11.11 Fine Structure of Hydrogen Atom

three contributions:

1) kinetic energy:

$$E_{KE} = \underbrace{E_n^{(0)}}_{} \alpha^2 \left\{ \frac{1}{n(l+\frac{1}{2})} - \frac{3}{4n^2} \right\}$$

lifting of degeneracy with respect to n

$$= -\underbrace{Ry}_{} \frac{1}{n^2}$$

$$= \frac{1}{2} mc^2 \alpha^2$$

$$\alpha^2 \approx \frac{1}{(137)^2} \approx 10^{-4}$$

2) spin-orbit coupling:

$$\hat{H}_{SO} = \frac{e^2}{8\pi\varepsilon_0 r^3 m^2 c^2} \cdot \hat{\vec{L}} \cdot \hat{\vec{S}}$$

is treated perturbatively

two basis sets for adding angular momenta: $\vec{J} = \vec{L} + \vec{S}$

A: eigenstates of $\vec{L}^2, \hat{L}_z, \vec{S}^2, \hat{S}_z$: disadvantageous $\rightarrow [\vec{L}\cdot\vec{S}, L_z]_- \neq 0 \neq [\vec{L}\cdot\vec{S}, S_z]_-$

B: eigenstates of $\vec{L}^2, \vec{S}^2, \vec{J}^2, \hat{J}_z$: advantageous $\rightarrow [\vec{L}\cdot\vec{S}, \vec{J}^2]_- = [\vec{L}\cdot\vec{S}, J_z]_- = 0$

In perturbation theory it is advantageous to choose a basis such that the perturbation, i.e. here $\vec{L}\cdot\vec{S}$, is already diagonal.

$$\Rightarrow \quad \mathcal{H}_l \otimes \mathcal{H}_{1/2=s} = \mathcal{H}_{l+\frac{1}{2}} \otimes \mathcal{H}_{l-\frac{1}{2}} \quad , \quad l > 0$$

basis states: $|\underline{n}, \underline{l}, \underline{\tfrac{1}{2}}, \underline{j}, \underline{m}\rangle \;\hat{=}\; R_{nl}(r) \cdot \underbrace{Y_{l\,\frac{1}{2}}^{l\pm\frac{1}{2}, m}(\vartheta, \varphi)}_{\text{spinoral spherical harmonics}}$

$$E_{SO} = \langle n, l, \tfrac{1}{2}, j, m \,|\, \hat{H}_{SO} \,|\, n, l, \tfrac{1}{2}, j, m\rangle$$

$$= \frac{e^2}{8\pi\varepsilon_0 m^2 c^2} \underbrace{\langle l, \tfrac{1}{2}, j, m | \hat{\vec{S}} \cdot \hat{\vec{L}} | l, \tfrac{1}{2}, j, m \rangle}_{①} \cdot \underbrace{\int_0^\infty dr\, r^2 R_{nl}^2(r) \frac{1}{r^3}}_{②}$$

due to $\hat{\vec{J}} = \hat{\vec{L}} + \hat{\vec{S}}$

$$= \langle l, \tfrac{1}{2}, j, m | \tfrac{1}{2}(\hat{\vec{J}}^2 - \hat{\vec{L}}^2 - \hat{\vec{S}}^2) | l, \tfrac{1}{2}, j, m \rangle$$

Case 1: $l = 0 \Rightarrow j = s = 1/2$

$$① = \frac{\hbar^2}{2} \left\{ \tfrac{1}{2}(\tfrac{1}{2}+1) - 0(0+1) - \tfrac{1}{2}(\tfrac{1}{2}+1) \right\} = 0$$

Case 2: $l > 0$

a) $j = l + 1/2$

$$① = \frac{\hbar^2}{2} \left\{ \underbrace{(l+\tfrac{1}{2})(l+\tfrac{1}{2}+1)}_{= l^2 + 2l + \frac{1}{2}} - l(l+1) - \tfrac{1}{2}(\tfrac{1}{2}+1) \right\} = \frac{\hbar^2}{2} l$$

b) $j = l - 1/2$

$$① = \frac{\hbar^2}{2} \left\{ (l-\tfrac{1}{2})(l+\tfrac{1}{2}) - l(l+1) - \tfrac{1}{2}(\tfrac{1}{2}+1) \right\} = -\frac{\hbar^2}{2}(l+1)$$

Evaluation of ② can be restricted to $l > 0$:

trick: Consider $\langle nlm | [\hat{H}_0, \hat{A}]_- | nlm \rangle$ $\hat{A}$: arbitrary

$$= \langle nlm | \hat{H}_0 \hat{A} - \hat{A} \hat{H}_0 | nlm \rangle$$

$$= \frac{\hat{p}_r^2}{2m} + \frac{\hat{\vec{L}}^2}{2mr^2} - \frac{e^2}{4\pi\varepsilon_0 r}$$

$$= \langle n l m | E_n^{(0)} \hat{A} - \hat{A} E_n^{(0)} | n l m \rangle \equiv 0$$

special choice: $\hat{A} = \hat{p}_r = \frac{\hbar}{i} \frac{\partial}{\partial r}$

$$0 = \langle n l m | \left[\cancel{\frac{\hat{p}_r^2}{2m}} + \frac{\hat{L}^2}{2m r^2} - \frac{e^2}{4\pi\varepsilon_0 r} , \hat{p}_r \right]_- | n l m \rangle$$

$$0 = \langle n l m | \left[\frac{\hbar^2 l(l+1)}{2m r^2} - \frac{e^2}{4\pi\varepsilon_0 r}, \frac{\hbar}{i}\frac{\partial}{\partial r} \right]_- | n l m \rangle$$

$$\Rightarrow \langle n l m | \frac{\partial}{\partial r} \left\{ \frac{\hbar^2 l(l+1)}{2m r^2} - \frac{e^2}{4\pi\varepsilon_0 r} \right\} | n l m \rangle = 0$$

$$\Rightarrow \left\langle \frac{1}{r^3} \right\rangle_{nl} = \frac{e^2 m}{4\pi\varepsilon_0 \hbar^2 l(l+1)} \left\langle \frac{1}{r^2} \right\rangle_{nl} \quad ; \quad l > 0$$

Problem 4 b): $\left\langle \frac{1}{r^2} \right\rangle_{nl} = \frac{8 E_n^{(0)2}}{\hbar^2 c^2 \alpha^2} \frac{n}{2l+1}$, $\alpha = \frac{e^2}{4\pi\varepsilon_0 \hbar c}$, $E_n^{(0)} = -\frac{1}{2} m c^2 \frac{\alpha^2}{n^2}$

$$\Rightarrow \left\langle \frac{1}{r^3} \right\rangle_{nl} = - \frac{2 e^2 m^2 E_n^{(0)}}{4\pi\varepsilon_0 \hbar^2} \frac{1}{n l (l+1)(l+\frac{1}{2})} = 2$$

Result for spin-orbit coupling:

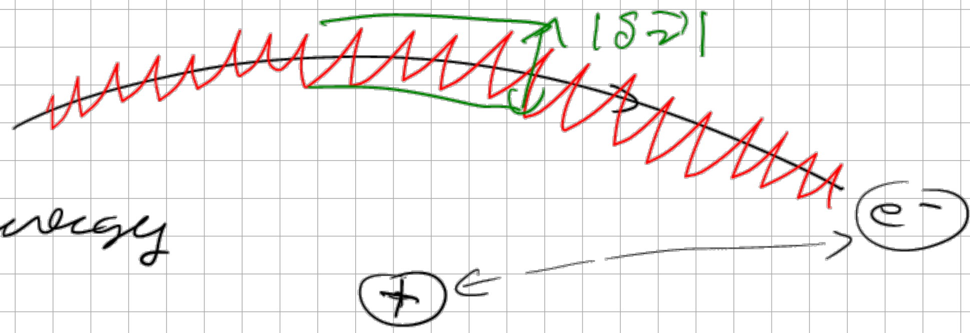
$$E_{SO} = \begin{cases} 0 & ; l = 0 \\ - E_n^{(0)} \frac{\alpha^2}{2n} \frac{1}{(l+\frac{1}{2})(l+1)} & ; j = l + \frac{1}{2} \\ + E_n^{(0)} \frac{\alpha^2}{2n} \frac{1}{l(l+\frac{1}{2})} & ; j = l - \frac{1}{2} \end{cases} \quad \Bigg\} \; l > 0$$

11.11.3 Darwin term:

This is an energy correction only affecting s-states. Physically it originates

from the fact that electron is not localised but fluctuates ("Zitterbewegung")
with the Compton wave length

$$|\delta \vec{r}| = \frac{\hbar}{mc} = \frac{\lambda_c}{2\pi}$$



This leads to a fluctuation of potential energy

$$V(\vec{r}) = -\frac{e^2}{4\pi\varepsilon_0 |\vec{r}|}$$

$$\underbrace{V(\vec{r}}_{\text{average coordinate}} + \underbrace{\vec{s}}_{\text{fluctuation ("Zitterbewegung")}}) = V(\vec{r}) + \sum_{i=1}^{3} \frac{\partial V(\vec{r})}{\partial r_i} s_i + \frac{1}{2} \sum_{i,j=1}^{3} \frac{\partial^2 V(\vec{r})}{\partial r_i \partial r_j} s_i s_j + \ldots$$

apply now average $\langle \cdot \rangle$

$$\langle V(\vec{r}+\vec{s})\rangle = V(\vec{r}) \underbrace{\langle 1 \rangle}_{=1} + \sum_{i=1}^{3} \frac{\partial V(\vec{r})}{\partial r_i} \underbrace{\langle s_i \rangle}_{=0} + \frac{1}{2} \sum_{i,j=1}^{3} \frac{\partial^2 V(\vec{r})}{\partial r_i \partial r_j} \underbrace{\langle s_i s_j \rangle}_{= \frac{1}{3}\langle \vec{s}^2\rangle \delta_{ij}} + \ldots$$

isotropy

$$\delta V(\vec{r}) := \langle V(\vec{r}+\vec{s})\rangle - V(\vec{r}) = \frac{1}{6} \underbrace{\Delta V(\vec{r})}_{= -\frac{e^2}{4\pi\varepsilon_0} \underbrace{\Delta \frac{1}{r}}_{-\frac{1}{4\pi}\delta(\vec{r})}} \underbrace{\langle \vec{s}^2 \rangle}_{= \left(\frac{\hbar}{mc}\right)^2} + \ldots$$

$$\delta V(\vec{r}) = + \frac{e^2 \hbar^2}{6 \varepsilon_0 m^2 c^2} \underbrace{\delta(\vec{r})}_{\text{affects only s-states}}$$

Darwin term due to Dirac theory: $\delta V_D(\vec{r}) = \dfrac{e^2 \hbar^2}{8 \varepsilon_0 m^2 c^2} \delta(\vec{r})$

$$E_D = \frac{e^2 \hbar^2}{8 \varepsilon_0 M^2 c^2} \underbrace{\langle \delta(\vec{r}) \rangle_{nl}}_{= |\psi^{(0)}_{nl}(\vec{0})|^2 = \frac{1}{\pi a_B^3 n}} \qquad a_B = \frac{4\pi \varepsilon_0 \hbar^2}{m e^2}$$

$$\Rightarrow \quad E_D = -\frac{\alpha^2}{n} E_n^{(0)}$$

11.11.4 Combining All Corrections:

$$E_{FS} = E_{KE} + E_{SO} + E_D$$

1. Case: $l = 0 \Rightarrow j = 1/2$

SO coupling

$$E_{FS} = \frac{E_n^{(0)} \alpha^2}{n} \left\{ \frac{1}{1/2} - \frac{3}{4n} \right\} + 0 - \frac{\alpha^2}{n} E_n^{(0)} = \frac{E_n^{(0)} \alpha^2}{n} \left\{ 1 - \frac{3}{4n} \right\}$$

$$= \frac{E_n^{(0)} \alpha^2}{n} \left\{ \frac{1}{j + \frac{1}{2}} - \frac{3}{4n} \right\} \Bigg|_{j = \frac{1}{2}}$$

2. Case: $l \geq 1$

a) $j = l + 1/2$

$$E_{FS} = \frac{E_n^{(0)} \alpha^2}{n} \left\{ \frac{1}{l + \frac{1}{2}} - \frac{3}{4n} \right\} - \frac{E_n^{(0)} \alpha^2}{2n} \frac{1}{(l+\frac{1}{2})(l+1)} + 0$$

$$= \frac{E_n^{(0)} \alpha^2}{n} \left\{ \frac{1}{l+1} - \frac{3}{4n} \right\} = \frac{E_n^{(0)} \alpha^2}{n} \left\{ \frac{1}{j + \frac{1}{2}} - \frac{3}{4n} \right\} \Bigg|_{j = l + 1/2}$$

Darwin

b) $j = l - 1/2$:

$$E_{FS} = \frac{E_n^{(0)} \alpha^2}{n} \left\{ \frac{1}{l + \frac{1}{2}} - \frac{3}{4n} \right\} + \frac{E_n^{(0)} \alpha^2}{2n} \frac{1}{l(l+\frac{1}{2})} + 0$$

$$= \frac{E_n^{(0)} \alpha^2}{n} \left\{ \frac{1}{l} - \frac{3}{4n} \right\} = \frac{E_n^{(0)} \alpha^2}{n} \left\{ \frac{1}{j + 1/2} - \frac{3}{4n} \right\} \Bigg|_{j = l - 1/2}$$

All 3 contributions together yield: $E_{FS} = \frac{E_n^{(0)}\alpha^2}{n}\left\{\frac{1}{j+1/2} - \frac{3}{4n}\right\}$

Comparison with Dirac theory:

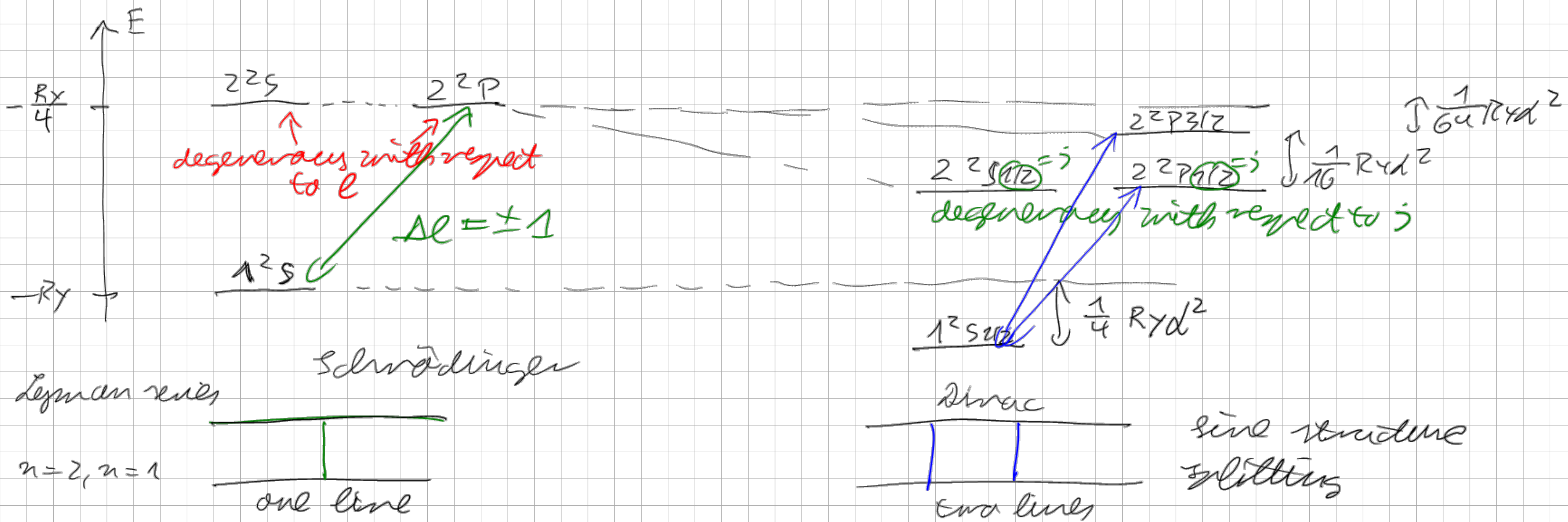
$$E_{nj} = mc^2\sqrt{1 - \frac{\alpha^2}{n^2 + 2\left(n - j - \frac{1}{2}\right)\left[(j+\frac{1}{2})^2 - \alpha^2\right] - j - \frac{1}{2}}}$$

Taylor expansion in α^2:

$$E_{nj} = \underbrace{mc^2}_{\text{rest energy}} - \frac{1}{2}\underbrace{mc^2\alpha^2}_{=Ry}\frac{1}{n^2} - \underbrace{\frac{Ry\,\alpha^2}{n^4}\left\{\frac{n}{j+1/2} - \frac{3}{4}\right\}}_{\text{Sommerfeld, Dirac}} + \dots$$

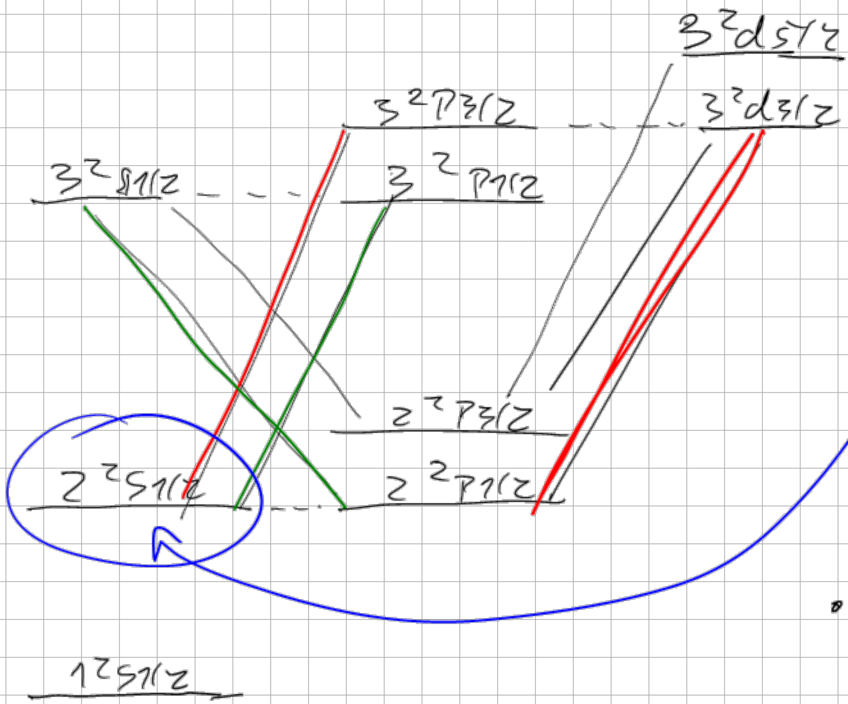
Bohr
Schrödinger

11.11.5 Discussion:



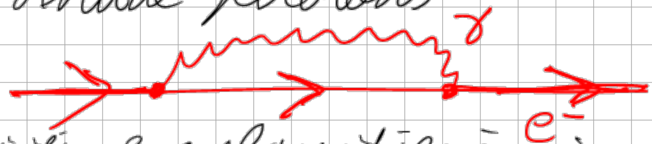
- first observed 1887 by Michelson
- precise measurements in 1925 by Hansen

Balmer series ($n = 3$, $n = 2$): H_α-line



- H_α-line splits into 5 lines due to degeneracies (—, —)
- Lamb shift: QFT effect, affects s-states $\Rightarrow$ 7 lines

- vacuum fluctuations: electron interacts with virtual photons



- heuristic explanation is similar to Darwin term

$$E_L = \frac{e^2}{6\varepsilon_0} |\psi_{nlm}(\vec{0})|^2 \underbrace{\langle \vec{s}^2 \rangle}$$

due to interaction with virtual photons

11.12 Magnetic Field

Now: interaction of electron with external homogeneous magnetic field

Interaction of charge $q = -e$ with static magnetic field $\vec{B}(\vec{x}) = \text{rot}\ \vec{A}(\vec{x})$ is described by minimal coupling

substitution rule: $\hat{\vec{p}} \Rightarrow \hat{\vec{p}} - q\vec{A}(\vec{x}) = \frac{\hbar}{i}\vec{\nabla} + e\vec{A}(\vec{x})$ (SI units)