STRONG / WEAK ZEEMAN EFFECT

We can now use all the power of perturbation theory to define more formally what happens to an atom located within a magnetic field. Let us start from the hydrogen atom Hamiltonian $H_{hydrogen}$

basic? no fine nor hyperfine structure terms!

$$H_{hydrogen} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r^2}$$

Our favorite set of eigenstates are described using the $|n,l,m\rangle$ quantum numbers: they are eigenstates of $\underline{3}$ operators, at the same time: $H_{hydrogen}, L^2, L_z$

and also S^2 spin of electron: it does not even appear in Hamiltonian, hence it commutes with it

$$\overset{\text{operator}}{H_{hydrogen}}|n,l,m\rangle = -\frac{13.6\ eV}{n^2}|n,l,m\rangle$$

$$L^2|n,l,m\rangle = \hbar^2 l(l+1)|n,l,m\rangle$$

$$L_z|n,l,m\rangle = \hbar m|n,l,m\rangle$$

The degeneracy of the energy eigenstates is $\underline{n^2}$: for a given n, each $l = 0,1,.,n-1$ state is allowed, and for each l there are $m = +l, l-1,..0,..-l+1,-l$ (2l+1, in total) possible values for m. You can easily prove that $\sum_{l=0}^{n-1}(2l+1) = n^2$.

We saw that the electron has a magnetic momentum proportional to its spin:

remember Stern-Gerlach

$$\vec{\mu} = -g\frac{\mu_B}{\hbar}\vec{S}$$

where $g = 2$ for electrons and μ_B is the Bohr magneton:

$$\mu_B = \frac{e\hbar}{2m} = 5.8\cdot10^{-5}\ eV/\underset{\text{Tesla}}{T}$$

A magnetic momentum interacts with a magnetic field, thus introducing the following term to my Hamiltonian:

$$\Delta H = -\vec{\mu}\cdot\vec{B}$$

We also saw that the hydrogen atom also has a magnetic moment proportional to its orbital angular momentum: $\longrightarrow$ remember first time we talked about Zeeman effect, before introducing spin

$$\vec{\mu} = -\frac{\mu_B \cdot \vec{L}}{\hbar}$$

(note the absence of the g-factor: we used a classical model of $|\vec{\mu}| = I \cdot A$ where I is the current created by the electron motion, and $A = \pi r^2$ is the area spanned by the electron, in this classical model)

When I put these together, I get:

$$H'_{Zeeman} = -\vec{\mu}_{total} \cdot \vec{B}_{ext} = \frac{\mu_B}{\hbar}(\vec{L} + \underset{\text{the g-factor!}}{\underset{\downarrow}{2}}\vec{S}) \cdot \vec{B}_{ext}$$

There is yet another interaction we left out so far: the spin-orbit interaction. The electron magnetic moment, proportional to its spin, interacts with a magnetic field produced by the current loop created by the relative motion of electron and nucleus; this magnetic field is proportional to the electron orbital angular momentum:

$$H'_{spin\text{-}orbit} = -\vec{\mu}_{electron} \cdot \underbrace{\frac{e\vec{L}}{8\pi\epsilon_0 m c^2 r^3}}_{\vec{B}_{int}\text{ : internal magnetic field}} = \frac{e^2}{8\pi\epsilon_0 m^2 c^2 r^3}\vec{L}\cdot\vec{S}$$

Now, $\vec{B}_{int} \sim 10T$ (Griffith's problem 6.20). We therefore have three regions:

1) WEAK ZEEMAN: spin-orbit dominates, and we know the correct eigenstates for $H^0 + H_{spin\text{-}orbit}$ are NOT $|n, \ell, m, \underset{\text{electron spin along } z}{\underset{\downarrow}{m_s}}\rangle$, but $|n, \ell, j, m_j\rangle$

Why? Because $H_{spin\text{-}orbit} \propto \vec{L}\cdot\vec{S}$ and neither L_z nor S_z commute with $\vec{L}\cdot\vec{S}$, but $\underset{|\vec{L}+\vec{S}|^2}{\underset{\parallel}{|\vec{J}|^2}}$ and $\underset{L_z+S_z}{\underset{\parallel}{J_z}}$ do!

2) INTERMEDIATE ZEEMAN : we will solve qualitatively, but one could use degenerate perturbation theory to find formulae for first-order energy corrections

3) STRONG ZEEMAN : $\vec{B}_{ext} >> \vec{B}_{int}$, we can ignore spin-orbit, and go back to using $|n, \ell, m, m_s\rangle$ as quantum numbers: the term $(\vec{L}+2\vec{S})\cdot\vec{B}_{ext}$ does commute with L^2, $\underbrace{L_z \text{ and } S_z}$.

provided we freely choose $\vec{B}_{ext} = B_z \cdot \hat{z}$

WEAK ZEEMAN

Let us consider $H^0 = H_{hydrogen} + H_{spin\text{-}orbit}$ as my unperturbed Hamiltonian.

The good eigenstates (i.e., the simultaneous eigenstates of H^0 and other operators) are :

$|n, \ell, j, m_j\rangle$:

$$H^0 |n, \ell, j, m_j\rangle = E_{nj\ell} |n, \ell, j, m_j\rangle$$

$$L^2 |n, \ell, j, m_j\rangle = \hbar^2 \ell(\ell+1) |n, \ell, j, m_j\rangle$$

election has spin 1/2! $\hbar^2 s(s+1) = 3\hbar^2/4$ →

$$S^2 |n, \ell, j, m_j\rangle = 3\hbar^2/4 \; |n, \ell, j, m_j\rangle$$

$$J^2 |n, \ell, j, m_j\rangle = \hbar^2 j(j+1) |n, \ell, j, m_j\rangle$$

$$J_z |n, \ell, j, m_j\rangle = \hbar m_j |n, \ell, j, m_j\rangle$$

What is $E_{nj\ell}$? I am going to provide a partial result, because so far we ignored relativistic correction to $H_{hydrogen}$, that provide contributions of the same order as $H_{spin\text{-}orbit}$. Let us put them aside for the time being.

$$\langle n, \ell, j, m_j | H_{hydrogen} | n, \ell, j, m_j\rangle = -\frac{13.6 \text{ eV}}{n^2}$$

$$\langle n, \ell, j, m_j | H_{spin\text{-}orbit} | n, \ell, j, m_j\rangle = \frac{e^2}{8\pi\varepsilon_0 m^2 c^2} \langle n, \ell, j, m_j | \frac{\vec{L}\cdot\vec{S}}{r^3} | n, \ell, j, m_j\rangle$$

$$= \frac{e^2 \hbar^2}{8\pi\varepsilon_0 m^2 c^2} \cdot \underbrace{\frac{1}{2}\left[j(j+1) - \ell(\ell+1) - \frac{3}{4} \right]}_{\vec{L}\cdot\vec{S} = \frac{1}{2}[J^2 - L^2 - S^2]} \cdot \underbrace{\left\langle \frac{1}{r^3} \right\rangle}_{\text{expectation value of } \frac{1}{r^3} \text{ : it not trivially depends on } n \text{ and } \ell}$$

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

Perturbation theory tells us that the first order correction to the energy is:

$$E^1_{zeeman} = \langle n, \ell, j, m_j | H' | n, \ell, j, m_j \rangle = \frac{e}{2m} \vec{B}_{ext} \cdot \underbrace{\langle \vec{L} + 2\vec{S} \rangle}_{\text{expectation value of unperturbed } H}$$

Here is the trick: $\vec{L} + 2\vec{S} = \vec{J} + \vec{S}$ and $\vec{J}$ is constant of motion (it commutes with $H_{hydrogen} + H_{spin\text{-}orbit}$). Let us remember that $\vec{B}_{int} >> \vec{B}_{ext}$: $\vec{L}$ and $\vec{S}$ are precessing rapidly around $\vec{J}$, therefore their (time) average is just their projection along $\vec{J}$:

$$\vec{S}_{average} = \frac{\vec{S} \cdot \vec{J}}{J^2} \cdot \vec{J}$$

Since $\vec{L} = \vec{J} - \vec{S}$, I have: $L^2 = J^2 + S^2 - 2\vec{J} \cdot \vec{S} \Longrightarrow$

$$\vec{S}_{average} = \frac{J^2 + S^2 - L^2}{2J^2} \vec{J}$$

Finally:

$$\langle \vec{L} + 2\vec{S} \rangle = \langle \vec{J} \rangle \cdot \vec{B}_{ext} \cdot \underbrace{\left[1 + \frac{j(j+1) + 3/4 - \ell(\ell+1)}{2j(j+1)} \right]}_{\text{this is called the Landé g-factor, } g_J}$$

Let us take $\vec{B}_{ext} = B_{ext} \cdot \hat{z}$, and get:

$$E^1_{zeeman} = \frac{e}{2m} B_{ext} \, g_J \underbrace{m_j \hbar}_{\text{expectation value of } J_z}$$

Examples of weak Zeeman effect

Consider the state $^2S_{1/2}$: $n = 2$, $\ell = 0$, $j = 1/2$, $m_j = \pm 1/2$.

The Landé g-factor is 2 :

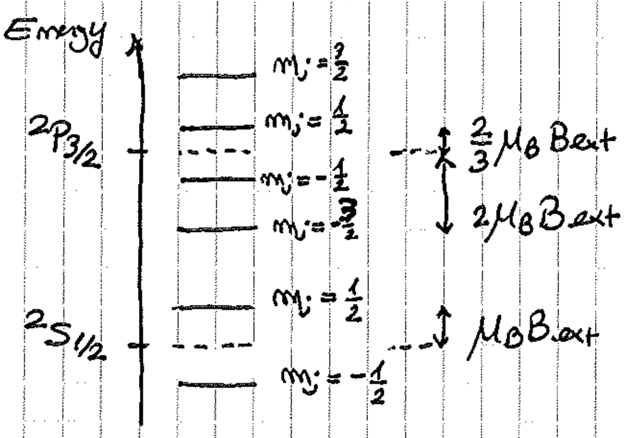
$$g_J = 1 + \frac{j(j+1) + 3/4 - \ell(\ell+1)}{2j(j+1)} = 1 + \frac{3/4 + 3/4 - 0}{2 \cdot 3/4} = 2$$

$$E^1_{\text{zeeman}} = \frac{e\hbar}{2m} B_{ext} \underbrace{g_J}_{2} \underbrace{m_j}_{\pm\frac{1}{2}} = \pm \frac{e\hbar}{2m} B_{ext} = \pm \underbrace{\mu_B}_{\text{Bohr magneton}} B_{ext}$$

Consider a second hydrogen atom in the state $^2P_{3/2}$: $n = 2$, $\ell = 1$, $j = 3/2$; $m_j = \pm 3/2, \pm 1/2$, four possible values of m_j.

$$g_J = 1 + \frac{j(j+1) + 3/4 - \ell(\ell+1)}{2j(j+1)} = 1 + \frac{15/4 + 3/4 - 2}{2 \cdot 15/4} = \frac{4}{3}$$

$$E^1_{\text{zeeman}} = \frac{4}{3} \mu_B B_{ext} \cdot m_j \text{ , where } m_j = \pm 3/2, \pm 1/2$$



(there is another state we left off: $^2P_{1/2}$ where is it located ?)

How many spectral lines will we see? Remember: there exist selection rules! We interpreted the $\Delta\ell = \pm 1$ rule as coming from the fact that our emitted photon carries off one unit of angular momentum. Now I can see that I need:

$$\underset{J_{initial}}{\text{initial atom}} \longrightarrow \underset{J_{final}}{\text{final atom}} + \underset{J=1}{\text{photon}} \Longrightarrow |J_{final} - 1| < J_{initial} < J_{final} + 1$$

The selection rule is $\Delta j = 0, \pm 1$, and $\Delta m_j = 0, \pm 1$

↳ photon can get away with spin = 1 by flipping electron

STRONG ZEEMAN

Now, $H_{zeeman} >> H_{spin\text{-}orbit}$; let us disregard $H_{spin\text{-}orbit}$ for the moment.

Then, let us also take $\vec{B}_{ext} = B_{ext}\,\hat{z}$. Good quantum numbers are n, ℓ, m and m_s, because $H_{hydrogen}+H_{zeeman}$, L^2, L_z, S_z all commute with each other [reminder : $H_{zeeman} \propto \vec{L}+2\vec{S}$]

What are the energies?

$$\langle n,\ell,m,m_s|\,H_{hydrogen}\,|n,\ell,m,m_s\rangle = -\frac{13.6\,eV}{n^2} \qquad \text{same as before}$$

$$\langle n,\ell,m,m_s|\,H_{zeeman}\,|n,\ell,m,m_s\rangle = \langle n,\ell,m,m_s|\,L_z+2S_z\,|n,\ell,m,m_s\rangle\frac{eB_{ext}}{2m}$$

$$= \frac{e\hbar}{2m}B_{ext}\,(m+2m_s)$$

Let us now consider the spin-orbit term as my perturbation:

$$H' = H_{spin\text{-}orbit} = \frac{e^2}{8\pi\varepsilon_0 m^2c^2r^3}\,\vec{L}\cdot\vec{S}$$

First order correction:

$$\langle n,\ell,m,m_s|\,H'\,|n,\ell,m,m_s\rangle = \frac{e^2}{8\pi\varepsilon_0 m^2c^2}\langle n\,\ell\,m\,m_s|\,\frac{\vec{L}\cdot\vec{S}}{r^3}\,|n\,\ell\,m\,m_s\rangle$$

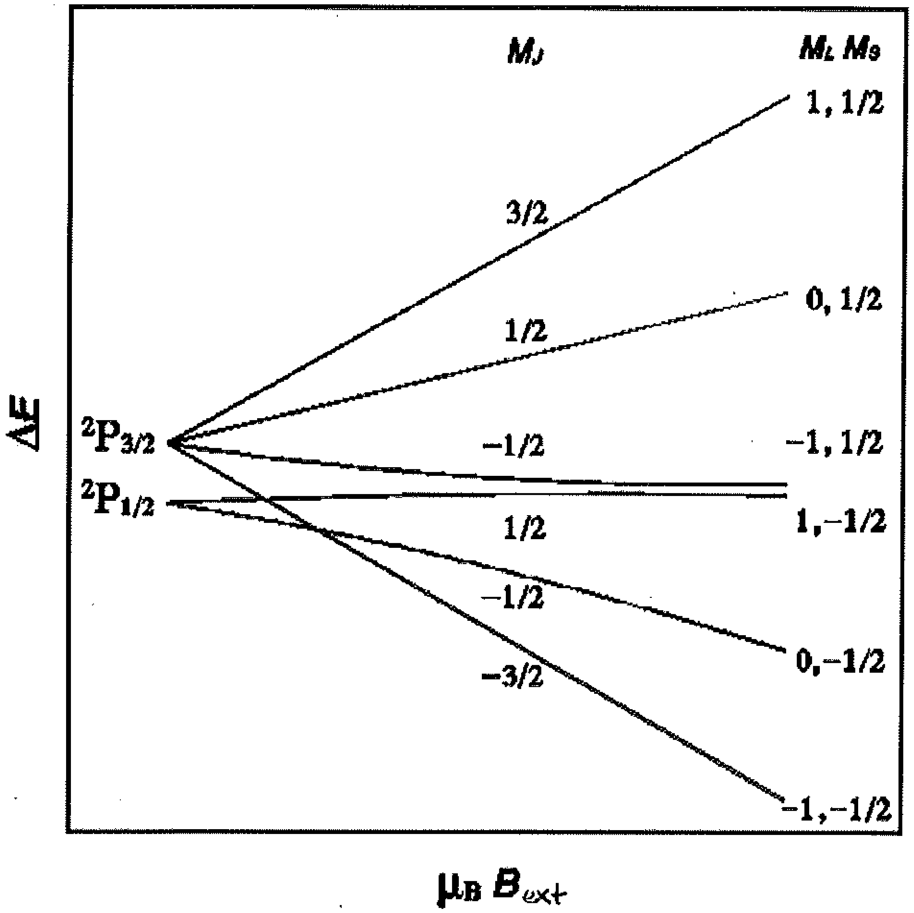
This is complicate (note the $1/r^3$ piece) but let's look at the numerator only. This is easy:

$$\langle n\,\ell\,m\,m_s|\,\vec{L}\cdot\vec{S}\,|n\,\ell\,m\,m_s\rangle = \overbrace{\langle\vec{L}\cdot\vec{S}\rangle}^{\text{expectation value}} = \underbrace{\underset{0}{\underset{\downarrow}{\langle L_x\rangle}}\underset{0}{\underset{\downarrow}{\langle S_x\rangle}}+\underset{0}{\underset{\downarrow}{\langle L_y\rangle}}\underset{0}{\underset{\downarrow}{\langle S_y\rangle}}}_{\text{my eigenstates are eigenstates of } L_z \text{ and } S_z\text{: their expectation values of } L_x, L_y, S_x, S_y \text{ are zero}}+\underset{\hbar m}{\underset{\downarrow}{\langle L_z\rangle}}\underset{\hbar m_s}{\underset{\downarrow}{\langle S_z\rangle}}$$

$$= \hbar^2\,\underset{\uparrow}{m}\cdot m_s$$

this results tells me that I can expect a term $m\cdot m_s$ inside the expression for $\underbrace{\left\langle\frac{\vec{L}\cdot\vec{S}}{r^3}\right\rangle}_{\text{expectation value}}$

Energy spectrum



S, P, D, F indicate $\ell=0,1,2,3$ states

Notes :

- $^2P_{3/2}$ identifies the $n=2$, $\ell=1$ (the P letter), $j=3/2$ states: there are four, corresponding to $m_j=\pm 3/2, \pm 1/2$. Similarly, $^2P_{1/2}$ indicates the $|\overset{n}{2}\ \overset{\ell}{1}\ \overset{j}{\frac{1}{2}}\ m_j\rangle$ states
- when $B_{ext}=0$, I have fine splitting: the six states $|n\,\ell\,m\,m_s\rangle = |2, 1, m=1,0,-1, m_s=\pm 1/2\rangle$ are not good eigenstates of the Hamiltonian with the spin-orbit term: Hspin-orbit lifts the 6-fold degeneracy! The good eigenstates are linear combinations of the $|n\,\ell\,m\,m_s\rangle$ states with defined J^2 and J_z ⇒ we used Clebsch-Gordan here
- when B_{ext} becomes very large, $E^1 \propto (m_L+2m_s)$ and the states $|n\ell m\, m_s\rangle$ return being (approximately) good eigenstates. Notice the birth of a degeneracy: $m_\ell+2m_s$ is the same if $m_L=1, m_s=-\frac{1}{2}$ or $m_\ell=-1, m_s=\frac{1}{2}$