Summary:

orbital angular momentum

$$\hat{\vec{L}}^2 |l, m_l\rangle = \hbar^2 l(l+1) |l, m_l\rangle$$

$$\hat{L}_z |l, m_l\rangle = \hbar m_l |l, m\rangle$$

$$|l, \underbrace{m_l}_{-l, \dots, +l}\rangle \hat{=} Y_l^{m_l}(\vartheta, \varphi)$$

spherical harmonics

spin angular momentum

$$\hat{\vec{S}}^2 |s, m_s\rangle = \hbar \underbrace{s}_{=1/2}(s+1) |s, m_s\rangle$$

$$\hat{S}_z |s, \underbrace{m_s}_{=\pm 1/2}\rangle = \hbar m_s |s, m_s\rangle$$

$$|\tfrac{1}{2}, \tfrac{1}{2}\rangle \hat{=} \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad |\tfrac{1}{2}, -\tfrac{1}{2}\rangle \hat{=} \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

total angular momentum $\hat{\vec{J}} = \hat{\vec{L}} + \hat{\vec{S}}$

$$\hat{\vec{J}}^2 |j, m_j\rangle = \hbar^2 j(j+1) |j, m\rangle$$

$$\hat{J}_z |\underbrace{j}_{=l \pm \frac{1}{2}}, \underbrace{m_j}_{-j, \dots, +j}\rangle = \hbar m_j |j, m\rangle$$

$$|j, m_j\rangle \hat{=} |Y_{l, \frac{1}{2}}^{l \pm \frac{1}{2}, m_j}\rangle$$

spinorial spherical harmonics

$$= \pm\sqrt{\frac{l \pm m_j + 1/2}{2l+1}} \, |\underbrace{m_j - \tfrac{1}{2}}_{=m_l}, \underbrace{\tfrac{1}{2}}_{=m_s}\rangle + \sqrt{\frac{l \mp m_j + 1/2}{2l+1}} \, |\underbrace{m_j + \tfrac{1}{2}}_{=m_l}, \underbrace{-\tfrac{1}{2}}_{m_s}\rangle$$

Applications:

1) Now: fine structure of hydrogen
2) Tomorrow: hydrogen in magnetic field (Zeeman or Paschen-Back effect)

11.11 Fine Structure of Hydrogen

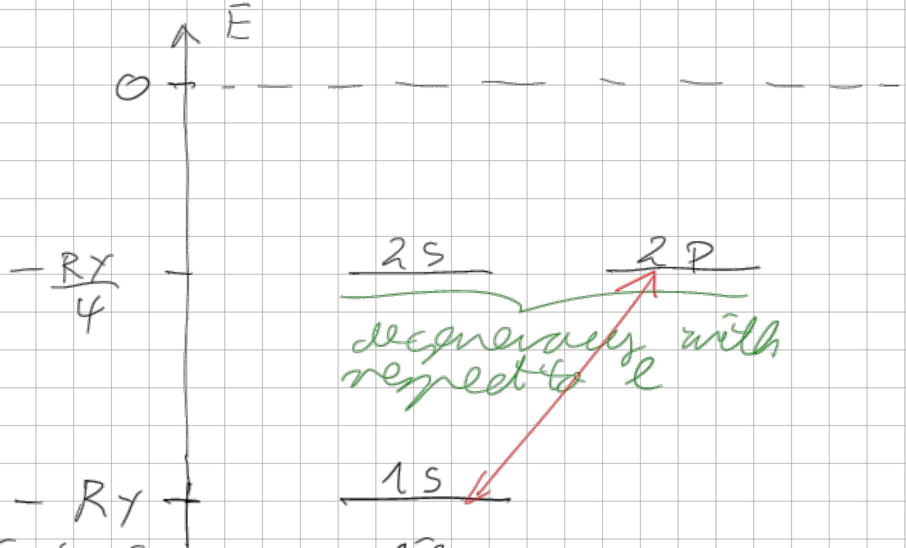
lecture QM I: deals with hydrogen

$$\hat{H}_0 = \frac{\vec{p}^2}{2m} - \frac{e^2}{4\pi\varepsilon_0 r}$$

$$E_n^{(0)} = -Ry\,\frac{1}{n^2}\,; \quad n = 1, 2, \ldots$$

$$Ry = \frac{1}{2}\underbrace{mc^2}_{0.5\,MeV}\alpha^2 = 13.6\,eV$$

Sommerfeld fine structure $\alpha \simeq 1/137$



Now: fine structure $\hat{=}$ special relativistic corrections of Schrödinger description

There are 3 types of special relativistic corrections which sum up to the total fine structure correction, determined by Dirac theory

11.11.1 Correction of Kinetic Energy: see problem 5 on sheet 2

$$T = \sqrt{\vec{p}^2c^2 + m^2c^4} \underset{|\vec{p}|c/mc^2 \ll 1}{=} mc^2\sqrt{1+\left(\frac{|\vec{p}|c}{mc^2}\right)^2} \simeq mc^2\left\{1 + \frac{1}{2}\frac{\vec{p}^2c^2}{m^2c^4} + \frac{1}{2}\frac{+1}{2}\frac{-3}{2}\frac{\vec{p}^4c^4}{m^4c^8} + \ldots\right\}$$

$$= \underbrace{mc^2}_{\text{rest energy}} + \underbrace{\frac{\vec{p}^2}{2m}}_{\text{classical kinetic energy}} \underbrace{\boxed{-\frac{\vec{p}^4}{8m^3c^2}}}_{\text{relativistic correction}} + \ldots$$

taken into account perturbatively

as an application of Feynman–Hellman theorem

$$\Delta E_{\text{kin. energy}} = E_n^{(0)} \cdot \alpha^2 \cdot \left\{ \frac{1}{n(\underbrace{l}+\frac{1}{2})} - \frac{3}{4n^2} \right\}$$

lifts degeneracy of $E_n^{(0)}$ with respect to l

but there are other corrections

11.11.2 Spin-orbit coupling:

According to Dirac theory the electron spin leads to magnetic moment

$$\left.\begin{aligned} \vec{\mu} &= - \underbrace{\mu_B}\ \underbrace{g_S}_{=2}\ \frac{\vec{S}}{\hbar} \\ &\text{Bohr magneton} \\ \mu_B &= \frac{e\hbar}{2M} \end{aligned}\right\} \quad \vec{\mu} = -\frac{e}{M}\vec{S} \quad (*)$$

- electron at rest: $\vec{E} = -\vec{\nabla}\varphi, \quad \varphi = -\frac{e}{4\pi\varepsilon_0 r}$
- lab frame: electron is moving with $\vec{v} = \frac{\vec{p}}{m}$ sees in addition a magnetic field

$$(**) \quad \vec{B} = \underbrace{\boxed{\frac{1}{2}}}\frac{\vec{v}}{c^2} \times \vec{E} \qquad \left(\frac{|\vec{v}|}{c} \ll 1\right) \quad (\text{Lorentz transformation})$$

Thomas precession: comes from connecting the Lorentz transformation to a rotation

- energy correction:

$$-\vec{\mu}\cdot\vec{B} \overset{(*)}{=} \frac{e}{m}\vec{S}\cdot\vec{B} \overset{(**)}{=} \frac{e}{2mc^2}\vec{S}\cdot(\underbrace{\vec{v}}_{=\vec{p}/m} \times \overbrace{\vec{E}}^{=-\vec{\nabla}\varphi}) = -\frac{e}{2m^2c^2}\vec{S}\cdot(\vec{p}\times\underbrace{\vec{\nabla}}_{\sim\vec{x}}\varphi)$$

with $\vec{\nabla}\varphi = \underbrace{\vec{e}_r}_{=\frac{\vec{x}}{r}}\frac{\partial}{\partial r}\varphi$ acting on isotropic potential

$$= \frac{e}{2m^2c^2} \frac{1}{r}\frac{\partial \varphi}{\partial r} \underbrace{(\vec{x} \times \vec{p})}_{=\vec{L}} \cdot \vec{S} = \underbrace{\frac{e^2}{8\pi\varepsilon_0 \cancel{r} 3 m^2 c^2}}_{\text{energy scale}} \underbrace{\vec{L}\cdot\vec{S}}_{\text{spin-orbit coupling}} = \hat{H}_{SO}$$

treat this perturbatively

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

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

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

It is advantageous in perturbation theory such a basis where the perturbation is already diagonal

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

③ basis states: $|n, l, \underbrace{\tfrac{1}{2}}_{=s}, j, m_j\rangle \hat{=} R_{nl}(r) \cdot \underbrace{Y_{l,\frac{1}{2}}^{l\pm\frac{1}{2}, m_j}(\vartheta, \varphi)}_{\text{spinorial spherical harmonics}}$

("two-component vector with spherical harmonics")

first-order perturbation theory

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

$$\frac{1}{2}\left(\hat{\vec{J}}^2 - \hat{\vec{L}}^2 - \hat{\vec{S}}^2\right)$$

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

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

evaluate ①:

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

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

Case 2: $\ell > 0$

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

$① = \frac{\hbar^2}{2}\left\{ \left(\ell+\frac{1}{2}\right)\left(\ell+\frac{3}{2}\right) - \ell(\ell+1) - \frac{1}{2}\frac{3}{2} \right\} = \frac{\hbar^2}{2}\ell$

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

$① = \ldots = -\frac{\hbar^2}{2}(\ell+1)$

Evaluation of ㉙: $\ell > 0$

trick: consider $\langle n\,\ell\,m | \underbrace{[\hat{H}_0, \hat{A}]_-}_{= \hat{H}_0\hat{A} - \hat{A}\hat{H}_0} | n,\ell,m\rangle$, $\hat{A}$ arbitrary

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

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

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

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

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

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

Problem 4.6): $\left\langle \frac{1}{r^2} \right\rangle_{nl} = \frac{8\, {E_n^{(0)}}^2}{\hbar^2 c^2 \alpha^2} \frac{n}{2l+1}$, $\alpha = \frac{e^2}{4\pi\varepsilon_0 \hbar c}$, $E_n^{(0)} = -\frac{1}{2} mc^2 \frac{\alpha^2}{n^2}$

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

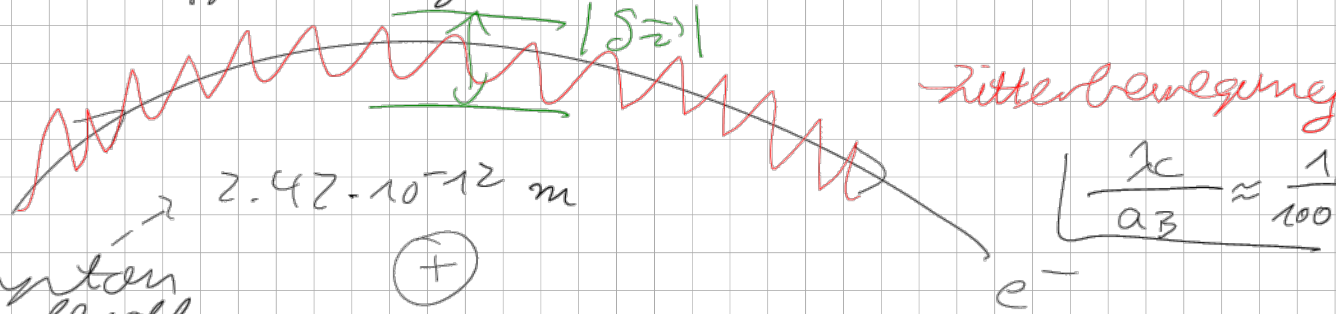
Result for spin-orbit coupling:

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

11.11.3 Darwin term:

This special relativistic correction affects only s-states

Physical origin: electron is not localized but fluctuates ("Zitterbewegung")



$\boxed{\frac{\lambda_C}{a_B} \approx \frac{1}{100}}$ $1/137$

$$|\delta \vec{r}| = \underbrace{\frac{\hbar}{mc}} = \frac{\lambda_C}{2\pi} \leftarrow \text{Compton wave length}$$

quantum mechanics (Heisenberg uncertainty relation)

+ largest momentum thinkable in special relativity

This leads to a fluctuating potential energy

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

$$V(\vec{r}+\vec{s}) \overset{\text{Taylor}}{=} V(\vec{r}) + \sum_{i=1}^{3} \frac{\partial V(\vec{r})}{\partial r_i} s_i + \frac{1}{2} \sum_{i,j=1}^{3} \frac{\partial^2 V(\vec{r})}{\partial r_i \partial r_j} s_i s_j + \dots$$

fixed fluctuation

apply average over fluctuations: $\langle \cdot \rangle$

$$\langle V(\vec{r}+\vec{s})\rangle = V(\vec{r})\underbrace{\langle 1\rangle}_{=1} + \sum_{i=1}^{3} \frac{\partial V(\vec{r})}{\partial r_i}\underbrace{\langle s_i\rangle}_{=0} + \frac{1}{2}\sum_{i=1}^{3}\sum_{j=1}^{3} \frac{\partial^2 V(\vec{r})}{\partial r_i \partial r_j}\underbrace{\langle s_i s_j\rangle}_{= \begin{cases} 0 & i\neq j \\ s_i^2 & i=j \end{cases}} + \dots$$

$$= \underbrace{\frac{1}{3}\langle \vec{s}^2\rangle}\ \underline{\delta_{ij}}$$

isotropy of fluctuations

$$\delta V(\vec{r}) = \langle V(\vec{r}+\vec{s})\rangle - \langle V(\vec{r})\rangle = \frac{1}{6}\underbrace{\Delta V(\vec{r})}\underbrace{\langle \vec{s}^2\rangle} + \dots$$

$$= -\frac{e^2}{4\pi\epsilon_0}\cdot \underbrace{\Delta\frac{1}{r}}_{= \frac{-1}{4\pi}\delta(\vec{r})} \qquad = \left(\frac{\hbar}{mc}\right)^2$$

$$\delta V(\vec{r}) = \underset{\text{repulsive}}{+}\ \frac{e^2\hbar^2}{6\epsilon_0 m^2 c^2}\ \underbrace{\delta(\vec{r})}_{\text{affects only s-states}}$$

Darwin term from Dirac theory

$$\delta V_D(\vec{r}) = \frac{e^2\hbar^2}{8\epsilon_0 m^2 c^2}\ \delta(\vec{r})$$