

12.4: Dirac Theory of the Hydrogen Atom

The theory of Paul Dirac represents an attempt to unify the theories of quantum mechanics and [special relativity](#). That is, one seeks a formulation of quantum mechanics which is [Lorentz invariant](#), and hence consistent with special relativity. For a free particle, relativity states that the energy is given by

$$E + p^2 c^2 + m^2 c^4 \quad (12.4.1)$$

Associating E with a Hamiltonian in quantum mechanics, one has

$$H^2 = p^2 c^2 + m^2 c^4 \quad (12.4.2)$$

If H and p are associated with the same operators as in Schrödinger theory, then one expects the wave equation

$$-\hbar \frac{\partial^2}{\partial t^2} \Psi = (-\hbar^2 \nabla^2 c^2 + m^2 c^4) \Psi \quad (12.4.3)$$

This is known as the *Klein-Gordon Equation*. Unfortunately, attempts to utilize this equation are not successful, since that which one would wish to interpret as a probability distribution turns out to be not **positive definite**. To alleviate this problem, the square root may be taken to get

$$H = \sqrt{p^2 c^2 + m^2 c^4} \quad (12.4.4)$$

However, this creates a new problem. What is meant by the square root of an operator? The approach is to guess the form of the answer, and the correct guess turns out to be

$$H = c \alpha \cdot p + \beta m c^2 \quad (12.4.5)$$

With this form of the Hamiltonian, the wave equation can be written

$$i\hbar \frac{\partial \chi}{\partial t} = (c \alpha \cdot p + \beta m c^2) \chi \quad (12.4.6)$$

In order for this to be valid, one hopes that when it is squared the **Klein-Gordon equation** is recovered. For this to be true, Equation 12.4.6 must be interpreted as a matrix equation, where α and β are at least 4×4 matrices and the wavefunction χ is a four-component column matrix.

It turns out that Equation 12.4.6 describes only a particle with spin 1/2. This is fine for application to the hydrogen atom, since the electron has spin 1/2, but why should it be so? The answer is that the linearization of the Klein-Gordon equation is not unique. The particular linearization used here is the simplest one, and happens to describe a particle of spin 1/2, but other more complicated Hamiltonians may be constructed to describe particles of spin 0, 1, 5/2 and so on. The fact that the relativistic Dirac theory automatically includes the effects of spin leads to an interesting conclusion - spin is a relativistic effect. It can be added by hand to the non-relativistic Schrödinger theory with satisfactory results, but spin is a natural consequence of treating quantum mechanics in a completely relativistic fashion.

Spin is a relativistic effect

Including the potential now in the Hamiltonian, Equation 12.4.6 becomes

$$i\hbar \frac{\partial \chi}{\partial t} = \left(c \alpha \cdot \mathbf{p} + \beta m c^2 - \frac{Z e^2}{r} \right) \chi. \quad (12.4.7)$$

When the square root was taken to linearize the Klein-Gordon equation, both a positive and a negative energy solution was introduced. One can write the wavefunction

$$\chi = \begin{pmatrix} \Psi_+ \\ \Psi_- \end{pmatrix}, \quad (12.4.8)$$

where Ψ_+ represents the two components of χ associated with the positive energy solution and Ψ_- represents the components associated with the negative energy solution. The physical interpretation is that Ψ_+ is the particle solution, and Ψ_- represents an anti-particle. Anti-particles are thus predicted by Dirac theory, and the discovery of anti-particles obviously represents a huge

triumph for the theory. In hydrogen, however, the contribution of Ψ_- is small compared to Ψ_+ . With enough effort, the equations for Ψ_+ and Ψ_- can be decoupled to whatever order is desired. When this is done, the Hamiltonian to order v^2/c^2 can be written

$$H + H_s + \Delta H_{rel} + \Delta H_{so} + \Delta H_d \quad (12.4.9)$$

where

- H_s is the original Schrödinger Hamiltonian,
- ΔH_{rel} is the relativistic correction to the kinetic energy,
- ΔH_{so} is the spin-orbit term, and
- ΔH_d is the previously mentioned Darwin term.

The Darwin Term

The physical origin of the Darwin term is a phenomenon in Dirac theory called *zitterbewegung*, whereby the electron does not move smoothly, but instead undergoes extremely rapid small-scale fluctuations, causing the electron to see a smeared-out Coulomb potential of the nucleus.

The Darwin term may be written

$$\Delta H_d = -\frac{e\hbar^2}{8m^2c^2} \nabla^2 \Psi \quad (12.4.10)$$

For the hydrogenic-atom potential $V = \frac{Ze}{r}$, Equation 12.4.10 is

$$H_d = -\frac{Ze^2\pi\hbar^2}{2m^2c^2} \delta^3(r) \quad (12.4.11)$$

When first-order perturbation theory is applied, the energy correction depends on $|\Psi(0)|^2$. This term will only contribute for s states (i.e., $(l=0)$), since only these wavefunctions have **non-zero probability** for finding the electron at the origin. The energy correction for $l = 0$ can be calculated to be

$$\Delta E_d = (Z\alpha)^4 mc^2 \frac{1}{2n^3} \quad (12.4.12)$$

Including this term, the fine-structure splitting can be reproduced for all l . All the effects that go into fine structure are thus a natural consequence of the Dirac theory.

The hydrogen atom can be solved exactly in Dirac theory, where the states found are simultaneous eigenstates of H , J^2 , and J_z , since these operators can be shown to mutually commute. The exact energy levels in Dirac theory are

$$E_{nj} = mc^2 \left[1 + \left(\frac{Z\alpha}{n - (j + \frac{1}{2}) + \sqrt{(j + \frac{1}{2})^2 - (Z\alpha)^2}} \right)^2 \right]^{-1/2}. \quad (12.4.13)$$

This can be expanded in powers of $Z\alpha$, yielding

$$E_{nj} = mc^2 \left\{ 1 - \frac{1}{2} \frac{(Z\alpha)^2}{n^2} \left[1 + \frac{(Z\alpha)^2}{n} \left(\frac{1}{j + \frac{1}{2}} - \frac{3}{4n} \right) \right] + \dots \right\} \quad (12.4.14)$$

This includes an amount mc^2 due to the relativistic energy associated with the rest mass of the electron, along with the principle energy levels and fine structure, in exact agreement to order $(Z\alpha)^4$ with what was previously calculated. However, even this exact solution in Dirac theory is not a complete description of the hydrogen atom, and so the next section describes further effects not yet discussed.

Footnote

See Bjorken and Drell Chapter 4 for a thorough discussion of the transfer

Contributors and Attributions

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