ZEEMAN EFFECT FOR N = 3: GENERAL CASE

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References: Griffiths, David J. (2005), Introduction to Quantum Mechanics, 2nd Edition; Pearson Education - Problem 6.26 (general field).

To complete our analysis of the $n=3$ line in the Zeeman effect, we need to calculate the general degenerate perturbation matrix W. We'll follow the same procedure as that for $n=2$ (except this time I'll do it for only one set of eigenstates!) and use the $|n\ell jj_z\rangle$ states as the basis for the matrix elements. We now have a total of 18 degenerate unperturbed states (the 8 we had for $n=2$ with $\ell=0,1$ plus 10 for $\ell=2$).

The eigenvalue equations we need to work out W are

$$H'_{fs}|n\ell jj_z\rangle = \frac{13.6\text{ eV}}{n^3}\alpha^2\left(\frac{3}{4n}-\frac{1}{j+\frac{1}{2}}\right)|n\ell jj_z\rangle \tag{1}$$

$$H'_Z|\ell\ell_z\rangle|ss_z\rangle = \mu_B B_{ext}(\ell_z+2s_z)|\ell\ell_z\rangle|ss_z\rangle \tag{2}$$

Here $n=3$, so we'll rewrite these equations to make them a bit more compact:

$$H'_{fs}|2\ell jj_z\rangle = \frac{13.6\text{ eV}}{27}\alpha^2\left(\frac{1}{4}-\frac{4}{4\left(j+\frac{1}{2}\right)}\right)|n\ell jj_z\rangle \tag{3}$$

$$= \frac{13.6\text{ eV}}{108}\alpha^2\left(1-\frac{4}{j+\frac{1}{2}}\right)|n\ell jj_z\rangle \tag{4}$$

$$\equiv \gamma\left(1-\frac{4}{j+\frac{1}{2}}\right)|n\ell jj_z\rangle \tag{5}$$

$$H'_Z|\ell\ell_z\rangle|ss_z\rangle = \mu_B B_{ext}(\ell_z+2s_z)|\ell\ell_z\rangle|ss_z\rangle \tag{6}$$

$$\equiv \beta(\ell_z+2s_z)|\ell\ell_z\rangle|ss_z\rangle \tag{7}$$

Note that the γ here is different from the one we used in the $n=2$ case.

Since the $\ell=0$ and $\ell=1$ states are the same as in the $n=2$ case, their decomposition into $|\ell\ell_z\rangle|ss_z\rangle$ states via Clebsch-Gordan coefficients is the same, so the matrix elements of H'_Z are the same as well. As a reminder, the $\ell=0$ and $\ell=1$ states are:

$$\psi_1 = \left|30\frac{1}{2}\frac{1}{2}\right\rangle = |00\rangle\left|\frac{1}{2}\frac{1}{2}\right\rangle \tag{8}$$

$$\psi_2 = \left|30\frac{1}{2}-\frac{1}{2}\right\rangle = |00\rangle\left|\frac{1}{2}-\frac{1}{2}\right\rangle \tag{9}$$

$$\psi_3 = \left|31\frac{3}{2}\frac{3}{2}\right\rangle = |11\rangle\left|\frac{1}{2}\frac{1}{2}\right\rangle \tag{10}$$

$$\psi_4 = \left|31\frac{3}{2}-\frac{3}{2}\right\rangle = |1-1\rangle\left|\frac{1}{2}-\frac{1}{2}\right\rangle \tag{11}$$

$$\psi_5 = \left|31\frac{3}{2}\frac{1}{2}\right\rangle = \sqrt{\frac{2}{3}}|10\rangle\left|\frac{1}{2}\frac{1}{2}\right\rangle + \sqrt{\frac{1}{3}}|11\rangle\left|\frac{1}{2}-\frac{1}{2}\right\rangle \tag{12}$$

$$\psi_6 = \left|31\frac{1}{2}\frac{1}{2}\right\rangle = -\sqrt{\frac{1}{3}}|10\rangle\left|\frac{1}{2}\frac{1}{2}\right\rangle + \sqrt{\frac{2}{3}}|11\rangle\left|\frac{1}{2}-\frac{1}{2}\right\rangle \tag{13}$$

$$\psi_7 = \left|31\frac{3}{2}-\frac{1}{2}\right\rangle = \sqrt{\frac{1}{3}}|1-1\rangle\left|\frac{1}{2}\frac{1}{2}\right\rangle + \sqrt{\frac{2}{3}}|10\rangle\left|\frac{1}{2}-\frac{1}{2}\right\rangle \tag{14}$$

$$\psi_8 = \left|31\frac{1}{2}-\frac{1}{2}\right\rangle = -\sqrt{\frac{2}{3}}|1-1\rangle\left|\frac{1}{2}\frac{1}{2}\right\rangle + \sqrt{\frac{1}{3}}|10\rangle\left|\frac{1}{2}-\frac{1}{2}\right\rangle \tag{15}$$

The matrix elements of H'_{fs} are different, however, as they depend on n and we're using a different value for γ. Since there are only 3 different values of j possible, we can work out the matrix elements of H'_{fs} for these:

$$E_{fs1}\left(j=\frac{1}{2}\right) = -3\gamma \tag{16}$$

$$E_{fs1}\left(j=\frac{3}{2}\right) = -\gamma \tag{17}$$

$$E_{fs1}\left(j=\frac{5}{2}\right) = -\frac{1}{3}\gamma \tag{18}$$

By following the $n=2$ procedure, we get the upper-left 8×8 block of W:

(19)

$$W_{1\rightarrow 8}=\left[\begin{array}{cccccccc}
\beta-3\gamma & 0 & 0 & 0 & 0 & 0 & 0 & 0\\
0 & -\beta-3\gamma & 0 & 0 & 0 & 0 & 0 & 0\\
0 & 0 & 2\beta-\gamma & 0 & 0 & 0 & 0 & 0\\
0 & 0 & 0 & -2\beta-\gamma & 0 & 0 & 0 & 0\\
0 & 0 & 0 & 0 & \frac{2}{3}\beta-\gamma & -\frac{\sqrt{2}}{3}\beta & 0 & 0\\
0 & 0 & 0 & 0 & -\frac{\sqrt{2}}{3}\beta & \frac{1}{3}\beta-3\gamma & 0 & 0\\
0 & 0 & 0 & 0 & 0 & 0 & -\frac{2}{3}\beta-\gamma & -\frac{\sqrt{2}}{3}\beta\\
0 & 0 & 0 & 0 & 0 & 0 & -\frac{\sqrt{2}}{3}\beta & -\frac{1}{3}\beta-3\gamma
\end{array}\right]$$

To get the lower-right 10×10 block of W, we need to use Clebsch-Gordan coefficients to write the $|n\ell j j_z\rangle$ states in terms of the $|\ell\ell_z\rangle\,|ss_z\rangle$ states so that we can calculate the matrix elements of H'_Z. We get

(20) $$\psi_9=\left|32\frac{5}{2}\frac{5}{2}\right\rangle=|22\rangle\left|\frac{1}{2}\frac{1}{2}\right\rangle$$

(21) $$\psi_{10}=\left|32\frac{5}{2}-\frac{5}{2}\right\rangle=|2-2\rangle\left|\frac{1}{2}-\frac{1}{2}\right\rangle$$

(22) $$\psi_{11}=\left|32\frac{5}{2}\frac{3}{2}\right\rangle=\sqrt{\frac{1}{5}}|22\rangle\left|\frac{1}{2}-\frac{1}{2}\right\rangle+\sqrt{\frac{4}{5}}|21\rangle\left|\frac{1}{2}\frac{1}{2}\right\rangle$$

(23) $$\psi_{12}=\left|32\frac{3}{2}\frac{3}{2}\right\rangle=\sqrt{\frac{4}{5}}|22\rangle\left|\frac{1}{2}-\frac{1}{2}\right\rangle-\sqrt{\frac{1}{5}}|21\rangle\left|\frac{1}{2}\frac{1}{2}\right\rangle$$

(24) $$\psi_{13}=\left|32\frac{5}{2}\frac{1}{2}\right\rangle=\sqrt{\frac{2}{5}}|21\rangle\left|\frac{1}{2}-\frac{1}{2}\right\rangle+\sqrt{\frac{3}{5}}|20\rangle\left|\frac{1}{2}\frac{1}{2}\right\rangle$$

(25) $$\psi_{14}=\left|32\frac{3}{2}\frac{1}{2}\right\rangle=\sqrt{\frac{3}{5}}|21\rangle\left|\frac{1}{2}-\frac{1}{2}\right\rangle-\sqrt{\frac{2}{5}}|20\rangle\left|\frac{1}{2}\frac{1}{2}\right\rangle$$

(26) $$\psi_{15}=\left|32\frac{5}{2}-\frac{1}{2}\right\rangle=\sqrt{\frac{3}{5}}|20\rangle\left|\frac{1}{2}-\frac{1}{2}\right\rangle+\sqrt{\frac{2}{5}}|2-1\rangle\left|\frac{1}{2}\frac{1}{2}\right\rangle$$

(27) $$\psi_{16}=\left|32\frac{3}{2}-\frac{1}{2}\right\rangle=\sqrt{\frac{2}{5}}|20\rangle\left|\frac{1}{2}-\frac{1}{2}\right\rangle-\sqrt{\frac{3}{5}}|2-1\rangle\left|\frac{1}{2}\frac{1}{2}\right\rangle$$

(28) $$\psi_{17}=\left|32\frac{5}{2}-\frac{3}{2}\right\rangle=\sqrt{\frac{4}{5}}|2-1\rangle\left|\frac{1}{2}-\frac{1}{2}\right\rangle+\sqrt{\frac{1}{5}}|2-2\rangle\left|\frac{1}{2}\frac{1}{2}\right\rangle$$

(29) $$\psi_{18}=\left|32\frac{3}{2}-\frac{3}{2}\right\rangle=\sqrt{\frac{1}{5}}|2-1\rangle\left|\frac{1}{2}-\frac{1}{2}\right\rangle-\sqrt{\frac{4}{5}}|2-2\rangle\left|\frac{1}{2}\frac{1}{2}\right\rangle$$

We can now work out the matrix elements as before to get the bottom-right 10×10 block:

(30)
$$W_{9\to 18} = \begin{bmatrix} 3\beta - \frac{1}{3}\gamma & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \\ 0 & -3\beta - \frac{1}{3}\gamma & 0 & 0 & 0 & 0 & 0 & 0 & \\ 0 & 0 & \frac{9}{5}\beta - \frac{1}{3}\gamma & -\frac{2}{5}\beta & 0 & 0 & 0 & 0 & \\ 0 & 0 & -\frac{2}{5}\beta & \frac{6}{5}\beta - \gamma & 0 & 0 & 0 & 0 & \\ 0 & 0 & 0 & 0 & \frac{3}{5}\beta - \frac{1}{3}\gamma & -\frac{\sqrt{6}}{5}\beta & 0 & 0 & \\ 0 & 0 & 0 & 0 & -\frac{\sqrt{6}}{5}\beta & \frac{2}{5}\beta - \gamma & 0 & 0 & \\ 0 & 0 & 0 & 0 & 0 & 0 & -\frac{3}{5}\beta - \frac{1}{3}\gamma & -\frac{\sqrt{6}}{5}\beta & \\ 0 & 0 & 0 & 0 & 0 & 0 & -\frac{\sqrt{6}}{5}\beta & -\frac{2}{5}\beta - \gamma & \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{9}{5}\beta \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & - \end{bmatrix}$$

The energies can now be obtained by finding the eigenvalues of the entire matrix, which isn't that hard since it consists of 6 solo diagonal elements and 6 2×2 blocks. We'll denote the energy corrections by ε_i for $i = 1..18$. The first 4 can be read off the first 4 diagonal entries in $W_{1\to 8}$:

$$\varepsilon_1 = \beta - 3\gamma \tag{31}$$
$$\varepsilon_2 = -\beta - 3\gamma \tag{32}$$
$$\varepsilon_3 = 2\beta - \gamma \tag{33}$$
$$\varepsilon_4 = -2\beta - \gamma \tag{34}$$

The next two are the eigenvalues of the sub-matrix $W_{5,6}$:

$$W_{5,6} = \begin{bmatrix} \frac{2}{3}\beta - \gamma & -\frac{\sqrt{2}}{3}\beta \\ -\frac{\sqrt{2}}{3}\beta & \frac{1}{3}\beta - 3\gamma \end{bmatrix} \tag{35}$$

which are:

$$\varepsilon_5 = -2\gamma + \frac{\beta}{2} + \sqrt{\gamma^2 + \frac{\gamma\beta}{3} + \frac{\beta^2}{4}} \tag{36}$$
$$\varepsilon_6 = -2\gamma + \frac{\beta}{2} - \sqrt{\gamma^2 + \frac{\gamma\beta}{3} + \frac{\beta^2}{4}} \tag{37}$$

We can carry on the same way to get the remaining energies:

$$\varepsilon_7 = -2\gamma - \frac{\beta}{2} + \sqrt{\gamma^2 - \frac{\gamma\beta}{3} + \frac{\beta^2}{4}} \tag{38}$$

$$\varepsilon_8 = -2\gamma - \frac{\beta}{2} - \sqrt{\gamma^2 - \frac{\gamma\beta}{3} + \frac{\beta^2}{4}} \tag{39}$$

$$\varepsilon_9 = 3\beta - \frac{1}{3}\gamma \tag{40}$$

$$\varepsilon_{10} = -3\beta - \frac{1}{3}\gamma \tag{41}$$

$$\varepsilon_{11} = -\frac{2}{3}\gamma + \frac{3\beta}{2} + \sqrt{\frac{\gamma^2}{9} + \frac{3\gamma\beta}{5} + \frac{\beta^2}{4}} \tag{42}$$

$$\varepsilon_{12} = -\frac{2}{3}\gamma + \frac{3\beta}{2} - \sqrt{\frac{\gamma^2}{9} + \frac{3\gamma\beta}{5} + \frac{\beta^2}{4}} \tag{43}$$

$$\varepsilon_{13} = -\frac{2}{3}\gamma + \frac{\beta}{2} + \sqrt{\frac{\gamma^2}{9} + \frac{\gamma\beta}{15} + \frac{\beta^2}{4}} \tag{44}$$

$$\varepsilon_{14} = -\frac{2}{3}\gamma + \frac{\beta}{2} - \sqrt{\frac{\gamma^2}{9} + \frac{\gamma\beta}{15} + \frac{\beta^2}{4}} \tag{45}$$

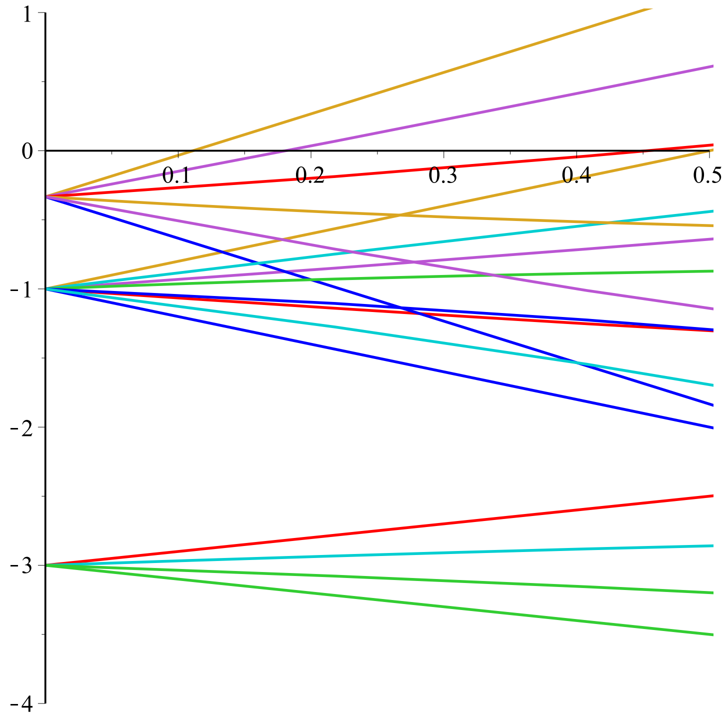
$$\varepsilon_{15} = -\frac{2}{3}\gamma - \frac{\beta}{2} + \sqrt{\frac{\gamma^2}{9} - \frac{\gamma\beta}{15} + \frac{\beta^2}{4}} \tag{46}$$

$$\varepsilon_{16} = -\frac{2}{3}\gamma - \frac{\beta}{2} - \sqrt{\frac{\gamma^2}{9} - \frac{\gamma\beta}{15} + \frac{\beta^2}{4}} \tag{47}$$

$$\varepsilon_{17} = -\frac{2}{3}\gamma - \frac{3\beta}{2} + \sqrt{\frac{\gamma^2}{9} - \frac{3\gamma\beta}{5} + \frac{\beta^2}{4}} \tag{48}$$

$$\varepsilon_{18} = -\frac{2}{3}\gamma - \frac{3\beta}{2} - \sqrt{\frac{\gamma^2}{9} - \frac{3\gamma\beta}{5} + \frac{\beta^2}{4}} \tag{49}$$

Plotting these energies as functions of β gives the following (where $\gamma = 1$):



A closer view shows the weak field case. Note the three distinct starting points for zero field, corresponding to the three values of $j=\frac{5}{2},\frac{3}{2},\frac{1}{2}$, reading from the top down.

Finally, we can check that these general results reduce to the weak and strong field values we had earlier. For the weak field case, $\beta\ll\gamma$ and we can expand the expressions for the energies to first order in β to get:

ε_1	ε_2	ε_3	ε_4	ε_5
$-3\gamma+\beta$	$-3\gamma-\beta$	$-\gamma+2\beta$	$-\gamma-2\beta$	$-\gamma+\frac{2}{3}\beta$
ε_{10}	ε_{11}	ε_{12}	ε_{13}	ε_{14}
$-\frac{1}{3}\gamma-3\beta$	$-\frac{1}{3}\gamma+\frac{9}{5}\beta$	$-\gamma+\frac{6}{5}\beta$	$-\frac{1}{3}\gamma+\frac{3}{5}\beta$	$-\gamma+\frac{2}{5}\beta$

ε_6	ε_7	ε_8	ε_9
$-3\gamma+\frac{1}{3}\beta$	$-\gamma-\frac{2}{3}\beta$	$-3\gamma-\frac{1}{3}\beta$	$-\frac{1}{3}\gamma+3\beta$
ε_{15}	ε_{16}	ε_{17}	ε_{18}
$-\frac{1}{3}\gamma-\frac{3}{5}\beta$	$-\gamma-\frac{2}{5}\beta$	$-\frac{1}{3}\gamma-\frac{9}{5}\beta$	$-\gamma-\frac{6}{5}\beta$

Comparing with the values obtained in the weak field approximation, we find the energies are the same, although they appear in a different order due to the way we labelled the rows in the matrix.

For the strong field limit, $\beta\gg\gamma$ and we get after expanding to first order in γ

ε_1	ε_2	ε_3	ε_4	ε_5
$-3\gamma+\beta$	$-3\gamma-\beta$	$-\gamma+2\beta$	$-\gamma-2\beta$	$-\frac{5}{3}\gamma+\beta$
ε_{10}	ε_{11}	ε_{12}	ε_{13}	ε_{14}
$-\frac{1}{3}\gamma-3\beta$	$-\frac{7}{15}\gamma+2\beta$	$-\frac{13}{15}\gamma+\beta$	$-\frac{3}{5}\gamma+\beta$	$-\frac{11}{15}\gamma$

ε_6	ε_7	ε_8	ε_9
$-\frac{7}{3}\gamma$	$-\frac{7}{3}\gamma$	$-\frac{5}{3}\gamma-\beta$	$-\frac{1}{3}\gamma+3\beta$
ε_{15}	ε_{16}	ε_{17}	ε_{18}
$-\frac{11}{15}\gamma$	$-\frac{3}{5}\gamma-\beta$	$-\frac{13}{15}\gamma-\beta$	$-\frac{7}{15}\gamma-2\beta$

Again, comparing with the strong field approximation, we find that the energies match.