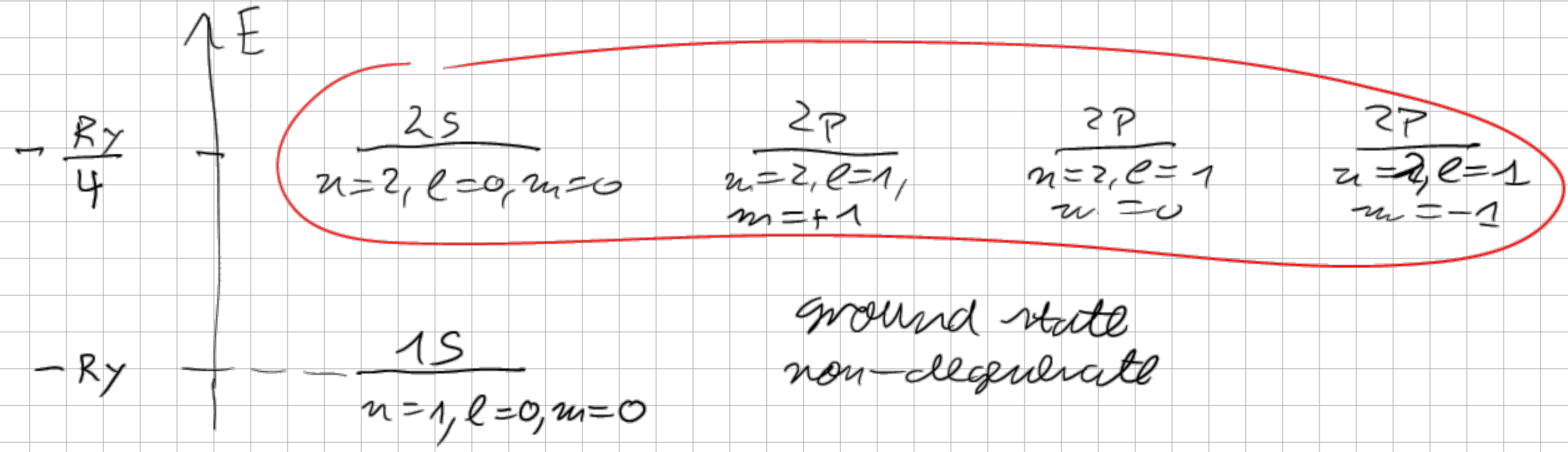
Chapter 3: Time-Independent Degenerate Perturbation Theory

Hydrogen Atom:

$$E_n = -Ry \cdot \frac{1}{n^2}, \quad n = 1, 2, \ldots \quad ; \text{degeneracies with respect to } l, m$$



first excited state is degenerate $d_2 = 4$

ground state non-degenerate

Concrete application for later: apply additional spatial-temporal homogeneous electric field $\vec{E} = \varepsilon \, \vec{e}_z \Rightarrow$ Stark effect

- first excited state: partial lift of degeneracy $\Rightarrow$ linear Stark effect
- ground state: quadratic Stark effect (downwards shift)

3.1 Motivation: see last time

$$\hat{H}_0 |\psi^{(0)}_{n\alpha_n}\rangle = E^{(0)}_n |\psi^{(0)}_{n\alpha_n}\rangle \qquad \alpha_n = 1, \ldots, d_n$$

no α_n dependence

degeneracy index

note

$$\langle \psi^{(0)}_{n\alpha_n} | \psi^{(0)}_{n\beta_n} \rangle = \delta_{\alpha_n, \beta_n}$$

d_n degenerate states $|\psi^{(0)}_{n1}\rangle \ldots |\psi^{(0)}_{nd_n}\rangle$

$$\underbrace{\hat{H}(\lambda)}_{\hat{H}_0+\lambda\hat{V}}|\tilde{\Psi}_{n\alpha_n}(\lambda)\rangle = \underbrace{E_{n\alpha_n}(\lambda)}_{\overset{\lambda\downarrow 0}{=} E_n^{(0)} + \lambda \underbrace{E^{(1)}_{n\alpha_n}} + \dots} \underbrace{|\tilde{\Psi}_{n\alpha_n}(\lambda)\rangle}_{\overset{\lambda\downarrow 0}{=} |\tilde{\Psi}^{(0)}_{n\alpha_n}\rangle + \lambda |\tilde{\Psi}^{(1)}_{n\alpha_n}\rangle + \dots}$$

1. result

$$\boxed{= \sum_{\beta_n=1}^{d_n} \underbrace{C^{(0)}_{n\alpha_n,\beta_n}}\, |\Psi^{(0)}_{n\beta_n}\rangle}$$

2. result

3. λ derivation:

$$\cancel{\hat{H}_0 |\tilde{\Psi}^{(0)}_{n\alpha_n}\rangle} + \lambda \hat{V} |\tilde{\Psi}^{(0)}_{n\alpha_n}\rangle + \cancel{\lambda \hat{H}_0 |\tilde{\Psi}^{(1)}_{n\alpha_n}\rangle} + \dots$$
$$= \cancel{E_n^{(0)} |\tilde{\Psi}^{(0)}_{n\alpha_n}\rangle} + \lambda E^{(1)}_{n\alpha_n} |\tilde{\Psi}^{(0)}_{n\alpha_n}\rangle + \cancel{\lambda E_n^{(0)} |\tilde{\Psi}^{(1)}_{n\alpha_n}\rangle} + \dots \quad \Big| : \lambda \quad \cdot \langle \Psi^{(0)}_{n\gamma_n}|$$

$$\sum_{\beta_n=1}^{d_n} C^{(0)}_{n\alpha_n,\beta_n} \underbrace{\hat{H}_0 |\Psi^{(0)}_{n\beta_n}\rangle}_{= E_n^{(0)} |\Psi^{(0)}_{n\beta_n}\rangle} = E_n^{(0)} |\tilde{\Psi}^{(0)}_{n\alpha_n}\rangle$$

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

drop n as we are in subspace n:

$$\underbrace{\langle \Psi^{(0)}_{\gamma} | \hat{V} | \tilde{\Psi}^{(0)}_{\alpha}\rangle}_{= \sum_\beta C^{(0)}_{\alpha\beta} \underbrace{\langle \Psi^{(0)}_\gamma | \hat{V} | \Psi^{(0)}_\beta \rangle}_{= V_{\gamma\beta}}} = E^{(1)}_\alpha \underbrace{\langle \Psi^{(0)}_\gamma | \tilde{\Psi}^{(0)}_\alpha \rangle}_{= C^{(0)}_{\alpha,\beta}\, \delta_{\beta,\gamma}}$$

$$\Rightarrow \sum_{\beta=1}^{d} C^{(0)}_{\alpha\beta} \left(V_{\gamma\beta} - E^{(1)}_\alpha \delta_{\beta\gamma} \right)$$

fixed α: d linear equations for the d coefficients $c^{(0)}_{\alpha\beta}$ as γ runs from $1,\dots,d$

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

eigenvalues   eigenstates

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

$\Rightarrow$ polynomial of degree d

$$\langle \tilde\psi^{(0)}_{n\alpha_n} | \tilde\psi^{(0)}_{m\beta_m} \rangle = \delta_{nm}\,\delta_{\alpha_n\beta_m}$$

- It could well be that some $E^{(1)}_\alpha$ still coincide
  $\Rightarrow$ degeneracy is only partially lifted

- It is complicated to discuss higher orders in degenerate perturbation theory, in particular until degeneracy is partially lifted
  $\Rightarrow$ Bleddinsen

3.3 Stark Effect of Hydrogen Atom

$$\vec E(\vec x) = \mathcal{E}\,\vec e_z = -\vec\nabla\,\Phi(\vec x) \quad \Rightarrow \quad \Phi(\vec x) = -\mathcal{E}\,z$$

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

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

=> electric field in lab => perturbation theory allowed

Preparatory work: $\boxed{z_{fi} = \int d^3x\, \psi^{(0)}_{n_f l_f m_f}(\vec{x})\, z\, \psi^{(0)}_{n_i l_i m_i}(\vec{x})}$ $r\cos\vartheta$

=> selection rules: which matrix elements vanish or not vanish

Appendix B: selection rules => matrix elements do not vanish provided (1) $\Delta l = l_f - l_i = \underbrace{\pm 1}_{}$, (2) $\Delta m = m_f - m_i = 0$

photon has spin 1

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

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

recurrence relation for associated Legendre polynomials

$$\underbrace{N_{l_i m_i}}_{} = \sqrt{\frac{2l_i+1}{4\pi}\frac{(l_i-m_i)!}{(l_i+m_i)!}}$$

$$\times\; P_l^{(m)}(x) = \frac{l+1-m}{2l+1} P^{(m)}_{l+1}(x) + \frac{l+m}{2l+1} P^{(m)}_{l-1}(x)$$

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

$$\Big\{ \underbrace{\frac{l_i+1-m_i}{2l_i+1} \cdot \frac{N_{l_i m_i}}{N_{l_i+1, m_i}}}_{\sqrt{\frac{l_i+1+m_i}{(2l_i+1)(2l_i+3)(l_i+1-m_i)}}} \cdot N_{l_i+1, m_i} P^{(m_i)}_{l_i+1}(\cos\vartheta) + \Big\}$$

$$= \delta_{m_i, m_f}\, \delta_{\ell_f, \ell_i+1} \sqrt{\frac{\ell_i+1+m_i}{(2\ell_i+1)(2\ell_i+3)(\ell_i+1-m_i)}}$$
$$+ \delta_{m_i, m_f}\, \delta_{\ell_f, \ell_i-1} \sqrt{}$$

→ selection rules

3.3.1 Linear Stark Effect:

(n, ℓ, m)

first excited states of hydrogen atom $\quad \alpha \in \{(2,0,0), (2,1,0), (2,1,1), (2,1,-1)\}$

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

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

$$V = V_{200,210} = e\mathcal{E} \int d^3x\, \underline{\psi_{200}(\vec{x})}\, z\, \underline{\psi_{210}(\vec{x})}$$

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

symmetry reasoning:

$$= \frac{4\pi}{3} \int_0^\infty dr\, r^4 f(r)$$

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

$$V = \frac{\sqrt{3}\, e \mathcal{E}}{4\pi} \frac{4\pi}{3} \int_0^\infty dr\, r^3 \underbrace{R_{20}(r)}\, R_{21}(r)$$

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

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

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

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

Eigenvalue problem:

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

1 = 200
2 = 210
3 = 211
4 = 21−1

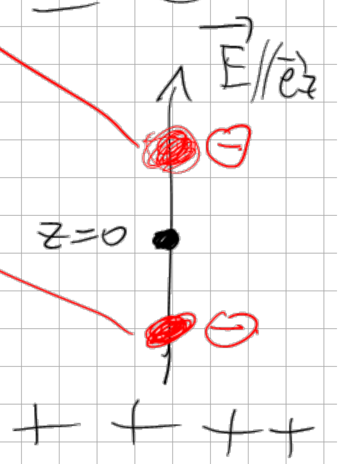
$E^{(1)}_{1} = \underline{-3e\mathcal{E}a_B < 0}$, $E^{(1)}_{2} = E^{(1)}_{3} = 0$, $E^{(1)}_{4} = +3e\mathcal{E}a_B > 0$

$\frac{1}{\sqrt{2}}(\psi_{200} - \psi_{210})$

$|200\rangle$ $|210\rangle$ $|211\rangle$ $|21-1\rangle$

$m = \pm 1$ $|211\rangle, |21-1\rangle$

$\frac{1}{\sqrt{2}}(\psi_{200} + \psi_{210})$



(1) $\begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \Rightarrow$

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