Texts and Monographs in Physics

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Relativistic Quantum Mechanics

Second Edition
With 21 Figures

Springer

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Library of Congress Control Number: 2005929195

ISSN 0172-5998

ISBN-10 3-540-25502-8 2nd ed. Springer Berlin Heidelberg New York
ISBN-13 978-3-540-25502-4 2nd ed.Springer Berlin Heidelberg New York
ISBN 3-540-43666-9 1st ed. Springer-Verlag Berlin Heidelberg New York

Typesetting: Data conversion by LE-TeX Jelonek, Schmidt & Vöckler GbR
Cover design: *design & production* GmbH, Heidelberg
Printed on acid-free paper SPIN 11414094 55/3141/YL 5 4 3 2 1 0

Preface to the Second Edition

This edition includes five new sections and a third appendix. Most other sections are expanded, in particular Sects. 5.2 and 5.6 on hyperfine interactions.

Section 3.8 offers an introduction to the important field of relativistic quantum chemistry. In Sect. 5.7, the coupling of the anomalous magnetic moment is needed for a relativistic treatment of the proton in hydrogen. It generalizes a remarkable feature of leptonium, namely the non-hermiticity of magnetic hyperfine interactions. In Appendix C, the explicit calculation of the expectation value of an operator which is frequently approximated by a delta-function confirms that the singularity of relativistic wave functions at the origin is correct.

The other three new sections cover dominantly nonrelaticistic topics, in particular the quark model. The coupling of three electron spins (Sect. 3.9) provides also the basis for the three quark spins of baryons (Sect. 5.9). For less than four particles, direct symmetry arguments are simpler than the representions of the permutation group which are normally used in the literature.

Another new topic of this edition is the confirmation of the E^2-dependence of atomic equations by the relativistic energy conservation in radiative atomic transitions, according to the time-dependent perturbation theory of Sect. 5.4. In the quark model, the E^2-theorem applies not only to mesons, but also to baryons as three-quark bound states. Unfortunately, the non-existence of free quarks prevents a precise formulation of the phenomenological "constituent quark model", which remains the most challenging problem of relativistic quantum mechanics.

Karlsruhe, May 2005 *Hartmut M. Pilkuhn*

Preface

Whereas nonrelativistic quantum mechanics is sufficient for any understanding of atomic and molecular spectra, relativistic quantum mechanics explains the finer details. Consequently, textbooks on quantum mechanics expand mainly on the nonrelativistic formalism. Only the Dirac equation for the hydrogen atom is normally included. The relativistic quantum mechanics of one- and two-electron atoms is covered by Bethe and Salpeter (1957), Mizushima (1970) and others. Books with emphasis on atomic and molecular applications discuss also effective "first-order relativistic" operators such as spin-orbit coupling, tensor force and hyperfine operators (Weissbluth 1978). The practical importance of these topics has led to specialized books, for example that of Richards, Trivedi and Cooper (1981) on spin-orbit coupling in molecules, or that of Das (1987) on the relativistic quantum mechanics of electrons. The further development in this direction is mainly the merit of quantum chemists, normally on the basis of the multi-electron Dirac-Breit equation. The topic is covered in reviews (Lawley 1987, Wilson et al. 1991); an excellent monograph by Strange (1998) includes solid-state theory.

Relativistic quantum mechanics is an application of quantum field theory to systems with a given number of massive particles. This is not easy, since the basic field equations (Klein-Gordon and Dirac) contain creation and annihilation operators that can produce unphysical negative-energy solutions in the derived single-particle equations. However, one has learned how to handle these states, even in atoms with two or more electrons. The methods are not particularly elegant; residual problems will be mentioned at the end of Chap. 3. But even there, the precision of these methods is impressive. For example, the influence of virtual electron-positron pairs is included by vacuum polarization, in the form of the Uehling, Kroll-Wichman and Källen-Sabry potentials (Sect. 5.3). For two-body problems, improved methods allow for a fantastic precision, which provides by far the most accurate test of quantum electrodynamics itself.

The present book introduces quantum mechanics in analogy with the Maxwell equations rather than classical mechanics; it emphasizes Lorentz invariance and treats the nonrelativistic version as an approximation. The important quantum field is the photon field, i.e. the electromagnetic field in the Coulomb gauge, but fields for massive particles are also needed. On the

other hand, the presentation is very different from that of books on quantum field theory, which include preparatory chapters on classical fields and relativistic quantum mechanics (for example Gross 1993, Yndurain 1996).

The Coulomb gauge is mandatory not only for atomic spectra, but also for the related "quark model" calculations of baryon spectra, which form an important part of the theory of strong interactions. A by-product of an entirely relativistic bound state formalism is a twofold degenerate spectrum, due to explicit charge conjugation invariance. Quark model calculations might benefit from such relatively simple improvements, even when the spectra may eventually be calculated "on the lattice".

A new topic of this book is a rather broad formalism for relativistic two-body ("binary") atoms: Nonrelativistically, the Schrödinger equation for an isolated binary can be reduced to an equivalent one-body equation, in which the electron mass is replaced by the "reduced mass". The extension of this treatment to two relativistic particles will be explained in Chap. 4. The case of two spinless particles was solved already in 1970, see the introduction to Sect. 4.5. The much more important "leptonium" case is treated in Sects. 4.6 and 4.7.

Stimulated by the enormous success of the single-particle Dirac equation, Bethe and Salpeter (1951) constructed a sixteen-component equation for two-fermion binaries. However, increasingly precise calculations disclosed weak points. An effective Dirac equation with a reduced mass cannot be derived from a sixteen-component equation except by an approximate "quasidistance" transformation. On the other hand, such a Dirac equation does follow very directly in an eight-component formalism, in which the relevant S-matrix is prepared as an 8×8-matrix. The principle will be explained in Sect. 4.6, the interaction is added in Sect. 4.7. Like in the Schrödinger equation with reduced mass, the coupling to the photon vector potential operator is treated perturbatively. The famous "Lamb shift" calculation will be presented in Sect. 5.5, extended to the two-body case.

A remarkable property of the new binary equations is the absence of "retardation". Its disappearance will be demonstrated in Sect. 4.9. Most fermions have an inner structure which requires extra operators already in the single-particle equation. As an example, the fine structure of antiprotonic atoms will be discussed in Sect. 5.6. The Uehling potential is also detailed for these and other "exotic" atoms.

Preparatory studies for this book have been supported by the Volkswagenstiftung. The book would have been impossible without the efforts of my students and collaborators, B. Melić and R. Häckl, M. Malvetti and V. Hund. A textbook by Hund, Malvetti and myself (1997) has provided some of its material.

I dedicate this book to the memory of Oskar Klein.

Karlsruhe, March 2002 *Hartmut M. Pilkuhn*

Contents

1 Maxwell and Schrödinger

1.1 Light and Linear Operators

Electromagnetic radiation is classified according to wavelength in radio and microwaves, infrared, visible and UV light, X- and Gamma rays. These names indicate that the particle aspect of the radiation dominates at short wavelengths, while the wave aspect dominates at long wavelengths. Nevertheless, the radiation is described at all wavelengths by electric and magnetic fields, $\boldsymbol{E}$ and $\boldsymbol{B}$, which obey wave equations. The quantum aspects of these fields will be discussed in Chap. 3. In vacuum, the equation for $\boldsymbol{E}$ is

$$(-c^{-2}\partial_t^2 + \partial_x^2 + \partial_y^2 + \partial_z^2)\boldsymbol{E} = 0, \quad \partial_t = \partial/\partial t, \;\; \partial_x = \partial/\partial x, \tag{1.1}$$

where $c = 299\,792\,458\,\mathrm{m/s}$ is the velocity of light in vacuum. For the time being, we are mainly interested in the form of this differential equation, which guided Schrödinger in the construction of his equation for electrons. In vectorial notation, $\boldsymbol{r} = (x, y, z)$ is the position vector, and $\nabla = (\partial_x, \partial_y, \partial_z) =$ "nabla" is the gradient vector; its square is the Laplacian Δ. Particularly in relativistic context, one prefers the notation $x^i = (x^1, x^2, x^3) = (x, y, z)$:

$$\nabla^2 = \Delta = \partial_x^2 + \partial_y^2 + \partial_z^2 = \sum_{i=1}^{3} \partial_i^2, \quad \partial_i \equiv \partial/\partial x^i. \tag{1.2}$$

The x^i is conveniently combined with $x^0 = ct$ into a four-vector $x^\mu = (x^0, x^i) = (x^0, \boldsymbol{r})$, and the $-c^2\partial_t^2$ of (1.1) is combined with ∇^2 into the d'Alembertian operator $\Box$, also called "quabla":

$$\Box \boldsymbol{E} = 0; \quad \Box = -\partial_0^2 + \nabla^2, \quad \partial_0 = \partial/\partial(ct). \tag{1.3}$$

The full use of this nomenclature will be postponed to Chap. 2. For the moment, t is expressed in terms of x^0 merely to suppress the constant c. Today, c is in fact used in the definition of the length scale, see Sect. 1.6.

Differential operators D are linear in the sense $D(\boldsymbol{E}_1 + \boldsymbol{E}_2) = D\boldsymbol{E}_1 + D\boldsymbol{E}_2$. If $\boldsymbol{E}_1$ and $\boldsymbol{E}_2$ are two different solutions of (1.1), $\boldsymbol{E} = \boldsymbol{E}_1 + \boldsymbol{E}_2$ is a third one. This is called the superposition principle. The intensity I of light is normally measured by $\boldsymbol{E}^2$, $I \sim \boldsymbol{E}^2 \equiv \mathrm{square}(\boldsymbol{E})$, but nonlinear operators such as "square" are not used in quantum mechanics. ∇ and ∇^2 are

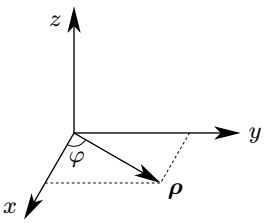

Fig. 1.1. Cylinder coordinates

both linear operators. The simplest operator is a multiplicative constant C, $C(\boldsymbol{E}_1 + \boldsymbol{E}_2) = C\boldsymbol{E}_1 + C\boldsymbol{E}_2$. We now recall some operators of classical electrodynamics, which will be needed in quantum mechanics. The Laplacian is in cylindrical coordinates (Fig. 1.1)

$$x = \rho\cos\phi, \quad y = \rho\sin\phi, \tag{1.4}$$

$$\nabla^2 = \partial_z^2 + \rho^{-1}\partial_\rho\rho\partial_\rho + \rho^{-2}\partial_\phi^2, \tag{1.5}$$

and in spherical coordinates (Fig. 1.2):

$$z = r\cos\theta, \quad \rho = r\sin\theta, \tag{1.6}$$

$$\nabla^2 = r^{-1}\partial_r^2 r + r^{-2}(\boldsymbol{r}\times\nabla)^2. \tag{1.7}$$

$\boldsymbol{r}\times\nabla$ is somewhat complicated, but its z-component is simple:

$$(\boldsymbol{r}\times\nabla)_z = x\partial_y - y\partial_x = \partial_\phi. \tag{1.8}$$

The square of $\boldsymbol{r}\times\nabla$ is also relatively simple,

$$(\boldsymbol{r}\times\nabla)^2 = \partial_\phi^2(1-u^2)^{-1} + \partial_u(1-u^2)\partial_u, \quad u = \cos\theta. \tag{1.9}$$

Two operators A and B are said to commute if the order in which they are applied to the wave function does not matter, $AB = BA$. For example, as $\boldsymbol{r}\times\nabla$ depends only on θ and ϕ, not on r, one has $r^{-2}(\boldsymbol{r}\times\nabla)^2 = (\boldsymbol{r}\times\nabla)^2 r^{-2}$. On the other hand, in the radial part $r^{-1}\partial_r^2 r$ of the Laplacian (1.7), the first

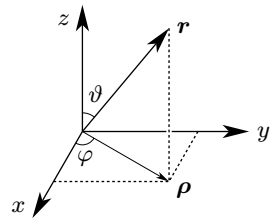

Fig. 1.2. Spherical coordinates

two operators do not commute, $r^{-1}\partial_r^2 \neq \partial_r^2 r^{-1}$ (otherwise one would have $r^{-1}\partial_r^2 r = \partial_r^2$). Valid alternative forms are

$$r^{-1}\partial_r^2 r = (\partial_r + 1/r)^2 = \partial_r^2 + 2r^{-1}\partial_r. \tag{1.10}$$

To check these, apply the operators to an arbitrary function $f(r)$ and use $\partial_r f(r) = f'(r)$, $\partial_r fg = f'g + fg'$, $(\partial_r + 1/r)^2 = (\partial_r + 1/r)(\partial_r + 1/r)$. Equation (1.1) has plane-wave solutions of the type

$$\boldsymbol{E} = \boldsymbol{E}_0 e^{i\boldsymbol{k}\boldsymbol{r} - i\omega t}, \quad \omega = 2\pi\nu. \tag{1.11}$$

$$\boldsymbol{k} = (k_x, k_y, k_z), \quad \lambda = 2\pi/k, \tag{1.12}$$

where $\boldsymbol{k}$ is the wave number vector, pointing into the direction of propagation of the plane wave, and λ is the wavelength. Insertion of

$$\partial_t \boldsymbol{E} = -i\omega \boldsymbol{E}, \quad \partial_z \boldsymbol{E} = ik_z \boldsymbol{E}, \ldots \tag{1.13}$$

shows that (1.11) is a solution of the wave equation (1.1) only for

$$\omega^2/c^2 = k^2 = k_x^2 + k_y^2 + k_z^2. \tag{1.14}$$

We shall also need cylindrical and spherical waves, where ∇^2 is required in the forms (1.5) and (1.7). Such waves can also be monochromatic, meaning that they contain only one (angular) frequency ω. The common wave equation for all monochromatic waves in vacuum is

$$\boldsymbol{E}(x^\mu) = e^{-i\omega t}\boldsymbol{E}_\omega(\boldsymbol{r}), \quad (\omega^2/c^2 + \nabla^2)\boldsymbol{E}_\omega(\boldsymbol{r}) = 0. \tag{1.15}$$

This "Helmholtz equation" is still a partial differential equation in three variables; we recall a few tricks for the solution of such equations. The main trick is to express ∇^2 in terms of commuting operators A, B, C, and then to construct "eigenfunctions" of these operators. When A is applied to any of its eigenfunctions f_n, it may be replaced simply by a constant a_n, called the eigenvalue:

$$Af_n = a_n f_n. \tag{1.16}$$

For example, the square of the operator ∂_ϕ occurs both in cylindrical and in spherical coordinates. The normalized eigenfunctions of ∂_ϕ are

$$\psi_{m_l}(\phi) = (2\pi)^{-1/2} e^{im_l\phi}, \quad m_l = 0, \pm 1, \pm 2 \ldots \tag{1.17}$$

In quantum mechanics, m_l is called the (orbital) magnetic quantum number (Sect. 1.4). The normalization is chosen such that

$$\int_0^{2\pi} \psi^*_{m_l} \psi_{m_l} d\phi = \int_0^{2\pi} |\psi_{m_l}|^2 d\phi = 1. \tag{1.18}$$

It fixes the scale of the eigenfunction. An essential point of (1.17) is the restriction of the eigenvalues m_l of $-i\partial_\phi$ to integer values, due to the required single-valuedness of ψ at all ϕ:

$$\psi_{m_l}(\phi + 2\pi) = \psi_{m_l}(\phi). \tag{1.19}$$

For such eigenfunctions, one may replace the operator ∂_ϕ^2 by one of its eigenvalues $-m_l^2$ in the operators (1.5) or (1.9). For commuting operators A and B there exist common eigenfunctions,

$$Af_{a_n,b_m} = a_n f_{a_n,b_m}, \;\; Bf_{a_n,b_m} = b_m f_{a_n,b_m}, \tag{1.20}$$

because $ABf = BAf = a_n Bf$ shows that Bf is also an eigenfunction of A, again with eigenvalue a_n. A rather trivial example of common eigenfunctions is given by the plane waves (1.11), which are eigenfunctions of $\partial_x, \partial_y, \partial_z$, with eigenvalues ik_x, ik_y, ik_z respectively. A famous example in spherical coordinates are the "spherical harmonics" $Y_l^m(\theta,\phi)$ (with simplified notation $m_l \equiv m$), which are not only eigenfunctions of ∂_ϕ, but also of $(\boldsymbol{r}\times\nabla)^2$ as given by (1.9):

$$Y_l^m(\theta,\phi) = \Theta_l^m(\theta)\psi_m(\phi), \tag{1.21}$$

$$(\boldsymbol{r}\times\nabla)^2 Y_l^m = -l(l+1)Y_l^m, \quad l = 0,\, 1,\, 2\ldots \quad -l \le m \le l. \tag{1.22}$$

Θ_l^m is a polynomial of degree $|m|$ in $\sin\theta$ and degree $l-|m|$ in $u = \cos\theta$. Some of these functions are collected in Table 1.1.

The Θ_l^0 are Legendre polynomials P_l, apart from a normalization constant:

$$\Theta_l^0 = (l+\tfrac{1}{2})^{\frac{1}{2}} P_l(u). \quad P_0 = 1,\; P_1 = u,\; P_2 = \tfrac{1}{2}(3u^3-1),\; P_3 = \tfrac{1}{2}(5u^3-3u). \tag{1.23}$$

When applied to the spherical harmonics, the Laplacian (1.6) effectively becomes a radial operator, i.e. independent of θ and ϕ. Thus $\boldsymbol{E}_\omega(\boldsymbol{r})$ has solutions of the form

$$\boldsymbol{E}_\omega(\boldsymbol{r}) = \boldsymbol{E}_0(\omega) R_{\omega,l}(r) Y_l^m(\theta,\phi), \tag{1.24}$$

$$(\omega^2/c^2 + \nabla^2)\boldsymbol{E}_\omega = \boldsymbol{E}_0 Y_l^m [\omega^2/c^2 + (\partial_r + 1/r)^2 - l(l+1)/r^2] R_{\omega,l}(r). \tag{1.25}$$

Table 1.1. Y_l^m for $l < 3$. Normalization (1.186), $x_\pm = \mp x - iy$.

$$\begin{aligned}
Y_0^0 &= (4\pi)^{-\frac{1}{2}},\\
Y_1^0 &= (3/4\pi)^{\frac{1}{2}}\cos\theta = (3/4\pi)^{\frac{1}{2}} z/r,\\
Y_1^{\pm1} &= \mp(3/8\pi)^{\frac{1}{2}}\sin\theta e^{\pm i\phi} = (3/8\pi)^{\frac{1}{2}} x_\pm/r,\\
Y_2^0 &= (5/16\pi)^{\frac{1}{2}}(3\cos^2\theta - 1) = (5/16\pi)^{\frac{1}{2}}(2z^2 + x_+x_-)/r^2,\\
Y_2^{\pm1} &= \mp(15/8\pi)^{\frac{1}{2}}\cos\theta\sin\theta e^{\pm i\phi} = (15/8\pi)^{\frac{1}{2}} x_\pm z/r^2,\\
Y_2^{\pm2} &= (15/32\pi)^{\frac{1}{2}} e^{\pm 2i\phi}\sin^2\theta = (15/32\pi)^{\frac{1}{2}} x_\pm^2/r^2.
\end{aligned}$$

Dividing off the first two factors, one finds the differential equation for the radial wave function $R(r)$,

$$[\omega^2/c^2 + (\partial_r + 1/r)^2 - l(l+1)/r^2]R_{\omega,l}(r) = 0. \tag{1.26}$$

Also this equation has simple solutions, to be discussed in Sect. 1.10.

$\boldsymbol{E}$ need not be an eigenfunction of any of these operators, but it may be expanded in terms of the eigenfunctions. Real light has a "spectral decomposition",

$$\boldsymbol{E}(t, \boldsymbol{r}) = \int_0^\infty d\omega \boldsymbol{E}_\omega(\boldsymbol{r}) e^{-i\omega t}, \tag{1.27}$$

which expresses a wave train (or wave packet) as a superposition of monochromatic waves. Similarly, there will be a double integral over the directions of $\boldsymbol{k}$ in (1.11), or equivalently a sum over l and m in (1.24). As a simple example of a summation, consider a wave in a waveguide along the z-axis. The walls of the waveguide in the x- and y-planes require standing waves along these directions, of the form $\sin(k_x x)\sin(k_y y)$. But

$$\sin(k_x x) = (2i)^{-1} e^{ik_x x} - (2i)^{-1} e^{-ik_x x} \tag{1.28}$$

displays a standing wave as a superposition of two counterpropagating plane waves. This also demonstrates that ∇^2 has real eigenfunctions. The solution (1.28) is an eigenfunction of ∂_x^2, even though it is not an eigenfunction of ∂_x. Similarly, the spherical harmonics are only complex because we insisted on using eigenfunctions of ∂_ϕ in (1.17), where $\sin\phi$ and $\cos\phi$ would have been equally possible from the point of view of ∂_ϕ^2.

We conclude with the solution of (1.26) for $l = 0$, $[\omega^2/c^2 + (\partial_r + 1/r)^2]R_{\omega,0}(r) = 0$. Also this equation has two solutions,

$$R_\pm = r^{-1} e^{\pm ikr}, \quad (\partial_r + 1/r)R_\pm = r^{-1}\partial_r e^{\pm ikr} = \pm ikR_\pm, \tag{1.29}$$

with $k^2 = \omega^2/c^2$, as usual. R_+ is the simplest example of an outgoing spherical wave. (It does not represent dipole radiation, because the Coulomb gauge condition $\mathrm{div}\boldsymbol{E} = 0$ has been ignored.) For complex $\boldsymbol{E}$, the intensity is $I \sim \boldsymbol{E}^*\boldsymbol{E}$ instead of $\boldsymbol{E}^2$. It decreases with r as r^{-2}, as expected.

1.2 De Broglies Idea and Schrödingers Equation

Although light does propagate according to the wave equation just discussed, it is nevertheless emitted and absorbed in quanta called photons. In monochromatic light of the type (1.15), each photon has the same energy $E = h\nu$, and in the case of a plane monochromatic wave (1.11), it also has a fixed momentum $\boldsymbol{p} = h\boldsymbol{k}/2\pi$:

$$E = h\nu = \hbar\omega = hc/\lambda, \quad \boldsymbol{p} = \hbar\boldsymbol{k}, \tag{1.30}$$

$$\hbar = h/2\pi = 6.58218 \times 10^{-16}\,\mathrm{eV\,s}, \tag{1.31}$$

where h is Planck's constant. The constants c and $\hbar$ ("hbar") are so fundamental in relativistic quantum mechanics that they are often taken as natural units (Sect. 1.6). On the basis of (1.30), Einstein (1905) translated the relation $\omega^2/c^2 = k^2$ into an energy-momentum relation for photons,

$$E^2/c^2 = p^2. \tag{1.32}$$

For massive particles, he had to reconcile Newton's expression $E_N = p^2/2m$ (m = particle mass, $\boldsymbol{p} = m\boldsymbol{v}$) with his photon formula (1.32). As Newtonian mechanics fixes E_N only up to a constant, Einstein put $E = mc^2 + E_N$ and interpreted this expression as an approximation for small p/mc of the function

$$E/c = \sqrt{m^2c^2 + p^2} = mc + p^2/2mc - p^4/8m^3c^3 \pm \dots \tag{1.33}$$

He thus postulated the energy-momentum relation

$$E^2/c^2 - p^2 = m^2c^2 \tag{1.34}$$

for all kinds of particles (including composite ones and even watches), and obtained (1.32) as a special case for zero-mass particles. It may also be noted that for $p/mc > 1$, the expansion (1.33) of the square root diverges. Instead, the expansion in terms of $mc/p < 1$ is now convergent:

$$E/c = p + m^2c^2/2p - m^4c^4/8p^3 \pm \dots \tag{1.35}$$

Comparing with the $E/c = p$ of (1.32), one may say that all particles of large momenta $mc/p \approx 0$ move also with the speed of light. There exist weakly interacting particles called neutrinos, which appear in beta decay. Their masses are not exactly zero, but are neglible in all terrestrial experiments, such that neutrinos move with the speed of light. In cosmic rays, electrons, protons and even heavier nuclei sometimes move with the speed of light, too. For most experiments, however, the system's total energy E is close to $\sum_i m_i c^2$, where the sum includes all particles which are explicitly considered. Even in a fully relativistic calculation, it is often practical to subtract this constant. Let us call the remaining energy E_N in honour of Newton, even when the calculation is relativistic. For example, when the energy levels of alkali atoms are approximated by a single-electron model, one sets

$$E = m_e c^2 + E_N, \quad m_e c^2 = 510.9989\,\mathrm{keV}. \tag{1.36}$$

Already before the discovery of quantum mechanics, Rydberg found an empirical formula for E_N,

$$E_N(n,l) = -R_\infty/(n-\beta)^2 \equiv -R_\infty/n_\beta^2, \quad n = 1,2,3\dots,\ R_\infty = 13.605691\,\mathrm{eV}. \tag{1.37}$$

R_∞ is the Rydberg constant for an infinitely heavy nucleus, n is the principal quantum number, n_β the "effective" principal quantum number, (also denoted by n^*), and $\beta = \beta(l, n)$ is a "quantum defect" at orbital angular momentum l (1.22). In alkali atoms, $\beta > 0$ is relatively large at small l where the valence electron sees an increasing fraction of the nuclear charge Ze inside the screening charge cloud of the other electrons. (Actually, $n = 1$ exists only for atomic hydrogen, which was studied later. Lithium ($Z = 3$) begins with $n = 2$, sodium (Na, $Z = 11$) with $n = 3$, see Sect. 3.8. The other two electrons of Li occupy the $n = 1$ "shell" which is "closed" according to Pauli (1925); the other ten electrons of Na occupy the closed $n = 1$ and $n = 2$ shells, nowadays called K and L shells.)

This book is mainly concerned with hydrogen-like atoms that have no further electrons. For pointlike nuclei, β is small and strictly independent of n, $\beta = \beta(l) \equiv \beta_l$. It will be shown in Sect. 1.6 that $1/n_\beta^2$ is the eigenvalue of the "standard form" of relativistic equations for hydrogenic atoms.

Long before Schrödinger found his equation (1926), Bohr (1913) interpreted the Rydberg formula as the energies of certain classical Kepler orbits:

$$E_N = -Z^2 R_\infty / n^2, \quad R_\infty = e^4 m_e / 2\hbar^2, \tag{1.38}$$

Z being the nulear charge. This form applies to the whole isoelectric sequence of hydrogen (H, He^+, Li^{++}, $Be^{+++}\ldots$). Together with Sommerfeld, Bohr established the quantization condition $\int pdq = nh$ for closed bound orbits. They also included a nuclear recoil in the form $R = R_\infty m_2/(m_2 + m_e)$, which amounts to replacing the electron mass by the "reduced mass" $m_e m_2/(m_e + m_2)$, m_2 being the nuclear mass. However, the orbits in many-electron atoms are confined but not closed. The hopping ("quantum jumps") from one orbit to another remained also obscure.

De Broglie (1923) proposed that an electron, bound or free, did not at all follow a path $\boldsymbol{r}_e = \boldsymbol{r}_e(t)$, but that its propagation was described by a wave equation. A bound electron would then correspond to a bound standing wave, analogous to a photon in a cavity. The cavity has eigenmodes n, say, with eigenfrequencies ω_n, which happen to obey Rydberg's law (1.37). Of course, de Broglie did not mean that atoms are confined by walls. Instead, the Coulomb attraction by the atomic nucleus would confine the wave to a finite volume. There is in fact an analogy with light reflection from a glass. Consider a plane wave $\exp\{i\boldsymbol{kr}\}$ incident on a window which is normal to the x-axis. Even under the conditions of total reflection, the wave equation excludes an abrupt jump to zero of the wave function. Instead, the factor $\exp\{ik_x x\}$ of $\exp\{i\boldsymbol{kr}\}$ becomes $\exp\{-\kappa x\}$, where $-\kappa$ corresponds to the continuation of k_x to an imaginary value, $k_x = i\kappa$, $ik_x = -\kappa$. Next, replace the plane wave in the vacuum by a spherical wave in a small bubble in the glass, for example by R_+ of (1.29). If now for some reason k is replaced by $i\kappa$ outside the bubble, then the wave function $\exp\{-\kappa r\}/r$ is exponentially falling in all directions. When the bubble shrinks to zero, only this "forbidden" region remains; the

complete wave function is then $R = \exp\{-\kappa r\}/r$, which is the asymptotic ($r \to \infty$) form of the hydrogen atom's wave functions, see Sect. 1.5. Taking now an electron instead of light, the volume filled by the electronic wave functions has a radius of the order of $\kappa^{-1} \equiv a_{\rm B}$. This must roughly correspond to the radius of Bohr's lowest classical circular orbit, which de Broglie knew from the Bohr-Sommerfeld model. For the nth orbit around a nucleus of electric charge Ze,

$$\kappa_n = Z/na_{\rm B}, \quad a_{\rm B} = \hbar^2/e^2 m_e = 0.05291772\,\text{nm}. \tag{1.39}$$

The Bohr radius is much smaller than the wavelength of visible light. This is the main reason for the late discovery of the wave equation for eletrons.

The quantitative result of de Broglie's hypothesis was that a free electron of momentum $\boldsymbol{p} = m_e \boldsymbol{v}$ propagates like the plane wave (1.11) in vacuum, with $\boldsymbol{k} = \boldsymbol{p}/\hbar$ and with the "de Broglie wavelength"

$$\lambda = 2\pi/k = 2\pi\hbar/p = h/m_e v. \tag{1.40}$$

Due to the smallness of λ, the verification of de Broglies idea came late. Today, electron diffraction is used in LEED (= low-energy electron diffraction; the low energy is needed for a sufficiently small value of v). The first application of particle interferometry came from low-energy neutron diffraction on crystals, analogous to X-ray diffraction.

Schrödinger (1926) constructed the wave equation for a free particle of mass m according to the ideas of de Broglie. He took Einstein's relation (1.34) and substituted backwards the values (1.30) for E and $\boldsymbol{p}$ for a plane monochromatic wave,

$$\hbar^2(\omega^2/c^2 - \boldsymbol{k}^2) = m^2c^2, \quad \psi = \psi_0 e^{i\boldsymbol{k}\boldsymbol{r} - i\omega t}. \tag{1.41}$$

We shall denote the wavefunctions of all kinds of particles except photons by ψ. The ψ_0 is analogous to the $\boldsymbol{E}_0$ in (1.11). In the case of spinless particles, it is a single constant. For spin-1/2 particles such as elctrons, protons and neutrons, it is a pair of constants called a spinor, just as the $\boldsymbol{E}_0$ is a triplet of constants called a vector. But spin was added one year later (Pauli 1927), and it is still customary to treat the electron as a spinless particle for a while. (Spin enters nonrelativistic equations only in a magnetic field, see (2.54).) In order to obtain a differential equation whose solutions satisfy the superposition principle, Schrödinger interpreted ω/c and $\boldsymbol{k}$ as eigenvalues of the operators $i\partial_0 = i\partial/\partial(ct)$ and $-i\nabla$, respectively:

$$[(i\hbar\partial_0)^2 - (-i\hbar\nabla)^2)]\psi = m^2c^2\psi. \tag{1.42}$$

Today, the "momentum operator" $-i\hbar\nabla$ is denoted by $\boldsymbol{p}$;

$$(-\hbar^2\partial_0^2 - \boldsymbol{p}^2 - m^2c^2)\psi = 0, \quad \boldsymbol{p} = -i\hbar\nabla. \tag{1.43}$$

The notation E is not used for $i\hbar\partial_t$, only for one of its eigenvalues (see also Sect. 1.4). The stationary free-particle Schrödinger equation

$$\psi(x^\mu) = e^{iEt/\hbar}\psi(\boldsymbol{r}), \quad (E^2/c^2 - \boldsymbol{p}^2 - m^2c^2)\psi(\boldsymbol{r}) = 0 \tag{1.44}$$

is the Helmholtz equation for a massive particle. In the notation of (1.15), it reads

$$(\omega^2/c^2 + \nabla^2 - m^2c^2/\hbar^2)\psi(\boldsymbol{r}) = 0, \tag{1.45}$$

which obviously reduces to (1.15) for $m = 0$. However, this form is not used, because the potentials of the next section would also have to be divided by $\hbar$. The significance of (1.44) will appear repeatedly in this book: for particles of arbitrary spins in Sect. 4.4, and for the asymptotic region of "binaries" in Sects. 4.5 and 4.6.

Example of wavelengths: The $n = 3$ to $n = 2$ transition in hydrogen emits a photon (the red H_α line) of energy $E = R_\infty(1/4 - 1/9) = 1.88\,\text{eV}$. Its wavelength is $\lambda = hc/E = 656.3\,\text{nm}$. The wavelength of a free electron with the same energy 1.88 eV is $\lambda_e = h/p = h/(2m_eE)^{1/2} = hc/E(2m_ec^2/E)^{1/2}$. With $2m_ec^2 \approx 10^6\,\text{eV}$ (1.36), the square root is of the order of 10^{-3}, and consequently $\lambda_e(1.88\,\text{eV}) \approx 0.9\,\text{nm}$. The neutron mass is $940 \times 10^6\,\text{eV}$, so λ_n is 43 times smaller.

1.3 Potentials and Gauge Invariance

The traditional method of including Coulomb and vector potentials in the Schrödinger equation of a charged particle uses a Hamiltonian formalism. But in the first place, this formalism applies to relativistic fields. The Hamiltonian of light in vacuum will be given in Sect. 3.1, that of the electron-positron field in (3.89). Relativistic quantum mechanics is the art of obtaining from these fields equations for systems with a fixed number of massive particles (in the cases of atoms, n_e electrons plus one nucleus). The resulting operators in differential equations are also called "Hamiltonians", but they are never exact. For the hydrogen atom, the old Dirac Hamiltonian is a good first approximation. For $n_e > 1$, the correct treatment of "negative-energy" states (Sect. 2.7) is rather tricky. As these problems disappear in the nonrelativistic limit, it may in fact be appropriate to first mention the nonrelativistic Hamiltonian, which the reader has certainly already seen somewhere.

The nonrelativistic Schrödinger equation is of first order in $i\partial_t$; the transformation of $-\partial_t^2$ into $i\partial_t$ is somewhat complicated. For the time being, we therefore consider the statinary equation (1.44) and replace E by $mc^2 + E_N$ as in (1.36):

$$(2mE_N + E_N^2/c^2 - \boldsymbol{p}^2)\psi(\boldsymbol{r}) = 0. \tag{1.46}$$

E_N^2/c^2 is neglected and (1.46) is rewritten as

$$E_N\psi(\boldsymbol{r}) = H_0\psi(\boldsymbol{r}), \quad H_0 = \boldsymbol{p}^2/2m. \tag{1.47}$$

In classical Hamiltonian mechanics, the complete Hamiltonian is the sum of the kinetic energy $\boldsymbol{p}^2(t)/2m$ (with $\boldsymbol{p}(t) = m\boldsymbol{v}(t)$) and the potential energy $V(\boldsymbol{r}(t))$:

$$H = \boldsymbol{p}^2/2m + V. \tag{1.48}$$

Bohr and Sommerfeld used this H, for an electron in the nuclear electrostatic potential $\phi = Ze/r$, $V = -e\phi = -Ze^2/r$ (the electron has charge $-e$). They calculated the resulting Kepler ellipses, subject to their quantization condition $\int \boldsymbol{p}d\boldsymbol{r} = nh$. Schrödinger also adopted H, but instead of taking $\boldsymbol{r} = \boldsymbol{r}(t)$ and $\boldsymbol{p} = m\boldsymbol{v}(t)$ of a classical path, he took $\boldsymbol{r}$ and $\boldsymbol{p}$ as time-independent operators acting on $\psi(\boldsymbol{r})$,

$$E_N\psi(\boldsymbol{r}) = H\psi(\boldsymbol{r}), \quad H = -\hbar^2\nabla^2/2m + V(r). \tag{1.49}$$

He solved this equation for bound states in the potential $V = -Ze^2/r$ and found that the eigenvalues $E_N(n,l)$ did reproduce the Bohr-Sommerfeld formula (1.38), independently of the quantum number l. Encouraged by this success, Schrödinger returned to his relativistic equation (1.32) and replaced $E \to E - V \to i\hbar\partial_t - V$:

$$(\pi^{0\,2} - \boldsymbol{p}^2 - m^2c^2)\psi = 0, \quad \pi^0 = (i\hbar\partial_t - V)/c = i\hbar\partial_0 - V/c. \tag{1.50}$$

However, the relativistic effects of this equation are complete only for spinless particles. After Dirac discovered his equation for relativistic electrons (1928), (1.50) was discarded for several years. Dirac was convinced that any wave equation, relativistic or not, had to be of the form $i\hbar\partial_t\psi = H\psi$. Today, (1.50) is known as the Klein-Gordon (KG) equation (Klein 1926, Gordon 1926). It describes the relativistic binding of pionic and kaonic atoms, where the pion π^- and kaon K^- are the negatively charged members of the spinless "mesons" π and K, with mc^2 of 139.57 and 493.68 MeV, respectively.

Maxwell's equations of electrodynamics have a peculiar "gauge invariance", and the best way to introduce interactions in quantum mechanics is by postulating gauge invariance also here. The method requires wave equations; it does not exist in classical mechanics. It has been known since long, but its universality became clear only after the discovery of the "electroweak" interaction. Like Lorentz invariance, gauge invariance is somewhat hidden in the standard form of Maxwell's equations:

$$\nabla\boldsymbol{B} = 0, \quad \nabla\times\boldsymbol{E} + \partial_0\boldsymbol{B} = 0, \quad \partial_0 = \partial/\partial(ct), \tag{1.51}$$

$$\nabla\boldsymbol{E} = 4\pi\rho_{\mathrm{el}}, \quad \nabla\times\boldsymbol{B} - \partial_0\boldsymbol{E} = 4\pi c^{-1}\boldsymbol{j}_{\mathrm{el}}. \tag{1.52}$$

The inhomogeneous equations (1.52) refer to the *cgs*-system, $4\pi\epsilon_0 = 11.12\times10^{-11}\,\mathrm{A\,s/V\,m}$; ρ_{el} and $\boldsymbol{j}_{\mathrm{el}}$ are the electric charge and current densities. The two vector fields $\boldsymbol{E}$ and $\boldsymbol{B}$ can be expressed in terms of a single "vector potential" $\boldsymbol{A}$ and a scalar potential $A^0 = \phi$,

$$\boldsymbol{B} = \nabla\times\boldsymbol{A}, \quad \boldsymbol{E} = -\nabla A^0 - \partial_0\boldsymbol{A}, \tag{1.53}$$

in which case the homogeneous equations (1.51) are automatically satisfied. The inhomogeneous equations become

$$-\nabla^2 A^0 - \nabla\partial_0 \boldsymbol{A} = 4\pi\rho_{\rm el}, \quad \nabla\times\nabla\times\boldsymbol{A} + \partial_0(\nabla A^0 + \partial_0\boldsymbol{A}) = 4\pi c^{-1}\boldsymbol{j}_{\rm el}. \tag{1.54}$$

Gauge transformation are defined as those transformations of $A^\mu = (A^0, \boldsymbol{A})$ which do not change $\boldsymbol{B}$ and $\boldsymbol{E}$:

$$A^{0\prime} = A^0 - \partial_0\Lambda, \quad \boldsymbol{A}' = \boldsymbol{A} + \nabla\Lambda, \quad \boldsymbol{B}' = \boldsymbol{B},\ \boldsymbol{E}' = \boldsymbol{E}. \tag{1.55}$$

The gauge function $\Lambda = \Lambda(x^0, \boldsymbol{r})$ must be unique and differentiable but is otherwise arbitrary. It need not be a scalar or a Lorentz invariant. As a rule, Λ is defined indirectly by a gauge fixing condition, for example

$$\text{Coulomb gauge}: \quad \nabla\boldsymbol{A} = 0, \tag{1.56}$$

$$\text{Lorentz gauge}: \quad \nabla\boldsymbol{A} + \partial_0 A^0 = 0. \tag{1.57}$$

An explicit Λ is then only required for a change of gauge, for example from Coulomb to Lorentz. The Coulomb gauge has $\nabla\partial_0\boldsymbol{A} = \partial_0\nabla\boldsymbol{A} = 0$ and $\nabla\times\nabla\times\boldsymbol{A} = \nabla(\nabla\boldsymbol{A}) - \nabla^2\boldsymbol{A} = -\nabla^2\boldsymbol{A}$, such that (1.54) is simplified as follows:

$$-\nabla^2 A^0 = 4\pi\rho_{\rm el}, \quad (\partial_0^2 - \nabla^2)\boldsymbol{A} + \nabla\partial_0 A^0 = 4\pi c^{-1}\boldsymbol{j}_{\rm el}. \tag{1.58}$$

The first of these equations is the Poisson equation, with the solution

$$A^0(t,\boldsymbol{r}) = \int d^3r'\rho_{\rm el}(t,\boldsymbol{r}')/|\boldsymbol{r}-\boldsymbol{r}'|, \quad |\boldsymbol{r}-\boldsymbol{r}'| = [(\boldsymbol{r}-\boldsymbol{r}')^2]^{1/2}. \tag{1.59}$$

In the Coulomb gauge, the nuclear charge density $\rho_{\rm el}(t,\boldsymbol{r}')$ is independent of t in the system where the nucleus is at rest. A pointlike nucleus has

$$\rho_{\rm el}(t,\boldsymbol{r}') = Ze\delta(\boldsymbol{r}'), \quad A^0 = \phi = Ze/r. \tag{1.60}$$

The Hamiltonian (1.48) and the KG equation (1.50) refer to that gauge.

Returning to quantum mechanics, gauge invariance is postulated as follows:

Wave equations are independent of local and temporal phases.

Let $q\Lambda(x^0,\boldsymbol{r})/\hbar c$ denote a change of phase of ψ, q being the particle's electric charge:

$$\psi' = e^{iq\Lambda/\hbar c}\psi. \tag{1.61}$$

Such a transformation does affect the differential operators, for example $i\partial_t$:

$$i\hbar\partial_0 e^{iq\Lambda/\hbar c}\psi = e^{iq\Lambda/\hbar c}(i\hbar\partial_0 - q[\partial_0,\Lambda]/c)\psi. \tag{1.62}$$

Here we have written $[\partial_0,\Lambda] \equiv \partial\Lambda/\partial x^0$ in order not to contradict the rule that operators apply to all expressions to their right, $\partial_0\Lambda\psi = \psi\partial_0\Lambda + \Lambda\partial_0\psi$,

analogous to $\partial_r fg$ following (1.10). To compensate the change of $i\hbar\partial_0$ under the time-dependent phase transformation, this operator must be accompanied by a function $-qA^0$, which is gauged according to (1.55). In other words, the interaction of a particle of charge q is obtained by replacing the free-particle operator $i\hbar\partial_0$ by

$$\pi^0 = i\hbar\partial_0 - qA^0/c. \tag{1.63}$$

This allows one to pull the phase to the left of the differential operator and eventually divide it off:

$$\pi^{0\prime}\psi' = e^{iq\Lambda/\hbar c}\pi^0\psi, \quad \pi^{0\prime 2}\psi' = e^{i\Lambda/\hbar c}\pi^{0 2}\psi. \tag{1.64}$$

Similarly, whenever $-i\hbar\nabla$ operates on ψ, it must be accompanied by a function $-qc^{-1}\boldsymbol{A}$ which cancels the gradient of Λ according to its gauge transformation (1.55):

$$\boldsymbol{\pi} = \boldsymbol{p} - qc^{-1}\boldsymbol{A} = -i\hbar\nabla - qc^{-1}\boldsymbol{A}. \tag{1.65}$$

Thus the phase-invariant relativistic Schrödinger (or KG) equation is

$$(\pi^{0 2} - \boldsymbol{\pi}^2 - m^2c^2)\psi = 0. \tag{1.66}$$

It is gauge transformed either by (1.55) at fixed phase of ψ, or by (1.61) at fixed A^μ. An example of the latter transformation is given in (1.174) below. The operators $\boldsymbol{\pi}$ and $\boldsymbol{p}$ are called kinetic and canonical momenta, respectively. They will appear again in the Dirac equation, and in slightly generalized forms in any local quantum field theory. It should also be warned that measurable nonlocal phase effects do exist (Aharanov and Bohm 1959).

The coupling provided by π^0 and $\boldsymbol{\pi}$ is called the "minimal coupling". But as $\boldsymbol{E}$ and $\boldsymbol{B}$ are gauge invariant, they may appear in additional couplings in (1.66), at least for composite particles.

In atomic theory, gauge invariance is more important than Lorentz invariance. The gauge-invariant form of the nonrelativistic Schrödinger equation (1.49) is

$$(c\pi_N^0 - \boldsymbol{\pi}^2/2m)\psi_N = 0, \quad \pi_N^0 \approx \pi^0 - mc. \tag{1.67}$$

The connection between ψ and ψ_N is postponed to Sect. 2.8. Also postponed are the Lorentz transformations of 4-vectors such as $x^\mu = (ct, \boldsymbol{r})$,

$$p^\mu = (p^0, \boldsymbol{p}) = i\hbar(\partial_0, -\nabla), \quad \pi^\mu = (\pi^0, \boldsymbol{\pi}) = p^\mu - qA^\mu/c. \tag{1.68}$$

For the moment, the 4-vector notation mainly implies that all 4 components have the same dimension, which can be helpful as a dimensionality check also in nonrelativistic equations such as (1.67) (note that mc has also the dimension of a momentum, according to (1.66)). However, as one is confronted with 4-vectors already in contexts such as classical electrodynamics, one may wonder why ∇ appears with a minus sign in p^μ, whereas x^μ has no minus sign

in front of $\boldsymbol{r}$. This sign arises from the combination $i\boldsymbol{k}\boldsymbol{r} - i\omega t$ in the exponent of the plane wave (1.11), combined with the avoidance of a minus sign in the eigenvalue equation $\boldsymbol{p}\psi = \hbar\boldsymbol{k}\psi$ (1.30). The 4-vectors introduced so far are all "contravariant". Later, some minus signs will be hidden in covariant 4-vectors. In addition to $\partial^\mu = (\partial_0, -\partial_i)$, one also uses $\partial_\mu = (\partial_0, \partial_i)$. But then minus sign appear in other places, for example in $A_\mu = (A^0, -\boldsymbol{A})$.

1.4 Stationary Potentials, Zeeman Shifts

Time-independent potentials are called stationary. The only operator which refers to t in the Schrödinger equation (relativistic or not) is then $i\hbar\partial_t$. Its eigenfunctions are $\exp\{-iE_n t/\hbar\}$, where the eigenvalues are denoted by E_n:

$$i\hbar\partial_t e^{-iE_n t/\hbar} = E_n e^{-iE_n t/\hbar}. \tag{1.69}$$

In this case, the equation has solutions of the type

$$\psi_{E_n}(t, \boldsymbol{r}) = e^{-iE_n t/\hbar}\psi_n(\boldsymbol{r}). \tag{1.70}$$

$\psi_n(\boldsymbol{r})$ is called a statinary solution, but in a sense the whole ψ_{E_n} is stationary, because $|\psi_{E_n}|^2$ is time-independent. A truly time-dependent solution must contain several different time exponents, which means several different values of E_n:

$$\psi(t, \boldsymbol{r}) = \sum_n c_n \psi_{E_n} = \sum_n c_n e^{-iE_n t/\hbar}\psi_n(\boldsymbol{r}). \tag{1.71}$$

It is analogous to the spectral decomposition (1.27) of $\boldsymbol{E}(t, \boldsymbol{r})$. The integral $\int d\omega$ is replaced here by a sum over discrete bound states n, but an additional integral over the continuous energies E of electron scattering states (which refer to an ionized atom) may also contribute. The coefficients c_n appear only when the functions $\psi_n(\boldsymbol{r})$ are separately normalized (Sect. 1.8). They are analogous to the $\boldsymbol{E}_0(\omega)$ in (1.24). Decently moving wave packets can be constructed for the harmonic oscillator (Sect. 1.8). In other potentials including the Coulomb potential, $|\psi|^2$ wobbles or disperses. The beginner should not waste time on classical trajectories as limits of moving wave packets.

In the following, we consider a stationary solution of the type (1.69) and drop the index $_n$. We may then replace $i\hbar\partial_0$ by E/c everywhere, and in particular in the gauge invariant combination π^0 (1.63). We also return to the Coulomb gauge and write $qA^0/c = V/c$ (1.50),

$$\pi^0 = (E - V)/c. \tag{1.72}$$

Insertion into the KG equation (1.66) gives

$$[(E - V)^2/c^2 - m^2c^2 - \boldsymbol{\pi}^2]\psi(\boldsymbol{r}) = 0. \tag{1.73}$$

This equation contains at least two constant operators, namely E^2/c^2 and m^2c^2. It is useful to combine these into a single constant,

$$E^2/c^2 - m^2c^2 = \hbar^2k^2. \tag{1.74}$$

In a region in space where the potentials vanish (called the asymptotic region in the case of the Coulomb potential, because it occurs at $r \to \infty$), ψ reduces to a free-particle solution,

$$(\hbar^2k^2 - \boldsymbol{p}^2)\psi_{\rm as} = 0. \tag{1.75}$$

The general form of $\psi_{\rm as}$ will be elaborated in Sect. 1.10. In solids V may tend to a constant (the chemical potential $V_{\rm chem}$) at large r. In such cases one would replace E by $E - V_{\rm chem}$ in the definition (1.74) of k^2. Apart from such trivial generalizations, (1.73) becomes

$$(\hbar^2k^2 - 2EV/c^2 + V^2/c^2 - \boldsymbol{\pi}^2)\psi(\boldsymbol{r}) = 0. \tag{1.76}$$

For comparison with the nonrelativistic limit (1.67), one may define a slightly energy-dependent "quasi-Hamiltonian",

$$2EV/c^2 - V^2/c^2 + \boldsymbol{\pi}^2 = 2mH_{\rm quasi}, \quad \hbar^2k^2\psi = 2mH_{\rm quasi}\psi. \tag{1.77}$$

The combination $2EV/c^2$ is normally close to $2mV$. When relativity was discovered, one noted that one had to replace m by E/c^2 in some places. One then called m the rest mass and E/c^2 the moving mass. The latter expression is not used any longer, as one wishes to emphasize the fact that energy and momentum form a 4-vector. Today, the rest mass is simply called "mass".

In Sect. 1.1, we saw that ∇^2 contains ∂_ϕ^2/ρ^2, and that ∂_ϕ^2 could be replaced by its eigenvalues $-m_l^2$ for the eigenfunctions (1.17). In spherical coordinates it contains $(\boldsymbol{r} \times \nabla)^2/r^2$, which reduces to $-l(l+1)/r^2$ for the spherical harmonics $Y_l^{m_l}$, independently of m_l. When V is independent of ϕ, $V = V(z, \rho)$ (cylindrical symmetry) or $V = V(r)$, $r = \sqrt{z^2 + \rho^2}$ (spherical symmetry), these eigenfunctions and eigenvalues can also be used in solving (1.77). In these cases, the addition of a small magnetic field $\boldsymbol{B}$ ($B^2 \approx 0$) produces energy shifts linear in Bm_l, provided the z-axis points along the direction of $\boldsymbol{B}$ (for $V = V(r)$, this is no loss of generality):

$$E(B) = E(0) + Be\hbar cm_l/2E(0). \tag{1.78}$$

This is already the relativistic formula, which is easily derived. $\boldsymbol{B}$ is taken constant over the atomic dimensions, and the z-axis is taken along $\boldsymbol{B}$. With $\boldsymbol{B} = \nabla \times \boldsymbol{A}$, the Coulomb gauge $\nabla \boldsymbol{A} = 0$ determines $\boldsymbol{A}$ only up to a constant, which is called b in the following:

$$\boldsymbol{A} = \begin{pmatrix} A_x \\ A_y \\ A_z \end{pmatrix} = B \begin{pmatrix} -by \\ (1-b)x \\ 0 \end{pmatrix}, \quad \boldsymbol{B} = \begin{pmatrix} 0 \\ 0 \\ B \end{pmatrix}, \tag{1.79}$$

plus linear terms $ax+c_x$ in A_x and $-ay+c_y$ in A_y (to keep $\partial_x A_x+\partial_y A_y=0$), which are rarely needed. $\boldsymbol{A}$ apears in the $\boldsymbol{\pi}^2$ of (1.76),

$$\boldsymbol{\pi}^2=(\boldsymbol{p}+e\boldsymbol{A}/c)^2=\boldsymbol{p}^2+(\boldsymbol{A}\boldsymbol{p}+\boldsymbol{p}\boldsymbol{A})e/c+e^2A^2/c^2. \tag{1.80}$$

There is a problem of notation here, which is the spatial analogue of $\dot{\Lambda}$ in (1.62). With $\boldsymbol{p}=-i\hbar\nabla$ and the Coulomb gauge $\nabla\boldsymbol{A}=0$, one might conclude $\boldsymbol{p}\boldsymbol{A}=0$. But since $\boldsymbol{p}\boldsymbol{A}$ operates on ψ, one has instead $\nabla\boldsymbol{A}\psi=\psi\nabla\boldsymbol{A}+\boldsymbol{A}\nabla\psi=\boldsymbol{A}\nabla\psi\neq 0$. Consequently, when $\boldsymbol{A}$ is used as an operator, one should not write $\nabla\boldsymbol{A}=0$. The alternative $\mathrm{div}\boldsymbol{A}=0$ is not good either, since the operators div, grad and rot are sometimes also meant to operate on everything to their right (unlike the dot in $\dot{\Lambda}\psi$, which is placed on top of its object). The quantum technicians have therefore elaborated special symbols for the redistribution of operators, in particular the commutator $[\,,]$ and anticommutator $\{\,,\}$. For any two operators A and B,

$$[A,B]=AB-BA,\quad \{A,B\}=AB+BA, \tag{1.81}$$

$$\{A,B\}=2AB-[A,B]=2AB+[B,A]. \tag{1.82}$$

A precise form of the Coulomb gauge in the context of operators is thus

$$[\nabla,\boldsymbol{A}]=0, \tag{1.83}$$

because its second term $-\boldsymbol{A}\nabla\psi$ cancels the $+\boldsymbol{A}\nabla\psi$ which is part of $\nabla\boldsymbol{A}\psi$. Similarly, when the ∇^2A^0 of (1.54) is needed as an operator on ψ, it must be replaced by the double commutator $[\nabla,[\nabla,A^0]]$, see (2.261).

Returning now to (1.79), the "circular gauge" $b=\frac{1}{2}$, maintains rotational symmetry around the z-axis:

$$\boldsymbol{A}_{\mathrm{ci}}=\tfrac{1}{2}\boldsymbol{B}\times\boldsymbol{r},\quad A_{\mathrm{ci}}^2=(x^2+y^2)B^2/4. \tag{1.84}$$

Then $2\boldsymbol{A}\boldsymbol{p}$ contains the combination $\boldsymbol{r}\times\boldsymbol{p}$ which is called angular momentum $\boldsymbol{l}$, in view of the corresponding combination in classical mechanics:

$$\boldsymbol{l}=\boldsymbol{r}\times\boldsymbol{p}=-i\hbar(\boldsymbol{r}\times\nabla), \tag{1.85}$$

$$2\boldsymbol{A}_{\mathrm{ci}}\boldsymbol{p}=(\boldsymbol{B}\times\boldsymbol{r})\boldsymbol{p}=\boldsymbol{B}\boldsymbol{l}=Bl_z=-iB\hbar\partial_\phi. \tag{1.86}$$

Electrons have an additional "spin" angular momentum; a more precise name for $\boldsymbol{l}$ is then "orbital angular momentum".

As spherical symmetry is a special case of cylindrical symmetry, we assume $V=V(z,\rho)$ and separate only the ϕ-dependence from $\psi(\boldsymbol{r})$,

$$\psi(\boldsymbol{r})=\psi(z,\rho)\psi_{m_l}(\phi),\quad -i\partial_\phi\psi=m_l\psi. \tag{1.87}$$

In $\boldsymbol{\pi}^2\psi$, one may then replace ∂_ϕ by im_l everywhere:

$$\boldsymbol{\pi}^2=-\hbar^2(\partial_z^2+\rho^{-1}\partial_\rho+\partial_\rho^2-m_l^2/\rho^2)+B\hbar m_l e/c+e^2B^2\rho^2/4c^2. \tag{1.88}$$

The function $\psi_{m_l}(\phi)$ can now be divided off. We also assume bound states in which the range of ρ^2 is confined by V, such that $B^2\rho^2$ may be neglected. The only remaining B-dependent operator in the KG-equation (1.73) is then the constant $-2B\hbar m_l e/c$, which may be included in the definition of $\hbar^2 k^2$ as in (1.74),

$$E^2/c^2 - m^2c^2 - B\hbar m_l e/c \equiv \hbar^2 k^2, \tag{1.89}$$

With this definition, one may use (1.76) with $\boldsymbol{\pi}^2 = \boldsymbol{p}^2 =$ first half of (1.88),

$$(\hbar^2 k^2 - 2EV/c^2 + V^2/c^2 - \boldsymbol{p}^2)\psi(z,\rho) = 0. \tag{1.90}$$

B is now completely hidden in the redefinition of k^2. For given k^2, the dependence of E on B follows from (1.89):

$$E(B) = (m^2c^4 + \hbar^2c^2k^2 + B\hbar m_l ec)^{\frac{1}{2}} = (E^2(0) + B\hbar m_l ec)^{\frac{1}{2}}. \tag{1.91}$$

To first order in B, expansion of the square root produces (1.78). In the nonrelativistic limit, the factor $1/E(0)$ is replaced by $1/mc^2$. One also defines the Bohr magneton μ_{B}:

$$\mu_{\mathrm{B}} = e\hbar/2mc, \quad E(B) \approx E(0) + B\mu_{\mathrm{B}} m_l. \tag{1.92}$$

A coincidence of n_d different energy levels is called an n_d-fold degeneracy. For $V = V(r)$ and $\psi(z,\rho) = R(r)\Theta_l^{m_l}(\theta)$ (1.21) $\boldsymbol{p}^2$ is independent of m_l according to (1.22). The energy levels $E_{l,m_l}(B=0)$ are then $2l+1$-fold degenerate, $\Sigma_{m_l=-l}^{l} = 2l+1$. The degeneracy is lifted by the Zeeman-splitting which is linear in Bm_l (Fig. 1.4). In the case of strictly vanishing quantum defects (1.37), different l-values become also degenerate, which may lead to the more complicated "quadratic Zeeman effect".

Whereas $\boldsymbol{p}^2 = -\hbar^2\nabla^2$ is a real operator with real eigenfunctions (remember (1.28)), $\boldsymbol{\pi}^2$ is complex and does require complex eigenfunctions. A real eigenfunction can only depend on m_l^2, not on m_l. The Zeeman shift demonstrates the necessity of complex functions. The eigenvalues E remain real, due to the hermiticity of operators, see Sect. 1.8.

1.5 Bound States

Conducting electrons in metals move like free particles in a constant potential of depth $-V_0$, which is measured from the ionization limit to the bottom of the conducting band. Due to the Pauli principle, they fill all levels of energies $E < E_{\mathrm{F}}$, where $E_{\mathrm{F}} < 0$ is the Fermi energy. It is customary here to shift the energy scale such that one has $V = 0$ inside the metal. The asymptotic region where (1.75) applies, $(k^2 + \nabla^2)\psi = 0$, is then inside the metal. The details of the metal surface are often unimportant, and it is convenient to use the limit $V = +V_0 \to \infty$ there. In this limit, ψ must vanish at the

surface, precisely as the standing waves in the waveguide mentioned near the end of Sect. 1.1. Consider now a wire along the z-axis, with a rectangular basis of dimensions L_x, L_y. The appropriate solutions of the wave equation are

$$\psi(x,y,z) = e^{ik_z z} \sin k_x x \sin k_y y, \quad \sin k_i L_i = 0 \ (i = 1,2). \tag{1.93}$$

The last two conditions imply

$$k_i = n_i \pi / L_i, \quad n_i = 1,2,3,4,5,\ldots \tag{1.94}$$

whereas k_z remains arbitrary, positive or negative. If one now cuts the wire at $z_{\max} = L_z$, k_z must also be positive and obey condition (1.94) for $i = 3$. The possible energy levels are then suddenly discrete or "quantized",

$$E = \sqrt{m^2c^4 + c^2\hbar^2 k^2} = \sqrt{m^2c^4 + c^2(n_x^2/L_x^2 + n_y^2/L_y^2 + n_z^2/L_z^2)h^2/4}, \tag{1.95}$$

with $\hbar\pi = h/2$. For a macroscopic piece of metal, one hastens to the limit $L_x = L_y = L_z \to \infty$, where the energy levels become again dense within the conducting band (thence the name "band"). Our point here is the opposite one, namely confining the wavefunction to a finite volume $L_x L_y L_z$ entails a discrete energy spectrum. This is the massive particle analogue of a microwave cavity, where the modes are quantized according to

$$E(n_x, n_y, n_z) = \hbar\omega = (n_x^2/L_x^2 + n_y^2/L_y^2 + n_z^2/L_z^2)^{1/2} ch/2. \tag{1.96}$$

But whereas a single cavity mode can host many photons, a mode in a metal can host at most two electrons, due to the Pauli principle (the factor 2 accounts for the electron spin). The modes for electrons are commonly called "orbitals". Such modes exist approximately also in a single many-electron atom. In the simplest form of the atomic shell model, the orbitals are successively filled with electrons. The word "state", on the other hand, means a precise wave function. In single-particle problems, there is hardly any difference. But the ground state of the helium atom has a wave function $\psi(\boldsymbol{r}_1, \boldsymbol{r}_2)$, which depends on the two electon positions $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$. It is an antisymmetrized product of orbitals only if the mutual repulsion of the two electrons is either neglected or approximated by an over-all weakening of binding. In the mathematical sense, the concept of a "state" is more general than a wave function, as will be explained in Sect. 1.9.

The wavefunction of a single spinless particle can be bound by an attractive, spherically symmetric potential $V(r) < 0$, $r = (x^2 + y^2 + z^2)^{1/2}$ according to (1.76), but now with $\boldsymbol{A} = 0$, $\boldsymbol{\pi}^2 = \boldsymbol{p}^2 = -\hbar^2\nabla^2$. In spherical coordinates (1.6), (1.22), $\psi(\boldsymbol{r})$ has solutions that factorize into angular and radial parts,

$$\psi_{k^2}(\boldsymbol{r}) = Y_l^{m_l}(\theta,\phi) R_{k^2,l}(r). \tag{1.97}$$

After (1.22) has been used, the angular part can be divided off, and the following equation is obtained for the radial part:

$$[k^2 - 2EV/c^2\hbar^2 + V^2/c^2\hbar^2 + (\partial_r + 1/r)^2 - l(l+1)/r^2]R_{k^2,l} = 0. \quad (1.98)$$

States with $l = 0, 1, 2, 3$ are called s, p, d, f, respectively. To solve the radial equation, consider first the asymptotic region, $V(r \to \infty) = 0$. For $r \to \infty$, $l(l+1)/r^2$ is also negligible. The solutions $R_{\rm as}(r) = R_{\pm}(r)$ of (1.98) have already been given in (1.29). For real k, they are not confined in space and correspond to an ionized electron. The general solution is a linear combination with two coefficients b_+ and b_-. Bound states require imaginary k,

$$k = i\kappa, \quad R_{\rm as}(r) = r^{-1}(b_+ e^{-\kappa r} + b_- e^{\kappa r}), \quad (1.99)$$

and the special value $b_- = 0$, to exclude exponential growth of $R(r)$ for $r \to \infty$. The solution of the complete equation (1.98) is now taken in the form

$$R_{k^2,l} = e^{-\kappa r} v(r), \quad (\partial_r + 1/r)^2 e^{-\kappa r} = e^{-\kappa r}(\partial_r + 1/r - \kappa)^2, \quad (1.100)$$

where both b_+ and r^{-1} have become parts of the new function v. The factor $e^{-\kappa r}$ is divided off, leading to

$$[-2EV/c^2\hbar^2 + V^2/c^2\hbar^2 + (\partial_r + 1/r)^2 - 2\kappa(\partial_r + 1/r) - l(l+1)/r^2]v = 0. \quad (1.101)$$

Although $R_{k^2,l}(r)$ is now bound, the values of $k^2 = -\kappa^2$ are not yet quantized. Quantization requires a second boundary condition, which arises at $r \to 0$. We first consider the case $l > 0$. With a finite nuclear charge distribution $\rho(r')$, $V(r = 0)$ remains finite according to (1.59). To find the singular part of (1.101) for $r \to 0$, one multiplies the equation by r^2 and then lets $r \to 0$:

$$[(\partial_r + 1/r)^2 - l(l+1)/r^2]v(r \to 0) = 0. \quad (1.102)$$

Also this equation has two linearly independent solutions,

$$v(r \to 0) = c_+ r^l + c_- r^{-l-1}. \quad (1.103)$$

The quantization of κ^2 arises only when one postulates both

$$b_- = 0, \quad c_- = 0. \quad (1.104)$$

These postulates are necessary to make $\psi(\boldsymbol{r})$ "normalizable", i.e. the integral

$$I = \int |\psi|^2 d^3r = \int \psi^*(\boldsymbol{r})\psi(\boldsymbol{r}) r^2 dr d\phi du \quad (1.105)$$

must be finite. Althought the electron itself is not "smeared out", its wave function implies an extended charge distribution $\rho_{\rm el}(t,\boldsymbol{r})$. Nonrelativistically,

$$\rho_{\rm el} = -e\rho \sim -e|\psi(t,\boldsymbol{r})|^2, \tag{1.106}$$

is to be used as one source of the scalar potential A^0, $-\nabla^2 A^0 = 4\pi\rho_{\rm el}$ according to Maxwell's equation (1.58). For stationary states, ρ is time-independent. And as the total charge must give the charge $-e$ of the electron, the nonrelativistic case requires $I = 1$. The spherical harmonics are separately normalized to unity by integration over $d\phi du$, such that one is left with

$$I = \int_0^\infty R^2_{k^2,l} r^2 dr = \int_0^\infty e^{-2\kappa r} v^2(r) r^2 dr. \tag{1.107}$$

This integral would diverge already for the smallest nonzero value $l = 1$, $v^2 = b_-^2 r^{-4}$, except for $c_- = 0$. An ordinary second-order differential equation such as (1.98) has two linearly independent solutions. With the two extra conditions (1.104), both solutions are killed, one is left with $\psi = 0$. However, when considered as a function of one of its parameters, the equation may have nontrivial solutions at certain discrete values of that parameter. In our case, that parameter is k^2, from which E follows according to (1.74) or (1.91). The above argument fails for $l = 0$, where both solutions of (1.101) are normalizable. Nonrelativistically and for $V = -Ze^2/r$, the second solution behaves like $r^{-1} - (2mZe^2/\hbar^2)\log r$ for small r. It gets excluded by more general arguments involving the kinetic energy operator $p^2/2m$. In the relativistic equation (1.101), the term $V^2/c^2\hbar^2$ contributes another r^{-2} -operator, which also leads to an equation of the type (1.102), but with l replaced by an $l_\alpha < l$. And with the relativistic form (1.197) below of the normalization integral, one finds that $c_- = 0$ is required for all values of l.

Exact solutions of (1.101) exist only for the point Coulomb potential, $V = -Ze^2/r$. For modified V, numerical integrations may use the point Coulomb k^2 as a starting value and integrate from large κr inwards, beginning with the function $e^{-\kappa r}$. The integration will end at $r = 0$ with $R(0) = +\infty$ or $-\infty$. By repeating the procedure with a slightly different κ one will be able to approach $R(0) = 0$ (for $l > 0$) or $R(r) = \text{const.}$ (for $l = 0$). Conversely, if one integrates from $r = 0$ outwards, starting with $R = r^l$, $R(\kappa r \gg 1)$ will behave as $b_- e^{+\kappa r}$, and modifications of κ will eventually lead to $b_- \sim 0$.

A spherical potential $V(r)$ is invariant under the parity transformation $\boldsymbol{r} \to -\boldsymbol{r}$, which in spherical coordinates (Fig. 1.2) means

$$r \to r, \quad \phi \to \phi + \pi, \quad \theta \to \pi - \theta \quad (u \to -u). \tag{1.108}$$

The parity of the bound states (1.97) is independent of their ϕ dependence,

$$\psi_{k^2}(-\boldsymbol{r}) = (-1)^l \psi_{k^2}(\boldsymbol{r}). \tag{1.109}$$

This follows from the decomposition (1.21) of $Y_l^{m_l}$. The factor $e^{im_l\phi}$ has the parity $(-1)^{m_l}$, while $\Theta_l^{m_l}$ has the parity $(-1)^{l-m_l}$ (note the invariance

of (1.9) under $u \to -u$). Consequently, a superposition of states (1.97) with different m_l remains a parity eigenstate. This gives rise to useful "selections rules", in particular for the "dipole operator" $\boldsymbol{r}$ itself,

$$\int \psi_l^{m_l'*} \psi_l^{m_l} \boldsymbol{r} d^3r = 0. \tag{1.110}$$

States that contain both even and odd l-values are not parity eigenstates. This applies for example to plane waves, which will be decomposed into spherical waves in Sect. 1.10. In the Dirac equation, parity eigenstates do contain both even and odd l-values, but the selection rule for dipole radiation remains (Sect. 5.4).

1.6 Spinless Hydrogenlike Atoms

We now turn to the complete solution of the radial equation (1.101) for a pointlike nucleus, $V = -Ze^2/r$. $Z > 1$ is needed for hydrogenlike ions, and also in some variational calculations. For $V/\hbar c$, we introduce Sommerfeld's fine structure constant, which has the pleasant property of being dimensionless:

$$e^2/\hbar c \equiv \alpha = (137.036)^{-1}, \tag{1.111}$$

$$[2EZ\alpha/\hbar cr - l_\alpha(l_\alpha+1)/r^2 + (\partial_r + 1/r)^2 - 2\kappa(\partial_r + 1/r)]v(r) = 0, \tag{1.112}$$

$$l_\alpha(l_\alpha+1) = l(l+1) - Z^2\alpha^2. \tag{1.113}$$

The notation $l_\alpha(l_\alpha+1)$ allows us to keep (1.101), with the replacement $l \to l_\alpha$. The orbital angular momentum quantum number l remains integer, of course, the spherical harmonics are not affected.

In this book, we shall use altogether three abbreviations for products of α with constants

$$\alpha_Z = Z\alpha, \quad \alpha_{\rm dip} = e_{\rm dip}^2/\hbar c, \quad \alpha_\pi = \alpha/\pi. \tag{1.114}$$

Ze is the nuclear charge, $e_{\rm dip}$ is the "dipole charge" (5.164). These symbols not only shorten the sometimes lengthy formulas, they also facilitate their understanding: α_Z occurs in the electron-nucleus interaction, $e_{\rm dip}$ occurs in the electric dipole radiation of the whole atom including the nucleus, and α_π arises from Cauchy integrals ("loops" in the language of Feynman diagrams) involving the electron alone (for example the anomalous magnetic moment (2.76)). Atomic dipole loops contains $\alpha_{\rm dip}/\pi$. A two-photon electron-nucleus loop will be mentioned in (5.196), which contains α_Z^2/π. It is quite common today to distinguish between α and α_Z even for $Z = 1$. The isolated α appears in multi-electron atoms, namely in the repulsive potential (3.80) between two electrons (and also in some small loop terms which contain $\pi\alpha_\pi$, see the remark following (C.25)). $\alpha_{\rm dip}$ and α_π will not be needed before Chap. 5.

To solve (1.112), one multiplies it by $r/2\kappa$ and expresses it in terms of the dimensionless variable $z = 2\kappa r$:

$$[n_\beta - l_\alpha(l_\alpha + 1)/z + z(\partial_z + 1/z)^2 - z\partial_z - 1]v(z) = 0, \tag{1.115}$$

$$z = 2\kappa r, \quad n_\beta = \alpha_Z E/\hbar c\kappa. \tag{1.116}$$

n_β will come out as the "effective principal quantum number" of the Rydberg formula.

The singular operator $-l_\alpha(l_\alpha + 1)/z$ is removed by the substitution

$$v(z) = z^{l_\alpha} w, \quad (\partial_z + 1/z)^2 z^{l_\alpha} = z^{l_\alpha}(\partial_z + 1/z + l_\alpha/z)^2 : \tag{1.117}$$

$$[n_\beta + z\partial_z^2 + 2\partial_z(1 + l_\alpha) - z\partial_z - l_\alpha - 1]w = 0. \tag{1.118}$$

This is the differential equation of the confluent hypergeometric function $F(z) = {}_1F_1(a, b, z)$:

$$[z\partial_z^2 + (b - z)\partial_z - a]F(a, b, z) = 0, \tag{1.119}$$

$$b = 2l_\alpha + 2, \quad a = l_\alpha + 1 - n_\beta. \tag{1.120}$$

F has the following power series in z:

$$\begin{aligned} F = 1 &+ za/b + a(a + 1)/[b(b + 1)]z^2/2! \\ &+ a(a + 1)(a + 2)/[b(b + 1)(b + 2)]z^3/3! \ldots \end{aligned} \tag{1.121}$$

To prove this, one writes $F = \Sigma_k a_k z^k$,

$$(b - z)F' = \Sigma_k z^k[b(k + 1)a_{k+1} - ka_k], \quad zF'' = \Sigma_k z^k k(k + 1)a_{k+1}, \tag{1.122}$$

which leads to the recurrence relation

$$a_{k+1}(k + 1)(k + b) = a_k(a + k). \tag{1.123}$$

For $k \to \infty$, $a_{k+1}/a_k = k$ shows that the series diverges as $e^z = \Sigma z^k/k!$ at large z. The precise relation between R and F is

$$R_{k^2,l} = e^{-\kappa r}(2\kappa r)^{l_\alpha} c_+ w = Ne^{-z/2} z^{l_\alpha} F(z), \tag{1.124}$$

such that R goes as $e^{-z/2}e^z = e^{z/2} = e^{\kappa r}$, as expected from (1.99). How can one avoid this rising exponent? There are certain values of the parameter a (1.120) for which F does not grow exponentially; for example $a = 0$ gives $F = 1$. More generally, when a is a negative integer $-n_r$, F reduces to a polynomial of degree n_r in z:

$$F = F(-n_r, b, z) = 1 - n_r z/b + (-n_r)(-n_r + 1)z^2/2!b(b + 1) \ldots,$$

$$F(n_r = 1) = 1 - z/b, \quad F(n_r = 2) = 1 - 2z/b + z^2/[b(b + 1)]. \tag{1.125}$$

Apart from normalization, these are the Laguerre polynomials (1.179) below. For each a (1.120) of F, E is now calculated using (1.116) and (1.120):

$$n_\beta = \alpha_Z E/\kappa\hbar c = n_r + l_\alpha + 1 \equiv n - \beta_l, \quad \beta_l = l - l_\alpha. \tag{1.126}$$

The integers n_r and n are the "radial" and "principal" quantum numbers, respectively,

$$n = n_r + l + 1. \tag{1.127}$$

The normalization constant N of (1.124) is given in Appendix A, the complete nonrelativistic wave functions for $n = 1$ and 2 are

$$\psi_{nlm}(\theta,\phi,r) = Y_l^m(\theta,\phi)(Z/na_\mathrm{B})^{3/2}e^{-Zr/na_\mathrm{B}}\hat{R}_{nl}(r),$$

$$\hat{R}_{10} = 2, \quad \hat{R}_{20} = 2 - Zr/a_\mathrm{B}, \quad \hat{R}_{21} = 3^{-1/2}Zr/a_\mathrm{B}. \tag{1.128}$$

For the calculation of E from (1.126), κ must be eliminated. $E^2 = m^2c^4 + c^2\hbar^2k^2 = m^2c^4 - \hbar^2c^2\kappa^2$ implies $\kappa\hbar c = (m^2c^4 - E^2)^{1/2}$, such that (1.126) becomes $\alpha_Z E/(m^2c^4 - E^2)^{1/2} = n_\beta$. Resolving this expression for E, one finds

$$E = mc^2\left(1 + \frac{\alpha_Z^2}{n_\beta^2}\right)^{-1/2}, \quad \hbar c\kappa = \frac{\alpha_Z E}{n_\beta} = mc^2\left(\frac{n_\beta^2}{\alpha_Z^2} + 1\right)^{-1/2}. \tag{1.129}$$

Note the absence of odd powers of α_Z. For $\alpha_Z^2/n_\beta^2 \ll 1$, one expands

$$[1 + \alpha_Z^2/n_\beta^2]^{-1/2} - 1 = -\tfrac{1}{2}\alpha_Z^2/n_\beta^2 + \tfrac{3}{8}\alpha_Z^4/n_\beta^4 - \tfrac{5}{16}\alpha_Z^6/n_\beta^6 \ldots \equiv f. \tag{1.130}$$

A more practical quantity is then $E_N = E - mc^2$ (1.36), which is given here to the order α_Z^8/n_β^8:

$$E_N = mc^2 f = -\tfrac{1}{2}mc^2\alpha_Z^2 n_\beta^{-2}(1 - \tfrac{3}{4}\alpha_Z^2/n_\beta^2 + \tfrac{5}{8}\alpha_Z^4/n_\beta^4 - \tfrac{35}{64}\alpha_Z^6/n_\beta^6). \tag{1.131}$$

The leading term gives Rydberg's expression (1.37). As $\beta_l \equiv \beta$ is also small, one expands

$$\alpha_Z^2/n_\beta^2 = \alpha_Z^2/(n-\beta)^2 = \alpha_Z^2/n^2(1 + 2\beta/n + 3\beta^2/n^2 + 4\beta^3/n^3). \tag{1.132}$$

Writing (1.113) in the form $(l_\alpha + 1/2)^2 = (l + 1/2)^2 - \alpha_Z^2$, one finds

$$\beta_l = l - l_\alpha = l + \tfrac{1}{2} - [(l + \tfrac{1}{2})^2 - \alpha_Z^2]^{1/2}. \tag{1.133}$$

Expansion of the square root in powers of α_Z^2 gives:

$$\beta_l = \alpha_Z^2(2l+1)^{-1}[1 + \alpha_Z^2/(2l+1)^2 + 2\alpha_Z^4/(2l+1)^4]. \tag{1.134}$$

It shows that the order α_Z^8 requires at most two powers of β_l in α_Z^4/n_β^4 and one power in α_Z^6/n_β^6:

$$\alpha_Z^4/n_\beta^4 = \alpha_Z^4 n^{-4}[1+4\beta/n+10\beta^2/n^2], \quad \alpha_Z^6/n_\beta^6 = \alpha_Z^6 n^{-6}(1+6\beta/n). \tag{1.135}$$

The expansion of E_N in n and l to order α_Z^3 is postponed to (2.149), where it is presented for the more important Dirac equation. As β_l arises from the inclusion of V^2 in the KG-equation, it need not be viewed as a relativistic effect. One may define a "KG potential" for use in the KG equation (1.76):

$$(\hbar^2 k^2 - 2EV_{\mathrm{KG}} - \boldsymbol{\pi}^2)\psi = 0, \quad V_{\mathrm{KG}} = V(1 - V/2E). \tag{1.136}$$

Even without the approximation $V/E \approx V/mc^2$, β_l is strictly independent of n. The expression for E_N to lowest nonvanishing order in α_Z^2 has of course $\beta_l = 0$, $E_N = -\alpha_Z^2 mc^2/2n^2$, in agreement with the Bohr-Sommerfeld formula. These energies depend on n_r and l only via their sum $n_r + l = n - 1$ according to (1.127). And as a given l-value contains already $2l + 1$ magnetic sublevels, the total degeneracy of the nonrelativistic energy levels of the spinless hydrogen atom is

$$g_{\mathrm{spinless}}(n) = \Sigma_{l=0}^{n-1}(2l + 1) = n^2. \tag{1.137}$$

A systematic degeneracy of this type (as opposed to accidental degeneracy for particular values of some parameters) can always be reduced to a symmetry argument. For spherically symmetric potentials, E is independent of m_l. For $V = -Ze^2/r$ and negligible V^2/E, E is also independent of l, which is a consequence of O_4 symmetry (its mechanical analogue is the conservation of the Runge-Lenz vector, which will not be discussed here). O_4 is a nonrelativistic symmetry which is broken in the relativistic case.

The operator $l(l + 1)/r^2$ may also be combined with V_{KG}, which is then called an effective potential:

$$V_{\mathrm{eff}} = V_{\mathrm{KG}} + l(l + 1)\hbar^2 c^2/2Er^2. \tag{1.138}$$

The second term corresponds to the centrifugal potential of classical mechanics. The nonrelativistic approximation $c^2/2E = 1/2m$ gives

$$V_{\mathrm{eff,\,nr}} = V + l(l + 1)\hbar^2/2mr^2. \tag{1.139}$$

This function is plotted in Fig. 1.3 for $V = -e^2/r$ and for $l = 0,\ 1,\ 2$ ("s"-, "p"-, "d"-states). The degeneracy of E_n in these very different potentials is not at all evident. It is reflected in the shell model of atoms. Electronic shells with $n = 1,\ 2,\ 3$ are called K, L, M. Examples of spinless hydrogenlike atoms are mesic atoms (pionic and kaonic atoms, normally with $Z > 1$). Their energy levels are influenced by strong interactions at short distances, which drastically reduce the lifetimes of mesic atoms in s-states, and for heavier nuclei also in p-states. For such atoms, the order α_Z^4-binding effects

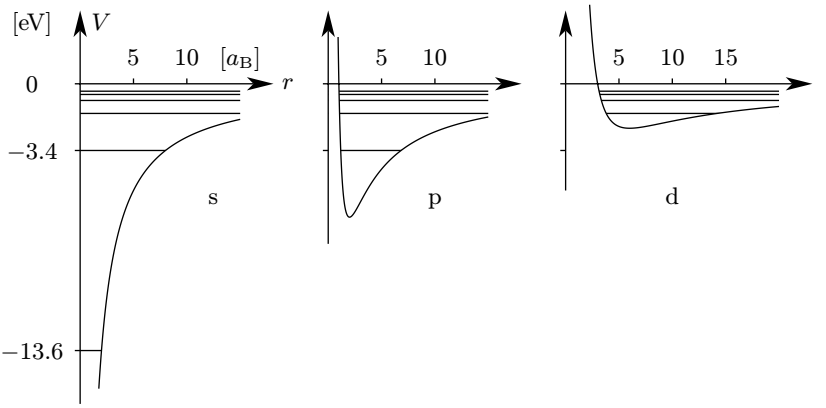

Fig. 1.3. The energy levels $E_N = -\alpha^2 mc^2/2n^2$ and $V_{\rm eff} = -e^2/r + \hbar^2\ell(\ell+1)/2mr^2$ for $\ell = 0, 1, 2,$ (s, p, d)

of the KG equation have been verified with moderate precision in p- and d-states. Foe a theoretician, the best test of these effects is a by-product of ordinary "electronic" hydrogenlike atoms, in the form of a fine-structure average (see the discussion following (2.149) below). The precise values of the electron mass and the Bohr radius $a_{\rm B}$ have already been given in Sect. 1.2. For scattering states (which contain one ion and one unbound electron), (1.98) applies with positive k^2; the substitution $k = i\kappa$ is then inappropriate. We therefore resubstitute in (1.120)

$$z = -2ikr, \quad a = l_\alpha + 1 + i\eta, \quad \eta = -\alpha_Z E/\hbar ck, \tag{1.140}$$

$$F = F(l_\alpha + 1 + i\eta,\, 2l_\alpha + 2,\, -2ikr). \tag{1.141}$$

$E > mc^2$ is now a continuous parameter, and the confluent hypergeometric function $F(a, b, z)$ contains both e^{ikr} and e^{-ikr} for $r \to \infty$. Such waves are called Coulomb distorted waves (see also (1.299) and Sect. 2.7); η is the "Sommerfeld parameter" (the distortion vanishes for $\eta = 0$). At very high energies, one has $V_{\rm KG} = V$, and the centrifugal potential at fixed l becomes also unimportant.

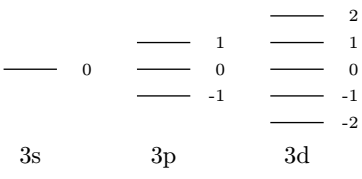

Fig. 1.4. The Zeeman splitting for the spinless hydrogen atom, at $n = 3$

The KG equation plays a central role in relativistic quantum mechanics, as the Dirac and binary equations can be reduced to the same form. It is therefore useful to simplify that form as much as possible. For the point Coulomb potential, multiplication of (1.76) by $(c/EZ\alpha)^2 = c^2/E^2\alpha_Z^2$ gives the "standard form"

$$(2/r_\epsilon + \alpha_Z^2/r_\epsilon^2 - \boldsymbol{\pi}_\epsilon^2)\psi = -(\hbar kc/E\alpha_Z)^2\psi, \tag{1.142}$$

$$\boldsymbol{r}_\epsilon = \boldsymbol{r}\alpha_Z E/\hbar c, \quad \boldsymbol{p}_\epsilon = c\boldsymbol{p}/\alpha_Z E. \tag{1.143}$$

It contains only two constants, namely α_Z^2 and n_β^{-2},

$$K\psi = -(\hbar kc/E\alpha_Z)^2\psi = n_\beta^{-2}\psi, \quad K = 2/r_\epsilon + \alpha_Z^2/r_\epsilon^2 - \boldsymbol{\pi}_\epsilon^2, \tag{1.144}$$

according to the definition (1.116) and $k^2 = -\kappa^2$ for bound states. The original KG equation is an "implicit" eigenvalue equation, i.e. the operator itself contains E. Its standard form is an explicit eigenvalue equation for n_β^{-2}, which is an advantage in perturbation theory of $\boldsymbol{\pi}^2$ (for example of the Zeeman shift calculation (2.307) in Sect. 2.9). This point is hidden in the four-component Dirac equation $H_D\psi_D = E\psi_D$ (Sect. 2.4), but becomes evident in the two-component "Kramers version" (2.135) below. The standard form of the nonrelativistic Schrödinger equation for $V = -\alpha_Z/r$ (1.49) is $(2/r_e - \boldsymbol{\pi}_e^2)\psi = n_\beta^{-2}\psi$; it is used in quantum defect theory (Seaton 1966). But there the advantage is less important, as (1.49) is already an explicit eigenvalue equation for E_N. Equation (1.119) is an explicit eigenvalue equation in z, with eigenvalue a.

Immediate results of the standard form are that it contains only α_Z^2, E^2 and m^2. Whereas the α^2-dependence survives in the nonrelativistic Schrödinger equation, the appearance of E^2 and m^2 is characteristic of relativity. It is already present in Einstein's relation (1.34) for freely moving objects. In particular, m is only defined as $\pm\sqrt{m^2}$. The sign of m is a matter of definition. Einstein should really have used a new symbol on the right-hand side of his equation (1.34), for example the letter s which will be introduced in (4.72) for the mass^2 of a composite particle. The arbitrariness in the sign of E is more difficult. In Sect. 3.2, negative energies will be needed for positrons, which are repelled by the hydrogen nucleus. But near the end of Sect. 4.7, it will become clear that the static KG and Dirac equations also represent limiting cases of relativistic two-body equations, in which hydrogen and antihydrogen appear as degenerate solutions with eigenvalue $s = (\pm E \pm m_{\text{nucleus}})^2$.

The natural units of relativistic quantum mechanics are $\hbar = c = 1$. A popular energy unit is the electron Volt, eV. From $\hbar$ (1.31) and c (1.1), one gets

$$1 = \hbar = \hbar c = 6.58218 \times 10^{-16}\,\text{eV s} = 1.973289 \times 10^{-5}\,\text{eV cm}. \tag{1.145}$$

Both cm and s have then the dimension eV^{-1}. As the precision of c exceeds that of the original Paris meter, the meter has been redefined as $1\,\text{m} = 1\,\text{s} \times c$.

The fine structure constant $e^2/\hbar c$ (1.111) remains dimensionless, $e^2 = \alpha = 1/137.036$. Measurements of α are discussed by Kinoshita (1996). Magnetic fields are quoted in Tesla,

$$1\,\mathrm{T} = 10\,000\,\mathrm{Gauss} = 692.76\,\mathrm{eV}^2. \tag{1.146}$$

With $m_e = 510\,999\,\mathrm{eV}$, the corresponding Larmor frequency ((1.173) below) is small,

$$\omega_{\mathrm{Larmor}} = \tfrac{1}{2}eB/m_e c = \tfrac{1}{2}(B/\mathrm{T})1.15768 \times 10^{-4}\,\mathrm{eV}. \tag{1.147}$$

The energy scale of thermal dirstibution is given by the Boltzman constant, $k_{\mathrm{B}} = 8.61734 \times 10^{-5}\,\mathrm{eV/K}$.

Unfortunately, some theorists use $\hbar = c = 1$ in connection with Heaviside-Lorentz units, where the 4π is missing in the inhomogeneous Maxwell equations (1.52). There are thus two different units of charge in use,

$$e = \sqrt{\alpha} = 0.08542, \quad e_{\mathrm{HL}} = e\sqrt{4\pi}, \quad \alpha = e_{\mathrm{HL}}^2/4\pi, \tag{1.148}$$

which is a permanent source of errors.

On the other hand, atomic theorists prefer "atomic" units, $\hbar = m_e = e = 1$. From $e^2/\hbar c = \alpha$, this fixes $c = 1/\alpha$. The Bohr radius is $a_{\mathrm{B}} = \hbar^2/e^2 m_e = 1$, the Rydberg constant $R_\infty = 1/2$. The smaller "Rydberg" unit $R_\infty = 1$ is also used, thus providing errors of factors 2.

1.7 Landau Levels and Harmonic Oscillator

A free spinless particle of charge $q = -e$ in a constant magnetic field is described by (1.76) for $V = 0$ and $\boldsymbol{\pi}^2$ given by (1.80):

$$(\hbar^2 k^2 - \boldsymbol{\pi}^2)\psi = (\hbar^2 k^2 - \boldsymbol{p}^2 - 2\boldsymbol{A}\boldsymbol{p}e/c - \boldsymbol{A}^2 e^2/c^2)\psi = 0. \tag{1.149}$$

As $\boldsymbol{A}$ (1.79) is independent of z, there exist solutions with plane waves along the z-axis,

$$\psi(\boldsymbol{r}) = e^{ik_z z}\psi(x,y), \quad (\hbar^2 k_t^2 - p_x^2 - p_y^2 - 2\boldsymbol{A}\boldsymbol{p}e/c - \boldsymbol{A}^2 e^2/c^2)\psi(x,y) = 0; \tag{1.150}$$

$$\hbar^2 k_t^2 = \hbar^2 k^2 - \hbar^2 k_z^2 = E^2/c^2 - m^2 c^2 - \hbar^2 k_z^2. \tag{1.151}$$

This equation may be solved both in cartesian and in cylindrical coordinates; the two sets of solutions are quite different. To understand their connection, it helps to recapitulate the corresponding classical paths. These follow from the Lorentz force

$$\dot{\boldsymbol{p}} = -e(\boldsymbol{E} + \boldsymbol{v} \times \boldsymbol{B}), \quad \boldsymbol{v} = \dot{\boldsymbol{r}} = d\boldsymbol{r}/dt \tag{1.152}$$

for the special case $\boldsymbol{E} = 0$. The relativistic form of $\boldsymbol{p}$ is $m\boldsymbol{u} = md\boldsymbol{r}/d\tau$, where τ is the particle's proper time. When the particle energy E is conserved, one has $t = \tau\gamma = \tau E/mc^2$ ("time dilatation") and $\dot{\boldsymbol{p}} = \ddot{\boldsymbol{r}}E/c^2$. Consequently, the relativistic Lorentz force contains m only indirectly via E, precisely as the Klein-Gordon equation (1.151). The classical path in three dimensions is a helix along the z-axis (the direction of the magnetic field), its projection on the xy-plane being a circle of radius

$$R = p_t/ecB. \tag{1.153}$$

Relativistic particle momenta are in fact measured from curvatures in magnetic fields. The relativistic Larmor frequency is $\omega_{\text{Larmor}} = ecB/2E$. The classical helix has its "guiding center" defined by its coordinates $(x_g,\ y_g)$ in the xy-plane. The quantum mechanical solutions of (1.149) have no orbits with x_g and y_g as simultaneous eigenvalues, as the corresponding operators do not commute. The circular gauge (1.84) contains orbits with guiding centers at a fixed distance ρ_g from the origin. The "Landau gauge" takes $b = 0$ in (1.79). Then $\boldsymbol{A}$ depends only on y, and x_g can be fixed. For general b, one obtains solutions with fixed ellipses of guiding centers. Rotated and shifted ellipses would require more parameters in (1.79).

The Landau levels are most easily calculated in the Landau gauge

$$b = 0, \quad A_z = A_x = 0, \quad A_y = Bx, \tag{1.154}$$

$$\psi(x, y) = e^{ik_y y}\psi(x), \quad [k_t^2 + \partial_x^2 - (k_y + xeB/\hbar c)^2]\psi(x) = 0. \tag{1.155}$$

The equation is rewritten as

$$[k_t^2 + \partial_x^2 - (eB/\hbar c)^2(x - x_0)^2]\psi = 0, \quad x_0 = -\hbar c k_y/eB. \tag{1.156}$$

It is made dimensionless and the x_0 is removed by the substitution

$$x - x_0 = s^{1/2}\xi, \quad \partial_x = s^{-1/2}\partial_\xi, \quad s = \hbar c/eB, \tag{1.157}$$

$$[k_t^2 s + \partial_\xi^2 - \xi^2]\psi(\xi) = 0. \tag{1.158}$$

The equation is equivalent to the nonrelativistic Schrödinger equation (1.49) in one dimension ($\nabla^2 \to \partial_x^2,\ E_N = \hbar^2 k^2/2m$) with the harmonic oscillator potential $V(x) = \frac{1}{2}m\omega_N^2(x - x_0)^2$, which will be commented on in Sects. 1.8 and 1.9, and also in Sect. 3.1 in connection with photons. The harmonic oscillator becomes dimensionless for $s = \hbar/m\omega_N$,

$$E_N\psi = \tfrac{1}{2}\hbar\omega_N(\xi^2 - \partial_\xi^2)\psi. \tag{1.159}$$

Note also that we have this time ignored our rule that the separation of the plane wave $\exp(ik_y y)$ in (1.155) replaces the constant k_t^2 by $k_x^2 = k_t^2 - k_y^2$, because k_y^2 was needed in the shift of variable (1.156). The physical range of ξ in the differential equation (1.158) is $-\infty < \xi < +\infty$; the point $\xi = 0$ is

harmless this time. The asymptotic solution at $\xi^2 \to \infty$ is found by setting $k_t^2 = 0$,

$$(\xi^2 - \partial_\xi^2)\psi_{\rm as} = 0, \quad \psi_{\rm as} = N_+ e^{\xi^2/2} + N e^{-\xi^2/2}, \tag{1.160}$$

The coefficient N_+ must vanish, because the function $\exp\{\xi^2/2\}$ explodes for $\xi \to \infty$. The complete solution for finite ξ is again taken as a product,

$$\psi_n(\xi) = N_n e^{-\xi^2/2} H_n(\xi). \tag{1.161}$$

The new label n refers to the nth eigenvalue k_{tn}^2 of (1.156). We shall find $n = 0$ for the lowest eigenvalue k_{t0}^2, where ψ_0 is called the ground state. (In the hydrogen atom, the ground state has the principal quantum number $n = 1$ and $l = 0$.) At this moment, the values of n are still open. The factor $\exp\{-\xi^2/2\}$ is again pulled to the left of all operators and then divided off:

$$\partial_\xi^2 e^{-\xi^2/2} = e^{-\xi^2/2}(\partial_\xi - \xi)^2 = e^{-\xi^2/2}(\partial_\xi^2 - \xi\partial_\xi - \partial_\xi\xi + \xi^2), \tag{1.162}$$

$$(\partial_\xi^2 - \xi\partial_\xi - \partial_\xi\xi + 2n')H_n(\xi) = 0, \quad n' = k_t^2 s. \tag{1.163}$$

One may of course also rewrite

$$\partial_\xi \xi = \xi\partial_\xi + 1, \tag{1.164}$$

remembering $\partial_\xi \xi H = \xi\partial_\xi H + H = (\xi\partial_\xi + 1)H$:

$$(\partial_\xi^2 - 2\xi\partial_\xi + 2n)H_n = 0, \quad n = n' - \tfrac{1}{2}. \tag{1.165}$$

This differential equation is solved by a power series expansion,

$$H_n = \sum_{\nu=0}^{\infty} a_\nu \xi^\nu, \quad 2(n - \xi\partial_\xi)\xi^\nu = 2(n-\nu)\xi^\nu, \quad \partial_\xi^2 \xi^\nu = \nu(\nu-1)\xi^{\nu-2}, \tag{1.166}$$

$$(\nu+2)(\nu+1)a_{\nu+2} + 2(n-\nu)a_\nu = 0. \tag{1.167}$$

The first term in (1.167) originates from $a_{\nu+2}\partial_\xi^2 \xi^{\nu+2}$. For $\nu \to \infty$, one has $a_{\nu+2}/a_\nu \approx 2/\nu$. The same ratio appears also in the power series expansion $\exp\{\xi^2\} = \Sigma_n (\xi^2)^n/n! = \Sigma_\nu \xi^\nu/(\nu/2)!$. As in the hydrogen case, it corresponds to the growing part of $\psi_{\rm as}$ (1.160). It can be avoided only if the series stops at a certain maximal power $\nu_{\max}$ of ξ. This requires the n of (1.165) to be an integer, $n = \nu_{\max}$; in that case $a_{\nu_{\max}+2}$ vanishes according to (1.167). The coefficients of the two highest powers of ξ follow from (1.167) by setting $\nu = n - 2$, and by Hermite's choice of normalization, $a_n = 2^n$.

$$n(n-1)a_n - 4a_{n-2} = 0, \quad H_n = 2^n[\xi^n - n(n-1)/4\xi^{n-2}\ldots] \tag{1.168}$$

The series begins with a_0 for even n and with a_1 for odd n,

$$H_0 = 1, \quad H_1 = 2\xi, \quad H_2 = 4\xi^2 - 2, \quad H_3 = 8\xi^3 - 12\xi. \tag{1.169}$$

The polynomials H_n are called Hermite polynomials. With $n' = n + \frac{1}{2}$ according to (1.165), the eigenvalues k_t^2 of (1.158) assume the values

$$k_{t,n}^2 = n' eB/\hbar c = (n + \tfrac{1}{2})/s, \quad n = 0,\ 1,\ 2 \ldots . \tag{1.170}$$

Thus the Landau levels are equidistant in k_t^2 and also in E^2 according to (1.151). At fixed k_z, one may also define a mass for the transverse motion,

$$m_t^2 = m^2 + \hbar^2 k_z^2/c^2, \tag{1.171}$$

$$E_n/c = \sqrt{m_t^2 c^2 + \hbar^2 k_t^2} = m_t c + n' eB\hbar/2m_t c^2 - n'^2 e^2 B^2 \hbar/8m_t^3 c^5 \ldots . \tag{1.172}$$

In the nonrelativistic limit, the third term is already negligible, such that the energy levels E_n themselves become equidistant,

$$E_{N,n} = n' \hbar \omega_{\text{Larmor}}, \quad \omega_{\text{Larmor}} = eB/2mc. \tag{1.173}$$

It is instructive to construct the Landau levels also in the gauge (1.79) with $b \neq 0$. For that purpose, we separate a phase from $\psi(x, y)$ (1.155) as in (1.61),

$$\psi(x, y) = e^{ie\Lambda/\hbar c} \psi'(x, y), \quad \Lambda = -bxyB, \tag{1.174}$$

$$-i\hbar\partial_x e^{\cdots} = e^{\cdots}(-i\hbar\partial_x + byeB/c), \quad -i\hbar\partial_y e^{\cdots} = e^{\cdots}(-i\hbar\partial_y + bxeB/c). \tag{1.175}$$

The equation for $\psi'(x, y)$ keeps the form (1.150), but now with $\boldsymbol{A}$ given by (1.79). In the circular gauge $b = \frac{1}{2}$, (1.84) and (1.86) give

$$(\hbar^2 k_t^2 - p_x^2 - p_y^2 + ieB\partial_\phi \hbar/c - e^2\rho^2 B^2/4c^2)\psi'(x, y) = 0, \quad \rho^2 = x^2 + y^2. \tag{1.176}$$

This is still the old equation, with solutions $\psi' = e^{-ie\Lambda/\hbar c} e^{-k_y y} \psi(x)$. However, it also has other simple solutions. They are found in cylindrical coordinates by the ansatz

$$\psi'(x, y) = \psi_{m_l}(\phi)\psi_{ci}(\rho), \tag{1.177}$$

where the $\psi_{m_l}(\phi)$ are the eigenfunctions of $-i\partial_\phi$, with eigenvalues $m_l = 0,\ \pm 1,\ \pm 2 \ldots$. The operator $\boldsymbol{\pi}^2$ is then given by (1.88), but with the additional simplification $\partial_z^2 \to -k_z^2$:

$$[k_t^2 + \rho^{-1}\partial_\rho + \partial_\rho^2 - m_l^2/\rho^2 - eBm_l/\hbar c - (e\rho B/2\hbar c)^2]\psi_{ci}(\rho) = 0. \tag{1.178}$$

The substitution $z = (e/2\hbar c)B\rho^2$ and the ansatz $\psi_{ci} = e^{-z/2} z^{|m_l|/2} w(z)$ lead again to the confluent hypergeometric differential equation for w, $w = F(a, b, z)$, this time with $b = 1 + |m_l|/2$, $-a = (k_t^2/eB - 1 - m_l - |m_l|)/2$. Its polynomial solutions have $-a = n_\rho$, $n' = n_\rho + m_l + |m_l| + 1)/2$. They are the ("associated") Laguerre polynomials L_q^p:

$$L_{n_\rho}^p = (n_\rho + p)!^2 (n_\rho! p!)^{-1} F(-n_\rho, p + 1, z), \tag{1.179}$$

with $p = |m_l|/2$, $q = n_\rho$, and the harmonic oscillator quantum number $n = p + n_\rho$.

1.8 Orthogonality and Measurements

The point Coulomb potential and the constant B-field ("harmonic oscillator") practically exhaust the list of explicit solutions not only for the KG-equation (1.73), but also for the Dirac equation below. The nonrelativistic Schrödinger equation has additional explicit solutions in cases that involve the conserved Runge-Lenz vector, but these are less interesting. In this situation, the analysis of implicit solutions becomes particularly important.

In linear algebra, an operator $A^\dagger$ Hermitian adjoint to A is defined over the space of square integrable functions $\psi,\ \psi'$ as follows:

$$\int \psi'^* A^\dagger \psi = \int \psi (A\psi')^* = \int \psi A^* \psi'^*. \tag{1.180}$$

The integration extends at least over those variables on which A acts. For $A = x,\ f(x),\ \partial_x, \partial_x^2$ etc. one may only have to integrate over x, even if $\psi(\boldsymbol{r})$ is also a function of the orthogonal coordinates y, z. But there are also wavefunctions $\psi(\boldsymbol{r}_1,\ \boldsymbol{r}_2)$ which are needed for atoms with two electrons, in which case a two-particle operator A_{12} might require integrals over d^3r_1 and d^3r_2 in (1.180). A popular notation is $\int d\tau$, without specification of τ. For $A^\dagger = A$, the operator is called "self-adjoint". The operator x (= multiplication by x) is self-adjoint, but ∂_x is not. $i\partial_x$ is self-adjoint for those functions that vanish at the integration limits. $(i\partial_x)^* = -i\partial_x$, and the minus sign is canceled by a partial integration, $\int \psi'^* \partial_x \psi = -\int \psi \partial_x \psi'^*$.

In practice, $A^\dagger = A$ may be weakened to apply to a class of integrals called "expectation values", to be defined in (1.206) below. This is called "hermiticity", $A_{\rm H}^\dagger = A_{\rm H}$. Eigenfunctions ψ_i of $A_{\rm H}$ have real eigenvalues, $a_i = a_i^*$. For the proof, we set $\psi = \psi_i,\ \psi' = \psi_i$ in (1.180):

$$\int \psi_i^* A_{\rm H} \psi_i = a_i \int \psi_i^* \psi_i = \int \psi_i (A_{\rm H}\psi_i)^* = a_i^* \int \psi_i^* \psi_i. \tag{1.181}$$

In physics, it has become customary to replace the term "self-adjoint" by "Hermitian", except perhaps in the discussion of "observables", see below.

Eigenfunctions ψ_i and ψ_j with two different eigenvalues of the same operator $A_{\rm H}$ are "orthogonal" to each other,

$$A\psi_i = a_i\psi_i, \quad A\psi_j = a_j\psi_j, \quad \int \psi_j^* \psi_i = 0 \text{ for } a_i \neq a_j. \tag{1.182}$$

For the proof, consider (1.181) with ψ_i^* replaced by ψ_j^*:

$$\int \psi_j^* A\psi_i = a_i \int \psi_j^* \psi_i = \int \psi_i (A\psi_j)^* = a_j \int \psi_i \psi_j^*, \tag{1.183}$$

in view of the reality of a_j. Consequently, $(a_i - a_j)\int \psi_j^* \psi_i = 0$ results in $\int \psi_j^* \psi_i = 0$ for $a_i - a_j \neq 0$. For $i = j$, the integral remains open, and a normalization constant N_i is used to get $\int |\psi_i|^2 = 1$. The functions are then said to be orthonormal,

$$\int \psi_j^* \psi_i = \delta_{ij} = \ (1 \text{ for } i = j,\ 0 \text{ for } i \neq j). \tag{1.184}$$

A trivial example of orthogonality relations is provided by the functions $\psi_{m_l}(\phi)$ (1.17), which have the universal normalization constant $N(m_l) = (2\pi)^{-1/2}$:

$$\int_0^{2\pi} d\phi \psi^*_{m'}(\phi)\psi_m(\phi) = \delta_{mm'}. \tag{1.185}$$

The piece $\partial_u(1-u^2)\partial_u$ of $(\boldsymbol{r}\times\boldsymbol{\nabla})^2$ is separately Hermitian in the variable $-1 < u < 1$, $u = \cos\theta$, such that $(\boldsymbol{r}\times\boldsymbol{\nabla})^2$ is also Hermitian (with eigenvalues $-l(l+1)$, as we know). Consequently, the spherical harmonics satisfy orthogonality relations in the two variables $u = \cos\theta$ and ϕ:

$$\int_0^{2\pi} d\phi \int_{-1}^{1} du Y_{l'}^{m'}(\theta,\phi) Y_l^m(\theta,\phi) \equiv \int d\Omega Y_{l'}^{m'*} Y_l^m = \delta_{mm'}\delta_{ll'}. \tag{1.186}$$

The operators ξ and $p_\xi = -i\partial_\xi$ are Hermitian for the harmonic oscillator wave funcions, and so is their combination $\xi^2 + p_\xi^2 = \xi^2 - \partial_\xi^2$. The resulting eigenvalues $n + \frac{1}{2}$ of $k^2\hbar c/eB$ (1.170) are real, so the eigenfunctions $\psi_n(\xi)$ are orthonormal:

$$\int d\xi N_m N_n e^{-\xi^2} H_m H_n = \delta_{mn}. \tag{1.187}$$

In this case, the normalization constant N_n is relatively complicated:

$$\int e^{-\xi^2} H_n^2 d\xi = \pi^{\frac{1}{2}} 2^n n!, \quad N_n = \left(\pi^{\frac{1}{2}} 2^n n!\right)^{-1/2}. \tag{1.188}$$

It will be derived by a simpler method in (1.227). If one wishes to normalize in the more physical coordinate x', the relation $dx' = sd\xi$ gives

$$N_{x,n} = \left[(\pi s)^{\frac{1}{2}} 2^n n!\right]^{-1/2}. \tag{1.189}$$

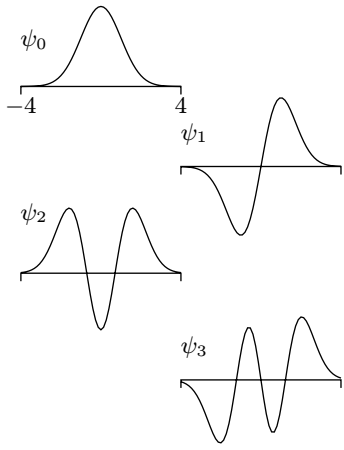

Fig. 1.5. The harmonic oscillator functions ψ_n for $n = 0$ to 3

Orthogonality relations of eigenfunctions of operators A with real eigenvalues a_i are taught in linear algebra. Their significance in quantum physics is also connected with the theory of measurements: The result of a measurement is the eigenvalue of a fixed and known operator. For example, the momentum $\hbar\boldsymbol{k}$ of a free particle is one of the infinitely many eigenvalues of the operator $\boldsymbol{p} = -i\hbar\boldsymbol{\nabla}$. But what happens with the hermiticity of $\boldsymbol{p}$ for plane waves which refuse to vanish at the integration limits? As an example, consider the functions

$$\psi = e^{ik_z z}\psi(x,y), \quad \psi' = e^{ik'_z z}\psi'(x,y).$$

$$\int_{z_{\min}}^{z_{\max}} \psi'^* \partial_z \psi = -\int_{z_{\min}}^{z_{\max}} \psi \partial_z \psi'^* + \psi'^*(z_{\max})\psi(z_{\max}) - \psi'^*(z_{\min})\psi(z_{\min}). \tag{1.190}$$

The "surface terms" must be eliminated in order to make $-i\hbar\partial_z$ a Hermitian operator. Two different methods are used here. The first one takes right away $z_{\min} = -\infty$, $z_{\max} = +\infty$, but replaces the phase $ik_z z$ by $ik_z z - \kappa|z|$ with $\kappa > 0$. In this case each surface term of (1.190) vanishes, and at the end of the calculation one may take $\kappa \to 0$. The second method uses a finite integration interval, $z_{\max} - z_{\min} = L_z$ as in Sect. 1.5, and imposes periodic boundary conditions, $\psi(z_{\max}, x, y) = \psi(z_{\min}, x, y)$. In this case the two surface terms of (1.190) cancel each other. At the end of the calcutation, one takes $L_z \to \infty$, see Sect. 2.2. In this method, the possible values of k_z are restricted to

$$k_z = n_z 2\pi/L_z, \quad n_z = 0, \pm1, \pm2, \pm3, \pm4 \ldots . \tag{1.191}$$

Their spacing is twice as large as in the case (1.94) for bound states, but negative values are now also allowed. The total number of states for large L_z is thus the same, and one is no longer restricted to standing waves $\sin k_z z$. Contrary to p_z, the component $l_z = -i\hbar\partial_\phi$ of the angular momentum operator $\boldsymbol{l} = \boldsymbol{r} \times \boldsymbol{p}$ (1.85) is automatically Hermitian, due to the periodicity condition $\psi(\phi) = \psi(\phi + 2\pi)$ of a single-valued function on a circle. This property has been converted into another useful trick for wavefunctions (1.190) that extend only over a finite region in x and y: The space is deformed into a torus of length $L_z = 2\pi R \to \infty$. The region $z > z_{\max}$ has a trivial meaning in this torus.

The stationary KG-equation (1.73) is of second order in $a_i = E_i$. For $V = 0$, the equation may be rewritten as $\boldsymbol{\pi}^2\psi = \hbar^2 k^2 \psi$, which is again an explicit eigenvalue equation $\boldsymbol{\pi}^2\psi_i = a_i\psi_i$, $a_i = \hbar^2 k^2$. (The fact that a_i contains E_i^2 instead of E_i is only relevant for the physical content.) A complication arises for $V \neq 0$, for those variables (normally only r) that occur in V.

For the derivation of orthogonality relations, one needs the KG-equation at energy E_i and its complex conjugate at energy E_j (the hydrogen atom without magnetic field has $E_i = E(n_i, l_i)$, $E_j = E(n_j, l_j)$, but one may immediately set $l_i = l_j$ in view of (1.186)):

$$[(E_i - V)^2/c^2 - m^2c^2 - \boldsymbol{\pi}^2]\psi_i = 0, \quad [(E_j - V)^2/c^2 - m^2c^2 - \boldsymbol{\pi}^{2^*}]\psi_j^* = 0. \tag{1.192}$$

We multiply the first equation by ψ_j^*, the second one by ψ_i and subtract the two products:

$$\psi_j^*(E_i^2 - 2E_iV - \boldsymbol{\pi}^2c^2)\psi_i - \psi_i(E_j^2 - 2E_jV - \boldsymbol{\pi}^{2^*}c^2)\psi_j^* = 0. \tag{1.193}$$

This is now integrated over all space. As $\boldsymbol{\pi} = \boldsymbol{p} + eA/c$ is Hermitian, the operators $\boldsymbol{\pi}^2$ and $\boldsymbol{\pi}^{2*}$ cancel each other after integration, and one is left with

$$\int \psi_j^*[E_i(E_i - 2V) - E_j(E_j - 2V)]\psi_i = 0. \tag{1.194}$$

Observing $E_i^2 - E_j^2 = (E_i - E_j)(E_i + E_j)$, one may extract a factor $(E_i - E_j)$;

$$\int \psi_j^*(E_i + E_j - 2V)\psi_i = 0 \ \text{ for } E_i \neq E_j. \tag{1.195}$$

For a spherically symmetric potential $V(\boldsymbol{r}) = V(r)$, (1.195) simplifies to

$$\int_0^\infty r^2 dr R_{k'^2,l} R_{k^2,l}(E + E' - 2V) = 0 \ \text{ for } E \neq E'. \tag{1.196}$$

These expressions generalize (1.182). The nonrelativistic limit takes $|V| \ll E$, in which case (1.182) remains correct also in the presence of V in the Schrödinger equation.

The normalization integral (the left-hand side of (1.196) for $E' = E$) can be set equal to 1 as in (1.184), but it is better to divide the expression by $2mc^2$ or by E in order to keep the nonrelativistic limit $E \sim E' \sim mc^2$, $V \sim 0$ in the form (1.184):

$$\int \psi_j^*(\tfrac{1}{2}E_j + \tfrac{1}{2}E_i - V)\psi_i/mc^2 = \delta_{ij}. \tag{1.197}$$

When the time exponents $\exp(-iE_it/\hbar)$ of ψ_i and $\exp(iE_jt/\hbar)$ of ψ_j^* are included, (1.197) may be written as

$$\langle j|i\rangle \equiv \int \psi_j^*(t,\boldsymbol{r})[(-\tfrac{1}{2}i\hbar\overleftarrow{\partial}_t + \tfrac{1}{2}i\hbar\partial_t - V)/mc^2]\psi_i(t,\boldsymbol{r}) = \delta_{ij}, \quad \psi^*\overleftarrow{\partial}_t \equiv \dot{\psi}^*. \tag{1.198}$$

This form applies also to truly time-dependent wave functions such as (1.71), for which Dirac introduced the compact notations of kets $|\rangle$ and bras $\langle|$:

$$|\psi\rangle = \sum_i c_i|i\rangle, \quad \langle\psi'| = \sum_i c_i'^*\langle i| \tag{1.199}$$

$$\langle\psi'|\psi\rangle = \sum_{ij} c_j'^* c_i\langle j|i\rangle = \sum_i c_i'^* c_i. \tag{1.200}$$

The Dirac notation is rather flexible, $|i\rangle = |\psi_i\rangle$. In nonrelativistic context, $\langle\psi'|\psi\rangle$ always means $\int \psi'^*\psi$. Two general solutions ψ and ψ' of an equation

are said to be orthogonal, $\langle\psi'|\psi\rangle = 0$ if they have not a single ψ_i in common, i.e. $c_i' = 0$ for $c_i \neq 0$. The normalization is

$$\langle\psi|\psi\rangle = \sum_i |c_i|^2 = 1. \tag{1.201}$$

The coefficient c_j of a specific state $|j\rangle$ is projected out of $|\psi\rangle$ (1.199) by means of (1.198), which defines the "scalar product" of $|j\rangle$ and $|\psi\rangle$;

$$c_j = \langle j|\psi\rangle = \int \psi_j^*(\tfrac{1}{2}E_j + \tfrac{1}{2}i\hbar\partial_t - V)\psi/mc^2. \tag{1.202}$$

The interpretation of a general state $|\psi\rangle$ is based on the observation of discrete and reproducible bound state energies, the superposition principle and on the orthogonality relations. In the absence of degeneracy, a measurement of E which results in the value E_i identifies the state $|i\rangle$, apart from a phase. Consider for example the states $|i\rangle = |n_i,\ l_i, m_i\rangle = \psi_{n_i,l_i,m_{li}}(r,\theta,\phi)$ of a hydrogen atom in a magnetic field, where the degeneracy with respect to the magnetic quantum number m_l is lifted by the Zeeman splitting (1.78). If the magnetic field B has been measured by some classical method, one can calculate the possible values E_i before measuring the atomic energies. The corresponding ψ_i play the role of unit vectors in the vector space of square integrable functions, $\langle\psi|\psi\rangle < \infty$, which is called a Hilbert space. This space has infinitely many dimensions, but in most cases one needs only a small number of components, namely those for which nonzero expansion coefficients c_i are expected in the actual energy measurement of the hydrogen atom. Hermititan operators that generate a complete set of states (see (1.250) below) are also called "observables".

Suppose now that a single hydrogen atom in a trap is excited at time $t = 0$ by a short laser pulse from its ground state ($n = 1,\ l = 0,\ m_l = 0$) to a mixture of its four $n = 2$-states (spin is neglected). The state $l = 0$ of $n = 2$ can only be excited by two-photon absorption, which is negligible. We thus expect a linear combination of the three states ($n = 2,\ l = 1,\ m_l = -1,\ 0,\ +1$), with coefficients $c_{-1},\ c_0$ and c_1, and of the unexcited ground state with coefficient c_{00}. However, in an actual measurement one finds only one of these four energies, for example from the frequency of the photon which is created in the atomic de-excitation. This frequency is always that of one of the discrete Zeeman components, never in between. The only possible interpretation of (1.201) is that $|c_i|^2$ is the probability to find that Zeeman component. As the single hydrogen atom in the trap can emit at most one photon, one cannot determine $|c_n|^2$ with a single pulse. One may either use many pulses with a sufficiently slow repetition rate, or one may fill the trap with many hydrogen atoms which are all in the atomic ground state. In the latter case, the gas must be sufficiently thin to avoid inter-atomic perturbances (and in particular recombination into molecular hydrogen H_2). In practice, it is easier to use a beam of atomic hydrogen. In that case, however, the "Doppler"

line broadening caused by the thermal velocity distribution must be much smaller than the Zeeman splitting. Such a beam is then described by a "density matrix". In any case, the outcome of these experiments will be the three positive numbers $|c_{-1}|^2$, $|c_0|^2$ and $|c_1|^2$, with $|c_{-1}|^2 + |c_0|^2 + |c_1|^2 < 1$. Different experiments are necessary to measure the relative phases between the c_i, for example the application of a probe laser pulse at time $t > 0$. A realistic theory of measurement in a given system may be quite complicated. As a rule, the precision of the apparatus has a natural limit. The preparation of a ψ with components in different energy eigenstates E_i requires a laser pulse with a correspondingly broad frequency band $\Delta\omega_{\text{laser}}$. According to (1.27) and the theory of Fourier transforms, this is achieved with a pulse length $\Delta t_{\text{laser}} \sim 1/\Delta\omega_{\text{laser}}$. The limit $\Delta t_{\text{laser}} \to 0$ would contain frequencies that lead to ionization of the atom.

The probability interpretation has some strange consequences. Registration of the decay photon at time t signals that the atom is now certainly in its de-excited state, which is normally the ground state, $c_i(t) = \delta_{i,00}$. Thus the wavefunction has "collapsed" on the state which has been identified by the measurement. Every energy measurement of a quantum state changes that state, except when it was already in a stationary state.

Equation (1.202) is rarely needed in the context of time-dependent problems, even in the analogous case of the Dirac equation for electrons. In our relativistic treatment of the spinless Zeeman effect, B^2-terms (mentioned in (1.88) and (1.91)) were neglected. This is equivalent to the use of first-order perturbation theory (Sects. 2.8 and 3.4), where the expansion coefficients may be calculated from the unperturbed wave function. The unperturbed atomic states (corresponding to $B = 0$) are degenerate at fixed l, and the simpler orthogonality relations (1.186) are sufficient. The magnetic components Y_l^m are projected out as follows:

$$|\psi/R_{nl}(r)\rangle = \sum_m c_m Y_l^m \equiv \sum_m c_m |lm\rangle; \tag{1.203}$$

$$c_{m'} = \int d\Omega Y_l^{m'*} \sum_m c_m Y_l^m \equiv \langle lm'|\psi/R_{nl}\rangle. \tag{1.204}$$

For $B = 0$, the $|c_m|^2$ may be measured not from the energies of the decay photons (which have converged to a single monochromatic line), but from their circular and linear polarizations.

For the point Coulomb potential $-Ze^2/r$, the explicit eigenvalue equation (1.144) leads again to orthogonality relations of the type (1.184),

$$\int d^3 r_\epsilon \psi_j^*(\boldsymbol{r}_\epsilon)\psi_i(\boldsymbol{r}_\epsilon) = \delta_{ij}, \tag{1.205}$$

where $\boldsymbol{r}_\epsilon$ is merely a complicated notation of the integration variable. In terms of the "physical" variable $\boldsymbol{r}$, one has $\psi_j(\boldsymbol{r}_\epsilon) = \psi_{j,\text{old}}(E_j \alpha_Z \boldsymbol{r})$. As the physical interpretation of ψ requires orthogonality relations, its relativistic

extension is not so obvious. In practice, measurements often result in pulses on an oscilloscope; their interpretation requires detailed knowledge of the apparatus. The integral

$$\int \psi^* A\psi \equiv \langle\psi|A|\psi\rangle \equiv \langle A\rangle_\psi \tag{1.206}$$

is called an expectation value. When A is Hermitian, ψ may be expanded in terms of its eigenfunctions ψ_i as in (1.199), and one finds

$$\langle A_{\rm H}\rangle_\psi = \sum_{j,i} c_j^* c_i a_i \langle j|i\rangle = \sum_i |c_i|^2 a_i. \tag{1.207}$$

This is the ordinary definition of a mean value: each possible outcome a_i of the measurement is weighted with its probability $|c_i|^2$. After each measurement, the state collapses onto the relevant eigenstate with probability one. It may there be verified at any later time, provided A commutes with the operator of the equation of motion, which in the case at hand is the KG-equation. In analogy with classical mechanics, one calls such an A a conserved operator. The measurement of eigenvalues of nonconserved operators is problematic. In particular, the x-component x of the position operator $\boldsymbol{r}$ does not commute with p_x^2 which occurs already in the free KG-equation.

The connection between quantum states and the classical motion of a particle seems simple only for the harmonic oscillator potential. Such a potential supports the "coherent states" below, which oscillate nearly rigidly with $\sin(\omega t)$. For a pendulum, $\omega = \omega_N$ is the classical pendulum frequency (see also Sect. 1.9). However, the most important application is to a nearly classical electromagnetic field (laser field) of a sharp frequency ω. In both cases, the equation $i\hbar\partial_t\psi = H\psi$ applies. For the pendulum, H is given by the right-hand side of (1.159). The laser field Hamiltonian has ξ and $-i\partial_\xi$ replaced by the "quadrature components" (3.34) of the monochromatic electric field. A necessary condition for the existence of solutions with the time dependence $\sin(\omega t)$ is an infinite spectrum of equidistant energy levels. Below, we shall discuss coherent relativistic Landau states, which are equidistant in the variable $k_t^2 = (E^2/c^2 - m^2c^2)/\hbar^2 - k_z^2$ according to (1.170).

Any energy eigenstate $\psi_n(\boldsymbol{r},t) = \psi_n(\boldsymbol{r})e^{-iE_nt/\hbar}$ has $\rho_n = \psi_n^*\psi_n E_n/mc^2 = |\psi_n(\boldsymbol{r})|^2 E_n/mc^2$ (the integrand of (1.197) for $V=0$) time-independent, which justifies the name "stationary". To obtain a time-dependent ρ, ψ must be a superposition of states ψ_i with different energies E_i. Only then are expectation values time dependent, $\langle\boldsymbol{r}\rangle = \langle\boldsymbol{r}\rangle(t)$, $\langle\boldsymbol{p}\rangle = \langle\boldsymbol{p}\rangle(t)$. If the coefficients c_i of this superposition are chosen at random, ρ will fluctuate rather unclassically within the range of the classical pendulum, subject only to the periodicity restriction $\rho(t + 2\pi/\omega) = \rho(t)$. Periodicity occurs of course also for a finite number of equidistant energy levels, for example for an arbitrary superposition of Zeeman sublevels.

At any given time, the coherent state is a shifted stationary state, shifted both in position ξ and velocity $-i\partial_\xi$. Normally the ground state ψ_0 is shifted,

such that the coherent state has a simple Gaussian form. The shift is accomplished by a Taylor expansion, which may be written in exponential form as in (1.275) below. The most general shift is best described by a complex parameter α,

$$\psi_\alpha(\xi, t=0) = D(\alpha)\psi_0(\xi), \quad D(\alpha) = \exp[\alpha(\xi - \partial_\xi)/\sqrt{2} - \alpha^*(\xi + \partial_\xi)/\sqrt{2}]. \tag{1.208}$$

α is the eigenvalue of a non-Hermitian operator,

$$a\psi_\alpha(\xi, t=0) = \alpha\psi_\alpha(\xi, t=0), \quad a = (\xi + \partial_\xi)/\sqrt{2}. \tag{1.209}$$

The complete coherent solution of $i\hbar\partial_t\psi = H\psi$, with H given in (1.159), is

$$\psi_\alpha = \Sigma_{n=0}^{\infty} e^{-i\omega_N t} c_n \psi_n(\xi), \quad c_n = e^{-|\alpha|^2/2}\alpha^n/\sqrt{n!}. \tag{1.210}$$

The $|c_n|^2$ are Poisson distributed, as shown in Fig. 1.6. Turning now to the relativistic Landau orbitals, we define a new variable $\tau(t)$ such that

$$\psi_\alpha(\xi, \tau) = \Sigma_{n=0}^{\infty} e^{-i\omega\tau} c_n \psi_n(\xi) \tag{1.211}$$

corresponds to the equidistance in k_t^2, and not in E. In terms of the Larmor frequency ω_{Larmor} (1.173), we find $\omega = 2\omega_{\text{Larmor}}$. τ is the wave packet's own "coherent time", each component having a slightly different time,

$$t_n = \tau E_n/mc^2. \tag{1.212}$$

Consequently, the wave packet of a relativistic particle in a constant magnetic field disperses in time, but not in its own "coherent time" (the component parallel to the field disperses always). However, this τ is not appropriate for the interaction with light, see (5.158).

Returning to a general operator A with eigenvalues a_i, the eigenvalues of A^2 are a_i^2, and the corresponding expectation value is

$$\langle A^2 \rangle = \sum_i |c_i|^2 a_i^2. \tag{1.213}$$

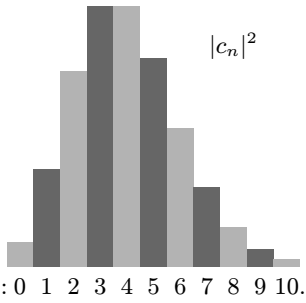

Fig. 1.6. The Poisson distribution for $|\alpha|^2 = 4$

This is the same as $\langle A\rangle^2$ only if the ψ in question is an eigenstate of A. The eigenstate ψ_j has $c_i = \delta_{ij}$. Otherwise, $\langle A^2\rangle - \langle A\rangle^2$ is positive. The distribution of $|c_i|^2$ (for example the $|c_n|^2$ of Fig. 1.6) may be characterized by a few parameters such as the "mean square deviation" and the "skewness". The former is

$$\sigma_A = \Big(\langle A^2\rangle - \langle A\rangle^2\Big)^{1/2} = \Big[\sum_i |c_i|^2 a_i^2 - \Big(\sum_i |c_i|^2 a_i\Big)^2\Big]^{1/2}. \tag{1.214}$$

For the distributions of two operators A ans B, one can prove the "triangle inequality"

$$(\langle A^2\rangle - \langle A\rangle^2)(\langle B^2\rangle - \langle B\rangle^2) \geq |\langle [A,B]\rangle/2|^2. \tag{1.215}$$

Applying this to the operators $A = x$, $B = p_x$, one finds from $[A,B] = i\hbar$ Heisenbergs "uncertainty relation"

$$(\langle x^2\rangle - \langle x\rangle^2)(\langle p_x^2\rangle - \langle p_x\rangle^2) \geq \hbar^2/4. \tag{1.216}$$

This is fascinating from the point of view of classical mechanics, because it implies that one cannot measure position and velocity of a particle at the same time, "$\Delta x \Delta p_x \geq \hbar/2$". In a loose sense, one may also regard the time variable t as a clock operator and put $A = t$, $B = i\hbar\partial_t$. which gives again $[A,B] = i\hbar$. As the eigenvalues of B are the energies E_n, this means that one can measure E with a prescribed precision ΔE only in a sufficiently long time interval Δt, see Sect. 5.4.

Books on nonrelativistic quantum mechanics define not only $\rho(\boldsymbol{r},t) = \psi^*(\boldsymbol{r},t)\psi(\boldsymbol{r},t)$ as the probability to find the electron at position $\boldsymbol{r}$, but also a probability current $\boldsymbol{j}(\boldsymbol{r},t) = -i\hbar(\psi^*\nabla\psi - \psi\nabla\psi^*)$, because this entails a continuity equation, $\partial_t\rho + \nabla\boldsymbol{j} = 0$. With $\langle\boldsymbol{r}\rangle(t) = \int \boldsymbol{r}\rho(t)$, it is then easily shown that $\langle\boldsymbol{r}\rangle(t)$ satisfies the relation of classical mechanics, $md\langle\boldsymbol{r}\rangle/dt = -i\langle\hbar\nabla\rangle = \langle\boldsymbol{p}\rangle(t)$ (Ehrenfest theorem). This is good for a classical motion where it exists, but it is of little use in quantum mechanics. $\psi^*\psi$ need not have a maximum at $\langle\boldsymbol{r}\rangle$, it may even vanish there. In (2.18) below, a continuity equation for the electric charge will be derived from the Maxwell equations. A separate equation for a flow of probability does not exist.

1.9 Operator Methods, Matrices

It was mentioned in Sect. 1.7 that the differential equation (1.158) for the Landau levels is equivalent to that of the harmonic oscillator,

$$E_N\psi = \hbar\omega\hat{H}\psi, \quad \hat{H} = \tfrac{1}{2}(\xi^2 - \partial_\xi^2). \tag{1.217}$$

The harmonic oscillator potential arises from the expansion of the potential $V(x)$ (in one dimension) about its minimum value at $x = x_0$:

$$V(x) \approx V(x_0) + \tfrac{1}{2}(x-x_0)^2\partial_x^2 V(x = x_0), \quad \partial_x^2 V(x = x_0) \equiv m\omega_N^2. \tag{1.218}$$

It is the favorite potential of nonrelativistic quantum mechanics because $V(x \to \infty) = \infty$ kills the dissociation continuum. A physical example is the effective potential between the two atoms of a diatomic molecule, where $x_0 > 0$ is the equilibrium distance and $\hbar\omega_N$ the approximately constant separation between those vibrational levels that are well below the dissociation energy (the mass m in the kinetic energy operator refers the reduced mass of the two atomic nuclei). A more hypothetical example is the quantum treatment of a pendulum.

In general quantum physics, $\hat{H}$ is related to the counting operator

$$N = \hat{H} - \tfrac{1}{2}, \quad N|n\rangle = n|n\rangle, \quad n = 0,\, 1,\, 2\ldots, \tag{1.219}$$

where $|n\rangle$ may represent the wavefunction $\psi_n(\xi)$. The eigenvalues n arose in (1.170) from the condition that the function $H(\xi)$ defined in (1.161) be a polynomial in ξ, the degree of which was called n. In the following, n and $|n\rangle$ are derived more directly, without referring to a wavefunction. One defines a non-Hermitian operator a and a Hermitian N,

$$a = 2^{-1/2}(\xi + \partial_\xi), \quad a^\dagger = 2^{-1/2}(\xi - \partial_\xi), \quad N = a^\dagger a. \tag{1.220}$$

The relation $\hat{H} = N + \frac{1}{2}$ follows from

$$[\partial_\xi, \xi] = 1, \quad [a, a^\dagger] \equiv aa^\dagger - a^\dagger a = 1. \tag{1.221}$$

The complete spectrum (1.219) will now be derived from $N = a^\dagger a$ and $[a.a^\dagger] = 1$.

We first show that if $|n\rangle$ is an eigenstate of N with some unknown eigenvalue n, then $a|n\rangle = |an\rangle$ is also an eigenstate, with eigenvalue $n - 1$:

$$Na = a^\dagger aa = (aa^\dagger - 1)a = a(a^\dagger a - 1) = a(N - 1), \tag{1.222}$$

$$Na|n\rangle = a(N-1)|n\rangle = a(n-1)|n\rangle = (n-1)a|n\rangle; \quad [N, a] = -a. \tag{1.223}$$

Apart from a constant, $|an\rangle$ is thus identical with the state $|n-1\rangle$. Normalizing $\langle n|n\rangle = 1$, we can from (1.223) calculate that constant:

$$\langle an|an\rangle = \langle n|a^\dagger a\ n\rangle = n\langle n|n\rangle = n, \tag{1.224}$$

$$a|n\rangle = n^{1/2}|n-1\rangle. \tag{1.225}$$

(A relative phase between states of different eigenvalues remains always open and is taken to vanish by definition.)

With a more explicit notation for $\langle an|an\rangle$, (1.224) reads $\int |a\psi_n|^2 d\xi = n$, which shows that n cannot be negative. If $n_{\min}$ denotes the smallest such value, what happens with (1.225) for $n = n_{\min}$? As $n_{\min} - 1$ is negative, the state $|n_{\min} - 1\rangle$ would have a negative norm, which is impossible according to the normalization integral. The only way out of this contradiction is

$$a|n_{\min}\rangle = 0, \quad (\xi + \partial_\xi)\psi_0 = 0. \tag{1.226}$$

This equation is satisfied with $\psi_0 = N_0 \exp(-\xi^2/2)$, which is in fact identical with the solution (1.161) for $n = 0$. Obviously, the ground state of the number operator $N = (\xi - \partial_\xi)(\xi + \partial_\xi)/2$ is already determined by its first factor acting on ψ (remember that mathematical formula, like semitic scripts, are read from right to left). Moreover, multiplication of (1.225) by $a^\dagger$ gives the recurrence relation

$$|n\rangle = n^{-1/2} a^\dagger |n-1\rangle, \quad \psi_n = (2n)^{-1/2}(\xi + \partial_\xi)\psi_{n-1}, \tag{1.227}$$

by means of which ψ_n is constucted iteratively, including its normalization factor (1.188). The operators $a^\dagger$ and a are called raising and lowering, or creation and annihilation operators. In Fig. 1.7, they are illustrated by steps on a ladder. They introduce addition and subtraction into quantum mechanics: $0 + 1 = 1$, $1 + 1 = 2$ and so on. Matrix elements of a and $a^\dagger$ between the more complicated Landau states (1.177) are derived in the review of Canuto and Ventura (1977), together with applications in astrophysics. The operator method can be extended to the angular momentum $\boldsymbol{l} = \boldsymbol{r} \times \boldsymbol{p}$. With $\boldsymbol{p} = -i\hbar\boldsymbol{\nabla}$, we set aside the factor $\hbar$ and define $\boldsymbol{l} = \hbar\hat{\boldsymbol{l}}$, $\hat{\boldsymbol{l}} = -i\boldsymbol{r} \times \boldsymbol{\nabla}$:

$$\hat{l}_x = -i(y\partial_z - z\partial_y), \quad \hat{l}_y = -i(z\partial_x - x\partial_z), \quad \hat{l}_z = -i(x\partial_y - y\partial_x), \tag{1.228}$$

$$[\hat{l}_x, \hat{l}_y] = i\hat{l}_z, \quad [\hat{l}_y, \hat{l}_z] = i\hat{l}_x, \quad [\hat{l}_z, \hat{l}_x] = i\hat{l}_y. \tag{1.229}$$

The second and third expressions follow from the first ones by the cyclic permutations $xyz \to yzx \to zxy$. The non-commutativity of $\boldsymbol{l}$ prevents common eigenstates $|l_x, l_y, l_z\rangle$, except for $l_x = l_y = l_z = 0$, $Y_0^0 = (4\pi)^{-1/2}$. Nevertheless, the operator $\hat{\boldsymbol{l}}^2$ does commute with each component $\hat{l}_i$; its eigenvalues $l(l+1)$ have already been mentioned in (1.22). To construct the eigenstates

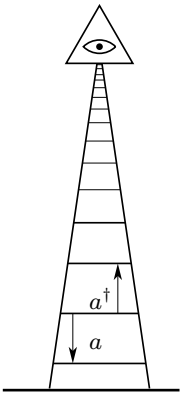

Fig. 1.7. Counting ladder

of $\hat{\boldsymbol{l}}^2$ and $\hat{l}_z$, we introduce operators $\hat{l}_\pm$ which change the eigenvalues of $\hat{l}_z$ by one unit:

$$\hat{l}_- = \hat{l}_x - i\hat{l}_y, \quad \hat{l}_+ = \hat{l}_-^\dagger = \hat{l}_x + i\hat{l}_y. \tag{1.230}$$

The eigenvalues of $\hat{l}_x$ would be changed by $\hat{l}_z \pm i\hat{l}_x$, but one prefers eigenstates of $\hat{l}_z$, in view of their simplicity (1.17) in spherical coordinates.

Insertion of the commutators (1.229) into (1.230) produces

$$[\hat{l}_z, \hat{l}_-] = -\hat{l}_-, \quad [\hat{l}_z, \hat{l}_+] = \hat{l}_+. \tag{1.231}$$

The first relation is reached from (1.222) with the substitutions $N \to \hat{l}_z$, $a \to \hat{l}_-$. To calculate the eigenvalues m of $\hat{l}_z$ by operator methods, we may translate (1.223) and (1.224) into

$$\hat{l}_z\hat{l}_-|m\rangle = (m-1)\hat{l}_-|m\rangle, \quad \langle\hat{l}_-m|\hat{l}_-m\rangle = \langle m|\hat{l}_+\hat{l}_-m\rangle \equiv n_-. \tag{1.232}$$

But whereas the eigenvalue n of $a^\dagger a$ was known in (1.224), the state $|\hat{l}_+\hat{l}_-m\rangle$ is as yet unknown. To begin with, we note that (1.231) implies that $\hat{l}_+\hat{l}_-$ commutes with $\hat{l}_z$:

$$\hat{l}_z\hat{l}_+\hat{l}_- = (\hat{l}_+ + \hat{l}_+\hat{l}_z)\hat{l}_- = \hat{l}_+\hat{l}_- + \hat{l}_+(\hat{l}_-\hat{l}_z - \hat{l}_-); \quad [\hat{l}_z, \hat{l}_+\hat{l}_-] = 0. \tag{1.233}$$

This ensures the existence of common eigenstates of $\hat{l}_z$ and $\hat{l}_+\hat{l}_-$:

$$\hat{l}_+\hat{l}_-|n_-, m\rangle = n_-|n_-, m\rangle, \quad \hat{l}_z|n_-, m\rangle = m|n_-, m\rangle. \tag{1.234}$$

And as the norm n_- of $|\hat{l}_-m\rangle$ (1.232) must not be negative, there is again a minimum of n_-, namely $n_{-\,\min} = 0$. To proceed, we must now isolate the m-dependence of n_-. The explicit expression

$$\hat{l}_+\hat{l}_- = (\hat{l}_x + i\hat{l}_y)(\hat{l}_x - i\hat{l}_y) = \hat{l}_x^2 + \hat{l}_y^2 + \hat{l}_z = \hat{\boldsymbol{l}}^2 - \hat{l}_z^2 + \hat{l}_z \tag{1.235}$$

shows that $\hat{l}_z$ commutes also with $\hat{\boldsymbol{l}}^2$. For the eigenstates (1.234), we have

$$n_- = \lambda - m^2 + m, \quad \hat{\boldsymbol{l}}^2|n_-, m\rangle = \lambda|n_-, m\rangle. \tag{1.236}$$

The claim is now that the eigenvalues λ of $\hat{\boldsymbol{l}}^2$ are independent of the eigenvalues m of $\hat{l}_z$. This is so because $\boldsymbol{l}^2$ contains l_x^2, l_y^2 and l_z^2 in a symmetrical way. Although none of the components commmute according to (1.229), they all commute with $\boldsymbol{l}^2$. Thus our choice of the basis of eigenfunctions of l_z is immaterial form the point of view of $\boldsymbol{l}^2$. In most textbooks, this symmetry is mentioned at the very beginning, and the fact that λ is independent of the eigenvalues of l_z is taken for granted. The relation $n_- = 0$ is then translated according to (1.236) into

$$m_{\min}(m_{\min} - 1) = \lambda. \tag{1.237}$$

The main deviation from the harmonic oscillator arises from the commutator

$$[\hat{l}_-, \hat{l}_+] = -2\hat{l}_z, \tag{1.238}$$

instead of the HO-relation $[a, a^\dagger] = +1$. Clearly, $|n_-, m\rangle$ is also an eigenstate of $\hat{l}_-\hat{l}_+$:

$$\hat{l}_-\hat{l}_+|n_-, m\rangle = n_+|n_-, m\rangle, \quad n_+ = n_- - 2m = \lambda - m(m+1). \tag{1.239}$$

Whereas $\hat{l}_-$ lowers the eigenvalues of $\hat{l}_z$, $\hat{l}_+$ lowers those of $-l_z$. Consequently, n_+ must vanish at the largest value of m,

$$m_{\max}(m_{\max}+1) = \lambda. \tag{1.240}$$

In combination with (1.236) this implies $m_{\min}(m_{\min}-1) = m_{\max}(m_{\max}+1)$, and as by definition $m_{\max} > m_{\min}$, this quadratic equation has only one solution,

$$m_{\max} = -m_{\min} \equiv l. \tag{1.241}$$

Finally, as m is lowered and raised in steps of 1, $m_{\max} - m_{\min} = 2l$ must be an integer, and insertion of (1.237) or (1.240) gives

$$\lambda = l(l+1), \quad n_- = \lambda - m(m-1) = (l+m)(l-m-1). \tag{1.242}$$

This is in agreement with the values of l and m quoted in (1.22), but it admits additional solutions in which l is half-integer. Such solutions are excluded in the KG-equation, but they will be needed in Sect. 2.5. There, $\boldsymbol{r} \times \boldsymbol{p}$ is not conserved (it does not commute with the Dirac operator, even if the potential is spherically symmetric). It is replaced by another conserved vector operator $\boldsymbol{j}$ with the same commutation relations.

The entity of eigenvalues of an operator is called its "spectrum". This definition may be used also in the case of implicit eigenvalue equations such

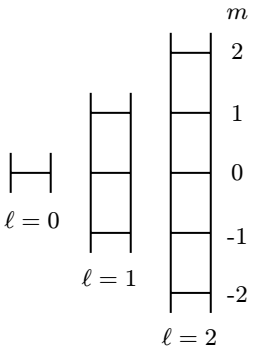

Fig. 1.8. The first three orbital angular momentum ladders

as the KG-equation in the presence of a Coulomb potential. The resulting E-spectrum has a discrete part (the bound states) and a continuous part (the scattering states). On the other hand, the operators N and $\hat{\boldsymbol{l}}$ have only discrete spectra. Their eigenstates are conveniently written as unit vectors, the operators as matrices. In the following, the eigenvalues are arranged in increasing order from bottom to top:

$$N = \begin{pmatrix} \ddots & & & & \\ & 3 & 0 & 0 & 0 \\ & 0 & 2 & 0 & 0 \\ & 0 & 0 & 1 & 0 \\ & 0 & 0 & 0 & 0 \end{pmatrix}, \quad |0\rangle = \begin{pmatrix} \vdots \\ 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}, \quad |1\rangle = \begin{pmatrix} \vdots \\ 0 \\ 0 \\ 1 \\ 0 \end{pmatrix}, \quad |2\rangle = \begin{pmatrix} \vdots \\ 0 \\ 1 \\ 0 \\ 0 \end{pmatrix} \tag{1.243}$$

For the following operators, the dots are omitted for brevity:

$$a = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 3^{\frac{1}{2}} & 0 & 0 & 0 \\ 0 & 2^{\frac{1}{2}} & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}, \; a^{\dagger} = \begin{pmatrix} 0 & 3^{\frac{1}{2}} & 0 & 0 \\ 0 & 0 & 2^{\frac{1}{2}} & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \end{pmatrix}, \; \xi = 2^{-\frac{1}{2}} \begin{pmatrix} 0 & 3^{\frac{1}{2}} & 0 & 0 \\ 3^{\frac{1}{2}} & 0 & 2^{\frac{1}{2}} & 0 \\ 0 & 2^{\frac{1}{2}} & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix} \tag{1.244}$$

One may now verify algebraic relationships such as (1.219)–(1.227) by matrix multiplication. The connection between these matrices and the differential operators of Sect. 1.8 follows from the scalar product (1.200) of two arbitrary vectors $|\psi\rangle = \Sigma_i \psi_i c_i$ and $\langle\psi'| = \Sigma_i \psi_i^* c_i'^*$. With $|\psi\rangle$ in the form of a column vector, $\langle\psi'|$ is a row vector, such that the scalar product is a (complex) number:

$$\langle\psi'| = (\ldots, c_2'^*, c_1'^*, c_0'^*), \quad |\psi\rangle = \begin{pmatrix} \vdots \\ c_2 \\ c_1 \\ c_0 \end{pmatrix}, \quad \langle\psi'|\psi\rangle = \sum_i c_i'^* c_i. \tag{1.245}$$

This notation is not quite conventional. As a page is written from top to bottom, one frequently begins with the state of lowest eigenvalue and then puts the dots further down when one gets tired or runs out of space. In a level scheme, on the other hand, the ground state appears always at the bottom. The excited states which appear further up are related to raising operators, at least at some stage of the formalism. Thus the notation chosen here avoids redefinitions in other sections.

For an arbitrary operator B, $B|\psi\rangle = |B\psi\rangle$ is again written as a column vector, namely as $\Sigma_i B|i\rangle c_i$ in terms of the eigenstates of N. Its j-component is obtained by multiplication with the unit vector $\langle j|$, giving $|B\psi\rangle_j = \langle j|\Sigma_i B|i\rangle c_i$. The matrix elements of B are now defined as

$$B_{ji} \equiv \langle j|B|i\rangle = \int \psi_j^* B \psi_i, \tag{1.246}$$

because this entails the rule for multiplication by a matrix B:

$$|B\psi\rangle_j = \Sigma_i B_{ji} c_i. \tag{1.247}$$

The multiplication rule for two matrices is more difficult to derive:

$$(AB)_{ji} = \langle j|AB|i\rangle = \Sigma_n \langle j|A|n\rangle\langle n|B|i\rangle. \tag{1.248}$$

The Σ_n extends over a complete set of eigenstates of a Hermitian operator. Unless stated differently, this operator is the same as in the definition of $|i\rangle$ and $\langle j|$, such that for example $\langle j|1|n\rangle = \delta_{nj}$. In our example, this is the number operator N. To derive (1.248), we must first derive a property of the "number wave function" $\psi_i(\xi)$ which is called "completeness". It follows from the fact (not proven here) that any square integrable but otherwise arbitrary function $\psi(\xi)$ can be expanded in terms of the ψ_n, $\psi(\xi) = \Sigma_n c_n \psi_n(\xi)$ (examples will follow in Sect. 4.2). A coefficient c_n of ψ is obtained by means of the orthogonality relations, which in the present example appear in the "nonrelativistic" form (1.184):

$$c_n = \int \psi_n^*(\xi')\psi(\xi')d\xi', \quad \psi(\xi) = \Sigma_n \int \psi_n^*(\xi')\psi(\xi')d\xi'\psi_n(\xi). \tag{1.249}$$

The last relation expresses the arbitrary function $\psi(\xi)$ in terms of $\psi(\xi')$ at different positions ξ'. This is only possible if the integrand is a delta function:

$$\Sigma_n \psi_n^*(\xi')\psi_n(\xi) = \delta(\xi - \xi'). \tag{1.250}$$

This is the desired completeness relation, also called closure. Turning now to (1.248), one may define $C = AB$, where $\langle j|C|i\rangle$ contains only a single integral, $\int d\xi$. It is converted into a double integral by means of the delta function, $\int d\xi = \int\int d\xi d\xi' \delta(\xi - \xi')$. The delta function is then replaced by the sum (1.250), which in Dirac's ket and bra notation reads

$$\Sigma_n |n\rangle\langle n| = 1, \tag{1.251}$$

or even shorter $|\rangle\langle| = 1$. The sum is inserted between A and B in (1.248).

In the case of the attractive Coulomb potential, the sum over the principal quantum number n must be extended to include the integral over the continuum states (the unbound Coulomb wave functions of Sect. 1.10), even when both indices $_j$ and $_i$ of (1.248) refer to bound states. This strongly reduces the use of the present method for matrix products. A more appropriate tool is the Coulomb Greens function of Appendix B.

In the relativistic case, the KG equation and also the Dirac equation have additional continuum solutions at negative E, which are also required in the completeness relation. On the other hand, these states decouple in many relativistic systems. For the number operator at hand, the relevant eigenvalue for the Landau levels is $\hbar^2 k^2 = E^2/c^2 - m^2 c^2$, and one merely needs a complete set of eigenvalues of $\hbar^2 k^2$. More generally, if $|i\rangle$ and $|j\rangle$ in

(1.248) are both positive-energy states and if either $\langle j|A|n\rangle$ or $\langle n|B|i\rangle$ vanish for all negative-energy states $|n\rangle$, then those states may simply be omitted. For example, this is the case for the angular momentum matrices $\boldsymbol{l}$, which commute with the KG-operator in the pure central Coulomb potential and thus do not change E.

The completeness relation for plane waves (in one dimension of length L) requires the normalized version of e^{ikx},

$$\hat{\psi}_k(x) = L^{-1/2}e^{ikx}, \quad L^{-1}\Sigma_n e^{ik_n x}e^{-ik_n x'} = \delta(x-x'), \tag{1.252}$$

with $k_n = 2\pi n/L$. The three-dimensional normalized plane wave is

$$\psi_{\boldsymbol{k}}(\boldsymbol{r}) = e^{i\boldsymbol{k}\boldsymbol{r}}V^{-1/2}, \quad V = L_x L_y L_z, \tag{1.253}$$

with V = normalization volume. As $L \to \infty$, the k_n-values become dense, and the sum approaches the integral over $dk = 2\pi dn/L$. This leads to the famous formula for the delta function,

$$\int_{-\infty}^{\infty} dk\, e^{ik(x-x')} = 2\pi\delta(x-x'). \tag{1.254}$$

We conclude with a few comments on Hermitian adjoint operators and matrices. Successive application of the definition (1.180) gives

$$\int \psi'^* A^{++}\psi = \int \psi A^{+*}\psi'^* = \int \psi'^* A^{**}\psi = \int \psi'^* A\psi, \tag{1.255}$$

as double complex conjugation gives the original operator. Another useful extension of (1.180) is obtained by replacing ψ by $B^+\psi$:

$$\int \psi'^* A^+ B^+\psi = \int (B^+\psi)A^*\psi'^* = \int \psi B^* A^*\psi'^* = \int \psi (BA)^*\psi'^*, \tag{1.256}$$

which shows that A^+B^+ is the Hermitian conjugate of BA,

$$(BA)^+ = A^+B^+. \tag{1.257}$$

As a special case, take $B = A^+$:

$$(A^+A)^+ = A^+A. \tag{1.258}$$

Thus already the mere definition of the number operator in terms of an arbitrary operator a guarantees that all its eigenvalues are real. The same remark applies to $\hat{l}_+\hat{l}_-$.

Turning now to matrices, the Hermitian conjugate of a matrix is the complex conjugate of its transposed,

$$B^+ = B^*_{tr}, \quad (B^+)_{ji} = (B^*)_{ij}. \tag{1.259}$$

In view of the definition (1.246), this is also the matrix representing the Hermitian adjoint operator. From (1.259), one also verifies $B^{++} = B^{**}_{trtr} = B$ and

$(BA)^+ = A^+B^+$. The elements of the unit matrix are called δ_{ij}; a diagonal matrix B_d has nonzero elements only in the diagonal positions $i = j$. The diagonal elements B_{ii} will be called b_i:

$$(B_d)_{ij} = b_i\delta_{ij}. \tag{1.260}$$

Vectors of the type $|n\rangle$ in (1.243) are eigenvectors of B, in the sense that matrix multiplication by B reproduces the vector up to a factor b_n, which is called the eigenvalue. Today, linear operators and matrices are synonymous expressions. For example, finding the eigenvalues of an operator is called diagonalization of the operator. The word "state" comprises a wave function and its representation by a vector. Eigenstates are eigenfunctions of an operator or eigenvectors of a matrix, and so on. The space of square integrable complex functions is called a Hilbert space. It is a linear vector space, which expresses the superposition principle: Linear combinations of states are again possible states. As a rule, states are taken to be normalized.

The elements $\hat{l}_{ij}$ of angular momentum matrices $\hat{\boldsymbol{l}}$ are characterized by index pairs, $i = (l, m)$, $j = (l', m')$, and $\hat{\boldsymbol{l}}^2$ is diagonal in both: $(\hat{\boldsymbol{l}}^2)_{l'm',lm} = l(l+1)\delta_{ll'}\delta_{mm'}$. All three matrices $\hat{\boldsymbol{l}}$ are diagonal in l:

$$(\hat{\boldsymbol{l}})_{l'm',lm} = \delta_{ll'}(\hat{\boldsymbol{l}}^{(l)})_{m'm}. \tag{1.261}$$

The submatrices $\hat{\boldsymbol{l}}^{(l)}$ have finite dimensions $(2l+1)(2l+1)$. For $l = 0$ one has $\hat{\boldsymbol{l}} = 0$ ($\hat{l}_z = \hat{l}_- = \hat{l}_+ = 0$), for $l = 1$ and $l = 2$

$$\hat{l}_z{}^{(1)} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}, \quad \hat{l}_-^{(1)} = \begin{pmatrix} 0 & 0 & 0 \\ 2^{\frac{1}{2}} & 0 & 0 \\ 0 & 2^{\frac{1}{2}} & 0 \end{pmatrix}, \quad \hat{l}_+^{(1)} = \begin{pmatrix} 0 & 2^{\frac{1}{2}} & 0 \\ 0 & 0 & 2^{\frac{1}{2}} \\ 0 & 0 & 0 \end{pmatrix} \tag{1.262}$$

$$\hat{l}_z{}^{(2)} = \begin{pmatrix} 2 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & -2 \end{pmatrix}, \quad \hat{l}_-^{(2)} = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 \\ 4^{\frac{1}{2}} & 0 & 0 & 0 & 0 \\ 0 & 6^{\frac{1}{2}} & 0 & 0 & 0 \\ 0 & 0 & 6^{\frac{1}{2}} & 0 & 0 \\ 0 & 0 & 0 & 4^{\frac{1}{2}} & 0 \end{pmatrix}. \tag{1.263}$$

Not shown is $\hat{l}_+^{(2)}$, which is the Hermitian adjoint of $\hat{l}_-^{(2)}$. Unit matrices may be written as 1, such that for example (1.235) reads

$$\hat{l}_+^{(l)}\hat{l}_-^{(l)} = l(l+1) - \hat{l}_z^2 + \hat{l}_z. \tag{1.264}$$

This convention becomes mandatory as more and more degrees of freedom are included, such as electronic spin (Sect. 2.3) and nuclear spin (Sects. 4.3, 4.4, 4.6). Without it, an operator A would have to be written as $A\otimes 1_s\otimes 1_t\otimes 1_u\ldots$, to indicate all the spaces s, t, $u\ldots$ in which A does not act.

It was mentioned in Sect. 1.8 after (1.202) that Hermitian operators have orthonormal sets of eigenstates $|i\rangle = \psi_i$ which can be used as basic unit vectors in a Hilbert space. An actual physical state ψ is specified by its components c_i along these vectors. Occasionally, one has to exchange this "coordinate system" with some other set of orthogonal unit vectors,

$$\psi = \Sigma_i c_i \psi_i = \Sigma_m c_m \psi'_m. \tag{1.265}$$

To avoid the infinitely many components of general Hilbert space vectors, consider an angular wave function $\psi(\theta, \phi)$ which happens to be an eigenfunction of $\hat{\boldsymbol{l}}^2$, such that it has only $2l + 1$ nonvanishing components. Normally, one would take the spherical harmonics Y_l^m as basic unit vectors in this case, $\psi_i = Y_l^i$. In vector notation $|i\rangle_z$ these are for $l = 1$

$$|+1\rangle_z = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \quad |0\rangle_z = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}, \quad |-1\rangle_z = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}, \tag{1.266}$$

where the index $_z$ is a reminder that these are eigenfunctions of $\hat{l}_z$. Suppose now that one wants to use the eigenvectors $\psi'_m = |m\rangle_x$ of $\hat{l}_x = (\hat{l}_- + \hat{l}_+)/2$ as an alternative set of coordinates. For $l = 1$,

$$\hat{l}_x^{(1)} = \frac{1}{\sqrt{2}} \begin{pmatrix} 0\,1\,0 \\ 1\,0\,1 \\ 0\,1\,0 \end{pmatrix}, \quad |\pm\rangle_x = \frac{1}{2} \begin{pmatrix} 1 \\ \pm 2^{1/2} \\ 1 \end{pmatrix}, \quad |0\rangle_x = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \\ 1 \end{pmatrix}. \tag{1.267}$$

They are linear combinations of the $Y_1^i(\theta, \phi)$,

$$\psi'_m = \Sigma_i U_{mi} \psi_i, \quad \psi'^*_n = \Sigma_j U^*_{nj} \psi^*_j. \tag{1.268}$$

The fact that both the ψ_i and the ψ'_m form orthonormal sets,

$$\langle j|i\rangle = \delta_{ij}, \quad \langle n|m\rangle = \delta_{nm}, \tag{1.269}$$

imposes a condition on the coefficients U_{mi}:

$$\delta_{nm} = \Sigma_j U^*_{nj} \langle j|\Sigma_i U_{mi}|i\rangle = \Sigma_{j,i} U^*_{nj} U_{mi} \delta_{ji} = \Sigma_j U^*_{nj} U_{mj}. \tag{1.270}$$

Taking the U_{mj} as elements of a matrix U, with $U^\dagger \equiv U^+ = U^*_{tr}$ (in components $U^*_{nj} = (U^\dagger)_{jn}$, see (1.259)), the matrix form of (1.270) becomes

$$1 = UU^\dagger. \tag{1.271}$$

Such a matrix is called unitary. Its Hermitian adjoint equals its inverse, $U^\dagger = U^{-1}$. Thus a change of basis in Hilbert space is accomplished by a unitary transformation. In our example it is a 3×3-matrix, the coefficients of which are just the elements of the state vectors (1.266). It is called $D_y^{(1)}(\pi/2)$,

as it has the meaning of rotating the cartesian coordinates by $\pi/2$ about the y-axis (which brings the x-axis into the position of the old z-axis). For $l = 2$, the corresponding matrix U is 5×5-dimensional: it is called $D^{(2)}(\pi/2)$.

Unitary transformations are used in many places, for example for a change of basis of the Landau levels. However, they are used most extensively in connection with rotations. In the following, we consider a particularly simple rotation, namely one by an angle α about the z-axis. Here each Y_l^m is transformed into itself, only its phase is changed: with $\phi' = \phi - \alpha$,

$$e^{im\phi'} = e^{im(\phi-\alpha)} = e^{-im\alpha} e^{im\phi}. \tag{1.272}$$

The resulting transformation matrix $D_z(\alpha)$ is diagonal,

$$(D_z(\alpha))_{mn} = \delta_{mn} e^{-im\alpha}, \quad D_z(\alpha) = e^{-i\hat{l}_z \alpha}. \tag{1.273}$$

The exponentiation of a general matrix M is defined by the converging series

$$e^M = 1 + M + M^2/2! + \ldots \tag{1.274}$$

In our example, $\hat{l}_z = i\partial_\phi$ in configuration space shows that (1.273) is nothing but the operatorized form of the Taylor expansion,

$$e^{-\alpha\partial_\phi} f(\phi) = f(\phi) - \alpha\partial_\phi f(\phi) + \frac{\alpha^2}{2!}\partial_\phi^2 f(\phi) \ldots = f(\phi - \alpha). \tag{1.275}$$

One says that the Hermitian $\hat{l}_z = -i\partial_\phi$ "generates" rotations about the z-axis. If fact, any Hermitian matrix H generates a unitary matrix U, as

$$U = e^{iH}, \quad U^\dagger = (e^{iH})^\dagger = e^{-iH^\dagger} = e^{-iH} = U^{-1}. \tag{1.276}$$

The simplest unitary matrix is a multiple of the unit matrix, $U_0 = e^{-i\alpha_0}$. For a given ψ in (1.265), it results in the multiplication of all expansion coefficients by $e^{i\alpha_0}$. But as an overall phase of all physical states remains unobservable, this change of expansion coefficients may be eliminated by multiplying ψ by $e^{-i\alpha_0}$. For definiteness, one sets $\alpha_0 \equiv 0$. This entails a restriction on the allowed matrices H in (1.276), namely $\operatorname{tr} H = 0$, for the following reason: Remembering $\det(AB) = (\det A)(\det B)$, $1 = UU^\dagger$ implies $\det(UU^\dagger) = |\det U|^2 = 1$ or $\det U = e^{-i\alpha_U}$ (the case $U = e^{-i\alpha_0}$ would have $\alpha_U = \alpha_0 \dim(U)$, where $\dim(U)$ is the number of diagonal elements of U). Therefore, any unitary matrix may be decomposed into a phase factor and a "special" or "unimodular" matrix SU of unit determinant:

$$U = e^{-i\alpha_U} SU, \quad \det SU = 1. \tag{1.277}$$

When SU is expressed as e^{iH}, one gets $\det SU = e^{i\operatorname{tr} H}$, and consequently H must be traceless (remember also that a unit matrix has $\det 1 = 1$, but $\operatorname{tr} 1 = \dim 1$).

1.10 Scattering and Phase Shifts

The scattering of particles on atoms may be formulated by a wave equation with an effective potential V_{eff}. For neutral atoms, V_{eff} is typically confined to a region $r < r_0$, and the asymptotic wave function ψ_{as} satisfies the free equation (1.75), $-\hbar^2\nabla^2\psi_{\text{as}} = \hbar^2 k^2 \psi_{\text{as}}$. For scattering on ions, the wave at $r > r_0$ suffers an additional Coulomb distortion, which will be mentioned below. Spin is again neglected.

Whereas the real scattering of a single particle is a time-dependent process, the idealized experiment contains a beam of particles of fixed momentum $\hbar\boldsymbol{k}$ (the direction of which is taken as the z-axis), plus a more complicated outward wave which is produced by the scatterer:

$$\psi_{\text{as}} = e^{ikru} + r^{-1} f_k(u) e^{ikr}, \quad u = \cos\theta, \quad d\sigma/d\Omega = |f|^2, \quad (d\Omega = dud\phi). \tag{1.278}$$

Here f_k is the scattering amplitude, and $d\sigma/d\Omega$ is the differential cross section for elastic scattering ($k' = k$) into the solid angle $u = u_k$, $\phi = \phi_k$. Superficially, the scatterer appears as a source, but $f_k(u)$ is negative in the forward direction $u = 1$ ($\theta = 0$), such that the total flux is conserved. The limitations on $f_k(u)$ follow from a partial-wave decomposition of (1.278),

$$\psi_{\text{as}} = \sum_{l=0}^{\infty} Y_l^0(u) R_l(kr) = (2\pi)^{-1/2} \sum_{l=0}^{\infty} (l + \tfrac{1}{2})^{1/2} P_l(u) R_l(kr). \tag{1.279}$$

After division by k^2, the radial equation becomes

$$[1 + (\partial_{kr} + 1/kr)^2 - l(l+1)/k^2 r^2] R_l(kr) = 0. \tag{1.280}$$

It is identical with (1.98) for $V = 0$, but the constant 1 was omitted in (1.102). Defining a dimensionless variable $kr = \rho$, the general solution of (1.280) is

$$R_l(\rho) = c_{l+}(k) j_l(\rho) + c_{l-}(k) n_l(\rho), \tag{1.281}$$

where j_l and n_l are the spherical Bessel and Neumann functions: j_l is regular at $\rho = 0$, $j_l(\rho \to 0) = \rho^l$, while $n_l(\rho \to 0) = \rho^{-l-1}$. For $l = 0$ and 1, one verifies

$$j_0 = \rho^{-1} \sin\rho, \quad n_0 = \rho^{-1} \cos\rho, \tag{1.282}$$

$$j_1 = \rho^{-2}(\sin\rho - \rho\cos\rho), \quad n_1 = \rho^{-2}(\cos\rho - \rho\sin\rho). \tag{1.283}$$

For $l > 0$, both j_l and n_l obey the recurrence relation

$$j_{l+1} = \rho^{-1}(2l+1) j_l - j_{l-1}. \tag{1.284}$$

The incident wave $e^{i\rho u}$ of (1.278) is decomposed into partial waves as follows:

$$e^{i\rho u} = \Sigma_l a_l j_l(\rho) P_l(u), \quad a_l = i^l(2l+1). \tag{1.285}$$

The values of a_l will be derived below.

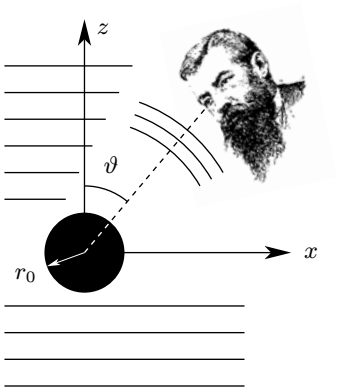

Fig. 1.9. Outgoing spherical waves

If (1.280) would apply at all r, then the normalizibility of ψ would require $c_{l-} = 0$ as in (1.103), and there would be no scattering. But as $\psi_{\rm as}$ is restricted to the region $r > r_0$, one may have $c_{l-} \neq 0$. Below the threshold energy for ionizing collisions, c_{l-}/c_{l+} remains real. The otherwise unknown $V_{\rm eff}$ is then real, and the complete KG-equation is also real. Another possible solution is then

$$R_l^*(kr) = c_{l+}^*(j_l + n_l c_{l-}/c_{l+}), \quad c_{l-}/c_{l+} \equiv -\tan\delta_l, \tag{1.286}$$

and since $\psi_{\rm as}$ is the unique continuation of the unknown inside wave ψ, R_l^* can differ from R_l at most by a constant phase, and $\tan\delta_l$ must be real. From the asymptotic forms of j_l and n_l,

$$j_l(\rho \to \infty) = \rho^{-1}\sin(\rho - l\pi/2) = (-i)^l(2i\rho)^{-1}(e^{i\rho} - (-1)^l e^{-i\rho}), \tag{1.287}$$

$$n_l(\rho \to \infty) = -\rho^{-1}\cos(\rho - l\pi/2) = (-i)^l(2\rho)^{-1}(e^{i\rho} + (-1)^l e^{-i\rho}), \tag{1.288}$$

one finds that δ_l causes a "phase shift" in R_l: With $\sin(\alpha+\delta) = \sin\alpha\sin\delta + \cos\alpha\cos\delta$,

$$R_l(\rho \to \infty) = c_{l+}(\rho\cos\delta_l)^{-1}\sin(\rho - l\pi/2 + \delta_l). \tag{1.289}$$

To calculate a coefficient a_l in the sum (1.285), it is projected out by means of the orthogonality relations (1.186) for the $Y_l^m(\theta,\phi)$, which are reduced to those of the Legendre polynomials by the substitution (1.279):

$$\int_{-1}^{1} du P_{l'}(u)P_l(u) = (l+\tfrac{1}{2})^{-1}\delta_{ll'}: \tag{1.290}$$

$$(l+\tfrac{1}{2})^{-1}a_l j_l = \int du P_l e^{i\rho u} = (i\rho)^{-1}[e^{i\rho u}P_l(u)|_{-1}^{1} - \int e^{i\rho u}P_l' du]. \tag{1.291}$$

For $\rho \to \infty$, the last integral vanishes relative to the first one, as a second partial integration produces a second factor $(i\rho)^{-1}$. Using also $P_l(1) = 1$, $P_l(-1) = (-1)^l$ and the asymptotic form (1.287), one has

$$(l + \tfrac{1}{2})^{-1} a_l (-i)^l (2i\rho)^{-1} [e^{i\rho} - (-1)^l e^{-i\rho}] = (i\rho)^{-1} [e^{i\rho} - (-1)^l e^{-i\rho}], \quad (1.292)$$

from which the value (1.285) follows. The form (1.292) shows also that the plane wave $e^{i\rho u}$ contains both outgoing $(e^{i\rho} P_l / i\rho)$ and incoming $(e^{-i\rho} P_l / i\rho)$ spherical waves. The scattered wave in (1.278) is purely outgoing, of course. The relation between $f_k(u)$ and δ_l follows after a partial wave decomposition of $f_k(u)$:

$$f_k(u) = \sum_{l=0}^{\infty} (2l + 1) f_l(k) P_l(u). \quad (1.293)$$

The total coefficient of $e^{ikr} P_l$ in (1.278) is thus $(l+\frac{1}{2})(i\rho)^{-1}(1+2ikf_l)$ according to (1.292). This must equal the form (1.289) for $R_l(\rho \to \infty)$. Rewriting

$$\sin(\rho - l\pi/2 + \delta_l) = (2i)^{-1} e^{-i\delta_l} [e^{i\rho} e^{2i\delta_l} - (-1)^l e^{-i\rho}] \quad (1.294)$$

(δ_l is called the phase shift), agreement is reached for

$$e^{2i\delta_l} = 1 + 2ikf_l, \quad f_l = k^{-1} \sin \delta_l e^{i\delta_l} = (2ik)^{-1} (e^{2i\delta_l} - 1). \quad (1.295)$$

The differential cross section becomes

$$d\sigma / d\Omega = |f_k|^2 = \Sigma_{l,l'} (2l + 1)(2l' + 1) P_l P_{l'} f_l f_{l'}^*. \quad (1.296)$$

The total cross section $\sigma = \int d\Omega d\sigma / d\Omega$ is simplified by the orthogonality relation (1.290),

$$\sigma = 4\pi \Sigma_l (2l + 1) |f_l|^2 = 4\pi / k^2 \Sigma_l (2l + 1) \sin^2 \delta_l. \quad (1.297)$$

The notation $d\Omega = du d\phi$ is common but not very adequate for the scattering of spinless particles on a central potential where $d\sigma$ is independent of ϕ, such that in practice $d\Omega = 2\pi du$.

So much about the scattering on neutral atoms. For the scattering on ions of total charge Z, the Coulomb potential cannot be dropped outside the ion radius r_0. The corresponding R_l was called $e^{ikr} v_l$ in (1.100), and the regular solution was $v_l = r^{l_\alpha} w = r^{l_\alpha} F(a, 2l_\alpha + 2, -2ikr)$, with a and η given in (1.140). Including a normalization constant N_l,

$$R_l = N_l (2\rho)^{l_\alpha} e^{ikr} F(l_\alpha + 1 + i\eta, 2l_\alpha + 2, -2ikr). \quad (1.298)$$

This is the generalization of j_l. The generalization of n_l is the irregular Coulomb function G_l. The wave function for the scattering by an ion has an asymptotic form similar to (1.289),

$$R_l(\rho \to \infty) = c_{l+} \rho^{-1} \sin[\rho - \eta \ln(2\rho) - l\pi/2 + \sigma_l], \quad (1.299)$$

where σ_l is a phase shift. For the scattering by a bare nucleus ($r_o = 0$), σ_l can be calculated explicitly:

$$\sigma_l = arg\Gamma(l_\alpha + 1 + i\eta) - \pi(l_\alpha - l)/2. \tag{1.300}$$

This is the (relativistic) Coulomb phase shift. The corresponding partial-wave Coulomb scattering amplitude f_l is again given by (1.293) and (1.295),

$$f_k(u) = (2ik)^{-1} \sum_{l=0}^{\infty} (2l+1) P_l(u)(e^{2i\sigma_l} - 1). \tag{1.301}$$

For nuclear reaction rates, one needs a normalized incident particle flux, corresponding to $c_{l+} = 1$ in (1.299) (see also the discussion in Sect. 4.2). This determines the original N_l of (1.298) as

$$N_l = e^{-\pi\eta/2} |\Gamma(l_\alpha + 1 + i\eta)| / \Gamma(2l_\alpha + 2). \tag{1.302}$$

The range r_0 of most nuclear reactions is so short that one may set $e^{ikr} = 1$ and $F = 1$. The factor $(2\rho)^{l_\alpha}$ practically excludes reactions with $l > 0$. In the approximation $l_\alpha = 0$, one finds

$$N_0^2 = 2\pi\eta(e^{2\pi\eta} - 1)^{-1}. \tag{1.303}$$

With charge $q_1 = Z_1 e > 0$ of the incident nucleus, $\eta = Z_1 Z_2 \alpha E/\hbar ck$ is positive and tends to infinity for $k \to 0$. N_0^2 is then known as Gamow's "Coulomb barrier penetration factor". It largely determines the thermonuclear reaction rates.

2 Lorentz, Pauli and Dirac

2.1 Lorentz Transformations

The Laplacian ∇^2 (1.2) is invariant under rotations of the coordinate system, $\boldsymbol{r}' = R\boldsymbol{r},\ \nabla' = R^{-1}\nabla$, where R is a 3×3 rotation matrix. Lorentz found additional transformations involving $x^0 = ct$ which leave the d'Alembertian $\Box$ (1.3) invariant. Today, the definition of Lorentz transformations is extended in one respect and narrowed in another one: A Lorentz transformation

$$x' = \Lambda x: \quad x'^{\mu} = \Lambda^{\mu}_0 x^0 + \sum_{i=1}^{3} \Lambda^{\mu}_i x^i \equiv \Lambda^{\mu}_{\rho} x^{\rho} \tag{2.1}$$

leaves $x^{02} - \boldsymbol{r}^2$ (and $\partial_0^2 - \nabla^2,\ \pi^{02} - \boldsymbol{\pi}^2$ etc.) invariant and has determinant $+1$. By this definition the rotations are a subgroup of Λ, namely those matrices having $x^{0\prime} = x^0$ and consequently $\Lambda^0_i = 0$:

$$\Lambda_R = \begin{pmatrix} 1 & \overrightarrow{0} \\ \downarrow 0 & R \end{pmatrix}. \tag{2.2}$$

An important subgroup of R are the rotations R_z about the z-axis. When viewed as Lorentz transformations, they are defined by $x^{0\prime} = x^0,\ z' = z$, $\det R = 1$. The invariance requirement is reduced to $x'^2 + y'^2 = x^2 + y^2$ and allows the parametrization of R in terms of one angle, called the rotation angle α:

$$\begin{matrix} z' = z, \\ x' = x\cos\alpha - y\sin\alpha, \\ y' = x\sin\alpha + y\cos\alpha \end{matrix} \quad R_z = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\alpha & -\sin\alpha \\ 0 & \sin\alpha & \cos\alpha \end{pmatrix}. \tag{2.3}$$

$\alpha = 0$ is the identity transformation $x'^{\mu} = x^{\mu}$, which is reached again at $\alpha = 2\pi$, due to the periodicity of $\cos\alpha$ and $\sin\alpha$. The matrix is further simplified by using Cartan components (z, x_+, x_-) instead of the des Cartes components (z, x, y)

$$x_{\pm} = \mp x - iy, \quad x'_+ = e^{i\alpha} x_+, \quad x'_- = e^{-i\alpha} x_-. \tag{2.4}$$

Perhaps Cartan simply diagonalized R_z. More likely, he wrote $x^2 + y^2 = (x + iy)(x - iy) = -x_+ x_-$ and required separate transformations for each bracket.

Turning now to general rotations, we set $\boldsymbol{r} = \boldsymbol{r}_1 + \boldsymbol{r}_2$ and find that $\boldsymbol{r}_1^2$, $\boldsymbol{r}_2^2$ and $\boldsymbol{r}_1\boldsymbol{r}_2$ are separate rotation invariants. In the standard vector formalism, these scalar products are $\boldsymbol{r}_2'\boldsymbol{r}_1' = r_{2,\mathrm{tr}} R_{\mathrm{tr}} R r_1$ where R_{tr} is the transposed of R. Thus the invariance condition reads

$$R_{\mathrm{tr}} R = 1: \quad \sum R_{ki} R_{kj} = \delta_{ij}. \tag{2.5}$$

Such matrices are called orthogonal. Their transpose equals their inverse, $R_{\mathrm{tr}} = R^{-1}$. The product of two such matrices is again orthogonal,

$$(R_2 R_1)_{\mathrm{tr}} R_2 R_1 = R_{1,\mathrm{tr}} R_{2,\mathrm{tr}} R_2 R_1 = R_{1,\mathrm{tr}} R_1 = 1. \tag{2.6}$$

With these two properties, the matrices form a group, the "rotation group". It allows one to construct complicated rotations from products of simpler ones. Euler wrote the most general $R(\alpha, \beta, \gamma)$ as the product of a rotation (2.3) about the z-axis, a rotation by β about the new y'-axis (which leaves $y'' = y'$), and a rotation by γ about the new z'-axis.

The determinant of a matrix product is the product of the determinants of its factors, and $\det(R_{\mathrm{tr}}) = \det R$. Consequently, (2.5) implies $\det^2(R) = 1$. The matrices $R^{(-)}$ of determinant -1 are not rotations (they do not form a group either, because $R^{(-)2}$ has determinant $+1$). They may be written as the product of a standard matrix $R_0^{(-)}$ and a rotation. In cases of 3-dimensional rotational invariance, the standard matrix is the space inversion

$$S: \quad x^{0\prime} = x^0, \quad \boldsymbol{r}' = -\boldsymbol{r} \;\; (z' = -z,\, x' = -x,\, y' = -y). \tag{2.7}$$

In many cases, however, external fields destroy rotational invariance except for rotations about a given axis, which is then taken as the z-axis. A reflection in the xy-plane,

$$R_{xy}: \quad z' = -z,\, x' = x,\, y' = y \tag{2.8}$$

may then be more practical. The two matrices are connected by a rotation by $\alpha = \pi$ about the z-axis, $S = R_z(\pi) R_{xy}$. The reason for denying the status "Lorentz transformation" to transformations with determinant -1 is mentioned at the end of this section and explained in Sect. 3.2, although it is irrelevant for this book.

The construction of "proper Lorentz transformations" Λ_{pr} is analogous. A Lorentz transformation along the z-axis is defined as a Λ_{pr} for which $x' = x$, $y' = y$. The resulting invariance condition is $(x^{0\prime})^2 - z'^2 = x^{02} - z^2 = (x^0 + z)(x^0 - z) \equiv x_+^0 x_-^0$. One merely has to replace the $\pm i\alpha$ in (2.4) by $\pm\eta$, where the "rapidity" η is real:

$$x_\pm^0 = x^0 \pm z, \quad x_+^{0\prime} = x_+^0 e^{\eta}, \quad x_-^{0\prime} = x_-^0 e^{-\eta}; \tag{2.9}$$

$$x^{0\prime} = x^0 \cosh\eta + z \sinh\eta, \quad z' = x^0 \sinh\eta + z \cosh\eta. \tag{2.10}$$

In classical mechanics, one uses an equivalent parametrization in terms of the velocity (1.152):

$$x^{0\prime} = \gamma(x^0 + zv/c), \quad z' = \gamma(x^0 v/c + z), \quad \gamma = (1 - v^2/c^2)^{-1/2}. \tag{2.11}$$

Comparison with (2.10) gives the connection,

$$\gamma = \cosh\eta, \quad v/c = \sinh\eta\,/\gamma. \tag{2.12}$$

Due to the simple exponential functions in (2.9), the addition law for two rapidities in the same direction is the same as for two rotations about the same axis:

$$\Lambda_{\rm pr}(\eta_1)\Lambda_{\rm pr}(\eta_2) = \Lambda_{\rm pr}(\eta_1 + \eta_2). \tag{2.13}$$

The addition law for velocities is complicated and leads to a limiting velocity $v = c$ for $\eta = \infty$. Speculations about tachyons (particles moving faster than light) look little attractive when formulated in terms of rapidity.

In covariant formulations that treat all four components of x^μ simultaneously, the relative minus sign in $\Box = -\partial_0^2 + \nabla^2$ must be somehow removed. It causes the minus sign in $x^{02} - \boldsymbol{r}^2$ and results in the definition of the Lorentz invariant scalar product of two 4-vectors A^μ and B^μ (for example $B^\mu = p^\mu$)

$$AB = A^0 B^0 - \boldsymbol{AB}. \tag{2.14}$$

The "archaic" solution of this formal problem is to set $x^0 = ix^4$, $\Box = \Sigma_{\mu=1}^4 x^\mu x^\mu$. It becomes very confusing for complex 4-vectors in connection with complex conjugation. Today, one defines for each (contravariant) 4-vector A^μ a covariant 4-vector A_μ as follows:

$$A_\mu = (A^0, -\boldsymbol{A}),\ B_\mu = (B^0, -\boldsymbol{B}), \quad AB = \sum_{\mu=0}^{3} A_\mu B^\mu \equiv A_\mu B^\mu = A^\mu B_\mu. \tag{2.15}$$

Alternatively, some authors define $A_\mu = (-A^0, \boldsymbol{A})$ in order to keep the sign of the Lorentz invariant scalar product of the archaic metric. They write $p^2 = -m^2c^2$ for a free particle, instead of the more common $p^2 = m^2c^2$.

The transformation between co- and contravariant 4-vectors is formalized by a "metric tensor" g,

$$A_\mu = g_{\mu\nu}A^\nu,\ A^\nu = g^{\nu\rho}A_\rho \quad g_{\mu\nu} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} = g^{\mu\nu}. \tag{2.16}$$

It is heavy machinery for a simple sign, but it may be familiar from general relativity. Remember that ∂_μ has no minus sign:

$$\partial_\mu = (\partial_0, \nabla),\ \partial^\mu = (\partial_0, -\nabla), \quad p^\mu = i\hbar(\partial_0, -\nabla),\ p_\mu = i\hbar(\partial_0, \nabla). \tag{2.17}$$

This distribution of minus signs is unusual but consistent with (2.14). As mentioned at the end of Sect. 1.3, it arises from the exponent of the plane

wave (1.11), $i(\boldsymbol{kr}-\omega t) = -ik_\mu x^\mu$. Another explanation for the "missing sign" in p_μ is based on the Maxwell equations: Maxwell added the term $-\partial_0 \boldsymbol{E}$ in (1.52) because he wanted a continuity equation for the charge-current density, $\operatorname{div} \boldsymbol{j} + \dot{\rho} = 0$. This term produced the Lorentz invariance; the 4-component version of the continuity equation being

$$j^\mu_{\rm el} = (c\rho_{\rm el}, \boldsymbol{j}_{\rm el}), \quad \partial_\mu j^\mu_{\rm el} = 0. \tag{2.18}$$

Lorentz combined $\boldsymbol{E}$ and $\boldsymbol{B}$ (1.53) into a single field strength tensor,

$$F^{\mu\nu} = \partial^\mu A^\nu - \partial^\nu A^\mu : \quad F^{i0} = \partial^i A^0 - \partial_0 A^i = E^i,\ F^{ij} = -B^k (ijk \text{ cyclic}), \tag{2.19}$$

which enabled him to summarize the inhomogeneous equations (1.52) by a single 4-component equation:

$$\partial_\mu F^{\mu\nu} = 4\pi j^\nu_{\rm el}/c. \tag{2.20}$$

The continuity equation is now necessary, because of $\partial_\nu \partial_\mu F^{\mu\nu} = \partial_\nu \partial_\mu (\partial^\mu A^\nu - \partial^\nu A^\mu) = 0$. Note also that the Lorentz gauge (1.57) is Lorentz invariant.

The metric tensor allows one to write the scalar product of two 4-vectors in terms of their contravariant components as follows:

$$AB = A^\mu g_{\mu\nu} B^\nu = A_{\rm tr} g B. \tag{2.21}$$

The Lorentz transformation Λ (2.1) must thus satisfy

$$\Lambda_{\rm tr} g \Lambda = g. \tag{2.22}$$

The proof that Lorentz transformations form a group is analogous to (2.6). Similarly, (2.22) implies $\det{}^2(\Lambda) = 1$. There are again matrices $\Lambda^{(-)}$ of determinant -1 which are not counted as Lorentz transformations. They may be written as $g\Lambda = S\Lambda$, where the metric tensor g plays the role of the space inversion S (2.7), and Λ has determinant $+1$. They may also be written as $-g\Lambda = T\Lambda'$, where T is the time reversal transformation:

$$T: \quad x^{0\prime} = -x^0, \ \ \boldsymbol{r}' = \boldsymbol{r}. \tag{2.23}$$

With these definitions, $ST = -1$ is a Lorentz transformation, although S and T are not. The reason is that $x^{0\prime} = -x^0,\ z' = -z$ can again be reached by a rotation analogous to (2.3), but now in the (x^0, z)-plane, with $\alpha = \pi$. The rotation looks trivial in the archaic metric $x^0 = ix^4,\ (x^{4\prime})^2 + z'^2 = (x^4)^2 + z^2$. However, in the region $0 < \alpha < \pi$, the mixing of x^4 and z produces complex values of x^0 and z. Nevertheless, there is no problem for operators such as $\Box$. In Sect. 3.2, ST will be identified with "CPT". There exists one very weak interaction which violates both CP and T but not CPT, which justifies the restriction of Lorentz transformations to $\det \Lambda = +1$.

The phase $\exp i(\boldsymbol{kr} - k_0 x^0)$ of a plane wave is Lorentz invariant, $k_0' x^{0\prime} - \boldsymbol{k}'\boldsymbol{r}' = k_0 x^0 - \boldsymbol{kr}$. It implies that k_μ is transformed like x_μ. With $k_0 = \omega/c$ and the z-axis along $\boldsymbol{v}$ as in (2.11), this gives

$$\omega' = \gamma(\omega + v k_z), \quad k_z' = \gamma(\omega v/c^2 + k_z). \tag{2.24}$$

An important application is the Doppler shift of the radiation emitted by an atom of velocity $\boldsymbol{v}$, as the frequency ω of the atomic calculation always refers to the atom at rest, $\boldsymbol{v} = 0$. When the atom moves away from the radiation detector, k_z is negative, and ω' is "redshifted".

2.2 Spinless Current, Density of States

Orthogonality relations were derived in Sect. 1.8 for the solutions of the KG-equation in a stationary potential $V(\boldsymbol{r}) = qA^0$ ($q = -e$), both for the stationary (1.197) and for the time-dependent (1.198) solutions. The latter form remains valid also for time-dependent $A^\mu = A^\mu(x^0, \boldsymbol{r})$, as will be seen now.

Quite generally, one first constructs a 4-current density $j^\mu(x^\nu) = (c\rho, \boldsymbol{j})$, which fulfills a continuity equation, $\partial_\mu j^\mu = 0$. Integrating $\partial_t \rho = -\nabla \boldsymbol{j}$ over all space and neglecting the surface integral according to the discussion in Sect. 1.8, one gets $\partial_t \int \rho d^3r = -\int \boldsymbol{j} d\boldsymbol{f} = 0$. Thus $\int j^0 d^3r$ is time-independent; it is used to define the scalar product.

Particles of charge $q \neq 0$ contribute to the electric 4-current density $j^\mu_{\rm el}$ on the right-hand side of the Maxwell equations (2.20). Also $j^\mu_{\rm el}$ obeys a continuity equation (2.18), and as long as the construction of j^μ is unique, $j^\mu_{\rm el}$ is identical with j^μ, apart from a constant:

$$j^\mu_{\rm el} = q j^\mu.$$

With the normalization $\int \rho d^3r = 1$, $q = \int \rho_{\rm el} d^3r$ is the system's total charge which is in fact conserved. In relativistic quantum mechanics, the number of each type of charged particles (pions, electrons, protons) is separately conserved, and charge conservation follows from Maxwell's equations. In the underlying quantum field theory, however, charged particles may be created in particle-antiparticle pairs (π^-, π^+), $(e^- e^+)$ and may also be transmuted as in β^+-decay, $\mathrm{p} \to \mathrm{n} e^+ \nu_e$. It appears that Maxwell got his conservation law by divine inspiration, because it remains correct also in these more general processes. In fact, both the neutron n and the neutrino ν_e have $q = 0$, and the electric charges of proton and positron are equal, $q(p) = q(e^+) = -q_e = e$.

In nonrelativistic quantum mechanics, $\rho(\boldsymbol{r}, t)$ may be interpreted as the probability to find the particle at the position $\boldsymbol{r}$ at time t. More precisely, $q\rho$ is taken as the probability to localize the charge at position $\boldsymbol{r}$. This interpretation becomes problematic in relativistic quantum mechanics. An instantaneous and precise localization measurement requires charged test projectiles

of high energy, which will always create photons in their collisions. In quantum field theory, $\boldsymbol{r}$ and t become continuous labels of the field operators, without any "physical" significance.

We now turn to the construction of j^μ from the KG-equation in covariant form. The 4-momentum $\pi^\mu = p^\mu - qA^\mu/c$ was derived already in (1.68), and the combination $\pi^{02} - \boldsymbol{\pi}^2$ is now recognized as $\pi_\mu \pi^\mu$:

$$\pi_\mu \pi^\mu \psi = m^2 c^2 \psi. \tag{2.25}$$

We shall also need the complex conjugate version,

$$\pi^*_\mu \pi^{\mu *} \psi^* = m^2 c^2 \psi^*. \tag{2.26}$$

From these two equations, we can verify that

$$j^\mu = \psi^* \pi^\mu \psi + \psi \pi^{\mu *} \psi^* \tag{2.27}$$

satisfies $\partial_\mu j^\mu = 0$. The first term in j^μ gives

$$\partial_\mu \psi^* \pi^\mu \psi = (\partial_\mu \psi^*) \pi^\mu \psi + \psi^* \partial_\mu \pi^\mu \psi. \tag{2.28}$$

In the second half of this expression, we express ∂_μ as

$$\partial_\mu = (\pi_\mu + qA_\mu/c)/i\hbar \tag{2.29}$$

and use (2.25). In the first half, on the other hand, we use

$$\partial_\mu = (-qA_\mu/c - \pi^*_\mu)/i\hbar, \tag{2.30}$$

and then (2.26). The corresponding substitutions are used in the first term of (2.27). With the superposition principle, $\psi = \psi_i + \psi_j$ of two solutions of the KG-equation, it follows that

$$j^\mu_{ji} = \psi^*_j (\overleftarrow{\pi}^{\mu *} + \pi^\mu) \psi_i, \quad \overleftarrow{\pi}^{\mu *} = -i\hbar \overleftarrow{\partial}^\mu - qA^\mu/c \tag{2.31}$$

also fulfills the continuity equation. Its 0-component j^0_{ji} is used for the scalar product $\langle j|i\rangle$, as discussed already in (1.198) for time-independent $V = qA^0$.

Consider now a plane wave,

$$\psi_{k^0, \boldsymbol{k}}(x) = e^{-ikx}, \quad kx = k_0 x^0 - \boldsymbol{kr}. \tag{2.32}$$

With $p^\mu \psi = \hbar k^\mu \psi$, it satisfies the KG-equation for

$$k_\mu k^\mu = k_0^2 - \boldsymbol{k}^2 = m^2 c^2/\hbar^2. \tag{2.33}$$

k_0 is then a function of $\boldsymbol{k}$, apart from a sign:

$$k_0 = \pm(\boldsymbol{k}^2 + m^2 c^2/\hbar^2)^{1/2}. \tag{2.34}$$

The sign will be fixed separately in the following, such that the index $_{k^0}$ of ψ may be dropped. For the construction of the scalar product of two plane waves, we use three times the one-dimensional integral

$$\int d^1x e^{ix(k_x - k'_x)} = 2\pi\delta(k_x - k'_x), \tag{2.35}$$

$$\langle \boldsymbol{k}'|\boldsymbol{k}\rangle = \hbar \int d^3r \psi^*_{\boldsymbol{k}'}(-i\overleftarrow{\partial_0} + i\partial_0)\psi_{\boldsymbol{k}} = 8\pi^3\hbar(k_0 + k'_0)\delta(\boldsymbol{k} - \boldsymbol{k}'). \tag{2.36}$$

As $\delta(\boldsymbol{k}' - \boldsymbol{k})$ requires $\boldsymbol{k}'^2 = \boldsymbol{k}^2$, one has $k'^2_0 = k^2_0$, and $k_0 + k'_0$ becomes $2k_0$ for equal signs and zero for opposite ones. In comparison with (1.197), we have dropped a factor $\hbar/2mc$, in order to comprise also massless particles. Very often, the factor $8\pi^3$ is also avoided by a normalization factor $(2\pi)^{-3/2}$ in front of the plane wave (2.32). In the quantum Maxwell field (Sect. 3.1), the factor $2k_0$ is likewise eliminated by means of a second normalization factor $(2k_0)^{-1/2} = (\hbar/2\omega)^{1/2}$. However, (2.36) is in fact more elegant because of its Lorentz invariance (see below).

A basic concept of quantum mechanics is the density dZ of free-particle states in the unbound continuum, or more precisely in a constant potential as mentioned in connection with (1.75). dZ is defined as the number of orthogonal states per interval d^3k and volume $V = L_xL_yL_z$. For large L_z, (1.191) may be written as $d(n_z/L_z) = dk_z/2\pi$, giving $dZ = d^3k/8\pi^3$. However, this is inconsistent with the scalar product (2.36), where dZ must cancel all factors. Consequently, one needs a Lorentz invariant density of states,

$$d^3_Lk \equiv d^3k/8\pi^3 2k_0, \quad \text{alternatively} \quad d^3_Lk = d^3kmc^2/8\pi^3E. \tag{2.37}$$

The second form is convenient for massive particles, because it agrees with the nonrelativistic form for $E = mc^2$. In many applications, one requires dZ as a function of an energy interval, dE or dk_0 instead of d^3k. One then uses spherical coordinates for the components of $\boldsymbol{k}$,

$$d^3k = k^2dkd\Omega = k_0kdk_0d\Omega, \tag{2.38}$$

due to the relation $kdk = k_0dk_0$ which follows from (2.34). Consequently,

$$dZ = kdk_0d\Omega/16\pi^3 \text{ or } = kdEd\Omega m/8\pi^3\hbar^2, \tag{2.39}$$

where the last expression has $k_0 = E/\hbar c = \omega/c$ inserted. The density of states is important in the theory of metals, where the Pauli principle allows only two electrons per state. The factor 2 accounts for the electron spin; particles of spin s have $2s + 1$ times the density of states of spinless particles. This is so because any free particle satisfies the KG-equation, as we shall see.

The factor mc^2/E in (2.36) may be regarded as a Lorentz contraction of the normalization volume in the direction of flight. For electrons, it becomes quite small in white dwarf stars where the high density (small volume per electron) pushes the electrons into relativistic orbitals, even at zero temperature. For bound electrons in a metal, on the other hand, mc^2/E is slightly larger than 1.

The Lorentz invariance of (2.37) is independent of the specific form of j^0. The Lorentz invariant differential is $d^4k = dk_0 d^3k$; the integral over k_0 is removed by a Lorentz invariant function, namely $\delta(k_\mu k^\mu - m^2c^2/\hbar^2)$. But with

$$\delta(k_0^2 - \boldsymbol{k}^2 - m^2c^2/\hbar^2) = \delta[(k_0 - \omega/c)(k_0 + \omega/c)]$$
$$= c(2\omega)^{-1}[\delta(k_0 - \omega/c) + \delta(k_0 + \omega/c)], \quad \omega/c \equiv (\boldsymbol{k}^2 - m^2c^2/\hbar^2)^{1/2}, \quad (2.40)$$

the second value $k_0 = -\omega/c$ must be removed by the step function, $\Theta(k_0) = 1$ for $k_0 > 0$ and 0 for $k_0 < 0$. $\Theta(k_0)$ is Lorentz invariant for $m^2 > 0$ (due to $\Lambda_0^0 \geq 1$, "tachyons" with $m^2 < 0$ are thus excluded). In summary, the Lorentz invariant form of (2.37) is

$$d_L^3 k = (2\pi)^{-3} d^4k \delta(k_\mu k^\mu - m^2c^2/\hbar^2)\Theta(k_0). \quad (2.41)$$

2.3 Pauli's Electron Spin

In one-electron atoms, the Zeeman splitting in a weak magnetic field B is given by a formula similar to (1.92),

$$E_{nljm_j}(B) = E_{nlj}(0) + B\mu_B g_{lj} m_j, \quad \mu_B = e\hbar/2mc. \quad (2.42)$$

The index $_j$ in $E_{nlj}(0)$ is a new quantum number which assumes two different values for $l > 0$, and the old magnetic quantum number m_l is replaced by a new one m_j which assumes equidistant values of either sign. With g_{lj} adjusted to the unit distance, m_j assumes half-integer values. For $l = 0$, m_j is $\pm 1/2$, while for $l = 1$ it is $\pm 1/2$ for one j and $\pm 1/2$, $\pm 3/2$ for the other one. In general, if one defines j in a clever way, then the multiplicity of m_j obeys a simple rule:

$$j = l \pm \tfrac{1}{2}, \quad -j \leq m_j \leq j. \quad (2.43)$$

In comparison with the spinless atom, the number of states at fixed n and l is doubled. With $\Sigma_{m_j} = 2j + 1$,

$$\Sigma_{j=l-1/2}^{l+1/2}(2j+1) = 2(l - \tfrac{1}{2}) + 1 + 2(l + \tfrac{1}{2}) + 1 = 2(2l+1). \quad (2.44)$$

For $l = 0$, the states $j = -1/2$ are absent, but (2.44) remains correct, as $2(0 - 1/2) + 1 = 0$. It is one of the first indications of the new two-valued degree of freedom of the electron, called "spin". The value of the "g-factor" in (2.42) was found by Landé:

$$g_{lj} = 1 + 2(j - l)/(2l + 1) = (2j + 1)/(2l + 1). \quad (2.45)$$

The simple formula (2.42) applies only when the total Zeeman splitting remains small in comparison with the j-splitting, $B\mu_B g_{lj}(2j + 1) < |E_{l+1/2} - E_{l-1/2}|$. For comparable splittings, the Zeeman effect becomes complicated, but for strong magnetic fields, a new simple pattern appears. The quantum numbers j and m_j are then inappropriate and are replaced by a new

two-valued quantum number, which is simply added to the spinless Zeeman formula (1.92). Anticipating a bit of theory in the notation, the normalized two eigenvalues are written as $2m_s$, $m_s = \pm 1/2$, where m_s is called the "spin magnetic quantum number":

$$E(B) = E_{nl}(0) + B\mu_{\mathrm{B}}(m_l + 2m_s). \tag{2.46}$$

This splitting in a strong magnetic field is called the "normal" Zeeman effect, because it was first understood. (The name referred originally to a similar formula for certain two-electron atoms, which is valid also for weak B). The Landé formula (2.42) got the name "anomalous Zeeman effect", which is still in use. Its theoretical complication arises from a "spin-orbit" potential, which is a relativistic spin effect in the Coulomb potential, see Sect. 2.8. For $l = 0$, however, (2.45) gives $g_{0j} = 2$, and both formulas are identical (the spin-orbit potential vanishes in this case). The situation is simpler in the absence of a Coulomb field, say for a free electron in a magnetic field. The relativistic Landau level formula (1.170) has n replaced by $n - m_s q/e$, for $q = \pm e$. An even more precise formula is

$$k_t^2(n, m_s) = [e(2n+1) - q g_{\mathrm{free}} m_s]B/\hbar c, \quad g_{\mathrm{free}} = 2.0023. \tag{2.47}$$

The constant g_{free} is called the g-factor of a free electron.

For $B = 0$ and in the absence of relativistic Coulomb effects such as the $V^2/c^2\hbar^2$ in (1.98), the electron spin becomes an "internal" or "hidden" quantum number, analogous to the two states of polarization of light in an optically inactive medium. But even then, the spin manifests itself in atoms and molecules via the Pauli principle, which allows at most one electron per orbital. If spin is not counted in the orbitals, the Pauli principle allows two electrons per orbital. For example, the total degeneracy of states in the nonrelativistic hydrogen atom is $g_{\mathrm{spin}}(n) = 2g_{\mathrm{spinless}}(n)$, with g_{spinless} given by (1.136).

Spin must be introduced into the electron wave function ψ_e in a manner that admits a rotational invariant coupling between the spin and a vector field such as $\boldsymbol{B}$. In the analogous case of light, the two polarization components must be incorporated in a 3-component vector $\boldsymbol{A}(\boldsymbol{r}, t)$, such that the operators $\boldsymbol{Ap}$ and $\boldsymbol{pA}$ in $\boldsymbol{\pi}^2$ (1.80) are rotational invariant. The Lorentz-invariant extension of these operators requires yet another component A^0 in combinations such as $A^\mu p_\mu$. For electrons, two components are sufficient, both for rotational invariance and for Lorentz invariance. In this section, only rotations are considered. The two-component electron wave function is called a spinor,

$$\psi_e \equiv \psi = \begin{pmatrix} \psi_{1/2}(x^\mu) \\ \psi_{-1/2}(x^\mu) \end{pmatrix} = \begin{pmatrix} \psi_+(x^\mu) \\ \psi_-(x^\mu) \end{pmatrix} = \psi_+(x^\mu)\chi_+ + \psi_-(x^\mu)\chi_-, \tag{2.48}$$

$$\chi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \chi(m_s = \tfrac{1}{2}), \quad \chi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \chi(m_s = -\tfrac{1}{2}). \tag{2.49}$$

χ_+ and χ_- are unit spinors, similar to the three unit vectors into which $\boldsymbol{A}(\boldsymbol{r},t)$ can be decomposed. An operator in this two-component space is a 2×2 matrix with at most 4 independent components. If no matrix is written, the 2×2 unit matrix is understood, which is also denoted by σ^0 in this context:

$$\sigma^0 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \equiv 1. \tag{2.50}$$

The other three matrices were chosen by Pauli (1927) as

$$\sigma^3 = \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad \sigma^1 = \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma^2 = \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}. \tag{2.51}$$

They are both Hermitian and unitary; their complete algebra can be written in a single line:

$$\sigma^i\sigma^j = \delta_{ij} + i\epsilon^{ijk}\sigma^k, \quad \epsilon^{123} = 1, \quad \epsilon^{jik} = -\epsilon^{ijk}. \tag{2.52}$$

For two vectors $\boldsymbol{a}$ and $\boldsymbol{b}$, it implies

$$(\boldsymbol{\sigma a})(\boldsymbol{\sigma b}) = \boldsymbol{ab} + i\boldsymbol{\sigma}(\boldsymbol{a}\times\boldsymbol{b}). \tag{2.53}$$

The development of the spin formalism has a complicated history (Enz 2002). It was first believed that the Zeeman effect involved the atomic core. Pauli suggested to Landé that is might be connected instead with the valence electron. Inspired by Pauli, Kronig suggested that the electron carries an intrinsic angular momentum $\frac{1}{2}\hbar$, but he was argued out of this by Pauli. Soon afterwards, Goudsmit and Uhlenbeck postulated spinning electrons, with a factor 2 between the spin and orbital magnetic moments, respectively. In classical relativity, Thomas calculated the relativistic precession of spin ("Thomas precession") in a magnetic field, which also contains the factor 2. Pauli still rejected a possible connection with the Zeeman effect, but was finally convinced by Frenkel. Next, the spin-orbit potential was explained by the Dirac equation (next section), where also the Zeeman operator followed very elegantly. This and the classical calculation by Thomas created the impression that spin is a relativistic effect. It was only found afterwards that the Zeeman operator is part of the nonrelativistic kinetic energy operator of (1.67), provided $\boldsymbol{\pi}^2$ is replaced by $\boldsymbol{\pi\sigma}^2$:

$$[c\pi_N^0 - (\boldsymbol{\pi\sigma})^2/2m]\psi_N = 0, \tag{2.54}$$

which will also be derived in Sect. 2.8 in the context of relativistic corrections, including the spin-orbit coupling. The name "Pauli equation" is associated both with (2.54) and with the relativistic corrections (2.248) below.

Mathematically, the Laplacian $\Delta = \nabla^2 = \partial_x^2 + \partial_y^2 + \partial_z^2$ is the square of a 2×2 matrix, which is called $\nabla\boldsymbol{\sigma}$ on the basis of the subsequent analysis. In its standard form, ∂_z appears in the diagonal:

$$\nabla\boldsymbol{\sigma} = \begin{pmatrix} \partial_z & \partial_- \\ \partial_+ & -\partial_z \end{pmatrix}, \quad \partial_\pm = \partial_x \pm i\partial_y. \tag{2.55}$$

Other forms follow from transformations with unitary 2×2 matrices. By matrix multiplication, one verifies the square:

$$(\nabla\boldsymbol{\sigma})^2 = \begin{pmatrix} \partial_z & \partial_- \\ \partial_+ & -\partial_z \end{pmatrix} \begin{pmatrix} \partial_z & \partial_- \\ \partial_+ & -\partial_z \end{pmatrix} = \begin{pmatrix} \partial_z^2 + \partial_-\partial_+ & \partial_z\partial_- - \partial_-\partial_z \\ \partial_+\partial_z - \partial_z\partial_+ & \partial_+\partial_- + \partial_z^2 \end{pmatrix} \tag{2.56}$$

$$= \begin{pmatrix} \nabla^2 & 0 \\ 0 & \nabla^2 \end{pmatrix} = \nabla^2\sigma^0. \tag{2.57}$$

In Schrödinger's (relativistic) free-particle equation (1.43) one now replaces $\boldsymbol{p}^2$ by $(\boldsymbol{p}\boldsymbol{\sigma})^2$

$$[-\hbar^2\partial_0^2 - (\boldsymbol{p}\boldsymbol{\sigma})^2 - m^2c^2]\psi = 0, \tag{2.58}$$

and then $\boldsymbol{p} \to \boldsymbol{\pi} = \boldsymbol{p} - q\boldsymbol{A}/c$ for an electron of charge $q = -e$:

$$[-\hbar^2\partial_0^2 - (\boldsymbol{\pi}\boldsymbol{\sigma})^2 - m^2c^2]\psi = 0. \tag{2.59}$$

This produces the desired new piece of the Zeeman operator,

$$(\boldsymbol{\pi}\boldsymbol{\sigma})^2 = \boldsymbol{\pi}^2 + \hbar e\boldsymbol{B}\boldsymbol{\sigma}/c, \quad \boldsymbol{B}\boldsymbol{\sigma} = \begin{pmatrix} B_z & B_- \\ B_+ & -B_z \end{pmatrix}, \quad B_\pm = B_x \pm iB_y. \tag{2.60}$$

Taking again $B_x = B_y = 0$, the new operator has the eigenvalues $\pm\hbar eB/c = 2m_s\hbar eB/c$ as required by the "normal" Zeeman effect (2.46). It arises from the replacement of p_-p_+ by $\pi_-\pi_+$ ($\pi_\pm = \pi_x \pm i\pi_y$) in one diagonal element (according to (2.56)) and of p_+p_- by $\pi_+\pi_-$ in the other one. The quadratic terms are equal in both products and produce the part $\pi_x^2 + \pi_y^2$ of $\boldsymbol{\pi}^2$. The mixed terms agree only in their anticommutators; $\pi_-\pi_+$ contains the combination

$$(\partial_x - i\partial_y)(A_x + iA_y) + (A_x + iA_y)(\partial_x - i\partial_y) = \{\partial_x, A_x\} + \{\partial_y, A_y\} + iB_z, \tag{2.61}$$

with $B_z = [\partial_x, A_y] - [\partial_y, A_x]$. $\pi_+\pi_-$ has a change of sign in its commutator part, and thus B_z replaced by $-B_z$.

For bound states, the approximation $E(0) \approx mc^2$ implicit in the use of the Bohr magneton (1.92) in (2.46) is consisitent with additional nonrelativistic approximations, to be discussed in Sect. 2.8. For $V = 0$, on the other hand, the exact validity of (2.59) shows that the relativistic Landau levels of electrons are obtained from the spinless Landau levels by the replacement $E^2/c^2 - \boldsymbol{\pi}^2 \longrightarrow E^2/c^2 - \boldsymbol{\pi}^2 - \hbar e\boldsymbol{\sigma}\boldsymbol{B}$. Consequently, they have simply the eigenvalues $2\hbar em_sB/c$ of this operator added to the spinless E^2-levels, which is precisely the statement of (2.47) in the approximation $g_{\text{free}} = 2$.

The raising and lowering matrices $\sigma_\pm$ are somewhat simpler than the Pauli matrices:

$$\sigma_+ = \tfrac{1}{2}(\sigma_x + i\sigma_y) = \begin{pmatrix} 0\ 1 \\ 0\ 0 \end{pmatrix}, \quad \sigma_- = \tfrac{1}{2}(\sigma_x - i\sigma_y) = \begin{pmatrix} 0\ 0 \\ 1\ 0 \end{pmatrix}. \tag{2.62}$$

The matrix $\boldsymbol{B\sigma}$ of (2.60) is decomposed into Pauli matrices as follows:

$$\boldsymbol{B\sigma} = B_z\sigma_z + B_-\sigma_+ + B_+\sigma_- = B_z\sigma_z + B_x\sigma_x + B_y\sigma_y. \tag{2.63}$$

This smells rotational invariance: One might argue that $\boldsymbol{B}$ is a vector, $\boldsymbol{\sigma}$ is a vector, so $\boldsymbol{B\sigma}$ is a scalar. The argument is not quite correct, however, as the Pauli matrices are fixed standard matrices. Rather, the spinor ψ (2.49) on which $\boldsymbol{B\sigma}$ acts must be transformed under rotations such that $\psi^\dagger\boldsymbol{\sigma}\psi$ becomes a vector, with $\psi^\dagger$ defined below. We use again the simplest form of a rotation, namely (2.3) which leaves the z-component invariant. The rotation of a vector field $\boldsymbol{B}(\boldsymbol{r})$ is complicated by the fact that its arguments $\boldsymbol{r} = (x, y, z)$ must also be rotated:

$$B'_z(\boldsymbol{r}') = B_z(\boldsymbol{r}), \quad B'_\pm(\boldsymbol{r}') = B_\pm(\boldsymbol{r})e^{\pm i\alpha}. \tag{2.64}$$

To simplify the notation, we assume again that $\boldsymbol{B}$ remains constant over atomic dimensions, and suppress its arguments. The scalar product of two spinors ψ_a and ψ_b is written as $\psi_b^\dagger\psi_a$; it implies a summation over the spinor components. For $\psi_b = \psi_a = \psi$,

$$\psi^\dagger = (\psi_+^*, \psi_-^*), \quad \psi^\dagger\psi = \psi_+^*\psi_+ + \psi_-^*\psi_-. \tag{2.65}$$

This combination is invariant under transformations by 2×2 unitary matrices, $U^\dagger = U^{-1}$:

$$\psi' = U\psi, \quad \psi'^\dagger = \psi^\dagger U^\dagger, \quad \psi'^\dagger\psi' = \psi^\dagger\psi. \tag{2.66}$$

It was mentioned at the end of Sect. 1.9 that rotations of the functions Y_l^m are represented by unitary matrices, see (1.276). If the combination $\psi^\dagger\sigma_z\psi$ is to transform like the z-component of a vector, the matrix $U_z(\alpha)$ for a rotation about the z-axis must commute with σ_z in order to keep $\psi'^\dagger\sigma_z\psi' = \psi^\dagger\sigma_z\psi$. And as a multiple $e^{i\alpha_0}$ of the unit matrix is excluded by definition, the only matrix available for U is σ_z:

$$U_z(\alpha) = e^{-i\alpha s\sigma_z} = \begin{pmatrix} e^{-i\alpha s} & 0 \\ 0 & e^{i\alpha s} \end{pmatrix}. \tag{2.67}$$

All 2×2 matrices of this type have automatically determinant $+1$, they are therefore SU_2 matrices in the sense of (1.277). A factor s will be necessary in order to also have $\psi^\dagger\sigma_\pm\psi$ transformed like the $\pm$-components of a vector:

$$\psi'^\dagger\sigma_\pm\psi' = \psi^\dagger U_z^\dagger\sigma_\pm U_z\psi = \psi^\dagger\sigma_\pm e^{\pm i\alpha}\psi. \tag{2.68}$$

We now study the full operator $\boldsymbol{\sigma B}$ (2.60); its rotated version is

$$\boldsymbol{B'\sigma} = \begin{pmatrix} B_z & B_-e^{-i\alpha} \\ B_+e^{i\alpha} & B_z \end{pmatrix}. \tag{2.69}$$

In order to get $\psi^\dagger U^\dagger \boldsymbol{B'\sigma} U\psi = \psi^\dagger \boldsymbol{B\sigma}\psi$, one needs

$$\boldsymbol{B'\sigma}U = U\boldsymbol{B\sigma}. \tag{2.70}$$

This requires $s = 1/2$ in (2.67): By matrix multiplication, one verifies

$$\boldsymbol{B'\sigma}U_z = \begin{pmatrix} B_z & B_- e^{-i\alpha} \\ B_+ e^{i\alpha} & -B_z \end{pmatrix} \begin{pmatrix} e^{-i\alpha/2} & 0 \\ 0 & e^{i\alpha/2} \end{pmatrix}, \tag{2.71}$$

$$\boldsymbol{B'\sigma}U_z = \begin{pmatrix} e^{-i\alpha/2} & 0 \\ 0 & e^{i\alpha/2} \end{pmatrix} \begin{pmatrix} B_z & B_- \\ B_+ & -B_z \end{pmatrix}. \tag{2.72}$$

The factor $s = 1/2$ is called the electron spin for the following reason: The Pauli matrices have the commutators

$$[\sigma_x, \sigma_y] = 2i\sigma_z, \quad [\sigma_y, \sigma_z] = 2i\sigma_x, \quad [\sigma_z, \sigma_x] = 2i\sigma_y \tag{2.73}$$

according to (2.52). Therefore, the "spin" operators $\boldsymbol{s} = \frac{1}{2}\boldsymbol{\sigma}$ satisfy the commutator algebra (1.229) of the angular momentum operators $\hat{\boldsymbol{l}}$. This restricts the possible eigenvalues $s(s+1)$ and m_s of $\boldsymbol{s}^2$ and s_z, and from $\boldsymbol{s} = \frac{1}{2}\boldsymbol{\sigma}$ and $\sigma_x^2 = \sigma_y^2 = \sigma_z^2 = 1$ one finds $\boldsymbol{s}^2 = 3/4$, ergo $s = 1/2$. One says that "SU_2-matrices form a two-dimensional representation of the rotation group". Strictly, only the inverse is true, because a rotation by 2π is identical with the unit operator. For the electron spinor, on the other hand, insertion of $s = 1/2$ and $\alpha = 2\pi$ into (2.67) gives

$$\psi_e(\alpha = 360^\circ) = \begin{pmatrix} e^{-i\pi} & 0 \\ 0 & e^{i\pi} \end{pmatrix} \psi_e(\alpha = 0) = -\psi_e. \tag{2.74}$$

The group SU_2 gains additional importance as a subgroup of $SL_2(C)$, of which the 4×4 Lorentz transformations Λ of Sect. 2.1 form a representation. This may justify the somewhat pedantic style of this section.

A general rotation may be characterized by a rotation axis $\hat{\boldsymbol{\alpha}}$ and a rotation angle α in the form of a rotation vector $\boldsymbol{\alpha} = \alpha\hat{\boldsymbol{\alpha}}$:

$$\psi'(\boldsymbol{\alpha}) = e^{-i\boldsymbol{\alpha}\boldsymbol{S}}\psi. \tag{2.75}$$

This form of the rotation applies in fact to particles of arbitrary spin s, where $\boldsymbol{S}$ is a vector of $(2s+1)(2s+1)$ matrices that satisfy the angular momentum algebra, for example the matrices (1.262) for $s = 1$.

The two pieces $\boldsymbol{\pi}^2$ and $(\hbar e/c)\boldsymbol{B\sigma}$ of $(\boldsymbol{\pi\sigma})^2$ are separately rotational invariant. They are also separately gauge invariant, as $\boldsymbol{B} = \nabla \times \boldsymbol{A}$ is not affected by the gauge transformations (1.55). One may thus admit an arbitrary factor $g_{\text{free}}/2$ in front of $\boldsymbol{B\sigma}$. The precise operator in the Pauli equation is in fact

$$(\boldsymbol{\pi\sigma})^2 + (\hbar e/c)\kappa_e \boldsymbol{B\sigma}, \quad \kappa_e = (g_{\text{free}} - 2)/2 = 0.00118 \approx \alpha/2\pi. \tag{2.76}$$

Dirac was lucky that the "anomalous magnetic moment" κ_e is so small. The proton has $\kappa_p = 1.79$, $g_p = 5.58$.

2.4 The Dirac Equation

While Pauli's equation (2.59) is correct as long as A^0 vanishes, its simplest extension $i\hbar\partial_0 \to \pi^0$,

$$[\pi^{02} - (\boldsymbol{\pi}\boldsymbol{\sigma})^2]\psi = m^2c^2\psi, \quad \pi^0 = i\hbar\partial_0 - qA^0/c \tag{2.77}$$

misses relativistic effects of A^0. Today, the name "Pauli equation" is reserved for the case where also $(\boldsymbol{\pi}\boldsymbol{\sigma})^2$ is treated nonrelativistically. In (1.67), the $\boldsymbol{\pi}^2/2m$ is then simply replaced by $(\boldsymbol{\pi}\boldsymbol{\sigma})^2/2m$. In the notation of nonrelativistic quantum mechanics, the equation (2.54) reads

$$i\hbar\partial_t\psi_N = H_P\psi_N, \quad H_P = (\boldsymbol{\pi}\boldsymbol{\sigma})^2/2m + V. \tag{2.78}$$

Relativistic corrections follow from the Dirac equation (Sect. 2.8). Those containing A^0 cannot be derived from (2.77), because the electric field

$$\boldsymbol{E} = -\nabla A^0 - \partial_0 \boldsymbol{A} \tag{2.79}$$

is missing. And as $\boldsymbol{E}$ and $\boldsymbol{B}$ are parts of the same tensor $F^{\mu\nu}$, (2.77) is not Lorentz invariant. Pauli mentioned this problem in letters to Dirac at Cambridge and Kramers at Copenhagen and urged them to solve it. When Dirac published his solution in 1928, Kramers had apparently also solved the problem, but in a rather different form. Looking at Dirac's more impressive form, Kramers was discouraged and published his own form much later (1933) in an inappropriate periodical. This form was practically ignored but was popularized 25 years later by Feynman and Gell-Mann (1958) in the context of parity violation. Its quantum field version was elaborated by Brown (1958) and Tonin (1959) and is today used in higher-order perturbative expansions (Chalmers and Siegel 1999). Here we first present the Kramers form, since it requires only Pauli matrices, and its proof of Lorentz invariance is a trivial modification of the proof of rotational invariance of the last section.

Kramers remembered the formula $a^2 - b^2 = (a+b)(a-b)$ for commuting operators a and b. When he made this replacement in the incorrect equation (2.77) with the noncommuting operators $a = \pi^0$, $b = \boldsymbol{\pi}\boldsymbol{\sigma}$,

$$(\pi^0 + \boldsymbol{\pi}\boldsymbol{\sigma})(\pi^0 - \boldsymbol{\pi}\boldsymbol{\sigma})\psi_r = m^2c^2\psi_r, \tag{2.80}$$

the commutator produced the missing $\boldsymbol{E}$:

$$[\boldsymbol{\pi}\boldsymbol{\sigma}, \pi^0] = \boldsymbol{\sigma}([i\hbar\nabla, qA^0/c] - [q\boldsymbol{A}/c, i\hbar\partial_0]) = -iq\hbar\boldsymbol{\sigma}\boldsymbol{E}/c. \tag{2.81}$$

For the electron, with $q = -e$, the explicit form of (2.80) is thus

$$[\pi_\mu\pi^\mu - \hbar e\boldsymbol{\sigma}(\boldsymbol{B} - i\boldsymbol{E})/c]\psi_r = m^2c^2\psi_r. \tag{2.82}$$

The correct equation thus contains both $\boldsymbol{B}$ and $\boldsymbol{E}$, but the proof of Lorentz invariance is easier in the form (2.80) with the factorizing operator. The formalism is further simplified by an auxiliary spinor ψ_l:

$$\psi_l = (mc)^{-1}(\pi^0 - \boldsymbol{\pi}\boldsymbol{\sigma})\psi_r. \tag{2.83}$$

With this definition, (2.80) assumes the form of two coupled linear equations:

$$\begin{aligned}(\pi^0 - \boldsymbol{\pi}\boldsymbol{\sigma})\psi_r &= mc\psi_l,\\ (\pi^0 + \boldsymbol{\pi}\boldsymbol{\sigma})\psi_l &= mc\psi_r.\end{aligned} \tag{2.84}$$

Kramers could equally well have used the opposite order of factors in (2.80), which changes the sign of the commutator:

$$(\pi^0 - \boldsymbol{\pi}\boldsymbol{\sigma})(\pi^0 + \boldsymbol{\pi}\boldsymbol{\sigma})\psi_l = m^2c^2\psi_l. \tag{2.85}$$

The two spinors that satisfy (2.80) and (2.85) are unequal; they are distinguished here by the indices $_r$ = "righthanded" and $_l$ = "lefthanded". Elimination of one of the two spinors from the linear equations produces the quadratic equation for the other one.

The operator $M = i\boldsymbol{\sigma}\boldsymbol{E}$ of (2.82) is anti-Hermitian, $M^\dagger = -M$. Moreover, it apparently destroys the invariance of the equation under the parity transformation $\boldsymbol{r} \to -\boldsymbol{r}$. The 4-potential A^μ transforms under parity as follows:

$$A^{0\prime}(\boldsymbol{r}') = A^0(\boldsymbol{r}), \quad \boldsymbol{A}'(\boldsymbol{r}') = -\boldsymbol{A}(\boldsymbol{r}). \quad \boldsymbol{r}' = -\boldsymbol{r}. \tag{2.86}$$

The substitution $\boldsymbol{r}' = -\boldsymbol{r}$ is the space inversion (2.7). Vectors that change sign under parity are called "polar", vectors that don't are called "axial". Both $\boldsymbol{A}$ and $\boldsymbol{E}$ (2.79) are polar, while $\boldsymbol{B} = \boldsymbol{\nabla} \times \boldsymbol{A}$ is axial. Thus the parity transform of $\boldsymbol{\sigma}(\boldsymbol{B} - i\boldsymbol{E})$ is $\boldsymbol{\sigma}(\boldsymbol{B} + i\boldsymbol{E})$, which is also the Hermitian conjugate.

Perhaps these unexpected complications confused Kramers. Dirac (1928) postulated a wave equation of the Hamiltonian type,

$$i\hbar\partial_0\psi_D = \frac{1}{c}H_D\psi_D, \quad \frac{1}{c}H_D = \frac{V}{c} + \boldsymbol{\pi}\boldsymbol{\alpha} + mc\beta, \tag{2.87}$$

with $V = -eA^0$. He then found out that $\boldsymbol{\alpha}$ and β had to be 4×4 matrices. Unlike the Pauli matrices, the Dirac matrices are used in two different standard forms. The form for (2.84) is called the chiral basis,

$$\psi_{ch} = \begin{pmatrix}\psi_r\\ \psi_l\end{pmatrix}, \quad \boldsymbol{\alpha}_{ch} = \begin{pmatrix}\boldsymbol{\sigma} & 0\\ 0 & -\boldsymbol{\sigma}\end{pmatrix}, \quad \beta_{ch} = \begin{pmatrix}0 & \sigma^0\\ \sigma^0 & 0\end{pmatrix}. \tag{2.88}$$

Insertion of these matrices reproduces precisely the pair of first-order equations that follows from the second-order Kramers equation (2.80). The Dirac matrices are Hermitian. The operator $\boldsymbol{\pi} = -i\hbar\nabla + e\boldsymbol{A}/c$ is a polar vector, $\boldsymbol{\pi}'(\boldsymbol{r}') = -\boldsymbol{\pi}(\boldsymbol{r})$. The parity transformation exchanges $\pi^0 - \boldsymbol{\pi}\boldsymbol{\sigma}$ with $\pi^0 + \boldsymbol{\pi}\boldsymbol{\sigma}$, which must be compensated by an exchange of ψ_r and ψ_l. Without the Dirac form, the parity transformation of (2.84) is

$$\psi_r'(\boldsymbol{r}') = \psi_l(\boldsymbol{r}), \quad \psi_l'(\boldsymbol{r}') = \psi_r(\boldsymbol{r}). \tag{2.89}$$

For the four-component Dirac spinor ψ_D, the same transformation is

$$\psi'_D(\boldsymbol{r}') = \gamma^0 \psi_D(\boldsymbol{r}), \quad \gamma^0 = \beta. \tag{2.90}$$

The second standard form uses the "parity basis", in which β is diagonal, see (2.151) below, where $\sigma^0 = 1$ is used. Unfortunately, Dirac concluded from his postulate that the relativistic Schrödinger equation must be wrong. In the context of quantum field theory, the equation was rehabilitated for spinless particles by Pauli and Weisskopf (1934). Instead of the abbreviation "KG-equation" used in this book, "SKGPW-equation" would be more correct.

Parity will be discussed more explicitly in Sect. 2.6. In the absence of the Kramers equation, emphasis was put on the 4×4 form of Dirac matrices. It is frequently easier to express $\boldsymbol{\alpha}$ in terms of the Pauli matrices,

$$\boldsymbol{\alpha} = \gamma^5 \boldsymbol{\sigma}, \quad \gamma^5_{ch} = \begin{pmatrix} \sigma^0 & 0 \\ 0 & -\sigma^0 \end{pmatrix}. \tag{2.91}$$

ψ_r and ψ_l are eigenspinors of the "chirality matrix" γ^5, with chiralities $+1$ and -1, respectively. The Dirac equation reads now

$$(\pi^0 - \gamma^5 \boldsymbol{\pi}\boldsymbol{\sigma})\psi_D = mc\beta\psi_D. \tag{2.92}$$

Contrary to parity, proper Lorentz transformations are diagonal in the chiral basis. The transformations were found by Weyl (1929) and Van der Waerden (1929). The chiral components ψ_r and ψ_l are also called Weyl or Van der Waerden spinors. In that context, $\psi_l \equiv \dot{\psi}$ is called a dotted spinor, $\psi_r \equiv \psi$ an undotted one.

As explained in Sect. 2.1, the Lorentz transformation of $x^0_+ = x^0 + z$ and $x^0_- = x^0 - z$ is obtained from the rotation of $x_+ = -x - iy$ and $x_- = x - iy$ by replacing the $i\alpha$ in the exponent of $x'_\pm = e^{\pm i\alpha} x_\pm$ by a new parameter η, which is real. The same substitutions apply to the spinor transformations (2.67). Dropping the i converts the matrix from unitary to Hermitian. Since its determinant continues to be 1, the matrix is now called SH:

$$\psi'_r = SH\psi_r, \quad SH = e^{-\eta\sigma_z/2} = \begin{pmatrix} e^{-\eta/2} & 0 \\ 0 & e^{\eta/2} \end{pmatrix}. \tag{2.93}$$

The matrix $\boldsymbol{B}\boldsymbol{\sigma}$ (2.60) which was used in the proof of rotational invariance is replaced by

$$\pi_\mu \sigma^\mu = \begin{pmatrix} \pi^0_- & \pi_+ \\ \pi_- & \pi^0_+ \end{pmatrix}, \quad \pi^0_\pm = \pi^0 \pm \pi_z, \ \pi_\pm = \pi_x \pm i\pi_y. \tag{2.94}$$

A Lorentz transformation along the z-axis,

$$\pi^{0\,\prime}_\pm = e^{\pm\eta}\pi^0_\pm, \quad \pi'_\pm = \pi_\pm \tag{2.95}$$

leads now to

$$\pi'_\mu \sigma^\mu SH = (SH)^{-1} \pi_\mu \sigma^\mu. \tag{2.96}$$

The explicit proof is analogous to (2.71), with $\boldsymbol{B'\sigma}$ replaced by $\pi'_\mu \sigma^\mu$. Thus $\psi_r^\dagger \pi_\mu \sigma^\mu \psi_r$ is Lorentz invariant as anticipated by the notation, but $\psi_r^\dagger \psi_r$ is not. Instead, it is transformed like the zero-component of a 4-vector,

$$\psi_r^{\dagger\prime} \psi'_r = \psi_r^\dagger (SH)^2 \psi_r = \psi_r^\dagger \begin{pmatrix} e^{-\eta} & 0 \\ 0 & e^{\eta} \end{pmatrix} \psi_r \tag{2.97}$$

$$= \psi_r^\dagger \psi_r \cosh\eta - \psi_r^\dagger \sigma_z \psi_r \sinh\eta. \tag{2.98}$$

The group of complex 2×2 matrices is called $L_2(C)$, its unimodular subgroup (which comprises the matrices with $\det(L_2(C)) = 1$) is $SL_2(C)$. Any such matrix may be decomposed into a matrix SU and a matrix SH:

$$SL_2(C) = SH_2 \otimes SU_2. \tag{2.99}$$

It has already been mentioned that a Lorentz transformation matrix Λ may be decomposed into a rotation matrix Λ_{R} (2.2) and a proper Lorentz transformation Λ_{pr}, $\Lambda = \Lambda_{\mathrm{R}} \Lambda_{\mathrm{pr}}$. Consequently, the group of real 4×4 Lorentz transformations represents the group $SL_2(C)$. It is presently speculated that the ultimate "theory of everything" could have more space-time dimensions than $3 + 1$. From the point of view of relativistic quantum theory, it should be more promising to try to extend $SL_2(C)$.

The phase between ψ_l and ψ_r in (2.84) is a matter of definition: a factor $e^{i\alpha}$ in front of $mc\psi_l$ would be compensated by a factor $e^{-i\alpha}$ in front of $mc\psi_r$ in the second equation. Similarly, m^2 in the Kramers equation (2.82) may be taken as the product of a lefthanded mass m_l that multiplies $c\psi_l$ and a righthanded mass m_r that multiplies $c\psi_r$ in the second equation:

$$m^2 = m_l m_r, \quad (\pi^0 - \boldsymbol{\pi\sigma})\psi_r = m_l c \psi_l, \quad (\pi^0 + \boldsymbol{\pi\sigma})\psi_l = m_r c \psi_r. \tag{2.100}$$

The corresponding Dirac version is

$$(\pi^0 - \gamma^5 \boldsymbol{\pi\sigma})\psi_D = mc\beta_{\mathrm{sim}} \psi_D, \quad \beta_{sim,ch} = \begin{pmatrix} 0 & (m_l/m_r)^{1/2} \\ (m_r/m_l)^{1/2} & 0 \end{pmatrix}. \tag{2.101}$$

The basis-independent form of β_{sim} is

$$\beta_{\mathrm{sim}} = \beta[m_r + m_l + (m_r - m_l)\gamma^5]/2m. \tag{2.102}$$

β_{sim} is a simple example of a new matrix in the "proper Dirac" space, which is spanned by the three matrices γ^5, β and $\gamma^5\beta$. To profit from the analogy with the Pauli matrices $\boldsymbol{\sigma}$, we now settle on one standard vector of 2×2 Dirac matrices in analogy with (2.51), $\boldsymbol{\beta} = (\beta_x,\ \beta_y,\ \beta_z)$. For reasons that will become clear later, the parity basis (2.151) below is preferred to the chiral basis, $\boldsymbol{\beta} = \boldsymbol{\beta}_{pa}$,

$$\beta = \beta_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad \gamma^5 = \beta_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad i\gamma^5\beta = \beta_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}. \tag{2.103}$$

$\boldsymbol{\sigma}$ and $\boldsymbol{\beta}$ reduce the algebra of the 15+1 4×4 Dirac matrices to two independent Pauli algebras. For example, the anticommutator of γ^5 and $\beta = \gamma^0$ which is normally written as

$$\gamma^5\gamma^0 + \gamma^0\gamma^5 = 0 \tag{2.104}$$

follows from

$$\beta_x\beta + \beta\beta_x = 0, \tag{2.105}$$

as in the case (2.52) of the Pauli matrices. The above matrix β_{sim} fulfills

$$\beta_{\text{sim}}^2 = 1, \quad \beta_{\text{sim}}\gamma^5 = -\gamma^5\beta_{\text{sim}}, \tag{2.106}$$

but it is not Hermitian. The transformation $\beta \to \beta_{\text{sim}}$ is a similarity transformation (Sect. 2.6). It is also the parity transformation matrix of the new basis.

In the field equations of quantum electrodynamics as well as in the derived many-electron equations, γ^5 appears only in the combination $\gamma^5\boldsymbol{\sigma}$. It justifies the abbreviation $\boldsymbol{\alpha} = \gamma^5\boldsymbol{\sigma}$, which is standard in the literature (a separate γ^5 appears only in parity violation, see (2.321)). However, in order to reduce the relativistic two-fermion problem to an effective one-body equation with a reduced mass, one must manipulate the two-fermion Dirac space independently of the two-fermion spin space (Sects. 3.6 and 4.6). The separate algebras of $\boldsymbol{\sigma}$ and $\boldsymbol{\beta}$ are then indispensable.

The Kramers equation shows that the sign of the mass has no physical significance. As the Dirac equation is linear in m, it must have an alternative form with m replaced by $-m$. The transformed ψ_D will be denoted by ψ_D^5:

$$\psi_D^5 = \gamma^5\psi_D, \quad (\pi^0 - \gamma^5\boldsymbol{\pi}\boldsymbol{\sigma})\psi_D^5 = -mc\beta\psi_D^5. \tag{2.107}$$

This form is obtained from (2.92) by the substitution $\psi_D = \gamma^5\psi_D^5$ and by multiplication by γ^5 from the left, using (2.104).

It may be noted that for $A^\mu = 0$, the Kramers equation (2.82) becomes the free KG equation $(p_\mu p^\mu - m^2c^2)\psi_r = 0$. In this case one need not reduce ψ_D to two components: Writing (2.92) as $(E - \gamma^5\boldsymbol{p}\boldsymbol{\sigma} - mc\gamma^0)\psi_D = 0$, multiplication by $E + \gamma^5\boldsymbol{p}\boldsymbol{\sigma} + mc\gamma^0$ gives

$$[E^2 - (\boldsymbol{p}\boldsymbol{\sigma})^2 - m^2c^2]\psi_D = (E^2 - \boldsymbol{p}^2 - m^2c^2)\psi_D = 0. \tag{2.108}$$

As classical mechanics uses Hamiltonian equations of motion, it was natural for Dirac to postulate an equation such as (2.87). In Chap. 3, we shall see that Hamiltonian equations do in fact occur in quantum field theory, which did not yet exist for electrons in 1928. However, equations for systems with given numbers of massive particles are derived from the quantum field equations in complicated iterative procedures. These procedures leave little room for separate postulates. Nevertheless, Dirac's Hamiltonian form remains useful for equations with several electrons, see (3.87) and particularly (3.112).

2.5 Addition of Angular Momenta

Setting $\pi^0 = (E - V)/c$, $\boldsymbol{\pi} = \boldsymbol{p}$, the Kramers equation (2.80) becomes

$$[(E - V)/c + \boldsymbol{\sigma p}][(E - V)/c - \boldsymbol{\sigma p}]\psi_r = m^2c^2\psi_r. \tag{2.109}$$

For a central potential, $V(\boldsymbol{r}) = V(r)$, one needs the vector of Pauli matrices in polar components:

$$\boldsymbol{\sigma} = \sigma_r(\hat{\boldsymbol{r}} + i\boldsymbol{\sigma} \times \hat{\boldsymbol{r}}) = (\hat{\boldsymbol{r}} - i\boldsymbol{\sigma} \times \hat{\boldsymbol{r}})\sigma_r. \tag{2.110}$$

By taking the scalar product of this equation with $\hat{\boldsymbol{r}}$, one finds its radial component,

$$\sigma_r = \boldsymbol{\sigma}\hat{\boldsymbol{r}} = \sigma_z \cos\theta + (\sigma_+ e^{-i\phi} + \sigma_- e^{i\phi}) \sin\theta. \tag{2.111}$$

The angular components are verified by taking the cross product with $\boldsymbol{r}$, using the rule $a \times (b \times c) = b(ac) - c(ab)$:

$$\hat{\boldsymbol{r}} \times \boldsymbol{\sigma} = i\sigma_r\hat{\boldsymbol{r}} \times (\boldsymbol{\sigma} \times \hat{\boldsymbol{r}}) = i\sigma_r(\boldsymbol{\sigma} \cdot 1 - \hat{\boldsymbol{r}}\sigma_r) = i(\sigma_r\boldsymbol{\sigma} - \hat{\boldsymbol{r}}), \tag{2.112}$$

as $\sigma_r^2 = 1$. This is the same as (2.110) multiplied by σ_r, again using $\sigma_r^2 = 1$.

The operator $\boldsymbol{\sigma p}$ follows from (2.110) as

$$\boldsymbol{\sigma p} = -i\hbar\sigma_r(\partial_r - \boldsymbol{\sigma}\hat{\boldsymbol{l}}/r) = -i\hbar(\partial_r + \boldsymbol{\sigma}\hat{\boldsymbol{l}}/r)\sigma_r, \tag{2.113}$$

with $\hat{\boldsymbol{l}} = \boldsymbol{r} \times \boldsymbol{p}/\hbar$. The product of these two forms shows $(\boldsymbol{\sigma p})^2 = \boldsymbol{p}^2$. In matrix form,

$$\sigma_r = \begin{pmatrix} \cos\theta & \sin\theta e^{-i\phi} \\ \sin\theta e^{i\phi} & -\cos\theta \end{pmatrix}, \quad \boldsymbol{\sigma}\hat{\boldsymbol{l}} = \begin{pmatrix} \hat{l}_z & \hat{l}_- \\ \hat{l}_+ & -\hat{l}_z \end{pmatrix}. \tag{2.114}$$

Neither of these matrices commutes with $\hat{\boldsymbol{l}}$. For example, from (1.231) one finds

$$[\hat{l}_z, \hat{\boldsymbol{l}}\boldsymbol{\sigma}] = -\sigma_+\hat{l}_- + \sigma_-\hat{l}_+. \tag{2.115}$$

On the other hand, using the corresponding commutators of the Pauli matrices,

$$\tfrac{1}{2}[\sigma_z, \sigma_\pm] = \pm\sigma_\pm, \tag{2.116}$$

$$\tfrac{1}{2}[\sigma_z, \hat{\boldsymbol{l}}\boldsymbol{\sigma}] = \sigma_+\hat{l}_- - \sigma_-\hat{l}_+. \tag{2.117}$$

This is just the opposite of (2.115), such that the sum of these two commutators vanishes. Similarly, one finds $[-i\partial_\phi + \sigma_z/2, \sigma_r] = 0$. One defines the total angular momentum $\boldsymbol{j}$ as follows:

$$\boldsymbol{j} \equiv \hat{\boldsymbol{l}} + \boldsymbol{\sigma}/2, \quad [\boldsymbol{j}, \hat{\boldsymbol{l}}\boldsymbol{\sigma}] = 0, \quad [\boldsymbol{j}, \sigma_r] = 0. \tag{2.118}$$

(In nonrelativistic quantum mechanics, $\boldsymbol{l} + \boldsymbol{s} = \hbar(\hat{\boldsymbol{l}} + \boldsymbol{\sigma}/2)$ is called $\boldsymbol{j}$. The definition (2.118) gives the opportunity to get rid of $\hbar$ in the angular momentum algebra without formally setting $\hbar = 1$). The commutators of $\boldsymbol{j}$ folow from those of its components:

$$[j_z, j_\pm] = \pm j_\pm, \quad [j_+, j_-] = 2j_z. \tag{2.119}$$

They imply $[\boldsymbol{j}^2, \boldsymbol{j}] = 0$ and the eigenvalues $j(j+1)$ of $\boldsymbol{j}^2$ and m_j of j_z. $-j \leq m_j \leq +j$. These eigenvalues explain the multiplet structure in the anomalous Zeeman splitting mentioned in Sect. 2.3. As $\boldsymbol{l}^2$ commutes with each component of $\boldsymbol{l}$, it commutes also with $\boldsymbol{l}\boldsymbol{\sigma}$. Already the total number of states led us to conclude that j assumes the two values $l \pm 1/2$. The eigenvalues of $\hat{\boldsymbol{l}}\boldsymbol{\sigma}$ follow then by squaring (2.118):

$$\hat{\boldsymbol{l}}\boldsymbol{\sigma} = \boldsymbol{j}^2 - \hat{\boldsymbol{l}}^2 - \boldsymbol{\sigma}^2/4 = j(j+1) - l(l+1) - 3/4. \tag{2.120}$$

A slightly more convenient operator is $\hat{\boldsymbol{l}}\boldsymbol{\sigma} + 1$; by inserting the two possible values of j, one verifies

$$\hat{\boldsymbol{l}}\boldsymbol{\sigma} + 1 = (j - l)(2j + 1). \tag{2.121}$$

In the Dirac equation, it is j that is conserved and fixed, while l assumes the two values $j \pm 1/2$. What is commonly called the electron's orbital angular momentum (= 0 for s-states, 1 for p-states etc) is the dominant value, see the next section.

For later applications, the general method of constructing eigenstates $|j(j_1 j_2)m\rangle$ from the product states $|j_1 m_1\rangle|j_2 m_2\rangle$ of two commuting angular momenta, $\boldsymbol{j} = \boldsymbol{j}_1 + \boldsymbol{j}_2$ will be explained. The j_i are kept fixed (our example has $j_1 = l$, $j_2 = s = 1/2$) and will be supressed, $|j(j_1 j_2)m\rangle = |jm\rangle$. The quantum number m_2 could also be supressed, as it is $m - m_1$. This follows from

$$j_z|jm\rangle = m|jm\rangle = (j_{z1} + j_{z2})|j_1 m_1\rangle|j_2 m_2\rangle = (m_1 + m_2)|j_1 m_1\rangle|j_2 m_2\rangle. \tag{2.122}$$

The new states $|jm\rangle$ are expressed in terms of the product states as follows:

$$|jm\rangle = \sum_{m_1} (m_1 m_2|jm)|j_1 m_1\rangle|j_2 m_2\rangle. \tag{2.123}$$

The coefficients $(m_1 m_2|jm)$ are Clebsch-Gordan (CG) coefficients; they are normally written in more detail, for example as $(j_1 j_2 m_1 m_2|j_1 j_2 jm)$. In the case at hand, m_1 assumes only the values $m \pm \frac{1}{2}$, as $m_2 = m_s$ is either $+\frac{1}{2}$ or $-\frac{1}{2}$. With the $|j_2 m_2\rangle = \chi(m_2)$ given by (2.49) and $|j_1 m_1\rangle = Y_l^m(\theta, \phi)$, we obtain the "spinor spherical harmonics"

$$|jm\rangle = \begin{pmatrix} (m - 1/2, 1/2|jm) Y_l^{m-1/2} \\ (m + 1/2, -1/2|jm) Y_l^{m+1/2} \end{pmatrix} \equiv \chi_l^{jm}(\theta, \phi). \tag{2.124}$$

The construction of $(m_1 m_2|jm)$ starts from the "stretched configuration", $m_1 = m_{1max} = j_1$, $m_2 = m_{2max} = j_2$, $m = m_{\max} = j_1 + j_2 = j_{\max}$. The single value $m = j_1 + j_2$ fixes both m_i at their maximal values j_i, the summation in (2.123) reduces to a single term, and from the normalization of $|jm\rangle$ one has

$$(j_1 j_2|j_{\max}, j_1 + j_2) = 1. \tag{2.125}$$

At the same time, this fixes the phases of all $|j_{\max}, m\rangle$, as the states with lower m-values are generated by the lowering operator $j_- = j_x - i j_y$ analogous to (1.230). According to (1.232), the lowering operator produces the state $|j, m-1\rangle$ with a proportionality constant $n_-^{1/2}$, where the value of n_- follows from (1.236), with $\lambda = j(j+1)$:

$$j_-|jm\rangle = n_-^{1/2}|j, m-1\rangle, \quad n_- = j(j+1) - m(m-1) = (j+m)(j-m+1). \tag{2.126}$$

Applying j_- to (2.123) and using $j_- = j_{1-} + j_{2-}$ on its right side, one gets

$$n_-^{1/2}|j, m-1\rangle = \sum_{m_1} (m_1 m_2|jm)[n_{1-}^{1/2}|j_1, m_1 - 1\rangle|j_2 m_2\rangle + n_{2-}^{1/2}|j_1 m_1\rangle|j_2, m_2 - 1\rangle].$$

Starting now from (2.125), one obtains all CG-coefficients for $j = j_{\max}$ from the recurrence relation

$$\begin{aligned} n_-^{1/2}(m_1 m_2|j, m-1) = {} & (j_1(j_1+1) - m_1(m_1+1))^{1/2}(m_1+1, m_2|jm) \\ & + (j_2(j_2+1) - m_2(m_2+1))^{1/2}(m_1, m_2+1|jm) \end{aligned}. \tag{2.127}$$

The relation applies in fact to all j provided one knows the state $|j, j\rangle$ also for $j < j_{\max}$. This state can be determined from orthogonality requirements. For example, application of j_- to the stretched configuration gives

$$j_{\max}^{1/2}|j_{\max}, j_1 + j_2 - 1\rangle = j_1^{1/2}|j_1, j_1 - 1\rangle|j_2 j_2\rangle + j_2^{1/2}|j_1 j_1\rangle|j_2, j_2 - 1\rangle. \tag{2.128}$$

Apart from an overall sign, the orthogonal combination with the same value of $m_1 + m_2$ is

$$j_{\max}^{1/2}|j_{\max} - 1, j_1 + j_2 - 1\rangle = -j_2^{1/2}|j_1, j_1 - 1\rangle|j_2 j_2\rangle + j_1^{1/2}|j_1 j_1\rangle|j_2, j_2 - 1\rangle \tag{2.129}$$

(remember the orthonormality of the states on the right-hand side, $\langle j_1 m_1|\langle j_2 m_2|j_1 m_1'\rangle|j_2 m_2'\rangle = \delta_{m_1' m_1}\delta_{m_2' m_2}$). One may of course also check directly that this is an eigenstate of $\boldsymbol{j}^2$. The overall sign was fixed by Clebsch and Gordan such that the coefficient of $|j_1 j_1\rangle$ is positive. Unfortumately, this depends on which of the two angular momenta is called $\boldsymbol{j}_1$. The asymmetry is removed in Wigner's $3j$-symbol

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = \frac{(-1)^{j_1 - j_2 - m_3}}{(2j_3+1)^{1/2}}(m_1 m_2|j_3, -m_3), \quad m_1 + m_2 + m_3 = 0. \tag{2.130}$$

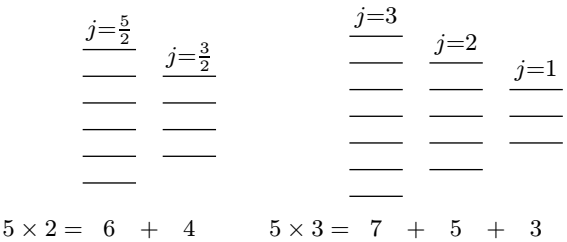

Fig. 2.1. Decomposition of $|2, m_1\rangle|1/2, m_2\rangle$ and $|2, m_1\rangle|1, m_2\rangle$ into $|j, m\rangle$

It is in fact totally symmetric under permutations of its three columns. For the coupling of three angular momenta, see for example Weissbluth (1978).

For $j_2 = 1/2$, $j_{\max} - 1 = j_1 - 1/2$ is already the minimal value of j. For $j_2 > 1/2$, a third state appears at $j_{\max} - 2$, which must be orthogonalized with respect to the two arising from the action of j_-. The resulting multiplet structure for $j_1 = 2$, $j_2 = 1$ is included in Fig. 2.1; the general CG-coefficients for $j_2 = 1$ are given in Table 2.1.

Returning to the present spinor case, one gets from (2.127) for fixed $j_1 = l$,

$$(m - \tfrac{1}{2}, \tfrac{1}{2}|l \pm \tfrac{1}{2}, m) = \pm[(l \pm m + \tfrac{1}{2})/(2l+1)]^{1/2},$$

$$(m + \tfrac{1}{2}, -\tfrac{1}{2}|l \pm \tfrac{1}{2}, m) = [(l \mp m + \tfrac{1}{2})/(2l+1)]^{1/2}, \tag{2.131}$$

$$\chi^{jm}_{j-\frac{1}{2}} = \frac{1}{\sqrt{2j}} \begin{pmatrix} (j+m)^{\frac{1}{2}} Y^{m-1/2}_{j-1/2} \\ (j-m)^{\frac{1}{2}} Y^{m+1/2}_{j-1/2} \end{pmatrix},$$

$$\chi^{jm}_{j+\frac{1}{2}} = \frac{1}{\sqrt{2j+2}} \begin{pmatrix} -(j+1-m)^{\frac{1}{2}} Y^{m-1/2}_{j+1/2} \\ (j+1+m)^{\frac{1}{2}} Y^{m+1/2}_{j+1/2} \end{pmatrix}. \tag{2.132}$$

As the $Y^{m\pm1/2}_l$ are normalized according to (1.186) and the transformation (2.124) is unitary, the χ^{jm}_l are automatically orthonormal:

$$\int d\Omega \chi^{j'm'\dagger}_{l'} \chi^{jm}_l = \delta_{l'l}\delta_{j'j}\delta_{m'm}. \tag{2.133}$$

Table 2.1. The CG-coefficients $(m_1 m_2|jm)$ for $j_2 = 1$ and $m_2 = +1$ (left column), $m_2 = 0$ (middle), and $m_2 = -1$ (right).

$j = j_1 + 1$:	$\left(\frac{(j_1+m)(j_1+m+1)}{(2j_1+1)(2j_1+2)}\right)^{\frac{1}{2}}$	$\left(\frac{(j_1+1)^2-m^2}{(2j_1+1)(j_1+1)}\right)^{\frac{1}{2}}$	$\left(\frac{(j_1-m)(j_1-m+1)}{(2j_1+1)(2j_1+2)}\right)^{\frac{1}{2}}$
$j = j_1$:	$-\left(\frac{(j_1+m)(j_1-m+1)}{2j_1(j_1+1)}\right)^{\frac{1}{2}}$	$m[j_1(j_1+1)]^{-\frac{1}{2}}$	$\left(\frac{(j_1-m)(j_1+m+1)}{2j_1(j_1+1)}\right)^{\frac{1}{2}}$
$j = j_1 + 1$:	$\left(\frac{(j_1-m)(j_1-m+1)}{2j_1(2j_1+1)}\right)^{\frac{1}{2}}$	$-\left(\frac{j_1^2-m^2}{j_1(2j_1+1)}\right)^{\frac{1}{2}}$	$\left(\frac{(j_1+m+1)(j_1+m)}{2j_1(2j_1+1)}\right)^{\frac{1}{2}}$

How does σ_r (2.111) act in this basis? Being pseudoscalar, it changes the parity of the state, at fixed j. It transforms χ_l^{jm} into $\chi_{\tilde{l}}^{jm}$, where $\tilde{l} = 2j - l$ is the other possible l-value. Moreover, $\sigma_r^2 = 1$ implies $\sigma_r \chi_l^{jm} = \pm\chi_{\tilde{l}}^{jm}$. Unfortunately, our choice $j_1 = l$, $j_2 = 1/2$ implies the minus sign:

$$\sigma_r \chi_l^{jm} = -\chi_{\tilde{l}}^{jm}, \quad \tilde{l} = 2j - l. \tag{2.134}$$

2.6 Hydrogen Atom and Parity Basis

The hydrogenic energy levels for an idealized, pointlike and infinitely heavy nucleus follow from the Dirac equation with the potential $V = -Ze^2/r = -\hbar c\alpha_Z/r$ ($\alpha_Z = Z\alpha$). Their lowering from the nonrelativistic value $E_N(n, l)$ is indicated in Fig. 2.2. Note the degeneracy of the levels $l = j - 1/2$ and $l = j + 1/2$ for all values of the principal quantum number n except $n = j + 1/2$, where the level with $l = j + 1/2 = n$ does not exist.

The levels are most easily calculated with the Kramers equation (2.109). Setting $E^2/c^2 - m^2c^2 = \hbar^2 k^2$ as usual and dividing by $\hbar^2$,

$$(k^2 + 2E\alpha_Z/\hbar cr + \alpha_Z^2/r^2 + \nabla^2 + i[\boldsymbol{\sigma}\boldsymbol{\nabla}, V/\hbar c])\psi_r = 0. \tag{2.135}$$

According to (2.113), one has

$$[\boldsymbol{\sigma}\boldsymbol{\nabla}, V] = \sigma_r[\partial_r, V] = \sigma_r V', \quad [\boldsymbol{\sigma}\boldsymbol{\nabla}, -\alpha_Z/r] = \sigma_r \alpha_Z/r^2. \tag{2.136}$$

This last operator is absent in the KG equation. It connects states of different l according to (2.134), such that a suitable ansatz for ψ_r requires both l-values:

$$\psi_{r+}(\boldsymbol{r}) = R_+(\chi_{j+1/2}^{jm} + i\hat{\beta}\chi_{j-1/2}^{jm}), \quad \psi_{r-}(\boldsymbol{r}) = R_-(-i\hat{\beta}\chi_{j+1/2}^{jm} + \chi_{j-1/2}^{jm}). \tag{2.137}$$

The terms proportional to $\hat{\beta}$ (see below) are the relativistic corrections with the "wrong" l-value. Writing the two χ-components of ψ_{r+} and ψ_{r-} on top of each other and decomposing $\nabla^2 = (\partial_r + 1/r)^2 - \hat{\boldsymbol{l}}^2/r^2$ as usual, one sees that (2.135) contains two 2×2 matrices acting on these components:

$$\chi = \begin{pmatrix} \chi_{j+1/2}^{jm} \\ \chi_{j-1/2}^{jm} \end{pmatrix}, \quad \hat{\boldsymbol{l}}^2 = \begin{pmatrix} (j+\frac{1}{2})(j+\frac{3}{2}) & 0 \\ 0 & j^2 - \frac{1}{4} \end{pmatrix}, \quad i\sigma_r = \begin{pmatrix} 0 & -i \\ -i & 0 \end{pmatrix}. \tag{2.138}$$

The elements of $\hat{\boldsymbol{l}}^2$ are the familiar $l(l+1)$, those of $i\sigma_r$ follow from (2.134). In (2.135), both matrices are multiplied by r^{-2}, such that their sum can be diagonalized independently of r. The diagonalization is simplified if one first subtracts from $\hat{\boldsymbol{l}}^2$ a multiple of the unit matrix, such that the rest is traceless:

$$\hat{\boldsymbol{l}}^2 = (j + \tfrac{1}{2})^2 - (\hat{\boldsymbol{l}}\boldsymbol{\sigma} + 1), \tag{2.139}$$

where $\hat{\boldsymbol{l}}\boldsymbol{\sigma}+1$ has the values $\pm(j+1/2)$ in the diagonal, according to (2.121):

$$\hat{\boldsymbol{l}}\boldsymbol{\sigma}+1+i\alpha_Z\sigma_r=\begin{pmatrix}-j_+ & -i\alpha_Z\\ -i\alpha_Z & j_+\end{pmatrix},\quad j_+\equiv j+\tfrac{1}{2}. \tag{2.140}$$

The eigenvalues of this matrix follow from its square, which is a multiple of the unit matrix:

$$(\hat{\boldsymbol{l}}\boldsymbol{\sigma}+1+i\alpha_Z\sigma_r)^2=\gamma^2, \tag{2.141}$$

$$\gamma=\sqrt{j_+^2-\alpha_Z^2}=\sqrt{(j+\tfrac{1}{2})^2-\alpha_Z^2}. \tag{2.142}$$

The two eigenvalues are thus $-\gamma$ and $+\gamma$, respectively. The other two r^{-2}-operators of (2.135), namely α_Z^2/r^2 and $-(j+\frac{1}{2})^2/r^2$ (which has been extracted from $-\hat{\boldsymbol{l}}^2/r^2$), combine into $-\gamma^2/r^2$, such that the two decoupled equations arising from the diagonalization can be summarized as follows:

$$(k^2+2E\alpha_Z/\hbar cr+(\partial_r+1/r)^2-\gamma(\gamma\pm1)/r^2)R_\pm=0. \tag{2.143}$$

The expansion (2.146) below shows that $\hat{\beta}$ is actually of the order α_Z. The substitution $k=i\kappa$, $R=e^{-\kappa r}v$ as in (1.100) produces again the radial KG-equation (1.112), for

$$l_{\alpha+}=\gamma\quad l_{\alpha-}=\gamma-1. \tag{2.144}$$

Its solutions (1.124), effective principal quantum numbers $n_\beta=n-\beta$, and eigenvalues E (1.129) remain valid, only the quantum defect β_l is replaced by $j+1/2-\gamma$, according to (2.144):

$$R_\pm=N_\pm e^{-z/2}z^{l_{\alpha\pm}}F(-n_r,2l_{\alpha\pm}+2,z)\quad z=2\kappa r,\quad l_{\alpha\pm}=l-\beta_j, \tag{2.145}$$

$$\beta_j\equiv\beta=j+1/2-\gamma=\alpha_Z^2/(2j+1)+\alpha_Z^4/(2j+1)^3\ldots. \tag{2.146}$$

The expansion differs from the spinless case (1.134) only by the replacement $l\to j$; insertion of (1.132) and (1.135) into (1.131) gives

$$E_N/mc^2=-\tfrac{1}{2}\alpha_Z^2/n^2(1+2\beta/n-\tfrac{3}{4}\alpha_Z^2/n^2+3\beta^2/n^2-\tfrac{3}{4}\alpha_Z^2\beta/n^3+\tfrac{5}{8}\alpha_Z^4/n^4 \tag{2.147}$$

$$+4\beta^3/n^3-\tfrac{15}{2}\alpha_Z^2\beta^2/n^4+\tfrac{15}{4}\alpha_Z^4\beta/n^5+\tfrac{35}{64}\alpha_Z^6/n^6). \tag{2.148}$$

The four terms in (2.148) are of the order α_Z^8. Finally, inserting the expansion (2.146) for β_j, one obtains to order α_Z^6,

$$\frac{E_N(j)}{mc^2}=-\frac{\alpha_Z^2}{2n^2}\left[1+\frac{2\alpha_Z^2/n}{2j+1}-\frac{3\alpha_Z^2}{4n^2}+\frac{\alpha_Z^4/n}{(2j+1)^3}+\frac{5\alpha_Z^4}{8n^4}+\frac{3\alpha_Z^4(n-2j-1)}{n^3(2j+1)^2}\right]. \tag{2.149}$$

The KG-energies have j replaced by l. The smallest j-value has $(2j+1)=2$, the smallest l-value has $(2l+1)=1$. To order α_Z^4, averaging over j at fixed l (with the weight $(2j+1)/2(2l+1)$ corresponding to the multiplicity $2j+1$)

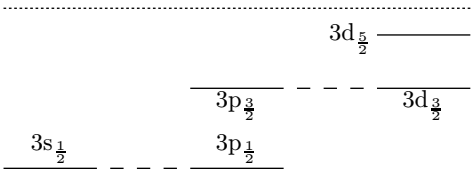

Fig. 2.2. Lowering of the hydrogen energy levels from the nonrelativistic value (upper dotted line) for $n = 3$

produces the spinless KG energies. In a perturbative treatment of spin, this is due to the vanishing traces of the Pauli matrices.

The wave functions for $l_{\alpha+}$ and $l_{\alpha-}$ are quite different. The condition $a = -n_r$ that the confluent hypergeometric function $F(a, b, z)$ reduces to a polynomial refers to n_r, not to $n_\beta = n_r + l_\alpha + 1$ which appears in the energy formula. A fixed value of n_β means $n_r = n_\beta - \gamma$ for $l_\alpha = \gamma$, and $n_r = n_\beta - \gamma + 1$ for $l_\alpha = \gamma - 1$. In particular, for $j = n - 1/2$, the first alternative is excluded by $n_r = -1$, $a = +1$.

Unfortunately, the ansatz (2.137) for ψ_r leads to parity eigenstates only for $j = n - 1/2$, which limits its use, for example in perturbation theory. In terms of ψ_r alone, the parity transformation (2.89) reads

$$\psi'_r(\boldsymbol{r}') = (mc)^{-1}(\pi^0 - \boldsymbol{\sigma\pi})\psi_r(\boldsymbol{r}) \tag{2.150}$$

according to (2.84). The ansatz (2.137) ignores this. The fact that a parity-invariant equation has solutions that are not parity eigenstates is not particularly strange; it happens in the excited states of the nonrelativistic hydrogen atom, and even plane waves are not parity eigenstates. What is embarrassing is the fact that the representations of the basic group $SL_2(C)$ are constrained by (2.150) in their parity eigenstates. In the 4-component Dirac formulation, this implies that γ^5 and γ^0 (2.91) do not commute. The appropriate basis for parity eigenstates has γ^0 diagonal. It is frequently called "Dirac" or "low-energy" basis; the name "parity basis" seems more appropriate:

$$\psi_{\rm pa} = \frac{1}{\sqrt{2}}\begin{pmatrix}\psi_r + \psi_l \\ \psi_r - \psi_l\end{pmatrix} \equiv \begin{pmatrix}\psi_g \\ \psi_f\end{pmatrix}, \quad \gamma^5_{\rm pa} = \begin{pmatrix}0 & 1 \\ 1 & 0\end{pmatrix}, \quad \beta_{\rm pa} = \begin{pmatrix}1 & 0 \\ 0 & -1\end{pmatrix}. \tag{2.151}$$

The index $_g$ stands for great or large, $_f$ for small. The small components vanish for $\boldsymbol{\sigma\pi} \to 0$. Parity eigenstates require two different radial wave functions $g(r)$ and $f(r)$, but they have only one l-value in ψ_g (see (1.109)) and only the other one (denonted by $\tilde{l}$ in the following) in ψ_f:

$$\psi_g = g(r)\chi_l^{jm}(\theta, \phi), \quad \psi_f = -if(r)\chi_{\tilde{l}}^{jm}(\theta, \phi). \quad \tilde{l} \equiv 2j - l. \tag{2.152}$$

The factor $-i$ compensates the i in the coupled radial equations below. Evidently, $\psi_{\rm pa}$ has parity $(-1)^l$, which derives from Y_l^m in the large components.

The opposite parity of Y_l^m in the small components is compensated by the eigenvalue -1 of γ^0. This allows one to define the "orbital angular momentum" l of an electron in a representation-independent way: For fixed j, the parity $(-1)^l$ determines l.

With $\boldsymbol{\alpha}_{\rm pa} = \gamma^5_{\rm pa}\boldsymbol{\sigma}$, the Dirac equation (2.87) assumes the form

$$\pi^0_- \psi_g = \boldsymbol{\sigma\pi}\psi_f, \quad \pi^0_+ \psi_f = \boldsymbol{\sigma\pi}\psi_g, \quad \pi^0_\pm = \pi^0 \pm mc. \tag{2.153}$$

The hydrogen atom has $\boldsymbol{\sigma\pi} = \boldsymbol{\sigma p}$ given by (2.113). When $\hat{\boldsymbol{l}}\boldsymbol{\sigma}+1$ acts on χ_l^{jm}, its eigenvalue is called $-\kappa_D$ ($_D$ for Dirac, to avoid confusion with $\kappa = -ik$). The other eigenvalue is then $+\kappa_D$ according to (2.121):

$$(\hat{\boldsymbol{l}}\boldsymbol{\sigma}+1)\chi_l^{jm} = -\kappa_D \chi_l^{jm}, \quad \kappa_D = (l-j)(2j+1),$$

$$\pi^0_- g = \hbar(\partial_r + 1/r - \kappa_D/r) f, \quad \pi^0_+ f = -\hbar(\partial_r + 1/r + \kappa_D/r) g. \tag{2.154}$$

The corresponding ansatz for ψ_r requires also two radial functions, say R_+ and R_- in (2.137), but the resulting coupled radial equations are second-order instead of first-order.

Before proceeding, it is convenient to separate a factor r^{-1} from g and f,

$$g = u_g/r, \quad f = u_f/r, \quad (\partial_r + r^{-1})r^{-1} = r^{-1}\partial_r. \tag{2.155}$$

This substitution is always practical in spherical coordinates; in the Laplacian it replaces $(\partial_r + r^{-1})^2$ by ∂_r^2, see (1.10). It removes a factor r^2 from the volume element $d^3r = r^2 dr d\Omega$, such that $i\partial_r$ becomes Hermitian, for example

$$\int r^2 dr g f = \int dr u_g u_f, \quad \int dr u_g (i\partial_r) u_f = \int dr u_f (-i\partial_r) u_g. \tag{2.156}$$

The equations for u_g and u_f are

$$\pi^0_- u_g = \hbar(\partial_r - \kappa_D/r) u_f, \quad \pi^0_+ u_f = -\hbar(\partial_r + \kappa_D/r) u_g. \tag{2.157}$$

It is possible to relate u_g and u_f to a single function u such that both equations for u become identical. The ansatz

$$u_g = [a\pi^0_+ + b\hbar(\partial_r - \kappa_D/r)]u, \quad u_f = [b\pi^0_- - a\hbar(\partial_r + \kappa_D/r)]u \tag{2.158}$$

with free parameters a and b produces

$$[\pi^0_+\pi^0_-/\hbar^2 + \partial_r^2 - \kappa_D(\kappa_D \pm 1)/r^2 \pm (b/a)^{\pm 1}\alpha_Z/r^2]u = 0. \tag{2.159}$$

These two equations become identical for $-\kappa_D + \alpha_Z b/a = \kappa_D - \alpha_Z a/b$, which determines b/a as

$$b/a = \kappa_D/\alpha_Z \mp (\kappa_D^2/\alpha_Z^2 - 1)^{1/2} = (\kappa_D \mp \gamma)/\alpha_Z. \tag{2.160}$$

With this expression, the r^{-2}-terms of (2.159) combine into $-\gamma^2 \mp \gamma$, and the equation becomes again (2.143), with $R = u/r$. Also, insertion of b/a into (2.158) gives

$$u_g = a[\pi_+^0 + (\hbar/\alpha_Z)(\kappa_D \mp \gamma)(\partial_r - \kappa_D/r)]u, \tag{2.161}$$

$$u_f = b[\pi_-^0 - (\hbar/\alpha_Z)(\kappa_D \pm \gamma)(\partial_r + \kappa_D/r)]u. \tag{2.162}$$

The second expression has been transformed using $(b/a)^{-1} = \alpha_Z/(\kappa_D \mp \gamma) = (\kappa_D \pm \gamma)/\alpha_Z$. The signs in front of γ must be chosen such that $\kappa_D \pm \gamma$ is of the order of α_Z^2.

Also these equations are greatly simplified for $n_r = 0$, $\kappa_D = -n$. With $F(n_r = 0) = 1$, $l_\alpha = \gamma - 1$, (1.124) gives

$$u(n_r = 0) = rR = Ne^{-\kappa r}(2\kappa r)^\gamma (2\kappa)^{-1}, \quad \gamma = (n^2 - \alpha_Z^2)^{1/2}. \tag{2.163}$$

The value of κ follows from (1.129), but now with $n_\beta = n - \beta_j \approx n - \alpha_Z^2/(2j+1)$:

$$\kappa = \frac{mc\alpha_Z}{\hbar n_\beta}\left(1 + \frac{\alpha_Z^2}{n_\beta^2}\right)^{-1/2} \approx \frac{mc\alpha_Z}{\hbar n}\left[1 + \frac{\alpha_Z^2}{2n}\left(\frac{1}{j+\frac{1}{2}} - \frac{1}{n}\right)\right]. \tag{2.164}$$

For $n = j + \frac{1}{2}$, the last bracket vanishes,

$$\kappa(n_r = 0) = \alpha_Z mc/\hbar n \equiv \kappa_{nr}. \tag{2.165}$$

Surprisingly, this is also the exact result, as insertion of $n_\beta^2 = \gamma^2$ into (1.129) shows. It happens to be the nonrelativistic expression (1.39), which appears in (1.38) for all n_r: $E_N = -\hbar^2\kappa_n^2/2m$. Insertion of u into (2.161) and (2.162) leads to the replacement $\partial_r \to \gamma/r - \kappa_n$. With $(\hbar/\alpha_Z)(-n+\gamma)[(\gamma+n)/r - \alpha_Z mc/\hbar n] = -\hbar\alpha_Z/r - mc(\gamma/n - 1)$ and $E/c = [m^2c^2 - \kappa_n^2]^{1/2} = mc\gamma/n$, the equation for u_g is reduced to

$$u_g = a[E/c + mc(2 - \gamma/n)]u = 2mcau. \tag{2.166}$$

The corresponding equation for u_f follows from (2.162) only up to a constant factor, which remains open in the solutions of the two identical equations (2.159). The precise expression for u_f follows instead from the original (2.157), $u_f = -(E/c + mc + \alpha_Z/r)^{-1}\hbar(\gamma/r - \kappa_n - n/r)u_g$. It takes some minutes to simplify this expression to

$$u_f = \alpha_Z^{-1}(n - \gamma)u_g, \tag{2.167}$$

the main tricks being the replacement of $E/c + mc$ in the denominator by $mc(\gamma+n)/n$ and of $\gamma + n$ by $-\alpha_Z^2/(\gamma - n)$. Otherwise, the only deviation from the nonrelativistic u_N is the replacement of r^{l+1} by r^γ. The main difference resides in the spinor $\chi_{\tilde{l}}^{jm}$ in ψ_f, which has $\tilde{l} = n$. For example, the ground state has

$$\chi_0^{1/2,m} = (4\pi)^{-1/2}\chi(m), \tag{2.168}$$

$$\chi_1^{1/2,m} = 3^{-1/2}[-(1 - m + \tfrac{1}{2})^{1/2}Y_1^{m-1/2}\chi(\tfrac{1}{2}) + (1 + m + \tfrac{1}{2})^{1/2}Y_1^{m+1/2}\chi(-\tfrac{1}{2})].$$

The elimination of the small components in a nonrelativistic expansion will be discussed in Sect. 2.8.

We have seen in (2.156) that $i\partial_r$ is Hermitian with respect to u_g and u_f, not with respect to g and f. It may be instructive to consider a volume element in a space of d dimensions, $d^d r = r^{d-1} dr d\Omega_{d-1}$. To make $i\partial_r$ a Hermitian operator, a factor $r^{(d-1)/2}$ must be absorbed by u and $u^\dagger$ each. The generalization of (2.155) is thus

$$g = r^{-(d-1)/2} u_g, \quad f = r^{-(d-1)/2} u_f,$$

$$r^{-(d-1)/2} \partial_r = [\partial_r + (d-1)/2r] r^{-(d-1)/2}.$$

For this reason,

$$\Delta_{r,d} = [\partial_r + (d-1)/2r]^2 = \partial_r^2 + (d-1) r^{-1} \partial_r + (d/2 - 3/2)(d/2 - 1/2) r^{-2} \tag{2.169}$$

may be identified with the radial part of the Laplacian in d dimensions. Rewriting the second factor in front of r^{-2} as $(d/2 - 3/2 + 1)$, one sees that the choice $d = 3+2l$ cancels the angular part $-l(l+1)r^{-2}$ of the 3-dimensional Laplacian. This trick has been discussed by Stillinger (1977) for the Coulomb Schrödinger equation. Relativistically, l is replaced by l_α, such that d is no longer integer.

The KG and Dirac equations may also be transformed into a radial harmonic oscillator in $d = 4 + 4l$ dimensions, by the substitution $r = s^2$ (see for example Dineykhan et al. 1995). However, none of these substitutions has produced practical progress yet.

Note that the 4×4 Dirac matrices $\boldsymbol{\alpha}$ and γ^0 are Hermitian, while the 2×2 matrix $\hat{\boldsymbol{l}}\boldsymbol{\sigma} + 1 + i\alpha_Z \sigma_r$ (2.140) is not. As the energies of bound states must be real, such non-Hermitian matrices in eigenvalue equations must have a property that guarantees real eigenvalues. In Sects. 1.8 and 1.9 we learnt that Hermitian matrices A ($A = A^\dagger$) have all eigenvalues real. In diagonal form, $A_{\text{diag}} \psi_i = a_i \psi_i$. We shall see now that the eigenvalues of any matrix remain unchanged under a "similarity transformation" with a matrix V,

$$A_{\text{sim}} = V A_{\text{diag}} V^{-1}. \tag{2.170}$$

With $V^{-1}V = 1$, this follows from

$$A_{\text{diag}} V^{-1} V \psi_i = a_i \psi_i, \quad V A_{\text{diag}} V^{-1} V \psi_i = a_i V \psi_i. \tag{2.171}$$

The eigenvalues are the solutions of the determinant equation, $\det(A_{\text{sim}} - a) = 0$, where $a = a \times 1$ is a multiple of the unit matrix. Writing $a = VaV^{-1}$, one obtains

$$\det[V(A_{\text{diag}} - a)V^{-1}] = \det(A_{\text{diag}} - a) = 0, \tag{2.172}$$

using $\det(VX) = \det(V)\det(X)$ (setting $a = a_i$, the diagonal matrix $A_{\text{diag}} - a_i$ has only zeros in the ith row, which makes the determinant vanish).

In nonrelativistic quantum mechanics, similarity transformations arise from changes of an orthonormal basis in Hilbert space (Sect. 1.9), in which case V is unitary ($V = U$, $U^{-1} = U^\dagger$), and $A_{\rm sim}$ is Hermitian. In relativistic quantum mechanics, non-unitary matrices V stem from the simultaneous use of two function spaces, ψ_r and ψ_l in the present case. Here one may impose $V^{-1} = V^*$, getting for (2.140)

$$A_{\rm sim} = \begin{pmatrix} -j_+ & -i\alpha_Z \\ -i\alpha_Z & j_+ \end{pmatrix} = V \begin{pmatrix} -\gamma & 0 \\ 0 & \gamma \end{pmatrix} V^*, \quad A_{\rm diag} = \begin{pmatrix} -\gamma & 0 \\ 0 & \gamma \end{pmatrix}, \tag{2.173}$$

$$V = \frac{\sqrt{\gamma + j_+}}{\sqrt{2\gamma}} \begin{pmatrix} 1 & i\alpha_Z(\gamma + j_+)^{-1} \\ -i\alpha_Z(\gamma + j_+)^{-1} & 1 \end{pmatrix}. \tag{2.174}$$

For $\psi_{r\pm}$ (2.137), the eigenstates of $A_{\rm diag}$ are now $V\psi_{r\pm}$. The value of $\hat{\beta}$ follows from (2.174) as

$$\hat{\beta} = (j + \tfrac{1}{2} - \gamma)/\alpha_Z = \beta/\alpha_Z. \tag{2.175}$$

However, such constructions fail for potentials other than $-\alpha_Z/r$. In general, the Kramers matrix element of an operator O follows from the orthogonality relations (2.207) below,

$$O_{fi} = \int \psi^\dagger_{l,f} O \psi_{r,i}. \tag{2.176}$$

The resulting form of hermiticity is $O^*_{fi} = O_{if}$. In the present example, the transformation (2.170) is unnecessary. Group theory became popular in quantum physics mainly after Wigner's book (1959); the correct statement that "observables may be represented by Hermitian matrices" has since been shortened to "observables are represented by Hermitian matrices". The counterexample of the Kramers equation was avoided in the Dirac equation. In Sect. 4.7, a normal, parity-invariant Dirac equation will be endowed with a non-Hermitian hyperfine operator $A_{\rm sim}$ which is necessary for positronium (Sect. 5.2).

The replacement of the nonrelativistic "centrifugal barrier potential" $l(l+1)/r^2$ by the smaller $\gamma(\gamma+1)/r^2$ becomes particularly important for nuclei of charge Ze, with $Z \gg 1$, $\alpha_Z \to 1$. For $j = 1/2$, γ becomes imaginary at $Z = 1/\alpha \approx 137$. For pionic atoms, $(l + \frac{1}{2})^2 - \alpha_Z^2$ becomes negative for $l = 0$ already at $Z = 1/2\alpha$. For ordinary atoms, the nuclear charge radius keeps $V(r)$ finite at $r = 0$. The "leptonium" bound states such as $e^-\mu^+$ have no helpful charge radius, but they have $Z = 1$, so there is no problem. Problems can arise when residual perturbations are approximated by operators that fail for $r \to 0$, see the next section.

Most operators of the quantum mechanical differential equations are expressed in terms of x^μ, ∂_μ, Pauli matrices $\boldsymbol{\sigma}$ etc. There are however several discrete operators for the classification of symmetry properties of the wave function. The parity transformation $\mathcal{P}$ was already defined in Sect. 1.5. One may formally write $\mathcal{P}\boldsymbol{r} = -\boldsymbol{r}\mathcal{P}$,

$$\mathcal{P} f(\boldsymbol{r}, t) = f(-\boldsymbol{r}, t), \quad \mathcal{P}^2 f = \mathcal{P} f(-\boldsymbol{r}, t) = f(\boldsymbol{r}, t). \tag{2.177}$$

Consequently, $\mathcal{P}^2 = 1$; the eigenvalues of $\mathcal{P}$ are $+1$ (even functions f) and -1 (odd ones). In this sense, it was said that the small components ψ_f (2.152) have the opposite parity of the large ones. The quantum mechanical parity transformation has an additional factor β, which is necessary to keep the Dirac equation invariant under the transformation $\boldsymbol{r} \to -\boldsymbol{r}$. Its connection with the classical space inversion (2.7) is in fact not unique, see Sect. 3.2 below. In any case, the transformation $\mathcal{P}\psi_D(\boldsymbol{r}, t) = \beta\psi_D(-\boldsymbol{r}, t)$ fulfills also $\mathcal{P}^2 = 1$. This property holds also for the operators $\mathcal{C}$ and $\mathcal{T}$ of Sect. 3.2, and for the two-particle exchange operator P_{12} which is needed for the formulation of the Pauli principle. The detailed quantum mechanical form of these operators follows from the appropriate wave equations, not from the Lorentz group of classical mechanics.

2.7 Alternative Form, Perturbations

The ansatz (2.161) for u_g and u_f leads to the radial solution $R = u/r$ of the Kramers equation, which is obtained from the solution of the KG-equation simply by replacing $l \to j$ in the quantum defect β. However, this approach seems to be restricted to the point Coulomb potential $V = -Ze^2/r$. In the presence of small additional operators, it is still possible to bring the radial equations (2.157) into a form that admits the extraction of the asymptotic factors $e^{-z/2}$ and $z^{l_\alpha+1}$ ($z = 2\kappa r$). We rewrite (2.157) as

$$\frac{mc^2 - c\pi^0}{2\hbar c\kappa} u_g + \left(\partial_z - \frac{\kappa_D}{z}\right) u_f = 0, \quad \frac{mc^2 + c\pi^0}{2\hbar c\kappa} u_f + \left(\partial_z + \frac{\kappa_D}{z}\right) u_g = 0, \tag{2.178}$$

with $c\pi^0 = E - V = E + Ze^2/r = E + 2\hbar c\kappa\alpha_Z/z$. Remembering $\hbar c\kappa = (m^2c^4 - E^2)^{1/2} = (mc^2 + E)^{1/2}(mc^2 - E)^{1/2}$, one sees that the constants to the left of u_g combine into $(mc^2 - E)/\hbar c\kappa = (mc^2 - E)^{1/2}/(mc^2 + E)^{1/2}$. We divide the equation by $(mc^2 - E)^{1/2}$ and define

$$(mc^2)^{1/2}(mc^2 + E)^{-1/2} u_g \equiv \hat{u}_g, \quad (mc^2)^{1/2}(mc^2 - E)^{-1/2} u_f \equiv \hat{u}_f. \tag{2.179}$$

After expressing u_f in terms of $\hat{u}_f$ also in the second equation (2.178), the square roots disappear again:

$$\left(\tfrac{1}{2} - \frac{\alpha_Z}{z}\frac{mc^2 + E}{\hbar c\kappa}\right) \hat{u}_g + \left(\partial_z - \frac{\kappa_D}{z}\right) \hat{u}_f = 0, \tag{2.180}$$

$$\left(\tfrac{1}{2} + \frac{\alpha_Z}{z}\frac{mc^2 - E}{\hbar c\kappa}\right) \hat{u}_f + \left(\partial_z + \frac{\kappa_D}{z}\right) \hat{u}_g = 0. \tag{2.181}$$

Next, we substitute

$$\hat{u}_g = u_+ + u_-, \quad \hat{u}_f = u_+ - u_-. \tag{2.182}$$

From the sum and difference of (2.180) and (2.181), one obtains

$$(\tfrac{1}{2}-n_\beta/z-\partial_z)u_- = z^{-1}(m_\beta+\kappa_D)u_+, \quad (\tfrac{1}{2}-n_\beta/z+\partial_z)u_+ = z^{-1}(m_\beta-\kappa_D)u_-, \tag{2.183}$$

$$n_\beta = \alpha_Z E/\hbar c\kappa, \quad m_\beta = \alpha_Z mc^2/\hbar c\kappa, \quad m_\beta^2 - n_\beta^2 = \alpha_Z^2. \tag{2.184}$$

We may now separate the factor $e^{-z/2}$, and then insert the first equation into the second one:

$$u_\pm = e^{-z/2}v_\pm, \quad v_+ = -(m_\beta+\kappa_D)^{-1}(z\partial_z + n_\beta - z)v_-, \tag{2.185}$$

$$[(\partial_z - n_\beta/z)(z\partial_z + n_\beta - z) + (m_\beta^2 - \kappa_D^2)/z]v_- = 0. \tag{2.186}$$

With $\kappa_D^2 = (j+\frac{1}{2})^2$, this equation does not distinguish between $l = j - \frac{1}{2}$ and $l = j + \frac{1}{2}$,

$$(z\partial_z^2 + (1-z)\partial_z + n_\beta - 1 - \gamma^2/z)v_- = 0. \tag{2.187}$$

The term $-\gamma^2/z$ is removed by the substitution

$$v_\pm = z^\gamma w_\pm, \quad [z\partial_z^2 + (2\gamma+1-z)\partial_z + n_\beta - \gamma - 1]w_- = 0. \tag{2.188}$$

This is again the confluent hypergeometric differential equation (1.119). Apart from a normalization constant, its present solution is

$$F_- = F(1-n_r', b_D, z), \quad n_r' = n_\beta - \gamma, \quad b_D = 2\gamma + 1. \tag{2.189}$$

For the exponentially falling functions F, n_r' must a positive integer. However, we can include the value $n_r' = 0$ by a zero in the normalization factor,

$$w_- = -N_\gamma x_- F_-, \quad x_- = \sqrt{(\gamma - n_\beta)(\kappa_D + m_\beta)}. \tag{2.190}$$

This implies $w_-(n_r'=0) = 0$, but the complete solution remains normalized, due to $w_+(n_r'=0) \neq 0$, see below. Comparison with the definition (1.126) $n_r = n_\beta - l_\alpha - 1$ shows $n_r = n_r'$ for $\gamma = l_\alpha + 1$ ($l = j - 1/2$), and $n_r = n_r' - 1$ for $\gamma = l_\alpha$ ($l = j + 1/2$). The case distinction of the previous section is now unnecessary. Insertion of v_- into (2.185) gives

$$v_+ = N_\gamma x_- (\kappa_D + m_\beta)^{-1} z^\gamma (z\partial_z - z + n_\beta + \gamma)F_-. \tag{2.191}$$

This expression is simplified using the relation

$$(z\partial_z - z + b - a - 1)F(1+a, b, z) = (b-a-1)F(a, b, z): \tag{2.192}$$

$$(z\partial_z - z + n_\beta + \gamma)F_- = (\gamma + n_\beta)F(-n_r', b_D, z).$$

Combination of the constants leads to

$$v_+ = N_\gamma x_+ z^\gamma F(-n_r', b_D, z), \quad x_+ = \sqrt{(\gamma + n_\beta)(\kappa_D - m_\beta)}. \tag{2.193}$$

This is so because

$$\gamma^2 - n_\beta^2 = \gamma^2 - m_\beta^2 + \alpha_Z^2 = \kappa_D^2 - m_\beta^2. \tag{2.194}$$

It is customary to denote n_r' by n_r, even if this is confusing for $l = j + \frac{1}{2}$, not only with the solution $R = u/r$ (2.145) of the Kramers equation, but also with the solutions u_g and u_f (2.158) in terms of the Kramers u. In summary, $g = u_g/r$ and $f = u_f/r$ have

$$u_{g,f} = N_\gamma e^{-z/2} z^\gamma (1 \pm E/mc^2)^{1/2} [x_+ F(-n_r, b_D, z) \mp x_- F(1 - n_r, b_D, z)]. \tag{2.195}$$

Note also that $b = 2l_\alpha + 2$ is near an even integer in u, whereas $b_D = 2\gamma + 1$ is near an odd one in u_g and u_f. Only for $j = n - \frac{1}{2}$, $n_r = 0$ implies $n_r F_- = 0$ and $u_g \sim u$ as in (2.166). The constant N_γ in (2.195) follows from the wave function normalization (Appendix A),

$$\int r^2 dr (g^2 + f^2) = \int dr (u_g^2 + u_f^2) = 1. \tag{2.196}$$

The unbound electrons have $E > mc^2$, $k = i\kappa = (E^2 - m^2c^4)^{1/2}/\hbar c > 0$. The effective principal quantum number n_β is replaced by the continuous parameter $-i\eta$ as in (1.140),

$$n_\beta = i\alpha_Z E/\hbar ck = -i\eta, \quad m_\beta = i\alpha_Z mc/\hbar k = -i\eta mc^2/E. \tag{2.197}$$

This implies $x_+^* = x_-$, and

$$x_- = e^{-i\xi}, \quad x_+ = e^{i\xi} = \sqrt{(\gamma - i\eta)/(\kappa_D - i\eta mc^2/E)}. \tag{2.198}$$

The exponential $e^{-z/2} = e^{-\kappa r}$ receives its original form e^{ikr}, and the second confluent hypergeometric function F_- of (2.195) is eliminated using

$$F(a, b, z) = e^z F(b - a, b, -z). \tag{2.199}$$

Finally, $(mc^2 - E)^{1/2} = i(E - mc^2)^{1/2}$, such that (2.195) becomes

$$\begin{pmatrix} u_g \\ u_f \end{pmatrix} = -2iN_\gamma (-2ikr)^\gamma \begin{pmatrix} (E + mc^2)^{1/2} Im \\ (E - mc^2)^{1/2} Re \end{pmatrix} e^{ikr + i\xi} F(\gamma + i\eta, b_D, -2ikr). \tag{2.200}$$

The solutions of the Dirac equation fulfill orthogonality relations, which may be written in various ways. The stationary form of (2.87), $H\psi = E\psi$ is the standard starting point, as it has the same appearance as the nonrelativistic Schödinger equation. The index $_D$ for Dirac is dropped here, but it must be remembered that $\psi = \psi_D$ has four components, both in the chiral (2.88) and parity (2.151) bases. The Dirac equation for $\boldsymbol{A} = 0$ and its Hermitian adjoint may be written as

$$H\psi_i = E_i \psi_i, \quad \psi_j^\dagger H^\dagger = E_j \psi_j^\dagger, \quad H^\dagger = V + c\boldsymbol{p}^\dagger \boldsymbol{\alpha} + mc^2 \beta. \tag{2.201}$$

The symbol $\boldsymbol{p}^\dagger$ is uncommon as $-i\hbar\nabla = \boldsymbol{p}$ is a Hermitian operator, but it is convenient here before integrating over all space, meaning $\psi^\dagger \boldsymbol{p}^\dagger = (-i\hbar\nabla\psi)^\dagger = \psi^\dagger i\hbar\overleftarrow{\nabla}$ in analogy with (1.198). Multiplying the first equation in (2.201) by $\psi_j^\dagger$, the second one by ψ_i from the right and integrating the difference of these two combinations over all space, one gets

$$\int \psi_j^\dagger (H - H^\dagger)\psi_i d^3r = 0 = (E_i - E_j) \int \psi_j^\dagger \psi_i d^3r, \tag{2.202}$$

from which the orthonormality relations follow as

$$\int \psi_j^\dagger \psi_i d^3r = \delta_{ij}. \tag{2.203}$$

The spin-angular functions χ_l^{jm} that form part of ψ in a spherically symmetric potential $V(r)$ are separately orthonormal in (l, j, m) according to (2.133), such that (2.202) is reduced to orthonormality relations for the radial functions $g = u_g/r$ and $f = u_f/r$,

$$\int r^2 dr(g_{n'} g_n + f_{n'} f_n) = \int dr(u_{g,n'} u_{g,n} + u_{f,n'} u_{f,n}) = \delta_{n'n}. \tag{2.204}$$

In the chiral basis, (2.203) becomes

$$\int (\psi_{rj}^\dagger \psi_{ri} + \psi_{lj}^\dagger \psi_{li}) d^3r = \delta_{ij}, \tag{2.205}$$

as (2.151) shows. If one now eliminates

$$\psi_{li} = (\pi_i^0 - \boldsymbol{\pi}\boldsymbol{\sigma})\psi_{ir}/mc, \quad \psi_{rj}^\dagger = \psi_{lj}^\dagger (\pi_j^0 + \overleftarrow{\boldsymbol{\pi}}^* \boldsymbol{\sigma})/mc, \tag{2.206}$$

one obtains again the KG form (1.197):

$$\int \psi_{lj}^\dagger (E_j + E_i - 2V)\psi_{ri} d^3r = mc^2 \delta_{ij}. \tag{2.207}$$

This result follows also directly from (2.80): When the "non-Hermitian" operator $(\pi^0 + \boldsymbol{\pi}\boldsymbol{\sigma})(\pi^0 - \boldsymbol{\pi}\boldsymbol{\sigma})$ operates on $\psi_l^\dagger$ to the left, the factors come in the order required by (2.85).

The perturbation theories of the Dirac equation and the nonrelativistic Schrödinger or Pauli equations are formally identical. The equation to be solved is

$$(H_0 + H_{\text{per}})\psi_n = E_n \psi_n, \tag{2.208}$$

where both H_0 and H_{per} are time-independent operators, and the unperturbed equation has known and exact solutions. The perturbed equation is solved by expanding both E_n and ψ_n in a power series of the matrix elements of H_0,

$$E_n = E_n^0 + E_n^1 + E_n^{(2)} \ldots, \tag{2.209}$$

$$\psi_n = \psi_n^0 + \psi_n^1 + \psi_n^{(2)} \ldots . \tag{2.210}$$

The unperturbed equation is

$$H_0\psi_n^0 = E_n^0\psi_n^0; \tag{2.211}$$

it is identical with one of the previously solved equations $H\psi_n = E_n\psi_n$. But as it does not solve (2.208), an index 0 is necessary in the formulas; it will be dropped in the final result. To second order in the matrix elements of $H_{\rm per}$, the series expansions (2.209) and (2.210) give

$$H_0\psi_n^1 + H_{\rm per}\psi_n^0 = E_n^0\psi_n^1 + E_n^1\psi_n^0, \tag{2.212}$$

$$H_0\psi_n^{(2)} + H_{\rm per}\psi_n^1 = E_n^0\psi_n^{(2)} + E_n^1\psi_n^1 + E_n^{(2)}\psi_n^0. \tag{2.213}$$

To solve (2.212), one multiplies it with $\psi_n^{0\dagger}$ and integrates over d^3r. For a normalized unperturbed wave function, $\int \psi_n^{0\dagger}\psi_n^0 = 1$, the result is

$$E_n^0 \int \psi_n^{0\dagger}\psi_n^1 + E_n^1 = \int \psi_n^{0\dagger} H_0\psi_n^1 + \int \psi_n^{0\dagger} H_{\rm per}\psi_n^0. \tag{2.214}$$

As H_0 is Hermitian, $H_0 = H_0^\dagger$, the integral with H_0 may be rewritten as

$$\int \psi_n^{0\dagger} H_0\psi_n^1 = \int (H_0\psi_n^0)^\dagger\psi_n^1 = E_n^0 \int \psi_n^{0\dagger}\psi_n^1. \tag{2.215}$$

This integral cancels in (2.214), leaving

$$E_n^1 = \int \psi_n^{0\dagger} H_{\rm per}\psi_n^0 \equiv \langle H_{\rm per}\rangle_n. \tag{2.216}$$

According to the definitions of Sect. 1.9, the energy shift E^1 in first-order perturbation theory is the expectation value of the perturbation in the unperturbed state. From (2.213), one can now express $E_n^{(2)}$ in terms of the nondiagonal matrix elements of $H_{\rm per}$. With the bra and ket notation (1.246) they read

$$\langle n|H_{\rm per}|k\rangle = \int \psi_n^\dagger H_{\rm per}\psi_k. \tag{2.217}$$

The index ^{0} of unperturbed states is now omitted. The hermiticity of H_0 gives $\langle n|H_0|n^{(2)}\rangle = E_n^0\langle n|n^{(2)}\rangle$ on the right-hand side of (2.213), such that the equation is simplified to

$$E_n^1\langle n|n^1\rangle + E_n^{(2)} = \langle n|H_{\rm per}|n^1\rangle, \tag{2.218}$$

where we have used the normalization $\langle n|n\rangle = 1$ for the coefficient of $E_n^{(2)}$. We still need the perturbed state $|n^1\rangle$, which we expand in terms of the complete set of unperturbed states $|k\rangle$ (of energies E_k^0) as in (1.199):

$$|n^1\rangle = \Sigma_k c_{kn}|k\rangle, \quad \langle k|n^1\rangle = c_{kn}, \quad \langle k|n\rangle = \delta_{kn}. \tag{2.219}$$

Multiplication of (2.212) by $\psi_k^{0\dagger}$ and integration gives the following relation for the c_{kn}:

$$E_n^0 c_{kn} + E_n^1\delta_{kn} = E_k^0 c_{kn} + \langle k|H_{\rm per}|n\rangle. \tag{2.220}$$

The term with $k = n$ leads again to the expression (2.216). The coefficient c_{nn} cancels out and cannot be determined this way; it is set equal to zero in order to keep the perturbed state $|n\rangle + |n^1\rangle$ normalized:

$$(\langle n| + \langle n^1|)(|n\rangle + |n^1\rangle) = \langle n|n\rangle = 1 : \quad \langle n|n^1\rangle \approx 0. \tag{2.221}$$

Geometrically, the small vector $|n^1\rangle$ must be orthogonal to $|n\rangle$ in order not to affect its length. Thus (2.220) gives

$$c_{kn} = (E_n^0 - E_k^0)^{-1}\langle k|H_{\rm per}|n\rangle. \tag{2.222}$$

Its insertion into (2.218 produces the final result

$$E_n^{(2)} = \Sigma_{k\neq n}\langle n|H_{\rm per}|k\rangle\langle k|H_{\rm per}|n\rangle(E_n^0 - E_k^0)^{-1}. \tag{2.223}$$

Unfortunately, many of the more complicated perturbative operators are calculated with nonrelativistic approximations, which normally deteriorate their behaviour for $r \to 0$. Examples to the order α_Z^4 will be given in the next section. In such cases, the relativistic wave function R cannot be used for s-states, where it diverges as $z^{l\alpha} = z^{l-\beta} = z^{-\beta}$. To the orders $\alpha_Z^6 \log \alpha_Z^2$ and α_Z^6, there exists a special nonrelativistic expansion of quantum electrodynamics (NRQED), with nonrelativistic field operators, in which the only allowed nonperturbative equation is the Schrödinger equation (see for example Kinoshita 1996). All terms beyond the Bohr formula are calculated perturbatively. A special "dimensional regularization" method yields in fact closed analytic results (Czarnecki et al., 1999). For a while, some of its results could only be derived from NRQED. However, relativistic equations are indispensable beyond α_Z^6, particularly for atoms and ions with high Z. In later chapters, the KG, Dirac etc. equations will be derived from the S-matrix of QED, which is both Lorentz invariant and easily calculated. The S-matrix is given in a Born series which has no bound states. Its reproduction by the solutions of differential (or integral) equations provides bound states, which are nonperturbative solutions of QED. As it is not possible to reproduce the full S-matrix in one step, many small elements must be included perturbatively. Every perturbation must be included with its correct analytic properties in coordinate space. This implies that perturbations from "loops" must be calculated from "dispersion integrals", which in coordinate space provide integrals over "Yukawa potentials", of the form $\int dx f(x) e^{-xr}/r$. This will be explained in Sect. 5.3 for the vacuum polarization ("Uehling potential") and in Appendix C. However, some of the effects can be anticipated by ad hoc modifications of the relativistic wave function, mainly for $r \to 0$.

Ordinary atoms have "Rydberg states", in which one electron occupies an orbital with n up to 100, and l up to 10, depending on the excitation mechanism. The resulting "Rydberg spectrum" is practically hydrogenic, corresponding to $V = -e^2/r$. There exists a vast literature on the modification of V for $r \to 0$ (Drake 1982, 1993). It comprises a "quantum defect theory" (Seaton 1966), even in a relativistic version (Johnson and Cheng 1979).

However, the problem is complicated by the presence of the "core" electrons (Sects. 3.5 and 3.8). It is clearest for the "leptonium" bound states, where no nuclear charge distribution "softens" V for $r \to 0$.

In the leptonium context, an approximate removal of the divergence of R was started by Fried and Yennie (1958). With $\beta = l - l_\alpha$, $z^{-\beta} = e^{-\beta \log z}$ is approximated by $1 - \beta \log z$. Insertion of $z = 2\kappa r = 2Er\kappa/E$ gives

$$\log z = \log(2\alpha_Z/n) + \log(Er). \tag{2.224}$$

Suppressing the index _ in the Kramers solution, one obtains for $l = 0$,

$$R/N = e^{-\kappa r}[1 - \beta \log(2\alpha_Z/n) - \beta \log(Er)]F(-n_r,\, 2 - 2\beta,\, z), \quad \beta_0 = \alpha_Z^2, \tag{2.225}$$

with $\beta_0 = \alpha_Z^2$ for KG and $\beta_{1/2} = \frac{1}{2}\alpha_Z^2$ for Kramers. Next, one may adjust the asymptotic behaviour of $R(z \to \infty)$, which is done here for arbitrary l: Using a relation explained in the course of Landau and Lifshitz (1977),

$$F(-n_r,\, b,\, z) \sim (-z)^{n_r} \Gamma(b)/\Gamma(n_r + b), \tag{2.226}$$

the first-order expansion of $\Gamma(n_r + b) = \Gamma(n_r + 2l + 2 - 2\beta_l)$ gives $\Gamma_{nr} - 2\beta_l \Gamma'_{nr}$ with $\Gamma_{nr} = \Gamma(n_r + 2l + 2)$. Consequently, for $l = 0$ and $z \to \infty$,

$$R(-n_r,\, -2\beta + 2,\, z) \sim R(-n_r\, 2,\, z)[1 + 2\beta(\Psi(n+1) - \Psi(1))], \tag{2.227}$$

$$\Psi = \Gamma'/\Gamma, \quad \Psi(1) = -\gamma_{\mathrm{Eu}}, \quad \Psi(n+1) - \Psi(1) = \Sigma_{i=1}^{n} i^{-1}. \tag{2.228}$$

($\gamma_{\mathrm{Eu}} = 0.5772\ldots$ is the Euler constant).

The remaining procedure in the adjustment of the relativistic wave function is still somewhat incomplete. Gupta et al. (1989) found an operator

$$r_G^{-3} = -\Delta[\log(\mu r)/r + \gamma_{\mathrm{Eu}}/r], \quad \Delta f = [\nabla, [\nabla, f]], \tag{2.229}$$

$$\langle r_G^{-3} \rangle = \langle r^{-3} \rangle \quad \text{for } l > 0, \tag{2.230}$$

where $\mu = m_1 m_2/m_{12}$ ($m_{12} = m_1 + m_2$). By partial integration,

$$\langle r_G^{-3} \rangle_{l=0} = 2\alpha_Z^3 \mu^3 n^{-3}[-\log(n/2\alpha_Z) + \Psi(n+1) + \gamma_{\mathrm{Eu}} - \tfrac{1}{2}n^{-1} + \tfrac{1}{2}]. \tag{2.231}$$

Inspection of the higher-order QED results shows that a first approximation for R is

$$R = R_{\beta=0}(1 - \beta \langle r_G^{-3} n^3 \rangle / \alpha_Z^3 \mu^3). \tag{2.232}$$

Note that $\langle r_G^{-3} \rangle_{l=0} < 0$ for small α_Z. Complete corrections to order α_Z^2 will be derived in Appendix C.

When the relativistic expectation value does not exist, both the zeroth and first-order in β expectation values must use (2.232). Higher orders in n_β^{-1} are included in the approximation $n_\beta = n$. For perturbations with a radial dependence r^{-2} (such as the hyperfine perturbation of Sect. 5.1), the expectation value is still the relativistic one. There is however a recoil correction

to first order in β, which has $1/\mu^3$ replaced by $1/\mu^2 m_{12}$. The Gupta operator occurs also in the "Salpeter shift", to be mentioned in connection with the Lamb shift of Sect. 5.5.

A precise formalism based on (2.232) does not exist. In a careful calculation of perturbations, singular operators such as $\delta(\boldsymbol{r})$ simply do not occur. Thus the factor $z^{-\beta}$ of R poses no problem. In the "quarkonium" model of mesons, the phenomenological potential is expected to be less singular than r^{-1} at $r = 0$ (see also Sect. 4.10).

The radial Dirac functions g and f may be regularized at $r = 0$ by defining $g_{\rm reg} = r^{\beta-1}u_g$, $f_{\rm reg} = r^{\beta-1}u_f$, provided the operator $\partial_r + r^{-1}$ is also modified, $(\partial_r + r^{-1} - \beta r^{-1})r^{\beta-1} = r^{\beta-1}\partial_r$, compare (2.169). But as the orthogonality relations (2.196) are also modified, nothing is gained for perturbation theory.

The Dirac equation may also be modified by a gauge vector potential, $\boldsymbol{A} = \boldsymbol{\nabla}\Lambda(r) \equiv \hat{\boldsymbol{r}}W(r)$, which does not contribute to $\boldsymbol{B}$ (see (1.53) and (1.55)). Suitable choices of W may then produce equations with exact solutions. The choice $W = \tilde{W} - \kappa_D/r$ (Alhaidari 2001) sets $\kappa_D = 0$ in (2.178) and produces an equation without any angular momentum, $\boldsymbol{j} = \hat{\boldsymbol{l}} + \boldsymbol{\sigma}/2 = 0$. That equation is solved exactly for Morse-type potentials, $V_{\rm Morse} = V_0[e^{-2(R-R_0)/a} - 2e^{-(R-R_0)/a}]$, where the variable R refers to the distance between the two nuclei of a diatomic molecule. To treat a molecule by an equation which suppresses the electronic coordinates requires an "adiabatic" approximation, valid for very slow nuclear motion. It is not clear that such a modified Dirac equation would be useful for relativistic effects in the adiabatic approximation.

2.8 The Pauli Equation

In the discussion of the KG equation, we mentioned the connection with the nonrelativistic Schrödinger equation in (1.77) for stationary solutions, where $\pi^0 = i\hbar\partial_0 - V/c$ is replaced by $(E - V)/c$. For time-dependent solutions, the connection is more complicated, as the KG equation is of second order in ∂_0, while the nonrelativistic equation is of first order. The Dirac equation, on the other hand, is already first-order, which slightly simplifies the derivation of the nonrelativistic Pauli equation. The derivation leads to familiar concepts such as kinetic energy and spin-orbit interaction, which are not at all evident from (2.153), let alone the chiral (2.84) or second-order (2.82) forms.

In the nonrelativistic reduction, the small components ψ_f may be eliminated from the first equation of (2.153) by means of the second one. One substitutes

$$\psi_D = e^{imcx_0/\hbar}\psi'_D, \tag{2.233}$$

which removes the mc from $\pi^0_- = \pi^0 - mc$, and adds mc to $\pi^0_+ = \pi^0 + mc$:

$$\pi^0_N\psi'_g = \boldsymbol{\sigma\pi}\psi'_f, \quad (\pi^0_N + 2mc)\psi'_f = \boldsymbol{\sigma\pi}\psi'_g. \tag{2.234}$$

The index $_N$ indicates that the eigenvalue of $i\hbar\partial_t$ is now $E_N = E - mc^2$. In nonrelativistic problems, the matrix elements of $V(r)$ and eigenvalues of $i\hbar\partial_t$ are both much smaller than mc^2, such that one may expand $\pi_N^0 + 2mc$ in terms of $\pi_N^0/2mc$:

$$\psi'_f = (\pi_N^0 + 2mc)^{-1}\boldsymbol{\sigma\pi}\psi'_g \approx (2mc)^{-1}(1 - \pi_N^0/2mc)\boldsymbol{\sigma\pi}\psi'_g. \tag{2.235}$$

One sets $\partial_0 = \partial_t/c$ and multiplies the first of (2.234) by c:

$$(i\hbar\partial_t - V)\psi'_g = [(\boldsymbol{\sigma\pi})^2/2m - \boldsymbol{\sigma\pi}c\pi_N^0\boldsymbol{\sigma\pi}/4m^2c^2]\psi'_g. \tag{2.236}$$

The first term on the right-hand side is brought to the other side and combined with V into the Pauli Hamiltonian

$$H_P = (\boldsymbol{\sigma\pi})^2/2m + V = (\boldsymbol{\pi}^2 + \hbar e\boldsymbol{\sigma B}/c)/2m + V \tag{2.237}$$

(the second form uses (2.60)). The rest is a relativistic "perturbation". The corresponding ψ'_g is the ψ_N of (1.67):

$$(i\hbar\partial_t - H_P)\psi_N = 0. \tag{2.238}$$

In the time-independent perturbation theory, the perturbing operator must not contain t or ∂_t. For the case at hand, the ∂_t which is part of $c\pi_N^0$ on the right-hand side of (2.236) was eliminated by Pauli. He substituted

$$\psi'_g = (1 - W^2/2)\psi, \quad W = \boldsymbol{\sigma\pi}/2mc, \tag{2.239}$$

multiplied the equation by $1 - W^2/2$ from the left and neglected these factors in connection with $\boldsymbol{\sigma\pi}c\pi_N^0\boldsymbol{\sigma\pi}/4m^2c^2$ which is already small:

$$(1 - W^2/2)(i\hbar\partial_t - H_P)(1 - W^2/2)\psi = (-i\hbar\partial_t W^2 + WVW)\psi. \tag{2.240}$$

Here we have used $W\partial_t W = \partial_t W^2$, assuming that W is time-independent. These terms cancel out in (2.240). Two new terms $W^2H_P/2$ and $H_PW^2/2$ arise on the left-hand side and are transferred to the right:

$$(i\hbar\partial_t - H_P)\psi = H_r\psi, \tag{2.241}$$

$$H_r = -\tfrac{1}{2}[W^2(\boldsymbol{\sigma\pi})^2 + (\boldsymbol{\sigma\pi})^2W^2]/2m - \tfrac{1}{2}W^2V - \tfrac{1}{2}VW^2 + WVW. \tag{2.242}$$

The last three terms make a double commutator:

$$H_r = -(\boldsymbol{\sigma\pi})^4/8m^3c^2 - \tfrac{1}{2}[W,[W,V]], \tag{2.243}$$

$$[W,V] = [\boldsymbol{\sigma\pi},V]/2mc = -i\hbar V'r^{-1}\boldsymbol{r\sigma}/2mc = -i\hbar V'\sigma_r/2mc, \tag{2.244}$$

$$-[W,[W,V]] = -i\hbar[\boldsymbol{\sigma\pi},V'\sigma_r]/4m^2c^2 = [-\hbar^2\Delta V - 2\hbar V'\boldsymbol{\sigma}(\boldsymbol{\pi}\times\hat{\boldsymbol{r}})]/4m^2c^2. \tag{2.245}$$

The symbol ΔV is a common abbreviation for $[\nabla,[\nabla,V]]$, to be evaluated below. With $\boldsymbol{\pi}=\boldsymbol{p}+e\boldsymbol{A}/c$, the term $-\boldsymbol{p}\times\hat{\boldsymbol{r}}$ is written as $r^{-1}\boldsymbol{r}\times\boldsymbol{p}=\hbar\hat{\boldsymbol{l}}/r$; this piece provides the spin-orbit potential:

$$V_{sl}=\hbar^2V'\boldsymbol{\sigma}\hat{\boldsymbol{l}}/4m^2c^2r. \tag{2.246}$$

The term

$$-\hbar^2\Delta V/8m^2c^2=V_{\mathrm{Da}} \tag{2.247}$$

is called the Darwin term. In summary, one has

$$H_r=-(\boldsymbol{\sigma\pi})^4/8m^3c^2+V_{\mathrm{Da}}+V_{sl}-\hbar eV'\boldsymbol{\sigma}(\boldsymbol{A}\times\boldsymbol{r})/4m^2c^3r. \tag{2.248}$$

The first operator in H_r is "kinematical", i.e. independent of V. Classically, one would have the expansion (1.33), with p^μ replaced by π^μ:

$$c\pi^0=(m^2c^4+c^2\boldsymbol{\pi}^2)^{1/2}=mc^2+\boldsymbol{\pi}^2/2m-\boldsymbol{\pi}^4/8m^3c^2\ldots \tag{2.249}$$

for an electron $\boldsymbol{\pi}^2$ is replaced by $(\boldsymbol{\sigma\pi})^2$.

The appearence of $(\boldsymbol{\sigma\pi})^4$ and other singular operators in H_r must not upset the basic structure of (2.241) as a second-order differential equation. This is achieved by the perturbation theory of Sect. 2.7, in which we now set $H_0=H_P$ and $H_{\mathrm{per}}=H_r$:

$$E_n^1=\int\psi_n^{0\dagger}H_r\psi_n^0\equiv\langle H_r\rangle_n. \tag{2.250}$$

The expectation value of the square of a Hermitian operator A_{H} may be evaluated symmetrically:

$$\int\psi_n^{0\,\dagger}A_{\mathrm{H}}^2\psi_n^0=\int(A_{\mathrm{H}}\psi_n^0)^\dagger A_{\mathrm{H}}\psi_n^0 \tag{2.251}$$

This is useful for $-(\boldsymbol{\sigma\pi})^4/8m^3c^2$, because one may then replace $(\boldsymbol{\sigma\pi})^2/2m\psi_n^0$ by $(E_{Nn}^0-V)\psi_n^0$. In this way one finds

$$\langle(\boldsymbol{\sigma\pi})^4/8m^3c^2\rangle_n=\langle(E_{Nn}^0-V)^2/2mc^2\rangle_n. \tag{2.252}$$

This correction appears unchanged in the nonrelativistic reduction of the KG equation, where $\boldsymbol{\pi}^4/8m^3c^2$ is eliminated by the nonrelativistic Schrödinger equation, $\boldsymbol{\pi}^2/2m\psi_n^0=(E_{Nn}^0-V)\psi_n^0$.

Whereas the Pauli equation with relativistic corrections is useful for more complex systems, the small components are more easily eliminated directly from (2.153),

$$(E-V-mc^2)\psi_g=\boldsymbol{\sigma\pi}c^2(E-V+mc^2)^{-1}\boldsymbol{\sigma\pi}\psi_g, \tag{2.253}$$

by expanding the denominator in terms of V alone:

$$(E+mc^2-V)^{-1}\approx(E+mc^2)^{-1}+V/(E+mc^2)^2. \tag{2.254}$$

The equation is now multiplied by $E + mc^2$, and the small term $c^2\boldsymbol{\sigma\pi}V\boldsymbol{\sigma\pi}/(E + mc^2)$ is approximated by $\boldsymbol{\sigma\pi}V\boldsymbol{\sigma\pi}/2m$:

$$[E^2 - m^2c^4 - (E + mc^2)V - (c\boldsymbol{\sigma\pi})^2 - \boldsymbol{\sigma\pi}V\boldsymbol{\sigma\pi}/2m]\psi_g = 0. \tag{2.255}$$

One may now rewrite $-\boldsymbol{\sigma\pi}V\boldsymbol{\sigma\pi}$ as $\frac{1}{2}[\boldsymbol{\sigma\pi}, [\boldsymbol{\sigma\pi}, V]] - \frac{1}{2}(\boldsymbol{\sigma\pi})^2V - \frac{1}{2}V(\boldsymbol{\sigma\pi})^2$ and replace both $\frac{1}{2}(\boldsymbol{\sigma\pi})^2V$ and $\frac{1}{2}V(\boldsymbol{\sigma\pi})^2$ by $m(E - mc^2 - V)V$ on account of their expectation values for ψ_N (2.238). The result is the old KG equation, augmented by the double commutator:

$$[E^2 - m^2c^4 - 2EV + V^2 - (c\boldsymbol{\sigma\pi})^2 + [\boldsymbol{\sigma\pi}, [\boldsymbol{\sigma\pi}, V]]/4m]\psi_g = 0. \tag{2.256}$$

It will be useful when hyperfine vector potentials are included in $\boldsymbol{\pi}$.

For the explicit calculation of $\langle H_r\rangle$ (indices are now supressed), one needs the expectation values of r^{-s} for $s = 1, 2, 3$. They are collected here for a hydrogen-like ion of nuclear charge Ze, for s up to 6:

$$\langle r^{-1}\rangle = \kappa_n/n, \quad \kappa_n \equiv \alpha_Z mc^2/\hbar cn = Z/a_{\mathrm{B}}n, \tag{2.257}$$

$$\langle r^{-2}\rangle = \kappa_n^2[n(l + \tfrac{1}{2})]^{-1}, \tag{2.258}$$

$$\langle r^{-3}\rangle = \kappa_n^3[L^2(l + \tfrac{1}{2})]^{-1}, \quad L^2 = l(l + 1), \tag{2.259}$$

$$\langle r^{-4}\rangle = \kappa_n^4 n^{-1}(3n^2/L^2 - 1)/(L^2 - 3/4)(2l + 1),$$

$$\langle r^{-5}\rangle = n\kappa_n\langle r^{-4}\rangle(5n^2 - 3L^2 + 1)/(3n^2 - L^2)(L^2 - 2),$$

$$\langle r^{-6}\rangle = \kappa_n^2\langle r^{-4}\rangle[35n^2 - 30L^2 + 25 + 3L^2(L^2 - 2)/n^2] \\ /(3n^2 - L^2)(L^2 - 2)(4L^2 - 15).$$

All $\langle r^{-s}\rangle$ are odd functions of n; $\langle r^{-2}\rangle$ and $\langle r^{-3}\rangle$ are both proportional to n^{-3}, which will be exploited below.

For the Darwin term, one also needs the wave function at the origin. With $|Y_0^0|^2 = 1/4\pi$ (Table 1.1) and the nonrelativistic normalization constant (A.13) for $l = 0$, $N^2(l = 0) = 4\kappa_n^3$,

$$|\psi(0)|^2 = N^2(l = 0)/4\pi = \kappa_n^3/\pi. \tag{2.260}$$

With $V' = dV/dr$ and $V = -Ze^2/r$, one has

$$\Delta V = [\nabla, [\nabla, V]] = V'' + 2V'/r = 0. \tag{2.261}$$

On the other hand, as $\boldsymbol{E} = -[\nabla, A^0] = [\nabla, V/e]$ is the nuclear electric field, the Maxwell equation (1.52) $[\nabla, \boldsymbol{E}] = 4\pi\rho_{\mathrm{el}}$ becomes

$$\Delta V = -e4\pi\rho_{\mathrm{el}}. \tag{2.262}$$

The point limit $Ze\delta(\boldsymbol{r})$ (1.62) of $\rho_{\rm el}$ gives $\Delta V = -4\pi\alpha_Z\delta(\boldsymbol{r})$:

$$\langle V_{\rm Da}\rangle = \hbar^2\langle -\Delta V\rangle/8m^2c^2 = \hbar^2\langle\alpha_Z 4\pi\delta(\boldsymbol{r})\rangle/8m^2c^2, \tag{2.263}$$

$$\langle V_{\rm Da}\rangle = \alpha_Z\hbar^2\delta_{l,0}\pi|\psi(0)|^2/2m^2c^2 = \alpha_Z\hbar^2\delta_{l,0}\kappa^3/2m^2c^2. \tag{2.264}$$

$\langle V_{sl}\rangle$ is now calculated as expectation value over the unperturbed wave function,

$$\psi^0 = R(r)\chi_l^{jm}(\theta,\ \phi), \tag{2.265}$$

where l is the orbital angular momentum of the large components, but m_l and m_s are still mixed according to the prescription (2.132) for χ_l^{jm}, such that one can use $\hat{\boldsymbol{l}}\boldsymbol{\sigma}\psi^0 = [(j-l)(2j+1)-1]\psi^0$ from (2.121). Insertion of a factor $1 = 4(j-l)^2$ gives

$$\hat{\boldsymbol{l}}\boldsymbol{\sigma} = (j-l)(-2j+4l+1), \tag{2.266}$$

$$\hat{\boldsymbol{l}}\boldsymbol{\sigma}(j = l+\tfrac{1}{2}) = l, \quad \hat{\boldsymbol{l}}\boldsymbol{\sigma}(j = l-\tfrac{1}{2}) = -(l+1). \tag{2.267}$$

For $l = 0$, one has $\langle\hat{\boldsymbol{l}}\boldsymbol{\sigma}\rangle = 0$, which reflects the spherical symmetry of Y_0^0, $\langle\hat{\boldsymbol{l}}\rangle_0 = 0$. However, (2.259) gives

$$\langle V'/r\rangle = Ze^2\kappa_n^3[l(l+1)(l+\tfrac{1}{2})]^{-1}, \tag{2.268}$$

which is infinite for $l = 0$. It has been customary to exclude the point $r = 0$ from $\langle V'/r\rangle$, getting $\langle V_{sl}\rangle_0 = 0$ on account of (2.266). For $l = 0$, $V_{\rm Da}$ takes over (Bethe and Salpeter, 1957). However, the factor l disappears from $\langle\hat{\boldsymbol{l}}\boldsymbol{\sigma}/r^3\rangle$, giving

$$\langle V_{\rm Da}(l=0)\rangle = \langle V_{sl}(l=0)\rangle = \alpha_Z^4 mc^2/2n^3. \tag{2.269}$$

It is thus possible to ignore the singular part of ΔV and to use $\langle V_{sl}(l=0)\rangle$ down to $l = 0$. This ambiguity arises because both r^{-3} and $\delta(r)$ prevent meanigful solutions of the differential equation, similar to the $(\boldsymbol{\sigma\pi})^4$. Both operators are eliminated by observing

$$\langle r^{-3}\rangle = \kappa_n n\langle r^{-2}\rangle/L^2 = \alpha_Z mc^2\langle r^{-2}\rangle/L^2\hbar c. \tag{2.270}$$

Dropping again the expectation brackets, one obtains the mathematically consistent form of the Pauli equation with relativistic corrections as

$$[E^2 - m^2c^4 - 2EV + V^2 - (c\boldsymbol{\sigma\pi})^2 - \tfrac{1}{2}\hbar c\alpha_Z V'\hat{\boldsymbol{l}}\boldsymbol{\sigma}/L^2]\psi_g = 0. \tag{2.271}$$

Moreover, $V' = \alpha_Z\hbar c/r^2$ may be combined with the other r^{-2}-operators of the radial KG equation into

$$L_\alpha^2 \equiv l_\alpha(l_\alpha+1) \equiv L^2 - \alpha_Z^2 + \tfrac{1}{2}\alpha_Z^2\hat{\boldsymbol{l}}\boldsymbol{\sigma}/L^2. \tag{2.272}$$

The l_α differs from the exact Dirac $l_{\alpha\pm}$ (2.144) only at the order α_Z^4. In summary, the radial KG equation (1.98)

$$[k^2 - 2EV/\hbar^2c^2 + (\partial_r + 1/r)^2 - L_\alpha^2/r^2]R_{k^2,l} = 0 \tag{2.273}$$

applies also to the Dirac equation to order α_Z^4, provided the l_α is chosen accordingly. The energy levels for $l = j \pm 1/2$ are still degenerate to this order. With $L_\alpha^2 = \gamma(\gamma \pm 1)$, the equation would again be exact as in (2.143) or (2.159).

Of practical interest is the fine structure of spectral lines, which arises from the splitting of energy levels by V_{sl} for fixed l and $j = l \pm \frac{1}{2}$. For that case one writes

$$\hat{\boldsymbol{l}}\boldsymbol{\sigma} = (j - l)(2l + 1) - \tfrac{1}{2} \tag{2.274}$$

and neglects the common downshift of E_n^1 due to the $-\frac{1}{2}$. The splitting follows then from (2.259) as

$$\Delta E_{\text{fine}} = \langle V_{sl}\rangle_{l+1/2} - \langle V_{sl}\rangle_{l-1/2} = \kappa_n^3\hbar\alpha_Z[2m^2c^2l(l+1)]^{-1}. \tag{2.275}$$

For s-states, $l = 0$ implies $j = \frac{1}{2}$, $\hat{\boldsymbol{l}}\boldsymbol{\sigma} = 0$, in which case ΔE_{fine} does not exist.

2.9 The Zeeman Effect

In the spinless case, the Zeeman operator arose from $\boldsymbol{\pi}^2 = \boldsymbol{p}^2 + eB\hbar\hat{l}_z/c + O(B^2)$, and $\hat{l}_z$ was replaced by one of its eigenvalues m_l. The Kramers equation (2.82) has $\boldsymbol{\pi}^2$ replaced by $\boldsymbol{\pi}\boldsymbol{\sigma}^2 = \boldsymbol{\pi}^2 + eB\hbar\sigma_z/c$. Neglecting again the $\boldsymbol{A}^2$ of $\boldsymbol{\pi}^2$, one has

$$(\boldsymbol{\pi}\boldsymbol{\sigma})^2 = \boldsymbol{p}^2 + eB\hbar(\hat{l}_z + \sigma_z)/c = \boldsymbol{p}^2 + eB\hbar(m_j + \sigma_z/2)/c. \tag{2.276}$$

j_z is replaced by one of its eigenvalues, which are called m_j in the following. However, as j_x and j_y do not commute with $\sigma_z/2$, $\boldsymbol{j}^2$ may be treated as a constant of motion only for the first-order Zeeman shift. Second-order effects may become important for small separations of different j-values. In fact, $j = l + \frac{1}{2}$ and $j = l - \frac{1}{2}$ are only separated by the spin-orbit potential V_{sl} (2.246), which was also derived by first-order perturbation theory. For the above use of j as a good quantum number, $|V_{sl}|$ must be much larger than the Zeeman splitting. This is the regime of the anomalous Zeeman effect. The splitting is then described by (2.42). In general, however, both perturbations must be considered. including the off-digonal elements of σ_z (those between the two j-values at fixed l and m_j). The resulting mixing is quite complicated in the Dirac equation. For this reason, we first use the Pauli operator H_P with its relativistic correction H_r. Insertion of (2.276) into (2.241) gives

$$(i\hbar\partial_t - V - \boldsymbol{p}^2/2m)\psi = [e\hbar B(\hat{l}_z + \sigma_z)/2mc + H_r]\psi. \tag{2.277}$$

For $H_r \approx 0$ (which implies $V_{sl} \approx 0$), $\hat{\boldsymbol{l}}$ becomes a useful operator for first-order perturbation theory. A set of good quantum numbers is then l, l_z and σ_z, for which (2.277) leads to the "normal" Zeeman effect (2.46), in which $\hat{l}_z$ and σ_z are replaced by their eigenvalues m_l and $2m_s$.

In H_r, the B-dependent terms appear as follows:

$$-(\boldsymbol{\sigma\pi})^4/8m^3c^2 = -\boldsymbol{p}^4/8m^3c^2 - eB\hbar B(\hat{l}_z + \sigma_z)\boldsymbol{p}^2/4m^3c^3, \tag{2.278}$$

$$[i\hbar\partial_t - H(B=0)]\psi = H_{\mathrm{Zee}}\psi, \tag{2.279}$$

$$H_{\mathrm{Zee}} = e\hbar[B(\hat{l}_z + \sigma_z)(1 - \boldsymbol{p}^2/2m^2c^2)/2mc - V'\boldsymbol{\sigma}(\boldsymbol{A}\times\boldsymbol{r})/4m^2c^3r]. \tag{2.280}$$

In H_{Zee}, all operators except $\boldsymbol{l}$ and $\boldsymbol{\sigma}$ may be replaced by their nonrelativistic expectation values, in particular

$$\langle \boldsymbol{p}^2\rangle = 2m(E_N - \langle V\rangle) = (\alpha_Z mc/n)^2, \tag{2.281}$$

and using $\boldsymbol{A} = \frac{1}{2}\boldsymbol{B}\times\boldsymbol{r}$,

$$\boldsymbol{\sigma}(\boldsymbol{A}\times\boldsymbol{r}) = \tfrac{1}{2}\boldsymbol{\sigma}(-r^2\boldsymbol{B} + \boldsymbol{r}Bz) = \tfrac{1}{2}r^2B(-\sigma_z + \sigma_r\cos\theta). \tag{2.282}$$

The factor r^2 is cancelled by $V' = Z\alpha/r^2$ in (2.280), which greatly simplifies the radial expectation value:

$$-\langle V'\boldsymbol{\sigma}(\boldsymbol{A}\times\boldsymbol{r})/r\rangle_{\mathrm{radial}} = \tfrac{1}{2}\langle V\rangle_{\mathrm{radial}}B(-\sigma_z + \sigma_r\cos\theta). \tag{2.283}$$

For the angular expectation value, one sets $\sigma_r = \sigma_z z + \sin\theta(\sigma_+ e^{-i\phi} + \sigma_- e^{i\phi})$; only $\sigma_z\cos^2\theta$ has a nonvanishing expectation value for parity eigenstates:

$$\langle -V'\boldsymbol{\sigma}(\boldsymbol{A}\times\boldsymbol{r})/4m^2c^3r\rangle = e\hbar B\sigma_z\alpha_Z^2(1 - \langle\cos^2\theta\rangle)/8n^2mc. \tag{2.284}$$

The total Zeeman operator with first-order relativistic corrections is thus

$$H_{\mathrm{Zee}} = \mu_{\mathrm{B}}B\{\hat{l}_z(1 - \alpha_Z^2/2n^2) + \sigma_z[1 - \alpha_Z^2(1 + \langle\cos^2\theta\rangle)/4n^2)]\}, \tag{2.285}$$

with $\mu_{\mathrm{B}} = e\hbar/2mc$ as usual. The ground state has $l = 0$, $n = 1$, $\langle\cos^2\theta\rangle = 1/3$ and thus $H_{\mathrm{B}} = \mu_{\mathrm{B}}B\sigma_z(1 - \alpha_Z^2/3)$.

For the fully relativistic calculation, we first consider the anomalous Zeeman effect, where only the diagonal matrix elements of σ_z in the spinor basis $\chi_l^{jm}(l = j \pm \frac{1}{2})$ are needed. We take the Kramers equation in the form

$$(\pi^{02} - \boldsymbol{p}^2 + i\hbar e\boldsymbol{\sigma}\boldsymbol{E}/c - m^2c^2)\psi_r = K_{\mathrm{per}}\psi_r, \quad K_{\mathrm{per}} = e\hbar B(m_j + \sigma_z/2)/c. \tag{2.286}$$

The perturbed energy $E = E^0 + E^1$ is part of π^0. To first order in E^1, one has

$$\pi^{02} = (E^0 + E^1 - V)^2/c^2 = (E^0 - V)^2/c^2 + 2E^1(E^0 - V)/c^2. \tag{2.287}$$

The perturbative form of the Kramers equation is thus

$$[K_r^0 + 2E^1(E^0 - V)/c^2]\psi_r = K_{\rm per}\psi_r, \tag{2.288}$$

$$K_r^0 = (E^0 - V)^2/c^2 - \boldsymbol{p}^2 + i\hbar e\boldsymbol{\sigma E}/c - m^2c^2. \tag{2.289}$$

Expanding also $\psi_r = \psi_r^0 + \psi_r^1$, the zeroth order equation is $K_r^0\psi_r^0 = 0$, and the first-order equation is

$$K_r^0\psi_r^1 + E^1 2(E^0 - V)c^{-2}\psi_r^0 = K_{\rm per}\psi_r^0. \tag{2.290}$$

From here on, the calculation of E^1 is a straightforward extension of the nonrelativistic procedure. One multiplies (2.290) by $\psi_l^{0\dagger}$, integrates over all space and uses

$$\int \psi_l^{0\dagger} K_r^0 \psi_r^1 = \int (K_l^0\psi_l^0)^\dagger \psi_r^1 = 0, \tag{2.291}$$

where K_l^0 differs from K_r^0 by the sign of $i\hbar e\boldsymbol{\sigma E}/c$. The factor $2(E^0 - V)/c^2$ following E^1 is absorbed in the orthogonality relation (2.207), leading to

$$E^1 = \int \psi_l^{0\dagger} K_{\rm per}\psi_r^0/mc \equiv \langle K_{\rm per}/mc\rangle. \tag{2.292}$$

This procedure is avoided in the literature, because the Dirac equation is an explicit eigenvalue equation, $H\psi = E\psi$, and its many-electron "Dirac-Breit" extension of Sect. 3.4 also has that form (which is only lost in the "improved Breitians"). There is then no difference between relativistic and nonrelativistic perturbation theory. However, the result (2.303) below follows rather directly from the Kramers equation with its implicit E-dependence and its non-Hermitian operator. This equation is a simple example of a more advanced class of relativistic equations. The example has a drawback, however, namely the degeneracy of states of opposite parities. When the unperturbed energies E_n^0 are degenerate, care must be taken that ψ_n^1 vanishes for $B \to 0$. This requires a diagonalization of $K_{\rm per}$ in the subspaces of degenerate states. In Sect. 2.6 we saw that for $n > j + \frac{1}{2}$, $l = l - \frac{1}{2}$ is degenerate with $l = j + \frac{1}{2}$ (for $n = j + \frac{1}{2}$, the state $l = j + \frac{1}{2} = n$ is absent). In the present case, $K_{\rm per}$ conserves parity; it is diagonal in Dirac's parity basis but not for the simpler states (2.137). Consequently, one must use

$$\psi_r = 2^{-1/2}(\psi_g + \psi_f), \quad \psi_l = 2^{-1/2}(\psi_g - \psi_f), \tag{2.293}$$

$$\langle K_{\rm per}\rangle = \tfrac{1}{2}\int (g\chi_l^\dagger - if\chi_{\tilde l}^\dagger)K_{\rm per}(g\chi_l - if\chi_{\tilde l}) = \tfrac{1}{2}\int (g^2\chi_l^\dagger K_{\rm per}\chi_l - f^2\chi_{\tilde l}^\dagger K_{\rm per}\chi_{\tilde l}). \tag{2.294}$$

With the normalization $\int(g^2+f^2) = 1$ one finds for the term $eB\hbar m_j/c$ of $K_{\rm per}$

$$E^1 = eB\hbar m_j(1 - 2\int f^2)/2mc = B\mu_{\rm B}m_j(1 - 2\int f^2), \quad \mu_{\rm B} = e\hbar/2mc. \tag{2.295}$$

The nonrelativistic limit has $\int f^2 = 0$. To first order in relativity, one may use (2.154) in the form

$$f \approx -(\hbar/2mc)(\partial_r + 1/r + \kappa_D/r)g. \tag{2.296}$$

The s-states have $l = 0$, $j = \frac{1}{2}$, $\kappa_D = -1$, $f \approx -(\hbar/2mc)g'$, $g \approx Ne^{-\kappa r}$, $\kappa = \alpha_Z mc/\hbar n$ according to (2.165), which leads to

$$\int f^2 = (\alpha_Z/2n)^2 \int g^2 = \alpha_Z^2/4n^2, \quad E^1(m_j) \approx B\mu_B m_j(1 - \alpha_Z^2/2n^2). \tag{2.297}$$

The general expression $\int f^2 = 1/2 - E/2m$ follows from (A.33). A simpler and even more general derivation is to combine in (2.286) the constants into a new mass m',

$$m^2c^2 + eB\hbar m_j/c \equiv m'^2c^2, \quad m' \approx m(1 + eB\hbar m_j/2m^2c^3), \tag{2.298}$$

and to use (2.149), with m replaced by m'. This also shows that (2.297) remains valid for $l > 0$. The expectation values of $\sigma_z/2$ follow from the spinor spherical harmonics (2.132),

$$\tfrac{1}{2}\langle\sigma_z\rangle_{l=j\pm1/2} = \mp m_j/(2l+1) = 2m_j(j-l)/(2l+1), \tag{2.299}$$

$$E^1(\sigma_z/2) = 2B\mu_B m_j \int [g^2(j-l)/(2l+1) - f^2(j-\tilde{l})/(2\tilde{l}+1)]. \tag{2.300}$$

The Landé g-factor g_{lj} (2.45) follows from (2.299). Use of $j - \tilde{l} = -(j-l)$ and of

$$(2\tilde{l}+1)^{-1} = (2l+1)^{-1} + 2(l-\tilde{l})(2\tilde{l}+1)^{-1}(2l+1)^{-1} = (2l+1)^{-1} + (l-j)/j(j+1) \tag{2.301}$$

produces the final results,

$$E^1(\sigma_z/2) = 2B\mu_B m_j[(j-l)/(2l+1) - [4j(j+1)]^{-1} \int f^2]. \tag{2.302}$$

With $\int f^2$ given above, the complete Zeeman shift becomes

$$E^1 = B\mu_B m_j[(2j+1)/(2l+1) - [1 + 1/4j(j+1)](1 - E/m)]. \tag{2.303}$$

For $l = 0$, this agrees with the $B\mu_B m_j(1 - \alpha_Z^2/3n^2)$ of (2.285).

As σ_z does not commute with $\hat{\boldsymbol{l}}\boldsymbol{\sigma}$, the fine structure and Zeeman splittings are not additive. V_{sl} is diagonal in the basis $\chi_l^{jm_j}$, but σ_z mixes $j = l + \frac{1}{2}$ with $j = l - \frac{1}{2}$ at fixed l and m_j. We consider only the nonrelativistic reduction of this mixing, where the value $\tilde{l}$ of the small components does not enter. Writing the state with $j = l + \frac{1}{2}$ above that with $j = l - \frac{1}{2}$, one has to diagonalize the matrix

$$M = \Delta E_{\text{fine}} \begin{pmatrix} 1/2 & 0 \\ 0 & -1/2 \end{pmatrix} + B\mu'_B \tfrac{1}{2}\sigma_z; \tag{2.304}$$

$$\mu'_B = \mu_B[1 - \alpha_Z^2(1 + \langle\cos^2\theta\rangle)/4n^2],$$

$$\tfrac{1}{2}\sigma_z = \frac{1}{2l+1} \begin{pmatrix} m_j & -w \\ -w & -m_j \end{pmatrix}; \quad w = \sqrt{(l+\tfrac{1}{2})^2 - m_j^2}. \tag{2.305}$$

The part $B\mu'_{\rm B}m_j$ of the Zeeman shift is a multiple of the unit matrix in this basis and is omitted together with the common downshift of $E_{\rm fine}$ (unit matrices have no influence on diagonalization). The diagonal elements of $\frac{1}{2}\sigma_z$ are adopted from (2.299); the nondiagonal elements follow from (2.132) as

$$\langle j = l + \tfrac{1}{2}|\tfrac{1}{2}\sigma_z|j = l - \tfrac{1}{2}\rangle = -\sqrt{l + \tfrac{1}{2} - m_j}\sqrt{l + \tfrac{1}{2} + m_j} = -w. \quad (2.306)$$

The eigenvalues of M are then

$$M_\pm = \pm\tfrac{1}{2}\sqrt{\Delta E_{\rm fine}^2 + 4\Delta E_{\rm fine}\mu'_{\rm B}Bm_j/(2l+1) + {\mu'_{\rm B}}^2B^2}.$$

The limit $B^2 \to 0$ gives $M_\pm = \pm\frac{1}{2}[\Delta E_{\rm fine} + 2\mu'_{\rm B}Bm_j/(2l+1)]$ and agrees with the anomalous Zeeman effect, while the opposite limit $\Delta E_{\rm fine} = 0$ gives the normal Zeeman effect (2.46). For s-states, $j = \frac{1}{2}$ implies $m_j^2 = 1/4$, $w = 0$, $M_+ = B\mu'_{\rm B}m_j$, and M_- does not exist. The ratio $\mu'_{\rm B}/\mu_{\rm B}$ is also called a "binding correction" to the free electron's g-factor $g_{\rm free}$.

Instead of the lengthy expression (2.242), one may also use (2.256) for the Zeeman shift calculation. The "standard form" (1.144) of the KG equation satisfies standard orthogonality relations, namely (A.36). Writing $K = K_0 - \delta K$, they lead to $\delta(n_\beta^{-2}) = \langle\delta K\rangle$. The linear expansion $n_\beta^{-2} = n_\beta^{-2}(E_0^2) + \delta(E^2)dn_\beta^{-2}/dE^2 = n_\beta^{-2}(E_0^2) - m^2\alpha_Z^2/E_0^4$ ($\hbar = c = 1$) gives

$$\delta(E^2) = \langle\delta K\rangle\alpha_Z^2E_0^4/m^2. \quad (2.307)$$

With $\boldsymbol{\pi}_\epsilon = \boldsymbol{p}_\epsilon + e\boldsymbol{A}(\boldsymbol{r}_\epsilon/E^2)$ (which is dimensionless), the linear Zeeman effect has $\delta K = \delta(\boldsymbol{\pi}_\epsilon)^2 = eB(l_z + \sigma_z)/E_0^2$. In this manner one finds

$$\delta E = \delta(E^2)/2E_0 = eB\langle\hat{l}_z + \sigma_z\rangle E_0/2m. \quad (2.308)$$

The factor E_0/m produces the correction $1 - \alpha_z^2/2n^2 = \langle 1 - \boldsymbol{p}^2/2m^2c^2\rangle$ of (2.280).

2.10 The Dirac Current. Free Electrons

We have so far studied the Dirac equation in a stationary potential, $V(\boldsymbol{r}) = qA_0(\boldsymbol{r})$. For time-dependent problems, one needs a conserved current, $\partial_\mu j^\mu = 0$, of which j^0 is then used for the scalar product. A compact notation of j^μ is $\overline{\psi}_D\gamma^\mu\psi_D$. It will be derived in the following from several more explicit forms. From (2.87), one finds with $\boldsymbol{\pi} = -i\hbar\nabla - c^{-1}q\boldsymbol{A}$,

$$i\hbar(\partial_0 + \nabla\boldsymbol{\alpha})\psi_D = c^{-1}q(A^0 - \boldsymbol{A}\boldsymbol{\alpha} + mc\beta)\psi_D, \quad q_e = -e. \quad (2.309)$$

Its Hermitian conjugate form is

$$i\hbar\psi_D^\dagger(\overleftarrow{\partial}_0 + \overleftarrow{\nabla}\boldsymbol{\alpha}) = -c^{-1}q\psi_D^\dagger(A^0 - \boldsymbol{A}\boldsymbol{\alpha} + mc\beta). \quad (2.310)$$

From these two equations, one verifies $\partial_0 j^0 + \nabla \boldsymbol{j} = 0$ for

$$j^0 = c\psi_D^\dagger \psi_D, \quad \boldsymbol{j} = c\psi_D^\dagger \boldsymbol{\alpha} \psi_D. \tag{2.311}$$

Note that $\psi_D^\dagger \psi_D$ is the zero-component of a 4-vector, not a Lorentz invariant. Its decomposition into chiral components follows from (2.88),

$$\psi_D^\dagger \psi_D = \psi_r^\dagger \psi_r + \psi_l^\dagger \psi_l \equiv \rho. \tag{2.312}$$

The Lorentz transformation of $\psi_r^\dagger \psi_r$ has been given in (2.97), that of $\psi_l^\dagger \psi_l$ has the rapidity η replaced by $-\eta$. They show that $\psi_l^\dagger \psi_r$ and $\psi_r^\dagger \psi_l$ are Lorentz invariants. Their sum is also parity invariant:

$$\psi_l^\dagger \psi_r + \psi_r^\dagger \psi_l = \psi_D^\dagger \gamma^0 \psi_D = \overline{\psi}_D \psi_D, \quad \overline{\psi}_D \equiv \psi_D^\dagger \gamma^0. \tag{2.313}$$

$\gamma^0 = \beta$ is given in the chiral basis by (2.88) and in the parity basis by (2.103). In the latter basis, on has

$$\overline{\psi}_D \psi_D = \psi_{\mathrm{pa}}^\dagger \gamma_{\mathrm{pa}}^0 \psi_{\mathrm{pa}} = \psi_g^\dagger \psi_g - \psi_f^\dagger \psi_f. \tag{2.314}$$

To express j^μ in terms of $\overline{\psi}_D$ and ψ_D, one defines

$$\boldsymbol{\gamma} = \gamma^0 \boldsymbol{\alpha} = \gamma^0 \gamma^5 \boldsymbol{\sigma}, \quad j^\mu = c\overline{\psi}_D \gamma^\mu \psi_D. \tag{2.315}$$

The variety of notations can be confusing; $\overline{\psi}_D \gamma^0 \psi_D$ is the same as $\psi_D^\dagger \psi_D$, because of $(\gamma^0)^2 = 1$. In the chiral basis, one would in the first place extend the Pauli matrices $\boldsymbol{\sigma}$ to two different sets of 4-vector matrices:

$$\sigma^\mu = (\sigma^0, \boldsymbol{\sigma}), \quad \sigma_\mu = (\sigma^0, -\boldsymbol{\sigma}) \equiv \sigma_l^\mu, \quad \sigma^0 = 1. \tag{2.316}$$

The pair of equations (2.84) reads then

$$\pi_\mu \sigma^\mu \psi_r = mc\psi_l, \quad \pi_\mu \sigma_l^\mu \psi_l = mc\psi_r. \tag{2.317}$$

The σ_l^μ appear only in front of lefthanded spinors; they may be called left-handed Pauli matrices. One may also define right- and lefthanded currents,

$$j_r^\mu = c\psi_r^\dagger \sigma^\mu \psi_r, \quad j_l^\mu = c\psi_l^\dagger \sigma_l^\mu \psi_l. \tag{2.318}$$

With the two expressions (2.29) and (2.30) for ∂_μ, one finds

$$i\partial_\mu j_r^\mu = mc^2(\psi_r^\dagger \psi_l - \psi_l^\dagger \psi_r) = -i\partial_\mu j_l^\mu. \tag{2.319}$$

Thus, for $mc^2 \neq 0$, there is only one conserved 4-current:

$$j^\mu = j_r^\mu + j_l^\mu = c\psi_r^\dagger \sigma^\mu \psi_r + c\psi_l^\dagger \sigma_l^\mu \psi_l. \tag{2.320}$$

But its two pieces j_l^μ occur separately in parity-violating weak interactions. When parity violation was finally discovered (Wu et al. 1957), it was for-

mulated within the existing standard Dirac notation by means of right- and left-handed projectors. According to the diagonal form (2.91) of γ^5,

$$P_r = \tfrac{1}{2}(1+\gamma^5), \quad P_l = \tfrac{1}{2}(1-\gamma^5), \tag{2.321}$$

$$j_r^\mu = \overline{\psi}_D \gamma^\mu P_r \psi_D, \quad j_l^\mu = \overline{\psi}_D \gamma^\mu P_l \psi_D. \tag{2.322}$$

This notation is still in use today. The Hamiltonian for beta decay $n \to p e^- \overline{\nu}$ is $H_\beta = 2^{1/2} G_\mu j_{e\nu}^{\mu,\dagger} g_{\mu\nu} j_{np}^\nu$,

$$j_{e\nu}^\mu = \overline{\Psi}_\nu \gamma^\mu P_l \Psi_e = \Psi_{\nu,l}^\dagger \sigma_l^\mu \Psi_{e,l} = j_{e\nu,l}^\mu \tag{2.323}$$

while j_r^μ is absent in H_β. (The field operators Ψ will be introduced in Sect. 3.2. The factor $2^{1/2}$ is a relict from the time when j_r^μ was coupled with equal strength. The nucleon current operator j_{np}^μ will be given in Sect. 5.8 in the quark model. Its matrix elements are discussed in textbooks on beta decay (Konopinski 1966, Pilkuhn 1979).)

One may also express j^μ in a form analogous to the spinless current (2.31),

$$j^\mu = \psi_l^\dagger \Gamma^\mu \psi_r / mc, \quad \Gamma^\mu = \overleftarrow{\pi}^{\mu *} + \pi^\mu + i\hbar \sigma^{\mu\nu} (\partial_\nu + \overleftarrow{\partial}_\nu), \tag{2.324}$$

where $\sigma^{\mu\nu}$ is the antisymmetric part of $\sigma_l^\mu \sigma^\nu$,

$$\sigma_l^\mu \sigma^\nu = g^{\mu\nu} + \sigma^{\mu\nu}, \quad \sigma^{\mu\nu} = -\sigma^{\nu\mu}. \tag{2.325}$$

$g^{\mu\nu}$ is the metric tensor (2.16), and

$$\sigma^{0j} = -\sigma^{j0} = \sigma_j, \quad \sigma^{ij} = i\sigma_k \text{ cyclic}. \tag{2.326}$$

However, j^μ is rarely used in this form.

The matrices γ^μ (2.315) are appropriate for the discussion of Lorentz properties in the four-component spinor formalism. One has

$$\gamma^\mu \gamma^\nu + \gamma^\nu \gamma^\mu = 2g^{\mu\nu}, \quad \gamma^\mu \gamma^\nu - \gamma^\nu \gamma^\mu \equiv 2\sigma_{4\times4}^{\mu\nu}. \tag{2.327}$$

$\sigma_{4\times4}^{\mu\nu}$ is the 4×4 version of (2.325). From (2.315), one finds

$$\sigma_{4\times4}^{0j} = \gamma^5 \sigma^{0j}, \quad \sigma_{4\times4}^{ij} = 1 \cdot \sigma^{ij}, \tag{2.328}$$

where 1 is the Dirac unit matrix.

Among the solutions of the free Dirac equation we discuss again plane waves,

$$\psi_D(\boldsymbol{k}) = e^{-i\omega t + i\boldsymbol{k}\boldsymbol{r}} u_D(\boldsymbol{k}, m_s). \tag{2.329}$$

In the chiral basis $u_D = (u_r, u_l)$, the components satisfy (2.84) in the form

$$(k^0 - \boldsymbol{k}\boldsymbol{\sigma}) u_r = (mc/\hbar) u_l, \quad (k^0 + \boldsymbol{k}\boldsymbol{\sigma}) u_l = (mc/\hbar) u_r. \tag{2.330}$$

These equations are solved by

$$u_r = (\hbar k^0 + \hbar \boldsymbol{\sigma}\boldsymbol{k})^{1/2} \chi, \quad u_l = (\hbar k^0 - \hbar \boldsymbol{\sigma}\boldsymbol{k})^{1/2} \chi, \tag{2.331}$$

because of $(k^{02} - \boldsymbol{k}^2)^{1/2} = mc/\hbar$. The spin states $\chi = \chi(m_s)$ refer to the electron at rest. When they are quantized along the direction $\hat{\boldsymbol{k}}$ of $\boldsymbol{k}$, they become eigenstates of the eigenvalue of $\boldsymbol{\sigma k}$. The eigenvalue of $\frac{1}{2}\boldsymbol{\sigma}\hat{\boldsymbol{k}}$ is called the helicity λ:

$$\tfrac{1}{2}\boldsymbol{\sigma k}\chi(\lambda, \hat{\boldsymbol{k}}) = \tfrac{1}{2}k\boldsymbol{\sigma}\hat{\boldsymbol{k}}\chi(\lambda, \hat{\boldsymbol{k}}) = \lambda k\chi(\lambda, \hat{\boldsymbol{k}}). \tag{2.332}$$

In this case (2.330) is solved by

$$u_r = (\hbar k^0 + 2\lambda\hbar k)^{1/2}\chi, \quad u_l = (\hbar k^0 - 2\lambda\hbar k)^{1/2}\chi, \tag{2.333}$$

In a general basis, the spinor $u_D(\boldsymbol{k}, m_s)$ is related to the spinor $u' = u_0(m_s)$ by the inverse of (2.93), which is called a "boost":

$$u_D(\boldsymbol{k}, m_s) = e^{\boldsymbol{\eta\alpha}/2}(mc)^{1/2}\chi(m_s). \tag{2.334}$$

From (2.12) one has

$$\cosh\eta = \gamma = E/mc^2, \quad \sinh\eta = \hbar k/mc, \tag{2.335}$$

$$e^{\boldsymbol{\eta\alpha}/2} = (e^{\boldsymbol{\eta\alpha}})^{1/2} = (E/mc^2 + \hbar\boldsymbol{k\alpha}/mc)^{1/2}, \quad \boldsymbol{\alpha} = \gamma^5\boldsymbol{\sigma}, \tag{2.336}$$

of which (2.333) is a special case in a special Dirac basis. With the angles of $\hat{\boldsymbol{k}}$ denoted by θ and ϕ, $\boldsymbol{\sigma}\hat{\boldsymbol{k}}$ is again the matrix σ_r in (2.114). The resulting helicity spinors are

$$\chi(\tfrac{1}{2}, \theta, \phi) = \begin{pmatrix} \cos\frac{1}{2}\theta \\ \sin\frac{1}{2}\theta e^{i\phi} \end{pmatrix}, \quad \chi(-\tfrac{1}{2}, \theta, \phi) = \begin{pmatrix} -\sin\frac{1}{2}\theta e^{-i\phi} \\ \cos\frac{1}{2}\theta \end{pmatrix}. \tag{2.337}$$

Their orthogonality relations are

$$\chi^\dagger(\lambda', \hat{\boldsymbol{k}})\chi(\lambda, \hat{\boldsymbol{k}}) = \delta_{\lambda,\lambda'}. \tag{2.338}$$

This leads to

$$u_r^\dagger u_r = \hbar(k^0 + 2\lambda k), \quad u_l^\dagger u_l = \hbar(k^0 - 2\lambda k), \quad u_D^\dagger u_D = 2\hbar k^0. \tag{2.339}$$

The plane wave orthogonality relations follow now from (2.35) as

$$\int \psi_D(\boldsymbol{k}')^\dagger\psi_D(\boldsymbol{k})d^3r = 8\pi^3\delta(\boldsymbol{k} - \boldsymbol{k}')\delta_{\lambda\lambda'}2\hbar k^0; \tag{2.340}$$

they agree with (2.36) of the spinless case. The density of free electrons is then again given by (2.37). The Lorentz invariance of $\overline{u}_D u_D$ is checked by (2.338) as follows:

$$\overline{u}_D u_D = u_r^\dagger u_l + u_l^\dagger u_r = \delta_{\lambda\lambda'}2(k^{02} - 4\lambda^2 k^2)^{1/2}\hbar = 2mc\delta_{\lambda\lambda'}. \tag{2.341}$$

The normalization differs from that chosen in Sects. 2.7 and 2.8 for an electron in an external Coulomb potential. The latter one breaks Lorentz invariance, but a normalization to $2k^0$ as in (2.340) is not excluded. For later use, we also collect the scalar products of helicity spinors that are quantized along

two different directions $\hat{\boldsymbol{k}}$ and $\hat{\boldsymbol{k}}'$. The z-axis is taken along $\hat{\boldsymbol{k}}$, such that $\chi(\lambda,0,0)=\chi(m_s=\lambda)$ are the standard unit spinors (2.49):

$$\chi'^{\dagger}\chi=\delta_{\lambda',\lambda}\cos\tfrac{1}{2}\theta+2\lambda'\delta_{\lambda',-\lambda}\sin\tfrac{1}{2}\theta e^{-2i\lambda'\phi}. \tag{2.342}$$

This leads to

$$u_D'^{\dagger}u_D=2\chi'^{\dagger}\chi(\delta_{\lambda',\lambda}\hbar k^0+\delta_{\lambda',-\lambda}mc). \tag{2.343}$$

We shall also need the nonrelativistic expansion of u_D. From (2.331) and with $(1+x)^{1/2}\approx 1+x/2-x^2/8$,

$$u_{r,l}=(\hbar k^0)^{1/2}(1\pm\boldsymbol{\sigma k}/k^0)^{1/2}\chi\approx(\hbar k^0)^{1/2}(1\pm\hbar\boldsymbol{\sigma k}/2mc-\hbar^2k^2/8m^2c^2)\chi. \tag{2.344}$$

In this limit, the large and small components (2.151) of u_D become useful,

$$u_g=2^{-1/2}(u_r+u_l)=(2mc)^{1/2}(1+\hbar^2k^2/8m^2c^2)\chi, \tag{2.345}$$

$$u_f=2^{-1/2}(u_r-u_l)=(2mc)^{-1/2}\hbar\boldsymbol{\sigma k}\chi, \tag{2.346}$$

because u_f vanishes for $\boldsymbol{k}\to 0$. However, (2.345) is dangerous because it suggests $+\hbar^2k^2/8m^2c^2$ as a relativistic correction to the nonrelativistic formalism. This is correct only if one renormalises $u_D^{\dagger}u_D$ to $2mc$ instead of the $2\hbar k^0$ of (2.339).

The helicity basis is by no means necessary for handling the Pauli matrices in Lorentz transformations. The algebra (2.52) shows that the most general function is in fact linear in $\boldsymbol{\sigma}$. And as $(\gamma^5)^2=1$, this applies also to the combination $\gamma^5\boldsymbol{\sigma}$. By squaring, one easily verifies

$$e^{\boldsymbol{\eta\alpha}/2}=(2\gamma+2)^{-1/2}(\gamma+1+\gamma^5\boldsymbol{\sigma k}\hbar/mc). \tag{2.347}$$

Nevertheless, the previous square roots are more compact. They are very convenient in bilinear forms. Consider for example the "spin summation"

$$\Sigma_u=\Sigma_{m_s}u(m_s)u^{\dagger}(m_s)=\hbar\Sigma_{m_s}(k^0+\gamma^5\boldsymbol{k\sigma})^{1/2}\chi(m_s)\chi^{\dagger}(m_s)(k^0+\gamma^5\boldsymbol{k\sigma})^{1/2}, \tag{2.348}$$

which appears in the calculation of probabilities. The Pauli spinors χ form a complete set:

$$\Sigma_{m_s}\chi(m_s)\chi^{\dagger}(m_s)=\begin{pmatrix}1&0\\0&1\end{pmatrix}\equiv 1. \tag{2.349}$$

In the Dirac chiral basis (2.91), Σ_u has the form

$$\Sigma_u=\begin{pmatrix}\Sigma_{rr}&\Sigma_{rl}\\ \Sigma_{lr}&\Sigma_{ll}\end{pmatrix}, \tag{2.350}$$

and with (2.331), one finds

$$\Sigma_u=\hbar(k^0+\gamma^5\boldsymbol{k\sigma})+mc\beta. \tag{2.351}$$

The mc arises as $\hbar(k^0\pm\boldsymbol{k\sigma})^{1/2}(k^0\mp\boldsymbol{k\sigma})^{1/2}$.

3 Quantum Fields and Particles

3.1 The Photon Field

In classical electrodynamics, the energy contained in the vacuum fields is

$$H_{\rm cl}^{\rm vac} = (8\pi)^{-1} \int d^3r (\boldsymbol{E}^2 + \boldsymbol{B}^2). \tag{3.1}$$

On the other hand, Planck's postulate (1901) requires that in a cavity with enumerable modes $i = 1, 2, 3, 4 \ldots$ of frequencies ω_i, the energy measurement in a given mode yields one of the possible values $E_{ni} = n_i \hbar \omega_i$, where n_i is the number of photons in that mode. The interaction between the photons is very small, such that the photon numbers in different modes can be determined simultaneously. The state of the electromagnetic field in a cavity can be expanded in "Fock states" with given photon numbers n_i in the modes $|i\rangle$,

$$\psi_F = |n_1, n_2, n_3, \ldots\rangle, \quad N_i \psi_F = n_i \psi_F. \tag{3.2}$$

The N_i are number operators, and the photon field Hamiltonian is

$$H_F = \sum_{i=1}^{\infty} \hbar \omega_i N_i. \tag{3.3}$$

Its lowest eigenvalue is zero, the corresponding Fock ground state is

$$\psi_F^{(0)} = |0,\, 0,\, 0, \ldots\rangle, \quad H_F \psi_F^{(0)} = 0. \tag{3.4}$$

A number operator $N = a^\dagger a$ was already discussed in Sect. 1.9; the matrix representations of a and $a^\dagger$ were given in (1.244). It was Dirac (1926, 1927) who proposed to use a_i and $a_i^\dagger$ as absorption and emission operators for photons in a mode $|i\rangle$. Thus a possible form for N_i arises from

$$[a_i, a_i^\dagger] = 1, \quad N_i = a_i^\dagger a_i. \tag{3.5}$$

The condition of simultaneous measurability of different modes, $[N_i, N_j] = 0$, is satisfied for

$$[a_i, a_j^\dagger] = \delta_{ij}, \quad [a_i, a_j] = 0. \tag{3.6}$$

When $\boldsymbol{E}$ and $\boldsymbol{B}$ are taken as linear combinations of these a_i and $a_i^\dagger$, a form similar to (3.1) leads automatically to (3.3), as will be seen below. It is convenient to express both $\boldsymbol{E}$ and $\boldsymbol{B}$ in terms of the four-potential A^μ and to keep time-independent parts of A^μ unquantized, as "classical" fields $A^\mu_{\rm cl}$. The Coulomb gauge $\nabla \boldsymbol{A} = 0$ is particularly convenient, as a static charge density $\rho_{\rm el}$ implies a time-independent A^0, $A^0 = A^0_{\rm cl}$. Thus only a part of the vector potential becomes a nontrivial operator,

$$\boldsymbol{A}_{\rm tot} = \boldsymbol{A}_{\rm cl}(\boldsymbol{r}) + \boldsymbol{A}, \quad \boldsymbol{A} = c\sum_i (h/\omega_i)^{1/2}(a_i \boldsymbol{A}_i + {\rm hc}), \quad \boldsymbol{A}_i = \boldsymbol{A}_i(\boldsymbol{r})e^{-i\omega_i t}, \tag{3.7}$$

where hc stands for "Hermitian conjugate", and $h = 2\pi\hbar$. The normalization factor $(h/\omega_i)^{1/2}$ refers to the following orthogonality relations

$$\langle i|j\rangle = \int d^3r \boldsymbol{A}_i^* \boldsymbol{A}_j = \delta_{ij}, \tag{3.8}$$

which will be verified below. The $\boldsymbol{A}_i$ satisfy the Helmholtz equation that follows from (1.58) in vacuum, and they also satisfy the Coulomb gauge condition:

$$(\omega_i^2/c^2 + \nabla^2)\boldsymbol{A}_i = 0, \quad \boldsymbol{\nabla}\boldsymbol{A}_i = 0. \tag{3.9}$$

Let $\boldsymbol{E}$ and $\boldsymbol{B}$ now denote the pure quantum fields:

$$\boldsymbol{E} = -\partial_t \boldsymbol{A}/c = i\sum_i (h\omega_i)^{1/2}[a_i \boldsymbol{A}_i(\boldsymbol{r})e^{-i\omega_i t} - {\rm hc}], \quad \boldsymbol{B} = \boldsymbol{\nabla}\times\boldsymbol{A}. \tag{3.10}$$

Clearly, the hermiticity of $\boldsymbol{E}$ and $\boldsymbol{B}$ requires $\boldsymbol{A} = \boldsymbol{A}^\dagger$. This introduces products $a_i a_j$ and $a_i^\dagger a_j^\dagger$ into the integrand of A (3.1) which change the photon numbers by two; these must somehow disappear from the final result (3.3). The Coulomb gauge condition admits two different modes i for fixed ω_i. Replacing the cavity walls by periodic boundary conditions allows the use of the convenient plane waves, normalized according to (1.253):

$$\boldsymbol{A}_i = \boldsymbol{\epsilon}^{(i)}(\boldsymbol{k})e^{i\boldsymbol{k}\boldsymbol{r}-i\omega t}V^{-1/2}, \quad \boldsymbol{k}\boldsymbol{\epsilon}^{(i)}(\boldsymbol{k}) = 0, \quad \omega^2 = c^2k^2. \tag{3.11}$$

The orthogonality of the two different polarization vectors $\boldsymbol{\epsilon}^{(i)}$ $(i = 1, 2)$ is understood in (3.8). When the z-axis is taken along $\boldsymbol{k}$, they may be taken as unit vectors along the x- and y-axes, $\boldsymbol{\epsilon}^{(1)} = (1, 0, 0)$, $\boldsymbol{\epsilon}^{(2)} = (0, 1, 0)$. But in the summation over many modes, it is best to keep a fixed coordinate system. The cartesian components of $\boldsymbol{k}$ are expressed in terms of their spherical ones:

$$\boldsymbol{k} = (k_x, k_y, k_z) = k(\sin\theta_k\cos\phi_k, \sin\theta_k\sin\phi_k, \cos\phi_k). \tag{3.12}$$

The transversality condition $\boldsymbol{k}\boldsymbol{\epsilon} = 0$ together with the choice $\epsilon_z^{(2)} = 0$ lead to

$$\boldsymbol{\epsilon}^{(1)} = (\cos\theta_k\cos\phi_k, \cos\theta_k\sin\phi_k, -\sin\theta_k), \tag{3.13}$$

$$\boldsymbol{\epsilon}^{(2)} = (-\sin\phi_k, \cos\phi_k, 0) = \widehat{z}\times\widehat{k}/\sin\theta_k. \tag{3.14}$$

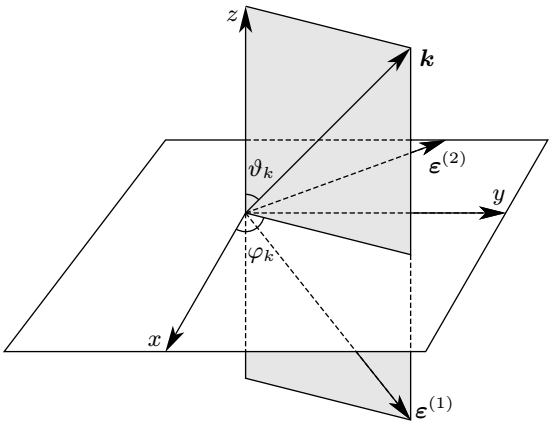

Fig. 3.1. The linear polarization vectors of $\boldsymbol{A}$. The vectors $\boldsymbol{k}, \boldsymbol{\varepsilon}^{(1)}, \boldsymbol{\varepsilon}^{(2)}$ form a rectangular system

For light of circular polarization ("helicity") $\lambda = \pm 1$, one uses

$$\boldsymbol{\epsilon}^{(\lambda)}(\boldsymbol{k}) = 2^{-1/2}(-\lambda\boldsymbol{\epsilon}^{(1)} - i\boldsymbol{\epsilon}^{(2)}). \tag{3.15}$$

We are now ready to insert $\boldsymbol{E}$ (3.10) into the form (3.1):

$$(8\pi)^{-1}\int d^3r\boldsymbol{E}^2 = -\hbar/4\int d^3r\Sigma_{i,j}(\omega_i\omega_j)^{1/2}(a_i\boldsymbol{A}_i - a_i^\dagger\boldsymbol{A}_i^*)(a_j\boldsymbol{A}_j - a_j^\dagger\boldsymbol{A}_j^*). \tag{3.16}$$

The products that contain one a and one $a^\dagger$ are reduced to a single sum by the orthogonality relations (3.8):

$$H_{E,d} = \tfrac{1}{4}\Sigma_i\hbar\omega_i(a_ia_i^\dagger + a_i^\dagger a_i) = \tfrac{1}{2}\Sigma_i\hbar\omega_i(N_i + \tfrac{1}{2}). \tag{3.17}$$

This is half of the desired operator H_F, plus an unwanted zero-point energy, $\frac{1}{2}\hbar\omega_i$ per mode. The zero-point energy is physical in cases where a harmonic oscillator potential is fitted to the minimum of the potential curve of a diatomic molecule, and also when Landau levels are joined to a region of vanishing magnetic field. Here, however, it is of no significance. It is eliminated by stipulating a "normal ordering" or "Wick product" in $\boldsymbol{E}^2$ and also in $\boldsymbol{B}^2$, in which all lowering operators a appear to the right of all raising operators $a^\dagger$:

$$H_F = (8\pi)^{-1}\int d^3r(:\boldsymbol{E}^2: + :\boldsymbol{B}^2:), \quad :aa^\dagger: \equiv a^\dagger a. \tag{3.18}$$

The integrals over $a_i\boldsymbol{A}_ia_j\boldsymbol{A}_j$ and $a_i^\dagger\boldsymbol{A}_i^*a_j^\dagger\boldsymbol{A}_j^*$ are also simplified by orthogonality relations. The plane waves $\boldsymbol{A}_i(\boldsymbol{r})$, (3.11) without the factor $e^{-i\omega t}$, satisfy

$$\boldsymbol{A}_i^*(\boldsymbol{r}) = \boldsymbol{A}_{-i}(\boldsymbol{r}), \tag{3.19}$$

where the index $-i$ stands for $-\boldsymbol{k}$ in this particular case. However, (3.19) applies to arbitrary modes if we understand i as an index for all addi-

tive quantum numbers of each mode. For spherical modes, for example, one has

$$(Y_l^m(\theta,\phi))^* = Y_l^{-m}(\theta,\phi). \tag{3.20}$$

The reason for this symmetry is the reality of the Helmholtz equation (3.9); $\boldsymbol{A}_i + \boldsymbol{A}_i^*$ is also a solution with the same ω_i; the modes in a cavity are in fact real, not complex (see below). Thus there remains the following nondiagonal sum in addition to (3.17):

$$H_{E,nd} = -\tfrac{1}{4}\Sigma_i \hbar\omega_i (a_i a_{-i} e^{-2i\omega_i t} + a_i^\dagger a_{-i}^\dagger e^{2i\omega_i t}). \tag{3.21}$$

It is cancelled by a corresponding term in $\int d^3r : \boldsymbol{B}^2 : /8\pi$; the cancellation is relatively complicated for arbitrary orbitals. One uses

$$\nabla(\boldsymbol{A}\times\boldsymbol{B}) = \boldsymbol{B}(\nabla\times\boldsymbol{A}) - \boldsymbol{A}(\nabla\times\boldsymbol{B}) \tag{3.22}$$

and inserts $\boldsymbol{B} = \nabla\times\boldsymbol{A}$:

$$(\nabla\times\boldsymbol{A})^2 = \nabla(\boldsymbol{A}\times(\nabla\times\boldsymbol{A})) + \boldsymbol{A}(\nabla\times(\nabla\times\boldsymbol{A})). \tag{3.23}$$

The first term is a divergence and vanishes after integration, and the second term may be rewritten as $-\boldsymbol{A}\nabla^2\boldsymbol{A}$ in the Coulomb gauge, see the derivation of (1.58). This equals $+\omega^2\boldsymbol{A}^2/c^2$ according to the Helmholtz equation. To summarize, the contributions of $\boldsymbol{E}^2$ and $\boldsymbol{B}^2$ to H_F are equal in the diagonal and opposite off-diagonal.

Knowing that the time-independence of H_F expresses the energy conservation of the free electromagnetic field, the proof that (3.18) is also time-independent can be greatly simplified, see Sect. 3.4.

Photons are the excitations of the free electromagnetic field. The commutators of the field operators can also be derived from the postulate of canonical field quantization, without reference to the excitation spectrum. The field equations are derived from a Lagrangian free field density,

$$L_F(\boldsymbol{A},\partial_\mu\boldsymbol{A}) = -(16\pi)^{-1}F_{\mu\nu}F^{\mu\nu} = (8\pi)^{-1}(\boldsymbol{E}^2 - \boldsymbol{B}^2), \tag{3.24}$$

(with $F_{\mu\nu}$ defined in (2.19)), by the principle of least action:

$$\delta_C \int d^3r dt L = 0. \tag{3.25}$$

The index C on the variational symbol δ restricts the variation of $\boldsymbol{A}$ to the space of functions satisfying the Coulomb gauge $\nabla\boldsymbol{A} = 0$. The canonical momentum field is

$$\boldsymbol{\Pi} = \partial L/\partial(\partial_0\boldsymbol{A}) = -\boldsymbol{E}, \tag{3.26}$$

and $H = \boldsymbol{\Pi}\partial_0\boldsymbol{A} - L$. The postulate of canonical field quantization is

$$[A_i(\boldsymbol{r}), \Pi_j(\boldsymbol{r}')] = i\hbar\delta_{ij}^{(t)}\delta(\boldsymbol{r}-\boldsymbol{r}'), \quad \delta_{ij}^{(t)} = \delta_{ij} - \partial_i\partial_j/\nabla^2. \tag{3.27}$$

The commutator is analogous to that of $\boldsymbol{r}$ and $\boldsymbol{p}$, but it is complicated here by the condition $\nabla \boldsymbol{A} = 0$, which requires $[\Sigma_{i=1}^{3} \partial_i A_i(\boldsymbol{r}), \Pi_j(\boldsymbol{r}')] = 0$.

In macroscopic matter, the electric polarization $\boldsymbol{p}$ of individual atoms of density $N_a(\boldsymbol{r})$ adds up to a macroscopic polarization $\boldsymbol{P} = N_a \boldsymbol{p}$. When the magnetic polarization is negligible, the macroscopic Maxwell equations are

$$\boldsymbol{D} = \boldsymbol{E} + 4\pi \boldsymbol{P}, \quad \nabla \boldsymbol{D} = 4\pi \rho_{\text{mov}}, \quad \nabla \times \boldsymbol{B} - \partial_0 \boldsymbol{D} = 4\pi \boldsymbol{j}_{\text{el}}/c, \tag{3.28}$$

where ρ_{mov} is the movable part of ρ_{el}. $\boldsymbol{P}$ can be written as a power series in the components E_i of $\boldsymbol{E}$, and frequently $\boldsymbol{P} = \chi(\boldsymbol{r})\boldsymbol{E}$ is a good approximation:

$$\boldsymbol{D} = \epsilon \boldsymbol{E} = -\epsilon \partial_0 \boldsymbol{A}, \quad \epsilon = 1 + \chi \equiv n^2, \tag{3.29}$$

where n is the index of refraction. Dielectrics have $\rho_{\text{mov}} = 0$, such that the Helmholtz and Coulomb gauge equations remain valid, although in slightly modified forms:

$$(\omega_i^2 n^2/c^2 + \nabla^2)\boldsymbol{A}_i = 0, \quad \nabla(\epsilon \boldsymbol{A}) = 0. \tag{3.30}$$

The Hamiltonian (3.18) is replaced by

$$H_F = (8\pi)^{-1} \int d^3 r : (\boldsymbol{E}\boldsymbol{D} + \boldsymbol{B}^2) : . \tag{3.31}$$

The canonical field quantization is changed accordingly, but the resulting form (3.3) of the energy operator does not change! One could write

$$[\tilde{a}_i, \tilde{a}_j^\dagger] = \delta_{ij}, \quad N_i = \tilde{a}_i^\dagger \tilde{a}_i \tag{3.32}$$

to notify that these operators refer to "polarons". For constant n, the modes of these particles have c replaced by c/n. The important point is that one has avoided complicated interactions by new decoupled modes. The corresponding quanta are frequently called quasiparticles. The underlying local fields (to the extent that they exist) are "quasifields" or "effective fields". Sometimes, quasiparticles exist only in a few selected modes. A spectacular example is "squeezed light", where in a certain mode m raising and lowering operators get mixed:

$$\tilde{a}_m = \mu a_m + \nu a_m^\dagger, \quad |\mu|^2 - |\nu|^2 = 1, \quad [\tilde{a}_m, \tilde{a}_m^\dagger] = 1, \quad \tilde{N}_m = \tilde{a}_m^\dagger \tilde{a}_m. \tag{3.33}$$

In some applications, a_i and $a_i^\dagger$ are eliminated in favour of their Hermitian components, which were called ξ and $-i\partial_\xi$ in the harmonic oscillator example. For light, one defines the "quadrature" components,

$$X_1 = \tfrac{1}{2}(a^\dagger + a), \quad X_2 = \tfrac{1}{2} i (a^\dagger - a), \quad [X_1, X_2] = \tfrac{1}{2} i, \tag{3.34}$$

for each mode separately. The electric field (3.10) for the plane waves (3.11) is then for real $\boldsymbol{\epsilon}$

$$\boldsymbol{E}(\boldsymbol{r},t) = 2(h\omega/V)^{1/2}\boldsymbol{\epsilon}(X_1\sin(\omega t - \boldsymbol{kr}) - X_2\cos(\omega t - \boldsymbol{kr})). \tag{3.35}$$

The matrix elements of a and $a^\dagger$ between Fock states follow from (1.225) and its Hermitian adjoint,

$$\langle n'|a|n\rangle = \delta_{n',n-1}\sqrt{n}, \quad \langle n'|a^\dagger|n\rangle = \delta_{n',n+1}\sqrt{n'}. \tag{3.36}$$

Consequently, all Fock expectation values vanish, $\langle n|\boldsymbol{A}|n\rangle = \langle \boldsymbol{A}\rangle_n = 0$. In the complete field operator $\boldsymbol{A}(\boldsymbol{r},t)$, each a_i and $a_i^\dagger$ changes the photon number of exactly one mode:

$$\begin{aligned}\langle n_1' n_2'|\boldsymbol{A}/c\hbar^{1/2}|n_1 n_2\rangle = {} & \omega_1^{\frac{1}{2}}\left(\delta_{n_1',n_1-1}\sqrt{n_1}\boldsymbol{A}_1 + \delta_{n_1',n_1+1}\sqrt{n_1'}\boldsymbol{A}_1^*\right)\delta_{n_2',n_2} \\ & + (1 \leftrightarrow 2)\,.\end{aligned} \tag{3.37}$$

However, actual fields can rarely be described by a single quantum state; they require a density matrix formalism.

In the continuum limit, one considers instead of H_F the energy density $e_F = H_F/V$,

$$e_F = H_F/V = \Sigma_\lambda \int d^3k N_\lambda(\boldsymbol{k})\hbar\omega/8\pi^3, \quad [a_\lambda(\boldsymbol{k}), a_{\lambda'}^\dagger(\boldsymbol{k})] = 8\pi^3\delta_{\lambda\lambda'}\delta_3(\boldsymbol{k}-\boldsymbol{k}'). \tag{3.38}$$

3.2 C, P and T

The Maxwell equations (2.20) are invariant under the charge conjugation operator C, which reverses the sign of the four-potential $A^\mu = (\phi, \boldsymbol{A})$:

$$A_C^\mu = -A^\mu: \quad \boldsymbol{E}_C = -\boldsymbol{E}, \;\; \boldsymbol{B}_C = -\boldsymbol{B}. \tag{3.39}$$

The extension of this invariance to quantum mechanics requires a sign change of the electric current, $j_{\mathrm{el},C}^\mu = -j_{\mathrm{el}}^\mu$. We have argued in Sect. 2.2 that j_{el}^μ differs from the 4-current density j^μ only by the constant q, $j_{\mathrm{el}}^\mu = qj^\mu$. Therefore C invariance of the Maxwell equations requires

$$j_C^\mu = -j^\mu. \tag{3.40}$$

With $\pi^\mu = i\hbar\partial^\mu - (q/c)A^\mu$, the charge-conjugate 4-momentum is

$$\pi_C^\mu = i\hbar\partial^\mu + (q/c)A^\mu = -\pi^{\mu *}, \tag{3.41}$$

where the star denotes complex conjugation. A Klein-Gordon equation (1.66) containing A_C^μ is

$$[(-\pi_\mu^*)(-\pi^{\mu *}) - m^2c^2]\psi_C = 0. \tag{3.42}$$

This is nothing but the complex conjugate of the original KG equation,

$$\psi_C = \psi^*. \tag{3.43}$$

In this sense, the KG equation is C-invariant. The antisymmetry of its current is satisfied by (2.27), $j^\mu = \psi^* \pi^\mu \psi + \psi \pi^{\mu *} \psi^*$; the minus sign arises from $\pi^\mu \to -\pi^{\mu *}$, $\pi^{\mu *} \to -\pi^\mu$.

The nonrelativistic Schrödinger equation (1.67) is not C-invariant, because it is linear in $\pi^0 = i\hbar\partial_0 - (q/c)A^0$. C invariance is responsible for the profound differences between nonrelativistic approximations and the relativistic formalism and its physical consequences. As the KG operator is second-order in π^0, the eigenvalue ω_n of $i\partial_t$ need not be positive. For a general $\psi(\boldsymbol{r}, t)$, the complete sum in (1.71) contains also negative energy states. The latter ones exist for ω down to $-\infty$. With interactions included, all charged particles could fall infinitely in energy, for example by emitting radiation. Without charge conjugation, one may rule that all expansion coefficients vanish when $\omega_n < 0$. But $\psi_C = \psi^*$ changes all $e^{-i\omega t}$ to $e^{+i\omega t}$ and turns all positive energies negative. On the other hand, possible negative energy states $\psi^{(-)}$ in ψ are turned into positive energy states. The only known way out is to replace ψ by an operator

$$\Psi = \Psi^{(+)} + \Psi^{(-)}, \quad \Psi^{(+)} = \Sigma_i a_i \psi_i e^{-i\omega_i t}, \quad \Psi^{(-)} = \Sigma_i a_{-i} \psi_{-i} e^{i\omega_i t}. \tag{3.44}$$

a_i is a meson lowering operator analogous to the a_i (3.5) for a photon in the mode i, and a_{-i} is a raising operator analogous to the $a_i^\dagger$ for a photon, but this time for a new particle, namely a meson of opposite electric charge. To emphasize this point already in the notation, one frequently writes

$$a_{-i} = b_i^\dagger, \quad a_{-i}^\dagger = b_i. \tag{3.45}$$

The neutral pion π^0 has no electric charge and has in fact $a_i = b_i$, which makes Ψ a Hermitian operator as in the case of light. For the π^- on the other hand, the new particle required by charge conjugation is the π^+, which is also called the antiparticle of the π^- (or vice versa). The operator Ψ is then not Hermitian, one has

$$\Psi^\dagger = \Sigma_i a_i^\dagger \psi_i^* e^{i\omega_i t} + \Sigma_i a_{-i}^\dagger \psi_{-i}^* e^{-i\omega_i t}. \tag{3.46}$$

Still, for $A^\mu = 0$, there is no formal difference, because the free KG equations for ψ and ψ^* are identical. For $A^\mu \neq 0$, there is also no difference as long as A^μ is charge conjugated according to (3.39). But if the total A^μ contains an external, "classical" piece as in (3.7), the states are different. In particular, an attractive Coulomb potential has bound states for π^- but not for π^+. The unbound scattering states of π^+ satisfy the equation for π^- at negative ω. More importantly, the positron wave functions in β^+ decays (see below) may be calculated from the Dirac equation for electrons.

Any closed system is charge conjugation invariant, apart from "weak interactions". Thus, if the Coulomb potential is provided by a proton nucleus p, there should also exist an "antiproton" nucleus $\overline{p}$, whose potential is repulsive for π^- but attractive for π^+. C invariance requires profound deviations from the traditional Hamiltonian quantum mechanics of binary atoms, to be discussed in Chap. 4.

Atoms have fixed numbers of electrons, but as Ψ removes an electron, it does not commute with the electron number operator. The connection between wave functions ψ and the operator Ψ is complicated. The aim of relativistic quantum mechanics is to approximate the action of Ψ by effective operators in the subspaces of fixed electron numbers. One normally sets $\Psi^{(-)} = 0$. When necessary, this can be formalized by projectors on positive-energy states. However, it would be inconsistent to keep such projectors in completeness relations.

The Dirac equation is also charge conjugation invariant, but the necessary transformation requires several steps. We take the form (2.8) but express $\boldsymbol{\alpha}$ as $\gamma^5\boldsymbol{\sigma}$ in order to separate the Pauli algebra from the Dirac algebra:

$$(\pi^0 - \gamma^5\boldsymbol{\sigma}\boldsymbol{\pi})\psi_D = mc\beta\psi_D, \quad (\pi^{0*} - \gamma^5\boldsymbol{\sigma}^*\boldsymbol{\pi}^*)\psi_D^* = mc\beta\psi_D^*. \tag{3.47}$$

σ_x and σ_z are real, but σ_y is imaginary, $\sigma_y^* = -\sigma_y$. There exists no unitary matrix that would transform all three $\boldsymbol{\sigma}^*$ back to $\boldsymbol{\sigma}$. It is however possible to transform $\boldsymbol{\sigma}^*$ into $-\boldsymbol{\sigma}$:

$$\boldsymbol{\sigma}^* = -U_C^\dagger\boldsymbol{\sigma}U_C, \quad U_C = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} = e^{-i\pi\sigma_y/2} = -i\sigma_y, \quad U_C^\dagger U_C = 1, \tag{3.48}$$

$$(\pi^{0*} + \gamma^5\boldsymbol{\sigma}\boldsymbol{\pi}^*)U_C\psi_D^* = mc\beta U_C\psi_D^*. \tag{3.49}$$

Next, the sign of the second operator in the bracket is changed by a β-transformation as in parity, using $\gamma^5\beta = -\beta\gamma^5$:

$$(\pi^{0*} - \gamma^5\boldsymbol{\sigma}\boldsymbol{\pi}^*)\beta U_C\psi_D^* = mcU_C\psi_D^*. \tag{3.50}$$

In the final step, the sign of the left-hand side of (3.50) is switched by a γ^5-transformation,

$$(-\pi^{0*} + \gamma^5\boldsymbol{\sigma}\boldsymbol{\pi}^*)\psi_C = mc\beta\psi_C, \quad \psi_C = \beta\gamma^5 U_C\psi_D^*. \tag{3.51}$$

This replaces the spinless transformation (3.42); it is surprisingly complicated. The joint operator CP fo charge conjugation and parity transformation is simpler, because the latter one brings another factor β,

$$\psi_{CP}(\boldsymbol{r}) = \gamma^5 U_C\psi_D^*(-\boldsymbol{r}). \tag{3.52}$$

It is accompanied by the CP-transformation of A^μ,

$$A^0_{CP}(\boldsymbol{r}) = -A^0(-\boldsymbol{r}), \quad \boldsymbol{A}_{CP}(\boldsymbol{r}) = \boldsymbol{A}(-\boldsymbol{r}). \tag{3.53}$$

It has been found that the weak interaction is neither C nor P-invariant, but that the ordinary beta decay ($p \to e^+\nu n$) is still CP invariant. In other forms of the weak interaction, CP violation is small. If one postulates the invariance of quantum mechanics under transformations that can represent classical Lorentz transformations including space inversion, then one can comprise beta decay only by taking CP as the space inversion operator. The problem is irrelevant from the mathematical point of view, as the group $SL_2(C)$ (2.99) has no space inversion.

The Maxwell, KG and Dirac equations are also invariant under time reversal T, $t' = -t$, $\boldsymbol{r}' = \boldsymbol{r}$:

$$A^0_T(t,\boldsymbol{r}) = A^0(-t,\boldsymbol{r}), \quad \boldsymbol{A}_T(t,\boldsymbol{r}) = -\boldsymbol{A}(-t,\boldsymbol{r}), \tag{3.54}$$

$$\pi^0_T = \pi^{0*}, \quad \boldsymbol{\pi}_T = -\boldsymbol{\pi}^*, \tag{3.55}$$

$A^{\mu *}$ is to be taken at time $-t$. For T, the matrix transformation (3.49) is already sufficient, because it changes exactly the signs of the three vector components:

$$\psi_T(t,\boldsymbol{r}) = U_C\psi^*_D(-t,\boldsymbol{r}). \tag{3.56}$$

The product CPT is particularly simple: With $U_C U^*_C = U^2_C = 1$ and $(\psi^*_D)^* = \psi_D$,

$$\psi_{CPT}(x^\mu) = \gamma^5\psi_D(-x^\mu) = \psi^5_D(-x^\mu) \tag{3.57}$$

in the notation of (2.107).

We still have to check the antisymmetry of the Dirac current $j^\mu = j^\mu_r + j^\mu_l$ (2.320) under charge conjugation, $j^\mu_C = -j^\mu$, as required by the Maxwell equations. We begin with $j^\mu_l/c = \psi^\dagger_l\sigma^\mu_l\psi_l$ and express this form in terms of the transposed spinors,

$$j^\mu_l/c = \psi_{l,\mathrm{tr}}\sigma^\mu_{l,\mathrm{tr}}\psi^*_l = \psi_{l,\mathrm{tr}}\sigma^{\mu *}_l\psi^*_l = \psi_{l,\mathrm{tr}}U^\dagger_C\sigma^\mu U_C\psi^*_l \tag{3.58}$$

according to (3.48). Looking now at (3.51), $\psi_C = \beta\gamma^5 U_C\psi^*_D$, writing σ^μ as $\gamma^5\beta\sigma^\mu\beta\gamma^5$ and remembering $\gamma^5 = -1$ for ψ_l as well as $\beta\psi_l = \psi_r$, one finds $j^\mu_l = j^\mu_{r,C}$ and correspondingly $j^\mu_r = j^\mu_{l,C}$, which disagrees with the expected $j^\mu_C = -j^\mu$. To resolve this contradiction, one must replace the Dirac spinor function $\psi_D(\boldsymbol{r},t)$ by an operator $\Psi_D(\boldsymbol{r},t)$ that lowers the charge of the state on which it operates by one unit: It destroys an electron with $\Psi^{(+)} \equiv \Psi_{De}$ and creates a positron with $\Psi^{(-)} \equiv \Psi_{Dp}$. The minus sign arises from the postulate that the components Ψ_α ($\alpha = 1,2,3,4$) of Ψ_D and $\Psi^\dagger_\beta$ of $\Psi^\dagger_D$ anticommute. The precise anticommutators will be derived in Sect. 3.3, they are

$$\{\Psi^\dagger_\alpha(\boldsymbol{r},t), \Psi_\beta(\boldsymbol{r}',t)\} = \delta_{\alpha\beta}\delta(\boldsymbol{r}-\boldsymbol{r}'), \quad \{\Psi_\alpha(\boldsymbol{r},t), \Psi_\beta(\boldsymbol{r}',t)\} = 0. \tag{3.59}$$

The Dirac current operator will be denoted by j^μ_Ψ in the following. As the form (3.58) has $\Psi^\dagger_l$ and Ψ_l in transposed order, it has in fact an extra minus sign from (3.59), and the correct form is $-\Psi_{l,\mathrm{tr}}\sigma^\mu_{l,\mathrm{tr}}\Psi^\dagger_{l,\mathrm{tr}} + 2\delta_{\mu 0}\delta(\boldsymbol{0})$. The

last term arises from $\Sigma_{\alpha,\beta}\delta_{\alpha\beta}\sigma^\mu_{l,\mathrm{tr},\alpha\beta} = \mathrm{tr}\,\sigma^\mu_l = 2\delta_{\mu 0}$. It is removed by an antisymmetrization of j^μ_Ψ,

$$j^\mu_\Psi/c = \tfrac{1}{2}[\overline{\Psi}^\dagger_D, \gamma^\mu \Psi_D] = \tfrac{1}{2}(\Psi^\dagger_r \sigma^\mu \Psi_r - \Psi_{r,\mathrm{tr}}\sigma^\mu_{\mathrm{tr}}\Psi^\dagger_{r,\mathrm{tr}} + \Psi^\dagger_l \sigma^\mu_l \Psi_l - \Psi_{l,\mathrm{tr}}\sigma^\mu_{l,\mathrm{tr}}\Psi^\dagger_{l,\mathrm{tr}}). \tag{3.60}$$

This antisymmetrization is always understood but rarely written explicitly. The resulting density operator ρ_Ψ is the antisymmetrised version of (2.312),

$$\rho_\Psi = \tfrac{1}{2}[\Psi^\dagger_D, \Psi_D] = \tfrac{1}{2}(\Psi^\dagger_r\Psi_r - \Psi_{r,\mathrm{tr}}\Psi^\dagger_{r,\mathrm{tr}} + \Psi^\dagger_l\Psi_l - \Psi_{l,\mathrm{tr}}\Psi^\dagger_{l,\mathrm{tr}}). \tag{3.61}$$

Commutators in (3.59) would lead to $\rho_\Psi = 0$. We shall see later that the anticommutator form (which is required by charge conjugation) entails the Pauli principle.

The precise meaning of the operators a_i and a_{-i} in Ψ (3.44) is best explained for a process in which a free electon of energy $\hbar c k^0$, momentum $\hbar\boldsymbol{k}$ and spin component m_s is removed, for example in the reaction $\mathrm{e}^-\mathrm{p} \to \nu\mathrm{n}$ (weak electron capture), where the proton (p) is transformed into a neutron (n), and the electron into a neutral and massless spinor particle called neutrino. The absorption of the initial and creation of the final particles requires the field operator product $\Psi^\dagger_n\Psi_p\Psi^\dagger_\nu\Psi$. For the electron field Ψ, we only need the component

$$\Psi_{\boldsymbol{k},m_s} = e^{i\boldsymbol{k}\boldsymbol{r}}[a_{\boldsymbol{k},m_s}e^{-i\omega t}u(k^0,\boldsymbol{k}) + a_{-,\boldsymbol{k},m_s}e^{i\omega t}u(-k^0,\boldsymbol{k})], \tag{3.62}$$

with u given by (2.331). The scattering theory of Sect. 4.2 predicts the conservation of energy and momentum, $\omega+\omega_p = \omega_n+\omega_\nu$, and $\boldsymbol{k}+\boldsymbol{k}_p = \boldsymbol{k}_n+\boldsymbol{k}_\nu$. These relations can only be saved if the antiparticle created by $a_{-,\boldsymbol{k},m_s}$ appears in the final state instead of the initial state, such that for negative ω, energy conservation reads

$$\omega_p = \omega_n + \omega_\nu + (-\omega). \tag{3.63}$$

Momentum conservation may be written as

$$\boldsymbol{k}_p = \boldsymbol{k}_n + \boldsymbol{k}_\nu + (-\boldsymbol{k}). \tag{3.64}$$

Consequently, the momentum of the object created by $a_{-,\boldsymbol{k},m_s}$ is $-\boldsymbol{k}$, not $\boldsymbol{k}$. The argument is extended to other quantum numbers which are additively conserved, in particular to the electric charge: As the removed electron has $q = -e$, a created anti-electron has $q = +e$, which explains the name "positron". When the $a_{\boldsymbol{k},m_s}$ of (3.62) contributes to $\mathrm{e}^-\mathrm{p} \to \nu\mathrm{n}$, the $a_{-,\boldsymbol{k},m_s}$ contributes to the "β^+-decay" $\mathrm{p} \to \mathrm{n}\nu\mathrm{e}^+$. As a free proton is lighter than a free neutron, β^+-decay occurs only in certain nuclei.

The summation index i of $\Psi^{(-)}$ is normally inverted to $-i$ as indicated already in (3.45). One thus writes

$$\psi_{-i} = e^{-i\boldsymbol{k}\boldsymbol{r}}iv, \quad v = \gamma^5 u(-k^0,-\boldsymbol{k},-m_s)/i = \gamma^5(\hbar k^0 + \hbar\boldsymbol{k}\boldsymbol{\alpha})^{1/2}\chi(-m_s); \tag{3.65}$$

$\gamma^5 v$ agrees with $-\beta\gamma^5 U_C u^*$ apart from a phase, $U_C\chi(m_s) = m_s\chi(-m_s)$. The γ^5 endows v_l with an extra minus sign, which ensures $\overline{u}v \sim -mc + mc = 0$, instead of $2mc$ as in (2.341).

3.3 Field Operators and Wave Equations

The replacement of the one-electron wave function ψ_D by an electron field operator Ψ_D has far-reaching consequences. The precise Dirac equation applies no longer to single-electron states as in (2.87), but to the field operator itself. With $\pi^\mu = i\hbar\partial^\mu + (e/c)A^\mu_{\rm tot}$,

$$i\hbar\partial_t\Psi_D = [-eA^0_{\rm tot} + (-ic\hbar\nabla + e\boldsymbol{A}_{\rm tot})\boldsymbol{\alpha} + mc^2\beta]\Psi_D, \tag{3.66}$$

where also $A^\mu_{\rm tot}$ contains field operators A^μ in addition to classical fields $A^\mu_{\rm cl}$:

$$\boldsymbol{A}_{\rm tot} = \boldsymbol{A}_{\rm cl} + \boldsymbol{A}, \quad A^0_{\rm tot} = A^0_{\rm cl} + A^0, \quad -eA^0_{\rm cl} = V(\boldsymbol{r}). \tag{3.67}$$

In the Coulomb gauge, $A^0_{\rm tot}$ satisfies the Poisson equation (1.58),

$$-\nabla^2 A^0_{\rm tot} = 4\pi(\rho_{\rm cl} - e\rho_\Psi + \rho'_{\rm el}). \tag{3.68}$$

In the case of atoms, $\rho_{\rm cl}$ is the nuclear charge density, ρ_Ψ is given by (3.61) and ρ' is the charge density of muon, pion etc fields. In the following, $\rho'_{\rm el}$ is neglected, and the antisymmetrization of ρ_Ψ is omitted. The solution (1.59) of the Poisson equation for the operator part A^0 is then

$$A^0(\boldsymbol{r},t) = -e\int d^3r'\rho_\Psi(\boldsymbol{r}',t)/|\boldsymbol{r}-\boldsymbol{r}'|, \quad \rho_\Psi = \Psi^\dagger_D(\boldsymbol{r}',t)\Psi_D(\boldsymbol{r}',t). \tag{3.69}$$

The physical meaning of $\boldsymbol{A}$ and A^0 is then very different: While $\boldsymbol{A}$ changes the photon number by ±1 according to our discussion of Sect. 3.1, A^0 creates or absorbs electron-positron pairs. After elimination of A^0, the Dirac equation becomes a nonlinear integro-differential equation for the field operator Ψ_D.

Wave equations for atoms with electrons are easily derived within a Fock space for electrons and positrons. We expand Ψ_D in terms of one-electron orbitals $\psi_{iD}(\boldsymbol{r})\exp(-i\omega_i t)$ and the complex conjugates of one-positron orbitals,

$$\Psi_D = \Psi_{De} + \Psi_{Dp}, \quad \Psi_{De} = \Sigma_i b_i\psi_{iD}(\boldsymbol{r})e^{-i\omega_i t}, \quad \Psi_{Dp} = \Sigma_i d^\dagger_i\psi_{iD-}(\boldsymbol{r})e^{i\omega_i t}. \tag{3.70}$$

The operator b_i is analogous to the a_i of Sect. 3.1; it removes and electron from the orbital $\psi_{iD}(\boldsymbol{r})$. $d^\dagger_i$ creates a positron, $b^\dagger_i$ creates an electron, and $N_i = b^\dagger_i b_i$ is the electron number operator for the orbital i. Surprisingly, this is consistent with the use of anticommutators (Jordan 1927, Jordan and Klein 1927)

$$b_i b^\dagger_j + b^\dagger_j b_i = \delta_{ij} \tag{3.71}$$

instead of the harmonic oscillator commutators $b_i b_j^\dagger - b_j^\dagger b_i = \delta_{ij}$, provided one has $b_i^2 = 0$: The necessary property of a raising operator $b^\dagger$ is

$$Nb^\dagger|n-1\rangle = n^{1/2}N|n\rangle, \quad N = b_i^\dagger b_i, \tag{3.72}$$

compare (1.227). For the special case $(b^\dagger)^2 = 0$ this is consistent with

$$b^\dagger b b^\dagger|n-1\rangle = b^\dagger(1 - b^\dagger b)|n-1\rangle = b^\dagger|n-1\rangle. \tag{3.73}$$

A good approximation for an electron bound in a state $|a\rangle$ to a nucleus is expressed in terms of the electron-positron vacuum $|0\rangle$ as follows:

$$\psi_a(\boldsymbol{r}_1, t) = \langle 0|\Psi_D(\boldsymbol{r}_1, t)b_a^\dagger|0\rangle, \tag{3.74}$$

because of $\langle 0|d_i^\dagger = 0$ and $\langle 0|b_i b_a^\dagger = 0$ for $i \neq a$. The index $i = a$ picks the desired orbital.

We now consider a simplified two-electron state, in which the repulsion between the two electrons is neglected. That is to say, the electrons occupy two orbitals $|a\rangle$ and $|b\rangle$:

$$\psi_{ab}(\boldsymbol{r}_1, \boldsymbol{r}_2, t) = 2^{-1/2}\langle 0|\Psi_D(\boldsymbol{r}_1, t)\Psi_D(\boldsymbol{r}_2, t)b_b^\dagger b_a^\dagger|0\rangle. \tag{3.75}$$

The factor $2^{-1/2}$ ensures normalization, see below. The operator product contains a double sum,

$$\Psi_D(\boldsymbol{r}_1, t)\Psi_D(\boldsymbol{r}_2, t) = \Sigma_{i,j} b_i b_j \psi_{iD}(\boldsymbol{r}_1)\psi_{jD}(\boldsymbol{r}_2)e^{-i(\omega_i+\omega_j)t}. \tag{3.76}$$

Two combinations of indices contribute to (3.75), namely $i = a,\ j = b$ and $i = b,\ j = a$. The first combination delivers the product $\psi_a(\boldsymbol{r}_1)\psi_b(\boldsymbol{r}_2)$. For the second one, the two Ψ_D's must be put into inverse order before $\Psi_D(\boldsymbol{r}_1, t)$ can compensate $b_b^\dagger$. This causes a change of sign according to (3.59). The resulting two-electron state is

$$\psi_{ab} = 2^{-1/2}[\psi_a(\boldsymbol{r}_1)\psi_b(\boldsymbol{r}_2) - \psi_b(\boldsymbol{r}_1)\psi_a(\boldsymbol{r}_2)]e^{i\omega t}, \quad \omega = \omega_a + \omega_b. \tag{3.77}$$

It vanishes for $a = b$, thus establishing the Pauli principle (Pauli 1925): an orbital can accomodate only one electron. Even in the absence of any interaction between the electrons, factorizing states $\psi_a(\boldsymbol{r}_1)\psi_b(\boldsymbol{r}_2)$ do not exist. Electrons cannot be numbered, $\boldsymbol{r}_1$ is used for the position of any of the elctrons.

As an operator in the photon Fock space, the "electron wave function" (3.74) satisfies (3.66) for $A^0 = 0$,

$$i\hbar\partial_t\psi_1 = H_1\psi_1, \quad H_1 = V(\boldsymbol{r}_1) + [-i\hbar\nabla_1 + e\boldsymbol{A}_{\rm cl}(\boldsymbol{r}_1) + e\boldsymbol{A}(\boldsymbol{r}_1, t)]\boldsymbol{\alpha}_1 + mc^2\beta_1. \tag{3.78}$$

As $\boldsymbol{A}(\boldsymbol{r}_1)$ changes the photon number by one unit, $\psi_a(\boldsymbol{r}_1, t)$ has no diagonal elements in the photon number space. The operator A^0 of (3.69) disappears because of $\langle 0|\Psi_D^\dagger = 0$. When (3.78) is applied to the result (3.77) for $|ab\rangle$, one gets

$$i\hbar\partial_t|ab\rangle = (H_1 + H_2)|ab\rangle, \tag{3.79}$$

which is of limited use because it misses the Coulomb repulsion between the two electrons,

$$V_{12} = e^2/r_{12}, \quad r_{12} = [(\boldsymbol{r}_1 - \boldsymbol{r}_2)^2]^{1/2}. \tag{3.80}$$

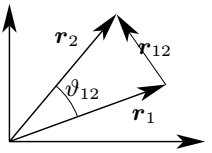

Fig. 3.2. The angle ϑ_{12}

For a more general state ψ_{D2} which is not an antisymmetrized product of orbitals, one must replace $b_a^\dagger b_b^\dagger|0\rangle$ by a state $|ee\rangle$ which is only specified indirectly by its eigenvalue $-2e$ of the total charge operator Q which is conserved:

$$Q = -e\int d^3r\rho_\Psi(\boldsymbol{r},t), \quad Q|ee\rangle = -2e|ee\rangle. \tag{3.81}$$

With the normalization left open, the generalization of the ansatz (3.75) is

$$\psi_{D2} = \langle 0|\Psi_D(\boldsymbol{r}_1,t)\Psi_D(\boldsymbol{r}_2,t)|ee\rangle \equiv \langle 0|\Psi_1\Psi_2|ee\rangle. \tag{3.82}$$

The field equation (3.66) for $\Psi_i = \Psi_D(\boldsymbol{r}_i,t)$ $(i=1,2)$ is now written in the more compact form

$$i\hbar\partial_t\Psi_i = [H_i - eA^0(\boldsymbol{r}_i,t)]\Psi_i. \tag{3.83}$$

And as H_2 does not operate on Ψ_1, one obtains for ψ_{D2}

$$(i\hbar\partial_t - H_1 - H_2)\psi_{D2} = \langle 0|[(i\hbar\partial_t - H_1)\Psi_1]\Psi_2 + \Psi_1[(i\hbar\partial_t - H_2)\Psi_2]|ee\rangle. \tag{3.84}$$

The combination $\langle 0|(i\hbar\partial_t - H_1)\Psi_1 = \langle 0|A^0(\boldsymbol{r}_1,t)\Psi_1$ vanishes again because of $\langle 0|A^0 = 0$. The second round bracket is $-eA^0(\boldsymbol{r}_2,t)$, for which we insert (3.69):

$$(i\hbar\partial_t - H_1 - H_2)\psi_{D2} = -e\langle 0|\Psi_1\int d^3r'\Psi'^\dagger\Psi'(e/|\boldsymbol{r}_2 - \boldsymbol{r}'|)\Psi_2|ee\rangle. \tag{3.85}$$

The operator $\Psi'^\dagger = \Psi^\dagger(\boldsymbol{r}',t)$ is now anticommuted to the left of Ψ_1, where one may use $\langle 0|\Psi'^\dagger = 0$. In this procedure, however, there remains the following anticommutator:

$$\sum_\beta \int d^3r' \frac{\{\Psi_{\alpha_1}(\boldsymbol{r}_1), \Psi_\beta^\dagger(\boldsymbol{r}')\Psi_\beta(\boldsymbol{r}')\}}{|\boldsymbol{r}_2 - \boldsymbol{r}'|} = \int d^3r' \frac{\delta(\boldsymbol{r}_1 - \boldsymbol{r}')\Psi_{\alpha_1}(\boldsymbol{r}')}{|\boldsymbol{r}_2 - \boldsymbol{r}'|} = \frac{\Psi_{\alpha_1}(\boldsymbol{r}_1)}{r_{12}}. \tag{3.86}$$

Thus, (3.84) finally becomes

$$(i\hbar\partial_t - H_1 - H_2 - V_{12})\psi_{D2} = 0, \tag{3.87}$$

which is the desired "Dirac-Coulomb" equation. The postulate of canonical field quantization was formulated for the electromagnetic field in (3.27), but it was not used there. Instead, the formalism was based on the counting operator N for free field quanta, namely photons or polarons. An analogous Fock space basis exists also for the electron field operator, but the decomposition into single-electron orbitals neglects their mutual Coulomb repulsion, as we have seen. For comparison, the interaction between photons or polarons is so weak that one can have large amounts of quanta before it is felt. For electrons, the canonical field quantization is most conveniently formulated if the field equation (in this case the Dirac equation) is already known: There exists a QED Hamiltonian $H_{\rm QED}$ as a space integral over products of field operators, such that the field equation follows from the commutator between the field and $H_{\rm QED}$,

$$i\hbar\partial_t\Psi(\boldsymbol{r}) = [\Psi(\boldsymbol{r}), H_{\rm QED}], \tag{3.88}$$

One piece of $H_{\rm QED}$ is already known, namely H_F (3.18), which commutes with $\Psi = \Psi_D$. We now add the electron-positron piece,

$$H_e = \int d^3r' \Psi_D^\dagger(\boldsymbol{r}')(V - \tfrac{1}{2}eA^0 + c\boldsymbol{\pi}\boldsymbol{\alpha} + mc^2\gamma^0)\Psi_D(\boldsymbol{r}'). \tag{3.89}$$

To obtain the field equation as a local differential equation from (3.88), it is clear that $\Psi(\boldsymbol{r})$ must either anticommute with $\Psi(\boldsymbol{r}')$, in which case its anticommutator with $\Psi^\dagger(\boldsymbol{r}')$ must have the form (3.59) in order to cancel the $\int d^3r'$, or it must commute with $\Psi(\boldsymbol{r}')$, in which case a commutator must be used (see below). For electrons and also for muons, charge conjugation invariance requires anticommutators, as we have seen. In the particular case of (3.89), note the factor $\frac{1}{2}$ in front of A^0. It disappears in the Dirac equation because $\Psi_D^\dagger A^0 \Psi_D$ is quadratic in $\Psi_D^\dagger$, compare (3.69). The complete Hamiltonian of quantum electrodynamics is

$$H_{\rm QED} = H_F + H_e + H_\mu + H_{\rm scalar} + \cdots \tag{3.90}$$

Here $H_{\rm scalar}$ contains the contributions of "scalar fields" for the charged spinless particles, such as $\pi^\pm$, see Sect. 4.9. The dots represent the Hamiltonians of possible additional fields that contribute also to $\rho'_{\rm el}$.

Both the Maxwell (2.20) and Dirac (3.66) field equations may be derived from the principle of least action (3.25), applied to the Lagrangian

$$L = (4\pi)^{-1}[\overline{\Psi}_D(\gamma_\mu\pi^\mu - m)\Psi_D - \tfrac{1}{4}F_{\mu\nu}F^{\mu\nu}], \quad \pi^\mu = i\hbar\partial^\mu - eA^\mu. \tag{3.91}$$

As we know these equations beforehand, there seems no need to define L. But the space integrals ("loops") of higher order perturbations are frequently di-

vergent, in gross contradiction with the spirit of small perturbations. Already the lowest nonvanishing "self-energy", depicted by graph a in Fig. 3.3 below, produces an infinite energy shift. It can be compensated in (3.91) by an ad hoc mass counterterm $\Delta m^{(1)}\overline{\Psi}_D\Psi_D$, such that m in (3.91) has little to do with the measured electron mass. The same complication arises with the electric charge e in (3.87), which gets "renormalized" by the "vacuum polarization". The first-order mass renormalization is nicely explained in the book of Sakurai (1967). A more convenient method is the "dimensional regularization" (see Sect. 5.3). For the QED Lagrangian (3.91), renormalization can be extended to all orders, leaving behind smaller and smaller finite terms. Such a field theory is called "renormalizable". Until Sect. 5.3, our masses and charges will be the physical, "renormalized" ones, e = 0.08542 (1.148) and $m_e c^2 = 511\,\mathrm{keV}$ for the electron. The corresponding L (3.91) is not particularly fundamental.

As the electron field operator disappears from equations such as (3.87), the Pauli principle becomes a separate postulate. The permutation operator P_{12} for two "identical particles" such as two electrons commutes with $H = H_1 + H_2 + V_{12}$, thus allowing common eigenstates of H and P_{12}:

$$P_{12}H = HP_{12}, \quad P_{12}\psi = \eta_{12}\psi. \tag{3.92}$$

With $P_{12}^2\psi = \psi$, the eigenvalues η_{12} are $+1$ and -1. The Pauli principle excludes the value $+1$ by hand.

Nuclear motion may be included in (3.87) by a nuclear Hamiltonian term, normally in a nonrelativistic form:

$$H_n = -\Sigma_i \nabla_{ni}^2/2m_{ni} + \Sigma_{i<j} Z_i Z_j e^2/r_{n,ij}.$$

Atoms have only one nucleus, but molecules such as H_2 or N_2 may have several identical nuclei. For any two identical particles i and j, the wave function $\psi_{e,n}$ of the complete system of electrons plus nuclei has $\eta_{ij} = (-1)^{2s_i}$, s_i being the spin of particle i. This is the famous "spin-statistics" theorem. For integer s_i, it is known as the "Bose-Einstein" principle. It has drastic consequences particularly for $s_i = 0$: In the vibrational ground state of N_2, all odd rotational excitations are missing, provided both nitrogen nuclei are of the spinless ^{14}N type.

Like the Pauli principle, the Bose-Einstein principle follows from quantum field theory: The spinless field operator satisfies a Klein-Gordon equation. The charge conjugation symmetry (3.40) of its current operator requires commutation relations instead of the anticommutation relations (3.59),

$$[\Psi^\dagger(\boldsymbol{r},t), \Psi(\boldsymbol{r}',t)] = \delta(\boldsymbol{r}-\boldsymbol{r}'), \quad [\Psi(\boldsymbol{r},t), \Psi(\boldsymbol{r}',t)] = 0. \tag{3.93}$$

However, local quantum fields for isotopes such as ^{14}N, ^{13}N are of little use in other contexts. The spin-statistics theorem is probably more fundamental.

3.4 Breit Operators

The "Dirac-Coulomb equation" (3.86) still contains the photon field operators $\boldsymbol{A}_i \equiv \boldsymbol{A}(\boldsymbol{r}_i, t)$. Although their expectation values $\langle \boldsymbol{A} \rangle_F$ vanish for all Fock states (3.2), it must be remembered that a general state of the electromagnetic field is a superposition of Fock states. The nondiagonal matrix elements of $\boldsymbol{A}$ (3.37) appear in second order perturbation theory. In that order, two terms arise from the combination $\boldsymbol{A}_1 \boldsymbol{A}_2$; they can be replaced to some extent by an equivalent "Breit" operator. For its calculation, we separate the full operator into an "unperturbed" operator H_C in which $\boldsymbol{A}$ is missing, and a perturbation $H_{\rm per}$ which is linear in $\boldsymbol{A}_1$ and $\boldsymbol{A}_2$:

$$H_{\rm per} = H_{p1} + H_{p2}, \quad H_{pi} = e\boldsymbol{A}(r_i, t)\boldsymbol{\alpha}_i. \tag{3.94}$$

The unperturbed Dirac-Coulomb equation reads

$$H_C \psi_n^0 = E_n^0 \psi_n^0, \quad H_C = H_{1C} + H_{2C} + e^2/r_{12}, \tag{3.95}$$

$$H_{iC} = V(\boldsymbol{r}_i) + \boldsymbol{\pi}_{i,\rm cl}\boldsymbol{\alpha}_i + mc^2\beta_i, \quad \boldsymbol{\pi}_{i,\rm cl} = -i\hbar\nabla_i + e\boldsymbol{A}_{\rm cl}(\boldsymbol{r}_i). \tag{3.96}$$

The standard time-independent perturbation theory for an eigenvalue equation $H\psi = E\psi$ is needed now to the second order. The first-order shift vanishes because of $\langle \boldsymbol{A} \rangle = 0$. This is good as $\boldsymbol{A}$ is time-dependent; the time dependence vanishes in the combination $\langle n|H_{\rm per}|k\rangle\langle k|H_{\rm per}|n\rangle$.

As $H_{\rm per}$ (3.94) contains two terms, two factors of $H_{\rm per}$ produce four terms, namely H_{p1}^2, H_{p2}^2, and $H_{p1}H_{p2} = H_{p2}H_{p1}$. The first two terms are "self-energies" and contribute to the Lamb shift (Sect. 5.5); the other two produce the Breit shift $E_{B,n}$ to order α^4:

$$E_{B,n} = 2\Sigma_{k\neq n}\langle n|H_{p1}|k\rangle\langle k|H_{p2}|n\rangle(E_n^0 - E_k^0)^{-1}. \tag{3.97}$$

In $\langle n|H_{p1}|k\rangle$, only the annihilation part $c\Sigma_i(h/\omega_i)^{1/2}a_i\boldsymbol{A}_i(\boldsymbol{r}_1)e^{-i\omega_i t}$ of $\boldsymbol{A}$ (3.7) contributes, and in $\langle k|H_{p2}|n\rangle$ only the corresponding creation part, containing $a_i^\dagger \boldsymbol{A}_i^*(\boldsymbol{r}_2)e^{i\omega_i t}$ with the same index i. In the product, the t-dependence disappears. The summation index k comprises the index i for the created photon and an index n' for the intermediate two-electron states. With $\langle 0|a_i a_i^\dagger|0\rangle = 1$,

$$E_{B,n} = 2e^2\Sigma_{i,n'}(hc/\omega_i)\int \psi_n^\dagger \boldsymbol{\alpha}_1 \psi_{n'}\boldsymbol{A}_i(\boldsymbol{r}_1)\int \psi_{n'}^\dagger \boldsymbol{\alpha}_2 \psi_n \boldsymbol{A}_i^*(\boldsymbol{r}_2')/\Delta E, \tag{3.98}$$

$$\Delta E = E_n^0 - E_{n'}^0 - \hbar\omega_i. \tag{3.99}$$

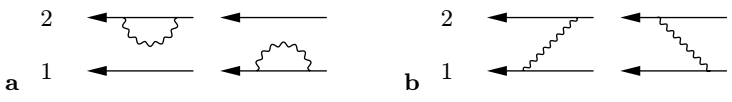

Fig. 3.3a,b. (**a**) Self interaction and (**b**) Photon exchange

The integration over $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ is understood in the first integral (remember that $\psi = \psi(\boldsymbol{r}_1, \boldsymbol{r}_2)$ is a two-electron wave function); the second integral has integration variables $\boldsymbol{r}'_1$, $\boldsymbol{r}'_2$. The $\Sigma_{n'}$ includes an integral over the continuum of unbound electrons, but the main contribution comes from states for which $E_n^0 - E_{n'}^0$ is significantly smaller than $\hbar\omega_i$. We use the approximation $\Delta E \approx -\hbar\omega_i$, which leads to a great simplification via the completeness relation (1.250), which in our case becomes

$$\Sigma_{n'} \psi_{n'}(\boldsymbol{r}_1, \boldsymbol{r}_2)\psi^\dagger_{n'}(\boldsymbol{r}'_1, \boldsymbol{r}'_2) = \delta_3(\boldsymbol{r}_1 - \boldsymbol{r}'_1)\delta_3(\boldsymbol{r}_2 - \boldsymbol{r}'_2), \tag{3.100}$$

$$E_{B,n} = -2e^2 hc \Sigma_i \int \psi^\dagger_n \boldsymbol{\alpha}_1 \boldsymbol{A}_i(\boldsymbol{r}_1)\boldsymbol{\alpha}_2 \boldsymbol{A}^*_i(\boldsymbol{r}_2)/\hbar\omega_i^2. \tag{3.101}$$

This has the form of an atomic expectation value. With $h = 2\pi\hbar$,

$$E_{B,n} = \langle H_B \rangle_n, \quad H_B = -4\pi e^2 \Sigma_i \omega_i^{-2} \boldsymbol{\alpha}_1 \boldsymbol{A}_i(\boldsymbol{r}_1)\boldsymbol{\alpha}_2 \boldsymbol{A}^*_i(\boldsymbol{r}_2). \tag{3.102}$$

H_B is the Breit operator, which reproduces $E_{B,n}$ already in first-order perturbation theory. For plane waves $\boldsymbol{A}(\boldsymbol{k})$ and in the continuum limit (3.38),

$$H_B = -e^2 \int d^3k (2\pi^2 k^2)^{-1} \Sigma_{i=1}^2 \alpha_1 e^{i\boldsymbol{k}\boldsymbol{r}_1} \boldsymbol{\epsilon}^{(i)} \alpha_2 e^{-i\boldsymbol{k}\boldsymbol{r}_2} \boldsymbol{\epsilon}^{*(i)}. \tag{3.103}$$

Due to the Coulomb gauge condition $\boldsymbol{k}\boldsymbol{\epsilon} = 0$, the tensor $T_{lm} = \Sigma_{i=1}^2 \epsilon_l^{(i)} \epsilon_m^{*(i)}$ is not simply δ_{lm} as for a complete set of vectors, but

$$T_{lm} = \Sigma_{i=1}^2 \epsilon_l^{(i)} \epsilon_m^{*(i)} = \delta_{lm} - k_l k_m / k^2, \tag{3.104}$$

such that $\boldsymbol{k} \cdot \boldsymbol{T}_m = 0$. Consequently,

$$H_B = -e^2 \int d^3k (2\pi^2 k^2)^{-1} [\boldsymbol{\alpha}_1 \boldsymbol{\alpha}_2 - (\boldsymbol{\alpha}_1 \boldsymbol{k})(\boldsymbol{\alpha}_2 \boldsymbol{k})/k^2] e^{i\boldsymbol{k}\boldsymbol{r}}, \quad \boldsymbol{r} = \boldsymbol{r}_1 - \boldsymbol{r}_2. \tag{3.105}$$

The first integral gives

$$\int d^3k (2\pi^2 k^2)^{-1} e^{i\boldsymbol{k}\boldsymbol{r}} = 1/r. \tag{3.106}$$

It follows from the inverse Fourier transformation (which contains a factor $(2\pi)^{-3}$) of (4.50) below. Strictly, the factor k^2 must be replaced by $(k^2 + a_s^{-2})^{-1}$; a_s is an "infrared cutoff" in this context: it removes the photons of wave numbers $\boldsymbol{k}$ having $k^2 < a_s^{-2}$ from the field $\boldsymbol{A}(\boldsymbol{r}, t)$. At the end of the calculation, one sends $a_s \to \infty$. The second integral is reduced to the first one in two steps: Firstly, one notes

$$\boldsymbol{k} e^{i\boldsymbol{k}\boldsymbol{r}} = -i\nabla e^{i\boldsymbol{k}\boldsymbol{r}} \tag{3.107}$$

and takes the ∇ outside the integration. Secondly, one writes

$$\boldsymbol{k}/k^4 = -\tfrac{1}{2}\nabla_k (1/k^2) \tag{3.108}$$

and performs a partial integration over $\boldsymbol{k}$:

$$-i\nabla_l \int d^3k e^{i\boldsymbol{kr}} k_m/(2\pi^2 k^4) = \tfrac{1}{2} i\nabla_l \int d^3k e^{i\boldsymbol{kr}} \partial_m (2\pi^2 k^2)^{-1} = \tfrac{1}{2}\nabla_l r_m, \tag{3.109}$$

$$\int d^3k e^{i\boldsymbol{kr}} k_l k_m/(2\pi^2 k^4) = \tfrac{1}{2}\delta_{lm}/r - \tfrac{1}{2} r_l r_m/r^3. \tag{3.110}$$

The complete final expression is thus (Breit 1929)

$$H_B = -\tfrac{1}{2} V_{12}[\boldsymbol{\alpha}_1\boldsymbol{\alpha}_2 + (\boldsymbol{\alpha}_1\boldsymbol{r})(\boldsymbol{\alpha}_2\boldsymbol{r})/r^2], \quad V_{12} = e^2/r. \tag{3.111}$$

Note the change of sign inside the bracket! The Dirac-Breit equation reads

$$(i\hbar\partial_t - H_1 - H_2 - V_{12} - H_B)\psi_{D2} = 0. \tag{3.112}$$

It is easily extended to more than two electrons.

Although H_{p1} and H_{p2} are time-dependent, the combination (3.97) is not. There exists a more elegant formalism which removes the t-dependence directly from $\boldsymbol{A} = \boldsymbol{A}(\boldsymbol{r}, t)$. Using the time-independence of $H_F = \Sigma_i \hbar\omega_i a_i^\dagger a_i$, one substitutes

$$\boldsymbol{A}(\boldsymbol{r}, t) = e^{itH_F/\hbar} \boldsymbol{A}_{\rm Sch} e^{-itH_F/\hbar}, \tag{3.113}$$

$$\boldsymbol{A}_{\rm Sch} = e^{-itH_F/\hbar} \boldsymbol{A}(\boldsymbol{r}, t) e^{itH_F/\hbar}. \tag{3.114}$$

The time derivative of $\boldsymbol{A}_{\rm Sch}$ is

$$i\hbar\partial_t \boldsymbol{A}_{\rm Sch} = e^{-itH_F/\hbar}(H_F\boldsymbol{A} - \boldsymbol{A}H_F + i\hbar[\partial_t, \boldsymbol{A}])e^{itH_F/\hbar}. \tag{3.115}$$

Any mode $\boldsymbol{A}_i$ in (3.7) satisfies

$$i\hbar[\partial_t, \boldsymbol{A}_i] = \omega_i \boldsymbol{A}_i, \quad i\hbar[\partial_t, \boldsymbol{A}_i^\dagger] = -\omega_i \boldsymbol{A}_i^\dagger, \tag{3.116}$$

which leads to

$$i\hbar[\partial_t, \boldsymbol{A}] = [\boldsymbol{A}, H_F], \tag{3.117}$$

and thus to $i\hbar\partial_t \boldsymbol{A}_{\rm Sch} = 0$. The operator $e^{itH_F/\hbar}$ has the physical meaning of a shift of the time variable by $-t$, compare (1.275); the connection between $\boldsymbol{A}$ and $\boldsymbol{A}_{\rm Sch}$ is simply

$$\boldsymbol{A}_{\rm Sch} = \boldsymbol{A}(\boldsymbol{r}, 0). \tag{3.118}$$

$\boldsymbol{A}_{\rm Sch}$ is called the Schrödinger picture of the vector potential operator, and $\boldsymbol{A}$ its Heisenberg picture. In the absence of external time dependene, all operators of the KG, Dirac, Dirac-Breit etc. equations are time-independent in the Schrödinger picture, which guarantees the existence of stationary solutions as in (1.44). The equations of nonrelativistic quantum mechanics have the form $i\hbar\partial_t\psi = H_{nr}\psi$, where H_{nr} is Hermitian, and time-independent for closed systems. In such cases, one may transform all operators as in (3.113), but with H_F replaced by the full H_{nr}. This Heisenberg picture has all time dependence of ψ moved to the operators. For example, the position operator $\boldsymbol{r}$ satisfies

$$i\hbar d\boldsymbol{r}/dt = [\boldsymbol{r}, H_{nr}]. \tag{3.119}$$

In this this book, only $\boldsymbol{A}$ is taken in the Heisenberg picture, which is called the "interaction picture". Here, t appears only in connection with the interaction between the charged particles and the photon field. The operators of relativistic quantum mechanics are often energy-dependent, in which case the Heisenberg picture is meaningless. This applies in particular to the KG and Kramers equations. The Dirac Hamiltonian which is derived from the Kramers operator (at the expense of doubling the number of components) is energy-independent, but replacing H_{nr} by H_D (2.87) in (3.119) still makes no sense. It leads to $d\boldsymbol{r}/dt \equiv v = c\boldsymbol{\alpha}$, which implies $v^2/c^2 = \boldsymbol{\alpha}^2 = (\gamma^5\boldsymbol{\sigma})^2 = 3$. This latter result shows also that H_B (3.111) cannot be used beyond first-order perturbation theory. In (3.168) below, it will be replaced by a better operator.

3.5 Two-Electron States and Pauli Principle

The Dirac-Breit equation in a nuclear Coulomb potential is difficult to handle except for nuclei of large electric charges Ze, where V_{12} and H_B may be treated perturbatively. For $Z \gg 1$, the unperturbed states of the inner electrons are determinants of one-electron orbitals ("Slater determinants"), which for two electrons have the form (3.77). The Dirac orbitals may then be taken as eigenstates of $\boldsymbol{j}_1^2$ and j_{1z}, $\boldsymbol{j}_2^2$ and j_{2z},

$$\boldsymbol{j}_1 = \hat{\boldsymbol{l}}_{\boldsymbol{1}} + \boldsymbol{\sigma}_1/2, \quad \boldsymbol{j}_2 = \hat{\boldsymbol{l}}_{\boldsymbol{2}} + \boldsymbol{\sigma}_2/2. \tag{3.120}$$

The effects of V_{12} and H_B require not only the combination of the product states $|j_1 m_1\rangle|j_2 m_2\rangle$ into states $|jm\rangle$ by means of CG-coefficients (2.123), but also a superposition of such states with different j_1 and j_2, at fixed j and m. The conserved total angular momentum operator of an isolated atom (with a spinless nucleus) is normally denoted by the capital letter $\boldsymbol{J}$; for a two-electron atom this is our $\boldsymbol{j}$:

$$\boldsymbol{J} = \boldsymbol{j}_1 + \boldsymbol{j}_2. \tag{3.121}$$

This basis of states is needed for "jj-coupling". For lighter atoms, however, V_{12} is more important than relativity, in which case the LS or "Russel-Saunders" coupling is more convenient. Here the orbital angular momenta $\hat{\boldsymbol{l}}_1$ and $\hat{\boldsymbol{l}}_2$ are first coupled to a total angular momentum $\hat{\boldsymbol{L}}$, to which the total spin operator $\boldsymbol{S} = \boldsymbol{\sigma}/2$ is added:

$$\boldsymbol{J} = \hat{\boldsymbol{L}} + \hat{\boldsymbol{S}}, \quad \hat{\boldsymbol{L}} = \hat{\boldsymbol{l}}_1 + \hat{\boldsymbol{l}}_2, \quad \boldsymbol{S} = \boldsymbol{\sigma}/2, \quad \boldsymbol{\sigma} = \boldsymbol{\sigma}_1 + \boldsymbol{\sigma}_2. \tag{3.122}$$

Capital letters S, P, D indicate the eigenstates of $\hat{\boldsymbol{L}}(\hat{\boldsymbol{L}}+1)$. Without relativistic effects and in the absence of magnetic fields, $\hat{\boldsymbol{L}}$ commutes with the total potential operator $V_{\rm tot}$,

$$[\hat{\boldsymbol{L}}, V_{\rm tot}] = 0, \quad V_{\rm tot} = V(r_1) + V(r_2) + V_{12}(r). \tag{3.123}$$

This is so because with $r = [(\boldsymbol{r}_1 - \boldsymbol{r}_2)^2]^{1/2}$, $[\hat{\boldsymbol{l}}_1, V_{12}(r)] = -[\hat{\boldsymbol{l}}_2, V_{12}(r)]$. It is also geometrically evident, as $\hat{\boldsymbol{L}}$ generates rotations of both electrons by the same angle: From (1.273), we have

$$D_z(\alpha) = \exp(-i\hat{L}_z\alpha) = \exp(-i\hat{l}_{1z}\alpha)\exp(-i\hat{l}_{2z}\alpha). \tag{3.124}$$

The distance r between the electrons is unchanged by this rotation.

In Sect. 3.6, we shall derive from the Dirac-Coulomb equation the nonrelativistic Pauli Hamiltonian for two spinor particles,

$$i\hbar\partial_t\psi_S = H_{nr}\psi_S, \quad H_{nr} = (\boldsymbol{\pi}_1\boldsymbol{\sigma}_1)^2/2m_1 + (\boldsymbol{\pi}_2\boldsymbol{\sigma}_2)^2/2m_2 + V_{\text{tot}}. \tag{3.125}$$

For $\boldsymbol{A} = 0$, H_{nr} reduces to a totally spin-independent operator,

$$H_{nr}(\boldsymbol{A} = 0) = \boldsymbol{p}_1^2/2m_1 + \boldsymbol{p}_2^2/2m_2 + V_{\text{tot}}. \tag{3.126}$$

In this approximation, spin has become an "internal degree of freedom". The corresponding solutions of (3.125) have a factorizing form,

$$\psi_S = \psi_{\text{spinless}}(\boldsymbol{r}_1, \boldsymbol{r}_2)\chi_{12}. \tag{3.127}$$

For two different spinor particles as in neutral muonic helium ($\alpha\mu^-e^-$, $\alpha =$ helium nucleus), χ_{12} may be taken as the direct product of eigenspinors χ_1 and χ_2 of σ_{1z} and σ_{2z}:

$$\chi_{12}(m_{s1}, m_{s2}) = \chi_1(m_{s1})\chi_2(m_{s2}). \tag{3.128}$$

For two electrons, however, these states exist only for $m_{s1} = m_{s2}$. The Pauli principle requires ψ_S to be antisymmetric under the simultaneous exchange $\boldsymbol{r}_1 \leftrightarrow \boldsymbol{r}_2$, $m_{s1} \leftrightarrow m_{s2}$. And as the solution (3.127) factorizes, one factor must be symmetric, the other antisymmetric. The symmetric $\chi_{12}(m_{s1} = m_{s2})$ requires an antisymmetric $\psi_{\text{spinless}} = \psi_{\text{as}}$. The resulting ψ_S is called "ortho":

$$\psi_{\text{ortho}} = \psi_{\text{as}}\,{}^3\chi^{m_s}, \quad m_s = m_{s1} + m_{s2}. \tag{3.129}$$

For $m_s = \pm 1$, one has indeed ${}^3\chi^{m_s} = \chi_1(m_s/2)\chi_2(m_s/2)$. For $m_s = 0$, on the other hand, the direct spinor product must be symmetrized by hand. Including a normalization coefficient $2^{-1/2}$,

$${}^3\chi^0 = 2^{-1/2}[\chi_1(\tfrac{1}{2})\chi_2(-\tfrac{1}{2}) + \chi_1(-\tfrac{1}{2})\chi_2(\tfrac{1}{2})]. \tag{3.130}$$

The notation ${}^3\chi^{m_s}$ merely means "triplet"; the triplet comprises the three values $m_s = 1, -1, 0$. The only antisymmetric combination,

$${}^1\chi^0 = 2^{-1/2}[\chi_1(\tfrac{1}{2})\chi_2(-\tfrac{1}{2}) - \chi_1(-\tfrac{1}{2})\chi_2(\tfrac{1}{2})], \tag{3.131}$$

is then a singlet. The corresponding ψ_{spinless} must be symmetric, the resulting ψ_S is called "para":

$$\psi_{\text{para}} = \psi_{\text{sy}}(\boldsymbol{r}_1, \boldsymbol{r}_2)\, {}^1\chi^0. \tag{3.132}$$

In the "orbital" approximation, the atomic ground state is $\psi_{00} = \psi_0(\boldsymbol{r}_1)\psi_0(\boldsymbol{r}_2)$. The ground states of two-electron atoms and ions are always spin singlets, even in cases such as H^- where the orbital approximation is insufficient (Sect. 3.8).

Note that the mere symmetries of the spin functions entail eigenstates of $\boldsymbol{S}^2 = \boldsymbol{\sigma}^2/4$. As $|m_s| = 1$ is the largest possible value of $|m_s|$, it belongs to the value 2 of $s(s+1)$. The lowering operator $S_- = S_{1-} + S_{2-}$ is symmetric under the exchange $1 \leftrightarrow 2$, it cannot transform a symmetric state into an antisymmetric one. According to the CG-construction (2.126), ${}^3\chi^0$ has thus also $s = 1$, and the remaining singlet state has $s = 0$. Of course, one may also verify the eigenvalues of $\boldsymbol{\sigma}^2$ directly by means of

$$\boldsymbol{\sigma}^2 = \boldsymbol{\sigma}_1^2 + \boldsymbol{\sigma}_2^2 + 2\boldsymbol{\sigma}_1\boldsymbol{\sigma}_2 = 6 + 2\sigma_{1z}\sigma_{2z} + 4(\sigma_{1+}\sigma_{2-} + \sigma_{1-}\sigma_{2+}), \tag{3.133}$$

where $\sigma_{i\pm}$ are the raising and lowering operators (2.62).

The situation for ψ_S is very different from that of the one-electron nonrelativistic and unperturbed state ψ^0, where a certain combination of $\chi_1(\frac{1}{2})$ and $\chi_1(-\frac{1}{2})$ was taken in (2.265) in anticipation of the relativistic perturbation V_{sl}. The present H_{nr} (3.125) contains no such perturbation; the form (3.126) contains no spin whatsoever.

The level scheme of helium is indicated in Fig. 3.4. The level notation is adopted from the uncoupled orbitals $|n_1, l_1\rangle|n_2, l_2\rangle$, even though the coupling due to the Coulomb potential e^2/r_{12} between the electrons is not neglected.

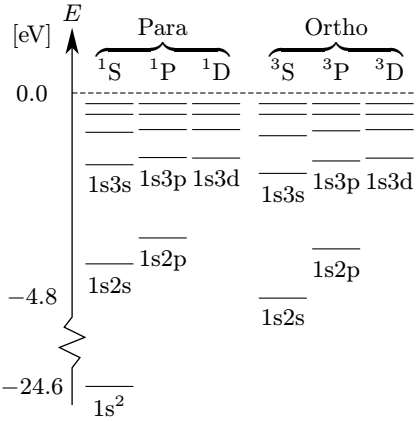

Fig. 3.4. Helium levels with one electron in the ground state 1s. The zero of E is chosen accordingly

One of the two electrons is always in the ground state, $|n_1, l_1\rangle = |1\mathrm{s}\rangle$. States with both electrons in excited states are auto-ionising: One electron de-excites and ejects the other one into the continuum ("Auger-electron"). The energy levels including the Coulomb repulsion in first-order nonrelativistic perturbation theory are

$$E = E_1 + E_2 + E_C^1, \quad E_1 + E_2 = -Z^2 R_\infty (1 + n_2^{-2}), \quad E_C^1 = \langle e^2/r_{12} \rangle. \tag{3.134}$$

As the spin functions are separately normalized, $\langle e^2/r_{12} \rangle$ needs only the orbital functions

$$\psi_{\mathrm{sy,\,as}} = 2^{-1/2}[\psi_{10}(\boldsymbol{r}_1)\psi_{n_2,l_2}(\boldsymbol{r}_2) \pm \psi_{10}(\boldsymbol{r}_2)\psi_{n_2,l_2}(\boldsymbol{r}_1)], \tag{3.135}$$

$$\langle e^2/r_{12} \rangle_{\mathrm{para,ortho}} = \int d^2r_1 d^3r_2 |\psi_{10}(\boldsymbol{r}_1)\psi_{n_2,l_2}(\boldsymbol{r}_2) \pm \psi_{10}(\boldsymbol{r}_2)\psi_{n_2,l_2}(\boldsymbol{r}_1)|^2 e^2/r_{12}. \tag{3.136}$$

There are altogether four integrals in (3.136), which are pairwise equal. One abbreviates

$$E_C^1 = \langle e^2/r_{12} \rangle_{\mathrm{para,ortho}} = J \pm K, \tag{3.137}$$

$$J = \int d^2r_1 d^3r_2 |\psi_{10}(\boldsymbol{r}_1)|^2 |\psi_{n_2,l_2}(\boldsymbol{r}_2)|^2 e^2/r_{12}, \tag{3.138}$$

$$K = \int d^2r_1 d^3r_2 \psi_{10}^*(\boldsymbol{r}_1)\psi_{n_2,l_2}(\boldsymbol{r}_1)\psi_{10}(\boldsymbol{r}_2)\psi_{n_2,l_2}^*(\boldsymbol{r}_2) e^2/r_{12}. \tag{3.139}$$

Both J and K are positive, such that the para-levels ly above the corresponding ortho-levels. J has a probability interpretation, as $|\psi_{10}(\boldsymbol{r}_1)|^2 |\psi_{n_2,l_2}(\boldsymbol{r}_2)|^2$ would be the joint probability to find the first particle at position $\boldsymbol{r}_1$ and the second one at position $\boldsymbol{r}_2$, provided the particles are distinguishable. For identical particles, this interpretation is excluded by the second integral K, which is called the "exchange energy". Both integrals can be performed analytically, but first one has to expand $1/r_{12}$ in terms of Legendre polynomials $P_l(u)$, with $u = \cos\theta_{12}$ and θ_{12} shown in Fig. 3.2:

$$\begin{aligned} r_{12}^{-1} &= (r_1^2 + r_2^2 - 2r_1 r_2 u)^{-1/2} = r_1^{-1}(1 + r_2^2/r_1^2 - 2ur_2/r_1)^{-1/2} \\ &= \sum_{l=0}^{\infty} r_2^l/r_1^{l+1} P_l(u). \end{aligned}$$

This expansion converges only for $r_2 < r_1$; otherwise r_2 must be extracted from the square root:

$$r_{12}^{-1} = \sum_{l=0}^{\infty} P_l(u)[r_2^l/r_1^{l+1}\Theta(r_1 - r_2) + r_1^l/r_2^{l+1}\Theta(r_2 - r_1)]. \tag{3.140}$$

Next, $P_l(\cos\theta_{12})$ is decomposed into products of spherical harmonics as follows:

$$P_l(\cos\theta_{12}) = 4\pi \sum_m Y_l^{m*}(\Omega_1) Y_l^m(\Omega_2). \tag{3.141}$$

All angular integrals are then performed by means of the orthogonality relations (1.186). Only $l = m = 0$ survives in J, and $l = l_2$, $m = m_2$ survives in K. The ground state $(1s)^2$ has

$$\psi_{10}(\boldsymbol{r}) = (4\pi)^{-1/2} R_{10}, \quad R_{10} = 2(Z/a_B)^{3/2} e^{-rZ/a_B}, \quad J = K = \tfrac{5}{8} Z R_\infty. \tag{3.142}$$

In the excited states $|1s\rangle|n_2 l_2\rangle$ with $l_2 > 0$, the factor $r_2^{l_2}$ pushes the maximum of $R_{n2,l2}$ to the region $r_2 \gg r_1$. This implies $\langle r_{12}\rangle \approx \langle r_2\rangle$ and suggests an asymmetric splitting of $V_{\rm tot}$ (3.123):

$$V_{\rm tot} = -Ze^2/r_1 - (Z-1)e^2/r_2 - e^2(1/r_2 - 1/r_{12}). \tag{3.143}$$

Neglect of the last bracket leads to

$$E \approx -Z^2 R_\infty - (Z-1)^2 R_\infty / n_2^2. \tag{3.144}$$

An improved treatment includes the multipole expansion (3.140) for $r_2 > r_1$,

$$r_2^{-1} - r_{12}^{-1} = r_1 r_2^{-2}[u + r_1 r_2^{-1} P_2(u) + \ldots]. \tag{3.145}$$

The decomposition (3.141) shows that every term in (3.145) has vanishing expectation value. However, second order perturbation theory does produce nonvanishing "polarization" energies. Here we only treat the dipole polarization, which arises from the first term in (3.145). The outer electron slightly displaces the wave function of the inner electron. This increases the mean distance between the electrons and reduces their mutual repulsion. The second-order perturbation theory of Sect. 2.7 leads to (2.218), which by $\langle\psi_0|\psi^1\rangle = 0$ reduces to

$$E^{(2)} = \langle\psi_0|H_{\rm per}|\psi^1\rangle, \quad H_{\rm per} = e^2 r_1 r_2^{-2} u. \tag{3.146}$$

The complicated expansion (2.219) of ψ^1 can be avoided in this case. The intrgration over $u = \cos\theta$ in $\langle\psi_0|H_{\rm per}|\psi^1\rangle$ shows that ψ^1 must also contain a factor u, which then gives $\int_{-1}^{1} u^2 du = 2/3$. From the point of view of the inner orbit, e^2/r_2^2 is a constant, (it is $-e$ times the electric field E caused by particle 2 at fixed distance r_2). It follows from (3.146) that $E^{(2)}$ will contain a factor e^4/r_2^4, which acts as an additional operator for the outer orbit. For the (non-degenerate) ground state of an arbitrary atom, one defines

$$E^{(2)} = -\tfrac{1}{2}\alpha_{e1} E^2 = -\tfrac{1}{2}\alpha_{e1} e^2/r_2^4, \tag{3.147}$$

where α_{e1} is called the electric polarizability.

The calculation inserts the ansatz $\psi^1 = uf(r)$ into the equation

$$(H_1 - E_1)\psi_1 = e^2 r r_2^{-2} u\psi_0 \tag{3.148}$$

for $r_1 \equiv r$, which is taken here in nonrelativistic form. The $-\nabla^2/2m$ of H_1 gives $-\nabla^2 u/2m = u(-\partial_r^2 - 2r^{-1}\partial_r + 2r^{-2})/2m$, after which the factor u cancels from (3.148). The resulting differential equation for f,

$$f'' + 2r^{-1}f' - 2r^{-2}f + (-Z^2/a_B^2 + 2Z/a_B r)f = (4\pi)^{-1/2}R_{10} \qquad (3.149)$$

is solved by

$$f = -(\pi a_B^3/Z^3)^{-1/2} r_2^{-2}(r a_B/Z + \tfrac{1}{2}r^2)e^{-rZ/a_B} \qquad (3.150)$$

and leads to $\alpha_{e1} = (9/2)(a_B/Z)^3$. This method has been extended to some other perturbations by Dalgarno and Lewis. Details can be found in the book by Schiff (1968). Relativistic corrections use Coulomb Greens functions (Zon et al. 1972). Kaneko (1977) includes higher multipoles. The energy $E^{(2)}(r_2)$ is now used as additional potential in the equation of motion of the outer electron. This is an "adiabatic" approximation, which neglects the influence of H_2 on the inner wave function, which after all does depend both on r_1 and r_2. Equation (2.259) shows that $\langle r^{-4}\rangle$ exists only for $L^2 > 0$, while $\langle r^{-6}\rangle$ exists only for $L^2 > 2$ ($l > 1$).

3.6 Elimination of Components

For a single electron, the small Dirac spinor components were eliminated in Sect. 2.8, and a transformation (2.239) was added in order to preserve the Hamiltonian form $i\hbar\partial_t\psi = H\psi$, see (2.241). A more general approximate elimination of components is due to Foldy and Wouthuysen (1950); it splits the Dirac equation into two separate Hamiltonian equations. The method has been extended to two fermions by Chraplyvy (1953), Barker and Glover (1955). In this section, we first present this "CBG"-method. Next, we eliminate the small components of the wave function for two electrons, which will yield (3.125) in the nonrelativistic limit. Finally, we turn to a very general method for eliminating half of the components of the Dirac-Coulomb-Breit equation for a closed system, which includes the nucleus as just another structureless fermion. Its anomalous magnetic moment coupling will be added in Sect. 5.7. Spinless nuclei are more complicated (Sect. 4.9). It will become clear in Chaps. 4 and 5 that closed relativistic systems have some general properties, which persist even in their coupling to the radiation field.

The CBG-method keeps β_1 and β_2 diagonal and eliminates γ_1^5 and γ_2^5. In the one-fermion case, one writes

$$H = \beta mc^2 + H_e + H_o, \qquad (3.151)$$

where the "even" operator H_e may contain β but not γ^5, and the "odd" operator H_o is proportional to γ^5. Otherwise, H_e and H_o need not be specified and may contain additional interactions, for example of additional nonrelativistic particles. A unitary transformation $\psi = e^{iS}\psi'$ that commutes with $i\hbar\partial_t$ gives after multiplication by e^{iS} the transformed Hamiltonian equation,

$$i\hbar\partial_t\psi' = H'\psi', \quad H' = e^{iS}He^{-iS}. \qquad (3.152)$$

Insertion of the exponential series (1.274) gives

$$H' = H + [iS, H] - \tfrac{1}{2}[S, [S, H]] - \tfrac{1}{6}[S, [S, [iS, H]]] \dots . \tag{3.153}$$

In a first approximation, H_o is removed by

$$S \approx S_1 = iH_o/2mc^2\beta. \tag{3.154}$$

The factor γ^5 in H_o gives for the main term βmc^2 of the first commutator

$$H_o\beta - \beta H_o = 2H_o\beta, \tag{3.155}$$

so H_o is in fact cancelled. The part $[iS, H_e]$ is a new odd operator which is eliminated in a second step. In this manner, one arrives at the Hamiltonian of Foldy and Wouthuysen,

$$H_{\rm FW} = \beta mc^2 + H_e + H_o^2\beta/2mc^2 - [[H_o, H_e], H_o]/8m^2c^4 - H_o^4\beta/8m^3c^6. \tag{3.156}$$

For two relativistic particles, (3.151) is generalized as follows:

$$H = \beta_1 m_1 c^2 + \beta_2 m_2 c^2 + H_{ee} + H_{oe} + H_{eo} + H_{oo}. \tag{3.157}$$

H_{oe} and H_{eo} contain factors γ_1^5 and γ_2^5, respectively, and H_{oo} contains a factor $\gamma_1^5\gamma_2^5$. In practice, H_{oo} is the Breit operator (3.111), which for the present purpose is put into the form

$$H_B = cb\gamma_1^5\gamma_2^5, \quad b = -\tfrac{1}{2}(\boldsymbol{\sigma}_1\boldsymbol{\sigma}_2 + \sigma_{1r}\sigma_{2r})V_{12}/c. \tag{3.158}$$

Removal of this operator requires a component S_{oo} in the transformation (3.153),

$$S_{oo} = (\beta_2 m_2 - \beta_1 m_1)H_{oo}/2c^2(m_2^2 - m_1^2). \tag{3.159}$$

The Chraplyvy-Barker-Glover Hamiltonian becomes

$$H_{\rm CBG} = \beta_1 m_1 c^2 + \beta_2 m_2 c^2 + H_{ee} + H_{oe}^2/2m_1^2c^2\beta_1 + H_{eo}^2/2m_2^2c^2\beta_2 \tag{3.160}$$

$$+[[H_{oe}, H_{ee}], H_{oe}]/8m_1^2c^4 + [[H_{eo}, H_{ee}], H_{eo}]/8m_2^2c^4$$

$$-H_{oe}^4/8m_1^3c^6\beta_1 - H_{eo}^4/8m_2^3c^6\beta_2 + \beta_1\beta_2\{\{H_{oe}, H_{oo}\}, H_{eo}\}/4m_1m_2c^4. \tag{3.161}$$

It represents four separate four-component equations, one for each eigenvalue of β_1 and β_2. For $\beta_1 = \beta_2 = 1$, both particle energies come out positive. The Dirac-Breit equation (3.112) has

$$H_{ee} = V_{\rm tot}, \quad H_{oe} = c\gamma_1^5\boldsymbol{\sigma}_1\boldsymbol{\pi}_1, \quad H_{oe}^2 = c^2(\boldsymbol{\sigma}_1\boldsymbol{\pi}_1)^2. \tag{3.162}$$

Equation (3.160) is the nonrelativistic Hamiltonian anticipated in (3.125). Among its many terms, the two spin-orbit potentials are quoted here for later reference:

$$V_{s1l}^{\mathrm{CBG}} = \boldsymbol{l}\boldsymbol{\sigma}_1 V'(\tfrac{1}{2}m_1^{-1} + m_2^{-1})/2m_1 r, \quad V_{s2l}^{\mathrm{CBG}} = \boldsymbol{l}\boldsymbol{\sigma}_2 V'(\tfrac{1}{2}m_2^{-1} + m_1^{-1})/2m_2 r. \tag{3.163}$$

Their expectation values are simplified by $\langle \boldsymbol{\sigma}_2 \rangle = \langle \boldsymbol{\sigma}_1 \rangle$, as $\langle \boldsymbol{\sigma}_1 - \boldsymbol{\sigma}_2 \rangle$ vanishes, both for triplet and for singlet spin states:

$$\langle V_{s1l}^{\mathrm{CBG}} + V_{s2l}^{\mathrm{CBG}} \rangle = \langle \boldsymbol{l}\boldsymbol{\sigma}_1 V'/2m_1 m_2 r \rangle (2 + m_2/2m_1 + m_1/2m_2). \tag{3.164}$$

H_{CBG} is a power series expansion in H_{oe}, H_{eo}, H_{oo} but not in H_{ee}. However, with $H_{oo} = H_B$ (3.158), one has $H_{oo}^2 = c^2 b^2 \sim V_{12}^2 \sim H_{ee}^2$, contrary to the assumed dominance of H_{ee}. As H_B was constructed using first-order perturbation theory, it is advisable to replace it by an operator with the same expectation value but with a negligible square (Malvetti and Pilkuhn 1990, 1994). For stationary states of total energy E, the following notation will be used:

$$V_{\mathrm{tot}} = V_1 + V_2 + V_{12}, \quad \pi^0 \equiv i\hbar\partial_0 - V_{\mathrm{tot}}/c, \quad \pi_1 \equiv \boldsymbol{\pi}_1\boldsymbol{\sigma}_1, \quad \pi_2 \equiv \boldsymbol{\pi}_2\boldsymbol{\sigma}_2 : \tag{3.165}$$

$$(\pi^0 - \gamma_1^5\pi_1 - \gamma_2^5\pi_2 - H_B/c)\psi_{D2} = c(m_1\beta_1 + m_2\beta_2)\psi_{D2}. \tag{3.166}$$

One substitutes

$$\psi_{D2} = (1 + H_B/2\pi^0 c)\psi_{DB}, \tag{3.167}$$

multiplies (3.166) by $1 + H_B/2\pi^0 c$ and sets all terms containing H_B^2 equal to zero. Due to $\{H_B, \beta_i\} = 0$, the right-hand side of (3.166) gets no linear terms:

$$(\pi^0 - \gamma_1^5\pi_1 - \gamma_2^5\pi_2 - \{H_B/2\pi^0 c, \gamma_1^5\pi_1 + \gamma_2^5\pi_2\})\psi_{DB} = c(m_1\beta_1 + m_2\beta_2)\psi_{DB}. \tag{3.168}$$

Insertion of (3.158) gives

$$\{H_B/2\pi^0 c, \gamma_1^5\pi_1 + \gamma_2^5\pi_2\} = \{b/2\pi^0, \gamma_2^5\pi_1 + \gamma_1^5\pi_2\}. \tag{3.169}$$

One now has $H_{oo} = 0$ in (3.157), and the series expansion is harmless. However, nonrelativistic expansions have another defect, which has been mentioned already in Sect. 2.8: Higher-order operators such as $\boldsymbol{\pi}^6$ in (2.249) become forbiddingly singular. Special "regularization" procedures must be introduced already at the order α_Z^6, which go under the name "nonrelativistic quantum electrodynamics" (NRQED). Each power of H_{oe} and H_{eo} contributes one power of ∇_1 and ∇_2, such that H_{CBG} is a "nonlocal" operator, with all powers of gradients. The original relativistic differential equations of quantum mechanics are local, however; they contain at most two derivatives.

We conclude the CBG elimination with an approximate reformulation of the unfamiliar operators (3.169), by inserting $\pi^0 \approx E/c \approx m_{12}c$ in $b/2\pi^0$, with $b = -(\boldsymbol{\sigma}_1\boldsymbol{\sigma}_2 + \sigma_{1r}\sigma_{2r})V_{12}/2c$:

$$\{b/2\pi^0, \pi_1\} = -\{(\boldsymbol{\sigma}_1\boldsymbol{\sigma}_2 + \sigma_{1r}\sigma_{2r})V_{12}, \boldsymbol{\pi}_1\boldsymbol{\sigma}_1\}/4m_{12}c^2. \tag{3.170}$$

With $V_{12} = e^2/r_{12}$ and the definition $\boldsymbol{\sigma}_{12}^{\times} = \boldsymbol{\sigma}_1 \times \boldsymbol{\sigma}_2$, one obtains for $\boldsymbol{A} = 0$, $\boldsymbol{\pi}_i = \boldsymbol{p}_i$, and for $j \neq i$.

$$-\{(\boldsymbol{\sigma}_1\boldsymbol{\sigma}_2+\sigma_{1r}\sigma_{2r})V_{12},\boldsymbol{p}_i\boldsymbol{\sigma}_i\}=-V_{12}(\boldsymbol{\sigma}_i\boldsymbol{p}_j+\sigma_{ir}p_{jr}+\sigma^{\times}_{12,r}/r_{12}). \quad (3.171)$$

The operator $-\gamma^5 V_{12}\sigma^{\times}_{12,r}/4m_{12}c^2r_{12}$ has the form of a hyperfine interaction (Sect. 4.7). The combination

$$b_{KD}=-\tfrac{1}{2}V_{12}(\boldsymbol{\sigma}_1\boldsymbol{p}_2+\sigma_{1r}p_{2r}) \quad (3.172)$$

is the Breit interaction between an electron and a spinless particle 2 (Sect. 4.9).

Now we come to our main topic, the fully relativistic elimination of components. We first treat (3.166) for two fermions. The operators $\gamma_1^5\gamma_2^5$ and $\beta_1\beta_2$ commute with each other; they have common eigenstates. The components of ψ_{D2} with eigenvalues ±1 of $\gamma_1^5\gamma_2^5$ will be called ψ and χ, respectively:

$$\psi_{D2}=\begin{pmatrix}\psi\\ \chi\end{pmatrix}, \quad \gamma_1^5\gamma_2^5\psi=\psi, \quad \gamma_1^5\gamma_2^5\chi=-\chi. \quad (3.173)$$

Their eigencomponents of $\beta_1\beta_2$ will be distinguished by a single index, g or f. They are expressed here in terms of the chiral components of ψ_{D2}:

$$\psi=\begin{pmatrix}\psi_g\\ \psi_f\end{pmatrix}=\frac{1}{\sqrt{2}}\begin{pmatrix}\psi_{rr}+\psi_{ll}\\ \psi_{rr}-\psi_{ll}\end{pmatrix}, \quad \chi=\begin{pmatrix}\chi_g\\ \chi_f\end{pmatrix}=\frac{1}{\sqrt{2}}\begin{pmatrix}\psi_{rl}+\psi_{lr}\\ \psi_{rl}-\psi_{lr}\end{pmatrix}. \quad (3.174)$$

The first index r or l refers to the eigenvalues $+1$ or -1 of γ_1^5, the second one to the eigenvalues of γ_2^5. Equal indices imply $\gamma_1^5\gamma_2^5=1$. β_i exchanges $r\leftrightarrow l$ in the ith index. In particular, the phase of χ has been chosen such that

$$\beta_2\psi=\chi, \quad \beta_2\chi=\psi. \quad (3.175)$$

ψ_g and χ_g are the "large" components of ψ and χ; their "small" components ψ_f and χ_f vanish in the nonrelativistic limit. More important is the fact that ψ_g, ψ_f and χ_g are symmetric under the exchange of their two indices, whereas χ_f is antisymmetric. It is the singlet in the space of "$D2$" states. In analogy with $(\boldsymbol{\sigma}_1+\boldsymbol{\sigma}_2)\,{}^1\chi^0=0$ in ordinary spin space, it fulfills

$$(\gamma_1^5+\gamma_2^5)\chi_f=0, \quad (\beta_1+\beta_2)\chi_f=0, \quad (3.176)$$

$$(\gamma_1^5\beta_1+\gamma_2^5\beta_2)\chi_f=0. \quad (3.177)$$

The last equation follows from

$$\gamma_1^5\beta_1+\gamma_2^5\beta_2=\tfrac{1}{2}(\gamma_1^5+\gamma_2^5)(\beta_1+\beta_2)-\tfrac{1}{2}(\beta_1+\beta_2)(\gamma_1^5+\gamma_2^5). \quad (3.178)$$

With the notation $\boldsymbol{\beta}=(\beta_x,\ \beta_y,\ \beta_z)\equiv(\gamma^5,\ i\gamma^5\beta,\ \beta)$, (3.176) and (3.177) can be summarized as

$$(\boldsymbol{\beta}_1+\boldsymbol{\beta}_2)\chi_f=0. \quad (3.179)$$

For two electrons, the Pauli principle admits χ_f only in connection with triplet spin states and symmetric states in $\boldsymbol{r}$-space, or in connection with

singlet spin states and antisymmetric states in $\boldsymbol{r}$-space. In the classification of helium levels (Fig. 3.4), such combinations are not mentioned because the terminology refers to the large components, as in the case of parity.

In the equation for ψ, one may now use $\gamma_2^5 = \gamma_1^5 \equiv \gamma^5$, while that for χ has $-\gamma_2^5 = \gamma_1^5 \equiv \gamma^5$. In addition, β_2 is eliminated by (3.175). With all Dirac matrices of particle 2 eliminated, we may abbreviate

$$\gamma_1^5 \equiv \gamma^5, \quad \beta_1 \equiv \beta, \quad m_2 + \beta m_1 \equiv m_+. \tag{3.180}$$

In the basis (3.173), (3.166) becomes a coupled pair of equations for ψ and χ. Using $c = 1$ from now on,

$$[\pi^0 - \gamma^5(\pi_1 + \pi_2) - b]\psi = m_+\chi, \quad [\pi^0 - \gamma^5(\pi_1 - \pi_2) + b]\chi = m_+\psi. \tag{3.181}$$

For $m_1 = m_2$, $m_+ = m_1(1 + \beta)$ vanishes for $\beta = -1$, which reduces (3.181) to

$$\pi^0\psi_f = \pi_{+b}\psi_g, \quad \pi^0\psi_g = 2m_1\chi_g + \pi_{+b}(\pi^0)^{-1}\psi_g\pi_{+b}\psi_g, \tag{3.182}$$

$$\pi^0\chi_f = \pi_{-b}\chi_g, \quad \pi^0\chi_g = 2m_1\psi_g + \pi_{-b}(\pi^0)^{-1}\psi_g\pi_{-b}\chi_g, \tag{3.183}$$

$$\pi_{\pm b} \equiv \pi_1 \pm \pi_2 \pm b. \tag{3.184}$$

Using (3.184) to eliminate χ_g, one obtains for ψ_g

$$[\pi^0 - \pi_{-b}(\pi^0)^{-1}\pi_{-b}][\pi^0 - \pi_{-b}(\pi^0)^{-1}\pi_{-b}]\psi_g = 4m_1^2\psi_g. \tag{3.185}$$

The approximations $b = 0$, $\pi^0 = 2m_1$ in the denominators and $\pi^0 = 2m_1 + i\partial/\partial_t$ in the numerators lead to (3.125) for $m_1 = m_2$.

Next, we consider arbitrary masses in (3.181) and eliminate χ by means of the first equation to obtain a second-order equation for ψ alone:

$$[\pi^0 - \gamma^5(\pi_1 - \pi_2) + b]m_+^{-1}[\pi^0 - \gamma^5(\pi_1 + \pi_2) - b]\psi = m_+\psi. \tag{3.186}$$

This equation is greatly simplified in the cms, where for $\boldsymbol{A} = 0$ $(\boldsymbol{p}_1\boldsymbol{\sigma}_1 - \boldsymbol{p}_2\boldsymbol{\sigma}_2)(\boldsymbol{p}_1\boldsymbol{\sigma}_1 + \boldsymbol{p}_2\boldsymbol{\sigma}_2) = p_1^2 - p_2^2 = 0$. It will turn out in Sect. 4.6 that (3.186) is not only of first order in $E\boldsymbol{p} \equiv \boldsymbol{p}_\rho$, but also of first order in E^2.

The parity transformation of ψ is

$$\psi'(\boldsymbol{r}_1, \boldsymbol{r}_2) = \beta\psi(-\boldsymbol{r}_1, -\boldsymbol{r}_2). \tag{3.187}$$

For $m_1 = m_2$, the Pauli principle requires a negative eigenvalue of the permutation operator P_{12} which exchanges $\boldsymbol{\pi}_1\boldsymbol{\sigma}_1$ with $\boldsymbol{\pi}_2\boldsymbol{\sigma}_2$:

$$P_{12}\psi = -\psi, \quad P_{12}\boldsymbol{\pi}_i\boldsymbol{\sigma}_i = \boldsymbol{\pi}_j\boldsymbol{\sigma}_j P_{12} \ \ (i \neq j). \tag{3.188}$$

However, setting $m_1 = m_2$ is not allowed in (3.186) because of $m_+^{-1} = 0$ for $\beta = -1$. Multiplication of (3.186)by m_+ removes m_+^{-1} everywhere except in connection with the first γ^5, because of

$$m_+\gamma^5 m_+^{-1} = \gamma^5 m_-/m_+ \equiv \gamma^{5\prime}, \quad m_- = m_2 - \beta m_1. \tag{3.189}$$

One may thus rewrite (3.186) as

$$[E - V_{\rm tot} - (\pi_1 - \pi_2)\gamma^{5\prime} + b][E - V_{\rm tot} - (\pi_1 + \pi_2)\gamma^5 - b]\psi = m_+^2\psi. \tag{3.190}$$

This equation will be greatly simplified in Chap. 4 for the isolated binary atom without a magnetic field. The presence of B excludes that simplification. In the next section, it will be simplified instead by the elimination of the small components ψ_f.

In the general case of a closed system of n Dirac particles, we call $n_e = n - 1$ the number of electrons (one of these particles could also be a muon). We define the total electronic chirality operator,

$$\gamma_e^5 = \Pi_{i=1}^{n_e}\gamma_i^5. \tag{3.191}$$

The general ψ_{Dn} is now decomposed into eigenstates ψ_{Dne} and χ_{Dne} of $\gamma_e^5\gamma_n^5$, with eigenvalues $+1$ and -1, respectively:

$$\gamma_n^5\psi_{Dne} = \gamma_e^5\psi_{Dne}, \quad \gamma_n^5\chi_{Dne} = -\gamma_e^5\chi_{Dne}. \tag{3.192}$$

Using in addition (3.175) for β_n, we have again eliminated the Dirac matrices of the last particle n. The pair of equations (3.186) is generalized to

$$[\pi^0 - \Sigma_i\gamma_i^5\pi_i - \gamma_e^5\pi_n - \Sigma_{ij}\gamma_i^5\gamma_j^5 b_{ij} - \Sigma_i\gamma_i^5\gamma_e^5 b_{in}]\psi = m_+\chi, \tag{3.193}$$

$$[\pi^0 - \Sigma_i\gamma_i^5\pi_i + \gamma_e^5\pi_n - \Sigma_{ij}\gamma_i^5\gamma_j^5 b_{ij} + \Sigma_i\gamma_i^5\gamma_e^5 b_{in}]\chi = m_+\psi. \tag{3.194}$$

The Σ_i and Σ_{ij} extend from 1 to $n_e = n - 1$, and

$$\pi^0 = E - \Sigma_i V_{in} - \Sigma_{ij}V_{ij}, \quad m_+ = m_n + \Sigma_i m_i\beta_i. \tag{3.195}$$

When all particles i are electrons, one has $m_+ = m_n + m_e\Sigma_i\beta_i$. The b_{ij} are the generalization of (3.158),

$$b_{ij} = -\tfrac{1}{2}(\boldsymbol{\sigma}_i\boldsymbol{\sigma}_j + \sigma_{ir}\sigma_{jr})V_{ij}. \tag{3.196}$$

Elimination of χ using (3.193) and multiplication by m_+ gives the following equation for ψ:

$$[E - V - \Sigma_i\gamma_i^{5\prime}\pi_i + \gamma_e^{5\prime}\pi_n - \Sigma_{ij}\gamma_i^{5\prime}\gamma_j^{5\prime}b_{ij} + \Sigma_i\gamma_i^{5\prime}\gamma_e^{5\prime}b_{in}] \tag{3.197}$$

$$\times[E - V - \Sigma_i\gamma_i^5\pi_i - \gamma_e^5\pi_n - \Sigma_{ij}\gamma_i^5\gamma_j^5 b_{ij} - \Sigma_i\gamma_i^5\gamma_e^5 b_{in}]\psi = m_+^2\psi.$$

$$\gamma_i^{5\prime} = m_+\gamma_i^5/m_+ = \gamma_i^5(1 - 2m_i\beta_i/m_+), \tag{3.198}$$

$$\gamma_e^{5\prime} = m_+\gamma_e^5/m_+ = \gamma_e^5 m_-/m_+, \quad m_- = m_n - \Sigma_i m_i\beta_i. \tag{3.199}$$

This is the generalization of (3.190) to $n_e > 1$ electrons.

3.7 Brown-Ravenhall Disease, Energy Projectors, Improved Breitian

The equation for n_e electrons, $\psi_{Dne} = \psi_D(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots \boldsymbol{r}_{ne})$ arises from a straightforward generalization of (3.82); it has 4^{n_e} components. Both the elimination of components and the transformation of Breitians of the previous section become ineffective for $n_e > 2$. But even for $n_e = 2$, the most precise calculations of helium-like ions in the region $Z\alpha \approx 1$ such as helium-like uranium (Indelicato and Desclaux 1990) are performed with 16-component Dirac-Breit equations. The eigenvalue $-n_e e$ of the charge (3.81) does not exclude the presence of electron-positron pairs in ψ_{D,n_e}. A corresponding wave function component would have the form $\psi_{D,n_e+1,p} = \psi_D(\boldsymbol{r}_1 \ldots \boldsymbol{r}_{n_e+1}; \boldsymbol{r}_p)$, where $\boldsymbol{r}_p$ are the positron coordinates. $\psi_D \approx \psi_{Dne}$ is called the "no-pair" approximation. It does allow for the creation and subsequent reabsorption of electron-positron pairs by higher orders of the interaction operators. Among these, the "vacuum polarization" will be calculated in Sect. 4.9, but by a rather different method.

Equations such as Dirac-Coulomb (3.87) (generalized to n_e electrons) are solved either by variational methods or by treating the electronic Coulomb repulsion V_{ij} as a perturbation of single-particle orbitals (properly antisymmetrized, of course). We first discuss the perturbative approach; the first-order shift E_C^1 was calculated already in Sect. 3.5. The second-order shift requires the perturbed states $|n^1\rangle$ expanded in a complete set of unperturbed states as in (2.219). The negative-energy states must be included here. They contain combinations in which one electron has a negative energy $E_1' < -m_e c^2$, while the other one has a much higher energy E_2', such that $E_1' + E_2'$ is degenerate with the unperturbed energy, $E_1' + E_2' = E_1 + E_2$. Consequently, all two-electron states are infinitely degenerate, and the perturbation theory breaks down. This was first noted by Brown and Ravenhall (1951), it became known as "Brown-Ravenhall disease". Over several decades, the influence of the negative-energy states was kept small by plausible assumptions, producing in fact increasingly precise results (Pyykkö 1988). The problem was reformulated by Sucher (1980) as "continuum dissolution", meaning that equations such as (3.112) have no bound states at all: An electron may fall and fall and transfer the energy difference to one or several other electrons by ejecting them, like in the Auger process mentioned in Sect. 3.5. In QED, the formally negative energies $-k^0$ in the electron field operator Ψ (3.62) appear in the energy balance with the correct positive sign, due to the Fock space operator a_-. In a wave function ψ, one can to some extent keep track of Fock space operators by means of energy sign projectors, one for each electron i:

$$\lambda_i^{(\pm)} = \tfrac{1}{2}[1 \pm H_i/(H_i^2)^{1/2}], \tag{3.200}$$

where H_i is the single-particle Hamiltonian (3.78) in the limit $\boldsymbol{A} \to 0$,

$$H_i = V(\boldsymbol{r}_i) + [-i\hbar\nabla_i + e\boldsymbol{A}_{\mathrm{cl}}(\boldsymbol{r}_i)]\boldsymbol{\alpha}_i + mc^2\beta_i. \tag{3.201}$$

The original proposal was to neglect also V and $\boldsymbol{A}_{\rm cl}$ in (3.201),

$$H_{i0} = -i\hbar\nabla_i\boldsymbol{\alpha}_i + mc^2\beta_i, \quad H_{i0}^2 = m^2c^4 - \hbar^2\nabla_i^2. \tag{3.202}$$

The resulting equation was elaborated among others by Mittleman (1981),

$$H\psi = E\psi, \quad H = \Sigma_i\lambda_i^{(+)}H_i\lambda_i^{(+)} + \Sigma_{i,j}\lambda_i^{(+)}\lambda_j^{(+)}V_{ij}\lambda_i^{(+)}\lambda_j^{(+)}. \tag{3.203}$$

It is the previous Dirac-Coulomb Hamiltonian, multiplied by positive-energy projectors.

The operators H_i in (3.203) still contain the photon field $\boldsymbol{A}$, which produces the Breit operators in second-order perturbation theory. The new form of the Breit operator is

$$H_{B,ij}^{(+)} = \lambda_i^{(+)}\lambda_j^{(+)}H_{B,ij}\lambda_i^{(+)}\lambda_j^{(+)}, \tag{3.204}$$

to be added to H in (3.203). It was mentioned in Sect. 3.6 that $H_{B,ij}^2 \approx V_{ij}^2$ makes $H_{B,ij}^2$ forbiddingly large. This defect is absent in $H_{B,ij}^{(+)}$ for the following reason: Each γ_i^5 of $H_{B,ij}$ connects the large components ψ_{gi} of ψ_i (in the parity basis (2.151)) with the small ones ψ_{fi}. It follows already from (2.153) with $\pi_\pm^0 = (E-V)/c \pm mc$ that $|\psi_g|$ is large and $|\psi_f|$ is small for $E \approx mc^2$. On the other hand, for $E \approx -mc^2$, $|\psi_g|$ is small and $|\psi_f|$ is large. The resulting $\langle\gamma^5\rangle$ is small in both cases, but the elements $\langle -E_i|\gamma_i^5|E_i\rangle$ and $\langle E_i|\gamma_i^5| - E_i\rangle$ are large. In $H_{B,ij}^{(+)}$, these matrix elements are set to zero by the projectors.

The decomposition of Ψ into $\Psi^{(+)}$ and $\Psi^{(-)}$ was given explicitly in (3.62) for a free electron field, but it was understood in (3.44) that a corresponding decomposition exists also in the presence of an external classical 4-potential $A_{\rm cl}^\mu$, and in particular in the presence of a Coulomb potential $V = -eA_{\rm cl}^0$. The formulation of QED in external fields is called the "Furry picture". Its validity is restricted to systems of relatively small electron numbers, depending on the strength of the external potential (Lindgren et al. 1955, Shabaev et al. 2000, Shabaev 2002). For a nucleus with $Z = 80$, $n_e = 2, 3, 4$ is unproblematic, while for $Z = 1$, $n_e = 3$ gives already nonsense: A proton cannot bind three electrons. On the other hand, $n_e = 20$ is also problematic for $Z = 80$, because the number of electron pairs is then $n_e(n_e-1)/2 = 190 > Z$. The formalism becomes more flexible when the external potential is replaced by an effective mean potential, but its connection with QED is then less clear.

For high Z and small n_e, the energy differences $E_n^0 - E_{n'}^0$ in ΔE (3.98) become increasingly important in Breit operators; they can be included in the Furry picture. The construction is somewhat complicated in the Coulomb gauge (Bethe and Salpeter 1957). Here we anticipate the covariant interaction of Chap. 4. The scattering amplitude is given in (4.255). With $q_0 = (E_1' - E_1)/\hbar c = (E_2 - E_2')/\hbar c$, the Fourier transform of $-t^{-1} = (\boldsymbol{q}^2 - q_0^2)^{-1}$ leads to e^{iq_0r}/r according to (4.117). Thus the complete interaction Hamiltonian between electrons 1 and 2 is

$$H_{12} = V_F(1 - \boldsymbol{\alpha}_1\boldsymbol{\alpha}_2), \quad V_F = e^{iq_0r_{12}}e^2/r_{12}, \tag{3.205}$$

The effects of keeping $q_0 \neq 0$ in t^{-1} are referred to as "retardation" (in classical electrodynamics they arise from the retarded interaction between two charged particles). The unretarded Hamiltonian is

$$H_{12}(q_0 = 0) = V_{12}(1 - \boldsymbol{\alpha}_1\boldsymbol{\alpha}_2), \quad V_{12} = e^2/r_{12}. \tag{3.206}$$

The piece $-\boldsymbol{\alpha}_1\boldsymbol{\alpha}_2 V_{12}$ is called the Gaunt interaction. Formally, it arises from H_B (3.111) by the replacement $(\boldsymbol{\alpha}_1\boldsymbol{r})(\boldsymbol{\alpha}_2\boldsymbol{r})/r^2 \to \boldsymbol{\alpha}_1\boldsymbol{\alpha}_2$. To get the complete Breit operator in the Furry picture, (3.205) is decomposed as follows:

$$H_{12} = V_{12} - \boldsymbol{\alpha}_1\boldsymbol{\alpha}_2 V_F + V_F - V_{12}, \tag{3.207}$$

and $V_F - V_{12}$ is expressed as a double commutator. The Furry states of particle 2 are eigenstates of H_2 with eigenvalues E_2 and E_2' in the initial and final states:

$$[H_2, V_F - V_{12}] = (E_2' - E_2)(V_F - V_{12}), \tag{3.208}$$

$$[H_1, [H_2, V_F - V_{12}]] = (E_1' - E_1)[H_2, V_F - V_{12}] = -\hbar^2 c^2 q_0^2 (V_F - V_{12}). \tag{3.209}$$

As $V_F - V_{12}$ contains neither gradients nor Dirac matrices, only the pieces $c\boldsymbol{p}_i\boldsymbol{\alpha}_i = -i\hbar c\boldsymbol{\alpha}_i\nabla_i$ of H_i (2.87) contribute to the commutators. And with $[\nabla_1, r_{12}] = -[\nabla_2, r_{12}] = [\nabla, r_{12}] = \boldsymbol{r}_{12}/r_{12}$, one obtains the following identity:

$$V_F - V_{12} = -\boldsymbol{\alpha}_1[\nabla, [\boldsymbol{\alpha}_2\nabla, V_F - V_{12}]]/q_0^2. \tag{3.210}$$

This is the exact result. For small q_0, one may expand

$$V_F - V_{12} = (e^{iq_0 r_{12}} - 1)e^2/r_{12} = ie^2 q_0 - \tfrac{1}{2}q_0^2 e^2/r_{12}, \tag{3.211}$$

$$\boldsymbol{\alpha}_2[\nabla, V_F - V_{12}] = -\tfrac{1}{2}q_0^2\boldsymbol{\alpha}_2\hat{\boldsymbol{r}}_{\mathbf{12}}, \quad \hat{\boldsymbol{r}}_{\mathbf{12}} = \boldsymbol{r}_{12}/r_{12}, \tag{3.212}$$

$$V_F - V_{12} = \tfrac{1}{2}[\boldsymbol{\alpha}_1\boldsymbol{\alpha}_2 - (\boldsymbol{\alpha}_1\hat{\boldsymbol{r}}_{12})(\boldsymbol{\alpha}_2\hat{\boldsymbol{r}}_{12})]. \tag{3.213}$$

When this is combined with the piece $-\boldsymbol{\alpha}_1\boldsymbol{\alpha}_2 V_F$ of (3.207), the old Breit operator emerges in the limit $q_0 \to 0$.

For $q^0 = 0$, (3.206) contradicts (3.213) where $V_{\rm ret}$ does not vanish. The contradiction is resolved by V_{12}^2 which arises from $\pi^{02} = (E - V_{12})^2$ after the elimination of χ in (3.190). V_{12}^2 is removed by the substitution (Schwinger 1973, Malvetti and Pilkuhn 1994)

$$(E - V_{12})^2 = (E + \alpha_Z/r_{12})^2 = E^2 + 2E\alpha_Z/r \equiv E^2 - 2EV. \tag{3.214}$$

To first order in α_Z, (3.214) merely shifts the origin of r_{12}:

$$r_{12} = r + \alpha_Z/2E, \quad \partial_{r12} = \partial_r. \tag{3.215}$$

The new "quasidistance" r applies in the cms of binary atoms, see Sects. 4.5–4.7, where $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ are not separately defined. It physical interval will be $0 < Er < \infty$. In the small Breit operator, $r_{12} - r$ is negligible. There remain

however changes in the kinetic energy operators $\boldsymbol{p}_i\boldsymbol{\sigma}_i$, to which π_1 and π_2 (3.165) reduce for $\boldsymbol{A}=0$. In (2.113), we found $\boldsymbol{\sigma p}=-i\hbar\sigma_r(\partial_r-\boldsymbol{\sigma}\hat{\boldsymbol{l}}/r)$, and in (2.155), an extra factor r^{-1} was extracted. Setting $(\boldsymbol{p}_1-\boldsymbol{p}_2)/2=\boldsymbol{p}_{12}$ in order to avoid confusion with $\boldsymbol{p}=-i\hbar\nabla_{\boldsymbol{r}}$, the substitution (3.215) in

$$r_{12}\boldsymbol{\sigma p}_{12}r_{12}^{-1}=-i\sigma_r[\partial_r-(\boldsymbol{\sigma}\hat{\boldsymbol{l}}+1)/r_{12}] \tag{3.216}$$

produces a correction which cancels $V_{\rm ret}$. This will be verified for the slightly simpler case of a spinless particle 2, see Sect. 4.9. On the other hand, the covariant form H_{12} (3.206) is to be inserted into the equation after the elimination of χ. Then H_{12}^2 vanishes by construction, one has $r_{12}=r$, and there is no retardation. With these simplifications, one can take $b=-V\boldsymbol{\sigma}_1\boldsymbol{\sigma}_2$ in (3.190), combine b with $V_{\rm tot}=V$ into $V_\pm=V(1\pm\boldsymbol{\sigma}_1\boldsymbol{\sigma}_2)$ and take $V_+V_-=0$ at the end:

$$[E-V_+-\gamma^{5\prime}\pi_-][E-V_--\gamma^5\pi_+]\psi=m_+^2\psi,\quad \pi_\pm=\pi_1\pm\pi_2. \tag{3.217}$$

With $V_+V_-=0$ and $m_\pm=m_2\pm\beta m_1$, this leads to

$$\begin{aligned}[E^2-2EV-m_+^2-(E-V_+)\gamma^5\pi_+-\pi_-(E-V_-)\gamma^5m_-/m_+\\ +\pi_-\pi_+m_+/m_-]\psi=0.\end{aligned} \tag{3.218}$$

One may now eliminate the small components, which have $\beta=-1$. Calling $m_2-m_1\equiv\delta m_{21}$ and $m_1+m_2=m_{12}$ as before,

$$\begin{aligned}[E^2-2EV-m_{12}^2+\pi_-\pi_+m_{12}/\delta m_{21}]\psi_g\\ =[(E-V_+)\pi_++\pi_-(E-V_-)\delta m_{21}/m_{12}]\psi_f,\end{aligned} \tag{3.219}$$

$$\begin{aligned}[E^2-2EV-\delta m_{21}^2+\pi_-\pi_+\delta m_{21}/m_{12}]\psi_f\\ =[(E-V_+)\pi_++\pi_-(E-V_-)m_{12}/\delta m_{21}]\psi_g.\end{aligned} \tag{3.220}$$

The last equation provides

$$\psi_f=D^{-1}[(E-V_+)\pi_++\pi_-(E-V_-)m_{12}/\delta m_{21}]\psi_g, \tag{3.221}$$

$$D=E^2-2EV-\delta m_{21}^2-\pi_-\pi_+\delta m_{21}/m_{12}. \tag{3.222}$$

The question arises whether this elimination covers the case of positronium, which has $m_1=m_2$, $m_{12}/\delta m_{21}=\infty$. The denominator D of ψ_f is harmless. The numerator appears in (3.219) for ψ_g in the combination

$$[(E-V_+)\pi_++\pi_-(E-V_-)\delta m_{21}/m_{12}]D^{-1}[(E-V_+)\pi_++\pi_-(E-V_-)m_{12}/\delta m_{21}]. \tag{3.223}$$

Expanding the denominator as in (2.254), one sees that the main singular term is canceled by the $\pi_-\pi_+m_{12}/\delta m_{21}$ of the left-hand side. In a relativistic treatment ot the binary Zeeman effect, the remaining singular terms are presently ambiguous because of the transformation (3.215). See also Sect. 4.10.

In principle, the Brown-Ravenhall disease can be cured by equations such as (3.197), in which the nucleus is included among the relativistic particles. The change of variables from $\boldsymbol{r}_i$ to

$$\boldsymbol{r}_{Ei} = \boldsymbol{r}_i/E, \quad \boldsymbol{p}_{Ei} = E\boldsymbol{p}_i = -i\nabla_{Ei} \tag{3.224}$$

makes (3.197) an equation in E^2 only. The potential energy V contains $-Z\alpha|\boldsymbol{r}_i - \boldsymbol{r}_n|^{-1}$ and $\alpha|\boldsymbol{r}_i - \boldsymbol{r}_j|^{-1}$, such that EV becomes $V(r_E) \equiv V_E$, in which each $\boldsymbol{r}_i$ and $\boldsymbol{r}_n$ is replaced by $\boldsymbol{r}_{Ei}$ and $\boldsymbol{r}_{En}$, respectively. We first demonstrate this E^2-theorem for the simpler equation (3.190). In the new variables, it becomes

$$[E^2 - m_+^2 - 2V_E - (\pi_{1E} - \pi_{2E})\gamma^{5\prime} - (\pi_{1E} + \pi_{2E})\gamma^5 - 2I_{hf}]\psi = 0, \tag{3.225}$$

$$2I_{hf} = [V_E + (\pi_{1E} - \pi_{2E})\gamma^{5\prime} - b_E][V_E + (\pi_{1E} + \pi_{2E})\gamma^5 + b_E]/E^2. \tag{3.226}$$

The form $-2I_{hf}$ in is chosen in analogy with the $-2V_E$, the index $_{hf}$ alludes to the hyperfine operator (4.235) below. In Chap. 4, r_E will also have the physical interval $0 < r_E < \infty$. Hopefully, the final version of relativistic quantum electrodynamics will completely dispense with energy projectors and Breitians.

Electronic Breitians (which do not involve particle n) occur only for $n_e > 1$. Here we return to (3.193), which we rewrite as

$$[E - V_E/E - (\Sigma_i\gamma_i^5\pi_{Ei} + \Sigma_{ij}\gamma_i^5\gamma_j^5 b_{Eij})/E - (\pi_{En} + \Sigma_i\gamma_i^5 b_{Ein})/E\gamma_n^5]\psi = m_+\chi. \tag{3.227}$$

The corresponding expression (3.194) is reformulated accordingly. The absence of even powers of E from the left-hand sides of these equations proves the E^2-theorem.

For even n_e, a complication arises from the parity transformation matrix β_e,

$$\beta_e = \Pi_{i=1}^{n_e}\beta_i, \quad \{\beta_e, \gamma_i^5\} = 0, \quad \beta_e\gamma_e^5 + (-1)^{n_e+1}\gamma_e^5\beta_e = 0. \tag{3.228}$$

It implies $\{\beta_e, \gamma_e^5\} = 0$ only for odd n_e. In that case, the parity transformation does not mix ψ with χ. For even n_e, it does. In that case, the problem disappears when particle n is spinless. However, its Klein-Gordon equation must be linearized before spinor particles can be added. This will be done in Sect. 4.9.

3.8 Variational Method, Shell Model

The ground state energy of an atom or molecule can be calculated by a variational principle. One takes a normalized trial function with one or several free parameters and expands it (virtually) in terms of the unknown exact solutions ψ_i of the differential equation, which has the form $H\psi_i = E_i\psi_i$:

$$\psi_{\text{trial}} = \Sigma_i c_i \psi_i. \tag{3.229}$$

The orthogonality relations of the exact solutions give the expectation value,

$$\langle H \rangle_{\text{trial}} = \Sigma_i |c_i|^2 E_i \geq E_g \Sigma_i |c_i|^2 = E_g, \tag{3.230}$$

where E_g is the smallest eigenvalue, namely that of the ground state. The best trial function gives the minimal value of $\langle H \rangle_{\text{trial}}$, which for well chosen parameters approaches E_g. For every parameter p_j, this means

$$\partial \langle H \rangle_{\text{trial}} / \partial p_j = 0. \tag{3.231}$$

Excited levels may be calculated by trial functions that are orthogonal to that of the ground state.

The variational calculation of the helium ground state by Hylleraas (1929) brought the final acceptance of the many-electron Schrödinger equation as the basis of nonrelativistic atomic theory. The Hamiltonian (3.125) is written as $H_{nr} = H_1 + H_2 + e^2/r_{12}$, with $H_i = \boldsymbol{p}_i^2/2m - Z\alpha/r_i$. Helium itself has $Z = 2$, but the calculation remains valid for Li^+, Be^{++} and other helium-like ions. In the simplest version, ψ_{trial} is assumed in factorizable form, $\psi_{\text{para, trial}} = \psi_{\text{trial}}(r_1)\psi_{\text{trial}}(r_2)^1\chi^0$, with Z replaced by an effective trial charge Z_{trial} in the ground state wave function R_{10} (3.142), $R_{\text{trial}} = 2(Z_{\text{trial}}/a_B)^{3/2} e^{-r_1 Z_{\text{trial}}/a_B}$. The trick of this ansatz is to express the correct H_1 in terms of Z_{trial},

$$H_1 = \boldsymbol{p}_1^2/2m + V_{\text{trial}} Z/Z_{\text{trial}}, \quad V_{\text{trial}} = -Z_{\text{trial}} e^2/r_1. \tag{3.232}$$

As R_{trial} solves the equation $(\boldsymbol{p}_1^2/2m + V_{\text{trial}} - E_{1,\text{trial}})R_{\text{trial}} = 0$ with $E_{1,\text{trial}} = -Z_{\text{trial}}^2 R_\infty$ according to (1.38), the nonrelativistic limit of the virial theorem (A.35) gives $\langle \boldsymbol{p}^2/2m \rangle_{\text{trial}} = -\frac{1}{2}\langle V_{\text{trial}} \rangle_{\text{trial}} = Z_{\text{trial}}^2 R_\infty$,

$$2\langle H_1 \rangle_{\text{trial}} = -2R_\infty (Z_{\text{trial}}^2 - 2ZZ_{\text{trial}}). \tag{3.233}$$

And most importantly, $\langle e^2/r_{12} \rangle_{\text{trial}}$ can be adopted from (3.142),

$$\langle e^2/r_{12} \rangle_{\text{trial}} = J_{\text{trial}} + K_{\text{trial}} = \tfrac{5}{4} Z_{\text{trial}}^2 R_\infty. \tag{3.234}$$

The total Z_{trial}-dependence of $\langle H_{nr} \rangle_{\text{trial}}$ is thus $2(Z_{\text{trial}}^2 - 2ZZ_{\text{trial}} + \frac{5}{8}Z_{\text{trial}})$. This function has a minimum for $\partial \langle H \rangle_{\text{trial}} / \partial Z_{\text{trial}} = 0$, at

$$Z_{\text{trial}} = Z - 5/16, \quad \langle H \rangle_{\text{trial}} = -2Z_{\text{trial}}^2 R_\infty. \tag{3.235}$$

$\langle H \rangle_{\min}$ is lower than the first order perturbative result of Sect. 3.5 by an amount $2(5/16)^2 R_\infty$ (the second order perturbation for the ground state is also negative as evidenced by (2.223), but is more difficult to calculate). The value $E_{\text{trial}} = -2 \times 2.85 R_\infty$ of (3.235) for $Z = 2$ is still above the experimental $-2 \times 2.904 R_\infty$ of helium. Application of this simplest variation to the H^- ion ($Z = 1$) gives $\langle H_1 \rangle_{\text{trial}} = -2(1 - 5/16)^2 R_\infty > -R_\infty$, which would mean

instability against the decay $H^- \to H + e^-$. Experimentally, H^- is stable by 0.75 keV. More precise variational calculations are explained by Bethe and Salpeter (1957).

An extension of the variational principle is the density-functional formalism, for systems with many electrons. The Thomas-Fermi model of an electron gas is an early example of this method. It describes the electrons by local plane waves $\exp\{i\boldsymbol{k}(r)\boldsymbol{r}\}$, which produce an electron density $\rho(\boldsymbol{r})$. The surprising successes of this method seem to result partly from good information on trial functions from other sources (Parr and Yang 1989).

Relativistic variational methods have been reviewed by Grant and Quiney (1988, 2002), mainly for "Dirac-Fock" calculations. They are complicated by the states of negative energies in Dirac-Coulomb equations, which exclude a stable ground state. In most cases, the trial functions can be chosen such that they avoid negative-energy components. The relativistic density-functional formalism has also been developed relatively early (Ramana and Rajagopal 1983, Engel et al. 1995). However, a consistent formalism can exclude the negative-energy states only if these are strictly avoided. We have seen in the last section that is accomplished by treating also the nucleus relativistically. It remains to find suitable orbitals for the variational trial functions. In terms of the 4-momenta k_i^μ and k_n^μ, they should satisfy effective equations with the Lorentz-invariant eigenvalues

$$E_{in}^2 = (k_i + k_n)^2, \quad E_{ij}^2 = (k_i + k_j)^2. \tag{3.236}$$

With $k_i^2 = m_i^2$ and $k_n^2 = m_n^2$, the desired E^2 results as

$$E^2 = (\Sigma_i k_i + k_n)^2 = \Sigma_i E_{in}^2 + \Sigma_{ij} E_{ij}^2 - \Sigma_i m_i^2 - m_n^2. \tag{3.237}$$

In the traditional static nucleus formulation, the total electronic energy E_e is the sum of the orbital energies, $E_e = \Sigma_i E_i$, and $E^2 = (E_e + m_n)^2$, apart from a nonrelativistic recoil correction as in (4.379) below. The effective two-particle orbitals would satisfy equations of the form (4.276) below. They may be written in terms of the effective principal quantum number $n_{\beta,i}$ as $K_i\psi_i = n_{\beta,i}^{-2}\psi_i$.

We now turn to a discussion of the periodic table of elements in terms of the single-electron orbitals of the atomic shell model. Only the atomic ground states are discussed. The notation for H and He is $(1s)^1$ and $(1s)^2$.

The Pauli principle pushes the next two elements, Li and Be, into the $n = 2$ shell. There they may choose between 2s and 2p, which in the limit of complete nuclear shielding by the two electrons of the "closed" shell would be degenerate, with energy $-R_\infty/n^2$, $n = 2$. The state $(1s)^2(2p)$ is close to this limit, similar to the $(1s)(2p)$ excited state of helium (compare (3.144), with $Z - 1$ replaced by $Z - 2$). The state $(1s)^2(2s)$ lies again lower, as the 2s wave function penetrates deeper into the electron cloud of the closed shell. Its outer electron energy may again be parametrized by $-Z_{\text{eff}}^2 R_\infty/n^2$, with $Z_{\text{eff}} \approx 1.25$. Consequently, the Li ground state is $(1s)^2(2s)$. Be ($Z = 4$) has two electrons

in the 2s-shell. In comparison with the Li ground state parametrization, one could associate two factors $-(Z_{\text{eff}}+1)^2 R_\infty$ with them, plus an extra mutual repulsion. This configuration is in fact lower than $(1s)^2(2s)^1(2p)^1$, where the last electron has again $Z_{\text{eff}} \approx 1$. Once the 2s-subshell is filled, the following six elements ($Z = 5 \to 10$) successively fill the 2p subshell. A general nl-shell can accommodate up to $2(2l+1)$ electrons, the factor 2 accounting for the electron spin.

The closed shells with $n = 1$ and 2 (He and Ne ($Z = 10$)) have the electrons so strongly bound that they refuse chemical binding; they make the lightest noble gases. The next noble gas is Ar ($Z = 18$), which has the 3s and 3p subshells filled. For the ten electrons in the 3d shell, Z_{eff} is again relatively small, such that the 4s-shell is filled first. Thus the 4th row of the periodic table successively fills 4s, 3d, and 4p. It ends with Kr ($Z = 36$). The 5th row fills 5s, 4d, 5p, ending with Xe ($Z = 54$). However, 4s and 3d as well as 5s and 4d are nearly degenerate. The d orbitals of rows 4 and 5 are filled in the order $(4s)^2(3d)^{n_d}$ and $(5s)^2(4d)^{n_d}$ respectively, with $n_d = 1 \ldots 10$, with the exception of the "coinage metals" Cu and Ag, which are $(4s)^1(3d)^{10}$ and $(5s)^1(4d)^{10}$, respectively. In Table 3.1, the 10 elements of the 3d and 4d subshells are listed in two separate rows, merely for compactness (in chemistry, this arrangement is used for the $2(2 \times 3 + 1) = 14$ 4f and 5f orbitals (lanthanides and actinides) of rows 5 and 6, which are omitted here).

Table 3.1. The periodic table of elements, including ionization energies in eV. The elements of the 3d and 4d subshells of the lower half of the table are to be inserted between the 4s and 4p, 5s and 5p subshells in the upper half. Not shown are row 6 and the 14 4f elements (lanthanides) of row 5.

Group	1	2	3–12		13	14	15	16	17	18
1s	H									He
eV	13.60									24.59
2s	Li	Be		2p:	B	C	N	O	F	Ne
eV	5.39	9.32			8.30	11.26	14.53	13.62	17.42	21.56
3s	Na	Mg		3p:	Al	Si	P	S	Cl	Ar
eV	5.14	7.65			5.99	8.15	10.49	10.36	12.97	15.76
4s	K	Ca	3d	4p:	Ga	Ge	As	Se	Br	Kr
eV	4.34	6.11			6.00	7.90	9.81	9.75	11.81	14.00
5s	Rb	Sr	4d	5p:	In	Sn	Sb	Te	I	Xe
eV	4.18	5.70			5.79	7.34	8.64	9.01	10.45	12.13
Group	3	4	5	6	7	8	9	10	11	12
3d	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
eV	6.54	6.82	6.74	6.77	7.44	7.87	7.86	7.64	7.73	9.39
4d	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
eV	6.38	6.84	6.88	7.10	7.28	7.37	7.46	8.34	7.58	8.99

The most stable atoms are the light noble gases, helium and neon. They have the largest ionization energies, 24.6 eV and 21.6 eV, respectively. Relativistic effects of the outermost or "valence" electrons are generally small, even in cases where they change the chemical properties. Larger effects occur in the isoelectric sequences of hydrogen (He^+, Li^{++}, $Be^{+++} \equiv Be^{3+}$, $B^{4+}, \ldots$), helium (Li^+, Be^{++}, $B^{3+}, \ldots$), and so on. To order α_Z^4, the binding energies of the hydrogenic sequence are given by (2.149) with $j = 1/2$, $n = 1$: $E_N/mc^2 = -Z^2\alpha^2(1 + Z^2\alpha^2/4)$. Xenon ($Z = 56$) has $Z^2\alpha^2/4 = 0.04$, which is already "large". For $Z \gg 3$, the helium isoelectric sequence has nearly twice the total binding energy of the hydrogenic one, as the repulsive potential e^2/r_{12} and the electronic Breit operator decrease as Z^{-1} relative to the nuclear attraction.

For neutral atoms, the single-electron binding energies of the inner shells (K, L, M) are approximately measured by X-ray absorption edges: With increasing X-ray energy, the absorption coefficient makes a jump at each inner-shell ionization threshold. The largest jumps occur for the last two shells, L(n = 2) and K(n = 1). The L-shell absorption contains three jumps, of wich the first two (L_{III} and L_{II}) arise from the $2p_{1/2}$ and $2p_{3/2}$ states, while the last one (L_I) arises from the $2s_{1/2}$ shell, which is more strongly bound, at least nonrelativistically. The splitting between $2p_{1/2}$ and $2p_{3/2}$ increases with increasing Z and eventually exceeds the $2p_{1/2} - 2s_{1/2}$ splitting, which would vanish according to the Dirac equation without mutual electron interaction.

Relativity increases the total atomic binding energy, thereby contracting the electron cloud. Orbitals with $j = 1/2$ contract most, those with $j = 3/2$ remain essentially unchanged up to $Z = 70$. The reason is that the contraction of $j = 1/2$ increases the shielding of the nuclear charge, such that Z_{eff} decreases for the orbitals with larger j. This indirect effect of relativity dominates for most of the d-shell ($j = 3/2$ and $5/2$). On the other hand, those valence orbitals that are already completely shielded without relativity, are not affected by inner shell contraction.

Turning now to the excited states of valence electrons, one would expect these to follow the Dirac equation for $Z_{\text{eff}} \approx 1$, at least for the alkaline atoms. After all, it was here that Rydberg discovered the principal quantum number n. The alkalines are the poor man's hydrogen. However, the nd states of Na show an "inverted" fine structure, in the sense that the $nd_{3/2}$ states are above the $nd_{1/2}$ states, rather than below as in the Dirac equation (see also Fig. 2.2), even for very large values of n (Rydberg atoms). Similar effects are observed in K and Rb, including hyperfine splittings. They arise from the stronger contraction of $j = l - 1/2$ states (relative to the $j = l + 1/2$ states), in combination with a negative exchange energy K (3.139) with the core electrons. The net result is an upshift of $j = l - 1/2$ which can overcompensate the Dirac downshift (Sternheimer 1963, Luc-Koenig 1976). Such effects become negligibly small in the alkaline isoelectric sequences (Johnson and Cheng 1979).

3.9 The Pauli Principle for Three Electrons

We now consider atoms or ions with three electrons, using the LS coupling scheme. A general three-spin state contains products $\chi_1(m_{sa}) \times \chi_2(m_{sb})\chi_3(m_{sc})$, which will be abbreviated by $|m_{sa}m_{sb}m_{sc}\rangle$. The largest possible value of $m_s = m_{sa} + m_{sb} + m_{sc}$ is $3/2$ and belongs to $S = 3/2$, $\chi(\frac{3}{2}\frac{3}{2}) = |\frac{1}{2}\frac{1}{2}\frac{1}{2}\rangle$. The other three state of this quartet are generated by the spin-lowering operator $\sigma_- = \sigma_{1-} + \sigma_{2-} + \sigma_{3-}$. The total symmetry of σ_- guarantees that it does not change the symmetry of the states on which it operates, which allows one to write down all $\chi(3/2, m_s)$ without using Clebsch-Gordan coefficients, for example

$$\chi(\tfrac{3}{2}, \tfrac{1}{2}) = 3^{-1/2}(|-\tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}\rangle + |\tfrac{1}{2}, -\tfrac{1}{2}, \tfrac{1}{2}\rangle + |\tfrac{1}{2}, \tfrac{1}{2}, -\tfrac{1}{2}\rangle). \tag{3.238}$$

The factor $3^{-1/2}$ follows from the normalization $\chi^\dagger\chi = 1$. However, these totally symmetric spin states require totally antisymmetric orbital states, which are rarely needed. In the orbital approximation, lithium and its isoelectric sequence always have two electrons in the 1s ground state, $\psi_1 = \psi_2 = \psi_{1s} \equiv \psi_0$. The third electron will be in a valence state ψ_v. The complete state must be constructed from the three orbital states $|00v\rangle$, $|0v0\rangle$, $|v00\rangle$ and the six spin states $|\frac{1}{2}, -\frac{1}{2}, m_s\rangle$, $|\frac{1}{2}, m_s, -\frac{1}{2}\rangle$ and $|m_s, \frac{1}{2}, -\frac{1}{2}\rangle$ with $m_s = \pm\frac{1}{2}$. The remaining two states $|\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\rangle$ and $|-\frac{1}{2}, -\frac{1}{2}, -\frac{1}{2}\rangle$ are excluded. By the symmetry of σ_-, combinations such as (3.238) are then also excluded. This implies that all totally antisymmetric combinations ψ_S of the above three orbital states and the available spin states automatically have $S = 1/2$, $m_s = \pm 1/2$.

In practice, one may then choose one value of m_s and take ψ_S as the normalized determinant,

$$\psi_S = 6^{-1/2} \begin{vmatrix} \psi_0(\boldsymbol{r}_1)\chi_1(\frac{1}{2}) & \psi_0(\boldsymbol{r}_1)\chi_1(-\frac{1}{2}) & \psi_v(\boldsymbol{r}_1)\chi_1(m_s) \\ \psi_0(\boldsymbol{r}_2)\chi_2(\frac{1}{2}) & \psi_0(\boldsymbol{r}_2)\chi_2(-\frac{1}{2}) & \psi_v(\boldsymbol{r}_2)\chi_2(m_s) \\ \psi_0(\boldsymbol{r}_3)\chi_3(\frac{1}{2}) & \psi_0(\boldsymbol{r}_3)\chi_3(-\frac{1}{2}) & \psi_v(\boldsymbol{r}_3)\chi_3(m_s) \end{vmatrix} \tag{3.239}$$

Expanding in the elements of the first row, one finds in the compact notation

$$\begin{aligned} \psi_S = 6^{-1/2}(&|00v\tfrac{1}{2}, -\tfrac{1}{2}, m_s\rangle - |0v0\tfrac{1}{2}, m_s, -\tfrac{1}{2}\rangle - |00v - \tfrac{1}{2}, \tfrac{1}{2}, m_s\rangle \\ &+ |0v0 - \tfrac{1}{2}, m_s, \tfrac{1}{2}\rangle + |v00m_s\tfrac{1}{2}, -\tfrac{1}{2}, \rangle - |v00m_s - \tfrac{1}{2}, \tfrac{1}{2}, \rangle). \end{aligned} \tag{3.240}$$

The determinant method ("Slater determinant") works for any number of electrons. For four or more electrons, however, it need not produce eigenstates $|S, m_s\rangle$ of $\boldsymbol{S}^2$. It is then helpful to first construct separate irreducible representations of the permutation group for spins and orbitals, respectively, and to combine these into the totally antisymmetric form afterwards. This can be done graphically by means of "Young diagrams" (Weissbluth 1978). The method works also for identical bosons, where the totally symmetric combination is needed (Pilkuhn 1979). See also Sect. 5.9.

4 Scattering and Bound States

4.1 Introduction

As mentioned in the Preface, the main goal of relativistic quantum mechanics is a precise and powerful basis for bound state calculations. The direct application of QED to bound states has been discussed in the last chapter; it is incomplete and needs improvements, even conceptual ones. Precise calculations include the nuclear charge distribution, which is normally measured in high-energy electron-nucleus scattering. This requires a connection between the bound state and scattering formalisms, which is provided by the Born series of Sect. 4.1.

In the analytic continuation of the S-matrix below the threshold for scattering, bound states appear as poles. For pointlike nuclei, these poles are found from solutions such as (1.298). They are then shifted by the form factors measured in electron or muon scattering.

As the various terms of the Born series have no bound state poles, a purely numerical continuation of the S-matrix seems excluded. One must have means to sum the Born series. These can be differential or integral equations. In the static limit (no nuclear recoil), one may simply modify the interactions in the already successful KG or Dirac equations such that their scattering amplitudes reproduce the Born series. In the simplest approximation, the potential is the Fourier transform of the first Born approximation.

Beyond the static limit, the Born series of two-body scattering is needed; it will be explained in Sect. 4.2. Again, the first Born approximation is normally sufficient, but it gains its full power only after reduction to irreducible submatrices. This delicate point will be discussed in Sect. 4.7.

In more general terms, one must find equations that produce calculable scattering amplitudes, and then adapt their Born series to that of QED as far as possible. The S-matrix of the synthetic equation is not exact, but it is both unitary and analytic. Its pole positions are the approximate atomic energy levels. They appear as the eigenvalues of the differential equation. The practical procedure will be explained in Sect. 4.5.

Conservation laws of QED such as energy-momentum conservation, Lorentz invariance etc are reproduced by the QED Born series. However, QED refers to electrons and photons only. Muons may be included without

profound alterations in the "electroweak" field theory, protons not. Nevertheless, we trust that the complicated quark-gluon structure of protons and other nuclei or even of atoms cannot destroy the consequences of such conservation laws in the scattering and decay of these objects. Relations that do not require explicit knowledge of the S-matrix go under the name "relativistic kinematics", they form the main part of Sect. 4.2. In particular, any system composed of two subsystems of 4-momenta k_1 and k_2 has $(k_1 + k_2)^2 = s$ as a Lorentz invariant. Setting $\boldsymbol{k}_1 + \boldsymbol{k}_2 = 0$ gives $s = (k_1^0 + k_2^0)^2$ where $k_1^0 + k_2^0$ is now the total cms energy. Relativistic two-body kinematics allows one to express $\boldsymbol{k}_1^2 = \boldsymbol{k}_2^2 \equiv k^2$ in terms of s alone, see (4.75). It combines the equations $\boldsymbol{p}_1^2\psi_1 = k^2\psi_1$ and $\boldsymbol{p}_2^2\psi_2 = k^2\psi_2$ into a single equation $\boldsymbol{p}^2\psi = k^2\psi$ (4.188) for the composite system in its cms. This asymptotic equation provides a check of whatever equation one may find. (Unfortunately, quarks have no well-defined S-matrix and no asymptotic equation, to which an interaction could be added.) Similarly, the kinematics of photon emission by atoms provides a test of time-dependent perturbation theory (Sect. 5.4).

4.2 Born Series and S-Matrix

Stationary scattering theory has been discussed in Sect. 1.10. In this section, the corresponding time-dependent formalism is explained. In principle, it requires wave packets instead of plane waves, such that one can define a time $-T$ at which the particle has not yet reached the scatterer, and a time $+T$ at which it has definitely left it. The complete solution at all times x^0 satisfies an integral equation, the "Lippmann-Schwinger" equation:

$$\psi(x) = \psi^{(0)}(x) + e \int d^4y G(x,y) K'(y) \psi(y), \tag{4.1}$$

where G and K' are the Greens function and kernel, respectively. Plane waves may be used instead of wave packets if K' is artificially "switched on" adiabatically at $x^0 = -T$, and again switched off at $x^0 = +T$. One may then idealize the initial state to an incoming plane wave,

$$\psi^{(0)}(x) = \psi_i(x) = e^{i\boldsymbol{k}_i\boldsymbol{r} - i\omega t} u_{Di}, \tag{4.2}$$

where u_{Di} is a possible free Dirac spinor as in (2.334). Similarly, $\psi(x_0 > +T)$ may be expanded in terms of outgoing plane waves:

$$\psi(x^0 > T) = \Sigma_f S_{if} \psi_f, \quad S_{if} = \lim_{t\to\infty} \langle \psi_f(\boldsymbol{x}, t) | \psi(\boldsymbol{x}, t) \rangle. \tag{4.3}$$

$$\psi_f^\dagger = e^{i\omega t - i\boldsymbol{k}_i\boldsymbol{r}} u_{Df}^\dagger. \tag{4.4}$$

The expansion coefficients S_{if} form the scattering matrix.

Born (1926) used an iterative solution of (4.1) (the Born series) for the construction of the S-matrix. The construction of the Born series begins with

the conversion of the equation of motion $K\psi = 0$ from differential to integral form, which is then solved by iteration. K is split into an operator K^0 with exact solutions $\psi^{(0)}$ and a remainder eK' which is treated perturbatively:

$$K = K^0 + eK', \quad K^0\psi^{(0)} = 0, \quad K^0\psi = -eK'\psi. \tag{4.5}$$

To solve the latter equation, one defines a Greens function G indirectly:

$$K^0 G(x,y) = -\delta_4(x-y) = -\delta(x^0 - y^0)\delta_3(\boldsymbol{x} - \boldsymbol{y}). \tag{4.6}$$

The formal solution of (4.5) is (4.1), because $\psi^{(0)}$ disappears from the left-hand side of (4.5), and $eK^0 \int d^4y G(x,y)$ replaces $eG(x,y)$ by $e\delta_4(x-y)$ according to (4.6). This produces the necessary $eK'(x)\psi(x)$ after y-integration.

In the following, we restrict ourselves to the free Greens function, $G_0 = \Delta(x,y) = \Delta(x-y)$; in the Dirac case this function is called $S(x-y)$:

$$(\partial_\mu \partial^\mu + m^2)\Delta(x) = \delta_4(x), \quad (i\partial^\mu \gamma_\mu - m)S(x) = \delta_4(x). \tag{4.7}$$

One sees that

$$S(x) = -(i\partial^\mu \gamma_\mu + m)\Delta(x) \tag{4.8}$$

reduces the equation for S to that for Δ. The integral equation (4.1) is then

$$\psi(x) = \psi^{(0)} - e \int d^4y \Delta(x-y)[i\{A_\mu(y), \partial^\mu\} + eA^2(y)]\psi(y), \tag{4.9}$$

while that for the Dirac equation becomes

$$\psi_D(x) = \psi_D^{(0)} - e \int d^4y S(x-y)\gamma^\mu A_\mu(y)\psi_D(y). \tag{4.10}$$

The construction of $\Delta(x)$ proceeds via momentum space. The relevant Fourier transforms are

$$\Delta(x) = (2\pi)^{-4} \int d^4p e^{-ipx}\Phi(p), \quad \delta_4(x) = (2\pi)^{-4} \int d^4p e^{-ipx} \tag{4.11}$$

and (4.7) reduces to

$$(m^2 - p_\mu p^\mu)\Phi(p) = 1. \tag{4.12}$$

This specifies Φ except on the "mass shell", $p_\mu p^\mu = m^2$, where it is adapted to the physical situation by "$i\epsilon$" rules. In scattering problems, $\psi^{(0)}(x) \sim e^{-ikx}$ represents an incident plane wave of 4-momentum k^μ. With $p^0 = \omega$,

$$\Phi(p^\mu) = (m^2 - \omega^2 + \boldsymbol{p}^2 - i\epsilon)^{-1} = (E^2 - \omega^2 - i\epsilon)^{-1}, \tag{4.13}$$

$$\Phi(p^\mu) = \frac{1}{2E}\left(\frac{1}{E - i\epsilon - \omega} + \frac{1}{E - i\epsilon + \omega}\right), \quad E = (m^2 + \boldsymbol{p}^2)^{1/2}. \tag{4.14}$$

The significance of the $i\epsilon_n$ in the denominator of (4.13) appears in the integration over ω in (4.11). The zero at $\omega = E_n$ is avoided by giving E_n a small

imaginary part, see Fig. 4.1. The integral is evaluated as a Cauchy integral, clockwise along a closed contour,

$$\oint (z-\omega)^{-1} d\omega f(\omega) = \begin{cases} 2\pi i f(z) & \text{for } z \text{ inside the contour} \\ 0 & \text{for } z \text{ outside the contour,} \end{cases} \tag{4.15}$$

provided f is regular inside and on the contour. For $x^0 > y^0$, the factor $\exp[-i\omega(x^0 - y^0)] = \exp[(-i\,\mathrm{Re}\,\omega + \mathrm{Im}\,\omega)(x^0 - y^0)]$ falls exponentially in the lower half of the complex ω-plane, such that the contour may be closed there by a large semicircle. Insertion of $f = (2E)^{-1} e^{-i\omega x^0}$ gives the socalled Feynman propagator Δ_F,

$$\Delta_F(x^0 > 0, \boldsymbol{x}) = i(2\pi)^{-3} \int \frac{d^3p}{2E} e^{i\boldsymbol{p}\boldsymbol{x}} e^{-iEx^0} \equiv \Delta_+(x). \tag{4.16}$$

In terms of $d_L^3 p$ (2.37), this may be also be written as

$$\Delta_+(x-y) = i \int d_L^3 p \psi_{\boldsymbol{p}}(x) \psi_{\boldsymbol{p}}^*(y), \quad \psi_{\boldsymbol{p}}(x) = e^{i\boldsymbol{p}\boldsymbol{x} - iEx^0}. \tag{4.17}$$

Before continuing, let us take a look at the "retarded propagator",

$$\Phi_R = (m^2 - \omega^2 + \boldsymbol{p}^2 - i\,\mathrm{sign}(\omega))^{-1}, \tag{4.18}$$

$$\Phi_R = \frac{1}{2E} \left(\frac{1}{E - i\epsilon - \omega} + \frac{1}{E + i\epsilon + \omega} \right), \tag{4.19}$$

which has both ω-poles in the lower half plane. The corresponding retarded Greens function $\Delta_R(x)$ for $x^0 > 0$ receives also contributions from the pole at $\omega = -E$, which in view of (4.16) corresponds to states of negative energies. The physical absence of such states excludes the use of Φ_R in the present treatment of scattering by equations such as (4.1) which are applied to wave functions. The correct equations (3.66) apply to the field operator Ψ. Their Greens functions are in fact the retarded ones, as will be seen in Sect. 5.3.

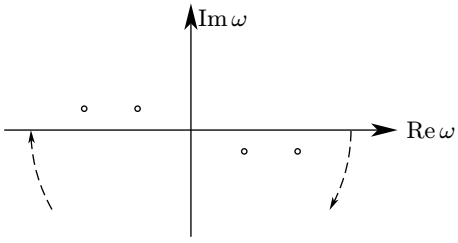

Fig. 4.1. Position of the poles of the Feynman propagator $\mathcal{G}_\omega$ in the complex ω-plane and closure of the integration path $-\infty < \omega < \infty$ by a semicircle at $|\omega| = \infty$ for $x^0 > y^0$

For $x^0 < y^0$, the factor $\exp[-i\omega(x^0 - y^0)]$ falls exponentially in the upper part of the complex ω-plane, such that Δ_F and Δ_R are evaluated by closing the integration path by a semicircle at $\mathrm{Im}\,\omega > 0$:

$$\Delta_F(x^0 < 0, \boldsymbol{x}) = i \int d_L^3 p e^{-i\boldsymbol{p}\boldsymbol{x}} e^{iEx^0} \equiv \Delta_-(x) = \Delta_+(-x^0, -\boldsymbol{x}), \tag{4.20}$$

$$\Delta_R(x^0 < 0) = 0. \tag{4.21}$$

Here Δ_F seems unreasonable, not only because it contains the "states of negative energies", but also because the resulting $\psi(x)$ (4.1) depends on later times, $y^0 > x^0$. However, it will be shown below that this part of the Feynman propagator describes the scattering of antiparticles, after a CPT transformation.

The Born series of particle scattering solves (4.1) iteratively,

$$\psi = \psi^{(0)} + \psi^{(1)} + \psi^{(2)}, \tag{4.22}$$

$$\psi^{(1)}(x) = e \int d^4y G(x,y) K'(y) \psi^{(0)}(y), \tag{4.23}$$

$$\psi^{(2)}(x) = e^2 \int d^4y G(x,y) K'(y) \int d^4z G(y,z) K'(z) \psi^{(0)}(z). \tag{4.24}$$

For spinless particles, the derivative of A_μ arising from the operator $i\partial^\mu A_\mu$ in (4.9) is avoided by a partial integration,

$$\psi - \psi^{(0)} = -ie \int d^4y \Delta(x-y)[iA_\mu \partial^\mu - i\overleftarrow{\partial}^\mu A_\mu + eA^2]\psi(y). \tag{4.25}$$

The S-matrix (4.3) is also constructed iteratively,

$$S = S^{(0)} + S^{(1)} + S^{(2)} \ldots, \quad S_{if}^{(0)} = \langle f|i\rangle. \tag{4.26}$$

The scalar product $\langle \psi_f(\boldsymbol{x},t)|\psi(\boldsymbol{x},t)\rangle$ contains an $\int d^3\boldsymbol{x}$, which is trivial, however: It produces a factor $16\pi^3 k_f^0 \delta(\boldsymbol{k}_f - \boldsymbol{p})$ according to (2.36) and the expression (4.20) for Δ_F. This factor is cancelled by the $d_L^3 p = (16\pi^3 p^0)^{-1} d^3p$. The result for S_{if} is thus simplified, and in particular

$$S_{if}^{(1)} = -ie \int d^4y A_\mu(y) j_{if}^{\mu\,\prime}(y), \tag{4.27}$$

$$j_{if}^{\mu\,\prime}(y) = \psi_{\boldsymbol{k}_f}^*(i\partial^\mu - i\overleftarrow{\partial}^\mu + eA^\mu)\psi_{\boldsymbol{k}_i}. \tag{4.28}$$

The term $-eA^\mu$ gives an e^2-contribution to $S_{if}^{(1)}$, which is moved to the next order $S_{if}^{(2)}$. The remainder will be called $j_{if}^\mu(y)$; it is the free-particle version of (2.31). Equation (4.27) applies also to electron scattering, where j^μ is one of the forms discussed in Sect. 2.10. One normally uses the compact notation (2.315),

$$j_{if}^\mu = \overline{\psi}_{k_f} \gamma^\mu \psi_{k_i}, \quad \overline{\psi} = \psi^\dagger \gamma^0. \tag{4.29}$$

To lowest order in e, ψ_{ki} and ψ_{kf} are plane waves of the type $e^{-iky} = e^{-ik_0y_0}e^{i\boldsymbol{ky}}$ as in (2.329). The y-dependence of j^μ_{if} is then explicitly

$$j^\mu_{if}(y) = J^\mu_{if}e^{-i(k_i-k_f)y} = J^\mu_{if}e^{-iqy}, \tag{4.30}$$

$$q^\mu = k^\mu_i - k^\mu_f:\ q^0 = k^0_i - k^0_f,\ \boldsymbol{q} = \boldsymbol{k}_i - \boldsymbol{k}_f. \tag{4.31}$$

The y-integration of (4.27) is trivial for the Fourier components $\tilde{A}_\mu$ of A_μ,

$$A_\mu(y) = \int d^4k e^{-iky}\tilde{A}_\mu(k), \tag{4.32}$$

$$\int d^4y e^{-iy(k+q)} = (2\pi)^4\delta_4(k+q), \tag{4.33}$$

$$S^{(1)}_{if} = -ie(2\pi)^4\int d^4k\delta_4(k+q)A_\mu(k)J^\mu_{if} = -ie(2\pi)^4\tilde{A}_\mu(-q)J^\mu_{if}. \tag{4.34}$$

The expression for J^μ_{if} for a spinless particle follows from (4.28) by $i\partial^\mu\psi_{\boldsymbol{k}_i} = k^\mu_i\psi_{\boldsymbol{k}_i}$, $\psi^*_{\boldsymbol{k}_f}(-i\overleftarrow{\partial}^\mu) = \psi^*_{\boldsymbol{k}_f}k^\mu_f$:

$$J^\mu_{if}(\mathrm{KG}) = k^\mu_i + k^\mu_f. \tag{4.35}$$

The matrix elements of the Dirac current follow from (2.329):

$$J^\mu_{if}(\mathrm{Dirac}) = \overline{u}_f\gamma^\mu u_i = \overline{u}_D(\boldsymbol{k}_f, m_f)\gamma^\mu u_D(\boldsymbol{k}_i, m_i). \tag{4.36}$$

The $A_\mu(y)$ produced by a stationary target such as a nucleus is independent of y_0, it requires the adiabatic switching on and off of A_μ at $y_0 = -T$ and $+T$, respectively:

$$\int_{-T}^{+T} dy_0 e^{-iq^0y_0} = 2\sin(q^0T)/q^0 \to 2\pi\delta(q^0). \tag{4.37}$$

The last expression appears in the limit $T \to \infty$. It should not be used in the calculation of the differential cross section $d\sigma_{if}$, which contains $|S_{if}|^2$. To be precise, $d\sigma_{if}$ is the differential transition rate (which is $d^3_Lk_f|S_{if}|^2/2T$) per incident particle flux (which is $v_i = k_i/k^0_i$. There is however an extra factor $(2k^0_i)^{-1}$ from the normalization of the initial state; the corresponding final state normalization factor is included in $d^3_Lk_f = d^3k/(8\pi^32k^0_f)$):

$$d\sigma_{if} = |S_{if}|^2d^3_Lk_f/4Tk^0_iv_i, \quad v_i = k_i/k^0_i. \tag{4.38}$$

In spherical coordinates for $\boldsymbol{k}_f$, $\boldsymbol{k}^2 = k^{02} - m^2$ implies $kdk = k^0dk^0$,

$$d^3_Lk_f = k^2_fdk_fd\Omega_f/(16\pi^3k^0_f) = k_fdk^0_fd\Omega_f/16\pi^3, \tag{4.39}$$

$$d\sigma_{if} = \lim_{T\to\infty}(|S_{if}|^2/2T)k_fdk^0_fd\Omega_f/(32\pi^3k_i). \tag{4.40}$$

With (4.37), the limit becomes

$$\lim_{T\to\infty}[2\sin(q^0T)/q^0]^2/2T = 2\pi\delta(q^0). \tag{4.41}$$

The dk_f^0 is cancelled by $\delta(q^0)$, which fixes not only $k_f^0 = k_i^0$ (energy conservation), but also $k_f = k_i$:

$$d\sigma_{if} = (16\pi^2)^{-1}d\Omega_f|e\int d^3y A_\mu(\boldsymbol{y})j_{if}^\mu(\boldsymbol{y})|^2. \tag{4.42}$$

To make the contact with the scattering amplitude f of the stationary scattering wave function (1.278), one defines

$$f_{if} = -(4\pi)^{-1}e\int d^3y A_\mu(\boldsymbol{y})j_{if}^\mu(\boldsymbol{y}), \quad d\sigma_{if} = |f_{if}|^2 d\Omega_f. \tag{4.43}$$

A spinless nucleus can only provide a Coulomb potential, $A^0(\boldsymbol{y}) = Ze/y$ for a point nucleus of charge Ze, and $\boldsymbol{A}(\boldsymbol{y}) = 0$. As mentioned above, we are primarily interested in deviations from the point potential, which are caused by an extended nuclear charge distribution $\rho_{\rm el}(r') = Ze\rho_N(r')$, $\int d^3r'\rho_N = 1$. The relevant A^0 is the solution (1.59) of the Poisson equation,

$$A^0(\boldsymbol{y}) = Ze\int d^3r'\rho_N(r')/|\boldsymbol{y}-\boldsymbol{r'}|, \quad V(r) = -eA^0(r). \tag{4.44}$$

Insertion of (4.30) gives

$$f_{if} = (4\pi)^{-1}J_{if}^0\int d^3y V(\boldsymbol{y})e^{i\boldsymbol{qy}}, \tag{4.45}$$

which is essentially the Fourier transform of V. We first integrate (4.44) over $\boldsymbol{r'}$ and then shift the integration variable $\boldsymbol{y}$ of the Fourier transform by $\boldsymbol{r'}$, $\boldsymbol{y} = \boldsymbol{r} + \boldsymbol{r'}$:

$$\int d^3y e^{i\boldsymbol{qy}}\int d^3r'\rho_N(r')/r = \int d^3r e^{i\boldsymbol{qr}}F_N(\boldsymbol{q}^2)/r, \tag{4.46}$$

$$F_N(\boldsymbol{q}^2) = \int d^3r' e^{i\boldsymbol{qr'}}\rho_N(r'), \quad F_N(0) = 1. \tag{4.47}$$

$F_N(q^2)$ is called the nuclear form factor; it is measured rather directly in high-energy scattering.

The Fourier transform in $\boldsymbol{r}$ is now performed in spherical coordinates, $\int d\Omega = dud\phi$, $\int d\phi = 2\pi$ and with $\boldsymbol{qr} = qru$:

$$\int d^3r\frac{e^{i\boldsymbol{qr}}}{r} = 2\pi\int_0^\infty rdr\int_{-1}^1 due^{iqru} = \frac{2\pi}{iq}\int_0^\infty dr(e^{iqr} - e^{-iqr}). \tag{4.48}$$

This integral does not converge at $r = \infty$. One defines an artificial charge screening radius a_s in the form of an extra factor e^{-r/a_s} and lets $a_s \to \infty$ in the final result:

$$\begin{aligned}\int_0^\infty dr[e^{r(iq-a_s^{-1})} - e^{r(-iq-a_s^{-1})}] &= -(iq-a_s^{-1})^{-1} - (iq+a_s^{-1})^{-1} \\ &= 2iq(q^2+a_s^{-2})^{-1}.\end{aligned} \tag{4.49}$$

In the final result, we write again $\boldsymbol{q}^2$ instead of q^2, in order to avoid confusion with $q_\mu q^\mu = q^{02} - \boldsymbol{q}^2$:

$$\int d^3r e^{i\boldsymbol{qr}} e^{-r/a_s}/r = 4\pi(\boldsymbol{q}^2 + a_s^{-2})^{-1} \to 4\pi/\boldsymbol{q}^2. \tag{4.50}$$

As already mentioned, it is the inverse Fourier transform which determines the point Coulomb potential:

$$V(r) = (2\pi)^{-3} \int d^3q e^{-i\boldsymbol{qr}}(-4\pi\alpha_Z/\boldsymbol{q}^2) = -\alpha_Z/r. \tag{4.51}$$

For the scattering of a spinless particle, one finds from (3.114)

$$J^0_{if}(\mathrm{KG}) = 2k_i^0 \equiv 2E, \quad f_{if} = -2\alpha_Z E F(\boldsymbol{q}^2)/\boldsymbol{q}^2. \tag{4.52}$$

And with $k_i^2 = k_f^2 \equiv k^2$, one obtains

$$q^2 = (\boldsymbol{k}_i - \boldsymbol{k}_f)^2 = 2k^2(1 - \cos\theta) = 4k^2 \sin^2(\theta/2), \tag{4.53}$$

where θ is the scattering angle. For electrons, the relevant matrix elements of $J^0_{if}(\mathrm{Dirac})$ have already been calculated in (2.343)

Because of many different units and normalization constants, it is advisable to check the dimensions of the final expressions. The differential cross section $d\sigma$ has the dimension of an area, cm^2 or $(\mathrm{eV})^{-2}$.

4.3 Two-body Scattering and Decay

In the S-matrix (4.27), we now replace the static limit $A^0(\boldsymbol{y})$ by the full $A_\mu(y)$ which is constructed from Maxwell's equations (2.20) in the Lorentz gauge $\partial_\mu A^\mu = 0$, now in units $c = 1$:

$$\partial_\mu \partial^\mu A^\nu = 4\pi j^\nu_{\mathrm{el}}. \tag{4.54}$$

The corresponding integral form uses the Greens function $D(y-x)$ satisfying

$$\partial_\mu \partial^\mu D(x) = \delta_4(x), \quad A_\mu(y) = \int d^4x D(y-x) 4\pi j_{\mathrm{el},\mu}(x). \tag{4.55}$$

Comparison with (4.7) shows $D(x) = \Delta(x,\ m^2 = 0)$, such that expressions (4.11) and (4.13) apply with $m^2 = 0$:

$$D(y-x) = (2\pi)^{-4} \int d^4p e^{-ipy} e^{ipx}(-p_\mu p^\mu - i\epsilon)^{-1}. \tag{4.56}$$

The $-i\epsilon$ is unessential in the following, because p^μ will be expressed in terms of in- and outgoing 4-momenta. For $j_{\mathrm{el},\mu}$ only the current density of the target nucleus is now relevant, $j_{\mathrm{el},\mu} = Z e j_{2,\mu}$. The notation must be extended to

the case of two different currents; our previous current of the projectile is now called j_1^μ. Also, we prefer to write $j_{2,\mu} = g_{\mu\nu} j_2^\nu$ and abbreviate again $Ze^2 = \alpha_Z$:

$$S_{if}^{(1)} = -4\pi i \alpha_Z \int d^4y d^4x D(y-x) j_1^\mu(y) g_{\mu\nu} j_2^\nu(x). \tag{4.57}$$

This expression is symmetric in j_1 and j_2, both currents must have the form (4.30):

$$j_1^\mu(y) = e^{-iq_1 y} J_{11'}^\mu, \quad j_2^\nu(x) = e^{-iq_2 x} J_{22'}^\nu, \quad q_j = k_j - k_j' \ (j = 1, 2). \tag{4.58}$$

The index i in S_{if} comprises the pair of indices $(1, 2)$, while f comprises the indices $(1', 2')$ of the final states. With the form (4.56) of $D(y-x)$, the x-integral gives

$$\int d^4x e^{ipx} e^{-iq_2 x} = (2\pi)^4 \delta_4(p - q_2), \tag{4.59}$$

while the y-integral gives $(2\pi)^4 \delta_4(p + q_1)$:

$$S_{if}^{(1)} = 4\pi i \alpha_Z (2\pi)^4 \int d^4p \delta_4(p - q_2) \delta_4(p + q_1) J_{11'}^\mu g_{\mu\nu} J_{22'}^\nu (p_\mu p^\mu)^{-1}. \tag{4.60}$$

The two δ_4-functions require

$$p^\mu = q_2^\mu = -q_1^\mu = k_2^\mu - k_2'^\mu = -k_1^\mu + k_1'^\mu. \tag{4.61}$$

We also define the total 4-momenta of the initial and final states,

$$k_i^\mu = k_1^\mu + k_2^\mu, \quad k_f^\mu = k_{1'}^\mu + k_{2'}^\mu, \tag{4.62}$$

such that S_{if} becomes

$$S_{if} = i(2\pi)^4 \delta_4(k_i - k_f) T_{if}, \tag{4.63}$$

$$T_{if}^{(1)} = 4\pi \alpha_Z J_{11'}^\mu g_{\mu\nu} J_{22'}^\nu / t, \quad t \equiv p_\mu p^\mu = q_1^{02} - \boldsymbol{q}_1^2. \tag{4.64}$$

In this form, $\delta_4(k_i - k_f) = \delta(k_i^0 - k_f^0) \delta_3(\boldsymbol{k}_i - \boldsymbol{k}_f)$ expresses conservation of the system's total energy and momentum. In the previous section, the energy k_1^0 of particle 1 was conserved, which entailed conservation of the magnitude of its momentum, but not of its direction. Perturbation theory in general is

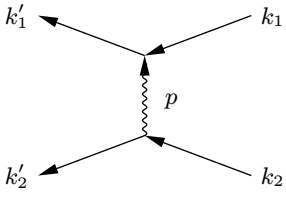

Fig. 4.2. The first Born graph for $ab \to a'b'$

illustrated by Feynman graphs. The Born series focuses on the number of exchanged "virtual" photons. The first Born graph is illustrated in Fig. 4.2. Two-photon exchange graphs are shown in Fig. 5.3 in Sect. 5.5.

Although (4.63) has been derived only for $S_{if}^{(1)}$, the energy-momentum conserving $\delta_4(k_i - k_f)$ arises in all orders, $T_{if} = T_{if}^{(1)} + T_{if}^{(2)} + \ldots$. The point at which a photon line begins or ends is called a "vertex" (points with two photon lines will be mentioned in Sect. 5.5). To begin with, each line section in a Feynman graph is associated with a certain 4-momentum. In $T^{(2)}$, the three 4-momenta on lines 1 and 2 may be called $k_1,\ k_1'',\ k_1'$ and $k_2,\ k_2'',\ k_2'$. As in (4.61), 4-momenta are conserved at each vertex. Calling q_1 and q_2 the two photon 4-momenta in the order in which they are emitted by particle 2, one has $k_2'' = k_2 - q_1 = k_2' + q_2$, and $k_1'' = k_1 + q_1 = k_1' - q_2$ in the "direct" graph, and $k_1'' = k_1 + q_1 = k_1' - q_2$ in the "crossed" graph where the photons end in inverse order on line 1. In the latter case, one rewrites k_1'' as $\frac{1}{2}(k_1 + k_1') + \frac{1}{2}(q_1 - q_2)$. In both cases, one finds $k_1 + k_2 = k_1'' + k_2'' = k_1' + k_2'$. Thus energy-momentum conservation proceeds stepwise in the higher order Born graphs. One of the two q_i remains unspecified; it is integrated over. Feynman rules are not used in this book; the final integrations over the unspecified momenta may be diverging and require intricate counterterms.

The k_1^0 and k_2^0 are in general not separately conserved. However, there exists a special coordinate system, called the center-of-mass or center-of-momentum system (cms), which is defined by

$$\boldsymbol{k}_i = \boldsymbol{k}_1 + \boldsymbol{k}_2 = 0 = \boldsymbol{k}_{1'} + \boldsymbol{k}_{2'} = \boldsymbol{k}_f. \tag{4.65}$$

The total energy in this system is frequently denoted by $\sqrt{s}$. One has

$$k_{i,\mathrm{cms}}^{\mu} = k_{f,\mathrm{cms}}^{\mu} = (\sqrt{s}, \mathbf{0}). \tag{4.66}$$

And as $k^2 \equiv k_\mu k^\mu$ is Lorentz invariant, the cms energy is also a Lorentz invariant,

$$k_i^2 = k_f^2 = s. \tag{4.67}$$

The individual energies k_1^0 and k_2^0 of the free ingoing particles in this system will be denoted by E_1 and E_2; they are also Lorentz invariants. Their sum is

$$E_1 + E_2 = \sqrt{s}, \tag{4.68}$$

while the difference of their squares follows from $E_1^2 - m_1^2 = \boldsymbol{k}_{1,\mathrm{cms}}^2 = E_2^2 - m_2^2$:

$$E_1^2 - E_2^2 = m_1^2 - m_2^2 \equiv -m_+ m_-. \tag{4.69}$$

The combination $m_+ m_-$ occurred already in (3.187). The lighter particle is called 1, the heavier one 2, such that $m_+ m_-$ is positive. Observing $E_1^2 - E_2^2 = (E_1 - E_2)\sqrt{s}$, one finds

$$E_1 = \tfrac{1}{2}(s - m_+ m_-)/\sqrt{s}, \quad E_2 = \tfrac{1}{2}(s + m_+ m_-)/\sqrt{s}. \tag{4.70}$$

The same formalism applies to the free outgoing particles, with $\boldsymbol{k}_{1,\mathrm{cms}}^2$ replaced by ${\boldsymbol{k}'_{1,\mathrm{cms}}}^2$. Consequently, $E_1 - E_{1'} = E_{2'} - E_2 = 0 = q^0_{1,\mathrm{cms}}$ in (4.61). In higher order Born graphs, expressions (4.70) need not apply to the intermediate energies E_1'' and E_2'', because the "virtual particles" associated with the sections between vertices need not fulfill the free-particle equations (they are then said to be "off the mass shell", $k_i^2 \neq m_i^2$). On the other hand, $\mathrm{Im}T^{(2)}$ has all particles onshell, due to the unitarity relation (4.99) below. This relation is used in a calculation of $T^{(2)}$ without Feynman rules.

Some expressions of the one-body kinematics of the last section can be taken over to the two-body kinematics in the cms. Defining $q^\mu_{1,\mathrm{cms}} \equiv q^\mu$, the Lorentz invariant t of (4.62) becomes $-\boldsymbol{q}^2$:

$$q^\mu \equiv q^\mu_{1,\mathrm{cms}} = (0, \boldsymbol{q}), \quad t = -\boldsymbol{q}^2. \tag{4.71}$$

The minus sign could have been avoided by defining $t = -q_\mu q^\mu$, but it is justified by a sign symmetry of the three Lorentz-invariant "Mandelstam variables",

$$s = (k_1 + k_2)^2 = (k_{1'} + k_{2'})^2,\ t = (k_1 - k_{1'})^2 = (k_{2'} - k_2)^2, \tag{4.72}$$

$$u = (k_1 - k_{2'})^2 = (k_2 - k_{1'})^2, \tag{4.73}$$

$$s + t + u = 2m_1^2 + 2m_2^2. \tag{4.74}$$

In the one-body case, we defined in (1.74) $E^2/c^2 - m^2c^2 \equiv \hbar^2 k^2$. This combination of constants occurs not only in the solutions of the KG equation, but also in those of the Dirac equation, compare (2.135). The corresponding cms value $\boldsymbol{k}_{1,\mathrm{cms}}^2 = \boldsymbol{k}_{2,\mathrm{cms}}^2$ will also be called k^2, dropping the boldface notation. From (4.69), we find

$$k^2 = E_1^2 - m_1^2 = E_2^2 - m_2^2 = [s + m_+^2 m_-^2/s - 2m_1^2 - 2m_2^2]/4. \tag{4.75}$$

It occurs frequently in the combination

$$4k^2 s = s^2 + m_+^2 m_-^2 - 2s(m_1^2 + m_2^2) \equiv \lambda(s, m_1^2, m_2^2). \tag{4.76}$$

The "triangle function" λ is symmetric in all three arguments,

$$\lambda(a, b, c) = a^2 + b^2 + c^2 - 2(ab + ac + bc). \tag{4.77}$$

More useful is the factorizing form

$$\lambda = [s - (m_2 + m_1)^2][s - (m_2 - m_1)^2]. \tag{4.78}$$

Physically, k is the wave number in the cms. The form (4.78) shows that it vanishes not only at the "threshold" $s_{\mathrm{th}} = (m_1 + m_2)^2$, but also at the "pseudothreshold" $s_{\mathrm{pth}} = (m_2 - m_1)^2$. Positive values of $\sqrt{s}$ refer to particle scattering, negative ones to the scattering of two antiparticles. Both k^2 and λ are Lorentz invariants.

In all measurable quantities, one is free to replace m_i by $-m_i$, even if they are derived from Dirac equations. When m_1 and m_2 are taken of opposite signs, $s_{\rm th}$ and $s_{\rm pth}$ exchange their roles.

The two-body generalization of the differential cross section $d\sigma_{if}$ (4.38) is somewhat artificial. A more fundamental concept is the transition rate density $\hat{r}_{if}$, which is the transition probability $|S_{if}|^2$ per time interval $2T$ and volume V, from a normalized initial state $|i\rangle = |1,2\rangle$ to a selected normalized final state $|f\rangle = |1',2'\rangle$. In the one-body case, we had to replace the energy-conserving delta-function, $\delta(q^0) = \delta(k_1^0 - k_1^{0\prime})$ by the adiabatic switching (4.37) in order to get a well-defined expression for δ^2. In the two-body case, the 4-dimensional $\delta_4(k_i - k_f)$ requires in addition also a large volume V, outside which the interaction vanishes at all times. Extending the arguments that led from $|S_{if}|^2/2T$ to $2\pi|T_{if}|^2\delta(q^0)$ to four dimensions, one gets

$$\hat{r}_{if} = |S_{if}|^2/2TV = (2\pi)^4\delta_4(k_i - k_f)|T_{if}|^2. \tag{4.79}$$

Alternatively, one may also use (4.63) directly but replace one of the two factors $(2\pi)^4\delta_4$ by

$$(2\pi)^4\delta_4(k_i - k_f) = \int d^4x e^{i(k_i - k_f)x}, \tag{4.80}$$

take $k_f = k_i$ in the exponent on account of the second factor, and then identify the resulting $\int d^4x$ with $2TV$, which cancels the denominator of (4.79).

The measurable rate density is proportional to the product of the macroscopic phase space densities $F_j(\boldsymbol{k}_j, \boldsymbol{R}, T)$ of the initial particles $j = 1, 2$. The particle density $\rho_j(\boldsymbol{R}, T)$ and particle numbers N_j are

$$\rho_j(\boldsymbol{R}, T) = \int d^3k_j F_j, \quad N_j = \int d^3r\rho_j. \tag{4.81}$$

The dependence of F on T and $\boldsymbol{R}$ must be sufficiently smooth in order to remain compatible with the limiting procedure $T \to \infty$, $V \to \infty$ required for energy-momentum conservation. A stationary particle beam of sharp momentum $\boldsymbol{p}$ has

$$F(\boldsymbol{k}, \boldsymbol{R}, T) = \delta_3(\boldsymbol{k} - \boldsymbol{p})\rho(\boldsymbol{R}, T); \tag{4.82}$$

ρ could be damped by absorption (or by decay in the case of unstable particles) along the beam direction $\hat{z}$,

$$\rho(\boldsymbol{R}, T) = \rho(x, y, 0)e^{-z/\lambda}, \tag{4.83}$$

where λ is a mean free path and $\rho(x, y, 0)$ a macroscopic beam profile. Remembering the covariant normalization $\langle j|j\rangle = 2k_j^0$, the actual transition rate density to a discrete final state $|f\rangle$ is

$$r_{if} = \Pi_j \int d^3k_j(2k_j^0)^{-1}F_j(\boldsymbol{k}_j, \boldsymbol{R}, T)\hat{r}_{if}. \tag{4.84}$$

For the collision of two stationary beams, $F_1F_2 = \delta_3(\boldsymbol{k}_1 - \boldsymbol{p}_1)\delta_3(\boldsymbol{k}_2 - \boldsymbol{p}_2)$ $\times\rho_1(\boldsymbol{R}, T)\rho_2(\boldsymbol{R}, T)$ makes r_{if} proportional to the product $\rho_1\rho_2$ at a common

time T in a common place $\boldsymbol{R}$. If the beams never meet, r_{if} remains zero. The case of a single unstable particle in $|i\rangle$ is discussed below.

In the continuum of unbound two-particle final states, one has a differential transition rate,

$$dr_{if} = \hat{r}_{if} d_L^3 k_1' d_L^3 k_2', \quad d_L^3 k = d^3k/16\pi^3 k^0, \tag{4.85}$$

where $d_L^3 k$ is again the Lorentz invariant momentum differential. The six differentials of dr_{if} can be rearranged such that four of them are cancelled by the $\delta_4(k_i - k_f)$ of $\hat{r}_{if}$. For this purpose, we define a "Lorentz invariant phase space" differential, which in the most general case comprises $n_f \geq 2$ particles of 4-momenta k_l in the final state:

$$\mathrm{dLips}(k_i, f) = (2\pi)^4 \Pi_{j=1}^{n_f} d_L^3 k_l \delta_4(k_i - k_f), \quad k_f = \Sigma_{j=1}^{n_f} k_l. \tag{4.86}$$

The differential transition rate is then

$$dr_{if} = |T_{if}|^2 \Pi_j \int d^3k_j (2k_j^0)^{-1} F_j \mathrm{dLips}(k_i, f). \tag{4.87}$$

For the special form (4.82) of F_1 and F_2, this gives

$$dr_{if} = \rho_1 \rho_2 (4k_1^0 k_2^0)^{-1} |T_{if}|^2 \mathrm{dLips}. \tag{4.88}$$

The differential cross section $d\sigma_{if}$ is now defined in terms of dr_{if} in a manner that reduces it to (4.38) in the static limit. One defines ad hoc a "relative velocity",

$$v_{12} = (2k_1^0 k_2^0)^{-1} \sqrt{\lambda}, \quad dr_{if} = \rho_1 \rho_2 v_{12} d\sigma_{if}. \tag{4.89}$$

The factor $(k_1^0 k_2^0)^{-1}$ is removed because it is not Lorentz invariant. In summary then,

$$d\sigma_{if} = (4k\sqrt{s})^{-1} |T_{if}|^2 \mathrm{dLips}(k_i, f). \tag{4.90}$$

In the cms and for $n_f = 2$, dLips is essentially the solid-angle differential $d\Omega_i$ of one of the two particles:

$$\mathrm{dLips} = (16\pi^2 E_1 E_2)^{-1} d^3k_1 d^3k_2 \delta(\sqrt{s} - E_1 - E_2) \delta_3(\boldsymbol{k}_1 + \boldsymbol{k}_2) \tag{4.91}$$

$$= k_1^2 dk_1 d\Omega_1 \delta(\sqrt{s} - E)/(16\pi^2 E_1 E_2), \quad E \equiv E_1 + E_2. \tag{4.92}$$

To cancel the last delta-function, one must express dk_1 in terms of dE. From $E_i^2 = m_i^2 + k_i^2$, one has $E_i dE_i = k_i dk_i$, and with $k_1 = k_2 \equiv k$,

$$dE = dE_1 + dE_2 = k dk (1/E_1 + 1/E_2) = k_1 dk_1 E/E_1 E_2. \tag{4.93}$$

After the cancellation, the delta-function implies $E = \sqrt{s}$, but we shall continue to use E as an alternative symbol for the cms energy:

$$\mathrm{dLips} = k d\Omega_1 / 16\pi^2 E, \quad E = \sqrt{s}. \tag{4.94}$$

Elastic scattering has $k_1 = k$ and consequently

$$d\sigma_{if} = d\Omega_1 |T_{if}|^2 / 64\pi^2 E^2. \tag{4.95}$$

Comparison with the one-particle formula (1.296), $d\sigma/d\Omega = |f_k|^2$, shows the connection

$$f_k = T_{if}/8\pi E. \tag{4.96}$$

The S-matrix has two fundamental properties, namely unitarity and analyticity, but both are largely lost in the Born series to any finite order. Unitarity ($S^\dagger S = 1$) results from the completeness of the initial and final states in the defintions (4.3) of the S-matrix. Adapting the notation of (1.270), one would write $\Sigma_j S^*_{fj} S_{ji} = \delta_{if}$. After a partial-wave expansion as in Sect. 1.10, one obtains a partial-wave S-matrix S_l, which in the simplest case of exclusively elastic scattering is a 1×1 matrix. Here unitarity requires $S_l = e^{2i\delta_l}$, where the phase shift $\delta_l(s)$ remains real up to a value s_{in} where inelastic scattering begins to contribute. In a more precise notation, one has

$$\Sigma_j S^*_{fj} S_{ji} \Pi_{n=1}^{n_j} d^3_L k_n = \langle i|f\rangle. \tag{4.97}$$

In terms of the T-matrix (4.63), this reads

$$-i(T_{if} - T^*_{fi}) = \Sigma_j \int \mathrm{dLips}(k_i, j) T^*_{fj} T_{ij}. \tag{4.98}$$

As practically all interactions are time-reversal invariant, one can find a spin basis in which T is symmetric, $T_{if} = T_{fi}$:

$$2\mathrm{Im} T_{if} = \Sigma_j \int \mathrm{dLips}(k_i, j) T^*_{fj} T_{ij}. \tag{4.99}$$

This relation connects different powers of T and is violated by any approximation that ends at a given power. For example, $T^{(1)}_{if}$ (4.64) is real, whereas the right-hand side of (4.99) is nonzero.

Analyticity says that $T_{if}(s,t)$ has an analytic continuation from the physical regions of s and t to the unphysical ones, and in particular to $s < s_{\mathrm{th}}$. While the Born amplitudes are analytic in t ($T^{(1)}_{if}$ has a pole a $t = 0$), they miss the poles at positions $s_n < s_{\mathrm{th}}$ that represent the atomic bound states (in the case of the Coulomb interaction, these poles accumulate near s_{th}. In a given partial wave, n may be identified with the principal quantum number, and $s_n = s_{\mathrm{th}} - \alpha^2_Z m_1 m_2/n^2$, as will be seen in Sect. 4.5). The situation may be illustrated by the function $f(x) = (1-x)^{-1} \approx 1 + x + x^2$, which is ∞ at $x = 1$, while its approximation is 3 there.

For the two-body states among j in (4.99), the analytic structure of dLips follows from (4.94) and the expressions (4.76) and (4.78) for k and λ:

$$\mathrm{dLips} = d\Omega_1 k/16\pi^2 s^{1/2} = d\Omega_1 \sqrt{s - s_{\mathrm{th}}}\sqrt{s - s_{\mathrm{pth}}}/32\pi^2 s. \tag{4.100}$$

It has a pole at $s = 0$ and two square root cuts, one starting at $s_{\mathrm{th}} = (m_1 + m_2)^2 = m^2_{12}$, the other at the pseudothreshold $s_{\mathrm{pth}} = (m_2 - m_2)^2$. By analytic continuation, the unitarity equation applies also in the region $t > 0$, where is supplies square root cuts at $t = t_{\mathrm{th}}$ and $t = t_{\mathrm{pth}}$. These cuts will be needed for the calculation of vacuum polarization in Sect. 5.3.

If the initial state consists of a single excited atom of energy E at rest, then its radiative decay into a photon and a atomic final state of energy E' gives a momentum $\boldsymbol{k}$ to the photon, and $-\boldsymbol{k}$ to the final atom. As the energy of an atom is normally quoted for the atom at rest, E' is to be taken as the mass m_2 in the expression (4.75) for k^2, while $m_1 = 0$ is the photon mass:

$$k^2 = (E^4 - 2E'^2E^2 + E'^4)/4E^2, \tag{4.101}$$

$$k = (E^2 - E'^2)/2E = E - E' - (E - E')^2/2E. \tag{4.102}$$

As E' is smaller than E, the subtracted term is positive. The energy $\hbar\omega$ of the emitted photon is not $E - E'$ as one might expect, but slightly smaller. The missing energy is carried away by the recoiling atom. Nonrelativistically, one has $2E = 2m$ (m = atomic mass) in the last denominator, giving $k = E - E' - k^2/2m$. In meson decays, there are some extreme cases like $\omega \to \gamma + \pi^0$ where $m_\pi^2 \ll m_\omega^2$ implies that the photon and the pion receive about equal energies, namely $\frac{1}{2}m_\omega$ each.

For the inverse process, one may direct a laser beam of photon momentum k' on the atoms of energy E' at rest. This requires $\hbar\omega' > E - E'$, because some energy is required for the motion of the excited atom. The total symmetry of the triangle function λ (4.77) implies that whenever one atom is at rest, the common (momentum)^2 of the photon and of the other atom is $\lambda/4$, divided by the cms (energy)^2 of the atom at rest, according to (4.76). The necessary momentum of a laser photon is thus

$$k' = \sqrt{\lambda}/2E' = (E^2 - E'^2)/2E' = E - E' + (E - E')^2/2E'. \tag{4.103}$$

Excited atoms and other unstable states may be included among the asymptotic initial states $|i\rangle$ of the S-matrix only if their decay rates may be calculated by first-order, time-dependent perturbation theory. The $\Pi_j d^3k_j(2k_j^0)^{-1}$ in (4.84) or (4.87) is then reduced to $d^3k_i/2k_i^0$; the decay rate density is

$$dr_{if} = |T_{if}|^2 \int d^3k_i(2k_i^0)^{-1}F_i\mathrm{dLips}(k_i, f). \tag{4.104}$$

A monoenergtic beam of unstable particles has $F_i = F(k_i, R, T)$ again given by (4.82). The decay rate is the integrated decay rate density, in which the density ρ of F disappears:

$$d\Gamma_{if}(k_i) = |T_{if}|^2(2k_i^0)^{-1}\mathrm{dLips}(k_i^0, \boldsymbol{k}_i, f). \tag{4.105}$$

For $\boldsymbol{k}_i = 0$, $k_i^0 = E$, a two-particle decay has dLips given by (4.94). And as $|T_{if}|^2$ is Lorentz invariant, the only difference for the lab system arises from the factor $(k_i^0)^{-1}$ in (4.105):

$$d\Gamma_{if}(k_i^0) = (k_i^0)^{-1}Ed\Gamma_{if}(E), \tag{4.106}$$

where $E = \sqrt{s}$ is the mass of the decaying state. The factor E/k_i^0 is the famous "time dilatation", which says that moving systems decay more slowly.

The total decay rate into the state $|f\rangle$ integrates over the decay angles Ω_1 in (4.94) and sums over the helicities λ_f of all decay products:

$$E\Gamma_{if}(E) = \int \sum_{\lambda_f} |T_{if}|^2 k_1 d\Omega_1 / 32\pi^2 E. \tag{4.107}$$

When $|i\rangle$ has vanishing total angular momentum (a "spinless particle"), the decay is isotropic in the cms, such that $\int d\Omega_1$ gives 4π. For a system of total angular momentum $j > 0$, the decay angular distribution depends on the magnetic quantum numbers m_j present in the initial state. By rotational invariance, the angular-integrated rate $\Gamma_{if}(E)$ is independent of m_j and may be calculated for a fixed value, say $m_j = 0$.

As an example, consider the decay of a vector meson into an electron-positron pair, $V \to e^- e^+$. Here one only needs one of the three m_j-values in the polarization vectors $\epsilon^\mu(m_j)$, say $\boldsymbol{e}(0)$ of (4.171) below. We may also set $\theta = 0$,

$$T(m_j = 0) = (4\pi)^{1/2} e_V J^z_{ep} = (4\pi)^{1/2} e_V \overline{u}_e \gamma_z v_p = (4\pi)^{1/2} e_V u_e^\dagger \alpha_z v_p. \tag{4.108}$$

The index p stands for positron. e_V is a coupling constant, and the $(4\pi)^{1/2}$ is included such that for the decay of a virtual photon, production and subsequent decay is again of the form (4.64), with $e_V = e$. The free Dirac spinors u_e and v_p are expressed in terms of Pauli's χ by (2.331) and (3.65),

$$u_e = \sqrt{E_e + \gamma^5 \boldsymbol{k}\boldsymbol{\sigma}}\chi(m_e), \quad v_p = \gamma^5 \sqrt{E_p + \gamma^5 \boldsymbol{k_p}\boldsymbol{\sigma}}\chi(-m_p). \tag{4.109}$$

In the cms, one has $E_e = E_p = E/2$ and $\boldsymbol{k}_p = -\boldsymbol{k}$. For the electron, we choose the explicit helicity spinors $\chi(\lambda)$ (2.337). The positron spinor is then $\chi_p(-m_p) = \chi(\lambda_p)$, because the positron helicity basis has the z-axis along the positron momentum, which is $-\boldsymbol{k}$. In this way, one finds

$$T = (4\pi)^{1/2} e_V \Sigma_{\gamma^5 = \pm 1} \sqrt{E/2 + 2\gamma^5 \lambda k} \sqrt{E/2 - 2\gamma^5 \lambda_p k}\, \langle \lambda | \sigma_z | \lambda_p \rangle, \tag{4.110}$$

$$\langle \lambda | \sigma_z | \lambda \rangle = 2\lambda (\cos^2 \tfrac{1}{2}\theta - \sin^2 \tfrac{1}{2}\theta) = 2\lambda \cos\theta, \tag{4.111}$$

$$\langle \lambda | \sigma_z | -\lambda \rangle = -2 \cos \tfrac{1}{2}\theta \sin \tfrac{1}{2}\theta e^{-i\phi} = -\sin\theta e^{-i\phi}, \tag{4.112}$$

$$T = (4\pi)^{1/2} 2 e_V (2\lambda m \cos\theta \delta_{\lambda,\lambda_p} - \tfrac{1}{2} E \sin\theta e^{-i\phi} \delta_{\lambda,-\lambda_p}), \tag{4.113}$$

$$\sum_{\lambda,\lambda_p} |T|^2 = 32\pi e_V^2 (m^2 \cos^2\theta + \tfrac{1}{4} E^2 \sin^2\theta). \tag{4.114}$$

Finally, the angular integral gives $\int d\Omega \cos^2\theta = 4\pi/3$,

$$E\Gamma(V \to e^- e^+) = \tfrac{2}{3} e_V^2 (2m^2 + E^2) k/E. \tag{4.115}$$

There are several applications of the two-body scattering formalism in which the cms does not exist. When two electrons scatter in the presence of

an external A^0, of an atomic atomic nucleus, the asymptotic states cannot be taken as plane waves any longer. They are eigenstates of single-particle Hamiltonians H_1 and H_2, with separate eigenvalues k_1^0 and k_2^0. The total lab energy $k_1^0 + k_2^0$ is conserved, but the S-matrix has nondiagonal elements, $S_{if} = \langle k_1^{0\prime} k_2^{0\prime} | S | k_1^0 k_2^0 \rangle$. The photon propagator is still given by (4.56); the index $_1$ of t (4.64) may be dropped:

$$t = p^\mu p_\mu = q_0^2 - \boldsymbol{q}^2, \quad q_0 = k_1^{0\prime} - k_1^0 = k_2^0 - k_2^{0\prime}. \tag{4.116}$$

The Fourier transform of the Born approximation still gives a local potential V_{12}, but this depends now on the energies of the asymptotic states. Replacing in (4.50) a_s^{-2} by $-q^{02}$, one finds

$$\int d^3 r e^{i\boldsymbol{q}\boldsymbol{r}} e^{iq_0 r}/r = 4\pi/(\boldsymbol{q}^2 - q_0^2), \quad V_{12}(r, q_0) = e^{iq_0 r} e^2/r. \tag{4.117}$$

(The zero of the denominator is neglected; it corresponds to atomic de-excitation.)

Explicit spin summations as in(4.114) are normally unelegant. The matrix element for scattering or collision of a single electron may be written in several forms,

$$T = \overline{u}' Q u = \chi^\dagger(\lambda') M \chi(\lambda). \tag{4.118}$$

Q is a linear combination of the sixteen matrices 1, γ^μ, $\sigma_{4\times4}^{\mu\nu}$, γ^5 and $\gamma^5\gamma^\mu$. M contains only the 2×2 matrices $\sigma^0 = 1$ and $\boldsymbol{\sigma}$; $M = M_0 + \boldsymbol{M}_\sigma \boldsymbol{\sigma}$. The cross section for unpolarized electrons avarages $|T|^2$ over λ;

$$\tfrac{1}{2} \Sigma_\lambda |T|^2 = \tfrac{1}{2} \Sigma_\lambda \chi^\dagger(\lambda') M \chi(\lambda) \chi^\dagger(\lambda) M^\dagger \chi(\lambda'). \tag{4.119}$$

This is simplified by the completeness relation

$$\Sigma_\lambda \chi(\lambda) \chi^\dagger(\lambda) = 1, \quad \Sigma_\lambda |T|^2 = \chi^\dagger(\lambda') M M^\dagger \chi(\lambda'). \tag{4.120}$$

When the polarization of the outgoing electron is irrelevant, one also has to sum over its helicity λ':

$$\Sigma_{\lambda,\lambda'} |T|^2 = \Sigma_{\lambda',ij} \chi_i^*(\lambda') \chi_j(\lambda') (M M^\dagger)_{ij} = \Sigma_{ii} (M M^\dagger)_{ii}. \tag{4.121}$$

In this way one obtains the simple expression

$$\tfrac{1}{2} \Sigma_{\lambda\lambda'} |T|^2 = \tfrac{1}{2} \mathrm{trace}(M M^\dagger) = |M_0|^2 + \boldsymbol{M}_\sigma \boldsymbol{M}_\sigma^*. \tag{4.122}$$

4.4 Current Matrix Elements, Form Factors

The forms (4.35) and (4.36) of current matrix elements ignore the inner structures of mesons and nuclei. Even the "elementary" leptons (electrons and muons) have some inner structure that follows from QED. In the present

section, the most general current matrix elements compatible with Lorentz and gauge invariance will be constructed.

Gauge invariance is simple; it is equivalent to current conservation:

$$q_\mu J^\mu_{if} = 0, \quad q^\mu = k^\mu_i - k^\mu_f. \tag{4.123}$$

When the meson or nucleus is not excited by the scattering, one has

$$k_i^2 = k_f^2 = m^2, \quad t = (k_i - k_f)^2 = 2m^2 - 2k_i k_f. \tag{4.124}$$

The general form of J^μ_{if} for a spinless particle is then

$$J^\mu_{if}(\mathrm{KG}) = (k_i + k_f)^\mu F(t), \quad F(0) = 1. \tag{4.125}$$

The first factor ensures (4.123), and $F(t)$ is a "form factor", which cannot be calculated exactly for mesons and nuclei. The nuclear form factor $F_N(\boldsymbol{q}^2)$ was introduced in (4.47) as the Fourier transform of the nuclear charge density, in the limit of a non-recoiling nucleus. In cms scattering, one has in fact $-t = \boldsymbol{q}^2$ according to (4.71). Thus $F(-t)$ is the Lorentz-invariant generalization of $F_N(\boldsymbol{q}^2)$. In principle, F is a function of all possible Lorentz invariants, $F = F(t, k_i^2, k_f^2, k_i k_f)$. But with (4.124), t is the only independent variable, for a fixed value m of the particle mass. At small t, F is paramatrized by its slope,

$$dF(t)/dt = \langle r^2_{ch} \rangle / 6, \tag{4.126}$$

where $\langle r^2_{ch} \rangle$ is the "mean square charge radius". The name derives from the relation (4.47) between F and the static charge density ρ_N at small $\boldsymbol{q}$,

$$\exp(i\boldsymbol{q}\boldsymbol{r}') \approx 1 + i\boldsymbol{q}\boldsymbol{r}' - \tfrac{1}{2}(\boldsymbol{q}\boldsymbol{r}')^2, \tag{4.127}$$

$$\tfrac{1}{2} \int d^3 r (\boldsymbol{q}\boldsymbol{r}')^2 \rho = \tfrac{1}{2} q^2 \int u^2 du r^4 dr \rho = q^2 \int r^4 dr \rho / 6 \equiv \langle r^2_{ch} \rangle q^2 / 6. \tag{4.128}$$

Qualitative arguments about the poles of analytic functions (which are handled by "uncertainty relations" in nonrelativistic quantum mechanics) show that particles with a large mean square radius have low-lying excited states. For nuclei, such state are produced in inelastic electron-nucleus collisions ("Coulomb excitation"). There one has

$$k_i^2 = m_i^2, \quad k_f^2 = m_f^2 > m_i^2. \tag{4.129}$$

The condition $q_\mu J^\mu_{if} = 0$ requires then instead of (4.125)

$$J^\mu_{if}(\mathrm{KG}) = [(k_i + k_f)^\mu t + q^\mu (m_f^2 - m_i^2)] G^0_{if}(t), \tag{4.130}$$

for a state f that is again spinless and has the same intrinsic parity as the ground state. For example, the α-particle (^{4}He nucleus) has among its excited states a state α^* that also has spin zero and positive parity (0^+). The Coulomb excitation cross section $d\sigma(e^-\alpha \to e^-\alpha^*)$ is given by (4.90).

The G^0_{if} in (4.130) is a transition form factor. Excited states appear also in the higher-order terms of the Born series for elastic scattering, beginning with the two-photon exchange (4.26):

$$S^{(2)}_{if} = -e^2 \int_{-\infty}^{+\infty} d^4y \int_{-\infty}^{y^0} dx^0 \int d^3x A_\mu(y) \sum_l j^{\mu\prime}_{il}(y) A_\nu(x) j^{\nu\ \prime}_{lf}(x). \quad (4.131)$$

We shall not discuss this expression any further, but note that A_μ is proportional to Ze (compare (4.55)), such that the second Born approximation is proportional to $Z^2e^4 = \alpha_Z^2$. The contribution of all excited states to the second Born approximation of elastic scattering is called the (electric) polarizability. Its calculation requires a good knowledge of nuclear theory. It frequently limits the precision of atomic bound state calculations, for example for atomic hydrogen. Heavy nuclei have both large $\langle r^2_{ch} \rangle$ and large Ze.

Turning now to spin-$\frac{1}{2}$ particles, the general form of the current matrix element may be taken as a combination of $\overline{u}_f(k_i + k_f)^\mu u_i$ and $\overline{u}_f \gamma^\mu u_i$:

$$J^\mu_{if} = \overline{u}_f [\gamma^\mu G_M(t) - F_2(t)(k_i + k_f)^\mu / 2m] u_i. \quad (4.132)$$

The two functions G_M and F_2 are the "magnetic" and "Pauli" form factors, respectively. The condition $q_\mu J^\mu_{if} = 0$ is satisfied by each term separately; the Dirac expression (4.36) for a structureless electron has $G_M = 1,\ F_2 = 0$. There is an alternative parametrization of J^μ_{if} which is better in the presence of potentials,

$$J^\mu_{if} = \overline{u}_f [\gamma^\mu F_1(t) + \sigma^{\mu\nu}_{4\times4} q_\nu F_2(t)/2m] u_i, \quad (4.133)$$

with $\sigma^{\mu\nu}_{4\times4}$ given by (2.327). Its equivalence with (4.132) is based on the Dirac equations for the free-particle spinors u_i and $\overline{u}_f$,

$$\begin{aligned} \overline{u}_f \sigma^{\mu\nu}_{4\times4} q_\nu u_i &= \tfrac{1}{2} \overline{u}_f [\gamma^\mu (k_i\gamma - k_f\gamma) - (k_i\gamma - k_f\gamma)\gamma^\mu] u_i \\ &= \overline{u}_f [\gamma^\mu (m_i + m_f) - k_i^\mu - k_f^\mu] u_i, \end{aligned} \quad (4.134)$$

after use of $k_i\gamma u_i = m_i u_i$, $\overline{u}_f k_f \gamma = m_f \overline{u}_f$, and with $\gamma^\nu\gamma^\mu = 2g^{\mu\nu} - \gamma^\mu\gamma^\nu$. For $m_i = m_f = m$ the connection between (4.132) and (4.133) is the "Gordon identity",

$$G_M(t) = F_1(t) + F_2(t). \quad (4.135)$$

$F_2(0)$ is the anomalous magnetic moment $\kappa_{\rm an}$ (2.76), as will be seen below. For leptons (electrons and muons), F_1 and F_2 may be calculated perturbatively as "radiative correction", caused by the emission and reabsorbtion of a virtual photon. They are then also called "vertex functions". The result is best expressed in terms of a new variable ξ (Lifshitz and Pitaevskii 1973) and a scaled coupling constant α_π,

$$\boldsymbol{q}^2 = -t \equiv m^2(1-\xi)^2/\xi, \quad \alpha_\pi \equiv \alpha/\pi, \quad (4.136)$$

$$F_2 = \alpha_\pi \xi \log \xi / (\xi^2 - 1), \quad F_2(0) = F_2(\xi = 1) = \tfrac{1}{2}\alpha_\pi = \kappa_{\rm an}. \quad (4.137)$$

In other words, a real electron is not quite structureless. The Gordon identity cannot be used in the presence of potentials. The form (4.133) is better than (4.132) because the normalization $F_1(0) = 1$ guarantees the correct value of the electric charge.

For nucleons (protons and neutrons), the large values $\kappa_p = 1.79$, $\kappa_n = -1.91$ cannot be calculated reliably; they are caused by the "hadronic structure" of these particles, which is qualitatively explained by the quark model, Sect. 5.9.

The vertex function $F_1(t)$ diverges for $t \to 0$. Like the factor $1/t$ in the main term $T_{if}^{(1)}$ (4.64), the divergence arises from the vanishing of the denominator of the photon propagator $D(y-x)$ (4.56), this time for the radiation emitted at position y and reabsorbed at position x. It can be handled by a charge screening radius a_s as in (4.50), but now a_s^{-1} is either called a photon mass or an infrared cutoff λ:

$$D_\lambda(y-x) = (2\pi)^{-4} \int d^4p e^{-ipy} e^{ipx} (\lambda^2 - p_\mu p^\mu - i\epsilon)^{-1}. \tag{4.138}$$

The resulting F_1 is complicated; for small $\boldsymbol{q}^2$ it is

$$F_1 = 1 - \alpha_\pi \boldsymbol{q}^2 m^{-2} (\tfrac{1}{3} \log(m/2\lambda) - \tfrac{1}{8}). \tag{4.139}$$

The removal of the unphysical parameter λ is postponed to Sect. 5.5. As the proton is also charged, it has the same form factor at very small $\boldsymbol{q}^2$. But normally, the inclusion of the hadronic charge radius (4.126) is more important. The proton has $\langle r_{ch}^2 \rangle \approx (0.85\,\mathrm{fm})^2$.

The fact that F_1 and F_2 follow from the Dirac equation (3.66) for the electron field operator emphasizes the exactness of that equation. However, as the calculation of radiative corrections is tedious, one prefers to work with effective field equations in which the dominant radiative corrections are replaced by auxiliary operators. The most important long-range operator arises in the approximation $F_1(t) = 1$, $F_2(t) = F_2(0) = \kappa_{\mathrm{an}}$. The resulting first-order S-matrix element for the scattering on a four-potential A^μ follows from the insertion of (4.133) into (4.30) and (4.27),

$$S_{if}^{(1)} = -ie \int d^4y A^\mu j_\mu = -ie \int d^4y A^\mu e^{-iqy} \overline{u}_f (\gamma_\mu + \sigma_{4\times4,\mu\nu} q^\nu \kappa_{\mathrm{an}}/2m) u_i. \tag{4.140}$$

The combination $e^{-iqy} q^\nu$ may be replaced by $i\partial^\nu e^{-iqy}$, and $\partial^\nu = \partial_y^\nu$ may be transferred to A^μ by partial integration:

$$S_{if}^{(1)} = -ie \int d^4y e^{-iqy} \overline{u}_f (A^\mu \gamma_\mu - i\partial^\nu A^\mu \sigma_{4\times4,\mu\nu} \kappa_{\mathrm{an}}/2m) u_i. \tag{4.141}$$

As $\sigma_{4\times4,\mu\nu} = (\gamma_\mu\gamma_\nu - \gamma_\nu\gamma_\mu)$ is antisymmetric in μ and ν, only the antisymmetric part of $\partial^\nu A^\mu$ contributes, which is $[\partial^\nu, A^\mu] = -F^{\mu\nu}/2$:

$$S_{if}^{(1)} = -ie \int d^4y e^{-iqy} \overline{u}_f (A^\mu \gamma_\mu + iF^{\mu\nu} \sigma_{4\times4,\mu\nu} \kappa_{\mathrm{an}}/4m) u_i. \tag{4.142}$$

The effective Dirac equation must reproduce this expression. It is unique only if one excludes additional derivatives. Remembering that the first term $A^\mu\gamma_\mu = \gamma^0(A^0 - \boldsymbol{A}\boldsymbol{\alpha})$ originates from the Dirac equation (2.92) in the form

$$(\gamma_\mu\pi^\mu - m)\psi_D = \gamma^0(\pi^0 - \gamma^5\boldsymbol{\sigma}\boldsymbol{\pi} - m\gamma^0)\psi_D = 0, \quad \boldsymbol{\pi} = \boldsymbol{p} + e\boldsymbol{A}, \tag{4.143}$$

one merely has to add the second term of (4.142) to the interaction operator of (4.143):

$$[\pi^0 - \gamma^5\boldsymbol{\sigma}\boldsymbol{\pi} - mc\gamma^0(1 - i\hbar e\kappa_{\rm an}F_{\mu\nu}\sigma^{\mu\nu}_{4\times4}/4m^2c^2)]\psi_{{\rm an}D} = 0. \tag{4.144}$$

This is the anomalous Dirac equation, which will be studied in some detail. The factors $\hbar$ and c have been included for that purpose. With appropriate restrictions, the equation also applies to an effective field operator $\Psi_{{\rm an}D}$ which removes electrons and emits and absorbs photons as in (3.66). The main restriction is of course that the reabsorption matrix element in the form connected with $F_2(t)$ in (4.133) is set equal to zero. For leptons, the second restriction is $\boldsymbol{q}^2/2m^2 \ll 1$, where m is the lepton mass. For nucleons, the same restriction holds, but here m is more of the order of the pion mass. The restriction also excludes the use of $\Psi_{{\rm an}D}$ for the creation of lepton-antilepton or nucleon-antinucleon pairs. A field theory with $\Psi_{{\rm an}D}$ is not renormalizable.

The space-space part $\sigma^{ij}_{4\times4} = \sigma^{ij} = i\sigma^k$ $(i, j = 1, 2, 3)$ of $\sigma^{\mu\nu}_{4\times4}$ contains no Dirac matrices according to (2.326). The $F_{\mu\nu}$ follows from (2.19). In the parity basis where $\gamma^0 = \beta$ is diagonal, (4.144) reads

$$(\pi^0 - m_{\rm an}c)\psi_g = (\boldsymbol{\pi}\boldsymbol{\sigma} - i\hbar\kappa_{\rm an}e\boldsymbol{\sigma}\boldsymbol{E}/2mc)\psi_f, \tag{4.145}$$

$$(\pi^0 + m_{\rm an}c)\psi_f = (\boldsymbol{\pi}\boldsymbol{\sigma} + i\hbar\kappa_{\rm an}e\boldsymbol{\sigma}\boldsymbol{E}/2mc)\psi_g, \tag{4.146}$$

$$m_{\rm an} = m + \hbar e\kappa_{\rm an}\boldsymbol{\sigma}\boldsymbol{B}/2mc, \quad \boldsymbol{E} = -\nabla A^0 - \partial_0\boldsymbol{A}. \tag{4.147}$$

The nonrelativistic limit of these equations gives $E = m_{\rm an}c^2 + H_P$. In the Pauli Hamiltonian H_P one may put $m_{\rm an} = m$, and the additional operator arising from $m_{\rm an}c^2$ may be shifted into H_P as follows:

$$H_{Pan} = V + \boldsymbol{\pi}^2/2m + \hbar e\boldsymbol{\sigma}\boldsymbol{B}g_{\rm free}/4mc, \quad g_{\rm free} = 2 + 2\kappa_{\rm an}. \tag{4.148}$$

Thus $\kappa_{\rm an}$ is in fact the anomalous magnetic moment defined in (2.76). Later, the Fourier transform of $F_1 - 1$ will be included as a modification of π^0.

Nuclei of ordinary atoms are nearly always nonrelativistic. They get an index $_2$ in the following, anticipating the application to binary atoms. Their Zeeman operators are expressed in terms of the nuclear magneton

$$H_{\rm Zee} = g_{2n}\boldsymbol{S}_2\boldsymbol{B}\mu_n, \quad \mu_n = e\hbar/2m_pc. \tag{4.149}$$

Here m_p is the proton mass, irrespective of the nuclear mass m_2, for all spins $s_2 > 0$. For $s_2 = 1/2$, $\boldsymbol{S}_2 = \boldsymbol{\sigma}_2/2$, this agrees with (4.148) only for the proton

itself. If one wants to treat a spin-1/2 nucleus as a Dirac particle, one must redefine its g-factor:

$$H_{\rm Zee} = \hbar Ze\boldsymbol{\sigma}\boldsymbol{B}g_2/4m_2c, \tag{4.150}$$

$$g_2 = g_{n2}m_2/Zm_p. \tag{4.151}$$

For example, the proton has $g_2 = g_{n2} = 5.58$, while the nucleus ^{3}He has $g_{n2} = -2.128$ and $g_2 \approx (3/2)g_{n2} = -3.185$. The most important manifestation of nuclear spin in atoms is the magnetic "hyperfine interaction" between $\boldsymbol{S}_2$ and the electrons. In classical electrodynamics, a nucleus with a magnetic moment

$$\boldsymbol{\mu}_n = g_{n2}\mu_n\boldsymbol{S}_2 \tag{4.152}$$

fixed at the origin produces a vector potential

$$\boldsymbol{A} = \boldsymbol{\mu}_n \times \boldsymbol{r}/r^3 = -\boldsymbol{\mu}_n \times [\boldsymbol{\nabla}, 1/r] = \nabla \times (\boldsymbol{\mu}_n/r). \tag{4.153}$$

This $\boldsymbol{A}$ is now used as an operator in the electron's Dirac equation. The procedure is analogous to the calculation of A^0 in (4.44), but it is more questionable here. For any finite Dirac g-factor g_2, g_{2n} vanishes in the limit $m_2 \to \infty$ according to (4.151), such that the static limit of (4.153) is strictly speaking zero. It is therefore of interest to see how $\boldsymbol{A}$ arises in the framework of two-body scattering: The vector components $\boldsymbol{J}_{if}$ of J^μ_{if} (4.133) contain

$$\overline{u}'\boldsymbol{\gamma}u = u'^\dagger\gamma^5\boldsymbol{\sigma}u = \chi'^\dagger[(\boldsymbol{\sigma}\boldsymbol{k}')\boldsymbol{\sigma} + \boldsymbol{\sigma}(\boldsymbol{\sigma}\boldsymbol{k})]\chi = \chi'^\dagger[\boldsymbol{k} + \boldsymbol{k}' + i\boldsymbol{\sigma} \times \boldsymbol{q}]\chi, \tag{4.154}$$

$$\overline{u}'\sigma^{i\nu}_{4\times4}q_\nu u = -\overline{u}'\sigma^{ij}q_j u = 2mi\chi'^\dagger(\boldsymbol{\sigma} \times \boldsymbol{q})_i\chi. \tag{4.155}$$

This shows that the part $\boldsymbol{J}(\boldsymbol{\sigma})_{if}$ which is proportional to $\boldsymbol{\sigma}$ does contain 1 and $\kappa_{\rm an}$ in the combination $1 + \kappa_{\rm an} = g_{\rm free}/2$:

$$\boldsymbol{J}_{if}(\boldsymbol{\sigma}) = \tfrac{1}{2}g_{\rm free}\overline{u}'\boldsymbol{\gamma}u = \tfrac{1}{2}ig_{\rm free}\chi'^\dagger\boldsymbol{\sigma} \times \boldsymbol{q}\chi. \tag{4.156}$$

The $\boldsymbol{\sigma}\boldsymbol{E}$ terms will be included relativistically in Sect. 5.6. Here we eliminate ψ_f (4.146) to obtain a nonrelativistic equation for ψ_g,

$$(\pi^0 - mc)\psi_g = [(\boldsymbol{\pi}\boldsymbol{\sigma})^2/2mc - i\hbar\kappa_{\rm an}[e\boldsymbol{\sigma}\boldsymbol{E}, \boldsymbol{\pi}\boldsymbol{\sigma}]/4m^2c^2]\psi_g. \tag{4.157}$$

With $e\boldsymbol{E} = [\nabla, V]$, the new operator adds a term $-\kappa_{\rm an}[W,[W,V]]$ in (2.243). It results in a factor $1 + 2\kappa_{\rm an}$ both in V_{sl} and in $V_{\rm Da}$ (2.246). For s-states, one finds

$$\langle V_{\rm Da}\rangle = (1 + \alpha_\pi)\alpha_Z^4\alpha m/2n^3 = \langle V_{sl}\rangle_{l=0}. \tag{4.158}$$

The analyticity of $\langle V_{sl}\rangle$ as a function of l is thus respected by F_2.

The Coulomb potential is modified by the inclusion of F_1 in the integrand of (4.51). With $\int d^3q e^{-i\boldsymbol{q}\boldsymbol{r}}\boldsymbol{q}^2/\boldsymbol{q}^2 = (2\pi)^3\delta(\boldsymbol{r})$, one finds

$$V(r) = -\alpha_Z/r + 4\pi\alpha_Z[\log(m/2\lambda) - 1/8]\delta(\boldsymbol{r})\alpha_\pi/m^2. \tag{4.159}$$

The modified Darwin potential is obtained from (2.263) as $\delta V_{\rm Da} = 2\kappa_{\rm an} V_{\rm Da} = \alpha_\pi \alpha_Z 4\pi\delta(\boldsymbol{r})/8m^2$, wich cancels the $-1/8$ of (4.159). It is thus advisable to use the spinless form factor,

$$F = F_1 - \tfrac{1}{8}\alpha_\pi \boldsymbol{q}^2 m^{-2} = 1 - (\alpha_\pi \boldsymbol{q}^2/m^2)\tfrac{1}{3}\log(m/2\lambda), \tag{4.160}$$

$$V(r) + \delta V_{\rm Da} = -\alpha_Z/r + 4\pi\alpha_Z \log(m/2\lambda)\delta(\boldsymbol{r})\alpha_\pi/m^2, \tag{4.161}$$

and to completely discard $\kappa_{\rm an}$ in s-states (except in the $\boldsymbol{\sigma B}$-term of (4.148), of course). For a spinless particle, one may simply set $V_{sl} = 0$, and identify F with the spinless form factor $F(t)$ in (4.125), to this order in α.

An order-of-magnitude estimate for λ is half the imaginary momentum $\kappa = -ik$ of the asymptotic wave function $e^{-\kappa r}$, $2\lambda \approx \kappa = Z\alpha m/n$, $F - 1 \approx -(\alpha_\pi \boldsymbol{q}^2/2m^2)\frac{1}{3}\log(n^2/\alpha_Z^2)$. Comparison with (4.126) leads to a kind of mean square radius of electrons and muons,

$$\langle r_{ch}^2 \rangle = (\alpha_\pi/m^2)\log(n^2/\alpha_Z^2), \tag{4.162}$$

although its dependence on $\alpha_Z = Z\alpha$ shows that it is a binding effect. It gives the leading contribution to the "Lamb shift", which lifts the Dirac degeneracy of $n{\rm s}_{1/2} - n{\rm p}_{1/2}$ states (compare Fig. 2.2). The complete Lamb shift will be calculated in Sect. 5.5. ($\langle r_{ch}^2 \rangle^{1/2}$ should not be confused with the "classical electron radius", $r_e = \alpha/m_e$, which enters the Compton cross section.)

Unfortunately, the introduction of the photon mass λ violates the gauge invariance of QED. A modification which does respect gauge invariance is a QED in d dimensions, where d need not be integer. It simplifies the cancellation of infrared divergences, see for example Brown (1992).

4.5 Particles of Higher Spins

In addition to the photon, the heavy bosons $\rm W^{\pm}$ and $\rm Z^0$ of the electroweak interaction have spin 1. All other particles of spin $> 1/2$ are composite, which limits the value of their "particle approximation", neglecting excitation and breakup. In atomic theory, nuclei are normally treated as single particles. In some long-range interactions, however, even a whole atom of total angular momentum j may be treated as a single particle of spin j.

It is postulated that any closed system of total energy $\hbar c k^0$ and total momentum $\hbar \boldsymbol{k}$ satisfies the Einstein relation (1.41), $\hbar^2 k_\mu k^\mu = m^2 c^2$, which leads to the differential equation (1.43), $(p_\mu p^\mu - m^2 c^2)\psi = 0$. For charged particles, gauge invariance requires the replacement of p^μ by π^μ, and additional spin operators $O(\boldsymbol{S})$ may appear. In units $\hbar = c = 1$, one thus has

$$[\pi_\mu \pi^\mu - m^2 - O(\boldsymbol{S})]\psi = 0, \quad \pi^\mu = p^\mu - qA^\mu. \tag{4.163}$$

Both the KG equation and the Kramers version (2.82) of the Dirac equation have that form.

A massive particle of spin 1 at rest is described by a wave function $\boldsymbol{V}(\boldsymbol{r},t)$, the three components $V_\pm = V_x \pm iV_y$ and $V_0 = V_z$ of which transform under rotations like the components of a vector field, for example like the magnetic field $\boldsymbol{B}$ (2.64) under rotations about the z-axis. A general rotation may be written as in (2.75), with the matrices $\boldsymbol{S}^{(1)}$ formally identical with the $\boldsymbol{l}^{(1)}$ of (1.263). This allows still for different Lorentz transformations. One usually chooses a 4-vector V^μ analogous to the electromagnetic potential A^μ. The fourth component is fixed by the Lorentz gauge condition $p_\mu V^\mu = 0$. For a free particle, this implies

$$k_\mu V^\mu = 0, \quad V^\mu(\boldsymbol{k}=0) = (0,\boldsymbol{V}), \tag{4.164}$$

because V^0 is a scalar under rotations, corresponding to a spinless particle. In the presence of electromagnetic fields, however, the condition itself must be gauge invariant,

$$\pi_\mu V^\mu = 0. \tag{4.165}$$

The solutions of (4.164) are similar to (3.11).

$$V^\mu(x^\nu) = e^{-ikx}\epsilon^\mu(\boldsymbol{k},\lambda), \quad k_\mu\epsilon^\mu = 0. \tag{4.166}$$

λ denotes the helicity, that is one of the eigenvalues of the spin operator along $\boldsymbol{k}$. For $k_y = 0,\ \phi = 0$, one finds

$$\epsilon^\mu(\pm 1) = 2^{-1/2}(0, \mp\cos\theta, -i, \pm\sin\theta), \tag{4.167}$$

$$\epsilon^\mu(0) = m^{-1}(k, k^0\sin\theta, 0, k^0\cos\theta). \tag{4.168}$$

The orthonormality and completeness relations are

$$\epsilon^*_\mu(\lambda')\epsilon^\mu(\lambda) = \epsilon^{0*}(\lambda')\epsilon^0(\lambda) - \boldsymbol{\epsilon}^*(\lambda')\boldsymbol{\epsilon}(\lambda) = -\delta_{\lambda'\lambda}, \tag{4.169}$$

$$\Sigma_\lambda\epsilon^\mu(k,\lambda)\epsilon^\nu(k,\lambda) = -g^{\mu\nu} + k^\mu k^\nu/m^2. \tag{4.170}$$

For $k = 0,\ k^0 = m$, one has

$$\epsilon^\mu = (0,\boldsymbol{e}), \quad \boldsymbol{e}(0) = (\sin\theta, 0, \cos\theta). \tag{4.171}$$

The interactions of particles of arbitrary spins are parametrized in the Born series. Their current matrix elements have been collected by Waldenström and Olsen (1971), see also (5.203). For spin 1,

$$J^\mu_{if} = -(k_i+k_f)^\mu[F_1\epsilon^*_f\epsilon_i - \tfrac{1}{2}m^{-2}F_2(\epsilon^*_f q)(\epsilon_i q)] - G_1[\epsilon^{*\mu}_f\epsilon_i q - \epsilon^\mu_i\epsilon^*_f q]. \tag{4.172}$$

$F_1,\ F_2$ and G_1 are three form factors. For small $|t|$, they are conveniently expressed in terms of the magnetic, charge and quadrupole form factors $F_M,\ F_C$ and F_Q. The "Breit" or "brick-wall" frame is used here, where the initial and final momenta $\boldsymbol{k}_i$ and $\boldsymbol{k}_f$ of the spin-one particle are as small as possible,

under the condition that its recoil effects are shared symmetrically between initial and final states:

$$\boldsymbol{k}_i = \boldsymbol{q}/2, \quad \boldsymbol{k}_f = -\boldsymbol{q}/2, \quad k_i^0 = k_f^0 \approx m(1+\tau/2), \quad \tau = \boldsymbol{q}^2/4m^2. \tag{4.173}$$

Taking the z-axis along $\boldsymbol{q}$, one finds

$$J_{if}^{\mu} = -(k_i+k_f)^{\mu}[F_1 \boldsymbol{e}_f^* \boldsymbol{e}_i + 2\tau e_{fz}^* e_{iz}(1+\tau)F_2] + G_1 q(\epsilon_f^{*\mu} e_{iz} - \epsilon_i^{\mu} e_{fz}^*)(1+\tfrac{1}{2}\tau). \tag{4.174}$$

The traceless part of $e_{fz}^* e_{iz}$ is the quadrupole operator

$$e_{fz}^* e_{iz} = \tfrac{1}{3}[\boldsymbol{e}_f^* \boldsymbol{e}_i + Q_{if}], \tag{4.175}$$

$$Q_{if} = 2e_{fz}^* e_{iz} - e_{fx}^* e_{ix} - e_{fy}^* e_{iy}. \tag{4.176}$$

F_C and F_Q are defined as the coefficients of $\boldsymbol{e}_f^* \boldsymbol{e}_i$ and of $Q_{if}/2\tau$ in $J^0/2k^0$, while F_M is the coefficient of $i\boldsymbol{q}\times\boldsymbol{S}/2m$ in $\boldsymbol{J}/2E$. In this manner, one obtains

$$F_Q = F_1 + (1+\tau)F_2 + G_1, \quad F_C = F_1 + \tfrac{2}{3}\tau F_Q, \quad F_M = G_1. \tag{4.177}$$

The magnetic and quadrupole moments are defined at $\tau = 0$,

$$\mu = eG_1(0)/2m, \quad Q = F_Q(0)/m^2. \tag{4.178}$$

Their effects on atomic spectra will be discussed in Chap. 5.

For particles of arbitrary spin s, there exists also a spinor wave function ψ_r with only $2s+1$ components, together with its parity transform ψ_l. (Fierz and Pauli 1939, Joos 1962, Weinberg 1964, Carruthers 1971). As for spin 1/2, one defines a 2×2 matrix γ^5 with eigenvalues $+1$ and -1 for ψ_r and ψ_l, respectively. A free "Dirac" spinor u_D is boosted from a spinor $\chi(m_s)$ in analogy with (2.334),

$$u_D^{(s)} = m^s e^{\gamma^5 \boldsymbol{\eta}\boldsymbol{S}} \chi^{(s)}. \tag{4.179}$$

For a boost to 4-momentum k^{μ} one has

$$\cosh\eta = k^0/m = \gamma, \quad \sinh\eta = k/m \tag{4.180}$$

as in (2.335). $e^{\boldsymbol{\eta}\boldsymbol{S}}$ is the square root of a polynomial of degree $2s$ in k^0 and $\boldsymbol{k}\boldsymbol{S}$. The polynomial is constructed from $e^{2\boldsymbol{\eta}\boldsymbol{S}}$ as in (2.336). One takes the z-axis along $\boldsymbol{k}$, such that $2\boldsymbol{\eta}\boldsymbol{S}$ reduces to $2\eta m_s$, where m_s is one of the eigenvalues of S_z. For $s=1$

$$S_z = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}; \quad e^{2\eta S_z} = \begin{pmatrix} e^{2\eta} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & e^{-2\eta} \end{pmatrix}, \tag{4.181}$$

$$e^{\pm 2\eta} = \cosh 2\eta \pm \sinh 2\eta = \cosh^2\eta + \sinh^2\eta \pm 2\cosh\eta\sinh\eta. \tag{4.182}$$

In this way one finds, in addition to $m^{1/2}e^{\boldsymbol{\eta S}^{(1/2)}} = (k^0 + \boldsymbol{k\sigma})^{1/2}$,

$$me^{\boldsymbol{\eta S}^{(1)}} = [m^2 + 2k^0\boldsymbol{kS} + 2(\boldsymbol{kS})^2]^{1/2}, \tag{4.183}$$

$$m^{3/2}e^{\boldsymbol{\eta S}^{(3/2)}} = [m^2(k^0 + 2\boldsymbol{kS}) + (k^0 + \tfrac{2}{3}\boldsymbol{kS})[2(\boldsymbol{kS})^2 - \tfrac{1}{2}\boldsymbol{k}^2]]^{1/2}, \tag{4.184}$$

$$m^2e^{\boldsymbol{\eta S}^{(2)}} = [m^4 + 2m^2(k^0 + \boldsymbol{kS})\boldsymbol{kS} + \tfrac{2}{3}(2k^0 + \boldsymbol{kS})\boldsymbol{kS}[(\boldsymbol{kS})^2 - \boldsymbol{k}^2]]^{1/2}. \tag{4.185}$$

These boosts depend only on $m_s = \lambda = \boldsymbol{kS}/k$, not on s. For example, (4.183) and (4.185) are identical for $|\lambda| < 2$. See also Sect. 4.8.

One may also construct $e^{\boldsymbol{\eta S}}$ from the direct product of $2s$ spin-1/2 boosts, with a set of Pauli matrices $\boldsymbol{\sigma}^{(i)}$. In that case, the product must be put into a form which contains only

$$\tfrac{1}{2}\Sigma_i\boldsymbol{\sigma}^{(i)} \equiv \boldsymbol{S}. \tag{4.186}$$

For $s = 1$,

$$me^{\boldsymbol{\eta S}^{(1)}} = (k^0 + \boldsymbol{k\sigma}^{(1)})^{1/2}(k^0 + \boldsymbol{k\sigma}^{(2)})^{1/2}. \tag{4.187}$$

Here one may use $k^{02} = m^2 + \boldsymbol{k}^2 = m^2 + \frac{1}{2}(\boldsymbol{k\sigma}^{(1)})^2 + \frac{1}{2}(\boldsymbol{k\sigma}^{(2)})^2$ and then combine $\frac{1}{2}(\boldsymbol{k\sigma}^{(1)})^2 + \frac{1}{2}(\boldsymbol{k\sigma}^{(2)})^2$ with $(\boldsymbol{k\sigma}^{(1)})(\boldsymbol{k\sigma}^{(2)})$ into $2(\boldsymbol{kS})^2$.

4.6 The Equation for Spinless Binaries

A study of the relativistic eikonal approximation (which is omitted in this book) led Brezin, Itzykson and Zinn-Justin (1970) to a bound state equation for two relativistic spinless particles ("spinless binaries"). The equation was rederived by Todorov (1971), who emphasized its exact solutions and also speculated about additional short-distance operators. In the following, essentially the original equation of Brezin, Itzykson and Zinn-Justin will be called "Todorov equation". The discoverers of the equation may console themselves that Schrödinger did not get his name attached to the Klein-Gordon equation either.

The Todorov equation is a KG equation with relativistic recoil. It applies for all mass combinations of the binary system, provided particle 2 is also spinless (spinor particles 2 are covered by the more complicated "Klein-Dirac" equation of Sect. 4.9). The relativistic effects of recoil are unmeasurably small already for the mesic helium atoms, which contain the lightest spinless nucleus. They become large in $\pi^-\pi^+$ and π^-K^+ and $K^-\pi^+$ atoms, but no precise data exist for such binaries. Like the KG equation, the Todorov equation is verified indirectly: It reproduces the spin-averaged energy levels of leptonium, which are known with excellent precision. The mathematical significance of the KG equation for the Dirac equation has been stressed in Chaps. 2 and 3; the Todorov equation is of comparable significance for leptonium.

In the two-body case, the interaction is constructed from the S-matrix in the cms, $\boldsymbol{p}_1 = -\boldsymbol{p}_2 \equiv \boldsymbol{p}$. With $\boldsymbol{p}_1^2 = \boldsymbol{p}_2^2 = \boldsymbol{p}^2$, two stationary free-particle equations (1.44) apply simultaneously in the asymptotic region $r \to \infty$ where the interaction vanishes,

$$(k^2 - \boldsymbol{p}_1^2)\psi_{\rm as}(\boldsymbol{r}) = 0, \quad (k^2 - \boldsymbol{p}_2^2)\psi_{\rm as}(\boldsymbol{r}) = 0, \quad k^2 = E_1^2 - m_1^2 = E_2^2 - m_2^2. \tag{4.188}$$

The complete equation has the interaction operator added. It is already known in the static limits ($m_1 \ll m_2$ and $m_2 \ll m_1$), namely $-2E_iV + V^2$ according to (1.90). If one now replaces the two limiting operatores $-2E_iV$ ($i = 1, 2$) by an interpolating $-2\epsilon V$, the resulting first Born scattering amplitude f_k reproduces exactly the cms Born amplitude $T_{if}^{(1)}$ (4.64) of QED, apart from the S-states (see below):

$$(k^2 - 2\epsilon V + V^2 - \boldsymbol{p}^2)\psi = 0. \tag{4.189}$$

The connection between f and T is given by (4.96). In the first Born approximation,

$$8\pi E f^{(1)} = T^{(1)} = 4\pi q_1 q_2 J^{\mu}_{11'} g_{\mu\nu} J^{\nu}_{22'} / \boldsymbol{q}^2. \tag{4.190}$$

Insertion of $J_1^{\mu} = (k_1 + k_1')^{\mu}$ (4.125) and $J_2^{\mu} = (k_2 + k_2')^{\mu}$ (in the approximation $F(t) = 1$) leads to

$$T_{if}^{(1)} = 4\pi q_1 q_2 (k_1 + k_1')^{\mu} (k_2 + k_2')_{\mu} / \boldsymbol{q}^2. \tag{4.191}$$

$k_1 k_2$ and $k_1' k_2'$ are fixed by $(k_1 + k_2)^2 = (k_1' + k_2')^2 = s$:

$$2k_1 k_2 = 2k_1' k_2' = s - m_1^2 - m_2^2. \tag{4.192}$$

Next, one may use ${k_1'}^{\mu} = k_1^{\mu} - q^{\mu}$ and ${k_2'}^{\mu} = k_2 + q^{\mu}$ to get

$$J_1 J_2 = (2k_1 - q)(2k_2 + q) = (2k_1' + q)(2k_2' - q). \tag{4.193}$$

Taking the average and observing $q(k_2 - k_2') = q(k_1' - k_1) = q^2 = -\boldsymbol{q}^2$, one finds the simple expression

$$T_{if}^{(1)} = 16\pi q_1 q_2 (k_1 k_2 / \boldsymbol{q}^2 - 1/4). \tag{4.194}$$

The Fourier transform of the second term $-q_1 q_2$ produces a delta function $\delta(\boldsymbol{r})$ which contributes only to S-states. The spinless particles known today (mesons and nuclei) all have internal structure which results in strong form factors $F_i(-\boldsymbol{q}^2)$. Their effects are negligible for larger orbital angular momenta l (normally $l > 0$ is sufficient), but the approximation (4.194) certainly breaks down for S-states. One may thus ignore the $-1/4$ in the bracket. Agreement with the scattering amplitude of (4.189) is then reached for

$$\epsilon = k_1 k_2 / \sqrt{s} = (s - m_1^2 - m_2^2)/2\sqrt{s}. \tag{4.195}$$

The relatively complicated expression (4.75) for k^2 in (4.136) is eliminated in favour of the relativistic reduced mass μ as follows

$$k^2 = \epsilon^2 - \mu^2, \quad \mu = m_1 m_2/\sqrt{s} = m_1 m_2/E, \tag{4.196}$$

$$[(\epsilon - V)^2 - \mu^2 - \boldsymbol{p}^2]\psi = 0. \tag{4.197}$$

Near the threshold $E = m_1 + m_2 \equiv m_{12}$, μ is close to its nonrelativistic limit $\mu_{nr} = m_1 m_2/m_{12}$. The equation is now in a familiar form, but it is better to remove the E^2 from denominators:

$$[(\tfrac{1}{2}(E^2 - m_1^2 - m_2^2) - EV)^2 - m_1^2 m_2^2 - E^2\boldsymbol{p}^2]\psi = 0. \tag{4.198}$$

Already the inclusion of the nonrelativistic binding energy, $E \approx m_{12} - \alpha_Z^2 \mu_{nr}/2n^2$ makes μ n-dependent, which is avoided in (4.198) (this n-dependence will enter the hyperfine operator of Sect. 5.1). The factor E in front of V and $\boldsymbol{p}$ is removed by taking $\boldsymbol{r}/E \equiv \boldsymbol{r}_E$ as independent variable, as in (3.224). At the same time, one may multiply the new variable by $m_1 m_2$ to make it dimensionless:

$$\boldsymbol{\rho} = m_1 m_2 \boldsymbol{r}_E = \mu \boldsymbol{r}, \quad \boldsymbol{p}_\rho = \boldsymbol{p}/\mu = -iE\boldsymbol{\nabla}/m_1 m_2. \tag{4.199}$$

$\boldsymbol{\rho}$ is close to the variable $\boldsymbol{\rho}_{nr} = \mu_{nr}\boldsymbol{r}$ of nonrelativistic quantum mechanics. The price paid for this pedagogical trick is another redefinition of $\boldsymbol{r}$. The possibility of such redefinitions stems from the fact that the "position operator" $\boldsymbol{r}$ is basically a nonrelativistic concept, for example in (3.119). Attempts to construct a corresponding operator for relativistic quantum mechanics result in a strange "Zitterbewegung". In quantum electrodynamics as the appropriate basis of relativistic quantum mechanics, both $\boldsymbol{r}$ and t serve as counting operators of fields.

The dimensionless Todorov equation is

$$[(\epsilon/\mu - V_\rho)^2 - 1 - \boldsymbol{p}_\rho^2]\psi = 0, \quad V_\rho = -\alpha_Z/\rho. \tag{4.200}$$

The form (4.197) of the Todorov equation follows from the KG equation by the substitutions

$$E_1 \to \epsilon, \quad m_1 \to \mu. \tag{4.201}$$

It guarantees the correctness of the operator V^2 only in the static limits. One additional energy shift is $\delta E_6 = \frac{1}{2}\langle V^2 L^2/r^2\rangle m_{12}/m_1^2 m_2^2$, which has been calculated by Elkhovskii (1996) in the nonrelativistic approximation for particle 2, to first order in m_1/m_2. It is of the order of α_Z^6. Its E^2-form is

$$\tfrac{1}{2}\delta E_6^2 = \tfrac{1}{2}\langle V_\rho^2 L^2/r^2\rangle. \tag{4.202}$$

With $\delta(\epsilon/\mu) = \frac{1}{2}\delta E^2/m_1 m_2$ according to (4.200), the corresponding operator can be included as a correction V_6 in the Todorov equation,

$$[(\epsilon - V)^2 - \mu^2 - \boldsymbol{p}^2 + V_6]\psi = 0, \quad V_6 = V^2 L^2/2r^2 m_1 m_2. \tag{4.203}$$

However, V_6 was calculated for two spinor particles, and its mere spin-independe does not prove its validity for spinless particles. Also, the radiative corrections of Sect. 5.5 are in fact larger.

The standard form of the Todorov equation is identical with (1.144), with new redefinitions of $\boldsymbol{r}_\epsilon$ and n_β. With $\hbar c = 1$,

$$\boldsymbol{r}_\epsilon = \boldsymbol{r}\alpha_z\epsilon, \quad n_\beta = \alpha_Z\epsilon/\kappa, \quad \kappa = (\mu^2 - \epsilon^2)^{1/2}. \tag{4.204}$$

But whereas the energy E_1 of particle 1 in the static limit is proportional to its mass m_1, $E_1 = m_1(1 + \alpha_Z^2/n_\beta^2)^{-1/2}$ according to (1.129), multiplication of the corresponding relation between ϵ and μ by E gives a linear relation between the square of the total cms energy and $m_1 m_2$:

$$E^2 - m_1^2 - m_2^2 = 2m_1 m_2(1 + \alpha_Z^2/n_\beta^2)^{-1/2}, \tag{4.205}$$

The threshold value of E^2 is $(m_1+m_2)^2 = m_{12}^2$. Its subtraction gives a relation analogous to (1.131) for E_N,

$$E^2 - m_{12}^2 = 2m_1 m_2 f, \quad f = (1 + \alpha_Z^2/n_\beta^2)^{-1/2} - 1. \tag{4.206}$$

The calculation of E requires yet another square root,

$$E = (2m_1 m_2 f + m_{12}^2)^{1/2} = m_{12} + f\mu_{nr} - \tfrac{1}{2}f^2\mu_{nr}^2/m_{12} + \tfrac{1}{2}f^3\mu_{nr}^3/m_{12}^2 \mp \ldots. \tag{4.207}$$

With f of the order of α_Z^2 and μ_{nr}/m_{12} vanishing in the static limit, the new expansion parameter $f\mu_{nr}/m_{12}$ is very small for electronic atoms. There, the terms f^2 are attributed to the "Braun recoil formula" for the Dirac equation (Braun 1973, Eides et al. 2001). Positronium has $\mu_{nr}/m_{12} = 1/4$.

As each expansion complicates the result, one may quote E^2 instead of E. We shall see later that fine and hyperfine splittings as well as radiative corrections contribute small corrections $\delta E^2 = 2E\delta E$, such that E^2 is the appropriate quantity also under more general circumstances.

It was mentioned already below eq. (4.96) in Sect. 4.2 that the T-matrix is an analytic function of the Mandelstam variables s and t. Consequently, the eigenvalues of any relativistic equation depend on E only via $s = E^2$. They are invariant under the replacement $E \to -E$. The symmetry in E of the spectra of closed systems follows already from CPT invariance. The field operators of spinless particles have $\Psi_{CPT}(x^\mu) = \Psi_{CPT}(-x^\mu)$, while spinor fields get an additional factor γ^5 according to (3.57). A closed system at total energy E has a time dependence e^{-iEt}, which is changed to $e^{+iEt} = e^{-i(-E)t}$ by CPT. Physically, the system of energy $-E$ is the antisystem of energy $+E$. An atom is transformed into its antiatom by CPT, for example hydrogen (e^-p) into antihydrogen ($e^+\overline{p}$).

An analogous argument applies also to the appearance of m_1^2 and m_2^2. Already in Sect. 1.6 it was mentioned that only m^2 has physical significance. This is obscured in the Dirac equation but is evident in its Kramers form,

(2.82) or (2.135). In the expression (4.205) for E^2, it seems contradicted by the requirement that $m_1 m_2$ must be positive. But this sign asymmetry may be traced back to the requirement that the bound state wave function must fall as $e^{-\kappa r}$ for $r \to \infty$, i.e. $\kappa = (\mu^2 - \epsilon^2)^{1/2}$ must be positive. With $\kappa = \mu(1+n_\beta^2/\alpha_Z^2)^{-1/2}$ as the generalization of (1.129), it is clear that negative $m_1 m_2$ requires the negative sign of the square root.

In the above formulas, $\boldsymbol{r} = \boldsymbol{r}_1 - \boldsymbol{r}_2$ has been replaced either by $\boldsymbol{\rho}$ or by $\boldsymbol{r}_\epsilon$:

$$\boldsymbol{\rho} = m_1 m_2 \boldsymbol{r}/E, \quad \boldsymbol{r}_\epsilon = \alpha_Z \epsilon \boldsymbol{r} = \tfrac{1}{2}\alpha_Z \boldsymbol{\rho}(E^2 - m_1^2 - m_2^2)/m_1 m_2. \tag{4.208}$$

The ranges of the new distance variables are $0 \le \rho \le \infty$ and $0 \le r_\epsilon \le \infty$ as usual, corresponding to $0 \le Er \le \infty$. Negative E thus requires the negative sign of the square root that defines r, $r = -[(\boldsymbol{r}_1 - \boldsymbol{r}_2)^2]^{1/2}$. The traditional distance variable in antiatoms is to be taken negative, at least in connection with C, CP or CPT transformations.

When particle 2 is a nucleus with a given charge density $\rho_N(r)$, the potential $V_N(r_\epsilon) = \int d^3 r' \rho_N(r') |\boldsymbol{r}_\epsilon - \boldsymbol{r}'/\alpha_Z \epsilon|^{-1}$ respects CPT only if ρ_N is the Fourier transform of the nuclear form factor $F(\boldsymbol{q}^2)$, and not some other convenient function. For a proof, define

$$\boldsymbol{q}_\epsilon = \boldsymbol{q}/\alpha_Z \epsilon, \tag{4.209}$$

such that $\exp(i\boldsymbol{q}\boldsymbol{r}) = \exp(i\boldsymbol{q}_\epsilon \boldsymbol{r}_\epsilon)$. Then V_N can be rewritten as

$$V_N(r_\epsilon) = \int d^3 r'_\epsilon (2\pi)^{-3} \int d^3 q_\epsilon e^{-i\boldsymbol{q}_\epsilon \boldsymbol{r}_\epsilon} F_N(\boldsymbol{q}_\epsilon^2 \alpha_Z^2 \epsilon^2) |\boldsymbol{r}_\epsilon - \boldsymbol{r}'_\epsilon|^{-1}. \tag{4.210}$$

The form factor introduces a weak ϵ^2-dependence into V_N, which does not break the invariance under $E \to -E$.

The KG orthogonality relations (1.197) do not directly apply to the solutions of the Todorov equation, due to the energy dependence of μ, $\mu_i = m_1 m_2/E_i$. One must first change the variable $\boldsymbol{r}$, either to $\boldsymbol{\rho}$ or to $\boldsymbol{r}_\epsilon$. The dimensionless Todorov equation (4.200) is most convenient, with $\epsilon/\mu = (E^2 - m_1^2 - m_2^2)/2m_1 m_2$:

$$\int \rho^2 d\rho R_j(\rho) R_i(\rho)(\epsilon_i/\mu_i + \epsilon_j/\mu_j - 2V_\rho) = 2\delta_{ij}\epsilon_i/\mu_i. \tag{4.211}$$

The generalized radial KG equation (2.273) may also be transformed to the variable ρ, because $L_\alpha^2 = l_\alpha(l_\alpha + 1)$ is independent of ϵ and μ:

$$[\epsilon^2/\mu^2 - 1 - 2V_\rho \epsilon/\mu + (\partial_\rho + 1/\rho)^2 - L_\alpha^2/\rho^2] R = 0. \tag{4.212}$$

It will be seen later that this equation carries the generalized KG equation to the two-body problem.

The first-order perturbation theory of the standard form, $K\psi = n_\beta^{-2}\psi$, is analogous to the formalism of Sect. 2.7:

$$(K_0 + K_{\rm per})\psi = [n_\beta^{-2} + (n_\beta^{-2})^1]\psi, \quad (n_\beta^{-2})^1 = \langle K_{\rm per} \rangle. \tag{4.213}$$

Here $n_\beta^{-2} = (n_\beta^{-2})^0$ is understood, and $(n_\beta^{-2})^1$ will be denoted by δn_β^{-2} in the following. With $n_\beta^{-2} = \kappa^2/\alpha_Z^2\epsilon^2 = \alpha_Z^{-2}(\mu^2/\epsilon^2 - 1)$, one obtains

$$\delta n_\beta^{-2} = \alpha_Z^{-2}\delta(\mu^2/\epsilon^2) = 4m_1^2m_2^2\alpha_Z^{-2}\delta(E^2 - m_1^2 - m_2^2)^{-2}. \tag{4.214}$$

The final result is

$$\delta E^2 = -\alpha_Z^2(\epsilon/\mu)^3 m_1 m_2 \delta n_\beta^{-2} = -\alpha_Z^2(\epsilon/\mu)^3 m_1 m_2 \langle K_{\rm per}\rangle. \tag{4.215}$$

$$\delta E = -\tfrac{1}{2}\alpha_Z^2(\epsilon/\mu)^3\mu\langle K_{\rm per}\rangle. \tag{4.216}$$

The nonrelativistic limit has $\epsilon/\mu = 1$, $\delta E^2 = 2m_{12}\delta E$, and thus $\delta E = \delta(-\frac{1}{2}\alpha_Z^2\mu/n_\beta^2) = \delta E_N$ as expected. The main advantage of the standard form is the expression for the second-order shift $(n_\beta^{-2})^{(2)}$, which is completely analogous to (2.223):

$$(n_\beta^{-2})^{(2)} = \Sigma_{k\neq n}\langle n|K_{\rm per}|k\rangle\langle k|K_{\rm per}|n\rangle(n_{\beta,n}^{-2} - n_{\beta,k}^{-2})^{-1}. \tag{4.217}$$

This form applies only to explicit eigenvalue equations.

The order α_Z^4 of E may be calculated from $T^{(1)}$ alone, setting $V^2 = 0$. One first expands all operators to first order in relativity and then uses gauge invariance $q_\mu J_1^\mu = q_\mu J_2^\mu = 0$. One keeps $q_0 \neq 0$ in the cms, because it will appear in the iteration of $T^{(1)}$. Instead, one splits $\boldsymbol{J}$ into a component $J_\parallel$ parallel to $\boldsymbol{q}$ and two perpendicular components,

$$\boldsymbol{J}_\perp = \boldsymbol{J} - \boldsymbol{q}(\boldsymbol{J}\boldsymbol{q})/\boldsymbol{q}^2. \tag{4.218}$$

This leads to

$$q_0 J^0 - qJ_\parallel = 0, \quad J_\parallel = q_0 J^0/q, \quad q = |\boldsymbol{q}|. \tag{4.219}$$

$$J_1^\mu J_{2\mu} = J_1^0 J_2^0(1 - q_0^2/\boldsymbol{q}^2) - \boldsymbol{J}_{1\perp}\boldsymbol{J}_{2\perp}. \tag{4.220}$$

Writing now $1 - q_0^2/\boldsymbol{q}^2 = -t/\boldsymbol{q}^2$, the t is cancelled in (4.64), and one is left with

$$J_1^\mu J_{2\mu}/t = -J_1^0 J_2^0/\boldsymbol{q}^2 - \boldsymbol{J}_{1\perp}\boldsymbol{J}_{2\perp}/(\boldsymbol{q}^2 - q_0^2). \tag{4.221}$$

The first term contains the "instantaneous" interaction, the second one the "retardation", which are familiar effects in classical electrodynamics. The retardation is frequently small and may be evaluated by setting $q_0 = 0$ in the denominator. Looking at the Breit operator H_B (3.105) from this point of view, we see that with a change of the name of the integration variable from $\boldsymbol{k}$ to $\boldsymbol{q}$, the square bracket is

$$\boldsymbol{\alpha}_{1\perp}\boldsymbol{\alpha}_{2\perp} = \boldsymbol{\alpha}_1\boldsymbol{\alpha}_2 - (\boldsymbol{\alpha}_1\boldsymbol{q})(\boldsymbol{\alpha}_2\boldsymbol{q})/\boldsymbol{q}^2. \tag{4.222}$$

A more precise treatment which keeps $q^0 \neq 0$ has been mentioned in Sect. 3.7.

In the spinless case $\boldsymbol{J} = \boldsymbol{k}' + \boldsymbol{k} = 2\boldsymbol{k} + \boldsymbol{q}$,

$$\boldsymbol{J}_\perp = 2\boldsymbol{k} - 2\boldsymbol{q}(\boldsymbol{k}\boldsymbol{q})/\boldsymbol{q}^2. \tag{4.223}$$

From $(\boldsymbol{k}'+\boldsymbol{k})\boldsymbol{q} = (\boldsymbol{k}'+\boldsymbol{k})(\boldsymbol{k}-\boldsymbol{k}') = k^2-k'^2$, one concludes that this formalism does not allow one to set $k^2 = k'^2$ either, because otherwise $J_\parallel = 0$, $\boldsymbol{J}_\perp = \boldsymbol{J}$. The modification (4.221) does reproduce the effect of V^2 to the order α_Z^4. Expansions to the order α_Z^6 also comprise retardation (Czarnecki et al., 1999).

4.7 The Leptonium Equation

There are six types of leptons, namely the electron e^-, muon μ^-, tau lepton τ^-, their antiparticles e^+ (positron), μ^+, τ^+, and their neutral massless partners, the neutrinos ν and antineutrinos $\overline{\nu}$. The tau lepton is very heavy and decays within 10^{-15} s which prevents bound states. The other charged leptons can form hydrogenlike "leptonium" bound states with each other, namely positronium e^-e^+, muonium $e^-\mu^+$, antimuonium $e^+\mu^-$ and muon-antimuon bound states $\mu^-\mu^+$. The muon decays after 2.2×10^{-6} s, which is long enough for precision measurements. Its mass is 200 times the electron mass. For this reason, muonium is chemically very similar to atomic hydrogen. As the muon is still ten times lighter than the proton, the main differences arise from the higher mobility of muonium. On the theoretical side, electrons and muons are ideal Dirac particles. Their anomalous magnetic moments are calculable from QED, they are very close to the $\alpha/2\pi$ given in (4.137). A consistent relativistic binary treatment of ordinary hydrogen is more difficult, due to the proton's inner structure which does not follow from QED. The theoretical study of leptonium is also of intererst for its possible analogy with a relativistic quarkonium model of mesons.

An essential issue in the description of two fermions is the number of components of the wave function ψ. In the presence of an external 4-potential $A^\mu_{\rm cl}$, $4 \times 4 = 16$ components are convenient, $\psi = \psi_{D2}$. This follows from the general ansatz (3.82) which leads to the Dirac-Coulomb equation with the Breit correction H_B (3.111). In Sect. 3.6, ψ_{D2} has been split into two octets ψ and χ, and χ has been eliminated in (3.186). Finally, ψ has been split into two quartets ψ_g and ψ_f (the large and small components of ψ, respectively), and elimination of ψ_f produces a four-component equation for ψ_g. Any systematic expansion ends up with four nonrelativistic components, for example the singlet and triplet spin components.

The construction of the binary equation from the S-matrix for $A^\mu_{\rm cl} = 0$ need not follow this procedure. For two spinless particles, we subtracted in (4.188) for noninteracting orbitals an interaction operator $I = 2\epsilon V - V^2$ and determined the linear operator $2\epsilon V$ from the first Born approximation. The V^2 was included because it is required in the two static limits (the two KG equations). Additional small "recoil operators" may be calculated from the

"straightforward" Born series up to arbitrary orders. When the differential equation is replaced by an integral equation, it is known as "Bethe-Salpeter" equation.

For two Dirac particles, one has traditionally taken an ansatz from the cms form of (3.166), replacing $\boldsymbol{\pi}_1 \to \boldsymbol{p}$, $\boldsymbol{\pi}_2 \to -\boldsymbol{p}$, $\pi^0 \to E - I_{16}$,

$$(E - I_{16} - \gamma_1^5 \boldsymbol{p}\boldsymbol{\sigma_1} + \gamma_2^5 \boldsymbol{p}\boldsymbol{\sigma_2})\psi_{D2} = m_+\psi_{D2}, \quad m_+ = m_1\beta_1 + m_2\beta_2, \tag{4.224}$$

and then adopted one of the two methods (V^2 or retardation) for the determination of I_{16}. Also in this case, agreement is reached at the order α_Z^4, but the details are irritating. If the procedure outlined in (4.220) is adopted, the first-order result is $I_{16}^{(1)} \approx V + H_B$, apart from necessary modifications by "positive-energy projectors". On the other hand, it follows from (3.206) that the "retardation" piece $V_{\rm ret}$ of H_B vanishes. It does so after the V^2 from $(E - V)^2$ is eliminated, see the discussion in Sect. 3.7 and the explicit calculation in Sect. 4.9. This indicates the existence of a simpler Born series for a reduced, 8×8 component T-matrix, from which an 8-component interaction I_8 is constructed, for direct subtraction in the free (= asymptotic) equation for the octet ψ. With $V = 0$, the asymptotic form of (3.186) is

$$[E - \gamma^5(p_1 - p_2)]m_+^{-1}[E - \gamma^5(p_1 + p_2)]\psi_{\rm as} = m_+\psi_{\rm as}. \tag{4.225}$$

With $\boldsymbol{p}_1 = -\boldsymbol{p}_2 \equiv \boldsymbol{p}$,

$$p_1 + p_2 = \boldsymbol{p}_1\boldsymbol{\sigma}_1 + \boldsymbol{p}_2\boldsymbol{\sigma}_2 = \boldsymbol{p}\boldsymbol{\Delta\sigma}, \quad p_1 - p_2 = \boldsymbol{p}_1\boldsymbol{\sigma}_1 - \boldsymbol{p}_2\boldsymbol{\sigma}_2 = \boldsymbol{p}\boldsymbol{\sigma}, \tag{4.226}$$

$$\boldsymbol{\Delta\sigma} = \boldsymbol{\sigma}_1 - \boldsymbol{\sigma}_2, \quad \boldsymbol{\sigma} = \boldsymbol{\sigma}_1 + \boldsymbol{\sigma}_2. \tag{4.227}$$

As the more practical form (3.186) has an extra factor m_+, the interaction operator $2I_8$ is introduced into (4.225) with a factor m_+^{-1},

$$[E - \gamma^5(p_1 - p_2)]m_+^{-1}E - \gamma^5(p_1 + p_2)] - m_+^{-1}2I_8 - m_+]\psi = 0. \tag{4.228}$$

Multiplication by m_+ and use of $(\boldsymbol{p\Delta\sigma})\boldsymbol{p\sigma} = 0$ gives

$$[E^2 - m_+^2 - 2I_8 - \gamma^5 E\boldsymbol{p}(\boldsymbol{\sigma}m_-/m_+ + \boldsymbol{\Delta\sigma})]\psi = 0. \tag{4.229}$$

By its construction from the first Born approximation, $2I_8^{(1)}$ is linear in V; the cancellation between first- and second-order Born terms induced by I_{16} is already done. More generally, (4.224) and (4.229) give different results at any given order of the Born series. Agreement is only reached when (4.224) includes higher orders than (4.229).

The single-particle Dirac equation exists also in two forms, namely the standard 4-component form and its 2-component Kramers reduction (2.82). But there it is the 4-component version which is superior in its relation to the Born series. As emphasized earlier in this chapter, the operator $\gamma_\mu A^\mu$ is the Fourier transform $I_4^{(1)}$ of the first Born approximation to the scattering

matrix. If one first reduces the S-matrix to 2×2, for example by the use of (2.324), and then uses its Fourier transform $I_2^{(1)}$ as interaction operator in the Kramers equation, one misses the quadratic operator, $A_\mu A^\mu = A^{02} - \boldsymbol{A}^2$, which follows from gauge invariance of that equation. In both cases, the formalism is influenced by parity invariance. The factorizing form (2.80) of the Kramers equation is parity invariant, but the form (2.82) is not suited for additions. If at fixed $\pi_\mu \pi^\mu$ the first-order operators are modified, parity invariance is lost. The asymptotic form of (4.224), on the other hand, has three parity transformations, namely $\psi_{D2}^{P1} = \beta_1 \psi_{D2}(-\boldsymbol{r}_1, \boldsymbol{r}_2)$, $\psi_{D2}^{P2} = \beta_2 \psi_{D2}(\boldsymbol{r}_1, -\boldsymbol{r}_2)$, and $\psi_{D2}^{P12} = \beta_1 \beta_2 \psi_{D2}(-\boldsymbol{r}_1, -\boldsymbol{r}_2)$. The first two transformations are useless because they are broken by I_{16}. Equation (4.229) has only one parity transformation, namely (3.187), which is respected by I_8. Obviously, the construction of the interaction from the S-matrix should be restricted to equations whose asymptotic forms do not require additional symmetries. This is also illustrated by the individual time shifting operators $p_1^0 = i\partial_{t1}$ and $p_2^0 = i\partial_{t2}$ of the two separate Dirac equations satisfied by $\psi_{D2,\mathrm{as}}$,

$$(\gamma_1^\mu p_{1\mu} - m_1)\psi_{D2,\mathrm{as}} = 0, \quad (\gamma_2^\mu p_{2\mu} - m_2)\psi_{D2,\mathrm{as}} = 0. \tag{4.230}$$

To obtain a useful two-fermion equation, one must multiply the first equation by γ_1^0, the second one by γ_2^0 and then add:

$$(p^0 - \gamma_1^5 \boldsymbol{p}_1 \boldsymbol{\sigma}_1 - \gamma_2^5 \boldsymbol{p}_2 \boldsymbol{\sigma}_2 - m_1\beta_1 - m_2\beta_2)\psi_{D2,\mathrm{as}} = 0, \quad p^0 = p_1^0 + p_2^0. \tag{4.231}$$

This aspect was absent in the nonperturbative method of Chap. 3, where only one time was used.

In the next section, the $2I_8$ of (4.229) will be constructed directly from the 8×8-component T-matrix of QED. However, $2I_8$ is also found from (3.225), by (i) omitting the retardation from the Breit operator, wich amounts to setting $b_E = -V_E \boldsymbol{\sigma}_1 \boldsymbol{\sigma}_2 / E$, and (ii) by omitting all V^2-operators in I_{hf} (3.226). With the abbreviations (4.226), there remains

$$I_{hf} = -V_E(1 + \boldsymbol{\sigma}_1 \boldsymbol{\sigma}_2)\boldsymbol{p}_E \Delta\boldsymbol{\sigma} \gamma^5 - \boldsymbol{p}_E \boldsymbol{\sigma} \gamma^{5\prime} V_E (1 - \boldsymbol{\sigma}_1 \boldsymbol{\sigma}_2)/E^2. \tag{4.232}$$

The second term vanishes, as $\boldsymbol{\sigma}$ operates only between triplet spin states, where $1 - \boldsymbol{\sigma}_1 \boldsymbol{\sigma}_2 = 0$. In the first term, the spin dependence is further simplified by

$$(\boldsymbol{\sigma}_1 \boldsymbol{\sigma}_2)\boldsymbol{\sigma}_1 = \boldsymbol{\sigma}_2 + i\boldsymbol{\sigma}_1 \times \boldsymbol{\sigma}_2, \quad (\boldsymbol{\sigma}_1 \boldsymbol{\sigma}_2)\boldsymbol{\sigma}_2 = \boldsymbol{\sigma}_1 - i\boldsymbol{\sigma}_1 \times \boldsymbol{\sigma}_2. \tag{4.233}$$

Insertion of $\Delta\boldsymbol{\sigma} = \boldsymbol{\sigma}_1 - \boldsymbol{\sigma}_2$ gives

$$(1 + \boldsymbol{\sigma}_1 \boldsymbol{\sigma}_2)\Delta\boldsymbol{\sigma} = 2i\boldsymbol{\sigma}_1 \times \boldsymbol{\sigma}_2 \equiv 2i\boldsymbol{\sigma}_{12}^\times, \tag{4.234}$$

$$I_8 = -V_E + I_{hf}, \quad I_{hf} = -i\gamma^5 \boldsymbol{\sigma}_{12}^\times V_E \boldsymbol{p}_E / E^2. \tag{4.235}$$

I_{hf} is the hyperfine operator, which will be discussed in the next section and in Chap. 5.

m_+ and m_- occur in (4.229) only in the combinations m_+^2 and m_-/m_+ of (3.189),

$$m_+^2 = m_1^2 + m_2^2 + 2m_1 m_2 \beta, \quad m_-/m_+ = (m_2 - m_1\beta)/(m_2 + m_1\beta). \tag{4.236}$$

For $I_8 = 0$, (4.229) must possess simpler forms such as

$$(E^2 - m_+^2 - 2\gamma^5 E\boldsymbol{p}\boldsymbol{\sigma}_1)\psi_{\text{as},1} = 0, \tag{4.237}$$

$$(E^2 - m_+^2 - 2\gamma^5 E\boldsymbol{p}\boldsymbol{\sigma}_2)\psi_{\text{as},2} = 0. \tag{4.238}$$

Only such forms lead to the asymptotic equation (4.188). To see this, we insert $E^2 - m_+^2 = E^2 - m_1^2 - m_2^2 - 2m_1 m_2\beta$ and divide (4.237) by $2E$ to get

$$(\epsilon - \mu\beta - \gamma^5 \boldsymbol{p}\boldsymbol{\sigma}_1)\psi_{\text{as},1} = 0, \tag{4.239}$$

with ϵ and μ defined in (4.195) and (4.197). This form of (4.237) is an effective one-body Dirac equation. Multiplication by $\epsilon + \mu\beta + \gamma^5 \boldsymbol{p}\boldsymbol{\sigma}_1$ gives

$$[\epsilon^2 - \mu^2 - (\boldsymbol{p}\boldsymbol{\sigma}_1)^2]\psi_{\text{as},1} = (k^2 - p^2)\psi_{\text{as},1} = 0, \tag{4.240}$$

as in (2.108).

The transformation from ψ_{as} to $\psi_{\text{as},1}$ must remove the factor m_-/m_+ from $\boldsymbol{\sigma}$ without changing $\boldsymbol{\Delta\sigma}$. It contains the "spin permutation" operator,

$$P_{\text{spin}} = \tfrac{1}{2}(1 + \boldsymbol{\sigma}_1\boldsymbol{\sigma}_2). \tag{4.241}$$

From (3.133) it follows that (see also (5.67) below)

$$\tfrac{1}{2}\boldsymbol{\sigma}_1\boldsymbol{\sigma}_2 = (\boldsymbol{\sigma}^2 - 6)/4 = s(s+1) - 3/2. \tag{4.242}$$

Consequently, P_{spin} has the eigenvalue $+1$ for the $s = 1$ states which are symmetric, and -1 for the $s = 0$ state which is antisymmetric, and $P_{\text{spin}}^2 = 1$. Consider now the transformation

$$\psi = C_1\psi_1, \quad C_1 = (m_+ m_-)^{-1/2}(m_2 + m_1\beta P_{\text{spin}}) \tag{4.243}$$

from this point of view. $\boldsymbol{\sigma}$ vanishes when it acts on a singlet state to its right or left. In the products $\boldsymbol{\sigma}C_1$ and $C_1\boldsymbol{\sigma}$, one may therefore replace P_{spin} by its triplet eigenvalue $+1$,

$$\boldsymbol{\sigma}C_1 = C_1\boldsymbol{\sigma} = \boldsymbol{\sigma}(m_+ m_-)^{-1/2}(m_2 + m_1\beta) = \boldsymbol{\sigma}(m_+/m_-)^{1/2}. \tag{4.244}$$

The inverse of C_1 is

$$C_1^{-1} = (m_+ m_-)^{-1/2}(m_2 - m_1\beta P_{\text{spin}}), \tag{4.245}$$

which explains the normalization factor $(m_+ m_-)^{-1/2} = (m_2^2 - m_1^2)^{-1/2}$. From $\beta\gamma^5 = \gamma^5(-\beta)$, one finds

$$C_1^{-1}\gamma^5 = \gamma^5 C_1. \tag{4.246}$$

Multiplying (4.229) by C_1^{-1} from the left, one observes

$$C_1^{-1}\gamma^5\boldsymbol{\sigma}C_1 = \gamma^5 C_1\boldsymbol{\sigma}C_1 = \gamma^5\boldsymbol{\sigma}m_+/m_-. \tag{4.247}$$

This removes the factor m_-/m_+ from $\boldsymbol{\sigma}$ in (4.229) as required. For $\Delta\sigma$, on the other hand, one finds

$$C_1^{-1}\gamma^5\Delta\boldsymbol{\sigma}C_1 = \gamma^5 C_1\Delta\boldsymbol{\sigma}C_1 = \gamma^5\Delta\boldsymbol{\sigma}, \tag{4.248}$$

because $\Delta\boldsymbol{\sigma}$ flips the spin symmetry: a triplet state to the right of $\Delta\boldsymbol{\sigma}$ is transformed into the singlet state (which has $P_{\text{spin}} = -1$) and vice versa. In this manner one achieves the combination $\Delta\boldsymbol{\sigma} + \boldsymbol{\sigma} = 2\boldsymbol{\sigma}_1$. The derivation of (4.238) is similar:

$$\psi = C_2\psi_2, \quad C_2 = P_{\text{spin}}C_1 = (m_+m_-)^{-1/2}(\beta m_1 + m_2 P_{\text{spin}}), \tag{4.249}$$

$$C_2^{-1}\gamma^5\boldsymbol{\sigma}C_2 = \gamma^5\boldsymbol{\sigma}m_+/m_-, \quad C_2^{-1}\gamma^5\Delta\boldsymbol{\sigma}C_2 = -\gamma^5\Delta\boldsymbol{\sigma}. \tag{4.250}$$

The extra minus sign in the operation of C_2 on $\Delta\boldsymbol{\sigma}$ produces the combination $-\Delta\boldsymbol{\sigma} + \boldsymbol{\sigma} = 2\boldsymbol{\sigma}_2$. The complete binary equation (4.229) is thus equivalent to two effective Dirac equations

$$(E^2 - m_+^2 - 2I_{81} - 2\gamma^5 E\boldsymbol{p}\boldsymbol{\sigma}_1)\psi_1 = 0, \tag{4.251}$$

$$(E^2 - m_+^2 - 2I_{82} - 2\gamma^5 E\boldsymbol{p}\boldsymbol{\sigma}_2)\psi_2 = 0, \tag{4.252}$$

$$I_{81} = C_1^{-1}I_8C_1, \quad I_{82} = C_2^{-1}I_8C_2. \tag{4.253}$$

The relation between ψ_1 and ψ_2 follows from the inversion of (4.249),

$$\psi_2 = C_2^{-1}C_1\psi_1 = C_1^{-1}P_{\text{spin}}C_1\psi_1 = P_{\text{spin}}\psi_1. \tag{4.254}$$

Thus P_{spin} exchanges $\boldsymbol{\sigma}_1$ with $\boldsymbol{\sigma}_2$ in the differential equation.

4.8 The Interaction in Leptonium

In the 16-component equation (4.224), the simplest interaction I_{16} would be the Fourier transform of the first-order Born approximation $T^{(1)}$ (4.64), (4.36),

$$T_{if}^{(1)} = 4\pi\alpha_Z\overline{u}_1'\gamma_1^\mu u_1\overline{u}_2'\gamma_{2,\mu}u_2/t. \tag{4.255}$$

To that one must at least add the retardation operators, as explained in Sect. 4.5. But if $T_{if}^{(1)}$ is first reduced to an 8×8 form (by (3.175) or by using the eliminations (4.260), (4.261) below), its Fourier transform $I_8 = I_{81}$ in (4.251) is both simpler and more precise. With $\overline{u}_i' = u_i'^\dagger\gamma_i^0$ and $\gamma_i^0\boldsymbol{\gamma}_i = \boldsymbol{\alpha}_i = \gamma_i^5\boldsymbol{\sigma}_i$, one obtains

$$T_{if}^{(1)} = 4\pi\alpha_Z u_1'^\dagger u_2'^\dagger(1 - \gamma_1^5\gamma_2^5\boldsymbol{\sigma}_1\boldsymbol{\sigma}_2)u_1u_2/t. \tag{4.256}$$

u_1 and u_2 are the 4-component spinors u_D (2.334) for momenta $\boldsymbol{k}$ and $\boldsymbol{k}_2 = -\boldsymbol{k}$, respectively. The free two-fermion spinors of ψ and χ will be called v and w. Here it is slightly more convenient to use simultaneous eigenstates of γ_1^5 and γ_2^5 instead of the states (3.174):

$$v = \begin{pmatrix} u_{1r}u_{2r} \\ u_{1l}u_{2l} \end{pmatrix}, \quad w = \begin{pmatrix} u_{1r}u_{2l} \\ u_{1l}u_{2r} \end{pmatrix}, \quad u_1 u_2 = \begin{pmatrix} v \\ w \end{pmatrix}, \quad \gamma_1^5\gamma_2^5 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{4.257}$$

The Hermitian adjoint final state spinors are

$$v'^\dagger = ({u'_{1r}}^\dagger {u'_{2r}}^\dagger,\ {u'_{1l}}^\dagger {u'_{2l}}^\dagger), \quad w'^\dagger = ({u'_{1r}}^\dagger {u'_{2l}}^\dagger,\ {u'_{1l}}^\dagger {u'_{2r}}^\dagger). \tag{4.258}$$

Inspection of (4.256) shows that $T_{if}^{(1)}$ can be rewritten as

$$T_{if}^{(1)} = 4\pi\alpha_Z[v'^\dagger(1 - \boldsymbol{\sigma}_1\boldsymbol{\sigma}_2)v + w'^\dagger(1 + \boldsymbol{\sigma}_1\boldsymbol{\sigma}_2)w]/t. \tag{4.259}$$

The general T_{if} may be decomposed into the elements of the four submatrices T_{vv}, T_{ww}, T_{vw} and T_{wv}, but T_{vw} and T_{wv} appear only for odd numbers of β_i (note that (4.256) contains no β_i). To get (4.259) as the elements of an 8×8 matrix, one may now use the free form of (3.181) to eliminate one of the two spinors:

$$w = m_+^{-1}(E - \gamma^5 \boldsymbol{\Delta\sigma k})v, \quad v = m_+^{-1}(E - \gamma^5 \boldsymbol{\sigma k})w, \tag{4.260}$$

or one of the two Hermitian adjoint final state spinors:

$$w'^\dagger = v'^\dagger(E - \gamma^5 \boldsymbol{\Delta\sigma k'})m_+^{-1}, \quad v'^\dagger = w'^\dagger(E - \gamma^5 \boldsymbol{\sigma k'})m_+^{-1}. \tag{4.261}$$

Here we choose to eliminate w and $v'^\dagger$; the resulting 8×8 matrix is called $m_+^{-1}M$:

$$T_{if} = w'^\dagger m_+^{-1} M v. \tag{4.262}$$

The form (4.262) is analogous to the one-fermion case, where the current operator was reduced to 2×2 components in the form $\psi_l'^\dagger \Gamma^\mu \psi_r$ in (2.324). It is not Hermitian, but it has instead simple Lorentz transformation properties, as $\psi_l^\dagger$ transforms inversely to ψ_r. From (4.259) and the elimination of w and $v'^\dagger$,

$$M = 4\pi\alpha_Z[m_+(E - \gamma^5 \boldsymbol{\sigma k'})m_+^{-1}(1 - \boldsymbol{\sigma}_1\boldsymbol{\sigma}_2) + (1 + \boldsymbol{\sigma}_1\boldsymbol{\sigma}_2)(E - \gamma^5 \boldsymbol{\Delta\sigma k})]/t. \tag{4.263}$$

The combination $\boldsymbol{\sigma}(1 - \boldsymbol{\sigma}_1\boldsymbol{\sigma}_2)$ vanishes as in (4.232). Consequently (and with $t = -\boldsymbol{q}^2$),

$$M = 4\pi\alpha_Z[2E - \gamma^5(1 + \boldsymbol{\sigma}_1\boldsymbol{\sigma}_2)\boldsymbol{\Delta\sigma k}]/(-\boldsymbol{q}^2). \tag{4.264}$$

Using (4.233) and (4.234),

$$M = -8\pi\alpha_Z(E - i\gamma^5 \boldsymbol{k\sigma}_{12}^\times)/\boldsymbol{q}^2, \quad \boldsymbol{\sigma}_{12}^\times \equiv \boldsymbol{\sigma}_1 \times \boldsymbol{\sigma}_2. \tag{4.265}$$

The operator $2I_8$ of (4.229) is the Fourier transform of $m_+^{-1}M$. The additional factor $(2E)^{-1}$ in (4.190) is taken care of in the transition to the form (4.239). The Fourier transform (4.51) of $-4\pi\alpha_Z/\boldsymbol{q}^2$ gives $V(r)$ as usual. In the second term of (4.265), $\boldsymbol{k}$ is the momentum of the initial state $\psi_{\boldsymbol{k}}(\boldsymbol{r})$; the corresponding operator is $\boldsymbol{p}$. Taken together, I_8 (4.235) results. Note that $V\boldsymbol{p}$ differs from $\boldsymbol{p}V$. The T_{if} in (4.262) arises from $\chi'^{\dagger}m_+^{-1}M\psi$, and $\chi'^{\dagger}\boldsymbol{p} = \chi'^{\dagger}\boldsymbol{k}'$. The final momentum $\boldsymbol{k}'$ has disappeared in (4.264).

For use in the simpler equations (4.251) or (4.252), I_8 must be transformed into I_{81} or I_{82} according to (4.253). Like $\Delta\boldsymbol{\sigma}$, $\boldsymbol{\sigma}_{12}^{\times}$ connects only singlets with triplets. Consequently,

$$C_1\boldsymbol{\sigma}_{12}^{\times}C_1 = \boldsymbol{\sigma}_{12}^{\times}, \quad C_2\boldsymbol{\sigma}_{12}^{\times}C_2 = -\boldsymbol{\sigma}_{12}^{\times} \equiv \boldsymbol{\sigma}_{21}^{\times}. \tag{4.266}$$

In this notation, $I_{81} = I_8$ and I_{82} have identical forms,

$$I_{8i} = EV(r) - i\gamma^5\boldsymbol{\sigma}_{ij}^{\times}V(r)\boldsymbol{p}. \tag{4.267}$$

Division by $2E$ exhibits the equations with the symbols of (4.239),

$$[\epsilon - \mu\beta - V(r) - \gamma^5\boldsymbol{p}\boldsymbol{\sigma}_i + i\gamma^5\boldsymbol{\sigma}_{ij}^{\times}V(r)\boldsymbol{p}/E]\psi_i = 0. \tag{4.268}$$

It is of course unnecessary to solve both equations. The symmetry under the exchange $1 \to 2$ is emphasized here because it is obscured by the notation in equations such as (4.251). As the reduced mass μ does not distinguish between the masses of the two particles; the Pauli matrix $\boldsymbol{\sigma}_i$ in (4.268) can be chosen freely. A continuous transition between ψ_1 and ψ_2 is achieved with the unitary operator

$$U(\alpha) = e^{iP_{\text{spin}}\alpha/2}, \quad U^{\dagger}\boldsymbol{\sigma}U = \boldsymbol{\sigma}, \tag{4.269}$$

$$U^{\dagger}\Delta\boldsymbol{\sigma}U = \cos\alpha\Delta\boldsymbol{\sigma} - \sin\alpha\boldsymbol{\sigma}_{12}^{\times}, \quad U^{\dagger}\boldsymbol{\sigma}_{12}^{\times}U = \cos\alpha\boldsymbol{\sigma}_{12}^{\times} + \sin\alpha\Delta\boldsymbol{\sigma}. \tag{4.270}$$

The last term in (4.268) is the hyperfine operator. For comparison, insertion of (4.153) in the Dirac equation (4.143) gives the static hyperfine operator,

$$\gamma^5\boldsymbol{\sigma}_1 e\boldsymbol{A} = \gamma^5\boldsymbol{\sigma}_1(g_{n2}/2m_p)s_2 \times [\boldsymbol{\nabla}, -e^2/r] = \gamma^5(g_{n2}/2Zm_p)\boldsymbol{\sigma}_1 \times \boldsymbol{s}_2[\nabla, V], \tag{4.271}$$

with $-e^2/r = V/Z$. For the special case $\boldsymbol{s}_2 = \boldsymbol{\sigma}_2/2$, $g_{n2} = 2$, $Z = 1$, the substitution $-[\nabla, V] = 2V\nabla - \{\nabla, V\}$ shows that the static hyperfine operator misses the anti-Hermitian $\{\nabla, V\}$ (the m_p^{-1} represents m_2^{-1}; it is replaced by $E^{-1} \approx (m_1 + m_2)^{-1}$ in the binary case).

The non-Hermitian $V\boldsymbol{p}$ in (4.268) does not lead to complex eigenvalues E. With the choice of phases (2.152) between large and small components, the coupled differential equations for g and f remain real. The kinetic energy operator $\gamma^5\boldsymbol{p}\boldsymbol{\sigma}_1$ is real because the explicit i in front of $f(r)$ makes $i\gamma^5$ real, and because the remaining $i\boldsymbol{\sigma}_1\boldsymbol{p} = \boldsymbol{\sigma}_1\nabla$ is real according to (2.36), where $\boldsymbol{\sigma}_1\boldsymbol{l}$ is real. Writing $\gamma^5\boldsymbol{\sigma}_1 \times \boldsymbol{s}_2 = (-i\gamma^5)(i\boldsymbol{\sigma}_1 \times \boldsymbol{s}_2)$, it remains to show that

$i\boldsymbol{\sigma}_1 \times \boldsymbol{s}_2$ is real. From $[s_{2x}, s_{2y}] = is_{2z}$ etc. and $[s_{1x}, s_{1y}] = is_{1z}$ etc., one obtains

$$i\boldsymbol{s}_1 \times \boldsymbol{s}_2 = [\boldsymbol{s}_2, \boldsymbol{s}_2\boldsymbol{s}_1] = -[\boldsymbol{s}_1, \boldsymbol{s}_2\boldsymbol{s}_1], \tag{4.272}$$

which is a generalization of (2.115) and (2.116). The $\boldsymbol{s}_1\boldsymbol{s}_2$ is obtained from the square of the total spin operator $\boldsymbol{S} = \boldsymbol{s}_1 + \boldsymbol{s}_2$,

$$\boldsymbol{S}^2 = \boldsymbol{s}_1^2 + \boldsymbol{s}_2^2 + 2\boldsymbol{s}_1\boldsymbol{s}_2 = 3/4 + s_2(s_2+1) + 2\boldsymbol{s}_1\boldsymbol{s}_2. \tag{4.273}$$

The resulting $2\boldsymbol{s}_1\boldsymbol{s}_2$ is diagonal in the space $|S, m_S\rangle$ of spin states, with elements s_2 and $-s_2 - 1$ for $S = s_2 \pm 1$, respectively. From the commutator (4.272), one thus obtains

$$\langle S', m'_S | i\boldsymbol{\sigma}_1 \times \boldsymbol{s}_2 | S, m_S\rangle = (S' - S)(s_2 + 1/2)\langle S', m'_S | \boldsymbol{\sigma}_1 | S, m_S\rangle, \tag{4.274}$$

for arbitrary magnetic quantum numbers m_S, m'_S. Equation (4.274) vanishes for $S' = S$, as required for a matrix that is both real and anti-Hermitian. The two coupled equations for g and f are thus real, and the resulting eigenvalues E are also real. The fact that the standard eigenfunctions are complex has a different origin, which was mentioned already in Sect. 1.1 in connection with the eigenfunctions of ∇^2.

The hyperfine operator will be treated later as a perturbation. In first order, only its expectation value enters; its anti-Hermitian part vanishes. At fixed total angular momentum f and orbital angular momentum $l > 0$ of the large components, the anti-Hermitian part mixes $j = l + 1/2$ with $j = l - 1/2$. As $f = j \pm 1/2$, this occurs only for $f = l > 0$. It is particularly important for positronium, where the hyperfine structure is of the same order of magnitude as the fine structure. Details will be given in Sect. 5.2.

The E^2 dependence of (4.268) is verified by the substitution $\boldsymbol{r} = \boldsymbol{\rho}/\mu = E\boldsymbol{r}_E$ as in (4.199). Division by μ gives the dimensionless leptonium equation,

$$(\epsilon/\mu - \beta - V_\rho - \gamma^5 \boldsymbol{p}_{\boldsymbol{\rho}}\boldsymbol{\sigma}_1 + i\gamma^5 \boldsymbol{\sigma}_{12}^{\times} V_\rho \boldsymbol{p}_\rho m_1 m_2/E^2)\psi_1 = 0. \tag{4.275}$$

When the E^{-2} in the last term is approximated by m_{12}^{-2}, one obtains the "chiral hamiltonian" form

$$h\psi = (\epsilon/\mu)\psi, \quad h = \beta + V_\rho + \gamma^5 \boldsymbol{p}_{\boldsymbol{\rho}}\boldsymbol{\sigma}_1 + i\gamma^5 \boldsymbol{\sigma}_{12}^{\times} V_\rho \boldsymbol{p}_\rho m_1 m_2/m_{12}^2, \tag{4.276}$$

where the dimensionless h is energy-independent. In Sect. 5.4, the time-dependent vector potential $\boldsymbol{A}(t)$ will be included in h. Using also $h^\dagger\chi = (\epsilon/\mu)\chi$, one obtains the orthogonality relations

$$\int d^3\rho \chi_j^\dagger \psi_i = \delta_{ij}. \tag{4.277}$$

The nonperturbative inclusion of the exact hyperfine operator (4.275) requires different orthogonality relations (Appendix A). Neglect of the hyperfine operator gives the two-body Dirac-Coulomb equation

$$(\epsilon/\mu-\beta-V_\rho-\gamma^5\boldsymbol{p_\rho}\boldsymbol{\sigma}_1)\psi_{1DC}=0,\quad \epsilon/\mu=(E^2-m_1^2-m_2^2)/2m_1m_2. \tag{4.278}$$

Equation (4.278) applies also to a spinless nucleus, as long as a correction $\alpha_Z^2 m_1^2/E^2$ in (4.371) below is neglected. This correction is smaller than hyperfine shifts, except of course in the limit $m_1/E \to 1$ (Klein-Gordon limit).

The Dirac-Breit equation of Chap. 3 does reproduce the results of (4.268), at least to the order α_Z^4. How is this possible, when it includes retardation and in its eightcomponent version (3.190) also the combination $\pi^{02} = E^2 - 2EV + V^2$, after the statement at the beginning of Sect. 4.6 that the V^2 must be dropped? The stunning answer is that the r in the two equations cover slightly different ranges. Denoting the r of the Dirac-Breit equation by r_{12}, its operator V_{12}^2 is eliminated by (3.214),

$$(E+\alpha_Z/r_{12})^2 = E^2 + 2E\alpha_Z/r. \tag{4.279}$$

With the approximation $E \approx m_{12} = m_1 + m_2$, this relation was found by Schwinger (1973). The equivalence of the two formulations will be demonstrated in Sect. 4.9.

The exact solutions of the Dirac-Coulomb equation (4.278) follow again most easily from its Kramers form as in (2.135), where the lefthanded components are eliminated:

$$(\epsilon^2/\mu^2-1-2V_\rho\epsilon/\mu+V_\rho^2+\nabla_\rho^2+i[\sigma_1\nabla_\rho,V_\rho])\psi_r=0,\quad V_\rho=-\alpha_Z/\rho, \tag{4.280}$$

with $\epsilon^2/\mu^2-1=k^2/\mu^2$. The equation differs from (2.135) only by notation. Its eigenvalues E^2 follow again from (4.206), with the effective principal quantum number n_β of the Dirac equation,

$$\epsilon/\mu=(1+\alpha_Z^2/n_\beta^2)^{-1/2},\quad n_\beta=n-\beta_j=n+\gamma-j-\tfrac{1}{2}. \tag{4.281}$$

Expansion of the square roots contained in f and $\gamma=\sqrt{(j+1/2)^2-\alpha_Z^2}$ gives to order α_Z^6 the already familiar result (2.149), this time for $\epsilon/\mu-1$. A final expansion for E according to (4.207) contains terms that had previously been calculated only by NRQED.

Again, the levels with $n=j+\frac{1}{2}=l+1$ have $n_\beta=\gamma$, and

$$(1+\alpha^2/n_\beta^2)^{-1/2}=\gamma/n,\quad E^2-m_1^2-m_2^2=2m_1m_2\gamma/n. \tag{4.282}$$

The nonrelativistic reduction of (4.278) follows the procedure of Sect. 2.8; one merely has to replace m by μ. The spin-orbit potential is now denoted by V_{s1l},

$$V_{s1l}=\hbar^2\hat{\boldsymbol{l}}\boldsymbol{\sigma}_1V'/4\mu^2c^2r. \tag{4.283}$$

It shows again that $\boldsymbol{\sigma}_1$ must not be interpreted as the spin operator of particle 1. Its l-dependence to order α_Z^4 is cancelled as in (2.273), as required by the parity degeneracy of the Dirac energy levels. This is in contrast to

$H_{\rm CBG}$, where both spin-orbit potentials (3.163) are needed for parity degeneracy. Setting $\boldsymbol{\sigma}_2 = 0$ in the CBG formalism implies a spinless nucleus, which will be confirmed in Sect. 4.9 below. Comments on the adjustment of the leptonium interaction to atomic hydrogen will be added in Sects. 5.6 and 5.7.

The charge conjugation of ψ_{D2} is the direct product of two single-fermion transformations (3.51), $\psi_{D2,C} = \beta_1\beta_2\gamma_1^5\gamma_2^5 U_{C1}U_{C2}\psi^*_{D2}$. The eight components ψ of ψ_D have $\beta_1\beta_2 = \beta$ and $\gamma_1^5\gamma_2^5 = 1$, which simplifies the transformation to

$$\psi_C = \beta U_{C1}U_{C2}\psi^*, \quad U_{Ci} = -i\sigma_{i,y}. \tag{4.284}$$

As in (3.48), one has

$$\boldsymbol{\sigma}_1^* = -U_{C1}^\dagger \boldsymbol{\sigma}_1 U_{C1}, \quad (i\boldsymbol{\sigma}^\times)^* = -U_{C1}^\dagger U_{C2}^\dagger i\boldsymbol{\sigma}^\times U_{C1}U_{C2}. \tag{4.285}$$

The eigenvalue E of $i\partial_{t1} + i\partial_{t2} \equiv i\partial_t$ is charge conjugated to $-E$, but as (4.275) depends explicitly only on E^2, no γ^5-transformation is required for a sign change. For $A^\mu = 0$, ψ and ψ_C satisfy the same equation. States with total magnetic quantum number $m_f = 0$ have $\psi^* = \beta\psi$, see (2.152) and (5.8) below. The CP and CPT transformations of ψ follow from (3.52) and (3.55) as

$$\psi_{CP}(\boldsymbol{r}) = U_{C1}U_{C2}\psi^*(-\boldsymbol{r}), \quad \psi_{CPT}(x^\mu) = \psi(-x^\mu). \tag{4.286}$$

In the static limit $m_1 \ll m_2$, $V(r)$ becomes an external potential, as explained in Sect. 3.2. The $e^-\mu^+$ system is then charge conjugated into $e^+\mu^+$ which has no bound states. But with the slightest recoil, the muon becomes a part of the dynamical system and must also be charge conjugated. The static limit has $E_2 = m_2$, $E = m_2 + E_1$. One can charge conjugate a whole atom of electronic energy $E_{\rm electrons}$, provided one extracts $-m_2$ in the case of negative E:

$$E_{\rm stat} = m_2 {\rm sign}(E) + E_{\rm electrons}. \tag{4.287}$$

Eigenstates of charge conjugation exist for all (neutral) atoms, but they are presently needed only for positronium. They are generated by $a_1^\dagger b_2^\dagger|0\rangle$, where $b_2^\dagger$ (3.45) creates the positron which is particle 2. This product is charge conjugated into $b_1^\dagger a_2^\dagger|0\rangle = -a_2^\dagger b_1^\dagger|0\rangle$, where the minus sign comes from the anticommutator. The latter sequence is the permutation P_{12} (3.188) of the original one, with the eigenvalues

$$P_{12}\psi = (-1)^{l+s+1}\psi, \tag{4.288}$$

l and s being the orbital angular momentum and spin of the large components. The small components have $\tilde{l} = l \pm 1$, $\tilde{s} \neq s$, such that ψ_C (4.284) gets the same phase for both values of β. This phase is $-P_{12} = (-1)^{l+s}$. It is $+1$ for the singlet ground state of positronium, which has $l = s = 0$.

From the definition (3.39) of C, a state of n photons has $C = (-1)^n$. By C-conservation, the above singlet ("para-positronium") decays into two photons. The triplet decays into three photons.Energy-momentum conser-

vation excludes the decay into a single photon, but the virtual one-photon intermediate state in electron-positron scattering produces an energy shift,

$$\Delta E_{1\gamma} = \tfrac{1}{2}\delta_{l,0}\delta_{s,1}\mu\alpha^4 n^{-3}, \quad \mu = m_e/2.$$

Outside QED, one uses differential equations with other potentials, for example meson-exchange potentials in nucleon-nucleon scattering. There, the potential of longest range comes from the exchange of a pion, which is spinless and has negative parity. It requires a factor γ_i^5 (pseudoscalar coupling) or $\gamma_i^5\gamma_i^\mu P_{i,\mu}$ (pseudovector coupling) at each vertex i. The resulting matrix M (4.263) has a nonvanishing coefficient of $m_+\gamma^5\boldsymbol{\sigma}\boldsymbol{k}'/m_+$ and thus contains a term with m_-/m_+. The same is true for the exchange of a scalar meson, which is often taken as an approximation for two-pion exchange. On the other hand, the anomalous magnetic moment couplings (Sect. 5.7) are again free from m_-/m_+. This shows that in the eight-component formalism, the QED interaction is privileged.

4.9 Binary Boosts

Here we discuss the transformation of the binary equation from the lab system to the "cms", where the total momentum vanishes. It is rarely needed in practice.

It is helpful to first recall the solution of the nonrelativistic binary Schrödinger equation in the lab system. The Hamiltonian (3.126) for $V_{\rm tot} = V_{12} \equiv V(r)$,

$$H_{nr} = \boldsymbol{p}_1^2/2m_1 + \boldsymbol{p}_2^2/2m_2 + V(r) \tag{4.289}$$

commutes with the generator of translations

$$\boldsymbol{P} = \boldsymbol{p}_1 + \boldsymbol{p}_2 = -i\hbar\boldsymbol{\nabla}_R. \tag{4.290}$$

With $r = \sqrt{(\boldsymbol{r}_1 - \boldsymbol{r}_2)^2}$, the following transformation of gradients is appropriate:

$$\boldsymbol{p}_1 = \boldsymbol{p}_{\rm lab} + c_1\boldsymbol{P}, \quad \boldsymbol{p}_2 = -\boldsymbol{p}_{\rm lab} + c_2\boldsymbol{P}, \quad c_1 + c_2 = 1. \tag{4.291}$$

The corresponding coordinate transformation is

$$\boldsymbol{r}_1 = \boldsymbol{R} + c_2\boldsymbol{r}_{\rm lab}, \quad \boldsymbol{r}_2 = \boldsymbol{R} - c_1\boldsymbol{r}_{\rm lab} \quad \boldsymbol{r}_{\rm lab} = \boldsymbol{r}_1 - \boldsymbol{r}_2. \tag{4.292}$$

The index "lab" is needed for the relativistic case, where $\boldsymbol{r}_{\rm lab}$ is Lorentz contracted along $\boldsymbol{P}$. The transformed Hamiltonian is

$$H_{nr} = \boldsymbol{p}_{\rm lab}^2/2\mu_{nr} + \boldsymbol{P}\boldsymbol{p}_{\rm lab}(c_1/m_1 - c_2/m_2) + \tfrac{1}{2}(c_1^2/m_1 + c_2^2/m_2)\boldsymbol{P}^2 + V(r), \tag{4.293}$$

$$1/\mu_{nr} = 1/m_1 + 1/m_2, \quad \mu_{nr} = m_1m_2/m_{12}, \quad m_{12} = m_1 + m_2. \tag{4.294}$$

The coupling operator $\boldsymbol{P}\boldsymbol{p}_{\rm lab}$ is removed by taking

$$c_1 = m_1/m_{12}, \quad c_2 = m_2/m_{12}. \tag{4.295}$$

$$H_{nr} = \boldsymbol{p}_{\rm lab}^2/2\mu_{nr} + V(r) + \boldsymbol{P}^2/2m_{12}. \tag{4.296}$$

H_{nr} is now the sum of two commuting operators, such that the Schrödinger equation $i\hbar\partial_t\psi_S = H_{nr}\psi_S$ has factorizing solutions,

$$\psi_S = e^{i\boldsymbol{K}\boldsymbol{R}}\psi_{\rm cms}(\boldsymbol{r}), \quad \boldsymbol{P}\psi_S = \hbar\boldsymbol{K}\psi_S. \tag{4.297}$$

The cms wave function $\psi_{\rm cms}(\boldsymbol{r})$ satisfies a Schrödinger equation for a fictitious particle of mass μ_{nr} with a cms energy operator,

$$(i\hbar\partial_t - \hbar^2\boldsymbol{K}^2/2m_{12})\psi_{\rm cms} = H_{\rm cms}\psi_{\rm cms}, \quad H_{\rm cms} = \boldsymbol{p}_{\rm lab}^2/2\mu_{nr} + V. \tag{4.298}$$

For an eigenvalue E of (4.298), the eigenvalue of the original energy operator is

$$E_{\rm lab} = E + \hbar^2\boldsymbol{K}^2/2m_{12}. \tag{4.299}$$

The coordinate transformation (4.292), (4.295) is of course known from classical nonrelativistic mechanics. It is repeated here on the quantum level because the corresponding relativistic transformation gives slightly different coefficients c_1 and c_2. There is however a shortcut derivation which avoids the coordinate transformation. One simply assumes translational invariance in space and time, which implies stationary solutions of the form

$$\psi_{\rm lab} = e^{-iK_\mu X^\mu}\psi(\boldsymbol{r}), \quad P^\mu\psi_{\rm lab} = \hbar K^\mu\psi_{\rm lab}(\boldsymbol{r}), \tag{4.300}$$

leaving $\boldsymbol{R}$ unspecified. One then solves the binary equation only for $\boldsymbol{K} = 0$, which is equivalent to setting $\boldsymbol{p}_1 = -\boldsymbol{p}_2 \equiv \boldsymbol{p}$ from the very beginning. This specifies the "center-of-momentum" system; the "center-of-mass" system is only known when $\boldsymbol{R}$ is explicitly given. However, one normally ignores this logical difference and abbreviates both systems as "cms". In the following, the index $_{\rm cms}$ will be omitted whenever possible. Where a distiction is necessary, the index $_{\rm lab}$ will be used for the laboratory system. In a final step, one calculates $E_{\rm lab}$ from the assumed Lorentz invariance of $K^\mu K_\mu$ $(= s = E^2)$,

$$E_{\rm lab} = \hbar cK^0 = \sqrt{E^2 + \hbar^2c^2\boldsymbol{K}^2}. \tag{4.301}$$

In the derivation of (4.299), a separate assumption of "Galilei invariance" was unnecessary.

In the relativistic case, one may use the single-time formalism of Sect. 3.3, which operates with two quantum fields $\Psi_a(\boldsymbol{r}_1, t)$, $\Psi_b(\boldsymbol{r}_2, t)$ at a common time t (Malvetti and Pilkuhn 1994). Field commutators at different times are more complicated.

For the verification of Lorentz invariance, the 8-component equation (3.218) is again convenient. We set

$$\pi^0 = K^0, \ \pi_\pm = p_\pm = \boldsymbol{p}_1\boldsymbol{\sigma}_1 \pm \boldsymbol{p}_2\boldsymbol{\sigma}_2, \tag{4.302}$$

where $\boldsymbol{p}_1$ and $\boldsymbol{p}_2$ refer to the lab system. The lab interaction $I_{\rm lab}$ is independent of $\boldsymbol{R}$ but otherwise unspecified:

$$(K^{02} - m_+^2 + p_- p_+ m_+/m_- - \gamma^5 K^0(p_+ + p_- m_-/m_+) - I_{\rm lab}(\boldsymbol{r}_{\rm lab}))\psi_{\rm lab} = 0. \tag{4.303}$$

It will be seen that $I_{\rm lab}$ depends both on $\boldsymbol{K}^2$ and on $\boldsymbol{r}_{\rm lab}\boldsymbol{K}$. The Dirac-Breit equation (3.112) avoids this complication, but it is not strictly Lorentz invariant. This is already evident from the approximation $q^0 = 0$ in (4.221). The merit of the DB-equation is that operators for external potentials are easily added, such that the equation is not restricted to closed systems. For (4.303), this is not yet the case; $I_{\rm lab}$ is constructed from the postulate of Lorentz invariance. Superficially, this looks like a defect of relativistic quantum mechanics as compared with relativistic quantum field theory, but one should remember that the interaction between quantum fields has also been constructed using Lorentz invariance among the postulates. In classical mechanics, the filling of a cup with coffee in a moving train also assumes Galilei invariance. Complications arise only when the train brakes.

The verification of Lorentz invariance of the remaining operators in (4.303) is instructive, but it is rarely needed. As emphasized in Sect. 4.5, the atomic spectrum is always calculated in the atomic rest frame, for which the coordinate transformation is unnecessary. If one really needs the radiation from a moving atom, one assumes the relation $K^0 = (E^2 + \boldsymbol{K}^2)^{1/2}$. In a second step, one then calculates the Doppler shifted radiation for a "Lorentz factor" $\gamma = K^0/E$. In a more careful treatment, one may use both $\gamma = K^0/E$ and $\gamma' = K^0/E'$, where $E' < E$ is the cms energy of the atomic final state, as explained in Sect. 4.2. In any case, explicit coordinate transformations are not needed for a calculation of the lab radiation spectrum. It must also be pointed out that a direct application of (4.303) is excluded for $m_1 = m_2$. A more direct approach on the basis of ideas explained in Sect. 4.10 below is not excluded.

Turning now to the Lorentz invariance of (4.303), one could in a first step insert $K^{02} \equiv E^2 + \boldsymbol{P}^2$, thus getting in the first two terms of (4.303) the combination $E^2 - m_+^2$ required by the cms equation (4.229). However, if c_1 and c_2 in (4.291) are to be free from Dirac operators, there is nothing in (4.303) that could cancel the $\boldsymbol{P}^2$. The only alternative is to let p_+p_- contain a piece $m_+m_-\boldsymbol{P}^2$ and then to combine $m_+^2\boldsymbol{P}^2$ with m_+^2. From (4.302),

$$p_-p_+ = p_1^2 - p_2^2 = (\boldsymbol{p}_1 - \boldsymbol{p}_2)\boldsymbol{P} = 2\boldsymbol{p}_{\rm lab}\boldsymbol{P} + (c_1 - c_2)\boldsymbol{P}^2, \tag{4.304}$$

one sees that $c_1 - c_2$ must be proportional to $m_+m_- = m_2^2 - m_1^2$. Using now $K^0 = \gamma E$, the desired cms combination is achieved in the form $\gamma^2(E^2 - m_+^2)$ for

$$c_1 - c_2 = -m_+m_-/E^2. \tag{4.305}$$

With that choice namely,

$$m_+^2 - (c_1 - c_2)\boldsymbol{P}^2 m_+/m_- = m_+^2(1 + \boldsymbol{P}^2/E^2) = m_+^2\gamma^2. \tag{4.306}$$

The separate values of c_1 and c_2 follow from $c_1 + c_2 = 1$:

$$c_1 = \tfrac{1}{2} - m_+m_-/2E^2 = E_1/E, \quad c_2 = \tfrac{1}{2} + m_+m_-/2E^2 = E_2/E. \quad (4.307)$$

For E near m_{12}, these values are close to the nonrelativistic ones (4.295).

The appearance of E^2 makes the coordinate transformation (4.292) state dependent. Already the approximation $E^2 \approx m_{12}^2 - m_1m_2\alpha_Z^2/n^2$ requires different coordinates for different values of n. It is then important to keep E fixed. In radiative decays E is the total cms energy before decay, see (5.160).

After the coordinate transformation, (4.303) becomes

$$\Big[K^{0\,2} - m_+^2(1 + \boldsymbol{P}^2/E^2) + 2\boldsymbol{P}\boldsymbol{p}_{\rm lab}m_+/m_- - \gamma^5\gamma E(p_+ + p_-m_-/m_+) - I_{\rm lab}\Big] \times \psi_{\rm lab} = 0, \quad (4.308)$$

$$p_+ \equiv (\boldsymbol{p}_{\rm lab} - \boldsymbol{P}m_+m_-/2E^2)\boldsymbol{\Delta\sigma} + \tfrac{1}{2}\boldsymbol{P}\boldsymbol{\sigma},$$
$$p_- \equiv (\boldsymbol{p}_{\rm lab} - \boldsymbol{P}m_+m_-/2E^2)\boldsymbol{\sigma} + \tfrac{1}{2}\boldsymbol{P}\boldsymbol{\Delta\sigma}. \quad (4.309)$$

Next, we use the ansatz (4.300), which reduces the bracket in (4.308) to γ^2. It is further simplified by taking the z-axis along $\boldsymbol{K}$,

$$\boldsymbol{K}\boldsymbol{p}_{\rm lab} = Kp_{z,\rm lab}. \quad (4.310)$$

To simplify the factors of γ^5, one γ is divided off. The resulting operator is called $\mathcal{K}_{\rm lab}$,

$$\mathcal{K}_{\rm lab}\psi_{\rm lab} = 0, \quad \mathcal{K}_{\rm lab} = \gamma(E^2 - m_+^2) + 2Kp_{z,\rm lab}m_+/\gamma m_- - \gamma^5 E\tilde{p} - I_{\rm lab}/\gamma. \quad (4.311)$$

$$\tilde{p} \equiv p_+ + p_-\frac{m_-}{m_+} = \left(\boldsymbol{p}_{\rm lab} - \boldsymbol{K}\frac{m_+m_-}{2E^2}\right)\left(\boldsymbol{\Delta\sigma} + \boldsymbol{\sigma}\frac{m_-}{m_+}\right) + \tfrac{1}{2}K\left(\sigma_z + \Delta\sigma_z\frac{m_-}{m_+}\right). \quad (4.312)$$

$$\gamma^5\tilde{p} = \gamma^5\boldsymbol{p}_{\rm lab}\left(\boldsymbol{\Delta\sigma} + \boldsymbol{\sigma}\frac{m_-}{m_+}\right) + \tfrac{1}{2}KE^{-2}\left[(E^2 - m_+^2)\gamma^5\sigma_z + (E^2 - m_-^2)\gamma^5\Delta\sigma_z\frac{m_-}{m_+}\right]. \quad (4.313)$$

Several problems remain: Firstly, one must find a transformation,

$$\psi_{\rm lab}(\boldsymbol{r}) = A_v(\boldsymbol{K})\psi(\boldsymbol{r}), \quad (4.314)$$

which transforms (4.311) into (4.229),

$$\mathcal{K}\psi = 0, \quad \mathcal{K} = E^2 - m_+^2 - \gamma^5 E\boldsymbol{p}(\boldsymbol{\Delta\sigma} + \boldsymbol{\sigma}m_-/m_+) - I_8. \quad (4.315)$$

Secondly, one must relate $\boldsymbol{p}_{\rm lab} = -i\nabla_{\rm lab}$ to $\boldsymbol{p} = -i\nabla$. This relation is anticipated here:

$$p_{z,\rm lab} = \gamma p_z, \quad p_{x,\rm lab} = p_x, \;\; p_{y,\rm lab} = p_y. \quad (4.316)$$

It is plausible from (4.311), because it simplifies $p_{z,\rm lab}/\gamma = p_z$.

The operator A_v may be adopted from a Lorentz transformation of the free-particle spinor v of ψ. It is the direct product of two single-particle transformations analogous to (2.336), but with the γ (2.335) of the particle boosts replaced by the γ for the Lorentz transformation from the cms to the lab system:

$$\cosh\eta_b = \gamma = K^0/E, \quad \sinh\eta_b = K/E \equiv \hat{K}, \quad \gamma^2 - \hat{K}^2 = 1. \tag{4.317}$$

Using $\gamma_1^5 v = \gamma_2^5 v = \gamma^5 v$,

$$A_v = (\gamma + \gamma^5\sigma_{1z}\hat{K})^{1/2}(\gamma + \gamma^5\sigma_{2z}\hat{K})^{1/2}. \tag{4.318}$$

In analogy with a single-particle boost from its rest system, it is the boost of the binary from its own rest system, in which E plays the role of the mass. Here we shall go in the opposite direction,

$$\psi = A_v^{-1}\psi_{\rm lab}, \quad A_v^{-1} = (\gamma - \gamma^5\sigma_{1z}\hat{K})^{1/2}(\gamma - \gamma^5\sigma_{2z}\hat{K})^{1/2}. \tag{4.319}$$

As always, the inverse boost A_v^{-1} has $\boldsymbol{K}$ replaced by $-\boldsymbol{K}$, or equivalently γ^5 by $-\gamma^5$. One may also combine the factors of A_v^{-1} under one square root,

$$A_v^{-1} = (1 - \hat{K}\gamma\gamma^5\sigma_z + \tfrac{1}{2}\hat{K}^2\sigma_z^2)^{1/2}, \tag{4.320}$$

using $\sigma_{1z}\sigma_{2z} = \sigma_z^2/2 - 1$. However, $\mathcal{K}\psi = 0$ and $\mathcal{K}A_v^{-1}\psi_{\rm lab} = 0$ do not imply $\mathcal{K}_{\rm lab} = \mathcal{K}A_v^{-1}$. Finally, one must find another matrix $A'_w(\boldsymbol{K})$ which achieves

$$\mathcal{K}_{\rm lab} = {A'_w}^{-1}\mathcal{K}A_v^{-1}. \tag{4.321}$$

In the corresponding single-particle case, the lab operator $\pi_\mu\sigma^\mu$ (2.94) could be expressed in terms of the cms operator $\pi'_\mu\sigma^\mu$ by means of (2.96), $\pi_\mu\sigma^\mu = SH\pi'_\mu\sigma^\mu SH$, and it was checked explicitly that the matrix to the left of $\pi'_\mu\sigma^\mu$ had to be the same as the one to the right, and not its inverse, for example. In the case at hand, the choice

$${A'_w}^{-1} = (1 - \hat{K}\gamma\gamma^5\Delta\sigma_z m_-/m_+ + \tfrac{1}{2}\hat{K}^2\Delta\sigma_z^2)^{1/2} \tag{4.322}$$

is successful. With $\sigma_z\Delta\sigma_z = 0$ and $(\sigma_z^2 + \Delta\sigma_z^2)/2 = 2 = 1 + (\sigma_z^2 + \Delta\sigma_z^2)/4$, it leads to

$${A'_w}^{-1}A_v^{-1} = \gamma - \tfrac{1}{2}\hat{K}\gamma^5(\sigma_z + \Delta\sigma_z m_-/m_+), \tag{4.323}$$

$${A'_w}^{-1}\beta A_v^{-1} = \beta A'_w A_v^{-1} = \beta[\gamma - \tfrac{1}{2}\hat{K}\gamma^5(\sigma_z - \Delta\sigma_z m_-/m_+)]. \tag{4.324}$$

It gives

$${A'_w}^{-1}(E^2 - m_+^2)A_v^{-1} = (E^2 - m_+^2)(\gamma - \tfrac{1}{2}\hat{K}\gamma^5\sigma_z) - (E^2 - m_-^2)\tfrac{1}{2}\hat{K}\gamma^5\Delta\sigma_z\frac{m_-}{m_+}. \tag{4.325}$$

The first product of (4.325) leads thus directly to terms of $\mathcal{K}_{\rm lab}$. For the remaining terms, one must observe that A commutes with σ_z and $\Delta\sigma_z$, while σ_{iz} anticommutes with σ_{ix} and σ_{iy}. A_v and A'_w may also be written without square roots, analogous to the single-particle boost (2.347):

$$A_v = \gamma + \tfrac{1}{2}\hat{K}\gamma^5\sigma_z - \tfrac{1}{2}\hat{K}^2\Delta\sigma_z^2/(2\gamma+2), \tag{4.326}$$

$$A'_w = \gamma + \tfrac{1}{2}\hat{K}\gamma^5\Delta\sigma_z m_-/m_+ - \tfrac{1}{2}\hat{K}^2\sigma_z^2/(2\gamma+2). \tag{4.327}$$

In checking these expressions by squaring, one uses $(\Delta\sigma_z)^4 = 4(\Delta\sigma_z)^2$, and $\hat{K}^4 = \hat{K}^2(\gamma^2-1)$. Having checked all this, one may of course try to find a more elegant derivation of A'_w:

$$A'_w = m_+ A_w/m_+, \tag{4.328}$$

$$A_w = (1+\hat{K}\gamma\gamma^5\Delta\sigma_z+\tfrac{1}{2}\Delta\sigma_z^2)^{1/2} = (\gamma+\gamma^5\sigma_{1z}\hat{K})^{1/2}(\gamma-\gamma^5\sigma_{2z}\hat{K})^{1/2}. \tag{4.329}$$

A_w is the boost for the free-particle spinor w of χ, it differs from A_v only by a change of sign of $\gamma^5\sigma_{2z}$, because of $\gamma_2^5 w = -\gamma^5 w$. The extra transformation with m_+ in (4.328) arises from the multiplication of the original equation (4.228) by m_+.

The more elegant forms (4.251) and (4.252) of the cms equation may also be boosted, of course. For (4.251),

$$\psi = C_1\psi_1, \quad \mathcal{K}_{\rm lab}\psi_{\rm lab} = \mathcal{K}_{\rm lab}A_v\psi = \mathcal{K}_{\rm lab}A_vC_1\psi_1 = 0, \tag{4.330}$$

one may write

$$\mathcal{K}_{\rm lab}\psi_{\rm lab} = \mathcal{K}_{\rm lab}C_1A_{v1}\psi_1, \quad A_{v1} = C_1^{-1}A_vC_1. \tag{4.331}$$

Multiplication by C_1^{-1} gives

$$\mathcal{K}_{\rm lab1}\psi_{\rm lab1} = 0, \quad \mathcal{K}_{\rm lab1} = C_1^{-1}\mathcal{K}_{\rm lab}C_1, \quad \psi_{\rm lab1} = A_{v1}\psi_1. \tag{4.332}$$

Thus ψ_1 is boosted with A_{v1}. Here it is useful to combine m_+/m_- with γ^5 into a matrix $\gamma^{5\prime}$:

$$\gamma^{5\prime} = \gamma_5 m_+/m_- = (m_-/m_+)^{1/2}\gamma^5(m_+/m_-)^{1/2}. \tag{4.333}$$

The last expression is mentioned merely to show that $\gamma^{5\prime}$ is diagonalized by a similarity transformation $V\gamma^5V^{-1}$ as in (2.170), with $V = (m_-/m_+)^{1/2} = V^\dagger$. Only the last two terms of $\mathcal{K}_L$ in (4.311) are changed by C_1:

$$C_1^{-1}\gamma^5\tilde{p}C_1 = 2\gamma^5\boldsymbol{p}_{\rm lab}\boldsymbol{\sigma}_1 + \tfrac{1}{2}KE^{-2}[(E^2-m_+^2)\gamma^{5\prime} + (E^2-m_-^2)\gamma^{5\prime\dagger}]\Delta\sigma_z, \tag{4.334}$$

which is again hermitian. The inverse boosts are

$$A_{v1}^{-1} = (1-\hat{K}\gamma\gamma^{5\prime}\sigma_z+\tfrac{1}{2}\hat{K}^2\sigma_z^2)^{1/2} = \gamma - \tfrac{1}{2}\hat{K}\gamma^{5\prime}\sigma_z - \tfrac{1}{2}\hat{K}^2\Delta\sigma_z^2/(2\gamma+2), \tag{4.335}$$

$$A'_{w1}{}^{-1} = (1-\hat{K}\gamma\gamma^{5\prime}\Delta\sigma_z+\tfrac{1}{2}\hat{K}^2\Delta\sigma_z^2)^{1/2} = \gamma - \tfrac{1}{2}\hat{K}\gamma^{5\prime\dagger}\Delta\sigma_z - \tfrac{1}{2}\hat{K}^2\sigma_z^2/(2\gamma+2), \tag{4.336}$$

The bilinear forms (4.323) and (4.324) become

$$A'_{w1}{}^{-1}A_{v1}^{-1} = \gamma - \tfrac{1}{2}\hat{K}(\gamma^{5\prime}\sigma_z + \gamma^{5\prime\dagger}\Delta\sigma_z), \tag{4.337}$$

$$A'_{w1}{}^{-1}\beta A_{v1}^{-1} = \beta[\gamma - \tfrac{1}{2}\hat{K}(\gamma^{5\prime}\sigma_z - \gamma^{5\prime\dagger}\Delta\sigma_z)]. \tag{4.338}$$

For the boost of the interaction, we take immediately the basis ψ_1. The Coulomb part $2EV$ is the same in I_8 and I_{81}; it is boosted with (4.337). The resulting $I^{(V)}_{\rm lab1}/\gamma$ of (4.311) is

$$I^{(V)}_{\rm lab1}/\gamma = {A'_{w1}}^{-1} 2EV A_{v1}^{-1} = 2K^0 V[1 - \tfrac{1}{2}K(\gamma^{5\prime}\sigma_z + \gamma^{5\prime\dagger}\Delta\sigma_z)/K^0]. \quad (4.339)$$

Here we have extracted a factor γ from (4.337) because this replaces EV by $E\gamma V = K^0 V$ appropriate for the lab system. However, also the appearance of V itself is modified. The transformation (4.316) of the gradient components requires the coordinate transformation

$$z_{\rm lab} = z/\gamma, \quad x_{\rm lab} = x, \quad y_{\rm lab} = y. \quad (4.340)$$

It corresponds to the "Lorentz contraction" along the direction of motion in classical special relativity. The result is

$$V = -\alpha_Z (x^2 + y^2 + z^2)^{-1/2} = -\alpha_Z (x^2 + y^2 + \gamma^2 z^2_{\rm lab})^{-1/2}. \quad (4.341)$$

The factor γ in front of $z_{\rm lab}$ compensates the Lorentz contraction, such that the Coulomb potential is isotropic in the cms. But the proper lab equation (4.303) contains $I^{(V)}_{\rm lab}$ and not $I^{(V)}_{\rm lab}/\gamma$, such that a second factor γ appears in front of V:

$$\gamma V = -\alpha_Z [(x^2 + y^2)/\gamma^2 + z^2_{\rm lab}]^{-1/2}. \quad (4.342)$$

Also this expression has an analogy in classical relativity: The field generated by a moving charge becomes increasingly transverse with increasing γ. Its analogy in quantum mechanics is known as the "Weizsäcker-Williams" approximation (Pilkuhn 1979).

When a binary is treated as a single particle, the spin $\boldsymbol{S}$ of that particle equals the total angular momentum $\boldsymbol{f} = \hat{\boldsymbol{l}} + \boldsymbol{s}_1 + \boldsymbol{s}_2$ in the cms. Setting $S_z = f_z$ in the particle boosts (4.183) to (4.185) ignores the binary structure. Nevertheless, for $\hat{l}_z = 0$, these boosts do agree with A_v (4.318) or (4.320),

$$A_v = [1 + K^0 \gamma^5 \boldsymbol{K}\boldsymbol{\sigma}/E^2 + \tfrac{1}{2}(\boldsymbol{K}\boldsymbol{\sigma}/E)^2]^{1/2}, \quad (4.343)$$

after the replacements $m \to E$ and $\boldsymbol{k}\boldsymbol{S} \to \boldsymbol{K}\boldsymbol{\sigma}/2$.

4.10 Klein-Dirac Equation, Hydrogen

Bound states of two spinless and two spinor particles have been discussed in Sects. 4.5 and 4.6, respectively. For the asymmetric combination of one spinor and one spinless particle, we now derive the "Klein-Dirac" equation. It reduces to the single-particle Dirac equation in the limit $m_1 \ll m_2$ and to the single-particle KG equation in the opposite limit $m_1 \gg m_2$. An example with $m_1 \approx m_2$ is $\mu^-\pi^+$ and $\mu^+\pi^-$, but the experimental information on this

"pi-muonium" (which appears as a by-product in $K^0 \to \pi\mu\nu$ decays) is still poor. Precision data are available for muonic helium $\mu^-\,{}^4\mathrm{He}$, where the ${}^4\mathrm{He}$ nucleus is the spinless alpha-particle. However, this example is already close to $m_1 \ll m_2$ and is normally treated by the Dirac equation with first-order recoil corrections. Spinless particles are discussed here mainly for a better understanding of the Todorov equation (4.189), and for checking the disappearance of retardation operators. We shall also mention the approximate "Grotch-Yennie" equation (which is a Dirac equation with shifted parameters) and the "original" Klein-Dirac equation (Pilkuhn 1984), which should really be called "Klein-Kramers" equation, because it has no Dirac form.

Two-body equations must contain ∂_{t1} and ∂_{t2} in the combination $\partial_{t1}+\partial_{t2}$, which is the total time shifting operator. The KG equation (1.66) for particle 2 is quadratic in $\pi_2^0 = i\partial_{t2} - q_2 A_2^0$. In applications to few-body systems, it must be linearized in π_2^0. One defines a "secondary field" $\Psi_s = \pi_2^0\Psi$ and expresses $\pi_2^{02}\Psi$ as $\pi_2^0\Psi_s$. The field equation is then a pair of two linear equations, their Hamiltonian form is (Malvetti and Pilkuhn 1994)

$$\Psi_H = \begin{pmatrix} \Psi \\ \Psi_s \end{pmatrix}, \quad H_2\Psi_H = i\partial_{t2}\Psi_H, \quad H_2 = \begin{pmatrix} q_2 A_2^0 & 1 \\ K_2 & q_2 A_2^0 \end{pmatrix}, \tag{4.344}$$

$$\Psi_s = \pi_2^0\Psi, \quad K_2 = m_2^2 + \pi_2^2. \tag{4.345}$$

A more complicated linearization has been proposed by Feshbach and Villars (1958), with large and small components as in the parity basis of the Dirac equation. However, the Dirac analogy does not help, as the KG operator does not factorize, unlike the Kramers operator (2.80). The scalar product is taken from the zero-component j^0 of the conserved vector current j^μ, as explained in Sect. 2.2. The index $_2$ is suppressed in the following formulas. With $j^0 = \Psi^\dagger\pi^0\Psi + \Psi\pi^{0*}\Psi^\dagger$ according to (2.27),

$$j^0 = \Psi^\dagger\Psi_s + \Psi_s^\dagger\Psi = \Psi_H^\dagger g\Psi_H, \quad g = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}. \tag{4.346}$$

In this notation, the scalar product of two single-particle states $|i\rangle$ and $|j\rangle$ becomes

$$\langle j|i\rangle = \int \Psi_{Hj}^\dagger g\psi_{Hi}. \tag{4.347}$$

The matrix g plays the role of a metric in the scalar product; it is necessary for hermiticity, $\langle i|j\rangle^* = \langle j|i\rangle$. Equation (4.347) is identical with the spinless scalar product that was already derived in (1.198).

The field commutators follow again from (3.88), where H_{scalar} is constructed such that it leads to the the KG equation in the form (4.344),

$$H_{\mathrm{scalar}} = \int d^3r'(\Psi_s^\dagger\Psi_s + \Psi^\dagger K_2\Psi), \tag{4.348}$$

$$[\Psi_s(\boldsymbol{r}'), \Psi^\dagger(\boldsymbol{r})] = [\Psi(\boldsymbol{r}), \Psi_s^\dagger(\boldsymbol{r}')] = \delta(\boldsymbol{r} - \boldsymbol{r}'). \tag{4.349}$$

The bound state wave function for particles 1 and 2 is now assumed as in (3.82),

$$\psi_{H12} = \langle 0|\Psi_D(\boldsymbol{r}_1)\Psi_H(\boldsymbol{r}_2)|12\rangle = \langle 0|\Psi_1\Psi_H|12\rangle. \tag{4.350}$$

Its time derivative gives

$$(i\partial_t - H_1)\psi_{H12} = \langle 0| - eA_1^0\Psi_1\Psi_H + \Psi_1 H_2\Psi_H|12\rangle = \langle 0|\Psi_1 H_2\Psi_H|12\rangle, \tag{4.351}$$

as $\langle 0|A^0 = 0$. H_1 is the Dirac Hamiltonian (3.78). ψ_{H12} has altogether eight components, four ψ_{12} and four ψ_{s12}. Insertion of (4.344) gives the following two Dirac spinor equations:

$$(i\partial_t - H_1)\psi_{12} = \langle 0|\Psi_1(q_2A_2^0\Psi_2 + \Psi_{2s})|12\rangle, \tag{4.352}$$

$$(i\partial_t - H_1)\psi_{s12} = \langle 0|\Psi_1(q_2A_2^0\Psi_{2s} + K_2\Psi_{2s})|12\rangle. \tag{4.353}$$

The operator A^0 satisfies the Poisson equation (3.68), where the spinless charge density is part of $\rho'_{\rm el}$. The spinless contribution $A^0_{\rm scalar}$ is given by (3.69), with ρ_Ψ replaced by $-\rho_{\rm scalar} = -j^0$ (4.346) (the minus sign accounts for $q_2 = -q_1 = +e$). But as $A^0_{\rm scalar}$ commutes with $\Psi_1 = \Psi_{D1}$, one arrives again at $\langle 0|A^0_{\rm scalar} = 0$, such that $A^0_{\rm scalar}$ is in fact unnecessary here. The rest is analogous to (3.85)–(3.87). With $\pi^0 = i\partial_t - V_{12} = i\partial_t + \alpha_Z/r_{12}$,

$$(\pi^0 - H_1)\psi_{12} = \psi_{s12}, \quad (\pi^0 - H_1)\psi_{s12} = K_2\psi_{12}. \tag{4.354}$$

The $\boldsymbol{\pi}_1$ in H_1 and the $\boldsymbol{\pi}_2^2$ in K_2 still contain the photon field operator $\boldsymbol{A}$ which must be included perturbatively, leading to a Breit operator H_B as in Sect. 3.4. One may use $\boldsymbol{\pi}_2^2 = \boldsymbol{p}_2^2 - 2q_2\boldsymbol{p}_2\boldsymbol{A}_2$, as $\boldsymbol{A}_2^2$ does not contribute. Comparison with (3.94) shows that one merely has to replace $\boldsymbol{\alpha}_2$ by

$$\boldsymbol{\alpha}_{\rm KG} = \boldsymbol{\pi}_2\gamma_{\rm KG}, \quad \gamma_{\rm KG} = \begin{pmatrix} 0 & 0 \\ 2 & 0 \end{pmatrix}. \tag{4.355}$$

The second equation in (4.354) is thus extended to

$$(\pi^0 - H_1)\psi_{s12} = (K_2 + K_B)\psi_{12}, \quad K_B = -V_{12}(\boldsymbol{\alpha}_1\boldsymbol{\pi}_2 + \alpha_{1r}\pi_{2r}). \tag{4.356}$$

Note that the factor $\frac{1}{2}$ of (3.111) is cancelled by the factor 2 from $\gamma_{\rm KG}$. The second spinor ψ_{s12} is eliminated from (4.356) by use of the first equation (4.354),

$$[(\pi^0 - H_1)^2 - K_2 - K_B]\psi_{12} = 0. \tag{4.357}$$

Insertion of $H_1 = m_1\beta + \boldsymbol{p}_1\boldsymbol{\alpha} \equiv H_1^0$ ((3.96) with $V(r_1) = 0$, $\boldsymbol{A}_{\rm cl} = 0$) gives

$$H_1^{02} = m_1^2 + (\boldsymbol{\sigma}\boldsymbol{\pi}_1)^2 \equiv K_1 : \tag{4.358}$$

$$[\pi^{02} - 2\pi^0 m_1\beta - \{\pi^0, \boldsymbol{p}_1\boldsymbol{\alpha}_1\} + K_1 - K_2 - K_B]\psi_{12} = 0. \tag{4.359}$$

This equation is solved in the following for $A^\mu = 0$ in the cms, $\boldsymbol{p}_1 = -\boldsymbol{p}_2 \equiv \boldsymbol{p}_{12}$,

$$\pi^0 = E - V_{12}, \quad K_1 - K_2 = m_1^2 - m_2^2, \quad E^2 + m_1^2 - m_2^2 = 2EE_1 : \quad (4.360)$$

$$[EE_1 - EV_{12} + V_{12}^2/2 - (E - V_{12})m_1\beta]\psi_{12} = \tfrac{1}{2}(\{\pi^0, \boldsymbol{p}_{12}\boldsymbol{\alpha}_1\} + H_B)\psi_{12}. \quad (4.361)$$

At this point, the "quasidistance" transformation (3.214) greatly simplifies the equation. We define

$$\pi_1^0 = E_1 - V_{12} + V_{12}^2/2E = E_1 - V, \quad V = -\alpha_Z/r, \quad (4.362)$$

divide by E and drop the index $_1$ of $\boldsymbol{\sigma}_1$. We also insert $\boldsymbol{\alpha}_1 = \gamma^5\boldsymbol{\sigma}$ and approximate $\boldsymbol{p}_{12} = \boldsymbol{p}$ everywhere except in $\{\pi^0, \boldsymbol{p}_{12}\boldsymbol{\alpha}_1\}$,

$$[\pi_1^0 - (1 - V_{12}/E)m_1\beta]\psi_{12} = \gamma^5[\boldsymbol{\sigma}\boldsymbol{p}_{12} - \{V/2E, \boldsymbol{\sigma}\boldsymbol{p}\} + V(\boldsymbol{\sigma}\boldsymbol{p} + \sigma_r p_r)/2E]\psi_{12}. \quad (4.363)$$

Miraculously, the square bracket on the right-hand side is just $\boldsymbol{\sigma}\boldsymbol{p}$, provided ψ_{12} is first expressed in terms of the corresponding u_{12} according to (2.155),

$$\psi_{12} = r_{12}^{-1}\psi_u = (r/r_{12})\psi. \quad (4.364)$$

(This reflects the change of volume element, from $d^3r_{12} = r_{12}^2 dr_{12} d\Omega$ in the variable $\boldsymbol{r}_{12}$ to $d^3r = r^2 dr d\Omega$ in the variable $\boldsymbol{r}$.) After the substitution $\psi_{12} = r_{12}^{-1}\psi_u$, $\boldsymbol{\sigma}\boldsymbol{p}_{12}$ is replaced by (3.216)

$$r_{12}\boldsymbol{\sigma}\boldsymbol{p}_{12}r_{12}^{-1} = -i\sigma_r[\partial_r - (\boldsymbol{\sigma}\hat{\boldsymbol{l}} + 1)(1/r - \alpha_Z/2Er^2)]. \quad (4.365)$$

The remaining terms inside the square bracket of (4.363) add up to

$$-\boldsymbol{\sigma}\boldsymbol{p}V/2E + V\sigma_r p_r/2E = i\sigma_r(\boldsymbol{\sigma}\hat{\boldsymbol{l}} + 1)\alpha_Z/2Er^2, \quad (4.366)$$

by use of $\partial_r V = V\partial_r - V/r$. They just cancel the term in the last bracket of (4.365). In this way, the retardation (which is part of the Breit operator) disappears. The result is a Dirac equation for particle 1, with an r-dependent mass $m_1(r)$,

$$[\pi_1^0 - m_1(r)\beta - \gamma^5\boldsymbol{\sigma}\boldsymbol{p}]\psi = 0, \quad m_1(r) = m_1(1 + \alpha_Z/Er_{12}). \quad (4.367)$$

From the point of view of the exact quasidistance transformation (3.214), $m_1(r)$ is the square root of $m_1^2(1 + \alpha_Z/Er_{12})^2$,

$$m_1^2(r) = m_1^2(1 + 2\alpha_Z/Er), \quad m_1(r) \approx m_1(1 + \alpha_Z/Er - \alpha_Z^2/2E^2r^2). \quad (4.368)$$

The modified Dirac equation is again solved by the ansatz (2.158), with $\pi_\pm^0$ replaced by $\pi_1^0 \pm m_1(r)$. The $\pi_1^{02} - m_1^2(r)$ in the solution (2.159) may be written in several ways. With $E_1^2 - m_1^2 = k^2 = \epsilon^2 - \mu^2$ and $E_1 - m_1^2/E = \epsilon$:

$$\pi_1^{02} - m_1^2(r) = k^2 - 2\epsilon V + V^2 = (\epsilon - V)^2 - \mu^2, \quad (4.369)$$

which agrees with the previous two-body equations. The α_Z/r^2 in the last term of (2.159) arises from $-\pi^{0\prime} = V'$ and is now generalized to $-(\pi_1^0 \pm$

$m_1(r))' \approx V'(1 \pm m_1/E)$. The derivative of the last term in $m_1(r)$ is negligible here. Thus the complete equations (2.159) become

$$[(\epsilon - V)^2 - \mu^2 + \partial_r^2 - \kappa_D(\kappa_D \pm 1)/r^2 \pm (b/a)^{\pm 1}(1 \pm m_1/E)\alpha_Z/r^2]u = 0. \quad (4.370)$$

They are equal for

$$b/a = (\kappa_D \mp \gamma_c)/\alpha_Z(1 - m_1/E), \quad \gamma_c = [\kappa_D^2 - \alpha_Z^2(1 - m_1^2/E^2)]^{1/2}. \quad (4.371)$$

This may be compared with the Dirac value (2.160) $(\kappa_D \mp \gamma)/\alpha_Z$, $\gamma = (\kappa_D^2 - \alpha_Z^2)^{1/2}$. In electronic atoms, $m_1^2/E^2 \approx m_1^2/m_2^2$ is very small, such that one can expand the square root about γ:

$$\gamma_c \approx \gamma + \alpha_Z^2 m_1^2/2E^2\gamma \approx \gamma + \alpha_Z^2 m_1^2/m_{12}^2(2j+1). \quad (4.372)$$

The complete coefficient of r^{-2} in (4.370) is then

$$\gamma^2 \pm \gamma_c \approx \gamma^2 \pm \gamma \pm \alpha_Z^2 m_1^2/2\gamma E^2. \quad (4.373)$$

To first order in m_1/E, the only difference between the E^2-levels of leptonium and KD is the absence of hyperfine splitting in the latter. To second order in m_1/E, one has to replace the $\beta_j = j + \frac{1}{2} - \gamma$ of (4.281) by

$$\beta_{jl} = j + \tfrac{1}{2} - \gamma - (l - j)(\alpha_Z m_1/E)^2/\gamma. \quad (4.374)$$

The change is small but nevertheless significant since it lifts the l-degeneracy of a given j-level (Barker and Glover 1955). In this way, it contributes to the "Lamb shift" of such atoms and is in fact the dominant shift in pi-muonium.

A recoil-corrected Dirac equation for the electron is obtained from (4.357) by defining $E \equiv m_2 + E_e$ and by shifting the V_{12} from π^0 to H_1. To avoid confusion, the external $V(r_1)$ is now called $-eA^0$.

$$[(m_2 + E_e - H_e)^2 - m_2^2 - \boldsymbol{\pi}_2^2 - K_B]\psi_{12} = 0, \quad (4.375)$$

$$H_e = \boldsymbol{\alpha}\boldsymbol{\pi}_1 + \beta m_1 + V_{12} - eA^0. \quad (4.376)$$

This is re-arranged into

$$[E_e - H_e - (\boldsymbol{\pi}_2^2 + K_B - (E_e - H_e)^2)/2m_2]\psi_{12} = 0. \quad (4.377)$$

The static limit $m_2 \gg E_e$ yields $H_e\psi_{12} = E_e\psi_{12}$. Using this as a zeroth approximation, one obtains the recoil-corrected Dirac equation of Grotch and Yennie (1967, 1969),

$$(H_{\rm GY} - E_e)\psi_{12} = 0, \quad H_{\rm GY} = H_e + (\boldsymbol{\pi}_2^2 + K_B)/2m_2, \quad (4.378)$$

with K_B of (4.356). Refinements are discussed by Sapirstein and Yennie (Kinoshita 1990). The equation was originally derived from the assumption that the Hamiltonian of a composite system should contain the sum of the Hamiltonians of its components. With the magnetic hyperfine interaction added as

an afterthought, the equation may be used for hydrogen. It has been converted into an equation for a field operator Ψ_{12}, which yields all first-order recoil corrections to arbitrary Feynman graphs of the static limit (Braun 1973). The V_6 (4.203) was originally derived by Braun's method. Further applications have been given by Pachucki and Grotch (1995). Nuclear size and structure corrections are collected in the review of Eides et al. (2001).

The Grotch-Yennie solution of (4.370) is obtained by substituting $b/a = (1 - m_1/E)^{1/2}(1 + m_1/E)^{-1/2}b'/a'$, which simplifies the last term to $(b'/a')^{\pm 1}\alpha_{\rm GY}/r^2$, where $\alpha_{\rm GY} = \alpha_Z(1 - m_1^2/E^2)^{1/2}$ is a reduced charge. This charge is then introduced in (4.369) by redefinitions of ϵ and μ, $\epsilon\alpha_Z/r = \epsilon_{\rm GY}\alpha_{\rm GY}/r$ and $\epsilon^2 - \mu^2 = \epsilon_{\rm GY}^2 - \mu_{\rm GY}^2$, but a small discrepancy remains in $V^2 = \alpha_{\rm GY}^2/r^2 + \alpha_Z^2 m_1^2/E^2 r^2$.

For atoms with several electrons, one simply assumes additivity of the kinetic energy operators. An atom with a nonrelativistic nucleus of mass m_n and momentum operator $\boldsymbol{\pi}_n = \boldsymbol{p}_n = -i\nabla_n$ has then $H_{\rm GY} = H_e + p_n^2/2m_n$, with H_e given by H (3.203), (3.204), or by H_{nr} (3.126) for two nonrelativistic electrons. The atomic rest frame has $\boldsymbol{p}_1 + \boldsymbol{p}_2 + \boldsymbol{p}_n = 0$, $p_n^2 = p_1^2 + p_2^2 + 2\boldsymbol{p}_1\boldsymbol{p}_2$. The squares can be combined with the $p_i^2/2m_e$ of H_{nr} into $p_i^2/2\mu_e$, $1/\mu_e = 1/m_e + 1/m_n$. The Hamiltonian of the total "Newtonian" energy $E_N = E - m_n - 2m_e$, $H_{\rm GY}\psi = E_N\psi$, assumes the form

$$H_{\rm GY} = H_e(m_e \to \mu_e) + H_{mp}, \quad H_{mp} = \boldsymbol{p}_1\boldsymbol{p}_2/m_n. \tag{4.379}$$

H_{mp} is called the mass polarization operator; its expectation value is frequently negligible. Surprisingly, (4.379) remains valid also for the relativistic $H(3.203) - 2m_e^2$.

The Klein-Dirac equation may be extended to atoms with a spinless nucleus and several electrons. For helium, the ansatz (5.75) is generalized to

$$\psi_{H123} = \langle 0|\Psi_D(\boldsymbol{r}_1)\Psi_D(\boldsymbol{r}_2)\Psi_H(\boldsymbol{r}_3)|123\rangle. \tag{4.380}$$

Using the same procedure as before, (4.357) is replaced by

$$(\pi_{\rm tot}^0 - H_1^0 - H_2^0 - H_B)^2\psi_{123} = (K_3 + K_{1B} + K_{2B})\psi_{123}, \tag{4.381}$$

$$\pi_{\rm tot}^0 = E - V_{13} - V_{23} - V_{12}, \quad K_3 = m_3^2 + (\boldsymbol{p}_1 + \boldsymbol{p}_2)^2, \tag{4.382}$$

where H_B is again given by (3.111), with $\boldsymbol{r} = \boldsymbol{r}_1 - \boldsymbol{r}_2$. The squares of H_1^0 and H_2^0 are conveniently combined with K_3,

$$K_3 - (H_1^0)^2 - (H_2^0)^2 = m_3^2 - 2m_e^2 + 2\boldsymbol{p}_1\boldsymbol{p}_2. \tag{4.383}$$

The "Klein-Kramers" equation is obtained from (2.135) by using the relativistic two-body kinematics (E replaced by ϵ and $k^2 = \epsilon^2 - \mu^2$) and by inserting an additional parameter c in front of σ_r (Pilkuhn 1984):

$$[(\epsilon - V)^2 - \mu^2 - \boldsymbol{p}^2 + ic\sigma_r V']\psi_r = 0. \tag{4.384}$$

As in the Todorov and quarkonium equations, the free parameter is obtained from the Fourier transform of the one-photon exchange in the cms, $T^{(1)} = -4\pi\alpha_Z J^{\mu}_{11'} g_{\mu\nu} J^{\nu}_{22'}/\boldsymbol{q}^2$, with $J^{\nu}_{22'} = (p_2 + p_2')^{\nu}$ for the spinless particle 2. The result is

$$c = (1 - m_1^2/E^2)^{1/2} \approx (1 - m_1^2/m_{12})^2. \tag{4.385}$$

For $V = -\alpha_Z/r$, the eigenvalues of the r^{-2}-operator are $\gamma^2 \pm \gamma_c$ as in (4.373),

$$\gamma_c = (\kappa_D - \alpha_{\mathrm{GY}}^2)^{1/2}, \quad \alpha_{\mathrm{GY}} = c\alpha_Z. \tag{4.386}$$

Contrary to (4.367), the radial equation has now exact solutions. One need not approximate V^2 by $\alpha_{\mathrm{GY}}^2/r^2$ as in the GY-equation. And contrary to the KD equation, the KK does not require $V = -\alpha_Z/r$. Remembering that the leptonium equation with hyperfine interactions has no exact solutions, the Todorov and the KK equations are the only ones with exact solutions to order α_Z^4.

From the theoretical point of view, the most important aspect of (4.384) is its parity transformation. It is formally identical with (2.89),

$$\psi'(\boldsymbol{r}') = \psi_l(\boldsymbol{r}), \quad [(\epsilon - V)^2 - \mu^2 - \boldsymbol{p}^2 - ic\sigma_r V']\psi_l = 0, \tag{4.387}$$

but a linear relation of the type (2.83) between ψ_r and ψ_l exists only for $c = 1$. The situation is analogous to (3.227), where the parity transformation for $n_e = 2$ brings in the spinor χ which is not linearly related to ψ after the expected cancellations in the quadratic equation. In the new E^2-equations, both P and C become rather special for bound states containing an odd number of fermions.

4.11 Dirac Structures of Binary Bound States

In Sect. 4.6, the eight-component equation for two free leptons was derived from the sixteen-component two-particle Dirac equation (4.231). A direct derivation from two Kramers equations is also possible. For atoms, nothing is gained by this method, but it could suggest improvements of the quark model, where the large-distance interaction is still unknown.

For two free leptons, the uncoupled equations are first taken as Pauli equations (2.58), including external vector potentials. Using again the compact notation $\pi_i = \boldsymbol{\pi}_i \boldsymbol{\sigma}_i$, they may be written in forms which also comprise KG particles,

$$p_i^{02}\psi_{\mathrm{as}} = K_i\psi_{\mathrm{as}}, \quad K_i = m_i^2 + \pi_i^2. \tag{4.388}$$

The first step is to combine the two equations into a single one which contains only a common time shift in the form $p_1^0 + p_2^0 \equiv p^0$. With $p_1^{02} - p_2^{02} = p^0(p_1^0 - p_2^0)$, the difference of the equations gives

$$(p_1^0 - p_2^0)p^0\psi_{\mathrm{as}} = (K_1 - K_2)\psi_{\mathrm{as}}. \tag{4.389}$$

An eigenvalue K^0 of p^0 will be assumed. As $p_1^0 - p_2^0$ commutes with K_1 and K_2, a second application of $p_1^0 - p_2^0$ gives

$$(p_1^0 - p_2^0)^2 \psi_{\rm as} = (K^0)^{-2}(K_1 - K_2)^2 \psi_{\rm as}. \tag{4.390}$$

Next, consider the sum of the two equations (4.388),

$$(p_1^{02} + p_2^{02} - K_1 - K_2)\psi_{\rm as} = 0. \tag{4.391}$$

With $p_1^0 = \frac{1}{2}K^0 + \frac{1}{2}(p_1^0 - p_2^0)$ etc, this leads to

$$[K^{02}/2 + (K_1 - K_2)^2/2K^{02} - K_1 - K_2]\psi_{\rm as} = 0. \tag{4.392}$$

In terms of the triangle function λ (4.76), $(K^0)^{-2}\lambda(K^{02}, K_1, K_2)\psi_{\rm as} = 0$. In the "constraint Hamiltonian mechanics" which dates back to Dirac, the coupling between the two particles is introduced already in equations (4.388), but practical success has been limited (Crater and Van Alstine 1994).

For particles of equal spins, λ may be decomposed symmetrically in the indices 1 and 2:

$$\lambda = (K^{02} - K_1 - K_2)^2 - 4K_1K_2. \tag{4.393}$$

With $m_2^2 - m_1^2 = m_+ m_-$,

$$\begin{aligned}\lambda = (K^{02} - m_1^2 - m_2^2)^2 &- 2\pi_1^2(K^{02} + m_+m_-) - 2\pi_2^2(K^{02} - m_+m_-) \\ &- 4m_1^2m_2^2 + (\pi_1^2 - \pi_2^2)^2. \end{aligned}\tag{4.394}$$

For $\boldsymbol{A} = 0$, the transformation (4.291), (4.307) of variables,

$$\boldsymbol{p}_1 = \boldsymbol{p}_{\rm lab} + \boldsymbol{K}E_1/E, \quad \boldsymbol{p}_2 = -\boldsymbol{p}_{\rm lab} + \boldsymbol{K}E_2/E, \quad E \equiv (K^{02} - \boldsymbol{K}^2)^{1/2}, \tag{4.395}$$

yields together with $p_{{\rm lab},x} = p_x$, $p_{{\rm lab},y} = p_y$, $p_{{\rm lab},z} = \gamma p_z$,

$$\lambda = \gamma^2[(E^2 - m_1^2 - m_2^2)^2 - 4m_1^2m_2^2 - 4E^2(p_x^2 + p_y^2 + p_{{\rm lab},z}^2/\gamma^2)]. \tag{4.396}$$

The factor γ^2 in front of the square bracket corresponds to the separation of one factor γ from (4.308). The square bracket is factorized by means of the Dirac matrices β, $\gamma^5 = \beta_x$ and $i\gamma^5\beta = \beta_y$ as follows:

$$\lambda/\gamma^2 = (f_0 + f_z\beta + f_x\beta_x + f_y\beta_y)(f_0 - f_z\beta - f_x\beta_x - f_y\beta_y), \tag{4.397}$$

$$f_0 = E^2 - m_1^2 - m_2^2, \quad f_z = 2m_1m_2, \quad f_x = 2E\boldsymbol{p}\boldsymbol{\sigma}_1, \quad f_y = 0. \tag{4.398}$$

The second factor of (4.398) is precisely that of the leptonium equation (4.237). More general forms include a rotation by an arbitrary angle ω_D about the β-axis in Dirac space (2.103), $f_x' = 2E\boldsymbol{p}\boldsymbol{\sigma}_1 \cos\omega_D$, $f_y' = 2E\boldsymbol{p}\boldsymbol{\sigma}_1 \sin\omega_D$, or a rotation (4.270) in the Pauli product space. For constant f_0, one may also take $f_y = 2E\boldsymbol{p}\boldsymbol{\sigma}_2 \sin\omega_D$, as $\sigma_{1i}\sigma_{1j}$ and $(\sigma_{1i}\cos\omega_D + i\sigma_{2i}\sin\omega_D)(\sigma_{1j}\cos\omega_D - i\sigma_{2j}\sin\omega_D)$ are identical in their symmetric tensor components. (In the quark

model, f_y is not excluded a priori even when f_0 is r-dependent. For small ω_D, it would mainly affect the hyperfine structure of quarkonium.)

The inclusion of $\boldsymbol{A}$ is trivial in the 16-component equation (3.186) or (3.190), whereas (3.218) is still unclear. The first-order relativistic Zeeman shift δE of the ground state has been calculated by Faustov (1970) and by Grotch and Hegstrom (1971). Besides the factor $(1-\alpha_Z^2/3)$ from H_{Zee} (2.285) in the Pauli reduction of the GY-equation (4.378), these authors find essentially a factor m_{12}/E in front of the nonrelativistic recoil corrections of the $\boldsymbol{\sigma}_i\boldsymbol{B}$ -terms. It represents the standard $\delta(E\epsilon) = \frac{1}{2}\delta E^2 = E\delta E$ of (4.398), and excludes additional energy functions such as $\sin^2\omega_D = E_1/E$ in the Pauli reduction. The complete relativistic recoil correction to the static approximation of Sect. 2.9 for $\boldsymbol{\sigma}_1\boldsymbol{B}$ is $(1+\mu\alpha_Z^2/2n^2m_{12})m_2/m_{12}$, and correspondingly for particle 2.

Leptonium in a constant magnetic field is translational invariant: All three components of the "pseudomomenta"

$$\boldsymbol{k}_i = \boldsymbol{\pi}_i + q_i\boldsymbol{B}\times\boldsymbol{r}_i \tag{4.399}$$

commute with the momentum operators $\boldsymbol{\pi}_{i,\mathrm{lab}} = \boldsymbol{p}_i - q_i\boldsymbol{A}(\boldsymbol{r}_i)$, although the different components of $\boldsymbol{k}_i$ don't commute among themselves. The $\boldsymbol{k}_i$ are the individual displacement operators in a magnetic field. The $(\boldsymbol{\sigma}_1\boldsymbol{\pi}_1)^2$ may be expressed as follows:

$$(\boldsymbol{\sigma}_1\boldsymbol{\pi}_1)^2 = \boldsymbol{k}_1^2 - 2q_1\boldsymbol{B}\boldsymbol{j}_1, \quad \boldsymbol{j}_1 = \boldsymbol{l}_1 + \tfrac{1}{2}\boldsymbol{\sigma}_1. \tag{4.400}$$

When the interaction is included, only the total displacer $\boldsymbol{k}_1+\boldsymbol{k}_2$ is conserved. For neutral atoms ($q_2 = -q_1 = e$),

$$\boldsymbol{k} = \boldsymbol{p}_1 + \boldsymbol{p}_2 - \tfrac{1}{2}e\boldsymbol{B}\times(\boldsymbol{r}_1 - \boldsymbol{r}_2), \tag{4.401}$$

its components do commute. Eigenfunctions of $\boldsymbol{k}$ with eigenvalue $\boldsymbol{K}$ are, for $\boldsymbol{p}_1 + \boldsymbol{p}_2 = -i\boldsymbol{\nabla}_R$,

$$\psi(\boldsymbol{K}) = e^{i\boldsymbol{K}\boldsymbol{R}}e^{ie\boldsymbol{B}(\boldsymbol{r}_1\times\boldsymbol{r}_2)/2}\psi(\boldsymbol{K}=0). \tag{4.402}$$

Despite this constant of motion, no extension of (4.398) has yet been found which could reproduce the simple $\delta(E\epsilon)$ mentioned above.

In the presence of external potentials V_i, the elimination of $p_1^0 - p_2^0$ is complicated. The Kramers equations

$$(\pi_i^0)^2\psi = K_i\psi, \quad \pi_i^0 = p_i^0 - V_i \tag{4.403}$$

may be linearized as in (4.344). With the abbreviation $\pi^0 = \pi_1^0 + \pi_2^0$, this leads to the following equation for $\psi_{H12} = \langle 0|\Psi_H(\boldsymbol{r}_1)\Psi_H(\boldsymbol{r}_2)|12\rangle$:

$$\pi^0\psi = \psi_{1s} + \psi_{2s}, \quad \pi^0\psi_{is} = \psi_{ss} + K_i\psi, \quad \pi^0\psi_{ss} = K_1\psi_{2s} + K_2\psi_{1s}. \tag{4.404}$$

Elimination of $\psi_{is} = (\pi^0)^{-1}(\psi_{ss} + K_i\psi)$ gives the following two equations:

$$(\pi^{02} - K)\psi = 2\psi_{ss}, \quad K = K_1 + K_2, \tag{4.405}$$

$$(\pi^0 - K/\pi^0)\psi_{ss} = [K_1(\pi^0)^{-1}K_2 + K_2(\pi^0)^{-1}K_1]\psi. \tag{4.406}$$

Multiplication of (4.405) by $\pi^0 - K/\pi^0$ permits the elimination of ψ_{ss}:

$$[\pi^{03} - \{\pi^0, K\} + \Delta K(\pi^0)^{-1}\Delta K]\psi = 0, \quad \Delta K = K_1 - K_2. \tag{4.407}$$

When the K_i are taken from (2.82) appropriate for ψ_r, (4.407) applies to the noninteracting components $\psi_{\mathrm{as},rr}$ of the two-particle Dirac spinor $\psi_{D2,\mathrm{as}}$ (4.231),

$$\psi_{D2,\mathrm{as},rr} = \psi_{1r}(\boldsymbol{r}_1)\psi_{2r}(\boldsymbol{r}_2). \tag{4.408}$$

This is checked by insertion into (4.407). For vanishing commutators, multiplication of (4.407) by π^0 reproduces (4.397). A "Dirac factorization" of (4.407) seems excluded.

5 Hyperfine Shifts, Radiation, Quarks

5.1 First-Order Magnetic Hyperfine Splitting

Atomic fine and hyperfine structures are normally small and may be treated as perturbations of the nonrelativistic Schrödinger Hamiltonian. However, many level splittings are measured so precisely that their calculation wound require second-order and even third-order perturbation theory. It is then much easier to take the fine structure from the Dirac equation, and to calculate the hyperfine structure as a perturbation of the Dirac equation. The experimental hyperfine splittings of the hydrogen and muonium ground states are 1 420 405.751767 kHz and 4 463 302.8 kHz, respectively (1 kHz $\approx$ 4.1357×10^{-12} eV). For such cases, the first-order hyperfine splitting of the Dirac equation follows from (5.11) below to all orders in α_Z.

In this section, the first order perturbation theory (Rose 1961) is adapted to the two-lepton equation (4.278) (Hund and Pilkuhn 2000). Its application to positronium requires modifications only in some particular states.

In Sect. 5.2, the magnetic hyperfine operator is modified in order to produce an equation with hyperfine wave functions as exact solutions. These wave functions may be used not only for the calculation of second-order hyperfine shifts, but also for the inclusion of other perturbations. The emission and re-absorption of another virtual photon produces several small shifts, of which only the anomalous magnetic moment and the "self-energy" shift survive in the static limit $m_1 \ll m_2$. The latter shift implies that the mass of a bound particle 1 differs from its unbound value m_1; it constitutes the main part of the socalled Lamb shift, which lifts the degeneracy of the two j-levels. The emission and re-absorption is a second-order process of the type (2.223), for which the Dirac-Coulomb Greens function may be used. This function will be discussed in Appendix B.

The derivation of the familiar first-order perturbation theory result, $E_n^1 = \langle H_{\rm per} \rangle_n$ requires hermiticity of the unperturbed operator H_0. For the hyperfine operator of (4.275),

$$H_{\rm per} = -\gamma^5 \boldsymbol{\sigma}_{12}^{\times} V_\rho \boldsymbol{\nabla}_\rho m_1 m_2 / E^2 \tag{5.1}$$

H_0 is the Dirac-Coulomb Hamiltonian H_ρ (4.276), which is Hermitian. The expectation value of the anti-Hermitian part of $H_{\rm per}$ contains $\langle i\{V, \boldsymbol{p}\}/2 \rangle$,

which vanishes by partial integration. The first-order shift of ϵ/μ in (4.275) contains only $i[V_\rho, \boldsymbol{p}_\rho]/2 = -\alpha_Z \hat{\boldsymbol{\rho}}/2\rho^2$:

$$(\epsilon/\mu)^1_n = \int \psi^{0\dagger}_n H_{\rm per} \psi^0_n d^3\rho \equiv \langle H_{\rm per}\rangle_n = \alpha_Z \langle \gamma^5 \boldsymbol{\sigma}^\times_{12} \hat{\boldsymbol{\rho}}/\rho^2\rangle m_1 m_2/2E^{02}_n. \quad (5.2)$$

The E^{02}_n in the denominator of (5.2) are the exact solutions of the Dirac-Coulomb equation. The extra increase of the hyperfine splitting with decreasing E^2 is largest for positronium, but it remains small even there. (The effect is much larger in the quarkonium model of mesons. The pseudoscalar and vector mesons represent the singlet and triplet quark-antiquark ground states, respectively. For the lightest members in each group, the pi and rho mesons, $m^2_\pi/m^2_\rho \approx 1/30$ excludes a perturbative treatment of the E^{-2}-dependence.)

On the left-hand side of (5.2), one has

$$(\epsilon/\mu)^1_n = (E^2)^1_n/2m_1 m_2 = E^0_n E^1_n/m_1 m_2, \quad (5.3)$$

as $(E^2)^1_n$ is the infinitesimal change of E^2_n, $\delta(E^2_n) = 2E_n \delta E_n = 2E^0_n E^1_n$. The Dirac expectation value gives

$$\langle \gamma^5 \boldsymbol{\sigma}^\times_{12} \hat{\boldsymbol{\rho}}/\rho^2\rangle = \int \psi^\dagger_D \gamma_5 \boldsymbol{\sigma}^\times_{12} \hat{\boldsymbol{\rho}} \psi_D/\rho^2 = \int (\psi^\dagger_g \boldsymbol{\sigma}^\times_{12} \hat{\boldsymbol{\rho}} \psi_f + \psi^\dagger_f \boldsymbol{\sigma}^\times_{12} \hat{\boldsymbol{\rho}} \psi_g)/\rho^2. \quad (5.4)$$

Insertion of (2.152) leads to

$$\langle \gamma^5 \boldsymbol{\sigma}^\times_{12} \hat{\boldsymbol{\rho}}/\rho^2\rangle = -i \int gf d\rho \int d\Omega (\chi^\dagger_{lj} \boldsymbol{\sigma}^\times_{12} \hat{\boldsymbol{\rho}} \chi_{\tilde{l}j} - \chi^\dagger_{\tilde{l}j} \boldsymbol{\sigma}^\times_{12} \hat{\boldsymbol{\rho}} \chi_{lj}). \quad (5.5)$$

The first angular integral is minus the second one (see below), such that the expectation value factorizes as follows:

$$\langle \gamma^5 \boldsymbol{\sigma}^\times_{12} \hat{\boldsymbol{\rho}}/\rho^2\rangle = 2 \int gf d\rho \int d\Omega \chi^\dagger_{\tilde{l}j} i \boldsymbol{\sigma}^\times_{12} \hat{\boldsymbol{\rho}} \chi_{lj}. \quad (5.6)$$

The notation χ_{lj} and $\chi_{\tilde{l}j}$ needs some clarification. The Dirac-Coulomb wave functions contain the spinor spherical harmonics χ^{j,m_j}_l (2.124) in their large components and $\chi^{j,m_j}_{\tilde{l}}$ in their small ones, where $\tilde{l} = 2j - l$ is the other possible value of l at fixed j. When the hyperfine operator is added, the only strictly conserved angular momentum operator is

$$\boldsymbol{f} = \hat{\boldsymbol{l}} + \tfrac{1}{2}\boldsymbol{\sigma}_1 + \tfrac{1}{2}\boldsymbol{\sigma}_2 = \hat{\boldsymbol{l}} + \tfrac{1}{2}\boldsymbol{\sigma} = \boldsymbol{j} + \tfrac{1}{2}\boldsymbol{\sigma}_2. \quad (5.7)$$

The eigenvalues of $\boldsymbol{f}^2$ and f_z are $f(f+1)$ and m_f, respectively. In first-order perturbation theory, only the unperturbed states appear, which do contain the quantum numbers l, $\tilde{l}$ and j. The quantum number m_j, on the other hand (which was called m in Sects. 2.5 and 2.6), cannot be kept fixed any longer, because the Dirac-Coulomb eigenvalues are degenerate in m_j. The appropriate states χ_{lj} and $\chi_{\tilde{l}j}$ in (5.6) are Clebsch-Gordan combinations of the χ^{j,m_j}_l,

$$\chi_{lj}^{f,m_f} = \Sigma_{m_j}(m_j, m_2|f, m_f)\chi_l^{j,m_j}\chi_2(m_2) \equiv \chi_{lj}, \tag{5.8}$$

where the $\chi_2(m_2)$ are the eigenstates of σ_{2z}, with eigenvalues $2m_2 = \pm 1$. The two arguments suppressed in the CG-coefficients $(m_j, m_2|f, m_f)$ are $j_1 = j$, $j_2 = 1/2$. The relevant coefficients are again given by (2.131), with $l \pm \frac{1}{2}$ replaced by $f = j \pm \frac{1}{2}$. The explicit construction below gives

$$\int d\Omega \chi_{lj}^{\dagger} i\boldsymbol{\sigma}_{12}^{\times}\hat{\boldsymbol{\rho}}\chi_{lj} = (f-j)8(l-j)(f+\tfrac{1}{2})^{-1}. \tag{5.9}$$

The radial integral is obtained from (A.31) and (A.45), with $\kappa_D = (l-j)(2j+1)$ and $\kappa/\mu = \alpha_Z(n_\beta^2 + \alpha_Z^2)^{-1/2}$,

$$I_r = \int gfd\rho = (\kappa/\mu)^3[2(1+\alpha_Z^2/n_\beta^2)^{-1/2}\kappa_D - 1]/[4\gamma(\gamma^2 - 1/4)]. \tag{5.10}$$

For $j = n - \frac{1}{2}$, it is again simplified by $n_\beta = \gamma$ as in (4.282), $\kappa/\mu = \alpha_Z/n$, and by $\kappa_D = -n$:

$$I_r = -\alpha_Z^3/[n^3\gamma(2\gamma - 1)]. \tag{5.11}$$

In general, one has to order α_Z^2

$$(n_\beta^2 + \alpha_Z^2)^{-3/2} = n^{-3}[1 + \tfrac{3}{2}\alpha_Z^2(n - j - \tfrac{1}{2})/n^2(j + \tfrac{1}{2})]. \tag{5.12}$$

A factor $4(l-j)$ may be extracted from the numerator of (5.10) by inserting $2\kappa_D = 4(l-j)(j+\frac{1}{2})$, and by rewriting $1 = 4(l-j)^2$. The $\gamma^2 - 1/4$ in the denominator may be put into the form

$$\gamma^2 - 1/4 = j(j+1) - \alpha_Z^2 = (l+\tfrac{1}{2})(\tilde{l}+\tfrac{1}{2}) - \alpha_Z^2, \tag{5.13}$$

with $\tilde{l} = 2j - l$. Then (5.10) becomes to order α_Z^5

$$I_r = \alpha_Z^3 \frac{l-j}{j+\frac{1}{2}} \frac{(n_\beta^2 + \alpha_Z^2)^{-\frac{3}{2}}}{2l+1} \left[1 + \frac{\alpha_Z^2/2}{(j+\frac{1}{2})^2} + \frac{\alpha_Z^2}{j(j+1)} - \frac{\alpha_Z^2(j+\frac{1}{2})}{n^2(2\tilde{l}+1)}\right]. \tag{5.14}$$

Collecting the various factors from (5.2) and (5.6), one obtains

$$(\epsilon/\mu)_{hf}^1 = \frac{\alpha_Z^4 m_1 m_2}{2E^2 n^3} \frac{2(f-j)}{(f+\frac{1}{2})(l+\frac{1}{2})(j+\frac{1}{2})} \left(1 + \alpha_Z^2 c^{(2)} + \ldots\right), \tag{5.15}$$

$$c^{(2)} = \left(\frac{3(n-j-\frac{1}{2})}{2n^2(j+1/2)} + \frac{1/2}{(j+\frac{1}{2})^2} + \frac{1}{j(j+1)} - \frac{j+1/2}{n^2(2\tilde{l}+1)}\right). \tag{5.16}$$

For S-states, one has to add to $c^{(2)}$ a "wave function correction" $c_{\rm wf}^{(2)}$, which can be expressed in terms of $\langle r_G^{-3}\rangle_{l=0}$ from (2.231),

$$c_{\rm wf}^{(2)} = 2\left[\log\frac{n}{2\alpha_Z} - \Psi(n+1) - \gamma_{\rm Eu} - \frac{n-1}{2n}\right]\frac{\mu}{m_{12}} = -\frac{n^3}{\alpha_Z^3\mu^2 m_{12}}\langle r_G^{-3}\rangle_{l=0}, \tag{5.17}$$

plus an n-independent correction which is omitted here. Insertion of (5.3), $(\epsilon/\mu)^1_{hf} = E\delta E_{hf}/m_1 m_2$ includes contributions to δE_{hf},

$$\delta E_{hf} = (\epsilon/\mu)_{hf} m_1 m_2/E = \tfrac{1}{2}\alpha_Z^4 m_1^2 m_2^2 (n m_{12} - \alpha_Z^2 \mu/2n)^{-3} \dots \tag{5.18}$$

that had previously to be calculated by NRQED.

In the following, the states χ_{lj}^{f,m_f} are given for $m_f = 0$. With the compact notation

$$\chi_1^1 = \chi_1(\tfrac{1}{2})\chi_2(\tfrac{1}{2}), \quad \chi_1^{-1} = \chi_1(-\tfrac{1}{2})\chi_2(-\tfrac{1}{2}), \quad \chi_1^0 = {}^3\chi^0, \quad \chi_0^0 = {}^1\chi^0 \tag{5.19}$$

and with ${}^3\chi^0$ and ${}^1\chi^0$ given in (3.130) and (3.131),

$$\chi^{f0}_{f-1,f-1/2} = (4f-2)^{-\frac{1}{2}}[(f-1)^{\frac{1}{2}}(Y^{-1}_{f-1}\chi_1^1 + Y^1_{f-1}\chi_1^{-1}) + (2f)^{\frac{1}{2}} Y^0_{f-1}\chi_1^0], \tag{5.20}$$

$$\chi^{f0}_{f+1,f+1/2} = (4f+6)^{-\frac{1}{2}}[(f+2)^{\frac{1}{2}}(Y^{-1}_{f+1}\chi_1^1 + Y^1_{f+1}\chi_1^{-1}) - (2f+2)^{\frac{1}{2}} Y^0_{f+1}\chi_1^0], \tag{5.21}$$

$$\chi^{f0}_{f,f-1/2} = (4f+2)^{-\frac{1}{2}}[(f+1)^{\frac{1}{2}}(-Y_f^{-1}\chi_1^1 + Y_f^1\chi_1^{-1}) - (2f)^{\frac{1}{2}} Y^0_f\chi_0^0], \tag{5.22}$$

$$\chi^{f0}_{f,f+1/2} = (4f+2)^{-\frac{1}{2}}[(f)^{\frac{1}{2}}(-Y_f^{-1}\chi_1^1 + Y_f^1\chi_1^{-1}) + (2f+2)^{\frac{1}{2}} Y^0_f\chi_0^0]. \tag{5.23}$$

Both χ_1^0 and χ_0^0 are normalized, and so are all four states χ_{lj}^{f0}. The spherical harmonics $Y_l^{m_l}$ occur for $l = f-1$ in (5.20), for $l = f+1$ in (5.21), and for $l = f$ in (5.22) and (5.23). This guarantees the orthogonality of the $\chi_{f\pm1,j}$ to each other and also to the two states with $l = f$. The latter two states, on the other hand, are combinations of identical components; they are orthonormal due to their coefficients. In particular, $\int d\Omega(-Y_l^{-1*}\chi_1^{1\dagger} + Y_l^{1*}\chi_1^{-1\dagger})(-Y_l^{-1}\chi_1^1 + Y_l^1\chi_1^{-1}) = 2$ makes the scalar product of the first terms in the square brackets $2f^{\frac{1}{2}}(f+1)^{\frac{1}{2}}$, which equals minus the scalar product of the last terms.

As $\boldsymbol{j}$ is not conserved by the hyperfine operator, an alternative basis may be used in which $\boldsymbol{S}^2 = \boldsymbol{\sigma}^2/4$ is diagonal, with eigenvalues $S(S+1)$. The appropriate CG-expansion is

$$\chi_{l,S}^{f,m_f} = \sum_{m_l} (m_l, m_s | f m_f\rangle Y_l^{m_l} \chi_S^{m_s}, \tag{5.24}$$

with $j_1 = l$ and $j_2 = S$ in (2.123). The $\chi_S^{m_s}$ are identical with the ones defined in (5.19). For $S = 0$, the expansion (5.24) requires $l = f$, where it reduces to a single term:

$$\chi_{f,0}^{f,m_f} = Y_f^{m_f}\chi_0^0. \tag{5.25}$$

Also simple is the expansion for $l = f,\ S = 1,\ m_f = 0$:

$$\chi_{f,1}^{f,0} = 2^{-1/2}(-Y_f^{-1}\chi_1^1 + Y_f^1\chi_1^{-1}). \tag{5.26}$$

The CG-coefficient of $Y_f^0\chi_1^0$ vanishes in $\chi_{f,1}^{f,0}$. Comparison with the states $\chi_{f,j}$ of (5.22) and (5.23) shows

$$\chi_{f,f-1/2}^{fm_f} = c\chi_{f,1}^{f,m_f} - s\chi_{f,0}^{f,m_f}, \quad \chi_{f,f+1/2}^{fm_f} = s\chi_{f,1}^{f,m_f} + c\chi_{f,0}^{f,m_f},$$

$$c \equiv [(f+1)/(2f+1)]^{-1/2}, \quad s \equiv [f/(2f+1)]^{-1/2}. \tag{5.27}$$

$c^2 + s^2 = 1$ shows that (5.27) is an orthogonal transformation. Such a "recoupling of angular momenta" is independent of m_f, see Sect. 5.6. In short,

$$\chi_{f,1} = c\chi_{f,f-1/2} + s\chi_{f,f+1/2}, \quad \chi_{f,0} = -s\chi_{f,f-1/2} + c\chi_{f,f+1/2}. \tag{5.28}$$

The CG-coefficients for $l = f \mp 1,\ S = 1$ are more complicated, see Table 2.1. On the other hand, a look at $\chi_{f\mp1,f\mp1/2}^{f0}$ shows that these contain only $\chi_1^{m_s}$; the singlet spin state χ_0^0 does not contribute. Consequently, the $\chi_{f\mp1,f\mp1/2}^{f0}$ are identical with the $\chi_{f\mp1,1}^{f0}$. Also these relations remain valid for all m_f:

$$\chi_{f-1,f-1/2}^{fm_f} = \chi_{f-1,1}^{fm_f}, \quad \chi_{f+1,f+1/2}^{fm_f} = \chi_{f+1,1}^{fm_f}. \tag{5.29}$$

The reason is that $l = f \mp 1$ requires not only $S = 1$, but also $j = f \mp 1/2 = l \pm 1/2$. The second lower index is unnecessary for the states (5.29) and is dropped in the following.

At fixed eigenvalue $f(f+1)$ of $\boldsymbol{f}^2$ and for all values of m_f, the operators $\boldsymbol{l}^2$, $\boldsymbol{\sigma}_1\boldsymbol{l}$, $\boldsymbol{\sigma}_2\boldsymbol{l}$ and $\boldsymbol{\sigma}^\times\boldsymbol{l}$ are 4×4 matrices. The upper indices f and m_f are now suppressed. A special symbol for the eigenvalues $f(f+1)$ of $\boldsymbol{f}^2$ will also be useful,

$$\boldsymbol{f}^2\chi = f(f+1)\chi \equiv F^2\chi, \quad F = \sqrt{f(f+1)}. \tag{5.30}$$

For example,

$$\boldsymbol{l}^2\chi_{f+1} = l(l+1)\chi_{f+1} = (f+1)(f+2)\chi_{f+1} = (F^2 + 2f + 2)\chi_{f+1}. \tag{5.31}$$

In the triplet-singlet basis, one thus gets

$$\chi_{l,S} = \begin{pmatrix} \chi_{f+1} \\ \chi_{f-1} \\ \chi_{f,1} \\ \chi_{f,0} \end{pmatrix}, \quad \boldsymbol{l}^2 = \begin{pmatrix} F^2+2f+2 & 0 & 0 & 0 \\ 0 & F^2-2f & 0 & 0 \\ 0 & 0 & F^2 & 0 \\ 0 & 0 & 0 & f^2 \end{pmatrix}, \tag{5.32}$$

$$\boldsymbol{\sigma}_{1,2}\boldsymbol{l} = \begin{pmatrix} -f-2 & 0 & 0 & 0 \\ 0 & f-1 & 0 & 0 \\ 0 & 0 & -1 & \pm F \\ 0 & 0 & \pm F & 0 \end{pmatrix}. \tag{5.33}$$

Note the sum check

$$\boldsymbol{\sigma}_1\boldsymbol{l} + \boldsymbol{\sigma}_2\boldsymbol{l} = \boldsymbol{\sigma}\boldsymbol{l} = \boldsymbol{f}^2 - \boldsymbol{l}^2 - \boldsymbol{\sigma}^2/4. \tag{5.34}$$

The matrix $\boldsymbol{\sigma}^\times \boldsymbol{l}$ has $\boldsymbol{\sigma}^\times = i\frac{1}{2}(1+\boldsymbol{\sigma}_1\boldsymbol{\sigma}_2)\boldsymbol{\Delta\sigma}$ according to (4.234), and as $\boldsymbol{\Delta\sigma l} = 0$ in the states with $l = f \pm 1$, we quote only its nonvanishing 2×2 submatrix in the lower right-hand corner of the 4×4 matrix, with an additional factor i which will be needed later:

$$i\boldsymbol{\sigma}^\times \boldsymbol{l} = \frac{1+\boldsymbol{\sigma}_1\boldsymbol{\sigma}_2}{2}\boldsymbol{\Delta\sigma l} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} 0 & 2F \\ 2F & 0 \end{pmatrix} = 2\begin{pmatrix} 0 & F \\ -F & 0 \end{pmatrix}. \tag{5.35}$$

In the $j = l \pm \frac{1}{2}$-basis for $l = f$, one has by inversion of (5.27)

$$\chi_j = \begin{pmatrix} \chi_{l+1/2} \\ \chi_{l-1/2} \end{pmatrix}, \quad \boldsymbol{\sigma}_{1,2}\boldsymbol{l} = \begin{pmatrix} s & c \\ c & -s \end{pmatrix}\begin{pmatrix} -1 & \pm F \\ \pm F & 0 \end{pmatrix}\begin{pmatrix} s & c \\ c & -s \end{pmatrix}, \tag{5.36}$$

$$\boldsymbol{\sigma}_1\boldsymbol{l} = \begin{pmatrix} l & 0 \\ 0 & -l-1 \end{pmatrix}, \quad \boldsymbol{\sigma}_2\boldsymbol{l} = \frac{1}{2l+1}\begin{pmatrix} -l(2l+3) & -2l(l+1) \\ -2l(l+1) & (2l-1)(l+1) \end{pmatrix}. \tag{5.37}$$

The eigenvalues of $\boldsymbol{\sigma}_1\boldsymbol{l}$ agree with (2.121). $\boldsymbol{\sigma}_2\boldsymbol{l}$ is diagonal in the j_2-basis ($\boldsymbol{j}_2 = \boldsymbol{l} + \boldsymbol{\sigma}_2/2$), with the same eigenvalues.

At large distances, hydrogenic atoms behave like particles of spin f. Their magnetic hyperfine interaction causes a quadrupole moment, which may be calculated from the Dirac equation (Baryshevsky and Kuten 1978).

5.2 Nonrelativistic Magnetic Hyperfine Operators

To the order α_Z^4, convenient magnetic hyperfine operators are obtained by elimination of the small components of the leptonium equation. We rewrite (4.268) as

$$(\epsilon - V - \mu\beta - \gamma^5\boldsymbol{\sigma}_1\boldsymbol{\pi})\psi_1 = 0, \tag{5.38}$$

$$\boldsymbol{\pi} = \boldsymbol{p} + e\boldsymbol{A}_{hf}, \quad e\boldsymbol{A}_{hf} = -iV\boldsymbol{\sigma}_2 \times \boldsymbol{p}/E. \tag{5.39}$$

By copying the steps of Sect. 2.8, one finds

$$(\epsilon - V - \mu)\psi_g = \boldsymbol{\sigma}_1\boldsymbol{\pi}(\epsilon - V + \mu)^{-1}\boldsymbol{\sigma}_1\boldsymbol{\pi}\psi_g. \tag{5.40}$$

Expansion of the denominator in $V/(\epsilon+\mu)$ gives (2.256),

$$[(\epsilon - V)^2 - \mu^2 - (\boldsymbol{\sigma}_1\boldsymbol{\pi})^2 + [\boldsymbol{\sigma}_1\boldsymbol{\pi}, [\boldsymbol{\sigma}_1\boldsymbol{\pi}, V]]/4\mu]\psi_g = 0. \tag{5.41}$$

The double commutator is a relativistic correction; to order α_Z^4, it may be evaluated in the limit $\boldsymbol{A}_{hf} = 0$. Consequently, also (2.271) applies again, in the form

$$[(\epsilon - V)^2 - \mu^2 - (\boldsymbol{\sigma}_1\boldsymbol{\pi})^2 - \tfrac{1}{2}\alpha_Z\boldsymbol{\sigma}_1\boldsymbol{l}V'/L^2]\psi_g = 0, \quad L^2 = l(l+1). \tag{5.42}$$

To the order α_Z^4, the hyperfine operator arises exclusively from $(\boldsymbol{\sigma}_1\boldsymbol{\pi})^2$. Insertion of $\boldsymbol{\sigma}_1\boldsymbol{\pi} = \boldsymbol{\sigma}_1\boldsymbol{p} - iV\boldsymbol{p}\boldsymbol{\sigma}^\times/E$ ($\boldsymbol{\sigma}^\times \equiv \boldsymbol{\sigma}_{12}^\times$) gives

$$(\boldsymbol{\sigma}_1\boldsymbol{\pi})^2 = \boldsymbol{p}^2 - i\{\boldsymbol{\sigma}_1\boldsymbol{p}, V\boldsymbol{p}\boldsymbol{\sigma}^\times\}/E - (V\boldsymbol{p}\boldsymbol{\sigma}^\times/E)^2. \tag{5.43}$$

The nonrelativistic hyperfine operator arises from the terms linear in V:

$$\{\boldsymbol{\sigma}_1\boldsymbol{p}, V\boldsymbol{p}\boldsymbol{\sigma}^\times\} = \boldsymbol{\sigma}_1[\boldsymbol{p}, V]\boldsymbol{p}\boldsymbol{\sigma}^\times + V\{\boldsymbol{\sigma}_1\boldsymbol{p}, \boldsymbol{p}\boldsymbol{\sigma}^\times\}. \tag{5.44}$$

The last anticommutator vanishes. Inserting $-i[\boldsymbol{p}, V] = -[\nabla, V] = -V'\boldsymbol{r}/r$, one obtains the complete nonrelativistic hyperfine operator from $(\boldsymbol{\sigma}_1\boldsymbol{\pi})^2/2\mu$,

$$-i\{\boldsymbol{\sigma}_1\boldsymbol{p}, V\boldsymbol{p}\boldsymbol{\sigma}^\times\}/2\mu E = -(V'/r)(\boldsymbol{\sigma}_1\boldsymbol{r})\boldsymbol{\sigma}_1(\boldsymbol{\sigma}_2 \times \boldsymbol{p})/2m_1m_2. \tag{5.45}$$

By (2.53),

$$(\boldsymbol{\sigma}_1\boldsymbol{r})\boldsymbol{\sigma}_1(\boldsymbol{\sigma}_2 \times \boldsymbol{p}) = \boldsymbol{r}(\boldsymbol{\sigma}_2 \times \boldsymbol{p}) + \boldsymbol{\sigma}_1(\boldsymbol{r} \times (\boldsymbol{\sigma}_2 \times \nabla)). \tag{5.46}$$

The hyperfine operator is then decomposed into two terms,

$$-i\{\boldsymbol{\sigma}_1\boldsymbol{p}, V\boldsymbol{p}\boldsymbol{\sigma}^\times\}/2\mu E = V_{s2l} + H'_{hf}. \tag{5.47}$$

V_{s2l} arises from the first operator in (5.46), it is independent of $\boldsymbol{\sigma}_1$,

$$V_{s2l} = V'\boldsymbol{\sigma}_2\boldsymbol{l}/2m_1m_2r. \tag{5.48}$$

As V_{s1l} (4.283) is still called the spin-orbit potential, the part V_{s2l} of the nonrelativistic hyperfine operator is called the "other" spin-orbit potential. It is always smaller than V_{s1l}. For $m_1 = m_2$, it is half as large. Both potentials V_{sil} are symmetric in m_1 and m_2 and must not be attributed to particles i (Pilkuhn 2001). The sum of their expectation values agrees with (3.164).

The remaining H'_{hf} of (5.47) requires a somewhat tricky decomposition of $\boldsymbol{r} \times (\boldsymbol{\sigma}_2 \times \nabla)$: The rule $\boldsymbol{a} \times (\boldsymbol{b} \times \boldsymbol{c}) = \boldsymbol{b}(\boldsymbol{a}\boldsymbol{c}) - (\boldsymbol{a}\boldsymbol{b})\boldsymbol{c}$ implies $\boldsymbol{r} \times (\boldsymbol{\sigma}_2 \times \nabla) = \boldsymbol{\sigma}_2(\boldsymbol{r}\nabla) - (\boldsymbol{r}\boldsymbol{\sigma}_2)\nabla$, thus giving

$$-(V'/r)\boldsymbol{\sigma}_1[\boldsymbol{r} \times (\boldsymbol{\sigma}_2 \times \nabla)] = (V'/r)[-\boldsymbol{\sigma}_1\boldsymbol{\sigma}_2(\boldsymbol{r}\nabla) + (\boldsymbol{\sigma}_2\boldsymbol{r})(\boldsymbol{\sigma}_1\nabla)]. \tag{5.49}$$

The last operator can be decomposed into the product of a spin operator and a tensor t in coordinate space, provided the summation indices which are hidden in the scalar products are written explicitly:

$$(\boldsymbol{\sigma}_2\boldsymbol{r})(\boldsymbol{\sigma}_1\nabla) = \sum_{i,j} \sigma_{2i}\sigma_{1j}t_{ij}, \quad t_{ij} = r_i\partial_j. \tag{5.50}$$

A tensor t has 3×3 components; it may be decomposed into three "irreducible" tensors which do not mix under rotations,

$$t = t^{(0)} + t^{(1)} + t^{(2)}, \tag{5.51}$$

$t^{(l)}$ transforms under rotations like an operator of angular momentum l; $t^{(0)}$ like a scalar, $t^{(1)}$ like a vector:

$$t^{(0)}_{ij} = \delta_{ij}\Sigma_k t_{kk}/3. \tag{5.52}$$

δ_{ij} are the elements of the unit matrix 1, which remains the unit matrix after a rotation. With trace(1) = 3, the remaining matrix $t^{(1)} + t^{(2)}$ is traceless; $t^{(1)}$ is its antisymmetric part:

$$t_{ij}^{(1)} = \tfrac{1}{2}(t_{ij} - t_{ji}). \tag{5.53}$$

It vanishes for $i = j$ and has only three independent components. The remaining tensor $t^{(2)}$ is now automatically symmetric and traceless and contains the remaining five independent components,

$$t_{ij}^{(2)} = \tfrac{1}{2}(t_{ij} + t_{ji}) - \delta_{ij}\Sigma_k t_{kk}/3. \tag{5.54}$$

One easily checks $t_{ij} = t_{ij}^{(0)} + t_{ij}^{(1)} + t_{ij}^{(2)}$. One writes symbolically $3\times3 = 1+3+5$. A general tensor is decomposed into its irreducible pieces by means of the "Clebsch-Gordan series". More about tensors in Sect. 5.6. The complicated decomposition of t_{ij} is not necessary, but it helps. In (5.50), $t_{ij} = r_i\partial_j$ gives

$$t_{ij}^{(0)} = \delta_{ij}\boldsymbol{r}\nabla/3 = \delta_{ij}r\partial_r/3, \tag{5.55}$$

$$t_{ij}^{(1)} = \tfrac{1}{2}(r_i\partial_j - r_j\partial_i) = \tfrac{1}{2}(\boldsymbol{r}\times\boldsymbol{\nabla})_k = \tfrac{1}{2}il_k. \tag{5.56}$$

The decomposition of H'_{hf} of (5.47) into irreducible pieces is

$$H'_{hf} = -(V'/r)\boldsymbol{\sigma}_1[\boldsymbol{r}\times(\boldsymbol{\sigma}_2\times\nabla)]/2m_1m_2 = H_{hf}^{(0)} + H_{hf}^{(1)} + H_{hf}^{(2)}, \tag{5.57}$$

where $H_{hf}^{(0)}$ includes the first term of (5.49):

$$H_{hf}^{(0)} = -(V'/r)\boldsymbol{\sigma}_1\boldsymbol{\sigma}_2(\boldsymbol{r}\nabla)/3m_1m_2, \tag{5.58}$$

$$H_{hf}^{(1)} = (V'/r)i\boldsymbol{\sigma}^{\times}\boldsymbol{l}/4m_1m_2 \equiv V_{s12l}, \tag{5.59}$$

$$H_{hf}^{(2)} = (V'/r)[\boldsymbol{\sigma}_2\boldsymbol{r}\boldsymbol{\sigma}_1\nabla/2 + \boldsymbol{\sigma}_1\boldsymbol{r}\boldsymbol{\sigma}_2\nabla/2 - \boldsymbol{\sigma}_1\boldsymbol{\sigma}_2(\boldsymbol{r}\nabla)/3]/2m_1m_2. \tag{5.60}$$

$H_{hf}^{(1)}$ is an anti-Hermitian spin-orbit potential. Its expectation value vanishes, such that it is needed in $E(\alpha_Z^4)$ only in the case of degeneracy (see below). The other two operators contribute only with their Hermitian parts. For s-states, these parts are formally too singular, as in the case of the Darwin term discussed at the end of Sect. 2.8. Also here, one can simply ignore the s-state operators and instead extrapolate the energy shifts in the orbital angular momentum l down to $l = 0$. In the following, the traditional method is presented, in which any operator containing $\boldsymbol{l}$ is taken to vanish for s-states. To illustrate the problem, set $\boldsymbol{r}\nabla = r\partial_r$ in $H_{hf}^{(0)}$. For $V = -\alpha_Z/r$, the Hermitian part of $-V'\partial_r = -\alpha_Z/r^2\partial_r$ is $\alpha_Z[\partial_r, r^{-2}]/2 = -\alpha_Z r^{-3}$, with $\langle r^{-3}\rangle_{l=0} = \infty$ according to (2.259). To obtain the correct result, one must return to the Hermitian part of the original operator (5.44), which means the re-substitution

$$(V'/r)\boldsymbol{r}\nabla = [\nabla, V]\nabla. \tag{5.61}$$

As $[\nabla, V]$ and ∇ are Hermitian and anti-Hermitian, respectively, the Hermitian part of (5.61) is

$$\tfrac{1}{2}[\nabla, V]\nabla - \tfrac{1}{2}\nabla[\nabla, V] = -\tfrac{1}{2}[\nabla[\nabla, V]] = -\tfrac{1}{2}\Delta V = 2\pi\alpha_Z\delta(\boldsymbol{r}). \tag{5.62}$$

The last expression follows from (2.262). The Hermitian part of $H_{hf}^{(0)}$ is called the Fermi contact term,

$$V_{\rm con} = \tfrac{1}{2}(H_{hf}^{(0)} + H_{hf}^{(0)\dagger}) = \tfrac{2}{3}\pi\alpha_Z\delta(\boldsymbol{r})\boldsymbol{\sigma}_1\boldsymbol{\sigma}_2/m_1m_2. \tag{5.63}$$

With $\boldsymbol{\sigma}_1\boldsymbol{\sigma}_2 = 1$ for triplet states and -3 for singlet states, the Fermi splitting of s-states, $E_F = E(\text{triplet}) - E(\text{singlet})$ is

$$E_F = \tfrac{8}{3}\alpha_Z^4\mu^3/n^3m_1m_2 = \tfrac{8}{3}\alpha_Z^4\mu^2/n^3m_{12}. \tag{5.64}$$

The expectation value of $H_{hf}^{(2)}$ vanishes for s-states by rotational invariance. And as $\langle\delta(\boldsymbol{r})\rangle$ vanishes for all other states, the operator $\boldsymbol{\sigma}_1\boldsymbol{\sigma}_2(\boldsymbol{r}\nabla)/3$ can be omitted from $H_{hf}^{(2)}$. The Hermitian parts of $[\partial_i, V]\partial_j$ and $[\partial_j, V]\partial_i$ are both $-\frac{1}{2}[\partial_j, [\partial_i, V]] = \frac{1}{2}\alpha_Z[3r_ir_j/r^5 - \delta_{ij}/r^3]$. Consequently,

$$H_{hf}^{(2)} = \alpha_Z\sigma_t/4m_1m_2r^3 = \sigma_tV'/4m_1m_2r \equiv V_t, \quad \sigma_t \equiv 3\sigma_{1r}\sigma_{2r} - \boldsymbol{\sigma}_1\boldsymbol{\sigma}_2. \tag{5.65}$$

This is the "tensor potential". In ordinary atoms, particle 2 is a nucleus with spin operator $\boldsymbol{s}_2$ and g-factor g_{2n}. There, $\boldsymbol{\sigma}_2/m_2$ is replaced by $g_{2n}\boldsymbol{s}_2/m_p$, where m_p arises from the use of the nuclear magneton μ_n as in the Zeeman operator (4.149).

To calculate σ_t, one observes that the pseudoscalar $\sigma_{ir} = \boldsymbol{\sigma}_i\boldsymbol{r}/r$ change l by one unit. In the triplet-singlet basis (5.32), one has

$$\sigma_{ir} = \begin{pmatrix} 0 & \hat{\sigma}_{ir} \\ \hat{\sigma}_{ir}^\dagger & 0 \end{pmatrix}, \quad \hat{\sigma}_{1r} = \begin{pmatrix} s & c \\ c & -s \end{pmatrix}, \quad \hat{\sigma}_{2r} = \begin{pmatrix} s & -c \\ c & s \end{pmatrix}. \tag{5.66}$$

The matrix $\hat{\sigma}_{1r}$ is the same as in (5.36); it arises from the transformation (5.27). The product $\sigma_{1r}\sigma_{2r}$ changes l by 0 or 2 units:

$$\sigma_{1r}\sigma_{2r} = \frac{1}{2f{+}1}\begin{pmatrix} -1 & 2F & 0 & 0 \\ 2F & 1 & 0 & 0 \\ 0 & 0 & 2f{+}1 & 0 \\ 0 & 0 & 0 & -2f{-}1 \end{pmatrix}, \quad \boldsymbol{\sigma}_1\boldsymbol{\sigma}_2 = \begin{pmatrix} 1&0&0&0 \\ 0&1&0&0 \\ 0&0&1&0 \\ 0&0&0&-3 \end{pmatrix}. \tag{5.67}$$

The anti-Hermitian V_{s12l} contributes to the α_Z^4 level splitting only in l-degenerate states at fixed f, for example in P states where it mixes ^{3}P with ^{1}P for $f = 1$. The nonvanishing submatrix of $i\boldsymbol{\sigma}^\times\boldsymbol{l}$ is given in (5.35). It is conveniently combined with the submatrices of σ_t and $\boldsymbol{\sigma}_2\boldsymbol{l}$:

$$\chi = \begin{pmatrix} \chi_{f,1} \\ \chi_{f,0} \end{pmatrix}, \quad \sigma_t = \begin{pmatrix} 2&0 \\ 0&0 \end{pmatrix}, \quad V_t + V_{s2l} + V_{s12l} = \begin{pmatrix} 0&0 \\ F&0 \end{pmatrix}\frac{-V'}{rm_1m_2}. \tag{5.68}$$

Writing moreover $1/m_1m_2 = \mu/E\mu^2$, this may be combined with the ordinary spin-orbit potential V_{s1l} into the total spin potential,

$$V_s = V_{s1l} + V_t + V_{s2l} + V_{s12l} = \begin{pmatrix} -1 & F \\ F(1-4\mu/E) & 0 \end{pmatrix} \frac{V'}{4r\mu^2}. \tag{5.69}$$

For its use in first-order perturbation theory, the matrix must be diagonalized; its eigenvalues will be denoted by $-2a_l^{(\pm)}l(l+1)$ for later purposes:

$$-2a_l^{(\pm)}l(l+1) = \tfrac{1}{2}[-1 \pm \sqrt{1+4l(l+1)(1-4\mu/E)}]. \tag{5.70}$$

Here we have inserted $F^2 = l(l+1)$. To first order in μ/E, this produces the ordinary fine and hyperfine splitting. Note in particular that $\mu/E = 0$ reduces the square bracket to

$$\tfrac{1}{2} \pm (l+\tfrac{1}{2}) = \tfrac{1}{2} + (l-j)(j+\tfrac{1}{2}), \tag{5.71}$$

where $j = l \pm \frac{1}{2}$ as in (2.121). Positronium, on the other hand, has $\mu/E \approx 4$,

$$2a_l^{(+)}l(l+1) = -1, \quad 2a_l^{(-)} = 0. \tag{5.72}$$

By charge conjugation, the factor $1 - 4\mu/E$ must in fact be replaced by a factor that vanishes exactly for $m_1 = m_2$. Such a factor is m_-^2/E^2 for $\beta = 1$, namely $\delta m^2/E^2 \equiv \delta\hat{m}^2$, with $\delta m = m_2 - m_1$:

$$V_s = A_{\rm sim}V'/4r\mu^2, \quad A_{\rm sim} = \begin{pmatrix} -1 & F \\ F\delta\hat{m}^2 & 0 \end{pmatrix}. \tag{5.73}$$

In the CBG-reduction of the 16-component formalism, a corresponding matrix $A^{\rm CBG}$ arises from $V_{s1l}^{\rm CBG} + V_{s2l}^{\rm CBG} + V_t^{\rm CBG}$ (see (3.164). As V_t (5.65) is both Hermitian and symmetric in (m_1, m_2), one has $V_t^{\rm CBG} = V_t$). The identical eigenvalues of $A_{\rm sim}$ and $A^{\rm CBG}$ imply a similarity transformation as in (2.170):

$$A_{\rm sim} = MA^{\rm CBG}M^{-1}, \quad A^{\rm CBG} = \begin{pmatrix} -1 & F\delta\hat{m} \\ F\delta\hat{m} & 0 \end{pmatrix}, \quad M = \begin{pmatrix} \delta\hat{m}^{-1/2} & 0 \\ 0 & \delta\hat{m}^{1/2} \end{pmatrix}. \tag{5.74}$$

The Hermitian form simplifies higher order perturbation theory.

Expansion of the square root of (5.70) to order $(\mu/E)^2$ produces energy shifts that are classified as quadratic hyperfine shifts. For the calculation of other second-order effects, one must either use second-order perturbation theory, or one must include the operators non-perturbatively. The latter possibility exists for the "generalized Todorov" equation (4.213), which is the two-body version of the generalized KG equation (2.273). One merely has to use the appropriate generalization of $l_\alpha(l_\alpha+1)$ (2.272),

$$L_\alpha^2 = L^2 - \alpha_Z^2 - \alpha_Z^2 A_l, \quad L^2 = l(l+1), \tag{5.75}$$

$$A_l = -[2l(l+1)]^{-1}[\boldsymbol{\sigma}_1\boldsymbol{l} + (2\boldsymbol{\sigma}_2\boldsymbol{l} + 2i\boldsymbol{\sigma}^\times\boldsymbol{l} + \sigma_t)\mu/m_{12}], \tag{5.76}$$

which is then diagonalized at fixed l. The eigenvalues are $a_l^{(\pm)}$, or a_{lf} in the case of $f = l \pm 1$. This form is only possible because $V'/r = \alpha_Z/r^3$ is equivalent to $r^{-2}\alpha_Z^2\mu/L^2$, or better $V'_\rho/\rho \approx \rho^{-2}\alpha_Z^2/L_\alpha^2$ according to (A.43), with $\epsilon/\mu \approx 1$. It is essential that the equivalence is independent of n, such that it remains valid also for the continuum states.

Note that $\langle\sigma_t\rangle_{l,0} = 0$, and that

$$\langle\sigma_t\rangle_{f-1} = 3/(2l+3) - 1 = -l/(l+3/2), \tag{5.77}$$

such that a_{ljf} remains finite for $l = 0$:

$$a_{f=l+1} = -(2l+2)^{-1} - (l+3/2)^{-1}\mu/m_{12}. \tag{5.78}$$

The part $-(2/3)\mu/m_{12}$ of $a_{0,1/2,1}$ is the triplet part of the Fermi splitting E_F, which in the nonrelativistic reduction arises from the contact term (5.63). Clearly, the extrapolation of the relativistic equation is simpler than the nonrelativistic reduction. Higher orders in α_Z may contain operators which cannot be extrapolated to $l = 0$. However, whenever the extrapolation is finite, it is also correct. The relativistic equation is a regular function of l, with no singularity at $l = 0$.

Defining the quantum defect $\beta_l = l - l_\alpha$ as in (1.126), one obtains the solutions of the nonrelativistic Schrödinger version (4.212) in the form of the quantum defect formula,

$$\epsilon/\mu - 1 = -\tfrac{1}{2}\alpha_Z^2(n-\beta_l)^{-2} \approx -\tfrac{1}{2}\alpha_Z^2(n^{-2} + 2\beta_l n^{-3} + 3\beta_l^2 n^{-4}), \tag{5.79}$$

$$\beta_l = l + 1/2 - \sqrt{(l+1/2)^2 - \alpha_Z^2(1+a_{ljf})} \approx \alpha_Z^2(1+a_{ljf})/(2l+1). \tag{5.80}$$

which differs from the original form (1.37) only by the substitutions $E_N \to \epsilon - \mu$ and $m_e \to \mu$. The nonrelativistic appearance of the hyperfine operator is not new: In the Pauli Hamiltonian (2.237), its static limit emerges from $(\boldsymbol{\pi}_1\boldsymbol{\sigma}_1)^2/2m_1$, with $\boldsymbol{\pi}_1 = \boldsymbol{p}_1 + (e/c)\boldsymbol{A}_{hf}$ and with $\boldsymbol{A}_{hf}$ from (4.153).

Generalizations of V_s for large g-factors will be given in Sect. 5.7.

5.3 Vacuum Polarization, Dispersion Relations

The Poisson equation (1.58) was solved in (1.60) for a nuclear point charge, $\rho_{\rm el} = Ze\delta(\boldsymbol{r})$, giving $A^0 = Ze/r$ and the familiar point Coulomb potential, $V = -eA^0 = -\alpha_Z/r$ in the equation of motion of a particle of charge $-e$. The quantum field version of that equation,

$$-\nabla^2 A^0_{\rm tot} = 4\pi[Ze\delta(\boldsymbol{r}) - e\Psi_D^\dagger\Psi_D + \rho'_{\rm el}] \tag{5.81}$$

gave the additional Coulomb potential $V_{ij} = e^2/r_{ij}$ between a pair (i,j) of electrons. But even for hydrogen-like, one-electron atoms the operator $e\Psi_D^\dagger\Psi_D$

makes a small contribution which is illustrated by the picture of "vacuum polarization": $\Psi_D^\dagger \Psi_D$ creates "virtual" electron-positron pairs, with a vanishing charge density in the absence of external charges. This "cloud" of virtual pairs gets polarized in the nuclear vicinity, which entails a partial screening of the nuclear charge. A bound electron is moving mainly outside the polarized cloud, where it sees the screened charge which is smaller than the "naked" charge of the nucleus inside. The cloud has a radius of about $1/2m_e$, which is much smaller than the electron Bohr radius (1.39), $a_\mathrm{B} = 1/\alpha m_e$. The naked nuclear charge appears only near $r = 0$, where the additional operator is well approximated by a function $\delta(\boldsymbol{r})$. For muonic, mesic or antiprotonic atoms, on the other hand, one must compare the cloud radius $1/2m_e$ with the extension of the wave function $e^{-\kappa r}/r$,

$$\kappa^{-1} = n/\alpha_Z \mu, \tag{5.82}$$

where $\mu \gg m_e$ is the reduced mass. These two radii are of the same order of magnitude, and the vacuum polarization produces a special potential V_U (Uehling 1935), which has been evaluated in great detail mainly for muonic atoms (Borie and Rinker 1982). A convenient form of V_U is a superposition of "Yukawa potentials" e^{-xr}/r,

$$V_U = \tfrac{2}{3} q_1 q_2 \alpha_\pi I(2m_e r)/r, \tag{5.83}$$

$$I = \int_1^\infty d\xi e^{-2m_e r\xi}(\xi^{-2} + \tfrac{1}{2}\xi^{-4})(\xi^2 - 1)^{1/2}, \tag{5.84}$$

with $\alpha_\pi = \alpha/\pi$. Hydrogenlike atoms have $q_1 q_2 = -Ze^2 = -\alpha_Z$, but the Uehling potential operates also in proton-nucleus scattering, where it increases the Coulomb repulsion. For hydrogenlike atoms, the total potential is

$$V = V_C + V_U, \quad V_C = -\alpha_Z/r. \tag{5.85}$$

This V is sometimes called the "electric" potential. It appears also in the hyperfine operator (4.235).

If one wants to derive V_U by the nonperturbative method of Chap. 3, one must modify the ansatz (3.69) for the bound state. Despite the above interpretation of the phenomenon, it is best calculated from the QED Born series. The calculation is complicated and entails a redefinition ("renormalization") of the electric charge, not only for nuclei, but for all particles.

In the higher orders of the QED Born series, one must really use the equations of motion for field operators Ψ, not for wave functions ψ. The "causality principle" of time-dependent perturbation theory postulates that a perturbation at time y^0 modifies the initial field $\Psi_\mathrm{in}(x) = \Psi_\mathrm{in}(x^0, \boldsymbol{x})$ only at times $y^0 > x^0$. The iterative solution of the equation for Ψ is again of the form (4.10), but now the propagator $S(x-y)$ must be taken as the retarded one,

$$\Psi(x) = \Psi_\mathrm{in}(x) - e \int d^4y S_R(x-y)\gamma^\mu A_\mu(y)\Psi(y), \quad S_R(y^0 < x^0) = 0. \tag{5.86}$$

According to (4.8),

$$S_R = -(i\partial^\mu \gamma_\mu + m_e)\Delta_R, \quad \Delta_R(x) = (2\pi)^{-4} \int d^4p e^{-ipx} \Phi_R(p^\mu), \tag{5.87}$$

where Φ_R is the retarded propagator (4.19). The current operator j (3.60) is expanded in powers of e,

$$j_\mu = \tfrac{1}{2}[\Psi^\dagger, \gamma_\mu \Psi] = j_\mu^{(0)} + j_\mu^{(1)} + \ldots, \tag{5.88}$$

$$j_\mu^{(0)} = \tfrac{1}{2}[\Psi_{\text{in}}^\dagger, \gamma_\mu \Psi_{\text{in}}], \tag{5.89}$$

$$-e j_\mu^{(1)} = \int d^4x' \Pi_{\mu\nu}(x - x') A^\nu, \tag{5.90}$$

$$\Pi_{\mu\nu} = \tfrac{1}{2} e^2 \{[\Psi_{\text{in}}^\dagger, \gamma_\mu S_R(x - x')\gamma_\nu \Psi_{\text{in}}(x')] + [\Psi_{\text{in}}^\dagger(x')\gamma_\nu S_R^\dagger(x - x'), \gamma_\mu \Psi_{\text{in}}]\}. \tag{5.91}$$

$$S_R^\dagger \equiv (i\partial^\mu \gamma_\mu - m_e)\Delta_R. \tag{5.92}$$

This expression can be used directly in the S-matrix of two-body scattering, for example by replacing in (4.57) the $g_{\mu\nu} j_2^\nu = j_{2,\mu}$ by $j_\mu^{(1)}$:

$$S_{if}^{(2)} = -4\pi i e^2 \int d^4y d^4x D(y - x) j_1^\mu(y) j_\mu^{(1)}(x). \tag{5.93}$$

The A^ν to be used in $j_\mu^{(1)}$ is again of the form (4.55), but with j_{el} replaced by the current Zej_2 of the other particle:

$$A^\nu(x') = \int d^4z D(x' - z) 4\pi Z e j_2^\nu(z). \tag{5.94}$$

In this manner, the final form of $S_{if}^{(2)}$ is again symmetric in j_1 and j_2. When neither j_1 nor j_2 contain electrons or positrons

$$S_{if}^{(2)} = i16\pi^2 \alpha_Z \int d^4y d^4z j_1^\mu(y) j_2^\nu(z) \int d^4x d^4x' D(y - x) D(x' - z) \Pi_{\mu\nu}^{(0)}(x - x'), \tag{5.95}$$

where the "vacuum polarization tensor" $\Pi_{\mu\nu}^{(0)}$ is the expectation value of $\Pi_{\mu\nu}$ with respect to the electron-positron vacuum:

$$\Pi_{\mu\nu}^{(0)} = \langle 0 | \Pi_{\mu\nu} | 0 \rangle. \tag{5.96}$$

The symmetry of (5.95) shows that vacuum polarization is not a property of one of the two particles. It modifies both charges, $q_1 = -e$ and $q_2 = Ze$. It is visualized by the Feynman graph of Fig. 4.3. For the details, one Fourier transforms D according to (4.56) and also $\Pi_{\mu\nu}^{(0)}$:

$$\Pi_{\mu\nu}^{(0)}(x - x') = (2\pi)^{-4} \int d^4q e^{-iq(x - x')} \Pi_{\mu\nu}(q). \tag{5.97}$$

The integrations over y, z, x and x' are then performed explicitly. Each integration produces a δ_4-function of some combination of 4-momenta. Three of these δ_4-functions are cancelled by the integrals over p, p' and q of the

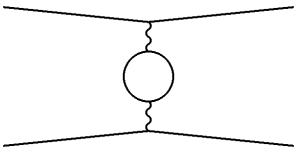

Fig. 5.1. The vacuum polarization graph

Fourier transforms. The remaining δ_4-function expresses energy-momentum conservation as in (4.63). The total T-matrix $T = T^{(1)} + T^{(2)}$ is then

$$T_{if} = 4\pi\alpha_Z J^{\mu}_{11'}(g_{\mu\nu}/t + \Pi_{\mu\nu}(q)/t^2)J^{\nu}_{22'}. \tag{5.98}$$

Current conservation requires $\partial^{\mu}\Pi^{(0)}_{\mu\nu} = \partial^{\nu}\Pi^{(0)}_{\mu\nu} = 0$. For $\Pi_{\mu\nu}(q)$, this entails the tensorial form

$$\Pi_{\mu\nu}(q) = (q_{\mu}q_{\nu} - g_{\mu\nu}t)\Pi(t), \quad t = q^{02} - \boldsymbol{q}^2. \tag{5.99}$$

For $q^0 > 0$, a dependence of Π on the sign of q^0 would be compatible with Lorentz invariance. But this is ruled out by CPT, which says that the inverse antiparticle scattering $\overline{f} \to \overline{i}$ is related to T_{if} simply by the reversal of all 4-momenta (see the end of Sect. 3.2):

$$T_{\overline{f},\overline{i}}(q^{\mu}, \ldots) = T_{if}(-q^{\mu}, - \ldots). \tag{5.100}$$

The additional 4-momenta are suppressed because they do not enter Π. If T_{if} for the particle scattering is evaluated in its cms $\boldsymbol{q} = 0$, $q^0 > 0$, $T_{\overline{f},\overline{i}}$ of the corresponding antiparticle scattering is identical to T_{if} at cms energy $-q^0$. Therefore, Lorentz invariance plus CPT implies

$$\Pi(q^0) = \Pi(-q^0). \tag{5.101}$$

On the other side, $J^{\mu}_{11'}q_{\mu} = 0$ and $J^{\nu}_{22'}q_{\nu} = 0$ eliminate a possible contribution of $q_{\mu}q_{\nu}$:

$$T_{if} = 4\pi\alpha_Z J^{\mu}_{11'}g_{\mu\nu}J^{\nu}_{22'}(1 - \Pi(t))/t. \tag{5.102}$$

When the potential $V(r)$ is calculated as the Fourier transform of T, its long-range limit $V(r \to \infty)$ depends only on $T(t \to 0)$, $V(r \to \infty) = -\alpha_Z(1 - \Pi(0))/r$. If one wants to keep the notation $V = -\alpha_Z/r$, one must identify the e in T_{if} with the "naked" charge e_n:

$$V_C = -Ze^2/r, \;\; e^2/\hbar c = \alpha, \quad e^2 = e_n^2(1 - \Pi(0)). \tag{5.103}$$

Alternatively, one may keep the symbol e for the naked charge, in which case the charge e in the Coulomb potential must be specified as "renormalized charge" e_r, with $e_r^2/\hbar c = \alpha$. This is less elegant because it turns out that the naked charge has no physical significance, to all orders in perturbative QED.

Although Π has been assumed to be small, it is in fact infinite. For small $\Pi(0)$, the combination $e_n^2(1-\Pi(t))$ in (5.102) may be rewritten as

$$e_n^2[1-\Pi(t)] = e^2[1-\Pi(t)+\Pi(0)], \tag{5.104}$$

neglecting terms of order Π^2. These terms are taken care of by higher order perturbation theory, and their measurable parts are tiny. The difference $\Pi(t)-\Pi(0)$ is small and produces the Uehling potential, which has been verified experimentally with good precision. In summary, T_{if} (5.98) is expressed in terms of the measured charge e by means of (5.104),

$$T_{if} = 4\pi Z e^2 J^{\mu}_{11'} g_{\mu\nu} J^{\nu}_{22'} t^{-1}[1+\Pi(0)-\Pi(t)]. \tag{5.105}$$

A standard way of calculating higher-order radiative corrections is by means of "Feynman rules" in momentum space. The "loop integrals" $\int d^4k$ diverge and need a momentum cutoff $\Lambda = k_{\max}$. Unfortunately, this procedure destroys gauge invariance. The contribution of $q_\mu q_\nu$ in (5.99) does not vanish and makes the integral diverge quadratically, i.e. as Λ^2. It has been customary to first postulate gauge invariance to get the form (5.102), and to introduce the cutoff afterwards. This inconsistent procedure was later replaced by t' Hooft and Veltman (1972) by the gauge invariant "dimensional regularization". It replaces the $\int d^4k$ by a $\int d^dk$, where $d<4$ is an artificially lowered dimension of space-time. This is technically simple in the Feynman parametrisation of Feynman integrals (see for example Ryder 1985, Itzykson and Zuber 1990, Brown 1992, Weinberg 1995). In the following, a different "dispersion relation" method is presented which uses unitarity and analyticity of the S-matrix. It is independent of the convergence of the Born series, and it is also more "physical" in that only the experimentally measured mass spectrum appears in the unitarity equation. Moreover, for vacuum polarization, it is by far the simplest procedure.

We begin with the Fourier inversion of (5.97) and take q^0 explicitly complex, $q^0 = \operatorname{Re} q^0 + i \operatorname{Im} q^0$. We also abbreviate $x^0 - x^{0\prime} = \Delta t$, and $\boldsymbol{x} - \boldsymbol{x}' = \Delta \boldsymbol{r}$:

$$\Pi_{\mu\nu}(q) = \int d^3r \Delta r e^{-i\boldsymbol{q}\Delta\boldsymbol{r}} \int_0^\infty d\Delta t e^{i\Delta t \operatorname{Re} q^0} e^{-\Delta t \operatorname{Im} q^0} \Pi_{\mu\nu}(\Delta t, \Delta \boldsymbol{r}). \tag{5.106}$$

The retarded Greens function S_R in (5.91) guarantees $\Pi_{\mu\nu}(x^0 - x^{0\prime}) = 0$ for $x^{0\prime} < x^0$, such that the $\int_{-\infty}^0 d\Delta t \ldots$ vanishes. Consequently, $\Pi_{\mu\nu}(q)$ falls exponentially for $\operatorname{Im} q^0 > 0$, which is the upper half of the complex q^0 plane. Calling $q^0 = z$ and $\Pi_{\mu\nu}(q^0) = f(z)$ for a moment, one can evaluate $f(z)$ by means of a Cauchy integral as in (4.15), which in the present case encloses the upper half z-plane counterclockwise:

$$f(z) = (2\pi i)^{-1} \int_{-\infty}^{\infty} dx f(x)(x-z)^{-1}. \tag{5.107}$$

Equation (5.107) is the origin of the factor π^{-1} in the $\alpha_\pi = \alpha/\pi$ defined in (1.114).

A direct use of the CPT symmetry (5.101) is not possible because it changes the sign of $\operatorname{Im} q^0$. An analytic function $f(z)$ is decomposed into its "real-analytic" and "imaginary-analytic" parts as follows:

$$f(z) = h(z) + g(z), \quad h^*(z) = h(z^*),\ g^*(z) = -g(z^*). \tag{5.108}$$

For real z, h and g are real and imaginary, respectively. We shall find below from unitarity that $\operatorname{Im} \Pi$ vanishes on a part of the real q^0-axis, namely $0 < q^0 < 2m_e$, $2m_e$ being the threshold for production of electron-positron pairs. By analytic continuation, a function which vanishes on a line vanishes everywhere. Thus $g = 0$; Π is real-analytic, $f(z^*) = f^*(z)$. f may be continued across this line from the upper half plane into the lower one, and the Cauchy integral may enclose the entire complex q^0 plane, except for the cut $2m_e < q^0 < \infty$ of the particle process and the cut $-\infty < q^0 < -2m_e$ of its antiparticle process. As the integration contour goes clockwise in the upper half plane, it goes counterclockwise in the lower half plane. Close to the real q^0-axis, this leads to the conbination $f(x_+) - f(x_-) = 2 \operatorname{Im} f(x_+)$, where

$$x_\pm = x \pm i\epsilon, \tag{5.109}$$

and $x = q^{0\prime}$ is now real. The Cauchy integral becomes

$$\Pi(q_+^0) = \pi^{-1} \left(\int_{-\infty}^{-2m_e} + \int_{2m_e}^{\infty} \right) \frac{dx}{x - q_+^0} \operatorname{Im} \Pi(x). \tag{5.110}$$

Equations of this type were first found by Kramers and Kronig for the index of refraction in optics; they are called dispersion relations. They result from the use of retarded propagators, which obey the causality postulate (see also Stone 2000). The case at hand is simplified as follows:

$$\pi^{-1} \int_{2m_e}^{\infty} \left(\frac{dx}{x - q_+^0} + \frac{dx}{x + q_-^0} \right) \operatorname{Im} \Pi(x) = \pi^{-1} \int_{2m_e}^{\infty} \frac{2x dx}{x^2 - q^{02} - i\epsilon} \operatorname{Im} \Pi(x). \tag{5.111}$$

In terms of the variable $t' = x^2$ with $2x dx = dt'$,

$$\Pi(t_+) = \pi^{-1} \int_{t_{\text{th}}}^{\infty} \frac{dt'}{t' - t_+} \operatorname{Im} \Pi(t'), \quad t_{\text{th}} = 4m_e^2. \tag{5.112}$$

With $\Pi = \operatorname{Re} \Pi + i \operatorname{Im} \Pi$, the imaginary part of the dispersion relation is an identity. To see this, call $t' - t - i\epsilon = x - i\epsilon$. In the integrand,

$$(x - i\epsilon)^{-1} = x(x^2 + \epsilon^2)^{-1} + i\epsilon(x^2 + \epsilon^2)^{-1} = \mathcal{P}/x + i\pi\delta(x). \tag{5.113}$$

$\mathcal{P}$ is the "principal value", which says that an infinitesimal interval δ on either side of $x = 0$ is omitted from the integral. For any function $f(x)$ which is regular at $x = 0$,

$$\int_{-\delta}^{\delta} \frac{x dx f(x)}{x^2 + \epsilon^2} = \int_{-\delta/\epsilon}^{\delta/\epsilon} \frac{y dy f(\epsilon y)}{y^2 + 1} \to f(0) \int_{-\delta/\epsilon}^{\delta/\epsilon} \frac{y dy}{y^2 + 1} = 0. \tag{5.114}$$

The imaginary part of (5.113) follows from

$$\int_{x_1}^{x_2} \frac{\epsilon dx f(x)}{x^2+\epsilon^2} = \tan^{-1}\left(\frac{x}{\epsilon}\right)_{x_1}^{x_2} - \int_{x_1}^{x_2} \tan^{-1}\left(\frac{x}{\epsilon}\right)\frac{df}{dx} = \pi f(0), \tag{5.115}$$

as $\tan^{-1}(x/\epsilon)$ is either $+\pi/2$ or $-\pi/2$ in the limit $\epsilon \to 0$, depending on the sign of x. The useful part of (5.112) is thus

$$\mathrm{Re}\,\Pi(t) = \pi^{-1}\mathcal{P}\int_{t_{\mathrm{th}}}^{\infty} \frac{dt'}{t'-t}\,\mathrm{Im}\,\Pi(t'). \tag{5.116}$$

A last difficulty is the divergence of the integral for $t' \to \infty$. It is removed by subtracting from (5.112) the relation for Π at a given point $t = t_s$. With $(t'-t)^{-1} - (t'-t_s)^{-1} = (t-t_s)/(t'-t)(t'-t_s)$,

$$\Pi(t) - \Pi(t_s) = \pi^{-1}\mathcal{P}(t-t_s)\int_{t_{\mathrm{th}}}^{\infty} \frac{dt'}{(t'-t)(t'-t_s)}\,\mathrm{Im}\,\Pi(t'). \tag{5.117}$$

The extra power of t' in the denominator makes the integral convergent. Insertion of $t = t_s$ in (5.117) shows that $\Pi(t_s)$ remains undetermined. The particular value of the subtraction point t_s is a matter of convenience. For atomic bound state calculations, it is advisable to set $t_s = 0$ in view of the asymptotic form (5.103) with its known value, $\alpha = 137.036^{-1}$: $\mathrm{Im}\,\Pi(t' < 4m_e^2) = 0$ implies that the principal value prescription is unnecessary for $t < 4m_e^2$,

$$t^{-1}[\Pi(t) - \Pi(0)]_{t<t_{\mathrm{th}}} = \pi^{-1}\int_{t_{\mathrm{th}}}^{\infty} dt'\,\mathrm{Im}\,\Pi(t')/t'(t'-t). \tag{5.118}$$

For possible bound states deep inside the vacuum polarization cloud, a value $t_s < 0$ could be chosen in order to subtract a constant value of the vacuum polarization. In that case

$$\alpha_Z(t_s) = \alpha_Z[1 + \Pi(0) - \Pi(t_s)] \tag{5.119}$$

is larger than α_Z. In the quarkonium model of mesons, the absence of the asymptotic region $V(r \to \infty) = 0$ makes $t_s = 0$ useless. There, the coupling constant $\alpha_s(t_s)$ is a decreasing function of t_s (a "running coupling constant").

The t-dependence of the left-hand side of (5.118) is precisely the combination occurring in T_{if} (5.105); its Fourier transform gives the Uehling potential V_U. The Fourier transformation can be carried out explicitly under the t'-integral for arbitrary $\mathrm{Im}\,\Pi(t')$. Calling $t = -\boldsymbol{q}^2$, the transformation assumes a form that has been calculated already in (4.50),

$$\int d^3r e^{i\boldsymbol{q}\boldsymbol{r}} e^{-r\sqrt{t'}}/r = 4\pi(\boldsymbol{q}^2 + t')^{-1}. \tag{5.120}$$

Apart from the product of coupling constants, the function $e^{-r\sqrt{t'}}/r$ is called a Yukawa potential. It corresponds to the exchange of a photon of "mass"

$\sqrt{t'} \equiv x$. The Uehling potential is thus an integral over Yukawa potentials. The explicit form (5.83) includes only the $e\overline{e}$ ($\equiv e^-e^+$)-contribution, which is by far the largest one.

$\mathrm{Im}\,\Pi(t')$ is now obtained from the imaginary part of (5.102) on one side, and from the unitarity equation (4.99) on the other. In the rest frame of the virtual photon, one has $J^0 = 0$,

$$\begin{aligned} \mathrm{Im}\,T_{if} &= 4\pi\alpha_Z \boldsymbol{J}_{1,1'}\boldsymbol{J}_{2,2'}t^{-1}\,\mathrm{Im}\,\Pi(t) \\ &= \tfrac{1}{2}\sum_{\lambda,\lambda_p}\int \mathrm{dLips}(t) T^*(f \to e\overline{e})T(i \to e\overline{e}). \end{aligned} \tag{5.121}$$

The equation applies at fixed value of the total magnetic quantum number m_j, and one may restrict oneself to $m_j = 0$ as in (4.108). With $e_V = e$,

$$T(i \to e\overline{e}, 0) = e_{\mathrm{HL}} J^z_{1,1'} t^{-1} T(0), \quad T(f \to e\overline{e}, 0) = e_{\mathrm{HL}} J^z_{2,2'} t^{-1} T(0). \tag{5.122}$$

Here we have abbreviated $\sqrt{4\pi}e = e_{\mathrm{HL}}$ mainly in order to shorten the expressions, but also to illustrate the advantage of the Heaviside-Lorentz units which are otherwise avoided in this book. Comparison between the two sides of (5.121) shows, with (4.115) and $e^2 = \alpha$, $E = \sqrt{t'}$,

$$\mathrm{Im}\,\Pi(t') = E\Gamma(\gamma \to e^-e^+) = \tfrac{2}{3}\alpha(1 + 2m_e^2/t')k/\sqrt{t'}. \tag{5.123}$$

k is the t-channel cms momentum at total energy $\sqrt{t'} \equiv x$,

$$k = \sqrt{t'/4 - m_e^2} = \sqrt{x^2/4 - m_e^2}. \tag{5.124}$$

The $e\overline{e}$-continuum begins at the threshold $x_{\mathrm{th}} = 2m_e$, which is conveniently extracted from k:

$$\sqrt{t'} = x = 2m_e\xi, \quad k = m_e\sqrt{\xi^2 - 1}. \tag{5.125}$$

The final integral over ξ in (5.118) is now performed using (C.18); its Fourier transform produces V_U as given by (5.83). In ordinary electronic atoms, $z = 2m_e r$ is $\gg 1$,

$$I(2m_e r \gg 1) = \tfrac{3}{4}(\pi/m_e r)^{1/2} e^{-2m_e r}/2rm_e. \tag{5.126}$$

In many muonic, mesic and antiprotonic atoms, $2m_e r < 1$ dominates (see Sect. 5.6). The $r\sqrt{t'}$ in the exponent of (5.120) becomes $2m_e\xi r$, such that the form (5.83) of the Uehling potential results.

In one-electron atoms, $2m_e r > 1$ domimates. There, $\langle V_U\rangle$ may be calculated as a power series in α_Z. With (C.19) and (C.23),

$$\langle V_U\rangle_{nr} = -4\alpha_\pi\alpha_Z^4\mu^3\delta_{l,0}/15n^3m_e^2 = -\alpha_\pi\alpha_Z\delta_{l,0}|\psi_n(0)|^2/15m_e^2, \tag{5.127}$$

with $|\psi(0)|^2 = 4(\alpha_Z\mu/n)^3\delta_{l,0}$. This forms a minor part of the Lamb shift. Its first-order relativistic correction is derived in (C.25).

As the relativistic $|\psi_n(0)|^2$ diverges, the wave function correction (2.232) appears at the order α_Z^6. The complete correction is derived in (C.46),

$$1 + \alpha_Z^2[\log(nm_e/2\alpha_Z\mu) - \Psi(n+1) + \Psi(2) + 2/n - 2/n^2 - 1/28n^2 + 326/105]. \tag{5.128}$$

The $\log(nm_e/2\alpha_Z\mu) = \log(m_e/2\kappa)$ is derived in (C.30). The term $2/n$ may be viewed as the sum of $1/2n$ which appears in $\langle r_G^{-3}\rangle$, and $3/2n$ which arises from the product of two quantum defects in the expansion (2.147). Keeping only the β-dependent terms, one has

$$E_N/mc^2 = -\alpha_Z^2 n^{-3}(\beta_{\rm el} + 3\beta_{\rm el}^2/2n\ldots), \quad \beta_{\rm el} = \beta_j + \beta_U. \tag{5.129}$$

Here β_U is the quantum defect caused by the short-range Uehling potential. $\beta_0 = \alpha_Z^2/2$ and β_U are both positive. The term linear in β produces the main energy shift (5.127), while the product $\alpha_Z^2\beta_U$ in β^2 gives the above $-3/2n$.

Higher-order corrections to the vacuum polarization have either two or more $e\overline{e}$ loops, or at least two more photon couplings ("vertices") on the electron loop of Fig. 5.1. Loops with an odd number of vertices vanish by charge conjugation invariance ("Furry's theorem". Each photon in the initial or final state brings a factor -1 to charge conjugation, see also the end of Sect. 4.7). The simplest correction has one additional photon emitted and reabsorbed by the loop ("Källén-Sabry potential"), which gives an additional factor of $e^2 = \alpha$. Next come two-photon corrections, either with one photon from the loop to the upper line, the other to the lower line (factor $\alpha\alpha_Z$), or with both photons to the upper line (factor α^2), or with both photons to the lower line (factor $\alpha_Z^2 = Z^2\alpha^2$). The last graph gives the potential of Wichman and Kroll (1956). It becomes the dominant correction for $Z^2\alpha > 1$. Our introductory picture of "vacuum polarization by the nucleus" is then at least partly correct. Results for such higher-order corrections are reviewed by Eides et al. (2001).

5.4 Atomic Radiation

With the exception of the ground states, atomic states are unstable. Some states above the ionization limit decay by electron emission ("auto-ionization"), all others decay by photon emission. By far the largest decay rates arise from electric dipole radiation, in which the orbital angular momentum of the atom changes by one unit, without a change of spin. The radiation has an indirect effect also on the ground state, in that its "dispersive" part shifts its energy (Lamb shift). The finite lifetimes of excited states cause a "natural line width", which is largest for states decaying by electric dipole radiation. The lifetime of the 2p state is 1.6 ns, its width is 41×10^{-8} eV (the lifetime is the inverse of the decay rate Γ, the width in eV is 6.582×10^{-16} times the lifetime). The 2s state decays by two-photon emission to the 1s ground state, with a rate of $8.22\,{\rm s}^{-1}$.

The decay rate is calculated by time-dependent perturbation theory (Dirac 1926, 1927),

$$(i\hbar\partial_t - H^0)\psi(\boldsymbol{r}_1, \boldsymbol{r}_2, t) = H_{\rm per}(\boldsymbol{r}_1, \boldsymbol{r}_2, t)\psi(\boldsymbol{r}_1, \boldsymbol{r}_2, t). \tag{5.130}$$

The units $\hbar$ and c are carried along for a while, because the atomic radiation is a basically new phenomenon. The notation is for two particles with position operators $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ as in Sect. 3.4; H^0 is typically the Dirac-Coulomb Hamiltonian (3.96),

$$H_C^0 = \Sigma_i(\boldsymbol{\alpha}_i\boldsymbol{\pi}_{i,cl} + m_i\beta_i) + V, \tag{5.131}$$

and

$$H_{\rm per}(\boldsymbol{r}_1, \boldsymbol{r}_2, t) = -q_1\boldsymbol{A}(\boldsymbol{r}_1, t)\boldsymbol{\alpha}_1 - q_2\boldsymbol{A}(\boldsymbol{r}_2, t)\boldsymbol{\alpha}_2 \tag{5.132}$$

is the "perturbing" time-dependent operator. The perturbative solution of (5.130) requires knowledge of the solutions $\psi_n^{(0)}$ of the unperturbed problem,

$$H^0\psi_n^{(0)} = E_n\psi_n^{(0)}, \quad \psi_n^{(0)} = u_n e^{-i\omega_n t}, \quad \omega_n = E_n/\hbar. \tag{5.133}$$

The complete solution is expanded in terms of the ψ_n with time-dependent coefficients,

$$\psi(\boldsymbol{r}_1, \boldsymbol{r}_2, t) = \Sigma_n c_n(t)u_n(\boldsymbol{r}_1, \boldsymbol{r}_2)e^{-i\omega_n t}. \tag{5.134}$$

The unperturbed $\psi_n^{(0)}$ cancel out on the left-hand side of (5.130), and with $\partial_t c_m \equiv \dot{c}_m$, one finds

$$\Sigma_m i\hbar\dot{c}_m u_m e^{-i\omega_m t} = \Sigma_n c_n H_{\rm per} u_n e^{-i\omega_n t}. \tag{5.135}$$

A single $\dot{c}_f$ (f for "final") is picked out of the sum by means of the orthogonality relations $\langle u_f|u_m\rangle = \delta_{m,f}$,

$$i\hbar\dot{c}_f = \Sigma_n c_n(t)\langle f|H_{\rm per}|n\rangle e^{i\omega_{fn}t}, \quad \omega_{fn} = \omega_f - \omega_n. \tag{5.136}$$

Next, the c_n are classified according to the power N of $H_{\rm per}$ on which they depend:

$$c_n(t) = \Sigma_N c_n^{(N)}(t), \quad c_n^{(0)}(t) = \delta_{n,i}\Theta(t - t_0). \tag{5.137}$$

The last equation specifies the atom to be in its "initial state" $|i\rangle$ at $t = t_0$. As a rule, one can assume that this state is suddenly created at $t_0 = 0$, but in second order pertubation theory the details of the preparation of $|i\rangle$ may become relevant. With the classification (5.137), (5.136) becomes a recurrence relation in the order N of the perturbation,

$$c_f^{(N)}(t) = -i\hbar^{-1}\int^t dt'\,\Sigma_n c_n^{(N-1)}(t')\langle f|H_{\rm per}(t')|n\rangle e^{i\omega_{fn}t'}. \tag{5.138}$$

To perform the integral, one must specify the time dependence of $H_{\rm per}$. Here it is convenient to decompose the vector potential $\boldsymbol{A}$ of $H_{\rm per}$ into modes of given

frequencies ω_i, $a_i \boldsymbol{A}_i(\boldsymbol{r}) e^{-i\omega_i t}$ and $a_i^\dagger \boldsymbol{A}_i^*(\boldsymbol{r}) e^{+i\omega_i t}$ according to (3.7). However, the index $_i$ is suppressed in the following. In first-order perturbation theory for decay, we could also contend ourselves with the "negative frequency" part which is proportional to $e^{+i\omega t}$, because only the operator $a^\dagger$ can create the outgoing photon. It is nevertheless instructive to keep the $e^{-i\omega t}$-part, which would describe the further excitation by an incident photon. We therefore decompose

$$H_{\rm per} = H_{\rm per}^{(+)} e^{i\omega t} + H_{\rm per}^{(-)} e^{-i\omega t}, \quad c_f^{(N)} = c_f^{(N+)} + c_f^{(N-)}. \tag{5.139}$$

The solution of (5.138) for $N = 1$ is then

$$c_f^{(1\pm)} = \sum_n \frac{\langle f|H^{(\pm)}|n\rangle}{\hbar(\omega_{fn} \pm \omega)} \left[e^{i(\omega_{fn} \pm \omega)t} - e^{i(\omega_{fn} \pm \omega)t_0} \right] \delta_{ni}. \tag{5.140}$$

In decay, the initial energy E_i is larger than the final one E_f, and ω_{fi} is negative. For this situation, we define

$$\Delta\omega = \omega + \omega_{fi} = \omega - \omega_{if} = \omega - (E_i - E_f)/\hbar. \tag{5.141}$$

We also abbreviate $\Delta t = t - t_0$ and obtain

$$c_f^{(1+)} = -\langle f|H^{(\pm)}|i\rangle e^{i\Delta\omega t_0} (e^{i\Delta\omega\Delta t} - 1)/\hbar\Delta\omega. \tag{5.142}$$

The probability to find the atom in the state $|f\rangle$ after a time Δt is $|c_f|^2$, and the decay rate is

$$\Gamma_{if} = |c_f|^2/\Delta t. \tag{5.143}$$

To compute $|c_f|^2$, one extracts a phase $e^{i\Delta\omega\Delta t/2}$ from the bracket in (5.142),

$$e^{i\Delta\omega\Delta t} - 1 = e^{i\Delta\omega\Delta t/2} \times 2\sin(\Delta\omega\Delta t/2), \tag{5.144}$$

and takes the limit $\Delta t \to \infty$:

$$4\sin^2(\Delta\omega\Delta t/2)/(\Delta\omega)^2\Delta t \to \pi\delta(\Delta\omega/2) = 2\pi\delta(\Delta\omega). \tag{5.145}$$

The decay rate is then independent of Δt.

Expression (5.143) refers to a single mode of the electromagnetic field. Examples are provided by an atom in a perfect cavity with non-degenerate modes, and by a single-mode laser beam where $(n_1')^{1/2}$ in (3.37) may assume very large values. In the latter case, the decay into mode 1 is called "induced" and may be much larger that the "spontaneous" decays into all other degenerate modes (which have $n_i = 0$, $n_i' = 1$). In the following, only spontaneous decays are considered. In the continuum limit, the differential decay rate into photons within a solid angle element $d\Omega_k$ of wavenumber $\boldsymbol{k}$ and helicity λ is

$$d\Gamma_{if} = (d^3k/8\pi^3)|\langle \boldsymbol{k}, \lambda, f|H^{(+)}|i\rangle|^2 2\pi\delta(\omega - \omega_{if})/\hbar^2, \tag{5.146}$$

with $d^3k = k^2 dk d\Omega_k$. One may use $dk = d\omega/c$ to cancel $d\omega$ against $\delta(\omega - \omega_{if})$, which then fixes the variable ω at the value ω_{if} as required by energy conservation:

$$d\Gamma_{if} = k^2 d\Omega_k |\langle \boldsymbol{k}, \lambda, f|H^{(+)}|i\rangle|^2 / 4\pi^2 c\hbar^2. \tag{5.147}$$

This is "Fermi's golden rule". One normally extracts from $H^{(+)}$ the additional normalization factors and the $n_f^{1/2}$ from the Fock matrix element of $a^\dagger$ (3.36),

$$H^{(+)} = c(\hbar n_f/\omega)^{1/2} \langle \boldsymbol{k}, \lambda, f|\hat{H}^{(+)}|i\rangle, \tag{5.148}$$

where $\hat{H}^{(+)} = -\Sigma_i q_i \boldsymbol{A}_f(\boldsymbol{r}_i)\boldsymbol{\alpha}_i$ still contains the desired radiation mode, for example a plane wave (3.11). The relations

$$\boldsymbol{\alpha}_i = i[H_C, \boldsymbol{r}_i], \quad \langle f|H_C \boldsymbol{r}_i - \boldsymbol{r}_i H_C|i\rangle = (E_f - E_i)\langle f|\boldsymbol{r}_i|i\rangle, \tag{5.149}$$

display $d\Gamma_{if}$ in terms of the dipole operators:

$$d\Gamma_{if} = (\omega^3 n(\boldsymbol{k})/2\pi c^2) d\Omega_k |\langle f|\boldsymbol{\epsilon}_\lambda^*(\boldsymbol{k}) \Sigma_i e^{-i\boldsymbol{k}\boldsymbol{r}_i} q_i \boldsymbol{r}_i|i\rangle|^2. \tag{5.150}$$

The same formula results if one or both particles are spinless, relativistic or not. In the latter case one starts from $H^{(+)} = -\Sigma_i q_i \boldsymbol{A}_f(\boldsymbol{r}_i)\boldsymbol{\pi}_i/m_i c$, where

$$[\Sigma_i \boldsymbol{r}_i, H_{\rm nr}] = [\Sigma_i \boldsymbol{r}_i, \boldsymbol{\pi}_i^2/2m_i] = i\hbar \Sigma_i \boldsymbol{\pi}_i/m_i. \tag{5.151}$$

Thus Fermi's golden rule is more general than one might have expected. It contains two powers of ω from parity conservation and one power from momentum space (the necessity of parity change was already mentioned in (1.110) for the nonrelativistic limit).

The total decay rate into the channel f follows after integration over $d\Omega_k$ as in (4.107). The atomic disappearance rate is of special interest, which also sums over different decay channels. In hydrogen for example, a 2p state can only decay into the 1s state, but a 3p state has the choice between 1s and 2s, which are called different "channels" in this context. The disappearance rate is defined as $\Gamma_i = \sum_f \Gamma_{if}$. Like $d\Gamma_{if}$ and Γ_{if}, it is time-independent according to (5.145). Denoting the surviving probability by $N_i(t)$, one has $dN_i/dt = \Gamma_i$, which by integration leads to the exponential decay law,

$$N_i(t) = N_i(t_0) e^{-\Gamma_i(t-t_0)}. \tag{5.152}$$

At finite $t - t_0$, this contradicts (5.137) which puts $c_i = 1$ for all times. A better ansatz is $c_n^{(0)}(t) = \delta_{n,i}\Theta(t - t_0)e^{-\Gamma_i(t-t_0)/2}$, as it includes already the exponentially falling survival probability. It is equivalent to shifting the unperturbed energies E_n by an amount $-i\hbar\Gamma_n/2$ into the lower complex plane,

$$\tilde{\omega}_n = \omega_n - i\Gamma_n/2 = (E_n - i\hbar\Gamma_n/2)/\hbar. \tag{5.153}$$

The resulting $c_f^{(1+)}$ is

$$c_f^{(1+)} = \frac{\langle f|H^{(+)}|i\rangle}{\hbar(\omega_{fi}+\omega-i\Gamma_i/2)}\left[e^{i(\omega_{fi}+\omega)t}e^{-\Gamma_i t/2} - e^{i(\omega_{fi}+\omega)t_0}e^{-i\Gamma_i t_0/2}\right]. \tag{5.154}$$

Setting $t_0 = 0$ and $t = \infty$ simplifies this to

$$c_f^{(1+)}(\infty) = \hbar^{-1}\langle f|H^{(+)}|i\rangle(\omega_{fi}+\omega-i\Gamma_i/2)^{-1}. \tag{5.155}$$

The corresponding transition probability is $dW_{if} = |c_f|^2$ as a function of ω:

$$dW_{if}/d\omega = (\Gamma_{if}/2\pi)(\Delta\omega^2+\Gamma_i^2/4)^{-1}. \tag{5.156}$$

This is conveniently expressed in terms of the "Lorentz curve",

$$L(\omega) = (\Gamma_i/2\pi)(\Delta\omega^2+\Gamma_i^2/4)^{-1}, \quad dW_{if}/d\omega = L(\omega)\Gamma_{if}/\Gamma_i. \tag{5.157}$$

In the limit $\Gamma_i \to 0$, L is normalized to $\delta(\Delta\omega)$. Γ_{if}/Γ_i is the "branching ration" for channel f, and $\Sigma_f\Gamma_{if}/\Gamma_i = 1$.

L has its maximum of $2(\pi\Gamma_i)^{-1}$ at $\Delta\omega = 0$, and half that value at $\Delta\omega = \pm\Gamma/2$. In the finite time interval $\Delta t \approx \Gamma_i$ granted by (5.152), $E_i = \hbar\omega$ is unsharp with $\Delta E \approx \hbar\Delta\omega \approx \hbar\Gamma_i/2$, such that $\Delta E\Delta t \approx \hbar/2$, in agreement with the "uncertainty relation" mentioned at the end of Sect. 1.8. The Lorentz curve is verified by precise measurements of the frequency distribution of the decay photon. Doppler shifts (2.24) from the thermal motion of the excited atoms superimpose a Boltzmann factor $Ne^{-E_{\rm kin}/k_{\rm B}T}$ on $dW_{if}/d\omega$, with $E_{\rm kin} = \frac{1}{2}Ev^2$ and $N = (E/2\pi k_{\rm B}T)^{3/2}$ in the nonrelativistic limit. The resulting curve is known as "Voigt profile".

For the inclusion of atomic recoil, the stationary binary equation (4.276) is extended to a time-dependent equation (Pilkuhn 2004). The unperturbed "chiral hamiltonian" is denoted by h^0 in the following (with $\hbar = c = 1$):

$$(i\partial_\tau - h^0)\psi_n = h_{\rm per}(t)\psi_n, \quad \tau = \mu t, \quad h^0\psi_n^{(0)} = (\epsilon/\mu)_n\psi_n^{(0)}. \tag{5.158}$$

The exponent $-i\omega_n t$ in (5.133) becomes $-i(\epsilon/\mu)_n\tau$, which implies that each state $|n\rangle$ has its individual time t_n (the proper time). Consequently, the factor $(\omega_i-\omega_f)t$ of the decay according to (5.141) is replaced by

$$[(\epsilon/\mu)_i - (\epsilon/\mu)_f]\tau = \tfrac{1}{2}\tau(E_i^2-E_f^2)/m_1m_2, \tag{5.159}$$

as the constants in $\epsilon/\mu = (E^2-m_1^2-m_2^2)/2m_1m_2$ are canceled. The $\delta(\Delta\omega)$ in (5.145) is replaced by $\delta(E_i\omega - E_i^2/2 + E_f^2/2)$, giving

$$\Delta\omega = \omega - (E_i^2-E_f^2)/2E_i, \tag{5.160}$$

as anticipated in (4.102). The Lorentz curve has its maximum shifted from $\omega = E_i - E_f$ to $\omega = (E_i^2-E_f^2)/2E_i = k$, as required by (4.102). Instead

of (5.153), the unperturbed E_n^2 are shifted by an amount $-i\hbar E_n \Gamma_n$ into the lower complex plane. The combination $E_n\Gamma_n$ does not depend on the sign of E_n, such that atoms and antiatoms have identical decay rates.

Unless one wants to measure the polarization of the emitted light (for example in connection with Zeeman splitting), one has to sum (5.150) over the helicity λ. This can be done with explicit expressions such as (3.13), but there is again a more elegant way based on (3.104): In cartesian components $\boldsymbol{\epsilon}_\lambda = (\epsilon_{\lambda i})$,

$$\Sigma_\lambda \epsilon^*_{\lambda i}\epsilon_{\lambda j} = \delta_{ij} - \hat{k}_i\hat{k}_j. \tag{5.161}$$

The integration over the photon angles Ω_k is then trivial. One has $\int d\Omega_k = 4\pi$, $\int \hat{k}_i\hat{k}_j d\Omega_k = \delta_{ij}\int d\Omega_k \hat{k}_i^2 = \delta_{ij}4\pi/3$,

$$\int d\Omega_k \Sigma_\lambda \epsilon^*_{\lambda i}\epsilon_{\lambda j} = \delta_{ij}8\pi/3. \tag{5.162}$$

Radiative transitions in atoms are classified into electric and magnetic multipoles (Lifshitz and Pitaevskii 1973). $\langle f|\boldsymbol{r}|i\rangle$ cannot be much larger than the atomic radius, which for hydrogenic atoms is the Bohr radius $a_\mathrm{B} = \hbar^2/Ze^2\mu$. In $k = \Delta\omega/c = \Delta E/\hbar c$ on the other hand, ΔE is certainly smaller than the ground state binding energy, $-E_1 = \alpha_Z^2\mu c^2/2 = \alpha_Z\hbar c/2a_\mathrm{B}$. The order of magnitude of $\langle f|\boldsymbol{kr}|i\rangle$ is thus $\alpha_Z/2$, which is small for moderate Z. For dipole radiation one approximates $e^{i\boldsymbol{kr}} = 1$, for quadrupole radiation $e^{i\boldsymbol{kr}} = 1 + i\boldsymbol{kr}$. With $q_1 = -e$, $q_2 = Ze$ and $\boldsymbol{r}_1 = \boldsymbol{R} + \boldsymbol{r}E_2/E$, $\boldsymbol{r}_2 = \boldsymbol{R} - \boldsymbol{r}E_1/E$ from (4.292) and (4.307), the sum in (5.150) simplifies in the dipole approxmation to

$$\Sigma_i e^{-i\boldsymbol{kr}_i} q_i \boldsymbol{r}_i = e^{-i\boldsymbol{kR}}[-(\boldsymbol{R} + \boldsymbol{r}E_2/E)e + (\boldsymbol{R} - \boldsymbol{r}E_1/E)Ze]. \tag{5.163}$$

The $\boldsymbol{R}$ in the square bracket does not induce dipole transitions. The only other $\boldsymbol{R}$-dependence in $d\Gamma_{if}$ is a factor $e^{-i\boldsymbol{KR}}$ from $\langle f|$, yielding $\int d^3\,\mathrm{Re}^{-i\boldsymbol{KR}}e^{-i\boldsymbol{kR}} = 8\pi^3\delta(\boldsymbol{k} + \boldsymbol{K})$. It expresses momentum conservation as anticipated in (4.102).

The remaining terms in (5.163) are combined into

$$-e_\mathrm{dip}\boldsymbol{r}, \quad e_\mathrm{dip} = e[1 + (Z-1)E_1/E], \quad E_1/E \approx m_1/m_{12}, \tag{5.164}$$

where e_dip is the effective "dipole radiation charge". In single-fermion ions, e_dip reaches its maximum for the nucleus ^{40}Ca, with $(Z-1)/m_2 \approx 19/40m_p = 0.475m_p$. The decay rate of the above-mentioned 2s-states contains a factor e_dip^4. $Z = 1$ gives $e_\mathrm{dip} = e$, but even there it may be useful to keep the distinction between e and e_dip, in view of a coherence classification (Sect. 5.5).

For binary atoms, the commutator (5.149) is replaced by $\boldsymbol{\alpha} = i[h^0, \boldsymbol{\rho}]$, and

$$\langle f|h^0\boldsymbol{\rho} - \boldsymbol{\rho}h^0|i\rangle = [(\epsilon/\mu)_f - (\epsilon/\mu)_i]\langle f|\boldsymbol{\rho}|i\rangle = -\omega\langle f|\boldsymbol{r}|i\rangle,$$

where $\hbar\omega \approx \Delta E(1 - \Delta E/2m_{12}c^2)$ is again the actual outgoing photon energy. Thus Fermi's golden rule for dipole emission from a relativistic binary becomes

$$\Gamma_{if,\mathrm{dip}} = (4\omega^3/3c^2)\alpha_{\mathrm{dip}}|\langle f|\boldsymbol{r}|i\rangle|^2, \quad \alpha_{\mathrm{dip}} = e_{\mathrm{dip}}^2/\hbar c. \tag{5.165}$$

Obviously, the factor ω^3 is independent of the detailed structure of H or h. For an arbitrary atom, the kinematically correct vaule of ω requires the h^0 in (5.158) to have eigenvalues $\frac{1}{2}(E_n^2 - \mathrm{const})/m_1m_2$, E_n being the total atomic mass of the state $|n\rangle$. This simple E^2-dependence is more restrictive than the requirement of invariance under $E \to -E$ of the eigenvalue equation itself.

5.5 Soft Photons, Lamb Shift

So far in this book, the interaction operator in the equations for binary atoms has been the Fourier transform of the one-photon exchange amplitude $T^{(1)}$ (4.64). Without form factors, the resulting interaction in the cms is the Coulomb potential, $V = -\alpha_Z/r$, possibly with additional hyperfine operators as in (4.268). Phenomenological form factors are particularly important for the atomic nucleus, giving rise to modified Coulomb potentials of the type (4.44), to phenomenological hyperfine operators (4.153) etc. Fortunately, these effects are supressed by large denominators. When particle 1 is an electron, the situation is qualitatively different. The form factors F_1 and F_2 ar small but do shift the energy by an amount $\Delta E^{(1)}$ (the upper index ^{1} is a reminder of the one-photon exchange) which is of the order of $m_e\alpha_Z^4\alpha_\pi$ ($\alpha_\pi = \alpha/\pi$). It is part of the "Lamb shift", which is larger than the α_Z^6 effects included in the Dirac etc. equations.

Whereas the modified Dirac equation with $F_2 \approx \kappa_{\mathrm{an}}$ is still (nearly) consistent, a direct inclusion of F (4.160) is ruled out by its infrared divergence $\log\lambda$. This problem is solved by adding to the elastic cross section the "nearly elastic" cross section σ_{soft} for the emission of an additional "soft" photon of energy smaller than a certain $\omega_{\max}$. With $\lambda \ll \omega_{\max}$, the infrared divergence disappears, at the expense of the new parameter $\omega_{\max}$. The result can be expressed in terms of an effective form factor $F_{\mathrm{eff}}(\omega_{\max})$, which is then used for the calculation of $\Delta E^{(1)}$.

It may be surprising that the high-energy approximation $T_{if} \approx T_{if}^{(1)}$ provides such a good potential for bound state equations. At the order $\alpha_Z^4\alpha_\pi$, this is only true for $\Delta E^{(1)}$. There is a low-energy piece $\Delta E_<$ which must be calculated perturbatively for the solutions of the binary equation. To the order $\alpha_Z^4\alpha_\pi$, the Schrödinger equation is sufficient here, and the dipole approximation may also be used. It is the whole atom which emits and reabsorbes the "virtual" photon by means of the dipole operator $e_{\mathrm{dip}}\boldsymbol{r}$ (5.164), including emission by one particle and absorption by the other one (compare

Fig. 3.3b, in the presence of the Coulomb potential). To order α_Z^4, such terms are included in the relativistic binary equation, but to order $\alpha_Z^4\alpha_\pi$, they are not. In most books, the Lamb shift is discussed in the static limit, where those exchange terms vanish. In the following, we also begin with this limit, in which particle 2 is unable to interact with photons. The T-matrix for the emission of a soft photon factorizes,

$$T_{\rm soft} = T_{if} M_{\rm soft}. \tag{5.166}$$

$M_{\rm soft}$ can be calculated classically as the soft dipole radiation emitted from accelerated charges, but it also follows from the Feynman rules. Restricting ourselves to the radiation from particle 1 (the electron), the in- and outgoing 4-momenta of that particle will be called p^μ and $p^{\mu\prime}$, while k^μ will denote the 4-momentum of the soft photon. When the electron emits the photon from the initial state before the proper scattering, its propagator to the scattering is

$$[m_1^2 - (p-k)_\mu (p-k)^\mu]^{-1} = (2pk)^{-1}, \tag{5.167}$$

according to (4.12) and with $p_\mu p^\mu = m_1^2,\ k_\mu k^\mu = \lambda^2 \approx 0$. For emission of the same photon after the scattering, the electron propagates with a 4-momentum $(p'+k)^\mu$, leading to

$$[m_1^2 - (p'+k)_\mu (p'+k)^\mu]^{-1} = -(2p'k)^{-1}. \tag{5.168}$$

The Feynman graph corresponding to this emission amplitude is shown in Fig. 5.2. There are altogether four emission amplitudes, one for each incoming and outgoing particle.

In the following, only the nonrelativistic limit is needed, $p^\mu = p'^\mu \approx (m_1, 0, 0, 0)$. The matrix elements for the photon emission are $-e\boldsymbol{\epsilon}^*\boldsymbol{p}$ and $-e\boldsymbol{\epsilon}^*\boldsymbol{p}'$, respectively, such that the complete matrix element for the additional emission of one soft photon from particle 1 is

$$T_{\rm soft} = T_{if} e\boldsymbol{\epsilon}^* (\boldsymbol{p}/pk - \boldsymbol{p}'/p'k)/2 = T_{if} e\boldsymbol{\epsilon}^* \boldsymbol{q}/m_1\omega. \tag{5.169}$$

The cross section for the emission of an extra photon is given by (4.90), where dLips (4.86) contains a factor $d^3k/16\pi^3\omega$ for the photon, but the normaliza-

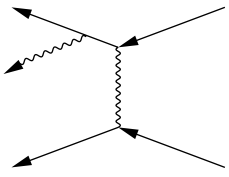

Fig. 5.2. Soft photon emission

tion factor $(h/\omega)^{1/2} = (4\pi\hbar/2\omega)^{1/2}$ brings an extra 4π. As k^μ is neglected in the δ_4-function of (4.86), one obtains the simple relation

$$d\sigma_{\text{soft}} = d\sigma_{if}\alpha_\pi(\boldsymbol{\epsilon}^*\boldsymbol{q}/m_1\omega)^2 d^3k/4\pi\omega. \tag{5.170}$$

This is integrated up to a value $\omega_{\max}$ which is small enough but nevertheless much larger than λ. With $\int d\Omega(\boldsymbol{qk})^2 = 4\pi q^2k^2/3$,

$$d\sigma_{\text{soft}} = d\sigma_{if}\alpha_\pi \boldsymbol{q}^2 m_1^{-2}\int_0^{\omega_{\max}} \left[1 - \frac{k^2}{3(k^2+\lambda^2)}\right]\frac{k^2dk}{(k^2+\lambda^2)^{3/2}}, \tag{5.171}$$

$$d\sigma_{\text{soft}} = d\sigma_{if}\alpha_\pi \boldsymbol{q}^2(\log(2\omega_{\max}/\lambda) - \tfrac{5}{6})\tfrac{2}{3}m_1^{-2}. \tag{5.172}$$

For sufficiently small $\omega_{\max}$, $d\sigma_{\text{soft}}$ will be counted as part of the elastic scattering cross section $d\sigma_{if}$, such that only the sum of the two quantities has a physical meaning. In $d\sigma_{if}$, one must at this order of precision also include the form factor F (4.160), $d\sigma_{if} = d\sigma_{if}^{(1)}F^2$. The cross section including linear terms in F is

$$d\sigma_{\text{soft}} + d\sigma_{if} = d\sigma_{if}^{(1)}[1 - \tfrac{2}{3}m_1^{-2}\alpha_\pi \boldsymbol{q}^2 m_1^2(\log(m_1/2\omega_{\max}) + \tfrac{5}{6})]. \tag{5.173}$$

$d\sigma_{if}^{(1)}$ is the first Born cross section, it has $F_1 = 1$ and $F_2 = 0$. The $\log\lambda$ terms have disappeared as expected. The result can be viewed as the Born cross section with a modified, "effective" form factor,

$$F_{\text{eff}} - 1 = -\tfrac{1}{3}m_1^{-2}\alpha_\pi \boldsymbol{q}^2 m_1^2(\log(m_1/2\omega_{\max}) + \tfrac{5}{6}). \tag{5.174}$$

The exchanged photon contributes a factor $1/\boldsymbol{q}^2$, the Fourier transform of $\boldsymbol{q}^2/\boldsymbol{q}^2 = 1$ introduces a factor $\delta_3(\boldsymbol{r})$, and with $\langle\delta_3\rangle = |\psi(0)|^2 = 4\delta_{l0}(\alpha_Z m_1/n)^3$ (compare (5.127)), the energy shift due to F_{eff} is

$$\Delta E^{(1)} = \alpha_Z^4\alpha_\pi \tfrac{4}{3}m_1 n^{-3}(\log(m_1/2\omega_{\max}) + \tfrac{5}{6}). \tag{5.175}$$

Turning now to the soft photon emission by particle 2, one simply replaces $-e$ by Ze, $\boldsymbol{p}$ by $-\boldsymbol{p}$ (in the cms), and m_1 by m_2, of course. The factor $e\boldsymbol{p}/m_1$ becomes $Ze\boldsymbol{p}/m_2$. The total soft photon emission matrix element contains the combination

$$e/m_1 + Ze/m_2 = e/\mu + (Z-1)e/m_2 = e_{\text{dip}}/\mu, \tag{5.176}$$

where e_{dip} is the dipole radiation charge (5.164) as expected. The square of (5.176) appears in $d\sigma_{\text{soft}}$,

$$\alpha_{\text{dip}}/\mu^2 = \alpha/m_1^2 + Z^2\alpha/m_2^2 + 2Z\alpha/m_1m_2. \tag{5.177}$$

The first term agrees with (5.170) and cancels the infrared singularity of F^2 as before. The second term is the analogous expression for particle 2, as its form factor $F(2)$ has e^2/m_1^2 replaced by $(Ze)^2/m_2^2$. The third term in (5.15) has

no partner among the form factors. Insisting on the cancellations of infrared singularities, one must add an "interference function" to the product of form factors in $d\sigma_{if}$,

$$d\sigma_{if} = d\sigma_{if}^{(1)}[F(1)^2F(2)^2 + 2F_{\rm int}], \tag{5.178}$$

$$F_{\rm int} = -\tfrac{2}{3}\alpha_\pi(Z\boldsymbol{q}^2/m_1m_2)[\log((m_1m_2)^{1/2}/2\lambda) - x]. \tag{5.179}$$

A finite function x remains open. The $\log(m_1m_2)^{1/2}$ is not necessary either, but it will be useful in connection with (5.195) below. This then leads to the very compact expression,

$$\Delta E^{(1)} = \tfrac{4}{3}\alpha_Z^4\alpha_{\rm dip}\mu(3\pi n^3)^{-1}[\log(\mu/2\omega_{\max}) + \tfrac{5}{6}]. \tag{5.180}$$

In the standard QED calculation with Feynman rules, the cancellation of infrared divergences appears automatically. $F_{\rm int}$ is then hidden in a two-photon exchange amplitude (that amplitude is normally calculated in a covariant gauge, in which A^0 contains also a field operator). Such calculations, which provide the complete "Salpeter shift" mentioned below, are more complicated.

In (5.180), $\omega_{\max}$ must be small enough to allow for the soft photon approximation, but it must be much larger than $\alpha_Z^2\mu$ where Coulomb distortion is important:

$$\alpha_Z^2\mu \ll \omega_{\max} \ll \mu. \tag{5.181}$$

Fortunately, it turns out that both conditions are satisfied, but the question arises how to calculate the residual energy shift $\Delta E_<$ from the region $E < \omega_{\max}$. Two procedures are possible here. In the first one, one solves the Schrödinger, KG of Dirac equation with $\boldsymbol{\pi} = \boldsymbol{p} + e\boldsymbol{A}$ to second order in the field operator $\boldsymbol{A}$ in the Schrödinger picture (3.118) in the dipole approximation $\boldsymbol{A}_{\rm Sch} = \boldsymbol{A}(\boldsymbol{0}, 0)$. The result has the form (2.223), cut off at $\omega_{\max}$. From this one has to subtract the corresponding energy shifts of the free (!) particles. The difference contains a term $\log\omega_{\max}$ which cancels the $-\log\omega_{\max}$ of (5.180). It implies a renormalization of particle masses, which is quite complicated in the relativistic case. It may be replaced by the more elegant dimensional renormalization, but even this is not at all trivial. For binary atoms, the renormalization must also be applied to particle 2, which is not really possible for composite particles such as protons.

The second method is based on unitarity and analyticity, as explained for the vacuum polarization. The complex energy $\tilde{\omega}_n$ (5.153) is calculated by first-order perturbation theory, where E_n still has its unperturbed value. Quite generally, one has for not too large Γ_n,

$$\tilde{\omega}_n = \omega_n + \Delta\omega_n = \omega_n + \Delta E_n - i\Gamma_n/2. \tag{5.182}$$

Dropping again $\hbar$ and c, (5.146) may be continued as follows:

$$\Delta E_i - i\Gamma_i/2 = -(8\pi^3)^{-1}\int d^3k|\langle k, \lambda, f|H^{(+)}|i\rangle|^2(\omega - \omega_{if} - i\epsilon)^{-1}, \tag{5.183}$$

by reading (5.113) backwards, $i\pi\delta(x)+\mathcal{P}/x=(x-i\epsilon)^{-1}$. The resulting ΔE_i agrees with (2.223), it is in the dipole approximation

$$\Delta E_i=\int d^3k(8\pi^3\omega)^{-1}\Sigma_f\omega_{if}^2\alpha_{\rm dip}|\langle f|\boldsymbol{r}\boldsymbol{\epsilon}|i\rangle|^2(\omega_{if}-\omega)^{-1}. \tag{5.184}$$

The Σ_f extends over all excited levels, including the ionization continuum. The ground state has $\omega_{if}<0$, its ΔE_i is negative, as always in second-order perturbation theory (compare also (2.223)). The k-integral diverges again. In the language of Feynman, such "ultraviolet" divergences arise in loop diagrams. The dispersion relation technique offers an attractive alternative. A diverging dispersion integral is simply replaced by its once subtracted form as explained in Sect. 5.3. The technique is quite general; it can be applied to the form factors F_1 and F_2 (Lifshitz and Pitaevskii 1973, Pilkuhn 1979). The proof of analyticity requires some theory of complex functions, however.

Unitarity and analyticity apply not only to scattering processes as in (4.99), but also to the decays of unstable particles or narrow resonances that are described by a complex energy as in (5.182). The δ-function limit (5.146) gives $\omega=\omega_{if}$ and thus

$$\Delta E_<=\int_0^{\omega_{\max}}d\omega\int d\Omega_k(8\pi^3)^{-1}\sum_f\omega_{if}^3\alpha_{\rm dip}|\langle f|\boldsymbol{r}\boldsymbol{\epsilon}|i\rangle|^2(\omega_{if}-\omega)^{-1}. \tag{5.185}$$

After the usual helicity summation and photon angular integration, one obtains, with $\omega_{if}=-\omega_{fi}$,

$$\Delta E_<=\int_0^{\omega_{\max}}d\omega\frac{2}{3\pi}\sum_f\omega_{if}^3\alpha_{\rm dip}\frac{|\boldsymbol{r}_{if}|^2}{\omega_{if}-\omega}=\frac{2\alpha_{\rm dip}}{3\pi}\sum_f\omega_{fi}^3|\boldsymbol{r}_{if}|^2\log\frac{\omega_{\max}}{\omega_{fi}}. \tag{5.186}$$

The Σ_f without the $\log(\omega_{\max}/\omega_{fi})$ is simple:

$$\Sigma_f\omega_{fi}^3|\boldsymbol{r}_{if}|^2=-\langle\Delta V\rangle/2\mu^2=2\mu\alpha_Z^4/n^3. \tag{5.187}$$

It follows from the Schrödinger equation $\omega_{fi}\boldsymbol{r}_{if}=\langle f|[\boldsymbol{r},H]|i\rangle=i\langle f|\boldsymbol{p}/\mu|i\rangle$ as in (5.151), and

$$\Sigma_f\omega_{fi}\langle f|\boldsymbol{p}^2|i\rangle=-\langle i|[\boldsymbol{p},H]\boldsymbol{p}|i\rangle=\langle\boldsymbol{p}[\boldsymbol{p},H]\rangle_i=-\tfrac{1}{2}\langle[\boldsymbol{p},[\boldsymbol{p},H]]\rangle_i=-\tfrac{1}{2}\langle\Delta V\rangle_i. \tag{5.188}$$

The logarithm may be decomposed as follows:

$$\log(\omega_{\max}/\omega_{fi})=\log(2\omega_{\max}/\mu)+\log(\mu/2\omega_{fi}), \tag{5.189}$$

$$\Delta E_<=\frac{4\alpha_{\rm dip}\mu\alpha_Z^4}{3\pi n^3}\log(2\omega_{\max}/\mu)+\frac{2\alpha_{\rm dip}}{3\pi}\sum_f\omega_{fi}^3|\boldsymbol{r}_{if}|^2\log(\mu/2\omega_{fi}). \tag{5.190}$$

The total self-energy shift $\Delta E = \Delta E_< + \Delta E^{(1)}$ from all frequencies $0 < \omega < \infty$ is thus free of $\log(2\omega_{\max}/\mu)$:

$$\Delta E = \tfrac{4}{3}\mu\alpha_{\rm dip}\alpha_Z^4(\pi n^3)^{-1}[\tfrac{5}{6} + n^3(\mu\alpha_Z^4)^{-1}\textstyle\sum_f \tfrac{1}{2}\omega_{fi}^3|\boldsymbol{r}_{if}|^2\log(\mu/2\omega_{fi})]. \tag{5.191}$$

The matrix elements $\boldsymbol{r}_{if}$ are proportional to α_Z/μ, and

$$\omega_{fi} = E_f - E_i = \alpha_Z^2\mu\tfrac{1}{2}(n_i^{-2} + 2E_f/\alpha_Z^2\mu) \tag{5.192}$$

is proportional to $\alpha_Z^2\mu$, even for the unbound states. The $\mu^{-1}\Sigma_f\ldots$ is therefore independent of μ, and its α_Z-dependence is given by $\log(\mu/2\omega_{fi}) = \log\alpha_Z^{-2} + \log(\mu\alpha_Z^2/2\omega_{fi})$:

$$\Delta E = \tfrac{4}{3}\mu\alpha_{\rm dip}\alpha_Z^4(\pi n^3)^{-1}[\tfrac{5}{6} + \log\alpha_Z^{-2} - \log k_0], \tag{5.193}$$

$$\log k_0 = -\tfrac{1}{2}n^3(\mu\alpha_Z^4)^{-1}\Sigma_f\omega_{fi}^3|\boldsymbol{r}_{if}|^2\log(\alpha_Z^2\mu/2\omega_{fi}). \tag{5.194}$$

$\log k_0$ is the Bethe logarithm. Numerical values of $\log k_0$ for $n_i = 1$, 2, 3, 4, and ∞ are 2.984, 2.812, 2.768, 2.750 and 2.721, respectively. The largest contribution to the Lamb shift comes from the term $\log(Z^{-2}\alpha^{-2})$ in (5.193); for the hydrogenic ground state it gives an upward shift of 1330 MHz out of 1040 MHz. It can be attributed to the electron mean square radius that was estimated already in (4.162). The Bethe logarithm is the net effect of second-order perturbation theory; it gives a downward shift as expected.

In most textbooks, one finds the vacuum polarization (5.127) added in ΔE, which gives $5/6 - 1/5 = 19/30$. However, $\langle V_U\rangle$ is proportional to α, not to $\alpha_{\rm dip}$, and contains a factor μ^2/m_e^2.

The calculations so far are entirely nonrelativistic and remain valid for particles of arbitrary spins 0, 1/2, 1, 3/2 ... which may appear when particle 2 is a nucleus. In contrast, the α_Z^4-contribution of Sect. 4.9 applies only for a binary of a Dirac particle (electron or muon) and a spinless nucleus.

A further correction to ΔE arises from the numerators of the logs in (5.174), in the corresponding expression for particle 2, and in (5.179). These are combined by a common factor $\alpha[1+(Z-1)m_1/m_{12}] = ee_{\rm dip}$. The resulting "$\Delta E_{\rm int}$" is

$$\Delta E_{\rm int} = -\frac{4\mu\alpha_Z^4}{3\pi n^3}ee_{\rm dip}\left[\frac{m_2}{m_{12}}\log\frac{m_2}{m_{12}} + Z\frac{m_1}{m_{12}}\log\frac{m_1}{m_{12}}\right]. \tag{5.195}$$

The factor $e_{\rm dip}$ indicates the soft photon origin of (5.195). Whereas a factor $e_{\rm dip}^2$ shows that the photon is emitted and absorbed coherently by the whole atom, a factor $ee_{\rm dip}$ implies that the photon is either emitted or absorbed coherently. Note also that (5.195) vanishes at both static limits.

The energy shift due to two-photon exchange was originally calculated by Salpeter (1952). With $\Delta E'_{\rm Sal} = \Delta E_{\rm Sal} - \Delta E_{\rm int}$,

$$\Delta E'_{\rm Sal} = -\frac{\alpha_Z^2/\pi}{m_1m_2}\left[\frac{7}{3}\langle r_G^{-3}\rangle - \left(\frac{\alpha_Z\mu}{n}\right)^3\left(\frac{7}{3}\log\frac{\mu}{m_{12}} - \frac{m_1^2+m_2^2}{m_+m_-}\log\frac{m_2}{m_1}\right)\right], \tag{5.196}$$

where r_G^{-3} is the operator (2.229). Also this shift vanishes at both static limits. It was recalculated by Gupta et al. (1989) from a potential $V^{(2)}$ obtained from the two-photon exchange graphs $T^{(2)}$ (Fig. 5.3) of the Born series. $V^{(2)}$ is the Fourier transform of that part of $T^{(2)}$ which does not arise from the iteration of the first Born graph. The method extends the calculation of $V(r)$ as the Fourier transform of the one-photon exchange $T^{(1)}$. The direct iteration of $T^{(1)}$ gives the imaginary part of $T^{(2)}$, see (4.99). In the differential (or integral) equations of quantum mechanics, it is automatically reproduced by V. Moreover, the static limit of $T^{(2)}$ is also reproduced by V. In $T^{(1)}$, $q^0_{\rm cms} = 0$ explains the absence of "retardation". In $T^{(2)}$, the energy transfers q_1^0 and q_2^0 of the exchanged photons are integration variables, subject to the condition $(q_1^0 + q_2^0)_{\rm cms} = 0$. But in the static limit, the treatment of Sect. 4.1 applies, where the energy of particle 1 is always conserved, $q_1^0 = q_2^0 = 0$. Consequently, the correction potential $V^{(2)}$ has no static limit.

The emission and reabsorption of n soft photons with $n > 1$ gives small corrections to the Lamb shift. In leading order, these graphs produce energy shifts proportional to $\log^n \alpha_Z^{-2}$, which may be calculated by special "renormalization group" equations (Manohar and Stewart 2000). This important aspect exists also in nonrelativistic quantum mechanics.

We conclude this section with some comments on Feynman graphs with more than one photon on a scattering particle. The number and shape of such graphs is the same in the KG and Kramers formalisms, while the Dirac formalism has fewer graphs. The operator $\pi^\mu \pi_\mu$ of KG and Kramers implies "contact graphs", where two photons originate from a single point on the particle line. In the Dirac linearization of the coupling, these graphs disappear. For example, the "Compton" scattering of a photon on a free electron has two Dirac graphs and three Kramers graphs (Brown 1958, Tonin 1959, Chalmers and Siegel 1999). Its contact graph is called "seagull" here, the two photons forming the wings (Fig. 5.4). In the nonrelativistic "Thomson" limit of Compton scattering, only this graph survives, which is somewhat unpractical for Dirac graphs where the seagull is eliminated by linearization. The Thomson scattering cross section is independent of the particle spin. The contact graphs for the soft photon emission of Fig. 5.2 have the photon emitted right at the main scattering, neither before nor after (remember that the description of the exchanged "photon" depends also on the choice of gauge).

Fig. 5.3a,b. (**a**) Direct two-photon exchange and (**b**) Crossed two-photon exchange

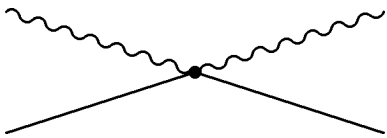

Fig. 5.4. The seagull graph

Fig. 5.3 has three contact terms, "V" where the two exchanged photons meet at the lower line, "Λ" where they meet at the upper line, and "O" where they meet at both lines. The amplitudes are normally different for particles of different spins. The results for spinless particles are expected to be particularly simple, but they have not yet been calculated for the two-photon exchange.

5.6 Antiprotonic Atoms, Quadrupole Potential

Whenever an antiproton ($\overline{p}$) hits a proton or a neutron in an s- or p-wave, it is immediately annihilated. The precision spectroscopy of antiprotonic atoms uses states of sufficiently large orbital angular momentum l, where the centrifugal barrier $l(l+1)/r^2$ prevents any contact between the $\overline{p}$ and the atomic nucleus, even for $Z = 90$.

The $\overline{p}$ is normally slowed down before it is captured on a neutral atom. It gets caught by ejection of a loosely bound electron ("Auger" electron). For an order-of-magnitude estimate, one assumes capture into a $\overline{p}$ Bohr orbit with principal quantum number n. The binding energy of that orbit must be comparable with that of the electron before ejection, which means $n \approx (m_p/m_e)^{1/2} \approx 40$. For atoms heavier than helium, the further de-excitation occurs in two phases. In phase 1, all remaining electrons are Auger-ejected. In phase 2, the $\overline{p}$ de-excites in a cascade of successive E1 transitions. Due to the very small Bohr radii of hydrogen-like $\overline{p}$ atoms, the emitted quanta are X-rays.

Protonium ($\overline{p}p$) is electrically neutral and gets de-excited by Stark mixing collisions with other hydrogen atoms. Antiprotonic helium ($\overline{p}^4$He or $\overline{p}^3$He) may end up in high-lying metastable states in which the last electron is protected against Auger emission by selection rules (Yamazaki et al., 2002). In such cases, the $\overline{p}$ must de-excite by the emission of optical photons, thus allowing for laser spectroscopy. These longlived $\overline{p}e^-$He bound states ("atomcules") are disregarded in the following because they require complicated molecular calculations.

The X-ray cascade puts the $\overline{p}$ preferentially into the "circular" orbits with $n_r = 0,\ n = l + 1$. The quantum defect $\beta_l = l - l_\alpha$ remains small in states with $l > 1$: $n_\beta = n - \beta_l$ (1.126) is close to n, such that the relevant states are not highly relativistic. The first-order relativistic correction is frequently sufficient,

$$E_N \approx -\tfrac{1}{2}\mu_{nr}(\alpha_Z^2/n_\beta^2)(1-3\alpha_Z^2/4n_\beta^2), \quad \mu_{nr}=m_1m_2/m_{12}. \tag{5.197}$$

The largest corrections arise from vacuum polarization and "recoil". The only spin-independent recoil correction in addition to μ_{nr} may be taken from the relativistic μ (4.196) of the Todorov equation, the vacuum polarization can be summarised by a term $a_v(n,l)$, and the spin structure (which is hidden in the β_l) can be summarized by terms a_{ljf} as in (5.75):

$$E_N = -\tfrac{1}{2}\mu_{nr}\frac{\alpha_Z^2}{n^2}\left[1+\frac{\alpha_Z^2}{n^2}\left(\frac{\mu_{nr}}{4m_{12}}-\frac{3}{4}+\frac{n}{l+1/2}(1+a_v+a_{ljf})\right)\right]. \tag{5.198}$$

Because of the antiproton's large g-factor, any form of Dirac equation requires essential modifications (see below), such that the generalized Todorov equation (4.212) is more convenient. The first term in the round bracket of (5.198) arises from (4.207). As a rule, a_v can be calculated perturbatively from the Uehling potential, but that potential may be large enough to modify the spin structure (Bohnert et al., 1985). At fixed integration variable ξ, the r-dependence of V_U (5.83) is that of a Yukawa potential, $e^{-2m_e r\xi}/r$. Its hydrogenic expectation value is expressed in (C.1) in terms of the standard integral $J_{\lambda 1}$, but with $\kappa=\epsilon/\alpha_Z n_\beta$ including recoil. As $y=\kappa/m_e\xi$ is relatively large, the form (C.7) of $J_{\lambda 1}$ is appropriate here:

$$\langle e^{-xr\xi}/r\rangle = 2\kappa\frac{\epsilon^2}{\mu^2}\frac{\Gamma(b+n_r)}{n_r!2n_\beta\Gamma(b)}y^{-2n_r}(1+1/y)^{-2n}F(-n_r,\,-n_r,\,b;\,y^2)\approx I'_n/n^3, \tag{5.199}$$

$$I'_n=(n+l)!(1+1/y)^{-2n}y^{-2n_r}F(-n_r,\,-n_r;2l+2;\,y^2)/(2l+1)!n_r!, \tag{5.200}$$

with $F=$ hypergeometric function. Special cases of I'_n are

$$I'_n(n=l+1)=(1+y^{-1})^{-2n}, \tag{5.201}$$

$$I'_n(l=0)=n(1+1/y)^{-2n}y^{-2n+2}F(-n+1,\,-n+1;2;\,y^2). \tag{5.202}$$

Generalizations of V_s (5.203) for large g-factors and for spins $\neq 1/2$, in particular $s_2=0,\ 1$ and $3/2$ have been given by Waldenström and Olsen (1971). To order α_Z^4, the spin-dependent potential in the Schrödinger equation with reduced mass follows from the CBG-reduction (Sect. 3.6) of the 16-component equation,

$$V_s^{\rm CBG}=c_1\boldsymbol{l}\boldsymbol{s}_1V'/\mu^2r+c_2\boldsymbol{l}\boldsymbol{s}_2V'/\mu^2r+V_t+V_Q, \tag{5.203}$$

$$c_i=(g_i/2s_i-\mu/m_i)\mu/2m_i, \tag{5.204}$$

$$V_t=c_tS_{12}V'/\mu^2r, \quad c_t=g_1g_2\mu/16m_{12}s_1s_2, \tag{5.205}$$

$$V_Q=-QS_{22}\alpha 2s_2(2s_2-1)/r^3, \quad S_{ij}=3s_{ir}s_{jr}-\boldsymbol{s}_1\boldsymbol{s}_2. \tag{5.206}$$

V_t is the generalization of the tensor potential (5.65). The g-factors are here defined as $g_i=2(\kappa_i+1)$ as in (2.76), corresponding to particles satisfying

the Pauli equation. They are related to the nuclear g-factors g_{n2} by (4.151). For $\boldsymbol{s}_i = \boldsymbol{\sigma}_i/2$ and $g_i = 2$, the two spin-orbit potentials agree with (3.163):

$$c_1 = \tfrac{1}{2}(1 - m_1^2/m_{12}^2), \quad c_2 = \tfrac{1}{2}(1 - m_2^2/m_{12}^2). \tag{5.207}$$

Q is the electric quadrupole moment of (4.178). Possible octupole moments of $s_2 = 3/2$ do not contribute at the order α_Z^4. The a_v of (5.200) is

$$a_v = (3\pi Z^2\alpha)^{-1} 2n(2l+1) \int_1^\infty d\xi I_n'(\xi)(\xi^2-1)^{1/2}(\xi^{-2} + \tfrac{1}{2}\xi^{-4}) \tag{5.208}$$

according to (5.83). This integral is best performed numerically. For example, the f-states of $\overline{p}^4$He have $a_v(l=3,\ n\to\infty) \approx 20$.

The a_{ljf} of (5.198) follow from (5.203) by removal of the common factor $V'/\mu^2 r$ and insertion of a factor $-2(\alpha_Z L^2)^{-1}$ ($\alpha_Z L^2$ from the conversion of r^{-3} to r^{-2}, a factor 2 from the replacement of $\boldsymbol{\sigma}_i$ by $\boldsymbol{s}_i$):

$$a_{ljf} = -2\langle c_1 \boldsymbol{l}\boldsymbol{s}_1 + c_2 \boldsymbol{l}\boldsymbol{s}_2 + c_t S_{12} - S_{22} Z^{-1} Q\mu^2\rangle_{ljf}/l(l+1). \tag{5.209}$$

In the presence of hyperfine mixing, one must diagonalize either the 2×2 matrix $\langle j'|a_{lf}|j\rangle$ for $j \equiv j_1 = l \pm \frac{1}{2}$, or the 2×2 matrix $\langle S'|a_{lf}|S\rangle$ for $S = s_2 \pm \frac{1}{2}$. The "stretched" configurations, $f = l + \frac{1}{2} + s_2$ and $f = l - \frac{1}{2} - s_2$ have no mixing, the values of j, j_2 and S are then fixed at their maximal and minimal values. Both spin-orbit operators $\boldsymbol{l}\boldsymbol{s}_i$ are automatically diagonal here:

$$\boldsymbol{l}\boldsymbol{s}_i = \tfrac{1}{2}(\boldsymbol{j}_i^2 - \boldsymbol{l}^2 - \boldsymbol{s}^2) = \tfrac{1}{2}[j_i(j_i+1) - l(l+1) - s_i(s_i+1)]. \tag{5.210}$$

The maximal value $j_i = l + s_i$ gives $\boldsymbol{l}\boldsymbol{s}_i = l s_i$. Similarly, the minimal value $j_i = l - s_i$ gives $\boldsymbol{l}\boldsymbol{s}_i = -(l+1)s_i$. In the first case, the factor l of the denominator in (5.209) is cancelled (as required for $l = 0$), in the other one the factor $l + 1$. Writing the sign as $2(j - l)$, one obtains for the spin-orbit operators,

$$a_{l,\, f=l\pm S} = 2(j-l)(j+\tfrac{1}{2})^{-1}(c_1 + 2s_2 c_2). \tag{5.211}$$

The tensor operator (5.206), $S_{12} = 3s_{1r}s_{2r} - \boldsymbol{s}_1\boldsymbol{s}_2$ has been constructed in (5.67) for $s_2 = 1/2$. For $s_2 = 1$, the three matrices $\boldsymbol{s}_2^{(1)}$ have the form of the $\hat{\boldsymbol{l}}^{(1)}$ of (1.262), from which s_{2r} is constructed as in (2.114). Its matrix elements for fixed j_2 are known from (5.210). For example, $j_2 = l + s_2 - 1$ gives $\boldsymbol{l}\boldsymbol{s}_2 = l(s_2 - 1) - s_2$. Whereas the operator is now easily constructed in the basis $|j_2, s_1, f, m_f\rangle$, it is actually needed in the basis $|j_1, s_2, f, m_f\rangle$, because the fine structure is diagonal there. A "recoupling of angular momenta" is needed. To minimize the confusion of indices, we first consider the transformation to the basis $|S, l, f, m_f\rangle$, where $S(S+1)$ is the eigenvalue of $\boldsymbol{S} = \boldsymbol{s}_1 + \boldsymbol{s}_2$ (for $s_2 = 1/2$, this is the basis shown in (5.32)). For the first basis, we write $\boldsymbol{f} = \boldsymbol{s}_1 + \boldsymbol{j}_2$, for the second one $\boldsymbol{f} = \boldsymbol{S} + \boldsymbol{l}$. The states $|f, m_f\rangle$ are thus constructed by

means of CG-coefficients in two different ways. Using the compact notation of Sect. 2.5,

$$|fm_f\rangle = \Sigma_{m_1}\langle m_1 m_{j2}|fm_f\rangle|s_1 m_1\rangle|j_2 m_{j2}\rangle = \Sigma_{m_S}\langle m_S m_l|fm_f\rangle|Sm_S\rangle|lm_l\rangle. \tag{5.212}$$

The states $|j_2 m_{j2}\rangle$ and $|Sm_S\rangle$ are now also CG-composed,

$$|j_2 m_{j2}\rangle = \Sigma_{m_2}\langle m_2 m_l|j_2 m_{j2}\rangle|s_2 m_2\rangle|lm_l\rangle, \tag{5.213}$$

$$|Sm_S\rangle = \Sigma_{m_1}\langle m_1 m_2|Sm_S\rangle|s_1 m_1\rangle|s_2 m_2\rangle. \tag{5.214}$$

$|fm_f\rangle$ is thus a double sum over $|s_1 m_1\rangle|s_2 m_2\rangle|lm_l\rangle$ in two different ways, namely firstly with coefficients $\langle m_1 m_{j2}|fm_f\rangle\langle m_2 m_l|j_2 m_{j2}\rangle$, and secondly with $\langle m_S m_l|fm_f\rangle\langle m_1 m_2|Sm_S\rangle$. By using the CG orthogonality relations, one may then express a state of the second form of $|fm_f\rangle$ in terms of states of the first form. In a shorthand notation,

$$|(s_1 s_2)Sl, fm_f\rangle = \Sigma_{j_2}|s_1(s_2 l)j_2, fm_f\rangle\langle s_1(s_2 l)j_2, f|(s_1 s_2)Sl, f\rangle. \tag{5.215}$$

Other notations are

$$\langle s_1(s_2 l)j_2, f|(s_1 s_2)Sl, f\rangle = (2j_2+1)^{1/2}(2S+1)^{1/2}W(s_1 s_2 fl; Sj_2), \tag{5.216}$$

$$W(s_1 s_2 fl; Sj_2) = (-1)^{s_1+s_2+l+f}\left\{\begin{array}{ccc} s_1 & s_2 & S \\ l & f & j_2 \end{array}\right\}. \tag{5.217}$$

W is called a Racah coefficient, and $\{\ldots\ldots\}$ is Wigner's $6j$-symbol. It is symmetric under the exchange of columns as well as interchange of upper and lower indices in any two columns. Tabulations are found e.g. in the book of Weissbluth (1978).

The $\boldsymbol{s}_1\boldsymbol{s}_2$ of the tensor operator is diagonal in the $|S, m_S\rangle$-basis, with elements $s_2/2$ and $-(s_2+1)/2$ according to (4.273).

The Dirac equation for one electron produces effects such as the modification of the spin-orbit interaction by the electric quadrupole potential, which for $Z > 1$ may exceed the nuclear recoil effects implied by (5.203). It is then better to include the nuclear spin operator $\boldsymbol{s}_2$ (normally denoted by $\boldsymbol{I}$) in the static approximation. There, the electric multipole interaction is derived from a nuclear wave function $\psi(\boldsymbol{r}_{p1}, \boldsymbol{r}_{p2}\ldots\boldsymbol{r}_{n1}\boldsymbol{r}_{n2}\ldots)$, in which $\boldsymbol{r}_{pi}$ and $\boldsymbol{r}_{ni}$ denote the positions of pointlike protons and neutrons. The Coulomb energy of a test particle of charge $-e$ at position $\boldsymbol{r}$ is $V(\boldsymbol{r}, \boldsymbol{r}_{pi}) = -\alpha/|\boldsymbol{r}-\boldsymbol{r}_{pi}|$, which is expanded as in (3.140) (the second step function is negligible as the antiproton must not enter the nucleus). The $Y_l^{m*}(\Omega_1)$ (3.141) in the expansion is conveniently rewritten as $Y_l^{-m}(\Omega_1)$; the summation indices l and m are replaced by k and m_k:

$$V(\boldsymbol{r}, \boldsymbol{r}_{pi}) = -4\pi\alpha\Sigma_{k=0}^{\infty} r^{-k-1}\Sigma_{pi=1}^{Z} r_{pi}^k \Sigma_m Y_k^{-m_k}(\Omega_1)Y_k^{m_k}(\Omega_{pi}). \tag{5.218}$$

The term with $k = 0$ is independent of r_{pi}; with $4\pi Y_0^0(\Omega_1)Y_0^0(\Omega(pi) = 1$ it gives Z identical terms, $V_0 = -Z\alpha/r$ as expected. The term with $k = 1$

changes the parity of the nuclear state. In the nonrelativistic limit, this follows essentially from (1.110). If the two lowest nuclear states would form a nearly degenerate parity doublet, the antiproton could in principle dipole excite the nucleus to its parity partner. In all other cases, the $k = 1$-term of (5.218) vanishes by parity conservation. The $k = 2$-term contains the interaction between the antiproton and the nuclear quadrupole moment, which is important for highly deformed nuclei. Nuclear quadrupole excitation may then be possible. However, the normal case is the quadrupole potential V_Q (5.206), where the nucleus is not excited.

Any operator t_{ij} of a closed system may be decomposed into irreducible tensor operators $t_k^{m_k}$, which transform under rotations like an angular momentum state $|k, m_k\rangle$. In atomic theory these quantum numbers are integer. Both $\boldsymbol{r}$ and the Pauli matrices $\boldsymbol{\sigma}$ are vector operators, these have $k = 1$ and $m_k = \pm 1, 0$. They are the Cartan components, z and $x_\pm$ (Table 1.1) in the case of $\boldsymbol{r}$, and σ_z (2.51) and $\sigma_\pm$ (2.62) in the case of $\boldsymbol{\sigma}$ (for $\sigma_\pm$, the factor $1/2$ must be replaced by $2^{-1/2}$ as in Table 1.1).

When $t_k^{m_k}$ operates on a state $|j_i m_i\rangle|n\rangle$ (the n comprises all additional quantum numbers), the resulting states transform under rotations as $|k, m_k\rangle|j_i m_i\rangle|n\rangle$ (Wigner-Eckart theorem). The product can be decomposed into states that transform like $|j' m'\rangle$. The matrix elements of $t_k^{m_k}$ are then

$$\langle n'|\langle j' m'_j|t_k^{m_k}|j_i m_i\rangle|n\rangle = (m_i m_k|j' m'_j)\langle n' j'||t||j_i n\rangle, \tag{5.219}$$

where $(m_i m_k|j' m'_j) = (j_1 j_2 m_1 m_2|j' m'_j)$ is the appropriate Clebsch-Gordan coefficient. The remaining "reduced" matrix element $\langle n' j'||t||j_i n\rangle$ is independent of m_i, m_k and m'_j. It may be calculated for any convenient combination of these magnetic quantum numbers, for example $m_k = 0$, $m'_j = m_i$. For the electric dipole interaction, this implies that only the matrix elements of $z = x^0$ is needed; the rest follows from CG's. By (5.219) and parity conservation, the electric dipole interaction changes the atomic orbital angular momentum by exactly one unit.

The electric quadrupole interaction is the product of the two operators with $k = 2$ in (5.218),

$$V_Q(\boldsymbol{r}, \boldsymbol{r}_{pi}) = -\alpha \Sigma_{m_k} t_2^{-m_k} Q_2^{m_k}, \tag{5.220}$$

$$t_2^{-m_k} = (4/5)^{1/2} r^{-3} Y_2^{-m_k}(\Omega_1), \tag{5.221}$$

$$Q_2^{m_k} = (4/5)^{1/2} \Sigma_{pi=1}^{Z} r_{pi}^2 Y_2^{m_k}(\Omega_{pi}). \tag{5.222}$$

The $Y_2^{-m_k}$ can change the atomic orbital momentum by 0 or 2; $\Delta l = 1$ is excluded by parity conservation. In this case, one may insert between $t_2^{-m_k}$ and $Q_2^{m_k}$ in (5.220) two different complete sets of angular momentum states. For the application of (5.219), one needs the set $|j' m'_j\rangle\langle j' m'_j|$ of atomic states. For the corresponding Wigner-Eckart theorem for $Q_2^{m_k}$, one needs the nuclear spin states, $|s'_2 m'_2\rangle\langle s'_2 m'_2|$. For fixed total angular momentum f, the second

basis is related to the first one by the recoupling coefficients (5.215), but now other quantum numbers are relevant. The resulting expectation value is

$$\langle \Sigma_{m_k} t_2^{-m_k} Q_2^{m_k} \rangle_{s_2 j f m_f} = (-1)^{f+j+s_2} \begin{Bmatrix} s_2 & j & f \\ j & s_2 & 2 \end{Bmatrix} \langle s_2 || Q_2 || s_2 \rangle \langle j || t_2 || j \rangle. \tag{5.223}$$

If one is not interested in nuclear structure, one may employ a more elegant formalism. In analogy with the magnetic hyperfine operator, the inner nuclear degrees of freedom are averaged out. As long as nuclear excitation is neglected, the only remaining operator for the atom is the total nuclear angular momentum $\boldsymbol{s}_2 = \boldsymbol{I}$ in this context. After the nuclear averageing, the $Q_k^{m_k}$ of (5.222) must be proportional to the only irreducible tensor of rank 2 that can be constructed from $\boldsymbol{I}$. In cartesian coordinates, it is given by (5.54) (Landau and Lifshitz 1977)

$$Q_{ij} = \tfrac{1}{2} C (I_i I_j + I_j I_i - \tfrac{2}{3} \delta_{ij} \boldsymbol{I}^2), \quad \boldsymbol{I}^2 = I(I+1). \tag{5.224}$$

The constant C is chosen such that $\langle Q_{zz} \rangle_{I_3 = I} = Q$,

$$C = 3Q(2I^2 - I)^{-1}. \tag{5.225}$$

We have already seen in Sect. 4.4 that the minimal value of $s_2 = I$ is 1, which gives $C = 3Q$. The Q_2^0 of (5.222) becomes $(5/16)^{1/2} Q_{33}$ according to Table 1.1, and $\langle Q_2^0 \rangle_{I_3 = I} = Q/2$.

The corresponding tensor operator t_{ik} is similarly constructed from the only atomic operator which remains conserved after inclusion of the fine structure, namely from $\boldsymbol{j} = \boldsymbol{l} + \boldsymbol{s}_1$:

$$t_{ik} = \frac{3Q_j}{2j(2j-1)} (j_i j_k + j_k j_i - \tfrac{2}{3} \delta_{ik} \boldsymbol{j}^2), \quad \boldsymbol{j}^2 = j(j+1). \tag{5.226}$$

Q_j is the atomic quadrupole moment, as seen from outside the atom. The hyperfine interaction needs the corresponding form inside the atom, which has $\boldsymbol{j}$ replaced by $\boldsymbol{l}$ and $l_i l_k$ by $\langle l_i l_k \rangle_j$:

$$t_{ik} = \frac{3Q_l}{2l(2l-1)} [\langle l_i l_k \rangle_j + \langle l_k l_i \rangle_j - \tfrac{2}{3} \boldsymbol{l}^2], \quad \boldsymbol{l}^2 = l(l+1), \tag{5.227}$$

where Q_l is the orbital angular momentum, which may differ from Q_j. The $\langle l_i l_k \rangle_j$ is defined as $\langle \Sigma_{i,k} j_i l_i l_k j_k \rangle_j = \langle (\boldsymbol{jl})^2 \rangle = (\boldsymbol{jl})^2$, because $\boldsymbol{jl} = \frac{1}{2}[j(j+1) - l(l+1) - s(s+1)]$ is a number. The second operator in (5.227) is $\langle \Sigma_{i,k} j_i l_k l_i j_k \rangle_j$, which can be rearranged using $[l_i, l_k] = i\epsilon_{ikl} l_l$, $[j_i, l_l] = i\epsilon_{ilm} l_m$. In this manner, one obtains

$$Q_j = Q_l [3\boldsymbol{jl}(2\boldsymbol{jl} - 1) - 2\boldsymbol{j}^2 \boldsymbol{l}^2][(j+1)(2j+3) l(2l-1)]^{-1}. \tag{5.228}$$

For $s_1 = \frac{1}{2}$, j assumes the values $l \pm \frac{1}{2}$:

$$Q_j(j = l + \tfrac{1}{2}) = Q_l, \quad Q_j(j = l - \tfrac{1}{2}) = (l-1)(2l+3)/l(2l+1). \tag{5.229}$$

Now back to antiprotonic atoms. When the hyperfine structure is negligible, V_s^{CBG} reduces to the antiprotonic spin-orbit coupling $c_1 \boldsymbol{l}\boldsymbol{s}_1 V'/\mu^2 r$. It is then useful to construct a relativistic equation of motion for the $\overline{p}$ which can be solved nonperturbatively. Its static limit has already been given in (4.145). For magnetic field $B = 0$, it reads, with $\pi_1^0 = E_1 - V(r)$,

$$(\pi_1^0 - m_1)\psi_g = (\boldsymbol{p}\boldsymbol{\sigma} - i\kappa_{\mathrm{an}} e\boldsymbol{\sigma}\boldsymbol{E}/2m_1)\psi_f, \tag{5.230}$$

$$(\pi_1^0 + m_1)\psi_f = (\boldsymbol{p}\boldsymbol{\sigma} + i\kappa_{\mathrm{an}} e\boldsymbol{\sigma}\boldsymbol{E}/2m_1)\psi_g. \tag{5.231}$$

And with $e\boldsymbol{E} = \boldsymbol{\nabla}V$, the electric field $\boldsymbol{E}$ is eliminated by the substitution

$$\psi = e^{a_1\beta V/2}\tilde{\psi}, \quad a_1 = \kappa_{\mathrm{an}}/m_1. \tag{5.232}$$

The equation for $\tilde{\psi}$ is

$$(\pi_1^0 - m_1)e^{a_1 V}\tilde{\psi}_g = \boldsymbol{p}\boldsymbol{\sigma}\tilde{\psi}_f, \quad (\pi_1^0 + m_1)e^{-a_1 V}\tilde{\psi}_f = \boldsymbol{p}\boldsymbol{\sigma}\tilde{\psi}_g. \tag{5.233}$$

The transformation

$$\tilde{\pi}_1^0 = \pi_1^0 \cosh(a_1 V) - m_1 \sinh(a_1 V), \quad \tilde{m}_1 = m_1 \cosh(a_1 V) - \pi_1^0 \sinh(a_1 V) \tag{5.234}$$

produces an ordinary Dirac equation,

$$(\tilde{\pi}_1^0 - \tilde{m}_1\beta - \gamma^5 \boldsymbol{p}\boldsymbol{\sigma})\tilde{\psi} = 0. \tag{5.235}$$

As $\tilde{\pi}_1^{02} - \tilde{m}_1^2 = \pi^{02} - m_1^2$, it is in fact only the spin structure which is modified by κ_{an}. To first order in $a_1 V = \kappa_{\mathrm{an}} V/m_1$, one approximates $\cosh(a_1 V) = 1$, $\sinh(a_1 V) = a_1 V$ and obtains for $V = -\alpha_Z/r$

$$\tilde{\pi}_1^0 = E_1 + (\alpha_Z/r)(1 + \kappa_{\mathrm{an}}), \quad \tilde{m}_1 = m_1 + (E_1 + \alpha_Z/r)\alpha_Z \kappa_{\mathrm{an}}/m_1 r. \tag{5.236}$$

With these approximations, (5.235) has the form of the Klein-Dirac equation (4.367); its solution can practically be adopted from (4.371),

$$\gamma_{\mathrm{an}} = [(j + \tfrac{1}{2})^2 - \alpha_Z^2(1 + 2\kappa_{\mathrm{an}})]^{1/2}. \tag{5.237}$$

This is the static limit $m_1/m_2 = 0$. The recoil effects follow from (4.371) and from the adaption of a_1 to c_1 (5.204), $a_{1,\mathrm{rec}} = a_1 m_2/m_{12}$. The recoil-corrected Klein-Dirac equation becomes (in its Kramers form)

$$[(\epsilon - V)^2 - \mu^2 - \boldsymbol{p}^2 + ic_{10}\sigma_{1r}V']\psi_r = 0, \tag{5.238}$$

$$c_{10} = (c_{\mathrm{an}}^2 - m_1^2/m_{12}^2)^{1/2}, \quad c_{\mathrm{an}} = (1 + 2\kappa_{\mathrm{an}} m_2/m_{12})^{1/2}. \tag{5.239}$$

Its solutions follow from (4.370), with γ_{an} replaced by the more general expression

$$\gamma_{c0} = [(j + \tfrac{1}{2})^2 - \alpha_Z^2(c_{\mathrm{an}}^2 - m_1^2/m_{12}^2)]^{1/2}. \tag{5.240}$$

A perturbative treatment of vacuum polarization will now automatically include its influence on the spin-orbit coupling.

For normal electronic atoms, recoil corrections beyond the reduced mass are normally negligible. This applies particularly to the "Barker-Glover" correction $\alpha_Z^2 m_1^2/m_{12}^2$ in γ_c. The new term $-2\alpha_Z^2 \kappa_{\rm an} m_2/m_{12} = -\frac{1}{2}\alpha_Z^3 \alpha_\pi$ (4.137) is much larger. It can influence relativistic polarizabilities and other perturbations.

5.7 The Magnetic Moment Interaction

The anomalous magnetic moments of fermions cause extra spin potentials. They will be derived by the method of Sect. 4.7, with $T_{if}^{(1)}$ given by (4.64) as before, but now with the general form (4.133) of J_{if}^μ, in the approximation $F_1 = 1,\ F_2 = \kappa_1$ and with $\boldsymbol{q} = \boldsymbol{k}_1 - \boldsymbol{k}_1' = \boldsymbol{k}_2' - \boldsymbol{k}_2$:

$$T_{if}^{(1)} = 4\pi\alpha_Z J_{11'}^\mu g_{\mu\nu} J_{22'}^\nu / t = 4\pi\alpha_Z (J_{11'}^0 J_{22'}^0 - \boldsymbol{J}_{11'}\boldsymbol{J}_{22'})/(q^{02} - \boldsymbol{q}^2), \quad (5.241)$$

$$J_{11'}^\mu = \overline{u}_1'(\gamma_1^\mu + \sigma_1^{\mu\nu} q_\nu \kappa_1/2m_1)u_1. \quad (5.242)$$

In the cms one has $q^0 = 0$, and with $\sigma^{0j} = \gamma^5\sigma^j$, $\sigma^{jk} = i\sigma_l$ (jkl cyclic),

$$J_{11'}^0 = u_1'^\dagger(1+\gamma_1^5\beta_1 \boldsymbol{q}\boldsymbol{\sigma}_1\kappa_1/2m_1)u_1, \quad \boldsymbol{J}_{11'} = u_1'^\dagger(\gamma_1^5\boldsymbol{\sigma}_1 - i\beta_1\boldsymbol{q}\times\boldsymbol{\sigma}_1\kappa_1/2m_1)u_1, \quad (5.243)$$

where $\overline{u}_1' = u_1'^\dagger\beta_1$ has been used. The corresponding $J_{22'}^\nu$ has $\boldsymbol{q}_2 = -\boldsymbol{q}$:

$$J_{22'}^0 = u_2'^\dagger(1-\gamma_2^5\beta_2 \boldsymbol{q}\boldsymbol{\sigma}_2\kappa_2/2m_2)u_2, \quad \boldsymbol{J}_{22'} = u_2'^\dagger(\gamma_2^5\boldsymbol{\sigma}_2 + i\beta_2\boldsymbol{q}\times\boldsymbol{\sigma}_2\kappa_2/2m_2)u_2, \quad (5.244)$$

This produces four terms in $T_{if}^{(1)}$,

$$T_{if}^{(1)} = T_D + \kappa_1 T_{\kappa 1} + \kappa_2 T_{\kappa 2} + \kappa_1\kappa_2 T_{\kappa 1,\kappa 2}. \quad (5.245)$$

T_D denotes our previous "Dirac" $T_{if}^{(1)}$ (4.256). We first evaluate the matrix element $T_{\kappa 1,\kappa 2}$:

$$T_{\kappa 1,\kappa 2} = -4\pi\alpha_Z u_1'^\dagger u_1'^\dagger[-\gamma_1^5\gamma_2^5(\boldsymbol{q}\boldsymbol{\sigma}_1)(\boldsymbol{q}\boldsymbol{\sigma}_2) - (\boldsymbol{q}\times\boldsymbol{\sigma}_1)(\boldsymbol{q}\times\boldsymbol{\sigma}_2)]\beta u_1 u_2/4m_1 m_2 \boldsymbol{q}^2. \quad (5.246)$$

The decomposition of $T_{\kappa 1,\kappa 2}$ gives again $T_{vw} = T_{wv} = 0$. In T_{vv}, one uses $\gamma_1^5\gamma_2^5\beta v = \beta\gamma_1^5\gamma_2^5 v = \beta v$, while T_{ww} has $w'^\dagger\gamma_1^5\gamma_2^5 = -w'^\dagger$. The matrix element $M_{\kappa 1,\kappa 2}$ is again constructed by expressing $w = m_+^{-1}(E - \gamma^5\boldsymbol{\Delta}\boldsymbol{\sigma}\boldsymbol{k})v$ and $v'^\dagger = w'^\dagger(E - \gamma^5\boldsymbol{\sigma}\boldsymbol{k})m_+^{-1}$, but this time we contend ourselves with the approximations $w = m_+^{-1}Ev$, $v'^\dagger = w'^\dagger E m_+^{-1}$. The sign change caused by $\gamma_1^5\gamma_2^5$ makes the factor of $(\boldsymbol{q}\boldsymbol{\sigma}_1)(\boldsymbol{q}\boldsymbol{\sigma}_2)$ vanish. And with $(\boldsymbol{q}\times\boldsymbol{\sigma}_1)(\boldsymbol{q}\times\boldsymbol{\sigma}_2) = \boldsymbol{q}^2\boldsymbol{\sigma}_1\boldsymbol{\sigma}_2 - (\boldsymbol{q}\boldsymbol{\sigma}_1)(\boldsymbol{q}\boldsymbol{\sigma}_2)$,

$$M_{\kappa 1,\kappa 2} \approx -8\pi\alpha_Z E[(\boldsymbol{q}\boldsymbol{\sigma}_1)(\boldsymbol{q}\boldsymbol{\sigma}_2) - \boldsymbol{q}^2\boldsymbol{\sigma}_1\boldsymbol{\sigma}_2]/4m_1 m_2 \boldsymbol{q}^2. \quad (5.247)$$

The procedure of Sect. 4.7 was to construct the Fourier transform $I_8(\boldsymbol{r})$ of M and then to use either $I_{81} = C_1^{-1} I_8 C_1$ as the interaction for ψ_1 (4.251), or $I_{82} = C_2^{-1} I_8 C_2$ for ψ_2 (4.252), in order to demonstrate the equivalence of the two equations. In the following, only the equation for ψ_1 will be considered. The indices $_{81}$ will be dropped, and the C_1-transformation will be applied before the Fourier transformation,

$$M^C = C_1^{-1} M C_1,\ I(\boldsymbol{r}) = E H_I(\boldsymbol{r}) = (2\pi)^{-3} \tfrac{1}{2} \int d^3q e^{-i\boldsymbol{qr}} M^C. \tag{5.248}$$

As $M_{\kappa 1,\kappa 2}$ contains no Dirac matrices and as $C_1^{-1}(\sigma_{1i}\sigma_{2j} + \sigma_{1j}\sigma_{2i})C = \sigma_{1i}\sigma_{2j} + \sigma_{1j}\sigma_{2i}$, one finds $M^C_{\kappa 1,\kappa 2} = M_{\kappa 1,\kappa 2}$. For the Fourier transform, one notes from (4.51)

$$(2\pi)^{-3} \int d^3q e^{-i\boldsymbol{qr}} q_i q_j (-4\pi\alpha_Z/q^2) = -\partial_i \partial_j V(r). \tag{5.249}$$

In the irreducible tensor part of $I(\boldsymbol{r})$ or $H_I(\boldsymbol{r})$, one subtracts $\delta_{ij}\partial_i^2/3$ from $\partial_i\partial_j$ as in (5.54), getting

$$H^{(2)}_{\kappa 1,\kappa 2} = \sigma_t V'/4m_1 m_2 r, \quad \sigma_t = 3\sigma_{1r}\sigma_{2r} - \boldsymbol{\sigma}_1\boldsymbol{\sigma}_2, \tag{5.250}$$

$$H^{(0)}_{\kappa 1,\kappa 2} = \tfrac{2}{3}\pi\alpha_Z \delta(\boldsymbol{r}) \boldsymbol{\sigma}_1\boldsymbol{\sigma}_2/m_1 m_2 = H_{\text{con}} \tag{5.251}$$

as in (5.65) and in (5.63).

The matrix elements $T_{\kappa 1}$ and $T_{\kappa 2}$ contain only one factor β_i and require a different elimination. Consider first

$$T_{\kappa 2} = -4\pi\alpha_Z u_1'^{\dagger} u_2'^{\dagger} \boldsymbol{q}(-\gamma_2^5 \boldsymbol{\sigma}_2 + i\gamma_1^5 \boldsymbol{\sigma}^{\times})\beta_2 u_1 u_2/2m_2\boldsymbol{q}^2. \tag{5.252}$$

With $\beta_2 w = v,\ v'^{\dagger}\beta_2 = w'^{\dagger}$, one finds this time $T_{vv} = T_{ww} = 0$,

$$T_{wv} = T_{vw} = -4\pi\alpha_Z \gamma^5 \boldsymbol{q}(\boldsymbol{\sigma}_2 + i\boldsymbol{\sigma}^{\times})/2m_2\boldsymbol{q}^2, \tag{5.253}$$

$$M_{\kappa 2} = -4\pi\alpha_Z \gamma^5 m_- \boldsymbol{q}(\boldsymbol{\sigma}_2 + i\boldsymbol{\sigma}^{\times})/m_2\boldsymbol{q}^2. \tag{5.254}$$

The C_1-transformation replaces $m_-\boldsymbol{\sigma}_2$ by

$$m_- \tfrac{1}{2}(\boldsymbol{\sigma} m_+/m_- - \boldsymbol{\Delta\sigma}) = \tfrac{1}{2}(\boldsymbol{\sigma} m_+ - \boldsymbol{\Delta\sigma} m_-) = \boldsymbol{\sigma}_2 m_2 + \beta\boldsymbol{\sigma}_1 m_1, \tag{5.255}$$

which leads to

$$M^C_{\kappa 2} = -4\pi\alpha_Z \gamma^5 \boldsymbol{q}[\boldsymbol{\sigma}_2 + i\boldsymbol{\sigma}^{\times} + \beta(\boldsymbol{\sigma}_1 - i\boldsymbol{\sigma}^{\times})m_1/m_2]/\boldsymbol{q}^2. \tag{5.256}$$

As there is no explicit factor E in $M^C_{\kappa 2}$, we quote $I(\boldsymbol{r})$ instead of $H_I(\boldsymbol{r})$. Using

$$(2\pi)^{-3} \int d^3q e^{-i\boldsymbol{qr}} \boldsymbol{q}(-4\pi\alpha_Z/q^2) = i\nabla V = i\boldsymbol{r}V'/r, \tag{5.257}$$

$$2I_{\kappa 2} = (V'/r)\gamma^5 \boldsymbol{r}[i\boldsymbol{\sigma}_2 - \boldsymbol{\sigma}^{\times} + \beta(i\boldsymbol{\sigma}_1 + \boldsymbol{\sigma}^{\times})m_1/m_2]. \tag{5.258}$$

For comparison with the static hyperfine operator (4.271), we neglect the terms proportional to m_1/m_2 and add $\kappa_2 I_{\kappa 2}$ to the previous I_8 of leptonium,

$$I_8+\kappa_2 I_{\kappa 2} = EV+\tfrac{1}{2}\gamma^5(\boldsymbol{\sigma}^\times(1+\kappa_2)[\nabla,V]-\boldsymbol{\sigma}^\times\{\nabla,V\}+i\kappa_2\boldsymbol{\sigma}_2[\nabla,V]). \quad (5.259)$$

The factor $(1+\kappa_2) = g_{n2}/2$ in the Hermitian part of the hyperfine operator produces the expected nuclear g-factor.

Next, we construct the four nonrelativistic hyperfine operators implied by (5.258), by eliminating the small components ψ_f as in (5.40). We immediately restrict ourselves to the terms linear in V',

$$V_{\kappa 2} = \{\boldsymbol{\sigma}_1\boldsymbol{p},(V'/r)\boldsymbol{r}(i\boldsymbol{\sigma}_2-\boldsymbol{\sigma}^\times)\}/4\mu E + [\boldsymbol{\sigma}_1\boldsymbol{p},(V'/r)\boldsymbol{r}(i\boldsymbol{\sigma}_1+\boldsymbol{\sigma}^\times)]/4m_2^2. \quad (5.260)$$

commutator arises from the extra factor β, because of $\beta\psi_g = \psi_g$, $\beta\psi_f = -\psi_f$.

The operator containing $\boldsymbol{\sigma}^\times\boldsymbol{r}V'/r$ in the anticommutator is the Hermitian part of the Dirac hyperfine operator, and we simply adopt the results (5.48), (5.65):

$$V_{s2l,\kappa 2} = V_{s2l} = V'\boldsymbol{\sigma}_2\boldsymbol{l}/2E\mu r, \quad V_{t,\kappa 2} = V_t = \tfrac{1}{2}\sigma_t V'/2E\mu r. \quad (5.261)$$

In the commutator, the part containing $i\boldsymbol{\sigma}_1$ is also Hermitian, giving

$$V_{s1l,\kappa 2} = V'\boldsymbol{\sigma}_1\boldsymbol{l}/2m_2^2 r. \quad (5.262)$$

For comparison, the CBG reduction finds only one potential for κ_2 from c_2 (5.204),

$$V_{\kappa 2}^{\mathrm{CBG}}(s_2=\tfrac{1}{2}) = \boldsymbol{\sigma}_2\boldsymbol{l}V'/2\mu m_2 r. \quad (5.263)$$

Again, there is agreement in the expectation values,

$$\langle V_{s2l,\kappa 2}+V_{s1l,\kappa 2}\rangle = \langle V_{\kappa 2}^{\mathrm{CBG}}\rangle, \quad (5.264)$$

but this time a discrepancy will appear in off-diagonal elements at the order $(\kappa_1 m_2-\kappa_2 m_1)^2$.

The part containing $\boldsymbol{\sigma}^\times$ in the commutator is anti-Hermitian and leads to

$$V_{s12l,\kappa 2} = -iV'\boldsymbol{\sigma}^\times\boldsymbol{l}/4m_2^2 r. \quad (5.265)$$

The operator $i\boldsymbol{\sigma}_2\boldsymbol{r}$ in the anticommutator is more complicated. With $i\boldsymbol{\sigma}_1\boldsymbol{p} = \sigma_{1r}(\partial_r-\boldsymbol{\sigma}_1\boldsymbol{l}/r) = (\partial_r+\boldsymbol{\sigma}_1\boldsymbol{l}/r)\sigma_{1r}$, one obtains, neglecting an operator $\sim \Delta V$, and with $\sigma_{1r}\sigma_{2r}$ from (5.67):

$$\chi = \begin{pmatrix}\chi_{f,1}\\ \chi_{f,0}\end{pmatrix}, \quad V_{ah,\kappa 2} = -[\sigma_{1r}\sigma_{2r},\boldsymbol{\sigma}_1\boldsymbol{l}]\frac{V'}{4E\mu r} = \begin{pmatrix}0 & F\\ -F & 0\end{pmatrix}\frac{V'}{2E\mu r}, \quad (5.266)$$

where the index $_{ah}$ stands for "anti-Hermitian".

The calculation of $T_{\kappa 1}$ and $I_{\kappa 1}$ is formally different, but the result follows from $I_{\kappa 2}$ simply by exchange of m_1 and m_2. The β_2 in (5.252) is replaced by $\beta_1 = \beta\beta_2$; the C-transformation replaces $m_-\boldsymbol{\sigma}_1\beta$ by

$$m_-\tfrac{1}{2}(\boldsymbol{\sigma}m_+/m_- + \Delta\boldsymbol{\sigma})\beta = (\boldsymbol{\sigma}_1 m_2+\beta\boldsymbol{\sigma}_2 m_1)\beta = \boldsymbol{\sigma}_2 m_1+\beta\boldsymbol{\sigma}_1 m_2, \quad (5.267)$$

which follows from (5.255) by the exchange of m_1 and m_2. As a result, the total operator proportional to κ_1 and κ_2 is

$$V_\kappa = \{(\boldsymbol{\sigma}_1\boldsymbol{l} - \tfrac{1}{2}i\boldsymbol{\sigma}^\times\boldsymbol{l})\hat{\kappa} + (\boldsymbol{\sigma}_2\boldsymbol{l} + \tfrac{1}{2}\sigma_t - \tfrac{1}{2}[\sigma_{1r}\sigma_{2r}, \boldsymbol{\sigma}_1\boldsymbol{l}])\kappa\}V'/2E\mu r, \quad (5.268)$$

$$\hat{\kappa} \equiv \kappa_1 m_2/m_1 + \kappa_2 m_1/m_2, \quad \kappa \equiv \kappa_1 + \kappa_2. \quad (5.269)$$

Collecting the matrices, one obtains

$$V_\kappa = \begin{pmatrix} -\hat{\kappa} & 0 \\ 2F(\hat{\kappa} - \kappa) & 0 \end{pmatrix} \frac{V'}{2E\mu r}, \quad \hat{\kappa} - \kappa = (\kappa_1 m_2 - \kappa_2 m_1)\frac{m_2 - m_1}{m_1 m_2}. \quad (5.270)$$

To this one has to add the tensor interaction $\kappa_1\kappa_2 H^{(2)}_{\kappa 1,\kappa 2}$ (5.250) and the Dirac spin matrix V_s (5.69),

$$V_{s,\mathrm{tot}} = \begin{pmatrix} -1 - 2y & F \\ Fx & 0 \end{pmatrix} \frac{V'}{4\mu^2 r}, \quad y = (\hat{\kappa} - \kappa_1\kappa_2)\mu/E, \quad (5.271)$$

$$x = 1 - 4(1 - \hat{\kappa} + \kappa)\mu/E = (m_2 - m_1)(m_2 - m_1 + 4\kappa_1 m_2 - 4\kappa_2 m_1)/E^2. \quad (5.272)$$

The eigenvalues of the matrix will again be called $-2a_l^{(\pm)}F^2$, with $F^2 = l(l+1)$ as in (5.70):

$$-2a_l^{(\pm)}F^2 = -\tfrac{1}{2} - y \pm \sqrt{(\tfrac{1}{2} + y)^2 + F^2 x}. \quad (5.273)$$

They may be compared with those of the CBG spin matrix. As the off-diagonal elements of a real 2×2 Hermitian matrix are equal, the corresponding x^{CBG} must be a square:

$$x^{\mathrm{CBG}} = (m_2 - m_1 + 2\kappa_1 m_2 - 2\kappa_2 m_1)^2/E^2 = x + 4(\kappa_1 m_2 - \kappa_2 m_1)^2/E^2. \quad (5.274)$$

The extra square is reminiscent of the V^2 in the form $(E - V)^2$ containing the Coulomb interaction. For leptonium, it may be canceled by higher-order vertex graphs. For hydrogen and for antiprotonic atoms, however, these graphs cannot be calculated. The factor m_1^2/E^2 in front of κ_2^2 shows that this part of x^{CBG} is a second-order hyperfine interaction.

Note that the indices of the spin matrices $\boldsymbol{\sigma}_1$ and $\boldsymbol{\sigma}_2$ remain disconnected from the particle indices. Whereas the original Born amplitude contains the combinations $\boldsymbol{\sigma}_1\kappa_1/m_1$ and $\boldsymbol{\sigma}_2\kappa_2/m_2$, the function multiplying $\boldsymbol{\sigma}_1\boldsymbol{l}$ is obtained from (5.262) as

$$V_{s1l,\kappa} = (V'/2r)\boldsymbol{\sigma}_1\boldsymbol{l}(\kappa_2/m_2^2 + \kappa_1/m_1^2). \quad (5.275)$$

The $m_1 \leftrightarrow m_2$ symmetry noted earlier in (5.48) is thus extended to a (κ_1, $m_1 \leftrightarrow \kappa_2$, m_2) symmetry.

5.8 SU_2, SU_3, Quarks

A short historical of the quark model may be in order. It all began with the "isospin" invariance of nuclear physics, which is based on the near equality of proton and neutron masses, $m_p = 938.28\,\mathrm{MeV}$, $m_n = 939.57\,\mathrm{MeV}$. Proton and neutron may be regarded as two isospin states of the "nucleon" N, with $I = 1/2$ and $I_3 = +1/2$ and $-1/2$, respectively. Strong interactions are invariant under unitary transformations SU_2 between p and n, which form an "isospin" doublet like the states χ_+ and χ_- (2.49) of ordinary fermion spin. When the pions π^+, π^0, π^- were found with nearly equal masses ($m_{\pi\pm} = 139.57\,\mathrm{MeV}$, $m_{\pi 0} = 134.96\,\mathrm{MeV}$), they were taken as an isotriplet. They have spin and parity 0^-, which allows one to formally treat them as $N\overline{N}$ bound states (Fermi and Yang 1949), with quantum numbers 1^1S_0. (The parity of a fermion-antifermion pair of orbital angular momentum l is $-(-1)^l$, the extra sign coming from the field anticommutator as for charge conjugation (4.288). Like the singlet state of positronium, the π^0 decays into $\gamma\gamma$). The Clebsch-Gordan series for $N\overline{N}$ gives $2 \times 2 = 3 + 1$. The components of the pion triplet may be adopted from (3.128) and (3.130), although modern textbooks normally use an extra minus sign for π^-. The predicted isosinglet state was found later in the form of the η meson (also 0^-, $m_\eta = 547.45\,\mathrm{MeV}$). The Fermi-Yang model also resulted in the "Goldberger-Treiman" relation for axial beta-decay, which has remained correct for different reasons.

Next found were the kaons $K = (K^+, K^-)$ and the isoscalar and isovector "hyperons" Λ and $\Sigma = (\Sigma^+, \Sigma^0, \Sigma^-)$, which decay weakly to nucleons. Strong interactions conserve a new "strangeness" quantum number which is $+1$ for K, -1 for $\overline{K}$ and -1 for the hyperons. Although $m_\Lambda - m_n = 176\,\mathrm{MeV}$ is not particularly small, the group of unitary transformations is sometimes extended from SU_2 to SU_3.

The group SU_n has $n^2 - 1$ generators of transformations. For SU_2, these are the three Pauli matrices $\boldsymbol{\sigma}$ which act on the fundamental spinors $\chi_\pm$ (2.49). SU_3 has eight 3×3 traceless generators λ^k, which act on the fundamental triplet, now called u (for isospin "up"), d (for isospin "down"), and s (for "strange"):

$$u = \begin{pmatrix} \chi_+ \\ 0 \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \quad d = \begin{pmatrix} \chi_- \\ 0 \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}, \quad s = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}. \tag{5.276}$$

The first three λ may be identified witht the σ which act only on u and d (compare (2.75)):

$$SU_3 = \exp\left\{ -\tfrac{1}{2} i \sum_{k=1}^{8} \alpha^k \lambda^k \right\}, \quad \lambda^{1,2,3} = \begin{pmatrix} \sigma^{1,2,3} & 0 \\ 0 & 0 \end{pmatrix}. \tag{5.277}$$

In analogy with σ^1 and σ^2 which exchange u with d, one defines $\lambda^6 = u^1$ and $\lambda^7 = u^2$ as thoses matrices which exchange d with s and leave u invariant:

$$\lambda^6 = \begin{pmatrix} 0\,0\,0 \\ 0\,0\,1 \\ 0\,1\,0 \end{pmatrix} \equiv u^1, \quad \lambda^7 = \begin{pmatrix} 0\,0\,0 \\ 0\,0\,-i \\ 0\,i\,0 \end{pmatrix} \equiv u^2. \tag{5.278}$$

The corresponding two matrices "v^1, v^2" which leave d invariant get the numbers 4 and 5:

$$\lambda^4 = \begin{pmatrix} 0\,0\,1 \\ 0\,0\,0 \\ 1\,0\,0 \end{pmatrix} \equiv v^1, \quad \lambda^5 = \begin{pmatrix} 0\,0\,-i \\ 0\,0\,0 \\ i\,0\,0 \end{pmatrix} \equiv v^2. \tag{5.279}$$

One could now identify the remaining λ^8 with u^3 or v^3 or with any linear combination of these two diagonal matrices. As SU_3 is much more broken than SU_2, one takes that combination which commutes with all three SU_2 generators λ^1, λ^2, λ^3:

$$\lambda^8 = 3^{-1/2} \begin{pmatrix} 1\,0\,0 \\ 0\,1\,0 \\ 0\,0\,-2 \end{pmatrix}. \tag{5.280}$$

The -2 in the last row follows from trace$\lambda^8 = 0$, the normalization factor $3^{-1/2}$ follows from trace$\lambda^i\lambda^i = 2\delta^{ik}$.

The generators of SU_n form the "regular" representation, of dimension $n^2 - 1$. It is a triplet (isospin 1) in SU_2, an octet in SU_3. For a while, one speculated that the baryons p, n and Λ could make the fundamental triplet. The triplet of Σ hyperons was taken as $\Lambda\pi$ bound states. Another isodoublet $\Xi = (\Xi^0, \Xi^-)$ of strangeness -2 at higher mass (Table 5.1) was taken as $\Lambda\overline{K}$ bound states. However, the identical spins and parities ($\frac{1}{2}^+$) of all these eight baryons pointed to the regular representation. In the limit of unbroken SU_3 symmetry, all eight baryons should have the same mass.

In analogy with the Clebsch-Gordan decomposition, one can use the u-spin lowering operator $u_- = u^1 - iu^2$ to generate from the neutron state n the complete "U-spin" triplet $|U, U_3\rangle$ for $U = 1$,

$$|1, 1\rangle_U = n, \quad |1, 0\rangle_U = \tfrac{1}{2}(3^{-1/2}\Lambda + \Sigma^0), \quad |1, -1\rangle_U = \Xi^0. \tag{5.281}$$

Gell-Mann and Okubo proposed that the SU_3-breaking "semistrong" interaction should also arise from one of the generators, in which case it must be λ^8 in order not to spoil SU_2. First-order perturbation theory predicts equal spacing between the masses of the U-spin triplet,

$$[m(\Xi^-) - \tfrac{1}{4}(3m(\Lambda) + m(\Sigma^0))]/[\tfrac{1}{4}(3m(\Lambda) + m(\Sigma^0)) - m(n)] = 1. \tag{5.282}$$

The experimental value of this ratio is 0.92. The E^2-theorem replaces the masses by their squares, in which case the ratio becomes 1.08. Similarly, the

Table 5.1. Masses and magnetic moments of baryons, from Review of Particle Physics (2004). The first column gives the (mass)^2. The last column gives the magnetic moment in the quark model.

baryon	m^2 [GeV]^2	m[GeV]	μ [μ_n]	μ (quark model)
p = (uud)	.880369	.938280	2.79285	$(4\mu_u - \mu_d)/3$
n = (ddu)	.882797	.939573	−1.91304	$(4\mu_d - \mu_u)/3$
Λ = (uds)	1.24475	1.11568	−.613	μ_s
Σ^+ = (uus)	1.41460	1.18937	2.46	$(4\mu_u - \mu_s)/3$
Σ^0 = (uds)	1.42239	1.19264		
Σ^- = (dds)	1.43389	1.19745	−1.16	$(4\mu_d - \mu_s)/3$
Ξ^0 = (ssu)	1.72879	1.31483	−1.25	$(4\mu_s - \mu_u)/3$
Ξ^- = (ssd)	1.74586	1.32131	−0.65	$(4\mu_s - \mu_d)/3$

pions form a pseudoscalar (i.e. spin-parity 0^-) octet together with η^0 and the kaon and antikaon doublets, $K^+ = u\overline{s}$, $K^0 = d\overline{s}$, $K^- = s\overline{u}$, $\overline{K}^0 = s\overline{d}$. The corresponding GMO mass relation is

$$m_\pi^2 + 3m_\eta^2 = 4m_K^2. \tag{5.283}$$

The pseudoscalar SU_3 singlet is called η'; the experimental mass of 950 MeV includes some SU_3-breaking $\eta - \eta'$-mixing.

In weak decays, the strangeness changes by at most one unit, such that the Ξ baryons cannot decay directly to nucleons. Instead, they decay in a "cascade" via the Λ and Σ hyperons, which earned them the name "cascade particles". As the "charm" quantum number below is also conserved in strong interactions, many of the "charmed baryons" have even longer decay sequences.

The Quark Model

One may distinguish between two periods of the quark model, one from the "eightfold way" of Gell-Mann (1964) and Zweig (1964) to the discovery of the J/ψ meson in 1974, and the post-1974 period which is dominated by quantum chromodynamics (QCD), a field theory analogous to QED. Its breakthrough came already in 1973 with papers by t'Hooft (unpublished), Politzer (1973) and by Gross and Wilczek (1973), who showed that the effective coupling constant between quarks vanishes at short distances (contrary to QED, where it is enhanced by vacuum polarization, see Sect. 5.3). Before the J/ψ discovery, all known mesons and meson resonances (such as the ρ resonance which decays immediately to two pions) could be identified with bound states of one of the three quarks $q = (u, d, s)$ (with electric charges 2/3, −1/3 and −1/3) and one of the three antiquarks $\overline{q} = (\overline{u}, \overline{d}, \overline{s})$.

Direct products of SU_3 multiplets are decomposed by the Clebsch-Gordan series, $3 \times \overline{3} = 8 + 1$ (SU_2 has $\overline{2} = -2$, see (3.95). In SU_3, no linear relation between $\overline{3}$ and 3 exists). Gell-Mann and Zweig interpreted baryons as bound states of three quarks qqq, with the SU_3-decomposition $3 \times 3 \times 3 = 3 \times (6 + \overline{3}) = 8 + 10 + 8 + 1$. The states $3 \times \overline{3}$ are absent. The baryon octet has spin 1/2, while the decuplet of resonances $\Delta = (\Delta^{++}, \Delta^{+}, \Delta^{0}, \Delta^{-})$, $\Sigma^{*} = (\Sigma^{*+}, \Sigma^{*0}, \Sigma^{*-}), \Xi = (\Xi^{*0}, \Xi^{*-})$ and Ω^{-} has spin 3/2 (the Ω^{-} has strangeness -3 and is in fact stable against strong decay). Attemps to ignore the "hyperfine" splitting led to an even larger symmetry group SU_6, which is not used any more.

After the J/ψ discovery, the quark model became much richer and more precise. Bound states of three heavy quarks c (charm), b (bottom), and t (top) (with charges 2/3, $-1/3$ and 2/3, respectively) were found. Today, one says that quarks come with the six "flavors" u, d, s, c, b, t. The heavy quark masses are so large that the extension of SU_3 to SU_{Nf} (N_f = number of flavours > 3) is useless. The above SU_3 is also called $SU_{3,\mathrm{flavor}}$, to distinguish it from the $SU_{3,\mathrm{color}}$ below. The J/ψ itself is $1^3S_1 c\overline{c}$. It is formed directly as a sharp resonance in $e^- e^+$ collisions at 3.098 GeV. The corresponding $2S$ and $3S$ states, $\psi' = \psi(2S)(3.6861)$ and $\psi'' = \psi(3S)(3.770)$ are also formed (the ψ'' decays strongly into $D\overline{D}$, where D stands for the charmed isodoublet $D^0 = c\overline{u}$, $D^+ = c\overline{d}$). The similarity with the positronium spectrum becomes even more spectacular for the $b\overline{b}$ resonances $\Upsilon(1S)(9.460) - \Upsilon(4S)(10.580)$; thence the name "quarkonium".

With so many striking parallels, it is natural to look again for an underlying field theory of mesons and baryons ("hadrons") as a rigorous basis. This field theory is called QCD, the "C" will be explained below. Its short-range interaction is sufficiently weak for a perturbative treatment in terms of Feynman graphs for high-energy processes (see for example the book by Yndurain 1999). As in QED, the Fourier transform of the Born series also provides the potential for bound states, but now only at short distances. At large distances, the interaction becomes too strong; presumably it diverges for $r \to \infty$. One defines a phenomenological "QCD parameter" $\Lambda_{\mathrm{QCD}} \approx 200\,\mathrm{MeV}$ and the "confinement radius" $R_c = \Lambda_{\mathrm{QCD}}^{-1}$, beyond which the treatment as an effective two- or three-body problem breaks down. As the Bohr radius a_B decreases with the reduced mass of the system, a sufficiently large reduced mass gives a ground state as well as a few excited states with wave functions essentially inside R_c. This explains the succes of QCD for charmonium and bottonium. Other systems such as $D = c\overline{l}$ ($l = u$ or d) have too large Bohr radii, but relations between the hyperfine operators (which are of short range) do persist (see for example Grozin 2004).

On the other hand, all pre-1974 hadrons would extend far beyond R_c according to QCD. One benefit of QCD remains, namely the "spontaneously broken" "chiral symmetry" of massless u, d, and perhaps even s quarks (see for example Donoghue et al. 1992). The pseudoscalar mesons π, K, η are

treated as Goldstone bosons, a concept which seems incompatible with the $q\overline{q}$ model. In the spontaneously broken symmetry, E^2 would be linear in the quark masses, $E^2 \approx B(m_1 + m_2)$, with B of the order of 1 GeV. The impressive "constituent quark" model of Gell-Mann and Zweig for all the mesons, nucleons, hyperons etc. before 1974 is not supported by QCD.

Connected with QCD is a hidden quantum number called "color", which is needed not only for the form of the interaction (its gauge transformations are nonabelian), but also for the Pauli principle of bound states. Consider the quark representation of Δ^{++}, which is $1Suuu_{3/2}$. The spin 3/2 state is totally symmetric under the exchange of the quark spins, and so is uuu. To avoid a breakdown of the spin-statistics theorem, each quark is endowed with a "color" which can assume three different values and which make each q a triplet in a new symmetry group SU_{3c}. Multiplication of $1Suuu_{3/2}$ by the totally antisymmetric combination of three colours saves the Pauli principle of bound states and the Fermi-Dirac statistics of the quark fields of QCD. $SU_{3\text{color}}$ is assumed to be strictly conserved, such that color singlets remain "colorless" forever.

However, the color of quarks must be well hidden such that it never shows up. In principle, the $c\overline{c}$ bound state could auto-ionize into $c + \overline{c}$, where even the widely separated quarks would still be in a color singlet. An analogy is known from the decay $\pi^0 \to \gamma\gamma$, where the two photons remain in a state of zero helicity, no matter how far they are apart (such states were called "verschränkt" (entangled) by Schrödinger and are considered for future quantum computation). The way out in QCD is that the c and $\overline{c}$ at distances $r > R$ "hadronize" into $(c\bar{l})$ and $(\overline{c}l)$, such that they appear as D and $\overline{D}$ in measurements.

The conclusion of QCD for the quark potential model of hadrons is thus gloomy. As no quark will ever be seen, its mass cannot be measured. Instead, quark masses must be estimated from the unprecise theory of bound states. Best suited are states with small relativistic effects. For example $m_{J/\psi} \approx 2m_c$. A presently acceptable range is $1.15\,\text{GeV} < m_c < 1.35\,\text{GeV}$. The masses of light quarks remain largely arbitrary. Nevertheless, the quarkonium model of the "old" hadrons is qualitatively and sometimes even quantitatively successful. The magnetic moment predictions of Table 5.1 will be discussed in Sect. 5.9. Here we discuss the decay width, which strongly support the binary bound state hypothesis.

Table 5.2 collects the masses, decay channels and widths of the nonet of the old "vector mesons" and the J/ψ. The ρ, ω and K^* are broad "resonances". The width of ω is comparatively small because the decay $\omega \to \pi^-\pi^+$ is forbidden by a combination of charge conjugation and isospin invariance, whereas the allowed decay $\omega \to \pi^-\pi^0\pi^+$ is supressed by a small phase space. The ϕ meson and the J/ψ have the same quantum numbers as the ω, but their three-pion decays have much larger phase spaces available. One would then expect widths of 100 MeV or more. The opposite is true. Before the

Table 5.2. The (masses)^2 and widths of the old vector meson resonances and of the J/ψ.

meson	I, S	m^2 [GeV]	main decay	Γ [MeV]
$\rho = (\rho^+, \rho^0, \rho^-)$	1 0	0.587	$\pi^+\pi^-$	150
ω	0 0	0.613	$\pi^+\pi^0\pi^-$	8.5
$K^* = (K^{*+}, K^{*0})$	1/2 1	0.796	$K\pi$	50
$\overline{K}^* = (\overline{K}^{*-}, \overline{K}^{*0})$	1/2 −1	"	$\overline{K}\pi$	"
ϕ	0 0	1.0393	$K\overline{K}$	4.3
J/ψ	0 0	9.591	hadrons	0.091

discovery of the J/ψ, the relative stability of ϕ was explained by the OZI (Okubo-Zweig-Iizuka) rule, saying that the quark and antiquark in the initial state are unwilling to annihilate. The ϕ is $s\overline{s}$ and thus forced to decay into a pair of kaons. The J/ψ is $c\overline{c}$. Here the charmonium model says that the $c\overline{c}$ annihilation rate is proportional to the square of the bound state wave function at the origin, which is small (at least in the nonrelativistic approximation). The success of the OZI rule shows that this argument applies also to the old vector mesons.

In quark loops, the color degree of freedom provides a factor 3, which is necessary both in the decay $\pi^0 \to \gamma\gamma$ and in the reaction $e^+e^- \to$ hadrons (Close 1979, Donoghue et al 1992). Outside loops, the (strong) hyperfine interaction in $q\overline{q}$ states is attractive as in positronium. Without color, it remains attractive there but turns repulsive in the qq subsystems of qqq, thus predicting spin 3/2 for the ground states of baryons (Close 1979). Here, however, the anti-Hermitian parts of the hyperfine operators $\boldsymbol{\sigma}_i \times \boldsymbol{\sigma}_j V \boldsymbol{p}_{ij}$ should be included. It might also be worth while to elaborate other possible Dirac structures such as $f_y = 2E\boldsymbol{p}\boldsymbol{\sigma}_2 \sin\omega_D$ in (4.397). The qqq states have not yet been analyzed from this point of view.

Perhaps it is possible to extend QCD to large distances. A new version might somehow restrict the separate fields for quarks and their "gluons" (which provide the interaction in QCD). At its extreme, it could return to the early theory of strong interactions, where mesons were "elementary" particles, created and absorbed by local fields. The new fields would have to be bilocal for mesons and trilocal for baryons. It is known that composite particles may be represented by fields in the local limit; an example has been given in (3.93) for ^{14}N. In the equations for the inner structure of these fields, one could keep the Dirac kinetic energy operators $\gamma_i^5 \boldsymbol{p}_i \boldsymbol{\sigma}_i$, but add new operators or omit old ones.

As an example, consider the Dirac equation (2.100) for quark 1 with right- and left-handed masses m_{1r} and m_{1l}, respectively. Its Dirac version is (2.101), even if in $m_1\beta_{1,\mathrm{sim}}$ (2.102) the γ_1^5 replaced by $\gamma_1^5\gamma_2^5$, because γ_2^5 does not operate in the Dirac space of quark 1:

$$m_1\beta_{1,\mathrm{sim}} = \tfrac{1}{2}\beta_1[m_{1r} + m_{1l} + (m_{1r} - m_{1l})\gamma_1^5\gamma_2^5], \tag{5.284}$$

and correspondingly for quark 2. On the other hand, one now has $m_1\beta_{1,\mathrm{sim}}\psi = m_{1r}\psi,\ m_1\beta_{1,\mathrm{sim}}\chi = m_{1l}\chi$. In the binary equation (3.217), one thus gets m_+^2 replaced by

$$m_{l+}m_{r+} = (m_{2l}+\beta m_{1l})(m_{2r}+\beta m_{1r}) = m_1^2+m_2^2+m_1m_2(x+1/x)\beta, \quad (5.285)$$

$$x = m_2m_{1r}/m_1m_{2r}. \quad (5.286)$$

Note that $x+1/x > 2$. The effect arises because the sum of the two similarity transformed operators is not a similarity transform of the original sum. This might be helpful for quarkonium models.

The standard QCD Lagrangian has little room for new operators. The three positively charged quark fields may be combined into a single spinor field Ψ_+, the three negatively charged ones into another spinor field Ψ_-, the masses into 3×3 diagonal matrices:

$$\Psi_+ = \begin{pmatrix}\Psi_u\\ \Psi_c\\ \Psi_t\end{pmatrix}, \quad \Psi_- = \begin{pmatrix}\Psi_d\\ \Psi_s\\ \Psi_b\end{pmatrix}, \quad (5.287)$$

$$m_+ = \begin{pmatrix}m_u & 0 & 0\\ 0 & m_c & 0\\ 0 & 0 & m_t\end{pmatrix}, \quad m_- = \begin{pmatrix}m_d & 0 & 0\\ 0 & m_s & 0\\ 0 & 0 & m_b\end{pmatrix}. \quad (5.288)$$

The six mass terms of the Lagrangian (3.91) appear then as

$$L_m = L_{m+} + L_{m-}, \quad L_{m+} = \overline{\Psi}_+ m_+ \Psi_+, \quad L_{m-} = \overline{\Psi}_- m_- \Psi_-. \quad (5.289)$$

Each $\overline{\Psi}\Psi$ is $\Psi_r^\dagger\Psi_l + \Psi_l^\dagger\Psi_r$. We shall see below that the Ψ_l are linear combinations of fields Ψ_l' that occur in the quark current of beta decay, $\Psi_{\pm,l} = S_\pm^\dagger \Psi'_{\pm,l}$. Admitting for completeness also similar transformations for righthanded fields, $\Psi_{\pm,r} = S_{\pm,r}^\dagger \Psi_r'$, one gets

$$L_{m+} = {\Psi'}^\dagger_{+l} m'_+ \Psi'_{+r} + {\Psi'_{+r}}^\dagger {m'_+}^\dagger \Psi'_{+l}, \quad (5.290)$$

$$m'_+ = S_+ m_+ S_{+r}^\dagger, \quad m'_- = S_- m_- S_{-r}^\dagger. \quad (5.291)$$

With $\det(S) = 1$, $m_\pm$ and $m'_\pm$ have identical eigenvalues; the $m'_\pm$ are similarity transforms of $m_\pm$. The non-unitary matrix V of (2.170) is now replaced by two unitary matrices. This is convenient for the construction of $m_\pm$ from $m'_\pm$. One first considers the product $m'm'^\dagger$ which is Hermitian:

$$m'm'^\dagger = SmS_r^\dagger S_r m^\dagger S^\dagger = Sm^2S^\dagger, \quad (5.292)$$

as $S_r^\dagger S_r = 1$ and $mm^\dagger = m^2$. After the diagonalization of $Sm^2S^\dagger$, one then obtains $m = (m^2)^{1/2}$.

The matrix $S_+^\dagger S_-$ (with $S_+ \equiv S_{+,l}$) enters the Lagrangian for beta decay. The decays $n \to pe^-\overline{\nu}$ and $\Lambda \to pe^-\overline{\nu}$ were originally attributed to two different currents j_{pn}^μ and $j_{\Lambda n}^\mu$ in (2.323), with G_μ replaced by two different

coupling constants G_n and G_Λ. Cabibbo (1963) noted a kind of universality, $G_n = G_\mu \cos\Theta_C$, $G_\Lambda = G_\mu \sin\Theta_C$. In terms of the quark model, Cabibbo's expression is

$$j^\mu = \Psi^\dagger_{u,l}\sigma^\mu_l(\cos\Theta_C\Psi_{dl} + \sin\Theta_C\Psi_{s,l}). \tag{5.293}$$

Already before the discovery of charm, this expression was generalized by Glashow, Iliopoulos and Maiani (1970) to

$$j^\mu_{\rm GIM} = {\Psi'_{+,l}}^\dagger\sigma^\mu_l S^\dagger_+ S_-\Psi_{-,l}, \tag{5.294}$$

where the index l of $\pm, l$ is again suppressed. The product of the two unitary matrices $S^\dagger_+$ and S_- is again unitary and can be kept real by a suitable choice of phases between the fields:

$$S^\dagger_+ S_- = \begin{pmatrix} \cos\Theta_C & \sin\Theta_C \\ -\sin\Theta_C & \cos\Theta_C \end{pmatrix}. \tag{5.295}$$

With the discovery of the b ("beauty") quark, a corresponding t quark of charge $+2/3$ was postulated, such that (5.295 could be generalized to a 3×3 unitary matrix (Kobayashi and Maskawa 1973). This KM matrix may be taken as SU_3, which fixes the relative phase between Ψ_+ and Ψ_-. Of its remaining 8 real parameters, two are eliminated by the relative phases in Ψ_+, and two by the relative phases in Ψ_-. This leaves 4 parameters, of which 3 may be taken as angles Θ_1, Θ_2, Θ_3, and the last one as a complex phase $e^{i\delta}$. It introduces complex coupling constants into beta decay, which violate CP invariance. This topic is treated in special books (Jarlskog 1989, Bigi and Sanda 2000). It was first discovered in decays of the long-lived neutral kaon K^0_L which is close to a CP eigenstate $|K^0_2\rangle = 2^{-1/2}|K^0 + \overline{K}^0\rangle$, and is presently under investigation for the B^0 states which are linear combinations of $|d\bar{b}\rangle$ and $|\bar{d}b\rangle$.

5.9 Baryon Magnetic Moments

With the possible exception of "pentaquarks", all baryons are described as three-quark bound states. Being color-singlets, they belong to the singlet representation "1" of $3\times 3\times 3$ color, which is totally antisymmetric in all three indices. As it is the same for all baryons, it may simply be ignored. Moreover, all three quarks in the baryon octet and decuplet are in the $(1s)^3$ state which is totally symmetric and which may be factored out as well. The remaining problem is then to find the (flavor, spin)-states of baryons. In the limit of SU_3 symmetry, it is analogous to finding totally antisymmetric (orbital, spin)-states for three electrons, which was discussed in Sect. 3.9. The states uuu, ddd, and sss contain three identical quarks. As their complete states including color must be antisymmetric, their spin states $\chi(S, m_s)$ must be totally symmetric. These are the states $\chi(3/2, m_s)$ mentioned in Sect. 3.9. They

are now rewritten in the most compact notation $\chi(+1/2)$ = "spin up" = $\uparrow$, $\chi(-1/2)$ = "spin down" = $\downarrow$:

$$\chi(\tfrac{3}{2},\tfrac{3}{2}) = \uparrow\uparrow\uparrow, \quad \chi(\tfrac{3}{2},\tfrac{1}{2}) = 3^{-1/2}(\downarrow\uparrow\uparrow + \uparrow\downarrow\uparrow + \uparrow\uparrow\downarrow). \tag{5.296}$$

In Sect. 3.9, they were rejected for the orbital combinations $|00v\rangle$ (two electrons in the ground state, one electron in a valence state). Now they are welcome for the orbital state $|000\rangle$ of three identical quarks, in particular for the Δ^{++} which is uuu. In perfect SU_2 symmetry, u and d are identical particles, which allows one to generate the other members Δ^+, Δ^0, Δ^- of this isospin quartet by quark lowering operators. For example, the state $|\frac{3}{2},\frac{3}{2}\rangle$ of Δ^+ is $3^{-1/2}(duu+udu+uud)\uparrow\uparrow\uparrow$, where the bracket results from the quark lowering operator, precisely as with spin. The spin state $|\frac{3}{2},\frac{1}{2}\rangle$ of Δ^+ is then

$$|\Delta^+\uparrow\rangle = \tfrac{1}{3}(duu+udu+uud)(\downarrow\uparrow\uparrow + \uparrow\downarrow\uparrow + \uparrow\uparrow\downarrow). \tag{5.297}$$

Our aim now is to construct the corresponding proton state $|p\uparrow\rangle$, which has $S = 1/2$, but which should nevertheless be totally symmetric in the limit of perfect isospin invariance.

There are two totally symmetric states in addition to (5.297), namely one which contains only those products in which d has $\downarrow$ and each u has $\uparrow$,

$$\psi_{\rm cor} = 3^{-1/2}(udu\uparrow\downarrow\uparrow + uud\uparrow\uparrow\downarrow + duu\downarrow\uparrow\uparrow), \tag{5.298}$$

and the rest, which contains the mixed products:

$$\psi_{\rm mix} = 6^{-1/2}[duu(\uparrow\downarrow\uparrow + \uparrow\uparrow\downarrow) + udu(\downarrow\uparrow\uparrow + \uparrow\uparrow\downarrow) + uud(\downarrow\uparrow\uparrow + \uparrow\downarrow\uparrow)], \tag{5.299}$$

Both states are normalized to 1. The desired proton state is that combination which is orthogonal to (5.297),

$$\langle\Delta^+\uparrow|a\psi_{\rm cor} + b\psi_{\rm mix}\rangle = 0, \tag{5.300}$$

with the normalization $a^2+b^2=1$. The result is $b = -2^{-1/2}a$, i.e. $a = (2/3)^{1/2}$, $b = 3^{-1/2}$, which gives explicitly

$$\begin{aligned}|p\uparrow\rangle = (18)^{-1/2}[&2(duu\downarrow\uparrow\uparrow + udu\uparrow\downarrow\uparrow + uud\uparrow\uparrow\downarrow) - uud(\uparrow\downarrow\uparrow + \downarrow\uparrow\uparrow)\\ &- udu(\uparrow\uparrow\downarrow + \downarrow\uparrow\uparrow) - duu(\uparrow\uparrow\downarrow + \uparrow\downarrow\uparrow)].\end{aligned} \tag{5.301}$$

To check the spin 1/2 of this state, one combines the terms such that two of the three spin always appear as singlets, for example

$$udu(2\uparrow\downarrow\uparrow - \uparrow\uparrow\downarrow - \downarrow\uparrow\uparrow) = udu[\uparrow(\downarrow\uparrow - \uparrow\downarrow) + (\uparrow\downarrow - \downarrow\uparrow)\uparrow]. \tag{5.302}$$

In the nonrelativistic Zeeman operator (4.150), the magnetic moment is expressed by (4.152), $\boldsymbol{\mu}_i = g_i\mu_n\boldsymbol{s}_i = \mu_i\boldsymbol{\sigma}_i$, $\mu_n = e\hbar/2m_pc$ being the nuclear magneton. In Table 5.1, $g_i/2$ is quoted, which would be 1 for a Dirac proton.

The last column gives the quark model values, $\mu_{\rm octet} = \Sigma_{i=1}^{3}\mu_i\sigma_{zi}$. For the proton and neutron, these are calculated from (5.301) and from the corresponding expression for $|n\uparrow\rangle$, which has u and d exchanged. The first three terms of (5.301) have $\sigma_{u1z} + \sigma_{u2z} = 2$, with a weight $4/18$, giving a total of $2 \cdot 3 \times 4/18 = 4/3$. The remaining six terms have $\sigma_{u1z} + \sigma_{u2z} = 0$. Similarly, the first three terms contribute $-\mu_d$ with a weight $4/18$ each, while the remaining six terms contribute $+\mu_d$ with a weight $1/18$ each, giving a total of $-\mu_d(12-6)/18 = -\mu_d/3$. For the up and down quarks, one obtains in this way

$$\mu_u = 1.85\mu_n, \quad \mu_d = -.972\mu_n. \tag{5.303}$$

As the masses of u and d quarks are not known, these values cannot be related to the $g = 2$ expected for Dirac quarks. From the quark charges $+2/3$ and $-1/3$, SU_2 symmetry predicts $\mu_u = -2\mu_d$, $\mu_p/\mu_n = -3/2$. The experimental value -1.53 is slightly larger, which seems related to the presence of virtual pions in the nucleons. Using the CG-coefficients (2.131) with $I_1 = 1,\ I_2 = 1/2$ instead of $j_1 = 1,\ j_2 = 1/2$, one finds for the virtual emission of pions by nucleons,

$$p \to (2/3)^{-1/2}\pi^+ n - 3^{-1/2}\pi^0 p, \quad n \to -(2/3)^{-1/2}\pi^- p + 3^{-1/2}\pi^0 n. \tag{5.304}$$

Consequently, the charged pions appear with weight $2/3$ in both cases. If they were the only source of magnetic moments, one would have $\mu_p/\mu_n = -1$. The early theory of strong interactions assumed that each baryon was surrounded by a cloud of virtual mesons, in which the pions dominate because of their small mass.

The virtual pion effect is particularly strong in Σ^-, which due to $m(\Sigma^-) - m_\Lambda = 82\,\mathrm{MeV}$ is relatively close to the dissociation limit $\Sigma \to \pi\Lambda$. The quark model prediction $\mu(\Sigma^+) - \mu(\Sigma^-) = 3.89\mu_n$ must be compared with the experimental value $3.62\mu_n$.

The Λ-hyperon is a singlet in isospace, which is antisymmetric. The symmetry of the complete wave function requires that also the corresponding spins appear in the antisymmetric combination,

$$\begin{aligned}|\Lambda\uparrow\rangle = (12)^{-1/2}[&(ud-du)(\uparrow\downarrow - \downarrow\uparrow)s\uparrow + s\uparrow(ud-du)(\uparrow\downarrow - \downarrow\uparrow)\\ &+(usd-dsu)(\uparrow\uparrow\downarrow - \downarrow\uparrow\uparrow)].\end{aligned} \tag{5.305}$$

In this combination, the magnetic moments of u and d disappear, the result being simply $\mu_\Lambda = \mu_s$. If one approximates the kinetic energies of quarks in baryons by $(\boldsymbol{\pi\sigma})^2/2m_i$, one can calculate their "constituent" masses from $\mu_q = Z_q/2m_q$, obtaining (Donoghue et al. 1992)

$$m_u = m_d \approx 320\,\mathrm{MeV}, \quad m_s \approx 510\,\mathrm{MeV}. \tag{5.306}$$

A Orthonormality and Expectation Values

The orthonormality relations (1.197) for two solutions ψ_i and ψ_j of the KG equation are

$$\int r^2 dr R_j R_i (E_j/2 + E_i/2 - V) = mc^2 \delta_{ij}. \tag{A.1}$$

The resulting normalization for $i = j,\ R_i = R_j = R$ is

$$\int r^2 dr R^2 (1 - V/E) = mc^2/E. \tag{A.2}$$

In the following we set $V = -Ze^2/r = -\alpha_Z \hbar c/r$, and $l_\alpha = [(l+\frac{1}{2})^2 - \alpha_Z^2]^{\frac{1}{2}} - \frac{1}{2}$:

$$R = N_{\rm KG} e^{-z/2} z^{l_\alpha} F, \quad z = 2\kappa r, \quad F = F(-n_r, b, z), \quad b = 2l_\alpha + 2. \tag{A.3}$$

The value of $N_{\rm KG}$ follows from insertion into (A.3):

$$N_{\rm KG}^2 (2\kappa)^{-3} \int_0^\infty dz e^{-z} z^b (1 + 2\alpha_Z \hbar c \kappa / zE) F^2 = mc^2/E. \tag{A.4}$$

This and similar integrals for $\langle r^{-s} \rangle$ follow from the formula

$$J_s = \int dz e^{-z} z^{b-s} F^2(-n_r, b, z) = n_r! \Gamma^{-1}(b + n_r) \Gamma(b) \Gamma(b + 1 - s)[1 + X], \tag{A.5}$$

$$X = n_r \frac{(s-2)(s-1)}{b} \left[1 + (n_r - 1) \frac{(s-3)s}{2^2(b+1)} \left(1 + (n_r - 2) \frac{(s-4)(s+1)}{3^2(b+2)} \right) \right], \tag{A.6}$$

where X is complete for $-3 < s < 6$. Using $\Gamma(b+1) = b\Gamma(b)$ and $b/2 + n_r = l_\alpha + 1 + n_r = n_\beta$, both J_0 and J_1 contain the following combination of gamma functions:

$$\Pi_\Gamma = \Gamma^2(b)/\Gamma(b + n_r). \tag{A.7}$$

The nonrelativistic limit of Π_Γ is

$$\Pi_{\Gamma,nr} = [(2l+1)!]^2/(l+n)!. \tag{A.8}$$

The first three values of J_s are

$$J_0 = n_r! 2 n_\beta \Pi_\Gamma, \quad J_1 = n_r! \Pi_\Gamma, \quad J_2 = n_r! \Pi_\Gamma/(b-1). \tag{A.9}$$

Insertion of J_0 and J_1 into (A.4) gives

$$N_{\mathrm{KG}}^{-2} mc^2/E = (2\kappa)^{-3} n_r!2(n_\beta + \alpha_Z \hbar c\kappa/E)\Pi_\Gamma. \tag{A.10}$$

The general definition of κ is $\hbar\kappa = (m^2c^2 - E^2/c^2)^{1/2}$. For bound states, $\hbar\kappa$ is quantized according to (1.129),

$$\hbar c\kappa = \alpha_Z E/n_\beta, \tag{A.11}$$

such that the second term in the bracket is α_Z^2/n_β. By means of (1.129), $1 + \alpha_Z^2/n_\beta^2 = m^2c^4/E^2$, N_{KG}^2 gets simplified:

$$N_{\mathrm{KG}}^2 = 4\kappa^3 [n_r! n_\beta \Gamma^2(b)]^{-1} \Gamma(b + n_r) E/mc^2. \tag{A.12}$$

The nonrelativistic limit has

$$N_{\mathrm{KG}}^2 \approx N^2 = 4\kappa^3 (n + l)!/[(2l + 1)!^2 n n_r!]. \tag{A.13}$$

The following expectation values are defined as in (1.206), $\langle r^{-s}\rangle \equiv \int \psi^* r^{-s} \psi d^3r$. For $s = 1, 2, 3, 4$, and with $l_\alpha(l_\alpha + 1) = L_\alpha^2$, they are

$$\langle r^{-1}\rangle = \kappa^2 a_B = \kappa^2/\alpha_Z m, \tag{A.14}$$

$$\langle r^{-2}\rangle = \kappa^3 a_B/(l_\alpha + \tfrac{1}{2}) = \kappa^3/\alpha_Z m(l_\alpha + \tfrac{1}{2}), \tag{A.15}$$

$$\langle r^{-3}\rangle = n_\beta \kappa^4 a_B/(l_\alpha + \tfrac{1}{2}) L_\alpha^2 = \alpha_Z E \langle r^{-2}\rangle / L_\alpha^2, \tag{A.16}$$

$$\langle r^{-4}\rangle = \kappa^5 a_B [3n_\beta^2 - L_\alpha^2 - 1]/L_\alpha^2 (l_\alpha^2 - 1/4)(l_\alpha + 3/2). \tag{A.17}$$

The last expression in each line sets $\hbar = c = 1$. The nonrelativistic approximations of $\langle r^{-s}\rangle$ are given in Sect. 2.8. $\langle r^{-3}\rangle_{l=0}$ and $\langle r^{-4}\rangle_{l=0}$ are only to be used in connection with an additional factor l_α. Note however that the first-order energy shift E^1 is not necessarily $\langle r^{-s}\rangle$: The KG perturbation theory is a special case of the Kramers perturbation theory of Sect. 2.9, where E^1 is given by (2.292). If the Coulomb potential is modified by a small V_{per}, then the $c^2\pi^{02}$ of (2.287) is generalized to

$$c^2\pi^{02} = (E^0 - V + E^1 - V_{\mathrm{per}})^2 \approx (E^0 - V)^2 + 2(E^1 - V_{\mathrm{per}})(E^0 - V). \tag{A.18}$$

In this case, the K_{per} of (2.288) is $V_{\mathrm{per}}(E^0 - V)$, and (2.292) becomes

$$E^1 = \langle V_{\mathrm{per}}(1 - V/E^0)\rangle = \int R^2 r^2 dr V_{\mathrm{per}}(E^0 - V)/mc^2. \tag{A.19}$$

For $V = -\alpha_Z/r$, this integral diverges for $V_{\mathrm{per}} \approx r^{-2}$. Physically relevant modifications of the point Coulomb potential have the Yukawa form, see Appendix C.

The Dirac-Coulomb equation has two types of solutions which are equivalent only for $j = n - \frac{1}{2}$. According to the orthogonality relations (2.207), the normalization constants $N_\pm$ of the solutions (2.145) equal the Klein-Gordon constant N_{KG}, taken at the appropriate value of b in Π_Γ (A.7):

$$N_\pm = N_{\mathrm{KG}}(b_\pm), \quad b_\pm = 2l_{\alpha\pm} + 2, \quad b_+ = 2\gamma + 2,\ b_- = 2\gamma. \tag{A.20}$$

The radial wave function components (g, f) of the parity eigenstates are normalized according to (2.196), $\int (g^2 + f^2) r^2 dr = 1$. A normalization constant N_γ has been defined in (2.195). However, it is customary to remove the square roots $x_\pm$ such that $F_- = F(1 - n_r, b_D, z)$ occurs with a factor $-n_r$ $(n_r = 0, 1, 2 \ldots)$ in the square bracket:

$$(g, f) = N_D (1 \pm E/m)^{1/2} e^{-z/2} z^{\gamma - 1} [\pm (m_\beta - \kappa_D) F(-n_r, b_D, z) - n_r F_-]. \tag{A.21}$$

The resulting N_D^2 is, with $m_\beta = \alpha_Z m/\kappa$ according to (2.184), and $b_D = 2\gamma + 1$,

$$N_D^2 = 4\kappa^3 [n_r! \Pi_\Gamma(b_D, n_r)[(m_\beta - \kappa_D)^2 + n_r(2\gamma + n_r)]]^{-1}. \tag{A.22}$$

Rewriting n_r as $n_\beta - \gamma$, one finds $n_r(2\gamma + n_r) = n_\beta^2 - \gamma^2 = m_\beta^2 - \kappa_D^2$, using $n_\beta^2 = m_\beta^2 - \alpha_Z^2$ according to (2.184). This allows one to simplify N_D^2 as follows:

$$\begin{gathered} N_D^2 = 2\kappa^3 [n_r! \Pi_\Gamma(b_D, n_r) m_\beta (m_\beta - \kappa_D)]^{-1}, \\ \kappa \approx \kappa_n [1 + \tfrac{1}{2}\alpha_Z^2 / n (1/(j + \tfrac{1}{2}) - 1/n)]. \end{gathered} \tag{A.23}$$

The approximate value of κ comes from (2.164). Insertion of the definition (2.184), $m_\beta = \alpha_Z m/\kappa$, gives

$$N_D^2 = 2\kappa^4 [\alpha_Z m n_r! \Gamma^2(b_D)(m_\beta - \kappa_D)]^{-1} \Gamma(b_D + n_r). \tag{A.24}$$

For $l = 0$, approximate expressions both for N_D^2 and N_{KG}^2 will be given in Appendix C. The Dirac expectation values of r^{-s} are, with $\kappa_D = (l - j)(2j + 1)$ and $\gamma = \sqrt{\kappa_D^2 - \alpha_Z^2}$,

$$\langle r^{-1} \rangle_D = \kappa^3 (\kappa_D^2 + n_r \gamma) / \gamma \alpha_Z^2 m^2 = (1 + \alpha_Z^2 / \gamma n_\beta) \langle r^{-1} \rangle, \tag{A.25}$$

$$\langle r^{-2} \rangle_D = 2\kappa^3 \kappa_D (2\kappa_D E/m - 1)[\gamma(4\gamma^2 - 1)\alpha_Z m]^{-1} E/m, \tag{A.26}$$

$$\langle r^{-3} \rangle_D = \frac{2\kappa^3}{\gamma(4\gamma^2 - 1)} \left[3\kappa_D E \frac{\kappa_D E/m - 1}{m(\gamma^2 - 1)} - 1 \right]. \tag{A.27}$$

The first-order energy shift caused by a perturbative potential $V^1 \approx r^{-s}$ is proportional to $\langle r^{-s} \rangle_D$. The corresponding energy shift in the KG equation is proportional to $\langle r^{-s}(1 + \alpha_Z / Er) \rangle$, according to (A.19). For $s = 1$, one finds from (A.14) and (A.15), $\delta E(s = 1) = \langle r^{-1} \rangle [1 + \alpha_Z^2 / n_\beta (l_\alpha + \frac{1}{2})]$, which is in fact close to the Dirac expression (A.25).

Nondiagonal matrix elements are given by Shabaev (1991), and by Martinez-y-Romero et al. (2001).

The expectation values of other operators follow from the "virial theorem" and its generalizations (Friar and Negele 1976, Goldman and Drake (1982), Shabaev, Martinez-y-Romero). Some relations are trivial, for example

$$\langle H\rangle = E, \quad H = V + \boldsymbol{p\alpha} + m\beta. \tag{A.28}$$

Others follow from an operator $\hat{O}$ as

$$\langle [H, \hat{O}]\rangle = \langle E\hat{O} - \hat{O}E\rangle = 0. \tag{A.29}$$

In particular, with $\hat{O} = \boldsymbol{rp}$ and $\hat{\boldsymbol{r}}\boldsymbol{p} = p_r$, one obtains

$$\langle \boldsymbol{p\alpha}\rangle = \langle rV'\rangle, \quad V' \equiv [\partial_r, V], \tag{A.30}$$

$$\langle r^{-1}(\boldsymbol{\alpha p} - \alpha_r p_r)\rangle = \langle V'\rangle, \tag{A.31}$$

The point Coulomb potential $V_C = -\alpha_Z/r$ has $rV_C' = -V_C$,

$$\langle \boldsymbol{p\alpha}\rangle = -\langle V_C\rangle. \tag{A.32}$$

This is the virial theorem. Insertion into (A.28) cancels V_C,

$$\langle \beta\rangle = E/m: \quad \int (g^2 - f^2) = E/m. \tag{A.33}$$

Taking for $\hat{O}$ any local function $f(r)$, one finds

$$\langle [\boldsymbol{\alpha\nabla}, f(r)]\rangle = 0. \tag{A.34}$$

Expectation values involving $\boldsymbol{p}^2$ follow most easily from the Kramers equation (2.135), as the expectation value of the anti-Hermitian operator $[\boldsymbol{\sigma p}, V]$ vanishes:

$$\langle \boldsymbol{p}^2\rangle = E^2 - m^2 - 2E\langle V\rangle + \langle V^2\rangle. \tag{A.35}$$

This applies again for any shape of V. Its nonrelativistic limit is obtained by setting $E \to E/c = mc + E_N/c$ and neglecting both E_N^2/c^2 and $\langle V^2\rangle$, $\langle \boldsymbol{p}^2/2m\rangle = E_N - \langle V\rangle$. It is identical with the expectation value of the nonrelativistic Schrödinger operator (1.49) and has nothing to do with the nonrelativistic virial theorem $\langle \boldsymbol{p}^2/2m\rangle \approx -\langle V_C/2\rangle$, which uses the Schrödinger expectation value of $\hat{O} = \boldsymbol{rp}$.

For $V = -\alpha_Z/r$, the orthogonality relations (A.1) are simplified by the transformation (1.143) of the distance variable, $\boldsymbol{r}_\epsilon = E\alpha_Z \boldsymbol{r}$.

$$\boldsymbol{r}_\epsilon = E\alpha_Z \boldsymbol{r}, \quad \int_0^\infty r_\epsilon^2 dr_\epsilon R_j(r_\epsilon/E_j) R_i(r_\epsilon/E_i) = \delta_{ij}. \tag{A.36}$$

The Dirac wave functions are normalized according to (2.203), $\int \psi_j^\dagger \psi_i = \delta_{ij}$, which is already as simple as possible. Introduction of $\boldsymbol{r}_\epsilon$ leaves $\beta m/E$ as the only energy-dependent operator. The resulting orthogonality relations are

$$\int d^3 r_\epsilon \psi_j^\dagger(\boldsymbol{r}_\epsilon/E_j)\beta\psi_i(\boldsymbol{r}_\epsilon/E_i) = 0 \quad \text{for } j \neq i. \tag{A.37}$$

The orthogonality relations of the solutions of the n_e-electron Dirac-Coulomb equation are in the standard Dirac form

$$\int d^3r_1 d^3r_2 \ldots \psi_j^\dagger(\boldsymbol{r}_1, \boldsymbol{r}_2 \ldots)\psi_i(\boldsymbol{r}_1, \boldsymbol{r}_2 \ldots) = \delta_{ij}. \tag{A.38}$$

The form analogous to (A.37) contains the total electronic energies E_j and E_i and has β replaced by $\Sigma\beta_e$. The method can be extended to the solutions of the Dirac-Breit equation, but the Breit operator of Sect. 3.4 can only be used as a first-order perturbation, of course.

The Kramers orthogonality relations have already been presented in (2.207). They have the same form as the KG orthogonality relations, except that $\psi_j^\dagger$ must be specified as the lefthanded $\psi_{l,j}^\dagger$ if ψ_i is taken as a righthanded Kramers spinor $\psi_{r,i}$:

$$\int \psi_{l,j}^\dagger (E_i + E_j - 2V)\psi_{r,i} = 2E\delta_{ij}. \tag{A.39}$$

The $\psi_l^\dagger$ is necessary because the Kramers operator K_r^0 is not Hermitian.

As long as hyperfine operators are treated perturbatively, the most convenient form of binary equations uses the variable $\boldsymbol{\rho} = \mu\boldsymbol{r}$, because the orthogonality relations (4.211)

$$\int \rho^2 d\rho R_j(\rho)R_i(\rho)(\epsilon_i/\mu_i + \epsilon_j/\mu_j - 2V_\rho) = 2\delta_{ij}\epsilon_i/\mu_i. \tag{A.40}$$

of the Todorov equation and (4.277) $\int d^3\rho \psi_j^\dagger \psi_i = \delta_{ij}$ of the leptonium equation are then form-identical with those of the single-particle equation, all differences being concentrated in the physical meaning of the single parameter μ. Equations (A.11, A.14, A.15) and (A.16) are generalized as follows:

$$\kappa = \alpha_Z\epsilon/\mu, \quad \langle\rho^{-1}\rangle = \kappa^2/\alpha_Z\mu^2 = \alpha_Z(\epsilon/n_\beta\mu)^2, \tag{A.41}$$

$$\langle\rho^{-2}\rangle = \kappa^3/\alpha_Z\mu^3(l_\alpha + 1/2) = \alpha_Z^2(\epsilon/n_\beta\mu)^3/(l_\alpha + 1/2), \tag{A.42}$$

$$\langle\rho^{-3}\rangle = \alpha_Z(\epsilon/\mu)\langle\rho^{-2}\rangle/L_\alpha^2. \tag{A.43}$$

In the Dirac case, (A.25) and (A.26) read

$$\langle\rho^{-1}\rangle_D = (\kappa/\mu)^3(\kappa_D^2 + n_r\gamma)/\gamma\alpha_Z^2, \tag{A.44}$$

$$\langle\rho^{-2}\rangle_D = 2(\kappa/\mu)^3\kappa_D[2\kappa_D(1 + \alpha_Z^2/n_\beta^2)^{-1/2} - 1]/\gamma(4\gamma^2 - 1), \tag{A.45}$$

with $\kappa/\mu = \alpha_Z(n_\beta^2 + \alpha_Z^2)^{-1/2}$ independent of μ.

The full leptonium equation (4.275) contains E^2, E^0 and E^{-2}. The E^{-2} in the hyperfine operator makes $\boldsymbol{\rho} = \mu\boldsymbol{r}$ inappropriate for orthogonality relations. Dividing the equation by E^2 and introducing $\boldsymbol{r}_\epsilon$ as a new independent variable, one obtains

$$[\tfrac{1}{2}(1 - m_+^2/E^2) + \alpha_Z^2/r_\epsilon - \alpha_Z\gamma^5\boldsymbol{p}_\epsilon\boldsymbol{\sigma}_1 + i(\alpha_Z^2/r_\epsilon)\gamma^5\boldsymbol{\sigma}_{12}^\times\alpha_Z\boldsymbol{p}_\epsilon]\psi_1 = 0. \tag{A.46}$$

The resulting orthogonality relations are

$$\int d^3 r_\epsilon \chi_j^\dagger(\boldsymbol{r}_\epsilon/E_j) m_+^2 \psi_i(\boldsymbol{r}_\epsilon/E_i) = 0 \quad \text{for } j \neq i. \tag{A.47}$$

χ are the eight components defined in (3.173); as in the Kramers equation, they appear because one of the operators (in this case the hyperfine operator) is not Hermitian. The $m_+^2 = m_1^2 + m_2^2 + 2m_1 m_2 \beta$ is the generalization of the β of the Dirac equation.

Without hyperfine interaction, the Kramers form of the leptonium equation has the following standard form in the variable $\boldsymbol{r}_\epsilon$:

$$K = 2/r_\epsilon + \alpha_Z^2/r_\epsilon^2 + [\boldsymbol{\sigma}_1 \boldsymbol{p}_\epsilon, \alpha_Z/r_\epsilon] - \boldsymbol{p}_\epsilon^2, \quad K\psi_r = n_\beta^{-2}\psi_r. \tag{A.48}$$

One of the early arguments against the KG equation was that the integrand of its normalization integral (A.1) can be negative at small r, whereas that of the Dirac equation is always positive, which is necessary for a probability interpretation. It is amusing to see that the opposite is true for the corresponding integrals (A.36) and (A.37).

B Coulomb Greens Functions

In nonrelativistic quantum mechanics, the higher-order effects of a perturbation H' (2.208)

$$(H + H_{\rm per})\psi = (E^0 + E^1 + E^{(2)} \ldots)\psi \tag{B.1}$$

may be calculated by means of a Greens function G which is defined by the following inhomogenenous differential equation

$$(E - H(\boldsymbol{r}, \boldsymbol{p}))G(\boldsymbol{r}, \boldsymbol{r}', E) = \delta(\boldsymbol{r} - \boldsymbol{r}'). \tag{B.2}$$

In atomic theory, $H = -\nabla^2/2m - \alpha_Z/r$ leads to the Coulomb Greens function. Its radial component is normally sufficient:

$$(E - H_l)G_l(\boldsymbol{r}, \boldsymbol{r}', E) = \delta(r - r'), \quad \nabla_l^2 = \partial_r^2 + (2/r)\partial_r - l(l+1)/r^2. \tag{B.3}$$

The use of these equations rests on the completeness (1.250) of the solutions ψ_n of the unperturbed equation $H\psi_n = E_n\psi_n$ (the upper index ^{0} is now suppressed)

$$\delta(\boldsymbol{r} - \boldsymbol{r}') = \Sigma_k \psi_k(\boldsymbol{r})\psi_k^*(\boldsymbol{r}'). \tag{B.4}$$

Using this expression in (B.2), one can for example calculate $E^{(2)}$ (2.223). Remember that the Coulomb spectrum includes a continuum of unbound electrons, which adds an $\int d^3k$ to the $\sum_k$ in (B.4). For G, on the other hand, one can construct forms in which the whole expression is reduced to a sum. The first such form was found by Schwinger, see the review by Maquet (1977). We shall consider the form of Hostler (1970),

$$G_l(\boldsymbol{r}, \boldsymbol{r}', E) = \Sigma_{n=l+1}^{\infty} R_{nlE}(r)R_{nlE}(r')(1 - \kappa_E/\kappa_n)^{-1}, \tag{B.5}$$

with $\kappa_n = \alpha_Z m/n$ and $\kappa_E = (-2mE)^{-1/2}$. R_{nlE} is the nonrelativistic limit of (A.3), but with κ_n replaced by κ_E:

$$R_{nlE}(r) = N(E)e^{-\kappa_E r}(2\kappa_E r)^l F(l + 1 - n,\ 2l + 2,\ 2\kappa_E r). \tag{B.6}$$

F is a polynomial of degree n_r.

The Dirac-Coulomb Greens function has also the nonrelativistic form, see (2.213) with $H_0 = H_C$ and (2.223). Its completeness relation has $\psi_k^*(\boldsymbol{r}')$ replaced by $\psi_k^\dagger(\boldsymbol{r}')$ to account for spin:

$$S(\boldsymbol{r}, \boldsymbol{r}', E) = \Sigma_k \psi_k(\boldsymbol{r}')\psi_k^\dagger(\boldsymbol{r}')(E - E_k)^{-1}. \tag{B.7}$$

However, the price of this formal simplicity is a 4×4 matrix. It seems easier to work with a 2×2 matrix G in spin space (Zon et al. 1972, Sapirstein and Yennie, in the book edited by Kinoshita (1990)). Instead of (B.1), one then has an implicit eigenvalue equation, $(K + K_{\rm per})\psi = 0$, where K is the KG or Kramers operator, and $K_{\rm per}$ is a perturbation. The Kramers operator is

$$K = E^2 - m^2 + 2E\alpha_Z/r + \nabla^2 + (\alpha_Z^2 + i\alpha_Z\sigma_r)/r^2, \tag{B.8}$$

and the relativistic Coulomb Greens function G is defined by

$$KG(\boldsymbol{r}, \boldsymbol{r}', E) = \delta(\boldsymbol{r} - \boldsymbol{r}'). \tag{B.9}$$

The Dirac-Coulomb Greens function S follows from G as

$$S(\boldsymbol{r}, \boldsymbol{r}', E) = (E - V + i\gamma^5\boldsymbol{\sigma}\boldsymbol{\nabla} + m\beta)G(\boldsymbol{r}, \boldsymbol{r}', E). \tag{B.10}$$

The more complicated E-dependence of K in (B.9) prevents simple solutions of the type (B.7). G satisfies the following integral equation:

$$G = G_S - \int d^3x G_S(\boldsymbol{r}, \boldsymbol{x})(\alpha_Z^2 + i\alpha_Z\boldsymbol{\sigma}\hat{\boldsymbol{x}})/x^2 G(\boldsymbol{x}, \boldsymbol{r}'), \tag{B.11}$$

where G_S satisfies (B.9) without the last two terms in K. G_S is a Schrödinger-Coulomb Greens function with relativistic kinematics. The method yields a closed expression for most of the Bethe logarithm.

The difficulties of relativistic Coulomb Greens functions should disappear with the use of the KG and Dirac equations in the dimensionless form (1.144). The interval $0 < r_\epsilon < \infty$ need not be expressed in terms of r. The perturbative expansion for K may be taken in the form

$$(K_0 + K_{\rm per})\psi_E = [(\kappa^2/E^2)^{(0)} + (\kappa^2/E^2)^{(1)} + \ldots]\psi_E. \tag{B.12}$$

The corresponding Greens function satisfies (B.3) in the form

$$(k^2/E^2 - p_{\epsilon,l\alpha}^2 - 2V_E + V_E^2)G_{E,l}(r_\epsilon, r'_\epsilon) = \delta(r_\epsilon - r'_\epsilon), \tag{B.13}$$

where $p_{\epsilon,l\alpha}^2$ has $l(l+1)/r^2$ replaced by $l_\alpha(l_\alpha+1)/r_\epsilon^2$. It has a Hostler solution (B.5) with new parameters, l_α and $\kappa_\epsilon = \kappa/E = \alpha_Z/n_\beta$,

$$R_{nlm_E} = N(m^2/E^2)e^{-\kappa_\epsilon r_\epsilon}(2\kappa_\epsilon r_\epsilon)^{l_\alpha} F(-n_r, 2l_\alpha + 2, 2\kappa_\epsilon r_\epsilon). \tag{B.14}$$

However, this formalism remains to be applied.

C Yukawa Expectation Values

Yukawa expectation values $\langle e^{-xr}/r\rangle$ are needed for the Uehling potential (5.83). More generally, they are useful for all interactions that can be written as dispersion integrals. For fermions, this includes the electric and magnetic form factor potentials. x is the integration variable of the dispersion relation, $x = x_{\rm th}\xi$; with the threshold value $x_{\rm th} = 2m_e$ both for the Uehling potential and for the electron's form factor potentials. First-order relativistic corrections are obtained by the Pauli reduction of Sect. 2.8, with the electric potential V_C+V_U (Pachucki 1996). Beyond the first order, one needs the fully relativistic expectation values. For the KG equation, the energy shift E^1 of first-order perturbation theory is obtained from (A.19)

$$\begin{aligned} E^1(\xi) &= \int R^2 e^{-xr}(r+\alpha_Z/E)dr(E/m) \\ &= (2\kappa)^{-2}\int R^2 e^{-zx/2\kappa}(z+2\kappa\alpha_Z/E)E/mdz. \end{aligned} \tag{C.1}$$

With R from (A.3), the total exponential becomes $e^{-\lambda z}$,

$$\lambda \equiv 1 + m_e\xi/\kappa \equiv 1 + 1/y, \tag{C.2}$$

$$E^1(\xi) = (2\kappa)^{-2} N_{\rm KG}^2 (J_{\lambda 1} + J_{\lambda 2})E/m \tag{C.3}$$

$$\begin{aligned} J_{\lambda 1} &= \int e^{-\lambda z} z^{b-1} F^2(-n_r, b, z)dz, \\ J_{\lambda 2} &= (2\kappa\alpha_Z/E)\int e^{-\lambda z} z^{b-2} F^2(-n_r, b, z)dz. \end{aligned} \tag{C.4}$$

The integral $J_{\lambda 1}$ is evaluated in closed form (Landau and Lifshitz 1977, Gradshteyn and Ryzhik 1980),

$$J_{\lambda 1} = \Gamma(b)\lambda^{-b-2n_r}(\lambda-1)^{2n_r} F(-n_r, -n_r, b; (\lambda-1)^{-2}), \tag{C.5}$$

where F is the hypergeometric function,

$$F(a, a', b; y) = 1 + aa'y/b + a(a+1)a'(a'+1)y^2/2!b(b+1) + \ldots \tag{C.6}$$

In (C.5), F is a polynomial of degree n_r. Insertion of $\lambda = 1 + 1/y$ gives

$$J_{\lambda 1} = \Gamma(b)(1+1/y)^{-b-2n_r} y^{-2n_r} F(-n_r, -n_r, b, y^2). \tag{C.7}$$

With $b = 2l_\alpha + 2,\ b + 2n_r$ gives $2n_\beta$. The integral $J_{\lambda 2}$ is more complicated. The two-body case has $\kappa = \alpha_Z\epsilon/n_\beta$; when ϵ is of the order of m_e, $m_e\xi/\kappa$

is much larger than 1. It is then useful to express $J_{\lambda 1}$ and $J_{\lambda 2}$ in powers of y,

$$F^2 = 1 - 2zn_r/b + z^2 n_r[n_r/b + (n_r - 1)/(b+1)]/b + \ldots, \tag{C.8}$$

and then use the basic integral

$$\int e^{-\lambda z} z^\nu dz = \Gamma(\nu+1)\lambda^{-\nu-1}: \tag{C.9}$$

$$J_{\lambda 1} = \Gamma(b) y^b [1 - 2n_\beta y + y^2(2n_\beta^2 + n_\beta)](1 + n_r^2 y^2/b). \tag{C.10}$$

The extra factor $2\kappa\alpha_Z/m \approx 2\alpha_Z^2/n$ in $J_{\lambda 2}$ is sufficient to make the y^2-terms negligible:

$$J_{\lambda 2} = 2(\kappa\alpha_Z/E)[\Gamma(b-1)y^{b-1} - 2n_r y^b \Gamma(b)/b]. \tag{C.11}$$

The last term is conveniently combined with the y^b of $J_{\lambda 1}$ into

$$J'_{\lambda 1} = \Gamma(b) y^b [1 - 4\alpha_Z^2 n_r/nb - 2ny + y^2(2n^2 + n + n_r^2/b)], \tag{C.12}$$

where we have also approximated n_β by n in the higher powers of y. In the remainder $J'_{\lambda 2}$ of $J_{\lambda 2}$, use of $\Gamma(b-1) = \Gamma(b)/(b-1) \approx \Gamma(b)/(2l+1)$ gives

$$J'_{\lambda 2} = 2\alpha_Z^2 n^{-1} \Gamma(b) y^{2l+1}/(2l+1). \tag{C.13}$$

The $\Gamma(b)$ is combined with the $(2\kappa)^{-2} N_{\mathrm{KG}}^2$ of (C.3) into

$$(2\kappa)^{-2} N_{\mathrm{KG}}^2 = (E/m)\kappa[n_r! n_\beta]^{-1} \Gamma(b + n_r)/\Gamma(b). \tag{C.14}$$

The KG energy shift of the Yukawa potential $e^{-2m_e\xi r}/r$ is thus

$$E^1(\xi) = \kappa \left(\frac{E}{m}\right) \frac{\Gamma(b+n_r)}{n_r! n_\beta \Gamma(b)} y^b \left[1 - 4\alpha_Z^2 \frac{n_r}{nb} - 2ny + y^{-1} \frac{2\alpha_Z^2}{n(2l+1)} + y^2(\ldots)\right]. \tag{C.15}$$

The energy shift of the Uehling potential is given by (5.83),

$$E_U^1 = -\tfrac{2}{3}\alpha_\pi (2\kappa)^{-2} N_{\mathrm{KG}}^2 \int_1^\infty d\xi (J'_{\lambda 1} + J'_{\lambda 2})(\xi^2 - 1)^{1/2}(\xi^{-2} + \tfrac{1}{2}\xi^{-4}). \tag{C.16}$$

The nonrelativistic limit of this integral has been calculated for the ground state ($n_r = 0$, $b = 2$), and recurrence relations have been constructed for other, not too large values of n_r and b (Pustovalov 1957). The corresponding Dirac ground state integral has been calculated by Karshenboim (1999). A convenient transformation of variable for this purpose is

$$\xi = (1 - v^2)^{-1/2}, \quad d\xi(\xi^2 - 1)^{1/2}\xi^{-2} = 2v^2 dv. \tag{C.17}$$

Approximate expressions for all $j = n - \frac{1}{2}$ are given in the limit of large κ/m_e. Such integrals are needed for antiprotonic and other exotic atoms

(Sect. 5.6). The ξ-integration in (C.16) results in integrals (Gradshtein and Ryzhik 1980),

$$\int d\xi(\xi^2-1)^{1/2}\xi^{-\nu} = \tfrac{1}{2}B(\tfrac{3}{2},\tfrac{\nu}{2}-1) = \tfrac{1}{2}\Gamma(\tfrac{3}{2})\Gamma(\tfrac{\nu}{2}-1)/\Gamma(\tfrac{\nu}{2}+\tfrac{1}{2}). \quad \text{(C.18)}$$

In (C.16), the ξ-integrals appear as

$$I_{U,\nu} = \int d\xi(\xi^2-1)^{1/2}\xi^{-\nu}(1+\tfrac{1}{2}\xi^{-2}) = \tfrac{3}{4}\frac{\nu}{\nu+1}B(\tfrac{3}{2},\tfrac{1}{2}\nu-1). \quad \text{(C.19)}$$

Neglecting the y^2-terms of (C.12),

$$E_U^1 = -\tfrac{2}{3}\alpha_\pi\kappa\frac{\kappa^b\Gamma(b+n_r)}{m_e^b n_r! n_\beta\Gamma(b)}\left[I_{U,b+2} - 2\alpha_Z\left(\frac{m}{m_e}I_{U,b+3} - \frac{1}{2l+1}\frac{m_e}{m}I_{U,b+1}\right)\right]. \quad \text{(C.20)}$$

Insertion of $b+2 = 2(l+2-\beta)$ leads to

$$I_{U,b+2} = \Gamma(3/2)\frac{\Gamma(l+1-\beta)}{\Gamma(l+5/2-\beta)}\frac{3}{4}\frac{l+2-\beta}{l+5/2-\beta}. \quad \text{(C.21)}$$

The index $_l$ of β_l is suppressed here, to facilitate the comparison with the Dirac case below. For $l=0$, (C.21) becomes

$$I_{U,4-\beta} = \Gamma(3/2)\frac{\Gamma(1-\beta)}{\Gamma(3/2-\beta)}\frac{3}{4}\frac{2-\beta}{(3/2-\beta)(5/2-\beta)}. \quad \text{(C.22)}$$

The expansion of Γ in powers of β introduces the function $\Psi = \Gamma'/\Gamma$; use of $\Psi(3/2) = -\gamma_{\rm Eu} - 2\log 2 + 2$ and $\Psi(1) = -\gamma_{\rm Eu}$ lead to

$$I_{U,\,l=0} \approx \tfrac{2}{5}[1+\beta(-2\log 2 + 2 - \tfrac{1}{2} + \tfrac{2}{3} + \tfrac{2}{5})]. \quad \text{(C.23)}$$

For $\nu = b+3$ and $b+1$, we only consider $l=0$ and take the limit $\alpha_Z^2 = 0$,

$$I_{U,b+3} = \tfrac{3}{4}\cdot\tfrac{5}{6}\Gamma^2(\tfrac{3}{2})/\Gamma(3) = \tfrac{5}{64}\pi, \quad I_{U,b+1} = \tfrac{18}{64}\pi. \quad \text{(C.24)}$$

with $\Gamma(3/2) = \frac{1}{2}\sqrt{\pi}$. Its contribution to E_U^1 is

$$E_U^1 = \tfrac{4}{3}\alpha_\pi\alpha_Z^2(\kappa/m_e)^3 m_e\pi(\tfrac{5}{64} - \tfrac{18}{64}m_e^2/m^2). \quad \text{(C.25)}$$

The presence of an extra π leads to the combination $\alpha_\pi\pi\alpha_Z^5 = \alpha\alpha_Z^5$, which shows that one-loop graphs do produce some terms without π^{-1}. Next, we expand the factors in front of the I_U in (C.20). For $l=0$, $n_r = n-1$, and to first order in α_Z^2, $b = 2-2\beta$, $n_\beta = n-\beta$:

$$\Gamma(b+n_r) = \Gamma(n+1-2\beta) = n![1-2\beta\Psi(n+1)], \quad \text{(C.26)}$$

$$(4\kappa^3)^{-1}\Gamma(b)N_{\rm KG}^2 = 1 - 2\beta[\Psi(n+1) - \Psi(2) - 1/2n] - \alpha_Z^2/2n^2, \quad \beta = \alpha_Z^2, \quad \text{(C.27)}$$

with $\Psi(n+1)-\Psi(2)=\Sigma_{i=2}^{n} i^{-1}$, see (2.228). The factor $(\kappa/m_e)^b$ of (C.15) is expanded as follows:

$$\kappa(\kappa/m_e)^b = m_e(\kappa/m_e)^{2l+3}(\kappa/m_e)^{-2\beta}, \tag{C.28}$$

$$(\kappa/m_e)^{-2\beta} = e^{-2\beta\log(\kappa_{nr}/m_e)} \approx 1-2\beta\log(\kappa_{nr}/m_e), \tag{C.29}$$

with $\kappa_{nr}=\alpha_Z\mu_{nr}/n$ (here and in the following, the one-body parameters E and m are replaced by the two-body quantities ϵ and μ). We can now check the correction $1-2\beta\log(2\alpha_Z/n)$, which has been guessed in Sect. 2.7 from the divergence of R^2/N^2 at $r=0$. The $-2\beta\log 2$ which is missing in (C.29) is provided by (C.23),

$$[1-2\beta\log(\kappa/m_e)]I_{U0} = \tfrac{2}{5}\{1+\beta[2\log(m_e/2\kappa)+\tfrac{3}{2}+\tfrac{2}{3}+\tfrac{2}{5}]\}. \tag{C.30}$$

The logarithmic correction is now complete, including the recoil factor m_e/μ.

The calculation of the Dirac expectation values $\langle e^{-xr}/r\rangle_D$ of the Yukawa potential is more complicated, yet the results are similar:

$$\langle e^{-xr}/r\rangle_D = \int(g^2+f^2)e^{-xr}rdr = (2\kappa)^{-2}\int(g^2+f^2)e^{-zx/2\kappa}zdz. \tag{C.31}$$

When V_U has a short range, one needs g^2+f^2 only at small z. An expansion of $F\equiv F(-n_r,b_D,z)$ and $F_-\equiv F(1-n_r,b_D,z)$ to order z^2 is then sufficient:

$$(m_\beta-\kappa_D)^2F^2+n_r^2F_-^2-2n_r(m_\beta-\kappa_D)(\epsilon/\mu)FF_- = c_0+c_1z+c_2z^2. \tag{C.32}$$

In c_0, one approximates ϵ/μ by $1-\alpha_Z^2/2n^2$,

$$c_0 = (m_\beta-\kappa_D-n_r)^2+n_r(m_\beta-\kappa_D)\alpha_Z^2/n^2. \tag{C.33}$$

In c_1 and c_2, one may take $\epsilon/\mu=1$:

$$c_1 = -2(m_\beta-\kappa_D-n_r)(m_\beta-\kappa_D-n_r+1), \tag{C.34}$$

$$\begin{aligned} c_2 = \frac{n_r}{b_D^2(b_D+1)}\big\{&[(m_\beta-\kappa_D)(m_\beta-\kappa_D-2n_r+2)+n_r^2-n_r] \\ &\times[n_r(2b_D+1)-b_D][n_r(2b_D+1)-b_D]-n_r(n_r-1)(2b_D+1)\big\} \end{aligned} \tag{C.35}$$

States with $l=j+\frac{1}{2}$ have $\kappa_D=j+\frac{1}{2}\approx\gamma+\alpha_Z^2/2\gamma$, $m_\beta-\kappa_D=n_r-\alpha_Z^2n_r/n(2j+1)$,

$$c_0(l=j+\tfrac{1}{2})=\alpha_Z^2n_r^2/n^2, \quad c_1(l=j+\tfrac{1}{2})=2\alpha_Z^2n_r/n(2j+1). \tag{C.36}$$

In comparison with the S-states, c_1 and c_2 are suppressed by a factor α_Z^2. This is in fact true for all P-states.

States with $l=j-\frac{1}{2}$ have $\kappa_D=-j-\frac{1}{2}$ and $m_\beta-\kappa_D\approx(n_r+2\gamma)[1+\alpha_Z^2/2n\gamma]$, where α_Z^2/γ serves merely as an abbreviation for $\alpha_Z^2/(j+\frac{1}{2})$. Dropping the argument $l=j-\frac{1}{2}$ of c_i, one obtains from (C.33)–(C.35)

$$c_0 = 4\gamma^2 + \alpha_Z^2(3 + 3\gamma/n - 1/n - \gamma/n^2), \quad c_1 = -4n_r\gamma, \tag{C.37}$$

$$c_2 = [n_r(2b_D - 1) - b_D + 1]n_r/b_D = n_r[2n_r - (n_r + 2\gamma)/(2\gamma + 1)]. \tag{C.38}$$

The index $b_D = 2\gamma + 1 \approx 2j + 2 = 2l + 3$ is then approximately one unit larger than the $b = 2l_\alpha + 2$ of the KG equation. To establish the contact with the nonrelativistic limit, the arguments of the gamma functions in $\Pi_\Gamma^{-1} = \Gamma(b_D + n_r)/\Gamma^2(b_D)$ in (A.24) must be lowered by one, using $\Gamma(2\gamma + 1 + n_r) = (2\gamma + n_r)\Gamma(2\gamma + n_r)$:

$$\tfrac{1}{2}\kappa^{-2}N_D^2 \approx \kappa^2\Gamma(2\gamma + n_r)[\alpha_Z\mu n_r!4\gamma^2\Gamma^2(2\gamma)(1 + \alpha_Z^2/2n\gamma)]^{-1}. \tag{C.39}$$

The integrand of (C.31) contains the combination

$$e^{-xr}zdz(g^2 + f^2) = z^{2\gamma-1}dze^{-\lambda z}(c_0 + c_1z + c_2z^2)N_D^2/2\kappa^2. \tag{C.40}$$

Using now the basic integral (C.9) with $\nu = b_D - 2 = 2\gamma - 1$, $\nu = 2\gamma$ and $\nu = 2\gamma + 1$, one arrives at

$$\langle e^{-xr}/r\rangle_D = \kappa^2\Gamma(2\gamma + n_r)[\alpha_Z\mu n_r!\Gamma(2\gamma)(1 + \alpha_Z^2/2n\gamma)]^{-1}y^{2\gamma}[\,]_y, \tag{C.41}$$

$$[\,]_y = c_0/4\gamma^2 - y(c_0 - c_1)/2\gamma + y^2(1 + 1/2\gamma)(c_0/2 - c_1 + c_2). \tag{C.42}$$

Rewriting the 2γ in (C.41) as $2j + 1 - 2\beta_j = 2l + 2 - 2\beta_j$, one sees that the only difference from $b = 2l + 2 - 2\beta_l$ in (C.15) is the replacement of β_l by $\beta_j \approx \alpha_Z^2/(2j+1)$ (2.146), except for the y^2-terms. In the following, we restrict ourselves again to S-states, where $\gamma = 1 - \alpha_Z^2/2$,$n_r + 1 = n$ and $n_r + 1 = n$:

$$(1 + 1/2\gamma)(c_0/2 - c_1 + c_2) = \tfrac{1}{2}(5n^2 + 1). \tag{C.43}$$

$$\Gamma(2\gamma + n_r)[n_r!\Gamma(2\gamma)n(1 + \alpha_Z^2/2n\gamma)]^{-1} = 1 - \alpha_Z^2[\psi(n + 1) - \psi(2) + 1/2n]. \tag{C.44}$$

The n^{-1}-term of (C.44) cancels that of c_0 (C.37). The only remaining n^{-1}-term arises from the κ^4 of N_D^2,

$$\kappa^4(l = 0) = \kappa_{nr}^4[1 + 2\alpha_Z^2(1/n - 1/n^2)] = \kappa_{nr}^4[1 + 2\alpha_Z^2n_r/n^2]. \tag{C.45}$$

Including a contribution from $I_{U,6} = 6/35$, the total α_Z^2-correction to $\langle V_{U0}\rangle$ is a factor

$$1 + \alpha_Z^2\left[\log\frac{nm_e}{2\alpha_Z\mu} - \Psi(n + 1) + \Psi(2) - \frac{1}{4n^2} + 2\frac{n_r}{n^2} + \frac{326}{105} + \frac{3}{14n^2}\right], \tag{C.46}$$

with $326/105 = 3/2 + 1/3 + 1/5 + 15/14$. The linear α_Z-correction is given by the first term in the bracket of (C.25), as the corresponding integrals differ only at the order α_Z^2.

The relativistic recoil correction in the Uehling energy shift E_U is small. With $r = \rho/\mu$, the dimensionless variable $z = 2\kappa r$ becomes $z = 2\rho\kappa/\mu$, and the Yukawa exponent $-2m_e r\xi$ becomes $-2\rho\xi m_e/\mu$. In summary, the use of

ρ replaces κ by κ/μ, and m_e by m_e/μ. The dimensionless $\langle V_U/\mu\rangle$ depends only on κ/m_e (see (C.28)) and remains unchanged. The only recoil correction for E_U comes from (5.3),

$$E_U = \mu(\epsilon/\mu)_U = \mu\langle V_U/\mu\rangle \approx \frac{m_1 m_2}{m_{12}}\left(1 + \frac{\alpha_Z^2 m_1 m_2}{2n^2 m_{12}^2}\right)\langle V_U/\mu\rangle. \qquad \text{(C.47)}$$

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