# 16. Relativistic corrections in atoms

## A talk for the Proseminar in Theoretical Physics


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22.04.2024

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# Motivation

# Motivation: Correction terms

Where do these terms come from?

$$H_1 = -\frac{(\vec{p}^2)^2}{8m^3} \qquad \text{Relativistic mass correction}$$

$$H_2 = \frac{e}{4m^2}\frac{1}{r}\frac{\partial \Phi}{\partial r}\vec{\sigma}\cdot\vec{L} \qquad \text{Spin-orbit coupling}$$

$$H_3 = \frac{e}{8m^2}\Delta\Phi \qquad \text{Darwin term}$$

As we will see, these terms arise from relativistic corrections but persist after taking the non-relativistic limit.

# Motivation: The Dirac equation

Relativistic corrections: starting point Dirac equation:

$$H\psi = (\vec{\alpha} \cdot \vec{p} + \beta m)\psi = i\frac{\partial}{\partial t}\psi$$

Unperturbed Hamiltonian:

$$H = \frac{p^2}{2m} + V$$

Dirac Equation (DE) yields solutions which are...

- ...electrically charged (optional)
- ...massive (optional)
- ...with spin 1/2
- ...relativistic

While considering $e^{-}$s, we want to examine the non-relativistic limit of the DE.

The DE is actually four coupled equations. Problem:

$$\beta = \begin{pmatrix} \mathbb{I}_2 & 0 \\ 0 & -\mathbb{I}_2 \end{pmatrix} \text{ is even, but } \vec{\alpha} = \begin{pmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{pmatrix} \text{ is odd!}$$

What does this mean, and why is this a problem?

Solutions of the DE are represented by 4-component spinors.

$$\psi = \begin{pmatrix} \varphi \\ \chi \end{pmatrix} = \begin{pmatrix} \text{"large" component, E > 0} \\ \text{"small" component, E < 0} \end{pmatrix} \xrightarrow{\frac{v}{c}\to 0} \begin{pmatrix} \varphi \\ 0 \end{pmatrix}$$

We want to decouple the DE into two 2-component equations.

$$\text{Even matrices: } \mathcal{E} = \begin{pmatrix} * & 0 \\ 0 & * \end{pmatrix} \quad \text{Odd matrices: } \mathcal{O} = \begin{pmatrix} * & * \\ * & * \end{pmatrix}$$

Goal: Block diagonalise the Hamiltonian!

Foldy–Wouthuysen transformation [2]:

- *Physical Review*, 1950
- Canonical unitary transformation
- Change of basis
- Must not change the spectrum

$$\psi \longrightarrow \psi' = e^{iS}\psi$$

$$i\partial_t \psi' \overset{!}{=} H'\psi'$$

$\rightarrow$ Blackboard

# Motivation: Foldy–Wouthuysen transformation

Foldy–Wouthuysen transformation [2]:

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$$\psi \longrightarrow \psi' = e^{iS}\psi$$

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$\rightarrow$ Blackboard

$$\Rightarrow H' = e^{iS}(H - i\partial_t)e^{-iS}$$

# Motivation: Foldy–Wouthuysen transformation

The goal is to derive the three corrections to the Hamiltonian analytically instead of heuristically.

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The goal is to derive the three corrections to the Hamiltonian analytically instead of heuristically.

We will do this once, so we will never have to do it again!

# Transformation of free particles

# Free particles: Ansatz

Dirac-Hamiltonian for free particles (V=0):

$$H = \vec{\alpha} \cdot \vec{p} + m\beta$$

We want to rotate in the spinor space. In order for $e^{iS_0}$ to be unitary, $S_0$ must be Hermitian. Ansatz:

$$iS_0 = \beta \frac{\vec{\alpha} \cdot \vec{p}}{|\vec{p}|} \vartheta(\vec{p})$$

$$\Rightarrow e^{\pm iS_0} = e^{\pm\beta \frac{\vec{\alpha} \cdot \vec{p}}{|\vec{p}|} \vartheta(\vec{p})} = cos\vartheta \pm \frac{\vec{\alpha} \cdot \vec{p}}{|\vec{p}|} sin\vartheta$$

Useful identities:

We have: $\{\alpha^i, \beta\} = 0$, i.e. $\alpha^i \beta = -\beta \alpha^i$

Furthermore, $(\vec{\alpha} \cdot \vec{p})^2 = |\vec{p}|^2$

$$(\beta \vec{\alpha} \cdot \vec{p})^2 = -|\vec{p}|^2$$

We want to compute

$$H' = e^{iS_0}(H - i\partial_t)e^{-iS_0}$$

$\rightarrow$ Blackboard

The computation yields

$$H' = \vec{\alpha} \cdot \vec{p} \underbrace{\left( cos2\vartheta - \frac{m}{|\vec{p}|} sin2\vartheta \right)}_{\stackrel{!}{=} 0} + \beta m \left( cos2\vartheta + \frac{|\vec{p}|}{m} sin2\vartheta \right)$$

$$\Rightarrow tan2\vartheta = \frac{|\vec{p}|}{m}$$

$$\Rightarrow sin2\vartheta = \frac{tan2\vartheta}{\sqrt{1 + tan^2 2\vartheta}} = \frac{|\vec{p}|}{\sqrt{m^2 + |\vec{p}|^2}}, \quad cos2\vartheta = \frac{m}{\sqrt{m^2 + |\vec{p}|^2}}$$

$$\Rightarrow H' = \beta \sqrt{|\vec{p}|^2 + m^2}$$

# Free particles: New Hamiltonian

Our transformed Hamiltonian

$$H' = \beta\sqrt{\vec{p}^2 + m^2}$$

is diagonalised!

$$H' = \begin{pmatrix} E & & & \\ & E & & \\ & & -E & \\ & & & -E \end{pmatrix} \text{ with } E > 0$$

This only works analytically for free particles.

# Transformation under Interaction with Electromagnetic Field

# EM interaction: Coupling of Hamiltonian

Couple to the electromagnetic field $\rightarrow$ modify the Dirac-Hamilton-Operator

$$\vec{p} \longrightarrow \vec{p} - e\vec{A} \quad V = 0 \longrightarrow e\Phi$$

$$\Rightarrow H = \vec{\alpha} \cdot (\vec{p} - e\vec{A}) + \beta m + e\Phi$$

$$= \beta m + \mathcal{E} + \mathcal{O}$$

with

$$\mathcal{E} = e\Phi \quad \text{and} \quad \mathcal{O} = \vec{\alpha} \cdot (\vec{p} - e\vec{A})$$

and $\vec{A}$: magnetic vector potential ($\vec{\nabla} \times \vec{A} = \vec{B}$)

# EM interaction: Ansatz

Recapitulate Ansatz and condition [4]:

$$iS_0 = \beta \frac{\vec{\alpha} \cdot \vec{p}}{|\vec{p}|} \vartheta \quad \text{and} \quad tan(2\vartheta) = \frac{|\vec{p}|}{m}$$

For small $\vartheta$ (non-relativistic case), we have:

$$S_0 \approx -\frac{i}{2m} \beta \vec{\alpha} \cdot \vec{p} \quad \Rightarrow \quad S = -\frac{i}{2m} \beta \mathcal{O}$$

as a new Ansatz. However, the coupling does not allow for an analytic expression for $e^{iS}$.

$\Rightarrow$ We expand $e^{iS}$ in $\frac{1}{m}$.

Baker-Campbell-Hausdorff identity:

$$\begin{aligned} e^A B e^{-A} &= \sum_{n=0}^{\infty} \frac{1}{n!}[A,B]_n \\ &= B + [A,B] + \cdots + \frac{1}{n!}[A,[A,\cdots,[A,B]\cdots]] + \cdots \end{aligned}$$

yields:

$$\begin{aligned} H' &= e^{iS}(H - i\partial_t)e^{-iS} \\ &= H + i[S,H] - \frac{1}{2}[S,[S,H]] - \frac{i}{6}[S,[S,[S,H]]] \\ &+ \frac{1}{24}[S,[S,[S,[S,H]]]] - \dot{S} - \frac{i}{2}[S,\dot{S}] \end{aligned}$$

with even terms up to $m^{-3}$ and odd terms up to $m^{-2}$.

# EM interaction: Evenness and Oddness

In this context, an operator $\mathcal{E}$ resp. $\mathcal{O}$ is *even* resp. *odd* iff

$$\beta\mathcal{E} = \mathcal{E}\beta \quad \text{resp.} \quad \beta\mathcal{O} = -\mathcal{O}\beta$$

Thus it follows:

$$\begin{aligned} \mathcal{E} \text{ even } &\Rightarrow \mathcal{E}^n \text{ even} && \forall n \in \mathbb{N} \\ \mathcal{O} \text{ odd } &\Rightarrow \mathcal{O}^{2n} \text{ even, } \mathcal{O}^{2n+1} \text{ odd} && \forall n \in \mathbb{N} \end{aligned}$$

End goal: transform away any $\mathcal{O}$'s.

# EM interaction: Foldy-Wouthuysen transformation 1

Brute force calculation:

$$
\begin{aligned}
H &= \beta m + \mathcal{E} + \mathcal{O} \\
S &= -\frac{i}{2m}\beta\mathcal{O} \\
i[S, H] &= -\mathcal{O} + \frac{\beta}{2m}[\mathcal{O}, \mathcal{E}] + \frac{1}{m}\beta\mathcal{O}^2 \\
-\frac{1}{2}[S, [S, H]] &= -\frac{\beta\mathcal{O}^2}{2m} - \frac{1}{2m^2}\mathcal{O}^3 - \frac{1}{8m^2}[\mathcal{O}, [\mathcal{O}, \mathcal{E}]] \\
-\frac{i}{6}[S, [S, [S, H]]] &= \frac{\mathcal{O}^3}{6m^2} - \frac{1}{6m^2}\beta\mathcal{O}^4 \\
\frac{1}{24}[S, [S, [S, [S, H]]]] &= \frac{\beta\mathcal{O}^4}{24m^3}
\end{aligned}
$$

# EM interaction: Foldy-Wouthuysen transformation 1

Brute force calculation:

$$H = \beta m + \mathcal{E} + \mathcal{O}$$

$$S = -\frac{i}{2m}\beta\mathcal{O}$$

$$-\dot{S} = \frac{i}{2m}\beta\dot{\mathcal{O}}$$

$$-\frac{i}{2}[S, \dot{S}] = -\frac{i}{8m^2}[\mathcal{O}, \dot{\mathcal{O}}]$$

Input of computed commutators into Hamiltonian:

$$\begin{aligned} H' =& H + i[S,H] - \frac{1}{2}[S,[S,H]] - \frac{i}{6}[S,[S,[S,H]]] \\ &+ \frac{1}{24}[S,[S,[S,[S,H]]]] - \dot{S} - \frac{i}{2}[S,\dot{S}] \\ &= \beta m + \beta\left(\frac{\mathcal{O}^2}{2m} - \frac{\mathcal{O}^4}{8m^3}\right) + \mathcal{E} - \frac{1}{8m^2}[\mathcal{O},[\mathcal{O},\mathcal{E}]] - \frac{i}{8m^2}[\mathcal{O},\dot{\mathcal{O}}] \\ &+ \frac{\beta}{2m}[\mathcal{O},\mathcal{E}] - \frac{\mathcal{O}^3}{3m^2} + \frac{i\beta\dot{\mathcal{O}}}{2m} \end{aligned}$$

Recall:

$$\begin{aligned} \mathcal{E} \text{ even } &\Rightarrow \mathcal{E}^n \text{ even} && \forall n \in \mathbb{N} \\ \mathcal{O} \text{ odd } &\Rightarrow \mathcal{O}^{2n} \text{ even, } \mathcal{O}^{2n+1} \text{ odd} && \forall n \in \mathbb{N} \end{aligned}$$

Pairing of terms:

$$\begin{aligned} H' &= \beta m + \left( \beta \left( \frac{\mathcal{O}^2}{2m} - \frac{\mathcal{O}^4}{8m^3} \right) + \mathcal{E} - \frac{1}{8m^2}[\mathcal{O}, [\mathcal{O}, \mathcal{E}]] - \frac{i}{8m^2}[\mathcal{O}, \dot{\mathcal{O}}] \right) \\ &+ \left( \frac{\beta}{2m}[\mathcal{O}, \mathcal{E}] - \frac{\mathcal{O}^3}{3m^2} + \frac{i\beta\dot{\mathcal{O}}}{2m} \right) \\ &\equiv \beta m + \mathcal{E}' + \mathcal{O}' \quad \Rightarrow \quad \mathcal{O}' \sim \frac{1}{m} \end{aligned}$$

$\mathcal{O}$ went away, but $\mathcal{O}'$ remains. What do we do?

# EM interaction: Foldy-Wouthuysen transformation 2

2nd Foldy-Wouthuysen transformation:

$$S = -\frac{i\beta}{2m}\mathcal{O}$$

implies new Ansatz

$$\begin{aligned} S' &= -\frac{i\beta}{2m}\mathcal{O}' \\ &= -\frac{i\beta}{2m}\left(\frac{\beta}{2m}[\mathcal{O},\mathcal{E}] - \frac{\mathcal{O}^3}{3m^2} + \frac{i\beta\dot{\mathcal{O}}}{2m}\right) \end{aligned}$$

# EM interaction: Foldy-Wouthuysen transformation 2

2nd Foldy-Wouthuysen transformation:

$$
\begin{aligned}
S' &= -\frac{i\beta}{2m}\left(\frac{\beta}{2m}[\mathcal{O},\mathcal{E}] - \frac{\mathcal{O}^3}{3m^2} + \frac{i\beta\dot{\mathcal{O}}}{2m}\right) \\
\Rightarrow H'' &= e^{iS'}(H' - i\partial_t)e^{-iS'} \\
&= \beta m + \mathcal{E}' + \left(\frac{\beta}{2m}[\mathcal{O}',\mathcal{E}'] + \frac{i\beta\dot{\mathcal{O}}'}{2m}\right) \\
&\equiv \beta m + \mathcal{E}' + \mathcal{O}'' \quad \Rightarrow \quad \mathcal{O}'' \sim \frac{1}{m^2}
\end{aligned}
$$

$\mathcal{O}'$ refuses to leave quite so easily. What do we do?

3rd Foldy-Wouthuysen transformation:

$$\begin{aligned} S'' &= -\frac{i\beta}{2m}\mathcal{O}'' = -\frac{i\beta}{2m}\left(\frac{\beta}{2m}[\mathcal{O}', \mathcal{E}'] + \frac{i\beta\dot{\mathcal{O}}'}{2m}\right) \\ \Rightarrow H''' &= e^{iS''}(H'' - i\partial_t)e^{-iS''} \\ &= \beta\left(m + \frac{\mathcal{O}^2}{2m} - \frac{\mathcal{O}^4}{8m^3}\right) + \mathcal{E} - \frac{1}{8m^2}\left[\mathcal{O}, [\mathcal{O}, \mathcal{E}] + i\dot{\mathcal{O}}\right] \\ &\equiv \beta m + \mathcal{E}' \end{aligned}$$

Finally! (Ignore new even terms of higher oder)

Modify the Dirac-Hamilton-Operator

$$H''' = \beta\left(m + \frac{\mathcal{O}^2}{2m} - \frac{\mathcal{O}^4}{8m^3}\right) + \mathcal{E} - \frac{1}{8m^2}\left[\mathcal{O}, [\mathcal{O}, \mathcal{E}] + i\dot{\mathcal{O}}\right]$$
$$= \beta m + \mathcal{E}'$$

with

$$\mathcal{E} = e\Phi \quad \text{and} \quad \mathcal{O} = \vec{\alpha}\cdot(\vec{p} - e\vec{A})$$

Brute force calculation:

$$\frac{\mathcal{O}^2}{2m} = \frac{1}{2m}(\vec{p} - e\vec{A})^2 - \frac{e}{2m}\vec{\Sigma} \cdot \vec{B}$$
$$\frac{\mathcal{O}^4}{8m^3} = \frac{1}{8m^3}[(\vec{p} - e\vec{A})^2 - e\vec{\Sigma} \cdot \vec{B}]^2 \approx \frac{\vec{p}^4}{8m^3}$$
$$\left[\mathcal{O}, [\mathcal{O}, \mathcal{E}] + i\dot{\mathcal{O}}]\right] = ie(\vec{p} \cdot \vec{E} + \vec{\Sigma} \cdot (\vec{\nabla} \times \vec{E}) - 2i\vec{\Sigma} \cdot (\vec{E} \times (\vec{p} - e\vec{A})))$$

with

$$\vec{\Sigma} = \begin{pmatrix} \vec{\sigma} & 0 \\ 0 & \vec{\sigma} \end{pmatrix} \quad rot\vec{E} = 0$$

Input into coupled Hamiltonian:

$$H''' = \beta\left(m + \frac{\mathcal{O}^2}{2m} - \frac{\mathcal{O}^4}{8m^3}\right) + \mathcal{E} - \frac{1}{8m^2}\left[\mathcal{O}, [\mathcal{O}, \mathcal{E}] + i\dot{\mathcal{O}}]\right]$$

$$= \beta\left(m + \frac{(\vec{p} - e\vec{A})^2}{2m} - \frac{e}{2m}\vec{\Sigma} \cdot \vec{B} - \frac{\vec{p}^4}{8m^3}\right) + e\Phi$$

$$- \frac{e}{8m^2}\left(2\vec{\Sigma} \cdot (\vec{E} \times (\vec{p} - e\vec{A})) - div\vec{E}\right)$$

Hamiltonian $H'''$ decoupled, apply to two-component spinor $\varphi$:

$$\psi \longrightarrow \begin{pmatrix} \varphi \\ 0 \end{pmatrix}, \quad \beta \longrightarrow \mathbb{I}_2, \quad \vec{\Sigma} \longrightarrow \vec{\sigma}$$

$$\begin{aligned} H''' &= \beta\left(m + \frac{(\vec{p} - e\vec{A})^2}{2m} - \frac{e}{2m}\vec{\Sigma}\cdot\vec{B} - \frac{\vec{p}^4}{8m^3}\right) + e\Phi \\ &- \frac{e}{8m^2}\left(2\vec{\Sigma}\cdot(\vec{E}\times(\vec{p} - e\vec{A})) - div\vec{E}\right) \\ \longrightarrow &\ m + \frac{1}{2m}(\vec{p} - e\vec{A})^2 + e\Phi - \frac{e}{2m}\vec{\sigma}\cdot\vec{B} \\ &- \frac{\vec{p}^4}{8m^3} - \frac{e}{4m^2}\vec{\sigma}\cdot(\vec{E}\times(\vec{p} - e\vec{A})) - \frac{e}{8m^2}div\vec{E} \end{aligned}$$

# EM interaction: Terms

What do those terms mean?

$$H''' = \overbrace{m}^{\text{rest mass}} + \overbrace{\frac{1}{2m}(\vec{p} - e\vec{A})^2}^{\text{kinetic energy}} + \overbrace{e\Phi}^{\text{potential}} - \overbrace{\frac{e}{2m}\vec{\sigma} \cdot \vec{B}}^{\text{coupling } \vec{\mu} \text{ to } \vec{B}}$$
$$- \underbrace{\frac{\vec{p}^4}{8m^3}}_{\text{mass correction}} - \underbrace{\frac{e}{4m^2}\vec{\sigma} \cdot (\vec{E} \times (\vec{p} - e\vec{A}))}_{\text{spin-orbit coupling}} - \underbrace{\frac{e}{8m^2} div\vec{E}}_{\text{Darwin term}}$$

Finally, application to hydrogen-like atoms:

$$\Phi \sim \frac{1}{r}, \quad \vec{E} = -\vec{\nabla}\Phi(r) = -\frac{1}{r}\frac{\partial \Phi}{\partial r}\vec{x}, \quad \vec{A} = 0, \quad \vec{\sigma}\cdot(\vec{E}\times\vec{p}) = -\frac{1}{r}\frac{\partial \Phi}{\partial r}\vec{\sigma}\cdot\vec{L}$$

$$H_1 = -\frac{(\vec{p}^2)^2}{8m^3}$$ Relativistic mass correction

$$H_2 = \frac{e}{4m^2}\frac{1}{r}\frac{\partial \Phi}{\partial r}\vec{\sigma}\cdot\vec{L}$$ Spin-orbit coupling

$$H_3 = \frac{e}{8m^2}\Delta\Phi$$ Darwin term

# Physical Interpretation

# Correction I: Relativistic Mass Correction

Heuristically: expand relativistic energy-momentum relation

$$E = E_0 + T = \sqrt{p^2 + m^2} = m + \frac{p^2}{2m} - \frac{p^4}{8m^3} + O(p^6)$$

$$\Rightarrow H_1 = -\frac{p^4}{8m^3}$$

Schrödinger equation a solid approximation, as by the virial theorem:

$$v \sim \alpha \simeq \frac{1}{137}$$

Would scale with $Z$.

# Correction II: Spin-Orbit Coupling

Interaction between magnetic moment of spin of electron

$$\mu_s = -g\mu_B \vec{S}, \quad \mu_B = \frac{e}{2m}, \quad g = 2$$

with the magnetic field generated by the angular momentum (Biot-Savart)[1]

$$\vec{B} = \vec{v} \times \vec{E}$$

$\rightarrow$ energy of magnetic moment in ”external” B-field:

$$H_2 = -\vec{\mu} \cdot \vec{B} = \frac{e}{m}\vec{S} \cdot (\vec{v} \times \vec{E}) = \frac{1}{r}\frac{\partial V(r)}{\partial r}\vec{L} \cdot \vec{S} = \frac{1}{r^3}\vec{L} \cdot \vec{S}$$

## Correction III: Darwin Term

Caused by the *Zitterbewegung* (vibration which obeys relativistic wave equation) of the electron. Position varies by reduced Compton wave length

$$\delta r = \frac{\lambda_C}{2\pi} = \frac{1}{m}$$

Electrostatic interaction of electron with potential no longer local, ”smearing” of the Coulomb interaction between electron and nucleus:

$$H_3 = \frac{e}{8m^2}\Delta\Phi$$

$\rightarrow$ Interference between positive- and negative-energy wave components

# Physical interpretation: Energy levels

First order pertubation theoretical correction:

$$E = E_{n,l,j=l\pm\frac{1}{2}} \pm \Delta E_{n,l,j=l\pm\frac{1}{2}}$$

$$\Delta E_{n,l,j=l\pm\frac{1}{2}} = \frac{RyZ^2}{n^2}\frac{(Z\alpha)^2}{n^2}\left(\frac{3}{4} - \frac{n}{j+\frac{1}{2}}\right)$$

$\Rightarrow$ Fine structure! ($\sim \alpha^2$)

# Physical interpretation: Fine structure

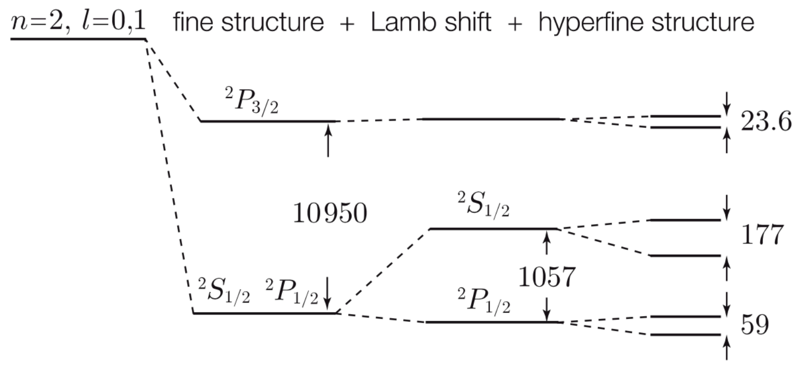


Figure 1: Consecutively finer splittings of the energy levels [3]

# Summary

# Summary

We've followed the following steps in this talk:

1. Find Ansatz for Hermitian $S$
2. Unitary transformation of Hamiltonian
3. Discard odd terms whenever possible
4. Repeat steps 1 - 3 if necessary
5. Decouple Hamiltonian and thus Dirac equation

to mathematically reaffirm known correction terms:

$$H_1 = -\frac{(\vec{p}^2)^2}{8m^3}$$ Relativistic mass correction

$$H_2 = \frac{e}{4m^2}\frac{1}{r}\frac{\partial\Phi}{\partial r}\vec{\sigma}\cdot\vec{L}$$ Spin-orbit coupling

$$H_3 = \frac{e}{8m^2}\Delta\Phi$$ Darwin term

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# Appendix: Further corrections

# Appendix: The lamb shift

Not predicted by Dirac theory, must refer to orbital theory. Deviation of energy levels of $^2S_{1/2}$ and $^2P_{1/2}$ orbitals by

$$\langle \Delta\Phi \rangle = \frac{\alpha^5 m}{6\pi} log\Big(\frac{1}{\pi\alpha}\Big) \sim 4.37 \mu eV$$

Caused by interactions between virtual photons and movement of electron in-between the two orbitals.

# Appendix: Hyperfine corrections

Not predicted by Dirac theory. Interaction between the magnetic moment of nucleus and the magnetic moment of electron (spin-spin interaction)

$$H_{HF} = \frac{e^2 g}{2\pi\varepsilon_0 \mu_K m} \vec{S} \cdot \left( -\vec{I} \Delta \frac{1}{r} + \vec{\nabla}(\vec{I} \cdot \vec{\nabla}) \frac{1}{r} \right)$$

$$\Rightarrow \Delta E \sim \alpha^4 \frac{m}{M}$$

Results in a splitting 1000 times more fine.

# Appendix: Splittings of energy levels