The Zeeman Effect

(Atoms in static fields)

So far, we've only considered "bare" atomic structure, i.e. the problem of atoms in the absence of applied fields.

We described important parts of this structure, namely the spin-orbit part of the fine structure and the hyperfine interactions as electron spins and nuclear spins interacting with an effective $B$-field, i.e.

Fine structure

$H_{s-o} = \mathbf{\mu}_e \cdot \mathbf{B}_{\text{eff}}$

$H_{s-o} \propto \mathbf{S} \cdot \mathbf{L}$

Hyperfine

$H_{hf} = -\mathbf{\mu}_n \cdot \mathbf{B}_{\text{eff}}$

$H_{hf} \propto \mathbf{I} \cdot \mathbf{J}$

It's natural to ask, "what effect does an external (static) magnetic field have on our states and their energies?"
General picture:

We've seen that the various angular momenta get "coupled" by their interactions, such that the symmetry of the Hamiltonian is changed and new quantum numbers / basis states are relevant.

i.e., for \( S_z, |S, m_s⟩ \) instead of \( |m_L, m_s⟩ \)
and for \( I \vec{z}, |I, m_F⟩ \) instead of \( |m_I, m_F⟩ \)

When the change in energy due to the applied field begins to dominate over the contribution due to these \((S_z, I \vec{z})\) interactions, the angular momenta will become uncoupled, and the states w/ well-defined angular momentum w/ respect to the \( z \)-axis (direction of applied field, breaking symmetry of the problem) for the respective components will become our good basis states.
Let's start by neglecting hyperfine (think $I=0$)

new term in Hamiltonian given by

$$H_B = -\vec{\mu} \cdot \vec{B}_{\text{ext}}$$

where

$$\vec{\mu} = \vec{\mu}_e + \vec{\mu}_s$$

due to electron

due to spin angular momentum

electron orbital angular momentum

$$\vec{\mu}_e = -\frac{m_e}{\hbar} \vec{L}$$

and

$$\vec{\mu}_s = -g_s \frac{m_e}{\hbar} \vec{S}$$

($\Delta E_{gs}$ is general)

For low fields, $E_{zeeman} \sim m_e B_z \ll E_{gs}$, $J, m_J$ will remain good quantum numbers, i.e. $\vec{L}$ and $\vec{S}$ will still be coupled as their interactions are the dominant term.

rewrite as

$$H_B = \frac{m_e}{\hbar} g_J \vec{J} \cdot \vec{B}_{\text{ext}}$$

where

$$g_J \vec{J} = \vec{L} + g_s \vec{S}$$

The Landé $g$-factor

$g_J$ can be found at low field

by considering the projection of $\vec{\mu}$ onto $\vec{J}$

$$g_J = \frac{\langle \vec{L} \cdot \vec{J} \rangle + g_s \langle \vec{S} \cdot \vec{J} \rangle}{\Delta (J(J+1) \hbar^2)}$$

with $g_s \approx 2$

$$g_J = 1 + \frac{\Delta (J(J+1) - L(L+1) + S(S+1))}{2(J(J+1))} = \frac{3}{2} + \frac{5(S+1) - L(L+1)}{2J(J+1)}$$

see Foot Ch 5.5
The 1st order energy shift at low fields will be
\[ \Delta E = \langle n, J, m_J | H_B | n, J, m_J \rangle = \frac{\mu_B}{h} g_J \langle n, J, m_J | J \cdot \vec{B} | n, J, m_J \rangle \]
with \( \vec{B} = Bz \hat{z} \)
\[ \Delta E = \frac{\mu_B}{h} g_J \langle n, J, m_J | J_z | n, J, m_J \rangle = \mu_B g_J m_J B_z \]
~ linear shift in energy according to \( m_J, g_J \) values

For an example:
- For \( I = 0, S = \frac{1}{2} \)
  - \( g_J = \frac{4}{3} \rightarrow n_0 P_{3/2} \)
  - \( g_J = \frac{2}{3} \rightarrow n_0 P_{1/2} \)

\[ \text{Note: in } H, \]
for the excited \( n_0 = 2 \) state:
\[ E_{5/2} > E_{3/2} \]

again, this low-field, linear Zeeman shift
regime will basically hold as long as \( E_{\text{Zeeman}} \ll \Delta E_{fs} \)

For \( H, \Delta E_{fs} \sim 10 \text{ GHz}, \mu_B \approx 1.4 \text{ MHz/G} \)

for heavy alkalis:
more like \( 10^{-4} - 10^{-3} \text{T} \)

\[ \approx 1T = 10,000 \text{ G} \]
for this to break down completely
High-field limit \[ \mu_B B_z \gg \Delta E_{fr} \]

In this limit, \( m_L \) and \( m_S \) are the "good" quantum numbers (states with well-defined angular momentum, \( \text{w.r.t.} \) the \( z \)-axis for both \( L \) & \( S \)), and the spin-orbit coupling is only a perturbation. This is referred to as the Paschen-Back limit:

\[
\mathbf{H}_0 = \frac{\mu_B}{k} (\mathbf{L} + g_S \mathbf{S}) \cdot \mathbf{B} = \frac{\mu_B}{k} (\mathbf{L} + 2 \mathbf{S}) \cdot \mathbf{B}
\]

and the Zeeman component of the energy is

\[
E_{mag} = \langle n, L, S, m_L, m_S | \mathbf{H}_0 | n, L, S, m_L, m_S \rangle = \mu_B B (m_L + 2m_S)
\]

For hydrogen, we'll find this limit for

\[ \mu_B B \gg \Delta E_{fr} \quad B \sim 10^3 \]

\[ \text{Li} \rightarrow \Delta E_{fr} \sim 10 \text{ GHz}, \text{ so roughly same as } H \]

For heavier alkalis, \( \Delta E_{fr} \sim \begin{cases} 0.5 \text{ THz for Na} \\ 2 \text{ THz for K} \\ 7 \text{ THz for Rb} \\ 16 \text{ THz for Cs} \end{cases} \]

\[ \rightarrow \quad \begin{cases} 10^2 \sim 10^4 \text{ T} \\ \text{or } 10^6 \sim 10^8 \text{ G} \end{cases} \]

Hard to get to Paschen-Back regime for fine structure.

Let's look at hyperfine structure.
Zeeman w/ hyperfine structure

The interaction of the various angular momentum components of an external field can again be written as

$$\mathbf{H} = -\mathbf{\mu} \cdot \mathbf{B}_{\text{ext}}$$

where

$$\mathbf{\mu} = \mathbf{\mu}_l + \mathbf{\mu}_s + \mathbf{\mu}_i$$

$$\mathbf{\mu}_i = \frac{-\mathbf{M}_i}{\hbar} \left( I + g_i S \right) + \mathbf{\mu}_i$$

we saw that the expression for $\mathbf{\mu}_i$ varies quite a bit from reference to reference. Both the sign and magnitude convention for $g_i$ vary

e.g. $M^i_l = + \frac{g_i M_i}{\hbar}$ or $M^i_+ = \frac{+g_i M_i}{\hbar}$

is sometimes used,

where $M_i = M_B m_e \frac{\mu_B}{m_p} \approx M_B \frac{1836}{10^{-3}}$

and $g_i$ is of order unity

Note: conventions w/ the opposite sign are also used

( Watch signs / magnitudes on HW questions - be consistent w/ Stock)
We'll write

$$H = \frac{MB}{\hbar} (I + g_s S) - \frac{g_I MN}{\hbar} \mathcal{I},$$

where $g_s \approx 2$ and $g_I$ is of order unity, depending on the atom's nuclear state.

Again, we saw that $F$ & $m_F$ were good quantum numbers in zero $B$-field, where the $I: \mathcal{I}$ interaction was the dominant perturbation to $H_{\text{HFS}}$.

**Low-field limit** $MBB \ll \Delta E_{\text{HFS}}$

$F$ & $m_F$ will remain good quantum numbers in this limit.

$$H_B = \frac{MB}{\hbar} \bar{g_F} \bar{F} \cdot \bar{B}$$

where

$$g_F = g_s \frac{F(F+1) - I(I+1) + J(J+1)}{2F(F+1)}$$

and

$$+ \frac{g_I MN}{MB} \frac{F(F+1) - J(J+1) + I(I+1)}{2F(F+1)}$$

smaller by roughly $10^{-3}$ factor

$$g_F \approx g_s \frac{F(F+1) - I(I+1) + J(J+1)}{2F(F+1)}$$
\[ \Delta E_{\text{Zeeman}}^{\text{low-field}} = \langle \hat{H}_B \rangle = \langle F, m_F | \mu_B g_F \hat{B} | F, m_F \rangle \]

for low fields

as before

\[ g_F = g_J = 2 \]

\[ B = B_Z \hat{z} \text{ w.r.t. } g \]

for \( ^{87}\text{Rb}, I = \frac{3}{2} \)

As in hydrogen, \( I = \frac{1}{2} \) for \( ^{15} \text{N}_2 \)

At high fields, where high means \( \Delta E_{\text{Zeeman}} \sim \mu_B B_Z \gg \Delta E_{\text{hf}} \),

Back - Goudsmit regime (also called Paschen - Back)

\[ I \text{ and } J \text{ are uncoupled, and states } \left| F, m_F \right> \text{ with well-defined } m_F \text{ w.r.t. } \hat{z} \text{ are eigenstates,} \]

so \( \left| F, m_F \right> \rightarrow \left| m_I, m_J \right> \)

at high fields - the hyperfine (\( I + J \)) interaction is just a perturbation that gets less important as \( B_Z \) increases.
\[ H^\text{high}_B = \left[ \frac{\mu_B}{k} \left( 1 + g_S \frac{S}{I} \right) - \frac{g_I \mu_N}{k} I \right] \cdot \vec{B} \]

\[ \Delta E^\text{high}_B = \langle I, m_I, J, m_J | H^\text{high}_B | I, m_I, J, m_J \rangle \]

\[ = \mu_B \left[ g_J m_J - \frac{g_I}{\mu_B} m_I \right] B_z \]

at which field this occurs, i.e. when the linear Zeeman effect fully breaks down, depends on the atom (i.e. on \( A_{hs} \)) as well as whether you're considering the s-level or excited states.

Typical value, for \( A \sim 1 \text{ GHz} \) and \( \mu_B = \frac{1.4 \times 10^6 \text{ MHz}}{\text{esu}} \),

will be roughly 100s of gauss

The \( \frac{S}{I} \) coupling will still have an absolute energy shift at high fields,

\[ \Delta E^\text{hy} = \langle I, m_z, J, m_J | \hbar A_{hs} \frac{S}{I} \frac{S}{I} | I, m_z, J, m_J \rangle = \hbar A_{hs} m_I m_J \]
Whole picture (for $^{57}$Rb, $I = 3/2$)

- $m_I = 3/2$
- $m_J = +1/2$
- $g_J = 2$

$I = 3/2$, $m_J \in \{-3/2, -1/2, 1/2, 3/2\}$

Change in symmetry of electron's eigenstates

You'll solve this numerically in HW 2

$F = 2$, $g_F = 1/2$

$F = 1$, $g_F = -1/2$

Low field

High field

Major note: $\mu = -\frac{dE}{dB}$, i.e. the slope of the energy vs. magnetic moment depends on $B$. 
\[ H = \hbar \alpha_{\text{F}} \frac{\mathbf{I} \cdot \mathbf{J}}{\hbar^2} - \mu_0 \mathbf{B} - \mu_1 \mathbf{B} \]

diagonal in \( \{|F, m_F\}\) basis

\[ H = \hbar \alpha_{\text{F}} \frac{\mathbf{I} \cdot \mathbf{J}}{\hbar^2} + \frac{\mathbf{m}_B}{\hbar} \left[ g_\Sigma J_z - g_I \frac{\mu_B}{\mathbf{m}_B} \mathbf{I} \cdot \mathbf{z} \right] B_z \]

diagonal in \( \{|m_I, m_J\}\) basis

w/ \( \mathbf{B} \) along \( \mathbf{z} \), express \( \mathbf{I} \cdot \mathbf{J} \) as

\[ H = \hbar \alpha_{\text{F}} \frac{\mathbf{I} \cdot \mathbf{J}}{\hbar^2} + \frac{\mathbf{m}_B}{\hbar} \left[ g_\Sigma J_z - g_I \frac{\mu_B}{\mathbf{m}_B} \mathbf{I} \cdot \mathbf{z} \right] B_z \]

need to express \( \mathbf{I} \) in terms of \( \{|I, m_I, J, m_J\}\) states

For the particular case of alkali ground states, there is an analytical solution (Breit-Rabi formula)

\[ L = 0 \]
\[ 5 = \mathbf{J} = \mathbf{S} \]
\[ \mathbf{I} \cdot \mathbf{J} = \mathbf{I} \cdot \mathbf{S} = \frac{\mathbf{S} \cdot \mathbf{S}}{2} \]

\[ \mathbf{S} = \mathbf{S}_z \]

Key task: construct \( \langle m_I', m_J' | I_+ S_- + I_- S_+ | m_I, m_J \rangle \)

terms, then solve

In HW#2, you'll write down \( H \) as a matrix and diagonalize it, solving for eigenstates and energies.

\[ \frac{1}{2} (I_+ S_+ + I_- S_-) \]

Diagonal

Off-diagonal
The solution, the Breit-Rabi formula, is

\[ E = -\frac{\Delta E_{hf}}{2(2I+1)} - \frac{g_I \mu_B m_I B_z}{\mu_B} + \frac{\Delta E_{hf}}{2} \sqrt{1 + \frac{4m x}{2I+1} + x^2} \]

where \( m = m_I \pm m_J \) depending on this sign.

\[ X = \left( g_J + g_I \frac{\mu_B}{\mu_N} \right) \frac{\mu_B B_z}{\Delta E_{hf}} \]

and\[ \Delta E_{hf} = \frac{(2I+1) \hbar A}{2} \]

(also) \[ |F, m_F\rangle = \alpha(B_2) |m_I = m_F - \frac{1}{2}, m_J = \frac{1}{2}\rangle \]

+ \[ \beta(B_2) |m_I = m_F + \frac{1}{2}, m_J = -\frac{1}{2}\rangle \]

change of \( \alpha, \beta \) w/ \( B_z \) relates to change of symmetry, change of eigenstates.

labelling state by the zero-field state to which it connects