Atoms in external (DC) Fields:

Zeeman Shifts:

Look at B-fields in regime $H_B, H_{S-O} \ll H_{re}$

ignore $\vec{I}$ for now.

$H_B \to -\vec{\mu}\cdot\vec{B}$, $H_{S-O} \to$ spin orbit, $H_{re} \to$ residual electrostatic

$\vec{L}, \vec{S}$ approximately good quantum numbers.

$\vec{B}$ is a classical field

$$H = H_0 + H_{SO} + H_B = H_0 + \beta_{SL}\,\vec{S}\cdot\vec{L} - \vec{\mu}\cdot\vec{B}$$

$$\vec{\mu} = -\mu_B \frac{\vec{L}}{\hbar} - g_s \mu_B \frac{\vec{S}}{\hbar}, \qquad \mu_B = \hbar e/2m_e, \quad g_s \simeq 2$$

If $H_B, H_{SO} \ll H_{re}$, we can ignore radial contributions and look entirely at angular momentum states.

For arbitrary $\vec{B}$, $\vec{J}$ is not a good quantum # (total J not conserved) but M_J is conserved.

Solution is a diagonalization of $\beta_{SL}\,\vec{S}\cdot\vec{L} - \vec{\mu}\cdot\vec{B}$ over the set of states

~~[illegible]~~ ~~[illegible]~~

$|M_J\rangle$ where several different states with the same M_J may exist.

a useful unit: Larmor frequency (precession frequency) for an electron in a B-field: $\omega_L/2\pi B = \dfrac{1.4\text{ MHz}}{\text{gauss}}$

Consider first $H_B << H_{SO}$:

J is a good quantum #, eigenstates of $\beta_{SL}\vec{S}\cdot\vec{L}$ are

$|J, M_J\rangle$ where $|L-S| < J\ |L+S|$

Treat H_B perturbatively, and use projection theorem on $\vec{\mu}$:

$$\vec{\mu} = \frac{\langle\vec{\mu}\cdot\vec{J}\rangle}{\hbar^2 J(J+1)}\vec{J}$$ where the expectation value can be taken for any m-level

$$H_B = -\vec{\mu}\cdot\vec{B} = -\frac{\langle\vec{\mu}\cdot\vec{J}\rangle}{\hbar^2 J(J+1)}\vec{J}\cdot\vec{B} \equiv g_J \mu_B \frac{\vec{J}}{\hbar}\cdot\vec{B}$$

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

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

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

If S, L, J are pretty good quantum #'s, $A^2 = \hbar^2 A(A+1)$ $A = S, J, L$

$$g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)} + \delta_a\left(\frac{1}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}\right)$$

where $g_s = 2 + \delta_a$, $\delta_a = 0.0023193043718(75)$

Examples:

$$H_B = g_J \mu_B \frac{\hat{J}_z}{\hbar} B_z \rightarrow \boxed{E = g_J \mu_B B_z m_J}$$

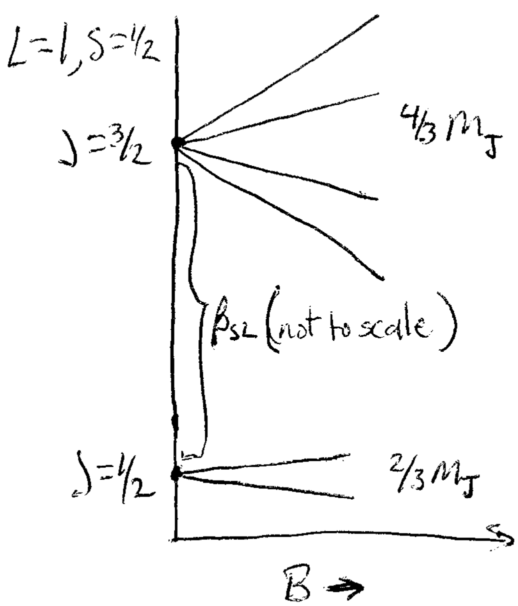
$L = 0,\ s = 1/2 \qquad g_J = 2 + \delta_a = g_s$

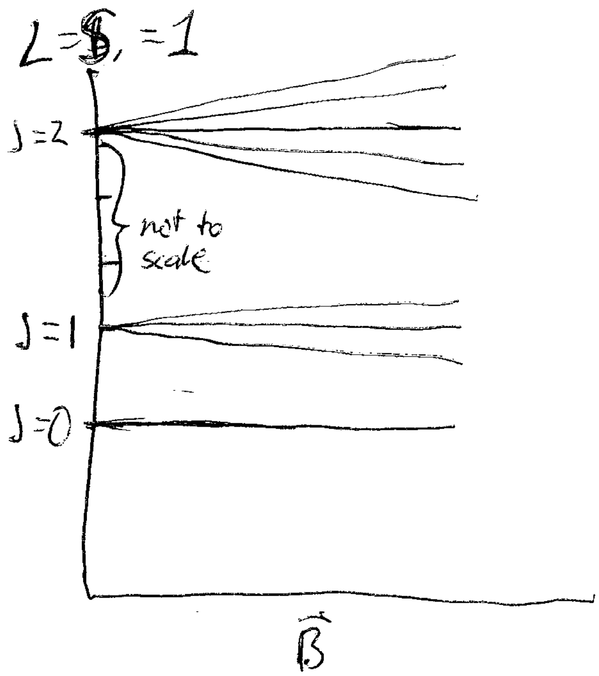
$L = 1,\ s = 1/2 \qquad g_J = \begin{cases} 4/3 & J = 3/2 \\ 2/3 & J = 1/2 \end{cases}$

$L,\ S = 1/2 \qquad g_J = \begin{cases} \dfrac{2(L+1)}{2L+1} & J = L + 1/2 \\ 2L/2L+1 & J = L - 1/2 \end{cases}$

$\left.\begin{matrix} L = 1,\ s = 1 \\ L = S \end{matrix}\right\} \longrightarrow g_J = 3/2$

$\delta_a \simeq 0$

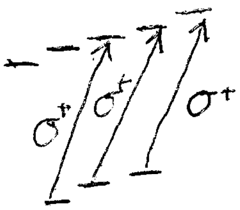




If g_J varies as a function of J, this gives rise to the anomalous Zeeman effect.

example: imagine an optical transition between singlet states, ${}^1D_2 \leftrightarrow {}^1P_1$ in a magnetic field.

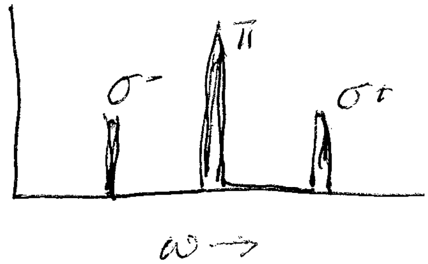
Since $S=0$, $g_J = 1$ for Both states.



all 3 σ^+ transitions have the same frequency, likewise for π, σ^-

Among the 9 possible transitions, only 3 frequencies.

spectrum =

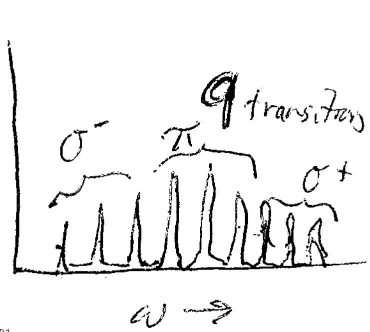


normal Zeeman effect.

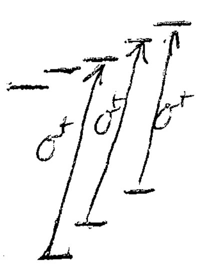
example: optical transition between ${}^3P_2 \longleftrightarrow {}^3S_1$

$g_J({}^3P_2) = 3/2$

$g_J({}^3S_1) = 2$



anomalous Zeeman



σ^+ now has 3 frequencies, likewise for π, σ^-

Now consider the other extreme:

$$H_B \gg H_{SO} \quad (\text{but both still} \ll H_{re})$$

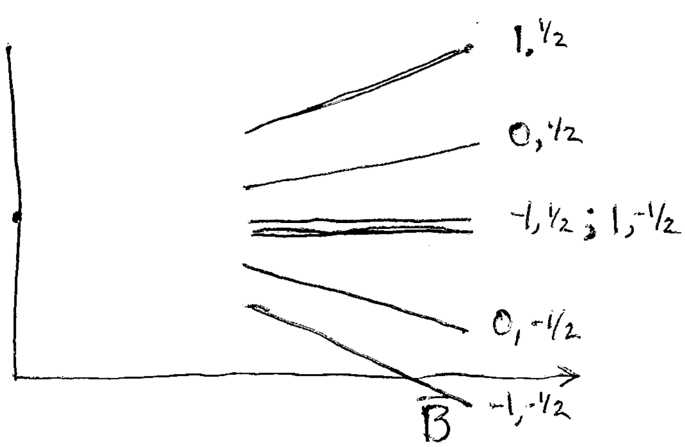
J, L, S bad quantum #s, but M_J, M_L, M_S are good.

$$H_B = -\vec{\mu}\cdot\vec{B} = \mu_B \frac{\vec{L}}{\hbar}\cdot\vec{B} + g_s \mu_s \frac{\vec{S}}{\hbar}\cdot\vec{B}$$

$$= \mu_B (M_L + 2M_S) B$$

example: $^4He^+$, $2p$ levels $J=1/2$, $J=3/2$ $\quad I=0$

$L=1$, $S=1/2$ $\quad \Delta_{SO} \simeq 175$ GHz



$|M_J\,(M_L, M_S)\rangle =$

$|3/2, 1, 1/2\rangle \qquad |1/2, 1, -1/2\rangle$

$|1/2, 0, 1/2\rangle \qquad |-1/2, 0, -1/2\rangle$

$|-1/2, -1, 1/2\rangle \qquad |-3/2, -1, -1/2\rangle$

ok for $\mu B \gg 175$ GHz
$\simeq 1.3$ Tesla

This is a large field, generally true that spin-orbit is large, and it gets larger for larger Z, so it is difficult to reach this regime for decoupling electron orbital + spin. (e.g. for Rb, $\Delta_{SO} \gtrsim 10^{12}$ Hz)
(Intermediate regime discussed in Mathematica Notebook)

~~Look at Hyperfine Zeeman~~

Intermediate regime:

neither H_{so} or H_B are diagonal. Pick a basis and diagonalize $H_{so} + H_B$

choose $|F, M_F\rangle$ basis, for example

H_{so} is diagonal: $\frac{\beta_{so}}{2}\left(J(J+1) - S(S+1) - L(L+1)\right)$

$\vec{\mu}\cdot\vec{B}$ is not diagonal, but can only mix same M_J states

Leads to diagonal elements
$$-\langle J M_J | \vec{\mu}\cdot\vec{B} | J M_J \rangle$$

and off-diagonal elements
$$-\langle J M_J | \vec{\mu}\cdot\vec{B} | J' M_J \rangle$$
($J' = J \pm 1, 0$, why?) (ie $J' \neq J+2$)

$$-\langle J M_J | \vec{\mu}\cdot\vec{B} | J' M_J \rangle = \sum_{M_L M_S} \frac{\mu_B}{\hbar} \langle J M_J | L_z + 2S_z | L M_L S M_S \rangle \langle L M_L S M_S | J' M_J \rangle$$

$$= \sum_{M_L M_S} \mu_B (M_L + 2M_S) \underbrace{\langle J M_J | L M_L S M_S \rangle \langle L M_L S M_S | J' M_J \rangle}_{\text{Clebsch-Gordan Coefficients.}}$$

it turns out that the on-diagonal terms are just $g_J \mu_B B m_J$

See Mathematica Notebook for example.

Consider nuclear moments:

$$\vec{\mu} = -g_J \frac{\mu_B}{\hbar} \vec{J} + g_I \frac{\mu_N}{\hbar} \vec{I} \simeq -g_J \frac{\mu_B}{\hbar} \vec{J}$$

(assume that the B-field is small enough that $\vec{\mu} \cdot \vec{B} \ll \beta_{SO}$, i.e. that J is always an approximately good quantum #. This is not so true for Hydrogen)

The Zeeman energy is approximately independent of $\bar{I}$, but the hyperfine splitting depends on $\bar{I}$, which affects eigenstates.

$$H_{HF} = A_J \vec{I} \cdot \vec{J} + \underbrace{B_J \frac{\left(3(\vec{I} \cdot \vec{J})^2 + \frac{3}{2}(\vec{I} \cdot \vec{J}) - I(I+1)J(J+1)\right)}{2I(2I-1)J(2J-1)}}_{J, I > 1/2}$$

The physics is almost the same as for fine-structure Zeeman effect, except 1) energies are smaller
2) $g_I \mu_N \simeq 0$, while $g_S \mu_B \cong 2\mu_B$

Hyperfine Zeeman effect:

Small field limit: $\boxed{E = g_F \mu_B B m_F}$

$|F, m_F\rangle$ initial state, $F \simeq$ good quantum #

projection theorem:

$$H_B \stackrel{\text{def}}{=} -\vec{\mu}_e \cdot \vec{B} = -\frac{\langle \vec{\mu}_e \cdot \vec{F} \rangle}{\hbar^2 F(F+1)} \vec{F} \cdot \vec{B} \equiv g_F \mu_B \frac{\vec{F} \cdot \vec{B}}{\hbar}$$

$$g_F = \frac{-\langle \mu_e \cdot \vec{F} \rangle}{\hbar \mu_B F(F+1)} = \frac{g_J \langle \vec{J} \cdot \vec{F} \rangle - g_I \mu_N/\mu_B \langle \vec{I} \cdot \vec{F} \rangle}{\hbar^2 F(F+1)}$$

$$g_F = \left(\frac{1}{2} + \frac{J(J+1) - I(I+1)}{2F(F+1)}\right) g_J - \left(\frac{1}{2} - \frac{J(J+1) - I(I+1)}{2F(F+1)}\right) g_I \underbrace{\frac{\mu_N}{\mu_B}}_{\simeq 0}$$

$$= \left(\frac{1}{2} + \frac{J(J+1) - I(I+1)}{2F(F+1)}\right)\left(g_J + g_I \frac{\mu_N}{\mu_B}\right) - g_I \frac{\mu_N}{\mu_B}$$

Large field limit:

$|M_F, M_J M_I\rangle$ are eigenstates of $\vec{\mu} \cdot \vec{B}$

since $\mu_N \simeq 0$, the states split into $2J+1$ groups of $2I+1$ states, each group has a slope of:

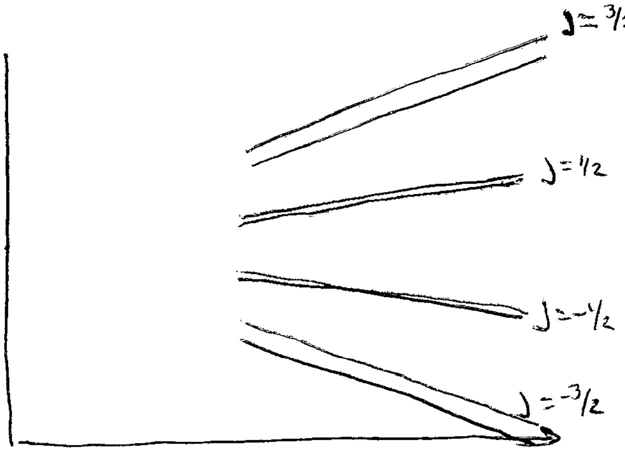
$g_J \mu_B M_J B$

They are spaced due to the hyperfine interaction A_{HF}

$\langle M_F, M_J, M_I | A_{HF} \vec{I} \cdot \vec{J} | M_F, M_J, M_I \rangle$.

Example: $J = 3/2$, $I = 1/2$

There are $(2J+1) \times (2I+1) = 8$ states total:



Overall slope is

$$g_J \mu_B B m_J$$

First order energy shift

$$\langle m_J m_I | \frac{A_{HF}}{\hbar^2} \vec{I} \cdot \vec{J} | m_J m_I \rangle$$

$$= \langle m_J m_I | \frac{A_{HF}}{\hbar^2} I_z J_z | m_J m_I \rangle$$

$$= A_{HF} \, m_J m_I$$

$\rightarrow$ offset is $\frac{A_{HF}}{4}$ or $\frac{A_{HF} 3}{4}$

Intermediate regime:

in the intermediate regime, the full Hamiltonian $H_{HF} + H_B$ must be diagonalized.

If, however, no more than 2 states at a time are coupled, then the diagonalization is easily dealt with analytically. (2x2 diagonalization)

$\rightarrow$ Breit-Rabi equation for Zeeman effect.

Example: $J = 1/2$, $I = 3/2$ (see mathematica code)

$F=2$, $m_F = \pm 2$ is the stretched state $\rightarrow$ no coupling to other states, slope is fixed.

$$E = \frac{3}{4} A_{HF} \pm \mu_B B \quad , \quad \Big(\overbrace{g_J}^{1/2} \, g_F \, \overset{2}{m_F} = 1 \Big)$$

Similar for other coupled m_F levels $F=2, m_F=1$ $F=1, m_F=1$

$\left.\begin{matrix} (F=2)\; m_F = 0 \\ (F=1)\; m_F = 0 \end{matrix}\right\}$ states are coupled (F is not a good quantum #)

diagonalize the sub-space

$$H_B = \begin{array}{cc} \begin{pmatrix} 0 & \mu_B B \\ \mu_B B & 0 \end{pmatrix} & \begin{array}{l} m_F = 0\ (F=2) \\ m_F = 0\ (F=1) \end{array} \end{array}$$

$$H_{A_H} = \begin{pmatrix} 3/4\, A_{HF} & 0 \\ 0 & -5/4\, A_{HF} \end{pmatrix}$$

(sometimes people set the offset to make this matrix symmetric around zero)

$$E = -\frac{A_{HF}}{4} \pm \sqrt{A_{HF}^2 + \mu_B^2 B^2}$$

In general: $$E = -\frac{A_{HF}}{(2I+1)} \pm \sqrt{A_{HF}^2 + \frac{4m\, A_{HF}}{(2I+1)} \frac{g_J}{2} \mu_B B + \left(\frac{g_J}{2}\right)^2 \mu_B^2 B^2}$$

See Mathematica code for more full example.