Single-Site Green-Function of the Dirac Equation for Full-Potential Electron Scattering

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Abstract

I present an elaborated analytical examination of the Green function of an electron scattered at single-site potential, for both the Schrödinger and the Dirac equation, followed by an efficient numerical solution, in both cases for potentials of arbitrary shape without an atomic sphere approximation.

A numerically stable way to calculate the corresponding regular and irregular wave functions and the Green function is via the angular Lippmann-Schwinger integral equations. These are solved based on an expansion in Chebyshev polynomials and their recursion relations, allowing to rewrite the Lippmann-Schwinger equations into a system of algebraic linear equations. Gonzales et. al. developed this method for the Schrödinger equation, where it gives a much higher accuracy compared to previous perturbation methods, with only modest increase in computational effort. In order to apply it to the Dirac equation, I developed relativistic Lippmann-Schwinger equations, based on a decomposition of the potential matrix into spin spherical harmonics, exploiting certain properties of this matrix. The resulting method was embedded into a Korringa-Kohn-Rostoker code for density functional calculations. As an example, the method is applied by calculating phase shifts and the Mott scattering of a tungsten impurity.

Contents

1 Introduction

A large portion of the technological progress seen over the past decades took place on grounds of materials research and condensed matter physics. Desired material properties are highly diverse, ranging from mechanical requirements for a reliably constructed aeroplane, over electrical specifications in solar cells, up to magnetoelectric properties in hard disk drives – to name just a few out of endless examples. The second half of the 20th century could be termed the microelectronics era. During this time, the world witnessed unprecedented and rapid changes in communication, information processing and information storing, starting from the earliest transistor up to having impressively powerful microprocessors in our mobile phones now, which would still have filled a supercomputing centre by the time I saw the light of day.

Most electronic devices nowadays work with binary digit data transmission, based on the presence or absence of electric charge (or, in other words, based on electrons and holes). Apart from the electron charge, another property is exploited: its spin. Storing data in a hard disk drive by changing the magnetisation of a bit, i.e. one tiny piece of magnetic material, is an example. This technology experienced a significant progression after the discovery of the Giant Magnetoresistance effect (GMR) by Grünberg in Jülich [1] and Fert in Paris [2], allowing a significantly higher information density. Their work, which was awarded the Nobel prize in 2007, can be seen as the birth of *magnetoelectronics*, i.e. the exploitation of magnetic fields in materials for the control of transport in electronic devices, from which thereafter developed the field of *spintronics* (short for spin electronics) [3, 4], which is the field of electronics based on the manipulation of the electrons' spin orientation.

It is, from my point of view, absolutely fascinating to see that all the electronic properties in spintronics and also condensed matter research in general emerge from just one single, small equation: the Dirac equation. Only the large number of particles is what makes it in practice impossible to solve the equation exactly in realistic solid state physics systems. This equation describes the behaviour of an electron under the influence of an electromagnetic potential, consistent with special relativity. It was proposed in 1928, just two years after the publication of the Schrödinger equation, which does not take special relativity into account. *Ab initio* methods aim to start from the Schrödinger or the Dirac equation, i.e. from quantum mechanical principles, to calculate physical properties from it within certain approximations but without introducing any adjustable parameters[1]. Such a method is *Density Functional Theory* (DFT), which addresses the problem of the immense amount of particles by using a density instead of wave functions as a central quantity, and results in effective single-particle Dirac or Schrödinger equations. Its first solid foundation dates back to the 1960s, when the Hohenberg-Kohn theorem [5] and the Kohn-Sham equations were published [6]. The often excellent accuracy with by far lower computational demands compared to wave function based methods, allowed it to rise from an initially peripheral position to a standard method in computational solid state physics and chemistry, including nowadays also fields such as organic chemistry or biochemistry. The Nobel prize in chemistry that Kohn and Pople were awarded in 1998 acknowledges the significance of the method.

One of the earliest schemes for the solution of the Kohn-Sham equations within DFT is

[1] The only parameters entering the theory are the electron mass and charge, Planck's constant and the speed of light in vacuum.

based on the KORRINGA-KOHN-ROSTOKER (KKR) method [7, 8]. Its roots are found even earlier than the ones of DFT, namely in the late 1940s, when it was developed as a wave function method for band structure calculations. It received only modest initial attention, yet when it was extended to a Green function method and embedded into DFT, it unveiled its full strength. The Green function can, in fact, be seen as the heart of the modern version of KKR [9, 10], containing all the information about the system and giving direct access to the electron density simply by an energy integration. It is first calculated for the single-site problem, i.e. the scattering of one electron at a single atomic potential, and then for the whole system, utilising a *multiple scattering* matching condition.

Historically, DFT was based on the Schrödinger equation as it has a simpler form compared to the Dirac equation, making it computationally less demanding. Notwithstanding, the Schrödinger equation is a serious approximation which is incapable of describing many important effects in solid state physics. Most strikingly, electron spin does not occur in the Schrödinger equation.

Expanding the Dirac Hamiltonian in powers of $1/c$, where c is the speed of light, (cf. section 6.4) enables to detect the leading correction terms compared to the Schrödinger Hamiltonian, out of which the most important ones are the relativistic mass increase and spin-orbit coupling. The latter, in turn, accounts for a long list of phenomena, which are the subject of current research. In magnetic materials these include, for instance, the magnetocrystalline anisotropy[2] [11], i.e. the spin alignment in a preferred direction. Understanding this anisotropy is crucial for the design of efficient data storage devices. The same is true for the DZYALOSHINSKII-MORIYA interaction [12, 13], which is an asymmetric spin interaction in systems with (bulk or surface) inversion asymmetry. In non-magnetic materials having such an inversion asymmetry spin-orbit interaction is responsible for the DRESSELHAUS effect [14] and the RASHBA effect [15]. Furthermore, it explains the formation of two-dimensional or three-dimensional *topological insulators.* [16, 17] The Rashba effect describes a spin splitting which can be observed in semiconductor quantum well structures with a conduction band building an antisymmetric potential well. The electrons in such a potential well form effectively a two-dimensional system (called the two-dimensional electron gas, 2DEG) in an effective electric field, which acts like a magnetic field in the rest frame of the electrons. As proposed by DATTA and DAS, by varying the voltage of a gate electrode the spin splitting can be manipulated which makes this effect so interesting for technological use, e.g. as a spin transistor. [18, 19, 20]

Quite in general, the spin-orbit interaction is essential for many spin related transport phenomena. To mention is the spin-relaxation, with the underlying ELLIOTT-YAFET [21] and DYAKONOV-PEREL [22] mechanisms. Spin relaxation determines how far the spin-polarisation of injected spin-polarised electrons can be transmitted in a wire. Besides spin-orbit coupling is central for all transport phenomena based on transversal conductance, such as the anomalous Hall effect, the spin Hall effect and the quantised versions of them (quantum anomalous Hall effect and quantum spin Hall effect). A microscopic understanding of these effects is not only at the forefront of science but also important for their perspective of technological applications. Proposals for technological use include not only the above mentioned the DATTA-DAS transistor [18] based on the Rashba effect, but also quantum

[2] Apart from the spin-orbit coupling, magnetocrystalline anisotropy is also caused by dipole-dipole interactions.

computation [23] or spin polarised solar batteries [24], to mention just a few examples. Whether or not such devices will really be realisable has yet to be seen in the future.

But it is not only in future high tech applications that relativistic effects play a role. Simple facts, like the colour of gold, can only be explained by relativistic calculations. In this example, the relativistic mass increase affects the s electrons (which are closer to the nucleus and thus move faster) more than the d electrons. As a consequence, the $5d$–$6s$ transition energy is decreased, which leads to an absorption of the blue colour, reflecting the part of the spectrum that is the golden colour we know. For silver the transition line lies in the invisible ultra-violet range, giving it its typical colour. In a non-relativistic world gold would have the same colour.

The KKR method was originally developed within the approximation of spherical potentials surrounding the atoms (atomic sphere approximation). Many of the examples above show, however, that asymmetries play an important role. Especially for structures with low symmetry or open structures it is important to take the full potential into account. Such structures include surfaces, interfaces, layered systems including van der Waals crystals, heterostructures, materials with covalent bonds, point defects, oxides or low-dimensional solids (graphene). Performing calculations in the atomic sphere approximation here results in errors in the electronic structure, for instance in the description of the interface or surface dipoles, in the description of split-off states of electrons or the formation energies of impurities.

To account for the importance of full-potential calculations, KKR (as well as other DFT methods, e.g. the FLAPW method [25]) was extended to a full-potential scheme [26], initially only for non-relativistic calculations. On the other hand, to describe relativistic effects as correctly as possible with an effort comparable to solving the Schrödinger equation, a scalar-relativistic approach was developed [27, 28], however initially for spherical potentials only. This approach does not use the full vector Dirac equation but only a scalar equation. It correctly describes the relativistic mass increase and the Darwin term, however, it does not include the important spin-orbit coupling. This restriction was overcome later on by the inclusion of a spin-orbit coupling term. As it remains an approximation, without a reference it is hard to give an exact answer to the question for which cases it holds and when it does not. On the other hand there was the development of a fully relativistic KKR scheme [29], however initially for spherical potentials only.

The history of these developments naturally raises the question if it would not be desirable to have a fully-relativistic full-potential scheme, or in other words: one scheme that includes all the requirements and effects mentioned above. Such a scheme would first serve as a valuable reference to control the applicability of the scalar relativistic or the atomic sphere approximation, but then, even more importantly, also be able to describe effects beyond the ones that the approximated schemes include once it has been tested successfully.

Publications approaching this problem are rare [30, 31], even though such implementations exist. The difficulty in formulating a practically applicable scheme, is an effective and numerically stable concept and algorithm for the fully-relativistic full-potential single-site scattering problem. Once this problem is solved, the remaining part of the calculation is the same as for a spherical fully-relativistic calculation.

In this thesis, I provide an efficient way to solve this problem. Gonzales et al. [32] presented a technique to compute the single-site scattering problem related to the Schrödinger

equation. They calculated the wave functions via the Lippmann-Schwinger integral equations, which they solved by applying Chebyshev quadrature and rewriting the equations into a system of linear equations. Once the wave functions are known, the Green function can be calculated simply from a sum (cf. section 10.3). Within the course of this work we will see that Lippmann-Schwinger equations of formally striking resemblance can also be formulated for the single-site problem of the full-potential Dirac scattering. The crucial ingredient in formulating these equations is an expansion of the potential into spin spherical harmonics, which I developed based on certain properties of the relativistic potential matrix (cf. section 10.5).

I implemented the method compatible for incorporation into a KKR impurity code that is currently under development in our group. By this means, direct comparisons between non-relativistic, scalar-relativistic and fully-relativistic calculations are accessible.

The single-site scattering problem, however, is even interesting on its own, apart from its significance for KKR and DFT. Using the code I developed, I performed calculations of the phase shift of electrons scattering at a tungsten impurity in a rubidium host. This system was chosen motivated by the aim to have a magnetic system with large relativistic effects: tungsten is a heavy element with strong spin-orbit coupling, rubidium is almost free-electron like with a low density, hence tungsten is magnetic in this system. The phase shifts beautifully show the energy splitting of the d states of tungsten. Furthermore, I calculated the $\mathbf{k}$-vector dependent scattering matrices for this impurity, showing the spin-dependent asymmetry in scattering, that is one of the so-called extrinsic contributions to the anomalous Hall effect.

These are just two examples of how the code can help to understand electronic properties on the atomic scale. This is what *ab initio* methods aim for. Another aim is to have predictive power, i.e. to not only reproduce experimental results, but predict properties. That this has been successful in describing various material properties can be seen in the fact that there are books successfully listing properties for a comprehensive list of metals [33] or other materials. By making as few approximations as possible, both concerning the shape of the potential and relativistic effects, I hope the developed method will show its potential in future calculations in the interesting field of the quantum theory of materials and the related field of spintronics.

The thesis is structured into four main parts. The first one describes the DFT and KKR methods. In the second part the non-relativistic theory is presented, in order to form a sound basis on which to develop the changes necessary in the relativistic case. The latter is treated in the following, third part, where I also develop the relativistic Lippmann-Schwinger equations and the corresponding decomposition of the potential matrix. In the last part I present the numerical methods used and explain the implemented algorithm. I conclude with calculations of scattering at a tungsten impurity in a rubidium host crystal.

Part I

Electronic Structure Calculations

2 Density Functional Theory

Density Functional Theory (DFT) it is an ab-initio method for electronic structure calculations of steadily growing popularity since the start of its development in the 1960s. From the initial, but in practice not exactly solvable, problem of the many-particle Hamiltonian of electrons and nuclei, DFT provides an efficient way to determine a solid's ground state properties of interest. It has been extended to include the electron spin (SDFT) and to a fully relativistic treatment (RDFT).

2.1 Quantum Mechanical Description of a Solid

The birth of quantum mechanics is marked by SCHRÖDINGER's groundbreaking publication [34] from the year 1926. With one single equation he was able to accurately describe arbitrary systems. After its successful validation for small systems, such as He and H_2, DIRAC is said to have explained that "chemistry has come to an end" . The essence is that this equation allows an *ab-initio* description, i.e. it is not necessary to introduce any empirical parameters from experimental measurements. Thus it has not only descriptive but also predictive power. Shortly after, however, it turned out that, although the Schrödinger equation correctly describes also large systems, the problem remains how to solve it.

A material consists of atomic nuclei and electrons. Its (non-relativistic) quantum mechanical description is therefore given by a Hamiltonian that includes the energy terms of all nuclei and all electrons of the respective material. Both, nuclei and electrons, move, giving them a kinetic energy contribution. Furthermore, due to their positive charge, there is a repulsive Coulomb interaction between the nuclei. Similarly, there is also a repulsive Coulomb interaction between the electrons due to their negative charge. And finally, between the nuclei and the electrons there is an attractive Coulomb interaction. Taking all the contributions together results in the Hamiltonian[3]

$$\begin{aligned}\hat{H}(\mathbf{R}_1,...,\mathbf{R}_N;\,\mathbf{r}_1,...,\mathbf{r}_n) \;=\; & \sum_{i=1}^{N}\frac{\hat{\mathbf{P}}_i^2}{2M_i}+\sum_{i=1}^{n}\frac{\hat{\mathbf{p}}_i^2}{2m} \\ & +\frac{1}{2}\sum_{\substack{i,j=1\\ i\neq j}}^{N}\frac{1}{4\pi\varepsilon_0}\frac{Z_iZ_je^2}{|\mathbf{R}_i-\mathbf{R}_j|}+\frac{1}{2}\sum_{\substack{i,j=1\\ i\neq j}}^{n}\frac{1}{4\pi\varepsilon_0}\frac{e^2}{|\mathbf{r}_i-\mathbf{r}_j|} \\ & -\sum_{i=1}^{N}\sum_{j=1}^{n}\frac{1}{4\pi\varepsilon_0}\frac{Z_ie^2}{|\mathbf{R}_i-\mathbf{r}_j|}.\end{aligned} \tag{2.1}$$

As this is a non-relativistic description, it is already an approximation that contains no relativistic corrections such as the electron spin, the magnetic field produced by the electrons

[3]Notation: N is the number of nuclei, n the number of electrons, M_i the mass of the i-th nucleus, $m \approx 9.109 \cdot 10^{-31}$ kg the electron mass, $e \approx 1.602 \cdot 10^{-19}$ C the absolute value of the electron charge and $\varepsilon_0 \approx 8.854 \cdot 10^{-12}$ $\mathrm{AsV^{-1}m^{-1}}$ the electric constant (or vacuum permittivity). The atomic positions are given by $\mathbf{R}_i$, the electron positions by $\mathbf{r}_i$ and their momenta by $\mathbf{P}_i$ and $\mathbf{p}_i$, respectively and the corresponding atomic number is given by Z_i. All variables are given in SI units.

and the resulting spin-orbit coupling. The corresponding stationary Schrödinger equation for the combined wave function $\Psi(\mathbf{R}_1, ..., \mathbf{R}_N; \mathbf{r}_1, ..., \mathbf{r}_n)$ of all nuclei and electrons is given by

$$\hat{H}\Psi(\mathbf{R}_1, ..., \mathbf{R}_N; \mathbf{r}_1, ..., \mathbf{r}_n) = E\Psi(\mathbf{R}_1, ..., \mathbf{R}_N; \mathbf{r}_1, ..., \mathbf{r}_n). \tag{2.2}$$

One of the simplest molecules is H_2^+, consisting of two protons (the nuclei) and one electron. Even this seemingly trivial three-body problem has no analytical solution in its general form. For a solid, the number of nuclei has the order of magnitude of 10^{23}. So obviously there is no chance for an analytic solution, but also a numerically exact solution is impossible even on today's most powerful supercomputers. Not only the CPU power is limiting the ability to perform such a calculation, but also just storing the wave function is a hopeless task. Hence there is the need for useful approximations and calculation concepts. Just shortly after the discovery of the Schrödinger equation the first rudimentary predecessor of DFT was developed by Thomas and Fermi [35, 36].

2.2 Born-Oppenheimer Approximation

On the way towards the DFT description of a solid, the first approximation is to treat electron and nucleon motions independently, exploiting the fact that their motions take place in different time scales. In simple words: electrons move a lot faster than the heavy nuclei. Consequently, it is a reasonable approximation to treat the nuclei as stationary within the electrons' reference system. After assuming that the complete wave function can be written as a product of the nucleus wave functions and the electron wave functions[4], the electron problem can be treated independently from the motion of the nuclei. This approximation was first proposed in 1927 by Born and Oppenheimer [37] and is also known as the *adiabatic approximation*. Before calculating the electron structure, one can still calculate the energetically optimal nucleon positions (*relaxation*).

The problem of calculating the electron wave function after applying the Born-Oppenheimer approximation is given by eq. (2.1) without the first summand (the kinetic energy of the nuclei) and with the third summand (the Coulomb interaction of the nuclei) being a constant.

2.3 Hohenberg-Kohn Theorem

Applying the Born-Oppenheimer approximation yields an equation for the electron wave function. The first approximative method to solve it was the Hartree method, developed in the 1930s. The idea in short is to treat the electron-electron interactions in a mean field approximation, write the nucleus-nucleus contribution as a potential independent from the electron positions and separate the many-electron wave function into a product of single-electron wave functions. It was improved by Fock and Slater, such that the Pauli principle was obeyed, by demanding an anti-symmetric many-electron wave function (written as a Slater determinant).

[4] This approximation neglects terms of the scalar product (of small magnitude) and excited electronic states.

The Hartree-Fock method is still used in certain cases. However, results in solids are often far from being accurate while the computational time scales unfavourably with system size.

The foundation in the development of the DFT method was laid by Hohenberg and Kohn in 1964 [5]. They were able to show that for an interacting electron system with non-degenerate ground state, in the influence of an external potential $V_{\text{ext}}(\mathbf{r})$, all ground state properties can be expressed as a unique functional $F[n(\mathbf{r})]$ of the electron density $n(\mathbf{r})$. For any such property and its corresponding functional, the energy can be expressed as $E = \int d\mathbf{r} n(\mathbf{r}) V_{\text{ext}}(\mathbf{r}) + F[n(\mathbf{r})]$. The density minimising the energy yields the correct ground state energy and ground state density. A generalised proof of this theorem was given by Levi in 1982 [38].

From the Hohenberg-Kohn theorem emerged the Kohn-Sham equations, effective one-electron equations that will be introduced in the following section.

2.4 Kohn-Sham Equations

The essence of the Kohn-Sham equations [6] is to describe a many-particle system by single particle equations. Kohn and Sham split the energy functional $E[n(\mathbf{r})]$ into several contributions:

$$E[n] = T_s[n] + V_H[n] + \int d\mathbf{r} n(\mathbf{r}) V_{\text{ext}}(\mathbf{r}) + E_{\text{xc}}[n]. \tag{2.3}$$

The first term $T_s[n]$ is the kinetic energy of non-interacting electrons:

$$T_s[n] = \sum_{i=1}^{n} \int d\mathbf{r} \psi_i^*(\mathbf{r}) \left(-\frac{\hbar^2}{2m} \Delta \right) \psi_i(\mathbf{r}), \tag{2.4}$$

where the electron density $n(\mathbf{r})$ is expressed in terms of the single electron wave functions

$$n(\mathbf{r}) = \sum_i |\psi_i(\mathbf{r})|^2 . \tag{2.5}$$

The second term is the Hartree energy, describing the Coulomb interaction between electrons:

$$V_H[n] = \frac{1}{4\pi\varepsilon_0} \frac{e^2}{2} \int \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \tag{2.6}$$

The third term describes the interaction of the electrons with an external potential. And the last term describes exchange-correlation effects between electrons. This term is unknown and can only be approximated, which is the important systematic limitation of DFT.

Varying the total energy and applying the Hohenberg-Kohn theorem yields the expression

$$V_{\text{eff}}(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + \frac{e^2}{4\pi\varepsilon_0} \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\delta E_{\text{xc}}}{\delta n(\mathbf{r})} \tag{2.7}$$

for the effective potential and the equations

$$\left(-\frac{\hbar^2}{2m} \Delta + V_{\text{eff}}(\mathbf{r}) \right) \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}) \tag{2.8}$$

for the single-electron wave functions. These equations have to be solved in a self-consistent manner.

2.5 Relativistic Spin-Current Density Functional Theory

The correct description of the electron including special relativity was given by DIRAC [39] just two years after the Schrödinger equation had been published. For heavy elements relativistic effects play an important role. Until today, however, the extension of the original DFT to a fully-relativistic scheme involves several difficulties concerning the approximation of the exchange-correlation energy. For this reason fully-relativistic implementations are rare. For an introduction to the topic cf. [40].

The basics of relativistic DFT were developed in the 1970s by RAJAGOPAL [41, 42, 43], VON BARTH and HEDIN [44] and MACDONALD and VOSKO [45]. In a fully relativistic treatment the four-vector current takes over the role of the electron density $n(\mathbf{r})$. With this change a generalisation of the Hohenberg-Kohn theorem is possible[5].

In the electrostatic limit, i.e. for a time-independent and purely electrostatic external potential, the four-vector current can be reduced to its time component as the only necessary variable, which is essentially the charge density. Instead of a covariant four-vector notation one can also use the electron density $n(\mathbf{r})$ and the current $\mathbf{j}(\mathbf{r}) = (j_x(\mathbf{r}), j_y(\mathbf{r}), j_z(\mathbf{r}))$. The analogue to eq. (2.3) is then given by

$$E[n,\mathbf{j}] = T_s[n,\mathbf{j}] + V_H[n] - \frac{1}{4\pi\varepsilon_0}\frac{1}{2c^2}\int\int \frac{\mathbf{j}_1(\mathbf{r}_1)\cdot\mathbf{j}_2(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}d\mathbf{r}_1 d\mathbf{r}_2 + \int d\mathbf{r} n(\mathbf{r}) V_{\text{ext}}(\mathbf{r}) + E_{\text{xc}}[n], \tag{2.9}$$

i.e. there is an additional term for the current-current contribution. This interaction term is usually negligible for single molecules, but not necessarily in a solid: it is the origin of the magnetocrystalline shape anisotropy through the spin-dipolar interaction it contains. It also explains the magnetic force between two (macroscopic) wires. In the non-relativistic limit the prefactor[6] $1/c^2$ vanishes, and with it the current-current contribution.

The Kohn-Sham equations (2.8), effective one-electron Schrödinger equations, now have to be replaced by Kohn-Sham-Dirac equations, which are effective one-electron Dirac equations[7]:

$$\left(c\boldsymbol{\alpha}\left(\hat{\mathbf{p}} - e\mathbf{A}_{\text{eff}}(\mathbf{r})\right) + \beta mc^2 + e\varphi_{\text{eff}}(\mathbf{r})\mathrm{I}_4\right)\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r}). \tag{2.10}$$

The wave functions ψ_i (Kohn-Sham orbitals) are now four-component Dirac spinors. The effective Kohn-Sham scalar and vector potentials φ_{eff} and $\mathbf{A}_{\text{eff}}$ are

$$\varphi_{\text{eff}}(\mathbf{r}) = \varphi_{\text{ext}}(\mathbf{r}) + \frac{e^2}{4\pi\varepsilon_0}\int\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' + \frac{\delta E_{\text{xc}}}{\delta n(\mathbf{r})}, \tag{2.11}$$

$$\mathbf{A}_{\text{eff}}(\mathbf{r}) = \mathbf{A}_{\text{ext}}(\mathbf{r}) - \frac{1}{4\pi\varepsilon_0}\frac{1}{c^2}\int\frac{\mathbf{j}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' + \frac{\delta E_{\text{xc}}}{\delta \mathbf{j}(\mathbf{r})}. \tag{2.12}$$

The term $\mathbf{A}_{\text{ext}}$ takes account of an external magnetic field and, accordingly, vanishes if there is no such external field.

[5] The uniqueness of the potential is no longer guaranteed in the relativistic case. However, it has been estimated that the practical consequences of this fact are not significant. For an overview of the discussion on this complicacy see [46] section 3.4 and references therein.

[6] The prefactor $1/c^2 = \varepsilon_0\mu_0/4\pi$ has its origin in the Biot-Savart law.

[7] The Dirac equation is discussed in chapter 6. In order to clarify the notation etc. it might be helpful to have a brief look at this chapter beforehand.

2.6 Relativistic Spin Density Functional Theory

Spin-current DFT brings with it the problem of finding a good approximation for the exchange-correlation contribution E_{xc}. To solve this problem and, furthermore, simplify the equations to a scheme more similar to the non-relativistic one, *spin-polarised DFT* is often used instead. An overview of the field is given for example in [47]. Compared to spin-current DFT the orbital currents are neglected here.

A Gordon decomposition[8] of the current density in the absence of a magnetic field yields

$$\mathbf{j}(\mathbf{r}) = \mathbf{j}_{\text{orb}}(\mathbf{r}) + \frac{1}{2m}\nabla \times \mathbf{m}(\mathbf{r}) \tag{2.13}$$

where $\mathbf{j}_{\text{orb}}$ is an orbital current, not discussed further here. $\mathbf{m}(\mathbf{r})$ is the spin magnetisation density. Neglecting the orbital currents $\mathbf{j}_{\text{orb}}$ the Kohn-Sham-Dirac equations take the form

$$\left(c\boldsymbol{\alpha}\hat{\mathbf{p}} + \beta mc^2 + \tilde{\tilde{V}}(\mathbf{r})\right)\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r}), \tag{2.14}$$

where $\tilde{\tilde{V}}$ is a 4×4 matrix given by[9]:

$$\begin{aligned}
\tilde{\tilde{V}}(\mathbf{r}) &= e\varphi_{\text{eff}}(\mathbf{r})\mathrm{I}_4 - \mu\beta\boldsymbol{\Sigma}\mathbf{B}(\mathbf{r}) \\
&= \begin{pmatrix} e\varphi(\mathbf{r})\mathrm{I}_2 - \mu\boldsymbol{\sigma}\mathbf{B}(\mathbf{r}) & 0 \\ 0 & e\varphi(\mathbf{r})\mathrm{I}_2 + \mu\boldsymbol{\sigma}\mathbf{B}(\mathbf{r}) \end{pmatrix} \\
&=: \begin{pmatrix} V^a(\mathbf{r}) & 0 \\ 0 & V^d(\mathbf{r}) \end{pmatrix}.
\end{aligned} \tag{2.15}$$

The $\mathbf{B}$ field and the scalar potential φ can be calculated from the above defined potentials V^a, V^d via

$$\varphi(\mathbf{r})\mathrm{I}_2 = \frac{1}{2e}\left(V^d(\mathbf{r}) + V^a(\mathbf{r})\right), \tag{2.16}$$

$$\boldsymbol{\sigma}\mathbf{B}(\mathbf{r}) = \frac{1}{2\mu}\left(V^d(\mathbf{r}) - V^a(\mathbf{r})\right). \tag{2.17}$$

Instead of the electron density $n(\mathbf{r})$ in the non-relativistic case or $n(\mathbf{r})$ and $\mathbf{j}(\mathbf{r})$ in the relativistic spin-current case, now the densities $n^{\uparrow\uparrow}(\mathbf{r})$, $n^{\uparrow\downarrow}(\mathbf{r})$, $n^{\downarrow\uparrow}(\mathbf{r})$, $n^{\downarrow\downarrow}(\mathbf{r})$ are used, defined as

$$n^{\alpha\beta}(\mathbf{r}) := \sum_i \varphi_i^{\alpha\dagger}(\mathbf{r})\varphi_i^{\beta}(\mathbf{r}), \;\; \alpha, \beta \in \{\uparrow, \downarrow\}. \tag{2.18}$$

In the method I implemented $\varphi_i^{\uparrow}$ and $\varphi_i^{\downarrow}$ are calculated by transforming the resulting four-vector wave function from the (κ, μ) basis into the (l, m_l, m_s) basis.

[8] The Gordon decomposition is a field theoretic method developed by W. Gordon [48], which allows to separate the current into an outer, orbital term and an inner part, depending on the internal state of the electron (the spin density term). The book by Strange [49] contains a section explaining the physics behind this decomposition.

[9] cf. section 6.3 for details

The (physically more intuitive) quantities, electron density $n(\mathbf{r})$ and spin magnetisation density $\mathbf{m}(\mathbf{r})$, can be calculated via

$$n(\mathbf{r}) = \sum_{\alpha} n^{\alpha\alpha}(\mathbf{r}) = n^{\uparrow\uparrow}(\mathbf{r}) + n^{\downarrow\downarrow}(\mathbf{r}) \tag{2.19}$$

$$\mathbf{m}(\mathbf{r}) = \sum_{\alpha,\beta} \boldsymbol{\sigma}^{\alpha\beta} n^{\alpha\beta}(\mathbf{r}) \tag{2.20}$$

where each σ matrix is written as

$$\sigma = \begin{pmatrix} \sigma^{\uparrow\uparrow} & \sigma^{\uparrow\downarrow} \\ \sigma^{\downarrow\uparrow} & \sigma^{\downarrow\downarrow} \end{pmatrix}. \tag{2.21}$$

2.7 Exchange-Correlation Energy Functionals

The exchange correlation energy is generally unknown. The simplest approximation for the non-relativistic case is the *local density approximation* (LDA):

$$E_{\mathrm{xc}}[n] = \int n(\mathbf{r}) \epsilon_{\mathrm{xc}}[n(\mathbf{r})] d\mathbf{r} \tag{2.22}$$

where $\epsilon_{\mathrm{xc}}[n]$ is the exchange correlation energy per electron of a homogeneous electron gas that has a constant density n. This quantity has to be evaluated only once and from then on calculating $E_{\mathrm{xc}}[n]$ means only evaluating the integral above. For a homogeneous electron gas the method is exact, but for other systems it often yields good results, even if their electron density is (globally) strongly inhomogeneous.

An attempt to improve LDA is the *generalised gradient approximation* (GGA) that includes also a gradient term. In some cases, however, GGA does not improve the results but, surprisingly, even worsens them.

In spin-polarised DFT calculations the *local spin density approximation* (LSD) can be used[10]:

$$E_{\mathrm{xc}}[n, \mathbf{m}] = \int n(\mathbf{r}) \epsilon_{\mathrm{xc}}[n(\mathbf{r}), |\mathbf{m}(\mathbf{r})|] d\mathbf{r}. \tag{2.23}$$

For possible approximations in spin-current DFT see Engel et al. [50]. Apart from an overview of different relativistic approximations of E_{xc} their accuracy for various systems is evaluated. However, a reliable approximation for E_{xc} remains a serious complication in spin-current DFT, also because this quantity plays a more dominant role here than in non-relativistic DFT. The reason is that the number of electrons in the core region increases with Z, so that the exchange-correlation contribution to the total energy also increases. Apart from that, with in increasing density also the electron momentum increases[11]. Therefore the speed of the electrons' motion is high for heavy elements, meaning that relativistic effects become non-negligible. Consequently, the exchange-correlation functional accounts for an increasing proportion of the total energy as the atomic number increases.

[10] Here the *non-collinear* approximation is shown. In the collinear approximation the projection of the spin magnetisation $\mathbf{m}$ to a certain axis (usually m_z) is used instead of the absolute value $|\mathbf{m}|$.

[11] To make this plausible consider for example the homogeneous electron gas, where the highest possible momentum is $k_F = \left(3\pi^2 n\right)^{1/3}$, for a given (constant) electron density n.

3 Korringa-Kohn-Rostoker Green Function Method

The KKR method is mostly used to calculate the electronic structure within the DFT formalism. Originally the method already emerged in the late 1940s but received only modest attention. It was extended by the Green function formalism, by incorporating full potentials, by changing the reference system for higher numerical efficiency (Screened KKR) and by the development of a fully-relativistic scheme, now making it a powerful electronic structure tool that is of advantage especially when dealing with systems of broken translational symmetry. This chapter outlines the main ideas of the multiple scattering Green function theory, as a context in which to understand the single-site problem, the focus of this work during the chapters that follow.

3.1 Overview and Historical Development

The *Korringa-Kohn-Rostoker* (KKR) method for the calculation of the electronic structure of materials was introduced as a band structure method already in 1947 by Korringa [8] and in 1954 by Kohn and Rostoker [7]. Accordingly its development started even earlier than the development of *Density Functional Theory* (DFT). However, its full strength became evident only after it was extended to a Green function method and embedded into the framework of DFT calculations. Good introductions to the methods are given in [51, 52].

The KKR method itself consists of two steps: first the single scattering problem is solved, i.e. the problem of one electron scattered at a single potential in free space. This problem is solved for each scattering potential, i.e. for each atom of the system under consideration, and its solution is described by the t matrix (cf. section 5.4). The second step is to solve the multiple scattering problem, which means solving the equation of one electron scattered at many different potentials. In order to do so, starting from the single-site scattering solutions, one applies the condition that the incident wave at each scattering centre has to be equal to the sum of the outgoing waves from all the other scattering centres. By splitting up the problem into these two steps one obtains a separation between the potential and structural properties of the system.

Originally the KKR method was designed for the simpler case of spherical potentials only. The generalisation to potentials of arbitrary shape [26, 53, 54] was an important improvement in the method, as the non-spherical contributions play an important role for systems with reduced symmetry.

Furthermore, even though KKR was originally developed for the Schrödinger equation, it is possible to formulate it for the Dirac equation, maintaining the structure of the key equations in the method [31]. This was first done for the spherical case, but then also for potentials of general shape [30]. Another improvement of the method was the development of *Screened* or *Tight-Binding KKR*. By replacing the free space reference system by a system of repulsive potentials, the numerical efficiency of the method can be strongly improved [55].

3.2 Introduction to Green Function Theory

Green functions form the basis of a technique for solving partial differential equations (PDE). A detailed examination from a mathematical point of view is given in the books by Roach [56] or Duffy [57], whereas Economou [58] provides a physicist's point of view. The aim of this section is to give an introduction pointing out the main concepts and properties important within the theory of multiple scattering without being mathematically completely rigorous.

For our purposes we need inhomogeneous linear first order (in the case of the Dirac equation) or second order (in the case of the Schrödinger equation) PDE in three (or four, in the time-dependent case) dimensions. Such a PDE can be expressed by a differential operator $\mathrm{L} = \mathrm{L}(\mathbf{r}, \frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}, \frac{\partial^2}{\partial x^2}, \frac{\partial^2}{\partial x \partial y}, ..., \frac{\partial^2}{\partial z^2})$ and a source term $f(\mathbf{r})$ as

$$\mathrm{L}u = f, \tag{3.1}$$

where $u(\mathbf{r})$ is the (unknown) solution of the PDE and $\mathbf{r} = (x, y, z)$. It would be convenient if one could invert the differential operator and solve the equation directly as $u = \mathrm{L}^{-1} f$. If L is a differential operator, obviously L^{-1} has to be an integral operator. That is exactly the philosophy of the Green function method. By the use of an auxiliary function $G(\mathbf{r}, \mathbf{r}')$, namely the Green function, the integral equation can be written as

$$u(\mathbf{r}) = \mathrm{L}^{-1} f(\mathbf{r}) = \int G(\mathbf{r}, \mathbf{r}') f(\mathbf{r}') d\mathbf{r}. \tag{3.2}$$

The Green function G is also called the kernel of the integral operator. As it is generally unknown and also depends on the boundary conditions, the problem of solving the PDE is transformed into the problem of finding the Green function and afterwards calculating the integral. However, G does not depend on f, and that is the main advantage of the method – once the Green function for a certain differential operator L is known, solving the inhomogeneous equation requires only the evaluation of an integral.

A useful tool within the Green function theory is the Dirac δ function. As $\mathrm{L}\mathrm{L}^{-1} = \mathrm{I}$, one may formally write

$$u(\mathbf{r}) = \mathrm{L}\mathrm{L}^{-1} u(\mathbf{r}) = \mathrm{L} \int G(\mathbf{r}, \mathbf{r}') u(\mathbf{r}') d\mathbf{r}' = \int \mathrm{L} G(\mathbf{r}, \mathbf{r}') u(\mathbf{r}') d\mathbf{r}'. \tag{3.3}$$

The δ function, which in fact is not a function but a distribution (also called a generalised function), is defined as the kernel of the integral above, i.e. it fulfils

$$u(\mathbf{r}) = \int \delta(\mathbf{r}' - \mathbf{r}) u(\mathbf{r}') d\mathbf{r}'. \tag{3.4}$$

The concept of distributions makes it possible to differentiate (generalised) functions at points where they are classically not differentiable. For example also the δ function is the derivative of a function (the Heaviside step function).

From equation (3.3) and the definition of the δ function (3.4) we obtain the relation

$$u(\mathbf{r}) = \int \delta(\mathbf{r}' - \mathbf{r}) u(\mathbf{r}') d\mathbf{r}' = \int \mathrm{L} G(\mathbf{r}, \mathbf{r}') u(\mathbf{r}') d\mathbf{r}'. \tag{3.5}$$

Thus, using the δ function, a Green function can formally be defined by the equation

$$\mathrm{L}G(\mathbf{r},\mathbf{r}') = \delta(\mathbf{r}'-\mathbf{r}). \tag{3.6}$$

With the Green function method we can determine a particular solution u^{part} of a non-homogeneous differential equation. The full set of solutions $\{u_i\}$ is then given by the set of the solutions $\{u_i^0\}$ of the homogeneous equation $Lu = 0$, plus the particular solution, found with the Green function method:

$$\{u_i\} = \{u^{\mathrm{part}} + u_i^0\}. \tag{3.7}$$

The differential operator which will first be of interest here is $\mathrm{L} = \Delta + k^2$, where Δ denotes the Laplace operator $\Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$. The corresponding differential equation is the Helmholtz equation

$$\left(\Delta + k^2\right) u = 0 \tag{3.8}$$

in the case of no source term (i.e. no potential) or, in the general case with a source term

$$\left(\Delta + k^2\right) u = f. \tag{3.9}$$

In the setting we will examine it will be $u = \psi$ and $f = V\psi$. We will see in chapter 4 how this equation emerges from the physical setting and how to determine its Green function.

3.3 Green Function and Electron Density

The Schrödinger equation for an electron in a potential (see eq. (4.2)) is an equation of the form $Lu = f$ (cf. eq. (3.1)) and it can thus be solved using Green functions. The same applies for the Dirac equation. In that way the calculation of all the eigenvalues E_n and corresponding eigenfunctions ψ_n can be avoided. The Green function contains all the information that the eigenfunctions contain, in particular the electron density (see eq. (2.5)) can be calculated as an integral of the Green function[12]:

$$n(\mathbf{r}) = -\frac{2}{\pi}\mathrm{Im}\int_{-\infty}^{E_F} G^{\mathrm{full}}(\mathbf{r},\mathbf{r},z)dz, \tag{3.10}$$

where the factor 2 arises from the spin degeneracy. Here G^{full} is the Green function of the complete system, which is calculated from the single-site Green functions G as described in the following section 3.4. To increase the numerical efficiency, the analytical properties of a Green function are used by introducing a complex energy $z = E + i\Gamma$ and solving the integral by a contour integration in the upper half of the complex plane. This avoids the singularities of the Green function on the real axis and thus leads to accurate results already for low numbers of quadrature points. The contour runs over all occupied states, i.e. it starts at an energy E_b below the bottom of the valence band and runs up to the Fermi energy E_F. Close to the Fermi energy the integration mesh should be chosen denser than the rest of the contour, since a higher accuracy is required here to obtain good results.

[12] This expression holds for non-relativistic calculations and scalar relativistic calculations without spin-polarisation.

3.4 Multiple Scattering

As it is the focus of this work, the single-site problem will be discussed in great detail in the following chapters. This section will give a short overview on how to proceed in obtaining the Green function for the full system using multiple scattering theory, once the single-site Green functions for all sites are known. All equations will be given for the relativistic case. However, they hold for the non-relativistic case, too, when replacing the index $\Lambda = (\kappa, \mu)$ by $L = (l, m)$.

In terms of wave functions ψ_i at the different sites i the multiple scattering condition (a detailed mathematical discussion gives [59]) says that the incoming wave at one site should be equal to the outgoing waves from all the scattering centres. This is schematically shown in figure 3.1, the corresponding formula is:

$$\psi_i^{\text{inc}}(\mathbf{r}) = \sum_{j \neq i} \psi_j^{\text{sc}}(\mathbf{r}). \tag{3.11}$$

From this condition one can derive a formula for the Green function of the whole system $G^{\text{full}}(\mathbf{r}, \mathbf{r}', W)$ from the single-site Green functions at the different sites $G^i(\mathbf{r}, \mathbf{r}', W)$, namely[13]

$$G^{\text{full}}(\mathbf{r} + \mathbf{R}^i, \mathbf{r}' + \mathbf{R}^j, W) = \delta_{ij} G^i(\mathbf{r}, \mathbf{r}', W) + \sum_{\Lambda} R^i_{\Lambda}(\mathbf{r}) \sum_{\Lambda'} G^{ij}_{\Lambda\Lambda'} \overline{R}^j_{\Lambda'}(\mathbf{r}'), \tag{3.12}$$

where W denotes the relativistic energy (cf. eq. (8.10)). The formula contains the wave functions R^i_{Λ} of all sites i in an angular momentum basis, that are determined from the Lippmann-Schwinger equation[14] . The wave functions depend on k (or, equivalently, on the energy W), however, this dependence is suppressed here to simplify the notation. Furthermore the formula contains the so-called structural Green functions $G^{ij}_{\Lambda\Lambda'}(W)$ that are also k-dependent (or, equivalently, energy-dependent) expansion coefficients. They can be calculated from the t matrix by the *Dyson equation:*

$$G^{ij}_{\Lambda\Lambda'} = g^{ij}_{\Lambda\Lambda'} + \sum_{\Lambda''} \sum_{n} g^{in}_{\Lambda\Lambda''} \sum_{\Lambda'''} t^n_{\Lambda''\Lambda'''} G^{nj}_{\Lambda'''\Lambda'}. \tag{3.13}$$

This is a system of linear equations that can be solved e.g. by Gauß elimination. $t^n_{\Lambda\Lambda'}$ are the single-site t matrices that can be calculated from the wave functions R^i_{Λ} (cf. eq. (5.34) in section 5.4 for the non-relativistic case or eq. (10.66) in section 10.4 for the relativistic case, see also [30, 60]). The coefficients $g^{ij}_{\Lambda\Lambda'}$ are, for fixed scattering centres, constants independent of the potentials, i.e. they only depend on the structure of the system under consideration. The index $\Lambda = (\kappa, \mu)$ denotes the quantum numbers in an angular momentum basis for the relativistic case (see section 7.5) and has to be replaced by $L = (l, m)$ in the non-relativistic case (see section 4.2).

A detailed derivation of the equations can be found in [26] for the full-potential Schrödinger case.

[13] Overlined letters, such as $\overline{R}^j_{k\Lambda'}$, denote left-hand side solutions. For details see chapters 8 and 10.
[14] cf. eq. (5.12) and eqs. (10.13) to (10.16) for the non-relativistic and relativistic case, respectively

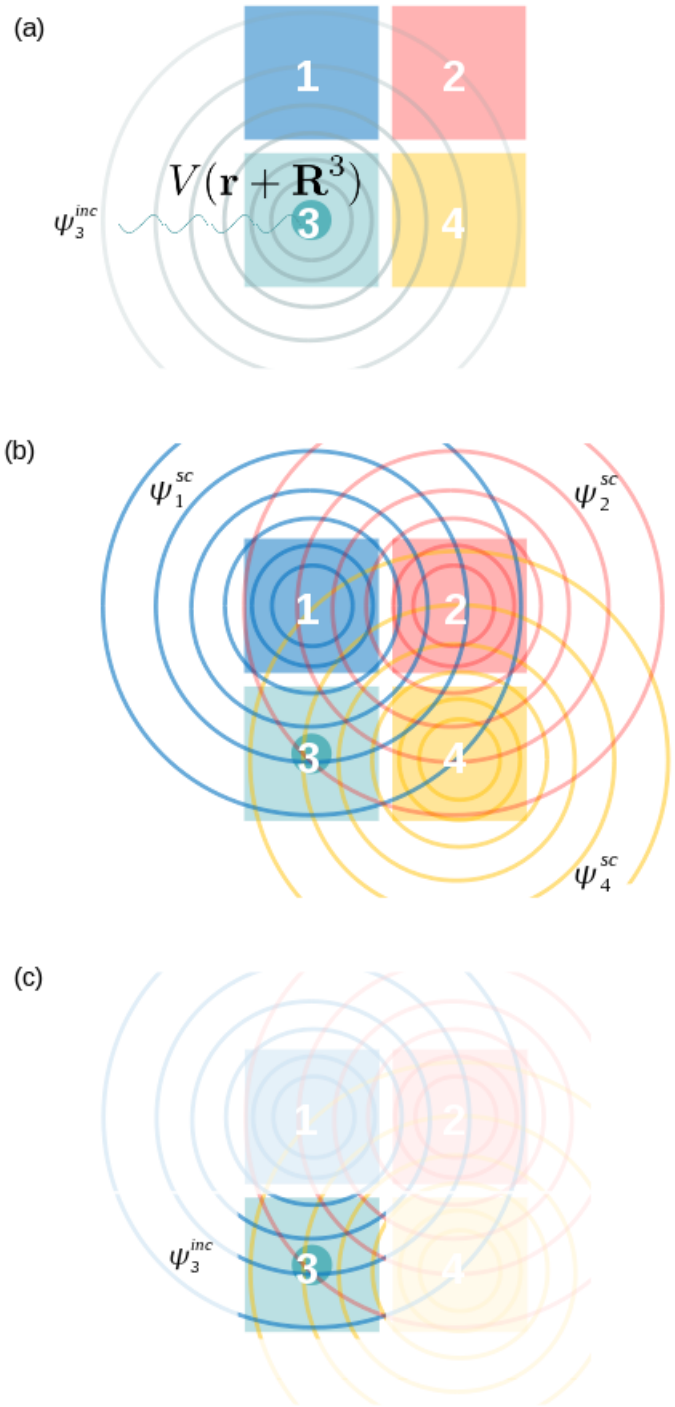


Figure 3.1: Schematic picture of the multiple scattering condition. (a) An incoming wave ψ_3^{inc} is scattered at the potential $V(\mathbf{r}+\mathbf{R}^3)$. The scattered wave strikes the other potentials. (b) Scattering at the other three potentials yields three scattered waves. Further orders, i.e. scattering of these waves, will be neglected in this schematic picture. (c) The scattered waves hit on the potential $V(\mathbf{r}+\mathbf{R}^3)$. According to the multiple scattering condition, the incoming wave for this potential must be equal to the scattered waves from all the other potentials.

3.5 Full Potential

In the original form of the KKR method one could only treat spherical potentials. Let us first consider the non-relativistic case. The restriction to spherical potential means that in a potential expansion of the form (cf. sections 5.2 and 5.3)

$$V(\mathbf{r}) = \sum_L V_L(r) Y_L(\hat{\mathbf{r}}) \tag{3.14}$$

only the first component with $L = (0, 0)$ is taken into account. Here r is the radial coordinate and $\hat{\mathbf{r}} = (\theta, \phi)$ denotes the angular coordinates, $Y_L(\hat{\mathbf{r}})$ are spherical harmonics[15]. This simplifies the calculations significantly, as instead of systems of coupled equations only decoupled single equations have to be solved (see section 10.8 for a detailed discussion in the relativistic case). The equations of the previous section 3.4 also become simpler when using spherical potentials only.

The generalisation to potentials of arbitrary shape [26], however, showed that the additional effort for calculations using the full potential scales only linearly with the number of non-equivalent atoms. As it is important for systems with broken symmetry, this modest increase in computational effort is totally acceptable and only in the full-potential scheme KKR shows its full strength in comparison to other electron structure methods. Such systems include surfaces, impurities in bulk material or on surfaces, tunnel junctions or interfaces. Also when calculating forces and lattice relaxations a full-potential treatment is required, as for these problems the spherical approximation fails completely [10].

Whereas in spherical potential calculations the Wigner-Seitz cells are approximated by spheres, in the full-potential treatment these spheres are replaced by the exact Wigner-Seitz cells, i.e. by space-filling and non-overlapping cells. This is realised by convoluting all integrals with shape functions $\Theta(\mathbf{r})$. They equal 1 inside a Wigner-Seitz cell and 0 outside. The shape functions are expanded in spherical harmonics, just like the potential:

$$\Theta(\mathbf{r}) = \sum_L \Theta_L(r) Y_L(\hat{\mathbf{r}}). \tag{3.15}$$

This type of expansion will also be applied to the wave functions, thus separating radial and angular parts of the equations, e.g. of the Lippmann-Schwinger equations.

In the relativistic case the idea remains unchanged. However the potential here is a 4×4 matrix, expanded in spin spherical harmonics. I derive an expansion for the potential in section 10.5, based on the hermicity of the 2×2 sub matrices, which has the form

$$V = \sum_{\Lambda} \sum_{\Lambda'} \begin{pmatrix} \chi_\Lambda(\hat{\mathbf{r}}) & 0 \\ 0 & \chi_{\overline{\Lambda}}(\hat{\mathbf{r}}) \end{pmatrix} \begin{pmatrix} v^a_{\Lambda\Lambda'}(r) & v^b_{\Lambda\Lambda'}(r) \\ v^c_{\Lambda\Lambda'}(r) & v^d_{\Lambda\Lambda'}(r) \end{pmatrix} \begin{pmatrix} \chi^\dagger_{\Lambda'}(\hat{\mathbf{r}}) & 0 \\ 0 & \chi^\dagger_{\overline{\Lambda}'}(\hat{\mathbf{r}}) \end{pmatrix}. \tag{3.16}$$

The first matrix has dimensions 4×2, the middle one 2×2 and the last one 2×4, resulting in a 4×4 matrix. From the potential expansion I derived an expansion of the relativistic Lippmann Schwinger equations (section 10.6).

[15] for the definition of spherical harmonics see the digression on page 43

3.6 KKR GF Algorithm

The chapter about the KKR Green function method will be concluded with an overview of the algorithm. It anticipates many equations from discussions in the following chapters, so when reading it for the first time it should only be seen as a rough overview without the need to understand it in full detail. After having further reading, it might be helpful as a reference for identifying which are the key steps within the calculation.

1. Starting point of the calculation is the Green function of a free electron $G^0(\mathbf{r}, \mathbf{r}', z)$, cf. eq. (4.15) or eq. (9.3) for the non-relativistic and the relativistic case, respectively. For this function there is an analytically known expression.

2. The system is divided into atomic cells and the wave functions for each cell are calculated from the Lippmann-Schwinger equation, that is eq. (5.12) in the non-relativistic case or equations (10.13) to (10.16) in the relativistic case, here shown for the regular right hand side solution:

$$R_\Lambda(\mathbf{r}) = J_\Lambda(\mathbf{r}) + \int d\mathbf{r}' G^0(\mathbf{r}, \mathbf{r}'; W) V(\mathbf{r}') R_\Lambda(\mathbf{r}). \tag{3.17}$$

   Mathematically, one has to solve an integral equation. The method chosen in this work is by using Chebyshev quadrature and rewriting the integral equation into a system of linear equations, as explained in chapter 11.

3. After the wave functions are known, the t matrix elements can be calculated. In the non-relativistic case this is done via eq. (5.34) or in the relativistic case via:

$$t_{\Lambda\Lambda'} = \int \overline{J}_{\Lambda'}(\mathbf{r}') V(\mathbf{r}') R_{\Lambda'}(\mathbf{r}') d\mathbf{r}. \tag{3.18}$$

4. The coefficients $g^{ij}_{\Lambda\Lambda'}$ have to be determined, see [26] for the formula and a derivation. They depend only on the position of the scattering centres, i.e. for fixed positions they are only energy-dependent.

5. The Dyson equation (cf. eq. (3.13))

$$G^{ij}_{\Lambda\Lambda'} = g^{ij}_{\Lambda\Lambda'} + \sum_{\Lambda''} \sum_n g^{in}_{\Lambda\Lambda''} \sum_{\Lambda'''} t^n_{\Lambda''\Lambda'''} G^{nj}_{\Lambda'''\Lambda'} \tag{3.19}$$

   for the structural Green functions $G^{ij}_{\Lambda\Lambda'}$ has to be solved. It is a system of linear equations that can be solved by standard methods.

6. The single-site Green function is also calculated from the wave-functions via eq. (10.19)

$$G(\mathbf{r}, \mathbf{r}', W) = \Theta(r' - r) \sum_\Lambda R_\Lambda(\mathbf{r}) \overline{S}_\Lambda(\mathbf{r}') + \Theta(r - r') \sum_\Lambda S_\Lambda(\mathbf{r}) \overline{R}_\Lambda(\mathbf{r}') \tag{3.20}$$

   for the relativistic case. For the non-relativistic case the same equation holds, except for changing the index Λ to L and using the non-relativistic wave functions instead.

7. The last step is the calculation of the Green function for the full system

$$G^{\text{full}}(\mathbf{r}+\mathbf{R}^i,\mathbf{r}'+\mathbf{R}^j,W)=\delta_{ij}G^i(\mathbf{r},\mathbf{r}',W)+\sum_{\Lambda}R^i_{\Lambda}(\mathbf{r})\sum_{\Lambda'}G^{ij}_{\Lambda\Lambda'}\overline{R}^j_{\Lambda'}(\mathbf{r}') \tag{3.21}$$

(cf. eq. (3.12)). This Green function contains the whole information, in particular it can be used to calculate the electron density via eq. (3.10).

Part II

Non-Relativistic Single-Site Scattering

4 Free Particle Green Function

The Green function of an electron moving freely without the influence of a potential plays an important role in the KKR theory. This is due to the fact that the free electron is the reference system used for calculating the Green function of the electron *with* the influence of a potential later on. The free space Green function can be calculated analytically, and in an angular momentum basis it can be expressed through the free space wave functions in this basis.

4.1 Derivation

As the Green function plays a vital role in multiple scattering methods, this function shall be calculated for the non-relativistic electron, i.e one that is moving at a speed which is small compared to the speed of light. The wave function ψ of such an electron is described by the (stationary) Schrödinger equation

$$\left(-\frac{\hbar^2}{2m}\Delta + V(\mathbf{r})\right)\psi(\mathbf{r}) = E\psi(\mathbf{r}), \tag{4.1}$$

where m is the electron mass, $\hbar$ the Planck constant, $V(\mathbf{r})$ a scattering potential and E the energy. This equation can be rewritten as

$$\frac{\hbar^2}{2m}\left(\Delta + k^2\right)\psi(\mathbf{r}) = \mathrm{V}(\mathbf{r})\psi(\mathbf{r}), \tag{4.2}$$

where k is defined by $\hbar^2k^2/2m := E$. It is helpful to consider first the problem of a free electron without any scattering potential – not only because this is easier to tackle but also because the result will be needed in future calculations of Green functions. In this case of a free electron the right hand side of the integral vanishes and what is left is the homogeneous differential equation

$$\frac{\hbar^2}{2m}\left(\Delta + k^2\right)\psi(\mathbf{r}) = 0 \tag{4.3}$$

which we recognise as the Helmholtz equation. The solutions of this equation for a given energy E are all the plane waves $\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{kr}}$ fulfilling $\hbar^2k^2/2m = E$. The corresponding Green function is defined by

$$\frac{\hbar^2}{2m}\left(\Delta + k^2\right)G^0_{nr}(\mathbf{r}, \mathbf{r}'; E) = \delta(\mathbf{r} - \mathbf{r}') \tag{4.4}$$

with the index nr indicating that it is the non-relativistic Green function. Here a third argument or parameter E is introduced to the Green function, to point out that it depends on the energy. To solve the equation, one can start from the integral representation of the Dirac δ function

$$\delta(\mathbf{r} - \mathbf{r}') = \frac{1}{(2\pi)^3}\int \mathrm{e}^{i\mathbf{q}(\mathbf{r}-\mathbf{r}')}d\mathbf{q}. \tag{4.5}$$

Inserting this into the definition of the Green function and bringing the differential operator to the other side of the equation yields

$$G^0_{nr}(\mathbf{r},\mathbf{r}';E) = \frac{2m}{\hbar^2}\left(\Delta+k^2\right)^{-1}\frac{1}{(2\pi)^3}\int \mathrm{e}^{i\mathbf{q}(\mathbf{r}-\mathbf{r}')}d\mathbf{q} \tag{4.6}$$

$$= \frac{2m}{\hbar^2}\frac{1}{(2\pi)^3}\int \left(\Delta+k^2\right)^{-1}\mathrm{e}^{i\mathbf{q}(\mathbf{r}-\mathbf{r}')}d\mathbf{q}. \tag{4.7}$$

Since

$$\left(\Delta+k^2\right)\frac{\mathrm{e}^{i\mathbf{q}(\mathbf{r}-\mathbf{r}')}}{k^2-q^2} = \mathrm{e}^{i\mathbf{q}(\mathbf{r}-\mathbf{r}')}, \tag{4.8}$$

as it can directly be verified by performing the differentiation, one obtains

$$G^0_{nr}(\mathbf{r},\mathbf{r}';E) = \frac{2m}{\hbar^2}\frac{1}{(2\pi)^3}\int \frac{\mathrm{e}^{i\mathbf{q}(\mathbf{r}-\mathbf{r}')}}{k^2-q^2}d\mathbf{q}. \tag{4.9}$$

The integral can first be rewritten into spherical coordinates. Defining $\mathbf{x} := \mathbf{r}-\mathbf{r}'$ and choosing the coordinate system in $\mathbf{x}$-direction, i.e. $\mathbf{x} = x\mathbf{e}_x$, one can simplify $\mathrm{e}^{i\mathbf{q}(\mathbf{r}-\mathbf{r}')} = \mathrm{e}^{iqx\cos\theta}$, so that

$$\begin{aligned}
G^0_{nr}(\mathbf{r},\mathbf{r}';E) &= \frac{2m}{\hbar^2}\frac{1}{(2\pi)^3}\int_0^{2\pi}d\phi\int_0^{\pi}d\theta\int_0^{\infty}q^2\sin\theta\frac{\mathrm{e}^{iqx\cos(\theta)}}{k^2-q^2}dq \\
&= \frac{2m}{\hbar^2}\frac{1}{(2\pi)^2}\int_0^{\pi}d\theta\int_0^{\infty}q^2\sin\theta\frac{\mathrm{e}^{iqx\cos(\theta)}}{k^2-q^2}dq \\
&= \frac{2m}{\hbar^2}\frac{1}{(2\pi)^2ix}\int_0^{\infty}q\frac{\mathrm{e}^{iqx}-\mathrm{e}^{-iqx}}{k^2-q^2}dq \\
&= \frac{2m}{\hbar^2}\frac{1}{(2\pi)^2ix}\left[\int_0^{\infty}q\frac{\mathrm{e}^{iqx}}{k^2-q^2}dq+\int_{-\infty}^{0}q\frac{\mathrm{e}^{iqx}}{k^2-q^2}dq\right] \\
&= \frac{2m}{\hbar^2}\frac{1}{(2\pi)^2ix}\int_{-\infty}^{\infty}q\frac{\mathrm{e}^{iqx}}{(k-q)(k+q)}dq.
\end{aligned} \tag{4.10}$$

The resulting integral has poles for $q=k$ and $q=-k$, both of order 1. Its value is therefore undefined unless a certain path of integration is specified. If we remember the previous section, where it was pointed out that the Green function depends on the boundary conditions, this makes sense – because so far we did not specify the boundary conditions. We will first choose a closed integration path γ with the pole at k lying within the path.

Digression: Residue Theorem

Let f be an analytic function (locally representable by a power series) within a simply-connected domain G except for isolated singular points. Then:

$$\int_\gamma f(z)dz = 2\pi i \sum_{l=1}^{N} \text{res}[f(z); a_l]$$

where γ is a closed, rectifiable ("piece-wise smooth") curve in G which does not intersect the singularities of f, and a_k, $k = 1, ..., N$ are the singular points within γ. The residue is

$$\text{res}[f(z), a] = \frac{1}{(m-1)!} \lim_{z\to a} \left(\frac{d^{m-1}}{dz^{m-1}} (z-a)^m f(z) \right)$$

for a pole of order m.

Using the residue theorem the integral can be solved:

$$G_{nr}^{0+}(\mathbf{r}, \mathbf{r}'; E) = \frac{2m}{\hbar^2} \frac{1}{(2\pi)^2 ix} \cdot 2\pi i \sum_{l=1}^{1} \text{res} \left[q \frac{\mathrm{e}^{iqx}}{(k-q)(k+q)}, a_l \right], \tag{4.11}$$

where $a_1 = k$ and

$$\begin{aligned} \text{res} \left[q \frac{e^{iqx}}{k^2 - q^2}, a_1 \right] &= \frac{1}{0!} \lim_{q\to k} \left((q-k) q \frac{\mathrm{e}^{iqx}}{(k-q)(k+q)} \right) \\ &= \lim_{q\to k} \frac{q}{(k+q)} \mathrm{e}^{iqx} \\ &= -\frac{1}{2} \mathrm{e}^{ikx}, \end{aligned} \tag{4.12}$$

thus

$$G_{nr}^{0+}(\mathbf{r}, \mathbf{r}'; E) = -\frac{2m}{\hbar^2} \frac{1}{4\pi x} \mathrm{e}^{ikx}. \tag{4.13}$$

Choosing a different integration path γ which contains the pole $q = -k$ and not $q = k$ and performing an analogue calculation yields

$$G_{nr}^{0-}(\mathbf{r}, \mathbf{r}'; E) = -\frac{2m}{\hbar^2} \frac{1}{4\pi x} \mathrm{e}^{-ikx}. \tag{4.14}$$

These two Green functions obviously have a different behaviour for $x \to \infty$. Thus the boundary conditions imposed on the Green function determine the value of the – otherwise undefined – integral which was seen in its calculation. There is also a physical interpretation of these boundary conditions: G_{nr}^{0+} describes an outgoing wave whereas G_{nr}^{0-} is an incoming wave. Here $G_{nr}^{0} := G_{nr}^{0+}$ is the function we are interested in. In short:

The Green function corresponding to the outgoing wave of a non-relativistic free electron is given by

$$G^0_{nr}(\mathbf{r},\mathbf{r}';E) = -\frac{2m}{\hbar^2}\frac{\mathrm{e}^{ik|\mathbf{r}-\mathbf{r}'|}}{4\pi|\mathbf{r}-\mathbf{r}'|}. \tag{4.15}$$

4.2 Angular Momentum Expansion

For calculations later on the angular momentum expansion of the Green function will be important. The reason being, that by writing down angular momentum expansions for all the relevant equations it will be possible to separate the problem and solve the sub-problems for different values of l and m.

Let us start by recalling the partial wave expansion of a plane wave: For a spherically symmetric scattering potential $V(\mathbf{r}) = V(r)$ states of different angular momentum are scattered independently. It is therefore convenient to expand the wave in terms of superposed partial waves with different angular momentum. This expansion shall not be derived here but just be stated:

$$\begin{aligned}\mathrm{e}^{i\mathbf{k}\cdot\mathbf{r}} = \mathrm{e}^{ikr\cos(\theta)} &= \sum_{l=0}^{\infty} i^l(2l+1)j_l(kr)P_l(\cos\theta) \\ &= 4\pi\sum_{l,m}^{\infty} i^l Y^*_{l,m}(\hat{\mathbf{k}})Y_{l,m}(\hat{\mathbf{r}})j_l(kr) \\ &= 4\pi\sum_{L} i^l Y^*_{L}(\hat{\mathbf{k}})Y_{L}(\hat{\mathbf{r}})j_l(kr).\end{aligned} \tag{4.16}$$

In the last step a combined index $L := (l,m)$ was introduced to simplify the notation and $\hat{\mathbf{r}} = (\phi,\theta)$ denotes the direction of the vector $\mathbf{r}$. Now let us look at the functions j_l, P_l and $Y_{l,m}$ in some short mathematical digressions. First an overview of Bessel and Hankel functions:

Digression: Bessel and Hankel functions

Bessel's differential equation

$$x^2\frac{d^2y}{dx^2} + x\frac{dy}{dx} + (x^2 - n^2)y = 0,$$

where n can be an arbitrary complex number (but in the cases of interest here will be an integer) has as solutions the *Bessel functions*. If n is not an integer, two linearly independent solutions are given by J_n and J_{-n}, where

$$J_n(x) := \sum_{r=0}^{\infty} \frac{(-1)^r (\frac{x}{2})^{2r+n}}{\Gamma(n+r+1)r!}.$$

These functions are also called the Bessel functions of first kind. In contrast, if n is an integer the two solutions are given by J_n and another function N_n which is called a Bessel function of second kind or also a Weber or a *Neumann function*:

$$N_n(x) := \lim_{p\to n} \frac{J_p(x)\cos(p\pi) - J_{-p}(x)}{\sin(p\pi)}.$$

Both sets of functions can alternatively be defined using integrals of trigonometric functions. They form a basis for the vector space of the solution of the differential equation. An alternative basis is given by the Hankel functions

$$H_n^{(\pm)}(x) := J_n(x) \pm iN_n(x).$$

For the partial wave expansion of a plane wave and also for the expansion of the Green function, the so-called spherical Bessel functions are needed. Thus a quick overview of those as well:

Digression: Spherical Bessel functions

When examining the free movement of a particle with a given angular momentum, one has to solve the Helmholtz equation

$$\left(\Delta + k^2\right)\psi = 0.$$

Separation of variables eventually yields the following radial part:

$$x^2\frac{d^2y}{dx^2} + 2x\frac{dy}{dx} + [x^2 - l(l+1)]y = 0.$$

Two linearly independent solutions are the spherical Bessel and spherical Neumann functions:

$$\begin{aligned} j_l(x) &:= \sqrt{\frac{\pi}{2x}}J_{l+1/2}(x) = (-x)^l\left(\frac{1}{x}\frac{d}{dx}\right)^l\frac{\sin x}{x}, \\ n_l(x) &:= \sqrt{\frac{\pi}{2x}}Y_{l+1/2}(x) = -(-x)^l\left(\frac{1}{x}\frac{d}{dx}\right)^l\frac{\cos x}{x}. \end{aligned}$$

Two different linearly independent solutions are given by the spherical Hankel functions:

$$\begin{aligned} h_l^{(1)}(x) &:= j_l(x) + in_l(x) \\ h_l^{(2)}(x) &:= j_l(x) - in_l(x). \end{aligned}$$

The Bessel function vanishes as $x \to 0$ if $l \geq 1$ and is called the *regular solution*. The Neumann and Hankel functions diverge and are called *irregular solutions*. Here only the function $h_l^{(1)}$ is of interest, thus the definition $h_l := h_l^{(1)}$ will be used throughout this work.

And finally the Legendre polynomials and spherical harmonics:

Digression: Legendre Polynomials and Spherical Harmonics

The Legendre polynomials are given by

$$P_n(x) = \frac{1}{2^n n!}\frac{d^n}{dx^n}[(x^2-1)^n].$$

They are solutions of Legendre's differential equation. Moreover, there is also a general Legendre equation, which is solved by the associated Legendre polynomials:

$$P_{l,m}(x) = \frac{(-1)^m}{2^l l!}(1-x^2)^{m/2}\ \frac{d^{l+m}}{dx^{l+m}}(x^2-1)^l.$$

They are also used to define complex spherical harmonics:

$$Y_{l,m}(\theta,\phi) = N\, e^{im\phi}\, P_{l,|m|}(\cos\theta).$$

N is a normalisation constant given by $N = A_{l,|m|}C_m$ (Condon-Shortley convention) where

$$\begin{aligned} A_{l,|m|} &= \sqrt{\frac{2l+1}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}} \\ C_m &= i^{m+|m|} = \begin{cases} 1, & m \le 0 \text{ or } m \text{ even} \\ -1, & m > 0 \text{ and } m \text{ odd.} \end{cases} \end{aligned}$$

The spherical harmonics are a set of solutions of the angular part of the Laplace equation. They fulfil the orthonormality relation

$$\int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta d\theta\, Y_{l,m}(\theta,\phi)Y^*_{l',m'}(\theta,\phi) = \delta_{ll'}\delta_{mm'}$$

and the completeness relation

$$\sum_{l=0}^{\infty}\sum_{m=-l}^{l} Y_{l,m}(\theta,\phi)Y^*_{l,m}(\theta',\phi') = \frac{1}{\sin\theta}\delta(\theta-\theta')\delta(\phi-\phi').$$

As a consequence, any complex square-integrable function can be expressed in terms of complex spherical harmonics:

$$f(\theta,\phi) = \sum_{l=0}^{\infty}\sum_{m=-l}^{l} f_{l,m}Y_{l,m}(\theta,\phi) = \sum_L f_L Y_L(\hat{\mathbf{r}}).$$

Here $L := (l,m)$ and $\hat{\mathbf{r}} = (\theta,\phi)$ are defined.

The starting point is to derive the expansion of the integral formula for the Green function (4.9), which can be rewritten as

$$G^0_{nr}(\mathbf{r},\mathbf{r}',E) = \frac{2m}{\hbar^2}\frac{1}{(2\pi)^3}\int \frac{1}{k^2-q^2}\mathrm{e}^{i\mathbf{q}\mathbf{r}}\mathrm{e}^{-i\mathbf{q}\mathbf{r}'}d\mathbf{q}. \tag{4.17}$$

Now insert the partial wave expansion of the plane wave eq. (4.16) into this expression, yielding $G^0_{nr}(\mathbf{r},\mathbf{r}',E) =$

$$\frac{2m}{\hbar^2}\frac{1}{(2\pi)^3}\int \frac{1}{k^2-q^2}\left[4\pi\sum_L i^l Y^*_L(\hat{\mathbf{q}})Y_L(\hat{\mathbf{r}})j_l(qr)\right]\left[4\pi\sum_{L'}(-i)^{l'}Y_{L'}(\hat{\mathbf{q}})Y^*_{L'}(\hat{\mathbf{r}}')j_{l'}(qr')\right]d\mathbf{q}. \tag{4.18}$$

This expression can be rearranged and rewritten into spherical coordinates, remembering that $\hat{\mathbf{r}} = (\theta_r,\phi_r)$ and $\hat{\mathbf{q}} = (\theta_q,\phi_q)$ represent the angular part in spherical coordinates of $\hat{\mathbf{r}}$ and $\hat{\mathbf{q}}$ respectively: $G^0_{nr}(\mathbf{r},\mathbf{r}',E)=$

$$\frac{2m}{\hbar^2}\frac{2}{\pi}\sum_{L,L'} i^l(-i)^{l'}Y_L(\hat{\mathbf{r}})Y^*_{L'}(\hat{\mathbf{r}}')\int\frac{j_l(qr)j_{l'}(qr')}{k^2-q^2}Y^*_L(\hat{\mathbf{q}})Y_{L'}(\hat{\mathbf{q}})d\mathbf{q} \tag{4.19}$$

$$= \frac{2m}{\hbar^2}\frac{2}{\pi}\sum_{L,L'}\left[i^l(-i)^{l'}Y_L(\hat{\mathbf{r}})Y^*_{L'}(\hat{\mathbf{r}}')\left(\int_0^\pi d\theta\int_0^{2\pi}d\phi\sin\theta Y^*_L(\hat{\mathbf{q}})Y_{L'}(\hat{\mathbf{q}})\right)\right.$$
$$\left.\cdot\left(\int_0^\infty dq\frac{q^2 j_l(qr)j_{l'}(qr')}{k^2-q^2}\right)\right].$$

Inserting the orthonormality relation for spherical harmonics as stated in the digression on the preceding page and, furthermore, using $i^l(-i)^{l'}\delta_{L,L'} = i^l(-i)^l = 1$ for $L = L'$, one obtains

$$\begin{aligned} G^0_{nr}(\mathbf{r},\mathbf{r}',E) &= \frac{2m}{\hbar^2}\frac{2}{\pi}\sum_L\left[Y_L(\hat{\mathbf{r}})Y^*_L(\hat{\mathbf{r}}')\left(\int_0^\infty\frac{q^2 j_l(qr)j_l(qr')}{k^2-q^2}dq\right)\right] \\ &= \frac{2m}{\hbar^2}\frac{1}{\pi}\sum_L\left[Y_L(\hat{\mathbf{r}})Y^*_L(\hat{\mathbf{r}}')\left(\int_{-\infty}^\infty\frac{q^2 j_l(qr)j_l(qr')}{k^2-q^2}dq\right)\right]. \end{aligned} \tag{4.20}$$

The last step uses the fact, that the integrand is an even function. That can easily be verified by inserting into the definition of the spherical Bessel functions

$$j_l(-x) = x^l\left(\frac{1}{(-x)}\frac{d}{d(-x)}\right)^l\frac{\sin(-x)}{(-x)} = x^l\left(\frac{1}{x}\frac{d}{dx}\right)^l\frac{\sin(x)}{x} = (-1)^l j_l(x) \tag{4.21}$$

and noting that $(-1)^{2l} = 1$. We proceed making the following definition:

$$G^0_{nr,l}(r,r',E) := \frac{1}{\pi}\int_{-\infty}^\infty\frac{q^2 j_l(qr)j_l(qr')}{k^2-q^2}dq. \tag{4.22}$$

This integral has to be solved by contour integration in the complex plane, again using the residue theorem. However, because $j_l(qr)j_{l'}(qr')$ does not vanish along a semi circle in the upper half plane, the expression has to be rewritten into spherical Hankel functions and

different cases have to be taken care of. The necessary steps can be found in [61]. The result is given by

$$G^0_{nr,l}(r,r',E) = -ikj_l(kr_<)h_l(kr_>), \tag{4.23}$$

where $r_< := \min\{r,r'\}$ and $r_> := \max\{r,r'\}$. Furthermore defining

$$\begin{aligned} J_{kL}(\mathbf{r}) &:= j_l(kr)Y_L(\hat{\mathbf{r}}), & (4.24)\\ \overline{J}_{kL}(\mathbf{r}) &:= j_l(kr)Y^*_L(\hat{\mathbf{r}}), & (4.25)\\ H_{kL}(\mathbf{r}) &:= h_l(kr)Y_L(\hat{\mathbf{r}}) \text{ and} & (4.26)\\ \overline{H}_{kL}(\mathbf{r}) &:= h_l(kr)Y^*_L(\hat{\mathbf{r}}), & (4.27) \end{aligned}$$

the final result for the Green function is obtained:

$$\begin{aligned} G^0_{nr}(\mathbf{r},\mathbf{r}',E) &= \frac{2m}{\hbar^2}\sum_L Y_L(\hat{\mathbf{r}})Y^*_L(\hat{\mathbf{r}}')G^0_{nr,l}(r,r',E) \qquad (4.28)\\ &= -ik\frac{2m}{\hbar^2}\sum_L Y_L(\hat{\mathbf{r}})Y^*_L(\hat{\mathbf{r}}')j_l(kr_<)h_l(kr_>)\\ &= -ik\frac{2m}{\hbar^2}\sum_L \left(\Theta(r-r')H_{kL}(\mathbf{r})\overline{J}_{kL}(\mathbf{r}') + \Theta(r'-r)J_{kL}(\mathbf{r})\overline{H}_{kL}(\mathbf{r}')\right) \end{aligned}$$

This important result in short[16]:

The partial wave expansion of the non-relativistic free electron Green function is given by

$$G^0_{nr}(\mathbf{r},\mathbf{r}',E) = -ik\frac{2m}{\hbar^2}\sum_L \left(\Theta(r-r')H_{kL}(\mathbf{r})\overline{J}_{kL}(\mathbf{r}') + \Theta(r'-r)J_{kL}(\mathbf{r})\overline{H}_{kL}(\mathbf{r}')\right). \tag{4.29}$$

[16]Remark: when using real spherical harmonics instead of the ("normal") complex ones used here, the functions $J_{\mathbf{k}L}$ and $\overline{J}_{\mathbf{k}L}$ are identical, the same holds for $H_{\mathbf{k}L}$ and $\overline{H}_{\mathbf{k}L}$. Hence, in that case the equation can be written in a more compact form. However, in the relativistic case that is not possible any more. Therefore, the form above is instructive inasmuch as it has exactly the same structure as the relativistic free particle Green function will have.

5 Particle in a Potential: Lippmann-Schwinger Equation

The Lippmann-Schwinger Equation is a reformulation of the Schrödinger equation (or later the Dirac equation) into an integral equation, derived by exploiting Green function theory. The integral equation contains the free space Green function, calculated in the previous chapter. From the Lippmann-Schwinger equation the solutions for the wave functions become accessible.

5.1 Derivation

Up to now only the case of a free electron has been examined. The Lippmann-Schwinger equation connects this free electron case with the general case, i.e. with the solution of the Schrödinger equation (4.2) for a particle (electron) under the influence of a potential V. Basically, it is nothing more than a general equation from Green function theory applied to the Schrödinger equation, namely the equation (3.2) that we first used to define a Green function. In the physical notation of the Schrödinger equation setting this equation is rewritten as

$$\psi^{\text{partc}}(\mathbf{r}) = \mathrm{L}^{-1}V(\mathbf{r})\psi^{\text{partc}}(\mathbf{r}) = \int G^0_{nr}(\mathbf{r},\mathbf{r}';E)V(\mathbf{r}')\psi^{\text{partc}}(\mathbf{r}')d\mathbf{r}'. \tag{5.1}$$

However, a complication here arises from the fact that the source term $V\psi$ itself contains the function ψ that we are looking for. Therefore, even after having found the Green function, the problem in this case consists not only of solving an integral but an integral equation.

As the notation ψ^{partc} already suggests, this is the particular solution, i.e. one out of many possible solutions of the inhomogeneous equation. According to the theory of differential equations, the general solution ψ of the inhomogeneous equation is given by the sum of the particular solution ψ^{partc} with the set of all solutions of the homogeneous equation $\{\psi^0_k\}$:

$$\psi_{\mathbf{k}} = \psi^{\text{partc}} + \psi^0_{\mathbf{k}} \tag{5.2}$$

The latter, as already mentioned, are all the plane waves

$$\psi^0_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{kr}}. \tag{5.3}$$

fulfilling the energy relation $\hbar^2k^2/2m = E$. So we obtain the general solution:

The general solution of the Schrödinger equation for a particle (electron) under the influence of a potential, is given by the Lippmann-Schwinger equation:

$$\psi_{\mathbf{k}}(\mathbf{r}) = \psi^0_{\mathbf{k}}(\mathbf{r}) + \int G^0_{nr}(\mathbf{r},\mathbf{r}';E)V(\mathbf{r}')\psi_{\mathbf{k}}(\mathbf{r}')d\mathbf{r}', \tag{5.4}$$

where $\psi^0_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{kr}}$, $\hbar^2k^2/2m = E$ and G^0_{nr} is given by eq. (4.29).

5.2 Angular Momentum Expansion

The next aim is to derive an angular momentum expansion of the Lippmann-Schwinger equation. In equation (4.16) we already saw the partial wave expansion of a plane wave, which we want to apply on $\psi^0_{\mathbf{k}}$ here. We first define

$$\psi^0_{kL}(\mathbf{r}) := Y_L(\hat{\mathbf{r}}) j_l(kr) \tag{5.5}$$

to obtain

$$\begin{aligned} \psi^0_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{kr}} &= 4\pi \sum_L i^l Y^*_L(\hat{\mathbf{k}}) Y_L(\hat{\mathbf{r}}) j_l(kr) &(5.6)\\ &= 4\pi \sum_L i^l Y^*_L(\hat{\mathbf{k}}) \psi^0_{kL}(\mathbf{r}). &(5.7)\end{aligned}$$

We then expand the solution $\psi_{\mathbf{k}}$ in a analogue manner

$$\psi_{\mathbf{k}}(\mathbf{r}) = 4\pi \sum_L i^l Y^*_L(\hat{\mathbf{k}}) \psi_{kL}(\mathbf{r}) \tag{5.8}$$

but with unknown functions $\psi_{\mathbf{k}L}$. Inserting (5.6) and (5.8) into the Lippmann-Schwinger equation (5.4), multiplying by $Y_{L'}(\hat{\mathbf{k}})$, integrating over $\hat{\mathbf{k}}$ and using the orthonormality of the spherical harmonics $\int Y^*_L(\hat{\mathbf{k}}) Y_{L'}(\hat{\mathbf{k}}) d\hat{\mathbf{k}} = \delta_{LL'}$ we obtain the following equation:

$$\sum_L i^l \psi_{kL}(\mathbf{r}) \delta_{LL'} = \sum_L i^l \left[\psi^0_{kL}(\mathbf{r}) + \int G^0_{nr}(\mathbf{r}, \mathbf{r}'; E) V(\mathbf{r}') \psi_{kL}(\mathbf{r}') d\mathbf{r}' \right] \delta_{LL'} \tag{5.9}$$

which is equivalent to

$$\psi_{kL}(\mathbf{r}) = \psi^0_{kL}(\mathbf{r}) + \int G^0_{nr}(\mathbf{r}, \mathbf{r}'; E) V(\mathbf{r}') \psi_{kL}(\mathbf{r}') d\mathbf{r}'. \tag{5.10}$$

Thus we can summarise:

The angular momentum expansion of the wave function $\psi_{\mathbf{k}}$ for a particle (electron) in a potential V is given by

$$\psi_{\mathbf{k}}(\mathbf{r}) = 4\pi \sum_L i^l Y^*_L(\hat{\mathbf{k}}) \psi_{kL}(\mathbf{r}) \tag{5.11}$$

where Y_L are (complex) spherical harmonics and $\psi_{\mathbf{k}L}$ are determined by a Lippmann-Schwinger type equation

$$\psi_{kL}(\mathbf{r}) = \psi^0_{kL}(\mathbf{r}) + \int G^0_{nr}(\mathbf{r}, \mathbf{r}'; E) V(\mathbf{r}') \psi_{kL}(\mathbf{r}') d\mathbf{r}'. \tag{5.12}$$

For this Lippmann-Schwinger equation there are two types of solutions, the regular and the irregular ones. The regular solutions R_{kL} are the ones that are not singular for $\mathbf{r} = 0$, whereas the irregular ones S_{kL} diverge as r goes to zero. Furthermore, for both of those solution there is a right-hand side solution and a left hand-hand side solution. In the

Lippmann-Schwinger equation this difference is taken account for by choosing a different source term out of eqs. (4.24) to (4.27). The regular solutions are defined as follows:

The Lippmann-Schwinger equations for the regular wave functions R_{kL} (right-hand side solution) and $\overline{R}_{kL}$ (left-hand side solution) are given by

$$R_{kL}(\mathbf{r}) = J_{kL}(\mathbf{r}) + \int G^0_{nr}(\mathbf{r}, \mathbf{r}'; E) V(\mathbf{r}') R_{kL}(\mathbf{r}') d\mathbf{r}' \tag{5.13}$$

$$\overline{R}_{kL}(\mathbf{r}) = \overline{J}_{kL}(\mathbf{r}) + \int G^0_{nr}(\mathbf{r}, \mathbf{r}'; E) V(\mathbf{r}') \overline{R}_{kL}(\mathbf{r}') d\mathbf{r}'. \tag{5.14}$$

The free space solutions J_{kL} and $\overline{J}_{kL}$ are defined by eqs. (4.24) and (4.25).

The source term of a Bessel function is chosen because the Bessel functions are regular at the origin. For the irregular solutions it will be Hankel functions instead, see eqs. (5.73) and (5.74).

5.3 Coupled Radial Equations

The Lippmann-Schwinger equations can be rewritten into radial equations, i.e. equations where the angular part is separated and the equation contains a one-dimensional radial integral only instead of the three dimensional integration of the previous section. The price for this simplification is that the resulting equations have double indices and form a system of coupled[17] equations. The derivation here will be shown for the regular right-hand side solution, however, the results are analogous for the other solutions.

We start from eq. (5.13), expand R_{kL} and V in terms of spherical harmonics and use the angular momentum expansion of the Green function (4.28):

$$V(\mathbf{r}') = \sum_L V_L(r') Y_L(\hat{\mathbf{r}}') \tag{5.15}$$

$$R_{\mathbf{k}L}(\mathbf{r}) = \sum_{L'} R_{L'L}(r) Y_{L'}(\hat{\mathbf{r}}) \tag{5.16}$$

$$G^0_{nr}(\mathbf{r}, \mathbf{r}', E) = \frac{2m}{\hbar^2} \sum_L Y_L(\hat{\mathbf{r}}) Y^*_L(\hat{\mathbf{r}}') G^0_{nr,l}(r, r', E) \tag{5.17}$$

Inserting the expansions into eq. (5.13) yields:

$$\begin{aligned} \sum_{L'''} R_{L'''L}(r) Y_{L'''}(\hat{\mathbf{r}}) = j_l(kr) Y_L(\hat{\mathbf{r}}) \quad + \quad & \frac{2m}{\hbar^2} \int \left[\left(\sum_{L'''} Y_{L'''}(\hat{\mathbf{r}}) Y^*_{L'''}(\hat{\mathbf{r}}') G^0_{nr,l'''}(r, r', E) \right) \right. \\ & \cdot \left(\sum_{L''''} V_{L''''}(r') Y_{L''''}(\hat{\mathbf{r}}') \right) \\ & \left. \cdot \left(\sum_{L''} R_{L''L}(r') Y_{L''}(\hat{\mathbf{r}}') \right) \right] d\mathbf{r}'. \end{aligned} \tag{5.18}$$

[17] In the case of a spherical potential they decouple, as shown for the relativistic case in section 10.8.

The next step is a multiplication by $Y^*_{L'}(\hat{\mathbf{r}})$, then integrating over $\hat{\mathbf{r}}$ and using the orthonormality, i.e. $\int Y^*_{L'}(\hat{\mathbf{r}})Y_L(\hat{\mathbf{r}})d\hat{\mathbf{r}} = \delta_{LL'}$:

$$\begin{aligned}\sum_{L'''} R_{L'''L}(r)\delta_{L'L'''} = j_l(kr)\delta_{LL'} \quad + \quad & \frac{2m}{\hbar^2}\int\Bigg[\left(\sum_{L'''}\delta_{L'L'''}Y^*_{L'''}(\hat{\mathbf{r}}')G^0_{nr,l'''}(r,r',E)\right)\\ & \cdot\left(\sum_{L''''}V_{L''''}(r')Y_{L''''}(\hat{\mathbf{r}}')\right)\\ & \cdot\left(\sum_{L''}R_{L''L}(r')Y_{L''}(\hat{\mathbf{r}}')\right)\Bigg]d\mathbf{r}'.\end{aligned} \tag{5.19}$$

Computing the sums over Kronecker δ yields:

$$\begin{aligned}R_{L'L}(r) = j_l(kr)\delta_{LL'} \quad + \quad & \frac{2m}{\hbar^2}\int\Bigg[\left(Y^*_{L'}(\hat{\mathbf{r}}')G^0_{nr,l'}(r,r',E)\right)\\ & \cdot\left(\sum_{L''''}V_{L''''}(r')Y_{L''''}(\hat{\mathbf{r}}')\right)\\ & \cdot\left(\sum_{L''}R_{L''L}(r')Y_{L''}(\hat{\mathbf{r}}')\right)\Bigg]d\mathbf{r}'.\end{aligned} \tag{5.20}$$

Using the relationship $d\mathbf{r} := r^2\sin(\theta)d\phi d\theta dr = r^2 dr d\hat{\mathbf{r}}$ the integral is rewritten into spherical coordinates:

$$\begin{aligned}R_{L'L}(r) = j_l(kr)\delta_{LL'} \quad + \quad & \frac{2m}{\hbar^2}\int_0^S dr' r'^2 G^0_{nr,l'}(r,r',E)\\ & \cdot\int d\hat{\mathbf{r}}' Y^*_{L'}(\hat{\mathbf{r}}')\left(\sum_{L''''}V_{L''''}(r')Y_{L''''}(\hat{\mathbf{r}}')\right)\\ & \cdot\left(\sum_{L''}R_{L''L}(r')Y_{L''}(\hat{\mathbf{r}}')\right),\end{aligned} \tag{5.21}$$

where S denotes the radius of a sphere outside of which the potential vanishes. This can be rewritten as

$$\begin{aligned}R_{L'L}(r) \quad = \quad & j_l(kr)\delta_{LL'} + \frac{2m}{\hbar^2}\int_0^S dr' r'^2 G^0_{nr,l'}(r,r',E)\\ & \cdot\sum_{L''L''''}\underbrace{\int d\hat{\mathbf{r}}'\left(Y^*_{L'}(\hat{\mathbf{r}}')Y_{L''''}(\hat{\mathbf{r}}')Y_{L''}(\hat{\mathbf{r}}')\right)}_{=:C^{L'}_{L''L''''}}\left(V_{L''''}(r')R_{L''L}(r')\right)\end{aligned} \tag{5.22}$$

and by defining

$$V_{L'L''}(r') = \sum_{L''''} C^{L'}_{L''L''''}V_{L''''}(r') \tag{5.23}$$

we can further simplify to obtain

$$R_{L'L}(r) \quad = \quad j_l(kr)\delta_{LL'} + \frac{2m}{\hbar^2}\int_0^S dr' r'^2 G^0_{nr,l'}(r,r',E)\sum_{L''}V_{L'L''}(r')R_{L''L}(r'). \tag{5.24}$$

The result and the necessary definitions summarised:

The regular solution of the angular momentum Lippmann-Schwinger type equation is given by

$$R_{\mathbf{k}L}(r) = \sum_{L'} R_{L'L}(r) Y_{L'}(\hat{\mathbf{r}}) \tag{5.25}$$

where

$$R_{L'L}(r) = j_l(kr)\delta_{LL'} + \frac{2m}{\hbar^2}\int_0^S dr' r'^2 G^0_{nr,l'}(r,r',E) \sum_{L''} V_{L'L''}(r') R_{L''L}(r'), \tag{5.26}$$

$$V_{L'L''}(r') = \sum_{L'''} C^{L'}_{L''L'''} V_{L'''}(r') \text{ and} \tag{5.27}$$

$$C^{L'}_{L''L'''} = \int d\hat{\mathbf{r}}' Y^*_{L'}(\hat{\mathbf{r}}') Y_{L'''}(\hat{\mathbf{r}}') Y_{L''}(\hat{\mathbf{r}}'). \tag{5.28}$$

The coefficients $C^{L'}_{L''L'''}$ are called *Gaunt coefficients*.

5.4 t Matrix

The t matrix[18] describes the transition between the incoming plane waves and the scattered waves. Therefore is interesting for to its physical meaning, but it will also be helpful later on to simplify the notation. A derivation of the expression for a full potential has been shown by Zeller [26].

Starting point is the angular momentum Lippmann-Schwinger equation for R_{kL} (5.13):

$$R_{kL}(\mathbf{r}) = j_l(kr)Y_L(\hat{\mathbf{r}}) + \int G^0_{nr}(\mathbf{r},\mathbf{r}';E) V(\mathbf{r}') R_{kL}(\mathbf{r}') d\mathbf{r}'. \tag{5.29}$$

Into this equation we insert the angular momentum expansion of the Green function (4.28)

$$G^0_{nr}(\mathbf{r},\mathbf{r}',E) = \frac{2m}{\hbar^2} \sum_{L'} Y_{L'}(\hat{\mathbf{r}}) Y^*_{L'}(\hat{\mathbf{r}}') G^0_{nr,l'}(r,r',E), \tag{5.30}$$

obtaining

$$R_{kL}(\mathbf{r}) = j_{l'}(kr)Y_{L'}(\hat{\mathbf{r}}) + \frac{2m}{\hbar^2}\int \left(\sum_{L'} Y_{L'}(\hat{\mathbf{r}}) Y^*_{L'}(\hat{\mathbf{r}}') G^0_{nr,l'}(r,r',E) \right) V(\mathbf{r}') R_{kL}(\mathbf{r}') d\mathbf{r}'. \tag{5.31}$$

Using expression (4.23) for the coefficients

$$G^0_{nr,l'}(r,r',E) = -ikj_{l'}(kr_<)h_{l'}(kr_>) \tag{5.32}$$

[18] The t matrix is closely related to the S matrix (where the S stands for scattering), first introduced by Wheeler [62].

for the case $r > r' > S \Longleftrightarrow r_< = r'$, $r_> = r$, this equation can be rewritten as

$$\begin{aligned} R_{kL}(\mathbf{r}) &= j_{l'}(kr)Y_{L'}(\hat{\mathbf{r}}) - ik\frac{2m}{\hbar^2}\sum_{L'}\left(\int Y^*_{L'}(\hat{\mathbf{r}}')j_{l'}(kr')V(\mathbf{r}')R_{kL}(\mathbf{r}')d\mathbf{r}'\right)Y_{L'}(\hat{\mathbf{r}})h_{l'}(kr) \\ &= j_{l'}(kr)Y_{L'}(\hat{\mathbf{r}}) - ik\frac{2m}{\hbar^2}\sum_{L'}t_{L'L}Y_{L'}(\hat{\mathbf{r}})h_{l'}(kr) \\ &= J_{kL'}(\mathbf{r}) - ik\frac{2m}{\hbar^2}\sum_{L'}t_{L'L}H_{kL'}(\mathbf{r}) \end{aligned} \tag{5.33}$$

where we defined

$$\begin{aligned} t_{LL'}: &= \int Y^*_L(\hat{\mathbf{r}}')j_l(kr')V(\mathbf{r}')R_{kL'}(\mathbf{r}')d\mathbf{r}'. \\ &= \int \overline{J}_{kL}(\mathbf{r}')V(\mathbf{r}')R_{kL}(\mathbf{r}')d\mathbf{r}'. \end{aligned} \tag{5.34}$$

The integration volume is the whole unity cell under consideration. Alternatively the t matrix can be written in such a manner that it only contains a radial integral. To derive this expression we compare the t matrix with equation (5.20), observing that the expression for the t matrix "almost" turns up in this equation – the only difference is that there is the function $G^0_{nr,l}$ instead of j_l. By following exactly the same steps as from eq. (5.20) up to eq. (5.24), that means by making an expansion in spherical harmonics and using the Gaunt coefficients, we can derive the alternative expression for the t matrix:

$$t_{LL'} = \int_0^S dr' r'^2 j_{l'}(kr')\sum_{L''}V_{L'L''}(r')R_{L''L}(r'). \tag{5.35}$$

A physical interpretation of the t matrix can be made looking at eq. (5.33): Incoming waves are represented in a basis of Bessel functions j_l (as their radial parts), with a dependence on the angular momentum quantum number l. These functions are regular at the origin, which is the centre of the scattering potential V. Outgoing waves are written in a basis of Hankel functions (that are irregular in the origin). The vector of Hankel functions is multiplied by the t matrix, in this way the matrix determines how incoming waves are scattered at the potential V. In case of a spherical potential the t matrix is diagonal, i.e. it has non-zero entries only for $L = L'$. This means that incoming waves with angular momentum quantum numbers l, m are only scattered to waves of the same angular momentum l, m and there is no mixing of the angular momentum channels as it is the case for potentials of arbitrary shape.

5.5 Radial Equations in PDE Formulation

Instead of using integral equations of Lippmann-Schwinger type it is also possible to find a system of differential equations for the radial solutions of the Schrödinger equation. This technique is not used within this work and will not be studied beyond this section, however, to give an idea of alternative solution techniques that are used to solve the radial equations, it should be mentioned here. As for the case of integral equations, the expansion parts $\psi_{\mathbf{k}L}$

and $V_{LL'}$ for different values of the angular momentum $\mathbf{L}$ are coupled, only in the case of a spherical potential the equations can be solved independently.

First we rewrite the Schrödinger equation into spherical coordinates. This can be done by using the Laplace operator in spherical coordinates (see eq. [63]) and the angular momentum operator $\hat{\mathbf{L}} = -i\hbar\mathbf{r} \times \nabla$, yielding:

$$\begin{aligned} & \left(-\frac{\hbar^2}{2m}\Delta + V(\mathbf{r})\right)\psi_{\mathbf{k}}(\mathbf{r}) = E\psi_{\mathbf{k}}(\mathbf{r}) \\ \Longleftrightarrow \quad & \left[-\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{\hbar^2 r^2}\hat{\mathbf{L}}^2 + \frac{2m}{\hbar^2}V(\mathbf{r}) - k^2\right]\psi_{\mathbf{k}}(\mathbf{r}) = 0. \end{aligned} \tag{5.36}$$

As before $\hbar^2k^2/2m = E$. The spherical harmonics are the eigenfunctions of $\hat{\mathbf{L}}^2$ (see e.g. [64] or another book on quantum mechanics):

$$\hat{\mathbf{L}}^2 Y_L(\hat{\mathbf{r}}) = \hbar^2 l(l+1) Y_L(\hat{\mathbf{r}}). \tag{5.37}$$

Since the first part of the operator in the Schrödinger equation depends only on r and the angular momentum operator $\hat{\mathbf{L}}$ depends only on the angular part $\hat{\mathbf{r}} = (\theta, \phi)$, the strategy to solve the equation is by separating the variables in the wave function. This is done by using the expansion (5.16) in terms of spherical harmonics. The potential is expanded in an analogous way as in (5.15):

$$V(\mathbf{r}) = \sum_{L'''} V_{L'''}(r) Y_{L'''}(\hat{\mathbf{r}}) \tag{5.38}$$

$$\psi_{\mathbf{k}L'}(r) = \sum_{L''} \psi_{\mathbf{k}L''L'}(r) Y_{L''}(\hat{\mathbf{r}}). \tag{5.39}$$

We insert this into the Schrödinger equation, obtaining

$$\begin{aligned} & \left[\left(-\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{2m}{\hbar^2}\left(\sum_{L'''} V_{L'''}(r) Y_{L'''}(\hat{\mathbf{r}})\right) - k^2\right) + \frac{1}{\hbar^2 r^2}\hat{\mathbf{L}}^2\right] \\ & \cdot \left[\sum_{L''} \psi_{\mathbf{k}L''L'}(r) Y_{L''}(\hat{\mathbf{r}})\right] = 0 \end{aligned} \tag{5.40}$$

This can be rearranged to

$$\begin{aligned} & \sum_{L''}\left(-\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{\hbar^2 r^2}\hat{\mathbf{L}}^2 - k^2\right)\psi_{\mathbf{k}L''L'}(r) Y_{L''}(\hat{\mathbf{r}}) \\ & + \frac{2m}{\hbar^2}\sum_{L''}\sum_{L'''} V_{L'''}(r) Y_{L'''}(\hat{\mathbf{r}})\psi_{\mathbf{k}L''L'}(r) Y_{L''}(\hat{\mathbf{r}}) = 0. \end{aligned} \tag{5.41}$$

Now we use the eigenvalue equation (5.37), multiply the whole equation by $Y_L^*(\hat{\mathbf{r}})$ and integrate over $\hat{\mathbf{r}}$. Using the orthonormality of the spherical harmonics, this gives us

$$\begin{aligned} & \sum_{L''}\left[\left(-\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{l(l+1)}{r^2} - k^2\right)\psi_{\mathbf{k}L''L'}(r)\delta_{LL''}\right] \\ & + \frac{2m}{\hbar^2}\sum_{L''}\sum_{L'''}\underbrace{\left(\int d\hat{\mathbf{r}} Y_L^*(\hat{\mathbf{r}}) Y_{L''}(\hat{\mathbf{r}}) Y_{L'''}(\hat{\mathbf{r}})\right)}_{=C^L_{L''L'''}} V_{L'''}(r)\psi_{\mathbf{k}L''L'}(r) = 0, \end{aligned} \tag{5.42}$$

where the coefficients $C^L_{L''L'''}$ are the Gaunt coefficients already defined in eq. (5.22). By using the definition of $V_{L''L}$ as in eq. (5.23) the equation can further be simplified:

$$\left(-\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{l(l+1)}{r^2}-k^2\right)\psi_{\mathbf{k}LL'}(r) + \frac{2m}{\hbar^2}\sum_{L''}\underbrace{\sum_{L'''}C^L_{L''L'''}V_{L'''}(r)}_{=V_{L''L}}\psi_{\mathbf{k}L''L'}(r)=0 \tag{5.43}$$

Finally, we obtain the coupled equations for the radial part of the wave function:

$$\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)-\frac{l(l+1)}{r^2}+k^2\right)\psi_{\mathbf{k}LL'}(r)=\frac{2m}{\hbar^2}\sum_{L''}V_{L''L}\psi_{\mathbf{k}L''L'}(r). \tag{5.44}$$

5.6 Operator Notation and Integral Equations for the Green Function

The Green function formalism and the Lippmann-Schwinger equation can also be expressed using an operator notation. It shortens the notation for calculating an integral equation for the Green function.

The free particle Green function was defined by eq. (4.1) and the following ones:

$$(E+\Delta)\,\psi(\mathbf{r}) = 0 \tag{5.45}$$
$$(E+\Delta)\,G^0_{nr}(\mathbf{r},\mathbf{r}',E) = \delta(\mathbf{r}-\mathbf{r}'). \tag{5.46}$$

For the particle in a potential V the corresponding Green function is analogously defined by

$$(E+\Delta-V)\,G_{nr}(\mathbf{r},\mathbf{r}',E)=\delta(\mathbf{r}-\mathbf{r}'). \tag{5.47}$$

Now this equation can be expressed as an operator equation by defining the operators $\hat{G}^0_{nr}$, $\hat{H}^0_{nr}$ and $\hat{H}_{nr}$ acting on a twice differentiable function f as:

$$\hat{G}^0_{nr}f := \int d\mathbf{r}'G_{nr}(\mathbf{r},\mathbf{r}',E)f(\mathbf{r}') \tag{5.48}$$
$$\hat{H}^0_{nr}f := -\Delta f(\mathbf{r}) \tag{5.49}$$
$$\hat{H}_{nr}f := (-\Delta+V(\mathbf{r}))\,f(\mathbf{r}). \tag{5.50}$$

Using these definitions and integrating equation (5.46) over $\mathbf{r}'$, it can be rewritten into

$$\int d\mathbf{r}'\,(E+\Delta)\,G^0_{nr}(\mathbf{r},\mathbf{r}',E) = \int d\mathbf{r}'\delta(\mathbf{r}-\mathbf{r}')$$
$$\iff \left(E-\hat{H}^0_{nr}\right)\hat{G}^0_{nr} = \mathbf{1}. \tag{5.51}$$

From this relation one can formally conclude

$$\hat{G}^0_{nr} = \left(E - \hat{H}^0_{nr}\right)^{-1}. \tag{5.52}$$

An analogous procedure for eq. (5.47) yields

$$\left(E - \hat{H}_{nr}\right)\hat{G}_{nr} = \mathbf{1}, \tag{5.53}$$

$$\hat{G}_{nr} = \left(E - \hat{H}_{nr}\right)^{-1} = \left(E - \hat{H}^0_{nr} - V\right)^{-1}. \tag{5.54}$$

Multiplying eq. (5.54) from the left by $\left(E - \hat{H}^0_{nr} - V\right)$ yields an operator representation of the Lippmann-Schwinger equation for the Green function:

$$\begin{aligned} & \left(E - \hat{H}^0_{nr} - V\right)\hat{G}_{nr} = \mathbf{1} \\ \Longleftrightarrow \quad & \underbrace{\left(E - \hat{H}^0_{nr}\right)}_{=\left(\hat{G}^0_{nr}\right)^{-1}}\hat{G}_{nr} = \mathbf{1} + V\hat{G}_{nr} \\ \Longleftrightarrow \quad & \hat{G}_{nr} = \hat{G}^0_{nr} + \hat{G}^0_{nr}V\hat{G}_{nr}. \end{aligned} \tag{5.55}$$

By using the definition of the operators the equation can be rewritten into a real space integral equation:

$$\begin{aligned} & \int d\mathbf{r}' G_{nr}(\mathbf{r}, \mathbf{r}', E) f(\mathbf{r}') \\ & = \int d\mathbf{r}' G^0_{nr}(\mathbf{r}, \mathbf{r}', E) f(\mathbf{r}') + \int d\mathbf{r}'' G^0_{nr}(\mathbf{r}, \mathbf{r}'', E) V(\mathbf{r}'') \int d\mathbf{r}' G_{nr}(\mathbf{r}'', \mathbf{r}', E) f(\mathbf{r}'), \end{aligned} \tag{5.56}$$

valid for any twice differentiable function f. Formally one obtains the integral equation for the Green function:

$$G_{nr}(\mathbf{r}, \mathbf{r}', E) = G^0_{nr}(\mathbf{r}, \mathbf{r}', E) + \int d\mathbf{r}'' G^0_{nr}(\mathbf{r}, \mathbf{r}'', E) V(\mathbf{r}'') G_{nr}(\mathbf{r}'', \mathbf{r}', E) \tag{5.57}$$

Multiplying eq. (5.54) from the right by the same factor as in eq. (5.55) gives:

$$\hat{G}_{nr} = \hat{G}^0_{nr} + \hat{G}_{nr} V \hat{G}^0_{nr}, \tag{5.58}$$

which, in real space, yields the integral equation

$$G_{nr}(\mathbf{r}, \mathbf{r}', E) = G^0_{nr}(\mathbf{r}, \mathbf{r}', E) + \int d\mathbf{r}'' G_{nr}(\mathbf{r}, \mathbf{r}'', E) V(\mathbf{r}'') G^0_{nr}(\mathbf{r}'', \mathbf{r}', E). \tag{5.59}$$

5.7 Fredholm and Volterra Integral Equations

During the derivation of the Green function for the particle in a potential, it will be useful to rewrite between two different types of integral equations, the *Fredholm* and the *Volterra integral equation*.

A *Fredholm integral equation* has the form[19]

$$y(\mathbf{r}) = f(\mathbf{r}) + \int d\mathbf{r}' G^0(\mathbf{r}, \mathbf{r}') V(\mathbf{r}') y(\mathbf{r}'). \tag{5.60}$$

For $f \neq 0$ it is called *inhomogeneous* or *of second kind*. The integration domain in this case is finite and does not depend on $\mathbf{r}$. G^0 is called the kernel of the integral, y is an unknown function and f, $G^0$and V are given.

One can directly see that the Lippmann-Schwinger equation is of this form, and therefore is a Fredholm integral equation.

The strategy for solving a Fredholm equation is by finding a resolvent kernel G, such that the unknown function y can be written as

$$y(\mathbf{r}) = f(\mathbf{r}) + \int d\mathbf{r}' G(\mathbf{r}, \mathbf{r}') V(\mathbf{r}') f(\mathbf{r}'). \tag{5.61}$$

The relationship between G and G^0 can be found using the operator notation exactly as it has been done in the previous section 5.6. Simply renaming the functions in the Lippmann-Schwinger equation (5.4) and in the resulting equations (5.57) and (5.59) we get the equations

$$G(\mathbf{r}, \mathbf{r}') = G^0(\mathbf{r}, \mathbf{r}') + \int d\mathbf{r}'' G^0(\mathbf{r}, \mathbf{r}'') V(\mathbf{r}'') G(\mathbf{r}'', \mathbf{r}'), \tag{5.62}$$

$$G(\mathbf{r}, \mathbf{r}') = G^0(\mathbf{r}, \mathbf{r}') + \int d\mathbf{r}'' G(\mathbf{r}, \mathbf{r}'') V(\mathbf{r}'') G^0(\mathbf{r}'', \mathbf{r}'). \tag{5.63}$$

A *Volterra integral equation* is of the same form as a Fredholm equation, with the only difference that the integral domain depends on $\mathbf{r}$. In this three-dimensional setting this can be written as

$$y(\mathbf{r}) = f(\mathbf{r}) + \int d\mathbf{r}' K^0(\mathbf{r}, \mathbf{r}') V(\mathbf{r}') f(\mathbf{r}') \tag{5.64}$$

where

$$K^0(\mathbf{r}, \mathbf{r}') = \Theta(r - r') \tilde{K}^0(\mathbf{r}, \mathbf{r}'). \tag{5.65}$$

That means the integration domain is limited to a sphere of radius $|\mathbf{r}|$. The equations for finding the integral kernel still hold, i.e. a solution of the Volterra equation is given by

$$y(\mathbf{r}) = f(\mathbf{r}) + \int d\mathbf{r}' K(\mathbf{r}, \mathbf{r}') V(\mathbf{r}') f(\mathbf{r}') \tag{5.66}$$

where

$$K(\mathbf{r}, \mathbf{r}') = K^0(\mathbf{r}, \mathbf{r}') + \int d\mathbf{r}'' K^0(\mathbf{r}, \mathbf{r}'') V(\mathbf{r}'') K(\mathbf{r}'', \mathbf{r}'). \tag{5.67}$$

[19] In the general form in Mathematics the term $V(\mathbf{r}')$ is not included. It can, however, simply be included by redefining G^0. In the form presented here the analogy to the Lippmann-Schwinger equation is directly obvious, which is why $V(\mathbf{r}')$ has been included.

For the calculation of the Green function it will be of advantage to rewrite the Lippmann-Schwinger equation from a Fredholm to a Volterra equation. How to do this will be explained in sections 10.3 and 10.9.

5.8 α and β Matrices and the Irregular Solution

The α matrix describes the behaviour at the origin of the regular angular single-site solutions with potential, $R_{kL}(\mathbf{r})$, and without potential, $J_{kL}(\mathbf{r})$.

The relationship between the two was given by equation (5.13):

$$R_{kL}(\mathbf{r}) = J_{kL}(\mathbf{r}) + \int d\mathbf{r}' G^0_{nr}(\mathbf{r},\mathbf{r}';E) V(\mathbf{r}') R_{kL}(\mathbf{r}'). \tag{5.68}$$

Inserting the partial wave expansion of the free space Green function, eq. (4.29), one gets

$$\begin{aligned} R_{kL}(\mathbf{r}) &= J_{kL}(\mathbf{r}) - ik\frac{2m}{\hbar^2}\sum_{L'}\Bigg(\int d\mathbf{r}'\Theta(r-r')H_{kL'}(\mathbf{r})\overline{J}_{kL'}(\mathbf{r}') \\ &\qquad +\Theta(r'-r)J_{kL'}(\mathbf{r})\overline{H}_{kL'}(\mathbf{r}')\Bigg)V(\mathbf{r}')R_{kL}(\mathbf{r}') \\ &= J_{kL}(\mathbf{r}) - ik\frac{2m}{\hbar^2}\Bigg(\sum_{L'}\int_{|\mathbf{r}'|\le|\mathbf{r}|} d\mathbf{r}' H_{kL'}(\mathbf{r})\overline{J}_{kL'}(\mathbf{r}')V(\mathbf{r}')R_{kL}(\mathbf{r}') \\ &\qquad +\int_{|\mathbf{r}'|>|\mathbf{r}|} d\mathbf{r}' J_{kL'}(\mathbf{r})\overline{H}_{kL'}(\mathbf{r}')V(\mathbf{r}')R_{kL}(\mathbf{r}')\Bigg). \end{aligned} \tag{5.69}$$

In the limit $|\mathbf{r}| \to 0$ the first integral vanishes, yielding

$$\begin{aligned} R_{kL}(\mathbf{r}) &= J_{kL}(\mathbf{r}) - ik\frac{2m}{\hbar^2}\sum_{L'} J_{kL'}(\mathbf{r})\int_{|\mathbf{r}'|>|\mathbf{r}|} d\mathbf{r}'\overline{H}_{kL'}(\mathbf{r}')V(\mathbf{r}')R_{kL}(\mathbf{r}') \\ &= \sum_{L'} J_{kL'}(\mathbf{r})\underbrace{\left(\delta_{LL'} - ik\frac{2m}{\hbar^2}\int_{|\mathbf{r}'|>|\mathbf{r}|} d\mathbf{r}'\overline{H}_{kL'}(\mathbf{r}')V(\mathbf{r}')R_{kL}(\mathbf{r}')\right)}_{=:\alpha_{LL'}}, \text{ as } |\mathbf{r}| \to 0. \end{aligned} \tag{5.70}$$

Hence[20]

$$R_{kL}(\mathbf{r}) = \sum_{L'}\alpha_{LL'}J_{kL'}(\mathbf{r}), \text{ as } |\mathbf{r}| \to 0, \tag{5.71}$$

where the α matrix was defined by

$$\alpha_{LL'} := \delta_{LL'} - ik\frac{2m}{\hbar^2}\int d\mathbf{r}\overline{H}_{kL'}(\mathbf{r})V(\mathbf{r})R_{kL}(\mathbf{r}). \tag{5.72}$$

As it has been seen in the expansion eq. (4.15), the non-relativistic free electron Green function can be written in terms of the regular and irregular solutions of the free Schrödinger

[20] Note that both α and β matrix have a dependence on k that is not indicated here explicitly.

equation. The goal later on will be finding a similar expansion for the Green function of an electron in a potential, i.e. in terms of regular and irregular solutions of the Dirac equation of an electron in a potential. This equation should, however, result in the equation for the free electron Green function when choosing $V = 0$. From eq. (5.68) one can see that $R_{kL} = J_{kL}$ for $V = 0$. Similarly, the irregular solution, denoted by S_{kL}, should be equal to the irregular solution of the free electron case, the Hankel function H_{kL}. Hence, the source term of the corresponding Lippmann-Schwinger equation is no longer a Bessel but now a Hankel function:

The irregular solutions $S_{kL}(\mathbf{r})$ of a particle in a potential are given by the Lippmann-Schwinger equations

$$S_{kL}(\mathbf{r}) = \sum_{L'} \beta_{LL'} H_{kL'}(\mathbf{r}) + \int d\mathbf{r}' G^0_{nr}(\mathbf{r}, \mathbf{r}', E) V(\mathbf{r}') S_{kL}(\mathbf{r}'), \tag{5.73}$$

$$\overline{S}_{kL}(\mathbf{r}) = \sum_{L'} \beta_{LL'} \overline{H}_{kL'}(\mathbf{r}) + \int d\mathbf{r}' G^0_{nr}(\mathbf{r}, \mathbf{r}', E) V(\mathbf{r}') \overline{S}_{kL}(\mathbf{r}'). \tag{5.74}$$

The source terms are defined in eqs. (4.26) and (4.27). Furthermore the β matrix is used, which is defined by its entries

$$\beta_{LL'} := \delta_{LL'} + ik \frac{2m}{\hbar^2} \int d\mathbf{r} \overline{S}_{kL'}(\mathbf{r}) V(\mathbf{r}) J_{kL}(\mathbf{r}). \tag{5.75}$$

In addition to the source term now being a Hankel function, there occurs, unexpectedly, also the multiplication by the β matrix. First note that for the case of a vanishing potential this matrix becomes the identity matrix, i.e. for $V = 0$ it is $S_{\mathbf{k}L} = H_{\mathbf{k}L}$ as it was required. As a source term any linear combination of Hankel functions can be used. Why the β matrix is introduced here and why this specific source term is chosen cannot be understood yet but only when deriving the expansion of the Green function in sections 5.9 and 10.3. There it will be seen that with this choice for the irregular solution the Green function for the particle in a potential can be written in a nice and simple form.

The equation for the irregular solution is a Fredholm integral equation. Thus, according to section 5.7, the solution is given by

$$S_{kL}(\mathbf{r}) = \sum_{L'} \beta_{LL'} \left[H_{kL'}(\mathbf{r}) + \int d\mathbf{r} G_{nr}(\mathbf{r}, \mathbf{r}', E) V(\mathbf{r}') H_{kL}(\mathbf{r}') \right]. \tag{5.76}$$

$$\overline{S}_{kL}(\mathbf{r}) = \sum_{L'} \beta_{LL'} \left[\overline{H}_{kL'}(\mathbf{r}) + \int d\mathbf{r} \overline{H}_{kL}(\mathbf{r}') V(\mathbf{r}') G_{nr}(\mathbf{r}', \mathbf{r}, E) \right]. \tag{5.77}$$

In a matrix notation the two matrices are given by

$$\alpha = (\alpha_{LL'})_{LL'}, \tag{5.78}$$

$$\beta = (\beta_{LL'})_{LL'} \in \mathbb{C}^{(n+1)^2 \times (n+1)^2}. \tag{5.79}$$

If l runs from 0 to n and $m \in \{-l, -(l-1), \ldots, l\}$ the combined index $L = (l, m)$ can take $(n+1)^2$ values, hence this is the dimension of the matrix. One can also define the vectors $\overline{S}$, $\overline{H}$ and $A \in \mathbb{C}^{(n+1)^2}$ by

$$\overline{S}(\mathbf{r}) = \left(\overline{S}_{kL}(\mathbf{r})\right)_L, \tag{5.80}$$

$$\overline{H}(\mathbf{r}) = \left(\overline{H}_{kL}(\mathbf{r})\right)_L, \tag{5.81}$$

$$A(\mathbf{r}) = \left(\int d\mathbf{r}' \overline{H}_{\mathbf{k}L}(\mathbf{r}') V(\mathbf{r}') G_{nr}(\mathbf{r}', \mathbf{r}, E)\right)_L, \tag{5.82}$$

i.e. they are column vectors containing the entries for different values of L. Using these definitions, equation (5.76) can then be written in a the compact form

$$\overline{S}(\mathbf{r}) = \beta \left[\overline{H}(\mathbf{r}) + A(\mathbf{r})\right]. \tag{5.83}$$

Even though it is not obvious to see, the α and β matrices are the inverse of each other:

The matrices α and β fulfil the relation

$$\alpha = \beta^{-1}. \tag{5.84}$$

Proof: Recall the Lippmann-Schwinger equation for the regular solution eq. (5.13):

$$R_{kL}(\mathbf{r}) = J_{kL}(\mathbf{r}) + \int d\mathbf{r}' G^0_{nr}(\mathbf{r}, \mathbf{r}'; E) V(\mathbf{r}') R_{kL}(\mathbf{r}') \tag{5.85}$$

According to section 5.7 its solution is

$$R_{kL}(\mathbf{r}) = J_{kL}(\mathbf{r}) + \int d\mathbf{r}' G_{nr}(\mathbf{r}, \mathbf{r}'; E) V(\mathbf{r}') J_{kL}(\mathbf{r}'). \tag{5.86}$$

Now insert this into the definition of the α matrix, eq. (5.72), to obtain

$$\begin{aligned} \alpha_{L'L} &= \delta_{LL'} - ik\frac{2m}{\hbar^2} \int d\mathbf{r} \overline{H}_{kL'}(\mathbf{r}) V(\mathbf{r}) \\ &\qquad \cdot \left(J_{kL}(\mathbf{r}) + \int d\mathbf{r}' G_{nr}(\mathbf{r}, \mathbf{r}'; E) V(\mathbf{r}') J_{kL}(\mathbf{r}')\right) \\ &= \delta_{LL'} - ik\frac{2m}{\hbar^2} \int d\mathbf{r} \overline{H}_{kL'}(\mathbf{r}) V(\mathbf{r}) J_{kL}(\mathbf{r}) \\ &\quad -ik\frac{2m}{\hbar^2} \int d\mathbf{r}' \left[\int d\mathbf{r} \overline{H}_{kL'}(\mathbf{r}) G_{nr}(\mathbf{r}, \mathbf{r}'; E) V(\mathbf{r})\right] V(\mathbf{r}') J_{kL}(\mathbf{r}'). \end{aligned} \tag{5.87}$$

Equation (5.83) can be rearranged as

$$A(\mathbf{r}) = \beta^{-1} \overline{S}(\mathbf{r}) - \overline{H}(\mathbf{r}) \tag{5.88}$$

which, in explicit notation, is equivalent to

$$\int d\mathbf{r}' \overline{H}_{kL}(\mathbf{r}') G_{nr}(\mathbf{r}, \mathbf{r}', E) V(\mathbf{r}') = \sum_{L'} \left(\beta^{-1}\right)_{LL'} \overline{S}_{kL'}(\mathbf{r}) - \overline{H}_{kL}(\mathbf{r}). \tag{5.89}$$

This is exactly the term in square brackets in the equation above. Replacing it yields

$$\begin{aligned}\alpha_{LL'} &= \delta_{LL'} - ik\frac{2m}{\hbar^2}\int d\mathbf{r}\overline{H}_{kL'}(\mathbf{r})V(\mathbf{r})J_{kL}(\mathbf{r}) \\ &\quad -ik\frac{2m}{\hbar^2}\int d\mathbf{r}'\left[\sum_{L''}\left(\beta^{-1}\right)_{LL''}\overline{S}_{kL''}(\mathbf{r}') - \overline{H}_{kL'}(\mathbf{r}')\right]V(\mathbf{r}')J_{kL}(\mathbf{r}') \\ &= \delta_{LL'} - \sum_{L'}\left(\beta^{-1}\right)_{LL'}\underbrace{ik\frac{2m}{\hbar^2}\int d\mathbf{r}'\overline{S}_{kL'}(\mathbf{r}')V(\mathbf{r}')J_{kL}(\mathbf{r}')}_{=\beta_{LL'}-\delta_{LL'},\text{ cf. eq. (5.75)}}.\end{aligned} \tag{5.90}$$

This equation can equivalently be written in a matrix notation

$$\alpha = \mathrm{I} - \beta^{-1}(\beta - \mathrm{I}) = \beta^{-1}, \tag{5.91}$$

where I denotes the identity matrix. From this equation follows the claim eq. (5.84), which completes the proof.

5.9 Angular Momentum Expansion of the Green function for a Particle in a Potential

In analogy to the angular momentum expansion of the free particle Green function (cf. eq. (4.28))

$$G^0_{nr}(\mathbf{r},\mathbf{r}',E) = -ik\frac{2m}{\hbar^2}\sum_L J_L(k\mathbf{r}_<)H_L(k\mathbf{r}_>) \tag{5.92}$$

the Green function a the particle in a potential can also be expanded. However, the spherical Bessel and Hankel functions J_L and H_L will here be replaced by the regular and irregular solutions of the Schrödinger equation for a particle in a potential. Thus, once these solutions are known, the Green function can be calculated from the expansion.

The non-relativistic Green function for a particle in a potential is given by

$$G_{nr}(\mathbf{r},\mathbf{r}';E) = -ik\frac{2m}{\hbar^2}\sum_L\left[\Theta(r-r')R_L(\mathbf{r}')\overline{S}_L(\mathbf{r}') + \Theta(r'-r)S_L(\mathbf{r}')\overline{R}_L(\mathbf{r}')\right] \tag{5.93}$$

with the regular wave functions R_Λ, $\overline{R}_\Lambda$, defined by eqs. (5.13) and (5.14), whereas the irregular wave functions S_Λ, $\overline{S}_\Lambda$ are defined by eqs. (5.73) and (5.74).

In section 10.3 it will be shown that an equation of the same form is valid in the relativistic case (cf. eq. (10.19)), together with a proof for the relativistic case. For the non-relativistic case this proof goes completely analogously, except for two differences: the first one is that here some functions are scalar, that will be vectors or matrices in the relativistic case. Hence in the relativistic case the order of multiplications matters, while in the non-relativistic case it does not. The second difference is that the indices L will be replaced by different indices Λ. As by replacing the indices the proof for the relativistic case can be adopted, no proof is given here.

Part III

Relativistic Single-Site Scattering

6 Dirac Equation

For an electron with a high kinetic energy the Schrödinger equation does no longer provide an adequate description, but the Dirac equation has to be used instead. It was already found two years after the Schrödinger equation was published and, using vectors with four entries, describes the motion of a spin 1/2 particle in accordance to special relativity.

6.1 Relativistic Quantum Mechanics

In 1905 EINSTEIN published his theory of special relativity [65], as it was later on termed. In contrast to the Galilean relativity, which explains the equivalence of all inertial system of uniform, linear motion with one universal time, the time in special relativity is no longer universal for all reference systems. The first experiment connected to special relativity was the MICHELSON-MORLEY experiment, conducted already in 1881. It aimed to find a medium in which light waves travel. However, no such medium and, accordingly, no distinguished inertial system was found. Einstein's special relativity explained the unexpected result of the experiment. As an important consequence of the theory, the vacuum light speed c must be finite.

In a mathematical description, a theory in accordance with Galilean relativity must be invariant under a Galilean transformation between two inertial systems. Newton's Laws, for example, are invariant under such a transformation. The relativistic counterpart is a Lorentz transformation, i.e. a theory in accordance with special relativity must be *covariant*, which means invariant under a Lorentz transformation. This transformation was part of Einstein's publication and also solved the problem that the Maxwell equations were not invariant under a Galilean transformation.

The Schrödinger equation, published in 1926, is not invariant under a Lorentz transformation and thus not in accordance with special relativity. Hence, the search for a relativistic equivalent started directly after Schrödinger's publication. An attempt to describe the relativistic movement of an electron was the Klein-Gordon equation, that was published in 1927. It turned out that this equation does not correctly describe relativistic electrons, however, it is correct for the description of relativistic Bosons. Dirac's publication in 1928 [39] solved the problem of describing relativistic electrons.

In the non-relativistic limit of small electron speed $v \ll c$ the Schrödinger equation correctly describes the electronic motion. With increasing energy and, accordingly, increasing speed of motion, relativistic properties become important. Consequences of the Dirac equation include negative energies, that were explained by Dirac by introducing antiparticles with opposite energy [66], also known as the hole theory. This theory furthermore allows, in accordance to the equivalence of energy and mass in special relativity, the annihilation and creation of particles, which means that the number of particles no longer is a conserved quantity. In contrast to the Schrödinger equation, it is also able to correctly describe all interaction processes between light and matter, such as emission and absorption or scattering of photons. Moreover, it includes the spin of an electron in the theory. This intrinsic angular momentum couples with the orbital angular momentum, known as *spin-orbit coupling.* It

becomes more and more important with increasing atomic number, as for heavy elements the electrons have a higher energy and thus move faster. There are several good introductory books to relativistic quantum mechanics [64, 67, 68, 69, 70, 71], whereas the books by Strange [49] and Rose [72] go further into the details and also treat aspects that are important in solid state physics.

6.2 The Free Electron

The relativistic description of an electron in free space is given by the Dirac equation

$$\hat{H}_0\Psi = i\hbar\frac{\partial\Psi}{\partial t} \tag{6.1}$$

with the Dirac Hamiltonian

$$\begin{aligned}\hat{H}_0 : &= \frac{\hbar c}{i}\left(\alpha_1\frac{\partial}{\partial x^1} + \alpha_2\frac{\partial}{\partial x^2} + \alpha_3\frac{\partial}{\partial x^3}\right) + \beta mc^2 &(6.2)\\ &= c\boldsymbol{\alpha}\hat{\mathbf{p}} + \beta mc^2 &(6.3)\end{aligned}$$

and

$$\hat{\mathbf{p}} = -i\hbar\nabla. \tag{6.4}$$

In the stationary case eq. (6.1) becomes

$$\hat{H}_0\psi = W\psi, \tag{6.5}$$

where W denotes the energy eigenvalue in the relativistic case. The quantities α_i and β are 4×4 matrices defined as

$$\beta = \begin{pmatrix} \mathrm{I}_2 & 0 \\ 0 & -\mathrm{I}_2 \end{pmatrix},\ \alpha_i = \begin{pmatrix} 0 & \sigma_i \\ \sigma_i & 0 \end{pmatrix} \tag{6.6}$$

where $i \in \{x, y, z\}$ is the cartesian coordinate and σ_i are the 2×2 Pauli matrices

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix},\ \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix},\ \sigma_x = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{6.7}$$

$\boldsymbol{\alpha}$ is a vector that contains the three matrices α_i as its entries. In contrast to the Schrödinger equation, which is a linear second order differential equation, the Dirac equation is a linear first order differential equation. However, according to the general theory of linear differential equations, any second order equation can be written as a coupled system of two first order equations. As the Dirac equation contains vectors with four entries and 4×4 matrices it can be seen as a system of four coupled equations, thus resolving this at first sight surprising difference to the Schrödinger equation.

6.3 Electron in a Potential

To include a scalar potential $e\varphi(\mathbf{r})$ and an electromagnetic vector potential $\mathbf{A}(\mathbf{r})$ in the Dirac equation, the following replacements are necessary (see e.g. [71]):

$$i\hbar\frac{\partial}{\partial t} \longrightarrow i\hbar\frac{\partial}{\partial t} - e\varphi(\mathbf{r}) \tag{6.8}$$

or for the stationary case

$$W \longrightarrow W - e\varphi(\mathbf{r}) \tag{6.9}$$

and

$$\hat{\mathbf{p}} \longrightarrow \hat{\mathbf{p}} - e\mathbf{A}(\mathbf{r}). \tag{6.10}$$

Therefore the Dirac Hamiltonian becomes

$$\begin{aligned} \hat{H}_D &= c\boldsymbol{\alpha}\left(\hat{\mathbf{p}} - e\mathbf{A}(\mathbf{r})\right) + \beta mc^2 + e\varphi(\mathbf{r}) \\ &= c\boldsymbol{\alpha}\hat{\mathbf{p}} + \beta mc^2 + V(\mathbf{r}) \end{aligned} \tag{6.11}$$

where the potential $V(\mathbf{r})$ is a 4×4 matrix defined by

$$\begin{aligned} V(\mathbf{r}): &= e\varphi(\mathbf{r})\mathrm{I}_4 - ce\boldsymbol{\alpha}\mathbf{A}(\mathbf{r}) \\ &= e \begin{pmatrix} \varphi(\mathbf{r})\mathrm{I}_2 & -c\boldsymbol{\sigma}\mathbf{A}(\mathbf{r}) \\ -c\boldsymbol{\sigma}\mathbf{A}(\mathbf{r}) & \varphi(\mathbf{r})\mathrm{I}_2 \end{pmatrix} \\ &= e \begin{pmatrix} \varphi(\mathbf{r}) & 0 & -cA_z(\mathbf{r}) & -cA_x(\mathbf{r}) + icA_y(\mathbf{r}) \\ 0 & \varphi(\mathbf{r}) & -cA_x(\mathbf{r}) - icA_y(\mathbf{r}) & +cA_z(\mathbf{r}) \\ -cA_z(\mathbf{r}) & -cA_x(\mathbf{r}) + icA_y(\mathbf{r}) & \varphi(\mathbf{r}) & 0 \\ -cA_x(\mathbf{r}) - icA_y(\mathbf{r}) & +cA_z(\mathbf{r}) & 0 & \varphi(\mathbf{r}) \end{pmatrix}. \end{aligned} \tag{6.12}$$

Assuming that φ and $\mathbf{A}$ have only real entries, this matrix is self-adjoint (Hermitian), i.e.

$$V(\mathbf{r}) = V^\dagger(\mathbf{r}). \tag{6.13}$$

Density functional calculations using this potential are called *Spin-Current DFT*. Usually the potential is approximated neglecting orbital currents (see e.g. [70]) and written in the following representation:

$$\begin{aligned} \tilde{\tilde{V}}(\mathbf{r}): &= e\varphi(\mathbf{r})\mathrm{I}_4 - \mu\beta\boldsymbol{\Sigma}\mathbf{B}(\mathbf{r}) \\ &= \begin{pmatrix} e\varphi(\mathbf{r})\mathrm{I}_2 - \mu\boldsymbol{\sigma}\mathbf{B}(\mathbf{r}) & 0 \\ 0 & e\varphi(\mathbf{r})\mathrm{I}_2 + \mu\boldsymbol{\sigma}\mathbf{B}(\mathbf{r}) \end{pmatrix} \\ &= \begin{pmatrix} e\varphi(\mathbf{r}) - \mu B_z(\mathbf{r}) & -\mu B_x(\mathbf{r}) + i\mu B_y(\mathbf{r}) & 0 & 0 \\ -\mu B_x(\mathbf{r}) - i\mu B_y(\mathbf{r}) & e\varphi(\mathbf{r}) + \mu B_z(\mathbf{r}) & 0 & 0 \\ 0 & 0 & e\varphi(\mathbf{r}) + \mu B_z(\mathbf{r}) & \mu B_x(\mathbf{r}) - i\mu B_y(\mathbf{r}) \\ 0 & 0 & \mu B_x(\mathbf{r}) + i\mu B_y(\mathbf{r}) & e\varphi(\mathbf{r}) - \mu B_z(\mathbf{r}) \end{pmatrix} \end{aligned} \tag{6.14}$$

where

$$\boldsymbol{\Sigma} = \begin{pmatrix} \boldsymbol{\sigma} & 0 \\ 0 & \boldsymbol{\sigma} \end{pmatrix} \tag{6.15}$$

and where $\mathbf{B}$ is the magnetic flux density and

$$\mu = \frac{e\hbar}{2m}. \tag{6.16}$$

Density functional calculations using this potential are called *spin-polarised DFT*. Just as the exact potential V, assuming that φ and $\mathbf{B}$ have real entries only, the approximated potential $\tilde{\tilde{V}}$ is also a self-adjoint matrix:

$$\tilde{\tilde{V}}(\mathbf{r}) = \tilde{\tilde{V}}^\dagger(\mathbf{r}). \tag{6.17}$$

6.4 Relativistic Corrections to the Schrödinger Equation

The wave functions resulting from the Dirac equation have four entries. The first two are commonly termed the large component, the remaining two the small component. In the Dirac equation, which is a system of four linear first-order differential equations, both components are coupled. By applying a so-called Foldy-Wouthuysen transformation of the Dirac Hamiltonian and neglecting the small component, one can derive the *Pauli operator*:

$$\hat{H}_{\text{Pauli}} = \underbrace{\frac{\hat{\mathbf{p}}^2}{2m} + e\varphi(\mathbf{r})}_{\hat{H}_{\text{Schrödinger}}} \underbrace{- \frac{e\hbar}{2m}\boldsymbol{\sigma}\cdot\mathbf{B}}_{(1)} \underbrace{- \frac{\hat{p}^4}{8m^3c^2}}_{(2)} \underbrace{+ \frac{e\hbar^2}{8m^2c^2}\nabla\cdot\mathbf{E}}_{(3)} \underbrace{- \frac{e\hbar}{4m^2c^2}\boldsymbol{\sigma}\cdot(\mathbf{E}\times\hat{\mathbf{p}})}_{(4)}. \tag{6.18}$$

This operator is applied only to the large component. The first term of the Pauli operator is equal to the Schrödinger Hamiltonian, followed by relativistic correction terms up to order $\mathcal{O}(1/c^2)$. Hence, the Pauli operator provides a way to include relativistic effects in otherwise non-relativistic calculations. The Dirac equation, of course, intrinsically contains all these terms (and more), so that the Pauli operator is not used anywhere within this work. It is however instructive in order to gain understanding for what are the main relativistic effects:

1. The first correction term describes the magnetic moment $\boldsymbol{\mu} = -e\hbar/2m\boldsymbol{\sigma}$ resulting from the electron spin. It gives rise, for example, to the dipole-dipole interaction of electrons, which is one factor contributing to magnetic shape anisotropy and magneto-crystalline anisotropy (the other one is spin-orbit coupling, cf. point 4).

2. With increasing speed the relativistic mass increases and differs more and more from the rest mass. The second correction term is the first contribution to this mass increase.

3. This correction in known as the *Darwin term*. It describes the fact that in a relativistic description one can only give a probability for finding an electron at a certain position. The fine structure correction in the description of Hydrogen is an example of the effect the Darwin term has.

4. The last term is called the *spin-orbit coupling* term, that is the main source of various relativistic effects in solid state physics, including the magnetic shape anisotropy mentioned above. More examples are listed in the introduction. For regions where the potential is in a good approximation spherical, i.e. close to the atom core, the spin-orbit contribution can be approximated [11, 73] by

$$\hat{H}_{\text{SO}} = \frac{e\hbar}{4m^2c^2}\boldsymbol{\sigma}\cdot(\mathbf{E}\times\mathbf{p}) \approx \xi(r)\hat{\mathbf{L}}\cdot\hat{\mathbf{S}}. \tag{6.19}$$

   Here $\xi(r)$ is the spin-orbit coupling constant, $\hat{\mathbf{L}}$ is the orbital angular momentum operator and $\hat{\mathbf{S}}$ is the spin operator. In the following chapter these operators and their eigenfunctions and eigenvalues will be discussed in detail.

7 Angular Momentum Operators, Eigenvalues and Eigenfunctions

Angular momentum expansions form an indispensable tool within the KKR-GF formalism. Whereas in the non-relativistic case spherical harmonics are used as a basis, now the so-called spin spherical harmonics take over this role. They are the eigenfunctions of the spin-orbit operator $\hat{K}$. To characterise the states one has the choice between two different basis sets, the (κ, μ)-basis and the (l, m_l, m_s)-basis. Explicit tables of the indices in the two basis sets, Clebsch-Gordan coefficients and the first spin spherical harmonics are presented as a groundwork for computational implementation.

7.1 Orbital Angular Momentum Operator

The orbital angular momentum operator $\hat{\mathbf{L}}$ is defined by

$$\hat{\mathbf{L}} = \mathbf{r} \times \hat{\mathbf{p}} \tag{7.1}$$

where $\hat{\mathbf{p}} = -i\hbar\nabla$ is the momentum operator. $\hat{\mathbf{L}}$ fulfils the commutation relations

$$\begin{aligned} \left[\hat{L}_x, \hat{L}_y\right] &= i\hbar\hat{L}_z \\ \left[\hat{L}_y, \hat{L}_z\right] &= i\hbar\hat{L}_x \\ \left[\hat{L}_z, \hat{L}_x\right] &= i\hbar\hat{L}_y. \end{aligned} \tag{7.2}$$

Using these relations, the cross-product of $\hat{L}$ with itself can be calculated:

$$\hat{\mathbf{L}} \times \hat{\mathbf{L}} = \begin{pmatrix} \hat{L}_y\hat{L}_z - \hat{L}_z\hat{L}_y \\ \hat{L}_z\hat{L}_x - \hat{L}_x\hat{L}_z \\ \hat{L}_x\hat{L}_y - \hat{L}_y\hat{L}_x \end{pmatrix} = \begin{pmatrix} \left[\hat{L}_y, \hat{L}_z\right] \\ \left[\hat{L}_z, \hat{L}_x\right] \\ \left[\hat{L}_x, \hat{L}_y\right] \end{pmatrix} = \begin{pmatrix} i\hbar\hat{L}_x \\ i\hbar\hat{L}_y \\ i\hbar\hat{L}_z \end{pmatrix} = i\hbar\hat{\mathbf{L}}. \tag{7.3}$$

The eigenfunctions of the squared orbital angular momentum operator and its z-component are spherical harmonics:

$$\hat{\mathbf{L}}^2 Y_{l,m}(\theta, \phi) = \hbar^2 l(l+1) Y_{l,m}(\theta, \phi) \tag{7.4}$$

$$\hat{L}_z Y_{l,m}(\theta, \phi) = \hbar m Y_{l,m}(\theta, \phi). \tag{7.5}$$

The angular versions of the creation and annihilation operators

$$\hat{L}_+ := \hat{L}_x + i\hat{L}_y \tag{7.6}$$

$$\hat{L}_- := \hat{L}_x - i\hat{L}_y \tag{7.7}$$

allow going from one m state to another:

$$\hat{L}_+ Y_{l,m} = \begin{cases} \sqrt{l(l+1) - m(m+1)} Y_{l,m+1} & \text{if } m < l \\ 0 & \text{otherwise} \end{cases} \tag{7.8}$$

$$\hat{L}_- Y_{l,m} = \begin{cases} \sqrt{l(l+1) - m(m-1)} Y_{l,m-1} & \text{if } m > -l \\ 0 & \text{otherwise.} \end{cases} \tag{7.9}$$

7.2 Spin Operator

The spin, experimentally observed in experiments of atoms in magnetic fields (Zeeman effect, Stern-Gerlach experiment), emerges from the Dirac equation as a new (rotational) degree of freedom compared to the Schrödinger equation. It can be described by the spin operator, which is defined as

$$\hat{\mathbf{S}} := \frac{\hbar}{2} \boldsymbol{\sigma} \tag{7.10}$$

where $\boldsymbol{\sigma}$ is a vector containing the Pauli matrices σ_x, σ_y and σ_z, which are given by

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{7.11}$$

For electrons, i.e. spin 1/2 particles, the operator fulfils the eigenvalue equations

$$\hat{\mathbf{S}}^2 \phi_{m_s} = \hbar^2 s(s+1) \phi_{m_s} \tag{7.12}$$

$$\hat{S}_z \phi_{m_s} = \hbar m_s \phi_{m_s} \tag{7.13}$$

where $s = 1/2$, $m_s = \pm s$ and the eigenfunctions ϕ_{m_s} are the spinors

$$\phi_{\frac{1}{2}} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \phi_{-\frac{1}{2}} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \tag{7.14}$$

The Pauli matrices have the following properties:

$$\sigma_i^2 = \mathrm{I}_2 \tag{7.15}$$

$$\sigma_x \sigma_y = i\sigma_z \text{ and cyclic permutations} \tag{7.16}$$

$$\sigma_x \sigma_y = -\sigma_y \sigma_x \text{ and cyclic permutations} \tag{7.17}$$

$$\sigma_x \sigma_y \sigma_z = i\mathrm{I}_2. \tag{7.18}$$

From these properties follows a general relation, valid for all commuting vector operators $\hat{\mathbf{A}}$ and $\hat{\mathbf{B}}$:

$$\sum_{i,j} \sigma_i \hat{A}_i \sigma_j \hat{B}_j = \sum_{i,j} \delta_{ij} \hat{A}_i \hat{B}_j + i \sum_{i,j,k} \epsilon_{ijk} \sigma_k \hat{A}_i \hat{B}_j \tag{7.19}$$

$$\iff (\boldsymbol{\sigma} \hat{\mathbf{A}})(\boldsymbol{\sigma} \hat{\mathbf{B}}) = \hat{\mathbf{A}} \hat{\mathbf{B}} + i\boldsymbol{\sigma}(\hat{\mathbf{A}} \times \hat{\mathbf{B}}) \tag{7.20}$$

The first line follows from the relation $\sigma_i \sigma_j = \delta_{ij} + \sum_k i\epsilon_{ijk}\sigma_k$ (here ϵ_{ikj} denotes the Levi-Civita symbol) which is equivalent to equations (7.15) and (7.16), the second line is just rewriting it using the sum notations for the scalar product and the cross product.

The spin operator $\hat{\mathbf{S}}$ fulfils

$$\left[\hat{S}_x, \hat{S}_y\right] = i\hbar\hat{S}_z \text{ and cyclic permutations.} \tag{7.21}$$

In analogy to the case of the orbital angular momentum in section 7.1, this implies

$$\hat{\mathbf{S}} \times \hat{\mathbf{S}} = i\hbar\hat{\mathbf{S}}. \tag{7.22}$$

We also note

$$\left[\hat{\mathbf{S}}, \hat{\mathbf{L}}\right] = \frac{\hbar}{2}\begin{pmatrix} \sigma_x\hat{L}_x - \hat{L}_x\sigma_x \\ \sigma_y\hat{L}_y - \hat{L}_y\sigma_y \\ \sigma_z\hat{L}_z - \hat{L}_z\sigma_z \end{pmatrix} = 0. \tag{7.23}$$

7.3 Total Angular Momentum Operator

In the Schrödinger theory the angular momentum $\mathbf{L}$ is equivalent to the total angular momentum. This is different in the relativistic case, where the total angular momentum is the sum of the orbital angular momentum and the spin. In operator notation:

$$\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}. \tag{7.24}$$

This sum of two operators has to be understood as the direct product of the corresponding quantum states, see eq. (7.50). The eigenvalues of $\hat{\mathbf{J}}^2$ are given by $j(j+1)$, where j is a non-negative half-integer, and those of $\hat{J}_z = \hat{L}_z + \hat{S}_z$ are given by $\mu := m + m_s$, where $m = -l, ..., l$ and $m_s = \pm s = \pm\frac{1}{2}$.

The eigenfunctions of this operator will be discussed in section 7.5.

7.4 Spin-Orbit Operator

7.4.1 The Dirac Hamiltonian in Spin-Orbit Operator Notation

Our aim here is to separate radial and angular parts of the Dirac Hamiltonian. This will later on allow us to apply the separation of variables onto the Dirac equation when calculating its eigenfunctions.

We will first rewrite the momentum operator $\hat{\mathbf{p}}$. The following identity holds:

$$\mathbf{e}_r \times (\mathbf{e}_r \times \hat{\mathbf{p}}) \overset{\text{Graßmann identity}}{=} \mathbf{e}_r(\mathbf{e}_r\hat{\mathbf{p}}) - (\mathbf{e}_r\mathbf{e}_r)\hat{\mathbf{p}} = \mathbf{e}_r(\mathbf{e}_r\hat{\mathbf{p}}) - \hat{\mathbf{p}}. \tag{7.25}$$

Rearranging and using the definition of the unit vector $\mathbf{e}_r = \mathbf{r}/r$ and of the angular momentum operator $\hat{\mathbf{L}} = \mathbf{r} \times \hat{\mathbf{p}}$ yields

$$\hat{\mathbf{p}} = \mathbf{e}_r(\mathbf{e}_r\hat{\mathbf{p}}) - \mathbf{e}_r \times (\mathbf{e}_r \times \hat{\mathbf{p}}) = \mathbf{e}_r(\mathbf{e}_r\hat{\mathbf{p}}) - \frac{1}{r}\mathbf{e}_r \times (\mathbf{r} \times \hat{\mathbf{p}}) = \mathbf{e}_r(\mathbf{e}_r\hat{\mathbf{p}}) - \frac{1}{r}\mathbf{e}_r \times \hat{\mathbf{L}}. \tag{7.26}$$

Hence

$$\boldsymbol{\sigma}\hat{\mathbf{p}} = (\boldsymbol{\sigma}\mathbf{e}_r)(\mathbf{e}_r\hat{\mathbf{p}}) - \frac{1}{r}\boldsymbol{\sigma}(\mathbf{e}_r \times \hat{\mathbf{L}}). \tag{7.27}$$

Now we define

$$\sigma_r := \boldsymbol{\sigma}\mathbf{e_r} \tag{7.28}$$

and note that the term $\mathbf{e}_r\hat{\mathbf{p}}$ is the directional derivative

$$\mathbf{e}_r\hat{\mathbf{p}} = -i\hbar\mathbf{e}_r\nabla = -i\hbar\frac{\partial}{\partial r}. \tag{7.29}$$

Hence equation (7.27) becomes

$$\boldsymbol{\sigma}\hat{\mathbf{p}} = -i\hbar\sigma_r\frac{\partial}{\partial r} - \frac{1}{r}\boldsymbol{\sigma}(\mathbf{e}_r \times \hat{\mathbf{L}}). \tag{7.30}$$

To rewrite the term $\mathbf{e}_r \times \hat{\mathbf{L}}$ the vector $\mathbf{e}_r$ and the operator $\hat{\mathbf{L}}$ are inserted into equation (7.20), which yields:

$$(\boldsymbol{\sigma}\mathbf{e_r})(\boldsymbol{\sigma}\hat{\mathbf{L}}) = \mathbf{e}_r\hat{\mathbf{L}} + i\boldsymbol{\sigma}(\mathbf{e}_r \times \hat{\mathbf{L}}). \tag{7.31}$$

Since the cross product $\hat{\mathbf{L}} = \mathbf{r} \times \hat{\mathbf{p}}$ is perpendicular to $\mathbf{r}$ and thus also to $\mathbf{e}_r$, the term $\mathbf{e}_r\hat{\mathbf{L}}$ equals zero. Now, inserting eq. (7.31) into (7.30) gives

$$\begin{aligned}
\boldsymbol{\sigma}\hat{\mathbf{p}} &= -i\hbar\sigma_r\frac{\partial}{\partial r} - \frac{1}{ir}\sigma_r\boldsymbol{\sigma}\hat{\mathbf{L}} \\
&= -i\hbar\sigma_r\frac{\partial}{\partial r} + i\frac{1}{r}\sigma_r\boldsymbol{\sigma}\hat{\mathbf{L}} \\
&= -i\sigma_r\left(\hbar\frac{\partial}{\partial r} - \frac{1}{r}\boldsymbol{\sigma}\hat{\mathbf{L}}\right).
\end{aligned} \tag{7.32}$$

By defining the

spin-orbit operator

$$\hat{K} := -\left(\hbar + \boldsymbol{\sigma}\hat{\mathbf{L}}\right) \tag{7.33}$$

the expression for $\boldsymbol{\sigma}\hat{\mathbf{p}}$ is rewritten as

$$\boldsymbol{\sigma}\hat{\mathbf{p}} = -i\sigma_r\left(\hbar\frac{\partial}{\partial r} + \frac{\hbar}{r} + \frac{\hat{K}}{r}\right). \tag{7.34}$$

Therefore

$$\boldsymbol{\alpha}\hat{\mathbf{p}} = -i\sigma_r\left(\hbar\frac{\partial}{\partial r} + \frac{\hbar}{r} + \frac{\hat{K}}{r}\right)\begin{pmatrix} 0 & \mathrm{I}_2 \\ \mathrm{I}_2 & 0 \end{pmatrix}. \tag{7.35}$$

Using this expression, the Dirac Hamiltonian for a free electron can be rewritten as

$$\hat{H}_D = -ci\sigma_r\left(\hbar\frac{\partial}{\partial r} + \frac{\hbar}{r} + \frac{\hat{K}}{r}\right)\begin{pmatrix} 0 & \mathrm{I}_2 \\ \mathrm{I}_2 & 0 \end{pmatrix} + \beta mc^2. \tag{7.36}$$

7.4.2 Eigenvalues of the Spin-Orbit Operator

The eigenvalues of the spin-orbit operator $\hat{K}$ are convenient to characterise the states of a free relativistic particle. To calculate them we first evaluate $\hat{K}^2$:

$$\hat{K}^2 = \hbar^2 + 2\hbar\boldsymbol{\sigma}\hat{\mathbf{L}} + (\boldsymbol{\sigma}\hat{\mathbf{L}})(\boldsymbol{\sigma}\hat{\mathbf{L}}). \tag{7.37}$$

Now we rewrite

$$\begin{aligned}(\boldsymbol{\sigma}\hat{\mathbf{L}})(\boldsymbol{\sigma}\hat{\mathbf{L}}) &\overset{\text{eq. (7.20)}}{=} \hat{\mathbf{L}}^2 + i\boldsymbol{\sigma}(\hat{\mathbf{L}}\times\hat{\mathbf{L}}) \\ &\overset{\text{eq. (7.3)}}{=} \hat{\mathbf{L}}^2 - \hbar\boldsymbol{\sigma}\hat{\mathbf{L}}.\end{aligned} \tag{7.38}$$

Inserting this into the expression for $\hat{K}^2$ yields

$$\hat{K}^2 = \hbar^2 + \hbar\boldsymbol{\sigma}\hat{\mathbf{L}} + \hat{\mathbf{L}}^2 \tag{7.39}$$

and hence

$$\hat{K}^2 + \hbar\hat{K} = \hat{\mathbf{L}}^2. \tag{7.40}$$

We denote the eigenvalues of $\hat{K}$ by $\hbar\kappa$, i.e. the eigenvalue equation is

$$\hat{K}\chi_\Lambda = \hbar\kappa\chi_\Lambda, \tag{7.41}$$

where χ_Λ denote the eigenfunctions and Λ is a combined index $\Lambda = (\kappa, \mu)$. Then from eq. (7.40) follows

$$\hbar^2\kappa^2 + \hbar^2\kappa = \hbar^2 l(l+1) \tag{7.42}$$

because $\hat{\mathbf{L}}^2$ has eigenvalues $\hbar^2 l(l+1)$. This means

$$\kappa(\kappa+1) = l(l+1) \tag{7.43}$$

which implies the two solutions $\kappa = l$ or $\kappa = -(l+1)$. The next step is to link these two solutions to the eigenvalues of the total angular momentum operator $\hat{\mathbf{J}}$. First we note

$$\hat{\mathbf{J}}^2 - \hat{\mathbf{L}}^2 - \hat{\mathbf{S}}^2 = \left(\hat{\mathbf{L}} + \hat{\mathbf{S}}\right)^2 - \hat{\mathbf{L}}^2 - \hat{\mathbf{S}}^2 = \hat{\mathbf{L}}\hat{\mathbf{S}} + \hat{\mathbf{S}}\hat{\mathbf{L}} \overset{\text{eq. (7.23)}}{=} 2\hat{\mathbf{S}}\hat{\mathbf{L}}. \tag{7.44}$$

Hence

$$\boldsymbol{\sigma}\hat{\mathbf{L}} \overset{\text{eq. (7.10)}}{=} \frac{2}{\hbar}\hat{\mathbf{S}}\hat{\mathbf{L}} = \frac{1}{\hbar}\left(\hat{\mathbf{J}}^2 - \hat{\mathbf{L}}^2 - \hat{\mathbf{S}}^2\right). \tag{7.45}$$

Inserting this into the definition of the spin-orbit operator yields

$$\hat{K} = -\left(\hbar + \boldsymbol{\sigma}\hat{\mathbf{L}}\right) = -\left(\hbar + \frac{1}{\hbar}\left(\hat{\mathbf{J}}^2 - \hat{\mathbf{L}}^2 - \hat{\mathbf{S}}^2\right)\right). \tag{7.46}$$

For its eigenvalues follows therefore

$$\hbar\kappa = -\left(\hbar + \hbar j(j+1) - \hbar l(l+1) - \hbar s(s+1)\right). \tag{7.47}$$

As for electrons the spin eigenvalue is $s = \frac{1}{2}$, it can further be simplified to

$$\kappa = -\left(j(j+1) - l(l+1) + \frac{1}{4}\right). \tag{7.48}$$

Inserting $\kappa = l$, the first solution we found for κ, into this equation yields $j = l - 1/2$. If the second solution $\kappa = -(l+1)$ is inserted, the relation $j = l + 1/2$ is obtained. Therefore we get the final result for the eigenvalues of $\hat{K}$:

$$\kappa = \begin{cases} l, & \text{if } j = l - \frac{1}{2} \\ -l-1, & \text{if } j = l + \frac{1}{2}. \end{cases} \tag{7.49}$$

7.5 Spin Spherical Harmonics

This section introduces the so-called spin spherical harmonics, which are the eigenfunctions of the spin-orbit operator $\hat{K}$. Furthermore, the angular momentum expansion in different basis sets is discussed, namely in the (l, m_l, m_s)-basis and the (κ, μ)-basis.

The definition of the spin spherical harmonics can be found in e.g. [69], [72] or [74], here they will be defined in 7.60.

A quantum state in the non-relativistic case is fully specified by the quantum numbers l and m, or by the combined index $L = (l, m)$. $l(l+1)$ is the value of the squared orbital angular momentum vector $\mathbf{L}^2$ and m is its z-component. We can denote the state in Dirac notation as $|l, m\rangle$.

In the relativistic case a further angular momentum occurs, the spin angular momentum $\mathbf{s}$. Since it is always $s = 1/2$, there is only one additional degree of freedom, the z-component of the spin, which is determined by $m_s = \pm 1/2$. To avoid confusion, we will rename m to m_l in the relativistic case. Thus a state is now characterised by four quantum numbers: $|l, m_l, s, m_s\rangle$, out of which one is fixed ($s = 1/2$). This state can be written as the product of the orbital angular momentum state and the spin angular momentum state:

$$|l, m_l, s, m_s\rangle = |l, m_l\rangle \otimes |s, m_s\rangle \,. \tag{7.50}$$

This product in an explicit representation is the product of (scalar) spherical harmonics Y_{l,m_l} with spinors ϕ_{m_s} :

$$|l, m_l, s, m_s\rangle = Y_{l,m_l}(\hat{\mathbf{r}})\phi_{m_s} \tag{7.51}$$

where the spinors are given by

$$\phi_{\frac{1}{2}} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \; \phi_{-\frac{1}{2}} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \tag{7.52}$$

The number of states up to a maximal l-value l_{cut} is given by

$$\text{number of states} = 2 \cdot (l_{\text{cut}} + 1)^2 \,. \tag{7.53}$$

Table 7.2a shows the 32 $(= 2 \cdot (3 + 1^2))$ possible states up to $l_{\text{cut}} = 3$.

For a given orbital angular momentum $\mathbf{L}$ and a given spin $\mathbf{S}$ the total angular momentum is defined by

$$\mathbf{J} = \mathbf{L} + \mathbf{S}. \tag{7.54}$$

One can calculate that the z-components of $\hat{\mathbf{L}}$ and $\hat{\mathbf{S}}$, given by the operators $\hat{L}_z$ and $\hat{S}_z$ with eigenvalues m_l and m_s, are no longer "good" quantum numbers in the case of this spin-orbit coupling, in the sense that these operators do not commute with the Dirac Hamiltonian $\hat{H}_D$. However the z-component of the combined angular momentum, given by the operator $\hat{J}_z = \hat{L}_z + \hat{S}_z$, does commute with $\hat{H}_D$. The eigenvalue of $\hat{J}_z$ is denoted by μ, and obviously it is

$$\mu \;:= m_j = \;\; m_l + m_s = m_l \pm \frac{1}{2}. \tag{7.55}$$

As an alternative to using the quantum numbers defining a state as $|l, m_l, s, m_s\rangle$, one can also define a state $|j, l, s, \mu\rangle$. This defines a different basis (the (κ,μ)-basis, as we will see later on). To go from one representation to the other, one has to calculate a linear combination of the states with suitable coefficients. Going from (l, m_l, s, m_s)-representation to (j, l, s, μ)-representation, it has the form:

$$|j, l, s, \mu\rangle = \sum_{m_s=\pm\frac{1}{2}} C(j, \mu, l, s|m_l, m_s)\, |l, m_l, s, m_s\rangle\,. \tag{7.56}$$

As only values for $\mu = m_l + m_s$ are allowed, the coefficients have to vanish for any other combination.

Now it turns out, that the eigenvalue κ of the spin-orbit operator $\hat{K}$, contains exactly the same information as j and l together. That means if κ is given, j and l can be calculated from it[21]

$$j \;\; = \;\; l - \frac{1}{2}\mathrm{sign}(\kappa) = l \pm \frac{1}{2} \tag{7.57}$$

$$l \;\; = \;\; \begin{cases} \kappa, & \text{if } j = l - \frac{1}{2} \Leftrightarrow \kappa > 0 \\ -\kappa - 1, & \text{if } j = l + \frac{1}{2} \Leftrightarrow \kappa < 0, \end{cases} \tag{7.58}$$

and on the other hand, if j and l are given, κ can be calculated:

$$\kappa = \begin{cases} l, & \text{if } j = l - \frac{1}{2} \\ -l - 1, & \text{if } j = l + \frac{1}{2}. \end{cases} \tag{7.59}$$

Thus it is completely equivalent to use the notation $|j, l, s, \mu\rangle$ or $|\kappa, s, \mu\rangle$. As it is always $s = 1/2$ this quantum number is usually omitted, and the states are named $|j, l, \mu\rangle$ or $|\kappa, \mu\rangle$ in the case of the total angular momentum basis or $|l, m_l, m_s\rangle$ for the former basis. The total angular momentum representation is normally called the (κ, μ)-representation. The following table shows how to calculate *within* this representation:

l	$j = l \pm 1/2$	κ
0	1/2	-1
1	1/2	1
	3/2	-2
2	3/2	2
	5/2	-3
3	5/2	3
	7/2	-4

[21] Note that the expression $j = l \pm \frac{1}{2}$ here means $j = l + s$, where $s = \pm\frac{1}{2}$. It is not equal to $l + m_s$.

Now we need an explicit expression for the basis functions $|\kappa, \mu\rangle$. Equation (7.56) already gives a definition, and in an explicit notation it is

$$\chi_\Lambda(\hat{\mathbf{r}}) = \sum_{m_s=\pm 1/2} C(l, j, \frac{1}{2}|\mu - m_s, m_s) Y_{l,\mu-m_s}(\hat{\mathbf{r}})\phi_{m_s} \tag{7.60}$$

where $\Lambda = (\kappa, \mu) = (j, l, \mu)$ is the combined index for the relativistic quantum numbers. These functions are called *spin spherical harmonics*. The coefficients C that occur here are called *Clebsch-Gordan coefficients* and are given by:

$C(l, j, \frac{1}{2}\|m_l, m_s)$	$m_s = 1/2$	$m_s = -1/2$
$j = l + 1/2$	$\sqrt{\frac{l+\mu+\frac{1}{2}}{2l+1}}$	$\sqrt{\frac{l-\mu+\frac{1}{2}}{2l+1}}$
$j = l - 1/2$	$-\sqrt{\frac{l-\mu+\frac{1}{2}}{2l+1}}$	$\sqrt{\frac{l+\mu+\frac{1}{2}}{2l+1}}$

Clebsch-Gordan coefficients are always needed when adding angular momenta. For details on how to calculate them see e.g. [64] or [72].

Furthermore one defines

$$\overline{\Lambda} = : (-\kappa, \mu) \tag{7.61}$$

$$\bar{l} = \begin{cases} \kappa - 1 & \text{if } \kappa > 0 \\ -\kappa & \text{if } \kappa < 0 \end{cases} \tag{7.62}$$

and

$$\chi_{\overline{\Lambda}}(\hat{\mathbf{r}}) = \sum_{m_s=\pm 1/2} C(\bar{l}, j, \frac{1}{2}|\mu - m_s, m_s) Y_{\bar{l},\mu-m_s}(\hat{\mathbf{r}})\phi_{m_s}. \tag{7.63}$$

One can show that the spin spherical harmonics are the eigenfunctions of the spin-orbit operator:

$$\hat{K}\chi_\Lambda(\hat{\mathbf{r}}) = \hbar\kappa\chi_\Lambda(\hat{\mathbf{r}}). \tag{7.64}$$

$$\hat{K}\chi_{\overline{\Lambda}}(\hat{\mathbf{r}}) = -\hbar\kappa\chi_{\overline{\Lambda}}(\hat{\mathbf{r}}). \tag{7.65}$$

For a given quantum number j the quantum number μ fulfils

$$|l - s| \leq \mu \leq l + s \tag{7.66}$$

where $s = 1/2$. The number of states up to a certain value of l is the same in the (κ, μ)-basis as it was in the (l, m_l, m_s)-basis, given by eq. (7.53). An explicit overview of the allowed values up to $l_{\text{cut}} = 3$ is given in table 7.2b.

The Clebsch-Gordan coefficients fulfil the following orthonormality properties (see e.g. [49] section 2.10):

$$\sum_j C(l, j, \frac{1}{2}|\mu - m_s, m_s) C(l, j, \frac{1}{2}|\mu' - m_s', m_s') = \delta_{m_s m_s'}\delta_{\mu\mu'} \tag{7.67}$$

$$\sum_{m_s} C(l, j, \frac{1}{2}|\mu - m_s, m_s) C(l, j', \frac{1}{2}|\mu - m_s, m_s) = \delta_{jj'}. \tag{7.68}$$

Table 7.1: An overview of the explicit expressions for the first ten spin spherical harmonics.

index	l	j	μ	κ	$\chi_\Lambda(\theta,\phi)$
1	0	1/2	-1/2	-1	$\begin{pmatrix} 0 \\ Y_{0,0}(\hat{\mathbf{r}}) \end{pmatrix} = \begin{pmatrix} 0 \\ \sqrt{\frac{1}{4\pi}} \end{pmatrix}$
2		1/2	1/2	-1	$\begin{pmatrix} Y_{0,0}(\hat{\mathbf{r}}) \\ 0 \end{pmatrix} = \begin{pmatrix} \sqrt{\frac{1}{4\pi}} \\ 0 \end{pmatrix}$
3	1	1/2	-1/2	1	$\begin{pmatrix} \sqrt{\frac{1}{3}}Y_{1,0}(\hat{\mathbf{r}}) \\ -\sqrt{\frac{2}{3}}Y_{1,-1}(\hat{\mathbf{r}}) \end{pmatrix} = \begin{pmatrix} \sqrt{\frac{1}{4\pi}}\cos(\theta) \\ -\sqrt{\frac{1}{4\pi}}\sin(\theta)\mathrm{e}^{-i\phi} \end{pmatrix}$
4		1/2	1/2	1	$\begin{pmatrix} -\sqrt{\frac{1}{3}}Y_{1,0}(\hat{\mathbf{r}}) \\ \sqrt{\frac{2}{3}}Y_{1,1}(\hat{\mathbf{r}}) \end{pmatrix} = \begin{pmatrix} -\sqrt{\frac{1}{4\pi}}\cos(\theta) \\ -\sqrt{\frac{1}{4\pi}}\sin(\theta)\mathrm{e}^{i\phi} \end{pmatrix}$
5		3/2	-3/2	-2	$\begin{pmatrix} 0 \\ Y_{1,-1}(\hat{\mathbf{r}}) \end{pmatrix} = \begin{pmatrix} 0 \\ \sqrt{\frac{3}{8\pi}}\sin(\theta)\mathrm{e}^{-i\phi} \end{pmatrix}$
6		3/2	-1/2	-2	$\begin{pmatrix} \sqrt{\frac{1}{3}}Y_{1,-1}(\hat{\mathbf{r}}) \\ \sqrt{\frac{2}{3}}Y_{1,0}(\hat{\mathbf{r}}) \end{pmatrix} = \begin{pmatrix} \sqrt{\frac{1}{8\pi}}\sin(\theta)\mathrm{e}^{-i\phi} \\ \sqrt{\frac{1}{2\pi}}\cos(\theta) \end{pmatrix}$
7		3/2	1/2	-2	$\begin{pmatrix} \sqrt{\frac{2}{3}}Y_{1,0}(\hat{\mathbf{r}}) \\ \sqrt{\frac{1}{3}}Y_{1,1}(\hat{\mathbf{r}}) \end{pmatrix} = \begin{pmatrix} \sqrt{\frac{1}{2\pi}}\cos(\theta) \\ -\sqrt{\frac{1}{8\pi}}\sin(\theta)\mathrm{e}^{i\phi} \end{pmatrix}$
8		3/2	3/2	-2	$\begin{pmatrix} Y_{1,1}(\hat{\mathbf{r}}) \\ 0 \end{pmatrix} = \begin{pmatrix} -\sqrt{\frac{3}{8\pi}}\sin(\theta)\mathrm{e}^{i\phi} \\ 0 \end{pmatrix}$
9	2	3/2	-3/2	2	$\begin{pmatrix} -\sqrt{\frac{4}{5}}Y_{2,-2}(\hat{\mathbf{r}}) \\ \sqrt{\frac{1}{5}}Y_{2,-1}(\hat{\mathbf{r}}) \end{pmatrix} = \begin{pmatrix} -\sqrt{\frac{3}{8\pi}}\sin^2(\theta)\mathrm{e}^{-2i\phi} \\ \sqrt{\frac{3}{8\pi}}\sin(\theta)\cos(\theta)\mathrm{e}^{-i\phi} \end{pmatrix}$
10		3/2	-1/2	2	$\begin{pmatrix} -\sqrt{\frac{3}{5}}Y_{2,-1}(\hat{\mathbf{r}}) \\ \sqrt{\frac{2}{5}}Y_{2,0}(\hat{\mathbf{r}}) \end{pmatrix} = \begin{pmatrix} -\sqrt{\frac{9}{8\pi}}\sin(\theta)\cos(\theta)\mathrm{e}^{-i\phi} \\ \sqrt{\frac{1}{8\pi}}\left(3\cos^2(\theta)-1\right) \end{pmatrix}$
$\vdots$					

Table 7.2: Allowed sets of quantum numbers in the different basis sets. Note that one state in the (κ, μ)-basis has no direct relation to a state in the (l, m_l, m_s)-basis, but is given by a linear combination of these states. However, the number of states up to a certain cutoff value l_{cut} is the same in both representations. Also the maximal index (2, 8, 18, 32, 50, 72, ...) corresponding to the cutoff-value l_{cut} and given by $2 \cdot (l_{\text{cut}} + 1)^2$, does not change.

(a) Different quantum states $|l, m_l, s, m_s\rangle$ in the (l, m_l, m_s)-basis.

index	l	m_l	m_s
1	0	0	-1/2
2			+1/2
3	1	-1	-1/2
4			+1/2
5		0	-1/2
6			+1/2
7		1	-1/2
8			+1/2
9	2	-2	-1/2
10			+1/2
11		-1	-1/2
12			+1/2
13		0	-1/2
14			+1/2
15		1	-1/2
16			+1/2
17		2	-1/2
18			+1/2
19	3	-3	-1/2
20			+1/2
21		-2	-1/2
22			+1/2
23		-1	-1/2
24			+1/2
25		0	-1/2
26			+1/2
27		1	-1/2
28			+1/2
29		2	-1/2
30			+1/2
31		3	-1/2
32			+1/2

(b) Different quantum states $|j, l, s, \mu\rangle$ in the (κ, μ)-basis. The left and right part of this table are equivalent, that means it is equivalent to use κ and μ or to use l, j and μ.

index	l	j	μ	κ	μ	orbital
1	0	1/2	-1/2	-1	-1/2	$s_{1/2}$
2		1/2	1/2	-1	1/2	
3	1	1/2	-1/2	1	-1/2	$p_{1/2}$
4		1/2	1/2	1	1/2	
5		3/2	-3/2	-2	-3/2	$p_{3/2}$
6		3/2	-1/2	-2	-1/2	
7		3/2	1/2	-2	1/2	
8		3/2	3/2	-2	3/2	
9	2	3/2	-3/2	2	-3/2	$d_{3/2}$
10		3/2	-1/2	2	-1/2	
11		3/2	1/2	2	1/2	
12		3/2	3/2	2	3/2	
13		5/2	-5/2	-3	-5/2	$d_{5/2}$
14		5/2	-3/2	-3	-3/2	
15		5/2	-1/2	-3	-1/2	
16		5/2	1/2	-3	1/2	
17		5/2	3/2	-3	3/2	
18		5/2	5/2	-3	5/2	
19	3	5/2	-5/2	3	-5/2	$f_{5/2}$
20		5/2	-3/2	3	-3/2	
21		5/2	-1/2	3	-1/2	
22		5/2	1/2	3	1/2	
23		5/2	3/2	3	3/2	
24		5/2	5/2	3	5/2	
25		7/2	-7/2	-4	-7/2	$f_{7/2}$
26		7/2	-5/2	-4	-5/2	
27		7/2	-3/2	-4	-3/2	
28		7/2	-1/2	-4	-1/2	
29		7/2	1/2	-4	1/2	
30		7/2	3/2	-4	3/2	
31		7/2	5/2	-4	5/2	
32		7/2	7/2	-4	7/2	

The spinors fulfil

$$\phi_{\frac{1}{2}}\phi^{\dagger}_{\frac{1}{2}} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \begin{pmatrix} 1 & 0 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \tag{7.69}$$

$$\phi_{-\frac{1}{2}}\phi^{\dagger}_{-\frac{1}{2}} = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \begin{pmatrix} 0 & 1 \end{pmatrix} = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} \tag{7.70}$$

and thus also

$$\sum_{m_s=\pm\frac{1}{2}} \phi_{m_s}\phi^{\dagger}_{m_s} = \phi_{\frac{1}{2}}\phi^{\dagger}_{\frac{1}{2}} + \phi_{-\frac{1}{2}}\phi^{\dagger}_{-\frac{1}{2}} = \mathrm{I}_2. \tag{7.71}$$

Furthermore they fulfil the orthonormality relation

$$\phi^{\dagger}_{m_s}\phi_{m'_s} = \delta_{m_s m'_s}. \tag{7.72}$$

From these relations also follows the orthonormality of the spin spherical harmonics:

$$\begin{aligned} \int d\hat{\mathbf{r}} \chi^{\dagger}_{\Lambda'}(\hat{\mathbf{r}})\chi_{\Lambda}(\hat{\mathbf{r}}) &= \delta_{\Lambda\Lambda'} \\ \int d\hat{\mathbf{r}} \chi^{\dagger}_{\overline{\Lambda}'}(\hat{\mathbf{r}})\chi_{\Lambda}(\hat{\mathbf{r}}) &= \delta_{\Lambda\overline{\Lambda}'} \\ \int d\hat{\mathbf{r}} \chi^{\dagger}_{\Lambda'}(\hat{\mathbf{r}})\chi_{\overline{\Lambda}}(\hat{\mathbf{r}}) &= \delta_{\overline{\Lambda}\Lambda'}. \end{aligned} \tag{7.73}$$

Another issue of importance is to transform between spin spherical harmonics expansions and spherical harmonics expansions. This can be done using the following formula:

$$\mathrm{I}_2 \sum_m Y_{l,m}(\hat{\mathbf{r}})Y^*_{l,m}(\hat{\mathbf{r}}') = \sum_{j,\mu} \chi_{\Lambda}(\hat{\mathbf{r}})\chi^{\dagger}_{\Lambda}(\hat{\mathbf{r}}'). \tag{7.74}$$

To verify its correctness start off the right hand side and insert the definition (7.60):

$$\begin{aligned} \sum_{j,\mu} \chi_{\Lambda}(\hat{\mathbf{r}})\chi^{\dagger}_{\Lambda}(\hat{\mathbf{r}}') &= \sum_{j,\mu}\sum_{m_s,m'_s} C(l,j,\tfrac{1}{2}|\mu-m_s,m_s)C^*(l,j,\tfrac{1}{2}|\mu-m'_s,m'_s) \\ &\qquad \cdot Y_{l,\mu-m_s}(\hat{\mathbf{r}})Y^*_{l,\mu-m'_s}(\hat{\mathbf{r}}')\phi_{m_s}\phi^{\dagger}_{m'_s} \\ &= \sum_{\mu}\sum_{m_s,m'_s}\left(\sum_j C(l,j,\tfrac{1}{2}|\mu-m_s,m_s)C^*(l,j,\tfrac{1}{2}|\mu-m'_s,m'_s)\right) \\ &\qquad \cdot \left(Y_{l,\mu-m_s}(\hat{\mathbf{r}})Y^*_{l,\mu-m'_s}(\hat{\mathbf{r}}')\phi_{m_s}\phi^{\dagger}_{m'_s}\right) \\ &\overset{\text{eq. (7.67)}}{=} \sum_{\mu}\sum_{m_s,m'_s}\delta_{m_s m'_s}\delta_{\mu\mu'}\left(Y_{l,\mu-m_s}(\hat{\mathbf{r}})Y^*_{l,\mu-m'_s}(\hat{\mathbf{r}}')\phi_{m_s}\phi^{\dagger}_{m'_s}\right) \\ &\overset{\text{eq. (7.55)}}{=} \sum_{m_l}\sum_{m_s=\pm\frac{1}{2}} Y_{l,m_l}(\hat{\mathbf{r}})Y^*_{l,m_l}(\hat{\mathbf{r}}')\phi_{m_s}\phi^{\dagger}_{m_s} \\ &\overset{\text{eq. (7.71)},\, m=m_l}{=} \mathrm{I}_2 \sum_m Y_{l,m}(\hat{\mathbf{r}})Y^*_{l,m}(\hat{\mathbf{r}}'). \end{aligned}$$

8 The Free Dirac Particle

A relativistic electron in free space is described by the potential-free Dirac equation. The solution of this equation is given by Dirac plane waves. After separating the radial and angular parts, one obtains spin spherical harmonics (discussed in the previous chapter) as the angular parts. To obtain the radial parts, the Bessel differential equation is solved, yielding Bessel, Hankel and Neumann functions.

8.1 Solution of the Free Dirac Equation: Dirac Plane Waves

In analogy to plane waves as the solution of the Schrödinger equation, one can calculate the solution of the Dirac Hamiltonian without a potential

$$\hat{H}_0 = c\boldsymbol{\alpha}\hat{\mathbf{p}} + \beta mc^2. \tag{8.1}$$

The solutions of the time dependent Dirac equation (6.1) are assumed to be of the form

$$\Psi(\mathbf{r},t) = \begin{pmatrix} \chi \\ \varphi \end{pmatrix} \mathrm{e}^{i\left(\mathbf{kr}-\frac{W}{\hbar}t\right)} = \psi(\mathbf{r})\mathrm{e}^{-\frac{i}{\hbar}Wt} \tag{8.2}$$

where $\psi(\mathbf{r})$ is the solution of the stationary equation, given by

$$\psi(\mathbf{r}) = \begin{pmatrix} \chi \\ \varphi \end{pmatrix} \mathrm{e}^{i\mathbf{kr}} = U\mathrm{e}^{i\mathbf{kr}}. \tag{8.3}$$

Here χ and φ a two-spinors that are called the large and small component of the double-spinor U.

Before moving on, first note that

$$\hat{\mathbf{p}}\mathrm{e}^{i\mathbf{kr}} = \hbar\mathbf{k}\mathrm{e}^{i\mathbf{kr}} \tag{8.4}$$

as it can easily be verified by applying the operator $\hat{\mathbf{p}}$ on the exponential function.

Inserting the form assumed for the solution ψ into the stationary Dirac equation (6.5) and using the relation above yields the equation

$$c\hbar \begin{pmatrix} 0 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & 0 \end{pmatrix} \begin{pmatrix} \chi \\ \varphi \end{pmatrix} \mathbf{k}\mathrm{e}^{i\mathbf{kr}} + mc^2 \begin{pmatrix} \mathrm{I}_2 & 0 \\ 0 & -\mathrm{I}_2 \end{pmatrix} \begin{pmatrix} \chi \\ \varphi \end{pmatrix} \mathrm{e}^{i\mathbf{kr}} = W \begin{pmatrix} \chi \\ \varphi \end{pmatrix} \mathrm{e}^{i\mathbf{kr}} \tag{8.5}$$

which can be rewritten into a system of two equations:

$$\begin{aligned} \left(W - mc^2\right)\chi - c\hbar\boldsymbol{\sigma}\mathbf{k}\varphi &= 0 && (8.6)\\ \left(W + mc^2\right)\varphi - c\hbar\boldsymbol{\sigma}\mathbf{k}\chi &= 0. && (8.7) \end{aligned}$$

For non-trivial solutions of this equation system its coefficient matrix must have a vanishing determinant:

$$\left(W - mc^2\right)\left(W + mc^2\right) - c^2\hbar^2\left(\boldsymbol{\sigma}\mathbf{k}\right)\left(\boldsymbol{\sigma}\mathbf{k}\right) = 0. \tag{8.8}$$

From the property (7.20) of Pauli matrices and commuting operators one can conclude

$$(\boldsymbol{\sigma}\mathbf{k})\,(\boldsymbol{\sigma}\mathbf{k}) = k^2, \tag{8.9}$$

which, inserted into (8.8), yields

$$W^2 \;\; = \;\; c^2\hbar^2k^2 + m^2c^4. \tag{8.10}$$

Furthermore, from (8.7) follows the relationship

$$\varphi = \frac{c\hbar\boldsymbol{\sigma}\mathbf{k}}{W + mc^2}\chi \tag{8.11}$$

between the large and the small component.

The basis vectors χ can be any two linearly independent vectors. Commonly, they are chosen as the eigenvectors of σ_z, which correspond to the states "spin up" ($m_s = +1/2$) and "spin down" ($m_s = -1/2$):

$$\phi_{\frac{1}{2}} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \;\; \phi_{-\frac{1}{2}} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \tag{8.12}$$

m_s determines the z-component of the spin angular momentum s and is given by

$$m_s = \pm s \tag{8.13}$$

where $s = 1/2$.

Using these results, the double-spinor U can be written as

$$U = U_{m_s} = \left(\frac{W + mc^2}{2W}\right)^{\frac{1}{2}} \begin{pmatrix} \phi_{m_s} \\ \frac{c\hbar\boldsymbol{\sigma}\mathbf{k}}{W+mc^2}\phi_{m_s} \end{pmatrix}, \tag{8.14}$$

where the normalisation constant is determined by the condition $U^2_{m_s} = 1$, using equations (8.9) and (8.10). Thus we can write:

The stationary right-hand side solutions of the free particle Dirac equation are:

$$\psi_{\mathbf{k}m_s}(\mathbf{r}) = \left(\frac{W + mc^2}{2W}\right)^{\frac{1}{2}} \begin{pmatrix} \phi_{m_s} \\ \frac{c\hbar\boldsymbol{\sigma}\mathbf{k}}{W+mc^2}\phi_{m_s} \end{pmatrix} \mathrm{e}^{i\mathbf{kr}} \tag{8.15}$$

where

$$W^2 = c^2\hbar^2k^2 + m^2c^4 \tag{8.16}$$

and

$$\phi_{\frac{1}{2}} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \;\; \phi_{-\frac{1}{2}} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \tag{8.17}$$

These solutions, as already mentioned above, are called the right-hand side solutions of the Dirac equation. They are two-spinor column vectors, i.e. of dimension 4×1, and solve the equation

$$\left(\hat{H}^0 - W\right)\psi_{\mathbf{k}m_s}(\mathbf{r}) = 0. \tag{8.18}$$

One can, however, also consider an equation of the form

$$\overline{\psi}_{\mathbf{k}m_s}(\mathbf{r})\left(\hat{H}^0 - W\right) = 0, \tag{8.19}$$

where $\overline{\psi}_{\mathbf{k}m_s}$ is a row vector, i.e. it has dimension 1×4 , and the operator $\hat{H}^0$ acts to the left. The solution of this equation is called the *left-hand side solution.*

8.2 Solution of the Free Dirac Equation for Separated Radial and Angular Parts

The previous section showed how to express the solution of the free Dirac equation in a basis set of Dirac plane waves. This section, in contrast, uses the representation eq. (7.36) of the Dirac equation to derive the solutions in a different basis set according to the eigenvalues $\Lambda = (\kappa, \mu)$ of the spin-orbit operator and the angular momentum operator.

Before actually starting, we consider how the different parts in equation (7.36) act on the spin spherical harmonics χ_Λ. We already saw in section 7.5 how the spin-orbit operator $\hat{K}$ acts on them. However, we have not yet looked on how σ_r acts on them. It is a few lines of calculus (cf. [49] p. 59) to show that

$$-\sigma_r\hat{K} = \hat{K}\sigma_r. \tag{8.20}$$

As $\hat{K}\chi_\Lambda = \hbar\kappa\chi_\Lambda$ after eq. (7.64), this implies

$$\hat{K}\left(-\sigma_r\chi_\Lambda\right) = -\hbar\kappa\left(-\sigma_r\chi_\Lambda\right). \tag{8.21}$$

Thus $-\sigma_r\chi_\Lambda$ must be an eigenfunction of $\hat{K}$. On the other hand we know that $-\hbar\kappa$ is the eigenvalue corresponding to the eigenfunction $\chi_{\overline{\Lambda}}$, where $\overline{\Lambda} = (-\kappa, \mu)$:

$$\hat{K}\chi_{\overline{\Lambda}} = -\hbar\kappa\chi_{\overline{\Lambda}}. \tag{8.22}$$

Comparing the two equations it follows that:

$$-\sigma_r\chi_\Lambda = \chi_{\overline{\Lambda}} \tag{8.23}$$

$$-\sigma_r\chi_{\overline{\Lambda}} = \chi_\Lambda. \tag{8.24}$$

Now we come back to the original problem of solving the stationary Dirac equation with the Hamiltonian given in eq. (7.36). The first step is to assume the solution is a wave function of the following form:

$$\psi(\mathbf{r}) = \psi_\Lambda(\mathbf{r}) = \begin{pmatrix} \psi^t(r)\chi_\Lambda(\hat{\mathbf{r}}) \\ i\psi^b(r)\chi_{\overline{\Lambda}}(\hat{\mathbf{r}}) \end{pmatrix}. \tag{8.25}$$

Inserting this into the Dirac equation yields:

$$-ic\sigma_r\left(\hbar\frac{\partial}{\partial r} + \hbar\frac{1}{r} + \frac{\hat{K}}{r}\right)\begin{pmatrix} i\psi^b(r)\chi_{\overline{\Lambda}}(\hat{\mathbf{r}}) \\ \psi^t(r)\chi_\Lambda(\hat{\mathbf{r}}) \end{pmatrix} + mc^2\begin{pmatrix} \psi^t(r)\chi_\Lambda(\hat{\mathbf{r}}) \\ -i\psi^b(r)\chi_{\overline{\Lambda}}(\hat{\mathbf{r}}) \end{pmatrix} = W\begin{pmatrix} \psi^t(r)\chi_\Lambda(\hat{\mathbf{r}}) \\ i\psi^b(r)\chi_{\overline{\Lambda}}(\hat{\mathbf{r}}) \end{pmatrix} \tag{8.26}$$

This can be regarded as a system of two equations. Using $\hat{K}\chi_\Lambda = \hbar\kappa\chi_\Lambda$ and $\hat{K}\chi_{\overline{\Lambda}} = -\hbar\kappa\chi_{\overline{\Lambda}}$, we obtain

$$\begin{aligned} c\sigma_r\hbar\left(\frac{\partial}{\partial r}+\frac{1}{r}-\frac{\kappa}{r}\right)\psi^b(r)\chi_{\overline{\Lambda}}(\hat{\mathbf{r}})+mc^2\psi^t(r)\chi_\Lambda(\hat{\mathbf{r}}) &= W\psi^t(r)\chi_\Lambda(\hat{\mathbf{r}}) \\ -ic\sigma_r\hbar\left(\frac{\partial}{\partial r}+\frac{1}{r}+\frac{\kappa}{r}\right)\psi^t(r)\chi_\Lambda(\hat{\mathbf{r}})-imc^2\psi^b(r)\chi_{\overline{\Lambda}}(\hat{\mathbf{r}}) &= iW\psi^b(r)\chi_{\overline{\Lambda}}(\hat{\mathbf{r}}). \end{aligned} \tag{8.27}$$

Applying equations (8.23) and (8.24) this is rewritten as

$$\begin{aligned} -c\hbar\left(\frac{\partial}{\partial r}+\frac{1}{r}-\frac{\kappa}{r}\right)\psi^b(r)\chi_\Lambda(\hat{\mathbf{r}})+mc^2\psi^t(r)\chi_\Lambda(\hat{\mathbf{r}}) &= W\psi^t(r)\chi_\Lambda(\hat{\mathbf{r}}) \\ c\hbar\left(\frac{\partial}{\partial r}+\frac{1}{r}+\frac{\kappa}{r}\right)\psi^t(r)\chi_{\overline{\Lambda}}(\hat{\mathbf{r}})-mc^2\psi^b(r)\chi_{\overline{\Lambda}}(\hat{\mathbf{r}}) &= W\psi^b(r)\chi_{\overline{\Lambda}}(\hat{\mathbf{r}}), \end{aligned} \tag{8.28}$$

which can be written in the form

$$\begin{aligned} c\hbar\frac{\partial}{\partial r}\psi^b(r) &= -c\hbar\frac{1-\kappa}{r}\psi^b(r)-\left(W-mc^2\right)\psi^t(r) \\ c\hbar\frac{\partial}{\partial r}\psi^t(r) &= -c\hbar\frac{1+\kappa}{r}\psi^t(r)+\left(W+mc^2\right)\psi^b(r). \end{aligned} \tag{8.29}$$

At this point the choice of the form assumed for the solution in the beginning becomes plausible: inserting the i in the second component eventually yields two real (i.e. non-complex) equations.

The next step is to make the substitutions

$$u_1(r) := r\psi^t(r),\ u_2(r) := r\psi^b(r), \tag{8.30}$$

yielding the equations

$$\begin{aligned} c\hbar\frac{\partial}{\partial r}\left(\frac{1}{r}u_2(r)\right) &= -c\hbar\frac{1-\kappa}{r^2}u_2(r)-\frac{(W-mc^2)}{r}u_1(r) \\ c\hbar\frac{\partial}{\partial r}\left(\frac{1}{r}u_1(r)\right) &= -c\hbar\frac{1+\kappa}{r^2}u_1(r)+\frac{(W+mc^2)}{r}u_2(r). \end{aligned} \tag{8.31}$$

After multiplying both equations by r and computing the differentiations, the second order differential terms cancel out, leaving the equations

$$\begin{aligned} \frac{\partial}{\partial r}u_2(r) &= \frac{\kappa}{r}u_2(r)-\frac{1}{c\hbar}\left(W-mc^2\right)u_1(r) \\ \frac{\partial}{\partial r}u_1(r) &= -\frac{\kappa}{r}u_1(r)+\frac{1}{c\hbar}\left(W+mc^2\right)u_2(r). \end{aligned} \tag{8.32}$$

This system of two linear first order differential equations can be rewritten into one second order equation. To do so, the second equation of (8.32) is rearranged:

$$u_2(r) = \frac{c\hbar}{W+mc^2}\left(\frac{\partial}{\partial r}u_1(r)+\frac{\kappa}{r}u_1(r)\right). \tag{8.33}$$

The obtained expression for u_2 is then inserted into the first equation:

$$\frac{c\hbar}{W+mc^2}\frac{\partial}{\partial r}\left(\frac{\partial}{\partial r}u_1(r)+\frac{\kappa}{r}u_1(r)\right)=\frac{c\hbar}{W+mc^2}\frac{\kappa}{r}\left(\frac{\partial}{\partial r}u_1(r)+\frac{\kappa}{r}u_1(r)\right)-\frac{W-mc^2}{c\hbar}u_1(r). \tag{8.34}$$

After computing the differentiation, this equation can be simplified to

$$\frac{\partial^2}{\partial r^2}u_1(r)-\frac{\kappa+\kappa^2}{r^2}u_1(r)+\frac{W^2-m^2c^4}{c^2\hbar^2}u_1(r)=0. \tag{8.35}$$

Inserting the relation (8.10) and multiplying the whole equation by r^2 it can be rewritten as

$$r^2\frac{\partial^2}{\partial r^2}u_1(r)+\left((kr)^2-\kappa(\kappa+1)\right)u_1(r)=0. \tag{8.36}$$

Resubstituting $u_1=r\psi^t$ and $u_2=r\psi^b$ yields

$$r^2\frac{\partial^2}{\partial r^2}r\psi^t(r)+\left((kr)^2-\kappa(\kappa+1)\right)r\psi^t(r) = 0 \tag{8.37}$$

$$\iff r^2\frac{\partial^2}{\partial r^2}\psi^t(r)+2r\frac{\partial}{\partial r}\psi^t(r)+\left((kr)^2-\kappa(\kappa+1)\right)\psi^t(r) = 0, \tag{8.38}$$

where $r\neq 0$ is required to divide the equation by r.

Equation (8.38) is known as the *Bessel differential equation*, cf. the digression on page 28. Its solutions are given by $j_l(kr)$ and $n_l(kr)$ and all linear combinations of these two functions. Here j_l denote spherical Bessel functions and n_l are spherical Neumann functions. The latter can be defined using spherical Hankel functions h_l and the relation $h_l=j_l+in_l$, cf. the digression on page 27. The spherical Bessel functions $j_l(kr)$ are regular, i.e. $j_l(kr)\to 0$ as $r\to 0$, whereas $n_l(kr)$ are irregular, i.e. they diverge. Consequently, they are called the regular and irregular solution respectively.

After the solution for ψ^t is known, the second component ψ^b can be calculated by using equation (8.33):

$$u_2(r) = \frac{c\hbar}{W+mc^2}\left(\frac{\partial}{\partial r}u_1(r)+\frac{\kappa}{r}u_1(r)\right) \tag{8.39}$$

$$\iff r\psi^b(r) = \frac{c\hbar}{W+mc^2}\left(\frac{\partial}{\partial r}+\frac{\kappa}{r}\right)r\psi^t(r) \tag{8.40}$$

$$\iff \psi^b(r) = \frac{c\hbar}{W+mc^2}\frac{1}{r}\left(\frac{\partial}{\partial r}+\frac{\kappa}{r}\right)rw_l(kr). \tag{8.41}$$

Here $w_l=j_l$ for the regular solution or $w_l=n_l$ for the irregular solution. In both cases, and also for $w_l=h_l$, the differentiation can be expressed by a recursion relation:

$$\frac{d}{dr}w_l(kr) = kw_{l-1}(kr)-\frac{l+1}{r}w_l(kr) \tag{8.42}$$

$$= \frac{l}{r}w_l(kr)-kw_{l+1}(kr) \tag{8.43}$$

Using equations (7.58) and (7.62), it follows that

$$\bar{l} = \begin{cases} l-1 & \text{if } \kappa > 0 \\ l+1 & \text{if } \kappa < 0. \end{cases} \tag{8.44}$$

Now, in the case $\kappa > 0$ it is convenient to work with eq. (8.42). Using eq. (7.58) it follows that $l = \kappa$, and the recursion can be written as

$$\frac{d}{dr} w_l(kr) = k w_{\bar{l}}(kr) - \frac{\kappa+1}{r} w_l(kr). \tag{8.45}$$

On the other hand, in the case $\kappa < 0$ it is convenient to work with eq. (8.43) and from (7.58) it follows that $l = -\kappa - 1$. Hence, this recursion can be written as

$$\frac{d}{dr} w_l(kr) = -\frac{\kappa+1}{r} w_l(kr) - k w_{\bar{l}}(kr). \tag{8.46}$$

Comparing that to the first case $\kappa > 0$, one notes that the two cases only differ by a sign. Therefore, an expression valid for both cases is

$$\frac{d}{dr} w_l(kr) = \text{sign}(\kappa) k w_{\bar{l}}(kr) - \frac{\kappa+1}{r} w_l(kr). \tag{8.47}$$

This recursion relation is now inserted into eq. (8.41):

$$\begin{aligned} \psi^b(\mathbf{r}) &= \frac{c\hbar}{W+mc^2} \frac{1}{r} \left(\frac{\partial}{\partial r} + \frac{\kappa}{r} \right) r w_l(kr) \\ &= \frac{c\hbar}{W+mc^2} \left(\frac{\kappa+1}{r} w_l(kr) + \frac{\partial}{\partial r} w_l(kr) \right) \\ &= \frac{c\hbar}{W+mc^2} \left(\frac{\kappa+1}{r} w_l(kr) + \text{sign}(\kappa) k w_{\bar{l}}(kr) - \frac{\kappa+1}{r} w_l(kr) \right) \\ &= \frac{c\hbar}{W+mc^2} k \,\text{sign}(\kappa) w_{\bar{l}}(kr) \end{aligned} \tag{8.48}$$

Replacing w_l by j_l and n_l respectively yields the final result for the regular and irregular right-hand side solution of the free particle Dirac equation in angular momentum basis:

$$\psi^{\text{reg}}_\Lambda(\mathbf{r}) : \quad = \quad J_\Lambda(\mathbf{r}) := \begin{pmatrix} j_l(kr)\chi_\Lambda(\hat{\mathbf{r}}) \\ \frac{ikc\hbar \cdot \text{sign}(\kappa)}{W+mc^2} j_{\bar{l}}(kr)\chi_{\overline{\Lambda}}(\hat{\mathbf{r}}) \end{pmatrix} \tag{8.49}$$

$$\psi^{\text{irr}}_\Lambda(\mathbf{r}) : \quad = \quad N_\Lambda(\mathbf{r}) := \begin{pmatrix} n_l(kr)\chi_\Lambda(\hat{\mathbf{r}}) \\ \frac{ikc\hbar \cdot \text{sign}(\kappa)}{W+mc^2} n_{\bar{l}}(kr)\chi_{\overline{\Lambda}}(\hat{\mathbf{r}}) \end{pmatrix}. \tag{8.50}$$

Now we also wish to calculate the left-hand side solution. This is a simple task. Instead of the form of the solution in eq. (8.25) we start from

$$\overline{\psi}_\Lambda(\mathbf{r}) = \begin{pmatrix} \overline{\psi}^t(r)\chi^\dagger_\Lambda(\hat{\mathbf{r}}) & -i\overline{\psi}^b(r)\chi^\dagger_{\overline{\Lambda}}(\hat{\mathbf{r}}) \end{pmatrix}. \tag{8.51}$$

Performing the same steps as in the previous case eventually results in the equation system (8.28). Hence

$$\overline{\psi}^{t}(r) = \psi^{t}(r),\ \overline{\psi}^{b}(r) = \psi^{b}(r) \tag{8.52}$$

and therefore the result is:

$$\overline{\psi}^{\mathrm{reg}}_{\Lambda}(\mathbf{r}) := \overline{J}_{\Lambda}(\mathbf{r}) := \begin{pmatrix} j_l(kr)\chi^{\dagger}_{\Lambda}(\hat{\mathbf{r}}) & -\frac{ikc\hbar\cdot\mathrm{sign}(\kappa)}{W+mc^2} j_{\bar{l}}(kr)\chi^{\dagger}_{\overline{\Lambda}}(\hat{\mathbf{r}}) \end{pmatrix} \tag{8.53}$$

$$\overline{\psi}^{\mathrm{irr}}_{\Lambda}(\mathbf{r}) := \overline{N}_{\Lambda}(\mathbf{r}) := \begin{pmatrix} n_l(kr)\chi^{\dagger}_{\Lambda}(\hat{\mathbf{r}}) & -\frac{ikc\hbar\cdot\mathrm{sign}(\kappa)}{W+mc^2} n_{\bar{l}}(kr)\chi^{\dagger}_{\overline{\Lambda}}(\hat{\mathbf{r}}) \end{pmatrix}. \tag{8.54}$$

As the Hankel functions h_l are a linear combination of Bessel and Neumann functions, it is also possible to use a basis of Bessel and Hankel functions instead[22]:

An alternative basis for the left-hand side solution of the free particle Dirac equation in an angular momentum basis is given by

$$J_{\Lambda}(\mathbf{r}) := \begin{pmatrix} j_l(kr)\chi_{\Lambda}(\hat{\mathbf{r}}) \\ \frac{ikc\hbar\cdot\mathrm{sign}(\kappa)}{W+mc^2} j_{\bar{l}}(kr)\chi_{\overline{\Lambda}}(\hat{\mathbf{r}}) \end{pmatrix} \tag{8.55}$$

$$H_{\Lambda}(\mathbf{r}) := \begin{pmatrix} n_l(kr)\chi_{\Lambda}(\hat{\mathbf{r}}) \\ \frac{ikc\hbar\cdot\mathrm{sign}(\kappa)}{W+mc^2} n_{\bar{l}}(kr)\chi_{\overline{\Lambda}}(\hat{\mathbf{r}}) \end{pmatrix}. \tag{8.56}$$

$$\overline{J}_{\Lambda}(\mathbf{r}) := \begin{pmatrix} j_l(kr)\chi^{\dagger}_{\Lambda}(\hat{\mathbf{r}}) & -\frac{ikc\hbar\cdot\mathrm{sign}(\kappa)}{W+mc^2} j_{\bar{l}}(kr)\chi^{\dagger}_{\overline{\Lambda}}(\hat{\mathbf{r}}) \end{pmatrix} \tag{8.57}$$

$$\overline{H}_{\Lambda}(\mathbf{r}) := \begin{pmatrix} h_l(kr)\chi^{\dagger}_{\Lambda}(\hat{\mathbf{r}}) & -\frac{ikc\hbar\cdot\mathrm{sign}(\kappa)}{W+mc^2} h_{\bar{l}}(kr)\chi^{\dagger}_{\overline{\Lambda}}(\hat{\mathbf{r}}) \end{pmatrix}. \tag{8.58}$$

This representation is the one that will be used from now on.

8.3 Angular Momentum Expansion of a Dirac Plane Wave

The Dirac plane waves from section 8.1 can be expanded in an angular momentum representation using the results from section 8.2. This is useful in order to express them in terms of spin spherical harmonics χ_{Λ}, which are eigenfunctions of the spin-orbit operator, rather than in terms of spinors ϕ_{m_s}. Once the results for the Dirac plane waves have been obtained, these results can further be used to derive an angular momentum expansion of the free particle Green function.

We start with the expression for the plane wave, eq. (8.15):

$$\psi_{\mathbf{k}m_s}(\mathbf{r}) = \left(\frac{W+mc^2}{2W}\right)^{\frac{1}{2}} \begin{pmatrix} \phi_{m_s} \\ \frac{c\hbar\boldsymbol{\sigma}\mathbf{k}}{W+mc^2}\phi_{m_s} \end{pmatrix} \mathrm{e}^{i\mathbf{kr}}. \tag{8.59}$$

The strategy is to write the term $\phi_{m_s}\mathrm{e}^{i\mathbf{kr}}$ as

$$\phi_{m_s}\mathrm{e}^{i\mathbf{kr}} = \sum_{\Lambda} a_{\Lambda} j_l(kr)\chi_{\Lambda}(\hat{\mathbf{r}}) \tag{8.60}$$

[22] This is a convention in the Jülich KKR group, the representation with Neumann functions, however, can equally well be used.

and determine the coefficients a_Λ fulfilling this relation. To do so, the equation is multiplied by $\chi_\Lambda^\dagger$ and then we integrate over $\hat{\mathbf{r}}$:

$$\int d\hat{\mathbf{r}}\chi_\Lambda^\dagger(\hat{\mathbf{r}})\phi_{m_s}\mathrm{e}^{i\mathbf{kr}} = \sum_{\Lambda'}\left[\int d\hat{\mathbf{r}}\chi_\Lambda^\dagger(\hat{\mathbf{r}})\chi_{\Lambda'}(\hat{\mathbf{r}})\right] a_{\Lambda'}j_{l'}(kr). \tag{8.61}$$

Using the orthonormality of the spin spherical harmonics, eq. (7.73), the term in square brackets simplifies to $\delta_{\Lambda\Lambda'}$, thus yielding the expression

$$\int d\hat{\mathbf{r}}\chi_\Lambda^\dagger(\hat{\mathbf{r}})\phi_{m_s}\mathrm{e}^{i\mathbf{kr}} = a_\Lambda j_l(kr). \tag{8.62}$$

Using the definition of the spin spherical harmonics eq. (7.60), $\chi_\Lambda^\dagger$ can be rewritten as

$$\chi_\Lambda^\dagger(\hat{\mathbf{r}}) = \sum_{m_s=\pm1/2} C(l,j,\frac{1}{2}|\mu-m_s,m_s)Y^*_{l,\mu-m_s}(\hat{\mathbf{r}})\phi^\dagger_{m_s}. \tag{8.63}$$

Inserting this into eq. (8.62) gives

$$\begin{aligned} a_\Lambda j_l(kr) &= \sum_{m_s'=\pm1/2} C(l,j,\frac{1}{2}|\mu-m_s',m_s')\int d\hat{\mathbf{r}}Y^*_{l,\mu-m_s'}(\hat{\mathbf{r}})\mathrm{e}^{i\mathbf{kr}}\underbrace{\phi^\dagger_{m_s'}\phi_{m_s}}_{\delta_{m_s'm_s}} \\ &= C(l,j,\frac{1}{2}|\mu-m_s,m_s)\int d\hat{\mathbf{r}}Y^*_{l,\mu-m_s}(\hat{\mathbf{r}})\mathrm{e}^{i\mathbf{kr}}, \end{aligned} \tag{8.64}$$

where in the second step the orthonormality of the spinors ϕ_{m_s} has been used.

For the term $\mathrm{e}^{i\mathbf{kr}}$ we already know an expansion from eq. (4.16):

$$\mathrm{e}^{i\mathbf{kr}} = 4\pi\sum_L i^l Y_L^*(\hat{\mathbf{k}})Y_L(\hat{\mathbf{r}})j_l(kr). \tag{8.65}$$

Inserting this into eq. (8.64) yields

$$\begin{aligned} a_\Lambda j_l(kr) &= 4\pi\sum_{l',m'} i^{l'}j_{l'}(kr)C(l,j,\frac{1}{2}|\mu-m_s,m_s)Y^*_{l',m'}(\hat{\mathbf{k}})\underbrace{\int d\hat{\mathbf{r}}Y^*_{l,\mu-m_s}(\hat{\mathbf{r}})Y_{l',m'}(\hat{\mathbf{r}})}_{\delta_{l',l}\delta_{m',\mu-m_s}} \\ &= 4\pi i^l j_l(kr)C(l,j,\frac{1}{2}|\mu-m_s,m_s)Y^*_{l,\mu-m_s}(\hat{\mathbf{k}}) \end{aligned} \tag{8.66}$$

Hence

$$a_\Lambda = 4\pi i^l C(l,j,\frac{1}{2}|\mu-m_s,m_s)Y^*_{l,\mu-m_s}(\hat{\mathbf{k}}). \tag{8.67}$$

This can be inserted into eq. (8.60), yielding

$$\phi_{m_s}\mathrm{e}^{i\mathbf{kr}} = \sum_\Lambda 4\pi i^l C(l,j,\frac{1}{2}|\mu-m_s,m_s)Y^*_{l,\mu-m_s}(\hat{\mathbf{k}})j_l(kr)\chi_\Lambda(\hat{\mathbf{r}}). \tag{8.68}$$

So far we found an expansion for the first component of the Dirac plane wave. The next step is to find an expansion for the second component, i.e. for the term $(\boldsymbol{\sigma}\mathbf{k})\,\phi_{m_s}\mathrm{e}^{i\mathbf{kr}}$. Since ϕ_{m_s} is a constant two-component vector, it is a simple consequence of eq. (8.4) that

$$\hbar\,(\boldsymbol{\sigma}\mathbf{k})\,\phi_{m_s}\mathrm{e}^{i\mathbf{kr}} = (\boldsymbol{\sigma}\hat{\mathbf{p}})\,\phi_{m_s}\mathrm{e}^{i\mathbf{kr}}. \tag{8.69}$$

Using eq. (7.34) we can write it as

$$(\boldsymbol{\sigma}\hat{\mathbf{p}})\,\phi_{m_s}\mathrm{e}^{i\mathbf{kr}} = -i\sigma_r\left(\hbar\frac{\partial}{\partial r}+\frac{\hbar}{r}+\frac{\hat{K}}{r}\right)\phi_{m_s}\mathrm{e}^{i\mathbf{kr}}. \tag{8.70}$$

In order to obtain an expansion like eq. (8.68), the question is how the $\boldsymbol{\sigma}\hat{\mathbf{p}}$ operator acts on $j_l(kr)\chi_\Lambda(\hat{\mathbf{r}})$. We know

$$\boldsymbol{\sigma}\hat{\mathbf{p}}j_l(kr)\chi_\Lambda(\hat{\mathbf{r}}) = -i\sigma_r\left(\hbar\frac{\partial}{\partial r}+\frac{\hbar}{r}+\frac{\hat{K}}{r}\right)j_l(kr)\chi_\Lambda(\hat{\mathbf{r}}) \tag{8.71}$$

and want to find the eigenvalues of this operator. Thus, let us look at the different parts of this expression:

- By using eq. (8.47) we know that

$$\hbar\frac{\partial}{\partial r}j_l(kr)\chi_\Lambda(\hat{\mathbf{r}}) = \hbar\left(\mathrm{sign}(\kappa)kj_{\bar{l}}(kr)-\frac{\kappa+1}{r}j_l(kr)\right)\chi_\Lambda(\hat{\mathbf{r}}). \tag{8.72}$$

- $\hat{K}$ acts only on the spherical part of a function, as it can be expressed in terms of the angular momentum operator $\hat{L}$, which only contains angular derivatives in spherical coordinates. Hence we get

$$\begin{aligned}\frac{\hat{K}}{r}j_l(kr)\chi_\Lambda(\hat{\mathbf{r}}) &= \frac{1}{r}j_l(kr)\hat{K}\chi_\Lambda(\hat{\mathbf{r}})\\ &= \frac{\hbar\kappa}{r}j_l(kr)\chi_\Lambda(\hat{\mathbf{r}}).\end{aligned} \tag{8.73}$$

Inserting these two results yields

$$\begin{aligned}\boldsymbol{\sigma}\hat{\mathbf{p}}j_l(kr)\chi_\Lambda(\hat{\mathbf{r}}) &= -i\sigma_r\hbar\left(\mathrm{sign}(\kappa)kj_{\bar{l}}(kr)-\frac{\kappa+1}{r}j_l(kr)+\frac{1}{r}j_l(kr)+\frac{\kappa}{r}j_l(kr)\right)\chi_\Lambda(\hat{\mathbf{r}})\\ &= -i\sigma_r\hbar\left(\mathrm{sign}(\kappa)kj_{\bar{l}}(kr)\right)\chi_\Lambda(\hat{\mathbf{r}}).\end{aligned} \tag{8.74}$$

Applying eq. (8.23) this becomes

$$\boldsymbol{\sigma}\hat{\mathbf{p}}j_l(kr)\chi_\Lambda(\hat{\mathbf{r}}) = i\hbar k\mathrm{sign}(\kappa)\cdot j_{\bar{l}}(kr)\chi_{\bar{\Lambda}}(\hat{\mathbf{r}}). \tag{8.75}$$

Now we can rewrite the expression for the plane wave:

$$\begin{aligned}\psi_{\mathbf{k}m_s}(\mathbf{r}) &= \left(\frac{W+mc^2}{2W}\right)^{\frac{1}{2}}\begin{pmatrix}\phi_{m_s}\\ \frac{c\hbar\boldsymbol{\sigma}\mathbf{k}}{W+mc^2}\phi_{m_s}\end{pmatrix}\mathrm{e}^{i\mathbf{kr}} \qquad (8.76)\\ &\overset{\text{Gl. (8.68)}}{=} \left(\frac{W+mc^2}{2W}\right)^{\frac{1}{2}}\sum_\Lambda 4\pi i^l C(l,j,\frac{1}{2}|\mu-m_s,m_s)Y^*_{l,\mu-m_s}(\hat{\mathbf{k}})\\ &\qquad\cdot\begin{pmatrix}j_l(kr)\chi_\Lambda(\hat{\mathbf{r}})\\ \frac{c\hbar\boldsymbol{\sigma}\mathbf{k}}{W+mc^2}\phi_{m_s}j_l(kr)\chi_\Lambda(\hat{\mathbf{r}})\end{pmatrix}\\ &\overset{\text{Gl. (8.75)}}{=} \left(\frac{W+mc^2}{2W}\right)^{\frac{1}{2}}\sum_\Lambda 4\pi i^l C(l,j,\frac{1}{2}|\mu-m_s,m_s)Y^*_{l,\mu-m_s}(\hat{\mathbf{k}})\\ &\qquad\cdot\begin{pmatrix}j_l(kr)\chi_\Lambda(\hat{\mathbf{r}})\\ \frac{ikc\hbar\cdot\mathrm{sign}(\kappa)}{W+mc^2}j_{\bar{l}}(kr)\chi_{\bar{\Lambda}}(\hat{\mathbf{r}})\end{pmatrix}.\end{aligned}$$

By using the definition eq. (8.55) of the functions J_Λ, this simplifies to the final result:

Angular momentum expansion of a Dirac plane wave:

$$\psi_{\mathbf{k}m_s}(\mathbf{r}) = \left(\frac{W+mc^2}{2W}\right)^{\frac{1}{2}} \sum_\Lambda 4\pi i^l C(l,j,\frac{1}{2}|\mu-m_s,m_s) Y^*_{l,\mu-m_s}(\hat{\mathbf{k}}) J_\Lambda(\mathbf{r}). \tag{8.77}$$

9 Free Particle Green Function

The Green function of the free particle is vital for setting up Lippmann-Schwinger equations. It is a 4×4 matrix that can be expressed in terms of the solutions of the free Dirac equation, namely spinors containing Bessel and Hankel functions (the radial part) multiplied by spin spherical harmonics (the angular part).

9.1 Derivation

We have seen in chapter 4 how the Green function of the potential free Schrödinger equation is derived. This expression will be useful when deriving the Green function of the Dirac equation, which will be derived now.

Starting point, of course, is the free particle Dirac Hamiltonian $\hat{H}_0$ as defined in eq. (8.1). For the stationary Dirac equation of the free electron

$$\hat{H}_0 \psi(\mathbf{r}) = W \mathrm{I}_4 \psi(\mathbf{r}) \tag{9.1}$$

the corresponding Green function is defined by

$$\left(\hat{H}_0 - W\mathrm{I}_4\right) G^0(\mathbf{r}, \mathbf{r}'; W) = -\delta(\mathbf{r} - \mathbf{r}')\mathrm{I}_4. \tag{9.2}$$

What will be shown in this section is the following proposition:

Once the non-relativistic free particle Green function G^0_{nr} is known, the relativistic one can be constructed from it by

$$G^0(\mathbf{r}, \mathbf{r}', W) = \frac{1}{2mc^2}\left(\hat{H}_0 + W\mathrm{I}_4\right) G^0_{nr}(\mathbf{r}, \mathbf{r}'; E) \tag{9.3}$$

$$\overset{\text{eq. (4.15) and (8.1)}}{=} - \frac{1}{c^2\hbar^2}\left(c\boldsymbol{\alpha}\hat{\mathbf{p}} + \beta mc^2 + W\mathrm{I}_4\right) \frac{\mathrm{e}^{ik|\mathbf{r}-\mathbf{r}'|}}{4\pi|\mathbf{r}-\mathbf{r}'|}. \tag{9.4}$$

Proof: To verify the statement let us first look at the following identity:

$$\begin{aligned}\left(\hat{H}_0 - W\mathrm{I}_4\right)\left(\hat{H}_0 + W\mathrm{I}_4\right) &= \hat{H}_0^2 - W^2\mathrm{I}_4 \\ &= c^2\left(\boldsymbol{\alpha}\hat{\mathbf{p}}\right)^2 + mc^3\left(\boldsymbol{\alpha}\hat{\mathbf{p}}\beta + \beta\boldsymbol{\alpha}\hat{\mathbf{p}}\right) + m^2c^4\beta^2 - W^2\mathrm{I}_4.\end{aligned} \tag{9.5}$$

We will simplify this term by term:

- Eq. (8.9), together with eq. (8.4), yields:

$$c^2\left(\boldsymbol{\alpha}\hat{\mathbf{p}}\right)^2 = c^2\hat{\mathbf{p}}^2 = c^2\left(-i\hbar\nabla\right)^2 = -c^2\hbar^2\Delta. \tag{9.6}$$

- It is easy to verify that for any 4×4 matrix

$$M = \begin{pmatrix} m_{11} & m_{12} \\ m_{21} & m_{22} \end{pmatrix}, \tag{9.7}$$

where the matrix elements m_{ij} themselves are 2×2 matrices, the following identity holds:

$$\beta M + M\beta = 2 \begin{pmatrix} m_{11} & 0 \\ 0 & -m_{22} \end{pmatrix}. \tag{9.8}$$

Thus, using expression (7.35) and putting $M = \boldsymbol{\alpha}\hat{\mathbf{p}}$ it follows

$$\boldsymbol{\alpha}\hat{\mathbf{p}}\beta + \beta\boldsymbol{\alpha}\hat{\mathbf{p}} = 0. \tag{9.9}$$

- The β matrix fulfils $\beta^2 = \mathrm{I}_4$.

Using these three identities we conclude

$$\begin{aligned} \left(\hat{H}_0 - W\mathrm{I}_4\right)\left(\hat{H}_0 + W\mathrm{I}_4\right) &= - \; c^2\hbar^2\Delta\mathrm{I}_4 + \left(m^2c^4 - W\right)\mathrm{I}_4 \\ &= - \; c^2\hbar^2\left(\Delta + k^2\right)\mathrm{I}_4 \end{aligned} \tag{9.10}$$

where in the second step eq. (8.10) has been inserted. Now we use the definition of the non-relativistic Green function in eq. (4.4) and insert an identity matrix I_4 on both sides of the equation:

$$\frac{\hbar^2}{2m}\left(\Delta + k^2\right)\mathrm{I}_4 G^0_{nr}(\mathbf{r}, \mathbf{r}'; E) = \mathrm{I}_4\delta(\mathbf{r} - \mathbf{r}'). \tag{9.11}$$

Replacing the term $\Delta + k^2$ in this equation with the result from eq. (9.10) yields

$$\frac{1}{2mc^2}\left(\hat{H}_0 - W\mathrm{I}_4\right)\left(\hat{H}_0 + W\mathrm{I}_4\right) G^0_{nr}(\mathbf{r}, \mathbf{r}'; E) = -\mathrm{I}_4\delta(\mathbf{r} - \mathbf{r}'). \tag{9.12}$$

Comparing that with the definition of the relativistic Green function G^0 in eq. (9.2) we obtain the result

$$G^0(\mathbf{r}, \mathbf{r}'; W) = \frac{1}{2mc^2}\left(\hat{H}_0 + W\mathrm{I}_4\right) G^0_{nr}(\mathbf{r}, \mathbf{r}'; E). \tag{9.13}$$

This completes the proof and forms an efficient way of calculating G^0. Note that G^0 no longer is a scalar as in the non-relativistic case, but it is now a 4×4 matrix.

9.2 Angular Momentum Expansion

The step is to find an angular momentum expansion of the free electron Green function. We recall the corresponding expansion in the non-relativistic case, eq. (4.28):

$$G^0_{nr}(\mathbf{r}, \mathbf{r}'; E) = -ik\frac{2m}{\hbar^2}\sum_L Y_L(\hat{\mathbf{r}})Y^*_L(\hat{\mathbf{r}}')j_l(kr_<)h_l(kr_>). \tag{9.14}$$

First let us consider the case $r > r'$, meaning that this equation reads as

$$G^0_{nr}(\mathbf{r}, \mathbf{r}'; E) = -ik\frac{2m}{\hbar^2}\sum_L Y_L(\hat{\mathbf{r}})Y^*_L(\hat{\mathbf{r}}')j_l(kr')h_l(kr). \tag{9.15}$$

In the previous section we derived a way to express the relativistic free particle Green function in terms of the non-relativistic one, eq. (9.3). Inserting the expression above into this equation we get

$$G^0(\mathbf{r},\mathbf{r}';W) = -\frac{ik}{c^2\hbar^2}\left(\hat{H}_0 + W\mathrm{I}_4\right)\sum_L Y_L(\hat{\mathbf{r}})Y_L^*(\hat{\mathbf{r}}')j_l(kr')h_l(kr). \tag{9.16}$$

Now we rewrite the term $\hat{H}_0 + W\mathrm{I}_4$ into a matrix form:

$$\begin{aligned}\hat{H}_0 + W\mathrm{I}_4 &= c\boldsymbol{\alpha}\hat{\mathbf{p}} + \beta mc^2 + W\mathrm{I}_4 \\ &= \begin{pmatrix} 0 & c\boldsymbol{\sigma}\hat{\mathbf{p}} \\ c\boldsymbol{\sigma}\hat{\mathbf{p}} & 0 \end{pmatrix} + \begin{pmatrix} mc^2\mathrm{I}_2 & 0 \\ 0 & -mc^2\mathrm{I}_2 \end{pmatrix} + \begin{pmatrix} W\mathrm{I}_2 & 0 \\ 0 & W\mathrm{I}_2 \end{pmatrix} \\ &= \begin{pmatrix} (W+mc^2)\,\mathrm{I}_2 & c\boldsymbol{\sigma}\hat{\mathbf{p}} \\ c\boldsymbol{\sigma}\hat{\mathbf{p}} & (W-mc^2)\,\mathrm{I}_2 \end{pmatrix}. \end{aligned} \tag{9.17}$$

Inserting this into the equation above we find a convenient form of the Green function G^0 (which is a 4×4 matrix) as a 2×2 matrix where its four entries G^0_{ij} itself are 2×2 matrices, too:

$$\begin{aligned} G^0(\mathbf{r},\mathbf{r}';W) &= -\frac{ik}{c^2\hbar^2}\begin{pmatrix} (W+mc^2)\,\mathrm{I}_2 & c\boldsymbol{\sigma}\hat{\mathbf{p}} \\ c\boldsymbol{\sigma}\hat{\mathbf{p}} & (W-mc^2)\,\mathrm{I}_2 \end{pmatrix}\sum_L Y_L(\hat{\mathbf{r}})Y_L^*(\hat{\mathbf{r}}')j_l(kr')h_l(kr) \\ &=: \begin{pmatrix} G^0_{11}(\mathbf{r},\mathbf{r}';W) & G^0_{12}(\mathbf{r},\mathbf{r}';W) \\ G^0_{21}(\mathbf{r},\mathbf{r}';W) & G^0_{22}(\mathbf{r},\mathbf{r}';W) \end{pmatrix} \end{aligned} \tag{9.18}$$

Now let us calculate the matrix elements one by one.

1. G^0_{11}: As defined above, it is

$$G^0_{11}(\mathbf{r},\mathbf{r}';W) = -\frac{ik}{c^2\hbar^2}\left(W+mc^2\right)\mathrm{I}_2\sum_L Y_L(\hat{\mathbf{r}})Y_L^*(\hat{\mathbf{r}}')j_l(kr')h_l(kr). \tag{9.19}$$

   Using eq. (7.74) we can replace the spherical harmonics by spin spherical harmonics:

$$\begin{aligned} G^0_{11}(\mathbf{r},\mathbf{r}';W) &= -\frac{ik}{c^2\hbar^2}\left(W+mc^2\right)\sum_l\left(\mathrm{I}_2\sum_m Y_{l,m}(\hat{\mathbf{r}})Y^*_{l,m}(\hat{\mathbf{r}}')\right)j_l(kr')h_l(kr) \\ &= -\frac{ik}{c^2\hbar^2}\left(W+mc^2\right)\sum_l\left(\sum_{j,\mu}\chi_\Lambda(\hat{\mathbf{r}})\chi^\dagger_\Lambda(\hat{\mathbf{r}}')\right)j_l(kr')h_l(kr) \\ &= -\frac{ik}{c^2\hbar^2}\left(W+mc^2\right)\sum_\Lambda j_l(kr')h_l(kr)\chi_\Lambda(\hat{\mathbf{r}})\chi^\dagger_\Lambda(\hat{\mathbf{r}}') \end{aligned} \tag{9.20}$$

2. G^0_{12}: Completely analogously to the first case, we can directly write

$$G^0_{12}(\mathbf{r},\mathbf{r}';W) = -\frac{ik}{c^2\hbar^2}c\boldsymbol{\sigma}\hat{\mathbf{p}}\sum_\Lambda j_l(kr')h_l(kr)\chi_\Lambda(\hat{\mathbf{r}})\chi^\dagger_\Lambda(\hat{\mathbf{r}}'). \tag{9.21}$$

   Now, using eq. (8.75) but replacing j_l by h_l (which is legitimate, because the equation is valid for $w_l = j_l, h_l, n_l$ as it can be seen from its derivation) we have

$$\boldsymbol{\sigma}\hat{\mathbf{p}}h_l(kr)\chi_\Lambda(\hat{\mathbf{r}}) = i\hbar k\,\mathrm{sign}(\kappa)\cdot h_{\bar{l}}(kr)\chi_{\overline{\Lambda}}(\hat{\mathbf{r}}). \tag{9.22}$$

Inserting this yields for the Green function:

$$G^0_{12}(\mathbf{r},\mathbf{r}';W) = \frac{k^2}{c\hbar}\sum \mathrm{sign}(\kappa)_\Lambda j_l(kr')h_{\bar{l}}(kr)\chi_{\overline{\Lambda}}(\hat{\mathbf{r}})\chi^\dagger_\Lambda(\hat{\mathbf{r}}'). \tag{9.23}$$

For the sake of a simpler notation later on, it is convenient to perform the following renaming:

$$\kappa \to -\kappa.$$

As the sum includes all values of κ, this does not change anything. Consequences of this renaming are:

$$\begin{aligned} \Lambda &\to \overline{\Lambda}, \quad \overline{\Lambda} \to \Lambda \\ l &\to \bar{l}, \quad \bar{l} \to l \\ \mathrm{sign}(\kappa) &\to -\mathrm{sign}(\kappa). \end{aligned}$$

Applying this to eq. (9.23) yields

$$G^0_{12}(\mathbf{r},\mathbf{r}';W) = -\frac{k^2}{c\hbar}\sum_\Lambda \mathrm{sign}(\kappa) j_{\bar{l}}(kr')h_l(kr)\chi_\Lambda(\hat{\mathbf{r}})\chi^\dagger_{\overline{\Lambda}}(\hat{\mathbf{r}}'). \tag{9.24}$$

3. G^0_{21}: This element is identical to G^0_{12}, thus we copy the result from eq. (9.23):

$$G^0_{21}(\mathbf{r},\mathbf{r}';W) = \frac{k^2}{c\hbar}\sum_\Lambda \mathrm{sign}(\kappa) j_l(kr')h_{\bar{l}}(kr)\chi_{\overline{\Lambda}}(\hat{\mathbf{r}})\chi^\dagger_\Lambda(\hat{\mathbf{r}}') \tag{9.25}$$

4. G^0_{22}: This can be adopted from the first case without any changes, except for one minus sign instead of a plus:

$$G^0_{22}(\mathbf{r},\mathbf{r}';W) = -\frac{ik}{c^2\hbar^2}\left(W - mc^2\right)\sum_\Lambda j_l(kr')h_l(kr)\chi_\Lambda(\hat{\mathbf{r}})\chi^\dagger_\Lambda(\hat{\mathbf{r}}'). \tag{9.26}$$

Again, for the sake of a simpler notation later on, we rename as in point 2, yielding:

$$G^0_{22}(\mathbf{r},\mathbf{r}';W) = -\frac{ik}{c^2\hbar^2}\left(W - mc^2\right)\sum_\Lambda j_{\bar{l}}(kr')h_{\bar{l}}(kr)\chi_{\overline{\Lambda}}(\hat{\mathbf{r}})\chi^\dagger_{\overline{\Lambda}}(\hat{\mathbf{r}}'). \tag{9.27}$$

Combining the results from points 1 to 4 yields: $G^0(\mathbf{r},\mathbf{r}';W) =$

$$\begin{aligned} &-\frac{ik}{c^2\hbar^2}\sum_\Lambda \begin{pmatrix} \left(W+mc^2\right) h_l(kr)\chi_\Lambda(\hat{\mathbf{r}})j_l(kr')\chi^\dagger_\Lambda(\hat{\mathbf{r}}') & -ic\hbar k\,\mathrm{sign}(\kappa)h_l(kr)\chi_\Lambda(\hat{\mathbf{r}})j_{\bar{l}}(kr')\chi^\dagger_{\overline{\Lambda}}(\hat{\mathbf{r}}') \\ ic\hbar k\,\mathrm{sign}(\kappa)h_{\bar{l}}(kr)\chi_{\overline{\Lambda}}(\hat{\mathbf{r}})j_l(kr')\chi^\dagger_\Lambda(\hat{\mathbf{r}}') & \left(W-mc^2\right) h_{\bar{l}}(kr)\chi_{\overline{\Lambda}}(\hat{\mathbf{r}})j_{\bar{l}}(kr')\chi^\dagger_{\overline{\Lambda}}(\hat{\mathbf{r}}') \end{pmatrix} \\ =-&\frac{ik\left(W+mc^2\right)}{c^2\hbar^2}\sum_\Lambda \begin{pmatrix} h_l(kr)\chi_\Lambda(\hat{\mathbf{r}})j_l(kr')\chi^\dagger_\Lambda(\hat{\mathbf{r}}') & \frac{-ic\hbar k\,\mathrm{sign}(\kappa)}{\left(W+mc^2\right)}h_l(kr)\chi_\Lambda(\hat{\mathbf{r}})j_{\bar{l}}(kr')\chi^\dagger_{\overline{\Lambda}}(\hat{\mathbf{r}}') \\ \frac{ic\hbar k\,\mathrm{sign}(\kappa)}{\left(W+mc^2\right)}h_{\bar{l}}(kr)\chi_{\overline{\Lambda}}(\hat{\mathbf{r}})j_l(kr')\chi^\dagger_\Lambda(\hat{\mathbf{r}}') & \frac{c^2\hbar^2k^2}{\left(W+mc^2\right)^2}h_{\bar{l}}(kr)\chi_{\overline{\Lambda}}(\hat{\mathbf{r}})j_{\bar{l}}(kr')\chi^\dagger_{\overline{\Lambda}}(\hat{\mathbf{r}}') \end{pmatrix}. \end{aligned} \tag{9.28}$$

In the second step the component G^0_{22} was rewritten using eq. (8.10):

$$\left(W+mc^2\right)\left(W-mc^2\right) = W^2 - m^2c^4 = c^2\hbar^2k^2. \tag{9.29}$$

The matrix can be rewritten into a product of two vectors: $G^0(\mathbf{r},\mathbf{r}';W) =$

$$-\frac{(W+mc^2)}{c^2\hbar^2}ik\sum_{\Lambda}\begin{pmatrix} h_l(kr)\chi_\Lambda(\hat{\mathbf{r}}) \\ \frac{ic\hbar k\,\mathrm{sign}(\kappa)}{W+mc^2}h_{\bar{l}}(kr)\chi_{\overline{\Lambda}}(\hat{\mathbf{r}}) \end{pmatrix}\begin{pmatrix} j_l(kr')\chi^\dagger_\Lambda(\hat{\mathbf{r}}') & -\frac{ic\hbar k\,\mathrm{sign}(\kappa)}{W+mc^2}j_{\bar{l}}(kr')\chi^\dagger_{\overline{\Lambda}}(\hat{\mathbf{r}}') \end{pmatrix}. \tag{9.30}$$

Now recall the definitions in eqs. (8.55) to (8.58):

$$J_\Lambda(\mathbf{r}): = \begin{pmatrix} j_l(kr)\chi_\Lambda(\hat{\mathbf{r}}) \\ \frac{ikc\hbar\cdot\mathrm{sign}(\kappa)}{W+mc^2}j_{\bar{l}}(kr)\chi_{\overline{\Lambda}}(\hat{\mathbf{r}}) \end{pmatrix} \tag{9.31}$$

$$H_\Lambda(\mathbf{r}): = \begin{pmatrix} h_l(kr)\chi_\Lambda(\hat{\mathbf{r}}) \\ \frac{ikc\hbar\cdot\mathrm{sign}(\kappa)}{W+mc^2}h_{\bar{l}}(kr)\chi_{\overline{\Lambda}}(\hat{\mathbf{r}}) \end{pmatrix} \tag{9.32}$$

$$\overline{J}_\Lambda(\mathbf{r}): = \begin{pmatrix} j_l(kr)\chi^\dagger_\Lambda(\hat{\mathbf{r}}) & -\frac{ikc\hbar\cdot\mathrm{sign}(\kappa)}{W+mc^2}j_{\bar{l}}(kr)\chi^\dagger_{\overline{\Lambda}}(\hat{\mathbf{r}}) \end{pmatrix} \tag{9.33}$$

$$\overline{H}_\Lambda(\mathbf{r}): = \begin{pmatrix} h_l(kr)\chi^\dagger_\Lambda(\hat{\mathbf{r}}) & -\frac{ikc\hbar\cdot\mathrm{sign}(\kappa)}{W+mc^2}h_{\bar{l}}(kr)\chi^\dagger_{\overline{\Lambda}}(\hat{\mathbf{r}}) \end{pmatrix}. \tag{9.34}$$

Using these functions, the Green function can be written as

$$G^0(\mathbf{r},\mathbf{r}';W) = -\frac{(W+mc^2)}{c^2\hbar^2}ik\sum_{\Lambda}H_\Lambda(\mathbf{r})\overline{J}_\Lambda(\mathbf{r}') \qquad \text{for } r>r'. \tag{9.35}$$

For the case $r'>r$ analogous calculations yield

$$G^0(\mathbf{r},\mathbf{r}';W) = -\frac{(W+mc^2)}{c^2\hbar^2}ik\sum_{\Lambda}J_\Lambda(\mathbf{r})\overline{H}_\Lambda(\mathbf{r}') \qquad \text{for } r>r'. \tag{9.36}$$

So the final result is:

Expansion of the Green function for a free Dirac particle:

$$G^0(\mathbf{r},\mathbf{r}';W) = -ik\frac{(W+mc^2)}{c^2\hbar^2}\sum_{\Lambda}\left[\Theta(r-r')H_\Lambda(\mathbf{r})\overline{J}_\Lambda(\mathbf{r}')+\Theta(r'-r)J_\Lambda(\mathbf{r})\overline{H}_\Lambda(\mathbf{r}')\right] \tag{9.37}$$

10 Relativistic Lippmann-Schwinger Equations

This chapter contains the most important analytical work of this thesis: the derivation of an expansion of the potential matrix into a radial and an angular part and, thereafter, such a separation for the relativistic Lippmann-Schwinger equations including a full potential. Within the derivation I introduce what I call D coefficients. They form the relativistic analogue to the Gaunt coefficients in the non-relativistic case. The analytical results found form the basis of the Dirac single-site solver that I implemented.

10.1 Derivation

The derivation of the relativistic version of the Lippmann-Schwinger equation is for the most part analogous to the non-relativistic case. The only noteworthy difference is that there are now two equations instead of one – one for the right-hand side solution and another one for the left-hand side solution.

The analogues of eq. (5.1) are the two equations for the particular solutions:

$$\psi^{\text{partc}}(\mathbf{r}) = \mathrm{L}^{-1}V(\mathbf{r})\psi(\mathbf{r}) = \int d\mathbf{r}' G^0(\mathbf{r},\mathbf{r}';W)V(\mathbf{r}')\psi(\mathbf{r}') \tag{10.1}$$

$$\overline{\psi}^{\text{partc}}(\mathbf{r}) = \overline{\psi}(\mathbf{r})\left(\mathrm{L}^{-1}V(\mathbf{r})\right)^t = \int d\mathbf{r}' \overline{\psi}(\mathbf{r}')V(\mathbf{r}')G^0(\mathbf{r}',\mathbf{r};W) \tag{10.2}$$

where ψ and ψ^{partc} are 4×1 column vectors whereas $\overline{\psi}$ and $\overline{\psi}^{\text{partc}}$ are 1×4 row vectors. Note that the differential operator L as well as the potential V are 4×4 matrices. t denotes the transpose.

The general solutions ψ, $\overline{\psi}$ of the inhomogeneous equation system are given by the sum of one particular solutions ψ^{partc}, $\overline{\psi}^{\text{partc}}$ plus the set of solutions of the homogeneous system, $\{\psi^0_{\mathbf{k}m_s}\}$ and $\left\{\overline{\psi}^0_{\mathbf{k}m_s}\right\}$:

$$\psi_{\mathbf{k}m_s} = \psi^{\text{partc}} + \psi^0_{\mathbf{k}m_s} \tag{10.3}$$

$$\overline{\psi}_{\mathbf{k}m_s} = \overline{\psi}^{\text{partc}} + \overline{\psi}^0_{\mathbf{k}m_s}. \tag{10.4}$$

The latter are Dirac plane waves, as defined in equations (8.15) and (8.19). We note this result:

The relativistic Lippmann-Schwinger equations for the right-hand side and left-hand side solutions are

$$\psi_{\mathbf{k}m_s}(\mathbf{r}) = \psi^0_{\mathbf{k}m_s}(\mathbf{r}) + \int d\mathbf{r}' G^0(\mathbf{r},\mathbf{r}';W)V(\mathbf{r}')\psi_{\mathbf{k}m_s}(\mathbf{r}') \tag{10.5}$$

$$\overline{\psi}_{\mathbf{k}m_s}(\mathbf{r}) = \overline{\psi}^0_{\mathbf{k}m_s}(\mathbf{r}) + \int d\mathbf{r}' \overline{\psi}_{\mathbf{k}m_s}(\mathbf{r}')V(\mathbf{r}')G^0(\mathbf{r}',\mathbf{r};W), \tag{10.6}$$

where $\psi^0_{\mathbf{k}m_s}$ and $\overline{\psi}^0_{\mathbf{k}m_s}$ are Dirac plane waves, given by equations (8.15) and (8.19).

10.2 Angular Momentum Expansion of the Lippmann-Schwinger Equations

The starting point for deriving the angular momentum expansion of the relativistic Lippmann-Schwinger equation is the expansion of Dirac plane, see eq. (8.15)

$$\psi^0_{\mathbf{k}m_s}(\mathbf{r}) = \left(\frac{W+mc^2}{2W}\right)^{\frac{1}{2}} \begin{pmatrix} \phi_{m_s} \\ \frac{c\hbar\boldsymbol{\sigma}\mathbf{k}}{W+mc^2}\phi_{m_s} \end{pmatrix} \mathrm{e}^{i\mathbf{kr}} \tag{10.7}$$

in an a spin angular momentum basis, as shown in eq. (8.77):

$$\psi^0_{\mathbf{k}m_s}(\mathbf{r}) = \left(\frac{W+mc^2}{2W}\right)^{\frac{1}{2}} \sum_{\Lambda} 4\pi i^l C(l,j,\frac{1}{2}|\mu-m_s,m_s) Y^*_{l,\mu-m_s}(\hat{\mathbf{k}}) J_\Lambda(\mathbf{r}). \tag{10.8}$$

The solution of the Lippmann-Schwinger equation (10.5) can be expanded in an analogue manner

$$\psi_{\mathbf{k}m_s}(\mathbf{r}) = \left(\frac{W+mc^2}{2W}\right)^{\frac{1}{2}} \sum_{\Lambda} 4\pi i^l C(l,j,\frac{1}{2}|\mu-m_s,m_s) Y^*_{l,\mu-m_s}(\hat{\mathbf{k}}) R_\Lambda(\mathbf{r}) \tag{10.9}$$

with an unknown function ψ_Λ. Inserting this expansion together with the expansion for the Dirac plane wave, eq. (10.8), into the Lippmann-Schwinger equation (10.5) yields

$$\begin{aligned} &\sum_{\Lambda} i^l C(l,j,\frac{1}{2}|\mu-m_s,m_s) Y^*_{l,\mu-m_s}(\hat{\mathbf{k}}) R_\Lambda(\mathbf{r}) \qquad (10.10)\\ = &\sum_{\Lambda} i^l C(l,j,\frac{1}{2}|\mu-m_s,m_s) Y^*_{l,\mu-m_s}(\hat{\mathbf{k}}) \left[J_\Lambda(\mathbf{r}) + \int d\mathbf{r} G^0(\mathbf{r},\mathbf{r}';W) V(\mathbf{r}') R_\Lambda(\mathbf{r}') \right]. \end{aligned}$$

The whole equation is multiplied by $Y_{\Lambda'}(\hat{\mathbf{k}}) = Y_{l',\mu'-m'_s}(\hat{\mathbf{k}})$. Integrating over $\hat{\mathbf{k}}$ and using the orthonormality of the spherical harmonics then results in

$$\begin{aligned} &\sum_{\Lambda} i^l C(l,j,\frac{1}{2}|\mu-m_s,m_s) R_\Lambda(\mathbf{r}) \delta_{\Lambda\Lambda'} \qquad (10.11)\\ = &\sum_{\Lambda} i^l C(l,j,\frac{1}{2}|\mu-m_s,m_s) \left[J_\Lambda(\mathbf{r}) + \int d\mathbf{r} G^0(\mathbf{r},\mathbf{r}';W) V(\mathbf{r}') R_\Lambda(\mathbf{r}') \right] \delta_{\Lambda\Lambda'}. \end{aligned}$$

Simplifying the equation gives

$$R_\Lambda(\mathbf{r}) = J_\Lambda(\mathbf{r}) + \int d\mathbf{r}' G^0(\mathbf{r},\mathbf{r}';W) V(\mathbf{r}') R_\Lambda(\mathbf{r}). \tag{10.12}$$

For the left hand side solution $\overline{R}_\Lambda$ the derivation is similar. The following box summarises the four Lippmann-Schwinger equations:

Angular momentum Lippmann-Schwinger equations for the regular solutions:

$$R_\Lambda(\mathbf{r}) = J_\Lambda(\mathbf{r}) + \int d\mathbf{r}' G^0(\mathbf{r},\mathbf{r}';W)V(\mathbf{r}')R_\Lambda(\mathbf{r}') \tag{10.13}$$

$$\overline{R}_\Lambda(\mathbf{r}) = \overline{J}_\Lambda(\mathbf{r}) + \int d\mathbf{r}' \overline{R}_\Lambda(\mathbf{r}')V(\mathbf{r}')G^0(\mathbf{r}',\mathbf{r};W) \tag{10.14}$$

Angular momentum Lippmann-Schwinger equations for the irregular solutions:

$$S_\Lambda(\mathbf{r}) = \sum_{\Lambda'} \overline{\beta}_{\Lambda'\Lambda} H_\Lambda(\mathbf{r}) + \int d\mathbf{r}' G^0(\mathbf{r},\mathbf{r}';W)V(\mathbf{r}')S_\Lambda(\mathbf{r}') \tag{10.15}$$

$$\overline{S}_\Lambda(\mathbf{r}) = \sum_{\Lambda'} \beta_{\Lambda'\Lambda} \overline{H}_{\Lambda'}(\mathbf{r}) + \int d\mathbf{r}' \overline{S}_\Lambda(\mathbf{r}')V(\mathbf{r}')G^0(\mathbf{r}',\mathbf{r};W). \tag{10.16}$$

Here the β and $\overline{\beta}$ matrices are defined by:

$$\begin{aligned}\beta_{\Lambda'\Lambda} &:= \delta_{\Lambda'\Lambda} + ik\frac{(W+mc^2)}{c^2\hbar^2}\int d\mathbf{r}\overline{H}_\Lambda(\mathbf{r})V(\mathbf{r})U_{\Lambda'}(\mathbf{r}) \qquad (10.17)\\ &= \delta_{\Lambda'\Lambda} + ik\frac{(W+mc^2)}{c^2\hbar^2}\int d\mathbf{r}\overline{S}_\Lambda(\mathbf{r})V(\mathbf{r})J_{\Lambda'}(\mathbf{r})\\ \overline{\beta}_{\Lambda'\Lambda} &:= \delta_{\Lambda'\Lambda} + ik\frac{(W+mc^2)}{c^2\hbar^2}\int d\mathbf{r}\overline{U}_{\Lambda'}(\mathbf{r})V(\mathbf{r})H_\Lambda(\mathbf{r}) \qquad (10.18)\\ &= \delta_{\Lambda'\Lambda} + ik\frac{(W+mc^2)}{c^2\hbar^2}\int d\mathbf{r}\overline{J}_{\Lambda'}(\mathbf{r})V(\mathbf{r})S_\Lambda(\mathbf{r})\end{aligned}$$

The reason for introducing the β matrix and for choosing exactly the source term above for the irregular solution can not be understood yet. It is because with this source term the irregular solution is chosen correctly to yield an easy expression for the Green function of a Dirac particle in a potential, as it will be shown in the next section, where also the equation for U_Λ will be given. The equivalence of the two representations for the β matrices will be proven in the next section, too.

10.3 Angular Momentum Expansion of the Relativistic Green Function for a Particle in a Potential

The objective of this work is to calculate the Green function of the single-site problem. Hence, this section shows how to calculate it from the wave functions of the single site problem and how the corresponding formula can be derived. A mathematically complete derivation for the non-relativistic case was given in [75]. The derivation here is based on this paper, however, the wave functions in the relativistic case are vectors with four entries instead of scalar wave functions, and the Green function and integration kernel are 4×4 matrices now. Hence, one has to pay attention to the order in which those vectors and matrices are multiplied. Apart from that, the derivation is analogous to the non-relativistic case.

The claim is that

the Green function for a Dirac particle in a potential is given by

$$G(\mathbf{r},\mathbf{r}';W) = -ik\frac{(W+mc^2)}{c^2\hbar^2}\sum_{\Lambda}\left[\Theta(r-r')R_\Lambda(\mathbf{r}')\overline{S}_\Lambda(\mathbf{r}') + \Theta(r'-r)S_\Lambda(\mathbf{r}')\overline{R}_\Lambda(\mathbf{r}')\right] \quad (10.19)$$

with the wave functions R_Λ, $\overline{R}_\Lambda$, S_Λ and $\overline{S}_\Lambda$ given by eqs. (10.13) to (10.16).

Proof: The proof will be split into eight steps, out of which the first seven describe the case $r > r'$, i.e. the first summand in the Green function, and the last step describes which changes are necessary in order to derive the second summand.

1. General technique of rewriting a Fredholm to a Volterra equation

Following a technique shown by RALL [76], a Fredholm integral equation can be rewritten into a Volterra integral equation.

A Fredholm equation is of the form

$$y(\mathbf{r}) = f(\mathbf{r}) + \int d\mathbf{r}' G^0(\mathbf{r},\mathbf{r}';W)V(\mathbf{r}')y(\mathbf{r}') \quad (10.20)$$

with arbitrary f. It has, according to section 5.7, the solution

$$y(\mathbf{r}) = f(\mathbf{r}) + \int d\mathbf{r}' G(\mathbf{r},\mathbf{r}';W)V(\mathbf{r}')f(\mathbf{r}'). \quad (10.21)$$

To solve it, it can be useful to rewrite it into a Volterra equation

$$y(\mathbf{r}) = f(\mathbf{r}) + \sum c_\Lambda J_\Lambda(\mathbf{r}) + \int d\mathbf{r}' K^0(\mathbf{r},\mathbf{r}';W)V(\mathbf{r}')y(\mathbf{r}') \quad (10.22)$$

by defining

$$K^0(\mathbf{r},\mathbf{r}';W) := G^0(\mathbf{r},\mathbf{r}';W) + ik\frac{(W+mc^2)}{c^2\hbar^2}\sum_{\Lambda} J_\Lambda(\mathbf{r})\overline{H}_\Lambda(\mathbf{r}') \quad (10.23)$$

$$c_\Lambda := -ik\frac{(W+mc^2)}{c^2\hbar^2}\int d\mathbf{r}\overline{H}_\Lambda(\mathbf{r})V(\mathbf{r})y(\mathbf{r}). \quad (10.24)$$

2. Rewriting the Lippmann-Schwinger equation to a Volterra equation

The technique from the first point can be applied to the Lippmann-Schwinger equation. Let us start with the regular right hand side solution, eq. (10.13)

$$R_\Lambda(\mathbf{r}) = J_\Lambda(\mathbf{r}) + \int d\mathbf{r}' G^0(\mathbf{r},\mathbf{r}';W)V(\mathbf{r}')R_\Lambda(\mathbf{r}'). \quad (10.25)$$

From eq. (9.37) we know the expansion of the Green function for the free Dirac particle, which in the case $r > r'$ is

$$G^0(\mathbf{r},\mathbf{r}';W) = -\frac{(W+mc^2)}{c^2\hbar^2}ik\sum_{\Lambda} H_\Lambda(\mathbf{r})\overline{J}_\Lambda(\mathbf{r}'). \quad (10.26)$$

Inserting this into the expression for K^0, eq. (10.23), yields the integration kernel for the Lippmann-Schwinger equation in a Volterra form:

$$K^0(\mathbf{r},\mathbf{r}';W) := -ik\frac{(W+mc^2)}{c^2\hbar^2}\Theta(r-r')\left(\sum_\Lambda H_\Lambda(\mathbf{r})\overline{J}_\Lambda(\mathbf{r}') - \sum_\Lambda J_\Lambda(\mathbf{r})\overline{H}_\Lambda(\mathbf{r}')\right). \quad (10.27)$$

The Lippmann-Schwinger equation itself is, rewritten into the Volterra representation, of the form of eq. (10.22). Thus, according to section 5.7, it has the solution

$$y(\mathbf{r}) = f(\mathbf{r}) + \sum_\Lambda c_\Lambda J_\Lambda(\mathbf{r}) + \int d\mathbf{r}' K(\mathbf{r},\mathbf{r}';W)V(\mathbf{r}')\left[f(\mathbf{r}') + \sum_\Lambda c_\Lambda J_\Lambda(\mathbf{r}')\right] \quad (10.28)$$

where K has to fulfil the relation

$$K(\mathbf{r},\mathbf{r}';W) = K^0(\mathbf{r},\mathbf{r}';W) + \int d\mathbf{r}'' K^0(\mathbf{r},\mathbf{r}'';W)V(\mathbf{r}'')K(\mathbf{r}'',\mathbf{r}';W). \quad (10.29)$$

By defining the two auxiliary functions

$$F(\mathbf{r}) = f(\mathbf{r}) + \int d\mathbf{r}' K(\mathbf{r},\mathbf{r}';W)V(\mathbf{r}')f(\mathbf{r}') \quad (10.30)$$

$$U_\Lambda(\mathbf{r}) = J_\Lambda(\mathbf{r}) + \int d\mathbf{r}' K(\mathbf{r},\mathbf{r}';W)V(\mathbf{r}')J_\Lambda(\mathbf{r}') \quad (10.31)$$

the solution of the Volterra equation can be written in the short form

$$y(\mathbf{r}) = F(\mathbf{r}) + \sum_\Lambda c_\Lambda U_\Lambda(\mathbf{r}). \quad (10.32)$$

3. Rewriting the c_Λ coefficients using the β matrix ($r > r'$)

For the part that follows the c_Λ coefficients have to be rewritten to a different form. In order to do so, we insert eq. (10.32) into the definition of the c_Λ coefficients, eq. (10.24):

$$\begin{aligned} c_\Lambda &= -ik\frac{(W+mc^2)}{c^2\hbar^2}\int d\mathbf{r}\overline{H}_\Lambda(\mathbf{r})V(\mathbf{r})\left(F(\mathbf{r}) + \sum_\Lambda c_\Lambda U_\Lambda(\mathbf{r})\right) \quad (10.33)\\ &= -ik\frac{(W+mc^2)}{c^2\hbar^2}\left(\int d\mathbf{r}\overline{H}_\Lambda(\mathbf{r})V(\mathbf{r})F(\mathbf{r}) + \sum_\Lambda c_\Lambda\int d\mathbf{r}\overline{H}_\Lambda(\mathbf{r})V(\mathbf{r})U_\Lambda(\mathbf{r})\right). \end{aligned}$$

This equation is equivalent to

$$\begin{aligned} &\sum_{\Lambda'} c_{\Lambda'}\left[\delta_{\Lambda'\Lambda} + ik\frac{(W+mc^2)}{c^2\hbar^2}\int d\mathbf{r}\overline{H}_{\Lambda'}(\mathbf{r})V(\mathbf{r})U_{\Lambda'}(\mathbf{r})\right] \quad (10.34)\\ &= -ik\frac{(W+mc^2)}{c^2\hbar^2}\int d\mathbf{r}\overline{H}_\Lambda(\mathbf{r})V(\mathbf{r})F(\mathbf{r}). \end{aligned}$$

Now the term in square brackets is defined as the β matrix:

$$\beta_{\Lambda'\Lambda} = \delta_{\Lambda'\Lambda} + ik\frac{(W+mc^2)}{c^2\hbar^2}\int d\mathbf{r}\overline{H}_{\Lambda}(\mathbf{r})V(\mathbf{r})U_{\Lambda'}(\mathbf{r}) \tag{10.35}$$

so that eq. (10.34) is viewed as an inhomogeneous linear equation with unknown c_Λ, and thus the c_Λ coefficients can be determined via matrix inversion

$$c_\Lambda = -ik\frac{(W+mc^2)}{c^2\hbar^2}\sum_{\Lambda'}\beta^{-1}_{\Lambda'\Lambda}\int d\mathbf{r}\overline{H}_{\Lambda'}(\mathbf{r})V(\mathbf{r})F(\mathbf{r}). \tag{10.36}$$

Here $\beta^{-1}_{\Lambda'\Lambda}$ denote the entries of the inverted matrix β^{-1} (and not the inverted entries of β). Inserting the definition of the auxiliary function F, eq. (10.30), into this expression yields

$$\begin{aligned}
c_\Lambda &= -ik\frac{(W+mc^2)}{c^2\hbar^2}\sum_{\Lambda'}\beta^{-1}_{\Lambda'\Lambda}\int d\mathbf{r}\overline{H}_{\Lambda'}(\mathbf{r})V(\mathbf{r})\left(f(\mathbf{r})+\int d\mathbf{r}'K(\mathbf{r},\mathbf{r}';W)V(\mathbf{r}')f(\mathbf{r}')\right)\\
&= -ik\frac{(W+mc^2)}{c^2\hbar^2}\sum_{\Lambda'}\beta^{-1}_{\Lambda'\Lambda}\left[\int d\mathbf{r}\overline{H}_{\Lambda'}(\mathbf{r})V(\mathbf{r})f(\mathbf{r})\right.\\
&\quad \left.+\int d\mathbf{r}\overline{H}_{\Lambda'}(\mathbf{r})V(\mathbf{r})\int d\mathbf{r}'K(\mathbf{r},\mathbf{r}';W)V(\mathbf{r}')f(\mathbf{r}')\right]\\
&= -ik\frac{(W+mc^2)}{c^2\hbar^2}\sum_{\Lambda'}\beta^{-1}_{\Lambda'\Lambda}\left[\int d\mathbf{r}\overline{H}_{\Lambda'}(\mathbf{r})V(\mathbf{r})f(\mathbf{r})\right.\\
&\quad \left.+\int d\mathbf{r}'\overline{H}_{\Lambda'}(\mathbf{r}')V(\mathbf{r}')\int d\mathbf{r}K(\mathbf{r},'\mathbf{r};W)V(\mathbf{r})f(\mathbf{r})\right]\\
&= -ik\frac{(W+mc^2)}{c^2\hbar^2}\sum_{\Lambda'}\beta^{-1}_{\Lambda'\Lambda}\int d\mathbf{r}\left[\overline{H}_{\Lambda'}(\mathbf{r})+\int d\mathbf{r}'\overline{H}_{\Lambda'}(\mathbf{r}')V(\mathbf{r}')K(\mathbf{r},'\mathbf{r};W)\right]V(\mathbf{r})f(\mathbf{r}).
\end{aligned} \tag{10.37}$$

We now define the function $\overline{S}_\Lambda$ as the term in square brackets:

$$\overline{S}_\Lambda(\mathbf{r}) = \overline{H}_\Lambda(\mathbf{r}) + \int d\mathbf{r}'\overline{H}_\Lambda(\mathbf{r}')V(\mathbf{r}')K(\mathbf{r}',\mathbf{r};W). \tag{10.38}$$

It will be shown in the seventh step of this proof that this definition is actually equivalent to the definition in eq. (10.16). Using this form for $\overline{S}_\Lambda$ the expression for the c_Λ coefficients simplifies to

$$c_\Lambda = -ik\frac{(W+mc^2)}{c^2\hbar^2}\sum_{\Lambda'}\beta^{-1}_{\Lambda'\Lambda}\int d\mathbf{r}\overline{S}_{\Lambda'}(\mathbf{r})V(\mathbf{r})f(\mathbf{r}). \tag{10.39}$$

4. Derivation of a preliminary expression for the Fredholm integration kernel ($r > r'$)

From eq. (10.39) we can insert the explicit expression for the c_Λ coefficients into the formal solution of a Volterra equation, eq. (10.32):

$$y(\mathbf{r}) = F(\mathbf{r}) - ik\frac{(W+mc^2)}{c^2\hbar^2}\sum_{\Lambda}\sum_{\Lambda'}\beta^{-1}_{\Lambda'\Lambda}\int d\mathbf{r}'\overline{S}_{\Lambda'}(\mathbf{r}')V(\mathbf{r}')f(\mathbf{r}')U_\Lambda(\mathbf{r}). \tag{10.40}$$

Inserting eq. (10.30) for the auxiliary function F yields

$$y(\mathbf{r}) = f(\mathbf{r}) + \int d\mathbf{r}' \Big[K(\mathbf{r},\mathbf{r}';W) - ik\frac{(W+mc^2)}{c^2\hbar^2} \sum_{\Lambda}\sum_{\Lambda'} \beta^{-1}_{\Lambda'\Lambda} \overline{S}_{\Lambda'}(\mathbf{r}') U_{\Lambda}(\mathbf{r}) V(\mathbf{r}') f(\mathbf{r}') \Big]. \tag{10.41}$$

By comparing this equation to the formal solution of a Fredholm equation, given in eq. (10.21), it follows that the Fredholm integration kernel G must be equal to the term in square brackets:

$$G(\mathbf{r},\mathbf{r}';W) = K(\mathbf{r},\mathbf{r}';W) - ik\frac{(W+mc^2)}{c^2\hbar^2} \sum_{\Lambda}\sum_{\Lambda'} \beta^{-1}_{\Lambda'\Lambda} \overline{S}_{\Lambda'}(\mathbf{r}') U_{\Lambda}(\mathbf{r}). \tag{10.42}$$

5. Rewriting the equation for U_Λ $(r > r')$

The defining equation for U_Λ, eq. (10.31), is such that U_Λ is the solution of the Volterra equation

$$U_\Lambda(\mathbf{r}) = J_\Lambda(\mathbf{r}) + \int d\mathbf{r}' K^0(\mathbf{r},\mathbf{r}';W) V(\mathbf{r}') U_\Lambda(\mathbf{r}') \tag{10.43}$$

with integration Kernel K. Inserting the expression for K^0 from eq. (10.27) it can be rewritten as

$$\begin{aligned} U_\Lambda(\mathbf{r}) &= J_\Lambda(\mathbf{r}) - ik\frac{(W+mc^2)}{c^2\hbar^2} \int d\mathbf{r}' \Big[\Theta(r-r') \sum_{\Lambda'} \Big(H_{\Lambda'}(\mathbf{r}) \overline{J}_{\Lambda'}(\mathbf{r}') \\ &\qquad - J_{\Lambda'}(\mathbf{r}) \overline{H}_{\Lambda'}(\mathbf{r}') \Big) \Big] V(\mathbf{r}') U_\Lambda(\mathbf{r}') \\ &\overset{r\geq r'}{=} J_\Lambda(\mathbf{r}) - ik\frac{(W+mc^2)}{c^2\hbar^2} \sum_{\Lambda'} H_{\Lambda'}(\mathbf{r}) \int d\mathbf{r}' \overline{J}_{\Lambda'}(\mathbf{r}') V(\mathbf{r}') U_\Lambda(\mathbf{r}') \\ &\quad + \sum_{\Lambda'} J_{\Lambda'}(\mathbf{r}) \underbrace{ik\frac{(W+mc^2)}{c^2\hbar^2} \int d\mathbf{r}'(\mathbf{r}) \overline{H}_{\Lambda'}(\mathbf{r}') V(\mathbf{r}') U_\Lambda(\mathbf{r}')}_{=\beta_{\Lambda\Lambda'} - \delta_{\Lambda\Lambda'} \text{ after eq. (10.35)}} \\ &= \sum_{\Lambda'} J_{\Lambda'}(\mathbf{r}) \beta_{\Lambda\Lambda'} - ik\frac{(W+mc^2)}{c^2\hbar^2} \sum_{\Lambda'} \int d\mathbf{r}' H_{\Lambda'}(\mathbf{r}) \overline{J}_{\Lambda'}(\mathbf{r}') V(\mathbf{r}') U_\Lambda(\mathbf{r}'). \end{aligned} \tag{10.44}$$

From eq. (9.37) we know the expansion for the free Dirac particle Green function, in the case $r > r'$ it is given by

$$G^0(\mathbf{r},\mathbf{r}';W) = -ik\frac{(W+mc^2)}{c^2\hbar^2} \sum_{\Lambda} H_\Lambda(\mathbf{r}) \overline{J}_\Lambda(\mathbf{r}'), \tag{10.45}$$

which, inserted into the equation above, yields

$$U_\Lambda(\mathbf{r}) = \sum_{\Lambda'} J_{\Lambda'}(\mathbf{r}) \beta_{\Lambda\Lambda'} + \int d\mathbf{r}' G^0(\mathbf{r},\mathbf{r}';W) V(\mathbf{r}') U_\Lambda(\mathbf{r}'). \tag{10.46}$$

By comparing this equation to the Lippmann-Schwinger equation that defines the regular right hand side solution R_Λ, eq. (10.13) it follows that

$$U_\Lambda(\mathbf{r}) = \sum_{\Lambda'} R_{\Lambda'}(\mathbf{r})\beta_{\Lambda\Lambda'}. \tag{10.47}$$

Inserting that into the preliminary expression eq. (10.42) that we found for the Green function G yields

$$G(\mathbf{r},\mathbf{r}';W) = K(\mathbf{r},\mathbf{r}';W) - ik\frac{(W+mc^2)}{c^2\hbar^2}\sum_{\Lambda'} R_\Lambda(\mathbf{r}')\overline{S}_{\Lambda'}(\mathbf{r}'). \tag{10.48}$$

Since $K(\mathbf{r},\mathbf{r}') = 0$ for $r > r'$ we obtain

$$G(\mathbf{r},\mathbf{r}';W) = ik\frac{(W+mc^2)}{c^2\hbar^2}\sum_{\Lambda} R_\Lambda(\mathbf{r}')\overline{S}_{\Lambda}(\mathbf{r}') \text{ for r} > \text{r}'. \tag{10.49}$$

6. Rewriting the β matrix solution ($r > r'$)

To complete the first part of the proof it remains to show that the definition for $\overline{S}_\Lambda$ in eq. (10.38) is equal to the one in eq. (10.16). In order to do so, we first define the α matrix by

$$\alpha_{\Lambda'\Lambda} := \delta_{\Lambda'\Lambda} - ik\frac{(W+mc^2)}{c^2\hbar^2}\int d\mathbf{r}\overline{H}_\Lambda(\mathbf{r})V(\mathbf{r})R_{\Lambda'}(\mathbf{r}). \tag{10.50}$$

Since this definition is, apart from different indices and a different prefactor, the same as in the non-relativistic case, eq. (5.72) in section (5.8), we know in analogy to this section that

$$\alpha^{-1}_{\Lambda'\Lambda} = \delta_{\Lambda'\Lambda} + ik\frac{(W+mc^2)}{c^2\hbar^2}\int d\mathbf{r}\overline{S}_\Lambda(\mathbf{r})V(\mathbf{r})J_{\Lambda'}(\mathbf{r}). \tag{10.51}$$

Now we first want to show that this matrix is equal to the β matrix defined in eq. (10.35). In order to do so insert eq. (10.47) into eq. (10.35), yielding

$$\beta_{\Lambda'\Lambda} = \delta_{\Lambda'\Lambda} + ik\frac{(W+mc^2)}{c^2\hbar^2}\int d\mathbf{r}\overline{H}_\Lambda V(\mathbf{r})\sum_{\Lambda''}\beta_{\Lambda'\Lambda''}R_{\Lambda''}(\mathbf{r}) \tag{10.52}$$

which can equivalently be expressed in a matrix notation as

$$\beta = \mathrm{I} + (\mathrm{I} - \alpha)\beta. \tag{10.53}$$

Rearranging this matrix equation yields

$$\beta = \alpha^{-1} \tag{10.54}$$

and hence

$$\beta_{\Lambda'\Lambda} = \delta_{\Lambda'\Lambda} + ik\frac{(W+mc^2)}{c^2\hbar^2}\int d\mathbf{r}\overline{S}_\Lambda(\mathbf{r})V(\mathbf{r})J_{\Lambda'}(\mathbf{r}). \tag{10.55}$$

7. Rewriting the irregular solution ($r > r'$)

Now, using the new expression for the β matrix, we can rewrite the equation for the irregular left hand side solution $\overline{S}_\Lambda$. We start from the defining Lippmann-Schwinger equation, eq. (10.16)

$$\overline{S}_\Lambda(\mathbf{r}) = \sum_{\Lambda'} \beta_{\Lambda'\Lambda} \overline{H}_{\Lambda'}(\mathbf{r}) + \int d\mathbf{r}' \overline{S}_\Lambda(\mathbf{r}') V(\mathbf{r}') G^0(\mathbf{r}', \mathbf{r}; W) \tag{10.56}$$

and insert the expression for the β matrix into this equation:

$$\begin{aligned} \overline{S}_\Lambda(\mathbf{r}) &= \sum_{\Lambda'} \left(\delta_{\Lambda'\Lambda} + ik \frac{(W + mc^2)}{c^2\hbar^2} \int d\mathbf{r}' \overline{S}_\Lambda(\mathbf{r}') V(\mathbf{r}') J_{\Lambda'}(\mathbf{r}') \right) \overline{H}_{\Lambda'}(\mathbf{r}) \\ &\quad + \int d\mathbf{r}' \overline{S}_\Lambda(\mathbf{r}') V(\mathbf{r}') G^0(\mathbf{r}', \mathbf{r}; W) \\ &= \overline{H}_{\Lambda'}(\mathbf{r}) + \int d\mathbf{r}' \overline{S}_\Lambda(\mathbf{r}') V(\mathbf{r}') \left[G^0(\mathbf{r}', \mathbf{r}; W) + ik \frac{(W + mc^2)}{c^2\hbar^2} \sum_{\Lambda'} J_{\Lambda'}(\mathbf{r}') \overline{H}_{\Lambda'}(\mathbf{r}) \right]. \end{aligned} \tag{10.57}$$

The term in square brackets is equal to $K^0(\mathbf{r}', \mathbf{r}; W)$ as defined in eq. (10.23), hence

$$\overline{S}_\Lambda(\mathbf{r}) = \overline{H}_\Lambda(\mathbf{r}) + \int d\mathbf{r}' \overline{S}_\Lambda(\mathbf{r}') V(\mathbf{r}') K^0(\mathbf{r}', \mathbf{r}; W). \tag{10.58}$$

This is a Volterra integral equation, which, according to section 5.7, has the solution

$$\overline{S}_\Lambda(\mathbf{r}) = \overline{H}_\Lambda(\mathbf{r}) + \int d\mathbf{r}' \overline{H}_\Lambda(\mathbf{r}') V(\mathbf{r}') K(\mathbf{r}', \mathbf{r}; W) \tag{10.59}$$

where the integration kernel K is defined by eq. (10.29).

8. Changes for the second case $r' > r$

The derivation of the second part of the Green function for the case $r' > r$ goes analogously to the first case. The Fredholm equation to start off now is given by

$$\overline{y}(\mathbf{r}) = \overline{f}(\mathbf{r}) + \int d\mathbf{r}' \overline{y}(\mathbf{r}') V(\mathbf{r}') G^0(\mathbf{r}', \mathbf{r}; W). \tag{10.60}$$

Note that the order of the functions in the integrand has changed and the arguments of G^0 have also been interchanged. The Volterra form of this equation is given by

$$\overline{y}(\mathbf{r}) = \overline{f}(\mathbf{r}) + \sum \bar{c}_\Lambda \overline{J}_\Lambda(\mathbf{r}) + \int d\mathbf{r}' \overline{y}(\mathbf{r}') V(\mathbf{r}') \overline{K}^0(\mathbf{r}', \mathbf{r}; W) \tag{10.61}$$

where $\overline{K}^0$ and $\bar{c}_\Lambda$ are given by

$$\overline{K}^0(\mathbf{r},' \mathbf{r}; W) := G^0(\mathbf{r}', \mathbf{r}; W) + ik \frac{(W + mc^2)}{c^2\hbar^2} \sum_{\Lambda} H_\Lambda(\mathbf{r}') \overline{J}_\Lambda(\mathbf{r}) \tag{10.62}$$

$$\bar{c}_\Lambda := -ik \frac{(W + mc^2)}{c^2\hbar^2} \int d\mathbf{r} \overline{H}_\Lambda(\mathbf{r}) V(\mathbf{r}) y(\mathbf{r}). \tag{10.63}$$

Following the steps from the first case and rewriting the equations then leads to the result

$$G(\mathbf{r}, \mathbf{r}'; W) = -ik \frac{(W + mc^2)}{c^2\hbar^2} \sum_{\Lambda'} S_\Lambda(\mathbf{r}') \overline{R}_{\Lambda'}(\mathbf{r}') \text{ for r' > r} \tag{10.64}$$

which, combined with eq. (10.49), gives the complete result

$$G(\mathbf{r},\mathbf{r}';W) = -ik\frac{(W+mc^2)}{c^2\hbar^2}\left[\sum_{\Lambda}\Theta(r-r')R_{\Lambda}(\mathbf{r}')\overline{S}_{\Lambda}(\mathbf{r}') + \Theta(r'-r)S_{\Lambda}(\mathbf{r}')\overline{R}_{\Lambda}(\mathbf{r}')\right] \tag{10.65}$$

and therefore completes the proof.

10.4 t Matrix and Phase Shift

The t matrix in the relativistic case (see also [60]) can be defined analogously to the non-relativistic case, i.e. to eq. (5.34), as

$$t_{\Lambda\Lambda'} = \int d\mathbf{r}\overline{J}_{\Lambda}(\mathbf{r})V(\mathbf{r})R_{\Lambda'}(\mathbf{r}). \tag{10.66}$$

The only difference to the non-relativistic case is, that the index L has been replaced by the index $\Lambda = (\kappa,\mu)$ and, correspondingly, the relativistic wave functions and the relativistic potential are inserted. The matrix elements, however, still remain scalar, since $\overline{J}_{\Lambda}$ is a 1×4 vector, V a 4×4 matrix and R_{Λ} a 4×1 vector.

The physical interpretation also remains unchanged compared to the non-relativistic case: incoming waves with angular momentum index Λ are scattered to the angular momentum channels Λ' with an amplitude given by the element $t_{\Lambda\Lambda'}$.

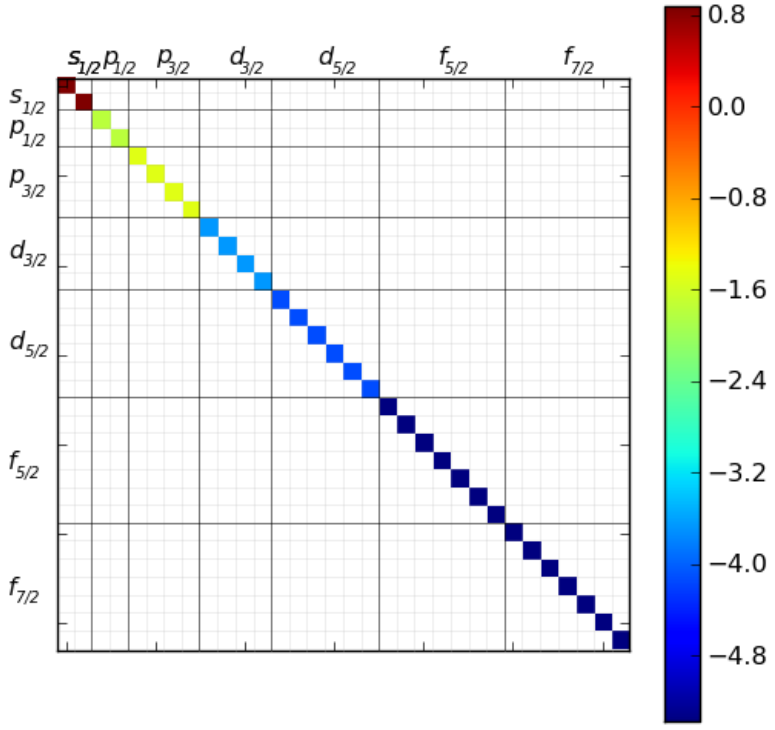
In the (κ,μ) representation the t matrix is diagonal for non-magnetic systems if the potential matrix V contains a spherical part only. That can be seen in figure 10.1a for the example of a tungsten impurity in a rubidium host, calculated with the fully-relativistic code that I implemented within my thesis. Note that this matrix, transformed into the (l,m_l,m_s) basis, would no longer be a diagonal matrix. The structure is the same as found within a scalar-relativistic calculation *with* additional spin-orbit coupling.

In a magnetic calculation, i.e. using a spin-dependent but still spherical potential, additional non-diagonal elements occur in the t matrix. They form a structure "parallel" to the diagonal, as shown in figure 10.1a. The same form has also been presented by Ebert et. al. [77].

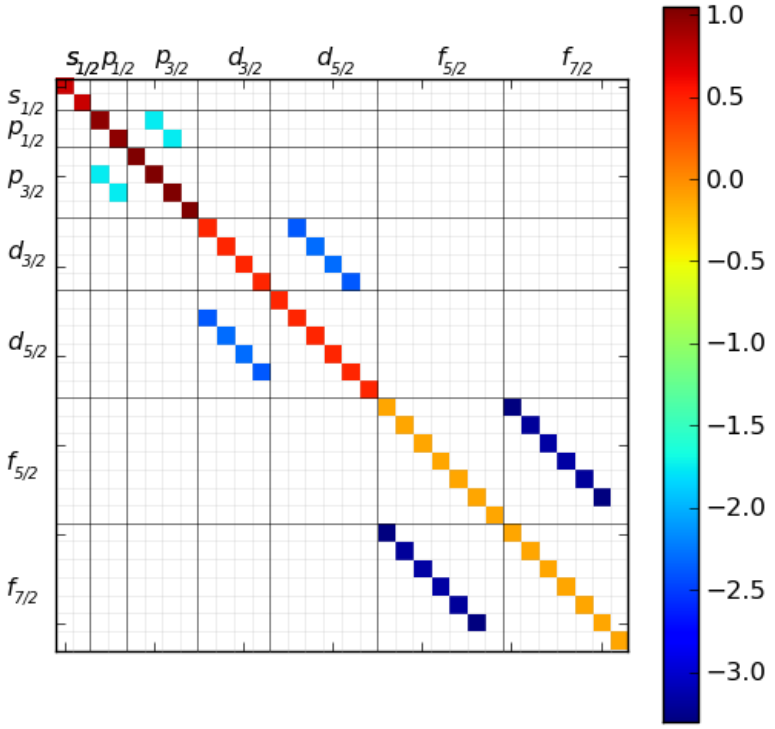
When comparing the result of a non-magnetic full-potential calculation in fig. 10.2a to the corresponding spherical potential calculation there is only little change in the structure of the t matrix. Note, however, the logarithmic scale. A similar structure does not mean that all the elements are exactly the same.

Fig. 10.2b shows the result of a magnetic full-potential calculation. Here additional non-diagonal elements can be observed. Rubidium has a body-centred cubic lattice structure, and for this lattice type Strange et.al. [78] give a general discussion of the form of the t matrix. The large elements in the matrix shown here are in accordance with their discussion. For the small elements ($< 10^{-8}$) there are deviations from their calculated form. This, however, is due to a small numerical inaccuracy.

To obtain a representation that can be more intuitively interpreted, we will also study the phase shift δ_{Λ}. This quantity describes the phase difference between the incoming wave with

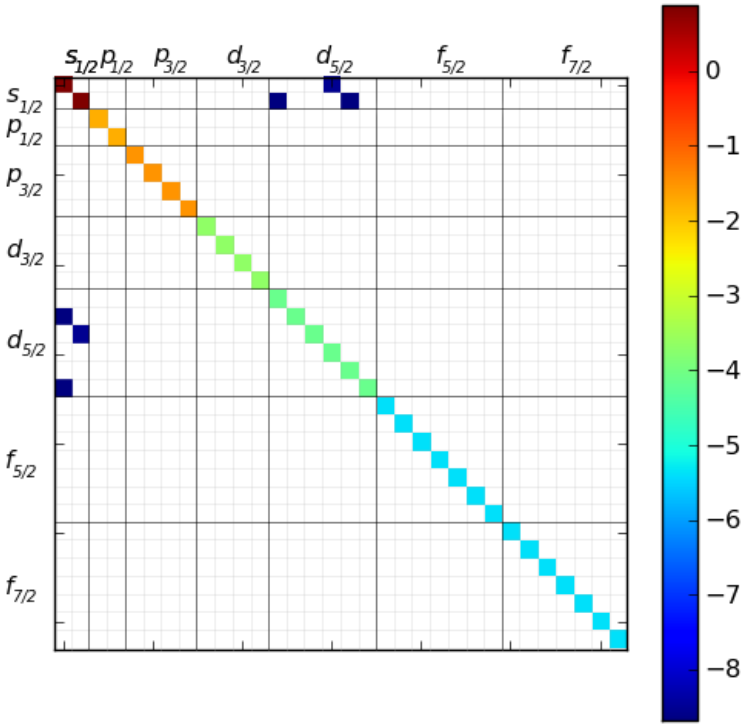


(a) Non-magnetic calculation with the spherically potential.

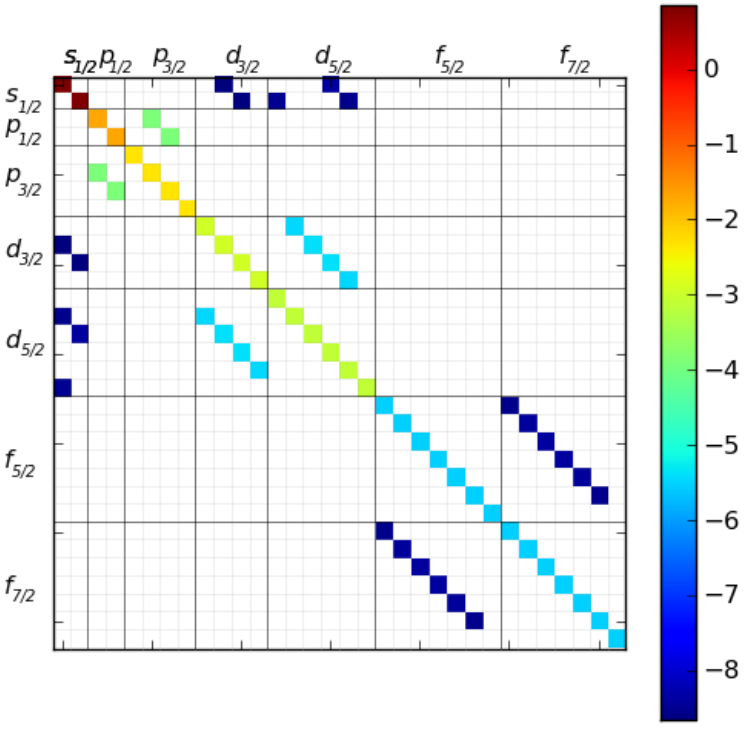


(b) Magnetic calculation with the spherically approximated potential.

Figure 10.1: Logarithmic plot of the t matrix elements, calculated fully-relativistically with a spherical potential for tungsten in a rubidium host in the (κ, μ) basis.



(a) Non-magnetic calculation with the full potential.



(b) Magnetic calculation with the full potential.

Figure 10.2: Logarithmic plot of the t matrix elements, calculated fully-relativistically for tungsten in a rubidium host in the (κ, μ) basis.

angular momentum index Λ and the outgoing scattered wave in the same angular momentum channel. Detailed descriptions can be found e.g. in [79, 80]. Such a description is possible for a spherical potential, meaning that there is no mixing between angular momentum channels, or in other words, where the t matrix is diagonal. Fig. 10.3 schematically depicts the phase shift of an incoming Bessel function j_l.

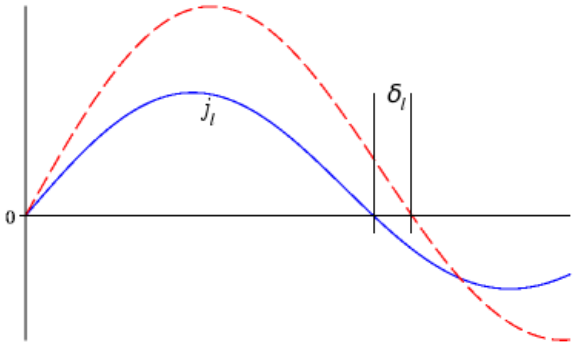


Figure 10.3: Schematic plot of the phase shift. The blue curve depicts the radial part of an incoming wave in an angular momentum decomposition, which is a Bessel function (here for $l = 1$). The red, dashed curve is the large component $R^t_{\Lambda\Lambda}$ of the scattered wave, with Λ corresponding to the given l value. Such a simplified picture is valid for spherical potentials, where there is no mixing of angular momentum channels.

For spherical potentials the following relation between the phase shift and the t matrix holds:

$$k\, t_{\Lambda\Lambda} = -\sin(\delta_\Lambda) \mathrm{e}^{i\delta_\Lambda}.$$

Fig. 10.4 shows the result of a calculation with the single-site Dirac solver that I implemented for the phase shifts of a tungsten impurity in a rubidium host. The calculation was non-magnetic and for a spherical potential, as only then the resulting t matrix is diagonal and the (non-generalised) phase shifts are defined. Interesting in the figure is the splitting between the two d orbitals. Such a splitting can be observed in relativistic calculations of heavy elements, as it depends on the spin-orbit coupling strength and therefore increases with the atomic number Z. For example, Strange et. al. [81] found a similar splitting in calculations for platinum.

Another interesting quantity is the $\mathbf{k}$-dependent t matrix, defined by its elements $T^{m_s m_s'}_{\mathbf{k}\mathbf{k}'}$. This matrix describes how an incoming wave with wave vector $\mathbf{k}$ and spin quantum number m_s is scattered into outgoing waves with wave vectors $\mathbf{k}'$ and spin quantum numbers m_s' and is defined as

$$T^{m_s m_s'}_{\mathbf{k}\mathbf{k}'} := \int d\mathbf{r} \overline{\psi}^0_{\mathbf{k}m_s}(\mathbf{r}) V(\mathbf{r}) \psi_{\mathbf{k}'m_s'}(\mathbf{r}). \tag{10.67}$$

This matrix can also be expressed in terms of the $t_{\Lambda\Lambda'}$ matrix elements. In order to show this, we insert the expansion of the free Dirac wave function, eq. (8.77), and the expansion

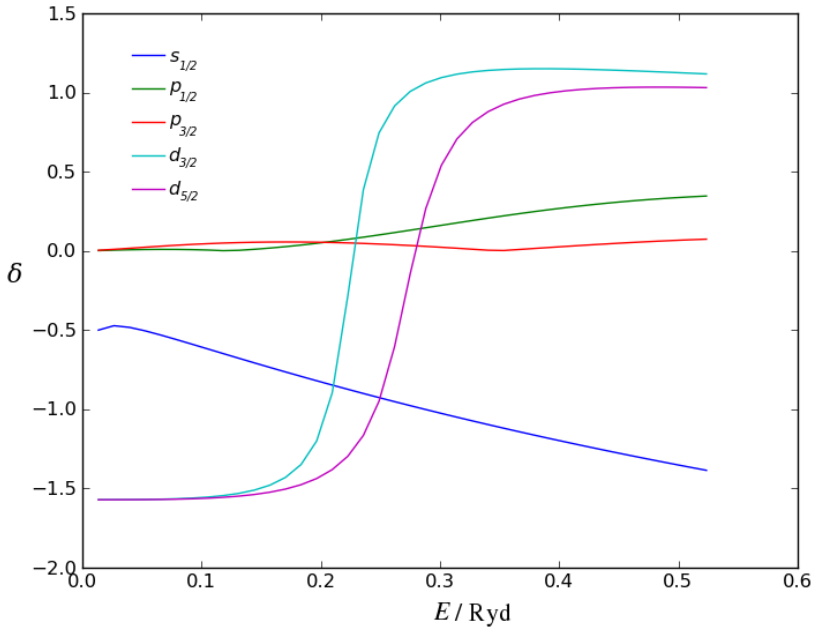


Figure 10.4: Phase shifts for tungsten in a rubidium host in a non-magnetic calculation with a spherical potential, which means that the $t_{\Lambda\Lambda}$ entries are the same for a given κ value. Plotted here are the values corresponding to the indices 1 to 18 in table 7.2b, corresponding to the given five orbitals.

of the solution $\psi_{\mathbf{k}'m_s'}$, eq. (10.9), into the definition above. This results in

$$\begin{aligned} T_{\mathbf{k}\mathbf{k}'}^{m_s m_s'} = \int d\mathbf{r} \sum_{\Lambda\Lambda'} \Bigg[& \left(\frac{W+mc^2}{2W}\right)^{\frac{1}{2}} \left(4\pi i^l C(l,j,\frac{1}{2}|\mu-m_s,m_s)\right)^* Y_{l,\mu-m_s}(\hat{\mathbf{k}}) \\ & \cdot \left(\frac{W+mc^2}{2W}\right)^{\frac{1}{2}} \left(4\pi i^l C(l',j',\frac{1}{2}|\mu'-m_s',m_s')\right) Y_{l',\mu'-m_s'}^*(\hat{\mathbf{k}}) \\ & \cdot \overline{J}_\Lambda(\mathbf{r}) V(\mathbf{r}) R_{\Lambda'}(\mathbf{r}) \Bigg]. \end{aligned} \tag{10.68}$$

Defining the coefficients

$$a_\Lambda(\mathbf{k}) = \left(\frac{W+mc^2}{2W}\right)^{\frac{1}{2}} 4\pi i^l C(l,j,\frac{1}{2}|\mu-m_s,m_s) Y_{l,\mu-m_s}^*(\hat{\mathbf{k}}) \tag{10.69}$$

it can be rewritten as

$$T_{\mathbf{k}\mathbf{k}'}^{m_s m_s'} = \sum_{\Lambda\Lambda'} a_\Lambda(\mathbf{k}) a_{\Lambda'}^*(\mathbf{k}') \int d\mathbf{r} \overline{J}_\Lambda(\mathbf{r}) V(\mathbf{r}) R_{\Lambda'}(\mathbf{r}). \tag{10.70}$$

The integral is by the definition in eq. (10.66) a $t_{\Lambda\Lambda'}$ element, hence

$$T_{\mathbf{k}\mathbf{k}'}^{m_s m_s'} = \sum_{\Lambda\Lambda'} a_\Lambda(\mathbf{k}) a_{\Lambda'}^*(\mathbf{k}') t_{\Lambda\Lambda'}. \tag{10.71}$$

10.5 Angular Momentum Expansion of the Potential

The angular momentum expansion of the potential is somewhat tricky in the relativistic case, thus we will devote a section to showing how it is done. This kind of expansion is *not* possible for an arbitrary 4×4 matrix but makes use of the property, that the potential matrices V or $\overset{\approx}{V}$ contain self-adjoint (or Hermitian) sub-matrices. These sub-matrices are defined as

$$V^a := \begin{pmatrix} V_{11} & V_{12} \\ V_{21} & V_{22} \end{pmatrix} = e \begin{pmatrix} \varphi & 0 \\ 0 & \varphi \end{pmatrix} \tag{10.72}$$

$$V^b := \begin{pmatrix} V_{13} & V_{14} \\ V_{23} & V_{24} \end{pmatrix} = ce \begin{pmatrix} -A_z & -A_x + iA_y \\ -A_x - iA_y & +A_z \end{pmatrix} \tag{10.73}$$

$$V^c := \begin{pmatrix} V_{31} & V_{32} \\ V_{41} & V_{42} \end{pmatrix} = ce \begin{pmatrix} -A_z & -A_x + iA_y \\ -A_x - iA_y & +A_z \end{pmatrix} \tag{10.74}$$

$$V^d := \begin{pmatrix} V_{33} & V_{34} \\ V_{43} & V_{44} \end{pmatrix} = e \begin{pmatrix} \varphi & 0 \\ 0 & \varphi \end{pmatrix} \tag{10.75}$$

so that the potential, cf. eq. (6.12), can be written as

$$V = \begin{pmatrix} V^a & V^b \\ V^c & V^d \end{pmatrix}. \tag{10.76}$$

Analogously, the potential $\overset{\approx}{V}$ that uses a $\mathbf{B}$ field instead of the vector potential $\mathbf{A}$, cf. eq. (6.14), is made up of the sub-matrices

$$\overset{\approx}{V}{}^a := \begin{pmatrix} \overset{\approx}{V}_{11} & \overset{\approx}{V}_{12} \\ \overset{\approx}{V}_{21} & \overset{\approx}{V}_{22} \end{pmatrix} = \begin{pmatrix} e\varphi - \mu B_z & -\mu B_x + i\mu B_y \\ -\mu B_x - i\mu B_y & e\varphi + \mu B_z \end{pmatrix} \tag{10.77}$$

$$\overset{\approx}{V}{}^b := \begin{pmatrix} \overset{\approx}{V}_{13} & \overset{\approx}{V}_{14} \\ \overset{\approx}{V}_{23} & \overset{\approx}{V}_{24} \end{pmatrix} = 0 \tag{10.78}$$

$$\overset{\approx}{V}{}^c := \begin{pmatrix} \overset{\approx}{V}_{31} & \overset{\approx}{V}_{32} \\ V_{41} & V_{42} \end{pmatrix} = 0 \tag{10.79}$$

$$\overset{\approx}{V}{}^d := \begin{pmatrix} \overset{\approx}{V}_{33} & \overset{\approx}{V}_{34} \\ \overset{\approx}{V}_{43} & \overset{\approx}{V}_{44} \end{pmatrix} = \begin{pmatrix} e\varphi + \mu B_z & \mu B_x - i\mu B_y \\ \mu B_x + i\mu B_y & e\varphi - \mu B_z \end{pmatrix} \tag{10.80}$$

and can consequently be written as

$$\overset{\approx}{V} = \begin{pmatrix} \overset{\approx}{V}{}^a & \overset{\approx}{V}{}^b \\ \overset{\approx}{V}{}^c & \overset{\approx}{V}{}^d \end{pmatrix}. \tag{10.81}$$

Now, the important thing to note is that for φ, $\mathbf{A}$ and $\mathbf{B}$ being real, all the sub-matrices are Hermitian:

$$V^x = V^{x\dagger}, \; \overset{\approx}{V}{}^x = \overset{\approx}{V}{}^{x\dagger}, \quad x = a, b, c, d. \tag{10.82}$$

We will now continue with the potential V. However, as $\tilde{\tilde{V}}$ also fulfils the property above, an analogous treatment is possible for this representation of the potential.

Exploiting a general property of Hermitian matrices, namely that they can be decomposed into their eigenvalues and eigenvectors, we can write

$$V^x = \sum_{i=1}^{2} \lambda_i^x u_i^x u_i^{x\dagger} \tag{10.83}$$

where $\{u_1^x, u_2^x\}$ are an orthonormal set of eigenvectors of V^x forming a basis of the matrix's eigenvalue spectrum, and $\{\lambda_1^x, \lambda_2^x\}$ are the corresponding eigenvalues. Using orthogonal but not necessarily normalised vectors, we can generalise

$$V^x = \sum_{i=1}^{2} \frac{\lambda_i^x}{\|u_i^x\|^2} u_i^x u_i^{x\dagger} \tag{10.84}$$

Digression: The spin spherical harmonics χ_Λ are 2×1 column vector functions depending on the two angular variables $\hat{\mathbf{r}} = (\theta, \phi)$. They form an orthonormal basis of the vector space of square integrable two-vector functions f on the surface of the unit sphere:

$$\begin{pmatrix} f_1 \\ f_2 \end{pmatrix} : [0, \pi) \times [-\pi, \pi) \to \mathbb{C}^2,\ (\theta, \phi) \mapsto \begin{pmatrix} f_1(\theta, \phi) \\ f_2(\theta, \phi) \end{pmatrix}$$

with the scalar product given by $\langle f, g \rangle := \int d\hat{\mathbf{r}} f^\dagger(\hat{\mathbf{r}}) g(\hat{\mathbf{r}})$. Hence, any function in that vector space can be expanded in terms of spin spherical harmonics: $f(\hat{\mathbf{r}}) = \sum_\Lambda \nu_\Lambda \chi_\Lambda(\hat{\mathbf{r}})$. If the function f depends not only on the angular but also on the radial variable, the coefficients ν_Λ have a radial dependence: $f(\mathbf{r}) = \sum_\Lambda \nu_\Lambda(r) \chi_\Lambda(\hat{\mathbf{r}})$.

Now let us take the eigenvalue $\lambda_i^a(\mathbf{r})$ one of the two eigenvectors $u_i^a(\mathbf{r})$. Exploiting the fact that there exists a χ_Λ-expansion of $\lambda_i^a u_i^a$, we write:

$$\lambda_i^a(\mathbf{r}) u_i^a(\mathbf{r}) = \sum_\Lambda \nu_{i\Lambda}^a(r) \chi_\Lambda(\hat{\mathbf{r}}) \quad \text{where } \nu_{i\Lambda}^a(r) = \int d\hat{\mathbf{r}} \chi_\Lambda^\dagger(\hat{\mathbf{r}}) \lambda_i^a(\mathbf{r}) u_i^a(\mathbf{r}). \tag{10.85}$$

One could also write this in Dirac notation as

$$|u_i^a\rangle = \sum_\Lambda |\chi_\Lambda\rangle \langle \chi_\Lambda | u_i^a \rangle . \tag{10.86}$$

Obviously, the same is valid for the adjoint of the eigenvector (that is not multiplied by the eigenvalue)

$$u_i^{a\dagger}(\mathbf{r}) = \sum_\Lambda \tilde{\nu}_{i\Lambda}^a(r) \chi_\Lambda^\dagger(\hat{\mathbf{r}}) \text{ where } \tilde{\nu}_{i\Lambda}^a(r) = \left(\int d\hat{\mathbf{r}} \chi_\Lambda^\dagger(\hat{\mathbf{r}}) u_i^a(\mathbf{r}) \right)^* = \int d\hat{\mathbf{r}} u_i^{a\dagger}(\mathbf{r}) \chi_\Lambda(\hat{\mathbf{r}}) \tag{10.87}$$

or in Dirac notation

$$\langle u_i^a| = \sum_\Lambda \langle \chi_\Lambda| \langle u_i^a |\chi_\Lambda\rangle\,, \tag{10.88}$$

as it follows simply by forming the adjoint equation. That means we can write

$$\begin{aligned}\lambda_i^a(\mathbf{r})u_i^a(\mathbf{r})u_i^{a\dagger}(\mathbf{r}) &= \left(\sum_\Lambda \nu_{i\Lambda}^a(r)\chi_\Lambda(\hat{\mathbf{r}})\right)\left(\sum_{\Lambda'} \tilde{\nu}_{i\Lambda'}^a(r)\chi_{\Lambda'}^\dagger(\hat{\mathbf{r}})\right)\\ &= \sum_\Lambda\sum_{\Lambda'} \nu_{i\Lambda}^a(r)\tilde{\nu}_{i\Lambda'}^a(r)\chi_\Lambda(\hat{\mathbf{r}})\chi_{\Lambda'}^\dagger(\hat{\mathbf{r}})\end{aligned} \tag{10.89}$$

Thus the 2×2 sub-matrices can be expanded as

$$\begin{aligned}V^a(\mathbf{r}) &= \sum_{i=1}^2\sum_\Lambda\sum_{\Lambda'} \nu_{i\Lambda}^a(r)\tilde{\nu}_{i\Lambda'}^a(r)\chi_\Lambda(\hat{\mathbf{r}})\chi_{\Lambda'}^\dagger(\hat{\mathbf{r}})\\ &= \sum_\Lambda\sum_{\Lambda'}\left(\sum_{i=1}^2 \nu_{i\Lambda}^a(r)\tilde{\nu}_{i\Lambda'}^a(r)\right)\chi_\Lambda(\hat{\mathbf{r}})\chi_{\Lambda'}^\dagger(\hat{\mathbf{r}})\\ &= \sum_\Lambda\sum_{\Lambda'} v_{\Lambda\Lambda'}^a(r)\chi_\Lambda(\hat{\mathbf{r}})\chi_{\Lambda'}^\dagger(\hat{\mathbf{r}})\end{aligned} \tag{10.90}$$

defining the term in brackets as

$$v_{\Lambda\Lambda'}^a(r) := \sum_{i=1}^2 \nu_{i\Lambda}^a(r)\tilde{\nu}_{i\Lambda'}^a(r) = \sum_{i=1}^2\left(\int d\hat{\mathbf{r}}\chi_\Lambda^\dagger(\hat{\mathbf{r}})\lambda_i^a(\mathbf{r})u_i^a\right)\left(\int d\hat{\mathbf{r}}u_i^{a\dagger}(\hat{\mathbf{r}})\chi_{\Lambda'}(\hat{\mathbf{r}})\right). \tag{10.91}$$

For the other sub-matrices the expansions are similar, however they are not exactly the same. For $x=b$ the term $\lambda_i^b u_i^b$ is expanded as before in the case $x=a$, however the part $u_i^{b\dagger}$ is expanded using $\chi_{\overline{\Lambda}}$ instead of χ_Λ. This is done just to obtain a simple notation in the end. For $x=c,d$ changes are similar. Here is an overview of the different coefficients:

$$\nu_{i\Lambda}^a(r) = \int d\hat{\mathbf{r}}\chi_\Lambda^\dagger(\hat{\mathbf{r}})\lambda_i^a(\mathbf{r})u_i^a(\mathbf{r}),\quad \tilde{\nu}_{i\Lambda}^a(r) = \int d\hat{\mathbf{r}}u_i^{a\dagger}(\mathbf{r})\chi_\Lambda(\hat{\mathbf{r}}) \tag{10.92}$$

$$\nu_{i\Lambda}^b(r) = \int d\hat{\mathbf{r}}\chi_\Lambda^\dagger(\hat{\mathbf{r}})\lambda_i^b(\mathbf{r})u_i^b(\mathbf{r}),\quad \tilde{\nu}_{i\Lambda}^b(r) = \int d\hat{\mathbf{r}}u_i^{b\dagger}(\mathbf{r})\chi_{\overline{\Lambda}}(\hat{\mathbf{r}}) \tag{10.93}$$

$$\nu_{i\Lambda}^c(r) = \int d\hat{\mathbf{r}}\chi_{\overline{\Lambda}}^\dagger(\hat{\mathbf{r}})\lambda_i^c(\mathbf{r})u_i^c(\mathbf{r}),\quad \tilde{\nu}_{i\Lambda}^c(r) = \int d\hat{\mathbf{r}}u_i^{c\dagger}(\mathbf{r})\chi_\Lambda(\hat{\mathbf{r}}) \tag{10.94}$$

$$\nu_{i\Lambda}^d(r) = \int d\hat{\mathbf{r}}\chi_{\overline{\Lambda}}^\dagger(\hat{\mathbf{r}})\lambda_i^d(\mathbf{r})u_i^d(\mathbf{r}),\quad \tilde{\nu}_{i\Lambda}^d(r) = \int d\hat{\mathbf{r}}u_i^{d\dagger}(\mathbf{r})\chi_{\overline{\Lambda}}(\hat{\mathbf{r}}) \tag{10.95}$$

$$v_{\Lambda\Lambda'}^a(r) = \sum_{i=1}^2 \nu_{i\Lambda}^a(r)\tilde{\nu}_{i\Lambda'}^a(r) = \sum_{i=1}^2\left(\int d\hat{\mathbf{r}}\chi_\Lambda^\dagger(\hat{\mathbf{r}})\lambda_i^a(\mathbf{r})u_i^a\right)\left(\int d\hat{\mathbf{r}}u_i^{a\dagger}(\hat{\mathbf{r}})\chi_{\Lambda'}(\hat{\mathbf{r}})\right) \tag{10.96}$$

$$v_{\Lambda\Lambda'}^b(r) = \sum_{i=1}^2 \nu_{i\Lambda}^b(r)\tilde{\nu}_{i\Lambda'}^b(r) = \sum_{i=1}^2\left(\int d\hat{\mathbf{r}}\chi_\Lambda^\dagger(\hat{\mathbf{r}})\lambda_i^b(\mathbf{r})u_i^b\right)\left(\int d\hat{\mathbf{r}}u_i^{b\dagger}(\hat{\mathbf{r}})\chi_{\overline{\Lambda}'}(\hat{\mathbf{r}})\right) \tag{10.97}$$

$$v_{\Lambda\Lambda'}^c(r) = \sum_{i=1}^2 \nu_{i\Lambda}^c(r)\tilde{\nu}_{i\Lambda'}^c(r) = \sum_{i=1}^2\left(\int d\hat{\mathbf{r}}\chi_{\overline{\Lambda}}^\dagger(\hat{\mathbf{r}})\lambda_i^c(\mathbf{r})u_i^c\right)\left(\int d\hat{\mathbf{r}}u_i^{c\dagger}(\hat{\mathbf{r}})\chi_{\Lambda'}(\hat{\mathbf{r}})\right) \tag{10.98}$$

$$v_{\Lambda\Lambda'}^d(r) = \sum_{i=1}^2 \nu_{i\Lambda}^d(r)\tilde{\nu}_{i\Lambda'}^d(r) = \sum_{i=1}^2\left(\int d\hat{\mathbf{r}}\chi_{\overline{\Lambda}}^\dagger(\hat{\mathbf{r}})\lambda_i^d(\mathbf{r})u_i^d\right)\left(\int d\hat{\mathbf{r}}u_i^{d\dagger}(\hat{\mathbf{r}})\chi_{\overline{\Lambda}'}(\hat{\mathbf{r}})\right) \tag{10.99}$$

As a consequence of these decompositions of the sub-matrices, there exists a decomposition of the whole potential matrix V:

$$\begin{aligned} V(\mathbf{r}) &= \sum_{\Lambda}\sum_{\Lambda'} \begin{pmatrix} v^a_{\Lambda\Lambda'}(r)\chi_{\Lambda}(\hat{\mathbf{r}})\chi^{\dagger}_{\Lambda'}(\hat{\mathbf{r}}) & v^b_{\Lambda\Lambda'}(r)\chi_{\Lambda}(\hat{\mathbf{r}})\chi^{\dagger}_{\overline{\Lambda}'}(\hat{\mathbf{r}}) \\ v^c_{\Lambda\Lambda'}(r)\chi_{\overline{\Lambda}}(\hat{\mathbf{r}})\chi^{\dagger}_{\Lambda'}(\hat{\mathbf{r}}) & v^d_{\Lambda\Lambda'}(r)\chi_{\overline{\Lambda}}(\hat{\mathbf{r}})\chi^{\dagger}_{\overline{\Lambda}'}(\hat{\mathbf{r}}) \end{pmatrix} \\ &= \sum_{\Lambda}\sum_{\Lambda'} \begin{pmatrix} \chi_{\Lambda}(\hat{\mathbf{r}}) & 0 \\ 0 & \chi_{\overline{\Lambda}}(\hat{\mathbf{r}}) \end{pmatrix} \begin{pmatrix} v^a_{\Lambda\Lambda'}(r) & v^b_{\Lambda\Lambda'}(r) \\ v^c_{\Lambda\Lambda'}(r) & v^d_{\Lambda\Lambda'}(r) \end{pmatrix} \begin{pmatrix} \chi^{\dagger}_{\Lambda'}(\hat{\mathbf{r}}) & 0 \\ 0 & \chi^{\dagger}_{\overline{\Lambda}'}(\hat{\mathbf{r}}) \end{pmatrix} \end{aligned} \tag{10.100}$$

We will later on make use of this expansion for separating the radial and angular part of the Lippmann-Schwinger equation.

To have an explicit expression as it can be programmed, we evaluate the products and get

$$V = \sum_{\Lambda}\sum_{\Lambda'} \begin{pmatrix} v^a_{\Lambda\Lambda'}\chi_{\Lambda(1)}\chi^*_{\Lambda'(1)} & v^a_{\Lambda\Lambda'}\chi_{\Lambda(1)}\chi^*_{\Lambda'(2)} & v^b_{\Lambda\Lambda'}\chi_{\Lambda(1)}\chi^*_{\overline{\Lambda}'(1)} & v^b_{\Lambda\Lambda'}\chi_{\Lambda(1)}\chi^*_{\overline{\Lambda}'(2)} \\ v^a_{\Lambda\Lambda'}\chi_{\Lambda(2)}\chi^*_{\Lambda'(1)} & v^a_{\Lambda\Lambda'}\chi_{\Lambda(2)}\chi^*_{\Lambda'(2)} & v^b_{\Lambda\Lambda'}\chi_{\Lambda(2)}\chi^*_{\overline{\Lambda}'(1)} & v^b_{\Lambda\Lambda'}\chi_{\Lambda(2)}\chi^*_{\overline{\Lambda}'(2)} \\ v^c_{\Lambda\Lambda'}\chi_{\overline{\Lambda}(1)}\chi^*_{\Lambda'(1)} & v^c_{\Lambda\Lambda'}\chi_{\overline{\Lambda}(1)}\chi^*_{\Lambda'(2)} & v^d_{\Lambda\Lambda'}\chi_{\overline{\Lambda}(1)}\chi^*_{\overline{\Lambda}'(1)} & v^d_{\Lambda\Lambda'}\chi_{\overline{\Lambda}(1)}\chi^*_{\overline{\Lambda}'(2)} \\ v^c_{\Lambda\Lambda'}\chi_{\overline{\Lambda}(2)}\chi^*_{\Lambda'(1)} & v^c_{\Lambda\Lambda'}\chi_{\overline{\Lambda}(2)}\chi^*_{\Lambda'(2)} & v^d_{\Lambda\Lambda'}\chi_{\overline{\Lambda}(2)}\chi^*_{\overline{\Lambda}'(1)} & v^d_{\Lambda\Lambda'}\chi_{\overline{\Lambda}(2)}\chi^*_{\overline{\Lambda}'(2)} \end{pmatrix} \tag{10.101}$$

were $\chi_{\Lambda(1)}$ and $\chi_{\Lambda(2)}$ are the two components of the spin spherical harmonic function.

Apart from the theoretical aspect that this expansion is possible, the coefficients $v^x_{\Lambda\Lambda'}$, as defined in eq. (10.91), are also explicitly needed for calculations. It is therefore necessary to calculate all the eigenvectors u^x_i and eigenvalues λ^x_i of the sub-matrices V^x. When using the potential $\tilde{\tilde{V}}$, these eigenvalues and eigenvectors are (obviously) different, so the coefficients $v^x_{\Lambda\Lambda'}$ are also modified compared to the exact theory.

Explicit calculations of the eigenvectors and eigenvalues for the potential V yield:

$$u^a_1 = \begin{pmatrix} 0 \\ 1 \end{pmatrix},\ u^a_2 = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \tag{10.102}$$

$$\lambda^a_1 = \lambda^a_2 = e\varphi \tag{10.103}$$

$$u^b_1 = \begin{pmatrix} \frac{-A_x+iA_y}{|\mathbf{A}|+A_z} \\ 1 \end{pmatrix},\ u^b_2 = \begin{pmatrix} \frac{-A_x+iA_y}{-|\mathbf{A}|+A_z} \\ 1 \end{pmatrix} \tag{10.104}$$

$$\lambda^b_1 = e\,|\mathbf{A}|\,,\ \lambda^b_2 = -e\,|\mathbf{A}| \tag{10.105}$$

$$u^c_i = u^b_i,\ \lambda^c_i = \lambda^b_i,\ u^d_i = u^a_i,\ \lambda^d_i = \lambda^a_i. \tag{10.106}$$

When using the potential $\tilde{\tilde{V}}$ the explicit expressions are

$$u^a_1 = \begin{pmatrix} \frac{-B_x+iB_y}{|\mathbf{B}|+B_z} \\ 1 \end{pmatrix},\ u^a_2 = \begin{pmatrix} \frac{-B_x+iB_y}{-|\mathbf{B}|+B_z} \\ 1 \end{pmatrix} \tag{10.107}$$

$$\lambda^a_1 = e\varphi + \mu\,|\mathbf{B}|\,,\ \lambda^a_2 = e\varphi - \mu\,|\mathbf{B}| \tag{10.108}$$

$$u^d_1 = \begin{pmatrix} \frac{B_x-iB_y}{|\mathbf{B}|-B_z} \\ 1 \end{pmatrix},\ u^d_2 = \begin{pmatrix} \frac{B_x-iB_y}{-|\mathbf{B}|-B_z} \\ 1 \end{pmatrix} \tag{10.109}$$

$$\lambda_1^d = e\varphi + \mu\,|\mathbf{B}|\,,\ \lambda_2^d = e\varphi - \mu\,|\mathbf{B}| \tag{10.110}$$

$$u_1^b = u_1^c = \begin{pmatrix} 0 \\ 1 \end{pmatrix},\ u_2^b = u_2^c = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \tag{10.111}$$

$$\lambda_i^b = \lambda_i^c = 0. \tag{10.112}$$

These eigenvectors are not yet normalised, i.e. in the calculation one has to replace these explicit expressions for u_i by $u_i / \|u_i\|$.

10.6 Coupled Radial Equations for Full-Potential Spin-Polarised KKR

As we have seen in section 10.3, once the regular and irregular solutions of the Dirac equation for the particle in a potential are known, the Green function can be calculated by using an expansion into those solutions. The latter can be calculated from the Lippmann-Schwinger equations (10.13) – (10.16). In order to do so, we will use a further angular momentum expansion, i.e. the potential and the Green function are expanded. This will result in coefficients $R_{\Lambda\Lambda'}$ from which the regular solutions R_Λ can be calculated.

We start off expanding R_Λ in terms of spin spherical harmonics:

$$R_\Lambda(\mathbf{r}) = \sum_{\Lambda'} \begin{pmatrix} R^a_{\Lambda'\Lambda}(r)\chi_{\Lambda'}(\hat{\mathbf{r}}) \\ iR^b_{\Lambda'\Lambda}(r)\chi_{\overline{\Lambda}'}(\hat{\mathbf{r}}) \end{pmatrix} = \sum_{\Lambda'} \begin{pmatrix} \chi_{\Lambda'}(\hat{\mathbf{r}}) & 0 \\ 0 & \chi_{\overline{\Lambda}'}(\hat{\mathbf{r}}) \end{pmatrix} \begin{pmatrix} R^a_{\Lambda'\Lambda}(r) \\ iR^b_{\Lambda'\Lambda}(r) \end{pmatrix}. \tag{10.113}$$

As we know that the spin spherical harmonics χ_Λ are 2×1 column vectors, the expression at the right hand side is a 4×2 matrix times a 2×1 column vector ($R^t_{\Lambda'\Lambda}$ and $R^t_{\Lambda'\Lambda}$ are scalar functions), thus yielding a 4×1 column vector. That is what the solution of the Dirac equation R_Λ (here in angular momentum representation) should be.

From eq. (8.55) we know we can write

$$J_\Lambda(\mathbf{r}) = \begin{pmatrix} J^a_\Lambda(r)\chi_\Lambda(\hat{\mathbf{r}}) \\ iJ^b_\Lambda(r)\chi_{\overline{\Lambda}}(\hat{\mathbf{r}}) \end{pmatrix} = \begin{pmatrix} \chi_\Lambda(\hat{\mathbf{r}}) & 0 \\ 0 & \chi_{\overline{\Lambda}}(\hat{\mathbf{r}}) \end{pmatrix} \begin{pmatrix} J^a_\Lambda(r) \\ iJ^b_\Lambda(r) \end{pmatrix} \tag{10.114}$$

where the following definition was made:

$$\begin{pmatrix} J^a_\Lambda(r) \\ iJ^b_\Lambda(r) \end{pmatrix} := \begin{pmatrix} j_l(kr) \\ \frac{ikc\hbar\cdot\mathrm{sign}(\kappa)}{W+mc^2} j_{\bar{l}}(kr) \end{pmatrix}. \tag{10.115}$$

Using eq. (9.28) we can write the Green function as

$$\begin{aligned} G^0(\mathbf{r},\mathbf{r}';W) &= -\frac{ik\,(W+mc^2)}{c^2\hbar^2} \sum_\Lambda \begin{pmatrix} G^a_\Lambda(r,r')\chi_\Lambda(\hat{\mathbf{r}})\chi^\dagger_\Lambda(\hat{\mathbf{r}}') & iG^b_\Lambda(r,r')\chi_\Lambda(\hat{\mathbf{r}})\chi^\dagger_{\overline{\Lambda}}(\hat{\mathbf{r}}') \\ iG^c_\Lambda(r,r')\chi_{\overline{\Lambda}}(\hat{\mathbf{r}})\chi^\dagger_\Lambda(\hat{\mathbf{r}}') & G^d_\Lambda(r,r')\chi_{\overline{\Lambda}}(\hat{\mathbf{r}})\chi^\dagger_{\overline{\Lambda}}(\hat{\mathbf{r}}') \end{pmatrix} \\ &= -\frac{ik\,(W+mc^2)}{c^2\hbar^2} \sum_\Lambda \begin{pmatrix} \chi_\Lambda(\hat{\mathbf{r}}) & 0 \\ 0 & \chi_{\overline{\Lambda}}(\hat{\mathbf{r}}) \end{pmatrix} \\ &\quad \cdot \begin{pmatrix} G^a_\Lambda(r,r') & iG^b_\Lambda(r,r') \\ iG^c_\Lambda(r,r') & G^d_\Lambda(r,r') \end{pmatrix} \begin{pmatrix} \chi^\dagger_\Lambda(\hat{\mathbf{r}}') & 0 \\ 0 & \chi^\dagger_{\overline{\Lambda}}(\hat{\mathbf{r}}') \end{pmatrix} \end{aligned} \tag{10.116}$$

with the definition

$$\begin{pmatrix} G^a_\Lambda(r,r') & iG^b_\Lambda(r,r') \\ iG^c_\Lambda(r,r') & G^d_\Lambda(r,r') \end{pmatrix} := \\ \Theta(r-r') \begin{pmatrix} h_l(kr)j_l(kr') & \frac{-ic\hbar k\,\mathrm{sign}(\kappa)}{(W+mc^2)} h_l(kr)j_{\bar{l}}(kr') \\ \frac{ic\hbar k\,\mathrm{sign}(\kappa)}{(W+mc^2)} h_{\bar{l}}(kr)j_l(kr') & \frac{c^2\hbar^2k^2}{(W+mc^2)^2} h_{\bar{l}}(kr)j_{\bar{l}}(kr') \end{pmatrix} \\ +\Theta(r'-r) \begin{pmatrix} h_l(kr')j_l(kr) & \frac{-ic\hbar k\,\mathrm{sign}(\kappa)}{(W+mc^2)} h_l(kr')j_{\bar{l}}(kr) \\ \frac{ic\hbar k\,\mathrm{sign}(\kappa)}{(W+mc^2)} h_{\bar{l}}(kr')j_l(kr) & \frac{c^2\hbar^2k^2}{(W+mc^2)^2} h_{\bar{l}}(kr')j_{\bar{l}}(kr) \end{pmatrix}. \quad (10.117)$$

Note that this matrix has dimension 2×2, whereas the full Green function $G^0(\mathbf{r},\mathbf{r}';W)$ is a 4×4 matrix. As the matrix of spin spherical harmonics multiplied from the left has dimensions 4×2 and the one multiplied from the right has dimensions 2×4, everything is well-defined.

And last but not least the potential is expanded in the following form:

$$V(\mathbf{r}) = \sum_\Lambda \sum_{\Lambda'} \begin{pmatrix} \chi_\Lambda(\hat{\mathbf{r}}) & 0 \\ 0 & \chi_{\bar{\Lambda}}(\hat{\mathbf{r}}) \end{pmatrix} \begin{pmatrix} v^a_{\Lambda\Lambda'}(r) & v^b_{\Lambda\Lambda'}(r) \\ v^c_{\Lambda\Lambda'}(r) & v^d_{\Lambda\Lambda'}(r) \end{pmatrix} \begin{pmatrix} \chi^\dagger_{\Lambda'}(\hat{\mathbf{r}}) & 0 \\ 0 & \chi^\dagger_{\bar{\Lambda}'}(\hat{\mathbf{r}}) \end{pmatrix}. \quad (10.118)$$

We continue from is the Lippmann-Schwinger equation (10.13)

$$R_\Lambda(\mathbf{r}) = J_\Lambda(\mathbf{r}) + \int d\mathbf{r}' G^0(\mathbf{r},\mathbf{r}';W) V(\mathbf{r}') R_\Lambda(\mathbf{r}'). \quad (10.119)$$

Inserting all the expansion into this equation yields

$$\sum_{\Lambda^5} \begin{pmatrix} \chi_{\Lambda^5}(\hat{\mathbf{r}}) & 0 \\ 0 & \chi_{\bar{\Lambda}^5}(\hat{\mathbf{r}}) \end{pmatrix} \begin{pmatrix} R^a_{\Lambda^5\Lambda}(r) \\ iR^b_{\Lambda^5\Lambda}(r) \end{pmatrix} \\ = \begin{pmatrix} \chi_\Lambda(\hat{\mathbf{r}}) & 0 \\ 0 & \chi_{\bar{\Lambda}}(\hat{\mathbf{r}}) \end{pmatrix} \begin{pmatrix} J^a_\Lambda(r) \\ iJ^b_\Lambda(r) \end{pmatrix} - \frac{ik\,(W+mc^2)}{c^2\hbar^2} \\ \cdot \int d\mathbf{r}' \sum_\Lambda \begin{pmatrix} \chi_\Lambda(\hat{\mathbf{r}}) & 0 \\ 0 & \chi_{\bar{\Lambda}}(\hat{\mathbf{r}}) \end{pmatrix} \begin{pmatrix} G^a_\Lambda(r,r') & iG^b_\Lambda(r,r') \\ iG^c_\Lambda(r,r') & G^d_\Lambda(r,r') \end{pmatrix} \begin{pmatrix} \chi^\dagger_\Lambda(\hat{\mathbf{r}}') & 0 \\ 0 & \chi^\dagger_{\bar{\Lambda}}(\hat{\mathbf{r}}') \end{pmatrix} \\ \cdot \sum_{\Lambda^2\Lambda^3} \begin{pmatrix} \chi_{\Lambda^2}(\hat{\mathbf{r}}') & 0 \\ 0 & \chi_{\bar{\Lambda}^2}(\hat{\mathbf{r}}') \end{pmatrix} \begin{pmatrix} v^a_{\Lambda^2\Lambda^3}(r') & v^b_{\Lambda^2\Lambda^3}(r') \\ v^c_{\Lambda^2\Lambda^3}(r') & v^d_{\Lambda^2\Lambda^3}(r') \end{pmatrix} \begin{pmatrix} \chi^\dagger_{\Lambda^3}(\hat{\mathbf{r}}') & 0 \\ 0 & \chi^\dagger_{\bar{\Lambda}^3}(\hat{\mathbf{r}}') \end{pmatrix} \\ \cdot \sum_{\Lambda^4} \begin{pmatrix} \chi_{\Lambda^4}(\hat{\mathbf{r}}') & 0 \\ 0 & \chi_{\bar{\Lambda}^4}(\hat{\mathbf{r}}') \end{pmatrix} \begin{pmatrix} R^a_{\Lambda^4\Lambda}(r') \\ iR^b_{\Lambda^4\Lambda}(r') \end{pmatrix}$$

Now multiplying by the matrix $\begin{pmatrix} \chi^\dagger_{\Lambda'}(\hat{\mathbf{r}}) & 0 \\ 0 & \chi^\dagger_{\bar{\Lambda}'}(\hat{\mathbf{r}}) \end{pmatrix}$ from the left, integrating by $\hat{\mathbf{r}}$ and using

the orthonormality of the spin spherical harmonics yields the equation

$$\begin{aligned}
&\begin{pmatrix} R^a_{\Lambda'\Lambda}(r) \\ iR^b_{\Lambda'\Lambda}(r) \end{pmatrix} = \begin{pmatrix} J^a_{\Lambda}(r) \\ iJ^b_{\Lambda}(r) \end{pmatrix} \delta_{\Lambda\Lambda'} \\
&-\frac{ik\,(W+mc^2)}{c^2\hbar^2} \int d\mathbf{r}' \begin{pmatrix} G^a_{\Lambda'}(r,r') & iG^b_{\Lambda'}(r,r') \\ iG^c_{\Lambda'}(r,r') & G^d_{\Lambda'}(r,r') \end{pmatrix} \begin{pmatrix} \chi^\dagger_{\Lambda'}(\hat{\mathbf{r}}') & 0 \\ 0 & \chi^\dagger_{\overline{\Lambda}'}(\hat{\mathbf{r}}') \end{pmatrix} \\
&\cdot \sum_{\Lambda^2\Lambda^3} \begin{pmatrix} \chi_{\Lambda^2}(\hat{\mathbf{r}}') & 0 \\ 0 & \chi_{\overline{\Lambda}^2}(\hat{\mathbf{r}}') \end{pmatrix} \begin{pmatrix} v^a_{\Lambda^2\Lambda^3}(r') & v^b_{\Lambda^2\Lambda^3}(r') \\ v^c_{\Lambda^2\Lambda^3}(r') & v^d_{\Lambda^2\Lambda^3}(r') \end{pmatrix} \begin{pmatrix} \chi^\dagger_{\Lambda^3}(\hat{\mathbf{r}}') & 0 \\ 0 & \chi^\dagger_{\overline{\Lambda}^3}(\hat{\mathbf{r}}') \end{pmatrix} \\
&\cdot \sum_{\Lambda^4} \begin{pmatrix} \chi_{\Lambda^4}(\hat{\mathbf{r}}') & 0 \\ 0 & \chi_{\overline{\Lambda}^4}(\hat{\mathbf{r}}') \end{pmatrix} \begin{pmatrix} R^a_{\Lambda^4\Lambda}(r') \\ iR^b_{\Lambda^4\Lambda}(r') \end{pmatrix}
\end{aligned} \tag{10.120}$$

From now on it is necessary to assume that we are using the potential $\tilde{\tilde{V}}$ with a $\mathbf{B}$ field and not one with a full vector field $\mathbf{A}$. If that is the case, it is $v^b_{\Lambda^2\Lambda^3} = v^c_{\Lambda^2\Lambda^3} = 0$, i.e. the 2×2 potential matrix only has diagonal entries and consequently it commutes with the matrices containing spin spherical harmonics. Therefore, one can take out the sums, write all the spin spherical harmonic matrices in a row and then write all the spin spherical harmonics into one matrix:

$$\begin{aligned}
&\begin{pmatrix} R^a_{\Lambda'\Lambda}(r) \\ iR^b_{\Lambda'\Lambda}(r) \end{pmatrix} = \begin{pmatrix} J^a_{\Lambda}(r) \\ iJ^b_{\Lambda}(r) \end{pmatrix} \delta_{\Lambda\Lambda'} \\
&-\frac{ik\,(W+mc^2)}{c^2\hbar^2} \int d\mathbf{r}' \begin{pmatrix} G^a_{\Lambda'}(r,r') & iG^b_{\Lambda'}(r,r') \\ iG^c_{\Lambda'}(r,r') & G^d_{\Lambda'}(r,r') \end{pmatrix} \\
&\cdot \sum_{\Lambda^2\Lambda^3\Lambda^4} \begin{pmatrix} \chi^\dagger_{\Lambda'}(\hat{\mathbf{r}})\chi_{\Lambda^2}(\hat{\mathbf{r}}')\chi^\dagger_{\Lambda^3}(\hat{\mathbf{r}}')\chi_{\Lambda^4}(\hat{\mathbf{r}}') & 0 \\ 0 & \chi^\dagger_{\overline{\Lambda}'}(\hat{\mathbf{r}})\chi_{\overline{\Lambda}^2}(\hat{\mathbf{r}}')\chi^\dagger_{\overline{\Lambda}^3}(\hat{\mathbf{r}}')\chi_{\overline{\Lambda}^4}(\hat{\mathbf{r}}') \end{pmatrix} \\
&\cdot \begin{pmatrix} v^a_{\Lambda^2\Lambda^3}(r') & 0 \\ 0 & v^d_{\Lambda^2\Lambda^3}(r') \end{pmatrix} \begin{pmatrix} R^a_{\Lambda^4\Lambda}(r'') \\ iR^b_{\Lambda^4\Lambda}(r'') \end{pmatrix}.
\end{aligned}$$

Separating angular and radial integral parts, this can be rewritten as:

$$\begin{aligned}
&\begin{pmatrix} R^a_{\Lambda'\Lambda}(r) \\ iR^b_{\Lambda'\Lambda}(r) \end{pmatrix} = \begin{pmatrix} J^a_{\Lambda}(r) \\ iJ^b_{\Lambda}(r) \end{pmatrix} \delta_{\Lambda\Lambda'} \\
&-\frac{ik\,(W+mc^2)}{c^2\hbar^2} \sum_{\Lambda^2\Lambda^3\Lambda^4} \int dr' \begin{pmatrix} G^a_{\Lambda'}(r,r') & iG^b_{\Lambda'}(r,r') \\ iG^c_{\Lambda'}(r,r') & G^d_{\Lambda'}(r,r') \end{pmatrix} \\
&\cdot \left[\int d\hat{\mathbf{r}}' \begin{pmatrix} \chi^\dagger_{\Lambda'}(\hat{\mathbf{r}})\chi_{\Lambda^2}(\hat{\mathbf{r}}')\chi^\dagger_{\Lambda^3}(\hat{\mathbf{r}}')\chi_{\Lambda^4}(\hat{\mathbf{r}}') & 0 \\ 0 & \chi^\dagger_{\overline{\Lambda}'}(\hat{\mathbf{r}})\chi_{\overline{\Lambda}^2}(\hat{\mathbf{r}}')\chi^\dagger_{\overline{\Lambda}^3}(\hat{\mathbf{r}}')\chi_{\overline{\Lambda}^4}(\hat{\mathbf{r}}') \end{pmatrix} \right] \\
&\cdot \begin{pmatrix} v^a_{\Lambda^2\Lambda^3}(r') & 0 \\ 0 & v^d_{\Lambda^2\Lambda^3}(r') \end{pmatrix} \begin{pmatrix} R^a_{\Lambda^4\Lambda}(r'') \\ iR^b_{\Lambda^4\Lambda}(r'') \end{pmatrix}.
\end{aligned}$$

Now, in analogy to the Gaunt coefficients in the non-relativistic case, the coefficient matrices

$$\begin{pmatrix} D_{\Lambda'\Lambda^2\Lambda^3\Lambda^4} & 0 \\ 0 & D_{\overline{\Lambda}'\overline{\Lambda}^2\overline{\Lambda}^3\overline{\Lambda}^4} \end{pmatrix}$$

are defined where

$$D_{\Lambda'\Lambda^2\Lambda^3\Lambda^4} := \int d\hat{\mathbf{r}}' \chi^\dagger_{\Lambda'}(\hat{\mathbf{r}}')\chi_{\Lambda^2}(\hat{\mathbf{r}}')\chi^\dagger_{\Lambda^3}(\hat{\mathbf{r}}')\chi_{\Lambda^4}(\hat{\mathbf{r}}') \tag{10.121}$$

Using these coefficients the equation can already be written as an exclusively radial equation. However, there are still three sums. By defining new potential coefficients given by

$$\begin{pmatrix} w^a_{\Lambda'\Lambda^4}(r') & 0 \\ 0 & w^d_{\Lambda'\Lambda^4}(r') \end{pmatrix} := \sum_{\Lambda^2\Lambda^3} \begin{pmatrix} D_{\Lambda'\Lambda^2\Lambda^3\Lambda^4} v^a_{\Lambda^2\Lambda^3}(r') & 0 \\ 0 & D_{\overline{\Lambda}'\overline{\Lambda}^2\overline{\Lambda}^3\overline{\Lambda}^4} v^d_{\Lambda^2\Lambda^3}(r') \end{pmatrix} \tag{10.122}$$

it can be simplified to the form

$$\begin{aligned} \begin{pmatrix} R^a_{\Lambda'\Lambda}(r) \\ iR^b_{\Lambda'\Lambda}(r) \end{pmatrix} &= \begin{pmatrix} J^a_\Lambda(r) \\ iJ^b_\Lambda(r) \end{pmatrix} \delta_{\Lambda\Lambda'} \\ -\frac{ik\,(W+mc^2)}{c^2\hbar^2} \sum_{\Lambda^2\Lambda^3\Lambda^4} \int dr' \begin{pmatrix} G^a_{\Lambda'}(r,r') & iG^b_{\Lambda'}(r,r') \\ iG^c_{\Lambda'}(r,r') & G^d_{\Lambda'}(r,r') \end{pmatrix} \\ \cdot \begin{pmatrix} w^a_{\Lambda'\Lambda^4}(r') & 0 \\ 0 & w^d_{\Lambda'\Lambda^4}(r') \end{pmatrix} \begin{pmatrix} R^a_{\Lambda^4\Lambda}(r'') \\ iR^b_{\Lambda^4\Lambda}(r'') \end{pmatrix} \end{aligned}$$

For convenience we rename $\Lambda^4 \to \Lambda''$.

The coupled radial relativistic Lippmann-Schwinger equations are given by

$$\begin{aligned} \begin{pmatrix} R^a_{\Lambda'\Lambda}(r) \\ iR^b_{\Lambda'\Lambda}(r) \end{pmatrix} &= \begin{pmatrix} J^a_\Lambda(r) \\ iJ^b_\Lambda(r) \end{pmatrix} \delta_{\Lambda\Lambda'} \\ -\frac{ik\,(W+mc^2)}{c^2\hbar^2} \int dr' r'^2 \begin{pmatrix} G^a_{\Lambda'}(r,r') & iG^b_{\Lambda'}(r,r') \\ iG^c_{\Lambda'}(r,r') & G^d_{\Lambda'}(r,r') \end{pmatrix} \\ \cdot \sum_{\Lambda''} \begin{pmatrix} w^a_{\Lambda'\Lambda''}(r') & 0 \\ 0 & w^d_{\Lambda'\Lambda''}(r') \end{pmatrix} \begin{pmatrix} R^a_{\Lambda''\Lambda}(r') \\ iR^b_{\Lambda''\Lambda}(r') \end{pmatrix}. \end{aligned} \tag{10.123}$$

The section is concluded with a closer look at the D coefficients. They are coefficients not depending on the position $\mathbf{r}$, i.e. the integrals can be calculated once and the values can be stored, without the need to calculate the integrals every time a Lippmann-Schwinger equation needs to be solved. The D coefficients have four indices, which means that for calculations up to Λ_{cut} one has to store Λ^4_{cut} values. If, for example, $l_{\text{cut}} = 3$ is chosen as the maximal l value in the calculation, Λ goes up to $\Lambda_{\text{cut}} = 32$. However, to include also the $\overline{\Lambda}$ coefficients, one has to go up to $\Lambda_{\text{cut}} = 40$. Storing all the $40^4 = 2560000$ coefficients yields a file size of roughly 90 MB (18 digits precision for non-zero values). This is still an acceptable size. However, for calculations using large l values, the following trick might be of interest.

Starting from the definition the integral is written as a double integral:

$$\begin{aligned} D_{\Lambda'\Lambda^2\Lambda^3\Lambda^4} : &= \int d\hat{\mathbf{r}} \chi^\dagger_{\Lambda'}(\hat{\mathbf{r}}) \chi_{\Lambda^2}(\hat{\mathbf{r}}) \chi^\dagger_{\Lambda^3}(\hat{\mathbf{r}}) \chi_{\Lambda^4}(\hat{\mathbf{r}}) \\ &= \int d\hat{\mathbf{r}} \int d\hat{\mathbf{r}}' \chi^\dagger_{\Lambda'}(\hat{\mathbf{r}}) \chi_{\Lambda^2}(\hat{\mathbf{r}}) \delta(\hat{\mathbf{r}} - \hat{\mathbf{r}}') \chi^\dagger_{\Lambda^3}(\hat{\mathbf{r}}') \chi_{\Lambda^4}(\hat{\mathbf{r}}'). \end{aligned} \tag{10.124}$$

Inserting the completeness relation of the spin spherical harmonics

$$\sum_{\Lambda} \chi^\dagger_{\Lambda}(\hat{\mathbf{r}}) \chi_{\Lambda}(\hat{\mathbf{r}}') = \delta(\hat{\mathbf{r}} - \hat{\mathbf{r}}') \tag{10.125}$$

one can rewrite

$$\begin{aligned} D_{\Lambda'\Lambda^2\Lambda^3\Lambda^4} : &= \int d\hat{\mathbf{r}} \int d\hat{\mathbf{r}}' \chi^\dagger_{\Lambda'}(\hat{\mathbf{r}}) \chi_{\Lambda^2}(\hat{\mathbf{r}}) \sum_{\Lambda} \chi^\dagger_{\Lambda}(\hat{\mathbf{r}}) \chi_{\Lambda}(\hat{\mathbf{r}}') \chi^\dagger_{\Lambda^3}(\hat{\mathbf{r}}') \chi_{\Lambda^4}(\hat{\mathbf{r}}') \\ &= \sum_{\Lambda} \left(\int d\hat{\mathbf{r}} \chi^\dagger_{\Lambda'}(\hat{\mathbf{r}}) \chi_{\Lambda^2}(\hat{\mathbf{r}}) \chi^\dagger_{\Lambda}(\hat{\mathbf{r}}) \right) \left(\int d\hat{\mathbf{r}}' \chi_{\Lambda}(\hat{\mathbf{r}}') \chi^\dagger_{\Lambda^3}(\hat{\mathbf{r}}') \chi_{\Lambda^4}(\hat{\mathbf{r}}') \right) \end{aligned} \tag{10.126}$$

Defining new coefficients

$$d_{\Lambda\Lambda^2\Lambda'} := \int d\hat{\mathbf{r}} \chi_{\Lambda}(\hat{\mathbf{r}}) \chi^\dagger_{\Lambda^2}(\hat{\mathbf{r}}) \chi_{\Lambda'}(\hat{\mathbf{r}}) \tag{10.127}$$

which are 2×1 vectors and have the property

$$d^\dagger_{\Lambda\Lambda^2\Lambda'} = \int d\hat{\mathbf{r}} \chi^\dagger_{\Lambda'}(\hat{\mathbf{r}}) \chi_{\Lambda^2}(\hat{\mathbf{r}}) \chi^\dagger_{\Lambda}(\hat{\mathbf{r}}) \tag{10.128}$$

the equation can be written as

$$D_{\Lambda'\Lambda^2\Lambda^3\Lambda^4} = \sum_{\Lambda} d^\dagger_{\Lambda\Lambda^2\Lambda'} d_{\Lambda\Lambda^3\Lambda^4}. \tag{10.129}$$

Hence, using the d coefficients, one has the chance to store only Λ^3_{cut} instead of Λ^4_{cut} values, however, with the disadvantage of having to calculate the sum of equation (10.129) for each quadruple of $(\Lambda', \Lambda^1, \Lambda^2, \Lambda^3)$ values.

The d coefficients can also be boiled down to sums over Clebsch-Gordan coefficients and Gaunt coefficients by writing the spin spherical harmonics in terms of spherical harmonics and replacing the occurring Gaunt coefficient terms.

10.7 Coupled Radial Equations for Full-Potential Spin-Current KKR

Fully relativistic calculations where the vector field $\mathbf{A}$ is not replaced by a magnetic field $\mathbf{B}$ are termed spin-current density functional theory. When using a magnetic field $\mathbf{B}$ the self-consistency circle is run for a spin-up potential $V^\uparrow$ and a spin-down potential $V^\downarrow$. From these two potentials one can calculate $\varphi(\mathbf{r})$ and $\mathbf{B}(\mathbf{r})$. Since a scalar-relativistic code needs the same two potentials, the necessary modifications in the KKR code to embed a fully relativistic single-site solver (given that the solver already exists) are small. In spin-current

calculations, however, the self-consistency circle has to be run for the potentials $\mathbf{A}$ and φ, which means that the whole KKR code needs to be modified to embed a fully relativistic spin-current single-site solver. A further difficulty is that the exchange-correlation potential for spin-current DFT is still under development.

Therefore, in the solver I implemented I used the approximation of a $\mathbf{B}$ field. Nonetheless, here I will present the coupled radial equations for a fully-relativistic full-potential spin-current single-site solver. The additional effort for the single-site problem is manageable and thus it might be interesting in the future to implement these equations.

I start from eq. (10.120). As the v^b and v^c coefficients are no longer vanishing, the next matrices do not any more nicely commute as they did before. However, the equation can be rewritten as

$$\begin{aligned}
&\begin{pmatrix} R^a_{\Lambda'\Lambda}(r) \\ iR^b_{\Lambda'\Lambda}(r) \end{pmatrix} = \begin{pmatrix} J^a_{\Lambda}(r) \\ iJ^b_{\Lambda}(r) \end{pmatrix} \delta_{\Lambda\Lambda'} \\
&-\frac{ik\,(W+mc^2)}{c^2\hbar^2} \sum_{\Lambda^2\Lambda^3\Lambda^4} \int d\mathbf{r}' \begin{pmatrix} G^a_{\Lambda}(r,r') & iG^b_{\Lambda}(r,r') \\ iG^c_{\Lambda}(r,r') & G^d_{\Lambda}(r,r') \end{pmatrix} \\
&\cdot \begin{pmatrix} \chi^\dagger_{\Lambda'}(\hat{\mathbf{r}}')\chi_{\Lambda^2}(\hat{\mathbf{r}}')\chi^\dagger_{\Lambda^3}(\hat{\mathbf{r}}')\chi_{\Lambda^4}(\hat{\mathbf{r}}')v^a_{\Lambda^2\Lambda^3}(r') & \chi^\dagger_{\Lambda'}(\hat{\mathbf{r}}')\chi_{\Lambda^2}(\hat{\mathbf{r}}')\chi^\dagger_{\overline{\Lambda}^3}(\hat{\mathbf{r}}')\chi_{\overline{\Lambda}^4}(\hat{\mathbf{r}}')v^b_{\Lambda^2\Lambda^3}(r') \\ \chi^\dagger_{\overline{\Lambda}'}(\hat{\mathbf{r}}')\chi_{\overline{\Lambda}^2}(\hat{\mathbf{r}}')\chi^\dagger_{\Lambda^3}(\hat{\mathbf{r}}')\chi_{\Lambda^4}(\hat{\mathbf{r}}')v^c_{\Lambda^2\Lambda^3}(r') & \chi^\dagger_{\Lambda'}(\hat{\mathbf{r}}')\chi_{\overline{\Lambda}^2}(\hat{\mathbf{r}}')\chi^\dagger_{\overline{\Lambda}^3}(\hat{\mathbf{r}}')\chi_{\overline{\Lambda}^4}(\hat{\mathbf{r}}')v^d_{\Lambda^2\Lambda^3}(r') \end{pmatrix} \\
&\cdot \begin{pmatrix} R^a_{\Lambda^4\Lambda}(r') \\ iR^b_{\Lambda^4\Lambda}(r') \end{pmatrix}
\end{aligned}$$

Separating radial and spherical integral parts is still possible:

$$\begin{aligned}
&\begin{pmatrix} R^a_{\Lambda'\Lambda}(r) \\ iR^b_{\Lambda'\Lambda}(r) \end{pmatrix} = \begin{pmatrix} J^a_{\Lambda}(r) \\ iJ^b_{\Lambda}(r) \end{pmatrix} \delta_{\Lambda\Lambda'} \\
&-\frac{ik\,(W+mc^2)}{c^2\hbar^2} \sum_{\Lambda^2\Lambda^3\Lambda^4} \int dr' \begin{pmatrix} G^a_{\Lambda}(r,r') & iG^b_{\Lambda}(r,r') \\ iG^c_{\Lambda}(r,r') & G^d_{\Lambda}(r,r') \end{pmatrix} \\
&\cdot \begin{pmatrix} \left[\int d\hat{\mathbf{r}}'\chi^\dagger_{\Lambda'}(\hat{\mathbf{r}}')\chi_{\Lambda^2}(\hat{\mathbf{r}}')\chi^\dagger_{\Lambda^3}(\hat{\mathbf{r}}')\chi_{\Lambda^4}(\hat{\mathbf{r}}')\right] v^a_{\Lambda^2\Lambda^3}(r') & \left[\int d\hat{\mathbf{r}}'\chi^\dagger_{\Lambda'}(\hat{\mathbf{r}}')\chi_{\Lambda^2}(\hat{\mathbf{r}}')\chi^\dagger_{\overline{\Lambda}^3}(\hat{\mathbf{r}}')\chi_{\overline{\Lambda}^4}(\hat{\mathbf{r}}')\right] v^b_{\Lambda^2\Lambda^3}(r') \\ \left[\int d\hat{\mathbf{r}}'\chi^\dagger_{\overline{\Lambda}'}(\hat{\mathbf{r}}')\chi_{\overline{\Lambda}^2}(\hat{\mathbf{r}}')\chi^\dagger_{\Lambda^3}(\hat{\mathbf{r}}')\chi_{\Lambda^4}(\hat{\mathbf{r}}')\right] v^c_{\Lambda^2\Lambda^3}(r') & \left[\int d\hat{\mathbf{r}}'\chi^\dagger_{\overline{\Lambda}'}(\hat{\mathbf{r}}')\chi_{\overline{\Lambda}^2}(\hat{\mathbf{r}}')\chi^\dagger_{\overline{\Lambda}^3}(\hat{\mathbf{r}}')\chi_{\overline{\Lambda}^4}(\hat{\mathbf{r}}')\right] v^d_{\Lambda^2\Lambda^3}(r') \end{pmatrix} \\
&\cdot \begin{pmatrix} R^a_{\Lambda^4\Lambda}(r') \\ iR^b_{\Lambda^4\Lambda}(r') \end{pmatrix}
\end{aligned}$$

Using the relativistic equivalent of the Gaunt-coefficients that I introduced in eq. (10.121), this can be written as

$$\begin{aligned}
&\begin{pmatrix} R^a_{\Lambda'\Lambda}(r) \\ iR^b_{\Lambda'\Lambda}(r) \end{pmatrix} = \begin{pmatrix} J^a_{\Lambda}(r) \\ iJ^b_{\Lambda}(r) \end{pmatrix} \delta_{\Lambda\Lambda'} \\
&-\frac{ik\,(W+mc^2)}{c^2\hbar^2} \sum_{\Lambda^2\Lambda^3\Lambda^4} \int dr' \begin{pmatrix} G^a_{\Lambda}(r,r') & iG^b_{\Lambda}(r,r') \\ iG^c_{\Lambda}(r,r') & G^d_{\Lambda}(r,r') \end{pmatrix} \\
&\cdot \begin{pmatrix} D_{\Lambda'\Lambda^2\Lambda^3\Lambda^4}v^a_{\Lambda^2\Lambda^3}('r) & D_{\Lambda'\Lambda^2\overline{\Lambda}^3\overline{\Lambda}^4}v^b_{\Lambda^2\Lambda^3}(r') \\ D_{\overline{\Lambda}'\overline{\Lambda}^2\Lambda^3\Lambda^4}v^c_{\Lambda^2\Lambda^3}(r') & D_{\overline{\Lambda}'\overline{\Lambda}^2\overline{\Lambda}^3\overline{\Lambda}^4}v^d_{\Lambda^2\Lambda^3}(r') \end{pmatrix} \\
&\cdot \begin{pmatrix} R^a_{\Lambda^4\Lambda}(r') \\ iR^b_{\Lambda^4\Lambda}(r') \end{pmatrix}.
\end{aligned}$$

Now I define the new potential coefficients as

$$\begin{aligned}\begin{pmatrix} w^a_{\Lambda'\Lambda^4}(r') & w^b_{\Lambda'\Lambda^4}(r') \\ w^c_{\Lambda'\Lambda^4}(r') & w^d_{\Lambda'\Lambda^4}(r') \end{pmatrix} :&= \sum_{\Lambda^2\Lambda^3} \begin{pmatrix} D_{\Lambda'\Lambda^2\Lambda^3\Lambda^4} v^a_{\Lambda^2\Lambda^3}(r') & D_{\Lambda'\Lambda^2\bar{\Lambda}^3\bar{\Lambda}^4} v^b_{\Lambda^2\Lambda^3}(r') \\ D_{\bar{\Lambda}'\bar{\Lambda}^2\Lambda^3\Lambda^4} v^c_{\Lambda^2\Lambda^3}(r') & D_{\bar{\Lambda}'\bar{\Lambda}^2\bar{\Lambda}^3\bar{\Lambda}^4} v^d_{\Lambda^2\Lambda^3}(r') \end{pmatrix} \\ &= \sum_{\Lambda\Lambda^2\Lambda^3} \begin{pmatrix} d^\dagger_{\Lambda\Lambda^2\Lambda'} d_{\Lambda\Lambda^3\Lambda^4} v^a_{\Lambda^2\Lambda^3}(r') & d^\dagger_{\Lambda\Lambda^2\Lambda'} d_{\Lambda\bar{\Lambda}^3\bar{\Lambda}^4} v^b_{\Lambda^2\Lambda^3}(r') \\ d^\dagger_{\Lambda\bar{\Lambda}^2\bar{\Lambda}'} d_{\Lambda\Lambda^3\Lambda^4} v^c_{\Lambda^2\Lambda^3}(r') & d^\dagger_{\Lambda\bar{\Lambda}^2\bar{\Lambda}'} d_{\Lambda\bar{\Lambda}^3\bar{\Lambda}^4} v^d_{\Lambda^2\Lambda^3}(r') \end{pmatrix}\end{aligned} \tag{10.130}$$

yielding the coupled radial equations (after renaming $\Lambda^4 \to \Lambda''$.):

The coupled radial relativistic Lippmann-Schwinger equations for full-potential spin-current calculations are given by

$$\begin{aligned}&\begin{pmatrix} R^a_{\Lambda'\Lambda}(r) \\ iR^b_{\Lambda'\Lambda}(r) \end{pmatrix} = \begin{pmatrix} J^a_\Lambda(r) \\ iJ^b_\Lambda(r) \end{pmatrix} \delta_{\Lambda\Lambda'} \\ &-\frac{ik\,(W+mc^2)}{c^2\hbar^2} \int dr' r'^2 \begin{pmatrix} G^a_{\Lambda'}(r,r') & iG^b_{\Lambda'}(r,r') \\ iG^c_{\Lambda'}(r,r') & G^d_{\Lambda'}(r,r') \end{pmatrix} \\ &\cdot \sum_{\Lambda''} \begin{pmatrix} w^a_{\Lambda'\Lambda''}(r') & w^b_{\Lambda'\Lambda''}(r') \\ w^c_{\Lambda'\Lambda''}(r') & w^d_{\Lambda'\Lambda''}(r') \end{pmatrix} \begin{pmatrix} R^a_{\Lambda''\Lambda}(r') \\ iR^b_{\Lambda''\Lambda}(r') \end{pmatrix}.\end{aligned} \tag{10.131}$$

These equation have the same form as the ones in eq. (10.123) except that the potential matrix does not any more have zero blocks.

10.8 Decoupled Radial Equations for a Spherical Potential without a Magnetic Field

For the special case of a spherical potential $\varphi(\mathbf{r}) = \varphi(r)$ without a magnetic field ($\mathbf{B} = 0$) the coefficients $v_{\Lambda\Lambda'}(r)$ and $w_{\Lambda\Lambda'}(r)$ have a simple form that can be calculated analytically. This can extremely speed up the calculation for this special case – there is no need to calculate the coefficients $D_{\Lambda'\Lambda^2\Lambda^3\Lambda^4}$ numerically and no angular integrals which would need to be calculated numerically. Furthermore, it forms a way to test a code designed for the general case and is good as an example to understand the procedure in the general setup.

The potential matrix for this special case has the simple form

$$V(r) = \begin{pmatrix} e\varphi(r) & & & \\ & e\varphi(r) & & \\ & & e\varphi(r) & \\ & & & e\varphi(r) \end{pmatrix} \tag{10.132}$$

and thus the eigenvectors and eigenvalues are

$$u^a_1 = \begin{pmatrix} 0 \\ 1 \end{pmatrix},\ u^a_2 = \begin{pmatrix} 1 \\ 0 \end{pmatrix},\ \lambda^a_1(r) = \lambda^a_2(r) = e\varphi(r) \tag{10.133}$$

$$u^d_1 = \begin{pmatrix} 1 \\ 0 \end{pmatrix},\ u^d_2 = \begin{pmatrix} 0 \\ 1 \end{pmatrix},\ \lambda^d_1(r) = \lambda^d_2(r) = e\varphi(r). \tag{10.134}$$

All the other eigenvalues are zero. As the eigenvectors are constant and the eigenvalues have no angular dependence, they can be taken out of the integral when calculating the $\nu_{i\Lambda}$ coefficients, for example

$$\begin{aligned} \nu^a_{1\Lambda}(r) &= \int d\hat{\mathbf{r}} \chi^\dagger_\Lambda(\hat{\mathbf{r}}) \lambda^a_i(\mathbf{r}) u^a_i(\mathbf{r}) && (10.135)\\ &= \left(\int d\hat{\mathbf{r}} \chi^\dagger_\Lambda(\hat{\mathbf{r}}) \right) \cdot e\varphi(r) \begin{pmatrix} 0 \\ 1 \end{pmatrix}. && (10.136) \end{aligned}$$

Now first look at the cases $\Lambda \in \{1, 2\}$. These are the only two values with $l = 0$ and $m = 0$. The integral of the spherical harmonic function $Y_{0,0} = 1/\sqrt{4\pi}$ is given by

$$\int d\hat{\mathbf{r}} Y_{0,0}(\hat{\mathbf{r}}) = \sqrt{4\pi}. \tag{10.137}$$

From table 7.1 it is known that

$$\chi_1(\hat{\mathbf{r}}) = \begin{pmatrix} Y_{0,0}(\hat{\mathbf{r}}) \\ 0 \end{pmatrix}, \ \chi_2(\hat{\mathbf{r}}) = \begin{pmatrix} 0 \\ Y_{0,0}(\hat{\mathbf{r}}) \end{pmatrix} \tag{10.138}$$

and thus it is

$$\int d\hat{\mathbf{r}} \chi^\dagger_1(\hat{\mathbf{r}}) = \begin{pmatrix} \sqrt{4\pi} & 0 \end{pmatrix}, \ \int d\hat{\mathbf{r}} \chi^\dagger_2(\hat{\mathbf{r}}) = \begin{pmatrix} 0 & \sqrt{4\pi} \end{pmatrix}. \tag{10.139}$$

For all values $\Lambda > 2$ the integral of the spin spherical harmonics is zero. This can easily be seen from the orthonormality relation of a spherical harmonic $Y_{l,m}$ with $Y_{0,0}$:

$$\begin{aligned} & \frac{1}{\sqrt{4\pi}} \int d\hat{\mathbf{r}} Y^*_{l,m}(\hat{\mathbf{r}}) = \int d\hat{\mathbf{r}} Y^*_{l,m}(\hat{\mathbf{r}}) Y_{0,0}(\hat{\mathbf{r}}) = \delta_{l,0}\delta_{m,0} \\ \Longrightarrow \quad & \int d\hat{\mathbf{r}} Y^*_{l,m}(\hat{\mathbf{r}}) = 0 \text{ for } (l, m) \neq (0, 0). \end{aligned} \tag{10.140}$$

Hence, the integral of the spin spherical harmonics for $\Lambda > 2$ is also vanishing:

$$\int d\hat{\mathbf{r}} \chi_\Lambda(\hat{\mathbf{r}}) = 0, \ \int d\hat{\mathbf{r}} \chi^\dagger_\Lambda(\hat{\mathbf{r}}) = 0 \text{ for } \Lambda > 2. \tag{10.141}$$

The other $\nu_{i\Lambda}$-coefficients can be calculated analogously. After that the $v_{\Lambda\Lambda'}$-coefficients can be calculated to be:

$$\begin{aligned} v^a_{\Lambda\Lambda'}(r) &= v^d_{\Lambda\Lambda'}(r) = \begin{cases} 4\pi e\varphi(r), & \Lambda = \Lambda', \ \Lambda \in \{1, 2\} \\ 0, & \text{otherwise} \end{cases} && (10.142)\\ v^b_{\Lambda\Lambda'}(r) &= v^c_{\Lambda\Lambda'}(r) = 0 \ \forall \Lambda, \Lambda'. \end{aligned}$$

The last step is to calculate the $w_{\Lambda\Lambda'}$-coefficients. Inserting the result above into the general formula yields

$$\begin{aligned} w^a_{\Lambda'\Lambda^4}(r) &= \sum_{\Lambda^2} \sum_{\Lambda^3} D_{\Lambda'\Lambda^2\Lambda^3\Lambda^4} v_{\Lambda^2\Lambda^3}(r) \\ &= \sum_{\Lambda^2} D_{\Lambda'\Lambda^2\Lambda^2\Lambda^4} v_{\Lambda^2\Lambda^2}(r) \\ &= (D_{\Lambda'11\Lambda^4} + D_{\Lambda'22\Lambda^4})\, 4\pi e\varphi(r). && (10.143) \end{aligned}$$

In the first step the property of the $v_{\Lambda\Lambda'}$-coefficients was used, that for $\Lambda \neq \Lambda'$ the coefficients vanish. In the second step the property that all coefficients for $\Lambda > 2$ vanish was used. The D-coefficients are calculated via

$$\begin{aligned} D_{\Lambda' 11 \Lambda^4} &= \int d\hat{\mathbf{r}} \chi^\dagger_{\Lambda'}(\hat{\mathbf{r}}) \chi_1(\hat{\mathbf{r}}) \chi^\dagger_1(\hat{\mathbf{r}}) \chi_{\Lambda^4}(\hat{\mathbf{r}}) \\ &= \int d\hat{\mathbf{r}} \chi^\dagger_{\Lambda'}(\hat{\mathbf{r}}) \begin{pmatrix} \frac{1}{\sqrt{4\pi}} \\ 0 \end{pmatrix} \begin{pmatrix} \frac{1}{\sqrt{4\pi}} & 0 \end{pmatrix} \chi_{\Lambda^4}(\hat{\mathbf{r}}) \\ &= \int d\hat{\mathbf{r}} \chi^\dagger_{\Lambda'}(\hat{\mathbf{r}}) \begin{pmatrix} \frac{1}{4\pi} & 0 \\ 0 & 0 \end{pmatrix} \chi_{\Lambda^4}(\hat{\mathbf{r}}) \qquad (10.144) \\ D_{\Lambda' 22 \Lambda^4} &= \int d\hat{\mathbf{r}} \chi^\dagger_{\Lambda'}(\hat{\mathbf{r}}) \begin{pmatrix} 0 & 0 \\ 0 & \frac{1}{4\pi} \end{pmatrix} \chi_{\Lambda^4}(\hat{\mathbf{r}}) \qquad (10.145) \end{aligned}$$

and thus

$$\begin{aligned} (D_{\Lambda' 11 \Lambda^4} + D_{\Lambda' 22 \Lambda^4}) &= \int d\hat{\mathbf{r}} \chi^\dagger_{\Lambda'}(\hat{\mathbf{r}}) \begin{pmatrix} \frac{1}{4\pi} & 0 \\ 0 & \frac{1}{4\pi} \end{pmatrix} \chi_{\Lambda^4}(\hat{\mathbf{r}}) \\ &= \frac{1}{4\pi} \int d\hat{\mathbf{r}} \chi^\dagger_{\Lambda'}(\hat{\mathbf{r}}) \chi_{\Lambda^4}(\hat{\mathbf{r}}) \\ &= \frac{1}{4\pi} \delta_{\Lambda' \Lambda^4}. \qquad (10.146) \end{aligned}$$

Inserting that into the formula for the $w_{\Lambda\Lambda'}$-coefficients yields

$$w^a_{\Lambda' \Lambda^4}(r) = \frac{1}{4\pi} \delta_{\Lambda' \Lambda^4} 4\pi e \varphi(r) = e\varphi(r) \delta_{\Lambda' \Lambda^4}. \qquad (10.147)$$

In analogy we have

$$\begin{aligned} w^d_{\Lambda' \Lambda^4}(r) &= \left(D_{\overline{\Lambda}' 22 \overline{\Lambda}^4} + D_{\overline{\Lambda}' 11 \overline{\Lambda}^4} \right) 4\pi e \varphi(r) = e\varphi(r) \delta_{\overline{\Lambda}' \overline{\Lambda}^4} \\ &= e\varphi(r) \delta_{\Lambda' \Lambda^4}. \qquad (10.148) \end{aligned}$$

This result means that all values for $\Lambda' \neq \Lambda^4$ vanish, which is important inasmuch as it means that the coupled radial Lippmann-Schwinger equations decouple in the case of a spherical potential without a **B** field. This decoupling is also found in the non-relativistic case of a spherical potential. When solving the single-site problem computationally, the coupling of the Lippmann-Schwinger equations results in a huge matrix that needs to be inverted. The inversion makes up a great part of the necessary computational effort, together with the calculation of the $w_{\Lambda\Lambda'}$-coefficients in the potential expansion. As both steps turn out obsolete in the case of a spherical scalar potential, it explains why this case is much simpler, both theoretically and with respect to the necessary computational effort, and therefore many investigations are limited to this special case.

10.9 From Fredholm to Volterra Representation

The Lippmann-Schwinger equations derived in sections 10.6 and 10.7 contain two types of radial integrals, one that goes from 0 to r and another one that goes from r to S, where S is a sphere outside which the potential vanishes. For computational implementation it is

favourable to have only one type of integral to solve. Hence, in this section the integral is rewritten to a Volterra equation, i.e. two integrals both with integration domain from 0 to r. The technique for rewriting the integral is the same as in section 10.3 in the first step of the proof.

Let us first insert the explicit form of the Green function, eq. (10.117), into the radial Lippmann-Schwinger equations (10.123), yielding:

$$\begin{aligned}
\begin{pmatrix} R^a_{\Lambda'\Lambda}(r) \\ iR^b_{\Lambda'\Lambda}(r) \end{pmatrix} &= \begin{pmatrix} J^a_\Lambda(r) \\ iJ^b_\Lambda(r) \end{pmatrix}\delta_{\Lambda\Lambda'} - \frac{ik\,(W+mc^2)}{c^2\hbar^2} \\
&\cdot\Bigg[\int_0^r dr' r'^2 \begin{pmatrix} j_{l'}(kr')h_{l'}(kr) & \frac{-ic\hbar k\,\mathrm{sign}(\kappa)}{(W+mc^2)} j_{\bar{l}'}(kr')h_{l'}(kr) \\ \frac{ic\hbar k\,\mathrm{sign}(\kappa)}{(W+mc^2)} j_{l'}(kr')h_{\bar{l}'}(kr) & \frac{c^2\hbar^2k^2}{(W+mc^2)^2} j_{\bar{l}'}(kr')h_{\bar{l}'}(kr) \end{pmatrix} \\
&\quad \sum_{\Lambda''} \begin{pmatrix} w^a_{\Lambda'\Lambda''}(r') & w^b_{\Lambda'\Lambda''}(r') \\ w^c_{\Lambda'\Lambda''}(r') & w^d_{\Lambda'\Lambda''}(r') \end{pmatrix} \begin{pmatrix} R^a_{\Lambda''\Lambda}(r') \\ iR^b_{\Lambda''\Lambda}(r') \end{pmatrix} \\
&\quad + \int_r^S dr' r'^2 \begin{pmatrix} j_{l'}(kr)h_{l'}(kr') & \frac{-ic\hbar k\,\mathrm{sign}(\kappa)}{(W+mc^2)} j_{\bar{l}'}(kr)h_{l'}(kr') \\ \frac{ic\hbar k\,\mathrm{sign}(\kappa)}{(W+mc^2)} j_{l'}(kr)h_{\bar{l}'}(kr') & \frac{c^2\hbar^2k^2}{(W+mc^2)^2} j_{\bar{l}'}(kr)h_{\bar{l}'}(kr') \end{pmatrix} \\
&\quad \sum_{\Lambda''} \begin{pmatrix} w^a_{\Lambda'\Lambda''}(r') & w^b_{\Lambda'\Lambda''}(r') \\ w^c_{\Lambda'\Lambda''}(r') & w^d_{\Lambda'\Lambda''}(r') \end{pmatrix} \begin{pmatrix} R^a_{\Lambda''\Lambda}(r') \\ iR^b_{\Lambda''\Lambda}(r') \end{pmatrix}\Bigg].
\end{aligned}$$

Taking the parts that do not depend on r' out of the integral, the equation can be rewritten as

$$\begin{aligned}
\begin{pmatrix} R^a_{\Lambda'\Lambda}(r) \\ iR^b_{\Lambda'\Lambda}(r) \end{pmatrix} &= \begin{pmatrix} J^a_\Lambda(r) \\ iJ^b_\Lambda(r) \end{pmatrix}\delta_{\Lambda\Lambda'} - \frac{ik\,(W+mc^2)}{c^2\hbar^2} \\
&\cdot\Bigg[\begin{pmatrix} h_{l'}(kr) \\ \frac{ic\hbar k\,\mathrm{sign}(\kappa)}{(W+mc^2)} h_{\bar{l}'}(kr) \end{pmatrix}\left(\int_0^r dr' r'^2 \begin{pmatrix} j_{l'}(kr') & -\frac{ikc\hbar\cdot\mathrm{sign}(\kappa)}{W+mc^2} j_{\bar{l}'}(kr') \end{pmatrix}\right) \\
&\quad \sum_{\Lambda''} \begin{pmatrix} w^a_{\Lambda'\Lambda''}(r') & w^b_{\Lambda'\Lambda''}(r') \\ w^c_{\Lambda'\Lambda''}(r') & w^d_{\Lambda'\Lambda''}(r') \end{pmatrix} \begin{pmatrix} R^a_{\Lambda''\Lambda}(r') \\ iR^b_{\Lambda''\Lambda}(r') \end{pmatrix} \\
&\quad + \begin{pmatrix} j_{l'}(kr) \\ \frac{ic\hbar k\,\mathrm{sign}(\kappa)}{(W+mc^2)} j_{\bar{l}'}(kr) \end{pmatrix}\left(\int_r^S dr' r'^2 \begin{pmatrix} h_{l'}(kr') & -\frac{ikc\hbar\cdot\mathrm{sign}(\kappa)}{W+mc^2} h_{\bar{l}'}(kr') \end{pmatrix}\right) \\
&\quad \sum_{\Lambda''} \begin{pmatrix} w^a_{\Lambda'\Lambda''}(r') & w^b_{\Lambda'\Lambda''}(r') \\ w^c_{\Lambda'\Lambda''}(r') & w^d_{\Lambda'\Lambda''}(r') \end{pmatrix} \begin{pmatrix} R^a_{\Lambda''\Lambda}(r') \\ iR^b_{\Lambda''\Lambda}(r') \end{pmatrix}\Bigg].
\end{aligned}$$

Now we use bold symbols for denoting two-entry vectors and 2×2 matrices and define[23]

$$\mathbf{R}_{\Lambda'\Lambda}(r) := \begin{pmatrix} R^a_{\Lambda'\Lambda}(r) \\ iR^b_{\Lambda'\Lambda}(r) \end{pmatrix} \tag{10.149}$$

$$\mathbf{J}_{\Lambda}(r) := \begin{pmatrix} J^a_{\Lambda}(r) \\ iJ^b_{\Lambda}(r) \end{pmatrix} = \begin{pmatrix} j_l(kr) \\ \frac{ic\hbar k \mathrm{sign}(\kappa)}{(W+mc^2)} j_{\bar{l}}(kr) \end{pmatrix} \tag{10.150}$$

$$\overline{\mathbf{J}}_{\Lambda}(r) := \begin{pmatrix} j_l(kr) & -\frac{ic\hbar k \mathrm{sign}(\kappa)}{(W+mc^2)} j_{\bar{l}}(kr) \end{pmatrix} \tag{10.151}$$

$$\mathbf{H}_{\Lambda}(r) := \begin{pmatrix} H^a_{\Lambda}(r) \\ iH^b_{\Lambda}(r) \end{pmatrix} = \begin{pmatrix} h_l(kr) \\ \frac{ic\hbar k \mathrm{sign}(\kappa)}{(W+mc^2)} h_{\bar{l}}(kr) \end{pmatrix} \tag{10.152}$$

$$\overline{\mathbf{H}}_{\Lambda}(r) := \begin{pmatrix} h_l(kr) & -\frac{ic\hbar k \mathrm{sign}(\kappa)}{(W+mc^2)} h_{\bar{l}}(kr) \end{pmatrix} \tag{10.153}$$

$$\mathbf{V}_{\Lambda'\Lambda}(r) := \begin{pmatrix} w^a_{\Lambda'\Lambda}(r) & w^b_{\Lambda'\Lambda}(r) \\ w^c_{\Lambda'\Lambda}(r) & w^d_{\Lambda'\Lambda}(r) \end{pmatrix}. \tag{10.154}$$

This allows us to rewrite the equation:

$$\begin{aligned} \mathbf{R}_{\Lambda'\Lambda}(r) = \mathbf{J}_{\Lambda'}(r)\delta_{\Lambda\Lambda'} - ik\frac{(W+mc^2)}{c^2\hbar^2}\Big[&\mathbf{H}_{\Lambda'}(r)\int_0^r dr' r'^2 \overline{\mathbf{J}}_{\Lambda'}(r') \sum_{\Lambda''} \mathbf{V}_{\Lambda'\Lambda''}(r')\mathbf{R}_{\Lambda''\Lambda}(r') \\ &+\mathbf{J}_{\Lambda'}(r)\int_r^S dr' r'^2 \overline{\mathbf{H}}_{\Lambda'}(r') \sum_{\Lambda''} \mathbf{V}_{\Lambda'\Lambda''}(r')\mathbf{R}_{\Lambda''\Lambda}(r')\Big]. \end{aligned} \tag{10.155}$$

Now we want to rewrite this mixed Fredholm equation into a Volterra equation. We start making the following definitions

$$A_{\Lambda'\Lambda}(r) := \delta_{\Lambda\Lambda'} - ik\frac{(W+mc^2)}{c^2\hbar^2}\int_r^S dr' r'^2 \overline{\mathbf{H}}_{\Lambda'}(r') \sum_{\Lambda''} \mathbf{V}_{\Lambda'\Lambda''}(r')\mathbf{R}_{\Lambda''\Lambda}(r') \tag{10.156}$$

$$B_{\Lambda'\Lambda}(r) := -ik\frac{(W+mc^2)}{c^2\hbar^2}\int_0^r dr' r'^2 \overline{\mathbf{J}}_{\Lambda'}(r') \sum_{\Lambda''} \mathbf{V}_{\Lambda'\Lambda''}(r')\mathbf{R}_{\Lambda''\Lambda}(r'), \tag{10.157}$$

which allow us to write the Fredholm equation as

$$\mathbf{R}_{\Lambda'\Lambda}(r) = A_{\Lambda'\Lambda}(r)\mathbf{J}_{\Lambda'}(r) + B_{\Lambda'\Lambda}(r)\mathbf{H}_{\Lambda'}(r). \tag{10.158}$$

In order to have integrals running from 0 to r only, we rewrite $A_{\Lambda'\Lambda}$ as follows:

$$\begin{aligned} A_{\Lambda'\Lambda}(r) &= \delta_{\Lambda\Lambda'} - ik\frac{(W+mc^2)}{c^2\hbar^2}\int_0^S dr' r'^2 \overline{\mathbf{H}}_{\Lambda'}(r') \sum_{\Lambda''} \mathbf{V}_{\Lambda'\Lambda''}(r')\mathbf{R}_{\Lambda''\Lambda}(r') \\ &\quad +ik\frac{(W+mc^2)}{c^2\hbar^2}\int_0^r dr' r'^2 \overline{\mathbf{H}}_{\Lambda'}(r') \sum_{\Lambda''} \mathbf{V}_{\Lambda'\Lambda''}(r')\mathbf{R}_{\Lambda''\Lambda}(r') \\ &= A_{\Lambda'\Lambda}(0) + ik\frac{(W+mc^2)}{c^2\hbar^2}\int_0^r dr' r'^2 \overline{\mathbf{H}}_{\Lambda'}(r') \sum_{\Lambda''} \mathbf{V}_{\Lambda'\Lambda''}(r')\mathbf{R}_{\Lambda''\Lambda}(r') \end{aligned} \tag{10.159}$$

[23] In my computational implementation the factor $(W+mc^2)/(c^2\hbar^2)$ is taken into the definition of the potential $\mathbf{V}$ to be consistent with the convention of the scalar relativistic solver.

Note that $A_{\Lambda'\Lambda}(0)$ is constant. Apart from the matrices A, B and $\mathbf{R}$ we also want to define the matrix

$$\tilde{\beta}: = A^{-1}(0) \text{ or} \tag{10.160}$$

$$\tilde{\beta}^{-1}_{\Lambda'\Lambda} = \delta_{\Lambda\Lambda'} - ik\frac{(W+mc^2)}{c^2\hbar^2}\int_0^S dr' r'^2 \overline{\mathbf{H}}_{\Lambda'}(r') \sum_{\Lambda''} \mathbf{V}_{\Lambda'\Lambda''}(r')\mathbf{R}_{\Lambda''\Lambda}(r'). \tag{10.161}$$

Note that this matrix is defined analogously to the matrix $\alpha = \beta^{-1}$ in eq. (10.50). It is not the same though, as the functions here are vectors with two entries instead of four.

Furthermore we define another three matrices by multiplying the first three matrices from the right hand side by $\tilde{\beta}$

$$\tilde{A}(r) := A(r)\tilde{\beta} \tag{10.162}$$

$$\tilde{B}(r) := B(r)\tilde{\beta} \tag{10.163}$$

$$\mathbf{U}(r) := \mathbf{R}(r)\tilde{\beta} \tag{10.164}$$

Explicitly written the entries are

$$\begin{aligned}\tilde{A}_{\Lambda'\Lambda}(r) &:= \sum_{\Lambda''} A_{\Lambda'\Lambda''}(r)\tilde{\beta}_{\Lambda''\Lambda} \\ &= \delta_{\Lambda\Lambda'} - ik\frac{(W+mc^2)}{c^2\hbar^2}\int_0^r dr' r'^2 \overline{\mathbf{H}}_{\Lambda'}(r') \sum_{\Lambda''} \mathbf{V}_{\Lambda'\Lambda''}(r')\mathbf{U}_{\Lambda''\Lambda}(r') \qquad (10.165)\\ \tilde{B}_{\Lambda'\Lambda}(r) &:= \sum_{\Lambda''} B_{\Lambda'\Lambda''}(r)\tilde{\beta}_{\Lambda''\Lambda} \\ &= -ik\frac{(W+mc^2)}{c^2\hbar^2}\int_0^r dr' r'^2 \overline{\mathbf{J}}_{\Lambda}(r') \sum_{\Lambda''} \mathbf{V}_{\Lambda'\Lambda''}(r')\mathbf{U}_{\Lambda''\Lambda}(r'). \qquad (10.166)\end{aligned}$$

Thus we get the equation

$$\mathbf{U}_{\Lambda'\Lambda}(r) = \mathbf{J}_{\Lambda'}(r)\tilde{A}_{\Lambda'\Lambda}(r) + \mathbf{H}_{\Lambda'}(r)\tilde{B}_{\Lambda'\Lambda}(r) \tag{10.167}$$

which is equivalent to:

Two-vector Volterra representation of the relativistic radial Lippmann-Schwinger equations:

$$\begin{aligned}\mathbf{U}_{\Lambda'\Lambda}(r) = \mathbf{J}_{\Lambda'}(r)&\left(\delta_{\Lambda\Lambda'} + ik\frac{(W+mc^2)}{c^2\hbar^2}\int_0^r dr' r'^2 \overline{\mathbf{H}}_{\Lambda}(r') \sum_{\Lambda''} \mathbf{V}_{\Lambda'\Lambda''}(r')\mathbf{U}_{\Lambda''\Lambda}(r')\right) \\ -\mathbf{H}_{\Lambda'}(r)&\left(ik\frac{(W+mc^2)}{c^2\hbar^2}\int_0^r dr' r'^2 \overline{\mathbf{J}}_{\Lambda}(r') \sum_{\Lambda''} \mathbf{V}_{\Lambda'\Lambda''}(r')\mathbf{U}_{\Lambda''\Lambda}(r')\right) \qquad (10.168)\end{aligned}$$

Part IV

Implementation and Applications

11 Numerical Techniques

The main challenge when solving the single-site Dirac equation is to solve the coupled radial Lippmann-Schwinger equations, in the method chosen here written in an integral from. Using Chebyshev quadrature formulae, the integral equations can be rewritten into linear equation systems that can be solved by matrix inversion.

Apart from the radial integration, there are also several integrations of the angular variables $\hat{\mathbf{r}} = (\phi, \theta)$, namely for the D coefficients and the ν coefficients, that are solved using the method by Lebedev and Laikov.

11.1 Chebyshev Quadrature

To solve the Lippmann-Schwinger integral equations for the Schrödinger equation, Gonzales et al. [82] proposed a method using Chebyshev polynomials (a good introduction can be found in [83], for details about the Chebyshev method see e.g. [84, 85, 86]). As the Lippmann-Schwinger equations derived here for the Dirac case have the same form, the same technique can be applied to solve them. The first component of the method is Chebyshev quadrature, which is based on a simple idea: a sufficiently smooth function is interpolated by a polynomial which is then integrated. Because the integral of a polynomial is known, the integration is easy and boils down to a recursion relation.

The intuitive try for interpolating a function might be to choose equidistant points within the integration interval. This, however, leads to large deviations between the interpolating polynomial and the interpolated function close to the boundaries of the interval in consideration. This problem is known as Runge's phenomenon (see [87]) and it can be overcome by using a different point set. The points that minimise the maximal error on the interval $[a, b]$ are given by

$$x_n = \frac{a+b}{2} + \frac{b-a}{2} \cos\left(\pi \frac{2n-1}{2N}\right), \; n = 1...N-1 \tag{11.1}$$

when using polynomials up to degree N. If $[a, b] = [-1, 1]$ these points are the zeroes of the Chebyshev polynomials T_n, which are defined by

$$T_n(x) := \cos(n \arccos(x)), \; n \in \mathbb{N}. \tag{11.2}$$

Although it is not obvious at first sight these functions are indeed polynomials. The first three are given by

$$\begin{aligned} T_0(x) &= 1 \\ T_1(x) &= x \\ T_2(x) &= 2x^2 - 1. \end{aligned} \tag{11.3}$$

When using the Chebyshev nodes, it is convenient to express the interpolating polynomial in a basis of Chebyshev polynomials. In order to derive a recursion relation for the differentiation of the polynomials one can use the trigonometric representation given above and

differentiate it, yielding

$$2T_n(x) = \frac{1}{n+1}\frac{d}{dx}T_{n+1}(x) - \frac{1}{n-1}\frac{d}{dx}T_{n-1}(x) \text{ for } n \geq 2. \tag{11.4}$$

Here, however, a recursion relation for the integration is needed. Integration the whole equation yields

$$\begin{aligned}
\int_{-1}^{r} T_n(x)dx &= \frac{1}{2\,(n+1)}T_{n+1}(x)\Big|_{x=-1}^{r} - \frac{1}{2\,(n-1)}T_{n-1}(x)\Big|_{x=-1}^{r} \\
&= \frac{1}{2\,(n+1)}\left(T_{n+1}(r) - (-1)^{n+1}\right) - \frac{1}{2\,(n-1)}\left(T_{n-1}(r) - (-1)^{n-1}\right) \\
&= \frac{1}{2\,(n+1)}T_{n+1}(r) - \frac{1}{2\,(n-1)}T_{n-1}(r) + \frac{(-1)^{n+1}}{n^2-1} \text{ for } n \geq 2.
\end{aligned} \tag{11.5}$$

To complete the recursion relation we need the case of $n = 0$ and $n = 1$, which can easily be calculated directly:

$$\int_{-1}^{r} T_0(x)dx = T_1(r) + 1 \tag{11.6}$$

$$\int_{-1}^{r} T_1(x)dx = \frac{1}{4}T_2(r) - \frac{1}{4}. \tag{11.7}$$

Hence, we have an integration formula for a single Chebyshev polynomial. Now let us look at an arbitrary polynomial of degree n (the interpolating polynomial) expressed in a basis of Chebyshev polynomials:

$$p(x) = \sum_{n=0}^{N} a_n T_n(x). \tag{11.8}$$

The integral of p will be a polynomial P of degree $N+1$ which, for the definite integral, can be written as

$$P(r) := \int_{-1}^{r} p(x)dx = \sum_{n=0}^{N+1} b_n T_n(r). \tag{11.9}$$

Let us directly look at the definite integral and evaluate the expression:

$$\begin{aligned}
\int_{-1}^{r} p(x)dx &= \sum_{n=0}^{N} a_n \int_{-1}^{r} T_n(x)dx \\
&\overset{\text{eqs. (11.5)–(11.7)}}{=} a_0\left(T_1(r) + T_0(r)\right) + \frac{a_1}{4}\left(T_2(r) - T_0(r)\right) \\
&\quad + \sum_{n=2}^{N} a_n \left(\frac{1}{2\,(n+1)}T_{n+1}(r) - \frac{1}{2\,(n-1)}T_{n-1}(r) + \frac{(-1)^{n+1}}{n^2-1}\right) \\
&= a_0\left(T_1(r) + T_0(r)\right) + \frac{a_1}{4}\left(T_2(r) - T_0(r)\right) \\
&\quad + \sum_{n=3}^{N+1} \frac{a_{n-1}}{2n}T_n(r) - \sum_{n=1}^{N-1} \frac{a_{n+1}}{2n}T_n(r) + \sum_{n=2}^{N} \frac{a_n(-1)^{n+1}}{n^2-1}
\end{aligned} \tag{11.10}$$

In order to maintain the basis we make the approximation of leaving out the $(N+1)$th term in the first sum. The equation can then be rewritten as

$$\begin{aligned}\int_{-1}^{r} p(x)dx &= a_0\left(T_1(r)+T_0(r)\right)+\frac{a_1}{4}\left(T_2(r)-T_0(r)\right)+\frac{a_{N-1}}{2N}T_N(r)-\frac{a_2}{2}T_1(r)\\ &\quad -\frac{a_3}{4}T_2(r)+\sum_{n=3}^{N-1}\frac{a_{n-1}-a_{n+1}}{2n}T_n(r)+\sum_{n=2}^{N}\frac{a_n(-1)^{n+1}}{n^2-1}. \end{aligned} \tag{11.11}$$

Rearranging and remembering that $T_0(r)=1$ yields

$$\begin{aligned}\int_{-1}^{r} p(x)dx &= \left(a_0-\frac{a_1}{4}+\sum_{n=2}^{N}\frac{a_n(-1)^{n+1}}{n^2-1}\right)T_0(r)+\left(a_0-\frac{a_2}{2}\right)T_1(r)\\ &\quad +\sum_{n=2}^{N-1}\frac{a_{n-1}-a_{n+1}}{2n}T_n(r)+\frac{a_{N-1}}{2N}T_N(r)\end{aligned} \tag{11.12}$$

Let us now define the coefficient vectors

$$\underline{p}:=\begin{pmatrix}a_0\\ a_1\\ \vdots\\ a_N\end{pmatrix},\ \underline{P}:=\begin{pmatrix}b_0\\ b_1\\ \vdots\\ b_N\end{pmatrix} \tag{11.13}$$

that contain the coefficients of the Chebyshev representation of the polynomials p and P. Again the term b_{N+1} has been omitted. From eq. (11.12) it can be seen that

$$\underline{P}:=\begin{pmatrix}a_0-\frac{a_1}{4}+\sum_{n=2}^{N}\frac{a_n(-1)^{n+1}}{n^2-1}\\ a_0-\frac{a_2}{2}\\ \frac{a_1-a_3}{4}\\ \frac{a_2-a_4}{6}\\ \vdots\\ \frac{a_{j-1}-a_{j+1}}{2j}\\ \vdots\\ \frac{a_{N-1}}{2N}\end{pmatrix}. \tag{11.14}$$

Now one can write in a matrix form:

$$\underline{\underline{M}}\cdot\underline{p}=\underline{P}, \tag{11.15}$$

which is explicitly written:

$$\begin{pmatrix} 1 & -\frac{1}{4} & -\frac{1}{3} & +\frac{1}{8} & -\frac{1}{15} & \cdots & \frac{(-1)^{j+1}}{j^2-1} & \cdots & & & \frac{(-1)^{N+1}}{N^2-1} \\ 1 & 0 & -\frac{1}{2} & & & & & & & & \\ & \frac{1}{4} & 0 & -\frac{1}{4} & & & & & & & \\ & & & 0 & & & & & & & \\ & & & & 0 & & & & & & \\ & & & & & \ddots & & & & & \\ & & & & & \frac{1}{2j} & 0 & -\frac{1}{2j} & & & \\ & & & & & & & \ddots & & & \\ & & & & & & & & \frac{1}{2(N-1)} & 0 & -\frac{1}{2(N-1)} \\ & & & & & & & & & \frac{1}{2N} & 0 \end{pmatrix} \begin{pmatrix} a_0 \\ a_1 \\ a_2 \\ \\ \\ \vdots \\ a_j \\ \vdots \\ \\ a_N \end{pmatrix} = \begin{pmatrix} b_0 \\ b_1 \\ b_2 \\ \\ \\ \vdots \\ b_j \\ \vdots \\ \\ b_N \end{pmatrix}. \tag{11.16}$$

Note that this is an $(N+1) \times (N+1)$ matrix and j runs from 0 to N.

The matrix differs slightly from the one calculated by Gonzales et al. [82], namely in the $(N+1)$th entry of the first line. This matrix includes a term that is neglected in the matrix by Gonzales. As a test, one can apply the integration onto the polynomials x^j. For $j < N$ both methods are numerically exact. For $j = N$ and $j = (N+1)$ I got results that were better by one order of magnitude for my example calculation ($N = 5$).

So far the method describes how to transform an integral to a matrix vector multiplication. In the case of the Lippmann-Schwinger equations, however, on has to solve an integral equation. In the scheme above that means that the coefficient vector $\underline{p}$ consists of unknown values that need to be determined. In order to do so, the matrix $\underline{\underline{M}}$ is inverted and the product $\underline{\underline{M}}^{-1}\underline{P}$ is evaluated. In other words, the integral equation is rewritten into a linear equation system that is solved by matrix inversion.

11.2 Chebyshev Expansion

The Chebyshev polynomials fulfil the following orthogonality relation:

$$\int_{-1}^{1} T_m(x) T_n(x) \left(1-x^2\right)^{-\frac{1}{2}} dx = \begin{cases} \frac{\pi}{2}\delta_{mn} & \text{if } m \neq 0 \text{ or } n \neq 0 \\ \pi & \text{if } m = n = 0. \end{cases} \tag{11.17}$$

Therefore a function f that is defined on the interval $[-1, 1]$ can be expanded in terms of Chebyshev polynomials as

$$f(x) = \sum_{n=0}^{\infty} a_n T_n(x) \tag{11.18}$$

where

$$a_n = \begin{cases} \frac{1}{\pi}\int_{-1}^{1} f(x)\left(1-x^2\right)^{-\frac{1}{2}} dx & \text{if } n = 0 \\ \frac{2}{\pi}\int_{-1}^{1} f(x) T_n(x)\left(1-x^2\right)^{-\frac{1}{2}} dx & \text{if } n \geq 1. \end{cases} \tag{11.19}$$

Apart from the continuous orthogonality relation, the Chebyshev polynomials also fulfil a discrete orthogonality relation:

$$\sum_{j=0}^{N} T_n(x_j) T_m(x_j) = \begin{cases} \frac{N}{2}\delta_{mn} & \text{if } m \neq 0 \text{ or } n \neq 0 \\ N & \text{if } m = n = 0, \end{cases} \tag{11.20}$$

where x_j are the Chebyshev nodes

$$x_j = \cos\left(\pi \frac{2n-1}{2N}\right), \; j = 0...N-1, \tag{11.21}$$

which are the special case of eq. (11.1) on the interval $[-1, 1]$. Inserting the function f into the orthogonality relation yields an approximative formula for the coefficients a_n:

$$a_n \approx \begin{cases} \frac{1}{N} \sum_{j=0}^{N-1} f(x_j) T_n(x_j) & if\ n = 0 \\ \frac{2}{N} \sum_{j=0}^{N-1} f(x_j) T_n(x_j) & \text{if } n \geq 1. \end{cases} \tag{11.22}$$

As this discrete formula is a sum instead of an integral, it is more useful for practical implementation of the Chebyshev method.

11.3 Lebedev-Laikov Quadrature

The Chebyshev method of the previous section can be applied to one-dimensional integrals, i.e. in the context of this thesis for the radial integration. For the angular momentum expansion of the potential, specifically for integrations when calculating the $\nu_{\Lambda\Lambda'}$ coefficients, equations (10.92) to (10.95), and the D coefficients, eq. (10.121), a quadrature method for integrations on a sphere is needed. The method used here was developed by Lebedev and Laikov [88, 89, 90, 91] and is a standard method for integrations on a sphere. A good introduction to the method can be found in [92].

The essence is to rewrite the integral to a summation

$$\int d\hat{\mathbf{r}} f(\hat{\mathbf{r}}) = \int_0^{\pi} d\theta \int_0^{2\pi} d\phi f(\theta, \phi) \approx \sum_i w_i f(\theta_i, \phi_i) \tag{11.23}$$

with adequately chosen points (θ_i, ϕ_i) on the sphere and corresponding weights. The points are chosen such that they are invariant under the octahedral rotational group with inversion. To construct the points one has to start from one representative of a certain class of points and then construct and then find the invariant points. The smallest number of points that can theoretically be used is six, corresponding to six vertices of an octahedron[24]. The weights are determined by demanding that the method is exact for integrating polynomials up to a given order.

Laikov provided a publicly available C code that generates integration points and corresponding weights. I used the original code to generate these values for my integration routine. As a test calculation I evaluated the orthonormality relation of spherical harmonics in the range of $l = 0$ up to $l = 6$. With 110 points I already obtained machine precision.

[24] The series of possible numbers of points is 6, 14, 26, 38, 50, 74, 86, 110, 146, 170, 194, 230, 266, 302, 350, 434, 590, 770, 974, ...

12 Dirac Single-Site Solver

The algorithm of the Dirac single-site solver that I implemented is explained here. As an application, the skew scattering of tungsten in rubidium is calculated, showing the expected asymmetry that is an extrinsic contribution to the anomalous Hall effect.

12.1 Algorithm

The algorithm for solving the single site problem has been implemented in Fortran 90. The most important steps up to the radial parts of the wave functions are described here in a diagrammatic scheme. For details of the steps refer to the respective equations given and the sections in which they appear. Expressions in `monospace` style refer to the corresponding Fortran files and subroutines.

Calculate and Expand the Potential (`Potential.f90`)

read the D coefficients from a file (`readDcoeff`)

for each r:
- calculate $\varphi(r,\phi,\theta)$ and $\mathbf{B}(r,\phi,\theta)$ (`getPotPhi`, `getPotB`)
- calculate the potential matrix $V(r)$
  - for each Λ: calculate the $\nu_\Lambda(r)$, $\tilde{\nu}_\Lambda(r)$ coefficients eqs. (10.92-10.95) performing integrations on a sphere (`nuCoefficients`)
  - for each tuple $\Lambda\Lambda'$: calculate the $v_{\Lambda\Lambda'}(r)$ coefficients by summing up the respective $\nu_\Lambda(r)$ coefficients eqs. (10.96-10.99) (`ExpansionCoefficients`)
  - calculate the sums for the $w_{\Lambda\Lambda'}(r)$ coefficients eq. (10.122) (`wPotentialExpansion`)

Prepare the Source Terms (`SourceTerms.f90`)

for each r: calculate a vector containing Bessel and Hankel functions $\mathbf{J}(r)$, $\mathbf{H}(r)$ for all Λ values, eqs. (10.150-10.153)

Set up and Solve the Linear Equation System (`calctmat.f90`, `rllsll.f90`)

write the equation as a huge matrix-vector multiplication with indices for the radial points r_i and the Λ value

multiply by the Chebyshev matrix to set up the linear equation system

invert the matrix

⇢ radial wave functions $\mathbf{R}_{\Lambda\Lambda'}(r)$, $\mathbf{S}_{\Lambda\Lambda'}(r)$

My code is written such that it is embedded into the KKR code that is recently under development in our institute (D. Bauer, R. Zeller, P. Mavropoulos).

The calculation for a given kinetic energy E starts by computing the magnetic field $\mathbf{B}$ and the scalar potential φ from the spin up $V^{\uparrow}$ and spin down potential $V^{\downarrow}$ in angular momentum representation, that is provided by the embedding KKR code. Once $\mathbf{B}$ and φ are known (in real space representation), the 4×4 potential matrix is set up and expanded into spin spherical harmonics. This expansion is done by making use of the $\nu_{\Lambda\Lambda'}$ coefficients. From these coefficients, the $w_{\Lambda\Lambda'}$ coefficients are calculated[25].

After the potential expansion has been computed, a second ingredient for setting up the Lippmann-Schwinger equations is to calculate the source terms, which contain Bessel and Hankel functions and spin spherical harmonics. Once they are calculated, the Lippmann-Schwinger equations are solved by the Chebyshev matrix. To obtain higher numerical accuracy without high computational effort, the integration domain is split into sub-intervals, resulting in smaller matrices. The solutions for the sub-intervals are matched by an analytically exact condition. The result is a large matrix, describing the system of linear equations which are equivalent to the Lippmann-Schwinger equations. The equation system is solved by matrix inversion, yielding the radial wave functions.

The two most time consuming steps in the algorithm are the calculation of the sum for the $w_{\Lambda\Lambda'}$ coefficients in eq. (10.122) and the matrix inversion. The former is a sum that has to be computed for Λ^2 coefficients, while for each of them Λ^2 summands have to be added, resulting in Λ^4 operations[26]. The current speed of the code is around four times slower compared to scalar relativistic calculations with spin-orbit coupling. While the matrix inversion is inevitable, the sum for the $w_{\Lambda\Lambda'}$ coefficients holds potential for future efficiency enhancement by examining the analytical properties of the $D_{\Lambda\Lambda'\Lambda^2\Lambda^3}$ coefficients, which are the relativistic counterparts of the Gaunt coefficients. As many of them are zero, the number of operations in the sum for each coefficient can be reduced if these properties are exploited.

Once the wave functions are known, they are transformed from the (κ, μ) basis to the (l, m_l, m_s) basis, so that they can be used within the currently existing embedding code without modifications. In the course of the wave function calculations, the (angular momentum dependent) t matrix is also calculated, as it is needed for the calculation of the Green function of the full system. The described procedure is done for many energies, afterwards the Green function can be calculated from an energy integration. The matrix $T^{m_s m_s'}_{\mathbf{k}\mathbf{k}'}$ is not part of this calculation, however, I wrote an add-on (in Python language) that calculates this matrix, in order to examine scattering in detail. Results are presented in the following section.

[25] For the case of spherical potentials with zero magnetic field $\mathbf{B}$ there is a faster routine, making use of analytical properties discussed in section 10.8, that calculates the $w_{\Lambda\Lambda'}$ coefficients directly. This routine is used if the parameter `spherical_only` in `DiracConfig.f90` is set to 1, otherwise the full-potential method is used.

[26] For example, if $l_{\text{cut}} = 3$ and hence $\Lambda_{\text{cut}} = 32$, this means that around 1 million operations have to be performed.

12.2 Skew Scattering at a Tungsten Impurity

If an electron is scattered at an (impurity) atom the interaction of the electron wave with the spin-orbit coupling of the impurity produces a direction dependent scattering, i.e. electrons have a higher probability of being scattered into a certain direction depending on whether they are in a spin up or spin down state. This effect has first been described by MOTT [93], who also examined the consequences for the conductivity in metals [94, 95]. It is one of the extrinsic contributions to the anomalous Hall effect [96], and in this context the term *skew scattering* is commonly used. The contribution to the spin Hall effect has recently been examined by FERT and LEVY [97].

The absolute squared value of the matrix $T^{m_s m_s'}_{\mathbf{k}\mathbf{k}'}$ defined in eq. (10.67) is proportional to the probability of a particle being scattered in a certain direction. I calculated this matrix, based on a calculation of a tungsten impurity in a rubidium host. The corresponding potential was calculated self-consistently within the local density approximation by the KKR method. Since rubidium is to a very good approximation a free-electron host, we can examine the Mott scattering in the free-electron approximation. Due to the cubic structure of rubidium, the tungsten potential has in reality small non-spherical components, that are neglected in the non-magnetic calculation and included in the magnetic calculation. In this calculation the incoming spin is oriented in z-direction, while the incoming wave has a wave vector $\mathbf{k}$ in the x-direction. In spherical coordinates this is equivalent to $\mathbf{k}$ having the angular part $(\theta, \phi) = (\frac{\pi}{2}, 0)$. The calculation was performed at the Fermi energy, hence the length of the wave vector is determined by $\hbar^2 k_F^2 / 2m = E_F$.

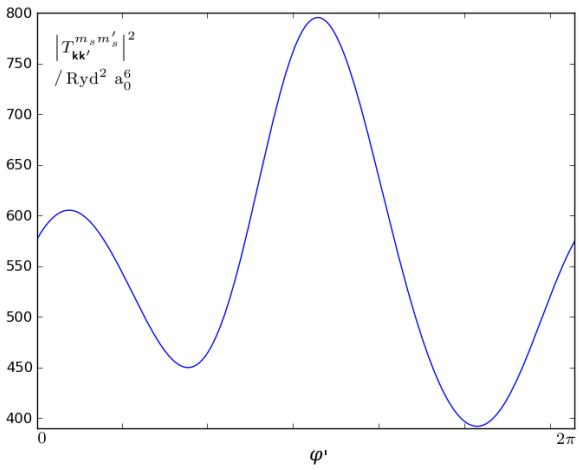
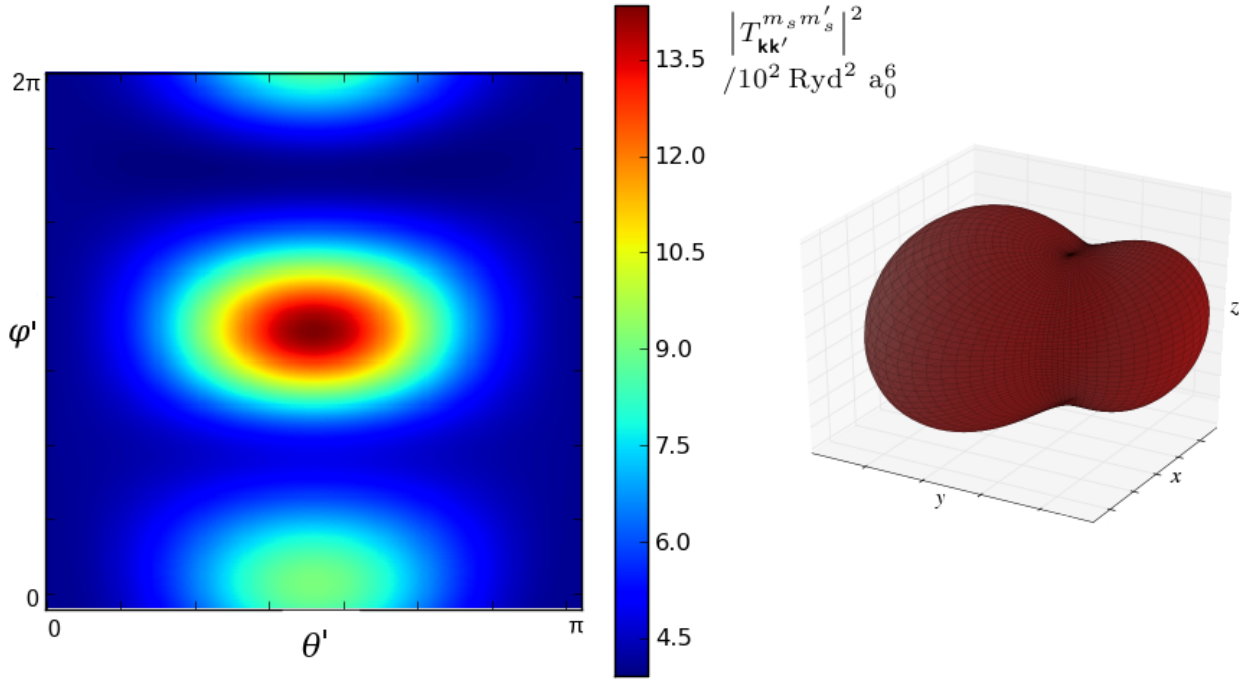


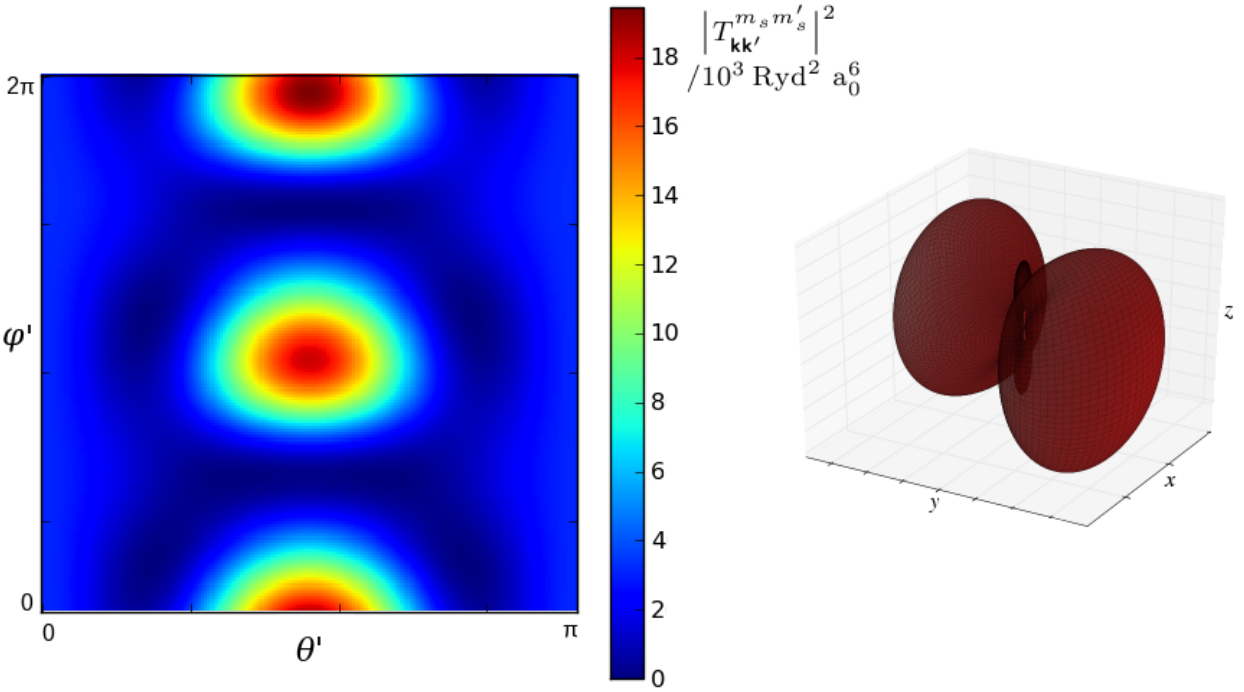
Figure 12.1: Scattering at a tungsten impurity in a rubidium host in a non-magnetic calculation with a spherically approximated potential. Depicted is the squared absolute value of the matrix $T^{m_s m_s'}_{\mathbf{k}\mathbf{k}'}$ where the absolute values of $\mathbf{k}$ and $\mathbf{k}'$ are equal (elastic scattering) and correspond to the Fermi energy. This figure shows the non-spinflip scattering, here for $m_s = m_s' = +\frac{1}{2}$ with the spin in z-direction. The incoming wave has a wave vector in the direction of the x-axis $\mathbf{k} = k_F \hat{\mathbf{e}}_x$. In spherical coordinates this corresponds to angles $\phi = 0$ and $\theta = \pi/2$. The shown curve is the ϕ'-dependence for a fixed value of $\theta' = \frac{3}{2}\pi$.

Fig. 12.2 shows the result of the calculation. Depicted is $\left|T^{m_s m_s'}_{\mathbf{k}\mathbf{k}'}\right|^2$ in terms of (θ', ϕ'), which are the angular coordinates of $\mathbf{k}$. The results shown are the part without spin-flip, i.e. $m_{s'} = m_s$. I computed this first in a non-magnetic calculation using only the spherical part of the potential (fig. 12.2a) and then in a magnetic calculation with full-potential (fig. 12.2b). The difference between a magnetic and non-magnetic calculation here is the dominating part of the difference.

The theoretically expected asymmetry between scattering to the left and to the right (in x-direction), corresponding to an asymmetry dependent on ϕ', can be observed in both calculations. It is more drastic in the magnetic full-potential case. For a more quantitative picture, in fig. 12.1 the ϕ'-dependent asymmetry is shown for a fixed θ value.



(a) Non-magnetic calculation with the spherically approximated potential.



(b) Magnetic calculation with the full potential.

Figure 12.2: Scattering at a tungsten impurity in a rubidium host. Depicted is the squared absolute value of the matrix $T_{\mathbf{kk'}}^{m_s m'_s}$ where the absolute values of $\mathbf{k}$ and $\mathbf{k}'$ are equal (elastic scattering) and correspond to the Fermi energy. This figure shows the non-spinflip scattering, here for $m_s = m'_s = +\frac{1}{2}$ with the spin in z-direction. The incoming wave has a wave vector in the direction of the x-axis $\mathbf{k} = k_F \hat{\mathbf{e}}_x$. In spherical coordinates this corresponds to angles $\phi = 0$ and $\theta = \pi/2$. The left plots show the angles of the wave vector $\mathbf{k}'$ of the scattered wave in spherical coordinates. In the right picture the same quantity is depicted, here by the distance from the origin.

13 Conclusion

Within this work it was my aim to present a comprehensive discussion of the full-potential electron scattering problem based on the Dirac equation. In the first part I set this work into the context of electronic structure calculations with the KKR method and DFT methods in general. The second part described the non-relativistic case, forming an important step in understanding the relativistic case later on. Additionally, the Green function in the relativistic case is based on the one of the non-relativistic case.

In the third part I addressed the main objective of this thesis. Starting point is the Dirac equation, which contains vectorial wave functions with four entries and a 4×4 potential matrix. This matrix has the important property that it is not only hermitian, but also consists of four sub-matrices, which themselves are again hermitian. Exploiting this property, I was able to expand the potential in spin spherical harmonics, such that the expansion coefficients form a 2×2 matrix. This fact is important, because based on this expansion I developed an expansion of the relativistic Lippmann-Schwinger equations with radial wave functions having only two and not four entries. Hence, the resulting matrix for the system of linear equations that has to be solved, in my method has only twice the dimensions (four times as many entries) as the matrix in the non-relativistic case, and not four times as many. The dimensions are the same as for scalar relativistic calculations with spin-orbit coupling, only the sum for the $w_{\Lambda\Lambda'}$ coefficients consumes additional computational time.

In the derivation of the potential expansion I considered both cases, the one of a $\mathbf{B}$ field representation and the one of using the full vector field $\mathbf{A}$. Hence I showed the theoretical framework of solving the single-site problem in a spin-current KKR method and discussed that the additional complicacy for the single-site problem is managable. In order to be compatible with the code, however, the implemented version is based on the $\mathbf{B}$ field representation (spin-polarised KKR).

Since the Lippmann-Schwinger equations I derived have the same structure as the ones in the non-relativistic case, the Chebyshev integration method, already applied by Gonzales et. al. to the Schrödinger equation, can be applied to the Dirac equation without major modifications in the integration methods. Hence the advantages of this method – immensely improved numerical accuracy at only modest increase in computational time and numerical stability, become accessible for fully-relativistic full-potential calculations.

I successfully implemented the method as part of the KKR code currently developed in Jülich. As a test, I compared some calculated wave functions to the ones calculated by the scalar-relativistic solver and, after artificially setting the vacuum speed of light in my programme to a much higher value (simulating the non-relativistic limit), to the non-relativistic solver, both with good agreement.

I applied the method to a tungsten impurity in a rubidium host. In this system tungsten is magnetic and furthermore, due to its high atomic number, tungsten shows strong spin-orbit coupling and, in general, strong relativistic effects. One of them is the splitting of the d orbitals which I could observe when calculating the phase shifts. Another property I examined was the scattering of electrons at this tungsten impurity (Mott scattering or skew scattering). Here a non-symmetric scattering behaviour can be observed, which forms one of the extrinsic contributions to the anomalous Hall effect.

To conclude it can be said that, based on a successful derivation of relativistic Lippmann-Schwinger equations, I was able to develop an efficient algorithm to determine the wave functions and the Green functions in fully-relativistic full-potential electron scattering. The calculations performed are able to simulate interesting quantum mechanical effects and are good accordance with expectations.

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