condition is sometimes referred to as the solution being **normalizable**. The wave function should also be 2π-periodic in θ, should vanish as $\rho \to \infty$, and should be bounded as $\rho \to 0^+$.

Separation of Variables (1 of 5)

Assume a product solution of the form $\Psi(\rho, \varphi, \theta, t) = T(t)R(\rho)F(\varphi, \theta)$.

$$i\hbar \frac{T'(t)}{T(t)} = -\frac{\hbar^2}{2\mu} \frac{\Delta \left[R(\rho)F(\varphi, \theta)\right]}{R(\rho)F(\varphi, \theta)} - \frac{e_0^2}{4\pi\epsilon_0\rho}$$

The left-hand side of this equation depends on t while the right-hand side depends on the spherical coordinate system variables, thus each side is equal to a constant denoted as E. Expanding the Laplacian in spherical coordinates result in

$$\begin{aligned} E &= -\frac{\hbar^2}{2\mu} \frac{\Delta \left[R(\rho)F(\varphi, \theta)\right]}{R(\rho)F(\varphi, \theta)} - \frac{e_0^2}{4\pi\epsilon_0\rho} \\ \left(E + \frac{e_0^2}{4\pi\epsilon_0\rho}\right) RF &= -\frac{\hbar^2}{2\mu} \left(R''F + \frac{2}{\rho} R'F\right) \\ &\quad - \frac{\hbar^2}{2\mu\rho^2} \left(RF_{\varphi\varphi} + \cot\varphi RF_{\varphi} + \csc^2\varphi RF_{\theta\theta}\right). \end{aligned}$$

Separation of Variables (2 of 5)

Multiply both sides by $2\mu\rho^2/(\hbar^2 RF)$ and move terms depending on ρ to the left-hand side.

$$\rho^2\left(\frac{R''}{R}+\frac{2}{\rho}\frac{R'}{R}+\frac{2\mu E}{\hbar^2}\right)+\frac{\mu e_0^2}{2\pi\epsilon_0\hbar^2}\rho=-\left(\frac{F_{\varphi\varphi}}{F}+\cot\varphi\frac{F_\varphi}{F}+\csc^2\varphi\frac{F_{\theta\theta}}{F}\right)$$

The radial variable ρ is separated from the angular variables (φ,θ). If both sides of the equation are equal to a constant λ then the partial differential equation for the angular variables becomes

$$F_{\varphi\varphi}+\cot\varphi F_\varphi+\csc^2\varphi F_{\theta\theta}+\lambda F=0.$$

If $\lambda=l(l+1)$ for $l=0,1,2,\ldots$, the solutions are the spherical harmonic functions $Y_l^m(\varphi,\theta)$.

Separation of Variables (3 of 5)

Setting the ρ-dependent side of the equation equal to $l(l+1)$ produces

$$\rho^2 R''(\rho) + 2\rho R'(\rho) + \left(\frac{2\mu E}{\hbar^2}\rho^2 + \frac{\mu e_0^2}{2\pi\epsilon_0\hbar^2}\rho - l(l+1)\right) R(\rho) = 0$$

This can be re-written as

$$xy''(x) + ((2l+1)+1-x)y'(x) + \left(e_0^2\sqrt{\frac{-\mu}{32\pi^2\epsilon_0^2 E\hbar^2}} - l - 1\right) y(x) = 0.$$

If the coefficient of $y(x)$ is a nonnegative integer, this is an example of the associated Laguerre differential equation.

Let $n = e_0^2\sqrt{-\mu/(32\pi^2\epsilon_0^2 E\hbar^2)}$, and thus when n is a positive integer such that $n \geq l+1$, there is a polynomial solution $y(x) = L_{n-l-1}^{2l+1}(x)$.

Separation of Variables (4 of 5)

Define $\alpha = \frac{2}{\hbar}\sqrt{-2\mu E}$ and the radial factor of the solution can be written as

$$R_{n,l}(\rho) = e^{-\frac{\alpha\rho}{2}}(\alpha\rho)^l L_{n-l-1}^{2l+1}(\alpha\rho)$$

for $l = 0, 1, 2, \ldots$ and n an integer for which $n \geq l + 1$.

The time-independent solution to the boundary value problem

$$R(\rho)F(\varphi, \theta) = e^{-\frac{\alpha\rho}{2}}(\alpha\rho)^l L_{n-l-1}^{2l+1}(\alpha\rho)Y_l^m(\varphi, \theta),$$

where l, m, and n are integers satisfying the inequality $|m| \leq l < n$ and $n \in \mathbb{N}$. To aid with notation, define $u_{l,m,n}(\rho, \varphi, \theta)$ to be the expression on the right-hand side of the last equation.

The assumption that n is a positive integer implies the possible values of E, the energy of the electron, are given by

$$E \equiv E_n = -\frac{\mu e_0^4}{32\pi^2\epsilon_0^2\hbar^2 n^2}.$$

These energies are called the energies of the bound (or stationary) states of the hydrogen atom.

Separation of Variables (5 of 5)

The time-dependent factor $T(t)$ of the product solution is

$$T'(t) = \frac{-iE_n}{\hbar} T(t),$$

and thus $T_n(t) = e^{-iE_n t/\hbar}$ for $n \in \mathbb{N}$.

Since the magnitude of $T_n(t)$ is one, the wave functions are normalized when $u_{l,m,n}(\rho, \varphi, \theta)$ is normalized.

$$\begin{aligned}
&\int_0^\infty \int_0^\pi \int_{-\pi}^\pi u_{l,m,n}(\rho,\varphi,\theta)\overline{u_{l,m,n}(\rho,\varphi,\theta)}\rho^2 \sin\varphi \, d\theta \, d\varphi \, d\rho \\
&= \int_0^\infty e^{-\alpha\rho}(\alpha\rho)^{2l}\left(L_{n-l-1}^{2l+1}(\alpha\rho)\right)^2 \rho^2 \, d\rho \int_0^\pi \int_{-\pi}^\pi Y_l^m(\varphi,\theta)\overline{Y_l^m(\varphi,\theta)} \sin\varphi \, d\theta \, d\varphi \\
&= \int_0^\infty e^{-\alpha\rho}(\alpha\rho)^{2l}\left(L_{n-l-1}^{2l+1}(\alpha\rho)\right)^2 \rho^2 \, d\rho \\
&= \frac{1}{\alpha^3}\int_0^\infty r^{2l+2}\left(L_{n-l-1}^{2l+1}(r)\right)^2 e^{-r} \, dr \\
&= \frac{(2n)\Gamma(n+l+1)}{\alpha^3 (n-l-1)!}.
\end{aligned}$$

Product Solution

$$\Psi_{l,m,n}(\rho,\varphi,\theta,t) = \sqrt{\frac{\alpha^3(n-l-1)!}{(2n)\Gamma(n+l+1)}}e^{-\frac{iE_n}{\hbar}t}e^{-\frac{\alpha}{2}\rho}(\alpha\rho)^l L_{n-l-1}^{2l+1}(\alpha\rho)Y_l^m(\varphi,\theta),$$

for $|m| \leq l < n$ and $n \in \mathbb{N}$.

- Index l is often called the **orbital** or **angular momentum quantum number**.
- Index m is the **magnetic quantum number**.
- Index n is the **principal** or **total quantum number**.

When the electron of the hydrogen atom is in energy state E_n, the wave function of the electron will be one of the n^2 functions given above.

Probability Density Function

The probability density function of the electron is

$$\begin{aligned} P_{l,m,n}(\rho,\varphi,\theta) &= \Psi_{l,m,n}(\rho,\varphi,\theta,t)\overline{\Psi_{l,m,n}(\rho,\varphi,\theta,t)} \\ &= \frac{\alpha^3(n-l-1)!}{(2n)\Gamma(n+l+1)} e^{-\alpha\rho}(\alpha\rho)^{2l}\left(L_{n-l-1}^{2l+1}(\alpha\rho)\right)^2 Y_l^m(\varphi,\theta)\overline{Y_l^m(\varphi,\theta)}. \end{aligned}$$

Example: $P_{2,0,3}(\rho, \varphi, \theta)$