The Zeeman effect

Just like in the case of an external electric field, placing an atom in an external magnetic field causes shifts of the energy levels. This effect is called the Zeeman effect.
Let us further focus on the case of a hydrogen-like atom. In general the electron has both the spin and the orbital angular momentum and magnetic moments associated with each of those. The perturbation Hamiltonian is given by

$$H' = -(\vec{\mu}_e + \vec{\mu}_s)\cdot\vec{B}$$

Here $\vec{\mu}_s = -\frac{e}{m}\vec{S}$ while $\vec{\mu}_e = -\frac{e}{2m}\vec{L}$, thus

$$H' = \frac{e}{2m}(\vec{L} + 2\vec{S})\cdot\vec{B}$$

The strenght of the external magnetic field $\vec{B}$ can be compared to the field created by the orbital motion of the electron (which causes spin-orbit interaction), which is about 12 Tesla in the hydrogen atom. Based on this comparison we can consider 3 regimes:

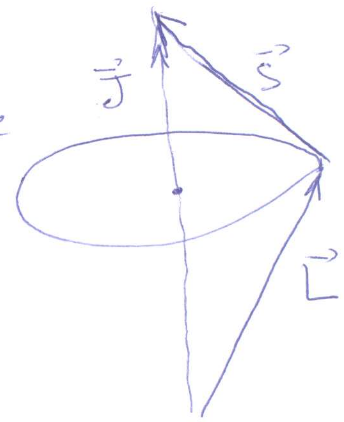
$|\vec{B}| << |\vec{B}_{internal}|$ weak-field Zeeman effect

$|\vec{B}| \sim |\vec{B}_{internal}|$ intermediate-field Zeeman effect

$|\vec{B}| >> |\vec{B}_{interal}|$ strong-field Zeeman effect

Let us first consider the weak-field regime. In this regime the fine structure effect obvioulsy dominate over the Zeeman effect. The good quantum numbers are n, l, j, m_j ($\vec{L}$ and $\vec{S}$ are not conserved separately)
The first order correction can be readily evaluated

$$E^{(1)} = \langle n\ell j m_j | H' | n\ell j m_j \rangle = \frac{e}{2m}\vec{B}\cdot\langle n\ell j m_j | \vec{L}+2\vec{S} | n\ell j m_j\rangle$$



As $\vec{L}$ and $\vec{S}$ precess rapidly around $\vec{J}$ vector (which is constant, while the $\vec{L}$ and $\vec{S}$ change direction) the time average of $\vec{S}$ is

$$\vec{S}_a = \frac{(\vec{S}\cdot\vec{J})}{J^2}\vec{J}$$

at the same time $\vec{L} = \vec{J} - \vec{S}$ and

$$L^2 = J^2 + S^2 - 2\vec{J}\cdot\vec{S}$$

or

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

when we act with $\vec{S}\cdot\vec{J}$ on $|n\ell j m_j\rangle$ we obtain

$$\frac{\hbar^2}{2}[j(j+1) + s(s+1) - \ell(\ell+1)]$$

Therefore

$$\langle n\ell j m_j | \vec{L}+2\vec{S} | n\ell j m_j\rangle = \langle \vec{J}+\vec{S}\rangle = \left\langle \left(1 + \frac{\vec{S}\cdot\vec{J}}{J^2}\right)\vec{J}\right\rangle =$$

$$= \underbrace{\left[1 + \frac{j(j+1) - \ell(\ell+1) + 3/4}{2j(j+1)}\right]}_{g_J \text{ - Landé g-factor}}\langle\vec{J}\rangle$$

If we chose z-axis to lie along $\vec{B}$ then

$$E^{(1)} = \frac{e}{2m}|\vec{B}|\, g_J \hbar m_j = \mu_B g_J |\vec{B}|\, m_j$$

$\mu_B \equiv \frac{e\hbar}{2m}$ - Bohr magneton

The total energy correction is the sum of $E^{(1)}$ and the larger spin-orbit correction, which we evaluated in the previous lecture.

Let us turn our attention to the case when

$|\vec{B}| \gg |\vec{B}_{internal}|$

The Zeeman effect dominates over spin-orbit interaction. ~~Now~~. n, ℓ, m_ℓ, and m_s are "good" quantum numbers

$$H' = \frac{e}{2m} B (L_z + 2S_z)$$

$$\langle n \ell m_\ell m_s | H' | n \ell m_\ell m_s \rangle = \cancel{-\frac{Ry}{n^2}} + \mu_B |\vec{B}| (m_\ell + 2m_s)$$

On top of the energy correction due to the Zeeman effect we can add (the smaller) fine structure correction

$$E^{(1)}_{fs} = \langle n \ell m_\ell m_s | H'_{relat} + H'_{so} | n \ell m_\ell m_s \rangle$$

The relativistic contribution was computed in a previous lecture

$$E^{(1)}_{relat} = -\frac{(E^{(0)}_n)^2}{2mc^2} \left[\frac{4n}{\ell + 1/2} - 3 \right]$$

For the spin-orbit term we need the average $\langle \vec{L} \cdot \vec{S} \rangle$

$$\langle \vec{S} \cdot \vec{L} \rangle = \underbrace{\langle S_x \rangle}_{=0} \underbrace{\langle L_x \rangle}_{=0} + \underbrace{\langle S_y \rangle}_{=0} \underbrace{\langle L_y \rangle}_{=0} + \langle S_z \rangle \langle L_y \rangle = \hbar^2 m_\ell m_s$$

With that

$$E^{(1)}_{fs} = \frac{Ry}{n^3} \alpha^2 \left(\frac{3}{4n} - \left[\frac{\ell(\ell+1) - m_\ell m_s}{\ell(\ell + 1/2)(\ell+1)} \right] \right)$$

Lastly we will consider the intermediate-field Zeeman effect. In this case neither of the two corrections (Zeeman & fine structure) dominates

$$H' = H'_Z + H'_{fs}$$

Let us focus our attention on the particular case of $n=2$. The total perturbation matrix is not diagonal. The most convenient choice of the basis for degenerate perturbation theory is $|n\ell j m_j\rangle$

Recall that $|j m_j \ell s\rangle = \sum_{m_\ell, m_s} |\ell m_\ell\rangle |s m_s\rangle C^{j m_j}_{\ell m_\ell s m_s}$

For $\ell = 0,1$ and $s=\frac{1}{2}$ the expansions are:

$$\left.\begin{array}{l} \psi_1 \equiv |\tfrac{1}{2}\tfrac{1}{2}\rangle = |00\rangle|\tfrac{1}{2}\tfrac{1}{2}\rangle \\ \psi_2 = |\tfrac{1}{2}-\tfrac{1}{2}\rangle = |00\rangle|\tfrac{1}{2}-\tfrac{1}{2}\rangle \end{array}\right\} \ell = 0$$

$$\psi_3 = |\tfrac{3}{2}\tfrac{3}{2}\rangle = |11\rangle|\tfrac{1}{2}\tfrac{1}{2}\rangle$$

$$\psi_4 = |\tfrac{3}{2}-\tfrac{3}{2}\rangle = |1-1\rangle|\tfrac{1}{2}-\tfrac{1}{2}\rangle$$

$$\psi_5 = |\tfrac{3}{2}\tfrac{1}{2}\rangle = \sqrt{\tfrac{2}{3}}\,|10\rangle|\tfrac{1}{2}\tfrac{1}{2}\rangle + \sqrt{\tfrac{1}{3}}\,|11\rangle|\tfrac{1}{2}-\tfrac{1}{2}\rangle$$

$$\psi_6 = |\tfrac{1}{2}\tfrac{1}{2}\rangle = -\sqrt{\tfrac{1}{3}}\,|10\rangle|\tfrac{1}{2}\tfrac{1}{2}\rangle + \sqrt{\tfrac{2}{3}}\,|11\rangle|\tfrac{1}{2}-\tfrac{1}{2}\rangle$$

$$\psi_7 = |\tfrac{3}{2}-\tfrac{1}{2}\rangle = \sqrt{\tfrac{1}{3}}\,|1-1\rangle|\tfrac{1}{2}\tfrac{1}{2}\rangle + \sqrt{\tfrac{2}{3}}\,|10\rangle|\tfrac{1}{2}-\tfrac{1}{2}\rangle$$

$$\psi_8 = |\tfrac{1}{2}-\tfrac{1}{2}\rangle = -\sqrt{\tfrac{2}{3}}\,|1-1\rangle|\tfrac{1}{2}\tfrac{1}{2}\rangle + \sqrt{\tfrac{1}{3}}\,|10\rangle|\tfrac{1}{2}-\tfrac{1}{2}\rangle$$

In this basis the nonzero matrix elements of H'_{fs} are all on the diagonal and are given by $E^{(1)}_{fs} = \frac{(E_n^{(0)})^2}{2mc^2}\left(3 - \frac{4n}{j+\frac{1}{2}}\right)$. The complete W H'_Z has four off-diagonal elements. The matrix is

$$\begin{pmatrix} 5\gamma-\beta &&&&&&& \\ & 5\gamma+\beta &&&&&& \\ && \gamma-2\beta &&&&& \\ &&& \gamma+2\beta &&&& \\ &&&& \gamma-\frac{2}{3}\beta & \frac{\sqrt{2}}{3}\beta && \\ &&&& \frac{\sqrt{2}}{3}\beta & 5\gamma-\frac{1}{3}\beta && \\ &&&&&& \gamma+\frac{2}{3}\beta & \frac{\sqrt{2}}{3}\beta \\ &&&&&& \frac{\sqrt{2}}{3}\beta & 5\gamma+\frac{1}{3}\beta \end{pmatrix}$$

with $\gamma \equiv \left(\frac{\alpha}{8}\right)^2 Ry \qquad \beta \equiv \mu_B |\vec{B}|$

Solving the eigenvalue problem then yields:

$$\varepsilon_1 = E_2^{(0)} - 5\gamma + \beta$$

$$\varepsilon_2 = E_2^{(0)} - 5\gamma - \beta$$

$$\varepsilon_3 = E_2 - \gamma + 2\beta$$

$$\varepsilon_4 = E_2 - \gamma - 2\beta$$

$$\varepsilon_5 = E_2 - 3\gamma + \frac{\beta}{2} + \sqrt{4\gamma^2 + \left(\frac{2}{3}\right)\gamma\beta + \frac{\beta^2}{4}}$$

$$\varepsilon_6 = E_2 - 3\gamma + \frac{\beta}{2} - \sqrt{4\gamma^2 + \left(\frac{2}{3}\right)\gamma\beta + \frac{\beta^2}{4}}$$

$$\varepsilon_7 = E_2 - 3\gamma - \beta/2 + \sqrt{4\gamma^2 - \left(\frac{2}{3}\right)\gamma\beta + \frac{\beta^2}{4}}$$

$$\varepsilon_8 = E_2 - 3\gamma - \frac{\beta}{2} - \sqrt{4\gamma^2 - \left(\frac{2}{3}\right)\gamma\beta + \frac{\beta^2}{4}}$$