Development and application of Muffin-Tin Orbital based Green’s function techniques to systems with magnetic and chemical disorder

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To my family
Abstract

Accurate electronic structure calculations are becoming more and more important because of the increasing need for information about systems which are hard to perform experiments on. Databases compiled from theoretical results are also being used more than ever for applications, and the reliability of the theoretical methods are of utmost importance. In this thesis, the present limits on theoretical alloy calculations are investigated and improvements on the methods are presented.

A short introduction to electronic structure theory is included as well as a chapter on Density Functional Theory, which is the underlying method behind all calculations presented in the accompanying papers. Multiple Scattering Theory is also discussed, both in more general terms as well as how it is used in the methods employed to solve the electronic structure problem. One of the methods, the Exact Muffin-Tin Orbital method, is described extensively, with special emphasis on the slope matrix, which energy dependence is investigated together with possible ways to parameterize this dependence.

Furthermore, a chapter which discusses different ways to perform calculations for disordered systems is presented, including a description of the Coherent Potential Approximation and the Screened Generalized Perturbation Method. A comparison between the Exact Muffin-Tin Orbital method and the Projector Augmented-Wave method in the case of systems exhibiting both compositional and magnetic disordered is included as well as a case study of the MoRu alloy, where the theoretical and experimental discrepancies are discussed.

The thesis is concluded with a short discussion on magnetism, with emphasis on its computational aspects. I further discuss a generalized Heisenberg model and its applications, especially to fcc Fe, and also present an investigation of the competing magnetic structures of FeNi alloys at different concentrations, where both collinear and non-collinear magnetic structures are included. For Invar-concentrations, a spin-flip transition is found and discussed. Lastly, I discuss so-called quantum corrals and possible ways of calculating properties, especially non-collinear magnetism, of such systems within perturbation theory using the force theorem and the Lloyd’s formula.
This thesis is the result of many different things. It is the result of my grandfather bringing me a small school bench and math books when I was 5 years old. It is the result of my family supporting me during my time living at home and studying. It is the result of me working in my grandfathers "snickeri", where I learned both that careful planning is essential for making bows from bamboo, and also not to drill myself in the foot. It is the result of climbing in the cliffs near my home in wintertime with ice everywhere, and not dying. It is the result of me and my friends playing Nintendo, Commodore 64, and Amiga games for days in a row; that is where I learned the seven wonders of the world, erroneously, from Civilization. It is the result of me playing chess everywhere and all the time, especially with big pieces in the city center against the city chief. He lost. It is the result of me deciding to study engineering at the university and then disdaining all the true engineering courses for physics. It is the result of Igor, my supervisor, accepting me as a graduate student in the Fysik IV group in Uppsala. It is also the result of quite a lot of work, believe it or not.

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Chapter 1

Introduction

1.1 A short essay on learning

This is my theory of how you learn things: First you spend quite some time trying to learn the language of the field you are studying. It might be Persian or Greek if you study languages, it might be Fortran if you study programming, and it might be mathematics if you study physics. After you have learned all the new terms and concepts, you must learn how to use them. You speak the language, write the programs, and read articles. This is where you think you know things. After this comes a phase where you can use these new concepts to formulate things yourself. Here you think that you most definitely really do understand the subject. Then comes the stage where you reformulate all the fancy terms and concepts in much more mundane terms, and are able to use your knowledge out of the usual context. This is when you finally begin to actually understand things, and also realize that you do not know much at all.

Unfortunately, I do not think that it is possible to start at this last stage when you try to teach someone about something; the way to go from abstract concepts to simpler terms is very personal, and what helps some might mean nothing to others. You can only show how you did it and hope that it helps someone. I greatly admire the late Professor John Ziman in this regard; I find his texts clear, to the point, and ascetic, but he is also not afraid of talking about his views of things instead of just relying on formulae. Although I do not make any pretense of being anything more than an, at best, adequate teacher, one of the main goals with this thesis is to gather the knowledge I have gained during my Ph. D. study time, and try to explain it in the best way I can. In many cases, it is probably much better to read a textbook on the matter, or to go to the original articles, but I have tried to gather all necessary theory in one place. I hope it will help some future student to gain some knowledge, and even if this is not the case, I have at least moved myself closer to realizing that I actually do not know much at all.

Before I move into the theoretical part of the thesis, I want to give a perspective
on the research I have done, and especially give a motivation to why this research is important.

1.2 An outlook

The field of material science is large and diverse. It encompasses many, very different, subjects. Some groups study how materials behave under stress and strain, or under pressure. Other groups manufacture materials that are hard to obtain, such as thin films or pure alloys, and measure properties of these materials. Yet other groups try to formulate theories for how the constituent atoms that make up the materials collaborate to produce the properties of the macroscopic samples that are used in everyday (and perhaps not so everyday) life, and use these models to make experiments with the help of computers. This gives a number of advantages in comparison to "real" experiments:

- Of course, computer experiments are usually much cheaper than real experiments. Even the most thorough computer experiment only wastes computer time, which is relatively cheap these days, while real experiments might be much more expensive. As an example high pressure experiments can be mentioned, where you sometimes have to sacrifice diamonds to be able to obtain high enough pressures. Other experiments, like calorimetric measurements, uses platinum wire by the meters. This is not cheap, and it is easily wasted, especially when new experimentalists try to build things with it, something I have learned myself the hard way.

- More importantly, it is easy to keep track of every parameter in a very careful way. When I say parameter, it might be parameters which have real life correspondences, like the volume of the sample, or parameters from a model you have made up yourself, like the local moment in a Heisenberg model of an itinerant electron system. This is an enormous advantage, and especially the possibility to "measure" made up variables makes it possible to try to understand the physics in terms of models that perhaps can be generalized to even more materials than the one examined, thus giving predictive power to the scientist.

- It is also possible to make the experiments (almost) anywhere and anytime. In real experiments, the experimental equipment is often very expensive, both to build and to maintain. Therefore many experimental groups have a joint facility where they take turns doing experiments. This means that you really have to prepare everything to be able to make as many experiments as possible when you finally get time at the facility. Often the graduate students (and it is always graduate students) keep vigil every night to maximize the output of the week in the lab. And if something interesting turns up, you may have to wait half a year to be able to verify the fact, or see that it was just some strange artifact of something.
1.3 The Problems

Recently, there has also been great interest in using theoretical databases for applications. This is because the theoretical methods have increased their efficiency and accuracy so that calculations often produces results as good as experimental data, but with calculations it is also possible to "measure" quantities that are hard to measure experimentally. There are no reasons to believe that these theoretical databases will not have increasing importance in the future, especially with the continuing development of theoretical methods.

At this stage, it is probably time to move into the more theoretical parts of the thesis, and this I do below.

1.3.1 Quantum mechanics and the Schrödinger equation

In the beginning of the 20th century, a number of experiments, like the Compton effect and the Franck-Hertz experiment, and some theoretical concepts, probably most notably the atom model of Niels Bohr, suggested that many things which had until then been described by smooth, continuous parameters, were actually quantized. Electrical charges, energies, and atomic orbits: They were all quantized; only some special, quantized, values could actually be obtained by the parameter in question. Since this is not a book on Modern Physics, I will not go through this in detail, but I will say a few things about one of the results of this time: The Schrödinger equation and its succession of the Newton laws as the way to describe the mechanics of particles. This is now known as quantum mechanics.

The Schrödinger equation can be derived in different ways, you could for example follow Landau’s derivation [1]. However you do it, you will get the same
result, and that is the time dependent Schrödinger equation:

\[ i \frac{\partial \Psi}{\partial t} = -\nabla^2 \Psi + U(r)\Psi, \]  

where \( U(r) \) is the potential energy part of the total energy, \(-\nabla^2\) is the momentum operator squared, and \( \Psi \) is the wave function of the system.

When one solves for the possible energies for the particles in a potential \( U \), the result is that you will have a continuous energy spectrum of free particles above the potential, and a discrete set of energy levels in the potential, see Fig.(1.1). The discrete set is called bound states and represent the energies of the particles, usually electrons, that are bound by the potential. This does not mean that the particles do not move, of course, only that they have a fix energy.

Another big discovery of the early 20th century was the theory of relativity. One of the most novel discoveries was that particles moving with a speed near the speed of light behaved in different ways than more mundane objects like cars or apples. Notions such as "time dilation", "the twin paradox", and "space-time continuum" became well known. Many times, you do not have to bother with using relativistic equations for the description of particle movements, but in some cases you do, e.g. when trying to describe particles in big accelerators, and then one has to use the "relativistic version" of the Schrödinger equation, known as the Dirac equation. In fact, this is what is implemented in the computer codes I will describe later, but notations become very complicated when dealing with the
1.3 The Problems

Dirac equation, and so the consensus has been reached to describe everything as if you were using the Schrödinger equation and then add at the end: "In reality, we are solving the Dirac equation.". I will change that here and now by mentioning it before I start. In reality, we are solving the Dirac equation. So. There it is. Here is also where the discussion becomes more technical, something I am afraid can not be avoided. Concepts from Hamiltonian mechanics and calculus of variations will be used, and for those unfamiliar with these concepts I recommend Goldstein’s *Classical Mechanics* [2] and Weinstock’s *Calculus of Variations* [3] respectively.

1.3.2 Separating the nuclei from the electrons

The total Hamiltonian $H$ for the system consisting of all the nuclei and electrons of the bulk matter can be written as:

$$
H = -\sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 - \frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|} + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J e^2}{|R_I - R_J|} - \sum_{i,I} \frac{Z_I e^2}{|r_i - R_I|},
$$

where $\hbar$ is Planck’s constant $\hbar$ divided by $2\pi$, $M_I$ are the masses of the nuclei, $m_e$ is the electron mass, $Z_I$ the nuclei charge, and $e$ the electron charge. Now, in Eq. (1.2), the first two terms are the kinetic energy of the electrons and the nuclei respectively, the third term is the electron-electron interaction, the fourth term is the nuclei-nuclei interaction, and finally the fifth term is the potential energy of the electrons in the field of the nuclei. Let us now try to find an eigenfunction for this Hamiltonian in the form of:

$$
\Psi = \psi(R, r)\Phi(R),
$$

where we demand that $\psi(R, r)$ satisfies the Schrödinger equation for the electrons in the potential of the now fixed nuclei at positions $R_I$:

$$
\left\{-\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + \sum_{i \neq j} \frac{e^2}{|r_i - r_j|} - \sum_{i,I} \frac{Z_I e^2}{|r_i - R_I|}\right\}\psi(R, r) = E_e(R)\psi(R, r),
$$

where the electron eigenvalues $E_e$ depend on the $R_I$.

If we now apply the Hamiltonian, Eq. (1.2), to the wave function, Eq. (1.3), we get:
\begin{align*}
H\Psi &= -\sum \frac{\hbar^2}{2M_I}\nabla_I^2 \Psi + \sum \frac{Z_I e^2}{|r_i - R_I|} \Psi + E_e(R)\Psi \\
&= \psi(R, r) \left\{ -\sum \frac{\hbar^2}{2M_I}\nabla_I^2 + E_e(R) + \sum \frac{Z_I e^2}{|r_i - R_I|} \right\} \Phi(R) \\
&\quad - \sum \frac{\hbar^2}{2M_I} \{ 2\nabla_I \Phi(R) \nabla_I \psi(R, r) + \Phi(R) \nabla_I^2 \psi(R, r) \}. \quad (1.5)
\end{align*}

If we can prove that the last line of Eq.(1.5) can be ignored, we can solve our complete problem, \( H\Psi = E\Psi \), by making \( \Phi(R) \) satisfy a Schrödinger-like equation:

\begin{align*}
\left\{ -\sum \frac{\hbar^2}{2M_I}\nabla_I^2 + E_e(R) + \sum \frac{Z_I e^2}{|r_i - R_I|} \right\} \Phi(R) &= E\Phi(R). \quad (1.6)
\end{align*}

This is what would be the Schrödinger equation for the nuclei alone, if not for the fact that the total energy of the electron system as a function of the nuclei positions enters as a contribution to the potential. So, if the last two terms in Eq.(1.5) vanished, we could solve the two parts of the bulk system, nuclei and electrons, separately, which would simplify things considerably. To see that these terms can be ignored, you first multiply with \( \Psi^* \) from the left and integrate to get the energy, and then integrate the first of these terms by parts (strictly speaking we have not yet made a transition to integrals from the sums, but this is elementary and will not be explained here), getting:

\begin{align*}
\int \psi^* \nabla_I \psi \, dr &= \frac{1}{2} \nabla_I \int \psi^* \psi \, dr \\
&= \frac{1}{2} \nabla_I n_e, \quad (1.7)
\end{align*}

where \( n_e \) is the total electron number, which is constant. The other term is more tricky, but one can get an estimate of the size by assuming the worst case: That the electrons are very tightly bound to the nuclei, which means that we can write:

\begin{align*}
\psi(R, r) = \psi(r - R). \quad (1.8)
\end{align*}

But then we get:

\begin{align*}
\int \psi^* \frac{\hbar^2}{2M_I} \nabla_I^2 \psi \, dr &= \int \psi^* \frac{\hbar^2}{2M_I} \nabla_I^2 \psi \, dr \\
&= \frac{m_e}{M_I} \int \psi^* \frac{\hbar^2}{2m_e} \nabla_I^2 \psi \, dr, \quad (1.9)
\end{align*}
where the last term is just the electron kinetic energy, multiplied with a number of the order $10^{-4} - 10^{-5}$. This can usually be neglected.

The derivation above has only been done for the diagonal terms in the so-called non-adiabatic terms (the last line in Eq.(1.5)). The neglect of the off-diagonal terms, meaning that you assume that the electrons do not change eigenstates as the nuclei move, is called the Born-Oppenheimer approximation [4], and can be used as long as the electron states are not degenerate.

### 1.3.3 Periodicity and the Bloch theorem

If not for the fact that most solids condense into periodic crystal structures, the field of condensed matter would not exist. The periodicity makes it possible to perform calculations for only one piece of the bulk matter (called a unit cell, see Fig.(1.2), or if you study properties with periodicities longer than a unit cell: supercell), which then yields the solution for the whole sample. In a macroscopic sample you have both surface atoms and bulk atoms. The number of surface atoms are of the order of $N^\frac{2}{3}$, or about 1 out of $10^8$ in a macroscopic sample. They are therefore neglected in the calculation of bulk properties, and only included if you want to study specifically some property with regard to surfaces. There are also always defects and impurities present in a sample, but these are, although interesting, neglected in the following discussion (and furthermore for the rest of
this thesis when ordered lattices can be assumed). The way to deal with the periodicity was found out in 1928 [5] and the result is called the Bloch theorem. It will be derived below, after a short discussion of what the periodicity means in terms of Fourier expansions to what is called the reciprocal lattice.

First we define the lattice vectors as the set of vectors $a_i$ that spans a unit cell of the lattice. Then we define a translation operator $T$ as any (sequence of) translation(s) that leaves the lattice invariant:

$$T = n_1a_1 + n_2a_2 + n_3a_3,$$

with $n_1, n_2, n_3$ integers.

Suppose now that we have a periodic function defined for the crystal, so that:

$$f(r + T) = f(r),$$

then we know that we can represent this function in terms of Fourier components at wave vectors $q$ defined in the reciprocal space. Furthermore, if we demand that each component must satisfy periodic boundary conditions, we get:

$$e^{iqa_1}N_1 = e^{iqa_2}N_2 = e^{iqa_3}N_3 = 1,$$

where $N_i$ is the number of unit cells in each dimension for the whole sample. This leads, after some manipulations [6], to the expression:

$$b_i \cdot a_j = 2\pi \delta_{ij},$$

where the $b_i$ now form the unit vectors of the reciprocal lattice. A picture of the bcc reciprocal cell can be seen in Fig.(1.3). In particular, the Wigner-Seitz cell of the reciprocal lattice is called the Brillouin zone, and is defined as the perpendicular bisectors of the vectors from the origin to the reciprocal lattice points.

Since the lattice is periodic, so is the external potential that enters the Schrödinger equation, and therefore we can state that because of the translational symmetry:

$$H(R) = H(0),$$

where $H$ is the Hamiltonian of the system, $0$ is some origin of a coordinate system, and $R$ is some lattice translation vector. We know that we have for the eigenstates of this Hamiltonian:

$$H(0)|0> = E|0>,$$

for an eigenstate $|0>$. By just relabeling of variables we also have:

$$H(R)|R> = E|R>.$$

But, with the help of Eq.(1.14), we can get:

$$H(0)|R> = E|R>,$$
Figure 1.3. The reciprocal cell of the bcc unit cell is actually an fcc (face centered cubic) unit cell, but with smaller dimensions. In the same way is the fcc reciprocal cell a bcc unit cell.

which means that the state $|R>$ is also a solution of the eigenvalue equation satisfied by $|0>$. Since the states are not identical, and of course any lattice translation $R'$ leads to another solution of the equations of motions, it must be that all these solutions are in some way related to each other. If we assume that the state $|0>$ is $n$-times degenerate, consisting of the states $|0>_i$, we know that a lattice translation $T_1$ in direction 1 of the lattice can produce a linear combination of the $n$ states:

$$
|T_1 >_1 = T_{11}^1 |0>_1 + T_{12}^1 |0>_2 + \cdots + T_{1n}^1 |0>_n \\
|T_1 >_2 = T_{21}^2 |0>_1 + T_{22}^2 |0>_2 + \cdots + T_{2n}^2 |0>_n \\
\vdots \\
|T_1 >_n = T_{n1}^n |0>_1 + T_{n2}^n |0>_2 + \cdots + T_{nn}^n |0>_n ,
$$

(1.18)

where we now see that $T_1$ is a matrix. Normalization demands that $T_1$ is unitary and it is also possible to diagonalize the matrix. The same is of course true for translations in the other directions. Since the translation operators commute, it will be possible to simultaneously diagonalize the translation matrices in all directions, and as they are unitary we can write the final result as: There exists
some wave vector \( \mathbf{q} \) so that:

\[
|\mathbf{R}\rangle = e^{i \mathbf{q} \cdot \mathbf{R}} |\mathbf{0}\rangle, \tag{1.19}
\]

where \( |\mathbf{0}\rangle \) is some transformed ground state \([7]\).

It can be shown that the choice of wave vector \( \mathbf{q} \) is not unique, but that every wave vector \( \mathbf{q}' = \mathbf{q} + \mathbf{b} \), where \( \mathbf{b} \) is any reciprocal wave vector, also satisfies the Bloch theorem. You usually choose the wave vector which lies in the Brillouin zone and represent the state by that wave vector. This now means that we can solve the Schrödinger equation just for the Brillouin zone and do not have to solve for the whole lattice.

Now we have reduced the problem to solving the Schrödinger equation for just one unit cell (actually even a primitive cell in the cases where it is possible to reduce the unit cell even more), and for separated electronic and nuclear degrees of freedom. Still, as long as we have more than two electrons, the problem is unmanageable. Therefore we must make more approximations in order to get some way to solve the problem. One of the most common approximations is the Hartree-Fock method \([8]\), in which the variational principle is used together with so called Slater determinants of electron orbitals to do calculations. One of the problems with this method is that you have to approximate the orbitals.

There is, however, another way to try to solve the problem. This is by using the electron density as the basic variable, and using approximations to functionals of this density instead of approximations to the electron orbitals. The theory is called Density Functional Theory, and Walter Kohn was awarded the Nobel prize in Chemistry 1998 for his work on it. I will describe it in the next chapter.
Chapter 2

Density functional theory

2.1 Introduction: The basic theorems

An alternative approach to the orbital theories of the many-electron problem was
developed at the same time as these theories [9, 10, 11, 12, 13], it was based on the
electron density of the systems considered and reduced the number of degrees of
freedom to a minimum, thereby also reducing the computational cost dramatically.
Unfortunately, this theory lacked in accuracy and was more or less considered a
dead end until Hohenberg and Kohn published the article [14] that was to be the
start of modern density functional theory.

Today, density functional theory is the underlying theory behind most solid
state calculations, even if traditional wave function methods are still used in
smaller systems, where the computational effort is not so big.

Good texts on the subject are the books by Parr and Wang [8] and Dreizler
and Gross [15], and the fabulous online textbook by Burke [16], upon which I have
based this chapter.

2.1.1 The Hohenberg-Kohn theorem

In their article from 1964, Hohenberg and Kohn proved that the density uniquely
determines the potential up to a constant, which does not matter since the poten-
tial is always determined up to a constant in any way. This means that the density
can be used as the basic variable of the problem, since the potential determines
all ground state properties of the system, as can be seen from the Schrödinger
equation. In the article, the proof is very simple, and done by contradiction:

Suppose that there are two different potentials, \( v(\mathbf{r}) \) and \( v'(\mathbf{r}) \) with ground
states \( \Psi(\mathbf{r}) \) and \( \Psi'(\mathbf{r}) \) respectively, which yield the same density. Then, unless
\( v'(\mathbf{r}) - v(\mathbf{r}) = \text{const.} \), \( \Psi'(\mathbf{r}) \) is different from \( \Psi(\mathbf{r}) \) since they solve different
Schrödinger equations. So, if the Hamiltonians and energies associated with \( \Psi'(\mathbf{r}) \)
and $\Psi(\mathbf{r})$ are denoted by $H'$, $H$ and $E'$, $E$, we have:

$$
E' = \langle \Psi'|H'|\Psi' \rangle < \langle \Psi|H'|\Psi \rangle = \langle \Psi|(H + v' - v)|\Psi \rangle,
$$

(2.1)

which gives:

$$
E' < E + \int (v'(\mathbf{r}) - v(\mathbf{r})) n(\mathbf{r}) d\mathbf{r}.
$$

(2.2)

Changing from primed quantities to unprimed quantities gives us:

$$
E < E' + \int (v(\mathbf{r}) - v'(\mathbf{r})) n(\mathbf{r}) d\mathbf{r}.
$$

(2.3)

But if we just add Eqs.(2.2) and (2.3) together, we get:

$$
E + E' < E' + E,
$$

(2.4)

which is obviously not true. So $v(\mathbf{r})$ is a functional of $n(\mathbf{r})$, and since $v(\mathbf{r})$ determines $H$, the whole system is a functional of $n(\mathbf{r})$. This proof is correct for densities with non-degenerate ground states and for local, non-spin dependent potentials.

Another thing can also be noticed: If we write the energy functional of $n(\mathbf{r})$ as:

$$
E_{v_0}[n] = \langle \Psi|n|\hat{T} + \hat{W} + \hat{V}_0|\Psi[n]\rangle,
$$

(2.5)

where $\hat{V}_0$ is the external potential of a system with ground state density $n_0(\mathbf{r})$, $\hat{T}$ is the kinetic energy operator, and $\hat{W}$ is the electron-electron interaction operator, we can use the Rayleigh-Ritz variational principle [17] and show that

$$
E_0 < E_{v_0}[n],
$$

(2.6)

where $E_0$ is the ground state energy and $n \neq n_0$ and, of course

$$
E_0 = E_{v_0}[n_0].
$$

(2.7)

So, the exact ground state density can be found by minimizing the functional $E_{v_0}[n]$ over all $n$. But we can write $E_{v_0}[n]$ as:

$$
E_{v_0}[n] = F_{HK}[n] + \int d\mathbf{r} v_0(\mathbf{r}) n(\mathbf{r}),
$$

(2.8)

where

$$
F_{HK}[n] = \langle \Psi|\hat{T} + \hat{W}|\Psi[n]\rangle
$$

(2.9)

is called the Hohenberg-Kohn functional. The Hohenberg-Kohn functional is said to be universal, since it does not depend on the external potential and thus is the same functional for all atoms, molecules, and solids.
2.1 Introduction: The basic theorems

2.1.2 \( \nu \)-representability and the Levy constrained search formalism

When we proved the Hohenberg-Kohn theorem above, we made the assumption that the density is \( \nu \)-representable. By this is meant that the density is a density associated with the anti-symmetric ground state wave function and some potential \( \nu(r) \). Why is this important? The reason is that we want to use the variational character of the energy functional:

\[
E_0 \leq E_{\nu_0}[n],
\]

where \( n \) is a \( \nu \)-representable density, to find the ground state energy. If our trial density that we put in this functional turns out to be non-\( \nu \)-representable, the variational principle is no longer valid. One would think that most "reasonable" densities would be \( \nu \)-representable, but many "reasonable" densities have actually been shown to be non-\( \nu \)-representable [18, 19]. The Levy constrained search formulation provides a way around the problem of \( \nu \)-representability and in the same way presents a constructive proof of the Hohenberg-Kohn theorem:

The minimization of \( E_{\nu_0}[n] \) can be written as:

\[
< \Psi_0|\hat{T} + \hat{W}||\Psi_0 > + \int d\boldsymbol{r} \nu(r)n(\boldsymbol{r}) \leq < \Psi_{n_0}|\hat{T} + \hat{W}||\Psi_{n_0} > + \int d\boldsymbol{r} \nu(r)n(\boldsymbol{r}),
\]

or

\[
< \Psi_0|\hat{T} + \hat{W}||\Psi_0 > \leq < \Psi_{n_0}|\hat{T} + \hat{W}||\Psi_{n_0} >.
\]

Here, the minimization is over all \( n \) which are \( N \)-representable. What this means is that \( n \) can be obtained from an anti-symmetric wave function, and that it
fulfills the following three conditions: It should be positive, it should integrate to \( N \), and it should be finite. This is obviously a much weaker condition than \( v \)-representability, and any "reasonable" density fulfills it. The word "constrained" in Levy constrained search method comes from the fact that the \( \Psi \)s that we search among are constrained to give the density \( n \).

### 2.1.3 Spin density functional theory

Since we want to be able to do calculations on magnetic materials, we must expand the formalism to allow for spin-dependent external potentials. This is quite easily done with the use of the Levy constrained search formulation.

As can be proven in exactly the same way as above, two different non-degenerate ground states will always lead to different four-vectors \( (n(r), m(r)) \) \[22, 23\], where \( n \) and \( \hat{m}_z \) can be related to the density of spin-up electrons \( n^+ \) and spin-down electrons \( n^- \) respectively as:

\[
n(r) = n^+(r) + n^-(r) \tag{2.14}
\]

and

\[
\hat{m}_z(r) = -\mu_0 (n^+(r) - n^-(r)). \tag{2.15}
\]

This means that we can write the energy functional

\[
E_{v_0,B_0}[n,m] = F_{HK}[n,m] + \int dr \left( v_0(r)n(r) - B_0(r)m(r) \right), \tag{2.16}
\]

where \( B_0 \) is the magnetic field. The functional has the same variational properties as in the non-magnetic case.

What has not yet been proven is that a given ground state corresponds to a unique vector of external fields \( (v(r), B(r)) \). The fact is that one can construct \[22\] external fields such that they yield common eigenstates of the corresponding non-interacting Hamiltonians, but it has not been shown that these eigenstates are actually ground states \[24\].

The difficulty of proving this is that each spin component only determines the potential up to a constant, and that we only can get rid of one of the constants by changing energy scales in our potential \[25\]. This is fortunately enough not a big problem when doing actual calculations, since we then have \( v(r) \) and \( B(r) \) given \[26\]. It has been shown that the Levy constrained search formulation can be extended without problems to the spin-dependent case \[27\].

### 2.2 The Kohn-Sham scheme

Now we know that it is possible to use the density as the fundamental variable, but is there a good way to do this? The answer is most certainly yes. The year after Hohenberg and Kohn published their article \[14\], Kohn and Sham published another article \[28\] in which they presented a computational scheme called the
2.2 The Kohn-Sham scheme

Kohn-Sham scheme. The main error in the earlier approaches to find a density functional theory was to approximate the kinetic energy as a local density functional. All of those approximations gave large errors, and it was clear that some new way had to be found to get around this problem.

In their paper, Kohn and Sham proposed to produce a system of non-interacting electrons with the same density as the physical system. Since we know that the ground state energy only depends on the density, a solution of this auxiliary system would yield the same energy as the solution of the real system. The main advantage with the non-interacting system was that the solution of the Kohn-Sham equations would produce the exact non-interacting kinetic energy, which is almost all of the true kinetic energy.

Let us have a look at the exact kinetic energy. In general, it is written as

\[ T = \sum_{i} \langle \Psi_i | -\frac{1}{2} \nabla^2 | \Psi_i \rangle, \]  

where we sum over all natural spin orbitals \( \Psi_i \) and their occupation numbers \( n_i \). If we were to have non-interacting electrons, the occupation numbers would reduce to 1 for \( N \) orbitals and to 0 for the rest. This would reduce the problem significantly, and would make it possible to solve a number of simple one-electron equations and just sum them up to get the total kinetic energy.

Since the Kohn-Sham system is a system of non-interacting electrons giving the same density as the real system, we can write for its orbitals:

\[ \{- \frac{1}{2} \nabla^2 + v_s(r)\} \phi_i(r), \]

where we also have

\[ n(r) = \sum_{i=1}^{N} |\phi_i(r)|^2. \]

Here the subscript \( s \) on the potential denotes that we are now solving single-electron equations, since we have a non-interacting system. But what is the potential in the equation above? By isolating the non-interacting kinetic energy \( (T_s) \) and the Coulomb interaction \( (U) \) in our energy functional \( E_{v0}(n) \) we get

\[ E_{v0}[n] = T_s[n] + U[n] + E_{ex}[n] + \int dr v_{ext}(r)n(r), \]

where \( U \) is the Hartree part of the electron-electron interaction energy and \( E_{ex}[n] \) is called the exchange-correlation energy and will be discussed below. If we now just use the usual variational methods to get the Euler equation for this system [15], we get:

\[ \mu = v_{eff}(r) + \frac{\delta T_s[n]}{\delta n(r)}. \]
where $\mu$ is the chemical potential. The Kohn-Sham effective potential $v_{\text{eff}}(\mathbf{r})$ is

\[
v_{\text{eff}}(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + \frac{\delta U}{\delta n(\mathbf{r})} + \frac{\delta E_{xc}}{\delta n(\mathbf{r})},
\]

which gives us

\[
v_s(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + v_{\text{coul}}[n](\mathbf{r}) + v_{xc}[n](\mathbf{r}),
\]

where

\[
v_{\text{coul}}[n](\mathbf{r}) = \int d\mathbf{r} \frac{n(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|},
\]

and

\[
v_{xc}[n](\mathbf{r}) = \frac{\delta E_{xc}}{\delta n(\mathbf{r})}.
\]

To get an expression for the energy we write

\[
E[n] = T_s[n] + U[n] + E_{xc}[n] + \int d\mathbf{r} v_{\text{ext}}(\mathbf{r}) n(\mathbf{r}),
\]

and note that

\[
\sum_i \epsilon_i = \sum_i <\Psi| - \frac{1}{2} \nabla^2 + v_{\text{eff}}|\Psi> = T_s[n] + \int d\mathbf{r} v_{\text{eff}}(\mathbf{r}) n(\mathbf{r})
\]

from the Schrödinger equation. This means that we can write for the total energy

\[
E[n] = \sum_i \epsilon_i - \int \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{xc}[n] - \int v_{xc}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r}.
\]

Note that the energy is not the sum of the one-electron energy eigenvalues since these are the energies for non-interacting electrons.

A sometimes overlooked fact is that the Kohn-Sham equation is exact at this stage. It is much easier to solve than the coupled Schrödinger equations that would have to be solved for the original system, since it decouples into single particle equations. The only problem is that we have introduced the exchange-correlation energy, which is an unknown quantity, and which must be approximated. Fortunately, it will turn out to be relatively easy to find reasonably good local approximations for it.
2.3 The exchange and correlation energies

The exchange energy $E_x$ is defined in density functional theory as

$$E_x[n] = \langle \Phi[n]|\hat{W}|\Phi[n]\rangle - U[n],$$

(2.29)

where the first term is just the electron-electron interaction evaluated on the Kohn-Sham orbitals and $U[n]$ is the direct Hartree contribution of the energy. If we can write our Kohn-Sham wave function as a single Slater determinant of orbitals, something that is almost always possible, $E_x$ is just the usual Fock integral of the Kohn-Sham orbitals, which should not, however, be confused with the usual Hartree-Fock orbitals, since they are orbitals which yield a given density, but are eigenstates of a single, non-orbital dependent, potential.

The correlation energy $E_c$ on the other hand is defined as the remaining unknown piece of energy


(2.30)

If we insert the definition of $F[n]$ (Eq.(2.9)) we can see that the correlation energy consists of two parts

$$E_c[n] = T_c[n] + U_c[n],$$

(2.31)

where $T_c$ is the kinetic contribution

$$T_c[n] = T[n] - T_s[n],$$

(2.32)

by definition the part of the kinetic energy that is not calculated exactly. $U_c[n]$ is the potential contribution


(2.33)

The unknown part of our energy functional is only this $E_{xc}[n] = E_x[n] + E_c[n]$ and we shall now take a look at some ways to get approximations for this functional.

2.3.1 The Local Density Approximation

What kind of approximation would be appropriate for the exchange-correlation energy? It is not so easy to guess, but we know that it would be very good if we could find a local approximation, since then the approximation would reduce to an integral over a function of the density

$$E_{xc}[n] = \int d\mathbf{r} f(n(\mathbf{r})),$$

(2.34)

where $f$ is some function. This would reduce computational time and simplify equations considerably. But how could we find an appropriate function? One first step would be to see that the local approximation is actually exact for the case of a uniform system, specifically a uniform electron gas.
For a uniform electron gas, the electrons are considered to be placed in an infinite region of space with an underlying positive background charge, which produces an overall charge neutrality. In this case, the kinetic energies and exchange energies would just be functions of the Kohn-Sham wave functions which would be plane waves, and the correlation energy could be extracted from Monte-Carlo calculations fitted to known limiting values, easy to get since we can solve the problems with the uniform electron gas analytically.

This approximation was first suggested by Kohn and Sham [28], but was not thought to be an especially good approximation, since the densities of true systems are far from uniform. Good results were nevertheless found even for strongly inhomogeneous systems, the reason of which we will return to a little later. It is not hard to come up with a formula for the exchange energy. If we calculate the Fock integral [8], we get for the exchange energy per atom

$$\epsilon_x^{\text{uniform}}[n] = \frac{3k_F}{4\pi},$$  

(2.35)

where $k_F$ is the Fermi wave vector. This leads to the exchange energy

$$E_{x}^{\text{LDA}} = A_X \int dr \, n^{4/3}(r),$$  

(2.36)

where $A_X = -(3/4)(3/\pi)^{1/3}$.

The correlation energy is not as easy, since it actually depends on the physical ground state wave function of the uniform gas, and not just the density. The usual way to include correlation is by introducing an enhancement factor $F_{xc}$ such that

$$\epsilon_{xc}[n] = F_{xc}[n] \epsilon_x[n].$$  

(2.37)

For high density system, the enhancement factor becomes unity, and exchange effects dominate over the correlation effects. When the density becomes lower, the enhancement factor kicks in and includes correlation effects into the exchange energies. The enhancement factor is not unique, but can be derived differently in different approximations. The most reliable ones are parameterizations of molecular Monte-Carlo data. Some well known, and regularly used, parameterizations have been made by Hedin and Lundqvist [29], von Barth and Hedin [22], Gunnarsson and Lundqvist [30], Ceperly and Adler [31], Vosko, Wilk, and Nusair [32], and Perdew and Zunger [27].

The Local Density Approximation was the standard approach for all density functional calculations until the early 1990s and is still used to a very large extent for solid state calculations. For atoms and molecules, exchange energies are underestimated with about 10%, while correlation energies are overestimated by 200-300%. Since these energies have different signs and sizes, the net effect is that the exchange-correlation energies are underestimated by about 7%.

### 2.3.2 The exchange-correlation hole

To understand why the LDA is such a surprisingly good approximation, it is helpful to rephrase the problem in terms of the exchange-correlation hole. To do
2.3 The exchange and correlation energies

This, some quantities first have to be defined.

The first-order density matrix is defined as

\[ \gamma(x, x') = N \int dx_2 \ldots \int dx_N \Psi^*(x, x_2, \ldots, x_N) \Psi(x', x_2', \ldots, x'_N), \]  

(2.38)

where \( \Psi(x_1, \ldots, x_N) \) is the many-body wave function. Here \( x \) symbolize both spatial and spin coordinates. The diagonal terms of the density matrix are the spin densities

\[ \gamma(x, x) = n(x). \]  

(2.39)

Moreover, we define the pair density as

\[ P(x, x') = N(N - 1) \int dx_3 \ldots \int dx_N |\Psi(x', x_2, \ldots, x'_N)|^2, \]  

(2.40)

the diagonal part of the second-order density matrix. The quantity \( P(r_\sigma, r_\sigma')drdr' \) is the probability of finding an electron of spin \( \sigma \) in \( dr \) around \( r \) and a second electron of spin \( \sigma' \) in \( dr' \) around \( r' \). This means that the pair density contains information about the correlation of the electrons.

The reason we defined this pair density, is that we can rewrite the electron-electron term \( W \) as

\[ W = \frac{1}{2} \int dx \int dx' P(x, x') \frac{|r - r'|}{r - r'|}. \]  

(2.41)

If we separate out the Hartree energy from this, which can easily be done since it can be written as an explicit density functional, we can define the exchange-correlation hole, \( n_{xc}(x, x') \), around an electron as

\[ P(x, x') = n(x)(n(x') + n_{xc}(x, x')). \]  

(2.42)

This hole is a measure of how other electrons are repelled by the electron around which it is centered, and integrates to -1 [8]:

\[ \int dx' n_{xc}(x, x') = -1. \]  

(2.43)

If we define \( u = r' - r \) we can write the exchange-correlation energy as

\[ E_{xc} = \int dr \ n(r) \int du \frac{n_{xc}(r, u)}{2u}. \]  

(2.44)

This means that we may interpret the exchange-correlation energy as the Coulomb interaction between the charge density and its surrounding exchange-correlation hole.
If we further separate the exchange-correlation hole into an exchange hole and a correlation hole, we find that the exchange hole is everywhere negative and that it satisfies a sum rule [8]:

$$\int d\mathbf{u} \ n_x(\mathbf{r}, \mathbf{u}) = -1.$$  \hfill (2.45)

The exchange hole gives the exchange energy as

$$E_x = \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{n(\mathbf{r})n_x(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}.$$  \hfill (2.46)

Since the correlation hole is everything that is not in the exchange hole, and since the whole exchange-correlation hole integrates to -1, we can immediately say that we have

$$\int d\mathbf{u} \ n_c(\mathbf{r}, \mathbf{u}) = 0,$$  \hfill (2.47)

and this means that the correlation hole has both positive and negative parts. This also means that occasionally, the exchange-correlation hole may be positive, although the exchange hole is everywhere negative.

The LDA exchange-correlation hole, of course, does not in general look like the exchange-correlation hole for a real system. A key realization to understanding why the LDA still works as well as it does for many systems, is that the quantity entering our energy functional is the spherically averaged, system averaged, exchange correlation hole:

$$< n_{xc}(\mathbf{u}) > = \int dx \ n(x) \int 4\pi \ r^2 n_{xc}(r) dr d\sigma.$$  \hfill (2.48)

As it turns out, this hole in LDA resembles the hole for real systems remarkably well. The reason for this is that the LDA exchange-correlation hole is the hole for the uniform electron gas, which is a real interacting electron system. This means that the LDA hole satisfies the same condition all (real) holes satisfy, including the sum rule and the fact that the exchange hole should be everywhere negative.

### 2.3.3 Gradient expansions

In the original article by Kohn and Sham [28] where the LDA was proposed, there was also a suggestion for improvement in the case of non-homogeneous systems. The suggestion was a gradient expansion

$$A_{GEA}[n] = \int d\mathbf{r} \ (a(n(\mathbf{r})) + b(n(\mathbf{r})))|\nabla n|^2 + ..),$$  \hfill (2.49)

for a general functional $A$. The coefficients and form of the corrections can be determined from e.g. scaling properties.

Unfortunately, the GEA did not really work as a good approximation for real systems. The reason for this is that although the GEA correctly enhances the
effects of exchange and correlation for small $u$, the behaviour of the exchange-correlation hole for larger values of $u$ is oscillatory and this makes the hole unphysical. This is because the hole is no longer modeled after a real system. To dampen out these oscillations one has to include some damping factor, but the method still fails [15].

Another, in some sense simpler, gradient correction is the Generalized Gradient Approximation (GGA) [33]. Here one simply throws away the oscillating part of the GEA exchange-correlation hole as soon as the hole integrates to -1, i.e., as soon as the sum rule is fulfilled. One also excludes the unphysical positive contributions from the hole before the cutoff. This, of course, looks very ugly in real space as the hole gets a kink, but since we are only interested in the spherically- and system-averaged hole, this is not a problem; the averaged hole remains smooth.

Usually, the GGA is implemented as an enhancement factor over the LDA energies, for example for the exchange energy we have

$$E_x^{\text{GGA}}[n] = \int dr \, e_x^{\text{LDA}}(n(r)) F_x(s(r)),$$

(2.50)

where $s$ is a reduced gradient $s = \frac{|\nabla n(r)|}{4\pi n(r)}$. For $F_x = 1$ we just have the usual LDA. In fact, one can write the GGA exchange-correlation energy as

$$E_x^{\text{GGA}}[n] = \int dr \, e_x^{\text{LDA}}(n(r)) F_{xc}(r_s(r), s(r)),$$

(2.51)

where all separate enhancement factors are special cases of the more general $F_{xc}$, which contains all information about correlation as well as the possible gradient corrections.

There are many different parametrizations for the GGA, e.g. [33, 34, 35]. They are all used in present day calculations and have similar properties.

To mention some differences between the GGA and the LDA, I must point to the fact that the GGA predicts ferro-magnetic Fe to have bcc as its ground state structure, as found in experiments. LDA does not. On the other hand, LDA produces better surface energies, and both LDA and GGA perform well for different materials. GGA often gives better volumes for the 3$d$ transition metals, while LDA gives better volumes for the 5$d$ metals. They are both used in applications today.

Here I will end my discussion on DFT, and instead move on to the problem of solving the Kohn-Sham equations.
Chapter 3

Multiple scattering theory

Before we get into the specifics of how to solve the single particle Kohn-Sham equation, it is helpful to do a small excursion into Multiple Scattering Theory (MST), the reason being that this is what is employed in the methods I have been using for the papers connected to the thesis.

Multiple Scattering Theory was first formulated by Lord Rayleigh [17] in a paper published in 1892 dealing with the propagation of heat or electricity through an inhomogeneous media. However, for most people the application to optics known as Huygens’ principle [36], is probably better known. It states that:

Each point on a moving wavefront acts as an independent source of wavelets. The surface of tangency to these wavelets determine the position of the wavefront at later times.

This was of course a rather bold statement giving that Maxwell’s theory of electromagnetism [37], describing light as electromagnetic waves, had not yet been formulated, but nevertheless it helped with the understanding of the nature of light. Since then, multiple scattering theory has been used in a wide variety of fields, e.g. scattering of sound or electromagnetic waves, or dielectric and elastic properties of materials, all within classical physics. Within quantum mechanics it has been used for studying low energy electron diffraction, point defects and disorder in alloys, and many other properties of materials. One should note one thing of importance: Although Huygen’s principle is actually wrong for classical optics, since the classical wave equation involves the second derivative with respect to time, requiring the specification of both the amplitude and its time derivative, it is correct for equations such as the Schrödinger equation, the Dirac equation, the Laplace equation, and the Poisson equation [38], which are the equations that govern the equations of motion in electronic structure theory.

This chapter is divided into three sections: In the first one I give a small, intuitive introduction to Multiple Scattering Theory, whereupon I expand a little
more formally in the second section, where also the scattering path operator used in muffin-tin orbital methods is introduced. In the third section I show the connection between the potential and the quantities used in the first two sections. The discussion follows closely the very nice book by Gonis and Butler [39], and anyone who wants a more thorough discussion is highly recommended to read that book.

3.1 Green’s functions and scattering

Suppose that we have no potentials in our system, but just free electrons. Then the Hamiltonian is simply $H_0 = -\nabla^2$, and the Schrödinger equation can be solved exactly in terms of the free-particle propagator, or Green’s function, $G_0(r, t; r', t')$, which satisfies the equation:

$$[i\frac{\partial}{\partial t} - H_0]G_0(r, t; r', t') = \delta(r - r')\delta(t - t').$$  \hspace{1cm} (3.1)

It can be seen that the Green’s function connects the value of a wave function at point $r$ and time $t$ to its value at a point $r'$ and time $t'$. In fact, we can get the wave function at time $t$ from the wave function at a time $t = 0$ as [39]:

$$\Psi(r, t) = \int dr' G_0(r - r', t)\Psi(r', 0).$$  \hspace{1cm} (3.2)

This means that, just as mentioned above about Huygen’s principle, every point where the wave function is non-zero at time $t = 0$ serves as a source for the wave function at a later time. Eq.(3.2) thus describes the propagation of the wave in free space between two different points and times, thereby giving the Green’s function its second name: the propagator. But what happens if we introduce a perturbing potential? We assume that the potential is a point-scatterer (that is, it has no extension) and that it is constant with respect to time, and denote it by $\hat{t}_1$, which is a measure of its strength. If we now also assumes that we only have one scatterer, located at $r_1$, the time development of the wave becomes:

$$\Psi(r, t) = \int dr' G_0(r - r', t)\Psi(r', 0)$$ 

$$\quad + \int_0^t dt_1 \int dr' G_0(r - r_1, t - t_1)\hat{t}_1 G_0(r_1 - r', t_1)\Psi(r', 0).$$  \hspace{1cm} (3.3)

We can see what happens: Either the wave propagates directly to $r$ without impinging on the scatterer (the first term), or propagates freely to the scatterer, scatters, and then propagates freely to $r$.

It is easy to introduce another scatterer, $\hat{t}_2$, and write down the propagation in that case: We will have one term without any scattering, now two terms with
scattering off of one scatterer (one each of $\hat{t}_1$ and $\hat{t}_2$), two terms where it scatters first off of one scatterer and then the next, and then an infinite number of more terms where it scatters back and forth between the two scatterers any number of times before coming to $\mathbf{r}$. This is just the sum of all ways that the wave can get from the initial position and time to the final position and time. Note also that there are no terms with more than one scattering in a row off of the same scatterer. This is because the scatterers ($t$-matrices) $\hat{t}$ are defined to describe fully the scattering off a scatterer. In Fig.(3.1) is a small picture which describes some possible two-scatterer event.

What we do now is to rewrite the scattering series for a general collection of scatterers as follows:

$$\Psi(\mathbf{r}, t) = \int d\mathbf{r}' G(\mathbf{r} - \mathbf{r}', t) \Psi(\mathbf{r}', 0),$$

(3.4)

where $G(\mathbf{r} - \mathbf{r}', t)$ is the total Green’s function, that describes the wave propaga-
tion in the presence of the scatterers. It can be written as:

\[
G(r - r', t - t') = G_0(r - r', t - t')
+ \int_0^t dt_1 \int_0^{t_1} dt_2 \int dr_1 \int dr_2 \ G_0(r - r_1, t - t_1) \\
\times \ T(r_1, r_2; t_1, t_2) G_0(r_2 - r', t_2 - t'),
\]  

(3.5)

where \( T \) is called the total system \textit{t-matrix}. It is given by:

\[
T = \sum_{i,j} T^{ij},
\]  

(3.6)

where the \( T^{ij} \) is the sum of all scattering event that starts at the scatterer \( i \) and ends on scatterer \( j \). It is given by (suppressing the integrations):

\[
T^{ij} = \hat{t}^i \delta_{ij} + \hat{t}^i G_0 \hat{t}^j (1 - \delta_{ij}) + \sum_{k \neq j,i} \hat{t}^i G_0 \hat{t}^k G_0 \hat{t}^j + \ldots
\]  

(3.7)

This can also be written as:

\[
T^{ij} = \hat{t}^i \delta_{ij} + \hat{t}^i \sum_{k \neq j} G_0 T^{kj},
\]  

(3.8)

which can be found by iteration. Although we have assumed point scatterers so far, all results are valid for any geometrical form of the scatterers as long as they do not overlap [39].

So far, we have kept everything time dependent, since it is very nice to think in terms of moving waves. In condensed matter theory, many phenomena are time independent, and this can of course also be treated with scattering theory. The only difference is that the time dependent waves become time independent standing waves. If one solves for the Green’s function in coordinate representation, one gets [39]:

\[
G_0(r - r'; E_i) = -\frac{1}{4\pi} e^{i\sqrt{E_i} |r - r'|}. 
\]  

(3.9)

The Green’s function satisfies:

\[
(\nabla^2 + E)G_0(r - r'; E) = \delta(r - r'),
\]  

(3.10)

and we can get the wave function in terms of this as:

\[
\Psi_{k_i}(r) = (2\pi)^{-3/2} e^{i k r} + \int G_0(r - r'; E_i) V(r') \Psi_{k_i}(r') dr',
\]  

(3.11)
where $V(r)$ is the (non-point) scatterer. Eq. (3.11) is the well known Lippman-Schwinger equation. Now we leave this part and try to make a little bit more formal treatment.

### 3.2 Hamiltonians and formal multiple scattering theory

We are going to formulate this in terms of Hamiltonians, which turn up naturally in discussions about Green’s functions. In fact, the Green’s function is defined in terms of the Hamiltonian, as we saw in the beginning of this chapter. Let us define $H_0$ to be the non-interacting Hamiltonian and $H = H_0 + V$ to be the Hamiltonian for the interacting system. We will assume that both systems have the same continuous (free electron) energy eigenstates, and that the interacting system also has a discrete spectrum of bound states below this continuum. This will almost always be the case for electronic structure calculations. Now suppose that $H_0$ has eigenstates $|\chi_\alpha>:

$$H_0|\chi_\alpha> = E_\alpha|\chi_\alpha>.$$  

(3.12)

The free particle Green function operator, $G_0$, and the full Green function, $G$, are given by definition respectively by:

$$G_0(E) = (E - H_0 \pm i\epsilon)^{-1},$$

(3.13)

and

$$G(E) = (E - H \pm i\epsilon)^{-1},$$

(3.14)

where $\epsilon$ is an infinitesimal number. This means that the scattered wave solutions of the interacting system, $|\psi_\alpha^\pm>$, satisfy both the usual eigenvalue equation

$$H|\psi_\alpha^\pm> = E_\alpha|\psi_\alpha^\pm>$$

(3.15)

as well as the Lippman-Schwinger equation, Eq.(3.11):

$$|\psi_\alpha^\pm(V) > = |\chi_\alpha > + (E - H_0 \pm i\epsilon)^{-1}V|\psi_\alpha^\pm>,$$

(3.16)

Both $|\psi_\alpha^+>$ and $|\psi_\alpha^->$ have the same eigenvalue $E_\alpha$ and correspond to the solutions which coincide with the free particle state $|\chi_\alpha>$ in the remote past or future respectively.

We can rewrite Eq.(3.16) in a number of ways:

$$|\psi_\alpha^\pm> = |\chi_\alpha > + G_0^\pm(E)V|\psi_\alpha^\pm>$$

$$= |\chi_\alpha > + G^\pm V|\chi_\alpha >$$

$$= |\chi_\alpha > + G_0^\pm(E)T^\pm(V)|\chi_\alpha >,$$

(3.17)
where $T^\pm$ are defined by:

$$T_{\alpha\alpha'}^+ = \langle \chi_\alpha(E_\alpha) | T^+ | \chi_{\alpha'}(E_{\alpha'}) \rangle = \langle \chi_\alpha(E_\alpha) | V | \psi_{\alpha'}^+(E_{\alpha'}) \rangle$$

and

$$T_{\alpha\alpha'}^- = \langle \chi_\alpha(E_\alpha) | T^- | \chi_{\alpha'}(E_{\alpha'}) \rangle = \langle \psi_{\alpha}^-(E_\alpha) | V | \chi_{\alpha'}(E_{\alpha'}) \rangle,$$

and are the t-matrix operators which describe the transition between different states. We will only have to work with the so called on the energy shell versions, since this is what is needed for multiple scattering theory [39]. This means that $E_\alpha = E_{\alpha'}$ and $T^+ = T^- = T(E)$, which can be recalled as the criterion for elastic scattering. By iteration of the first line in Eq.(3.17) we can now show:

$$T(V) = V + VG_0V + VG_0VG_0V + \ldots,$$

which, if it converges, satisfies the Dyson equation:

$$T(V) = V + VG_0T(V),$$

with the formal solution:

$$T(V) = (1 - VG_0)^{-1}V = (V^{-1} - G_0)^{-1}.$$

One can also write this in terms of the Green’s functions:

$$G = G_0 + G_0VG = (G_0^{-1} - V)^{-1} = G_0 + G_0T(V)G_0.$$

As a matter of fact, we have not made any assumptions about the potentials, and may therefore equally well set $V = \sum_i V^i$ in Eq.(3.20) where each $V^i$ is one of the cell potentials. This works as long as the potentials are non-overlapping, and gives us the equation:

$$T = T[\sum_i V^i] = \sum_i V^i + \sum_i V^i G_0 \sum_j V^j + \ldots.$$  

By grouping all terms containing only one cell potential, we can rewrite the equation above in terms of the cell t-matrices:

$$T[\sum_i V^i] = \sum_i t^i + \sum_{i \neq j} t^i G_0 \sum_j t^j + \ldots.$$
3.2 Hamiltonians and formal multiple scattering theory

Now we can again introduce $T^{ij}$ as the sum of all scattering events starting with $t^i$ and ending at $t^j$ and get:

$$T = \sum_{i,j} T^{ij} = ((\sum_i V^i)^{-1} - G_0)^{-1},$$

(3.26)

and it can be shown by iteration that the $T^{ij}$s satisfy:

$$T^{ij} = t^i \delta_{ij} + t^i G_0 \sum_{k \neq i} T^{kj}.$$  (3.27)

Let us now try to interpret these equations in terms of incoming and outgoing waves. Eq.(3.17) gives:

$$V^i |\psi> = t^i |\chi>,$$

(3.28)

in the case of a single potential $V^i$ in vacuum. Here $|\chi>$ can be thought of as an incoming wave, which is scattered into the outgoing wave $|\psi>$. To deal with a large collection of scatterers, let us introduce the notation $|\psi^{in;i}>$ for the state which describes the wave incident on cell $i$. We can still write the same equation as above:

$$V^i |\psi> = t^i |\psi^{in;i}>,$$

(3.29)

where we have just change from vacuum to the potential field of all other scatterers than $i$. Now Eq.(3.17) also gives us the relation

$$\sum_i V^i |\psi> = \sum_{i,j} T^{ij} |\chi> = \sum_i T^i |\chi>,$$

(3.30)

where $T^i$ is defined by

$$T^i = \sum_{i \neq j} T^{ij},$$

(3.31)

and describes all scattering from the cell $i$. Eq.(3.27) can now be rewritten as:

$$T^i = t^i [1 + G_0 \sum_{k \neq i} T^k].$$

(3.32)

Combining a few of the equations above we can further see that we have

$$V^i |\psi> = T^i |\chi>$$

$$= t^i [1 + G_0 \sum_{k \neq i} T^k] |\chi>$$

$$= t^i |\psi^{in;i}>.$$

(3.33)
Using these derived equations above, we can now write:

\[ |\psi_{in,i}^\text{in} > = [1 + G_0 \sum_{k \neq i} T^k]|\chi >, \tag{3.34} \]

or perhaps for clarity:

\[ |\psi_{in,i}^\text{in} > = |\chi > + G_0 \sum_{k \neq i} t^k|\psi_{in,k}^\text{in} >, \tag{3.35} \]

which describe the incoming wave at cell \(i\) as the sum of an incident wave \(|\chi >\) and incoming waves at all other sites that are scattered there and then propagated to site \(i\) via \(G_0\). The wave function for the total system can thus be written

\[ |\psi > = |\chi > + G_0 T|\chi > = |\chi > + G_0 \sum_i t^i|\psi_{in,i}^\text{in} >. \tag{3.36} \]

This is a multi-center expansion of the wave function in terms of the incoming waves of the system. It can also be expressed as a single center expansion

\[ |\psi > = |\psi_{in,i}^\text{in} > + |\psi_{out,i}^\text{out} >, \tag{3.37} \]

by defining

\[ |\psi_{out,i}^\text{out} > = G_0 t_i|\psi_{in,i}^\text{in} >. \tag{3.38} \]

As can be seen from these equations, there is no need for an incident wave \(|\chi >\) in order to get bounded states. Manipulation of Eq.(3.35) into

\[ \sum_j [\delta_{ij} - G_0 t^j (1 - \delta_{ij})]|\psi_{in,j}^\text{in} > = |\chi >, \tag{3.39} \]

further gives us that nontrivial solutions to the standing waves in the absence of an incident wave exists only if

\[ ||\delta_{ij} - G_0 t^i (1 - \delta_{ij})|| = 0. \tag{3.40} \]

If we can find a representation which converges reasonably fast, this will just be a determinant that has to be solved to find the bound states. Furthermore, if the determinant of \(t^i\) is not zero, we can rewrite this as

\[ \det[M] = ||m^i - G_0 (1 - \delta_{ij})|| = 0, \tag{3.41} \]

where \(m^i = t^{i-1}\). In muffin-tin formalism, it is customary to introduce \(\tau^{ij}\) as the inverse of \(M^{ij}\). \(\tau^{ij}\) is called the scattering path operator [40], though it is not really an operator, but a matrix. The scattering path operator (here in angular momentum representation for later convenience) satisfies the equation:

\[ \tau^{ll'} = t^l \delta_{ll'} + \sum_{l'' \neq l} t^j G_0(E) \tau^{j,l'}, \tag{3.42} \]
3.3 The connection between the $t$-matrices and the potential

which means that if we have the same $t$ matrix on all sites, we can get the scattering path operator from:

$$
\tau_{nn}^{t} = \frac{1}{V} \int dq \left( \frac{1}{t^{-1} - G(q)} \right)_{L',L},
$$

(3.43)

where $G$ is the Fourier transformation of $G_0$ and $V$ is the volume of the Brillouin zone.

It is also interesting to investigate how the introduction of an impurity on a site influences the scattering path operator. This means that $t$ goes to $t'$ on one site. The result [39] is that $\tau$ obeys a Dyson-like equation:

$$
\tau_{new,ij}^{t'} = \tau_{old,ij}^{t'} + \tau_{old,ij}^{t'} \Delta t^{-1} \tau_{new,ij}^{t'}. 
$$

(3.44)

These results will be used in Chapter 5 in connection with alloys.

3.3 The connection between the $t$-matrices and the potential

Since we will be dealing mostly with spherical symmetric potentials, this is what will be discussed here. The generalization to non-spherical potentials is, although cumbersome both computationally and notationally, not any different conceptually.

In scattering theory, it can be proven that the scattered wave function, outside the effective radius from the scattering potential, should look like [39]:

$$
\Psi_{k_i}(r) \rightarrow A(e^{i k_i \cdot r} + f(\theta, \phi) e^{i k r}),
$$

(3.45)

as $r \rightarrow \infty$. Here $A$ is an independent (of all variables in the equation) constant, and $f(\theta, \phi)$ is called the scattering amplitude. It can be noticed that the scattered wave consists of the incoming wave and a scattered wave, and that all information about the scattering potential is buried in the scattering amplitude. We will now try to connect this scattering amplitude to the $t$-matrices and to the potential.

The solution to the Schrödinger equation for a spherical symmetric potential can be written as:

$$
\Psi(k_i, r) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} c_{ml}(k) R_{lm}(k, r) Y_{lm}(\theta, \phi)
$$

$$
= \sum_{L} c_{L} R_{L}(k, r) Y_{lm}(\theta, \phi),
$$

(3.46)
where $L = (l, m)$ and the $Y$s are spherical harmonics [41]. The $R$s are solutions to the spherical symmetric radial Schrödinger equation and can in the case of no potential (the free electron case) be expressed in terms of the spherical Bessel functions ($j_l$), the spherical Neumann functions ($n_l$), and the spherical Hankel functions ($h_l^{(±)}$) of first (+) and second (-) order [41]. One usually also introduces $u_l(k,r) = rR_l(k,r)$ for notational reasons. For this spherical symmetric potential, we can write a general solution as:

$$u_l(kr) = kr[C_l^1(k)j_l(kr) + C_l^2(k)n_l(kr)],$$

where the integration constants $C$ may still depend on $k$.

There is a well known expansion theorem to expand the plane wave solution (which are the solutions to the free particle equation) in terms of Bessel functions as well [39]:

$$e^{ikr} = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^{l} i^l j_l(kr)Y_{lm}^*(\hat{k}_i)Y_{lm}(\hat{r}).$$

One should note that for an incoming wave, the coefficients $c_{lm}$ from Eq.(3.46) are found to be [39]:

$$c_{0lm}^0 = i^l[4\pi(2l + 1)]^{1/2}\delta_{m,0},$$

and the rest vanish.

For large $x$, the Bessel/Neumann functions behave like:

$$j_l(x) \rightarrow \frac{1}{x} \sin(x - \frac{l\pi}{2})$$

and

$$n_l(x) \rightarrow -\frac{1}{x} \cos(x - \frac{l\pi}{2}),$$

which means that we can write

$$u_l(k,r) \rightarrow A_l(k) \sin(kr - \frac{l\pi}{2} + \delta_l(k)),$$

where

$$A_l(k) = (|C_l^1(k)|^2 + |C_l^2(k)|^2)^{1/2}$$

and

$$\tan(\delta_l(k)) = -\frac{C_l^2(k)}{C_l^1(k)}.$$
3.3 The connection between the $t$-matrices and the potential

just from trigonometric identities. Here $\delta_l(k)$ is called the phase shift for the $l$ partial wave, and this parameter determines how the incoming wave is affected by the scattering.

Now we will try to match the asymptotic expansion of the partial waves (Eq.(3.46)) to the scattering wave (Eq.(3.45)). Using the expansion in Eq.(3.48) and the result Eq.(3.49) we get:

$$
\Psi_{k_i} \lim_{r \to \infty} = A(k) \left[ \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{[4\pi(2l+1)]^{1/2} i^l}{2ikr} e^{i(kr - \frac{l\pi}{2} + \delta_l(k))} \right. \\
\times \left. Y_{lm} (\hat{r}) \delta_{m,0} + f(k, \theta, \phi) \frac{e^{ikr}}{r} \right].
$$

But we can also consider Eq.(3.46):

$$
\Psi_{k_i} \lim_{r \to \infty} = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} c_{lm}(k) A_l(k) \frac{1}{2ikr} \\
\times [e^{i(kr - \frac{l\pi}{2} + \delta_l(k))} - e^{-i(kr - \frac{l\pi}{2} + \delta_l(k))}] Y_{lm} (\hat{r}).
$$

If we now compare the coefficients between these two expressions, we find:

$$
c_{lm}(k) = \frac{A(k)}{k A_l(k)} [4\pi(2l+1)]^{1/2} i^l e^{i\delta_l} \delta_{m,0}.
$$

This means that we can write the partial wave expansion (Eq.(3.46)) as:

$$
\Psi_{k_i}(k, r) = A(k) \sum_{l=0}^{\infty} \frac{\sqrt{4\pi(2l+1)}}{k A_l(k)} i^l e^{i\delta_l} R_l(k, r) Y_{l,0} (\theta).
$$

When we now finally compare the outgoing waves in Eq.(55) and Eq.(56) we find:

$$
f(k, \theta) = \frac{1}{2ik} \sum_{l=0}^{\infty} (2l+1) e^{2i\delta_l(k)-1} P_l(\cos \theta),
$$

where $P_l(\cos \theta)$ are Legendre polynomials [41]. If one introduces the so-called partial wave amplitude

$$
a_l(k) = \frac{1}{2ik} (e^{2i\delta_l(k)-1}),
$$
Multiple scattering theory

we can write

\[ f(k, \theta) = \sum_{l=0}^{\infty} (2l + 1)a_l(k)P_l(\cos \theta). \] (3.62)

What is left now is to relate these \( a_l \)s to the \( t \)-matrices and the potentials, and to specify the \( A \) coefficients, which mostly determine wave function normalization. It can be shown \[42\] that one can link the phase shift to some integral equations, which depend on the wave function normalization.

For example, we can get:

\[ t_l(k) = -\frac{e^{i\delta_l(k)}}{k} \sin \delta_l(k) = \int_{0}^{\infty} j_l(kr)V(r)R_l(k,r)r^2 dr, \] (3.63)

where the normalization is now defined as:

\[ \lim_{r \to \infty} R_l(k, r) = [j_l(kr) - \tan \delta_l(k)n_l(kr)]. \] (3.64)

This last equation clearly shows how the incoming wave has been transformed to a combination of the incoming wave and an outgoing scattered wave, the scattering defined by \( \delta_l(k) \).

Another way is to match the inside and outside solution at the muffin-tin radius \( r_{MT} \) \[40\]:

\[ \delta_l(k) = \cot^{-1} \left[ \frac{\sqrt{E_n}(\sqrt{E_{MT}}) - \gamma_l(E)n_l(\sqrt{E_{MT}})}{\sqrt{E_j}(\sqrt{E_{MT}}) - \gamma_l(E)n_l(\sqrt{E_{MT}})} \right], \] (3.65)

where the prime denotes the derivative with respect to \( r \) and \( \gamma \) is the logarithmic derivative of \( R \) calculated at the muffin-tin radius.

In the next chapter, we will investigate how the angular momentum representation for multiple scattering theory is used in the Exact Muffin-Tin Orbital (EMTO) method.
Chapter 4

Muffin-Tin Orbital methods

4.1 A short historical exposé

Before going into the theory for the Exact Muffin-Tin Orbital method, I want to give a short historical overview of muffin-tin based methods. This is done in order to put the method, and the development of the quantities used in the method, in a historical context.

The first method for solving the MST problem in angular momentum representation was made by Korringa [43] and Kohn and Rostocker [44] separately. The method came to be called the KKR method for electronic structure calculations and used the Green’s function technique from Chapter 3 to solve the electronic structure problem. The separation into potential- and structure dependent parts made the method conceptually clean and also speeded up calculations, since the structural dependent part could be calculated once and for all for each structure. Furthermore, the Green’s function technique made the method very suitable for the treatment of disordered alloys, since the Coherent Potential Approximation [45] could easily be implemented.

With the later introduction of the Linear Muffin-Tin Orbital (LMTO) method [46, 47, 48, 49, 50], a formulation of the multiple scattering problem in terms of Hamiltonians was introduced. This provided another way to gain more knowledge about the KKR method, which, although elegant, was not so easily understood. In the LMTO method one had to use energy linearizations of the MTOs to be able to put it into a Hamiltonian formalism. The two methods (KKR and LMTO) were shown [51] to be very closely related within the Atomic Sphere Approximation (ASA) [46, 52], which was used in conjunction with the LMTO method to provide an accurate and computationally efficient technique.

In 1984, it was also realized that it was possible to transform the original, so called bare (or canonical), structure constants into other types of structure constants using so-called screening transformations [53]. This allowed one to trans-
form the originally long ranged (one had to use reciprocal space Ewald summation to calculate them) bare structure constants into, e.g., short ranged, tight binding, structure constants. The latter were much more localized, and made it possible to calculate the structure constants in real space, which, in its turn, made a formulation of efficient order-\(N\) methods possible [54, 55, 56, 57].

Not until the so called third generation of LMTOs [58], was there a way to properly include the interstitial part of the muffin-tin potential and perform calculations without the ASA, in fact it was possible to perform calculations for exact muffin-tins using the Exact Muffin-Tin Orbitals (EMTO) method. Since the structural dependent part is called the slope matrix in the EMTO method, this is the name I will use for the rest of this thesis when discussing the EMTO method.

There has also been recent interest in so called NMTOs [59], where the energy dependence is expressed in a quantized polynomial approximation. In this method it is possible to obtain a minimal, short-ranged basis set, making it very useful for providing understanding of chemical bonding, amongst other things. Outside the LMTO/EMTO methods, there has also been a development of the screened KKR (SKKR) method [60, 61, 62, 63], where the long ranged bare KKR structure constants are screened in a similar fashion as in the screening transformations in LMTO/EMTO.

But let us take a look into how the MST problem is solved in the EMTO method, since this is the method that has been used for almost all calculations in this thesis.

### 4.2 The Exact Muffin-Tin Orbital Method

Since the language of the Exact Muffin-Tin Orbital (EMTO) method is phrased in terms of wave functions and the solution to the Schrödinger equation, and not in terms of Green’s functions, I will also start with this formulation, and then later make the transition into Green’s functions when appropriate. Some papers with a good account of the methodology are Refs.[58, 64, 65]

Our main goal is, of course, to solve the one-electron Kohn-Sham equations, as discussed in Chapter 2:

\[
[-\nabla^2 + v(\mathbf{r})] \Phi_i(\mathbf{r}) = E \Phi_i(\mathbf{r}).
\]  

We will also use the so called muffin-tin approximation for the potential:

\[
v(\mathbf{r}) \approx v_{MT} = v_0 + \sum_R [v_R(r_R) - v_0],
\]

where \(R\) runs through all lattice sites and \(v_R(r_R)\) are spherical symmetric potentials, which are augmented by a constant \(v_0\), the muffin-tin zero, outside radii \(s_R\).
4.2 The Exact Muffin-Tin Orbital Method

called the muffin-tin radii.

To solve Eq. (4.1) one expands the wave function in a complete basis set:

\[ \Phi_i(r) = \sum_{RL} \tilde{\Psi}_{RL}^a(E, r_R)u_{RL,i}^a. \]  

(4.3)

Here \( L \) stands for the \((l,m)\) set of quantum numbers, and will do so throughout this thesis. The \( \tilde{\Psi}_{RL}^a \) are the EMTOs, which will be defined below.

The method above seems to be quite straightforward, but there is of course not so easy to find a complete basis set that converges fast enough to be of use here. What I mean with this is that one could use, e.g., a plane wave basis set. This is complete. The problem then is that plane waves look nothing at all like the wave function within the potential sphere, and one would need a very large number of basis functions to get a good representation of the true wave function, thus reducing the computational efficiency tremendously. In the same way is partial waves a complete basis set, and they are also reasonably close to the wave function inside the potential sphere to converge quickly, but in the interstitial the true wave function should be plane wave like, and then the partial waves will converge badly. The way to get around this problem is to use one basis set inside the potential spheres, and another basis set in the interstitial, that is, the space between the potential spheres. While it is possible to use partial waves in the potential spheres, the use of plane waves in the interstitial is still too badly convergent to be used with maximal computational efficiency, but there are other sets available.

In the EMTO method, the basis set used is called screened spherical waves \([58]\) and will be discussed and defined below. The reason for choosing this basis set, also called screened Neumann/Hankel functions, is that the solutions in terms of this basis set are relatively well localized for energies of interest, and can therefore be easily calculated in real space. Unfortunately, these screened Neumann/Hankel functions are irregular at the origin and diverge, so they have to be augmented by partial waves \( \phi_{RL}(E, r_R) \), which are the solutions to the Schrödinger equation inside the potential spheres. A short walk-through of these well known waves are given below before we move to the screened spherical waves.

### 4.2.1 Partial waves

Since we are dealing with spherical symmetric potentials, the solution to the Schrödinger equation inside the spheres can be written as:

\[ \phi_{RL}(E, r) = \phi_{RL}(E, r)Y_L(\hat{r}). \]  

(4.4)

The functions \( Y_L(\hat{r}) \) are the well known spherical harmonics \([41]\) which are purely angular functions. The functions \( \phi_{RL}(E, r) \) are the solutions to the radial Schrödinger
Muffin-Tin Orbital methods

The equation [66]:

\[
\frac{\partial^2 [r_R \phi_{RL}(E,r_R)]}{\partial r^2_R} = \left\{ \frac{l(l+1)}{r_R^2} + v_R(r_R) - E \right\} r_R \phi(E,r_R).
\] (4.5)

Since we are going to match the screened spherical waves to these partial waves in order to get a solution in all space, we will need some way to match that includes all information about the muffin-tin wells. This is done by matching the radial logarithmic derivative at a radius \( r_R \):

\[
D \{ \phi_{RL}(E,r_R) \} = \frac{r_R \phi'_{RL}(E,r_R)}{\phi_{RL}(E,r_R)}.
\] (4.6)

Matching the logarithmic derivative is equivalent to making the values and first derivatives of the functions you are matching continuous at that radius, and this is what is needed for a solution to the Schrödinger equation. Now we need to find a solution \( \psi(E,r) \) at energy \( E \) of the wave equation in the interstitial, and match it as:

\[
\frac{r_R \psi'_{RL}(E,r_R)}{\psi_{RL}(E,r_R)} = D \{ \phi_{RL}(E,r_R) \}
\] (4.7)

for all \( RL \). Here \( \psi(E,r_R) \) is the projection of \( \psi(E,r) \) onto the spherical harmonic at a sphere of radius \( r \). We can then use this condition to find the values of \( E \) for which a solution exists, which in its turn means that we can determine the \( u_{RL,i}^a \) in Eq.(4.3) and with that the exact muffin-tin orbitals. But now we focus on the screened spherical waves.

### 4.2.2 Screened spherical waves

In the interstitial between the potential spheres, the potential is \( v_0 \), and the Schrödinger equation reduces to:

\[
[\nabla^2 + \kappa^2] \psi_{RL}^a(\kappa,r_R) = 0,
\] (4.8)

where \( \kappa^2 = E - v_0 \). The screened spherical waves are similar to plane waves, but are localized in both \( r \)-space and energy. They also, as mentioned, diverges at the sites \( R \). They are furthermore defined as the solution to the Helmholtz wave equation, Eq.(4.8) with boundary conditions at non-overlapping hard (impenetrable) spheres with radii \( a_{RL} \) centered at each site \( R \) and which may be different for each \( l \) channel. The basis is defined as the solution to the wave equation whose spherical harmonic \( Y_L(\hat{r}_R) \) projection on its own \( a_R \) sphere is unity and whose \( Y_L'(\hat{r}_{R'}) \) projection vanishes, for low \( l \) values, on all other \( a_{RL'} \) channels:

\[
\int \delta(r_{RL'} - a_{RL'}) Y_L'(\hat{r}_{RL'}) \psi_{RL}^a(\kappa,r_R,\hat{r}_{RL'}) \, d^3r = \delta_{RL} \delta_{LL'}.
\] (4.9)

This set is complete in the so called \( a \) interstitial, the space between these hard \( a \)-spheres. An \( l \) value is considered "low" if the logarithmic derivative of the partial
waves at the potential sphere boundary deviates substantially from the constant value \( l \) in the energy range of interest. In general \( l \leq 3 \). For \( l \) values larger than this cut-off, the \( a \)-spheres are set to zero in order to automatically satisfy the matching condition \([58]\). This definition forces the low \( l \) components of the screened spherical waves to be quite localized when \( \kappa^2 \) is below the hard sphere continuum, that is, the energies where there exists localized, bound states for the hard spheres.

One can notice that it is possible to express the screened spherical waves in terms of two functions \( f \) and \( g \), called the "value" and "slope" function respectively \([58]\), and defined by:

\[
\begin{align*}
 f_{RL}^{a}(\kappa, r)|_{aRL} &= 1 \quad \text{and} \quad \frac{\partial f_{RL}^{a}(\kappa, r)}{\partial r}|_{aRL} = 0, \\
 g_{RL}^{a}(\kappa, r)|_{aRL} &= 0 \quad \text{and} \quad \frac{\partial g_{RL}^{a}(\kappa, r)}{\partial r}|_{aRL} = \frac{1}{a_{RL}}.
\end{align*}
\] (4.10)

The screened spherical waves then look like:

\[
\psi_{RL}^{a}(\kappa^2, \mathbf{r}) = f_{RL}^{a}(\kappa, r_{R})Y_{L}(\hat{r}_{R})\delta_{RL}\delta_{L'L'} + \\
+ \sum_{L'} g_{RL}^{a}(\kappa, r_{R'})Y_{L'}(\hat{r}_{R'})S_{RL'RL}^{a}(\kappa^2),
\] (4.12)

where the expansion coefficients \( S_{RL'RL}^{a}(\kappa^2) \) are the slope matrix of the EMTO method.

The \( f \) and \( g \) functions can in their turn be expanded in terms of Bessel and Neumann/Hankel functions \([41]\) as

\[
\begin{align*}
 f_{RL}^{a}(\kappa, r) &= t_{RL}n_{i}(\kappa r) + t_{RL}j_{i}(\kappa r) \\
g_{RL}^{a}(\kappa, r) &= -t_{RL}n_{i}(\kappa r) - t_{RL}j_{i}(\kappa r),
\end{align*}
\] (4.13, 4.14)

where the \( t_{RL} \)s are the elements of the screening matrix:

\[
\begin{pmatrix}
 t_{RL}(\kappa) & 2t_{RL}(\kappa) \\
 3t_{RL}(\kappa) & 4t_{RL}(\kappa)
\end{pmatrix} = 2\frac{a_{RL}^2}{w} \begin{pmatrix}
 \frac{\partial j_{i}(\kappa a_{RL})}{\partial r} & -\frac{\partial n_{i}(\kappa a_{RL})}{\partial r} \\
 -\frac{\partial j_{i}(\kappa a_{RL})}{\partial r} & \frac{\partial n_{i}(\kappa a_{RL})}{\partial r}
\end{pmatrix},
\] (4.15)

where \( w \) is the average atomic radius.

Finally, in order to match the solution which has boundary conditions on the MT-spheres (the partial waves) with the solution with boundary conditions on
the $a$-spheres (the screened spherical waves), a free-electron solution $\bar{\phi}_R^a(E, r_R)$, where we have [64]

$$\bar{\phi}_R^a(E, r_R) = f_{RL}^a(\kappa, r) + g_{RL}^a(\kappa, r)D\{\bar{\phi}_R^a(E, a_R)\},$$  \hspace{1cm} (4.16)$$

is introduced from the MT-sphere to the $a$-sphere. This joins continuously and differentiably the partial waves at the potential sphere boundary and continuously the screened spherical waves at the hard sphere boundary. This means that there might be up to three different solutions for some radii. The EMTOs are then:

$$\Psi_{RL}^a(E, r_R) = (\bar{\phi}_R^a(E, r_R) - \bar{\phi}_R^a(E, r_R))Y_{L}(\hat{r}_{R}) + \psi_{RL}^a(\kappa^2, r_R),$$ \hspace{1cm} (4.17)$$

where the radial parts of $\phi_R^a$ and $\bar{\phi}_R^a$ are truncated outside the MT-sphere, $s_R$, and inside the hard sphere, $a_R$, respectively. One can notice that it is not possible to write the EMTOs as a product of a radial function and a spherical harmonic. Also, the low $l$ projections of $\psi_{RL}^a$ are truncated inside the $a_R$ sphere while the high $l$ projections are allowed to penetrate into the hard spheres. The EMTO basis set is continuous and differentiable in the whole space, except for at the $a$ sphere boundary, where they are only continuous and exhibit kinks.

### 4.2.3 The kink cancellation matrix and the slope matrix

To get a solution to the Schrödinger equation valid in all space, we must now make these kinks disappear, and this is done by formulating a kink cancellation equation [58], which can be written as:

$$\sum_{RL} a_R \{ S_{RL}^0(\kappa_j) \delta_{RL}^a - \delta_{RL'}^a D\{\bar{\phi}_R^a(E_j, a_R)\}\} \psi_{RL,j}^a = 0,$$ \hspace{1cm} (4.18)$$

and which yields energy eigenvalues and wave vectors.

In actual calculations one does not solve this equation, but instead calculates the poles of the scattering path operator to the kink matrix. Nevertheless, it is clear that we need to find an expression for the slope matrix. This can be derived from the bare (or canonical) KKR structure constant matrix $S_{RL}^0(\kappa^2)$, and this will be shown below, as well as how to compute the first energy derivative of the slope matrix.

The EMTO slope matrix can be obtained from the bare KKR structure constant matrix $S_{RL}^0(\kappa^2)$ as [58]

$$S_{RL}^{a}(\kappa^2) = \frac{1}{3t_{RL}^a} \delta_{RL}^a \delta_{L' L}^a \left[ S_{RL}^0(\kappa^2) - \frac{4t_{RL}^a}{3t_{RL}^a} \right]^{-1} a_R \frac{2a_R}{w^2},$$ \hspace{1cm} (4.19)$$

where one calculates this in real space for a small cluster chosen just big enough for the slope matrix to converge.
4.2 The Exact Muffin-Tin Orbital Method

The bare structure constants are defined as

\[
S^0_{R'L'RL}(\kappa^2) = -8\pi \sum_{L''} C_{LL''}^{\prime\prime} \frac{(2l'' - 1)!!}{(2l' - 1)!!(2l - 1)!!} \times \left[ -\frac{1}{(k\omega)^2} \right]^{\frac{l' + l'' - l}{2}} (-1)^{l''} \kappa n_{L''}(\kappa, R' - R), \tag{4.20}
\]

where \(C_{LL''}^{\prime\prime}\) are the real Gaunt coefficients \([41]\). In order to express the energy derivatives of the slope matrix, we introduce the dimensionless energy parameter \(\omega \equiv (kw)^2\). After rearranging Eq.(4.19), we get

\[
\sum_{R''L''B_{R'L''RL}(\omega)A_{R'L''RL}(\omega) = -2a_{R}w \delta_{R'R} \delta_{L'L}, \tag{4.21}
\]

where

\[
A_{R'L'RL}(\omega) \equiv \frac{1}{3} t_{R'I}(\omega) \delta_{R'R} \delta_{L'L} - S^0_{R'R'RL}(\omega), \tag{4.22}
\]

and

\[
B_{R'L'RL}(\omega) \equiv 3 t_{R'I}(\omega) \left[ 4 t_{R'I}(\omega) \delta_{R'R} \delta_{L'L} + S^0_{R'R'RL}(\omega) \right]. \tag{4.23}
\]

Note that the screening parameters, and likewise the slope matrix, depend on energy through \(\omega\). Applying the product rule, from Eq.(4.21) we obtain the \(n\)-th energy derivative of the slope matrix as

\[
\frac{d^n S^0(\omega)}{d\omega^n} = B(\omega)^{-1} \left[ \sum_{i=0}^{n-1} \frac{n!}{(n-i)!i!} \frac{d^{n-i} A(\omega)}{d\omega^{n-i}} + 2a_{R}w \delta_{n,0} \right] \\
+ \frac{d^n}{d\omega^n} \frac{1}{3} t_{R'I}(\omega), \tag{4.24}
\]

where the RL subscripts have been dropped and matrix multiplication is implied.

The energy derivatives of the bare structure constant \(S^0(\omega)\) are calculated directly from Eq.(4.20). The derivatives of the screening parameters are obtained from the energy derivatives of the Bessel and Neumann functions.

When the slope matrix is calculated only on the real energy axis, one should use Bessel and Neumann functions for positive \(\omega\), and Bessel and Hankel functions for negative \(\omega\) as basis functions. In this case the slope matrix will be real on the real energy axis. If one wants to calculate the slope matrix for a general complex energy, it is more convenient to use everywhere Bessel and Hankel functions as basis functions. In this case, the slope matrix is complex for the positive real energy axis, while still being real on the negative real energy axis.
4.2.4 Introducing the scattering path operator

Now, in an EMTO calculation, one should find the zeroes of the kink cancellation equation, Eq.(4.18), with a search over all energies, and then perform an integration over these energies up to the Fermi energy. This is not the exact way this is performed in the EMTO method though. Instead the scattering path operator mentioned in Chapter 3 is introduced, but named \( g \) instead of \( \tau \) since it is called the auxiliary Green’s function in this formalism:

\[
\sum_{R' L' R'' L''} K_{R' L' R R'' L''}^a(z, k) g_{R' R'' L'}^a(z, k) = \delta_{R' R} \delta_{L' L},
\]

where \( z \) is the (complex) energy and \( k \) runs over the whole Brillouin zone. Since \( g \) is analytical in the whole complex plane, except for the poles at the real axis corresponding to the one-electron energies, we can use the residue theorem:

\[
\frac{1}{2\pi i} \oint_C f(z) \, dz = \sum_{k=1}^n R_{zh}[f(z)],
\]

where \( R_{zh}[f(z)] \) are the residues at the poles. The residues for \( g = \frac{1}{K} \) are just \( \dot{K} \) where the dot represent derivatives with respect to energy. Rearranging terms we get:

\[
N(E_F) = \frac{1}{2\pi i} \oint_{E_F} \sum_{R' L' R L} \int_{BZ} g_{R' L' R L}^a(z, k) \dot{K}_{R L R' L'}^a(z, k) dkdz,
\]

where \( N(E_F) \) is the integrated density of states. The reason for using residue calculus instead of doing a direct integration along the real energy axis is because it was found very early [67] that the scattering path operator is very structured close to the poles, and the mesh in \( k \)-space needed for good accuracy was very big. This could be avoided by performing the integral in the complex plane, where the scattering path operator is smooth. We have

\[
\dot{K}_{R L R' L'}^a(z, k) = a_{RL}[\delta^a_{R L R' L'}(z - v_0, k) - \delta_{R L} \delta_{R' L'} D_{RL}^a(z)],
\]

and it is not too hard to calculate the derivatives of the slope matrix from the relation, Eq.(4.24), given earlier in the chapter. The derivatives of the potential functions \( D \) are just derivatives of Bessel/Hankel functions. There is one thing to be careful of though, and that is that the normalization of the integrated density of states done above, when we divided the energy integral with the value of the residue, has introduced some unphysical poles of \( \dot{D} \). These should not be included in the integrals, and can be taken care of rather easily; one just subtracts these poles by doing the integration as:

\[
N(E_F) = \frac{1}{2\pi i} \oint_{E_F} G(z) \, dz,
\]
where
\[
G(z) = \sum_{R' L' R L} \int_{BZ} g_{R' L' RL}^a(z, k) \bar{K}_{\alpha}(z, k) - \sum_{R L} \left[ \frac{\bar{D}_{RL}^a(z)}{D_{RL}^a(z)} - \sum_{E_{RL}^D} \frac{1}{z - E_{RL}^D} \right].
\]
(4.30)

Here \(E_{RL}^D\) are the zeroes of the potential function \(D_{RL}^a(z)\). In this way, the poles of \(\bar{D}\) is exactly cancelled by the poles of the last term in Eq.(4.30).

In this integration, the slope matrix should be calculated at each energy point on the integration contour. It should also be noticed that the contour changes every self-consistent iteration, since the Fermi energy is determined as well as the density each iteration. To recalculate the slope matrix for each new energy point would be very inefficient. Fortunately, it was found that the slope matrix exhibited a weak energy dependence in quite a big energy range \([65]\). In a self-consistent EMTO calculation, one needs the slope matrix for energies where the states you treat as valence states are localized. In many cases, you has a pretty narrow valence band, and a deeper lying core, but sometimes there are states which lie quite close to the valence states, called semi-core states, see Fig.(4.1).

It is sometimes possible to treat these states as core states, but often, especially when alloying with another element, hybridization broadens the valence band and the semi-core states and creates a continuous band, and in this case the semi-core states have to be treated as valence states.

In a generic EMTO calculation, the slope matrix is calculated at an expansion center and later Taylor expanded to the energy points on the integration contour:

\[
S^a(\omega) = S^a(\omega_0) + \frac{1}{1!} dS^a(\omega) (\omega - \omega_0) + \frac{1}{2!} \frac{d^2 S^a(\omega)}{d\omega^2} (\omega - \omega_0)^2 + \ldots,
\]
(4.31)

where the energy derivatives are computed using the analytic expression derived above, Eq.(4.24). Usually, the expansion center \(\omega_0\) is chosen somewhere close to 0. Because of the weak energy dependence, this is often a good approximation, especially when the valence band is narrow, which means that a small integration contour can be used. In other cases, when the valence band is broad and especially if the system has a large volume (as the slope matrix depends on \((\kappa w)^2\)), where \(w\) is the Wigner-Seitz radius), the contour is very deep, and the Taylor expansion breaks down.

One way to improve on the convergence of the expansion is to use another expansion center at a large negative \((\kappa w)^2\), but this creates some problems when trying to join the two expansions. A better way is to use information from another energy point in a two-center Taylor expansion:
Figure 4.1. The density of states in hcp La. The semi-core states can be seen as two peaks in the density of states located around -1.20 Ry. The valence band can be seen around the Fermi level.

\[
S^a(\omega) \approx S^{n,m}(\omega; \omega_1, \omega_2) =
\begin{align*}
  &a_0 + \frac{1}{1!}a_1(\omega - \omega_1) + \frac{1}{2!}a_2(\omega - \omega_1)^2 + \ldots + \frac{1}{n!}a_n(\omega - \omega_1)^n \\
  &+ \frac{1}{(n+1)!}a_{n+1}(\omega - \omega_1)^{n+1} + \frac{1}{(n+2)!}a_{n+2}(\omega - \omega_1)^{n+2} + \ldots \\
  &+ \frac{1}{(n+m)!}a_{n+m+1}(\omega - \omega_1)^{n+m+1}.
\end{align*}
\] (4.32)

The first \( n + 1 \) coefficients we can get from:

\[
a_i = \frac{d^iS^a(\omega_1)}{d\omega^i} \text{ for } i = 0, 1, 2, \ldots, n,
\] (4.33)

while the last \( m + 1 \) coefficients are obtained from:
4.2 The Exact Muffin-Tin Orbital Method

Figure 4.2. The relative error of the expansion of (a) the slope matrix using a one-center Taylor expansion and (b) using a two-center expansion. The error is defined in Eq. (4.35) and the expansion center is (0,0) for the one center expansion, and (0,0) and (-10,0) for the two-center expansion.

$$S_{n,m}(\omega_2;\omega_1,\omega_2) = S^a(\omega_2),$$

$$\frac{dS_{n,m}(\omega;\omega_1,\omega_2)}{d\omega} \bigg|_{\omega=\omega_2} = \frac{dS^a(\omega)}{d\omega} \bigg|_{\omega=\omega_2}, \quad (4.34)$$

These conditions lead to a system of linear equations for $a_{n+1}, a_{n+2}, \ldots$. Solving these equations, we obtain a $(n+m+1)$th order expansion for $S^a$. In Paper I, this expansion is examined and compared with the old one-center Taylor expansion. The results show a marked improvement in the expansion of the fcc slope matrix, see Fig.(4.2), and we also find some cases where it is necessary to use the two-center expansion in order to produce correct results. The error in Fig.(4.2) is defined as

$$\text{Err} = \frac{(\text{Re}\{S_{\text{calc.}}\} - \text{Re}\{S_{\text{expan.}}\})^2 + (\text{Im}\{S_{\text{calc.}}\} - \text{Im}\{S_{\text{expan.}}\})^2)^{1/2}}{(\text{Re}\{S_{\text{calc.}}\}^2 + \text{Im}\{S_{\text{calc.}}\}^2)^{1/2}}. \quad (4.35)$$

where $S_{\text{calc.}}$ is the calculated value of the slope matrix and $S_{\text{expan.}}$ is the value of the slope matrix expanded from the energy point (0,0) using a Taylor expansion.

Another idea we had, was to try to set the expansion center somewhere out in the complex plane instead for on the real energy axis. In Fig.(4.3) is shown the real (a) and imaginary (b) part of the ss element of the fcc slope matrix.
One can see that the real part is relatively smooth for small energy values, but that it rises to a peak, which actually becomes a sharp pole at higher energies. This is the first of the original free-electron energy values, which has been shifted towards higher energies by the screening employed for the screened spherical waves. The large absolute value of the slope matrix here introduces numerical instabilities in the inversion routines used for the screening, and makes calculations impossible. Our idea was to calculate the slope matrix a bit out in the complex plane instead, where the absolute value is much smaller. This indeed brings an improvement in that it is possible to actually calculate the slope matrix, and in that the expansion generally is slightly better if the expansion center is placed in the center of the energy contour. Unfortunately, the improvement was very small, and furthermore we found that it was still not possible to Taylor expand to the real axis, because the Taylor expansion was unable to capture the sharp pole like behaviour at the axis.

Another possible future usage of the EMTO method is to try to go beyond the traditional Local Density Approximation with, e.g., the Dynamical Mean Field Theory [68, 69, 70]. In this method, the slope matrix at large imaginary energies is needed in order to integrate over so-called Matsubara frequencies. In Paper I, we also investigated the behaviour of the slope matrix for large imaginary parts of the energies, and derived formulae for the asymptotic behaviour. The results are that all elements die exponentially with distance from the real axis, except for the diagonal terms of the first energy derivative of the slope matrix, which dies as
4.2 The Exact Muffin-Tin Orbital Method

The behaviour of the real (a) and imaginary (b) part of the ss-block of the fcc EMTO slope matrix. The approach to the asymptotic limit is quite slow, and is not reached until a value of 250-300 of the imaginary part of $\omega$.

\[ S_{ll}^{\omega}(\omega) = l - \sqrt{\omega} \frac{h_{l+1}(\sqrt{\omega})}{h_{l}(\sqrt{\omega})}, \quad (4.36) \]

where $h_{l}(\sqrt{\omega})$ is a Hankel function. For large imaginary values of $\sqrt{\omega}$, this expression goes to the same limit, $i\sqrt{\omega} - 1$, regardless of the value of $l$. In Fig.(4.4) one can see that the slope matrix has converged to the asymptotic value at a value of 250-300 for the imaginary part of $\omega$.

If we now return to the determination of the density, it can be written as:

\[ n(r) = \sum_{E_j \leq E_F} |\phi_j(r)|^2, \quad (4.37) \]

where one sums over all one-electron states below the Fermi energy. Inside a Wigner-Seitz cell at $R$ this can be transformed into a one-center expansion:

\[ n(r) = \sum_{R} n_R(r) = \sum_{RL} n_{RL}(r_R)Y_L(\hat{r}_R). \quad (4.38) \]

$n(r_R)$ can in its turn be expressed as:

\[ n_{RL}(r_R) = \frac{1}{2\pi i} \oint_{E_F} \sum_{L''L'} C_{L''L'}^{L} Z_{RR''}^{a}(z, r_R) \tilde{g}_{RL''RL'}^{a}(z) \times Z_{RR'}^{a}(z, r_R)dz, \quad (4.39) \]

where the $L''$ and $L'$ summations include the higher terms. In Eq.(4.39) some notations need to be clarified:
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\[ Z_{Ri}(z, r_R) = \begin{cases} 
N_R \phi_R(z, r_R) & \text{if } l \leq l_{\text{max}} \text{ and } r_R < R \\
\phi_R(z, r_R) & \text{if } l \leq l_{\text{max}} \text{ and } r_R > s_R \\
-j_l(k r_R) & \text{if } l > l_{\text{max}} \text{ for all } r_R
\end{cases} \]

and

\[ \tilde{g}_{RL'}^{a}(z) \equiv \begin{cases} 
g_{RL'}^{a}(z) + \frac{4 \pi}{s_R \Omega_R^a(z)} \left( \frac{\Omega_R^a(z)}{s_R} - \sum E_{RL'}^a - \frac{1}{E_{RL'}} \right) \\
\sum_{R' L''} g_{RL'}^{a} g_{R'L''L''}(z) S_{RL'}^{a} S_{RL'}^{a}(k) g_{RL'}^{a} g_{R'L''L''}(z) S_{RL'}^{a} S_{RL'}^{a}(k) \\
\sum_{R'' L''} S_{RL'}^{a} S_{RL'}^{a}(k) g_{RL'}^{a} g_{R'L''L''}(z) S_{RL'}^{a} S_{RL'}^{a}(k)
\end{cases} \]

where the first line is for \( l, l' \leq l_{\text{max}} \), the second line for \( l' \leq l_{\text{max}} \) and \( l > l_{\text{max}} \), and the third line for \( l', l > l_{\text{max}} \). The charge density is normalized within the unit cell, and is reasonably continuous over the cell boundaries [64].

From the density, it is now possible to construct the potential for the next iteration, and also to calculate total energies. During the self-consistency loop, we make a spherical approximation to the potential. This is because the computational cost for using the full potential is very high, and that the density converges rather badly in the corners of the unit cell. In order not to confuse matters with the ASA (Atomic Sphere Approximation) this is named the Spherical Cell Approximation (SCA) [65]. If we denote the volume of the Wigner-Seitz cell centered at \( R \) by \( \Omega_R \), we have \( \Omega_R = \Omega_{wR} = (4 \pi / 3) w_R^3 \), where \( w \) is the Wigner-Seitz radius. This means that the whole space is covered by spheres, just as in the ASA. We will soon see why this is practical, when we try to create the potential.

### 4.2.5 Creating the potential and calculating the energy

We want to get the best possible representation of the full potential by using the (possibly overlapping) muffin-tin potentials defined in Eq.(4.2). For non-overlapping muffin-tin potentials, it is not hard to find the spherical symmetric part of the muffin-tin potential:

\[ v_R(r_R) = \frac{1}{4 \pi} \int v(\mathbf{r})d\mathbf{r}_R. \]  \hspace{1cm} (4.40)

The muffin-tin constant \( v_0 \) is simply fixed to the average of the full potential in the space outside the potential sphere, but inside the unit cell: the interstitial. If the muffin-tins overlap, one can get another equation for the muffin-tin constant [50]:

\[ \sum_{R} 4 \pi \int_0^{s_R} \left[ v_R(r_R) - v_0 \right] r_R^2 dr + v_0 = \frac{1}{\Omega} \int v(\mathbf{r})d\mathbf{r}, \]  \hspace{1cm} (4.41)
where \( s_R \) is the potential sphere radius and \( \Omega \) is the unit cell volume. In the present implementation, the spherical part of the muffin-tin potential is given by Eq.(4.40) whether the muffin-tins overlap or not. In this case we also get \( v_0 \) as:

\[
v_0 = \frac{1}{\Omega - \sum_R V_R} \left[ \int v(r) dr - \sum_R \int_{V_R} v(r) dr \right], \quad (4.43)
\]

where \( V_R \) is the potential sphere volume at \( R \). This equation can also be written as:

\[
v_0 = \sum_R \left[ \int_{\Omega_R} v(r) dr - \int_{\Omega_R^w} v(r) dr \right], \quad (4.44)
\]

where \( \Omega_R^I \) is the interstitial at \( R \) and \( \Omega_R^w \) is the overlapping part of the potential cell at \( R \). This means that we need the full potential for parts of the unit cell, but since the calculation of this is very time consuming, we here use the SCA. The expression for \( v_0 \) is the same whether we have \( s_R > w_R \) or \( s_R < w_R \), where \( w \) is the Wigner-Seitz radius, and is [65]:

\[
v_0 = \frac{\sum_R \int_{s_R}^{w_R} r^2 \left[ \int v(r) dr \right] dr}{\sum_R W_R}, \quad (4.45)
\]

where \( W_R = 4\pi (w^3_R - s^3_R)/3 \). Both the spherical part of the muffin-tin potential and the muffin-tin constant are thus given by the spherical average of the full potential. Now it is just to construct this average potential.

The electrostatic potential is the solution to Poisson’s equation:

\[
\nabla^2 v^C(r) = -8\pi \left[ n(r) - \sum_R Z_R \delta(r_R) \right], \quad (4.46)
\]

where \( Z_R \) is the protonic charge at \( R \). This potential can be divided into contributions from inside and outside the potential sphere. The intercell contribution, the Madelung potential, can be gotten from:

\[
v^M_R(r_R) = \frac{1}{w} \sum_{R' L'} M_{R(0,0)R' L'} Q^{SCA}_{R' L'}, \quad (4.47)
\]

where \( w \) is the average atomic radius, \( M \) is the Madelung matrix, and the multipole moments \( Q^{SCA}_{RL} \) are calculated within the SCA as [65]:

\[
Q^{SCA}_{RL} = \frac{\sqrt{4\pi}}{2l + 1} \int_{0}^{w_R} \left( \frac{r_R}{w} \right) \frac{n_{RL}(r_R)}{r_R^2} dr_R 
- Z_R \delta_{L,(0,0)} + \delta^{SCA}_{L,(0,0)}, \quad (4.48)
\]
Since the density is normalized within the unit cell, and the integral in Eq.(4.48) is over the spherical cell, the monopole moments have to be renormalized, and this is done by adding/subtracting the constant \( \delta_{SCA} \) in accordance with charge neutrality of the spherical cell.

The intracell contribution can be written as [65]:

\[
v_I^f(r_R) = 8\pi \frac{1}{2} \int_0^{r_R} \int_0^{r_R'} n_{R,(0,0)}(r_R') dr_R' + 8\pi \int_{r_R}^{w_R} r_R' n_{R,(0,0)}(r_R') dr_R' - \frac{2Z_R}{r_R},
\]  
(4.49)

If the spherical part of the exchange-correlation potential \( \mu_{xcR}(r_R) \) is used as well, we get a potential which just depends on the spherical symmetric part of the charge density \( n(r_R) \), which looks like:

\[
v_R(r_R) = v_I^f(r_R) + v_M^R + \mu_{xcR}(r_R).
\]  
(4.50)

So far, we have used the spherical symmetric muffin-tin potentials in our calculations, but now we are going to make a final iteration using the full charge density, that is, the electronic density corresponding to the full potential. In the EMTO one first calculates the full potential and the corresponding full density, and then the total energy is calculated. The kinetic energy part is calculated from:

\[
T[n] = \frac{1}{2\pi i} \oint_{E_F} zG(z) dz - \sum_R \int_{\Omega_R} v_{MT}(r_R)n_R(r_R) dr
= \sum J E_j - \sum_R \int_{\Omega_R} v_{MT}(r_R)n_R(r_R) dr,
\]  
(4.51)

where the \( E_j \)s are the one-electron energies. This is just taken from Eq.(2.27). This is the exact kinetic energy for the muffin-tin potential, and the use of this instead of the kinetic energy for the full potential is one of the largest approximations in the EMTO-FCD method. The improvement on this energy, with a correction for the full potential should be very desirable, and work is in progress. The Coulomb and exchange-correlation parts of the total energy functional are calculated with the use of shape functions [71, 72, 73]. The shape functions \( \sigma_{RL}(r_R) \) are defined to be one inside the unit cell, and zero outside it. If we then multiply our integrands with these functions and integrate over a circumscribing spherical cell with radius \( w_R \), the integrals turn from three dimensional integrals to one dimensional radial
integrals, something which greatly reduces computational costs. In this way, we can introduce

\[
\tilde{n}_{RL}(r_R) = \sum_{L', L''} C_{L', L''}^L n_{RL'}(r_R) \sigma_{RL''}(r_R) \tag{4.52}
\]

and express the energy contributions in terms of this. The intracell part is [64]

\[
F_{\text{intra}}^{R}[n_R] = \frac{\sqrt{4\pi}}{w} \sum_{L} \int_{0}^{w_R} \tilde{n}_{RL}(r_R) \left[ \left( \frac{r_R}{w} \right)^l P_{RL}(r_R) \right. \\
+ \left. \left( \frac{r_R}{w} \right)^{-l-1} Q_{RL}(r_R) \right] r_R^2 dr_R,
\tag{4.53}
\]

where

\[
P_{RL}(r_R) = \frac{\sqrt{4\pi}}{2l + 1} \int_{r_R}^{w_R} \tilde{n}_{RL}(r'_R) \left( \frac{r'_R}{w} \right)^{-l-1} r'^2_{RL} dr'_R \tag{4.54}
\]

and

\[
Q_{RL}(r_R) = \frac{\sqrt{4\pi}}{2l + 1} \int_{0}^{r_R} \tilde{n}_{RL}(r'_R) \left( \frac{r'_R}{w} \right)^l r'^2_{RL} dr'_R - \delta_{L,(0,0)} Z_R. \tag{4.55}
\]

The intercell energy can be written as [71, 74]

\[
F_{\text{inter}}^{R}[n] = -\frac{1}{2w} \sum_{L} \sum_{R' \neq R} \frac{b_{RR'}}{w} \left[ Y_L(\hat{b}_{RR'}) \right. \\
\times \sum_{L', L''} Q_{RL'} \frac{4\pi(2l'' - 1)!!}{(2l - 1)!!(2l' - 1)!!} C_{L', L''}^L \delta_{l', l''} \\
\times \sum_{L'''} S_{RL''': R' + b_{RR'}, L'''} Q_{R'L''}, \tag{4.56}
\]

where \( S_{RL':R''} \) are the standard LMTO structure constants [50] and \( b_{RR'} \) is introduced in Ref.([75]), and discussed in Refs.([71, 74]). Finally one has to add the exchange-correlation energy, which is integrated as [64]

\[
E_{xcR}[n] = \int_{0}^{2\pi} \int_{0}^{\pi} \int_{0}^{w_R} \epsilon_{xc}[n(r)] \sum_{L} \sigma_{RL}(r_R) Y_L(\hat{r}_R) r^2_R dr_R \\
\times \sin \theta d\theta d\phi. \tag{4.57}
\]
The total energy is then the sum of these contributions:

$$E_{tot} = T[n] + \sum_{R} (F_{intra}^{R}[n_R] + E_{xc}^{R}[n_R]) + F_{inter}[n],$$  \hspace{1cm} (4.58)

where $R$ runs through the different sites in the unit cell. This expression will be slightly modified when we discuss alloys in the next chapter.

### 4.3 Other Muffin-Tin Orbital methods

Two other methods that have been used in this thesis are the Bulk Green’s Function method (BGFM) [76, 77] and the Local Self-Consistent Green’s Function method (LSGF) [78, 79]. I will not say much about BGFM since it is very similar to the EMTO method; I will just point out some of the big differences between the two methods. The BGFM is a KKR-ASA method, in which you solve the multiple scattering equations in exactly the same way as in the EMTO method, with the difference being that the ASA is used for the potential. The Atomic Sphere Approximation (ASA) [46, 52] is made by approximating the potential as spherical cells with the same volume as the Wigner-Seitz cells, thereby filling the space totally, and then choosing the value of the kinetic energy in the interstitial, $\kappa = E - v_0$, to be constant, usually zero. This makes the structure constants energy independent and significantly simplifies calculations at the cost of accuracy. The reason for fixing the kinetic energy to zero is that it was found that both the structure constants and phase shifts were strongly energy dependent, and it was further found out [51] that the wave function depends on $\kappa$ through the wavelength $2\pi/\kappa$, which is a much larger wavelength than the length scales of the potential. The strong $\kappa$-dependence was therefore thought to be unphysical, and also disappeared at the solutions of the KKR equations [80]. It was then decided to fix $\kappa$ to $E - v_0$ and thereby get rid of the interstitial.

In the BGFM, the ASA+M technique [57] is used to improve on the ASA energies. In the ASA+M, the multipole moments which are lost in the ASA (that is, all but the spherical $l = 0$ monopole moment) are added to the Madelung potential and energy. This significantly increases the accuracy [81], and makes the BGFM a reliable method in many cases [76, 82].

The LSGF method on the other hand is an order-$N$ method for calculation of the electronic system. It is based on a supercell (which may just be one unit cell) with periodic boundary conditions, see Fig.(4.5), and the concept of a Local Interaction Zone (LIZ), which is embedded in an effective medium, usually chosen to be the Coherent Potential Approximation medium (see next chapter). For each atom in the supercell, one uses the Dyson equation to solve the electronic structure problem as an impurity problem in the effective medium. The ASA is employed as well as the ASA+M correction described above. The total energy is defined to
be the averaged energy from all atoms in the supercell:

\[ E_{tot} = \frac{1}{N} \sum_{i=1}^{N} E_i, \]

where the \( E_i \)'s are calculated analogous to how it is done in BGFM.

In Fig.(4.6) the main idea is shown: In (a) is shown the original supercell with some effective medium substituted on all sites. In (b) we have centered on one atom and its LIZ. For this atom one calculates, using the Dyson equation, the Green's function for the LIZ embedded in the effective medium, and calculates the total energy of the central site from that Green's function. Then one moves to another site (c), and calculates its new Green's function, and so on for the whole supercell. In (d) is shown another possibility for a (slightly larger) LIZ. With a good choice of effective medium, preferably the CPA effective medium, the method converges fast with respect to LIZ size.

The LSGF method will be mentioned in the next chapter when I describe how to use it to correct the CPA method for some problems with charge transfer that appears when you calculate properties for alloys.
Figure 4.6. An LSGF method supercell with (a) an effective medium, a small LIZ around one of the atoms in the supercell (b), the same LIZ around another atom (c), and a larger LIZ around one of the atoms in the supercell (d).
Chapter 5

Alloys: The problem of disorder

One of the big problems in electronic structure theory is alloying. If the alloy forms an ordered structure, everything is still fine, but very often this is not the case: the alloy forms a disordered, random, structure. This introduces a problem in that the translational symmetry that we have assumed all the time breaks down. The reason is simple: When you have a disordered alloy, the atoms place themselves at the lattice positions in a random manner, making each ion unique because of the different environments. Since we cannot really do without translational symmetry, we must try to mimic this randomness in one way or another. One way would be to calculate a lot of big supercells where you have placed your alloying atoms in a random manner, and then average the results from the calculations. This is not a very good idea. It is very hard to get a good representation of the randomness by this method, it is hard to do the averaging in a consistent manner, and the computational time is very great. Especially if one wants to calculate odd concentrations, because then one has to use very large supercells: For 1% or 49% concentrations of one alloy component, you would need at least 100 or 98 atoms in order to obtain the correct concentration, 0.1% requires 1000 atoms.

Another way would be to set up a supercell where one tries to mimic the randomness by demanding that the Warren-Cowley short range order parameters [83] should be zero for the first few nearest neighbour shells, just like they should be for a random alloy, where they are all zero. This is the Special Quasirandom Structure (SQS) method [83]. It is still quite computationally heavy, since the supercells have to be large to be able to bring the short range order parameters to zero, and it is hard to get good supercells for low concentrations. The averaging on the other hand, is of course no longer necessary, since the supercell is supposed to be a good model of the alloy as it is, and you just have to make one calculation.

A third way is to try to keep the translational symmetry of the underlying lattice by creating an effective medium which is then placed on the lattice sites.
If this could be realized it would be very nice, since it would be computationally efficient. The problem is how to construct this effective medium. Two very nice reviews on the problem [84, 85] are highly recommended for further reading. I will do a short summary below, with just two alloy components and one atom per unit cell. The extension to more components is relatively simple.

5.1 Effective medium approaches to the alloy problem

Early on, the Virtual Crystal Approximation (VCA) was tried. Here one just puts
\[ v_{\text{eff}} = c_A v_A + c_B v_B, \] (5.1)
that is, one sets the concentration average of the different potentials as the new potential representing the alloy. Here \( c_i \) is the concentration and \( v_i \) the potential of alloy component \( i \). Though the derivation from Rayleigh-Schrödinger perturbation theory seemed sound at first, it was later discovered that it was not possible to use that perturbation theory to describe the transition from order to disorder since no finite number of perturbation steps could make the transition [84]. The method worked when the potentials were similar from the start, but failed when they were not.

Another attempt was made by Korringa [86], who tried to average the scattering amplitudes, which are equivalent to the \( t \) matrices, on each site:
\[ t_{\text{eff}} = c_A t_A + c_B t_B. \] (5.2)
Many properties were qualitatively correct, such as the inelasticity of the effective scatterers leading to finite lifetimes for states in the alloy. This is so because the possibility of two different scatterings of an electron wave at a site creates waves which tend to cancel out due to negative interference. A problem though was that the potential turned out to be complex and energy dependent, and that the energy eigenvalues and eigenfunctions turned out to be wrong. This lessened the use of the method, but it was still the best approximation until the birth of the Coherent Potential Approximation (CPA) [87].

The CPA can be understood by thinking of the scattering in an alloy and what we want the effective potential to actually do. We want to have an effective potential that on average differs as little as possible from the alloy, that is, an electron moving through the effective medium should scatter from the effective potential as close as possible to what it would experience in a random alloy. This can be formulated as:
\[ \tau_{\text{eff}} = c_A \tau_A + c_B \tau_B, \] (5.3)
where $\tau$ is the scattering path operator. The main idea is depicted in Fig.(5.1). We have already showed in Chapter 3 that for a monatomic solid, such as the effective medium with the coherent potential, it is easy to find the scattering path operator [88]:

$$\tau_{L' L}^{nn} = \frac{1}{V} \int_V dq \left( \frac{1}{1 - S(q)} \right)^{L' L}.$$  \hfill (5.4)

where $S(q)$ is the Fourier transformed structure constants, and from Eq.(3.44) it is easy to find an expression for the impurity scattering path operator for an atom of kind $A$ on site $n$:

$$\tau_{L' L}^{A,nn} = \left( \frac{\tau^{C,nn}}{1 - [t^A]^{-1} - (t^C)^{-1} \tau^{C,nn}} \right)^{L' L},$$  \hfill (5.5)

where $\tau^{C,nn}$ and $t^C$ are the coherent scattering path operator and $t$-matrix respectively. The same equation can of course be written for the case with an atom of kind $B$, and the final result is [88]:

$$\tau_{L' L}^{C,nn} = c \frac{\tau^{C,nn}}{1 - [(t^A)^{-1} - (t^C)^{-1}] \tau^{C,nn}} + (1 - c) \frac{\tau^{C,nn}}{1 - [(t^B)^{-1} - (t^C)^{-1}] \tau^{C,nn}}.$$  \hfill (5.6)
We can now solve self-consistently for the effective medium: From the electronic structure calculation we get the $t$'s for the different atomic kinds and the $S$ matrix. Then we solve Eq.(5.6) to get the $t^c$ for the effective medium, which we use in Eq.(5.4) to get the scattering path operator for the effective medium. This then gives the new scattering path operators for the different atomic kinds by using Eq.(3.44) for the impurity problem. These are what is needed to restart the calculations for the next iteration.

The resulting effective medium is called the Coherent Potential Approximation (CPA) medium, and is the best possible single site approximation to a random alloy. As a matter of fact, it is very often good enough to get reliable results from your calculations. To anticipate discussions in Chapter 7, I also want to mention that the CPA can be used for modeling paramagnetic systems. Paramagnetism is when you have magnetic moments which are pointing in random directions, so the net magnetic moment is zero. This can be modeled with an alloy consisting of 50% spin-up moments and 50% spin-down moments, and the technique is called the Disordered Local Moment method [89]. In this model, the spin-up and spin-down components of the density is treated as an alloy with the CPA, and it can be shown that one in this way describes a paramagnetic state within the CPA [89].

In the EMTO-CPA method, the total energy for an alloy is gotten from the expression:

$$E_{\text{tot}} = T[n] + \sum_R \sum_i c^i(F_{\text{intra}}^i[n^i] + E_{\text{xc}}^i[n^i]) + F_{\text{inter}}[n]$$

$$- \sum_i c^i \frac{\alpha_c \beta_c}{w} (Q_{i,s}^R - Q_s^R)^2,$$

(5.7)

where the $R$ sum is over sub-lattices in the unit cell, and the potential for atom kind $i$ is calculated from:

$$v_{\text{R}}^i(r_R) = v_{\text{R}}^i(v_R) + v_{\text{R}}^M + \mu_{\text{xc}} [n_{R,L_0}^i(r_R)] - \frac{2\alpha_c}{w} (Q_{i,s}^R - Q_s^R).$$

(5.8)

Equations (5.7) and (5.8) are derived in Refs.([90, 91, 92]), except for the last terms which are explained below. As can be seen, the Madelung part of the energy and potential is calculated using the effective medium $[n]$, while the intrasite part is solved for the atom kind density, and this leads to a non-vanishing net charge for the alloy component systems. This is corrected for by using the Screened Impurity Model (SIM) [93, 81, 94, 95] and leads to the last terms in the above equations.

The Screened Impurity Model deals with these so-called charge transfer problems (because charge is transfered from one alloy component to another), by assuming that the missing/extra charge is placed at the boundary of the potential sphere of each alloy and represents the screening of the missing/extra charge. In this way, you do not have to have different effective media for the different alloy components, but instead just modify the alloy component potential.
5.2 The short range order problem

The $\alpha_c$ is called the *on-site screening constant*, and is different for different alloys. It can be obtained from calculations with the LSGF method by treating $\alpha_c$ as a free parameter and trying to reproduce the LSGF method charge transfer by varying $\alpha_c$. Since the LSGF method treats the Madelung part exactly, this gives an $\alpha_c$ that is correct. For the total energy, this $\alpha_c$ will still underestimate the Madelung energy because it does not include multipole-multipole interactions. This is remedied by introducing yet another fitting parameter $\beta_c$ to the Madelung energy term. This in its turn is gotten from the same kind of calculations by using it as a parameter and trying to reproduce the total energy from the LSGF method.

There are still some effects that are not properly taken into account. The fact that we are using a single site approximation means that we are totally neglecting short range order effects as well as local lattice relaxations. There are ways of addressing these shortcomings, although they are not perfect. To get an estimation of the local relaxations, a semi-phenomenological method, the Effective Tetrahedron Method (ETM) [96] was recently developed. In the ETM, the assumption is that the relaxation energy of the smallest cluster in the underlying alloy lattice is a function mainly of the change in volume of that cluster. A harmonic spring model is introduced, and the bond lengths of the clusters are then allowed to relax as a function of bond lengths and bulk moduli of the alloy and pure elements. The ETM only accounts for pure volume relaxations, and inhomogeneous lattice distortions are completely neglected, making it perilous to use close to phase transitions. Otherwise, the comparisons in Ref.([96]) show a very good agreement with supercell methods.

5.2 The short range order problem

The problem of order and disorder in alloys is a very old problem. It is discussed very thoroughly in Ref.([97]), and a large part of a very nice book by Ducastelle [98] also deals with it. All methods have one thing in common: The use of an effective Hamiltonian in terms of effective cluster interactions, which can be used to find the configurational energy. Often a statistical Monte-Carlo [99, 100, 101] program is used to find optimizing configurations. The general idea is discussed in Ref.([98]), and it is as follows: Suppose that we want to find the configurational energy for an alloy. We can then write that energy as [102, 103]:

$$E_{\text{config.}}(\sigma_i^a) = E_{\text{rand.}}(c) + E'(\sigma_i^a),$$

(5.9)

where $E_{\text{rand.}}$ is the energy of the random alloy (taken to be the CPA alloy in the rest of the discussion), which depends on the concentration but not on the configuration. $E'$ on the other hand is the configurational dependent part, which can be written in terms of the occupation numbers $P_i$, which takes the value 0 or 1 depending on if the $i$th site is occupied with atom kind $a$ or not, or in terms of the spin-like variables $\sigma_i^a = 2P_i - 1$ which is 1 or -1. The alloy configuration can
now be uniquely defined by the set of numbers for each order \( n \) of clusters (there are \( n \) sites in the cluster) and type \( s \) labeling geometrical class:

\[
\tilde{\xi}_s^{(n)} = \frac{1}{n} \sum_{p \in s} \prod_{i=1}^{n} \sigma_i^p,
\]

where the summation is over all clusters in the system. It has been proven [104] that these correlation functions constitute a complete basis for expanding thermodynamic properties, if the range of the interactions are finite. One can therefore write the configurational energy as

\[
E_{\text{config.}} = \sum_{n,s} \tilde{V}_s^{(n)} \tilde{\xi}_s^{(n)},
\]

where \( \tilde{V}_s^{(n)} \) is the effective cluster interaction for the cluster of order \( n \) and type \( s \). But these can be rewritten in terms of interatomic potentials \( \nu \) as [105]:

\[
\tilde{V}_s^{(n)} = \frac{1}{2n} \sum_{\sigma} \nu^{(n)}(\sigma) \prod_{i=1}^{n} \sigma_i = \frac{1}{2n} V_s^{(n)},
\]

where the \( V_s^{(n)} \) interactions have been introduced. These appear in the configurational Hamiltonian if one uses occupation numbers instead of the spin variables as the basis, and are what I will use in the following.

Now we must find a way to calculate them. One common way is by using the Connolly-Williams, or Structure Inverse Method (SIM) [106, 107], in which one maps the total energies of some ordered structures onto an Ising-type Hamiltonian. This method often works fine, but it has some shortcomings in the fact that it is very hard to use in the case of multi-component alloys and the fact that one has to decide in beforehand which interactions are important. Another way is to use the Generalized Perturbation Method [98, 108]. This is a method which is based on perturbation theory applied to the CPA medium, and which is very convenient in that you can calculate all the interactions you need, and then converge the configurational energy with relative ease.

The perturbation theory is based on the so-called force theorem [109], whose equivalence allowing for magnetism [110, 111] will be of use later in Chapter 7. The force theorem basically states that the changes in energy when a small perturbation to the density (and spin density) is made, is equal to the change in the one-electron energies and the change in electrostatic interactions due to the perturbation. The one-electron energies can be derived explicitly from the so-called Lloyd’s formula [112], which starts from the integrated density of states

\[
N(E) = \int_{-\infty}^{E} n(E)dE,
\]

and uses the relations
\[ n(E) = \frac{1}{V} \sum_n \delta(E - E_n) \]
\[ = \frac{1}{V} \text{Tr} \delta(E - H), \quad (5.14) \]

where \( V \) is the volume for the system, \( E \) the energy eigenvalues of the Hamiltonian \( H \), and \( \text{Tr} \) denotes the trace. If one then writes the Hamiltonian as the sum of kinetic and potential energies:

\[ H = k^2 + \Gamma, \quad (5.15) \]

and writes the delta function as:

\[ \delta(x) = -\frac{\text{Im}}{\pi} \frac{1}{x + i\epsilon}, \quad (5.16) \]

we can write

\[ N(E) = -\frac{\text{Im}}{\pi V} \text{Tr} \ln \left( (k^2 + \Gamma - E - i\epsilon) \delta_{kk'} + <k|\Gamma|k'> \right), \quad (5.17) \]

where we have used the relation \( \text{Tr} \ln(A) = \ln(\text{det} \|A\|) \), from linear algebra. If this expression is transformed to position representation, it instead reads [112]:

\[ N(E) = N_0 - \frac{\text{Im}}{\pi V} \ln \left( \text{det} \| \delta_{LL'} \delta_{ll'} + t^L G_{LL'}(l - l') \| \right), \quad (5.18) \]

where \( N_0 \) is the free electron density of states

\[ N_0(E) = \frac{k^3}{6\pi^2}, \quad (5.19) \]

\( t^L \) is the \( t \)-matrix at site \( L \), and \( G \) is the Green’s function of the system. This can also be written

\[ N(E) = N_0 + \frac{\text{Im}}{\pi} \text{Tr} \ln \tau(E), \quad (5.20) \]

where \( \tau \) is the scattering path operator. We can now find the change in the one-electron energies from a perturbation as:

\[ \delta E = \int_{-\infty}^{E_F} dE E \delta n(E) = E_F \delta z - \int_{-\infty}^{E_F} dE \delta N(E) \]
\[ = -\int_{-\infty}^{E_F} dE \delta N(E), \quad (5.21) \]
by integration by parts. Here $\delta z$ is the change in electron numbers, which is zero, because we just do a small perturbation. For a general perturbation at site $i$, the energy change becomes:

$$\delta E = \frac{1}{\pi} \int_{-\infty}^{E_F} dE \Im \Tr \ln(1 + \delta t_i^{-1} \tau).$$  \hfill (5.22)

This expression will be used in Chapter 7 to calculate magnetic interactions and to discuss quantum corrals.

Now it is not too hard to find the cluster interactions. They are found by the expression $[113]$:

$$V_{(n)-\text{one el}} = -\frac{1}{\pi} \Im \int_{-\infty}^{E_F} dE \Tr \ln[\prod_{p \in A-\text{even}} Q_p (\prod_{p \in A-\text{odd}} Q_p)^{-1}],$$  \hfill (5.23)

where $A$-odd is the clusters with an odd-number of $A$ atoms, $A$-even the clusters with an even number of $A$ atoms, and

$$Q_{ij} = \delta_{ij} - t_i^j (1 - \delta_{ij}).$$  \hfill (5.24)

For a pair interaction, it is simply

$$V_{(n)-\text{pair}} = -\frac{1}{\pi} \Im \int_{-\infty}^{E_F} dE \Tr \ln[Q_{AA}Q_{BB}(Q_{AB}Q_{BA})^{-1}].$$  \hfill (5.25)

To get the GPM effective interaction we expand the logarithm in Eq.(5.23), assuming that $\delta t \tau$ is small, and keep the interactions only the lowest order of scattering on each cluster:

$$V_{(n)-\text{GPM}} = -\frac{1}{\pi} \Im \int_{-\infty}^{E_F} dE \sum_{p \in s} \Tr(\delta t_i^j \tau_{ij} \delta t^j \ldots \delta t_k \tau_{ki}^s),$$  \hfill (5.26)

where the summation is over all irreducible paths in the clusters. There is also a way to partly take account of the higher order scatterings by calculating the expression $[114]$:

$$V_{(n)-\text{GPM}} = -\frac{1}{\pi} \Im \int_{-\infty}^{E_F} dE \sum_{p \in s} \Tr[\ln[1 - \delta t_i^j \tau_{ij} \delta t^j \ldots \delta t_k \tau_{ki}^s]].$$  \hfill (5.27)

In the limit of $c \to 0(1)$, this takes into account the higher order scattering, but overestimates these interaction around $c = 0.5$. A better method is to just calculate the energy difference $AABB - ABAB$ in Eq.(5.22).
Of course, even in the case of GPM interactions, we have the problem of charge transfer: The perturbation should include the screening cloud of the perturbing atoms. The right way to take care of this is in exactly the same way as the above discussed screened coulomb interactions, one adds a shift to the GPM-interaction according to the screening constant as for the Coulomb potential [81, 105]. We write:

\[ V^{(2)}(R) = V^{(2)-GPM}(R) + V^{(2)}_{\text{scr}}(R), \]  
\[ (5.28) \]

where

\[ V^{(2)}_{\text{scr}}(R) = \frac{e^2}{2} (q_A - q_B)^2 \frac{\alpha_{\text{scr}}(R)}{S} \]  
\[ (5.29) \]

is the screened Coulomb interaction of the pair \(AB\). As can be seen in Ref.[105]), these interactions reproduce ordering energies very accurately, and can be used with confidence in thermodynamic simulations.
Chapter 6

Calculations on alloys

6.1 Calculations on magnetic alloys

Now I have introduced a lot of different methods and theories, but how well do they actually work? Can they reproduce experimental values, and are they in the same accuracy range as full potential methods? Part of these questions were addressed in Paper II for the FCD-EMTO-CPA method, where calculations were performed for magnetic alloys with both compositional and magnetic disorder. This is one of the hardest test one can make for an electronic structure calculation method, and the results are presented in Fig.(6.1)(a) and (b). In Fig.(6.1)(a) are shown calculations of the mixing energy $E_{\text{mix}}$, defined as

$$E_{\text{mix}} = E_{\text{alloy}}(c) - cE_{\text{ss}}^a - (1 - c)E_{\text{ss}}^b,$$

where $E_{\text{ss}}$ is the total energy of the standard states from which you are measuring the mixing energy.

In Fig.(6.1)(b) are shown calculations of the mixing enthalpy, which is defined analogous to the mixing energy, but here the enthalpy is measured instead. In the $T = 0K$ limit, they coincide. For the ordered alloys, we have calculated ferromagnetic alloys, and ferromagnetic reference states with the structure fcc for the L1$_0$ and bcc for the B2 structure. We have used both the FCD-EMTO-CPA method and the full potential Projector Augmented Wave (PAW) method [115] as a benchmark. The results can be seen to agree quite well. We also calculated a ferromagnetic random fcc alloy, where we have used the SQS supercell [83] technique for the PAW calculations. Even here the results agree. This gave us confidence enough to do a calculation for a disordered magnetic alloy, which we chose to be a paramagnetic fcc FeCo alloy. This alloy was treated as a four-component alloy $Fe_{x/2}^{\uparrow}Fe_{x/2}^{\downarrow}Co_{(1-x)/2}^{\uparrow}Co_{(1-x)/2}^{\downarrow}$, where $x$ is the total concentration of Fe. The calculations were then compared with experimental values [116] for paramagnetic FeCo. Once again we find a very good agreement between the two curves (Fig.(6.1)(b)).
66 Calculations on alloys

FeCo FeNi FeCu FeCo FeNi FeCu FeCo FeNi FeCu

-20 -10 0 10 20

Mixing energy [mRy/atom]

EMTO PAW

Random/SQSL1

B2

0 20 40 60 80 100

Concentration of Fe (at. %)

-5 -4 -3 -2 -1 0

Mixing enthalpy [mRy/atom]

EMTO, fcc random Experiment, fcc random EMTO, B2 ordered

Fe-Co (a) (b)

Figure 6.1. In (a) is shown calculations for the mixing energy of the ferromagnetic ordered alloys on the B2 and L1₀ lattices, as well as for the ferromagnetic random fcc alloy with 50% Fe and 50% Ni. In (b) is shown the calculated results for the paramagnetic fcc FeCo alloy over the whole concentration range, as well as experimental values and one point of the paramagnetic ordered B2 structure.

These results indicate that the FCD-EMTO-CPA method is a reliable method for electronic structure calculations, even in the case of systems with both configurational and magnetic disorder. I will now present a slightly larger case study of the binary MoRu alloy system, which I have been working on for some time.

6.2 The case of MoRu

The MoRu project, which is described in Papers III, IV, and V, started when professor Larry Kaufman contacted us about the possibility to cooperate with a project intended to investigate the differences between CALPHAD interpolation techniques [117] and \textit{ab initio} methods. One of these differences are the structural energy differences, which usually agrees very well, but for some elements, Nb, Mo, Ru, Rh, for example, the difference between CALPHAD and \textit{ab initio} values is very big. The idea was to start from the equation for the mixing enthalpy of the alloy:

\[
\Delta H_{hcp}^{hcp}[Ru(x)Mo(1-x)] = E_{hcp}^{hcp}[Ru(x)Mo(1-x)] - (1-x)E_{Mo}^{bcc} - xE_{Ru}^{hcp},
\]  

(6.2)

where \(E_{hcp}^{hcp}[Ru(x)Mo(1-x)]\) is the energy of the hcp alloy and \(E_{Mo}^{bcc}\) and \(E_{Ru}^{hcp}\) are the energies of bcc Mo and hcp Ru respectively. If we now add and subtract the quantity \((1-x)E_{Mo}^{hcp}\) to the right hand side of Eq.(6.2), we can rewrite it as:
The case of MoRu

6.2 The case of MoRu

Figure 6.2. Mixing enthalpies for the random bcc, fcc, and hcp alloys, as well as an experimental curve for the Ru-rich hcp alloy.

\[
\Delta H_{hcp}[Ru(x)Mo(1-x)] = H_{hcp}[Ru(x)Mo(1-x)] - (1-x)[E_{hcp}M_{0} - E_{hcp}Ru], \quad (6.3)
\]

where \( H_{hcp}[Ru(x)Mo(1-x)] \) is the isostructural mixing enthalpy of the hcp phase, defined by

\[
H_{hcp}[Ru(x)Mo(1-x)] = E_{hcp}[Ru(x)Mo(1-x)] - (1-x)[E_{hcp}M_{0} - xE_{hcp}Ru]. \quad (6.4)
\]

In this equation, we have now separated the contribution from the structural energy difference of Mo, and can treat it as a fitting parameter, if we so choose. If the isostructural mixing enthalpy can be calculated with enough accuracy, we might then be able to draw conclusions with regards to the structural energy difference. Fortunately, we have a method that has proven capable of calculating these isostructural mixing enthalpies, the EMTO method [118, 119], and the calculated results for the random alloy using the theoretical value of the Mo structural energy difference can be seen in Fig.(6.2), where also experimental results and theoretical results from another group [120] are presented. The experimental curve is from Ref.(121).

As can be seen, the theoretical results are not in agreement with the experimental values. Here we have first calculated the Coulomb screening parameters
α and β discussed above with the LSGF method, using the procedure mentioned in the discussion about these screening parameters. Of course, all ordering is neglected, and this might contribute quite a lot to the enthalpy, so we also calculated the mixing enthalpy of the ordered and partially ordered DO$_{19}$ phase, which is an hcp version of the more familiar L1$_2$ for the fcc structure [98]. A partially ordered alloy is an alloy where the order is kept on some sublattices, and disorder is allowed on others. This allows for calculations of concentrations which do not match the stoichiometric conditions of the ordered alloy, but retains some of the ordering.

In Fig.(6.3)(a) and (b) is shown the mixing enthalpy with the theoretical and CALPHAD value of the structural energy difference respectively. As can be seen, the CALPHAD value gives results much closer to the experimental values than the ab initio calculation does. The conclusion from Paper III was that the recipe of using ab initio isostructural mixing enthalpies coupled with CALPHAD structural energy differences seemed to improve upon the results, although no explanation for this could be given. In the conclusion to Paper III was also mentioned the fact that an independent experimental measurement of the mixing enthalpy would be very interesting, in order to verify the results. Contact with J. C. Gachon at Laboratoire de Chimie du Solide Mineral (LCSM) in Nancy, France was made. Although he had all the necessary equipment, he was currently under-staffed, and so it was decided that I would go to Nancy and perform the experiments myself, something that would turn out to be easier said than done.

6.3 Direct Reaction Calorimetry

Calorimetry is the name of methods where one tries to extract properties like enthalpies of formation, heat capacities, heat of transformations, etc. of a substance
6.3 Direct Reaction Calorimetry

by measuring how heat effects the substance in question. This can be done in different ways and with different kinds of devices. The most common method is solution calorimetry, which I will describe very shortly below.

In solution calorimetry, the constituents of the compound you want to measure the mixing enthalpy of are placed in a vessel inside a furnace, the vessel is heated until the constituent elements melt and form the desired compound, and during this process the heat is measured carefully. Then the compound is allowed to solidify by lowering the temperature to room temperature again. The mixing enthalpy is then measured as

\[
\Delta H_{\text{mix}} = c_A \Delta H_{A}^{\text{heat}} + c_B \Delta H_{B}^{\text{heat}} - \Delta H_{c_Ac_B}^{\text{heat}},
\]

(6.5)

where \( \Delta H_{A}^{\text{heat}} \) and \( \Delta H_{B}^{\text{heat}} \) consists of the enthalphy of heating up the solid from room temperature to the melting temperature, the heat of melting of the component, and the limited partial heat of solution in the liquid aluminium bath where the reaction takes place. The \( \Delta H_{c_Ac_B}^{\text{heat}} \) just includes the part from dissolution in the bath.

Direct Reaction Calorimetry (DRC) works slightly different. It is a form of calorimetric measurements where you synthesize the alloys directly in the crucible (container), where you also measure the heats. The method will be described very quickly here, for further reading one could consult Refs.[122, 123, 124]. In this method you have a crucible made of ceramic aluminium, in which several thermoelectric elements (usually made of a platinum alloy) are lodged. With the help of these one can then measure the heat of the reaction and get the mixing enthalpy from

\[
\Delta H_{\text{mix}} = Q - (c_A \Delta H_{A}^{\text{heat}} + c_B \Delta H_{B}^{\text{heat}}),
\]

(6.6)

where the \( Q \) is the heat measured during the process of dropping the samples at room temperature into the crucible, heating them, and letting them react. The \( \Delta H_{A}^{\text{heat}} \) and \( \Delta H_{B}^{\text{heat}} \) is here the enthalpy for heating the constituent elements from room temperature to reaction temperature.

The samples themselves are prepared in a glove box, where powders of the elements are manually pressed into a pellet, which are then put into a sealed dispenser which is put on the calorimeter. Interspersed with these pellets are also aluminium samples, which are used for calibrating the heat curves. The calorimeter is then heated, and the samples dropped one after each other into the crucible, and the heat is measured from integration of the temperature curve which one gets out of the experiment. In most cases, this is an excellent method for measuring mixing enthalpies, but it has its advantages and disadvantages. The big plus is that you can go to very high temperatures, even temperatures of 1800 C are possible [122]. The higher the temperature though, the faster the thermoelectric elements oxidize and have to be changed. This is not an easy job, I tried it myself with mixed results. The brittleness of these elements increases with each measurements as
they oxidize, and they then break from the shock when samples are dropped into the crucible, or during insertion/retrievement of the crucible from the calorimeter. When this happens you have to let the calorimeter cool, and then remake the crucible. All this takes time, and the method itself is also fairly time consuming, just like all other calorimetric experiment techniques. An experiment consists of the preparation of the samples in a glove box, the heating of the calorimeter, the measurement itself, letting the calorimeter cool, and then the retrieval of the samples. It takes at least one day, if you work the whole day from 7am to 11pm.

After you have taken out the samples, they are first put into a resin and polished, and then investigated with both X-ray diffraction and electron microprobe analysis, to see that you have obtained the right structure, and that the samples have reacted properly so that you have a homogeneous sample.

I spent roughly one month learning to prepare samples, using the equipment and making the experiments, of course with the help from both Professor Gaouchon and also Dr. Gilberto Coelho from Lorena, Brazil, who was there to learn the technique. The experiments seemed to go well, but all of them either failed the test for homogeneity or produced very strange results. The expected mixing enthalpy is very small, and the tolerance of my measurements turned out to be very big. Unfortunately, I did not have time to complete the experiments, but they were continued without me. It was found out that there were big problems with oxidation of Mo, which reacted very strongly, and which made the pellets impractical both because of their big surface to volume ratio and because of their small size. Experiments using a monolayer technique was employed, but the results were inconclusive, and although the experiments continue, no measurement has yet been conclusive.

6.4 Continued theoretical investigations of the MoRu system

In Paper IV, we investigate the MoRu alloy more carefully, especially with regards to ordering. We were not quite satisfied with the idea of using \textit{ab initio} isostuctural mixing enthalpies with CALPHAD structural energy differences, since it was not motivated from a theoretical point of view. There had been more theoretical investigations performed [120], and although the results were not exactly the same (especially near pure Mo, the reason being the different value for the structural energy difference of Mo), in the Ru rich region they were practically identical, and supported our old results in that it was not possible to obtain the experimental values of the mixing enthalpy. We therefore did an investigation of more ordered structures, among them the sigma phase which appears in the experimental phase diagram at a Ru concentration of roughly one third. The sigma phase is not stable at room temperature, but becomes stable at about 1143 C and then becomes unstable again near the melting point at 2000 C. In paper V we performed calcula-
6.4 Continued theoretical investigations of the MoRu system

![Figure 6.4](image_url)

Figure 6.4. The mixing enthalpy for all the possible configurations of the MoRu sigma phase. One can see that configuration #8 has the lowest mixing enthalpy, as expected from the experimental phase diagram.

We investigated relaxation effects by first calculating the hcp c/a ratio dependence on the mixing enthalpy. It was found to be very small with a maximum of 0.2 mRy. We also minimized all calculations with respect to volume, so it was only local relaxation effects that could play a role in this system. The ETM mentioned earlier was used, with the result that the maximum relaxation energy was 0.3 mRy around 75% Ru for the hcp alloy. We tried to verify this by the means of PAW calculations of 64 atoms SQS supercells. Those calculations produced larger relaxation energies, for example a result of 0.9 mRy at 75% Ru. Although this was bigger than the ETM result, it was still very small compared to the difference between the experimental values and the calculated mixing enthalpy. Here, both we and Shin et al. [120] found that it was not possible to relax the structure at certain concentrations (for Mo-rich alloys) without having the atoms deform from the hcp lattice. This is discussed more thoroughly in Ref.([120]), where an investigation of this is made. The reason is that hcp Mo is dynamically unstable [125, 126]. One reason that the ETM and PAW-SQS relaxation energies differ so
much might be that the system is close to a dynamical instability. Nevertheless, since the relaxation energies were small compared to the big difference in mixing enthalpy, we decided not to consider relaxation effects for the rest of the calculations.

The ordering effects were investigated with the use of partially ordered structures as explained above, and also with the use of (screened) GPM interactions (for a discussion about the screening, see above and Ref.([105]). We investigated the GPM interactions by calculating the ordering energy for a number of structures, using both direct calculations and energies from Monte-Carlo calculations using the GPM interactions. The results (see Paper IV) agreed quite well, and so we performed a ground state search, using different large sized supercells, to get an estimate of ordering effects. All possible configurations of atoms in the supercell were examined to find the one lowest in energy. Although we found two new ground states at different concentrations, presented in Fig.(6.5) and (6.6), they are not necessarily the true ground states, because of our use of relatively small supercells. They should nevertheless give a good estimate of the maximal ordering energy because there are no experimentally found ordered structures in Ru-rich MoRu.

The results for the mixing enthalpy of all the ordered structures can be seen in Fig.(6.7). It can be seen that even though there are some slightly lowering of the mixing enthalpy by ordering, there is still a big discrepancy between our values and the experimental values. The calculated mixing enthalpy is at least 4mRy away from the experimental curve at every point.

The results of the investigation of the MoRu alloy system is thus that it seems to be impossible to reconcile theoretical and experimental values, quite independent of which theoretical method one uses. Although it is possible to get quite close to the experimental curve by using the \textit{ab initio} isostructural mixing enthalpy with the CALPHAD structural energy difference, there is no obvious reason for using this method. One can also find that no reasonable (non-negative) value of the Mo
6.4 Continued theoretical investigations of the MoRu system

Figure 6.6. A 24 atom ground state structure found in the ground state search using the GPM interactions.

Figure 6.7. The mixing enthalpy for both the random as well as all the ordered and partially ordered structures mentioned in the thesis. Although ordering brings the experimental curve and the theoretical values into better agreement, the discrepancy is still very big, with at least 4mRy between the two curves at every point.
hcp-bcc structural energy difference can bring the experimental and theoretical curves to coincide in the dilute limit. Another point to make is the slightly odd curvature of the experimental curve. These points, together with big experimental difficulties, might suggest that the experimental results are questionable, and that an independent experimental measurement is very interesting, both with regards to the mixing enthalpy, but also to the discussion about the discrepancy between the \textit{ab initio} and CALPHAD values of the structural energy difference for some elements.
Chapter 7

Computational Magnetism

Magnetism is a phenomenon that can be present in nearly every form of matter. There are magnetic atoms and ions, there are magnetic ions and atoms in otherwise nonmagnetic lattices, there are magnetic semi-conductors, and of course magnetic metals, just to mention a few systems where magnetism is of importance. One of the big divisions that are possible to make, is between localized and itinerant magnetism. Localized magnetism is when the magnetic electrons are localized at some nuclei and one can calculate properties with this assumption. In metals on the other hand, the magnetic electrons are itinerant, which means that they move about in the lattice and are not localized. This creates problems from a computational aspect, since the concept of a local moment is very appealing, both from a computational and a conceptual point of view.

In many cases, one can introduce a local moment in spite of the itinerancy of the electrons. This is because of the two time scales in the problem. The first one is the time scale given by the electron hopping. This determines the instantaneous moment on a site, which fluctuates rapidly. The other time scale is that of the expectation value of the moment at the site. This is a much slower time scale, and makes it possible to introduce a local moment variable [89]. This is usually called the adiabatic principle.

It is also possible to further divide the field into the problem of ground state magnetism and magnetism of excited states. Another division could be made between theoretical and computational (not to talk about experimental) work. To define my research area, we finally end up in: calculations of ground state properties of itinerant electron systems where the magnetism is treated as local moments. This is what I will talk about in this chapter. I start with a small introduction to magnetism in general, continue with a discussion about magnetic ordering, and then present my own research.

For a deeper discussion of the subject, I refer to a book by Yosida [127] and, for itinerant magnetism and general solid state physics with any relation to magnetism, a book by Kübler [128].
7.1 Basic facts

That magnetism is a purely quantum mechanical phenomenon was discovered already in the 30s by Bohr and van Leeuwen, who showed that a classical partition function based on the Hamiltonian of electrons in a magnetic field does not depend on the magnetic field, and therefore:

\[ M = k_B T \frac{\partial}{\partial H} \ln Z = 0, \]  

(7.1)

where \( M \) is the magnetization, \( H \) the magnetic field, \( T \) the temperature, \( k_B \) Boltzmann’s constant, and \( Z \) the partition function. In classical physics, there is no magnetism.

With the formulation of quantum mechanics, came the notion of spin, which is the intrinsic angular momentum of a particle. The interaction of the spin with a magnetic field \( H \) is given by

\[ \Delta E_{\text{magn.}} = -\mathbf{m} \cdot \mathbf{H}, \]  

(7.2)

where \( \mathbf{m} = g_0 \frac{e}{2m} \mathbf{s} \). Here \( c \) is the speed of light, \( m \) is the electron mass, \( e \) is the electron charge, \( \hbar \) is Planck’s constant \( h \) divided by \( 2\pi \) and \( \mathbf{s} \) the spin. One of the great triumphs of the relativistic Dirac equation was to predict the value of \( g_0 \) to be \( 2(1 + \frac{\alpha^2}{\pi} + O(\alpha^4)) \), where \( \alpha = \frac{e^2}{\hbar c} \).

One might expect that magnetic interactions arise from dipole-dipole interactions between the magnetic moments, but the fact is that magnetic interactions are largely effects of electrostatic interactions. To see this, we can consider a Hydrogen molecule with the Hamiltonian:

\[ H = \frac{\mathbf{p}_1^2 + \mathbf{p}_2^2}{2m} + e^2 \left( \frac{1}{R} + \frac{1}{r_{12}} - \frac{1}{r_{a1}} - \frac{1}{r_{a2}} - \frac{1}{r_{b1}} - \frac{1}{r_{b2}} \right), \]  

(7.3)

where \( \mathbf{p}_i \) is the electron momentum operator, \( m \) and \( e \) the electron mass and charge respectively, and \( r_{\alpha\beta} \) is the distance between particles \( \alpha \) and \( \beta \), where 1,2 denotes electrons and \( a \) and \( b \) the protons. This Hamiltonian does not depend on the spin-variables explicitly, so we can write the wave function for the electrons as a product of a spatial (\( \phi \)) and a spin (\( \chi \)) wave function:

\[ \Psi(r_1\sigma_1, r_2\sigma_2) = \phi(r_1, r_2)\chi(\sigma_1, \sigma_2), \]  

(7.4)

where \( \sigma \) is the spin projection along some axis. According to the Pauli principle [66], the total wave function for fermions (among which electrons are) must be anti-symmetric under exchange of two particles. This means that for a symmetric spin function, the spatial wave function must be anti-symmetric, and vice versa. Now, the addition rules for two spin \( \frac{1}{2} \) particles give four spin wave functions for the system in terms of the two electrons [66]:

\[ \chi_s = \frac{1}{\sqrt{2}} ( |\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle), \]  

(7.5)
and

\[ \chi_t = \frac{1}{\sqrt{2}} (|\uparrow\uparrow> + |\downarrow\downarrow>) \]  

(7.6)

where \(|\uparrow>\) means that the spin is pointing up along the quantization axis and \(|\downarrow>\) that it is pointing down. It can be seen that \(\chi_s\), the singlet state, is anti-symmetric with respect to electron exchange, while the states \(\chi_t\), the triplet states, are all symmetric. We now denote the symmetric spatial wave function \(\phi_s\) and the anti-symmetric wave function \(\phi_a\), and assume that the hydrogen atoms are far from each other, so that the Heitler-London approximation [129] of the wave function can be used:

\[ \phi_s(r_1, r_2) = C_1 (\phi(r_a_1)\phi(r_b_2) + \phi(r_a_2)\phi(r_b_1)), \]  

(7.7)

and

\[ \phi_a(r_1, r_2) = C_2 (\phi(r_a_1)\phi(r_b_2) - \phi(r_a_2)\phi(r_b_1)), \]  

(7.8)

where \(\phi(r_{ai})\) is the normalized hydrogen atom wave function of the \(i\)th electron and the \(\alpha\)th nucleus, and the \(C_i\) are normalization factors.

The energies for the two different states are now

\[ E_{\uparrow\uparrow}(r) = \int \phi_s^*(r_1, r_2) H \phi_s(r_1, r_2) dr_1 dr_2 \]  

(7.9)

and

\[ E_{\uparrow\downarrow}(r) = \int \phi_a^*(r_1, r_2) H \phi_a(r_1, r_2) dr_1 dr_2, \]  

(7.10)

which gives, on substitution of the wave functions

\[ E_{\uparrow\uparrow}(r) = C_2 \sqrt{2} (A(r) - B(r)) \]  

(7.11)

and

\[ E_{\uparrow\downarrow}(r) = C_1 \sqrt{2} (A(r) + B(r)), \]  

(7.12)

where

\[ A(r) = \int U(r) \phi^2(r_{a_1})\phi^2(r_{b_2}) dr_1 dr_2 \]  

(7.13)

and

\[ B(r) = \int U(r) \phi(r_{a_1})\phi(r_{b_1})\phi(r_{a_2})\phi(r_{b_2}) dr_1 dr_2, \]  

(7.14)
with
\[ U(r) = e^2 \left( \frac{1}{r} + \frac{1}{r_1} - \frac{1}{r_{a2}} - \frac{1}{r_{b1}} \right). \] (7.15)

If we now let the separation of the two nuclei increase, the difference in energy between the two states becomes \( E^{\uparrow \downarrow} - E^{\uparrow \uparrow} = 2B(r) \), and for the hydrogen molecule \( B(r) \) is negative in this limit, meaning that the state with the anti-parallel spins is lower in energy than the state with parallel spins. \( B(r) \) is called the exchange energy, because it consists of the overlap of the states where the two electrons exchange positions. Since the atomic orbitals \( \phi(r_{ai}) \) are localized, \( B \) quickly goes to zero with increasing distance between the nuclei. In this way we see that magnetism is really a consequence of electrostatic interactions, the dipole-dipole energy of two magnetic moments interacting is several order of magnitudes smaller than the exchange interaction.

It should also be noted that in general, the magnetic density is a vector field, and this would introduce some problems with computational efficiency, since the sizes of matrices would increase. In both the EMTO method and the BGFM, an approximation called the Atomic Moment Approximation is made. This is an approximation where you assume that the spin direction is the same within each atomic sphere. This can be motivated by noticing that the spin density often is centered around the nuclei, and that it is almost collinear around each nuclei [128]. In this way, one can coarse grain the problem, from a big mesh of the whole vector field to a much smaller mesh consisting of only the nuclei.

### 7.2 Magnetic ordering

There are many ways for the spins to order in a material. If we only go through the transition metal series we find a remarkably large number of magnetic orderings depending on volume and structure: bcc Fe, fcc Ni, and fcc Co orders ferromagnetically, see Fig.(7.1)(a), bcc Mn, bcc Cr, and fcc Fe favour anti-ferromagnetic ordering, Fig.(7.1)(b) (although the anti-ferromagnetic ordering for both fcc Fe and bcc Cr is not the simple one depicted here), and there are many more structures, such as double layer anti-ferromagnetic solutions, spin-density waves, and spin spirals (see Fig.(7.2) and discussion below). At higher temperatures, above the ordering temperature known as the Curie temperature for ferromagnetic ordering and Néel temperature for anti-ferromagnetic ordering, the spins disorder, resulting in what is known as a paramagnetic state, Fig(7.1)(c).

In the present implementation of the EMTO method and in the BGFM implementation of the KKR-ASA method, you do not allow for anything but collinear magnetism, which includes more magnetic orderings than just the ferromagnetic ordering you might expect: the anti-ferromagnetic ordering and many other special orderings can be achieved with the help of several sublattices, where the spins point in the same directions on each sublattice, but in different directions between sublattices. Paramagnetism can also be treated reasonably well by the DLM-method discussed in section 5.1 in chapter 5. There is also another general set of
7.2 Magnetic ordering

Figure 7.1. In (a) is shown a ferromagnetic ordering, in (b) an anti-ferromagnetic ordering, and in (c) paramagnetic disorder. Here the lattice is one-dimensional, but the general idea is evident.

Figure 7.2. An incommensurate spin spiral. Only a few of the atoms have had their spins marked in the figure, but they of course all have spins. The figure is from Ref.[128].

orderings, incommensurate spin spirals, see Fig.(7.2), which can be implemented without having to resort to a vector field description of magnetism.

A spin spiral \( \mathbf{m} \) is defined by

\[
\mathbf{m}_{\tau \nu} = m_{\nu} [\cos(q \cdot \mathbf{R}_n + \phi_{\nu}) \sin \theta_{\nu}, \sin(q \cdot \mathbf{R}_n + \phi_{\nu}) \sin \theta_{\nu}, \cos \theta_{\nu}],
\]

where \( m_{\nu} \) is the magnetic moment at site \( \tau_{\nu} \), \( n \) labels the atom at \( \mathbf{R}_n \) and \( (q \cdot \mathbf{R}_n + \phi_{\nu}) \) and \( \theta_{\nu} \) are the polar and azimuthal angles, see Fig.(7.2). At a first look, this seems to destroy the periodicity of the lattice, but all atoms separated by a translation are actually equivalent. Furthermore, it was found out [130, 131, 132] that if you combined a lattice translation \( \mathbf{R}_n \) with a spin rotation around the \( z \)-axis by an angle \( q \cdot \mathbf{R}_n \), it leaves the spin spiral structure invariant, and these
symmetry operations are part of a so-called **spin-space group**. We denote these generalized translations by \{-q \cdot \mathbf{R}_n | e | \mathbf{R}_n \}, where \( e \) is a unity space rotation, and note that a spinor transform as

\[
\{ -q \cdot \mathbf{R}_n | e | \mathbf{R}_n \} \Psi(r) = \begin{pmatrix} e^{-i q \cdot \mathbf{R}_n / 2} & 0 \\ 0 & e^{i q \cdot \mathbf{R}_n / 2} \end{pmatrix} \Psi(r - \mathbf{R}_n). \tag{7.17}
\]

The spinors further commute with the Kohn-Sham Hamiltonian and obey a commutative multiplication law, thereby making them an Abelian group isomorphic to the usual translation group [133]. But this means that they have the same irreducible representation, which is the Bloch theorem. So, we therefore have the generalized Bloch theorem:

\[
\{ -q \cdot \mathbf{R}_n | e | \mathbf{R}_n \} \Psi_k(r) = e^{-ik \cdot \mathbf{R}_n} \Psi_k(r). \tag{7.18}
\]

It should also be noted that if we denote by the \( k \)-vector \( k_0 \) the Bloch function for the non-magnetic state, then Eq.(7.17) and the usual Bloch law give us, in the case of \( \theta_\nu = 0 \)

\[
\{ -q \cdot \mathbf{R}_n | e | \mathbf{R}_n \} \Psi(r) = \begin{pmatrix} e^{[-i(q/2+k_0) \cdot \mathbf{R}_n]} & 0 \\ 0 & e^{-i(-q/2+k_0) \cdot \mathbf{R}_n] \end{pmatrix} \Psi(r), \tag{7.19}
\]

which, when compared with Eq.(7.18) gives

\[
k = k_0 + \frac{1}{2} \sigma q, \tag{7.20}
\]

where \( \sigma \) is an Ising spin variable. These results now show that we can calculate spin spirals in the EMTO method and in the BGFM by transforming the structure constants according to

\[
\tilde{S}(\tau_\nu - \tau_{\nu'}, \mathbf{k}) = U(\theta_\nu, \phi_\nu) \begin{pmatrix} S(\tau_\nu - \tau_{\nu'} , k - \frac{1}{2} q) \\ 0 \end{pmatrix} \times U^+(\theta_{\nu'}, \phi_{\nu'}), \tag{7.21}
\]

where \( S \) is the Fourier transformed structure constants/slope matrix and \( U \) is the spin \( \frac{1}{2} \) rotation matrix:

\[
U(\theta_\nu, \phi_\nu) = \begin{pmatrix} \cos \frac{\theta}{2} & \sin \frac{\theta}{2} \\ -\sin \frac{\theta}{2} & \cos \frac{\theta}{2} \end{pmatrix} \begin{pmatrix} e^{i \phi_\nu / 2} & 0 \\ 0 & e^{-i \phi_{\nu'} / 2} \end{pmatrix}. \tag{7.22}
\]

The multiplication of the rotation matrices comes from the need to transform the potential function matrices to the global spin quantization axis. Instead of doing this, the whole secular equation is rotated, meaning that the potential functions become constant, but the structure constants have to be rotated instead. This has been implemented in both the EMTO method and the BGFM and is used in Papers VI, VII, and VIII.
7.3 A generalized Heisenberg approach to magnetism

A very well known and useful technique for gaining new knowledge in solid state physics, is the mapping of the ground state energetics onto some classical model. We have already seen an example of this in the case of ordering energies in alloys in terms of the GPM, where one maps the problem onto an Hamiltonian which then depends on clusters of atoms and energies of interaction of these clusters. In the field of magnetism, the classical Heisenberg model is the most used mapping. Here the energetics are mapped onto clusters of classical spins, and the effective exchange interaction between these clusters of spin. The simplest version, with just pair interactions, can be written as:

\[ E = -\sum_{ij} J_{ij}^{(2)} s_i \cdot s_j, \quad (7.23) \]

where the \( \{s_i\} \) are unit vectors and the \( J_{ij}^{(2)} \) are effective (pair) exchange interactions. Note that these effective exchange interactions do not equal the classical exchange interactions, which are always positive, but are the effects of all possible exchange interactions which have been mapped into one interaction. The validity of this expansion will not be discussed here, this is already done in Paper VI and in Ref.[89]. There are several different ways to get these exchange interactions, but they can all be divided into two classes: (i) structure inverse methods and (ii) perturbation theory methods, just as in the GPM-case. As discussed earlier in the part about the GPM, they both have their advantages and disadvantages, and I will just focus on the perturbative approach from this point on.

The effective exchange interactions \( J_{ij}^{(2)} \) (and higher order terms) can be found from the change in energy of embedding two (or more) spins in some effective medium, and rotating them an "infinitesimal" angle \( \theta \) while subtracting the energy for rotating each of the spin separately

\[ \Delta E' = \Delta E - \sum_i \delta E_i, \quad (7.24) \]

where \( \Delta E' \) is the pair interaction energy, \( \Delta E \) is the total change in energy of the rotation, and \( \delta E_i \) is the change in energy of rotating one atom at site \( i \). From our previously derived Eq.(5.22), this can be written as

\[ \Delta \tilde{E} = \frac{1}{\pi} \text{Im} \int_{-\infty}^{\infty} dE \text{ Tr } \ln \tilde{T}, \quad (7.25) \]

where

\[ \tilde{T}_{ii} = 1 \quad (7.26) \]
and

\[ \tilde{T}_{ij} = (1 + \delta P_{t gi})^{-1} \delta P_{t gij}, \quad (7.27) \]

where \( P \) is the KKR-ASA potential function, and \( g \) is the scattering path operator of the reference medium.

One way to calculate the \( J^{(2)}_{ij} \)s is to assume that we are starting from a ferromagnetic reference medium [110, 111], calculate the changes in the \( t \)-matrices from twisting them an angle \( \theta \) in the medium, and then expanding the resulting logarithm of the matrix and equate terms in the expansion for the energy change with the terms of the Heisenberg expansion in terms of the angle \( \theta \). This leads to the expression:

\[ J^{\text{FM}}_{ij} = \frac{1}{4\pi} \text{Im} \int_{-\infty}^{E_F} dE \, \text{Tr} \, \Delta_i g_{ij}^\uparrow \Delta_j g_{ji}^\uparrow, \quad (7.28) \]

where \( \Delta_i = P^\uparrow_i - P^\downarrow_i \) (where \( P^\sigma \) is the potential function), and \( g_{ij} \) is the scattering path operator.

One can also assume a disordered, DLM, medium as the reference state [134], and make the same expansions to get the exchange parameters, that now reads [105]:

\[ J^{\text{DLM}}_{ij} = \frac{1}{\pi} \text{Im} \int_{-\infty}^{E_F} dE \, \text{Tr} \, t_i - g_{ij} t_j - g_{ji}, \quad (7.29) \]

where \( t_- = \frac{1}{2} (t^\uparrow - t^\downarrow) \) and \( g \) is the coherent path operator of the DLM medium.

In Paper VI, we compared the expansions with the ferromagnetic and DLM state as reference states. The DLM state used as the reference state in this paper is not the DLM state for the self-consistent magnetic moment, but a constrained DLM state where the magnetic moment is fixed to the ground state moment. This means that we no longer use the DLM as a model of the self consistently obtained paramagnetic state, but of a disordered magnetic state with the ground state moment.

In Fig.(7.3) are shown calculations of a planar spin spiral (meaning that \( \theta = \pi/2 \)) using both direct calculations with the BGFM and energies from the Heisenberg model with exchange interactions from the magnetic force theorem with both the ferromagnetic (FM-MFT) and DLM reference states (DLM-MFT). bcc Fe, fcc Ni, and fcc Co have been studied. The fcc and bcc special points represent points in the Brillouin zone with high symmetry [128], as an example can be mentioned that the \( \Gamma \) point is at the center of the zone. For a planar spin spiral, a calculation at \( \mathbf{q} = \Gamma = (0,0,0) \) means that the spin spiral actually describes a ferromagnetic state, while a calculation at \( \mathbf{q} = X \) (for fcc) means a simple anti-ferromagnetic structure. In between these points, and at the other special points, we have true
7.3 A generalized Heisenberg approach to magnetism

Figure 7.3. Planar spin spiral energetics for bcc Fe, fcc Co, and fcc Ni directly calculated from the BGFM (filled symbols) and evaluated using the magnetic force theorem with ferromagnetic (FM-MFT, dashed lines) and disordered local moment reference states (DLM-MFT, continuous lines). Energies are measured relative to the NM energy, and the moment is fixed to the ground state moment.

Incommensurate spin spirals. In this way the planar spin spirals contain both the limits, ferromagnetic and non-collinear, that we want to investigate.

As can be seen in Fig.(7.3), the FM reference state provides a better description of the spin spiral around the ferromagnetic Γ point (if we take into account that for this reference state, the energies should be measured with respect to the FM state for a fair comparison), while the DLM reference state agrees better with direct calculations away from the Γ point. A very interesting fact here is that the FM-MFT interactions do a very bad job in reproducing the spin spirals for Fe, while for Co and Ni, both the FM-MFT and the DLM-MFT provide good agreement over the whole spectrum, except maybe for the DLM-MFT around the Γ point in Ni. An explanation to this might be that one needs many more interactions in the Heisenberg expansion for the FM-MFT in order to capture the correct behaviour of the interactions in weak ferromagnets such as Fe (meaning that both the spin-up and spin-down band has large density of states at the Fermi level). This means that the asymptotic behaviour leads to long ranged RKKY decays [135] and to a possible increase in multisite interactions. For strong ferromagnets, the interactions die out exponentially, diminishing the effect of multi-site interactions. For the DLM-MFT, the interactions always die out exponentially due to
Figure 7.4. Small $\theta$ spin spiral energetics for bcc Fe, fcc Co, and fcc Ni directly calculated from the BGFM (filled symbols) and evaluated using the magnetic force theorem with ferromagnetic (FM-MFT, dashed lines) and disordered local moment (DLM-MFT, continuous lines) reference state. Energies are measured relative to the FM energy, and the moment is fixed to the ground state moment.

A case where the FM-MFT should work very well, is for small $\theta$ spin spirals, where in our calculations we have set $\theta = \pi/10$. This is also the fact, as shown in Fig.(7.4).

The FM-MFT seems to give almost exact results for both fcc Co and Ni, while it is a bit off for Fe near the H point, where effects of the RKKY interactions can be seen. These effects are of course absent from the DLM-MFT because of its short ranged interactions. The DLM-MFT overestimates the energy of the small $\theta$ spin spirals rather much, except for fcc Co, which again seems to be quite well described by both methods.

One of the big problems of the classical Heisenberg Hamiltonian is the lack of possibility to account for longitudinal fluctuations of the moments. One way to take this into consideration is to introduce a moment size dependence of the exchange interactions and to introduce an on-site term, which couples the intrasite
exchange and the intersite exchange:

\[ E(\{s_i\}, \{m_i\}) = \sum_i J_i^{(0)}(m_i) - \sum_{ij} J_{ij}^{(2)}(\{s_i\}, \{m_i\}) s_i \cdot s_j. \] (7.30)

This should be an improvement to having only transverse effects. To find these on-site terms \( J^{(0)} \), it can be noticed that if one uses the DLM-MFT, the spin product vanishes, leading to:

\[ E_{\text{DLM}}(m^2) = \sum_i J_i^{(0)}(m^2), \] (7.31)

where the \( m \)-dependence is now on \( m^2 \) because of the \( m = -m \) symmetry of the DLM effective medium. This means that the \( m \)-dependence is the same as that for the DLM state itself. Furthermore it can be found that the \( m \)-dependence of the \( J_{ij}^{(2)} \)’s can be found from the CPA impurity equation from embedding two spins of moments \( m_i \) and \( m_j \) in an effective medium with net moment \( \bar{m} \):

\[ J_{ij}^{(2)}(\bar{m}, m_i, m_j) = \frac{1}{4\pi} \text{Im} \int_{-\infty}^{E_F} dE \text{Tr}(\Delta t_i(\bar{m}, m_i) g_{ij}(\bar{m}) \Delta t_j(\bar{m}, m_j) g_{ji}(\bar{m})). \] (7.32)

We can now rewrite Eq.(7.30) as

\[ E(\{s_i\}, \{m_i\}) = \sum_i J_i^{(0), \text{DLM}}(m^2) - \sum_{ij} J_{ij}^{(2)}(\bar{m}, m_i, m_j) s_i \cdot s_j. \] (7.33)

In actual calculations, \( J_i^{(0), \text{DLM}} \) and \( J_{ij}^{(2)} \) have to be parameterized as functions of \( m \).

To see how good this theory is, we again calculated the planar spin spirals for bcc Fe, fcc Ni, and fcc Co, but this time letting the moment relax to the equilibrium value instead of being fixed to the ground state value. The results are shown in Fig.(7.5).

The agreement is excellent in all cases, except possibly around the \( \Gamma \) point for Fe. In Fig.(7.6) are the relaxation energies for the spin spirals, defined as the difference in energy between the spin spirals with equilibrium moments and the ones with moments fixed to the ground state moments. The agreement is again good, especially for Ni and Co, while for Fe there are some problems with the path between the \( N \) and \( \Gamma \) points. This is of course expected, since for Fe hybridization effects are important and they depend explicitly on \( q \), something that the reference states obviously can not capture. It is quite remarkable how the interactions derived from the DLM state can capture the energetics for the ferromagnetic state in addition to the non-collinear spin spirals. Spurred on by this success, we decided to tackle the fcc Fe-problem.
Figure 7.5. Relaxation of the magnetic moment of planar spin spirals in fcc Ni, fcc Co, and bcc Fe. Shown are both the results of direct calculation via the BGFM (open circles) and evaluation from the $m$-dependent magnetic force theorem approach.

Figure 7.6. Relaxation energy of planar spin spirals in fcc Ni, fcc Co, and bcc Fe. Shown are both the results of direct calculation with the BGFM (open and filled symbols) and evaluation from the $m$-dependent magnetic force theorem approach (dashed lines).
7.4 Spin spirals in fcc Fe

In Paper VII we studied fcc Fe and the use of the generalized Heisenberg model for its spin spirals. The magnetic ground state structure for fcc Fe, or $\gamma$-Fe, has been one of the most challenging problems for band structure methods. fcc Fe is only stable for high temperatures, but a low temperature phase can be realized experimentally as Fe precipitates in fcc Cu. For these Fe-clusters, the magnetic ordering is a spin spiral with $q = [0, \xi_{XW}, 1]$, where $\xi_{XW} = 0.127$ [136], when the cluster radius is less than 40nm. For larger clusters there is a structural phase transformation to a periodic shear wave structure [137]. The clusters can be stabilized by alloying with Co, and with just 4% of Co, it is possible to go up to 100nm radius clusters and still keep the spin spiral structure, although $\xi_{XW}$ shifts to higher values with alloying [136].

Another spin spiral with $q = [0, 0, \xi_{ΓX}]$ with $\xi_{ΓX} = 0.5 - 0.6$ depending on volume, was found theoretically very early [138, 139, 140, 141, 142], but it was only recently that a spin spiral with a wave vector near the experimental value was found theoretically [143, 144], and then at much lower volumes. In all these calculations one has assumed bulk geometry, which seems reasonable since the number of Fe atoms is quite big: $10^5 - 10^7$. The other common approximation is the use of local or semi-local exchange-correlation functionals, and this might be one of the reasons for the failure of reproducing experimental results.

In Fig.(7.7) are shown calculations with the BGFM of a number of different magnetic structures. Except for the non-magnetic and the ferromagnetic curve (showing the typical double minima structure), an anti-ferromagnetic curve (denoted by X for the corresponding special point for planar spin spirals), a DLM curve, and the two spin spirals denoted by $q_{XW}$ and $q_{ΓX}$ respectively can be seen. Furthermore is shown calculations for a number of magnetic orderings, which are supercells of $2n$ (100) layers with the spin arranged as $\uparrow \ldots \uparrow \downarrow \ldots \downarrow$ where $n = 1$ is the anti-ferromagnetic structure and $n = 2$ is a double-layer anti-ferromagnetic structure. Lastly, the $2k$ and $3k$ structures are given by

$$\sigma_j = \frac{1}{\sqrt{2}} (e^{i q_1 \cdot r_j}, e^{i q_2 \cdot r_j}, 0)$$  \hspace{1cm} (7.34)

and

$$\sigma_j = \frac{1}{\sqrt{3}} (e^{i q_1 \cdot r_j}, e^{i q_2 \cdot r_j}, e^{i q_3 \cdot r_j})$$  \hspace{1cm} (7.35)

respectively, where $\{q\}$ are the inequivalent members of the $<100>$ star in the fcc Brillouin zone. As can be seen in the figure, there are many competing structures within a very narrow energy range. Especially for low volumes, the ground state structure cannot be discernible by mere observation from the diagram. I will leave further discussion about the sequence of ground states to Paper VII, and instead concentrate on the spin spirals.
Figure 7.7. Total energies vs. volume, with the energies measured relative to the energy of non-magnetic $\gamma$-Fe at the lattice parameter of 6.78 a.u. Bars at the top indicate the corresponding ground state structure amongst those considered.

Figure 7.8. The upper and lower panels show the moments and the total energy respectively, as a function of the spin spiral wave vector. The numbers attached to curves in the lower panel indicate the corresponding lattice parameter at which the spectrum is calculated. In the upper panel these labels are not shown since the moment increases monotonically with volume for all $q$ vectors. The inset provides a close up of the spectrum in the low volume limit.
In Fig.(7.8) are shown direct calculations of the planar spin spirals as a function of moment and of volume. One can see that the spin spiral \( q_{XW} \) is stable for low volumes and moments, while the spin spiral \( q_{\Gamma X} \) is stable at higher volumes and moments. Now, we calculate the spin spirals for fixed moments, both with the BGFM and with with the Heisenberg model with both FM and DLM interactions, just as described above for bcc Fe, fcc Ni, and fcc Co. We also calculate the spin spirals directly with the force theorem without the Heisenberg expansion by doing one calculation with the potentials from either the ferromagnetic or anti-ferromagnetic solution and the new spin spiral structure. The results can be seen in Fig.(7.9).

It is clear that for the low moment case, both the FM-MFT and the DLM-MFT give qualitatively good agreement with the calculated results, although the FM-MFT is quantitatively off. As the moment increases, the splitting around the X point becomes smaller, until the X point becomes the lowest point, which is very different from the calculations, where the minima to the left of the X point moves toward the \( \Gamma \) point, and then the \( \Gamma \) point stabilizes. The DLM interactions instead show a flattening of the spectrum after which the \( \Gamma \) point becomes stable. The FM-MFT curve, lastly, shows a very pronounced minima around the X point before eventually making the \( \Gamma \) point stable at the high moment limit. Both Heisenberg expansions fail to produce the intermediate moment \( q_{\Gamma X} \) spin spiral, while predicting the low moment \( q_{XW} \) in agreement with calculations.

If we assume that the force theorem is correct for this system, the other pos-
Possible reason for this failure is the expansion in orders of $\theta$. To investigate this, force theorem calculations without the small $\theta$ expansion were made. As can be seen in Fig. (7.9), these agree very well with the directly calculated results with both the ferromagnetic and the anti-ferromagnetic structures as reference states. The failure thus lies in the small $\theta$ expansion, which is not so surprising since the $q_{\Gamma X}$ spin spiral is stabilized by a hybridization gap at the Fermi level and the symmetry of the spin spiral. When doing force theorem calculations without the small $\theta$ expansion, this hybridization can be captured since one uses the full Green’s function. But when doing the small $\theta$ expansion, this feature is removed by the expansion in terms of powers of the effective interaction parameters, which have been obtained from a specific reference state.

We have also calculated the on-site exchange interaction $J^{(0)}$ for fcc Fe at different volumes, since this is needed for the generalized, $m$-dependent Heisenberg model, together with the $m$-dependent bilinear $J^{(2)}$ interactions. The results can be seen in Fig. (7.10) and show a pronounced change in the on-site term as a function of volume. For low volumes, the on-site term is monotonically rising as a function of moment, while for larger volumes it shows a deep minima for moments at around $2 \mu_B$. The intersite term, on the other hand, does not change much with volume. This means that the change of volume enters the generalized Heisenberg model mainly through the on-site term for fcc Fe, and this means that fixed moment spin spirals should be quite independent of volume, when the energy is measured from the DLM state at each volume. This can also be seen in Fig. (7.11), where are shown spin spirals with both the moment relaxed, and with

Figure 7.10. Left panel shows the intrasite exchange interactions used in the generalized Heisenberg model. Shown on the right hand panel are the (bilinear) intersite exchange interactions.
7.5 An investigation of magnetic structures of fcc FeNi alloys

Fe is one of the most used materials in the world. It and its alloys are used in the building of houses, railroads, and ships, just to mention some obvious application. As have already been shown above, pure Fe is in itself very fascinating, with a multitude of different magnetic structures for the fcc phase, although Fe is stabilized in the bcc phase at room temperature. When alloying Fe with other elements, things become even more complicated. The alloying may stabilize Fe in the bcc or fcc phase, depending on material and composition, and there has

Figure 7.11. Upper panels show spin spirals with relaxed moments for two different lattice parameters. Bottom panels show the magnetization energy of fixed moment spin spirals with the intrasite exchange energy subtracted.

fixed moment calculations with the intrasite energy removed.

The equilibrium spin spirals (in the top two panels) look very different for the two volumes, but the underlying behaviour of the spin ordering is very similar for the two cases, as can be seen from the lower panels. This means that there might be many different behaviours of fcc Fe, given by differences in the basis set used, exchange correlation functional used etc., even if the part of the energetics that determines moment orientation is roughly the same.

7.5 An investigation of magnetic structures of fcc FeNi alloys
recently been a great deal of research on how magnetism in the alloys strongly influence the thermodynamic properties, phase stabilities, and elastic properties of the materials [145, 146, 147].

One of the most interesting effects is the so-called Invar-effect, which is observed in FeNi alloys. This was noted already 1897 by Guillaume [148], and consists of a vanishing of the thermal expansion coefficient of FeNi steels at Ni concentrations around 35%, the alloy does not expand when heated. In recent years theoretical as well as experimental communities have expressed an increased interest in the problem [149, 150, 151, 152, 153, 154, 155, 156, 157], because of new suggestions of the origin of the Invar effect in the FeNi system related to an observation of noncollinear magnetic structures in the alloy [158].

Earlier attempts at doing systematic studies of FeNi alloys have been made [149, 159, 160, 161, 162, 163, 164, 165], but always considering only collinear magnetic structures. Investigations of the alloy at a Ni concentration of 35%, with the use of a supercell method, have shown that noncollinear structures indeed seem to exist in the alloy [166]. Furthermore, van Schilfgaarde et al. [158] discovered a continuous transition from a ferromagnetic high-moment state at large volumes, to increasingly noncollinear disordered structures at smaller volumes, also using a supercell method. Investigations have shown that there exists an anomalous behaviour of the exchange parameters for certain volumes and electron concentrations [167, 150], and local chemical environment effects have also been studied [151]. Nevertheless, no systematic study has yet been made for the FeNi alloys, where noncollinear magnetic states have been included.

Another problem is that for fcc Fe, the Generalized Gradient Approximation (GGA) is assumed to be the most accurate approximation for the exchange-correlation potential, but most of the studies on the FeNi alloys have been made using the Local Spin Density Approximation (LSDA). Therefore, it was of some importance to perform an exhaustive study of FeNi alloys using the GGA, and this was done in Paper VIII, where we have investigated the FeNi alloys from pure Fe to alloys with a Ni concentration of 50%.

In Figs. (7.12) and (7.13) are shown the spin spiral spectra for two concentrations of Ni, in (7.12) 10% and in (7.13) 36%. The calculations are here done with the BGFM, but the spin spiral spectra calculated with the EMTO method show the same trends, if one takes into account the small shift in volume that the EMTO method introduces. As can be seen in Fig. (7.12), the onset of magnetism starts at a Wigner-Seitz radius around 2.50 a.u. at the \( \mathbf{q} = \mathbf{q}_{\Gamma_X} \) and \( \mathbf{q} = \mathbf{q}_{XW} \) spin spirals discussed in the section about fcc Fe above. The spin spiral minima at \( \mathbf{q}_{XW} \) is not so close to the \( \mathbf{q}_{\Gamma_X} \) spin spiral for the alloys as for pure fcc Fe, though. Otherwise the same trend can be seen as in fcc Fe, with the ferromagnetic \( \Gamma \) point stabilizing with increasing volume. In (7.13) the spectrum is quite different, the \( \Gamma \) point becomes stable at much lower volumes, and the \( \mathbf{q}_{XW} \) spin spiral has disappeared, or rather has been raised in energy with respect to the \( \mathbf{W} \) point. These two spectra show the general trend when one passes from pure Fe to an alloy with a Ni concentration of 50%. At all concentrations there is a flattening
Figure 7.12. Calculations of the spin spiral spectrum of the FeNi alloy with an Ni concentration of 10%. SWS denotes the Wigner-Seitz radius.

Figure 7.13. Calculations of the spin spiral spectrum of the FeNi alloy with an Ni concentration of 36%. SWS denotes the Wigner-Seitz radius.
Figure 7.14. Total energy calculations of different magnetic structures for an FeNi alloy with 10% Ni. SWS denotes the Wigner-Seitz radius. The inset shows the $\mathbf{q}$ vector of the spin spiral and the moment of the alloy components in the spin spiral structure as functions of volume.

of the $\mathbf{q}_{\text{X}}$ minimum with increasing volumes, which stabilizes the ferromagnetic solution at different volumes depending on the Ni concentration. The $\mathbf{q}_{\text{XW}}$ spin spiral also moves up in energy with respect to the $\mathbf{q}_{\text{X}}$ minima with increasing Ni concentration.

In Figs. (7.14) and (7.15) are presented total energy calculations for some of the different magnetic structures mentioned above when fcc Fe was discussed. The DLMX/Y structures are just DLM states with different concentrations of the two atom species used (see discussion above about the DLM-method). DLM50/50 is a paramagnetic state with net moment zero, while all the other DLMX/Y have a net moment coming from the fact that there is a concentration of X% spin-up atoms and Y% spin-down atoms. The calculations have been performed with the EMTO-FCD method. The general trend is quite clear: While in pure fcc Fe there are many competing magnetic structures, alloying with Ni tends to stabilize the ferromagnetic solution. Already at Ni concentration of 10%, the anti-ferromagnetic solutions no longer appear as the structure with lowest energy for any volume, and although the $\mathbf{q}_{\text{X}}$ spin spiral is the ground state structure at low volumes, it is never the global ground state structure. This is instead always the ferromagnetic solution, which is stabilized at lower volumes with increasing Ni concentration. At first sight, this is a little depressing, since no evident connection to the Invar effect can be found among these magnetic phase transitions, but in all these calculations we have neglected local environment effects, which are known to be important for
7.5 An investigation of magnetic structures of fcc FeNi alloys

![Graph showing energy calculations for different magnetic structures of FeNi alloy.]

**Figure 7.15.** Total energy calculations of different magnetic structures for an FeNi alloy with 36\% Ni. SWS denotes the Wigner-Seitz radius. The inset shows the \( q \) vector of the spin spiral and the moment of the alloy components in the spin spiral structure as functions of volume.

...the system according to the earlier discussion.

In Fig.(7.16) is therefore presented calculations using the PAW method with a 64 atom SQS supercell of both the ferromagnetic structure and what is called a spin-flip structure. This is just calculations for the same supercell as above, but with the spin flipped on an Fe atom with many (here 9) nearest neighbours being Fe. It has recently been shown [168] that this spin-flip transition occurs at sites with a large number of Fe atoms, due to the anti-ferromagnetic coupling of Fe nearest neighbour atoms to other Fe atoms. In Fig.(7.16) the spin-flip transition occurs at a Wigner-Seitz radius of 2.62 a.u., while the equilibrium volume for the Invar alloy Fe\(_{0.66}\)Ni\(_{0.35}\) is around 2.65 a.u.. If one notices that the calculated transition is seen for an Fe atom with 9 nearest neighbours being Fe, it can be assumed that for an atom with 12 nearest neighbours being Fe, the transition volume would be even higher, perhaps around the equilibrium volume. This would then mean that this spin-flip transition might participate in the Invar behaviour.

A summary of the magnetic phase transitions in the Invar alloy is thus that all transitions occur at much lower volumes than the ferromagnetic ground state volume, except the spin-flip transition, which is predicted to occur somewhere around this equilibrium volume, and which must therefore be taken into account in models for the Invar behaviour.
Figure 7.16. Calculations of the ferromagnetic structure and the spin-flip structure (see text) for the Fe$_{0.65}$Ni$_{0.35}$ alloy.

7.6 Quantum Corrals done perturbatively

I will end the thesis with a small discussion on perturbative approaches to calculations of noncollinear order in quantum corrals. This project was started quite some time ago, but everything that could go wrong went wrong, and then it was time to write this thesis. This meant that I did not have time to follow the project to conclusion, but nevertheless I think that it have been to much help for me personally in understanding many things better, and I also spent very much time writing computer codes for the project, so I could not just leave it out of the thesis. Therefore a small introduction to the field of quantum corrals and the project will be presented here, although there is not yet an article to accompany it.

Quantum corrals are fascinating structures, which consist of atoms positioned in a geometrical pattern on a noble metal (111) surface. They are built atom by atom using scanning tunneling microscopes (STM), which can then be used to study the properties of the corral as well.

The corrals exhibit standing-wave patterns of electrons, and the first idea was to use the corrals to study ”quantum chaos” [169, 170, 171, 172]. Unfortunately, the walls leaked too much for the electrons to bounce around long enough to detect any chaotic effects [173]. In 2000, Manoharan et al. [174] performed an experiment on an elliptic quantum corral, where a ”quantum mirage” of a Co atom at one of the focus points of the ellipse was seen when a Co atom was placed at the other
focus point. The image for $dI/dV$ shows an uncanny resemblance to the wave-pattern in mercury, when one drops mercury into one of the focus points, see Fig. (7.17).

The reason for this behaviour is the presence of Shockley surface states [176] on the noble metal surfaces. On these surfaces, the Fermi energy is placed in a band gap for electrons propagating normal to the surface. This leads to exponentially decaying solutions both into the bulk and into the vacuum, and creates a two-dimensional electron gas at the surface. The gas can often be treated with very simple quantum mechanical models [177, 178], and much research has been done, especially with regards to Kondo physics [179, 180, 181]. There has also been attempts to do ab initio calculations of quantum corrals [182, 183], with in general excellent results.

The problems with performing ab initio calculations for quantum corrals is the very long computational time that is needed, especially if one would want to do big supercell calculations. Even with the help of the force theorem, and perturbative approaches to the problem, one has so far had to diagonalize very big matrices, which makes it hard to perform exhaustive searches for quantities of interest. There has also been interest in engineering quantum corrals to achieve specified electronic properties [184], and also here the problem of finding optimized quantum corral structures appears.

Up until now, the ab initio approach has been to consider the quantum corral as
a perturbation on the surface, and then solve the Dyson equation for the scattering path operator for these sites and selected empty sites. Except for the problem of choosing interesting empty sites, this approach involves the inversion of a large matrix, which makes exhaustive searches of, for example spin structures, very time consuming.

Another method would be to write Eq. (7.25) as

\[ \Delta \tilde{E} = \frac{1}{\pi} \text{Im} \int_{-\infty}^{E_p} dE \ln \det ||\tilde{T}||, \tag{7.36} \]

instead, where \( T \) is defined in Eqs. (7.26) and (7.27). Here one can use matrix operations and properties of the determinant to significantly simplify the problem. The determinant can be calculated very fast, especially if one notices that the quantities needed to evaluate Eq. (7.36) is the perturbed potentials, which are generated as input parameters, and the scattering path operators \( g_{ij} \) for all perturbed sites. These \( g_{ij} \)s can be calculated once and for all for a large zone including the interesting sites and then stored, making the evaluation of Eq. (7.36) almost instantaneous for changes at these sites. Combined with numerical optimization routines, this is an excellent tool for exhaustive searches of spin configurations in quantum corrals.

Another way to deal with the \( g_{ij} \)s is to note that they are obtained from a Fourier transform of the scattering path operator in \( \mathbf{k} \)-space:

\[ g_{ij}(E) = \frac{1}{V_{BZ}} \int_{BZ} e^{-i(\mathbf{r}_i - \mathbf{r}_j) \cdot \mathbf{k}} g(\mathbf{k}, E) d\mathbf{k}. \tag{7.37} \]

From this equation, it can be seen that it is possible to separate out the "phase" \( e^{-i(\mathbf{r}_i - \mathbf{r}_j) \cdot \mathbf{k}} \), and calculate \( g(\mathbf{k}, E) \) once and for all and store it. Then it would be very fast to calculate the \( g_{ij} \)s for any \( \mathbf{r}_{ij} \) one wants, and then evaluate Eq. (7.36), again very fast.

The problem here is to calculate \( g(\mathbf{k}, E) \) with enough accuracy. For small \( \mathbf{r}_{ij} \)s, this is not a problem, but when \( \mathbf{r}_{ij} \) becomes large, the "phase" oscillates rapidly, which makes it important to have very good accuracy in \( g(\mathbf{k}, E) \), since otherwise the integral of the product with the "phase" would give erroneous results. In Fig. (7.18) are presented calculations of the imaginary part of \( g(\mathbf{k}, E) \) for a number of different \( \mathbf{k} \)-meshes for a line through the Brillouin zone. The energy is here very close to the real axis, where the scattering path operators has most structures; for most of the energy points, the \( \mathbf{k} \)-mesh can be quite coarse without losing accuracy.

As can be seen, one needs at least 100 points on this path to capture the general behaviour of \( g(\mathbf{k}, E) \), although even then one looses some of the finer details. As a comparison can be mentioned that for a self-consistent calculation, the total energy is converged down to 0.1 mRy for some structures with \( \mathbf{k} \)-meshes equivalent to just between 10 and 20 points on this path. This makes the calculation of \( g(\mathbf{k}, E) \) rather slow for some of the energy points, and a better way of solving the problem would
Figure 7.18. The imaginary part of $g(k, E)$ calculated for an energy close to the real axis, for a path through the Brillouin zone. The number in the legends is the number of $k$ points on that path.

be to keep a reasonably good accuracy, good enough for a small range of $r_{ij}$s, and then use asymptotic forms for larger $r_{ij}$s.

The method is presently under development, but the possible fields of applications are many and diverse, including order-$N$ methods and alloy ordering problems outside of the quantum corrals.
Bibliography


Bibliography


