Dissertation

The full-potential screened KKR method

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Kurzfassung

Die vorliegende Arbeit befasst sich mit der Formulierung einer KKR Theorie für sogenannte volle Potentiale, die von dem Konzept des “Screening” Gebrauch macht. Im Falle anisotroper Ladungsverteilungen sind Näherungen, die das Potential in Kristallverbänden als sphärisch symmetrisch darstellen, wie die “Atomic Sphere Approximation” (ASA) oder die “Muffin Tin” Näherung, keine guten Beschreibungen mehr. Besonders Systeme mit Fremdatomen, Oberflächen oder andere ausgedehnte Störungen bedürfen einer Beschreibung durch die volle Potential Methode. In der Arbeit wird gezeigt, wie man ein System von Potentialen in eine raumfüllende Anordnung von Wigner-Seitz Zellen zerlegen, und wie das Einfachstreuproblem für eine einzelne solcher Zellen gelöst werden kann. Anschließend wird gezeigt, dass die Gleichungen der Vielfachstreutheorie auch im Falle der vollen Potentiale ihre Gültigkeit behalten. Schließlich wird das Konzept des “Screening”, das den numerischen Aufwand reduziert, vorgestellt.

Weiters ist es wichtig die Gesamt-Energie berechnen zu können. Man stößt dabei aber auf das Problem, dass die üblicherweise verwendete Multi-Pol Entwicklung, die für Muffin Tins konvergiert, für benachbarte Zellen divergent ist. Führt man jedoch einen Verschiebungsvektor ein, kann man dieses Problem vermeiden und erhält wieder eine konvergente Summe. Die Poisson Gleichung kann unter Verwendung desselben Prinzips ebenfalls gelöst, und die Gesamt-Energie unter Verwendung des resultierenden Potentials ausgedrückt werden.

Schlussendlich wird ein verbesserter, auf dem Predictor-Corrector Verfahren basierender Algorithmus zur Lösung der radialen Schrödinger Gleichung vorgestellt, der sich eines Interpolationsverfahrens bedient. Dabei wird die Anzahl der verwendeten radialen Stützstellen während der Integration erhöht, was zu einer Verringerung der Schrittweite zwischen den Punkten und gleichzeitig zu einer drastischen Verbesserung der Genauigkeit des Verfahrens führt.

Abstract

This thesis develops a KKR theory using full potentials and the concept of screening. For anisotropic charge distributions the atomic sphere approximation or a muffin-tin geometry for the atomic potentials in a crystal structure are insufficient descriptions. Especially for systems with impurities, at surfaces or other extended defects a full potential treatment is needed. It is shown how an arrangement of potentials can be translated into a collection of space-filling Wigner-Seitz cells, and how for one potential of polyhedral shape the single-site scattering problem can be solved. As an algorithm for solving the resulting coupled radial equations the Born-approximation may be applied. Subsequently the validity of the multiple scattering equations for full potentials is shown and the concept of screening as a means of reducing the computational effort is introduced.

It is furthermore essential to be able to calculate the total energy of a system. However, one runs into problems when the usual multipole expansion, which is always convergent for muffin-tin geometries, is used, as for neighbouring cells this (angular momentum) expansion is divergent. By introducing a certain displacement vector the expansion can be lead to convergence once again. Using this very concept the Poisson equation my be solved and an expression for the total energy in terms of the resulting potential is derived.

Finally an improved algorithm, based on the predictor-corrector scheme, for solving the radial Schrödinger equation is introduced which relies on an interpolation scheme that increases the number of radial mesh points used during the integration. By this means the step size between neighbouring points is decreased which improves the accuracy of the scheme drastically.

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1

Introduction

Electronic structure calculations are being applied with increasing success, as the methods have become more and more sophisticated, in order to understand the underlying features of macroscopically observable quantities. It is not only of interest to explain and comprehend experimental data by relating them to the underlying electronic structure, but also to predict properties of possible new materials. Especially the properties of alloys, their surfaces and multilayer systems have attracted considerable attention over the past decade, due to the rapid advances in the computer industry. Clearly enough the applicability of electronic structure calculations has emerged hand in hand with the enormous progress in developing ever more powerful computers, and it has been only this development that made the computation of large scale systems possible.

Within the numerous methods comprised by the label of electronic structure calculations, the *ab-initio* type approaches feature prominently in condensed matter physics. Such methods start out from fundamental quantum mechanics (i.e. the Schrödinger equation) to derive structural and dynamical properties of solids, while only the atomic numbers of given elements and usually some structural information have to be supplied as input parameters.

There exist two different types of approaches to such *first principles* calculations: one approach uses wave functions, the other makes use of Green's functions. Wave function methods, however, are of limited use when one wants to describe e.g. substitutional disorder or true semi-infinite geometries. There Green's function type techniques are much better suited. Once the Green's function of a system is known, essential quantities like the charge density, density of states, and subsequently total energies can be computed. Then from the knowledge of the total energy structural parameters and other quantities may be deduced.

One method that make use of Green's functions is the Korringa-Kohn-Rostoker (KKR) [KR54][Kor47] method in association with multiple scattering. The KKR method has been developed in the 1950s and since then undergone various modifications and refinements [HS61][Zim65][WJM72][LS72][Hol75]. Initially the formulae were derived for collections of muffin-tin type potentials but in the actual applications, the atomic sphere approximation (ASA) was also successfully used. Then the theory was applied to layered structures, and computation was made more efficient by the introduction of the concept of screening [SÚWK94b][WZD97] , or – as it is also referred to – by the tight-binding [ZDS+95] version [ZDS+95] of the KKR method. Another method that makes use of Green's functions is the closely related LMTO method [Skr84] and its tight binding version (TB-LMTO) [TDK+97].

During the 1980s and early 90s a vital discussion took place whether the KKR theory could be extended to a full potential treatment, i.e., to a formulation where no approximation on the shape of a potential is assumed. Since the charge distribution around impurities, at surfaces, or other extended defects is certainly anisotropic, the assumption that the potentials are of spherical shape and only radially dependent is an insufficient approximation. In order to apply multiple scattering theory also to such systems it was necessary to remove this limitation, by showing that the relevant formulations are also valid for potentials of general shape. The main concern was that some angular momentum expansions are not convergent and that certain "Near Field Corrections" have to be taken into account. Faulkner [Fau86], Gonis [Gon86a], Zeller [Zel87], Badralexe [BF87b], and Brown and Ciftan [BC86] contributed most notably to this discourse. Nowadays it seems that the issue is settled and it is agreed that the implementation of arbitrarily shaped potentials is possible, even though actual codes and calculations are rare. This is probably due to the computational demand, when the method is to be applied to large scale systems, the large amount of test calculations needed, and some conceptual difficulties.

It is for the above reasons that this thesis tries to provide a rigorous theoretical formulation of a *full potential screened KKR* (FP-SKKR) method, with the aim to develop a computationally efficient program. The prospects are to apply the resulting code to surfaces and interfaces and extend it to a fully relativistic, spin-polarized formulation.

This thesis is consequently grouped along the following line: first the single site problem for a potential of general shape is discussed, and the concept of an algorithm for the computation of the regular and irregular wave functions and the single site t matrix is provided. Then the theory is extended to multiple scattering and it is shown that the resulting equations are valid for a space-filling cell geometry. To complete the chapter on multiple scattering the concept of screening is also introduced. Using the expression for the charge density obtained in that chapter, it is subsequently shown how the total energy can be calculated. Again emphasis is put on the differences to potentials of spherical shape. Furthermore the subsequent chapter is devoted to the problem of solving Poisson's equation, and finally, in the appendix, an improved algorithm, which has been developed in the course of this work, for obtaining coupled solutions of the radial Schrödinger equation is explained. From test calculations one sees that the resulting wave functions are highly accurate. A discussion of some further numerical methods concludes the thesis.

At present it seems that the use of density functional theory [HK64][KS65] in self-consistent electronic structure calculations is so self-evident that I decided not to include a discussion on it in this thesis. Density functional theory has now reached such an important status, that the Nobel prize for its development in 1998 has come as no surprise. Hence it should be noted that the FP-SKKR theory has to be thought of as being contained within the concept of density functional theory and the electrostatic potential as being a self-consistent one.

2

Scattering at a Potential of Arbitrary Shape

While for a spherically symmetric scatterer the single site t matrix is totally determined through the phase shifts, this is no longer true for an anisotropic potential, where additional contributions from the non-spherically symmetric parts of the potential have to be added. This is a consequence of the fact that the angular momentum channels are no longer decoupled, and the radial solutions have to be obtained from a set of coupled equations. However, as will be shown in the next chapter, the scattering problem can be split up into a spherically and a non-spherically symmetric one, treating the latter as a perturbation.

In this chapter the solutions of the coupled radial equations for the single site problem will be discussed.

2.1

The Free Particle Green's Function

As we are assuming, that the scattering potential is of finite range, i.e. zero for $|\boldsymbol{r}| > S$, it is necessary to discuss the Schrödinger equation for a free particle. The energy, E, refers to the relative energy between the scatterer and the incoming particle. It is positive and not quantized which means that we deal with a continuous energy spectrum. In the presence of a single scattering potential, $V(\boldsymbol{r})$, the stationary Schrödinger equation for a particle with energy E can be written in atomic units as

$$\left(\nabla^2 + k^2\right) \psi(\boldsymbol{r}) = V(\boldsymbol{r})\, \psi(\boldsymbol{r}) \quad , \tag{2.1}$$

where $k^2 = E$. The discussion now follows closely the one given in [Daw92]. At a large distance from the scattering center, the particles feel no influence of the potential, move freely, and can be described as plane waves:

$$\varphi(\boldsymbol{r}) = \exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}) \quad , \tag{2.2}$$

which are solutions of the homogeneous Schrödinger equation:

$$\left(\nabla^2 + k^2\right)\varphi(\boldsymbol{r}) = 0 \quad . \tag{2.3}$$

The solution to equation (2.1) is easy to find by using the *Green's function* corresponding to the operator on the left hand side of (2.3) which describes the free motion of particles. This function, $G^0(\boldsymbol{r},\boldsymbol{r'};E)$, satisfies the following equation:

$$\left(\nabla^2 + k^2\right) G^0(\boldsymbol{r},\boldsymbol{r'};E) = \delta(\boldsymbol{r}-\boldsymbol{r'}) \quad . \tag{2.4}$$

First, let us find the solution of equation (2.4) by rewriting it as:

$$G^0(\boldsymbol{r},\boldsymbol{r'};E) = \left(\nabla^2 + k^2\right)^{-1}\delta(\boldsymbol{r}-\boldsymbol{r'}) \quad . \tag{2.5}$$

In the integral representation the Dirac's delta function is of the form

$$\delta(\boldsymbol{r}-\boldsymbol{r'}) = (2\pi)^{-3}\int \exp\left[\mathrm{i}\boldsymbol{q}\cdot(\boldsymbol{r}-\boldsymbol{r'})\right]\mathrm{d}^3\boldsymbol{q} \quad , \tag{2.6}$$

and can be substituted into (2.5) to yield

$$G^0(\boldsymbol{r},\boldsymbol{r'};E) = (2\pi)^{-3}\int \frac{\exp\left[\mathrm{i}\boldsymbol{q}\cdot(\boldsymbol{r}-\boldsymbol{r'})\right]}{k^2-q^2}\,\mathrm{d}^3\boldsymbol{q} \quad . \tag{2.7}$$

Evaluating the angular part of the integral reduces the expression to

$$G^0(\boldsymbol{r},\boldsymbol{r'};E) = (4\pi^2\mathrm{i}|\boldsymbol{r}-\boldsymbol{r'}|)^{-1}\int_{-\infty}^{\infty} \frac{q\exp\left(\mathrm{i}q|\boldsymbol{r}-\boldsymbol{r'}|\right)}{k^2-q^2}\,\mathrm{d}q \quad , \tag{2.8}$$

where $q = |\boldsymbol{q}|$. The value of the integral depends on how the contour integration is performed. One can include either one of the two poles, $q = \pm k$, in the integration path. It follows from the boundary conditions of $G^0(\boldsymbol{r},\boldsymbol{r'};E)$ for $|\boldsymbol{r}-\boldsymbol{r'}| \to \infty$ which is the proper path to be chosen. Choosing $\mathrm{Im}\,k > 0$ results in outgoing waves

$$G^0_{(+)}(\boldsymbol{r},\boldsymbol{r'};E) = -\frac{\exp(\mathrm{i}k|\boldsymbol{r}-\boldsymbol{r'}|)}{4\pi|\boldsymbol{r}-\boldsymbol{r'}|} \quad , \tag{2.9}$$

and $\mathrm{Im}\, k < 0$ in incoming waves

$$G^0_{(-)}(\boldsymbol{r}, \boldsymbol{r'}; E) = -\frac{\exp(-\mathrm{i}k|\boldsymbol{r} - \boldsymbol{r'}|)}{4\pi|\boldsymbol{r} - \boldsymbol{r'}|} \quad . \tag{2.10}$$

For a further discussion the angular momentum expansion of the free particle Green's function is needed. It is well known that a plane wave can be expanded in a partial wave basis:

$$\exp(\mathrm{i}\boldsymbol{q} \cdot \boldsymbol{r}) = 4\pi \sum_L \mathrm{i}^\ell\, j_\ell(qr)\, Y_L^*(\hat{\boldsymbol{q}})\, Y_L(\hat{\boldsymbol{r}}) \quad , \tag{2.11}$$

where $L = (\ell, m)$, $j_\ell(qr)$ are spherical Bessel functions, Y_L are complex spherical harmonics, and Y_L^* denote their complex conjugates. Inserting this expression in (2.7) one obtains instead of (2.8):

$$G^0(\boldsymbol{r}, \boldsymbol{r'}; E) = \pi^{-1} \sum_L Y_L(\hat{\boldsymbol{r}})\, Y_L^*(\hat{\boldsymbol{r}}') \int\limits_{-\infty}^{\infty} \frac{j_\ell(qr)\, j_\ell(qr')}{k^2 - q^2}\, q^2 \mathrm{d}q \quad . \tag{2.12}$$

In shorthand notation this defines the coefficients of the angular momentum expansion, $G^0_\ell(r, r'; E)$:

$$G^0(\boldsymbol{r}, \boldsymbol{r'}; E) = \sum_L Y_L(\hat{\boldsymbol{r}})\, G^0_\ell(r, r'; E)\, Y_L^*(\hat{\boldsymbol{r}}') \quad . \tag{2.13}$$

It is shown in the appendix that by evaluating the integral in (2.12) the partial wave expansion of the free particle Green's function is given by

$$G^0(\boldsymbol{r}, \boldsymbol{r'}; E) = -\mathrm{i}k \sum_L j_L(k\boldsymbol{r}_<)\, h_L(k\boldsymbol{r}_>) \quad , \tag{2.14}$$

if one keeps in mind that the complex conjugated spherical harmonic is associated with the second argument of the Green's function, and therefore

$$G^0_\ell(r, r'; E) = -\mathrm{i}k\, j_\ell(kr_<)\, h_\ell(kr_>) \quad . \tag{2.15}$$

Here $r_>$ and $r_<$ denote the larger and smaller value of r and r', and $h_L(k\boldsymbol{r}) = h_\ell(kr)\, Y_L(\hat{\boldsymbol{r}})$ and $j_L(k\boldsymbol{r}) = j_\ell(kr)\, Y_L(\hat{\boldsymbol{r}})$. The definition of the spherical Hankel functions of the first kind used here is

$$h_\ell(kr) = j_\ell(kr) + \mathrm{i}\, n_\ell(kr) \quad . \tag{2.16}$$

Equation (2.14) is an expansion of the Green's function in terms of the solutions of the corresponding Schrödinger equation. This concept will reappear several times throughout this thesis.

The Lippmann-Schwinger Equation

It is the aim of this discussion to find the two linearly independent solutions of (2.1). One of these solutions is regular at the origin and subsequently called regular solution. The other, the irregular solution, exhibits a singular behaviour for $r \to 0$. It is convenient to write these solutions in terms of integral instead of differential equations, as there the boundary conditions are contained implicitly. Inside the potential region the solutions are inherently different from the solutions on the outside. The solutions in the outside region, however, differ from the solutions of the homogeneous Schrödinger equation (2.3), i.e., from the solutions in the absence of any potential. In the case of spherical potentials the difference in the asymptotic behaviour is determined by a phase shift only, whereas in the general case certain *phase functions* – the generalization of the phase shifts – can be defined (see [Gon92] or [Wei90] for a discussion of the phase functions).

The Green's function and its expansion in terms of spherical harmonics, which has been derived in the previous section, can be used to find the solution to (2.1). From the theory of Green's function (see e.g. [Ric80]) it is well known that if $G^0(\boldsymbol{r},\boldsymbol{r'};E)$ is the solution of

$$\left(\nabla^2 + k^2\right) G^0(\boldsymbol{r},\boldsymbol{r'};E) = \delta(\boldsymbol{r}-\boldsymbol{r'}) \quad , \tag{2.17}$$

then the solution of

$$\left(\nabla^2 + k^2\right) \psi(\boldsymbol{r}) = A(\boldsymbol{r}) \quad , \tag{2.18}$$

is of the form

$$\psi(\boldsymbol{r}) = \varphi(\boldsymbol{r}) + \int G^0(\boldsymbol{r},\boldsymbol{r'};E)\, A(\boldsymbol{r'})\, \mathrm{d}\boldsymbol{r'} \quad , \tag{2.19}$$

which is the *Lippmann-Schwinger equation* [LS50]. If on the right hand side of (2.18) $A(\boldsymbol{r}) = V(\boldsymbol{r})\,\psi(\boldsymbol{r})$, then we have

$$\psi(\boldsymbol{r}) = \varphi(\boldsymbol{r}) + \int G^0(\boldsymbol{r},\boldsymbol{r'};E)\, V(\boldsymbol{r'})\, \psi(\boldsymbol{r'})\, \mathrm{d}\boldsymbol{r'} \quad . \tag{2.20}$$

Before further discussion the implicit directional dependence of $\psi(\boldsymbol{r})$ on $\hat{\boldsymbol{k}}$ can be separated off by using the following expansions:

$$\varphi(\boldsymbol{r}) = 4\pi \sum_L \mathrm{i}^\ell\, Y_L(\hat{\boldsymbol{k}})\, \varphi_L(\boldsymbol{r}) \quad , \tag{2.21}$$

$$\psi(\boldsymbol{r}) = 4\pi \sum_L \mathrm{i}^\ell\, Y_L(\hat{\boldsymbol{k}})\, \psi_L(\boldsymbol{r}) \quad . \tag{2.22}$$

Substitution, multiplication by $Y_L(\hat{\boldsymbol{k}})$, and integration over $\hat{\boldsymbol{k}}$ yields

$$\psi_L(\boldsymbol{r}) = \varphi_L(\boldsymbol{r}) + \int G^0(\boldsymbol{r},\boldsymbol{r'};E)\,V(\boldsymbol{r'})\,\psi_L(\boldsymbol{r'})\,\mathrm{d}\boldsymbol{r'} \quad . \tag{2.23}$$

The above equation is the starting point for a further discussion of the regular and irregular solutions in the subsequent sections. In the following all equations are valid for all "regular" potentials of arbitrary shape. As a consequence a set of coupled radial equations is obtained. For the special case of a spherically symmetric potential these equations decouple and a solution is straightforward. But for arbitrary potentials the solution is more complicated and more work is needed.

2.2.1 **Regular Solutions**

The regular solutions are commonly denoted by $R_L(\boldsymbol{r})$. However, due to a special normalization at the boundary of the potential (see also section 2.2.3), later on the so called *scattering solutions*, denoted by $Z_L(\boldsymbol{r})$, will be used instead. For a potential that vanishes in all space we can write the regular solution as

$$\varphi_L(\boldsymbol{r}) = j_\ell(kr)\,Y_L(\hat{\boldsymbol{r}}) \quad . \tag{2.24}$$

Then using (2.23), the regular solution in the presence of a scattering potential is given by

$$R_L(\boldsymbol{r}) = j_\ell(kr)\,Y_L(\hat{\boldsymbol{r}}) + \int G^0(\boldsymbol{r},\boldsymbol{r'};E)\,V(\boldsymbol{r'})\,R_L(\boldsymbol{r'})\,\mathrm{d}\boldsymbol{r'} \quad . \tag{2.25}$$

In terms of a physical picture the above expression describes the scattering of an incoming partial wave $j_\ell(kr)Y_L(\hat{\boldsymbol{r}})$ by a potential $V(\boldsymbol{r})$. The integration in (2.25) is three dimensional and for convenience and numerical purposes it is possible to derive an expression that contains only a one dimensional radial integration. This can be straightforwardly done, by using (2.13) and the expansions for the wave function and the potential [Dri91]

$$\begin{aligned} V(\boldsymbol{r}) &= \sum_L V_L(r)\,Y_L(\hat{\boldsymbol{r}}) \qquad &(2.26)\\ R_L(\boldsymbol{r}) &= \sum_{L'} R_{L'L}(r)\,Y_{L'}(\hat{\boldsymbol{r}}) \quad . &(2.27)\end{aligned}$$

Substitution in (2.25) yields explicitly

$$\begin{aligned}\sum_{L'} R_{L'L}(r)\, Y_{L'}(\hat{\boldsymbol{r}}) \quad &= \quad j_\ell(kr)\, Y_L(\hat{\boldsymbol{r}}) \\ &\quad + \int \mathrm{d}\boldsymbol{r}' \left(\sum_L Y_L(\hat{\boldsymbol{r}})\, G^0_\ell(r, r'; E)\, Y^*_L(\hat{\boldsymbol{r}}') \right) \\ &\quad \times \left(\sum_{L'} V_{L'}(r')\, Y_{L'}(\hat{\boldsymbol{r}}') \right) \\ &\quad \times \left(\sum_{L''} R_{L''L'''}(r')\, Y_{L''}(\hat{\boldsymbol{r}}') \right) \quad . \end{aligned} \tag{2.28}$$

Multiplication with $Y^*_L(\hat{\boldsymbol{r}})$, integration over $\hat{\boldsymbol{r}}$, and using the orthonormality of the spherical harmonics which removes the spherical harmonic with the unprimed argument from the integral leaves

$$\begin{aligned} R_{LL'}(r) \quad &= \quad \delta_{LL'}\, j_\ell(kr) + \int \mathrm{d}\boldsymbol{r}'\, G^0_\ell(r, r'; E)\, Y^*_L(\hat{\boldsymbol{r}}') \\ &\quad \times \left(\sum_{L'} V_{L'}(r')\, Y_{L'}(\hat{\boldsymbol{r}}') \right) \left(\sum_{L''} R_{L''L'''}(r')\, Y_{L''}(\hat{\boldsymbol{r}}') \right) \quad . \end{aligned} \tag{2.29}$$

Then by rewriting this equation and using spherical (polar) coordinates one obtains

$$R_{LL'}(r) = \delta_{LL'}\, j_\ell(kr) + \int_0^S r'^2\, \mathrm{d}r'\, G^0_\ell(r, r'; E) \sum_{L'L''} C^L_{L'L''}\, V_{L'}(r')\, R_{L''L'''}(r') \quad , \tag{2.30}$$

where S is the radius of the circumscribed sphere and the *Gaunt coefficients*, $C^L_{L'L''}$ are defined as follows:

$$C^L_{L'L''} = \int \mathrm{d}\hat{\boldsymbol{r}}\, Y^*_L(\hat{\boldsymbol{r}})\, Y_{L'}(\hat{\boldsymbol{r}})\, Y_{L''}(\hat{\boldsymbol{r}}) \quad . \tag{2.31}$$

Now, by using

$$V_{LL''}(r) = \sum_{L'} C^L_{L'L''}\, V_{L'}(r) \quad , \tag{2.32}$$

we can finally write (after renaming $L''' \to L'$):

$$R_{LL'}(r) = \delta_{LL'}\, j_\ell(kr) + \int_0^S r'^2\, \mathrm{d}r'\, G^0_\ell(r, r'; E) \sum_{L''} V_{LL''}(r')\, R_{L''L'}(r') \quad . \tag{2.33}$$

2.2.2 The α and t Matrices

While the behaviour of the wave function in the presence of a potential for $r \to 0$ is usually formulated in terms of a matrix, denoted in the following by α, the t matrix, which also contains the information about the potential, is a transition operator between the incoming, plane waves and the scattered waves. The t matrix can therefore be used to match the wave functions inside and outside the potential at its boundary. In order to be able to define these two quantities the expansion coefficients of the free particle Green's function as given in (2.13) will be used. Then (2.25) becomes

$$\begin{aligned} R_L(\boldsymbol{r}) &= j_\ell(kr)\, Y_L(\hat{\boldsymbol{r}}) \\ &\quad + \int \mathrm{d}\boldsymbol{r}' \left(\sum_{L'} Y_{L'}(\hat{\boldsymbol{r}})\, G^0_{\ell'}(r, r'; E)\, Y^*_{L'}(\hat{\boldsymbol{r}}') \right) V(\boldsymbol{r}')\, R_L(\boldsymbol{r}')\,. \end{aligned} \tag{2.34}$$

With (2.15) and by rearranging the terms we get for $r > r'$:

$$\begin{aligned} R_L(\boldsymbol{r}) &= j_\ell(kr)\, Y_L(\hat{\boldsymbol{r}}) \\ &\quad - \mathrm{i}k \sum_{L'} \left(\int \mathrm{d}\boldsymbol{r}'\, j_{\ell'}(kr')\, Y^*_{L'}(\hat{\boldsymbol{r}}')\, V(\boldsymbol{r}')\, R_L(\boldsymbol{r}') \right) h_{\ell'}(kr)\, Y_{L'}(\hat{\boldsymbol{r}}) \qquad (2.35) \\ &= j_\ell(kr)\, Y_L(\hat{\boldsymbol{r}}) - \mathrm{i}k \sum_{L'} t_{LL'}\, h_{\ell'}(kr)\, Y_{L'}(\hat{\boldsymbol{r}}) \quad . \qquad (2.36) \end{aligned}$$

As can be seen from (2.36) the angular momentum representation of the t matrix is defined by

$$t_{LL'} = \int \mathrm{d}\boldsymbol{r}'\, j_{\ell'}(kr')\, Y^*_{L'}(\hat{\boldsymbol{r}}')\, V(\boldsymbol{r}')\, R_L(\boldsymbol{r}') \quad . \tag{2.37}$$

Once again one can find a representation of the t matrix which contains only a radial integral. First (2.27) on the left hand side of (2.36) and the orthogonality of the spherical harmonics are used

$$R_{LL'}(r) = \delta_{LL'}\, j_\ell(kr)\ - \mathrm{i}k \left(\int \mathrm{d}\boldsymbol{r}'\, j_\ell(kr')\, Y^*_L(\hat{\boldsymbol{r}}')\, V(\boldsymbol{r}')\, R_L(\boldsymbol{r}') \right) h_\ell(kr) \quad . \tag{2.38}$$

Then using again (2.26) and (2.27) in the integrand, and by following the same steps as in the derivation of (2.33), one obtains an expression for the regular solution outside the scattering region:

$$R_{LL'}(r) = \delta_{LL'}\, j_\ell(kr)\ - \mathrm{i}k\, t_{LL'}\, h_\ell(kr) \quad , \tag{2.39}$$

where $t_{LL'}$ is given by

$$t_{LL'} = \int_0^S r'^2\, \mathrm{d}r'\, j_\ell(kr') \sum_{L''} V_{LL''}(r')\, R_{L''L'}(r') \quad . \tag{2.40}$$

$V_{LL''}$ has been defined in (2.32) and S again refers to the radius of the circumscribed sphere containing a whole cell. This means that (2.37) and (2.40) are equivalent representations of the t-matrix.

The behaviour of the regular solution in the vicinity of the origin can be investigated by rewriting (2.33) using (2.15):

$$\begin{aligned} R_{LL'}(r) \;=\;& \delta_{LL'}\, j_\ell(kr) \\ & -\mathrm{i}k \left(\int\limits_0^r r'^2\,\mathrm{d}r'\, j_\ell(kr') \sum_{L''} V_{LL''}(r')\, R_{L''L'}(r') \right) h_\ell(kr) \\ & -\mathrm{i}k \left(\int\limits_r^S r'^2\,\mathrm{d}r'\, h_\ell(kr') \sum_{L''} V_{LL''}(r')\, R_{L''L'}(r') \right) j_\ell(kr) \quad . \end{aligned} \tag{2.41}$$

Since for $r \to 0$ the first integral vanishes, in this limit the radial amplitudes $R_{LL'}(r)$ are of the form:

$$R_{LL'}(r) \cong \alpha_{LL'}\, j_\ell(kr) \quad , \tag{2.42}$$

where the matrix elements $\alpha_{LL'}$ are obtained from

$$\alpha_{LL'} = \delta_{LL'} - \mathrm{i}k \left(\int\limits_0^S r'^2\,\mathrm{d}r'\, h_\ell(kr') \sum_{L''} V_{LL''}(r')\, R_{L''L'}(r') \right) \quad . \tag{2.43}$$

Equation (2.42) expresses the amplification of the regular solution of the homogeneous Schrödinger equation – the unperturbed wave – in the presence of a potential around the origin.

2.2.3 Equivalent Formulation

The formulation of the regular solution given in the previous section is a very natural way to express scattering theory as it leads to a picture of incoming and outgoing waves. However, it is possible to reformulate the expressions with respect to the normalization at the potential cell boundary as originally proposed by Faulkner [Fau79]. Up to now the regular solution has been expanded in angular momentum components, each of which have to satisfy certain boundary conditions. The angular momentum expansion can be written in a more general form as

$$\psi(\boldsymbol{r}) = \sum_L b_L\, R_L(\boldsymbol{r}) \quad . \tag{2.44}$$

While $R_L(\boldsymbol{r})$ has been derived in (2.36):

$$R_L(\boldsymbol{r}) = j_\ell(kr)\,Y_L(\hat{\boldsymbol{r}}) - \mathrm{i}k\sum_{L'} h_{\ell'}(kr)\,Y_{L'}(\hat{\boldsymbol{r}})\,t_{L'L} \quad , \tag{2.45}$$

in complete analogy we can define another function, $Z_L(\boldsymbol{r})$, and identify it as components of the expansion:

$$\psi(\boldsymbol{r}) = \sum_L a_L\,Z_L(\boldsymbol{r}) \quad . \tag{2.46}$$

Using the negative of the inverse of the Wigner reaction matrix, with elements $c_{LL'}$, the new functions are normalized such that outside the scattering region, they are given by

$$Z_L(\boldsymbol{r}) = k\,n_\ell(kr)\,Y_L(\hat{\boldsymbol{r}}) - \sum_{L'} j_{\ell'}(kr)\,Y_{L'}(\hat{\boldsymbol{r}})\,c_{L'L} \quad , \tag{2.47}$$

or by

$$Z_L(\boldsymbol{r}) = \sum_{L'} j_{\ell'}(kr)\,Y_{L'}(\hat{\boldsymbol{r}})\,t^{-1}_{L'L} - \mathrm{i}k\,h_\ell(kr)\,Y_L(\hat{\boldsymbol{r}}) \quad , \tag{2.48}$$

where the spherical Bessel functions $j_\ell(kr)$ have been used together with spherical Neumann $n_\ell(kr)$ and Hankel $h_\ell(kr)$ functions respectively. The Wigner reaction matrix, $\boldsymbol{K}$, is defined as

$$\boldsymbol{K} = \boldsymbol{t}\,(1 - \mathrm{i}k\boldsymbol{t})^{-1} \quad , \tag{2.49}$$

where $\boldsymbol{t}$ is the t-matrix with elements $t_{LL'}$ as defined in (2.40), and the elements of $\boldsymbol{K}$ can be obtained from:

$$K_{LL'} = \sum_{L''} t_{LL''}\,\left(\delta_{L''L'} - \mathrm{i}\,k\,t_{L''L'}\right)^{-1} \quad . \tag{2.50}$$

Finally the matrix $\boldsymbol{c}$ in (2.47) is the negative of the inverse of the reaction matrix:

$$\boldsymbol{c} = -\boldsymbol{K}^{-1} \quad . \tag{2.51}$$

The two solutions are connected via the relation

$$R_L(\boldsymbol{r}) = \sum_{L'} Z_{L'}(\boldsymbol{r})\,t_{L'L} \quad , \tag{2.52}$$

which can be verified by direct substitution of expression (2.47) and using (2.45). Hence (2.44) and (2.46) are equivalent formulations as long as the coefficients are related via

$$a_L = \sum_{L'} t_{LL'} \, b_{L'} \quad . \tag{2.53}$$

Again the components of the angular momentum matrix, $Z_{LL'}(r)$, have to be calculated. In the same manner as in the previous section we use

$$Z_L(\boldsymbol{r}) = \sum_{L'} Z_{L'L}(r) \, Y_{L'}(\hat{\boldsymbol{r}}) \quad , \tag{2.54}$$

and the orthogonality of the spherical harmonics which yields

$$Z_{LL'}(r) = \delta_{LL'} \, k \, n_\ell(kr) - j_\ell(kr) \, c_{LL'} \, , \quad r \geq S \quad . \tag{2.55}$$

2.2.4 **Irregular Solutions**

We now turn to the properties of the solution of the radial Schrödinger equation which is not regular at the origin and hence called irregular solution. Approaching the origin the function diverges as $r^{-\ell-1}$ and smoothly joins a spherical Bessel function at the boundary of the potential. As for the regular solution a Lippmann-Schwinger equation can be formulated:

$$J_L(\boldsymbol{r}) = J_L^0(\boldsymbol{r}) + \int G^0(\boldsymbol{r}, \boldsymbol{r}'; E) \, V(\boldsymbol{r}') \, J_L(\boldsymbol{r}') \, \mathrm{d}\boldsymbol{r}' \quad . \tag{2.56}$$

In there $J_L(\boldsymbol{r})$ is the irregular solution in the presence of a scattering potential $V(\boldsymbol{r})$, and $J_L^0(\boldsymbol{r})$ is the solution of (2.1) in the absence of a potential.

Outside the scattering region the wave function is given by spherical Bessel functions:

$$J_L(\boldsymbol{r}) = j_\ell(kr) \, Y_L(\hat{\boldsymbol{r}}) \, , \quad r \geq S \quad . \tag{2.57}$$

From this condition an expression for the free space solution, $J_L^0(\boldsymbol{r})$, can be deduced. We can write:

$$\begin{aligned} J_L^0(\boldsymbol{r}) &= j_\ell(kr) \, Y_L(\hat{\boldsymbol{r}}) - \int \mathrm{d}\boldsymbol{r}' \, G^0(\boldsymbol{r}, \boldsymbol{r}'; E) \, V(\boldsymbol{r}') \, J_L(\boldsymbol{r}') & (2.58) \\ &= j_\ell(kr) \, Y_L(\hat{\boldsymbol{r}}) \\ &\quad + \mathrm{i}k \sum_{L'} \left(\int \mathrm{d}\boldsymbol{r}' \, j_{\ell'}(kr') \, Y_{L'}^*(\hat{\boldsymbol{r}}') \, V(\boldsymbol{r}') \, J_L(\boldsymbol{r}') \right) h_{\ell'}(kr) \, Y_{L'}(\hat{\boldsymbol{r}}) & (2.59) \\ &= j_\ell(kr) \, Y_L(\hat{\boldsymbol{r}}) + \mathrm{i}k \sum_{L'} \tilde{t}_{LL'} \, h_{\ell'}(kr) \, Y_{L'}(\hat{\boldsymbol{r}}) \quad . & (2.60) \end{aligned}$$

The above equations are valid for $r \geq S$ and in the last step a matrix equivalent to the t matrix for the regular solution has been defined for the irregular solution as

$$\tilde{t}_{LL'} = \int \mathrm{d}\boldsymbol{r}' \, j_{\ell'}(kr') \, Y^*_{L'}(\hat{\boldsymbol{r}}') \, V(\boldsymbol{r}') \, J_L(\boldsymbol{r}') \quad . \tag{2.61}$$

2.2.5 **Coupled Equations**

Instead of Lippmann-Schwinger type equations the corresponding set of differential equations, from which the coupling of the angular momentum components ("L-channels") is more obvious, can be investigated. The coupling arises from the non-spherical shape of the spatially bounded scatterer and it can be shown that the channels decouple in the case of spherical symmetry. Let us denote the coupled equations as [Gon92]:

$$\left(\nabla^2 + k^2 - \frac{\ell(\ell+1)}{r^2} \right) \psi_{LL''}(r) = \sum_{L'} V_{LL'}(r) \, \psi_{L'L''}(r) \quad . \tag{2.62}$$

As has been previously defined, the angular momentum components of the general potential $V(\boldsymbol{r})$ are given by

$$V_{LL'}(r) = \sum_{L''} C^{L}_{L'L''} \, V_{L''}(r) \quad , \tag{2.63}$$

or alternatively by

$$V_{LL'}(r) = \int \mathrm{d}\hat{\boldsymbol{r}} \, Y^*_L(\hat{\boldsymbol{r}}) \, V(\boldsymbol{r}) \, Y_{L'}(\hat{\boldsymbol{r}}) \quad , \tag{2.64}$$

which follows directly from (2.63) if the potential is expanded in terms of spherical harmonics as in (2.26). Now if the potential has spherical symmetry, then the expansion reduces to the first term, i.e.

$$V(\boldsymbol{r}) = \sum_L V_L(r) \, Y_L(\hat{\boldsymbol{r}}) \tag{2.65}$$

$$V(\boldsymbol{r}) = V(r) = \frac{1}{\sqrt{4\pi}} V_{(0,0)}(r) \quad . \tag{2.66}$$

If the last identity is used in (2.64), only the diagonal elements remain

$$V_{LL'}(r) = \delta_{LL'} \, V(r) = \delta_{LL'} \, \frac{1}{\sqrt{4\pi}} V_{(0,0)}(r) \quad , \tag{2.67}$$

the radial equations decouple and the only components of the radial solutions are the diagonal ones:

$$\psi_{LL'}(r) = \delta_{LL'}\,\psi_\ell(r) \quad . \tag{2.68}$$

Then (2.62) reduces to its well known form for a spherically symmetric scatterer

$$\left(\nabla^2 + k^2 - \frac{\ell(\ell+1)}{r^2}\right)\psi_\ell(r) = V(r)\,\psi_\ell(r) \quad . \tag{2.69}$$

It follows from (2.62) that the coupling of the angular momentum components arises due to the anisotropic contributions to the potential.

2.3

Solutions of the Coupled Equations

This section deals with the solutions of the coupled, radial equations (2.62). It is possible to solve this system of equations directly by employing a proper algorithm (c.f. [Dri91]). However, the procedure is numerically demanding and not very efficient and we will therefore not proceed in that direction. Another possibility is to treat the problem in a perturbation type approach. This is motivated by the fact that the spherically symmetric part of the potential is by far the most dominating one, and the deviation from spherical symmetry occurs only in the outermost regions. Then the potential can be looked at as consisting of a part that depends only on the distance from the origin and an anisotropic one. The radial solutions are then obtained via a Born approximation, where the 0-th approximations are the solutions of the spherically symmetric problem. Hence the scheme of this section is the following. First we have to show that the total radial solutions can be written in terms of spherically symmetric solutions. For this it is necessary to show that the Green's function for the single site problem can be expanded in terms of regular and irregular solution in the same manner as the free particle Green's function. To achieve this, an operator formalism will be introduced, which leads to the definition of the T-operator. Furthermore some useful relations between Green's functions and between Green's functions and the T-operator are found. After having obtained expressions for the regular and irregular solutions, the normalization of these wave functions will again be discussed. Finally a description of the iterative scheme of the Born approximation will be given.

2.3.1 **Expansion of the Green's Function in Terms of Regular and Irregular Scattering Solutions**

To arrive at such an expansion let us first introduce the following operator formalism and write the free particle Green's function, whose coordinate representation has been introduced in a previous chapter, in the following way:

$$\hat{G}^0 = (z - \hat{H}^0)^{-1} \quad , \tag{2.70}$$

where $\hat{H}^0$ is the Hamiltonian of free space and $z = E + \mathrm{i}\varepsilon$ is a complex energy. In the same manner the Green's function of a system with a single scatterer, represented by the potential $\hat{V}$, can be written as:

$$\hat{G} = (z - \hat{H})^{-1} = (z - \hat{H}^0 - \hat{V})^{-1} \quad . \tag{2.71}$$

This last expression can be manipulated in such a way that the operator $\hat{G}$ can be expressed in a Dyson equation involving also $\hat{G}^0$ and $\hat{V}$. Thus multiplication from the left with $(z - \hat{H})$ yields:

$$\begin{aligned} (z - \hat{H}^0 - \hat{V})\,\hat{G} &= \mathbf{1} && (2.72)\\ (\hat{G}^0)^{-1}\,\hat{G} &= \mathbf{1} + \hat{V}\,\hat{G} && (2.73)\\ \hat{G} &= \hat{G}^0 + \hat{G}^0\,\hat{V}\,\hat{G} \quad . && (2.74) \end{aligned}$$

On the other hand, if (2.71) is multiplied with $(z - \hat{H})$ from the right we get:

$$\begin{aligned} \hat{G}\,(z - \hat{H}^0 - \hat{V}) &= \mathbf{1} && (2.75)\\ \hat{G}\,(\hat{G}^0)^{-1} &= \mathbf{1} + \hat{G}\,\hat{V} && (2.76)\\ \hat{G} &= \hat{G}^0 + \hat{G}\,\hat{V}\,\hat{G}^0 \quad . && (2.77) \end{aligned}$$

The T-Operator

It is useful to define the following operator $\hat{T}$ [Wei90]:

$$\hat{T} := \hat{V} + \hat{V}\,\hat{G}\,\hat{V} \quad . \tag{2.78}$$

Now using (2.74) once yields the Lippmann-Schwinger or *Dyson equation* for the T-operator:

$$\begin{aligned} \hat{T} &= \hat{V} + \hat{V}\,\hat{G}^0\,\hat{V} + \hat{V}\,\hat{G}^0\,\hat{V}\,\hat{G}\,\hat{V} && (2.79)\\ &= \hat{V} + \hat{V}\,\hat{G}^0\,(\hat{V} + \hat{V}\,\hat{G}\,\hat{V}) && (2.80)\\ &= \hat{V} + \hat{V}\,\hat{G}^0\,\hat{T} \quad . && (2.81) \end{aligned}$$

If (2.78) is multiplied from the left with $\hat{G}^0$ one gets:

$$\begin{aligned} \hat{G}^0\,\hat{T} &= \hat{G}^0\,\hat{V} + \hat{G}^0\,\hat{V}\,\hat{G}\,\hat{V} && (2.82)\\ &= (\hat{G}^0 + \hat{G}^0\,\hat{V}\,\hat{G})\,\hat{V} && (2.83)\\ &= \hat{G}\,\hat{V} \quad . && (2.84) \end{aligned}$$

With this it follows from (2.77) that

$$\hat{G} = \hat{G}^0 + \hat{G}^0\,\hat{T}\,\hat{G}^0 \quad . \tag{2.85}$$

Coordinate Representations

Now all of the above abstract operator equations can be written in corresponding coordinate representations, which makes them useful for practical calculations. A Green's function is then the representation of the operator $\hat{G}$ in the limit $\varepsilon \to 0$. Hence the coordinate representations of equations (2.74) and (2.77) are:

$$\begin{aligned} G(\boldsymbol{r},\boldsymbol{r}') &= G^0(\boldsymbol{r},\boldsymbol{r}') + \int \mathrm{d}\boldsymbol{r}''\, G^0(\boldsymbol{r},\boldsymbol{r}'')\, V(\boldsymbol{r}'')\, G(\boldsymbol{r}'',\boldsymbol{r}') && (2.86)\\ G(\boldsymbol{r},\boldsymbol{r}') &= G^0(\boldsymbol{r},\boldsymbol{r}') + \int \mathrm{d}\boldsymbol{r}''\, G(\boldsymbol{r},\boldsymbol{r}'')\, V(\boldsymbol{r}'')\, G^0(\boldsymbol{r}'',\boldsymbol{r}') \quad . && (2.87) \end{aligned}$$

The T-operator in (2.78) can be written as [ZG89b]:

$$T(\boldsymbol{r},\boldsymbol{r}') = V(\boldsymbol{r})\,\left(\delta(\boldsymbol{r}-\boldsymbol{r}') + \int \mathrm{d}\boldsymbol{r}''\, G(\boldsymbol{r},\boldsymbol{r}'')\, V(\boldsymbol{r}'')\right) \quad , \tag{2.88}$$

or alternatively as

$$T(\boldsymbol{r},\boldsymbol{r}') = V(\boldsymbol{r})\,\left(\delta(\boldsymbol{r}-\boldsymbol{r}') + \int \mathrm{d}\boldsymbol{r}''\, G^0(\boldsymbol{r},\boldsymbol{r}'')\, T(\boldsymbol{r}'',\boldsymbol{r}')\right) \quad , \tag{2.89}$$

which is equation (2.81). Finally the relation between the Green's function of the single scatterer system and the T-operator in equation (2.85) is

$$\begin{aligned} G(\boldsymbol{r},\boldsymbol{r}') &= G^0(\boldsymbol{r},\boldsymbol{r}') \\ &\quad + \iint \mathrm{d}\boldsymbol{r}''\mathrm{d}\boldsymbol{r}'''\, G^0(\boldsymbol{r},\boldsymbol{r}'')\, T(\boldsymbol{r}'',\boldsymbol{r}''')\, G^0(\boldsymbol{r}''',\boldsymbol{r}') \quad . && (2.90) \end{aligned}$$

The aim of this section is to show that the Green's function defined in (2.71) can be expanded in terms of regular and irregular scattering solutions in analogy to equation (2.14):

$$G^0(\boldsymbol{r},\boldsymbol{r'}) = -\mathrm{i}k \sum_L j_L(k\boldsymbol{r}_<)\, h_L(k\boldsymbol{r}_>) \quad . \tag{2.91}$$

Using this expansion in (2.90), we obtain:

$$\begin{aligned} G(\boldsymbol{r},\boldsymbol{r}') &= -\mathrm{i}k \sum_L j_L(k\boldsymbol{r}_<)\, h_L(k\boldsymbol{r}_>) \\ &\quad -k^2 \sum_{LL'} \iint \mathrm{d}\boldsymbol{r}''\mathrm{d}\boldsymbol{r}'''\, j_L(k\boldsymbol{r}_<)\, h_L(k\boldsymbol{r}_>)\, T(\boldsymbol{r}'',\boldsymbol{r}''')\, j_{L'}(k\boldsymbol{r}_<)\, h_{L'}(k\boldsymbol{r}_>)\,. \end{aligned} \tag{2.92}$$

Now taking account of $\boldsymbol{r}_<$ and $\boldsymbol{r}_>$ and using the notation Ω_r for a sphere of radius r and Ω_{r-S} for a hollow sphere with the thickness $S-r$, we can write:

$$\begin{aligned} G(\boldsymbol{r},\boldsymbol{r}') &= -\mathrm{i}k \sum_L j_L(k\boldsymbol{r}_<)\, h_L(k\boldsymbol{r}_>) \\ &\quad - k^2 \sum_{LL'} \left[h_L(k\boldsymbol{r}) \left(\int\limits_{\Omega_r}\int\limits_{\Omega_r} \mathrm{d}\boldsymbol{r}''\mathrm{d}\boldsymbol{r}'''\, j^\dagger_L(k\boldsymbol{r}'')\, T(\boldsymbol{r}'',\boldsymbol{r}''')\, j_{L'}(k\boldsymbol{r}''') \right) h^\dagger_{L'}(k\boldsymbol{r}') \right. \\ &\quad + h_L(k\boldsymbol{r}) \left(\int\limits_{\Omega_r}\int\limits_{\Omega_{r-S}} \mathrm{d}\boldsymbol{r}''\mathrm{d}\boldsymbol{r}'''\, j^\dagger_L(k\boldsymbol{r}'')\, T(\boldsymbol{r}'',\boldsymbol{r}''')\, h_{L'}(k\boldsymbol{r}''') \right) j^\dagger_{L'}(k\boldsymbol{r}') \\ &\quad + j_L(k\boldsymbol{r}) \left(\int\limits_{\Omega_{r-S}}\int\limits_{\Omega_r} \mathrm{d}\boldsymbol{r}''\mathrm{d}\boldsymbol{r}'''\, h^\dagger_L(k\boldsymbol{r}'')\, T(\boldsymbol{r}'',\boldsymbol{r}''')\, j_{L'}(k\boldsymbol{r}''') \right) h^\dagger_{L'}(k\boldsymbol{r}') \\ &\quad \left. + j_L(k\boldsymbol{r}) \left(\int\limits_{\Omega_{r-S}}\int\limits_{\Omega_{r-S}} \mathrm{d}\boldsymbol{r}''\mathrm{d}\boldsymbol{r}'''\, h^\dagger_L(k\boldsymbol{r})\, T(\boldsymbol{r}'',\boldsymbol{r}''')\, h_{L'}(k\boldsymbol{r}''') \right) j^\dagger_{L'}(k\boldsymbol{r}') \right] \end{aligned} \tag{2.93}$$

where † refers to the complex conjugation of spherical harmonics in $j^\dagger_L(k\boldsymbol{r})$ and $h^\dagger_L(k\boldsymbol{r})$:

$$j^\dagger_L(k\boldsymbol{r}) = j_\ell(kr)\, Y^*_L(\hat{\boldsymbol{r}}) \quad , \tag{2.94}$$

$$h^\dagger_L(k\boldsymbol{r}) = h_\ell(kr)\, Y^*_L(\hat{\boldsymbol{r}}) \quad . \tag{2.95}$$

Clearly for $r \geq S$ the last three terms vanish and we are left with

$$G(\boldsymbol{r},\boldsymbol{r}') = -\mathrm{i}k\sum_L j_L(k\boldsymbol{r}_<)\,h_L(k\boldsymbol{r}_>)$$
$$-k^2\sum_{LL'} h_L(k\boldsymbol{r})\left(\iint \mathrm{d}\boldsymbol{r}''\mathrm{d}\boldsymbol{r}'''\,j_L^\dagger(k\boldsymbol{r}'')\,T(\boldsymbol{r}'',\boldsymbol{r}''')\,j_{L'}(k\boldsymbol{r}''')\right)\,h_{L'}^\dagger(k\boldsymbol{r}') \tag{2.96}$$

If only one scatterer is present we can identify the term inside the brackets as the t matrix:

$$t_{LL'} = \iint \mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{r}'\,j_L^\dagger(k\boldsymbol{r})\,T(\boldsymbol{r},\boldsymbol{r}')\,j_{L'}(k\boldsymbol{r}') \quad , \tag{2.97}$$

then we can write the Green's function again in terms of spherical Bessel and Hankel functions (for $r' > r$) as:

$$G(\boldsymbol{r},\boldsymbol{r}') = -\mathrm{i}k\sum_L j_L(k\boldsymbol{r}_<)\,h_L(k\boldsymbol{r}_>) - k^2\sum_{LL'} h_L(k\boldsymbol{r}_<)\,t_{LL'}\,h_{L'}(k\boldsymbol{r}_>) \quad . \tag{2.98}$$

We could have arrived at the same expression if we had expanded the Green's function in terms of regular and irregular solutions:

$$G(\boldsymbol{r},\boldsymbol{r}') = -\mathrm{i}k\sum_L R_L(\boldsymbol{r}_<)\,H_L(\boldsymbol{r}_>) \quad , \tag{2.99}$$

and then used the expressions

$$R_L(\boldsymbol{r}) \;=\; j_L(k\boldsymbol{r}) - \mathrm{i}k\sum_{L'} h_{L'}(k\boldsymbol{r})\,t_{L'L} \quad , \tag{2.100}$$
$$H_L(\boldsymbol{r}) \;=\; h_L(k\boldsymbol{r}) \quad , \tag{2.101}$$

which are the proper normalizations of these functions and are valid for $r \geq S$.

Now we want to find an expansion of the Green's function if the radial solutions for a spherically symmetric scatterer are used. For this purpose let us rewrite (2.99) as:

$$G(\boldsymbol{r},\boldsymbol{r}') = \sum_{LL'} Y_L(\hat{\boldsymbol{r}})\,G_{LL'}(r,r')\,Y_{L'}^*(\hat{\boldsymbol{r}}') \quad , \tag{2.102}$$

where the matrix $G_{LL'}(r,r')$ is given by

$$G_{LL'}(r,r') = -\mathrm{i}k\sum_{L''} R_{LL''}(r_<)\,H_{L''L'}(r_>) \quad . \tag{2.103}$$

If the potential has spherical symmetry then the solutions are diagonal in angular momenta:

$$R_{LL''}(r) = \delta_{LL''}\, R_{\ell''}(r)\,, \quad H_{L''L'}(r) = \delta_{L''L'}\, H_{\ell''}(r)\,. \tag{2.104}$$

Hence for such a potential the expansion in (2.102) reduces to

$$G(\boldsymbol{r}, \boldsymbol{r}') = -\mathrm{i}k \sum_{L} Y_L(\hat{\boldsymbol{r}})\, R_\ell(r_<)\, H_\ell(r_>)\, Y_L^*(\hat{\boldsymbol{r}}') \quad , \tag{2.105}$$

and instead of (2.103) we can write:

$$G_\ell(r, r') = -\mathrm{i}k\, R_\ell(r_<)\, H_\ell(r_>) \quad . \tag{2.106}$$

Comparing the last two equations to (2.14) and (2.15) one sees that this is the analogy to the expansion of the free particle Green's function for a single scattering potential.

2.3.2 Separating the Scattering Problem

The underlying idea of the following is that the potential can be separated into a spherically symmetric and a non-spherically symmetric contribution. In contrast to the symmetric contribution the non-spherical one is finite only in the outer regions of the potential and can be treated as a perturbation. Exactly where the "outer region" starts, i.e., at what distance from the origin is a matter of experience and differs from system to system. According to (2.26) the potential can be expanded as:

$$V(\boldsymbol{r}) = \sum_{L} V_L(r)\, Y_L(\hat{\boldsymbol{r}}) \quad . \tag{2.107}$$

It has been shown in section 2.2.5 that the spherical symmetric part of the potential is just the first term of the summation. Hence we can express the total potential as the following sum:

$$V(\boldsymbol{r}) = V(r) + \sum_{\mathfrak{L}>1} V_{\mathfrak{L}}(r)\, Y_{\mathfrak{L}}(\hat{\boldsymbol{r}}) \quad , \tag{2.108}$$

where $V(r) = 1/4\pi\, V_1(r)$ and $\mathfrak{L} = \ell(\ell+1) + m + 1$ has been used. If we define the perturbation part of the potential as:

$$\Delta V(\boldsymbol{r}) = \sum_{\mathfrak{L}>1} V_{\mathfrak{L}}(r)\, Y_{\mathfrak{L}}(\hat{\boldsymbol{r}}) \quad , \tag{2.109}$$

then the potential can be expressed as the sum of two terms:

$$V(\boldsymbol{r}) = V(r) + \Delta V(\boldsymbol{r}) \quad . \tag{2.110}$$

The angular momentum notation for the spherical symmetric part is given by equation (2.67), and for $\Delta V_{LL'}(r)$ we get:

$$\Delta V_{LL'}(r) = V_{LL'}(r) - \delta_{LL'} V(r) \quad . \tag{2.111}$$

We would now like to find a Lippmann-Schwinger equation in which the solution of the Schrödinger equation for an anisotropic potential is expressed in terms of a solution of the equation containing the spherical symmmetric part of the full potential. In order to find such a relation let us first denote the Lippmann-Schwinger equation of (2.23):

$$\psi_L(\boldsymbol{r}) = \varphi_L(\boldsymbol{r}) + \int \mathrm{d}\boldsymbol{r}' \, G^0(\boldsymbol{r},\boldsymbol{r}') \, V(\boldsymbol{r}') \, \psi_L(\boldsymbol{r}') \quad , \tag{2.112}$$

where $\varphi_L(\boldsymbol{r})$ is a solution of the homogeneous Schrödinger equation. Then we can make use of relation (2.87):

$$G(\boldsymbol{r},\boldsymbol{r}') = G^0(\boldsymbol{r},\boldsymbol{r}') + \int \mathrm{d}\boldsymbol{r}'' \, G(\boldsymbol{r},\boldsymbol{r}'') \, V(r'') \, G^0(\boldsymbol{r}'',\boldsymbol{r}') \quad , \tag{2.113}$$

where it is important to note that $G(\boldsymbol{r},\boldsymbol{r}')$ is now the Green's function for a Schrödinger equation for a spherically symmetric potential. This equation can be rewritten so that we obtain a relation for $G^0(\boldsymbol{r},\boldsymbol{r}')$:

$$G^0(\boldsymbol{r},\boldsymbol{r}') = G(\boldsymbol{r},\boldsymbol{r}') - \int \mathrm{d}\boldsymbol{r}'' \, G(\boldsymbol{r},\boldsymbol{r}'') \, V(r'') \, G^0(\boldsymbol{r}'',\boldsymbol{r}') \quad . \tag{2.114}$$

Substitution of the above expression into the Lippmann-Schwinger equation (2.112) yields:

$$\begin{aligned} \psi_L(\boldsymbol{r}) = \varphi_L(\boldsymbol{r}) &+ \int \mathrm{d}\boldsymbol{r}' \, G(\boldsymbol{r},\boldsymbol{r}') \, V(\boldsymbol{r}') \, \psi_L(\boldsymbol{r}') \\ &- \int \mathrm{d}\boldsymbol{r}'' \, G(\boldsymbol{r},\boldsymbol{r}'') \, V(r'') \left(\int \mathrm{d}\boldsymbol{r}' \, G^0(\boldsymbol{r}'',\boldsymbol{r}') \, V(\boldsymbol{r}') \, \psi_L(\boldsymbol{r}') \right) \quad . \end{aligned} \tag{2.115}$$

The term inside the parentheses already appeared in (2.112) and consequently we can write:

$$\begin{aligned} \psi_L(\boldsymbol{r}) \;\; = \;\; & \varphi_L(\boldsymbol{r}) + \int \mathrm{d}\boldsymbol{r}' \, G(\boldsymbol{r},\boldsymbol{r}') \, V(r') \, \varphi_L(\boldsymbol{r}') \\ & + \int \mathrm{d}\boldsymbol{r}' \, G(\boldsymbol{r},\boldsymbol{r}') \, \left(V(\boldsymbol{r}') - V(r') \right) \, \psi_L(\boldsymbol{r}') \quad . \end{aligned} \tag{2.116}$$

In this equation the first two terms are a Lippmann-Schwinger equation for the spherically symmetric solution, which will be denoted by $\psi_\ell(r)$, because it contains the

Green's function of the system which is perturbed by the potential $V(r)$. The last term contains the difference between the full and the spherically symmetric potential and according to (2.110) this is nothing but $\Delta V(\boldsymbol{r})$. With these observations (2.116) reduces to:

$$\psi_L(\boldsymbol{r}) = \psi_\ell(r) + \int \mathrm{d}\boldsymbol{r}'\, G(\boldsymbol{r},\boldsymbol{r}')\, \Delta V(\boldsymbol{r}')\, \psi_L(\boldsymbol{r}') \quad . \tag{2.117}$$

In analogy to the previous sections this integral equation can be rewritten in a form that contains only a one-dimensional radial integration. For the derivation one has to make use of the following identities (c.f. (2.33), (2.87), (2.111)):

$$\begin{aligned} \psi_{LL'}(r) &= \varphi_\ell(r) + \int r'^2 \mathrm{d}r'\, G^0_\ell(r,r') \sum_{L''} V_{LL''}(r')\, \psi_{L''L'}(r') & (2.118)\\ G^0_\ell(r,r') &= G_\ell(r,r') - \int r''^2 \mathrm{d}r''\, G_\ell(r,r'')\, V(r'')\, G^0_\ell(r'',r') & (2.119)\\ V_{LL'}(r) &= \delta_{LL'} V(r) + \Delta V_{LL'}(r) \quad . & (2.120) \end{aligned}$$

The expression for the radial wave function $\psi_{LL'}(r)$ is finally:

$$\psi_{LL'}(r) = \psi_\ell(r) + \int_0^S r'^2 \mathrm{d}r'\, G_\ell(r,r') \sum_{L''} \Delta V_{LL''}(r')\, \psi_{L''L'}(r') \quad . \tag{2.121}$$

Regular Solutions

For the regular solutions, (2.121) is given through:

$$R_{LL'}(r) = R_\ell(r) + \int_0^S r'^2 \mathrm{d}r'\, G_\ell(r,r') \sum_{L''} \Delta V_{LL''}(r')\, R_{L''L'}(r') \quad . \tag{2.122}$$

This equation closely resembles (2.33). But now instead of free space, the reference system is the isotropic part of the potential, $V(r)$. By making use of (2.106) equation (2.122) acquires the following structure:

$$\begin{aligned} R_{LL'}(r) &= R_\ell(r) - \mathrm{i}k \left(\int_0^r r'^2 \mathrm{d}r'\, R_\ell(r') \sum_{L''} \Delta V_{LL''}(r')\, R_{L''L'}(r') \right) H_\ell(r) \\ &\quad - \mathrm{i}k \left(\int_r^S r'^2 \mathrm{d}r'\, H_\ell(r') \sum_{L''} \Delta V_{LL''}(r')\, R_{L''L'}(r') \right) R_\ell(r) & (2.123)\\ R_{LL'}(r) &= A_{LL'}\, R_\ell(r) + B_{LL'}\, H_\ell(r) \quad , & (2.124) \end{aligned}$$

where in the last step the two coefficients $A_{LL'}$ and $B_{LL'}$ have been defined as:

$$A_{LL'} = \delta_{LL'} - \mathrm{i}k \int\limits_{r}^{S} r'^2 \mathrm{d}r'\, H_\ell(r') \sum_{L''} \Delta V_{LL''}(r')\, R_{L''L'}(r') \tag{2.125}$$

$$B_{LL'} = -\,\mathrm{i}k \int\limits_{0}^{r} r'^2 \mathrm{d}r'\, R_\ell(r') \sum_{L''} \Delta V_{LL''}(r')\, R_{L''L'}(r') \quad . \tag{2.126}$$

Irregular Solutions

The irregular solutions can be denoted in the same way as above, however, the different boundary conditions have to be taken account of. Hence, with $V(r)$ as the reference system, the solutions are given by:

$$H_{LL'}(r) = \varphi_\ell(r) + \int\limits_{0}^{S} r'^2 \mathrm{d}r'\, G_\ell(r,r') \sum_{L''} \Delta V_{LL''}(r')\, H_{L''L'}(r') \quad , \tag{2.127}$$

where $\varphi_\ell(r)$ contains the boundary conditions which will be included in the following. The asymptotic behaviour of the wave functions outside the scattering region is the following:

$$H_{LL'}(r) = H_\ell(r)\,, \quad \text{for} \quad r \geq S\,. \tag{2.128}$$

If the reference system was free space, i.e., $V(r) = 0$, then $H_\ell(r)$ could be identified by spherical Hankel functions of the first kind. It follows with equation (2.106) that $\varphi_\ell(r)$ is of the form:

$$\varphi_\ell(r) = H_\ell(r) + \mathrm{i}k\, H_\ell(r) \int\limits_{0}^{S} r'^2 \mathrm{d}r'\, R_\ell(r') \sum_{L''} \Delta V_{LL''}(r')\, H_{L''L'}(r') \quad . \tag{2.129}$$

This can be substituted into (2.127) to yield a radial Lippmann-Schwinger equation for the irregular solutions, written exclusively in terms of the anisotropic contributions of the potential:

$$\begin{aligned} H_{LL'}(r) \;=\; & H_\ell(r) + \mathrm{i}k\, H_\ell(r) \int\limits_{0}^{S} r'^2 \mathrm{d}r'\, R_\ell(r') \sum_{L''} \Delta V_{LL''}(r')\, H_{L''L'}(r') \\ & + \int\limits_{0}^{S} r'^2 \mathrm{d}r'\, G_\ell(r,r') \sum_{L''} \Delta V_{LL''}(r')\, H_{L''L'}(r') \quad . \end{aligned} \tag{2.130}$$

Using again the expression for $G_\ell(r,r')$ of equation (2.106) one obtains:

$$\begin{aligned} H_{LL'}(r) \;&=\; H_\ell(r) + \mathrm{i}k\, H_\ell(r) \int\limits_0^S r'^2 \mathrm{d}r'\, R_\ell(r') \sum_{L''} \Delta V_{LL''}(r')\, H_{L''L'}(r') \\ &\quad -\mathrm{i}k\, H_\ell(r) \int\limits_0^r r'^2 \mathrm{d}r'\, R_\ell(r') \sum_{L''} \Delta V_{LL''}(r')\, H_{L''L'}(r') \\ &\quad -\mathrm{i}k\, R_\ell(r) \int\limits_r^S r'^2 \mathrm{d}r'\, H_\ell(r') \sum_{L''} \Delta V_{LL''}(r')\, H_{L''L'}(r') \quad , \end{aligned} \tag{2.131}$$

and finally we get

$$\begin{aligned} H_{LL'}(r) \;&=\; H_\ell(r) + \mathrm{i}k\, H_\ell(r) \int\limits_r^S r'^2 \mathrm{d}r'\, R_\ell(r') \sum_{L''} \Delta V_{LL''}(r')\, H_{L''L'}(r') \\ &\quad -\mathrm{i}k\, R_\ell(r) \int\limits_r^S r'^2 \mathrm{d}r'\, H_\ell(r') \sum_{L''} \Delta V_{LL''}(r')\, H_{L''L'}(r') \quad . \end{aligned} \tag{2.132}$$

Once more we can write this in a shorthand notation as:

$$H_{LL'}(r) = C_{LL'}\, R_\ell(r) + D_{LL'}\, H_\ell(r) \quad , \tag{2.133}$$

where the coefficients are given by the following expressions:

$$C_{LL'} \;=\; -\mathrm{i}k \int\limits_r^S r'^2 \mathrm{d}r'\, H_\ell(r') \sum_{L''} \Delta V_{LL''}(r')\, H_{L''L'}(r') \tag{2.134}$$

$$D_{LL'} \;=\; \delta_{LL'} + \mathrm{i}k \int\limits_r^S r'^2 \mathrm{d}r'\, R_\ell(r') \sum_{L''} \Delta V_{LL''}(r')\, H_{L''L'}(r') \quad . \tag{2.135}$$

2.3.3 **The t Matrix**

For the present case of an anisotropic, arbitrarily shaped potential, the single site t matrix is no longer diagonal in angular momentum indices. As in the case of the radial wave functions we can separate the problem into the calculation of the t matrix for the spherical part of the potential, and into the calculation of the non-diagonal contributions to the t matrix which correspond to the perturbative, anisotropic part of the total potential.

Outside the scattering region the regular solution for the potential $V(r) = V(\boldsymbol{r}) - \Delta V(\boldsymbol{r})$, $R_\ell(r)$, is given by the well known expression:

$$R_\ell(r) = j_\ell(kr) - \mathrm{i}k\, t_\ell\, h_\ell(kr) \quad . \tag{2.136}$$

In the previous section it has been mentioned that the irregular solution is normalized to smoothly join a spherical Hankel function of the first kind in free space, thus:

$$H_\ell(r) = h_\ell(kr)\,, \quad \text{for} \quad r \geq S \quad . \tag{2.137}$$

Furthermore the coefficients in equations (2.125) and (2.126) reduce outside the scattering region, i.e. $r \geq S$, to:

$$\begin{aligned} A_{LL'} &= \delta_{LL'} && (2.138)\\ B_{LL'} &= -\mathrm{i}k \int\limits_0^S r'^2 \mathrm{d}r'\, R_\ell(r') \sum_{L''} \Delta V_{LL''}(r')\, R_{L''L'}(r') && (2.139)\\ &= -\mathrm{i}k\, \Delta t_{LL'} \quad . && (2.140) \end{aligned}$$

In the last step the additional contribution to the total t matrix has been identified by comparison with (2.40) as:

$$\Delta t_{LL'} = \int\limits_0^S r'^2 \mathrm{d}r'\, R_\ell(r') \sum_{L''} \Delta V_{LL''}(r')\, R_{L''L'}(r') \quad . \tag{2.141}$$

Then for $r \geq S$, (2.124) is given by:

$$\begin{aligned} R_{LL'}(r) &= j_\ell(kr) - \mathrm{i}k\, t_\ell\, h_\ell(kr) - \mathrm{i}k\, \Delta t_{LL'}\, h_\ell(kr) && (2.142)\\ &= j_\ell(kr) - \mathrm{i}k\, t_{LL'}\, h_\ell(kr) \quad , && (2.143) \end{aligned}$$

where the total t matrix was identified as:

$$t_{LL'} = t_\ell + \Delta t_{LL'} \quad . \tag{2.144}$$

2.3.4 **Numerical Solution with the Born Approximation**

Equations (2.124) and (2.133) can be used to obtain solutions for the Lippmann-Schwinger equations through an iterative scheme. The idea is that in a first step the wave functions $R_{LL'}(r)$ and $H_{LL'}(r)$, respectively, which appear in the integrands, can be approximated by the solutions to the radially symmetric problem. So for the 0-th approximation we can write:

$$\begin{aligned} R^{(0)}_{LL'}(r) &= R_\ell(r) && (2.145) \\ H^{(0)}_{LL'}(r) &= H_\ell(r) \quad . && (2.146) \end{aligned}$$

Inserting these into (2.124) and (2.133) results in the first approximations, $R^{(1)}_{LL'}(r)$ and $H^{(1)}_{LL'}(r)$. Then they are again inserted into the equations to yield the second Born approximation. This iteration scheme can be repeated several times, but experience has shown that the results of the second Born approximation is sufficiently accurate [Dri91]. The radial integrations are all performed by Simpson's method which is described in the appendix.

So once the radial solutions $R_{LL'}(r)$ have been obtained the t matrix can be calculated according to (2.141) and (2.144).

2.4

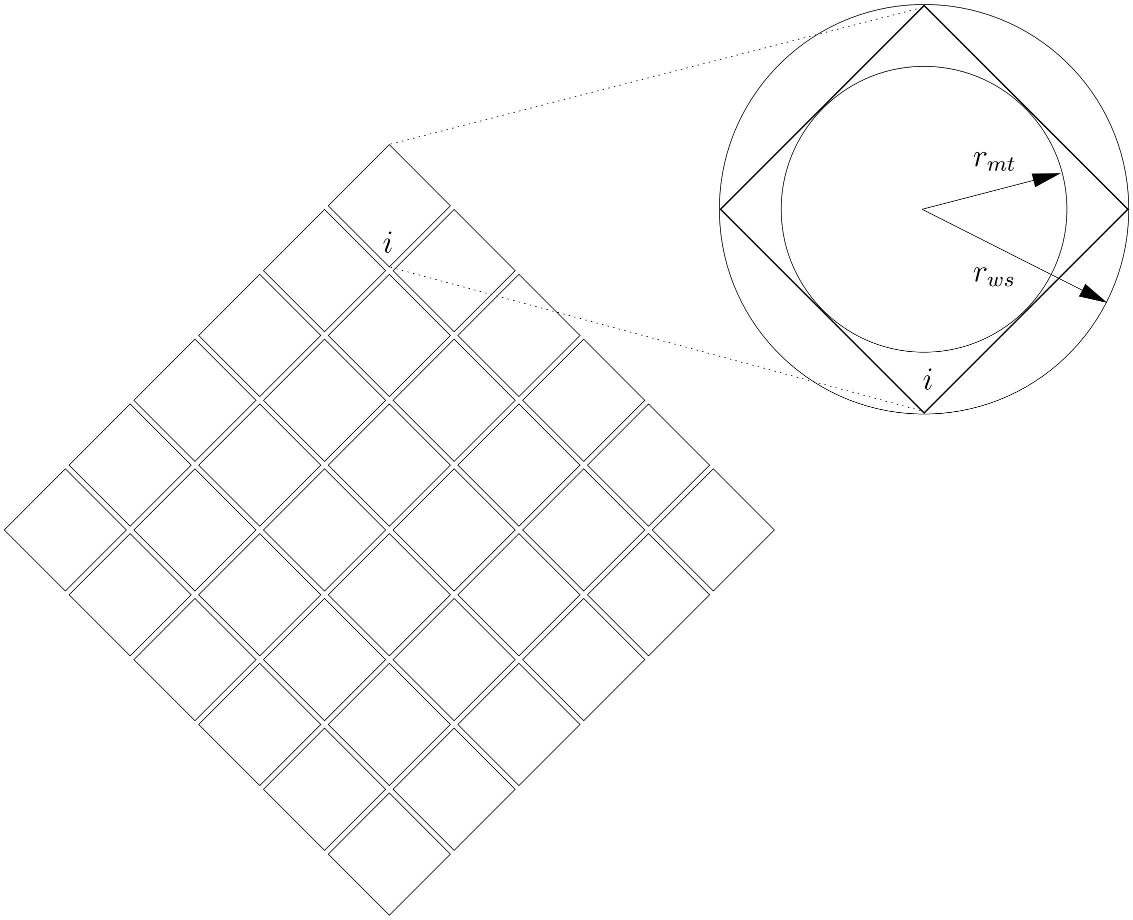
The Shape Function Technique

As should be clear by now from the discussion in the previous sections, the potential is, apart from being anisotropic, of non-spherical shape. Furthermore we require that a periodic arrangement of this potential ought to fill up all space. The latter requirement is achieved by the division of space into Wigner-Seitz cells. Clearly the individual potentials are then of polyhedral shape and we have to take account of this fact by some means. Here the introduction of so called *shape functions* [AW73][WSF94] helps out. These are nothing but unit step functions, which are defined to have the value 1 inside a given Wigner-Seitz cell and 0 outside. Denoting the step function of the i-th cell by $\sigma_i(\boldsymbol{r})$ we may write:

$$\sigma_i(\boldsymbol{r}) = \begin{cases} 1 & , \quad \text{if } \boldsymbol{r} \text{ inside the } i\text{−th cell} \\ 0 & , \quad \text{otherwise} \end{cases} \quad . \qquad (2.147)$$

As is illustrated in figure 2.1, the shape functions are equal to 1 as long as $r \leq r_{mt}$ and equal to 0 if $r > r_{ws}$. For values of r between those characteristic radii the shape functions acquire values of either 1 or 0 depending on the direction of $\boldsymbol{r}$. It should be noted that r_{ws} denotes the radius of a sphere circumscribing a Wigner-Seitz cell, and

Figure 2.1: *A collection of Wigner-Seitz cells. Around each cell a bounding sphere of radius r_{ws}, and inside each cell a sphere with the muffin tin radius r_{mt} can be drawn. A shape function cuts out those parts of the bounding sphere which do not lie inside the i-th cell.*



should not be confused with the Wigner-Seitz radius which specifies the radius of a sphere equal in volume with a Wigner-Seitz cell.

Consider now a potential $V(\boldsymbol{r})$ belonging to an atom at a lattice position, which we label by i, that is anisotropic but of unspecified shape and extent. Then by folding this potential with the shape function of cell i we do not only limit the maximum range of the potential but also "cut" it into a certain shape. This potential is then given by:

$$v_i(\boldsymbol{r}) = V(\boldsymbol{r})\,\sigma_i(\boldsymbol{r}) \quad . \tag{2.148}$$

Of course the shape functions can also be expanded in terms of their angular momentum components and spherical harmonics as:

$$\sigma(\boldsymbol{r}) = \sum_L \sigma_L(r)\,Y_L(\hat{\boldsymbol{r}}) \quad . \tag{2.149}$$

Accordingly the expansion coefficients may then by calculated from:

$$\sigma_L(r) = \int \mathrm{d}\hat{\boldsymbol{r}}\, Y_L^*(\hat{\boldsymbol{r}})\, \sigma(\boldsymbol{r}) \quad . \tag{2.150}$$

From the definition of the shape functions it is clear that these coefficients can easily by calculated for $r \leq r_{mt}$ and $r > r_{ws}$, where they are given by:

$$\sigma_L(r) = \delta_{\ell 0}\, \delta_{m0} \sqrt{4\pi}\,, \quad r \leq r_{mt} \quad , \tag{2.151}$$

and

$$\sigma_L(r) = 0\,, \quad r > r_{ws} \quad . \tag{2.152}$$

The difficulty now is to obtain the expansion coefficients in the intermediate region by solving (2.150). Prescriptions on how to solve this integral can be found in the literature [SAZ90][SZ91][BtVB88][AP89]. As is shown there the integration has – at least partially – to be performed numerically.

While the shape functions are anisotropic in the region between the muffin tin and the bounding sphere, the potential also has anisotropic contributions that extend into the muffin tin. This is schemetically displayed in figure 2.2. The part of the potential that is spherically symmetric lies inside the muffin tin radius and has n_{sph} mesh points. Beyond the corresponding radius r_{sph} are so-called non-spherical contributions to the potential which lie on n_{nsph} radial points and extend up to the maximum radius r_{ws}. Therefore the solutions of the coupled radial equations have to be obtained on these n_{nsph} mesh points. The value of r_{sph} is more or less arbitrary, is due to experience, and differs from system to system.

In systems with high symmetry, not all of the angular momentum components are finite. Taking the case of cubic systems one can use the so-called cubic harmonics, i.e., we only have non-zero components for $\ell = 0, 4, 6, 8, 10, 12, \ldots$ and $m = 0 \bmod(4)$.

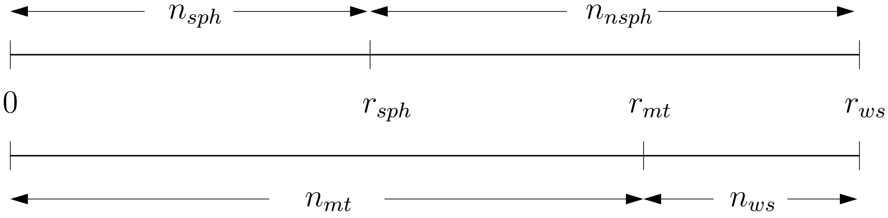
Returning now to equation (2.148) and expanding all quantities in terms of spherical harmonics we get the following identity:

$$\sum_L v_{iL}(r)\, Y_L(\hat{\boldsymbol{r}}) = \sum_{LL'} V_L(r)\, \sigma_{iL'}(r)\, Y_L(\hat{\boldsymbol{r}})\, Y_{L'}(\hat{\boldsymbol{r}}) \quad . \tag{2.153}$$

Multiplication with $Y_{L''}^*(\hat{\boldsymbol{r}})$, an angular integration and renaming indices yields the result:

$$v_{iL}(r) = \sum_{L'L''} V_{L'}(r)\, \sigma_{iL''}(r)\, C_{L'L''}^{L} \quad , \tag{2.154}$$

Figure 2.2: *The critical radii in relation to the regions of a Wigner-Seitz cell which are considered to be spherically symmetric and non-spherically symmetric.* r_{sph} *is an arbitrarily chosen radius up to which the potential is considered to be spherically symmetric and contains* n_{sph} *mesh points. Then* n_{nsph} *mesh points up to the Wigner-Seitz radius* r_{ws} *constitute the radial mesh of the non-spherical contributions to the potential. There are* n_{mt} *points up to the muffin tin radius* r_{mt} *and finally the number of points has to be the same, i.e.:* $n_{sph} + n_{nsph} = n_{mt} + n_{ws}$.



where once more the Gaunt coefficients have been defined as:

$$C^{L}_{L'L''} = \int \mathrm{d}\hat{\boldsymbol{r}}\, Y^{*}_{L}(\hat{\boldsymbol{r}})\, Y_{L'}(\hat{\boldsymbol{r}})\, Y_{L''}(\hat{\boldsymbol{r}}) \quad . \tag{2.155}$$

The "folding" of the potential with a shape function has the consequence that the angular momentum components of the potential acquire the properties of the shape function components. Since the first derivative of the latter is not continuous on the whole r-mesh also the components of the potential have this feature. The points where these discontinuities occur are those values of r where a corner, or a face is touched. E.g. in the case of an fcc lattice the intervals where the functions and their first derivatives are continuous are:

$$I_1 = \left[\frac{a}{\sqrt{8}}, \frac{a}{\sqrt{6}}\right] \quad , \tag{2.156}$$

$$I_2 = \left[\frac{a}{\sqrt{6}}, \frac{a\sqrt{3}}{4}\right] \quad , \tag{2.157}$$

$$I_3 = \left[\frac{a\sqrt{3}}{4}, \frac{a}{2}\right] \quad . \tag{2.158}$$

The first interval, I_1, corresponds to the difference of the radial distances between the centers of two faces of the cell, while the second interval, I_2, is the difference in distance between a face and a corner. Finally the third interval, I_3 contains the region between that corner and another corner whose radial distance from the cell center is identical to the Wigner-Seitz radius, r_{ws}. This has the effect that when the radial equation is solved the algorithm has to be stopped and restarted at these critical points. Hence we get integration intervals where the first and last point of each interval is always a critical point. One can use either exponential radial meshes in each interval, or alternatively use an exponential mesh between the origin and r_{mt} and equidistant distributions of r points in the intervals between r_{mt} and r_{ws}.

It is interesting to investigate how many angular momentum components have to be taken into account when the shape functions are calculated. We assume that we have calculated the wave functions up to ℓ_{max}. Then while solving the coupled equations (2.62) the double indexed components of the potential $V_{LL'}(r)$ enter. These are given by equation (2.63) as:

$$V_{LL'}(r) = \sum_{L''} C^{L}_{L'L''} V_{L''}(r) \quad , \tag{2.159}$$

It follows from the selection rules of the Gaunt numbers (c.f. section B.2.1 of the appendix) that $\ell'' = \ell + \ell'$, and therefore we need to compute $V_L(r)$ up to $2\ell_{max}$. Consequently we can see by inspecting equation (2.154) that we need the components of the shape functions up to $4\ell_{max}$.

3

Multiple Scattering and KKR

The presence of more than one scatterer necessitates the extension of the theory to multiple scattering. In the case of a large or infinite collection of potentials, which have to be non overlapping and are spatially bounded, the theory becomes especially useful, as then the electronic bandstructure and hence the physical properties of a periodic, infinite solid can be calculated. However, it is also possible to extend the theory to systems with interfaces or a surface.

Multiple scattering theory can either be developed by using wave functions or, alternatively, using operators and Green's functions. The latter case provides a straightforward, formal way to arrive at the final expressions. Hence we will proceed in that direction in the following.

The first section is devoted to the introduction of the *scattering path operator* which goes back to traditions introduced by Györffy [GS77]. Then a short discussion about the meaning of being *on the energy shell* follows. A rather extended section subsequently deals with a derivation of the Green's function of the system in terms of the scattering path operator and scattering solutions. A discussion of the structure constants and of the calculation of physical observables finally concludes the chapter.

3.1

The Scattering Path Operator

As a first principle let us assume that the potential in the system is the sum of non overlapping potentials centered at lattice sites labelled by i. Then in an operator notation we can write:

$$\hat{V} = \sum_i v_i \,, \quad D(v_i) \cap D(v_j) = \emptyset \quad , \tag{3.1}$$

where $D(v_i)$ refers to the domain of v_i. If only one potential v_i is present in the whole system then the operator $\hat{T}$ defined in (2.81) reduces to the single site t matrix. This can be denoted as:

$$t^i = v_i + v_i \, \hat{G}^0 \, t^i = \left(\mathbf{1} - v_i \, \hat{G}^0\right)^{-1} v_i \quad . \tag{3.2}$$

Returning to the case of more than one potential being present, instead of (2.81) we can write with equation (3.1):

$$\hat{T} = \sum_i \left(v_i + v_i \, \hat{G}^0 \, \hat{T}\right) = \sum_i \hat{Q}_i \quad , \tag{3.3}$$

where in the last step the quantities $\hat{Q}_i$ were defined. They can now be manipulated in the following manner:

$$\hat{Q}_i = v_i + v_i \, \hat{G}^0 \, \hat{T} = v_i + v_i \, \hat{G}^0 \sum_j \hat{Q}_j \quad , \tag{3.4}$$

and hence

$$\hat{Q}_i = v_i + v_i \, \hat{G}^0 \, \hat{Q}_i + v_i \, \hat{G}^0 \sum_{j \neq i} \hat{Q}_j \quad . \tag{3.5}$$

We would now like to express this operator in terms of the t matrix, which can be achieved by first rewriting (3.5) as:

$$\left(\mathbf{1} - v_i \, \hat{G}^0\right) \hat{Q}_i = v_i + v_i \, \hat{G}^0 \sum_{j \neq i} \hat{Q}_j \quad , \tag{3.6}$$

which then leads to:

$$\hat{Q}_i = \left(\mathbf{1} - v_i \, \hat{G}^0\right)^{-1} v_i \left(\mathbf{1} + \hat{G}^0 \sum_{j \neq i} \hat{Q}_j\right) \tag{3.7}$$

$$= t^i \left(\mathbf{1} + \hat{G}^0 \sum_{j \neq i} \hat{Q}_j\right) = t^i + t^i \, \hat{G}^0 \sum_{j \neq i} \hat{Q}_j \quad . \tag{3.8}$$

Repeated application of $\hat{Q}_i$ in this last identity results in the following expansion:

$$\hat{Q}_i = t^i + t^i \, \hat{G}^0 \sum_{j \neq i} t^j + t^i \, \hat{G}^0 \sum_{j \neq i} t^j \, \hat{G}^0 \sum_{k \neq j} t^k + \ldots \quad . \tag{3.9}$$

Accordingly for the $\hat{T}$ operator one obtains:

$$\hat{T} = \sum_i t^i + \sum_i t^i \, \hat{G}^0 \sum_{j \neq i} t^j + \sum_i t^i \, \hat{G}^0 \sum_{j \neq i} t^j \, \hat{G}^0 \sum_{k \neq j} t^k + \ldots \quad . \tag{3.10}$$

It can easily be shown that the above expansion can be written in a more compact form as:

$$\hat{T} = \sum_{ij} \tau^{ij} \quad , \tag{3.11}$$

if the *scattering path operator*, τ^{ij} [GS77] [FS80], is denoted by:

$$\begin{aligned} \tau^{ij} &= t^i \, \delta_{ij} + t^i \, \hat{G}^0 \sum_{k \neq i} \tau^{kj} & (3.12) \\ &= t^i \, \delta_{ij} + \sum_{k \neq j} \tau^{ik} \, \hat{G}^0 \, t^j \quad . & (3.13) \end{aligned}$$

These identities can be used to derive some expressions that will be useful later on. Considering a specific site n in the following we can write with the above identities:

$$\tau^{nj} = t^n \, \delta_{nj} + t^n \, \hat{G}^0 \sum_{i \neq n} \tau^{ij} \quad . \tag{3.14}$$

Then summing also over j, leaving out site n and multiplying both sides of the equation by $\hat{G}^0$ yields:

$$\sum_{j \neq n} \tau^{nj} \, \hat{G}^0 = t^n \, \hat{G}^0 \sum_{\substack{i \neq n \\ j \neq n}} \tau^{ij} \, \hat{G}^0 \quad . \tag{3.15}$$

In the same way another expression can be obtained:

$$\tau^{in} = t^n \, \delta_{in} + \sum_{k \neq n} \tau^{ik} \, \hat{G}^0 \, t^n \quad . \tag{3.16}$$

Summing over i, multiplying with $\hat{G}^0$ and renaming k to j results in:

$$\sum_{i \neq n} \tau^{in} \, \hat{G}^0 = \sum_{\substack{i \neq n \\ j \neq n}} \tau^{ij} \, \hat{G}^0 \, t^n \, \hat{G}^0 \quad . \tag{3.17}$$

Furthermore the diagonal element of the scattering path operator is given by:

$$\tau^{nn} = t^n + \sum_{j \neq n} \tau^{nj} \, \hat{G}^0 \, t^n \quad , \tag{3.18}$$

which leads with (3.15) to:

$$\tau^{nn} = t^n + t^n \, \hat{G}^0 \sum_{\substack{i \neq n \\ j \neq n}} \tau^{ij} \, \hat{G}^0 \, t^n \quad . \tag{3.19}$$

From equation (2.85) we know a relation between $\hat{G}$ and $\hat{T}$ namely:

$$\hat{G} = \hat{G}^0 + \hat{G}^0 \, \hat{T} \, \hat{G}^0 \quad , \tag{3.20}$$

which with (3.11) is identical to:

$$\hat{G} = \hat{G}^0 + \hat{G}^0 \sum_{ij} \tau^{ij} \, \hat{G}^0 \quad , \tag{3.21}$$

or, taking the diagonal element at site n out of the summation:

$$\hat{G} = \hat{G}^0 + \hat{G}^0 \, \tau^{nn} \, \hat{G}^0 + \hat{G}^0 \sum_{i \neq n} \tau^{in} \, \hat{G}^0 + \hat{G}^0 \sum_{j \neq n} \tau^{nj} \, \hat{G}^0 + \hat{G}^0 \sum_{\substack{i \neq n \\ j \neq n}} \tau^{ij} \, \hat{G}^0 \quad . \tag{3.22}$$

Now the reason for making the above transformations has become clear and we can use the identities (3.15), (3.17), and (3.19) in (3.22) to get the lengthy expression:

$$\begin{aligned} \hat{G} \; = \; & \hat{G}^0 + \hat{G}^0 \, t^n \, \hat{G}^0 + \hat{G}^0 \, t^n \, \hat{G}^0 \sum_{\substack{i \neq n \\ j \neq n}} \tau^{ij} \, \hat{G}^0 \, t^n \, \hat{G}^0 + \hat{G}^0 \sum_{\substack{i \neq n \\ j \neq n}} \tau^{ij} \, \hat{G}^0 \, t^n \, \hat{G}^0 \\ & + \hat{G}^0 \, t^n \, \hat{G}^0 \sum_{\substack{i \neq n \\ j \neq n}} \tau^{ij} \, \hat{G}^0 + \hat{G}^0 \sum_{\substack{i \neq n \\ j \neq n}} \tau^{ij} \, \hat{G}^0 \quad . \end{aligned} \tag{3.23}$$

In the presence of no other scatterer than the one at site n, (2.85) is identical to:

$$\hat{G}^n = \hat{G}^0 + \hat{G}^0 \, t^n \, \hat{G}^0 \quad , \tag{3.24}$$

which is the Green's function for an electron moving under the sole influence of the potential $v_n(\boldsymbol{r})$. Then using this definition, (3.23) can be written as:

$$\hat{G} = \hat{G}^n + \hat{G}^n \sum_{\substack{i \neq n \\ j \neq n}} \tau^{ij} \, \hat{G}^n \quad . \tag{3.25}$$

On the Energy Shell

In order to clarify the conception of being on the energy shell, a short excursion to the coordinate representation of the t matrix will be made in this section. To begin with let us denote equation (2.89), which is an expression for a t matrix corresponding to the potential v_i at site i, in the following way (leaving out the implicitly assumed energy dependence):

$$t^i(\boldsymbol{r},\boldsymbol{r}') = v_i(\boldsymbol{r})\,\delta(\boldsymbol{r}-\boldsymbol{r}') + v_i(\boldsymbol{r})\int \mathrm{d}\boldsymbol{r}'' G^0(\boldsymbol{r},\boldsymbol{r}'')\,t^i(\boldsymbol{r}'',\boldsymbol{r}') \quad . \tag{3.26}$$

In the next step consider the elements of the t matrix in a plane wave representation, $t^i(\boldsymbol{k},\boldsymbol{k}')$, which can be obtained from [GS77]:

$$t^i(\boldsymbol{k},\boldsymbol{k}') = \iint \mathrm{d}\boldsymbol{r}\,\mathrm{d}\boldsymbol{r}'\,\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\boldsymbol{r}}\,t^i(\boldsymbol{r},\boldsymbol{r}')\,\mathrm{e}^{\mathrm{i}\boldsymbol{k}'\boldsymbol{r}'} \quad . \tag{3.27}$$

These elements are defined for any combination of k vectors of incoming and outgoing plane waves. However, when one talks about elastic scattering a situation is meant where $\boldsymbol{k}^2 = \boldsymbol{k}'^2 = E$. Then $t^i(\boldsymbol{k},\boldsymbol{k}')$ is the probability amplitude that a state with wave vector $\boldsymbol{k}$ scatters into a state with wave vector $\boldsymbol{k}'$. Hence being "on the energy shell" refers to elastic scattering. To proceed, the famous expansion (2.11):

$$\mathrm{e}^{\mathrm{i}\boldsymbol{k}\boldsymbol{r}} = 4\pi\sum_L \mathrm{i}^\ell\, j_L(k\boldsymbol{r})\,Y_L^*(\hat{\boldsymbol{k}}) \quad , \tag{3.28}$$

can be used in (3.27), which yields:

$$t^i(\boldsymbol{k},\boldsymbol{k}') = 16\pi^2\sum_{LL'} \mathrm{i}^{-\ell+\ell'}\,Y_L(\hat{\boldsymbol{k}})\,t^i_{LL'}\,Y^*_{L'}(\hat{\boldsymbol{k}}') \quad . \tag{3.29}$$

In the above equation the "on the energy shell" matrix elements $t^i_{LL'}$ were defined as:

$$t^i_{LL'} = \iint \mathrm{d}\boldsymbol{r}\,\mathrm{d}\boldsymbol{r}'\,j_\ell(kr)\,Y_L^*(\hat{\boldsymbol{r}})\,t^i(\boldsymbol{r},\boldsymbol{r}')\,Y_{L'}(\hat{\boldsymbol{r}}')\,j_{\ell'}(kr') \quad . \tag{3.30}$$

The Equation of Motion

Györffy and Stocks have given some insight into the physical meanings of the operators t^i, τ^{ij}, and $\hat{T}$ in one of their articles [GS77]. In their picture t^i is the operator that (due to v_i) generates the scattered wave from the incident wave. Then the scattering path operator τ^{ij} produces a scattered wave from site j incident at site i by operating on the incident wave at site j and including all the scattering in between. Continuing along this line of thought, $\hat{T}$ then sums over all incident waves at all sites and turns them into scattered waves emanating from all other sites and adds up all the scattering.

The task now is to find a relation between the on the energy shell components of the t matrix and the scattering path operator which subsequently provides a powerful tool for bandstructure calculations. In order to derive such an expression we will initially rewrite equation (3.12) in a coordinate representation:

$$\tau^{ij}(\boldsymbol{r}_i, \boldsymbol{r}'_j) = t^i(\boldsymbol{r}_i, \boldsymbol{r}'_i) + \sum_{k \neq i} \iint \mathrm{d}\boldsymbol{r}'_i \, \mathrm{d}\boldsymbol{r}''_k \, t^i(\boldsymbol{r}_i, \boldsymbol{r}'_i) \, G^0(\boldsymbol{r}'_i, \boldsymbol{r}''_k) \, \tau^{kj}(\boldsymbol{r}''_k, \boldsymbol{r}'_j) \quad , \tag{3.31}$$

where the vector indices refer to the lattice sites at which the vectors are centered. This means that two vectors, one centered at i the other at k, connecting to one and the same point in the cell centered at k are related in the following way:

$$\boldsymbol{r}_i = \boldsymbol{R}_k - \boldsymbol{R}_i + \boldsymbol{r}_k = \boldsymbol{S}_{ik} + \boldsymbol{r}_k \quad . \tag{3.32}$$

With this observation it is possible to make use of the following expansion of the free particle Green's function ($r'_i > r_i$):

$$\begin{aligned} G^0(\boldsymbol{r}'_i, \boldsymbol{r}''_i) &= G^0(\boldsymbol{r}'_i, \boldsymbol{r}''_k + \boldsymbol{S}_{ik}) = G^0(\boldsymbol{r}'_i, \boldsymbol{r}''_k) && (3.33) \\ &= -\mathrm{i}k \sum_L Y_L(\hat{\boldsymbol{r}}'_i) \, j_\ell(kr'_i) \, h_\ell(k|\boldsymbol{r}''_k + \boldsymbol{S}_{ik}|) \, Y^*_L(\widehat{\boldsymbol{r}''_k + \boldsymbol{S}}_{ik}) \quad . && (3.34) \end{aligned}$$

Utilizing furthermore the addition theorem [FR54] giving rise to the structure constants $G_{LL'}(\boldsymbol{S}_{ik})$:

$$-\mathrm{i}k \, h_\ell(k|\boldsymbol{r}''_k + \boldsymbol{S}_{ik}|) \, Y^*_L(\widehat{\boldsymbol{r}''_k + \boldsymbol{S}}_{ik}) = \sum_{L'} G_{LL'}(\boldsymbol{S}_{ik}) \, j_{\ell'}(kr''_k) \, Y^*_{L'}(\hat{\boldsymbol{r}}''_k) \quad , \tag{3.35}$$

leads to

$$\begin{aligned} G^0(\boldsymbol{r}'_i, \boldsymbol{r}''_k) &= \sum_{LL'} Y_L(\hat{\boldsymbol{r}}'_i) \, j_\ell(kr'_i) \, G_{LL'}(\boldsymbol{S}_{ik}) \, j_{\ell'}(kr''_k) \, Y^*_{L'}(\hat{\boldsymbol{r}}''_k) && (3.36) \\ &= \sum_{LL'} j_L(k\boldsymbol{r}'_i) \, G_{LL'}(\boldsymbol{S}_{ik}) \, j^\dagger_{L'}(k\boldsymbol{r}''_k) \quad . && (3.37) \end{aligned}$$

The structure constants are given by:

$$G_{LL'}(\boldsymbol{S}_{ik}) = -4\pi k\, \mathrm{i}^{\ell-\ell'+1} \sum_{L''} \mathrm{i}^{\ell''}\, C^{L'}_{LL''}\, h_{L''}(k\boldsymbol{S}_{ik}) \quad , \tag{3.38}$$

where the notation of the spherical Hankel functions refers to:

$$h_L(k\boldsymbol{S}_{ik}) = h_\ell(kS_{ik})\, Y_L(\hat{\boldsymbol{S}}_{ik}) \quad . \tag{3.39}$$

Now we can write instead of (3.31):

$$\begin{aligned} \tau^{ij}(\boldsymbol{r}_i, \boldsymbol{r}'_j) &= t^i(\boldsymbol{r}_i, \boldsymbol{r}'_i) \\ &+ \sum_{k\neq i} \sum_{LL'} \iint \mathrm{d}\boldsymbol{r}'_i\, \mathrm{d}\boldsymbol{r}''_k\, t^i(\boldsymbol{r}_i, \boldsymbol{r}'_i)\, j_L(k\boldsymbol{r}'_i)\, G_{LL'}(\boldsymbol{S}_{ik})\, j^\dagger_{L'}(k\boldsymbol{r}''_k)\, \tau^{kj}(\boldsymbol{r}''_k, \boldsymbol{r}'_j) \quad . \end{aligned} \tag{3.40}$$

Then turning to a plane wave representation as in the previous section and taking only the on the energy shell elements on both sides of the equation, we obtain a central result of multiple scattering theory namely the *equation of motion* for the scattering path operator or, as it is also referred to, the *fundamental equation of multiple scattering*:

$$\tau^{ij}_{LL'} = \delta_{ij}\, t^i_{LL'} + \sum_{k\neq i} \sum_{L''L'''} t^i_{LL''}\, G_{L''L'''}(\boldsymbol{S}_{ik})\, \tau^{kj}_{L'''L'} \quad , \tag{3.41}$$

where the on the energy shell elements of the t matrix and the τ operator have been defined as:

$$\tau^{ij}_{LL'} = \iint \mathrm{d}\boldsymbol{r}_i\, \mathrm{d}\boldsymbol{r}'_j\, j^\dagger_L(k\boldsymbol{r}_i)\, \tau^{ij}(\boldsymbol{r}_i, \boldsymbol{r}'_j)\, j_{L'}(k\boldsymbol{r}'_j) \tag{3.42}$$

$$t^i_{LL'} = \iint \mathrm{d}\boldsymbol{r}_i\, \mathrm{d}\boldsymbol{r}'_i\, j^\dagger_L(k\boldsymbol{r}_i)\, t^i(\boldsymbol{r}_i, \boldsymbol{r}'_i)\, j_{L'}(k\boldsymbol{r}'_i) \quad . \tag{3.43}$$

Subsequently multiplying (3.41) with $m^i_{LL'} = (t^i_{LL'})^{-1}$ from the left we get:

$$\sum_{L''} \delta_{ij}\, m^i_{LL''}\, \tau^{ij}_{L''L'} = 1 + \sum_{k\neq i} \sum_{L''} G_{LL''}(\boldsymbol{S}_{ik})\, \tau^{kj}_{L''L'} \quad , \tag{3.44}$$

and furthermore

$$\sum_k \sum_{L''} \left(\delta_{ki}\, m^k_{LL''} - (1-\delta_{ki})\, G_{LL''}(\boldsymbol{S}_{ik})\right)\, \tau^{kj}_{L''L'} = 1 \quad . \tag{3.45}$$

3.3.1 **Bandstructure Calculation**

By using the method of lattice Fourier transforms one can manipulate (3.41) to arrive at an expression that is especially suitable for obtaining the dispersion relation E vs. $\boldsymbol{k}$. The following is valid for a material of ideal structure and infinite, three dimensionally periodic, extent. Following Gonis [Gon92] let us first define the $\boldsymbol{k}$ representation of the scattering path operator by

$$\begin{aligned}
\tau_{LL'}(\boldsymbol{k},\boldsymbol{k}') &= \frac{1}{N}\sum_{ij}\tau^{ij}_{LL'}\,\mathrm{e}^{\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{R}_i-\boldsymbol{k}'\cdot\boldsymbol{R}_j)} && (3.46)\\
&= \frac{1}{N}\sum_{ij}\tau^{ij}_{LL'}\,\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{R}_i-\boldsymbol{R}_j)-\mathrm{i}\boldsymbol{R}_j\cdot(\boldsymbol{k}'-\boldsymbol{k})} && (3.47)\\
&= \frac{1}{N}\sum_{j}\mathrm{e}^{\mathrm{i}\boldsymbol{R}_j\cdot(\boldsymbol{k}'-\boldsymbol{k})}\left[\sum_i\tau^{ij}_{LL'}\,\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{R}_i-\boldsymbol{R}_j)}\right]\quad , && (3.48)
\end{aligned}$$

N being the number of lattice sites. The term inside the brackets can be replaced by the quantity:

$$\tau_{LL'}(\boldsymbol{k}) = \sum_i\tau^{ij}_{LL'}\,\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{R}_i-\boldsymbol{R}_j)}\quad , \tag{3.49}$$

and the sum over j is easily identified as:

$$\frac{1}{N}\sum_j\mathrm{e}^{\mathrm{i}\boldsymbol{R}_j\cdot(\boldsymbol{k}'-\boldsymbol{k})} = \delta(\boldsymbol{k}'-\boldsymbol{k})\quad . \tag{3.50}$$

Therefore we can denote the following identity:

$$\tau_{LL'}(\boldsymbol{k},\boldsymbol{k}') = \tau_{LL'}(\boldsymbol{k})\,\delta(\boldsymbol{k}'-\boldsymbol{k})\quad . \tag{3.51}$$

Furthermore the product of the structure constants and the scattering path operator in (3.41) may by written in a shorthand notation as:

$$\sum_k G_{LL''}(\boldsymbol{S}_{ik})\,\tau^{kj}_{L''L'} = \sum_k G^{ik}_{LL''}\,\tau^{kj}_{L''L'} = M^{ij}_{LL'}\quad . \tag{3.52}$$

The $\boldsymbol{k}$ representation of $M^{ij}_{LL'}$ is obtained as above:

$$M_{LL'}(\boldsymbol{k},\boldsymbol{k}') = \frac{1}{N}\sum_j\mathrm{e}^{\mathrm{i}\boldsymbol{R}_j\cdot(\boldsymbol{k}'-\boldsymbol{k})}\left[\sum_i M^{ij}_{LL'}\,\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{R}_i-\boldsymbol{R}_j)}\right]\quad . \tag{3.53}$$

Insertion of (3.52) yields:

$$M_{LL'}(\boldsymbol{k},\boldsymbol{k}') = \frac{1}{N}\sum_j \mathrm{e}^{\mathrm{i}\boldsymbol{R}_j\cdot(\boldsymbol{k}'-\boldsymbol{k})}\left[\sum_{ik} G^{ik}_{LL''}\,\tau^{kj}_{L''L'}\,\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{R}_i-\boldsymbol{R}_k)}\,\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{R}_k-\boldsymbol{R}_j)}\right] \quad . \tag{3.54}$$

The terms inside the brackets are simply the lattice Fourier transform of the structure constants and the τ operator:

$$G^0_{LL'}(\boldsymbol{k}) = \sum_i G^{ik}_{LL'}\,\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{R}_i-\boldsymbol{R}_k)} \tag{3.55}$$

$$\tau_{LL'}(\boldsymbol{k}) = \sum_k \tau^{kj}_{LL'}\,\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{R}_k-\boldsymbol{R}_j)} \quad . \tag{3.56}$$

Hence we have obtained the following identity:

$$M_{LL'}(\boldsymbol{k},\boldsymbol{k}') = M_{LL'}(\boldsymbol{k})\,\delta(\boldsymbol{k}'-\boldsymbol{k}) \tag{3.57}$$

$$= G^0_{LL''}(\boldsymbol{k})\,\tau_{L''L'}(\boldsymbol{k}) \quad . \tag{3.58}$$

Because the t matrix is site diagonal it is identical to its lattice Fourier transform:

$$t^i_{LL'} = t_{LL'}(\boldsymbol{k}) \quad , \tag{3.59}$$

and we can write instead of (3.41):

$$\tau_{LL'}(\boldsymbol{k}) = t_{LL'}(\boldsymbol{k}) + \sum_{L''L'''} t_{LL''}(\boldsymbol{k})\,G^0_{L''L'''}(\boldsymbol{k})\,\tau_{L'''L'}(\boldsymbol{k}) \quad . \tag{3.60}$$

It is now straightforward to obtain a solution for the scattering path operator in $\boldsymbol{k}$ representation, which is nothing but:

$$\tau_{LL'}(\boldsymbol{k}) = \left[m_{LL'}(\boldsymbol{k}) - G^0_{LL'}(\boldsymbol{k})\right]^{-1} \quad . \tag{3.61}$$

Clearly the quantity $m_{LL'}(\boldsymbol{k})$ denotes the inverse of the t matrix.

3.4

Screened KKR Formalism

The idea behind the so called *screening* transformation [SÚW95][ZDS+95] [Zel97][SÚWK94b][WZD97] is that one has complete freedom in choosing a suitable reference system. Originally [KR54] [Kor47] this reference system was taken to be free space, but one might think of a more favourable one. It would be especially pleasing to construct it such that the KKR structure constants, which are to be discussed in one of the following sections, are short ranged. Then beyond a few neighbouring shells of atoms the structure constants are virtually zero. Therefore the matrices with respect to lattice sites reduce in size and are easier to handle computationally.

First let us see how such a reference system might be constructed. One can think of a reference system that consists of a collection of constant repulsive potentials centered at lattice sites. Denoting the collection of reference potentials as $V^r(\boldsymbol{r})$ we can write:

$$V^r(\boldsymbol{r}) = \sum_i v_i^r(\boldsymbol{r}) \quad . \tag{3.62}$$

Furthermore the individual reference potentials are constant inside a certain distance d and 0 beyond it:

$$v_i^r(\boldsymbol{r}) = \left\{ \begin{array}{ccc} const. & , & |\boldsymbol{r}| \leq d \\ 0 & , & otherwise \end{array} \right. \quad . \tag{3.63}$$

Note that the domains of the actual potential $v_i(\boldsymbol{r})$ and the screening potential $v_i^r(\boldsymbol{r})$ should be identical. Then the distance d can in principle be either identical to the muffin tin radius, in which case we obviously talk about a collection of repulsive muffin tin spheres. Or we use ASA spheres, or we could also use a collection of Wigner-Seitz polyhedra of constant potential. According to Dederichs [Ded] the screening is best achieved by using muffin tins. However, there are no conclusive investigations of a “full potential” reference system to date.

3.4.1 Relations between Green’s Functions and τ Operators

To show how the new reference system can be used within the theory, we first have to find some relations between the operator $\hat{G}$ which was defined in (2.77) and (3.20), and the scattering path operator. Inserting the expansion of the operator $\hat{T}$ as given from (3.10), into (3.20) results in an expansion of $\hat{G}$ in terms of single site t matrices:

$$\begin{aligned} \hat{G} \;=\; & \hat{G}^0 + \hat{G}^0 \sum_i t^i \hat{G}^0 + \hat{G}^0 \sum_i t^i \hat{G}^0 \sum_{j \neq i} t^j \hat{G}^0 \\ & + \hat{G}^0 \sum_i t^i \hat{G}^0 \sum_{j \neq i} t^j \hat{G}^0 \sum_{k \neq j} t^k \hat{G}^0 + \ldots \quad . \end{aligned} \tag{3.64}$$

We can subsequently make use of lattice Fourier transforms as in the previous section. By, for reasons of simplicity, switching to a matrix notation, where the general matrix $\underline{A}(\boldsymbol{k})$ is simply:

$$\underline{A}(\boldsymbol{k}) = \{A_{LL'}(\boldsymbol{k})\} \quad , \tag{3.65}$$

we can write the above expansion in terms of the respective Fourier components as:

$$\underline{G}(\boldsymbol{k}) = \underline{G}^0(\boldsymbol{k}) + \underline{G}^0(\boldsymbol{k})\,\underline{t}(\boldsymbol{k})\,\underline{G}^0(\boldsymbol{k}) + \underline{G}^0(\boldsymbol{k})\,\underline{t}(\boldsymbol{k})\,\underline{G}^0(\boldsymbol{k})\,\underline{t}(\boldsymbol{k})\,\underline{G}^0(\boldsymbol{k}) + \cdots \quad . \tag{3.66}$$

It is easily seen that we can cast this equation in the form of a Dyson equation:

$$\begin{aligned} \underline{G}(\boldsymbol{k}) &= \underline{G}^0(\boldsymbol{k}) + \underline{G}^0(\boldsymbol{k})\,\underline{t}(\boldsymbol{k})\,\underline{G}(\boldsymbol{k}) && (3.67)\\ &= \underline{G}^0(\boldsymbol{k}) + \underline{G}(\boldsymbol{k})\,\underline{t}(\boldsymbol{k})\,\underline{G}^0(\boldsymbol{k}) \quad , && (3.68) \end{aligned}$$

and therefore we can write:

$$\begin{aligned} \underline{G}(\boldsymbol{k}) &= \left[\mathbf{1} - \underline{G}^0(\boldsymbol{k})\,\underline{t}(\boldsymbol{k})\right]^{-1}\,\underline{G}^0(\boldsymbol{k}) && (3.69)\\ &= \underline{G}^0(\boldsymbol{k})\,\left[\mathbf{1} - \underline{t}(\boldsymbol{k})\,\underline{G}^0(\boldsymbol{k})\right]^{-1} \quad . && (3.70) \end{aligned}$$

By furthermore denoting equation (3.61) in the same fashion:

$$\underline{\tau}(\boldsymbol{k}) = \left[\underline{m}(\boldsymbol{k}) - \underline{G}^0(\boldsymbol{k})\right]^{-1} \quad , \tag{3.71}$$

we can find relations between the scattering path operator and the Green's function. From rearranging the above equation one can find the relation:

$$\underline{t}(\boldsymbol{k}) = \underline{\tau}(\boldsymbol{k})\,\left[\mathbf{1} + \underline{G}^0(\boldsymbol{k})\,\underline{\tau}(\boldsymbol{k})\right]^{-1} \quad , \tag{3.72}$$

which can be used in (3.67) to yield after some basic manipulations:

$$\underline{G}(\boldsymbol{k}) = \underline{G}^0(\boldsymbol{k}) + \underline{G}^0(\boldsymbol{k})\,\underline{\tau}(\boldsymbol{k})\,\underline{G}^0(\boldsymbol{k}) \quad . \tag{3.73}$$

Rewriting (3.71) once more to find an expression for $\underline{G}^0(\boldsymbol{k})$, namely:

$$\underline{G}^0(\boldsymbol{k}) = \underline{m}(\boldsymbol{k}) - \underline{\tau}^{-1}(\boldsymbol{k}) \quad , \tag{3.74}$$

the following result is obtained after insertion into (3.67):

$$\underline{G}(\boldsymbol{k}) = \underline{m}(\boldsymbol{k})\,\underline{\tau}(\boldsymbol{k})\,\underline{m}(\boldsymbol{k}) - \underline{m}(\boldsymbol{k}) \quad . \tag{3.75}$$

3.4.2 **Screening Transformations**

Clearly an expansion like (3.66) can also be written with respect to the t matrices of the reference system. If such a t matrix is denoted as $\underline{t}^r(\boldsymbol{k})$, we get for the Green's function of the reference system:

$$\begin{aligned} \underline{G}^r(\boldsymbol{k}) &= \left[\mathbf{1} - \underline{G}^0(\boldsymbol{k})\,\underline{t}^r(\boldsymbol{k})\right]^{-1}\,\underline{G}^0(\boldsymbol{k}) && (3.76)\\ &= \underline{G}^0(\boldsymbol{k})\,\left[\mathbf{1} - \underline{G}^0(\boldsymbol{k})\,\underline{t}^r(\boldsymbol{k})\right]^{-1} \quad . && (3.77) \end{aligned}$$

It follows immediately that:

$$\underline{G}^0(\boldsymbol{k}) = [\mathbf{1} + \underline{G}^r(\boldsymbol{k})\,\underline{t}^r(\boldsymbol{k})]^{-1}\,\underline{G}^r(\boldsymbol{k}) \quad . \tag{3.78}$$

If this identity is used in (3.70):

$$\underline{G}(\boldsymbol{k}) = \underline{G}^0(\boldsymbol{k})\,\left[\mathbf{1} - \underline{t}(\boldsymbol{k})\,\underline{G}^0(\boldsymbol{k})\right]^{-1} \quad , \tag{3.79}$$

one in fact obtains after some straightforward manipulations:

$$\underline{G}(\boldsymbol{k}) = \underline{G}^r(\boldsymbol{k})\,[\mathbf{1} - \underline{\alpha}(\boldsymbol{k})\,\underline{G}^r(\boldsymbol{k})]^{-1} \quad . \tag{3.80}$$

Above the matrix $\underline{\alpha}(\boldsymbol{k})$ is simply the difference between the two t matrices:

$$\underline{\alpha}(\boldsymbol{k}) = \underline{t}(\boldsymbol{k}) - \underline{t}^r(\boldsymbol{k}) \quad . \tag{3.81}$$

Using the t matrix and the Green's function of the reference system, a τ-operator can be defined as:

$$\underline{\tau}^r(\boldsymbol{k}) = \left[\underline{\alpha}^{-1}(\boldsymbol{k}) - \underline{G}^r(\boldsymbol{k})\right]^{-1} \quad . \tag{3.82}$$

If from this equation we deduce an equality for $\underline{\alpha}(\boldsymbol{k})$:

$$\underline{\alpha}(\boldsymbol{k}) = [\mathbf{1} + \underline{\tau}^r(\boldsymbol{k})\,\underline{G}^r(\boldsymbol{k})]^{-1}\,\underline{\tau}^r(\boldsymbol{k}) \quad , \tag{3.83}$$

and use it in (3.80) we find the relation:

$$\underline{G}(\boldsymbol{k}) = \underline{G}^r(\boldsymbol{k}) + \underline{G}^r(\boldsymbol{k})\,\underline{\tau}^r(\boldsymbol{k})\,\underline{G}^r(\boldsymbol{k}) \quad , \tag{3.84}$$

and in analogy to (3.75) we find:

$$\underline{G}(\boldsymbol{k}) = \underline{\alpha}^{-1}(\boldsymbol{k})\,\underline{\tau}^r(\boldsymbol{k})\,\underline{\alpha}^{-1}(\boldsymbol{k}) - \underline{\alpha}^{-1}(\boldsymbol{k}) \quad . \tag{3.85}$$

The operator in (3.82) can be referred to as the *screened* scattering path operator. Using (3.75) and (3.85) one can easily read off the following expression for the "unscreened" scattering path operator in terms of t matrices and the screened scattering path operator:

$$\underline{\tau}(\boldsymbol{k}) = \underline{t}(\boldsymbol{k}) - \underline{t}(\boldsymbol{k})\,\underline{\alpha}^{-1}(\boldsymbol{k})\,\underline{t}(\boldsymbol{k}) + \underline{t}(\boldsymbol{k})\,\underline{\alpha}^{-1}(\boldsymbol{k})\,\underline{\tau}^{r}(\boldsymbol{k})\,\underline{\alpha}^{-1}(\boldsymbol{k})\,\underline{t}(\boldsymbol{k}) \quad . \tag{3.86}$$

The resulting *screened Korringa-Kohn-Rostoker* (KKR) method has been successfully applied to bulk, as well as surface systems [ÚSW96][ÚSBW96][ÚSW95][SÚWK94a] [SÚWS96][SÚW95][SÚW97][SÚPW98][SÚB^{+}97][SZU^{+}98][ZPU^{+}98][ZUB^{+}98][PZU^{+}99].

3.5

Green's Function

The most important quantity for the calculation of physical quantities is the Green's function of the system, as from its knowledge all quantities such as the density of states, the charge density, and consequently the total energy or magnetic moments can be derived. It is the purpose of this section to show how this Green's function is connected to single site quantities, namely the regular and irregular scattering solutions and the t matrix, and to the diagonal elements of the scattering path operator. The starting point is equation (3.25) in coordinate representation:

$$G(\boldsymbol{r}_n,\boldsymbol{r}'_n) = G^n(\boldsymbol{r}_n,\boldsymbol{r}'_n) + \sum_{\substack{i\neq n\\ j\neq n}} \iint \mathrm{d}\boldsymbol{r}_i\,\mathrm{d}\boldsymbol{r}_j\, G^n(\boldsymbol{r}_n,\boldsymbol{r}_i)\,\tau(\boldsymbol{r}_i,\boldsymbol{r}_j)\,G^n(\boldsymbol{r}_j,\boldsymbol{r}'_n) \quad . \tag{3.87}$$

One can easily check that outside the scattering region where the regular and irregular solutions respectively are normalized in the following way:

$$\begin{aligned} Z_L(\boldsymbol{r}_n) &= -\mathrm{i}k\,h_L(k\boldsymbol{r}_n) + \sum_{L'} j_{L'}(k\boldsymbol{r}_n)\,m^n_{L'L} && (3.88)\\ J_L(\boldsymbol{r}_n) &= j_L(k\boldsymbol{r}_n) \quad , && (3.89)\end{aligned}$$

the single scatterer Green's function $G^n(\boldsymbol{r}_n,\boldsymbol{r}'_n)$ can be expressed by either:

$$G^n(\boldsymbol{r}_n,\boldsymbol{r}'_n) = -\mathrm{i}k \sum_{LL'} Z_L(\boldsymbol{r}_n)\,t^n_{LL'}\,h^{\dagger}_{L'}(k\boldsymbol{r}'_n) \quad , \tag{3.90}$$

or alternatively by

$$G^n(\boldsymbol{r}_n,\boldsymbol{r}'_n) = \sum_{LL'} Z_L(\boldsymbol{r}_n)\,t^n_{LL'}\,Z^{\dagger}_L(\boldsymbol{r}'_n) - \sum_{L} Z_L(\boldsymbol{r}_n)\,J^{\dagger}_L(\boldsymbol{r}'_n) \quad . \tag{3.91}$$

Here the superscript † refers to the complex conjugation of only the spherical harmonics which e.g. for the Hankel functions means:

$$h^\dagger_L(k\boldsymbol{r}) = h_\ell(kr)\, Y^*_L(\hat{\boldsymbol{r}}) \quad . \tag{3.92}$$

To proceed we have to use two center expansions of the Green's functions G^n which appear in the integrand. By using

$$\boldsymbol{r}'_n = \boldsymbol{r}_i + \boldsymbol{S}_{ni} \quad , \tag{3.93}$$

and

$$\boldsymbol{r}_n = \boldsymbol{r}_j + \boldsymbol{S}_{nj} \quad , \tag{3.94}$$

we can expand expression (3.90) as:

$$\begin{aligned} G^n(\boldsymbol{r}_n, \boldsymbol{r}'_n) &= G^n(\boldsymbol{r}_n, \boldsymbol{r}_i + \boldsymbol{S}_{ni}) = G^n(\boldsymbol{r}_n, \boldsymbol{r}_i) && (3.95)\\ &= \sum_{LL'L''} Z_L(\boldsymbol{r}_n)\, t^n_{LL'}\, G_{L'L''}(\boldsymbol{S}_{ni})\, j^*_{L''}(k\boldsymbol{r}_i) \quad , && (3.96) \end{aligned}$$

or with respect to cell j as:

$$\begin{aligned} G^n(\boldsymbol{r}_n, \boldsymbol{r}'_n) &= G^n(\boldsymbol{r}_j + \boldsymbol{S}_{nj}, \boldsymbol{r}'_n) = G^n(\boldsymbol{r}_j, \boldsymbol{r}'_n) && (3.97)\\ &= -\mathrm{i}k \sum_{LL'} h_L(k\boldsymbol{r}_n)\, t^n_{LL'}\, Z^\dagger_{L'}(\boldsymbol{r}'_n) && (3.98)\\ &= \sum_{LL'L''} j_L(k\boldsymbol{r}_j)\, G_{LL'}(\boldsymbol{S}_{nj})\, t^n_{L'L''}\, Z^\dagger_{L''}(k\boldsymbol{r}'_n) \quad , && (3.99) \end{aligned}$$

In the next step the expansions (3.91), (3.96), and (3.99) are substituted into equation (3.87) which gives:

$$\begin{aligned} G(\boldsymbol{r}_n, \boldsymbol{r}'_n) = \; & -\sum_L Z_L(\boldsymbol{r}_n)\, J^\dagger_L(\boldsymbol{r}'_n) + \sum_{LL'} Z_L(\boldsymbol{r}_n)\, t^n_{LL'}\, Z^\dagger_L(\boldsymbol{r}'_n)\\ & + \sum_{\substack{i\neq n\\ j\neq n}} \sum_{\substack{LL'L''\\ L'''L^{iv}L^v}} \iint \mathrm{d}\boldsymbol{r}_i\, \mathrm{d}\boldsymbol{r}_j\, Z_L(\boldsymbol{r}_n)\, t^n_{LL'}\, G_{L'L''}(\boldsymbol{S}_{ni})\, j^*_{L''}(k\boldsymbol{r}_i)\\ & \times \tau(\boldsymbol{r}_i, \boldsymbol{r}_j)\, j_{L'''}(k\boldsymbol{r}_j)\, G_{L'''L^{iv}}(\boldsymbol{S}_{nj})\, t^n_{L^{iv}L^v}\, Z^\dagger_{L^v}(k\boldsymbol{r}'_n) \quad . \end{aligned} \tag{3.100}$$

Once again the on the energy shell elements of the scattering path operator can be identified from the above expression as:

$$\tau^{ij}_{L''L'''} = \iint \mathrm{d}\boldsymbol{r}_i\, \mathrm{d}\boldsymbol{r}_j\, j^*_{L''}(k\boldsymbol{r}_i)\, \tau(\boldsymbol{r}_i, \boldsymbol{r}_j)\, j_{L'''}(k\boldsymbol{r}_j) \quad . \tag{3.101}$$

Clearly in the calculations the elements of the scattering path operator are not evaluated by solving the above integrals. Instead equation (3.61) is used which involves the determination of the single site t matrices, the structure constants and a matrix inversion. The difficult part being the inversion of an, in general, infinite matrix.

After defining $\tau^{ij}_{L''L'''}$ we are now left with the following identity:

$$\begin{aligned} G(\boldsymbol{r}_n, \boldsymbol{r}'_n) &= -\sum_{L} Z_L(\boldsymbol{r}_n)\, J^{\dagger}_L(\boldsymbol{r}'_n) + \sum_{LL'} Z_L(\boldsymbol{r}_n)\, t^n_{LL'}\, Z^{\dagger}_L(\boldsymbol{r}'_n) \\ &\quad + \sum_{\substack{i\neq n\\ j\neq n}} \sum_{\substack{LL'L''\\ L'''L^{iv}L^{v}}} Z_L(\boldsymbol{r}_n)\, t^n_{LL'}\, G_{L'L''}(\boldsymbol{S}_{ni}) \\ &\quad \times \tau^{ij}_{L''L'''} G_{L'''L^{iv}}(\boldsymbol{S}_{nj})\, t^n_{L^{iv}L^{v}}\, Z^{\dagger}_{L^{v}}(k\boldsymbol{r}'_n) \quad . \end{aligned} \tag{3.102}$$

To proceed let us first rewrite the equation of motion (3.41) in a shorthand notation (by leaving out the dependence on angular momentum indices):

$$\tau^{ij} = t^i\, \delta_{ij} + \sum_{k\neq i} t^i\, G(\boldsymbol{S}_{ik})\, \tau^{kj} \tag{3.103}$$

$$\quad = t^i\, \delta_{ij} + \sum_{k\neq j} \tau^{ik}\, G(\boldsymbol{S}_{kj})\, t^j \quad . \tag{3.104}$$

These equations are similar to (3.12) and (3.13) except that this time the “on the energy shell” elements of the respective quantities are meant. We can, for example, manipulate (3.104) in the following way:

$$\tau^{nn} = t^n + \sum_{j\neq n} \tau^{nj}\, G(\boldsymbol{S}_{nj})\, t^n \quad . \tag{3.105}$$

Multiplication with $m^n = (t^n)^{-1}$ from the right and rearrangement leads to:

$$\sum_{j\neq n} \tau^{nj}\, G(\boldsymbol{S}_{nj}) = (\tau^{nn} - t^n)\, m^n \quad . \tag{3.106}$$

Then using (3.103) one can write:

$$\tau^{nj} = t^n\, \delta_{nj} + \sum_{i\neq n} t^n\, G(\boldsymbol{S}_{ni})\, \tau^{ij} \quad . \tag{3.107}$$

If both sides are multiplied by $G(\boldsymbol{S}_{nj})$ and a summation over the index j not including site n is added we find

$$\sum_{j\neq n} \tau_{nj}\, G(\boldsymbol{S}_{nj}) = \sum_{\substack{i\neq n\\ j\neq n}} t^n\, G(\boldsymbol{S}_{ni})\, \tau^{ij}\, G(\boldsymbol{S}_{nj}) \tag{3.108}$$

$$\quad = (\tau^{nn} - t^n)\, m^n \quad . \tag{3.109}$$

The final step is to multiply with m^n from the left yielding:

$$\sum_{\substack{i\neq n\\ j\neq n}} G(\boldsymbol{S}_{ni})\,\tau^{ij}\,G(\boldsymbol{S}_{nj}) = m^n\,(\tau^{nn}-t^n)\,m^n \quad , \tag{3.110}$$

an identity that can be used in (3.102). We are then left with:

$$\begin{aligned} G(\boldsymbol{r}_n,\boldsymbol{r}'_n) &= -\sum_L Z_L(\boldsymbol{r}_n)\,J^\dagger_L(\boldsymbol{r}'_n) + \sum_{LL'} Z_L(\boldsymbol{r}_n)\,t^n_{LL'}\,Z^\dagger_L(\boldsymbol{r}'_n) \\ &\quad + \sum_{\substack{LL'L''\\ L'''L^{iv}L^{v}}} Z_L(\boldsymbol{r}_n)\,t^n_{LL'}m^n_{L'L''} \\ &\quad \times (\tau^{nn}_{L''L'''} - t^n_{L''L'''})\,m^n_{L'''L^{iv}}\,t^n_{L^{iv}L^{v}}\,Z^\dagger_{L^v}(\boldsymbol{r}'_n) \quad . \end{aligned} \tag{3.111}$$

Because of $t^n_{LL'}m^n_{L'L''} = \delta_{LL''}$ one obtains:

$$\begin{aligned} G(\boldsymbol{r}_n,\boldsymbol{r}'_n) &= -\sum_L Z_L(\boldsymbol{r}_n)\,J^\dagger_L(\boldsymbol{r}'_n) + \sum_{LL'} Z_L(\boldsymbol{r}_n)\,t^n_{LL'}\,Z^\dagger_L(\boldsymbol{r}'_n) \\ &\quad + \sum_{LL'} Z_L(\boldsymbol{r}_n)\,\tau^{nn}_{LL'}\,Z^\dagger_{L'}(\boldsymbol{r}'_n) - \sum_{LL'} Z_L(\boldsymbol{r}_n)\,t^n_{LL'}\,Z^\dagger_{L'}(\boldsymbol{r}'_n) \quad , \end{aligned} \tag{3.112}$$

and finally the Green's function is given by:

$$G(\boldsymbol{r}_n,\boldsymbol{r}'_n) = \sum_{LL'} Z_L(\boldsymbol{r}_n)\,\tau^{nn}_{LL'}\,Z^\dagger_{L'}(\boldsymbol{r}'_n) - \sum_L Z_L(\boldsymbol{r}_n)\,J^\dagger_L(\boldsymbol{r}'_n) \quad . \tag{3.113}$$

Even though this equation was derived for $\boldsymbol{r}_n$ and $\boldsymbol{r}'_n$ outside the scattering region (through the use of the corresponding expressions of the wave functions outside the scattering region), it is valid also for the interior region because the Green's function fulfills the defining Schrödinger equation and the proper boundary conditions [Gon92].

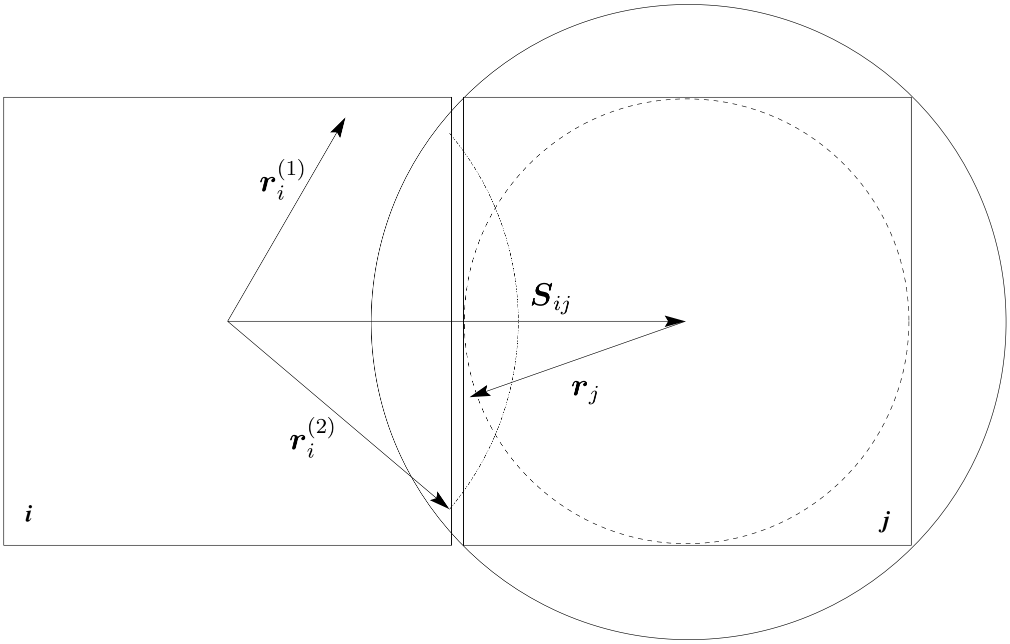
3.5.1 **Validity for Space-Filling Cell Potentials**

Equation (3.113) was solemnly derived for muffin tin potentials and it is not a priori clear that its validity can be extended to general potentials of arbitrary shape. The nature of the problem becomes apparent by considering two vectors in adjacent cells, as is illustrated in figure 3.1. Expansions of the type:

$$G^0(\boldsymbol{r}_i,\boldsymbol{r}'_i) = \sum_{LL'} j_L(k\boldsymbol{r}_i)\,G_{LL'}(\boldsymbol{S}_{ij})\,j_{L'}(k\boldsymbol{r}'_j) \quad , \tag{3.114}$$

are only valid for $|\boldsymbol{r}_i| < |\boldsymbol{S}_{ij}+\boldsymbol{r}_j|$ which is the case for the vector $\boldsymbol{r}_i^{(1)}$. The vector $\boldsymbol{r}_i^{(2)}$, however, does not necessarily fulfill this condition. But if $|\boldsymbol{r}_i| > |\boldsymbol{S}_{ij}+\boldsymbol{r}_j|$ the

Figure 3.1: *Two neighbouring cells where the region in which the muffin tin condition is not valid is indicated.*



angular momentum expansion is not valid in general. Hence the formal derivation of the scattering path operator is inhibited by this difficulty and it is not immediately evident that (3.113) is valid for the case of non muffin tin potentials.

Along with this mathematically, formal argument comes a physical argument. Consider a spherical wave emanating from the center of cell j with a wavefront indicated in figure 3.1 by a dashed circle. In that moment when the wavefront crosses the cell boundary the scattering starts. But then the wave is also scattered by the neighbouring cells before it even finished the full scattering process in cell j. Then the prominent feature of multiple scattering theory in the muffin tin approximation, namely that the scattering events may be treated on an individual basis, is lost. The scattering and the structural aspects would be coupled in a very complicated way. Therefore is has been suggested that certain “Near Field Corrections” [Fau88][Fau85][Fau86](which vanish in the muffin tin case) have to be taken into account.

Gonis [ZG89b][Gon92][ZG89b][ZG89a][Gon86a][Gon86b][GZD$^+$90] has provided counterarguments to the mathematical as well as the physical question. Evidently a cell of arbitrary shape can be approximated by a collection of non overlapping spheres (of various sizes) to any degree of accuracy. By thinking of the cell as such a collection of scatterers the expanding wavefront of this cell consist of the interference of wavefronts emanating from the centers of all the spheres. Hence we are once again confronted with a muffin tin geometry where the Near Field Corrections are identically zero. This can also be shown mathematically by either treating the cells as collection of muffin tin spheres or, alternatively, by considering individual cells. In both cases the Near Field

Corrections vanish.

According to Zeller [Zel87][Zel88] the convergence of the angular momentum expansion is not of interest as long as only the physically relevant angular momentum values are taken into account.

Further arguments for the validity of the multiple scattering equations are that a proper physical theory should be independent of a particular representation. Hence it cannot depend on the way in which the potential is partitioned in a given space.

The validity of the multiple scattering equations for full potentials is now generally accepted [MGZC89][ZGM89][GZN88][Nes90][Nes92][dKF96][BF87a][Bad89][BF88a][BF88b][BC86][BC89] and test calculations using this method [YCNB90][WZB⁺92] as well as applications to bulk systems [Set99][DWZD89][ZD79][SBZD87][PZDS97b][PZDS97a][KPZD98] have been reported.

We will now proceed with a discussion of the structural Green's function.

3.6

The Structural Green's Function

In order to gain some insight in the physical meaning of the structure constants two similar approaches for their derivation shall be presented in this section. The first one involves a boundary value problem for the homogeneous Schrödinger equation and the second one uses an integral or Lippmann-Schwinger type equation for the wave function.

Following Kohn and Rostocker [KR54] we want to find the solution of (2.4):

$$\left(\nabla^2 + k^2\right) G^0(\boldsymbol{r}, \boldsymbol{r}') = \delta(\boldsymbol{r} - \boldsymbol{r}') \quad , \tag{3.115}$$

under periodic, three dimensional (cyclic) boundary conditions:

$$G(\boldsymbol{r} + \boldsymbol{R}, \boldsymbol{r}') = G(\boldsymbol{r}, \boldsymbol{r}') = \mathrm{e}^{\mathrm{i}\boldsymbol{kR}} G^0(\boldsymbol{r}, \boldsymbol{r}') \quad . \tag{3.116}$$

In the last equation $\boldsymbol{R}$ is a fundamental lattice translation vector. According to (2.10), the solution of (3.115) is given by:

$$G^0(\boldsymbol{r}, \boldsymbol{r}') = -\frac{\mathrm{e}^{\mathrm{i}k|\boldsymbol{r}-\boldsymbol{r}'|}}{4\pi|\boldsymbol{r} - \boldsymbol{r}'|} \quad . \tag{3.117}$$

By transition to cell centered coordinates, i.e. $\boldsymbol{r} = \boldsymbol{R}_i + \boldsymbol{r}_i$ and $\boldsymbol{r}' = \boldsymbol{R}_j + \boldsymbol{r}'_j$ the lattice translation can be expressed as:

$$\boldsymbol{S}_{ij} = \boldsymbol{R}_j - \boldsymbol{R}_i \quad , \tag{3.118}$$

and by summing over all cells we obtain the following Green's function as a solution for (3.115) under periodic boundary conditions:

$$G(\boldsymbol{r}_i, \boldsymbol{r}'_j) = -\frac{1}{4\pi} \sum_j \frac{\mathrm{e}^{\mathrm{i}k|\boldsymbol{r}_i - \boldsymbol{r}'_j - \boldsymbol{S}_{ij}|}}{|\boldsymbol{r}_i - \boldsymbol{r}'_j - \boldsymbol{S}_{ij}|} \, \mathrm{e}^{\mathrm{i}\boldsymbol{k}\boldsymbol{S}_{ij}} \quad . \tag{3.119}$$

Alternatively let us consider a solution of the inhomogeneous Schrödinger equation in integral form, which is given by:

$$\psi(\boldsymbol{r}) = \int \mathrm{d}\boldsymbol{r}' \, G^0(\boldsymbol{r}, \boldsymbol{r}') \, V(\boldsymbol{r}') \, \psi(\boldsymbol{r}') \quad . \tag{3.120}$$

As first conditions we can demand that the potential is periodic, i.e.:

$$V(\boldsymbol{r} + \boldsymbol{R}) = V(\boldsymbol{r}) \quad , \tag{3.121}$$

and that therefore the wave function satisfies the Bloch condition:

$$\psi(\boldsymbol{r} + \boldsymbol{R}) = \mathrm{e}^{\mathrm{i}\boldsymbol{k}\boldsymbol{R}} \, \psi(\boldsymbol{r}) \quad . \tag{3.122}$$

Using these properties together with (3.117) we may write instead of (3.120):

$$\psi(\boldsymbol{r}) = -\frac{1}{4\pi} \sum_j \int\limits_{\Omega_j} \mathrm{d}\boldsymbol{r}' \, V(\boldsymbol{r}') \, \psi(\boldsymbol{r}') \, \mathrm{e}^{\mathrm{i}\boldsymbol{k}\boldsymbol{R}} \, \frac{\mathrm{e}^{\mathrm{i}k|\boldsymbol{r} - \boldsymbol{r}'|}}{|\boldsymbol{r} - \boldsymbol{r}'|} \quad . \tag{3.123}$$

Changing once again to cell centered coordinates and noting that the potential is given as the sum of individual potentials centered at lattice sites:

$$V(\boldsymbol{r}') = \sum_j v_j(\boldsymbol{r}'_j) \quad , \tag{3.124}$$

we get the following expression:

$$\psi(\boldsymbol{r}) = -\frac{1}{4\pi} \sum_j \int\limits_{\Omega_j} \mathrm{d}\boldsymbol{r}'_j \, v_j(\boldsymbol{r}'_j) \, \psi(\boldsymbol{r}'_j) \, \mathrm{e}^{\mathrm{i}\boldsymbol{k}\boldsymbol{S}_{ij}} \, \frac{\mathrm{e}^{\mathrm{i}k|\boldsymbol{r}_i - \boldsymbol{r}'_j - \boldsymbol{S}_{ij}|}}{|\boldsymbol{r}_i - \boldsymbol{r}'_j - \boldsymbol{S}_{ij}|} \quad . \tag{3.125}$$

Now we only have to perform an integration over a unit cell Ω_j and can identify the *structural Green's function* as:

$$G(\boldsymbol{r}_i, \boldsymbol{r}'_j) = G(\boldsymbol{k}; \boldsymbol{r}_i, \boldsymbol{r}'_j) = -\frac{1}{4\pi} \sum_j \frac{\mathrm{e}^{\mathrm{i}k|\boldsymbol{r}_i - \boldsymbol{r}'_j - \boldsymbol{S}_{ij}|}}{|\boldsymbol{r}_i - \boldsymbol{r}'_j - \boldsymbol{S}_{ij}|} \, \mathrm{e}^{\mathrm{i}\boldsymbol{k}\boldsymbol{S}_{ij}} \quad , \tag{3.126}$$

which is identical to (3.119). It is easy to see that the structural Green's function is nothing but the lattice Fourier transform of $G^0(\boldsymbol{r},\boldsymbol{r}')$. This observation allows us to write:

$$G(\boldsymbol{k};\boldsymbol{r}_i,\boldsymbol{r}'_j) = -\frac{1}{4\pi}\sum_j \mathrm{e}^{\mathrm{i}\boldsymbol{k}\boldsymbol{S}_{ij}}\, G^0(\boldsymbol{r},\boldsymbol{r}') \quad . \tag{3.127}$$

It is shown in the appendix that the following relation holds:

$$\frac{1}{(2\pi)^3}\int \mathrm{d}\boldsymbol{q}\,\frac{\mathrm{e}^{\mathrm{i}\boldsymbol{q}(\boldsymbol{r}-\boldsymbol{r}')}}{q^2-k^2} = \frac{1}{4\pi}\,\frac{\mathrm{e}^{\mathrm{i}k|\boldsymbol{r}-\boldsymbol{r}'|}}{|\boldsymbol{r}-\boldsymbol{r}'|} \quad , \tag{3.128}$$

implying a small imaginary part ε in the denominator in the limit $\varepsilon \rightarrow 0$. Substitution of this identity into (3.126) leads to:

$$\begin{aligned} G(\boldsymbol{k};\boldsymbol{r}_i,\boldsymbol{r}'_j) &= -\frac{1}{(2\pi)^3}\sum_j \mathrm{e}^{\mathrm{i}\boldsymbol{k}\boldsymbol{S}_{ij}}\int \mathrm{d}\boldsymbol{q}\,\frac{\mathrm{e}^{\mathrm{i}\,\boldsymbol{q}(\boldsymbol{r}_i-\boldsymbol{r}'_j-\boldsymbol{S}_{ij})}}{q^2-k^2} && (3.129)\\ &= -\frac{1}{(2\pi)^3}\sum_j \int \mathrm{d}\boldsymbol{q}\,\frac{\mathrm{e}^{\mathrm{i}\,\boldsymbol{q}(\boldsymbol{r}_i-\boldsymbol{r}'_j)}\,\mathrm{e}^{\mathrm{i}\boldsymbol{S}_{ij}(\boldsymbol{k}-\boldsymbol{q})}}{q^2-k^2} \quad . && (3.130)\end{aligned}$$

If use is made of the relation:

$$\sum_j \mathrm{e}^{\mathrm{i}\boldsymbol{S}_{ij}(\boldsymbol{k}-\boldsymbol{q})} = \sum_n \frac{(2\pi)^3}{V_\Omega}\,\delta(\boldsymbol{K}_n+\boldsymbol{k}-\boldsymbol{q}) \quad , \tag{3.131}$$

where V_Ω refers to the volume of a unit cell and $\boldsymbol{K}_n$ is a lattice vector in reciprocal space, we are left with:

$$G(\boldsymbol{k};\boldsymbol{r}_i,\boldsymbol{r}'_j) = -\frac{1}{V_\Omega}\sum_n \int \mathrm{d}\boldsymbol{q}\,\frac{\mathrm{e}^{\mathrm{i}\boldsymbol{q}(\boldsymbol{r}_i-\boldsymbol{r}'_j)}\,\delta(\boldsymbol{K}_n+\boldsymbol{k}-\boldsymbol{q})}{q^2-k^2} \quad . \tag{3.132}$$

The integral on the right hand side can now be easily evaluated because it is only finite for $\boldsymbol{q}=\boldsymbol{K}_n+\boldsymbol{k}$. Therefore we obtain the famous expression for the structural Green's function:

$$G(\boldsymbol{k};\boldsymbol{r}_i,\boldsymbol{r}'_j) = -\frac{1}{V_\Omega}\sum_n \frac{\mathrm{e}^{\mathrm{i}\,(\boldsymbol{K}_n+\boldsymbol{k})(\boldsymbol{r}_i-\boldsymbol{r}'_j)}}{|\boldsymbol{K}_n+\boldsymbol{k}|^2-k^2} \quad . \tag{3.133}$$

Calculation of Physical Oberservables

The usefulness of going through all the trouble of calculating the Green's function should become clear in this section. Once the Green's function is known, physical observables can be derived from it in a straightforward manner. To understand this we first note that the Green's function is the solution of:

$$\big(-\nabla^2 + V(\boldsymbol{r}) - E\big)\, G(\boldsymbol{r}, \boldsymbol{r}'; E) = \delta(\boldsymbol{r} - \boldsymbol{r}') \quad , \tag{3.134}$$

where the energy dependence was explicitly added. It has been discussed previously that this equation corresponds to the eigenvalue problem:

$$\big(-\nabla^2 + V(\boldsymbol{r})\big)\, \psi_n(\boldsymbol{r}) = E_n\, \psi_n(\boldsymbol{r}) \quad , \tag{3.135}$$

where E_n denotes the eigenvalues. Clearly the eigenfunctions $\psi_n(\boldsymbol{r})$ fulfill the conditions of orthonormality and completeness:

$$\int \mathrm{d}\boldsymbol{r}\, \psi_m(\boldsymbol{r})\, \psi_n^*(\boldsymbol{r}) \;=\; \delta_{mn} \tag{3.136}$$

$$\sum_n \psi_n(\boldsymbol{r})\, \psi_n^*(\boldsymbol{r}') \;=\; \delta(\boldsymbol{r} - \boldsymbol{r}') \quad . \tag{3.137}$$

With this it is a known result [TDK$^+$97][Fau82][Wei90][Str98] that the Green's function may be expressed in a spectral representation as:

$$G(\boldsymbol{r}, \boldsymbol{r}'; E) = \lim_{\varepsilon \to 0} \sum_n \frac{\psi_n(\boldsymbol{r})\, \psi_n^*(\boldsymbol{r}')}{E - E_n + \mathrm{i}\varepsilon} \quad , \tag{3.138}$$

for any positive ε. Taking the trace, i.e.,

$$\mathrm{Tr}\, G(\boldsymbol{r}, \boldsymbol{r}'; E) = G(\boldsymbol{r}, \boldsymbol{r}; E) \quad , \tag{3.139}$$

and integrating over $\boldsymbol{r}$ yields because of (3.137) the result:

$$\int \mathrm{d}\boldsymbol{r}\, G(\boldsymbol{r}, \boldsymbol{r}; E) = \lim_{\varepsilon \to 0} \sum_n \frac{1}{E - E_n + \mathrm{i}\varepsilon} \quad . \tag{3.140}$$

Consider now definition (B.10) of the delta function in the form:

$$\delta(x - x_0) = \frac{1}{\pi} \lim_{\varepsilon \to 0} \frac{\varepsilon}{(x - x_0)^2 + \varepsilon^2} \quad . \tag{3.141}$$

Then since

$$\lim_{\varepsilon\to 0}\frac{1}{(x-x_0)+\mathrm{i}\varepsilon} = \lim_{\varepsilon\to 0}\left[\frac{(x-x_0)-\mathrm{i}\varepsilon}{(x-x_0)^2+\varepsilon^2}\right] \tag{3.142}$$

$$= \frac{1}{(x-x_0)} - \lim_{\varepsilon\to 0}\frac{\mathrm{i}\varepsilon}{(x-x_0)^2+\varepsilon^2} \quad , \tag{3.143}$$

we can write

$$\lim_{\varepsilon\to 0}\frac{1}{(E-E_n)+\mathrm{i}\varepsilon} = \frac{1}{(E-E_n)} - \mathrm{i}\pi\,\delta(E-E_n) \quad . \tag{3.144}$$

It follows that the imaginary part of this expression is simply equal to the delta function:

$$-\frac{1}{\pi}\,\mathrm{Im}\left[\lim_{\varepsilon\to 0}\frac{1}{(E-E_n)+\mathrm{i}\varepsilon}\right] = \delta(E-E_n) \quad . \tag{3.145}$$

Combination of this identity with (3.140) results in the following relation between the imaginary part of the Green's function and the delta function:

$$-\frac{1}{\pi}\,\mathrm{Im}\int \mathrm{d}\boldsymbol{r}\,G(\boldsymbol{r},\boldsymbol{r};E) = \sum_n \delta(E-E_n) \quad . \tag{3.146}$$

The right hand side of this equation can be interpreted as the density of states because by integrating over an energy interval $\Delta E = 2\varepsilon$:

$$\sum_n \int_{E-\varepsilon}^{E+\varepsilon} \mathrm{d}E\,\delta(E-E_n) = N \quad , \tag{3.147}$$

N being the number of states in the interval. From this argument we may conclude that the density of states $n(E)$ is given by:

$$n(E) = -\frac{1}{\pi}\,\mathrm{Im}\int \mathrm{d}\boldsymbol{r}\,G(\boldsymbol{r},\boldsymbol{r};E) \quad . \tag{3.148}$$

In a similar fashion an expression for the charge density can be found. According to density functional theory the charge density is given by:

$$\rho(\boldsymbol{r}) = \sum_n \psi_n(\boldsymbol{r})\psi_n^*(\boldsymbol{r}) \quad , \tag{3.149}$$

where the summation runs over all occupied states. Integrating the Green's function up to the Fermi energy we can derive an expression for the charge density in terms of the imaginary part of the Green's function. We may write:

$$\begin{aligned}
\int\limits_{-\infty}^{E_F} \mathrm{d}E\, G(\boldsymbol{r},\boldsymbol{r};E) &= \lim_{\varepsilon\to 0}\sum_n \int\limits_{-\infty}^{E_F} \mathrm{d}E\, \frac{\psi_n(\boldsymbol{r})\psi_n^*(\boldsymbol{r})}{E-E_n+\mathrm{i}\varepsilon} && (3.150)\\
&= \sum_n \psi_n(\boldsymbol{r})\psi_n^*(\boldsymbol{r}) \lim_{\varepsilon\to 0}\int\limits_{-\infty}^{E_F} \mathrm{d}E\, \frac{1}{E-E_n+\mathrm{i}\varepsilon} && (3.151)\\
&= \sum_n \psi_n(\boldsymbol{r})\psi_n^*(\boldsymbol{r}) \int\limits_{-\infty}^{E_F} \mathrm{d}E\, \left[\frac{1}{E-E_n} - \mathrm{i}\pi\,\delta(E-E_n)\right] . && (3.152)
\end{aligned}$$

Because the product of wave functions is real, by taking the imaginary part of both sides of the last equality one only has to deal with the delta function in the integrand. The integration of the delta function reduces the summation over all states to a summation over only the occupied states. Hence we obtain the following equality:

$$\rho(\boldsymbol{r}) = -\frac{1}{\pi}\,\mathrm{Im}\int\limits_{-\infty}^{E_F} \mathrm{d}E\, G(\boldsymbol{r},\boldsymbol{r};E) \quad . \tag{3.153}$$

Note that the energy is in general complex and the energy integration has to be performed along a contour – usually either a semi circle or a straight line parallel to the real energy axis – in the complex plane. To evaluate the expressions for the density of states and the charge density, respectively, in terms of the specific Green's function derived previously, we can rewrite equation (3.113) (denoting the energy dependence explicitly):

$$G(\boldsymbol{r}_n,\boldsymbol{r}'_n;E) = \sum_{LL'} Z_L(\boldsymbol{r}_n;E)\,\tau^{nn}_{LL'}\,Z^\dagger_{L'}(\boldsymbol{r}'_n;E) - \sum_L Z_L(\boldsymbol{r}_n;E)\,J^\dagger_L(\boldsymbol{r}'_n;E)\,, \tag{3.154}$$

by first taking the trace and then using the angular momentum expansions for the regular and irregular solutions. This is done in the following manner:

$$\begin{aligned}
G(\boldsymbol{r}_n,\boldsymbol{r}_n;E) &= \mathrm{Tr}\,G(\boldsymbol{r}_n,\boldsymbol{r}'_n;E) && (3.155)\\
&= \sum_{LL'} Z_L(\boldsymbol{r}_n;E)\,\tau^{nn}_{LL'}\,Z^\dagger_{L'}(\boldsymbol{r}_n;E) - \sum_L Z_L(\boldsymbol{r}_n;E)\,J^\dagger_L(\boldsymbol{r}_n;E) && (3.156)\\
&= \sum_{\substack{LL'\\L''L'''}} Z_{LL''}(r_n;E)\,Y_{L''}(\hat{\boldsymbol{r}}_n)\,\tau^{nn}_{LL'}\,Z_{L'L'''}(r_n;E)\,Y^*_{L'''}(\hat{\boldsymbol{r}}_n) && (3.157)\\
&\quad - \sum_{LL'L''} Z_{LL'}(r_n;E)\,Y_{L'}(\hat{\boldsymbol{r}}_n) J_{LL''}(r_n;E)\,Y^*_{L''}(\hat{\boldsymbol{r}}_n) && (3.158)\\
&= \sum_{LL'} G^{nn}_{LL'}(r_n;E)\,Y_L(\hat{\boldsymbol{r}}_n)\,Y^*_{L'}(\hat{\boldsymbol{r}}_n) \quad . && (3.159)
\end{aligned}$$

In the last step we have defined:

$$\begin{aligned} G^{nn}_{LL'}(r_n;E) &= \sum_{L''L'''} Z_{LL''}(r_n;E)\,\tau^{nn}_{L''L'''}\,Z_{L'''L'}(r_n;E) && (3.160)\\ &\quad - \sum_{L''} Z_{LL''}(r_n;E)\,J_{LL''}(r_n;E) \quad . && (3.161)\end{aligned}$$

Furthermore, by making use of the identity:

$$Y_L(\hat{\boldsymbol{r}}_n)\,Y^*_{L'}(\hat{\boldsymbol{r}}_n) = \sum_{L''} C^{L'}_{LL''}\,Y^*_{L''}(\hat{\boldsymbol{r}}_n) \quad , \tag{3.162}$$

where the $C^{L'}_{LL''}$ are the Gaunt coefficients as defined in the appendix and the identity can be easily verified by multiplying both sides by $Y_L(\hat{\boldsymbol{r}}_n)$ and integrating over the unit sphere, we can write:

$$G(\boldsymbol{r}_n,\boldsymbol{r}_n;E) = \sum_{LL'L''} G^{nn}_{LL'}(r_n;E)\,C^{L'}_{LL''}\,Y^*_{L''}(\hat{\boldsymbol{r}}_n) \quad . \tag{3.163}$$

Finally, with the definition

$$G^{nn}_{L}(r_n;E) = \sum_{L'L''} G^{nn}_{L'L''}(r_n;E)\,C^{L''}_{L'L} \quad , \tag{3.164}$$

we obtain the following shorthand notation for the Green's function:

$$G(\boldsymbol{r}_n,\boldsymbol{r}_n;E) = \sum_{L} G^{nn}_{L}(r_n;E)\,Y^*_{L}(\hat{\boldsymbol{r}}_n) \quad . \tag{3.165}$$

Using this result we can rewrite the charge density (3.153) as:

$$\begin{aligned} \rho(\boldsymbol{r}_n) &= -\frac{1}{\pi}\,\mathrm{Im}\int\limits_{-\infty}^{E_F} \mathrm{d}E\,G(\boldsymbol{r}_n,\boldsymbol{r}_n;E) && (3.166)\\ &= -\frac{1}{\pi}\,\mathrm{Im}\sum_{L}\int\limits_{-\infty}^{E_F} \mathrm{d}E\,G^{nn}_{L}(r_n;E)\,Y^*_{L}(\hat{\boldsymbol{r}}_n) && (3.167)\\ &= \mathrm{Im}\sum_{L} \rho_L(r_n)\,Y^*_{L}(\hat{\boldsymbol{r}}_n) \quad . && (3.168)\end{aligned}$$

Above the coefficients of the angular momentum expansion were identified as

$$\rho_L(r_n) = -\frac{1}{\pi}\int\limits_{-\infty}^{E_F} \mathrm{d}E\,G^{nn}_{L}(r_n;E) \quad . \tag{3.169}$$

Similarly an expression for the density of states can be derived. Starting from (3.148) we can write:

$$\begin{aligned} n(E) &= -\frac{1}{\pi}\,\mathrm{Im}\int \mathrm{d}\boldsymbol{r}_n\, G(\boldsymbol{r}_n,\boldsymbol{r}_n;E) && (3.170)\\ &= -\frac{1}{\pi}\,\mathrm{Im}\sum_L \int \mathrm{d}\boldsymbol{r}_n\, G^{nn}_L(r_n;E)\, Y^*_L(\hat{\boldsymbol{r}}_n) \quad . && (3.171)\end{aligned}$$

The evaluation of the integral can be done by making use of the shape function technique. Using:

$$\sigma(\boldsymbol{r}_n) = \sum_L \sigma_L(r_n)\, Y_L(\hat{\boldsymbol{r}}_n) \quad , \tag{3.172}$$

we can write:

$$\begin{aligned} n(E) &= -\frac{1}{\pi}\,\mathrm{Im}\sum_{LL'} \int_{BS} \mathrm{d}\boldsymbol{r}_n\, G^{nn}_L(r_n;E)\,\sigma_{L'}(r_n)\, Y_{L'}(\hat{\boldsymbol{r}}_n)\, Y^*_L(\hat{\boldsymbol{r}}_n) && (3.173)\\ &= -\frac{1}{\pi}\,\mathrm{Im}\sum_{LL'} \int_0^S r_n^2\,\mathrm{d}r_n\, G^{nn}_L(r_n;E)\,\sigma_{L'}(r_n) \int \mathrm{d}\hat{\boldsymbol{r}}_n\, Y_{L'}(\hat{\boldsymbol{r}}_n)\, Y^*_L(\hat{\boldsymbol{r}}_n) && (3.174)\\ &= -\frac{1}{\pi}\,\mathrm{Im}\sum_{L} \int_0^S r_n^2\,\mathrm{d}r_n\, G^{nn}_L(r_n;E)\,\sigma_{L}(r_n) && (3.175)\\ &= \mathrm{Im}\sum_L n_L(E) \quad . && (3.176)\end{aligned}$$

In the final step the partial density of states was defined as:

$$\begin{aligned} n_L(E) &= -\frac{1}{\pi} \int_0^S r_n^2\,\mathrm{d}r_n\, G^{nn}_L(r_n;E)\,\sigma_L(r_n) && (3.177)\\ &= -\frac{1}{\pi} \sum_{L'L''} C^{L''}_{L'L} \int_0^S r_n^2\,\mathrm{d}r_n\, G^{nn}_{L'L''}(r_n;E)\,\sigma_L(r_n) \quad . && (3.178)\end{aligned}$$

4

Calculation of the Total Energy

According to density functional theory the total energy may be decomposed into a universal functional $G[\rho]$ that contains the kinetic energy $T[\rho]$ of non-interacting particles of density ρ and the exchange-correlation energy $E_{xc}[\rho]$, and a functional $F[\rho]$, which includes all Coulomb contributions [KS65]. Then we can write the total energy $E[\rho]$ as

$$E[\rho] \equiv G[\rho] + F[\rho] \quad . \tag{4.1}$$

In view of what has been said above, $G[\rho]$ is defined by

$$G[\rho] \equiv T[\rho] + E_{xc}[\rho] \quad , \tag{4.2}$$

and the Coulomb contribution to the total energy is in general given by (using Rydberg units, i.e. $e^2 = 2$):

$$F[\rho] \equiv \int \mathrm{d}\boldsymbol{r}\, \rho(\boldsymbol{r})\, \upsilon(\boldsymbol{r}) + U[\rho] \tag{4.3}$$

In there $\upsilon(\boldsymbol{r})$ is some external potential, and $U[\rho]$ is the Coulomb energy:

$$U[\rho] = \iint \mathrm{d}\boldsymbol{r}\, \mathrm{d}\boldsymbol{r}'\, \frac{\rho(\boldsymbol{r})\, \rho(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} \quad . \tag{4.4}$$

Hence in the absence of an external potential the total energy is nothing but the sum of the kinetic, exchange-correlation, and Coulomb energy

$$E_{tot}[\rho] = T[\rho] + E_{xc}[\rho] + U[\rho] \quad . \tag{4.5}$$

These three terms, that add up to give the total energy, will be separately discussed in the following sections, as each of them requires special considerations.

Kinetic Energy

It follows from the Kohn-Sham equations that the kinetic energy functional can be calculated from

$$T[\rho] = E_{one} - \int \mathrm{d}\boldsymbol{r}\, \rho(\boldsymbol{r})\, V(\boldsymbol{r}) \quad . \tag{4.6}$$

The potential $V(\boldsymbol{r})$ in the integrand has to be understood as the effective potential in the Kohn-Sham equations which contains the Coulomb potential, the exchange-correlation, and the external potential, if one is present.

The *one-electron energy*, E_{one}, can be split up into a contribution stemming from the core and one from the valence electrons:

$$E_{one} = E_c + E_v \quad . \tag{4.7}$$

The core contribution is given simply as the sum over the electron states in the core region

$$E_c = \sum_{i_{core}} E_{i_{core}} \quad . \tag{4.8}$$

The second contribution is also referred to as *band energy* and can be evaluated from the integral

$$E_v = \int\limits_{-\infty}^{E_F} \mathrm{d}E\, E\, n(E) \quad , \tag{4.9}$$

where $n(E)$ is the density of states for the valence electrons.

The evaluation of the one-electron energies is rather straightforward, whereas the computation of the integral in (4.6) requires some consideration.

First of all it has to be noted that the charge density, which up to now is defined in all space, can be written as the sum over the contributions from individual Wigner Seitz cells. The region of a particular Wigner Seitz cell around a lattice position R will be denoted by Ω_R. Then the charge density in all space is given by

$$\rho(\boldsymbol{r}) = \sum_{R} \rho_R(\boldsymbol{r} - \boldsymbol{R}) \quad , \tag{4.10}$$

where $\rho_R(\boldsymbol{r}) = 0$ if $\boldsymbol{r} \notin \Omega_R$. Of course the same idea applies to the effective potential since both of them are interrelated via the Poisson equation. Then

$$V(\boldsymbol{r}) = \sum_R V_R(\boldsymbol{r} - \boldsymbol{R}) \quad , \tag{4.11}$$

again with the condition that $V_R(\boldsymbol{r}) = 0$ if $\boldsymbol{r} \notin \Omega_R$.

For a particular Wigner Seitz cell, the integral has now to be performed over a bounding sphere (BS) which contains the whole cell. The angular integration however has to take account of the polyhedral shape of such a cell and can be carried out be making use of the shape functions $\sigma_R(\boldsymbol{r})$. Hence we can write

$$\int\limits_{\Omega_R} \mathrm{d}\boldsymbol{r}\, \rho_R(\boldsymbol{r})\, V_R(\boldsymbol{r}) = \int\limits_{BS} \mathrm{d}\boldsymbol{r}\, \sigma_R(\boldsymbol{r})\, \rho_R(\boldsymbol{r})\, V_R(\boldsymbol{r}) \quad . \tag{4.12}$$

Now employing the following expansions in terms of complex spherical harmonics

$$\rho_R(\boldsymbol{r}) = \sum_L \rho_{RL}(r)\, Y_L^*(\hat{\boldsymbol{r}}) \quad , \tag{4.13}$$

$$V_R(\boldsymbol{r}) = \sum_L V_{RL}(r)\, Y_L(\hat{\boldsymbol{r}}) \quad , \tag{4.14}$$

$$\sigma_R(\boldsymbol{r}) = \sum_L \sigma_{RL}(r)\, Y_L(\hat{\boldsymbol{r}}) \quad , \tag{4.15}$$

where as should be noted the charge density is expanded in terms of the complex conjugated spherical harmonics, one obtains after inserting all sums into (4.12)

$$\begin{aligned} \int\limits_{BS} \mathrm{d}\boldsymbol{r}\, \sigma_R(\boldsymbol{r})\, \rho_R(\boldsymbol{r})\, V_R(\boldsymbol{r}) &= \int\limits_{BS} \mathrm{d}\boldsymbol{r} \sum_{LL'L''} Y_L(\hat{\boldsymbol{r}})\, Y_{L'}^*(\hat{\boldsymbol{r}})\, Y_{L''}(\hat{\boldsymbol{r}})\, \sigma_{RL}(r)\, \rho_{RL'}(r)\, V_{RL''}(r) \\ &= \sum_{LL'L''} \int\limits_{BS} \mathrm{d}\boldsymbol{r}\, Y_L(\hat{\boldsymbol{r}})\, Y_{L'}^*(\hat{\boldsymbol{r}})\, Y_{L''}(\hat{\boldsymbol{r}})\, \sigma_{RL}(r)\, \rho_{RL'}(r)\, V_{RL''}(r) \\ &= \sum_{L''} \int\limits_0^S r^2\, \mathrm{d}r \sum_{LL'} C_{LL''}^{L'}\, \sigma_{RL}(r)\, \rho_{RL'}(r)\, V_{RL''}(r) \quad . \end{aligned}$$

By defining a modified charge density, $\tilde{\rho}_{RL}(r)$, as

$$\tilde{\rho}_{RL''}(r) := \sum_{LL'} C_{LL''}^{L'}\, \sigma_{RL}(r)\, \rho_{RL'}(r) \quad , \tag{4.16}$$

we can rename indices and finally write

$$\int\limits_{BS} \mathrm{d}\boldsymbol{r}\, \sigma_R(\boldsymbol{r})\, \rho_R(\boldsymbol{r})\, V_R(\boldsymbol{r}) = \sum_L \int\limits_0^S r^2\, \mathrm{d}r\, \tilde{\rho}_{RL}(r)\, V_{RL}(r) \tag{4.17}$$

Summarizing, one can compute the kinetic energy for a cell centered at position $\boldsymbol{R}$ from the following expression

$$T_R[\rho] = \sum_{i_{core}} E_{i_{core}} + \int\limits_{-\infty}^{E_F} \mathrm{d}E\, E\, n_R(E) - \sum_L \int\limits_0^S r^2\, \mathrm{d}r\, \tilde{\rho}_{RL}(r)\, V_{RL}(r) \quad . \tag{4.18}$$

4.2

Exchange-Correlation Energy

If the density ρ is sufficiently slowly varying, the exchange-correlation energy can, according to [KS65], be calculated from

$$E_{xc}[\rho] = \int \mathrm{d}\boldsymbol{r}\, \rho(\boldsymbol{r})\, \epsilon_{xc}[\rho(\boldsymbol{r})] \quad , \tag{4.19}$$

where $\epsilon_{xc}[\rho(\boldsymbol{r})]$ is the exchange correlation energy per electron of a uniform electron gas and is assumed to be known from some approximation.

The integral can be evaluated in analogy to the previous section. Again we want to compute the energy per Wigner Seitz cell and label the energy term accordingly. Then we get for the expansion in terms of spherical harmonics

$$\epsilon_{xc,R}[\rho_R(\boldsymbol{r})] = \sum_L \epsilon_{xc,RL}(r)\, Y_L(\hat{\boldsymbol{r}}) \quad . \tag{4.20}$$

As can be seen immediately, the expansion coefficients have to be obtained from the angular integration

$$\epsilon_{xc,RL}(r) = \int \mathrm{d}\hat{\boldsymbol{r}}\, Y_L^*(\hat{\boldsymbol{r}})\, \epsilon_{xc,R}[\rho_R(\boldsymbol{r})] \quad , \tag{4.21}$$

which has to be computed numerically by means of e.g. a Gauss quadrature.

Then following the same steps as in the evaluation of (4.12) and using definition (4.16), the expression for the exchange-correlation energy for a Wigner Seitz cell at position R is given by

$$E_{xc,R}[\rho] = \sum_L \int\limits_0^S r^2\, \mathrm{d}r\, \tilde{\rho}_{RL}(r)\, \epsilon_{xc,RL}(r) \quad . \tag{4.22}$$

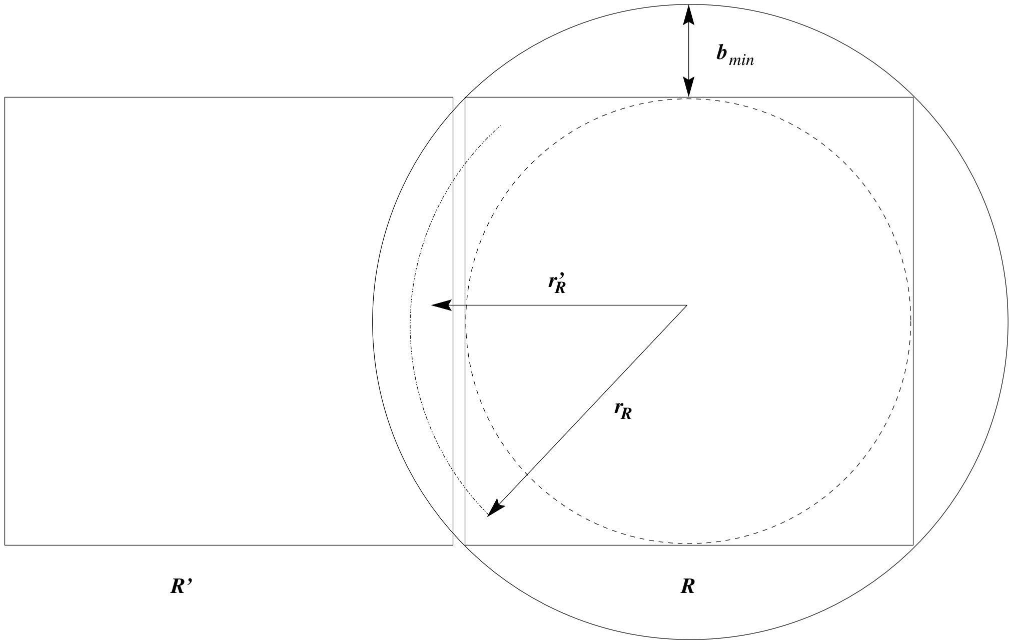
Coulomb Energy

In this section an expression for the Coulomb energy of an assembly of arbitrary charge distributions will be derived. Since the corresponding expression for charge densities confined in a non-overlapping muffin tin geometry are not valid in general, an alternative approach is needed.

The problem arises from the fact that the solution to Poisson's equation from classical electrodynamics, which describes the potential due to a charge distribution by an expansion in terms of multipole moments [Jac92] is no longer valid in the case of a space filling geometry, such as can be constructed from Wigner Seitz cells, for neighbouring cells. There one has to consider what has been called *moon* region by Gonis [Gon92]. This region is the complement of the Wigner-Seitz cell and its circumscribed sphere. If the vector $\boldsymbol{r}'_R$, which extends into the neighbouring cell, is inside this region, its length may be shorter than that of the vector $\boldsymbol{r}_R$, inside the cell. Then the common expansion becomes invalid and the sum does not converge [GSS91].

It is now useful to divide the Coulomb energy into an *intra-cell* part, which includes all

Figure 4.1: *The moon region of two adjacent cells for which the muffin tin condition is not satisfied. It can be seen from this sketch that the vector* $\boldsymbol{r}'_R$*, even though it extends into the neighbouring cell,* R'*, can be shorter than the vector* $\boldsymbol{r}_R$ *in cell* R*, hence invalidating the angular momentum expansion. The minimum length of the displacement vector is indicated by* $\boldsymbol{b}_{min}$*.*



contributions from within the cell at position $\boldsymbol{R}$, and a *inter-cell* part, that describes the effects from all the other charge distributions in the crystal. Then we can write:

$$U_R[\rho] = U_R^{intra}[\rho] + U_R^{inter}[\rho] \quad . \tag{4.23}$$

The intra-cell part of the Coulomb energy is computationally more straightforward and therefore we start with its derivation.

4.3.1 **Intra-Cell Contribution**

In order to find an expression for this part of the energy, we will rewrite the expression (4.4). Then let us denote the total Coulomb energy with respect to cell $\boldsymbol{R}$ in the following way:

$$U[\rho] = \tag{4.24}$$
$$\iint \mathrm{d}\boldsymbol{r}_R\, \mathrm{d}\boldsymbol{r}'_R \, \frac{\Big(\rho(\boldsymbol{r}_R) - \sum_{R'} \mathrm{Z}_{R'}\, \delta(\boldsymbol{r}_R - \boldsymbol{S}_{RR'})\Big)\Big(\rho(\boldsymbol{r}'_R) - \sum_{R''} \mathrm{Z}_{R''}\, \delta(\boldsymbol{r}'_R - \boldsymbol{S}_{RR''})\Big)}{|\boldsymbol{r}_R - \boldsymbol{r}'_R|} \quad ,$$

where the Z_R are the atomic numbers and the occurring vectors have the following meaning:

$$\boldsymbol{r}_R = \boldsymbol{r} - \boldsymbol{R} \quad , \tag{4.25}$$
$$\boldsymbol{r}'_R = \boldsymbol{r}' - \boldsymbol{R} \quad , \tag{4.26}$$
$$\boldsymbol{S}_{RR'} = \boldsymbol{R}' - \boldsymbol{R} \quad . \tag{4.27}$$

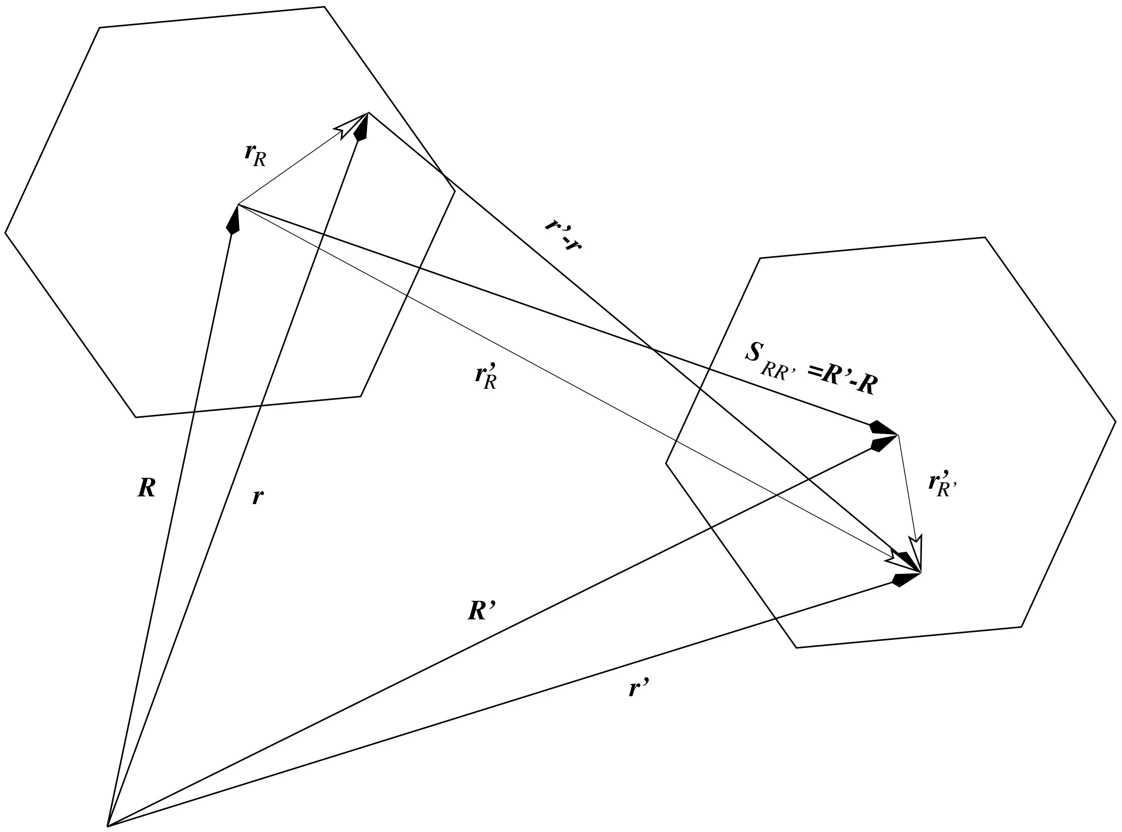
From (4.24) one finds after multiplication and rearrangement of the terms, that

$$\begin{aligned} U[\rho] \;=\; & \int \mathrm{d}\boldsymbol{r}_R\, \rho(\boldsymbol{r}_R) \left(\int \mathrm{d}\boldsymbol{r}'_R \, \frac{\rho(\boldsymbol{r}'_R)}{|\boldsymbol{r}_R - \boldsymbol{r}'_R|} - \sum_{R'} \frac{2\,\mathrm{Z}_{R'}}{|\boldsymbol{r}_R - \boldsymbol{S}_{RR'}|} \right) \\ & + \sum_{\substack{R'R'' \\ R''\neq R'}} \frac{\mathrm{Z}_{R'}\,\mathrm{Z}_{R''}}{|\boldsymbol{R}' - \boldsymbol{R}''|} \quad . \end{aligned} \tag{4.28}$$

It is then possible to write the charge density in all space as the sum of the contributions of individual cells, with the aim to substitute the resulting sum into the integral inside the brackets. Then:

$$\rho(\boldsymbol{r}'_R) = \sum_{R'} \rho_{R'}(\boldsymbol{r}'_R - \boldsymbol{S}_{RR'})\,, \quad \text{with} \quad \rho_{R'}(\boldsymbol{r}'_{R'}) = 0\,, \quad \text{if} \quad \boldsymbol{r}'_{R'} \notin \Omega_{R'}\,, \tag{4.29}$$

Figure 4.2: *Illustration of the notation of the vectors used in the derivation of the electrostatic energy.*



where Ω_R denotes the cell centered at position $\boldsymbol{R}$. One thus obtains by substitution, interchanging the integral and summation, and with $\boldsymbol{r}'_R - \boldsymbol{S}_{RR'} = \boldsymbol{r}'_{R'}$:

$$\begin{aligned} U[\rho] &= \int \mathrm{d}\boldsymbol{r}_R\, \rho(\boldsymbol{r}_R) \sum_{R'} \left(\int_{\Omega_{R'}} \mathrm{d}\boldsymbol{r}'_{R'}\, \frac{\rho_{R'}(\boldsymbol{r}'_{R'})}{|\boldsymbol{r}_{R'} - \boldsymbol{r}'_{R'}|} - \frac{2\,\mathrm{Z}_{R'}}{|\boldsymbol{r}_R - \boldsymbol{S}_{RR'}|} \right) \\ &\quad + \sum_{\substack{R'R'' \\ R'' \neq R'}} \frac{\mathrm{Z}_{R'}\,\mathrm{Z}_{R''}}{|\boldsymbol{R}' - \boldsymbol{R}''|} \quad . \end{aligned} \tag{4.30}$$

Now taking only the term of the summation with $\boldsymbol{R}' = \boldsymbol{R}$, extending the first integral only over Ω_R, and noting that, since also $\boldsymbol{R}'' = \boldsymbol{R}$, the last term gives no contribution we obtain:

$$U_R^{intra}[\rho] = \int_{\Omega_R} \mathrm{d}\boldsymbol{r}_R\, \rho_R(\boldsymbol{r}_R) \left(\int_{\Omega_R} \mathrm{d}\boldsymbol{r}'_R\, \frac{\rho_R(\boldsymbol{r}'_R)}{|\boldsymbol{r}_R - \boldsymbol{r}'_R|} - \frac{2\,\mathrm{Z}_R}{|\boldsymbol{r}_R|} \right) \quad . \tag{4.31}$$

This is the intra-cell Coulomb energy (in Rydberg units) for a cell labelled by the index

R, because the integrals extend only over the region bounded by Ω_R and the charge density is confined to that region only.

Computation of the Intra-Cell Coulomb Energy

To find a representation of (4.31) that is of computational use, we have to recall the expansions (4.13), (4.15), and (B.35). Then we get instead of (4.31):

$$\begin{aligned}
U_R^{intra}[\rho] \;&=\; \sum_{LL'L''} \int \mathrm{d}\hat{\boldsymbol{r}}_R\, Y^*_{L'}(\hat{\boldsymbol{r}}_R)\, Y_{L''}(\hat{\boldsymbol{r}}_R) \int_0^S r_R^2\, \mathrm{d}r_R\, \rho_{RL'}(r_R)\, \sigma_{RL''}(r_R) \\
&\quad \times \left(\frac{4\pi}{2\ell+1} Y_L(\hat{\boldsymbol{r}}_R) \int \mathrm{d}\hat{\boldsymbol{r}}_R\, Y^*_L(\hat{\boldsymbol{r}}'_R)\, Y^*_{L'}(\hat{\boldsymbol{r}}'_R)\, Y_{L''}(\hat{\boldsymbol{r}}'_R) \right. \\
&\quad \times \left. \int_0^S r'^2_R\, \mathrm{d}r_R\, \frac{r_<^\ell}{r_>^{\ell+1}}\, \rho_{RL'}(r'_R)\, \sigma_{RL''}(r'_R) - \frac{2\mathrm{Z}_R}{r_R} \right) \quad . \qquad (4.32)
\end{aligned}$$

Using the definition of the Gaunt coefficients leads to

$$\begin{aligned}
U_R^{intra}[\rho] \;&=\; \sum_{LL'L''} C_{LL''}^{L'} \int_0^S r_R^2\, \mathrm{d}r_R\, \rho_{RL'}(r_R)\, \sigma_{RL''}(r_R) \\
&\quad \times \left(\frac{4\pi}{2\ell+1}\, C_{L''}^{LL'} \int_0^S r'^2_R\, \mathrm{d}r'_R\, \frac{r_<^\ell}{r_>^{\ell+1}}\, \rho_{RL'}(r'_R)\, \sigma_{RL''}(r'_R) - \frac{2\mathrm{Z}_R}{r_R} \right) . \qquad (4.33)
\end{aligned}$$

The two Gaunt coefficients in this expression are different because complex spherical harmonics are used and they are not proportional to each other. But still it is possible to define two modified charge densities, to make the computation more efficient, as:

$$\tilde{\rho}^{(1)}_{RL}(r_R) \;=\; \sum_{L'L''} C_{LL''}^{L'}\, \rho_{RL'}(r_R)\, \sigma_{RL''}(r_R) \qquad (4.34)$$

$$\tilde{\rho}^{(2)}_{RL}(r_R) \;=\; \sum_{L'L''} C_{L''}^{LL'}\, \rho_{RL'}(r_R)\, \sigma_{RL''}(r_R) \quad . \qquad (4.35)$$

Using these definitions we can write

$$\begin{aligned}
&U_R^{intra}[\rho] = \\
&\quad \sum_L \frac{4\pi}{2\ell+1} \int_0^S r_R^2\, \mathrm{d}r_R\, \tilde{\rho}^{(1)}_{RL}(r_R) \left(\int_0^S r'^2_R\, \mathrm{d}r'_R\, \frac{r_<^\ell}{r_>^{\ell+1}}\, \tilde{\rho}^{(2)}_{RL}(r'_R) - \frac{2\mathrm{Z}_R}{r_R} \right) \quad . \qquad (4.36)
\end{aligned}$$

The integral in the brackets has to be rewritten in the following way:

$$\int_0^S r_R'^2 \, \mathrm{d}r_R' \, \frac{r_<^\ell}{r_>^{\ell+1}} \, \tilde{\rho}^{(2)}_{RL}(r_R') =$$

$$\int_0^{r_R} r_R'^2 \, \mathrm{d}r_R' \, \frac{(r_R')^\ell}{r_R^{\ell+1}} \, \tilde{\rho}^{(2)}_{RL}(r_R') + \int_{r_R}^S r_R'^2 \, \mathrm{d}r_R' \, \frac{r_R^\ell}{(r_R')^{\ell+1}} \, \tilde{\rho}^{(2)}_{RL}(r_R') \quad . \tag{4.37}$$

With this the intra-cell contribution to the Coulomb energy can be expressed in a compact form:

$$U_R^{intra}[\rho] = \sum_L \frac{4\pi}{2\ell+1} \int_0^S \tilde{\rho}^{(1)}_{RL}(r_R) \, \left(r_R^{-\ell-1} \, A_{RL}(r_R) + r_R^\ell \, B_{RL}(r_R) \right) r_R^2 \, \mathrm{d}r_R \quad , \tag{4.38}$$

where the functions $A_{RL}(r_R)$ and $B_{RL}(r_R)$ are given by

$$A_{RL}(r_R) \;=\; \int_0^{r_R} \mathrm{d}r_R' \, r_R'^{\ell+2} \, \tilde{\rho}^{(2)}_{RL}(r_R') - 2 \, \delta_{\ell 0} \, \delta_{m0} \, \mathrm{Z}_R \quad , \tag{4.39}$$

$$B_{RL}(r_R) \;=\; \int_{r_R}^S \mathrm{d}r_R' \, (r_R')^{-\ell+1} \, \tilde{\rho}^{(2)}_{RL}(r_R') \quad . \tag{4.40}$$

4.3.2 **Inter-Cell Contribution**

All the energy terms that are not included in (4.31) form the Inter-Cell energy. We inspect again equation (4.24) and find that the outer integration still extends only over Ω_R because we want to compute the Coulomb energy for the charge distribution $\rho(\boldsymbol{r}_R)$ in that cell times the contribution from all other cells whose charge distribution is given by $\rho(\boldsymbol{r}_R') = \sum_{R' \neq R} \rho_{R'}(\boldsymbol{r}_{R'}' - \boldsymbol{S}_{RR'})$. Therefore the second integration does not include Ω_R. Let us denote what has been said as:

$$U_R^{inter}[\rho] = \tag{4.41}$$

$$\int_{\Omega_R} \mathrm{d}\boldsymbol{r}_R \int_{\Omega \backslash \Omega_R} \mathrm{d}\boldsymbol{r}_R' \, \frac{\Big(\rho_R(\boldsymbol{r}_R) - \mathrm{Z}_R \, \delta(\boldsymbol{r}_R) \Big) \Big(\rho(\boldsymbol{r}_R') - \sum_{R'} \mathrm{Z}_{R'} \, \delta(\boldsymbol{r}_R' - \boldsymbol{S}_{RR'}) \Big)}{|\boldsymbol{r}_R - \boldsymbol{r}_R'|} \, ,$$

where the notation $\Omega \setminus \Omega_R$ indicates that the integration extends over all cells except Ω_R. Now it is essential to consider the contributions from neighbouring cells and such cells which do not have intersecting bounding spheres separately. In order to treat the nearest neighbours, i.e., cells whose bounding spheres do intersect the bounding sphere of the cell at $\boldsymbol{R}$, a multipole expansion of the inverse of the difference vector in the denominator of (4.41) will be made use of, which is the tedious part in the derivation. This expansion then leads to a description of the electrostatic energy (and of course also of the Coulomb potential) in terms of multipole moments, which is analogous to the muffin tin case. First let us introduce a vector $\boldsymbol{b}$ for which the relation $b < |\boldsymbol{r}_R - \boldsymbol{r}'_R - \boldsymbol{b}|$ is always true. Adding and subtracting this vector we can write:

$$\frac{1}{|\boldsymbol{r}_R - \boldsymbol{r}'_R|} = \frac{1}{|-\boldsymbol{b} - (\boldsymbol{r}_R - \boldsymbol{r}'_R - \boldsymbol{b})|} \quad . \tag{4.42}$$

It is advantageous to choose a particular vector $\boldsymbol{b}$ in the direction of the vector connecting the centers of a given pair of neighbouring cells centered at $\boldsymbol{R}$ and $\boldsymbol{R}'$ respectively. Hence $\boldsymbol{b}$ will be denoted in the following as $\boldsymbol{b}_{RR'}$. Then the expansion of equation (B.35) is made use of, yielding:

$$\frac{1}{|-\boldsymbol{b}_{RR'} - (\boldsymbol{r}_R - \boldsymbol{r}'_R - \boldsymbol{b}_{RR'})|} = \sum_L \frac{4\pi}{2\ell+1}\, b^{\ell}_{RR'}\, Y^*_{\ell m}(-\hat{\boldsymbol{b}}_{RR'})\, \frac{Y_{\ell m}(\widehat{\boldsymbol{r}_R - (\boldsymbol{r}'_R + \boldsymbol{b}_{RR'})})}{|\boldsymbol{r}_R - (\boldsymbol{r}'_R + \boldsymbol{b}_{RR'})|^{\ell+1}} \quad . \tag{4.43}$$

To proceed, one condition has to be imposed on the minimum length of the vector $\boldsymbol{b}_{RR'}$. It has to be at least equal to the distance between the radius of the circumscribing sphere and the length from the cell center to the center of a face (c.f. figure (4.1). This means that $r_R < |\boldsymbol{r}'_R + \boldsymbol{b}_{RR'}|$, and the expansion (B.36) can be applied, which leads to:

$$\begin{aligned}\frac{1}{|-\boldsymbol{b}_{RR'} - (\boldsymbol{r}_R - \boldsymbol{r}'_R - \boldsymbol{b}_{RR'})|} &= \sum_L \frac{(-1)^{\ell}\,(4\pi)^2}{2\ell+1}\, b^{\ell}_{RR'}\, Y^*_{\ell m}(\hat{\boldsymbol{b}}_{RR'}) \\ &\times \sum_{L'} (-1)^{\ell}\, \frac{(2(\ell+\ell')-1)!!}{(2\ell-1)!!\,(2\ell'+1)!!}\, C^{\ell' m'}_{\ell m,(\ell+\ell')(m'-m)} \\ &\times \frac{Y^*_{(\ell+\ell')(m'-m)}(\widehat{\boldsymbol{r}'_R + \boldsymbol{b}_{RR'}})}{|\boldsymbol{r}'_R + \boldsymbol{b}_{RR'}|^{\ell+\ell'+1}}\, r^{\ell'}_R\, Y_{\ell' m'}(\hat{\boldsymbol{r}}_R) \,.\end{aligned} \tag{4.44}$$

The summations over L and L' in (4.44) are both infinite. Because the inner sum, over L', is dependent on the value of L, the double summation is conditionally convergent and its order cannot be interchanged. Therefore we continue by using the identity:

$$\boldsymbol{r}'_R + \boldsymbol{b}_{RR'} = \boldsymbol{r}'_{R'} - (\boldsymbol{S}_{R'R} - \boldsymbol{b}_{RR'}) \quad . \tag{4.45}$$

With this and (B.36) the following expansion is found:

$$
\begin{aligned}
&\frac{Y^{*}_{(\ell+\ell')(m'-m)}(\widehat{\boldsymbol{r}'_R+\boldsymbol{b}_{RR'}})}{|\boldsymbol{r}'_R+\boldsymbol{b}_{RR'}|^{\ell+\ell'+1}} = \\
&\qquad \sum_{L''}(-1)^{\ell+\ell'}\,4\pi\,\frac{(2(\ell+\ell'+\ell'')-1)!!}{(2(\ell+\ell')-1)!!\,(2\ell''+1)!!}\,C^{\ell''m''}_{(\ell+\ell')(m'-m),(\ell+\ell'+\ell'')(m''-m'+m)} \\
&\qquad \times\,\frac{Y_{(\ell+\ell'+\ell'')(m''-m'+m)}(\widehat{\boldsymbol{S}_{R'R}-\boldsymbol{b}_{RR'}})}{|\boldsymbol{S}_{R'R}-\boldsymbol{b}_{RR'}|^{\ell+\ell'+\ell''+1}}\,r'^{\ell''}_{R'}\,Y^{*}_{\ell''m''}(\hat{\boldsymbol{r}}'_{R'}) \quad . \qquad (4.46)
\end{aligned}
$$

which requires $r'_{R'} < |\boldsymbol{S}_{RR'}+\boldsymbol{b}_{RR'}|$. This expansion is now inserted into (4.44). Then making use of the following identity (where for simplicity the arguments are left out and the definitions $m''' = m'-m$, $m^{iv} = m''-m'+m$, and $\{m\} = mm'm''m'''m^{iv}$ are used):

$$
\begin{aligned}
&\sum_{\{m\}} Y^{*}_{\ell m}\,Y_{\ell'm'}\,Y^{*}_{\ell''m''}\,Y_{(\ell+\ell'+\ell'')m^{iv}}\,C^{\ell'm'}_{\ell m,(\ell+\ell')m'''}\,C^{\ell''m''}_{(\ell+\ell')m''',(\ell+\ell'+\ell'')m^{iv}} = \\
&\qquad \sum_{\{m\}} Y_{\ell m}\,Y_{\ell'm'}\,Y^{*}_{\ell''m''}\,Y^{*}_{(\ell+\ell'+\ell'')m^{iv}}\,C^{(\ell+\ell')m'''}_{\ell m,\ell'm'}\,C^{(\ell+\ell')m'''}_{\ell''m'',(\ell+\ell'+\ell'')m^{iv}} \quad , \qquad (4.47)
\end{aligned}
$$

we arrive by combining (4.44) and (4.46) at the final expression

$$
\begin{aligned}
\frac{1}{|\boldsymbol{r}_R-\boldsymbol{r}'_R|} &= 2\pi\sum_{L} b^{\ell}\,Y_{\ell m}(\hat{\boldsymbol{b}}_{RR'})\sum_{L'} r^{\ell'}_{R}\,Y_{\ell'm'}(\hat{\boldsymbol{r}}_R)\,C^{(\ell+\ell')(m+m')}_{\ell m,\ell'm'} \\
&\qquad \times\sum_{L''} B_{LL'L''}(\boldsymbol{S}_{RR'}+\boldsymbol{b}_{RR'})\,\sqrt{4\pi}\,r'^{\ell''}_{R'}\,Y^{*}_{\ell''m''}(\hat{\boldsymbol{r}}'_{R'}) \quad , \qquad (4.48)
\end{aligned}
$$

where the coefficients $B_{LL'L''}(\boldsymbol{S}_{RR'}+\boldsymbol{b}_{RR'})$ have been defined as

$$
\begin{aligned}
&B_{LL'L''}(\boldsymbol{S}_{RR'}+\boldsymbol{b}_{RR'}) := (-1)^{\ell''}\,\frac{8\pi\;(2(\ell+\ell'+\ell'')-1)!!}{(2\ell+1)!!\,(2\ell'+1)!!\,(2\ell''+1)!!} \\
&\qquad \times\sqrt{4\pi}\,C^{(\ell+\ell')(m+m')}_{\ell'm',(\ell+\ell'+\ell'')(m+m'-m'')}\,\frac{Y^{*}_{(\ell+\ell'+\ell'')(m+m'-m'')}(\widehat{\boldsymbol{S}_{RR'}+\boldsymbol{b}_{RR'}})}{|\boldsymbol{S}_{RR'}+\boldsymbol{b}_{RR'}|^{\ell+\ell'+\ell''+1}} \quad . \qquad (4.49)
\end{aligned}
$$

Now (4.48) and (4.29) can be used in (4.41) to yield an expression for the contribution to the Inter-Cell Coulomb energy from neighbouring cells:

$$
\begin{aligned}
U^{inter}_{R,nn}[\rho] &= \sqrt{\pi}\sum_{\mathcal{R}}\sum_{L} b^{\ell}_{RR'}\,Y_{\ell m}(\hat{\boldsymbol{b}}_{RR'}) \\
&\qquad \times\sum_{L'}\sqrt{4\pi}\int_{\Omega_R}\mathrm{d}\boldsymbol{r}_R\,\Big(\rho_R(\boldsymbol{r}_R)-\mathrm{Z}_R\,\delta(\boldsymbol{r}_R)\Big)\,r^{\ell'}_{R}\,Y_{\ell'm'}(\hat{\boldsymbol{r}}_R) \\
&\qquad \times C^{(\ell+\ell')(m+m')}_{\ell m,\ell'm'}\sum_{L''} B_{LL'L''}(\boldsymbol{S}_{RR'}+\boldsymbol{b}_{RR'}) \\
&\qquad \times\sqrt{4\pi}\int_{\Omega_{R'}}\mathrm{d}\boldsymbol{r}'_{R'}\,r'^{\ell''}_{R'}\,Y^{*}_{\ell''m''}(\hat{\boldsymbol{r}}'_{R'})\,\Big(\rho_{R'}(\boldsymbol{r}'_{R'})-\mathrm{Z}_{R'}\,\delta(\boldsymbol{r}'_{R'})\Big) \quad , \qquad (4.50)
\end{aligned}
$$

where the outer sum (over $\mathcal{R}$) runs over nearest neighbour cells, such that $\mathcal{R}$ contains the following set of vectors $\boldsymbol{R}'$:

$$\mathcal{R} = \left\{ \boldsymbol{R}' \in \mathcal{L} \,\middle|\, |\boldsymbol{R}' - \boldsymbol{R}| < 2\, S_R \right\} \quad , \tag{4.51}$$

if $\mathcal{L}$ denotes a lattice and S_R is the radius of the circumscribing sphere around $\boldsymbol{R}$. Furthermore it is illustrated in figure 4.3 in which way the bounding spheres are shifted apart in the directions of the vectors $\boldsymbol{b}_{RR'}$ for different pairs of neighbouring cells. Equation (4.50) has been written such that the multipole moments $\hat{Q}_{RL}$

$$\hat{Q}_{RL} = \sqrt{4\pi} \int\limits_{\Omega_R} \mathrm{d}\boldsymbol{r}_R\, \rho_R(\boldsymbol{r}_R)\, r_R^\ell\, Y_L^*(\hat{\boldsymbol{r}}_R) \;-\; \delta_{\ell 0}\, \delta_{m0}\, \mathrm{Z}_R \quad , \tag{4.52}$$

can easily be read off. Using this definition, (4.50) can be written in a compact form as [GSS91, KVS99]:

$$\begin{aligned} U^{inter}_{R,nn}[\rho] \;&=\; \sqrt{\pi} \sum_{\mathcal{R}} \sum_{L} b^\ell_{RR'}\, Y_{\ell m}(\hat{\boldsymbol{b}}_{RR'}) \sum_{L'} \hat{Q}^*_{RL'}\, C^{(\ell+\ell')(m+m')}_{\ell m,\ell' m'} \\ &\quad \times \sum_{L''} B_{LL'L''}(\boldsymbol{S}_{RR'} + \boldsymbol{b}_{RR'})\, \hat{Q}_{R'L''} \,. \end{aligned} \tag{4.53}$$

The multipole moments may be readily computed by using the shape function technique and expansions (4.13) and (4.15). One then gets

$$\hat{Q}_{RL} = \sqrt{4\pi} \sum_{L'L''} C^{L'}_{LL''} \int\limits_0^S \mathrm{d}r_R\, r_R^{2+\ell}\, \rho^{(2)}_{RL'}(r_R)\, \sigma_{RL''}(r_R) - \delta_{\ell 0}\, \delta_{m0}\, \mathrm{Z}_R \quad , \tag{4.54}$$

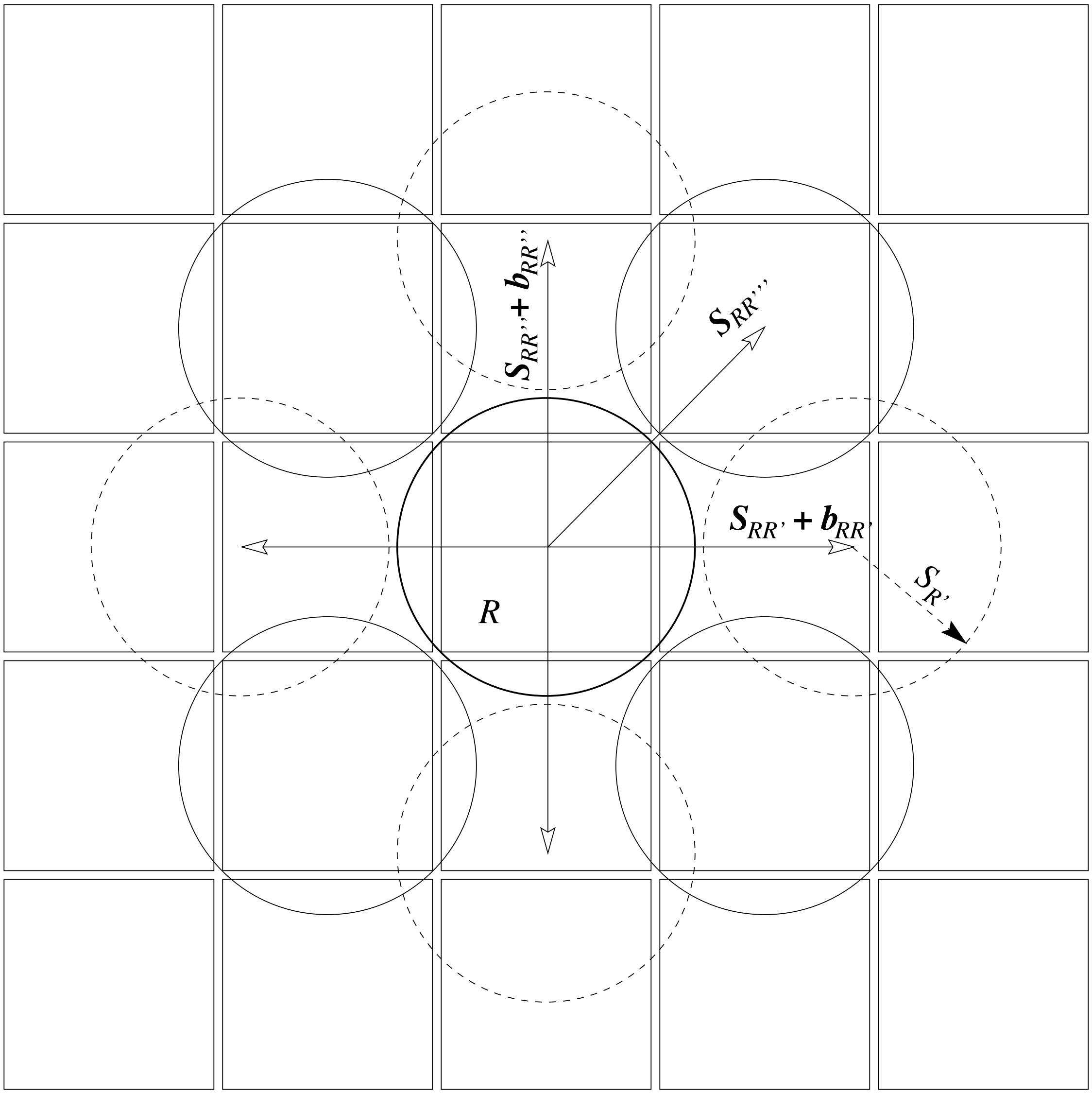
where S again refers to the radius of the bounding sphere. Then with definition (4.16) the expression for the multipole moments containing only radial integrations is given by

$$\hat{Q}_{RL} = \sqrt{4\pi} \int\limits_0^S \mathrm{d}r_R\, r_R^{2+\ell}\, \tilde{\rho}^{(2)}_{RL}(r_R) - \delta_{\ell 0}\, \delta_{m0}\, \mathrm{Z}_R \quad . \tag{4.55}$$

For cells with non-overlapping (*no*) bounding spheres, one can choose $b = 0$ and find that, because the only contribution from the first sum comes from $L = (0, 0)$ and using relation (B.34):

$$U^{inter}_{R,no}[\rho] = \frac{1}{4\sqrt{\pi}} \sum_{\mathcal{S}} \sum_{L} \hat{Q}^*_{RL} \sum_{L'} B_{LL'}(\boldsymbol{S}_{RR'})\, \hat{Q}_{R'L'} \,, \tag{4.56}$$

Figure 4.3: *The bounding spheres of neighbouring cells, which would overlap with the bounding sphere of the cell at* $\boldsymbol{R}$ *are shifted away along the direction of* $\boldsymbol{S}_{RR'}$*. From this illustration it is clear that it is of advantage to align* $\boldsymbol{S}_{RR'}$ *and* $\boldsymbol{b}_{RR'}$ *parallel*



if $\mathcal{S}$ is the set of position vectors of cells with non-overlapping bounding spheres such that:

$$\mathcal{S} = \left\{ \boldsymbol{R}' \in \mathcal{L} \,\middle|\, |\boldsymbol{R}' - \boldsymbol{R}| \geq 2\, S_R \right\} \quad . \tag{4.57}$$

The $B_{LL'}(\boldsymbol{S}_{RR'})$ are now given by:

$$\begin{aligned} B_{LL'}(\boldsymbol{S}_{RR'}) \;&=\; (-1)^{\ell'} \, \frac{8\pi \; (2(\ell+\ell')-1)!!}{(2\ell+1)!!\,(2\ell'+1)!!} \sqrt{4\pi}\, C^{\ell m}_{\ell' m',(\ell+\ell')(m-m')} \\ &\quad \times \frac{Y^{*}_{(\ell+\ell')(m-m')}(\hat{\boldsymbol{S}}_{RR'})}{|\boldsymbol{S}_{RR'}|^{\ell+\ell'+1}} \quad . \end{aligned} \tag{4.58}$$

An interpretation of the derivation of (4.53) is the following. Initially the neighbouring cells are displaced by the vector $\boldsymbol{b}_{RR'}$ until the bounding spheres are at least not overlapping anymore. Then the energy can be expressed in terms of the multipole moments of the undisplaced cell which corresponds to the inner summation over L'' in (4.53). Then by means of the outer sum (over L) the cells are shifted back to their original position [GSS91].

The convergence of the summations depends sensitively on $\boldsymbol{b}_{RR'}$, and different authors have given different prescriptions on how the vector $\boldsymbol{b}_{RR'}$ should be chosen. According to Gonis, its length should be approximately of the size of the inter-cell vector. But Kollar *et al.* find that the *displacement* vector $\boldsymbol{b}_{RR'}$ is related to the radii of the circumscribing spheres of the neighbouring cells by

$$|\boldsymbol{S}_{RR'} + \boldsymbol{b}_{RR'}| = (1+\alpha)(S_R + S'_R) \quad , \tag{4.59}$$

where the parameter α is the ratio between $\ell_{\max}$ and $\ell'_{\max}$, i.e.

$$\alpha = \frac{\ell_{\max}}{\ell'_{\max}} \quad , \tag{4.60}$$

and S_R is the radius of the circumscribing sphere of cell R.

4.4

Relationship to the 3D KKR Structure Constants

The coefficients $B_{LL'}(\boldsymbol{S}_{RR'})$ which appeared in the above derivation of the inter-cell Coulomb energy are closely related to the traditional KKR structure constants in the $k \to 0$ limit. To see this we first have to note that the KKR structure constants are the coefficients of the following expansion [Szu90]:

$$-\mathrm{i}k\, h^{+}_{\ell}(k|\boldsymbol{r}_R - \boldsymbol{S}_{RR'}|)\, Y^{*}_{\ell m}(\widehat{\boldsymbol{r}_R - \boldsymbol{S}_{RR'}}) = \sum_{L'} G_{LL'}(\boldsymbol{S}_{RR'};k)\, j_{\ell'}(kr_R)\, Y^{*}_{\ell' m'}(\hat{\boldsymbol{r}}_R) \quad .(4.61)$$

The meaning of this identity is that the function $h^{+}_{L}(k(\boldsymbol{r}_R - \boldsymbol{S}_{RR'})) = h^{+}_{\ell}(k|\boldsymbol{r}_R - \boldsymbol{S}_{RR'}|)\, Y^{*}_{\ell m}(\widehat{\boldsymbol{r}_R - \boldsymbol{S}_{RR'}})$, whose argument is centered around the lattice site $\boldsymbol{R}'$, is expanded around the site $\boldsymbol{R}$ by making use of the structure constants which are given by:

$$G_{LL'}(\boldsymbol{S}_{RR'};k) = -4\pi\, k\, \mathrm{i}^{\ell-\ell'+1} \sum_{L''} \mathrm{i}^{\ell''}\, C^{\ell m}_{\ell' m', \ell'' m''}\, h^{+}_{\ell''}(kS_{RR'})\, Y^{*}_{\ell'' m''}(\hat{\boldsymbol{S}}_{RR'}) \quad , \tag{4.62}$$

where $S_{RR'} = |\boldsymbol{S}_{RR'}|$ was used for ease of notation. By inspecting the limiting behaviour of this function a relation to $B_{LL'}(\boldsymbol{S}_{RR'})$ can be found. The only term that depends on k are the spherical Hankel functions of the first kind and for small arguments they behave as:

$$h_\ell^+(z) \xrightarrow{z\to 0} \frac{z^\ell}{(2\ell+1)!!} - \mathrm{i}\,\frac{(2\ell-1)!!}{z^{\ell+1}} \quad . \tag{4.63}$$

As the first term vanishes, only the second term contributes to the structure constants in this limit. We can further write:

$$\begin{aligned} \lim_{k\to 0} G_{LL'}(\boldsymbol{S}_{RR'};k) &= -4\pi\,\mathrm{i}^{\ell-\ell'+1}\sum_{L''}\mathrm{i}^{\ell''}\,C^{\ell m}_{\ell' m',\ell'' m''} \\ &\times\left[k^{\ell''+1}\,\frac{S^{\ell''}_{RR'}}{(2\ell''+1)} - \mathrm{i}\,\frac{1}{k^{\ell''}}\,\frac{(2\ell''-1)!!}{S^{\ell''+1}_{RR'}}\right] Y^*_{\ell'' m''}(\hat{\boldsymbol{S}}_{RR'}) \end{aligned} \tag{4.64}$$

However, the second term inside the parentheses is divergent. But because of the selection rules of the Gaunt coefficients according to which $\ell'' \le \ell+\ell'$ and $m'' = m-m'$, the term does not diverge (in the limit $k \to 0$) if the expression is multiplied by $k^{\ell+\ell'}$ so that we get:

$$\begin{aligned} \lim_{k\to 0}\left[k^{\ell+\ell'}\,G_{LL'}(\boldsymbol{S}_{RR'};k)\right] &= -4\pi\,\mathrm{i}^{\ell-\ell'+1}\sum_{L''}\mathrm{i}^{\ell''}\,C^{\ell m}_{\ell' m',\ell'' m''} \\ \times\left[k^{\ell+\ell'+\ell''+1}\,\frac{S^{\ell''}_{RR'}}{(2\ell''+1)} - \mathrm{i}\,k^{\ell+\ell'-\ell''}\,\frac{(2\ell''-1)!!}{S^{\ell''+1}_{RR'}}\right] &Y^*_{\ell'' m''}(\hat{\boldsymbol{S}}_{RR'}) \quad . \end{aligned} \tag{4.65}$$

As mentioned above the first term inside the brackets vanishes in the $k \to 0$ limit, whereas the second term vanishes only if $\ell'' \neq \ell+\ell'$. Hence we obtain with $\ell'' = \ell+\ell'$ and $m'' = m-m'$:

$$\begin{aligned} \lim_{k\to 0}\left[k^{\ell+\ell'}\,G_{LL'}(\boldsymbol{S}_{RR'};k)\right] &= (-1)^{\ell+1}\,4\pi\,C^{\ell m}_{\ell' m',(\ell+\ell')(m-m')} \\ &\times\frac{(2(\ell+\ell')-1)!!}{S^{\ell+\ell'+1}_{RR'}}\,Y^*_{(\ell+\ell')(m-m')}(\hat{\boldsymbol{S}}_{RR'}) \quad . \end{aligned} \tag{4.66}$$

Then by comparison with (4.58) one finds the following identity:

$$\lim_{k\to 0}\left[k^{\ell+\ell'}\,G_{LL'}(\boldsymbol{S}_{RR'};k)\right] = (-1)^{\ell+\ell'+1}\,\frac{(2\ell+1)!!\,(2\ell'+1)!!}{4\sqrt{\pi}}\,B_{LL'}(\boldsymbol{S}_{RR'}) \quad . \tag{4.67}$$

Or otherwise writing $B_{LL'}(\boldsymbol{S}_{RR'})$ in terms of the KKR structure constants:

$$B_{LL'}(\boldsymbol{S}_{RR'}) = (-1)^{\ell+\ell'+1}\frac{4\sqrt{\pi}}{(2\ell+1)!!\,(2\ell'+1)!!}\,\lim_{k\to 0}\left[k^{\ell+\ell'}\,G_{LL'}(\boldsymbol{S}_{RR'};k)\right] \quad . \tag{4.68}$$

5

Solution of Poisson's Equation for Space Filling Cells

Within the self-consistency cycle the electrostatic potential has to be calculated from the charge density by solving Poisson's equation in each iteration. If the charge distribution is spherically symmetric this can be done in a rather straightforward manner by using expansions in terms of multipole moments. However, as has been explained in chapter 4, in the case of a space filling cell geometry these expansions are no longer valid for neighbouring cells because of their overlapping bounding spheres. Several solutions to this problem have been suggested. One way is to numerically evaluate the integrals over the charge density which however is computationally demanding, cumbersome, and not a very elegant way to resolve this matter [Pai81]. Another approach which is especially suited for FLAPW methods has been suggested by Weinert [Wei80]. There the Fourier components of the interstitial charge density are matched to the multipole moments of the charge density inside non-overlapping spheres. For the construction of the potential within the KKR Method this approach is not a natural one, as an artificial division between an interstitial and a charge density inside muffin tins would have to be made. Furthermore the Fourier components, which are already present in the FLAPW method, would have to be computed first. Therefore the approach suggested by Gonis *et al.* [MGZC89] will be used in this work which is valid for a three dimensional periodic arrangement of potentials. The principle of the method has already been explained in section 4.3 and references to certain expressions derived there will be made.

In a first step the calculation of the electrostatic potential from the charge density will be explained for a three dimensional, periodic system. Then an expression for the total energy in terms of this potential will be obtained and a remark on spin-polarization concludes the chapter.

The Coulomb Potential

As the basic principle we assume that the Coulomb potential filling all space can be written as a superposition of potentials confined to Wigner Seitz cells around each lattice point in an infinite, periodic lattice. This can be denoted as:

$$V^c(\boldsymbol{r}) = \sum_R V^c_R(\boldsymbol{r}_R) \quad , \tag{5.1}$$

where $V^c_R(\boldsymbol{r}_R) = 0$ if $\boldsymbol{r}_R \notin \Omega_R$, and the notation of vectors has been given in section 4.3. Then the Coulomb potential of a cell centered at lattice point $\boldsymbol{R}$ denoted by $V^c_R(\boldsymbol{r}_R)$, which interacts with all electrostatic potentials in the system is (in Rydberg units) given by:

$$V^c_R(\boldsymbol{r}_R) = 2\int \mathrm{d}\boldsymbol{r}'_R \, \frac{\rho(\boldsymbol{r}'_R)}{|\boldsymbol{r}_R - \boldsymbol{r}'_R|} - \sum_{R'} \frac{2\mathrm{Z}_{R'}}{|\boldsymbol{r}_R - \boldsymbol{S}_{RR'}|} \quad , \tag{5.2}$$

where the integration extends over all space. When the integral is expressed as a sum of local integrals over Wigner-Seitz cells by using

$$\rho(\boldsymbol{r}'_R) = \sum_{R'} \rho_{R'}(\boldsymbol{r}'_R - \boldsymbol{S}_{RR'}) \, , \quad \rho_{R'}(\boldsymbol{r}'_R - \boldsymbol{S}_{RR'}) = 0 \text{ if } \boldsymbol{r}'_R - \boldsymbol{S}_{RR'} \notin \Omega_{R'} \, , \tag{5.3}$$

the following expression is obtained:

$$V^c_R(\boldsymbol{r}_R) = 2\sum_{R'} \left(\int_{\Omega_{R'}} \mathrm{d}\boldsymbol{r}'_{R'} \, \frac{\rho_{R'}(\boldsymbol{r}'_{R'})}{|\boldsymbol{r}_{R'} - \boldsymbol{r}'_{R'}|} - \frac{\mathrm{Z}_{R'}}{|\boldsymbol{r}_R - \boldsymbol{S}_{RR'}|} \right) \quad . \tag{5.4}$$

Two physically different terms can now be distinguished from the above summation. One term contains only contributions from the cell under consideration at lattice position $\boldsymbol{R}$. This is the *intra-cell* term and is explicitly given by:

$$V^{c,intra}_R(\boldsymbol{r}_R) = 2\int_{\Omega_R} \mathrm{d}\boldsymbol{r}'_R \, \frac{\rho_R(\boldsymbol{r}'_R)}{|\boldsymbol{r}_R - \boldsymbol{r}'_R|} - \frac{2\mathrm{Z}_R}{|\boldsymbol{r}_R|} \quad . \tag{5.5}$$

All the remaining terms of (5.4) form the *inter-cell* contribution as they describe how the potential at $\boldsymbol{R}$ is influenced by the charge distributions in all the other cells in the crystal. We can write the inter-cell terms in the following way:

$$V^{c,inter}_R(\boldsymbol{r}_R) = 2\sum_{\substack{R' \\ R' \neq R}} \left(\int_{\Omega_{R'}} \mathrm{d}\boldsymbol{r}'_{R'} \, \frac{\rho_{R'}(\boldsymbol{r}'_{R'})}{|\boldsymbol{r}_{R'} - \boldsymbol{r}'_{R'}|} - \frac{\mathrm{Z}_{R'}}{|\boldsymbol{r}_R - \boldsymbol{S}_{RR'}|} \right) \quad . \tag{5.6}$$

The intra-cell potential can be calculated in a straight forward manner, while more work is needed to compute the inter-cell potential because of the infinite summation and the fact that contributions from neighbouring cells have to be treated separately.

5.1.1 **The Intra-Cell Coulomb Potential**

This part of the Coulomb potential can be simply calculated by making use of the shape function technique and expansion (B.35). Hence by using shape functions to integrate over the exact shape of the Wigner-Seitz cell and by using the expansions (4.13) and (4.15) we get for the integral in (5.5):

$$\begin{aligned} \int\limits_{\Omega_R} \mathrm{d}\boldsymbol{r}'_R \, \frac{\rho_R(\boldsymbol{r}'_R)}{|\boldsymbol{r}_R - \boldsymbol{r}'_R|} &= \int\limits_{BS_R} \mathrm{d}\boldsymbol{r}'_R \, \frac{\rho_R(\boldsymbol{r}'_R)\, \sigma_R(\boldsymbol{r}'_R)}{|\boldsymbol{r}_R - \boldsymbol{r}'_R|} && (5.7) \\ &= \sum_{LL'} \int\limits_0^S r'^2_R \, \mathrm{d}r'_R \, \rho_{RL}(r'_R)\, \sigma_{RL'}(r'_R) \int \mathrm{d}\hat{\boldsymbol{r}}'_R \, \frac{Y^*_L(\hat{\boldsymbol{r}}'_R)\, Y_{L'}(\hat{\boldsymbol{r}}'_R)}{|\boldsymbol{r}_R - \boldsymbol{r}'_R|} \, . && (5.8) \end{aligned}$$

Now making use of the expansion

$$\frac{1}{|\boldsymbol{r}_R - \boldsymbol{r}'_R|} = \sum_{L''} \frac{4\pi}{2\ell''+1} \, \frac{r_<^{\ell''}}{r_>^{\ell''+1}} \, Y_{L''}(\hat{\boldsymbol{r}}_R)\, Y^*_{L''}(\hat{\boldsymbol{r}}'_R) \quad , \tag{5.9}$$

leads to the following expression for the integral:

$$\begin{aligned} &\int\limits_{\Omega_R} \mathrm{d}\boldsymbol{r}'_R \, \frac{\rho_R(\boldsymbol{r}'_R)}{|\boldsymbol{r}_R - \boldsymbol{r}'_R|} = \\ &\qquad \sum_{LL'L''} \frac{4\pi}{2\ell''+1} \int\limits_0^S r'^2_R \, \mathrm{d}r'_R \, \frac{r_<^{\ell''}}{r_>^{\ell''+1}} \, \rho_{RL}(r'_R)\, \sigma_{RL'}(r'_R)\, C^{L'}_{LL''}\, Y_{L''}(\hat{\boldsymbol{r}}_R) \quad . \end{aligned} \tag{5.10}$$

In the actual calculations we are in fact not interested in the potential that depends on three dimensional coordinates, but in the only radially dependent (and therefore L dependent) expansion coefficients of the following series:

$$V_R^{c,intra}(\boldsymbol{r}_R) = \sum_L V_{RL}^{c,intra}(r_R)\, Y_L(\hat{\boldsymbol{r}}_R) \quad . \tag{5.11}$$

Comparison of this expansion with (5.10) and taking the term containing the nuclear charge in (5.5) into account, yields an expression for the expansion coefficients:

$$V_{RL}^{c,intra}(r_R) = \frac{4\pi}{2\ell+1} \int\limits_0^S r'^2_R \, \mathrm{d}r'_R \, \frac{r_<^{\ell}}{r_>^{\ell+1}} \, \tilde{\rho}^{(2)}_{RL}(r'_R) - \frac{2\mathrm{Z}_R}{r_R} \sqrt{4\pi}\, \delta_{\ell 0}\, \delta_{m0} \quad , \tag{5.12}$$

where the indices L and L'' have been renamed and a modified charge density was defined through:

$$\tilde{\rho}^{(2)}_{RL}(r'_R) = \sum_{L'L''} C^{L'}_{LL''}\, \sigma_{RL'}(r'_R)\, \rho_{RL''}(r'_R) \quad . \tag{5.13}$$

As a final step the radial integral in (5.12) needs to be expressed in a computationally useful way. To do this we make use of (4.37) to obtain:

$$\begin{aligned} V^{c,intra}_{RL}(r_R) &= \frac{4\pi}{2\ell+1} \int_0^{r_R} r'^2_R\, \mathrm{d}r'_R\, \frac{r'^{\ell}_R}{r^{\ell+1}_R}\, \tilde{\rho}^{(2)}_{RL}(r'_R) \\ &\quad + \frac{4\pi}{2\ell+1} \int_{r_R}^{S} r'^2_R\, \mathrm{d}r'_R\, \frac{r^{\ell}_R}{r'^{\ell+1}_R}\, \tilde{\rho}^{(2)}_{RL}(r'_R) - \frac{2\mathrm{Z}_R}{r_R} \sqrt{4\pi}\, \delta_{\ell 0}\, \delta_{m0} \quad . \end{aligned} \tag{5.14}$$

This can be written in a more transparent form by defining the two functions:

$$A_{RL}(r_R) = \frac{4\pi}{2\ell+1} \int_0^{r_R} \mathrm{d}r'_R\, r'^{\ell+2}_R\, \tilde{\rho}^{(2)}_{RL}(r'_R) \quad , \tag{5.15}$$

$$B_{RL}(r_R) = \frac{4\pi}{2\ell+1} \int_{r_R}^{S} \mathrm{d}r'_R\, r'^{-\ell+1}_R\, \tilde{\rho}^{(2)}_{RL}(r'_R) \quad . \tag{5.16}$$

Hence as a final expression for the expansion coefficients of the intra cell Coulomb potential we can write:

$$V^{c,intra}_{RL}(r_R) = r^{-\ell-1}_R\, A_{RL}(r_R) + r^{\ell}_R\, B_{RL}(r_R) - \frac{2\mathrm{Z}_R}{r_R} \sqrt{4\pi}\, \delta_{\ell 0}\, \delta_{m0} \quad . \tag{5.17}$$

5.1.2 **The Inter-Cell Coulomb Potential**

Turning now to the inter-cell potential we have to evaluate equation (5.6):

$$V^{c,inter}_{R}(\boldsymbol{r}_R) = 2 \sum_{\substack{R' \\ R' \neq R}} \int_{\Omega_{R'}} \mathrm{d}\boldsymbol{r}'_{R'}\, \frac{\rho_{R'}(\boldsymbol{r}'_{R'})}{|\boldsymbol{r}_{R'} - \boldsymbol{r}'_{R'}|} - \sum_{\substack{R' \\ R' \neq R}} \frac{2\mathrm{Z}_{R'}}{|\boldsymbol{r}_R - \boldsymbol{S}_{RR'}|} \quad . \tag{5.18}$$

In order to calculate this expression three terms can be distinguished. One term that describes the contributions from neighbouring cells (superscript *nn*), one that includes all remaining cells (labelled by the superscript *no* for the “non overlapping” bounding spheres), and one term that sums over the nuclear charges (superscript *nuc*):

$$V^{c,inter}_{R}(\boldsymbol{r}_R) = V^{c,nn}_{R}(\boldsymbol{r}_R) + V^{c,no}_{R}(\boldsymbol{r}_R) + V^{c,nuc}_{R}(\boldsymbol{r}_R) \quad . \tag{5.19}$$

Consequently the three terms are explicitly given by:

$$V_R^{c,nn}(\boldsymbol{r}_R) = 2\sum_{\mathcal{R}} \int_{\Omega_{R'}} \mathrm{d}\boldsymbol{r}'_{R'} \, \frac{\rho_{R'}(\boldsymbol{r}'_{R'})}{|\boldsymbol{r}_{R'} - \boldsymbol{r}'_{R'}|} \quad , \tag{5.20}$$

$$V_R^{c,no}(\boldsymbol{r}_R) = 2\sum_{\mathcal{S}} \int_{\Omega_{R'}} \mathrm{d}\boldsymbol{r}'_{R'} \, \frac{\rho_{R'}(\boldsymbol{r}'_{R'})}{|\boldsymbol{r}_{R'} - \boldsymbol{r}'_{R'}|} \quad , \tag{5.21}$$

$$V_R^{c,nuc}(\boldsymbol{r}_R) = -\sum_{\substack{R' \\ R' \neq R}} \frac{2Z_{R'}}{|\boldsymbol{r}_R - \boldsymbol{S}_{RR'}|} \quad . \tag{5.22}$$

It is didactically of advantage to start with the evaluation of the second and third equation and consider the term containing the nearest neighbour contributions at the end.

Non Overlapping Bounding Spheres

Once more the shape function technique is used to evaluate the integral in (5.21). Hence by furthermore making use of $\boldsymbol{r}_{R'} = \boldsymbol{r}_R - \boldsymbol{S}_{RR'}$ the integral transforms to:

$$\begin{aligned} V_R^{c,no}(\boldsymbol{r}_R) &= 2\sum_{\mathcal{S}} \int_{BS_{R'}} \mathrm{d}\boldsymbol{r}'_{R'} \, \frac{\rho_{R'}(\boldsymbol{r}'_{R'})\,\sigma_{R'}(\boldsymbol{r}'_{R'})}{|\boldsymbol{r}_R - \boldsymbol{r}'_{R'} - \boldsymbol{S}_{RR'}|} & (5.23) \\ &= \sum_L r_R^\ell \, Y_L(\hat{\boldsymbol{r}}_R) \, \frac{8\pi}{2\ell+1} \\ &\quad \times \sum_{\mathcal{S}} \int_{BS_{R'}} \mathrm{d}\boldsymbol{r}'_{R'} \, \rho_{R'}(\boldsymbol{r}'_{R'})\,\sigma_{R'}(\boldsymbol{r}'_{R'}) \frac{Y_L^*(\widehat{\boldsymbol{r}'_{R'} + \boldsymbol{S}_{RR'}})}{|\boldsymbol{r}'_{R'} + \boldsymbol{S}_{RR'}|^{\ell+1}} \quad , & (5.24) \end{aligned}$$

where in the second step expansion (B.35) and the fact that $r_R < |\boldsymbol{r}'_{R'} + \boldsymbol{S}_{RR'}|$ is always true has been used. Subsequently inserting the following expansion:

$$\begin{aligned} \frac{Y_{\ell m}^*(\widehat{\boldsymbol{r}'_{R'} + \boldsymbol{S}_{RR'}})}{|\boldsymbol{r}'_{R'} + \boldsymbol{S}_{RR'}|^{\ell+1}} &= \sum_{L'} (-1)^{\ell'} \frac{4\pi \; (2(\ell+\ell')-1)!!}{(2\ell-1)!!\,(2\ell+1)!!} \, C_{\ell m,(\ell+\ell')(m'-m)}^{\ell' m'} \\ &\quad \times \frac{Y_{(\ell+\ell')(m'-m)}(\hat{\boldsymbol{S}}_{RR'})}{|\boldsymbol{S}_{RR'}|^{\ell+\ell'+1}} \, r'^{\ell'}_{R'} \, Y_{\ell' m'}^*(\hat{\boldsymbol{r}}'_{R'}) \quad , & (5.25) \end{aligned}$$

where use of the identity

$$Y_{(\ell+\ell')(m'-m)}(\hat{\boldsymbol{S}}_{R'R}) = (-1)^{\ell+\ell'} \, Y_{(\ell+\ell')(m'-m)}(\hat{\boldsymbol{S}}_{RR'}) \quad , \tag{5.26}$$

has already been made, we arrive at an equation for this part of the Coulomb potential:

$$\begin{aligned} V_R^{c,no}(\boldsymbol{r}_R) &= \sum_L r_R^\ell \, Y_L(\hat{\boldsymbol{r}}_R) \sum_{\mathcal{S}} \sum_{L'} (-1)^{\ell'} \frac{32\pi^2 \; (2(\ell+\ell')-1)!!}{(2\ell-1)!! \, (2\ell+1)!!} \, C^{\ell' m'}_{\ell m,(\ell+\ell')(m'-m)} \\ &\quad \times \frac{Y_{(\ell+\ell')(m'-m)}(\hat{\boldsymbol{S}}_{RR'})}{|\boldsymbol{S}_{RR'}|^{\ell+\ell'+1}} \\ &\quad \times \int\limits_{BS_{R'}} \mathrm{d}\boldsymbol{r}'_{R'} \, \rho_{R'}(\boldsymbol{r}'_{R'}) \, \sigma_{R'}(\boldsymbol{r}'_{R'}) \, r'^{\ell'}_{R'} \, Y^*_{\ell' m'}(\hat{\boldsymbol{r}}'_{R'}) \quad . \end{aligned} \tag{5.27}$$

In order to be able to define structure constants in the same way as in (4.58) the following relation can be substituted into the above equation:

$$\begin{aligned} &\sum_{m'} C^{\ell' m'}_{\ell m,(\ell+\ell')(m'-m)} \, Y_{(\ell+\ell')(m'-m)}(\hat{\boldsymbol{S}}_{RR'}) \, Y^*_{\ell' m'}(\hat{\boldsymbol{r}}'_{R'}) = \\ &\qquad \sum_{m'} C^{\ell m}_{\ell' m',(\ell+\ell')(m-m')} \, Y^*_{(\ell+\ell')(m-m')}(\hat{\boldsymbol{S}}_{RR'}) \, Y^*_{\ell' m'}(\hat{\boldsymbol{r}}'_{R'}) \quad . \end{aligned} \tag{5.28}$$

With this we can write instead of (5.27):

$$V_R^{c,no}(\boldsymbol{r}_R) = \sum_L r_R^\ell \, Y_L(\hat{\boldsymbol{r}}_R) \sum_{\mathcal{S}} \sum_{L'} B_{LL'}(\boldsymbol{S}_{RR'}) \, Q_{R'L'} \quad . \tag{5.29}$$

Now in there the constants $B_{LL'}(\boldsymbol{S}_{RR'})$ which depend only on the position of the lattice points have been defined through:

$$\begin{aligned} B_{LL'}(\boldsymbol{S}_{RR'}) &= (-1)^{\ell'} \frac{8\pi \; (2(\ell+\ell')-1)!!}{(2\ell+1)!! \, (2\ell'+1)!!} \sqrt{4\pi} \, C^{\ell m}_{\ell' m',(\ell+\ell')(m-m')} \\ &\quad \times \frac{Y^*_{(\ell+\ell')(m-m')}(\hat{\boldsymbol{S}}_{RR'})}{|\boldsymbol{S}_{RR'}|^{\ell+\ell'+1}} \quad , \end{aligned} \tag{5.30}$$

and the multipole moments Q_{RL} were defined as usually by:

$$Q_{RL} := \sqrt{4\pi} \int\limits_{BS_R} \mathrm{d}\boldsymbol{r}_R \, \rho_R(\boldsymbol{r}_R) \, \sigma_R(\boldsymbol{r}_R) \, r_R^\ell \, Y^*_{\ell m}(\hat{\boldsymbol{r}}_R) \quad . \tag{5.31}$$

Alternatively the multipole moments can be written in terms of only a radial integral making use of (5.13):

$$Q_{RL} = \sqrt{4\pi} \int\limits_0^S r_R^{\ell+2} \, \mathrm{d}r_R \, \tilde{\rho}^{(2)}_{RL}(r_R) \quad . \tag{5.32}$$

To proceed we will evaluate equation (5.22) by inserting expansion (B.35). Clearly $|\boldsymbol{r}_R| < |\boldsymbol{S}_{RR'}|$ is true if r_R is confined to the Wigner-Seitz cell around $\boldsymbol{R}$ and we obtain:

$$V_R^{c,nuc}(\boldsymbol{r}_R) = -\sum_L r_R^\ell \, Y_L(\hat{\boldsymbol{r}}_R) \, \frac{8\pi}{2\ell+1} \sum_{\substack{R' \\ R' \neq R}} \frac{Y_L^*(\hat{\boldsymbol{S}}_{RR'})}{|\boldsymbol{S}_{RR'}|^{\ell+1}} \, \mathrm{Z}_{R'} \quad . \tag{5.33}$$

Returning now to the structure constants defined in (5.30) we can calculate the term for $L' = (0,0)$ which is then given by:

$$B_{L(0,0)}(\boldsymbol{S}_{RR'}) = \frac{8\pi}{2\ell+1} \, \frac{Y_{\ell m}^*(\hat{\boldsymbol{S}}_{RR'})}{|\boldsymbol{S}_{RR'}|^{\ell+1}} \quad . \tag{5.34}$$

Making use of this identity, the expression for $V_R^{c,nuc}(\boldsymbol{r}_R)$ can be rewritten in the following way:

$$V_R^{c,nuc}(\boldsymbol{r}_R) = -\sum_L r_R^\ell \, Y_L(\hat{\boldsymbol{r}}_R) \sum_{\substack{R' \\ R' \neq R}} B_{L(0,0)}(\boldsymbol{S}_{RR'}) \, \mathrm{Z}_{R'} \quad . \tag{5.35}$$

Contrary to equation (5.29) the summation here also includes neighbouring cells with overlapping bounding spheres. However by using the following redefinition of the multipole moments:

$$\hat{Q}_{RL} := Q_{RL} - \delta_{\ell 0} \, \delta_{m0} \, \mathrm{Z}_{R'} \quad , \tag{5.36}$$

the two potentials can be added up and as can be easily shown one gets the compact expression:

$$\begin{aligned} V_R^{c,no}(\boldsymbol{r}_R) + V_R^{c,nuc}(\boldsymbol{r}_R) \quad &= \quad \sum_L r_R^\ell \, Y_L(\hat{\boldsymbol{r}}_R) \sum_{L'} \sum_{\substack{R' \\ R' \neq R}} B_{LL'}(\boldsymbol{S}_{RR'}) \, \hat{Q}_{R'L'} \\ &\quad - \sum_L r_R^\ell \, Y_L(\hat{\boldsymbol{r}}_R) \sum_{L'} \sum_{\mathcal{R}} B_{LL'}(\boldsymbol{S}_{RR'}) \, Q_{R'L'} \quad . \end{aligned} \tag{5.37}$$

The problems involved in the calculation of the terms coming from neighbouring cells have already been explained in section 4.3. Therefore use can be made of some results already derived there. Let's first denote the expression that has to be evaluated once again:

$$V_R^{c,nn}(\boldsymbol{r}_R) = 2\sum_{\mathcal{R}} \int\limits_{\Omega_{R'}} \mathrm{d}\boldsymbol{r}'_{R'}\, \frac{\rho_{R'}(\boldsymbol{r}'_{R'})}{|\boldsymbol{r}_{R'} - \boldsymbol{r}'_{R'}|} \quad . \tag{5.38}$$

Since $|\boldsymbol{r}_{R'} - \boldsymbol{r}'_{R'}| = |\boldsymbol{r}_R - \boldsymbol{r}'_R|$ we can use the result that has been found in section 4.3, namely that the inverse of the difference vector in this equation can be written as (c.f. (4.48)):

$$\begin{aligned} \frac{1}{|\boldsymbol{r}_R - \boldsymbol{r}'_R|} &= 2\pi \sum_L b_{RR'}^{\ell}\, Y_{\ell m}(\hat{\boldsymbol{b}}_{RR'}) \sum_{L'} r_R^{\ell'}\, Y_{\ell' m'}(\hat{\boldsymbol{r}}_R)\, C_{\ell m,\ell' m'}^{(\ell+\ell')(m+m')} \\ &\quad \times \sum_{L''} B_{LL'L''}(\boldsymbol{S}_{RR'} + \boldsymbol{b}_{RR'})\, \sqrt{4\pi}\; r_{R'}^{\prime \ell''}\, Y_{\ell'' m''}^{*}(\hat{\boldsymbol{r}}'_{R'}) \quad , \end{aligned} \tag{5.39}$$

where the constants $B_{LL'L''}(\boldsymbol{S}_{RR'} + \boldsymbol{b}_{RR'})$ are given by 4.49. Inserting this expansion into (5.38) we get for this potential:

$$\begin{aligned} V_R^{c,nn}(\boldsymbol{r}_R) &= \sum_{\mathcal{R}} \sum_L b_{RR'}^{\ell}\, Y_{\ell m}(\hat{\boldsymbol{b}}_{RR'}) \sum_{L'} r_R^{\ell'}\, Y_{\ell' m'}(\hat{\boldsymbol{r}}_R)\, 4\pi\, C_{\ell m,\ell' m'}^{(\ell+\ell')(m+m')} \\ &\quad \times \sum_{L''} B_{LL'L''}(\boldsymbol{S}_{RR'} + \boldsymbol{b}_{RR'})\, Q_{R'L''} \quad . \end{aligned} \tag{5.40}$$

Where once more the multipole moments have been identified as:

$$Q_{R'L''} = \sqrt{4\pi} \int\limits_{\Omega_{R'}} \mathrm{d}\boldsymbol{r}'_{R'}\, r_{R'}^{\prime \ell''}\, Y_{\ell'' m''}^{*}(\hat{\boldsymbol{r}}'_{R'})\, \rho_{R'}(\boldsymbol{r}'_{R'}) \quad . \tag{5.41}$$

Combining the results (5.37) and (5.40) an expression for the inter-cell potential can now be given. Either the three terms can be simply added up or by observing the fact that the structural constants $B_{LL'L''}(\boldsymbol{S}_{RR'} + \boldsymbol{b}_{RR'})$ simply reduce to $B_{LL'}(\boldsymbol{S}_{RR'} + \boldsymbol{b}_{RR'})$ (c.f. definition in (5.30)) for $L = (0,0)$ we obtain the result:

$$\begin{aligned} V_R^{c,inter}(\boldsymbol{r}_R) &= \sum_L r_R^{\ell}\, Y_L(\hat{\boldsymbol{r}}_R) \sum_{\substack{R' \\ R' \neq R}} \sum_{L'} B_{LL'}(\boldsymbol{S}_{RR'})\, \hat{Q}_{R'L'} \\ &\quad + \sum_L r_R^{\ell}\, Y_L(\hat{\boldsymbol{r}}_R) \sum_{\mathcal{R}} \sum_{L'} \left[B_{LL'}(\boldsymbol{S}_{RR'} + \boldsymbol{b}_{RR'}) - B_{LL'}(\boldsymbol{S}_{RR'})\right] Q_{R'L'} \\ &\quad + \sum_{\mathcal{R}} \sum_{\substack{L \\ \ell > 0}} b_{RR'}^{\ell}\, Y_{\ell m}(\hat{\boldsymbol{b}}_{RR'}) \sum_{L'} r_R^{\ell'}\, Y_{\ell' m'}(\hat{\boldsymbol{r}}_R)\, 4\pi\, C_{\ell m,\ell' m'}^{(\ell+\ell')(m+m')} \\ &\quad \times \sum_{L''} B_{LL'L''}(\boldsymbol{S}_{RR'} + \boldsymbol{b}_{RR'})\, Q_{R'L''} \quad . \end{aligned} \tag{5.42}$$

The Coulomb Energy in Terms of the Electrostatic Potential

Within the code it is of advantage to compute the Coulomb energy in terms of the Coulomb potential which reduces the computational effort. Otherwise expressions which are more or less identical have to be calculated twice, which is not very efficient. In order to arrive at such a formulation we use equation (4.30) as a starting point:

$$\begin{aligned} U[\rho] \;&=\; \int \mathrm{d}\boldsymbol{r}_R\, \rho(\boldsymbol{r}_R) \sum_{R'} \left(\int\limits_{\Omega_{R'}} \mathrm{d}\boldsymbol{r}'_{R'}\, \frac{\rho_{R'}(\boldsymbol{r}'_{R'})}{|\boldsymbol{r}_{R'} - \boldsymbol{r}'_{R'}|} - \frac{2\,\mathrm{Z}_{R'}}{|\boldsymbol{r}_R - \boldsymbol{S}_{RR'}|} \right) \\ &\quad + \sum_{\substack{R'R'' \\ R''\neq R'}} \frac{\mathrm{Z}_{R'}\,\mathrm{Z}_{R''}}{|\boldsymbol{R}' - \boldsymbol{R}''|} \quad . \end{aligned} \tag{5.43}$$

According to (5.4) the electrostatic potential is generally given by

$$V^c_R(\boldsymbol{r}_R) = 2 \sum_{R'} \left(\int\limits_{\Omega_{R'}} \mathrm{d}\boldsymbol{r}'_{R'}\, \frac{\rho_{R'}(\boldsymbol{r}'_{R'})}{|\boldsymbol{r}_{R'} - \boldsymbol{r}'_{R'}|} - \frac{\mathrm{Z}_{R'}}{|\boldsymbol{r}_R - \boldsymbol{S}_{RR'}|} \right) \quad . \tag{5.44}$$

Then by comparison with the previous equation the electrostatic energy can also be written in terms of $V^c_R(\boldsymbol{r}_R)$ as:

$$\begin{aligned} U[\rho] \;&=\; \frac{1}{2} \int \mathrm{d}\boldsymbol{r}_R\, \rho(\boldsymbol{r}_R)\, V^c_R(\boldsymbol{r}_R) - \int \mathrm{d}\boldsymbol{r}_R\, \rho(\boldsymbol{r}_R) \left(\sum_{R'} \frac{\mathrm{Z}_{R'}}{|\boldsymbol{r}_R - \boldsymbol{S}_{RR'}|} \right) \\ &\quad + \sum_{\substack{R'R'' \\ R''\neq R'}} \frac{\mathrm{Z}_{R'}\,\mathrm{Z}_{R''}}{|\boldsymbol{R}' - \boldsymbol{R}''|} \end{aligned} \tag{5.45}$$

$$\begin{aligned} &=\; \frac{1}{2} \int \mathrm{d}\boldsymbol{r}_R\, \rho(\boldsymbol{r}_R)\, V^c_R(\boldsymbol{r}_R) \\ &\quad - \sum_{R'} \mathrm{Z}_{R'} \left(\int \mathrm{d}\boldsymbol{r}_R\, \frac{\rho(\boldsymbol{r}_R)}{|\boldsymbol{r}_R - \boldsymbol{S}_{RR'}|} - \sum_{\substack{R'' \\ R''\neq R'}} \frac{\mathrm{Z}_{R''}}{|\boldsymbol{R}' - \boldsymbol{R}''|} \right) \quad . \end{aligned} \tag{5.46}$$

The integral inside the parentheses can be rewritten as a sum over individual cells by using:

$$\rho(\boldsymbol{r}_R) = \sum_{R''} \rho_{R''}(\boldsymbol{r}_R - \boldsymbol{S}_{RR''}) = \sum_{R''} \rho_{R''}(\boldsymbol{r}_{R''}) \quad , \tag{5.47}$$

so that we get

$$\int \mathrm{d}\boldsymbol{r}_R \, \frac{\rho_R(\boldsymbol{r}_R)}{|\boldsymbol{r}_R - \boldsymbol{S}_{RR'}|} = \sum_{R''} \int\limits_{\Omega_{R''}} \mathrm{d}\boldsymbol{r}_{R''} \, \frac{\rho_{R''}(\boldsymbol{r}_{R''})}{|\boldsymbol{r}_{R''} - \boldsymbol{S}_{R''R'}|} \quad . \tag{5.48}$$

Using (5.47) and (5.48) in the formula for the Coulomb energy one obtains:

$$\begin{aligned} U[\rho] &= \frac{1}{2} \sum_{R'} \int\limits_{\Omega_{R'}} \mathrm{d}\boldsymbol{r}_{R'} \, \rho_{R'}(\boldsymbol{r}_{R'}) \, V^c_{R'}(\boldsymbol{r}_{R'}) \\ &\quad - \sum_{R'} \mathrm{Z}_{R'} \left(\sum_{R''} \int\limits_{\Omega_{R''}} \mathrm{d}\boldsymbol{r}_{R''} \, \frac{\rho_{R''}(\boldsymbol{r}_{R''})}{|\boldsymbol{r}_{R''} - \boldsymbol{S}_{R''R'}|} - \sum_{\substack{R'' \\ R'' \neq R'}} \frac{\mathrm{Z}_{R''}}{|\boldsymbol{R}' - \boldsymbol{R}''|} \right) \quad . \end{aligned} \tag{5.49}$$

We have once again written all global integrals now in terms of local integrals over all cells in the system. The above expression can be further modified. By taking the term with $R'' = R'$ out of the summation over R'' we consequently get after some rearrangement of the terms:

$$\begin{aligned} U[\rho] &= \frac{1}{2} \sum_{R'} \left[\int\limits_{\Omega_{R'}} \mathrm{d}\boldsymbol{r}_{R'} \, \rho_{R'}(\boldsymbol{r}_{R'}) \left(V^c_{R'}(\boldsymbol{r}_{R'}) - \frac{2\mathrm{Z}_{R'}}{|\boldsymbol{r}_{R'}|} \right) \right. \\ &\quad \left. - \, 2\mathrm{Z}_{R'} \sum_{\substack{R'' \\ R'' \neq R'}} \left(\int\limits_{\Omega_{R''}} \mathrm{d}\boldsymbol{r}_{R''} \, \frac{\rho_{R''}(\boldsymbol{r}_{R''})}{|\boldsymbol{r}_{R''} - \boldsymbol{S}_{R''R'}|} - \frac{\mathrm{Z}_{R''}}{|\boldsymbol{R}' - \boldsymbol{R}''|} \right) \right] \quad . \end{aligned} \tag{5.50}$$

The last term in this equation deserves some consideration. Recalling the expression for the inter-cell Coulomb potential, equation (5.6), which can be rewritten as:

$$V^{c,inter}_{R'}(\boldsymbol{r}'_{R'}) = 2 \sum_{\substack{R'' \\ R'' \neq R'}} \left(\int\limits_{\Omega_{R''}} \mathrm{d}\boldsymbol{r}_{R''} \, \frac{\rho_{R''}(\boldsymbol{r}_{R''})}{|\boldsymbol{r}_{R''} - \boldsymbol{r}'_{R'} - \boldsymbol{S}_{R''R'}|} - \frac{\mathrm{Z}_{R'}}{|\boldsymbol{r}'_{R'} + \boldsymbol{R}' - \boldsymbol{R}''|} \right) , \tag{5.51}$$

this function can be evaluated for $\boldsymbol{r}'_{R'} = 0$:

$$V^{c,inter}_{R'}(0) = 2 \sum_{\substack{R'' \\ R'' \neq R'}} \left(\int\limits_{\Omega_{R''}} \mathrm{d}\boldsymbol{r}_{R''} \, \frac{\rho_{R''}(\boldsymbol{r}_{R''})}{|\boldsymbol{r}_{R''} - \boldsymbol{S}_{R''R'}|} - \frac{\mathrm{Z}_{R'}}{|\boldsymbol{R}' - \boldsymbol{R}''|} \right) \quad . \tag{5.52}$$

One can easily see that the Coulomb energy per cell can now be written in the following way:

$$U_R[\rho] = \frac{1}{2} \int\limits_{\Omega_R} \mathrm{d}\boldsymbol{r}_R \, \rho_R(\boldsymbol{r}_R) \left(V^c_R(\boldsymbol{r}_R) - \frac{2\mathrm{Z}_R}{|\boldsymbol{r}_R|} \right) - \frac{1}{2} \, \mathrm{Z}_R \, V^{c,inter}_R(0) \quad . \tag{5.53}$$

5.2.1 **An Expression for the Total Energy**

Finally, with the same argument as above, namely in order to avoid calculating things twice we can use the last equation (5.53) to obtain a compact expression for the total energy. We have seen in chapter 4 that the total energy per cell is the sum of kinetic, Coulomb, and exchange-correlation terms. Summarizing we can write this as:

$$\begin{aligned} E_{R,tot} &= E_{R,c} + E_{R,v} - \int\limits_{\Omega_R} \mathrm{d}\boldsymbol{r}_R\, \rho_R(\boldsymbol{r}_R)\, V_R(\boldsymbol{r}_R) \\ &\quad + \frac{1}{2} \int\limits_{\Omega_R} \mathrm{d}\boldsymbol{r}_R\, \rho_R(\boldsymbol{r}_R) \left(V_R^c(\boldsymbol{r}_R) - \frac{2\mathrm{Z}_R}{|\boldsymbol{r}_R|} \right) - \frac{1}{2}\, \mathrm{Z}_R\, V_R^{c,inter}(0) \\ &\quad + \int\limits_{\Omega_R} \mathrm{d}\boldsymbol{r}_R\, \rho_R(\boldsymbol{r})\, \epsilon_{xc}\left[\rho_R(\boldsymbol{r})\right] \quad , \end{aligned} \tag{5.54}$$

where $V_R(\boldsymbol{r})$ represents the sum of Coulomb and exchange-correlation potential:

$$V_R(\boldsymbol{r}_R) = V_R^c(\boldsymbol{r}_R) + V_R^{xc}(\boldsymbol{r}_R) \quad . \tag{5.55}$$

With this and some rearrangement of terms one finds that the total energy may be cast in the following form:

$$\begin{aligned} E_{R,tot} &= E_{R,c} + E_{R,v} - \frac{1}{2} \int\limits_{\Omega_R} \mathrm{d}\boldsymbol{r}_R\, \rho_R(\boldsymbol{r}_R) \left(V_R^c(\boldsymbol{r}_R) - \frac{2\mathrm{Z}_R}{|\boldsymbol{r}_R|} \right) \\ &\quad - \frac{1}{2}\, \mathrm{Z}_R\, V_R^{c,inter}(0) + \int\limits_{\Omega_R} \mathrm{d}\boldsymbol{r}_R\, \rho_R(\boldsymbol{r}_R) \left(\epsilon_{xc}\left[\rho_R(\boldsymbol{r}_R)\right] - V_R^{xc}(\boldsymbol{r}_R) \right) \quad . \end{aligned} \tag{5.56}$$

5.2.2 **Note on Spin-Polarization**

In the case of spin-polarized calculations, one ends up with charge densities for *spin up* and *spin down* electrons. Hence the total charge density is the sum of these two terms:

$$\rho_R(\boldsymbol{r}) = \rho_R^{\uparrow}(\boldsymbol{r}) + \rho_R^{\downarrow}(\boldsymbol{r}) \quad . \tag{5.57}$$

Accordingly, the exchange-correlation potential has a spin up and a spin down component. The corresponding integral, which appears in the expression for the kinetic energy is then actually given by:

$$\int\limits_{\Omega_R} \mathrm{d}\boldsymbol{r}\, \rho_R(\boldsymbol{r})\, V_R^{xc}(\boldsymbol{r}) = \int\limits_{\Omega_R} \mathrm{d}\boldsymbol{r}\, \left(\rho_R^{\uparrow}(\boldsymbol{r})\, V_R^{xc,\uparrow}(\boldsymbol{r}) + \rho_R^{\downarrow}(\boldsymbol{r})\, V_R^{xc,\downarrow}(\boldsymbol{r}) \right) \quad . \tag{5.58}$$

The term on the right hand side of this equation can be further manipulated in the following way:

$$\begin{aligned}\int\limits_{\Omega_R} \mathrm{d}\boldsymbol{r}\,\rho_R(\boldsymbol{r})\,V_R^{xc}(\boldsymbol{r}) \;&=\; \int\limits_{\Omega_R} \mathrm{d}\boldsymbol{r}\,\left(\rho_R^{\uparrow}(\boldsymbol{r})+\rho_R^{\downarrow}(\boldsymbol{r})\right)\,\frac{V_R^{xc,\uparrow}(\boldsymbol{r})+V_R^{xc,\downarrow}(\boldsymbol{r})}{2}\\ &\quad+\int\limits_{\Omega_R} \mathrm{d}\boldsymbol{r}\,\left(\rho_R^{\uparrow}(\boldsymbol{r})-\rho_R^{\downarrow}(\boldsymbol{r})\right)\,\frac{V_R^{xc,\uparrow}(\boldsymbol{r})-V_R^{xc,\downarrow}(\boldsymbol{r})}{2} \qquad (5.59)\\ &=\; \int\limits_{\Omega_R} \mathrm{d}\boldsymbol{r}\,\rho_R(\boldsymbol{r})\,\bar{V}_R^{xc}(\boldsymbol{r})\\ &\quad+\int\limits_{\Omega_R} \mathrm{d}\boldsymbol{r}\,\left(\rho_R^{\uparrow}(\boldsymbol{r})-\rho_R^{\downarrow}(\boldsymbol{r})\right)\,B_R^{xc}(\boldsymbol{r}) \quad . \qquad (5.60)\end{aligned}$$

In the last step the obvious definitions:

$$B_R^{xc}(\boldsymbol{r}) = \frac{V_R^{xc,\uparrow}(\boldsymbol{r})-V_R^{xc,\downarrow}(\boldsymbol{r})}{2} \quad , \tag{5.61}$$

and

$$\bar{V}_R^{xc}(\boldsymbol{r}) = \frac{V_R^{xc,\uparrow}(\boldsymbol{r})+V_R^{xc,\downarrow}(\boldsymbol{r})}{2} \quad , \tag{5.62}$$

have been used.

A

Solutions and Numerical Treatment of the Radial Schrödinger Equation

Within the full potential KKR theory it is necessary to compute the regular and irregular solutions to the radial Schrödinger or Dirac equation. Though the solutions of these equations for a full potential are angular dependent the problem may be separated into a spherically symmetric and a non-spherical portion. But initially one has to obtain only the solutions for the spherically symmetric problem, for which the regular and irregular solutions depend only on the distance from the origin of the potential sphere. This has to be done only for one atomic site and hence this is called the single site problem. By computing the radial solutions one can determine the single site t-matrix which is an important quantity in multiple scattering theory. The t-matrix is site–diagonal and, for a non-spherical potential, non-diagonal in the angular momentum indices. However, for a muffin tin or ASA potential it is diagonal with respect to site as well as in angular momenta and for that reason easy to calculate.

The regular and irregular solutions $R_\ell(r)$ and $I_\ell(r)$ mathematically have to fulfill the Wronski relation,

$$R_\ell(r)I'_\ell(r) - R'_\ell(r)I_\ell(r) \neq 0 \quad , \tag{A.1}$$

where $f'(r) = \mathrm{d}f(r)/\mathrm{d}r$. Hence any pair of regular and irregular, linear independent solutions necessarily need to meet this requirement. Since for an arbitrary potential the solutions are seldom known analytically, they have to be computed by numerical integration. Standard procedures are e.g. Adams or Adams-Bashforth integration routines together with Runge-Kutta [Frö85][GW89] [FM87] extrapolation for initial values. Their accuracy is however limited and can in principle only be improved by reducing the step size of the integration–mesh or by enhancing the order of the algorithms as will be exhaustively explained later.

In order to choose the proper algorithm it is necessary to know the asymptotic behaviour of the regular and irregular wave functions. At a large distance from the scattering potential they behave as if no potential was present except for a phase shift δ_ℓ. So for non-relativistic electrons the Schrödinger equation for a vanishing potential has to be solved in that region (see e.g. [Wei90]). The resulting wave functions need to be matched at the maximum radius of the potential sphere with the numerically computed wave functions inside the sphere.

A.1

Regular and Irregular Solutions

The initial task is now to solve the single–site problem, which means that the regular and irregular solutions for a single potential at an atomic site have to be obtained. In the (non-relativistic) Schrödinger equation

$$H\psi(\boldsymbol{r}) = \left(-\nabla^2 + U(\boldsymbol{r})\right)\psi(\boldsymbol{r}) = E\psi(\boldsymbol{r}) \tag{A.2}$$

has to be solved. This can be facilitated by dividing the space–filling potential, U, the so–called *full potential*, into a spherical and a non–spherical partition, $V(r)$ and $\Delta V(\mathbf{r})$, such that

$$U(\boldsymbol{r}) = V(r) + \Delta V(\boldsymbol{r}) \tag{A.3}$$

For the part of the general potential that depends only on the distance from the origin the general solution of equation (A.2) can be expressed as a superposition of partial waves and products of solely radial and angular dependent functions:

$$\psi(\boldsymbol{r}) = \sum_L \phi_\ell(\boldsymbol{r}) Y_L(\theta,\varphi) \quad , L \equiv (\ell, m) \tag{A.4}$$

which leads with the substitution

$$R_\ell(r) = r\phi_\ell(r) \tag{A.5}$$

to the second order differential equation:

$$\frac{d^2 R_\ell}{dr^2} + \left(E - V(r) - \frac{\ell(\ell+1)}{r^2}\right) R_\ell = 0 \quad . \tag{A.6}$$

The potential $V(r)$ is of the following shape:

$$V(r) = \left\{ \begin{array}{ccc} V(r) & , & r \leq r_s \\ V_0 & , & else \end{array} \right. \quad , \tag{A.7}$$

where r_s is the radius of the potential sphere.

A.1.1 **Regular Solution**

One solution of the radial equation (A.6) is regular at the origin and behaves in the following manner:

$$R_\ell(r) \overset{r\to 0}{\longrightarrow} \sim r^\ell \tag{A.8}$$

At the sphere boundary r_s it has to be matched to a solution of this equation for $V(r) = V_0$ which is constructed from two linear independent solutions. This can be done by either combining spherical Bessel ($j_\ell(kr)$) and Neumann ($n_\ell(kr)$) functions, or equivalently spherical Bessel and Hankel functions of the first kind ($h_\ell^+(kr)$). Therefore the solution at the sphere boundary is given by the two equivalent expressions:

$$\begin{aligned} R_\ell(r_s) &= \cos\delta_\ell(k) j_\ell(kr_s) - \sin\delta_\ell(k) n_\ell(kr_s) && \text{(A.9)} \\ &= e^{-i\delta_\ell}\left(j_\ell(kr_s) - ikt_\ell(k)h_\ell^+(kr_s)\right) \quad . && \text{(A.10)} \end{aligned}$$

According to equation (A.9) the corresponding derivative at $r = r_s$ is given by

$$R'_\ell(r_s) = k\left[\cos\delta_\ell(k) j'_\ell(kr_s) - \sin\delta_\ell(k) n'_\ell(kr_s)\right] \quad , \tag{A.11}$$

where $k = \sqrt{E - V_0}$.

In order to obtain an expression for the single site t–matrix, $t_\ell(k)$, the ℓ-like phase shifts may be derived from the relation

$$\tan\delta_\ell(k) = \frac{L_\ell(r_s, E) j_\ell(kr_s) - kj'_\ell(kr_s)}{L_\ell(r_s, E) n_\ell(kr_s) - kn'_\ell(kr_s)} \tag{A.12}$$

where $L_\ell(r_s, E) = R'_\ell(r_s, E)/R_\ell(r_s, E)$ defines the logarithmic derivative of the wave function at the sphere boundary. Using equation (A.12) the reactance [Fau79][Wig46], $K_\ell(k)$, is defined as:

$$K_\ell(k) = -\frac{1}{k}\tan\delta_\ell(k) \quad . \tag{A.13}$$

Then the diagonal elements of the t–matrix are given by

$$t_\ell(k) = \frac{K_\ell(k)}{1 + ikK_\ell(k)} \quad . \tag{A.14}$$

For computational purposes equation (A.9) can be manipulated such that a normalization factor, $A_\ell(k)$, may be derived. Furthermore, instead of $R_\ell(r,E)$ the quantities $Z_\ell(r,E)$ as originally defined by Faulkner, the so called scattering solutions, [Fau79] are used. Dividing by $\sin\delta_\ell(k)$ and multiplying by $-k$ yields

$$\begin{aligned} -\frac{kR_\ell(r)}{\sin\delta_\ell(k)} &= A_\ell(k)R_\ell(r) = Z_\ell(r) \\ &= r\left(kn_\ell(kr) + K_\ell^{-1}(k)j_\ell(kr)\right)\,. \end{aligned} \tag{A.15}$$

Now the coefficient $A_\ell(k)$ can be calculated from the condition that equation (A.9) is valid at the boundary r_s as:

$$A_\ell(k) = \frac{r_s\,\left(kn_\ell(kr_s) + K_\ell^{-1}(k)j_\ell(kr_s)\right)}{R_\ell(r_s)} \tag{A.16}$$

A.1.2 **Irregular Solution**

There is another, though unphysical, solution to equation (A.6) which, due to its behaviour in the vicinity of the origin, is referred to as irregular solution. Following Faulkner, this wave function joins smoothly to $j_\ell(r)$, for $r > r_s$, and is denoted by $J_\ell(r)$. It diverges as its argument approaches zero as $r^{-\ell}$, i.e.,

$$J_\ell(r) \xrightarrow{r\to 0} \sim r^{-\ell-1}\,. \tag{A.17}$$

The general expression for the irregular solution $J_\ell(r)$ is given as a superposition of regular and irregular wave functions, which is still an irregular solution:

$$J_\ell(r) = B_\ell(r)R_\ell(r) + C_\ell(r)I_\ell(r)\,, \tag{A.18}$$

with

$$I_\ell(r) = r\phi_\ell^i(r)\,, \tag{A.19}$$

where $\phi_\ell^i(r,E)$ is the second solution of (A.2).

In the actual calculation, R_ℓ and I_ℓ are the functions that are directly obtained from the integration. The functions denoted by Z_ℓ and J_ℓ are the normalized solutions.

Normalization

The continuity condition at the boundary of the potential sphere can be used to calculate the normalization coefficients $B_\ell(k)$ and $C_\ell(k)$:

$$\begin{aligned} B_\ell(k)R_\ell(r_s) + C_\ell(k)I_\ell(r_s) &= r_s\, j_\ell(kr_s) \quad , \\ B_\ell(k)R'_\ell(r_s) + C_\ell(k)I'_\ell(r_s) &= j_\ell(kr_s) + r_s k j'_\ell(kr_s) \quad . \end{aligned} \tag{A.20}$$

From the above conditions the following expressions for the coefficients are obtained:

$$\begin{aligned} B_\ell(k) &= \frac{-\beta_\ell(kr_s)I_\ell(r_s) + r_s\, j_\ell(kr_s)I'_\ell(r_s)}{R_\ell(r_s)I'_\ell(r_s) - R'_\ell(r_s,E)I_\ell(r_s,E)}\,, \\ C_\ell(k) &= \frac{\beta_\ell(kr_s)R_\ell(r_s) - r_s\, j_\ell(kr_s)R'_\ell(r_s)}{R_\ell(r_s)I'_\ell(r_s) - R'_\ell(r_s)I_\ell(r_s)}\,, \end{aligned} \tag{A.21}$$

where

$$\beta_\ell(kr_s) = j_\ell(kr_s) + rkj'_\ell(kr_s) = (\ell+1)j_\ell(kr_s) - rkj_{\ell+1}(kr_s)\,. \tag{A.22}$$

A.2

Numerical Treatment of the Schrödinger Equation

In order to solve the Schrödinger equation numerically, it first has to be transformed from a single, second order differential equation to two, first order differential equations. Then by means of a suitable algorithm it is possible to solve those two equations numerically. But let's start with the transformation.

A.2.1 Coupled Radial Equations

The second order differential equation to be solved is given by equation (A.6):

$$P_\ell'' + \left(E - V - \frac{\ell(\ell+1)}{r^2} \right) P_\ell = 0 \quad . \tag{A.23}$$

In there and in the following the notation is $P_\ell = P_\ell(r, E)$, $P_\ell' = \mathrm{d}P_\ell/\mathrm{d}r$, $P_\ell'' = \mathrm{d}^2 P_\ell/\mathrm{d}r^2$ and

$$P_\ell = R_\ell \quad \text{or} \quad I_\ell \,. \tag{A.24}$$

Now, let's define the quantity $Q_\ell = Q_\ell(r, E)$ as [Lou67]:

$$Q_\ell = P_\ell' - \frac{P_\ell}{r} \,. \tag{A.25}$$

Consequently P_ℓ' and P_ℓ'' turn out to be

$$\begin{aligned} P_\ell' &= Q_\ell + \frac{P_\ell}{r} && \text{(A.26)} \\ P_\ell'' &= Q_\ell' + \frac{P_\ell'}{r} - \frac{P_\ell}{r^2} \,. && \text{(A.27)} \end{aligned}$$

With

$$\frac{P_\ell'}{r} - \frac{P_\ell}{r^2} = \frac{Q_\ell}{r} \,, \tag{A.28}$$

substitution of (A.27) into equation (A.23) yields

$$Q_\ell' + \frac{Q_\ell}{r} + \left(E - V - \frac{\ell(\ell+1)}{r^2} \right) P_\ell = 0 \,. \tag{A.29}$$

Finally the coupled equations to be solved numerically are:

$$\boxed{\begin{aligned} Q'_\ell &= -\frac{Q_\ell}{r} + \left(\frac{\ell(\ell+1)}{r^2} + (V-E)\right) P_\ell \\ Q_\ell &= P'_\ell - \frac{P_\ell}{r} \end{aligned}} \tag{A.30}$$

Furthermore for computational purposes it is necessary to use an equally spaced mesh along which the wave functions have to be evaluated. While the radial distance from the origin, r, is usually given on an exponential mesh, the equidistant variable x may be defined and used for the calculations, where

$$x = \ln(r)\,, \tag{A.31}$$

and therefore

$$\frac{\mathrm{d}P_\ell}{\mathrm{d}r} = e^{-x}\frac{\mathrm{d}P_\ell}{\mathrm{d}x} \quad , \quad \frac{\mathrm{d}Q_\ell}{\mathrm{d}r} = e^{-x}\frac{\mathrm{d}Q_\ell}{\mathrm{d}x}\,. \tag{A.32}$$

With these transformations the coupled radial equations (A.30) for evaluation on an equally spaced mesh become

$$\boxed{\begin{aligned} Q'_\ell &= -Q_\ell + \left(\frac{\ell(\ell+1)}{e^x} + e^x(V-E)\right) P_\ell \\ Q_\ell &= e^{-x}(P'_\ell - P_\ell) \end{aligned}} \tag{A.33}$$

Separation of a ℓ-dependent Factor

For numerical accuracy it is sometimes convenient to separate a factor r^ℓ off the regular solution and $r^{-\ell}$ off the irregular solution, which leads to two different sets of coupled radial equations. First consider the regular, radial solution and write it as

$$P_\ell = \tilde{P}_\ell\, r^\ell \quad , \quad Q_\ell = \tilde{Q}_\ell\, r^\ell\,. \tag{A.34}$$

Then the derivatives are

$$P'_\ell = \ell\, r^{\ell-1}\, \tilde{P}_\ell + \tilde{P}'_\ell\, r^\ell \tag{A.35}$$

$$= r^\ell\left(\frac{\ell}{r}\tilde{P}_\ell + \tilde{P}'_\ell\right) \quad , \tag{A.36}$$

$$Q'_\ell = r^\ell\left(\frac{\ell}{r}\tilde{P}_\ell + \tilde{P}'_\ell\right) \quad . \tag{A.37}$$

Substitution of these expressions into (A.30) yields the following two, coupled equations:

$$\boxed{\begin{aligned}\tilde{Q}'_\ell &= -\left(\frac{\ell+1}{r}\right)\tilde{Q}_\ell + \left(\frac{\ell(\ell+1)}{r^2} + (V-E)\right)\tilde{P}_\ell \\ \tilde{Q}_\ell &= \tilde{P}'_\ell + \left(\frac{\ell-1}{r}\right)\tilde{P}_\ell\end{aligned}} \tag{A.38}$$

For a better numerical treatment of the irregular solutions a factor $r^{-\ell}$ is extracted. This is especially helpful since the irregular wave function diverges at extremely high rates around the origin. In this case the new functions and their derivatives are:

$$P_\ell = \tilde{P}_\ell\, r^{-\ell} \quad , \tag{A.39}$$

$$P'_\ell = -\ell\, r^{-\ell-1}\,\tilde{P}_\ell + \tilde{P}'_\ell\, r^{-\ell} \tag{A.40}$$

$$= r^{-\ell}\left(-\frac{\ell}{r}\tilde{P}_\ell + \tilde{P}'_\ell\right) \quad , \tag{A.41}$$

$$Q_\ell = \tilde{Q}_\ell\, r^{-\ell} \quad , \tag{A.42}$$

$$Q'_\ell = r^{-\ell}\left(-\frac{\ell}{r}\tilde{Q}_\ell + \tilde{Q}'_\ell\right) \quad . \tag{A.43}$$

Then the final, new coupled equations for the irregular solutions are:

$$\boxed{\begin{aligned}\tilde{Q}'_\ell &= \left(\frac{\ell-1}{r}\right)\tilde{Q}_\ell + \left(\frac{\ell(\ell+1)}{r^2} + (V-E)\right)\tilde{P}_\ell \\ \tilde{Q}_\ell &= \tilde{P}'_\ell - \left(\frac{\ell+1}{r}\right)\tilde{P}_\ell\end{aligned}} \tag{A.44}$$

A.2.2 **Numerical Evaluation of the Regular Solution**

Because of its nice and regular behaviour in the vicinity of the origin the regular solution is relatively easy to integrate. The best way to obtain such a solution is to start with small values of the wave function close to the origin and integrate outwards with a predictor-corrector algorithm. Because the value of the wave function is initially very small, the error one makes at the beginning is very small. If the wave function subsequently increases the initial error does not cause problems as it becomes less significant compared to the size of the wave function. Therefore the final deviation of the numerical wave function from the "real" wave function arises almost solely from the accuracy of the numerical algorithm. So for the regular solution one does not have difficulties with what can be called "intrinsic" errors. Those come from the fact that one always makes a small error at the initial value or values because the exact values are not known and because the numerical accuracy of the computer is limited. When the initial values, however, are very large and the size of the subsequent values of the computed function decreases an intrinsic error causes problems. Then the initial value is large compared to the size of the wave function and the error can have an exponential character and cause the solution to be unstable, even though the algorithm may be extremely accurate.

Assume the exact solution of the differential equation is given by a function $F(x)$, the numerically computed approximate solution is $f(x)$, and the initial values are calculated at x_0. Then the approximate solution is given by [Sch97]:

$$f(x) = \left(f(x_0) - F(x_0)\right) e^{\lambda x} + F(x)\,. \tag{A.45}$$

If the initial value $f(x_0)$ exactly equals the correct solution at that point then the first term vanishes and no intrinsic error inhibits an exact solution. However, in reality there will always be a small error due to the limitation of computational accuracy and thus an intrinsic error is always present. If the error, as in equation (A.45), is of exponential character or has a similar behaviour, then of course one can run into trouble especially if the solution varies over several orders of magnitude from large to small values.

But in the case of the regular solution no such problems have been encountered in the course of the present work. The method that has been chosen to evaluate the regular solution is to calculate Coulomb functions around the origin and use those as starting values for an outward integration up to the sphere boundary using an Adams–Bashforth–Moulton predictor-corrector algorithm.

Coulomb Functions

In the vicinity of the origin the effect of the electrons on the potential may be neglected, the charge can be approximated by the nuclear charge (Z), and a potential, $V(r)$, is given by

$$V(r) = -\frac{2Z}{r}\,. \tag{A.46}$$

Assuming that for small r the above term is much larger than the energy, equation (A.6) becomes [AS73]

$$\frac{d^2}{dr^2} R_\ell(r) + \left(1 - \frac{2Z}{r} - \frac{\ell(\ell+1)}{r^2}\right) R_\ell(r) = 0\,. \tag{A.47}$$

Equation (A.47) is called *Coulomb equation.* Following Abramowitz and Stegun the regular solutions to this equation, the *Coulomb functions* are given by

$$R_\ell(r) = C_\ell(Z) r^{\ell+1} \phi_\ell(Z, r)\,, \tag{A.48}$$

with

$$\phi_\ell(Z, r) = \sum_{k=\ell+1}^{\infty} A_k^\ell(Z) r^{k-\ell-1}\,, \tag{A.49}$$

and where $C_\ell(Z)$ and $A_k^\ell(Z)$ are constants. The first derivative of the regular Coulomb function, $R'_\ell(r) = \mathrm{d}R_\ell(r)/\mathrm{d}r$, is then obtained as

$$R'_\ell(r) = C_\ell(Z) r^{\ell} \phi_\ell^\dagger(Z, r)\,, \tag{A.50}$$

with

$$\phi_\ell^\dagger(Z, r) = \sum_{k=\ell+1}^{\infty} k A_k^\ell(Z) r^{k-\ell-1}\,. \tag{A.51}$$

The advantage of Coulomb functions is, that they are known analytically and can be computed according to equations (A.48) and (A.50).

Predictor-Corrector Method

The predictor-corrector method (see e.g. [Sch97]) is a multiple step method in the sense that n+1 preceding values, $P_{i-n}, P_{i-n+1}, \ldots, P_{n-1}, P_i$ are used to get the next, new value P_{i+1}. P_{i+1} is then the approximate value for the exact solution $F(x_{i+1})$.

Such a method can be applied to solve a set of first order differential equations in one variable, involving an initial value problem of the kind

$$\begin{aligned} F'(x) &= f(x, F(x)) = f(x, F_1, F_2, \ldots, F_3) \quad \text{for} \quad x \in [x_{-n}, x_{N-n}] \\ F(x_{-n}) &= F_{-n}\,. \end{aligned} \tag{A.52}$$

For this method it is necessary that the interval between the grid points x_i, i.e. the step size $h_i := x_{i+1} - x_i > 0$, is constant along the whole grid. The starting values $F_i = F(x_i)$ are calculated for the first n grid points:

$$x_{-n} < x_{-n+1} < \cdots < x_0\,. \tag{A.53}$$

The resulting set of points $(x_i, F(x_i))$ for $i = -n, 0$ are the initial values used to calculate the approximate values $P_i = P(x_i)$ for the exact function $F(x_i), i = 1, N-n$.

In order to obtain the starting values, either a Runge Kutta procedure can be employed, or as in the present case the values are given by an analytic function, or they are known or computed by any other means.

Using the fundamental theorem of calculus, equation (A.52) becomes

$$F(x_{i+1}) = F(x_i) + \int\limits_{x_i}^{x_{i+1}} f(x, F(x))\, dx \quad \text{for} \quad i = 0, \ldots, N - n - 1\,. \tag{A.54}$$

It is subsequently possible to replace the function $f(x, F(x))$ with an interpolating polynomial φ_n through the points $(x_k, F_k), k = i - n, \ldots, i$. Then φ_n is integrated over the interval $[x_i, x_{i+1}]$ to yield the approximate value P_{i+1}. When the interpolating polynomial and hence the right hand side of equation (A.54) contains only values up to P_i the formula is an *explicit formula* and is called the *predictor*.

If also the grid point x_{i+1} is used for obtaining the polynomial φ_n then also P_{i+1} is contained on the right hand side of the integral equation (A.54). It is therefore an *implicit formula* and called a *corrector*.

Explicit and implicit formula can be combined to form the so called *predictor-corrector method*.

From the discussion above it is clear that the points P_{i+1} are only an approximation to the *real* values F_{i+1}, which, however, are not known. Hence, obviously, the following equation, which defines the procedural error ε_{i+1} holds:

$$F_{i+1} = P_{i+1} + \varepsilon_{i+1}\,. \tag{A.55}$$

By replacing $f(x, F(x))$ with $\varphi_n(x)$ one obtains an integral equation for the approximate values P_{i+1}

$$P_{i+1} = P_i + \int\limits_{x_i}^{x_{i+1}} \varphi_n(x)\, dx\,, \tag{A.56}$$

which is the *Adams–Bashforth* formula.

As explicit Adams-Bashforth formula, for $h_i = h = const.$, i.e. for an equidistant grid, used as a predictor in the present calculations, the following expression is denoted:

$$
\begin{aligned}
n = 5: \qquad P_{i+1} &= P_i + \frac{h}{1440}(4277 f_i - 7923 f_{i-1} + 9982 f_{i-2} \\
&\quad -7298 f_{i-3} + 2877 f_{i-4} - 475 f_{i-5}) \qquad \text{(A.57)} \\
\varepsilon_{i+1} &\sim \frac{19087}{60480} h^7
\end{aligned}
$$

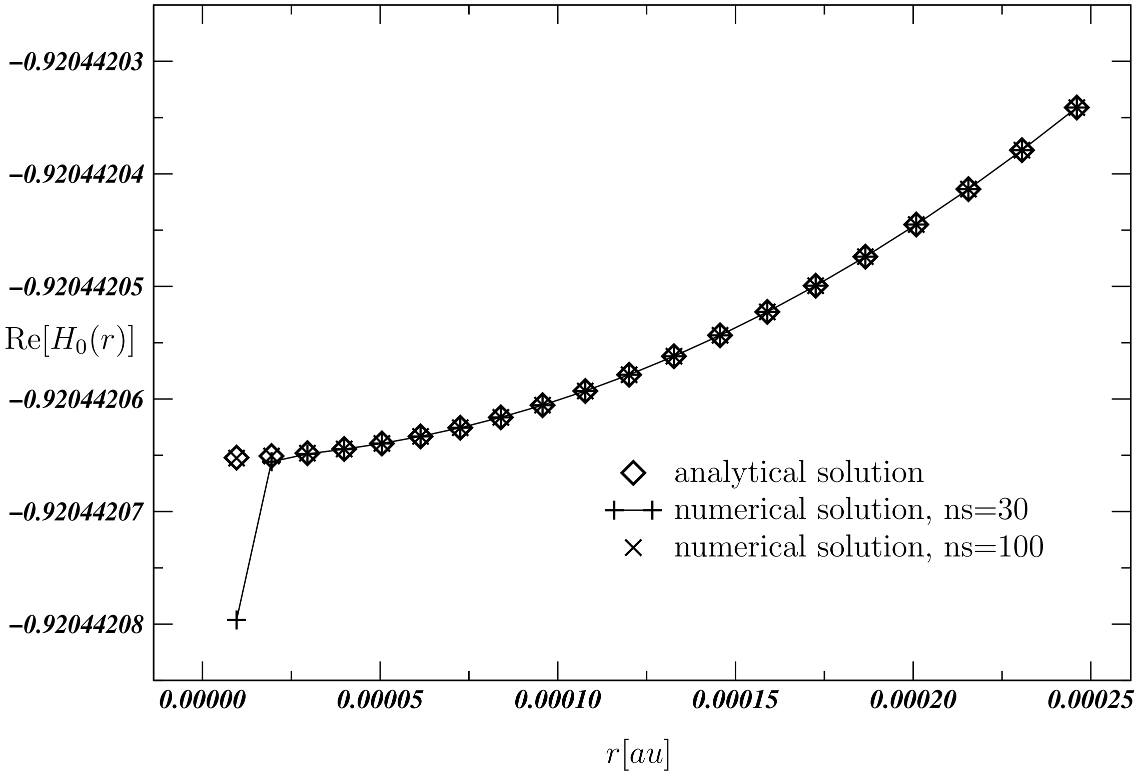
Since the *procedural error* ε_{i+1} is proportional to h^{n+2} the quality of the integration can be improved by reducing the step size of the grid points. Also an Adams–Bashforth formula of higher order can be used. But the best way to improve the quality of the procedure is to reduce the step size. How small h ought to be depends of course on the specific differential equation to be evaluated.

As mentioned above the predictor formula should be combined with a corrector or *Adams–Moulton* formula. The best way to do this is to use a corrector with an error order one higher than the predictor. Next the corrector formula used in the present calculations is given:

$$
\begin{aligned}
n = 6: \qquad P_{i+1}^{\nu+1} &= P_i + \frac{h}{60480}(19087 f_{i+1}^{\nu} + 65112 f_i - 46461 f_{i-1} \\
&\quad +37504 f_{i-2} - 20211 f_{i-3} + 6312 f_{i-4} - 863 f_{i-5}) \qquad \text{(A.58)} \\
\varepsilon_{i+1} &\sim -\frac{275}{24192} h^8
\end{aligned}
$$

In there f_{i+1}^{ν} is calculated from the predicted value of equation (A.57). Then it is used to compute $P_{i+1}^{\nu+1}$, and the resulting value is compared to the predicted value P_{i+1}. If the two values match well enough, which is determined within the program by a convergence condition, one can proceed to the next point. On the other hand if the values are not close enough, another cycle of prediction – correction is performed. But this time the corrected value $P_{i+1}^{\nu+1}$ is used to compute f_{i+1}^{ν} and a new corrector. The old corrector becomes the new predictor and is compared with the new corrector and so forth until the convergence condition is met. If the step size is small enough, usually one or two iterations suffice.

Figure A.1: *Comparison of the numerically computed real part of the solution to the free space Schrödinger equation for two different numbers of interpolation points, ns, with the analytic solution (in this case the spherical Neumann functions) for* $\ell = 0$.



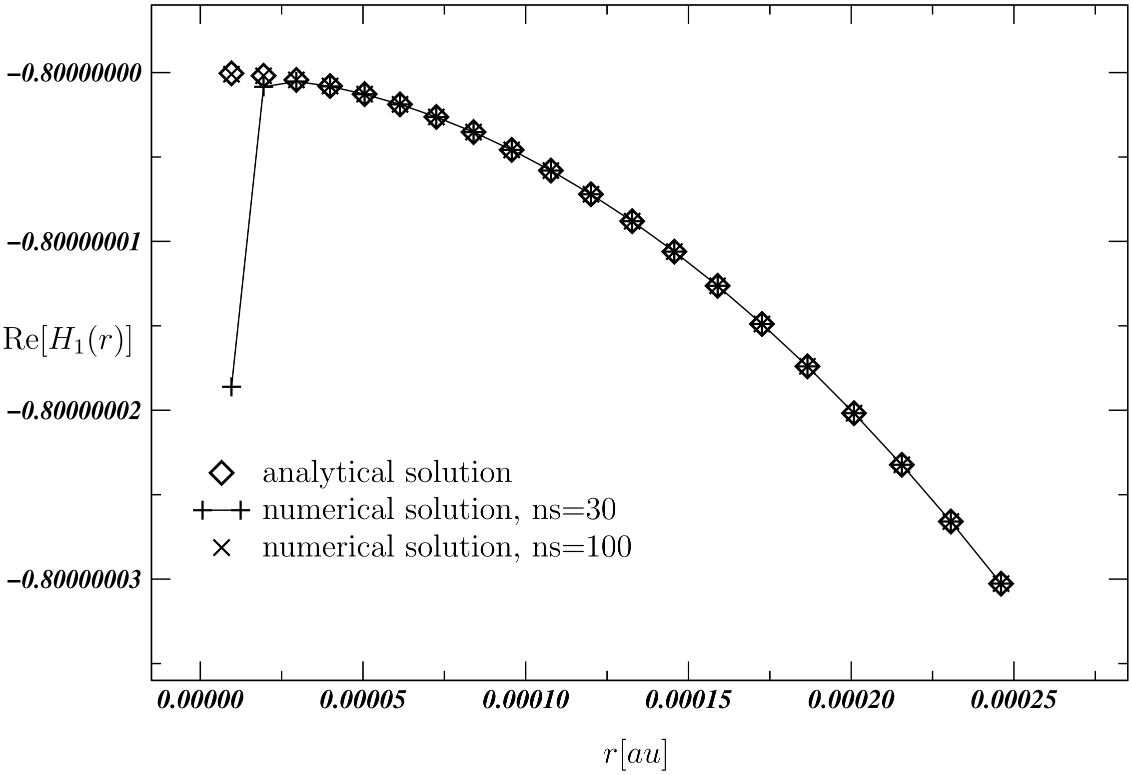
Interpolation Scheme

The reduction of the step size has been done in the following manner: typically the potential is given on an exponential, radial mesh containing about 350 to 500 mesh points. It is an easy task to interpolate the potential on a mesh about thirty to one hundred times denser and therefore reducing the step size by that factor. Of course this can only be achieved at the expense of computation time, but the solutions obtained with such an interpolation method are very stable and reliable. The Wronski determinant in equation (A.1) has been computed and an accuracy up to 10^{-12} over the whole mesh could be achieved.

So consider a given mesh of radial points r_i, $i = 1, n$. The increment between to neighbouring points on the mesh is denoted by $\Delta_i(h)$. This increment is not necessarily a constant – it can be, for example, an exponential expression – but h is, as demanded by the predictor-corrector algorithm discussed above. Hence we can write

$$r_i + \Delta_i(h) = r_{i+1} \quad \forall i \quad . \tag{A.59}$$

Figure A.2: *Comparison of the numerically computed real part of the solution to the free space Schrödinger equation for two different numbers of interpolation points, ns, with the analytic solution (in this case the spherical Neumann functions) for $\ell = 1$.*



Then let us define an interpolating mesh, s_j, of m points such that

$$r_i < s_j \leq r_{i+1}\,, \quad j = 1, 2, \ldots, m \quad . \tag{A.60}$$

The corresponding array of functional values for all r_i is $f(r_i)$. As for the radial mesh we define an increment for the interpolation mesh such that

$$s_j + \Delta_j(h/m) = s_{j+1} \quad \forall j \quad . \tag{A.61}$$

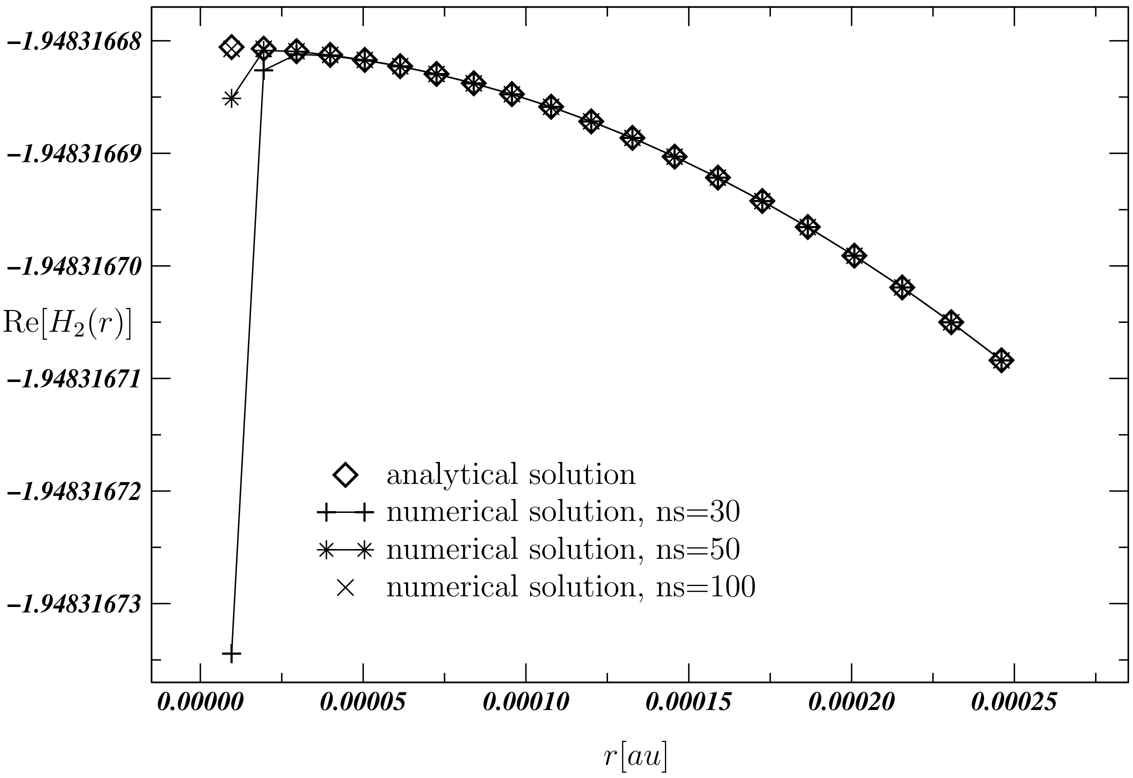
And lets denote the values on the interpolation mesh as $\tilde{f}(s_j)$. Then the values of $\tilde{f}(s_j)$ at the last point of the interpolation mesh have to match the values of $f(r_i)$, thus

$$f(r_{i+1}) = \tilde{f}(s_m) \quad , \tag{A.62}$$

and furthermore the function value of the first interpolation point is equal to the function value of

$$f(r_i + \Delta_i(h/m)) = \tilde{f}(s_1) \quad . \tag{A.63}$$

Figure A.3: *Comparison of the numerically computed real part of the solution to the free space Schrödinger equation for three different numbers of interpolation points, ns, with the analytic solution (in this case the spherical Neumann functions) for $\ell = 2$.*



From the above it is clear that the step size is now reduced by a factor m:

$$h \to \frac{h}{m} \quad , \tag{A.64}$$

and the procedural error of the predictor formula (A.57) is

$$\varepsilon_{i+1} \sim \frac{19087}{60480} \left(\frac{h}{m} \right)^7 \quad . \tag{A.65}$$

Keeping in mind these considerations the following algorithm can be performed: we start with the first mesh point, r_1. For the corresponding function $f(r_1)$, an initial value has to be determined. In the case of the regular solution, this can be a more or less arbitrary value, but it is wise to use a rather small, positive value. Then the mesh points s_j have to be determined between r_1 and r_2. In order to obtain the wave function on this mesh, the potential has to be interpolated using a Lagrangian interpolation scheme. Having computed these values, the coupled equations are solved for s_j, $j = 1, m$. Then the last value of the interpolating wave function, $\tilde{f}(s_m)$, is stored in $f(r_2)$. Now we move on to the next radial value, r_3, and proceed in the same manner. This scheme is repeated until the final mesh point r_n has been reached.

In figures A.1, A.2, and A.3 the results of test calculations are shown. The numerical solution of the free space Schrödinger equation is plotted against the analytically obtained values of the spherical Neumann function. Here one solution of the Schrödinger equation is taken to be $H_\ell(r) = \mathrm{i}\, r\, h_\ell(kr)$, where $h_\ell(kr)$ is a spherical Hankel function. Then the real part of this function is just the spherical Neumann function. From the figures one can see the high accuracy of the interpolation scheme. Already for 30 interpolation points the numerical values are identical to the analytical values except for a few radial points closest to the origin. By using 50 interpolation points the error for those points can be dramatically reduced and when the number is increased to 100 points the values are virtually identically over the whole mesh. Note however, that the functions, that are displayed in the plots are practically constant lines. Hence the errors occur at the 8th, 9th, or 10th position after the comma and are actually extremely small.

A.2.3 **Numerical Evaluation of the Irregular Solution**

Evaluating the irregular solution to equation (A.6) is a numerically challenging task when one tries to apply the same procedure as described above for the regular solution. The problem here is, as has already been indicated earlier, the unpleasant behaviour of the wave function around the origin. There it diverges as $r^{-\ell}$, i.e. with increasing angular momentum quantum number, ℓ, it goes to infinity at higher and higher rates. Hence when trying to start with some values of the Coulomb approximation (which means to use values of the Coulomb functions) close to the origin one has to use large values beyond the numerical accuracy of most computers. Therefore the initial error is rather large. Even worse, the irregular solution decreases in size as the sphere boundary is approached and tends to zero. So one starts with a large error, which becomes more and more significant as the size of the wave function decreases, and a situation as described in section (A.2.2) is encountered. It is therefore, for angular momentum quantum numbers $\ell > 1$ impossible to obtain stable solutions, even if the step size of the predictor-corrector algorithm is reduced to extremely small increments.

A different approach to the solution of the coupled differential equations is thus needed. The method of choice for this problem is an inwards integration using again the predictor-corrector method and starting values which have to be obtained from a Runge-Kutta extrapolation. To start this algorithm the boundary condition of equation (A.20) can be used. The Runge–Kutta method uses the spherical Bessel function at the sphere boundary to extrapolate a few points and subsequently a predictor-corrector algorithm performs an inwards integration, again interpolating the potential on a thirty to one hundred times denser mesh. The only difference to the formulas for the outwards integration (equations (A.57) and (A.58)) is, that $h \to -h$. Using this procedure, very stable irregular solutions can be obtained.

For completeness, below the expressions for the employed Runge–Kutta procedure are given [FM87]. For the system of coupled differential equations

$$P' = f(P,Q) \quad , \quad Q' = g(P,Q)\,, \tag{A.66}$$

where $f(P,Q)$ and $g(P,Q)$ are for example given by (A.30), the following coefficients have to be computed

$$\begin{aligned} k_1 &= h\,f(P_i,Q_i)\,, & m_1 &= h\,g(P_i,Q_i)\,,\\ k_2 &= h\,f(P_i+(k_1/2),Q_i+(m_1/2))\,, & m_2 &= h\,g(P_i+(k_1/2),Q_i+(m_1/2))\,,\\ k_3 &= h\,f(P_i+(k_2/2),Q_i+(m_2/2))\,, & m_3 &= h\,g(P_i+(k_2/2),Q_i+(m_2/2))\,,\\ k_4 &= h\,f(P_i+k_3,Q_i+m_3)\,. & m_4 &= h\,g(P_i+k_3,Q_i+m_3)\,. \end{aligned}$$

Then the next function values on the mesh are obtained from

$$P_{i+1} \cong P_i + \frac{1}{6}\,(k_1+2k_2+2k_3+k_4) \quad , \tag{A.67}$$

$$Q_{i+1} \cong Q_i + \frac{1}{6}\,(m_1+2m_2+2m_3+m_4) \quad . \tag{A.68}$$

In figure A.4 the accuracy of the algorithm is tested by comparing the numerical solutions to the free space Schrödinger equation with analytical Hankel functions. For the numerical solution an inwards integration has been performed using different numbers of interpolation points. The results for 30 and 100 points are shown. It can be seen from the numbers that the numerical results are correct up to the 12th digit after the comma for almost all of the points on the r-mesh. Only for the last eight (30 interpolation points) and the last two (100 interpolation points) points on the mesh the deviations from the analytical solutions are larger, but still correct to the 8th, 9th or even 10th digit. However, by using even more interpolation points this small error can be suppressed further and almost any desired accuracy can be obtained. Of course, all this is at the cost of computation time, but tests have shown that with 50 interpolation points the accuracy is sufficient and the computation time reasonable.

Finally it should be noted that the results in figures A.4, A.5, and A.6 are in fact representative, since the same accuracy was obtained for even higher angular momenta, the imaginary parts of the wave functions, different potentials (square well and Coulomb potentials), and different energies.

Figure A.4: *Comparison of the real part of the analytic irregular solutions of the Schrödinger equation in free space, the spherical Hankel functions (here the Neumann functions) of the first kind with the real part of the numerical solutions, for* $\ell = 0$*, using the interpolation scheme with 30 and 100 interpolation points.*

$V = 0$, $E = (1 + \mathrm{i}0.5)\mathrm{Ry}$	**analytical solution**	numerical solution	numerical solution
r_i	$\mathrm{Re}(h_0^+)r_i$	$\mathrm{Re}(H_0)r_i$, $ns = 30$	$\mathrm{Re}(H_0)r_i$, $ns = 100$
r_{484} = 0.335355000000E+01	0.417488923552E+00	0.417488923552E+00	0.417488923552E+00
r_{483} = 0.334507282062E+01	0.418617707912E+00	0.418617707912E+00	0.418617707912E+00
r_{482} = 0.333659564124E+01	0.419717448200E+00	0.419717448200E+00	0.419717448200E+00
r_{481} = 0.332811846186E+01	0.420787936002E+00	0.420787936002E+00	0.420787936002E+00
r_{480} = 0.331964128248E+01	0.421828964400E+00	0.421828964400E+00	0.421828964400E+00
r_{479} = 0.331116410310E+01	0.422840327993E+00	0.422840327993E+00	0.422840327993E+00
r_{478} = 0.330268692372E+01	0.423821822921E+00	0.423821822921E+00	0.423821822921E+00
r_{477} = 0.329420974434E+01	0.424773246887E+00	0.424773246887E+00	0.424773246887E+00
r_{476} = 0.328573256496E+01	0.425694399181E+00	0.425694399181E+00	0.425694399181E+00
r_{475} = 0.327725538558E+01	0.426585080701E+00	0.426585080701E+00	0.426585080701E+00
r_{474} = 0.326877820620E+01	0.427445093978E+00	0.427445093978E+00	0.427445093978E+00
r_{473} = 0.326030102682E+01	0.428274243193E+00	0.428274243193E+00	0.428274243193E+00
r_{472} = 0.325182384744E+01	0.429072334209E+00	0.429072334209E+00	0.429072334209E+00
r_{471} = 0.324334666806E+01	0.429839174585E+00	0.429839174585E+00	0.429839174585E+00
r_{470} = 0.323486948868E+01	0.430574573601E+00	0.430574573601E+00	0.430574573601E+00
r_{469} = 0.322639230930E+01	0.431278342284E+00	0.431278342284E+00	0.431278342284E+00
r_{468} = 0.321791512992E+01	0.431950293426E+00	0.431950293426E+00	0.431950293426E+00
r_{467} = 0.320943795054E+01	0.432590241608E+00	0.432590241608E+00	0.432590241608E+00
r_{466} = 0.320096077116E+01	0.433198003222E+00	0.433198003222E+00	0.433198003222E+00
r_{465} = 0.319248359178E+01	0.433773396494E+00	0.433773396494E+00	0.433773396494E+00
r_{464} = 0.318400641240E+01	0.434316241507E+00	0.434316241507E+00	0.434316241507E+00
r_{463} = 0.317552923302E+01	0.434826360219E+00	0.434826360219E+00	0.434826360219E+00
r_{462} = 0.316705205364E+01	0.435303576490E+00	0.435303576490E+00	0.435303576490E+00
r_{461} = 0.315857487426E+01	0.435747716102E+00	0.435747716102E+00	0.435747716102E+00
r_{460} = 0.315009769488E+01	0.436158606780E+00	0.436158606780E+00	0.436158606780E+00
$\vdots$	$\vdots$	$\vdots$	$\vdots$
r_{21} = 0.246053484867E-03	-0.920442034110E+00	-0.920442034110E+00	-0.920442034110E+00
r_{20} = 0.230613699437E-03	-0.920442037896E+00	-0.920442037896E+00	-0.920442037896E+00
r_{19} = 0.215555123668E-03	-0.920442041353E+00	-0.920442041353E+00	-0.920442041353E+00
r_{18} = 0.200868345460E-03	-0.920442044500E+00	-0.920442044500E+00	-0.920442044500E+00
r_{17} = 0.186544185097E-03	-0.920442047355E+00	-0.920442047355E+00	-0.920442047355E+00
r_{16} = 0.172573689515E-03	-0.920442049936E+00	-0.920442049936E+00	-0.920442049936E+00
r_{15} = 0.158948126696E-03	-0.920442052261E+00	-0.920442052261E+00	-0.920442052261E+00
r_{14} = 0.145658980223E-03	-0.920442054343E+00	-0.920442054343E+00	-0.920442054343E+00
r_{13} = 0.132697943945E-03	-0.920442056200E+00	-0.920442056200E+00	-0.920442056200E+00
r_{12} = 0.120056916793E-03	-0.920442057844E+00	-0.920442057844E+00	-0.920442057844E+00
r_{11} = 0.107727997714E-03	-0.920442059289E+00	-0.920442059289E+00	-0.920442059289E+00
r_{10} = 0.957034807307E-04	-0.920442060547E+00	-0.920442060548E+00	-0.920442060547E+00
r_{9} = 0.839758501299E-04	-0.920442061631E+00	-0.920442061632E+00	-0.920442061631E+00
r_{8} = 0.725377757604E-04	-0.920442062553E+00	-0.920442062554E+00	-0.920442062553E+00
r_{7} = 0.613821084533E-04	-0.920442063321E+00	-0.920442063324E+00	-0.920442063321E+00
r_{6} = 0.505018755533E-04	-0.920442063948E+00	-0.920442063954E+00	-0.920442063948E+00
r_{5} = 0.398902765609E-04	-0.920442064441E+00	-0.920442064459E+00	-0.920442064441E+00
r_{4} = 0.295406788810E-04	-0.920442064811E+00	-0.920442064883E+00	-0.920442064811E+00
r_{3} = 0.194466136784E-04	-0.920442065065E+00	-0.920442065578E+00	-0.920442065067E+00
r_{2} = 0.960177183360E-05	-0.920442065212E+00	-0.920442079626E+00	-0.920442065253E+00

Figure A.5: *Comparison of the real part of the analytic irregular solutions of the Schrödinger equation in free space, the spherical Hankel functions (here the Neumann functions) of the first kind with the real part of the numerical solutions, for $\ell = 1$, using the interpolation scheme with 30 and 100 interpolation points.*

$V = 0$, $E = (1 + \mathrm{i}0.5)\mathrm{Ry}$	**analytical solution**	numerical solution	numerical solution
r_i	$\mathrm{Re}(h_0^+)r_i^{\ell+1}$	$\mathrm{Re}(H_0)r_i^{\ell+1}$, $ns = 30$	$\mathrm{Re}(H_0)r_i^{\ell+1}$, $ns = 100$
r_{484} = 0.335355000000E+01	0.500301926230E+00	0.500301926230E+00	0.500301926230E+00
r_{483} = 0.334507282062E+01	0.488298737784E+00	0.488298737784E+00	0.488298737784E+00
r_{482} = 0.333659564124E+01	0.476268738534E+00	0.476268738534E+00	0.476268738534E+00
r_{481} = 0.332811846186E+01	0.464212949352E+00	0.464212949352E+00	0.464212949352E+00
r_{480} = 0.331964128248E+01	0.452132393060E+00	0.452132393060E+00	0.452132393060E+00
r_{479} = 0.331116410310E+01	0.440028094326E+00	0.440028094326E+00	0.440028094326E+00
r_{478} = 0.330268692372E+01	0.427901079579E+00	0.427901079579E+00	0.427901079579E+00
r_{477} = 0.329420974434E+01	0.415752376868E+00	0.415752376868E+00	0.415752376868E+00
r_{476} = 0.328573256496E+01	0.403583015782E+00	0.403583015782E+00	0.403583015782E+00
r_{475} = 0.327725538558E+01	0.391394027336E+00	0.391394027336E+00	0.391394027336E+00
r_{474} = 0.326877820620E+01	0.379186443861E+00	0.379186443861E+00	0.379186443861E+00
r_{473} = 0.326030102682E+01	0.366961298906E+00	0.366961298906E+00	0.366961298906E+00
r_{472} = 0.325182384744E+01	0.354719627120E+00	0.354719627120E+00	0.354719627120E+00
r_{471} = 0.324334666806E+01	0.342462464154E+00	0.342462464154E+00	0.342462464154E+00
r_{470} = 0.323486948868E+01	0.330190846547E+00	0.330190846547E+00	0.330190846547E+00
r_{469} = 0.322639230930E+01	0.317905811615E+00	0.317905811615E+00	0.317905811615E+00
r_{468} = 0.321791512992E+01	0.305608397362E+00	0.305608397362E+00	0.305608397362E+00
r_{467} = 0.320943795054E+01	0.293299642345E+00	0.293299642344E+00	0.293299642344E+00
r_{466} = 0.320096077116E+01	0.280980585578E+00	0.280980585578E+00	0.280980585578E+00
r_{465} = 0.319248359178E+01	0.268652266426E+00	0.268652266426E+00	0.268652266426E+00
r_{464} = 0.318400641240E+01	0.256315724491E+00	0.256315724491E+00	0.256315724491E+00
r_{463} = 0.317552923302E+01	0.243971999504E+00	0.243971999504E+00	0.243971999504E+00
r_{462} = 0.316705205364E+01	0.231622131214E+00	0.231622131214E+00	0.231622131214E+00
r_{461} = 0.315857487426E+01	0.219267159282E+00	0.219267159282E+00	0.219267159282E+00
r_{460} = 0.315009769488E+01	0.206908123161E+00	0.206908123161E+00	0.206908123161E+00
$\vdots$	$\vdots$	$\vdots$	$\vdots$
r_{21} = 0.246053484867E-03	-0.800000030270E+00	-0.800000030269E+00	-0.800000030269E+00
r_{20} = 0.230613699437E-03	-0.800000026590E+00	-0.800000026590E+00	-0.800000026590E+00
r_{19} = 0.215555123668E-03	-0.800000023231E+00	-0.800000023231E+00	-0.800000023231E+00
r_{18} = 0.200868345460E-03	-0.800000020173E+00	-0.800000020173E+00	-0.800000020173E+00
r_{17} = 0.186544185097E-03	-0.800000017399E+00	-0.800000017398E+00	-0.800000017398E+00
r_{16} = 0.172573689515E-03	-0.800000014890E+00	-0.800000014890E+00	-0.800000014890E+00
r_{15} = 0.158948126696E-03	-0.800000012632E+00	-0.800000012631E+00	-0.800000012631E+00
r_{14} = 0.145658980223E-03	-0.800000010608E+00	-0.800000010607E+00	-0.800000010607E+00
r_{13} = 0.132697943945E-03	-0.800000008804E+00	-0.800000008804E+00	-0.800000008804E+00
r_{12} = 0.120056916793E-03	-0.800000007207E+00	-0.800000007206E+00	-0.800000007206E+00
r_{11} = 0.107727997714E-03	-0.800000005803E+00	-0.800000005802E+00	-0.800000005802E+00
r_{10} = 0.957034807307E-04	-0.800000004580E+00	-0.800000004579E+00	-0.800000004579E+00
r_9 = 0.839758501299E-04	-0.800000003526E+00	-0.800000003526E+00	-0.800000003525E+00
r_8 = 0.725377757604E-04	-0.800000002631E+00	-0.800000002632E+00	-0.800000002630E+00
r_7 = 0.613821084533E-04	-0.800000001884E+00	-0.800000001886E+00	-0.800000001883E+00
r_6 = 0.505018755533E-04	-0.800000001275E+00	-0.800000001282E+00	-0.800000001275E+00
r_5 = 0.398902765609E-04	-0.800000000796E+00	-0.800000000818E+00	-0.800000000795E+00
r_4 = 0.295406788810E-04	-0.800000000436E+00	-0.800000000528E+00	-0.800000000436E+00
r_3 = 0.194466136784E-04	-0.800000000189E+00	-0.800000000848E+00	-0.800000000190E+00
r_2 = 0.960177183360E-05	-0.800000000045E+00	-0.800000018614E+00	-0.800000000098E+00

Figure A.6: *Comparison of the real part of the analytic irregular solutions of the Schrödinger equation in free space, the spherical Hankel functions (here the Neumann functions) of the first kind with the real part of the numerical solutions, for $\ell = 2$, using the interpolation scheme with 30 and 100 interpolation points.*

$V = 0$, $E = (1 + \mathrm{i}0.5)\mathrm{Ry}$	**analytical solution**	numerical solution	numerical solution
r_i	$\mathrm{Re}(h_0^+)r_i^{\ell+1}$	$\mathrm{Re}(H_0)r_i^{\ell+1}$, $ns = 30$	$\mathrm{Re}(H_0)r_i^{\ell+1}$, $ns = 100$
r_{484} = 0.335355000000E+01	-0.426599604829E+01	-0.426599604829E+01	-0.426599604829E+01
r_{483} = 0.334507282062E+01	-0.429052849709E+01	-0.429052849709E+01	-0.429052849709E+01
r_{482} = 0.333659564124E+01	-0.431467427802E+01	-0.431467427802E+01	-0.431467427802E+01
r_{481} = 0.332811846186E+01	-0.433843354141E+01	-0.433843354141E+01	-0.433843354141E+01
r_{480} = 0.331964128248E+01	-0.436180647733E+01	-0.436180647733E+01	-0.436180647733E+01
r_{479} = 0.331116410310E+01	-0.438479331537E+01	-0.438479331537E+01	-0.438479331537E+01
r_{478} = 0.330268692372E+01	-0.440739432450E+01	-0.440739432450E+01	-0.440739432450E+01
r_{477} = 0.329420974434E+01	-0.442960981290E+01	-0.442960981290E+01	-0.442960981290E+01
r_{476} = 0.328573256496E+01	-0.445144012776E+01	-0.445144012776E+01	-0.445144012776E+01
r_{475} = 0.327725538558E+01	-0.447288565514E+01	-0.447288565515E+01	-0.447288565515E+01
r_{474} = 0.326877820620E+01	-0.449394681974E+01	-0.449394681975E+01	-0.449394681975E+01
r_{473} = 0.326030102682E+01	-0.451462408474E+01	-0.451462408474E+01	-0.451462408474E+01
r_{472} = 0.325182384744E+01	-0.453491795157E+01	-0.453491795158E+01	-0.453491795158E+01
r_{471} = 0.324334666806E+01	-0.455482895978E+01	-0.455482895978E+01	-0.455482895978E+01
r_{470} = 0.323486948868E+01	-0.457435768675E+01	-0.457435768676E+01	-0.457435768676E+01
r_{469} = 0.322639230930E+01	-0.459350474758E+01	-0.459350474758E+01	-0.459350474758E+01
r_{468} = 0.321791512992E+01	-0.461227079476E+01	-0.461227079477E+01	-0.461227079477E+01
r_{467} = 0.320943795054E+01	-0.463065651808E+01	-0.463065651809E+01	-0.463065651809E+01
r_{466} = 0.320096077116E+01	-0.464866264433E+01	-0.464866264433E+01	-0.464866264433E+01
r_{465} = 0.319248359178E+01	-0.466628993710E+01	-0.466628993710E+01	-0.466628993710E+01
r_{464} = 0.318400641240E+01	-0.468353919655E+01	-0.468353919655E+01	-0.468353919655E+01
r_{463} = 0.317552923302E+01	-0.470041125919E+01	-0.470041125920E+01	-0.470041125920E+01
r_{462} = 0.316705205364E+01	-0.471690699763E+01	-0.471690699764E+01	-0.471690699764E+01
r_{461} = 0.315857487426E+01	-0.473302732035E+01	-0.473302732036E+01	-0.473302732036E+01
r_{460} = 0.315009769488E+01	-0.474877317146E+01	-0.474877317147E+01	-0.474877317147E+01
⋮	⋮	⋮	⋮
r_{21} = 0.246053484867E-03	-0.194831670838E+01	-0.194831670839E+01	-0.194831670839E+01
r_{20} = 0.230613699437E-03	-0.194831670500E+01	-0.194831670501E+01	-0.194831670501E+01
r_{19} = 0.215555123668E-03	-0.194831670191E+01	-0.194831670191E+01	-0.194831670191E+01
r_{18} = 0.200868345460E-03	-0.194831669909E+01	-0.194831669910E+01	-0.194831669910E+01
r_{17} = 0.186544185097E-03	-0.194831669654E+01	-0.194831669655E+01	-0.194831669655E+01
r_{16} = 0.172573689515E-03	-0.194831669423E+01	-0.194831669424E+01	-0.194831669424E+01
r_{15} = 0.158948126696E-03	-0.194831669215E+01	-0.194831669216E+01	-0.194831669216E+01
r_{14} = 0.145658980223E-03	-0.194831669029E+01	-0.194831669029E+01	-0.194831669029E+01
r_{13} = 0.132697943945E-03	-0.194831668863E+01	-0.194831668863E+01	-0.194831668863E+01
r_{12} = 0.120056916793E-03	-0.194831668716E+01	-0.194831668716E+01	-0.194831668716E+01
r_{11} = 0.107727997714E-03	-0.194831668586E+01	-0.194831668587E+01	-0.194831668587E+01
r_{10} = 0.957034807307E-04	-0.194831668474E+01	-0.194831668475E+01	-0.194831668475E+01
r_9 = 0.839758501299E-04	-0.194831668377E+01	-0.194831668378E+01	-0.194831668378E+01
r_8 = 0.725377757604E-04	-0.194831668294E+01	-0.194831668296E+01	-0.194831668295E+01
r_7 = 0.613821084533E-04	-0.194831668226E+01	-0.194831668227E+01	-0.194831668226E+01
r_6 = 0.505018755533E-04	-0.194831668170E+01	-0.194831668173E+01	-0.194831668170E+01
r_5 = 0.398902765609E-04	-0.194831668125E+01	-0.194831668133E+01	-0.194831668126E+01
r_4 = 0.295406788810E-04	-0.194831668092E+01	-0.194831668120E+01	-0.194831668093E+01
r_3 = 0.194466136784E-04	-0.194831668070E+01	-0.194831668262E+01	-0.194831668071E+01
r_2 = 0.960177183360E-05	-0.194831668056E+01	-0.194831673445E+01	-0.194831668072E+01

Scalar Relativistic Approximation

The scalar relativistic approximation (SRA) is an attempt to describe relativistic effects by sticking to non–relativistic quantum numbers at the expense of excluding spin–orbit coupling. The radial dependent part of the full solution to the Dirac equation is given by:

$$\psi_\kappa(r) = \begin{pmatrix} g_\kappa(r,E) \\ \mathrm{i} f_\kappa(r,E) \end{pmatrix} \tag{A.69}$$

The component $f_\kappa(r,E)$ is usually referred to as the small component because it is of the order $1/c$ smaller than $g_\kappa(r,E)$, the large component. Defining now the following two quantities:

$$\begin{aligned} P_\kappa(r,E) &= r\, g_\kappa(r,E) && \text{(A.70)} \\ Q_\kappa(r,E) &= c\, r\, f_\kappa(r,E) \quad , && \text{(A.71)} \end{aligned}$$

the radial Dirac equations can be written as

$$\begin{aligned} P'_\kappa &= \left(\frac{E-V}{c^2}+1\right) Q_\kappa - \frac{\kappa}{r}\, P_\kappa \\ Q'_\kappa &= \frac{\kappa}{r}\, Q_\kappa - (E-V) P_\kappa \end{aligned} \tag{A.72}$$

where κ is defined as

$$\ell = \begin{cases} \kappa & , \quad \kappa > 0 \\ -\kappa - 1 & , \quad \kappa < 0 \end{cases} \tag{A.73}$$

With the definition

$$B = B(r) = 1 + \frac{E - V(r)}{c^2}\,, \tag{A.74}$$

by noting that $\kappa^2 + \kappa = \ell(\ell+1)$ and after some elementary manipulations the following equation can be derived:

$$\frac{P''_\kappa}{B} + \frac{V'}{B^2c^2}\left(P'_\kappa - \frac{P_\kappa}{r}\right) + \frac{V'}{B^2c^2}\frac{\kappa+1}{r}\, P_\kappa + \left(\frac{\ell(\ell+1)}{Br^2} + V - E\right) P_\kappa \quad = \quad 0 \tag{A.75}$$

Redefining Q as

$$B\, Q_\kappa = P'_\kappa - \frac{P_\kappa}{r}\,, \tag{A.76}$$

and differentiating with respect to r, an expression for P''_κ is obtained:

$$P''_\kappa = \left(\frac{B}{r} - \frac{V'}{c^2}\right) Q_\kappa + B\,Q'_\kappa\,. \tag{A.77}$$

If in equation (A.75) the term that includes the quantum number κ, the spin–orbit coupling term, is neglected and equation (A.77) is inserted into equation (A.75), one gets

$$\frac{Q_\kappa}{r} + Q'_\kappa - \frac{\ell(\ell+1)}{Br^2}\,P_\kappa + (E-V)\,P_\kappa = 0\,. \tag{A.78}$$

Rewriting (A.78), using equation (A.76), and renaming the index κ to ℓ (because κ has been eliminated) a new set of coupled radial equations similar to the non–relativistic ones is obtained (c.f. (A.30)):

$$\boxed{\begin{aligned} Q'_\ell &= -\frac{Q_\ell}{r} + \left(\frac{\ell(\ell+1)}{Br^2} + (V-E)\right) P_\ell \\ P'_\ell &= \frac{P_\ell}{r} + B\,Q_\ell \end{aligned}} \tag{A.79}$$

A.3.1 **Wronskian**

In order to compute correctly the Wronskian of the second order differential equation (A.75), some care has to be taken as compared to the non–relativistic case. Assume two linear independent, differentiable functions, $Z_\ell(r)$ and $J_\ell(r)$, which are both solutions and form the fundamental set of equation (A.75). Then the determinant of the *solution matrix* is the *Wronskian* $W(Z_\ell, J_\ell)$ associated to $Z_\ell(r)$ and $J_\ell(r)$:

$$W(Z_\ell, J_\ell)(r) = \begin{vmatrix} Z_\ell(r) & J_\ell(r) \\ Z'_\ell(r) & J'_\ell(r) \end{vmatrix} \quad = \quad Z_\ell(r)J'_\ell(r) - Z'_\ell(r)J_\ell(r) \quad . \tag{A.80}$$

The Wronskian can then be used to obtain information of the linear dependence or independence of two solutions. Two solution of the same differential equation are thus linear independent if

$$W(Z_\ell, J_\ell)(r) \neq 0 \quad , \tag{A.81}$$

and linear dependent if $W(Z_\ell, J_\ell)(r) = 0$. Equation (A.75) is of the general form

$$P'' + b(r)P' + c(r)P = 0 \quad . \tag{A.82}$$

Let one solution be denoted as $Z_\ell(r)$, then a second, linear independent solution is given by

$$J_\ell(r) = Z_\ell(r)\nu_\ell(r) \quad . \tag{A.83}$$

Forming the first and second derivatives, substitution of the results into (A.82) and performing some easy manipulations, the function defined in (A.80) is then of the following form:

$$W(Z_\ell, J_\ell)(r) = W(Z_\ell, J_\ell)(r_0)\ \exp\left(-\int\limits_{r_0}^{r} b(x)\,dx\right) \quad . \tag{A.84}$$

In there the coefficient $b(x)$ is given by

$$b(x) = \frac{V'(x)}{c^2 + E - V(x)} \quad . \tag{A.85}$$

Hence the integral to be evaluated in equation (A.84) is

$$\begin{aligned} -\int\limits_{r_0}^{r} b(x)\,dx &= -\int\limits_{r_0}^{r} \frac{V'(x)}{c^2 + E - V(x)}\,dx & \text{(A.86)} \\ &= \ln\left(\frac{c^2 + E - V(r)}{c^2 + E - V(r_0)}\right) \quad . & \text{(A.87)} \end{aligned}$$

Finally the Wronskian is determined from the function:

$$W(Z_\ell, J_\ell)(r) = W(Z_\ell, J_\ell)(r_0)\,\frac{c^2 + E - V(r)}{c^2 + E - V(r_0)} \quad . \tag{A.88}$$

In the non–relativistic case $b(r) = 0$ and hence the exponential in equation (A.84) is equal to 1.

B

Special Functions and Expansions

B.1

The Delta Function

The delta function of a variable x is commonly denoted as $\delta(x)$. It has the property of being zero for all values of x except at $x = 0$. There it is infinite in such a manner that its integral that contains the point $x = 0$ is equal to 1:

$$\int\limits_{-\infty}^{\infty} \delta(x)\,\mathrm{d}x = 1 \quad . \tag{B.1}$$

If ε is any positive number the following identity is also true:

$$\int\limits_{a-\varepsilon}^{a+\varepsilon} \delta(x-a)\,\mathrm{d}x = 1 \quad . \tag{B.2}$$

An important property of the delta function is that if it is multiplied by any continuous function $F(x)$ and the resulting product is integrated it results in

$$\int\limits_{-\infty}^{\infty} F(x)\,\delta(x-a)\,\mathrm{d}x = F(a) \quad . \tag{B.3}$$

$F(x)$ may be any kind of continuous function and can be a scalar, a vector, or a tensor. The usefulness of the delta function is not its value for a specific argument, but the evaluation of the product of a function with the delta function by an integral. In this sense the delta function is a generalized function.

The delta function can also be represented as a limit of an analytical function such as

$$\delta(x) = \lim_{L\to\infty} \frac{\sin(xL)}{\pi x} \quad , \tag{B.4}$$

where for $x = 0$, $\sin(xk)/\pi x = L/\pi$. This function has the same properties as the delta function. Using expression (B.4), the proof of the equation

$$(2\pi)^{-1} \int\limits_{-\infty}^{\infty} \mathrm{e}^{\mathrm{i}kx}\,\mathrm{d}k = \delta(x) \tag{B.5}$$

is simple:

$$(2\pi)^{-1} \int\limits_{-\infty}^{\infty} \mathrm{e}^{\mathrm{i}kx}\,\mathrm{d}k = \lim_{L\to\infty} (2\pi)^{-1} \int\limits_{-L}^{L} \mathrm{e}^{\mathrm{i}kx}\,\mathrm{d}k = \lim_{L\to\infty} \frac{\sin(xL)}{\pi x} = \delta(x) \quad . \tag{B.6}$$

The delta function can be extended to three dimensions where it is defined as:

$$\delta(\boldsymbol{r}) = \delta(x)\,\delta(y)\,\delta(z) = (2\pi)^{-3} \int \mathrm{e}^{\mathrm{i}\boldsymbol{kr}}\mathrm{d}\boldsymbol{k} \tag{B.7}$$

As in the one dimensional case, when multiplied with a function and after integration the following relation results:

$$\int \delta(\boldsymbol{r})\, F(\boldsymbol{r})\,\mathrm{d}\boldsymbol{r} = F(0) \quad , \tag{B.8}$$

if $\boldsymbol{r}= 0$ is contained in the integration region. Finally there are some useful relations:

$$\delta(\boldsymbol{r}) = \frac{\delta(r)}{2\pi r^2}\,, \qquad \delta(\boldsymbol{r'} - \boldsymbol{r}) = \frac{2}{r^2}\,\delta(\boldsymbol{n'} - \boldsymbol{n})\,\delta(r' - r) \quad , \tag{B.9}$$

where $\boldsymbol{n}$ and $\boldsymbol{n'}$ are unit vectors in the direction of $\boldsymbol{r}$ and $\boldsymbol{r'}$. Further definitions of the delta function are:

$$\begin{aligned}
\delta(x) &= \frac{1}{\pi} \lim_{\varepsilon\to 0} \frac{\varepsilon}{x^2+\varepsilon^2} \quad , && \text{(B.10)}\\
&= \lim_{\varepsilon\to 0} \varepsilon\,|x|^{\varepsilon-1} \quad , && \text{(B.11)}\\
&= \lim_{\varepsilon\to 0^+} \frac{1}{2\sqrt{\pi\varepsilon}}\,\mathrm{e}^{-x^2/(4\varepsilon)} \quad , && \text{(B.12)}\\
&= \lim_{\varepsilon\to 0} \frac{1}{\varepsilon}\,\mathrm{Ai}(x/\varepsilon) \quad , && \text{(B.13)}\\
&= \lim_{\varepsilon\to 0} \frac{1}{\varepsilon}\,J_{1/\varepsilon}\left(\frac{x+1}{\varepsilon}\right) \quad , && \text{(B.14)}
\end{aligned}$$

$$= \lim_{\varepsilon\to 0}\left|\frac{1}{\varepsilon}\,\mathrm{e}^{-x^2/\varepsilon}\,L_n\left(\frac{2x}{\varepsilon}\right)\right| \quad , \tag{B.15}$$

$$= \lim_{n\to\infty}\frac{1}{2\pi}\,\frac{\sin[(n+\frac{1}{2})\,x]}{\sin(\frac{1}{2}\,x)} \quad , \tag{B.16}$$

where $\mathrm{Ai}(x)$ is an Airy function, $J_n(x)$ is a Bessel function of the first kind, and $L_n(x)$ is a Laguerre polynomial of arbitrary positive integer order.

B.2

Complex Spherical Harmonics in Condon-Shortley Convention

In the literature various expression for the spherical harmonics can be found which differ by the choice of the phase factor. Furthermore, care has to be taken whether real or complex functions are used. Throughout this work complex spherical harmonics with the phase convention of Condon and Shortley [CS59][Jac92] are used and the expressions will be given below.

Let us define the spherical harmonics in the following manner:

$$Y_{\ell m}(\theta,\varphi) = C_m A_{\ell|m|} P_\ell^{|m|}(\cos\theta) e^{\mathrm{i}m\varphi} \quad , \tag{B.17}$$

where the coefficients are defined by

$$A_{\ell|m|} = \sqrt{\frac{2\ell+1}{4\pi}\frac{(\ell-|m|)!}{(\ell+|m|)!}} \quad , \tag{B.18}$$

and

$$C_m = \mathrm{i}^{m+|m|} = \begin{cases} \ \ 1 \quad , & \text{if} \quad m\le 0 \quad \text{or} \quad m \quad \text{even} \\ -1 \quad , & \text{if} \quad m>0 \quad \text{and} \quad m \quad \text{odd} \end{cases} \quad .$$

The *associated Legendre functions*, $P_\ell^{|m|}(\cos\theta)$, are the solution of the generalized Legendre equation (see e.g. [Jac92])

$$\frac{\mathrm{d}}{\mathrm{d}\cos\theta}\left(\left(1-\cos^2\theta\right)\frac{\mathrm{d}P_\ell^m}{\mathrm{d}\cos\theta}\right) + \left(\ell(\ell+1) - \frac{m^2}{1-\cos^2\theta}\right) P_\ell^m = 0 \quad . \tag{B.19}$$

Using Rodrigues' formula for the representation of the *Legendre polynomials*, $P_\ell(\cos\theta)$

$$P_\ell(\cos\theta) = \left(2^\ell \ell!\right)^{-1}\frac{\mathrm{d}^\ell}{\mathrm{d}(\cos\theta)^\ell}\left(\cos^2\theta - 1\right)^\ell \quad , \tag{B.20}$$

the Legendre functions can be expressed in terms of these as

$$P_\ell^{|m|}(\cos\theta) = (-1)^{|m|}\left(1-\cos^2\theta\right)^{|m|/2}\frac{\mathrm{d}^m}{\mathrm{d}(\cos\theta)^m}\,P_\ell(\cos\theta) \quad . \tag{B.21}$$

Then for negative m the following relation can be obtained:

$$P_\ell^{-m}(\cos\theta) = (-1)^m\,\frac{(\ell-|m|)!}{(\ell+|m|)!}\,P_\ell^m(\cos\theta) \quad . \tag{B.22}$$

Therefore for the spherical harmonics one has:

$$Y_{\ell,-m}(\theta,\varphi) = (-1)^m\,Y_{\ell m}^*(\theta,\varphi) \quad . \tag{B.23}$$

Another useful relation is that for a space reflection

$$Y_{\ell m}(\pi-\theta,\varphi+\pi) = (-1)^\ell\,Y_{\ell m}(\theta,\varphi) \quad . \tag{B.24}$$

Finally the normalization and orthogonality conditions are given by

$$\int\limits_0^{2\pi}\mathrm{d}\varphi\int\limits_0^{\pi}\sin\theta\,\mathrm{d}\theta\,Y_{\ell m}(\theta,\varphi)\,Y_{\ell' m'}^*(\theta,\varphi) = \delta_{\ell\ell'}\,\delta_{mm'} \quad , \tag{B.25}$$

and the completeness relation is obtained from the sum over the angular momentum quantum numbers:

$$\sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell}Y_{\ell m}(\theta,\varphi)\,Y_{\ell m}^*(\theta',\varphi') = \delta(\varphi'-\varphi)\,\delta(\cos\theta'-\cos\theta) \quad . \tag{B.26}$$

In this work the equivalent notations

$$Y_L(\hat{\boldsymbol{r}}) \equiv Y_{\ell m}(\theta,\varphi) \quad , \tag{B.27}$$

are used simultaneously. Finally from (B.23) it follows that

$$\sum_{m=-\ell}^{\ell}Y_{\ell m}(\theta,\varphi)\,Y_{\ell m}^*(\theta',\varphi') = \sum_{m=-\ell}^{\ell}Y_{\ell m}^*(\theta,\varphi)\,Y_{\ell m}(\theta',\varphi') \quad . \tag{B.28}$$

B.2.1 **Gaunt Coefficients**

An important set of constants that appears frequently in the derivations is the angular integral over a triple product of spherical harmonics:

$$C_{LL''}^{L'} = \int \mathrm{d}\hat{\boldsymbol{r}}\, Y_L(\hat{\boldsymbol{r}})\, Y_{L'}^*(\hat{\boldsymbol{r}})\, Y_{L''}(\hat{\boldsymbol{r}}) \quad . \tag{B.29}$$

Here the upper index denotes the index of the complex conjugated spherical harmonic. These quantities are often referred to as *Gaunt coefficients* and as for the spherical harmonics the equivalent notations

$$C_{LL''}^{L'} = C_{\ell m,\ell'' m''}^{\ell' m'} \quad , \tag{B.30}$$

will be used. Not all of these coefficients are non-zero but only those for which $m' = m + m''$, $\ell + \ell' + \ell''$ even, $\ell + \ell' \geq \ell''$, $\ell' + \ell'' \geq \ell$, and $\ell + \ell'' \geq \ell'$ [LS72]. From these selection rules (triangular conditions) follow the relations for the double primed indices:

$$|\ell - \ell'| \leq \ \ell'' \ \leq \ell + \ell' \tag{B.31}$$

$$m'' \ = \ m' - m \quad . \tag{B.32}$$

Since the Gaunt coefficients are real one finds that

$$C_{LL''}^{L'} = C_{L'}^{LL''} \quad . \tag{B.33}$$

And due to the othonormality of the spherical harmonics we get the useful relation

$$C_{L,(0,0)}^{L'} = C_{(0,0),L}^{L'} = \frac{\delta_{LL'}}{\sqrt{4\pi}} \quad . \tag{B.34}$$

B.2.2 **Useful Expansions**

Two important expansions in terms of spherical harmonics that are used in this work are (c.f. [Mes69], [Jac92],[LS72],[Skr84]):

$$\frac{1}{|\boldsymbol{r} - \boldsymbol{r}'|} = \sum_L \frac{4\pi}{2\ell + 1} \frac{r_<^\ell}{r_>^{\ell+1}} Y_L(\hat{\boldsymbol{r}})\, Y_L^*(\hat{\boldsymbol{r}}') \quad , \tag{B.35}$$

and

$$\begin{aligned} \frac{1}{|\boldsymbol{r} - \boldsymbol{r}'|^{\ell+1}} Y_{\ell m}(\widehat{\boldsymbol{r} - \boldsymbol{r}'}) \quad &= \quad \sum_{L'} (-1)^\ell \frac{4\pi\ (2(\ell + \ell') - 1)!!}{(2\ell - 1)!!\,(2\ell' + 1)!!} C_{\ell m,(\ell+\ell')(m'-m)}^{\ell' m'} \\ &\times \ Y_{(\ell+\ell')(m'-m)}^*(\hat{\boldsymbol{r}}') \frac{1}{(r')^{\ell+\ell'+1}} r^{\ell'} Y_{\ell' m'}(\hat{\boldsymbol{r}}) \quad . \end{aligned} \tag{B.36}$$

The Green's Function for Free Electrons

In this section the expressions (2.9) and (2.10) will be derived in detail. The starting point is equation (2.7):

$$G^0(\boldsymbol{r},\boldsymbol{r'};E) = (2\pi)^{-3} \int \frac{\exp\left[\mathrm{i}\boldsymbol{q}\cdot(\boldsymbol{r}-\boldsymbol{r'})\right]}{k^2-q^2}\,\mathrm{d}\boldsymbol{q} \quad . \tag{B.37}$$

Changing to spherical coordinates

$$\begin{aligned} \mathrm{d}\boldsymbol{q} &= q^2\,\mathrm{d}q\,\mathrm{d}\hat{\boldsymbol{q}} \\ \mathrm{d}\hat{\boldsymbol{q}} &= \sin\theta\,\mathrm{d}\theta\,\mathrm{d}\varphi \quad , \end{aligned}$$

with $0 \le q < \infty$, $0 \le \varphi \le 2\pi$, and $0 \le \theta \le \pi$, the integral transforms to

$$G^0(\boldsymbol{r},\boldsymbol{r'};E) = (2\pi)^{-3} \int_0^\infty \mathrm{d}q\,\frac{q^2}{k^2-q^2} \int \mathrm{d}\hat{\boldsymbol{q}}\,\exp(\mathrm{i}q|\boldsymbol{r}-\boldsymbol{r'}|\cos\theta) \quad , \tag{B.38}$$

where $\boldsymbol{q}\cdot\boldsymbol{r}= qr\cos\theta$ has been used. Next the integration over $\mathrm{d}\hat{\boldsymbol{q}}$ is performed:

$$\begin{aligned} \int \mathrm{d}\hat{\boldsymbol{q}}\,\exp(\mathrm{i}q|\boldsymbol{r}-\boldsymbol{r'}|\cos\theta) &= \int_0^{2\pi}\mathrm{d}\varphi \int_0^{\pi}\mathrm{d}\theta\,\sin\theta\,\exp(\mathrm{i}q|\boldsymbol{r}-\boldsymbol{r'}|\cos\theta) & \text{(B.39)} \\ &= -2\pi\,\frac{\exp(-\mathrm{i}q|\boldsymbol{r}-\boldsymbol{r'}|)-\exp(\mathrm{i}q|\boldsymbol{r}-\boldsymbol{r'}|)}{\mathrm{i}q|\boldsymbol{r}-\boldsymbol{r'}|} \quad . & \text{(B.40)} \end{aligned}$$

After substitution and rearrangement in (B.38), only the one dimensional radial integral is left:

$$\begin{aligned} G^0(\boldsymbol{r},\boldsymbol{r'};E) &= \frac{1}{4\pi^2\mathrm{i}|\boldsymbol{r}-\boldsymbol{r'}|}\int_0^\infty \frac{q\left[\exp(\mathrm{i}q|\boldsymbol{r}-\boldsymbol{r'}|)-\exp(-\mathrm{i}q|\boldsymbol{r}-\boldsymbol{r'}|)\right]}{k^2-q^2}\,\mathrm{d}q & \text{(B.41)} \\ &= -\frac{1}{4\pi^2\mathrm{i}|\boldsymbol{r}-\boldsymbol{r'}|}\int_{-\infty}^\infty \frac{q\exp(\mathrm{i}q|\boldsymbol{r}-\boldsymbol{r'}|)}{q^2-k^2}\,\mathrm{d}q \quad . & \text{(B.42)} \end{aligned}$$

The last expression contains a complex function of the variable q in the integral, which has two simple poles at $q = k$ and $q = -k$. For the evaluation of the integral a proper integration path in the upper half of the complex plane has to be chosen, which includes either one of the two poles. According to standard analysis [WW92] an integral of the type (B.42) is evaluated as

$$\int\limits_{-\infty}^{\infty} f(z)\,\mathrm{d}z = 2\pi\mathrm{i}\sum_{k=0}^{n}\mathrm{Res}_{z=z_k}\,f(z)\,,\quad \mathrm{Im}(z_k)>0 \quad , \tag{B.43}$$

where z is a complex variable, z_k are the poles of $f(z)$, and $\mathrm{Res}f(z)$ refers to the residuum of the function $f(z)$, which can be evaluated from

$$\mathrm{Res}_{z=z_k}\,f(z) = \lim_{z\to z_k}(z-z_k)f(z) \quad . \tag{B.44}$$

With

$$\mathrm{Res}_{q=k}\left\{\frac{q\exp(\mathrm{i}q|\boldsymbol{r}-\boldsymbol{r'}|)}{q^2-k^2}\right\} = \frac{1}{2}\exp(\mathrm{i}k|\boldsymbol{r}-\boldsymbol{r'}|) \quad , \tag{B.45}$$

evaluation of the integral in (B.42) yields

$$G^0_{(+)}(\boldsymbol{r},\boldsymbol{r'};E) = -\frac{\exp(\mathrm{i}k|\boldsymbol{r}-\boldsymbol{r'}|)}{4\pi|\boldsymbol{r}-\boldsymbol{r'}|} \quad , \tag{B.46}$$

which is equation (2.9). If the residuum for the second pole, $q=-k$, is calculated, equation (2.10) is obtained:

$$G^0_{(-)}(\boldsymbol{r},\boldsymbol{r'};E) = -\frac{\exp(-\mathrm{i}k|\boldsymbol{r}-\boldsymbol{r'}|)}{4\pi|\boldsymbol{r}-\boldsymbol{r'}|} \quad . \tag{B.47}$$

B.3.1 **Partial Wave Expansion of the Free Particle Green's Function**

A commonly used description of the free particle Green's function is its expansion in terms of solutions of the free space Schrödinger equation and its partial wave components. We start off by rewriting equation (2.7)

$$G^0(\boldsymbol{r},\boldsymbol{r'};E) = (2\pi)^{-3}\int \exp\left(\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}\right)\,\frac{1}{k^2-q^2}\,\exp\left(-\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}'\right)\,\mathrm{d}\boldsymbol{q} \quad . \tag{B.48}$$

Using the expansion (2.11), which is also known as Bauer's identity, we have

$$\begin{aligned} G^0(\boldsymbol{r},\boldsymbol{r'};E) &= (2\pi)^{-3}\int \mathrm{d}\boldsymbol{q}\left(\sum_L 4\pi\mathrm{i}^\ell\,j_\ell(qr)\,Y^*_L(\hat{\boldsymbol{q}})\,Y_L(\hat{\boldsymbol{r}})\right) \\ &\quad \times\frac{1}{k^2-q^2}\left(\sum_{L'}4\pi(-\mathrm{i}^{\ell'})\,j_{\ell'}(qr')\,Y_{L'}(\hat{\boldsymbol{q}})\,Y^*_{L'}(\hat{\boldsymbol{r}}')\right) \quad . \end{aligned} \tag{B.49}$$

Transformation to spherical coordinates and some rearrangement yields

$$G^0(\boldsymbol{r},\boldsymbol{r'};E) \;=\; \frac{2}{\pi}\int\limits_0^\infty \frac{q^2\,\mathrm{d}q}{k^2-q^2}\sum_{LL'} \mathrm{i}^\ell(-\mathrm{i}^{\ell'})\, j_\ell(qr) j_{\ell'}(qr')\, Y_L(\hat{\boldsymbol{r}}) Y^*_{L'}(\hat{\boldsymbol{r}}') \\ \times \int \mathrm{d}\hat{\boldsymbol{q}}\, Y^*_L(\hat{\boldsymbol{q}}) Y_{L'}(\hat{\boldsymbol{q}}) \quad . \tag{B.50}$$

Now the orthogonality of the complex spherical harmonics can be used

$$\int \mathrm{d}\hat{\boldsymbol{q}}\, Y^*_L(\hat{\boldsymbol{q}}) Y_{L'}(\hat{\boldsymbol{q}}) = \delta_{LL'} \quad , \tag{B.51}$$

and with $\mathrm{i}^\ell(-\mathrm{i}^\ell) = 1$, one can write

$$G^0(\boldsymbol{r},\boldsymbol{r'};E) = \frac{2}{\pi}\int\limits_0^\infty \frac{q^2\,\mathrm{d}q}{k^2-q^2}\sum_{L} j_\ell(qr) j_\ell(qr')\, Y_L(\hat{\boldsymbol{r}}) Y^*_L(\hat{\boldsymbol{r}}') \quad . \tag{B.52}$$

Following from the fact that the integrand is even in q, this formula can be rewritten to yield equation (2.12)

$$G^0(\boldsymbol{r},\boldsymbol{r'};E) = \pi^{-1}\sum_L Y_L(\hat{\boldsymbol{r}})\, Y^*_L(\hat{\boldsymbol{r}}') \int\limits_{-\infty}^{\infty} \frac{j_\ell(qr)\, j_\ell(qr')}{k^2-q^2}\, q^2 \mathrm{d}q \quad . \tag{B.53}$$

Hence we can define

$$G^0_\ell(r,r';E) = \pi^{-1}\int\limits_{-\infty}^{\infty} \frac{j_\ell(qr)\, j_\ell(qr')}{k^2-q^2}\, q^2 \mathrm{d}q \quad . \tag{B.54}$$

The evaluation of the integral has to be done by contour integration in the complex q plane. However, because the product $j_\ell(qr)\, j_\ell(qr')$ does not vanish along the semi circle in the upper half plane [MMZ87] some care has to be taken. Following Gonis [Gon92] for $r' > r$ the relation

$$j_\ell(qr') = \frac{1}{2}\left[h_\ell(qr') + h^*_\ell(qr')\right] \quad , \tag{B.55}$$

where $h_\ell(qr')$ is a spherical Hankel function of the first kind, helps out. After substitution in (B.53) the solutions to two integrals have to be found:

$$\mathrm{I}_1 \;=\; \frac{1}{2}\int\limits_{-\infty}^{\infty} \frac{q^2\, j_\ell(qr)\, h_\ell(qr')}{k^2-q^2}\,\mathrm{d}q \quad , \tag{B.56}$$

$$\mathrm{I}_2 \;=\; \frac{1}{2}\int\limits_{-\infty}^{\infty} \frac{q^2\, j_\ell(qr)\, h^*_\ell(qr')}{k^2-q^2}\,\mathrm{d}q \quad . \tag{B.57}$$

The integral I_1 can be solved by using the pole at $q = +k$ from

$$\begin{aligned}
\mathrm{I}_1 &= \tfrac{1}{2}\, 2\pi\mathrm{i}\, \mathrm{Res}_{q=+k} \left[\frac{q^2\, j_\ell(qr)\, h_\ell(qr')}{k^2 - q^2} \right] && \text{(B.58)} \\
&= \pi\mathrm{i} \left[-\frac{1}{2}\, k\, j_\ell(kr)\, h_\ell(kr') \right] && \text{(B.59)} \\
&= -\tfrac{1}{2}\, \mathrm{i}\pi k\, j_\ell(kr)\, h_\ell(kr')\,, \quad r' > r \quad . && \text{(B.60)}
\end{aligned}$$

The second integral can be evaluated by closing the contour in the lower half plane and thereby including the second pole $q = -k$. One then gets

$$\begin{aligned}
\mathrm{I}_2 &= \tfrac{1}{2}\, 2\pi\mathrm{i}\, \mathrm{Res}_{q=-k} \left[\frac{q^2\, j_\ell(qr)\, h^*_\ell(qr')}{k^2 - q^2} \right] && \text{(B.61)} \\
&= -\tfrac{1}{2}\, \mathrm{i}\pi k\, j_\ell(-kr)\, h^*_\ell(-kr') \quad . && \text{(B.62)}
\end{aligned}$$

With the identities $j_\ell(-kr) = (-1)^{\ell+1} j_\ell(kr)$ and $h^*_\ell(-kr) = (-1)^\ell\, h_\ell(kr)$, I_2 finally yields an contribution identical to I_1:

$$\mathrm{I}_2 = -\tfrac{1}{2}\, \mathrm{i}\pi k\, j_\ell(kr)\, h_\ell(kr')\,, \quad r' > r \quad . \tag{B.63}$$

In total we have

$$\mathrm{I}_1 + \mathrm{I}_2 = -\mathrm{i}\pi k\, j_\ell(kr)\, h_\ell(kr')\,, \quad r' > r \quad . \tag{B.64}$$

The same procedure has to be used for $r > r'$ which gives the identical result, and in summary we can write

$$\mathrm{I}_1 + \mathrm{I}_2 = -\mathrm{i}\pi k\, j_\ell(kr_<)\, h_\ell(kr_>) \quad , \tag{B.65}$$

and therefore

$$G^0_\ell(r, r'; E) = -\mathrm{i}k\, j_\ell(kr_<)\, h_\ell(kr_>) \quad , \tag{B.66}$$

where $r_< := \min\{r, r'\}$ and $r_> := \max\{r, r'\}$. With this result the partial wave expansion of the free particle Green's function is given by

$$G^0(\boldsymbol{r}, \boldsymbol{r'}; E) = -\mathrm{i}k \sum_L j_\ell(kr_<)\, h_\ell(kr_>)\, Y_L(\hat{\boldsymbol{r}})\, Y^*_L(\hat{\boldsymbol{r}}') \quad , \tag{B.67}$$

and with the definitions:

$$\begin{aligned}
j_L(k\boldsymbol{r}) &= j_\ell(kr)\, Y_L(\hat{\boldsymbol{r}}) && \text{(B.68)} \\
h_L(k\boldsymbol{r}) &= h_\ell(kr)\, Y_L(\hat{\boldsymbol{r}}) \quad , && \text{(B.69)}
\end{aligned}$$

we can finally write

$$G^0(\boldsymbol{r}, \boldsymbol{r'}; E) = -\mathrm{i}k \sum_L j_L(k\boldsymbol{r}_<)\, h_L(k\boldsymbol{r}_>) \quad , \tag{B.70}$$

which is equation (2.14).

C

Numerical Methods

C.1

Numerical Integration - Quadratures

In the SKKR program, essentially three types of integrals appear. One type are Brillouin zone integrals, where for a layered system the integration has to be performed over a two dimensional plane in reciprocal space. A second type are complex energy integrations which appear e.g. in the evaluation of the charge density or by computing the Band energy part to the kinetic energy. And a third type are one dimensional radial integrals, which are frequently used within the program. Below an account of the mathematical basis for the numerical evaluation of these kinds of integrals is given.

The basic principle of numerical integration is to approximate the integrand $f(x)$ by an interpolating polynomial. Two types of approximations are possible. In one case a function is known on a given (equidistant) mesh, in the other the mesh is chosen to yield the highest possible accuracy [Sch97]. Initially the former case will be treated.

C.1.1 Newton-Cotes Quadrature and Lagrange Interpolation

Lagrange Interpolation

The basis of all that follows is the existence and uniqueness of polynomial interpolation. Given $n+1$ discrete mesh points $x_0, x_1, x_2, \ldots, x_n$ and the corresponding values $y_0, y_1, y_2, \ldots, y_n$, we then want to find a polynomial of n-th order

$$P_n(x) = a_0 + a_1 x + a_2 x^2 + \ldots + a_n x^n \quad , \tag{C.1}$$

which satisfies the condition that

$$P_n(x_i) = y_i\,, \quad i = 0, 1, 2, \ldots, n\,. \tag{C.2}$$

To see that such a polynomial, whose highest order is n, will always exist for any given pair of mesh points and corresponding values, we can inspect certain *Lagrange polynomials*, $L_i(x)$ for the $n+1$ mesh points:

$$L_i(x) := \prod_{\substack{j=0 \\ j\neq i}}^{n} \frac{x - x_j}{x_i - x_j}\,, \quad i = 0, 1, 2, \ldots, n\,. \tag{C.3}$$

With this definition the Lagrange polynomials have the following property:

$$L_i(x_k) = \delta_{ik} = \begin{cases} 1, & i = k \\ 0, & i \neq k \end{cases} \quad . \tag{C.4}$$

Now the polynomial $P_n(x)$ can be written as

$$P_n(x) = \sum_{i=0}^{n} y_i\, L_i(x) \quad , \tag{C.5}$$

which can easily be seen when (C.4) is used:

$$P_n(x_k) = \sum_{i=0}^{n} y_i\, L_i(x_k) = \sum_{i=0}^{n} y_i\, \delta_{ik} = y_k\,, \quad k = 0, 1, 2, \ldots, n\,. \tag{C.6}$$

The uniqueness of this polynomial can also be shown [Sch97].

These results can be used to find a computationally useful scheme for the general interpolation of a function given on a certain mesh - the *Lagrange interpolation* which has already been defined through equation (C.5). Now using (C.3) in (C.5), we find for $x \neq x_i$:

$$P_n(x) = \sum_{i=0}^{n} y_i \prod_{\substack{j=0 \\ j\neq i}}^{n} \frac{x - x_j}{x_i - x_j} = \sum_{i=0}^{n} y_i \frac{1}{x - x_i} \left[\prod_{\substack{j=0 \\ j\neq i}}^{n} \frac{1}{x_i - x_j} \right] \prod_{k=0}^{n} (x - x_k)\,. \tag{C.7}$$

The expression in the brackets depends only on the mesh points and can be defined as coefficients, thus

$$\pi_i := \prod_{\substack{j=0 \\ j\neq i}}^{n} \frac{1}{x_i - x_j}\,, \quad i = 0, 1, 2, \ldots, n \quad . \tag{C.8}$$

Defining the following quantity that depends also on the new mesh point x

$$\varpi_i := \frac{\pi_i}{x - x_i}\,, \quad i = 0, 1, 2, \ldots, n \quad , \tag{C.9}$$

we can write

$$P_n(x) = \sum_{i=0}^{n} \varpi_i \, y_i \prod_{k=0}^{n} (x - x_k) \quad . \tag{C.10}$$

Finally we have to find an useful expression for the last product. This can be found by observing that for $y_i = 1$ also $P_n(x) = 1$ for all i. With this it follows that

$$1 = \sum_{i=0}^{n} \varpi_i \prod_{k=0}^{n} (x - x_k) \quad , \tag{C.11}$$

and then the product is determined through the weights ϖ_i as

$$\prod_{k=0}^{n} (x - x_k) = \frac{1}{\sum\limits_{i=0}^{n} \varpi_i} \quad . \tag{C.12}$$

Now we have found a formula for the Lagrange interpolation (C.5):

$$P_n(x) = \frac{\sum\limits_{i=0}^{n} \varpi_i \, y_i}{\sum\limits_{i=0}^{n} \varpi_i} \quad , \tag{C.13}$$

which can be used in actual calculations. Within the SKKR code the subroutine that is based on this interpolation scheme is called *ylag.f.*

Newton-Cotes Quadrature

Now lets turn to the numerical evaluation of integrals and start with the following considerations: we want to integrate a real, continuous function $f(x)$, which is given on $n + 1$ mesh points $x_0 < x_1 < x_2 < \ldots < x_n$, on the closed interval $[a, b]$ which contains the whole mesh. The integral is denoted as

$$I = \int\limits_{a}^{b} f(x) \, \mathrm{d}x \, . \tag{C.14}$$

According to the previous section for the mesh points and the corresponding values $f(x_k)$ there exists a unique interpolation polynomial $P_n(x)$ which can be denoted using the Lagrange polynomials $L_k(x)$:

$$P_n(x) = \sum_{k=0}^{n} f(x_k)\, L_k(x) \quad , \tag{C.15}$$

as then

$$P_n(x_k) = f(x_k) \quad . \tag{C.16}$$

In order to approximate the integral we substitute (C.15) in (C.14):

$$I_n = \int\limits_a^b P_n(x)\,\mathrm{d}x = \sum_{k=0}^{n} f(x_k) \int\limits_a^b L_k(x)\,\mathrm{d}x \quad . \tag{C.17}$$

If the *integration weights* w_k are defined as

$$w_k := \frac{1}{b-a} \int\limits_a^b L_k(x)\,\mathrm{d}x\,, \quad k = 0, 1, 2, \ldots, n\,, \tag{C.18}$$

we obtain as an approximation to the integral in (C.14) the interpolating quadrature formula

$$I_n = (b-a) \sum_{k=0}^{n} w_k\, f(x_k) \quad . \tag{C.19}$$

Simpson's Rule

Let us consider an equidistant mesh in the interval $[a, b]$ such that:

$$x_i = a + ih\,, \quad i = 0, 1, 2, \ldots, n\,, \qquad h = \frac{b-a}{n}\,. \tag{C.20}$$

To evaluate the expression (C.18) we need to use the definition of the Lagrange polynomials (C.3) and make the substitution

$$x = a + (b-a)\xi\,, \quad dx = (b-a)\mathrm{d}\xi \quad , \tag{C.21}$$

which leads to:

$$w_k := \frac{1}{b-a} \int\limits_a^b \prod_{\substack{i=0\\i\neq k}}^{n} \frac{x-x_i}{x_k-x_i}\,\mathrm{d}x = \int\limits_0^1 \prod_{\substack{i=0\\i\neq k}}^{n} \frac{n\xi-i}{k-i}\,\mathrm{d}\xi \quad . \tag{C.22}$$

Taking $n = 2$ leads to the three weighting factors:

$$w_0 = \int\limits_0^1 \frac{(2\xi-1)(2\xi-2)}{(-1)(-2)}\,\mathrm{d}\xi = \frac{1}{2}\int\limits_0^1 (4\xi^2-6\xi+2)\,\mathrm{d}\xi = \frac{1}{6}\,, \tag{C.23}$$

$$w_1 = \int\limits_0^1 \frac{2\xi(2\xi-2)}{(-1)}\,\mathrm{d}\xi = -\int\limits_0^1 (4\xi^2-4\xi)\,\mathrm{d}\xi = \frac{2}{3}\,, \tag{C.24}$$

$$w_2 = \int\limits_0^1 \frac{2\xi(2\xi-1)}{2}\,\mathrm{d}\xi = \frac{1}{2}\int\limits_0^1 (4\xi^2-2\xi)\,\mathrm{d}\xi = \frac{1}{6}\,, \tag{C.25}$$

which can be substituted into the quadrature formula to yield *Simpson's rule*:

$$I_2 = \frac{b-a}{6}\,\left(f(x_0)+4\,f(x_1)+f(x_2)\right) = \frac{h}{3}\,\left(f(x_0)+4\,f(x_1)+f(x_2)\right) \quad . \tag{C.26}$$

A better approximation of the integral is obtained if the interval $[a, b]$ is divided into N intervals of equal length. Then the above formula is applied on each interval and the results are added up to give a modified Simpson's rule:

$$S_2 = \frac{h}{3}\left(f(a)+4\,f(x_1)+f(b)+2\sum_{k=1}^{N-1}\left[f(x_{2k})+2\,f(x_{2k+1})\right]\right) \quad , \tag{C.27}$$

where

$$h = \frac{b-a}{2N}\,, \quad x_k = a+kh\,, \quad k = 1,2,\ldots,2N-1\,. \tag{C.28}$$

The function that performs this integration in the code is *rsimp.f*.

C.1.2 **Gaussian Quadrature**

The difference to the quadrature formulas discussed above is that now the weights w_k and the mesh points x_k are chosen to give a quadrature formula of the highest possible accuracy. In close analogy to the results obtained above such a formula is given by

$$I_n = \sum_{k=1}^{n} w_k \, f(x_k) \,, \quad x_k \in [-1,1] \,. \tag{C.29}$$

The n mesh points x_k are the zeros of the n-th Legendre polynomial, (for a proof see reference [Sch97]) which has been defined in (B.20), and the weights w_k are

$$w_k = \int_{-1}^{1} \prod_{\substack{j=1 \\ j\neq k}}^{n} \left(\frac{x - x_j}{x_k - x_j} \right)^2 \mathrm{d}x > 0 \,, \quad k = 1,2,\ldots,n \,. \tag{C.30}$$

It is common to choose the integration interval to be $[-1,1]$ as any finite interval $[a,b]$ may be obtained through a linear transformation. One advantage of this choice is that the nodes x_k lie symmetric around the origin and therefore the knowledge of the non-negative nodes and their corresponding weights suffices.

Using a Gaussian quadrature to calculate an integral of the general form

$$I = \int_{a}^{b} f(\xi) \, \mathrm{d}\xi \quad , \tag{C.31}$$

a variable substitution of the type

$$\xi = \frac{b-a}{2} \, x + \frac{a+b}{2} \quad , \tag{C.32}$$

has to be used. Then the integral transforms to

$$I = \frac{b-a}{2} \int_{-1}^{1} f\left(\frac{b-a}{2} \, x + \frac{a+b}{2} \right) \mathrm{d}x \quad , \tag{C.33}$$

and the quadrature formula is

$$I_n = \frac{b-a}{2} \sum_{k=1}^{n} w_k \, f\left(\frac{b-a}{2} \, x_k + \frac{a+b}{2} \right) = \frac{b-a}{2} \sum_{k=1}^{n} w_k \, f(\xi_k) \quad . \tag{C.34}$$

Complex Energy Integration

The Gaussian quadrature is used within the program to compute integrals over functions of the complex energy. To perform these integrals a special parameterization can be chosen such that the complex energy lies on a semicircular contour and the mesh is denser approaching the Fermi energy. The integral to be evaluated is of the form [TDK+97]

$$I = \int\limits_{E_B}^{E_F} f(z)\,\mathrm{d}z \quad , \tag{C.35}$$

where z is some complex energy and E_B denotes the bottom of the valence band which in practical calculations is an energy point below the valence band. Clearly E_F is the Fermi energy. To evaluate this integral we turn to a parameterization of the complex energy that makes use of an angle φ and the radius r whose meanings are illustrated in figure C.1. The radius is thus defined as

$$r = \frac{E_F - E_B}{2} \quad , \tag{C.36}$$

and by defining $z_0 = E_B + r$, the complex energy is given by

$$z = r\,\mathrm{e}^{\mathrm{i}\varphi} + z_0 \quad . \tag{C.37}$$

In order to obtain the desired distribution of the complex energy points φ is given by

$$\varphi = \varepsilon\left(\mathrm{e}^{-y} - 1\right) \quad , \tag{C.38}$$

where ε is some small number and y is

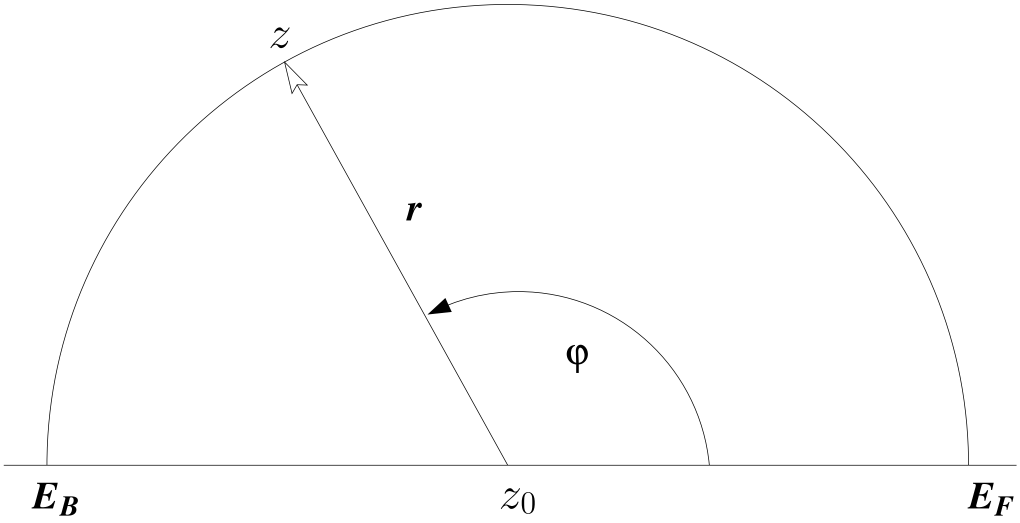
$$y = \frac{1}{2}\left(y_2 - y_1\right) x_k + \frac{1}{2}\left(y_2 + y_1\right) \quad . \tag{C.39}$$

There the x_k are the zeros of the Legendre polynomials and y_1 and y_2 define the first and the last point on the contour as they are calculated from

$$y_1 = -\ln\left(\frac{\varepsilon + \varphi_1}{\varepsilon}\right) \quad , \tag{C.40}$$

$$y_2 = -\ln\left(\frac{\varepsilon + \varphi_2}{\varepsilon}\right) \quad , \tag{C.41}$$

Figure C.1: *Parameterization of the semicircular contour for the complex energy integration.*



Hence for $\varphi_1 = \pi$ and $\varphi_2 = 0$ it can be easily checked that with $x_k = -1$ we get $z = z_0 - r$ and with $x_k = 1$ we get $z = z_0 + r$. Now with this parameterization the initial integral can be evaluated from

$$I = \sum_{k=1}^{n} \rho_k \, f(z_k) \quad , \tag{C.42}$$

where the parametrized weights ρ_k and the nodes z_k are given by

$$\rho_k = -\frac{\mathrm{i}\,\varepsilon\,\mathrm{e}^{-y}\,(y_2 - y_1)\,(z_k - z_0)\,w_k}{2} \quad , \tag{C.43}$$

$$z_k = r\,\mathrm{e}^{\mathrm{i}\varphi} + z_0 \tag{C.44}$$

The routine that performs this parameterization is *zmesh.f.*

Complex Energy Integration Along a Straight Line

If instead of the semi circle an integration parallel to the energy axis is desired, things are less complicated. Then the distribution of energy points is equidistant with an increment Δz:

$$\Delta z = \frac{E_F - E_B}{N - 1} \quad , \tag{C.45}$$

if N is the number of energy points. Hence the complex energies are given by

$$z_k = z_{k-1} + \Delta z + \mathrm{i}\varepsilon \quad , \tag{C.46}$$

where ε is some small number. The corresponding weights are real and simply

$$w_k = \Delta z \quad , \tag{C.47}$$

except for $k = 1$ and $k = N$, for which we use $w_k = \Delta z/2$.

C.3

Brillouin Zone Integration

The integration over a Brillouin zone [LT72][FV76][Ban75][Kle83][Has61][HWK90][HKS84][JA84][PS85] is in principle performed by a simple Newton-Cotes quadrature (c.f. equation (C.19)). Since we are dealing with layered structures, two dimensional integrations have to be performed in reciprocal space. The sets of mesh points and weights have to be chosen in accordance with the direction of the crystal planes and hence are different for the (001), (110), and (111) directions. Care has to be taken when the two dimensional reciprocal lattice is constructed since the final results are different depending on whether it is obtained from the two dimensional, direct lattice or from the three dimensional one. In the following the constructions of two dimensional lattices for the three major crystallographic planes in an fcc lattice will be discussed.

Figure C.2: *The 2D real space, primitive vectors $\boldsymbol{a}_1$, $\boldsymbol{a}_2$ and the corresponding vectors in reciprocal space labelled by $\boldsymbol{b}_1$, $\boldsymbol{b}_2$. One can see that $\boldsymbol{b}_1$ ($\boldsymbol{b}_2$) is perpendicular to $\boldsymbol{a}_2$ ($\boldsymbol{a}_1$).*

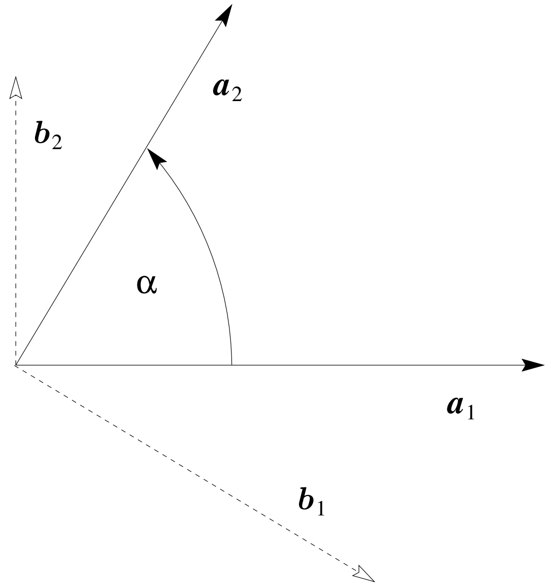


Figure C.3: *Fcc (001) plane. The lengths of the diagonals are equal to the 3D lattice constant a.*

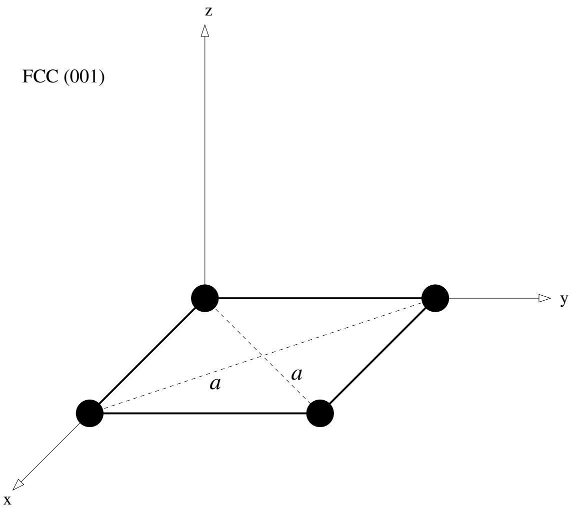
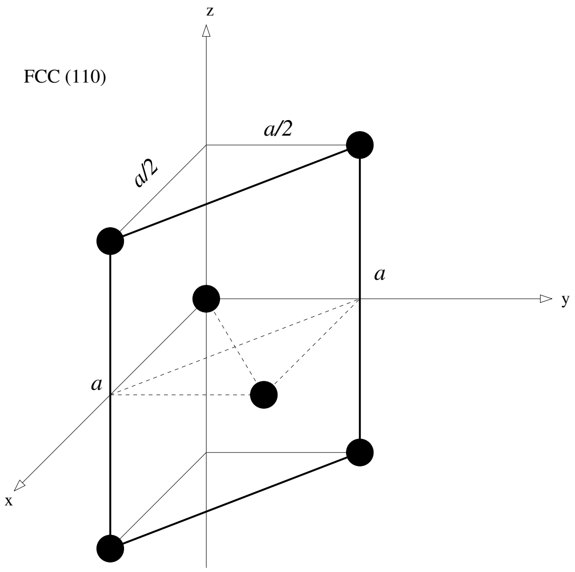


Figure C.4: *Fcc (110) plane. Indicated are the relations to the 3D lattice constant a.*



But first let us investigate the general construction of the two dimensional reciprocal lattice.

Generally, the two basis vectors forming the primitive cell in direct space are given by

$$\boldsymbol{a}_1 = a_{2D} \begin{pmatrix} 1 \\ 0 \end{pmatrix} , \quad \boldsymbol{a}_2 = \beta\, a_{2D} \begin{pmatrix} \cos\alpha \\ \sin\alpha \end{pmatrix} \quad , \tag{C.48}$$

where α is the angle between $\boldsymbol{a}_1$ and $\boldsymbol{a}_2$, and β is the *asymmetry ratio* of the primitive cell, i.e. it is equal to 1 if the vectors have the same length. The 2D lattice constant a_{2D} of the direct lattice is related to the 3D lattice constant in ways depending on the crystallographic plane under consideration. Because of the relation (c.f. figure C.2)

$$\boldsymbol{a}_i\, \boldsymbol{b}_j = 2\pi\, \delta_{ij}\,, \quad i,j = 1,2 \quad , \tag{C.49}$$

it follows that the primitive vectors of the reciprocal lattice, $\boldsymbol{b}_1$ and $\boldsymbol{b}_2$ are given by

$$\boldsymbol{b}_1 = \frac{2\pi}{a_{2D}\sin\alpha} \begin{pmatrix} \sin\alpha \\ -\cos\alpha \end{pmatrix} , \quad \boldsymbol{b}_2 = \frac{2\pi}{\beta\, a_{2D}\sin\alpha} \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad . \tag{C.50}$$

With this we can now investigate the three different planes.

Figure C.5: *Distribution of k points in the irreducible part of the Brillouin zone of a two dimensional square lattice for a fcc or bcc (001) plane.*

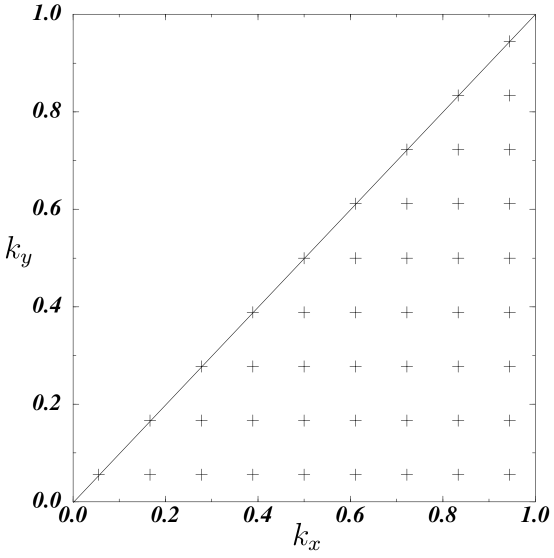
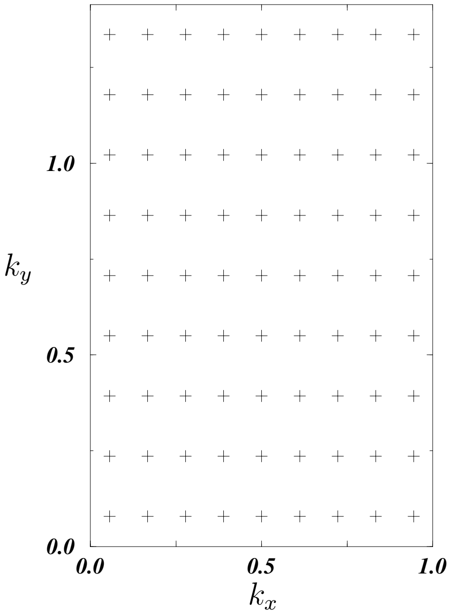


Figure C.6: *Distribution of k points in the irreducible part of the Brillouin zone of a two dimensional rectangular lattice for a fcc (110) plane.*



C.3.1 **Fcc (001) Plane**

In this plane, which is illustrated in figure C.3, the 2D lattice constant is related to the 3D lattice constant a via

$$a_{2D} = \frac{a}{\sqrt{2}} \quad . \tag{C.51}$$

The lattice is of square type and therefore $\alpha = \pi/2$ and $\beta = 1$. Hence according to (C.48) the vectors in real space are given by

$$\boldsymbol{a}_1 = a_{2D} \begin{pmatrix} 1 \\ 0 \end{pmatrix} , \quad \boldsymbol{a}_2 = a_{2D} \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad , \tag{C.52}$$

and with (C.50) the basis vectors in reciprocal space are

$$\boldsymbol{b}_1 = \frac{2\pi}{a_{2D}} \begin{pmatrix} 1 \\ 0 \end{pmatrix} , \quad \boldsymbol{b}_2 = \frac{2\pi}{a_{2D}} \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad . \tag{C.53}$$

Now the Brillouin zone can be constructed around each lattice point. Then the irreducible part of the zone, as illustrated in figure C.5, is bounded by the vectors:

$$\boldsymbol{k}_1 = \frac{\pi}{a_{2D}} \begin{pmatrix} 1 \\ 0 \end{pmatrix} , \quad \boldsymbol{k}_2 = \frac{\pi}{a_{2D}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \quad . \tag{C.54}$$

Figure C.7: *Distribution of k points in the irreducible part of the Brillouin zone of a two dimensional hexagonal lattice on a fcc or bcc (111) plane.*

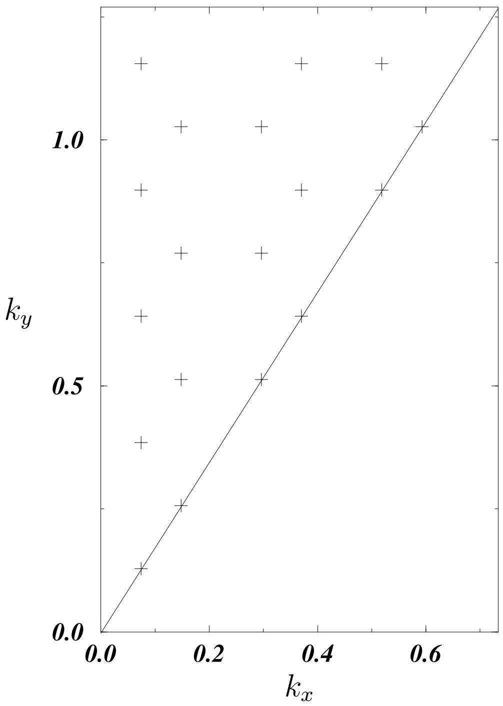
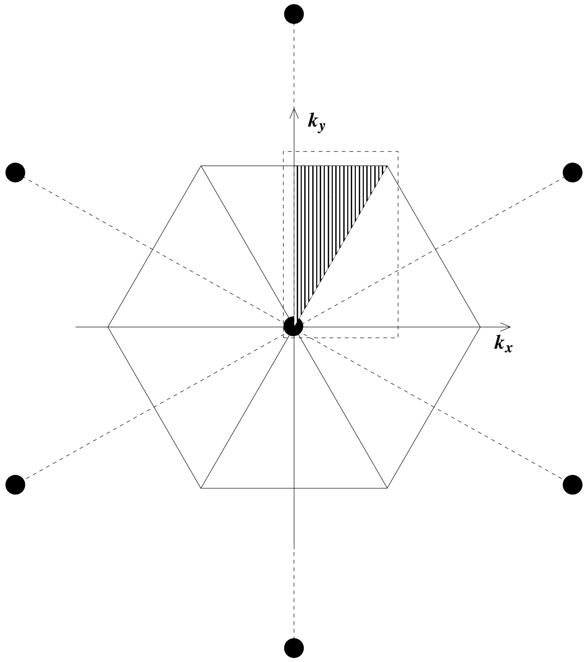


Figure C.8: *First Brillouin zone in a two dimensional hexagonal lattice with the lattice points indicated by filled, black circles.*



The points for the integration are distributed equally along the k_x and k_y direction. If n is the number of points in the k_x direction then the total number of points in the irreducible part is $n(n+1)/2$.

C.3.2 **Fcc (110) Plane**

In the direct lattice, displayed in figure C.4, the 2D lattice constant is $a_{2D} = a$, however the lattice is rectangular ($\alpha = \pi/2$) and $\beta = 1/\sqrt{2}$. Therefore the vectors are given by

$$\boldsymbol{a}_1 = a_{2D} \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \boldsymbol{a}_2 = \frac{a_{2D}}{\sqrt{2}} \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad , \tag{C.55}$$

and with this the reciprocal vectors are obtained as

$$\boldsymbol{b}_1 = \frac{2\pi}{a_{2D}} \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \boldsymbol{b}_2 = \frac{2\sqrt{2}\,\pi}{a_{2D}} \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad . \tag{C.56}$$

The k_x and the k_y directions are subdivided into an equal number of intervals, which means that there is the same number of points in each direction. Because of this arrangement, n^2 points are used for the integration if there are n points in one direction.

C.3.3 Fcc (111) Plane

In the (111) direction, which is illustrated in figure C.9, a hexagonal lattice is obtained. Then also the reciprocal lattice is hexagonal. The 2D lattice constant in direct space is given by

$$a_{2D} = \frac{a}{\sqrt{2}} \quad , \tag{C.57}$$

β is equal to 1 and $\alpha = \pi/3$. Hence the vectors forming the two dimensional primitive cell are

$$\boldsymbol{a}_1 = a_{2D} \begin{pmatrix} 1 \\ 0 \end{pmatrix} , \quad \boldsymbol{a}_2 = a_{2D} \begin{pmatrix} 1/2 \\ \sqrt{3}/2 \end{pmatrix} \quad . \tag{C.58}$$

It follows that the reciprocal, primitive vectors are given by

$$\boldsymbol{b}_1 = \frac{4\pi}{a_{2D}\sqrt{3}} \begin{pmatrix} \sqrt{3}/2 \\ -1/2 \end{pmatrix} , \quad \boldsymbol{b}_2 = \frac{4\pi}{a_{2D}\sqrt{3}} \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad . \tag{C.59}$$

The corresponding first Brillouin zone is illustrated in C.8 and from simple Algebra it follows that the two vectors defining the irreducible part are simply

$$\boldsymbol{k}_1 = \frac{\pi}{a_{2D}} \begin{pmatrix} 2/3 \\ 0 \end{pmatrix} , \quad \boldsymbol{k}_2 = \frac{\pi}{a_{2D}} \begin{pmatrix} 2/3 \\ 2/\sqrt{3} \end{pmatrix} \quad . \tag{C.60}$$

In figure C.7 the distribution of k points in this region is displayed. Contrary to the previous cases, the points are not distributed evenly but in a special manner.

Figure C.9: *Fcc (111) plane. Indicated are the relations to the 3D lattice constant a.*

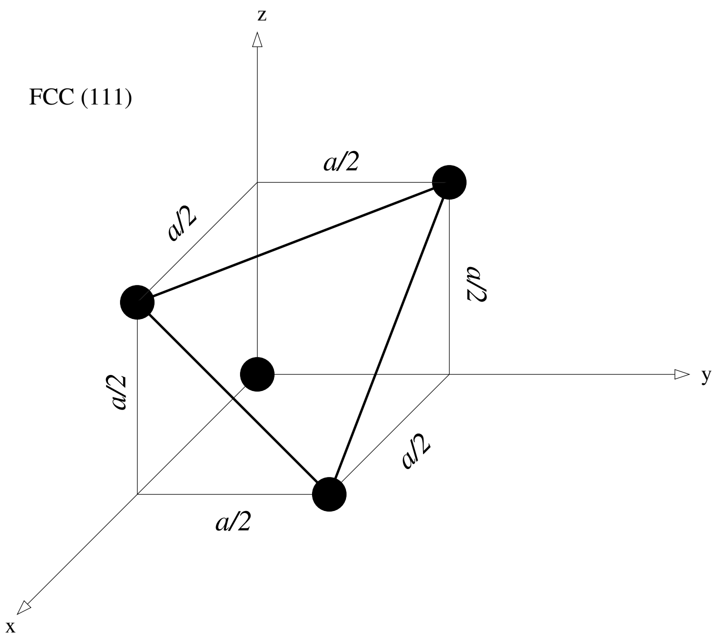


Figure C.10: *Bcc (001) plane. Indicated are the relations to the 3D lattice constant a*

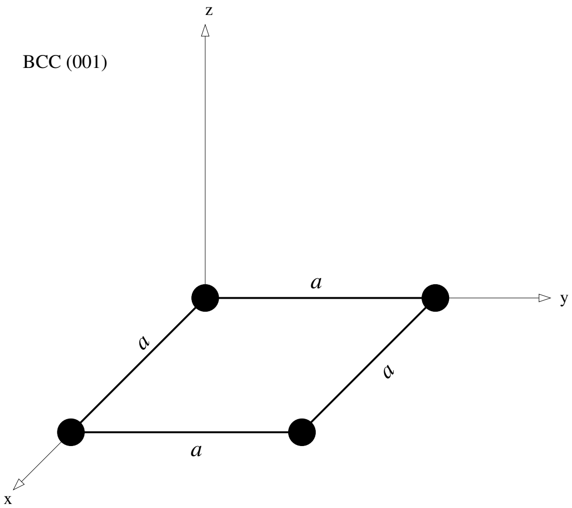
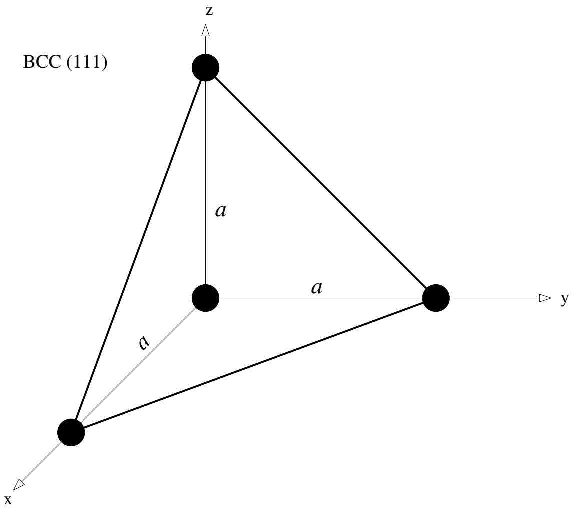


Figure C.11: *Bcc (111) plane. Indicated are the relations to the 3D lattice constant a*



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