DRAFT VERSION

Einstein-Cartan-Evans Unified Field Theory

The Geometrical Basis of Physics

Volume 2: Quantum Physics

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Layout created with the Legrand Orange Book style by LaTeXTemplates.com.

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Creation date: November 17, 2023

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11.1 Introduction

In Volume 1 of this textbook [1], all relevant subjects of classical physics were revisited from the perspective of ECE theory. In particular, this includes the unification of classical dynamics, electrodynamics, and fluid dynamics. A number of new connections among these subjects were revealed and new insights were discussed. In this second volume, we extend the unification to quantum mechanics. We will show that the quantum realm can be described by the same Cartan geometry that was used for the classical realm, and this requires only a quantization of physical variables has to be performed, which we do in the canonical way known from standard quantum mechanics.

The Dirac equation 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. We do this similarly to how we handled Maxwell's equations in electrodynamics, and in so doing we are even able to simplify Dirac's structure (which is based on 4x4 matrices) to the 2x2 Pauli matrices. We call the resulting equation the "Fermion equation", because it holds for fermions in the same way as the Dirac equation.

After we develop this fundamental result, we will discuss far-reaching consequences of ECE quantum mechanics in later chapters. In particular, some of these 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

We start by recapitulating selected basics of standard quantum mechanics that are relevant to this aspect of ECE theory. This section cannot present the whole subject area of quantum mechanics. A reader who is not familiar with quantum mecahnics, can find supplementary information in standard textbooks such as [2].

A quantum-mechanical state is described by its complex valued *wave function* $\psi(x^\mu)$, which depends on the coordinates x^μ of 4-space. The wave function is also called the *probability amplitude*. A quantum state has a *probability distribution* that is defined by

$$p(x^\mu) = |\psi(x^\mu)|^2 = \psi^*(x^\mu)\psi(x^\mu), \tag{11.1}$$

and it always has 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,

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

which is often written as

$$W = \langle \psi | W_{op} | \psi \rangle = \langle W_{op} \rangle . \tag{11.3}$$

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:

$$W_{ij} = \left\langle \psi_i | W_{op} | \psi_j \right\rangle . \tag{11.4}$$

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

$$\left\langle \psi_i | \psi_j \right\rangle = \int \psi_i^* \psi_j d^3 r, \tag{11.5}$$

and this integral also called the *overlap* between wave functions. Wave functions have to be normalized and, for an orthonormal set of wave functions, the following relation holds:

$$\left\langle \psi_i | \psi_j \right\rangle = \delta_{ij} \tag{11.6}$$

(with δ being the Kronecker symbol).

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

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

and in contravariant form it is

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

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

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

$$\mathbf{p} \rightarrow -i\hbar \boldsymbol{\nabla}. \tag{11.10}$$

In 4-space, we obtain the covariant and contravariant momentum operators, denoted by $\widehat{p}_\mu$ and $\widehat{p}^\mu$:

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

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

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 $\widehat{H}$ and energy operator $\widehat{E}$, it reads:

$$\widehat{H}\psi = \widehat{E}\psi. \tag{11.13}$$

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

$$\frac{\widehat{\mathbf{p}}^2}{2m} = -\frac{\hbar^2}{2m}\nabla^2, \tag{11.14}$$

and the *energy operator* is

$$\widehat{E} = i\hbar\frac{\partial}{\partial t}. \tag{11.15}$$

Hence, the Schrödinger equation takes the following form:

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

The *probability density* is

$$\rho = |\psi|^2 = \psi^*\psi, \tag{11.17}$$

and is positive definite. The *probability current* is

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

11.2.2 Klein-Gordon equation

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

$$E^2 = c^2p^2 + mc^2 \tag{11.19}$$

by the quantization rules (11.9, 11.10) and obtain

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

This equation is of second order and leads to negative probability densities. The latter point motivated Paul Dirac to derive an equation that gives only positive probability densities. The spin of electrons requires further modifications for spin-1/2 particles, which require the use 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 specification of two different 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 ensures that the rotational symmetry of these states will be described adequately.

By using group theory, the group of rotations in three-dimensional Euclidean space can 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:

$$RR^T = R^T R = I, \tag{11.21}$$

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 to its inverse, that is, if

$$U^{*T} = U^{-1}. \tag{11.22}$$

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

$$UU^{*T} = UU^{+} = I. \tag{11.23}$$

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

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

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

$$|a|^2 + |b|^2 = 1 \tag{11.25}$$

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]

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

■ **Example 11.1** In this example, we illustrate the relation between SU(2) and O(3) rotations. We rotate the spinors by progressing angles on the complex unit circle by defining

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

$$\xi_2 = \frac{1}{\sqrt{2}}, \tag{11.28}$$

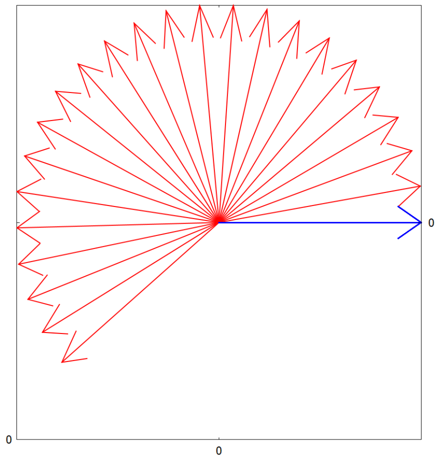


Figure 11.1: Example of a rotation in SU(2) geometry; red: ξ_1, blue: ξ_2.

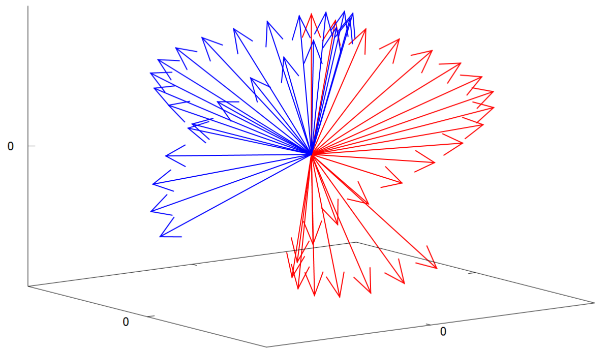


Figure 11.2: (ξ_1,ξ_2), transformed to O(3) geometry; red and blue: real and imaginary parts of (X,Y,Z), respectively.

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 [16]). 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 to 3D space by Eq. (11.26). These vectors have real and imatinary parts. 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 following form:

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

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

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

The 2D spinor rotates by half of the angle as the 3D vector. This leads to a topological distinction between the rotation groups. Increasing the angle α by 2π gives the result $U\to -U$ for the SU(2) rotation, while giving $R\to R$ for the O(3) rotation. Any rotation in SU(2) corresponds to a rotation by twice that 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 that depend on the spin state. The three *Pauli matrices* are

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

Sometimes, an additional unit matrix is used:

$$\sigma^0 = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}. \tag{11.32}$$

The Pauli matrices are self-inverse:

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

The commutator relation is

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

and the anti-commutator relation is

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

A vector of Pauli matrices is defined by

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

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

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

This is a unitary matrix, ant this can be seen by comparing it to 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 $\widehat{\mathbf{p}}$ operator written out according to (11.11), the helicity operator is

$$\widehat{h} = \hbar \begin{bmatrix} i\partial_3 & \partial_2 + i\partial_1 \\ -\partial_2 + i\partial_1 & -i\partial_3 \end{bmatrix}. \tag{11.38}$$

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 has only been possible by extending the 2-dimensional spinors of non-relativistic Pauli theory to 4-dimensional spinors that allow a Lorentz-invariant description. Consequently, 4x4 matrices, the γ *matrices*, had to be defined, analogously to the Pauli matrices. These matrices, in *Weyl* *representation* [2] (also called the *spinor representation*) are given by

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

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

$$\gamma^0_{\text{Dirac}} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix}. \tag{11.40}$$

The Dirac equation in covariant form is

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

or, with the momentum operators written out,

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

where ψ is the 4-spinor of wave functions:

$$\psi = \begin{bmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{bmatrix}. \tag{11.43}$$

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

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

The components ψ_1 and ψ_3 correspond to spin-up states, while ψ_2 and ψ_4 describe spin-down states. Also, the components ψ_1 and ψ_2 describe right-handedness, while ψ_3 and ψ_4 describe left-handedness. Each handedness has a spin-up and spin-down component. The pairs of handedness are combined to form *2-spinors*, ϕ_R and ϕ_L, in the following way:

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

which allows the Dirac equation (11.41) to also be written in the following form:

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

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

$$j^\mu = \bar{\psi}\gamma^\mu\psi \tag{11.47}$$

with the *adjoint spinor*

$$\bar{\psi} = \psi^{*T}\gamma^0. \tag{11.48}$$

It follows that

$$\rho = |\psi_1|^2 + |\psi_2|^2 + |\psi_3|^2 + |\psi_4|^2, \tag{11.49}$$

which satisfies the condition of being positive definite. For computational details regarding the Pauli and Dirac matrices, as well as the Dirac equation, see computer algebra code [17].

A problem with 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:

$$\gamma^0 E\psi = mc^2\psi. \tag{11.50}$$

This is an eigenvalue equation for γ_0, with eigenvalues +1 and -1, each of them with a multiplicity of 2. In the classical limit, we therefore obtain two equations for the rest energy:

$$E = +mc^2, \tag{11.51}$$

$$E = -mc^2. \tag{11.52}$$

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 to be filled with vacuum states of negative energy, and pulling up an electron would produce a hole, which would then be filled by an electron with positive mass energy E, falling down to energy state $-E$, representing a positron. These problematic interpretations can be averted by using 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

$$\widehat{E}\begin{bmatrix}0&0&1&0\\0&0&0&1\\1&0&0&0\\0&1&0&0\end{bmatrix}\begin{bmatrix}\psi_1\\\psi_2\\\psi_3\\\psi_4\end{bmatrix} + c\begin{bmatrix}\begin{matrix}0&0\\0&0\end{matrix}&\boldsymbol{\sigma}\cdot\widehat{\mathbf{p}}\\-\boldsymbol{\sigma}\cdot\widehat{\mathbf{p}}&\begin{matrix}0&0\\0&0\end{matrix}\end{bmatrix}\begin{bmatrix}\psi_1\\\psi_2\\\psi_3\\\psi_4\end{bmatrix} = mc^2\begin{bmatrix}\psi_1\\\psi_2\\\psi_3\\\psi_4\end{bmatrix} \tag{11.53}$$

with the 2x2 helicity operator

$$\widehat{h} = \boldsymbol{\sigma}\cdot\widehat{\mathbf{p}} = \begin{bmatrix}\widehat{p}_3 & \widehat{p}_1 - i\widehat{p}_2\\ \widehat{p}_1 + i\widehat{p}_2 & -\widehat{p}_3\end{bmatrix}. \tag{11.54}$$

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 derived from 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:

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

which are column vectors. By using them, we can define a 2x2 tetrad

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

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 $q^a{}_\mu$, 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

$$V^a = q^a{}_\mu V^\mu. \tag{11.57}$$

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

$$\begin{bmatrix} V^R \\ V^L \end{bmatrix} = \begin{bmatrix} q^R{}_1 & q^R{}_2 \\ q^L{}_1 & q^L{}_2 \end{bmatrix} \begin{bmatrix} V^1 \\ V^2 \end{bmatrix}. \tag{11.58}$$

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 [18] shows that Eq. (11.53) can be cast into the following form:

$$\widehat{E} \begin{bmatrix} \psi_3 & \psi_1 \\ \psi_4 & \psi_2 \end{bmatrix} + c\boldsymbol{\sigma} \cdot \widehat{\mathbf{p}} \begin{bmatrix} \psi_3 & -\psi_1 \\ \psi_4 & -\psi_2 \end{bmatrix} = mc^2 \begin{bmatrix} \psi_1 & \psi_3 \\ \psi_2 & \psi_4 \end{bmatrix}. \tag{11.59}$$

This is already in the tetrad form that is being sought. In this equation, the orignial ψ tetrad (11.56) has been permuted in two different ways as follows. This equation can be expressed by the Pauli matrices and the transpose of the ψ tetrad,

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

to obtain

$$\widehat{E}\psi^T \sigma^1 + c\boldsymbol{\sigma} \cdot \widehat{\mathbf{p}} (\sigma^1 \psi)^T \sigma^3 = mc^2 \psi^T \tag{11.61}$$

(see computer algebra code [18]). An additional transposition of this equation gives the Fermion equation in the following form:

$$\boxed{\widehat{E}\sigma^1 \psi + c\sigma^3 \sigma^1 \psi (\boldsymbol{\sigma} \cdot \widehat{\mathbf{p}})^T = mc^2 \psi.} \tag{11.62}$$

It should be noted that $(\boldsymbol{\sigma}\cdot\widehat{\mathbf{p}})^T$ is a left-operator. Written out in components, this equation is

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

These equations are identical to the four single Eqs. (11.44) that comprise the Dirac equation. The left-operator in (11.62) can be avoided by writing the Fermion equation in the following alternative form:

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

(see [4] and computer algebra code [18]). The negative sign of the $\widehat{p}_2$ term prevents further simplification. However, this sign becomes positive, if we redefine the sign of the Pauli matrix:

$$\sigma^2 \to -\sigma^2. \tag{11.65}$$

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

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

and, for completeness,

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

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

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

Eq. (11.64) can now be written in the following form:

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

We define a matrix-form of 4-momentum by

$$\pi_\mu = (\pi_0, \pi_1, \pi_2, \pi_3) \tag{11.70}$$

with

$$\pi_0 = \sigma'^0 p_0, \quad \pi_i = -\sigma'^3 p_i, \tag{11.71}$$

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

$$\boxed{\widehat{\pi}_\mu\psi\sigma'^\mu = mc\sigma'^1\psi.} \tag{11.72}$$

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 the equivalent here, but within the framework of Cartan geometry. The ECE wave equation is identical to the Evans Lemma (2.258), which is a differential equation of second order for the tetrad elements:

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

and which uses the d'Alembert operator:

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

(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. By comparing Eq. (11.73) to the Dirac equation, we see that

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

and has the correct 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 following form:

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

We will now factorize the wave equation, and we start with the Einstein energy equation

$$E^2 - c^2 p^2 = m^2 c^4, \tag{11.77}$$

which can be factorized on the classical level into

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

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

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

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

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

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

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

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

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

$$\begin{aligned}
c\,(\widehat{p}_1 - i\widehat{p}_2)\,\psi_4 + \left(c\,\widehat{p}_3 + \widehat{E}\right)\,\psi_3 &= m c^2\,\psi_1,\\
c\,(\widehat{p}_1 + i\widehat{p}_2)\,\psi_3 + \left(-c\,\widehat{p}_3 + \widehat{E}\right)\,\psi_4 &= m c^2\,\psi_2,\\
c\,(-\widehat{p}_1 + i\widehat{p}_2)\,\psi_2 + \left(-c\,\widehat{p}_3 + \widehat{E}\right)\,\psi_1 &= m c^2\,\psi_3,\\
c\,(-\widehat{p}_1 - i\widehat{p}_2)\,\psi_1 + \left(c\,\widehat{p}_3 + \widehat{E}\right)\,\psi_2 &= m c^2\,\psi_4.
\end{aligned} \tag{11.83}$$

These equations are again identical to those of (11.63) that, in turn, are identical to the original Dirac equation (see computer algebra code [18]).

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

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

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

For the spinor components, we use the following approach:

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

These are plane waves with a different wave number, $+k_{Z1}$ or $-k_{Z2}$, for each spin direction. We will now show that this is a solution of the Fermion equation within specific constraints. By inserting these functions into Eqs. (11.84, 11.85), and taking the real parts, we obtain the following component equations:

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

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

(see computer algebra code [19]). The left and right sides of these equations are compatible, if

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

and

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

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

$$\hbar\omega_0 = mc^2. \tag{11.91}$$

If the fermion has a non-vanishing momentum, then 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, 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, the form shown in Eq. (11.62)), it follows that

$$E\psi = mc^2\sigma_1\psi, \tag{11.92}$$

or, in the form of component equations:

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

The same result is obtained for the rest fermion 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 2x2 matrix and not a 4x4 matrix as it is in the Dirac case, the eigenvalues are not twofold degenerate; nevertheless, the two signs remain. To investigate this further, we analyze 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

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

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

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

which can be reduced to a quadratic equation with the solutions

$$E_{1,2} = \pm mc^2 \tag{11.96}$$

(see computer algebra code [18]). 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

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

This represents a phase shift in the wave functions ψ_1 and ψ_2, but leaves their absolute values unaltered, thus 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, and 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 had de facto already been solved years ago. Another argument against the introduction of negative energies is that 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.

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

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

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 textbooks, 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 trace matrix was used, which gives the right probability density, but the current densities differ from those of Dirac theory. We prefer the method shown below, because it 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 will rewrite the definition of the Dirac current j^μ in the corresponding form:

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

where a "+" denotes the adjoint spinor. From computer algebra [17, 18], it follows that the current density is identical to that of Dirac's theory. When we denote the real and imaginary parts of the wave functions ψ_j by

$$\psi_j = \phi_j + i\chi_j, \tag{11.100}$$

the current densities become

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

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

$$j^0 = |\psi_1|^2 + |\psi_2|^2 + |\psi_3|^2 + |\psi_4|^2, \tag{11.102}$$

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 $\widehat{h} = \boldsymbol{\sigma} \cdot \widehat{\mathbf{p}}$ is the helicity operator, which describes a projection of spin in the direction of linear momentum. Changing 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:

$$P(h) = -h. \tag{11.103}$$

Similarly, parity reverses the coordinates X, Y and Z for a given frame **i**, **j** and **k** in cartesian coordinates. So, for a position vector **r**,

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

or, in short-hand notation:

$$P \to -P. \tag{11.105}$$

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

$$T(h) = h, \tag{11.106}$$

or, in short-hand notation:

$$T \to T. \tag{11.107}$$

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

$$C(e) = -e. \tag{11.108}$$

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

$$CPT \to (-C)(-P)T = CPT, \tag{11.109}$$

so 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) then describe a positron. This means that the character of the wave functions remains as is. When both spinor equations, and the term $c\boldsymbol{\sigma} \cdot \widehat{\mathbf{p}}$, undergo a helicity change, the wave functions interchange according to $P(\Phi^R) = \Phi^L$ and $P(\Phi^L) = \Phi^R$, so that the spinor equations (11.81, 11.82),

$$(\widehat{E} - c\boldsymbol{\sigma} \cdot \widehat{\mathbf{p}})\Phi^R = mc^2\Phi^L, \tag{11.110}$$
$$(\widehat{E} + c\boldsymbol{\sigma} \cdot \widehat{\mathbf{p}})\Phi^L = mc^2\Phi^R, \tag{11.111}$$

remain the same:

$$(\widehat{E} + c\boldsymbol{\sigma} \cdot \widehat{\mathbf{p}})\Phi^L = mc^2\Phi^R, \tag{11.112}$$
$$(\widehat{E} - c\boldsymbol{\sigma} \cdot \widehat{\mathbf{p}})\Phi^R = mc^2\Phi^L. \tag{11.113}$$

When a fermion collides with an antifermion, the momenta cancel out. Then adding the first and fourth equations, (11.110) and (11.113), gives us

$$2E\Phi^R = 2mc^2\Phi^L, \tag{11.114}$$

and doing the same with the second and third equations gives us

$$2E\Phi^L = 2mc^2\Phi^R. \tag{11.115}$$

Finally, adding these two new equations gives us

$$2E(\Phi^R + \Phi^L) = 2mc^2(\Phi^R + \Phi^L), \tag{11.116}$$

which is 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's 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, then the frequencies at which resonant absorption takes place are observed. Absorption can occur by induction of molecular rotations/vibrations or lattice vibrations in solids. This appears in the microwave and infrared ranges. For higher frequencies, transitions in the electronic shells are induced, up to emission of electrons from atomic compounds. Excitations of nucleons in atomic nuclei can also arise. Widely used spectroscopy methods are, for example, ESR (electron spin resonance), PES/XPS (photo or X-ray emission spectroscopy), NMR (nuclear magnetic resonance) and Raman spectroscopy, and an overview of these methods is given in [5].

12.1 g factor and spin-orbit coupling

12.1.1 g factor

To describe quantum mechanical excitations using ECE theory, electromagnetic fields have to be incorporated into the Fermion equation. We will use methods similar to those used for the Dirac equation [2, 6]. In the presence of an electromagnetic field, the generalized terms for energy and momentum are

$$E \rightarrow E - e\Phi, \tag{12.1}$$

$$\mathbf{p} \rightarrow \mathbf{p} - e\mathbf{A}, \tag{12.2}$$

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:

$$\widehat{E} \rightarrow \widehat{E} - e\Phi, \tag{12.3}$$

$$\widehat{\mathbf{p}} \rightarrow \widehat{\mathbf{p}} - e\mathbf{A}. \tag{12.4}$$

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

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

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

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

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

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

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

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

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

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

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

(see computer algebra code [20]). To be mathematically exact, we would have to add the unit matrix σ^0 on the right side, but this matrix is often omitted by convention as well. Relation (12.10) is a special case of the *Pauli algebra theorem*

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

for vectors $\mathbf{F}$ and $\mathbf{G}$, which has also been proven by computer algebra [20]. In Eq. (12.10), we have the special case

$$\mathbf{F} = \mathbf{G} = \mathbf{p} - e\mathbf{A}, \tag{12.12}$$

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

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

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

$$\widehat{\mathbf{p}} = -i\hbar\boldsymbol{\nabla}, \tag{12.14}$$

so that (12.13) becomes

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

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

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

where we have applied both the product rule for the Nabla operator and the definition of the magnetic field from electrodynamics:

$$\mathbf{B} = \boldsymbol{\nabla} \times \mathbf{A}. \tag{12.17}$$

This definition is also present in in ECE2 theory, if we identify the vector potential **A** with the ECE2 vector potential **W** (see Section 6.1.3, Eq. (6.122)).

By inserting this result into (12.9), we obtain

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

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

$$\Phi = 0. \tag{12.19}$$

Eq. (12.18) then becomes

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

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

$$p^2c^2 = E^2 - m^2c^4. \tag{12.21}$$

Consequently, Eq. (12.18) is changed into

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

Introducing the Hamiltonian $\widehat{H}$ allows us to write this equation in the following form:

$$E_{\mathrm{kin}}\Phi^R = \widehat{H}\Phi^R, \tag{12.23}$$

with

$$E_{\mathrm{kin}} = \frac{p^2}{2m} \tag{12.24}$$

and

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

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

$$\widehat{H}_{\mathrm{int}} = -\frac{1}{2m}e\hbar\boldsymbol{\sigma}\cdot\mathbf{B} = -\frac{e\hbar}{2m}\begin{bmatrix} B_Z & 0 \\ 0 & -B_Z \end{bmatrix} = -\frac{e}{m}\mathbf{S}\cdot\mathbf{B} \tag{12.26}$$

with the spin angular momentum

$$\mathbf{S} = \frac{\hbar}{2}\boldsymbol{\sigma}. \tag{12.27}$$

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

$$\mathbf{m}_L = -\frac{e\hbar}{2m}\mathbf{L}, \tag{12.28}$$

and the magnetic moment of the total angular momentum is

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

which requires a "correction factor" g, called the *gyromagnetic factor*, *g factor* or *Landé factor*. The ECE Fermion equation produces a g factor of 2 for the electron, without the use of negative energy. The exact g factor deviates from 2 by radiative corrections, so 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:

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

We assume that there is no magnetic vector potential **A**, but rather an electric potential Φ. Then, this equation becomes

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

Dividing by $E-e\Phi$ gives us

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

and then by adding $mc^2\Phi^R$ to both sides we obtain

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

Next, we use the non-relativistic approximation

$$E=\gamma mc^2\approx mc^2, \tag{12.34}$$

and obtain

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

Multiplying by $E-e\Phi$ gives

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

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

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

which leads to

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

We can write this equation in the following form:

$$E\Phi^R=\widehat{H}\Phi^R \tag{12.39}$$

with the Hamiltonian

$$\widehat{H}=mc^2+e\Phi+c^2\frac{\boldsymbol{\sigma}\cdot\mathbf{p}\,\boldsymbol{\sigma}\cdot\mathbf{p}}{2mc^2-e\Phi}. \tag{12.40}$$

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

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

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

$$\widehat{H}_{\text{s-o}} = \frac{e}{4m^2c^2}\boldsymbol{\sigma}\cdot\mathbf{p}\,\Phi\,\boldsymbol{\sigma}\cdot\mathbf{p}. \tag{12.42}$$

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

We will now 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 this seems to be arbitrary. However, once we replace the momentum p with its operator, it will make a difference where we place a function that originally stood behind multiple operators. The present choice is justified by the fact that the correct experimental results follow. Similarly, when we decide whether one or both functions $\mathbf{p}$ should be replaced with an operator, we will select the configuration that gives results that match experimental values. At this point, quantum mechanics becomes empirical.

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

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

In the last line, we have introduced the electric field strength:

$$\mathbf{E} = -\boldsymbol{\nabla}\Phi. \tag{12.44}$$

This 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 of 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 very selective application of quantization rules.

Next, we apply the Pauli algebra theorem

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

and obtain for (12.43):

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

Taking the real part, and omitting the third term on the right side, gives us the spin-orbit Hamiltonian:

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

With the spin operator

$$\widehat{\mathbf{S}} = \frac{1}{2}\hbar\boldsymbol{\sigma}, \tag{12.48}$$

it follows that

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

By inserting the Coulomb potential of the proton,

$$\Phi = \frac{e}{4\pi\varepsilon_0 r}, \tag{12.50}$$

we obtain the electric field of the Hydrogen atom:

$$\mathbf{E} = -\boldsymbol{\nabla}\Phi = \frac{e^2}{4\pi\varepsilon_0}\frac{\mathbf{r}}{r^3}. \tag{12.51}$$

Using the classical angular momentum,

$$\mathbf{L} = \mathbf{r} \times \mathbf{p}, \tag{12.52}$$

and treating it as an operator, allows us to finally write the spin-orbit Hamiltonian as

$$\widehat{H}_{\text{s-o}} = -\frac{e^2}{4\pi\varepsilon_0 r^3}\frac{\widehat{\mathbf{S}}\cdot\widehat{\mathbf{L}}}{2m^2c^2}, \tag{12.53}$$

or

$$\widehat{H}_{\text{s-o}} = -\xi(r)\,\widehat{\mathbf{S}}\cdot\widehat{\mathbf{L}}, \tag{12.54}$$

with the spin-orbit function

$$\xi(r) = \frac{e^2}{8\pi\varepsilon_0 m^2c^2r^3}. \tag{12.55}$$

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 it is easily detectable and grows with the fourth power of the ordinal number of atoms. Alternatively, the derivation in this section can be based on the Dirac equation in spinor representation, but the Fermion equation, which is a part of ECE quantum mechanics, is simpler. Both derivations contain non-relativistic approximations and a very tricky use of quantum operators.

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

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

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

$$\widehat{H}_{\text{Darwin}}\Phi^R = -\frac{e\hbar^2}{4m^2c^2}\boldsymbol{\nabla}\Phi\boldsymbol{\nabla}\Phi^R. \tag{12.57}$$

The Darwin term can be interpreted as an interaction of the nucleus with the electron, and is effective only close to the nucleus, because there the term $\boldsymbol{\nabla}\Phi$ 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 an effect only on *s* orbitals, because other orbitals (*p*, *d*, ...) have a vanishing probability density at the origin, where the proton resides. ■

12.2 ESOR

In this section, a new type of spectroscopic effect, called *electron-spin-orbit resonance (ESOR)*, is investigated. It is derived from the anomalous Zeeman effect, which will be described first.

12.2.1 Standard Hamiltonian of the anomalous Zeeman effect

In Section 12.1.1, we derived an expression for the interaction of a magnetic field with the spin angular momentum of the electron. Now, we will do this for the interaction of a magnetic field with the spin, and with the orbital momentum, of the electron. 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):

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

This equation was obtained by applying several approximations 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 which gives us

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

Next, we first 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 $\boldsymbol{\sigma}\cdot(\mathbf{p}-e\mathbf{A})$, thus obtaining a Hamiltonian of the linear parts:

$$\widehat{H}_1 = -\frac{1}{2m}\left(\boldsymbol{\sigma}\cdot\mathbf{A}\,\boldsymbol{\sigma}\cdot\mathbf{p}+\boldsymbol{\sigma}\cdot\mathbf{p}\,\boldsymbol{\sigma}\cdot\mathbf{A}\right). \tag{12.60}$$

The Pauli algebra theorem (12.11) gives us

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

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

If we treat $\boldsymbol{\sigma}$ as a function, it follows that

$$\widehat{H}_1 = -\frac{e}{2m}\left(\mathbf{A}\cdot\mathbf{p}+\mathbf{p}\cdot\mathbf{A}+i\boldsymbol{\sigma}\cdot(\mathbf{A}\times\mathbf{p})+i\boldsymbol{\sigma}\cdot(\mathbf{p}\times\mathbf{A})\right). \tag{12.63}$$

For a uniform magnetic field, the vector potential is

$$\mathbf{A} = \frac{1}{2}\mathbf{B}\times\mathbf{r} \tag{12.64}$$

(see computer algebra code [20]). It follows that

$$\widehat{H}_1 = -\frac{e}{4m}\left((\mathbf{B}\times\mathbf{r})\cdot\mathbf{p}+\mathbf{p}\cdot(\mathbf{B}\times\mathbf{r})+i\boldsymbol{\sigma}\cdot((\mathbf{B}\times\mathbf{r})\times\mathbf{p})+i\boldsymbol{\sigma}\cdot(\mathbf{p}\times(\mathbf{B}\times\mathbf{r}))\right). \tag{12.65}$$

Treating $\mathbf{p}$ as a function gives us the following triple product:

$$\mathbf{B}\times\mathbf{r}\cdot\mathbf{p} = \mathbf{p}\cdot\mathbf{B}\times\mathbf{r} = \mathbf{B}\cdot\mathbf{r}\times\mathbf{p} = \mathbf{B}\cdot\mathbf{L}, \tag{12.66}$$

where $\mathbf{L}$ is the classical angular momentum. Then, the Hamiltonian (12.63/12.65), applied to the wave function ψ, becomes

$$\widehat{H}_1\psi = -\frac{e}{2m}\left(\mathbf{L}\cdot\mathbf{B}+i\boldsymbol{\sigma}\cdot(\mathbf{A}\times\mathbf{p})+i\boldsymbol{\sigma}\cdot(\mathbf{p}\times\mathbf{A})\right)\psi. \tag{12.67}$$

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

$$\mathbf{p} = -i\hbar\boldsymbol{\nabla}, \tag{12.68}$$

which results in

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

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

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

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

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

By using the spin operator

$$\widehat{\mathbf{S}} = \frac{\hbar}{2}\boldsymbol{\sigma}, \tag{12.72}$$

this equation can be written in the following form:

$$\widehat{H}_1\psi = -\frac{e}{2m}\left(\widehat{\mathbf{L}}\cdot\mathbf{B} + 2\widehat{\mathbf{S}}\cdot\mathbf{B}\right)\psi = -\frac{e}{2m}\widehat{\mathbf{J}}\cdot\mathbf{B}\;\psi \tag{12.73}$$

with the total angular momentum operator

$$\widehat{\mathbf{J}} = \widehat{\mathbf{L}} + 2\widehat{\mathbf{S}}. \tag{12.74}$$

For multi-electron systems, we have to insert the Landé factor g_J:

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

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

$$J = L+S, \ldots, |L-S|. \tag{12.76}$$

Thus, the general result for (12.73) is

$$\boxed{\widehat{H}_1\psi = -\frac{e}{2m}g_J\widehat{\mathbf{J}}\cdot\mathbf{B}\;\psi.} \tag{12.77}$$

This Hamiltonian describes the *anomalous Zeeman effect*, which is the absorption of light by electrons (where the net spin of the electrons is non-zero) when in the presence of a magnetic field. This Hamiltonian, together with the Hamiltonian of spin-orbit coupling (12.54), produce the ESR spectra. The complete ESR Hamiltonian is

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

When we derived $\widehat{H}_1$, we used the operators for $\mathbf{p}$ in both instances of its occurrence in Eq. (12.67). For deriving $\widehat{H}_{s-o}$, only the first occurrence of $\mathbf{p}$ was converted into an operator. In the final result (12.54), $\mathbf{S}\cdot\mathbf{L}$ was treated as an operator, which has the known eigenvalues

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

for a single electron. Please note that, while we have the option of using $\mathbf{p}$ and $\boldsymbol{\sigma}$ either as functions or operators, our choice was guided by the scientific requirement of conforming to experimental results (which this does).

12.2.2 ESOR Hamiltonian

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

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

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

(see computer algebra code [20]). The product of these equations is

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

Because

$$\mathbf{r}\cdot\mathbf{A}=0 \tag{12.83}$$

(see [20]), this equation simplifies to

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

According to another theorem of the Pauli algebra [20], we have

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

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

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

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

thus Eq. (12.85) becomes

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

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

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

which, because of (12.83), simplifies to

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

According to the Pauli algebra, we additionally have

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

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

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

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

consequently, like as (12.88),

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

Next, we again consider the Hamiltonian (12.59), from which the Hamiltonian $\widehat{H}_1$ (Eq. (12.60)) was derived. We use different choices for operators and functions, and call this Hamiltonian $\widehat{H}_2$. We start with following (written as functions):

$$\widehat{H}_2\psi = -\frac{e}{2m}(\mathbf{p}\cdot\mathbf{A}+\mathbf{A}\cdot\mathbf{p})\,\psi. \tag{12.95}$$

We have derived expressions for the scalar products of **p** and **A** before. By inserting these expressions (Eqs. (12.86, 12.92)), we obtain

$$\widehat{H}_2\psi = -\frac{e}{2m}\frac{1}{r^2}(\boldsymbol{\sigma}\cdot\mathbf{L}\,\boldsymbol{\sigma}\cdot(\mathbf{A}\times\mathbf{r}) + \boldsymbol{\sigma}\cdot(\mathbf{A}\times\mathbf{r})\,\boldsymbol{\sigma}\cdot\mathbf{L})\,\psi. \tag{12.96}$$

For the scalar products in (12.95), it holds that $\mathbf{p}\cdot\mathbf{A} = \mathbf{A}\cdot\mathbf{p}$, and therefore we equate the corresponding terms in Eq. (12.96), which gives us

$$\widehat{H}_2\psi = -\frac{e}{mr^2}\boldsymbol{\sigma}\cdot(\mathbf{A}\times\mathbf{r})\,\boldsymbol{\sigma}\cdot\mathbf{L}\psi. \tag{12.97}$$

Introducing the spin operator,

$$\widehat{\mathbf{S}} = \frac{1}{2}\hbar\boldsymbol{\sigma}, \tag{12.98}$$

and treating **L** as an operator as well, gives us an expectation value, according to standard quantum mechanics, of

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

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

$$\mathbf{A} = \frac{1}{2}\mathbf{B}\times\mathbf{r}, \tag{12.100}$$

from which we obtained

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

(see computer algebra code [20]). By inserting this into Eq. (12.97), we obtain the *ESOR Hamiltonian*:

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

If the magnetic field is aligned in the Z direction, then

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

We assume that the sample is isotropic, so on average

$$\frac{Z^2}{X^2+Y^2+Z^2}=\frac{1}{3}\,. \tag{12.104}$$

Thus, the corresponding part of the ESOR Hamiltonian becomes

$$\widehat{H}\psi=E\psi \tag{12.105}$$

with energy eigenvalues

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

Resonance occurs at the frequency

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

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:

$$\Delta l=\pm 1,\ \Delta m_l=0,\pm 1. \tag{12.108}$$

The conventional Zeeman resonances arise from the term

$$\widehat{H}_Z\psi=-\frac{e}{2m}\widehat{\mathbf{L}}\cdot\mathbf{B}\psi=-\frac{e}{2m}m_l B_Z\psi, \tag{12.109}$$

which is the spin-less version of Eq. (12.77) with $m_l=-l,\ldots,l$, and is called the *(standard) Zeeman effect* (which appears when the net spin of the electrons is zero).

■ **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

$$\langle\widehat{H}_2\rangle=\int\psi^*\widehat{H}_2\psi d^3r=E_{\mathrm{ESOR}}. \tag{12.110}$$

Using

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

it follows that

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

with normalized wave functions

$$\int\psi^*\psi d^3r=1. \tag{12.113}$$

In spherical polar coordinates,

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

and the infinitesimal volume element is

$$d^3r = r^2\sin\theta\, dr\, d\theta\, d\phi \tag{12.115}$$

with

$$r^2 = X^2+Y^2+Z^2. \tag{12.116}$$

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

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

thus

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

For the ESOR Energy, we can then split the result in the following way:

$$E_{\text{ESOR}} = E_1 + E_2 \tag{12.119}$$

with

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

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

where we have abbreviated the quantum number term by

$$F_j = j(j+1) - l(l+1) - s(s+1). \tag{12.122}$$

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

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

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 external tables, 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 [21]. The ordinal number is $Z = 1$ for Hydrogen. The normalization has been checked by computing the integral

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

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

$$\frac{e\hbar}{2m} \cdot 1\mathrm{T} = 3.63695 \cdot 10^{-4}\ \mathrm{eV}. \tag{12.125}$$

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 additional possibilities for defining new spectra, for which numerical examples of hydrogenic wave functions are given in [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 then becomes

$$E \rightarrow E - e\Phi + m\phi, \tag{12.126}$$

where $-e$ is the charge and m is the mass of the electron, and this approach has to be used with 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 should be 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

Up to this point, development of new types of spectroscopy has been based on the Dirac or the Fermion equation. We will now derive these new types directly from Einstein's energy equation. This direct derivation is an independent advancement within the ECE2 theory framework [12].

12.3.1 Spin-orbit coupling

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

$$E^2 = p^2c^2 + m^2c^4, \tag{12.127}$$

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

$$\mathbf{p} = \gamma m\mathbf{v} = \gamma\mathbf{p}_0. \tag{12.128}$$

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

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

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

$$E = \gamma mc^2. \tag{12.130}$$

When we use the relativistic 4-momenta,

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

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

Eq. (12.127) takes the covariant form

$$p^\mu p_\mu = m^2c^2. \tag{12.133}$$

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

$$U = -e\Phi. \tag{12.134}$$

This potential energy enters the relativistic Hamiltonian, which is defined by

$$H = E + U. \tag{12.135}$$

Thus, Eq. (12.127) takes the following form:

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

After factorizing

$$(H-U)^2 - m^2c^2 = p^2c^2 \tag{12.137}$$

into

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

we obtain from Eq. (12.137):

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

Next, we introduce the reduced relativistic Hamiltonian

$$H_0=H-mc^2, \tag{12.140}$$

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

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

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

$$H_{\text{n-r}}=\frac{p_0^2}{2m}+U, \tag{12.142}$$

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

$$\mathbf{p}=\gamma\mathbf{p}_0 \;\to\; \mathbf{p}_0. \tag{12.143}$$

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

$$H \approx mc^2, \tag{12.144}$$

which leads to

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

Therefore, Dirac assumed that

$$E=H-U \;\approx\; mc^2-U=\gamma mc^2, \tag{12.146}$$

and therefore Dirac's Lorentz factor is

$$\gamma_D=1-\frac{U}{mc^2}. \tag{12.147}$$

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

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

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

$$\frac{p_0^2}{2m} \;\approx\; -U. \tag{12.149}$$

After this result is inserted into Eq. (12.142), it follows that

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

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 that

$$|U| \ll 2mc^2, \tag{12.151}$$

thus

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

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 as

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

This is the same as Eq. (12.42) with $U = -e\Phi$. As discussed earlier, the placement of U is mathematically unconstrained; nevertheless, the position is 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):

$$\widehat{H}_{\text{s-o}} = -\frac{e^2}{8\pi\varepsilon_0 m^2c^2r^3}\widehat{\mathbf{S}}\cdot\widehat{\mathbf{L}}. \tag{12.154}$$

We now turn our attention to the usage of momenta. In the development of Eq. (12.53), the quantization rule has been used for the *relativistic* momentum. Although the following is almost never mentioned in textbooks, it is assumed that the relativistic rules for quantization are the same as those 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):

$$\mathbf{p}_0\psi \to -i\hbar\psi, \tag{12.155}$$

$$\mathbf{p}\psi_r \to -i\hbar\psi_r. \tag{12.156}$$

The second $\mathbf{p}$ in Eq. (12.153) has been treated 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:

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

$$\widehat{L}_{0Z}\psi = \hbar m_l\psi. \tag{12.158}$$

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

$$\widehat{H}_{\text{s-o}} = -\frac{e^2}{8\pi\varepsilon_0 m^2c^2r^3}\,\gamma\,\widehat{\mathbf{S}}\cdot\widehat{\mathbf{L}}_0. \tag{12.159}$$

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

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

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

$$J = L+S,\ldots,|L-S|. \tag{12.161}$$

For a single electron, we have

$$S = \pm\frac{1}{2}, \tag{12.162}$$

so

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

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

$$\widehat{H}_{\text{s-o}} = -\frac{e^2}{8\pi\varepsilon_0 m^2c^2r^3}\left(1+\frac{1}{2}\frac{p_0^2}{m^2c^2}\right)\widehat{\mathbf{S}}\cdot\widehat{\mathbf{L}}_0. \tag{12.164}$$

The momentum p_0 determines the non-relativistic kinetic energy

$$T = \frac{1}{2}mv^2 = \frac{p_0^2}{2m}, \tag{12.165}$$

and, according to the Virial theorem, we have

$$U = -2T, \tag{12.166}$$

thus for the non-relativistic Hamiltonian it follows that

$$H_{\text{n-r}} = T+U = -T. \tag{12.167}$$

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

$$\frac{1}{2}\frac{p_0^2}{m^2c^2} = \frac{p_0^2}{2m}\frac{1}{mc^2} = \frac{T}{mc^2} = -\frac{H_{\text{n-r}}}{mc^2}. \tag{12.168}$$

For Hydrogen, the expectation value of this term is

$$-\frac{1}{mc^2}\langle H_{\text{n-r}}\rangle = \frac{1}{mc^2}\frac{e^4m}{32\pi^2\varepsilon_0^2\hbar^2n^2} = \frac{e^4}{32\pi^2\varepsilon_0^2\hbar^2c^2n^2}, \tag{12.169}$$

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

$$\lambda_C = \frac{\hbar}{mc}, \tag{12.170}$$

the fine-structure constant:

$$\alpha = \frac{e^2}{4\pi\varepsilon_0 c\hbar} \tag{12.171}$$

and the Bohr radius:

$$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{e^2 m} = \frac{\hbar}{mc\alpha} = \frac{\lambda_C}{\alpha}, \tag{12.172}$$

we can write

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

and

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

(see computer algebra code [22]). 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

$$\widehat{H}_{\text{s-o}} = -\frac{e^2}{8\pi\varepsilon_0 m^2 c^2 r^3}\left(1+\frac{\alpha^2}{2n^2}\right)\widehat{\mathbf{S}}\cdot\widehat{\mathbf{L}}_0, \tag{12.175}$$

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

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

so that the expectation value of $\widehat{H}_{\text{s-o}}$ becomes

$$\begin{aligned}\left\langle\widehat{H}_{\text{s-o}}\right\rangle &= -\frac{e^2}{8\pi\varepsilon_0 m^2 c^2}\left(1+\frac{\alpha^2}{2n^2}\right)\frac{1}{2}\hbar^2(J(J+1)-L(L+1)-S(S+1)) \\ &\quad\cdot\int\psi^*\frac{1}{r^3}\psi\, d^3r.\end{aligned} \tag{12.177}$$

(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

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

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

$$\left\langle\widehat{H}_{\text{s-o}}\right\rangle = -\frac{e^2\hbar^2}{16\pi\varepsilon_0 m^2 c^2}\frac{J(J+1)-L(L+1)-S(S+1)}{a_0^3 L(L+\frac{1}{2})(L+1)n^3}\left(1+\frac{\alpha^2}{2n^2}\right). \tag{12.179}$$

■ **Example 12.3** We compute the constants in Eq. (12.179). These are, according to computer algebra [22],

$$\frac{e^2\hbar^2}{16\pi\varepsilon_0 m^2 c^2 a_0^3 n^3} = \frac{\alpha\lambda_C\hbar c}{4a_0^3 n^3} = \frac{3.622608\cdot 10^{-4}}{n^3}\text{eV}, \tag{12.180}$$

and

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

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 $L > 0$. Therefore, the smallest value appears for $n = 2$, and 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 to only 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 Hamiltonian is Eq. (12.141):

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

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

$$H_{\text{n-r}} = \frac{p_0^2}{2m} + U \tag{12.183}$$

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

$$\mathbf{p} = \gamma \mathbf{p}_0, \tag{12.184}$$

thus giving

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

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

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

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

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

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

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

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

These 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 for types I and IV. According to Eq. (12.148), we have

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

By using the relation

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

in the limit $v \ll c$ we obtain

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

Insertion of

$$p_0^2 = 2m(H_0 - U) \tag{12.194}$$

gives us

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

This result can be inserted into the Class I Hamiltonian (12.187) while omitting U therein:

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

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

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

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 in the following way. In the presence of a magnetic field, as usual, we replace the momentum $\mathbf{p}_0$ with its generalized form:

$$\mathbf{p}_0 \to \mathbf{p}_0 - e\mathbf{A}. \tag{12.198}$$

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

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

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

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

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

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

From (12.174) we have

$$\langle H_{\text{n-r}}\rangle = -mc^2\frac{\alpha^2}{2n^2}, \tag{12.202}$$

and from the Virial theorem we have

$$\langle U\rangle = 2\langle H_{\text{n-r}}\rangle, \tag{12.203}$$

$$\langle T\rangle = \left\langle \frac{p_0^2}{2m}\right\rangle = \langle H_{\text{n-r}}\rangle - \langle U\rangle = \langle H_{\text{n-r}}\rangle - 2\langle H_{\text{n-r}}\rangle = -\langle H_{\text{n-r}}\rangle. \tag{12.204}$$

Therefore,

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

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

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

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

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

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

The non-relativistic version is

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

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

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

where, in accordance with Eq. (12.203), we insert

$$\langle U\rangle = \int\psi^*U\psi d^3r = -\frac{e^2}{4\pi\varepsilon_0}\int\psi^*\frac{1}{r}\psi d^3r \approx 2\langle H_{\text{n-r}}\rangle = -mc^2\frac{\alpha^2}{n^2} \tag{12.211}$$

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

■ **Example 12.4** We calculate the relativistic energy levels of Hydrogen, inlcuding spin-orbit coupling (see computer algebra code [23]). 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 with a relativistic correction factor, resulting in Eq. (12.179):

$$\left\langle \widehat{H}_{\text{s-o}} \right\rangle = -\frac{e^2\hbar^2}{16\pi\varepsilon_0 m^2 c^2} \frac{J(J+1)-L(L+1)-S(S+1)}{a_0^3 L(L+\frac{1}{2})(L+1)n^3} \left(1+\frac{\alpha^2}{2n^2}\right). \tag{12.212}$$

To describe the total energy of the electron, including this coupling, we have to add the kinetic and potential energies. 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):

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

where the numerical value of the correction factor is

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

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

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

The total energy is then

$$\begin{aligned} E &= E_{\text{kin}} + E_{\text{pot}} + \left\langle \widehat{H}_{\text{s-o}} \right\rangle \\ &= \left(1+\frac{3}{4}\frac{\alpha^2}{n^2}\right) mc^2 \frac{\alpha^2}{2n^2} - mc^2 \frac{\alpha^2}{n^2} \\ &\quad - \frac{e^2\hbar^2}{16\pi\varepsilon_0 m^2 c^2} \frac{J(J+1)-L(L+1)-S(S+1)}{a_0^3 L(L+\frac{1}{2})(L+1)n^3} \left(1+\frac{\alpha^2}{2n^2}\right). \end{aligned} \tag{12.216}$$

In contrast, the total energy in Dirac's theory is the above equation without the relativistic extension factors:

$$E_D = mc^2 \frac{\alpha^2}{2n^2} - mc^2 \frac{\alpha^2}{n^2} - \frac{e^2\hbar^2}{16\pi\varepsilon_0 m^2 c^2} \frac{J(J+1)-L(L+1)-S(S+1)}{a_0^3 L(L+\frac{1}{2})(L+1)n^3}. \tag{12.217}$$

Because the kinetic energy is amplified in this improved ECE 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 schema of Figs. 12.1-12.6. The energies are given in Hartree units (1 H = 2 Ryd = 27.211384 eV). The term schemas show (column-wise) the non-relativistic energy, the Dirac splitting, and the shift and splitting by ECE2 theory. In the latter, the spin-orbit splitting itself is changed only by a relative factor of about $1+10^{-5}$, as was discussed earlier 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.

■

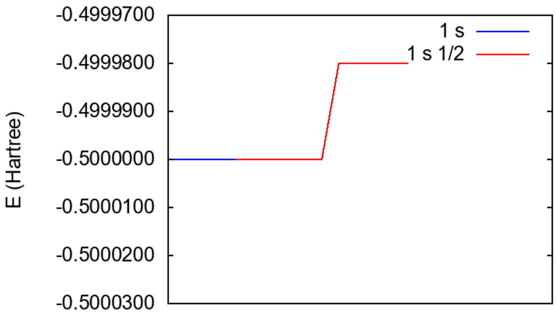


Figure 12.1: Energy schema for 1s states (non-rel., Dirac theory, ECE2 theory).

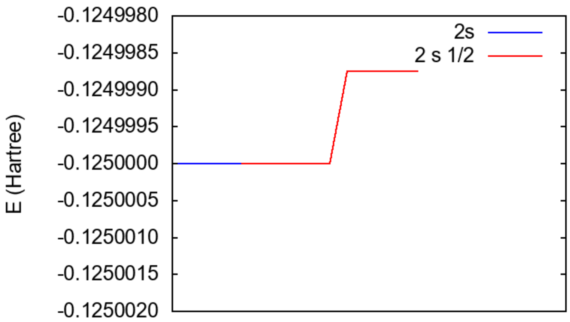


Figure 12.2: Energy schema for 2s states (non-rel., Dirac theory, ECE2 theory).

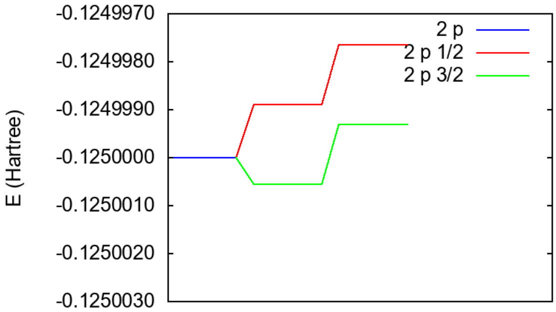


Figure 12.3: Energy schema for 2p states (non-rel., Dirac theory, ECE2 theory).

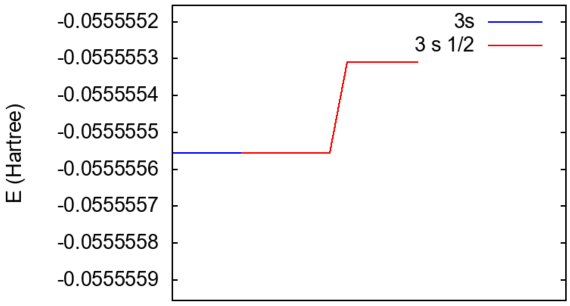


Figure 12.4: Energy schema for 3s states (non-rel., Dirac theory, ECE2 theory).

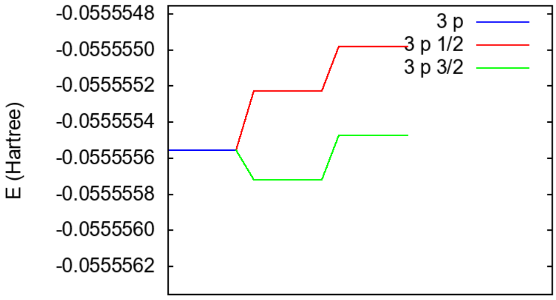


Figure 12.5: Energy schema for 3p states (non-rel., Dirac theory, ECE2 theory).

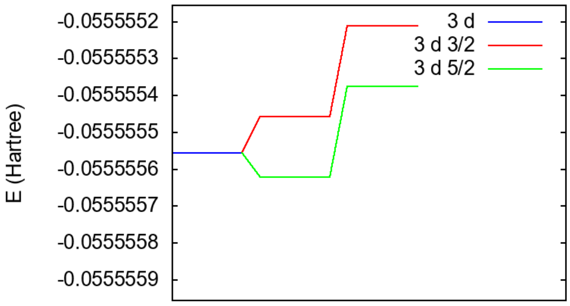


Figure 12.6: Energy schema for 3d states (non-rel., Dirac theory, ECE2 theory).

■ **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 [24]). 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 the 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 regard to the spin of the electron). To accomplish this, we have to replace the quantum number J with l in the equations and omit the gyromagnetic factor g_J. The result is

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

with

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

If we restrict Eq. (12.218) to the non-relativistic kinetic energy, this equation becomes

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

and the pure non-relativistic result (completely without the correction factor) is

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

l and m_l are the quantum numbers of the angular momentum and its Z component, respectively. m_l takes values between -l and l. Please notice that the formulas for the Zeeman effect do not depend on the quantum number l; this dependence only exists 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, Δl is always equal to 1.

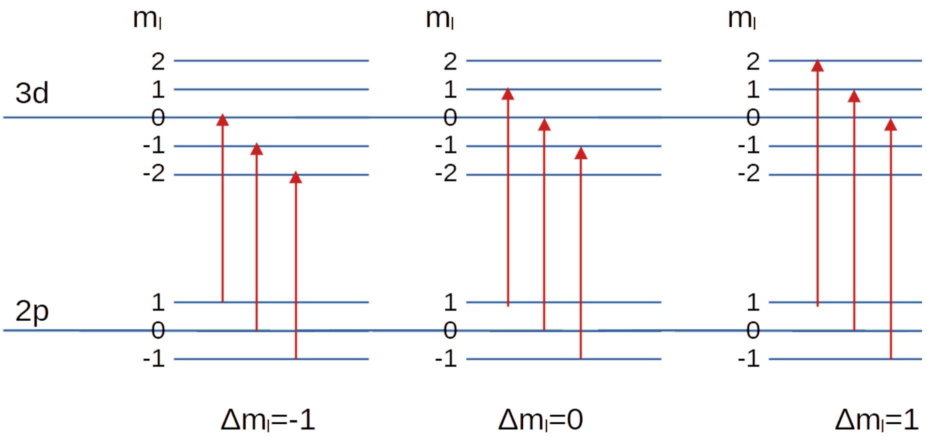


Figure 12.7: Transition lines $2p \rightarrow 3d$ in the Zeeman spectrum.

Consider, for example, the transition
$(n=2,\ l=1,\ m_l=0) \to (n=3,\ l=2,\ m_l=1)$.

Assuming a magnetic field strength of 0.1 T, from the above formulas we obtain for the initial and final states (in Hartree units):

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

and

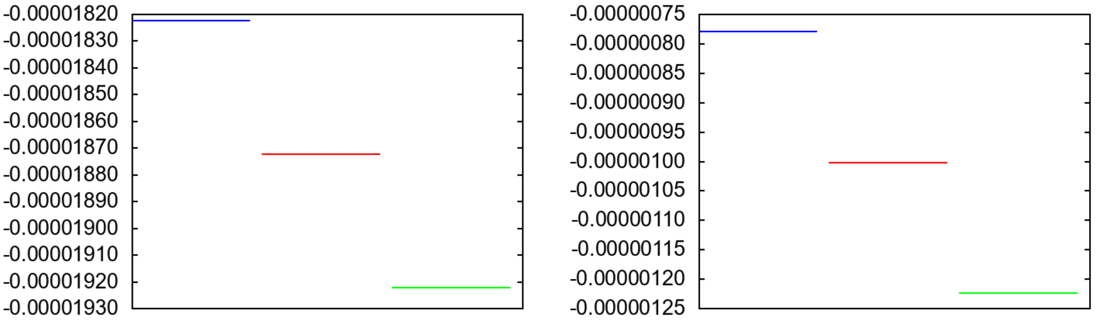
$$\begin{aligned} E_{\text{n-r}}(2) &= -0.10555555, \\ E_{\text{n-r-kin}}(2) &= -0.10555578, \\ E(2) &= -0.10555553. \end{aligned} \tag{12.223}$$

We can see that, for $m_l > 0$, the splitting is partially compensated, because the correction for the kinetic energy is positiv, while the correction for the Zeeman term is negative. Because these corrections depend only on the principal quantum numbers, there is, for example, no difference between the transitions
$(n=3,\ l=1,\ m_l=0) \to (n=4,\ l=2,\ m_l=1)$

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

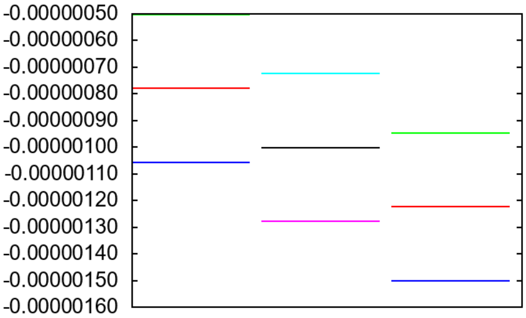
which differ only in the angular momentum of the final state.

A few representative relativistic corrections to the Zeeman spectra are graphed in Figs. 12.8 (a)-(i). In each diagram, the three columns represent the corrections to 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. Please notice that the scales are different. The higher the 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 cases would not be visible. In the non-relativistic case, it is always true that $\Delta E = 0$. The deviations should be observable by high-resolution spectroscopy. ■

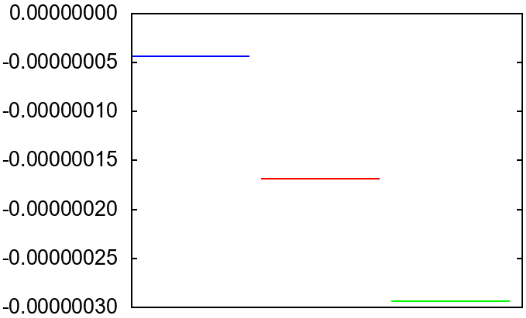


(a) 1s --> 2p

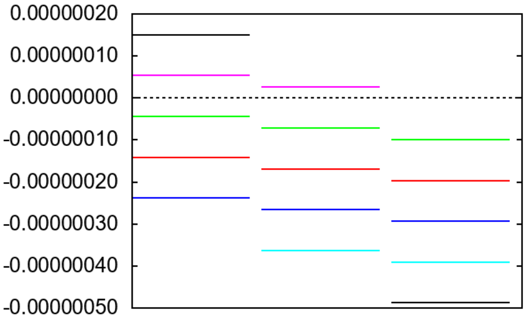
(b) 2s --> 3p



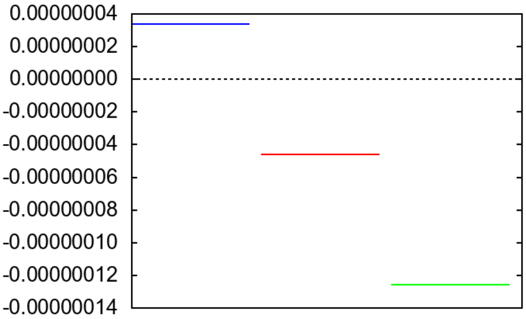
(c) 2p --> 3d



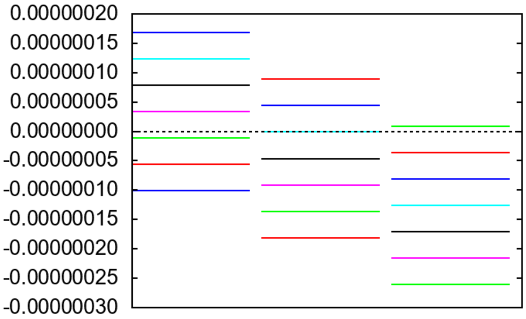
(d) 3s --> 4p



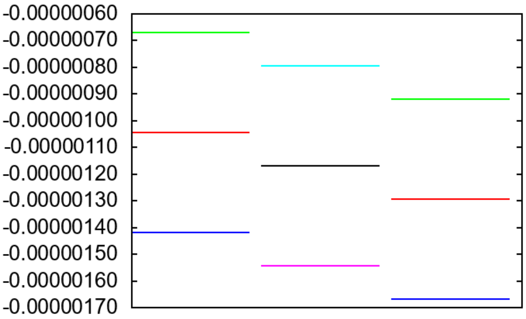
(e) 3d --> 4f



(f) 4s --> 5p



(g) 4f --> 5g



(h) 2p --> 4d

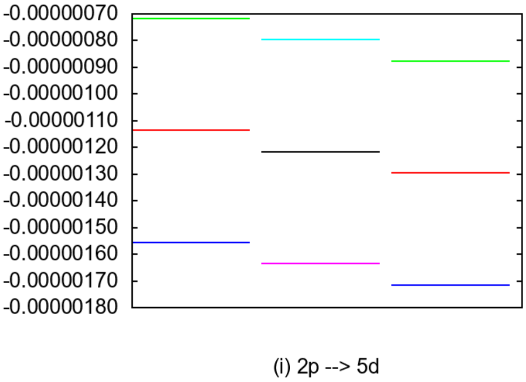


Figure 12.8: (a)-(i): Relativistic Zeeman corrections of ECE2 theory, in Hartree units; $\Delta m_l = -1, 0, 1;$ (a)-(g): $\Delta n = 1;$ (h)-(i): $\Delta n > 1$.

In this chapter, we developed a number of new approaches that are important for spectroscopy. Development was first based either on the Dirac equation or on the equivalent Fermion equation (which is derived from Cartan geometry, and which also averts problematic interpretations). These approaches were then re-developed from Einstein's energy equation directly, which is an advancement unique to ECE2 theory. Different quantization methods were applied, and the physical effects and their computational bases are listed in Table 12.3, below. The new ESOR method was also introduced.

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.

The mathematics applied throughout this chapter was the Pauli algebra for SU(2) symmetry, which led to quite complex mathematical derivations. Pauli algebra was used in several different ways to quantize classical quantities like linear and angular momentum. The method for doing this presents several mathematically equivalent options, which makes this part of quantum mechanics somewhat ambiguous. However, whenever experimental results were available, we selected configurations whose results matched experimental values, which makes this part of quantum mechanics quasi empirical.

13. Improvements of standard quantum theory

After we have introduced the Fermion equation and have described new types of spectroscopy, we present additional aspects of quantum mechanics. Some of them are new, others are given a different interpretation, compared to standard physics.

13.1 Pauli exclusion principle

In 1925, Wolfgang Pauli formulated a principle to explain the structure of atoms using quantum theory. This is called *Pauli exclusion principle*, also known as the *Pauli principle*, for short. In its original version, it states that two electrons in an atom cannot have a set of identical quantum numbers. In the modern formulation, the Pauli principle states that the wave function of a quantum system that consists of fermions (having half-integer spin) is antisymmetric with respect to the permutation of two fermions. As a consequence, fermions are "mutually exclusive", meaning that two fermions in the same quantum system cannot co-exist with the same set of quantum numbers. This is the only way to understand the differentiated structure of matter consisting of atoms and molecules. The Pauli principle does not hold for bosons that have an integer spin. Therefore, fermions and bosons follow a different quantum statistics concerning the occupied orbitals.

The Pauli exclusion principle was considered to be an empirical fact so far. In the following, we will show how this principle can be derived from the solutions of the Fermion equation (see also the original Paper [14]). First, we describe these solutions. The solution method can be found in the standard literature [6] and is the same as for the Dirac theory. The left and right Pauli spinors Φ^L and Φ^R are replaced with a combination of auxiliary spinors Φ^L_S and Φ^R_S:

$$\Phi^R = \Phi^R_S - \Phi^L_S, \tag{13.1}$$
$$\Phi^L = \Phi^R_S + \Phi^L_S. \tag{13.2}$$

These replacements are inserted into the spinor equations (11.81, 11.82):

$$(\widehat{E} - c\boldsymbol{\sigma}\cdot\widehat{\mathbf{p}})\Phi^R = mc^2\Phi^L, \tag{13.3}$$
$$(\widehat{E} + c\boldsymbol{\sigma}\cdot\widehat{\mathbf{p}})\Phi^L = mc^2\Phi^R, \tag{13.4}$$

and lead to the solutions

$$\Phi_S^R = F(r) Y_{l_-}^{jm}, \tag{13.5}$$

$$\Phi_S^L = -i f(r) Y_{l_+}^{jm}, \tag{13.6}$$

where $F(r)$ and $f(r)$ are radial functions, and $Y_{l_\pm}^{jm}$ are the spinor spherical harmonics [13] with total, orbital and spin quantum numbers

$$j = l + s, \tag{13.7}$$

$$l_\pm = j \pm \frac{1}{2}, \tag{13.8}$$

and $s = \pm\frac{1}{2}$. Therefore, the Pauli spinors are

$$\Phi^R = F(r) Y_{l_-}^{jm} + i f(r) Y_{l_+}^{jm}, \tag{13.9}$$

$$\Phi^L = F(r) Y_{l_-}^{jm} - i f(r) Y_{l_+}^{jm}. \tag{13.10}$$

We now investigate the effect of parity. For the solution of the Dirac equations, (13.5, 13.6), it is known that applying the parity operator P to them gives

$$P(F(r)) = F(r), \tag{13.11}$$

$$P(f(r)) = -f(r). \tag{13.12}$$

When we insert the auxiliary spinors into Eqs. (13.3, 13.4), we obtain

$$(\widehat{E} - mc^2)\Phi_S^R + c\boldsymbol{\sigma} \cdot \widehat{\mathbf{p}}\, \Phi_S^L = 0, \tag{13.13}$$

$$(\widehat{E} + mc^2)\Phi_S^L + c\boldsymbol{\sigma} \cdot \widehat{\mathbf{p}}\, \Phi_S^R = 0. \tag{13.14}$$

Applying the parity operator to these equations, and with

$$P(\boldsymbol{\sigma} \cdot \widehat{\mathbf{p}}) = -\boldsymbol{\sigma} \cdot \widehat{\mathbf{p}}, \tag{13.15}$$

it follows that the same equations come out again (see computer algebra code [25]). In Section 11.3.5, however, it was explained that applying the parity operator to the original spinor equations (13.3, 13.4) gives an interchange $\Phi^R \to \Phi^L$ and $\Phi^L \to \Phi^R$, leading to two equations with interchanged wave functions. This is not the case for Φ_S^R and Φ_S^L in the above equations (13.13, 13.14). Even worse, the problem of negative energies reappears. Therefore, the auxiliary spinors are not the physical solutions of the original spinor equations and, consequently, not of the Fermion equation (11.72). We have to use the "back-transformed" spinors (13.1, 13.2) instead.

The total wave function of multi-fermion systems is the product of the one-particle wavefunctions. In the simplest case of a Helium atom, we have two electrons with single orbital wave functions $\psi_{n_1 l_1 m_1}(\mathbf{r}_1)$, $\psi_{n_2 l_2 m_2}(\mathbf{r}_2)$, and the two-particle wave function with quantum number sets $(n_1,\, l_1,\, m_1)$ and $(n_2,\, l_2,\, m_2)$ then is

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_{n_1 l_1 m_1}(\mathbf{r}_1)\psi_{n_2 l_2 m_2}(\mathbf{r}_2). \tag{13.16}$$

If the electron spin is now included, we obtain, for electrons A and B, products of the form

$$\psi_1^R(A)\ \psi_1^R(B),\ \ldots,\ \psi_2^L(A)\ \psi_2^L(B), \tag{13.17}$$

where 1 and 2 are the spin indices of the spinors Φ^R and Φ^L. Using the abbreviations

$$F_1^-(A) = F_1(A) Y_{l_-}^{jm}(A), \tag{13.18}$$

$$f_1^+(A) = f_1(A) Y_{l_+}^{jm}(A), \tag{13.19}$$

and so on, we can write, for example,

$$\begin{aligned} \psi_1^R(A)\ \psi_1^R(B) &= \Big(F_1^-(A) + i f_1^+(A)\Big)\Big(F_1^-(B) + i f_1^+(B)\Big) \\ &= F_1^-(A)F_1^-(B) - f_1^+(A)f_1^+(B) + i\Big(F_1^-(A)f_1^+(B) + f_1^+(A)F_1^-(B)\Big). \end{aligned} \tag{13.20}$$

Applying the parity operator, we obtain

$$\begin{aligned} &P\Big(\psi_1^R(A)\ \psi_1^R(B)\Big) \\ &\quad = F_1^-(A)F_1^-(B) - f_1^+(A)f_1^+(B) - i\Big(F_1^-(A)f_1^+(B) + f_1^+(A)F_1^-(B)\Big). \end{aligned} \tag{13.21}$$

Interchanging the factors in the sums gives

$$\begin{aligned} &P\Big(\psi_1^R(A)\ \psi_1^R(B)\Big) \\ &\quad = F_1^-(B)F_1^-(A) - f_1^+(B)f_1^+(A) - i\Big(F_1^-(B)f_1^+(A) + f_1^+(B)F_1^-(A)\Big), \end{aligned} \tag{13.22}$$

which is the same result as for interchanging the particles A and B:

$$P\Big(\psi_1^R(A)\ \psi_1^R(B)\Big) = \psi_1^R(B)\ \psi_1^R(A). \tag{13.23}$$

Applying the parity operation to the 2-particle wave function conserves the antisymmetry properties introduced in Eqs. (13.11, 13.12). We conclude that the Pauli principle follows from the solutions of the Fermion equation.

13.2 Quantum-Hamilton and force equations

In this section, we derive quantum mechanical equations that are equivalent to equations of classical mechanics [15]. In the standard literature, these equations are not completely handled in this form so far. They are based on commutators, and as a by-product of inspecting commutator properties, we derive Heisenberg's uncertainty principle. We show that this principle is not tenable in its generalized form used today.

13.2.1 Commutators and Heisenberg's uncertainty principle

First, we consider properties of quantum-mechanical commutators. The *commutator* of two operators $\hat{A}$ and $\hat{B}$ is defined by

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}. \tag{13.24}$$

This is the definition on the abstract operator level. The operators have to be applied to a wave function, so what is meant with the above equations is

$$[\hat{A}, \hat{B}]\psi = \hat{A}\hat{B}\psi - \hat{B}\hat{A}\psi. \tag{13.25}$$

The expectation value of a commutator for a quantum state ψ is then defined in the usual way by

$$\begin{aligned} <[\hat{A},\hat{B}]> &= \int \psi^*(\hat{A}\hat{B}-\hat{B}\hat{A})\psi d^3r \\ &= \int \psi^*\hat{A}\hat{B}\psi d^3r - \int \psi^*\hat{B}\hat{A}\psi d^3r. \end{aligned} \tag{13.26}$$

As an example, we consider the commutator of the linear momentum and the position coordinate in one dimension, $[\hat{p},\hat{x}]$. The momentum operator has the common quantized form

$$\hat{p}\psi = -i\hbar\frac{\partial \psi}{\partial x}, \tag{13.27}$$

and the operator of the position coordinate x is simply

$$\hat{x} = x. \tag{13.28}$$

According to Eq. (13.25), it is

$$[\hat{p},\hat{x}]\psi = -i\hbar[\frac{\partial}{\partial x},x]\psi = -i\hbar\left(x\frac{\partial \psi}{\partial x} + \psi - x\frac{\partial \psi}{\partial x}\right) = -i\hbar\psi, \tag{13.29}$$

i.e., the result is proportional to the wave function. According to the above definitions and the product rule, the expectation value of this commutator is

$$\begin{aligned} <[\hat{p},\hat{x}]> &= -i\hbar\int \psi^*(\hat{p}\hat{x}-\hat{x}\hat{p})\psi d^3r \\ &= -i\hbar\int \psi^*\hat{p}(\hat{x}\psi)d^3r - \int \psi^*\hat{x}\hat{p}\psi d^3r \\ &= -i\hbar\left(\int \psi^* x\frac{\partial \psi}{\partial x}d^3r + \int \psi^*\psi d^3r - \int \psi^* x\frac{\partial \psi}{\partial x}d^3r\right) \\ &= -i\hbar\int \psi^*\psi d^3r \\ &= -i\hbar. \end{aligned} \tag{13.30}$$

This result means that interchanging both operators gives different results. If two operators can be interchanged, we have

$$[\hat{A},\hat{B}] = 0. \tag{13.31}$$

The relation (13.30) is

$$\boxed{<[\hat{x},\hat{p}]> = i\hbar,} \tag{13.32}$$

and it follows that the eigenvalues of position and momentum cannot be specified simultaneously, which is called *Heisenberg's uncertainty principle* in the Copenhagen interpretation of quantum mechanics. By working out and combining the expectation values of $<\hat{x}>$ and $<\hat{p}>$, as well as their statistical variances, it can be shown [8] that the product of the variances Δx and Δp obeys the inequality

$$\Delta x\Delta p \geq \frac{\hbar}{2}. \tag{13.33}$$

This is the uncertainty principle of position and linear momentum. If one of them is defined relatively exactly, i.e. the Delta value is quite small, this equation requires that the Delta value of the other variable must be quite large to satisfy the uncertainty principle. Besides for position and momentum, the principle holds for all complementary variables, for example, angular coordinate and angular momentum.

In addition to the commutator of two operators $\hat{A}$ and $\hat{B}$, we also define the *anti-commutator* with a plus sign instead of a minus sign between the operator products:

$$\{\hat{A}\hat{B}\} = \hat{A}\,\hat{B} + \hat{A}\,\hat{B}. \tag{13.34}$$

We use curly brackets for the anti-commutator. Both the commutator and the anti-commutator are important. In a system described in cartesian coordinates, restricted to one dimension, we have

$$\hat{x} = x, \tag{13.35}$$

$$\hat{p} = -i\hbar\frac{\partial}{\partial x}. \tag{13.36}$$

Computer algebra [26] gives the results

$$[\hat{x}^2, \hat{p}^2] = 4\hbar^2\frac{\partial\psi}{\partial x}x + 2\hbar^2\psi, \tag{13.37}$$

$$\{\hat{x}, \hat{p}\} = -2i\hbar\frac{\partial\psi}{\partial x}x - i\hbar\psi, \tag{13.38}$$

so that we obtain

$$[\hat{x}^2, \hat{p}^2] = 2i\hbar\{\hat{x}, \hat{p}\}. \tag{13.39}$$

This is a relation between commutator and anti-commutator. In the following examples, we compute several expectation values of both by using well known eigenfunctions of simple quantum mechanical systems. Details on the systems investigated in Examples 13.1 - 13.3 can be found in [8].

■ **Example 13.1** The wave function of the harmonic oscillator is

$$\psi_v(x) = N_v H_v(\alpha x)\exp(-\frac{\alpha x^2}{2}), \tag{13.40}$$

where α is a constant, N_v is a normalization factor and $H_v(\alpha x)$ is the Hermite polynomial of degree v. Details can be found in [6] and in the computer algebra code [27]. The results for several commutators and anticommutators are listed in Table 13.1. The commutator $[x, p_x]$ is $i\hbar$ as expected from the Heisenberg principle. All other commutators and anticommutators are zero except the anticommutator $\{x^2, p_x^2\}$ for the squared position and momentum.

v	$[x, \hat{p}_x]$	$\{x, \hat{p}_x\}$	$[x, \hat{p}_x^2]$	$\{x, \hat{p}_x^2\}$	$[x^2, \hat{p}_x]$	$\{x^2, \hat{p}_x\}$	$[x^2, \hat{p}_x^2]$	$\{x^2, \hat{p}_x^2\}$
0	$i\hbar$	0	0	0	0	0	0	$-\frac{\hbar^2}{2}$
1	$i\hbar$	0	0	0	0	0	0	$\frac{3\hbar^2}{2}$
2	$i\hbar$	0	0	0	0	0	0	$\frac{11\hbar^2}{2}$
3	$i\hbar$	0	0	0	0	0	0	$\frac{23\hbar^2}{2}$

Table 13.1: Commutators of the harmonic oscillator.

■

■ **Example 13.2** The wave function of a particle on a ring is

$$\psi_m(\phi) = \frac{1}{\sqrt{2\pi}} \exp(im\phi), \tag{13.41}$$

where m is the magnetic quantum number that takes values between the angular momentum quantum numbers $-l$ and l. In polar coordinates (r, ϕ), the angular momentum operator around the Z axis is

$$\hat{L}_Z = -i\hbar \frac{\partial}{\partial \phi}. \tag{13.42}$$

Several commutators of the wave function have been computed by computer algebra code [28] and are listed in Table 13.2. The canonical coordinate is ϕ, and the canonical momentum is $\hat{L}_Z$. Consequently, it is $< [\phi, \hat{L}_Z] >= i\hbar$, according to the Heisenberg principle. All other expectation values are non-zero and have specific values. Obviously, the operator relation (13.39) is also satisfied by the polar coordinates of a particle on a ring.

$[\phi, \hat{L}_Z]$	$\{\phi, \hat{L}_Z\}$	$[\phi, \hat{L}_Z^2]$	$\{\phi, \hat{L}_Z^2\}$
$i\hbar$	$\hbar(2\pi m - i)$	$2im\hbar^2$	$2m\hbar^2(\pi m - i)$
$[\phi^2, \hat{L}_Z$	$\{\phi^2, \hat{L}_Z\}$	$[\phi^2, \hat{L}_Z^2]$	$\{\phi^2, \hat{L}_Z^2\}$
$2i\pi\hbar$	$\frac{2}{3}\pi\hbar(4\pi m - 3i)$	$2\hbar^2(2i\pi m + 1)$	$\frac{2}{3}\hbar^2(4\pi^2 m^2 - 6i\pi m - 3)$

Table 13.2: Commutators of a particle on a ring.

■

■ **Example 13.3** In the third example, we compute the commutators for the radial wave functions of the Hydrogen atom. These functions have been listed in Table 12.1. n and l are the principal and angular quantum number, r is the radial coordinate, and $\hat{p}_r$ is the radial part of the angular momentum:

$$\hat{p}_r = -i\hbar \frac{\partial}{\partial r}. \tag{13.43}$$

The expectation values of the commutators have been evaluated by computer algebra code [29] and are listed in Table 13.3. Again, the canonical pair $(r, \hat{p}_r)$ has the Heisenberg value. The commutator and anticommutator of the pair $(r, \hat{p}_r)$ are identical for all combinations of quantum numbers. ■

l, m	$[r, \hat{p}_r]$	$\{r, \hat{p}_r\}$	$[r, \hat{p}_r^2]$	$\{r, \hat{p}_r^2\}$	$[r^2, \hat{p}_r]$	$\{r^2, \hat{p}_r\}$	$[r^2, \hat{p}_r^2]$	$\{r^2, \hat{p}_r^2\}$
$0, 0$	$i\hbar$	$2i\hbar$	0	$\frac{\hbar^2}{a_0}$	$3ia_0\hbar$	$3ia_0\hbar$	0	0
$1, 0$	$i\hbar$	$2i\hbar$	0	$\frac{\hbar^2}{a_0}$	$12ia_0\hbar$	$12ia_0\hbar$	0	$3\hbar^2$
$1, 1$	$i\hbar$	$2i\hbar$	0	$\frac{\hbar^2}{2a_0}$	$10ia_0\hbar$	$10ia_0\hbar$	0	$\hbar^2$
$2, 0$	$i\hbar$	$2i\hbar$	0	$\frac{\hbar^2}{a_0}$	$27ia_0\hbar$	$27ia_0\hbar$	0	$8\hbar^2$
$2, 1$	$i\hbar$	$2i\hbar$	0	$\frac{7\hbar^2}{9a_0}$	$25ia_0\hbar$	$25ia_0\hbar$	0	$6\hbar^2$
$2, 2$	$i\hbar$	$2i\hbar$	0	$\frac{\hbar^2}{3a_0}$	$21ia_0\hbar$	$21ia_0\hbar$	0	$2\hbar^2$

Table 13.3: Commutators of radial wave functions of the hydrogen atom (a_0 is the Bohr radius).

As can be seen from Tables 13.1 - 13.3, the expectation value of the commutator of generalized coordinates q,p is always $i\hbar$, which is the well known Heisenberg uncertainty. However, for the harmonic oscillator, the commutator of squared operators $\hat{q}^2, \hat{p}^2$ is zero. The same holds for the radial wave functions of the H atom. This means that the observabls q and p are precisely known. The claims of general uncertainty cannot be true at the same time for the same operators applied to the same wave functions. The Copenhagen interpretation is therefore an invalid overinterpretation. This shows the inconsistency of the Heisenberg concept. Obviously, q or p cannot be "unknowable" and also "knowable" as in the claim made originally by Bohr and Heisenberg independently circa 1927. Obviously the Heisenberg result (13.33) has been overinterpreted without evaluation of other cases.

Myron Evans writes in [15]:

Copenhagen is refuted because in that interpretation it makes no sense for an expectation value of a commutator of operators to be both zero and non-zero for the same pair of operators. One of the operators could be "absolutely unknowable" and the other "precisely knowable" if the expectation value were non-zero, and both "precisely knowable" if it were zero. These two interpretations refer respectively to non-zero and zero commutator expectation values, and both interpretations cannot be true for the same pair of operators.

Prior to this paper, commutators of a given pair of operators were thought to be either zero or non- zero, never both zero and non-zero, so a clear refutation of Copenhagen was never realized. In ECE quantum mechanics, Copenhagen and its unscientific jargon are not used, and the expectation values are straightforward consequences of the fundamental operators introduced by Schroedinger. The latter immediately rejected Copenhagen as did Einstein, de Broglie and their Schools.

13.2.2 Quantum-Hamilton equations

The quantum Hamilton equations will show that x and p are specified simultaneously in quantum mechanics. We will derive equations on quantum level that are the equivalent to the classical Hamilton equations:

$$\frac{dq}{dt} = \frac{\partial H}{\partial p}, \tag{13.44}$$

$$\frac{dp}{dt} = -\frac{\partial H}{\partial q} \tag{13.45}$$

with generalized coordinate q and momentum p, and with Hamilton function H.

Time derivative of an expectation value

First, we compute the time derivative of an operator. To do this, we use the time-dependent Schrödinger equation

$$i\hbar\frac{\partial \psi}{\partial t} = \hat{H}\psi \tag{13.46}$$

and its conjugate complex form

$$-i\hbar\frac{\partial \psi^*}{\partial t} = \hat{H}\psi^*, \tag{13.47}$$

where $\hat{H}$ is the Hamilton operator. Additionally, we use the momentum operator $\hat{p}$ as given in Eq. (13.27) and the hermiticity of an operator $\hat{A}$, expressed by

$$\int \psi^* A\psi d^3r = \int (A\psi)^* \psi d^3r. \tag{13.48}$$

Then, the time derivative of the expectation value of $\hat{A}$ is

$$\begin{aligned}\frac{d}{dt} < \hat{A} > &= \frac{d}{dt}\int \psi^*(t)\hat{A}\psi(t)d^3r \\ &= \int \frac{\partial \psi^*}{\partial t}\hat{A}\psi(t)d^3r + \int \psi(t)\hat{A}\frac{\partial \psi(t)}{\partial t}d^3r \\ &= \frac{1}{i\hbar}\left(-\int \hat{H}\psi(t)^*\hat{A}\psi(t)d^3r + \int \psi(t)^*\hat{A}\hat{H}\psi(t)d^3r\right) \\ &= \frac{1}{i\hbar}\left(-\int \psi(t)^*\hat{H}\hat{A}\psi(t)d^3r + \int \psi(t)^*\hat{A}\hat{H}\psi(t)d^3r\right) \\ &= \frac{1}{i\hbar}\int \psi(t)^*(\hat{A}\hat{H} - \hat{H}\hat{A})\psi(t)d^3r.\end{aligned} \tag{13.49}$$

The result is

$$\boxed{\frac{d}{dt} < \hat{A} >= \frac{i}{\hbar} < [\hat{H},\hat{A}] > .} \tag{13.50}$$

This is the first intermediate result on our way to derive the quantum Hamilton equations. In a similar way, the spatial derivative of an expectation value of operator $\hat{A}$ can be computed. With regard to later computations, we remark that the wave function here is considered as a function of the position coordinate: $\psi = \psi(x)$. This is also called the *position representation*. Besides this, we have to make a specific definition for computing expectation values of space (and later, momentum) coordinates. We introduce a minus sign for the expectation value of a spatial derivative of an operator $\hat{A}$:

$$\frac{d}{dx} < \hat{A} >= -\int \psi^* A\psi d^3r. \tag{13.51}$$

This is a new axiom of quantum mechanics. With this definition in mind, and with the replacements made for computing the time derivative (13.49), we obtain

$$\begin{aligned}\frac{d}{dx} < \hat{A} > &= -\frac{d}{dx}\int \psi^*\hat{A}\psi d^3r \\ &= -\left(\int \frac{\partial \psi^*}{\partial x}\hat{A}\psi d^3r + \int \psi\hat{A}\frac{\partial \psi}{\partial x}d^3r\right) \\ &= -\frac{1}{i\hbar}\left(\int \hat{p}\psi^*\hat{A}\psi d^3r - \int \psi^*\hat{A}\hat{p}\psi d^3r\right) \\ &= -\frac{1}{i\hbar}\left(\int \psi^*\hat{p}\hat{A}\psi d^3r - \int \psi^*\hat{A}\hat{p}\psi d^3r\right) \\ &= -\frac{1}{i\hbar}\int \psi^*(\hat{p}\hat{A} - \hat{A}\hat{p})\psi d^3r.\end{aligned} \tag{13.52}$$

In total, we have the result

$$\boxed{\frac{d}{dx} < \hat{A} >= \frac{i}{\hbar} < [\hat{p},\hat{A}] > .} \tag{13.53}$$

Since $\hat{A}$ is an arbitrary operator, we can insert $\hat{x}$ for it in Eq. (13.53). By definition it must be

$$\frac{d}{dx} < \hat{x} >= 1. \tag{13.54}$$

Then Eq. (13.53) gives us

$$\frac{d}{dx} < \hat{x} >= 1 = \frac{i}{\hbar} < [\hat{p},\hat{x}] > \tag{13.55}$$

or

$$< [\hat{x},\hat{p}] >= i\hbar, \tag{13.56}$$

which is the Heisenberg principle. This is also a proof that the choice of the minus sign in Eq. (13.51) was correct. Otherwise we would have a sign change in the Heisenberg principle, which was derived from the operators $\hat{x}$ and $\hat{p}$ directly in (13.30).

In order to compute the derivative of an expectation value with respect to momentum, we have to use the *momentum representation* of the wave function in the form $\psi = \psi(p)$. In addition, we have to use the momentum representation of the position operator. This is defined analogously to the momentum operator in position space:

$$\hat{x}\psi(p) = i\hbar\frac{\partial\psi(p)}{\partial p}, \tag{13.57}$$

and in its conjugate complex form:

$$\hat{x}\psi^*(p) = -i\hbar\frac{\partial\psi^*(p)}{\partial p}, \tag{13.58}$$

By proceeding as in the above calculation (13.52), we obtain

$$\begin{aligned}\frac{d}{dp} < \hat{A} > &= -\frac{d}{dp}\int \psi^*\hat{A}\psi d^3r \\ &= -\left(\int \frac{\partial\psi^*}{\partial p}\hat{A}\psi d^3r + \int \psi\hat{A}\frac{\partial\psi}{\partial p}d^3r\right) \\ &= -\frac{1}{i\hbar}\left(-\int \hat{x}\psi^*\hat{A}\psi d^3r + \int \psi^*\hat{A}\hat{x}\psi d^3r\right) \\ &= -\frac{1}{i\hbar}\left(-\int \psi^*\hat{x}\hat{A}\psi d^3r + \int \psi^*\hat{A}\hat{x}\psi d^3r\right) \\ &= -\frac{1}{i\hbar}\int \psi^*(-\hat{x}\hat{A}+\hat{A}\hat{x})\psi d^3r.\end{aligned} \tag{13.59}$$

The result is

$$\boxed{\frac{d}{dp} < \hat{A} >= -\frac{i}{\hbar} < [\hat{x},\hat{A}] > .} \tag{13.60}$$

Equations (13.53) and (13.60) merge into one another by interchanging x and p with a sign change. Since $\hat{A}$ is an arbitrary operator, we can insert $\hat{p}$ for it in Eq. (13.60). By definition it must be

$$\frac{d}{dp} < \hat{p} >= 1. \tag{13.61}$$

Then Eq. (13.60) gives us

$$\frac{d}{dp} < \hat{p} >= 1 = -\frac{i}{\hbar} < [\hat{x},\hat{p}] > \tag{13.62}$$

or

$$< [\hat{x}, \hat{p}] >= i\hbar, \tag{13.63}$$

which is the Heisenberg principle again.

Another result is that from (13.53) follows

$$\frac{d}{dx} < \hat{p} >= 0, \tag{13.64}$$

and from (13.60):

$$\frac{d}{dp} < \hat{x} >= 0. \tag{13.65}$$

This proves that x and p are independent variables as is the case in classical mechanics.

Now we can put all parts together to derive the quantum Hamilton equations. In (13.50) we replace the operator $\hat{A}$ by the generalized position coordinate $q = \hat{q}$, which gives us

$$\frac{d}{dt} < \hat{q} >= -\frac{i}{\hbar} < [\hat{q}, \hat{H}] > . \tag{13.66}$$

In In (13.60) we replace $\hat{A}$ by $\hat{H}$ and $\hat{x}$ by $\hat{q}$:

$$\frac{d}{dp} < \hat{H} >= -\frac{i}{\hbar} < [\hat{q}, \hat{H}] > . \tag{13.67}$$

The right sides of the last two equations are equal, so we have

$$\frac{d}{dt} < \hat{q} >= \frac{d}{dp} < \hat{H} > . \tag{13.68}$$

This is the first quantum Hamilton equation. To obtain the second equation, we replace $\hat{A}$ by $\hat{p}$ in (13.50) and $\hat{A}$ by $\hat{H}$ in (13.53). This gives us

$$\frac{d}{dt} < \hat{p} >= -\frac{i}{\hbar} < [\hat{p}, \hat{H}] >, \tag{13.69}$$

$$\frac{d}{dq} < \hat{H} >= \frac{i}{\hbar} < [\hat{p}, \hat{H}] > . \tag{13.70}$$

It follows that the second Quantum Hamilton equation is

$$\frac{d}{dt} < \hat{p} >= -\frac{d}{dq} < \hat{H} > . \tag{13.71}$$

In the general case, where more than one canonical variable q and p is present, we have to use the partial derivatives for q_i and p_j, and the quantum Hamilton equations are

$$\boxed{\begin{aligned} \frac{d}{dt} < \hat{q}_i > &= \frac{\partial}{\partial p_j} < \hat{H} >, & (13.72) \\ \frac{d}{dt} < \hat{p}_j > &= -\frac{\partial}{\partial q_i} < \hat{H} > . & (13.73) \end{aligned}}$$

These are relations between the expectation values of $\hat{q}$, $\hat{p}$ and $\hat{H}$ and have the same form as the Hamilton equations (13.44, 13.45) of classical mechanics. The equations are non-relativistic, because they have been derived by using the Schrödinger equation.

13.2.3 Quantum force equation

The second quantum Hamilton equation (13.73) describes a force law. With $q = x$ (in one dimension) the force is

$$\boxed{F = \frac{d}{dt} < \hat{p} > = -\frac{\partial}{\partial x} < \hat{H} > = -\frac{i}{\hbar} < [\hat{p}, \hat{H}] > .} \tag{13.74}$$

This is the *quantum force equation*. The Hamilton operator is

$$\hat{H} = \hat{T} + U = -\frac{\hat{p}^2}{2m} + U(x) \tag{13.75}$$

with kinetic energy operator $\hat{T}$ and potential energy U. Since p and x are canonical variables, they are independent of one another, and the kinetic energy term does not depend on x. It follows that

$$\frac{\partial \hat{H}}{\partial x} = \frac{\partial U}{\partial x} \tag{13.76}$$

and, consequently, for the expectation values:

$$< \frac{\partial \hat{H}}{\partial x} > = < \frac{\partial U}{\partial x} > = \int \psi^* \frac{\partial U}{\partial x} \psi d^3x = \frac{\partial U}{\partial x}. \tag{13.77}$$

Then, from (13.74), the force is

$$F = -\frac{\partial U}{\partial x}, \tag{13.78}$$

which is the classical result. On the other hand, the classical Hamiltonian is

$$H = -\frac{p^2}{2m} + U(x) \tag{13.79}$$

and its derivative is

$$\frac{\partial H}{\partial x} = \frac{\partial U}{\partial x} \tag{13.80}$$

To transform this to quantum mechanics, we have to show that

$$\frac{\partial < \hat{H} >}{\partial x} = < \frac{\partial \hat{H}}{\partial x} > . \tag{13.81}$$

Because of

$$< H > = H \tag{13.82}$$

it follows

$$\frac{\partial < \hat{H} >}{\partial x} = \frac{\partial U}{\partial x}. \tag{13.83}$$

Because the right sides of Eqs. (13.77) and (13.83) are equal, Eq. (13.81) follows directly.

The force can be practically computed by deriving the Schrödinger equation with respect to x:

$$\frac{\partial}{\partial x}(\hat{H}\psi) = \frac{\partial}{\partial x}(E\psi). \tag{13.84}$$

Applying the product rule, and noting that E is a constant, it follows that

$$\frac{\partial \hat{H}}{\partial x}\psi + \hat{H}\frac{\partial \psi}{\partial x} = E\frac{\partial \psi}{\partial x}, \tag{13.85}$$

and with (13.76):

$$\frac{\partial U}{\partial x}\psi + \hat{H}\frac{\partial \psi}{\partial x} = E\frac{\partial \psi}{\partial x}. \tag{13.86}$$

Insertion of (13.78) gives

$$-F\psi + \hat{H}\frac{\partial \psi}{\partial x} = E\frac{\partial \psi}{\partial x} \tag{13.87}$$

or

$$\boxed{F\psi = (\hat{H}-E)\frac{\partial \psi}{\partial x},} \tag{13.88}$$

which is the quantum force equation in a different form that allows computing the force within quantum systems easily, when the solutions of the Schrödinger equation ψ and E are known. This is an important result for quantum chemistry, for example. The force distribution within a quantum system is obtained directly from the solutions of the Schrödinger equation. An expectation value for the force distribution can be computed by

$$< F >= \int \psi^*(\hat{H}-E)\frac{\partial \psi}{\partial x}d^3x. \tag{13.89}$$

We consider some examples of the quantum force, using the same quantum systems as in Examples 13.1 - 13.3.

■ **Example 13.4** We compute the quantum force for the harmonic oscillator using Eq. (CH13:EQ88) (see computer algebra code [30]). The Hamiltonian is

$$\widehat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}m\omega^2 x^2, \tag{13.90}$$

and the solutions are the wave functions given in Eq. (13.40). The first energy eigenvalues and force values are listed in Table 13.4. According to Eq. (CH13:EQ88), the force eigenvalues are

$$\boxed{F = \frac{1}{\psi}(\hat{H}-E)\frac{\partial \psi}{\partial x},} \tag{13.91}$$

The forces are the same as for the zero order eigenvalue in all cases. Obviously, the result is independent on the quantum number n and is the well known restoring force.

n	E	F
0	$\frac{1}{2}\hbar\omega$	$-m\omega^2 x$
1	$\frac{3}{2}\hbar\omega$	$-m\omega^2 x$
2	$\frac{5}{2}\hbar\omega$	$-m\omega^2 x$
3	$\frac{7}{2}\hbar\omega$	$-m\omega^2 x$

Table 13.4: Energy and force eigenvalues for the harmonic oscillator.

■

■ Example 13.5 We continue with the quantum force of a particle on a ring. The Hamiltonian of a particle with mass m at a polar angle ϕ is

$$\widehat{H} = -\frac{\hbar^2}{2mr^2}\frac{\partial^2}{\partial\phi^2} \tag{13.92}$$

and has the solutions (13.41, containing the quantum number m_j. Since we have a rotational motion, the force is actually a torque. As can be seen from Table 13.5, the force eigenvalues vanish for all values of m_j (see computer algebra code [31]). A non-zero torque would require a 3-dimensional motion.

Quantum Number	E	F
m_j	$\frac{\hbar^2}{2mr^2}m_j^2$	0

Table 13.5: Energy and force eigenvalues for a particle on a ring.

■

■ Example 13.6 The most interesting force eigenvalues are certainly those of the Hydrogen atom. The energy eigenvalues only depend on the principal quantum number n. The radial wave functions were taken from Table 12.1 as in Example 13.3. For the evaluation of the force eigenvalues, the Hamiltonian of Hydrogen is required, whose radial part, applied to the wave function ψ (in spherical coordinates), is

$$\widehat{H}\psi = -\frac{\hbar^2}{2mr^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{\hbar^2 l(l+1)}{2mr^2}\psi - \frac{\hbar^2}{a_0 mr}\psi. \tag{13.93}$$

The resulting force eigenvalues are listed in Table 13.6 for the first s, p and d orbitals (see computer algebra code [32]). All force eigenvalues for quantum number combinations $(n,\ l)$ are different, and there is no force for the $1s$ state.

The forces and radial wave functions are graphed in Figs. 13.1-13.6 . The $2s$ and $3s$ states are attractive near to the nucleus while the other states are not. In most cases, there are poles of the force where the wave function has a zero crossing. This could mean that there is a separation effect to positive and negative values of the wave function (or the corresponding charge densities). For molecules, this could have to do with the fact that the same type of orbitals can be binding or anti-binding, depending on symmetry. The force eigenvalues have the potential of giving new insight into chemical bonding and stability mechanisms.

Since the quantum force F is a function of space coordinates, it makes sense to compute the expectation value of F with the wave functions by Eq. (13.89). Since the radial integration is weighted by the factor r^2, the behavior of F near to $r = 0$ plays no role. The results are listed in Table 13.7 (in atomic units) and give the astonishing result that only the $2s$ and $3s$ states produce a net force. This does not mean that no other forces are present, these would be torques of the angular coordinates. It has been shown in other papers of ECE theory that the spherical harmonics (that are the angular solutions for the Hydrogen atom) show a quantum force [15]. In addition, the results of Table 13.7 show that the poles of the force eigenvalues are integrable because there the wave functions enforce zero contributions.

n	l	E	F
1	0	$-\frac{\hbar^2}{2ma_0^2}$	0
2	0	$-\frac{\hbar^2}{8ma_0^2}$	$-\frac{\hbar^2}{a_0 m r^2}$
2	1	$-\frac{\hbar^2}{8ma_0^2}$	$-\frac{\hbar^2 (r-2a_0)}{2a_0 m r^3}$
3	0	$-\frac{\hbar^2}{18ma_0^2}$	$-\frac{\hbar^2 \left(10r^2-114a_0r+243{a_0}^2\right)}{3a_0 m r^2 (2r^2-18a_0r+27{a_0}^2)}$
3	1	$-\frac{\hbar^2}{18ma_0^2}$	$-\frac{2\hbar^2 \left(2r^2-18a_0r+27{a_0}^2\right)}{3a_0 m r^3 (r-6a_0)}$
3	2	$-\frac{\hbar^2}{18ma_0^2}$	$-\frac{2\hbar^2 (r-6a_0)}{3a_0 m r^3}$

Table 13.6: Energy and force functions for the radial wave functions of the Hydrogen atom (a_0: Bohr radius).

n	l	$< F >$
1	0	0
2	0	$-\frac{\hbar^2}{4{a_0}^3 m}$
2	1	0
3	0	$-\frac{2\hbar^2}{9{a_0}^3 m}$
3	1	0
3	2	0

Table 13.7: Expectation values of force for the Hydrogen atom.

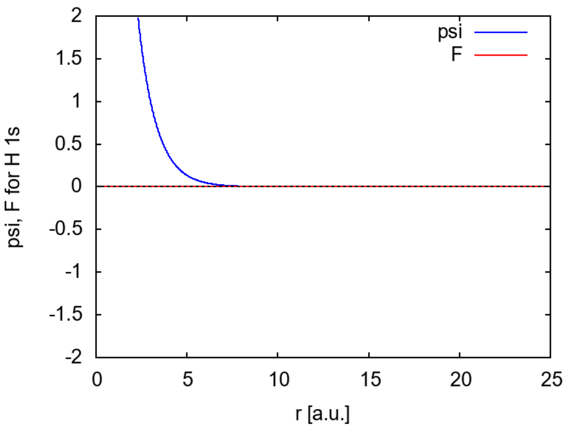


Figure 13.1: Hydrogen 1*s* radial function and quantum force.

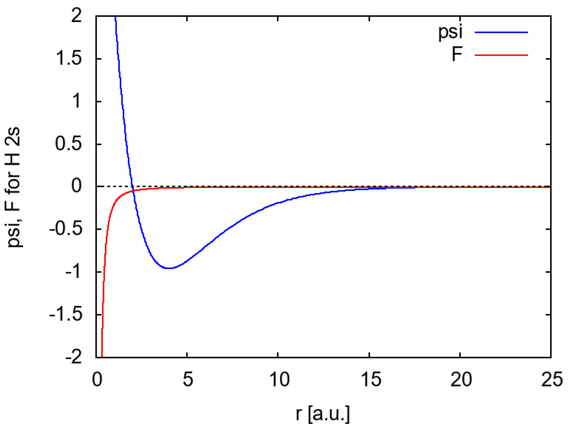


Figure 13.2: Hydrogen 2*s* radial function and quantum force.

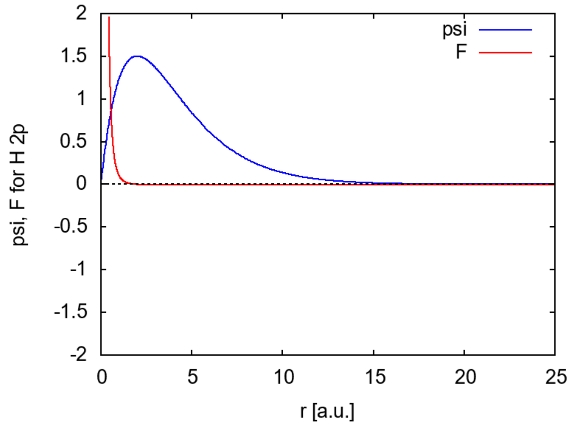


Figure 13.3: Hydrogen $2p$ radial function and quantum force.

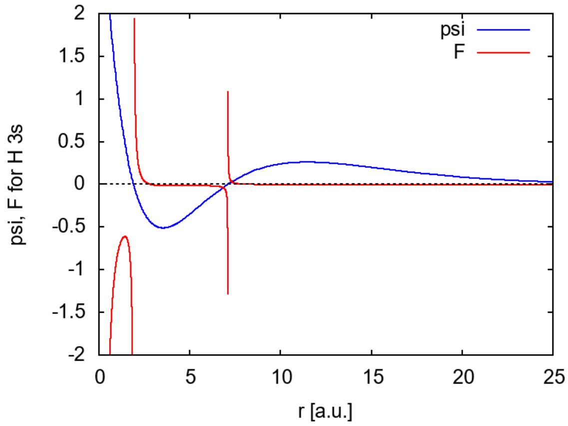


Figure 13.4: Hydrogen $3s$ radial function and quantum force.

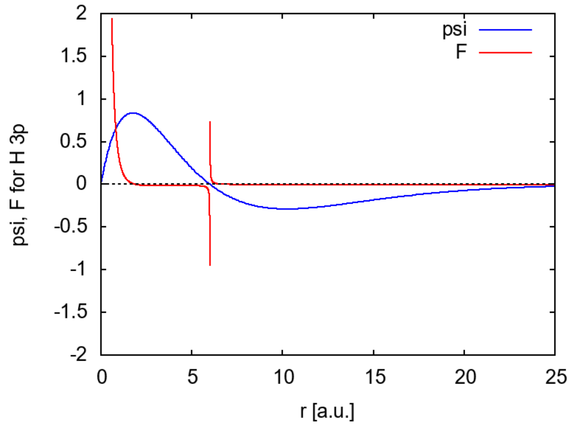


Figure 13.5: Hydrogen $3p$ radial function and quantum force.

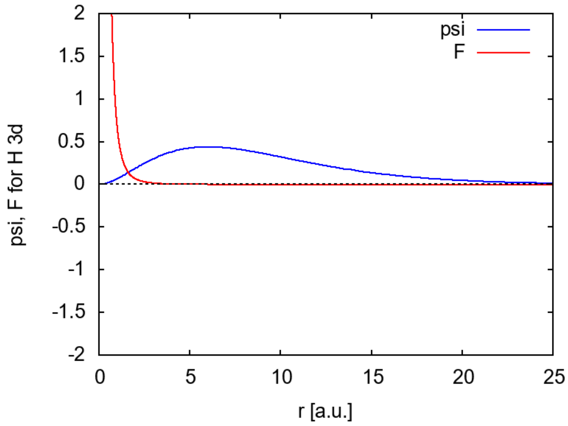


Figure 13.6: Hydrogen $3d$ radial function and quantum force.

■

Relativistic quantum force equations

We compute a relativistic version of the quantum force equation by taking into account spin-orbit coupling. In Sections 12.1.2 and 12.3.1, the Hamilton operator was derived in the form

$$\widehat{H} = mc^2 + U + \widehat{H}_{\text{kin}} + \widehat{H}_{\text{s-o}} \tag{13.94}$$

with potential energy U, kinetic energy operator $\widehat{H}_{\text{kin}}$ and spin-orbit coupling operator $\widehat{H}_{\text{s-o}}$. In non-relativistic approximation, the kinetic energy operator is

$$\widehat{H}_{\text{kin}} = -\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2. \tag{13.95}$$

The spin-orbit coupling operator is given by

$$\widehat{H}_{\text{s-o}} = -\xi(r)\,\widehat{\mathbf{S}}\cdot\widehat{\mathbf{L}} \tag{13.96}$$

with spin and orbital angular momenta $\widehat{\mathbf{S}}$ and $\widehat{\mathbf{L}}$ and spin-orbit function

$$\xi(r) = \frac{e^2}{8\pi\varepsilon_0 m^2 c^2 r^3}. \tag{13.97}$$

According to Eq. (12.79), the expectation value of the operator product is

$$\langle \widehat{\mathbf{S}} \cdot \widehat{\mathbf{L}} \rangle = \frac{\hbar^2}{2} \left(j(j+1) - l(l+1) - s(s+1) \right) \tag{13.98}$$

with quantum numbers j, l and s for a single electron. The expectation value of $\xi(r)$ with the hydrogenic radial functions depends on n, l and was given by Eq. (12.178):

$$\left\langle \frac{1}{r^3} \right\rangle_{n,l} = \int \psi^* \frac{1}{r^3} \psi \, d^3r = \frac{1}{a_0^3 \, l(l+\frac{1}{2})(l+1)n^3}. \tag{13.99}$$

The expectation value of the spin-orbit operator is the spin-orbit energy contribution, which, using Eq. (13.96), is

$$E_{\text{s-o}} = \left\langle \widehat{H}_{\text{s-o}} \right\rangle = -\frac{e^2\hbar^2}{16\pi\varepsilon_0 m^2 c^2} \frac{j(j+1) - l(l+1) - s(s+1)}{a_0^3 \, l(l+\frac{1}{2})(l+1)n^3}. \tag{13.100}$$

This equation is identical to Eq. (12.179) without the additional relativistic α term correction. In our representation, the spin-orbit operator is an extension to the non-relativistic Schrödinger theory. Therefore, we omit the constant rest energy and write:

$$\widehat{H}_{\text{r}} = -\frac{\hbar^2}{2m} \nabla^2 + U + \widehat{H}_{\text{s-o}}. \tag{13.101}$$

Using this Hamiltonian, the force eigenvalues follow from Eq. (13.88):

$$F\psi = (\widehat{H}_{\text{r}} - E) \frac{\partial \psi}{\partial x}. \tag{13.102}$$

The total energy E is the sum of that of the Hydrogen atom and the expectation value of spin-orbit splitting:

$$E = E_{\text{H}} - E_{\text{s-o}}, \tag{13.103}$$

where

$$E_{\text{H}} = -\frac{\hbar^2}{2m a_0^2 n^2} \tag{13.104}$$

is the energy eigenvalue of the non-relativistic calculation.

■ **Example 13.7** We show the effect of spin-orbit splitting for the quantum force of Hydrogen (see computer algebra code [33]). In Table 13.8 the force eigenvalues are compiled, similar to Table 13.6, but with the spin-orbit energies added. E_{so} has not been worked out further for clarity. For the s states, there is no spin-orbit splitting. If we set $E_{so} = 0$, we obtain the values of Table 13.6 again.

The full evaluation of E_{so} according ot Eq. (13.100) gives quite complicated expressions. Therefore, we represent the impact of spin-orbit splitting on the force eigenvalues graphically in Figs. 13.7 - 13.9. The effect is very small, because the spin-orbit splitting in Hydrogen is in the order of 10^{-5}eV. To be able to represent the effects graphically, E_{so} was increased by a factor of 10^6, 10^7 and 10^8 for the 2p, 3p and 3d states, respectively. The graphs are shown in atomic units. These examples for Hydrogen should be representative for heavier atoms also. The signs of the forces differ for large radii in all cases. ■

n	l	E	F
1	0	$-\frac{\hbar^2}{2ma_0^2}$	0
2	0	$-\frac{\hbar^2}{8ma_0^2}$	$-\frac{\hbar^2}{a_0 m r^2}$
2	1	$-\frac{\hbar^2}{8ma_0^2}$	$-\frac{m r^2 (r-2a_0) E_{so} + \hbar^2 (r-2a_0)}{2a_0 m r^3}$
3	0	$-\frac{\hbar^2}{18ma_0^2}$	$-\frac{\hbar^2 \left(10r^2-114a_0 r+243{a_0}^2\right)}{3a_0 m r^2 (2r^2-18a_0 r+27{a_0}^2)}$
3	1	$-\frac{\hbar^2}{18ma_0^2}$	$-\frac{m r^2 \left(r^2-12a_0 r+18{a_0}^2\right) E_{so}+2\hbar^2 \left(2r^2-18a_0 r+27{a_0}^2\right)}{3a_0 m r^3 (r-6a_0)}$
3	2	$-\frac{\hbar^2}{18ma_0^2}$	$-\frac{m r^2 (r-6a_0) E_{so}+2\hbar^2 (r-6a_0)}{3a_0 m r^3}$

Table 13.8: Energy and force functions for the radial wave functions of the Hydrogen atom with spin-orbit coupling.

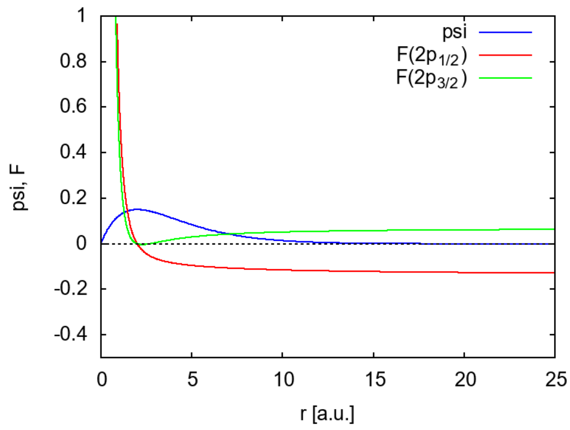


Figure 13.7: Hydrogen quantum force with spin-orbit coupling, 2p states.

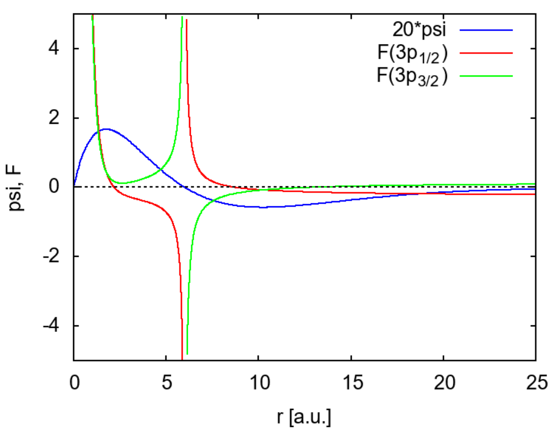


Figure 13.8: Hydrogen quantum force with spin-orbit coupling, 3p states.

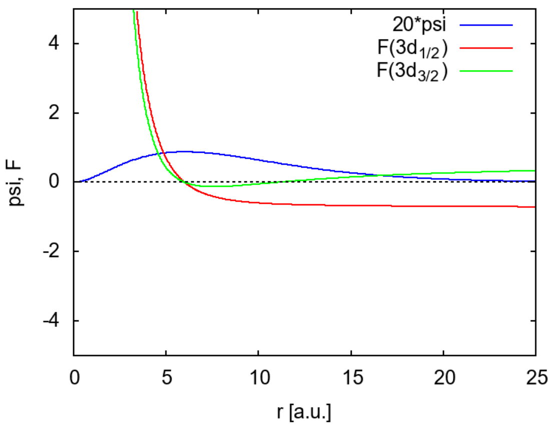


Figure 13.9: Hydrogen quantum force with spin-orbit coupling, 3d states.

Magnetic splitting of quantum force

Besides spin-orbit splitting, another type of the splitting the force eigenvalues happens by external magnetic fields. Degenerate spectral lines are split as known by the Zeeman and Paschen-Back effect. In this case, the Hamiltonian in non-relativistic approximation is given by

$$\widehat{H} = -\frac{\hbar^2}{2m}\nabla^2 + U - \frac{e\hbar}{2m}\boldsymbol{\sigma}\cdot\mathbf{B}. \tag{13.105}$$

This follows from Eq. (12.71), when only the electron spin is considered. Assuming that the magnetic field is positioned in Z direction, it has only a Z, which leads to

$$\boldsymbol{\sigma}\cdot\mathbf{B} = \begin{bmatrix} B_Z & 0 \\ 0 & -B_Z \end{bmatrix}, \tag{13.106}$$

Thus, we obtain two signs for the corresponding part of the Hamiltonian, denoting it by

$$\widehat{H}_+ = -\frac{\hbar^2}{2m}\nabla^2 + U - \frac{e\hbar}{2m}B_Z \tag{13.107}$$

and

$$\widehat{H}_- = -\frac{\hbar^2}{2m}\nabla^2 + U + \frac{e\hbar}{2m}B_Z. \tag{13.108}$$

■ **Example 13.8** We evaluate the quantum force for the Zeeman effect by the Hydrogenic wave functions (see computer algebra code [34]). Assuming a weak magnetic field, the wave function of the Hydrogen atom in the undistorted state can be taken to evaluate the force eigenvalues, and we denote them by F_+ and F_-. Using Eq. (13.88), they are

$$F_+\psi = (\widehat{H}_+ - E)\frac{\partial\psi}{\partial x} \tag{13.109}$$

and

$$F_-\psi = (\widehat{H}_- - E)\frac{\partial\psi}{\partial x}. \tag{13.110}$$

The results are shown in Table 13.9, where only the positive value for B_Z has been taken. F_- is obtained by changing sign of B_Z. Setting $B_Z = 0$ gives the force values for the undistorted atom as shown earlier in Table 13.6.

In Figs.13.10 - 13.15, the force eigenvalues are shown in an enlarged scale in order to make the effects visible. The radially weighted probability density$\psi \cdot r^2$ is graphed for comparison. F_+ and F_- show a symmetric splitting of the original F (with $B_Z = 0$) that is also shown. Beyond a certain nodal point, the splitting is nearly quadratically increasing with the radius coordinate. Also the s state is split, where no F is present without a magnetic field. Where poles in the forces appear, the behavior is similar to spin-orbit splitting.

n	l	E	F
1	0	$-\frac{\hbar^2}{2ma_0^2}$	$\frac{B_Z \hbar e}{2a_0 m}$
2	0	$-\frac{\hbar^2}{8ma_0^2}$	$\frac{B_Z \hbar e r^2 (r-4a_0)-4\hbar^2 (r-2a_0)}{4a_0 m r^2 (r-2a_0)}$
2	1	$-\frac{\hbar^2}{8ma_0^2}$	$\frac{B_Z \hbar e r^2 (r-2a_0)-2\hbar^2 (r-2a_0)}{4a_0 m r^3}$
3	0	$-\frac{\hbar^2}{18ma_0^2}$	$\frac{B_Z \hbar e r^2 \left(2r^2-30a_0 r+81{a_0}^2\right)-2\hbar^2 \left(10r^2-114a_0 r+243{a_0}^2\right)}{6a_0 m r^2 (2r^2-18a_0 r+27{a_0}^2)}$
3	1	$-\frac{\hbar^2}{18ma_0^2}$	$\frac{B_Z \hbar e r^2 \left(r^2-12a_0 r+18{a_0}^2\right)-4\hbar^2 \left(2r^2-18a_0 r+27{a_0}^2\right)}{6a_0 m r^3 (r-6a_0)}$
3	2	$-\frac{\hbar^2}{18ma_0^2}$	$\frac{B_Z \hbar e r^2 (r-6a_0)-4\hbar^2 (r-6a_0)}{6a_0 m r^3}$

Table 13.9: Energy and force eigenvalues of the Hydrogen atom with with Zeeman splitting.

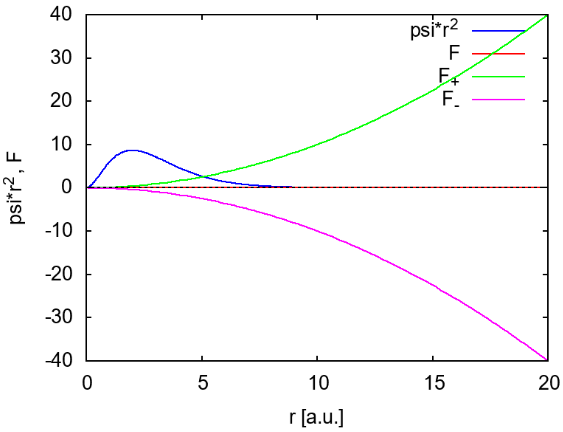


Figure 13.10: Hydrogen 1s probability density and Zeeman quantum forces.

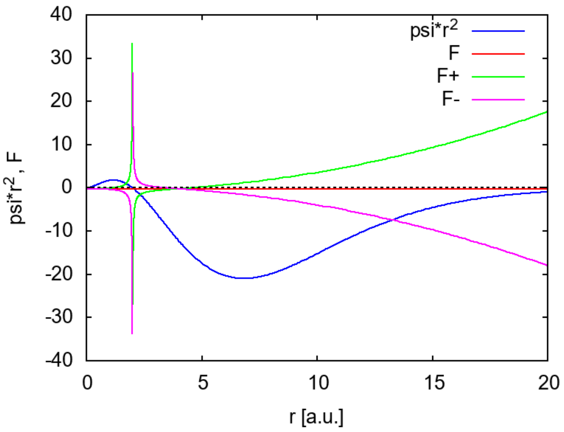


Figure 13.11: Hydrogen 2s probability density and Zeeman quantum forces.

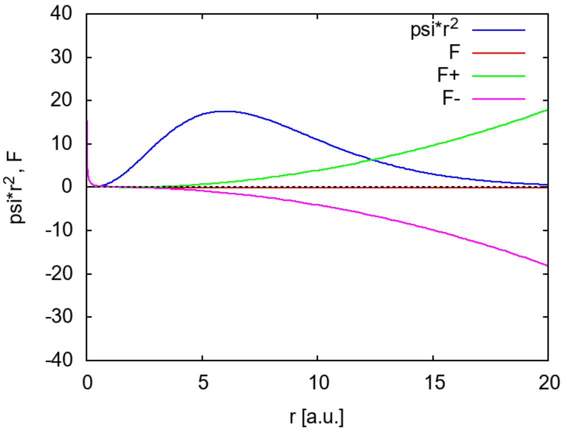


Figure 13.12: Hydrogen 2p probability density and Zeeman quantum forces.

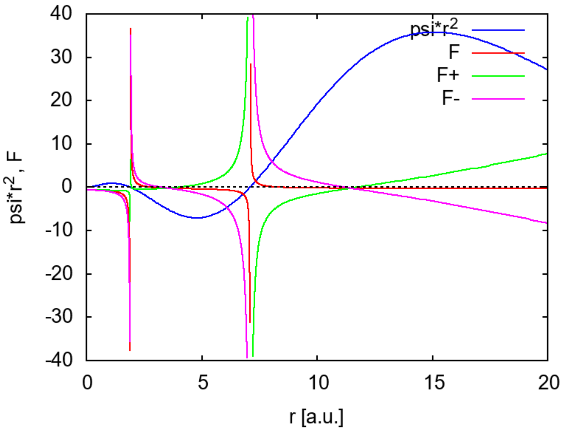


Figure 13.13: Hydrogen 3s probability density and Zeeman quantum forces.

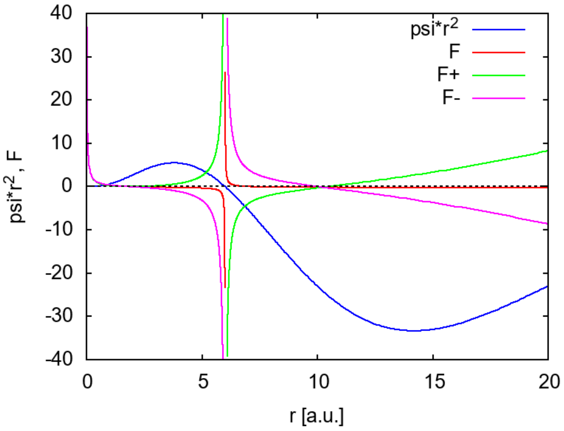


Figure 13.14: Hydrogen 3*p* probability density and Zeeman quantum forces.

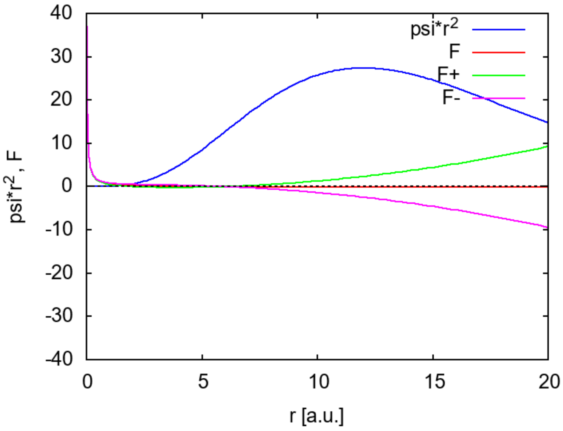


Figure 13.15: Hydrogen 3*d* probability density and Zeeman quantum forces.

■

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[12] Papers 329-335, Unified Field Theory (UFT) Section of www.aias.us.

Chapter 13

[13] https://en.wikipedia.org/wiki/Spinor_spherical_harmonics.

[14] Paper 174, Unified Field Theory (UFT) Section of www.aias.us.

[15] Papers 175-178, Unified Field Theory (UFT) Section of www.aias.us.

Computer algebra code (Maxima)

(This code is available in http://aias.us/documents/uft/ECE-Code-2.zip)

[16] Ex11.1.wxm - Transformation example SU(2) → O(3)

[17] Ex11.1a.wxm - Pauli and Dirac theory

[18] Ex11.1b.wxm - Fermion equation

[19] Ex11.2.wxm - Example solution for the Fermion equation

[20] Ex12.1.wxm - Pauli algebra and related theorems

[21] Ex12.2.wxm - ESOR energies of Hydrogen

[22] Ex12.3.wxm - Parameters of the Hydrogen atom

[23] Ex12.4.wxm - Relativistic spin-orbit coupling of Hydrogen

[24] Ex12.5.wxm - Relativistic anomalous Zeeman transitions of Hydrogen

[25] Ex13.1.wxm - Pauli principle

[26] Ex13.1a.wxm - Commutator-anticommutator relation

[27] Ex13.1b.wxm - Commutators for the harmonic oscillator

[28] Ex13.2.wxm - Commutators for a particle on the ring

[29] Ex13.3.wxm - Commutators for the radial wave functions of Hydrogen

[30] Ex13.4.wxm - Energy and force eigenvalues for the harmonic oscillator

[31] Ex13.5.wxm - Energy and force eigenvalues for a particle on the ring

[32] Ex13.6.wxm - Energy and force eigenvalues for the radial wave functions of Hydrogen

[33] Ex13.7.wxm - Force eigenvalues of Hydrogen with spin-orbit splitting

[34] Ex13.8.wxm - Force eigenvalues of Hydrogen for the Zeeman effect

External figures and pictures

[35] Source: Wikimedia Commons - https://commons.wikimedia.org/wiki/File:3D_Spherical.svg#/media/File:3D_Spherical.svg

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Acknowledgments

I am grateful to the AIAS colleagues for valuable hints concerning this textbook. In particular, I would like to thank John Surbat for the careful proofreading.