Degenerate Perturbation Theory

$$\hat{H}_0 \, |\psi^{(0)}_{n\alpha_n}\rangle = E^{(0)}_n \, |\psi^{(0)}_{n\alpha_n}\rangle \quad , \quad \langle \psi^{(0)}_{n\alpha_n} | \psi^{(0)}_{n\beta_n}\rangle = \delta_{\alpha_n,\beta_n}$$

degeneracy index : $\alpha_n = 1, \ldots, d_n$

$$\hat{H}(\lambda) = \hat{H}_0 + \lambda \hat{V}$$

lifting of degeneracy

$$\hat{H}(\lambda) \, |\tilde{\psi}_{n\alpha_n}(\lambda)\rangle = E_{n\alpha_n}(\lambda) \, |\tilde{\psi}_{n\alpha_n}(\lambda)\rangle$$

$$= E^{(0)}_n + \underbrace{\lambda E^{(1)}_{n\alpha_n}}_{\text{1. goal}} + \lambda^2 + \ldots$$

$$= \underbrace{|\tilde{\psi}^{(0)}_{n\alpha_n}\rangle}_{\text{2. goal}} + \lambda |\tilde{\psi}^{(1)}_{n\alpha_n}\rangle + \ldots$$

Derivation: first order

$$\cancel{\hat{H}_0 |\tilde{\psi}^{(0)}_{n\alpha_n}\rangle} + \lambda \hat{V} |\tilde{\psi}^{(0)}_{n\alpha_n}\rangle + \cancel{\hat{H}_0 \lambda |\tilde{\psi}^{(1)}_{n\alpha_n}\rangle} + \ldots$$

$$= \cancel{E^{(0)}_n \underbrace{|\tilde{\psi}^{(0)}_{n\alpha_n}\rangle}} + \lambda E^{(1)}_{n\alpha_n} |\tilde{\psi}^{(0)}_{n\alpha_n}\rangle + \cancel{E^{(0)}_n \lambda |\tilde{\psi}^{(1)}_{n\alpha_n}\rangle} + \ldots \quad \Big| \cdot \langle \psi^{(0)}_{n\gamma_n} |$$

$$\Big| : \lambda$$

$$= \sum_{\beta_n=1}^{d_n} C^{(0)}_{n\alpha_n\beta_n} |\tilde{\psi}^{(0)}_{n\beta_n}\rangle$$

$$\Rightarrow \quad \langle \psi^{(0)}_{n\gamma_n} | \hat{V} | \tilde{\psi}^{(0)}_{n\alpha_n}\rangle = E^{(1)}_{n\alpha_n} \langle \psi^{(0)}_{n\gamma_n} | \tilde{\psi}^{(0)}_{n\alpha_n}\rangle$$

our choice   result

drop n, i.e. we fix ~~the~~ degenerate subspace to be investigated

$$\langle \psi_\gamma^{(0)} | \hat{V} | \underbrace{\tilde{\psi}_\alpha^{(0)} \rangle} = E_\alpha^{(1)} \langle \psi_\gamma^{(0)} | \tilde{\psi}_\alpha \rangle$$

$$= \sum_\beta c_{\alpha\beta}^{(0)} | \psi_\beta^{(0)} \rangle$$

$$\sum_\beta c_{\alpha\beta}^{(0)} \underbrace{\langle \psi_\gamma^{(0)} | \hat{V} | \psi_\beta^{(0)} \rangle}_{= V_{\gamma\beta}} = E_\alpha^{(1)} \sum_\beta c_{\alpha\beta}^{(0)} \underbrace{\langle \psi_\gamma^{(0)} | \psi_\beta^{(0)} \rangle}_{= \delta_{\beta\gamma}}$$

$$\sum_{\beta=1}^{d} c_{\alpha\beta}^{(0)} \left(V_{\gamma\beta} - E_\alpha^{(1)} \delta_{\beta\gamma} \right) = 0$$

fix α: d linear equations for d coefficients $c_{\alpha\beta}^{(0)}$ as γ runs from 1 to d

$$\begin{pmatrix} V_{11} - E_\alpha^{(1)} & V_{12} & \cdots & V_{1d} \\ V_{21} & V_{22} - E_\alpha^{(1)} & \cdots & V_{2d} \\ \vdots & \vdots & \ddots & \vdots \\ V_{d1} & V_{d2} & \cdots & V_{dd} - E_\alpha^{(1)} \end{pmatrix} \begin{pmatrix} c_{\alpha 1}^{(0)} \\ c_{\alpha 2}^{(0)} \\ \vdots \\ c_{\alpha n}^{(0)} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ \vdots \\ 0 \end{pmatrix}$$

$$\det \left(V_{\gamma\beta} - E_\alpha^{(1)} \delta_{\gamma\beta} \right) = 0$$

- condition for non-trivial solution for $E_\alpha^{(1)}$
- polynomial of degree d: d solutions
- It could well be that some $E_\alpha^{(1)}$ still coincide, i.e. $\hat{V}$ lifted in first order

the degeneracy only partially

- It is complicated to go to higher orders in degenerate perturbation theory, in particular if degeneracies are only partially lifted in first order

$\rightarrow$ Blochinzew

Stark Effect for Hydrogen Atom

$$\vec{E}(\vec{x}) = \mathcal{E}\,\vec{e}_z = -\vec{\nabla}\,\Phi(\vec{x}) \qquad \Phi(\vec{x}) = -\mathcal{E} z$$

potential energy: $V(\vec{x}) = \underbrace{q}_{=-e}\,\Phi(\vec{x}) = e\,\mathcal{E}\,z$

atomic electric field strength: $\mathcal{E}_{atom} = \dfrac{e}{4\pi\varepsilon_0 a_B^2} = 5.8\ 10^{11}\ \dfrac{V}{m}$

$\mathcal{E}_{lab} \ll \mathcal{E}_{atom} \Rightarrow$ perturbation theory valid ✓

preparatory work

$$z_{fi} = \int d^3x\ \underline{\psi^{(0)}_{n_f l_f m_f}}(\vec{x})\ \overset{r\cos\vartheta}{\overline{z}}\ \underline{\psi^{(0)}_{n_i l_i m_i}}(\vec{x})$$

final ↗ ↖ initial

selection rules: which matrix elements vanish or do not vanish

$$\psi^{(0)}_{nlm}(r,\vartheta,\varphi) = R_{nl}(r)\,Y_{lm}(\vartheta,\varphi) \Rightarrow z_{fi} = I_r \cdot I_{\vartheta,\varphi}$$

$$I_{\vartheta,\varphi} = \int_0^{\pi} d\vartheta\,\sin\vartheta \int_0^{2\pi} d\varphi\ Y^*_{l_f m_f}(\vartheta,\varphi)\ \boxed{\cos\vartheta}\ \underbrace{Y_{l_i m_i}(\vartheta,\varphi)}$$

$$= N_{l_i m_i}\, P^{(m_i)}_{l_i}(\cos\vartheta)\, e^{i m_i \varphi}$$

recursion formula for associated Legendre polynomials:

$$x P_l^{(m)}(x) = \frac{l+1-m}{2l+1} P_{l+1}^{(m)}(x) + \frac{l+m}{2l+1} P_{l-1}^{(m)}(x)$$

$$I_{f,i} = \int_0^{\pi} d\vartheta \sin\vartheta \int_0^{2\pi} d\varphi \; N_{l_f m_f} P_{l_f}^{(m_f)}(\cos\vartheta)\, e^{-i m_f \varphi} \quad e^{i m_i \varphi}$$

$$\left\{ N_{l_i m_i} \frac{l_i+1-m_i}{2l+1} P_{l_i+1}^{(m_i)}(\cos\vartheta) + \frac{l_i+m_i}{2l+1} P_{l_i-1}^{(m_i)}(\cos\vartheta) \right\}$$

$$= \int d\Omega \quad Y^*_{l_f m_f}(\vartheta,\varphi) \left\{ C_1 Y_{l_i+1\, m_i}(\vartheta,\varphi) + C_2 Y_{l_i-1\, m_i}(\vartheta,\varphi) \right\}$$

$$= \left(\circledast \; \delta_{l_f, l_i+1} + \circledast \; \delta_{l_f, l_i-1} \right) \delta_{m_f, m_i}$$

$\Rightarrow$ selection rules: $\Delta l = l_f - l_i = \pm 1$, $\Delta m = m_f - m_i = 0$

Linear Stark Effect:

first excited states of hydrogen atom:

$$\alpha \in \{ \underbrace{(2,0,0)}_{=(n,l,m)}, (2,1,0), (2,1,1), (2,1,-1) \}$$

$$\quad 1 \qquad\qquad 2 \qquad\qquad 3 \qquad\qquad 4$$

$$V_{\alpha\beta} = \int d^3x \; \psi^*_\alpha(\vec{x})\, e \mathcal{E} z \; \psi_\beta(\vec{x})$$

$$(V_{\alpha\beta}) = \begin{pmatrix} \cancel{V_{200,200}} & \boxed{V_{200,210}} & & \\ \boxed{V_{210,200}} & \cancel{V_{210,210}} & & \\ \cancel{V_{211,200}} & \cancel{V_{211,210}} & \cancel{V_{211,211}} & \\ \cancel{V_{21-1,200}} & \cancel{V_{21-1,210}} & \cancel{V_{21-1,211}} & \cancel{V_{21-1,21-1}} \end{pmatrix}$$

— : forbidden due to selection rules

— : allowed " " "

$$V = V_{200,210} = e\,\mathcal{E} \int d^3x\, \underbrace{\psi_{200}(\vec{x})}_{R_{20}(r)\,\underbrace{Y_{00}(\vartheta,\varphi)}_{=\frac{1}{\sqrt{4\pi}}}}\; z\; \underbrace{\psi_{210}(\vec{x})}_{R_{21}(r)\,\underbrace{Y_{10}(\vartheta,\varphi)}_{=\sqrt{\frac{3}{4\pi}}\cos\vartheta}}$$

$$\cos\vartheta = \frac{z}{r}$$

$$= \frac{\sqrt{3}\, e\mathcal{E}}{4\pi} \int d^3x\, \frac{R_{20}(r) R_{21}(r)}{r}\, z^2$$

symmetry consideration:

$$\int d^3x\, \rho(r)\, z^2 = \frac{1}{3} \int d^3x\, \rho(r) (x^2 + y^2 + z^2) = \frac{1}{3} \int d^3x\, \rho(r)\, r^2$$

$$= \frac{\sqrt{3}\, e\mathcal{E}}{4\pi}\, \frac{1}{3}\, \underbrace{\int d^3 x}_{4\pi \int_0^\infty dr\, r^2}\; r\, R_{20}(r) R_{21}(r)$$

$$R_{21}(r) = \frac{1}{2\sqrt{6}\, a_B^{3/2}}\, \frac{r}{a_B}\, e^{-\frac{r}{2a_B}}$$

$$R_{20}(r) = \frac{1}{2\sqrt{2}\, a_B^{3/2}} \left(2 - \frac{r}{a_B}\right) e^{-\frac{r}{2a_B}}$$

$$\varrho = \frac{r}{a_B}$$

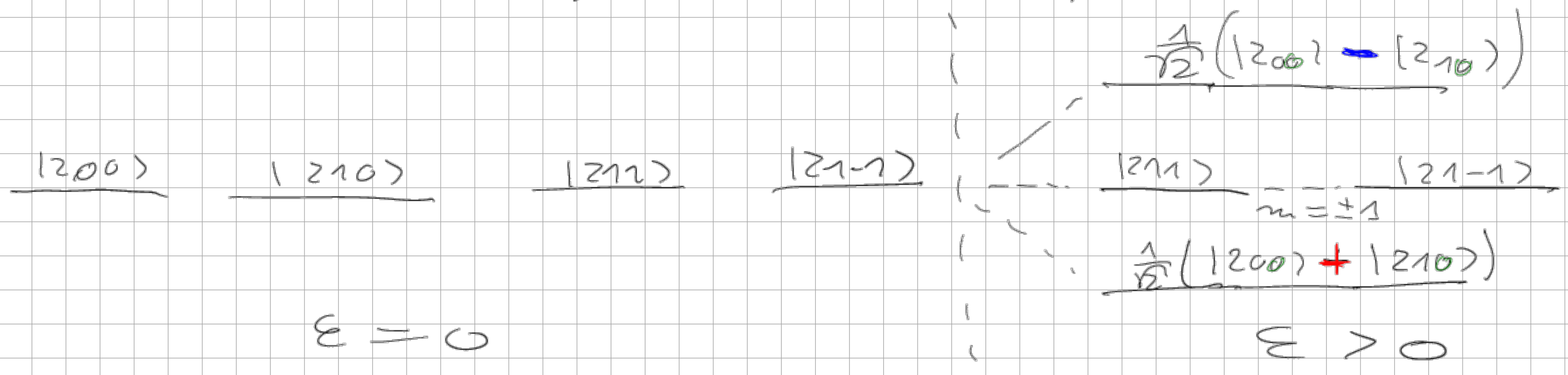
$$= \frac{e\mathcal{E} a_B}{24} \int_0^\infty d\varrho\, (2\varrho^4 - \varrho^5)\, e^{-\varrho}\,; \qquad \int_0^\infty d\varrho\, \varrho^k e^{-\varrho} = k! = \Gamma(k+1)$$

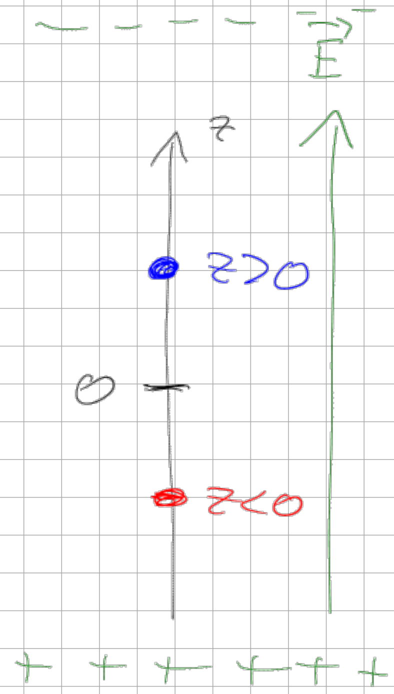
$$\Rightarrow V = -3\, e\, \mathcal{E}\, a_B$$

Eigenvalue problem

$$\begin{pmatrix} -E^{(1)} & -3e\mathcal{E}a_B & 0 & 0\\ -3e\mathcal{E}a_B & -E^{(1)} & 0 & 0 \\ 0 & 0 & -E^{(1)} & 0\\ 0 & 0 & 0 & -E^{(1)}\end{pmatrix}\begin{pmatrix}c_1\\c_2\\c_3\\c_4\end{pmatrix}=\begin{pmatrix}0\\0\\0\\0\end{pmatrix}$$

$$E^{(1)}_{①} = -3e\mathcal{E}a_B < 0, \quad E^{(1)}_{②} = E^{(1)}_{③} = 0, \quad E^{(1)}_{④} = +3e\mathcal{E}a_B > 0$$

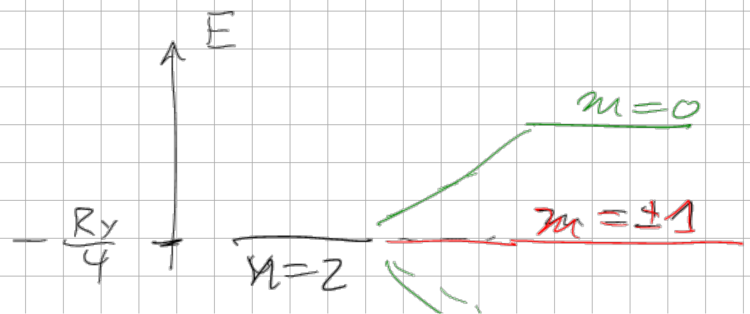




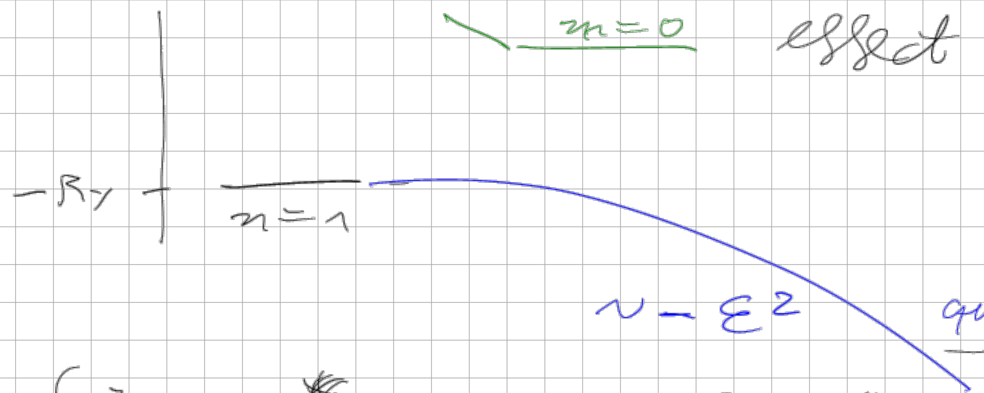
$$①: \begin{pmatrix}1 & -1\\ -1 & 1\end{pmatrix}\begin{pmatrix}c_1\\c_2\end{pmatrix}=\begin{pmatrix}0\\0\end{pmatrix} \Rightarrow c_1 = c_2 = \frac{1}{\sqrt2}$$

$$\frac{1}{\sqrt2}\left(|200\rangle \mp |\psi_{210}\rangle\right) = \frac{1}{8\sqrt{\pi}\,a_B^{3/2}}\left(2-\frac{r}{a_B}\mp\frac{z}{\sqrt3\,a_B}\right)e^{-\frac{r}{a_B}}$$

node: $2-\frac{z}{a_B}\left(1\pm\frac{1}{\sqrt3}\right)=0$



linear Stark } degenerate perturbation theory



} non-degenerate perturbation theory

quadratic Stark effect

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

$\uparrow$ $\Delta l = \pm 1, \ \Delta m = 0$

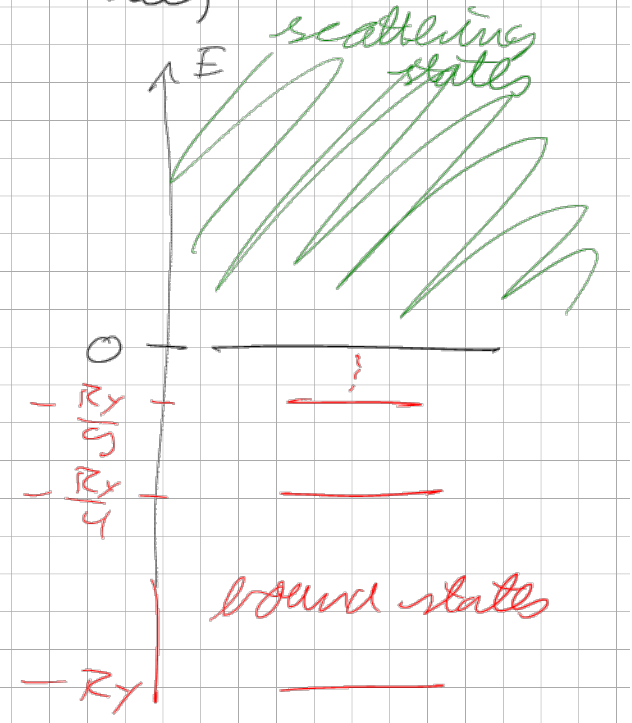
$$E_1^{(2)} \underset{\substack{\uparrow \\ \text{general}}}{=} \sum_{n\neq 1} \frac{|V_{1n}|^2}{E_1^{(0)} - E_n^{(0)}} \underset{\substack{\uparrow \\ \text{hydrogen}}}{=} \sum_{n=2}^{\infty} \sum_{l=0}^{n-1} \sum_{m=-l}^{+l} \frac{|V_{100,nlm}|^2}{E_1^{(0)} - E_n^{(0)}} \underset{\text{selection rules}}{=}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

BUT: This is wrong!

Introduce a more precise relation:

$$E_1^{(2)} = \cancel{\sum}\!\!\!\!\int_{n\neq 1} \frac{|V_{1n}|^2}{E_1^{(0)} - E_n^{(0)}}$$

complicated to evaluate! What shall we do?



Sum rules: circumvents evaluation of summation / integration

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

diagonal expectation values

$W(\vec{x})$ is a solution of

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

2nd partial differential equation for W

Next time:

- derive this
- possible generalisation for higher orders
- apply for quadratic Stark effect