SECOND-ORDER CORRECTION TO ZEEMAN EFFECT IN HYDROGEN

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Shankar, R. (1994), *Principles of Quantum Mechanics*, Plenum Press. Exercise 14.5.2.

[If some equations are too small to read easily, use your browser's magnifying option (Ctrl + on Chrome, probably something similar on other browsers).]

Shankar derives the interaction Hamiltonian between a magnetic moment and a magnetic field in quantum theory in his equations 14.4.11 to 14.4.15, so we won't repeat the derivation here. Rather we can summarize the main points.

The starting point is the classical Hamiltonian for the electromagnetic force

$$H=\frac{\left|\mathbf{p}-q\mathbf{A}/c\right|^{2}}{2m}+q\phi \tag{1}$$

In the current example, there is no electrostatic field, so $\phi=0$, and we make the transition to quantum theory by interpreting $\mathbf{p}$ as the momentum operator $\mathbf{P}$. This gives

$$H=\frac{\left|\mathbf{P}\right|^{2}}{2m}-\frac{q}{2mc}\left(\mathbf{P}\cdot\mathbf{A}+\mathbf{A}\cdot\mathbf{P}\right)+\frac{q^{2}\left|\mathbf{A}\right|^{2}}{2mc^{2}} \tag{2}$$

We then assume that we have a constant magnetic field that points along the z axis, which can be produced by taking the vector potential $\mathbf{A}$ to be

$$\mathbf{A}=\frac{B}{2}\left(-y\hat{\mathbf{x}}+x\hat{\mathbf{y}}\right) \tag{3}$$

Using the standard relation between the vector potential and field, we have

$$\mathbf{B}=\nabla\times\mathbf{A}=B\hat{\mathbf{z}} \tag{4}$$

Shankar then assumes that the field is fairly weak, so we can ignore the last term in 2. He then shows that the middle term in 2 comes out to

$$H = -\mu \cdot \mathbf{B} \tag{5}$$

where the magnetic moment is defined as

$$\mu \equiv \frac{q}{2mc}\mathbf{L} \tag{6}$$

where $\mathbf{L}$ is the orbital angular momentum.

For the hydrogen atom, this analysis leads to the prediction of energy levels for the state $|nlmm_x\rangle$ of

$$E = -\frac{\text{Ry}}{n^2} + \frac{eB\hbar}{2m_e c}(m + 2m_s) \tag{7}$$

Here, m_e is the mass of the electron, m is the z component of orbital angular momentum (Shankar confusingly uses the same symbol m for the electron mass and z component of orbital angular momentum) and m_s is the z component of spin (both in units of $\hbar$). The Rydberg (Ry) has a value of 13.6 eV and is the energy level of the ground state of hydrogen. Also, note that all these equations use the Gaussian system of units (rather than SI, which we used in both of Griffiths's books). For calculation, it's useful to use the Bohr magneton for the electron, which is (using Gaussian units):

$$\mu_B \equiv \frac{e\hbar}{2m_e c} \tag{8}$$

$$= \frac{\left(4.8 \times 10^{-10}\text{ esu}\right)\left(1.05 \times 10^{-27}\text{ erg s}\right)}{2\left(9.1 \times 10^{-28}\text{ g}\right)\left(3 \times 10^{10}\text{ cm s}^{-1}\right)} \tag{9}$$

$$= 9.23 \times 10^{-21}\text{ erg G}^{-1} \tag{10}$$

$$\simeq 0.6 \times 10^{-8}\text{ eV G}^{-1} \tag{11}$$

To see the effect of the level splitting on the ground state (this is the Zeeman effect for $l = 0$, which we treated earlier), we have $n = 1$ and $m = 0$ with $m_s = \frac{1}{2}$, so the size of the level splitting is

$$\Delta E = \mu_B B \tag{12}$$

For $B = 1000$ kG $= 10^6$ G we have $\Delta E \simeq 0.6 \times 10^{-2}$ eV so the relative size, compared to the ground state energy, is

$$\frac{\Delta E}{E} = \frac{0.6 \times 10^{-2}}{13.6} = 4.4 \times 10^{-4} \tag{13}$$

[In Shankar's answer at the back of the book, he says the relative size is about one in a million, which seems much too small.]

We can also calculate the effect that we neglected by ignoring the $|\mathbf{A}|^2$ term in 2. If we assume that the electron is in a classical orbit of radius a_0 (the Bohr radius), then from 3, we have

$$|\mathbf{A}|^2 = \frac{B^2 a_0^2}{4} \tag{14}$$

The neglected term is therefore (using $a_0 \simeq 5.3\times10^{-9}$ cm)

$$\frac{e^2B^2a_0^2}{8mc^2} = \frac{\left(4.8\times10^{-10}\text{ esu}\right)^2 B^2\left(5.3\times10^{-9}\text{ cm}\right)^2}{8\left(9.1\times10^{-28}\text{ g}\right)\left(3\times10^{10}\text{ cm s}^{-1}\right)^2} \tag{15}$$

$$\simeq 10^{-32}B^2\text{ erg} \tag{16}$$

$$= 6\times10^{-19}B^2\text{ eV} \tag{17}$$

Thus in order for this term to make much of a difference, it would need to be the same order of magnitude as ΔE in 12. That is, we're looking for B such that

$$\Delta E \simeq \frac{e^2B^2a_0^2}{8mc^2} \tag{18}$$

$$\mu_B B \simeq \frac{e^2B^2a_0^2}{8mc^2} = 6\times10^{-19}B^2\text{ eV} \tag{19}$$

$$B \simeq \frac{\mu_B}{6\times10^{-19}} \tag{20}$$

$$= \frac{0.6\times10^{-8}}{6\times10^{-19}} \tag{21}$$

$$= 10^{10}\text{ G} \tag{22}$$