Lecture 15 – 10/30

Topics: "all the multi-'level'" stuff ...:

- hyperfine interaction
- atoms in fields:
  - → magnetic (i.e. interaction with mgn dipoles)
  - → electric (change of transitions)

What is the "quantization axis"? How is it determined?

① What is it?

→ Angular mom. has $\boxed{\text{two}}$ quantum numbers, one connected to its strength: $\vec{J}^2 \to J(J+1)$, one to its projection to the z-axis $J_z \to m_J$. This z-axis is the "quantization axis" (i.e., the direction along which the projection is quantized.)

② How to choose?

Since the physics is determined by what is measurable, ultimately, the quantization axis has to be the measurement direction. (If we measure scalars, i.e. scalar products, we can choose the most convenient direction.

③ What happens when there are several important directions?

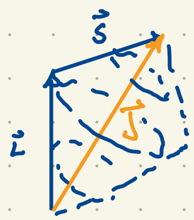
→ Make a judgement call... Often in these cases, we look at the extreme cases in both directions and interpolate / diagonalize

- Landé g-factors

$\vec{J} = \vec{L} + \vec{S}$ gives good q. numbers (Dirac)

(for zero or low magnetic field)

→ g_S, g_L don't contribute independently!



(only $|\vec{L}|, |\vec{S}|, L_z, S_z$ defined. For zero mgn. field: $\vec{J} \parallel$ quantization axis $\hat{=}\ \hat{z}$)

⇒ find sum of projections of $\vec{\mu}_s$ and $\vec{\mu}_L$ on $\vec{J}$.

$\vec{L}: \mu_{L,J} = -\frac{\mu_0 |\vec{L}|}{\hbar} \frac{\vec{L}\cdot\vec{J}}{|\vec{L}|\cdot|\vec{J}|}$ $\qquad$ $\vec{S}: \mu_{S,J} = -g_s \frac{\mu_0 |\vec{S}|}{\hbar} \frac{\vec{S}\cdot\vec{J}}{|\vec{S}||\vec{J}|}$

$\vec{\mu}_J = -g_J \mu_0 \frac{\vec{J}}{\hbar}$ $\qquad$ $g_J = -\frac{\hbar}{\mu_0} \frac{\mu_{L,J} + \mu_{S,J}}{|\vec{J}|}$

$$g_J = \frac{g_L \vec{L}\cdot(\vec{L}\cdot\vec{S}) + g_s \vec{S}\cdot(\vec{L}+\vec{S})}{|\vec{J}|^2} =$$

Note: $\vec{L}\cdot\vec{S} = \frac{1}{2}(\vec{J}^2 - \vec{L}^2 - \vec{S}^2)$

$$= 1 + \frac{j(j+1) + s(s+1) - \ell(\ell+1)}{2j(j+1)}$$

(ignore $\vec{I}$: $U = -\vec{\mu}_J \cdot \vec{B}$,
$\vec{F} = \vec{I} + \vec{J}$: same logic)

Transitions: level j' ↔ level j'' (or F', F'')

three or more lines: "Zeeman"

(low magnetic fields)

e.g. $\Delta m (\equiv m_{j'} - m_{j''})$

$$\boxed{\Delta E = (g_{j'} m_{j'} - g_{j''} m_{j''}) \mu_0 B}$$ (from 5.1)

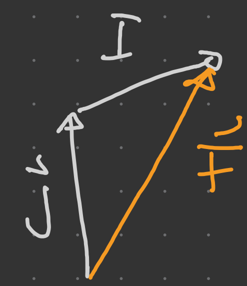
ΔE: change of transition frequency

$$\vec{\mu}_J = -g_J \mu_0 \frac{\vec{J}}{\hbar} \qquad g_J = -\frac{\hbar}{\mu_0} \frac{\mu_{L,J} + \mu_{S,J}}{|\vec{J}|}$$

$$g_J = \frac{g_L \vec{L}\cdot(\vec{L}+\vec{S}) + g_S \vec{S}\cdot(\vec{L}+\vec{S})}{|\vec{J}|^2} =$$

Noh: $\vec{L}\cdot\vec{S} = \frac{1}{2}\left(\vec{J}^2 - \vec{L}^2 - \vec{S}^2\right)$

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



$$\vec{\mu}_F = -g_F \mu_0 \frac{\vec{F}}{\hbar} \qquad g_F = -\frac{\hbar}{\mu_0} \frac{\mu_{J,F} + \mu_{I,F}}{|\vec{F}|}$$

$$\vec{L}: \ \mu_{L,J} = -\frac{\mu_0 |\vec{L}|}{\hbar} \frac{\vec{L}\cdot\vec{J}}{|\vec{L}|\cdot|\vec{J}|}$$

$$\mu_{J,F} = -\frac{\mu_0 |\vec{J}|}{\hbar} \frac{\vec{J}\cdot\vec{F}}{|\vec{J}|\cdot|\vec{F}|}$$

$$\mu_{I,F} = +\frac{\mu_N |\vec{I}|}{\hbar} \cdot \frac{\vec{I}\cdot\vec{F}}{|\vec{I}||\vec{F}|} = \frac{\mu_N}{\mu_0} \frac{\mu_0 |\vec{I}|}{\hbar} \frac{\vec{I}\cdot\vec{F}}{|\vec{I}||\vec{F}|}$$

$$\Rightarrow g_F = +\frac{\cancel{\hbar}}{\cancel{\mu_0}} \frac{1}{|\vec{F}|}\left(+ \frac{\cancel{\mu_0}|\cancel{\vec{J}}|}{\underbrace{\cancel{\hbar}}_{\tilde{g}_I}} \frac{\vec{J}\cdot\vec{F}}{|\cancel{\vec{J}}||\vec{F}|} - \frac{\mu_N}{\mu_0} \frac{\cancel{\mu_0}|\cancel{\vec{I}}|}{\cancel{\hbar}} \frac{\vec{I}\cdot\vec{F}}{|\cancel{\vec{I}}||\vec{F}|}\right) =$$

$$= \frac{g_J \vec{J}\cdot(\vec{J}+\vec{I}) - \tilde{g}_I \vec{I}(\vec{J}+\vec{I})}{F(F+1)}$$

$\vec{J}\cdot\vec{I} = \frac{1}{2}\left(F(F+1) - J(J+1) - I(I+1)\right)$

$$= \frac{g_J\left(J(\cancel{J+1}) + \frac{1}{2}(F(F+1) + J(J+1) - I(I+1))\right) - \tilde{g}_I\left(I(\cancel{I+1}) + \frac{1}{2}(F(F+1) - J(J+1) + I(I+1))\right)}{F(F+1)}$$

$$= \frac{(g_J - \tilde{g}_I)F(F+1) + (g_J + \tilde{g}_I)J(J+1) - (g_J + \tilde{g}_I)I(I+1)}{2F(F+1)}$$

for $g_{J'} = g_{J''}$ or $j'=0$ or $j''=0$: <u>one</u> ΔE

(three total shifts: $\Delta m = 0, \pm 1$,
otherwise more!

<u>Hyperfine structure + magn. field</u>

$$H = a_h \vec{I}\cdot\vec{J} - \vec{\mu}_J \vec{B} - \vec{\mu}_I \cdot \vec{B}$$

$$\vec{\mu}_J = -g_J \mu_0 \frac{\vec{J}}{\hbar} \quad ; \quad \vec{\mu}_I = -g_I \mu_N \frac{\vec{I}}{\hbar}$$

- <u>low field</u>: F, m_F are good q. numbers ($\hat{\vec{F}}$ is quantization axis)

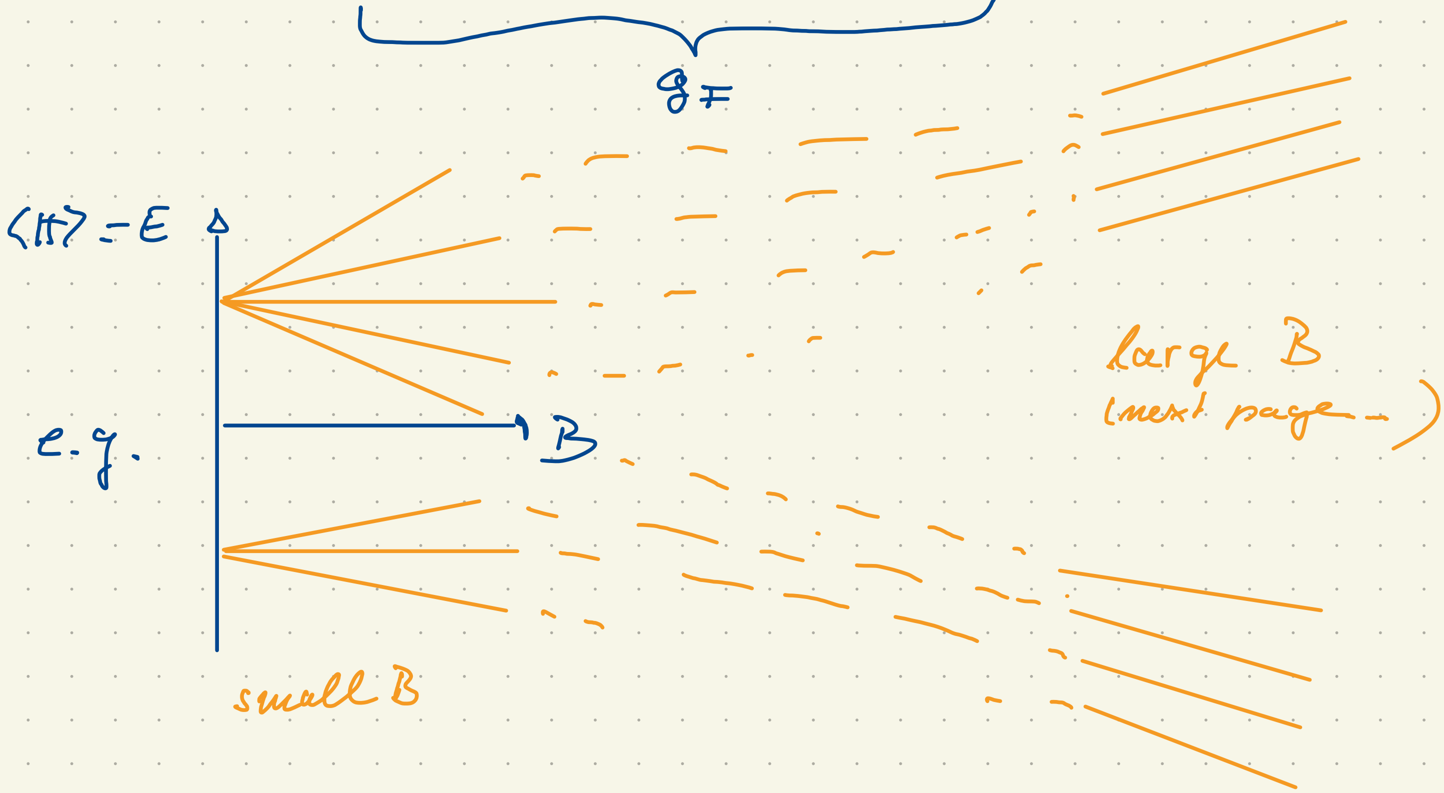
$\Rightarrow$ $H_B = -(\vec{\mu}_J + \vec{\mu}_I)\cdot\vec{B}$ is perturbation

↓ neglect ....

$$\Rightarrow \langle \vec{J}\cdot\vec{B}\rangle = \frac{\langle \vec{J}\cdot\vec{F}\rangle \cdot \vec{F}\cdot\vec{B}}{|\vec{F}^2|}$$

$$\langle \vec{J}\cdot\vec{F}\rangle = \langle \vec{J}\cdot(\vec{J}+\vec{I})\rangle = \frac{1}{2}\left(F(F+1) + j(j+1) - I(I+1)\right)$$

$$H_B \approx \underbrace{\frac{g_J}{2}\,\frac{F(F+1)+j(j+1)-I(I+1)}{F(F+1)}}_{g_F}\,\mu_0 m_F B$$



large B field: quantize along B!

I, m_I, J, m_J are good q. numbers

$\Rightarrow H \approx a\,h\, m_I \cdot m_J + \underbrace{g_J\, m_J\, \mu_0 B}_{\text{largest!}} - g_I\, m_I\, \mu_N B$

general solution: (any B)

diagonalize H!

analytic solution only for 2×2 ($I \leq \frac{1}{2}$ or $J \leq \frac{1}{2}$)

i.e. 2 hf states

Example: "Breit-Rabi formula"

diagram

from Wolfram: for $F = I \pm \frac{1}{2}$

b) Atoms in DC electric fields

(i) Consideration of parity

"parity" – effect under space inversion:

$$\hat{\vec{r}} \longrightarrow -\hat{\vec{r}}$$

• Define a parity operator: $\hat{\pi}$: $\boxed{\hat{\pi}\,\hat{\vec{r}}\,\hat{\pi}^{+} = -\hat{\vec{r}}}$

with $\hat{\pi}^{+} = \hat{\pi}$

(use just x-coord - same for y, z)

$\hat{x}\,|\vec{r}\rangle = x\,|\vec{r}\rangle$ $\left(\Rightarrow \hat{\vec{r}}\,|\vec{r}\rangle = \vec{r}\,|\vec{r}\rangle\right)$

$\Rightarrow \hat{x}\,\hat{\pi}\,|\vec{r}\rangle = -\hat{\pi}\,\hat{x}\,|\vec{r}\rangle = -\hat{\pi}\,x\,|\vec{r}\rangle = -x\,\hat{\pi}\,|\vec{r}\rangle$

$\Rightarrow \hat{\pi}\,|\vec{r}\rangle$ is eigenfunction of $\hat{\vec{r}}$ with eigenvalue $-\vec{r}$.

use space inversion ($\hat{\pi}$) twice will give identity!

$$|\hat{\pi}^2| = 1 \Rightarrow \text{eigenvalues } \langle\hat{\pi}\rangle = \pm 1$$

behavior	state	operator
"odd parity"	$\hat{\pi}\,|\alpha\rangle = -|\alpha\rangle$	$\hat{\pi}\,\hat{A}\,\hat{\pi} = -\hat{A}$
"even parity"	$\hat{\pi}\,|\alpha\rangle = |\alpha\rangle$	$\hat{\pi}\,A\,\hat{\pi} = \hat{A}$

$\hat{\vec{r}}, \hat{\vec{p}} \rightarrow$ odd ("polar") vectors

$\vec{L} = \vec{r} \times \vec{p}$ even $\rightarrow$ "axial" vectors

"pseudo-" vectors

• spherical harmonics:

$$\hat{\pi}\,|Y_{\ell m}\rangle = (-1)^{\ell}\,|Y_{\ell m}\rangle$$

$\Rightarrow$ selection rules:

$\langle\alpha|\,\hat{A}\,|\beta\rangle \neq 0$ "allowed"

(transition

$\Rightarrow$ selection rules:

$\langle \alpha | \hat{A} | \beta \rangle \neq 0$ "allowed" (transition from $|\beta\rangle$ to $|\alpha\rangle$ using interaction $\hat{A}$)

$= 0$ "forbidden"

'coupling'/interaction operator, e.g. $e\hat{\vec{r}}$.

parity selection rules:

$\hat{\pi} |\alpha\rangle = p_\alpha |\alpha\rangle$, $\hat{\pi} |\beta\rangle = p_\beta |\beta\rangle$ $\qquad p_\alpha, p_\beta = \pm 1$

$$\langle \beta | \hat{\vec{r}} | \alpha \rangle = \langle \underbrace{\beta | \hat{\pi}^+}_{\langle \beta | p_\beta} \underbrace{\hat{\pi}\, \hat{\vec{r}}\, \hat{\pi}^+}_{-\hat{\vec{r}}} \underbrace{\hat{\pi} | \alpha}_{p_\alpha |\alpha\rangle} \rangle = - p_\alpha p_\beta \langle \beta | \hat{\vec{r}} | \alpha \rangle$$

$\Rightarrow$ "allowed" only for $p_\alpha = - p_\beta$

(same for any odd coupling operator)

even coupling operator: "allowed" for $p_\alpha = p_\beta$

$$\boxed{[H_0, \hat{\pi}] = 0} \qquad H_0 \propto \vec{p}^{\,2}, \frac{1}{r^{2n}}, \frac{1}{|\vec{r}|} \text{ (even)}$$

$\Rightarrow$ eigenfunctions of (undisturbed) atomic Hamiltonian all odd or even! (as a basis)

Same if magnetic field is present: $\vec{B}$ even, $\vec{J}$ even

<u>(ii) Static DC field</u>

Perturbation theory:

- <u>non-degenerate</u> energy levels: $\vec{E} = E\hat{z}$

$$\Delta E_n^{(1)} = eE \langle n | \hat{z} | n \rangle = 0 \qquad (H|n\rangle = E_n|n\rangle)$$

$$\Delta E_n^{(2)} = (eE)^2 \sum_{m \neq n} \frac{|\langle m|\hat{z}|n\rangle|^2}{E_n - E_m} \qquad (\neq 0 \text{ in general})$$

$$\propto E^2 \Rightarrow \text{"quadratic Stark effect"}$$

$$|\tilde{n}'\rangle = |n\rangle + eE \sum_{m \neq n} \frac{|\langle m|\hat{z}|n\rangle|^2}{E_n - E_m} |m\rangle$$

$\Rightarrow$ $|n'\rangle$ <u>not</u> eigenfct of $\hat{\Pi}$!

N electrons: $\hat{z} \to \sum_{i=1}^{N} \hat{z}_i$ (same)

- polarizability α_d:

$$\vec{d} = -e\langle n'|\hat{z}|n'\rangle =$$

$$= 2e^2 \sum_{m \neq n} \frac{|\langle m|\hat{z}|n\rangle|^2}{E_n - E_m} E + \mathcal{O}(E^2)$$

$$\equiv \alpha_d \vec{E}$$

$\Rightarrow$ quadratic Stark effect:

$$\boxed{\Delta E_n^{(2)} = -\frac{\alpha_d}{2} E^2}$$

- <u>Degenerate</u> energy levels

$\Delta E_n^{(1)} \neq 0$ in general:

Example: $n=2$:

$$H \propto \begin{array}{cc} \begin{pmatrix} E_1 & 0 & 0 & eE\langle z\rangle_{14} & 0 \\ 0 & E_2 & 0 & 0 & 0 \\ 0 & 0 & E_2 & 0 & 0 \\ eE\langle z\rangle_{41} & 0 & 0 & E_2 & eE\langle z\rangle_{45} \\ 0 & 0 & 0 & eE\langle z\rangle_{54} & E_2 \end{pmatrix} & \begin{array}{ll} |100\rangle & 1 \\ |211\rangle & 2 \\ |21{-1}\rangle & 3 \\ |210\rangle & 4 \\ |200\rangle & 5 \end{array} \end{array}$$

all "0" b/o $\Delta m \neq 0$, or $\Delta l = 0$ diagonalize...

Ex: $\frac{1}{\sqrt{2}}\left(|210\rangle \pm |200\rangle\right)$ – eigenstate with $E_2 \pm eE\langle z\rangle$

w/ $\langle z\rangle = |\langle 210|\hat{z}|200\rangle|$

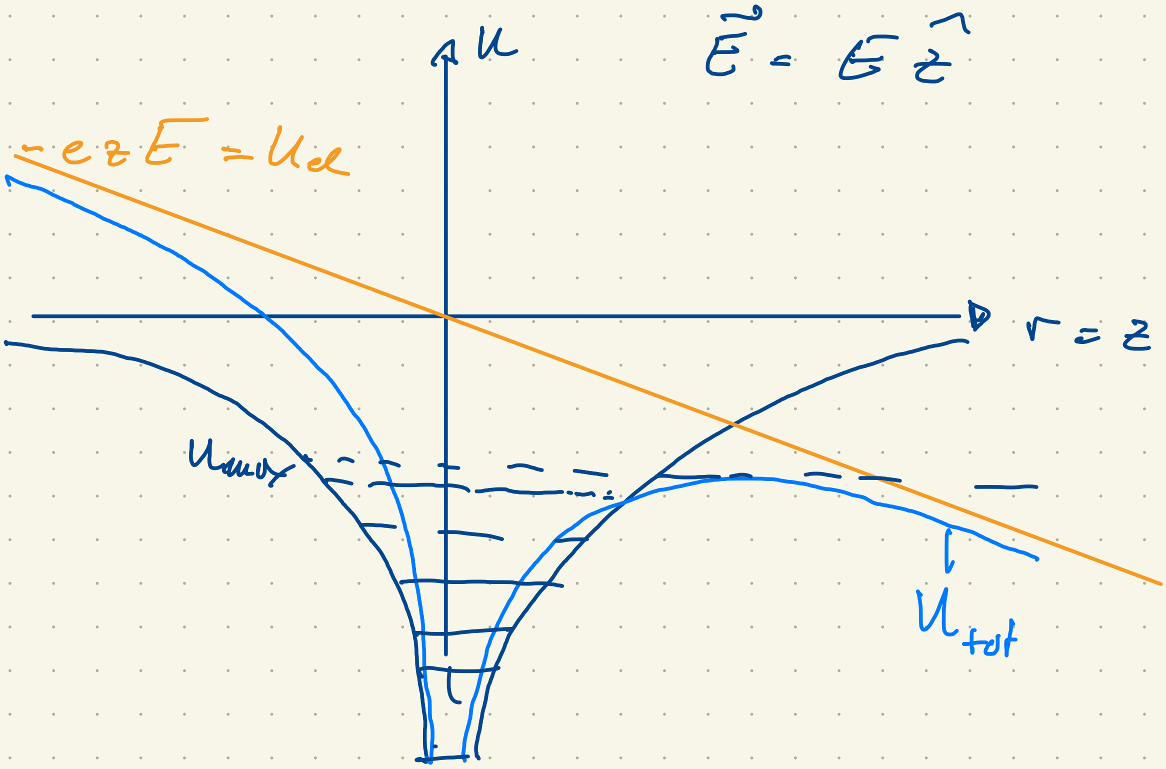
linear in E !

$\Rightarrow$ linear Stark effect

(see effect H. Friedrich)

Careful: calculation changes if $\vec{E} \not\parallel$ quantiz. axis

(iii) Strong fields: Field ionization



$$U_{tot} = U_{atom} + U_{el} = -\frac{Z\tilde{e}^2}{|z|} - eEz$$

$$\Rightarrow U_{max} \text{ for } z = \sqrt{\frac{Ze}{4\pi\epsilon_0 E}}$$

for $\langle H\rangle = U_{max}$

Here: H atomic Hamiltonian

$$E_{ion} = \frac{\langle H\rangle^2}{4\tilde{e}^2 Z} \approx \frac{3.2\cdot 10^8}{Z n^{*4}} \frac{V}{cm}$$

$(n^* = n - \delta_{nl})$

This estimate is correct to ~20%

neglected: - effect of $\vec{E}$ on $\hat{H}$

- tunneling ...

(iv) <u>Oscillating electric field</u>

assume case where $H' = -d E \hat{z} \cos \nu t$, but where $\hbar\nu$ is potentially very far away from any transition resonance (⇒ no transition necessarily)

Assume multiple (≥ 2) states: $|\psi\rangle = \sum_n a_n e^{-i\omega_n t} |n\rangle$

$$\dot{a}_k = \frac{1}{i\hbar} \sum_n \langle k | H' | n \rangle a_n e^{i\omega_{kn} t}$$

⇒ solve for $\vec{d} = \langle \psi | e\vec{r} | \psi \rangle$

(similar calc. as for classical dipole in chapter 1)

⇒ $d(\nu, t) = \alpha(\nu) E \cos \nu t$ with

$$\boxed{\alpha(\nu) = \frac{2e^2}{\hbar} \sum_k \frac{\omega_{kg} |\langle k | \hat{r} | g \rangle|^2}{\omega_{kg}^2 - \nu^2}}$$

AC polarizability