Fine structure of hydrogen

$$\Delta E_{FS} = E_{kin} + E_{SO} + E_D$$

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

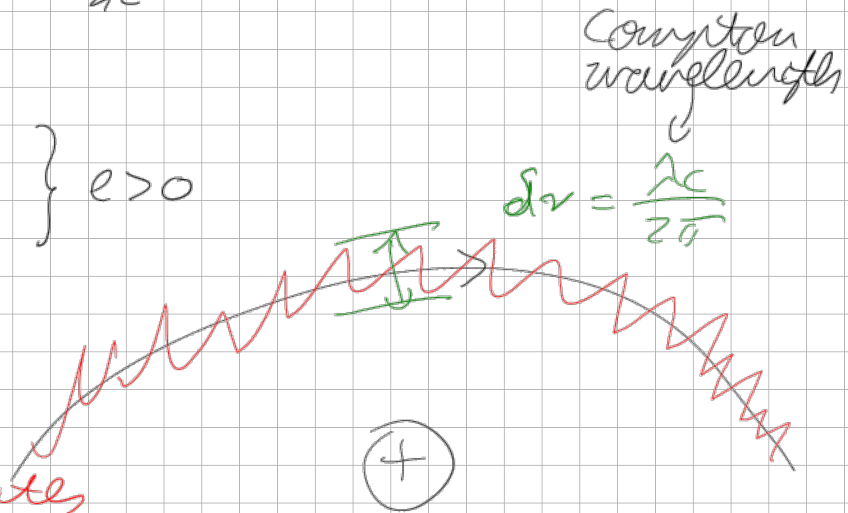
$$E_{SO} = \begin{cases} 0 & ; \; l = 0 \\ -E_n^{(0)} \frac{\alpha^2}{2n} \frac{1}{(l+\frac{1}{2})(l+1)} & ; \; j = l + \frac{1}{2} \\ +E_n^{(0)} \frac{\alpha^2}{2n} \frac{1}{l(l+\frac{1}{2})} & ; \; j = l - \frac{1}{2} \end{cases} \Bigg\} \; l > 0$$

heuristic derivation of Darwin

$$\delta V_D(\vec{r}) = +\frac{e^2 \hbar^2}{8 \varepsilon_0 m^2 c^2} \delta(\vec{r})$$

repulsive (instead of 6)

affects only s-states



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

$$= -\frac{\alpha^2}{n} E_n^{(0)} > 0$$

Combine all 3 corrections:

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

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

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

2. case: $\ell > 0$

a) $j = \ell + 1/2$

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

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

b) $j = \ell - 1/2$

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

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

Summing all 3 terms gives one formula:

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

Comparison with Dirac theory:

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

Taylor expansion in α^2

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

Bohr, Schrödinger

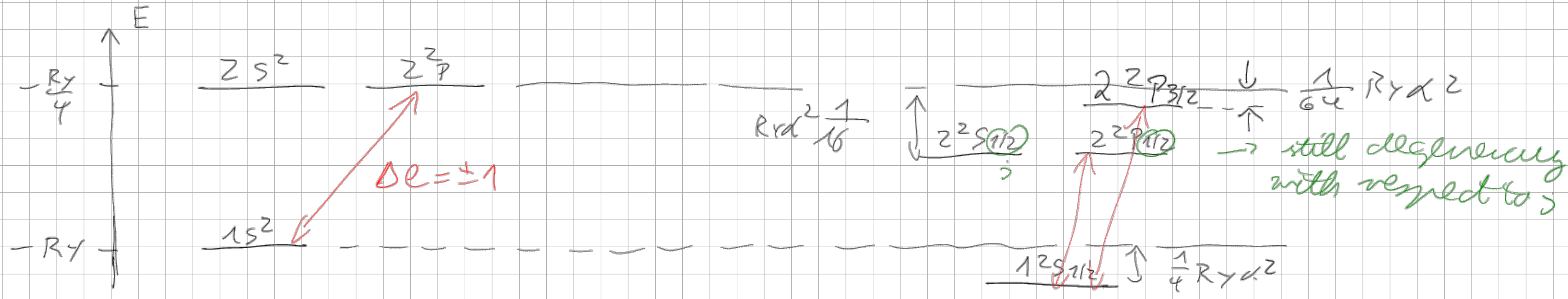
Sommerfeld, Dirac

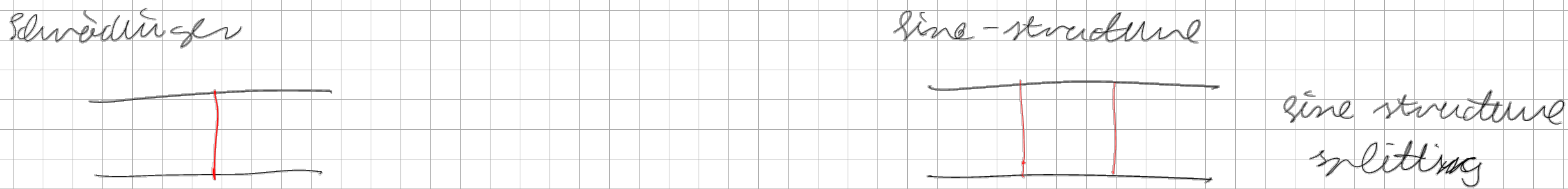
$M(v) = \frac{M}{\sqrt{1-\frac{v^2}{c^2}}}$

diving trajectories ("Tauchbahnen")

Discussion:

1) Lyman series: $n = 2 \leftrightarrow n = 1$

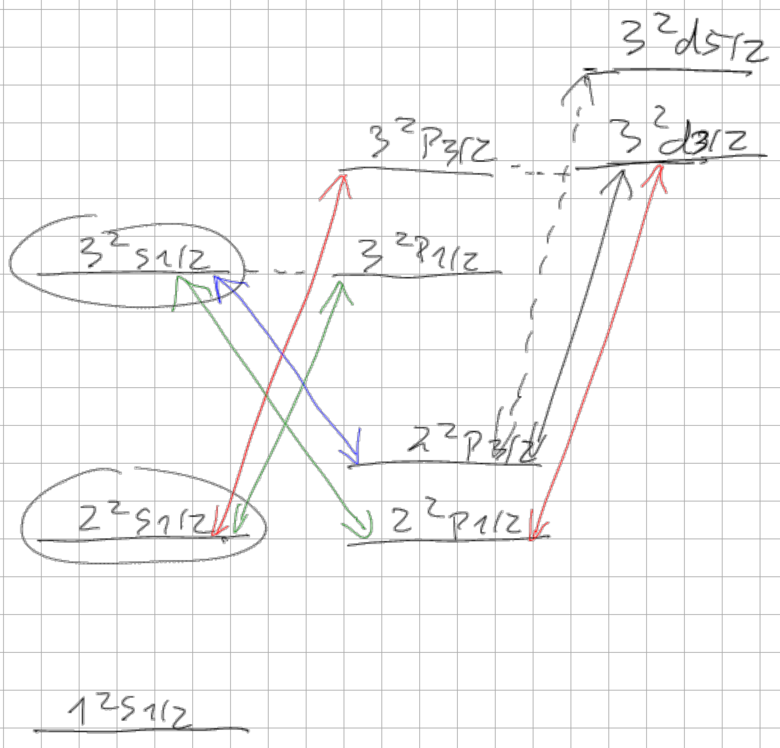




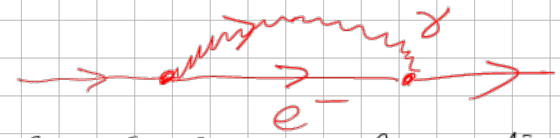
- first observed 1887 by Michelson
- precise measurements in 1925 by Hansen

2) Balmer series: $n = 3 \leftrightarrow n = 2 \Rightarrow H\alpha$-line

- $H\alpha$-line (in Schrödinger) splits into 5 lines (with transitions —, — having the same frequency)
- In experiments you see 7 lines: —, — degenerate frequencies are splitted due to a QFT effect ⇒ Lamb shift



- vacuum fluctuations: electron interacts with virtual photons



- heuristic explanation similar to Darwin term

$$E_{LS} = \underbrace{+}_{>0} \frac{e^2}{6\varepsilon_0} |\psi_{nem}(\vec{0})|^2 \langle \vec{s}^2 \rangle$$

$\Rightarrow$ quantum optics lecture notes

11.12 Hydrogen in magnetic field

Zeeman effect (weak B) $\longleftrightarrow$ Paschen-Back effect (strong B)

11.12.1 Minimal coupling:

Interaction of charge $q = -e$ with a magnetic field $\vec{B}(\vec{x}) = \text{rot}\,\vec{A}(\vec{x})$ follows from minimal coupling:

$$\hat{\vec{p}} \longrightarrow \hat{\vec{p}} - q\vec{A}(\vec{x}) = \frac{\hbar}{i}\vec{\nabla} + e\vec{A}$$

kinetic energy:

$$\hat H_{kin} = \frac{\hat{\vec p}^2}{2m} \Rightarrow \frac{1}{2m}\left[\frac{\hbar}{i}\vec\nabla + e\vec A(\vec x)\right]^2$$

$$= -\frac{\hbar^2}{2m}\Delta + \frac{e}{2m}\left\{\frac{\hbar}{i}\vec\nabla \vec A + \vec A(\vec x)\frac{\hbar}{i}\vec\nabla\right\} + \frac{e^2}{2m}\vec A^2(\vec x)$$

wave function

$$= -\frac{\hbar^2}{2m}\Delta + \frac{e}{m}\left\{\boxed{\vec A \frac{\hbar}{i}\vec\nabla} + \frac{\hbar}{2i}\cancel{\operatorname{div}\vec A}\right\} + \frac{e^2}{2m}\vec A^2$$

homogeneous magnetic field: $\vec A(\vec x) = \frac{1}{2}\vec B \times \vec x$, $\operatorname{rot}\vec A(\vec x) = \underbrace{\vec B}_{\text{konst.}}$

$$\vec B(\vec x) = B\,\vec e_z \Rightarrow \vec A(\vec x) = \frac{B}{2}\begin{pmatrix}-y\\ x\\ 0\end{pmatrix} \text{ with } \operatorname{div}\vec A(\vec x) = 0$$

$$\hat H_{kin} = -\frac{\hbar^2}{2m}\Delta + \underbrace{\frac{e}{2m}\underbrace{B}_{\text{linear in } B}\underbrace{\left(x\frac{\hbar}{i}\frac{\partial}{\partial y} - y\frac{\hbar}{i}\frac{\partial}{\partial x}\right)}_{=\hat L_z}}_{\text{linear Zeeman effect}} + \underbrace{\frac{e^2}{2m}(x^2+y^2)\underbrace{B^2}_{\text{quadratic in } B}}_{\text{quadratic Zeeman effect}}$$

neglect this here

linear energy shift is due ~~to~~ orbital angular momentum

$$\hat H_B = \frac{eB}{2m}\hat L_z = \underbrace{\frac{e\hbar}{2m}}_{\text{Bohr magneton} = \mu_B}\underbrace{g_e}_{=1}\vec B\cdot\frac{\hat{\vec L}}{\hbar}$$

← Landé factor

We expect a similar shift due to spin angular momentum:

$$\hat H_B = \frac{e\hbar}{2m}\underbrace{g_S}_{=2}\vec B\,\frac{\vec S}{\hbar}$$

Total energy shift: $\hat H_B = \frac{eB}{2m}\left(\hat L_z + 2\hat S_z\right)$

Total Hamiltonian: $\hat H = \hat H_0 + \left(\hat H_{kin} + \underbrace{\hat H_{SO}}_{\sim \vec L\cdot\vec S} + \hat H_D\right) + \hat H_B$

$E_{SO} \gg E_B$

weak B

Zeeman

$E_{SO} \ll E_B$

strong B

Paschen-Back

Linear Zeeman Effect

B-term can be treated perturbatively

unperturbed $\hat{H}_{SO}$ is diagonal with respect to $|j, m_j\rangle$

$$E_B = \langle j, m_j | \hat{H}_B | j, m_j\rangle = \frac{eB}{2\hbar}\langle j, m_j | \underbrace{\hat{L}_z + 2\hat{S}_z}_{\underbrace{\hat{L}_z + \hat{S}_z}_{=\hat{J}_z} + \hat{S}_z} | j, m_j\rangle$$

$$= \frac{eB\hbar}{2\hbar}\left\{ m_j + \langle j, m_j | \boxed{\frac{\hat{S}_z}{\hbar}} | j, m_j\rangle \right\}$$

Recall spinorial spherical harmonics:

$$|j = \ell \pm \tfrac{1}{2}, m_j\rangle = \pm\sqrt{\frac{\ell \pm m_j + 1/2}{2\ell+1}}\,|m_\ell = m_j - \tfrac{1}{2}, \boxed{m_s = +\tfrac{1}{2}}\rangle$$

$$+\sqrt{\frac{\ell \mp m_j + 1/2}{2\ell+1}}\,|m_\ell = m_j + \tfrac{1}{2}, \boxed{m_s = -\tfrac{1}{2}}\rangle$$

$$\langle j, m_j | \frac{\hat{S}_z}{\hbar} | j, m_j\rangle = \frac{1}{2}\cdot\frac{\ell \pm m_j + 1/2}{2\ell+1} + \left(-\frac{1}{2}\right)\cdot\frac{\ell \mp m_j + 1/2}{2\ell+1}$$

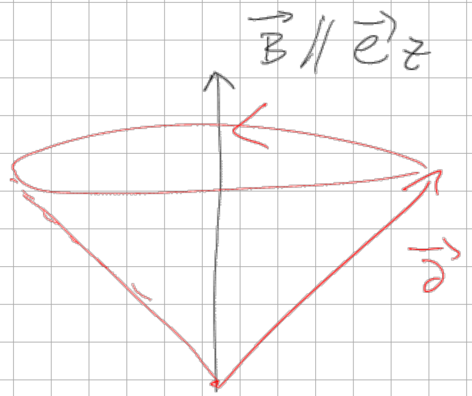
$$= \pm\frac{m_j \hbar}{2\ell+1}$$

$$E_B = \frac{e\hbar}{2M} B m_j \left\{ 1 \pm \frac{1}{2\ell+1} \right\} = \underbrace{\frac{e\hbar}{2M}}_{\mu_B} \underbrace{g_j}_{} B m_j$$

Landé factor of total angular momentum

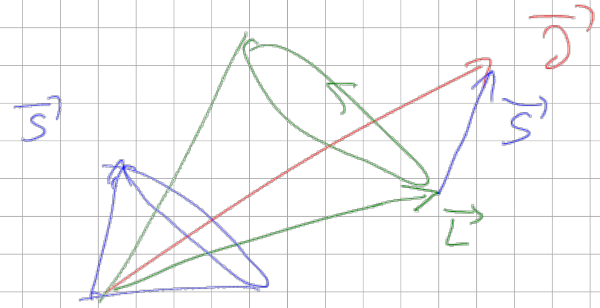
$$\Rightarrow g_j = 1 \pm \frac{1}{2\ell+1}$$

This result also follows from semiclassical vector model (based on Wigner-Eckart theorem)



slow precession due to weak magnetic field

?



fast precession due to strong SO coupling

Due to fast precession of $\vec{L}$ and $\vec{S}$ around $\vec{J}$ only their temporal averages are physically relevant in direction of $\vec{J}$

$$\langle \vec{S} \rangle = \left(\frac{\vec{S}\cdot\vec{J}}{|\vec{J}|} \right) \frac{\vec{J}}{|\vec{J}|}, \quad \langle \vec{L} \rangle = \left(\frac{\vec{L}\cdot\vec{J}}{|\vec{J}|} \right) \frac{\vec{J}}{|\vec{J}|}$$