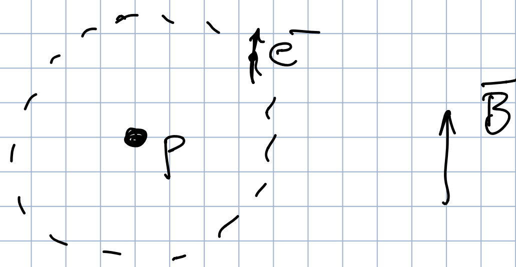
$\Longrightarrow$ VORLESUNG 21 QM

6. ZEIT-UNABHÄNGIGE STÖRUNGSTHEORIE



$$H_{INT} = -\vec{\mu} \cdot \vec{B}$$

$$\rightsquigarrow \quad H^{(0)} |\psi_n^{(0)}\rangle = E_n^{(0)} |\psi_n^{(0)}\rangle$$

(0) : UNGESTÖRTE PROBLEM

STÖRING $H^{(1)}$ e.g. $H^{(1)} = -\vec{\mu} \cdot \vec{B}$

$$H = H^{(0)} + \lambda H^{(1)}$$

KLEIN

(AM ENDE $\lambda \Rightarrow 1$)

$$H |\psi_n\rangle = E_n |\psi_n\rangle$$

1. FALL: KEINE ENTARTUNG

$$E_n^{(0)} \neq E_m^{(0)} \qquad n \neq m$$

$$\longrightarrow \quad E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots$$

$$\longrightarrow \quad |\psi_n\rangle = |\psi_n^{(0)}\rangle + \lambda |\psi_n^{(1)}\rangle + \lambda^2 |\psi_n^{(2)}\rangle + \dots$$

$$\left(H^{(0)} + \lambda H^{(1)}\right)\left(|\psi_n^{(0)}\rangle + \lambda |\psi_n^{(1)}\rangle + \lambda^2 |\psi_n^{(2)}\rangle + \dots\right)$$

$$= \left(E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots\right) \cdot \left(|\psi_n^{(0)}\rangle + \lambda |\psi_n^{(1)}\rangle + \lambda^2 |\psi_n^{(2)}\rangle + \dots\right)$$

$\big\downarrow$ ENTWICKLUNG IN λ

ORDNUNG λ^0

$$H^{(0)} |\psi_n^{(0)}\rangle = E_n^{(0)} |\psi_n^{(0)}\rangle$$

ORDNUNG λ^1

$$H^{(1)} | \psi_n^{(0)} \rangle + H^{(0)} | \psi_n^{(1)} \rangle$$

$$= E_n^{(0)} | \psi_n^{(1)} \rangle + E_n^{(1)} | \psi_n^{(0)} \rangle$$

ORDNUNG λ^2

$$H^{(0)} | \psi_n^{(2)} \rangle + H^{1} | \psi_n^{(1)} \rangle$$

$$= E_n^{(0)} | \psi_n^{(2)} \rangle + E_n^{(1)} | \psi_n^{(1)} \rangle + E_n^{(2)} | \psi_n^{(0)} \rangle$$

$$\vdots$$

$\Rightarrow$ 1. ORDNUNG

- $E_n^{(1)}$?

$$\langle \psi_n^{(0)} |$$

$$\langle \psi_n^{(0)} | H^{(1)} | \psi_n^{(0)} \rangle + \langle \psi_n^{(0)} | H^{(0)} | \psi_n^{(1)} \rangle$$

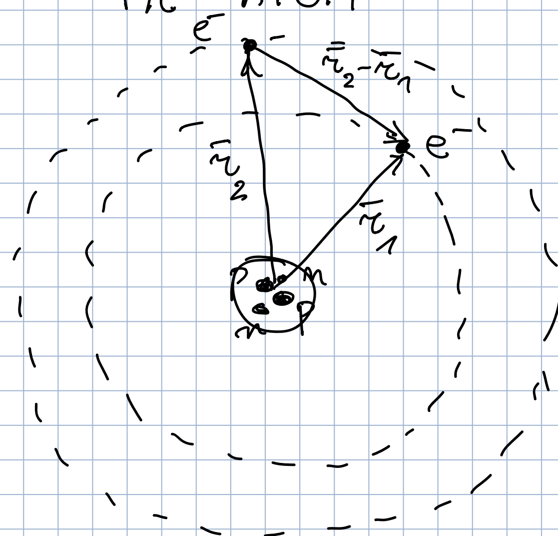
$$= E_n^{(0)} \langle \psi_n^{(0)} | \psi_n^{(1)} \rangle + E_n^{(1)} \underbrace{\langle \psi_n^{(0)} | \psi_n^{(0)} \rangle}_{1}$$

$$\langle \psi_n^{(0)} | H^{(1)} | \psi_n^{(0)} \rangle + E_n^{(0)} \cancel{\langle \psi_n^{(0)} | \psi_n^{(1)} \rangle}$$

$$= E_n^{(0)} \cancel{\langle \psi_n^{(0)} | \psi_n^{(1)} \rangle} + E_n^{(1)}$$

$$\therefore \quad \boxed{E_n^{(1)} = \langle \psi_n^{(0)} | H^{(1)} | \psi_n^{(0)} \rangle}$$

e.g. He ATOM



$$\underline{\underline{H^{(1)}}} = \frac{(\alpha \hbar c)}{|\bar{r}_2 - \bar{r}_1|}$$

$$E_n^{(0)} \rightsquigarrow E_n^{(1)}$$

- $|\psi_n^{(1)}\rangle$?

$$H^{(1)}|\psi_n^{(0)}\rangle + H^{(0)}|\psi_n^{(1)}\rangle$$

$$= E_n^{(0)}|\psi_n^{(1)}\rangle + E_n^{(1)}|\psi_n^{(0)}\rangle$$

$$\left(H^{(0)} - E_n^{(0)}\right)|\psi_n^{(1)}\rangle = \left(E_n^{(1)} - H^{(1)}\right)|\psi_n^{(0)}\rangle$$

$|\psi_n^{(0)}\rangle$ BILDEN EINEN VOLLSTÄNDIGEN SATZ

$$|\psi_n^{(1)}\rangle = \sum_{m \neq n} c_m^{(n)} |\psi_m^{(0)}\rangle$$

$$\sum_{m \neq n} c_m^{(n)} \left(H^{(0)} - E_n^{(0)}\right)|\psi_m^{(0)}\rangle = \left(E_n^{(1)} - H^{(1)}\right)|\psi_n^{(0)}\rangle$$

$m = n$? $\Longrightarrow 0$

$$\sum_{m \neq n} c_m^{(n)} \left(E_m^{(0)} - E_n^{(0)}\right)|\psi_m^{(0)}\rangle$$

$$= \left(E_n^{(1)} - H^{(1)}\right)|\psi_n^{(0)}\rangle$$

$$\langle \psi_l^{(0)} |$$

① $\underline{\underline{l = n}}$

$$\langle \psi_n^{(0)} | \psi_m^{(0)} \rangle = 0 \qquad m \neq n$$

$$0 = \langle \psi_n^{(0)} | E_n^{(1)} - H^{(1)} | \psi_n^{(0)} \rangle$$

$$E_n^{(1)} \underbrace{\langle \psi_n^{(0)} | \psi_n^{(0)} \rangle}_{1} = \langle \psi_n^{(0)} | H^{(1)} | \psi_n^{(0)} \rangle$$

② $\underline{\underline{l \neq n}}$

$$\sum_{m \neq n} c_m^{(n)} \left(E_m^{(0)} - E_n^{(0)} \right) \underbrace{\langle \psi_l^{(0)} | \psi_m^{(0)} \rangle}_{\delta_{lm}}$$

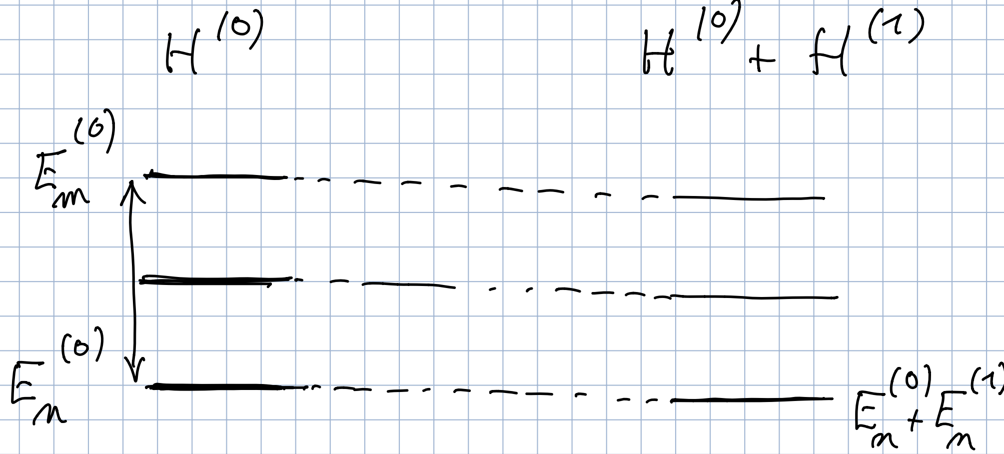
$$= \langle \psi_l^{(0)} | E_n^{(1)} - H^{(1)} | \psi_n^{(0)} \rangle$$

$$c_l^{(n)} \left(E_l^{(0)} - E_n^{(0)} \right) = - \langle \psi_l^{(0)} | H^{(1)} | \psi_n^{(0)} \rangle$$

$$c_l^{(n)} = \frac{\langle \psi_l^{(0)} | H^{(1)} | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_l^{(0)}} \qquad l \neq n$$

KEINE ENTARTUNG !

$$|\psi_n^{(1)}\rangle = \sum_{m \neq n} \frac{\langle \psi_m^{(0)} | H^{(1)} | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} |\psi_m^{(0)}\rangle$$



- 2. ORDNUNG

$$H^{(0)} |\psi_n^{(2)}\rangle + H^{(1)} |\psi_n^{(1)}\rangle$$

$$= E_n^{(0)} |\psi_n^{(2)}\rangle + E_n^{(1)} |\psi_n^{(1)}\rangle + E_n^{(2)} |\psi_n^{(0)}\rangle$$

$$\langle \psi_n^{(0)} |$$

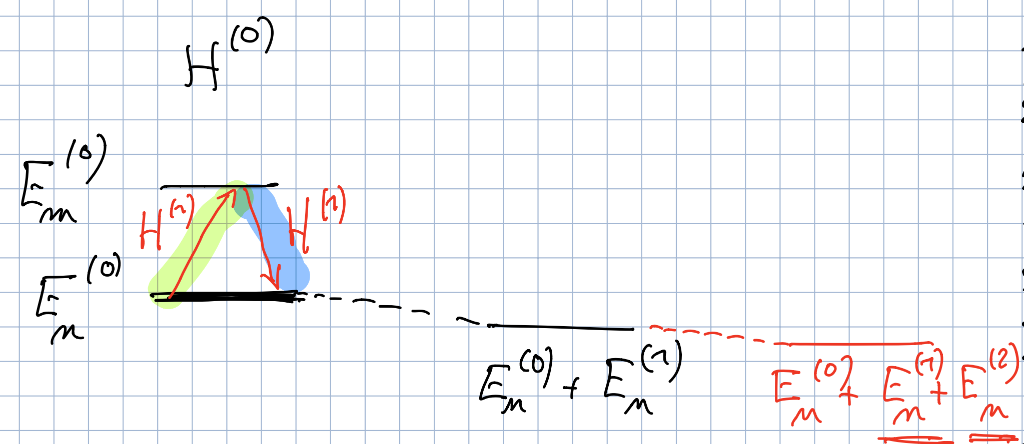
$$\langle \psi_n^{(0)} | H^{(1)} | \psi_n^{(1)} \rangle$$

$$= E_n^{(1)} \underbrace{\langle \psi_n^{(0)} | \psi_n^{(1)} \rangle}_{0} + E_n^{(2)} \underbrace{\langle \psi_n^{(0)} | \psi_n^{(0)} \rangle}_{1}$$

$$E_n^{(2)} = \langle \psi_n^{(0)} | H^{(1)} | \underline{\psi_n^{(1)}} \rangle$$

$$= \sum_{m \neq n} \frac{\langle \psi_m^{(0)} | H^{(1)} | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} \underbrace{\langle \psi_n^{(0)} | H^{(1)} | \psi_m^{(0)} \rangle}_{\langle \psi_m^{(0)} | H^{(1)} | \psi_n^{(0)} \rangle^*}$$

$$\boxed{E_n^{(2)} = \sum_{m \neq n} \frac{\left| \langle \psi_m^{(0)} | H^{(1)} | \psi_n^{(0)} \rangle \right|^2}{E_n^{(0)} - E_m^{(0)}}}$$



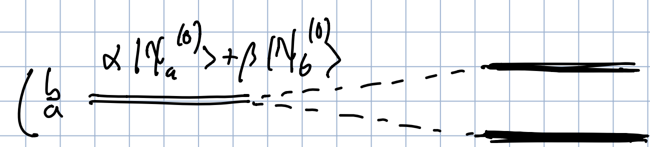
$$\langle \psi_n^{(0)} | H^{(1)} | \psi_m^{(0)} \rangle \langle \psi_m^{(0)} | H^{(1)} | \psi_n^{(0)} \rangle$$

2. FALL: ENTARTUNG IN ENERGIE

$\Rightarrow$ **2-FACH ENTARTUNG**

$$E_a^{(0)} = E_b^{(0)} = E^{(0)}$$

$$H^{(0)} \Longrightarrow H^{(0)} + H^{(1)}$$



$$\begin{cases} H^{(0)}|\psi_a^{(0)}\rangle = E^{(0)}|\psi_a^{(0)}\rangle \\ H^{(0)}|\psi_b^{(0)}\rangle = E^{(0)}|\psi_b^{(0)}\rangle \end{cases}$$

$$\langle\psi_a^{(0)}|\psi_a^{(0)}\rangle = \langle\psi_b^{(0)}|\psi_b^{(0)}\rangle = 1$$

$$\langle\psi_a^{(0)}|\psi_b^{(0)}\rangle = 0$$

$$(H^{(0)} + \lambda H^{(1)})|\psi\rangle = E|\psi\rangle$$

$$E = E^{(0)} + \lambda E^{(1)} + \dots$$

$$|\psi\rangle = |\psi^{(0)}\rangle + \lambda|\psi^{(1)}\rangle + \dots$$

$$|\psi^{(0)}\rangle = \alpha\,|\psi_a^{(0)}\rangle + \beta\,|\psi_b^{(0)}\rangle$$

ORDNUNG λ^0

$$H^{(0)}|\psi^{(0)}\rangle = E^{(0)}|\psi^{(0)}\rangle$$

$$H^{(0)}|\alpha\,\psi_a^{(0)} + \beta\,\psi_b^{(0)}\rangle \stackrel{!}{=} E^{(0)}|\alpha\,\psi_a^{(0)} + \beta\,\psi_b^{(0)}\rangle$$

ORDNUNG λ^1

$$H^{(0)}|\psi^{(1)}\rangle + H^{(1)}|\psi^{(0)}\rangle$$

$$= E^{(0)}|\psi^{(1)}\rangle + E^{(1)}|\psi^{(0)}\rangle$$

$$\left(H^{(0)} - E^{(0)}\right)|\psi^{(1)}\rangle = \left(E^{(1)} - H^{(1)}\right)|\psi^{(0)}\rangle$$

$$\longrightarrow \quad \langle\psi_a^{(0)}| \quad , \quad \langle\psi_b^{(0)}|$$

$$\alpha\,\langle\psi_a^{(0)}| + \beta\,\langle\psi_b^{(0)}|$$

$$(1) \quad 0 = E^{(1)} \langle \psi_a^{(0)} | \psi^{(0)} \rangle - \langle \psi_a^{(0)} | H^{(1)} | \psi^{(0)} \rangle$$

$$(2) \quad 0 = E^{(1)} \langle \psi_b^{(0)} | \psi^{(0)} \rangle - \langle \psi_b^{(0)} | H^{(1)} | \psi^{(0)} \rangle$$

$$(1) \quad E^{(1)} \Big(\alpha \underbrace{\langle \psi_a^{(0)} | \psi_a^{(0)} \rangle}_{1} + \beta \underbrace{\langle \psi_a^{(0)} | \psi_b^{(0)} \rangle}_{0} \Big)$$

$$= \alpha \langle \psi_a^{(0)} | H^{(1)} | \psi_a^{(0)} \rangle + \beta \langle \psi_a^{(0)} | H^{(1)} | \psi_b^{(0)} \rangle$$

$$= \alpha E^{(1)}$$

$$(2) \quad \beta E^{(1)}$$

$$= \beta \langle \psi_b^{(0)} | H^{(1)} | \psi_b^{(0)} \rangle + \alpha \langle \psi_b^{(0)} | H^{(1)} | \psi_a^{(0)} \rangle$$

$$\langle \psi_i^{(0)} | H^{(1)} | \psi_j^{(0)} \rangle \equiv W_{ij}$$

HERMITISCH

$i, j = a, b$

$$W_{ji} = W_{ij}^*$$

$$W = \begin{pmatrix} W_{aa} & W_{ab} \\ W_{ba} & W_{bb} \end{pmatrix}$$

$$W_{ba} = W_{ab}^{*}$$

$$(1) \quad \alpha W_{aa} + \beta W_{ab} = \alpha E^{(1)}$$

$$(2) \quad \alpha W_{ba} + \beta W_{bb} = \beta E^{(1)}$$

$$\begin{pmatrix} W_{aa} & W_{ab} \\ W_{ba} & W_{bb} \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = E^{(1)} \begin{pmatrix} \alpha \\ \beta \end{pmatrix}$$

EIGENZUSTÄNDE EIGENWERTE

(GUTE UNGESTÖRTE ZUSTÄNDE)

EIGENWERTE $E^{(1)}$

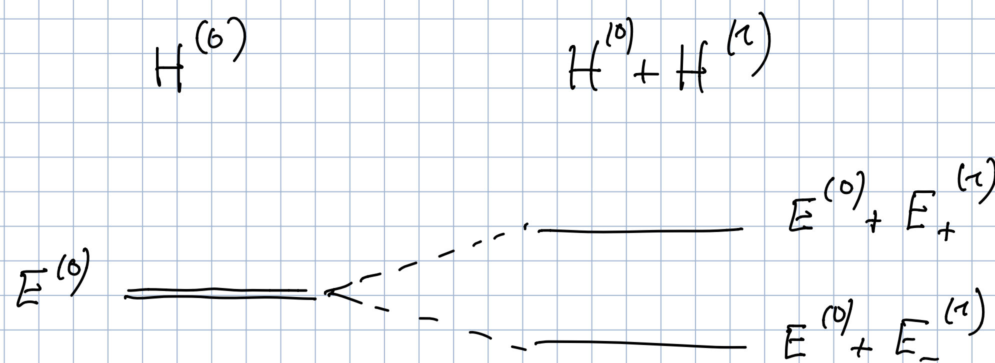
$$\begin{vmatrix} W_{aa} - E^{(1)} & W_{ab} \\ W_{ab}^{*} & W_{bb} - E^{(1)} \end{vmatrix} = 0$$

$$\left(W_{aa} - E^{(1)}\right)\left(W_{bb} - E^{(1)}\right) - |W_{ab}|^2 = 0$$

$$0 = \left(E^{(1)}\right)^2 - E^{(1)}\left(W_{aa} + W_{bb}\right) + W_{aa}W_{bb} - |W_{ab}|^2$$

$$E^{(1)} = \frac{1}{2}\left[\left(W_{aa}+W_{bb}\right) \pm \sqrt{\left(W_{aa}+W_{bb}\right)^2 - 4\left(W_{aa}W_{bb} - |W_{ab}|^2\right)}\right]$$

$$E^{(1)}_{\pm} = \frac{1}{2}\left[W_{aa}+W_{bb} \pm \sqrt{\left(W_{aa}-W_{bb}\right)^2 + 4|W_{ab}|^2}\right]$$



- $\alpha = 1 \;,\; \beta = 0$

$$\alpha|\psi_a^{(0)}\rangle + \beta|\psi_b^{(0)}\rangle = |\psi_a^{(0)}\rangle$$

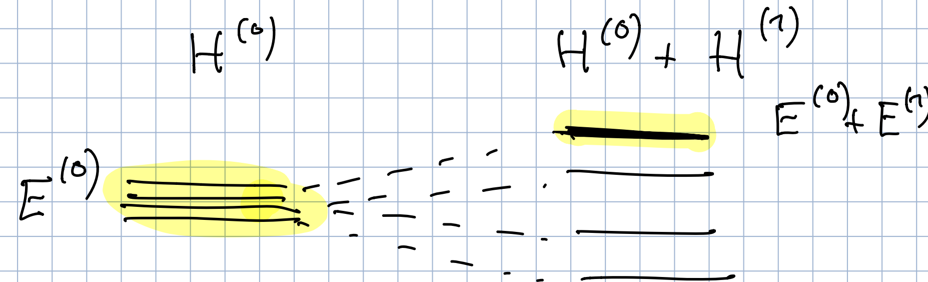
$$\begin{pmatrix} W_{aa} & W_{ab} \\ W_{ba} & W_{bb} \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = E^{(1)}\begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

$$W_{aa} = E^{(1)}$$

$$W_{ba} = 0$$

$$E^{(1)} = W_{aa} = \langle \psi_a^{(0)} | H^{(1)} | \psi_a^{(0)} \rangle$$

$\Rightarrow$ <u>n – FACH ENTARTUNG</u>



$$|\psi_1^{(0)}\rangle, \dots, |\psi_n^{(0)}\rangle \Rightarrow E^{(0)}$$

1) $$W_{ij} = \langle \psi_i^{(0)} | H^{(1)} | \psi_j^{(0)} \rangle$$

$$i, j = 1 \dots n$$

$$\begin{pmatrix} W_{11} & \dots & W_{1n} \\ \vdots & & \\ W_{n1} & \dots & W_{nn} \end{pmatrix} \begin{pmatrix} \alpha_1 \\ \vdots \\ \alpha_n \end{pmatrix} = E^{(1)} \begin{pmatrix} \alpha_1 \\ \vdots \\ \alpha_n \end{pmatrix}$$

2) $|\psi^{(0)}\rangle = \underline{\underline{\alpha_1}} |\psi_1^{(0)}\rangle + \dots + \underline{\underline{\alpha_n}} |\psi_n^{(0)}\rangle$

n EIGENWERTE $E^{(1)}$