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Chapter 3

Fine Structure and Lamb Shift

3.1 Fine Structure

Immediately adjacent to Michelson and Morley's announcement of their failure to find the ether in an 1887 issue of the Philosophical Journal is a paper by the same authors reporting that the H_α line of hydrogen is actually a doublet, with a separation of 0.33 cm^{-1}. In 1915 Bohr suggested that this "fine structure" of hydrogen is a relativistic effect arising from the variation of mass with velocity. Sommerfeld, in 1916, solved the relativistic Kepler problem and using the old quantum theory, as it was later christened, accounted precisely for the splitting. Sommerfeld's theory gave the lie to Einstein's dictum "The Good Lord is subtle but not malicious", for it gave the right results for the wrong reason: his theory made no provision for electron spin, an essential feature of fine structure. Today, all that is left from Sommerfeld's theory is the fine structure constant $\alpha = e^2/\hbar c$.

The theory for the fine structure in hydrogen was provided by Dirac whose relativistic electron theory (1926) was applied to hydrogen by Darwin and Gordon in 1928. They found the following expression for the energy of an electron bound to a proton of infinite mass:

$$\frac{E}{mc^2} = \left[\frac{1}{\sqrt{\frac{\alpha Z}{n-k+\sqrt{k^2-\alpha^2 Z^2}}}} \right]^2 \tag{3.1}$$

where n is the principal quantum number, $k = j+1/2$, and $j = \ell \pm 1/2$. The Dirac equation is not nearly as illuminating as the Pauli equation, which is the approximation to the Dirac equation to the lowest order in v/c.

$$H = mc^2 + \frac{p^2}{2m} - \frac{e^2}{r} + H_{FS} \tag{3.2}$$

The first term is the electron's rest energy; the following two terms are the non relativistic Hamiltonian, and the last term, the fine structure interaction, is given by

$$H_{FS} = -\frac{p^4}{8m^3c^2} + \frac{\hbar^2 e^2}{2m^2c^2}\frac{1}{r^3}\mathbf{L}\cdot\mathbf{S} - \frac{\hbar^2}{8m^2c^2}\nabla^2\frac{e^2}{r} \tag{3.3}$$

The relativistic contributions can be described as the *kinetic, spin-orbit,* and *Darwin* terms, $H_{\rm kin}$, $H_{\rm so}$, and $H_{\rm Dar}$, respectively. Each has a straightforward physical interpretation.

3.1.1 Kinetic contribution

Relativistically, the total electron energy is E $= \sqrt{(mc^2)^2 + (pc)^2}$. The kinetic energy is

$$T = E - mc^2 = (mc^2)\left[\sqrt{1 + \frac{p^2}{m^2c^2}} - 1\right] = \frac{p^2}{2m} - \frac{1}{8}\frac{p^4}{m^3c^2} + \cdots \tag{3.4}$$

Thus

$$H_{\text{kin}} = \frac{1}{8}\frac{p^4}{m^3c^2} \tag{3.5}$$

3.1.2 Spin-Orbit Interaction

According to the Dirac theory the electron has intrinsic angular momentum $\hbar S$ and a magnetic moment $\vec{\mu}_2 = -g_e\mu_0\mathbf{S}$. The electron g-factor, $g_e = 2$. As the electron moves through the electric field of the proton it "sees" a motional magnetic field

$$\mathbf{B}_{\text{mot}} = -\frac{v}{c} \times \mathbf{E} = -\frac{v}{c} \times \frac{e}{r^3}\mathbf{r} = \frac{e\hbar}{mc}\frac{1}{r^3}\mathbf{L} \tag{3.6}$$

where $\hbar\mathbf{L} = \mathbf{r} \times m\mathbf{v}$. However, there is another contribution to the effective magnetic field arising from the Thomas precession.

The relativistic transformation of a vector between two moving co- ordinate systems which are moving with different velocities involve not only a dilation, but also a rotation (cf Jackson, *Classical Electrodynamics*). The rate of rotation, the Thomas precession, is

$$\vec{\Omega}_T = \frac{1}{2}\frac{\mathbf{a} \times \mathbf{v}}{c^2} \tag{3.7}$$

Note that the precession vanishes for co-linear acceleration. However, for a vector fixed in a co-ordinate system moving around a circle, as in the case of the spin vector of the electron as it circles the proton, Thomas precession occurs. From the point of view of an observer fixed to the nucleus, the precession of the electron is identical to the effect of a magnetic field.

$$\mathbf{B}_T = \frac{1}{\gamma_e}\vec{\Omega}_T. \tag{3.8}$$

Substituting $\gamma_e = e/mc$, and $\mathbf{a} = -e^2\mathbf{r}/mr^3$ into Eq. 3.7 gives

$$\mathbf{B}_T = -\frac{1}{2}\frac{e\hbar}{mc}\frac{1}{r^3}\mathbf{L} \tag{3.9}$$

Hence the total effective magnetic field is

$$\mathbf{B}' = \frac{1}{2}\frac{e\hbar}{mc}\frac{1}{r^3}\mathbf{L} \tag{3.10}$$

This gives rise to a total spin-orbit interaction

$$H_{so} = -\vec{\mu} \cdot \mathbf{B}' = \frac{e^2\hbar^2}{2m^2c^2}\frac{1}{r^3}\mathbf{S} \cdot \mathbf{L} \tag{3.11}$$

3.1.3 The Darwin Term

Electrons exhibit "Zitterbewegung", fluctuations in position on the order of the Compton wavelength, $\hbar/mc$. As a result, the effective Coulombic potential is not $V(r)$, but some suitable average $\overline{V}(\mathbf{r})$, where the average is over the characteristic distance $\hbar/mc$. To evaluate this, expand $V(\mathbf{r})$ about $\mathbf{r}$ in terms of a displacement $\mathbf{s}$,

$$\mathbf{V}(\mathbf{r}+\mathbf{s}) = V(\mathbf{r}) + \vec{\nabla}V \cdot \mathbf{s} + \frac{1}{2}\sum_{ij} \mathbf{s}_{xi}\mathbf{s}_{xj}\frac{\partial^2 V}{\partial x_i \partial x_j} + \cdots \tag{3.12}$$

Assume that the fluctuations are isotropic. Then the time average of $V(\mathbf{r}+\mathbf{s}) - V(\mathbf{r})$ is

$$\Delta V \sim \frac{1}{2}\left[\frac{1}{3}\left(\frac{\hbar}{mc}\right)^2\right]\nabla^2 V = -\frac{1}{6}\frac{e^2\hbar^2}{m^2c^2}\nabla^2\left(\frac{1}{r}\right) \tag{3.13}$$

The precise expression for the Darwin term is

$$H_{\text{Dar}} = -\frac{1}{8}\frac{e^2\hbar^2}{m^2c^2}\nabla^2\left(\frac{1}{r}\right) \tag{3.14}$$

The coefficient of the Darwin term is 1/8, rather than 1/6.

3.1.4 Evaluation of the fine structure interaction

The spin orbit-interaction is not diagonal in $\mathbf{L}$ or $\mathbf{S}$ due to the term $\mathbf{L}\cdot\mathbf{S}$. However, it is diagonal in $\mathbf{J} = \mathbf{L} + \mathbf{S}$. H_{so} and H_{Dar} are likewise diagonal in $\mathbf{J}$. Hence, finding the energy level structure due to the fine structure interaction involves evaluating $< n, \ell, S, j, m_j | H_{\text{FS}} | n, l, S, j, m_j >$. Note that $< H_{\text{so}} >$ vanishes in an S state, and that $< H_{\text{Dar}} >$ vanishes in all states but an S state. It is left as an exercise to show that

$$E_{\text{FS}}(n,j) = (\alpha^2 mc^2)\left(-\frac{\alpha^2}{2n^4}\right)\left(\frac{n}{j+1/2} - \frac{3}{4}\right) \tag{3.15}$$

Note that states of a given n and j are degenerate. This degeneracy is a crucial feature of the Dirac theory.

3.2 The Lamb Shift

According to the Dirac theory, states of the hydrogen atom with the same values of n and j are degenerate. Hence, in a given term, $({}^2S_{1/2}, {}^2P_{1/2})$, $({}^2P_{3/2}, {}^2D_{3/2})$, $({}^2D_{5/2}, {}^2F_{5/2})$, etc. form degenerate doublets. However, as described in Chapter 1, this is not exactly the case. Because of vacuum interactions, not taken into account, in the Dirac theory, the degeneracy is broken. The largest effect is in the $n = 2$ state. The energy splitting between the ${}^2S_{1/2}$ and ${}^2P_{1/2}$ states is called the Lamb Shift. A simple physical model due to Welton and Weisskopf demonstrate its origin.

Because of zero point fluctuation in the vacuum, empty space is not truly empty. The electromagnetic modes of free space behave like harmonic oscillators, each with zero-point energy $h\nu/2$. The density of modes per unit frequency interval and per volume is given by the well known expression

$$\rho(\nu)d\nu = 8\pi\frac{\nu^2}{c^3}d\nu \tag{3.16}$$

Consequently, the zero-point energy density is

$$W_\nu = \frac{1}{2}h\nu\rho(\nu) = 4\pi\frac{h\nu^3}{c^3} \tag{3.17}$$

With this energy we can associate a spectral density of radiation

$$W_\nu = \frac{1}{8\pi}\left(\overline{E_\nu^2} + \overline{B_\nu^2}\right) = \frac{1}{8\pi}E_\nu^2 \tag{3.18}$$

The bar denotes a time average and E_ν and B_ν are the field amplitudes. Hence,

$$E_\nu^2 = \frac{32\pi^2 h\nu^3}{c^3} \tag{3.19}$$

For the moment we shall treat the electron as if it were free. Its motion is given by

$$m\ddot{s}_\nu = eE_\nu \cos 2\pi\nu t \tag{3.20}$$

$$\overline{s_\nu^2} = \frac{e^2}{32\pi^4 m^2\nu^4}E_\nu^2 \quad = \frac{e^2 h}{\pi^2 m^2 c^3}\frac{1}{\nu} \tag{3.21}$$

The effect of the fluctuation $\mathbf{s}_\nu$ is to cause a change ΔV in the average potential

$$\Delta V = \overline{V(r + s_\nu)} - V(r) \tag{3.22}$$

$V(\mathbf{r} + \mathbf{s}_\nu)$ can be found by a Taylor's expansion:

$$V(\mathbf{r} + \mathbf{s}_\nu) = V(\mathbf{r}) + \Delta V \cdot \mathbf{s}_\nu + \frac{1}{2}\sum_{ij}\frac{\partial^2 V}{\partial s_{\nu,i}\partial s_{\nu,j}}s_{\nu,i}s_{\nu,j} + \cdots \tag{3.23}$$

When we average this in time, the second term vanishes because $\mathbf{s}$ averages to zero. For the same reason, in the final term, only contributions with $i = j$ remain. We have, taking the average,

$$\overline{V(\mathbf{r} + \mathbf{s}_\nu)} = V(\mathbf{r}) + \frac{1}{2}\sum_i \frac{\partial^2 V_i}{\partial s_{\nu,i}^2}\overline{s_{\nu,i}^2} \tag{3.24}$$

Since $\overline{s_{\nu,i}^2} = \overline{s_\nu^2}/3$ we obtain finally

$$\overline{V(r + s_\nu)} = \frac{s_\nu^2}{6}\nabla^2 V(r) \tag{3.25}$$

Since $\nabla^2 V(\mathbf{r}) = 4\pi Ze\delta(\mathbf{r})$, we obtain the following expression for the change in energy

$$\delta W_\nu = \frac{2\pi}{2}e^2 s_\nu^2 < n', \ell', m'|\delta(\mathbf{r})|n, \ell, m > \tag{3.26}$$

The matrix element gives contributions only for S states, where its value is

$$|\Psi_{n,0,0}(0)|^2 = \frac{Z^3}{\pi n^3 a_0^3} \tag{3.27}$$

Combining Eqs. 3.21, 3.27 into Eq. 3.26 yields

$$\delta W_\nu = \frac{2}{3} e^2 s_\nu^2 \frac{Z^4}{n^3 a_0^3} = \frac{2}{3} \frac{e^4 Z^4}{m^2 c^3 \pi^2} \frac{1}{n^3 a_0^2} \frac{h}{\nu} \tag{3.28}$$

Integrating over some yet to be specified frequency limits, we obtain

$$\delta W = \frac{2}{3} \frac{e^4}{m^2 c^3} \frac{Z^4}{\pi^2} \frac{h}{n^3 a_0^3} \ln\left(\frac{\nu_{\text{max}}}{\nu_{\text{min}}}\right) \tag{3.29}$$

At this point, atomic units come in handy. Converting by the usual prescription, we obtain

$$\delta W = \frac{4}{3\pi} \alpha^3 \frac{Z^4}{n_3} \ln\left(\frac{\nu_{\text{max}}}{\nu_{\text{min}}}\right) \tag{3.30}$$

The question remaining is how to choose the cut-off frequencies for the integration. It is reasonable that ν_{min} is approximately the frequency of an orbiting electron, Z^2/n^3 in atomic units. At lower energies, the electron could not respond. For the upper limit, a plausible guess is the rest energy of the electron, mc^2. Hence, $\nu_{\text{max}}/\nu_{\text{min}} \sim Z^2/(n^3\alpha^2)$.
For the $2S$ state, this gives

$$\delta W = \frac{1}{6\pi} \alpha^3 \ln \frac{8}{\alpha^2} = 2.46 \times 10^{-7} \text{ atomic units} = 1,600 \text{ MHz} \tag{3.31}$$

The actual value is 1,058 MHz.

Bibliography

[1] John M. Blatt, Journal of Comp. Phys. **1**, 382 (1967).