The Quantum Theory of the Hydrogen Atom

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Nomenclature

CM	Center-of-mass
CMS	Center-of-mass-system
LRL	Laplace-Runge-Lenz (vector/operator)
OS	On-shell (renormalization scheme)
QED	Quantum electrodynamics
QFT	Quantum field theory
US	ultra soft (energy scale)

Chapter 1

Introduction

The hydrogen atom has a long history as a testing ground for new physical ideas. It is one of the most simple bound states one could imagine, consisting of a single electron and a much heavier proton and thus it is very easy to treat theoretically and to measure very subtle effects experimentally. Balmer (1885) first discovered the spectral lines of hydrogen due to transitions of the electron from higher excited states to the first excited state above the ground state. Balmer found that the wavelengths corresponding to the spectral lines, the so called Balmer series, follow the law

$$\frac{1}{\lambda_n} \propto \frac{1}{2^2} - \frac{1}{n^2}, \qquad n \in \mathbb{N}. \tag{1.1}$$

Already in 1888, Rydberg presented an empirical formula,

$$\frac{1}{\lambda_{fi}} = \mathrm{Ryd}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right), \qquad n_f, n_i \in \mathbb{N}, \qquad n_f > n_i, \tag{1.2}$$

which describes the wavelengths of transitions between two different states of excitation in terms of two integer numbers. Later these were identified with the principal quantum number of the hydrogen atom, of course. The Rydberg constant Ryd introduced in eq. (1.2) amounts to $\approx 1.1 \cdot 10^7$ m^{-1}, which corresponds to an energy of approximately 13.6 eV. The series of spectral lines originating from transitions to the ground state were found by Lyman (1906) in the ultra violet and more spectral series of hydrogen have been discovered in later years at lower energies.

The first theoretical model that explained the hydrogen spectrum was developed by Bohr (1913) in a series of papers. In this model, the electron orbits the proton on classical trajectories, like a planet orbits the sun, but the angular momentum of the electron is set to be quantized, $L = n \in \mathbb{N}$.

This in turn leads to discrete energy levels,

$$E_n = -\frac{\mathrm{Ryd}}{n^2}, \qquad \mathrm{Ryd} = \frac{m\alpha^2}{2}, \tag{1.3}$$

where m is the reduced mass of the electron in the hydrogen atom and α the fine-structure constant, introduced by Sommerfeld in 1916. The Rydberg constant follows here as a prediction of the theory. The transitions between the different Bohr levels lead to the emission of photons with wavelengths given by the Rydberg formula (1.2).

Already Michelson (1892) found that the spectral lines were actually multiplets of lines very close together. At first this could be explained in the more refined Bohr-Sommerfeld model (Sommerfeld, 1916) but it was only with the upcoming of the new quantum mechanics that a satisfying answer could be found.

In 1925 Heisenberg introduced a new perspective on the microscopic processes of atoms, which he called matrix mechanics. It was elaborated rigorously by Born and Jordan (1925) and Born, Heisenberg and Jordan (1926) and is nowadays known as the operator formalism. Using this new formalism Pauli (1926) was able to derive the Bohr energy levels (1.3). Very soon afterwards, Schrödinger (1926) introduced the wave function and with it the equation named after him. From this equation he was able to derive the energy levels (1.3) but with the wave function he also found the spatial distribution for the probability to find the electron in the hydrogen atom. Again soon afterwards Dirac (1928a,b) developed a quantum theory which incorporated special relativity at its basis. The equation named after him naturally includes the spin of the electron and reduces to the Schrödinger equation in the non-relativistic limit. The Dirac equation can also be solved for the hydrogen atom (Gordon, 1928) and features the line splittings found by Michelson (1892), which are due to the electron spin (spin-orbit coupling) and relativistic corrections.

In 1947 Lamb and Retherford found yet another very small splitting between spectral lines which could not be explained by Dirac's theory. This additional shift, called Lamb shift, originates from quantum effects of the electromagnetic field. Its theoretical description makes it necessary to quantize the electromagnetic field. The effort to extend the quantum mechanics of point particles, interacting via a classical electromagnetic field, to a full quantum field theory had already started much earlier in the late 1920s and involved contributions by many physicists. It is a theory of quantized fermion and photon fields and was called quantum electrodynamics (QED). For two decades, however, serious divergences which occurred in the calculation of observable quantities made it unclear how to make use of this theory. The

experiment of Lamb and Retherford (1947) constituted an important guide for the theoretical development in this point, because soon Bethe (1947) found a way of how to extract useful information out of QED despite divergent expressions. Subsequently the theory was elaborated mainly in several series of papers by Tomonaga (1946), Koba et al. (1947a,b), Kanesawa and Tomonaga (1948a,b), Tomonaga and Oppenheimer (1948) and independently by Schwinger (1948a,b, 1949a,b) but also independently by Feynman (1948c,a,b, 1949b,a, 1950) and also by Dyson (1949a,b). Salpeter and Bethe (1951) then elaborated a field theoretic framework for the treatment of relativistic bound states in which dynamics is governed by the Bethe-Salpeter equation. The theoretical predictions derived from QED are able to reproduce experimental results to an accuracy never seen before.

This is, however, not the end of the story. Feynman (1948c) proposed a new way to view quantum mechanics, which he called the spacetime-approach, and is nowadays known as the path integral formalism. This formalism is equivalent to Heisenberg's matrix mechanics and Schrödinger theory and is especially useful in the field theoretic context of QED. Solving the path integral of the hydrogen atom, however, turns out to be very complicated and involves much more elaborate calculations than in previous approaches. It took a long time until this problem was finally solved by Duru and Kleinert (1979).

Meanwhile progress was made using the methods of group theory to understand the symmetries governing the dynamics of the hydrogen atom. Already the derivation of the energy levels by Pauli (1926) relied on its SO(4) symmetry. It was shown by Kleinert (1968a,b) that all properties of the hydrogen atom that were known from Schrödinger theory could be formulated in terms of group operations of its symmetry group SO(4,2), which is therefore called the dynamic group of the hydrogen atom.

to be mentioned: effective field theory

This script gives an overview over the fundamental, theoretical methods in the treatment of the hydrogen atom since the upcoming of the "new" quantum mechanics in 1925. At the current moment it comprises the non-relativistic treatment via the formalisms of Heisenberg, Schrödinger and Feynman, including group theoretic methods, and relativistic treatments using the Dirac equation both for the electron and for the two-particle system of electron and proton. Also the lowest order of radiative corrections ($O(m\alpha^5)$) is reviewed in the context of QED.

The only experimental input that enters into the calculations are the fine-structure constant α and the masses of electron m_e and proton m_p from

which the total mass $M = m_e + m_p$ and the reduced mass $m = m_e m_p/M$ are calculated. The values of these quantities are taken from Nakamura and Particle Data Group (2010),

$$\begin{aligned} \alpha &= 7.2973525698(24) \cdot 10^{-3} \\ m_e &= 0.510998928(11)\ \text{MeV} \\ m_p &= 938.272046(21)\ \text{MeV} \\ M &= 938.783045\ \text{MeV} \\ m &= 0.510720781\ \text{MeV}. \end{aligned} \tag{1.4}$$

It is also a common way to represent the value of the fine-structure constant as $\alpha^{-1} = 137.035999074(44)$. The theoretical energy levels which are calculated will be compared to the experimentally measured values which are taken from NIST and can also be found in Kramida (2010). Table 1.1 displays the experimental results for the ground state $1s$ up to the $4f$ state as well as the relative deviation of the energy levels from Bohr and Schrödinger theory and from Dirac theory. One can see that even without radiative corrections from full QED, the theoretical models reproduce the experimental values very accurately.

To be included in the future:

1. **effective field theory**

Table 1.1: Experimental values of the hydrogen energy levels as given in (Kramida, 2010) and the relative deviation of the theoretical energy levels from the non-relativistic theories of Bohr, Heisenberg and Schrödinger ($O(\alpha^2)$), from the relativistic Dirac theory, expanded up to order α^4, and from the QED calculations up to order α^5.

State	Experiment (eV)	Dev. $O(\alpha^2)$	Dev. $O(\alpha^4)$	Dev. $O(\alpha^5)$
$1S_{1/2}$	0			
$2P_{1/2}$	10.1988055286	$9 \cdot 10^{-6}$	$3 \cdot 10^{-6}$	$3 \cdot 10^{-8}$
$2S_{1/2}$	10.1988099034600	$9 \cdot 10^{-6}$	$3 \cdot 10^{-6}$	$3 \cdot 10^{-8}$
$2P_{3/2}$	10.1988508929	$1 \cdot 10^{-5}$	$3 \cdot 10^{-6}$	$3 \cdot 10^{-8}$
$3P_{1/2}$	12.087492922	$1 \cdot 10^{-5}$	$3 \cdot 10^{-6}$	$3 \cdot 10^{-8}$
$3S_{1/2}$	12.087494224	$1 \cdot 10^{-5}$	$3 \cdot 10^{-6}$	$3 \cdot 10^{-8}$
$3D_{3/2}$	12.087506341	$1 \cdot 10^{-5}$	$3 \cdot 10^{-6}$	$3 \cdot 10^{-8}$
$3P_{3/2}$	12.087506364	$1 \cdot 10^{-5}$	$3 \cdot 10^{-6}$	$3 \cdot 10^{-8}$
$3D_{5/2}$	12.087510821	$1 \cdot 10^{-5}$	$3 \cdot 10^{-6}$	$3 \cdot 10^{-8}$
$4P_{1/2}$	12.74853166921	$1 \cdot 10^{-5}$	$3 \cdot 10^{-6}$	$3 \cdot 10^{-8}$
$4S_{1/2}$	12.74853221952	$1 \cdot 10^{-5}$	$3 \cdot 10^{-6}$	$3 \cdot 10^{-8}$
$4D_{3/2}$	12.7485373313	$1 \cdot 10^{-5}$	$3 \cdot 10^{-6}$	$3 \cdot 10^{-8}$
$4P_{3/2}$	12.74853733962	$1 \cdot 10^{-5}$	$3 \cdot 10^{-6}$	$3 \cdot 10^{-8}$
$4D_{5/2}$	12.74853922041	$1 \cdot 10^{-5}$	$3 \cdot 10^{-6}$	$3 \cdot 10^{-8}$
$4F_{5/2}$	12.748539221	$1 \cdot 10^{-5}$	$3 \cdot 10^{-6}$	$3 \cdot 10^{-8}$
$4F_{7/2}$	12.7485401632	$1 \cdot 10^{-5}$	$3 \cdot 10^{-6}$	$3 \cdot 10^{-8}$
Continuum	13.598433770784	$1 \cdot 10^{-5}$	$2 \cdot 10^{-6}$	$3 \cdot 10^{-8}$

Chapter 2

Heisenberg's matrix mechanics

Given the problems that the "old quantum mechanics" of the models of Bohr (1913), Sommerfeld (1916) had and the fact that these models were based on quantities which are in principle unobservable, such as position and orbital period of the electrons in an atom, Heisenberg invented a novel way to think about the microcosmos. Only observable entities enter his approach, which is somewhat similar to classical physics concerning its overall structure but completely different in character.

The seminal ideas of Heisenberg (1925) were elaborated further mathematically by Born and Jordan (1925), Born et al. (1926) to become the "new quantum mechanics", called matrix mechanics. Since there are many books on basic quantum mechanics, their formalism is presented here only briefly in a modern notation.

2.1 Matrix mechanics

Let $\mathcal{H}$ be a Hilbert space and $\mathcal{H}^*$ its dual and $|\psi\rangle$ and $\langle\chi|$ their respective elements (i.e. vectors and covectors). We denote the scalar product on $\mathcal{H}$ as $\langle\chi|\psi\rangle$. The state of a quantum mechanical system is represented by a vector in $\mathcal{H}$. Given the components $\psi_n = \langle n|\psi\rangle$ with respect to a basis $|n\rangle$ the components of $\langle\psi|$ are given by $\psi_n^* = \langle\psi|n\rangle$. From this we deduce the relation $\langle\chi|\psi\rangle^\dagger = \langle\psi|\chi\rangle$. Observables are given by operators $\hat{A}$ acting on the vectors $|\psi\rangle$, which represent quantum mechanical systems. Every possible outcome of a measurement of the quantity $\hat{A}$ corresponds to an eigenvalue a in its spectrum,

$$\hat{A}|\psi\rangle = a|\psi\rangle. \tag{2.1}$$

The expectation value of an operator is denoted by

$$\langle \hat{A} \rangle = \frac{\langle \psi | \hat{A} | \psi \rangle}{\langle \psi | \psi \rangle}. \tag{2.2}$$

One of the "axioms" of matrix mechanics is that the vectors $|\psi\rangle$ are constant in time, while the evolution of operators $\hat{A}$ is generated by the Hamiltonian operator $\hat{H}$,

$$\dot{\hat{A}} = \partial_t \hat{A} + \frac{1}{i}[\hat{A}, \hat{H}], \tag{2.3}$$

where $d\hat{A}/dt = \dot{\hat{A}}$. This equation is called the Heisenberg equation. The Hamiltonian operator $\hat{H}$ (from now on simply Hamiltonian) is easily obtained from the classical Hamiltonian function H by substituting dynamical variables with operators. For example the Hamiltonian for a single particle of charge q in an external 4-vector potential $(\Phi, \vec{A})$ is obtained from the classical Hamiltonian function as

$$H = \frac{(\vec{p} - q\vec{A}(t, \vec{x}))^2}{2m} + q\Phi(t, \vec{x}) \quad \rightarrow \quad \hat{H} = \frac{(\hat{\vec{p}} - q\vec{A}(t, \hat{\vec{x}}))^2}{2m} + q\Phi(t, \hat{\vec{x}}). \tag{2.4}$$

However, since operators do not commute in general, this correspondence principle does not determine the Hamiltonian uniquely. This is to be expected since one can only derive classical mechanics from the more fundamental quantum mechanics and not the other way around.

From the Heisenberg equation (2.3) it follows that an operator which does not explicitly depend on time represents a conserved quantity, if and only if it commutes with the Hamiltonian. For the momentum and position operators, correspondingly, we have

$$\dot{\hat{\vec{p}}} = \frac{1}{i}[\hat{\vec{p}}, \hat{H}], \qquad \dot{\hat{\vec{x}}} = \frac{1}{i}[\hat{\vec{x}}, \hat{H}]. \tag{2.5}$$

The second "axiom" is given by the commutation relations of the position operators $\hat{x}^j$ and momentum operators $\hat{p}_j$,

$$[\hat{x}^j, \hat{x}^k] = 0, \qquad [\hat{p}_j, \hat{p}_k] = 0, \qquad [\hat{x}^j, \hat{p}_k] = \delta^j{}_k. \tag{2.6}$$

One might now wonder why this formalism is called matrix mechanics and also why we even introduced the Hilbert space $\mathcal{H}$ and its elements $|\psi\rangle$ if dynamics are given by the operators, anyway. First, if we chose a basis $|n\rangle$ every operator $\hat{A}$ is equivalent to a matrix with components $a_{mn} = \langle m | \hat{A} | n \rangle$. In the early papers on quantum mechanics such as the ones referred to in this

work, a basis that diagonalizes the Hamiltonian $\hat{H}$ is always chosen implicitly so that all operators are indeed given by matrices in the energy eigenbasis. The second point needs a little more explanation. One can write down a formal solution to eq. (2.3) for operators that do not explicitly depend on time, $\partial_t \hat{A} = 0$. If we define the unitary time-evolution operator $\hat{\mathcal{U}}$ as

$$\hat{\mathcal{U}}(t_N, t_0) = \hat{T} \exp\left[-i \int_{t_0}^{t_N} dt\, \hat{H}(t)\right] = \lim_{N\to\infty} \hat{T} \prod_{n=0}^{N-1} \left(1 - i\Delta t \hat{H}(t_n)\right), \quad (2.7)$$

where $t_{n+1} = \Delta t + t_n$, $\Delta t = (t_N - t_0)/N$. The action of the time-ordering operator $\hat{T}$ is such that all expressions on its right get ordered with later times to the left, i.e.

$$\hat{\mathcal{U}}(t_N, t_0) = \left(1 - i\Delta t \hat{H}(t_{N-1})\right) \ldots \left(1 - i\Delta t \hat{H}(t_1)\right) \left(1 - i\Delta t \hat{H}(t_0)\right). \quad (2.8)$$

Obviously $\hat{\mathcal{U}}$ has the properties

$$\begin{aligned} \hat{\mathcal{U}}(t_i, t_f) &= \hat{\mathcal{U}}^\dagger(t_f, t_i), & \hat{\mathcal{U}}(t_f, t_i) &= \hat{\mathcal{U}}(t_f, t_0)\hat{\mathcal{U}}(t_0, t_i), \\ \frac{d\hat{\mathcal{U}}(t_f, t_i)}{dt_f} &= -i\hat{H}(t_f)\hat{\mathcal{U}}(t_f, t_i), & \frac{d\hat{\mathcal{U}}(t_f, t_i)}{dt_i} &= +i\hat{\mathcal{U}}(t_f, t_i)\hat{H}(t_i). \end{aligned} \quad (2.9)$$

The solution to eq. (2.3) then reads

$$\hat{A}(t) = \hat{\mathcal{U}}^\dagger(t, t_0)\hat{A}(t_0)\hat{\mathcal{U}}(t, t_0). \quad (2.10)$$

In this expression lies the answer to why we introduced the Hilbert space $\mathcal{H}$. Outcomes of measurements $a(t)$ are given by expectation values

$$a(t) = \langle \hat{A}(t) \rangle = \langle \psi | \hat{A}(t) | \psi \rangle, \qquad |\psi\rangle \equiv |\psi(t_0)\rangle. \quad (2.11)$$

Since the prescription (2.10) basically shifts time-evolution to the operator $\hat{\mathcal{U}}$ we do not change the predicted outcome of measurements by attaching $\hat{\mathcal{U}}$ to the vectors $|\psi\rangle$,

$$a(t) = \langle \psi(t) | \hat{A} | \psi(t) \rangle, \qquad |\psi(t)\rangle = \hat{\mathcal{U}}(t, t_0)|(t_0)\rangle, \qquad \hat{A} \equiv \hat{A}(t_0). \quad (2.12)$$

In going from eq. (2.11) to eq. (2.12) we did not change the formalism, but only the picture of the quantum dynamics. The prescription corresponding to eq. (2.11), where operators evolve and states are constant is called the Heisenberg picture, whereas the prescription corresponding to eq. (2.12), where operators are constant and states evolve, is called the Schrödinger picture. In the Heisenberg picture dynamics are completely given by the

operators, thus it is justified to call it matrix mechanics. One should note that in the Schrödinger picture, eq. (2.12) implies the equation of motion

$$i\frac{d|\psi(t)\rangle}{dt} = i\partial_t|\psi(t)\rangle = \hat{H}|\psi(t)\rangle, \tag{2.13}$$

which is the time-dependent Schrödinger equation (see chapter 3) for the abstract vector $|\psi(t)\rangle$.

Before we proceed to the actual derivation of the hydrogenic energy levels, let us write down some important relations. Concerning the commutators of the position and momentum operators one can show by induction that

$$\begin{aligned} [\hat{p}_j, (\hat{x}^k)^n] &= -in(\hat{x}^j)^{n-1}\delta^{(k)}{}_{(j)} \quad \Rightarrow \quad [\hat{\vec{p}}, f(\hat{\vec{x}})] = -i\vec{\nabla}_{\hat{x}} f(\hat{\vec{x}}), \\ [\hat{x}^j, (\hat{p}_k)^n] &= +in(\hat{p}_k)^{n-1}\delta^{(j)}{}_{(k)} \quad \Rightarrow \quad [\hat{\vec{x}}, f(\hat{\vec{p}})] = +i\vec{\nabla}_{\hat{p}} f(\hat{\vec{x}}). \end{aligned} \tag{2.14}$$

A very important quantity is given by the angular momentum operator,

$$\hat{\vec{L}} = \hat{\vec{x}} \times \hat{\vec{p}}, \tag{2.15}$$

which satisfies the commutation relations

$$\begin{aligned} [\hat{x}^j, \hat{L}^k] &= i\varepsilon^{jkl}\hat{x}_l, & [\hat{p}^j, \hat{L}^k] &= i\varepsilon^{jkl}\hat{p}_l, \\ [\hat{L}^j, \hat{L}^k] &= i\varepsilon^{jkl}\hat{L}_l, & [f(\hat{r}), \hat{L}^k] &= 0. \end{aligned} \tag{2.16}$$

The properties of eigenstates of the angular momentum operator are needed for the derivation of the energy levels. Therefore an individual section is devoted to them.

2.2 Angular momentum eigenstates

Let us consider the commutation relations among the components of the angular momentum operator,

$$[\hat{L}^i, \hat{L}^j] = i\varepsilon^{ijk}\hat{L}_k. \tag{2.17}$$

This commutator defines the Lie algebra of SU(2) and SO(3). The square of the total angular momentum operator commutes with all three of its components,

$$\hat{\vec{L}}^2 = (\hat{L}^1)^2 + (\hat{L}^2)^2 + (\hat{L}^3)^2, \qquad [\hat{\vec{L}}^2, \hat{L}^i] = 0. \tag{2.18}$$

Let us define states of the form $|m\rangle$ that diagonalize $\hat{L}^3$,

$$\hat{L}^3|m\rangle = m|m\rangle. \tag{2.19}$$

Since $\hat{L}^3$ and $\hat{\vec{L}}^2$ commute, this bases diagonalizes $\hat{\vec{L}}^2$ as well. From eqs. (2.17) and (2.18) one can see that the raising and lowering operators,

$$\hat{L}^\pm = \hat{L}^1 \pm i\hat{L}^2, \tag{2.20}$$

satisfy the commutation relations

$$[\hat{L}^+, \hat{L}^-] = 2\hat{L}^3, \qquad [\hat{\vec{L}}^2, \hat{L}^\pm] = 0, \qquad [\hat{L}^3, \hat{L}^\pm] = \pm\hat{L}^\pm. \tag{2.21}$$

From these relations it follows that

$$\hat{L}^3(\hat{L}^\pm)^n|m\rangle = (m \pm n)(\hat{L}^\pm)^n|m\rangle \quad \Rightarrow \quad (\hat{L}^\pm)|m\rangle \propto |m \pm n\rangle. \tag{2.22}$$

Thus the operators $\hat{L}^\pm$ indeed raise and lower the quantum numbers of angular momentum eigenstates. Let us now consider finite dimensional representations of the Lie group underlying the Lie algebra (2.17). Thus we label every state by an additional quantum number l, which limits the values that m is allowed to take. Let us now write

$$\hat{L}^\pm|l, m\rangle = c^\pm_{l,m}|l, m \pm 1\rangle, \qquad c^\pm_{l,m} \in \mathbb{C}, \tag{2.23}$$

where for a finite-dimensional representation, we have $c^+_{l,l} = c^-_{l,-l} = 0$. Since $\hat{L}^\pm$ changes the quantum number m only by one, l and m have to be half integers,

$$|m| \leq l, \qquad 2|m|, 2l \in \mathbb{N}. \tag{2.24}$$

In order to determine the $c^\pm_{l,m}$, we consider the square of the total angular momentum operator. It may be written in terms of the raising and lowering operators as

$$\hat{\vec{L}}^2 = \hat{L}^-\hat{L}^+ + \hat{L}^3 + (\hat{L}^3)^2 = \hat{L}^+\hat{L}^- - \hat{L}^3 + (\hat{L}^3)^2. \tag{2.25}$$

Since $\hat{\vec{L}}^2$ commutes with $\hat{L}^\pm$ its eigenvalues are independent of m,

$$\langle l, m|\hat{\vec{L}}^2|l, m\rangle = \langle l, \pm l|\hat{\vec{L}}^2|l, \pm l\rangle = l(l+1). \tag{2.26}$$

We can further use the fact that $(\hat{L}^\pm)^\dagger = \hat{L}^\mp$,

$$|c^\pm_{l,m}|^2 = |\hat{L}^\pm|l, m\rangle|^2 = \langle l, m|\hat{L}^\mp\hat{L}^\pm|l, m\rangle$$

$$= \langle l,m|(\hat{\vec{L}}^2 \mp \hat{L}^3 - (\hat{L}^3)^2)|l,m\rangle = l(l+1) - m(m\pm 1). \qquad (2.27)$$

Since we are free to chose the phase, we set all $c^{\pm}_{l,m}$ to be real,

$$c^{+}_{l,m} = c_{l,m} = \sqrt{(l-m)(l+m+1)}, \qquad c^{-}_{l,m} = c_{l,m-1}. \qquad (2.28)$$

Thus every state $|l,m\rangle$ may be represented as $\hat{L}^{\pm}$ acting $l-m$ times on $|l,\pm l\rangle$,

$$|l,m\rangle = \sqrt{\frac{(l\pm m)!}{(2l)!(l\mp m)!}}\,(\hat{L}^{\mp})^{l\mp m}|l,\pm l\rangle. \qquad (2.29)$$

2.3 Derivation of the hydrogen energy levels

Let us now consider the Hamiltonian $\hat{H}_{\text{tot}}$ of the proton and electron in the hydrogen atom,

$$\hat{H}_{\text{tot}} = \frac{\hat{\vec{p}}_p^{\,2}}{2m_p} + \frac{\hat{\vec{p}}_e^{\,2}}{2m_e} - \frac{\alpha}{|\hat{\vec{x}}_p - \hat{\vec{x}}_e|}, \qquad (2.30)$$

where the position and momentum operators of the proton commute with those of the electron. Analogous to classical mechanics we introduce center-of-mass (CM) and relative coordinates and momenta,

$$\begin{aligned} \hat{\vec{r}} &= \hat{\vec{x}}_p - \hat{\vec{x}}_e, & \hat{\vec{R}} &= (m_p\hat{\vec{x}}_p + m_e\hat{\vec{x}}_e)/M, \\ \hat{\vec{p}} &= (m_e\hat{\vec{p}}_p - m_p\hat{\vec{p}}_e)/M & \hat{\vec{P}} &= \hat{\vec{p}}_p + \hat{\vec{p}}_e, \end{aligned} \qquad (2.31)$$

where $M = m_p + m_e$. The total Hamiltonian (2.30) then separates into a CM and relative part,

$$\hat{H}_{\text{tot}} = \frac{\hat{\vec{P}}^2}{2M} + \hat{H}, \qquad \hat{H} = \frac{\hat{\vec{p}}^{\,2}}{2m} - \frac{\alpha}{\hat{r}}. \qquad (2.32)$$

In the following we will only concentrate on the relative part $\hat{H}$. The equations of motion for this system read, analogous to classical mechanics,

$$\dot{\hat{\vec{p}}} = -\vec{\nabla}_{\hat{x}}\hat{H} = -\frac{\alpha\hat{\vec{x}}}{\hat{r}^3}, \qquad \dot{\hat{\vec{x}}} = \vec{\nabla}_{\hat{p}}\hat{H} = \frac{\hat{\vec{p}}}{m}. \qquad (2.33)$$

Using these results, we can directly show that the angular momentum operator $\hat{\vec{L}}$ represents a conserved quantity,

$$\frac{d\hat{\vec{L}}}{dt} = \frac{1}{i}[\hat{\vec{L}},\hat{H}] = \hat{\vec{x}}\times\frac{1}{i}[\hat{\vec{p}},\hat{H}] + \frac{1}{i}[\hat{\vec{x}},\hat{H}]\times\hat{\vec{p}} = 0. \qquad (2.34)$$

From this it also follows that,

$$[\hat{\vec{x}}, \hat{\vec{L}}^2] = i(\hat{\vec{L}} \times \hat{\vec{x}} - \hat{\vec{x}} \times \hat{\vec{L}}), \quad [\hat{\vec{p}}, \hat{\vec{L}}^2] = i(\hat{\vec{L}} \times \hat{\vec{p}} - \hat{\vec{p}} \times \hat{\vec{L}}), \quad [\hat{\vec{p}}^2, \hat{L}^k] = 0. \tag{2.35}$$

Further we define an operator that represents the Laplace-Runge-Lenz (LRL) vector,

$$\begin{aligned} \hat{\vec{U}} = \frac{[\hat{\vec{p}}, \hat{\vec{L}}^2]}{2im\alpha} + \frac{\hat{\vec{x}}}{\hat{r}} &= \frac{\hat{\vec{L}} \times \hat{\vec{p}} - \hat{\vec{p}} \times \hat{\vec{L}}}{2m\alpha} + \frac{\hat{\vec{x}}}{\hat{r}} \\ &= \frac{\hat{\vec{L}} \times \hat{\vec{p}}}{m\alpha} - \frac{i\hat{\vec{p}}}{m\alpha} + \frac{\hat{\vec{x}}}{\hat{r}} = -\frac{\hat{\vec{p}} \times \hat{\vec{L}}}{m\alpha} + \frac{i\hat{\vec{p}}}{m\alpha} + \frac{\hat{\vec{x}}}{\hat{r}}, \end{aligned} \tag{2.36}$$

where the different representations will become useful in different situations. As in classical mechanics, this operator also represents a conserved quantity,

$$\begin{aligned} \frac{d\hat{\vec{U}}}{dt} = \frac{1}{i}[\hat{\vec{U}}, \hat{H}] &= -\frac{[[\hat{\vec{p}}, \hat{H}], \hat{\vec{L}}^2]}{2m\alpha} + \frac{1}{i}\left[\frac{\hat{\vec{x}}}{\hat{r}}, \hat{H}\right] \\ &= \frac{\hat{\vec{x}} \times \hat{\vec{L}} - \hat{\vec{L}} \times \hat{\vec{x}}}{2m\hat{r}^3} + \left\{\frac{\mathbb{1}\hat{r}^2 - \hat{\vec{x}} \otimes \hat{\vec{x}}}{\hat{r}^3}, \frac{\hat{\vec{p}}}{2im}\right\} = 0. \end{aligned} \tag{2.37}$$

The LRL operator $\hat{\vec{U}}$ serves to find the energy eigenvalues of the system. For this purpose, using $\mathrm{Ryd} = m\alpha^2/2$ again, we calculate its square,

$$\begin{aligned} \hat{\vec{U}}^2 &= \left(\frac{\hat{\vec{L}} \times \hat{\vec{p}}}{m\alpha} - \frac{i\hat{\vec{p}}}{m\alpha} + \frac{\hat{\vec{x}}}{\hat{r}}\right)\left(-\frac{\hat{\vec{p}} \times \hat{\vec{L}}}{m\alpha} + \frac{i\hat{\vec{p}}}{m\alpha} + \frac{\hat{\vec{x}}}{\hat{r}}\right) \\ &= 1 + \frac{\hat{H}}{\mathrm{Ryd}}(1 + \hat{\vec{L}}^2). \end{aligned} \tag{2.38}$$

Further we calculate the commutator of its components with themselves and with those of the angular momentum operator,

$$[\hat{U}^i, \hat{U}^j] = -\frac{\hat{H}}{\mathrm{Ryd}} i\varepsilon^{ijk}\hat{L}_k, \qquad [\hat{U}^i, \hat{L}^j] = i\varepsilon^{ijk}\hat{U}_k. \tag{2.39}$$

Analogous to section 2.2 we define raising and lowering operators for the LRL operator,

$$\hat{U}^{\pm} = \hat{U}^1 \pm i\hat{U}^2. \tag{2.40}$$

They satisfy the commutation relations

$$\begin{aligned}
[\hat{U}^+, \hat{U}^-] &= -\frac{2\hat{H}\hat{L}^3}{\mathrm{Ryd}}, & [\hat{U}^3, \hat{U}^\pm] &= \mp\frac{\hat{H}\hat{L}^\pm}{\mathrm{Ryd}}, \\
[\hat{U}^\pm, \hat{L}^\mp] &= \pm 2\hat{U}^3, & [\hat{U}^\pm, \hat{L}^3] &= \mp\hat{U}^\pm, \\
[\hat{U}^\pm, \hat{\vec{L}}^2] &= \pm 2(\hat{U}^3\hat{L}^\pm - \hat{U}^\pm(\hat{L}^3 \pm 1)), & [\hat{U}^3, \hat{\vec{L}}^2] &= \hat{L}^-\hat{U}^+ - \hat{U}^-\hat{L}^+. \quad (2.41)
\end{aligned}$$

The square of the LRL operator may thus be written alternatively as

$$\hat{\vec{U}}^2 = \hat{U}^+\hat{U}^- + \frac{\hat{H}\hat{L}^3}{\mathrm{Ryd}} + (\hat{U}^3)^2 = \hat{U}^-\hat{U}^+ - \frac{\hat{H}\hat{L}^3}{\mathrm{Ryd}} + (\hat{U}^3)^2. \quad (2.42)$$

Let us now investigate the action of $\hat{U}^3$ and $\hat{U}^\pm$ on a state $|E, l, m\rangle$, which is an eigenstate of the Hamiltonian $\hat{H}$ with eigenvalue E,

$$\hat{H}|E, l, m\rangle = E|E, l, m\rangle, \quad (2.43)$$

and angular momentum and magnetic quantum numbers l and m according to section 2.2. From the commutators of $\hat{U}^3$ and $\hat{U}^\pm$ with $\hat{L}^3$ we can see that the first leaves m invariant while the second raises/lowers m by one,

$$\begin{aligned}
\langle E', l', m'|\hat{U}^3|E, l, m\rangle &\propto \delta_{E',E}\delta_{m',m}, \\
\langle E', l', m'|\hat{U}^\pm|E, l, m\rangle &\propto \delta_{E',E}\delta_{m',m\pm1}, \quad (2.44)
\end{aligned}$$

where the energy-δ is a result of $[\hat{H}, \hat{U}^i] = 0$. But the components of the LRL operator can also change the angular momentum l of a state as can be seen from the third line of eq. (2.41). From these commutators we can deduce the relations

$$\begin{aligned}
\langle E, l', m+1|\hat{U}^+|E, l, m\rangle &= -\frac{2c_{l,m}}{\mathcal{L} - 2(m+1)} \langle E, l', m+1|\hat{U}^3|E, l, m+1\rangle, \\
\langle E, l', m|\hat{U}^-|E, l, m+1\rangle &= \frac{2c_{l,m}}{\mathcal{L} + 2m} \langle E, l', m|\hat{U}^3|E, l, m\rangle, \\
\langle E, l', m|\hat{U}^3|E, l, m\rangle &= \frac{c_{l,m}}{\mathcal{L}} \langle E, l', m|\hat{U}^-|E, l, m+1\rangle \\
&\quad - \frac{c_{l',m}}{\mathcal{L}} \langle E, l', m+1|\hat{U}^+|E, l, m\rangle, \quad (2.45)
\end{aligned}$$

where we have defined $\mathcal{L} = l'(l'+1) - l(l+1)$. Using $(\hat{U}^+)^\dagger = \hat{U}^-$, we obtain from eqs. (2.45) the two relations

$$\langle E, l', m|\hat{U}^3|E, l, m\rangle = \frac{c_{l',m}}{c_{l,m}} \frac{\mathcal{L} + 2m}{\mathcal{L} + 2(m+1)} \langle E, l', m+1|\hat{U}^3|E, l, m+1\rangle$$

$$= \frac{c_{l,m}}{c_{l',m}} \frac{\mathcal{L} - 2m}{\mathcal{L} - 2(m+1)} \langle E, l', m+1 | \hat{U}^3 | E, l, m+1 \rangle. \tag{2.46}$$

The consistency of the two lines in eq. (2.46) allows only three values of l',

$$\mathcal{L} = 0 \quad \Leftrightarrow \quad l' = l, \qquad \mathcal{L} = 1 \pm (2l+1) \quad \Leftrightarrow \quad l' = l \pm 1. \tag{2.47}$$

Let us consider the case $l' = l$. Eq. (2.46) then yields

$$\langle E, l, 0 | \hat{U}^3 | E, l, 0 \rangle = \langle E, l, l | \hat{U}^3 | E, l, l \rangle = 0, \tag{2.48}$$

but also

$$\frac{\langle E, l, m | \hat{U}^3 | E, l, m \rangle}{m} = \frac{\langle E, l, m' | \hat{U}^3 | E, l, m' \rangle}{m'}, \tag{2.49}$$

for arbitrary $m, m' \neq 0$. Setting $m' = l$, however, shows that the matrix elements of $\hat{U}^3$ with $l' = l$ all vanish and so do the matrix elements of $\hat{U}^\pm$ according to eqs. (2.45). Thus we obtain

$$\begin{aligned} \hat{U}^3 | E, l, m \rangle &= C_{l+1,l} \sqrt{(l+1)^2 - m^2}\, | E, l+1, m \rangle \\ &\quad + C_{l,l-1} \sqrt{l^2 - m^2}\, | E, l-1, m \rangle \\ \hat{U}^\pm | E, l, m \rangle &= \mp C_{l+1,l} \sqrt{(l \pm m + 1)(l \pm m + 2)}\, | E, l+1, m \pm 1 \rangle \\ &\quad \pm C_{l,l-1} \sqrt{(l \mp m)(l \mp m - 1)}\, | E, l-1, m \pm 1 \rangle, \end{aligned} \tag{2.50}$$

where $C_{l+1,l}$ is symmetric in its two indices due to the hermiticity of $\hat{U}^3$ and does not depend on m. Writing $E = -\,\mathrm{Ryd}\,\mathcal{E}$ we may conclude from these relations that

$$2m\mathcal{E} = \langle E, l, m | [\hat{U}^+, \hat{U}^-] | E, l, m \rangle = 2m(C_{l,l-1}^2 (2l-1) - C_{l+1,l}^2 (2l+3)), \tag{2.51}$$

which for general m implies

$$C_{l,l-1} = \sqrt{\frac{\mathcal{E} + (2l+3) C_{l+1,l}^2}{2l-1}}. \tag{2.52}$$

Let us define a quantum number $n \in \mathbb{N}$ that labels energy eigenvalues, $E \to E_n$, $C_{l,l-1} \to C_{l,l-1}^n$ such that n determines the maximum angular momentum compatible with the energy E_n via $l < n$. Inserting $C_{n,n-1}^n = 0$ into relation (2.52) then yields,

$$C_{l,l-1}^n = \sqrt{\mathcal{E}_n \frac{n^2 - l^2}{(2l+1)(2l-1)}}. \tag{2.53}$$

Table 2.1: Experimental values of the hydrogen energy levels as given in Kramida (2010) are compared with the non-relativistic energy levels ΔE_n in eq. (2.56). The relative deviation from the experimental values is of the order 10^{-5}.

State	Exp. levels (eV)	ΔE_n (eV)	Deviation
$1S_{1/2}$	0	0	
$2P_{1/2}$	10.1988055286	10.1987150105746	$9 \cdot 10^{-6}$
$2S_{1/2}$	10.1988099034600		$9 \cdot 10^{-6}$
$2P_{1/2}$	10.1988508929		$1 \cdot 10^{-5}$
$3P_{1/2}$	12.087492922	12.0873659384587	$1 \cdot 10^{-5}$
$3S_{1/2}$	12.087494224		$1 \cdot 10^{-5}$
$3D_{1/2}$	12.087506341		$1 \cdot 10^{-5}$
$3P_{1/2}$	12.087506364		$1 \cdot 10^{-5}$
$3D_{1/2}$	12.087510821		$1 \cdot 10^{-5}$
$4P_{1/2}$	12.74853166921	12.7483937632182	$1 \cdot 10^{-5}$
$4S_{1/2}$	12.74853221952		$1 \cdot 10^{-5}$
$4D_{1/2}$	12.7485373313		$1 \cdot 10^{-5}$
$4P_{1/2}$	12.74853733962		$1 \cdot 10^{-5}$
$4D_{1/2}$	12.74853922041		$1 \cdot 10^{-5}$
$4F_{1/2}$	12.748539221		$1 \cdot 10^{-5}$
$4F_{1/2}$	12.7485401632		$1 \cdot 10^{-5}$
Continuum	13.598433770784	13.5982866807661	$1 \cdot 10^{-5}$

We can now determine the energy eigenvalues E_n from the expectation value of $\hat{\vec{U}}^2$ for states $|E_n, l, m\rangle = |n, l, m\rangle$,

$$\begin{aligned}\langle n,l,m|\hat{\vec{U}}^2|n,l,m\rangle &= 1 - \mathcal{E}_n(1 + l(l+1)) \\ &= (C^n_{l+1,l})^2(l+m+1)(2l+3) \\ &\quad + (C^n_{l,l-1})^2(l-m)(2l-1) + m\mathcal{E}_n. \end{aligned} \tag{2.54}$$

Inserting eq. (2.52) yields the energy levels

$$\mathcal{E}_n = \frac{1}{n^2}, \qquad E_n = -\frac{\mathrm{Ryd}}{n^2}, \tag{2.55}$$

which are identical to the ones derived by Bohr (1913). Electronic transitions to the hydrogen ground state then liberate the energy

$$\Delta E_n = \mathrm{Ryd}\left(1 - \frac{1}{n^2}\right), \tag{2.56}$$

which are compared the experimental values in table 2.1.

Chapter 3

The Schrödinger equation

Soon after Heisenberg's new formulation of quantum mechanics Schrödinger (1926) found another approach to the field. Even though the two formalisms looked completely different at first sight and seemed to have a different philosophy at their base, it turns out they are completely equivalent to each other. With the Schrödinger equation one has a partial differential equation at hand which determines (up to normalization) a function ψ, the wave function, which is defined on spacetime and the absolute square of which gives the probability density to find the particle (electron) at the given event. In this chapter we introduce Schrödinger's formalism and use it to find the solution for the hydrogen atom.

3.1 Schrödinger's formalism and its relation to matrix mechanics

Schrödinger (1926) started out from the Hamilton-Jacobi equation for a time-independent Hamiltonian

$$H\left(\vec{x}, \vec{\nabla} S_0\right) = E, \qquad S_0(\vec{x}; \vec{x}_0) = \int_{\vec{x}_0}^{\vec{x}} d\vec{x}\, \vec{p}, \tag{3.1}$$

where S_0 is the reduced action. Schrödinger's ansatz was now to introduce a function ψ via

$$S_0(\vec{x}) = \ln \psi(\vec{x}), \tag{3.2}$$

where the reduced action S_0 is viewed as a function of the end point. For a Hamiltonian of the form

$$H(\vec{x}, \vec{p}) = \frac{\vec{p}^2}{2m} + V(\vec{x}), \tag{3.3}$$

eq. (3.1) implies

$$\frac{(\vec{\nabla}\psi(\vec{x}))^2}{2m} + (V(\vec{x}) - E)\psi^2(\vec{x}) = 0. \tag{3.4}$$

This is however not the equation Schrödinger was looking for but the (double) Hamiltonian density of a variational problem with action J,

$$J = \frac{1}{2}\int_V d^3x\, \psi(\vec{x}) \left(-\frac{\Delta}{2m} + V(\vec{x}) - E\right) \psi(\vec{x}). \tag{3.5}$$

Variation with respect to ψ then gives the famous (stationary) Schrödinger equation,

$$\left(-\frac{\Delta}{2m} + V(\vec{x}) - E\right) \psi(\vec{x}) = 0, \tag{3.6}$$

provided that the surface integral

$$\int_{\partial V} d^2x\, \delta\psi\, \vec{n}_V \vec{\nabla}\psi, \tag{3.7}$$

which results from a partial integration, vanishes. These are the historical arguments by which Schrödinger "derived" the equation (3.6) named after him. It is not manifest that the formalisms of Heisenberg (see chapter 2) and Schrödinger are indeed equivalent. Heisenberg's formalism is concerned with the evolution of operators, such as the position and momentum operators $\hat{\vec{x}}$ and $\hat{\vec{p}}$ that act on vectors $|\psi\rangle$ living in a Hilbert space $\mathcal{H}$. The Schrödinger formalism, on the other hand, deals with a wave function ψ, where positions are given by vectors $\vec{x}$ in configuration space and momenta have been replaced by derivatives. Nowadays one would rather express Schrödinger's formalism in a different way that makes the connection to the Heisenberg formalism obvious.

Let us consider matrix mechanics in the Schrödinger picture as given in eq. (2.12). We now choose a continuous basis $|\vec{x}\rangle$ that diagonalizes the position operators $\hat{\vec{x}}$,

$$\hat{\vec{x}}|\vec{x}\rangle = \vec{x}|\vec{x}\rangle, \qquad \mathbb{1} = \int d^3x\, |\vec{x}\rangle\langle\vec{x}|, \qquad \langle\vec{y}|\vec{x}\rangle = \delta^3(\vec{x} - \vec{y}), \tag{3.8}$$

i.e. we can define a function $\psi(t, \vec{x})$ as

$$\psi(t, \vec{x}) = \langle\vec{x}|\psi(t)\rangle. \tag{3.9}$$

Thus the function ψ is defined on the configuration space and $|\psi(t,\vec{x})|^2$ gives the probability density to find the particle at time t at position $\vec{x}$. The expectation value of an operator $\hat{A}$ reads

$$\langle \hat{A}(t)\rangle = \int d^3x \, \langle \vec{x}|\hat{A}|\vec{x}\rangle |\psi(t,\vec{x})|^2, \tag{3.10}$$

as given in the position eigenbasis $|\vec{x}\rangle$. Acting with a vector $|\vec{x}\rangle$ on eqs. (2.14) gives us the matrix elements of the momentum operator in the position eigenbasis,

$$[\hat{\vec{p}}, f(\hat{\vec{x}})]|\vec{x}\rangle = |\vec{x}\rangle(-i\vec{\nabla})f(\vec{x}) \quad \Rightarrow \qquad \langle \vec{y}|\hat{\vec{p}}|\vec{x}\rangle = \delta^3(\vec{x}-\vec{y})(-i\vec{\nabla}). \tag{3.11}$$

Let us now act with $\langle \vec{x}|$ on eq. (2.13),

$$\begin{aligned} i\partial_t \psi(t,\vec{x}) &= \int d^3y \, \langle \vec{x}|\hat{H}(t,\hat{\vec{x}},\hat{\vec{p}})|\vec{y}\rangle \, \psi(t,\vec{y}) \\ &= H(t,\vec{x},-i\vec{\nabla})\psi(t,\vec{x}), \end{aligned} \tag{3.12}$$

where $H(t,\vec{x},-i\vec{\nabla})$ in the second line means the classical Hamilton function with momenta $\vec{p}$ replaced by $-i\vec{\nabla}$. This equation is known as the time-dependent Schrödinger equation[1]. The Hamiltonian corresponding to the example (2.4) reads in this formalism

$$H(t,\vec{x},-i\vec{\nabla}) = -\frac{(\vec{\nabla} - iq\vec{A}(t,\vec{x}))^2}{2m} + q\Phi(t,\vec{x}). \tag{3.13}$$

Of course, all ambiguities of the Heisenberg formalism concerning the transition from classical mechanics to the quantum mechanical analogue (and not the other way around) remain.

Thus the Schrödinger formalism is simply concerned with the evolution of the components $\psi(t,\vec{x})$ of the Hilbert space-vector $|\psi(t)\rangle$ with respect to the position eigenbasis $|\vec{x}\rangle$ in the Schrödinger picture of matrix mechanics. The advantage of Schrödinger's formalism is clearly its much more intuitive notion of a function ψ defined on spacetime with its absolute square $|\psi|^2$ representing a probability density (if the term "intuitive" applies to quantum mechanics at all) as opposed to the abstract formalism of matrix mechanics. Also different formalisms have different strengths and weaknesses so it is very useful to have alternative formulations at hand to be able to switch to the one which is most

[1] Quite frankly, the $i\partial_t$ in eq. (3.12) may be viewed as the matrix element of an operator $\hat{p}^t = -\hat{p}_t$ in a spacetime basis $|t,\vec{x}\rangle$. The 4-momentum operator would then read $\hat{p}_\mu = -i\partial_\mu$.

efficient for a given problem. Especially in the case of the hydrogen atom the stationary wave function $\psi(\vec{x})$ gives us valuable information about the spatial probability distribution to find the electron. In the next section we will therefore solve the Schrödinger equation for the hydrogen atom, which yields the same Bohr energy levels as found in the previous chapter, but also inspect the properties of the resulting wave function.

3.2 The hydrogen wave functions

In this section we derive the solution to the hydrogen atom using the non-relativistic Schrödinger equation, i.e. we solve the equation

$$\left(-\frac{\Delta_p}{2m_p} - \frac{\Delta_e}{2m_e} - \frac{\alpha}{|\vec{x}_p - \vec{x}_e|} - i\partial_t\right)\psi(t, \vec{x}_p, \vec{x}_e) = 0, \tag{3.14}$$

where $\vec{x}_p$ and $\vec{x}_e$ are the positions of proton and electron, respectively. Let us introduce center-of-mass (CM) and relative coordinates,

$$\vec{r} = \vec{x}_p - \vec{x}_e, \qquad \vec{R} = (m_p\vec{x}_p + m_e\vec{x}_e)/M, \qquad M = m_p + m_e. \tag{3.15}$$

Making the separation ansatz $\psi(t, \vec{x}_p, \vec{x}_e) = \psi(t, \vec{R})\psi(t, \vec{r})$, we obtain

$$\psi(t, \vec{r})\left(-\frac{\Delta_R}{2M} - i\partial_t\right)\psi(t, \vec{R}) + \psi(t, \vec{R})\left(-\frac{\Delta_r}{2m} - \frac{\alpha}{r} - i\partial_t\right)\psi(t, \vec{r}) = 0, \tag{3.16}$$

where $m = m_p m_e/M$ is the reduced mass as given in eq. (1.4). Obviously the CM-Schrödinger equation is solved by the one-parameter family of solutions

$$\psi_K(t, \vec{R}) = e^{i\vec{K}\vec{R} - i\vec{K}^2 t/(2M)}. \tag{3.17}$$

These wave functions satisfy the completeness relation

$$\int \frac{d^3K}{(2\pi)^3}\,\psi_K(t, \vec{R}_1)\psi_K^*(t, \vec{R}_2) = \delta^3(\vec{R}_1 - \vec{R}_2). \tag{3.18}$$

Since we consider a bound state, the solution of the remaining part of the Schrödinger equation will have a discrete spectrum. Due to the spherical and time translation symmetry of the problem we write

$$\psi_{nlm}(t, \vec{r}) = e^{-iE_n t}\frac{g_{nl}(r)}{r}Y_{lm}(\theta, \varphi), \tag{3.19}$$

where Y_{lm} is a spherical harmonic (see appendix B). In order for the wave function to be orthonormal, the wave function ψ and its radial part g have to satisfy the conditions,

$$\int d^3r\, \psi^*_{n'l'm'}(t,\vec{r})\psi_{nlm}(t,\vec{r}) = \delta_{nn'}\delta_{ll'}\delta_{mm'},$$
$$\int_0^\infty dr\, g^*_{nl}(r)g_{n'l}(r) = \delta_{nn'}. \tag{3.20}$$

In spherical coordinates, the Schrödinger equation becomes

$$\left(-\frac{\partial_r^2}{2m} + \frac{l(l+1)}{2mr^2} - \frac{\alpha}{r} - E_n\right) g_{nl}(r) = 0. \tag{3.21}$$

Defining $C_n = \sqrt{-2mE_n}$ and $x = 2C_n r$ we have

$$\left(\partial_x^2 - \frac{l(l+1)}{x^2} + \frac{m\alpha}{C_n x} - \frac{1}{4}\right) g_{nl}(r) = 0. \tag{3.22}$$

From the asymptotic behavior in the limits $x \to 0$ and $x \to \infty$, we get the form

$$g_{nl}(r) = x^{l+1}e^{-x/2}u_{nl}(x). \tag{3.23}$$

The equation for u then reads

$$\left(x\partial_x^2 + (2l+2-x)\partial_x + \frac{m\alpha}{C_n} - l - 1\right) u_{nl}(x) = 0. \tag{3.24}$$

Up to normalization u is given by the Kummer function,

$$u_{nl}(x) \propto M(l+1-m\alpha/C_n, 2l+2, x). \tag{3.25}$$

Since the bound-state wave function ought to be normalizable, the first argument of the Kummer function has to be a negative integer,

$$l+1-m\alpha/C_n = -n_r, \quad \text{where} \quad n_r \in \mathbb{N}, \quad \text{say.} \tag{3.26}$$

Let $n = n_r + l + 1 \in \mathbb{N}^+$ and $\mathrm{Ryd} = m\alpha^2/2$, then

$$C_n = \frac{m\alpha}{n}, \qquad E_n = -\frac{\mathrm{Ryd}}{n^2}. \tag{3.27}$$

These are the same energy levels found by Bohr (1913) and Pauli (1926) and which are given in eq. (2.55). A comparison with the experimentally

measured has been given in table 2.1. Now will proceed with our calculation of the wave functions, however.

For negative integer values of its first argument one may express the Kummer function in terms of the Laguerre polynomials,

$$M(-n_r, 2l+2, 2C_n r) = \frac{\Gamma(n_r+1)\Gamma(2l+2)}{\Gamma(n_r+2l+2)} L_{n_r}^{2l+1}(2C_n r). \tag{3.28}$$

The radial bound state wave function then reads

$$g_{nl}(r) = \mathcal{A}_{nl} x^{l+1} e^{-x/2} L_{n-l-1}^{2l+1}(x). \tag{3.29}$$

The normalization constant $\mathcal{A}$ may be calculated according to eq. (3.20), using the generating function of the Laguerre polynomials (see appendix B),

$$\begin{aligned}
1 &\stackrel{!}{=} \int_0^\infty dr\, (g_{nl}(r))^2 = \frac{\mathcal{A}_{nl}^2}{2C_n} \int_0^\infty dx\, x^{2l+2} e^{-x} (L_{n-l-1}^{2l+1}(x))^2 \\
&= \frac{\mathcal{A}_{nl}^2}{2C_n} \int_0^\infty dx\, x^{2l+2} e^{-x}\, \frac{\partial_y^{n-l-1}\partial_z^{n-l-1}}{((n-l-1)!)^2} \frac{\exp\left[-\frac{xy}{1-y} - \frac{xz}{1-z}\right]}{(1-y)^{2l+2}(1-z)^{2l+2}}\bigg|_{y=z=0} \\
&= \frac{\mathcal{A}_{nl}^2}{2C_n} \frac{(2l+2)!}{((n-l-1)!)^2}\, \partial_y^{n-l-1}\partial_z^{n-l-1} \frac{1-y-z+yz}{(1-yz)^{2l+3}}\bigg|_{y=z=0} \\
&= \frac{\mathcal{A}_{nl}^2}{2C_n} \frac{(n+l+1)! + (n-l-1)(n+l)!}{(n-l-1)!} \\
&= \frac{\mathcal{A}_{nl}^2}{C_n} \frac{n(n+l)!}{(n-l-1)!}.
\end{aligned} \tag{3.30}$$

Thus we obtain the final result for the radial wave function,

$$g_{nl}(r) = \sqrt{\frac{C_n}{n} \frac{(n-l-1)!}{(n+l)!}}\, (2C_n r)^{l+1} e^{-C_n r} L_{n-l-1}^{2l+1}(2C_n r). \tag{3.31}$$

The first few radial wave functions g_{nl} that belong to the energy values in table 2.1 are displayed in figure 3.2. They are labeled by their principle and angular quantum numbers n and l, using the numerical value of n and the scheme S, P, D, F, G, H, ... for $l = 0, 1, 2, 3, 4, 5, \ldots$ The explicit expressions of the first few radial wave functions read

$$\begin{aligned}
g_{10}(r) &= \sqrt{C_1}\, x_1 e^{-x_1/2} \\
g_{20}(r) &= \frac{\sqrt{C_2}}{2}\, x_2 e^{-x_2/2}\, (2 - x_2)
\end{aligned}$$

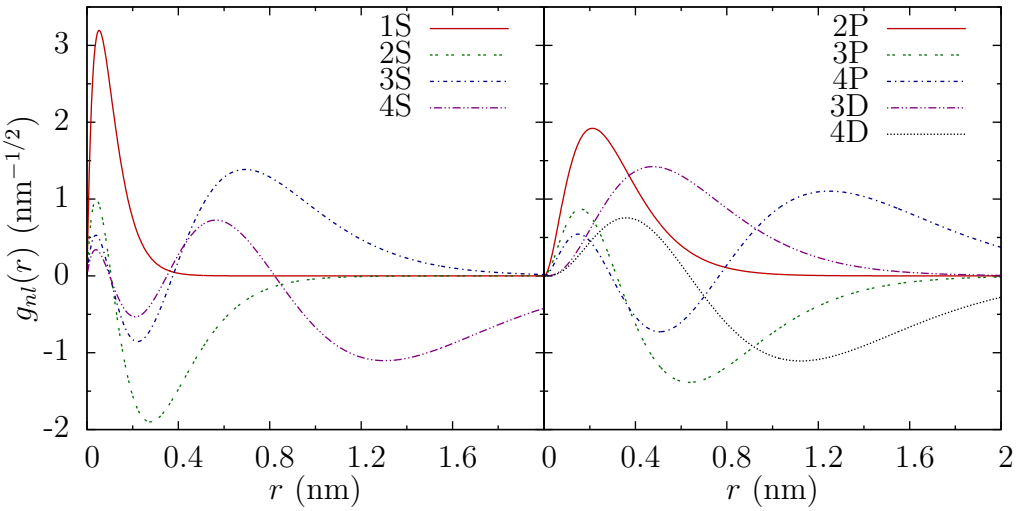

Figure 3.1: Bound state radial Schrödinger wave functions g_{nl} as given in eq. (3.31) for $n \leq 4$ and $l \leq 2$. See text for the nomenclature of the different states.

$$
\begin{aligned}
g_{21}(r) &= \sqrt{\frac{C_2}{12}}\, x_2^2 e^{-x_2/2} \\
g_{30}(r) &= \frac{\sqrt{C_3}}{3}\, x_3 e^{-x_3/2} \left(3 - 3x_3 + \frac{x_3^2}{2}\right) \\
g_{31}(r) &= \sqrt{\frac{C_3}{72}}\, x_3^2 e^{-x_3/2} \left(4 - x_3\right) \\
g_{32}(r) &= \sqrt{\frac{C_3}{360}}\, x_3^3 e^{-x_3/2}
\end{aligned}
\tag{3.32}
$$

3.2.1 Orthogonality of radial wave functions

Let us show explicitly that the orthonormality relation (3.20) holds, following the approach of Dunkl (2003). Since g_{nl} is already normalized, we only need to show that the right hand side of eq. (3.20) vanishes for $n \neq n'$. Consequently we will drop all irrelevant prefactors in the following calculation:

$$
\begin{aligned}
0 &\stackrel{!}{=} \int_0^\infty dr\, g_{nl}(r) g_{n'l}(r) \\
&\propto \int_0^\infty dx_1\, \frac{x_1^{2l+2}}{(nn')^{l+1}} e^{-\frac{x_1}{2}\left(\frac{1}{n}+\frac{1}{n'}\right)} L_{n-l-1}^{2l+1}\left(\frac{x_1}{n}\right) L_{n'-l-1}^{2l+1}\left(\frac{x_1}{n'}\right)
\end{aligned}
$$

$$\propto \int_0^\infty dy\, y^{2l+2} e^{-y} L_{n-l-1}^{2l+1}(ay) L_{n'-l-1}^{2l+1}(by), \tag{3.33}$$

where we have defined

$$y = \frac{x_1}{2}\left(\frac{1}{n} + \frac{1}{n'}\right), \qquad a = \frac{2n'}{n+n'}, \qquad b = \frac{2n}{n+n'}. \tag{3.34}$$

Writing further

$$N = n - l - 1, \qquad N' = n' - l - 1, \qquad \alpha = 2l + 1, \tag{3.35}$$

we can combine eqs. (B.16) and (B.17) to obtain

$$\begin{aligned} L_N^\alpha(ay) &= L_N^{\alpha+1}(ay) - L_{N-1}^{\alpha+1}(ay) \\ &= \sum_{k=0}^{N} Q(N,\alpha,k,a) \left(\frac{a}{1-a}\right)^k L_k^{\alpha+1}(y)\,(k - N'b), \\ Q(N,\alpha,k,a) &= \frac{(1-a)^{N-1}}{N+\alpha+1} \begin{pmatrix} N+\alpha+1 \\ N-k \end{pmatrix}. \end{aligned} \tag{3.36}$$

Inserting this into the last line of eq. (3.33) and using the standard orthogonality relation of the associated Laguerre polynomials (B.18) yields

$$\begin{aligned} &\int_0^\infty dy\, y^{\alpha+1} e^{-y} L_N^\alpha(ay) L_{N'}^\alpha(by) \\ &\quad = \sum_{k=0}^{N}\sum_{p=0}^{N'} Q(N,\alpha,k,a) Q(N',\alpha,p,b) \left(\frac{a}{1-a}\right)^k \left(\frac{b}{1-b}\right)^p \\ &\qquad\qquad \cdot (k - N'b)(p - Na) \int_0^\infty dy\, y^{\alpha+1} e^{-y} L_k^{\alpha+1}(y) L_p^{\alpha+1}(y) \\ &\quad \propto \Sigma(N, N', \alpha, a, b), \end{aligned} \tag{3.37}$$

where we have defined Σ as the sum

$$\Sigma(N,N',\alpha,a,b) = \sum_{k=0}^{\min(N,N')} \frac{(k - N'b)(k - Na)}{(N-k)!(N'-k)!(k+\alpha+1)!} \frac{\gamma^k}{k!}, \tag{3.38}$$

thereby introducing the parameter

$$\gamma = \frac{ab}{(1-a)(1-b)} = \frac{ab}{ab-1} = -\frac{4nn'}{(n-n')^2}. \tag{3.39}$$

Reformulating the numerator in terms of γ,

$$(k - N'b)(k - Na) = \frac{\gamma(N-k)(N'-k) - k(k+\alpha+1)}{\gamma - 1}, \tag{3.40}$$

we see that Σ vanishes,

$$\begin{aligned}\Sigma(N, N', \alpha, a, b) \propto & \sum_{k=0}^{\min(N,N')-1} \frac{1}{(N-k-1)!(N'-k-1)!(k+\alpha+1)!} \frac{\gamma^{k+1}}{k!} \\ & - \sum_{k=1}^{\min(N,N')} \frac{1}{(N-k)!(N'-k)!(k+\alpha)!} \frac{\gamma^k}{(k-1)!}, \\ = & \ 0. \end{aligned} \tag{3.41}$$

Hence we have explicitly shown that the radial wave functions satisfy the orthonormality relation (3.20).

3.2.2 Radial expectation values

Of great importance are the expectation values of powers of the radial coordinate, $\langle r^s \rangle$,

$$\langle r^s \rangle_{nl} = \int d^3x \, |\psi_{nlm}(\vec{x})|^2 r^s = \int_0^\infty dr \, (g_{nl}(r))^2 r^s. \tag{3.42}$$

From eq. (3.21) one can deduce the following relation between the expectation values of different powers,

$$(s+1)C_n^2 \langle r^s \rangle_{nl} - (2s+1)m\alpha \langle r^{s-1} \rangle_{nl} + s\left(l(l+1) - \frac{s^2-1}{4}\right) \langle r^{s-2} \rangle_{nl} = 0. \tag{3.43}$$

From $\langle 1 \rangle = 1$, one can easily derive $\langle r^{-1} \rangle$ as well as expectation values of larger integer powers of r. Both $\langle r^{-2} \rangle$ and $\langle r^{-3} \rangle$ are also very important expectation values. However, $\langle r^{-2} \rangle$ has to be calculated explicitly,

$$\begin{aligned}\left\langle \frac{1}{r^2} \right\rangle_{nl} &= \int_0^\infty dr \, \frac{(g_{nl}(r))^2}{r^2} = 2C_n \mathcal{A}_{nl}^2 \int_0^\infty dx \, x^{2l} e^{-x} (L_{n-l-1}^{2l+1}(x))^2 \\ &= \frac{2C_n \mathcal{A}_{nl}^2 (2l)!}{((n-l-1)!)^2} \, \partial_y^{n-l-1} \partial_z^{n-l-1} \frac{1}{1-y} \frac{1}{1-z} \frac{1}{(1-yz)^{2l+1}} \bigg|_{y=z=0}\end{aligned}$$

$$
\begin{aligned}
&= \frac{2C_n\mathcal{A}_{nl}^2(2l)!}{((n-l-1)!)^2} \\
&\qquad \cdot \sum_{j=0}^{n-l-1} \left[\begin{pmatrix} n-l-1 \\ j \end{pmatrix} \right]^2 \frac{((n-l-1-j)!)^2\, j!\, (2l+j)!}{(2l)!} \\
&= 2C_n\mathcal{A}_{nl}^2(2l)! \sum_{j=0}^{n-l-1} \begin{pmatrix} 2l+j \\ 2l \end{pmatrix} = 2C_n\mathcal{A}_{nl}^2(2l)! \begin{pmatrix} n+l \\ 2l+1 \end{pmatrix} \\
&= \frac{C_n^2}{n(l+1/2)}.
\end{aligned}
$$

Thus we may present the most commonly required radial expectation values,

$$
\begin{aligned}
\langle r^2\rangle_{nl} &= \frac{n^2(5n^2-3l(l+1)+1)}{2m^2\alpha^2}, & \langle r\rangle_{nl} &= \frac{3n^2-l(l+1)}{2m\alpha}, \\
\langle r^{-1}\rangle_{nl} &= \frac{m\alpha}{n^2}, & \langle r^{-2}\rangle_{nl} &= \frac{m^2\alpha^2}{n^3(l+1/2)}, \\
\langle r^{-3}\rangle_{nl} &= \frac{m^3\alpha^3}{n^3 l(l+1/2)(l+1)}. & &
\end{aligned} \tag{3.44}
$$

3.3 Continuum wave functions

In section 3.2 we have derived bound state solutions to the quantum mechanical Coulomb problem, as it applies to the hydrogen atom. These states, however, do not form a complete set since a free electron might as well be influenced by the presence of the proton as it is the case in e.g. a scattering scenario. Thus we also have to consider the continuum states, where the energy $E > 0$ may take any positive real value. The bound states together with the continuum states form a complete set,

$$
\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\left(\sum_{n=l+1}^{\infty}|nlm\rangle\langle nlm| + \int_0^{\infty} dk\,|klm\rangle\langle klm|\right) = 1, \tag{3.45}
$$

where $k = \sqrt{2mE}$ means the absolute value of the wave vector. Obviously $|nlm\rangle$ and $|klm\rangle$ are closely related to each other since they are eigenstates of the same Hamiltonian (3.14). Let us write the stationary continuum wave functions as

$$
\chi_{klm}(\vec{x}) = \frac{h_{kl}(r)}{r} Y_{lm}(\theta,\varphi). \tag{3.46}
$$

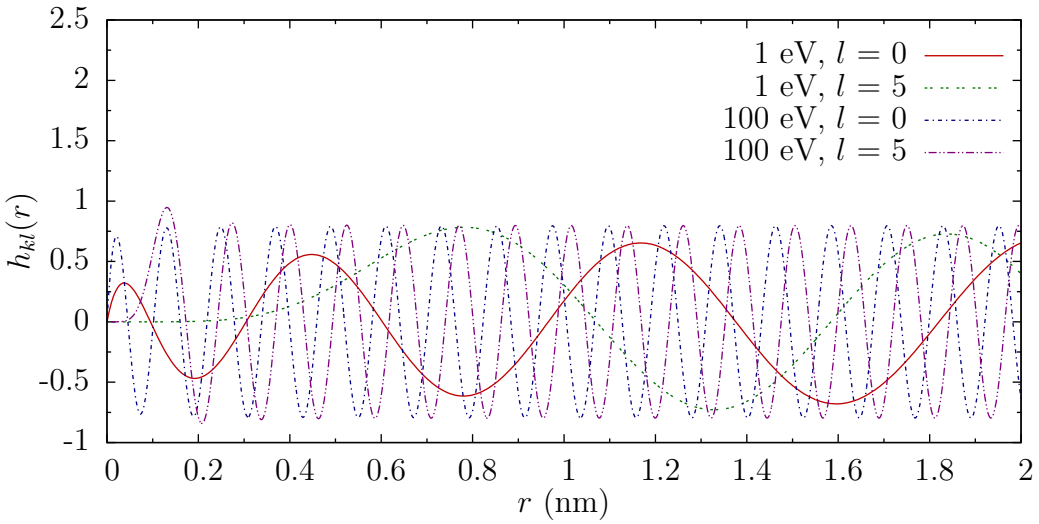

Figure 3.2: Continuum radial Schrödinger wave functions h_{kl} as given in eq. (3.50) for angular momentum $l = 0$, 5 and energy $E = 1$ eV, 100 eV, respectively.

In order to find the radial continuum wave functions h_{kl} we simply have to drop the constraint on eq. (3.25) that the wave function be normalizable over an infinite volume,

$$h_{kl}(r) \propto M(l + 1 - i\nu, 2l + 2, -2ix), \tag{3.47}$$

where $\nu = m\alpha/k$ and $x = kr$, i.e. we make the replacement $C_n \to -ik$, $E_n \to -E$ as compared to the bound case. The normalization constant of the continuum wave function is chosen such that the completeness relation (3.45) is satisfied. We may rewrite eq. (3.45) in position space as

$$\sum_{l=0}^{\infty} \sum_{m=-l}^{l} \left(\sum_{n=l+1}^{\infty} \psi_{nlm}(\vec{x}_2)\psi^*_{nlm}(\vec{x}_1) + \int_0^{\infty} dk\, \chi_{klm}(\vec{x}_2)\chi^*_{klm}(\vec{x}_1) \right) = \delta^3(\vec{x}_2 - \vec{x}_1), \tag{3.48}$$

which together with eq. (B.12) implies that for every l we have

$$\sum_{n=l+1}^{\infty} g_{nl}(r_2)g^*_{nl}(r_1) + \int_0^{\infty} dk\, h_{kl}(r_2)h^*_{kl}(r_1) = \delta(r_2 - r_1). \tag{3.49}$$

The normalization constant is most easily derived from the branch cut of fixed-energy amplitude in the complex energy plane. The concept of the

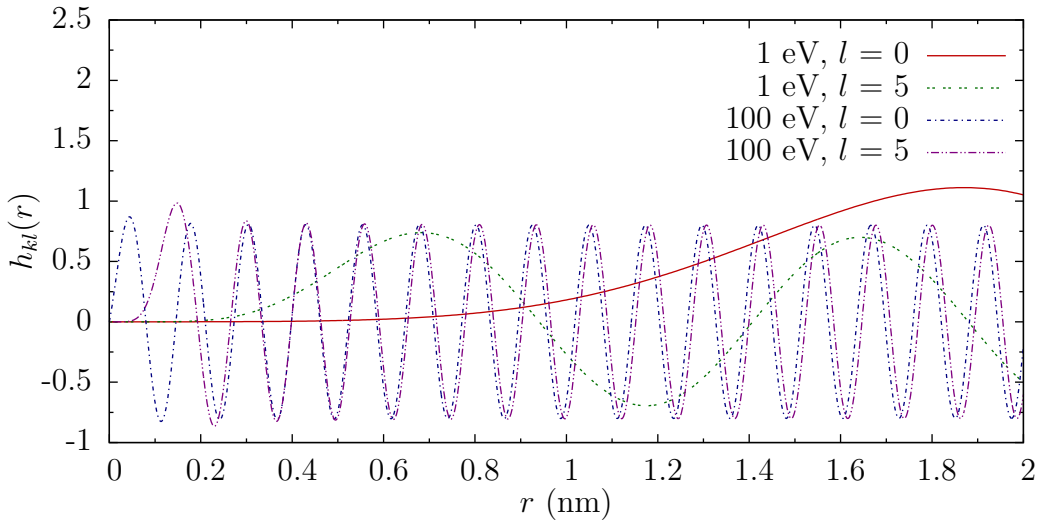

Figure 3.3: Continuum radial Schrödinger wave functions h_{kl} as given in eq. (3.50) for a repulsive Coulomb potential, i.e. negative ν, for angular momentum $l = 0$, 5 and energy $E = 1$ eV, 100 eV, respectively.

fixed-energy amplitude is explained in chapter 5. Here we will only write down the result which is also given in eq. (5.144),

$$\begin{aligned} h_{kl}(r) &= \frac{|\Gamma(l+1-i\nu)|}{\sqrt{2\pi}\,\Gamma(2l+2)} e^{\pi\nu/2+ikr}(2kr)^{l+1} M(l+1-i\nu, 2l+2, -2ikr) \\ &= \sqrt{\frac{2}{\pi}}\, F_l(-\nu, kr), \end{aligned} \tag{3.50}$$

where F_l means the Coulomb wave function. Note that the wave functions for a repulsive Coulomb potential, $\alpha \to -\alpha$, may be readily obtained from eq. (3.50) by replacing $\nu \to -\nu$. Due to the lack of bound state solutions in this case we may infer from eq. (3.49) the following completeness relation for the Coulomb wave functions,

$$\int_0^\infty dk\, F_l\left(\frac{\mu}{k}, kr_2\right) F_l\left(\frac{\mu}{k}, kr_1\right) = \frac{\pi}{2}\,\delta(r_2 - r_1), \qquad \mu \geq 0. \tag{3.51}$$

3.4 Parabolic coordinates

Apart from the previous treatment in section 3.2 it is also very instructive to solve the relative-motion, stationary Schrödinger equation (3.16),

$$\left(-\frac{\Delta}{2m} - \frac{\alpha}{r} - E\right)\psi(\vec{x}) = 0, \tag{3.52}$$

in parabolic coordinates (X, Y, φ). They are related to the usual cartesian coordinates (x^1, x^2, x^3) via

$$\begin{aligned} x^1 &= \sqrt{XY}\cos\varphi, & x^2 &= \sqrt{XY}\sin\varphi, \\ x^3 &= \frac{X-Y}{2}, & |\vec{x}| = r &= \frac{X+Y}{2}, \end{aligned} \tag{3.53}$$

while the inverse relations read

$$\begin{aligned} X &= r + x^3, & Y &= r - x^3, \\ \varphi &= \arctan\frac{x^1}{x^2}, & XY &= (x^1)^2 + (x^2)^2. \end{aligned} \tag{3.54}$$

In these coordinate we have the metric g,

$$g = (dx^1)^2 + (dx^2)^2 + (dx^3)^2 = \frac{r}{2}\left(\frac{dX^2}{X} + \frac{dY^2}{Y}\right) + XY d\varphi^2, \tag{3.55}$$

and its inverse g^{-1},

$$g^{-1} = \partial_1^2 + \partial_2^2 + \partial_3^2 = \frac{2}{r}\left(X\partial_X^2 + Y\partial_Y^2\right) + \frac{1}{XY}\partial_\varphi^2, \tag{3.56}$$

respectively. The determinant of the metric then yields $\det g = r^2/4$. The Schrödinger equation (3.52) may expressed in parabolic coordinates via

$$\begin{aligned} \Delta = \frac{1}{\sqrt{|\det g|}}\vec{\nabla} g^{-1}\sqrt{|\det g|}\vec{\nabla} &= \frac{1}{\sqrt{|\det g|}}\partial_i g^{ij}\sqrt{|\det g|}\partial_j \\ &= \frac{2}{r}\left(\partial_X X\partial_X + \partial_Y Y\partial_Y\right) + \frac{1}{XY}\partial_\varphi^2. \end{aligned} \tag{3.57}$$

Multiplying eq. (3.52) by $-mr$ then yields

$$\begin{aligned} \Bigg(\partial_X X\partial_X + \partial_Y Y\partial_Y + \frac{1}{4}\left(\frac{1}{X} + \frac{1}{Y}\right)\partial_\varphi^2 \\ + m\alpha + \frac{mE}{2}(X+Y)\Bigg)\psi(X,Y,\varphi) = 0. \end{aligned} \tag{3.58}$$

The fact that this equation separates in X and Y makes it apparent why this coordinate system is so well suited for solving for the hydrogen wave functions. Let us now make the definitions

$$C = \sqrt{-2mE}, \qquad \nu = \frac{m\alpha}{C}, \qquad x = CX, \qquad y = CY, \tag{3.59}$$

to rewrite eq. (3.58) as

$$\left(\partial_x x\partial_x - \frac{x}{4} + \frac{1}{4x}\partial_\varphi^2 + \partial_y y\partial_y - \frac{y}{4} + \frac{1}{4y}\partial_\varphi^2 + \nu\right)\psi(X,Y,\varphi) = 0. \tag{3.60}$$

We now make the separation ansatz

$$\psi(X,Y,\varphi) \propto e^{im\varphi} g_x(x) g_y(y) \tag{3.61}$$

to obtain

$$\begin{aligned} g_y(y)\left(\partial_x x\partial_x - \frac{x}{4} - \frac{m^2}{4x}\right) g_x(x) \\ + g_x(x) \underbrace{\left(\partial_y y\partial_y - \frac{y}{4} - \frac{m^2}{4y}\right) g_y(y)}_{=B g_y(y)} + \nu g_x(x) g_y(y) = 0. \end{aligned} \tag{3.62}$$

Since the two terms on the left-hand side are independent of each other, they must be constants times $g_x g_y$, adding up to $-\nu g_x g_y$. It is sufficient to consider the equation satisfied by g_x,

$$\left(\partial_x x\partial_x - \frac{x}{4} - \frac{m^2}{4x} + \nu + B\right) g_x(x) = 0. \tag{3.63}$$

From the analogue with eq. (3.22) for spherical coordinates we set

$$g_x(x) = x^{|m|/2} e^{-x/2} L_x(x), \tag{3.64}$$

which yields the analogue of eq. (3.24)

$$\left(x\partial_x^2 + (|m| + 1 - x)\partial_x + \nu + B - \frac{|m|+1}{2}\right) L_x(x) = 0. \tag{3.65}$$

This equation is again solved by Kummer's function,

$$L_x(x) \propto M((|m|+1)/2 - \nu - B, |m|+1, x). \tag{3.66}$$

To obtain the corresponding expression for $g_y(y)$ from $g_x(x)$ we must replace $x \to y$ and $\nu + B \to -B$ in eqs. (3.64) and (3.66). Like in section 3.2 we are interested in normalizable, bound state solutions. Therefore we require that the first argument of the Kummer function must be a negative integer so that g_x and g_y may be expressed in terms of Laguerre polynomials,

$$\nu + B - \frac{|m|+1}{2} = n_1, \qquad -B - \frac{|m|+1}{2} = n_2, \qquad n_1, n_2 \in \mathbb{N}. \tag{3.67}$$

This yields

$$\nu = n_1 + n_2 + |m| + 1 := n, \tag{3.68}$$

where we have identified the principal quantum number n of the Bohr energy levels. The resulting wave function $\psi(X, Y, \varphi)$ is now characterized by the quantum numbers n_1, n_2 and m,

$$\psi_{n_1,n_2,m}(X,Y,\varphi) = \mathcal{A}_{n_1,n_2,m}\,\frac{e^{im\varphi}}{\sqrt{2\pi}}\,(C_n^2 XY)^{|m|/2}\,e^{-C_n(X+Y)/2} \cdot L_{n_1}^{|m|}(C_n X) L_{n_2}^{|m|}(C_n Y), \tag{3.69}$$

where L_n^α are again the associated Laguerre polynomials. Let us now calculate the normalization constant, using the measure $dXdYd\varphi\,(X+Y)/4$, to obtain

$$\begin{aligned} 1 &\stackrel{!}{=} \int_0^\infty dXdY\,\frac{X+Y}{4}\int_0^{2\pi} d\varphi\,|\psi_{n_1,n_2,m}(X,Y,\varphi)|^2 \\ &= \frac{\mathcal{A}_{n_1,n_2,m}^2}{4C_n^3}\int_0^\infty dxdy\,(x+y)(xy)^{|m|}e^{-(x+y)}\left(L_{n_1}^{|m|}(x)L_{n_2}^{|m|}(y)\right)^2 \\ &= \frac{\mathcal{A}_{n_1,n_2,m}^2}{4C_n^3}\left(I_{n_1}^{|m|,1}I_{n_2}^{|m|,0} + I_{n_2}^{|m|,1}I_{n_1}^{|m|,0}\right), \end{aligned} \tag{3.70}$$

where

$$I_n^{\alpha,\beta} = \int_0^\infty dx\,x^{\alpha+\beta}e^{-x}\left(L_n^\alpha(x)\right)^2. \tag{3.71}$$

With analogous calculations as in eq. (3.30) we obtain

$$I_n^{\alpha,0} = \frac{\Gamma(n+1+\alpha)}{n!}, \qquad I_n^{\alpha,1} = \frac{\Gamma(n+1+\alpha)}{n!}(2n+1+\alpha). \tag{3.72}$$

Inserting into eq. (3.70) yields

$$\mathcal{A}_{n_1,n_2,m} = \sqrt{\frac{2C_n^3}{n}\frac{n_1!}{(n_1+|m|)!}\frac{n_2!}{(n_2+|m|)!}}. \tag{3.73}$$

Chapter 4

The Dirac equation

In 1928 Dirac presented a relativistic treatment of the quantum theory of the electron. It does not constitute a new formulation of quantum mechanics but a relativistic generalization of the formalisms of Heisenberg and Schrödinger, where the non-relativistic Hamiltonian in e.g. eqs. (2.4) and (3.13) is replaced with a corresponding relativistic version. The relativistic equation of motion for the wave function, called Dirac equation, was very soon after its discovery solved by Gordon (1928) for the case of the hydrogen atom.

The Dirac equation can be formulated in a Lorentz-invariant manner and naturally includes the electron spin as a degree of freedom which was missing in the previous non-relativistic approaches. Also the Dirac equation predicts the existence of antiparticles which, according to Feynman and Stückelberg, can be interpreted as particles of opposite quantum numbers which travel backwards in time. The antiparticle of the electron, the positron, was discovered in 1933 by Anderson.

4.1 Motivation and properties of the Dirac equation

Let us start from a non-covariant classical Hamiltonian for a relativistic particle and its naive quantum mechanical counter part,

$$H = \sqrt{\vec{p}^{\,2} + m^2} \qquad \rightarrow \qquad \hat{H} = \sqrt{\hat{\vec{p}}^{\,2} + m^2}. \tag{4.1}$$

Simply promoting the dynamical variables to operators obviously yields an expression which we do not know how to deal with. Dirac's idea, however, proposed a Hamiltonian of the type

$$\hat{H} = \hat{\vec{\alpha}}\hat{\vec{p}} + \hat{\beta}m, \tag{4.2}$$

where the operators $\hat{\vec{\alpha}}$ and $\hat{\beta}$ are called Dirac matrices and are set to commute with $\hat{\vec{p}}$ and $\hat{\vec{x}}$. However, eqs. (4.1) and (4.2) can only be equivalent if

$$\hat{\vec{\alpha}}\hat{\vec{p}} + \hat{\beta}m = \sqrt{(\hat{\vec{\alpha}}\hat{\vec{p}} + \hat{\beta}m)^2} \stackrel{!}{=} \sqrt{\hat{\vec{p}}^2 + m^2}. \tag{4.3}$$

This in turn implies for $\hat{\vec{\alpha}}$ and $\hat{\beta}$

$$\{\hat{\alpha}^i, \hat{\alpha}^j\} = 2\delta^{ij}, \qquad \{\hat{\alpha}^i, \hat{\beta}\} = 0, \qquad \hat{\beta}^2 = 1. \tag{4.4}$$

If given with respect to a basis, these operators become matrices $\vec{\alpha}$, β. From the above relations we can easily show that all four matrices have only eigenvalues ± 1 and that $\operatorname{Tr}\beta = \operatorname{Tr}\alpha^i = 0$. Thus the Dirac matrices can only be of even dimension and at least 4×4, since we need four independent matrices. Throughout this work we will chose the basis such that $\vec{\alpha}$ and β are given in the Dirac representation,

$$\beta = \begin{pmatrix} \mathbb{1} & 0 \\ 0 & -\mathbb{1} \end{pmatrix}, \qquad \vec{\alpha} = \begin{pmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{pmatrix}, \tag{4.5}$$

where the blocks in these expressions are 2×2-blocks and $\vec{\sigma}$ represents the 2×2-Pauli-matrices,

$$\sigma^1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \qquad \sigma^2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \qquad \sigma^3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \tag{4.6}$$

which satisfy the relations

$$\{\sigma^i, \sigma^j\} = 2\delta^{ij}, \qquad [\sigma^i, \sigma^j] = 2i\varepsilon^{ijk}\sigma_k. \tag{4.7}$$

In the following we will use a position eigenbasis so the Dirac equation for a particle in an external 4-vector potential $(\Phi, \vec{A})$ reads,

$$\left(-i(\partial_t + iq\Phi(x)) - i\vec{\alpha}(\vec{\nabla} - iq\vec{A}(x)) + \beta m\right)\Psi(x) = 0, \tag{4.8}$$

where $x = (t, \vec{x})$. In this equation, the wave function has four components, $\Psi(x) = (\Psi_a)(x) = \langle a, x|\psi\rangle$, $a \in \{1, 2, 3, 4\}$. Inspecting the properties of the Dirac equation we find that Ψ is most conveniently written in the form

$$\Psi(x) = \begin{pmatrix} \varphi(x) \\ \chi(x) \end{pmatrix}, \tag{4.9}$$

where the two-dimensional quantities φ and χ are Weyl spinors which transform in the spinor and conjugate spinor representation of the Lorentz group,

respectively. The quantity Ψ, which is called a Dirac spinor, thus transforms in a mixed spinor and conjugate spinor representation.

Eq. (4.8) may be easily reformulated in a Lorentz-invariant manner by defining the γ-matrices,

$$\gamma^0 = \beta, \qquad \vec{\gamma} = \beta\vec{\alpha} = \begin{pmatrix} 0 & \vec{\sigma} \\ -\vec{\sigma} & 0 \end{pmatrix}, \tag{4.10}$$

as well as the matrix γ_5,

$$\gamma_5 = i\varepsilon_{\mu\nu\rho\sigma}\gamma^\mu\gamma^\nu\gamma^\rho\gamma^\sigma = i\gamma^0\gamma^1\gamma^2\gamma^3 = \begin{pmatrix} 0 & \mathbb{1} \\ \mathbb{1} & 0 \end{pmatrix}, \tag{4.11}$$

and multiplying eq. (4.8) by γ^0 from the left

$$(-i\gamma^\mu(\partial_\mu - iqA_\mu) + m)\,\Psi(x) = 0, \tag{4.12}$$

where $A_0 = -\Phi$. From eqs. (4.4) we infer the anti-commutation relations,

$$\{\gamma^\mu, \gamma^\nu\} = -2\eta^{\mu\nu}, \qquad \{\gamma^\mu, \gamma_5\} = 0. \tag{4.13}$$

The matrices γ^μ transform as vectors under Lorentz transformations while γ_5 is a pseudo-scalar,

$$\gamma^\mu \to \gamma'^\mu = \Lambda^\mu{}_\nu\gamma^\nu, \qquad \gamma_5 \to \gamma_5' = \det\Lambda\,\gamma_5. \tag{4.14}$$

Further we define the operation of Dirac conjugation as

$$\bar{\Psi} = \Psi^\dagger\gamma^0, \qquad \bar{\gamma}^\mu = \gamma^0\gamma^{\mu\dagger}\gamma^0 = \gamma^\mu, \qquad \bar{\gamma}_5 = \gamma^0\gamma_5^\dagger\gamma^0 = \gamma_5, \tag{4.15}$$

and introduce the Feynman slash notation, $\not{A} = \gamma^\mu A_\mu$, so that eq. (4.12) reads

$$\left(-i\not{\partial} - q\not{A}(x) + m\right)\Psi(x) = 0. \tag{4.16}$$

Let $\Psi^{(\pm)}$ denote solutions to eq. (4.16) for particles with charge $\pm q$. Using

$$\varepsilon\vec{\sigma}\varepsilon = \vec{\sigma}^*, \qquad \varepsilon = i\sigma^2 = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}, \tag{4.17}$$

one finds that the two solutions are related to each other by the operation of charge conjugation,

$$\Psi^{(-)} = \mathcal{C}\Psi^{(+)*}, \qquad \mathcal{C} = i\gamma^2, \tag{4.18}$$

i.e. eq. (4.16) is invariant under the exchange

$$\Psi^{(+)} \leftrightarrow \Psi^{(-)}, \qquad +q \leftrightarrow -q. \tag{4.19}$$

Writing the Dirac equation in terms of the Weyl spinors φ and χ yields

$$\begin{aligned}(-i\partial_t + q\Phi(x) + m)\varphi(x) &= i\vec{\sigma}(\vec{\nabla} - iq\vec{A}(x))\chi(x),\\ (i\partial_t - q\Phi(x) + m)\chi(x) &= -i\vec{\sigma}(\vec{\nabla} - iq\vec{A}(x))\varphi(x).\end{aligned} \tag{4.20}$$

It is easy to see that for a time-independent 4-vector potential, we may write

$$\Psi(x) = e^{-iEt}\begin{pmatrix}\varphi(\vec{x})\\ \chi(\vec{x})\end{pmatrix}, \tag{4.21}$$

so that

$$\begin{aligned}(m - E + q\Phi(\vec{x}))\varphi(\vec{x}) &= i\vec{\sigma}(\vec{\nabla} - iq\vec{A}(\vec{x}))\chi(\vec{x}),\\ (m + E - q\Phi(\vec{x}))\chi(\vec{x}) &= -i\vec{\sigma}(\vec{\nabla} - iq\vec{A}(\vec{x}))\varphi(\vec{x}).\end{aligned} \tag{4.22}$$

Charge conjugation is performed in eqs. (4.22) by the replacement

$$\begin{aligned}E \to -E, &\qquad q \leftrightarrow -q,\\ \varphi(\vec{x}) \leftrightarrow \varepsilon\chi^*(\vec{x}), &\qquad \chi(\vec{x}) \leftrightarrow -\varepsilon\varphi^*(\vec{x}).\end{aligned} \tag{4.23}$$

Hence we find that if $\Psi^{(+)}$ is a solution to the Dirac equation with positive energy E then the charge-conjugated Dirac spinor $\Psi^{(-)}$ represents a solution with negative energy $-E$. The negative energy solution corresponds to an antiparticle (positron), i.e. a particle (electron) of opposite charge which travels backwards in time.

We can see from eq. (4.22) that it is possible to express the spinor χ in terms of φ. For a non-relativistic system we have $W = E - m \ll m$ and $q\Phi \ll m$, so that eqs. (4.22) become

$$\begin{aligned}(q\Phi(\vec{x}) - W)\varphi(\vec{x}) &= \frac{[\vec{\sigma}(\vec{\nabla} - iq\vec{A}(\vec{x}))]^2}{2m}\varphi(\vec{x}),\\ \chi(\vec{x}) &= \frac{-i\vec{\sigma}(\vec{\nabla} - iq\vec{A}(\vec{x}))}{2m}\varphi(\vec{x}).\end{aligned} \tag{4.24}$$

The dynamics are now completely determined by the Weyl spinor φ. The equation of motion (4.24) for φ is called the Pauli equation, which was proposed to explain the properties of an electron in an external magnetic field

$\vec{B} = \vec{\nabla} \times \vec{A}$ (Pauli, 1927). Using the properties of the Pauli-matrices (4.7) we may reformulate eq. (4.24) as

$$\left(-\frac{(\vec{\nabla} - iq\vec{A}(\vec{x}))^2}{2m} - \frac{gq\vec{s}\vec{B}}{2m} + q\Phi(\vec{x}) - W \right) \varphi(\vec{x}) = 0, \tag{4.25}$$

where $\vec{s} = \vec{\sigma}/2$ is the spin operator and $g = 2$ the Landé g-factor. Obviously the Pauli equation (4.25) reduces to the Schrödinger equation (3.13) if the effect of spin is neglected.

4.2 The free Dirac equation

Before we proceed with the solution for the hydrogen atom we will briefly consider the Dirac equation for a free particle. This will be of much use in later chapters. The Dirac equation for a free particle reads

$$(-i\partial\!\!\!/ + m)\Psi(x) = 0. \tag{4.26}$$

Performing a Fourier transform yields

$$(p\!\!\!/ + m)\tilde{\Psi}(p) = 0, \tag{4.27}$$

where $p = (p^0, \vec{p})$. This equation has non-trivial solutions only if

$$p^0 = \pm E, \qquad E = \sqrt{\vec{p}^{\,2} + m^2}. \tag{4.28}$$

Two eigenvectors of this matrix equation can be easily found for $p = (m, 0)$,

$$u_\pm(0) = \sqrt{2m} \begin{pmatrix} \xi_\pm \\ 0 \end{pmatrix}, \qquad \xi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \qquad \xi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \tag{4.29}$$

We can now obtain general expressions for $u_s(\vec{p})$ via a Lorentz transformation $S(\Lambda)$. Regarding that the Dirac spinor Ψ transforms in a mixed spinor representation under Lorentz transformations (see e.g. Srednicki, 2007), we may perform an active boost on u_s with the matrix

$$\begin{aligned} S(\Lambda(\vec{y})) = S(\vec{y}) &= \exp\left[-\frac{1}{4}[\vec{y}\vec{\gamma}, \gamma^0] \right] = \mathbb{1} \cosh\frac{|\vec{y}|}{2} + \vec{n}\vec{\alpha} \sinh\frac{|\vec{y}|}{2} \\ &= \sqrt{\frac{E+m}{2m}} \begin{pmatrix} \mathbb{1} & \frac{\vec{p}\vec{\sigma}}{E+m} \\ \frac{\vec{p}\vec{\sigma}}{E+m} & \mathbb{1} \end{pmatrix}, \end{aligned} \tag{4.30}$$

where $\vec{n} = \vec{y}/|\vec{y}|$, $\vec{p}/m = \vec{n}\sinh|\vec{y}|$ and $E/m = \cosh|\vec{y}|$. The transformation yields

$$S(\vec{y})(-m\gamma^0 + m)S^{-1}(\vec{y})S(\vec{y})u_s(0) = (\not{p} + m)u_s(\vec{p}) = 0, \tag{4.31}$$

where $s = \pm$ and

$$u_s(\vec{p}) = \begin{pmatrix} \sqrt{E+m}\,\xi_s \\ \frac{\vec{\sigma}\vec{p}}{\sqrt{E+m}}\,\xi_s \end{pmatrix}. \tag{4.32}$$

Solutions corresponding to negative energy states, $p^0 = -E$, are obtained by charge conjugation of u_s,

$$v_s(\vec{p}) = \mathcal{C}u_s^*(\vec{p}) = s\begin{pmatrix} \frac{\vec{\sigma}\vec{p}}{\sqrt{E+m}}\,\xi_{-s} \\ \sqrt{E+m}\,\xi_{-s} \end{pmatrix}. \tag{4.33}$$

The two Dirac spinors v_s satisfy the equation

$$(-\not{p} + m)v_s(\vec{p}) = 0. \tag{4.34}$$

Also the four Dirac spinors u_s and v_s satisfy several important relations,

$$\begin{aligned} \bar{u}_r(\vec{p})u_s(\vec{p}) &= 2m\delta_{r,s}, & u_r^\dagger(\vec{p})u_s(\vec{p}) &= v_r^\dagger(\vec{p})v_s(\vec{p}) = 2E\delta_{r,s}, \\ \bar{v}_r(\vec{p})v_s(\vec{p}) &= -2m\delta_{r,s}, & \bar{u}_r(\vec{p})v_s(\vec{p}) &= 0, \\ \sum_{s=\pm} u_s(\vec{p})\bar{u}_s(\vec{p}) &= -\not{p} + m, & \sum_{s=\pm} v_s(\vec{p})\bar{v}_s(\vec{p}) &= -\not{p} - m, \end{aligned} \tag{4.35}$$

as well as the following completeness relations,

$$\begin{aligned} \sum_{s=\pm}\left(u_s(\vec{p})\bar{u}_s(\vec{p}) - v_s(\vec{p})\bar{v}_s(\vec{p})\right) &= 2m, \\ \sum_{s=\pm}\left(u_s(\vec{p})u_s^\dagger(\vec{p}) + v_s(-\vec{p})v_s^\dagger(-\vec{p})\right) &= 2E. \end{aligned} \tag{4.36}$$

Let us define the time-independent wave functions

$$\Psi_{s,\vec{p}}^{(+)}(\vec{x}) = e^{i\vec{p}\vec{x}}u_s(\vec{p}), \qquad \Psi_{s,\vec{p}}^{(-)}(\vec{x}) = e^{-i\vec{p}\vec{x}}v_s(\vec{p}), \tag{4.37}$$

which are solutions to the time-independent, free Dirac equation,

$$(\mp E\gamma^0 - i\vec{\gamma}\vec{\nabla} + m)\Psi_{s,\vec{p}}^{(\pm)}(\vec{x}) = 0, \tag{4.38}$$

and satisfy the completeness relation

$$\int \widetilde{dp} \sum_{s=\pm} \left(\Psi^{(+)}_{s,\vec{p}}(\vec{x}) \Psi^{(+)\dagger}_{s,\vec{p}}(\vec{x}') + \Psi^{(-)}_{s,\vec{p}}(\vec{x}) \Psi^{(-)\dagger}_{s,\vec{p}}(\vec{x}') \right) = \delta^3(\vec{x} - \vec{x}'), \tag{4.39}$$

where $\widetilde{dp} = d^3p/((2\pi)^3 2E)$. We may expand any function $\Psi(t, \vec{x})$ in terms of $\Psi^{(\pm)}_{s,\vec{p}}$,

$$\begin{aligned} \Psi(t, \vec{x}) &= \int \widetilde{dp} \sum_{s=\pm} \left(\Psi^{(+)}_{s,\vec{p}}(\vec{x}) A^{(+)}_{s,\vec{p}}(t) + \Psi^{(-)}_{s,\vec{p}}(\vec{x}) A^{(-)}_{s,\vec{p}}(t) \right), \\ A^{(\pm)}_{s,\vec{p}}(t) &= \int d^3x \, \Psi^{(\pm)\dagger}_{s,\vec{p}}(\vec{x}) \Psi(t, \vec{x}). \end{aligned} \tag{4.40}$$

4.3 The relativistic hydrogen wave functions

Now we consider the hydrogen atom in the context of relativistic quantum theory using the Dirac equation. However, we postpone the rigorous treatment of the relativistic Coulomb problem as a two-particle problem to chapter 8. Here, we consider the hydrogen atom as a single particle problem with a particle of reduced mass m in an external Coulomb potential $-\alpha/r$. The Dirac equation for this problem reads

$$H\Psi(x) = 0, \qquad H = -i\partial\!\!\!/ + m - \gamma^0 \frac{\alpha}{r}. \tag{4.41}$$

We make the ansatz

$$\Psi(x) = e^{-iEt}\Psi(\vec{x}), \qquad \Psi(\vec{x}) = \begin{pmatrix} \varphi(\vec{x}) \\ \chi(\vec{x}) \end{pmatrix}, \tag{4.42}$$

and insert it into eq. (4.41) to obtain

$$\begin{aligned} \left(E + \frac{\alpha}{r} - m \right) \varphi &= -i\vec{\sigma}\vec{\nabla}\chi, \\ \left(E + \frac{\alpha}{r} + m \right) \chi &= -i\vec{\sigma}\vec{\nabla}\varphi. \end{aligned} \tag{4.43}$$

Let us consider the angular momentum operator $\vec{J} = \vec{L} + \vec{S}$, with the orbital momentum operator $\vec{L}$ and the electron spin operator $\vec{S}$,

$$\vec{L} = -i\vec{x} \times \vec{\nabla}, \qquad \vec{S} = \begin{pmatrix} \vec{s} & 0 \\ 0 & \vec{s} \end{pmatrix}, \qquad \vec{s} = \frac{\vec{\sigma}}{2}. \tag{4.44}$$

We find

$$\left[\vec{J}, H\right] = \left[\vec{L}, H\right] + \left[\vec{S}, H\right] = \vec{\gamma} \times \vec{\nabla} - \vec{\gamma} \times \vec{\nabla} = 0. \tag{4.45}$$

Thus there exists a basis which simultaneously diagonalizes the Hamiltonian and the angular momentum operator. We can use this fact in the following ansatz

$$\varphi_{nk}(\vec{x}) = \frac{g_{nk}(r)}{r}\,\Omega_{km}(\theta,\varphi), \qquad \chi_{nk}(\vec{x}) = \frac{i f_{nk}(r)}{r}\,\Omega_{-km}(\theta,\varphi). \tag{4.46}$$

The Weyl spinor Ω is defined as

$$\Omega_{km} = \sum_{m_l=-l}^{l} \sum_{m_s=\pm 1/2} \langle\theta,\varphi|l,m_l;\frac{1}{2},m_s\rangle\langle l,m_l;\frac{1}{2},m_s|j,m\rangle \tag{4.47}$$

$$= \frac{1}{\sqrt{2k+1}} \begin{pmatrix} \sqrt{k+\frac{1}{2}-m}\; Y_{k,m-1/2}(\theta,\varphi) \\ -\operatorname{sgn} k \sqrt{k+\frac{1}{2}+m}\; Y_{k,m+1/2}(\theta,\varphi) \end{pmatrix}, \tag{4.48}$$

where Y_{lm} means the spherical harmonics. The quantum number k is defined as

$$k = \mp\left(j+\frac{1}{2}\right) = \begin{cases} -l-1, & j = l+1/2 \\ l, & j = l-1/2 \end{cases}, \tag{4.49}$$

where $j = l \pm 1/2$ is the total momentum quantum number. By means of the identity

$$\vec{\sigma}\vec{a}\;\vec{\sigma}\vec{b} = \vec{a}\vec{b} + i\vec{\sigma}\vec{a} \times \vec{b} \tag{4.50}$$

we may insert unity in the form $1 = (\vec{\sigma}\vec{e}_r)^2$ into eqs. (4.43) to rewrite

$$\vec{\sigma}\vec{\nabla}\;\vec{\sigma}\vec{e}_r = \partial_r + \frac{2}{r} - i\vec{\sigma}\vec{e}_r \times \vec{\nabla} = \frac{1}{r}\left(\partial_r r + K\right), \tag{4.51}$$

where we have defined the operator

$$K = 1 + 2\vec{s}\vec{L} = 1 + \vec{J}^2 - \vec{L}^2 - \vec{s}^2. \tag{4.52}$$

Eqs. (4.43) then read

$$\begin{aligned} \left(E_{nk} + \frac{\alpha}{r} - m\right) g_{nk}\,\Omega_{km} &= \left(\partial_r + \frac{K}{r}\right) f_{nk}\vec{\sigma}\vec{e}_r\Omega_{-km}, \\ \left(E_{nk} + \frac{\alpha}{r} + m\right) f_{nk}\,\Omega_{-km} &= -\left(\partial_r + \frac{K}{r}\right) g_{nk}\vec{\sigma}\vec{e}_r\Omega_{km}. \end{aligned} \tag{4.53}$$

Note that Ω is an eigenstate of K,

$$K\Omega_{km} = -k\Omega_{km}. \tag{4.54}$$

Further we obtain with the properties of the spherical harmonics

$$\vec{\sigma}\vec{e}_r\Omega_{km} = \Omega_{-km}. \tag{4.55}$$

Thus we may rewrite eqs. (4.53) as

$$\begin{aligned}\left(\left(\partial_r - \frac{k}{r}\right) f - \left(E + \frac{\alpha}{r} - m\right) g\right)\Omega_{km} = 0,\\ \left(\left(\partial_r + \frac{k}{r}\right) g + \left(E + \frac{\alpha}{r} + m\right) f\right)\Omega_{-km} = 0,\end{aligned} \tag{4.56}$$

or equivalently

$$\partial_r \begin{pmatrix} g \\ f \end{pmatrix} = \underbrace{\begin{pmatrix} -\frac{k}{r} & -E - \frac{\alpha}{r} - m \\ E + \frac{\alpha}{r} - m & \frac{k}{r} \end{pmatrix}}_{=:M} \begin{pmatrix} g \\ f \end{pmatrix}. \tag{4.57}$$

Gordon (1928) has attacked this equation directly by a power series ansatz of the form $r^\rho e^{-\lambda r}\sum_i a_i r^i$. The simplest way to solve eq. (4.57), however, which also shows the analogy to the non-relativistic case of chapter 3, is to bring it into a Schrödinger type form by performing another derivative,

$$\begin{aligned}\partial_r^2 \begin{pmatrix} g \\ f \end{pmatrix} &= \left[M^2 + \partial_r M\right] \begin{pmatrix} g \\ f \end{pmatrix} \\ &= \left[\left(\frac{k^2 - \alpha^2}{r^2} - \frac{2E\alpha}{r} + m^2 - E^2\right)\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\right. \\ &\qquad \left. + \frac{1}{r^2}\begin{pmatrix} k & \alpha \\ -\alpha & -k \end{pmatrix}\right] \begin{pmatrix} g \\ f \end{pmatrix}.\end{aligned} \tag{4.58}$$

The second matrix in cornered parenthesis has the eigenvalues

$$\lambda_\pm = \pm\gamma, \qquad \gamma = \sqrt{k^2 - \alpha^2}. \tag{4.59}$$

Taking care of the fact that k can be both positive and negative, we diagonalize it by the transformation $B' = A^{-1}\,B\,A$, where

$$\begin{aligned}A &= \frac{1}{\sqrt{2k(k-\gamma)}}\begin{pmatrix} \alpha & -(k-\gamma) \\ -(k-\gamma) & \alpha \end{pmatrix}, \\ A^{-1} &= \frac{k}{\gamma}\frac{1}{\sqrt{2k(k-\gamma)}}\begin{pmatrix} \alpha & k-\gamma \\ k-\gamma & \alpha \end{pmatrix}.\end{aligned} \tag{4.60}$$

With the definition

$$\begin{pmatrix} g \\ f \end{pmatrix} = A\begin{pmatrix} u^+ \\ u^- \end{pmatrix}, \tag{4.61}$$

as well as

$$x = 2Cr, \qquad C = \sqrt{m^2 - E^2}, \tag{4.62}$$

eq. (4.58) becomes

$$\partial_x^2 u^\pm = \left[\frac{\gamma(\gamma \pm 1)}{x^2} - \frac{E\alpha}{C}\frac{1}{x} + \frac{1}{4} \right] u^\pm. \tag{4.63}$$

This reminds of the non-relativistic, radial Schrödinger equation (3.22). Correspondingly, we make the ansatz

$$\begin{pmatrix} u^+ \\ u^- \end{pmatrix} = x^\gamma e^{-x/2} \begin{pmatrix} \mathcal{A}_+ x L^+ \\ \mathcal{A}_- L^- \end{pmatrix} \tag{4.64}$$

so we obtain from (4.63)

$$x\partial_x^2 L^\pm + (2\gamma + 1 \pm 1 - x)\,\partial_x L^\pm + \left(\underbrace{\frac{E\alpha}{C} - \gamma}_{=:n_r} - \frac{1}{2} \mp \frac{1}{2} \right) L^\pm = 0. \tag{4.65}$$

As in chapter 3, we are interested in bound state solutions, which have to be normalizable and so we require

$$0 \leq n_r - \frac{1}{2} \mp \frac{1}{2}, \qquad\qquad n_r \in \mathbb{N}. \tag{4.66}$$

Consequently, if $n_r = 0$ the only solution for L^+ in eq. (4.65) is the trivial one, $L^+|_{n_r=0} = 0$.

The two solutions to eq. (4.65) may again be written in terms of the Laguerre polynomials L_n^α. From the normalization condition we obtain the energy levels

$$C = \frac{\alpha m}{\sqrt{\alpha^2 + (n_r + \gamma)^2}}, \qquad\qquad E = \frac{m}{\sqrt{1 + \frac{\alpha^2}{(n_r+\gamma)^2}}}. \tag{4.67}$$

The expansion up to order α^4 of this expression yields

$$\frac{E_{nk}}{m} \approx 1 - \frac{\alpha^2}{2n^2} + \frac{\alpha^4}{2n^3}\left(\frac{3}{4n} - \frac{1}{|k|} \right) \pm O(\alpha^6), \tag{4.68}$$

where we have reintroduced the principal quantum number $n = n_r + |k|$ by comparison with the non-relativistic energy levels from chapters 2 and 3. The energy difference between a state (nk) and the ground state is given by

$$\Delta E_{nk} = E_{nk} - E_{1,-1}$$

Table 4.1: Experimental values of the hydrogen energy levels as given in Kramida (2010) are compared with the fourth order expansion in α of the energy levels E_{nk} as given in eq. (4.69). The relative deviation of the relativistic Dirac theory from the experimental values is about three times smaller than for the non-relativistic Schrödinger theory.

State	Exp. levels (eV)	ΔE_{nk} (eV)	Deviation
$1S_{1/2}$	0	0	
$2P_{1/2}$	10.1988055286	10.1988394699345	$3 \cdot 10^{-6}$
$2S_{1/2}$	10.1988099034600		$3 \cdot 10^{-6}$
$2P_{3/2}$	10.1988508929	10.1988847278836	$3 \cdot 10^{-6}$
$3P_{1/2}$	12.087492922	12.087526855611	$3 \cdot 10^{-6}$
$3S_{1/2}$	12.087494224		$3 \cdot 10^{-6}$
$3D_{3/2}$	12.087506341	12.0875402653737	$3 \cdot 10^{-6}$
$3P_{3/2}$	12.087506364		$3 \cdot 10^{-6}$
$3D_{5/2}$	12.087510821	12.0875447352946	$3 \cdot 10^{-6}$
$4P_{1/2}$	12.74853166921	12.7485656019936	$3 \cdot 10^{-6}$
$4S_{1/2}$	12.74853221952		$3 \cdot 10^{-6}$
$4D_{3/2}$	12.7485373313	12.7485712592372	$3 \cdot 10^{-6}$
$4P_{3/2}$	12.74853733962		$3 \cdot 10^{-6}$
$4D_{5/2}$	12.74853922041	12.7485731449851	$3 \cdot 10^{-6}$
$4F_{5/2}$	12.748539221		$3 \cdot 10^{-6}$
$4F_{7/2}$	12.7485401632	12.748574087859	$3 \cdot 10^{-6}$
Continuum	13.598433770784	13.5984677125623	$2 \cdot 10^{-6}$

$$= \mathrm{Ryd}\left(1 - \frac{1}{n^2} + \alpha^2\left(\frac{1}{4} + \frac{3}{4n^4} - \frac{1}{|k|n^3}\right)\right) \pm O(\alpha^6). \qquad (4.69)$$

The Dirac energy levels include the fine structure of the hydrogen atom, which is given by the order α^4 correction in eq. (4.68). The fine structure includes a relativistic correction to the motion of the electron and a correction due to the spin-orbit coupling. The deviation of the Dirac energy levels from experiment is of the order 10^{-6} and improves the accuracy of the Schrödinger energy levels (3.27) roughly by a factor of three (see table 4.1).

One should note that the definition of n in eq. (4.68) is indeed equal to the non-relativistic one when k is negative so that $|k| = l + 1$. When k is positive, however, we have $k = l$, so that n_r has to be larger by one as compared to eq. (3.26) to obtain the same n. Specifically, we require $n_r > 0$ for $k = l$ since the principal quantum should satisfy $n > l$. In brief we will see that this condition is indeed always satisfied.

To continue we write the solutions for $u^{\pm}$ in analogy to chapter 3 as,

$$\begin{pmatrix} u^+_{nk} \\ u^-_{nk} \end{pmatrix} = x^\gamma e^{-x/2} \begin{pmatrix} \mathcal{A}_+ x L^{2\gamma+1}_{n-|k|-1} \\ \mathcal{A}_- L^{2\gamma-1}_{n-|k|} \end{pmatrix}. \tag{4.70}$$

However, since we have obtained this solution by differentiation of eq. (4.57) it is too general. This reflects in the fact that we have two unknowns, $\mathcal{A}_+$ and $\mathcal{A}_-$. Note, that in the special case $n = |k|$ the upper component in eq. (4.70) vanishes, $u^+ = 0$, so that $\mathcal{A}_-$ remains as the only unknown variable. In order to fix the ratio $\mathcal{F} = \mathcal{A}_-/\mathcal{A}_+$ for $n > |k|$ we plug our solution into eq. (4.57),

$$\begin{aligned} \partial_x \begin{pmatrix} u^+ \\ u^- \end{pmatrix} &= \frac{1}{2C} A^{-1} M A \begin{pmatrix} u^+ \\ u^- \end{pmatrix} \\ &= \left[-\frac{\gamma}{x} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \right. \\ &\qquad \left. + \frac{1}{2C\gamma} \begin{pmatrix} E\alpha & -(Ek+\gamma m) \\ Ek-\gamma m & -E\alpha \end{pmatrix} \right] \begin{pmatrix} u^+ \\ u^- \end{pmatrix}. \end{aligned} \tag{4.71}$$

Considerung the case $n = |k|$ we have $u^+ = 0$ so the upper component of eq. (4.71) yields

$$Ek + \gamma m = 0 \qquad \text{for} \qquad n_r = 0. \tag{4.72}$$

Hence we have found that $n_r = 0$ enforces negative values of k and thus $n > l$ as we had argued above. For $n > |k|$ we may derive the ratio $\mathcal{F}$ from eq. (4.71). Since the individual orders in x have to cancel each other, we consider only terms of the order x^γ in the upper row of eq. (4.71),

$$(\gamma+1) \begin{pmatrix} n_r + 2\gamma \\ n_r - 1 \end{pmatrix} = -\gamma \begin{pmatrix} n_r + 2\gamma \\ n_r - 1 \end{pmatrix} - \frac{Ek+\gamma m}{2C\gamma} \mathcal{F} \begin{pmatrix} n_r + 2\gamma - 1 \\ n_r \end{pmatrix} \tag{4.73}$$

$$\begin{aligned} \Rightarrow \mathcal{F} &= -\frac{C n_r (n_r + 2\gamma)}{Ek + \gamma m} = \frac{\gamma m - kE}{C} \\ &= \frac{1}{\alpha} \left(\gamma \sqrt{\alpha^2 + (n_r + \gamma)^2} - k(n_r + \gamma) \right). \end{aligned} \tag{4.74}$$

Thus we know the relation between u^+ and u^- and see that u^-/u^+ is of the order α if $k > 0$ and $1/\alpha$ if $k < 0$. In the ladder case the factor $1/\alpha$ is canceled by a corresponding factor in $\mathcal{A}_+$. The constants $\mathcal{A}_\pm$ may be determined from the normalization condition,

$$1 \stackrel{!}{=} \int d^3x \, \Psi^\dagger_{nkm} \Psi_{nkm} = \int_0^\infty dr \left(g^2_{nk} \int d\Omega \, |\Omega_{km}|^2 + f^2_{nk} \int d\Omega \, |\Omega_{-km}|^2 \right)$$

$$= \int_0^\infty dr \left(g_{nk}^2 + f_{nk}^2\right) = \int_0^\infty dr \left({u_{nk}^+}^2 + {u_{nk}^-}^2 - 2\frac{\alpha}{k} u_{nk}^+ u_{nk}^-\right). \tag{4.75}$$

The individual terms are calculated by means of the generating function of the Laguerre polynomials (see appendix B),

$$\begin{aligned}
\int_0^\infty dr\, {u_{nk}^+}^2 &= \frac{\mathcal{A}_+^2}{2C} \int dx\, x^{2\gamma+2} e^{-x} (L_{n_r-1}^{2\gamma+1}(x))^2 \\
&= \frac{\mathcal{A}_+^2}{2C} \int dx\, x^{2\gamma+2} e^{-x} \\
&\qquad \cdot \frac{\partial_y^{n_r-1} \partial_z^{n_r-1}}{((n_r-1)!)^2} \frac{\exp\left[-\frac{xy}{1-y} - \frac{xz}{1-z}\right]}{(1-y)^{2\gamma+2}(1-z)^{2\gamma+2}} \Bigg|_{y=z=0} \\
&= \frac{\mathcal{A}_+^2}{2C} \frac{\Gamma(2\gamma+3)}{((n_r-1)!)^2}\, \partial_y^{n_r-1} \partial_z^{n_r-1} \frac{1-y-z+yz}{(1-yz)^{2\gamma+3}} \Bigg|_{y=z=0} \\
&= \frac{\mathcal{A}_+^2}{2C} \frac{\Gamma(n_r+2\gamma+2) + (n_r-1)\Gamma(n_r+2\gamma+1)}{(n_r-1)!} \\
&= \frac{\mathcal{A}_+^2}{C} \frac{(n_r+\gamma)\Gamma(n_r+2\gamma+1)}{(n_r-1)!},
\end{aligned} \tag{4.76}$$

$$\int_0^\infty dr\, {u_{nk}^-}^2 = \frac{\mathcal{A}_-^2}{C} \frac{(n_r+\gamma)\Gamma(n_r+2\gamma)}{n_r!}, \tag{4.77}$$

$$-2\frac{\alpha}{k} \int_0^\infty dr\, u_{nk}^+ u_{nk}^- = \frac{2\alpha}{k} \frac{\mathcal{A}_+ \mathcal{A}_-}{C} \frac{\Gamma(n_r+2\gamma+1)}{(n_r-1)!}. \tag{4.78}$$

Using these results in eq. (4.75) implies for $n_r > 0$

$$1 \overset{!}{=} \frac{\mathcal{A}_+^2}{C} \frac{(n_r+\gamma)\Gamma(n_r+2\gamma+1)}{(n_r-1)!} \left(1 + \frac{\mathcal{F}^2}{n_r(n_r+2\gamma)} + 2\frac{\alpha}{k}\frac{\mathcal{F}}{n_r+\gamma}\right), \tag{4.79}$$

so that we finally obtain the normalization constants as

$$\begin{aligned}
\mathcal{A}_+ &= \sqrt{\frac{C}{n_r+\gamma} \frac{(n_r-1)!}{\Gamma(n_r+2\gamma+1)} \frac{1}{2} \left(\left(\frac{Ek}{\gamma m}\right)^2 + \frac{Ek}{\gamma m}\right)} \\
&= \sqrt{\frac{C\,(n_r-1)!}{\Gamma(n_r+2\gamma+1)} \frac{n_r+\gamma+\frac{\gamma}{k}\sqrt{\alpha^2+(n_r+\gamma)^2}}{2\frac{\gamma^2}{k^2}\left(\alpha^2+(n_r+\gamma)^2\right)}},
\end{aligned}$$

$$\mathcal{A}_- = \sqrt{\frac{C\, n_r!}{\Gamma(n_r+2\gamma)} \frac{n_r+\gamma-\frac{\gamma}{k}\sqrt{\alpha^2+(n_r+\gamma)^2}}{2\frac{\gamma^2}{k^2}\left(\alpha^2+(n_r+\gamma)^2\right)}}. \tag{4.80}$$

For $n = |k|$ we simply set $\mathcal{A}_+ = 0$ while the expression for $\mathcal{A}_-$ remains valid with $n_r = 0$.

4.3.1 A short summary

Let us briefly summarize the results in the previous section. The wave function reads

$$\Psi_{nkm}(r,\theta,\varphi) = \begin{pmatrix} \frac{g_{nk}(r)}{r}\Omega_{km}(\theta,\varphi) \\ \frac{if_{nk}(r)}{r}\Omega_{-km}(\theta,\varphi) \end{pmatrix}, \tag{4.81}$$

where

$$\Omega_{km} = \frac{1}{\sqrt{2k+1}} \begin{pmatrix} \sqrt{k+\frac{1}{2}-m}\, Y_{k,m-1/2}(\theta,\varphi) \\ -\operatorname{sgn} k \sqrt{k+\frac{1}{2}+m}\, Y_{k,m+1/2}(\theta,\varphi) \end{pmatrix} \tag{4.82}$$

and

$$\begin{pmatrix} g_{nk}(r) \\ f_{nk}(r) \end{pmatrix} = \frac{1}{\sqrt{2k(k-\gamma)}} \begin{pmatrix} \alpha & -(k-\gamma) \\ -(k-\gamma) & \alpha \end{pmatrix} \begin{pmatrix} u^+_{nk}(r) \\ u^-_{nk}(r) \end{pmatrix}. \tag{4.83}$$

For the functions $u^\pm$ we have obtained

$$\begin{pmatrix} u^+_{nk}(r) \\ u^-_{nk}(r) \end{pmatrix} = (2C_{nk}r)^\gamma\, e^{-C_{nk}r} \begin{pmatrix} \mathcal{A}_{+,nk}\, 2C_{nk}r\, L^{2\gamma+1}_{n_r-1}(2C_{nk}r) \\ \mathcal{A}_{-,nk} L^{2\gamma-1}_{n_r}(2C_{nk}r) \end{pmatrix}, \tag{4.84}$$

where,

$$\begin{aligned} \mathcal{A}_{+,nk} &= \sqrt{\frac{C_{nk}\,(n_r-1)!}{\Gamma(n_r+2\gamma+1)} \frac{n_r+\gamma+\frac{\gamma}{k}\sqrt{\alpha^2+(n_r+\gamma)^2}}{2\frac{\gamma^2}{k^2}\left(\alpha^2+(n_r+\gamma)^2\right)}}, \\ \mathcal{A}_{-,nk} &= \sqrt{\frac{C_{nk}\, n_r!}{\Gamma(n_r+2\gamma)} \frac{n_r+\gamma-\frac{\gamma}{k}\sqrt{\alpha^2+(n_r+\gamma)^2}}{2\frac{\gamma^2}{k^2}\left(\alpha^2+(n_r+\gamma)^2\right)}}. \end{aligned} \tag{4.85}$$

The constants C_{nk}, E_{nk} and γ are given by

$$E_{nk} = \frac{m}{\sqrt{1+\frac{\alpha^2}{(n_r+\gamma)^2}}}, \qquad C_{nk} = \sqrt{m^2-E^2_{nk}}, \qquad \gamma = \sqrt{k^2-\alpha^2}, \tag{4.86}$$

where

$$n_r = n-|k|, \qquad k = \mp\left(j+\frac{1}{2}\right) = \begin{cases} -l-1, & j = l+1/2 \\ l, & j = l-1/2 \end{cases}. \tag{4.87}$$

4.4 Expansion of the wave functions

In chapter 6 we will calculate radiative corrections of the order α^5 to the Dirac energy levels (4.68). Thus we will have to take care to which order in α each term contributes. For this purpose we expand the Dirac wave functions (4.81) to the linear order in α,

$$\begin{aligned}
\begin{pmatrix} u^+_{nk}(r) \\ u^-_{nk}(r) \end{pmatrix} &= \sqrt{\frac{C_n}{n}\frac{(n-|k|-1)!}{(n+|k|)!}}\,(2C_nr)^{|k|}\;e^{-C_nr} \\
&\quad\cdot\begin{pmatrix} 2C_nr\,L^{2|k|+1}_{n-|k|-1}(2C_nr) \\ \alpha\frac{n^2-k^2}{2n|k|}L^{2|k|-1}_{n-|k|}(2C_nr) \end{pmatrix} + O(\alpha^2), \qquad k>0, \\
\begin{pmatrix} u^+_{nk}(r) \\ u^-_{nk}(r) \end{pmatrix} &= \sqrt{\frac{C_n}{n}\frac{(n-|k|)!}{(n+|k|-1)!}}\,(2C_nr)^{|k|}\;e^{-C_nr} \\
&\quad\cdot\begin{pmatrix} \frac{\alpha}{2|k|n}\,2C_nr\,L^{2|k|+1}_{n-|k|-1}(2C_nr) \\ L^{2|k|-1}_{n-|k|}(2C_nr) \end{pmatrix} + O(\alpha^2), \quad k<0, \qquad (4.88)
\end{aligned}$$

where now $C_{nk} \approx C_n = m\alpha/n$. Thus, to linear order in α, the radial wave function reads

$$\begin{aligned}
\begin{pmatrix} g_{nk}(r) \\ f_{nk}(r) \end{pmatrix} &= \begin{pmatrix} \Theta(k)u^+_{nk}(r) + \Theta(-k)u^-_{nk}(r) \\ \Theta(k)[u^-_{nk}(r) - \frac{\alpha}{2|k|}u^+_{nk}(r)] + \Theta(-k)[u^+_{nk}(r) + \frac{\alpha}{2|k|}u^-_{nk}(r)] \end{pmatrix} \\
&\quad + O(\alpha^2), \qquad (4.89)
\end{aligned}$$

where the upper line is completely of order 1, while the lower one is of order α. Let us define the function g^S_{nl} as the non-relativistic radial Schrödinger wave function as derived in chapter 3, i.e.

$$g^S_{nl}(r) = \sqrt{\frac{C_n}{n}\frac{(n-l-1)!}{(n+l)!}}\,(2C_nr)^{l+1}e^{-C_nr}L^{2l+1}_{n-l-1}(2C_nr), \qquad (4.90)$$

where $l \geq 0$ as usual. In this non-relativistic limit the large component g_{nl} of the Dirac spinor is given in terms of the Schrödinger wave function as

$$g_{nk}(r) = \Theta(k)g^S_{n|k|}(r) + \Theta(-k)g^S_{n,|k|-1}(r) = g^S_{nl}(r). \qquad (4.91)$$

Up to higher orders in α this expression is exactly the same as eq. (3.31). The small component, however, takes a different form depending on whether k is positive or negative,

$$f_{nk}(r) = \frac{\alpha}{2|k|}\left[\Theta(k)\left(g^S_{n,|k|-1}(r)\sqrt{1-\frac{k^2}{n^2}} - g^S_{n|k|}(r)\right)\right.$$

$$+\Theta(-k)\left(g^S_{n,|k|-1}(r)+g^S_{n|k|}(r)\sqrt{1-\frac{k^2}{n^2}}\right)\Bigg],$$

$$=\begin{cases}\frac{\alpha}{2l}\left(g^S_{n,l-1}(r)\sqrt{1-\frac{l^2}{n^2}}-g^S_{nl}(r)\right), & k>0\\ \frac{\alpha}{2(l+1)}\left(g^S_{nl}(r)+g^S_{n,l+1}(r)\sqrt{1-\frac{(l+1)^2}{n^2}}\right), & k<0\end{cases}. \tag{4.92}$$

4.5 Proton recoil and reduced mass

In section 4.3 we have silently assumed that a particle with the reduced mass m of the electron in the hydrogen atom is subject to an external potential $-\alpha/r$. In chapters 2 and 3 we could perform the same coordinate transformation to relative and CM coordinates as in classical mechanics. Thus we could separate the CM- from the relative motion-Hamiltonian. The situation is not so simple, however, in the case of the Dirac equation, because already in classical special relativity the notion of the CM coordinate requires the specification of a certain coordinate system. In chapter 8 we rigorously solve the Dirac equation for the two-particle system of electron and proton but in this chapter we help ourselves in a much simpler way.

Consider the electron in the rest-system of the proton. We then obtain the same solution to the Dirac equation as in section 4.3 but with m replaced by m_e. The 4-momenta of electron and proton read, respectively,

$$p=\begin{pmatrix}E_e\\ \vec{p}\end{pmatrix}, \qquad P=\begin{pmatrix}m_p\\ \vec{o}\end{pmatrix}, \tag{4.93}$$

where the electron energy E_e is the one obtained in section 4.3,

$$E_e=\frac{m_e}{A}, \qquad A=\sqrt{1+\frac{\alpha^2}{(n_r+\gamma)^2}}. \tag{4.94}$$

The total energy of the system then reads

$$E_{\rm tot}=\sqrt{-(p+P)^2}=\sqrt{m_p^2+m_e^2+2m_pE_e}$$
$$=M\sqrt{1-\frac{2m}{M}(1-A^{-1})}. \tag{4.95}$$

Expanding $E_{\rm tot}/M$ to second order in m/M and A to fourth order in α yields

$$\frac{E_{\rm tot}}{M}\approx 1-\frac{m}{M}(1-A^{-1})-\frac{m^2}{2M^2}(1-A^{-1})^2$$

$$\approx 1 - \frac{\mathrm{Ryd}}{M}\left(\frac{1}{n^2} + \alpha^2\left(\frac{1}{|k|n^3} - \frac{3 - m/M}{4n^4}\right)\right). \tag{4.96}$$

Hence we should modify eq. (4.69) to read

$$\Delta E_{nk} = \mathrm{Ryd}\left(1 - \frac{1}{n^2} + \alpha^2\left(\frac{1 + m/M}{4} + \frac{3 - m/M}{4n^4} - \frac{1}{|k|n^3}\right)\right). \tag{4.97}$$

However, since $\alpha^4 m/M < \alpha^5$ this correction is of no consequence for the order α^4 energy levels considered in this chapter. Higher order recoil corrections are only important if even higher accuracy is envisaged than the order α^5 radiative corrections calculated in chapter 6. Therefore the $\alpha^4 m/M$ will not be considered in this work.

Chapter 5

Feynman's path integral

In 1948 Feynman proposed a third formulation of quantum mechanics which he called the "spacetime approach" and which is very different at first glance and yet equivalent to matrix mechanics and Schrödinger theory. The focus of this formalism is neither on state vectors living in a Hilbert space nor on wave functions but on a probability amplitude called propagator which describes the transition of a system from one state into another. This transition amplitude is calculated by integrating over all possible intermediate states. In the case of position states, i.e. the transition of a particle from one location to another, the intermediate states constitute paths. Consequently one integrates over all paths from the initial to the final position which is way Feynman's spacetime approach is nowadays known as "path integral formalism".

Regarding the date of discovery of the formalism, this chapter is in the right historical order, as the previous chapters. However, the solution to the hydrogen atom in the path integral formalism was not found until 1979 by Duru and Kleinert. At first it was doubted that the method they used was indeed valid until it was reviewed by Kleinert (1987) in a rigorous manner. In this chapter we perform the calculation of Duru and Kleinert (1979), which is already far more involved than the calculations in previous chapters and which includes a change of variables that transforms the flat three-dimensional position space into a four-dimensional space with curvature and torsion and spinor-valued coordinates. A treatment of the subtle issues that arise in this calculation is beyond the scope of this work and can be found in Kleinert (2004).

Feynman used the path integral formalism in his original formulation of quantum electrodynamics (QED) in the late 1940's and it is also the way quantum field theory is presented in chapter 6. Hence this formalism is reviewed a bit more carefully than the other approaches presented so far.

5.1 Non-relativistic path integrals

The central question in the path integral approach is: Given a system has been measured in state $|\psi(t_i)\rangle$ at time t_i, what is the probability that it will be measured in state $|\chi(t_f)\rangle$ at time t_f? Let us illustrate this formalism for the special case of a charged particle in an external 4-vector potential $(\Phi, \vec{A})$, governed by the Hamiltonian

$$\hat{H} = \frac{(\hat{\vec{p}} - q\vec{A}(t, \hat{\vec{x}}))^2}{2m} + q\Phi(t, \hat{\vec{x}}). \tag{5.1}$$

Let us recall the time-evolution operator as given in eq. (2.7),

$$\hat{\mathcal{U}}(t_N, t_0) = \hat{T} \exp\left[-i \int_{t_0}^{t_N} dt\, \hat{H}(t)\right] = \lim_{N\to\infty} \hat{T} \prod_{n=1}^{N} \left(1 - i\varepsilon \hat{H}(t_k)\right), \tag{5.2}$$

where $t_{n+1} = \varepsilon + t_n$, $\varepsilon = (t_N - t_0)/N$ and $\hat{T}$ is the time-ordering operator as explained in chapter 2. We now want to investigate the amplitude

$$\begin{aligned} K(t_f, \chi; t_i, \psi) &= \langle \chi(t_f) | \hat{\mathcal{U}}(t_f, t_i) | \psi(t_i) \rangle \\ &= \int d^3x_f d^3x_i \, \langle \chi(t_f) | \vec{x}_f \rangle \langle \vec{x}_f | \hat{\mathcal{U}}(t_f, t_i) | \vec{x}_i \rangle \langle \vec{x}_i | \psi(t_i) \rangle \\ &= \int d^3x_f d^3x_i \, \chi^\dagger(t_f, \vec{x}_f) K(t_f, \vec{x}_f; t_i, \vec{x}_i) \psi(t_i, \vec{x}_i). \end{aligned} \tag{5.3}$$

Thus the amplitude $K(t_f, \chi; t_i, \psi)$ for the transition $|\psi(t_i\rangle \to |\chi(t_f\rangle$ has been formulated in terms of the amplitude $K(t_f, \vec{x}_f; t_i, \vec{x}_i)$ for the transition $(t_f, \vec{x}_f) \to (t_i, \vec{x}_i)$. The quantity $K(t_f, \vec{x}_f; t_i, \vec{x}_i)$ is called the propagator since it represents the amplitude that the particle propagates from $\vec{x}_i$ to $\vec{x}_f$ in the time span $t_f - t_i$. First of all, from the properties of $\mathcal{U}$ it is clear that for $t_f = t_i$

$$K(t_i, \vec{x}_f; t_i, \vec{x}_i) = \langle \vec{x}_f | \vec{x}_i \rangle = \delta^3(\vec{x}_f - \vec{x}_i), \tag{5.4}$$

i.e. the particle can not travel a finite distance in zero time. Let us now separate the path under consideration into N infinitesimal sections,

$$\begin{aligned} &\vec{x}_n = \vec{x}(t_n), && \vec{x}_0 = \vec{x}(t_i), && \vec{x}_N = \vec{x}(t_f) \\ &t_n = t_{n-1} + \varepsilon, && t_0 = t_i, && \varepsilon = \frac{t_f - t_i}{N}, \end{aligned} \tag{5.5}$$

to approximate

$$K(t_f,\vec{x}_f;t_i,\vec{x}_i)=\langle\vec{x}_f|\mathcal{U}(t_f,t_i)|\vec{x}_i\rangle\approx\langle\vec{x}_f|\hat{T}\prod_{k=1}^{N}\left(1-i\varepsilon\hat{H}(t_k,\hat{\vec{x}},\hat{\vec{p}})\right)|\vec{x}_i\rangle. \tag{5.6}$$

We now insert a complete set of momentum eigenstates into every factor to obtain

$$\begin{aligned}
K(t_f,\vec{x}_f;t_i,\vec{x}_i)=\prod_{k=1}^{N}\int\frac{d^3p_k}{(2\pi)^3}\cdot\prod_{l=1}^{N-1}\int d^3x_l\cdot\hat{T}\prod_{j=1}^{N}\langle\vec{x}_j|\Bigg[&\left(1-i\varepsilon\frac{\hat{\vec{p}}^2}{2m}\right)|\vec{p}_j\rangle\langle\vec{p}_j|\\
&-i\varepsilon\left(\frac{q^2\vec{A}^{\,2}(t_j,\hat{\vec{x}})}{8m}-\frac{q\vec{A}(t_j,\hat{\vec{x}})\hat{\vec{p}}}{2m}+\frac{1}{2}q\Phi(t_j,\hat{\vec{x}})\right)|\vec{p}_j\rangle\langle\vec{p}_j|\\
&-i\varepsilon|\vec{p}_j\rangle\langle\vec{p}_j|\left(\frac{q^2\vec{A}^{\,2}(t_j,\hat{\vec{x}})}{8m}-\frac{\hat{\vec{p}}q\vec{A}(t_j,\hat{\vec{x}})}{2m}+\frac{1}{2}q\Phi(t_j,\hat{\vec{x}})\right)\\
&-i\varepsilon\frac{q^2\vec{A}(t_j,\hat{\vec{x}})|\vec{p}_j\rangle\langle\vec{p}_j|\vec{A}(t_j,\hat{\vec{x}})}{4m}\Bigg]|\vec{x}_{j-1}\rangle\\
=\prod_{k=1}^{N}\int\frac{d^3p_k}{(2\pi)^3}\cdot\prod_{l=1}^{N-1}\int d^3x_l\cdot\prod_{j=1}^{N}&e^{iS_c(t_j,\vec{x}_j;t_{j-1},\vec{x}_{j-1})}\\
=\int\mathcal{D}^3p\mathcal{D}^3x\,e^{iS_c(t_f,\vec{x}_f;t_i,\vec{x}_i)},&
\end{aligned} \tag{5.7}$$

where

$$\begin{aligned}
S_c(t_j,\vec{x}_j;t_{j-1},\vec{x}_{j-1})&=\vec{p}_j(\vec{x}_j-\vec{x}_{j-1})\\
&\quad-i\varepsilon\left[\frac{\left(\vec{p}_j-q\frac{\vec{A}(t_j,\vec{x}_j)+\vec{A}(t_j,\vec{x}_{j-1})}{2}\right)^2}{2m}+q\frac{\Phi(t_j,\vec{x}_j)+\Phi(t_j,\vec{x}_{j-1})}{2}\right],\\
\mathcal{D}^3p&=\prod_{k=1}^{N}\left(\frac{i\varepsilon}{2\pi m}\right)^{3/2}d^3p_k,\\
\mathcal{D}^3x&=\left(\frac{m}{2\pi i\varepsilon}\right)^{3/2}\prod_{l=1}^{N-1}\left(\frac{m}{2\pi i\varepsilon}\right)^{3/2}d^3x_l.
\end{aligned} \tag{5.8}$$

Let us make the following approximation which is justified in the continuum limit,

$$\frac{\Phi(t_j,\vec{x}_j)+\Phi(t_j,\vec{x}_{j-1})}{2}\approx\Phi\left(t_j,\frac{\vec{x}_j+\vec{x}_{j-1}}{2}\right), \tag{5.9}$$

and similarly for $\vec{A}$. We recognize S_c as the classical, canonical (but not minimized) action. Abbreviating $x = (t, \vec{x})$ we may express it in the continuum limit as

$$S_c(x_f; x_i) = \int_{x_i}^{x_f} \left[d\vec{x} \cdot \vec{p} - dt\, H(t, \vec{x}, \vec{p}) \right]. \tag{5.10}$$

Note that the momentum states in eq. (5.7) could have been inserted differently, resulting in a slightly different result for the times-sliced, classical action S_c. E.g. in the case of the hydrogen atom ($\vec{A} = 0$) it is convenient use S_c in the form

$$S_c(x_j; x_{j-1}) = \vec{p}_j(\vec{x}_j - \vec{x}_{j-1}) - i\varepsilon \left(\frac{\vec{p}_j{}^2}{2m} + q\Phi(\vec{x}_{j-1}) \right), \tag{5.11}$$

The difference between these two versions of S_c is an overall, constant factor of $e^{-i\varepsilon q(\Phi(\vec{x}_N) - \Phi(\vec{x}_0))/2}$ which vanishes in the continuum limit.

Writing $\bar{\vec{A}}_k = \vec{A}(t_k, (x_k + x_{k-1})/2)$, the p-integral in eq. (5.7) can be readily performed,

$$\prod_{k=1}^{N} \left(\frac{i\varepsilon}{2\pi m} \right)^{3/2} \int d^3 p_k\, e^{i\vec{p}_k(\vec{x}_k - \vec{x}_{k-1}) - \frac{i\varepsilon}{2m}\left(\vec{p}_k - q\bar{\vec{A}}_k\right)^2} = \prod_{k=1}^{N} e^{\frac{im(\vec{x}_k - \vec{x}_{k-1})^2}{2\varepsilon} + i(\vec{x}_k - \vec{x}_{k-1})q\bar{\vec{A}}_k}, \tag{5.12}$$

so that

$$\int \mathcal{D}^3 p\, e^{iS_c(x_f; x_i)} = e^{iS(x_f; x_i)}, \tag{5.13}$$

where S means the classical action in Lagrangian form

$$\begin{aligned} S(x_f; x_i) &= \int_{t_i}^{t_f} dt\, L(t, \vec{x}, \dot{\vec{x}}), \\ L(t, \vec{x}, \dot{\vec{x}}) &= \frac{m\dot{\vec{x}}^2}{2} + \dot{\vec{x}} q\vec{A}(x) - q\Phi(x). \end{aligned} \tag{5.14}$$

The meaning of this new formalism can be easily interpreted. The propagator, i.e. the amplitude $K(x_f; x_i)$ to find a particle at the event $(t_f, \vec{x}_f)$ given it has been found at $(t_i, \vec{x}_i)$, where $t_i < t_f$, is given by the a summation over

all possible paths which connect $\vec{x}_f$ with $\vec{x}_i$. This is expressed in the path integral measure $\mathcal{D}^3x \propto \Pi_n d^3x_n$, where all intermediate steps are integrated over the whole space and the limit of infinitely many steps is performed. Every path is weighted by a phase, however, which is given by the exponential of the classical action integrated along the path. The propagator is thus given by

$$K(x_f; x_i) = \int_{x_i}^{x_f} \mathcal{D}^3x \, e^{iS(x_f;x_i)}. \tag{5.15}$$

In the path integral formulation it is especially easy to see how classical mechanics arises from quantum mechanics in the limit of "large" systems. The situation becomes most vivid if we introduce an imaginary time $\tau = it$ and define the so called euclidean action $S_E = -iS$,

$$\begin{aligned} K(x_f; x_i) &= \int_{x_i}^{x_f} \mathcal{D}^3x \, e^{-S_E(x_f;x_i)}, \\ S_E(x_f; x_i) &= \int_{it_i}^{it_f} d\tau \, \left[\frac{m}{2} \left(\frac{d\vec{x}}{d\tau} \right)^2 - i \frac{d\vec{x}}{d\tau} q\vec{A}(x) + q\Phi(x) \right]. \end{aligned} \tag{5.16}$$

Eqs. (5.16) show clearly that K receives the largest contribution from those paths which are attributed to the smallest euclidean action. Paths corresponding to larger S_E are exponentially suppressed. The most important paths are thus centered around the classical path where $\delta S_E = 0$. The centering around the classical path gets more and more pronounced the larger the euclidean action S_E of the system is. Thus it comes that for macroscopic systems in very good approximation only the one path with $\delta S_E = 0$ contributes. This argument does not change substantially if we return to the real time formalism. A sizable change in the action between neighboring paths results in a rapidly oscillating phase factor e^{iS} unless they are close to the classical path where the action becomes extremal, $\delta S = 0$. Therefore the contribution of neighboring paths far from the classical one are not exponentially damped but instead cancel each other out due to the oscillating phase factor e^{iS}. Only those paths contribute where the action does not change substantially from its extremum.

Let us draw the connection between the path integral formalism and Schrödinger theory. Since Schrödinger's formalism is equivalent to matrix mechanics, this will also show the equivalence of path integrals to the latter.

Let us note that from eq. (5.15) and the path integral measure (5.8) it is immediately clear that

$$K(x_3;x_1) = \int_{x_1}^{x_3} \mathcal{D}^3x\, e^{iS(x_3;x_1)} = \int d^3x_2 \int_{x_2}^{x_3} \mathcal{D}^3x\, e^{iS(x_3;x_2)} \int_{x_1}^{x_2} \mathcal{D}^3x\, e^{iS(x_2;x_1)}$$
$$= \int d^3x_2\, K(x_3;x_2)K(x_2;x_1), \tag{5.17}$$

where $t_3 > t_2 > t_1$, i.e. the amplitude to propagate from x_1 to x_3 is given by the amplitudes for $x_1 \to x_2$ and $x_2 \to x_3$, integrated over all possible intermediate positions $\vec{x}_2$. Using this property we can show that the propagator (5.15) satisfies the Schrödinger equation. Let us consider the change of the propagator within an infinitesimal time step ε,

$$K(t+\varepsilon,\vec{x};x_0) = \int_{x_0}^{(t+\varepsilon,\vec{x})} \mathcal{D}^3x\, e^{iS(t+\varepsilon,\vec{x};x_0)}$$
$$= \int d^3y \left(\frac{m}{2\pi i\varepsilon}\right)^{3/2} K(t,\vec{y};x_0) \exp\left[\frac{im(\vec{x}-\vec{y})^2}{2\varepsilon}\right.$$
$$\left. + iq(\vec{x}-\vec{y})\vec{A}\left(t+\varepsilon,\frac{\vec{x}+\vec{y}}{2}\right) - i\varepsilon q\Phi\left(t+\varepsilon,\frac{\vec{x}+\vec{y}}{2}\right)\right]. \tag{5.18}$$

Let us make the shift $\vec{y} \to \vec{x}+\vec{y}$ and further define for convenience $\epsilon = i\varepsilon$ and $\vec{z} = \vec{y}\sqrt{m/\epsilon}$. The rate of change in time $\partial_t K(t,\vec{x};x_0)$, expanded in powers of ϵ then reads,

$$i\partial_t K(t,\vec{x};x_0) = \lim_{\epsilon\to 0} \frac{K(t,\vec{x};x_0) - K(t+\varepsilon,\vec{x};x_0)}{\epsilon}$$
$$= \lim_{\epsilon\to 0} \frac{1}{\epsilon}\left[K(t,\vec{x};x_0) - \int \frac{d^3z\, e^{-\vec{z}^2/2}}{(2\pi)^{3/2}} \cdot \left(1 - \epsilon q\Phi(x)\right.\right.$$
$$- iq\sqrt{\frac{\epsilon}{m}}\vec{z}\left(1 + \frac{1}{2}\sqrt{\frac{\epsilon}{m}}(\vec{z}\vec{\nabla})\right)\vec{A}(x) - \frac{\epsilon(\vec{z}q\vec{A}(x))^2}{2m} + O(\epsilon^{3/2})\Big)$$
$$\left.\cdot\left(1 + \sqrt{\frac{\epsilon}{m}}\vec{z}\vec{\nabla} + \frac{\epsilon}{2m}(\vec{z}\vec{\nabla})(\vec{z}\vec{\nabla}) + O(\epsilon^{3/2})\right)K(t,\vec{x};x_0)\right]$$
$$= \lim_{\epsilon\to 0} \frac{1}{\epsilon}\left[1 - \int \frac{d^3z\, e^{-\vec{z}^2/2}}{(2\pi)^{3/2}}\left(1 - \epsilon q\Phi(x)\right.\right.$$
$$\left.\left. + \frac{\epsilon\vec{z}^2}{6m}\left(\vec{\nabla} - iq\vec{A}(x)\right)^2\right)\right]K(t,\vec{x};x_0)$$

$$= \left[\frac{\left(-i\vec{\nabla} - q\vec{A}(x)\right)^2}{2m} + q\Phi(x) \right] K(t, \vec{x}; x_0). \tag{5.19}$$

Thus the propagator obeys the same dynamics as the wave function. $K(x; x_0)$ also satisfies the Schrödinger equation with respect to x_0 if one exchanges $\partial_t \to -\partial_{t_0}$, $\vec{\nabla} \to \vec{\nabla}_0$, $\hat{H} \to \hat{H}^\dagger$,

$$\begin{aligned} \left(-i\partial_t + \hat{H}(x, -i\vec{\nabla})\right) K(x; x_0) = 0, \\ \left(+i\partial_{t_0} + \hat{H}^\dagger(x_0, -i\vec{\nabla}_0)\right) K(x; x_0) = 0. \end{aligned} \tag{5.20}$$

The propagator can hence be used to propagate the Schrödinger wave function in time. Let the state of a system at time t_i be $|\psi(t_i)\rangle$. At a later time t_f the state is then $|\psi(t_f)\rangle$. We may then express the wave function $\psi(x_f) = \langle \vec{x}_f | \psi(t_f) \rangle$ in terms of the propagator as

$$\begin{aligned} \psi(x_f) = \langle \vec{x}_f | e^{-i\hat{H}(t_f - t_i)} | \psi(t_i) \rangle &= \int d^3x_i \, \langle \vec{x}_f | e^{-i\hat{H}(t_f - t_i)} | \vec{x}_i \rangle \langle \vec{x}_i | \psi(t_i) \rangle \\ &= \int d^3x_i \, K(x_f; x_i) \psi(x_i). \end{aligned} \tag{5.21}$$

This reflects the fact that the amplitude $\psi(x_f)$ to find the particle at x_f is equal to the amplitude $K(x_f; x_i)$ that the particle propagates from x_i to x_f times the amplitude to find the particle $\psi(x_i)$ at x_i, integrated over all possible initial positions $\vec{x}_i$. Eq. (5.21) also makes it clear that if the propagator satisfies the Schrödinger equation so does the wave function and vice versa.

There is also another, very important relation between the propagator and the wave functions. Inserting a complete set of eigenstates of the Hamiltonian in the first line of eq. (5.7) and writing $T = t_f - t_i$ yields

$$K(x_f; x_i) = \sum_n \psi_n(\vec{x}_f) \psi_n^\dagger(\vec{x}_i) e^{-iE_n T} + \int dp \, \psi_p(\vec{x}_f) \psi_p^\dagger(\vec{x}_i) e^{-iE_p T}, \tag{5.22}$$

with the wave functions $\psi_{n/p}(\vec{x}) = \langle \vec{x} | E_{n/p} \rangle$ for discrete and continuous eigenvalues, respectively.

In the next section we will calculate explicit expressions for propagators of some simple systems. Before we proceed, however, it should be noted that in a non-relativistic context one is usually interested in the so called causal propagator,

$$K^>(x_f; x_i) = \Theta(t_f - t_i) K(x_f; x_i), \tag{5.23}$$

which allows only for evolution of states forward in time. Combining the property (5.4) with eqs. (5.20) we find that the causal propagator is basically the Green's function of the Schrödinger equation,

$$\begin{aligned}\left(-i\partial_t + \hat{H}(x, -i\vec{\nabla})\right) K^>(x; x_0) &= -i\delta^4(x - x_0),\\ \left(+i\partial_{t_0} + \hat{H}^\dagger(x_0, -i\vec{\nabla}_0)\right) K^>(x; x_0) &= -i\delta^4(x - x_0).\end{aligned} \tag{5.24}$$

In the following all calculations will always be concerned with the propagator K if not stated otherwise since the causal propagator $K^>$ can always be obtained by a simple multiplication of the Θ-function.

5.1.1 The propagator of the forced harmonic oscillator

The harmonic oscillator is a system which is perfectly suited for the path integral formalism. The fact that the electromagnetic field is essentially a field of forced harmonic oscillators distributed throughout space explains why QED is so easily formulated in terms of Feynman's path integral approach (see e.g. Feynman, 1949a).

The harmonic oscillator also plays a major role in the calculation of the path integral for the hydrogen atom. Due to a Kustaanheimo-Stiefel transformation it is possible to transform the three-dimensional Coulomb problem into a four-dimensional harmonic oscillator in terms of spinor-valued coordinates. Thus we will take a closer look at the path integral of the harmonic oscillator. For preparation of the field theory treatment in chapter 6 we will also consider the forced harmonic oscillator.

The classical action of an harmonic oscillator, driven by a force $\vec{F}$ reads

$$S(x_f; x_i) = \int_{t_i}^{t_f} dt \left(m\frac{\dot{\vec{x}}^2 - \omega^2\vec{x}^2}{2} + \vec{F}\vec{x} \right). \tag{5.25}$$

Since this action is additive in every dimension the full, three-dimensional propagator will simply be a product of one-dimensional propagators

$$K(t_f, \vec{x}_f; t_i, \vec{x}_i) = K(t_f, x_f; t_i, x_i)K(t_f, y_f; t_i, y_i)K(t_f, z_f; t_i, z_i). \tag{5.26}$$

Let us separate the (one-dimensional) path given by positions $\{x(t)\}$, $t_i \leq t \leq t_f$ into a part which extremizes the action of the free harmonic oscillator $\{z(t)\}$, i.e. the classical path, plus quantum fluctuations $\{y(t)\}$,

$$x(t) = z(t) + y(t), \qquad \frac{\delta S}{\delta x}[z]\Big|_{F=0} = 0. \tag{5.27}$$

Since the end points of the paths $\{x(t)\}$ are held fixed, we have

$$\begin{aligned} z(t_i) &= x_i, & z(t_f) &= x_f, \\ y(t_i) &= 0, & y(t_f) &= 0. \end{aligned} \tag{5.28}$$

Thus we may write the one-dimensional action of the forced harmonic oscillator as

$$\begin{aligned} S = \underbrace{m\int_{t_i}^{t_f} dt \frac{\dot{z}^2 - \omega^2 z^2}{2}}_{=:S_{z,0}} + \underbrace{\int_{t_i}^{t_f} dt\, Fz}_{=:S_{z,F}} - m\int_{t_i}^{t_f} dt\, y \underbrace{\left(\ddot{z} + \omega^2 z\right)}_{=0} \\ + \underbrace{\int_{t_i}^{t_f} dt \left(m\frac{\dot{y}^2 - \omega^2 y^2}{2} + Fy\right)}_{=:S_{y,F}}. \end{aligned} \tag{5.29}$$

It is easy to see why the third term in the first line vanishes. If we expand the action around the path $x = z$, we obtain

$$S[z+y] = S[z] + \int dt\, y \frac{\delta S}{\delta z}[z] + \frac{1}{2}\int dt\, y^2 \frac{\delta^2 S}{\delta z^2}[z] + \ldots. \tag{5.30}$$

It is always possible to expand the action in this way and the linear term in y always vanishes by definition of the classical path z in eq. (5.27). In the special case of the harmonic oscillator, however, this series truncates after the quadratic term since the full action itself is only quadratic in the position variable. This is the reason why the path integral approach is so well suited for the harmonic oscillator.

By a purely classical calculation we obtain

$$\begin{aligned} z(t) &= \frac{x_f \sin(\omega(t - t_i)) + x_i \sin(\omega(t_f - t))}{\sin \omega T}, \\ S_{z,0} &= \frac{m\omega}{2\sin\omega T}\left((x_f^2 + x_i^2)\cos\omega T - 2x_f x_i\right), \end{aligned} \tag{5.31}$$

where $T = t_f - t_i$. We insert this into the one-dimensional propagator

$$K_{fi} = e^{iS_{z,0} + iS_{z,F}} \int \mathcal{D}y\, e^{iS_{y,F}}, \tag{5.32}$$

where $K_{fi} \equiv K(t_f, x_f; t_i, x_i)$ and

$$S_{y,F} = -\frac{m}{2}\int_{t_i}^{t_f} dt \left(y\left(\partial_t^2 + \omega^2\right) y - 2y\frac{F}{m}\right)$$

$$= -\frac{m}{2}\int_{t_i}^{t_f} dt \left(y - \frac{F}{m}\frac{1}{\partial_t^2+\omega^2}\right)\left(\partial_t^2+\omega^2\right)\left(y - \frac{1}{\partial_t^2+\omega^2}\frac{F}{m}\right) +$$

$$+ \frac{1}{2m}\int_{t_i}^{t_f} dt\, F\frac{1}{\partial_t^2+\omega^2}F \tag{5.33}$$

The first part of this equation can be brought into the form

$$-\frac{m}{2}\int_{t_i}^{t_f} dt\, y\left(\partial_t^2+\omega^2\right) y \tag{5.34}$$

by a constant shift of the path y, which leaves the measure $\mathcal{D}y$ invariant. The discretized version of this expression reads

$$-\frac{m}{2\varepsilon}\sum_{n=1}^{N-1} y_n\left(y_{n+1} - (2-\omega^2\varepsilon^2)y_n + y_{n-1}\right) = \frac{m}{2\varepsilon} yAy, \tag{5.35}$$

with the $(N-1)\times(N-1)$ matrix

$$A = \begin{pmatrix} 2-\omega^2\varepsilon^2 & -1 & 0 & 0 & \dots \\ -1 & 2-\omega^2\varepsilon^2 & -1 & 0 & \ddots \\ 0 & -1 & 2-\omega^2\varepsilon^2 & -1 & \ddots \\ 0 & 0 & -1 & 2-\omega^2\varepsilon^2 & \ddots \\ \vdots & \ddots & \ddots & \ddots & \ddots \end{pmatrix}. \tag{5.36}$$

Since the second part of eq. (5.33) is independent of y one may write the propagator as

$$K_{fi} = e^{iS_{z,0}+iS_{z,F}+iS_{FGF}}\int \mathcal{D}y e^{\frac{im}{2\varepsilon}yAy},$$

$$= \sqrt{\frac{m}{2\pi i\varepsilon\det A}}\, e^{iS_{z,0}+iS_{z,F}+iS_{FGF}}, \tag{5.37}$$

where we have defined

$$S_{FGF} = \frac{1}{2m}\int_{t_i}^{t_f} dt\, F\frac{1}{\partial_t^2+\omega^2}F. \tag{5.38}$$

Let $d^n = \det(A^n)$ denote the determinant of the $(n-1)\times(n-1)$ submatrix $A^n = (A_{ij})$, where $i,j < n$. The determinant of the matrix $A = A^N$ is then given by d^N. One can show by mathematical induction that the relation

$$\frac{d^{n+1} - 2d^n + d^{n-1}}{\varepsilon^2} + \omega^2 d^n = 0, \qquad 1 < n < N-1, \tag{5.39}$$

holds among the set of determinants $\{d^n\}$. The first term on the left-hand side has the form of a discretized, second order derivative so that eq. (5.39) resembles the equation of motion of a harmonic oscillator. Hence we find the solution

$$d^n = \alpha \sin(\tilde{\omega}\varepsilon n) + \beta \cos(\tilde{\omega}\varepsilon n), \qquad \tilde{\omega} = \frac{\arcsin(\omega\varepsilon/2)}{\varepsilon/2}, \tag{5.40}$$

which is periodic in n. The constants α and β may be determined by considering the case of a free particle ($\omega = 0$), where eq. (5.39) may be readily solved,

$$d^n\Big|_{\omega=0} = n \qquad \Rightarrow \quad \alpha = \frac{1}{\tilde{\omega}\varepsilon}, \qquad \beta = 0. \tag{5.41}$$

Let us perform the limit $N \gg \omega T$ in d^N, which yields

$$\det A = d^N = \frac{\sin(\tilde{\omega}\varepsilon N)}{\tilde{\omega}\varepsilon} \approx \frac{\sin \omega T}{\omega\varepsilon}. \tag{5.42}$$

Thus we obtain for the one-dimensional propagator

$$K_{fi} = \sqrt{\frac{m\omega}{2\pi i \sin \omega T}}\, e^{iS_{z,0} + iS_{z,F} + iS_{FGF}}, \tag{5.43}$$

where z and $S_{z,0}$ are given in eqs. (5.31). In order to solve the problem of the forced harmonic oscillator we rewrite eq. (5.38) as follows,

$$S_{FGF} = \frac{1}{2m} \int_{t_i}^{t_f} dt dt'\, F(t) \frac{1}{\partial_t^2 + \omega^2} \delta(t - t') F(t'). \tag{5.44}$$

The quantity sandwiched in between the F's is the Green's function G of the harmonic oscillator

$$G(t,t') = \frac{1}{\partial_t^2 + \omega^2} \delta(t - t'), \tag{5.45}$$

which satisfies the equations

$$\left(\partial_t^2 + \omega^2\right) G(t,t') = \left(\partial_{t'}^2 + \omega^2\right) G(t,t') = \delta(t-t'). \tag{5.46}$$

Implementing the boundary conditions $y(t_i) = y(t_f) = 0$, it is given by

$$\begin{aligned} G(t,t') = \Theta(t-t')&\frac{\sin\omega(t-t_f)\sin\omega(t'-t_i)}{\omega\sin\omega T} \\ &+ \Theta(t'-t)\frac{\sin\omega(t'-t_f)\sin\omega(t-t_i)}{\omega\sin\omega T}. \end{aligned} \tag{5.47}$$

Due to the symmetry with respect to interchange of the times $t \leftrightarrow t'$ we may express S_{FGF} as

$$S_{FGF} = \frac{1}{m\omega\sin\omega T}\int_{t_i}^{t_f} dt\, F(t)\sin(\omega(t-t_f))\int_{t_i}^{t} dt'\sin(\omega(t'-t_i))F(t'). \tag{5.48}$$

For given F the propagator (5.43) may now be calculated by the evaluation of ordinary one-dimensional integrals. Here we want to give explicit solutions to several simple but important special cases.

First let us consider the case of a constant force, $F(t) = f = const.$,

$$S_{z,F} = f\,\frac{x_f + x_i}{2}\,\frac{4\sin^2\frac{\omega T}{2}}{\omega\sin\omega T}, \tag{5.49}$$

$$S_{FGF} = \frac{f^2 T}{2m\omega^2}\left(1 - \frac{4\sin^2\frac{\omega T}{2}}{\omega T\sin\omega T}\right). \tag{5.50}$$

Taken all together, we obtain for the three-dimensional propagator

$$\begin{aligned} K_{fi} = \left(\frac{m\omega}{2\pi i\sin\omega T}\right)^{3/2}&\exp\left[\frac{im\omega}{2\sin\omega T}\left(\vec{X}^2\cos^2\frac{\omega T}{2}\right.\right. \\ &\left.\left. - 4\left(\vec{\bar{X}} - \frac{\vec{f}}{m\omega^2}\right)^2\sin^2\frac{\omega T}{2} + \frac{\vec{f}^2 T\sin\omega T}{m^2\omega^3}\right)\right], \end{aligned} \tag{5.51}$$

where $\vec{X} = \vec{x}_f - \vec{x}_i$ and $\vec{\bar{X}} = (\vec{x}_f + \vec{x}_i)/2$. From this result we may now derive the propagator for a free harmonic oscillator ($\vec{f} = 0$),

$$K_{fi} = \left(\frac{m\omega}{2\pi i\sin\omega T}\right)^{3/2}\exp\left[\frac{im\omega}{2\sin\omega T}\left(\vec{X}^2\cos^2\frac{\omega T}{2} - 4\vec{\bar{X}}^2\sin^2\frac{\omega T}{2}\right)\right], \tag{5.52}$$

whereas for a particle under the influence of a constant force ($\omega = 0$) we obtain

$$K_{fi} = \left(\frac{m}{2\pi i T}\right)^{3/2} \exp\left[\frac{im\vec{X}^2}{2T} + i\vec{f}\vec{\bar{X}}T - \frac{i\vec{f}^2T^3}{24m}\right], \tag{5.53}$$

while the free particle propagator ($\omega = \vec{f} = 0$) reads

$$K_{fi} = \left(\frac{m}{2\pi i T}\right)^{3/2} \exp\left[\frac{im\vec{X}^2}{2T}\right]. \tag{5.54}$$

As a last point we note that for the free particle case eqs. (5.24) allow for a much simpler derivation of the causal propagator $K^{>}_{fi}$ and hence K_{fi},

$$\begin{aligned} K^{>}_{fi} &= \frac{-i}{-i\partial_{t_f} - \Delta_f/(2m) - i0^+}\delta^4(x_f - x_i) \\ &= \int \frac{d^4p}{(2\pi)^4}\frac{-ie^{ip(x_f-x_i)}}{-p^0 + \vec{p}^2/(2m) - i0^+} \\ &= \Theta(T)\int \frac{d^3p}{(2\pi)^3}\exp\left[-\frac{i\vec{p}^2T}{2m} + i\vec{p}\vec{X}\right] \\ &= \Theta(T)\left(\frac{m}{2\pi i T}\right)^{3/2}\exp\left[\frac{im\vec{X}^2}{2T}\right] \\ &= \Theta(T)K_{fi}. \end{aligned} \tag{5.55}$$

In the second line, 0^+ means a very small, positive quantity which is supposed to approach 0 as soon as it is safe to due so.

5.1.2 The path integral in spherical coordinates

For a spherically symmetric problem such as the hydrogen atom it is useful to reformulate the path integral in spherical coordinates. For convenience we use the imaginary time formulation of eqs. (5.16) and consider the case of a central potential. The discretized expressions then read

$$\begin{aligned} K_{fi} &= \int \mathcal{D}^3x\, e^{-S}, \\ \mathcal{D}^3x &= \left(\frac{m}{2\pi\varepsilon}\right)^{3N/2}\prod_{n=1}^{N-1} dr_n r_n^2 d\cos\theta_n d\varphi_n, \\ S &= \sum_{n=1}^{N}\left(\frac{m}{2\varepsilon}\left(r_n^2 + r_{n-1}^2 - 2r_nr_{n-1}\cos\gamma_n\right) + \varepsilon V(r_{n-1})\right), \end{aligned} \tag{5.56}$$

$$\cos\gamma_n = \cos\theta_n\cos\theta_{n-1} + \sin\theta_n\sin\theta_{n-1}\cos(\varphi_n - \varphi_{n-1}), \tag{5.57}$$

where $\varepsilon = iT/N$. We may express the exponential of the cosine in terms of a spherical modified Bessel function of the first kind,

$$e^{h\cos\gamma_n} = \sum_{l=0}^{\infty}(2l+1)i_l(h)P_l(\cos\gamma_n), \tag{5.58}$$

which are connected to the modified Bessel functions of the first kind via

$$i_l(x) = \sqrt{\frac{\pi}{2x}}I_{l+1/2}(x), \tag{5.59}$$

and where P_l means the Legendre polynomials. The latter are connected to the spherical harmonics via the addition theorem

$$P_l(\cos\gamma_n) = \frac{4\pi}{2l+1}\sum_{m=-l}^{l}Y_{lm}(\theta_n,\varphi_n)Y^*_{lm}(\theta_{n-1},\varphi_{n-1}). \tag{5.60}$$

Consequently the path integral may be written as

$$\begin{aligned} K_{fi} = \int \mathcal{D}^3x \prod_{n=1}^{N}\Bigg\{ &\exp\left[-\left(\frac{m}{2\varepsilon}\left(r_n^2 + r_{n-1}^2\right) + \varepsilon V(r_{n-1})\right)\right] \\ &\cdot 4\pi\sum_{l_n=0}^{\infty} i_{l_n}\left(\frac{mr_nr_{n-1}}{\varepsilon}\right)\sum_{m_n=-l_n}^{l_n}Y_{l_nm_n}(\theta_n,\varphi_n)Y^*_{l_nm_n}(\theta_{n-1},\varphi_{n-1})\Bigg\}. \end{aligned} \tag{5.61}$$

Due to the orthonormality of the spherical harmonics the angular integration merely yields a product of δ-functions so that only one sum over l and m remains and only the spherical harmonics at the end points survive,

$$\begin{aligned} K_{fi} &= \sum_{l=0}^{\infty}\sum_{m=-l}^{l}\frac{Y_{lm}(\theta_f,\varphi_f)}{r_f}\frac{Y^*_{lm}(\theta_i,\varphi_i)}{r_i}\mathcal{R}_{fi,l}, \\ \mathcal{R}_{fi,l} &= \int \mathcal{D}'r\exp\left[-\sum_{n=1}^{N}\left(\frac{m}{2\varepsilon}\left(r_n^2 + r_{n-1}^2\right) - \ln i_l\left(\frac{mr_nr_{n-1}}{\varepsilon}\right) + \varepsilon V(r_{n-1})\right)\right], \\ \mathcal{D}'r &= r_fr_i\left(4\pi\right)^N\left(\frac{m}{2\pi\varepsilon}\right)^{3N/2}\prod_{n=1}^{N-1}dr_nr_n^2. \end{aligned} \tag{5.62}$$

For large arguments, i.e. small ε, the Bessel function features the asymptotic behavior

$$i_l(x) \overset{x\to\infty}{\to} \frac{e^x}{2x}\left(1 - \frac{l(l+1)}{2x} \pm \dots\right). \tag{5.63}$$

The second term in bracket constitutes the well known centrifugal barrier. We want to filter this term out by introducing a further modification to the Bessel function,

$$\tilde{i}_l(x) := 2x\, e^{-x} i_l(x), \tag{5.64}$$

so that the radial path integral in eqs. (5.62) reads

$$\begin{aligned}
\mathcal{R}_{fi,l} &= \int \mathcal{D}r\, e^{-S_r}, \\
S_r &= \sum_{n=1}^{N} \left(\frac{m}{2\varepsilon} (r_n - r_{n-1})^2 - \ln \tilde{i}_l \left(\frac{m r_n r_{n-1}}{\varepsilon} \right) + \varepsilon V(r_{n-1}) \right), \\
\mathcal{D}r &= \sqrt{\frac{m}{2\pi\varepsilon}} \prod_{n=1}^{N-1} \sqrt{\frac{m}{2\pi\varepsilon}}\, dr_n.
\end{aligned} \tag{5.65}$$

Up to the appearance of the Bessel function this expression look very similar to the one-dimensional, cartesian case. Naively one could approximate the Bessel function by the centrifugal barrier to obtain the action

$$S_r^{\text{naive}} = \sum_{n=1}^{N} \left(\frac{m}{2\varepsilon} (r_n - r_{n-1})^2 + \varepsilon \frac{l(l+1)}{2 m r_n r_{n-1}} + \varepsilon V(r_{n-1}) \right). \tag{5.66}$$

However, this approximation is invalid for $l \neq 0$ since we have to integrate over all paths whereas the paths converge slower towards the continuum limit the closer they approach the central singularity of this r^{-2}-potential. The solution to this problem is elucidated in the next subsection.

5.1.3 The fixed-energy amplitude

The propagator K_{fi} describes the transition of an initial state $|\psi_i\rangle = |\psi(t_i)\rangle$ into a final state $|\psi_f\rangle = |\psi(t_f)\rangle$ in time. Thinking of a particle it describes the particle's propagation in spacetime. It is, however, very helpful instead of the transition $(t_i, \vec{x}_i) \to (t_f, \vec{x}_f)$ to consider the transition $\vec{x}_i \to \vec{x}_f$ at fixed energy E. More generally this means

$$(t_i, |\psi_i\rangle) \to (t_f, |\psi_f\rangle) \qquad \longrightarrow \qquad |\psi_i\rangle \overset{E=const.}{\to} |\psi_f\rangle, \tag{5.67}$$

for some initial and final states. The amplitude for this transition between states at constant energy is called the fixed-energy amplitude and is given by the Fourier transform of the causal propagator

$$G_{fi} \equiv G(\vec{x}_f; \vec{x}_i | E) = \int dT\, e^{iET} K^{>}(t_i + T, \vec{x}_f; t_i, \vec{x}_i), \tag{5.68}$$

where we have written $T = t_f - t_i$. More specifically, for a time independent Hamiltonian, we obtain for G_{fi},

$$G_{fi} = \int_0^\infty dT \, \langle \vec{x}_f | e^{-i(\hat{H}-E)T} | \vec{x}_i \rangle = \langle \vec{x}_f | \frac{-i}{\hat{H} - E - i0^+} | \vec{x}_i \rangle, \tag{5.69}$$

where 0^+ means a very small, positive quantity which is supposed to approach 0 as soon as it is safe to due so. The operator $-i/(\hat{H} - E)$ is called "the resolvent" and the $-i0^+$ insertion in eq. (5.69) tells us how to avoid the singularities. Consequently, the fixed-energy amplitude is nothing but the matrix elements of the resolvent. In the case of e.g. a free particle we obtain

$$G_{fi} = \int_0^\infty dT \left(\frac{m}{2\pi i T}\right)^{3/2} e^{\frac{im\vec{X}^2}{2T} + iET} = \frac{m}{2\pi i |\vec{X}|} e^{i|\vec{X}|\sqrt{2mE}}. \tag{5.70}$$

Writing the propagator K_{fi} as in eq. (5.22) yields the following expression for the fixed-energy amplitude,

$$iG_{fi} = \sum_n \frac{\psi_n(\vec{x}_f)\psi_n^*(\vec{x}_i)}{E_n - E - i0^+} + \int dp \, \frac{\psi_p(\vec{x}_f)\psi_p^*(\vec{x}_i)}{E_p - E - i0^+}. \tag{5.71}$$

Consequently the fixed-energy amplitude has poles at the positions which correspond to the actual particle energy. From eq. (5.71) we may calculate the discontinuity along the real axis in the complex energy plane,

$$\begin{aligned} \text{disc}\,(G_{fi}) &= G(\vec{x}_f; \vec{x}_i | E + i0^+) - G(\vec{x}_f; \vec{x}_i | E - i0^+) \\ &= \sum_n 2\pi\delta(E_n - E)\, \psi_n(\vec{x}_f)\psi_n^*(\vec{x}_i) \\ &\qquad + \int dp \, 2\pi\delta(E_p - E)\, \psi_p(\vec{x}_f)\psi_p^*(\vec{x}_i). \end{aligned} \tag{5.72}$$

Since the eigenstates if the Hamiltonian satisfy the completeness relation

$$\sum_n |n\rangle\langle n| + \int dp \, |p\rangle\langle p| = 1, \tag{5.73}$$

we obtain for the energy integral over the discontinuity,

$$\int_{-\infty}^\infty \frac{dE}{2\pi} \, \text{disc}\,(G_{fi}) = \sum_n \psi_n(\vec{x}_f)\psi_n^*(\vec{x}_i) + \int dk \, \psi_k(\vec{x}_f)\psi_k^*(\vec{x}_i)$$

$$= \langle \vec{x}_f | \left(\sum_n |n\rangle\langle n| + \int dp\, |p\rangle\langle p| \right) |\vec{x}_i\rangle$$
$$= \langle \vec{x}_f | \vec{x}_i \rangle = \delta^3(\vec{x}_f - \vec{x}_i). \tag{5.74}$$

From eq. (5.69) we see that the fixed-energy amplitude virtually emerges from an integration over propagators which describe time-evolution with an effective Hamiltonian operator

$$\hat{\mathcal{H}} = \hat{H} - E. \tag{5.75}$$

The fixed-energy amplitude has a remarkable property which yields the solution to the centrifugal barrier-problem we encountered in the last subsection in eqs. (5.65) and which eventually allows us to solve the path integral for the hydrogen atom. This property is based on the additional integration over the time interval T, which allows for arbitrary, invertible reparameterizations.

First we note that we may complement the resolvent on the left and right with regularization operators $\hat{\lambda}_L$ and $\hat{\lambda}_R$,

$$\frac{1}{\hat{\mathcal{H}}} = \hat{\lambda}_L \frac{1}{\hat{\lambda}_R \hat{\mathcal{H}} \hat{\lambda}_L} \hat{\lambda}_R. \tag{5.76}$$

Classically this corresponds to the reparameterization $dT = ds\, \lambda$. In the following we consider reparameterizations of the form $\hat{\lambda}_{L/R} = \hat{\lambda}_{L/R}(\vec{x})$ even though an s- or $\vec{p}$-dependence would be possible as well.

Let us now consider a Hamiltonian of the form

$$\hat{H} = \frac{\hat{\vec{p}}^2}{2m} + V(\hat{\vec{x}}). \tag{5.77}$$

We may now formulate the fixed-energy amplitude as a path integral,

$$G_{fi} = \int_0^\infty ds\, \langle \vec{x}_f |\, \hat{\lambda}_L e^{-i\hat{\lambda}_R \hat{\mathcal{H}} \hat{\lambda}_L s} \hat{\lambda}_R\, |\vec{x}_i\rangle$$
$$= \int_0^\infty ds\, \lambda_{L,f} \lambda_{R,i} \int \prod_{j=1}^{N-1} d^3x_j \prod_{k=1}^{N} \langle \vec{x}_k | e^{-i\hat{\lambda}_R \hat{\mathcal{H}} \hat{\lambda}_L \varepsilon} | \vec{x}_{k-1} \rangle$$
$$\approx \int_0^\infty ds\, \lambda_{L,f} \lambda_{R,i} \int \prod_{j=1}^{N-1} d^3x_j \prod_{k=1}^{N} \langle \vec{x}_k | \left(1 - i\hat{\lambda}_R \hat{\mathcal{H}} \hat{\lambda}_L \varepsilon \right) |\vec{x}_{k-1}\rangle. \tag{5.78}$$

Let us insert a complete set of momentum eigenstates $|\vec{p}\rangle$ for every factor,

$$\int \frac{d^3p_k}{(2\pi)^3} \langle \vec{x}_k | \left(|\vec{p}_k\rangle\langle \vec{p}_k| - i\hat{\lambda}_R \hat{\mathcal{H}} |\vec{p}_k\rangle\langle \vec{p}_k| \hat{\lambda}_L \varepsilon \right) |\vec{x}_{k-1}\rangle, \tag{5.79}$$

so that the fixed-energy amplitude reads

$$G_{fi} = \int_0^\infty ds\, \lambda_{L,f}\lambda_{R,i} \int \mathcal{D}^3x\mathcal{D}^3p\, e^{iS},$$
$$S = \sum_{n=1}^{N} \left[\vec{p}_n(\vec{x}_n - \vec{x}_{n-1}) - \varepsilon\lambda_n \left(\frac{\vec{p}_n^{\,2}}{2m} + V_n - E\right)\right], \tag{5.80}$$

where we have defined $\lambda_n = \lambda_{L,n-1}\lambda_{R,n}$, as well as

$$\mathcal{D}^3p = \prod_{k=1}^{N} \left(\frac{i\varepsilon\lambda_n}{2\pi m}\right)^{3/2} d^3p_k,$$
$$\mathcal{D}^3x = \left(\frac{m}{2\pi i\varepsilon\lambda_N}\right)^{3/2} \prod_{l=1}^{N-1} \left(\frac{m}{2\pi i\varepsilon\lambda_l}\right)^{3/2} d^3x_l. \tag{5.81}$$

Of course we can perform the $\mathcal{D}^3p$ integration again which yields

$$G_{fi} = \int_0^\infty ds\, \lambda_{L,f}\lambda_{R,i} \int \mathcal{D}^3x\, e^{iS},$$
$$S = \sum_{n=1}^{N} \left[\frac{m(\vec{x}_n - \vec{x}_{n-1})^2}{2\varepsilon\lambda_n} - \varepsilon\lambda_n\,(V_n - E)\right]. \tag{5.82}$$

Let us now investigate how we can use the gauge freedom we have obtained from the functions $\lambda_{L/R}$ to prevent singular potentials like the Coulomb potential and the centrifugal barrier in eqs. (5.65) to cause any trouble. Repeating the steps that lead to eqs. (5.65) and using an imaginary parameter, $s \to -is$, yields the fixed-energy amplitude in radial coordinates,

$$iG_{fi} = \int_0^\infty ds\, \lambda_{L,f}\lambda_{R,i} \sum_{l=0}^{\infty} \mathcal{R}_{fi,l} \sum_{m=-l}^{l} \frac{Y_{lm}(\theta_f,\varphi_f)}{r_f} \frac{Y^*_{lm}(\theta_i,\varphi_i)}{r_i},$$
$$\mathcal{R}_{fi,l} = \int \mathcal{D}r\, e^{-S_{r,l}},$$
$$\mathcal{D}r = \sqrt{\frac{m}{2\pi\varepsilon\lambda_N}} \prod_{n=1}^{N-1} dr_n \sqrt{\frac{m}{2\pi\varepsilon\lambda_n}},$$
$$S_{r,l} = \sum_{n=1}^{N} \left[\frac{m(r_n - r_{n-1})^2}{2\varepsilon\lambda_n} + \varepsilon\lambda_n\,(V_n - E) - \ln \tilde{i}_l\left(\frac{mr_nr_{n-1}}{\varepsilon\lambda_n}\right)\right]. \tag{5.83}$$

The appearance of λ in the argument of the Bessel function allows us to get rid of the singular centrifugal barrier. The choice $\lambda_n = r_n r_{n-1}$, for example, yields the action

$$S_{r,l} = \sum_{n=1}^{N} \left[\frac{m(r_n - r_{n-1})^2}{2\varepsilon r_n r_{n-1}} + \varepsilon r_n r_{n-1} (V_n - E) + \varepsilon \frac{l(l+1)}{2m} \right]. \tag{5.84}$$

Generally this means that any r^{-2}-potential where we may approximate

$$r_n r_{n-1} \cdot \frac{1}{r_n^2} \approx 1 \tag{5.85}$$

can simply be absorbed into the centrifugal barrier. If we have, say, a potential of the form

$$V(r) = V_0(r) + \frac{L^2}{2mr^2}, \tag{5.86}$$

we may simply write the action as

$$S_{r,l} = \sum_{n=1}^{N} \left[\frac{m(r_n - r_{n-1})^2}{2\varepsilon r_n r_{n-1}} + \varepsilon r_n r_{n-1} (V_{0,n} - E) + \varepsilon \frac{l_{\text{eff}}(l_{\text{eff}}+1)}{2m} \right], \tag{5.87}$$

where

$$l_{\text{eff}} = -\frac{1}{2} + \sqrt{\left(l + \frac{1}{2}\right)^2 + L^2}. \tag{5.88}$$

Since the Bessel functions $\tilde{i}_l$ are defined for any real l we may simply reformulate eq. (5.87) by reintroducing λ and $\tilde{i}_{l_{\text{eff}}}$. Consequently, any r^{-2}-potentials may be treated in spherical coordinates by ignoring them initially and in the end substituting $l \to l_{\text{eff}}$ in $\mathcal{R}_{fi,l}$.

Now way have gathered all the tools necessary to solve the path integral for the hydrogen atom, which we will attack in the next section.

5.2 The solution to the path integral for the hydrogen atom

We now want to calculate the path integral for the hydrogen atom. Since the Coulomb potential is singular at the origin we first have to calculate the fixed-energy amplitude so we can make use of the additional gauge freedom

as described in the previous subsection. In the continuum limit the action of the Coulomb problem is given by

$$S = \int_0^s ds \left(\frac{m\dot{\vec{x}}^2}{2\lambda} + \lambda \left(\frac{\alpha}{r} + E \right) \right), \tag{5.89}$$

where the dot means a derive with respect to s, $\dot{\vec{x}} = d\vec{x}/ds$, and the arbitrary function λ represents our gauge freedom. The central singularity can be cured by the choice $\lambda = r$. Schematically this yields

$$\begin{aligned} S\big|_{\lambda=r} &= \alpha s + \int_0^s ds \left(\frac{m\dot{\vec{x}}^2}{2r} + Er \right) \\ &\text{"}=\text{"}\ \alpha s + \frac{m}{2} \int_0^s ds \left(\dot{\sqrt{r}}^2 - \sqrt{\frac{-2E}{m}}^2 \sqrt{r}^2 \right). \end{aligned} \tag{5.90}$$

The result would look something like a harmonic oscillator with angular frequency $\omega = \sqrt{-2E/m}$ for $E < 0$, which is a problem that has already been solved in subsection 5.1.1. However, we still need to make a suitable choice of coordinates u in order to make sense of the term $\dot{\vec{x}}^2/r$. The hint lies in the expression $r = \vec{u}^2$, since, loosely speaking, the square root of a vector is a spinor. So let us write

$$z = \begin{pmatrix} u^1 + iu^2 \\ u^3 + iu^4 \end{pmatrix}, \qquad \vec{x} = z^\dagger \vec{\sigma} z = \begin{pmatrix} 2(u^1u^3 + u^2u^4) \\ 2(u^1u^4 - u^2u^3) \\ {u^1}^2 + {u^2}^2 - {u^3}^2 - {u^4}^2 \end{pmatrix}, \tag{5.91}$$

where $\vec{\sigma}$ means the Pauli matrices. Further we write

$$\vec{x} = A'(u)\,\vec{u}, \qquad A' = \begin{pmatrix} u^3 & u^4 & u^1 & u^2 \\ u^4 & -u^3 & -u^2 & u^1 \\ u^1 & u^2 & -u^3 & -u^4 \end{pmatrix}. \tag{5.92}$$

Indeed for these spinor-valued coordinates we have

$$r = \vec{u}^2. \tag{5.93}$$

In order to calculate the Jacobi-determinant that belongs to this change of coordinates we have to introduce an auxiliary dimension, parameterized by the coordinate x^4. Our choice of x^4 is guided by the symmetry of the resulting 4×4-matrix,

$$dx^4 = u^2du^1 - u^1du^2 + u^4du^3 - u^3du^4. \tag{5.94}$$

We thus obtain

$$d\vec{x} = 2A\, d\vec{u}, \qquad A = \begin{pmatrix} u^3 & u^4 & u^1 & u^2 \\ u^4 & -u^3 & -u^2 & u^1 \\ u^1 & u^2 & -u^3 & -u^4 \\ u^2 & -u^1 & u^4 & -u^3 \end{pmatrix}, \tag{5.95}$$

with the four-dimensional vector $\vec{x} = (x^1, x^2, x^3, x^4)$. The measure of the path integral may be augmented by a fourth dimension through an insertion of unity,

$$1 = \prod_{n=1}^{N} dx_{n-1}^4 \sqrt{\frac{m}{2\pi i\varepsilon\lambda_n}} \exp\left[\frac{im(x_n^4 - x_{n-1}^4)^2}{2\varepsilon\lambda_n}\right], \tag{5.96}$$

so that the measure reads

$$\mathcal{D}^4x = dx_0^4 \left(\frac{m}{2\pi i\varepsilon\lambda_N}\right)^2 \prod_{n=1}^{N-1} d^4x_n \left(\frac{m}{2\pi i\varepsilon\lambda_{n+1}}\right)^2. \tag{5.97}$$

Note that we also have to integrate over x_N^4. The action is still given by

$$S = \sum_{n=1}^{N} \left(\frac{m(\vec{x}_n - \vec{x}_{n-1})^2}{2\varepsilon\lambda_n} - \varepsilon\lambda_n(V_n - E)\right), \tag{5.98}$$

but now $\vec{x}$ means the four-dimensional vector. Now we can perform the coordinate transformation. Noting that

$$A^T A = \vec{u}^2, \tag{5.99}$$

we obtain the following expression for the metric

$$g = d\vec{x}^{\,2} = 4\vec{u}^{\,2} d\vec{u}^{\,2}, \tag{5.100}$$

while the four-dimensional integral measure reads

$$d^4x = 16\vec{u}^{\,4} d^4u. \tag{5.101}$$

Further we obtain

$$\vec{x}_n - \vec{x}_{n-1} = A(\vec{u}_n + \vec{u}_{n-1}) \cdot (\vec{u}_n - \vec{u}_{n-1}). \tag{5.102}$$

With respect to these coordinates the action and integration measure read, respectively,

$$S = \sum_{n=1}^{N} \left(\frac{m(\vec{u}_n + \vec{u}_{n-1})^2(\vec{u}_n - \vec{u}_{n-1})^2}{2\varepsilon\lambda_n} - \varepsilon\lambda_n(V_n - E)\right),$$

$$\mathcal{D}^4x = \frac{dx_0^4}{16\vec{u}_N^4}\left(\frac{2m\vec{u}_N^2}{\pi i\varepsilon\lambda_N}\right)^2 \prod_{n=1}^{N-1} d^4u_n \left(\frac{2m\vec{u}_n^2}{\pi i\varepsilon\lambda_n}\right)^2. \tag{5.103}$$

In order to regularize the Coulomb potential we set

$$\lambda_{L,n} = 1, \quad \lambda_{R,n} = r_n \qquad \Rightarrow \qquad \lambda_n = r_n = \vec{u}_n^2. \tag{5.104}$$

The expression $(\vec{u}_n + \vec{u}_{n-1})^2$ in eq. (5.103) can be approximated by $4\vec{u}_n^2$ to lowest order in $\Delta\vec{u}_n = \vec{u}_n - \vec{u}_{n-1}$. This yields

$$S = \alpha s + \sum_{n=1}^{N}\left(\frac{2m(\vec{u}_n - \vec{u}_{n-1})^2}{\varepsilon} + \varepsilon E\vec{u}_n^2\right),$$

$$\mathcal{D}^4x = \frac{dx_i^4}{16r_i^2}\left(\frac{2m}{\pi i\varepsilon}\right)^2 \prod_{n=1}^{N-1} d^4u_n \left(\frac{2m}{\pi i\varepsilon}\right)^2. \tag{5.105}$$

The whole procedure concerning the transformation of the action and the integral measure is in fact quite involved since one changes from a flat space to a space with curvature and torsion. More details on this issue can be found in Kleinert (1987, 2004).

It is now safe to perform the continuum limit. Setting

$$\mathcal{D}^4u = \left(\frac{2m}{\pi i\varepsilon}\right)^2 \prod_{n=1}^{N-1} d^4u_n \left(\frac{2m}{\pi i\varepsilon}\right)^2, \tag{5.106}$$

we obtain for the fixed-energy amplitude

$$\begin{aligned} G_{fi} &= \int_0^\infty ds \int \frac{dx_i^4}{16r_i} \int \mathcal{D}^4u\, e^{i\alpha s + 2im\int_0^s ds\left(\dot{\vec{u}}^2 - \omega^2\vec{u}^2\right)} \\ &= \int_0^\infty ds \int \frac{dx_i^4}{16r_i}\left(\frac{2m\omega}{i\pi\sin\omega s}\right)^2 e^{i\alpha s + \frac{2im\omega}{\sin\omega s}\left((\vec{u}_f^2 + \vec{u}_i^2)\cos\omega s - 2\vec{u}_f\vec{u}_i\right)}, \end{aligned} \tag{5.107}$$

where $\omega = \sqrt{-E/(2m)}$. Comparing with eq. (5.52) shows that this result is closely related to the propagator of a four-dimensional harmonic oscillator. In order to obtain an explicit expression for G_{fi} we have to perform the x^4-integration. For this purpose it is helpful to express the spinor z, defined in eq. (5.91), in spherical coordinates,

$$z = \sqrt{r}\begin{pmatrix} \cos(\theta/2)\, e^{-i(\varphi+\gamma)/2} \\ \sin(\theta/2)\, e^{i(\varphi-\gamma)/2} \end{pmatrix}, \tag{5.108}$$

where $\gamma \in [0, 4\pi[$. The definition of x^4 in eq. (5.94) then yields

$$dx^4 = r\left(\cos\theta\, d\varphi + d\gamma\right). \tag{5.109}$$

Since the endpoints in eq. (5.107) are held fixed the x_i^4-integration reduces to an integration over γ_i. The only quantity in eq. (5.107) that depends on γ_i is $\vec{u}_f\vec{u}_i$. To find the exact dependence we briefly consider the case of two dimensions, where $\vec{u}$ is given by

$$u^1 + iu^2 = \sqrt{r}e^{i\varphi/2}. \tag{5.110}$$

In this case we would obtain

$$\vec{u}_f\vec{u}_i = \sqrt{r_f r_i}\cos\frac{\varphi_f - \varphi_i}{2}, \qquad \vec{x}_f\vec{x}_i = r_f r_i\cos(\varphi_f - \varphi_i)$$

$$\Rightarrow \vec{u}_f\vec{u}_i = \sqrt{\frac{r_f r_i + \vec{x}_f\vec{x}_i}{2}}. \tag{5.111}$$

The form of eq. (5.111) shall be the role model for the following calculation. In the four-dimensional case we have with eq. (5.108)

$$\begin{aligned}
\vec{u}_f\vec{u}_i &= \sqrt{\frac{r_f r_i + \vec{x}_f\vec{x}_i}{2}}\cos\chi,\\
\cos\chi &= \sqrt{\frac{2r_f r_i}{r_f r_i + \vec{x}_f\vec{x}_i}}\left(\cos\frac{\theta_f}{2}\cos\frac{\theta_i}{2}\cos\frac{\varphi_f - \varphi_i + \gamma_f - \gamma_i}{2}\right.\\
&\qquad\left. + \sin\frac{\theta_f}{2}\sin\frac{\theta_i}{2}\cos\frac{\varphi_f - \varphi_i - \gamma_f + \gamma_i}{2}\right)\\
&= \sqrt{\frac{2r_f r_i}{r_f r_i + \vec{x}_f\vec{x}_i}}\left(\cos\frac{\theta_f - \theta_i}{2}\cos\frac{\varphi_f - \varphi_i}{2}\cos\frac{\gamma_f - \gamma_i}{2}\right.\\
&\qquad\left. - \cos\frac{\theta_f + \theta_i}{2}\sin\frac{\varphi_f - \varphi_i}{2}\sin\frac{\gamma_f - \gamma_i}{2}\right),
\end{aligned} \tag{5.112}$$

and further

$$\vec{x}_f\vec{x}_i = r_f r_i\left(\sin\theta_f\sin\theta_i\cos(\varphi_f - \varphi_i) + \cos\theta_f\cos\theta_i\right). \tag{5.113}$$

The expression for $\cos\chi$ in eqs. (5.112) may be rewritten as

$$\cos\chi = \frac{\cos(\gamma_f - \gamma_i)/2 - \frac{\cos(\theta_f+\theta_i)/2\,\sin(\varphi_f-\varphi_i)/2}{\cos(\theta_f-\theta_i)/2\,\cos(\varphi_f-\varphi_i)/2}\,\sin(\gamma_f - \gamma_i)/2}{\sqrt{1 + \left(\frac{\cos(\theta_f+\theta_i)/2\,\sin(\varphi_f-\varphi_i)/2}{\cos(\theta_f-\theta_i)/2\,\cos(\varphi_f-\varphi_i)/2}\right)^2}}. \tag{5.114}$$

This is now an expression of the form $\cos a \cos b - \sin a \sin b$, so it follows that

$$\chi = \frac{\gamma_f - \gamma_i + \beta}{2}, \tag{5.115}$$

where

$$\beta = 2 \arctan \left(\frac{\cos(\theta_f + \theta_i)/2 \, \sin(\varphi_f - \varphi_i)/2}{\cos(\theta_f - \theta_i)/2 \, \cos(\varphi_f - \varphi_i)/2} \right). \tag{5.116}$$

Using the identity

$$e^{z \cos \varphi} = \sum_{m=-\infty}^{\infty} I_m(z) e^{im\varphi} \tag{5.117}$$

and writing $s = -i\sigma$ yields the fixed-energy amplitude

$$G_{fi} = \frac{-i}{4\pi} \int_0^\infty d\sigma \left(\frac{2m\omega}{\sinh \omega\sigma} \right)^2 I_0 \left(\frac{4m\omega}{\sinh \omega\sigma} \sqrt{\frac{r_f r_i + \vec{x}_f \vec{x}_i}{2}} \right) \cdot e^{\alpha\sigma - 2m\omega(r_f + r_i) \coth \omega\sigma}. \tag{5.118}$$

This expression may be further rewritten if we define

$$k = 2m\omega, \qquad \nu = \frac{\alpha}{2\omega}, \qquad y = \omega\sigma, \tag{5.119}$$

and make use of the identity

$$I_0(z \cos(\psi/2)) = \frac{2}{z} \sum_{l=0}^{\infty} (2l+1) P_l(\cos \psi) I_{2l+1}(z) \tag{5.120}$$

to obtain

$$G_{fi} = \frac{-im}{2\pi\sqrt{r_f r_i}} \int_0^\infty \frac{dy}{\sinh y} e^{2\nu y - k(r_f + r_i) \coth y} \cdot \sum_{l=0}^{\infty} (2l+1) P_l(\cos \gamma_{fi}) I_{2l+1} \left(\frac{2k\sqrt{r_f r_i}}{\sinh y} \right), \tag{5.121}$$

where γ_{fi} means the angle formed by $\vec{x}_f$ and $\vec{x}_i$. Using eq. (5.60) yields a separation into spherical and radial parts according to eq. (5.62),

$$G_{fi} = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{Y_{lm}(\theta_f, \varphi_f)}{r_f} \frac{Y^*_{lm}(\theta_i, \varphi_i)}{r_i} \mathcal{R}_{fi,l},$$

$$\mathcal{R}_{fi,l} = -2im\sqrt{r_f r_i}\int\limits_0^\infty \frac{dy}{\sinh y} e^{2\nu y - k(r_f+r_i)\coth y} I_{2l+1}\left(\frac{2k\sqrt{r_f r_i}}{\sinh y}\right). \quad (5.122)$$

This integral may be written in closed form in terms of Whittaker functions,

$$\mathcal{R}_{fi,l} = -\frac{im}{k}\frac{\Gamma(l+1-\nu)}{\Gamma(2l+2)} W_{\nu,l+1/2}\left(2kr_f\right) M_{\nu,l+1/2}\left(2kr_i\right). \quad (5.123)$$

In the following we would rather use the Kummer functions which have already encountered in chapter 3. The Whittaker functions are related to the Kummer functions via

$$\begin{aligned} M_{a,b}(z) &= z^{b+1/2}\, e^{-z/2}\, M(1/2+b-a, 1+2b, z) \\ W_{a,b}(z) &= z^{b+1/2}\, e^{-z/2}\, U(1/2+b-a, 1+2b, z), \end{aligned}$$

which yields the radial fixed-energy amplitude

$$\begin{aligned} \mathcal{R}_{fi,l} = -\frac{im}{k}\frac{\Gamma(l+1-\nu)}{\Gamma(2l+2)} &(2kr_f)^{l+1}(2kr_i)^{l+1}\, e^{-kr_f-kr_i} \\ &\cdot U(l+1-\nu, 2l+2, 2kr_f) M(l+1-\nu, 2l+2, 2kr_f). \end{aligned} \quad (5.124)$$

From eq. (5.71) we know that the fixed-energy amplitude has isolated poles at the bound state energy levels. In eq. (5.124) the Γ function has isolated poles for negative integer arguments,

$$\nu - l - 1 = n' \in \mathbb{N} \quad \Rightarrow \quad \nu = n \in \mathbb{N},\ n > l+1. \quad (5.125)$$

Thus we are able to identify the bound states of the Coulomb system. In the limit $\nu \to n$ the Γ function behaves like

$$\begin{aligned} (-1)^{n'} n'!\, \Gamma(-n'+n-\nu) &\approx \frac{1}{n-\nu} \approx \frac{2n}{n^2-\nu^2} \\ &= \frac{2}{n}\frac{E}{E + m\alpha^2/(2n^2)} = \frac{2}{n}\frac{k^2}{2m}\frac{1}{E_n - E}, \end{aligned} \quad (5.126)$$

where we have identified the bound state energy levels $E_n = -m\alpha^2/(2n^2)$ in the last step. Let us write the fixed-energy amplitude in the form of eq. (5.71),

$$\mathcal{R}_{fi,l} = \sum_{n=l+1}^{\infty} \frac{1}{i}\frac{R_{nl}(r_f) R^*_{nl}(r_i)}{E_n - E} \ + \ \int \big(\text{continuum states}\big). \quad (5.127)$$

Comparing with eq. (5.124) shows that we first have to express U in terms of M. The identity

$$U(a,b,z) = \frac{\pi}{\sin \pi b}\left(\frac{M(a,b,z)}{\Gamma(1+a-b)\Gamma(b)} - z^{1-b}\frac{M(1+a-b,2-b,z)}{\Gamma(a)\Gamma(2-b)}\right) \tag{5.128}$$

may be rewritten for $-a \in \mathbb{N}$ as

$$U(a,b,z) = (-1)^a \frac{\Gamma(b-a)}{\Gamma(b)} M(a,b,z) + z^{1-b}\frac{\Gamma(b-1)}{\Gamma(a)} M(1+a-b,2-b,z), \tag{5.129}$$

where we have used that

$$\frac{\pi}{\sin \pi z} = \Gamma(1-z)\Gamma(z) = (-1)^n \Gamma(1-n-z)\Gamma(n+z). \tag{5.130}$$

However, since $-a \in \mathbb{N}$, the second term on the right-hand side in eq. (5.129) vanishes so that

$$\begin{aligned}\mathcal{R}_{fi,l} = \sum_{n=l+1}^{\infty} \frac{1}{i}\frac{k}{n}\frac{(2kr_f)^{l+1}(2kr_i)^{l+1}}{E_n - E} e^{-kr_f - kr_i} \frac{\Gamma(n+l+1)}{\Gamma(n-l)\Gamma^2(2l+2)} \\ \cdot M(l+1-n,2l+2,2kr_f) M(l+1-n,2l+2,2kr_i) \\ + \int \big(\text{continuum states}\big).\end{aligned} \tag{5.131}$$

As before we express the Kummer function in terms of the associated Laguerre polynomials,

$$M(-n,\alpha,z) = \frac{\Gamma(n+1)\Gamma(\alpha)}{\Gamma(n+\alpha)} L_n^{\alpha-1}(z), \tag{5.132}$$

and, for $k = \sqrt{-2mE_n} = m\alpha/n = C_n$, obtain the same result for the radial bound state wave functions as in eq. (3.31),

$$g_{nl}(r) = \sqrt{\frac{C_n}{n}\frac{\Gamma(n-l)}{\Gamma(n+l+1)}}\,(2C_n r)^{l+1} e^{-C_n r} L_{n-l-1}^{2l+1}(2C_n r). \tag{5.133}$$

The complete, stationary wave function reads

$$\psi_{nlm}(\vec{x}) = \frac{g_{nl}(r)}{r} Y_{lm}(\theta,\varphi). \tag{5.134}$$

The continuum or scattering states may be obtain by the replacements

$$\omega \to -i\omega, \qquad k \to -ik, \qquad \nu \to i\nu, \tag{5.135}$$

where now $\omega = \sqrt{E/(2m)}$. The radial fixed-energy amplitude now reads

$$\mathcal{R}_{fi,l} = \frac{m}{k}\,\frac{\Gamma(l+1-i\nu)}{\Gamma(2l+2)} W_{i\nu,l+1/2}\left(-2ikr_f\right) M_{i\nu,l+1/2}\left(-2ikr_i\right), \tag{5.136}$$

and the discontinuity across the branch cut then yields the continuum states,

$$\begin{aligned}
\mathrm{disc}\left(\mathcal{R}_{fi,l}\right) &= 2\ \mathrm{Re}\left\{\mathcal{R}_{fi,l}\right\} \\
&= \frac{m}{k}\,\frac{\Gamma(l+1-i\nu)}{\Gamma(2l+2)} W_{i\nu,l+1/2}\left(-2ikr_f\right) M_{i\nu,l+1/2}\left(-2ikr_i\right) \\
&\qquad + \frac{m}{k}\,\frac{\Gamma(l+1+i\nu)}{\Gamma(2l+2)} W_{-i\nu,l+1/2}\left(2ikr_f\right) M_{-i\nu,l+1/2}\left(2ikr_i\right) \\
&= \frac{m}{k}\,\frac{M_{i\nu,l+1/2}\left(-2ikr_i\right)}{\Gamma(2l+2)}\big[\Gamma(l+1-i\nu) W_{i\nu,l+1/2}\left(-2ikr_f\right) + \\
&\qquad + (-1)^{l+1}\Gamma(l+1+i\nu) W_{-i\nu,l+1/2}\left(2ikr_f\right)\big].
\end{aligned} \tag{5.137}$$

The expression in square brackets in the last line may be reformulated by means of the identity

$$\begin{aligned}
M_{\kappa,\mu}(z) = \frac{\Gamma(2\mu+1)}{\Gamma(1/2+\mu+\kappa)} e^{i\pi\kappa} e^{-i\pi(\mu+1/2)} W_{\kappa,\mu}(z) \\
+ \frac{\Gamma(2\mu+1)}{\Gamma(1/2+\mu-\kappa)} e^{i\pi\kappa} W_{-\kappa,\mu}(z\, e^{i\pi}),
\end{aligned} \tag{5.138}$$

to yield

$$\mathrm{disc}\left(\mathcal{R}_{fi,l}\right) = \frac{m}{k}\,\frac{\left|\Gamma(l+1-i\nu)\right|^2}{\Gamma^2(2l+2)} e^{\pi\nu} M_{i\nu,l+1/2}\left(-2ikr_f\right) M_{-i\nu,l+1/2}\left(2ikr_i\right). \tag{5.139}$$

The radial wave functions can now be derived from the completeness relation,

$$\int_0^\infty \frac{dE}{2\pi}\,\mathrm{disc}\left(\mathcal{R}_{fi,l}\right) + \sum_n g_{nl}(r_f) g^*_{nl}(r_i) = \delta(r_f - r_i), \tag{5.140}$$

where

$$\int_0^\infty \frac{dE}{2\pi}\,\mathrm{disc}\left(\mathcal{R}_{fi,l}\right) = \int_0^\infty dk\, h_{kl}(r_f) h^*_{kl}(r_i). \tag{5.141}$$

Since $dE = kdk/m$ we may combine this relation with eq. (5.139) to obtain the complete, stationary continuum wave functions,

$$\chi_{klm}(\vec{x}) = \frac{h_{kl}(r)}{r} Y_{lm}(\theta, \varphi), \tag{5.142}$$

with the radial wave functions

$$h_{kl}(r) = \frac{|\Gamma(l+1-i\nu)|}{\sqrt{2\pi}\,\Gamma(2l+2)} e^{\pi\nu/2} M_{i\nu,l+1/2}\left(-2ikr\right), \tag{5.143}$$

or expressed in terms of the Kummer functions and Coulomb wave functions, respectively,

$$\begin{aligned} h_{kl}(r) &= \frac{|\Gamma(l+1-i\nu)|}{\sqrt{2\pi}\,\Gamma(2l+2)} e^{\pi\nu/2+ikr} (2kr)^{l+1} M(l+1-i\nu, 2l+2, -2ikr) \\ &= \sqrt{\frac{2}{\pi}}\, F_l(-\nu, kr), \end{aligned} \tag{5.144}$$

where we have dropped an unobservable prefactor of $(-i)^{l+1}$ as compared to eq. (5.143). This is the same result we already found in chapter 3 without having to derive the normalization factor.

Chapter 6

Radiative Corrections

In this chapter we will derive the radiative corrections of order α^5 to the relativistic energy levels given in chapter 4. For this purpose it will be necessary to introduce some concepts of quantum field theory (QFT) so we can make use of the quantum action formalism. This will allow us to derive a modified version of the Dirac equation (4.41) that includes quantum corrections.

We will consider an electron moving in a background Coulomb field and then calculate quantum corrections for the interaction of the electron with the background field and with its own electromagnetic field. More elaborate calculations concerning the vacuum polarization and the 3-point vertex function can be found in appendix A.

6.1 Quantum electrodynamics

In this section we proceed from the theory of quantum mechanics used in the previous chapters to the theory of quantum electrodynamics (QED). We elaborate some basic principles of QFT which are needed to calculate the lowest order radiative corrections to the relativistic energy levels. The calculations in this section follow or are inspired by Feynman and Hibbs (1965), Feynman (1962), Itzykson and Zuber (1980), Peskin and Schroeder (1995), Kleinert (2004), Srednicki (2007).

6.1.1 Towards quantum field theory

In previous chapters we have considered the quantum properties of an electron, both relativistically and non-relativistically, in the fixed background field of the much heavier proton, i.e. we treated the electromagnetic field like a classical field. The results of the relativistic quantum theory of the

electron deviates from experiment by a fraction of $\sim 3 \cdot 10^{-6}$. The main part of the deviation is due to the quantum nature of the electromagnetic field itself.

In order to treat the quantum properties of the electromagnetic field, we consider the classical action of a free 4-vector potential $A = (\Phi, \vec{A})$,

$$S[t_f, A_f; t_i, A_i] = \frac{1}{2} \int_{t_i}^{t_f} dt \int d^3x \, A_\mu \left(\eta^{\mu\nu} \partial^2 - \partial^\mu \partial^\nu \right) A_\nu, \tag{6.1}$$

where $A_{f/i} = A(t_{f/i}, \vec{x})$. While it is totally legitimate to use the action (6.1) for the electromagnetic field to calculate its propagator from an expression like,

$$\int_{A_i}^{A_f} \mathcal{D}A \, e^{iS[t_f, A_f; t_i, A_i]}, \tag{6.2}$$

it will not be useful to do so in many instances. The explicit choice of t_i and t_f specifies a reference frame and thus breaks the Lorentz covariance which is present in the classical theory. In the hydrogen atom relativistic corrections represent only a small contribution to the essentially non-relativistic nature of the system and often times we will have to choose the CMS as reference frame. In many cases in this chapter, however, we will perform fully relativistic calculations and thus it would be very useful to think about a relativistically covariant alternative to eqs. (6.1) and (6.2).

Let us start by defining an infinitesimal 4-volume element of spacetime δ such that

$$\int d^4x = \sum_x \delta, \tag{6.3}$$

where the sum goes over all resulting cells in the discretized spacetime. Now let us consider some complex scalar field ψ and an integration of the form

$$\int \mathcal{D}\psi \mathcal{D}\psi^\dagger \propto \prod_x d\psi_x d\psi_x^\dagger, \tag{6.4}$$

where we have written $\psi_x = \psi(x)$. This integral is no longer a path integral like in chapter 5 but a functional integral, since we now integrate over all configurations of a field ψ defined on the whole spacetime. Let us normalize the functional integral measure in the following way:

$$1 = \int \mathcal{D}\psi \mathcal{D}\psi^\dagger \, e^{iS_0},$$

$$S_0 = \sum_x |\psi_x|^2 \delta \approx \int d^4x \, |\psi_x|^2,$$
$$\mathcal{D}\psi\mathcal{D}\psi^\dagger = \prod_x \frac{d\psi_x d\psi_x^\dagger}{2\pi i/\delta}, \tag{6.5}$$

For the verification of the first line one needs to make the replacement $\delta \to \delta + i0^+$. This functional integral satisfies the relation

$$\int \mathcal{D}\psi\mathcal{D}\psi^\dagger \, \psi(x_2)\psi^\dagger(x_1) \, e^{iS_0} = \begin{cases} 0, & x_1 \neq x_2 \\ i/\delta, & x_1 = x_2 \end{cases} . \tag{6.6}$$

The right-hand side of this equation evaluates to either zero or infinity in the continuum limit. From eq. (6.3) it further follows that the spacetime integral evaluates to i so that we may write

$$\int \mathcal{D}\psi\mathcal{D}\psi^\dagger \, \psi(x_2)\psi^\dagger(x_1) \, e^{iS_0} = i\delta^4(x_2 - x_1). \tag{6.7}$$

Using this representation of the δ function we can find an alternative way to calculate the causal propagator according to eq. (5.55) for a system with Hamiltonian $\hat{H}$,

$$\begin{aligned} K_{fi}^{>} &= \frac{-i}{-i\partial_{t_f} + \hat{H}_f - i0^+} \delta^4(x_f - x_i) \\ &= \frac{\int \mathcal{D}\psi\mathcal{D}\psi^\dagger \, \frac{1}{i\partial_{t_f} - \hat{H}_f + i0^+} \psi(x_f)\psi^\dagger(x_i) \, e^{iS_0}}{\int \mathcal{D}\psi\mathcal{D}\psi^\dagger \, e^{iS_0}} \\ &= \frac{\int \mathcal{D}\psi\mathcal{D}\psi^\dagger \, \psi(x_f)\psi^\dagger(x_i) \, e^{iS}}{\int \mathcal{D}\psi\mathcal{D}\psi^\dagger \, e^{iS}}, \end{aligned} \tag{6.8}$$

where now

$$S = \int d^4x \, \psi^\dagger(i\partial_t - \hat{H} + i0^+)\psi. \tag{6.9}$$

In the second line in eq. (6.8) we have made a change of variables, $\psi \to (i\partial_t - \hat{H} + i0^+)\psi$. The resulting new factors emerging from the functional integral measure are canceled out by the numerator.

Let us summarize our recent findings: In chapter 5 we have calculated the non-relativistic, causal propagator $K_{fi}^{>}$ by considering the two events x_i and x_f, where $t_f \geq t_i$, and integrating over all spatial paths which connect $\vec{x}_i$ with $\vec{x}_f$, weighted with e^{iS}. Now we have found that the causal propagator can also be calculated by defining a Lorentz invariant action (6.9) in which

a Lagrangian density is integrated over the whole spacetime. The causal propagator then emerges from the expectation value $\langle\psi(x_f)\psi^\dagger(x_i)\rangle$, which measures the correlation between excitations of the field ψ at the two events x_i and x_f. In other words, the causal propagator $K^>_{fi}$ to find a particle at x_f, which had been found before at x_i, is given by the expectation value $\langle\psi(x_f)\psi^\dagger(x_i)\rangle$ that an excitation at x_i of the field ψ is correlated with an excitation at x_f. The field ψ is in this case not the Schrödinger wave function of course but rather connected to an operator $\hat{\psi}^\dagger(x)$ which adds to a multi-particle state $|\Phi\rangle$ a particle of species ψ at the event x. Correspondingly, the operator $\hat{\psi}(x)$ removes such a particle at the event x.

6.1.2 Electrons in an external potential

In the previous subsection we have introduced the concept of QFT to calculate causal propagators (in the following we will simply call them propagators) in a relativistic context. Here we will as a first step consider a scenario which is already familiar from the quantum mechanical treatment in the previous chapters: the interaction of an electron with an external 4-vector potential V. As before the electron is treated as a test charge of reduced mass m in this classical potential and we assume that the Dirac equation corresponding to this problem may be solved analytically.

According to eq. (6.9) the action of such a system reads

$$S_{\Psi,V} = \int d^4x\, \bar{\Psi}(-\mathcal{H}_{\Psi,V})\Psi, \qquad \mathcal{H}_{\Psi,V} = -i\partial\!\!\!/ + eV\!\!\!/ + m, \tag{6.10}$$

where Ψ is a Dirac spinor representing the electron field, which is moreover Grassman-valued, i.e. it obeys the following anti-commuting algebra,

$$\{\Psi(x_1), \Psi(x_2)\} = 0, \qquad \{\Psi(x_1), \bar{\Psi}(x_2)\} = 0. \tag{6.11}$$

Functional derivatives of Ψ and $\bar{\Psi}$ are hence calculated according to

$$\begin{aligned} \delta_{\Psi(x_1)}\Psi(x_2) &= -\Psi(x_2)\overleftarrow{\delta}_{\Psi(x_1)} = \delta^4(x_1 - x_2), \\ \delta_{\bar{\Psi}(x_1)}\bar{\Psi}(x_2) &= -\bar{\Psi}(x_2)\overleftarrow{\delta}_{\bar{\Psi}(x_1)} = \delta^4(x_1 - x_2), \\ \delta_{\Psi(x_1)}\bar{\Psi}(x_2) &= \delta_{\bar{\Psi}(x_1)}\Psi(x_2) = 0. \end{aligned} \tag{6.12}$$

In this relativistic, field theoretic context the expectation value of an operator is calculated via

$$\langle\hat{O}[\bar{\Psi}, \Psi]\rangle = \frac{\int \mathcal{D}\Psi\mathcal{D}\bar{\Psi}\, O[\bar{\Psi}, \Psi]\, e^{iS_{\Psi,V}[\bar{\Psi},\Psi]}}{\int \mathcal{D}\Psi\mathcal{D}\bar{\Psi}\, e^{iS_{\Psi,V}[\bar{\Psi},\Psi]}}. \tag{6.13}$$

The denominator in this expression is an integral over all possible field configurations and hence represents the partition function Z of the theory,

$$Z = \int \mathcal{D}\Psi\mathcal{D}\bar{\Psi}\, e^{iS_{\Psi,V}[\bar{\Psi},\Psi]}. \tag{6.14}$$

Defining now Dirac-spinor valued Grassman fields η and $\bar{\eta}$ as external sources for the fields $\bar{\Psi}$ and Ψ, respectively, we can turn the partition function Z into a generating functional $Z[\eta,\bar{\eta}]$ for correlation functions,

$$Z[\eta,\bar{\eta}] = \int \mathcal{D}\Psi\mathcal{D}\bar{\Psi}\, e^{iS_{\Psi,V}[\bar{\Psi},\Psi]+\int d^4x\,\left(\bar{\Psi}\eta+\bar{\eta}\Psi\right)}. \tag{6.15}$$

However, it is even more practical to define the connected generating functional $W[\eta,\bar{\eta}]$ via

$$W[\eta,\bar{\eta}] = \ln Z[\eta,\bar{\eta}], \tag{6.16}$$

so that expectation values may be calculated according to eq. (6.13) very conveniently by differentiating W with respect to η and $\bar{\eta}$,

$$\langle\hat{O}[\bar{\Psi},\Psi]\rangle = O[-\delta_\eta,\delta_{\bar{\eta}}]W[\eta,\bar{\eta}]\Big|_{\eta=\bar{\eta}=0}. \tag{6.17}$$

The minus sign in front of δ_η is due to the anti-commuting nature of the Grassman fields. Completing the square in the exponent of the generating functional and shifting variables like in eqs. (5.33) and (5.34) yields

$$\begin{aligned} Z[\eta,\bar{\eta}] &= Z_0\, e^{\int d^4x d^4x'\,\bar{\eta}(x)S_V(x,x')\eta(x')}, \\ Z_0 &= \int \mathcal{D}\Psi\mathcal{D}\bar{\Psi}\, e^{iS_{\Psi,V}[\bar{\Psi},\Psi]} \equiv 1, \\ S_V(x,x') &= \frac{1}{-\mathcal{H}_{\Psi,V}+i0^+} i\delta(x-x'), \end{aligned} \tag{6.18}$$

where we have rescaled the functional integral measure such that the partition function, i.e. the generating functional in the absence of external sources, is equal to unity, $Z[0,0] = Z_0 = 1$. Obviously the quantity S_V which appears in the exponent of the generating functional is the (causal) propagator of the electron under the influence of the classical, external potential V.

An important quantity which may be readily calculated from eqs. (6.18) is the electron propagator S in the absence of the external potential, $V = 0$,

$$\begin{aligned} S_{V=0}(x_f,x_i) &\equiv S(x_f-x_i) \\ &= \frac{1}{i\partial\!\!\!/_f - m + i0^+} i\delta(x_f-x_i) \end{aligned}$$

$$
\begin{aligned}
&= \frac{-i\not{\partial}_f - m}{-\partial_f^2 + m^2 - i0^+} i\delta(x_f - x_i) \\
&= i \int \frac{d^4p}{(2\pi)^4} \frac{(\not{p} - m) e^{ip(x_f - x_i)}}{p^2 + m^2 - i0^+} \\
&= \int \widetilde{dp}\, e^{-iE|T|} \sum_{s=\pm} \Big[\Theta(T) \Psi^{(+)}_{s,\vec{p}}(\vec{x}_f) \bar{\Psi}^{(+)}_{s,\vec{p}}(\vec{x}_i) \\
&\qquad\qquad - \Theta(-T) \Psi^{(-)}_{s,\vec{p}}(\vec{x}_f) \bar{\Psi}^{(-)}_{s,\vec{p}}(\vec{x}_i) \Big], \qquad (6.19)
\end{aligned}
$$

where $T = t_f - t_i$ as usual and we have used the time-independent, free wave functions $\Psi^{(\pm)}_{s,\vec{p}}(\vec{x})$ defined in eqs. (4.37) and the relativistic energy $E = (\vec{p}^{\,2} + m^2)^{1/2}$. Note that for $V = 0$ the theory becomes invariant under spacetime translations so that the propagator only depends on the difference $x_f - x_i$ in this case. While remaining integral in eq. (6.19) can be done in closed form, the resulting expression is rarely useful so we would like to keep it in the current form.

Apparently the (causal) propagator has picked up contributions from paths which travel backwards in time. In the case of fermions like the electron these correspond to antiparticle contributions but they are also present in the photon propagator. It is now clear that we would lack these contributions had we calculated the propagator from a functional integral like in eq. (6.2).

6.1.3 The free electromagnetic field

Our second step towards the full theory of QED is to consider the QFT of the free electromagnetic field, i.e. the theory of non-interacting photons. According to eq. (6.9) the action for this system is simply given by the classical one,

$$S_A = \int d^4x \, \frac{1}{2} A_\mu (\eta^{\mu\nu} \partial^2 - \partial^\mu \partial^\nu) A_\nu, \qquad (6.20)$$

where A is the well known 4-vector potential. The action S_A is invariant under the gauge transformation,

$$A \to A + \partial\Gamma, \qquad (6.21)$$

for some arbitrary function $\Gamma(x)$ of spacetime. The gauge freedom of the photon field A allows us to replace the term $\partial^\mu \partial^\nu$ in its Hamiltonian with

some operator $\mathcal{G}^{\mu\nu}$ which is in accord with the choice of gauge and drops out in gauge invariant expressions,

$$S_A = \int d^4x \, \frac{1}{2} A_\mu (-\mathcal{H}_A^{\mu\nu}) A_\nu, \qquad \mathcal{H}_A^{\mu\nu} = -\eta^{\mu\nu}\partial^2 - \mathcal{G}^{\mu\nu}. \tag{6.22}$$

Like in eqs. (6.15) and (6.16) we define the generating functional of the free electromagnetic field in the presence of a 4-vector valued, external source J and the connected generating functional as

$$Z[J] = \int \mathcal{D}A \, e^{iS_A[A] + \int d^4x \, J^\mu A_\mu}, \qquad W[J] = \ln Z[J]. \tag{6.23}$$

As for eqs. (6.18) we complete the square in the exponent of the generating functional and shift variables to obtain

$$\begin{aligned} Z[J] &= Z_0 \, e^{\int d^4x d^4x' \, \frac{1}{2} J^\mu(x) D_{\mu\nu}(x-x') J^\nu(x')}, \\ Z_0 &= \int \mathcal{D}A \, e^{iS_A[A]} \equiv 1, \\ D_{\mu\nu}(x-x') &= \frac{1}{-\mathcal{H}_A^{\mu\nu}(x) + i0^+} i\delta(x-x'), \end{aligned} \tag{6.24}$$

where we have scaled the functional integral measure such that the partition function is equal to unity, $Z[0] = Z_0 = 1$. Expectation values of operators $\langle \hat{O}[A] \rangle$ may be calculated analogous to eq. (6.17) by differentiating W with respect to J,

$$\langle \hat{O}[A] \rangle = O[\delta_J] W[J] \Big|_{J=0}. \tag{6.25}$$

Calculating the free photon propagator D is fairly easy. However, we first have to inspect the influence of gauge freedom on the propagator and the partition function more closely. Focusing on the partition function we see from eq. (6.23) that in the absence of the source J a gauge transformation according to eq. (6.21) yields

$$Z[0] = \int \mathcal{D}A \, e^{iS_A[A]} = \int \mathcal{D}A' \, e^{iS_A[A']}. \tag{6.26}$$

Simply renaming the field $A' \to A$ shows that the partition function is invariant under gauge transformations. This remains true if a source J is added since it may be defined to couple to the transformed field instead. Since two fields A and A' correspond to the same physical situation if they are related to each other by a gauge transformation we have to fix a gauge to enforce

that every physically inequivalent field configuration is counted only once. To do this formally we will use the method of Faddeev and Popov (1967), i.e. we insert unity into the partition function (6.26) in the form

$$1 = \int \mathcal{D}\Gamma\, \delta[G[A']] \left| \det \frac{\delta G[A']}{\delta \Gamma} \right|, \qquad A' = A + \partial\Gamma, \tag{6.27}$$

where $\delta[f]$ is the functional generalization of the δ-function and $G[A']$ is some condition that the gauge transformed field A' has to satisfy. E.g. Lorenz-gauge is enforced by $G[A'] = \partial_\mu A'^\mu$ while Coulomb-gauge needs $G[A'] = \vec{\nabla}\vec{A}'$, etc. In the following the determinant in eq. (6.27) will be independent of A so that we can treat it as a constant under the functional integral. Inserting eq. (6.27) into eq. (6.26) then yields

$$Z[0] = \int \mathcal{D}A\mathcal{D}\Gamma \left| \det \frac{\delta G[A']}{\delta \Gamma} \right| \delta[G[A']]\, e^{iS_A[A]}. \tag{6.28}$$

Transforming $A \to A'$ and then renaming yields

$$Z[0] = \left(\int \mathcal{D}\Gamma \left| \det \frac{\delta G[A]}{\delta \Gamma} \right| \right) \int \mathcal{D}A\, \delta[G[A]]\, e^{iS_A[A]}. \tag{6.29}$$

We have thus managed to formally extract an infinitely large prefactor out of the functional integral and instead integrate only over physically inequivalent field configurations. Since such a prefactor always cancels out when an expectation value is calculated we may simply redefine the generating functional and the partition function as

$$\begin{aligned} Z[J] &= Z_0\, e^{\int d^4x d^4x' \, \frac{1}{2} J^\mu(x) D_{\mu\nu}(x-x') J^\nu(x')}, \\ Z_0 &= \int \mathcal{D}A\, \delta[G[A]]\, e^{iS_A[A]} \equiv 1, \end{aligned} \tag{6.30}$$

where a proper rescaling of the functional integral measure has also been performed. Let us now calculate the free photon propagator. First, in the Coulomb gauge, $\vec{\nabla}\vec{A} = 0$, we have

$$D_{i0}(x) = 0, \qquad D_{ij}(x) = \left(\delta_i{}^k - \frac{\partial_i \partial^k}{\Delta} \right) D_{kj}(x). \tag{6.31}$$

Hence the propagator reads

$$D_{00}(x_f - x_i) = \frac{1}{-\Delta_f^2}\, i\delta^4(x_f - x_i)$$

$$
\begin{aligned}
&= i\delta(T)\int \frac{d^3k}{(2\pi)^3}\frac{e^{i\vec{k}\vec{X}}}{\vec{k}^2} = \frac{i\delta(T)}{4\pi|\vec{X}|},\\
D_{ij}(x_f-x_i) &= \left(\eta_{ij}-\frac{\partial_{f,i}\partial_{f,j}}{\Delta_f}\right)\frac{1}{\partial_f^2+i0^+}\,i\delta^4(x_f-x_i)\\
&= i\int\frac{d^4k}{(2\pi)^4}\left(\eta_{ij}-\frac{k_ik_j}{\vec{k}^2}\right)\frac{e^{ik(x_f-x_i)}}{-k^2+i0^+}\\
&= \int\widetilde{dk}\,e^{i\vec{k}\vec{X}}\left(\eta_{ij}-\frac{k_ik_j}{\vec{k}^2}\right)\left(\Theta(T)e^{-i\omega T}+\Theta(-T)e^{i\omega T}\right), \quad (6.32)
\end{aligned}
$$

where $\vec{X}=\vec{x}_f-\vec{x}_i$ as well as $\omega=|\vec{k}|$ and $\widetilde{dk}=d^3k/((2\pi)^3 2\omega)$. While the remaining integral in eqs. (6.32) can be done in closed form, the resulting expression is rarely useful so we would like to keep it in the current form. Also very important is Lorenz gauge, $\partial_\mu A^\mu=0$, where the propagator satisfies

$$
D_{\mu\nu}(x) = \left(\delta_\mu{}^\rho-\frac{\partial_\mu\partial^\rho}{\partial^2}\right)D_{\rho\nu}(x), \quad (6.33)
$$

so that we obtain

$$
\begin{aligned}
D_{\mu\nu}(x_f-x_i) &= \left(\eta_{\mu\nu}-\frac{\partial_\mu\partial_\nu}{\partial^2}\right)\frac{1}{\partial_f^2+i0^+}\,i\delta^4(x_f-x_i)\\
&= i\int\frac{d^4k}{(2\pi)^4}\left(\eta_{\mu\nu}-\frac{k_\mu k_\nu}{k^2}\right)\frac{e^{ik(x_f-x_i)}}{-k^2+i0^+}\\
&= \int\widetilde{dk}\,e^{i\vec{k}\vec{X}}\left(\eta_{\mu\nu}-\frac{k_\mu k_\nu}{k^2}\right)\left(\Theta(T)e^{-i\omega T}+\Theta(-T)e^{i\omega T}\right).
\end{aligned} \quad (6.34)
$$

Finally, in Feynman gauge we have

$$
\begin{aligned}
D_{\mu\nu}(x_f-x_i) &= \frac{\eta_{\mu\nu}}{\partial_f^2+i0^+}\,i\delta^4(x_f-x_i)\\
&= i\eta_{\mu\nu}\int\frac{d^4k}{(2\pi)^4}\frac{e^{ik(x_f-x_i)}}{-k^2+i0^+}\\
&= \eta_{\mu\nu}\int\widetilde{dk}\,e^{i\vec{k}\vec{X}}\left(\Theta(T)e^{-i\omega T}+\Theta(-T)e^{i\omega T}\right). \quad (6.35)
\end{aligned}
$$

6.1.4 Quantum electrodynamics

The theory of QED emerges when the electron field from subsection 6.1.2 is allowed to interact with the free photon field from subsection 6.1.3. In the

case of the hydrogen atom it is very helpful to separate the photon field into a classical, external potential V like in subsection 6.1.2, which represents the Coulomb potential and a quantum field A which give rise to the Lamb shift. In the following, however, we will only consider the quantum field A to clear up the notation. The external potential can be restored anytime by the replacement $A \to A + V$.

Naively we might write the full QED action as,

$$S_{\text{naive}} = S_{\Psi,0} + S_A + S_{\text{int}}, \qquad S_{\text{int}} = -e \int d^4x \, \bar{\Psi} \not{A} \Psi, \tag{6.36}$$

where $S_{\Psi,0}$ and S_A are given in eqs. (6.10), with $V = 0$, and (6.22), respectively. However, the interaction of photons with matter gives the fields A and Ψ and parameters e and m a different meaning than before. In subsections 6.1.2 and 6.1.3 we could identity these quantities with observables like field strength, electron charge and (reduced) mass. The interaction represented by S_{int}, however, includes self interaction of the electron with its own electromagnetic field, thus effectively changing its mass from m. But the interaction with the own electromagnetic field also changes how the electron interacts with photons from other sources and hence effectively changes e. The fields A and Ψ are effected in the same way. To account for this change of parameters due to the omnipresent interaction we have to replace the action (6.36) by

$$S = \int d^4x \, \left[\frac{Z_A}{2} A_\mu (\eta^{\mu\nu} \partial^2 + \mathcal{G}^{\mu\nu}) A_\nu + \bar{\Psi} (Z_\Psi i \not{\partial} - Z_m m - Z_e e \not{A}) \Psi \right]. \tag{6.37}$$

This action is obtained from eq. (6.36) by simply rescaling $A \to Z_A^{1/2} A$ and similar for Ψ, e and m. Perturbative calculations show that $Z_i = 1 + O(\alpha)$. We may adjust the Z-factors such that A, Ψ, e and m take certain values under certain conditions, i.e. we impose renormalization conditions. E.g. we might want to adjust m such that it equals the measured (reduced) mass of an electron. Other normalizations might be useful as well, depending on the situation.

Since we will have to resort to perturbation theory to calculate radiative corrections to the hydrogen energy levels we have to separate the action (6.37) into a part which we now how to handle analytically plus a perturbative part which we call S_{int}. For the present case we set

$$S = S_A + S_\Psi + S_{\text{int}} \tag{6.38}$$

with the the same S_A and $S_\Psi = S_{\Psi,0}$ as in subsections 6.1.2 and 6.1.3,

$$S_A = \int d^4x \, \frac{1}{2} A_\mu (-\mathcal{H}_A^{\mu\nu}) A_\nu, \qquad \mathcal{H}_A^{\mu\nu} = -\eta^{\mu\nu} \partial^2 - \mathcal{G}^{\mu\nu},$$

$$S_\Psi = \int d^4x\, \bar\Psi(-\mathcal{H}_\Psi)\Psi, \qquad\qquad \mathcal{H}_\Psi = -i\partial\!\!\!/ + m, \tag{6.39}$$

and with the interaction part

$$S_{\text{int}} = \int d^4x \left[\frac{1}{2}A_\mu(-\delta\mathcal{H}_A^{\mu\nu})A_\nu + \bar\Psi(-\delta\mathcal{H}_\Psi - Z_e e A\!\!\!/)\Psi\right], \tag{6.40}$$

where, setting $Z_i = 1 + \delta_i$,

$$\delta\mathcal{H}_A^{\mu\nu} = -\delta_A(\eta^{\mu\nu}\partial^2 + \mathcal{G}^{\mu\nu}), \qquad \delta\mathcal{H}_\Psi = -\delta_\Psi i\partial\!\!\!/ + \delta_m m. \tag{6.41}$$

Thus we have separated the full QED action (6.37) into a part containing the free electromagnetic and electron fields and into another part containing the interaction of electrons with the electromagnetic field and the corresponding rescaling terms.

A peculiarity of this separation is that in perturbative calculations the contributions from highly energetic sub-processes cause certain correction terms to become infinitely large. However, all problematic terms of this kind may be regulated such that they diverge only in a well defined limit and thus can be absorbed into the renormalizing Z-factors.

Historically the appearance of these divergences and the necessity of renormalization represented a major problem for the theory of QED, which was finally solved by Tomonaga, Schwinger, Feynman and Dyson.

While it is surprising at first that e.g. the correction term $\delta_m m$ to the electron mass is infinitely large, one might consider the following: Say, that we have adjusted the Z-factors such that the parameter m is equal to the free electron mass as measured in experiment, $m = m_{\text{ex,free}}$. Say further, we compare the mass of a free electron to that of an electron in a bound state,

$$m_{\text{ex,free}} - m_{\text{ex,bound}} = (\delta_{m,\text{free}} - \delta_{m,\text{bound}})m_{\text{ex,free}}. \tag{6.42}$$

We now find that the infinite parts in the Z-factors cancel out in this expression since highly energetic processes are insensitive to whether the electron is bound or not. The remaining correction is indeed small and in excellent agreement with experiment. The tricky part in the separation in eq. (6.38) is that S_Ψ actually describes an unphysical "uncharged electron". A physical electron with charge $-e$, however, is always interacting with its own electromagnetic field which moreover becomes stronger the closer the electron is approached. Therefore self interaction becomes more important the higher the energy of the photons under consideration. Consequently, the mass difference relative to the "uncharged electron" becomes infinite in the absence of a cut off (or a different regularization) on the photon energy.

Let us now proceed by inspecting the action of QED a little closer. While the naive action S_{naive} is invariant under the simultaneous gauge transformation,

$$A \to A + \partial\Gamma, \qquad \Psi \to e^{iq\Gamma}\Psi, \qquad \bar{\Psi} \to e^{-iq\Gamma}\bar{\Psi}, \tag{6.43}$$

for some arbitrary function $\Gamma(x)$ of spacetime, this is only true for S in eq. (6.37) if $Z_\Psi = Z_e$. Fortunately this is ensured by an identity due to (Ward, 1950) so that the action S is also invariant under the gauge transformation (6.43).

Following the procedure of subsections 6.1.2 and 6.1.3 we define the generating functional $Z[\eta, \bar{\eta}, J]$ and the connected generating functional $W[\eta, \bar{\eta}, J]$ of QED using the Dirac-spinor and 4-vector valued, external sources η, $\bar{\eta}$ and J,

$$\begin{aligned} Z[\eta, \bar{\eta}, J] &= \int \mathcal{D}\Psi\mathcal{D}\bar{\Psi}\mathcal{D}A\, \delta[G[A]]\, e^{iS[\bar{\Psi},\Psi,A]+\int d^4x \left(\bar{\Psi}\eta+\bar{\eta}\Psi+J^\mu A_\mu\right)}, \\ W[\eta, \bar{\eta}, J] &= \ln Z[\eta, \bar{\eta}, J]. \end{aligned} \tag{6.44}$$

As before expectation values may be calculated very conveniently by differentiating W with respect to η, $\bar{\eta}$ and J,

$$\langle \hat{O}[\bar{\Psi}, \Psi, A] \rangle = O[-\delta_\eta, \delta_{\bar{\eta}}, \delta_J] W[\eta, \bar{\eta}, J]\Big|_{\eta=\bar{\eta}=J=0}. \tag{6.45}$$

As usual we complete the square in the exponent of the generating functional and shift variables to obtain

$$\begin{aligned} Z[\eta, \bar{\eta}, J] &= e^{iS_{\text{int}}[-\delta_\eta,\delta_{\bar{\eta}},\delta_J]} Z_0[\eta, \bar{\eta}, J], \\ Z_0[\eta, \bar{\eta}, J] &= Z_0\, e^{\int d^4x d^4x' \left(\bar{\eta}(x)S(x-x')\eta(x')+\frac{1}{2}J^\mu(x)D_{\mu\nu}(x-x')J^\nu(x')\right)}, \\ Z_0 &= \int \mathcal{D}\Psi\mathcal{D}\bar{\Psi}\mathcal{D}A\, \delta[G[A]]\, e^{iS_A[A]+iS_\Psi[\bar{\Psi},\Psi]} \equiv 1, \end{aligned} \tag{6.46}$$

where we have scaled the functional integral measure such that the partition function of the non-interacting theory is equal to unity, $Z_0[0, 0, 0] = Z_0 = 1$.

From eqs. (6.45) and (6.46) we may write the electron and photon propagators, $\mathcal{S}$ and $\mathcal{D}$, of the full theory as

$$\begin{aligned} \mathcal{S}(x_f - x_i) &= -\delta_{\bar{\eta}(x_f)}\delta_{\eta(x_i)} W[\eta, \bar{\eta}, J]\Big|_{\eta=\bar{\eta}=J=0} \\ &= S(x_f - x_i) + \frac{1}{Z[\eta, \bar{\eta}, J]} e^{iS_{\text{int}}[-\delta_\eta,\delta_{\bar{\eta}},\delta_J]} \\ &\cdot \int d^4x\, S(x_f - x)\eta(x) \int d^4y\, \bar{\eta}(y) S(y - x_i) \cdot Z_0[\eta, \bar{\eta}, J]\Big|_{\eta=\bar{\eta}=J=0}, \end{aligned}$$

$$\begin{aligned}\mathcal{D}_{\mu\nu}(x_f - x_i) &= \delta_{J^\mu(x_f)}\delta_{J^\nu(x_i)} W[\eta,\bar\eta,J]\Big|_{\eta=\bar\eta=J=0} \\ &= D_{\mu\nu}(x_f - x_i) + \frac{1}{Z[\eta,\bar\eta,J]} e^{iS_{\rm int}[-\delta_\eta,\delta_{\bar\eta},\delta_J]} \\ \cdot \int d^4x\, D_{\mu\alpha}(x_f - x) J^\alpha(x) &\int d^4y\, J^\beta(y) D_{\beta\nu}(y - x_i) \cdot Z_0[\eta,\bar\eta,J]\Big|_{\eta=\bar\eta=J=0}.\end{aligned} \tag{6.47}$$

From these expressions it is apparent that indeed the electron and photon propagators of the non-interacting theory, where $S_{\rm int} = 0$, are simply given by S and D in the exponent of the generating functional,

$$\begin{aligned}\mathcal{S}(x_f - x_i)\Big|_{S_{\rm int}=0} &= S(x_f - x_i), \\ \mathcal{D}(x_f - x_i)\Big|_{S_{\rm int}=0} &= D_{\mu\nu}(x_f - x_i).\end{aligned} \tag{6.48}$$

Let us now define the self energy Σ of the electron and the vacuum polarization Π of the photon in the following way:

$$\begin{aligned}\mathcal{S}^{-1}(x-y) &= S^{-1}(x-y) - i\Sigma(x-y), \\ (\mathcal{D}^{-1})^{\mu\nu}(x-y) &= (D^{-1})^{\mu\nu}(x-y) - i\Pi^{\mu\nu}(x-y).\end{aligned} \tag{6.49}$$

The quantities Σ and Π capture the effect of self interaction of the electron and photon, respectively, that we had mentioned above. One should keep in mind that the presence of an external potential would most likely destroy the translational invariance of $\mathcal{S}$, $\mathcal{D}$, Σ and Π, i.e. $\mathcal{S}(x,y) \neq \mathcal{S}(x-y)$, etc. Performing a Fourier transform in eqs. (6.49) and inverting yields the very useful expressions

$$\begin{aligned}\mathcal{S}(x) &= \frac{1}{i}\int \frac{d^4p}{(2\pi)^4} \frac{e^{ipx}}{\not p + m - \Sigma(p) - i0^+}, \\ \mathcal{D}_{\mu\nu}(x) &= \int \frac{d^4k}{(2\pi)^4} \frac{e^{ikx}}{(\widetilde{D}^{-1})^{\mu\nu}(k) - i\Pi^{\mu\nu}(k)},\end{aligned} \tag{6.50}$$

with the Fourier transformed expressions

$$\Sigma(p) = \int d^4x\, e^{-ipx}\Sigma(x), \qquad \Pi(k) = \int d^4x\, e^{-ikx}\Pi(x). \tag{6.51}$$

The exact form of $\mathcal{D}$ is specific to choice of gauge of course. E.g. in the case of Coulomb gauge, we obtain

$$\mathcal{D}_{00}(x) = i\int \frac{d^4k}{(2\pi)^4} \frac{e^{i\vec k\vec x}}{\vec k^2 + \Pi^{00}(k)},$$

$$\mathcal{D}_{ij}(x) = \frac{1}{i}\int \frac{d^4k}{(2\pi)^4}\left(\delta_i{}^l - \frac{k_i k^l}{\vec{k}^2}\right)\frac{e^{i\vec{k}\vec{x}}}{k^2\eta^{lj} - \Pi^{lj}(k) - i0^+}, \tag{6.52}$$

while in Lorenz gauge we have

$$\mathcal{D}_{\mu\nu}(x) = \frac{1}{i}\int \frac{d^4k}{(2\pi)^4}\left(\delta_\mu{}^\rho - \frac{k_\mu k^\rho}{k^2}\right)\frac{e^{i\vec{k}\vec{x}}}{k^2\eta^{\rho\nu} - \Pi^{\rho\nu}(k) - i0^+}. \tag{6.53}$$

Finally, in Feynman gauge we have

$$\mathcal{D}_{\mu\nu}(x) = \frac{1}{i}\int \frac{d^4k}{(2\pi)^4}\frac{e^{i\vec{k}\vec{x}}}{k^2\eta^{\mu\nu} - \Pi^{\mu\nu}(k) - i0^+}. \tag{6.54}$$

Further we may expand eqs. (6.49) in a geometric series for $\mathcal{S}$ and $\mathcal{D}$,

$$\begin{aligned}
\mathcal{S}_{fi} &= S_{fi} + \int_{a,b} S_{fa} i\Sigma_{ab} S_{bi} + \int_{a,b,c,d} S_{fa} i\Sigma_{ab} S_{bc} i\Sigma_{cd} S_{di} + \dots, \\
\mathcal{D}_{\mu\nu,fi} &= D_{\mu\nu,fi} + \int_{a,b} D_{\mu\rho,fa} i\Pi^{\rho\sigma}_{ab} D_{\sigma\nu,bi} \\
&\qquad + \int_{a,b,c,d} D_{\mu\rho,fa} i\Pi^{\rho\sigma}_{ab} D_{\sigma\alpha,bc} i\Pi^{\alpha\beta}_{cd} D_{\beta\nu,di} + \dots,
\end{aligned} \tag{6.55}$$

where $\int_{a,b,\dots} = \int d^4a d^4b \dots$ and $\Sigma_{ab} = \Sigma(a-b)$, etc. In order to calculate the $O(\alpha^5)$ corrections to the hydrogen energy levels we have to consider the $O(\alpha)$ contributions to Σ and Π. From eqs. (6.47) we may infer the expressions,

$$\begin{aligned}
\Sigma(x-y) &= ie^2\gamma^\mu S(x-y) D_{\mu\nu}(x-y)\gamma^\nu \\
&\qquad - \delta\mathcal{H}_\Psi(x)\delta^4(x-y) + O(\alpha^2), \\
\Pi^{\mu\nu}(x-y) &= -ie^2\,\mathrm{Tr}[S(x-y)\gamma^\mu S(y-x)\gamma^\nu] \\
&\qquad - \delta\mathcal{H}^{\mu\nu}_A(x)\delta^4(x-y) + O(\alpha^2).
\end{aligned} \tag{6.56}$$

6.1.5 The quantum action

The field theoretic formalism developed in subsections 6.1.1 to 6.1.4 is very powerful but in the context of a bound state we can go even further with the quantum action formalism.

The Legendre transform Γ of the connected generating functional W defined in eq. (6.44) is called the quantum action or effective action,

$$i\Gamma[\Omega,\bar{\Omega},B] = W[\eta,\bar{\eta},J] - \int d^4x\left(\bar{\Omega}[\eta]\eta + \bar{\eta}\Omega[\bar{\eta}] + J^\mu B_\mu[J]\right). \tag{6.57}$$

The functionals W and Γ satisfy the relations

$$\begin{aligned} \delta_{\bar\eta} W &= \Omega, & i\delta_\Omega \Gamma &= \bar\eta, \\ \delta_\eta W &= -\bar\Omega, & i\delta_{\bar\Omega}\Gamma &= -\eta, \\ \delta_J W &= B, & i\delta_B \Gamma &= -J. \end{aligned} \tag{6.58}$$

The equations in the right row are called the quantum equations of motion for the fields $\bar\Omega$, Ω and B. The meaning of these variables can be elucidated by considering eq. (6.45),

$$\Omega[\bar\eta] = \langle\Psi\rangle_{\bar\eta}, \qquad \bar\Omega[\eta] = \langle\bar\Psi\rangle_\eta, \qquad B = \langle A\rangle_J. \tag{6.59}$$

Thus the functionals $(\Omega, \bar\Omega, B)$ correspond to the expectation values of the fields $(\Psi, \bar\Psi, A)$, i.e. their classical values in the presence of non-vanishing sources $(\eta, \bar\eta, J)$.

Let us now expand the quantum action Γ in terms of the fields $(\Omega, \bar\Omega, B)$ and only keep the first few terms,

$$\begin{aligned} \Gamma[\Omega,\bar\Omega,B] = &\int d^4x d^4y\, \bar\Omega(x) \frac{\delta^2\Gamma}{\delta\Omega(y)\delta\bar\Omega(x)}\Omega(y) \\ &+ \frac{1}{2}\int d^4x d^4y\, B_\mu(x) \frac{\delta^2\Gamma}{\delta B_\mu(x)\delta B_\nu(y)} B_\nu(y) \\ &+ \int d^4x d^4y d^4z\, \bar\Omega(x) \frac{\delta^3\Gamma}{\delta\Omega(y)\delta\bar\Omega(x)\delta B_\mu(z)}\Omega(y)B_\mu(z) + \dots . \end{aligned} \tag{6.60}$$

Higher orders in the expansion will not be needed in the rest of this work. Obviously the quantum action Γ is gauge invariant just like W and hence not all combinations of Ω, $\bar\Omega$ and B can arise in the expansion. Also from the non-interacting theory one easily finds that $\Gamma[0,0,0] = 0$. From differentiations of the relations (6.58), taking care of the anti-commutativity of the Grassman-valued fields, we obtain

$$\begin{aligned} \delta^4(x-y) &= \delta_{\Omega(x)}\Omega(y) = \delta_{\Omega(x)}\delta_{\bar\eta(y)} W \\ &= \int d^4z\, [\delta_{\Omega(x)}\eta(z)]\, [\delta_{\eta(z)}\delta_{\bar\eta(y)} W] \\ &= \int d^4z\, [\delta_{\Omega(x)}\delta_{\bar\Omega(z)} i\Gamma]\, [\delta_{\bar\eta(y)}\delta_{\eta(z)} W], \\ \delta^\mu{}_\nu \delta^4(x-y) &= \delta_{B_\mu(x)} B_\nu(y) = \delta_{B_\mu(x)}\delta_{J^\nu(y)} W \\ &= \int d^4z\, [\delta_{B_\mu(x)} J^\rho(z)]\, [\delta_{J^\rho(z)}\delta_{J^\nu(y)} W] \end{aligned}$$

$$= -\int d^4z\,[\delta_{B_\mu(x)}\delta_{B_\rho(z)}i\Gamma]\,[\delta_{J^\rho(z)}\delta_{J^\nu(y)}W]. \tag{6.61}$$

Hence, according to eqs. (6.47), we obtain for vanishing sources, $\eta = \bar{\eta} = J = 0$,

$$\frac{\delta^2\Gamma}{\delta\bar{\Omega}(x)\delta\Omega(y)} = i\mathcal{S}^{-1}(x-y), \qquad \frac{\delta^2\Gamma}{\delta B_\mu(x)\delta B_\nu(y)} = i(\mathcal{D}^{-1})^{\mu\nu}(x-y). \tag{6.62}$$

Similarly the remaining coefficient in eq. (6.60) may be calculated as follows:

$$\begin{aligned} 0 &= \delta_{B_\mu(w)}\delta^4(x-y) \\ &= \delta_{B_\mu(w)}\int d^4z\,[\delta_{\Omega(x)}\delta_{\bar{\Omega}(z)}i\Gamma]\,[\delta_{\bar{\eta}(y)}\delta_{\eta(z)}W] \\ &= \int d^4z\,[\delta_{\Omega(x)}\delta_{\bar{\Omega}(z)}\delta_{B_\mu(w)}i\Gamma]\,[\delta_{\bar{\eta}(y)}\delta_{\eta(z)}W] \\ &\quad - \int d^4zd^4v\,[\delta_{B_\mu(w)}\delta_{B_\nu(v)}i\Gamma]\,[\delta_{\Omega(x)}\delta_{\bar{\Omega}(z)}i\Gamma]\,[\delta_{J^\nu(v)}\delta_{\bar{\eta}(y)}\delta_{\eta(z)}W]. \end{aligned} \tag{6.63}$$

Again setting $\eta = \bar{\eta} = J = 0$, we define the 3-point vertex function $\mathcal{V}_3$ as

$$\begin{aligned} -e\mathcal{V}_3^\mu(x,y,z) &= \delta_{\Omega(y)}\delta_{\bar{\Omega}(x)}\delta_{B_\mu(z)}\Gamma \\ &= i\int d^4ud^4vd^4w\,\mathcal{S}^{-1}(y-u)(\mathcal{D}^{-1})^{\mu\nu}(z-v) \\ &\qquad \cdot[\delta_{J^\nu(v)}\delta_{\bar{\eta}(u)}\delta_{\eta(w)}W]\,\mathcal{S}^{-1}(w-x). \end{aligned} \tag{6.64}$$

Inserting these results into eq. (6.60) for the quantum action yields

$$\begin{aligned} \Gamma[\Omega,\bar{\Omega},B] = \int d^4xd^4y\,\Big[\bar{\Omega}(x)\left(i\mathcal{S}^{-1}(x-y) - (e\mathcal{V}_3B)(x,y)\right)\Omega(y) \\ + \frac{i}{2}B_\mu(x)(\mathcal{D}^{-1})^{\mu\nu}(x-y)B_\nu(y)\Big], \end{aligned} \tag{6.65}$$

where

$$(e\mathcal{V}_3B)(x,y) = \int d^4z\,e\mathcal{V}_3^\mu(x,y,z)B_\mu(z). \tag{6.66}$$

Using the relations (6.58) we may derive from Γ the quantum equations of motion for the fields Ω and B ,

$$\delta_{\bar{\Omega}}\Gamma = 0, \qquad\qquad \delta_B\Gamma = 0, \tag{6.67}$$

which yields

$$\int d^4y\,i\mathcal{S}^{-1}(x-y)\Omega(y) = \int d^4y\,(e\mathcal{V}_3B)(x,y)\Omega(y),$$

$$\int d^4y\, i(\mathcal{D}^{-1})^{\mu\nu}(x-y)B_\nu(y) = \int d^4y d^4z\, \bar{\Omega}(y) e\mathcal{V}_3(y,z,x)\Omega(z). \qquad (6.68)$$

Analogous to eqs. (6.56) we expand the 3-point vertex function to first order in α,

$$\begin{aligned}\mathcal{V}_3^\mu(x,y,z) &= \gamma^\mu\delta^4(x-z)\delta^4(y-z) + \delta\mathcal{V}_3^\mu(x,y,z),\\ \delta\mathcal{V}_3^\mu(x,y,z) &= \delta_e\gamma^\mu\delta^4(x-z)\delta^4(y-z)\\ &\quad - e^2\gamma^\alpha S(x-z)\gamma^\mu S(z-y)\gamma^\beta D_{\alpha\beta}(x-y) + O(\alpha^2), \qquad (6.69)\end{aligned}$$

where we have assumed that $\delta_e = Z_e - 1 = O(\alpha)$. It will be helpful to use eqs. (6.49) and (6.69) to write the quantum action in the form

$$\begin{aligned}\Gamma[\Omega,\bar{\Omega},B] &= \int d^4x \left(\bar{\Omega}\left[-\mathcal{H}_\Psi - e\not{B}\right]\Omega - \frac{1}{2}B_\mu\mathcal{H}_A^{\mu\nu}B_\nu\right)\\ &\quad + \int d^4x d^4y \left(\bar{\Omega}(x)\left[\Sigma(x-y) - (\delta\mathcal{V}_3 eB)(x,y)\right]\Omega(y)\right.\\ &\quad \left. + \frac{1}{2}B_\mu(x)\Pi^{\mu\nu}(x-y)B_\nu(y)\right). \qquad (6.70)\end{aligned}$$

Apparently the first two lines of eq. (6.70) are just equal to the classical action like in eq. (6.36). Similarly the quantum equations of motion (6.68) may be rewritten as

$$\begin{aligned}\left[\mathcal{H}_\Psi + e\not{B}(x)\right]\Omega(x) &= \int d^4y\, \left[\Sigma(x-y) - (\delta\mathcal{V}_3 eB)(x,y)\right]\Omega(y),\\ \mathcal{H}_A^{\mu\nu}B_\nu(x) &= \int d^4y\, \Pi^{\mu\nu}(x-y)B_\nu(y)\\ &\quad - \int d^4y d^4z\, \bar{\Omega}(y) e\mathcal{V}_3(y,z,x)\Omega(z). \qquad (6.71)\end{aligned}$$

Now we have reached a good starting point for the calculation of radiative corrections to the relativistic energy levels.

6.2 The quantum equations of motion for the hydrogen atom

In this section we apply the quantum action formalism elaborated in the previous section to the case of the hydrogen atom. The calculation of the corrections to the hydrogen energy levels is performed in section 6.3.

We will rename the electron and photon fields from the previous section, $(\Omega, \bar{\Omega}, B)$, back to their original names,

$$(\Omega, \bar{\Omega}, B) \to (\Psi, \bar{\Psi}, A). \tag{6.72}$$

Keep in mind, however, that their meaning has changed from the quantum fields in subsection 6.1.4 to their expectation values as in subsection 6.1.5. Further we will regard the photon field A as a pure background field, while the dynamical quantum part of A is to be considered in the self energy Σ of the electron.

The quantum equation of motion for an electron in an external photon field A as given in eq. (6.71) is a Dirac equation for Ψ that includes radiative corrections,

$$\left[-i\partial\!\!\!/ + m + eA\!\!\!/(x)\right] \Psi(x) = \int d^4y \, \left[\Sigma(x-y) - (\delta \mathcal{V}_3 eA)(x,y)\right] \Psi(y). \tag{6.73}$$

The correction terms on the right-hand side of this equation comprise a variety of contributions which are collectively denoted as Lamb shift and the major part of which is due to the modified self energy of the electron in the hydrogen atom as compared to a free electron.

In this chapter we will calculate the order α^5 corrections to the energy levels. In order to do this we have to discriminate photons of different wavelengths against each other. *Hard* photons, with momenta of the order of the rest mass m, are important only in the immediate vicinity of the proton, i.e. over distance scales $\sim m^{-1}$. They contribute only to high energy processes which are encountered e.g. in the Uehling potential. The coulombic part of the proton potential is generated by *soft* photons with momenta of the order of the electron momentum, $m\alpha$. Their wavelengths are of the order of the atomic size, $\sim (m\alpha)^{-1}$. Their contributions to the vacuum polarization are derived in appendix A in the limit of small photon momenta since $m\alpha \ll m$. However, there is another energy scale to cover, the *ultra soft* (US) scale, consisting of photons with momenta of the order of the binding energy, $m\alpha^2$. Those photons do not contribute to the Coulomb potential but to a shift of the energy levels. Will we introduce an ultra soft cutoff $\mathcal{K}$, which satisfies

$$m\alpha^2 \ll \mathcal{K} \sim m\alpha \ll m \tag{6.74}$$

to separate the ultra soft from the soft contributions. It is important to realize that this procedure breaks Lorentz covariance. In the following when we speak of soft and ultra soft photon momenta or non-relativistic electrons we refer to the CMS. Throughout the whole chapter we will perform calculations for ultra soft and soft photons separately.

6.2.1 The photon field

Let us apply the above mentioned separation to the photon field A by dividing A into two parts,

$$A = A^> + A^<, \tag{6.75}$$

where $A^>$ contains only contributions from soft photons (momentum $k \gtrsim \mathcal{K}$) and $A^<$ those from ultra soft photons ($k \ll \mathcal{K}$). The ultra soft part is simply taken as a free photon field whereas the soft part yields the background potential of the proton. $A^>$ is taken to be the solution to the second line of eq. (6.68), where the right-hand side is set to be the 4-current of a proton at rest in the origin,

$$\int d^4y\, (\mathcal{D}^{-1})^{\mu\nu}(x-y) A^>_\nu(y) = -iJ^\nu(x), \qquad J^\nu = e\delta^\nu{}_0 \delta^3(\vec{x}). \tag{6.76}$$

Let us choose the Coulomb gauge, $\vec{\nabla}\vec{A}^> = 0$, and use eqs. (6.32) and (6.52) to write down the solution to this equation,

$$\begin{aligned} eA^>_\mu(x) &= -ie \int d^4y\, \mathcal{D}_{\mu\nu}(x-y) J^\nu(y) = \eta_{\mu 0} e^2 \int \frac{d^3k}{(2\pi)^3} \frac{e^{i\vec{k}\vec{x}}}{\vec{k}^2 + \Pi^{00}(0,\vec{k})} \\ &= \eta_{\mu 0} \frac{\alpha}{r} + e\delta A^>_\mu(x), \\ e\delta A^>_\mu(x) &\approx -\eta_{\mu 0} e^2 \int \frac{d^3k}{(2\pi)^3} \frac{e^{i\vec{k}\vec{x}}}{\vec{k}^4} \Pi^{00}(0,\vec{k}). \end{aligned} \tag{6.77}$$

In the modification $e\delta A^>$ to the Coulomb potential we have kept the first non-trivial term of the geometric series (6.55) since it contributes to the $O(\alpha^5)$-corrections to the energy levels. The vacuum polarization Π is calculated in A.1 to the first order in α for soft photon momenta, $k^2 \ll m^2$. $e\delta A^>$ is then obtained from eq. A.15 as

$$\begin{aligned} e\delta A^>_\mu(x) &= \eta_{\mu 0} e^2 \int \frac{d^3k}{(2\pi)^3} \frac{e^{i\vec{k}\vec{x}}}{\vec{k}^2} \Pi(0,\vec{k}) \\ &= \eta_{\mu 0} \frac{4\alpha^2}{15m^2}\, \delta^3(\vec{x}). \end{aligned} \tag{6.78}$$

We will solve eq. (6.73) with the Coulomb part of $A^>$ and treat the correction term $\delta A^>$ as well as the ultra soft field $A^<$ as a perturbation. The ultra soft contributions then appear to lowest order only in the electron self energy and not in the three point vertex function,

$$(\delta\mathcal{V}_3 eA) = \delta\mathcal{V}_3^> eA^>, \qquad \Sigma = \Sigma^> + \Sigma^<. \tag{6.79}$$

Correspondingly the soft field contains the Coulomb potential and corrections to it, while the soft vertex function contains corrections to the way the electron interacts with the potential. The complete contribution of the ultra soft field, however, is accounted for in the ultra soft self energy $\Sigma^<$.

In the following we will consider the electron field Ψ to be the exact solution to the equation

$$\left[-i\not{\partial} + m - \gamma^0 \frac{\alpha}{r}\right] \Psi(x) = 0, \tag{6.80}$$

while the remaining terms in eq. (6.73) are included in a perturbation Hamiltonian $\hat{H}^{(1)}$,

$$\hat{H}^{(1)}\Psi(x) = e\delta\not{A}^>(x)\Psi(x) - \int d^4y \left[\Sigma(x-y) - (\delta\mathcal{V}_3^> eA^>)(x,y)\right]\Psi(y). \tag{6.81}$$

The solutions to eq. (6.80) are of course the ones derived in chapter 4, while the radiative corrections to the Dirac energy levels are given by the expectation value of the perturbation Hamiltonian $\hat{H}^{(1)}$.

6.2.2 The soft vertex function

Let us write down the Fourier transform of $\delta\mathcal{V}_3 eA$,

$$(\delta\mathcal{V}_3 eA)(x,y) = \int \frac{d^4p}{(2\pi)^4}\frac{d^4p'}{(2\pi)^4}\, e^{ipx-ip'y}\delta\mathcal{V}_3^\mu(p,p')e\widetilde{A}_\mu(p'-p), \tag{6.82}$$

with the momentum space expression in Feynman gauge,

$$\delta\mathcal{V}_3^\mu(p,p') = ie^2\int \frac{d^4l}{(2\pi)^4}\frac{\gamma_\nu\tilde{S}(p'+l)\gamma^\mu\tilde{S}(p+l)\gamma^\nu}{l^2+m_\gamma^2-i0^+} + \delta_e\gamma^\mu + O(\alpha^2). \tag{6.83}$$

The correction to the vertex function is given in appendix A.2 in the limit of small photon momenta as

$$\delta\mathcal{V}_3^\mu(p,p') = \gamma^\mu\frac{\alpha}{3\pi}\frac{q^2}{m^2}\left(\ln\frac{m_\gamma}{m}+\frac{3}{8}\right) - \frac{\alpha}{2\pi}\frac{iS^{\mu\nu}q_\nu}{m}, \qquad q = p'-p, \tag{6.84}$$

This expression includes contributions from all scales. We have to exclude the ultra soft photons, however, since these are to be considered in the ultra soft self energy $\Sigma^<$ only. Thus we have to calculate the first order correction to the vertex function, $\delta\mathcal{V}_3^<$, from eq. (6.83) by inserting the ultra soft cutoff $\mathcal{K}$ and using free electron propagators,

$\bar{u}_{s'}(\vec{p}')\delta\mathcal{V}_3^{<\mu}(p,p')u_s(\vec{p})$

$$
\begin{aligned}
&= \delta_e^< \bar{u}_{s'}(\vec{p}')\gamma^\mu u_s(\vec{p}) - ie^2 \int_{\mathcal{K}} \frac{d^4l}{(2\pi)^4} \\
&\quad \cdot \frac{\bar{u}_{s'}(\vec{p}')\gamma^\nu \left(\not{p}' + \not{l} - m\right)\gamma^\mu \left(\not{p} + \not{l} - m\right)\gamma_\nu u_s(\vec{p})}{((p'+l)^2 + m^2 - i0^+)\left((p+l)^2 + m^2 - i0^+\right)\left(l^2 + m_\gamma^2 - i0^+\right)} \\
&\approx \delta_e^< \bar{u}_{s'}(\vec{p}')\gamma^\mu u_s(\vec{p}) \\
&\quad - ie^2 \int_{\mathcal{K}} \frac{d^4l}{(2\pi)^4} \frac{4pp'\bar{u}_{s'}(\vec{p}')\gamma^\mu u_s(\vec{p})}{(2p'l - i0^+)\left(2pl - i0^+\right)\left(l^2 + m_\gamma^2 - i0^+\right)} \\
&\quad = \bar{u}_{s'}(\vec{p}')\gamma^\mu u_s(\vec{p}) \left(\delta_e^< + \frac{\alpha}{\pi} I(p,p')\right), \qquad (6.85)
\end{aligned}
$$

where $Z_e^< = 1 + \delta_e^<$ is the renormalization factor specific to the ultra soft regime,

$$Z_e = Z_e^> + Z_e^<. \qquad (6.86)$$

In going to the second line of eq. (6.85) we have neglected $\not{l}$ against m in the numerator and l^2 against pl and $p'l$ in the denominator. We calculate $\delta\mathcal{V}_3^<$ for non-relativistic electrons, i.e. in the CMS we have

$$p = E\begin{pmatrix} 1 \\ \vec{v} \end{pmatrix}, \quad p' = E'\begin{pmatrix} 1 \\ \vec{v}\,' \end{pmatrix}, \quad q = p' - p \approx E\begin{pmatrix} 0 \\ \vec{v}\,' - \vec{v} \end{pmatrix}, \qquad (6.87)$$

where

$$E' \approx E = \frac{m}{\sqrt{1-v^2}}, \qquad \vec{v}^2 \approx \vec{v}\,'^2 = v^2, \qquad \vec{v}\vec{v}\,' \approx v^2\cos\theta. \qquad (6.88)$$

To calculate the integral I we perform the l^0-integration in the complex plane, closing the contour above the real axis. Further we write

$$l = |\vec{l}|, \qquad \hat{l} = \frac{\vec{l}}{l}, \qquad E_l = \sqrt{l^2 + m_\gamma^2}, \qquad (6.89)$$

so that

$$
\begin{aligned}
I(p,p') &= \frac{p'p}{E^2} \int_0^{\mathcal{K}} \frac{dl\, l^2}{E_l^3} \int \frac{d\Omega}{4\pi} \frac{1}{1 - \vec{v}\vec{l}/E_l} \frac{1}{1 - \vec{v}\,'\vec{l}/E_l} \\
&= \frac{p'p}{E^2} \int_0^{\mathcal{K}} \frac{dl\, l^2}{E_l^3} \int_0^1 dx \int_{-1}^1 \frac{d\cos\vartheta}{2(1 - (l/E_l)|x\vec{v} + (1-x)\vec{v}\,'|\cos\vartheta)^2} \\
&= \frac{p'p}{E^2} \int_0^{\mathcal{K}} \frac{dl\, l^2}{E_l^3} \int_0^1 \frac{dx}{1 - (l/E_l)^2(x\vec{v} + (1-x)\vec{v}\,')^2}. \qquad (6.90)
\end{aligned}
$$

For non-relativistic electrons (in the CMS) we have $v \ll 1$ and may expand $I(p', p)$ to linear order in v^2, using $q^2 \approx 4m^2 v^2 \sin^2\theta/2$,

$$\begin{aligned} I(p',p) &= -\int_0^{\mathcal{K}} \frac{dl\, l^2}{E_l^3}(1 - v^2\cos\theta) \int_0^1 dx \left(1 + \frac{l^2}{E_l^2}(x\vec{v} + (1-x)\vec{v}')^2\right) \\ &\approx -\int_0^{\mathcal{K}} \frac{dl\, l^2}{E_l^3}\left(1 - v^2 + \frac{q^2}{2m^2} + \frac{l^2}{E_l^2}\left(v^2 - \frac{q^2}{6m^2}\right)\right) \\ &= -\Bigg[\left(\operatorname{arsinh}\frac{\mathcal{K}}{m_\gamma} - 1\right)\left(1 - v^2 + \frac{q^2}{2m^2}\right) \\ &\qquad + \left(\operatorname{arsinh}\frac{\mathcal{K}}{m_\gamma} - \frac{4}{3}\right)\left(v^2 - \frac{q^2}{6m^2}\right)\Bigg] \\ &\approx -\left[\frac{q^2}{3m^2}\left(\ln\frac{2\mathcal{K}}{m_\gamma} - \frac{5}{6}\right) - \frac{v^2}{3} - 1 + \ln\frac{2\mathcal{K}}{m_\gamma}\right]. \end{aligned} \tag{6.91}$$

The definition of the electron charge,

$$\bar{u}_{s'}(\vec{p}')\delta\mathcal{V}_3^{<\mu}\bar{u}_s(\vec{p})\Big|_{\substack{p^2 = p'^2 = -m^2 \\ q^2 = 0}} = 0, \tag{6.92}$$

enforces

$$Z_e^< = Z_\Psi^< = 1 - \frac{\alpha}{\pi}\left[\frac{v^2}{3} + 1 - \ln\frac{2\mathcal{K}}{m_\gamma}\right]. \tag{6.93}$$

It appears worrisome that the velocity v^2 appears in the counter term since it will become $-\Delta/m^2$ in position space. In order to check that this term can indeed be absorbed into a counter-term, we have to inspect the derivative of the ultra soft self energy, $\partial_{\not p}\Sigma^<$. So far, however, the soft vertex function reads

$$\delta\mathcal{V}_3^> = \delta\mathcal{V}_3 - \delta\mathcal{V}_3^< = \gamma^\mu \frac{\alpha}{3\pi}\frac{q^2}{m^2}\left(\ln\frac{2\mathcal{K}}{m} - \frac{11}{24}\right) - \frac{\alpha}{2\pi}\frac{iS^{\mu\nu}q_\nu}{m}. \tag{6.94}$$

Thus we are able write down the first part of the perturbation Hamiltonian (6.81) explicitly,

$$\begin{aligned} \hat{H}^{(1)}\Psi(x) = \gamma^0 &\left[\frac{4\alpha^2}{3m^2}\left(\ln\frac{m}{2\mathcal{K}} + \frac{31}{120}\right)\delta^3(\vec{x}) - \frac{i\alpha^2}{4\pi m}\frac{\vec{\gamma}\vec{x}}{r^3}\right]\Psi(x) + \\ &+ \int d^4y\, \Sigma(x-y)\Psi(y). \end{aligned} \tag{6.95}$$

6.2.3 Renormalization of the free ultra soft self energy

In this subsection we check that the renormalization of the free ultra soft self energy is consistent with the result (6.93) for the soft vertex function. Let us write the self energy of a free electron in terms of its Fourier transform,

$$\Sigma_{\rm free}(x-y) = \int \frac{d^4p}{(2\pi)^4}\, e^{ip(x-y)}\Sigma_{\rm free}(p), \tag{6.96}$$

with the momentum space expression in Feynman gauge,

$$\Sigma_{\rm free}(p) = e^2 \int \frac{d^4l}{(2\pi)^4} \frac{\gamma_\mu \widetilde{S}(\not{p}+\not{l})\gamma^\mu}{l^2+m_\gamma^2-i0^+} - \delta_\Psi \not{p} - \delta_m m + O(\alpha^2). \tag{6.97}$$

The self energy is renormalized such that it vanishes for a free electron, and that the residue of the free electron propagator is one,

$$\bar{u}_s(\vec{p})\Sigma_{\rm free}(p)u_s(\vec{p}) = 0, \qquad \bar{u}_s(\vec{p})\partial_{\not{p}}\Sigma_{\rm free}(p)u_s(\vec{p}) = 0. \tag{6.98}$$

These are the two conditions which constrain Z_Ψ and Z_m. We make the separation $Z_i = Z_i^> + Z_i^<$ again. The electron propagator in eq. (6.97) is substituted by a free propagator, so that

$$\begin{aligned}
&\bar{u}_s(\vec{p})[\Sigma^<_{\rm free}(\not{p}) + \delta^<_m - \delta^<_\Psi]u_s(\vec{p}) \\
&\qquad = -ie^2 \int \frac{d^4l}{(2\pi)^4} \frac{\bar{u}_s(\vec{p})\gamma_\mu\left(-\not{p}-\not{l}+m\right)\gamma^\mu u_s(\vec{p})}{(l^2+m_\gamma^2-i0^+)((p+l)^2+m^2-i0^+)} \\
&\qquad \approx ie^2 m\, \bar{u}_s(\vec{p})u_s(\vec{p}) \int \frac{d^4l}{(2\pi)^4} \frac{1}{(l^2+m_\gamma^2-i0^+)(pl-i0^+)} \\
&\qquad = e^2 m\, \bar{u}_s(\vec{p})u_s(\vec{p}) \int \frac{d^3l}{(2\pi)^3 2E_l^2} \frac{1}{E-\vec{v}\vec{l}/E_l} \\
&\qquad = \frac{m\alpha}{\pi E}\bar{u}_s(\vec{p})u_s(\vec{p}) \int_0^{\mathcal{K}} \frac{dl\, l^2}{E_l^2} \frac{1}{-2vl/E_l} \ln\frac{1-vl/E_l}{1+vl/E_l} \\
&\qquad \approx \frac{\alpha}{\pi}\bar{u}_s(\vec{p})u_s(\vec{p}) \left(1-\frac{v^2}{2}\right) \int_0^{\mathcal{K}} \frac{dl\, l^2}{E_l^2} \left(1+\frac{v^2}{3}\frac{l^2}{E_l^2}\right).
\end{aligned} \tag{6.99}$$

In the limit of $m_\gamma \to 0$ we have

$$\int_0^{\mathcal{K}} \frac{dl\, l^2}{E_l^2} = \mathcal{K} - \int_0^{\mathcal{K}} \frac{dl\, m_\gamma^2}{E_l^2} \to \mathcal{K},$$

$$\int_0^{\mathcal{K}} \frac{dl\, l^4}{E_l^4} = \int_0^{\mathcal{K}} dl \left(1 - \frac{2m_\gamma^2}{E_l^2} + \frac{m_\gamma^4}{E_l^4}\right) \to \mathcal{K} - \frac{m_\gamma^3}{2}\partial_{m_\gamma}\frac{\arctan\frac{l}{m_\gamma}}{m_\gamma} \to \mathcal{K},$$

so that we obtain a condition for the Z-factors,

$$Z_m^< - Z_\Psi^< = \frac{\alpha\mathcal{K}}{\pi}\left(1 - \frac{v^2}{6}\right). \tag{6.100}$$

Let us now check our result from subsection 6.2.2 on $Z_e^< = Z_\Psi^<$ by calculating the derivative of $\Sigma_{\text{free}}^<$,

$$\begin{aligned}&\bar{u}_s(\vec{p})[\partial_{\not p}\Sigma_{\text{free}}^<(\not p) + Z_\Psi^< - 1]u_s(\vec{p}) \\ &\quad = -ie^2\bar{u}_s(\vec{p})\left[\partial_{\not p}\int \frac{d^4l}{(2\pi)^4}\frac{1}{(l^2 + m_\gamma^2 - i0^+)}\gamma^\mu\frac{1}{\not p + \not l + m - i0^+}\gamma_\mu\right]u_s(\vec{p}).\end{aligned} \tag{6.101}$$

In order to calculate the derivative with respect to $\not p$ we note that

$$\partial_{\not p} = (\gamma_\mu)^{-1}\partial_{p^\mu} = -\gamma^\mu\partial_{p^\mu} \tag{6.102}$$

and hence

$$\partial_{\not p}\gamma^\mu\frac{1}{\not p + A}\gamma_\mu = \gamma^\alpha\gamma^\mu\frac{1}{\not p + A}\gamma_\alpha\frac{1}{\not p + A}\gamma_\mu. \tag{6.103}$$

For the present case we thus obtain

$$\bar{u}_s(\vec{p})[\partial_{\not p}\Sigma_{\text{free}}^<(\not p) + \delta_\Psi^<]u_s(\vec{p}) = -ie^2\int \frac{d^4l}{(2\pi)^4}\frac{\bar{u}_s(\vec{p})u_s(\vec{p})}{(l^2 + m_\gamma^2 - i0^+)}\frac{m^2}{(pl - i0^+)^2}, \tag{6.104}$$

which can be calculated using

$$\int_0^{\mathcal{K}} \frac{dl\, l^2}{E_l^3} = \operatorname{arsinh}\frac{\mathcal{K}}{m_\gamma} - 1 \to \ln\frac{2\mathcal{K}}{m_\gamma} - 1, \qquad \int_0^{\mathcal{K}} \frac{dl\, l^2 m_\gamma^2}{E_l^5} = \frac{1}{3}. \tag{6.105}$$

According to eq. (6.98) we then obtain

$$Z_e^< = Z_\Psi^< = 1 - \frac{\alpha}{\pi}\left(\frac{v^2}{3} + 1 - \ln\frac{2\mathcal{K}}{m_\gamma}\right), \tag{6.106}$$

in agreement with eq. (6.93).

6.3 Calculation of the energy corrections

Now we will calculate the radiative corrections to the energy levels. One should note that to the order α^5 only the Schrödinger energy levels enter the calculation. For the same reason we will often times approximate the Dirac wave function by the non-relativistic Schrödinger pendant.

6.3.1 The energy corrections

The shift of the energy levels caused by the perturbation Hamiltonian (6.81) is given by

$$\delta E_{nk} = \frac{1}{T} \int d^4x \, \bar{\Psi}_{nkm}(x) \hat{H}^{(1)} \Psi_{nkm}(x), \tag{6.107}$$

where T is the temporal extent of the integration range. In previous chapters we have simply calculated the energy levels and afterwards presented them like in eqs. (2.56) and (4.69) as measured relative to the ground state. In QFT, however, we will on several occasions encounter intermediate results containing divergent terms. Those unphysical contributions may be absorbed into the Z-factors in eqs. (6.83) and (6.97) by specifying renormalization conditions on Σ, $\partial\!\!\!/ \Sigma$ and $\delta\mathcal{V}_3$. Additionally, we have introduced the arbitrary cutoff $\mathcal{K}$ so we can not make sense of the direct result of eq. (6.107). In any case, however, the unphysical, arbitrary terms cancel out whenever a measurable quantity is calculated. E.g. Bethe (1947) derived a physical result from eq. (6.107) by simply calculating the difference $\delta E_{nk} - \delta E_{\text{free}}$, where δE_{free} is the energy shift of a free electron that follows from eq. (6.107). In the following we will therefore calculate the quantity

$$\Delta E_{nk} = \delta E_{nk} - \delta E_{1,-1} \tag{6.108}$$

so we save ourselves a lot of trouble by directly canceling out the Z-factors, the $\mathcal{K}$-dependent terms and a lot of other terms that we otherwise would have to carry through the calculation.

Inserting eq. (6.81) into eq. (6.108) yields

$$\begin{aligned} T\Delta E_{nk} = &\int d^4x \big[\bar{\Psi}_{nkm}(x) e \delta \not{A}^{>}(x) \Psi_{nkm}(x) - \bar{\Psi}_{1,-1,0}(x) e \delta \not{A}^{>}(x) \Psi_{1,-1,0}(x)\big] \\ &- \int d^4x d^4y \big[\bar{\Psi}_{nkm}(x) \Sigma(x-y) \Psi_{nkm}(y) - \bar{\Psi}_{1,-1,0}(x) \Sigma(x-y) \Psi_{1,-1,0}(y)\big] \\ &+ \int d^4x d^4y \big[\bar{\Psi}_{nkm}(x) (\delta\mathcal{V}_3^{>} e A^{>})(x,y) \Psi_{nkm}(y) \end{aligned}$$

$$- \bar{\Psi}_{1,-1,0}(x)(\delta\mathcal{V}_3^{>} eA^{>})(x,y)\Psi_{1,-1,0}(y)\big]. \quad (6.109)$$

In order to calculate the main part of the Lamb shift we need to consider eq. (6.97) where $S = S_c$ represents an electron propagator in the Coulomb field. We separate Σ into soft and ultra soft parts again,

$$\Sigma = \Sigma^{>} + \Sigma^{<}. \quad (6.110)$$

However, soft and hard photons do not feel the binding of the electron in the hydrogen atom so the electron looks nearly free at these energies and $\int \bar{\Psi}\Sigma\Psi$ changes only negligibly for the different bound state levels. We may thus approximate

$$\int \left[\bar{\Psi}_{nkm}\Sigma\Psi_{nkm} - \bar{\Psi}_{1,-1,0}\Sigma\Psi_{1,-1,0}\right] \approx \int \left[\bar{\Psi}_{nkm}\Sigma^{<}\Psi_{nkm} - \bar{\Psi}_{1,-1,0}\Sigma^{<}\Psi_{1,-1,0}\right]. \quad (6.111)$$

The remaining self energy comprises only ultra soft contributions, or more specifically,

$$\Sigma^{<}(x-y) = ie^2\gamma^\mu\Delta^{<}_{\mu\nu}(x-y)S_c(x-y)\gamma^\nu, \quad (6.112)$$

$$\Delta^{<}_{\mu\nu}(x-y) = \eta_{\mu\nu}\int_{\mathcal{K}} \widetilde{dq}\, e^{-i|\vec{q}||y^0-x^0|+i\vec{q}(\vec{y}-\vec{x})}, \quad (6.113)$$

$$S_c(x-y) = \mathrm{sgn}(x^0-y^0)\sum_{n'k'm'} \Psi^{(\pm)}_{n'k'm'}(\vec{x})\bar{\Psi}^{(\pm)}_{n'k'm'}(\vec{y})\, e^{-iE_{n'k'}|x^0-y^0|} + (\text{continuum states}), \quad (6.114)$$

where we have employed Feynman gauge in the photon propagator. Substituting the propagators (6.113) and (6.114) into the self energy (6.112) yields

$$\Sigma^{<}(x-y) = i\,\mathrm{sgn}(x^0-y^0)\,\frac{\alpha}{\pi}\sum_{n'k'm'}\int_0^{\mathcal{K}} \frac{dq\, q\, d\Omega}{4\pi}\cdot \cdot \gamma_\mu\Psi_{n'k'm'}(\vec{x})\bar{\Psi}_{n'k'm'}(\vec{y})\gamma^\mu e^{i\vec{q}(\vec{x}-\vec{y})-i(E_{n'k'}+q)|x^0-y^0|}, \quad (6.115)$$

where $q = |\vec{q}|$ and the sum $\sum_{n'k'm'}$ is understood to include continuum states. This result is to be inserted into eqs. (6.95) and (6.109).

6.3.2 Soft contributions

Let us separate the energy shift into two parts,

$$\delta E_{nk} = \delta E^{\mathrm{S}}_{nk} + \delta E^{\mathrm{US}}_{nk}, \quad (6.116)$$

due to soft (S) and ultra soft photons (US). According to eq. (6.95), we have

$$\begin{aligned}\delta E^{\mathrm{S}}_{nk} &= \int d^3x\, \Psi^\dagger_{nkm}(\vec{x}) \left[\frac{4\alpha^2}{3m^2}\left(\ln\frac{m}{2\mathcal{K}}+\frac{31}{120}\right)\delta^3(\vec{x}) - \frac{i\alpha^2}{4\pi m}\frac{\vec{\gamma}\vec{x}}{r^3}\right]\Psi_{nkm}(\vec{x}) \\ &= \frac{4\alpha^2}{3m^2}\left(\ln\frac{m}{2\mathcal{K}}+\frac{31}{120}\right)|\Psi_{nkm}(\vec{o})|^2 \\ &\qquad - \frac{i\alpha^2}{4\pi m}\int d^3x\, \Psi^\dagger_{nkm}(\vec{x})\frac{\vec{\gamma}\vec{x}}{r^3}\Psi_{nkm}(\vec{x}). \end{aligned} \tag{6.117}$$

To order α^5, only the lowest order parts of $|\Psi|^2$ contribute. According to the results of section 4.4 this leaves only us with

$$\begin{aligned}|\Psi_{nkm}(\vec{o})|^2 &\approx \lim_{r\to 0}\left|\frac{u^-_{n,-1}(r)}{r}\right|^2 \delta_{k,-1} = \frac{C^3_{n,-1}}{\pi n^2}(L^1_{n-1}(0))^2\delta_{k,-1} \\ &= \frac{C^3_{n,-1}}{\pi}\delta_{k,-1} \approx \frac{m^3\alpha^3}{\pi n^3}\delta_{k,-1}, \end{aligned} \tag{6.118}$$

where, of course, it is more common to write $\delta_{k,-1} = \delta_{l,0}$. The first part of $\delta E^{\mathrm{S}}_{nk}$ is thus obtained as

$$\frac{4m\alpha^5}{3\pi n^3}\left(\ln\frac{m}{2\mathcal{K}}+\frac{31}{120}\right)\delta_{l,0}. \tag{6.119}$$

Let us now turn to the second part of eq. (6.117),

$$\begin{aligned}-\frac{i\alpha^2}{4\pi m}\int d^3x\, \Psi^\dagger\frac{\vec{\gamma}\vec{x}}{r^3}\Psi &= -\frac{i\alpha^2}{4\pi m}\int d^3x\, \left[\varphi^\dagger\frac{\vec{\sigma}\vec{x}}{r^3}\chi - \chi^\dagger\frac{\vec{\sigma}\vec{x}}{r^3}\varphi\right] \\ &= -\frac{\alpha^2}{8\pi m^2}\int d^3x\, \left[\varphi^\dagger\frac{\vec{\sigma}\vec{x}}{r^3}\vec{\sigma}\vec{\nabla}\varphi + (\vec{\sigma}\vec{\nabla}\varphi)^\dagger\frac{\vec{\sigma}\vec{x}}{r^3}\varphi\right] \\ &= \frac{\alpha^2}{8\pi m^2}\int d^3x\, \varphi^\dagger\left[\vec{\sigma}\vec{\nabla}, \frac{\vec{\sigma}\vec{x}}{r^3}\right]\varphi, \end{aligned} \tag{6.120}$$

where we have used eq. (4.43) to write $\chi \approx -i\vec{\sigma}\vec{\nabla}\varphi/(2m)$ in the second line and performed a partial integration in the third line. The commutator may be written as

$$\left[\vec{\sigma}\vec{\nabla}, \frac{\vec{\sigma}\vec{x}}{r^3}\right] = 4\pi\delta^3(\vec{x}) + \frac{2(K-1)}{r^3}, \tag{6.121}$$

where $K = 1 + 2\vec{S}\vec{L} = \vec{J}^2 - \vec{L}^2 - \vec{S}^2$ as in chapter 4. Again we approximate the Dirac wave function by its Schrödinger equivalent so that the result of eq. (6.120) becomes

$$\frac{m\alpha^5}{2\pi n^3}\left(\delta_{l,0} - (1-\delta_{l,0})\frac{1+k}{l(l+1)(2l+1)}\right). \tag{6.122}$$

The last term is not present for $l = 0$, i.e. $k = -1$. Thus we may write this expression most conveniently as

$$-\frac{m\alpha^5}{2\pi n^3(2l+1)k}. \tag{6.123}$$

Taking eqs. (6.119) and (6.123) together, we obtain

$$\begin{aligned}\delta E^{\mathrm{S}}_{nlk} &= \frac{4m\alpha^5}{3\pi n^3}\left(\ln\frac{m}{2\mathcal{K}}+\frac{31}{120}\right)\delta_{l,0} - \frac{m\alpha^5}{2\pi n^3(2l+1)k} \\ &= \frac{m\alpha^5}{\pi n^3}\left[\left(\frac{4}{3}\ln\frac{m}{2\mathcal{K}}+\frac{31}{90}\right)\delta_{l,0} - \frac{1}{2k(2l+1)}\right].\end{aligned} \tag{6.124}$$

Despite the fact that soft contributions to the Lamb shift are rather small, they are still very important from the theoretical side because they allows us to eliminate the arbitrary parameter $\mathcal{K}$ in combination with the ultra soft contributions.

6.3.3 Ultra soft contributions

The largest fraction of the Lamb shift originates from the ultra soft self energy (6.115) which we are now going to calculate. Since we aim to calculate the difference $\Delta E_{nk} = \delta E_{nk} - \delta E_{1,-1}$ we will drop any contributions occuring in the calculation that do not depend on the hydrogen quantum numbers n, k, m. The ultra soft contribution to the energy levels reads

$$\delta E^{\mathrm{US}}_{nk} = \frac{\alpha}{\pi}\sum_{n'k'm'}\int_0^{\mathcal{K}}\frac{dq\,q\,d\Omega}{4\pi}\,|I^{n'k'm'}_{nkm}|^2\left(\frac{1}{E_n+E'_n+q}+\frac{1}{E_n-E'_n-q}\right), \tag{6.125}$$

$$(I^\mu)^{n'k'm'}_{nkm} = \int d^3x\,\bar\Psi_{n'k'm'}(\vec x)\gamma^\mu e^{i\vec q\vec x}\Psi_{nkm}(\vec x). \tag{6.126}$$

Keep in mind, however, that the sum $\sum_{n'k'm'}$ also includes continuum states. Let us abbreviate $I = I^{n'k'm'}_{nkm}$, $\Psi = \Psi_{nkm}$, $\Psi' = \Psi_{n'k'm'}$ and separate I into a transverse and a longitudinal (and temporal) part,

$$|I|^2 = |I_\parallel|^2 + |I_\perp|^2, \tag{6.127}$$

where

$$|I_\parallel|^2 = -|I^0|^2 + |\vec I\vec q|^2/q^2, \qquad |I_\perp|^2 = |(\mathbb{1} - \vec q\otimes\vec q/q^2)\vec I|^2. \tag{6.128}$$

The first term in brackets in eq. (6.125) is approximately $1/(2m)$ and therefore we make only a small error be writing

$$\sum_{n'k'm'} \frac{|I|^2}{E_n + E'_n + q} \approx \sum_{n'k'm'} \int d^3x d^3y \, \frac{\bar{\Psi}(\vec{y})\gamma_\mu \Psi'(\vec{y}) e^{i\vec{q}(\vec{x}-\vec{y})} \bar{\Psi}'(\vec{x})\gamma^\mu \Psi(\vec{x})}{2m}$$
$$\approx \int d^3x d^3y \, \frac{\bar{\Psi}(\vec{x})\gamma_\mu \gamma^0 \delta^3(\vec{x}-\vec{y})\gamma^\mu \Psi(\vec{y})}{2m} = \frac{1}{m}. \quad (6.129)$$

Hence this part approximately cancels out in the difference (6.108) and may be dropped. Next let us look at the longitudinal part of I in the remaining part of eq. (6.125),

$$\frac{|I_\parallel|^2}{E_n - E'_n - q} = \frac{-q^2 |\int d^3x \, \Psi'^\dagger e^{i\vec{q}\vec{x}} \Psi|^2 + |\int d^3x \, \Psi'^\dagger \gamma^0 \vec{\gamma}\vec{q} e^{i\vec{q}\vec{x}} \Psi|^2}{q^2(E_n - E'_n - q)}. \quad (6.130)$$

Using

$$\left(-i\gamma^0 \vec{\gamma}\vec{\nabla} + \gamma^0 m - \frac{\alpha}{r}\right) \Psi_n(\vec{x}) = E_n \Psi_n(\vec{x}) \quad (6.131)$$

we may rewrite the second term as

$$\left| \int d^3x \, \Psi'^\dagger \left[-i\gamma^0 \vec{\gamma}\vec{\nabla} + \gamma^0 m - \frac{\alpha}{r}, e^{i\vec{q}\vec{x}} \right] \Psi \right|^2 = (E_n - E_{n'})^2 \left| \int d^3x \, \Psi'^\dagger e^{i\vec{q}\vec{x}} \Psi \right|^2. \quad (6.132)$$

The longitudinal part thus reads

$$\frac{|I_\parallel|^2}{E_n - E'_n - q} = \frac{E_n - E'_n + q}{q^2} \left| \int d^3x \, \Psi'^\dagger e^{i\vec{q}\vec{x}} \Psi \right|^2. \quad (6.133)$$

Since the wave function is exponentially damped by a factor of the order $m\alpha$, while the phase factor of the ultra soft photon varies with angular velocity $q \sim m\alpha^2$, we may use the dipole approximation and set $e^{i\vec{q}\vec{x}} \approx 1$. Then by the orthonormality of the wave functions,

$$\int d^3x \, \Psi'^\dagger \Psi = \delta_{nn'}\delta_{kk'}\delta_{mm'} \qquad \Rightarrow \qquad \sum_{n'k'm'} \frac{|I_\parallel|^2}{E_n - E'_n - q} \approx \frac{1}{q}. \quad (6.134)$$

Thus we may also drop the longitudinal part since it only gives a constant contribution. Let us turn to the transverse part. We may again use the dipole approximation and perform the spherical integral to obtain

$$\int \frac{d\Omega}{4\pi} |I_\perp|^2 = \frac{2}{3} \left| \int d^3x \, \bar{\Psi}' \vec{\gamma} \Psi \right|^2 = \frac{2}{3} |\vec{I}|^2. \quad (6.135)$$

Again we make use of the dipole approximation so that the energy shift reads

$$\delta E_{nk}^{\mathrm{US}} = \frac{2\alpha}{3\pi} \sum_{n',k',m'} |\vec{I}|^2 \left(-\mathcal{K} + (E_{n'} - E_n) \ln \frac{\mathcal{K}}{|E_n - E_{n'}|} \right), \tag{6.136}$$

where we have used that $\mathcal{K} \gg |E_n - E_{n'}|$. Let us consider the first term on the right-hand side. The sum over the squared integral reads

$$\sum_{n',k',m'} |\vec{I}|^2 \approx \sum_{n',k',m'} \int d^3x d^3y \, \bar{\Psi}(\vec{y}) \vec{\gamma} \Psi'(\vec{y}) \bar{\Psi}'(\vec{x}) \vec{\gamma} \Psi(\vec{x}). \tag{6.137}$$

Due to the negligible overlap we make only a small error by using completeness relation to replace

$$\sum_{n',k',m'} \Psi'(\vec{y}) \Psi'^{\dagger}(\vec{x}) \to \delta^3(\vec{x} - \vec{y}). \tag{6.138}$$

This replacement together with the orthonormality condition of the wave functions yields a constant result for the first term in eq. (6.136) so it may be dropped. We now want to combine our result for $\delta E_{nk}^{\mathrm{S}}$ from eq. (6.124) with $\delta E_{nk}^{\mathrm{US}}$ in order to get rid of the arbitrary and unphysical scale $\mathcal{K}$. For this we need to calculate the quantity $\sum |\vec{I}|^2 (E_{n'} - E_n)$. Using eq. (4.43) to write $\chi \approx -i\vec{\sigma}\vec{\nabla}\varphi/(2m)$, we may rewrite the overlap integral as

$$\vec{I} = \int d^3x \, \bar{\Psi}' \vec{\gamma} \Psi \approx \int d^3x \, \frac{\varphi'^{\dagger} \{\vec{\sigma}, -i\vec{\sigma}\vec{\nabla}\} \varphi}{2m} = \int d^3x \, \frac{\varphi'^{\dagger} \vec{\nabla} \varphi}{im}. \tag{6.139}$$

Then we note that, to this order of accuracy, $H_S \varphi_{nkm} = E_n \varphi_{nkm}$, where $H_S = -\Delta/(2m) - \alpha/r$ is the relative-motion, stationary Schrödinger Hamiltonian from eq. (3.16). With this knowledge, let us first inspect the quantity

$$\begin{aligned} \sum_{n',k',m'} |\vec{I}|^2 (E_{n'} - E_n) &= -\frac{1}{2m^2} \int d^3x \, \varphi^{\dagger} \left(\vec{\nabla} \left[H_S, \vec{\nabla} \right] + \left[\vec{\nabla}, H_S \right] \vec{\nabla} \right) \varphi \\ &= -\frac{1}{2m^2} \int d^3x \, \varphi^{\dagger} \left(\vec{\nabla} \left[-\frac{\alpha}{r}, \vec{\nabla} \right] + \left[\vec{\nabla}, -\frac{\alpha}{r} \right] \vec{\nabla} \right) \varphi \\ &= \frac{2\pi\alpha}{m^2} |\varphi(\vec{o})|^2 \approx \frac{2m\alpha^4}{n^3} \delta_{k,-1}. \end{aligned} \tag{6.140}$$

In the second line we have performed a partial integration of one integral, which gives us a minus sign, and then rewritten the factor $E_{n'} - E_n$ as H_S acting on φ. This allows us to make use of the completeness relation to take

out φ' and one integral. The resulting commutator simply yields a δ-function. Consequently, to this order of accuracy, we have

$$\delta E_{nk}^{\mathrm{US}} = \frac{4m\alpha^5}{3\pi n^3}\delta_{l,0}\ln\mathcal{K} + \frac{2\alpha^3}{3\pi}\sum_{n',k',m'}|\alpha^{-1}\vec{I}|^2(E_{n'}-E_n)\ln\frac{1}{|E_n-E_{n'}|}, \tag{6.141}$$

where we have regarded the fact that $\vec{I} = \vec{I}_{nkm}^{n'k'm'}$, given in eq. (6.139), is of the order α. First we observe that the logarithmic term containing $\mathcal{K}$ vanishes for non-S-wave states and hence we may replace $\mathcal{K}$ with some arbitrary value as, for example $\mathrm{Ryd} = m\alpha^2/2$. But the dependence on $\mathcal{K}$ vanishes even for $l = 0$ since combining eqs. (6.124) and (6.141) yields the total energy shift

$$\begin{aligned}\delta E_{nk} = \frac{4m\alpha^5}{3\pi n^3}&\left[\left(\frac{31}{120}+\ln\frac{1}{\alpha^2}\right)\delta_{l,0} - \frac{3}{8k(2l+1)}\right] \\ &+ \frac{2\alpha^3}{3\pi}\sum_{n',k',m'}|\alpha^{-1}\vec{I}|^2(E_{n'}-E_n)\ln\frac{\mathrm{Ryd}}{|E_n-E_{n'}|}.\end{aligned} \tag{6.142}$$

Following Bethe (1947) we now introduce the average of the logarithm in eq. (6.142), the so called Bethe logarithm, via[1]

$$\ln\gamma(n,l) = \frac{n^3}{4}\sum_{n',k',m'}|\alpha^{-1}\vec{I}_{nkm}^{n'k'm'}|^2\left(\frac{1}{n^2}-\frac{1}{n'^2}\right)\ln\frac{|E_n-E_{n'}|}{\mathrm{Ryd}}, \tag{6.143}$$

which is independent of the magnetic quantum number m as we will show in subsection 6.3.4. In this notation the fifth-order correction to the energy levels reads

$$\delta E_{nk} = \frac{4m\alpha^5}{3\pi n^3}\left[\left(\frac{31}{120}+\ln\frac{1}{\alpha^2}\right)\delta_{l,0} - \frac{3}{8k(2l+1)} - \ln\gamma(n,l)\right]. \tag{6.144}$$

Thus the final values for the energy levels, relative to the ground state, including the result of the Dirac theory (4.68) read

$$\Delta E_{nk} = \mathrm{Ryd}\left[1 - \frac{1}{n^2} + \alpha^2\left(\frac{1}{4}+\frac{3}{4n^4}-\frac{1}{|k|n^3}\right) - \frac{8\alpha^3}{3\pi}\left(\frac{19}{30}+\ln\frac{1}{\alpha^2\gamma(n,l)}\right)\right.$$

[1]Strictly speaking this can only be interpreted as an actual average in the case of S-states, where may we rewrite eq. (6.143) as

$$\ln\gamma(n,l) = \frac{\sum'|\alpha^{-1}\vec{I}|^2(E'-E)\ln\frac{|E-E'|}{\mathrm{Ryd}}}{\sum'|\alpha^{-1}\vec{I}|^2(E'-E)}.$$

For $l \neq 0$, however, the denominator in this expression would vanish.

$$+\frac{8\alpha^3}{3\pi n^3}\left(\left(\frac{31}{120}+\ln\frac{1}{\alpha^2}\right)\delta_{l,0}-\frac{3}{8k(2l+1)}-\ln\gamma(n,l)\right)\Bigg]\pm O(\alpha^6). \tag{6.145}$$

6.3.4 Calculating the Bethe logarithm

Let us reformulate the overlap integral

$$\vec{I}=\int d^3x\,\frac{\varphi'^{\dagger}\vec{\nabla}\varphi}{im} \tag{6.146}$$

by writing $-i\vec{\nabla}/m=[H_S,\vec{r}]$ and hence

$$\begin{aligned}\vec{I}^{n'k'm'}_{nkm}&=(E_{n'}-E_n)J^{n'k'}_{nk}\vec{G}^{k'm'}_{km},\\ J^{n'k'}_{nk}&=\int_0^\infty dr\,r\,g_{n'k'}(r)g_{nk}(r),\\ \vec{G}^{k'm'}_{km}&=\int d\Omega\,\Omega^{\dagger}_{k'm'}\vec{e}_r\Omega_{km}.\end{aligned} \tag{6.147}$$

From eq. (4.91) we see that, to this order in α, J may be solely expressed by the radial Schrödinger wave functions g^S_{nl}. Also from eq. (B.13) we see that only allowed values are $m'=m$, $m\pm1$ and $l'=l\pm1$, or in terms of k and k',

$$k'=k\pm1,\ -k-1\pm1. \tag{6.148}$$

Inserting this into the sum of the Bethe logarithm (6.143) yields

$$\begin{aligned}\sum_{k'=-n'}^{n'-1}\sum_{m'=-|k'|+1/2}^{|k'|-1/2}|\vec{I}^{n'k'm'}_{nkm}|^2&=(E_{n'}-E_n)^2\\ &\cdot\Bigg[|J^{n',l-1}_{nl}|^2\sum_{m'=m-1}^{m+1}\left(|\vec{G}^{l-1,m'}_{lm}|^2+|\vec{G}^{-l,m'}_{lm}|^2\right)\\ &+|J^{n',l+1}_{nl}|^2\sum_{m'=m-1}^{m+1}\left(|\vec{G}^{l+1,m'}_{lm}|^2+|\vec{G}^{-l-2,m'}_{lm}|^2\right)\Bigg].\end{aligned} \tag{6.149}$$

From eq. (B.13) we have $\vec{G}^{-l-2,m\pm1}_{lm}=\vec{G}^{-l-2,m}_{lm}=0$ as well as

$$\vec{G}^{l-1,m\pm1}_{lm}=\pm\vec{e}_{\pm}\frac{\sqrt{(l-\frac{1}{2}\mp m)(l-\frac{3}{2}\mp m)}}{\sqrt{2}(2l-1)},\quad \vec{G}^{l-1,m}_{lm}=\vec{e}_z\frac{\sqrt{(l-\frac{1}{2})^2-m^2}}{2l-1},$$

$$\vec{G}_{lm}^{l+1,m\pm1} = \mp\vec{e}_{\pm}\frac{\sqrt{(l+\frac{1}{2}\pm m)(l+\frac{3}{2}\pm m)}}{\sqrt{2}(2l+1)}, \quad \vec{G}_{lm}^{l+1,m} = \vec{e}_z\frac{\sqrt{(l+\frac{1}{2})^2-m^2}}{2l+1},$$
$$\vec{G}_{lm}^{-l,m\pm1} = \vec{e}_{\pm}\sqrt{2}\frac{\sqrt{l^2-(\frac{1}{2}\pm m)^2}}{(2l-1)(2l+1)}, \qquad \vec{G}_{lm}^{-l,m} = \vec{e}_z\frac{2m}{(2l-1)(2l+1)}. \tag{6.150}$$

The sum in the Bethe logarithm thus becomes

$$\sum_{k',m'}|\vec{I}_{nkm}^{n'k'm'}|^2 = (E_{n'}-E_n)^2\frac{l|J_{nl}^{n',l-1}|^2+(l+1)|J_{nl}^{n',l+1}|^2}{2l+1} \tag{6.151}$$

so the complete Bethe logarithm (6.143) reads

$$\ln\gamma(n,l) = \frac{m^2\alpha^2n^3}{16}\sum_{n'}\frac{l|J_{nl}^{n',l-1}|^2+(l+1)|J_{nl}^{n',l+1}|^2}{2l+1} \cdot\left(\frac{E_{n'}-E_n}{\mathrm{Ryd}}\right)^3\ln\frac{|E_n-E_{n'}|}{\mathrm{Ryd}}, \tag{6.152}$$

where we have to regard the fact that J is of the order $(m\alpha)^{-1}$. The major contribution to eq. (6.152) comes from the continuum states. This expression has to be evaluated numerically and a simple numerical calculation performed by the author yields

$$\begin{aligned}\ln\gamma(1,0) &= 2.985, & \delta E_{1,-1} &= 3.359\cdot10^{-5}\ \mathrm{eV},\\ \ln\gamma(2,0) &= 2.817, & \delta E_{2,-1} &= 4.293\cdot10^{-6}\ \mathrm{eV}.\end{aligned} \tag{6.153}$$

But already this crude result improves the results of the Dirac theory tremendously. The shift of the ground state energy level $\delta E_{1,-1}$ is by far the largest and simply including this shift in eq. (6.145) and ignoring all other order $m\alpha^5$-contributions reduces the relative deviation from experiment down to $\sim 3\cdot10^{-8}$ i.e. two orders of magnitude for all non-S states. But even for the S states this already reduces the deviation below $5\cdot10^{-7}$. And also the shift for the 2S state in eqs. (6.153) accounts for 1038 MHz of the 1057 MHz measured for the $2S_{1/2}$-$2P_{1/2}$ splitting by Lamb and Retherford (1947). Over the years detailed calculations of the Bethe logarithm have been performed. In table 6.1 we present very accurate results from Drake and Swainson (1990) for the states displayed in the previous tables. These values have also been used to compute the energy levels corrected up to order α^5 from eq. (6.145) in table 6.2. Jentschura and Mohr (2005) have calculated the Bethe logarithm

Table 6.1: Numerical results for the Bethe logarithm from Drake and Swainson (1990) for some of the lowest lying hydrogen states and the corresponding fifth-order corrections from eq. (6.144).

State	$\ln \gamma(n, l)$	δE_{nk} (eV)
$1S_{1/2}$	2.984128555765498	$3.35940976992458 \cdot 10^{-5}$
$2S_{1/2}$	2.811769893120563	$4.29589892444639 \cdot 10^{-6}$
$2P_{1/2}$	-0.030016708630213	$-5.32544917436815 \cdot 10^{-8}$
$2P_{3/2}$		$4.01908763410275 \cdot 10^{-8}$
$3S_{1/2}$	2.767663612491822	$1.28018610080462 \cdot 10^{-6}$
$3P_{1/2}$	-0.038190229385312	$-1.44212817216688 \cdot 10^{-8}$
$3P_{3/2}$		$1.32662347478746 \cdot 10^{-8}$
$3D_{3/2}$	-0.005232148140883	$-3.28393634350078 \cdot 10^{-9}$
$3D_{5/2}$		$5.02231859736224 \cdot 10^{-9}$
$4S_{1/2}$	2.749811840454057	$5.41329635333724 \cdot 10^{-7}$
$4P_{1/2}$	-0.041954894598086	$-5.82013533143648 \cdot 10^{-9}$
$4P_{3/2}$		$5.86053567915214 \cdot 10^{-9}$
$4D_{3/2}$	-0.006740938876975	$-1.27966851564170 \cdot 10^{-9}$
$4D_{5/2}$		$2.22453278753488 \cdot 10^{-9}$
$4F_{5/2}$	-0.001733661482126	$-1.12999848892155 \cdot 10^{-9}$
$4F_{7/2}$		$1.21501976498660 \cdot 10^{-10}$

for states up to $n \leq 200$. One can see that radiative corrections improve the results of the Dirac theory by roughly a factor one hundred. Also the famous splitting between the $2S_{1/2}$ and $2P_{1/2}$ levels is calculated to this order of accuracy to yield ≈ 1051.62 MHz which deviates only by 0.6% from the experimentally observed 1057.83653507 MHz.

Table 6.2: Experimental values of the hydrogen energy levels as given in Kramida (2010) are compared with the relativistic energy levels E_{nk} including corrections up to fifth order in α as given in eq. (6.145). The lowest order radiative corrections improve the accuracy of the pure Dirac theory by roughly a factor one hundred.

State	Exp. levels (eV)	ΔE_{nk} (eV)	Deviation
$1S_{1/2}$	0	0	
$2P_{1/2}$	10.1988055286	10.1988058225823	$3 \cdot 10^{-8}$
$2S_{1/2}$	10.1988099034600	10.1988101717357	$3 \cdot 10^{-8}$
$2P_{3/2}$	10.1988508929	10.1988511739767	$3 \cdot 10^{-8}$
$3P_{1/2}$	12.087492922	12.087493247092	$3 \cdot 10^{-8}$
$3S_{1/2}$	12.087494224	12.0874945416994	$3 \cdot 10^{-8}$
$3D_{3/2}$	12.087506341	12.087506667992	$3 \cdot 10^{-8}$
$3P_{3/2}$	12.087506364	12.0875066845422	$3 \cdot 10^{-8}$
$3D_{5/2}$	12.087510821	12.0875111462192	$3 \cdot 10^{-8}$
$4P_{1/2}$	12.74853166921	12.7485320020757	$3 \cdot 10^{-8}$
$4S_{1/2}$	12.74853221952	12.7485325492255	$3 \cdot 10^{-8}$
$4D_{3/2}$	12.7485373313	12.7485376638598	$3 \cdot 10^{-8}$
$4P_{3/2}$	12.74853733962	12.748537671	$3 \cdot 10^{-8}$
$4D_{5/2}$	12.74853922041	12.7485395531119	$3 \cdot 10^{-8}$
$4F_{5/2}$	12.748539221	12.7485395497574	$3 \cdot 10^{-8}$
$4F_{7/2}$	12.7485401632	12.7485404938828	$3 \cdot 10^{-8}$
Continuum	13.598433770784	13.5984341184646	$3 \cdot 10^{-8}$

Chapter 7

The group theoretic approach

Group theory has many applications in physics as it approaches the concept of symmetries in a systematic way. Symmetries put restrictions on the states and dynamics of physical systems. The orbital eigenstates of the hydrogen atom follow from its manifest SO(3) symmetry and the energy levels from its hidden SO(4) symmetry. In this light sections 2.2 and 2.3 already presented applications of group theory.

Further properties of the hydrogen atom can be derived from its symmetry group SO(4,1) (Bander and Itzykson, 1966a,b, and references therein). In a series of papers, Kleinert (1968a,b), Barut and Kleinert (1967a,b,c) showed that the hydrogen atom possesses the even larger symmetry group SO(4,2), the dynamic group, from which not only energy levels and states but also the matrix elements of the dipole and momentum operators can be derived. Thus all properties of the hydrogen atom that are known from Schrödinger theory can also be derived from group theory.

This chapter is restricted to the derivation of the bound state energy levels and radial eigenstates from the SO(4) and SO(2,1) symmetry groups, respectively. We compare the results to Schrödinger theory and briefly introduce the generators of the dynamical group SO(4,2). More information on the application of group theory to the hydrogen atom can be found e.g. in Kleinert (2004), Kibler (2004), Gilmore (2008).

7.1 Deriving hydrogen energy levels from the SO(4) symmetry group

As a first application of group theory we will derive the hydrogen energy levels. Important ground work has already been done in sections 2.2 and 2.3, where we worked out algebraic properties of the angular momentum and

LRL operators $\hat{\vec{L}}$ and $\hat{\vec{U}}$, respectively. The derivation of the energy levels, however, is much simpler with the group theoretic approach presented in this section.

Let us rewrite the most important results from chapter 2, which are the commutation relations (2.17) and (2.39) of angular momentum and LRL operator among each other,

$$\begin{aligned}
[\hat{L}^j, \hat{L}^k] &= i\varepsilon^{jkl}\hat{L}_l, \\
[\hat{U}^j, \hat{L}^k] &= i\varepsilon^{jkl}\hat{U}_l, \\
[\hat{U}^j, \hat{U}^k] &= -\frac{\hat{H}}{\mathrm{Ryd}} i\varepsilon^{jkl}\hat{L}_l,
\end{aligned} \tag{7.1}$$

with the Hamiltonian, eqs. (2.34) and (2.37),

$$[\hat{L}^j, \hat{H}] = 0, \qquad [\hat{U}^j, \hat{H}] = 0, \tag{7.2}$$

and the square of the LRL operator, eq. (2.38),

$$\hat{\vec{U}}^2 = 1 + \frac{\hat{H}}{\mathrm{Ryd}}(1 + \hat{\vec{L}}^2). \tag{7.3}$$

The commutation relations in the first line of eq. (7.1), define the Lie algebra of SO(3). The fact that the angular momentum operator commutes with $\hat{H}$ means, that SO(3) is a symmetry group of the Hamiltonian, i.e. $\hat{H}$ is invariant under SO(3) transformations. Since the LRL operator commutes with $\hat{H}$ as well, means that the symmetry group is even larger.

The angular momentum and LRL operator together can serve as generators of SO(4), where the latter has to be rescaled first. In order to show this, we define the 4×4-matrix-valued, totally antisymmetric operator $\hat{T}_{AB}$ as

$$\hat{T}_{jk} = \varepsilon_{jkl}\hat{L}^l, \qquad \hat{T}_{j4} = \sqrt{\frac{\mathrm{Ryd}}{-\hat{H}}}\,\hat{U}_j, \tag{7.4}$$

where uppercase indices take values $\{1, 2, 3, 4\}$ while lowercase indices are restricted to the usual values $\{1, 2, 3\}$. The components $\hat{T}_{AB}$ satisfy the commutation relations of SO(4) generators,

$$\begin{aligned}
[\hat{T}_{AB}, \hat{T}_{CD}] &= i\left(g_{AC}\hat{T}_{BD} - g_{AD}\hat{T}_{BC} - g_{BC}\hat{T}_{AD} + g_{BD}\hat{T}_{AC}\right), \\
(g_{AB}) &= \mathrm{diag}(1, 1, 1, 1),
\end{aligned} \tag{7.5}$$

where g is the metric of four dimensional euclidean space. Hence we find that SO(4) is also a symmetry of the Hamiltonian. In order to derive the energy levels, we now define the operators

$$\begin{aligned}\hat{\vec{J}} &= \frac{1}{2}\left(\hat{\vec{L}} + \sqrt{\frac{\mathrm{Ryd}}{-\hat{H}}}\,\hat{\vec{U}}\right),\\ \hat{\vec{K}} &= \frac{1}{2}\left(\hat{\vec{L}} - \sqrt{\frac{\mathrm{Ryd}}{-\hat{H}}}\,\hat{\vec{U}}\right).\end{aligned} \tag{7.6}$$

They obviously commute with the Hamiltonian,

$$[\hat{J}^j, \hat{H}] = 0, \qquad [\hat{K}^j, \hat{H}] = 0, \tag{7.7}$$

and further satisfy the following commutation relations among each other

$$\begin{aligned}[\hat{J}^j, \hat{J}^k] &= i\varepsilon^{jkl}\hat{J}_l,\\ [\hat{K}^j, \hat{K}^k] &= i\varepsilon^{jkl}\hat{K}_l,\\ [\hat{J}^j, \hat{K}^k] &= 0.\end{aligned} \tag{7.8}$$

The first two lines are identical to the first line of eq. (7.1), which means that both operators are generators of SO(3). Their eigenvalues and eigenvectors can thus be found completely analogous to the procedure for the angular momentum operator in section 2.2. Since both operators commute with each other we can even find a basis $|j, m_j, k, m_k\rangle$ which diagonalizes them both simultaneously,

$$\begin{aligned}\hat{J}^3|j, m_j, k, m_k\rangle &= m_j|j, m_j, k, m_k\rangle,\\ \hat{K}^3|j, m_j, k, m_k\rangle &= m_k|j, m_j, k, m_k\rangle,\\ \hat{\vec{J}}^2|j, m_j, k, m_k\rangle &= j(j+1)|j, m_j, k, m_k\rangle,\\ \hat{\vec{K}}^2|j, m_j, k, m_k\rangle &= k(k+1)|j, m_j, k, m_k\rangle.\end{aligned} \tag{7.9}$$

The quantum numbers j, m_j, k, m_k are allowed to take the same values as l and m in section 2.2. Making use of

$$\hat{\vec{U}}\hat{\vec{L}} = \hat{\vec{L}}\hat{\vec{U}} = 0, \tag{7.10}$$

we readily calculate squares of $\hat{\vec{J}}$ and $\hat{\vec{K}}$,

$$\hat{\vec{J}}^2 = \hat{\vec{K}}^2 = -\frac{1}{4}\left(1 + \frac{\mathrm{Ryd}}{\hat{H}}\right), \tag{7.11}$$

and find them to be equal. This implies that their eigenvalues must be equal as well,

$$j \equiv k. \tag{7.12}$$

Their eigenvectors can thus be characterized by only three quantum numbers,

$$|j, m_j, k, m_k\rangle = |j, m_j, m_k\rangle. \tag{7.13}$$

Using eq. (7.11) we may express the Hamiltonian in terms of $\hat{\vec{J}}$,

$$\hat{H} = -\frac{\text{Ryd}}{1 + 4\hat{\vec{J}}^2}. \tag{7.14}$$

The action of the Hamiltonian on a state $|j, m_j, m_k\rangle$ is then readily calculated,

$$\hat{H}|j, m_j, m_k\rangle = -\frac{\text{Ryd}}{(2j+1)^2}|j, m_j, m_k\rangle. \tag{7.15}$$

Since m_j and m_k are independent from each other, the multiplicity of states with quantum number j is $(2j+1)^2$, which is consistent with the expected multiplicity of states with principal quantum number n. We can thus identify $n = 2j + 1$ to obtain the well known energy levels

$$E_n = -\frac{\text{Ryd}}{n^2}, \tag{7.16}$$

which we previously presented in eq. (2.55) and which are compared to the experimentally measured values in table 2.1. The group theoretic approach, utilizing the SO(4) symmetry of the Hamiltonian, however, has greatly simplified the derivation of the energy levels as compared to section 2.3.

7.2 Deriving radial wave functions from the SO(2,1) symmetry group

In sections 3.2 and 3.3 we derived the wave functions from Schrödinger theory. Due to the underlying SO(3) symmetry, these factorize into radial and spherical parts as in eq. (3.19). For the abstract hydrogen states, $|n, l, m\rangle$, we therefore expect a factorization of the form,

$$|n, l, m\rangle = |n, l\rangle \otimes |l, m\rangle, \tag{7.17}$$

where the spherical part, $|l,m\rangle$, is an eigenstate of the angular momentum operator as given in eq. (2.29). Its position space components are given by the spherical harmonics, $Y_{lm}(\theta,\varphi) = \langle\vec{x}|l,m\rangle$. Hence we already succeeded in deriving the spherical wave functions from a group theoretic approach. In this section we will also derive the radial part, $|n,l\rangle$, which encodes most of the physics of the hydrogen atom.

In a first step, let us separate the radial and spherical parts in the Hamiltonian by defining the radial momentum operator,

$$\hat{p}_r = \frac{1}{\hat{r}^2}(\hat{\vec{x}}\hat{\vec{p}})\hat{r}, \tag{7.18}$$

which translates to $-i/r \cdot \partial_r r$ in position space. We find that in terms of $\hat{p}_r$, the Hamiltonian reads

$$\hat{H} = \frac{\hat{p}_r^2}{2m} + \frac{\hat{\vec{L}}^2}{2m\hat{r}^2} - \frac{\alpha}{\hat{r}}. \tag{7.19}$$

Further, $\hat{p}_r$ has the commutation relations

$$[\hat{r},\hat{p}_r] = i, \qquad [\hat{p}_r,\hat{L}^j] = 0, \qquad [\hat{p}_r,\hat{H}] = \frac{i\hat{\vec{L}}^2}{m\hat{r}^3} - \frac{i\alpha}{\hat{r}^2}. \tag{7.20}$$

The action of the Hamiltonian on an eigenstate $|n,l,m\rangle$, with energy E_n, leads to the equation

$$\begin{aligned} 0 &= \left(\hat{H} - E_n\right)|n,l,m\rangle \\ &= \left(\frac{\hat{p}_r^2}{2m} + \frac{l(l+1)}{2m\hat{r}^2} - \frac{\alpha}{\hat{r}} - E_n\right)|n,l,m\rangle, \end{aligned} \tag{7.21}$$

where we applied eq. (2.26) according to the factorization in eq. (7.17). In order to derive the radial wave functions we will consider the action of an operator $\hat{\mathcal{H}}_l$ on the radial states $|n,l\rangle$, where

$$\hat{\mathcal{H}}_l = \frac{\hat{r}\hat{p}_r^2}{2m\alpha} + \frac{l(l+1)}{2m\alpha\hat{r}} - 1. \tag{7.22}$$

This is equal to $\hat{r}\hat{H}/\alpha$ after the angular momentum eigenstate $|l,m\rangle$ has acted on it. For simplicity we will omit the index l and just write $\hat{\mathcal{H}} \equiv \hat{\mathcal{H}}_l$. Thus, the radial states are governed by the equation,

$$0 = \left(\hat{\mathcal{H}} - \frac{\hat{r}}{\alpha}E_n\right)|n,l\rangle. \tag{7.23}$$

The operator $\hat{\mathcal{H}}$ has the commutation relations

$$\begin{aligned}
[\hat{r}, \hat{\mathcal{H}}] &= \frac{i\hat{r}\hat{p}_r}{m\alpha}, \\
[\hat{p}_r, \hat{\mathcal{H}}] &= \frac{i}{\hat{r}}\left(-\frac{\hat{r}\hat{p}_r^2}{2m\alpha} + \frac{l(l+1)}{2m\alpha\hat{r}}\right), \\
[\hat{r}\hat{p}_r, \hat{\mathcal{H}}] &= i\left(\frac{\hat{r}\hat{p}_r^2}{2m\alpha} + \frac{l(l+1)}{2m\alpha\hat{r}}\right).
\end{aligned} \tag{7.24}$$

These relations lead us to the definition of the following operators:

$$\begin{aligned}
\hat{w}^1 &= \hat{r}\hat{p}_r, \\
\hat{w}^2 &= \frac{1}{2}\left(\frac{\hat{r}\hat{p}_r^2}{m\alpha} - m\alpha\hat{r} + \frac{l(l+1)}{m\alpha\hat{r}}\right), \\
\hat{w}^3 &= \frac{1}{2}\left(\frac{\hat{r}\hat{p}_r^2}{m\alpha} + m\alpha\hat{r} + \frac{l(l+1)}{m\alpha\hat{r}}\right).
\end{aligned} \tag{7.25}$$

In terms of these operators, we may express,

$$\begin{aligned}
\hat{\mathcal{H}} &= \frac{\hat{w}^2 + \hat{w}^3}{2} - 1, \\
m\alpha\hat{r} &= \hat{w}^3 - \hat{w}^2.
\end{aligned} \tag{7.26}$$

From their commutation relations among each other,

$$\begin{aligned}
[\hat{w}^1, \hat{w}^2] &= i\hat{w}^3, \\
[\hat{w}^2, \hat{w}^3] &= -i\hat{w}^1, \\
[\hat{w}^3, \hat{w}^1] &= -i\hat{w}^2,
\end{aligned} \tag{7.27}$$

we see that the $\hat{w}^i$ are generators of SO(2,1). We will investigate the properties of the eigenstates of $\hat{w}^3$ in close analogy to the procedure for SO(3) in section 2.2. Let $|\chi_{w,l}\rangle$ be the eigenstate of $\hat{w}^3$ with eigenvalue w,

$$\hat{w}^3|\chi_{w,l}\rangle = w|\chi_{w,l}\rangle. \tag{7.28}$$

We can then define raising and lowering operators,

$$\hat{w}^\pm = \hat{w}^2 \pm i\hat{w}^1, \tag{7.29}$$

which satisfy the commutation relations

$$[\hat{w}^3, \hat{w}^\pm] = \pm\hat{w}^\pm, \qquad [\hat{w}^-, \hat{w}^+] = 2\hat{w}^3, \tag{7.30}$$

and thus allow the transformation of one eigenstate into another,

$$\hat{w}^{\pm}|\chi_{w,l}\rangle = C^{\pm}_{w,l}|\chi_{w\pm1,l}\rangle. \tag{7.31}$$

By repeated application of the raising and lowering operators we can calculate all eigenstates of $\hat{w}^3$ once the state $|\chi_{w,l}\rangle$ for a given value of w is known. Since the energy spectrum of the hydrogen atom is bounded from below, we expect the spectrum of $\hat{w}^3$ to have a lower bound as well. I.e. for some value k, we have

$$\hat{w}^{-}|\chi_{k,l}\rangle = 0. \tag{7.32}$$

The operator $\hat{\Omega}$ is the SO(2,1) analogue of $\hat{\vec{L}}^2$,

$$\begin{aligned}\hat{\Omega} &= (\hat{w}^3)^2 - (\hat{w}^2)^2 - (\hat{w}^1)^2 \\ &= (\hat{w}^3)^2 - \hat{w}^3 - \hat{w}^+\hat{w}^- \\ &= (\hat{w}^3)^2 + \hat{w}^3 - \hat{w}^-\hat{w}^+. \end{aligned} \tag{7.33}$$

It commutes with all $\hat{w}$-operators,

$$[\hat{\Omega}, \hat{w}^j] = 0, \tag{7.34}$$

so its eigenvalues are independent of w. Indeed, using the definition of the $\hat{w}$-operators, we see that

$$\hat{\Omega} = l(l+1). \tag{7.35}$$

Acting with the lowest state $|\chi_{k,l}\rangle$ on $\hat{\Omega}$ and using the second line of eq. (7.33) yields

$$k(k-1) = l(l+1), \tag{7.36}$$

and hence $k = l+1$ or $k = -l$. We need to make sure the spectrum of $\hat{w}^3$ has no upper limit as the physical application requires. Let us assume there was such an upper limit k' for which the equation

$$\hat{w}^{+}|\chi_{k',l}\rangle \stackrel{!}{=} 0 \tag{7.37}$$

is satisfied. From the third line of eq. (7.33) we then infer

$$k'(k'+1) = l(l+1), \tag{7.38}$$

and hence $k' = -l - 1$ or $k' = l$. It follows that the eigenvalues of physical states must satisfy

$$w \geq l + 1. \tag{7.39}$$

Before we proceed with the construction of a complete basis of eigenstates of $\hat{w}^3$, we first investigate how these states relate to the eigenstates of $\hat{\mathcal{H}}$. In terms of the of the $\hat{w}$-operators, eq. (7.23) reads

$$\left(\hat{w}^2 \frac{1-\mathcal{E}_n}{2} + \hat{w}^3 \frac{1+\mathcal{E}_n}{2} - 1\right) |n, l\rangle = 0, \tag{7.40}$$

where we have written $E_n = -\mathcal{E}_n \,\mathrm{Ryd}$ for the energy levels. We will now eliminate $\hat{w}^2$ from this equation by means of a n-dependent unitary transformation matrix

$$\hat{U}_n = e^{i\vartheta_n(\hat{w}^1 - i/2)}. \tag{7.41}$$

The transformed $\hat{w}^3$ may be calculated using eq. (7.27) in combination with the Baker-Campbell-Hausdorff formula (see appendix B),

$$\hat{U}_n \hat{w}^3 \hat{U}_n^\dagger = \hat{w}^3 \cosh\vartheta_n - \hat{w}^2 \sinh\vartheta_n. \tag{7.42}$$

Setting $\vartheta_n = (1/2)\ln\mathcal{E}_n$, we obtain

$$\hat{U}_n \hat{w}^3 \hat{U}_n^\dagger = \frac{1}{\sqrt{\mathcal{E}_n}} \left(\hat{w}^2 \frac{1-\mathcal{E}_n}{2} + \hat{w}^3 \frac{1+\mathcal{E}_n}{2}\right). \tag{7.43}$$

Hence we may write eq. (7.40) as

$$\hat{U}_n \left(\hat{w}^3 \sqrt{\mathcal{E}_n} - 1\right) \hat{U}_n^\dagger |n, l\rangle = 0. \tag{7.44}$$

We now identify the principal quantum number n with the eigenvalues of $\hat{w}^3$ and make the Ansatz

$$|n, l\rangle = \hat{U}_n |\chi_{n,l}\rangle, \tag{7.45}$$

to obtain the equation

$$\hat{U}_n \left(n\sqrt{\mathcal{E}_n} - 1\right) |\chi_{n,l}\rangle = 0. \tag{7.46}$$

This implies $\mathcal{E}_n = 1/n^2$ and yields the well known energy levels

$$E_n = -\frac{\mathrm{Ryd}}{n^2}. \tag{7.47}$$

Let us now return to the construction of the radial wave functions from the eigenvectors of $\hat{w}^3$. In position space the action of the ladder operators $\hat{w}^\pm$ on the states $|\chi_{n,l}\rangle$ yields the equation

$$\langle\vec{x}|\hat{w}^\pm|\chi_{n,l}\rangle = \left(\pm\partial_r r - \frac{1}{2}\left(\frac{\partial_r^2 r}{m\alpha} + m\alpha r - \frac{l(l+1)}{m\alpha r}\right)\right)\chi_{n,l}(r), \tag{7.48}$$

where $\chi_{n,l}(r) = \langle\vec{x}|\chi_{n,l}\rangle$ is the position space eigenfunction. With the definition $x = 2m\alpha r$, we now make the general ansatz

$$\chi_{n,l}(r) = x^l e^{-x/2} h_{n,l}(x). \tag{7.49}$$

Inserting this into eqs. (7.48) and (7.31), yields the following recurrence relations for $h_{n,l}$,

$$\begin{aligned} C^+_{n,l} h_{n+1,l}(x) &= -\left(x\partial_x^2 + 2(l+1-x)\partial_x - 2(l+1) + x\right) h_{n,l}(x), \\ C^-_{n,l} h_{n-1,l}(x) &= -\left(x\partial_x^2 + 2(l+1)\partial_x\right) h_{n,l}(x). \end{aligned} \tag{7.50}$$

Since the lowest state gets annihilated by $\hat{w}^-$, we have $C^-_{l+1,l} = 0$ in which case the second line implies

$$h_{l+1,l}(x) = const. \tag{7.51}$$

Inserting the solutions repeatedly into the first line of eq. (7.50) yields the non-constant parts of the lowest few functions,

$$\begin{aligned} &h_{l+1,l}(x) \propto const., \\ &h_{l+2,l}(x) \propto 2l + 2 - x, \\ &h_{l+3,l}(x) \propto x^2 - 2x(2l+3) + (2l+2)(2l+3). \end{aligned} \tag{7.52}$$

As these expressions are proportional to the associated Laguerre polynomials L_n^α, we suspect that all $h_{n,l}$ take the following form,

$$h_{n,l}(x) = A_{n,l} L^{2l+1}_{n-l-1}(x), \tag{7.53}$$

with some normalization constant $A_{n,l}$. Let us prove this claim by induction. The expressions for the lowest few functions above may serve as base case. For the induction step we need to show that the right hand sides of eq. (7.50) are proportional to L^{2l+1}_{n-l} and L^{2l+1}_{n-l-2}, respectively. Making repeated use of the relations in eq. (B.17) and omitting the argument x to unclutter notation, we can show that

$$\left(x\partial_x^2 + 2(l+1-x)\partial_x - 2(l+1) + x\right) L^{2l+1}_{n-l-1}$$

$$
\begin{aligned}
&= xL^{2l+3}_{n-l-3} - 2(l+1-x)L^{2l+2}_{n-l-2} + (x-2l-2)L^{2l+1}_{n-l-1} \\
&= (n+l)L^{2l+2}_{n-l-3} + (2x-n-l)L^{2l+2}_{n-l-2} + (x-2l-2)L^{2l+1}_{n-l-1} \\
&= (n+l)L^{2l+1}_{n-l-2} + (x-2n)L^{2l+1}_{n-l-1} \\
&= -(n-l)L^{2l+1}_{n-l}, \qquad (7.54)
\end{aligned}
$$

for the right hand side of the first line of eq. (7.50). Performing the same calculation for the second line yields

$$
\begin{aligned}
\left(x\partial_x^2 + 2(l+1)\partial_x\right) L^{2l+1}_{n-l-1} &= xL^{2l+3}_{n-l-3} - 2(l+1)L^{2l+2}_{n-l-2} \\
&= (n+l)(L^{2l+2}_{n-l-3} - L^{2l+2}_{n-l-2}) \\
&= -(n+l)L^{2l+1}_{n-l-2}. \qquad (7.55)
\end{aligned}
$$

And hence we have proven our claim (7.53). Inserting the results into eq. (7.50) yields expressions for the coefficients $C^{\pm}_{n,l}$,

$$
\begin{aligned}
C^{+}_{n,l} &= (n-l)\frac{A_{n,l}}{A_{n+1,l}}, \\
C^{-}_{n,l} &= (n+l)\frac{A_{n,l}}{A_{n-1,l}}. \qquad (7.56)
\end{aligned}
$$

The normalization factor $A_{n,l}$ can be determined by the normalization condition of the full hydrogen state $|n,l,m\rangle$,

$$
\begin{aligned}
1 = \langle n,l,m|n,l,m\rangle &= \int_0^\infty dr\, r^2 |\chi_{n,l}|^2 \\
&= \frac{|A_{nl}|^2}{(2m\alpha)^3}\int_0^\infty dx\, x^{2l+2}e^{-x}(L^{2l+1}_{n-l-1})^2. \qquad (7.57)
\end{aligned}
$$

This integral has already been evaluated in eq. (3.30). The normalization factor is therefore readily obtained,

$$
A_{n,l} = \sqrt{\frac{(2m\alpha)^3}{2n}\frac{(n-l-1)!}{(n+l)!}}. \qquad (7.58)
$$

For the coefficients $C^{\pm}_{n,l}$ we then obtain

$$
C^{+}_{n,l} = \sqrt{\frac{n+1}{n}(n-l)(n+l+1)},
$$

$$C^-_{n,l} = \sqrt{\frac{n-1}{n}(n+l)(n-l-1)}. \tag{7.59}$$

Finally, the action of the ladder operators $\hat{w}^\pm$ can be written in abstract notation as

$$\hat{w}^\pm|\chi_{n,l}\rangle = \sqrt{\frac{n\pm1}{n}(n\mp l)(n\pm(l+1))}\,|\chi_{n\pm1,l}\rangle. \tag{7.60}$$

The radial states $|n,l\rangle$ can then be raised and lowered using

$$\hat{U}_{n\pm1}\hat{w}^\pm\hat{U}_n^\dagger|n,l\rangle = \sqrt{\frac{n\pm1}{n}(n\mp l)(n\pm(l+1))}\,|n\pm1,l\rangle. \tag{7.61}$$

Now there is only one task left that needs to be done and that is to draw the connection from the radial wave functions $\chi_{n,l}$ derived in this section to the ones derived in section 3.2 using the Schrödinger equation. Let us write $\chi_{n,l}(r)$ for clarity,

$$\chi_{n,l}(r) = \sqrt{\frac{4C_1^3}{n}\frac{(n-l-1)!}{(n+l)!}}\,(2C_1r)^l e^{-C_1r}L^{2l+1}_{n-l-1}(2C_1r), \tag{7.62}$$

where we have used eq. (3.27) to write $x = 2C_1r$. The total radial wave function reads

$$\langle\vec{x}|n,l\rangle = \langle\vec{x}|\hat{U}_n|\chi_{n,l}\rangle = e^{\vartheta_n\partial_r r+\vartheta_n/2}\chi_{n,l}(r). \tag{7.63}$$

The operator $e^{\vartheta_n\partial_r r}$ is actually called tilt operator (see Kleinert, 1968a, Kleinert, 2004). One can show that its action on any function that can be expanded in powers of r amounts to

$$e^{\vartheta_n\partial_r r}f(r) = e^{\vartheta_n}f(e^{\vartheta_n}r). \tag{7.64}$$

This result is frankly not restricted to position space but is valid in any basis. Consequently, the total radial wave function reads

$$\begin{aligned}\langle\vec{x}|n,l\rangle &= \frac{\chi_{n,l}(r/n)}{n^{3/2}} \\ &= 2C_n\sqrt{\frac{C_n}{n}\frac{(n-l-1)!}{(n+l)!}}\,(2C_nr)^l e^{-C_nr}L^{2l+1}_{n-l-1}(2C_nr).\end{aligned} \tag{7.65}$$

This expression is indeed equal to the radial wave function $g_{n,l}/r$, defined in eqs. (3.19) and (3.31).

7.3 The generators of SO(4,2)

The dynamical group of the hydrogen atom is SO(4,2). It contains the SO(4) and SO(2,1) subgroups from which we derived the hydrogen eigenstates and energy levels in previous sections. Dynamical quantities like the dipole and momentum operators can be expressed in terms of SO(4,2) group operations. In this section we merely present its generators in terms of the physical operators $\hat{\vec{p}}$ and $\hat{\vec{x}}$. In depth information, including other representations in terms of spinors or the square root coordinates (u^1, u^2, u^3, u^4) introduced in section 5.2, can be found in Kleinert (1968a,b), Kleinert (2004).

Let $\hat{T}_{AB}$ be a 6×6-matrix-valued, totally antisymmetric operator whose components are equal to the fifteen generators of SO(4,2). The $\hat{T}_{AB}$ must then satisfy the commutation relations

$$\begin{aligned}[\hat{T}_{AB}, \hat{T}_{CD}] &= i\left(g_{AC}\hat{T}_{BD} - g_{AD}\hat{T}_{BC} - g_{BC}\hat{T}_{AD} + g_{BD}\hat{T}_{AC}\right), \\ (g_{AB}) &= \mathrm{diag}(1,1,1,1,-1,-1)\end{aligned} \tag{7.66}$$

where uppercase indices take values $\{1,2,3,4,5,6\}$ and g is the metric of six dimensional Minkowski space with two timelike dimensions. In the following we will find expressions for all of the components $\hat{T}_{AB}$.

From previous considerations we already know that the components of the angular momentum operator span a SO(3) subgroup and are thus among the generators of SO(4,2). The LRL operator, however, is not an advantageous choice as a generator in the representation we are developing. In the last section we introduced the $\hat{w}$-operators. Now we introduce the following set of closely related operators:

$$\begin{aligned}\hat{W}^1 &= \hat{\vec{x}}\hat{\vec{p}} - i, \\ \hat{W}^2 &= \frac{1}{2}\left(\frac{\hat{r}\hat{\vec{p}}^2}{m\alpha} - m\alpha\hat{r}\right), \\ \hat{W}^3 &= \frac{1}{2}\left(\frac{\hat{r}\hat{\vec{p}}^2}{m\alpha} + m\alpha\hat{r}\right),\end{aligned} \tag{7.67}$$

which are equal to the $\hat{w}$-operators when expressed in terms of $\hat{p}_r$ and after $\hat{\vec{L}}^2$ has been replaced by its eigenvalue. Consequently they have the same commutation relations among each other,

$$\begin{aligned}[\hat{W}^1, \hat{W}^2] &= i\hat{W}^3, \\ [\hat{W}^2, \hat{W}^3] &= -i\hat{W}^1,\end{aligned}$$

$$[\hat{W}^3, \hat{W}^1] = -i\hat{W}^2. \tag{7.68}$$

We readily verify that the $\hat{W}^j$ and $\hat{L}^k$ commute with each other,

$$[\hat{W}^j, \hat{L}^k] = 0. \tag{7.69}$$

The $\hat{W}^i$ generate a SO(2,1) subgroup of SO(4,2) and hence we already know six of the total fifteen generators. In order to find the remaining generators, we consider the following commutation relations

$$\begin{aligned}
[\hat{r}, \hat{L}^j] &= 0, & [\hat{p}^j, \hat{L}^k] &= i\varepsilon^{jkl}\hat{p}_l, \\
[\hat{r}, \hat{W}^1] &= i\hat{r}, & [\hat{p}^j, \hat{W}^1] &= -i\hat{p}^j, \\
[\hat{r}, \hat{W}^2] &= \frac{i\hat{W}^1}{m\alpha}, & [\hat{p}^j, \hat{W}^2] &= -i\frac{\hat{x}^j}{\hat{r}^2}\hat{W}^2, \\
[\hat{r}, \hat{W}^3] &= \frac{i\hat{W}^1}{m\alpha}, & [\hat{p}^j, \hat{W}^3] &= -i\frac{\hat{x}^j}{\hat{r}^2}\hat{W}^3.
\end{aligned} \tag{7.70}$$

These relations lead us to the definition of the operator $\hat{\vec{\Gamma}}$,

$$\hat{\vec{\Gamma}} = \hat{r}\hat{\vec{p}}. \tag{7.71}$$

Its commutators with $\hat{\vec{L}}$ and the $\hat{W}$-operators read

$$\begin{aligned}
[\hat{\Gamma}^j, \hat{\Gamma}^k] &= -i\varepsilon^{jkl}\hat{L}_l, \\
[\hat{\Gamma}^j, \hat{L}^k] &= i\varepsilon^{jkl}\hat{\Gamma}_l, \\
[\hat{\Gamma}^j, \hat{W}^1] &= 0, \\
[\hat{\Gamma}^j, \hat{W}^2] &= i\left(\frac{\hat{W}^1\hat{p}^j}{m\alpha} - \frac{\hat{x}^j}{\hat{r}}\hat{W}^2\right), \\
[\hat{\Gamma}^j, \hat{W}^3] &= i\left(\frac{\hat{W}^1\hat{p}^j}{m\alpha} - \frac{\hat{x}^j}{\hat{r}}\hat{W}^3\right).
\end{aligned} \tag{7.72}$$

The first three lines look very promising. However, if $\hat{\vec{\Gamma}}$ is indeed a generator of SO(4,2) then the right hand sides of the last two lines need to be generators as well so that eq. (7.66) can be satisfied. Hence we define

$$\begin{aligned}
\hat{\vec{\mathcal{U}}} &= \frac{\hat{\vec{x}}}{\hat{r}}\hat{W}^2 - \frac{\hat{W}^1\hat{\vec{p}}}{m\alpha}, \\
\hat{\vec{\mathcal{V}}} &= \frac{\hat{\vec{x}}}{\hat{r}}\hat{W}^3 - \frac{\hat{W}^1\hat{\vec{p}}}{m\alpha}.
\end{aligned} \tag{7.73}$$

The commutators of these new operators with allr the previously found generators read

$$\begin{aligned}
[\hat{\mathcal{U}}^j, \hat{L}^k] &= i\varepsilon^{jkl}\hat{\mathcal{U}}_l, & [\hat{\mathcal{V}}^j, \hat{L}^k] &= i\varepsilon^{jkl}\hat{\mathcal{V}}_l, \\
[\hat{\mathcal{U}}^j, \hat{\Gamma}^k] &= i\delta^{jk}\hat{W}^2, & [\hat{\mathcal{V}}^j, \hat{\Gamma}^k] &= i\delta^{jk}\hat{W}^3, \\
[\hat{\mathcal{U}}^j, \hat{W}^1] &= -i\hat{\mathcal{V}}^j, & [\hat{\mathcal{V}}^j, \hat{W}^1] &= -i\hat{\mathcal{U}}^j, \\
[\hat{\mathcal{U}}^j, \hat{W}^2] &= -i\hat{\Gamma}^j, & [\hat{\mathcal{V}}^j, \hat{W}^2] &= 0, \\
[\hat{\mathcal{U}}^j, \hat{W}^3] &= 0, & [\hat{\mathcal{V}}^j, \hat{W}^3] &= i\hat{\Gamma}^j.
\end{aligned} \tag{7.74}$$

Among each other, they have the commutators,

$$\begin{aligned}
[\hat{\mathcal{U}}^j, \hat{\mathcal{U}}^k] &= i\varepsilon^{jkl}\hat{L}_l, \\
[\hat{\mathcal{V}}^j, \hat{\mathcal{V}}^k] &= -i\varepsilon^{jkl}\hat{L}_l, \\
[\hat{\mathcal{U}}^j, \hat{\mathcal{V}}^k] &= i\delta^{jk}\hat{W}^1.
\end{aligned} \tag{7.75}$$

Now we are able to populate the entries of $\hat{T}_{AB}$ in the following way,

$$\begin{aligned}
\hat{T}_{jk} &= \varepsilon_{jkl}\hat{L}^l, & \hat{T}_{45} &= \hat{W}^1, \\
\hat{T}_{j4} &= \hat{\mathcal{U}}_j, & \hat{T}_{46} &= \hat{W}^2, \\
\hat{T}_{j5} &= \hat{\mathcal{V}}_j, & \hat{T}_{56} &= \hat{W}^3, \\
\hat{T}_{j6} &= \hat{\Gamma}_j, & &
\end{aligned} \tag{7.76}$$

or written in matrix notation,

$$(\hat{T}_{AB}) = \begin{pmatrix}
0 & \hat{L}^3 & -\hat{L}^2 & \hat{\mathcal{U}}_1 & \hat{\mathcal{V}}_1 & \hat{\Gamma}_1 \\
-\hat{L}^3 & 0 & \hat{L}^1 & \hat{\mathcal{U}}_2 & \hat{\mathcal{V}}_2 & \hat{\Gamma}_2 \\
\hat{L}^2 & -\hat{L}^1 & 0 & \hat{\mathcal{U}}_3 & \hat{\mathcal{V}}_3 & \hat{\Gamma}_3 \\
-\hat{\mathcal{U}}^1 & -\hat{\mathcal{U}}^2 & -\hat{\mathcal{U}}^3 & 0 & \hat{W}^1 & \hat{W}^2 \\
-\hat{\mathcal{V}}^1 & -\hat{\mathcal{V}}^2 & -\hat{\mathcal{V}}^3 & -\hat{W}^1 & 0 & \hat{W}^3 \\
-\hat{\Gamma}^1 & -\hat{\Gamma}^2 & -\hat{\Gamma}^3 & -\hat{W}^2 & -\hat{W}^3 & 0
\end{pmatrix}. \tag{7.77}$$

Using the commutation relations worked out in this section, one can verify that this definition of $\hat{T}_{AB}$ indeed satisfies eq. (7.66). All dynamical variables can be expressed in terms of the generators of SO(4,2),

$$\begin{aligned}
m\alpha\hat{x}_j &= \hat{T}_{j5} - \hat{T}_{j4}, & \frac{\hat{p}_j}{m\alpha} &= (\hat{T}_{56} - \hat{T}_{46})^{-1}\hat{T}_{j6}, \\
m\alpha\hat{r} &= \hat{T}_{56} - \hat{T}_{46}, & \frac{\hat{\vec{p}}^2}{(m\alpha)^2} &= (\hat{T}_{56} - \hat{T}_{46})^{-1}(\hat{T}_{56} + \hat{T}_{46}).
\end{aligned} \tag{7.78}$$

Chapter 8

The two-particle Dirac equation

In the non-relativistic approach to the hydrogen atom in chapter 2, we considered the two-particle system of proton and electron and introduced CM and relative coodinates. This lead to a separation of the Hamiltonian and reduced the problem to a single particle of reduced mass m interacting with an external potential $-\alpha/r$. There is no simple way in the relativistic treatment of the hydrogen atom that leads to an analogous separation of the Dirac Hamiltonian. For this reason we started directly with the single-particle Hamiltonian in eq. (4.41) in chapter 4. A rigorous treatment of the relativistic hydrogen atom, however, should start with the full two-particle Hamiltonian. An analytic solution for this relativistic problem was only obtained by Marsch in 2005. This chapter illustrates his approach.

8.1 Preparations

Let us consider the relativistic two-particle system consisting of electron and proton bound together in a hydrogen atom. The general Dirac equation for a single particle of mass m and charge e reads in the Hamiltonian formulation

$$i\partial_t \Psi(x) = \left(-eA_0 - i\gamma^0\vec{\gamma}\vec{\nabla} - e\gamma^0\vec{\gamma}\vec{A} + \gamma^0 m\right)\Psi(x), \tag{8.1}$$

where Ψ is a four-component Dirac spinor as familiar from chapter 4. In the case of the two-particle problem, however, we consider Ψ to be an element of the two-particle Fock space,

$$\Psi(x) = \Psi_p(x) \otimes \Psi_e(x), \tag{8.2}$$

where Ψ_p and Ψ_e represent four-component Dirac spinors describing the proton and electron, respectively. Analogous to chapter 3 we call the positions

of proton and electron $\vec{x}_p$ and $\vec{x}_e$, respectively and change to the CMS,

$$\begin{aligned} \vec{R} &= \frac{m_p\vec{x}_p + m_e\vec{x}_e}{M} \equiv 0, & \vec{r} &= \vec{x}_e - \vec{x}_p, \\ \vec{\nabla}_R &= \vec{\nabla}_p + \vec{\nabla}_e \equiv 0, & \vec{\nabla} &\equiv \vec{\nabla}_r = \vec{\nabla}_e = -\vec{\nabla}_p, \end{aligned} \tag{8.3}$$

where $M = m_p + m_e$ and we let the vector potential A represent the Coulomb potential,

$$eA = -\frac{\alpha}{r}\, e_t, \tag{8.4}$$

The Hamiltonian for this system then reads

$$H = \left(-\frac{\alpha}{r} + i\gamma^0\vec{\gamma}\vec{\nabla} + \gamma^0 m_p\right) \otimes \left(-\frac{\alpha}{r} - i\gamma^0\vec{\gamma}\vec{\nabla} + \gamma^0 m_e\right), \tag{8.5}$$

where m_p and m_e means the proton and electron mass, respectively. Further we define the nuclear and electron spin operators,

$$\vec{I} = \frac{1}{2}(\gamma_5\gamma^0\vec{\gamma}) \otimes \mathbb{1}, \qquad \vec{S} = \frac{1}{2}\mathbb{1} \otimes (\gamma_5\gamma^0\vec{\gamma}), \tag{8.6}$$

to obtain the following explicit expression for the Hamiltonian of the hydrogen atom

$$H = \begin{pmatrix} -\frac{\alpha}{r} + m_p & 2i\vec{I}\vec{\nabla} \\ 2i\vec{I}\vec{\nabla} & -\frac{\alpha}{r} - m_p \end{pmatrix} \otimes \begin{pmatrix} -\frac{\alpha}{r} + m_e & -2i\vec{S}\vec{\nabla} \\ -2i\vec{S}\vec{\nabla} & -\frac{\alpha}{r} - m_e \end{pmatrix} \tag{8.7}$$

In the following it will be useful to express the Hamiltonian in a spin basis,

$$e_1 = |+\rangle \otimes |+\rangle, \quad e_2 = |+\rangle \otimes |-\rangle, \quad e_3 = |-\rangle \otimes |+\rangle, \quad e_4 = |-\rangle \otimes |-\rangle. \tag{8.8}$$

Again, we make the ansatz suitable for a stationary problem,

$$\Psi(t, \vec{x}) = e^{-iEt}\Psi(\vec{x}), \tag{8.9}$$

and obtain for eqs. (8.1) and (8.7),

$$\begin{pmatrix} -E - \frac{\alpha}{r} + M & -2i\vec{S}\vec{\nabla} & 2i\vec{I}\vec{\nabla} & 0 \\ -2i\vec{S}\vec{\nabla} & -E - \frac{\alpha}{r} + \mu M & 0 & 2i\vec{I}\vec{\nabla} \\ 2i\vec{I}\vec{\nabla} & 0 & -E - \frac{\alpha}{r} - \mu M & -2i\vec{S}\vec{\nabla} \\ 0 & 2i\vec{I}\vec{\nabla} & -2i\vec{S}\vec{\nabla} & -E - \frac{\alpha}{r} - M \end{pmatrix} \Psi(\vec{x}) = 0, \tag{8.10}$$

where $M = m_p + m_e$ und $\mu = (m_p - m_e)/M$. Before we proceed to the actual derivation of the solution let us consider the total angular momentum operator,

$$\vec{J} = \vec{L} + \vec{S} + \vec{I}, \tag{8.11}$$

where $\vec{L} = -i\vec{r} \times \vec{\nabla}$. One finds that

$$\begin{aligned}\left[H, \vec{J}\right] = &\underbrace{(\gamma^0\vec{\gamma} \times \vec{\nabla}) \otimes \mathbb{1} - \mathbb{1} \otimes (\gamma^0\vec{\gamma} \times \vec{\nabla})}_{=\left[H,\vec{L}\right]} \\ &\underbrace{-(\gamma^0\vec{\gamma} \times \vec{\nabla}) \otimes \mathbb{1}}_{=\left[H,\vec{I}\right]} \underbrace{+\mathbb{1} \otimes (\gamma^0\vec{\gamma} \times \vec{\nabla})}_{=\left[H,\vec{S}\right]} = 0.\end{aligned} \tag{8.12}$$

Correspondingly there exists a basis which diagonalizes the Hamiltonian and the total angular momentum operator simultaneously. This will proof useful.

8.2 Derivation of the solution to the spherical Dirac equation

We define the operators

$$K_I = 1 + 2\vec{I}\vec{L}, \qquad K_S = 1 + 2\vec{S}\vec{L}. \tag{8.13}$$

Before in inspecting their spectrum and eigenbasis, we note that

$$\begin{aligned}-i\vec{\sigma}\vec{\nabla} &= -i\vec{\sigma}\vec{e}_r\,\vec{\sigma}\vec{e}_r\,\vec{\sigma}\vec{\nabla} = h\left(-i\partial_r + \vec{\sigma}\vec{e}_r \times \vec{\nabla}\right) \\ &= ih\left(-\partial_r + \frac{2\vec{S}\vec{L}}{r}\right) \quad \text{or} \quad ih\left(-\partial_r + \frac{2\vec{I}\vec{L}}{r}\right) \\ &= \frac{i}{r}h\left(-\partial_r r + K_{S/I}\right),\end{aligned} \tag{8.14}$$

where we have defined a helicity operator

$$h = \vec{\sigma}\vec{e}_r = \begin{pmatrix} \cos\theta & e^{-i\varphi}\sin\theta \\ e^{i\varphi}\sin\theta & \cos\theta \end{pmatrix}. \tag{8.15}$$

Further we introduce the variables

$$x = Mr, \qquad e = \frac{E}{M}, \qquad D_{S/I} = -\partial_x x + K_{S/I} \tag{8.16}$$

so that the Dirac equation (8.10) reads

$$\begin{pmatrix} -e-\frac{\alpha}{x}+1 & \frac{i}{x}h_S D_S & -\frac{i}{x}h_I D_I & 0 \\ \frac{i}{x}h_S D_S & -e-\frac{\alpha}{x}+\mu & 0 & -\frac{i}{x}h_I D_I \\ -\frac{i}{x}h_I D_I & 0 & -e-\frac{\alpha}{x}-\mu & \frac{i}{x}h_S D_S \\ 0 & -\frac{i}{x}h_I D_I & \frac{i}{x}h_S D_S & -e-\frac{\alpha}{x}-1 \end{pmatrix} \Psi(x) = 0. \tag{8.17}$$

Let us now consider the operators $K_{S/I}$. Their commutator reads

$$[K_S, K_I] = 4i\left(\vec{S}\times\vec{I}\right)\vec{L} \stackrel{!}{=} 0. \tag{8.18}$$

In order to solve eq. (8.17) we have to find a basis, in which the commutator (8.18) vanishes. Let us insvestigate the algebraic properties of $K_{S/I}$. The total spin operator is given by

$$\vec{Q} = \vec{S} + \vec{I}. \tag{8.19}$$

One should note that

$$K_I + K_S = 2 + \vec{J}^2 - \vec{L}^2 - \vec{Q}^2. \tag{8.20}$$

In the following we seek a basis of eigenvectors,

$$K_{I/S}\Psi = k\Psi, \tag{8.21}$$

or, using eq. (8.20),

$$k = 1 + \frac{1}{2}\left(j(j+1) - l(l+1) - q(q+1)\right) = \begin{cases} 1, & q=0, & j=l \\ l+1, & q=1 & j=l+1 \\ -l, & q=1 & j=l-1 \end{cases}. \tag{8.22}$$

One can see that $k \equiv 1$ for the singulet state and $k = \pm 1, \pm 2, ...$ for the triplet states. In the spin basis of eq. (8.8) the matrix elements of $K_{S/I}$ read

$$K_S = \begin{pmatrix} 1+L_3 & L_- & 0 & 0 \\ L_+ & 1-L_3 & 0 & 0 \\ 0 & 0 & 1+L_3 & L_- \\ 0 & 0 & L_+ & 1-L_3 \end{pmatrix} \tag{8.23}$$

$$K_I = \begin{pmatrix} 1+L_3 & 0 & L_- & 0 \\ 0 & 1+L_3 & 0 & L_- \\ L_+ & 0 & 1-L_3 & 0 \\ 0 & L_+ & 0 & 1-L_3 \end{pmatrix}. \tag{8.24}$$

We now make the following ansatz,

$$\Psi(\vec{x}) = \psi_1(x)\phi_1(\theta,\varphi)+\psi_2(x)\phi_2(\theta,\varphi)+\psi_3(x)\phi_3(\theta,\varphi)+\psi_4(x)\phi_4(\theta,\varphi), \quad (8.25)$$

where

$$\phi_1 = Y_{l,m-1}e_1, \qquad \phi_2 = Y_{lm}e_2, \qquad \phi_3 = Y_{lm}e_3, \qquad \phi_4 = Y_{l,m+1}e_4, \qquad (8.26)$$

and where Y_{lm} are the spherical harmonics. The operators $K_{S/I}$ then become

$$K_S = \begin{pmatrix} m & B(-m) & 0 & 0 \\ B(-m) & 1-m & 0 & 0 \\ 0 & 0 & 1+m & B(m) \\ 0 & 0 & B(m) & -m \end{pmatrix} \quad (8.27)$$

$$K_I = \begin{pmatrix} m & 0 & B(-m) & 0 \\ 0 & 1+m & 0 & B(m) \\ B(-m) & 0 & 1-m & 0 \\ 0 & B(m) & 0 & -m \end{pmatrix}, \quad (8.28)$$

where $L_\pm Y_{lm} = B(\pm m)Y_{l,m\pm1}$ and

$$B(m) = \sqrt{(l-m)(l+m+1)} = \sqrt{(k+m)(k-m-1)}. \quad (8.29)$$

Note that $B(m-1) = B(-m)$. We now choose a new basis such that the singlet and triplet states live in different subspaces,

$$\begin{aligned} \Phi_0 &= \frac{1}{\sqrt{2}}(e_2 - e_3)\, Y_{lm}, & \Phi_1 &= Y_{l,m-1}e_1, \\ \Phi_2 &= \frac{1}{\sqrt{2}}(e_2 + e_3)\, Y_{lm}, & \Phi_3 &= Y_{l,m+1}e_4. \end{aligned} \quad (8.30)$$

The change of the basis (8.26) to (8.30) is conducted via the orthogonal transformation matrix

$$U = \begin{pmatrix} 0 & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} & 0 \\ 1 & 0 & 0 & 0 \\ 0 & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \quad , \quad U^{-1} = U^T = \begin{pmatrix} 0 & 1 & 0 & 0 \\ \frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} & 0 \\ -\frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}. \quad (8.31)$$

In this new basis the operators $K_{S/I}$ become $K'_{S/I} = UK_{S/I}U^{-1} = K_+ \pm K_-$, where

$$K_+ = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & m & B(-m)/\sqrt{2} & 0 \\ 0 & B(-m)/\sqrt{2} & 1 & B(m)/\sqrt{2} \\ 0 & 0 & B(m)/\sqrt{2} & -m \end{pmatrix} \quad (8.32)$$

$$K_- = \begin{pmatrix} 0 & B(-m)/\sqrt{2} & -m & -B(m)/\sqrt{2} \\ B(-m)/\sqrt{2} & 0 & 0 & 0 \\ -m & 0 & 0 & 0 \\ -B(m)/\sqrt{2} & 0 & 0 & 0 \end{pmatrix}. \tag{8.33}$$

The matrix K_+ has the eigenvalues 0, $-l$, $l+1$, where 0 has to e excluded as we have seen in the algebraic treatment ($k \neq 0$). The corresponding eigenvectors read

$$\lambda = l+1 = k: \quad E_1 = \frac{1}{\sqrt{2(l+1)(2l+1)}} \begin{pmatrix} \sqrt{(l+m)(l+m+1)} \\ \sqrt{2}\sqrt{(l-m+1)(l+m+1)} \\ \sqrt{(l-m)(l-m+1)} \end{pmatrix} \tag{8.34}$$

$$\lambda = -l = k: \quad E_2 = \frac{1}{\sqrt{2l(2l+1)}} \begin{pmatrix} \sqrt{(l-m)(l-m+1)} \\ -\sqrt{2}\sqrt{(l-m)(l+m)} \\ \sqrt{(l+m)(l+m+1)} \end{pmatrix}. \tag{8.35}$$

In terms of the quantum number k there exists a common expression for both eigenvectors,

$$E_1\Big|_{k>0} = E_2\Big|_{k<0} = \frac{1}{\sqrt{2k(2k-1)}} \begin{pmatrix} \sqrt{(k+m)(k+m-1)} \\ \operatorname{sgn} k\sqrt{2}\sqrt{(k+m)(k-m)} \\ \sqrt{(k-m)(k-m-1)} \end{pmatrix}. \tag{8.36}$$

Note further that $K_- E_{1/2} = 0$. Obviously the triplet and singlet states do not mix. The same should be true for Φ_0. Setting $K_-\Phi_0 = 0$ implies, however, that $l = 0$ i. e. $k = 1$. There we define

$$\begin{aligned} {}^T\Omega_{km}(\theta,\varphi) &= \frac{1}{\sqrt{2k(2k-1)}} \Big[\sqrt{(k+m)(k+m-1)}\, Y_{-k,m-1}(\theta,\varphi)\, |+\rangle \otimes |+\rangle + \\ &+ \operatorname{sgn} k \sqrt{(k+m)(k-m)}\, Y_{-k,m}(\theta,\varphi)\, (|+\rangle \otimes |-\rangle + |-\rangle \otimes |+\rangle) + \\ &+ \sqrt{(k-m)(k-m-1)}\, Y_{-k,m+1}(\theta,\varphi)\, |-\rangle \otimes |-\rangle \Big], \end{aligned} \tag{8.37}$$

$$= \sqrt{\frac{k^2-m^2}{2k(2k-1)}} \begin{pmatrix} \sqrt{\frac{k+m-1}{k-m}}\, Y_{-k,m-1}(\theta,\varphi) \\ \operatorname{sgn} k\, Y_{-k,m}(\theta,\varphi) \\ \operatorname{sgn} k\, Y_{-k,m}(\theta,\varphi) \\ \sqrt{\frac{k-m-1}{k+m}}\, Y_{-k,m+1}(\theta,\varphi) \end{pmatrix}, \tag{8.38}$$

(8.39)

as well as,

$$ {}^{S}\Omega_{km}(\theta,\varphi) = \frac{\delta_{k1}}{\sqrt{8\pi}}\left(|+\rangle\otimes|-\rangle - |-\rangle\otimes|+\rangle\right) = \frac{\delta_{k1}}{\sqrt{8\pi}}\begin{pmatrix} 0 \\ 1 \\ -1 \\ 0 \end{pmatrix}. \tag{8.40} $$

These objects satisfy $K_{I/S}\,{}^{S/T}\Omega_{km} = k\Omega_{km}$. They represent solutions of the spherical Dirac equation with quantum numbers (k,m). Further we note that $\{K_{I/S}, h_{I/S}\} = 0$ and ${h_{I/S}}^2 = 1$ implies

$$ K_{I/S}h_{I/S}\Omega_{km} = -kh_{I/S}\Omega_{km}. \tag{8.41} $$

Thus the explicit expression for $h_{I/S}\Omega$ reads

$$ h_{S/I}\,{}^{T}\Omega_{km}(\theta,\varphi) = \sqrt{\frac{k^2-m^2}{2k(2k+1)}}\begin{pmatrix} \sqrt{\frac{k-m+1}{k-m}}\,Y_{k,m-1}(\theta,\varphi) \\ \mp\operatorname{sgn}k\sqrt{\frac{k+m}{k-m}}\,Y_{k,m}(\theta,\varphi) \\ \pm\operatorname{sgn}k\sqrt{\frac{k-m}{k+m}}\,Y_{k,m}(\theta,\varphi) \\ -\sqrt{\frac{k+m+1}{k+m}}\,Y_{k,m+1}(\theta,\varphi) \end{pmatrix}. \tag{8.42} $$

Finally we may write the wave function (8.25) as

$$ \Psi(r,\theta,\varphi) = \left(F_1(x), ih_SF_2(x), ih_IF_3(x), h_Sh_IF_4(x)\right)\frac{\Omega_{km}(\theta,\varphi)}{x}, \tag{8.43} $$

where we have already included an ansatz for the radial Dirac equation (8.17).

8.3 Solving the radial Dirac equation

Inserting eq. (8.43) with the new ansatz for the radial part into eq. (8.17) we obtain

$$ \begin{pmatrix} -e-\frac{\alpha}{x}+1 & \partial_x+\frac{k}{x} & -\partial_x-\frac{k}{x} & 0 \\ -\partial_x+\frac{k}{x} & -e-\frac{\alpha}{x}+\mu & 0 & \partial_x+\frac{k}{x} \\ \partial_x-\frac{k}{x} & 0 & -e-\frac{\alpha}{x}-\mu & -\partial_x-\frac{k}{x} \\ 0 & -\partial_x+\frac{k}{x} & \partial_x-\frac{k}{x} & -e-\frac{\alpha}{x}-1 \end{pmatrix} F(x) = 0. \tag{8.44} $$

Keeping in mind our previous experience with the Coulomb problem we make the ansatz

$$ \vec{F}(x) = z^{\gamma}e^{-z}\vec{H}(z), \qquad z = \kappa x, \qquad \gamma,\kappa > 0 \tag{8.45} $$

to obtain, after a multiplication by -1,

$$\begin{pmatrix} e_1+\frac{\alpha}{z} & -\partial_z+1-\frac{k+\gamma}{z} & \partial_z-1+\frac{k+\gamma}{z} & 0 \\ \partial_z-1-\frac{k-\gamma}{z} & e_2+\frac{\alpha}{z} & 0 & -\partial_z+1-\frac{k+\gamma}{z} \\ -\partial_z+1+\frac{k-\gamma}{z} & 0 & e_3+\frac{\alpha}{z} & \partial_z-1+\frac{k+\gamma}{z} \\ 0 & \partial_z-1-\frac{k-\gamma}{z} & -\partial_z+1+\frac{k-\gamma}{z} & e_4+\frac{\alpha}{z} \end{pmatrix} \vec{H}(z)=0, \tag{8.46}$$

where we have defined

$$e_1=(e-1)/\kappa, \quad e_2=(e-\mu)/\kappa \quad e_3=(e+\mu)/\kappa \quad e_4=(e+1)/\kappa. \tag{8.47}$$

Let us make the ansatz

$$\vec{H}(z)=\sum_{i=0}^{N}\vec{a}_i z^i, \tag{8.48}$$

where $N<\infty$, which is required to make the wave function normalizable. Using the substitution $r=\gamma+i$ yields the recursive relation

$$\begin{pmatrix} \alpha & -k-r & k+r & 0 \\ -k+r & \alpha & 0 & -k-r \\ k-r & 0 & \alpha & k+r \\ 0 & -k+r & k-r & \alpha \end{pmatrix} \vec{a}_i = \begin{pmatrix} -e_1 & -1 & 1 & 0 \\ 1 & -e_2 & 0 & -1 \\ -1 & 0 & -e_3 & 1 \\ 0 & 1 & -1 & -e_4 \end{pmatrix} \vec{a}_{i-1}, \tag{8.49}$$

or shorter,

$$\mathcal{M}_i\vec{a}_i=\mathcal{N}\vec{a}_{i-1}. \tag{8.50}$$

Four constraints may be derived from eq. (8.50). First we have

$$\mathcal{M}_0\vec{a}_0=0 \quad \Rightarrow \quad \det\mathcal{M}_0=0 \quad \Rightarrow \quad \gamma=\sqrt{k^2-\frac{\alpha^2}{4}}, \tag{8.51}$$

and second,

$$\vec{a}_0\propto\begin{pmatrix} k+\gamma \\ \alpha/2 \\ -\alpha/2 \\ k-\gamma \end{pmatrix}, \tag{8.52}$$

the third and fourth constraints read, respectively,

$$\det\mathcal{N}=0 \quad \Rightarrow \qquad 0=e_1e_2e_3e_4+(e_1+e_4)(e_2+e_3), \tag{8.53}$$

$$\mathcal{N}\vec{a}_N = 0 \quad \Rightarrow \qquad \vec{a}_N = \begin{pmatrix} -e_4 \\ \frac{e_1 e_3 e_4}{e_2+e_3} \\ -\frac{e_1 e_2 e_4}{e_2+e_3} \\ e_1 \end{pmatrix}, \tag{8.54}$$

where the first line is required in order to exclude the trivial solution of the second line. From eq. (8.53) we obtain the following relation for κ,

$$\kappa = \sqrt{\frac{(1-e^2)(e^2-\mu^2)}{4e^2}}. \tag{8.55}$$

The as usual the energy levels may be derived from the termination of the power series,

$$\mathcal{M}_N \vec{a}_N = \mathcal{N}\vec{a}_{N-1}. \tag{8.56}$$

By Gaussian elimination we can make one line on the right-hand side vanish. This line then contains the following information

$$\vec{Q}\vec{a}_N = 0, \qquad \vec{Q} = \begin{pmatrix} ((k-r)e_1 - \alpha)e_2 e_3 e_4 \\ (\alpha + re_2)e_3(e_1+e_4) - ke_2e_3(e_1-e_4) \\ -(\alpha + re_3)e_2(e_1+e_4) + ke_2e_3(e_1-e_4) \\ ((k+r)e_4 + \alpha)e_1 e_2 e_3 \end{pmatrix}. \tag{8.57}$$

Using eq. (8.54) for $\vec{a}_N$ we obtain the relation

$$(e_2+e_3)(e_1+e_4) = \frac{\alpha}{2r}\left(e_2e_3\frac{e_1^2+e_4^2}{e_1+e_4} + e_1e_4\frac{e_2^2+e_3^2}{e_2+e_3}\right). \tag{8.58}$$

Substituting the expressions from eq. (8.47) yields the equation

$$\begin{aligned} 4e^2 &= \frac{\alpha}{2r\kappa}\left((e^2-\mu^2)\frac{e^2+1}{2e} + (e^2-1)\frac{e^2+\mu^2}{2e}\right) \\ \Leftrightarrow \quad \frac{\alpha}{2r}\frac{e^4-\mu^2}{e^2} &= \sqrt{(1-e^2)(e^2-\mu^2)}. \end{aligned} \tag{8.59}$$

This equation implies that $\mu \leq e \leq 1$. We may thus write $e = 1-\zeta$ and expand the square of eq. (8.59) up to quadratic order in ζ,

$$\begin{aligned} 0 &\approx 2\zeta(1-\mu^2) - \zeta^2(5-\mu^2) - \frac{\alpha^2}{4r^2}(1-4\zeta+6\zeta^2-\mu^2)^2(1+2\zeta+3\zeta^2)^2 \\ &\approx \sqrt{2\zeta(1-\mu^2)-\zeta^2(5-\mu^2)} - \frac{\alpha}{2r}(1-4\zeta+6\zeta^2-\mu^2)(1+2\zeta+3\zeta^2) \end{aligned} \tag{8.60}$$

$$0 = \left(\frac{\alpha}{2r}\right)^2 \left(\frac{e^4 - \mu^2}{e^2}\right)^2 - (1 - e^2)(e^2 - \mu^2). \tag{8.61}$$

In terms of the variable $y = e^2$ we obtain the quartic equation

$$\left(1 + \left(\frac{\alpha}{2r}\right)^2\right) y^4 - \left(1 + \mu^2\right) y^3 + \left(1 - 2\left(\frac{\alpha}{2r}\right)^2\right) y^2 + \mu^4 \left(\frac{\alpha}{2r}\right)^2 = 0. \tag{8.62}$$

Appendix A

Elementary calculations in QED

In this appendix we perform one-loop QED calculations concerning the vacuum polarization Π and 3-point vertex function $\mathcal{V}_3$, given in eqs. (6.56) and (6.69), to the extend needed for the calculations in chapter 6. We consider unbound electrons and use the on-shell (OS) renormalization scheme. For definitions and notation see chapter 6.

A.1 The vacuum polarization

In this section we calculate the vacuum polarization Π in the limit of small photon momenta, $k^2 \ll m^2$, to the linear order in α. Let us start from the second line of eq. (6.56),

$$\begin{aligned}\Pi^{\mu\nu}(x-y) = &-ie^2 \operatorname{Tr}[S(x-y)\gamma^\mu S(y-x)\gamma^\nu] \\ &+ \delta_A(\eta^{\mu\nu}\partial_x^2 + \mathcal{G}^{\mu\nu}(x))\delta^4(x-y) + O(\alpha^2). \qquad \text{(A.1)}\end{aligned}$$

Let us choose Lorenz gauge, i.e. $\mathcal{G}^{\mu\nu} = -\partial^\mu\partial^\nu$. Using eqs. (6.19) and defining $P^{\mu\nu} = \eta^{\mu\nu} - k^\mu k^\nu/k^2$, the Fourier transform of Π reads

$$\begin{aligned}\Pi^{\mu\nu}(k) + \delta_A k^2 P^{\mu\nu} &= -ie^2 \int \frac{d^4l}{(2\pi)^4} \operatorname{Tr}\left(\tilde{S}(l-k)\gamma^\mu \tilde{S}(l)\gamma^\nu\right) \\ &= ie^2 \int \frac{d^4l}{(2\pi)^4} \operatorname{Tr} \frac{(\not{l}+\not{k}-m)\gamma^\mu(\not{l}-m)\gamma^\nu}{((l+k)^2+m^2)\,(l^2+m^2)} \\ &= 4ie^2 \int dF_2 \int \frac{d^4l}{(2\pi)^4} \frac{N^{\mu\nu}}{(x_1(l+k)^2 + x_2 l^2 + m^2)^2}\end{aligned}$$

$$= -4e^2 \int_0^1 dx \int \frac{d^4\bar{q}}{(2\pi)^4} \frac{N^{\mu\nu}}{(\bar{q}^2 + D)^2}. \tag{A.2}$$

In the third line we have introduced Feynman parameters $\{x_i\}$ with integration measure

$$\int dF_n = (n-1)! \int_0^1 \left(\prod_{i=1}^n dx_i \right) \delta \left(\sum_{i=1}^n x_i - 1 \right), \tag{A.3}$$

also we have performed a Wick rotation in the fourth line,

$$\bar{q} = (-iq^0, \vec{q}), \qquad\qquad q = l + x_1 k, \tag{A.4}$$

and, replacing $x_1 \to x$, made the substitutions

$$\begin{aligned} N^{\mu\nu} &= 2(l+k)^{(\mu} l^{\nu)} - \left(l(l+k) + m^2 \right) \eta^{\mu\nu} \\ &= 2\bar{q}^\mu \bar{q}^\nu + 2x(1-x)k^2 P^{\mu\nu} - \left(\bar{q}^2 + D \right) \eta^{\mu\nu} + (\text{linear in } \bar{q}), \\ D &= x(1-x)k^2 + m^2. \end{aligned} \tag{A.5}$$

Since the integral in eq. (A.2) diverges we have to choose a way to regularize it so the infinite parts may be absorbed properly into δ_A. We choose dimensional regularization, i.e. we perform the integral in $d - \epsilon$ dimensions, where $d = 4$. Also we replace $e \to e\tilde{\mu}^{\epsilon/2}$ to keep e non-dimensional in $d - \epsilon$ dimensions. Inserting $\alpha = e^2/(4\pi)$ and using the formulae

$$\int \frac{d^d\bar{q}}{(2\pi)^d} \frac{(\bar{q}^2)^a}{(\bar{q}^2 + D)^b} = \frac{\Gamma\left(b - a - \frac{d}{2}\right) \Gamma\left(a + \frac{d}{2}\right)}{(4\pi)^{d/2} \Gamma(b) \Gamma\left(\frac{d}{2}\right)} D^{-b+a+d/2}, \tag{A.6}$$

and

$$\int d^d q \, q^\mu q^\nu f(q^2) = \frac{1}{d} \eta^{\mu\nu} \int d^d q \, f(q^2), \tag{A.7}$$

we obtain for eq. (A.2)

$$\begin{aligned} &\Pi^{\mu\nu}(k) + \delta_A k^2 P^{\mu\nu} \\ &\quad = -16\pi\alpha\tilde{\mu}^\epsilon \int_0^1 dx \Bigg[\left(\frac{2}{4-\epsilon} - 1 \right) \frac{4-\epsilon}{2} \frac{\Gamma\left(-1 + \frac{\epsilon}{2}\right)}{(4\pi)^{2-\epsilon/2}} D^{1-\epsilon/2} \eta^{\mu\nu} \\ &\qquad + \left(2x(1-x)k^2 P^{\mu\nu} - D\eta^{\mu\nu} \right) \frac{\Gamma\left(\frac{\epsilon}{2}\right)}{(4\pi)^{2-\epsilon/2}} D^{-\epsilon/2} \Bigg] \end{aligned}$$

$$= -16\pi\alpha\tilde{\mu}^{\epsilon} \int_0^1 dx \, \frac{\Gamma\left(\frac{\epsilon}{2}\right)}{(4\pi)^{2-\epsilon/2}} D^{-\epsilon/2} \cdot 2x(1-x)k^2 P^{\mu\nu}. \tag{A.8}$$

Writing $\Pi^{\mu\nu}(k) = \Pi(k)k^2 P^{\mu\nu}$ yields

$$\Pi(k^2) = -\frac{2\alpha}{\pi} \int_0^1 dx \, \Gamma\left(\frac{\epsilon}{2}\right) \left(\frac{4\pi\tilde{\mu}^2}{D}\right)^{\epsilon/2} x(1-x) - \delta_A. \tag{A.9}$$

In the limit $\epsilon \to 0$ we make use of the two approximations

$$\Gamma\left(\frac{\epsilon}{2}\right) = \frac{2}{\epsilon} - \gamma + O(\epsilon), \qquad A^{\epsilon/2} = 1 + \frac{\epsilon}{2}\ln A + O(\epsilon^2), \tag{A.10}$$

with the Euler-Mascheroni constant. Substituting further $\mu^2 = 4\pi e^{-\gamma}\tilde{\mu}^2$, we obtain

$$\Pi(k^2) = \frac{2\alpha}{\pi} \int_0^1 dx \, x(1-x) \ln\frac{D}{\mu^2} - \frac{\alpha}{3\pi}\frac{2}{\epsilon} - \delta_A. \tag{A.11}$$

In the OS-scheme, the polarization tensor is set to satisfy the renormalization condition

$$\Pi(0) = 0, \tag{A.12}$$

which constrains δ_A to

$$\delta_A = -\frac{\alpha}{3\pi}\left(\frac{2}{\epsilon} - \ln\frac{m^2}{\mu^2}\right). \tag{A.13}$$

Thus we are left with

$$\Pi(k^2) = \frac{2\alpha}{\pi} \int_0^1 dx \, x(1-x) \ln\frac{D}{m^2}. \tag{A.14}$$

While the integral can be done in closed form, it will suffice for our purposes to consider the case where photon momenta are small compared to the electron mass, $k^2 \ll m^2$ (soft photons, see chapter 6). In this case we may expand the logarithm in eq. (A.14) to first order in k^2/m^2 which yields

$$\Pi(k^2) = \frac{\alpha}{15\pi}\frac{k^2}{m^2} + O\left(\frac{k^4}{m^4}\right). \tag{A.15}$$

This expression causes a modification of the electron-proton interaction potential which is hence no longer a pure Coulomb potential. The influence on the relativistic energy levels is calculated in chapter 6.

A.2 The 3-point vertex function

In this section we calculate the 3-point vertex function $\mathcal{V}_3$ in the limit of small photon momenta, $k^2 \ll m^2$, to the linear order in α. Let us start from eq. (6.69),

$$\begin{aligned}\mathcal{V}_3^\mu(x,y,z) &= \gamma^\mu\delta^4(x-z)\delta^4(y-z) + \delta\mathcal{V}_3^\mu(x,y,z)\\ \delta\mathcal{V}_3^\mu(x,y,z) &= \delta_e\gamma^\mu\delta^4(x-z)\delta^4(y-z)\\ &\quad - e^2\gamma^\alpha S(x-z)\gamma^\mu S(z-y)\gamma^\beta D_{\alpha\beta}(x-y) + O(\alpha^2). \quad \text{(A.16)}\end{aligned}$$

Employing Feynman gauge the Fourier transform of $\mathcal{V}_3$ reads

$$\begin{aligned}\mathcal{V}_3^\mu(p,p') &= Z_e\gamma^\mu - e^2\int\frac{d^4l}{(2\pi)^4}\gamma^\nu\tilde{S}(p'+l)\tilde{D}_{\nu\rho}(l)\gamma^\mu\tilde{S}(p+l)\gamma^\rho\\ &= Z_e\gamma^\mu - ie^2\int\frac{d^4l}{(2\pi)^4}\frac{\gamma^\nu\left(\not{p}'+\not{l}-m\right)\gamma^\mu\left(\not{p}+\not{l}-m\right)\gamma_\nu}{\left((p'+l)^2+m^2\right)\left((p+l)^2+m^2\right)\left(l^2+m_\gamma^2\right)}\\ &= Z_e\gamma^\mu - ie^2\int dF_3\int\frac{d^4\bar{q}}{(2\pi)^4}\frac{\gamma^\nu\bar{\not{q}}\gamma^\mu\bar{\not{q}}\gamma_\nu + N^\mu}{\left(\bar{q}^2+D\right)^3}\\ &= Z_e\gamma^\mu - ie^2\int dF_3\int\frac{d^d\bar{q}}{(2\pi)^d}\frac{\frac{(d-2)^2}{d}\bar{q}^2\gamma^\mu + N^\mu}{\left(\bar{q}^2+D\right)^3}\\ &= Z_e\gamma^\mu + \frac{e^2}{16\pi^2}\int dF_3\left(\frac{4\pi\tilde{\mu}}{D}\right)^{\epsilon/2}\left((1-\epsilon)\,\Gamma\left(\frac{\epsilon}{2}\right)\gamma^\mu + \frac{1}{2}\frac{N^\mu}{D}\right)\\ &= Z_e\gamma^\mu + \frac{\alpha}{4\pi}\int dF_3\left(\left(\frac{2}{\epsilon} - 2 - \ln\frac{D}{\mu^2}\right)\gamma^\mu + \frac{1}{2}\frac{N^\mu}{D}\right). \quad \text{(A.17)}\end{aligned}$$

In the third line we have introduced Feynman parameters, substituted the variable $q = l + x_1p + x_2p'$ and performed a Wick rotation. In line four we have continued the integral to $d = 4-\epsilon$ dimensions, performed it in line five and expanded the resulting expression for small ϵ in line six. Further we have introduced the variables

$$\begin{aligned}D &= x_1(1-x_1)p^2 + x_2(1-x_2)p'^2 - 2pp'x_1x_2 + (x_1+x_2)m^2 + x_3m_\gamma,\\ N^\mu &= \gamma^\nu\left(-x_1\not{p} + (1-x_2)\not{p}' - m\right)\gamma^\mu\left((1-x_1)\not{p} - x_2\not{p}' - m\right)\gamma_\nu\\ &= 2\left((1-x_1)\not{p} - x_2\not{p}'\right)\gamma^\mu\left(-x_1\not{p} + (1-x_2)\not{p}'\right) -\\ &\quad - 4m\left((1-2x_1)p + (1-2x_2)p'\right)^\mu + 2m^2\gamma^\mu. \quad \text{(A.18)}\end{aligned}$$

In the OS-scheme we impose the renormalization condition such that e is equal to the elementary charge as measured in low-energy experiments, i.e.

$$\bar{u}_{s'}(\vec{p}\,')e\mathcal{V}_3^\mu(p,p')u_s(\vec{p})\Big|_{\substack{p^2=p'^2=-m^2\\ k^2=0}} = e\bar{u}_{s'}(\vec{p}\,')\gamma^\mu u_s(\vec{p})\Big|_{\substack{p^2=p'^2=-m^2\\ k^2=0}}, \quad \text{(A.19)}$$

where $k = p' - p$. We make use of the relations

$$\left(\not{p} + m\right) u_s(\vec{p}) = 0, \qquad \bar{u}_s(\vec{p}) \left(\not{p} + m\right) = 0, \tag{A.20}$$

as well as

$$\bar{u}_{s'}(\vec{p}\,') \left(p' + p\right)^\mu u_s(\vec{p}) = \bar{u}_{s'}(\vec{p}\,') \left(2m\gamma^\mu + 2iS^{\mu\nu}k_\nu\right) u_s(\vec{p}), \tag{A.21}$$

where $S^{\mu\nu} = \frac{i}{4}\left[\gamma^\mu, \gamma^\nu\right]$, to rewrite $\bar{u}Nu$ as

$$\begin{aligned}
&\frac{1}{2}\bar{u}_{s'}(\vec{p}\,')N^\mu u_s(\vec{p}) \\
&\quad = \left(2pp'(x_3 + x_1x_2) + m^2(2(1-x_3) - x_1^2 - x_2^2)\right) \bar{u}_{s'}(\vec{p}\,')\gamma^\mu u_s(\vec{p}) - \\
&\qquad - m\, x_3(1-x_3)\, \bar{u}_{s'}(\vec{p}\,') \left(p + p'\right)^\mu u_s(\vec{p}) \\
&\qquad - m\, (x_2 - x_1)(2 - x_3)\, \bar{u}_{s'}(\vec{p}\,')k^\mu u_s(\vec{p}) \\
&\quad \to \left(2pp'(x_3 + x_1x_2) + m^2(2(1-x_3)^2 - x_1^2 - x_2^2)\right) \bar{u}_{s'}(\vec{p}\,')\gamma^\mu u_s(\vec{p}) - \\
&\qquad - 2im\, x_3(1-x_3)\bar{u}_{s'}(\vec{p}\,')S^{\mu\nu}k_\nu u_s(\vec{p}),
\end{aligned} \tag{A.22}$$

where we have used the symmetry in x_1, x_2 in the last line. Thus the sandwiched 3-point vertex function reads

$$\bar{u}_{s'}(\vec{p}\,')\mathcal{V}_3^\mu(p, p')u_s(\vec{p}) = \bar{u}_{s'}(\vec{p}\,') \left(F_1(k)\gamma^\mu - \frac{i}{m}F_2(k)S^{\mu\nu}k_\nu\right) u_s(\vec{p}), \tag{A.23}$$

where

$$\begin{aligned}
F_1(k) &= Z_e - \frac{\alpha}{4\pi}\int dF_3 \left(2 - \frac{2}{\epsilon} + \ln\frac{D}{\mu^2} - \frac{1}{2}\frac{\tilde{N}}{D}\right), \\
F_2(k) &= \frac{\alpha}{2\pi}\int dF_3\, \frac{m^2 x_3(1-x_3)}{D},
\end{aligned} \tag{A.24}$$

and

$$\tilde{N} = 4pp'(x_3 + x_1x_2) + 2m^2(2(1-x_3)^2 - x_1^2 - x_2^2). \tag{A.25}$$

Considering on-shell electrons we can set $p^2 = p'^2 = -m^2$ and $pp' = -m^2 - k^2/2$ to obtain

$$\begin{aligned}
D &= k^2 x_1 x_2 + (1-x_3)^2 m^2 + x_3 m_\gamma^2, \\
\tilde{N} &= 2m^2(1 - 4x_3 + x_3^2) - 2k^2(x_3 + x_1x_2).
\end{aligned} \tag{A.26}$$

For $k^2 \ll m^2$ we calculate the integral for F_2 in the second line of eqs. (A.24) to the zeroth order in k^2/m^2 since the coefficient of F_2 in eq. (A.23) already includes k,

$$F_2(k) \approx F_2(0) = \frac{\alpha}{2\pi}. \tag{A.27}$$

The first integral for F_1 in eqs. (A.24) may be expanded to first order in k^2/m^2 to yield

$$\begin{aligned}\int dF_3 \, \ln \frac{D}{\mu^2} &\approx \ln \frac{m^2}{\mu^2} + \int dF_3 \left(2\ln(1-x_3) + \frac{k^2}{m^2} \frac{x_1 x_2}{(1-x_3)^2} \right) \\ &= \ln \frac{m^2}{\mu^2} - 1 + \frac{k^2}{2m^2}. \end{aligned} \tag{A.28}$$

The second integral in the expression for F_1 is also expanded to first order in k^2/m^2 to yield

$$\begin{aligned} -\frac{1}{2} \int dF_3 \frac{\tilde{N}}{D} &= -I_1 + \frac{k^2}{m^2}(I_2 + I_3), \\ I_1 &= \int dF_3 \, \frac{(1 - 4x_3 + x_3^2)}{(1-x_3)^2 + x_3 m_\gamma^2/m^2} = 5 + 4\ln \frac{m_\gamma}{m}, \\ I_2 &= \int dF_3 \, \frac{x_3 + x_1 x_2}{(1-x_3)^2 + x_3 m_\gamma^2/m^2} = -\frac{11}{6} - 2\ln \frac{m_\gamma}{m}, \\ I_3 &= \int dF_3 \, \frac{x_1 x_2 (1 - 4x_3 + x_3^2)}{((1-x_3)^2 + x_3 m_\gamma^2/m^2)^2} = \frac{5}{6} + \frac{2}{3}\ln \frac{m_\gamma}{m}. \end{aligned} \tag{A.29}$$

We insert these results into the first line of eq. (A.24) to obtain

$$\begin{aligned} F_1(k) = Z_e + \frac{\alpha}{2\pi} \Bigg(2 + \frac{1}{\epsilon} - \ln \frac{m}{\mu} + 2\ln \frac{m_\gamma}{m} \\ + \frac{k^2}{m^2} \left(\frac{1}{4} + \frac{2}{3} \ln \frac{m_\gamma}{m} \right) + O\left(\frac{k^4}{m^4} \right) \Bigg). \end{aligned} \tag{A.30}$$

The renormalization constraint of the OS-scheme (A.19) enforces $F_1(0) = 1$ and hence we set Z_e to equal

$$Z_e = 1 - \frac{\alpha}{2\pi} \left(2 + \frac{1}{\epsilon} - \ln \frac{m}{\mu} + 2\ln \frac{m_\gamma}{m} \right). \tag{A.31}$$

Finally, we may write the 3-point vertex function to the linear order in α and k^2/m^2 as

$$\mathcal{V}_3^\mu(k) = \gamma^\mu \left(1 + \frac{\alpha}{3\pi} \frac{k^2}{m^2} \left(\ln \frac{m_\gamma}{m} + \frac{3}{8} \right) \right) - \frac{\alpha}{2\pi} \frac{i S^{\mu\nu} k_\nu}{m}. \tag{A.32}$$

The order α corrections to the 3-point vertex function modify the way the electron interacts with photons. They represent yet another contribution to the level shift calculated in chapter 6.

Appendix B

Useful formulae and special functions

In this appendix many definitions, relations and identities are listed, which have been used in the course of this dissertation. Concerning the special functions, most of the relations are taken from the book of Abramowitz and Stegun (1968).

Associated Legendre functions The associated Legendre functions are solutions to the equation

$$\left[(1-x^2)\,\partial_x^2 - 2x\,\partial_x + l(l+1) - \frac{m^2}{1-x^2}\right] P_{lm}(x) = 0, \tag{B.1}$$

where $l, |m| \in \mathbb{N}$, $|m| \leq l$. Explicitly, they are given by

$$P_{lm}(x) = \sum_{k=0}^{\lfloor (l-m)/2 \rfloor} (-1)^{k+m} \frac{(2l-2k)!\, x^{l-m-2k}\, (1-x^2)^{\frac{m}{2}}}{2^l\, k!\, (l-k)!\, (l-m-2k)!}. \tag{B.2}$$

If $m = 0$ the associated Legendre functions are equal to the Legendre polynomials, $P_{l0} = P_l$. Since $-l$ is equivalent to $l-1$ in eq. (B.1), one can define $P_{-l,m} := P_{l-1,m}$. The Legendre functions have the properties

$$\begin{aligned} P_{l,-m} &= (-1)^m \frac{(l-m)!}{(l+m)!} P_{lm}, \\ xP_{lm} &= \frac{(l+m)P_{l-1,m} + (l-m+1)P_{l+1,m}}{2l+1}, \\ \sqrt{1-x^2}P_{lm} &= \frac{P_{l-1,m+1} - P_{l+1,m+1}}{2l+1}. \end{aligned} \tag{B.3}$$

The Legendre functions also satisfy the orthogonality relation

$$\int_{-1}^{1} dx\, P_{km}(x) P_{lm}(x) = \frac{2}{2l+1} \frac{(l+m)!}{(l-m)!}\, \delta_{kl}. \tag{B.4}$$

Spherical harmonics The spherical harmonics are solutions to the equation

$$\left[(1-x^2)\, \partial_x^2 - 2x\, \partial_x + l(l+1) + \frac{1}{1-x^2} \partial_\varphi^2 \right] Y_{lm}(x,\varphi) = 0, \tag{B.5}$$

where $l \in \mathbb{N}$. Comparing with eq. (B.1) makes the close connection to Legendre functions obvious. Consequently, the spherical harmonics are given by

$$Y_{lm}(x,\varphi) = \sqrt{\frac{2l+1}{4\pi} \frac{(l-m)!}{(l+m)!}}\, P_{lm}(x)\, e^{im\varphi}, \tag{B.6}$$

where $|m| \in \mathbb{N}$, $|m| \leq l$. From the identities (B.3) follows

$$Y_{-l,m} = Y_{l-1,m}, \qquad\qquad Y_{l,-m} = (-1)^m Y^*_{l,m}, \tag{B.7}$$

$$xY_{lm} = \sqrt{\frac{(l+m)(l-m)}{(2l+1)(2l-1)}} Y_{l-1,m} + \sqrt{\frac{(l+m+1)(l-m+1)}{(2l+1)(2l+3)}} Y_{l+1,m}, \tag{B.8}$$

$$\begin{aligned} \sqrt{1-x^2} e^{i\varphi} Y_{lm} = & \sqrt{\frac{(l-m-1)(l-m)}{(2l+1)(2l-1)}} Y_{l-1,m+1} \\ & - \sqrt{\frac{(l+m+1)(l+m+2)}{(2l+1)(2l+3)}} Y_{l+1,m+1}. \end{aligned} \tag{B.9}$$

From these relations it also follows that

$$\begin{aligned} \sqrt{1-x^2} e^{-i\varphi} Y_{lm} = & -\sqrt{\frac{(l+m-1)(l+m)}{(2l+1)(2l-1)}} Y_{l-1,m-1} \\ & + \sqrt{\frac{(l-m+1)(l-m+2)}{(2l+1)(2l+3)}} Y_{l+1,m-1}. \end{aligned} \tag{B.10}$$

The spherical harmonics satisfy the orthonormality relation,

$$\int_{-1}^{1} dx \int_{0}^{2\pi} d\varphi\, Y^*_{lm}(x,\varphi) Y_{kn}(x,\varphi) = \delta_{kl} \delta_{mn}, \tag{B.11}$$

and the completeness relation

$$\sum_{l=0}^{\infty}\sum_{m=-l}^{l} Y^*_{lm}(x,\varphi)Y_{lm}(x',\varphi') = \delta(x-x')\delta(\varphi-\varphi'). \tag{B.12}$$

Taking the previous relations together, one can derive another important relation,

$$\begin{aligned}
&\int_{-1}^{1} dx \int_{0}^{2\pi} d\varphi\, Y_{lm}(x,\varphi)\, \vec{e}_r\, Y^*_{l'm'}(x,\varphi) \\
&\quad= \int_{-1}^{1} dx \int_{0}^{2\pi} d\varphi\, Y_{lm}(x,\varphi) \left[\tfrac{\sqrt{1-x^2}e^{i\varphi}}{2}\,\vec{e}_+ + \tfrac{\sqrt{1-x^2}e^{-i\varphi}}{2}\,\vec{e}_- + x\,\vec{e}_z\right] Y^*_{l'm'}(x,\varphi) \\
&\quad= \vec{e}_+\,\frac{\delta_{m+1,m'}}{\sqrt{2}}\left[\delta_{l-1,l'}\sqrt{\tfrac{(l-m-1)(l-m)}{(2l+1)(2l-1)}} - \delta_{l+1,l'}\sqrt{\tfrac{(l+m+1)(l+m+2)}{(2l+1)(2l+3)}}\,\right] + \\
&\qquad+ \vec{e}_-\,\frac{\delta_{m-1,m'}}{\sqrt{2}}\left[-\delta_{l-1,l'}\sqrt{\tfrac{(l+m-1)(l+m)}{(2l+1)(2l-1)}} + \delta_{l+1,l'}\sqrt{\tfrac{(l-m+1)(l-m+2)}{(2l+1)(2l+3)}}\,\right] + \\
&\qquad+ \vec{e}_z\,\delta_{m,m'}\left[\delta_{l-1,l'}\sqrt{\tfrac{(l+m)(l-m)}{(2l+1)(2l-1)}} + \delta_{l+1,l'}\sqrt{\tfrac{(l+m+1)(l-m+1)}{(2l+1)(2l+3)}}\,\right],
\end{aligned} \tag{B.13}$$

where $\vec{e}_\pm = (1, \mp i, 0)/\sqrt{2}$.

Associated Laguerre polynomials The associated Laguerre polynomials are solutions to the equation

$$\left[x\,\partial_x^2 + (\alpha+1-x)\,\partial_x + n\right] L_n^\alpha(x) = 0, \tag{B.14}$$

where $n \in \mathbb{N}$, $\alpha \in \mathbb{R}$. Explicitly, they are given by

$$\begin{aligned}
L_n^\alpha(x) &= \sum_{k=0}^{n} \binom{n+\alpha}{n-k} \frac{(-x)^k}{k!} \\
&= \frac{1}{n!}\,\partial_z{}^n\, \frac{e^{-\frac{xz}{1-z}}}{(1-z)^{1+\alpha}}\bigg|_{z=0} \\
&= \oint_{\mathcal{C}} \frac{dz}{2\pi i}\, \frac{e^{-\frac{xz}{1-z}}}{(1-z)^{1+\alpha} z^{n+1}},
\end{aligned} \tag{B.15}$$

where the contour $\mathcal{C}$ encircles the origin $z=0$ counterclockwise but not the singularity at $z=1$. If $\alpha = 0$ the associated Laguerre polynomials reduce to

the ordinary ones, $L_n^0 = L_n$. From the contour description, one can derive the rescaling relation

$$L_n^\alpha(ax) = \sum_{k=0}^{n} \left(\begin{array}{c} n+\alpha \\ n-k \end{array} \right) a^k (1-a)^{n-k} L_k^\alpha(x), \tag{B.16}$$

where $a \in \mathbb{R}$. Useful recurrence relations are

$$\begin{aligned} \partial_x L_n^\alpha(x) &= -L_{n-1}^{\alpha+1}(x), \\ L_n^\alpha(x) &= L_{n+1}^\alpha(x) - L_{n+1}^{\alpha-1}(x), \\ x L_n^\alpha(x) &= (n+\alpha) L_n^{\alpha-1}(x) - (n+1) L_{n+1}^{\alpha-1}(x). \end{aligned} \tag{B.17}$$

The associated Laguerre polynomials satisfy the orthogonality relation

$$\int_0^\infty dx\, x^\alpha e^{-x} L_n^\alpha(x) L_m^\alpha(x) = \frac{\Gamma(n+\alpha+1)}{n!} \delta_{nm}. \tag{B.18}$$

Kummer function The Kummer function satisfies the equation,

$$\left[x\, \partial_x{}^2 + (b-x)\, \partial_x - a \right] M(a,b,x) = 0. \tag{B.19}$$

Explicitly, it is given by

$$M(a,b,x) = \sum_{j=0}^{\infty} \frac{(a)^{\overline{j}}\, x^j}{(b)^{\overline{j}}\, j!} = 1 + \frac{a}{b}\frac{x}{1!} + \frac{a(a+1)}{b(b+1)}\frac{x^2}{2!} + \ldots, \tag{B.20}$$

where $(a)^{\overline{j}} = \Gamma(a+j)/\Gamma(a)$ means the ascending factorial. If a is a negative integer, the Kummer function may be expressed in terms of the aforementioned Laguerre polynomials,

$$M(-n,b,x) = \frac{n!}{(b)^{\overline{n}}}\, L_n^{b-1}(x), \qquad\qquad n \in \mathbb{N}. \tag{B.21}$$

Other useful relations are given by

$$\begin{aligned} M(a,b,x) &= e^x M(b-a,b,-x), \\ x\partial_x M(a,b,x) &= a(M(a+1,b,x) - M(a,b,x)) \\ &= (b-1)(M(a,b-1,x) - M(a,b,x)) \\ &= (b-a)M(a-1,b,x) + (a-b+x)M(a,b,x) \\ &= x\frac{a-b}{b} M(a,b+1,x) + xM(a,b,x) \end{aligned} \tag{B.22}$$

Coulomb wave functions The Coulomb wave functions are solutions to the equation

$$\left[x^2\partial_x^2 + x^2 - 2\eta x - l(l+1)\right] F_l(x) = 0. \tag{B.23}$$

They are expressed most conveniently they in terms of the aforementioned Kummer function,

$$F_l(\eta, x) = \frac{|\Gamma(l+1+i\eta)|}{2\,\Gamma(2l+2)}(2x)^{l+1}e^{-ix-\pi\eta/2}M(l+1-i\eta, 2l+2, 2ix). \tag{B.24}$$

Very important is the expansion in terms of spherical Bessel functions, j_l,

$$F_l(\eta, x) = \frac{|\Gamma(l+1+i\eta)|}{\Gamma(2l+2)}\,2^l(2l+1)!!\,x\,e^{-\pi\eta/2}\sum_{k=l}^{\infty} b_k j_k(x), \tag{B.25}$$

$$b_l = 1, \qquad b_{l+1} = \frac{2l+3}{l+1}\eta,$$

$$b_k = \frac{2k+1}{k(k+1)-l(l+1)}\left(2\eta\, b_{k-1} - \frac{(k-1)(k-2)-l(l+1)}{2k-3}\, b_{k-2}\right),$$

for $k > l+1$. In the special case $\eta = 0$ this reduces to

$$F_l(0, x) = x j_l(x). \tag{B.26}$$

For positive $\eta = \mu/k$ the Coulomb wave functions satisfy the completeness relation

$$\int_0^\infty dk\, F_l\left(\frac{\mu}{k}, kr\right) F_l\left(\frac{\mu}{k}, kr'\right) = \frac{\pi}{2}\,\delta(r-r'), \qquad \mu \geq 0. \tag{B.27}$$

Bessel functions The Bessel functions and spherical Bessel functions of the first kind, J and j, respectively, satisfy the equations

$$\left[x^2\,\partial_x^2 + x\,\partial_x + x^2 - \nu^2\right] J_\nu(x) = 0, \tag{B.28}$$

$$\left[x^2\,\partial_x^2 + 2x\,\partial_x + x^2 - l(l+1)\right] j_l(x) = 0, \tag{B.29}$$

where $\nu \in \mathbb{C}$ and $l \in \mathbb{Z}$. The spherical and ordinary Bessel functions of the first kind are related to each other by

$$j_l(x) = \sqrt{\frac{\pi}{2x}} J_{l+1/2}(x). \tag{B.30}$$

Explicitly, they are given by

$$J_\nu(x) = \left(\frac{x}{2}\right)^\nu \sum_{k=0}^{\infty} \frac{(-x^2/4)^k}{\Gamma(\nu+k+1)\,k!},$$

$$j_l(x) = \left(\frac{x}{2}\right)^l \sum_{k=0}^{\infty} \frac{(-x^2/2)^k}{(3/2)^{\overline{l+k}}\, k!}. \tag{B.31}$$

The Bessel functions J_ν satisfy the very important completeness relation,

$$\int_0^\infty dk\, k\, J_\nu(kr) J_\nu(kr') = \frac{\delta(r-r')}{r}. \tag{B.32}$$

Baker-Campbell-Hausdorff formula Let $\hat{A}$ and $\hat{B}$ be operators. We then have

$$\begin{aligned} e^{\hat{A}} \hat{B} e^{-\hat{A}} &= \sum_{k=0}^{\infty} \frac{\hat{R}_k}{k!}, \\ \hat{R}_k &= \sum_{m=0}^{k} \left(\begin{array}{c} k \\ m \end{array} \right) \hat{A}^m \hat{B} (-\hat{A})^{k-m}. \end{aligned} \tag{B.33}$$

By means of the well known relation of the binomial coefficients,

$$\left(\begin{array}{c} k+1 \\ m \end{array} \right) = \left(\begin{array}{c} k \\ m \end{array} \right) + \left(\begin{array}{c} k \\ m-1 \end{array} \right), \tag{B.34}$$

it is easy to show that the coefficients $\hat{R}_k$ obey the recursive relation

$$\hat{R}_0 = \hat{B}, \qquad\qquad \hat{R}_{k+1} = [\hat{A}, \hat{R}_k]. \tag{B.35}$$

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