Phys 506 lecture 18: Hydrogen in a Magnetic Field

1 Introduction

The effect of a small magnetic field is smaller than the fine-structure splitting, so we can solve the problem in two steps:

1. Find the fine structure.

2. Perturb the fine structure due to the field.

This weak field regime is called the **Zeeman regime**. When H is large, the fine structure is small compared to the energy shifts due to the field (called the **Paschen-Back regime**). We will solve the general case and then extract the limiting behavior.

2 Setting up the perturbation

The orbital magnetic moment of the electron is:

$$\mu_{\text{orb}} = -\mu_0 \hat{\mathbf{L}},$$

where $\mu_0 = \frac{e\hbar}{2mc}$ is the Bohr magneton and has the value of 0.579×10^{-8} eV/gauss. The spin magnetic moment is:

$$\mu_{\text{spin}} = -2\mu_0 \hat{\mathbf{S}}.$$

It is the extra factor of 2 that makes life difficult.

$$\hat{V}_{\text{mag}} = \mu_0 \mathbf{H} \cdot (\hat{\mathbf{L}} + 2\hat{\mathbf{S}}) = \mu_0 \mathbf{H} \cdot (\hat{\mathbf{J}} + \hat{\mathbf{S}}).$$

Choose the z-direction along $\mathbf{H}$, so $\mathbf{H} = H\mathbf{e}_z$. Then $\hat{S}^2$, $\hat{L}^2$, $\hat{L}_z$, and $\hat{S}_z$ commute with $\hat{V}_{\text{mag}}$. But $\hat{L}_z$ and $\hat{S}_z$ do not separately commute with $\hat{V}_{\text{fine structure}}$, only the sum does. This implies the field will mix states, and we do not know the parallel directions in the degenerate subspace.

One important note: $\hat{L}_z + 2\hat{S}_z$ is an even parity operator, so it cannot connect states with different parity. Therefore ℓ must be the same or differ by a multiple of 2, as $\ell + 1$ is different parity from ℓ. This reduces a lot of our work.

3 Symmetry analysis

We have eight degenerate energy levels $2P_{3/2}, 2P_{1/2}, 2S_{1/2}$ with degeneracies of 4, 2, and 2 respectively. Because of the parity argument, the $2S_{1/2}$ state cannot connect to $2P_{3/2}$ or $2P_{1/2}$. Therefore S is a parallel direction. Similarly, $2P_{3/2}m = \pm 3/2$ cannot couple, since $\hat{J}_z$ is a good quantum number, as $\hat{L}_z + \hat{S}_z$ commutes with $\hat{H}$. So only $2P_{3/2}(m{=}\pm\frac{1}{2}$ and $2P_{1/2}(m{=}\pm\frac{1}{2})$ couple (positive to positive and negative to negative).

Hence, we reduce from an 8×8 subspace to four 1×1 subspaces:

$$2P_{3/2}(m{=}\tfrac{3}{2}),\quad 2P_{3/2}(m{=}-\tfrac{3}{2}),\quad 2S_{1/2}(m{=}\tfrac{1}{2}),\quad 2S_{1/2}(m{=}-\tfrac{1}{2})$$

and two 2×2 subspaces:

$$\begin{array}{l} 2P_{3/2}(m{=}\tfrac{1}{2}),\quad 2P_{1/2}(m{=}\tfrac{1}{2}) \\ 2P_{3/2}(m{=}-\tfrac{1}{2}),\quad 2P_{1/2}(m{=}-\tfrac{1}{2}). \end{array}$$

4 Calculate the perturbative corrections

First, examine the 1×1 subspaces, which can be analyzed with non-degenerate perturbation theory.

$$\Delta E_{\text{mag}} = \langle nljm|(\hat{J}_z + \hat{S}_z)|nljm\rangle\, \mu_0 H = \mu_0 H \left(m + \langle nljm|\hat{S}_z|nljm\rangle\right).$$

The radial part of the overlap is 1. The angular momentum is tricky—need to change the basis from $jmsl$ to $lm_l sm_s$:

$$\langle slm|s_z l_z sm_s\rangle = \sum_{m_l m_s} \langle sl|lm_l sm_s\rangle\langle lm_l sm_s|s_z l_z sm_s\rangle = \sum_{m_l m_s} |\langle slm|lm_l sm_s\rangle|^2$$

where $\langle slm|lm_l sm_s\rangle$ are your Clebsch-Gordon coefficients.

We already showed:

$$\left|\ell{+}\frac{1}{2}, m\right\rangle = \sqrt{\frac{\ell+m+\frac{1}{2}}{2\ell+1}}\left|m_\ell = m{-}\frac{1}{2}, m_s = +\frac{1}{2}\right\rangle + \sqrt{\frac{\ell-m+\frac{1}{2}}{2\ell+1}}\left|m_\ell = m{+}\frac{1}{2}, m_s = -\frac{1}{2}\right\rangle$$

and

$$\left|\ell{-}\frac{1}{2}, m\right\rangle = -\sqrt{\frac{l-m+\frac{1}{2}}{2l+1}}\left|m_\ell = m{-}\frac{1}{2}, m_s = +\frac{1}{2}\right\rangle + \sqrt{\frac{\ell+m+\frac{1}{2}}{2\ell+1}}\left|m_\ell = m{+}\frac{1}{2}, m_s = -\frac{1}{2}\right\rangle$$

so for $j = \ell + 1/2$, only two m_ℓ terms contribute to each sum and so we get:

$$= \frac{1}{2}\frac{\ell+m+\frac{1}{2}}{2\ell+1} + \frac{1}{2}\frac{\ell-m+\frac{1}{2}}{2\ell+1} = \frac{m}{2\ell+1}$$

and for $j = \ell - \frac{1}{2}$, only two m_s terms contribute, and we get:

$$= \frac{1}{2}\frac{\ell - m + \frac{1}{2}}{2\ell+1} + \frac{1}{2}\frac{\ell + m + \frac{1}{2}}{2\ell+1} = -\frac{m}{2\ell+1}.$$

So:

$$\langle s\ell jm|s_z|s\ell jm\rangle = \pm\frac{m}{2\ell+1}$$

for $j = \ell \pm \frac{1}{2}$, and:

$$\Delta E_{\text{mag}} = \mu_0 H\left(m + \frac{m}{2\ell+1}\right) = \mu_0 Hm\left(\frac{2\ell+1\pm 1}{2\ell+1}\right).$$

Now recall:

$$\Delta E_{\text{FS}} = E_2^0\frac{\alpha^2}{n^2}\left[\frac{1}{j+\frac{1}{2}} - \frac{3}{4}\right].$$

So:

$$\begin{cases} \Delta E(2P_{3/2}, m = \pm\frac{3}{2}) = E_2^0\frac{\alpha^2}{4}\left[\frac{1}{4}\right] + \mu_0 H\frac{3}{2}\cdot\frac{4}{3} = E_2^0\frac{\alpha^2}{16} + 2\mu_0 H \\ \Delta E(2S_{1/2}, m = \pm\frac{1}{2}) = E_2^0\frac{\alpha^2}{4}\left[\frac{5}{4}\right] + \mu_0 H\frac{1}{2}\cdot 2 = E_2^0\frac{5\alpha^2}{16} + \mu_0 H. \end{cases}$$

Now onto the 2×2 cases. The diagonal fine-structure matrix elements are:

$$\begin{cases} \Delta^2 E_2^0\frac{\alpha^2}{4}\left[\frac{2}{2} - \frac{3}{4}\right] = \frac{E_2^0\alpha^2}{16}, \quad j = \frac{3}{2}, \\ \Delta^2 E_2^0\frac{\alpha^2}{4}\left[\frac{5}{16}\right] = \frac{5E_2^0\alpha^2}{16}, \quad j = \frac{1}{2}. \end{cases}$$

The diagonal magnetic matrix elements are:

$$\mu_0 Hm\frac{2\ell+1\pm 1}{2\ell+1} = \begin{cases} \pm\frac{2}{3}\mu_0 H \quad j = \frac{3}{2},\ \text{since}\ \pm\frac{1}{2}\times\frac{4}{3} \\ \pm\frac{1}{3}\mu_0 H \quad j = \frac{1}{2},\ \text{since}\ \pm\frac{1}{2}\times\frac{2}{3} \end{cases}$$

The off-diagonal elements are:

$$\begin{aligned} \langle P_{1/2}, m|S_z|P_{3/2}, m\rangle &= \sum_{m_\ell, m_s}\langle s = \frac{1}{2}, \ell = 1, j = \frac{1}{2}, m|s = \frac{1}{2}, \ell = 1, m_\ell, m_s\rangle \\ &\qquad\times\langle s = \frac{1}{2}, \ell = 1, m_\ell, m_s|s = \frac{1}{2}, \ell = 1, j = \frac{3}{2}, m\rangle \\ &= \sum_{m_\ell, m_s}\langle s = \frac{1}{2}, \ell = 1, j = \frac{1}{2}, m|s = \frac{1}{2}, \ell = 1, m_\ell, m_s\rangle \\ &\qquad\times\langle s = \frac{1}{2}, \ell = 1, m_\ell, m_s|s = \frac{1}{2}, \ell = 1, j = \frac{3}{2}, m\rangle \end{aligned}$$

Since only the two m_ℓ values contribute, we get:

$$= \frac{1}{2}\left(-\sqrt{\frac{\ell - m + \frac{1}{2}}{2\ell+1}}\sqrt{\frac{\ell + m + \frac{1}{2}}{2\ell+1}} - \frac{1}{2}\sqrt{\frac{\ell - m + \frac{1}{2}}{2\ell+1}}\sqrt{\frac{\ell + m + \frac{1}{2}}{2\ell+1}}\right)$$

$$= -\frac{1}{2}\frac{1}{2\ell+1}\left(\sqrt{(\ell + \tfrac{1}{2})^2 - m^2}\right)2$$

Hence, for $m = \pm\frac{1}{2}, \ell = 1$, we get:

$$= -\frac{1}{3}\sqrt{\frac{4}{4} - \frac{1}{4}} = -\frac{\sqrt{2}}{3}$$

Hence, the off diagonal elements are $-\mu_0 H\sqrt{2}/3$. We can write the matrix in full, subtract off $\epsilon\mathbb{I}$ and take its determinant, setting it to zero:

$$\det\begin{pmatrix} \frac{\alpha^2 E_2^0}{16} + \frac{2}{3}\mu_0 H - \epsilon & -\mu_0 H\frac{\sqrt{2}}{3} \\ -\mu_0 H\frac{\sqrt{2}}{3} & \frac{5\alpha^2 E_2^0}{16} \pm \frac{1}{3}\mu_0 H - \epsilon \end{pmatrix} = 0.$$

to find:

$$\epsilon^2 - \epsilon\left(\frac{3}{8}\alpha^2 E_2^0 + \mu_0 H\right) + \frac{5}{256}\alpha^4 (E_2^0)^2 \pm \frac{11}{48}\alpha^2 E_2^0 \mu_0 H = 0$$

Solving for ϵ gives:

$$\epsilon = \frac{3}{16}\alpha^2 E_2^0 \pm \frac{1}{2}\mu_0 H \pm \frac{1}{2}\sqrt{\left(\frac{1}{16}\alpha^2 E_2^0\right)^2 \mp \frac{1}{2}\alpha^2 E_2^0 \mu_0 H + \mu_0^2 H^2}.$$

The first and third $\pm$ and $\mp$ correspond to $m_j = \pm\frac{1}{2}$. The second $\pm$ corresponds to the fact that we have two roots. As a result, we have:

$$\begin{cases} \Delta E(2P_{3/2}\&2P_{1/2}, m_j = \frac{1}{2}) = \frac{3}{16}\alpha^2 E_2^0 \pm \frac{1}{2}\mu_0 H + \frac{1}{2}\sqrt{\left(\frac{1}{16}\alpha^2 E_2^0\right)^2 - \frac{1}{2}\alpha^2 E_2^0 \mu_0 H + \mu_0^2 H^2} \\ \Delta E(2P_{3/2}\&2P_{1/2}, m_j = -\frac{1}{2}) = \frac{3}{16}\alpha^2 E_2^0 - \frac{1}{2}\mu_0 H \pm \frac{1}{2}\sqrt{\left(\frac{1}{16}\alpha^2 E_2^0\right)^2 + \frac{1}{2}\alpha^2 E_2^0 \mu_0 H + \mu_0^2 H^2} \end{cases}$$

5 Limiting behavior

In the small H limit, we get the following simplifications. For $m_j = \pm\frac{1}{2}$, we have:

$$\frac{3}{16}\alpha^2 E_0^2 + \frac{1}{8}\alpha^2 E_0^2 + \frac{1}{3}\mu_0 H + \frac{1}{3}\alpha^2 E_0^2\left(\frac{16}{6}\frac{\mu_0 H}{\alpha^2 E_0^2}\right)^{\frac{1}{2}}$$

$$\frac{5}{16}\alpha^2 E_0^2 + \frac{1}{3}\mu_0 H$$

$$\frac{1}{16}\alpha^2 E_0^2 + \frac{2}{3}\mu_0 H.$$

And for $m_j = -\frac{1}{2}$, we have:

$$\frac{3}{16}\alpha^2 E_0^2 + \frac{1}{8}\alpha^2 E_0^2 - \frac{1}{3}\mu_0 H + \frac{1}{3}\alpha^2 E_0^2\left(\frac{16}{6}\frac{\mu_0 H}{\alpha^2 E_0^2}\right)^{\frac{1}{2}}$$

$$\frac{5}{16}\alpha^2 E_0^2 - \frac{1}{3}\mu_0 H$$

$$\frac{1}{16}\alpha^2 E_0^2 - \frac{2}{3}\mu_0 H.$$

which can be read of the above matrix with H small. In the large H limit, we instead get for $m_j = +\frac{1}{2}$:

$$\frac{\mu_0 H}{2} \pm \frac{\mu_0 H}{2} = \begin{cases} \mu_0 H \\ 0 \end{cases}$$

and for $m_j = -\frac{1}{2}$:

$$-\frac{\mu_0 H}{2} \pm \frac{\mu_0 H}{2} = \begin{cases} -\mu_0 H \\ 0 \end{cases}$$

This is $\hat{J}_z \pm \hat{S}_z$ when we think of $\hat{J}_z$ and $\hat{S}_z$ as independent.