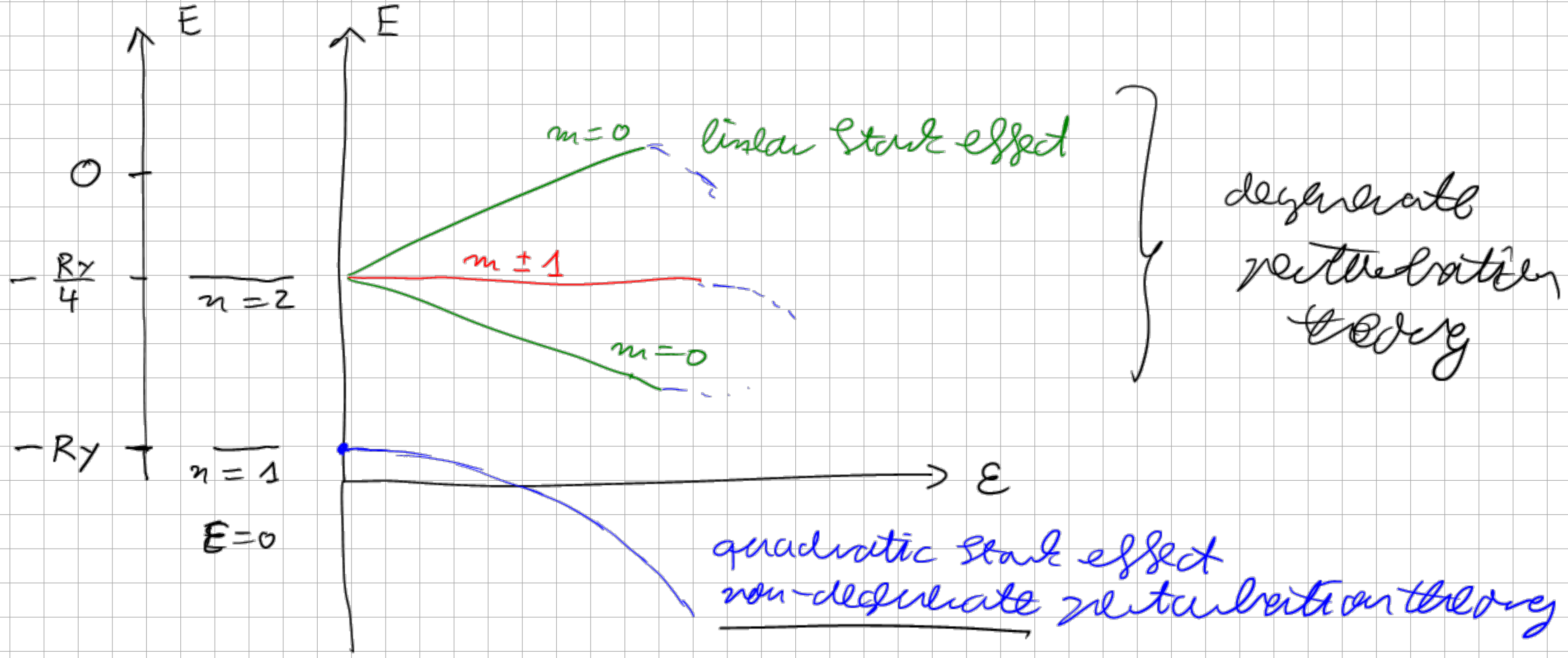
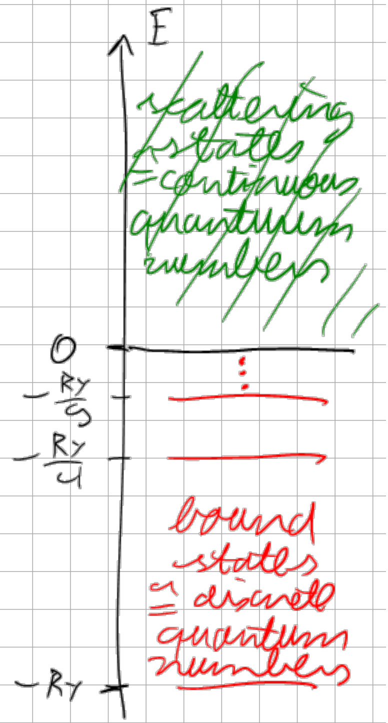
Stark effect $\hat{=}$ hydrogen atom + electric field





$$E_1^{(1)} = \int d^3x\, \psi^*_{100}(\vec{x}) \underbrace{e\mathcal{E}z}_{=V(\vec{x})} \psi_{100}(\vec{x}) \underset{\uparrow}{=} 0$$

$\Delta l = \pm 1, \Delta m = 0$ (selection rules)

$$E_1^{(2)} \underset{\uparrow}{=} \sum_{n\neq 1} \frac{|V_{1,n}|^2}{E_1^{(0)} - E_n^{(0)}} \underset{\uparrow}{=} \sum_{n=2}^{\infty} \sum_{l=0}^{n-1} \sum_{m=-l}^{+l} \frac{|V_{100,nlm}|^2}{E_1^{(0)} - E_n^{(0)}} \underset{\uparrow}{=} \sum_{n=2}^{\infty} \frac{|V_{100,n10}|^2}{E_1^{(0)} - E_n^{(0)}}$$

general formula   hydrogen atom   selection rules

But: WRONG! $\Rightarrow$ Scattering states are missing

Introduce a more precise notation: $E_1^{(2)} = \sum\!\!\!\!\!\!\int_n \frac{|V_{1,n}|^2}{E_1^{(0)} - E_n^{(0)}}$

⇒ complicated to evaluate ⇒ What shall we do ?

Sum rule : circumvents evaluation of summation / integration

$$E_n^{(2)} = \frac{2M}{\hbar^2}\left\{ (V\,W)_{nn} - V_{nn}\, W_{nn} \right\}$$

diagonal expectation values

$$= \langle \psi_n^{(0)} | \hat{O} | \psi_n^{(0)} \rangle$$

$$(O)_{nn} = \int d^3x\, \psi_n^{*(0)}(\vec{x})\, O(\vec{x})\, \psi_n^{(0)}(\vec{x})$$

$W(\vec{x})$ is a solution of: $\Delta W(\vec{x})\, \underbrace{\psi_n^{(0)}(\vec{x})}_{\text{unperturbed wave function}} + 2\vec{\nabla} W(\vec{x}) \cdot \vec{\nabla}\psi_n^{(0)}(\vec{x}) = \underbrace{V(\vec{x})}_{\text{given perturbation}}\psi_n^{(0)}(\vec{x})$

Derivation: non-degenerate perturbation theory ⇒ $n \neq m$

$$\left\{-\frac{\hbar^2}{2M}\Delta + V_{pot.}(\vec{x})\right\}\psi_n^{(0)}(\vec{x}) = E_n^{(0)}\psi_n^{(0)}(\vec{x}) \quad \Big|\ \int d^3x\, \psi_m^{(0)*}(\vec{x})\, W(\vec{x})$$

$$\left\{-\frac{\hbar^2}{2M}\Delta + V_{pot.}(\vec{x})\right\}\psi_m^{(0)}(\vec{x}) = E_m^{(0)}\psi_m^{(0)}(\vec{x}) \quad \Big|\ \int d^3x\, \psi_n^{(0)}(\vec{x})\, W(\vec{x}) \quad \text{complex conjec.}$$

$$-\frac{\hbar^2}{2M}\int d^3x\, \underbrace{W(\vec{x})\left\{\psi_m^{(0)*}(\vec{x})\overset{=\vec{\nabla}^2}{\Delta}\psi_n^{(0)}(\vec{x}) - \psi_n^{(0)}\overset{\vec{\nabla}^2}{\Delta}\psi_m^{(0)*}(\vec{x})\right\}} = (E_n^{(0)} - E_m^{(0)})\int d^3x\, \psi_m^{(0)*}(\vec{x})\, W(\vec{x})\, \psi_n^{(0)}(\vec{x})$$

⇒ $V_{pot.}(\vec{x})$ drops out

$$= \vec{\nabla}\left\{ W(\vec{x})\psi_m^{(0)*}(\vec{x})\,\vec{\nabla}\psi_n^{(0)}(\vec{x}) - W(\vec{x})\psi_n^{(0)}(\vec{x})\,\vec{\nabla}\psi_m^{(0)*}(\vec{x}) \right\} \xrightarrow[\text{Satz}]{\text{Gauß}} 0$$

$$- \vec{\nabla}W(\vec{x})\,\psi_m^{(0)*}(\vec{x})\,\vec{\nabla}\psi_n^{(0)}(\vec{x}) - \cancel{W(\vec{x})\,\vec{\nabla}\psi_m^{(0)*}(\vec{x})\,\vec{\nabla}\psi_n^{(0)}(\vec{x})}$$

$$+ \vec{\nabla}W(\vec{x})\,\psi_n^{(0)}(\vec{x})\,\vec{\nabla}\psi_m^{(0)*}(\vec{x}) + \cancel{W(\vec{x})\,\vec{\nabla}\psi_n^{(0)}(\vec{x})\,\vec{\nabla}\psi_m^{(0)*}(\vec{x})}$$

$$\int d^3x \left\{ \boxed{\psi_m^{(0)*}(\vec{x})}\, \vec{\nabla} w(\vec{x}) \cdot \vec{\nabla} \psi_n^{(0)}(\vec{x}) - \psi_n^{(0)}(\vec{x})\, \vec{\nabla} w(\vec{x}) \cdot \boxed{\vec{\nabla} \psi_m^{(0)*}(\vec{x})} \right\}$$

$$= \frac{2M}{\hbar^2} \boxed{(E_n^{(0)} - E_m^{(0)})} \int d^3x\, \psi_m^{(0)*}(\vec{x})\, w(\vec{x})\, \psi_n^{(0)}(\vec{x})$$

$$= -\vec{\nabla}\left\{ \psi_n^{(0)}(\vec{x})\, \vec{\nabla} w(\vec{x})\, \psi_m^{(0)*}(\vec{x}) \right\} \xrightarrow[\text{dirichlet}]{\text{Gauß}} 0$$

$$+ \psi_m^{(0)*}(\vec{x}) \left\{ \psi_n^{(0)}(\vec{x})\, \Delta w(\vec{x}) + \vec{\nabla} \psi_n^{(0)} \cdot \vec{\nabla} w(\vec{x}) \right\}$$

$$\int d^3x\, \psi_m^{(0)*}(\vec{x}) \underbrace{\left\{ \psi_n^{(0)}(\vec{x})\, \Delta w(\vec{x}) + 2\, \vec{\nabla} w(\vec{x}) \cdot \vec{\nabla} \psi_n^{(0)}(\vec{x}) \right\}}_{\stackrel{!}{=}\, V(\vec{x})\, \psi_n^{(0)}(\vec{x})} =$$

$w(\vec{x})$ is at our disposal!

$\uparrow$ $w(\vec{x})$ should solve this differential equation

$$E_n^{(2)} = \sum_{m \neq n} \frac{|V_{n,m}|^2}{E_n^{(0)} - E_m^{(0)}}$$

$$\frac{1}{E_n^{(0)} - E_m^{(0)}} \underbrace{\int d^3x\, \psi_m^{(0)*}(\vec{x})\, V(\vec{x})\, \psi_n^{(0)}(\vec{x})}_{= \langle \psi_m^{(0)} | \hat{V} | \psi_n^{(0)} \rangle} = \frac{2M}{\hbar^2} \underbrace{\int d^3x\, \psi_m^{(0)*}(\vec{x})\, w(\vec{x})\, \psi_n^{(0)}(\vec{x})}_{= \langle \psi_m^{(0)} | \hat{w} | \psi_n^{(0)} \rangle} \quad \Bigg\| \cdot \sum_{m \neq n} \langle \psi_n^{(0)} | \hat{V} | \psi_m^{(0)} \rangle$$

$$= \sum_{m \neq n} \frac{\langle \psi_m^{(0)} | \hat{V} | \psi_n^{(0)} \rangle^* \langle \psi_m^{(0)} | \hat{V} | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} \stackrel{\hat{V} = \hat{V}^\dagger}{=} \sum_{m \neq n} \frac{\langle \psi_n^{(0)} | \hat{V} | \psi_m^{(0)} \rangle \langle \psi_m^{(0)} | \hat{V} | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}}$$

$$E_n^{(2)} = \frac{2M}{\hbar^2} \sum_{m \neq n} \langle \psi_n^{(0)} | \hat{V} | \psi_m^{(0)} \rangle \langle \psi_m^{(0)} | \hat{w} | \psi_n^{(0)} \rangle$$

$$= \frac{2M}{\hbar^2} \langle \psi_n^{(0)} | \hat{V} \sum_{m \neq n} | \psi_m^{(0)} \rangle \langle \psi_m^{(0)} | \hat{w} | \psi_n^{(0)} \rangle =$$

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

$$= \frac{2m}{\hbar^2}\left\{ (VW)_{nn} - V_{nn} \cdot W_{nn} \right\}$$

Outlook: Once W is known, in principle, a sum rule is possible to derive for any perturbative order

Now: back to quadratic effect $\Rightarrow$ W is needed!

$$\Delta W(\vec{x})\, \psi_{100}^{(0)}(\vec{x}) + 2\, \vec{\nabla} W(\vec{x})\, \vec{\nabla} \psi_{100}^{(0)}(\vec{x}) = \underbrace{V(\vec{x})}_{= e\mathcal{E}\underbrace{z}_{= r\cos\vartheta}}\ \underbrace{\psi_{100}^{(0)}(\vec{x})}_{= \frac{2}{a_B^{3/2}} e^{-r/a_B}}$$

$\to$ inhomogeneous differential equation

Particular solution found as follows:

$P_1(x) = x \,|\, = P_1(\cos\vartheta)$

$$\vec{\nabla}\psi_{100}^{(0)}(\vec{x}) = -\frac{1}{a_B}\psi_{100}^{(0)}(\vec{x})\,\vec{e}_r$$

- ground state: isotropic
- perturbation due to electric field: cylinder-symmetric

$\Rightarrow$ $W(\vec{x})$ is suspected to be cylinder-symmetric

$$\underbrace{W(\vec{x})}_{= W(r,\vartheta)} = \sum_{\ell=0}^{\infty} W_\ell(r)\, \underbrace{P_\ell(\cos\vartheta)}_{\text{complete}}$$

: most general ansatz for a cylinder-symmetric problem

$$\Delta = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\left(\frac{\partial^2}{\partial \vartheta^2} + \frac{\cos\vartheta}{\sin\vartheta}\frac{\partial}{\partial\vartheta} + \frac{1}{\sin^2\vartheta}\frac{\partial^2}{\partial\varphi^2} \right)$$

$$\vec{\nabla} = \frac{\partial}{\partial r}\vec{e}_r + \frac{1}{r}\frac{\partial}{\partial\vartheta}\vec{e}_\vartheta + \frac{1}{r\sin\vartheta}\frac{\partial}{\partial\varphi}\vec{e}_\varphi$$

$$\Rightarrow \quad w_l''(r) + 2\left(\frac{1}{r} - \frac{1}{a_B}\right) w_l'(r) - \frac{l(l+1)}{r^2} w_l(r) = e\mathcal{E} r \, \delta_{l,1}$$

$$\Rightarrow \quad w_l(r) = -\frac{1}{4} e\mathcal{E} a_B (r + 2a_B) r \, \delta_{l,1}$$

$$\Rightarrow \quad w(r,\vartheta,\varphi) = -\frac{1}{4} e\mathcal{E} a_B (r + 2a_B) r \cos\vartheta$$

$$E^{(2)}_{100} = \frac{\hbar^2}{2M}\left\{ (V w)_{100,100} - \cancel{\underbrace{V_{100,100}}_{= E^{(1)}_{100} = 0} \cdot W_{100,100}} \right\}$$

$$= -\frac{1}{4} e^2 \mathcal{E}^2 a_B \int d^3x \, (r + 2a_B) \underbrace{z^2}_{\to \frac{r^2}{3}} \left|\psi^{(0)}_{100}(r)\right|^2$$

$$= -\frac{1}{12} e^2 \mathcal{E}^2 a_B \, 4\pi \int_0^\infty dr \, r^2 (r + 2a_B) \, r^2 \, \frac{4}{a_B^3} \, e^{-\frac{2r}{a_B}}$$

$$\downarrow \quad \rho = \frac{2r}{a_B} \quad , \quad \int_0^\infty d\rho \, \rho^k e^{-\rho} = k!$$

$$= -\frac{9 m e^2}{4\hbar^2} a_B^4 \mathcal{E}^2$$

Interpretation: external electric field yield electric dipole moment

$$\vec{p} \sim \vec{E} \, , \qquad \vec{p} = \varepsilon_0 \underbrace{\alpha_p}_{\text{polarizability}} \vec{E}$$

$$E = -\int_0^{\vec{E}} \vec{p} \, d\vec{E} = -\frac{\varepsilon_0}{2} \alpha_p \underbrace{\vec{E}^2}_{= \mathcal{E}^2}$$

$$\alpha_p = 18\pi a_B^3 \quad (\text{SI units})$$

$$\varepsilon_0 \Rightarrow \frac{1}{4\pi}$$

$$\alpha_p = \frac{9}{2} a_B^3 \quad (\text{cgs units})$$

$$\frac{e^2}{4\pi\varepsilon_0 r} \qquad \frac{e^2}{r}$$

Back to general theory: third-order sum rule?

$$E_n^{(3)} = \sum_{l,l' \neq n} \frac{V_{nl} V_{ll'} V_{l'n}}{(E_n^{(0)}-E_l^{(0)})(E_n^{(0)}-E_{l'}^{(0)})} - V_{nn} \sum_{l \neq n} \frac{V_{nl} V_{ln}}{(E_n^{(0)}-E_n^{(0)})^2}$$

previously: $\frac{V_{ln}}{E_n^{(0)}-E_l^{(0)}} = \frac{2m}{\hbar^2} W_{ln}$ $\xrightarrow[\text{conjugation and } \hat{V}=\hat{V}^+, \hat{W}=\hat{W}^+]{\text{complex}}$ $\frac{V_{nl}}{E_n^{(0)}-E_l^{(0)}} = \frac{2m}{\hbar^2} W_{nl}$

1) $$\sum_{l,l' \neq n} \frac{V_{nl}}{E_n^{(0)}-E_l^{(0)}} V_{ll'} \frac{V_{l'n}}{E_n^{(0)}-E_{l'}^{(0)}}$$

$$= \left(\frac{2m}{\hbar^2}\right)^2 \sum_{l\neq n} \sum_{l' \neq n} \underbrace{W_{nl} V_{ll'} W_{l'n}}_{\langle \psi_n^{(0)} | \hat{W} | \psi_l^{(0)} \rangle \langle \psi_l^{(0)} | \hat{V} | \psi_{l'}^{(0)} \rangle \langle \psi_{l'}^{(0)} | \hat{W} | \psi_n^{(0)} \rangle}$$

$$= \langle \psi_n^{(0)} | \hat{W} \left(1 - |\psi_n^{(0)}\rangle\langle\psi_n^{(0)}|\right) \hat{V} \left(1 - |\psi_n^{(0)}\rangle\langle\psi_n^{(0)}|\right) \hat{W} | \psi_n^{(0)} \rangle$$

$$= (WVW)_{nn} - (W)_{nn} (VW)_{nn} - (WV)_{nn} W_{nn} + W_{nn}^2 V_{nn}$$

2) $\left(\frac{2m}{\hbar^2}\right)^2 \underbrace{\sum_{l\neq n} W_{nl} W_{ln}}_{\underbrace{\langle n|\hat{W}|1-|n\rangle\langle n|\hat{W}|n\rangle}_{=(W^2)_{nn}-(W)_{nn}^2}}$

Add 1) and 2): sum rule for third order:

$$E_n^{(3)} = \left(\frac{2m}{\hbar^2}\right)^2 \left\{ (\cancel{V}W^2)_{nn} - 2 W_{nn} \underbrace{(VW)_{nn}}_{\to E_n^{(2)}} - V_{nn} (W^2)_{nn} + 2 W_{nn}^2 V_{nn} \right\}$$

$E_n^{(1)}$

$$E_n^{(3)} = \left(\frac{2m}{\hbar^2}\right)^2 (VW)^2_{nn} - 2 \frac{2m}{\hbar^2} E_n^{(2)} \underline{W_{nn}} - \left(\frac{2m}{\hbar^2}\right)^2 E_n^{(1)} \underline{W_{nn}^2}$$

$$E_n^{(2)} = \frac{2m}{\hbar^2} \left\{ (VW)_{nn} - \underbrace{V_{nn}}_{=E_n^{(1)}} W_{nn} \right\}$$

$$E_n^{(1)} = V_{nn}$$

2nd cumulant

Conjecture: $E_n^{(k)} = \left(\frac{2m}{\hbar^2}\right)^{k-1} \underline{(V W^{k-1})^{c}_{nn}}$