Zeeman effect: a H-atom in external magnetic field

depends only on $\hat{L}^2$

$$\hat{H} = \frac{1}{2m}\left(\vec{p} - \frac{e}{c}\vec{A}\right)^2 - \frac{e}{r} - \frac{p^4}{8m^3c^2} - \vec{\mu}_s\cdot\vec{B} + \frac{1}{2}\frac{e^2}{m^2c^2}\frac{1}{r^3}\hat{\vec{L}}\hat{\vec{S}}$$

where $\vec{\mu}_s$ – spin magn. moment

For a homogeneous magnetic field $\vec{B} = B\cdot\vec{e}_z$

$$\vec{A} = \frac{1}{2}(\vec{B}\times\vec{r})$$

$$\hat{H} = \frac{p^2}{2m} - \frac{e^2}{r} - \frac{e\hbar}{2m_ec}B\cdot\hat{L}_z + \frac{e^2}{8mc^2}B^2(x^2+y^2) - \frac{2e\hbar}{2m_ec}B\cdot\frac{\hat{S}_z}{\hbar} +$$

$$+ \frac{1}{2}\frac{e^2}{m^2c^2}\frac{1}{r^3}\hat{\vec{L}}\hat{\vec{S}} + \underbrace{\hat{H}_{rel}}_{\text{neglect}}$$

The term $\propto B^2(x^2+y^2)$ is negligeabl (for H-atoms)

$$\hat{H} = \underbrace{\frac{p^2}{2m} - \frac{e^2}{r}}_{\hat{H}_0} + \underbrace{\frac{1}{2}\frac{e^2}{m^2c^2}\frac{1}{r^3}\langle\hat{\vec{L}}\hat{\vec{S}}\rangle}_{\hat{V}_{SO}} \underbrace{- \frac{e\hbar}{2m_ec}(\hat{L}_z - 2\hat{L}_s)B}_{\hat{V}_{zeeman}}$$

$$+ \underbrace{\frac{e^2}{8mc^2}B^2(x^2+y^2)}_{\text{quadratic Zeeman term}}$$

$$\hat{V}_{zeeman} = \vec{\mu}_{tot}\cdot\vec{B} = \mu_B(\hat{\vec{L}} + 2\hat{\vec{S}})$$

"intrinsic" total magnetic moment

Both corrections – spin-orbit coupling and Zeeman effect – are much smaller than $E_n^{(0)}$; however, their relative value determines the leading behavior.

a) Weak magnetic field $\langle V_{zeeman} \rangle \ll \langle V_{SO} \rangle$

Spin-orbit coupling partially lifts L-degeneracy

"Proper basis" $|l s j m_j\rangle$ — total angular momentum

We are going to use these states as unperturbed "zero"-approximation wave function.

$$\Delta \hat{V}_{zeeman} = -\mu \vec{B} \frac{(\vec{L} + 2\vec{S})}{\hbar} = -\mu B \frac{1}{\hbar}(\hat{J}_z + \hat{S}_z)$$

$$E_{zeeman} = -\mu B \frac{1}{\hbar}(\langle J_z \rangle + \langle \hat{S}_z \rangle)$$

$$\langle J_z \rangle = \langle l s j m_j | \hat{J}_z | l s j m \rangle = \hbar m_j$$

$\langle S_z \rangle$ – ?

We can show that $\langle l s j m_j | S_z | l s j m_j' \rangle = 0$ for $m_j \neq m_j'$

Indeed

$$|l s j m_j\rangle = \alpha\, |l, s, m_l = m_j + 1/2, m_s = -\tfrac{1}{2}\rangle + \beta\, |l, s, m_l = m_j - 1/2, m_s = +\tfrac{1}{2}\rangle$$

since $\langle m_s | \hat{S} | m_{s'} \rangle = 0$ for $m_s \neq m_{s'}$ and it does not affect m_l =>

m_j does not change

One can use Wigner–Eckart projection theorem

$$\langle j\, m_j | \vec{S} | j, m_j \rangle = \underbrace{\frac{\langle j, m_j | \vec{J} \cdot \vec{S} | j, m_j \rangle}{\langle j, m | J^2 | j m \rangle}}_{\pm \frac{1}{2l+1} \quad j = l \pm 1/2} \langle j\, m_j | \vec{J} | j m \rangle$$

more generally $\vec{J}$ is the only "known" direction in the problem, so

$$\vec{S} = \text{const} \cdot \vec{J}$$

$$\langle S_z \rangle = \text{const} \langle J_z \rangle = \text{const} \cdot \hbar m_j$$

$$\langle \vec{S}\vec{J} \rangle = \text{const} \langle J^2 \rangle = \text{const}\ \hbar^2 j(j+1)$$

on the other hand

$$\langle \hat{L}^2 = (\hat{\vec{J}} - \hat{\vec{S}})^2 = \hat{J}^2 + \hat{S}^2 - 2\vec{J}\vec{S} \Rightarrow \vec{J}\vec{S} = \frac{1}{2}\left[\hat{J}^2 + \hat{S}^2 - \hat{L}^2\right]$$

Thus, $\text{const} \cdot \hbar^2 j(j+1) = \frac{\hbar^2}{2}(j(j+1) + s(s+1) - l(l+1))$

$$\text{const} = \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)}$$

$$\langle S_z \rangle = \hbar m_j \cdot \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)}$$

and

$$E_{zeeman} = -\mu_B B m_j \left(\frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)} + 1 \right)$$

$$\boxed{E_{zeeman} = -\mu_B B g m_j}$$

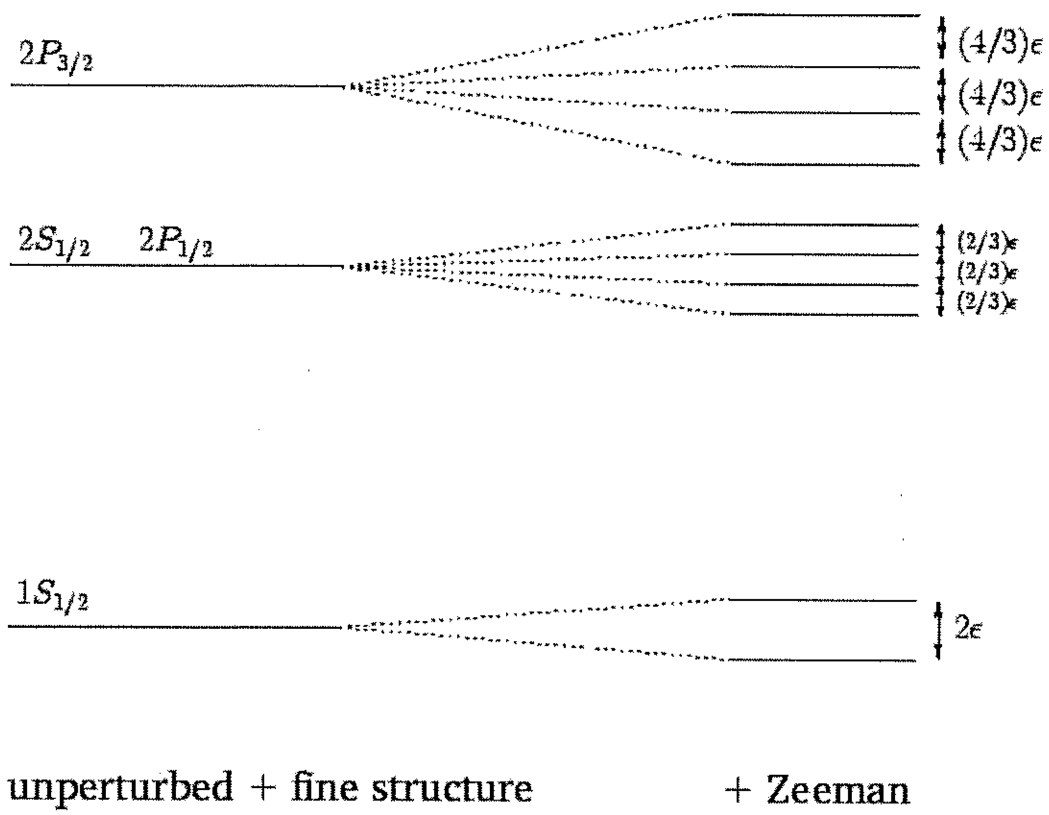
where $g = 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)}$ gyromagnetic ratio

magnetic field lifts the m_j - degeneracy

for $s = 1/2$ $j = l \pm 1/2$

$$\frac{j(j+1) + 3/4 - l(l+1)}{2j(j+1)} = \begin{cases} \dfrac{\overbrace{\cancel{l^2} + 2l + 3/4 + 3/4 - \cancel{l^2} - l}^{= l + 3/2}}{2(l+1/2)(l+3/2)} = \dfrac{1}{2l+1} \\[2ex] \dfrac{\overbrace{\cancel{l^2} - 1/4 + 3/4 - \cancel{l^2} - l}^{= -l + 1/2}}{2(l-1/2)(l+1/2)} = -\dfrac{1}{2l+1} \end{cases}$$

$$g_{J \pm 1/2} = \left(1 \pm \frac{1}{2l+1}\right)$$


$2P_{3/2}$
$(4/3)\epsilon$
$(4/3)\epsilon$
$(4/3)\epsilon$
$2S_{1/2}$ $2P_{1/2}$
$(2/3)\epsilon$
$(2/3)\epsilon$
$(2/3)\epsilon$
$1S_{1/2}$
2ϵ
unperturbed + fine structure
+ Zeeman

Limit of a strong magnetic field (Paschen - Back limit)

Can go back to our original basis!

$|l, m_l, s, m_s\rangle$

$$\hat{V}_{zeeman} = -\mu_B B (\hat{L}_z + 2\hat{S}_z)$$

$$\Delta E_{zeeman} = -\mu_B B (m_l + 2 m_s)$$

In this basis V_{SO} is a small correction

$$\langle \vec{L}\cdot\vec{S}\rangle = \langle l m_l s m_s | \hat{l}_x \hat{S}_x + \hat{l}_y \hat{S}_y + \hat{l}_z \hat{S}_z | l m_l s m_s\rangle =$$

$$= \langle l m_l s m_s | \hat{l}_z \hat{S}_z | l m_l s m_s\rangle = \hbar^2 m_l m_s$$

$$\Delta E_{SO} = \frac{\hbar^2}{2m^2c^2} \cdot m_l m_s \left\langle \frac{1}{r}\frac{dV_c}{dr}\right\rangle_{nl}$$

Example: n=2 state of H-atom

P-state: $l = 1$, $s = 1/2$

Weak magn. field $\mu_e B \ll \alpha^2 E_0$

$j = 1/2$ $\quad 2P_{1/2}$ $\quad m_j = \pm 1/2$ double degenerate

$j = 3/2$ $\quad 2P_{3/2}$ $\quad m_j = \pm 1/2, \pm 3/2$ - 4-fold degenerate

S-state: $l = 0$, $s = 1/2 \Rightarrow j = 1/2$ $\quad m_j = \pm 1/2$

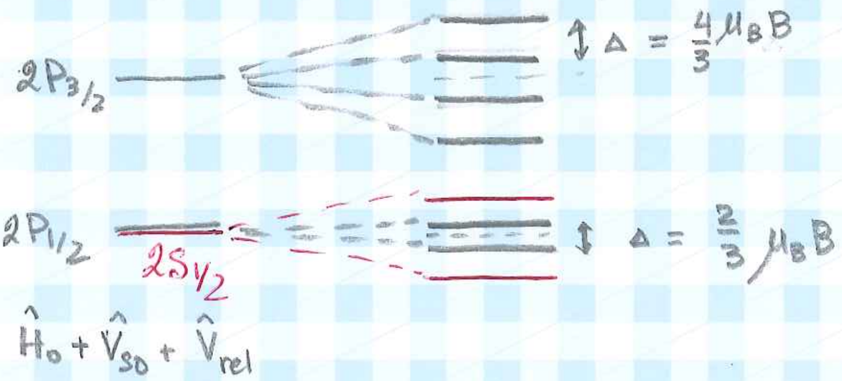
gyromagnetic ratio: s-state $l = 0$ $\quad g = 2$

p-state: $l = 1$ $\quad j = 3/2$ $\quad g = 1 + \frac{1}{2l+1} = \frac{4}{3}$

$j = 1/2$ $\quad g = 1 - \frac{1}{2l+1} = \frac{2}{3}$

2S state	$2P_{1/2}$ state	$2P_{3/2}$ state
$\Delta E = \pm 2 \cdot \mu_B B \cdot \frac{1}{2} = \pm \mu_B B$	$\Delta E = \frac{2}{3}\mu_B B(\pm 1/2) = \pm 1/3 \mu_B B$	$\Delta E = \frac{4}{3}\mu_B B(\pm\frac{1}{2}; \pm\frac{3}{2}) = \pm 2/3 \mu_B B; \pm 2 \mu_B B$

H- atom $n=2$ state with spin-orbit and relativistic corrections



equidistant spectrum all degeneracy is lifted

again, all degeneracy is lifted

Strong magnetic field $\mu_B B \gg \alpha^2 E_0$

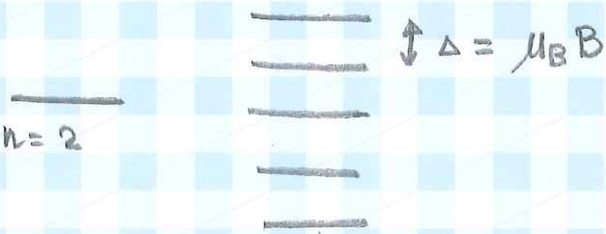
$l = 1 \quad m_l = 0, \pm 1$ $\qquad$ $l = 0 \quad m_e = \pm 1/2$

$s = 1/2 \quad m_s = \pm 1/2$

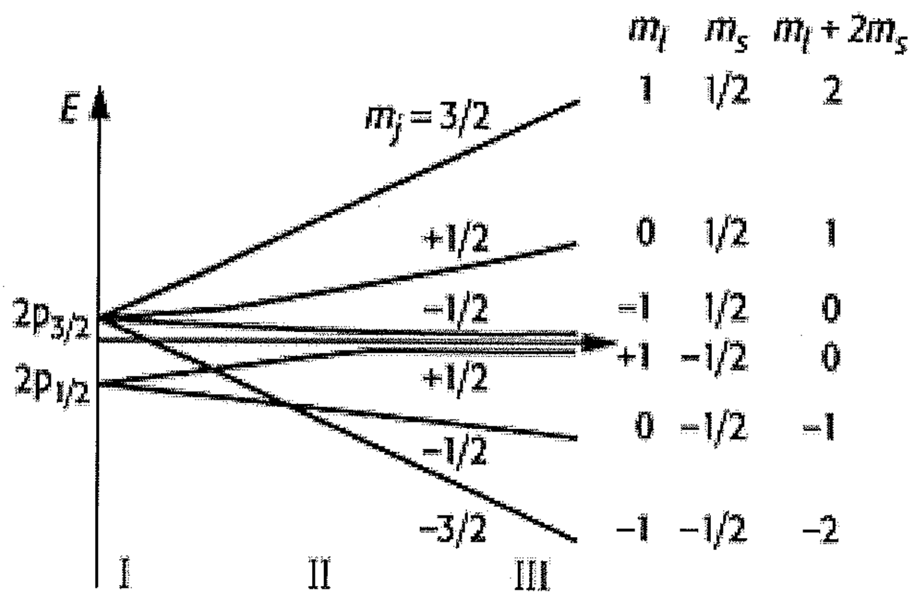
$m_l + 2m_s$: $0 \pm 1 \Rightarrow \pm 1$ $\qquad$ $m_l + 2m_s$: ± 1

$\pm(1 \pm 1) \Rightarrow \pm 0, \pm 2$

6 states, one double degenerate $\qquad$ 2 states



double- degenerate


E
$2p_{3/2}$
$2p_{1/2}$
$m_j = 3/2$
+1/2
−1/2
+1/2
−1/2
−3/2
I
II
III
m_l m_s $m_l + 2m_s$
1 1/2 2
0 1/2 1
−1 1/2 0
+1 −1/2 0
0 −1/2 −1
−1 −1/2 −2

Hyperfine structure

To fully describe the energy structure of the alkali-metals, one has to take into account the interaction with the nucleus, that also has an angular moment $\vec{I}$

$$\vec{\mu}_I = g_I \mu_N (\vec{I}/\hbar) \qquad \mu_N = \frac{e}{2m_pc} \text{ nuclear Bohr magneton}$$

$$\frac{\mu_N}{\mu_e} = \frac{m_e}{m_n} \sim \frac{1}{2000}$$

expected correction is $\sim \frac{1}{2000} \hat{H}_{SO}$

Interactions contributing to H_{HF}

dominates:
- "contact" interaction: $\bar{e}$ magnetic dipole interacts with the magnetic field of the nucleus $\propto \vec{S}\cdot\vec{I}\,\delta(r)$

- the nucleus magnetic moment interacts with the field of the electron $\propto \vec{L}\cdot\vec{I}\cdot\frac{1}{R^3}$
- dipole-dipole interaction b/w $\vec{S}$ and $\vec{I}$

$$\hat{H}_{HF} = A\,\hat{\vec{I}}\cdot\hat{\vec{J}}$$

easiest to evaluate for $l=0$ states $\vec{J}=\vec{S}$

$j = s = 1/2$

$\vec{F} = \vec{I} + \vec{J} = \vec{I} + \vec{S}$

For an H-atom $I = 1/2$ (proton)

$F = 0, 1$

New wavefunctions $|n\, l\, s\, j\, i\, \underline{F, m_F}\rangle$ with $l, s, j \to 0, \tfrac{1}{2}, \tfrac{1}{2}$

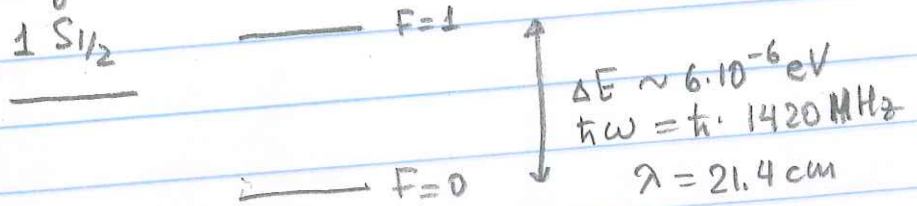
good quantum numbers

Using again $\hat{I}\hat{S} = \frac{1}{2}(\hat{F}^2 - \underbrace{\hat{I}^2}_{= 3/4} - \underbrace{\hat{S}^2}_{= 3/4})$

$$E^{(1)}_{HF} = \langle F, m_F | \hat{H}_{HF} | F, m_F \rangle =$$

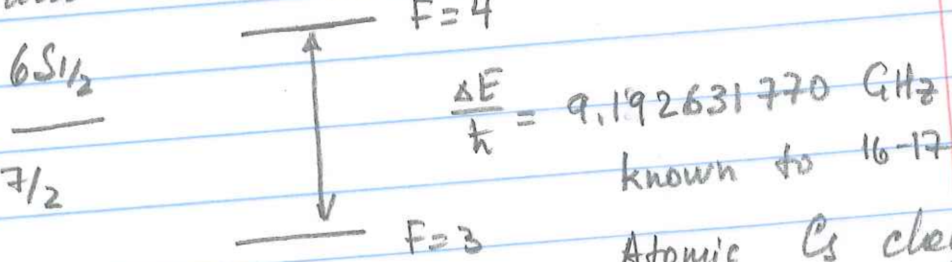
$$= \frac{1}{2} A \left(F(F+1) - 3/2 \right) = \begin{cases} 1/4 A & F = 1 \\ -3/4 A & F = 0 \end{cases}$$

Hydrogen



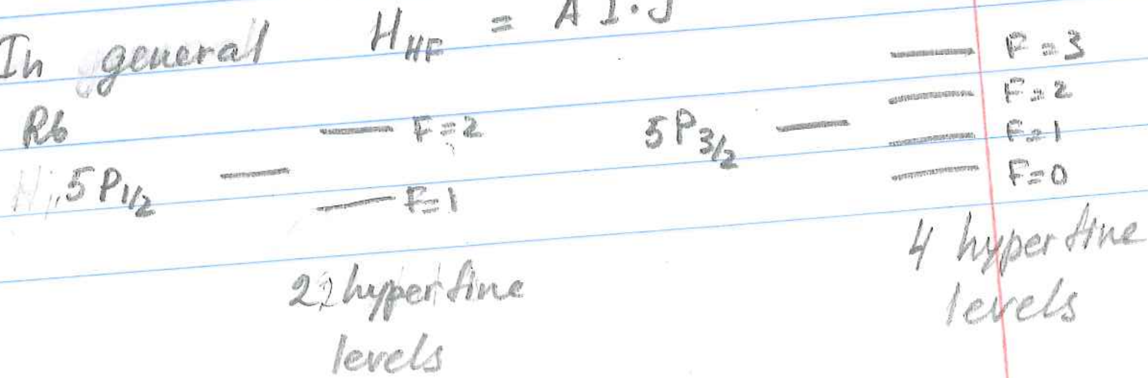
First maser operated on this transition
Cosmic microwave background - radiation of this transition

Cesium



known to 16-17 digits
Atomic Cs clocks operates on this transition

In general $\hat{H}_{HF} = A \hat{I} \cdot \hat{J}$



What if the magnetic field is weak enough to take into account the hyperfine splitting?

$$\hat{H} = \hat{H}_0 + \underbrace{\hat{V}_{SO}}_{\text{dominant correction}} + \underbrace{\frac{A}{\hbar^2}\vec{I}\cdot\vec{J}}_{\hat{V}_{HF}} - \mu_B(\vec{L}+2\vec{S})\vec{B} - g_I\mu_n\,\vec{I}\cdot\vec{B}$$

$$\mu_n = \frac{\hbar e}{2m_n c} \quad \text{nucleus}$$

$$\hat{V}_{HF} = \frac{A}{\hbar^2}\,\vec{I}\cdot\vec{J} \longrightarrow$$ need to use total angular momentum $\vec{F} = \vec{I} + \vec{J}$

$$\Delta E_{HF} = \frac{A}{\hbar^2}\langle lsjIFm_F|\,\vec{I}\cdot\vec{J}\,|lsjIFm_F\rangle$$

$$\vec{I}\cdot\vec{J} = \frac{1}{2}\left(\hat{F}^2 - \hat{J}^2 - \hat{I}^2\right)$$

$$\Delta E_{HF} = \frac{A}{2}\left(F(F+1) - I(I+1) - J(J+1)\right)$$

Weak zeeman field

$$\hat{V}_{zeeman} = -\left(\mu_B(\vec{J}+\vec{S}) + \underbrace{g_I\mu_N\vec{I}}_{\text{small correction}}\right)\vec{B} \qquad \frac{\mu_N}{\mu_B} \sim \frac{1}{2000}$$

$$E_{HF\,zeeman} = \langle F m_F|\,\hat{V}_{zeeman}\,|F m_F\rangle$$

we can show that

$$E_{zeeman} \simeq g_F\,\mu_B\,B\cdot m_F \qquad \boxed{g_F \simeq \frac{F(F+1)+S(S+1)-I(I+1)}{F(F+1)}}$$

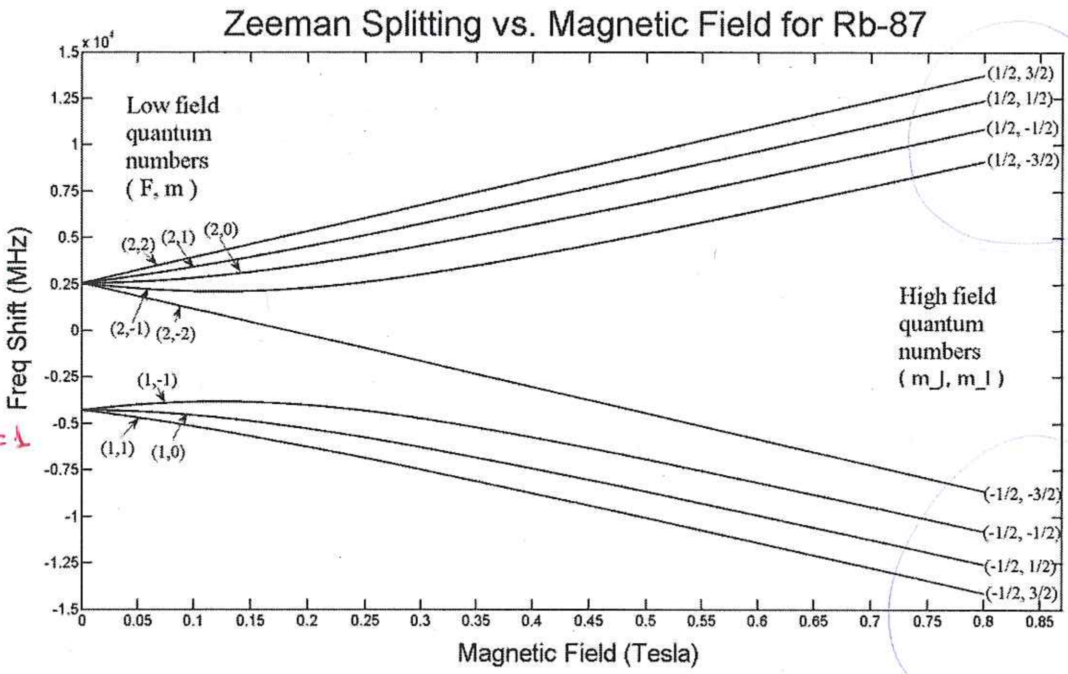
For strong magnetic field we can use the same procedure!

F is not a good quantum number use m_j and m_I

$$E_{HF\,\text{Paschen-Back}} = \left(g_j m_j \mu_B + g_I m_I \mu_B\right)$$

F=2

F=1



$J = 1/2$

$J = -1/2$

Rb^{87} ground state $\ell = 0$ $s = 1/2 \Rightarrow J = 1/2$

$I = 3/2$

$F = I \pm J = 1, 2$