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8 Übungsblatt Atom- und Molekülphysik

8.1

We will get ourselves a useful relation before starting the calculation.

$$\int_0^\infty dr\, r^n e^{-\alpha r} = \underbrace{\left[-r^n \frac{1}{\alpha} e^{-\alpha r}\right]_0^\infty}_{=0} + \frac{n}{\alpha}\int_0^\infty dr\, r^{n-1} e^{-\alpha r}$$

$$= 0 + \frac{n(n-1)}{\alpha^2}\int_0^\infty dr\, r^{n-2} e^{-\alpha r}$$

$$\vdots$$

$$= \frac{n!}{\alpha^n}\int_0^\infty dr\, e^{-\alpha r}$$

$$= \frac{n!}{\alpha^{n+1}} ,$$

which we will verify by induction:

$n=0$: $\int_0^\infty dr\, r^0 e^{-\alpha r} = \int_0^\infty dr\, e^{-\alpha r} = \frac{1}{\alpha} = \frac{0!}{\alpha^{0+1}}$ ✓

$n \to n+1$: $\frac{n!}{\alpha^{n+1}} \longrightarrow \frac{(n+1)!}{\alpha^{n+2}}$, can be shown by

$$\int_0^\infty dr\, r^{n+1} e^{-\alpha r} = \underbrace{\left[-\frac{1}{\alpha} r^{n+1} e^{-\alpha r}\right]_0^\infty}_{=0} + \frac{n+1}{\alpha}\underbrace{\int_0^\infty dr\, r^n e^{-\alpha r}}_{=\frac{n!}{\alpha^{n+1}}\ \text{(because of precondition)}}$$

$$= \frac{(n+1)!}{\alpha^{n+2}} \quad ✓$$

$$\Rightarrow \int_0^\infty dr\, r^{n+1} e^{-\alpha r} = \frac{n!}{\alpha^{n+1}} .$$

a)

$$|2p_z\rangle = \sqrt{\frac{1}{\pi}} \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \left(\frac{Zr}{2a_0}\right) e^{-\frac{Zr}{2a_0}} \cos\theta \quad \text{(script 7.233 and 8.20)}$$

(ψ_{210})

$$\rightarrow \langle e\vec{r}\rangle = \langle 2p_z| e \begin{pmatrix} r\sin\theta\cos\varphi \\ r\sin\theta\sin\varphi \\ r\cos\theta \end{pmatrix} |2p_z\rangle$$, we calculate the components one by one:

$\langle ex\rangle = \frac{e}{\pi}\left(\frac{Z}{2a_0}\right)^5 \int_0^\infty dr \int_0^{2\pi} d\varphi \int_0^\pi d\theta\, r^5 e^{-\frac{Zr}{a_0}} \sin^2\theta\cos^2\theta\cos\varphi = 0$, while

$\int_0^{2\pi}\cos\varphi = [\sin\varphi]_0^{2\pi} = 0$.

$\langle ey\rangle = \frac{e}{\pi}\left(\frac{Z}{2a_0}\right)^5 \int_0^\infty dr \int_0^{2\pi} d\varphi \int_0^\pi d\theta\, r^5 e^{-\frac{Zr}{a_0}} \sin^2\theta\cos^2\theta\sin\varphi = 0$, while

$\int_0^{2\pi}\sin\varphi = [-\cos\varphi]_0^{2\pi} = -1+1 = 0$.

$\langle ez\rangle = \frac{e}{\pi}\left(\frac{Z}{a_0}\right)^5 \int_0^\infty dr \int_0^{2\pi} d\varphi \int_0^\pi d\theta\, r^5 e^{-\frac{Zr}{a_0}} \sin\theta\cos^3\theta = 0$, while

$\int_{-1}^1 d\cos\theta\cos^3\theta = \frac{1}{4}[\cos\theta]_0^{2\pi} = \frac{1}{4}[1-1] = 0$.

Resulting in a permanent dipole moment of:

$$\langle e\vec{r}\rangle = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$$, meaning that there is none.

8.1

b)

The average distance of the electron from the nucleus is:

$$
\begin{aligned}
\langle r \rangle &= \frac{1}{\pi}\left(\frac{Z}{2a_0}\right)^5 \int_0^\infty dr \int_0^{2\pi} d\varphi \int_0^\pi d\theta \, r^5 \sin\theta \cos^2\theta \, e^{-\frac{Zr}{a_0}} \\
&= 2\left(\frac{Z}{2a_0}\right)^5 \underbrace{\int_0^\infty dr \, r^5 e^{-\frac{Zr}{a_0}}}_{\text{use shown formula on page -1-}} \underbrace{\int_{-1}^{1} d\cos\theta \cos^2\theta}_{=\frac{2}{3}} \\
&= \frac{4}{3}\left(\frac{Z}{2a_0}\right)^5 \cdot \frac{5!}{\left(\frac{Z}{a_0}\right)^6} \\
&= \frac{\cancel{2}^{2}}{\cancel{3}} \frac{1}{2^{\cancel{5}}} \cdot 5 \cdot \cancel{2}^{3} \cdot \cancel{3} \frac{a_0}{Z} = 5\frac{a_0}{Z} \quad , \text{for } Z=1 \text{ (hydrogen)} \\
&= 5a_0 .
\end{aligned}
$$

8-2

a) Die Term Symbole lauten:

$1s : (n=1\,;\; s=\frac{1}{2}\,;\; l=0\,;\; j=\frac{1}{2})$

$1^2S_{1/2}$

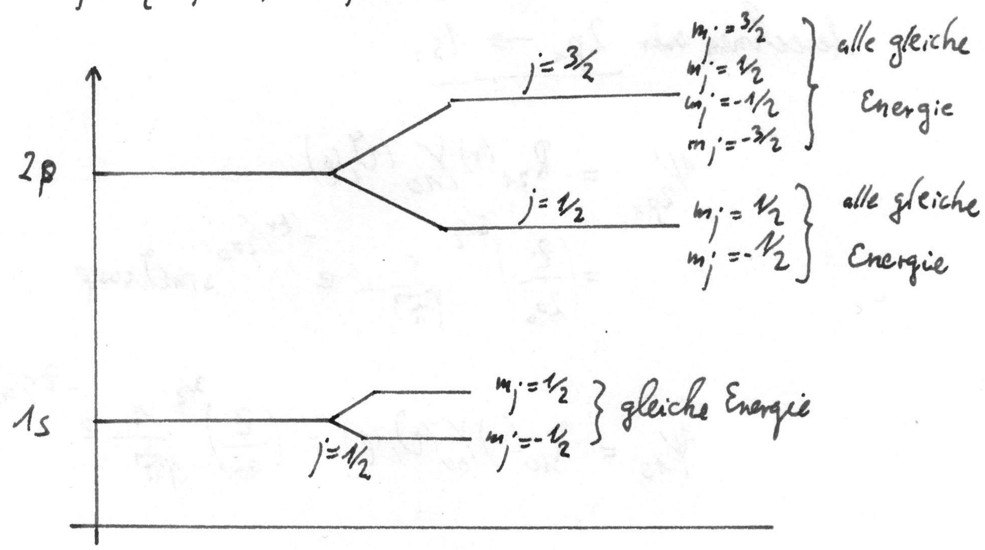
Für 2p kann s $\frac{1}{2}$ oder $-\frac{1}{2}$ werden.

$2p : (n=2,\, s=\pm\frac{1}{2},\, l=1,\, j=\frac{1}{2}, 3/2)$

$2^2P_{1/2}$ $\qquad$ $2^2P_{3/2}$

Sofern kein externes Feld anliegt ist m_j entartet:

$m_j \in \{-|j+s|, \ldots, |j+s|\}$



Energien : siehe 8-2 b)

b) Die erlaubten Übergänge sind

$$2p_x \to 1s \qquad 2p_y \to 1s \qquad 2p_z \to 1s$$

aufgrund der Auswahlregeln

$$\Delta l = \pm 1; \quad \Delta m_l = 0, \pm 1 \quad ; \quad \Delta j = 0, \pm 1$$

jeweils noch mit $j = 3/2$ oder $\frac{1}{2}$ im p- Zustand.

Die Übergangsraten für x, y, z müssen gleich sein, da keine Richtung ausgezeichnet ist.

Bei folgender Formel für die Einstein-Koeffizienten

(*) $$A_{j \to k} = \frac{4}{3} \frac{1}{4\pi \varepsilon_0} \frac{\omega_{jk}^3 e^2}{\hbar c^3} |\langle j | \vec{r} | k \rangle|^2$$

berechnen wir <u>$2p_x \to 1s$</u>:

$$\psi_{2p_x} = R_{21}(r) Y_{10}(\vartheta, \varphi)$$
$$= \left(\frac{Z}{2a_0}\right)^{5/2} \frac{r}{\sqrt{\pi}} e^{-Zr/2a_0} \sin\vartheta \cos\varphi$$

$$\psi_{1s} = R_{10}(r) Y_{00}(\vartheta, \varphi) = \left(\frac{Z}{a_0}\right)^{3/2} \frac{1}{\sqrt{\pi}} e^{-Zr/a_0}$$

Damit folgt

$$\langle \Psi_{2p_x} | \vec{r} | \Psi_{1s} \rangle = \iiint dr\, d\vartheta\, d\varphi \; r^2 \sin\vartheta \left(\frac{Z}{2a_0}\right)^{5/2} \frac{1}{\sqrt{\pi}}\, r e^{-Zr/2a_0}$$

$$\cdot \sin\vartheta \cos\varphi \cdot \begin{pmatrix} r\sin\vartheta\cos\varphi \\ r\sin\vartheta\sin\varphi \\ r\cos\vartheta \end{pmatrix} \cdot \left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0} \frac{1}{\sqrt{\pi}}$$

$$= \iiint dr\, d\vartheta\, d\varphi \; \frac{2^{-5/2}}{\pi} \left(\frac{Z}{a_0}\right)^4 r^4 e^{-3Zr/2a_0} \sin^2\vartheta \cos\varphi \begin{pmatrix} \sin\vartheta\cos\varphi \\ \sin\vartheta\sin\varphi \\ \cos\vartheta \end{pmatrix}$$

Betrachtet man die Integrale einzeln:

$$\int_0^{2\pi} d\varphi \cos\varphi = \Big[\sin\varphi\Big]_0^{2\pi}$$

$$\int_0^{2\pi} d\varphi \sin\varphi\cos\varphi \underset{x=\sin\varphi}{=} \int_0^0 dx\, x = 0$$

$$\int_0^{2\pi} 1\, d\varphi = \int_0^{2\pi} \cos^2\varphi + \sin^2\varphi \, d\varphi = 2\pi \Rightarrow \int_0^{2\pi} d\varphi \cos^2\varphi = \pi$$

$$\int_0^{\pi} d\vartheta \sin^3\vartheta \underset{x=\cos\vartheta}{=} -\int_1^{-1} (1-x^2)\, dx = \int_{-1}^{1} (1-x^2)\, dx$$

$$= \left[x - \frac{x^3}{3}\right]_{x=-1}^{1} = \frac{4}{3}$$

Damit behalten wir nur ein Komponente und eine Integrationsvariable:

$$\langle \psi_{2p_x} | \vec{r} | \psi_{1s} \rangle = \int dr\, r^4\, 2^{-5/2} \left(\frac{Z}{a_0}\right)^4 \frac{4}{3} e^{-3Zr/2a_0} \underbrace{\begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}}_{=\vec{e}_Z}$$

Hier benutzen wir wieder die Integrationsregel

$$\int_0^\infty dr\, r^n e^{-\alpha r} = n!\, \alpha^{-(n+1)}$$

$$\langle \psi_{2p_x} | \vec{r} | \psi_{1s} \rangle = 24 \cdot \frac{4}{3} \left(\frac{2}{3}\right)^5 \frac{a_0}{Z} \vec{e}_Z = \frac{128\sqrt{2}}{243} \frac{a_0}{Z} \vec{e}_Z$$

Nun müssen wir noch die Energiewerte der einzelnen Zustände berechnen. Dazu verwenden wir (10.45)

$$E_{nj}^{exact} = mc^2 \left(\sqrt{1 + \left(\frac{Z\alpha}{n - j - \frac{1}{2} + \sqrt{(j+\frac{1}{2})^2 - Z^2\alpha^2}} \right)^2} - 1 \right)$$

Dies eingesetzt erhalten wir: $(Z=1)$

$$E_{1\frac{1}{2}} = 13.606235\, eV$$

$$E_{2\frac{3}{2}} = 3.401457\, eV$$

$$E_{2\frac{1}{2}} = 3.401507\, eV$$

Mit Hilfe von (*) folgen die Einstein-Koeffizienten:

$$A_{2p,\uparrow \to 1s} = 1.880776 \cdot 10^{9} \frac{1}{s}$$

$$A_{2p,\downarrow \to 1s} = 1.880751 \cdot 10^{9} \frac{1}{s}$$

8.3

$$H = \begin{pmatrix} \varepsilon_1 & Ve^{-ix} \\ Ve^{ix} & \varepsilon_2 \end{pmatrix}, \quad H_{12} = Ve^{ix}, \quad x = k \cdot r - \omega t, \quad V \in \mathbb{R}, \quad \underbrace{|1\rangle, |2\rangle}_{\text{energy levels}}$$

with energies $\varepsilon_1, \varepsilon_2$

a)

$$\det\begin{pmatrix} \varepsilon_1 - \lambda & Ve^{-ix} \\ Ve^{ix} & \varepsilon_2 - \lambda \end{pmatrix} \stackrel{!}{=} 0 = (\varepsilon_1 - \lambda)(\varepsilon_2 - \lambda) - V^2$$

$$\Rightarrow \quad \varepsilon_1\varepsilon_2 - \lambda\varepsilon_1 - \lambda\varepsilon_2 + \lambda^2 - V^2 = 0$$

$$\Leftrightarrow \quad \lambda^2 - (\varepsilon_1 + \varepsilon_2)\lambda + \varepsilon_1\varepsilon_2 - V^2 = 0$$

$$\Rightarrow \quad \lambda_{1,2} = \frac{\varepsilon_1 + \varepsilon_2}{2} \pm \sqrt{\frac{(\varepsilon_1 + \varepsilon_2)^2}{4} - \varepsilon_1\varepsilon_2 + V^2}$$

$$\varepsilon_\pm = \lambda_{1,2} = \frac{\varepsilon_1 + \varepsilon_2}{2} \pm \frac{1}{2}\sqrt{\varepsilon_1^2 + 2\varepsilon_1\varepsilon_2 + \varepsilon_2^2 - 4\varepsilon_1\varepsilon_2 + 4V^2}$$

$$\varepsilon_\pm = \frac{\varepsilon_1 + \varepsilon_2}{2} \pm \frac{1}{2}\sqrt{(\varepsilon_1 - \varepsilon_2)^2 + 4V^2}$$

The eigenstates are:

$$\varepsilon_+ = \frac{\varepsilon_1 + \varepsilon_2}{2} + \frac{1}{2}\sqrt{(\varepsilon_1 - \varepsilon_2)^2 + 4V^2}$$

$$\varepsilon_- = \frac{\varepsilon_1 + \varepsilon_2}{2} - \frac{1}{2}\sqrt{(\varepsilon_1 - \varepsilon_2)^2 + 4V^2}$$

b)

$$|\psi_+\rangle = \cos\theta \, e^{-i\frac{x}{2}} |1\rangle + \sin\theta \, e^{i\frac{x}{2}} |2\rangle$$

$$|\psi_-\rangle = -\sin\theta \, e^{-i\frac{x}{2}} |1\rangle + \cos\theta \, e^{i\frac{x}{2}} |2\rangle$$

$$\tan 2\theta = \frac{2V}{\varepsilon_1 - \varepsilon_2} \quad \Rightarrow \quad \varepsilon_\pm = \frac{\varepsilon_1 + \varepsilon_2}{2} \pm \frac{1}{2}(\varepsilon_1 - \varepsilon_2)\sqrt{1 + \frac{4V^2}{(\varepsilon_1 - \varepsilon_2)^2}}$$

$$\varepsilon_\pm = \frac{\varepsilon_1 + \varepsilon_2}{2} \pm \frac{1}{2}(\varepsilon_1 - \varepsilon_2)\sqrt{\underbrace{1 + \tan^2 2\theta}_{\frac{\cos^2 2\theta + \sin^2 2\theta}{\cos^2 2\theta}}}$$

$$\varepsilon_\pm = \frac{\varepsilon_1 + \varepsilon_2}{2} \pm \frac{1}{2}(\varepsilon_1 - \varepsilon_2)\frac{1}{\cos 2\theta}$$

We are meant to confirm the eigenstates $|\psi_+\rangle$ and $|\psi_-\rangle$. This is possible using:

$$(H - \varepsilon_+ I_{2\times 2})|\psi_+\rangle = 0 \quad \text{and} \quad (H - \varepsilon_- I_{2\times 2})|\psi_-\rangle = 0,$$

We just need to calculate and proof those two equations.

8.3

b)

$$\begin{pmatrix} (\varepsilon_1-\varepsilon_+) & Ve^{-i\chi} \\ Ve^{i\chi} & (\varepsilon_2-\varepsilon_+) \end{pmatrix} \begin{pmatrix} \cos\theta \, e^{-i\frac{\chi}{2}} \\ \sin\theta \, e^{i\frac{\chi}{2}} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

$$\Rightarrow \text{I} \; (\varepsilon_1-\varepsilon_+)\cos\theta \, e^{-i\frac{\chi}{2}} + V\sin\theta \, e^{-i\frac{\chi}{2}} = 0$$
$$\text{II} \; (\varepsilon_2-\varepsilon_+)\sin\theta \, e^{i\frac{\chi}{2}} + V\cos\theta \, e^{i\frac{\chi}{2}} = 0$$

$$\Rightarrow \text{I} \; (\varepsilon_1-\varepsilon_+) + V\tan\theta = 0 \qquad \Bigg| \; \varepsilon_+ = \frac{\varepsilon_1}{2}\left(1+\frac{1}{\cos 2\theta}\right) + \frac{\varepsilon_2}{2}\left(1-\frac{1}{\cos 2\theta}\right)$$
$$\text{II} \; (\varepsilon_2-\varepsilon_+)\tan\theta + V = 0$$

Inserting ε_+ in I:

$$\text{I} \; \frac{(\varepsilon_1-\varepsilon_2)}{2}\left(1-\frac{1}{\cos 2\theta}\right) + V\tan\theta = 0 \quad (*)$$

Inserting $\varepsilon_1-\varepsilon_2 = \frac{2V}{\tan 2\theta}$:

$$\text{I} \; \frac{V}{\tan 2\theta}\left(1-\frac{1}{\cos 2\theta}\right) + V\tan\theta = 0$$

$$\Leftrightarrow \frac{\cos 2\theta - 1}{\sin 2\theta} = -\tan\theta$$

$$\Leftrightarrow \frac{-2\sin^2\theta}{2\sin\theta\cos\theta} = -\tan\theta \quad \checkmark$$

This means $|\psi_+\rangle$ is eigenstate.

$$\begin{pmatrix} (\varepsilon_1-\varepsilon_-) & Ve^{-i\chi} \\ Ve^{i\chi} & (\varepsilon_2-\varepsilon_-) \end{pmatrix} \begin{pmatrix} -\sin\theta \, e^{-i\frac{\chi}{2}} \\ \cos\theta \, e^{i\frac{\chi}{2}} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

$$\Rightarrow \text{I} \; (\varepsilon_1-\varepsilon_-)(-\sin\theta) e^{-i\frac{\chi}{2}} + V\cos\theta \, e^{-i\frac{\chi}{2}} = 0$$
$$\text{II} \; (\varepsilon_2-\varepsilon_-)\cos\theta \, e^{i\frac{\chi}{2}} - V\sin\theta \, e^{i\frac{\chi}{2}} = 0$$

$$\Rightarrow$$
$$\text{I} \; (\varepsilon_1-\varepsilon_-)\tan\theta - V = 0 \qquad \Bigg| \; \varepsilon_- = \frac{\varepsilon_1}{2}\left(1-\frac{1}{\cos 2\theta}\right) + \frac{\varepsilon_2}{2}\left(1+\frac{1}{\cos 2\theta}\right)$$
$$\text{II} \; (\varepsilon_2-\varepsilon_-) - V\tan\theta = 0$$

Inserting ε_- in II:

$$\text{II} \; \frac{\varepsilon_2-\varepsilon_1}{2}\left(1-\frac{1}{\cos 2\theta}\right) - V\tan\theta = 0 \Leftrightarrow \frac{(\varepsilon_1-\varepsilon_2)}{2}\left(1-\frac{1}{\cos 2\theta}\right) + V\tan\theta = 0$$

Where the last term equals $(*)$, which means $|\psi_-\rangle$ is eigenstate.

8.3

c)

$$U(t,t_0) = \left(|\Psi_+\rangle\langle\Psi_+| \, e^{-\frac{i}{\hbar}\varepsilon_+(t-t_0)} \right) + \left(|\Psi_-\rangle\langle\Psi_-| \, e^{-\frac{i}{\hbar}\varepsilon_-(t-t_0)} \right)$$

$t_0 = 0$ and atom in state $|1\rangle$. The time dependence of the population of level 2 is given by:

$$P_{21}(t) = |\langle 2| U(t, t_0 = 0) |1\rangle|^2$$

We can use the orthonormality $\langle 1|1\rangle = 1 = \langle 2|2\rangle$ and $\langle 1|2\rangle = \langle 2|1\rangle = 0$

$$\Rightarrow \quad \langle 2| U(t,0) |1\rangle = \sin\theta \, e^{i\frac{\varkappa}{2}} e^{-\frac{i}{\hbar}\varepsilon_+ t} \cos\theta \, e^{i\frac{\varkappa}{2}} + \cos\theta \, e^{i\frac{\varkappa}{2}} e^{-\frac{i}{\hbar}\varepsilon_- t} (-\sin\theta) e^{i\frac{\varkappa}{2}}$$

$$= \sin\theta\cos\theta \, e^{i\varkappa} \left(e^{-\frac{i}{\hbar}\varepsilon_+ t} - e^{-\frac{i}{\hbar}\varepsilon_- t} \right),$$

mit $\frac{\varepsilon_+ - \varepsilon_-}{\hbar} = \frac{1}{\hbar}\sqrt{(\varepsilon_1 - \varepsilon_2)^2 + 4V^2} = \Omega$ folgt:

$$\langle 2| U |1\rangle = \sin\theta\cos\theta \, e^{i\varkappa} e^{-\frac{i}{\hbar}\varepsilon_+ t} \left(1 - e^{i\Omega t} \right),$$

Calculating $|\langle 2|U|1\rangle|^2$ leads to:

$$|\langle 2|U|1\rangle|^2 = \langle 2|U|1\rangle^* \langle 2|U|1\rangle = \sin^2\theta\cos^2\theta \left(1 - e^{-i\Omega t}\right)\left(1 - e^{i\Omega t}\right)$$

$$= \sin^2\theta\cos^2\theta \left(1 - e^{-i\Omega t} - e^{i\Omega t} + 1 \right)$$

$$= \sin^2\theta\cos^2\theta \left(2 - 2\left(\frac{e^{-i\Omega t} + e^{i\Omega t}}{2} \right) \right)$$

$$= 2\sin^2\theta\cos^2\theta \left(1 - \cos\Omega t \right)$$

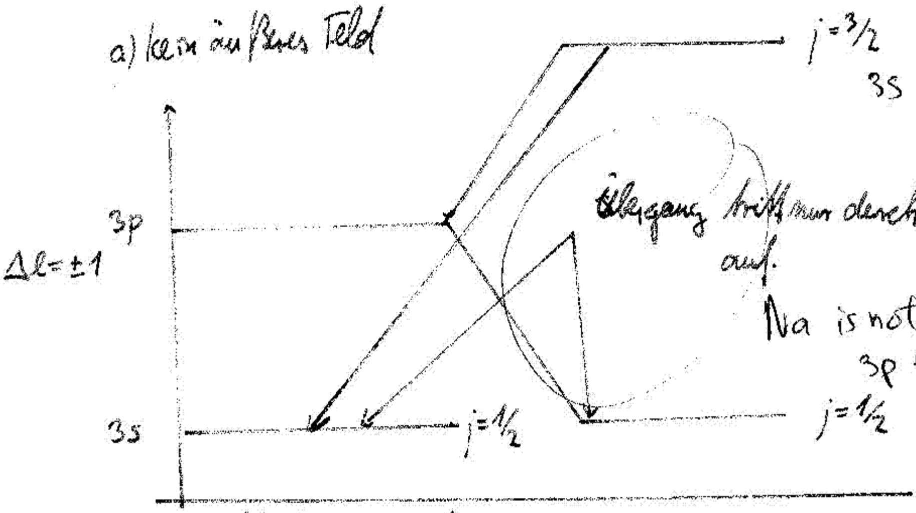
$$= (2\sin\theta\cos\theta)^2 \, \frac{1}{2} \left(1 - 1 + 2\sin^2\left(\frac{\Omega t}{2}\right) \right)$$

$$P_{21}(t) = \sin^2 2\theta \, \sin^2\left(\frac{\Omega t}{2}\right)$$

8-4 Wir haben die 3 folgenden Situationen

3p

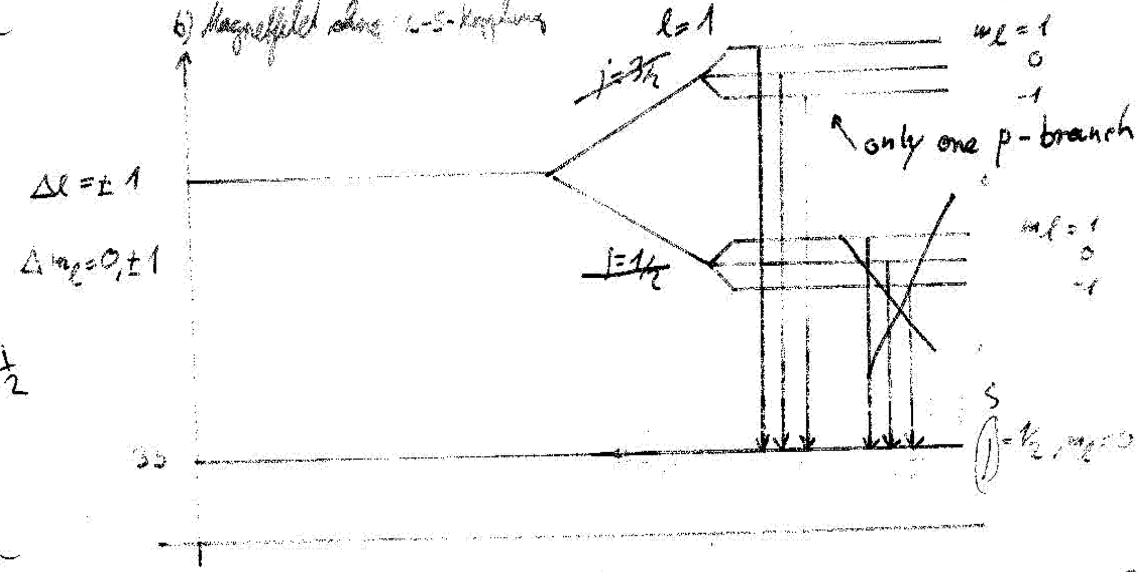
a) kein äußeres Feld



Übergang tritt nur durch Lamb-Shift auf.

Na is not H
3p levels lie much higher in energy than 3S

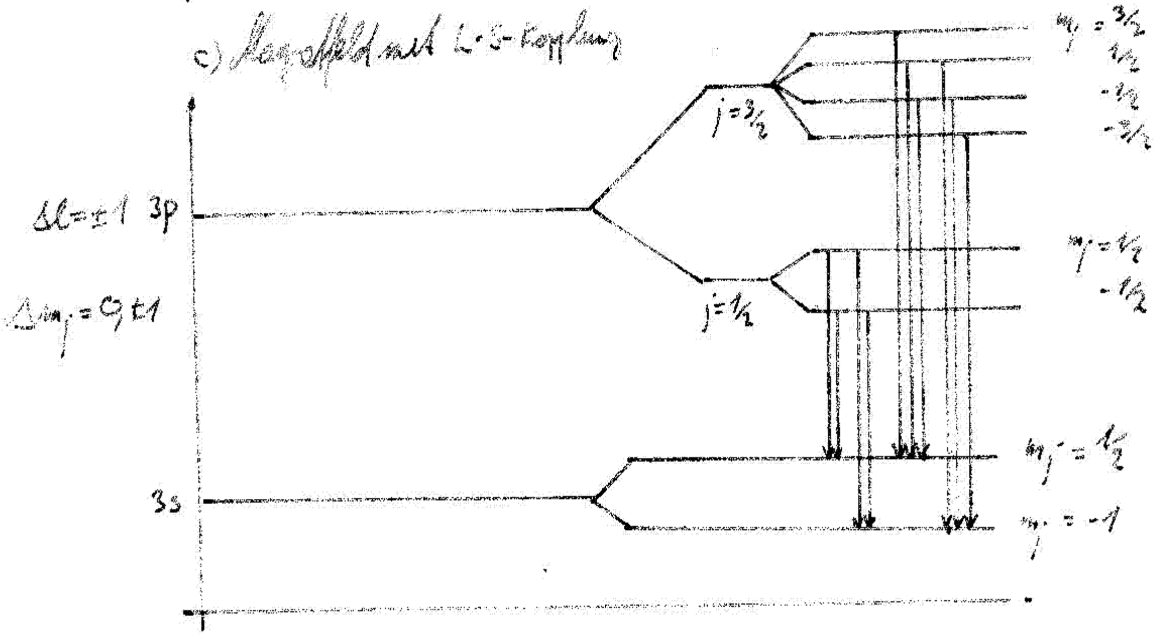
b) Magnetfeld ohne L-S-Kopplung



only one p-branch

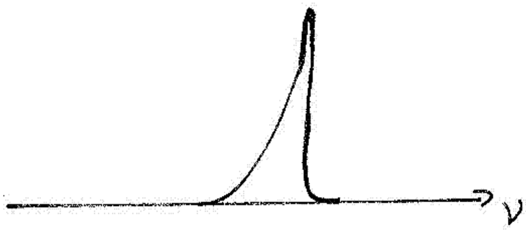
$1\frac{1}{2}$

c) Magnetfeld mit L-S-Kopplung

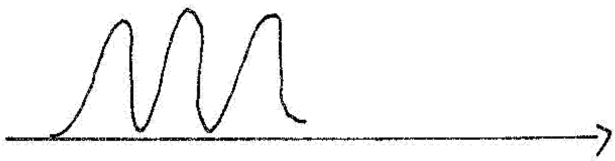


Absorption spectra:

a)



b)



c)