B. Zeeman Effects : First Encounter

- Phenomena: One spectral line splits into several lines in the presence of an external (applied) magnetic field $\vec{B}$

Zeeman effect →

- Key Point: There is an externally applied $\vec{B}$ field

- In this first encounter, we consider how far we can go in explaining the phenomenon only taking into account of the orbital angular momentum $\vec{L}$ of the electron in the atom.

[Meaning: Ignore electron spin (for now)]

Effect of Applied $\vec{B}$ field?

- $\vec{B}$ interacts with magnetic dipole moment

$$\vec{\mu}_L = \frac{-e}{2m_e}\vec{L} \quad (1)$$ [see notes on Angular Momentum]

$\vec{\mu}_L$: magnetic dipole moment due to $\vec{L}$; $\vec{L}$: orbital angular momentum

$$\boxed{\vec{\mu}_L = -\underbrace{\left(\frac{e\hbar}{2m_e}\right)}_{\mu_B}\frac{1}{\hbar}\vec{L} = -\mu_B\frac{1}{\hbar}\vec{L} = -g_L\frac{\mu_B}{\hbar}\vec{L}} \quad (2)$$

Bohr magneton: μ_B — set the scale of atomic $|\vec{\mu}_L|$

$g_L = 1$[+]

interaction energy between $\vec{\mu}_L$ and $\vec{B}$:

$$\boxed{U_{\text{magnetic}} = -\vec{\mu}_L\cdot\vec{B}} \quad (3)$$

It is energy that goes into Hamiltonian

physics: $\vec{B}$ tends to make $\vec{\mu}_L$ align in its direction

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[+] g_L is introduced here although $g_L = 1$. It is called the g-factor. Same form is appliable to other AM's

Go Quantum: $\hat{U}_{magnetic} = -\hat{\vec{\mu}}_L \cdot \vec{B}$

- Applied $\vec{B}$ field $\Rightarrow$ a direction specified by direction of $\vec{B}$

  Call that direction $\hat{z}$ direction (this is general), $\vec{B} = B\hat{z}$

$$\boxed{\hat{U}_{magnetic} = -\underbrace{(\hat{\vec{\mu}}_L \cdot \hat{z})}_{\text{pick up } z\text{-component of } \vec{\mu}_L} B = -\hat{\mu}_{L,z} B = \underbrace{\mu_B B}_{\text{unit of energy}} \frac{\hat{L}_z}{\hbar}} \quad (4)$$

see Eq.(2)

Addition term in Hamiltonian for atom in $\vec{B}$-field

unit of energy

$\frac{\mu_B B}{\hbar} \equiv \frac{eB}{2m_e}$ (Larmor frequency)

$\mu_B = 5.79 \times 10^{-5}$ eV/Tesla ; B-field in lab ~ 10 Tesla

National lab ~ 50-80 Tesla (short duration)

$\Rightarrow \mu_B B \sim \underbrace{10^{-4}\,\text{eV (tiny compared with} \sim \text{eV)}}_{\text{concept}}$

$\vec{B} = 0$	$\vec{B} \neq 0$
$\hat{H} = \hat{H}_{atom}$ (solvable for Hydrogen)	$\hat{H} = \hat{H}_{atom} + \hat{U}_{magnetic} = \hat{H}_{atom} + \frac{\mu_B B}{\hbar} \hat{L}_z \quad (5)$

Tool Box

- Solve exactly
- Perturbation Theories
- Big Matrix

What to do?

For Hydrogen atom in $\vec{B}$-field (but ignoring spin), this problem can be solved exactly.[+]

[+] But the prediction is <u>incorrect</u> when compared with exp't. for <u>hydrogen</u>!

Key Effect: $\vec{B}$-field "lifts" the degeneracy caused by m_ℓ

No $\vec{B}$-field

$$\hat{H} = \hat{H}_{atom} = -\frac{\hbar^2}{2m}\nabla^2 + \underbrace{U(r)}_{\frac{-e^2}{4\pi\varepsilon_0 r}}$$ for H-atom

$$E_n = -\frac{13.6}{n^2}\,\text{eV} \quad \text{(H-atom)}$$

[for general $U(r)$, $E_{n\ell}$] doesn't depend on m_ℓ

$\therefore$ m_ℓ lead to degeneracy

- $B=0$, given ℓ, there are $(2\ell+1)$ values of m_ℓ and all of them correspond to the same energy

[Recall: $Y_{\ell m_\ell}(\theta,\phi)$]

$(2\ell+1)$ values for given ℓ

With $\vec{B}$-field (but consider $\vec{\mu}_L$ only)+

$$\hat{H} = \hat{H}_{atom} + \hat{U}_{magnetic}$$
$$= \hat{H}_{atom} - \hat{\vec{\mu}}_L\cdot\vec{B}$$

[Once $\vec{B}$ is applied, $\vec{B}$ specifies a direction.]

Take $\vec{B} = B\hat{z}$

$$\hat{H} = \hat{H}_{atom} - \hat{\mu}_z B$$
$$= \hat{H}_{atom} + \frac{eB}{2m_e}\hat{L}_z = \hat{H}_{atom} + \frac{\mu_B B}{\hbar}\hat{L}_z \quad (5)$$

z-component of orbital angular momentum

- $B\neq 0$: $(2\ell+1)$ values of m_ℓ now correspond to different energies!

$\therefore$ Degeneracy due to m_ℓ is "removed" or "lifted" ($\because \hat{L}_z Y_{\ell m_\ell} = m_\ell\hbar Y_{\ell m_\ell}$)

+Note: Ignored "Spin" so far.

The QM Problem becomes $\hat{H}\psi = E\psi$ with

$$\hat{H} = \underbrace{\hat{H}_{atom}}_{\text{no } \vec{B}\text{-field}} + \underbrace{\frac{\mu_B B}{\hbar}\hat{L}_z}_{\text{due to } -\hat{\vec{\mu}}_L \cdot \vec{B}} \qquad (5)$$

Do perturbation theory?

- No! It is too "high-tech"!

<u>Then what?</u>

$\hat{H}\psi = E\psi$ can be <u>solved exactly</u> <u>without any effort</u>

<u>How?</u> $\hat{H}_{atom}$ generally satisfies ($U(\vec{r}) = U(r)$ only, i.e. spherically symmetric)

$$\hat{H}_{atom}\psi_{n\ell m_\ell} = E_{n\ell}\psi_{n\ell m_\ell}$$

[<u>Recall</u>: Hydrogen is a <u>special case</u> for which E_n depends on n only]

The atomic states $\psi_{n\ell m_\ell}(r,\theta,\phi)$

eigenstate of $\hat{L}^2$ (eigenvalue $\ell(\ell+1)\hbar^2$)

$\boxed{\text{eigenstate of } \hat{L}_z \text{ (eigenvalue } m_\ell\hbar) \quad \hat{L}_z \psi_{n\ell m_\ell} = (m_\ell\hbar)\psi_{n\ell m_\ell}}$ ← Key Point

of energy eigenvalue $E_{n\ell}$ are also eigenstates of $\hat{L}^2$ and $\hat{L}_z$.

i.e. $\boxed{\psi_{n\ell m_\ell}(r,\theta,\phi) \text{ are simultaneous eigenstates of } \hat{H}_{atom},\ \hat{L}^2, \text{ and } \hat{L}_z}$

Now

$$\hat{H} = \hat{H}_{atom} + \frac{\mu_B B}{\hbar}\hat{L}_z \quad (5)$$

$\therefore$ $\boxed{\psi_{n\ell m_\ell}(r,\theta,\phi) \text{ are eigenstates of } \hat{H}}$ ($\because$ additional term $\sim \hat{L}_z$) (6)

$\Rightarrow$ Done!

$$\hat{H}\psi_{n\ell m_\ell} = \hat{H}_{atom}\psi_{n\ell m_\ell} + \frac{\mu_B B}{\hbar}\underbrace{\hat{L}_z\psi_{n\ell m_\ell}}$$

$$= E_{n\ell}\psi_{n\ell m_\ell} + \frac{\mu_B B}{\hbar}\cdot\overbrace{m_\ell\hbar\,\psi_{n\ell m_\ell}}$$

$$= \underbrace{\left(E_{n\ell} + m_\ell \mu_B B\right)}_{\text{new energy eigenvalue (depends on } \mu_B B \text{ and } m_\ell)}\psi_{n\ell m_\ell} \qquad (7) \ (\text{Exact})^{+}$$

Removes the $(2\ell+1)$ degeneracy due to m_ℓ

$\therefore$ $\boxed{\psi_{n\ell m_\ell} \text{ is an eigenstate of } \hat{H} \text{ with eigenvalue } (E_{n\ell} + m_\ell \mu_B B)}$

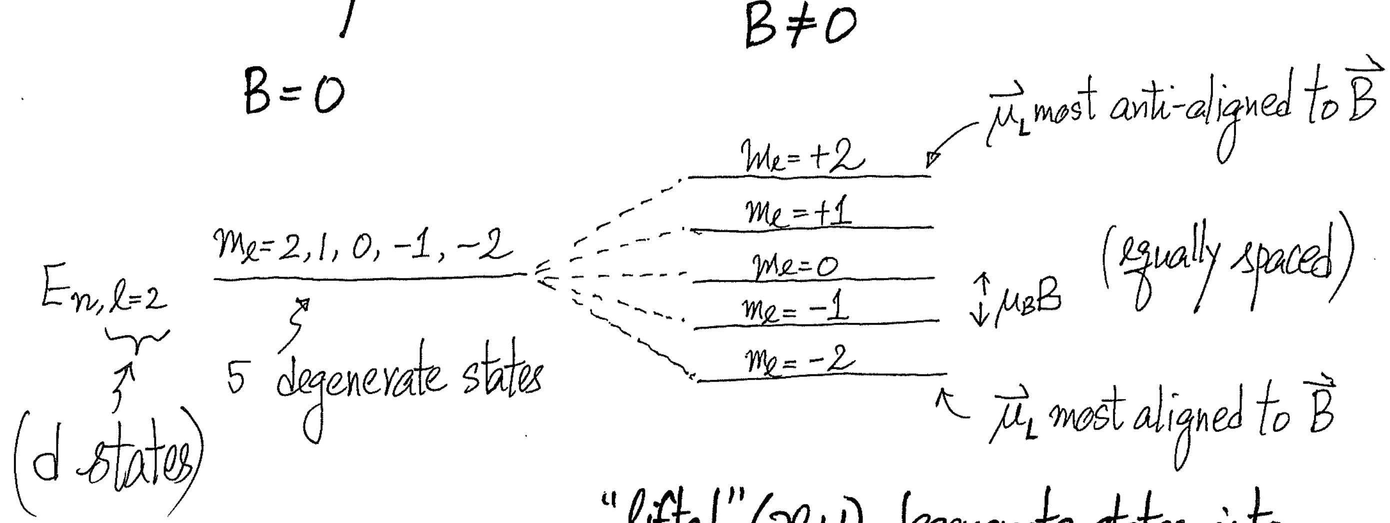
also!

$E_{n\ell}$: eV order; $m_\ell \mu_B B$: $\underbrace{10^{-4}\,\text{eV order}}_{\text{a tiny shift with observable consequence!}}$

Recall: Given ℓ, $m_\ell = \underbrace{\ell, \ell-1, \cdots, 0, \cdots, -\ell}_{(2\ell+1)\text{ values}}$ "Order 1"

+ For those who like 1st order perturbation theory, you are "lucky" in that it gives the exact result because $\int \psi^*_{n\ell m_\ell}\left(\frac{\mu_B B}{\hbar}\hat{L}_z\right)\psi_{n\ell m_\ell}\,d^3r = m_\ell \mu_B B$. There is a good reason for it. Why?

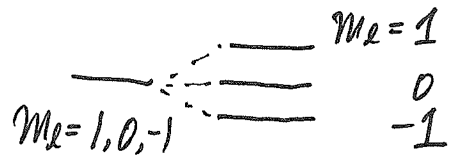
Schematically (l=2) (d states)



"lifted" $(2l+1)$-degenerate states into $(2l+1)$ equally spaced states with $\underbrace{\mu_B B}_{\sim 10^{-5} - 10^{-4}\,\text{eV}}$ between adjacent states

Similar effect for $\underbrace{l=1 \text{ (p states)}}$

$\Downarrow$



Because spectral lines come from transition between atomic states $\Rightarrow$ splitting in states due to $\vec{B}$-field leads to splitting of spectral lines (Zeeman Effect)

Aside: What is this in Big Matrix Picture? (Optional)

$$\hat{H}_{atom}\,\psi_{n\ell m_\ell} = E_{n\ell}\,\psi_{n\ell m_\ell}$$

$\{\psi_{n\ell m_\ell}\}$ set of basis functions

Matrix of $\hat{H}_{atom}$ in $\{\psi_{n\ell m_\ell}\}$

$$H^{atom}_{ji} = \int \psi^*_{n'\ell' m_\ell'}(\vec{r})\,\underbrace{\hat{H}_{atom}\,\psi_{n\ell m_\ell}(\vec{r})}_{E_{n\ell}\,\psi_{n\ell m_\ell}(\vec{r})}\,d^3r$$

$$= E_{n\ell}\,\delta_{nn'}\,\delta_{\ell\ell'}\,\delta_{m_\ell m_\ell'}$$

$\Rightarrow$ diagonal matrix

same E_{21} degenerate due to $m_\ell = -1, 0, +1$

$$\begin{array}{c}\left(\begin{array}{cccccccc}
E_{10} & 0 & 0 & 0 & 0 & & & \\
0 & E_{20} & 0 & 0 & 0 & & & \\
0 & 0 & E_{21} & 0 & 0 & & & \\
0 & 0 & 0 & E_{21} & 0 & 0 & & \\
 & & & 0 & E_{21} & 0 & & \\
 & & & 0 & 0 & E_{30} & 0 & 0 \\
 & & & & & & & \ddots
\end{array}\right)\end{array}
\begin{array}{l} \\ \\ \left.\begin{array}{l}\psi_{21-1}\\ \psi_{210}\\ \psi_{211}\end{array}\right\} \\ \\ \\ \end{array}$$

diagonal elements are exact energy eigenvalues

Matrix of $\underbrace{\left(\hat{H}_{atom} + \frac{\mu_B B}{\hbar}\hat{L}_z\right)}_{\hat{H}}$ in $\{\psi_{n\ell m_\ell}\}$ is <u>also diagonal</u>!

$$\because \quad H_{ji} = \int \psi^*_{n'\ell' m_\ell'} \hat{H} \psi_{n\ell m_\ell} d^3r \overset{\text{Eq.(7)}}{=} \left(E_{n\ell} + m_\ell \mu_B B\right) \delta_{nn'} \delta_{\ell\ell'} \delta_{m_\ell m_\ell'}$$

$$
\begin{array}{ll}
(100)\ 1s & \\
(200)\ 2s & \\
(21\text{-}1) & \\
(210)\ 2p & \\
(211) & \\
(300)\ 3s & \\
(31\text{-}1) & \\
(310)\ 3p & \\
(311) & \\
\vdots &
\end{array}
\begin{pmatrix}
E_{10} & & & & & & & & & \\
& E_{20} & & & & \text{all zeros!} & & & & \\
& & E_{21}-\mu_B B & & & & & & & \\
& & & E_{21} & & & & & & \\
& & & & E_{21}+\mu_B B & & & & & \\
& & & & & E_{30} & & & & \\
& \text{all zeros!} & & & & & E_{31}-\mu_B B & & & \\
& & & & & & & E_{31} & & \\
& & & & & & & & E_{31}+\mu_B B & \\
& & & & & & & & & \ddots
\end{pmatrix}
$$

B-field <u>removes</u> the degeneracy due to m_ℓ

- Diagonal because $\{\psi_{n\ell m_\ell}\}$ are exact solutions to the $\hat{H}$ problem
- "First order perturbation" (ignore all off-diagonal elements)

  ↑ they are zeros! (ignore them is right!)
  (or nothing to ignore)

$$E = E_{n\ell} + m_\ell \mu_B B$$

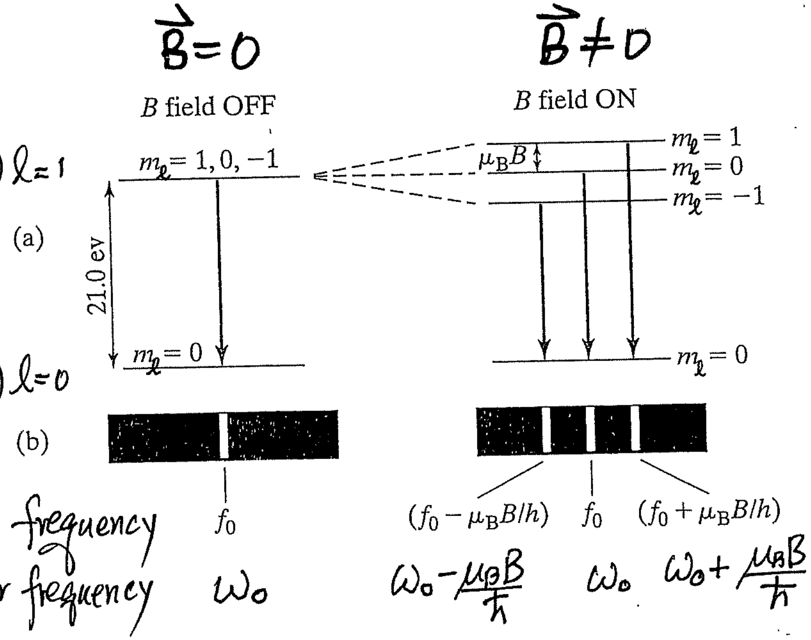
is exact

- Degenerate Perturbation Theory? $(21{-}1)\,(210)\,(211)$ are degenerate to begin with?
  Fine! Read out 3×3 & do it exactly. It is $\begin{pmatrix} E_{21}-\mu_B B & 0 & 0 \\ 0 & E_{21} & 0 \\ 0 & 0 & E_{21}+\mu_B B \end{pmatrix}$.
  So, it is already treated exactly.

- All because $\underbrace{\{\psi_{n\ell m_\ell}\}}_{\text{simultaneous eigenstates of } \hat{H} \text{ \& } \hat{H}_{atom}}$ are exact eigenstates of $\underbrace{\hat{H} \text{ and } \hat{H}_{atom}}_{\text{they commute}}$.

What to expect?

Note → **(a)** The ground state ($l = 0$) and one of the excited levels ($l = 1$) of helium. When a magnetic field is applied, the upper level splits into three, while the ground state is unaffected. (The splitting of the levels is greatly exaggerated since, even in the strongest magnetic fields obtainable in a lab — about 40 T — the separation is only $\mu_B B \approx 2 \times 10^{-3}$ eV.) **(b)** With the magnetic field on, there are three distinct transitions possible and hence three distinct spectral lines, as shown on the right.



[Taken from TZD (Taylor, Zafiratos, Dubson) "Modern Physics for scientists and engineers"]

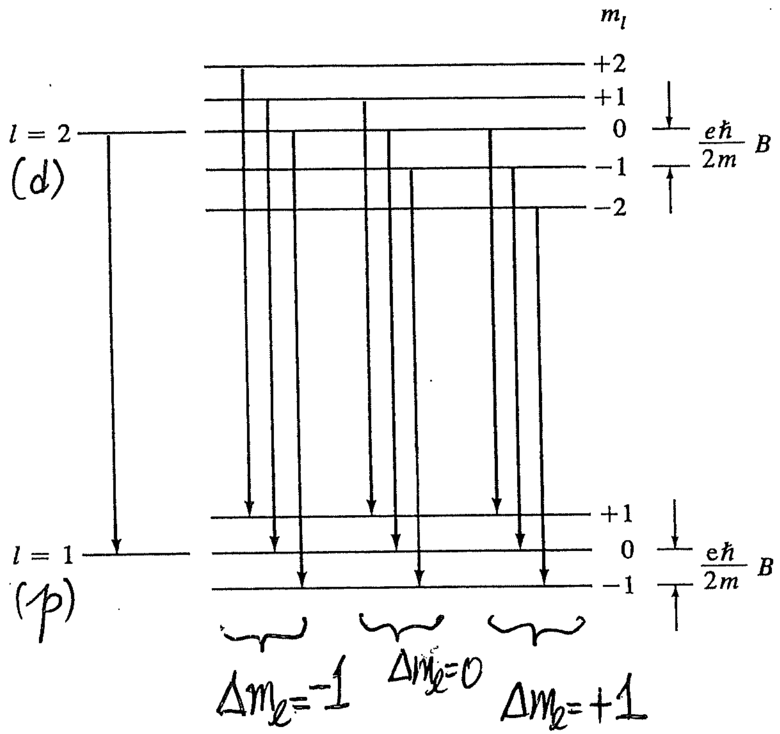
There is a selection rule† for allowed transitions given by $\Delta m_l = 0, \pm 1$ (selection rule involving quantum number m_l)

Expected to see: A spectral line ($\vec{B}=0$) from transition between different l is split into 3 components.

→ This is the "Normal" Zeeman Effect

† The physics behind selection rules will be discussed later. Briefly, when light is incident onto atom, there is a $\hat{H}'$. Perturbation theory hints at integral of the form $\int \psi^*_{final} \hat{H}' \psi_{initial} \, d\tau$ that is important. If this integral does not vanish, the transition is allowed.

Between d states and p states



The normal Zeeman splitting of the spectral line for a d to p transition into three lines. Only three lines are expected because the energy splitting is the same for the initial and final states and only transitions that obey the selection rule $\Delta m_\ell = 0, \pm 1$ are allowed.

[Taken from Blatt, "Modern Physics"]

$\Delta m_\ell = 0, \pm 1$ (selection rules)

There are 9 transitions.

Only three energy differences are involved.

$\hbar\omega_0 + \mu_B B \quad \hbar\omega_0 \quad \hbar\omega - \mu_B B$

$\vec{B} = 0$: One spectral line corresponding to $\hbar\omega_0$

$\vec{B} \neq 0$: Split into 3 lines $\begin{cases} \hbar\omega_0 - \mu_B B \\ \hbar\omega_0 \\ \hbar\omega_0 + \mu_B B \end{cases}$

The "Normal" Zeeman Effect (Why put quotation marks in normal?)

- Due to $-\vec{\mu}_L \cdot \vec{B}$ interaction
- One spectral line splits into three closely separated lines

$\vec{B}=0$:

angular freq: ω_0

energy: $\hbar\omega_0$

$\vec{B} \neq 0$

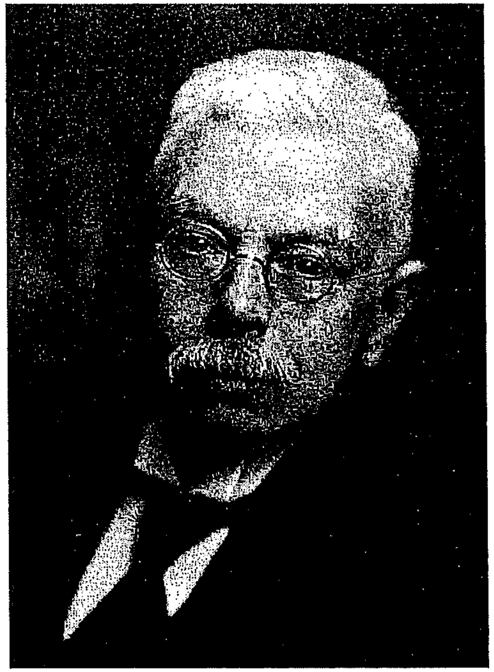
Zeeman (~1896)

angular freq.: $\omega_0 - \frac{\mu_B B}{\hbar}$ $\quad \omega_0 \quad$ $\omega_0 + \frac{\mu_B B}{\hbar}$

energy: $\hbar\omega_0 - \underbrace{\mu_B B}_{\text{tiny}}$ $\quad \hbar\omega_0 \quad$ $\hbar\omega_0 + \underbrace{\mu_B B}_{\text{tiny}}$

Pieter Zeeman

(1865–1943, Dutch)



At the suggestion of his teacher Lorentz, Zeeman investigated the effect of magnetic fields on atomic spectra. The results confirmed Lorentz's suspicion that atomic spectra are somehow connected to the motion of electrons in the atoms. Zeeman and Lorentz shared the 1902 Nobel Prize in physics for this work.

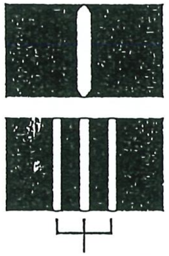
Well before QM was formulated!

[Taken from TZD]

Anomalous Zeeman Effect

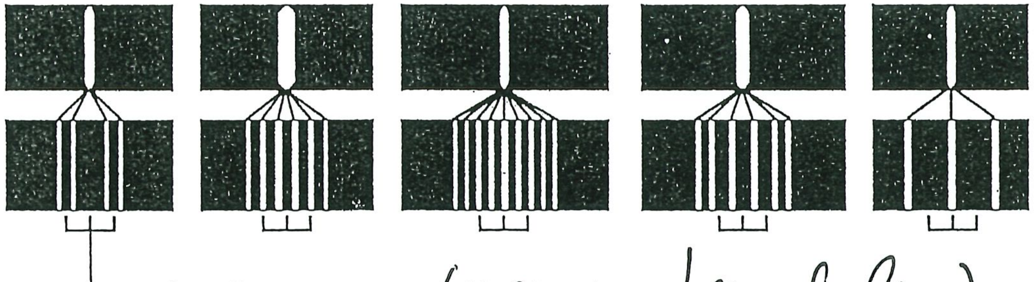
$\vec{B} \neq 0$

Normal



(due to $-\vec{\mu}_L \cdot \vec{B}$ effect)

(3 lines)



(Why?)

(even number of lines)

The normal and anomalous Zeeman effects in various spectral lines.

The "Normal Zeeman effect" is NOT normally seen! It only appears when effects of spin is absent.

[First Lyman line in H-atom splits into many (even #) in $\vec{B}$-field. How many?]

What we did so far is NOT sufficient to explain hydrogen's Zeeman effect!

When could we ignore spin effects?

- Not for Hydrogen atom because there is only $\underbrace{\text{one } (s=\tfrac{1}{2}) \text{ electron}}_{\text{up or down } (\alpha_z \text{ or } \beta_z) \text{ spin state}}$

- Multiple-electron atoms (Some of them)

  e.g. Helium atom ground state [2 electrons (one "up" & one "down")]

$$\vec{S} = \vec{s}_1 + \vec{s}_2$$

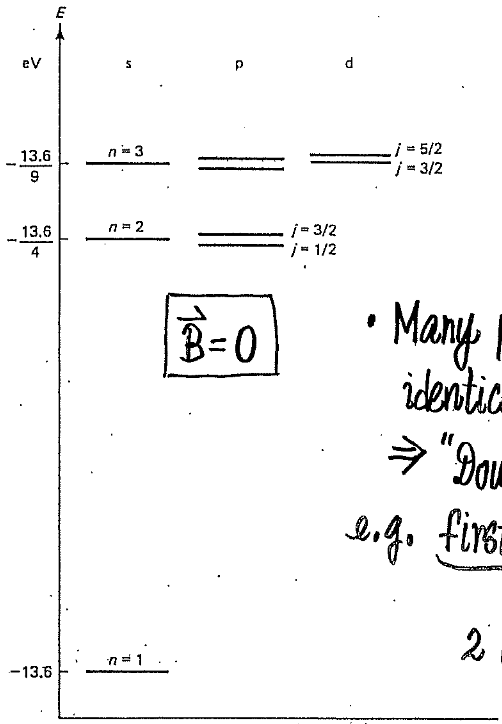
total spin Angular Momentum; 1st and 2nd electrons

$\vec{S} = 0$ (then can ignore spin effects)

What's next?

- Need to include spin effects
  - What is the physics behind the anomalous Zeeman effect?
  - Spectroscopic data (no applied field $\vec{B} = 0$)

(Not to scale)



Fine structure of the lowest energy levels of hydrogen. The splitting between the doublets is typically $\simeq 10^{-5}$ eV. In the energy-level diagram, the splitting has been exaggerated for the sake of clarity.

- Many pairs of nearly identical spectral lines
  $\Rightarrow$ "Doublets" (but $\vec{B} = 0$)

  e.g. $\underbrace{\text{first Balmer line}}$;
  $\downarrow$
  2 lines differ by ~ 0.1 Å (in wavelength)

"Fine Structure"

- Why?
- What are the labels j?