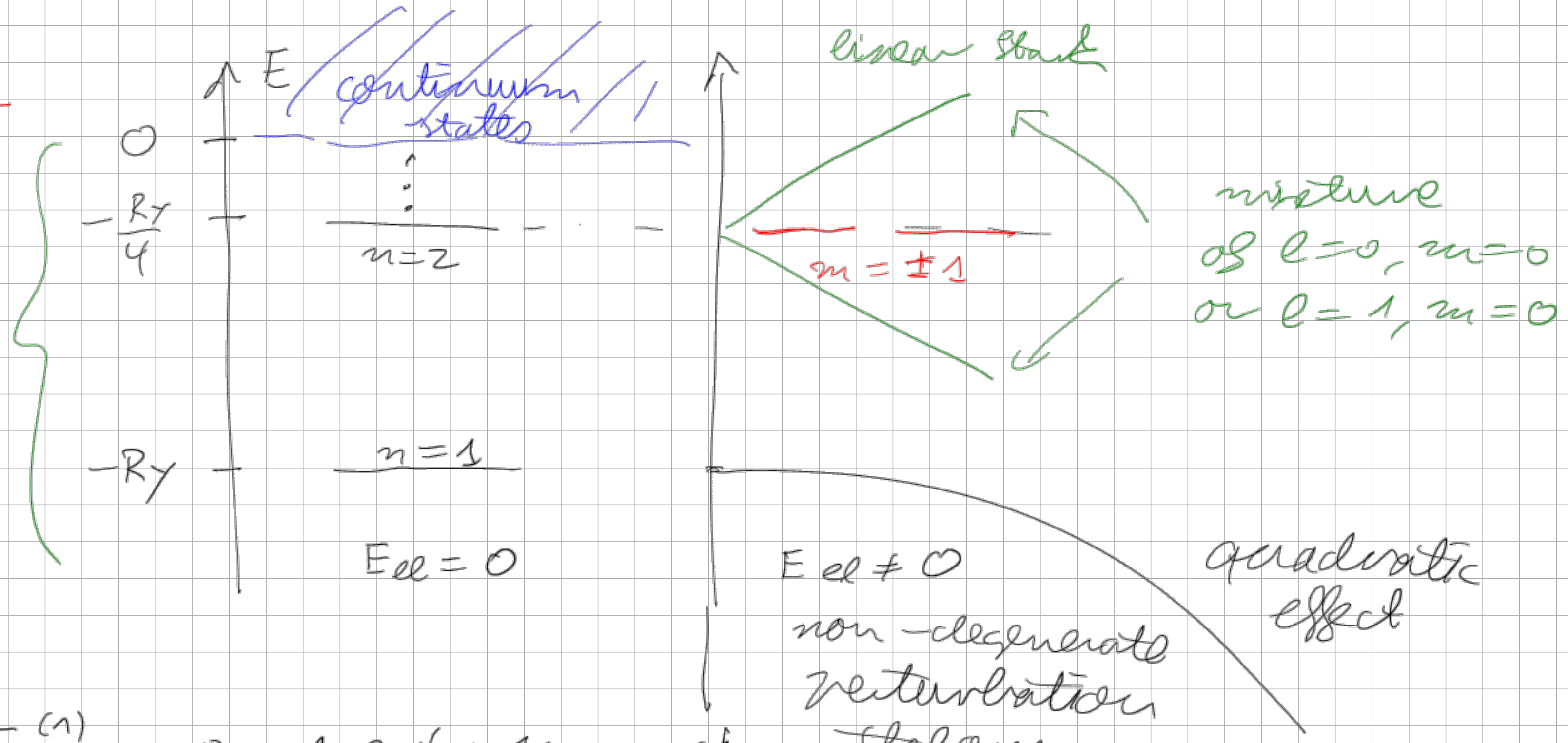
Reminder:

bound states



last time: $E_1^{(1)} = 0$ due to symmetry

$$\underset{n=1}{E_1^{(2)}} \overset{\text{order}}{} = \sum_{n=2}^{\infty} \frac{|V_{100,n10}|^2}{E_1^{(0)} - E_n^{(0)}}$$ naive expectation **WRONG**

potential: perturbation

$$\overset{\text{true}}{=} \sum_{n\neq 1}\!\!\!\!\!\int \frac{|V_{1,n}|^2}{E_1^{(0)} - E_n^{(0)}}$$

too complicated to consider:
1) continuum states are known
2) sum is cumbersome

SUM RULE:

derivation relies on non-degenerate perturbation theory ($n \neq m$)

$$\left\{-\frac{\hbar^2}{2m}\Delta + V(\vec{x})\right\}\psi_n^{(0)}(\vec{x}) = E_n^{(0)}\psi_n^{(0)}(\vec{x})$$

not degenerate $\left|\int d^3x\, \psi_m^{(0)*}(\vec{x})\, W(\vec{x})\right.$

potential of unperturbed problem

not ϵ Coulomb potential (hydrogen atom)

unknown

$$\left\{-\frac{\hbar^2}{2m}\Delta + V_{pot}(\vec x)\right\}\psi_m^{(0)*}(\vec x) = E_m^{(0)}\,\psi_m^{(0)*}(\vec x) \qquad \Big| \int d^3x\, \psi_n^{(0)}(\vec x)\, w(\vec x)$$

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

$$= \vec\nabla\left\{w(\vec x)\psi_m^{(0)*}(\vec x)\vec\nabla\psi_n^{(0)}(\vec x) - w(\vec x)\psi_n^{(0)}(\vec x)\vec\nabla\psi_m^{(0)*}(\vec x)\right\} \xrightarrow{\text{Gauß}} \text{boundary term} \to 0$$

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

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

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

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

$$- \vec\nabla\left\{\psi_n^{(0)}(\vec x)\,\vec\nabla w(\vec x)\,\psi_m^{(0)*}(\vec x)\right\} \xrightarrow{\text{Gauß}} \text{boundary term} \to 0$$

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

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

fix $w(\vec x)$:

$w(\vec{x})$ should solve: inhomogeneous linear differential equation of second order

$$\psi_n^{(0)}(\vec{x})\,\Delta w(\vec{x}) + 2\,\vec{\nabla} w(\vec{x})\cdot\vec{\nabla}\psi_n^{(0)}(\vec{x}) = \underbrace{V(\vec{x})}_{\text{perturbation}}\,\psi_n^{(0)}(\vec{x})$$

$$\underbrace{\int d^3x\, \psi_m^{(0)*}(\vec{x})\, V(\vec{x})\, \psi_n^{(0)}(\vec{x})}_{=V_{mn}} = \frac{2m}{\hbar^2}\left(E_n^{(0)} - E_m^{(0)}\right)\int d^3x\, \psi_m^{(0)*}(\vec{x})\, w(\vec{x})\, \psi_n^{(0)}(\vec{x})$$

$$\frac{1}{E_n^{(0)} - E_m^{(0)}}\,\underbrace{V_{mn}}_{\langle\psi_m^{(0)}|\hat{V}|\psi_n^{(0)}\rangle} = \frac{2m}{\hbar^2}\langle\psi_m^{(0)}|w|\psi_n^{(0)}\rangle$$

$\hat{V}=\hat{V}^+$

$$\underbrace{=\langle\psi_m^{(0)}|\hat{V}|\psi_n^{(0)}\rangle}$$

$\sum\!\!\!\!\!\!\int_m V_{nm}$

$$E_n^{(2)} = \sum\!\!\!\!\!\!\int_{m\neq n}\frac{|V_{n,m}|^2}{E_n^{(0)} - E_m^{(0)}} = \sum\!\!\!\!\!\!\int_{m\neq n}\frac{\langle\psi_n^{(0)}|\hat{V}|\psi_m^{(0)}\rangle\langle\psi_n^{(0)}|\hat{V}|\psi_m^{(0)}\rangle^*}{E_n^{(0)} - E_m^{(0)}}$$

$$= \frac{2m}{\hbar^2}\underbrace{\sum\!\!\!\!\!\!\int_{m\neq n}\langle\psi_n^{(0)}|\hat{V}|\psi_m^{(0)}\rangle\langle\psi_m^{(0)}|\hat{w}|\psi_n^{(0)}\rangle}$$

$$= \langle\psi_n^{(0)}|\hat{V}\underbrace{\sum\!\!\!\!\!\!\int_{m\neq n}|\psi_m^{(0)}\rangle\langle\psi_m^{(0)}|}_{=1-|\psi_n^{(0)}\rangle\langle\psi_n^{(0)}|}\hat{w}|\psi_n^{(0)}\rangle$$

basic assumption:
all states m (= bound + continuum) represent a basis of Hilbert space

$$\Rightarrow E_n^{(2)} = \frac{2m}{\hbar^2}\left\{\underbrace{(Vw)_{nn}}_{\langle\psi_n^{(0)}|Vw|\psi_n^{(0)}\rangle = \int d^3x\,\psi_n^{(0)*}(\vec{x})\psi_n^{(0)}(\vec{x})\,V(\vec{x})\,w(\vec{x})} - (V)_{nn}(w)_{nn}\right\}$$

$(V)_{nn} = E_n^{(1)}$

Once W is known, a sum rule allows to determine 2nd non-degenerate perturbative result.

$\uparrow \vec{E} \parallel \vec{e}_z$

Outlook: generalizable to higher orders

Now back to quadratic Stark effect: W is needed

$$\underline{\Delta \boxed{W(\vec{x})}}\, \cancel{\psi^{(0)}_{100}(\vec{x})} + 2\, \underline{\vec{\nabla} \boxed{W(\vec{x})}} \cdot \underbrace{\vec{\nabla} \psi^{(0)}_{100}(\vec{x})}_{= -\frac{1}{a_B}\cancel{\psi^{(0)}_{100}(\vec{x})}\,\underline{\vec{e}_r}} = \underbrace{V(\vec{x})}_{= e\mathcal{E} \underbrace{z}_{= r\cos\vartheta}} \underbrace{\cancel{\psi^{(0)}_{100}(\vec{x})}}_{= \frac{2}{a_B^{3/2}}\, e^{-\frac{r}{a_B}}}$$

symmetries:

- ground state: isotropic
- cylinder symmetry due to $V(\vec{x})$

} Expectation: $W(\vec{x})$ is also cylinder symmetric

$$\Rightarrow W(\vec{x}) = W(r, \vartheta) = \sum_{l=0}^{\infty} W_l(r) \underline{P_l(\cos\vartheta)}$$

$\hat{=}$ basis functions

$$\Delta = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} - \frac{\vec{L}^2}{\hbar^2 r^2}$$

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

$$\sum_{l=0}^{\infty}\left\{ W_l''(r) + \frac{2}{r}W_l'(r) - \frac{l(l+1)}{r^2}W_l(r)\right\} P_l(\cos\vartheta)$$

$$+ 2\sum_{l=0}^{\infty} \frac{-1}{a_B} W_l'(r) P_l(\cos\vartheta) = e\mathcal{E} r \underbrace{\cos\vartheta}_{= P_1(\cos\vartheta)}$$

$$\int_0^{\pi} \sin\vartheta \, P_{l'}(\cos\vartheta)\, d\vartheta$$

$$x = \cos\vartheta$$

$$dx = -\sin\vartheta\, d\vartheta$$

$$\int_{-1}^{+1} dx \; P_\ell(x)\, P_{\ell'}(x) = \delta_{\ell\ell'}$$

$$w_\ell''(r) + 2\left(\frac{1}{r} - \frac{1}{a_B}\right) w_\ell'(r) - \frac{\ell(\ell+1)}{r^2}\, w_\ell(r) = e\varepsilon r\, \delta_{\ell,1}$$

$$w_\ell(r) = -\frac{1}{4}\, e\, \varepsilon\, a_B (r + 2a_B)\, r\, \delta_{\ell,1}$$ particular solution

$$\boxed{w(r,\vartheta) = -\frac{1}{4}\, e\, \varepsilon\, a_B (r + 2a_B)\, r \cos\vartheta}$$

$$E^{(2)}_{100} = \frac{\hbar^2}{2m}\left\{ \underline{(VW)_{100,100}} - \underbrace{(V)_{100,100}}_{=0} \cdot (W)_{100,100} \right\}$$

$$= -\frac{\hbar^2}{2m}\, \frac{1}{4} e^2 \varepsilon^2 a_B \int d^3x\, (r + 2a_B) \underbrace{(r\cos\vartheta)^2}_{= z^2 \;\hat{=}\; \frac{1}{3} r^2} \frac{4}{a_B^2}\, e^{-\frac{2r}{a_B}}$$

symmetry

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

note: $\int_0^\infty d\rho\, \rho^n e^{-\rho} = n!$

$$\Rightarrow \quad E^{(2)}_{100} = -\frac{9 m e^2}{4\hbar^2}\, a_B^4\, \varepsilon^2$$

reduction of energy

quadratic in ε

How to interprete ?

electric field induces an electric dipole moment:

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

$E = -\int_0^{\vec{E}} \vec{p} \cdot d\vec{E} = -\frac{\varepsilon_0}{2} \alpha_P \vec{E}^2$

α_P (cgs)

$\Rightarrow$ polarizability of hydrogen atom in ground state

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

$\downarrow$ $\varepsilon_0 = \frac{1}{4\pi}$

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