Week 9 Worksheet
Fine Structure of Hydrogen

Jacob Erlikhman

March 14, 2024

Exercise 0. Warm up.

a) What are the physical effects that make up fine structure?

b) Write down H_r, the relativistic hamiltonian, and explain its physical origin.
Hint: Expand the relativistic energy for $v \ll c$.

c) Do the same for H_{SO}, but don't feel obligated to get every factor of 2 right.
Hint: $H = -\boldsymbol{\mu} \cdot \mathbf{B}$.

This is done in Griffiths.

Exercise 1. Darwin Term. In class, you found that the spin-orbit coupling gave a first-order correction to the energy

$$E^1_{\text{SO}} = \frac{{E_n}^2}{mc^2} \frac{n[j(j+1) - \ell(\ell+1) - 3/4]}{\ell(\ell+1/2)(\ell+1)}.$$

a) What is E^1_{SO} for s-states, i.e. those with $\ell = 0$?
Hint: If $\ell = 0$, then what values can $\mathbf{L} \cdot \mathbf{S}$ take?

b) There is an additional effect for s-states called the **Darwin term**:

$$H_D = \frac{\hbar^2}{8m^2c^2} \nabla^2 V_C,$$

where $V_C = -e/r$ is the Coulomb potential. This term can be derived from the Dirac equation, but we can get a handle on it using non-relativistic QM. To see where the term comes from, the Dirac equation (relativistic quantum mechanics) predicts that the electron does not have a constant position. Instead, it undergoes a frantic jittering motion due to the creation of virtual position-electron pairs. The lifetime of these is given by the uncertainty principle $\Delta t \Delta E = \hbar$, so $\Delta t = \hbar/mc^2$. The position of the electron is smeared out due to this motion by the characteristic distance associated to this lifetime, the Compton wavelength: $\lambda_c \equiv c\Delta t = \hbar/mc \approx 4 \cdot 10^{-11}$ cm. So the potential energy is not at a particular position; rather, it is an average around that point. Suppose that r_0 is the average position, and expand the potential $V_C(r)$ as a Taylor expansion to second order about r_0.

c) Use symmetry to argue that the expectation value of the first term in the expansion is 0.

d) Use the same symmetry and dimensional analysis to argue that

$$\langle V_C(r)\rangle \approx V_C(r_0) + A\frac{\hbar^2}{m^2c^2}4\pi e^2\delta^{(3)}(\mathbf{r}),$$

where A is a dimensionless constant. We call the second term the **Darwin term**. Calculate A, and show that this reproduces H_D exactly, *assuming that the characteristic length is actually* $3\lambda_c/4$.

e) Argue that this term has an expectation value only for s-states.

f) Use the fact that $R_{n0}(0) = 2/(na_0)^{3/2}$, where $a_0 = \hbar^2/me^2$, and that

$$E_r^1 = -\frac{{E_n}^2}{2mc^2}(8n-3)$$

for s-states to calculate E_{fs}^1 for such states. Compare to the formula in Griffiths,

$$E_{\text{fs}}^1 = -\frac{2{E_n}^2}{mc^2}\left(\frac{n}{j+1/2} - 3/4\right).$$

Hint: Note that $E_n = -mc^2\alpha^2/2n^2$.

Remark 1. This calculation agrees with the physical intuition that in s-states the spin-orbit coupling should be 0. It explains the fine structure energy correction derived in Griffiths. There, Griffiths makes the assumption that E_{SO}^1 is *not* zero for s-states in order to complete the derivation.

Remark 2. You may have noticed that we kind of cheated by assuming that the characteristic length was $3\lambda_c/4$ rather than just λ_c. Unfortunately, there isn't a good justification for this. The Darwin term and all of fine structure can be derived rigorously from the Dirac equation, and that's all there is to it. The Schrödinger theory just isn't a good theory for dealing with truly relativistic effects.

a) In s-states, the electron has no orbital angular momentum, so it can't couple to the proton's spin. Thus, $E_{\text{SO}}^1 = 0$.

b) Suppose we perturb around $\mathbf{r}_0$ by $\delta\mathbf{r}$. Then we can expand

$$V_C(r) = V_C(r_0) + \delta\mathbf{r}\cdot\nabla V_C(r_0) + \frac{1}{2}\delta r_i\delta r_j\nabla_i V_C(r_0)\nabla_j V_C(r_0) + \cdots,$$

where the final term is a double sum.

c) It's key to notice that when we take expectation values, we integrate *over* r_0. This is because the idea of the perturbation is that it occurs *at each point* in space where the wavefunction takes values. Hence, we perturb each point by $\delta\mathbf{r}$, which itself has dependence on the specific point we are perturbing about. Now, since the jittering motion is spherically symmetric, the expectation value of the first term must be 0. This is because

$$\langle\delta\mathbf{r}\cdot\nabla V_C(r)\rangle$$

will have angular dependence in the integral and so will vanish in the spherically symmetric s-state. To see this, just notice that there is no way we can make the integrand depend only on the magnitude of $\mathbf{r}$.

d) Similarly, spherical symmetry gives us that the final term can only depend on the magnitude squared of the vector $\delta\mathbf{r}$, namely $\delta r_i \delta r_i = (\delta r)^2$. Thus, we find that it must be proportional to δ_{ij}. To find the dimensionful proportionality constant, we need to find a constant with units of length squared. This is given by

$$\frac{\hbar c^2}{m^2 c^4} = \frac{\hbar^2}{m^2 c^2} = \lambda_c{}^2.$$

Next, note that

$$\nabla^2 V_C(r_0) = 4\pi e \delta^{(3)}(\mathbf{r}_0).$$

Finally, to find the constant A, note that there is a factor of 1/2 coming from the Taylor expansion as well as a factor of 1/3:

$$(\delta r_i \delta r_j)_{\text{avg}} \nabla_i \nabla_j V_C(r) = \frac{1}{6}(\delta r)^2 4\pi e \delta^{(3)}(\mathbf{r}),$$

where $(\delta r)^2$ is the magnitude squared of the characteristic length scale in question. The reason we get the 1/3 is because the average value of $\delta r_i \delta r_j$ is exactly

$$\frac{1}{3}(\delta r_{\text{avg}})^2 \delta_{ij}.$$

Plugging in $\delta r_{\text{avg}} = \lambda_c \sqrt{3/4}$, we arrive at the answer.

e) Since states with $\ell \neq 0$ have wavefunctions which vanish at the origin, they will have no contribution from the Darwin term due to the delta function.

f) We plug in (remembering that $Y_{00} = 1/\sqrt{4\pi}$):

$$\begin{aligned} E_D^1 &= \frac{\hbar^2}{8m^2c^2} 4\pi e^2 \cdot \frac{4}{4\pi n^3}\left(\frac{me^2}{\hbar^2}\right)^3 \\ &= \frac{mc^2}{2n^3}\alpha^4 \\ &= \frac{2n E_n{}^2}{mc^2}. \end{aligned}$$

Adding this to the relativistic correction we find exactly the fine structure correction for $\ell = 0$!