

The Zeeman Effect

As we mentioned in Chapter 3, the splitting of spectral lines when an atom is placed in an external magnetic field was looked for by Faraday, predicted on the basis of classical theory by Lorentz, and first observed by Zeeman,¹⁷ for whom the effect is now named.

In quantum mechanics, a shift in the frequency and wavelength of a spectral line implies a shift in the energy level of one or both of the states involved in the transition. The Zeeman effect that occurs for spectral lines resulting from a transition between *singlet* states is traditionally called the *normal* effect, while that which occurs when the total spin of either the initial or final states, or both, is nonzero is called the *anomalous* effect.¹⁸ There is no fundamental difference between the two, however, so we will generally not distinguish between them, save for one exception: the large value of the electron's magnetic moment complicates the explanation of the anomalous effect a bit, so we will discuss the Zeeman effect in transitions between singlet states first.

Normal Zeeman Effect

For singlet states, the spin is zero and the total angular momentum \mathbf{J} is equal to the orbital angular momentum \mathbf{L} . When placed in an external magnetic field, the energy of the atom changes because of the energy of its magnetic moment in the field, which is given by

$$\Delta E = -\boldsymbol{\mu} \cdot \mathbf{B} = -\mu_z B \quad 7-68$$

where the z direction is defined by the direction of \mathbf{B} (compare with Equation 7-54). Using Equation 7-45 for μ_z , we have $\mu_z = -m_\ell \mu_B = -m_\ell (e\hbar/2m_e)$, and

$$\Delta E = +m_\ell \frac{e\hbar}{2m_e} B = m_\ell \mu_B B \quad 7-69$$

Since there are $2\ell + 1$ values of m_ℓ , each energy level splits into $2\ell + 1$ levels. Figure 7-28 shows the splitting of the levels for the case of a transition between a state with $\ell = 2$ and one with $\ell = 1$. The selection rule $\Delta m_\ell = \pm 1$ restricts the number of possible lines to the nine shown.

Because of the uniform splitting of the levels, there are only three different transition energies: $E_0 + e\hbar B/2m_e$, E_0 , and $E_0 - e\hbar B/2m_e$, corresponding to the transitions with $\Delta m_\ell = +1$, $\Delta m_\ell = 0$, and $\Delta m_\ell = -1$. We can see that

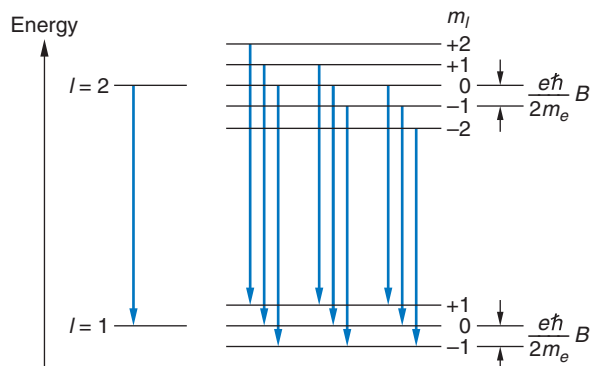


FIGURE 7-28 Energy-level splitting in the normal Zeeman effect for singlet levels $\ell = 2$ and $\ell = 1$. Each level is split into $2\ell + 1$ terms. The nine transitions consistent with the selection rule $\Delta m = 0, \pm 1$, give only three different energies because the energy difference between adjacent terms is $e\hbar B/2m_e$ independent of ℓ .

there will only be these energies for any initial and final values of ℓ . The change in the frequency of the emitted spectral line is the energy change divided by h . The frequency changes are therefore $\pm eB/2m_e$ or 0.

Anomalous Zeeman Effect

As stated above, the anomalous Zeeman effect occurs when the spin of either the initial or the final states, or both, is nonzero. The calculation of the energy-level splitting is complicated a bit by the fact that the magnetic moment due to spin is 1 rather than $\frac{1}{2}$ Bohr magneton, and as a result the total magnetic moment is not parallel to the total angular momentum. Consider an atom with orbital angular momentum \mathbf{L} and spin \mathbf{S} . Its total angular momentum is

$$\mathbf{J} = \mathbf{L} + \mathbf{S}$$

whereas the total magnetic moment is

$$\boldsymbol{\mu} = -g_\ell \mu_B \frac{\mathbf{L}}{\hbar} - g_s \mu_B \frac{\mathbf{S}}{\hbar}$$

Since $g_\ell = 1$ and $g_s = 2$ (approximately—see Equation 7-47), we have

$$\boldsymbol{\mu} = -\frac{\mu_B}{\hbar} (\mathbf{L} + 2\mathbf{S}) \quad 7-70$$

Figure 7-29 shows a vector model diagram of the addition of $\mathbf{L} + \mathbf{S}$ to give \mathbf{J} . The magnetic moments are indicated by the darker vectors. Such a vector model can be used to calculate the splitting of the levels, but since the calculation is rather involved, we will discuss only the results.¹⁹

Each energy level is split into $2j + 1$ levels, corresponding to the possible values of m_j . For the usual laboratory magnetic fields, which are weak compared with the internal magnetic field associated with the spin-orbit effect, the level splitting is small compared with the fine-structure splitting. Unlike the case of the singlet levels in the normal effect, the Zeeman splitting of these levels depends on j , ℓ , and s , and in general there are more than three different transition energies due to the fact that the upper and lower states are split by different amounts. The level splitting, that is, the energy shift relative to the position of the no-field energy level, can be written

$$\Delta E = g m_j \left(\frac{e\hbar B}{2m_e} \right) = g m_j \mu_B B \quad 7-71$$

where g , called the Landé g factor,²⁰ is given by

$$g = 1 + \frac{j(j+1) + s(s+1) - \ell(\ell+1)}{2j(j+1)} \quad 7-72$$

Note that for $s = 0$, $j = 1$, and $g = 1$, Equation 7-71 also gives the splitting in the normal Zeeman effect, as you would expect. Figure 7-30 shows the splitting of sodium doublet levels ${}^2P_{1/2}$, ${}^2P_{3/2}$, and ${}^2S_{1/2}$. The selection rule $\Delta m_j = \pm 1$ or 0 gives four lines for the transition ${}^2P_{1/2} \rightarrow {}^2S_{1/2}$ and six lines for the transition ${}^2P_{3/2} \rightarrow {}^2S_{1/2}$, as indicated. The energies of these lines can be calculated in terms of $e\hbar B/2m_e$ from Equations 7-71 and 7-72.

If the external magnetic field is sufficiently large, the Zeeman splitting is greater than the fine-structure splitting. If B is large enough so that we can neglect the fine-structure splitting, the Zeeman splitting is given by

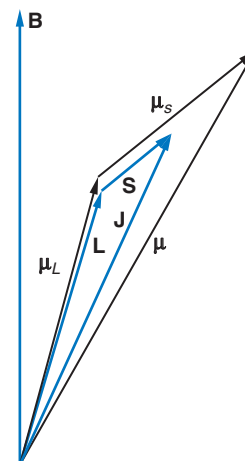
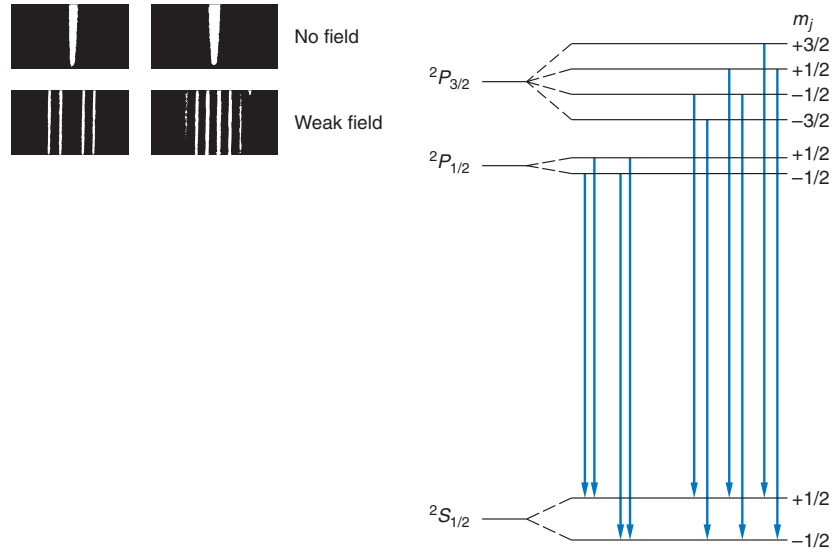


FIGURE 7-29 Vector diagram for the total magnetic moment when S is not zero. The moment is not parallel to the total angular momentum \mathbf{J} , because μ_s/S is twice μ_L/L . (The directions of $\boldsymbol{\mu}_L$, $\boldsymbol{\mu}_s$, and $\boldsymbol{\mu}$ have been reversed in this drawing for greater clarity.)

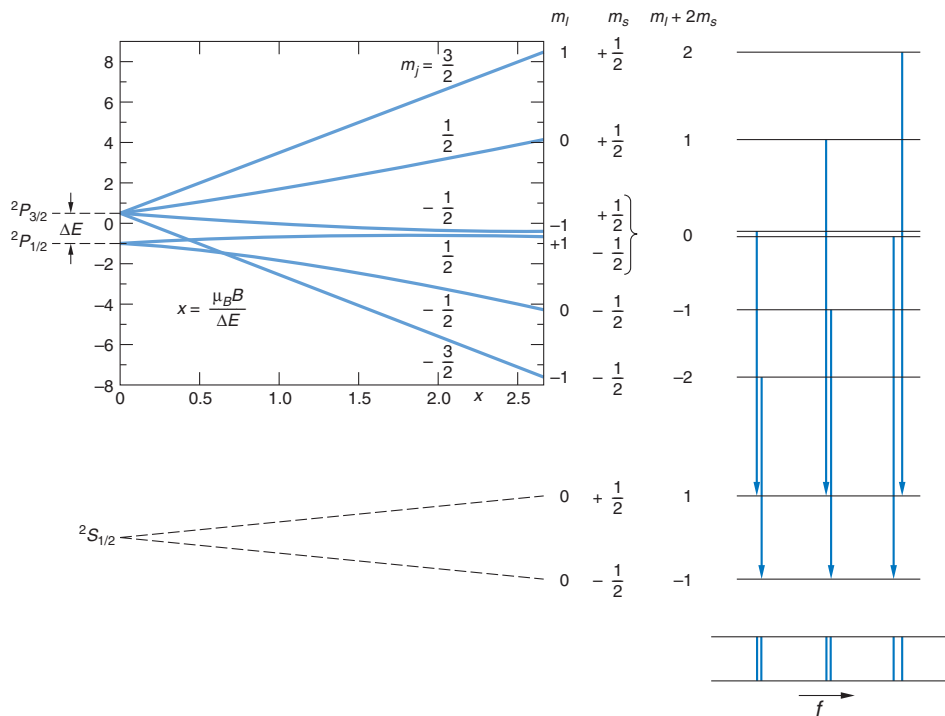
FIGURE 7-30 Energy-level splitting in a magnetic field for the $^2P_{3/2}$, $^2P_{1/2}$, and $^2S_{1/2}$ energy levels for sodium, showing the anomalous Zeeman effect. These are the D_1 and D_2 lines in Figure 7-22. The splitting of the levels depends on L , S , and J , leading to more than the three lines seen in the normal effect. [Photo from H.E. White, *Introduction to Atomic Spectra*, New York: McGraw-Hill Book Company, 1934. Used by permission of the publisher.]



$$\Delta E = (m_\ell + 2m_s) \left(\frac{e\hbar B}{2m_e} \right) = (m_\ell + 2m_s) \mu_B B$$

The splitting is then similar to the normal Zeeman effect and only three lines are observed. This behavior in large magnetic fields is called the Paschen-Back effect after its discoverers, F. Paschen and E. Back. Figure 7-31 shows the transition of the splitting of the levels from the anomalous Zeeman effect to the Paschen-Back effect as the magnitude of \mathbf{B} increases. The basic reason for the change in the appearance of the anomalous effect as \mathbf{B} increases is that the external magnetic field overpowers the

FIGURE 7-31 Paschen-Back effect. When the external magnetic field is so strong that the Zeeman splitting is greater than the spin-orbit splitting, effectively decoupling L and S , the level splitting is uniform for all atoms and only three spectral lines are seen, as in the normal Zeeman effect. Each of the three lines is actually a closely spaced doublet, as illustrated by the transitions shown at the right. These are the same transitions illustrated in Figure 7-30. Levels shown are for $x = 2.7$.



spin-orbit effect and decouples \mathbf{L} and \mathbf{S} so that they precess about \mathbf{B} nearly independently; thus, the projections of \mathbf{L} behave as if $\mathbf{S} \approx 0$, and the effect reduces to three lines, each of which is a closely spaced doublet.

EXAMPLE 7-5 Magnetic Field of the Sun The magnetic field of the Sun and stars can be determined by measuring the Zeeman-effect splitting of spectral lines. Suppose that the sodium D_1 line emitted in a particular region of the solar disk is observed to be split into the four-component Zeeman effect (see Figure 7-30). What is the strength of the solar magnetic field B in that region if the wavelength difference $\Delta\lambda$ between the shortest and the longest wavelengths is 0.022 nm? (The wavelength of the D_1 line is 589.8 nm.)

SOLUTION

The D_1 line is emitted in the $3^2P_{1/2} \rightarrow 3^2S_{1/2}$. From Equation 7-72 we compute the Landé g factors to use in computing the ΔE values from Equation 7-71 as follows:

For the $3^2P_{1/2}$ level:

$$g = 1 + \frac{1/2(1/2 + 1) + 1/2(1/2 + 1) - 1(1 + 1)}{(2)(1/2)(1/2 + 1)} = 2/3$$

For the $3^2S_{1/2}$ level:

$$g = 1 + \frac{1/2(1/2 + 1) + 1/2(1/2 + 1) - 0}{(2)(1/2)(1/2 + 1)} = 2$$

and from Equation 7-71,

For the $3^2P_{1/2}$ level:

$$\Delta E = (2/3)(\pm 1/2)(5.79 \times 10^{-9} \text{ eV/gauss})B$$

For the $3^2S_{1/2}$ level:

$$\Delta E = (2)(\pm 1/2)(5.79 \times 10^{-9} \text{ eV/gauss})B$$

The longest-wavelength line ($m_j = -\frac{1}{2} \rightarrow m_j = +\frac{1}{2}$) will have undergone a net energy shift of

$$-1.93 \times 10^{-9} B - 5.79 \times 10^{-9} B = -7.72 \times 10^{-9} B \text{ eV}$$

The shortest-wavelength line ($m_j = +\frac{1}{2} \rightarrow m_j = -\frac{1}{2}$) will have undergone a net energy shift of

$$1.93 \times 10^{-9} B + 5.79 \times 10^{-9} B = 7.72 \times 10^{-9} B \text{ eV}$$

The total energy difference between these two photons is

$$\Delta E = -1.54 \times 10^{-8} B \text{ eV}$$

Since $\lambda = c/f = hc/E$, then $\Delta\lambda = -(hc/E^2)\Delta E = 0.022 \text{ nm}$. We then have that

$$\Delta E = -0.022 \text{ nm}(E^2/hc) = -1.54 \times 10^{-8} B$$

where $E = hc/\lambda = hc/(589.9 \text{ nm})$. Finally, we have

$$B = \frac{(0.022 \times 10^{-9} \text{ nm})hc}{(589.8 \times 10^{-9} \text{ nm})^2(1.54 \times 10^{-8} \text{ eV/T})(1.60 \times 10^{-19} \text{ J/eV})}$$

$$B = 0.51 \text{ T} = 5100 \text{ gauss}$$

For comparison, the Earth's magnetic field averages about 0.5 gauss.