

12.1 We showed in Chapter 7 that the Laplacian operator that represents the square of the momentum can be written in terms of the angular momentum as [see Eq. (7.71)]

$$p^2 \doteq (-i\hbar\nabla)^2 = -\hbar^2\nabla^2 = -\hbar^2 \left[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) - \frac{1}{\hbar^2 r^2} \mathbf{L}^2 \right]$$

Use this to find the commutator of  $p^2$  with the angular momentum operator  $\mathbf{L}^2$  is

$$\begin{aligned} [p^2, \mathbf{L}^2] &\doteq \left( -\hbar^2 \left[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) - \frac{1}{\hbar^2 r^2} \mathbf{L}^2 \right] \right) \mathbf{L}^2 \\ &\quad - \mathbf{L}^2 \left( -\hbar^2 \left[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) - \frac{1}{\hbar^2 r^2} \mathbf{L}^2 \right] \right) \\ &\doteq -\hbar^2 \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) \mathbf{L}^2 + \hbar^2 \mathbf{L}^2 \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) \end{aligned}$$

$\mathbf{L}^2$  has derivatives only with respect to angular variables, so its order with respect to radial variables can be changed, giving

$$[p^2, \mathbf{L}^2] \doteq -\hbar^2 \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) \mathbf{L}^2 + \hbar^2 \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) \mathbf{L}^2 = 0,$$

so they commute. Similarly, the commutator of  $p^2$  with the angular momentum component operator  $L_z$  is (use  $[\mathbf{L}^2, L_z] = 0$ )

$$\begin{aligned} [p^2, L_z] &\doteq \left( -\hbar^2 \left[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) - \frac{1}{\hbar^2 r^2} \mathbf{L}^2 \right] \right) L_z \\ &\quad - L_z \left( -\hbar^2 \left[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) - \frac{1}{\hbar^2 r^2} \mathbf{L}^2 \right] \right) \\ &\doteq -\hbar^2 \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) L_z + L_z \hbar^2 \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) \end{aligned}$$

$L_z$  has derivatives with respect to angular variables only ( $\phi$ ), so it's order with respect to radial variables can be changed, giving

$$[p^2, L_z] \doteq -\hbar^2 \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) L_z + \hbar^2 \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) L_z = 0$$

so they commute. Now we know that

$$\begin{aligned} [p^2, \mathbf{L}^2] &= 0 \\ [p^2, L_z] &= 0 \end{aligned}$$

Use these to find the commutators with  $p^4$ :

$$\begin{aligned} [p^4, \mathbf{L}^2] &= p^4 \mathbf{L}^2 - \mathbf{L}^2 p^4 = p^2 p^2 \mathbf{L}^2 - \mathbf{L}^2 p^2 p^2 = p^2 \mathbf{L}^2 p^2 - \mathbf{L}^2 p^2 p^2 = \mathbf{L}^2 p^2 p^2 - \mathbf{L}^2 p^2 p^2 = 0 \\ [p^4, L_z] &= p^4 L_z - L_z p^4 = p^2 p^2 L_z - L_z p^2 p^2 = p^2 L_z p^2 - L_z p^2 p^2 = L_z p^2 p^2 - L_z p^2 p^2 = 0 \end{aligned}$$


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12.2  $\mathbf{L} \cdot \mathbf{S}$  is diagonal in the coupled basis because the operators  $\mathbf{J}^2$ ,  $\mathbf{L}^2$ , and  $\mathbf{S}^2$  are diagonal in the coupled basis. The  $n=2$  state has 8 states. Using Eq. (12.39)

$$\mathbf{L} \cdot \mathbf{S} = \frac{1}{2} (\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2),$$

we arrive at the diagonal 8x8 matrix

$$\mathbf{L} \cdot \mathbf{S} \doteq \left( \begin{array}{cccccccc} \hbar^2/2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \hbar^2/2 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \hbar^2/2 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \hbar^2/2 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1\hbar^2 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1\hbar^2 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0\hbar^2 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0\hbar^2 \end{array} \right) \begin{array}{l} 1, \frac{1}{2}, \frac{3}{2}, \frac{3}{2} \\ 1, \frac{1}{2}, \frac{3}{2}, \frac{1}{2} \\ 1, \frac{1}{2}, \frac{3}{2}, \frac{-1}{2} \\ 1, \frac{1}{2}, \frac{3}{2}, \frac{-3}{2} \\ 1, \frac{1}{2}, \frac{1}{2}, \frac{1}{2} \\ 1, \frac{1}{2}, \frac{1}{2}, \frac{-1}{2} \\ 0, \frac{1}{2}, \frac{1}{2}, \frac{1}{2} \\ 0, \frac{1}{2}, \frac{1}{2}, \frac{-1}{2} \end{array}$$

where we label the rows with  $\ell s j m_j$ .

$\mathbf{L} \cdot \mathbf{S}$  is not diagonal in the uncoupled basis because the angular momentum ladder operators connect adjacent states, just as we found for the  $\mathbf{S} \cdot \mathbf{I}$  matrix in Eq. (11.38) for the hyperfine structure calculation. Use Eq. (12.40):

$$\mathbf{L} \cdot \mathbf{S} = \frac{1}{2} (L_+ S_- + L_- S_+) + L_z S_z$$

The ladder operator matrices are found using Eq. (11.23):

$$J_{\pm} |j, m_j\rangle = \hbar [j(j+1) - m_j(m_j \pm 1)]^{1/2} |j, m_j \pm 1\rangle.$$

For example, the matrix elements of  $L_+$  are:

$$\begin{aligned} \langle n \ell s m'_\ell m'_s | L_+ | n \ell s m_\ell m_s \rangle &= \langle n \ell s m'_\ell m'_s | \hbar [\ell(\ell+1) - m_\ell(m_\ell + 1)]^{1/2} | n \ell s, m_\ell + 1, m_s \rangle \\ &= \hbar [\ell(\ell+1) - m_\ell(m_\ell + 1)]^{1/2} \langle n \ell s m'_\ell m'_s | n \ell s, m_\ell + 1, m_s \rangle \\ &= \hbar [\ell(\ell+1) - m_\ell(m_\ell + 1)]^{1/2} \delta_{m'_\ell, m_\ell + 1} \delta_{m'_s, m_s} \end{aligned}$$

Thus the matrix representation of  $L_+$  in the uncoupled basis is:

$$L_+ \doteq \begin{pmatrix} 0 & 0 & \sqrt{2}\hbar & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \sqrt{2}\hbar & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \sqrt{2}\hbar & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \sqrt{2}\hbar & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \begin{array}{l} 1, \frac{1}{2}, 1, \frac{1}{2} \\ 1, \frac{1}{2}, 1, -\frac{1}{2} \\ 1, \frac{1}{2}, 0, \frac{1}{2} \\ 1, \frac{1}{2}, 0, -\frac{1}{2} \\ 1, \frac{1}{2}, -1, \frac{1}{2} \\ 1, \frac{1}{2}, -1, -\frac{1}{2} \\ 0, \frac{1}{2}, 0, \frac{1}{2} \\ 0, \frac{1}{2}, 0, -\frac{1}{2} \end{array}$$

where we label the rows with  $\ell s m_\ell m_s$ . Likewise, the matrix representation of  $L_-$  in the uncoupled basis is:

$$L_- \doteq \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ \sqrt{2}\hbar & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \sqrt{2}\hbar & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \sqrt{2}\hbar & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \sqrt{2}\hbar & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \begin{array}{l} 1, \frac{1}{2}, 1, \frac{1}{2} \\ 1, \frac{1}{2}, 1, -\frac{1}{2} \\ 1, \frac{1}{2}, 0, \frac{1}{2} \\ 1, \frac{1}{2}, 0, -\frac{1}{2} \\ 1, \frac{1}{2}, -1, \frac{1}{2} \\ 1, \frac{1}{2}, -1, -\frac{1}{2} \\ 0, \frac{1}{2}, 0, \frac{1}{2} \\ 0, \frac{1}{2}, 0, -\frac{1}{2} \end{array}$$

The matrix representations of  $S_+$  and  $S_-$  in the uncoupled basis are:

$$S_+ \doteq \begin{pmatrix} 0 & \hbar & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \hbar & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \hbar & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & \hbar \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \begin{array}{l} 1, \frac{1}{2}, 1, \frac{1}{2} \\ 1, \frac{1}{2}, 1, -\frac{1}{2} \\ 1, \frac{1}{2}, 0, \frac{1}{2} \\ 1, \frac{1}{2}, 0, -\frac{1}{2} \\ 1, \frac{1}{2}, -1, \frac{1}{2} \\ 1, \frac{1}{2}, -1, -\frac{1}{2} \\ 0, \frac{1}{2}, 0, \frac{1}{2} \\ 0, \frac{1}{2}, 0, -\frac{1}{2} \end{array}$$

$$S_- \doteq \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ \hbar & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \hbar & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \hbar & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \hbar & 0 & 0 \end{pmatrix} \begin{array}{l} 1, \frac{1}{2}, 1, \frac{1}{2} \\ 1, \frac{1}{2}, 1, -\frac{1}{2} \\ 1, \frac{1}{2}, 0, \frac{1}{2} \\ 1, \frac{1}{2}, 0, -\frac{1}{2} \\ 1, \frac{1}{2}, -1, \frac{1}{2} \\ 1, \frac{1}{2}, -1, -\frac{1}{2} \\ 0, \frac{1}{2}, 0, \frac{1}{2} \\ 0, \frac{1}{2}, 0, -\frac{1}{2} \end{array}$$

The  $z$ -component matrices are obtained by inspection of the eigenvalue equations:

$$L_z \doteq \begin{pmatrix} \hbar & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \hbar & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -\hbar & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -\hbar & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \begin{array}{l} 1, \frac{1}{2}, 1, \frac{1}{2} \\ 1, \frac{1}{2}, 1, -\frac{1}{2} \\ 1, \frac{1}{2}, 0, \frac{1}{2} \\ 1, \frac{1}{2}, 0, -\frac{1}{2} \\ 1, \frac{1}{2}, -1, \frac{1}{2} \\ 1, \frac{1}{2}, -1, -\frac{1}{2} \\ 0, \frac{1}{2}, 0, \frac{1}{2} \\ 0, \frac{1}{2}, 0, -\frac{1}{2} \end{array}$$
  

$$S_z \doteq \begin{pmatrix} \hbar/2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -\hbar/2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \hbar/2 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\hbar/2 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \hbar/2 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -\hbar/2 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \hbar/2 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\hbar/2 & 0 \end{pmatrix} \begin{array}{l} 1, \frac{1}{2}, 1, \frac{1}{2} \\ 1, \frac{1}{2}, 1, -\frac{1}{2} \\ 1, \frac{1}{2}, 0, \frac{1}{2} \\ 1, \frac{1}{2}, 0, -\frac{1}{2} \\ 1, \frac{1}{2}, -1, \frac{1}{2} \\ 1, \frac{1}{2}, -1, -\frac{1}{2} \\ 0, \frac{1}{2}, 0, \frac{1}{2} \\ 0, \frac{1}{2}, 0, -\frac{1}{2} \end{array}$$

Substituting into  $\mathbf{L} \cdot \mathbf{S} = \frac{1}{2}(L_+ S_- + L_- S_+) + L_z S_z$ , we obtain the result

$$\mathbf{L} \cdot \mathbf{S} \doteq \begin{pmatrix} \hbar^2/2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -\hbar^2/2 & \hbar^2/\sqrt{2} & 0 & 0 & 0 & 0 & 0 \\ 0 & \hbar^2/\sqrt{2} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \hbar^2/\sqrt{2} & 0 & 0 & 0 \\ 0 & 0 & 0 & \hbar^2/\sqrt{2} & -\hbar^2/2 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \hbar^2/2 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \begin{array}{l} 1, \frac{1}{2}, 1, \frac{1}{2} \\ 1, \frac{1}{2}, 1, \frac{-1}{2} \\ 1, \frac{1}{2}, 0, \frac{1}{2} \\ 1, \frac{1}{2}, 0, \frac{-1}{2} \\ 1, \frac{1}{2}, -1, \frac{1}{2} \\ 1, \frac{1}{2}, -1, \frac{-1}{2} \\ 0, \frac{1}{2}, 0, \frac{1}{2} \\ 0, \frac{1}{2}, 0, \frac{-1}{2} \end{array}$$


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12.3 Start with the results in the text [Eqs. (12.30) and (12.46)]

$$\begin{aligned} E_{fs}^{(1)} &= E_{rel}^{(1)} + E_{SO}^{(1)} \\ &= \frac{1}{4} \alpha^4 m c^2 \frac{j(j+1) - \ell(\ell+1) - \frac{3}{4}}{n^3 \ell(\ell + \frac{1}{2})(\ell+1)} - \frac{1}{2} \alpha^4 m c^2 \left[ \frac{1}{n^3 (\ell + \frac{1}{2})} - \frac{3}{4n^4} \right] \\ &= \frac{1}{4} \alpha^4 m c^2 \left\{ \frac{j(j+1) - \ell(\ell+1) - \frac{3}{4}}{n^3 \ell(\ell + \frac{1}{2})(\ell+1)} - \frac{2}{n^3 (\ell + \frac{1}{2})} + \frac{3}{2n^4} \right\} \end{aligned}$$

Now treat the two possible cases  $j = \ell \pm 1/2$  separately. First,  $j = \ell + 1/2$ , so  $\ell = j - 1/2$ :

$$\begin{aligned} E_{fs}^{(1)} &= \frac{1}{4} \alpha^4 m c^2 \left\{ \frac{j(j+1) - (j - \frac{1}{2})(j + \frac{1}{2}) - \frac{3}{4}}{n^3 (j - \frac{1}{2}) j (j + \frac{1}{2})} - \frac{2}{n^3 j} + \frac{3}{2n^4} \right\} \\ &= \frac{1}{4} \alpha^4 m c^2 \left\{ \frac{(j - \frac{1}{2})}{n^3 (j - \frac{1}{2}) j (j + \frac{1}{2})} - \frac{2}{n^3 j} + \frac{3}{2n^4} \right\} \\ &= \frac{1}{4} \alpha^4 m c^2 \left\{ \frac{1 - 2(j + \frac{1}{2})}{n^3 j (j + \frac{1}{2})} + \frac{3}{2n^4} \right\} = \frac{1}{4} \alpha^4 m c^2 \left\{ \frac{-2j}{n^3 j (j + \frac{1}{2})} + \frac{3}{2n^4} \right\} \\ &= -\frac{1}{2} \alpha^4 m c^2 \frac{1}{n^3} \left\{ \frac{1}{j + \frac{1}{2}} - \frac{3}{4n} \right\} \end{aligned}$$

Next, consider  $j = \ell - 1/2$ , so  $\ell = j + 1/2$ :

$$\begin{aligned}
 E_{fs}^{(1)} &= \frac{1}{4} \alpha^4 mc^2 \left\{ \frac{j(j+1) - (j+\frac{1}{2})(j+\frac{3}{2}) - \frac{3}{4}}{n^3(j+\frac{1}{2})(j+1)(j+\frac{3}{2})} - \frac{2}{n^3(j+1)} + \frac{3}{2n^4} \right\} \\
 &= \frac{1}{4} \alpha^4 mc^2 \left\{ \frac{(-j-\frac{3}{2})}{n^3(j+\frac{1}{2})(j+1)(j+\frac{3}{2})} - \frac{2}{n^3(j+1)} + \frac{3}{2n^4} \right\} \\
 &= \frac{1}{4} \alpha^4 mc^2 \left\{ \frac{-1 - 2(j+\frac{1}{2})}{n^3(j+\frac{1}{2})(j+1)} + \frac{3}{2n^4} \right\} = \frac{1}{4} \alpha^4 mc^2 \left\{ \frac{(-2j-2)}{n^3(j+\frac{1}{2})(j+1)} + \frac{3}{2n^4} \right\} \\
 &= -\frac{1}{2} \alpha^4 mc^2 \frac{1}{n^3} \left\{ \frac{1}{j+\frac{1}{2}} - \frac{3}{4n} \right\}
 \end{aligned}$$

Both cases give the same result, with no divergence.

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12.4 The Zeeman perturbation Hamiltonian is

$$H'_Z = -\mu \cdot \mathbf{B} = \frac{\mu_B}{\hbar} (g_\ell \mathbf{L} + g_e \mathbf{S}) \cdot \mathbf{B} = \frac{\mu_B B}{\hbar} (g_\ell L_z + g_e S_z)$$

The uncoupled basis states  $|n\ell sm_\ell m_s\rangle$  are eigenstates of the commuting operators  $H_0$ ,  $\mathbf{L}^2$ ,  $\mathbf{S}^2$ ,  $L_z$ , and  $S_z$  while the coupled basis states  $|n\ell sjm_j\rangle$  are eigenstates of the commuting operators  $H_0$ ,  $\mathbf{L}^2$ ,  $\mathbf{S}^2$ ,  $\mathbf{J}^2$ , and  $J_z$ . Operators are always diagonal when represented in their own bases, so  $H_0$ ,  $\mathbf{L}^2$ ,  $\mathbf{S}^2$ ,  $L_z$ , and  $S_z$  are diagonal in the uncoupled basis states  $|n\ell sm_\ell m_s\rangle$ , while  $H_0$ ,  $\mathbf{L}^2$ ,  $\mathbf{S}^2$ ,  $\mathbf{J}^2$ , and  $J_z$  are diagonal in the coupled basis states  $|n\ell sjm_j\rangle$ . The Zeeman perturbation Hamiltonian includes the operators  $L_z$  and  $S_z$ , so it is diagonal in the uncoupled basis states  $|n\ell sm_\ell m_s\rangle$ , but not in the coupled basis states  $|n\ell sjm_j\rangle$ . So the short answer is that the Zeeman perturbation Hamiltonian is diagonal in the uncoupled basis because those basis states are eigenstates of the same operators comprising the Zeeman perturbation.

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12.5 For the hydrogen  $2p$  states  $n=2$ ,  $\ell=1$ , and  $s=1/2$ . The uncoupled basis  $|n\ell sm_\ell m_s\rangle$  comprises six states:

$$|21\frac{1}{2}1\frac{1}{2}\rangle, |21\frac{1}{2}1\frac{-1}{2}\rangle, |21\frac{1}{2}0\frac{1}{2}\rangle, |21\frac{1}{2}0\frac{-1}{2}\rangle, |21\frac{1}{2}, -1\frac{1}{2}\rangle, |21\frac{1}{2}, -1\frac{-1}{2}\rangle$$

The eigenvalue equations for  $L_z$  and  $S_z$  are

$$\begin{aligned}
 L_z |n\ell sm_\ell m_s\rangle &= m_\ell \hbar |n\ell sm_\ell m_s\rangle \\
 S_z |n\ell sm_\ell m_s\rangle &= m_s \hbar |n\ell sm_\ell m_s\rangle
 \end{aligned}$$

Find the matrix elements of  $L_z$  using the eigenvalue equation:

$$\begin{aligned}
 \langle n\ell sm'_\ell m'_s | L_z | n\ell sm_\ell m_s \rangle &= \langle n\ell sm'_\ell m'_s | m_\ell \hbar | n\ell sm_\ell m_s \rangle = m_\ell \hbar \langle n\ell sm'_\ell m'_s | n\ell sm_\ell m_s \rangle \\
 &= m_\ell \hbar \delta_{m_\ell m'_\ell} \delta_{m_s m'_s}
 \end{aligned}$$

The Kronecker deltas ensure that the  $L_z$  matrix is diagonal in the uncoupled basis:

$$L_z \doteq \begin{pmatrix} \hbar & 0 & 0 & 0 & 0 & 0 \\ 0 & \hbar & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -\hbar & 0 \\ 0 & 0 & 0 & 0 & 0 & -\hbar \end{pmatrix} \begin{array}{l} 1, \frac{1}{2}, 1, \frac{1}{2} \\ 1, \frac{1}{2}, 1, -\frac{1}{2} \\ 1, \frac{1}{2}, 0, \frac{1}{2} \\ 1, \frac{1}{2}, 0, -\frac{1}{2} \\ 1, \frac{1}{2}, -1, \frac{1}{2} \\ 1, \frac{1}{2}, -1, -\frac{1}{2} \end{array}$$

Where we label the rows with  $\ell s m_\ell m_s$ . Now find the matrix elements of  $S_z$ :

$$\begin{aligned} \langle n \ell s m'_\ell m'_s | S_z | n \ell s m_\ell m_s \rangle &= \langle n \ell s m'_\ell m'_s | m_s \hbar | n \ell s m_\ell m_s \rangle = m_s \hbar \langle n \ell s m'_\ell m'_s | n \ell s m_\ell m_s \rangle \\ &= m_s \hbar \delta_{m_\ell m'_\ell} \delta_{m_s m'_s} \end{aligned}$$

The Kronecker deltas ensure that the  $S_z$  is also diagonal:

$$S_z \doteq \begin{pmatrix} \hbar/2 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -\hbar/2 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \hbar/2 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\hbar/2 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \hbar/2 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -\hbar/2 & 0 \end{pmatrix} \begin{array}{l} 1, \frac{1}{2}, 1, \frac{1}{2} \\ 1, \frac{1}{2}, 1, -\frac{1}{2} \\ 1, \frac{1}{2}, 0, \frac{1}{2} \\ 1, \frac{1}{2}, 0, -\frac{1}{2} \\ 1, \frac{1}{2}, -1, \frac{1}{2} \\ 1, \frac{1}{2}, -1, -\frac{1}{2} \end{array}$$


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12.6 From Problem 12.5 (or by inspection of the eigenvalue equations), we know the matrix elements of  $L_z$  and  $S_z$  in the uncoupled basis:

$$\begin{aligned} \langle n \ell s m'_\ell m'_s | L_z | n \ell s m_\ell m_s \rangle &= m_\ell \hbar \delta_{m_\ell m'_\ell} \delta_{m_s m'_s} \\ \langle n \ell s m'_\ell m'_s | S_z | n \ell s m_\ell m_s \rangle &= m_s \hbar \delta_{m_\ell m'_\ell} \delta_{m_s m'_s} \end{aligned}$$

The Clebsch-Gordan coefficients in Table 11.3 give us the coupled basis states in terms of the uncoupled basis states

$$\begin{aligned} \left| \frac{3}{2} \frac{3}{2} \right\rangle &= \left| 1 \frac{1}{2} 1 \frac{1}{2} \right\rangle \\ \left| \frac{3}{2} \frac{1}{2} \right\rangle &= \frac{1}{\sqrt{3}} \left| 1 \frac{1}{2} 1 \frac{-1}{2} \right\rangle + \sqrt{\frac{2}{3}} \left| 1 \frac{1}{2} 0 \frac{1}{2} \right\rangle \\ \left| \frac{3}{2} \frac{-1}{2} \right\rangle &= \sqrt{\frac{2}{3}} \left| 1 \frac{1}{2} 0 \frac{-1}{2} \right\rangle + \frac{1}{\sqrt{3}} \left| 1 \frac{1}{2}, -1 \frac{1}{2} \right\rangle \\ \left| \frac{3}{2} \frac{-3}{2} \right\rangle &= \left| 1 \frac{1}{2}, -1 \frac{-1}{2} \right\rangle \\ \left| \frac{1}{2} \frac{1}{2} \right\rangle &= \sqrt{\frac{2}{3}} \left| 1 \frac{1}{2} 1 \frac{-1}{2} \right\rangle - \frac{1}{\sqrt{3}} \left| 1 \frac{1}{2} 0 \frac{1}{2} \right\rangle \\ \left| \frac{1}{2} \frac{-1}{2} \right\rangle &= \frac{1}{\sqrt{3}} \left| 1 \frac{1}{2} 0 \frac{-1}{2} \right\rangle - \sqrt{\frac{2}{3}} \left| 1 \frac{1}{2}, -1 \frac{1}{2} \right\rangle \end{aligned}$$

Using these expansions, we calculate the matrix elements of  $L_z$  in the coupled basis in terms of uncoupled-basis matrix elements. For example,

$$\langle \frac{3}{2} \frac{3}{2} | L_z | \frac{3}{2} \frac{3}{2} \rangle = \langle 1 \frac{1}{2} 1 \frac{1}{2} | L_z | 1 \frac{1}{2} 1 \frac{1}{2} \rangle = \hbar \langle 1 \frac{1}{2} 1 \frac{1}{2} | 1 \frac{1}{2} 1 \frac{1}{2} \rangle = \hbar .$$

The other diagonal terms are:

$$\begin{aligned}\langle \frac{3}{2} \frac{1}{2} | L_z | \frac{3}{2} \frac{1}{2} \rangle &= \left( \frac{1}{\sqrt{3}} \langle 1 \frac{1}{2} 1 \frac{-1}{2} | + \sqrt{\frac{2}{3}} \langle 1 \frac{1}{2} 0 \frac{1}{2} | \right) L_z \left( \frac{1}{\sqrt{3}} | 1 \frac{1}{2} 1 \frac{-1}{2} \rangle + \sqrt{\frac{2}{3}} | 1 \frac{1}{2} 0 \frac{1}{2} \rangle \right) = \frac{1}{3} 1 \hbar + \frac{2}{3} 0 \hbar = \frac{1}{3} \hbar \\ \langle \frac{3}{2} \frac{-1}{2} | L_z | \frac{3}{2} \frac{-1}{2} \rangle &= \left( \sqrt{\frac{2}{3}} \langle 1 \frac{1}{2} 0 \frac{-1}{2} | + \frac{1}{\sqrt{3}} \langle 1 \frac{1}{2}, -1 \frac{1}{2} | \right) L_z \left( \sqrt{\frac{2}{3}} | 1 \frac{1}{2} 0 \frac{-1}{2} \rangle + \frac{1}{\sqrt{3}} | 1 \frac{1}{2}, -1 \frac{1}{2} \rangle \right) = \frac{-1}{3} \hbar \\ \langle \frac{3}{2} \frac{-3}{2} | L_z | \frac{3}{2} \frac{-3}{2} \rangle &= (\langle 1 \frac{1}{2}, -1 \frac{-1}{2} |) L_z (\langle 1 \frac{1}{2}, -1 \frac{-1}{2} |) = -\hbar \\ \langle \frac{1}{2} \frac{1}{2} | L_z | \frac{1}{2} \frac{1}{2} \rangle &= \left( \sqrt{\frac{2}{3}} \langle 1 \frac{1}{2} 1 \frac{-1}{2} | - \frac{1}{\sqrt{3}} \langle 1 \frac{1}{2} 0 \frac{1}{2} | \right) L_z \left( \sqrt{\frac{2}{3}} | 1 \frac{1}{2} 1 \frac{-1}{2} \rangle - \frac{1}{\sqrt{3}} | 1 \frac{1}{2} 0 \frac{1}{2} \rangle \right) = \frac{2}{3} \hbar \\ \langle \frac{1}{2} \frac{-1}{2} | L_z | \frac{1}{2} \frac{-1}{2} \rangle &= \left( \frac{1}{\sqrt{3}} \langle 1 \frac{1}{2} 0 \frac{-1}{2} | - \sqrt{\frac{2}{3}} \langle 1 \frac{1}{2}, -1 \frac{1}{2} | \right) L_z \left( \frac{1}{\sqrt{3}} | 1 \frac{1}{2} 0 \frac{-1}{2} \rangle - \sqrt{\frac{2}{3}} | 1 \frac{1}{2}, -1 \frac{1}{2} \rangle \right) = \frac{-2}{3} \hbar\end{aligned}$$

Likewise, we calculate all the non-zero off-diagonal elements:

$$\begin{aligned}\langle \frac{3}{2} \frac{1}{2} | L_z | \frac{1}{2} \frac{1}{2} \rangle &= \left( \frac{1}{\sqrt{3}} \langle 1 \frac{1}{2} 1 \frac{-1}{2} | + \sqrt{\frac{2}{3}} \langle 1 \frac{1}{2} 0 \frac{1}{2} | \right) L_z \left( \sqrt{\frac{2}{3}} | 1 \frac{1}{2} 1 \frac{-1}{2} \rangle - \frac{1}{\sqrt{3}} | 1 \frac{1}{2} 0 \frac{1}{2} \rangle \right) = \frac{\sqrt{2}}{3} \hbar \\ \langle \frac{3}{2} \frac{-1}{2} | L_z | \frac{1}{2} \frac{-1}{2} \rangle &= \left( \sqrt{\frac{2}{3}} \langle 1 \frac{1}{2} 0 \frac{-1}{2} | + \frac{1}{\sqrt{3}} \langle 1 \frac{1}{2}, -1 \frac{1}{2} | \right) L_z \left( \frac{1}{\sqrt{3}} | 1 \frac{1}{2} 0 \frac{-1}{2} \rangle - \sqrt{\frac{2}{3}} | 1 \frac{1}{2}, -1 \frac{1}{2} \rangle \right) = \frac{\sqrt{2}}{3} \hbar\end{aligned}$$

plus the Hermitian conjugates of these. The  $L_z$  matrix is thus

$$L_z \doteq \begin{pmatrix} \hbar & 0 & 0 & 0 & 0 & 0 & \frac{3}{2}, \frac{3}{2} \\ 0 & \frac{1}{3} \hbar & 0 & 0 & \frac{\sqrt{2}}{3} \hbar & 0 & \frac{3}{2}, \frac{1}{2} \\ 0 & 0 & \frac{-1}{3} \hbar & 0 & 0 & \frac{\sqrt{2}}{3} \hbar & \frac{3}{2}, \frac{-1}{2} \\ 0 & 0 & 0 & -\hbar & 0 & 0 & \frac{3}{2}, \frac{-3}{2} \\ 0 & \frac{\sqrt{2}}{3} \hbar & 0 & 0 & \frac{2}{3} \hbar & 0 & \frac{1}{2}, \frac{1}{2} \\ 0 & 0 & \frac{\sqrt{2}}{3} \hbar & 0 & 0 & \frac{-2}{3} \hbar & \frac{1}{2}, \frac{-1}{2} \end{pmatrix}$$

Now calculate the matrix elements of  $S_z$  in the coupled basis in terms of uncoupled-basis matrix elements. For example

$$\langle \frac{3}{2} \frac{3}{2} | S_z | \frac{3}{2} \frac{3}{2} \rangle = \langle 1 \frac{1}{2} 1 \frac{1}{2} | S_z | 1 \frac{1}{2} 1 \frac{1}{2} \rangle = \frac{1}{2} \hbar \langle 1 \frac{1}{2} 1 \frac{1}{2} | 1 \frac{1}{2} 1 \frac{1}{2} \rangle = \frac{1}{2} \hbar$$

The other diagonal terms are:

$$\begin{aligned}\langle \frac{3}{2} \frac{1}{2} | S_z | \frac{3}{2} \frac{1}{2} \rangle &= \left( \frac{1}{\sqrt{3}} \langle 1 \frac{1}{2} 1 \frac{-1}{2} | + \sqrt{\frac{2}{3}} \langle 1 \frac{1}{2} 0 \frac{1}{2} | \right) S_z \left( \frac{1}{\sqrt{3}} | 1 \frac{1}{2} 1 \frac{-1}{2} \rangle + \sqrt{\frac{2}{3}} | 1 \frac{1}{2} 0 \frac{1}{2} \rangle \right) = \frac{1}{3} \left( \frac{-1}{2} \hbar \right) + \frac{2}{3} \left( \frac{1}{2} \hbar \right) = \frac{1}{6} \hbar \\ \langle \frac{3}{2} \frac{-1}{2} | S_z | \frac{3}{2} \frac{-1}{2} \rangle &= \left( \sqrt{\frac{2}{3}} \langle 1 \frac{1}{2} 0 \frac{-1}{2} | + \frac{1}{\sqrt{3}} \langle 1 \frac{1}{2}, -1 \frac{1}{2} | \right) S_z \left( \sqrt{\frac{2}{3}} | 1 \frac{1}{2} 0 \frac{-1}{2} \rangle + \frac{1}{\sqrt{3}} | 1 \frac{1}{2}, -1 \frac{1}{2} \rangle \right) = \frac{-1}{6} \hbar \\ \langle \frac{3}{2} \frac{-3}{2} | S_z | \frac{3}{2} \frac{-3}{2} \rangle &= (\langle 1 \frac{1}{2}, -1 \frac{-1}{2} |) S_z (\langle 1 \frac{1}{2}, -1 \frac{-1}{2} |) = \frac{-1}{2} \hbar \\ \langle \frac{1}{2} \frac{1}{2} | S_z | \frac{1}{2} \frac{1}{2} \rangle &= \left( \sqrt{\frac{2}{3}} \langle 1 \frac{1}{2} 1 \frac{-1}{2} | - \frac{1}{\sqrt{3}} \langle 1 \frac{1}{2} 0 \frac{1}{2} | \right) S_z \left( \sqrt{\frac{2}{3}} | 1 \frac{1}{2} 1 \frac{-1}{2} \rangle - \frac{1}{\sqrt{3}} | 1 \frac{1}{2} 0 \frac{1}{2} \rangle \right) = \frac{-1}{6} \hbar \\ \langle \frac{1}{2} \frac{-1}{2} | S_z | \frac{1}{2} \frac{-1}{2} \rangle &= \left( \frac{1}{\sqrt{3}} \langle 1 \frac{1}{2} 0 \frac{-1}{2} | - \sqrt{\frac{2}{3}} \langle 1 \frac{1}{2}, -1 \frac{1}{2} | \right) S_z \left( \frac{1}{\sqrt{3}} | 1 \frac{1}{2} 0 \frac{-1}{2} \rangle - \sqrt{\frac{2}{3}} | 1 \frac{1}{2}, -1 \frac{1}{2} \rangle \right) = \frac{1}{6} \hbar\end{aligned}$$

Likewise, we calculate all the non-zero off-diagonal elements:

$$\begin{aligned}\langle \frac{3}{2} \frac{1}{2} | S_z | \frac{1}{2} \frac{1}{2} \rangle &= \left( \frac{1}{\sqrt{3}} \langle 1 \frac{1}{2} 1 \frac{-1}{2} | + \sqrt{\frac{2}{3}} \langle 1 \frac{1}{2} 0 \frac{1}{2} | \right) S_z \left( \sqrt{\frac{2}{3}} | 1 \frac{1}{2} 1 \frac{-1}{2} \rangle - \frac{1}{\sqrt{3}} | 1 \frac{1}{2} 0 \frac{1}{2} \rangle \right) = \frac{-\sqrt{2}}{3} \hbar \\ \langle \frac{3}{2} \frac{-1}{2} | S_z | \frac{1}{2} \frac{-1}{2} \rangle &= \left( \sqrt{\frac{2}{3}} \langle 1 \frac{1}{2} 0 \frac{-1}{2} | + \frac{1}{\sqrt{3}} \langle 1 \frac{1}{2}, -1 \frac{1}{2} | \right) S_z \left( \frac{1}{\sqrt{3}} | 1 \frac{1}{2} 0 \frac{-1}{2} \rangle - \sqrt{\frac{2}{3}} | 1 \frac{1}{2}, -1 \frac{1}{2} \rangle \right) = \frac{-\sqrt{2}}{3} \hbar\end{aligned}$$

plus the Hermitian conjugates of these. The  $S_z$  matrix is thus

$$S_z \doteq \begin{pmatrix} \frac{1}{2} \hbar & 0 & 0 & 0 & 0 & 0 & \frac{3}{2}, \frac{3}{2} \\ 0 & \frac{1}{6} \hbar & 0 & 0 & -\frac{\sqrt{2}}{3} \hbar & 0 & \frac{3}{2}, \frac{1}{2} \\ 0 & 0 & \frac{-1}{6} \hbar & 0 & 0 & -\frac{\sqrt{2}}{3} \hbar & \frac{3}{2}, \frac{-1}{2} \\ 0 & 0 & 0 & \frac{-1}{2} \hbar & 0 & 0 & \frac{3}{2}, \frac{-3}{2} \\ 0 & -\frac{\sqrt{2}}{3} \hbar & 0 & 0 & \frac{-1}{6} \hbar & 0 & \frac{1}{2}, \frac{1}{2} \\ 0 & 0 & -\frac{\sqrt{2}}{3} \hbar & 0 & 0 & \frac{1}{6} \hbar & \frac{1}{2}, \frac{-1}{2} \end{pmatrix}$$


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12.7 In Problem 12.6, we found the  $L_z$  and  $S_z$  operators in the coupled basis for the  $2p$  states. Now we must add in the  $2s$  states. For the  $2s$  states,  $\ell = 0$  and  $s = \frac{1}{2}$ , so  $j = \frac{1}{2}$  and the Clebsch-Gordan coefficients are trivial, giving

$$\begin{aligned}|\frac{1}{2} \frac{1}{2}\rangle &= |0 \frac{1}{2} 0 \frac{1}{2}\rangle \\ |\frac{1}{2} \frac{-1}{2}\rangle &= |0 \frac{1}{2} 0 \frac{-1}{2}\rangle\end{aligned}$$

Hence we get only diagonal matrix elements:

$$\begin{aligned}\langle \frac{1}{2} \frac{1}{2} | L_z | \frac{1}{2} \frac{1}{2} \rangle &= \langle 0 \frac{1}{2} 0 \frac{1}{2} | L_z | 0 \frac{1}{2} 0 \frac{1}{2} \rangle = 0 \hbar \\ \langle \frac{1}{2} \frac{-1}{2} | L_z | \frac{1}{2} \frac{-1}{2} \rangle &= \langle 0 \frac{1}{2} 0 \frac{-1}{2} | L_z | 0 \frac{1}{2} 0 \frac{-1}{2} \rangle = 0 \hbar \\ \langle \frac{1}{2} \frac{1}{2} | S_z | \frac{1}{2} \frac{1}{2} \rangle &= \langle 0 \frac{1}{2} 0 \frac{1}{2} | S_z | 0 \frac{1}{2} 0 \frac{1}{2} \rangle = \frac{1}{2} \hbar \\ \langle \frac{1}{2} \frac{-1}{2} | S_z | \frac{1}{2} \frac{-1}{2} \rangle &= \langle 0 \frac{1}{2} 0 \frac{-1}{2} | S_z | 0 \frac{1}{2} 0 \frac{-1}{2} \rangle = -\frac{1}{2} \hbar\end{aligned}$$

Adding these elements to the results from Problem 12.6 gives for the  $j = \frac{1}{2}$  states

$$L_z \doteq \begin{pmatrix} 0 & 0 & 0 & 0 & \frac{1}{2}, \frac{1}{2} & 2s \\ 0 & 0 & 0 & 0 & \frac{1}{2}, \frac{-1}{2} & 2s \\ 0 & 0 & \frac{2}{3} \hbar & 0 & \frac{1}{2}, \frac{1}{2} & 2p \\ 0 & 0 & 0 & \frac{-2}{3} \hbar & \frac{1}{2}, \frac{-1}{2} & 2p \end{pmatrix}$$

and

$$S_z \doteq \begin{pmatrix} \frac{1}{2}\hbar & 0 & 0 & 0 \\ 0 & -\frac{1}{2}\hbar & 0 & 0 \\ 0 & 0 & -\frac{1}{6}\hbar & 0 \\ 0 & 0 & 0 & \frac{1}{6}\hbar \end{pmatrix} \begin{array}{ll} \frac{1}{2}, \frac{1}{2} & 2s \\ \frac{1}{2}, -\frac{1}{2} & 2s \\ \frac{1}{2}, \frac{1}{2} & 2p \\ \frac{1}{2}, -\frac{1}{2} & 2p \end{array}$$

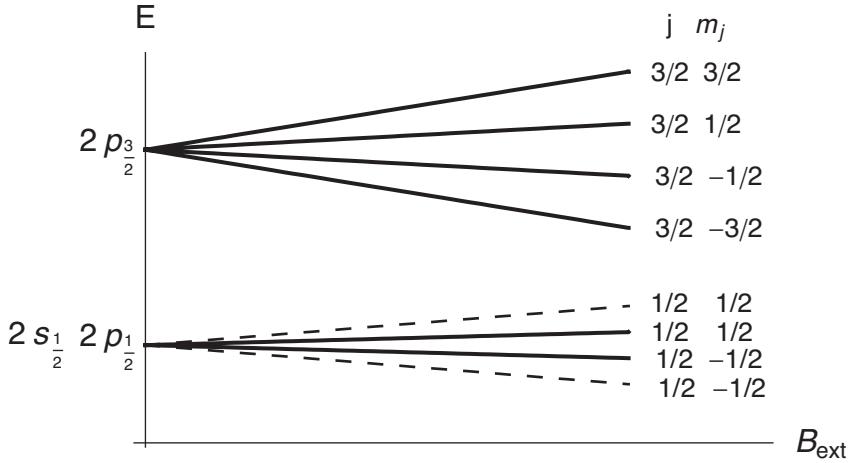
Which gives the Zeeman operator as

$$H'_Z = \frac{\mu_B B}{\hbar} (g_\ell L_z + g_e S_z) \doteq \mu_B B \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & \frac{1}{3} & 0 \\ 0 & 0 & 0 & -\frac{1}{3} \end{pmatrix} \begin{array}{ll} \frac{1}{2}, \frac{1}{2} & 2s \\ \frac{1}{2}, -\frac{1}{2} & 2s \\ \frac{1}{2}, \frac{1}{2} & 2p \\ \frac{1}{2}, -\frac{1}{2} & 2p \end{array}$$

using the gyromagnetic ratios:  $g_\ell = 1$ ,  $g_e = 2$ . There are no off-diagonal elements, so the energies are obtained by inspection

$$E_Z^{(1)} = \langle H'_Z \rangle = \langle n\ell s j m_j | H'_Z | n\ell s j m_j \rangle = \mu_B B, -\mu_B B, \frac{1}{3}\mu_B B, -\frac{1}{3}\mu_B B$$

in agreement with Eq. (12.78). The plot below shows all the  $n=2$  energies (see Fig. 12.8) with the new 2s levels shown as dashed lines.




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12.8 The spin-orbit interaction is not diagonal in the uncoupled basis because we can write  $\mathbf{L} \cdot \mathbf{S}$  as [see Eq. (12.40)]

$$\mathbf{L} \cdot \mathbf{S} = \frac{1}{2} (L_+ S_- + L_- S_+) + L_z S_z$$

and the angular momentum ladder operators connect adjacent states. An example of an off-diagonal element is

$$\begin{aligned} \langle n\ell s m'_\ell m'_s | L_+ S_- | n\ell s m_\ell m_s \rangle &= \langle n\ell s (m_\ell + 1)(m_s - 1) | L_+ S_- | n\ell s m_\ell m_s \rangle \\ \Rightarrow m'_\ell &= m_\ell + 1 \quad \text{and} \quad m'_s = m_s - 1 \end{aligned}$$

The Zeeman energies in a strong field are

$$\Delta E_{\text{Zeeman}} = \mu_B B (m_\ell + 2m_s)$$

so two states  $|n\ell sm_\ell m_s\rangle$  and  $|n\ell sm'_\ell m'\rangle$  are degenerate when

$$m_\ell + 2m_s = m'_\ell + 2m'_s$$

Using the values for the non-zero off-diagonal elements from above gives

$$m'_\ell + 2m'_s = m_\ell + 1 + 2(m_s - 1) = m_\ell + 2m_s - 1 \neq m_\ell + 2m_s$$

so that the non-zero off-diagonal matrix elements of  $\mathbf{L} \cdot \mathbf{S}$  do not coincide with the degenerate states of the Zeeman string field perturbation.

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12.9. In the coupled basis  $|n\ell sjm_j\rangle$ ,  $H'_{fs}$  is diagonal but  $H'_Z$  is not diagonal. The sum is [Eq. (12.87)]

$$H' \doteq \begin{pmatrix} -a+2b & 0 & 0 & 0 & 0 & 0 \\ 0 & -a+\frac{2}{3}b & 0 & 0 & \frac{-\sqrt{2}}{3}b & 0 \\ 0 & 0 & -a-\frac{2}{3}b & 0 & 0 & \frac{-\sqrt{2}}{3}b \\ 0 & 0 & 0 & -a-2b & 0 & 0 \\ 0 & \frac{-\sqrt{2}}{3}b & 0 & 0 & -5a+\frac{1}{3}b & 0 \\ 0 & 0 & \frac{-\sqrt{2}}{3}b & 0 & 0 & -5a-\frac{1}{3}b \end{pmatrix} \begin{matrix} \frac{3}{2}, \frac{3}{2} \\ \frac{3}{2}, \frac{1}{2} \\ \frac{3}{2}, \frac{-1}{2} \\ \frac{3}{2}, \frac{-3}{2} \\ \frac{1}{2}, \frac{1}{2} \\ \frac{1}{2}, \frac{-1}{2} \end{matrix}$$

where we define

$$a = \frac{1}{128} \alpha^4 mc^2$$

$$b = \mu_B B$$

To diagonalize, it is useful to reorder the rows and columns to make the matrix block diagonal:

$$H' \doteq \begin{pmatrix} -a+2b & 0 & 0 & 0 & 0 & 0 \\ 0 & -a-2b & 0 & 0 & 0 & 0 \\ 0 & 0 & -a+\frac{2}{3}b & \frac{-\sqrt{2}}{3}b & 0 & 0 \\ 0 & 0 & \frac{-\sqrt{2}}{3}b & -5a+\frac{1}{3}b & 0 & 0 \\ 0 & 0 & 0 & 0 & -a-\frac{2}{3}b & \frac{-\sqrt{2}}{3}b \\ 0 & 0 & 0 & 0 & \frac{-\sqrt{2}}{3}b & -5a-\frac{1}{3}b \end{pmatrix} \begin{matrix} \frac{3}{2}, \frac{3}{2} \\ \frac{3}{2}, \frac{-3}{2} \\ \frac{3}{2}, \frac{1}{2} \\ \frac{1}{2}, \frac{1}{2} \\ \frac{3}{2}, \frac{-1}{2} \\ \frac{1}{2}, \frac{-1}{2} \end{matrix}$$

The characteristic equation is

$$[\lambda - (-a + 2b)][\lambda - (-a - 2b)] \left\{ [\lambda - (-a + \frac{2}{3}b)][\lambda - (-5a + \frac{1}{3}b)] - \left(\frac{-\sqrt{2}}{3}b\right)^2 \right\} \times \\ \times \left\{ [\lambda - (-a - \frac{2}{3}b)][\lambda - (-5a - \frac{1}{3}b)] - \left(\frac{-\sqrt{2}}{3}b\right)^2 \right\} = 0$$

and gives 4 equations:

$$\begin{aligned}\lambda &= (-a + 2b) \\ \lambda &= (-a - 2b) \\ \lambda^2 + \lambda(6a - b) + 5a^2 - \frac{11}{3}ab &= 0 \\ \lambda^2 + \lambda(6a + b) + 5a^2 + \frac{11}{3}ab &= 0\end{aligned}$$

The first two equations give the eigenvalues:

$$\lambda_{1,2} = -a \pm 2b$$

Solving the quadratic equations gives

$$\begin{aligned}\lambda_{3,4,5,6} &= -\frac{(6a \boxed{\pm} b)}{2} \pm \sqrt{\left(\frac{(6a \pm b)}{2}\right)^2 - \left(5a^2 \boxed{\pm} \frac{11}{3}ab\right)} \\ &= -\frac{(6a \boxed{\pm} b)}{2} \pm \sqrt{9a^2 + \frac{1}{4}b^2 \boxed{\pm} 3ab - \left(5a^2 \boxed{\pm} \frac{11}{3}ab\right)} \\ &= -\frac{(6a \boxed{\pm} b)}{2} \pm \sqrt{4a^2 + \frac{1}{4}b^2 \boxed{\pm} \frac{2}{3}ab} = -3a \boxed{\pm} \frac{b}{2} \pm 2a \sqrt{1 + \frac{1}{16} \left(\frac{b}{a}\right)^2 \boxed{\pm} \frac{1}{6} \frac{b}{a}}\end{aligned}$$

where the boxed  $\pm$  go together. Setting  $b = 0$  gives the field-free fine-structure levels  $-a$  ( $2p_{3/2}$ ) and  $-5a$  ( $2p_{1/2}$ ) as expected. The weak-field limit ( $b \ll a$ ) is

$$\begin{aligned}\lambda_{1,2} &= -a \pm 2b \\ \lambda_{3,4,5,6} &= -3a \boxed{\pm} \frac{b}{2} \pm 2a \sqrt{1 + \frac{1}{16} \left(\frac{b}{a}\right)^2 \boxed{\pm} \frac{1}{6} \frac{b}{a}} \equiv -3a \boxed{\pm} \frac{b}{2} \pm 2a \pm \boxed{\pm} \frac{1}{6} b \\ &\equiv \begin{cases} -a \pm \frac{4}{3}b \\ -5a \pm \frac{2}{3}b \end{cases}\end{aligned}$$

These are consistent with Eqs. (12.47) and (12.78) and the plot in Fig. 12.8.

The strong-field limit ( $b \gg a$ ) is

$$\begin{aligned}\lambda_{1,2} &= -a \pm 2b \\ \lambda_{3,4,5,6} &= -3a \left[ \pm \frac{b}{2} \pm 2a \sqrt{1 + \frac{1}{16} \left( \frac{b}{a} \right)^2} \right] = -3a \left[ \pm \frac{b}{2} \pm \frac{b}{2} \sqrt{1 \pm \frac{8}{3} \frac{a}{b} + \left( \frac{4a}{b} \right)^2} \right] \\ &\cong -3a \left[ \pm \frac{b}{2} \pm \frac{b}{2} \pm \left[ \pm \frac{2}{3} a \right. \right. \\ &\quad \left. \left. \cong \begin{cases} -\frac{7}{3}a + \{b, 0\} \\ -\frac{11}{3}a + \{0, -b\} \end{cases} \right]\right]\end{aligned}$$

These are consistent with Eqs. (12.82) and (12.86) and the plot in Fig. 12.9.

The 2s states are the same in the coupled or uncoupled basis:

$$\begin{aligned}\left| \frac{1}{2} \frac{1}{2} \right\rangle &= \left| 0 \frac{1}{2} 0 \frac{1}{2} \right\rangle \\ \left| \frac{1}{2} \frac{-1}{2} \right\rangle &= \left| 0 \frac{1}{2} 0 \frac{-1}{2} \right\rangle\end{aligned}$$

so the Zeeman perturbation is diagonal in either basis. Eqs. (12.78) and (12.82) both give

$$H_z = \begin{pmatrix} b & 0 \\ 0 & -b \end{pmatrix}$$

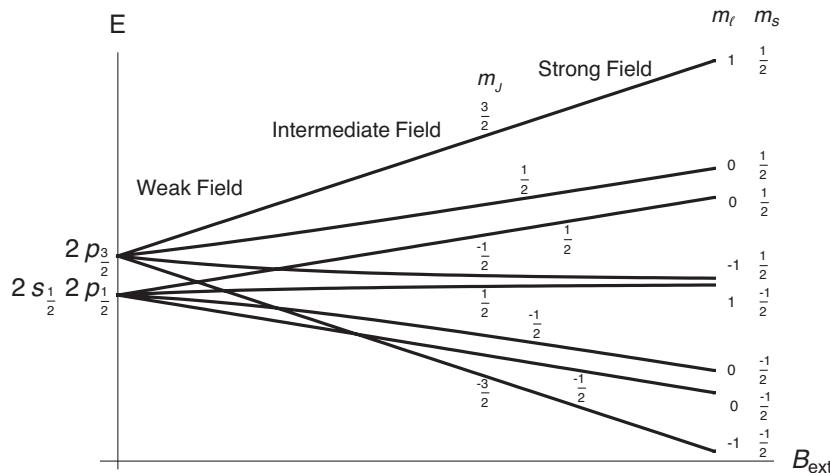
Adding in the fine structure (Eq. 12.47) gives

$$H' = \begin{pmatrix} -5a+b & 0 \\ 0 & -5a-b \end{pmatrix}$$

The resultant energy shifts are

$$E_{7,8} = -5a \pm b$$

All 8 energy levels are shown in the plot:



12.10 In the uncoupled basis  $|n\ell s m_\ell m_s\rangle$ ,  $H'_z$  is diagonal but  $H'_{fs}$  is not diagonal. First do  $H'_z$ : Eq. (12.57) gives  $H'_z = \mu_B B(g_\ell L_z + g_e S_z)/\hbar$ . Substituting the values  $g_\ell = 1$  and  $g_e = 2$  yields

$$H'_z = \frac{\mu_B B}{\hbar} (L_z + 2S_z)$$

$L_z$  and  $S_z$  are both diagonal in the uncoupled basis. The required matrix elements are

$$\begin{aligned} & \langle \ell s m'_\ell m'_s | L_z | \ell s m_\ell m_s \rangle \\ & \langle \ell s m'_\ell m'_s | S_z | \ell s m_\ell m_s \rangle \end{aligned}$$

Use the eigenvalue equations  $L_z |\ell s m_\ell m_s\rangle = m_\ell \hbar |\ell s m_\ell m_s\rangle$  and  $S_z |\ell s m_\ell m_s\rangle = m_s \hbar |\ell s m_\ell m_s\rangle$  to get

$$\begin{aligned} \langle \ell s m'_\ell m'_s | L_z | \ell s m_\ell m_s \rangle &= \langle \ell s m'_\ell m'_s | m_\ell \hbar | \ell s m_\ell m_s \rangle = m_\ell \hbar \langle \ell s m'_\ell m'_s | \ell s m_\ell m_s \rangle = m_\ell \hbar \delta_{m'_\ell m_\ell} \delta_{m'_s m_s} \\ \langle \ell s m'_\ell m'_s | S_z | \ell s m_\ell m_s \rangle &= \langle \ell s m'_\ell m'_s | m_s \hbar | \ell s m_\ell m_s \rangle = m_s \hbar \langle \ell s m'_\ell m'_s | \ell s m_\ell m_s \rangle = m_s \hbar \delta_{m'_\ell m_\ell} \delta_{m'_s m_s} \end{aligned}$$

which shows that the matrices are diagonal. Now write them down:

$$L_z \doteq \begin{pmatrix} \hbar & 0 & 0 & 0 & 0 & 0 \\ 0 & \hbar & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -\hbar & 0 \\ 0 & 0 & 0 & 0 & 0 & -\hbar \end{pmatrix} \begin{matrix} 1, \frac{1}{2} \\ 1, -\frac{1}{2} \\ 0, \frac{1}{2} \\ 0, -\frac{1}{2} \\ -1, \frac{1}{2} \\ -1, -\frac{1}{2} \end{matrix}$$

$$S_z \doteq \begin{pmatrix} \hbar/2 & 0 & 0 & 0 & 0 & 0 \\ 0 & -\hbar/2 & 0 & 0 & 0 & 0 \\ 0 & 0 & \hbar/2 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\hbar/2 & 0 & 0 \\ 0 & 0 & 0 & 0 & \hbar/2 & 0 \\ 0 & 0 & 0 & 0 & 0 & -\hbar/2 \end{pmatrix} \begin{matrix} 1, \frac{1}{2} \\ 1, -\frac{1}{2} \\ 0, \frac{1}{2} \\ 0, -\frac{1}{2} \\ -1, \frac{1}{2} \\ -1, -\frac{1}{2} \end{matrix}$$

Put these together to find the Zeeman matrix:  $H'_z = \mu_B B(L_z + 2S_z)/\hbar$ :

$$H'_z \doteq \begin{pmatrix} 2\mu_B B & 0 & 0 & 0 & 0 & 0 & 1, \frac{1}{2} \\ 0 & 0 & 0 & 0 & 0 & 0 & 1, -\frac{1}{2} \\ 0 & 0 & \mu_B B & 0 & 0 & 0 & 0, \frac{1}{2} \\ 0 & 0 & 0 & -\mu_B B & 0 & 0 & 0, -\frac{1}{2} \\ 0 & 0 & 0 & 0 & 0 & 0 & -1, \frac{1}{2} \\ 0 & 0 & 0 & 0 & 0 & -2\mu_B B & -1, -\frac{1}{2} \end{pmatrix}$$

Now find  $H'_{fs}$ . Use Eq. (12.30) to get the relativistic term, which is diagonal, and has the same value for all the  $2p$  states:

$$\begin{aligned} E_{rel}^{(1)} &= -\frac{1}{2}\alpha^4 mc^2 \left[ \frac{1}{n^3(\ell + \frac{1}{2})} - \frac{3}{4n^4} \right] \\ &= -\frac{1}{2}\alpha^4 mc^2 \left[ \frac{1}{2^3(1 + \frac{1}{2})} - \frac{3}{4(2)^4} \right] \\ &= -\frac{7}{384}\alpha^4 mc^2 \end{aligned}$$

The relativistic matrix is

$$H'_{rel} \doteq \begin{pmatrix} -\frac{7}{384}\alpha^4 mc^2 & 0 & 0 & 0 & 0 & 0 & 1, \frac{1}{2} \\ 0 & -\frac{7}{384}\alpha^4 mc^2 & 0 & 0 & 0 & 0 & 1, -\frac{1}{2} \\ 0 & 0 & -\frac{7}{384}\alpha^4 mc^2 & 0 & 0 & 0 & 0, \frac{1}{2} \\ 0 & 0 & 0 & -\frac{7}{384}\alpha^4 mc^2 & 0 & 0 & 0, -\frac{1}{2} \\ 0 & 0 & 0 & 0 & -\frac{7}{384}\alpha^4 mc^2 & 0 & -1, \frac{1}{2} \\ 0 & 0 & 0 & 0 & 0 & -\frac{7}{384}\alpha^4 mc^2 & -1, -\frac{1}{2} \end{pmatrix}$$

Use Eqs. (12.38) and (12.40) to get the spin-orbit term

$$H'_{so} = \frac{e^2}{8\pi\epsilon_0 m^2 c^2 r^3} \vec{L} \cdot \vec{S} = \frac{e^2}{8\pi\epsilon_0 m^2 c^2 r^3} \left( \frac{1}{2}(L_+ S_- + L_- S_+) + L_z S_z \right)$$

We already have the  $L_z$  and  $S_z$  matrices from above, so we need the matrix for  $(L_+ S_- + L_- S_+)$ . To find these matrix elements proceed as in Eqs. (11.36) and (11.37). Many terms are zero. For example,  $(L_+ S_- + L_- S_+) |1\frac{1}{2} 1\frac{1}{2}\rangle = 0$ . The only terms that exist are ones like

$$\begin{aligned} (L_+ S_- + L_- S_+) |1\frac{1}{2} 0\frac{1}{2}\rangle &= \hbar [1(1+1) - 0(0+1)]^{1/2} \hbar [\frac{1}{2}(\frac{1}{2}+1) - \frac{1}{2}(\frac{1}{2}-1)]^{1/2} |1\frac{1}{2} 1\frac{-1}{2}\rangle \\ &= \hbar^2 \sqrt{2} |1\frac{1}{2} 1\frac{-1}{2}\rangle \end{aligned}$$

that connect  $|1\frac{1}{2}0\frac{1}{2}\rangle$  to  $|1\frac{1}{2}1\frac{-1}{2}\rangle$  and also  $|1\frac{1}{2}0\frac{-1}{2}\rangle$  to  $|1\frac{1}{2},-1\frac{1}{2}\rangle$ . The final result for  $\vec{\mathbf{L}} \cdot \vec{\mathbf{S}}$  is (see Problem 12.2)

$$\vec{\mathbf{L}} \cdot \vec{\mathbf{S}} \doteq \begin{pmatrix} \hbar^2/2 & 0 & 0 & 0 & 0 & 0 \\ 0 & -\hbar^2/2 & \hbar^2/\sqrt{2} & 0 & 0 & 0 \\ 0 & \hbar^2/\sqrt{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \hbar^2/\sqrt{2} & 0 \\ 0 & 0 & 0 & \hbar^2/\sqrt{2} & -\hbar^2/2 & 0 \\ 0 & 0 & 0 & 0 & 0 & \hbar^2/2 \end{pmatrix} \begin{matrix} 1,\frac{1}{2} \\ 1,\frac{-1}{2} \\ 0,\frac{1}{2} \\ 0,\frac{-1}{2} \\ -1,\frac{1}{2} \\ -1,\frac{-1}{2} \end{matrix}$$

Hence, the spin orbit matrix is

$$H'_{SO} \doteq \begin{pmatrix} \frac{1}{96}\alpha^4 mc^2 & 0 & 0 & 0 & 0 & 0 \\ 0 & -\frac{1}{96}\alpha^4 mc^2 & \frac{1}{48\sqrt{2}}\alpha^4 mc^2 & 0 & 0 & 0 \\ 0 & \frac{1}{48\sqrt{2}}\alpha^4 mc^2 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{1}{48\sqrt{2}}\alpha^4 mc^2 & 0 \\ 0 & 0 & 0 & \frac{1}{48\sqrt{2}}\alpha^4 mc^2 & -\frac{1}{96}\alpha^4 mc^2 & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{1}{96}\alpha^4 mc^2 \end{pmatrix} \begin{matrix} 1,\frac{1}{2} \\ 1,\frac{-1}{2} \\ 0,\frac{1}{2} \\ 0,\frac{-1}{2} \\ -1,\frac{1}{2} \\ -1,\frac{-1}{2} \end{matrix}$$

Define  $a = \alpha^4 mc^2 / 128$  and we get for the fine structure matrix:

$$H'_{fs} \doteq \begin{pmatrix} -a & 0 & 0 & 0 & 0 & 0 \\ 0 & -\frac{11}{3}a & \frac{4\sqrt{2}}{3}a & 0 & 0 & 0 \\ 0 & \frac{4\sqrt{2}}{3}a & -\frac{7}{3}a & 0 & 0 & 0 \\ 0 & 0 & 0 & -\frac{7}{3}a & \frac{4\sqrt{2}}{3}a & 0 \\ 0 & 0 & 0 & \frac{4\sqrt{2}}{3}a & -\frac{11}{3}a & 0 \\ 0 & 0 & 0 & 0 & 0 & -a \end{pmatrix} \begin{matrix} 1,\frac{1}{2} \\ 1,\frac{-1}{2} \\ 0,\frac{1}{2} \\ 0,\frac{-1}{2} \\ -1,\frac{1}{2} \\ -1,\frac{-1}{2} \end{matrix}$$

Define  $b = \mu_B B$  and add the Zeeman and fine structure matrices to get

$$H'_z + H'_{fs} \doteq \begin{pmatrix} 2b-a & 0 & 0 & 0 & 0 & 0 \\ 0 & -\frac{11}{3}a & \frac{4\sqrt{2}}{3}a & 0 & 0 & 0 \\ 0 & \frac{4\sqrt{2}}{3}a & b-\frac{7}{3}a & 0 & 0 & 0 \\ 0 & 0 & 0 & -b-\frac{7}{3}a & \frac{4\sqrt{2}}{3}a & 0 \\ 0 & 0 & 0 & \frac{4\sqrt{2}}{3}a & -\frac{11}{3}a & 0 \\ 0 & 0 & 0 & 0 & 0 & -2b-a \end{pmatrix} \begin{matrix} 1, \frac{1}{2} \\ 1, -\frac{1}{2} \\ 0, \frac{1}{2} \\ 0, -\frac{1}{2} \\ -1, \frac{1}{2} \\ -1, -\frac{1}{2} \end{matrix}$$

The characteristic equation is

$$[\lambda - (2b-a)][\lambda - (-2b-a)] \left\{ [\lambda - (-\frac{11}{3}a)][\lambda - (b - \frac{7}{3}a)] - (\frac{4\sqrt{2}}{3}a)^2 \right\} \times \\ \times \left\{ [\lambda - (-b - \frac{7}{3}a)][\lambda - (-\frac{11}{3}a)] - (\frac{4\sqrt{2}}{3}a)^2 \right\} = 0$$

which gives 4 equations:

$$\begin{aligned} \lambda &= (2b-a) \\ \lambda &= (-2b-a) \\ \lambda^2 + \lambda(6a-b) + 5a^2 - \frac{11}{3}ab &= 0 \\ \lambda^2 + \lambda(6a+b) + 5a^2 + \frac{11}{3}ab &= 0 \end{aligned}$$

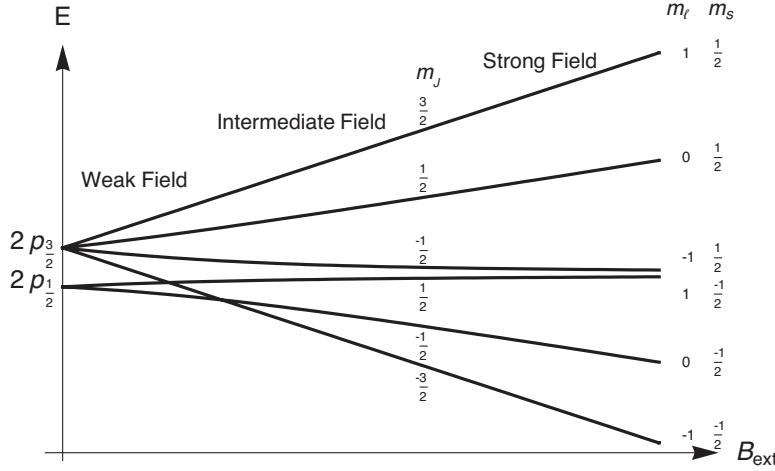
The first two equations give the eigenvalues:

$$\lambda_{1,2} = -a \pm 2b$$

Solving the quadratic equations gives

$$\begin{aligned} \lambda_{3,4,5,6} &= -\frac{(6a \pm b)}{2} \pm \sqrt{\left(\frac{(6a \pm b)}{2}\right)^2 - (5a^2 \pm \frac{11}{3}ab)} \\ &= -\frac{(6a \pm b)}{2} \pm \sqrt{9a^2 + \frac{1}{4}b^2 \pm 3ab - (5a^2 \pm \frac{11}{3}ab)} \\ &= -\frac{(6a \pm b)}{2} \pm \sqrt{4a^2 + \frac{1}{4}b^2 \pm \frac{2}{3}ab} = -3a \pm \frac{b}{2} \pm 2a\sqrt{1 + \frac{1}{16}\left(\frac{b}{a}\right)^2 \pm \frac{1}{6}\frac{b}{a}} \end{aligned}$$

where the boxed  $\pm$  go together. These result in the plot below.



12.11 The Zeeman perturbation matrix in the intermediate field in the coupled basis is [Eq. (12.87)]

$$H' \doteq \begin{pmatrix} -a+2b & 0 & 0 & 0 & 0 & 0 & \frac{3}{2}, \frac{3}{2} \\ 0 & -a+\frac{2}{3}b & 0 & 0 & -\frac{\sqrt{2}}{3}b & 0 & \frac{3}{2}, \frac{1}{2} \\ 0 & 0 & -a-\frac{2}{3}b & 0 & 0 & -\frac{\sqrt{2}}{3}b & \frac{3}{2}, -\frac{1}{2} \\ 0 & 0 & 0 & -a-2b & 0 & 0 & \frac{3}{2}, -\frac{3}{2} \\ 0 & -\frac{\sqrt{2}}{3}b & 0 & 0 & -5a+\frac{1}{3}b & 0 & \frac{1}{2}, \frac{1}{2} \\ 0 & 0 & -\frac{\sqrt{2}}{3}b & 0 & 0 & -5a-\frac{1}{3}b & \frac{1}{2}, -\frac{1}{2} \end{pmatrix}$$

Rearrange the rows (and columns of course) to put the off-diagonal elements adjacent to the diagonal

$$H' \doteq \begin{pmatrix} -a+2b & 0 & 0 & 0 & 0 & 0 & \frac{3}{2}, \frac{3}{2} \\ 0 & -a-2b & 0 & 0 & 0 & 0 & \frac{3}{2}, -\frac{3}{2} \\ 0 & 0 & -a+\frac{2}{3}b & -\frac{\sqrt{2}}{3}b & 0 & 0 & \frac{3}{2}, \frac{1}{2} \\ 0 & 0 & -\frac{\sqrt{2}}{3}b & -5a+\frac{1}{3}b & 0 & 0 & \frac{1}{2}, \frac{1}{2} \\ 0 & 0 & 0 & 0 & -a-\frac{2}{3}b & -\frac{\sqrt{2}}{3}b & \frac{3}{2}, -\frac{1}{2} \\ 0 & 0 & 0 & 0 & -\frac{\sqrt{2}}{3}b & -5a-\frac{1}{3}b & \frac{1}{2}, -\frac{1}{2} \end{pmatrix}$$

From this, we see that the states  $|\frac{3}{2} \frac{3}{2}\rangle$  and  $|\frac{3}{2} -\frac{3}{2}\rangle$  are not coupled to any other states and so have the same field dependence at low and high fields. The states  $|\frac{3}{2} \frac{1}{2}\rangle$  and  $|\frac{1}{2} \frac{1}{2}\rangle$  couple to each other, so they repel each other in Fig. 12.10. Likewise the states  $|\frac{3}{2} -\frac{1}{2}\rangle$  and  $|\frac{1}{2} -\frac{1}{2}\rangle$  couple to each other and repel each other in Fig. 12.10.

12.12 For weak fields, we include the hyperfine structure in the zeroth-order Hamiltonian, use the coupled states  $|FM_F\rangle$  as the "good" basis because the hyperfine Hamiltonian is diagonal in that basis, and treat the Zeeman effect as a perturbation. For strong fields, we include the Zeeman effect in the zeroth-order Hamiltonian, use the uncoupled states  $|SIm_S m_I\rangle$  as the "good" basis because the Zeeman Hamiltonian is diagonal in that basis, and treat the hyperfine interaction as a perturbation.

Starting in the weak field case, the hyperfine Hamiltonian in the coupled basis is [from Eq. (12.91)]:

$$H'_{\text{hfs}} \doteq \frac{A}{4} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -3 \end{pmatrix} \begin{array}{l} 11 \\ 10 \\ 1,-1 \\ 00 \end{array}$$

so the zeroth-order energies are  $+A/4$  and  $-3A/4$ , as we found in Eq. (11.64). The Zeeman Hamiltonian is

$$H'_z = \frac{2\mu_B B}{\hbar} S_z$$

so we need to find  $S_z$  in the coupled basis. Just as in Sec. 12.3.2, we use the Clebsch-Gordan expansions:

$$\begin{aligned} |11\rangle &= |++\rangle \\ |10\rangle &= \frac{1}{\sqrt{2}}[|+-\rangle + |-+\rangle] \\ |1,-1\rangle &= |--\rangle \\ |00\rangle &= \frac{1}{\sqrt{2}}[|+-\rangle - |-+\rangle] \end{aligned}$$

$S_z$  is diagonal in the uncoupled basis [Eq. (11.32)], but is not diagonal in the coupled basis. The only non-zero matrix elements are

$$\begin{aligned} \langle 11 | S_z | 11 \rangle &= \langle ++ | S_z | ++ \rangle = +\frac{\hbar}{2} \\ \langle 1,-1 | S_z | 1,-1 \rangle &= \langle -- | S_z | -- \rangle = -\frac{\hbar}{2} \\ \langle 10 | S_z | 00 \rangle &= \frac{1}{\sqrt{2}}(\langle +- | + \langle -+ |) S_z \frac{1}{\sqrt{2}}(|+-\rangle - |-+\rangle) = \frac{1}{2}\left(+\frac{\hbar}{2} - \left(-\frac{\hbar}{2}\right)\right) = +\frac{\hbar}{2} \\ \langle 00 | S_z | 10 \rangle &= \frac{1}{\sqrt{2}}(\langle +- | - \langle -+ |) S_z \frac{1}{\sqrt{2}}(|+-\rangle + |-+\rangle) = \frac{1}{2}\left(+\frac{\hbar}{2} - \left(-\frac{\hbar}{2}\right)\right) = +\frac{\hbar}{2} \end{aligned}$$

The resultant Zeeman matrix in the coupled basis is

$$H'_z \doteq \mu_B B \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & -1 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} \begin{array}{l} 11 \\ 10 \\ 1,-1 \\ 00 \end{array}$$

As we found in the fine-structure case, the off-diagonal matrix elements couple states that are non-degenerate, so the Zeeman matrix is diagonal within each degenerate manifold (the  $F=1$  states and the  $F=0$  state). The first-order Zeeman corrections are thus the diagonal elements

$$E_Z^{(1)} = \langle H'_Z \rangle = \langle FM_F | H'_Z | FM_F \rangle$$

which we find by inspection to be

$$\begin{aligned} E_Z^{(1)} &= M_F \mu_B B \\ &= \mu_B B, 0, -\mu_B B, 0 \quad \text{for the } |11\rangle, |10\rangle, |1,-1\rangle, |00\rangle \text{ states} \end{aligned}$$

as expected. Hence the total energies (neglecting the -13.6 eV term) are

$$E_{hf}^{(0)} + E_Z^{(1)} = \begin{cases} +\frac{A}{4} + \mu_B B & |11\rangle \\ +\frac{A}{4} & |10\rangle \\ +\frac{A}{4} + \mu_B B & |1,-1\rangle \\ -\frac{3A}{4} & |00\rangle \end{cases}$$

as seen in Fig. 12.11.

For the strong-field case, we treat the Zeeman effect in zeroth-order, which means we use the uncoupled basis. The Zeeman Hamiltonian is

$$H'_Z = \frac{2\mu_B B}{\hbar} S_z \doteq \frac{2\mu_B B}{\hbar} \frac{\hbar}{2} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} \begin{array}{l} ++ \\ +- \\ -+ \\ -- \end{array}$$

Hence the zeroth-order energies are, by inspection,  $+\mu_B B$  for the  $|++\rangle$  and  $|+-\rangle$  states and  $-\mu_B B$  for the  $|-\rangle$  and  $|--\rangle$  states. The hyperfine Hamiltonian in the uncoupled basis was found in Eq. (11.39) to be

$$H'_{hf} \doteq \frac{A}{4} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 2 & 0 \\ 0 & 2 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{array}{l} ++ \\ +- \\ -+ \\ -- \end{array}$$

This is diagonal within each degenerate manifold ( $m_s = \pm 1/2$ ), so the first-order hyperfine corrections in a strong field are the diagonal terms

$$\begin{aligned} E_{hf}^{(1)} &= \langle H'_{hf} \rangle = \langle 1sIm_s m_I | H'_{hf} | 1sIm_s m_I \rangle \\ &= \begin{cases} +\frac{A}{4} & \text{for } |++\rangle, |--\rangle \\ -\frac{A}{4} & \text{for } |+-\rangle, |-+\rangle \end{cases} \end{aligned}$$

Hence the total energies (neglecting the -13.6 eV term) are

$$E_z^{(0)} + E_{hf}^{(1)} = \begin{cases} +\mu_B B + \frac{A}{4} & |++\rangle \\ +\mu_B B - \frac{A}{4} & |+-\rangle \\ -\mu_B B + \frac{A}{4} & |--\rangle \\ -\mu_B B - \frac{A}{4} & |-+\rangle \end{cases}$$

as seen in Fig. 12.11.

The intermediate field region is where the Zeeman and hyperfine corrections are of the same order of magnitude. Equating the two corrections:

$$\mu_B B = A ,$$

we get a magnetic field strength

$$\begin{aligned} B &= \frac{A}{\mu_B} = \frac{1420 \text{ MHz}}{1.4 \text{ MHz/Gauss}} \\ \Rightarrow B &= 1000 \text{ Gauss} = 0.1 \text{ Tesla} \end{aligned}$$


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12.13 The hyperfine Hamiltonian in the coupled basis is [from Eq. (12.91)]:

$$H'_{hfs} \doteq \frac{A}{4} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -3 \end{pmatrix} \begin{matrix} 11 \\ 10 \\ 1,-1 \\ 00 \end{matrix}$$

The Zeeman perturbation in the coupled basis is [from Eq. (12.92)]:

$$H'_Z \doteq \mu_B B \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & -1 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} \begin{matrix} 11 \\ 10 \\ 1,-1 \\ 00 \end{matrix}$$

The sum of these two gives the full perturbation:

$$H' = H'_{hfs} + H'_Z \doteq \begin{pmatrix} \mu_B B + \frac{1}{4}A & 0 & 0 & 0 \\ 0 & \frac{1}{4}A & 0 & \mu_B B \\ 0 & 0 & -\mu_B B + \frac{1}{4}A & 0 \\ 0 & \mu_B B & 0 & -\frac{3}{4}A \end{pmatrix} \begin{matrix} 11 \\ 10 \\ 1,-1 \\ 00 \end{matrix}$$

Now diagonalize this:

$$\begin{vmatrix} \mu_B B + \frac{1}{4}A - \lambda & 0 & 0 & 0 \\ 0 & \frac{1}{4}A - \lambda & 0 & \mu_B B \\ 0 & 0 & -\mu_B B + \frac{1}{4}A - \lambda & 0 \\ 0 & \mu_B B & 0 & -\frac{3}{4}A - \lambda \end{vmatrix} = 0$$

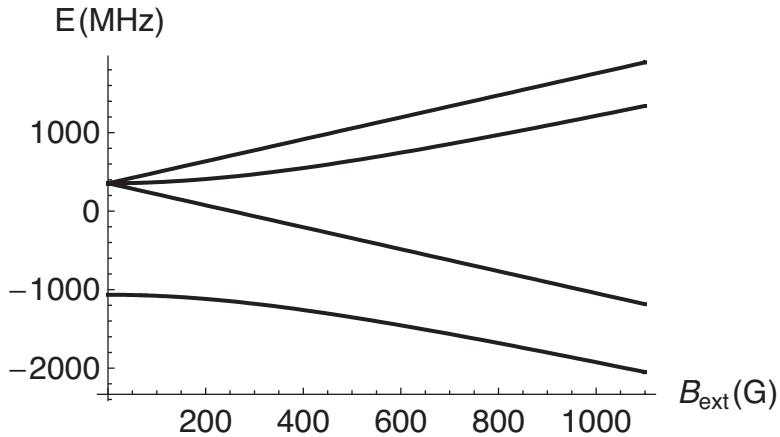
$$(\mu_B B + \frac{1}{4}A - \lambda) \{ (\frac{1}{4}A - \lambda)(-\mu_B B + \frac{1}{4}A - \lambda)(-\frac{3}{4}A - \lambda) + \mu_B B(-\mu_B B)(-\mu_B B + \frac{1}{4}A - \lambda) \} = 0$$

$$(\mu_B B + \frac{1}{4}A - \lambda)(-\mu_B B + \frac{1}{4}A - \lambda) \{ (\frac{1}{4}A - \lambda)(-\frac{3}{4}A - \lambda) + \mu_B B(-\mu_B B) \} = 0$$

$$(\mu_B B + \frac{1}{4}A - \lambda)(-\mu_B B + \frac{1}{4}A - \lambda) \left\{ \lambda^2 + \frac{1}{2}A\lambda - \frac{3}{16}A^2 - (\mu_B B)^2 \right\} = 0$$

$$\lambda = \mu_B B + \frac{1}{4}A, -\mu_B B + \frac{1}{4}A, -\frac{1}{4}A \pm \sqrt{\left(\frac{1}{2}A\right)^2 + (\mu_B B)^2}$$

Let's use MHz as our energy units, with  $A = 1420 \text{ MHz}$  and  $\mu_B = 1.4 \text{ MHz/G}$ . This yields the following plot:



- 12.14 a) The energy difference between the  $n = 1$  and  $n = 2$  states BEFORE any perturbations are considered. We know that for the H atom with no spin considered,  $E_n = -mc^2\alpha^2/2n^2 = -13.6eV/n^2$  where  $\alpha = e^2/4\pi\epsilon_0\hbar c = 1/137$  is the fine structure constant. Thus

$$\Delta E_{2 \rightarrow 1}^{(0)} = -\frac{mc^2\alpha^2}{2} \left( \frac{1}{4} - \frac{1}{1} \right) = \frac{3}{4} \frac{mc^2\alpha^2}{2} = \frac{3}{4} 13.6eV = 10.2eV$$

This corresponds to a wavelength of

$$\lambda = \frac{hc}{\Delta E_{2 \rightarrow 1}^{(0)}} = \frac{1240 \text{ eV nm}}{10.2 \text{ eV}} \approx 122 \text{ nm}.$$

- b) The correction to the  $n = 1$  and  $n = 2$  states due to spin-orbit coupling. The correction to the energies due to **spin-orbit coupling** is [from Eq. (12.46)]

$$\begin{aligned}\Delta E_{SO}^{(1)} &= \frac{1}{4} \alpha^4 mc^2 \frac{[j(j+1) - \ell(\ell+1) - s(s+1)]}{n^3 \ell(\ell + \frac{1}{2})(\ell+1)} = \frac{13.6 \text{ eV}}{137^2} \frac{[j(j+1) - \ell(\ell+1) - s(s+1)]}{2n^3 \ell(\ell + \frac{1}{2})(\ell+1)} \\ &= 0.073 \text{ eV} \frac{[j(j+1) - \ell(\ell+1) - s(s+1)]}{2n^3 \ell(\ell + \frac{1}{2})(\ell+1)}\end{aligned}$$

Notice that this looks troublesome for  $\ell = 0$ , but for this case  $\hat{L} = 0$ , so that  $H_{SO} = 0$ . But if we ignore this problem and rewrite the spin-orbit energy in terms of  $j$ , using  $j = \ell + 1/2 \Rightarrow \ell = j - 1/2$ , we get an expression that we call spin-orbit, but is really the Darwin term for  $s$ -states:

$$\begin{aligned}\Delta E_{SO(D)}^{(1)} &= \frac{1}{4} \alpha^4 mc^2 \frac{[j(j+1) - (j - \frac{1}{2})(j + \frac{1}{2}) - \frac{1}{2}(\frac{1}{2} + 1)]}{n^3 (j - \frac{1}{2}) j (j + \frac{1}{2})} = \frac{1}{2} \alpha^2 mc^2 \alpha^2 \frac{[j^2 + j - j^2 + \frac{1}{4} - \frac{3}{4}]}{2n^3 (j - \frac{1}{2}) j (j + \frac{1}{2})} \\ &= \frac{1}{2} \alpha^2 mc^2 \alpha^2 \frac{(j - \frac{1}{2})}{2n^3 (j - \frac{1}{2}) j (j + \frac{1}{2})} = \frac{1}{2} \alpha^2 mc^2 \alpha^2 \frac{1}{2n^3 j (j + \frac{1}{2})} = 0.073 \text{ eV} \frac{1}{2n^3 j (j + \frac{1}{2})}\end{aligned}$$

Let's make a table of these corrections:

$n, \ell, j$	$1, 0, \frac{1}{2}$	$2, 0, \frac{1}{2}$	$2, 1, \frac{1}{2}$	$2, 1, \frac{3}{2}$
Term notation	${}^2S_{1/2}$	${}^2S_{1/2}$	${}^2P_{1/2}$	${}^2P_{3/2}$
$\Delta E_{s-o(D)}^{(1)}$	$\frac{1}{2} \alpha^4 mc^2$	$\frac{1}{16} \alpha^4 mc^2$	$-\frac{1}{48} \alpha^4 mc^2$	$\frac{1}{96} \alpha^4 mc^2$
meV	0.725	0.091	-0.030	0.015
GHz	175.2	21.9	-7.3	3.6

c) The correction to the  $n = 1$  and  $n = 2$  states due to the relativistic term. The correction to the energies due to the **relativistic term** in the kinetic energy is [Eq. (12.30)]

$$\Delta E_{rel}^{(1)} = -\frac{1}{2} \alpha^4 mc^2 \left[ \frac{1}{n^3 (\ell + \frac{1}{2})} - \frac{3}{4n^4} \right] = -0.073 \text{ eV} \left[ \frac{1}{n^3 (\ell + \frac{1}{2})} - \frac{3}{4n^4} \right]$$

Let's make a table of corrections:

$n, \ell, j$	$1, 0, \frac{1}{2}$	$2, 0, \frac{1}{2}$	$2, 1, \frac{1}{2}$	$2, 1, \frac{3}{2}$
Term notation	${}^2S_{1/2}$	${}^2S_{1/2}$	${}^2P_{1/2}$	${}^2P_{3/2}$
$\Delta E_{rel}^{(1)}$	$-\frac{5}{8} \alpha^4 mc^2$	$-\frac{13}{128} \alpha^4 mc^2$	$-\frac{7}{384} \alpha^4 mc^2$	$-\frac{7}{384} \alpha^4 mc^2$
meV	-0.906	-0.147	-0.026	-0.026
GHz	-219.0	-35.6	-6.4	-6.4

d) The total correction to these states. Now we add the corrections:

$n, \ell, j$	$1, 0, \frac{1}{2}$	$2, 0, \frac{1}{2}$	$2, 1, \frac{1}{2}$	$2, 1, \frac{3}{2}$
Term notation	$^2S_{1/2}$	$^2S_{1/2}$	$^2P_{1/2}$	$^2P_{3/2}$
$\Delta E_{s-o(D)}^{(1)} + \Delta E_{rel}^{(1)}$	$-\frac{1}{8}\alpha^4 mc^2$	$-\frac{5}{128}\alpha^4 mc^2$	$-\frac{5}{128}\alpha^4 mc^2$	$\frac{-1}{128}\alpha^4 mc^2$
meV	-0.181	-0.0566	-0.0566	-0.0113
GHz	-43.8	-13.7	-13.7	-2.74

Compare to Eq. (12.47), which gives the correction for the **total fine structure**:

$$\Delta E_{fs}^{(1)} = -\frac{1}{2}\alpha^4 mc^2 \frac{1}{n^3} \left[ \frac{1}{(j + \frac{1}{2})} - \frac{3}{4n} \right].$$

- (e) What wavelength resolution must your detector have to be able to resolve the two lines in the  $n = 2$  to  $n = 1$  transition? Be careful here. When you include the correction, you will find that it is *very small* compared to the unperturbed value. Be sensible about how to include the effects.

The two transitions are from

- (i) the  $j = 3/2$  level of the  $n = 2$  state to the  $n = 1$  state ( $j = 1/2$ ), or in spectroscopic notation,  $^2P_{3/2} \rightarrow ^2S_{1/2}$ .
- (ii) the  $j = 1/2$  level of the  $n = 2$  state to the  $n = 1$  state ( $j = 1/2$ ), or in spectroscopic notation,  $^2P_{1/2} \rightarrow ^2S_{1/2}$ .

The wavelength of the transition is basically 122 nm as calculated in (a) above (this corresponds to about 10.2 eV). The difference in energy between the  $^2P_{3/2}$  and the  $^2P_{1/2}$  states is  $\frac{4}{128}\alpha^4 mc^2 = \frac{1}{32}\alpha^4 mc^2 = \frac{1}{32}\alpha^2 27.2 eV = 0.045 meV$  (about 4 parts in  $10^{-6}$  of the total energy spacing). Our job is to figure out how this translates into a wavelength difference.

The energy and wavelength of the photon emitted in a transition are related by

$$\begin{aligned} \lambda &= \frac{hc}{E_{ph}} \\ \Rightarrow d\lambda &= -\frac{hc}{E_{ph}^2} dE_{ph} = -\frac{\lambda}{E_{ph}} dE_{ph} \\ \Rightarrow \frac{\Delta\lambda}{\lambda} &= -\frac{\Delta E_{ph}}{E_{ph}} \end{aligned}$$

Since we're interested in magnitude only, we take the absolute value, and plug in the appropriate numbers:

$$|\Delta\lambda| = \lambda \frac{\Delta E_{ph}}{E_{ph}} = 122 \text{ nm} \frac{0.045 \text{ meV}}{10.2 \text{ eV}} = 0.00054 \text{ nm} = 0.0054 \text{ \AA}.$$

- (f) Is it important to use the reduced mass of the electron in your calculations or is it OK to use the rest mass? As always, it depends ..... The reduced mass of the electron differs from the rest mass by about 5 parts in  $10^4$ :

$$\begin{aligned}\frac{m - m_{red}}{m_{red}} &= \frac{m}{m_{red}} - 1 = \frac{m(m+M)}{mM} - 1 \\ &= \frac{m^2 + mM - mM}{mM} = \frac{m}{M} \approx \frac{1}{1840} \approx 0.0005\end{aligned}$$

Thus the energy difference between the two emitted photons would change by only this amount, which is negligible by ordinary lab standards. On the other hand, transitions of this type are used to measure fundamental constants to a precision of better than 1 part in  $10^{14}$ . In this case, it is very important to apply this correction.

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12.15. The Hamiltonian from Eq. (13.9) is  $H'_{hf} = A\mathbf{I} \cdot \mathbf{S}/\hbar^2$ . The spin of the deuteron is  $I = 1$ , so the allowed values of the coupled angular momentum  $\mathbf{F} = \mathbf{S} + \mathbf{I}$  with  $s = 1/2$  for the electron are  $F = \frac{1}{2}, \frac{3}{2}$ . Do the calculation in the coupled basis, like we did in Eq. (11.61). The hyperfine Hamiltonian from Eq. (11.60) is

$$H'_{hf} = \frac{A}{\hbar^2} \mathbf{S} \cdot \mathbf{I} = \frac{A}{2\hbar^2} (\mathbf{F}^2 - \mathbf{S}^2 - \mathbf{I}^2)$$

The matrix elements are

$$\begin{aligned}\langle F'M'_F | H'_{hf} | FM_F \rangle &= \frac{A}{2\hbar^2} \langle F'M'_F | \vec{\mathbf{F}}^2 - \vec{\mathbf{J}}^2 - \vec{\mathbf{I}}^2 | FM_F \rangle \\ &= \frac{A}{2\hbar^2} [F(F+1) - s(s+1) - I(I+1)] \hbar^2 \langle F'M'_F | FM_F \rangle \\ &= \frac{A}{2} [F(F+1) - s(s+1) - I(I+1)] \delta_{F'F} \delta_{M'_FM_F}\end{aligned}$$

For deuterium,  $I = 1$ ,  $s = 1/2$ , and  $F = \frac{1}{2}, \frac{3}{2}$ , giving the diagonal elements

$$\langle FM_F | H'_{hf} | FM_F \rangle = \begin{cases} \frac{1}{2}A; & F = \frac{3}{2} \\ -A; & F = \frac{1}{2} \end{cases}$$

and the matrix

$$H'_{hf} \doteq \left( \begin{array}{cccccc} A/2 & 0 & 0 & 0 & 0 & 0 & \frac{3}{2}, \frac{3}{2} \\ 0 & A/2 & 0 & 0 & 0 & 0 & \frac{3}{2}, \frac{1}{2} \\ 0 & 0 & A/2 & 0 & 0 & 0 & \frac{3}{2}, \frac{-1}{2} \\ 0 & 0 & 0 & A/2 & 0 & 0 & \frac{3}{2}, \frac{-3}{2} \\ 0 & 0 & 0 & 0 & -A & 0 & \frac{1}{2}, \frac{1}{2} \\ 0 & 0 & 0 & 0 & 0 & -A & \frac{1}{2}, \frac{-1}{2} \end{array} \right)$$

The two hyperfine levels are split by the amount

$$\Delta E = \frac{3}{2} A$$

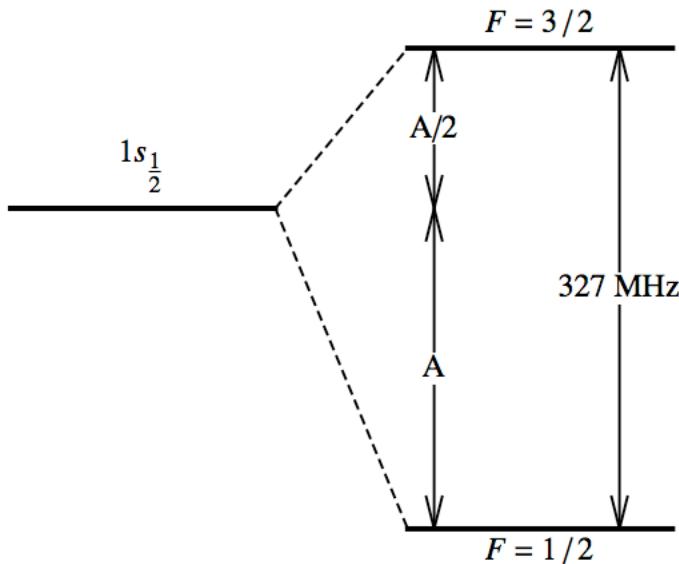
For deuterium  $g_D = 0.857$ , compared to  $g_p = 5.59$ . Hence, for deuterium

$$A_D = \frac{g_D}{g_p} A_H = \frac{0.857}{5.59} 1420.4 \text{ MHz} = 217.8 \text{ MHz}$$

and the splitting is

$$\boxed{\Delta E = \frac{3}{2} A_D = 326.6 \text{ MHz}}$$

The ground state hyperfine structure of deuterium is shown below.



- b) Now find the Zeeman splitting. The Zeeman Hamiltonian from Eq. (12.90) is  $H'_Z = 2\mu_B B S_z / \hbar$ . We can do the calculation in either basis—one matrix will be non-diagonal. Let's do the coupled basis, like we did in Sec. 12.3.3. The hyperfine Hamiltonian matrix is given above and is diagonal. The Zeeman matrix is not diagonal in the coupled basis and we can find it by using the Clebsch-Gordan coefficients like we did in Sec. 12.3.2, where we considered the 2p state of hydrogen with  $\ell = 1$  and  $s = 1/2$ . For the deuterium ground state we have  $I = 1$  and  $s = 1/2$ , which gives the same Clebsch-Gordan coefficients and hence the same angular momentum matrices. Hence the  $S_z$  matrix for deuterium ground state is equivalent to the  $S_z$  matrix in Eq. (12.64):

$$S_z \doteq \hbar \begin{pmatrix} \frac{1}{2} & 0 & 0 & 0 & 0 & 0 \\ 0 & \frac{1}{6} & 0 & 0 & \frac{-\sqrt{2}}{3} & 0 \\ 0 & 0 & \frac{-1}{6} & 0 & 0 & \frac{-\sqrt{2}}{3} \\ 0 & 0 & 0 & \frac{-1}{2} & 0 & 0 \\ 0 & \frac{-\sqrt{2}}{3} & 0 & 0 & \frac{-1}{6} & 0 \\ 0 & 0 & \frac{-\sqrt{2}}{3} & 0 & 0 & \frac{1}{6} \end{pmatrix} \begin{pmatrix} \frac{3}{2}, \frac{3}{2} \\ \frac{3}{2}, \frac{1}{2} \\ \frac{3}{2}, \frac{-1}{2} \\ \frac{3}{2}, \frac{-3}{2} \\ \frac{1}{2}, \frac{1}{2} \\ \frac{1}{2}, \frac{-1}{2} \end{pmatrix}$$

Giving a Zeeman matrix (using  $b = \mu_B B$ )

$$H_Z \doteq \begin{pmatrix} b & 0 & 0 & 0 & 0 & 0 \\ 0 & \frac{1}{3}b & 0 & 0 & \frac{-2\sqrt{2}}{3}b & 0 \\ 0 & 0 & \frac{-1}{3}b & 0 & 0 & \frac{-2\sqrt{2}}{3}b \\ 0 & 0 & 0 & -b & 0 & 0 \\ 0 & \frac{-2\sqrt{2}}{3}b & 0 & 0 & \frac{-1}{3}b & 0 \\ 0 & 0 & \frac{-2\sqrt{2}}{3}b & 0 & 0 & \frac{1}{3}b \end{pmatrix} \begin{pmatrix} \frac{3}{2}, \frac{3}{2} \\ \frac{3}{2}, \frac{1}{2} \\ \frac{3}{2}, \frac{-1}{2} \\ \frac{3}{2}, \frac{-3}{2} \\ \frac{1}{2}, \frac{1}{2} \\ \frac{1}{2}, \frac{-1}{2} \end{pmatrix}$$

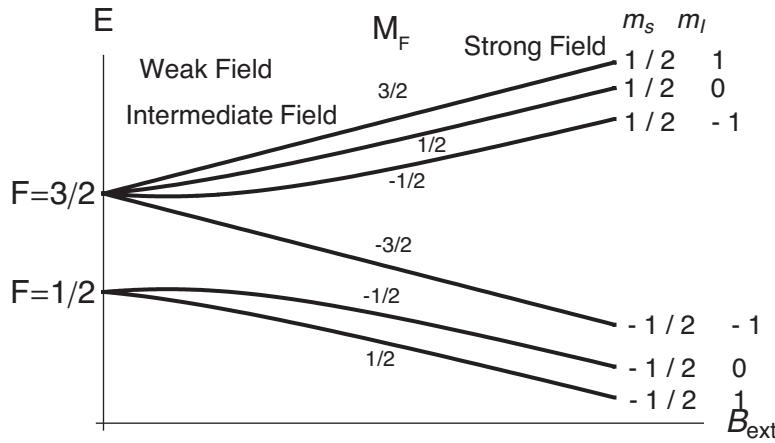
and a total perturbation matrix

$$H_{hf} + H_Z \doteq \begin{pmatrix} A/2 + b & 0 & 0 & 0 & 0 & 0 \\ 0 & A/2 + \frac{1}{3}b & 0 & 0 & \frac{-2\sqrt{2}}{3}b & 0 \\ 0 & 0 & A/2 - \frac{1}{3}b & 0 & 0 & \frac{-2\sqrt{2}}{3}b \\ 0 & 0 & 0 & A/2 - b & 0 & 0 \\ 0 & \frac{-2\sqrt{2}}{3}b & 0 & 0 & -A - \frac{1}{3}b & 0 \\ 0 & 0 & \frac{-2\sqrt{2}}{3}b & 0 & 0 & -A + \frac{1}{3}b \end{pmatrix} \begin{pmatrix} \frac{3}{2}, \frac{3}{2} \\ \frac{3}{2}, \frac{1}{2} \\ \frac{3}{2}, \frac{-1}{2} \\ \frac{3}{2}, \frac{-3}{2} \\ \frac{1}{2}, \frac{1}{2} \\ \frac{1}{2}, \frac{-1}{2} \end{pmatrix}$$

Diagonalizing this matrix yields the six energies:

$$\begin{aligned} & \frac{A}{2} - b, \frac{A}{2} + b, \\ & \frac{1}{4} \left( -A - \sqrt{9A^2 - 8Ab + 16b^2} \right), \frac{1}{4} \left( -A + \sqrt{9A^2 - 8Ab + 16b^2} \right), \\ & \frac{1}{4} \left( -A - \sqrt{9A^2 + 8Ab + 16b^2} \right), \frac{1}{4} \left( -A + \sqrt{9A^2 + 8Ab + 16b^2} \right) \end{aligned}$$

Plot below.



12.16 The effective magnetic moment of the atom is given by the slope  $-\partial E_z^{(1)} / \partial B$  of the Zeeman energy plot. In the ground state of hydrogen, the Zeeman energies are shown in Fig. 12.11 and the energies found in Problem 12.13 are

$$E_z^{(1)} = \mu_B B + \frac{1}{4} A, -\mu_B B + \frac{1}{4} A, -\frac{1}{4} A \pm \sqrt{\left(\frac{1}{2} A\right)^2 + (\mu_B B)^2}$$

where  $A$  is the hyperfine splitting. The effective magnetic moment is

$$\mu_{eff} = \frac{-\partial E_z^{(1)}}{\partial B} = \mu_B, -\mu_B, \pm \frac{2\mu_B^2 B}{2\sqrt{\left(\frac{1}{2} A\right)^2 + (\mu_B B)^2}}$$

This exact expression holds in intermediate fields, so there are four beams in a Stern-Gerlach device. In weak magnetic fields ( $\mu_B B \ll A$ ), the moment becomes

$$\mu_{eff,weak} \cong \mu_B, -\mu_B, \pm \frac{2\mu_B^2 B}{A} \cong \mu_B, -\mu_B, 0$$

so there are three beams in a Stern-Gerlach device. In strong magnetic fields ( $\mu_B B \gg A$ ), the moment becomes

$$\mu_{eff,weak} \cong \mu_B, -\mu_B, \pm \frac{\mu_B^2 B}{\mu_B B} \cong \mu_B, -\mu_B$$

so there are two beams in a Stern-Gerlach device.