4. Influence of External (Static) Magnetic Field

(1) Zeeman Effect:

In 1896, Peter Zeeman found that when a light source was placed in a magnetic field, the emitted light spectral line was split into spectral lines. The splitting of spectral line indicates the splitting and shift of corresponding energy levels. This phenomenon is called the Zeeman effect. It is the influence result from the the interaction of atomic magnetic moments and the external static magnetic field.

(2) Interaction of static magnetic field with atoms:

The Hamiltonian operator $\Delta\hat{H}_{mag}$ corresponding to the interaction of a (homogeneous) static external magnetic field with an atom is give by:

$$\Delta\hat{H}_{mag} = -\hat{\vec{\mu}} \cdot \hat{\vec{B}}$$

where $\hat{\vec{\mu}}$ is the total magnetic moments that an atom has, $\hat{\vec{B}}$ is the external magnetic field. In atomic dimension, $\vec{B}$ can be regarded as homogeneous.

The total magnetic moment $\hat{\vec{\mu}}$ can be regarded as

$$\hat{\vec{\mu}} = \hat{\vec{\mu}}_l + \hat{\vec{\mu}}_s + \hat{\vec{\mu}}_I + \hat{\vec{\mu}}_{induced}$$

Where: $\hat{\vec{\mu}}_l = -g_l \mu_B \hat{\vec{l}}$ is the electron orbital magnetic moment,

$\hat{\vec{\mu}}_s = -g_s \mu_B \hat{\vec{S}}$ is the electron spin magnetic moment.

$\hat{\vec{\mu}}_I = g_I \mu_N \hat{\vec{I}} = g_I' \mu_B \hat{\vec{I}}$ is the nuclear spin magnetic momen

$\hat{\vec{\mu}}_{induced} = -\frac{\alpha^4}{2} \langle r^2 \sin^2\theta \rangle B$ is the induced magnetic moment under the external magnetic field.

Note that the nuclear magnetic moment is about 3 order of magnitude smaller than $\hat{\vec{\mu}}_\ell$ and $\hat{\vec{\mu}}_s$. In weak field, the induced magnetic moment is far smaller than the intrinsic magnetic moments ($\hat{\vec{\mu}}_\ell$ and $\hat{\vec{\mu}}_s$). But pay attention to the "−" sign in the $\hat{\vec{\mu}}_{induced}$ equation, which means the property of diamagnetism of any atoms. The induced magnetic moment will show effects in high excited states under very strong magnetic field. Here, we will ignore its influence.

$$
\begin{aligned}
\Delta \hat{H}_{mag} &= -\hat{\vec{\mu}} \cdot \hat{\vec{B}} \\
&\cong -(\hat{\vec{\mu}}_\ell + \hat{\vec{\mu}}_s + \hat{\vec{\mu}}_I) \cdot \hat{\vec{B}} \\
&= -(\mu_{\ell z} + \mu_{sz} + \mu_{Iz}) B \\
&= -\mu_B (g_\ell m_\ell + g_s m_s - g_I' m_I) B .
\end{aligned}
$$

(3) Zeeman Effect in Fine Structure

Consider single electron case (hydrogen atom or hydrogen-like ions), we analyze the influence of external magnetic field to the fine structure energy levels and spectral lines.

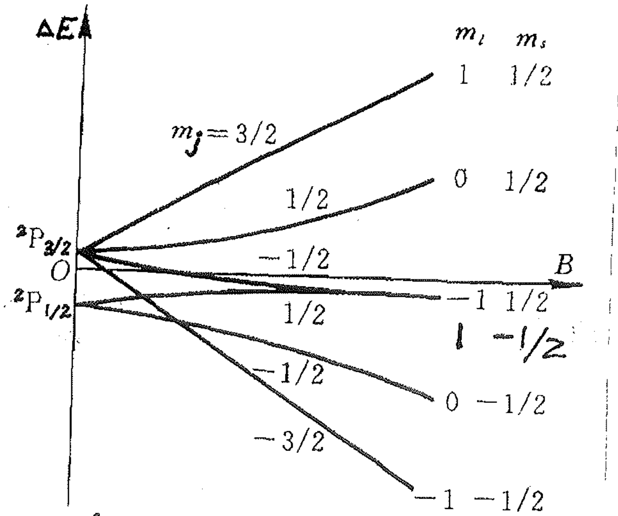
Here, the g_I' is too small to consider ($g_I' \sim \frac{m_e}{M_p} g_\ell$ (or g_s)).

Depending on the magnetic field strength, the Zeeman effect could be comparable to the electron spin-orbital coupling interaction. Therefore, these two interactions should be considered together. The corresponding Hamiltonian operator $\Delta\hat{H}$ is:

$$\Delta\hat{H} = a(r)\,\hat{\vec{l}}\cdot\hat{\vec{s}} - (\hat{\vec{\mu}}_l + \hat{\vec{\mu}}_s)\cdot\hat{\vec{B}}$$

This $\Delta\hat{H}$ can be treated as a perturbation to the main Hamiltonian operator, and then the energy shift caused by $\Delta\hat{H}$ can be derived from time-independent perturbation theory. This is the advantage of using QM to solve these problems. But the procedure is rather complicated, and we will only show the QM results below:

for ^2p state ($s=\frac{1}{2}$, $l=1$).



(X-aix is magnetic field strength)

* In very weak magnetic field, l-s coupling (i.e., spin-orbit coupling) is dominant. So we have $j=\frac{1}{2}$ and $j=\frac{3}{2}$ two cases. That's on the far-most left side of the plot. Each j corresponds to $m_j=\pm\frac{1}{2}$ and $m_j=\pm\frac{3}{2}, \pm\frac{1}{2}$ magnetic sublevels. That's why we see the splitting of the sublevels when $\vec{B}$ gradually increases.

* These sublevels could cross with each other as $\vec{B}$ continues increasing (in the intermedium case).

* In very strong magnetic field, there ~~is~~ is no longer l-s coupling, i.e; j and m_j are no longer good quantum numbers as they are not conservative. In this case, l, m_l, S, and m_s are approximately good quantum numbers.

$$m_l = 0, \pm 1, \quad m_s = \pm 1/2$$

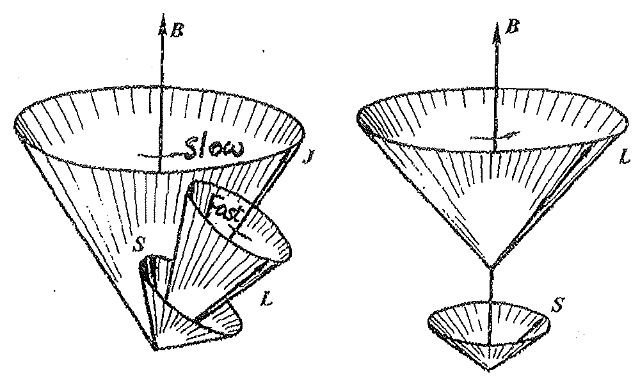
The combination of m_l and m_s is

m_l	1	0	−1	1	0	−1
m_s	½	½	½	−½	−½	−½

That's what is shown at the far-most right side of the plot.

The intermedium case can only be solved by QM. But in the two extreme cases (very weak and very strong $\vec{B}$), we can simplify the problem and use vector model to help us to understand the zeeman effect.

① In weak field approximation:
Under weak field, l-S coupling is dominant, so they form fine structure energy levels.
Use ^2P as an example, $^2P_{1/2}$ and $^2P_{3/2}$ states.



(a) Weak field (b) Strong Field
Figure. Vector model of spin-orbit coupling

We use the $|l s j m_j\rangle$ representation, regard the Hamiltonian operator $\Delta \hat{H}_{weak} = -(\hat{\vec{\mu}}_l + \hat{\vec{\mu}}_s) \cdot \hat{\vec{B}}$ as perturbation to the $a(r)\hat{\vec{l}} \cdot \hat{\vec{s}}$ coupling term.

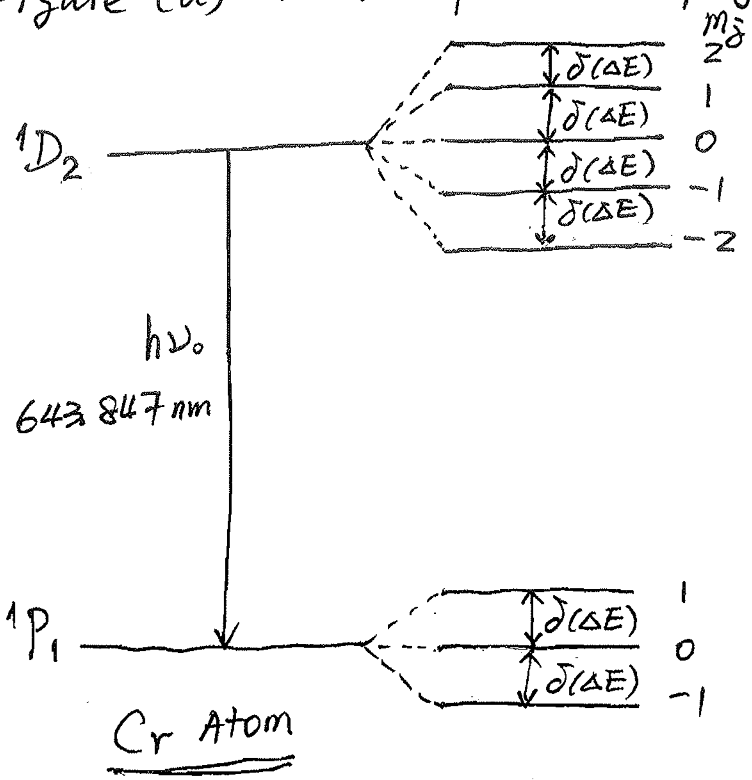
The energy shift caused by this perturbation (relative to the fine structure energy level) is given by

$$\Delta E_{mag} = \langle \Delta \hat{H}_{weak} \rangle$$
$$= \langle -(\hat{\vec{\mu}}_\ell + \hat{\vec{\mu}}_s)\cdot \hat{\vec{B}} \rangle \quad \left(\text{recall } \mu_{jz} = -g_j m_j \mu_B\right)$$
$$= \langle -\mu_{jz} B \rangle$$
$$= g_j m_j \mu_B B$$

where $g_j = \frac{3}{2} + \frac{1}{2}\,\frac{s(s+1) - \ell(\ell+1)}{j(j+1)}$ (See appendix for the derivation of g_j)

The vector model for weak field is that angular momentum $\hat{\vec{L}}$ and $\hat{\vec{S}}$ do fast precession around $\hat{\vec{J}}$ direction and form the total angular momentum $\hat{\vec{J}}$, while the $\hat{\vec{J}}$ will process slowly around the external magnetic field $\vec{B}$ (See Figure (a) in the previous page).

Example:



$\left.\begin{array}{l} s=0 \\ \ell=2 \\ j=2, \end{array}\right\} \Rightarrow g_j = 1$, $m_j = 0, \pm1, \pm2$

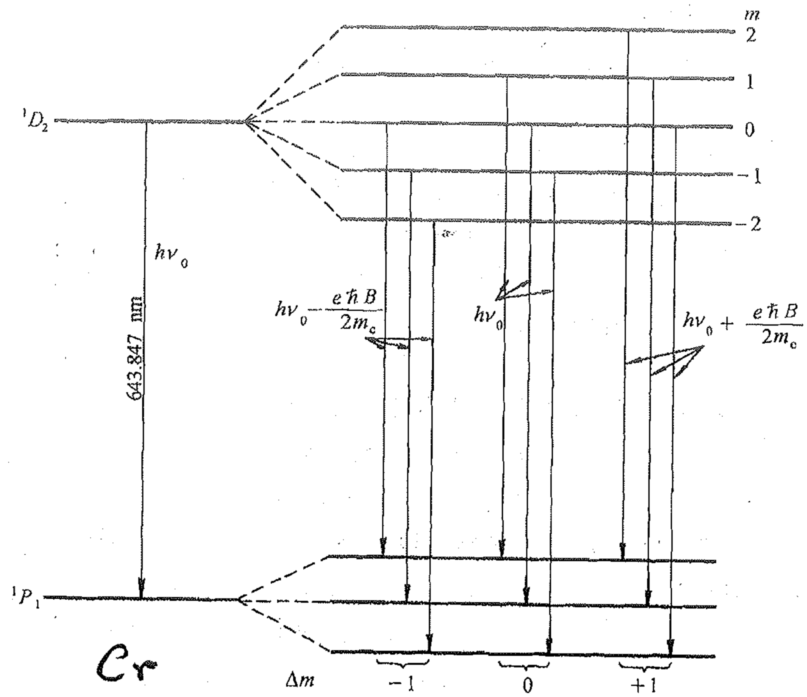
$$\delta(\Delta E) = \Delta E(m_j=2) - \Delta E(m_j=1)$$
$$= g_j \,\Delta m_j\, \mu_B B$$
$$= 1\times 1\times \mu_B B$$
$$= \mu_B B = \frac{e\hbar}{2m_e} B$$

$s=0,\ \ell=1,\ j=1 \Rightarrow g_j = 1$

$m_j = 0, \pm 1,$

$$\delta(\Delta E) = \Delta E(m_j=1) - \Delta E(m_j=0)$$
$$= g_j\,\Delta m_j\,\mu_B B$$
$$= \mu_B B = \frac{e\hbar}{2m_e} B.$$

Could you try to figure out the Zeeman splitting and spectral line splitting by yourself?



Selection rules $\Delta m_j = 0, \pm 1$.

If E_2 and E_1 are the energy for the upper and lower levels when there is no external magnetic field, then after adding external field, the energy levels become

$$\begin{cases} E_2' = E_2 + m_2 g_2 \mu_B B \\ E_1' = E_1 + m_1 g_1 \mu_B B \end{cases} \qquad (h\nu = E_2 - E_1)$$

$\therefore$ The transition frequency is changed to

$$h\nu' = E_2' - E_1' = (E_2 - E_1) + (m_2 g_2 - m_1 g_1)\mu_B B$$

$$= h\nu + (m_2 g_2 - m_1 g_1)\mu_B B,$$

$\because$ $g_2 = g_1 = 1$ in this case,

$$\therefore \quad h\nu' = h\nu + (m_2 - m_1)\mu_B B = h\nu + \Delta m \mu_B B.$$

Due to the selection rule $\Delta m_j = 0, \pm 1$, there will be three different wavelengths / frequencies:

$$h\nu' = h\nu + \begin{Bmatrix} +\mu_B B \\ 0 \\ -\mu_B B \end{Bmatrix}.$$

i.e., we will see 3 spectral lines, although there are 9 transitions.

② In strong field approximation:

Strong magnetic field prevents $l-s$ coupling. The result is that the spin and orbital angular momentums precess around the external magnetic field separatly (as shown in Figure (b)).

Use $|l s m_l m_s\rangle$ representation, the $\hat{\vec{l}}\cdot\hat{\vec{S}}$ coupling term is small so it is neglected.

$$\Delta\hat{H}_{strong} = a(r)\,\hat{\vec{l}}\cdot\hat{\vec{S}} - (\hat{\vec{\mu}}_l + \hat{\vec{\mu}}_s)\cdot\hat{\vec{B}}$$
$$\approx -(\hat{\vec{\mu}}_l + \hat{\vec{\mu}}_s)\cdot\hat{\vec{B}}$$
$$= \frac{e}{2m_e}(g_l\hat{\vec{l}} + g_s\hat{\vec{S}})\cdot\hat{\vec{B}}$$

The energy shift

$$\Delta E_{strong} = \langle\Delta\hat{H}_{strong}\rangle$$
$$= \langle\frac{e}{2m_e}(g_l\hat{\vec{l}} + g_s\hat{\vec{S}})\cdot\hat{\vec{B}}\rangle$$
$$= \frac{e\cdot B}{2m_e}(g_l l_z + g_s S_z)$$
$$= (g_l m_l + g_s m_s)\frac{e\hbar}{2m_e}B$$
$$= (g_l m_l + g_s m_s)\mu_B B$$

For ^2P energy level, $l=1$, $S=1/2$, $g_l=1$, $g_s=2$.

∴ for the combination of m_l, m_s,

m_l	1	0	−1	1	0	−1
m_s	½	½	½	−½	−½	−½
$g_l m_l + g_s m_s$	2	1	0	0	−1	−2

i.e; $(m_l=-1, m_s=\frac{1}{2})$ and $(m_l=1, m_s=-\frac{1}{2})$ two states have the same energy value under strong magnetic field.

That's why these two energy levels merge to one level at the far-most right side of ^2P figure.

The energy level splitting under very strong magnetic field is called Paschen-Back effect.

The selection rules are $\Delta m_s = 0$, $\Delta m_\ell = 0, \pm 1$.