Vector Representation of the Hydrogen Atom

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1 Introduction

The hydrogen atom, consisting of a single proton and an electron, is one of the fundamental systems in quantum mechanics and electromagnetism. Its simplicity allows for analytical solutions to the Schrödinger equation, making it a cornerstone of atomic physics.

In classical terms, the hydrogen atom can be described by the relative position of the electron with respect to the proton. This is represented by the position vector $\mathbf{r}$, which extends from the proton (at the origin) to the electron. Additionally, the center of mass (COM) of the system provides a useful reference point for analyzing motion in a two-body system.

A visual representation of these vectors is provided in Figure 1, where the proton is fixed at the origin, and the electron is located at some arbitrary point. The unit vector $\hat{\mathbf{r}}$ denotes the normalized direction of $\mathbf{r}$, useful for expressing forces and fields acting on the system.

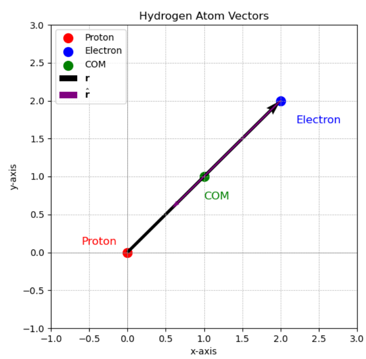

Figure 1: A labeled vector diagram showing the proton (red), electron (blue), center of mass (green), and the vectors $\mathbf{r}$ and $\hat{\mathbf{r}}$.

2 Analytical Solution

Building on this geometric framework, we now derive the wavefunction of the hydrogen atom by solving the time-independent Schrödinger equation in spherical coordinates. Given the central Coulomb potential, the problem naturally lends itself to separation of variables, leading to distinct radial and angular components. The following derivation outlines each step in detail, from the formulation of the governing equation to the final expression of the hydrogenic wavefunctions in terms of associated Laguerre and Legendre polynomials.

2.1 Step 1: Write the Time-Independent Schrödinger Equation

The time-independent Schrödinger equation (TISE) for a hydrogen atom is:

$$-\frac{\hbar^2}{2m}\nabla^2\psi - \frac{e^2}{4\pi\epsilon_0 r}\psi = E\psi \tag{1}$$

Expanding the Laplacian in spherical coordinates:

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2} \tag{2}$$

Substituting into Schrödinger's equation:

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

2.2 Step 2: Apply Separation of Variables

Assume that the wavefunction ψ can be separated as:

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

Substituting this into the Schrödinger equation and dividing by RY, we get:

$$\left[\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2m}{\hbar^2}\left(E + \frac{e^2}{4\pi\epsilon_0 r}\right)r^2\right] + \frac{1}{Y}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right] = 0 \tag{5}$$

Since each term depends only on either r or (θ,ϕ), they must be equal to a constant, defined as $\ell(\ell+1)$.

This gives two separate differential equations:

1. **Angular equation**:

$$\frac{1}{Y}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right] = -\ell(\ell+1) \tag{6}$$

2. **Radial equation**:

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2m}{\hbar^2}\left(E+\frac{e^2}{4\pi\epsilon_0 r}\right)r^2=\ell(\ell+1) \tag{7}$$

2.3 Step 3: Solve the Angular Equation

We assume a separable solution:

$$Y(\theta,\phi)=\Theta(\theta)\Phi(\phi) \tag{8}$$

Solving for $\Phi(\phi)$:

$$\frac{d^2\Phi}{d\phi^2}+m^2\Phi=0 \tag{9}$$

The solutions are exponentials:

$$\Phi_m(\phi)=e^{im\phi} \tag{10}$$

For $\Theta(\theta)$, defining $x=\cos\theta$, we get Legendre's equation:

$$\frac{d}{dx}\left((1-x^2)\frac{d\Theta}{dx}\right)+\left[\ell(\ell+1)-\frac{m^2}{1-x^2}\right]\Theta=0 \tag{11}$$

The solutions are associated Legendre polynomials:

$$\Theta_{\ell m}(\theta)=P_\ell^m(\cos\theta) \tag{12}$$

2.4 Step 4: Solve the Radial Equation

Define:

$$\rho=\frac{2r}{na_0} \tag{13}$$

This transforms into Laguerre's equation, with solutions:

$$R_{n\ell}(r)=\frac{1}{r}\rho^\ell e^{-\rho/2}L_{n-\ell-1}^{2\ell+1}(\rho) \tag{14}$$

The energy levels are:

$$E_n=-\frac{me^4}{8\epsilon_0^2h^2}\frac{1}{n^2},\quad n=1,2,3,... \tag{15}$$

2.5 Step 5: Construct the Full Wavefunction

$$\psi_{n\ell m}(r,\theta,\phi) = R_{n\ell}(r)Y_\ell^m(\theta,\phi) \tag{16}$$

where: - $R_{n\ell}(r)$ is the radial wavefunction (Laguerre polynomials) - $Y_\ell^m(\theta,\phi)$ is the angular wavefunction (Legendre polynomials and exponentials)

3 The Radial Schrödinger Equation

Next, we apply the finite difference scheme to the radial equation of the hydrogen problem:

$$\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) - \frac{2\mu r^2}{\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\frac{1}{r} - \frac{l(l+1)\hbar^2}{2\mu r^2} - E\right)R = 0. \tag{17}$$

Using the substitution:

$$\rho \equiv rR \quad \Rightarrow \quad R = \frac{\rho}{r}, \tag{18}$$

the differential operator transforms as follows:

$$\begin{aligned}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\frac{\rho}{r}\right) &= \frac{\partial}{\partial r}\left[r^2\frac{1}{r}\frac{\partial\rho}{\partial r} + r^2\rho\left(-\frac{1}{r^2}\right)\right] \\ &= \frac{\partial\rho}{\partial r} + r\frac{\partial^2\rho}{\partial r^2} - \frac{\partial\rho}{\partial r} \\ &= r\frac{\partial^2\rho}{\partial r^2}.\end{aligned} \tag{19}$$

Thus, the equation simplifies to:

$$r\frac{\partial^2\rho}{\partial r^2} - \frac{2\mu r^2}{\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\frac{1}{r} - \frac{l(l+1)\hbar^2}{2\mu r^2} - E\right)\frac{\rho}{r} = 0. \tag{20}$$

Dividing by r, we obtain:

$$\frac{\partial^2\rho}{\partial r^2} - \frac{2\mu}{\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\frac{1}{r} - \frac{l(l+1)\hbar^2}{2\mu r^2} - E\right)\rho = 0. \tag{21}$$

Rewriting in operator form:

$$-\frac{\hbar^2}{2\mu}\frac{\partial^2\rho}{\partial r^2} + \frac{e^2}{4\pi\epsilon_0}\frac{1}{r}\rho - \frac{l(l+1)\hbar^2}{2\mu r^2}\rho = E\rho. \tag{22}$$

This equation is now in a form where we can apply the finite difference method.

4 Finite Difference Discretization

We discretize the radial coordinate using an equidistant grid of N elements with a spacing Δr. The discretized Hamiltonian consists of three terms.

4.1 Laplacian Term

The Laplace operator is approximated using a three-point stencil, leading to a tridiagonal matrix:

$$-\frac{\hbar^2}{2\mu}\begin{bmatrix} -2 & 1 & 0 & \cdots & 0 \\ 1 & -2 & 1 & \cdots & 0 \\ 0 & 1 & -2 & \ddots & 0 \\ \vdots & \vdots & \ddots & \ddots & 1 \\ 0 & 0 & 0 & 1 & -2 \end{bmatrix}. \tag{23}$$

4.2 Potential Terms

The Coulomb potential term results in a diagonal matrix:

$$\frac{e^2}{4\pi\epsilon_0}\begin{bmatrix} \frac{1}{r_1} & 0 & 0 & \cdots & 0 \\ 0 & \frac{1}{r_2} & 0 & \cdots & 0 \\ 0 & 0 & \frac{1}{r_3} & \ddots & 0 \\ \vdots & \vdots & \ddots & \ddots & 0 \\ 0 & 0 & 0 & 0 & \frac{1}{r_N} \end{bmatrix}. \tag{24}$$

Similarly, the centrifugal term gives another diagonal matrix:

$$-\frac{\hbar^2}{2\mu}\begin{bmatrix} \frac{1}{r_1^2} & 0 & 0 & \cdots & 0 \\ 0 & \frac{1}{r_2^2} & 0 & \cdots & 0 \\ 0 & 0 & \frac{1}{r_3^2} & \ddots & 0 \\ \vdots & \vdots & \ddots & \ddots & 0 \\ 0 & 0 & 0 & 0 & \frac{1}{r_N^2} \end{bmatrix}. \tag{25}$$

4.3 Hamiltonian Matrix

The sum of these three matrices forms the Hamiltonian matrix:

$$H = -\frac{\hbar^2}{2\mu}D + V_{\text{Coulomb}} + V_{\text{centrifugal}}. \tag{26}$$

To solve for the energy levels, we diagonalize the Hamiltonian matrix. The eigenvalues E_n correspond to the energy states of the system, and the eigenvectors ρ_n are related to the radial wave functions R_n through the relation:

$$R_n = \frac{\rho_n}{r}. \tag{27}$$