

## ZEEMAN EFFECT: DEGENERATE PERTURBATION THEORY FOR N = 2

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References: Griffiths, David J. (2005), *Introduction to Quantum Mechanics*, 2nd Edition; Pearson Education - Problem 6.25.

When considering the Zeeman effect in the two limiting cases of a strong field and a weak field we could simplify things by assuming either the Zeeman effect or the fine structure (due to relativistic and spin-orbit coupling corrections) was dominant and then getting an approximate value for the energy perturbation by using non-degenerate perturbation theory, even though the unperturbed energy levels of hydrogen are highly degenerate.

If the Zeeman effect and fine structure are of roughly equal magnitude, however, these approximate methods don't work and we need to do a proper analysis using degenerate perturbation theory. The perturbation hamiltonian in this case is

$$H' = H'_Z + H'_{fs} \quad (1)$$

and we need to construct the matrix  $W$  whose elements are the matrix elements  $W_{ab} = \langle a | H' | b \rangle$  where the states used to calculate the matrix elements are eigenstates of the unperturbed hamiltonian.

When we calculated fine structure, we used the eigenstates  $|nljj_z\rangle$ , that is, eigenstates of the angular momentum operators  $L^2$ ,  $J^2$  and  $J_z$ , since these states are also eigenstates of  $H'_{fs}$ . However, they are not eigenstates of  $H'_Z$ ; for that calculation, we used the eigenstates  $|n\ell\ell_z s_z\rangle = |\ell\ell_z\rangle |ss_z\rangle$  of the operators  $L^2$ ,  $L_z$  and  $S_z$ . (Note that both sets of states are eigenstates of  $S^2$ , since we are always dealing with spin  $\frac{1}{2}$ .) To calculate  $W$ , we need to choose one of these sets. Griffiths chooses to use  $|nljj_z\rangle$  so we'll go with that to start.

The eigenvalue equations we need to work out  $W$  are

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

$$H'_Z |\ell\ell_z\rangle |ss_z\rangle = \mu_B B_{ext} (\ell_z + 2s_z) |\ell\ell_z\rangle |ss_z\rangle \quad (3)$$

Here  $n = 2$ , so we'll rewrite these equations to make them a bit more compact:

$$H'_{fs} |2\ell jj_z\rangle = \frac{13.6 \text{ eV}}{8} \alpha^2 \left( \frac{3}{8} - \frac{8}{8(j + \frac{1}{2})} \right) |n\ell jj_z\rangle \quad (4)$$

$$= \frac{13.6 \text{ eV}}{64} \alpha^2 \left( 3 - \frac{8}{j + \frac{1}{2}} \right) |n\ell jj_z\rangle \quad (5)$$

$$\equiv \gamma \left( 3 - \frac{8}{j + \frac{1}{2}} \right) |n\ell jj_z\rangle \quad (6)$$

$$H'_Z |\ell\ell_z\rangle |ss_z\rangle = \mu_B B_{ext} (\ell_z + 2s_z) |\ell\ell_z\rangle |ss_z\rangle \quad (7)$$

$$\equiv \beta (\ell_z + 2s_z) |\ell\ell_z\rangle |ss_z\rangle \quad (8)$$

In order to calculate the matrix elements of  $H'_Z$  in this basis, we need to express  $|2\ell jj_z\rangle$  in terms of  $|\ell\ell_z\rangle |ss_z\rangle$ , which we can do by using Clebsch-Gordan coefficients. In this case, we are combining the angular momenta  $\ell$  and  $s$  to produce a fixed total  $j$ . The results are given in Griffiths, but the procedure is the same as that given in the link in the previous sentence. The results are, defining  $\psi_i$  as shorthand for the states:

$$\psi_1 = \left| 20 \frac{1}{2} \frac{1}{2} \right\rangle = |00\rangle \left| \frac{1}{2} \frac{1}{2} \right\rangle \quad (9)$$

$$\psi_2 = \left| 20 \frac{1}{2} - \frac{1}{2} \right\rangle = |00\rangle \left| \frac{1}{2} - \frac{1}{2} \right\rangle \quad (10)$$

$$\psi_3 = \left| 21 \frac{3}{2} \frac{3}{2} \right\rangle = |11\rangle \left| \frac{1}{2} \frac{1}{2} \right\rangle \quad (11)$$

$$\psi_4 = \left| 21 \frac{3}{2} - \frac{3}{2} \right\rangle = |1-1\rangle \left| \frac{1}{2} - \frac{1}{2} \right\rangle \quad (12)$$

$$\psi_5 = \left| 21 \frac{3}{2} \frac{1}{2} \right\rangle = \sqrt{\frac{2}{3}} |10\rangle \left| \frac{1}{2} \frac{1}{2} \right\rangle + \sqrt{\frac{1}{3}} |11\rangle \left| \frac{1}{2} - \frac{1}{2} \right\rangle \quad (13)$$

$$\psi_6 = \left| 21 \frac{1}{2} \frac{1}{2} \right\rangle = -\sqrt{\frac{1}{3}} |10\rangle \left| \frac{1}{2} \frac{1}{2} \right\rangle + \sqrt{\frac{2}{3}} |11\rangle \left| \frac{1}{2} - \frac{1}{2} \right\rangle \quad (14)$$

$$\psi_7 = \left| 21 \frac{3}{2} - \frac{1}{2} \right\rangle = \sqrt{\frac{1}{3}} |1-1\rangle \left| \frac{1}{2} \frac{1}{2} \right\rangle + \sqrt{\frac{2}{3}} |10\rangle \left| \frac{1}{2} - \frac{1}{2} \right\rangle \quad (15)$$

$$\psi_8 = \left| 21 \frac{1}{2} - \frac{1}{2} \right\rangle = -\sqrt{\frac{2}{3}} |1-1\rangle \left| \frac{1}{2} \frac{1}{2} \right\rangle + \sqrt{\frac{1}{3}} |10\rangle \left| \frac{1}{2} - \frac{1}{2} \right\rangle \quad (16)$$

From here it's a matter of applying the eigenvalue relations above to these states, remembering that the states within each basis are all orthonormal. For example

$$W_{56} = \langle \psi_5 | H'_Z | \psi_6 \rangle = \langle \psi_5 | H'_Z \left[ -\sqrt{\frac{1}{3}} |10\rangle \left| \frac{1}{2} \frac{1}{2} \right\rangle + \sqrt{\frac{2}{3}} |11\rangle \left| \frac{1}{2} -\frac{1}{2} \right\rangle \right] \quad (17)$$

$$= \langle \psi_5 | \left[ -\sqrt{\frac{1}{3}} \beta \left( 0 + 2 \times \frac{1}{2} \right) |10\rangle \left| \frac{1}{2} \frac{1}{2} \right\rangle + \sqrt{\frac{2}{3}} \beta \left( 1 - 2 \times \frac{1}{2} \right) |11\rangle \left| \frac{1}{2} -\frac{1}{2} \right\rangle \right] \quad (18)$$

$$= -\frac{\sqrt{2}}{3} \beta \quad (19)$$

The other elements of  $W$  can be worked out similarly, with the result

$$W = \begin{bmatrix} \beta - 5\gamma & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -\beta - 5\gamma & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 2\beta - \gamma & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -2\beta - \gamma & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{2}{3}\beta - \gamma & -\frac{\sqrt{2}}{3}\beta & 0 & 0 \\ 0 & 0 & 0 & 0 & -\frac{\sqrt{2}}{3}\beta & \frac{1}{3}\beta - 5\gamma & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -\frac{2}{3}\beta - \gamma & -\frac{\sqrt{2}}{3}\beta \\ 0 & 0 & 0 & 0 & 0 & 0 & -\frac{\sqrt{2}}{3}\beta & -\frac{1}{3}\beta - 5\gamma \end{bmatrix} \quad (20)$$

The energy corrections are the eigenvalues of this matrix. The first four eigenvalues can just be read off the top 4 diagonal elements and the other four can be found by finding the eigenvalues of the two  $2 \times 2$  submatrices with non-zero entries. The results are:

$$E_{2,1} = \begin{cases} -5\gamma \pm \beta \\ -\gamma \pm 2\beta \\ \frac{\beta}{2} - 3\gamma \pm \frac{1}{6} \sqrt{9\beta^2 + 24\beta\gamma + 144\gamma^2} \\ -\frac{\beta}{2} - 3\gamma \pm \frac{1}{6} \sqrt{9\beta^2 - 24\beta\gamma + 144\gamma^2} \end{cases} \quad (21)$$

Comparing this with the results for a weak field we see that the first two lines match the weak field energies with slopes of  $\pm 1$  and  $\pm 2$ . For a weak field,  $\beta \ll \gamma$  so we can approximate the square roots. We get

$$\frac{1}{6}\sqrt{9\beta^2 \pm 24\beta\gamma + 144\gamma^2} = 2\gamma\sqrt{1 \pm \frac{\beta}{6\gamma} + \frac{\beta^2}{16\gamma^2}} \quad (22)$$

$$\approx 2\gamma\left(1 \pm \frac{\beta}{12\gamma}\right) \quad (23)$$

$$= 2\gamma \pm \frac{\beta}{6} \quad (24)$$

Therefore the energy correction terms become

$$E_{2,1} = \begin{cases} -5\gamma \pm \beta \\ -\gamma \pm 2\beta \\ \pm \frac{2\beta}{3} - \gamma \\ \pm \frac{\beta}{3} - \gamma \end{cases} \quad (25)$$

which matches the energies obtained using the weak field approximation.

In the strong field limit,  $\gamma \ll \beta$  so we get

$$\frac{1}{6}\sqrt{9\beta^2 \pm 24\beta\gamma + 144\gamma^2} = \frac{\beta}{2}\sqrt{1 \pm \frac{8}{3}\frac{\gamma}{\beta} + 16\frac{\gamma^2}{\beta^2}} \quad (26)$$

$$\approx \frac{\beta}{2}\left(1 \pm \frac{4}{3}\frac{\gamma}{\beta}\right) \quad (27)$$

$$= \frac{\beta}{2} \pm \frac{2}{3}\gamma \quad (28)$$

Plugging this approximation into the energy formulas reproduces the energies we worked out earlier using the strong field approximation (though it's a bit tedious).

To use the other set of eigenstates  $|\ell\ell_z\rangle |ss_z\rangle$ , we need to express these in terms of the  $|n\ell jj_z\rangle$  set so that we can calculate the matrix elements for  $H'_{fs}$ . To do this, we can use the Clebsch-Gordan coefficients again, except this time we read off the coefficients from a row rather than a column. For example, the state  $|10\rangle \left|\frac{1}{2} - \frac{1}{2}\right\rangle$  must have  $j_z = -\frac{1}{2}$  so we look in the table for combining spins 1 and  $\frac{1}{2}$  in the row for  $\ell_z = 0$  and  $s_z = -\frac{1}{2}$  and we get

$$|10\rangle \left|\frac{1}{2} - \frac{1}{2}\right\rangle = \sqrt{\frac{2}{3}} \left|\frac{3}{2} - \frac{1}{2}\right\rangle + \sqrt{\frac{1}{3}} \left|\frac{1}{2} - \frac{1}{2}\right\rangle \quad (29)$$

We can work out the other entries the same way and we get, defining  $\zeta_i$  to be shorthand for the eigenstates:

$$\zeta_1 = |00\rangle \left| \frac{1}{2} \frac{1}{2} \right\rangle = \left| 20 \frac{1}{2} \frac{1}{2} \right\rangle \quad (30)$$

$$\zeta_2 = |00\rangle \left| \frac{1}{2} - \frac{1}{2} \right\rangle = \left| 20 \frac{1}{2} - \frac{1}{2} \right\rangle \quad (31)$$

$$\zeta_3 = |11\rangle \left| \frac{1}{2} \frac{1}{2} \right\rangle = \left| 21 \frac{3}{2} \frac{3}{2} \right\rangle \quad (32)$$

$$\zeta_4 = |11\rangle \left| \frac{1}{2} - \frac{1}{2} \right\rangle = \sqrt{\frac{1}{3}} \left| 21 \frac{3}{2} \frac{1}{2} \right\rangle + \sqrt{\frac{2}{3}} \left| 21 \frac{1}{2} \frac{1}{2} \right\rangle \quad (33)$$

$$\zeta_5 = |10\rangle \left| \frac{1}{2} \frac{1}{2} \right\rangle = \sqrt{\frac{2}{3}} \left| 21 \frac{3}{2} \frac{1}{2} \right\rangle - \sqrt{\frac{1}{3}} \left| 21 \frac{1}{2} \frac{1}{2} \right\rangle \quad (34)$$

$$\zeta_6 = |10\rangle \left| \frac{1}{2} - \frac{1}{2} \right\rangle = \sqrt{\frac{2}{3}} \left| 21 \frac{3}{2} - \frac{1}{2} \right\rangle + \sqrt{\frac{1}{3}} \left| 21 \frac{1}{2} - \frac{1}{2} \right\rangle \quad (35)$$

$$\zeta_7 = |1-1\rangle \left| \frac{1}{2} \frac{1}{2} \right\rangle = \sqrt{\frac{1}{3}} \left| 21 \frac{3}{2} - \frac{1}{2} \right\rangle - \sqrt{\frac{2}{3}} \left| 21 \frac{1}{2} - \frac{1}{2} \right\rangle \quad (36)$$

$$\zeta_8 = |1-1\rangle \left| \frac{1}{2} - \frac{1}{2} \right\rangle = \left| 21 \frac{3}{2} - \frac{3}{2} \right\rangle \quad (37)$$

The matrix elements of  $H'_Z$  are non-zero only on the diagonal but there will now be 4 off-diagonal non-zero elements for  $H'_{fs}$ :

$$W_{45} = \langle \zeta_4 | H'_{fs} | \zeta_5 \rangle = W_{54} = \frac{4\sqrt{2}}{3} \gamma \quad (38)$$

$$W_{67} = W_{76} = \frac{4\sqrt{2}}{3} \gamma \quad (39)$$

We can work out the matrix elements in the same way as before and get

$$W = \begin{bmatrix} \beta - 5\gamma & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -\beta - 5\gamma & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 2\beta - \gamma & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\frac{11}{3}\gamma & \frac{4\sqrt{2}}{3}\gamma & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{4\sqrt{2}}{3}\gamma & \beta - \frac{7}{3}\gamma & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -\beta - \frac{7}{3}\gamma & \frac{4\sqrt{2}}{3}\gamma & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{4\sqrt{2}}{3}\gamma & -\frac{11}{3}\gamma & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -2\beta - \gamma \end{bmatrix} \quad (40)$$

This matrix has the same eigenvalues as the previous one, so as we would hope, we get the same solutions for the energy corrections.

#### PINGBACKS

Pingback: Zeeman effect for  $n = 3$ : general case