

# I. Zeeman Effect - Revisited

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

Additional interaction energies (terms) in Hamiltonian

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

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

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

$$\begin{aligned}
 \hat{H}'_{\text{Zeeman}} &= \hat{H}'_z = -\hat{\mu}_L \cdot \vec{B}_{\text{ext}} - \hat{\mu}_S \cdot \vec{B}_{\text{ext}} = -\hat{\mu}_{\text{total}} \cdot \vec{B}_{\text{ext}} \\
 &= \frac{e}{2m_e} \hat{\vec{L}} \cdot \vec{B}_{\text{ext}} + \frac{e}{m_e} \hat{\vec{S}} \cdot \vec{B}_{\text{ext}} \quad \left[ \hat{\mu}_{\text{total}} = \hat{\mu}_L + \hat{\mu}_S \right] \\
 &= \frac{e}{2m_e} (\hat{\vec{L}} + 2\hat{\vec{S}}) \cdot \vec{B}_{\text{ext}} \quad (30) \text{ "Zeeman term" that goes} \\
 &\quad \text{into Hamiltonian}
 \end{aligned}$$

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

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

$$\hat{H} = \hat{H}_{\text{atom}} + \underbrace{\hat{H}'_{\text{so}}}_{\text{spin-orbit interaction}} + \underbrace{\hat{H}'_z}_{\text{Zeeman}} + \underbrace{\hat{H}'_{\text{rel}}}_{\text{even a relativistic correction}} \quad (31)$$

What to do?

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

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

[ignore here!]  
[less important in atoms other than hydrogen]

Think like a physicist!

$$\hat{H} = \hat{H}_{\text{atom}} + \underbrace{\hat{H}'_{\text{so}} + \hat{H}'_{\text{z}}}_{(32)}$$

- 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.  $\vec{B}_{\text{ext}}$

## The Big Picture

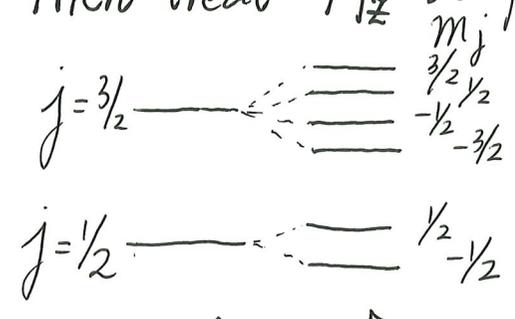
- Strong  $\vec{B}_{\text{ext}}$  field:  $\hat{H} = \underbrace{(\hat{H}_{\text{atom}} + \hat{H}'_{\text{z}})}_{\text{handle more accurately}} + \underbrace{\hat{H}'_{\text{so}}}_{\text{perturbation}} \quad (32a)$   
 $(\hat{H}'_{\text{z}} \propto \vec{B}_{\text{ext}})$  more important

- Weak  $\vec{B}_{\text{ext}}$  field:  $\hat{H} = \underbrace{(\hat{H}_{\text{atom}} + \hat{H}'_{\text{so}})}_{\text{treated under spin-orbit interaction}} + \hat{H}'_{\text{z}} \quad (32b)$   
 $B_{\text{int}}$  more important (order  $\sim 1$  Tesla)  
 $\hat{H}'_{\text{so}}$

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  $\hat{H}'_z$  as perturbation
 

$j = 3/2$  ———  $\begin{matrix} \text{---} & m_j = 3/2 \\ \text{---} & m_j = 1/2 \\ \text{---} & m_j = -1/2 \\ \text{---} & m_j = -3/2 \end{matrix}$   
 $j = 1/2$  ———  $\begin{matrix} \text{---} & m_j = 1/2 \\ \text{---} & m_j = -1/2 \end{matrix}$

$\left[ \text{due to } \hat{H}'_{so} \right]$        $\left[ \text{due to } \hat{H}'_z \right]$   
 (fine structure)

[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.

## Moral of the Story

- Work on the more important thing first! (Common Sense!)  
(人生道理)

Q: What if  $\hat{H}_{s0}'$  and  $\hat{H}_{z}'$  are comparable in effects?

- Most difficult case
- tune Best to avoid this

(a) Strong Field Zeeman Effect

$$\hat{H}_{\text{atom}} \psi_{n l m_l s m_s} \xrightarrow{s=1/2 \text{ always}} = E_n \psi_{n l m_l s m_s} \quad \left[ \begin{array}{l} \text{for } U(r) \text{ [spherically symmetric, assumed for atoms]} \\ \text{[0th order problem]} \end{array} \right]$$

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  $(\hat{H}_{\text{atom}} + \hat{H}'_z)$  <sup>↑ "n only" for H-atom</sup>

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

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

$$\therefore (\hat{H}_{\text{atom}} + \hat{H}'_z) \psi_{n l m_l(s) m_s} = \left[ -\frac{13.6}{n^2} + \mu_B B_{\text{ext}} (m_l + 2m_s) \right] \psi_{n l m_l(s) m_s} \quad (33)$$

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

↑  
for H-atom [removed degeneracies behind  $m_l$  and  $m_s$ ]  
(OR  $E_n$ )

$\therefore$  For  $(\hat{H}_{\text{atom}} + \hat{H}'_z)$ , the description  $\psi_{n l m_l (s) m_s}$  is preferred over  $\psi_{n l (s) j m_j}$

Aside:

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

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

Similarly,

$$\hat{S}_z \alpha_z = \underbrace{+\frac{\hbar}{2}}_{m_s \hbar} \alpha_z \quad ; \quad \hat{S}_z \beta_z = \underbrace{-\frac{\hbar}{2}}_{m_s \hbar} \beta_z \quad [ \because \hat{S}_z \text{ sees } \alpha_z, \beta_z ]$$

$(m_s = +1/2)$    $(m_s = -1/2)$

$\therefore$  Eq. (33) follows.

$$\hat{H} = \underbrace{(\hat{H}_{\text{atom}} + \hat{H}_z)}_{\text{treated exactly (plays the role of } \hat{H}_0 \text{) using } \psi_{n,l,m_l(s),m_s}} + \hat{H}'_{so} \leftarrow \text{treat it perturbatively}$$

• Apply 1<sup>st</sup> order perturbation theory:

$$E_{so}^{(1)} = \int \psi_{n,l,m_l(s),m_s}^* (f(r) \underbrace{\hat{S} \cdot \hat{L}}_{\hat{S}_x \hat{L}_x + \hat{S}_y \hat{L}_y + \hat{S}_z \hat{L}_z}) \psi_{n,l,m_l(s),m_s} d\tau \quad [\text{used 1<sup>st</sup> order formula}]$$

$$= \underbrace{\langle f(r) \rangle}_{\int |R_{nl}(r)|^2 f(r) r^2 dr \text{ (depends on } n, l)} \left[ \underbrace{\langle \hat{S}_x \rangle}_{\text{expectation value over spin state specified by } m_s} \underbrace{\langle \hat{L}_x \rangle}_{\text{expectation value over orbital AM state specified by } l, m_l} + \langle \hat{S}_y \rangle \langle \hat{L}_y \rangle + \underbrace{\langle \hat{S}_z \rangle}_{m_s \hbar} \underbrace{\langle \hat{L}_z \rangle}_{m_l \hbar} \right]$$

$$= m_l m_s \hbar^2 \langle f(r) \rangle \quad (\text{Key result}) \quad (34)$$

\* See next page on handling the spin part, e.g.  $\psi_{n,l,m_l(s),\frac{1}{2}} = \psi_{n,l,m_l}(r, \theta, \phi) \cdot \alpha_x$

## Arguments

Q: Why  $\langle \hat{S}_x \rangle = 0$ ?  $\psi_{n l m_l (s) m_s}$  is a state with definite  $S_z$   $\left\{ \begin{array}{l} +\frac{\hbar}{2} \text{ (} m_s = \frac{1}{2} \text{)} \\ -\frac{\hbar}{2} \text{ (} m_s = -\frac{1}{2} \text{)} \end{array} \right.$

- Such state is NOT an eigenstate of  $\hat{S}_x$  ( $\because [\hat{S}_z, \hat{S}_x] \neq 0$ )
- Go through the thought of multiple copies of states [definite (s)  $m_s$ ] and measure  $S_x$ 
  - $\rightarrow$  50%  $S_x = +\frac{\hbar}{2}$
  - $\rightarrow$  50%  $S_x = -\frac{\hbar}{2}$ $\therefore \langle S_x \rangle = 0$

Q: Why  $\langle \hat{L}_x \rangle = 0$  for  $\psi_{n l m_l (s) m_s}$ ?

$\psi_{n l m_l (s) m_s}$  is a state of definite  $L_z$  (equals  $m_l \hbar$ )  
Such state is NOT an eigenstate of  $\hat{L}_x$

... [same thoughts]  $\langle \hat{L}_x \rangle = 0$

Thus Eq.(34) follows.

- also works for  $\langle \hat{S}_y \rangle = 0$  &  $\langle \hat{L}_y \rangle = 0$

Math Details: Zooming into  $\langle \hat{S}_x \rangle = 0$  <sup>Why?</sup> also called  $\alpha_z$

$\psi_{n, l, m_l, m_s}$  related to spin  $|s, m_s\rangle = \begin{cases} |1/2, 1/2\rangle & \text{for } S_z = \frac{\hbar}{2} \text{ (up) state} \\ |1/2, -1/2\rangle & \text{for } S_z = -\frac{\hbar}{2} \text{ (down) state} \end{cases}$  also called  $\beta_z$

$\therefore \langle \hat{S}_x \rangle$  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)

By Math:  $\langle \alpha_z | \hat{S}_x | \alpha_z \rangle = (1^* \ 0^*) \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = 0$

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

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

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

# Putting results together (Strong field):

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

(35) (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. (35)):  $-\frac{13.6}{n^2}$  ----- ( $l=1$ ) (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

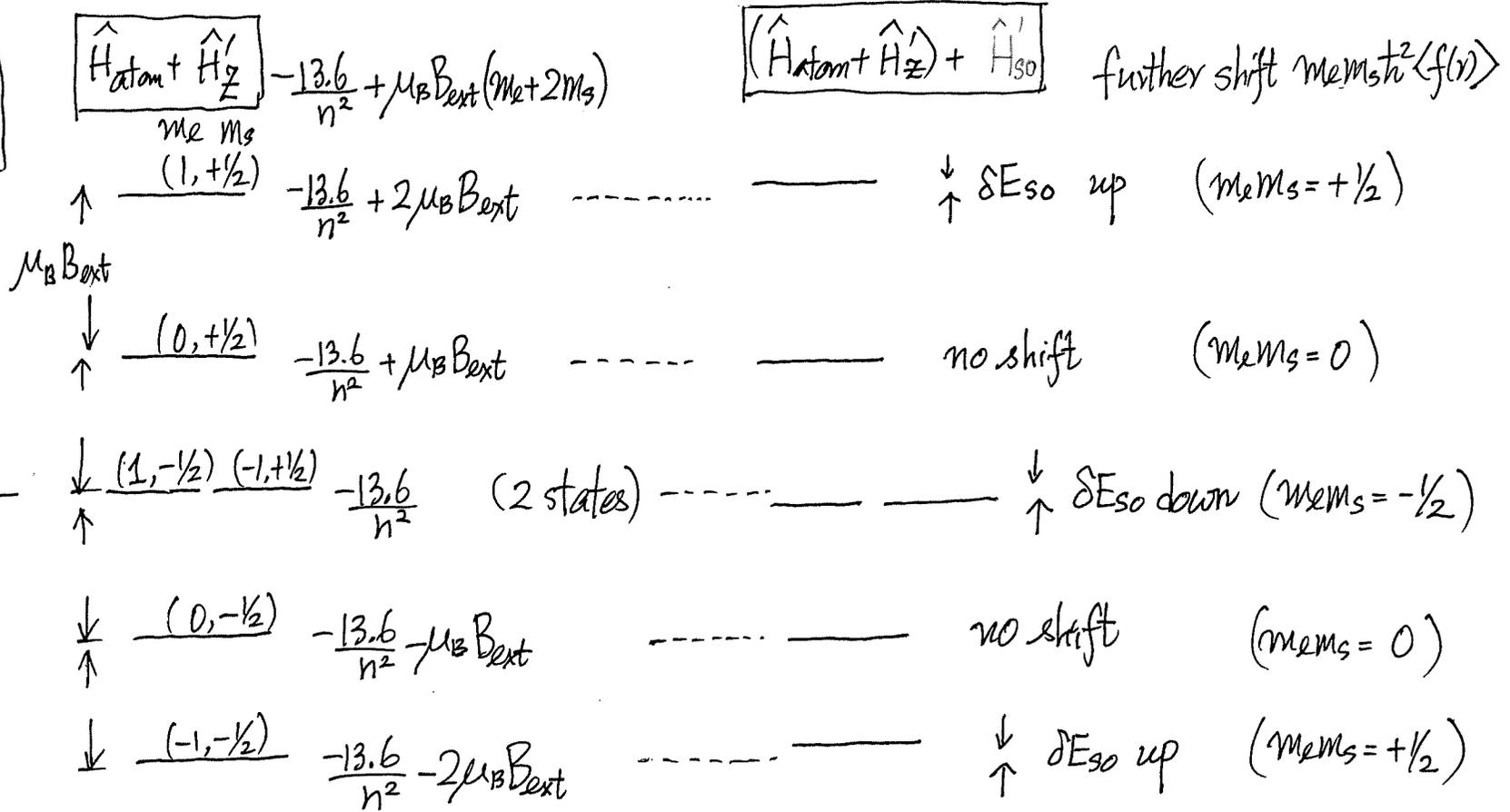
$m_l m_s$ †
+1/2
0
-1/2
-1/2
0
+1/2

\* Useful for  $\hat{H}'_z$  term

† Useful for  $\hat{H}'_{so}$  term  
(See Eq. (35))

AP-II-(12)

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  $\vec{B}_{ext}$ )

- In atomic physics, the strong field case is called the "Paschen-Back Effect"
- The observed phenomena are similar to Normal Zeeman Effect

(b) Weak Field Zeeman Effect

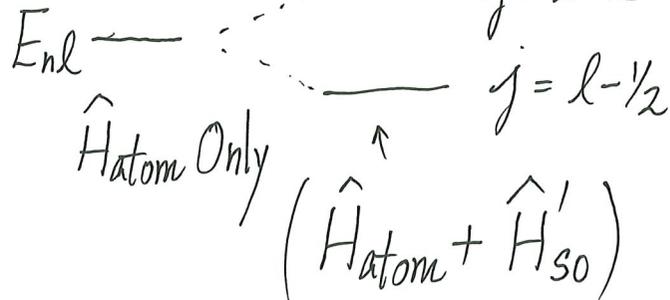
$\hat{H}_{atom}$  term:  $\psi_{n,l,m_l(s),m_s}$  and  $\psi_{n,l(s),j,m_j}$  are equally good ↗ both with  $E_{nl}$

Weak field  $\Rightarrow$   $\hat{H}'_{so}$  is more important than  $\hat{H}'_{z}$   
 $B_{int}$   $B_{ext}$  (weak)

Do  $(\hat{H}_{atom} + \hat{H}'_{so})$  first

(Done! Fine structure)

$\psi_{n,l(s),j,m_j}$  are preferred over  $\psi_{n,l,m_l(s),m_s}$  due to  $\hat{H}'_{so}$



makes  $\vec{J}$  important  
 not  $L_z$ , not  $S_z$   
 they lost their identities

Then  $\hat{H}'_z = -\hat{\mu}_{total} \cdot \vec{B}_{ext} = \frac{e}{2m_e} \vec{B}_{ext} \cdot (\hat{L} + 2\hat{S})$  is treated as perturbation  
 $(\hat{H}_{atom} + \hat{H}'_z)$  requires  $\psi_{n l (s) j m_j} \leftarrow$  "unperturbed states"

$$E_{Zeeman}^{(1)} = \langle n l (s) j m_j | (-\hat{\mu}_{total} \cdot \vec{B}_{ext}) | n l (s) j m_j \rangle \quad (1^{st} \text{ order perturbation})$$

$$= \langle n l (s) j m_j | \underbrace{\frac{e}{2m_e} \vec{B}_{ext} \cdot (\hat{L} + 2\hat{S})}_{\neq \hat{J}} | n l (s) j m_j \rangle \quad (36)$$

Problem arises from:

$$\hat{\mu}_{total} = -\frac{e}{2m_e} (\hat{L} + 2\hat{S}) = -\frac{e}{2m} (\hat{J} + \overbrace{\hat{S}}^{\text{extra!}}) \neq g \left( \frac{-e}{2m_e} \right) \hat{J} \quad \text{as in } \begin{cases} \vec{\mu}_L = (1) \left( \frac{-e}{2m_e} \right) \vec{L} \\ \vec{\mu}_S = (2) \left( \frac{-e}{2m_e} \right) \vec{S} \end{cases}$$

Not true

Not easy! Need further approximation

Idea: It will be nice if  $\vec{\mu}_{\text{total}} \approx \vec{\mu}_{\text{J (approx)}} = g \left( \frac{-e}{2m_e} \right) \vec{J}$  (37)

If so,  $-\vec{B}_{\text{ext}} \cdot \hat{\vec{\mu}}_{\text{J (approx)}} |n l (s) j m_j\rangle$

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

$$(\vec{B}_{\text{ext}} = B_{\text{ext}} \hat{z})$$

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

$$(\hat{J}_z |j m_j\rangle = m_j \hbar |j m_j\rangle)$$

$$= B_{\text{ext}} \frac{e \hbar}{2m_e} g m_j |n l (s) j m_j\rangle$$

(Done!?! What's g?)

and

$$E_{\text{Zeeman}}^{(1)} \cong \langle n l (s) j m_j | (-\vec{B}_{\text{ext}} \cdot \hat{\vec{\mu}}_{\text{J (approx)}}) | n l (s) j m_j \rangle$$

$$= g \mu_B B_{\text{ext}} m_j$$

(38)

( $|n l (s) j m_j\rangle$  are normalized)

∴ If approximation (37) is made, life becomes easy &  $E_{\text{Zeeman}}^{(1)}$  is given by Eq. (38)

How to approximate  $\vec{\mu}_{\text{total}} = \frac{-e}{2m_e} (\vec{L} + 2\vec{S})$  reasonably by  $\vec{\mu}_{\text{J(approx)}} = g \left( \frac{-e}{2m_e} \right) \vec{J}$  ?

Idea: Project  $(\vec{L} + 2\vec{S})$  along  $\vec{J}$  (as the approximation)

$= \vec{J} + \vec{S}$   
 along  $\vec{J}$  OK  $\leftarrow$  Project  $\vec{S}$  in direction of  $\vec{J}$  and ignore the rest

Approximate  $\vec{S}$  by:

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

$\vec{J}$   
 unit vector  
 in direction  
 of  $\vec{J}$

$$\vec{J} = \vec{L} + \vec{S}$$

$$\Rightarrow \vec{L} = \vec{J} - \vec{S}$$

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

$$\Rightarrow \vec{S} \cdot \vec{J} = \frac{J^2 - L^2 + S^2}{2}$$

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

Then  $E_{\text{Zeeman}}^{(1)}$  becomes (for  $\vec{B}_{\text{ext}} = B_{\text{ext}} \hat{z}$ ):

$$\begin{aligned} E_{\text{Zeeman}}^{(1)} &\approx \langle n l (s) j m_j | B_{\text{ext}} \frac{e\hbar}{2m_e} m_j \left( 1 + \frac{\hat{J}^2 - \hat{L}^2 + \hat{S}^2}{2\hat{J}^2} \right) | n l (s) j m_j \rangle \\ &= \langle n l (s) j m_j | B_{\text{ext}} \mu_B m_j \left( 1 + \frac{j(j+1) - l(l+1) + s(s+1)}{2j(j+1)} \right) | n l (s) j m_j \rangle \\ &= g_{\text{Landé}} \mu_B B_{\text{ext}} m_j \quad (39) \quad [\text{Done!}] \end{aligned}$$

where

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

Landé  $g$ -factor

a number (not necessarily integer)  
(order 1)

← depending on  $j$   
and how that value of  $j$   
comes about ( $l$  and  $s$ )  
(How important is spin-orbit  
interaction)

- Same form as previously found in normal Zeeman effect

Normal [ignores spin]

$$E_{\text{Zeeman}} = g_L \mu_B B m_l$$

Including spin (anomalous Zeeman effect)

$$E_{\text{Zeeman}} \approx g_{\text{Landé}} \mu_B B m_j$$

This is because we have effectively approximated  $\vec{\mu}_{\text{total}}$  by

$$\vec{\mu}_{\text{J (approx)}} = g_{\text{Landé}} \left( \frac{-e}{2m} \right) \vec{J} \quad (40)$$

which has the same form<sup>†</sup>

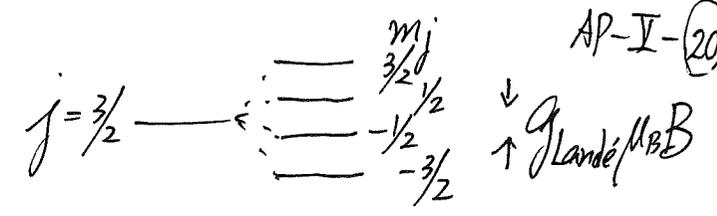
$$\text{as } \vec{\mu}_L = g_L \left( \frac{-e}{2m_e} \right) \vec{L}$$

$$\vec{\mu}_S = g_S \left( \frac{-e}{2m_e} \right) \vec{S}$$

---

<sup>†</sup> But  $g_{\text{Landé}}$  takes on a value that depends on  $j$  AND ( $l$  and  $s$ ) [Termo symbol]

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



removes degeneracy due to  $m_j$

Example

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

Ignoring everything

$\hat{H}_{\text{atom}}$  only

+

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

+

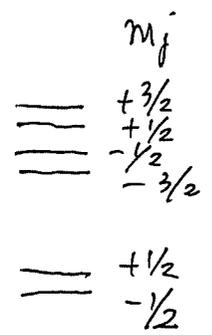
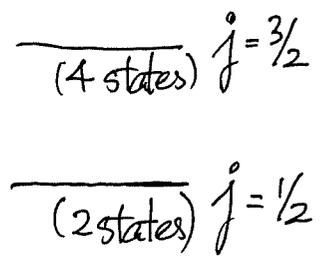
Weak field with  $\hat{H}'_{\text{z}}$

Weak Field

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

$\uparrow$

$l=1$   
( $s=1/2$ )



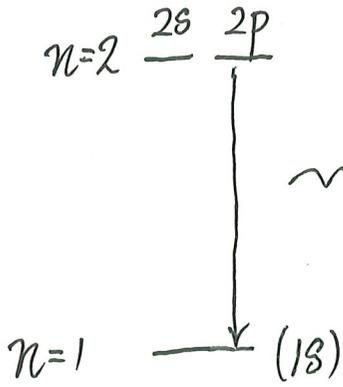
With  $\hat{H}'_{\text{so}}$  only,  
energy depends on  
 $n$  and  $j$   
(see fine-structure  
discussion)

Next lifts degeneracy  
as  
 $E_{\text{Zeeman}}^{(1)} = g_{\text{Landé}} \mu_B m_j B_{\text{ext}}$   
depending on  $m_j$

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

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

$\hat{H}_{atom}$  only



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

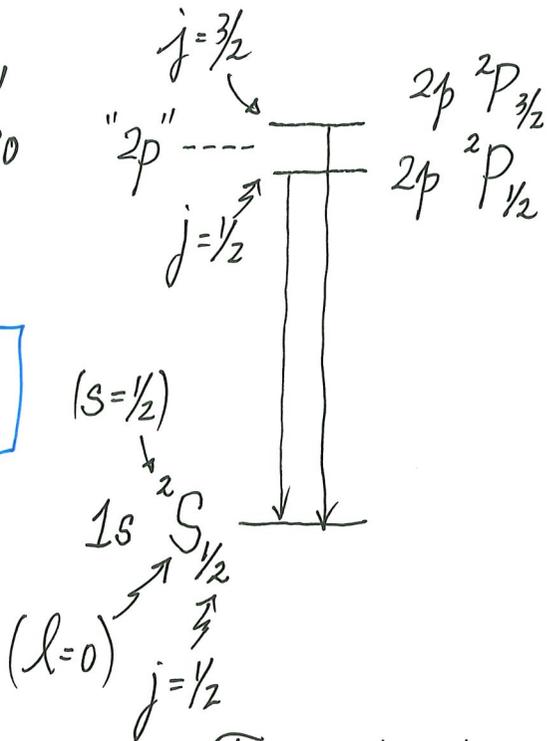
spectrum



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

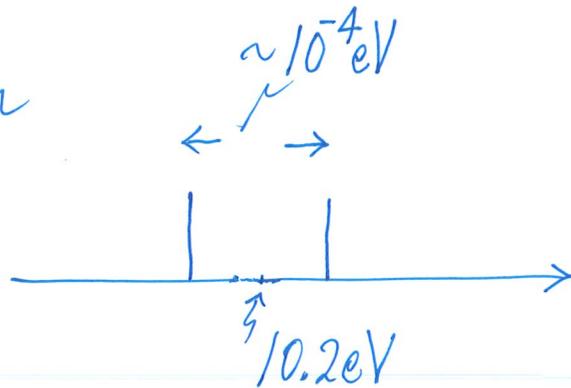
$\hat{H}_{atom} + \hat{H}'_{so}$   
( $\vec{B}_{ext} = 0$ )

[spin-orbit coupling only]



Fine structure

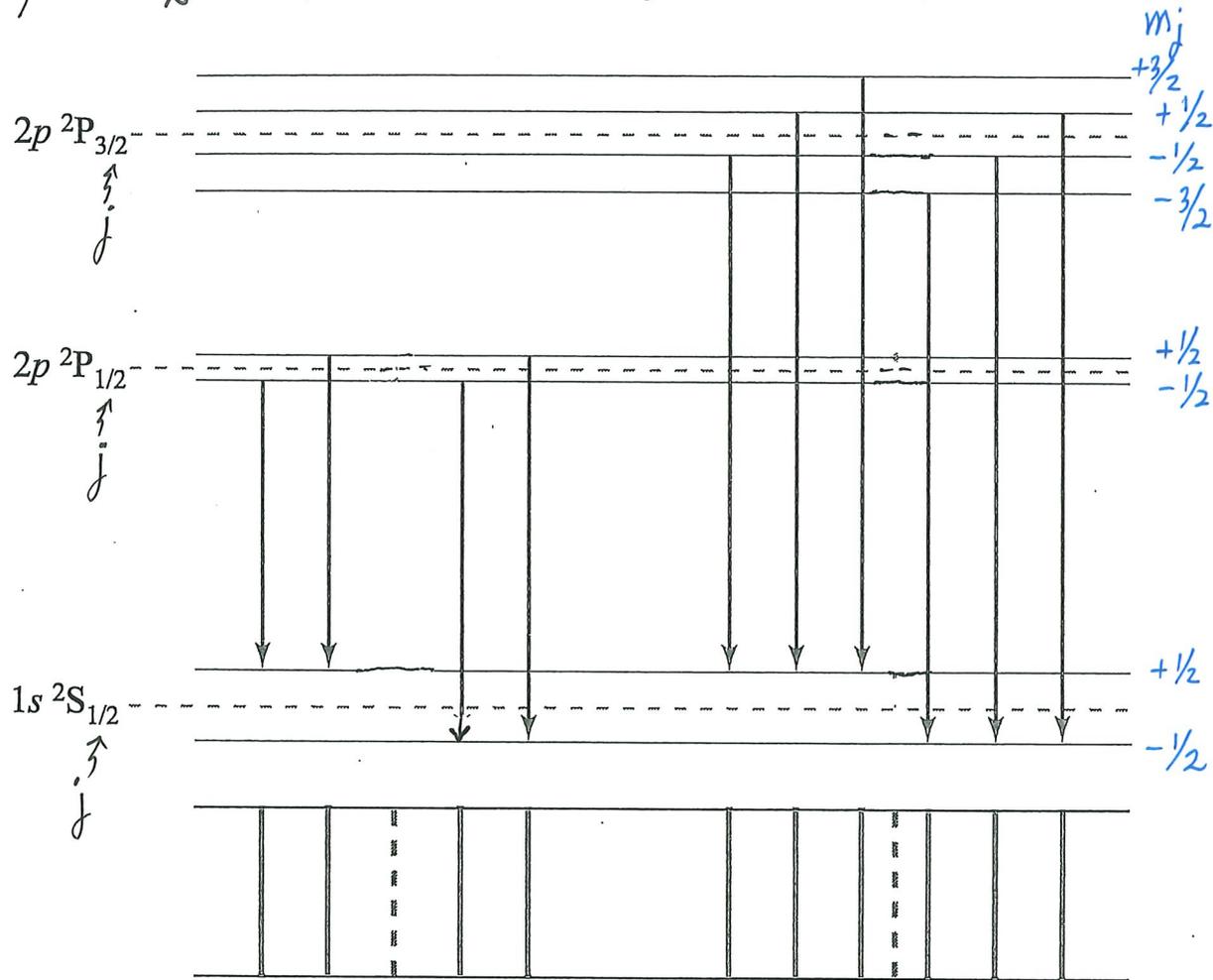
spectrum



due to spin-orbit interaction  
(fine structure)

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

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



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

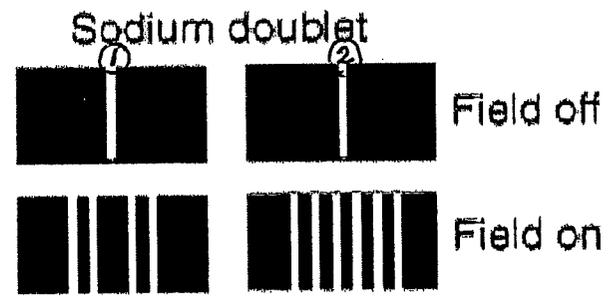
10 lines  
in weak  $\vec{B}_{\text{ext}}$

Anomalous  
Zeeman  
Effect

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

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.

# Same Works for Sodium



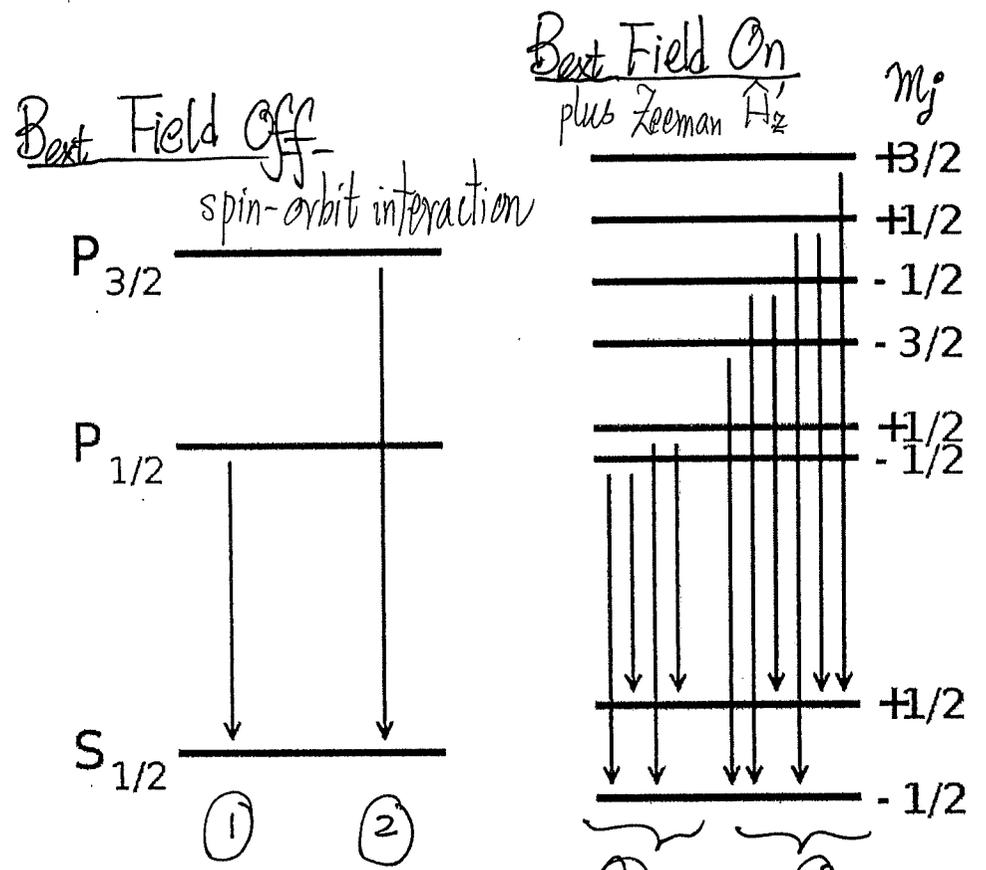
▪  $\hat{H}'_{so}$  only  
Sodium D lines (doublet)

▪ 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

becomes 4 lines      becomes 6 lines (10 lines)  
[even # of lines]

## Final Remarks

- The study on Zeeman effect had led to key developments in ideas/concepts<sup>+</sup> 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,  $g_{Landé}$  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 : " $-\vec{\mu}_z \cdot \vec{B}$ "  
 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.