

The Hydrogen Atom

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Abstract

Schrödinger's solution of both the relativistic and the nonrelativistic Coulomb problem in its Wave Mechanics formulation is reviewed.

1 The Wave Equations

Schrödinger's derivation of a wave equation for a particle of mass m began with the relativistic dispersion relation for the free particle: $p^\mu p_\mu = g_{\mu\nu} p^\mu p^\nu = (mc)^2$. In terms of the energy E and the three-momentum \mathbf{p} this is

$$E^2 - (\mathbf{p}c)^2 = (mc^2)^2 \quad (1)$$

Interaction of a particle of charge q with the electromagnetic field is described by the Principle of Minimal Electromagnetic Coupling: $p_\mu \rightarrow \pi_\mu = p_\mu - \frac{q}{c} A_\mu$, where the four-vector potential A consists of the scalar potential Φ and the vector potential \mathbf{A} . These obey $\mathbf{B} = \nabla \times \mathbf{A}$ and $\mathbf{E} = -\nabla\Phi - \frac{1}{c} \frac{\partial \mathbf{A}}{\partial t}$. For an electron $q = -e$, where e is the charge on the proton, positive by convention. In the Coulomb field established by a proton, $\Phi = e/r$ and $\mathbf{A} = \mathbf{0}$, so that $E \rightarrow E + e^2/r$. Here r is the proton-electron distance. The Schrödinger prescription for converting a dispersion relation to a wave equation is to replace $\mathbf{p} \rightarrow (\hbar/i)\nabla$ and allow the resulting equation to act on a spacial function $\psi(\mathbf{x})$. This prescription results in the wave equation

$$\begin{array}{l} \text{Klein-} \\ \text{Gordon} \\ \text{Equation:} \end{array} \quad \left\{ E^2 - (mc^2)^2 + 2E \left(\frac{e^2}{r} \right) + \left(\frac{e^2}{r} \right)^2 - (-i\hbar c \nabla)^2 \right\} \psi(x) = 0 \quad (2)$$

This equation exhibits spherical symmetry in the sense that it is unchanged (invariant) in form under rotations: $\langle S'|H|S' \rangle = \langle S|H|S \rangle$, where $\langle S'|S \rangle \in SO(3)$. Schrödinger solved this equation, compared its predictions with the spectral energy measurements on the hydrogen atom, was not convinced his theory was any good, and buried this approach in his desk drawer.

Sometime later he reviewed this calculation and took its nonrelativistic limit. Since the binding energy is about 13.6 eV and the electron rest energy mc^2 is about 510,000 eV, it makes sense to write $E = mc^2 + W$, where the principle part of the relativistic energy E is the electron rest energy and the nonrelativistic energy W is a small perturbation of either ($\simeq 0.0025\%$). Under this substitution, and neglecting terms of order $(W + e^2/r)^2/mc^2$, we obtain the nonrelativistic form of Eq. (14.4):

$$\begin{array}{l} \text{Schrödinger} \\ \text{Equation:} \end{array} \quad \left\{ \frac{\mathbf{p} \cdot \mathbf{p}}{2m} - \frac{e^2}{r} - W \right\} \psi(\mathbf{x}) = \left\{ -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{r} - W \right\} \psi(\mathbf{x}) = 0 \quad (3)$$

Eq.(2) is now known as the Klein-Gordon equation and its nonrelativistic limit Eq.(3) is known as the Schrödinger equation, although the former was derived by Schrödinger before he derived his namesake equation.

Remark: Schrödinger began his quest for a theory of atomic physics with Maxwell's Equations, in particular, the eikonal form of these equations. It is no surprise that his theory inherits key characteristics of electromagnetic theory: solutions that are amplitudes, the superposition principle for solutions, and interference effects that come about by squaring amplitudes to obtain intensities. Had he started from classical mechanics, there would be no amplitude-intensity relation and the only superposition principle would have been the superposition of forces or their potentials. The elegant but forced relation between Poisson brackets and commutator brackets $([A, B]/i\hbar = \{A, B\})$ is an attempt to fit quantum mechanics into the straitjacket of classical mechanics.

2 Quantization Conditions

The standard approach to solving partial differential equations is to separate variables. Since the two equations derived above have spherical symmetry, it is useful to introduce spherical coordinates: (r, θ, ϕ) . In this coordinate system the Laplacian is

$$\nabla^2 = \left(\frac{1}{r} \frac{\partial}{\partial r} r \right)^2 + \frac{\mathcal{L}^2(S^2)}{r^2} \quad (4)$$

$$\mathcal{L}^2(S^2) = \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \quad (5)$$

The second order differential operator $\mathcal{L}^2(S^2)$ is the Laplacian on the sphere S^2 . Its eigenfunctions are the spherical harmonics $Y_m^l(\theta, \phi)$ and its spectrum of eigenvalues is $\mathcal{L}^2(S^2)Y_m^l(\theta, \phi) = -l(l+1)Y_m^l(\theta, \phi)$. The integers (l, m) satisfy $l = 0, 1, 2, \dots$ and $-l \leq m \leq +l$. The negative sign and discrete spectrum characteristically indicate that S^2 is compact.

The partial differential equations Eqs.(2) and (3) are reduced to ordinary differential equations by substituting the ansatz

$$\psi(r, \theta, \phi) \rightarrow \frac{1}{r} R(r) Y_m^l(\theta, \phi) \quad (6)$$

into these equations, replacing the angular part of the Laplacian by the eigenvalue $-l(l+1)$, and multiplying by r on the left. This gives the simple second order ordinary differential equation

$$\left(\frac{d^2}{dr^2} + \frac{A}{r^2} + \frac{B}{r} + C \right) R(r) = 0 \quad (7)$$

The values of the coefficients A, B, C that are obtained for the Klein-Gordon equation and the Schrödinger equation are

| Equation | A | B | C |
|--------------|-----------------------------|---------------------|--------------------------------|
| Klein-Gordon | $-l(l+1) + (e^2/\hbar c)^2$ | $2Ee^2/(\hbar c)^2$ | $[E^2 - (mc^2)^2]/(\hbar c)^2$ |
| Schrödinger | $-l(l+1)$ | $2me^2/\hbar^2$ | $2mW/\hbar^2$ |

(8)

There is a standard procedure for solving simple ordinary differential equations of the type presented in Eq.(7). This is the Frobenius method. The steps involved in this method, and the result of each step, are summarized in Table 1.

The energy eigenvalues for the bound states of both the relativistic and nonrelativistic problems are expressed in terms of the radial quantum number $n = 0, 1, 2, \dots$ and the angular momentum

Table 1: Left column lists the steps followed in the Frobenius method for finding the square-integrable solutions of simple ordinary differential equations. Right column shows the result of applying the step to Eq.(7).

| Procedure | Result |
|--|---|
| 1 Locate singularities | $0, \infty$ |
| 2 Determine analytic behavior at singular points | $r \rightarrow 0 : R \simeq r^\gamma, \quad \gamma(\gamma - 1) + A = 0$ $r \rightarrow \infty : R \simeq e^{\lambda r}, \quad \lambda^2 + C = 0$ |
| 3 Keep only \mathcal{L}^2 solutions | $\gamma = \frac{1}{2} + \sqrt{\left(\frac{1}{2}\right)^2 - A}, \quad \lambda = -\sqrt{-C}$ |
| 4 Look for solutions with proper asymptotic behavior | $R = r^\gamma e^{\lambda r} f(r)$ |
| 5 Construct DE for $f(r)$ | $[(rD^2 + 2\gamma D) + (2\lambda\gamma + B + 2\lambda r D)] f(r) = 0$ |
| 6 Construct recursion relation | $f_{j+1} = -\frac{2\lambda(j+\gamma)+B}{j(j+1)+2\gamma(j+1)} f_j$ |
| 7 Look at asymptotic behavior | $f \simeq e^{-2\lambda r}$ if series doesn't terminate $\simeq e^{+1\lambda r}$ if series does terminate ($\lambda < 0$) |
| 8 Construct quantization condition | $2\lambda(n + \gamma) + B = 0$ or $n + \frac{1}{2} + \sqrt{\left(\frac{1}{2}\right)^2 - A} = \frac{B}{2\sqrt{-C}}$ |
| 9 Construct explicit solutions | $E = \frac{mc^2}{\sqrt{1+(\alpha/N')^2}} \quad W = -\frac{1}{2}mc^2\alpha^2 \frac{1}{N^2}$ $N' = n + \frac{1}{2} + \sqrt{\left(l + \frac{1}{2}\right)^2 - \alpha^2} \quad N = n + l + 1$ |

quantum number $l = 0, 1, 2, \dots$, mass m of the electron, or more precisely the reduced mass of the proton-electron pair $m_{red}^{-1} = m_e^{-1} + M_p^{-1}$, and the fine structure constant

$$\alpha = \frac{e^2}{\hbar c} = \frac{1}{137.035\,999\,796(70)} = 0.007\,297\,352\,531\,3(3\,8) \quad (9)$$

This is a dimensionless ratio of three physical constants that are fundamental in three “different” areas of physics: e (electromagnetism), \hbar (quantum mechanics), and c (relativity). It is one of the most precisely measured of the physical constants. The bound state energy eigenvalues are

| | | |
|--|--|------|
| <p>Klein-Gordon Equation</p> $E(n, l) = \frac{mc^2}{\sqrt{1 + (\alpha/N')^2}}$ $N' = n + \frac{1}{2} + \sqrt{\left(l + \frac{1}{2}\right)^2 - \alpha^2}$ | <p>Schrödinger Equation</p> $W(n, l) = -\frac{1}{2}mc^2\alpha^2 \frac{1}{N^2}$ $N = n + l + 1$ | (10) |
|--|--|------|

Both the nonrelativistic and relativistic energies have been plotted in Fig. 1. The nonrelativistic energies for the hydrogen atom appear as the darker lines. The nonrelativistic energy has been normalized by dividing by the hydrogen atom ground state energy $|W_1| = \frac{1}{2}mc^2\alpha^2$. These normalized energy levels decrease to zero like $1/N^2$, where $N = n + l + 1$ is the principle quantum number. The energies are displayed as a function of the orbital angular momentum l . The relativistic energies of

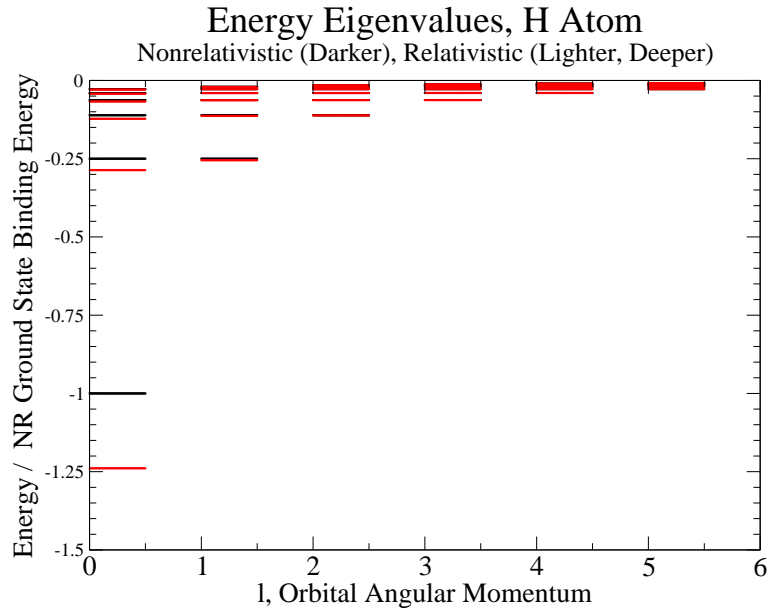


Figure 1: Spectrum of the hydrogen atom, normalized by the energy of the nonrelativistic ground state. The nonrelativistic spectrum is darker. The relativistic spectrum has been computed for $Z = 50$. These energies are computed by replacing $\alpha \rightarrow Z\alpha$ everywhere.

the bound states for the proton-electron system converge to the rest energy mc^2 as N' increases. When this limit is removed these energies (also rescaled by dividing by $\frac{1}{2}mc^2\alpha^2$) can be plotted on the same graph. At the resolution shown, the two sets of rescaled energies are indistinguishable. To illustrate the difference, we have instead computed and plotted the bound state spectrum for a single electron in a potential with positive charge Z . The energies in this case are obtained by the substitution $\alpha \rightarrow Z\alpha$ everywhere. The energies of these bound states have been renormalized by subtracting the limit mc^2 and dividing by the nonrelativistic energy for the same ion: $\frac{1}{2}mc^2(Z\alpha)^2$. The energy difference between the $1s$ ground states is pronounced; this difference decreases rapidly as the principle quantum number increases.