

# Chapter 7

## Relativistic Quantum Mechanics

In the previous chapters we have investigated the Schrödinger equation, which is based on the non-relativistic energy-momentum relation. We now want to reconcile the principles of quantum mechanics with special relativity. Schrödinger actually first considered a relativistic equation for de Broglie's matter waves, but was deterred by discovering some apparently unphysical properties like the existence of plane waves with unbounded negative energies  $E = -\sqrt{p^2c^2 + m^2c^4}$ : Classically a particle on the positive branch of the square root will keep  $E \geq mc^2$  forever but quantum mechanically interactions can induce a jump to the negative branch releasing  $\delta E \geq 2mc^2$ . Schrödinger hence arrived at his famous equation in the non-relativistic context.

Two years later Paul A.M. Dirac found a linearization of the relativistic energy-momentum relation, which explained the gyromagnetic ratio  $g = 2$  of the electron as well as the fine structure of hydrogen. While his equation missed its original task of eliminating negative energy solutions, it was too successful to be wrong so that Dirac went on, inspired by Pauli's exclusion principle, to solve the problem of unbounded negative energies by inventing the particle-hole duality that is nowadays familiar from semiconductors. In the relativistic context the holes are called anti-particles. While Dirac first tried to identify the anti-particle of the electron with the proton (the only other particle known at that time) this did not work for several reasons and he concluded that there must exist a positively charged particle with the same mass as the electron. The positron was then discovered in cosmic rays in 1932. Dirac thus made the first prediction of a new particle on theoretical grounds and, more generally, showed the existence of antimatter as an implication of the consistency of quantum mechanics with special relativity. This initiated the long development of the modern quantum field theory of elementary particles and interactions.

After a brief discussion of the problem with negative energy solutions we now construct the Dirac equation and analyze its nonrelativistic limit. The issue of Lorentz transformations and further symmetries will be taken up in the chapter on symmetries and transformation groups.

**The Klein-Gordon-equation.** If we start with the relativistic energy-momentum relation

$$E^2 = m^2c^4 + c^2\vec{p}^2. \quad (7.1)$$

and use the correspondence rule  $E \rightarrow i\hbar\partial_t$  and  $\vec{p} \rightarrow \frac{\hbar}{i}\vec{\nabla}$  we obtain

$$(i\hbar\partial_t)^2 \psi(\vec{x}, t) = (m^2c^4 - c^2\hbar^2\Delta)\psi(\vec{x}, t), \quad (7.2)$$

which can be written as

$$\boxed{\left(\square + \frac{m^2 c^2}{\hbar^2}\right)\psi(\vec{x}, t) = 0} \quad (7.3)$$

in terms of the d'Alembert operator  $\square := \frac{1}{c^2} \frac{\partial^2}{\partial t^2} - \Delta$ , briefly called “*box*.” While Schrödinger already knew this relativistic wave equation, it was later named after Klein and Gordon who first published it. An immediate problem for the use of (7.3) as an equation for quantum mechanical wave functions is the existence of negative energy solutions

$$\psi_E(\vec{x}, t) = e^{-\frac{i}{\hbar} E t + \frac{i}{\hbar} \vec{p} \vec{x}}, \quad E = -\sqrt{m c^2 + p^2 c^4} \leq -m c^2 \quad (7.4)$$

with an energy that is unbounded from below. Once interactions are turned on electrons could thus emit an infinite amount of energy, which is clearly unphysical.

If we try to avoid the negative energy solutions of the Klein-Gordon equation (7.3) by using an expansion of the positive square root,

$$E = m c^2 \sqrt{1 + \frac{p^2}{m^2 c^2}} = m c^2 + \frac{p^2}{2m} - \frac{p^4}{8m^3 c^2} + \frac{p^6}{16m^5 c^4} - \dots \geq m c^2, \quad (7.5)$$

the Hamiltonian becomes an infinite series with derivatives of arbitrary order and we lose locality. More concretely, it can be shown that localized wavepackets cannot be constructed without contributions from plane waves with negative energies [Itzykson, Zuber].

## 7.1 The Dirac-equation

Dirac tried to avoid the problem with the negative energy solutions by linearization of the equation for the energy. We get an idea for how this could work by recalling the equation  $\sigma_i \sigma_j = \delta_{ij} \mathbb{1} + i \varepsilon_{ijk} \sigma_k$  for the Pauli matrices  $\sigma_i$ , which implies  $(\vec{\sigma} \vec{v})^2 = \sigma_i v_i \sigma_j v_j = \vec{v}^2 \mathbb{1}$ . For massless particles we thus obtain the relativistic energy-momentum relation from a linear equation

$$E \psi = \pm c \vec{\sigma} \vec{p} \psi \quad \Rightarrow \quad E^2 \mathbb{1} = c^2 (\vec{p} \vec{\sigma})^2 = c^2 p^2 \mathbb{1}. \quad (7.6)$$

Upon quantization the suggested Hamiltonian  $H = \pm c \vec{p} \vec{\sigma}$  becomes a  $2 \times 2$  matrix of momentum operators because

$$\vec{\sigma} = \left( \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \right) \Rightarrow \vec{p} \vec{\sigma} = p_i \sigma_i = \begin{pmatrix} p_3 & p_1 - i p_2 \\ p_1 + i p_2 & -p_3 \end{pmatrix} = \frac{\hbar}{i} \begin{pmatrix} \partial_3 & \partial_1 - i \partial_2 \\ \partial_1 + i \partial_2 & -\partial_3 \end{pmatrix} \quad (7.7)$$

Equation (7.6) indeed shows up as the massless case of the Dirac equation. It is called Weyl equation and it describes the massless neutrinos of the standard model of particle physics.

In 1928 Dirac made the following ansatz for a linear relation between energy and momenta

$$E \cdot \mathbb{1} = c p_i \alpha_i + m c^2 \beta \quad (7.8)$$

with four dimensionless Hermitian matrices  $\alpha_i$  and  $\beta$ . Taking squares and demanding the relativistic energy-momentum relation (7.1) we find

$$E^2 \mathbb{1} = (m^2 c^4 + c^2 p_i p_i) \mathbb{1} = c^2 \alpha_i \alpha_j p_i p_j + m c^3 p_i (\alpha_i \beta + \beta \alpha_i) + \beta^2 m^2 c^4, \quad (7.9)$$

which is equivalent to the matrix equations

$$\boxed{\beta^2 = \mathbb{1}, \quad \{\alpha_i, \beta\} = 0, \quad \{\alpha_i, \alpha_j\} = 2\delta_{ij}\mathbb{1},} \quad (7.10)$$

where  $\{A, B\} = AB + BA$  denotes the anticommutator. Assuming the existence of a solution we arrive at the free Dirac equation

$$i\hbar\partial_t\psi = H\psi, \quad H = \frac{\hbar}{i}c\alpha_i\partial_i\psi + \beta mc^2 \quad (7.11)$$

with  $H = H^\dagger$ . The coupling to electromagnetic fields is achieved as in the non-relativistic case with the replacement  $\vec{p} \rightarrow \frac{\hbar}{i}\vec{\nabla} - \frac{e}{c}\vec{A}$  and  $E \rightarrow i\hbar\partial_t - V$ . With  $V = e\phi$  this leads to the **interacting Dirac equation**

$$\boxed{\left(i\hbar\frac{\partial}{\partial t} - e\phi\right)\psi = c\alpha_i\left(\frac{\hbar}{i}\partial_i - \frac{e}{c}A_i\right)\psi + \beta mc^2\psi,} \quad (7.12)$$

for charged particles in an electromagnetic field, where we still need to find matrices  $\alpha_i$  and  $\beta$  representing the Dirac algebra (7.10).

While  $\alpha_i = \sigma_i$  would satisfy  $\{\alpha_i, \alpha_j\} = \delta_{ij}\mathbb{1}$  it is impossible to find a further  $2 \times 2$  matrix  $\beta$  solving (7.10). A simple argument shows that the dimension of the Dirac matrices has to be even: Since  $\beta^2 = \mathbb{1}$  and  $\alpha_i\beta = -\beta\alpha_i$  cyclicity of the trace  $\text{tr}(M\beta) = \text{tr}(\beta M)$  implies

$$\text{tr}\alpha_i = \text{tr}\alpha_i\beta^2 = \text{tr}(\alpha_i\beta)\beta = \text{tr}\beta(\alpha_i\beta) = -\text{tr}\beta(\beta\alpha_i) = -\text{tr}\alpha_i \quad (7.13)$$

and hence  $\text{tr}\alpha_i = 0$  (similarly  $\text{tr}\beta = \text{tr}(\beta\alpha_1)\alpha_1 = \text{tr}\alpha_1(\beta\alpha_1) = -\text{tr}\alpha_1(\alpha_1\beta) = -\text{tr}\beta$  shows that the trace of  $\beta$  also has to vanish). On the other hand,  $\alpha_i^2 = \beta^2 = \mathbb{1}$  implies that all eigenvalues of  $\alpha_i$  and  $\beta$  must be  $\pm 1$  so that  $\text{tr}\alpha_i = \text{tr}\beta = 0$  entails that half of the eigenvalues are  $+1$  and the other half are  $-1$ . This is only possible for even-dimensional matrices. Dirac hence tried an ansatz with  $4 \times 4$  matrices and found the solution

$$\alpha_i = \begin{pmatrix} 0 & \sigma_i \\ \sigma_i & 0 \end{pmatrix}, \quad \beta = \begin{pmatrix} \mathbb{1} & 0 \\ 0 & -\mathbb{1} \end{pmatrix}, \quad \begin{aligned} \alpha_i &= \alpha_i^\dagger = \alpha_i^{-1} \\ \beta &= \beta^\dagger = \beta^{-1} \end{aligned} \quad (7.14)$$

where we used a block notation with  $2 \times 2$  matrices  $\mathbb{1}, 0$  and  $\sigma_i$  as matrix entries. In full gory detail the Dirac matrices read  $\alpha_1 = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}$ ,  $\alpha_2 = \begin{pmatrix} 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \\ 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \end{pmatrix}$ ,  $\alpha_3 = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{pmatrix}$ ,  $\beta = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$ , but one should *never use these explicit expressions* and rather work with the defining equations (7.10), or possibly with the block notation (7.14) if a splitting of the 4-component spinor wave function  $\psi = (\psi_1, \psi_2, \psi_3, \psi_4)^T$  into two 2-component spinors is unavoidable like in the non-relativist limit (see below). It can be shown that (7.14) is the unique irreducible unitary representation of the Dirac algebra (7.10), up to unitary equivalence  $\alpha_i \rightarrow U\alpha_iU^{-1}$ ,  $\beta \rightarrow U\beta U^{-1}$  with  $UU^\dagger = \mathbb{1}$ .

**Relativistic spin.** In order to derive the spin operator for relativistic electrons we observe that the orbital angular momentum  $\vec{L} = \vec{X} \times \vec{P}$  is not conserved for the free Dirac Hamiltonian

$$[H, L_i] = [c\vec{\alpha}\vec{P} + \beta mc^2, \varepsilon_{ijk}X_jP_k] = \frac{\hbar}{i}c\varepsilon_{ijk}\alpha_jP_k \neq 0 \quad (7.15)$$

because  $[P_l, X_j] = \frac{\hbar}{i}\delta_{lj}$ . A conserved operator  $\vec{J} = \vec{L} + \vec{S}$  can be constructed by observing that

$$\begin{aligned} [H, \varepsilon_{ijk}\alpha_j\alpha_k] &= \varepsilon_{ijk}[c\vec{\alpha}\vec{P}, \alpha_j\alpha_k] = \varepsilon_{ijk}cP_l(\{\alpha_l, \alpha_j\}\alpha_k - \alpha_j\{\alpha_l, \alpha_k\}) \\ &= \varepsilon_{ijk}cP_l(2\delta_{lj}\alpha_k - 2\delta_{lk}\alpha_j) = 4c\varepsilon_{ijk}P_j\alpha_k \end{aligned} \quad (7.16)$$

because  $[A, BC] = ABC + BAC - BAC - BCA = \{A, B\}C - B\{A, C\}$ . The spin operator

$$S_i = \frac{\hbar}{4i} \varepsilon_{ijk} \alpha_j \alpha_k = \frac{\hbar}{2} \begin{pmatrix} \sigma_i & 0 \\ 0 & \sigma_i \end{pmatrix} \quad (7.17)$$

therefore yields a conserved total angular momentum  $\vec{J} = \vec{L} + \vec{S}$ .

**Lorentz covariant form of the Dirac equation.** Multiplication with the matrix  $\frac{1}{c}\beta$  from the left recasts the relation  $E - e\phi = c\vec{\alpha}(\vec{p} - \frac{e}{c}\vec{A}) + \beta mc^2$  into

$$\left( \beta \left( \frac{1}{c}E - \frac{e}{c}\phi \right) - \beta \vec{\alpha} \left( \vec{p} - \frac{e}{c}\vec{A} \right) - mc \right) \psi = 0. \quad (7.18)$$

The standard combination of coordinates, energy-momenta and gauge potentials into 4-vectors

$$x^\mu = (ct, \vec{x}), \quad \partial_\mu = \left( \frac{1}{c}\partial_t, \vec{\nabla} \right), \quad p^\mu = \left( \frac{1}{c}E, \vec{p} \right), \quad A^\mu = (\phi, \vec{A}), \quad (7.19)$$

which entails the relativistic version  $p_\mu \rightarrow P_\mu = i\hbar\partial_\mu$  of the quantum mechanical correspondence (2.3), suggests the combination of  $\beta$  and  $\beta\alpha_i$  into a 4-vector  $\gamma^\mu$  of  $4 \times 4$  matrices as

$$\gamma^\mu = (\beta, \beta\vec{\alpha}) \quad \Rightarrow \quad \boxed{\{\gamma^\mu, \gamma^\nu\} = 2g^{\mu\nu}\mathbb{1}} \quad \text{with} \quad g^{\mu\nu} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}. \quad (7.20)$$

Putting everything together and dividing (7.18) by  $\hbar$  we obtain the Lorentz-covariant equation

$$\boxed{\left( \gamma^\mu (i\partial_\mu - \frac{e}{\hbar c} A_\mu) - \frac{c}{\hbar} m \right) \psi = 0.} \quad (7.21)$$

Since  $(\beta\alpha_i)^\dagger = \alpha_i\beta = -\beta\alpha_i$  the gamma matrices  $\gamma^\mu$  are unitary, but for  $\mu \neq 0$  not Hermitian

$$\boxed{(\gamma^\mu)^\dagger = (\gamma^\mu)^{-1} \equiv \gamma_\mu,} \quad (7.22)$$

where the second equality should be interpreted as a numerical coincidence due to (7.20) and our convention  $g_{\mu\nu} = \text{diag}(1, -1, -1, -1)$  and not as a covariant equation! When we will come to the discussion of symmetries we will see that the non-Hermiticity of  $\gamma^\mu$  with  $\mu \neq 0$  is related to the fact that Lorentz-boosts are represented by non-unitary transformations, as one might expect to be required by consistency of probability density interpretations with Lorentz contractions.

**The Dirac sea.** The Dirac algebra  $\{\gamma^\mu, \gamma^\nu\} = 2g^{\mu\nu}\mathbb{1}$  implies  $(\gamma^\mu p_\mu)^2 = \gamma^\mu \gamma^\nu p_\mu p_\nu = p^2$  and

$$(\gamma^\mu p_\mu + mc)(\gamma^\nu p_\nu - mc) = (p^2 - m^2 c^2)\mathbb{1} = \frac{1}{c^2} (E^2 - (p^2 c^2 + m^2 c^4))\mathbb{1}. \quad (7.23)$$

Every component  $\psi_1, \dots, \psi_4$  of a solution  $\psi$  of the free Dirac equation  $(p^\nu \gamma_\nu - mc)\psi = 0$  is hence a solution of the Klein Gordon equation. In turn, the operator  $p^\mu \gamma_\mu + mc$  can be used to construct plan wave solutions

$$\psi(t, \vec{x}) = e^{\frac{i}{\hbar} \left( \frac{E}{c} t - i\vec{p}\vec{x} \right)} (\gamma^\mu p_\mu + mc) \psi_0 \quad \text{with} \quad E = \pm \sqrt{p^2 c^2 + m^2 c^4} \quad (7.24)$$

in terms of constant spinors  $\psi_0$ . For each momentum  $\vec{p}$  two of the four spinor polarizations have positive and two have negative energy. This is most easily seen in the rest frame  $\vec{p} = 0$

where  $\gamma^\mu p_\mu + mc = mc(\mathbb{1} \pm \beta)$  for  $E = \pm mc$ . For positive energies  $\frac{1}{2}(\mathbb{1} + \beta)$  projects onto  $\psi_{1,2}$  while for negative energies  $\frac{1}{2}(\mathbb{1} - \beta)$  projects onto  $\psi_{3,4}$ .

As negative energy states are thus unavoidable in the relativistic quantum theory Dirac concluded that what we observe as the vacuum is a state where all (infinitely many!) negative energy eigenstates are filled by electrons. This vacuum is called *Dirac sea*. Pauli's exclusion principle then forbids transitions to negative energy states because they are already occupied. But the existence of this sea implies that, when interactions are turned on, a sufficient amount of energy  $E \geq 2mc^2$  can be used to bring an electron into a positive energy state while leaving a hole in the vacuum. A missing negative charge in a uniform background density, however, acts like a positive charge so that the holes are perceived as positively charged particles, called positrons, and a particle-antiparticle pair has been created out of the vacuum.

The same story can now be told for other particles, but for bosons there is no Pauli exclusion principle and the Dirac sea has to be replaced by the more powerful concept of field quantization where wave functions are replaced by (superpositions of particle creation and annihilation) operators [Itzykson,Zuber]. This is true, in particular, for the quanta of the electromagnetic field, called photons. We will further discuss the concept of particle creation and annihilation in chapter 10 (many particle theory). While the relativistic Dirac sea should hence not be taken too literally it is still a very powerful intuitive concept and later found important applications in solid state physics.

## 7.2 Nonrelativistic limit and the Pauli-equation

In this section we show that the Pauli-equation, as well as the fine structure of the hydrogen atom, can be obtained from a non-relativistic approximation of the Dirac-equation. Assuming that the potentials  $V = e\phi$  and  $\vec{A}$  are time-independent we make the stationary ansatz

$$\psi(\vec{x}, t) = w(\vec{x}) e^{-\frac{i}{\hbar}Et} = \begin{pmatrix} u(\vec{x}) \\ v(\vec{x}) \end{pmatrix} e^{-\frac{i}{\hbar}Et} \quad (7.25)$$

for energy eigenfunctions  $\psi$  where we decomposed the 4-spinor  $w(\vec{x})$  into two 2-component spinors  $u = \begin{pmatrix} u_1 \\ u_2 \end{pmatrix}$  and  $v = \begin{pmatrix} v_1 \\ v_2 \end{pmatrix}$ . For convenience we introduce the notation

$$\vec{\Pi} = \vec{P} - \frac{e}{c}\vec{A} \quad \text{with} \quad \vec{P} = \frac{\hbar}{i}\vec{\nabla} \quad (7.26)$$

for the gauge-invariant physical momentum  $\vec{\Pi} = \vec{p} - \frac{e}{c}\vec{A}$  and insert  $\vec{\alpha} = \begin{pmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{pmatrix}$ ,  $\beta = \begin{pmatrix} \mathbb{1} & 0 \\ 0 & -\mathbb{1} \end{pmatrix}$  into the stationary Dirac-equation  $Ew = Hw$  with  $H = c\vec{\alpha}\vec{\Pi} + V + \beta mc^2$ . Putting everything together we obtain

$$\begin{pmatrix} E - V - mc^2 & 0 \\ 0 & E - V + mc^2 \end{pmatrix} \begin{pmatrix} u \\ v \end{pmatrix} = \begin{pmatrix} 0 & c\vec{\sigma}\vec{\Pi} \\ c\vec{\sigma}\vec{\Pi} & 0 \end{pmatrix} \begin{pmatrix} u \\ v \end{pmatrix} \quad (7.27)$$

For positive energies

$$E' \equiv E - mc^2 > 0 \quad (7.28)$$

equation (7.25) is now written as a coupled system of two differential equations

$$(E' - V) u = c(\vec{\sigma}\vec{\Pi}) v \quad (7.29)$$

$$(E' + 2m_0c^2 - V) v = c(\vec{\sigma}\vec{\Pi}) u \quad (7.30)$$

for two spinor wave functions  $u$  and  $v$ .

In the *non-relativistic approximation* we now assume that all energies, momenta and electromagnetic potentials are small

$$V, \vec{A}, \vec{p}, E' \ll mc^2. \quad (7.31)$$

Then we can solve (7.30) for the *small components*  $v$  of the 4-spinor  $w$  as

$$v = \frac{f(\vec{x})}{2mc} \vec{\sigma} \vec{\Pi} u \quad \text{with} \quad f(\vec{x}) = \frac{1}{1 + \frac{E' - V(\vec{x})}{2mc^2}} \approx 1 - \frac{E' - V(\vec{x})}{2mc^2}. \quad (7.32)$$

Inserting  $v$  into equation (7.29) yields

$$(E' - V) u = \frac{(\vec{\sigma} \vec{\Pi}) f(\vec{x}) (\vec{\sigma} \vec{\Pi})}{2m} u \quad (7.33)$$

which can be interpreted as a non-relativistic Schrödinger equation with the Hamilton operator

$$H_{non-rel} = \frac{1}{2m} (\vec{\sigma} \vec{\Pi} f(\vec{x}) \vec{\sigma} \vec{\Pi}) + V. \quad (7.34)$$

and non-relativistic energy  $E'$ .

In the evaluation of the resulting operator we now assume a *centrally symmetric potential*  $V(\vec{x}) = V(r)$ . With  $\frac{\partial f(r)}{\partial x_i} = f'(r) \frac{x_i}{r}$ ,  $\sigma_i \sigma_j = \delta_{ij} + i \varepsilon_{ijk} \sigma_k$  and  $\vec{\Pi} = \frac{\hbar}{i} \vec{\nabla} - \frac{e}{c} \vec{A}$  we find

$$(\vec{\sigma} \vec{\Pi}) f(r) (\vec{\sigma} \vec{\Pi}) = \Pi_i f \Pi_j \sigma_i \sigma_j = \left( f \Pi_i \Pi_j + \frac{\hbar}{i} \frac{\partial f}{\partial x_i} \Pi_j \right) (\delta_{ij} + i \varepsilon_{ijk} \sigma_k) \quad (7.35)$$

whose decomposition according to (anti)symmetry in  $ij$  yields four terms,

$$\boxed{\Pi_i f \Pi_j \sigma_i \sigma_j = f \Pi_i \Pi_j \delta_{ij} + i f \varepsilon_{ijk} \sigma_i \Pi_j \Pi_k - i \hbar f' \frac{x_i}{r} \Pi_j \delta_{ij} + \hbar f' \frac{x_i}{r} \Pi_j \varepsilon_{ijk} \sigma_k} \quad (7.36)$$

which we now discuss in turn. We will neglect higher order corrections that lead to energy corrections of higher order in the fine structure constant  $\alpha = \frac{e^2}{\hbar c} \approx \frac{1}{137}$  and that are hence suppressed by additional powers of  $\frac{\alpha}{2\pi} \approx 10^{-3}$ .

- **Angular momentum term.** We begin with the evaluation of the first term

$$f \Pi^2 = f \Pi_i \Pi_j \delta_{ij} = f \left( \vec{p}^2 - \frac{e}{c} (\vec{p} \vec{A} + \vec{A} \vec{p}) + \frac{e^2}{c^2} \vec{A}^2 \right) \quad (7.37)$$

For a constant magnetic field  $\vec{B} = \nabla \times \vec{A}$  we choose the vector potential  $A_i = -\frac{1}{2} \varepsilon_{ijk} x_j B_k$  that satisfies the Coulomb gauge condition  $\text{div } \vec{A} = \partial_i A_i = 0$  and neglect the last term, which is quadratic in  $B$ . Since  $\partial_i A_i \psi = (\partial_i A_i) \psi + A_i \partial_i \psi = A_i \partial_i \psi$  in Coulomb gauge and

$$-2 \frac{e}{c} \vec{A} \vec{p} = -2 \frac{e}{c} \left( -\frac{1}{2} \varepsilon_{ijk} x_j B_k \right) p_i = -\frac{e}{c} \vec{B} \vec{L} \quad (7.38)$$

the leading contribution  $\frac{1}{2m} f \approx \frac{1}{2m}$  yields the leading kinetic term and the angular momentum coupling

$$\frac{1}{2m} \vec{\Pi}^2 = \frac{1}{2m} \left( \vec{p}^2 - \frac{e}{c} (\vec{L} \vec{B}) \right) + \mathcal{O}(B^2). \quad (7.39)$$

**Relativistic kinetic energy.** Since  $\vec{p}^2/2m$  is the leading non-relativist term we should

also keep its combination with the next-to-leading term in the expansion  $f = 1 - \frac{E'-V}{2mc^2} + \dots$ . In the resulting correction term we insert  $E' = V + p^2/2m + \dots$  and obtain

$$\boxed{H_{rel} = -\frac{\vec{p}^4}{8m^3c^2}} \quad (7.40)$$

in agreement with (6.20).

- **Gyromagnetic ratio.** The next term that we need to consider is  $\frac{1}{2m}$  times

$$i\varepsilon_{ijk}\sigma_i\Pi_j\Pi_k = -\frac{e}{c}i\varepsilon_{ijk}\sigma_k(p_iA_j + A_ip_j) = -\frac{e}{c}i\varepsilon_{ijk}\sigma_k(p_iA_j - A_jp_i). \quad (7.41)$$

Since  $(p_iA_j - A_jp_i)\psi = (p_iA_j)\psi$  this expression becomes

$$-\frac{e}{c}\varepsilon_{ijk}\hbar(\partial_iA_j)\sigma_k = -\frac{e\hbar}{c}(\text{rot}\vec{A})_k\sigma_k = -\frac{e\hbar}{c}\vec{B}\vec{\sigma} = -2\frac{e}{c}\vec{B}\vec{S} \quad (7.42)$$

which amounts to a  $g$ -factor  $g = 2$  in the magnetic coupling  $-\frac{e}{2mc}(\vec{L} + g\vec{S})\vec{B}$ .

- **Darwin term.** For the contribution  $\frac{1}{2m}\frac{\hbar}{i}f'\frac{x_i}{r}\Pi_i$  of the third term in (7.36) we insert the derivative  $f' \approx V'/2mc^2$  of the r.h.s. of (7.32) and find

$$\frac{1}{2m}\frac{\hbar}{i}f'\frac{x_i}{r}\Pi_i \approx \frac{\hbar}{4im^2c^2}\frac{V'}{r}(\vec{x}\vec{p} - \frac{e}{c}\vec{x}\vec{A}) \approx -\frac{\hbar^2}{4m^2c^2}\partial_iV\partial_i \quad (7.43)$$

where we used  $\frac{x_i}{r}V' = \partial_iV$  and dropped the vector potential contribution, which is quadratic in the electromagnetic fields. This term is equivalent to the Darwin term

$$\boxed{H_{Darwin} = \frac{\hbar^2}{8m^2c^2}\Delta V} \quad (7.44)$$

because the expectation values of the Hamiltonians agree by partial integration of  $\int u\partial_iV\partial_iu = \frac{1}{2}\int\partial_iV\partial_i(u^2) = -\frac{1}{2}\int(\Delta V)u^2$  for real eigenfunctions  $u$ .

- **Spin-orbit coupling.** Since  $\vec{S} = \frac{\hbar}{2}\vec{\sigma}$  the term  $\frac{\hbar}{i}\frac{f'}{r}i\varepsilon_{ijk}x_ip_j\sigma_k$  yields

$$\frac{\hbar}{i}\frac{f'}{r}i\varepsilon_{ijk}x_ip_j\sigma_k = \frac{f'}{r}\hbar\mathcal{L}_k\sigma_k \approx \frac{dV}{dr}\frac{1}{mc^2r}\vec{\mathcal{L}}\vec{S}, \quad (7.45)$$

which completes our evaluation of the terms in eq. (7.36).

Collecting all relevant contributions we thus obtain the *Pauli-equation*

$$\boxed{H_{Pauli}u = \left( \frac{\vec{p}^2}{2m} + V - \frac{e}{2mc}\vec{B}(\vec{L} + 2\vec{S}) + \frac{dV}{dr}\frac{\vec{L}\vec{S}}{2m^2c^2r} \right) u,} \quad (7.46)$$

which contains the spin-orbit coupling and explains the observed gyromagnetic ratio. In addition we find the *relativistic energy correction* (7.40) and the *Darwin term* (7.44), which together with (7.46) explain the complete fine structure of the energy levels of the hydrogen atom.