Schrödinger Equation for the Hydrogen Atom

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In this paper, I derive the general equation of the wave function of the hydrogen atom by solving the Schrödinger equation in spherical coordinates.

I. INTRODUCTION

The hydrogen atom is the simplest system in quantum mechanics. It consists of an electron orbiting a positively charged nucleus (proton). The quantum description of this system is based on solving the time-dependent Schrödinger equation for the electron under the influence of the Coulomb potential of the proton. Next, I will now derive the general equation of the wave function of the hydrogen atom.

II. SCHRÖDINGER EQUATION IN SPHERICAL COORDINATES

The time-independent Schrödinger equation in Cartesian coordinates is:

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi(\mathbf{r}) + V(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r}), \tag{1}$$

where μ is the reduced mass of the electron-proton system, $V(\mathbf{r})$ is the Coulomb potential, and E is the total energy of the system.

The Coulomb potential that describes the interaction between the electron and the proton is:

$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r}, \tag{2}$$

where e is the charge of the electron and ϵ_0 is the vacuum permittivity. To solve this equation in spherical coordinates (r, θ, φ) [1], it is convenient to rewrite the Laplacian operator ∇^2 in these coordinates, which gives the following form of the Schrödinger equation:

$$\left\{-\frac{\hbar^2}{2\mu r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right] - \frac{e^2}{4\pi\epsilon_0 r}\right\}\psi(r,\theta,\varphi) = E\psi(r,\theta,\varphi) \tag{3}$$

where $\hbar$ is the reduced Planck constant, μ is the reduced electron mass, r, θ, φ are the spherical coordinates, $V(r)$ is the Coulomb potential between the electron and the nucleus, E is the total energy of the system.

III. SEPARATION OF VARIABLES

To solve this equation, we use the method of separation of variables, assuming that the total wave function $\psi(r, \theta, \varphi)$ can be written as the product of a radial function $R(r)$ and an angular function $Y(\theta, \varphi)$, that is:

$$\psi(r,\theta,\varphi) = R(r)Y(\theta,\varphi). \tag{4}$$

Substituting this into the Schrödinger equation and separating the variables, we obtain two independent equations: one for the radial part $R(r)$ and one for the angular part $Y(\theta, \varphi)$.

A. Angular Part

The angular part of the equation is associated with the angular momentum of the electron. The angular equation is:

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\varphi^2} = -l(l+1)Y(\theta,\varphi), \tag{5}$$

where l is the angular momentum quantum number. The solutions of this equation are the spherical harmonics $Y_l^m(\theta, \varphi)$, which are given by:

$$Y_l^m(\theta,\varphi) = \sqrt{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}}P_l^m(\cos\theta)e^{im\varphi}, \tag{6}$$

where $P_l^m(\cos\theta)$ are the associated Legendre polynomials [2], and m is the magnetic quantum number.

$$\begin{aligned} P_l^m(x) &= (-1)^m(1-x^2)^{m/2}\frac{d^m}{dx^m}P_l(x) \\ &= \frac{(-1)^m}{2^l l!}(1-x^2)^{m/2}\frac{d^{l+m}}{dx^{l+m}(x^2-1)^l} \end{aligned} \tag{7}$$

B. Radial Part

The radial part of the Schrödinger equation is:

$$\begin{aligned} &\frac{d^2R(r)}{dr^2} + \frac{2}{r}\frac{dR(r)}{dr} - \frac{l(l+1)}{r^2}R(r) \\ &+\frac{2\mu}{\hbar^2}\left(E + \frac{e^2}{4\pi\epsilon_0 r}\right)R(r) = 0. \end{aligned} \tag{8}$$

The solution of this equation involves the use of associated Laguerre polynomials, and the physical solutions are given by:

$$R_{nl}(r) = \sqrt{\left(\frac{2Z}{na_0}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}} e^{-Zr/na_0} \times \left(\frac{2Zr}{na_0}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2Zr}{na_0}\right), \quad (9)$$

where L_{n-l-1}^{2l+1} are the generalized Laguerre polynomials, Z is the number of protons in the nucleus (for hydrogen, $Z = 1$), and a_0 is the Bohr radius.

IV. FULL WAVE FUNCTION

The full wave function of the hydrogen atom is the product of the radial part $R_{nl}(r)$ and the angular part $Y_l^m(\theta, \varphi)$:

$$\psi_{nlm}(r, \theta, \varphi) = R_{nl}(r) Y_l^m(\theta, \varphi), \quad (10)$$

where n is the principal quantum number, l is the angular momentum quantum number, and m is the magnetic quantum number.

V. DISCUSSION

I have derived the general equation of the wave function of the hydrogen atom by solving the Schrödinger equation in spherical coordinates. The solution consists of a radial function and an angular function, which describe the probability distribution of the electron in the atom. It is the basis for the derivation of more complex atomic systems.

The solution of the Schrödinger equation for a Coulomb potential is indispensable for advanced analysis in quantum mechanics. For instance, in time-independent perturbation theory. In a future work, the way to calculate the energy correction to quantum states when the Hamiltonian of the system is modified by small perturbations will be presented. For the case of Hydrogen, perturbation theory allows us to find corrections to the energy levels of the hydrogen atom due to fine structure, external fields, or other small interactions.

[1] "Spherical Harmonic – from Wolfram MathWorld." https://mathworld.wolfram.com/SphericalHarmonic.html.

[2] "Associated Legendre Polynomial – from Wolfram MathWorld." https://mathworld.wolfram.com/AssociatedLegendrePolynomial.html.