

Week 7 Worksheet

Fine Structure of Hydrogen

Jacob Erlikhman

October 8, 2025

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

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

But this formula does not tell us what happens for $\ell = 0$ states, called “ s -states” (see part (a) below). There is an additional effect for s -states called the **Darwin term**:

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

where $V(r) = -e/r$ is the Coulomb potential. This term can be derived from the Dirac equation, but in this problem you will get a handle on it using non-relativistic QM.

- What is E_{so}^1 for s -states, i.e. those with $\ell = 0$?
Hint: If $\ell = 0$, then what values can $\mathbf{L} \cdot \mathbf{S}$ take?
- If we confine an electron to a box of side length L , write down what physical constants p must be proportional to.
Hint: Recall that $p = \hbar k$. What is k for the infinite square well?
- If $p = mc$, the characteristic momentum at which relativistic effects become significant, write down the characteristic length associated to this momentum. This is called the Compton wavelength, λ_C . Its value is $\lambda_C \approx 4 \cdot 10^{-11}$ cm.
- If we confine an electron to a distance $\sim \lambda_C$, show that the energy of the associated momentum (from the uncertainty principle) is $\sim mc^2$. This implies that virtual electron-positron pair creation becomes possible.
- The lifetime of these pairs is given by the uncertainty principle $\Delta t \Delta E = \hbar$, so $\Delta t = \hbar/mc^2$. If the virtual particle pair moves at the speed of light, show that it covers a distance λ_C before disappearing again.

- f) The effect of the creation of this pair is to smear out the position of the electron over a distance of order λ_C . Thus, the potential energy is not at a particular position; rather, it is an average around that point. To model the smearing, we might suppose that

$$V(r) = \int d^3\epsilon f(\epsilon) V(\mathbf{r} + \epsilon),$$

where $f(\epsilon)$ is some “smearing function” of width λ_C , normalized so that $\int f(\epsilon) d^3\epsilon = 1$. For example, we could take

$$f(\epsilon) = \frac{3}{4\pi\lambda_C^3} \theta(\lambda_C - \epsilon) = \begin{cases} 0, & \epsilon > \lambda_C \\ \frac{3}{4\pi\lambda_C^3}, & \epsilon < \lambda_C \end{cases}.$$

Expand the potential $V(\mathbf{r} + \epsilon)$ as a Taylor expansion to second order about \mathbf{r} .

- g) Use symmetry to argue that the expectation value of the first term in the expansion of $V(r)$ is 0, supposing that $f(\epsilon) = f(\epsilon)$ is spherically symmetric in ϵ .
Hint: Note that $\epsilon \cdot \nabla V = \epsilon |\nabla V| \cos(\theta)$, and you can choose this θ to be the usual polar angle θ (why?).
- h) Use the same symmetry and the form for f given in part (f) to compute $V(r)$ to second order in ϵ .
Hint: You can argue that the $\epsilon_i \epsilon_j$ terms with $i \neq j$ vanish. Why?
- i) Plug in the Coulomb potential, and show that the second order term reproduces H_D exactly, *assuming that the characteristic length is actually $\lambda_C \sqrt{5/4}$* .
- j) Argue that this term has an expectation value only for s -states.
- k) 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,

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

Hints: Note that $E_n = -mc^2\alpha^2/2n^2$. You can determine α by combining the fundamental constants of the hydrogen atom (\hbar , e , c) into a dimensionless constant. By the way, why does m not appear in the fine structure constant?

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 cheated by assuming that the characteristic length was $\lambda_C \sqrt{3/4}$ rather than just λ_C . In this problem, we assumed the smearing was given by a step function. In fact, the smearing comes from a more complicated “smearing function,” but there is no way to derive it without using relativistic QM and the Dirac equation. The Darwin term and all of fine structure can be derived rigorously from the Dirac equation, and that’s all there is to it. Unfortunately, the Schrödinger theory just isn’t a good theory for dealing with truly relativistic effects.