FY2045 Quantum Mechanics I

Fall 2023

Henning Goa Hugdal

Week 13

Hydrogen atom revisited

— Fine structure and hyperfine structure

Background

The Schrödinger equation,

$$i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r},t) = \left[\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right]\Psi(\mathbf{r},t),$$

is not Lorentz invariant — the time and space derivatives enter differently — and is not consistent with the theory special relativity.

The electron spin was proposed by Goudsmit and Uhlenbeck to explain experimental results — “duplexity phenomena” — and added “by hand” by Pauli.

Background

The question remains as to why Nature should have chosen this particular model for the electron instead of being satisfied with the point-charge. One would like to find some incompleteness in the previous methods of applying quantum mechanics to the point-charge electron such that, when removed, the whole of the duplexity phenomena follow without arbitrary assumptions. In the present paper it is shown that this is the case, the incompleteness of the previous theories lying in their disagreement with relativity, or, alternatively, with the general transformation theory of quantum mechanics. It appears that the simplest Hamiltonian for a point-charge electron satisfying the requirements of both relativity and the general transformation theory leads to an explanation of all duplexity phenomena without further assumption.

P.A.M. Dirac, *The quantum theory of the electron*, Proc. R. Soc. Lond. A **117** 610–624 (1928).

Background

Dirac proposed a new wave equation consistent with special relativity,

$$i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r},t) = \left[-ic\hbar\boldsymbol{\alpha}\cdot\boldsymbol{\nabla} + \beta mc^2 + V(\mathbf{r})\right]\Psi(\mathbf{r},t),$$

where α_i, β are 4×4 matrices, which naturally included and justified **spin** and predicted **antimatter**.

In the non-relativistic limit, $|\mathbf{p}|c \ll mc^2$, the Dirac equation simplifies to the Schrödinger equation[1], but we will now look at a situation where we have to include relativistic corrections in order to get agreement between experiment and theory.

[1] Loosely speaking. It is more correct to say that the leading order terms in an expansion of the Dirac equation in powers of $|\mathbf{p}|/(mc)$ agrees with the Pauli equation — the Schrödinger equation for spin ½ particles.

Fine structure and hyperfine structure

When we studied the hydrogen atom, we used

$$H_0 = -\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 - \frac{e^2}{4\pi\epsilon_0}\frac{1}{r},$$

and got the energy levels E_n with eigenfunctions $\psi_{nlm}(\mathbf{r})$. However, the experimental spectra for hydrogen show more energy levels than those predicted using the above Hamiltonian. There are additional corrections:

Fine structure: Relativistic corrections and spin-orbit coupling.

Lamb shift: Associated with the quantization of the electromagnetic field.

Hyperfine splitting: Interaction between the spins of the electron and proton.

Fine structure

Relativistic correction to kinetic energy:

Taylor expanding relativistic energy expression (or Dirac equation) in powers of p/mc,

$$T \approx \frac{p^2}{2m} - \frac{p^4}{8m^3c^2} + \ldots,$$

leads to additional term in Hamiltonian

$$H_r = -\frac{p^4}{8m^3c^2}.$$

First order correction:

$$E_r^1 = -\frac{E_n^2}{2mc^2}\left[\frac{4n}{l+\frac{1}{2}} - 3\right].$$

Fine structure

Darwin term:

From the Dirac equation, one also gets relativistic correction to potential energy,

$$H_D = \frac{\hbar^2 \pi}{2m^2 c^2} \left(\frac{e^2}{4\pi\epsilon_0} \right) \delta(\mathbf{r}).$$

Since $\psi_{nlm}(0) = 0$ for $l > 0$, only s-orbitals are affected by the perturbations.

First order correction:

$$E_D^1 = \frac{2n}{mc^2} E_n^2, \quad (l = 0).$$

Fine structure

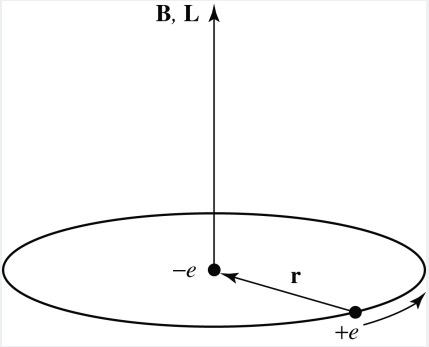
Spin-orbit coupling:

Classical picture: In the *electron's rest frame*, the proton rotates about the electron. The circulating current sets up a magnetic field $\mathbf{B}$ that exerts a torque on the magnetic moment $\boldsymbol{\mu}$ of the electron,

$$H = -\boldsymbol{\mu} \cdot \mathbf{B}.$$

Since $\boldsymbol{\mu} \propto \mathbf{S}$ and $\mathbf{B} \propto \mathbf{L}$, this results in a **spin-orbit coupling**

$$H_{SO} \propto \mathbf{L} \cdot \mathbf{S}.$$



Fine structure

Spin-orbit coupling:

From the Dirac equation, one finds for the hydrogen atom

$$H_{SO} = \left(\frac{e^2}{8\pi\epsilon_0}\right)\frac{1}{m^2c^2r^3}\mathbf{L}\cdot\mathbf{S}.$$

First order correction:

$$E^1_{SO} = \frac{2E_n^2}{mc^2}\frac{n\left[j(j+1) - l(l+1) - \frac{3}{4}\right]}{l(2l+1)(l+1)} \quad (l > 0).$$

Fine structure

Gathering all terms, we get the first-order fine-structure corrections

$$E^1_{fs} = \frac{E_n^2}{2mc^2}\left[3 - \frac{4n}{j+\frac{1}{2}}\right].$$

Hence, the new energy levels are

$$E_{nj} = -\frac{13.6\text{ eV}}{n^2}\left[1 + \frac{\alpha^2}{n^2}\left(\frac{n}{j+\frac{1}{2}} - \frac{3}{4}\right)\right]$$

with **fine structure constant**[1]

$$\alpha \equiv \frac{e^2}{4\pi\epsilon_0\hbar c} \approx \frac{1}{137}.$$

[1] For recent experimental results on the variation of α in nearby stars, see *A limit on variations in the fine-structure constant from spectra of nearby Sun-like stars*, Murphy *et al.* (2022).

The end of the periodic table?

From the Dirac equation the exact energies for an atom with nuclear charge Ze is

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

Feynman suggested[2] that neutral atoms could not exist for $Z > 137$, since the energy of the inner electron would turn imaginary. This is likely not the case due to other details, and the theorized extended periodic table goes past $Z = 170$.[3] The highest known atomic number is $Z = 118$, oganesson.

[2] This is probably more of a folk legend.

[3] See e.g. The extended periodic table — Elements above the atomic number 137.

Hyperfine structure

Both the proton and electron have a magnetic dipole moment

$$\boldsymbol{\mu}_p = \frac{g_p e}{2m_p}\mathsf{S}_p, \quad \boldsymbol{\mu}_e = -\frac{g_e e}{2m_e}\mathsf{S}_e,$$

with $g_p \approx 5.59$ and $g_e \approx 2$. A magnetic dipole sets up a magnetic field, leading to a **spin-spin coupling**

$$H_{\mathrm{hf}} = \frac{\mu_0 g_p e^2}{8\pi m_p m_e}\frac{3(\mathsf{S}_p \cdot \hat{r})(\mathsf{S}_e \cdot \hat{r}) - \mathsf{S}_p \cdot \mathsf{S}_e}{r^3} + \frac{\mu_0 g_p e^2}{3m_p m_e}\mathsf{S}_p \cdot \mathsf{S}_e \delta(\mathsf{r}).$$

We consider the correction for the ground state only, $|nlm\rangle = |100\rangle$.

Hyperfine structure

Since the proton and electron spins are coupled, the "good" quantum numbers are the total spin quantum numbers s and m_s, with "good" states

$$|100; 1m_s\rangle,\ m_s = -1, 0, 1 \qquad (s = 1,\ \text{triplet}),$$
$$|100; 00\rangle, \qquad (s = 0,\ \text{singlet}).$$

We then get the first order corrections

$$E^1_{hf} = E_0 \alpha^2 \frac{8 g_p m_e}{3 m_p} \times \begin{cases} -\frac{1}{4}, & \text{triplet}, \\ +\frac{3}{4}, & \text{singlet}, \end{cases}$$

leading to a splitting of $\Delta E = 5.88 \times 10^{-6}$ eV.