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 consider the case of a hydrogen-like atom. In general, the electron has both the spin and orbital angular momentum. Hence, there are magnetic moments corresponding to each of those. The perturbation Hamiltonian describing the interaction of the magnetic moment with an external magnetic field is given by

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

Here $\vec{\mu}_s = -\frac{e}{m}\vec{S}$, while $\vec{\mu}_e = -\frac{e}{2m}\vec{L}$ (the gyromagnetic ratio is different for spin and orbital angular momentum). Thus,

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

The strength of the external magnetic field $\vec{B}$ can be compared to the magnetic field associated with the orbital motion of the electron (which causes spin-orbit interaction), which is about 25 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

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

Let us consider the weak-field regime first. In this regime the fine structure effect obviously dominates 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:

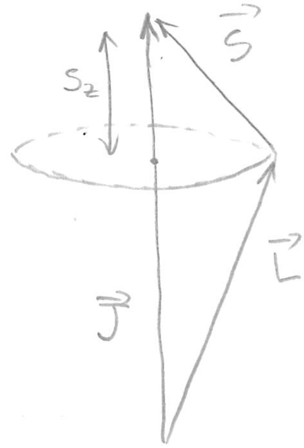
$$E^{(1)} = \langle n\ell j m_j | H' | n\ell j m_j \rangle = \frac{e}{2m} \vec{B} \cdot \langle n\ell j m_j | \vec{L} + 2\vec{S} | n\ell j m_j \rangle$$

$$= \frac{e}{2m} \vec{B} \cdot \langle n\ell j m_j | \vec{J} + \vec{S} | n\ell j m_j \rangle$$

If we assume $\vec{B}$ to be along the z-axis then it becomes

$$E^{(1)} = \frac{e}{2m} B \langle n\ell j m_j | J_z + S_z | n\ell j m_j \rangle \qquad (B = B_z)$$

It may not be immediately obvious that the off-diagonal matrix elements of the perturbation operator H' are zeros in basis $|n\ell j m_j\rangle$. However, we can demonstrate that S_z (and H') commute with J_z (eigenfunction of which $|n\ell j m_j\rangle$ are) "on average".



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

$$\vec{S}_{ave} = \frac{(\vec{S} \cdot \vec{J})}{J^2} \vec{J} \qquad S_{ave\,z} = \frac{(\vec{S} \cdot \vec{J})}{J^2} J_z$$

At the same time we know that

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

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

When we act with operator $\vec{S}\cdot\vec{J}$ on $|nljm_j\rangle$ we obtain

$$\vec{S}\cdot\vec{J}\,|nljm_j\rangle = \frac{\hbar^2}{2}\left[j(j+1)+s(s+1)-l(l+1)\right]|nljm_j\rangle$$

Therefore

$$\langle nljm_j|\,J_z+S_z\,|nljm_j\rangle = \langle nljm_j|\left(1+\frac{(\vec{S}\cdot\vec{J})}{J^2}\right)J_z\,|nljm_j\rangle =$$

$$= \underbrace{\left[1+\frac{j(j+1)+s(s+1)-l(l+1)}{2\,j(j+1)}\right]}_{g_J}\underbrace{\langle nljm_j|\,J_z\,|nljm_j\rangle}_{\hbar m_j}$$

The quantity g_J is called the Lande g-factor.

With that we obtain

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

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

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

Now let us turn our attention to the case when $|\vec{B}| >> |\vec{B}_{internal}|$. This regime is call the Paschen-Back effect. Here the Zeeman splitting dominates over the spin-orbit interaction. Quantum numbers n, ℓ, m_ℓ, and m_s are now "good" quantum numbers. H', which has the form

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

is diagonal in the basis $|n \ell m_\ell m_s\rangle$:

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

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 in $E^{(1)}_{fs}$ 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, $H'_{so} = \frac{Ze^2}{8\pi\varepsilon_0 m^2 c^2} \frac{1}{r^3} \vec{L} \cdot \vec{S}$, we need the average $\langle \vec{L} \cdot \vec{S} \rangle$:

$$\langle \vec{S} \cdot \vec{L} \rangle = \langle S_x \rangle \langle L_x \rangle + \langle S_y \rangle \langle L_y \rangle + \langle S_z \rangle \langle L_z \rangle$$

Here averaging over the spin variables and spatial variables is independent. Now, in the states with a definite L_z and S_z projection we have

$$\langle L_x \rangle = \langle L_y \rangle = 0 \qquad \langle S_x \rangle = \langle S_y \rangle = 0$$

This somewhat intuitive statement (based in symmetry) is derived in the appendix

With that we get

$$\langle \vec{S}\cdot\vec{L}\rangle = \langle S_z\rangle\langle L_z\rangle = \hbar^2 m_e m_s .$$

Recalling that $\langle n\ell|\frac{1}{r^3}|n\ell\rangle = \frac{1}{\ell(\ell+\frac{1}{2})(\ell+1)\,n^3 a^3}$ $(\ell>0)$

we obtain

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

$$+\frac{2(E_n^{(0)})^2 n}{mc^2}\,\frac{m_e m_s}{\ell(\ell+\frac{1}{2})(\ell+1)} = \frac{(E_n^{(0)})^2\, 2n}{mc^2}\left[\frac{3}{4n}-\frac{\ell(\ell+1)-m_e m_s}{\ell(\ell+\frac{1}{2})(\ell+1)}\right]$$

$$= \frac{Ry\,\alpha^3}{n^3}\left[\frac{3}{4n}-\frac{\ell(\ell+1)-m_e m_s}{\ell(\ell+\frac{1}{2})(\ell+1)}\right]$$

where $Ry \equiv \frac{m Z^2 e^4}{32\hbar^2\pi^2\varepsilon_0^2}$ $= 13.6\ \text{eV}\ (Z=1)$

$$E_n^{(0)} = -\frac{mZ^2e^4}{32\hbar^2\pi^2\varepsilon_0^2 n^2} = -\frac{Ry}{n^2}$$

Lastly, let us consider the Zeeman effect in the intermediate-field regime. In this case neither of the two corrections (Zeeman and fine structure) dominates

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

Let us consider a particular case, $n=2$. 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 $$|j m_j \ell s\rangle = \sum_{\substack{m_e, m_s\\ m_e+m_s=m_j}}' C^{j m_j}_{\ell m_e s m_s}\,|\ell m_e\rangle|s m_s\rangle$$

For $l = 0, 1$ and $s = \frac{1}{2}$ these states look as follows

$$\left.\begin{aligned} \psi_1 &= \left|\tfrac{1}{2}\tfrac{1}{2}\right\rangle = |00\rangle\left|\tfrac{1}{2}\tfrac{1}{2}\right\rangle \\ \psi_2 &= \left|\tfrac{1}{2}\,-\tfrac{1}{2}\right\rangle = |00\rangle\left|\tfrac{1}{2}\,-\tfrac{1}{2}\right\rangle \end{aligned}\right\} \begin{array}{l} l=0 \\ \text{states} \end{array}$$

$$\left.\begin{aligned} \psi_3 &= \left|\tfrac{3}{2}\tfrac{3}{2}\right\rangle = |11\rangle\left|\tfrac{1}{2}\tfrac{1}{2}\right\rangle \\ \psi_4 &= \left|\tfrac{3}{2}\,-\tfrac{3}{2}\right\rangle = |1,-1\rangle\left|\tfrac{1}{2},-\tfrac{1}{2}\right\rangle \\ \psi_5 &= \left|\tfrac{3}{2}\tfrac{1}{2}\right\rangle = \sqrt{\tfrac{2}{3}}\,|10\rangle\left|\tfrac{1}{2}\tfrac{1}{2}\right\rangle + \sqrt{\tfrac{1}{3}}\,|11\rangle\left|\tfrac{1}{2}\,-\tfrac{1}{2}\right\rangle \\ \psi_6 &= \left|\tfrac{1}{2}\tfrac{1}{2}\right\rangle = -\sqrt{\tfrac{1}{3}}\,|10\rangle\left|\tfrac{1}{2}\tfrac{1}{2}\right\rangle + \sqrt{\tfrac{2}{3}}\,|11\rangle\left|\tfrac{1}{2}\,-\tfrac{1}{2}\right\rangle \\ \psi_7 &= \left|\tfrac{3}{2}\,-\tfrac{1}{2}\right\rangle = \sqrt{\tfrac{1}{3}}\,|1,-1\rangle\left|\tfrac{1}{2}\tfrac{1}{2}\right\rangle + \sqrt{\tfrac{2}{3}}\,|10\rangle\left|\tfrac{1}{2},-\tfrac{1}{2}\right\rangle \\ \psi_8 &= \left|\tfrac{1}{2},-\tfrac{1}{2}\right\rangle = -\sqrt{\tfrac{2}{3}}\,|1,-1\rangle\left|\tfrac{1}{2}\tfrac{1}{2}\right\rangle + \sqrt{\tfrac{1}{3}}\,|10\rangle\left|\tfrac{1}{2}\,-\tfrac{1}{2}\right\rangle \end{aligned}\right\} \begin{array}{l} l=1 \\ \text{states} \end{array}$$

It turns out that in this basis nonzero matrix elements of H'_{fs} are all on the diagonal and are given by

$$E^{(1)}_{fs} = \frac{(E^{(0)}_n)^2}{2mc^2}\left(3 - \frac{4n}{j+\frac{1}{2}}\right)$$

H'_Z has only four nonzero off-diagonal elements. The complete perturbation matrix $H' = H'_Z + H'_{fs}$ looks as follows

$$
-\begin{pmatrix}
5\gamma-\beta & & & & & & & \\
 & 5\gamma+\beta & & & & & 0 & \\
 & & \gamma-2\beta & & & & & \\
 & & & \gamma+2\beta & & & & \\
 & & & & \gamma-\frac{2}{3}\beta & \frac{\sqrt{2}}{3}\beta & & \\
 & 0 & & & \frac{\sqrt{2}}{3}\beta & 5\gamma-\frac{1}{3}\beta & & \\
 & & & & & & \gamma+\frac{2}{3}\beta & \frac{\sqrt{2}}{3}\beta \\
 & & & & & & \frac{\sqrt{2}}{3}\beta & 5\gamma+\frac{1}{3}\beta
\end{pmatrix}
$$

where

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

Solving this 8×8 eigenvalue problem yields:

$$E_1^{(1)} = -5\gamma+\beta \qquad E_5^{(1)} = -3\gamma+\frac{\beta}{2}+\sqrt{4\gamma^2+\left(\frac{2}{3}\right)\gamma\beta+\frac{\beta^2}{4}}$$

$$E_2^{(1)} = -5\gamma-\beta \qquad E_6^{(1)} = -3\gamma+\frac{\beta}{2}-\sqrt{4\gamma^2+\left(\frac{2}{3}\right)\gamma\beta+\frac{\beta^2}{4}}$$

$$E_3^{(1)} = -\gamma+2\beta \qquad E_7^{(1)} = -3\gamma-\frac{\beta}{2}+\sqrt{4\gamma^2-\left(\frac{2}{3}\right)\gamma\beta+\frac{\beta^2}{4}}$$

$$E_4^{(1)} = -\gamma-2\beta \qquad E_8^{(1)} = -3\gamma-\frac{\beta}{2}-\sqrt{4\gamma^2-\left(\frac{2}{3}\right)\gamma\beta+\frac{\beta^2}{4}}$$

Appendix: Let us show that $\langle L_x\rangle = \langle L_y\rangle = 0$ in any state with a definite value of L_z

For this we can consider the action of the ladder operators $L_\pm$ on $|\ell m\rangle$:

$$L_\pm |\ell m\rangle = \hbar\sqrt{\ell(\ell+1) - m(m\pm 1)}\,|\ell, m\pm 1\rangle \qquad L_\pm = L_x \pm i L_y$$

The expectation value of L_x is then:

$$\langle \ell m| L_+ |\ell m\rangle = \langle \ell m| L_x + iL_y |\ell m\rangle$$

$$\langle \ell m| \sqrt{\ell(\ell+1) - m(m+1)}\,|\ell, m+1\rangle = \langle \ell m|L_x|\ell m\rangle + i\langle \ell m| L_y |\ell m\rangle$$

$$0 = \langle L_x\rangle + i\langle L_y\rangle$$

Both $\langle L_x\rangle$ and $\langle L_y\rangle$ must be real because L_x and L_y are hermitian operators. Hence we can conclude that $\langle L_x\rangle = \langle L_y\rangle = 0$