

I. Zeeman Effect - Revisited

- No external \vec{B} -field ($\vec{B}_{\text{ext}} = 0$), we have \vec{B}_{int} that leads to spin-orbit interaction (thus \hat{H}'_{so}) [always there!]
- Zeeman Effect: There is an externally applied \vec{B} -field ($\vec{B}_{\text{ext}} \neq 0$)

Additional interaction energies (terms) in Hamiltonian

$$\begin{aligned} \bullet \vec{L} \rightarrow \vec{\mu}_L = -\frac{e}{2m_e} \vec{L} \quad \text{leads to } & \left(-\vec{\mu}_L \cdot \vec{B}_{\text{ext}} \right) \leftarrow \begin{array}{l} \text{considered in} \\ \text{"Normal Zeeman} \\ \text{effect"} \end{array} \\ \bullet \vec{S} \rightarrow \vec{\mu}_S = -\frac{e}{m_e} \vec{S} \quad \text{leads to } & \left(-\vec{\mu}_S \cdot \vec{B}_{\text{ext}} \right) \end{aligned}$$

Cannot avoid it
as \vec{S} is already invoked
in \hat{H}_{so} (spin-orbit interaction)

new terms in Hamiltonian
when $\vec{B}_{\text{ext}} \neq 0$

$$\begin{aligned}
 \hat{H}'_{Zeeman} &= \hat{H}'_z = -\hat{\mu}_L \cdot \vec{B}_{ext} - \hat{\mu}_S \cdot \vec{B}_{ext} = -\hat{\mu}_{total} \cdot \vec{B}_{ext} \\
 &= \frac{e}{2m_e} \hat{L} \cdot \vec{B}_{ext} + \frac{e}{m_e} \hat{S} \cdot \vec{B}_{ext} \quad \left[\hat{\mu}_{total} = \hat{\mu}_L + \hat{\mu}_S \right] \\
 &= \frac{e}{2m_e} (\hat{L} + 2\hat{S}) \cdot \vec{B}_{ext} \quad (35) \text{ "Zeeman term" that goes into Hamiltonian}
 \end{aligned}$$

[Note: $\vec{L} + 2\vec{S} \neq \vec{J}$ as $\vec{J} = \vec{L} + \vec{S}$]

Atom in \vec{B}_{ext} : The full QM problem is to solve TISE with

$$\hat{H} = \hat{H}_{atom} + \underbrace{\hat{H}'_{so}}_{\text{spin-orbit interaction}} + \underbrace{\hat{H}'_z}_{\text{Zeeman}} \left(+ \hat{H}'_{rel} \right) \quad (36)$$

What to do?

$f(r) \vec{S} \cdot \vec{L}$
[independent of \vec{B}_{ext}]

$$\frac{e}{2m_e} (\vec{L} + 2\vec{S}) \cdot \vec{B}_{ext}$$

even a relativistic correction
[ignore here!]
[less important in atoms other than hydrogen]

Think like a physicist!

$$\hat{H} = \hat{H}_{\text{atom}} + \underbrace{\hat{H}'_{\text{so}} + \hat{H}'_{\text{z}}}$$

- Two things to do? Do the more important thing (part) first and do it more seriously (rigorously)!

- Which term is more important?
 - No standard answer!
 - Depends on situation, i.e. \vec{B}_{ext}

The Big Picture

- Strong \vec{B}_{ext} field: $\hat{H} = \underbrace{(\hat{H}_{\text{atom}} + \hat{H}'_{\text{z}})}_{\text{handle more accurately}} + \underbrace{\hat{H}'_{\text{so}}}_{\text{perturbation}}$ (37a)

($\hat{H}'_{\text{z}} \propto \vec{B}_{\text{ext}}$) more important

- Weak \vec{B}_{ext} field: $\hat{H} = \underbrace{(\hat{H}_{\text{atom}} + \hat{H}'_{\text{so}})}_{\text{treated under spin-orbit interaction}} + \hat{H}'_{\text{z}}$ (37b)

B_{int} more important (order ~ 1 Tesla)

\hat{H}'_{so}

Strong \vec{B}_{ext}

- Treat $\hat{H}'_z = \frac{eB_{ext}}{2m} (\hat{L}_z + 2\hat{S}_z)$ first
 - states labelled by (n, l, m_l, s, m_s) are eigenstates of $(\hat{H}_{atom} + \hat{H}'_z)$
 - \hat{H}'_z removes degeneracies behind m_l and m_s
- With $\psi_{n l m_l s m_s}$, treat \hat{H}'_{so} as perturbation

Weak \vec{B}_{ext}

- Treat $\hat{H}'_{so} = f(r) \vec{S} \cdot \vec{L}$ first
 - states labelled by (n, l, s, j, m_j) are good for \hat{H}'_{so}
- Then treat \hat{H}'_z
 - $j = 3/2$ ——— $\begin{matrix} \text{---} & m_j \\ \text{---} & 3/2 \\ \text{---} & 1/2 \\ \text{---} & -1/2 \\ \text{---} & -3/2 \end{matrix}$
 - $j = 1/2$ ——— $\begin{matrix} \text{---} & 1/2 \\ \text{---} & -1/2 \end{matrix}$

[due to \hat{H}'_{so}] ↑ [due to \hat{H}'_z]

[It is $|\vec{B}_{ext}|$ vs $|\vec{B}_{int}|$ that decides which term is more important]

$\downarrow \hat{H}'_z$ $\downarrow \hat{H}'_{so}$ ($\vec{B}_{int} \sim 1$ Tesla)

Keep this Big Picture in mind as we fill in the math.

(a) Strong Field Zeeman Effect

$$\hat{H}_{\text{atom}} \psi_{n l m_l s m_s} \stackrel{s=1/2 \text{ always}}{=} E_n \psi_{n l m_l s m_s} \quad \text{for } U(r) \text{ [spherically symmetric, e.g. atoms]} \quad \text{[0th order problem]}$$

for H-atom, becomes $E_n = -\frac{13.6}{n^2} \text{ eV}$

The same $\{\psi_{n l m_l(s) m_s}\}$ also solve $(\hat{H}_{\text{atom}} + \hat{H}'_z)$: ^{^ "n only" for H-atom}

$$\therefore \hat{H}'_z \psi_{n l m_l(s) m_s} = \frac{e}{2m} B_{\text{ext}} (\hat{L}_z + 2\hat{S}_z) \psi_{n l m_l(s) m_s} = \frac{e\hbar}{2m_e} B_{\text{ext}} (m_l + 2m_s) \psi_{n l m_l(s) m_s}$$

↑ picks up $(m_l\hbar)$
↑ picks up $(m_s\hbar)$
↑ eigenvalue of \hat{H}'_z

$$\therefore (\hat{H}_{\text{atom}} + \hat{H}'_z) \psi_{n l m_l(s) m_s} = \left[-\frac{13.6}{n^2} + \mu_B B_{\text{ext}} (m_l + 2m_s) \right] \psi_{n l m_l(s) m_s} \quad (38)$$

Solved $(\hat{H}_{\text{atom}} + \hat{H}'_z)$ exactly!

↑
eigenvalues now depend on m_l, m_s

for H-atom [removed degeneracies behind m_l and m_s]

Aside:

Recall $\psi_{n l m_l (s) m_s} = \underbrace{\psi_{n l m_l}(r, \theta, \phi)}_{R_{nl}(r) \cdot Y_{lm_l}(\theta, \phi)} \cdot \begin{cases} \alpha_z & (\text{if } m_s = +1/2) \text{ "up"} \\ \beta_z & (\text{if } m_s = -1/2) \text{ "down"} \end{cases}$

$\therefore \hat{L}_z \psi_{n l m_l} = m_l \hbar \psi_{n l m_l}$ ($\because Y_{lm_l}(\theta, \phi)$ is eigenstate of \hat{L}_z with eigenvalue $m_l \hbar$)

Similarly, $\hat{S}_z \alpha_z = \underbrace{+\frac{\hbar}{2}}_{m_s \hbar} \alpha_z$; $\hat{S}_z \beta_z = \underbrace{-\frac{\hbar}{2}}_{m_s \hbar} \beta_z$
 $(m_s = +1/2)$ $(m_s = -1/2)$

\therefore Eq. (38) follows.

Remarks: Zooming into $\langle \hat{S}_x \rangle = 0$ ^{Why?} also called α_z

$\psi_{nl m_l (s) m_s} \quad |s m_s\rangle = \begin{cases} |1/2 \ 1/2\rangle & \text{for } S_z = \frac{\hbar}{2} \text{ (up) state} \\ |1/2 \ -1/2\rangle & \text{for } S_z = -\frac{\hbar}{2} \text{ (down) state} \end{cases}$

related to spin also called β_z

$\therefore \langle \hat{S}_x \rangle$ is either $\langle \alpha_z | \hat{S}_x | \alpha_z \rangle$ or $\langle \beta_z | \hat{S}_x | \beta_z \rangle$

- States of definite S_z have completely uncertain S_x ($\because [\hat{S}_z, \hat{S}_x] \neq 0$)
- $\therefore \langle \hat{S}_x \rangle = 0$ (by argument)

More explicitly, $\langle \alpha_z | \hat{S}_x | \alpha_z \rangle = (1 \ 0) \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = 0$ (by math)

$$\langle \beta_z | \hat{S}_x | \beta_z \rangle = (0 \ 1) \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = 0$$

- $\langle \hat{L}_x \rangle = \int Y_{lm}^*(\theta, \phi) \hat{L}_x Y_{lm}(\theta, \phi) d\Omega = 0$ (same argument)

- Similar consideration for $\langle \hat{S}_y \rangle$ and $\langle \hat{L}_y \rangle$

Putting results together (Strong field):

AP-V-9

$$E_{nl m_l(s) m_s} \approx \underbrace{-\frac{13.6}{n^2}}_{\substack{\text{ignored} \\ \text{everything} \\ \text{(QM I) (H-atom)}}} + \underbrace{\mu_B B_{\text{ext}} (m_l + 2m_s)}_{\substack{\text{due to } \hat{H}'_z \text{ (thus } B_{\text{ext}}) \\ \text{treated exactly}}} + \underbrace{m_l m_s \hbar^2 \langle f(r) \rangle}_{\substack{\text{due to } \hat{H}'_{so} \\ \text{1st order perturbation}}}$$

(40)
(Done!)

Example: $l=1$ states (p states) $m_l = \begin{cases} 1 \\ 0 \\ -1 \end{cases}$ and $m_s = \begin{cases} +1/2 \text{ (up)} \\ -1/2 \text{ (down)} \end{cases}$ total of 6 states

• ignore everything (1st term in Eq. (34)): $-\frac{13.6}{n^2}$ ----- ($l=1$) (6 states)

6 states have

m_l	m_s
1	+1/2
0	+1/2
1	-1/2
-1	+1/2
0	-1/2
-1	-1/2

$m_l + 2m_s$
2
1
0
0
-1
-2

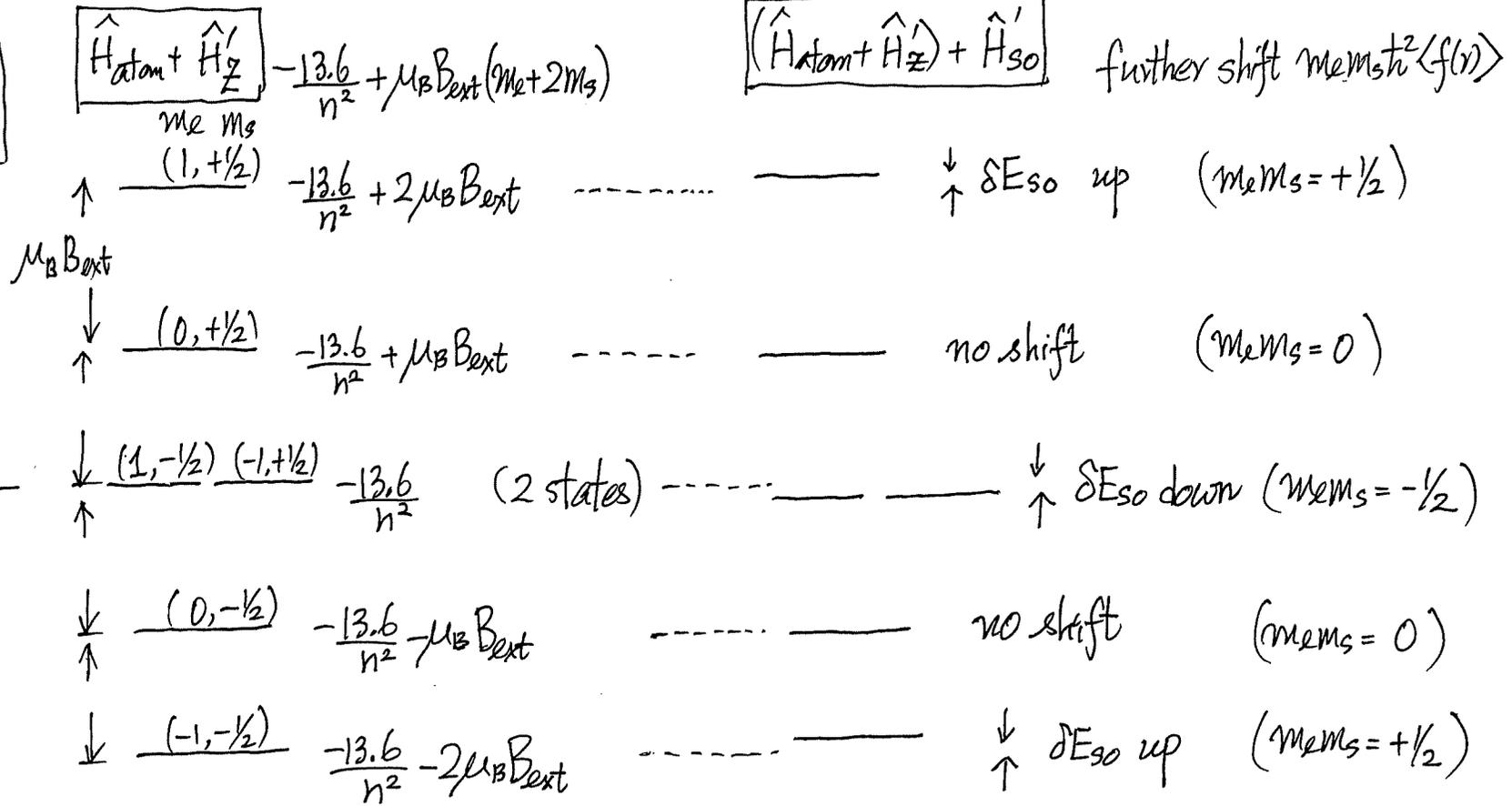
$m_l m_s$
+1/2
0
-1/2
-1/2
0
+1/2

* Useful for \hat{H}'_z term

+ Useful for \hat{H}'_{so} term
(See Eq. (40))

AP-II-(10)

ignore everything
 \hat{H}_{atom} only



Strong Field

[Split the p states by strong B_{ext} into 5 levels]
 (cf. without spin, split into 3 states only) (normal Zeeman effect)

where $\delta E_{so} = \frac{1}{2} \hbar^2 \langle f(r) \rangle$
 tiny shifts due to \hat{H}'_{so}

- In any case, the key message is that degenerate states are split in \vec{B}_{ext} .
- Similar consideration for other l.
- Transitions [e.g. $2p \rightarrow 1s$] lead to Zeeman Effect (splitting of spectral line in \vec{B}_{ext})

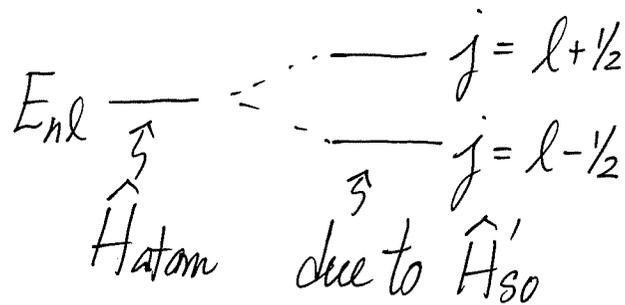
(b) Weak Field Zeeman Effect

▪ \hat{H}'_{so} is more important than \hat{H}'_z [recall: $|B_{int}| \sim \text{Tesla}$ leads to spin-orbit interaction]

▪ Do $(\hat{H}_{atom} + \hat{H}'_{so})$ first [Done! see spin-orbit interaction]

use states $\psi_{n l (s) j m_j}$ \rightarrow for $s = 1/2, l \neq 0$: $j = l + 1/2, l - 1/2$
 \rightarrow for $s = 1/2, l = 0$: $j = 1/2$ only

then



(j, m_j) refer to total angular momentum $\vec{J} = \vec{L} + \vec{S}$

∴ \hat{H}'_{so} makes \vec{J} important (not L_z , not S_z , they lost their identities)

$\psi_{n l (s) j m_j}$ play the role of the "unperturbed" states

■ Treat $\hat{H}'_z = -\hat{\mu}_L \cdot \vec{B}_{\text{ext}} - \hat{\mu}_S \cdot \vec{B}_{\text{ext}} = -\underbrace{\hat{\mu}_{\text{total}}}_{(\vec{\mu}_L + \vec{\mu}_S)} \cdot \vec{B}_{\text{ext}} = \frac{e}{2m_e} \vec{B}_{\text{ext}} \cdot (\hat{L} + 2\hat{S})$
 by 1st order perturbation theory

$$\begin{aligned}
 E_{\text{Zeeman}}^{(1)} &= \langle n l (s) j m_j | -\hat{\mu}_{\text{total}} \cdot \vec{B}_{\text{ext}} | n l (s) j m_j \rangle \\
 &= \langle n l (s) j m_j | \frac{e}{2m_e} \vec{B}_{\text{ext}} \cdot (\hat{L} + 2\hat{S}) | n l (s) j m_j \rangle \quad (41)
 \end{aligned}$$

• Need approximation to do (41):

Why? $(j m_j)$ refer to \vec{J} , but $\hat{L} + 2\hat{S} = \vec{J} + \vec{S} \neq \vec{J}$

OR $\vec{\mu}_{\text{total}} \neq \underbrace{g}_{\text{some number}} \left(\frac{-e}{2m_e} \right) \vec{J}$ (strictly speaking)

formally, $\vec{\mu}_{\text{total}}$ is NOT anti-parallel to \vec{J} as in $\begin{cases} \vec{\mu}_L = (1) \cdot \frac{-e}{2m_e} \vec{L} \\ \vec{\mu}_S = (2) \cdot \frac{-e}{2m_e} \vec{S} \end{cases}$

Find a way out?

Approximate $\vec{\mu}_{\text{total}}$ (not $\propto -\vec{J}$) by $\boxed{\vec{\mu}_{\text{J (approx)}} \propto -\vec{J}}$

How? Take the projection of $\vec{\mu}_{\text{total}}$ along \vec{J}

i.e. project $(\vec{L} + 2\vec{S})$ along \vec{J} ($\because \vec{\mu}_{\text{total}} = \frac{-e}{2m_e}(\vec{L} + 2\vec{S})$)

$$\vec{L} + \vec{S} + \vec{S} = \vec{J} + \vec{S} \leftarrow \text{project } \vec{S} \text{ along } \vec{J}$$

↑
already along \vec{J} (OK)

• Approximate \vec{S} as a vector along direction of \vec{J} by projecting \vec{S} along \vec{J} :

$$\hookrightarrow \left(\frac{\vec{S} \cdot \vec{J}}{|\vec{J}|} \right) \frac{\vec{J}}{|\vec{J}|} = \frac{(\vec{S} \cdot \vec{J})}{J^2} \vec{J} = \frac{J^2 - L^2 + S^2}{2J^2} \vec{J}$$

↑
unit vector in
direction of \vec{J}

$$(\because \vec{L} = \vec{J} - \vec{S} \Rightarrow L^2 = J^2 + S^2 - 2\vec{S} \cdot \vec{J})$$

$$\therefore \vec{L} + 2\vec{S} \underset{\substack{\uparrow \\ \text{approximation}}}{\approx} \left(1 + \frac{J^2 - L^2 + S^2}{2J^2} \right) \vec{J} \quad (\text{now along } \vec{J}) \quad (42)$$

From Eq. (41), $E_{\text{Zeeman}}^{(1)} \cong \langle n l (s) j m_j | \frac{e}{2m_e} \vec{B}_{\text{ext}} \cdot \left(1 + \frac{\hat{J}^2 - \hat{L}^2 + \hat{S}^2}{2\hat{J}^2} \right) \hat{J} | n l (s) j m_j \rangle$

$$= \langle n l (s) j m_j | \underbrace{\left(1 + \frac{j(j+1) - l(l+1) + s(s+1)}{2j(j+1)} \right)}_{\text{just a number of order 1 (Landé } g\text{-factor)}} \frac{e}{2m_e} \hat{J} \cdot \vec{B}_{\text{ext}} | n l (s) j m_j \rangle$$

($\vec{B}_{\text{ext}} = B_{\text{ext}} \hat{z}$)
 [no loss of generality]

$$= \langle n l (s) j m_j | g_{\text{Landé}} \frac{e}{2m_e} \hat{J} \cdot \vec{B}_{\text{ext}} | n l (s) j m_j \rangle \quad (43)$$

$$= \langle n l (s) j m_j | g_{\text{Landé}} \frac{e}{2m_e} \hat{J}_z B_{\text{ext}} | n l (s) j m_j \rangle$$

$$= g_{\text{Landé}} \frac{e \hbar}{2m_e} m_j B_{\text{ext}} = g_{\text{Landé}} \mu_B B_{\text{ext}} m_j \quad (\text{Done!}) \quad (44)$$

- Inspect Eq. (37), it is equivalent to having approximated $\vec{\mu}_{\text{total}}$ by

$$\vec{\mu}_{\text{J (approx)}} = g_{\text{Landé}} \left(\frac{-e}{2m_e} \right) \vec{J} \quad (45)$$

[retained standard form]

$$\text{with } g_{\text{Landé}} \equiv 1 + \frac{j(j+1) - l(l+1) + s(s+1)}{2j(j+1)}$$

(for the state under consideration)

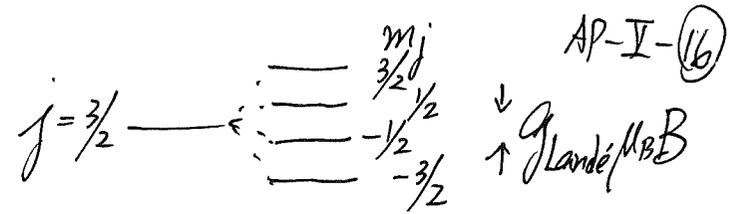
- Retained the standard form between $\vec{\mu}$ and AM, $[\vec{J} = \vec{L} + \vec{S}]$
 $(j) \quad (l) \quad (s)$ all in!
 and put all the complications into $g_{\text{Landé}}$, which can be determined experimentally

Eq. (44): $E_{\text{Zeeman}}^{(1)} = \underbrace{g_{\text{Landé}}}_{\substack{g_{\text{Landé}} \\ m_j}} \mu_B B m_j \quad \underline{\text{vs}} \quad \underbrace{g \mu_B B m_e}_{\substack{g \\ m_e}} \quad \text{for "Normal Zeeman effect" due to } \vec{\mu}_L \text{ only.}$

same form

$\underline{\text{vs}}$
 $\underline{\text{vs}}$

$$\therefore E_{\text{Zeeman}}^{(1)} = g_{\text{Landé}} \mu_B B m_j$$



removes degeneracy due to m_j

Example

$l=1$ (p states)
(6 states with spin)

Ignoring everything

\hat{H}_{atom} only

+

Including \hat{H}'_{so} only

+

Weak field with \hat{H}'_Z

Weak Field

$n p$ states $-\frac{13.6\text{eV}}{n^2}$ -----
(e.g. $2p$) (6 states)
(H-atom)

----- $j=3/2$
(4 states)

----- $j=1/2$
(2 states)

m_j

----- $+3/2$
----- $+1/2$
----- $-1/2$
----- $-3/2$

----- $+1/2$
----- $-1/2$

With \hat{H}'_{so} only,
energy depends on
 n and j
(see fine-structure)
discussion

[no external field
here, $B_{\text{ext}}=0$]

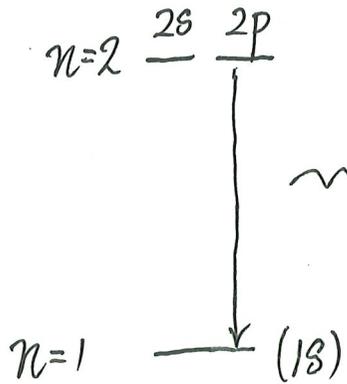
B_{ext} lifts degeneracy
as

$$E_{\text{Zeeman}}^{(1)} = g_{\text{Landé}} \mu_B m_j B_{\text{ext}}$$

depending on m_j

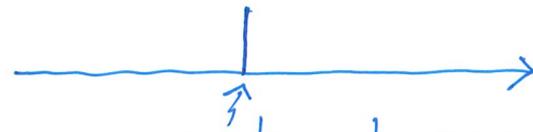
Consequences : Look into the first Lyman line (Weak Field)

\hat{H}_{atom} only



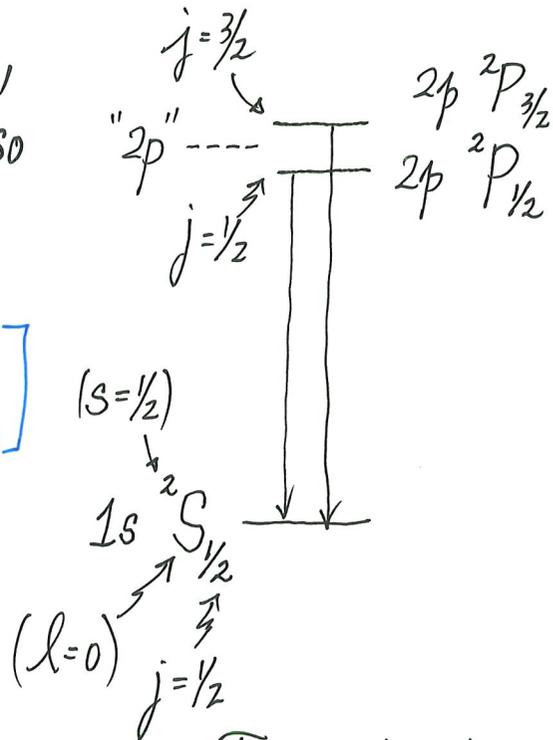
$\rightarrow h\nu = \Delta E = -\frac{13.6}{4} - \left(-\frac{13.6}{1}\right) \approx 10.2 \text{ eV}$

spectrum



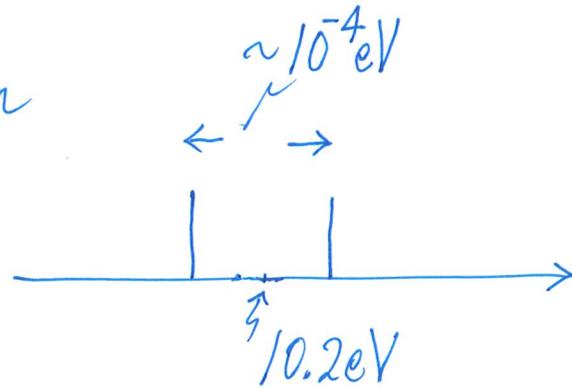
one line at $\sim 10.2 \text{ eV}$ (in Lyman Series)

$\hat{H}_{atom} + \hat{H}'_{so}$
 $(\vec{B}_{ext} = 0)$
 [spin-orbit coupling only]



Fine structure

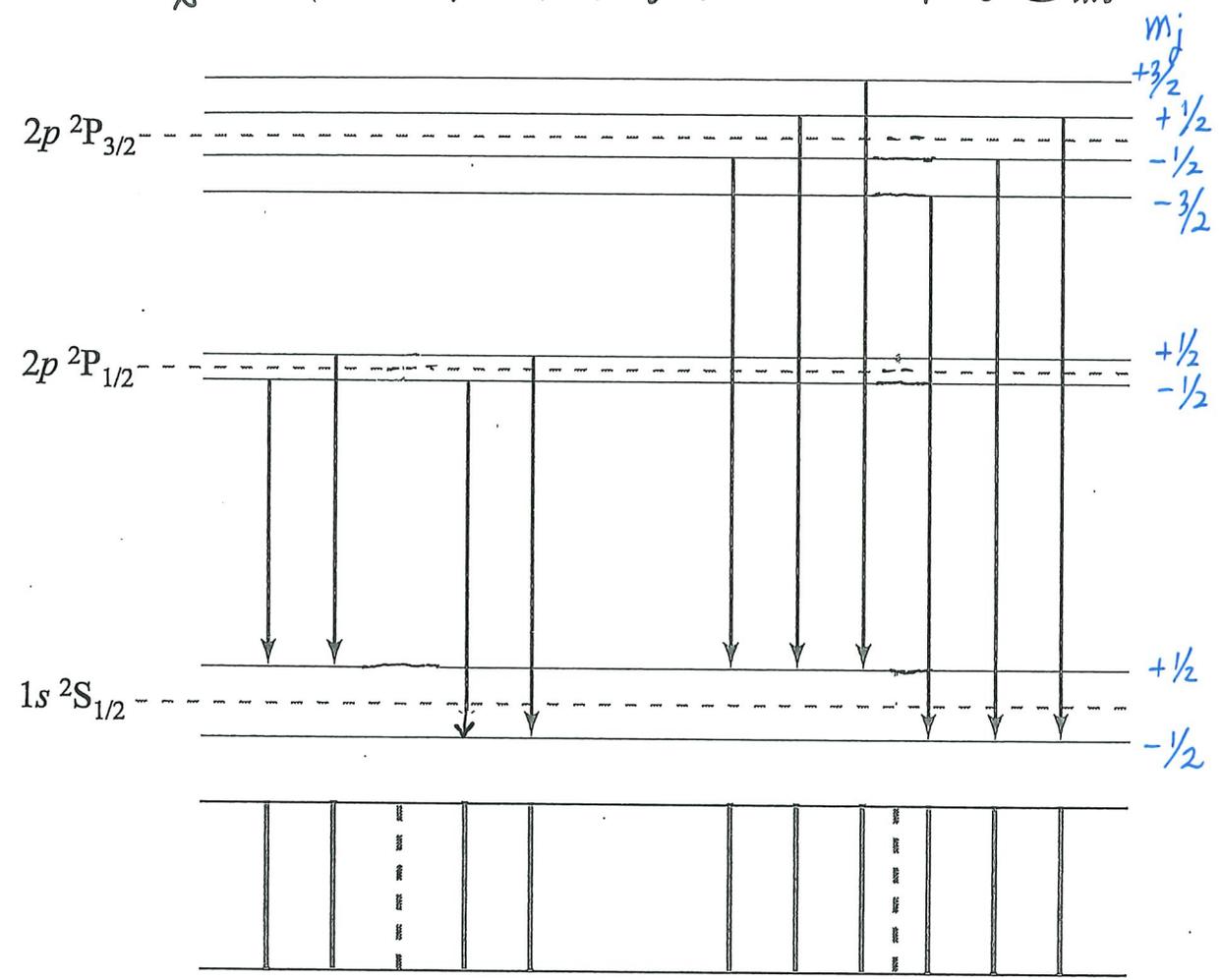
spectrum



due to spin-orbit interaction

$$\hat{H}_{atom} + \hat{H}'_{so} + \hat{H}'_z \quad (\vec{B}_{ext} \neq 0, \text{ but weaker than } \vec{B}_{int} \text{ in spin-orbit interaction})$$

Hydrogen
($n=2 \rightarrow n=1$)



Selection rules
for allowed
transitions
 $\Delta m_j = 0, \pm 1$

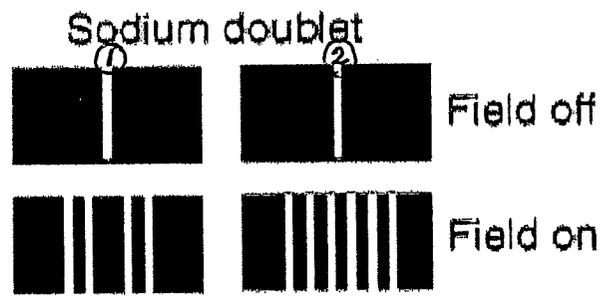
10 lines
in weak \vec{B}_{ext}

fine structure when $\vec{B}_{ext} = 0$

The Zeeman effect for the 1s and 2p levels of atomic hydrogen in a weak external magnetic field, showing the allowed transitions. A schematic diagram of the resulting spectrum is shown at the bottom. The dashed lines show the fine structure that is present in the absence of an external magnetic field.

Anomalous
Zeeman
Effect

Same Works for Sodium



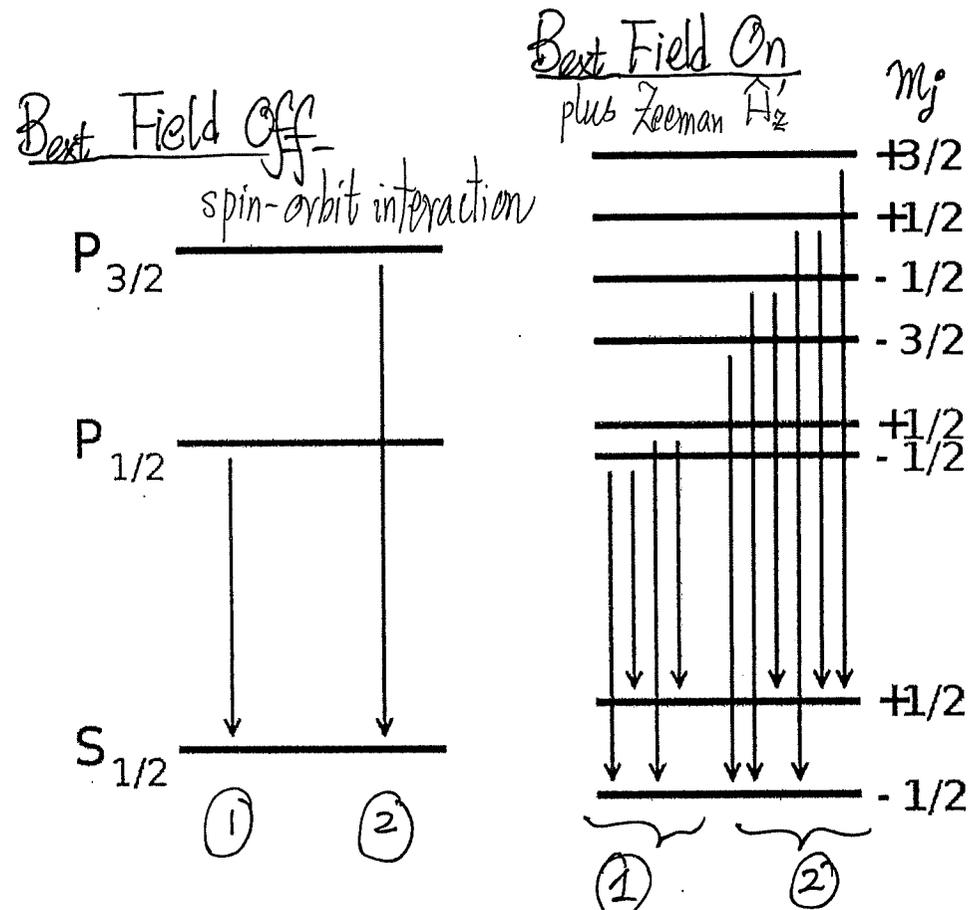
▪ \hat{H}'_{so} only
Sodium D lines (doublet)

▪ With \vec{B}_{ext} , each line in doublet split

▪ This example uses Na atom

▪ Bigger atoms have stronger \hat{H}'_{so}

▪ Thus, weak \vec{B}_{ext} case is often observed in heavier atoms



Zeeman term leads to $g_L \mu_B m_j B_{ext}$

$\Delta m_j = 0, \pm 1$
selection rules

① becomes 4 lines

② becomes 6 lines

(10 lines)
[even # of lines]

Final Remarks

- The study on Zeeman effect had led to key developments in ideas⁺/concepts⁺ in Quantum Mechanics
- QM and spin, plus techniques (approximations), are key to understand Fine structure and Zeeman effect
- Ideas: \vec{J} , spin-orbit interaction \hat{H}_{so} , \hat{H}_z , strong/weak field cases... are introduced within the context of hydrogen atom here.
But ideas/techniques are applicable to other atoms
[need to add up \vec{L} 's and \vec{S} 's of many electrons]
- Historically, Landé was introduced (1921) to describe exp'tal data before QM and spin were established. Its value informs us how important spin-orbit interaction is in an atom.

An appreciation...

Modern/Quantum Physics level : Descriptive

Zeeman : " $-\vec{\mu}_L \cdot \vec{B}$ "
 Spin-orbit : " $\vec{S} \cdot \vec{L}$ "
 Hydrogen's relative correction : "ignored"
 Strong & Weak Field Zeeman : "not treated"

Applied Quantum Mechanics :

A bit of Quantum Mechanics (TISE, Angular Momenta in QM, Think classical and go quantum (look for \hat{H}'_{so} and \hat{H}'_z)) and approximation methods (perturbation theory, physical sense) can take us to a deeper and quantitative understanding that backs up the qualitative descriptions.