

DRAFT VERSION

Einstein-Cartan-Evans Unified Field Theory

The Geometrical Basis of Physics

Volume 2: Quantum Physics

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11. The ECE Fermion equation

11.1 Introduction

In Volume 1 of this textbook [1], all relevant subjects of classical physics have been revisited under the concept of ECE theory. This is in particular the unification of classical dynamics, electrodynamics, and fluid dynamics. A number of new connections between these subjects and new insights have been revealed. In this Volume 2, we extend the unification to quantum mechanics. We will show that the quantum realm can be described by the same Cartan geometry as the classical realm. Solely, a quantization of physical variables has to be performed. We do this in the canonical way known from standard quantum mechanics. Applying this to the ECE wave equation, we obtain the Dirac equation, which is the state-of-the-art relativistic basis of quantum mechanics in the sense of special relativity. In ECE theory, however, we derive an equivalent equation that is generally covariant and is an equation of general relativity, similar as we did for Maxwell's equations in electrodynamics. We are even able to simplify Dirac's structure that was based on 4×4 matrices to the 2×2 Pauli matrices, and we call the equation the "Fermion equation", because it holds for fermions in the same way as the Dirac equation.

Having developed this fundamental result, we will discuss far-reaching consequences of ECE quantum mechanics in later chapters. In particular, some of the consequences are extensions of the standard theory. For example, we will derive the Pauli exclusion principle mathematically, and we will develop a novel quantum force equation that connects quantum mechanics with classical physics.

11.2 Standard quantum mechanics

11.2.1 Quantization

First, we recapitulate certain basics of standard quantum mechanics that are relevant for our ECE developments. This section cannot present the whole subject area of quantum mechanics. The reader should be familiar with this area from his own university studies or by studying standard textbooks [2].

A quantum-mechanical state is described by its complex valued *wave function* $\psi(x^t)$, which

depends on the coordinates x^μ of 4-space. The wave function is also called *probability amplitude*. A quantum state has a *probability distribution* that is given by

$$p(x^\mu) = |\psi(x^\mu)|^2 = \psi^*(x^\mu)\psi(x^\mu) \quad (11.1)$$

and has always to be positive definite which is guaranteed by this definition. While wave functions are complex valued, probability distributions are real valued. Measurable physical quantities are the expectation values of a corresponding operator, applied to the wave function. The measured value of a quantity W is, therefore,

$$W = \int \psi^* W_{op} \psi d^3 r, \quad (11.2)$$

which is often written as

$$W = \langle \psi | W_{op} | \psi \rangle = \langle W_{op} \rangle. \quad (11.3)$$

W_{op} is the operator for the observable W . Integrals with two different wave functions ψ_i, ψ_j are called matrix elements of an operator:

$$W_{ij} = \langle \psi_i | W_{op} | \psi_j \rangle. \quad (11.4)$$

The wave functions must be square-integrable functions. Such functions, together with a scalar product, form a *Hilbert space*, a mathematical space of functions. The scalar product between two functions ψ_i, ψ_j in this space is defined by the integral

$$\langle \psi_i | \psi_j \rangle = \int \psi_i^* \psi_j d^3 r \quad (11.5)$$

and is also called the *overlap* between wave functions. These have to be normalized, and, for an orthonormal set of wave functions, the relation holds:

$$\langle \psi_i | \psi_j \rangle = \delta_{ij} \quad (11.6)$$

with the Kronecker symbol δ .

The 4-momentum was defined in Eqs. (7.139) and (9.91) of Vol. 1. Its 0-component is the energy E and its vector components are the momentum components p_i . In covariant form, the 4-momentum is

$$p_\mu = \begin{bmatrix} p_0 \\ p_1 \\ p_2 \\ p_3 \end{bmatrix} = \begin{bmatrix} E/c \\ -\mathbf{p} \end{bmatrix} = \begin{bmatrix} E/c \\ -p_X \\ -p_Y \\ -p_Z \end{bmatrix}, \quad (11.7)$$

and in contravariant form:

$$p^\mu = \begin{bmatrix} p^0 \\ p^1 \\ p^2 \\ p^3 \end{bmatrix} = \begin{bmatrix} E/c \\ \mathbf{p} \end{bmatrix} = \begin{bmatrix} E/c \\ p_X \\ p_Y \\ p_Z \end{bmatrix}. \quad (11.8)$$

Standard quantum mechanics uses quantization rules to describe quantization of energy and momentum. An essential constant is the quantum of angular momentum $\hbar = h/(2\pi)$, where h is Planck's quantum of action. The standard quantization rules are

$$E \rightarrow i\hbar c \partial_0 = i\hbar \frac{\partial}{\partial t}, \quad (11.9)$$

$$\mathbf{p} \rightarrow -i\hbar \nabla. \quad (11.10)$$

In 4-space, we obtain the covariant and contravariant momentum operators, denoted by \hat{p}_μ and \hat{p}^μ :

$$p_\mu = \begin{bmatrix} E/c \\ -p_X \\ -p_Y \\ -p_Z \end{bmatrix} \rightarrow \hat{p}_\mu = i\hbar \begin{bmatrix} c\partial_0 \\ \partial_1 \\ \partial_2 \\ \partial_3 \end{bmatrix}, \quad (11.11)$$

$$p^\mu = \begin{bmatrix} E/c \\ p_X \\ p_Y \\ p_Z \end{bmatrix} \rightarrow \hat{p}^\mu = i\hbar \begin{bmatrix} c\partial_0 \\ -\partial_1 \\ -\partial_2 \\ -\partial_3 \end{bmatrix}, \quad (11.12)$$

with $\partial_0 = \partial/\partial_{ct}$, $\partial_1 = \partial/\partial_X$, etc.

These operators appear in the *Schrödinger equation*, which is the non-relativistic equation of quantum states. With Hamilton operator \hat{H} and energy operator \hat{E} , it reads

$$\hat{H}\psi = \hat{E}\psi. \quad (11.13)$$

For a free particle (without potential energy), the *Hamilton operator* is the kinetic energy

$$\frac{\hat{\mathbf{p}}^2}{2m} = -\frac{\hbar^2}{2m}\nabla^2, \quad (11.14)$$

and the *energy operator* is

$$\hat{E} = i\hbar\frac{\partial}{\partial t}. \quad (11.15)$$

Hence, the Schrödinger equation takes the form

$$-\frac{\hbar^2}{2m}\nabla^2\psi = i\hbar\frac{\partial}{\partial t}\psi. \quad (11.16)$$

The *probability density* is

$$\rho = |\psi|^2 = \psi^*\psi \quad (11.17)$$

and is positive definite. The *probability current* is

$$\mathbf{j} = -\frac{i\hbar}{2m}(\psi^*\nabla\psi - \psi\nabla\psi^*). \quad (11.18)$$

11.2.2 Klein-Gordon equation

For spin-0 particles with mass m and momentum p we can quantize Einstein's energy equation

$$E^2 = c^2p^2 + mc^2 \quad (11.19)$$

by the quantization rules (11.9, 11.10) and obtain

$$\hbar^2\frac{\partial^2\psi}{\partial t^2} = c^2\hbar^2\nabla^2\psi - mc^2\psi. \quad (11.20)$$

This equation is of second order and leads to negative probability densities. The latter point motivated Paul Dirac to derive an equation that gives positive probability densities only. The spin of electrons requires further modifications for spin-1/2 particles, which require the usage of another symmetry group.

11.2.3 SU(2) symmetry

In quantum mechanics, we have to respect the spin of electrons, which is quantized in two directions and therefore requires the distinction of spin states. Thus, a wave function has to consist of at least two components, one for each spin direction. The mathematics for spin states must be developed in a way that rotational symmetry of these states can be described adequately.

Using group theory, the group of rotations in three-dimensional euclidean space is described by the group called $O(3)$, represented by a 3x3 rotation matrix. This is an *orthogonal matrix*, meaning that the transpose of such a matrix R is its inverse:

$$RR^T = R^T R = I, \quad (11.21)$$

where I is the unit matrix. Each rotation around the coordinate origin preserves the length of a vector, therefore the determinant of the rotation matrix is ± 1 . To conserve the orientation (handedness of space), the determinant must be $+1$, which defines the *special rotation group* named $SO(3)$.

We are now interested in the rotational representation of wave functions with two components. Since these functions are complex-valued, we have to consider rotations in a two-dimensional space of complex numbers, and to relate them to three-dimensional rotations.

A complex square matrix U is called *unitary*, if its conjugate transpose is identical with its inverse, that is, if

$$U^{*T} = U^{-1}. \quad (11.22)$$

Another notation for U^{*T} is U^+ . It follows directly that, for unitary matrices, it holds

$$UU^{*T} = UU^+ = I. \quad (11.23)$$

The group of unitary 2x2 matrices with $\det(U) = 1$ is called $SU(2)$. Then, U has the general form [2]

$$U = \begin{bmatrix} a & b \\ -b^* & a^* \end{bmatrix} \quad (11.24)$$

with complex numbers a and b , for which the normalization condition

$$|a|^2 + |b|^2 = 1 \quad (11.25)$$

holds. a and b consist of four parameters that are constrained by the above equation, so that we have three independent parameters as is required for describing a rotation in three-dimensional space. A 2-vector or *spinor* (ξ_1, ξ_2) in $SU(2)$ is related to a complex 3-vector (X, Y, Z) in $O(3)$ via the relation [2]

$$\begin{aligned} X &= \frac{1}{2} (\xi_2^2 - \xi_1^2), \\ Y &= \frac{1}{2i} (\xi_2^1 + \xi_1^2), \\ Z &= \xi_1 \xi_2. \end{aligned} \quad (11.26)$$

■ **Example 11.1** The relation between $SU(2)$ and $O(3)$ rotations is illustrated by an example. We rotate the spinors by certain progressing angles on the complex unit circle by defining

$$\xi_1 = \frac{1}{\sqrt{2}} \left(\cos \frac{4(n-1)}{N} + i \sin \frac{4(n-1)}{N} \right), \quad (11.27)$$

$$\xi_2 = \frac{1}{\sqrt{2}}, \quad (11.28)$$

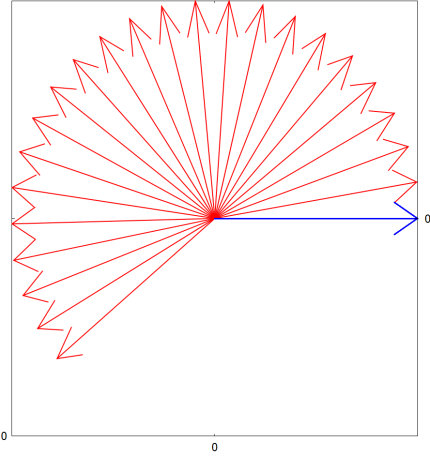


Figure 11.1: Example of a rotation in SU(2) geometry, red: ξ_1 , blue: ξ_2 .

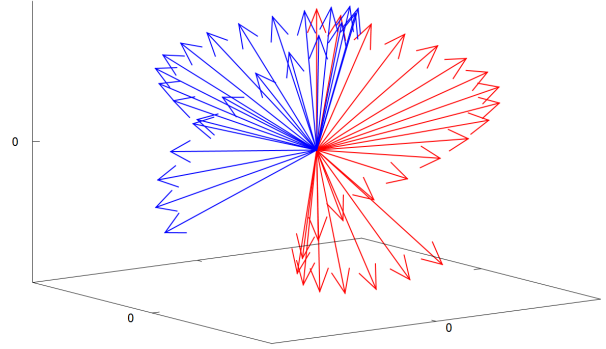


Figure 11.2: (ξ_1, ξ_2) , transformed to O(3) geometry. red and blue: real and imaginary parts of (X, Y, Z) .

for n running in a loop between 1 and $N = 12$. This is a rotation sequence in the complex plane with unit vectors $|\xi_1|^2 + |\xi_2|^2 = 1$ (see computer algebra code [13]). The real and imaginary parts of ξ_1 and ξ_2 are graphed in Fig. 11.1. Since ξ_2 is constant, there is only one arrow for ξ_2 in the complex plane. ξ_1 describes rotated vectors for somewhat more than a half-circle. The ξ vectors have been transformed into 3D space by Eq. (11.26). There are real and imaginary parts of these vectors. The real parts describe a kind of helix, while the imaginary parts are more irregular (see Fig. 11.2). ■

For pure rotations by an angle α , the SU(2) rotation matrix takes the form

$$U = \begin{bmatrix} e^{i\alpha/2} & 0 \\ 0 & e^{-i\alpha/2} \end{bmatrix}, \quad (11.29)$$

while, for a 3D rotation around the Z axis in O(3) space, the corresponding rotation matrix is

$$R = \begin{bmatrix} \cos \alpha & \sin \alpha & 0 \\ -\sin \alpha & \cos \alpha & 0 \\ 0 & 0 & 1 \end{bmatrix}. \quad (11.30)$$

The 2D spinor rotates by half the angle as the 3D vector does. This leads to a topological distinction between both rotation groups. Increasing the angle α by 2π gives the result $U \rightarrow -U$ for the SU(2) rotation, while it gives $R \rightarrow R$ for the O(3) rotation. Any rotation in SU(2) corresponds to a rotation by the doubled angle in O(3). This is the deeper cause for the g factor and the Thomas factor in quantum mechanics.

11.2.4 Pauli matrices

As we have mentioned, the description of spin states requires SU(2) symmetry. The Pauli matrices are Hermitian and unitary 2x2 matrices. They are the basis of the spin operators, which describe observables depending on the spin state. The three *Pauli matrices* are

$$\sigma^1 = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \quad \sigma^2 = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \quad \sigma^3 = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}. \quad (11.31)$$

Sometimes, an additional unit matrix is used:

$$\sigma^0 = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}. \quad (11.32)$$

The Pauli matrices are self-inverse:

$$\begin{aligned} (\sigma^1)^{*T} &= (\sigma^1)^{-1} = \sigma^1, \\ (\sigma^2)^{*T} &= (\sigma^2)^{-1} = \sigma^2, \\ (\sigma^3)^{*T} &= (\sigma^3)^{-1} = \sigma^3. \end{aligned} \quad (11.33)$$

The commutator relation is

$$\begin{aligned} [\sigma^1, \sigma^2] &= i\sigma^3, \\ [\sigma^2, \sigma^3] &= i\sigma^1, \\ [\sigma^3, \sigma^1] &= i\sigma^2, \end{aligned} \quad (11.34)$$

and the anti-commutator relation is

$$\{\sigma^i, \sigma^j\} = \sigma^i \sigma^j + \sigma^j \sigma^i = 2\delta_{ij} \sigma^0. \quad (11.35)$$

A vector of Pauli matrices is defined by

$$\boldsymbol{\sigma} = [\sigma^1, \sigma^2, \sigma^3]. \quad (11.36)$$

This is the *Pauli vector* that contains the three Pauli matrices as components. Its scalar product with the momentum operator $\hat{\mathbf{p}}$ is defined as the *helicity operator* or *handedness* and is a 2x2 matrix:

$$\hat{h} = \boldsymbol{\sigma} \cdot \hat{\mathbf{p}} = \begin{bmatrix} \hat{p}_3 & \hat{p}_1 - i\hat{p}_2 \\ \hat{p}_1 + i\hat{p}_2 & -\hat{p}_3 \end{bmatrix} = \begin{bmatrix} -\hat{p}_Z & -\hat{p}_X + i\hat{p}_Y \\ -\hat{p}_X - i\hat{p}_Y & \hat{p}_Z \end{bmatrix}. \quad (11.37)$$

This is a unitary matrix, as can be seen by comparison with Eq. (11.24). It represents the helicity of a spin vector, i.e., it describes the rotation direction of spin, in relation to the direction of motion of a particle. More precisely, it is the projection of spin on a given direction of linear momentum. With the $\hat{\mathbf{p}}$ operator written out according to (11.11), the helicity operator is

$$\hat{h} = \hbar \begin{bmatrix} i\partial_3 & \partial_2 + i\partial_1 \\ -\partial_2 + i\partial_1 & -i\partial_3 \end{bmatrix}. \quad (11.38)$$

11.2.5 Dirac equation

The Schrödinger equation is a differential equation of first order. Equations of second order like the wave equation or the Klein-Gordon equation require initial conditions for velocities, which would make the solutions dependent on the state of motion. This is not desirable for fundamental equations of quantum mechanics. It was therefore preferable to find a first-order equation for the spin states in SU(2) representation that was invariant in the sense of special relativity. Historically, this was only possible by extending the 2-dimensional spinors of non-relativistic Pauli theory to 4-dimensional spinors that allow a Lorentz-invariant description.

In analogy to the Pauli matrices, 4x4 matrices had to be defined, the γ matrices. These are in *Weyl representation* [2], also called the *spinor representation*, given by

$$\begin{aligned} \gamma^0 &= \begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix}, & \gamma^1 &= \begin{bmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & -1 & 0 & 0 \\ -1 & 0 & 0 & 0 \end{bmatrix}, \\ \gamma^2 &= \begin{bmatrix} 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \\ 0 & i & 0 & 0 \\ -i & 0 & 0 & 0 \end{bmatrix}, & \gamma^3 &= \begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix}. \end{aligned} \quad (11.39)$$

In Dirac's original work, the matrix γ^0 was given by a different matrix:

$$\gamma_{\text{Dirac}}^0 = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix}. \quad (11.40)$$

The Dirac equation is in covariant form

$$(c\gamma^\mu \hat{p}_\mu - mc^2)\psi = 0, \quad (11.41)$$

or, with the momentum operators written out,

$$(ic\hbar\gamma^\mu \partial_\mu - mc^2)\psi = 0, \quad (11.42)$$

where ψ is the 4-spinor of wave functions

$$\psi = \begin{bmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{bmatrix}. \quad (11.43)$$

The Dirac equation (11.41) consists of four single equations, which, fully written out, are

$$\begin{aligned} c(\hat{p}_1 - i\hat{p}_2)\psi_4 + (c\hat{p}_3 + \hat{E})\psi_3 &= mc^2\psi_1, \\ c(\hat{p}_1 + i\hat{p}_2)\psi_3 + (-c\hat{p}_3 + \hat{E})\psi_4 &= mc^2\psi_2, \\ c(-\hat{p}_1 + i\hat{p}_2)\psi_2 + (-c\hat{p}_3 + \hat{E})\psi_1 &= mc^2\psi_3, \\ c(-\hat{p}_1 - i\hat{p}_2)\psi_1 + (c\hat{p}_3 + \hat{E})\psi_2 &= mc^2\psi_4. \end{aligned} \quad (11.44)$$

The components ψ_1 and ψ_3 correspond to spin-up states, while ψ_2 and ψ_4 describe spin-down states. The first and last two components describe the handedness (right or left). Each of them has a spin-up and spin-down component. The pairs of handedness are combined to 2-spinors ϕ_R and ϕ_L by

$$\phi_R = \begin{bmatrix} \psi_1 \\ \psi_2 \end{bmatrix}, \quad \phi_L = \begin{bmatrix} \psi_3 \\ \psi_4 \end{bmatrix}, \quad (11.45)$$

so that the Dirac equation (11.41) can also be written in the form

$$(c\gamma^\mu \hat{p}_\mu - mc^2) \begin{bmatrix} \phi_R \\ \phi_L \end{bmatrix} = 0. \quad (11.46)$$

The current density must be defined in a way that its 0-component, the probability density ρ , is positive definit. In Dirac theory, the *4-current density* is

$$j^\mu = \bar{\psi} \gamma^\mu \psi \quad (11.47)$$

with the *adjoint spinor*

$$\bar{\psi} = \psi^{*T} \gamma^0. \quad (11.48)$$

It follows that

$$\rho = |\psi_1|^2 + |\psi_2|^2 + |\psi_3|^2 + |\psi_4|^2, \quad (11.49)$$

which fulfills the condition of being positive definite. For computational details of the Pauli and Dirac matrices, as well as the Dirac equation, see computer algebra code [14].

A problem of Dirac theory is that, for each solution with positive energy, there is also a solution with negative energy. This can be seen when we consider a particle at rest. Then we have $\mathbf{p} = \mathbf{0}$, and the Dirac equation (11.41) reads

$$\gamma^0 E \psi = mc^2 \psi. \quad (11.50)$$

This is an eigenvalue equation for γ_0 , with eigenvalues +1 and -1, each of them with twofold multiplicity. In the classical limit, we obtain therefore two equations for the rest energy:

$$E = +mc^2, \quad (11.51)$$

$$E = -mc^2. \quad (11.52)$$

Physical particle energies should always be positive. The negative energies are interpreted as a negative “Dirac sea”, in which each particle with positive energy has a negative counterpart. Because of the Pauli principle, each energy state is allowed to be occupied only once. Several interpretations have been given; for example, the Dirac sea was considered as filled with vacuum states of negative energy, and pulling up an electron would produce a hole, which is filled by an electron with positive mass energy E , falling down to energy state $-E$, representing a positron. These problematic interpretations can be abandoned by the Fermion equation of ECE theory, as we will see next.

11.3 Fermion equation

11.3.1 Derivation from the Dirac equation

The aim of this section is to derive an equation equivalent to the Dirac equation, but based on the principles of Cartan geometry. The Dirac equation uses a 4-spinor as wave function. Written out in matrix form, the Dirac equation (11.41) is

$$\hat{E} \begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix} \begin{bmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{bmatrix} + c \begin{bmatrix} 0 & 0 & \sigma \cdot \hat{\mathbf{p}} \\ 0 & 0 & 0 & 0 \\ -\sigma \cdot \hat{\mathbf{p}} & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{bmatrix} = mc^2 \begin{bmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{bmatrix} \quad (11.53)$$

with the 2x2 helicity operator

$$\hat{h} = \sigma \cdot \hat{\mathbf{p}} = \begin{bmatrix} \hat{p}_3 & \hat{p}_1 - i\hat{p}_2 \\ \hat{p}_1 + i\hat{p}_2 & -\hat{p}_3 \end{bmatrix}. \quad (11.54)$$

In ECE theory, all fundamental fields of physics are derived from tetrad elements, as is defined in the ECE axioms of mechanics, electrodynamics and fluid dynamics. Therefore, it follows that the wave functions should also be tetrad elements. In $SU(2)$ geometry, we have right- and left-handed 2-component spinors Φ^R and Φ^L , as introduced in Section 11.2.5:

$$\phi_R = \begin{bmatrix} \psi_1 \\ \psi_2 \end{bmatrix}, \quad \phi_L = \begin{bmatrix} \psi_3 \\ \psi_4 \end{bmatrix}, \quad (11.55)$$

which are column vectors. Using these, we can define a 2x2 tetrad

$$\psi = \begin{bmatrix} q^{(1)}_1 & q^{(1)}_2 \\ q^{(2)}_1 & q^{(2)}_2 \end{bmatrix} = \begin{bmatrix} \psi_1 & \psi_2 \\ \psi_3 & \psi_4 \end{bmatrix} = \begin{bmatrix} (\Phi^R)^T \\ (\Phi^L)^T \end{bmatrix}. \quad (11.56)$$

This tetrad contains the transposed spinors (as line vectors). The spinor indices R and L denote the ECE polarization index a of the tetrad elements q^a_μ , and the lower indices correspond to the spin indices 1 and 2. As introduced in Section 2.5.1, the tetrad is a transformation between the base manifold and the tangent space. A vector V^μ of the base manifold is transformed into a vector V^a of tangent space via the transformation

$$V^a = q^a_\mu V^\mu. \quad (11.57)$$

This holds in general for any dimension of base manifolds and tangent spaces. Applied to quantum mechanics, this means that the wave function matrix (11.56) is a 2x2 tetrad. It transforms spin states V^1, V^2 into spinors (or helicity vectors) V^R, V^L via

$$\begin{bmatrix} V^R \\ V^L \end{bmatrix} = \begin{bmatrix} q^R_1 & q^R_2 \\ q^L_1 & q^L_2 \end{bmatrix} \begin{bmatrix} V^1 \\ V^2 \end{bmatrix}. \quad (11.58)$$

What we have to do is to rewrite the Dirac equation (11.53), so that it contains a tetrad matrix instead of Dirac's 4-spinors. Computer algebra [15] proves that Eq. (11.53) can be cast into the form

$$\hat{E} \begin{bmatrix} \psi_3 & \psi_1 \\ \psi_4 & \psi_2 \end{bmatrix} + c\sigma \cdot \hat{\mathbf{p}} \begin{bmatrix} \psi_3 & -\psi_1 \\ \psi_4 & -\psi_2 \end{bmatrix} = mc^2 \begin{bmatrix} \psi_1 & \psi_3 \\ \psi_2 & \psi_4 \end{bmatrix}. \quad (11.59)$$

This is already the tetrad form sought for. The original ψ tetrad has been permuted in one way or another. This equation can be expressed by the Pauli matrices and the transpose of the ψ tetrad,

$$\psi^T = \begin{bmatrix} \psi_1 & \psi_3 \\ \psi_2 & \psi_4 \end{bmatrix}, \quad (11.60)$$

to obtain:

$$\hat{E}\psi^T\sigma^1 + c\sigma \cdot \hat{\mathbf{p}}(\sigma^1\psi)^T\sigma^3 = mc^2\psi^T. \quad (11.61)$$

(see computer algebra code [15]). An additional transposition of this equation gives the Fermion equation in the form:

$$\boxed{\hat{E}\sigma^1\psi + c\sigma^3\sigma^1\psi(\sigma \cdot \hat{\mathbf{p}})^T = mc^2\psi} \quad (11.62)$$

It has to be noticed that $(\sigma \cdot \hat{\mathbf{p}})^T$ is a left-operator. Written out in components, this equation is

$$\begin{aligned} c(\hat{p}_1 - i\hat{p}_2)\psi_4 + (c\hat{p}_3 + \hat{E})\psi_3 &= mc^2\psi_1, \\ c(\hat{p}_1 + i\hat{p}_2)\psi_3 + (-c\hat{p}_3 + \hat{E})\psi_4 &= mc^2\psi_2, \\ c(-\hat{p}_1 + i\hat{p}_2)\psi_2 + (-c\hat{p}_3 + \hat{E})\psi_1 &= mc^2\psi_3, \\ c(-\hat{p}_1 - i\hat{p}_2)\psi_1 + (c\hat{p}_3 + \hat{E})\psi_2 &= mc^2\psi_4. \end{aligned} \quad (11.63)$$

These equations are identical with the single Eqs. (11.44) of the Dirac equation. The left-operator in (11.62) can be avoided by writing the Fermion equation in the alternative form

$$\boxed{\widehat{E}\psi - c\sigma^3(\widehat{p}_1\psi\sigma^1 - \widehat{p}_2\psi\sigma^2 + \widehat{p}_3\psi\sigma^3) = mc^2\sigma^1\psi} \quad (11.64)$$

(see [4] and computer algebra code [15]). The negative sign of the \widehat{p}_2 term prevents a further simplification. This sign would become positive by redefining the sign of the Pauli matrix

$$\sigma^2 \rightarrow -\sigma^2. \quad (11.65)$$

Such a sign change means a mirroring of the Y axis. A modified set of Pauli matrices σ' (primed Pauli matrices) can then be defined by

$$\sigma'^1 = \sigma^1 = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \quad \sigma'^2 = -\sigma^2 = \begin{bmatrix} 0 & i \\ -i & 0 \end{bmatrix}, \quad \sigma'^3 = \sigma^3 = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}, \quad (11.66)$$

and, for completeness,

$$\sigma'^0 = \sigma^0 = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}. \quad (11.67)$$

Then, the commutator relation (11.34) produces a sign change on the right sides:

$$\begin{aligned} [\sigma'^1, \sigma'^2] &= -i\sigma'^3, \\ [\sigma'^2, \sigma'^3] &= -i\sigma'^1, \\ [\sigma'^3, \sigma'^1] &= -i\sigma'^2. \end{aligned} \quad (11.68)$$

Eq. (11.64) can now be written as

$$\sigma^0\widehat{E}\psi\sigma^0 - c\sigma'^3(\widehat{p}_1\psi\sigma'^1 + \widehat{p}_2\psi\sigma'^2 + \widehat{p}_3\psi\sigma'^3) = mc^2\sigma'^1\psi. \quad (11.69)$$

We define a matrix-form of 4-momentum

$$\pi_\mu = (\pi_0, \pi_1, \pi_2, \pi_3) \quad (11.70)$$

with

$$\pi_0 = \sigma'^0 p_0, \quad \pi_i = -\sigma'^3 p_i, \quad (11.71)$$

where the p_μ are the covariant momentum components (11.11). The momentum π_μ can be made an operator that replaces the \widehat{p}_μ 's, and we can write the Fermion equation (11.64) in the covariant form

$$\boxed{\widehat{\pi}_\mu\psi\sigma'^\mu = mc\sigma'^1\psi} \quad (11.72)$$

This equation is fully equivalent to the Dirac equation with 4-spinors.

11.3.2 Derivation by factorizing the ECE wave equation

The Dirac equation was originally derived from the wave equation by factorization [2]. We do this similarly in a framework of Cartan geometry. The ECE wave equation is identical with the Evans Lemma (2.258) that is a differential equation of second order for the tetrad elements:

$$(\square + R)q^a{}_\mu = 0 \quad (11.73)$$

with the d'Alembert operator

$$\square = \partial^\mu \partial_\mu = \frac{1}{c^2} \frac{\partial^2}{\partial t^2} - \frac{\partial^2}{\partial X^2} - \frac{\partial^2}{\partial Y^2} - \frac{\partial^2}{\partial Z^2} \quad (11.74)$$

(see Section 2.5.5). The eigenvalue R is a scalar curvature and brings general relativity into this equation. In particular, it allows gravitation and quantum mechanics to be coupled. Here, we restrict ourselves to a constant value of R , i.e., to special relativity. From comparison with the Dirac equation, it is

$$R = - \left(\frac{mc}{\hbar^2} \right)^2 \quad (11.75)$$

and has the right dimension of inverse square meters. Then the tetrad matrix, interpreted as a wave function as introduced in Eq. (11.56), appears in the wave equation in the form

$$\left(\square - \left(\frac{mc}{\hbar^2} \right)^2 \right) \psi = 0. \quad (11.76)$$

In the following, we will factorize the wave equation. We start with the Einstein energy equation

$$E^2 - c^2 p^2 = m^2 c^4, \quad (11.77)$$

which can be factorized on the classical level into

$$(E - cp)(E + cp) = m^2 c^4. \quad (11.78)$$

Now, we introduce the operators \hat{E} and $\hat{\mathbf{p}}$. We have to respect SU(2) symmetry, therefore the term cp in Einstein's energy equation is to be replaced by $c\boldsymbol{\sigma} \cdot \hat{\mathbf{p}}$, and the energy operator is $\sigma^0 \hat{E}$. The factorization then is

$$(\hat{E} - c\boldsymbol{\sigma} \cdot \hat{\mathbf{p}})(\hat{E} + c\boldsymbol{\sigma} \cdot \hat{\mathbf{p}}) = m^2 c^4. \quad (11.79)$$

This is a pure operator equation. In order to switch to quantum mechanics, we have to apply the operators to wave functions. Doing it in the way

$$(\hat{E} - c\boldsymbol{\sigma} \cdot \hat{\mathbf{p}})\Phi^R (\hat{E} + c\boldsymbol{\sigma} \cdot \hat{\mathbf{p}})\Phi^L = m^2 c^4 \Phi^R \Phi^L, \quad (11.80)$$

this equation can be written as the product of two single equations:

$$(\hat{E} - c\boldsymbol{\sigma} \cdot \hat{\mathbf{p}})\Phi^R = mc^2 \Phi^L, \quad (11.81)$$

$$(\hat{E} + c\boldsymbol{\sigma} \cdot \hat{\mathbf{p}})\Phi^L = mc^2 \Phi^R. \quad (11.82)$$

This procedure may look somewhat arbitrary, but both equations can also be obtained by applying Lorentz boost transforms in momentum representation of Φ^R and Φ^L [2]. Writing out both equations in components, this gives us

$$\begin{aligned} c(\hat{p}_1 - i\hat{p}_2)\psi_4 + (c\hat{p}_3 + \hat{E})\psi_3 &= mc^2\psi_1, \\ c(\hat{p}_1 + i\hat{p}_2)\psi_3 + (-c\hat{p}_3 + \hat{E})\psi_4 &= mc^2\psi_2, \\ c(-\hat{p}_1 + i\hat{p}_2)\psi_2 + (-c\hat{p}_3 + \hat{E})\psi_1 &= mc^2\psi_3, \\ c(-\hat{p}_1 - i\hat{p}_2)\psi_1 + (c\hat{p}_3 + \hat{E})\psi_2 &= mc^2\psi_4. \end{aligned} \quad (11.83)$$

These equations are identical again to those of (11.63) that in turn are identical to the original Dirac equation (see computer algebra code [15]).

■ **Example 11.2** We discuss a solution of the Fermion equation as an example. We assume a momentum in Z direction for simplicity. Then, the Fermion equations (11.81, 11.82) read, with operators written out:

$$\left(i\hbar \begin{bmatrix} \frac{\partial}{\partial t} & 0 \\ 0 & \frac{\partial}{\partial t} \end{bmatrix} - i\hbar c \begin{bmatrix} \frac{\partial}{\partial Z} & 0 \\ 0 & -\frac{\partial}{\partial Z} \end{bmatrix} \right) \Phi^R = mc^2 \Phi^L, \quad (11.84)$$

$$\left(i\hbar \begin{bmatrix} \frac{\partial}{\partial t} & 0 \\ 0 & \frac{\partial}{\partial t} \end{bmatrix} + i\hbar c \begin{bmatrix} \frac{\partial}{\partial Z} & 0 \\ 0 & -\frac{\partial}{\partial Z} \end{bmatrix} \right) \Phi^L = mc^2 \Phi^R. \quad (11.85)$$

For the spinor components, we make the approach

$$\begin{aligned} \psi_1 &= \exp(-i(\omega_0 t + k_{Z1} Z)), \\ \psi_2 &= \exp(-i(\omega_0 t - k_{Z2} Z)), \\ \psi_3 &= \exp(-i(\omega_0 t + k_{Z1} Z)), \\ \psi_4 &= \exp(-i(\omega_0 t - k_{Z2} Z)). \end{aligned} \quad (11.86)$$

These are plane waves with different wave numbers $+k_{Z1}$ and $-k_{Z2}$ for both spin directions. We show that this is a solution of the Fermion equation within certain constraints. Inserting these functions into Eqs. (11.84, 11.85), and taking the real parts, we obtain for both spinors the component equations

$$\hbar(\omega_0 + c k_{Z1}) \cos(\omega_0 t + k_{Z1} Z) = mc^2 \cos(\omega_0 t + k_{Z1} Z), \quad (11.87)$$

$$\hbar(\omega_0 + c k_{Z2}) \cos(\omega_0 t - k_{Z2} Z) = mc^2 \cos(\omega_0 t - k_{Z2} Z). \quad (11.88)$$

(see computer algebra code [16]). The left and right sides of these equations are compatible, if

$$\hbar(\omega_0 + c k_{Z1}) = mc^2 \quad (11.89)$$

and

$$\hbar(\omega_0 + c k_{Z2}) = mc^2. \quad (11.90)$$

Obviously, we can identify ω_0 with the de Broglie matter frequency. In the case of the rest fermion ($p=0$), we obtain the exact de Broglie relation

$$\hbar\omega_0 = mc^2. \quad (11.91)$$

If the fermion has a non-vanishing momentum, this momentum energy has to be added to the rest energy $\hbar\omega_0$ to obtain the total energy. It has to be mentioned, however, that this is not Einstein's energy equation. For that equation, the summation of the squared energies would be required. ■

11.3.3 Rest fermion

The equations for the fermion at rest are obtained from the Fermion equation with $\mathbf{p} = \mathbf{0}$. From the Fermion equation, for example Eq. (11.62), it follows:

$$E\psi = mc^2 \sigma_1 \psi, \quad (11.92)$$

or, in form of component equations,

$$\begin{aligned} E\psi_1 &= mc^2 \psi_3, \\ E\psi_2 &= mc^2 \psi_4, \\ E\psi_3 &= mc^2 \psi_1, \\ E\psi_4 &= mc^2 \psi_2. \end{aligned} \quad (11.93)$$

The same result for the rest fermion is obtained from the Dirac equation. Concerning negative energy solutions, the arguments are the same as for the Dirac equation. The matrix σ^1 has eigenvalues $+1$ and -1 . Because σ^1 is a 2×2 matrix and not a 4×4 matrix as it is in the Dirac case, the eigenvalues are not two-fold degenerated, but the two signs remain. To investigate this further, we analyse the equation system (11.93). This is a homogeneous system for the variables $\psi_1, \psi_2, \psi_3, \psi_4$. The coefficient matrix is

$$C = \begin{bmatrix} E & 0 & -mc^2 & 0 \\ 0 & E & 0 & -mc^2 \\ -mc^2 & 0 & E & 0 \\ 0 & -mc^2 & 0 & E \end{bmatrix}. \quad (11.94)$$

In order to obtain non-vanishing solutions, the coefficient determinant must be zero. This leads to a quartic equation for E ,

$$E(E^3 - Em^2c^4) - mc^2(E^2mc^2 - m^3c^6) = 0, \quad (11.95)$$

which can be reduced to a quadratic equation with the solutions

$$E_{1,2} = \pm mc^2 \quad (11.96)$$

(see computer algebra code [15]). E must be either positive or negative for the complete equation set (11.93). It is, however, not required to assume the existence of negative energies. In the equation set (11.93), we can propagate the negative sign to the wave functions in the way

$$\begin{aligned} E(-\psi_1) &= mc^2\psi_3, \\ E(-\psi_2) &= mc^2\psi_4, \\ E\psi_3 &= mc^2(-\psi_1), \\ E\psi_4 &= mc^2(-\psi_2). \end{aligned} \quad (11.97)$$

This represents a phase shift in the wave functions ψ_1 and ψ_2 but leaves their absolute values unaltered. There is no need to introduce negative energies. The sign change is a consequence of the fact that there is no external momentum, so there is obviously an additional degree of freedom in the choice of the phase. This choice is consistent over all equations. This argument can also be applied to the Dirac equation in Weyl representation, therefore the problem of negative energies has de facto been solved already years ago. Another argument is: In the spinor form (11.81, 11.82) of the Fermion equation, only positive energies appear for both types of spinors. There is no Pauli matrix present that would allow for negative eigenvalues.

Only when we use the Dirac representation for the γ_0 matrix, Eq. (11.40), the component equations for the rest fermion (11.89) take the decoupled form

$$\begin{aligned} E\psi_1 &= mc^2\psi_1, \\ E\psi_2 &= mc^2\psi_2, \\ -E\psi_3 &= mc^2\psi_3, \\ -E\psi_4 &= mc^2\psi_4. \end{aligned} \quad (11.98)$$

In this case, the phase factor argument does not apply, and there would be real negative energies. We assume that the discussion about negative energies arose from this original set of equations for the Dirac equation. In modern text books, the Weyl representation is used, remedying the problem, but the discussion on negative energy solutions has survived in the literature to this day.

11.3.4 Probability current density

The probability density and current of the Dirac equation have been given in Eqs. (11.47-11.49). For the Fermion equation, they should follow from expressions with Pauli matrices instead of Dirac's γ matrices. In [4], a method with a tracematrix was used, which gives the right probability density, but the current densities differ from those of Dirac theory. Therefore, we prefer a method that gives the same results for both theories. Since the Dirac spinor consists of the same 2-spinors Φ^R and Φ^L that are used in the Fermion equation, we rewrite the definition of the Dirac current j^μ in the suitable form

$$\begin{aligned} j^0 &= (\Phi^R)^+ \sigma^0 \Phi^R + (\Phi^L)^+ \sigma^0 \Phi^L, \\ j^1 &= -(\Phi^R)^+ \sigma^1 \Phi^R + (\Phi^L)^+ \sigma^1 \Phi^L, \\ j^2 &= -(\Phi^R)^+ \sigma^2 \Phi^R + (\Phi^L)^+ \sigma^2 \Phi^L, \\ j^3 &= -(\Phi^R)^+ \sigma^3 \Phi^R + (\Phi^L)^+ \sigma^3 \Phi^L, \end{aligned} \quad (11.99)$$

where a "+" denotes the adjoint spinor. From computer algebra [14, 15], it follows that the current density is identical to that of the Dirac theory. When we denote the real and imaginary parts of the wave functions ψ_j by

$$\psi_j = \phi_j + i\chi_j, \quad (11.100)$$

the current densities are

$$\begin{aligned} j^0 &= \phi_4^2 + \phi_3^2 + \phi_2^2 + \phi_1^2 + \chi_4^2 + \chi_3^2 + \chi_2^2 + \chi_1^2, \\ j^1 &= 2(\phi_3\phi_4 - \phi_1\phi_2 + \chi_3\chi_4 - \chi_1\chi_2), \\ j^2 &= -2(\chi_3\phi_4 - \chi_4\phi_3 - \chi_1\phi_2 + \chi_2\phi_1), \\ j^3 &= -(\phi_4^2 - \phi_3^2 - \phi_2^2 + \phi_1^2 + \chi_4^2 - \chi_3^2 - \chi_2^2 + \chi_1^2). \end{aligned} \quad (11.101)$$

The probability density j^0 is positive definite as required:

$$j^0 = |\psi_1|^2 + |\psi_2|^2 + |\psi_3|^2 + |\psi_4|^2, \quad (11.102)$$

and the current components j^1, j^2, j^3 are real-valued.

11.3.5 CPT invariance

As already discussed in Section 11.2.4, the operator $\hat{h} = \boldsymbol{\sigma} \cdot \hat{\mathbf{p}}$ is the helicity operator, describing a projection of spin on the direction of linear momentum. An inversion of the sign of the operator changes the helicity. This can be seen directly from the equations (11.81, 11.82). Changing the sign of the operator interchanges Φ^R with Φ^L at the same time. This is a parity change operation and can be written by using the parity operator P as

$$P(h) = -h. \quad (11.103)$$

Similarly, parity reverses the coordinates X, Y and Z for a given sense of frame \mathbf{i}, \mathbf{j} and \mathbf{k} in cartesian coordinates. So, for a position vector \mathbf{r} ,

$$P(\mathbf{r}) = -\mathbf{r}, \quad (11.104)$$

or, in short-hand notation:

$$P \rightarrow -P. \quad (11.105)$$

A reversal of time leaves the helicity unchanged, therefore, for the time reversal operator T ,

$$T(h) = h, \quad (11.106)$$

or, in short-hand notation:

$$T \rightarrow T. \quad (11.107)$$

The charge conjugation operator flips the sign of an electric charge. For example, an electron is changed to a positron and vice versa:

$$C(e) = -e. \quad (11.108)$$

In physics, various combinations of the fundamental symmetry operators are used. For the three operators, it holds that

$$CPT \rightarrow (-C)(-P)T = CPT, \quad (11.109)$$

so that physical states remain unchanged under this combination. This is called *CPT conservation*. Therefore, when parity is changed, the charge is also changed, and the Fermion equations (11.62) and (11.72) describe a positron in this case. This means that the character of the wave functions remains as is. Therefore, under a helicity change, the spinor equations (11.81, 11.82),

$$(\hat{E} - c\boldsymbol{\sigma} \cdot \hat{\mathbf{p}})\Phi^R = mc^2\Phi^L, \quad (11.110)$$

$$(\hat{E} + c\boldsymbol{\sigma} \cdot \hat{\mathbf{p}})\Phi^L = mc^2\Phi^R, \quad (11.111)$$

take the form:

$$(\hat{E} + c\boldsymbol{\sigma} \cdot \hat{\mathbf{p}})\Phi^R = mc^2\Phi^L, \quad (11.112)$$

$$(\hat{E} - c\boldsymbol{\sigma} \cdot \hat{\mathbf{p}})\Phi^L = mc^2\Phi^R. \quad (11.113)$$

When a fermion collides with an antifermion, the momenta cancel out, and summing up the first and third equation of the groups above, we obtain:

$$2E\Phi^R = 2mc^2\Phi^L, \quad (11.114)$$

and for the second and fourth equation:

$$2E\Phi^L = 2mc^2\Phi^R. \quad (11.115)$$

In total, we have

$$2E(\Phi^R + \Phi^L) = 2mc^2(\Phi^R + \Phi^L), \quad (11.116)$$

leaving an equation of energy. This corresponds to producing a pair of photons, as is well known from particle processes.

11.3.6 Comparison with Dirac theory

We conclude this section with some of Myron Evans' original and illuminating comments [3]:

By using a 2x2 tetrad wavefunction, the Dirac equation is greatly simplified to Eq. (11.72), which may be generalized to one of unified field theory. This appears to be the first time that the equation of the fermion has been expressed in terms of 2x2 matrices, and so this disposes with the need for 4x4 matrix Dirac algebra, a major advance in mathematics and physics. This basic

advance works its way into fermion, electroweak, strong field and particle theory and this will be the subject of future work.

When an electron and a positron collide, they produce two photons, pure energy as in Eqs. (11.114) and (11.115). The production of the positron from the Dirac equation on the other hand is a non-Baconian process in which the well known Dirac sea has to be used. The Dirac sea is an ad-hoc concept and is asserted without experimental evidence to be the vacuum filled with antifermions that obey the Pauli exclusion principle, another ad-hoc concept but one which happens to work well in spectroscopy. By definition, the Dirac sea is not directly observable, and so is not a Baconian concept. Otherwise, Dirac was a deterministic scientist and rejected the Copenhagen interpretation of quantum mechanics and of his own equation. Indeterminacy is the archetypical non-Baconian concept of the twentieth century, in which physics as a subject was thereby weakened towards the end of the century by a plethora of unobservables such as confined quarks, strings, superstrings, multiple dimensions, spontaneous symmetry breaking, black holes, big bang, dark matter, ark flow, dark universe, the unobserved Higgs boson with undefined energy, abstract internal spaces of gauge theory, approximate symmetries and so forth. These unobservables are rejected in ECE theory wherever they occur. The Einstein field equation has been shown to be mathematically erroneous due to its neglect of spacetime torsion, and Einsteinian cosmology has been replaced by a torsion-based cosmology.

The interpretation of the Dirac equation is greatly complicated by negative energy. It is not clear why the unphysical idea of negative energy was introduced, because it was rejected by Einstein on the classical level. The Dirac antifermion is therefore postulated ad hoc, by invoking an unobservable and non-Baconian Dirac sea to get rid of an unobservable and non-Baconian negative energy. This convoluted thinking leads to the necessity for second quantization, and to the ad-hoc introduction of the Dirac-Jordan-Wigner anticommutator. This anticommutator is claimed to produce antifermions and to “explain” the Pauli exclusion principle. This is a wholly obscure argument, because it is based only on the reversal of sign of phase. In second quantization, the Dirac spinor is expanded in a Fourier series consisting of Hermitian operators. These are conventionally claimed to be creation and annihilation operators acting on number states. However, all that is really happening is a Fourier expansion. For a rest fermion, the Dirac equation is conventionally interpreted in terms of two spinors with positive phase, and two with negative phase. The sign of phase is arbitrarily associated with a change of sign of energy.

In the ECE interpretation of the fermion, things are Baconian and simple. The observable positron is produced from the observable electron by changing helicity and conserving CPT. The ECE equations of the electron and positron are satisfactory single particle equations, and are both positive energy equations. The ECE fermion and antifermion equations also give rigorously non-zero probability density.

12. New spectroscopy

In spectroscopy, electromagnetic waves are radiated onto atoms, molecules and matter, and it is observed, for which frequencies a resonant absorption takes place. Absorption can occur by induction of molecular rotations/vibrations or lattice vibrations in solids. This appears in the microwave and infrared range. For higher frequencies, transitions in the electronic hull are induced, up to emission of electrons from the compound of atoms. Excitations of nucleons in atomic nuclei can arise also. Widely used methods are, for example, ESR (electron spin resonance), PES/XPS (photo or X-ray emission spectroscopy), NMR (nuclear magnetic resonance) and Raman spectroscopy. An overview on the experimental methods is given in [5].

12.1 g factor and spin-orbit coupling

12.1.1 g factor

To describe excitations by the theory, electromagnetic fields have to be incorporated into the Fermion equation. We do this in a similar way as is usually worked out for the Dirac equation [2, 6]. In the presence of an electromagnetic field, the generalized terms for energy and momentum are:

$$E \rightarrow E - e\Phi, \quad (12.1)$$

$$\mathbf{p} \rightarrow \mathbf{p} - e\mathbf{A}, \quad (12.2)$$

where $-e$ is the charge of the electron, Φ is the electric potential and \mathbf{A} is the vector potential of the external electromagnetic field. So far, this is classical electrodynamics. The same modification is assumed for the operators:

$$\hat{E} \rightarrow \hat{E} - e\Phi, \quad (12.3)$$

$$\hat{\mathbf{p}} \rightarrow \hat{\mathbf{p}} - e\mathbf{A}. \quad (12.4)$$

With these generalizations, the Fermion equation in chiral representation, Eqs. (11.81, 11.82), reads

$$\left(\hat{E} - e\Phi - c\boldsymbol{\sigma} \cdot (\hat{\mathbf{p}} - e\mathbf{A}) \right) \Phi^R = mc^2 \Phi^L, \quad (12.5)$$

$$\left(\hat{E} - e\Phi + c\boldsymbol{\sigma} \cdot (\hat{\mathbf{p}} - e\mathbf{A}) \right) \Phi^L = mc^2 \Phi^R. \quad (12.6)$$

Φ^R and Φ^L are the 2-spinors, as defined in Eq. (11.55):

$$\phi_R = \begin{bmatrix} \psi_1 \\ \psi_2 \end{bmatrix}, \quad \phi_L = \begin{bmatrix} \psi_3 \\ \psi_4 \end{bmatrix}, \quad (12.7)$$

Now, we replace the operators in (12.5, 12.6) by the original quantities E and \mathbf{p} , multiply both equations and divide formally by Φ^L . We obtain

$$((E - e\Phi)^2 - c^2[\boldsymbol{\sigma} \cdot (\mathbf{p} - e\mathbf{A})][\boldsymbol{\sigma} \cdot (\mathbf{p} - e\mathbf{A})]) \Phi^R = m^2 c^4 \Phi^R. \quad (12.8)$$

The expressions $\boldsymbol{\sigma} \cdot (\mathbf{p} - e\mathbf{A})$ are 2x2 matrices by definition. The square brackets are omitted by convention, assuming that the dot between $\boldsymbol{\sigma}$ and $\mathbf{p} - e\mathbf{A}$ has mathematical operator precedence. Then, we can write

$$((E - e\Phi)^2 - c^2 \boldsymbol{\sigma} \cdot (\mathbf{p} - e\mathbf{A}) \boldsymbol{\sigma} \cdot (\mathbf{p} - e\mathbf{A})) \Phi^R = m^2 c^4 \Phi^R. \quad (12.9)$$

For the product of the Pauli vectors, we find by computer algebra:

$$\boldsymbol{\sigma} \cdot (\mathbf{p} - e\mathbf{A}) \boldsymbol{\sigma} \cdot (\mathbf{p} - e\mathbf{A}) = (\mathbf{p} - e\mathbf{A})^2, \quad (12.10)$$

(see computer algebra code [17]). To be mathematically exact, we would had to add the unit matrix σ^0 on the right-hand side. This matrix is often omitted as well. Relation (12.10) is a special case of the *Pauli algebra*

$$\boldsymbol{\sigma} \cdot \mathbf{F} \boldsymbol{\sigma} \cdot \mathbf{G} = \mathbf{F} \cdot \mathbf{g} + i\boldsymbol{\sigma} \cdot (\mathbf{F} \times \mathbf{G}) \quad (12.11)$$

for vectors \mathbf{F} and \mathbf{G} and has also been proven by computer algebra [17]. In Eq. (12.10), we have the special case

$$\mathbf{F} = \mathbf{G} = \mathbf{p} - e\mathbf{A}, \quad (12.12)$$

and with $\mathbf{p} \times \mathbf{p} = \mathbf{A} \times \mathbf{A} = \mathbf{0}$, Eq. (12.11) takes the form:

$$\boldsymbol{\sigma} \cdot (\mathbf{p} - e\mathbf{A}) \boldsymbol{\sigma} \cdot (\mathbf{p} - e\mathbf{A}) = (\mathbf{p} - e\mathbf{A})^2 - ie\boldsymbol{\sigma} \cdot (\mathbf{p} \times \mathbf{A} + \mathbf{A} \times \mathbf{p}). \quad (12.13)$$

The term on the far right would also vanish, if we stayed with the vector algebra, but we now re-introduce the operator

$$\hat{\mathbf{p}} = -i\hbar\nabla, \quad (12.14)$$

so that (12.13) becomes

$$\boldsymbol{\sigma} \cdot (\hat{\mathbf{p}} - e\mathbf{A}) \boldsymbol{\sigma} \cdot (\hat{\mathbf{p}} - e\mathbf{A}) = (\hat{\mathbf{p}} - e\mathbf{A})^2 - ie\boldsymbol{\sigma} \cdot (\hat{\mathbf{p}} \times \mathbf{A} + \mathbf{A} \times \hat{\mathbf{p}}). \quad (12.15)$$

The cross product terms on the right-hand side do not cancel out. Written out, this part, applied to Φ^R , is

$$\begin{aligned} -ie\boldsymbol{\sigma} \cdot (\hat{\mathbf{p}} \times \mathbf{A} + \mathbf{A} \times \hat{\mathbf{p}}) \Phi^R &= -e\hbar\boldsymbol{\sigma} \cdot (\nabla \times \mathbf{A} + \mathbf{A} \times \nabla) \Phi^R \\ &= -e\hbar\boldsymbol{\sigma} \cdot (\nabla \times (\mathbf{A}\Phi^R) + \mathbf{A} \times \nabla\Phi^R) \\ &= -e\hbar\boldsymbol{\sigma} \cdot ((\nabla \times \mathbf{A})\Phi^R + \nabla\Phi^R \times \mathbf{A} + \mathbf{A} \times \nabla\Phi^R) \\ &= -e\hbar\boldsymbol{\sigma} \cdot (\nabla \times \mathbf{A})\Phi^R \\ &= -e\hbar(\boldsymbol{\sigma} \cdot \mathbf{B})\Phi^R, \end{aligned} \quad (12.16)$$

where we have applied the product rule for the Nabla operator and the definition of the magnetic field

$$\mathbf{B} = \nabla \times \mathbf{A}. \quad (12.17)$$

This is the definition of classical electrodynamics, which is the same as in ECE2 theory, if we identify the vector potential \mathbf{A} with the ECE2 vector potential \mathbf{W} (see Section 6.1.3, Eq. (6.122)).

Inserting this result into (12.9), we obtain

$$((E - e\Phi)^2 - m^2 c^4) \Phi^R = c^2 ((\mathbf{p} - e\mathbf{A})^2 - e\hbar\boldsymbol{\sigma} \cdot \mathbf{B}) \Phi^R. \quad (12.18)$$

For simplicity and clarity, we assume that there is no external electric potential:

$$\Phi = 0. \quad (12.19)$$

Eq. (12.18) then becomes

$$(E^2 - m^2 c^4) \Phi^R = c^2 ((\mathbf{p} - e\mathbf{A})^2 - e\hbar\boldsymbol{\sigma} \cdot \mathbf{B}) \Phi^R. \quad (12.20)$$

We replace $E^2 - m^2 c^4$ with the relativistic momentum p by using Einstein's energy equation:

$$p^2 c^2 = E^2 - m^2 c^4. \quad (12.21)$$

Then, Eq. (12.18) becomes

$$\frac{1}{2m} p^2 \Phi^R = \frac{1}{2m} ((\mathbf{p} - e\mathbf{A})^2 - e\hbar\boldsymbol{\sigma} \cdot \mathbf{B}) \Phi^R. \quad (12.22)$$

Introducing the Hamiltonian \hat{H} , we can write this equation in the form

$$E_{\text{kin}} \Phi^R = \hat{H} \Phi^R \quad (12.23)$$

with

$$E_{\text{kin}} = \frac{p^2}{2m} \quad (12.24)$$

and

$$\hat{H} = \frac{1}{2m} ((\mathbf{p} - e\mathbf{A})^2 - e\hbar\boldsymbol{\sigma} \cdot \mathbf{B}). \quad (12.25)$$

This is a relativistic form of the Schrödinger equation. The second term of the Hamiltonian describes the magnetic interaction energy \hat{H}_{int} , which is a matrix and reads for a magnetic field only in the Z direction:

$$\hat{H}_{\text{int}} = -\frac{1}{2m} e\hbar\boldsymbol{\sigma} \cdot \mathbf{B} = -\frac{e\hbar}{2m} \begin{bmatrix} B_Z & 0 \\ 0 & -B_Z \end{bmatrix} = -\frac{e}{m} \mathbf{S} \cdot \mathbf{B} \quad (12.26)$$

with the spin angular momentum

$$\mathbf{S} = \frac{\hbar}{2} \boldsymbol{\sigma}. \quad (12.27)$$

This result is verified experimentally in ESR and NMR. The magnetic dipole moment of the orbital angular momentum is

$$\mathbf{m}_L = -\frac{e\hbar}{2m} \mathbf{L}. \quad (12.28)$$

and the magnetic moment of the total angular momentum is

$$\mathbf{m}_{\text{tot}} = -\frac{e\hbar}{2m} (\mathbf{L} + g\mathbf{S}), \quad (12.29)$$

requiring a ‘‘correction factor’’ g , called *gyromagnetic factor*, *g factor* or *Landé factor*. The ECE Fermion equation produces the g factor of 2 for the electron without the use of negative energy. The exact g factor deviates from 2 by radiative corrections, so that it actually amounts to $g \approx 2.00233$.

12.1.2 Spin-orbit coupling

We start again with the Fermion equation in chiral representation, Eqs. (11.81, 11.82), from which Eq. (12.9) was derived:

$$\left((E - e\Phi)^2 - c^2 \boldsymbol{\sigma} \cdot (\mathbf{p} - e\mathbf{A}) \boldsymbol{\sigma} \cdot (\mathbf{p} - e\mathbf{A}) \right) \Phi^R = m^2 c^4 \Phi^R. \quad (12.30)$$

We assume that there is no magnetic vector potential \mathbf{A} , but an electric potential Φ . Then, this equation becomes

$$\left((E - e\Phi)^2 - c^2 \boldsymbol{\sigma} \cdot \mathbf{p} \boldsymbol{\sigma} \cdot \mathbf{p} \right) \Phi^R = m^2 c^4 \Phi^R. \quad (12.31)$$

Dividing by $E - e\Phi$, we obtain

$$\left(E - e\Phi - c^2 \frac{\boldsymbol{\sigma} \cdot \mathbf{p} \boldsymbol{\sigma} \cdot \mathbf{p}}{E - e\Phi} \right) \Phi^R = \frac{m^2 c^4}{E - e\Phi} \Phi^R, \quad (12.32)$$

and by adding $mc^2 \Phi^R$ on both sides:

$$\left(E + mc^2 - e\Phi - c^2 \frac{\boldsymbol{\sigma} \cdot \mathbf{p} \boldsymbol{\sigma} \cdot \mathbf{p}}{E - e\Phi} \right) \Phi^R = \left(\frac{m^2 c^4}{E - e\Phi} + mc^2 \right) \Phi^R. \quad (12.33)$$

Now we use the non-relativistic approximation

$$E = \gamma mc^2 \approx mc^2 \quad (12.34)$$

and obtain

$$\left(2mc^2 - e\Phi - c^2 \frac{\boldsymbol{\sigma} \cdot \mathbf{p} \boldsymbol{\sigma} \cdot \mathbf{p}}{E - e\Phi} \right) \Phi^R = \left(\frac{m^2 c^4}{E - e\Phi} + mc^2 \right) \Phi^R. \quad (12.35)$$

Multiplying by $E - e\Phi$ gives

$$(2mc^2 - e\Phi) (E - e\Phi) \Phi^R = (c^2 \boldsymbol{\sigma} \cdot \mathbf{p} \boldsymbol{\sigma} \cdot \mathbf{p} + mc^2 (mc^2 + E - e\Phi)) \Phi^R, \quad (12.36)$$

and repeating the above non-relativistic approximation on the right side gives

$$(2mc^2 - e\Phi) (E - e\Phi) \Phi^R = (c^2 \boldsymbol{\sigma} \cdot \mathbf{p} \boldsymbol{\sigma} \cdot \mathbf{p} + mc^2 (2mc^2 - e\Phi)) \Phi^R, \quad (12.37)$$

which leads to

$$(E - e\Phi) \Phi^R = \left(c^2 \frac{\boldsymbol{\sigma} \cdot \mathbf{p} \boldsymbol{\sigma} \cdot \mathbf{p}}{2mc^2 - e\Phi} + mc^2 \right) \Phi^R. \quad (12.38)$$

We can write this equation in the form

$$E \Phi^R = \hat{H} \Phi^R \quad (12.39)$$

with the Hamiltonian

$$H = mc^2 + e\Phi + c^2 \frac{\boldsymbol{\sigma} \cdot \mathbf{p} \boldsymbol{\sigma} \cdot \mathbf{p}}{2mc^2 - e\Phi}. \quad (12.40)$$

Because of $e\Phi \ll mc^2$, the denominator of the momentum term can be approximated, resulting in

$$H = mc^2 + e\Phi + \frac{1}{2m} \boldsymbol{\sigma} \cdot \mathbf{p} \left(1 + \frac{e\Phi}{2mc^2} \right) \boldsymbol{\sigma} \cdot \mathbf{p}. \quad (12.41)$$

Here, we have written the approximated term between both terms $\boldsymbol{\sigma} \cdot \mathbf{p}$, which was a deliberate decision (see discussion below). The term with $e\Phi/2mc^2$ is the *spin-orbit coupling* term, therefore this part of the Hamiltonian is

$$H_{s-o} = \frac{e}{4m^2c^2} \boldsymbol{\sigma} \cdot \mathbf{p} \Phi \boldsymbol{\sigma} \cdot \mathbf{p}. \quad (12.42)$$

The extra factor of 2 in the denominator is the *Thomas factor*. When a spinning electron makes one rotation in the observer frame around the atomic nucleus, it made two spin rotations in its local frame.

We have to explain why we wrote the term with Φ in Eq. (12.41) in the middle between the two terms $\boldsymbol{\sigma} \cdot \mathbf{p}$. So far, we have not introduced operators, so that this seems to be arbitrary. However, as soon as we replace the momentum \mathbf{p} by its operator, it makes a difference where to place a function standing originally behind multiple operators. The current choice is arbitrary and only justified by the fact that the right experimental results follow. The situation gets even more arbitrary when we decide which functions \mathbf{p} have to be replaced by an operator, one or both of them. This decision depends again on the correctness of the results, when they are compared with experimental values. Quantum mechanics is empirical at this point.

We develop the spin-orbit term with the first momentum function rewritten as operator:

$$\begin{aligned} \boldsymbol{\sigma} \cdot \mathbf{p} \Phi \boldsymbol{\sigma} \cdot \mathbf{p} &= -i\hbar \boldsymbol{\sigma} \cdot \nabla (\Phi \boldsymbol{\sigma} \cdot \mathbf{p}) \\ &= -i\hbar \boldsymbol{\sigma} \cdot (\nabla \Phi) \boldsymbol{\sigma} \cdot \mathbf{p} + \Phi \boldsymbol{\sigma} \cdot \mathbf{p} \boldsymbol{\sigma} \cdot \mathbf{p} \\ &= i\hbar (\boldsymbol{\sigma} \cdot \mathbf{E}) (\boldsymbol{\sigma} \cdot \mathbf{p}) + \Phi p^2. \end{aligned} \quad (12.43)$$

In the last line, we have introduced the electric field strenght

$$\mathbf{E} = -\nabla \Phi. \quad (12.44)$$

The usage of the momentum operator is quite tricky. In the first line, we have to apply the product rule to $\Phi \boldsymbol{\sigma} \cdot \mathbf{p}$. The application to the first factor Φ is standard, but instead applying it to the second factor in the next summand, we have inserted the momentum function again. Therefore, this term reads $\Phi \boldsymbol{\sigma} \cdot \mathbf{p} \boldsymbol{\sigma} \cdot \mathbf{p}$. Finally, the Pauli identity $\boldsymbol{\sigma} \cdot \mathbf{p} \boldsymbol{\sigma} \cdot \mathbf{p} = p^2$ has been applied in the last line. This is indeed a tricky and very selective application of quantization rules.

Next, we apply the Pauli algebra

$$\boldsymbol{\sigma} \cdot \mathbf{E} \boldsymbol{\sigma} \cdot \mathbf{p} = \mathbf{E} \cdot \mathbf{p} + i\boldsymbol{\sigma} \cdot (\mathbf{E} \times \mathbf{p}). \quad (12.45)$$

So we obtain for (12.43):

$$\boldsymbol{\sigma} \cdot \mathbf{p} \Phi \boldsymbol{\sigma} \cdot \mathbf{p} = i\hbar \mathbf{E} \cdot \mathbf{p} - \hbar \boldsymbol{\sigma} \cdot (\mathbf{E} \times \mathbf{p}) + \Phi p^2. \quad (12.46)$$

Taking the real part and omitting the third term on the right-hand side, the spin-orbit Hamiltonian is

$$\hat{H}_{s-o} = -\frac{e\hbar}{4m^2c^2} \boldsymbol{\sigma} \cdot (\mathbf{E} \times \mathbf{p}). \quad (12.47)$$

With the spin operator

$$\hat{\mathbf{S}} = \frac{1}{2} \hbar \boldsymbol{\sigma}, \quad (12.48)$$

it follows that

$$\hat{H}_{s-o} = -\frac{e}{2m^2c^2} \hat{\mathbf{S}} \cdot (\mathbf{E} \times \mathbf{p}). \quad (12.49)$$

By insertion of the Coulomb potential of the proton,

$$\Phi = \frac{e}{4\pi\epsilon_0 r}, \quad (12.50)$$

we obtain the electric field of the Hydrogen atom:

$$\mathbf{E} = -\nabla\Phi = \frac{e^2}{4\pi\epsilon_0} \frac{\mathbf{r}}{r^3}. \quad (12.51)$$

Using the classical angular momentum,

$$\mathbf{L} = \mathbf{r} \times \mathbf{p}, \quad (12.52)$$

and considering it as an operator, the spin-orbit Hamiltonian can finally be written as

$$\hat{H}_{s-o} = -\frac{e^2}{4\pi\epsilon_0 r^3} \frac{\hat{\mathbf{S}} \cdot \hat{\mathbf{L}}}{2m^2 c^2} \quad (12.53)$$

or

$$\hat{H}_{s-o} = -\xi(r) \hat{\mathbf{S}} \cdot \hat{\mathbf{L}} \quad (12.54)$$

with the spin-orbit function

$$\xi(r) = \frac{e^2}{8\pi\epsilon_0 m^2 c^2 r^3}. \quad (12.55)$$

Spin-orbit coupling is a coupling between the spin and orbital angular momenta. The spin-orbit splitting of spectra in Hydrogen is small (about 10^{-5} eV) but well detectable and grows with the fourth power of the ordinal number of atoms. The derivation in this section can alternatively be based on the Dirac equation in spinor representation, but the Fermion equation is simpler and a part of ECE quantum mechanics. The derivation contains non-relativistic approximations and a very tricky usage of quantum operators.

■ **Example 12.1** As an example for a different usage of the quantization rules, we derive the *Darwin term*, which is observed in the fine structure of spectra. In Eq. (12.42), we have quantized only the first appearance of $\boldsymbol{\sigma} \cdot \mathbf{p}$. Now, we apply quantization to the second term also. This term operates on the wave function. The Pauli vector $\boldsymbol{\sigma}$ is considered as a function, not as a spin operator. Then, we obtain:

$$\boldsymbol{\sigma} \cdot \mathbf{p} \Phi \boldsymbol{\sigma} \cdot \mathbf{p} \Phi^R = -\hbar^2 \boldsymbol{\sigma} \cdot \nabla (\Phi \boldsymbol{\sigma} \cdot \nabla \Phi^R) = -\hbar^2 (\nabla \Phi \nabla \Phi^R + \Phi \nabla^2 \Phi^R). \quad (12.56)$$

With the constants from Eq. (12.42), the Hamiltonian of the Darwin term is the first term and operates as

$$\hat{H}_{\text{Darwin}} \Phi^R = -\frac{e\hbar^2}{4m^2 c^2} \nabla \Phi \nabla \Phi^R. \quad (12.57)$$

The Darwin term can be interpreted as an interaction of the nucleus with the electron and is effective only near to the nucleus, because there the term $\nabla \Phi$ of the Coulomb potential Φ is largest. In the picture of quantum oscillations, this is a smearing out of the electrostatic interaction between the electron and the nucleus. It has only an effect on s orbitals, because other orbitals (p, d, \dots) have a vanishing probability density at the origin, where the proton resides. ■

12.2 ESOR

A new type of spectroscopic effect is investigated, called *electron-spin-orbit resonance (ESOR)*. This is derived from the anomalous Zeeman effect, which will be described before the specific ESOR is developed.

12.2.1 Standard Hamiltonian of the anomalous Zeeman effect

In Section 12.1.1, we have derived an expression for the interaction of a magnetic field with the spin angular momentum of the electron. Now, we will do this for an electron including both the spin and orbital momentum. In the preceding section and in Example 12.1, we have already seen that different forms of operator equations can be derived from the equation for spin-orbit coupling (12.41):

$$H = mc^2 + e\Phi + \frac{1}{2m} \boldsymbol{\sigma} \cdot \mathbf{p} \left(1 + \frac{e\Phi}{2mc^2} \right) \boldsymbol{\sigma} \cdot \mathbf{p}. \quad (12.58)$$

This equation was obtained by several approximations applied to the chiral Fermion equation. Now, we add a vector potential, using the generalized momentum $\mathbf{p} - e\mathbf{A}$, and insert this into the above equation:

$$H = mc^2 + e\Phi + \frac{1}{2m} \boldsymbol{\sigma} \cdot (\mathbf{p} - e\mathbf{A}) \left(1 + \frac{e\Phi}{2mc^2} \right) \boldsymbol{\sigma} \cdot (\mathbf{p} - e\mathbf{A}). \quad (12.59)$$

First, we omit the spin-orbit coupling term, because this was already considered separately in the preceding section. Then, we omit the quadratic terms in the product of the terms of $\boldsymbol{\sigma} \cdot (\mathbf{p} - e\mathbf{A})$, obtaining a Hamiltonian of the linear parts:

$$H_1 = -\frac{1}{2m} (\boldsymbol{\sigma} \cdot \mathbf{A} \boldsymbol{\sigma} \cdot \mathbf{p} + \boldsymbol{\sigma} \cdot \mathbf{p} \boldsymbol{\sigma} \cdot \mathbf{A}). \quad (12.60)$$

The Pauli algebra (12.11) gives us:

$$\boldsymbol{\sigma} \cdot \mathbf{A} \boldsymbol{\sigma} \cdot \mathbf{p} = \mathbf{A} \cdot \mathbf{p} + i\boldsymbol{\sigma} \cdot (\mathbf{A} \times \mathbf{p}), \quad (12.61)$$

$$\boldsymbol{\sigma} \cdot \mathbf{p} \boldsymbol{\sigma} \cdot \mathbf{A} = \mathbf{p} \cdot \mathbf{A} + i\boldsymbol{\sigma} \cdot (\mathbf{p} \times \mathbf{A}). \quad (12.62)$$

By regarding $\boldsymbol{\sigma}$ as a function, it follows

$$H_1 = -\frac{e}{2m} (\mathbf{A} \cdot \mathbf{p} + \mathbf{p} \cdot \mathbf{A} + i\boldsymbol{\sigma} \cdot (\mathbf{A} \times \mathbf{p}) + i\boldsymbol{\sigma} \cdot (\mathbf{p} \times \mathbf{A})). \quad (12.63)$$

For a uniform magnetic field, the vector potential is

$$\mathbf{A} = \frac{1}{2} \mathbf{B} \times \mathbf{r} \quad (12.64)$$

(see computer algebra code [17]). It follows that

$$H_1 = -\frac{e}{4m} ((\mathbf{B} \times \mathbf{r}) \cdot \mathbf{p} + \mathbf{p} \cdot (\mathbf{B} \times \mathbf{r}) + i\boldsymbol{\sigma} \cdot ((\mathbf{B} \times \mathbf{r}) \times \mathbf{p}) + i\boldsymbol{\sigma} \cdot (\mathbf{p} \times (\mathbf{B} \times \mathbf{r}))). \quad (12.65)$$

By regarding \mathbf{p} as a function, the triple product is:

$$\mathbf{B} \times \mathbf{r} \cdot \mathbf{p} = \mathbf{p} \cdot \mathbf{B} \times \mathbf{r} = \mathbf{B} \cdot \mathbf{r} \times \mathbf{p} = \mathbf{B} \cdot \mathbf{L}, \quad (12.66)$$

where \mathbf{L} is the classical angular momentum. Then, the Hamiltonian (12.63), applied to the wave function ψ , becomes

$$H_1 \psi = -\frac{e}{2m} (\mathbf{L} \cdot \mathbf{B} + i\boldsymbol{\sigma} \cdot (\mathbf{A} \times \mathbf{p}) + i\boldsymbol{\sigma} \cdot (\mathbf{p} \times \mathbf{A})) \psi. \quad (12.67)$$

At this stage, \mathbf{p} is regarded as an operator:

$$\mathbf{p} = -i\hbar\nabla, \quad (12.68)$$

which results in

$$\hat{H}_1 \psi = -\frac{e}{2m} (\mathbf{L} \cdot \mathbf{B} + \hbar\boldsymbol{\sigma} \cdot (\mathbf{A} \times \nabla) + \hbar\boldsymbol{\sigma} \cdot (\nabla \times \mathbf{A})) \psi. \quad (12.69)$$

Inserting the definition $\mathbf{B} = \nabla \times \mathbf{A}$ gives

$$\hat{H}_1 \psi = -\frac{e}{2m} (\mathbf{L} \cdot \mathbf{B} + \hbar\boldsymbol{\sigma} \cdot (\mathbf{A} \times \nabla) + \hbar\boldsymbol{\sigma} \cdot \mathbf{B}) \psi. \quad (12.70)$$

Neglecting the term with $\mathbf{A} \times \nabla \psi$, we finally obtain

$$\hat{H}_1 \psi = -\frac{e}{2m} (\mathbf{L} \cdot \mathbf{B} + \hbar\boldsymbol{\sigma} \cdot \mathbf{B}) \psi. \quad (12.71)$$

Using the spin operator

$$\hat{\mathbf{S}} = \frac{\hbar}{2}\boldsymbol{\sigma}, \quad (12.72)$$

this equation can be written in the form

$$\hat{H}_1 \psi = -\frac{e}{2m} (\hat{\mathbf{L}} \cdot \mathbf{B} + 2\hat{\mathbf{S}} \cdot \mathbf{B}) \psi = -\frac{e}{2m} \hat{\mathbf{J}} \cdot \mathbf{B} \psi \quad (12.73)$$

with the total angular momentum operator

$$\hat{\mathbf{J}} = \hat{\mathbf{L}} + 2\hat{\mathbf{S}}. \quad (12.74)$$

For multi-electron systems, the Landé factor g_J has to be inserted, which is

$$g_J = 1 + \frac{J(J+1) - S(S+1) - L(L+1)}{2J(J+1)}, \quad (12.75)$$

where J is the quantum number of the total angular momentum:

$$J = L + S, \dots, |L - S|. \quad (12.76)$$

So the general result of (12.73) is

$$\boxed{\hat{H}_1 \psi = -\frac{e}{2m} g_J \hat{\mathbf{J}} \cdot \mathbf{B} \psi} \quad (12.77)$$

This Hamiltonian describes the *anomalous Zeeman effect*, which is the absorption of light by electrons with spin in a magnetic field. Together with the Hamiltonian of spin-orbit coupling (12.54), the ESR spectra are produced. The complete ESR Hamiltonian is

$$\hat{H} = \hat{H}_1 + \hat{H}_{s-o} = -\frac{e}{2m} g_J \hat{\mathbf{J}} \cdot \mathbf{B} - \xi(r) \hat{\mathbf{S}} \cdot \hat{\mathbf{L}}. \quad (12.78)$$

When we derived H_1 , we have used the operators for \mathbf{p} in both cases of its occurrence in Eq. (12.67). For deriving H_{s-o} , only the first occurrence of \mathbf{p} was converted to an operator. In the final result (12.54), $\mathbf{S} \cdot \mathbf{L}$ was considered as an operator, which has the known eigenvalues

$$\langle \hat{\mathbf{S}} \cdot \hat{\mathbf{L}} \rangle = \frac{\hbar^2}{2} (j(j+1) - l(l+1) - s(s+1)) \quad (12.79)$$

for a single electron. It is seen that the use of \mathbf{p} and $\boldsymbol{\sigma}$ as functions or operators is arbitrary. The results are accepted because they are correct experimentally.

12.2.2 ESOR Hamiltonian

In the following, we derive the *electron spin-orbit resonance* (ESOR) Hamiltonian, a new type of resonance. We proceed according to [7] and start with the relations of the Pauli algebra:

$$\boldsymbol{\sigma} \cdot \mathbf{p} = \frac{1}{r^2} \boldsymbol{\sigma} \cdot \mathbf{r} (\mathbf{r} \cdot \mathbf{p} + i \boldsymbol{\sigma} \cdot \mathbf{L}), \quad (12.80)$$

$$\boldsymbol{\sigma} \cdot \mathbf{A} = \frac{1}{r^2} \boldsymbol{\sigma} \cdot \mathbf{r} (\mathbf{r} \cdot \mathbf{A} + i \boldsymbol{\sigma} \cdot (\mathbf{r} \times \mathbf{A})) \quad (12.81)$$

(see computer algebra code [17] for a proof). The product of both equations is

$$\begin{aligned} \boldsymbol{\sigma} \cdot \mathbf{p} \boldsymbol{\sigma} \cdot \mathbf{A} &= \frac{1}{r^2} (\mathbf{r} \cdot \mathbf{p} \mathbf{r} \cdot \mathbf{A} - \boldsymbol{\sigma} \cdot \mathbf{L} \boldsymbol{\sigma} \cdot (\mathbf{r} \times \mathbf{A})) \\ &\quad + \frac{i}{r^2} (\mathbf{r} \cdot \mathbf{p} \boldsymbol{\sigma} \cdot (\mathbf{r} \times \mathbf{A}) + \boldsymbol{\sigma} \cdot \mathbf{L} \mathbf{r} \cdot \mathbf{A}). \end{aligned} \quad (12.82)$$

Because of

$$\mathbf{r} \cdot \mathbf{A} = 0 \quad (12.83)$$

(see [17]), this equation simplifies to

$$\boldsymbol{\sigma} \cdot \mathbf{p} \boldsymbol{\sigma} \cdot \mathbf{A} = \frac{1}{r^2} \boldsymbol{\sigma} \cdot \mathbf{L} \boldsymbol{\sigma} \cdot (\mathbf{A} \times \mathbf{r}) + \frac{i}{r^2} \mathbf{r} \cdot \mathbf{p} \boldsymbol{\sigma} \cdot (\mathbf{r} \times \mathbf{A}). \quad (12.84)$$

According to another theorem of the Pauli algebra [17], we have

$$\boldsymbol{\sigma} \cdot \mathbf{p} \boldsymbol{\sigma} \cdot \mathbf{A} = \mathbf{p} \cdot \mathbf{A} + i \boldsymbol{\sigma} \cdot (\mathbf{p} \times \mathbf{A}). \quad (12.85)$$

Comparing the real and imaginary parts of the last two equations, it follows that

$$\mathbf{p} \cdot \mathbf{A} = \frac{1}{r^2} \boldsymbol{\sigma} \cdot \mathbf{L} \boldsymbol{\sigma} \cdot (\mathbf{A} \times \mathbf{r}), \quad (12.86)$$

$$\boldsymbol{\sigma} \cdot (\mathbf{p} \times \mathbf{A}) = \frac{1}{r^2} \mathbf{r} \cdot \mathbf{p} \boldsymbol{\sigma} \cdot (\mathbf{r} \times \mathbf{A}), \quad (12.87)$$

so that Eq. (12.85) becomes

$$\boldsymbol{\sigma} \cdot \mathbf{p} \boldsymbol{\sigma} \cdot \mathbf{A} = \frac{1}{r^2} \boldsymbol{\sigma} \cdot \mathbf{L} \boldsymbol{\sigma} \cdot (\mathbf{A} \times \mathbf{r}) + \frac{i}{r^2} \mathbf{r} \cdot \mathbf{p} \boldsymbol{\sigma} \cdot (\mathbf{r} \times \mathbf{A}). \quad (12.88)$$

On the other hand, we obtain from the identities (12.80, 12.81) for the interchanged factors on the left side:

$$\boldsymbol{\sigma} \cdot \mathbf{A} \boldsymbol{\sigma} \cdot \mathbf{p} = \frac{1}{r^2} (\mathbf{r} \cdot \mathbf{A} + i \boldsymbol{\sigma} \cdot (\mathbf{r} \times \mathbf{A})) (\mathbf{r} \cdot \mathbf{p} + i \boldsymbol{\sigma} \cdot \mathbf{L}), \quad (12.89)$$

which, because of (12.83), simplifies to

$$\begin{aligned} \boldsymbol{\sigma} \cdot \mathbf{A} \boldsymbol{\sigma} \cdot \mathbf{p} &= \frac{i}{r^2} \boldsymbol{\sigma} \cdot (\mathbf{r} \times \mathbf{A}) (\mathbf{r} \cdot \mathbf{p} + i \boldsymbol{\sigma} \cdot \mathbf{L}) \\ &= \frac{1}{r^2} (\boldsymbol{\sigma} \cdot (\mathbf{A} \times \mathbf{r}) \boldsymbol{\sigma} \cdot \mathbf{L} + i \boldsymbol{\sigma} \cdot (\mathbf{r} \times \mathbf{A}) \mathbf{r} \cdot \mathbf{p}). \end{aligned} \quad (12.90)$$

According to the Pauli algebra, we have

$$\boldsymbol{\sigma} \cdot \mathbf{A} \boldsymbol{\sigma} \cdot \mathbf{p} = \mathbf{A} \cdot \mathbf{p} + i \boldsymbol{\sigma} \cdot (\mathbf{A} \times \mathbf{p}) \quad (12.91)$$

Equating the real and imaginary parts of the last two equations, we obtain

$$\mathbf{A} \cdot \mathbf{p} = \frac{1}{r^2} \boldsymbol{\sigma} \cdot (\mathbf{A} \times \mathbf{r}) \boldsymbol{\sigma} \cdot \mathbf{L}, \quad (12.92)$$

$$\boldsymbol{\sigma} \cdot (\mathbf{A} \times \mathbf{p}) = \frac{1}{r^2} \boldsymbol{\sigma} \cdot (\mathbf{r} \times \mathbf{A}) \mathbf{r} \cdot \mathbf{p}, \quad (12.93)$$

so that, similarly as before,

$$\boldsymbol{\sigma} \cdot \mathbf{A} \boldsymbol{\sigma} \cdot \mathbf{p} = \frac{1}{r^2} \boldsymbol{\sigma} \cdot (\mathbf{A} \times \mathbf{r}) \boldsymbol{\sigma} \cdot \mathbf{L} + \frac{i}{r^2} \boldsymbol{\sigma} \cdot (\mathbf{r} \times \mathbf{A}) \mathbf{r} \cdot \mathbf{p}, \quad (12.94)$$

Now, we consider again the Hamiltonian (12.59), from which the the Hamiltonian H_1 (Eq. (12.60)) was derived. We use a different derivation concerning operators and functions, and call this Hamiltonian H_2 . At the starting point, we have, written as functions,

$$H_2 \psi = -\frac{e}{2m} (\mathbf{p} \cdot \mathbf{A} + \mathbf{A} \cdot \mathbf{p}) \psi. \quad (12.95)$$

We have derived expressions for the scalar products of \mathbf{p} and \mathbf{A} before. Inserting these expressions (Eqs. 12.86, 12.92)), we obtain

$$H_2 \psi = -\frac{e}{2m} \frac{1}{r^2} (\boldsymbol{\sigma} \cdot \mathbf{L} \boldsymbol{\sigma} \cdot (\mathbf{A} \times \mathbf{r}) + \boldsymbol{\sigma} \cdot (\mathbf{A} \times \mathbf{r}) \boldsymbol{\sigma} \cdot \mathbf{L}) \psi. \quad (12.96)$$

For the scalar products in (12.95) holds $\mathbf{p} \cdot \mathbf{A} = \mathbf{A} \cdot \mathbf{p}$, therefore we equate both corresponding terms in Eq. (12.96). So we have

$$H_2 \psi = -\frac{e}{mr^2} \boldsymbol{\sigma} \cdot (\mathbf{A} \times \mathbf{r}) \boldsymbol{\sigma} \cdot \mathbf{L} \psi. \quad (12.97)$$

Introducing the spin operator

$$\widehat{\mathbf{S}} = \frac{1}{2} \hbar \boldsymbol{\sigma} \quad (12.98)$$

and considering \mathbf{L} as an operator also, the expectation value is, according to standard quantum mechanics,

$$\langle \widehat{\mathbf{S}} \cdot \widehat{\mathbf{L}} \rangle = \frac{\hbar^2}{2} (j(j+1) - l(l+1) - s(s+1)), \quad (12.99)$$

where $j = l + s, \dots, |l - s|$ and $s = 1/2$ for an electron. During this derivation, we have made use of Eq. (12.64):

$$\mathbf{A} = \frac{1}{2} \mathbf{B} \times \mathbf{r}, \quad (12.100)$$

from which we have

$$\mathbf{A} \times \mathbf{r} = \frac{1}{2} (\mathbf{B} \times \mathbf{r}) \times \mathbf{r} = \frac{1}{2} (\mathbf{r}(\mathbf{r} \cdot \mathbf{B}) - \mathbf{B}r^2). \quad (12.101)$$

(see computer algebra code [17]). Inserting this into Eq. (12.97), we obtain the *ESOR Hamiltonian*

$$\boxed{\widehat{H}_2 \psi = \frac{e}{m\hbar} \boldsymbol{\sigma} \cdot \left(\mathbf{B} - \frac{\mathbf{r}}{r^2} (\mathbf{r} \cdot \mathbf{B}) \right) \widehat{\mathbf{S}} \cdot \widehat{\mathbf{L}} \psi} \quad (12.102)$$

If the magnetic field is aligned in Z direction, then

$$\boldsymbol{\sigma} \cdot \frac{\mathbf{r}}{r^2} (\mathbf{r} \cdot \mathbf{B}) = \frac{\sigma_Z Z^2 B_Z}{X^2 + Y^2 + Z^2}. \quad (12.103)$$

We assume that the sample is isotropic, so it is on average

$$\frac{Z^2}{X^2 + Y^2 + Z^2} = \frac{1}{3}. \quad (12.104)$$

Thus, the corresponding part of the ESOR Hamiltonian becomes

$$\hat{H}\psi = E\psi \quad (12.105)$$

with energy eigenvalues

$$E = -\frac{1}{6} \frac{e\hbar}{m} \sigma_Z B_Z (j(j+1) - l(l+1) - s(s+1)). \quad (12.106)$$

Resonance occurs at the frequency

$$\omega = \frac{|E|}{\hbar} = \frac{1}{3} \frac{eB_Z}{m} (j(j+1) - l(l+1) - s(s+1)). \quad (12.107)$$

This is electron-spin-orbit resonance (ESOR) in an isotropic sample. The electric dipole selection rules are the same as for the conventional description of the Zeeman effect:

$$\Delta l = \pm 1, \Delta m_l = 0, \pm 1. \quad (12.108)$$

The conventional Zeeman resonances arise from the term

$$\hat{H}_Z \psi = -\frac{e}{2m} \hat{\mathbf{L}} \cdot \mathbf{B} \psi = -\frac{e}{2m} m_l B_Z \psi, \quad (12.109)$$

which is the spin-less version of Eq. (12.77) with $m_l = -l, \dots, l$, called (*standard*) Zeeman effect.

■ **Example 12.2** We compute the energies of atomic Hydrogen that produce the ESOR spectra. The energy expectation value of the ESOR Hamiltonian (12.102) is

$$\langle \hat{H}_2 \rangle = \int \psi^* \hat{H}_2 \psi d^3 r = E_{\text{ESOR}}. \quad (12.110)$$

With

$$\hat{S} \cdot \hat{L} \psi = \frac{\hbar^2}{2} (j(j+1) - l(l+1) - s(s+1)) \psi \quad (12.111)$$

it follows that

$$E_{\text{ESOR}} = \frac{e\hbar}{2m} (j(j+1) - l(l+1) - s(s+1)) \left(\boldsymbol{\sigma} \cdot \mathbf{B} \int \psi^* \psi d^3 r - \int \psi^* \frac{\boldsymbol{\sigma} \cdot \mathbf{r}}{r^2} \mathbf{r} \cdot \mathbf{B} \psi d^3 r \right) \quad (12.112)$$

with normalized wave functions

$$\int \psi^* \psi d^3 r = 1. \quad (12.113)$$

In spherical polar coordinates

$$\begin{aligned} X &= r \sin \theta \cos \phi, \\ Y &= r \sin \theta \sin \phi, \\ Z &= r \cos \theta, \end{aligned} \quad (12.114)$$

the infinitesimal volume element is

$$d^3 r = r^2 \sin \theta dr d\theta d\phi \quad (12.115)$$

with

$$r^2 = X^2 + Y^2 + Z^2. \quad (12.116)$$

In Eqs. (12.103, 12.104), we have assumed that the magnetic field is aligned in parallel to the Z axis and the sample is isotropic. For a non-isotropic sample, we have

$$\frac{Z^2}{X^2 + Y^2 + Z^2} = \cos^2 \theta, \quad (12.117)$$

so that

$$\int \psi^* \frac{\boldsymbol{\sigma} \cdot \mathbf{r}}{r^2} \mathbf{r} \cdot \mathbf{B} \psi d^3 r = \sigma_Z B_Z \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} \int_{r=0}^{\infty} \psi^* \cos^2 \theta \psi r^2 \sin \theta dr d\theta d\phi. \quad (12.118)$$

For the ESOR Energy, we then can split the result in the form

$$E_{\text{ESOR}} = E_1 + E_2 \quad (12.119)$$

with

$$E_1 = \frac{e\hbar}{2m} F_j \sigma_Z B_Z, \quad (12.120)$$

$$E_2 = -\frac{e\hbar}{2m} F_j \sigma_Z B_Z \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} \int_{r=0}^{\infty} \psi^* \cos^2 \theta \psi r^2 \sin \theta dr d\theta d\phi, \quad (12.121)$$

where we have abbreviated the quantum number term by

$$F_j = j(j+1) - l(l+1) - s(s+1). \quad (12.122)$$

The integral E_2 has to be evaluated with the Hydrogenic wave functions, which can be assumed to be identical to those of the unperturbed atom in good approximation. The wave functions are known analytically and are, in spherical coordinates, defined by

$$\psi(r, \theta, \phi) = R_{nl}(r) Y_{lm}(\theta, \phi), \quad (12.123)$$

where n is the principal quantum number, and l, m are the quantum numbers of angular momentum. R_{nl} are the radial parts of the wave functions, and Y_{lm} are the spherical harmonics that represent the angular parts. The spherical harmonics are listed in [8, 9], for example. In some tabular works, the radial wave functions are given with wrong normalization factors. Therefore, we have listed them in Table 12.1, where they have been evaluated by computer algebra [18]. The ordinal number is $Z = 1$ for Hydrogen. The normalization has been checked by executing the integral

$$N = \int_0^{\infty} R_{nl}(r)^2 r^2 dr. \quad (12.124)$$

The norm evaluates to $N = 1$ in all cases.

The results for E_1 and E_2 are listed in Table 12.2. We have assumed a magnetic field of 1 Tesla. The energies are given in multiples of $e\hbar/(2m)$. There is no contribution from s states. The numerical factor in eV is

$$\frac{e\hbar}{2m} \cdot 1\text{T} = 3.63695 \cdot 10^{-4} \text{ eV}. \quad (12.125)$$

This is only a small spectral correction, but it is in the order of spin-orbit coupling and therefore detectable. It has to be multiplied by the results given in Table 12.2 to obtain the quantum-number dependent energy values. ■

n	l	R_{nl}
1	0	$2 \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{-\frac{rZ}{a_0}}$
2	0	$\frac{\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}}{2^{\frac{3}{2}}} \left(2 - \frac{rZ}{a_0}\right) e^{-\frac{rZ}{2a_0}}$
2	1	$\frac{Z}{2\sqrt{6}a_0} \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} r e^{-\frac{rZ}{2a_0}}$
3	0	$\frac{\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}}{3^{\frac{5}{2}}} \left(\frac{4r^2Z^2}{9a_0^2} - \frac{4rZ}{a_0} + 6\right) e^{-\frac{rZ}{3a_0}}$
3	1	$\frac{2Z}{27\sqrt{6}a_0} \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} r \left(4 - \frac{2rZ}{3a_0}\right) e^{-\frac{rZ}{3a_0}}$
3	2	$\frac{4Z^2}{81\sqrt{30}a_0^2} \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} r^2 e^{-\frac{rZ}{3a_0}}$

Table 12.1: Radial wave functions for the Hydrogenic orbitals.

Besides the ESOR Hamiltonian described in this section, there are some more possibilities of defining new spectra, for which numerical examples for hydrogenic wave functions are given [10]. It is also possible to include spin-orbit interaction of the gravitational potential ϕ in addition to that of the electric potential Φ [11]. The minimal prescription for extending the energy operator is then:

$$E \rightarrow E - e\Phi + m\phi, \quad (12.126)$$

where $-e$ is the charge and m is the mass of the electron. This approach has to be inserted into the starting equation (12.30) of spin-orbit development. Since the gravitational interaction is weaker than the electromagnetic interaction by about 20 orders of magnitude, gravitational effects play no role in terrestrial laboratories. The results show that such effects are pronounced only in heavy systems with small radii such as neutron stars. So, if there is a Hydrogen atom at the surface of a neutron star, its fine structure spectrum is measurably different from the same spectrum in a terrestrial laboratory.

n	l	m_l	j	s	m_s	m_j	F_j	E_1	E_2	$E_1 + E_2$
1	0	0	1/2	1/2	-1/2	-1/2	0	0	0	0
1	0	0	1/2	1/2	1/2	-1/2	0	0	0	0
2	0	0	1/2	1/2	-1/2	-1/2	0	0	0	0
2	0	0	1/2	1/2	1/2	-1/2	0	0	0	0
2	1	-1	3/2	1/2	-1/2	-3/2	1	1	$-\frac{1}{5}$	$\frac{4}{5}$
2	1	-1	3/2	1/2	1/2	-1/2	1	1	$-\frac{1}{5}$	$\frac{4}{5}$
2	1	0	1/2	1/2	-1/2	-1/2	-1	-1	$\frac{3}{5}$	$-\frac{2}{5}$
2	1	0	3/2	1/2	1/2	1/2	1	1	$-\frac{3}{5}$	$\frac{2}{5}$
2	1	1	1/2	1/2	-1/2	1/2	-1	-1	$\frac{1}{5}$	$-\frac{4}{5}$
2	1	1	3/2	1/2	1/2	3/2	1	1	$-\frac{1}{5}$	$\frac{4}{5}$
3	0	0	1/2	1/2	-1/2	-1/2	0	0	0	0
3	0	0	1/2	1/2	1/2	-1/2	0	0	0	0
3	1	-1	3/2	1/2	-1/2	-3/2	1	1	$-\frac{1}{5}$	$\frac{4}{5}$
3	1	-1	3/2	1/2	1/2	-1/2	1	1	$-\frac{1}{5}$	$\frac{4}{5}$
3	1	0	1/2	1/2	-1/2	-1/2	-1	-1	$\frac{3}{5}$	$-\frac{2}{5}$
3	1	0	3/2	1/2	1/2	1/2	1	1	$-\frac{3}{5}$	$\frac{2}{5}$
3	1	1	1/2	1/2	-1/2	3/2	-1	-1	$\frac{1}{5}$	$-\frac{4}{5}$
3	1	1	5/2	1/2	1/2	-5/2	1	1	$-\frac{1}{5}$	$\frac{4}{5}$
3	2	-2	5/2	1/2	-1/2	-5/2	2	2	$-\frac{2}{7}$	$\frac{12}{7}$
3	2	-2	5/2	1/2	1/2	-3/2	2	2	$-\frac{2}{7}$	$\frac{12}{7}$
3	2	-1	3/2	1/2	-1/2	-3/2	-2	-2	$\frac{6}{7}$	$-\frac{8}{7}$
3	2	-1	5/2	1/2	1/2	-1/2	2	2	$-\frac{6}{7}$	$\frac{8}{7}$
3	2	0	3/2	1/2	-1/2	-1/2	-2	-2	$\frac{22}{21}$	$-\frac{20}{21}$
3	2	0	5/2	1/2	1/2	1/2	2	2	$-\frac{22}{21}$	$\frac{20}{21}$
3	2	1	3/2	1/2	-1/2	1/2	-2	-2	$\frac{6}{7}$	$-\frac{8}{7}$
3	2	1	5/2	1/2	1/2	3/2	2	2	$-\frac{6}{7}$	$\frac{8}{7}$
3	2	2	3/2	1/2	-1/2	3/2	-2	-2	$\frac{2}{7}$	$-\frac{12}{7}$
3	2	2	5/2	1/2	1/2	5/2	2	2	$-\frac{2}{7}$	$\frac{12}{7}$

Table 12.2: Energies E_1 , E_2 and E in units of $e\hbar/(2m)$, related to $B_Z = 1$ T.

12.3 Beyond the Dirac approximation

So far, the developments of new types of spectroscopy were based on the Dirac or Fermion equation. Now, we derive such types from Einstein's energy equation directly, which is an independent development within the ECE2 theory framework [12].

12.3.1 Spin-orbit coupling

In textbook physics, the spin-orbit coupling is developed with significant approximations made by Dirac and others (see Section 12.1.2). In this section, we derive spin-orbit coupling from the rigorous relativistic theory based on Einstein's energy equation of special relativity. This equation reads

$$E^2 = p^2 c^2 + m^2 c^4, \quad (12.127)$$

where m is the particle mass and \mathbf{p} is the relativistic momentum

$$\mathbf{p} = \gamma m \mathbf{v} = \gamma \mathbf{p}_0. \quad (12.128)$$

\mathbf{v} is the particle velocity, $\mathbf{p}_0 = m \mathbf{v}$ is the non-relativistic momentum, and γ is the Lorentz factor

$$\gamma = \left(1 - \frac{v^2}{c^2}\right)^{-1/2} = \left(1 - \frac{p_0^2}{m^2 c^2}\right)^{-1/2}. \quad (12.129)$$

With the Lorentz factor, the total energy E can be written as

$$E = \gamma m c^2. \quad (12.130)$$

Using the relativistic 4-momenta,

$$p^\mu = \left(\frac{E}{c}, \mathbf{p}\right), \quad (12.131)$$

$$p_\mu = \left(\frac{E}{c}, -\mathbf{p}\right), \quad (12.132)$$

Eq. (12.127) takes the covariant form

$$p^\mu p_\mu = m^2 c^2. \quad (12.133)$$

Einstein's energy equation relates to free particle motion. In atoms and molecules, there is an external potential Φ that leads to a potential energy U of the particle and is not contained in Einstein's equation. For electrons with charge $-e$, the potential energy is

$$U = -e\Phi. \quad (12.134)$$

This enters the relativistic Hamiltonian, defined by

$$H = E + U. \quad (12.135)$$

Thus, Eq. (12.127) takes the form

$$(H - U)^2 = p^2 c^2 + m^2 c^2. \quad (12.136)$$

Factorizing

$$(H - U)^2 - m^2 c^2 = p^2 c^2 \quad (12.137)$$

in the form

$$(H - U)^2 - m^2 c^2 = (H - U - mc^2)(H - U + mc^2), \quad (12.138)$$

we obtain from Eq. (12.137):

$$H - U - mc^2 = \frac{p^2 c^2}{H - U + mc^2}. \quad (12.139)$$

Now, we introduce the reduced relativistic Hamiltonian

$$H_0 = H - mc^2, \quad (12.140)$$

which does not contain the rest energy. From (12.139), it follows:

$$\begin{aligned} H_0 &= \frac{p^2 c^2}{H - U + mc^2} + U = \frac{p^2 c^2}{E + mc^2} + U = \frac{p^2 c^2}{(1 + \gamma)mc^2} + U \\ &= \frac{p^2}{(1 + \gamma)m} + U, \end{aligned} \quad (12.141)$$

which is another way of writing the Einstein energy equation, augmented by the potential energy U . In the non-relativistic limit $\gamma \rightarrow 1$, this expression reduces to the non-relativistic Hamiltonian

$$H_{n-r} = \frac{p_0^2}{2m} + U, \quad (12.142)$$

where $p_0^2/(2m)$ is the classical, non-relativistic kinetic energy, for which we have used the transition

$$\mathbf{p} = \gamma \mathbf{p}_0 \rightarrow \mathbf{p}_0. \quad (12.143)$$

Dirac approximated the Hamiltonian in the denominator of Eq. (12.141) by

$$H \approx mc^2, \quad (12.144)$$

which leads to

$$H_0 \approx \frac{p^2 c^2}{2mc^2 - U} + U = \frac{p^2}{2m \left(1 - \frac{U}{2mc^2}\right)} + U. \quad (12.145)$$

So Dirac assumed

$$E = H - U \approx mc^2 - U = \gamma mc^2, \quad (12.146)$$

so that Dirac's Lorentz factor is

$$\gamma_D = 1 - \frac{U}{mc^2}. \quad (12.147)$$

However, according to Eq. (12.129), the correct γ is

$$\gamma = \left(1 - \frac{p_0^2}{m^2 c^2}\right)^{-1/2} \approx 1 + \frac{1}{2} \frac{p_0^2}{m^2 c^2} \quad (12.148)$$

for $v \ll c$. Comparing (12.147) and (12.148), we obtain

$$\frac{p_0^2}{2m} \approx -U. \quad (12.149)$$

Inserting this result into Eq. (12.142), it follows

$$H_{n-r} = \frac{p_0^2}{2m} + U \approx 0, \quad (12.150)$$

i.e., in the non-relativistic approximation, no energy is produced by the Hamiltonian. This seems not to be a meaningful result, although the Dirac approximation has been used for over 90 years.

Accepting this approximation for the sake of argument, Eq. (12.145) is traditionally developed by assuming

$$|U| \ll 2mc^2, \quad (12.151)$$

so

$$H_0 \approx \frac{p^2}{2m} \left(1 - \frac{U}{2mc^2}\right) + U = \frac{p^2}{2m} - \frac{U}{4m^2c^2} p^2 + U. \quad (12.152)$$

where p is the *relativistic* momentum. The first term was developed in Section 12.2.1 and gives the fine structure of the Zeeman effect. The second term is the spin-orbit term and is written in the SU(2) basis:

$$H_{s-o} = -\frac{1}{4m^2c^2} \boldsymbol{\sigma} \cdot \mathbf{p} U \boldsymbol{\sigma} \cdot \mathbf{p}. \quad (12.153)$$

This is the same as Eq. (12.42) with $U = -e\Phi$. As discussed earlier, the placement of U is arbitrary and chosen in such a way that the correct experimental results come out. The subsequent calculation in Section 12.2.1 gives the final result (12.53):

$$\hat{H}_{s-o} = -\frac{e^2}{8\pi\epsilon_0 m^2 c^2 r^3} \hat{\mathbf{S}} \cdot \hat{\mathbf{L}}. \quad (12.154)$$

The usage of momenta deserves some attention. In the development of Eq. (12.53), the quantization rule has been used for the *relativistic* momentum. Although this is nearly nowhere mentioned in textbooks, it is assumed that the relativistic rules for quantization are the same as for non-relativistic quantization in Schrödinger theory. The difference is only that in one case the operator is applied to a non-relativistic theory (with wave function ψ), while in the other case it is applied to a relativistic theory (with wave function ψ_r):

$$\mathbf{p}_0 \psi \rightarrow -i\hbar \nabla \psi, \quad (12.155)$$

$$\mathbf{p} \psi_r \rightarrow -i\hbar \nabla \psi_r. \quad (12.156)$$

The second \mathbf{p} in the Eq. (12.153) has been taken as a function and is used to introduce the angular momentum \mathbf{L} . This is the *relativistic* angular momentum by construction. However, the well-known eigenvalues of the angular momentum are *non-relativistic* eigenvalues:

$$\hat{\mathbf{L}}_0^2 \psi = \hbar^2 l(l+1) \psi, \quad (12.157)$$

$$\hat{L}_{0z} \psi = \hbar m_l \psi. \quad (12.158)$$

Therefore, the angular momentum in Eq. (12.154) is the *relativistic* angular momentum, and the equation has to be written with the γ factor:

$$\hat{H}_{s-o} = -\frac{e^2}{8\pi\epsilon_0 m^2 c^2 r^3} \gamma \hat{\mathbf{S}} \cdot \hat{\mathbf{L}}_0. \quad (12.159)$$

The eigenvalues of $\widehat{\mathbf{S}} \cdot \widehat{\mathbf{L}}_0$ are

$$\widehat{\mathbf{S}} \cdot \widehat{\mathbf{L}}_0 \psi = \frac{1}{2} \hbar^2 (J(J+1) - L(L+1) - S(S+1)) \psi \quad (12.160)$$

with quantum numbers written in capital letters for multi-electron systems:

$$J = L + S, \dots, |L - S|. \quad (12.161)$$

For a single electron, it is

$$S = \pm \frac{1}{2}, \quad (12.162)$$

so

$$J = L + \frac{1}{2} \quad \text{and} \quad J = L - \frac{1}{2}. \quad (12.163)$$

The γ factor in Eq. (12.159) can be approximated as in Eq. (12.148), which gives

$$\widehat{H}_{s-o} = -\frac{e^2}{8\pi\epsilon_0 m^2 c^2 r^3} \left(1 + \frac{1}{2} \frac{p_0^2}{m^2 c^2}\right) \widehat{\mathbf{S}} \cdot \widehat{\mathbf{L}}_0. \quad (12.164)$$

The momentum p_0 determines the non-relativistic kinetic energy

$$T = \frac{1}{2} m v^2 = \frac{p_0^2}{2m}, \quad (12.165)$$

and, according to the Virial theorem, we have

$$U = -2T, \quad (12.166)$$

so that for the non-relativistic Hamiltonian follows:

$$H_{n-r} = T + U = -T. \quad (12.167)$$

So, the term containing p_0^2 in (12.164) can be transformed into

$$\frac{1}{2} \frac{p_0^2}{m^2 c^2} = \frac{p_0^2}{2m} \frac{1}{m c^2} = \frac{T}{m c^2} = -\frac{H_{n-r}}{m c^2}. \quad (12.168)$$

The expectation value of this term is for Hydrogen:

$$-\frac{1}{m c^2} \langle H_{n-r} \rangle = \frac{1}{m c^2} \frac{e^4 m}{32\pi^2 \epsilon_0^2 \hbar^2 n^2} = \frac{e^4}{32\pi^2 \epsilon_0^2 \hbar^2 c^2 n^2}, \quad (12.169)$$

where n is the principal quantum number. Using the definitions of the Compton wavelength

$$\lambda_C = \frac{\hbar}{m c}, \quad (12.170)$$

the finestructure constant

$$\alpha = \frac{e^2}{4\pi\epsilon_0 c \hbar} \quad (12.171)$$

and the Bohr radius

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{e^2m} = \frac{\hbar}{mc\alpha} = \frac{\lambda_C}{\alpha}, \quad (12.172)$$

we can write

$$\langle H_{n-r} \rangle = -\frac{1}{2} \frac{\hbar c}{a_0} \frac{\alpha}{n^2} = -mc^2 \frac{\alpha^2}{2n^2} \quad (12.173)$$

and

$$\frac{1}{mc^2} \langle H_{n-r} \rangle = -\frac{1}{2} \frac{\lambda_C}{a_0} \frac{\alpha}{n^2} = -\frac{\alpha^2}{2n^2} \quad (12.174)$$

(see computer algebra code [19]). This is an elegant expression of the total energy of the electron in Hydrogen and demonstrates that this non-relativistic expression contains the “relativistic” energy mc^2 . Eq. (12.164) can be written as

$$\hat{H}_{s-o} = -\frac{e^2}{8\pi\epsilon_0m^2c^2r^3} \left(1 + \frac{\alpha^2}{2n^2}\right) \hat{\mathbf{S}} \cdot \hat{\mathbf{L}}_0 \quad (12.175)$$

and now contains a correction term that makes the spin-orbit splitting dependent on the principal quantum number n . We can furthermore introduce the eigenvalues of

$$\hat{\mathbf{S}} \cdot \hat{\mathbf{L}}_0 \psi = \frac{1}{2} \hbar^2 (J(J+1) - L(L+1) - S(S+1)) \psi, \quad (12.176)$$

so that the expectation value of \hat{H}_{s-o} becomes

$$\begin{aligned} \langle \hat{H}_{s-o} \rangle &= -\frac{e^2}{8\pi\epsilon_0m^2c^2} \left(1 + \frac{\alpha^2}{2n^2}\right) \frac{1}{2} \hbar^2 (J(J+1) - L(L+1) - S(S+1)) \\ &\quad \cdot \int \psi^* \frac{1}{r^3} \psi d^3r. \end{aligned} \quad (12.177)$$

(Please notice that the expectation value of $1/r^3$ stems from the denominator of the first fraction.) The integral, taken with the undisturbed wave functions of the Hydrogen atom, is analytically solvable and gives

$$\left\langle \frac{1}{r^3} \right\rangle = \int \psi^* \frac{1}{r^3} \psi d^3r = \frac{1}{a_0^3 L(L + \frac{1}{2})(L+1)n^3}. \quad (12.178)$$

In total, the expectation value of the relativistically corrected theory of spin-orbit splitting is

$$\langle \hat{H}_{s-o} \rangle = -\frac{e^2\hbar^2}{16\pi\epsilon_0m^2c^2} \frac{J(J+1) - L(L+1) - S(S+1)}{a_0^3 L(L + \frac{1}{2})(L+1)n^3} \left(1 + \frac{\alpha^2}{2n^2}\right). \quad (12.179)$$

■ **Example 12.3** We compute the constants in Eq. (12.179). These are, according to computer algebra [19],

$$\frac{e^2\hbar^2}{16\pi\epsilon_0m^2c^2a_0^3n^3} = \frac{\alpha\lambda_C\hbar c}{4a_0^3n^3} = \frac{3.622608 \cdot 10^{-4}}{n^3} \text{eV}, \quad (12.180)$$

$$\frac{1}{2} \frac{\lambda_C}{a_0} \frac{\alpha}{n^2} = mc^2 \frac{\alpha^2}{2n^2} = \frac{2.662568 \cdot 10^{-5}}{n^2}. \quad (12.181)$$

The spin-orbit splitting has the order of magnitude of $10^{-4}/n^3$ eV. It would be largest for the 1s state, but the equation is only defined for $L > 0$. So the smallest value appears for $n = 2$ that gives an effective order of magnitude of 10^{-5} eV.

The second constant is a dimensionless, relative number, by which the spin-orbit splitting is increased. Since it is added to unity, it leads only to a slight change of transition energies between states of different principal quantum numbers. More details will be discussed in later examples. ■

12.3.2 Anomalous Zeeman effect

In order to develop the anomalous Zeeman effect without using the Dirac equation, we start with the relativistic Hamiltonian H_0 without rest energy that was derived from the Einstein energy equation in the previous section. This is Eq. (12.141):

$$H_0 = \frac{p^2}{(1+\gamma)m} + U \quad (12.182)$$

with relativistic momentum p , particle mass m and potential energy U . In the non-relativistic limit $\gamma \rightarrow 1$, this becomes the classical Hamiltonian

$$H_{n-r} = \frac{p_0^2}{2m} + U \quad (12.183)$$

with the non-relativistic momentum p_0 . The Einstein energy equation can be written entirely using p_0 by applying the definition of the relativistic momentum

$$\mathbf{p} = \gamma \mathbf{p}_0, \quad (12.184)$$

giving

$$H_0 = \frac{1}{m} \frac{\gamma^2}{1+\gamma} p_0^2 + U. \quad (12.185)$$

In the SU(2) basis, this equation reads:

$$H_0 = \frac{1}{m} \frac{\gamma^2}{1+\gamma} \boldsymbol{\sigma} \cdot \mathbf{p}_0 \boldsymbol{\sigma} \cdot \mathbf{p}_0 + U. \quad (12.186)$$

The factor $\gamma^2/(1+\gamma)$ can be written at different positions in this equation. This does not matter, as long as \mathbf{p}_0 is considered as a function, but makes a difference, as soon as operators for \mathbf{p}_0 are used. Essentially, there are four possibilities:

$$H_0^I = \frac{1}{m} \boldsymbol{\sigma} \cdot \mathbf{p}_0 \frac{\gamma^2}{1+\gamma} \boldsymbol{\sigma} \cdot \mathbf{p}_0 + U, \quad (12.187)$$

$$H_0^{II} = \frac{\gamma}{m} \boldsymbol{\sigma} \cdot \mathbf{p}_0 \frac{\gamma}{1+\gamma} \boldsymbol{\sigma} \cdot \mathbf{p}_0 + U, \quad (12.188)$$

$$H_0^{III} = \frac{\gamma^2}{m} \boldsymbol{\sigma} \cdot \mathbf{p}_0 \frac{1}{1+\gamma} \boldsymbol{\sigma} \cdot \mathbf{p}_0 + U, \quad (12.189)$$

$$H_0^{IV} = \frac{1}{m} \frac{\gamma^2}{1+\gamma} \boldsymbol{\sigma} \cdot \mathbf{p}_0 \boldsymbol{\sigma} \cdot \mathbf{p}_0 + U. \quad (12.190)$$

The four classes of H_0 give four different types of hyperfine structure. In the presence of a magnetic field, intricate new effects appear, notably in ESR and NMR.

Next, we develop the Lorentz factors in type I and IV. According to Eq. (12.148), we have

$$\gamma = \left(1 - \frac{p_0^2}{m^2 c^2}\right)^{-1/2} \approx 1 + \frac{1}{2} \frac{p_0^2}{m^2 c^2}. \quad (12.191)$$

Using the relation

$$\frac{\gamma^2}{1+\gamma} = \left(\frac{1}{\gamma^2} + \frac{1}{\gamma}\right)^{-1} = \left(1 - \frac{p_0^2}{m^2 c^2} + \left(1 - \frac{p_0^2}{m^2 c^2}\right)^{1/2}\right)^{-1}, \quad (12.192)$$

we obtain in the limit $v \ll c$:

$$\frac{\gamma^2}{1+\gamma} = \left(2 - \frac{3p_0^2}{2m^2c^2}\right)^{-1} = \frac{1}{2} \left(1 - \frac{3p_0^2}{4m^2c^2}\right)^{-1} \approx \frac{1}{2} \left(1 + \frac{3p_0^2}{4m^2c^2}\right). \quad (12.193)$$

Insertion of

$$p_0^2 = 2m(H_0 - U) \quad (12.194)$$

gives us

$$\begin{aligned} \frac{\gamma^2}{1+\gamma} &\approx \frac{1}{2} \left(1 + \frac{3(H_0 - U)}{2mc^2}\right) = \frac{1}{2} \left(1 - \frac{U}{2mc^2} + \frac{3}{2} \frac{H_0}{mc^2} - \frac{U}{mc^2}\right) \\ &= \frac{1}{2} \left(1 - \frac{U}{2mc^2} + \frac{1}{mc^2} \left(\frac{H_0}{2} + \frac{p_0^2}{2m}\right)\right) \end{aligned} \quad (12.195)$$

This result can be inserted into the class I Hamiltonian (12.187), omitting U :

$$H_1 = \frac{1}{2m} \boldsymbol{\sigma} \cdot \mathbf{p}_0 \left(1 - \frac{U}{2mc^2}\right) \boldsymbol{\sigma} \cdot \mathbf{p}_0 + \frac{1}{2m^2c^2} \boldsymbol{\sigma} \cdot \mathbf{p}_0 \left(\frac{H_0}{2} + \frac{p_0^2}{2m}\right) \boldsymbol{\sigma} \cdot \mathbf{p}_0. \quad (12.196)$$

Rearranging this equation and regarding the vectors \mathbf{p}_0 as functions in the second summand, we obtain (omitting the kinetic energy)

$$H_1 = -\frac{1}{2m} \boldsymbol{\sigma} \cdot \mathbf{p}_0 \frac{U}{2mc^2} \boldsymbol{\sigma} \cdot \mathbf{p}_0 + \frac{p_0^2}{2m^2c^2} \left(\frac{H_0}{2} + \frac{p_0^2}{2m}\right). \quad (12.197)$$

The first summand is the spin-orbit coupling Hamiltonian (12.153) and the second summand describes non-linear corrections to the kinetic energy that are parts of the hyperfine structure.

The anomalous Zeeman effect can be derived from a class IV Hamiltonian as follows. In presence of a magnetic field, we replace the momentum \mathbf{p}_0 by its generalized form as usual:

$$\mathbf{p}_0 \rightarrow \mathbf{p}_0 - e\mathbf{A}. \quad (12.198)$$

Then, the class IV Hamiltonian (12.190) becomes (without potential energy U)

$$H_4 = \frac{1}{m} \frac{\gamma^2}{1+\gamma} \boldsymbol{\sigma} \cdot (\mathbf{p}_0 - e\mathbf{A}) \boldsymbol{\sigma} \cdot (\mathbf{p}_0 - e\mathbf{A}), \quad (12.199)$$

The development proceeds in the same way as in Section 12.2.1, resulting in Eq. (12.77), which, for a magnetic field in Z direction, now reads

$$H_Z \psi = -\frac{\gamma^2}{1+\gamma} \frac{e\hbar}{m} g_J m_J B_Z \psi. \quad (12.200)$$

The γ factor corrections are multiplicative factors. The kinetic energy has to be added to give a complete Hamiltonian (we can omit U that does not impact the transitions between energy levels). Therefore, we have to write

$$H_4 \psi = \frac{\gamma^2}{1+\gamma} \left(\frac{p_0^2}{m} - \frac{e\hbar}{m} g_J m_J B_Z\right) \psi. \quad (12.201)$$

From (12.174):

$$\langle H_{n-r} \rangle = -mc^2 \frac{\alpha^2}{2n^2}. \quad (12.202)$$

From the Virial theorem:

$$\langle U \rangle = 2 \langle H_{n-r} \rangle, \quad (12.203)$$

$$\langle T \rangle = \left\langle \frac{p_0^2}{2m} \right\rangle = \langle H_{n-r} \rangle - \langle U \rangle = \langle H_{n-r} \rangle - 2 \langle H_{n-r} \rangle = - \langle H_{n-r} \rangle, \quad (12.204)$$

so:

$$\left\langle \frac{p_0^2}{2m} \right\rangle = mc^2 \frac{\alpha^2}{2n^2}, \quad (12.205)$$

$$\langle U \rangle = -mc^2 \frac{\alpha^2}{n^2}. \quad (12.206)$$

Eq. (12.195) can then be written in the form

$$\begin{aligned} \left\langle \frac{\gamma^2}{1+\gamma} \right\rangle &= \frac{1}{2} \left(1 - \frac{\langle U \rangle}{2mc^2} + \frac{1}{mc^2} \left(\frac{\langle H_{n-r} \rangle}{2} + \left\langle \frac{p_0^2}{2m} \right\rangle \right) \right) \\ &= \frac{1}{2} \left(1 - \frac{\langle H_{n-r} \rangle}{mc^2} + \frac{1}{mc^2} \left(\frac{\langle H_{n-r} \rangle}{2} - \langle H_{n-r} \rangle \right) \right) \\ &= \frac{1}{2} \left(1 - \frac{3 \langle H_{n-r} \rangle}{2 mc^2} \right) \\ &= \frac{1}{2} \left(1 + \frac{3 \alpha^2}{4 n^2} \right). \end{aligned} \quad (12.207)$$

This expression converges to the non-relativistic limit of $1/2$ for $n \rightarrow \infty$ and is greater than $1/2$ in general. The expectation value of the anomalous Zeeman effect (12.201) then becomes

$$\begin{aligned} \langle H_4 \rangle &= \left\langle \frac{\gamma^2}{1+\gamma} \right\rangle \left(\left\langle \frac{p_0^2}{m} \right\rangle - \frac{e\hbar}{m} g_J m_J B_Z \right) \\ &= \frac{1}{2} \left(1 + \frac{3 \alpha^2}{4 n^2} \right) \left(mc^2 \frac{\alpha^2}{n^2} - \frac{e\hbar}{m} g_J m_J B_Z \right). \end{aligned} \quad (12.208)$$

The non-relativistic version is

$$\langle H_{4,n-r} \rangle = \frac{1}{2} \left(mc^2 \frac{\alpha^2}{n^2} - \frac{e\hbar}{m} g_J m_J B_Z \right). \quad (12.209)$$

For the total energy, the expectation value of the potential energy has to be added:

$$E = \frac{1}{2} \left(1 + \frac{3 \alpha^2}{4 n^2} \right) \left(mc^2 \frac{\alpha^2}{n^2} - \frac{e\hbar}{m} g_J m_J B_Z \right) + \langle U \rangle, \quad (12.210)$$

where we insert, according to Eq. (12.203):

$$\langle U \rangle = \int \psi^* U \psi d^3 r = -\frac{e^2}{4\pi\epsilon_0} \int \psi^* \frac{1}{r} \psi d^3 r \approx 2 \langle H_{n-r} \rangle = -mc^2 \frac{\alpha^2}{n^2} \quad (12.211)$$

in the non-relativistic approximation. Eq. (12.210) is the total energy for the anomalous Zeeman effect with corrections of special relativity.

■ **Example 12.4** We calculate the relativistic energy levels of Hydrogen including spin-orbit coupling (see computer algebra code [20]). The level splitting due to spin-orbit coupling has been

derived in Section 12.3.1. The expectation values of the spin-orbit coupling operator have been augmented by a relativistic correction factor, result in Eq. (12.179):

$$\langle \hat{H}_{s-o} \rangle = -\frac{e^2 \hbar^2}{16\pi\epsilon_0 m^2 c^2} \frac{J(J+1) - L(L+1) - S(S+1)}{a_0^3 L(L+\frac{1}{2})(L+1)n^3} \left(1 + \frac{\alpha^2}{2n^2}\right). \quad (12.212)$$

To describe the total energy of the electron including this coupling, we have to add the kinetic and potential energy. A relativistic expression for the kinetic energy was obtained as a “by-product” of the derivation of the anomalous Zeeman effect in this section. It is the non-Zeeman term in Eq. (12.210):

$$E_{\text{kin}} = \left(1 + \frac{3}{4} \frac{\alpha^2}{n^2}\right) mc^2 \frac{\alpha^2}{2n^2} \quad (12.213)$$

with the numerical value of the correction factor

$$\frac{3}{4} \frac{\alpha^2}{n^2} = \frac{3.993852 \cdot 10^{-5}}{n^2}. \quad (12.214)$$

For the potential energy, we use the expectation value of the potential U in non-relativistic approximation, i.e., taken with the non-relativistic wave functions of Hydrogen. According to Eq. (12.211), this expectation value is

$$E_{\text{pot}} = \langle U \rangle = -mc^2 \frac{\alpha^2}{n^2}. \quad (12.215)$$

The total energy is then

$$\begin{aligned} E &= E_{\text{kin}} + E_{\text{pot}} + \langle \hat{H}_{s-o} \rangle \\ &= \left(1 + \frac{3}{4} \frac{\alpha^2}{n^2}\right) mc^2 \frac{\alpha^2}{2n^2} - mc^2 \frac{\alpha^2}{n^2} \\ &\quad - \frac{e^2 \hbar^2}{16\pi\epsilon_0 m^2 c^2} \frac{J(J+1) - L(L+1) - S(S+1)}{a_0^3 L(L+\frac{1}{2})(L+1)n^3} \left(1 + \frac{\alpha^2}{2n^2}\right). \end{aligned} \quad (12.216)$$

In comparison, the total energy of the Dirac theory is the above equations without the relativistic extension factors:

$$E_D = mc^2 \frac{\alpha^2}{2n^2} - mc^2 \frac{\alpha^2}{n^2} - \frac{e^2 \hbar^2}{16\pi\epsilon_0 m^2 c^2} \frac{J(J+1) - L(L+1) - S(S+1)}{a_0^3 L(L+\frac{1}{2})(L+1)n^3}. \quad (12.217)$$

Because the kinetic energy is enlarged in this improved version of the total energy E , the term schema of energy levels is lifted, compared to Dirac’s theory. This can be seen in the graphical representation scheme in Figs. 12.1-12.6. The energies are given in Hartree units (1 H = 2 Ryd = 27.211384 eV). The term schemes show the non-relativistic energy, the Dirac splitting and the shift and splitting by ECE2 theory. In the latter, the spin-orbit splitting itself is only changed by a relative factor of about $1 + 10^{-5}$, as was already discussed in Example 12.3. This effect is smaller by orders of magnitude compared to the lifting of kinetic energy levels, but the shift should be detectable in high-resolution atomic spectra. ■

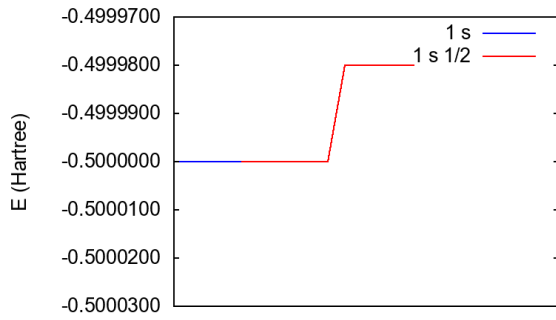


Figure 12.1: Energy schema for $1s$ states (non-rel., Dirac theory, ECE2 theory).

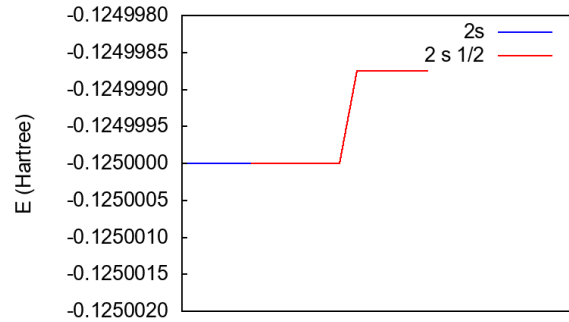


Figure 12.2: Energy schema for $2s$ states (non-rel., Dirac theory, ECE2 theory).

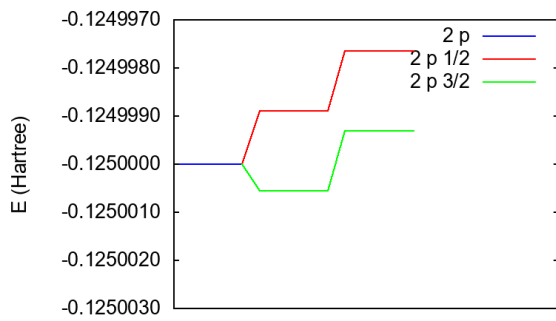


Figure 12.3: Energy schema for $2p$ states (non-rel., Dirac theory, ECE2 theory).

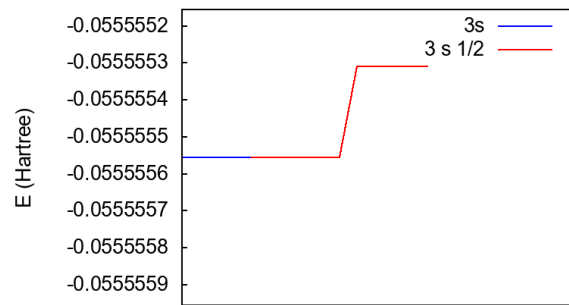


Figure 12.4: Energy schema for $3s$ states (non-rel., Dirac theory, ECE2 theory).

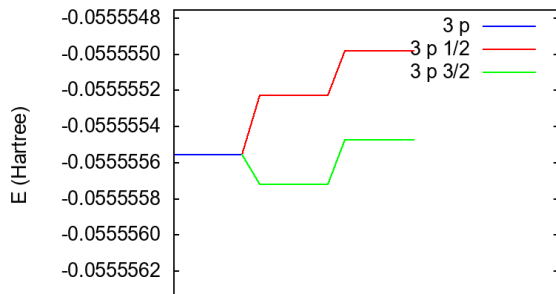


Figure 12.5: Energy schema for $3p$ states (non-rel., Dirac theory, ECE2 theory).

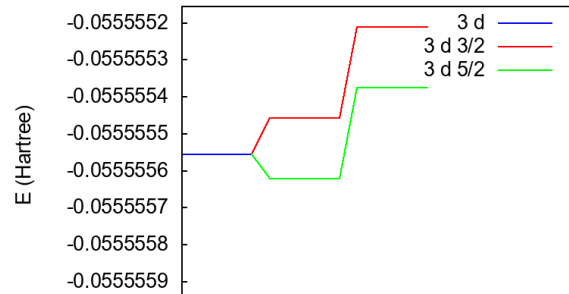


Figure 12.6: Energy schema for $3d$ states (non-rel., Dirac theory, ECE2 theory).

■ **Example 12.5** We compute the transition energies that should be observed in the spectra of the Zeeman effect with relativistic corrections (see computer algebra code [21]). In particular, an additional splitting of lines due to these corrections should appear. In Eqs. (12.209-12.211), the total electronic energy in a magnetic field in Z direction, derived from a class I Hamiltonian (12.187), is given for the anomalous Zeeman effect. In this example, we restrict consideration to the normal Zeeman effect (without respecting the spin of the electron). For this, we have to replace the quantum number J by l in the equations and have to omit the gyromagnetic factor g_J . The result is:

$$E = \frac{1}{2} \left(1 + \frac{3}{4} \frac{\alpha^2}{n^2} \right) \left(mc^2 \frac{\alpha^2}{n^2} - \frac{e\hbar}{m} m_l B_Z \right) + \langle U \rangle \quad (12.218)$$

with

$$\langle U \rangle = -mc^2 \frac{\alpha^2}{n^2}. \quad (12.219)$$

If we take the non-relativistic kinetic energy, Eq. (12.218) becomes

$$E_{n-r-kin} = -mc^2 \frac{\alpha^2}{2n^2} - \left(1 + \frac{3}{4} \frac{\alpha^2}{n^2} \right) \left(\frac{e\hbar}{2m} m_l B_Z \right), \quad (12.220)$$

and the pure non-relativistic result is

$$E_{n-r} = \left(mc^2 \frac{\alpha^2}{2n^2} - \frac{e\hbar}{2m} m_l B_Z \right) + \langle U \rangle = -mc^2 \frac{\alpha^2}{2n^2} - \frac{e\hbar}{2m} m_l B_Z. \quad (12.221)$$

l and m_l are the quantum numbers of the angular momentum and its Z component. m_l takes values between $-l$ and l . Please notice that the formulas of the Zeeman effect do not depend on the quantum number l , this would only be the case for the anomalous Zeeman effect. The selection rules for transitions are

$$\begin{aligned} \Delta l &= \pm 1, \\ \Delta m_l &= -1 \quad \text{for left-circularly polarized light,} \\ \Delta m_l &= 0 \quad \text{for linearly polarized light,} \\ \Delta m_l &= +1 \quad \text{for right-circularly polarized light} \end{aligned}$$

(see Fig. 12.7). For light absorption as in the Zeeman effect, there is always $\Delta l = 1$.

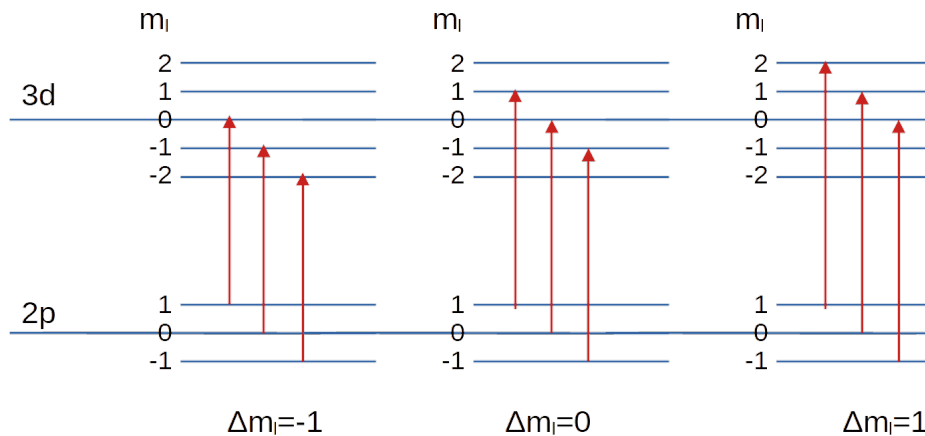


Figure 12.7: Transition lines $2p \rightarrow 3d$ in the Zeeman spectrum.

Consider, for example, a transition
 $(n = 2, l = 1, m_l = 0) \rightarrow (n = 3, l = 2, m_l = 1)$.
 Assuming a magnetic field strength of 0.1 T, we obtain for the initial and final state from the above formulas (in Hartree units):

$$\begin{aligned} E_{n-r}(1) &= -0.125 & (12.222) \\ E_{n-r-kin}(1) &= -0.125 \\ E(1) &= -0.12499875 \end{aligned}$$

and

$$\begin{aligned} E_{n-r}(2) &= -0.10555555 & (12.223) \\ E_{n-r-kin}(2) &= -0.10555578 \\ E(2) &= -0.10555553 \end{aligned}$$

We can see that, for $m_l > 0$, the splitting is partially compensated, because the correction for the kinetic energy is positive and that for the Zeeman term is negative in this case. Because these corrections depend only on the principal quantum numbers, there is, for example, no difference between the transitions

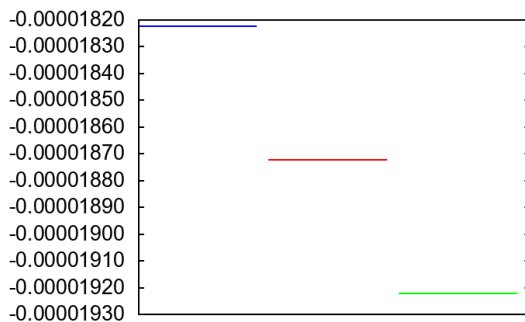
$$(n = 3, l = 1, m_l = 0) \rightarrow (n = 4, l = 2, m_l = 1)$$

and

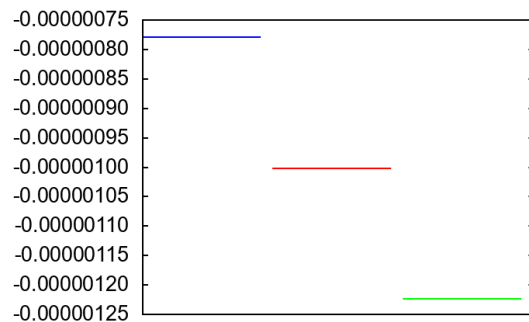
$$(n = 3, l = 1, m_l = 0) \rightarrow (n = 4, l = 3, m_l = 1),$$

which differ only in the angular momentum of the final state.

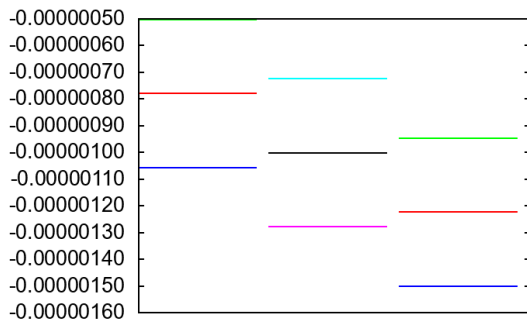
Some exemplary relativistic corrections to the Zeeman spectra are graphed in Figs. 12.8 (a)-(i). In each diagram, the three columns represent the corrections of the transition energies for $\Delta m_l = -1, 0, 1$. The transitions (a)-(g) are between neighboring principal quantum numbers n , (h)-(i) are for larger differences of n . The different scales should be noticed. The higher n , the smaller the energy corrections. It is not possible to graph the absolute transition energies, because then the differences between the non-relativistic and relativistic case would not become visible. In the non-relativistic case, it is always $\Delta E = 0$. The deviations should be observable by high-resolution spectroscopy. ■



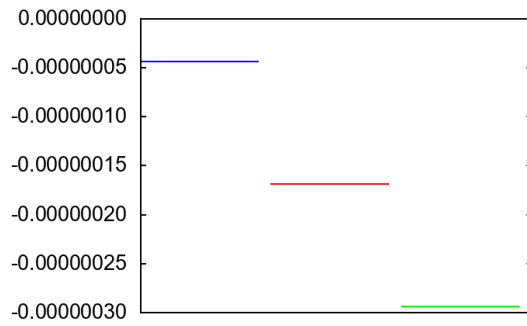
(a) 1s \rightarrow 2p



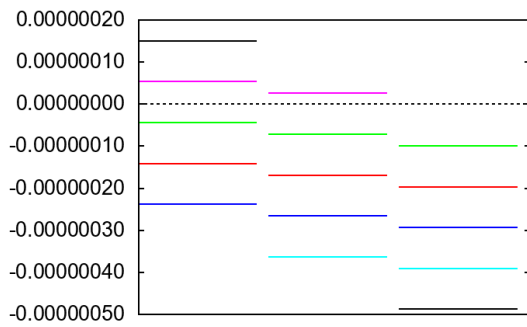
(b) 2s \rightarrow 3p



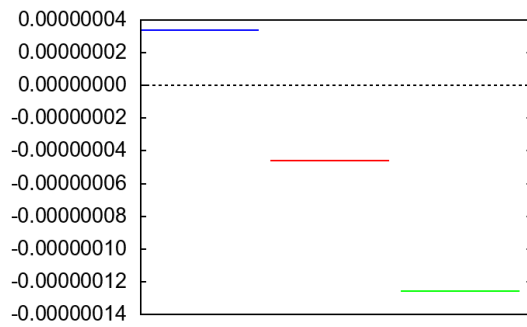
(c) 2p --> 3d



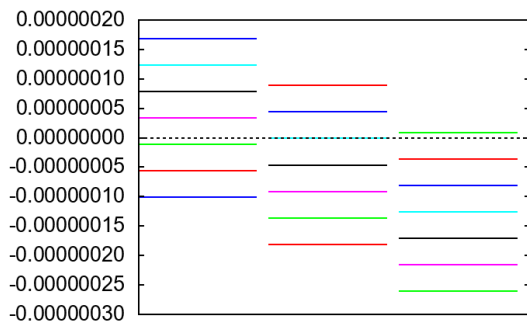
(d) 3s --> 4p



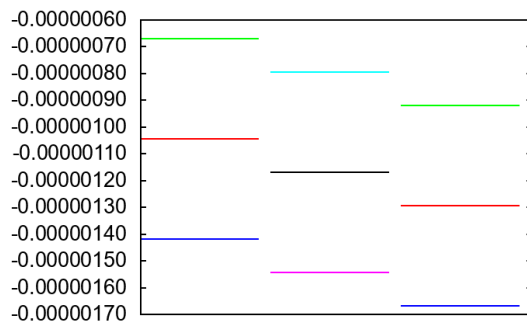
(e) 3d --> 4f



(f) 4s --> 5p



(g) 4f --> 5g



(h) 2p --> 4d

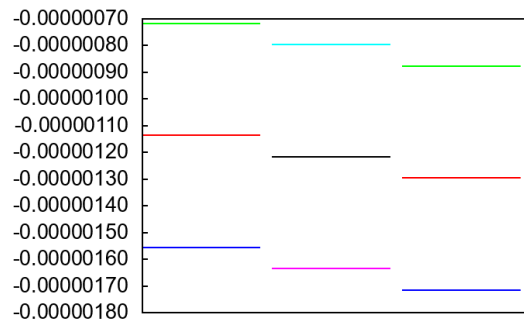
(i) 2p \rightarrow 5d

Figure 12.8: (a)-(i): Relativistic Zeeman corrections of ECE2 theory in Hartree units, $\Delta m_l = -1, 0, 1$, (a)-(g): $\Delta n = 1$, (h)-(i): $\Delta n > 1$.

Summarizing this chapter, we have developed a number of effects important for spectroscopy, first based on the Dirac/Fermion equation, then based on the Einstein energy equation directly. Different quantization methods have been applied. The physical effects and their computational basis are listed in Table 12.3. The ESOR method was newly introduced. The method of Dirac leads to inconsistencies but obviously to the right experimental results. By quantizing Einstein's energy equation directly, we obtain relativistic corrections to the spectra, leading to shifts and splittings that should be observable by high-resolution spectroscopic methods.

The mathematics applied throughout this chapter was the Pauli algebra for $SU(2)$ geometry. This led to quite complex mathematical derivations. Pauli algebra was used in diverse variants for quantizing classical quantities like linear and angular momentum. How to do this, is highly non-unique and depends on whether the results are experimentally found or not. This makes this part of quantum mechanics ambiguous and quasi "experimental".

Method	Equation basis	Equation	Type of theory
g factor	Dirac/ECE2	(12.29)	rel./non-rel.
spin-orbit coupling	Dirac/ECE2	(12.53)	rel./non-rel.
Darwin term	Dirac/ECE2	(12.57)	rel./non-rel.
anomalous Zeeman effect	Dirac/ECE2	(12.77)	rel./non-rel.
ESOR	Dirac/ECE2	(12.102)	rel./non-rel.
Zeeman effect	Dirac/ECE2	(12.109)	rel./non-rel.
spin-orbit coupling	ECE2 type I	(12.179)	rel.
spin-orbit coupling	ECE2 type IV	(12.197)	rel.
anomalous Zeeman effect	ECE2 type IV	(12.210)	rel.
Zeeman effect	ECE2 type IV	(12.218)	rel.

Table 12.3: Summary of developments in Chapter 12.



Bibliography

Chapter 11

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- [9] <http://mathworld.wolfram.com/SphericalHarmonic.html>
- [10] Papers 251, 252, Unified Field Theory (UFT) Section of www.aias.us.
- [11] Paper 253, Unified Field Theory (UFT) Section of www.aias.us.
- [12] Papers 329-335, Unified Field Theory (UFT) Section of www.aias.us.

Computer algebra code (Maxima)

(You can find this code on <http://aias.us/documents/uft/ECE-Code.zip>.)

- [13] Ex11.1.wxm - Example 11.1
- [14] Ex11.1a.wxm - Pauli and Dirac theory
- [15] Ex11.1b.wxm - Fermion equation
- [16] Ex11.2.wxm - Example solution for Fermion equation
- [17] Ex12.1.wxm - Pauli algebra and related theorems
- [18] Ex12.2.wxm - ESOR energies of Hydrogen
- [19] Ex12.3.wxm - Parameters of Hydrogen atom
- [20] Ex12.4.wxm - Relativistic spin-orbit coupling of Hydrogen
- [21] Ex12.5.wxm - Relativistic anomalous Zeeman transitions of Hydrogen

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