

Collaborators

I worked with **Andrew Binder** to complete this assignment. Sorry for the late submission, most of the time spent doing this problem set was actually typing up the solutions rather than doing the problems themselves.

Problem 1

Derive the fine structure formula (Equation 7.68) from the relativistic correction (Equation 7.58) and the spin-orbit coupling (Equation 7.67). *Hint:* Note that $j = \ell \pm 1/2$ (except for $\ell = 0$, where only the plus sign occurs); treat the plus sign and the minus sign separately, and you'll find that you get the same final answer either way.

Solution: We use $j = l \pm \frac{1}{2}$, following the hint. Starting with $J = l + \frac{1}{2}$, recall the spin-orbit corrections written in terms of l :

$$E_{\text{rel}} = -\frac{E_n^2}{2mc^2} \left[\frac{4n}{n+1/2} - 3 \right] \quad E_{\text{SO}} = \frac{E_n^2}{mc^2} \left[\frac{n(j(j+1) - l(l+1) - \frac{3}{4})}{l(l+1/2)(l+1)} \right]$$

Now using the relation that $l = j - 1/2$, we can get the following corrections:

$$\begin{aligned} E_{\text{rel}} &= -\frac{E_n^2}{2mc^2} \left[\frac{4n}{j} - 3 \right] \\ E_{\text{SO}} &= \frac{E_n^2}{mc^2} \left[\frac{n(j(j+1) - (j-1/2)(j+1/2) - 3/4)}{(j-1/2)j(j+1/2)} \right] \\ &= \frac{E_n^2}{mc^2} \left[\frac{n(j-1/2)}{(j-1/2)j(j+1/2)} \right] \\ &= \frac{E_n^2 n}{mc^2 j(j+1/2)} \end{aligned}$$

Adding these together to get the fine structure correction:

$$\begin{aligned} E_{\text{FS}} &= \frac{E_n^2}{mc^2} \left(\frac{n}{j(j+1/2)} \right) - \frac{E_n^2}{2mc^2} \left(\frac{4n}{j} - 3 \right) \\ &= \frac{E_n^2}{mc} \left(\frac{n}{j(j+1/2)} - 1/2 \left(\frac{4n}{j} - 3 \right) \right) \\ &= \frac{E_n^2}{mc} \left(\frac{n}{j(j+1/2)} - \frac{2n}{j} + \frac{3}{2} \right) \\ &= \frac{E_n^2}{2mc} \left[\frac{2(n - 2n(j+1/2))}{j+1/2} + 3 \right] \\ &= \frac{E_n^2}{2mc} \left[3 - \frac{4nj}{j(j+1/2)} \right] \\ &= \frac{E_n^2}{2mc} \left[3 - \frac{4n}{j+1/2} \right] \end{aligned}$$

Which is the fine structure, as desired. Now using $j = l - 1/2$, we get the following corrections for the relativistic and spin orbit corrections:

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

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

Adding the two together, we get:

$$\begin{aligned} E_{\text{FS}} &= -\frac{E_n^2}{2mc^2} \left(\frac{4n}{j+1} - 3 \right) + \frac{E_n^2}{mc^2} \left(-\frac{n}{(j+1/2)(j+1)} \right) \\ &= -\frac{E_n^2}{2mc^2} \left[\frac{4n}{j+1} - 3 + \frac{2n}{(j+1/2)(j+1)} \right] \\ &= -\frac{E_n^2}{2mc^2} \left[\frac{4n(j+1/2) + 2n}{(j+1)(j+1/2)} - 3 \right] \\ &= -\frac{E_n^2}{2mc^2} \left[\frac{4n(j+1)}{(j+1)(j+1/2)} - 3 \right] \\ &= \frac{E_n^2}{2mc^2} \left[3 - \frac{4n}{j+1/2} \right] \end{aligned}$$

as desired. □

Problem 2

The most prominent feature of the hydrogen spectrum in the visible region is the Balmer line, coming from the transition $n = 3$ to $n = 2$. First of all, determine the wavelength and frequency of this line according to the Bohr theory. Fine structure splits this line into several closely spaced lines; the question is: *How many, and what is their spacing?* *Hint:* First determine how many sublevels the $n = 2$ level splits into, and find E_{fs}^1 for each of these, in eV. Then do the same for $n = 3$. Draw an energy level diagram showing all possible transitions from $n = 3$ to $n = 2$. The energy released (in the form of a photon) is $(E_3 - E_2) + \Delta E$, the first part being common to all of them, and ΔE (due to fine structure) varying from one transition to the next. Find ΔE (in eV) for each transition. Finally, convert to photon frequency, and determine the spacing between adjacent spectral lines (in Hz) – *not* the frequency interval between each line and the *unperturbed* line, (which is, of course, unobservable), but the frequency interval between each line and the *next* one. Your final answer should take the form: “The red Balmer line splits into (???) lines. In order of increasing frequency, they come from the transitions (1) $j = (???)$ to $j = (???)$, (2) $j = (???)$ to $j = (???)$, ... The frequency spacing between line (1) and line (2) is (???) Hz, the spacing between line (2) and line (3) is (???) Hz, ...”

Solution: The energy transition is from $n = 3$ to $n = 2$, so the change in energy is given by:

$$\Delta E = E_3 - E_2 = E_1 \left(\frac{1}{9} - \frac{1}{4} \right) = -\frac{5E_1^0}{36}$$

Solving for the wavelength, we get:

$$\frac{2\pi\hbar c}{\lambda} = -\frac{5E_1^0}{36} \implies \lambda \approx 655 \text{ nm}$$

And we can also solve for f :

$$f = \frac{c}{\lambda} \approx 4.58 \times 10^{14} \text{ Hz}$$

Now we are asked to determine how the fine structure splits these two lines. We will follow the hint closely to arrive at the final answer. First, based on the fine-structure correction, we know that (from the previous problem)

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

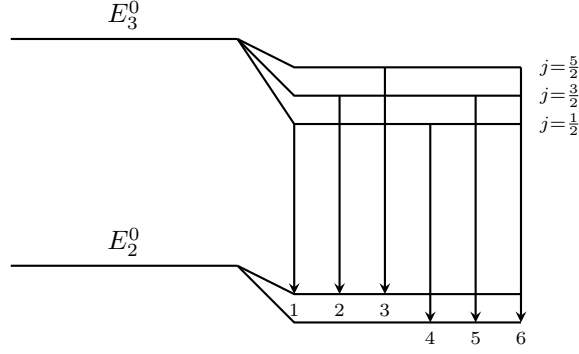
So the degeneracy lies in $j = l + 1/2$. For $n = 2$, we have $l = 0$ or $l = 1$, so the fine structure splits this into two energy levels (recall that $j = l + 1/2$):

$$\begin{aligned} l = 0 \ (j = 1/2) : \quad E_2^1 &= \frac{E_2^2}{2mc^2} \left(3 - \frac{4(2)}{1/2 + 1/2} \right) = -\frac{5E_2^2}{2mc^2} = -\frac{5}{32} \frac{E_1^2}{mc^2} \approx -5.66 \times 10^{-5} \text{ eV} \\ l = 1 \ (j = 3/2) : \quad E_2^1 &= \frac{E_2^2}{2mc^2} \left(3 - \frac{4(2)}{(3/2 + 1/2)} \right) = -\frac{E_2^2}{2mc^2} = -\frac{1}{32} \frac{E_1^2}{mc^2} \approx -1.13 \times 10^{-5} \text{ eV} \end{aligned}$$

For the $n = 3$ case, we now have $l = 0, 1, 2$ so the fine structure will split this into three energy levels:

$$\begin{aligned} l = 0 \ (j = 1/2) : \quad E_3^1 &= \frac{E_3^2}{2mc^2} \left(3 - \frac{4(3)}{1/2 + 1/2} \right) = -\frac{9E_3^2}{2mc^2} = -\frac{1}{18} \frac{E_1^2}{mc^2} \approx 2.01 \times 10^{-5} \text{ eV} \\ l = 1 \ (j = 3/2) : \quad E_3^1 &= \frac{E_3^2}{2mc^2} \left(3 - \frac{4(3)}{3/2 + 1/2} \right) = -\frac{3E_3^2}{2mc^2} = -\frac{1}{54} \frac{E_1^2}{mc^2} \approx -0.67 \times 10^{-5} \text{ eV} \\ l = 2 \ (j = 5/2) : \quad E_3^1 &= \frac{E_3^2}{2mc^2} \left(3 - \frac{4(3)}{5/2 + 1/2} \right) = -\frac{E_3^2}{2mc^2} = -\frac{1}{162} \frac{E_1^2}{mc^2} \approx -0.22 \times 10^{-5} \text{ eV} \end{aligned}$$

We can plot these to see what the transitions look like (credit goes to Andrew Binder for the TikZ diagram):



So we have six transitions to calculate the energy for. In terms of the notation, I will label $E_{k,m}$ to denote the change in energy from the k -th state in $n = 3$ to the m -th state in $n = 2$ with the states arranged in order of increasing j . So for instance, $E_{1,2}$ would correspond to the transition from the lowest energy state in E_3 in the split down to the highest energy state in E_2 .

$$\begin{aligned}\Delta E_{1,2} &= \left(-\frac{1}{18} + \frac{1}{32}\right) \frac{E_1^2}{mc^2} \approx 8.8 \times 10^{-6} \text{ eV} \\ \Delta E_{2,2} &= \left(-\frac{1}{54} + \frac{1}{32}\right) \frac{E_1^2}{mc^2} \approx 4.6 \times 10^{-6} \text{ eV} \\ \Delta E_{3,2} &= \left(-\frac{1}{162} + \frac{1}{32}\right) \frac{E_1^2}{mc^2} \approx 9.1 \times 10^{-6} \text{ eV} \\ \Delta E_{1,1} &= \left(-\frac{1}{18} + \frac{5}{32}\right) \frac{E_1^2}{mc^2} \approx 36.5 \times 10^{-6} \text{ eV} \\ \Delta E_{2,1} &= \left(-\frac{1}{54} + \frac{5}{32}\right) \frac{E_1^2}{mc^2} \approx 49.9 \times 10^{-6} \text{ eV} \\ \Delta E_{3,1} &= \left(-\frac{1}{162} + \frac{5}{32}\right) \frac{E_1^2}{mc^2} \approx 54.3 \times 10^{-6} \text{ eV}\end{aligned}$$

So now finally writing out the answer in the format from the hint:

The red balmer line splits into 6 lines. In order of increasing frequency, they come from the following transitions:

- $j = 1/2$ to $j = 3/2$
- $j = 3/2$ to $j = 3/2$
- $j = 5/2$ to $j = 5/2$
- $j = 1/2$ to $j = 1/2$
- $j = 3/2$ to $j = 1/2$
- $j = 5/2$ to $j = 1/2$

The frequency spacing between line (1) and line (2) is 3.23×10^9 Hz, the spacing between line (2) and (3) is 1.08×10^9 Hz, the spacing between line (3) and (4) is 6.60×10^9 Hz, the spacing between line (4) and (5) is 3.23×10^9 Hz, and finally the spacing between line (5) and (6) is 1.08×10^9 Hz. In general, the frequency spacing between line n and line $n + 1$ is given by

$$f_n = \frac{\Delta E_{n+1} - \Delta E_n}{2\pi\hbar}$$

□

Problem 3

Consider the (eight) $n = 2$ states $|2\ell\ j\ m_j\rangle$. Find the energy of each state, under weak-field Zeeman splitting, and construct a diagram like Figure 710 to show how the energies evolve as B_{ext} increases. Label each line clearly, and indicate its slope.

Solution: For $n = 2$, we have 8 states, which we will label $|n\rangle$:

$$\begin{aligned} |1\rangle &= |2, 0, 1/2, -1/2\rangle \\ |2\rangle &= |2, 0, 1/2, 1/2\rangle \\ |3\rangle &= |2, 1, 1/2, -1/2\rangle \\ |4\rangle &= |2, 1, 1/2, 1/2\rangle \\ |5\rangle &= |2, 1, 3/2, -3/2\rangle \\ |6\rangle &= |2, 1, 3/2, -1/2\rangle \\ |7\rangle &= |2, 1, 3/2, 1/2\rangle \\ |8\rangle &= |2, 1, 3/2, 3/2\rangle \end{aligned}$$

For the weak Zeeman effect, we need to consider both the fine structure energy and the Zeeman correction. Starting with the Zeeman correction, we calculate the g-factor for the states $l = 0$ with $j = 1/2$ and $l = 1$ with $j = 1/2, 3/2$:

$$\begin{aligned} g_J^{0,1/2} &= 1 + \frac{(1/2)(1/2 + 1) - 0(1) + 1/2(1/2 + 1)}{2(1/2)(1/2 + 1)} = 1 + 1 = 2 \\ g_J^{1,1/2} &= 1 + \frac{(1/2)(1/2 + 1) - 1(2) + 1/2(1/2 + 1)}{2(1/2)(3/2 + 1)} = 1 - \frac{1}{3} = \frac{2}{3} \\ g_J^{1,3/2} &= 1 + \frac{3/2(3/2 + 1) - 1(2) + 1/2(1/2 + 1)}{2(3/2)(3/2 + 1)} = 1 + \frac{5}{15} = \frac{4}{3} \end{aligned}$$

Now we can calculate the Zeeman effect $E_z = \mu_B g_J B_{ext} m_j$:

$$\begin{aligned} E_{Z,1}^1 &= -2\mu_B B_{ext} \\ E_{Z,2}^1 &= 2\mu_B B_{ext} \\ E_{Z,3}^1 &= -\frac{1}{3}\mu_B B_{ext} \\ E_{Z,4}^1 &= \frac{1}{3}\mu_B B_{ext} \\ E_{Z,5}^1 &= -\frac{2}{3}\mu_B B_{ext} \\ E_{Z,6}^1 &= \frac{2}{3}\mu_B B_{ext} \\ E_{Z,7}^1 &= -2\mu_B B_{ext} \\ E_{Z,8}^1 &= 2\mu_B B_{ext} \end{aligned}$$

Now incorporating the fine structure energy, which only depends on j :

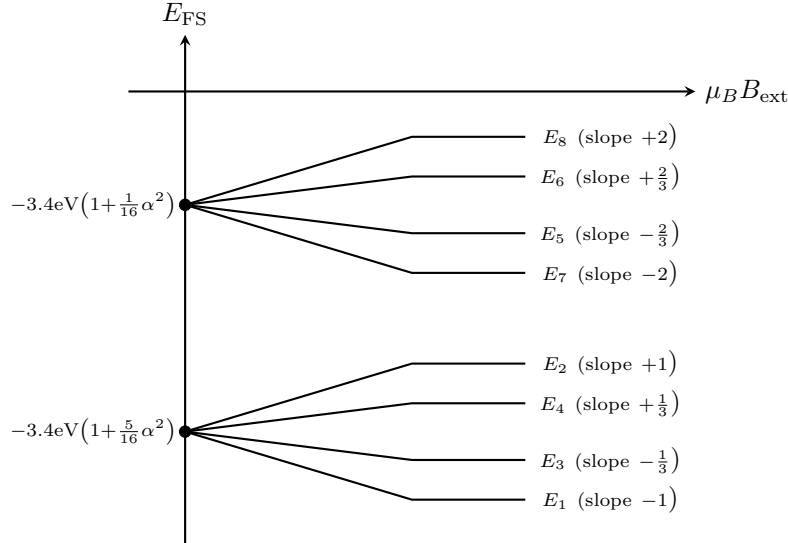
$$E_{FS,1/2} = -\frac{13.6 \text{ eV}}{2^2} \left[1 + \frac{\alpha^2}{2} \left(\frac{2}{1/2 + 1/2} - \frac{3}{4} \right) \right] = -3.4 \text{ eV} \left(1 + \frac{5}{16} \alpha^2 \right)$$

$$E_{FS,3/2} = -\frac{13.6 \text{ eV}}{2^2} \left[1 + \frac{\alpha^2}{2} \left(\frac{2}{3/2 + 1/2} - \frac{3}{4} \right) \right] = -3.4 \text{ eV} \left(1 + \frac{1}{16} \alpha^2 \right)$$

Putting these together, we get:

$$\begin{aligned} E_1 &= E_{FS,1/2} - \mu_B B_{ext} \\ E_2 &= E_{FS,1/2} + \mu_B B_{ext} \\ E_3 &= E_{FS,1/2} - \frac{1}{3} \mu_B B_{ext} \\ E_4 &= E_{FS,1/2} + \frac{1}{3} \mu_B B_{ext} \\ E_5 &= E_{FS,3/2} - \frac{2}{3} \mu_B B_{ext} \\ E_6 &= E_{FS,3/2} + \frac{2}{3} \mu_B B_{ext} \\ E_7 &= E_{FS,3/2} - 2 \mu_B B_{ext} \\ E_8 &= E_{FS,3/2} + 2 \mu_B B_{ext} \end{aligned}$$

Plotting these out (again thanks to Andrew for the TikZ diagram):



□

Problem 4

If $\ell = 0$, then $j = s, m_j = m_s$ and the “good” states are the same ($|n m_s\rangle$) for weak *and* strong fields. Determine E_Z^1 (from Equation 7.74) and the fine structure energies (Equation 7.69), and write down the general result for the $l = 0$ Zeeman effect – *regardless* of the strength of the field. Show that the strong-field formula (Equation 7.86) reproduces this result, provided that we interpret the indeterminate term in square brackets as 1.

Solution: In the case where $l = 0$, then we have $j = s = 1/2$ and $m_j = m_s$ as a result. We can rewrite the Zeeman energy to reflect this:

$$E_Z = \frac{eB_{ext}}{2m}(2m_s\hbar) = 2m_s\mu_B B_{ext}$$

The fine structure correction, which is dependent on j , then becomes:

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

So the total energy correction is the sum of these two:

$$E = -\frac{13.6 \text{ eV}}{n^2} \left[1 + \frac{\alpha^2}{n^2} \left(n - \frac{3}{4} \right) \right] + 2m_s\mu_B B_{ext}$$

We now want to show that Equation 7.86 also reproduces this result provided that the term in square brackets is 1. Doing so, we obtain the equation:

$$\begin{aligned} E_{fs}^1 &= \frac{13.6 \text{ eV}}{n^3} \alpha^2 \left(\frac{3}{4n} - 1 \right) \\ &= \frac{13.6 \text{ eV}}{n^4} \alpha^2 \left(\frac{3}{4} - n \right) \\ &= -\frac{13.6 \text{ eV}}{n^4} \alpha^2 \left(n - \frac{3}{4} \right) \end{aligned}$$

So combining this back, we see that the energy correction becomes:

$$\begin{aligned} E &= -\frac{13.6 \text{ eV}}{n^2} - \frac{13.6 \text{ eV}}{n^4} \alpha^2 \left(n - \frac{3}{4} \right) + 2m_s\mu_B B_{ext} \\ &= -\frac{13.6 \text{ eV}}{n^2} \left[1 + \frac{\alpha^2}{n^2} \left(n - \frac{3}{4} \right) \right] + 2m_s\mu_B B_{ext} \end{aligned}$$

which is the same result as before, as desired. □

Problem 5

The eigenstates of a rotating dumbbell, with moment of inertia I

$$E_l = \frac{\hbar^2 l(l+1)}{2I}$$

are $(2l+1)$ -fold degenerate. In the event that the dumbbell is equally and oppositely charged at its ends, it becomes a dipole. The interaction energy between such a dipole and a constant, uniform electric field \mathcal{E} is

$$\hat{H}' = -d \cdot \mathcal{E} \quad (\hat{H} - \mathbf{d} \cdot \mathcal{E})$$

The dipole moment of the dumbbell is \mathbf{d} . Show that to terms of first order, this perturbing potential *does not separate* the degenerate E_l eigenstates.

Solution: I will argue this both qualitatively and quantitatively. Qualitatively speaking, we know that degeneracy arises when we have symmetry in the problem, and that introducing a perturbation which depends on that symmetric parameter now breaks the symmetry. For instance, the Zeeman effect arises when we now introduce a term which breaks the symmetry for m_l , causing a split in the energy levels as a result.

Since the magnetic moment is $\mathbf{d} = e\mathbf{r}$, then we know that this value actually only depends on r , so there is no L_z component, meaning that the perturbation should not depend on the value of m_l . Since the degeneracies in this problem arise from the degeneracies in m_l , then the fact that d does not depend on m_l means that we should not expect it to separate the E_l eigenstates.

Quantitatively, we can calculate the energy change due to this perturbation and show that it is in fact equal to zero. The eigenfunctions of the dumbbell are those of the rigid rotor, which are the spherical harmonics. Calculating the energy correction:

$$\Delta E = \langle lm | -\mathcal{E} \cdot \mathbf{d} | lm \rangle = -\mathcal{E} \langle lm | \mathbf{d} | lm \rangle = -\mathcal{E} \langle lm | e\mathbf{r} | lm \rangle = -\mathcal{E} e \langle lm | r | lm \rangle$$

Since $|lm\rangle$ has no r component, this expectation value is zero, as expected. □

Problem 6

Consider again the dipole moment described in Problem 13.14. If both ends are equally charged, the rotating dipole constitutes a magnetic dipole. If the dipole has angular momentum \mathbf{L} , the corresponding magnetic dipole moment is

$$\boldsymbol{\mu} = \frac{e}{2mc} \mathbf{L}$$

where e is the net charge of the dipole. The interaction energy between this magnetic dipole and a constant, uniform magnetic field \mathcal{B} is

$$\hat{H}' = -\hat{\boldsymbol{\mu}} \cdot \mathcal{B} = -\frac{e}{2mc} \hat{\mathbf{L}} \cdot \mathcal{B} \quad (\hat{H} = \hat{H}_0 - \hat{\boldsymbol{\mu}} \cdot \mathcal{B})$$

- a) If \mathcal{B} points in the z direction, show that \hat{H}' separates the $(2l+1)$ -fold degenerate E_l energies of the rotating dipole.

Solution: To show that the degeneracy splits, we show that the energy correction is nonzero. If \mathcal{B} points in the \hat{z} direction, then taking the dot product with L :

$$\hat{\mathbf{L}} \cdot \mathcal{B} = \hat{L}_x \mathcal{B}_x + \hat{L}_y \mathcal{B}_y + \hat{L}_z \mathcal{B}_z = \hat{L}_z \mathcal{B}_z$$

Note that the first two terms go to zero because \mathcal{B} points only in the \hat{z} direction. Now, calculating the expectation value:

$$\begin{aligned} \langle lm | -\frac{e}{2mc} \hat{\mathbf{L}} \cdot \mathcal{B} | lm \rangle &= -\frac{e}{2mc} \langle lm | \hat{L}_z \mathcal{B}_z | lm \rangle \\ &= -\frac{e \mathcal{B}_z}{2mc} \langle lm | \hat{L}_z | lm \rangle \\ &= -\frac{e \mathcal{B}_z \hbar m_l}{2mc} \end{aligned}$$

□

- b) Apply these results to one-electron atoms to find the splitting of the P states. (Neglect spin-orbit coupling.) (*Note:* This phenomenon is an example of the *Zeeman effect* discussed previously in Problems 12.15 et seq.)

Solution: We repeat the same calculation as before, but now using the wavefunctions for single particle atoms, which happens to just be that of the hydrogen atom:

$$\begin{aligned} \langle nlm | -\frac{e}{2mc} \hat{L}_z \mathcal{B}_z | nlm \rangle &= -\frac{e \mathcal{B}_z}{2mc} \langle nlm | \hat{L}_z | nlm \rangle \\ &= -\frac{e \mathcal{B}_z}{2mc} \langle nl | \langle lm | \hat{L}_z | lm \rangle | nl \rangle \\ &= -\frac{e \mathcal{B}_z}{2mc} \langle lm | \hat{L}_z | lm \rangle \\ &= -\frac{e \mathcal{B}_z \hbar m_l}{2mc} \end{aligned}$$

□