Tuesday, October 28, 2025

Zeeman substructure

The interaction of an atom with an external $\vec{B}$-field is given by

positive 1.4 MHz/G

$$H_{Zeeman} = \frac{+\mu_B}{\hbar}\left[g_S \vec{S} + g_L \vec{L} + g_I \vec{I} \right] \cdot \vec{B}$$

$S_z \quad L_z \quad I_z \quad B_z$

where $g_L = 1 - \frac{m_e}{M_{nucleus}} \simeq 1$

for $\vec{B} = B\hat{z}$
$\hookrightarrow \hat{z}$ = quantization axis

$$g_S = \underbrace{2.0023193043 62}_{\text{9 digits of agreement with QED theory}} \simeq 2$$

g_I = nuclear g-factor $\simeq -9.95141 \times 10^{-4}$ for ^{87}Rb

$$\mu_B = \frac{e\hbar}{2m_e} = +9.27408 \times 10^{-24}\ J/T \simeq +1.4\ MHz/G$$

If the Zeeman energy shift is small compared to the fine structure splitting, then according to perturbation theory

lots of math

very small

$$E(J, m_J) = \langle J, m_J | H_{Zeeman} | J, m_J \rangle = \frac{\mu_B}{\hbar}\left(g_J J_z + g_I I_z \right) B_z$$

with the Landé factor g_J given by

$$g_J = g_L \frac{J(J+1) - S(S+1) + L(L+1)}{2J(J+1)} + g_S \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

for $g_s = 2$, $g_L = 1$, then $g_J = 1 + \dfrac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$

Setting $g_I = 0$, we can see this in the following manner

$\hookrightarrow$ $H_{zeeman} \propto J_z B_z$

$$E(J, m_J) = \langle J, m_J | H_{zeeman} | J, m_J \rangle$$

$$= \langle J, m_J | \frac{\mu_B}{\hbar} (\vec{L} + 2\vec{S}) \cdot \vec{B} | J, m_J \rangle$$

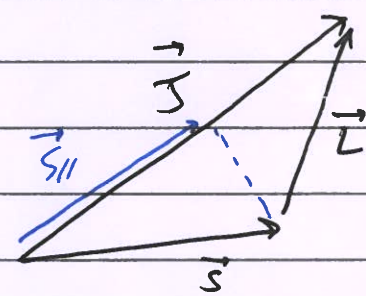
$$= \langle J, m_J | \frac{\mu_B}{\hbar} (\vec{J} + \vec{S}) \cdot \vec{B} | J, m_J \rangle$$

The $\{|J, m_J\rangle\}$ basis forms a subspace in the larger space spanned by the $\{|L, m_L\rangle \otimes |S, m_s\rangle\}$ basis.

The Wigner–Eckart Projection Theorem states that

$$\boxed{\langle J, m_J | \vec{S} | J, m_J \rangle = \frac{\langle J, m_J | \vec{J} \cdot \vec{S} | J, m_J \rangle}{\langle J, m_J | \vec{J}^2 | J, m_J \rangle} \vec{J} = \vec{S}_{\parallel}}$$

Geometric picture:



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

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

thus $E(J, m_J) = \langle J, m_J | \frac{\mu_B}{\hbar} \vec{J} \cdot \vec{B} | J, m_J \rangle + \frac{\mu_B}{\hbar} \frac{\langle J, m_J | \vec{J} \cdot \vec{S} | J, m_s \rangle}{\langle J, m_J | \vec{J}^2 | J, m_J \rangle} \langle J, m_J | \vec{J} \cdot \vec{B} | J, m_J \rangle$

$$\Rightarrow \quad E(J, m_J) = \frac{\mu_B}{\hbar} \langle J, m_J | \left(1 + \frac{1}{2} \frac{J(J+1) + S(S+1) - L(L+1)}{J(J+1)} \right) \underbrace{\vec{J} \cdot \vec{B}}_{J_z B_z} | J, m_J \rangle$$

If the Zeeman Energy shift is small compared to the hyperfine splitting, then we can write

$$H_{\text{Zeeman}} = \frac{\mu_B}{\hbar} g_F \underbrace{\vec{F} \cdot \vec{B}}_{F_z B_z} = \mu_B g_F m_F B_z$$

with the hyperfine Landé g-factor given by

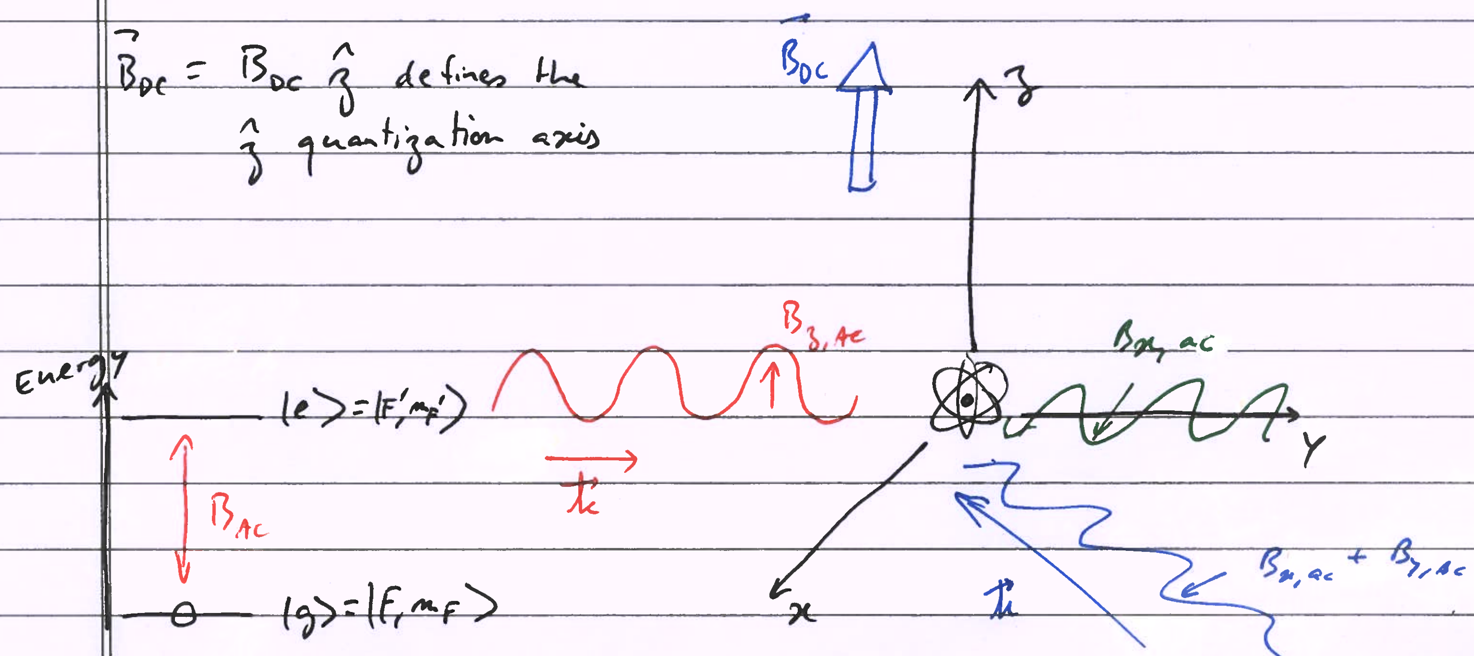
$$g_F = g_J \frac{F(F+1) - I(I+1) + J(J+1)}{2F(F+1)} + g_I \underbrace{\frac{F(F+1) + I(I+1) - J(J+1)}{2F(F+1)}}_{\text{neglect}}$$

very small

Transition Selection Rules

Consider M1 transitions at low DC $\vec{B}_{DC}$-field. These are driven by an oscillating magnetic field $\vec{B}_{AC}$.

$\vec{B}_{DC} = B_{DC}\,\hat{z}$ defines the $\hat{z}$ quantization axis



The Rabi frequency is $\boxed{\Omega = \dfrac{\langle e|\, H_{Zeeman,AC}\, |g\rangle}{\hbar}}$

$$\Rightarrow \quad \Omega = \langle F', m_F'|\, \frac{\mu_B}{\hbar^2}\, g_F\, \vec{F}\cdot\vec{B}_{AC}\, |F, m_F\rangle$$

Case 1: π-polarization : $\vec{B}_{AC} = B_{AC}\,\hat{z}$

$$\Omega = \frac{\mu_B}{\hbar^2}\, g_F\, |B_{AC}|\, \underbrace{\langle F, m_F'|\, F_z\, |F, m_F\rangle}_{\text{Wigner-Eckart theorem assumed } F=F'}$$

$$= \frac{\mu_B}{\hbar^2}\, g_F\, m_F\, |B_{AC}|\, \delta_{FF'}\, \delta_{m_F m_F'}$$

π – transition requires $\Delta m_F = 0 \implies |g\rangle = |e\rangle$

↳ not really a transition!!

For $F \neq F'$ ($L = 0$ here)

$$\Omega = \frac{\mu_B}{\hbar^2} g_s |\vec{B}_{AC}| \underbrace{\langle F', m_F' | S_z | F, m_F \rangle}_{cst \, \delta_{F,F'+1} \, \delta_{m_F m_F'}}$$

↳ how do you calculate the constant?

↳ use Clebsch-Gordan decomposition!

$$\implies \boxed{\begin{array}{l} \pi\text{-transition requires } \Delta m_F = 0, \Delta F = \pm 1 \\ \left[\vec{B}_{AC} \parallel z\text{-axis or } \vec{B}_{AC} \parallel \vec{B}_{DC}\right] \end{array}}$$

stopped here

Case 2: σ – polarization $\vec{B}_{AC} \perp \vec{B}_{DC}$ (or $\hat{z}$)

$$\implies \Omega = \frac{\mu_B}{\hbar^2} g_F \langle F, m_F' | F_x B_x + F_y B_y | F, m_F \rangle$$

but $F_x = \dfrac{F_+ + F_-}{2}$ and $F_y = \dfrac{F_+ - F_-}{2i}$

so $$\Omega = \frac{\mu_B}{\hbar^2} g_F \langle F, m_F' | \left(\frac{F_+ + F_-}{2}\right) B_x + \left(\frac{F_+ - F_-}{2i}\right) B_y | F, m_F \rangle$$

$$\implies \Omega = \frac{\mu_B}{\hbar^2} g_F \langle F, m_F' | F_+ \underbrace{\left(\frac{B_x - iB_y}{2}\right)}_{B_-} + F_- \underbrace{\left(\frac{B_x + iB_y}{2}\right)}_{B_+} | F, m_F \rangle$$

$$\iff \Omega = \frac{\mu_B}{\hbar^2} g_F \langle F, m_F' | F_+ B_- + F_- B_+ | F, m_F \rangle$$