Zeeman effect

Now let us go back to Pauli Eq^n with the present $\vec{A}$

Recall, we had derived,

$$H\Psi = \left[-\frac{\hbar^2\nabla^2}{2m} + \frac{i\hbar q}{m}\left(\vec{A}\cdot\vec{\nabla} + \frac{(\vec{\nabla}\cdot\vec{A})}{2}\right) + \frac{q^2}{2m}\vec{A}\cdot\vec{A} + q\Phi_0\right]\Psi$$

We need to include $\frac{e\hbar}{2m}(\vec{\sigma}\cdot\vec{B})$ Recall $\vec{S} = \frac{\hbar}{2}\vec{\sigma}$

To describe $\vec{B}$ which is assumed to be invariant over the length scale of the system (atom or molecule)

we choose $\vec{A} = \frac{1}{2}(\vec{B}\times\vec{r}) \Rightarrow \vec{B} = \vec{\nabla}\times\vec{A}$

Also $(\vec{\nabla}\cdot\vec{A}) = \vec{\nabla}\cdot\frac{1}{2}(\vec{B}\times\vec{r}) = \frac{1}{2}\underset{0}{\underbrace{(\vec{\nabla}\times\vec{B})}}\cdot\vec{r} - \frac{1}{2}\underset{0}{\underbrace{(\vec{\nabla}\times\vec{r})}}\cdot\vec{B}$

linear in A

$$\frac{i\hbar q}{m}\vec{A}\cdot\nabla\Psi = \frac{i\hbar q}{2m}(\vec{B}\times\vec{r})\cdot\nabla\Psi$$
$$= -\frac{q}{2m}(\vec{B}\times\vec{r})\cdot\hat{p}\Psi$$
$$= -\frac{q}{2m}\vec{B}\cdot(\vec{r}\times\hat{p})\Psi$$
$$= -\frac{q}{2m}\vec{B}\cdot\hat{L}\Psi \sim \frac{e\hbar|\vec{B}|}{2m}, \quad (q=-e)$$

Quadratic in A

$$\frac{q^2}{2m}\vec{A}\cdot\vec{A} = \frac{e^2}{8m}(\vec{B}\times\vec{r})^2 = \frac{e^2}{8m}\left[|B|^2 r^2 - (\vec{B}\cdot\vec{r})^2\right]$$
$$\sim \frac{e^2}{8m}|B|^2 a_0^2$$

$\langle r^2\rangle \sim a_0^2$

$$\therefore \frac{\left|\left\langle \frac{q^2}{2m}\vec{A}\cdot\vec{A}\right\rangle\right|}{\left|\left\langle \frac{i\hbar q}{m}\vec{A}\cdot\nabla\right\rangle\right|} \sim \left[\frac{e\, a_0^2|B|}{4\hbar}\right] \approx |B|\, 10^{-6}$$

$\rightarrow$ dimensionless $\rightarrow \frac{q\cdot(LT^{-1})B}{E} = \frac{(qvB)L}{E}$

$(q=-e)$

Define $\hat{\mu}_L = -\frac{e}{2m}\hat{L} = -\mu_B\hat{L}/\hbar$

magnetic Dipole moment

Recall,

$$\hat{\mu}_s = -g_s\frac{e}{2m}\hat{S} = -\frac{g_s\mu_B}{\hbar}\hat{S}$$

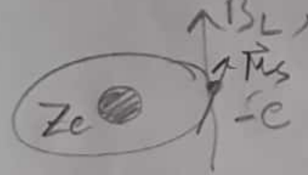
∴ Neglecting the quadratic term in $\vec{A}$ and retaining only the spin orbit term (since the other terms are diagonal in $n\, l\, m_l\, m_s$) and the Pauli spin term

$$\left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{(4\pi\epsilon_0)r} + \xi(r)\hat{L}\cdot\hat{S} + \frac{e}{2m}\vec{B}\cdot\hat{L} + \frac{e\hbar}{2m}\vec{\sigma}\cdot\vec{B}\right]\underline{\Psi} = E\underline{\Psi}$$

$$\Rightarrow \left[H_0 + \xi(r)\hat{L}\cdot\hat{S} + \frac{1}{\hbar}\mu_B\vec{B}\cdot\hat{L} + \frac{2}{\hbar}\mu_B\vec{S}\cdot\vec{B}\right]\underline{\Psi} = E\underline{\Psi}$$

$$\Rightarrow \left[H_0 + \xi(r)\hat{L}\cdot\hat{S} + \frac{1}{\hbar}\mu_B(\hat{L} + 2\hat{S})\cdot\vec{B}\right]\underline{\Psi} = E\underline{\Psi}$$

If $|B_{ext}| \gg |\vec{B}_L|$ then $\vec{M}_s$ gets completely oriented by B_{ext} → Strong field limit



If $|\vec{B}_{ext}| \sim |\vec{B}_L|$

$\vec{M}_s$ responds to both.

→ Weak field limit.

<u>Strong field</u>

$$\left(H_0 + \frac{1}{\hbar}\mu_B(\hat{L} + 2\hat{S})\cdot\vec{B}\right)\underline{\Psi} = E\underline{\Psi}$$

Note that $(\hat{L} + 2\hat{S})\cdot\vec{B}$ is diagonal in $\underline{\Psi}_{n l m_l m_s}$

<u>Let $\vec{B} \parallel \hat{z}$</u>

$$\therefore E = E_n + \mu_B B_z(m_l + 2m_s)$$

→ degeneracy in m_l is removed by breaking the spatial symmetry in direction

	m_l	$2m_s$
$\mu_B B$	1	1
	0	1
$n, l=1$	1	−1
	−1	1
	0	−1
	−1	−1

$m_l = -1, 0, 1$

$m_s = +\frac{1}{2}, -\frac{1}{2}$

$2m_s = 1, -1$

<u>Recall selection rules</u>

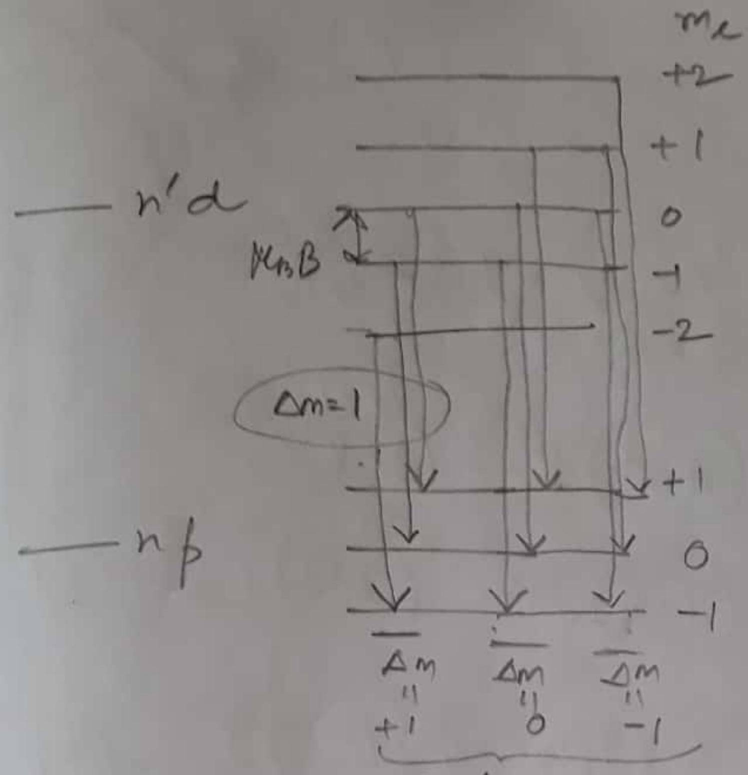
$\Delta m_l = 0, \pm 1$

$\Delta l = \pm 1$

for strong fields these two are enough + <u>$\Delta m_s = 0$</u>

from the transition dipole term.

trivially commutes with $\hat{S}^2, \hat{S}_z$



$\Delta m = 0 : E_n \to E_{n'}$

π line

$\omega_\pi = (E_{n'} - E_n)/\hbar$

$\Delta m = \pm 1 : \sigma$ lines

$\omega_{\sigma-} = \frac{(E_{n'} - E_n)}{\hbar} - \frac{\mu_B B}{\hbar}$ ($\Delta m = +1$)

$\omega_{\sigma+} = \frac{(E_{n'} - E_n)}{\hbar} + \frac{\mu_B B}{\hbar}$ ($\Delta m = -1$)

3 lines ∴

Lorentz triplet.

visible not only for strong fields but also for those system whose net spin is zero. → no spin-orbit coupling.

Recall also: $\Delta m = +1 \to$ emission of Right circularly polarized light with helicity $+\hbar$

∴ $\sigma+ \to$ emits helicity $+\hbar$

$\sigma- \to$ " " $-\hbar$

Intermediate field $\quad |B_{ext}| > |\vec{B}_L|$ but the effect of $\vec{B}_L$ can be treated perturbatively

$$\therefore \Delta E = \langle n \ell s m_\ell m_s | \xi(r) \hat{L} \cdot \hat{S} | n \ell s m_\ell m_s \rangle$$

$$= \underbrace{\int |R_{n\ell}|^2 \xi(r) r^2 dr}_{\lambda_{n\ell}} \langle \ell s m_\ell m_s | \hat{L} \cdot \hat{S} | \ell s m_\ell m_s \rangle$$

$L_x S_x + L_y S_y + L_z S_z$

Write in terms of raising lowering operators to understand that these two terms will not contribute.

$= \lambda_{n\ell} m_\ell m_s$

$\downarrow$

$$-\frac{\alpha^2 Z^2}{n} E_n \frac{1}{\ell (\ell + \frac{1}{2})(\ell + 1)}$$

Note that the divergence at $\ell = 0$ is avoided by $m_\ell = 0$

Strong field term

Source of lifting of m_s degeneracy in strong fields

$$\Rightarrow \omega = \frac{E_{n'} - E_n}{\hbar} + \frac{\mu_B B_z}{\hbar}(m_\ell - m_{\ell'}) + (\lambda_{n'\ell'} m_{\ell'} - \lambda_{n\ell} m_\ell) m_s$$

Weak field $|B_L| \sim |B_{ext}|$

Recall

$$H\psi = \Big[\underbrace{-\frac{\hbar^2\nabla^2}{2m} - \frac{Ze^2}{(4\pi\varepsilon_0)r} + \xi(r)\vec{L}\cdot\hat{\vec{S}}}_{\text{consider as } H_0} + \underbrace{\frac{\mu_B}{\hbar}(\hat{L}_z + 2\hat{S}_z)}_{H'}\Big]\psi$$

consider as H_0 $\Downarrow$ $\psi_0 = \Psi_{nlsjm_j}$

H' perturbation (opposite of PB effect at intermediate field.)

$$H' = \frac{\mu_B B_z}{\hbar}(\hat{L}_z + 2\hat{S}_z) = \frac{\mu_B}{\hbar}(J_z + S_z)B_z$$

The problem is with finding $\langle nlsjm_j | S_z | nlsjm_j\rangle$

We can do it in two ways.

1. Expand $|nlsjm_j\rangle$ in terms of $|nlsm_lm_s\rangle$ using the CG coeffecients. since $\hat{S}_z$ is diagonal in $|nlsm_lm_s\rangle$
2. Use a general result derived from the Wigner-Eckart theorem that for any vector operator $\hat{V} = \hat{i}\hat{V}_x + \hat{j}\hat{V}_y + \hat{k}\hat{V}_z$ that it holds from the properties of sph harmonics that

$$j(j+1)\hbar^2\langle lsjm_j|V|lsjm_j\rangle$$
$$= \underbrace{\langle lsjm_j|}_{\sum_{m_lm_s} CG^*_{jm_j,m_lm_s}\underbrace{\langle lsm_lm_s|}_{\text{sph harmonics}}}(V\cdot J)J|lsjm_j\rangle$$

Identify $\hat{\vec{S}}$ as $\hat{\vec{V}}$ and collect only the z component;

$$j(j+1)\hbar^2\langle lsjm_j|S_z|lsjm_j\rangle = \langle lsjm_j|(\hat{\vec{S}}\cdot\hat{\vec{J}})J_z|lsjm_j\rangle$$
$$= m_j\hbar\langle lsjm_j|(\hat{\vec{S}}\cdot\hat{\vec{J}})|lsjm_j\rangle \quad \Big| \text{ Recall } \hat{\vec{J}} = \hat{\vec{L}} + \hat{\vec{S}}$$
$$= m_j\hbar\langle|\frac{1}{2}(J^2 + S^2 - L^2)|\rangle$$
$$= m_j\hbar\,[\,j(j+1) + s(s+1) - l(l+1)\,]$$

$$\therefore \Delta E_{m_j} = \frac{\mu_B}{\hbar}\langle|J_z + S_z|\rangle B_z = \frac{\mu_B B_z}{\hbar}m_j\hbar\left[1 + \frac{j(j+1) + s(s+1) - l(l+1)}{j(j+1)}\right]$$
$$= \mu_B B_z m_j g_L \rightarrow \text{Lande's } g \text{ factor}$$

Note that Landé's g factor is 2 for spin $\begin{pmatrix} l=0 \\ j=\frac{1}{2} \end{pmatrix}$

However it is not exactly same as the gyromagnetic ratio introduced in Pauli eq^n.
Note that the value of gyromagnetic ratio 2 was naturally arrived at from Dirac theory which seem to be same as the Landé's g factor.
But a more exact QED framework gives a value of gyromagnetic ratio slightly more than 2 for spin (ie an electron in 1s orbital), whereas the Landé's g factor is strictly 2.
Also note that the g factor is sourced at the gyromagnetic ratio since the g factor would not have arrived if gyromagnetic ratio had been 1, ie H' would have been $= (L_z + S_z)\frac{\mu_B B_z}{\hbar}$ instead of $(L_z + 2S_z)\frac{\mu_B B_z}{\hbar}$.

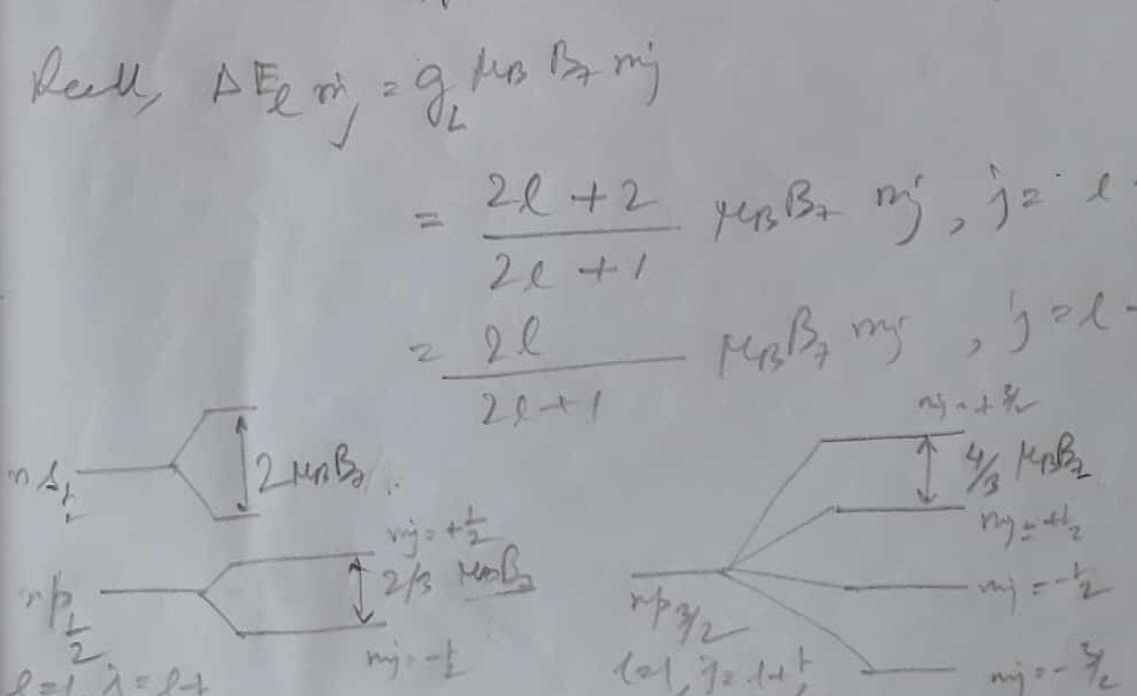
Putting all together at weak field:

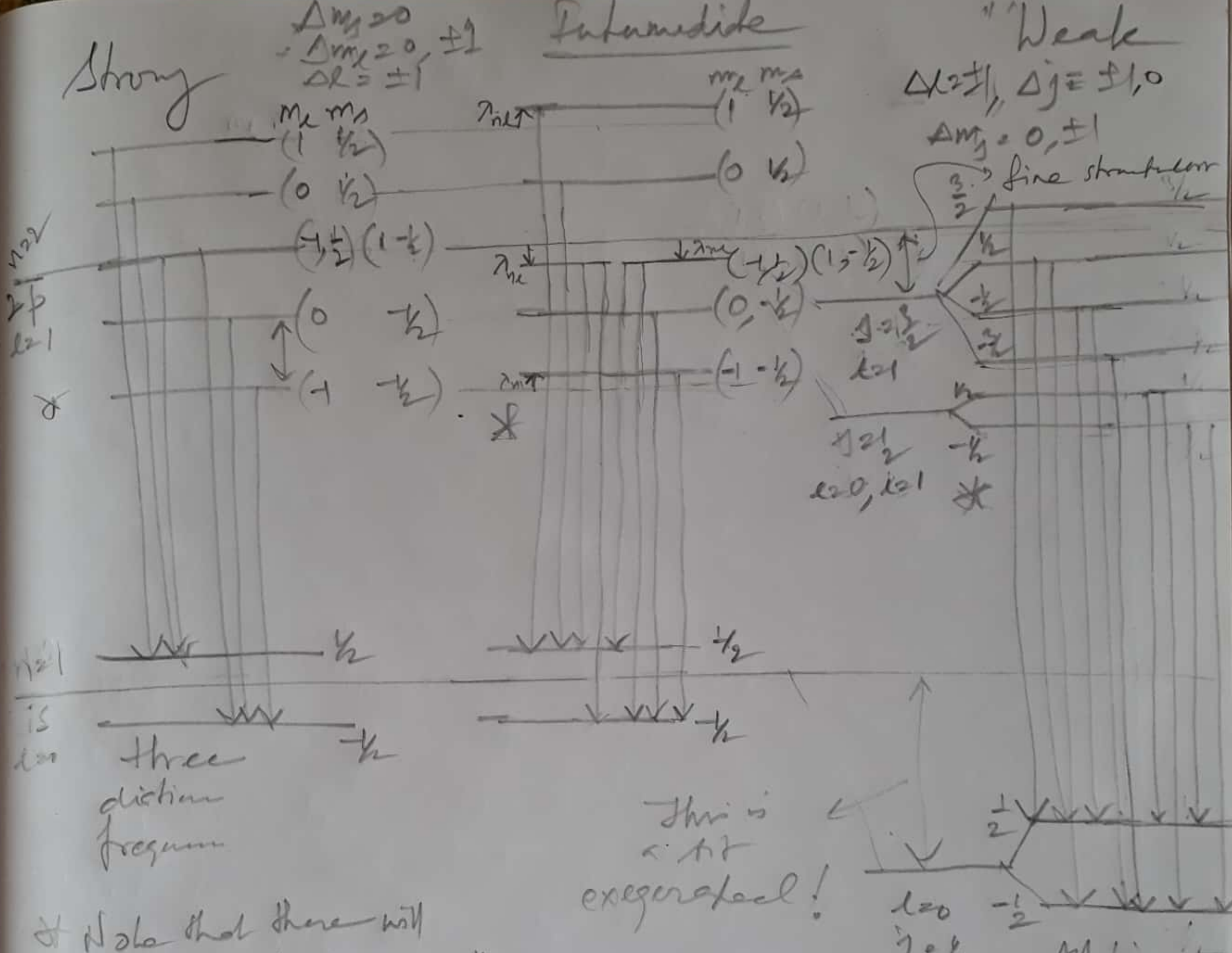
$$E_{njm_j} = \underbrace{E_n}_{\text{non-relativistic energy}} + \underbrace{\Delta E_{nj}}_{\text{fine structure correction}} + \underbrace{\Delta E_{l m_j}}_{\text{correction due to weak magnetic field}}$$

Recall, $\Delta E_{l m_j} = g_L \mu_B B_z m_j$

$$= \frac{2l+2}{2l+1}\mu_B B_z m_j, \quad j = l + \frac{1}{2}$$

$$= \frac{2l}{2l+1}\mu_B B_z m_j, \quad j = l - \frac{1}{2}$$





* Note that there will be transitions for $\Delta l = \pm 1$ within $n=2$ but we are not considering them here because we are looking for splitting of levels from $n=1$ to $n=2$ in visible range.