Electronic Transport in Strained Materials

THOMAS DZIEKAN
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Abstract

In this thesis the conductivity of strained materials has been investigated using density functional theory and a semiclassical transport theory based on the Boltzmann equation.

In transition metals trends are reproduced without adjustable parameters. The introduction of one temperature dependent cross section allowed the reproduction of resistivity trends between 10 and 1000K.

The effect of strain on transition metals in bcc and fcc structure was studied deforming the unit cell along the tetragonal deformation path. The anisotropy of the conductivity varied on wide range of the c/a-ratio. The orbitals at the Fermi level determined the principal behavior. Pairs of elements with permuted number of electrons and holes in the 4d band showed similar behavior. The concept of the tetragonal deformation was also applied on semiconductors.

The deformation of Vanadium in X/V superlattices (X=Cr, Fe, Mo) due to Hydrogen loading depends on the properties of X. It was found that counteracting effects due to the presence of Hydrogen influence the conductivity.

It is shown that a small magnetic moment of the V host reduces the hydrogen solubility. Depending on the magnitude of the tetragonal distortion of V, the hydrogen dissolution becomes favored for larger moments.

Finally, extra charge filling of the bandstructure of Cr and Mo decreases the Fermi velocity and increases the density of states at the Fermi energy.

Keywords: Conductivity, Strain, Transport, Boltzmann theory, Transition metal, Hydrogen loading, Electronic structure, Density functional theory, Bulk material, Multilayer

Thomas Dziekan, Department of Physics and Materials Science, Ångström laboratoriet, Lägerhyddsv. 1, Box 530, Uppsala University, SE-75121 Uppsala, Sweden

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for my family and friends...
List of Papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.

I  **Trends and anomalies in 3d, 4d, and 5d transition metal conductivity**  
V. Meded, T. Dziekan, P. Zahn, S. Shallcross, S. Mirbt  
*Phys. Rev. B, Accepted for publication* (2008)

II  **Piezoresistivity of Metals: Manifestation of orbital orientation**  
T. Dziekan, V. Meded, S. Mirbt, P. Zahn  
*In manuscript*

III  **Theoretical calculations of mobility enhancement in strained silicon**  
T. Dziekan, P. Zahn, V. Meded, S. Mirbt  

IV  **Conductivity variation upon hydrogen loading within Cr/V multilayers**  
T. Dziekan, P. Zahn, S. Mirbt  
*In manuscript*

V  **Influence of Vanadium spin-polarization on the dissolution of hydrogen in vanadium**  
T. Dziekan, P. Zahn, V. Meded, S. Shallcross, B. Hjörvarsson, S. Mirbt  
*Submitted to Phys. Rev. B*

VI  **Conductivity dependence on extra charge in bulk Cr and Mo**  
T. Dziekan, P. Zahn, S. Mirbt  
*In manuscript*

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1. Introduction

The transport of information and energy can be done in many ways. An elegant and clean method is using electrical current. Since more than hundred years its advantages are used extensively. First as a replacement for the steam power technologies in factories and a safer alternative for the street light formerly driven with natural gas, it changed the daily life of everybody within a few decades. Later on the broadcasting of information was improved by radio and television both based on electronic devices.

In the fiftieth of the last century semiconductors started to be used in electronic devices. They were much smaller and had a lower power consumption than the so far used electronic tubes which wasted tremendous amounts of the input energy for heating. With miniaturization and growing complexity of the semiconductor devices, soon computers solely based on integrated circuits appeared. They are the reason for an ongoing revolutionary change of our life, replacing more and more physical work by information processing.

In order to meet the requirements of our information society, it is of vital interest to improve the abilities how information is processed. A first evolutionary step forward, based on the technologies already available, is to improve the properties of the present semiconductors. One is to increase the mobility of the carriers so that they can transport information more efficiently. Another challenge is to generate and distribute electrical energy in order to be reliably available. Therefore a good microscopic knowledge about conducting materials is necessary. And, it is always exciting to find out what last but not least the physical reasons are that a certain material just reveals its properties in the way it does.

But not only that. Sometimes the motivation for the investigation of the conductivity is as simple as in paper IV, where the conductivity dependence upon hydrogen loading was investigated. It is experimentally exploited in order to define the achievement of a steady state during hydrogen loading into vanadium in multilayer systems under a certain pressure. The conductivity dependence upon hydrogen pressure is nonlinear and is depending on the composition of the host material. We could show that under certain circumstances localized states at the central vanadium sites occur influencing the global conductivity.

As a site project the influence of magnetism on the hydrogen loading into bulk vanadium is presented in paper V. It contributes in conjunction with the other work to the insight that the hydrogen uptake is to some extent influ-
enced by magnetic interactions. The last paper (VI) outlines the research on systems, which obtain extra charge. It is a nice example how important it is to thoroughly investigate the interplay between cause and effect. At a first glance the effect simulated in paper VI could help to explain the conductivity behavior in paper IV, but this is misleading. Nevertheless the conductivity changes of the former neutral bulk systems, due to small amounts of additional charge, is impressive in itself.

But before coming to the hydrogen induced change of conductivity in the second part of the result presentation the anomalous low conductivity of Mn/Tc/Re compared to other transition metals is evaluated in paper I. Here in the first place strain induced change have not been considered. But it is illustrative to learn how the conductivity is influenced by the electronic configuration and the nearest neighbour distance in the lattices of the elements in the investigated series. The concept has been extended in paper II where the 4d series elements underwent tetragonal distortions. Again it could be shown that the nearest neighbour distance or better the orbital orientation and their overlaps and the electronic configuration are mainly influencing the conductivity. In paper III the mobility enhancement of Si upon strain was calculated and analyzed. Here the methods have been successfully transferred and applied to semiconductors. We have investigated doped Si which has still a band gap in the range of ambient tetragonal distortions of its zinc-blend structure. Si in such a distorted zinc-blend structure, which is equivalent to an fcc lattice with a basis, shows the same conductivity trends as the investigated materials mentioned above around fcc.

The conductivity in all papers was computed within the semi-classical Boltzmann approach which has the advantage that the conductivity properties of the system under consideration can be explained by means of its electronic structure. The numerical methods and tools used to compute the electronic structure are proved, and their properties and shortcomings are well known. The focus of this work is on general trends due to distortion. That is why the influence of the lattice, through defects or phonons, is mainly neglected by assuming isotropic coherent scattering. Otherwise the proper description of such effects within the Boltzmann theory is done by the relaxation time, which is difficult to estimate.

The work is outlined as follows. First the basic numerical methods are briefly reviewed. They are divided into two parts, because the Boltzmann approach requires the electronic band structure as an input, the chapter 3 explains the steps and corresponding approximations in order to calculate the band structure. Thereafter, in chapter 4, a short outline of the used Boltzmann theory itself is given and the most important formulas are presented. In chapter 5 the results represented in the papers are summarized and explained. First the results of the investigation of the conductivity trends in the 3d, 4d, and 5d transition metal series together with the conductivity enhancement in strained silicon are shown. The chapter concludes with the representation of the re-
sults related to hydrogen loading. Finally, chapter 6 will give an outlook about possible future tasks.
2. Introduktion på svenska


För att kunna bemöta kraven från vårt informationssamhälle är det av yttersta vikt att förbättra vår förmåga att bearbeta information. Ett första evolutionärt steg framåt baserat på den redan existerande teknologin är att förbättra egenskaperna av dagens halvledare. Ett sätt är att höja mobiliteten av ladningsbärare så att dem kan transporterera information mera effektivt. En annan utmaning är framställningen och fördelningen av elektrisk energi på ett pålitligt sätt. Därför är en god och mikroskopiskt baserad förståelse av strömbärande material nödvändig. Och därutöver är det alltid spännande att förstå fysiken som gör att ett visst material har just de egenskaper det har.

Men inte bara det, ibland är motivationen för en undersökning av ledningsförmågan så enkel som i manuskript IV, där vi undersökte ledningsförmågans beroende av väteupptagningen. Experimentellt används detta för att definiera jämviktstillståndet vid ett givet tryck för väteupptagningen i vanadin. Ledningsförmågans beroende av vätetrycket är ickelinjärt och beror av sammansättningen av material som tar upp väte. Vi visar att detta har sin förklaring i existensen av ett lokaliserat tillstånd i de centrala vanadinskikten under speciella omständigheter.

Som sidoprojekt presenteras inverkan av magnetism på vanadins väteupptagningsförmåga i manuskript V. Tillsammans med andra arbeten bidrar detta till insikten att väteupptagningen påverkas till viss grad av magnetiska växelverkan. Den sista artikeln i avhandlingen skisserar vår forskning kring sys-

Dock innan vi kommer till den väteinducerade ändringen av ledningsförmågan i andra delen av resultatavsnittet jämför vi den anomal låga ledningsförmågan av Mn/Tc/Re med andra övergångsmetaller i artikel I. Töjningsinducerade ändringar har inte blivit undersökt i första hand men det är illustrativt att lära sig om hur ledningsförmågan påverkas av den elektroniska uppbyggnaden och avståndet till de närmaste grannarna i grundämnenas gitter av den undersökte serien. Detta koncept har utökats i artikel II där den 4d-serien av grundämnena genomgår tetragonal distorsion. Återigen kunde visas att avståndet till de närmaste grannarna eller bättre sagt deras orbitalutrirkning och överlapp och elektronisk uppbyggnad påverkar ledningsförmågan mest. I artikel III beräknades och analyserades mobilitetsökningen av Si genom töjning. Här har metoderna framgångsrikt överförts till och använts på halvledare. Vi har undersökt dopad Si som fortfarande har ett bandgapsvärde av samma slag som tetragonal distorsioner som förekommer i zinkblende-strukturen. Si i denna distorterade struktur, som är ekivalent till ett fcc-gitter med en bas, visar samma trender som de ovannämnda materialen omkring fcc.


3. Electronic structure calculation

3.1 Density functional theory

Any kind of atom contains electrons, protons and neutrons and can be specified by its atomic number, weight and so on. But how the atom interacts with its surrounding environment is almost exclusively determined by its electronic configuration. The electronic configuration, expressed in wavefunctions, can be obtained by solving the atomic Schrödinger equation. But already here one faces the problem that it is not possible to solve this equation for more than three involved particles, either protons or electrons. How is it then possible to make statements and predictions about properties of solids, which consists of an almost infinite number of atoms? This chapter will give an overview how to obtain the essential information that is needed later on as the input for the transport calculations.

In order to answer the question mentioned above, the required steps are first listed in reverse order and will be explained later in the text. To make statements why solids behave in the way they do or to calculate the conductivity with the approach we have used, one needs information about the density of (electronic) states and the electronic band structure. They can be derived from a set of electronic wavefunctions, obeying the Schrödinger equation, describing the solid. In order to keep things simple the system is considered to be time independent and non-relativistic.

A solid seen as a non-relativistic, time-independent quantum system can be described by a Schrödinger equation of the form

$$\hat{H}\Psi_s(\{r_i\}, \{R_l\}) = E_s \Psi_s(\{r_i\}, \{R_l\}).$$

(3.1)

The nuclei and electrons as the constituents of the solid are labeled with the respective coordinates $R_l$ and $r_i$. The total Hamiltonian $\hat{H}$ describes the dynamical properties of the system where all the information about the actual state, indexed by $s$, is contained in $\Psi_s$, the antisymmetric many body wavefunction. To each eigenstate of the full system belongs an energy $E_s$.

In the following the dependencies and arguments of the used functions and operators are clearly stated the first time they occur, but later on the non-ambiguous arguments may be omitted for the sake of readability.

The Hamiltonian $\hat{H}$ consists of an electronic part, an ionic part describing the nuclei and one part describing the external effects on the electrons including the interaction between the ions and the electrons,

$$\hat{H} = \hat{H}_{el} + \hat{H}_{ion} + \hat{H}_{ext}. \quad (3.2)$$
The parts of the Hamiltonian (3.2) are explicitly

\[ \hat{H}_{el} = \hat{T} + \hat{V}_{\text{int}} = -\sum_i \frac{\hbar^2}{2m_0} \nabla_i^2 + \sum_{i<j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}, \]

\[ \hat{H}_{\text{ion}} = \hat{T}_n + \hat{V}_{nn} = -\sum_l \frac{\hbar^2}{2M_l} \nabla_l^2 + \sum_{l<m} Z_l Z_m e^2 |\mathbf{R}_l - \mathbf{R}_m|, \]

\[ \hat{H}_{\text{ext}} = \hat{V}_{\text{ext}} = -\sum_{i,l} Z_l e^2 |\mathbf{r}_i - \mathbf{R}_l|. \]

In \( \hat{H}_{el} \) the first term is the kinetic energy operator for the electrons with a mass \( m_0 \) and an elementary charge \( e \), \( \hbar \) is Planck’s constant over \( 2\pi \). The second term stands for the contribution due to the electron-electron Coulomb interaction. In analogy to \( \hat{H}_{el} \) the operator \( \hat{H}_{\text{ion}} \) contains the corresponding terms for the ions, apart from the fact that each nucleus has a multiple \( Z_l \) of the elementary charge. \( M_l \) are the nuclei masses.

The solution of equation (3.1) with the Hamiltonian (3.3) describes correctly the system within the quantum theory. But this solution is not feasible. Therefore the problem must be simplified. For problems, as the here presented work, usually the following approximations are done:

- Born Oppenheimer Approximation: separated electron problem,
- Hohenberg-Kohn theorems: electronic density as main variable,
- Ansatz of Kohn-Sham: effective single electron equation,
- Local density approximation: approximated exchange-correlation energy,
- Bloch theorem: Fourier transformed Schrödinger equation,
- Pseudopotentials: Reduced number of plane waves.

Since a long time back [7] a first step is to separate the ionic cores and the electrons. The heavy ionic cores form the lattice and the light electrons ( \( M_l/m_e \approx 1800 \) ) are in the space between the ions. In addition, in the case of low temperature, the electrons usually have higher kinetic energies than the ions. That means, that the electrons follow instantaneously the ionic movement or vice versa, on the timescale in which the electrons reach a stationary state the ions do not move. So the ions can be considered as fixed.

Therefore the solution of the pure electronic system can be written as \( \psi_n = \psi_n (\{\mathbf{r}_i\}, \{\mathbf{R}_l\}) \) with the coordinate set of the nuclei \( \{\mathbf{R}_l\} \) as parameters,

\[ [\hat{H}_{el} + \hat{V}_{\text{ext}}] \psi_n = \varepsilon_n (\{\mathbf{R}_l\}) \psi_n. \]  

(3.4)

The total wavefunction for certain lattice configuration \( \{\mathbf{R}_l\} \) is then a linear combination of the complete and orthonormal set of the electronic wave functions \( \{\psi_n\} \)

\[ \Psi_s = \sum_n \chi_{sn} (\{\mathbf{R}_l\}) \psi_n (\{\mathbf{r}_i\}, \{\mathbf{R}_l\}). \]  

(3.5)

After replacing the wave function in (3.1) with the right-hand side of (3.5) the total Hamiltonian can be rearranged in such a way that the equation is divided
into one part which is merely dependent on the \{R_i\} and one which couples
the electrons and ions

\[
[H_{\text{ion}} + \varepsilon_n (\{R_i\}) - E_s] \chi_{sm} (\{R_i\}) = \sum_m \hat{O}_{nm} (\{r_i\}, \{R_i\}) \chi_{sm} (\{R_i\}). \tag{3.6}
\]

The adiabatic or Born-Oppenheimer approximation is to neglect the \(\hat{O}\) terms
which describe the energy contribution due to the interaction between the elec-
trons and the ions.

Because of the large difference between the masses of a nucleus and an
electron and the higher kinetic energy of electrons the electron distribution
will always adapt itself instantaneously to the comparable slow change of the
ionic configuration. Therefore the electrons are assumed to remain in the same
state as the ions move and the \(\hat{O}\)-terms can be neglected. It has to be mentioned
that this is only valid for low temperatures since the kinetic energy of the ions
increases with higher temperature.

In the next sections the numerical method, that is used in this work to solve
the electronic Schrödinger equation, is outlined.

3.1.1 Hohenberg-Kohn theorems

This section will provide a short overview about the basic theorems of the
density functional theory (DFT) which is an widely used method to solve the
many particle problem by providing solutions in arbitrary good approxima-
tion. The basic theorems of the DFT are found by Hohenberg and Kohn [17].
They will be presented first. Then follows the ansatz of Kohn and Sham [21],
which maps the many particle problem onto the Kohn-Sham equations. These
equations finally can be solved numerically with desired accuracy.

If one tries to describe a many particle system, like electrons, interacting
with each other, one will always obtain a set of coupled differential equations
reflecting that each particle is influenced by the others. An example for a solu-
tion of such a system is the multivariate many electron wavefunction \(\psi_n (\{r_i\})\)
that depends on the coordinates of all electrons.

Things would become much simpler if one could express a certain state of
the electronic system through a univariate function, for instance the electron
density. Since in a solid electrons are indistinguishable, the electron density
can be written as

\[
n(r) = N \int dr_2 \ldots dr_N \psi (r, r_2, \ldots, r_N)^\dagger \psi (r, r_2, \ldots, r_N)
= N \langle \psi | \delta (r - r_1) | \psi \rangle \tag{3.7}
\]

which depends only on the spatial coordinate \(r\).

Then the energy of the system \(E\) could be written as a functional \(E_{HK}[n]\) of
the electron density \(n(r)\). Dividing the energy contributions in the same way
as the Hamiltonian in (3.3) one obtains

\[ E_{HK}[n] = T[n] + E_{int}[n] + \int dr V_{ext}(r)n(r) + E_{nn} \]

(3.8)

\[ F_{HK}[n] = T[n] + E_{int}[n]. \]

The functional \( F_{HK}[n] \) contains only the energies of the interacting electrons and therefore it is also universal, which means it is the same for all kinds of electron systems.

Nevertheless, the problem of this representation is hidden in the electronic interaction \( E_{int}[n] \),

\[ E_{int} = \sum_{i<j}^N \int dr_1...dr_N \psi^*(r_1,...,r_N) \frac{e^2}{|r_i-r_j|} \psi(r_1,...,r_N). \]  

(3.9)

\( E_{int} \) contains pair densities for each \( i, j \)-integral, which can neither be neglected nor do they allow a simply one-to-one mapping of the electron density onto the state of the system.

This problem was overcome by Hohenberg and Kohn. They showed in their theorems [17] that, first, for any system of interacting particles in an external potential \( V_{ext}(r) \), the external potential is uniquely determined by the ground state particle density \( n_0(r) \) (except for a constant). And second, that the ground state energy of the system \( E_0 \) is the global minimum of the energy functional \( E_{HK}[n] \) for a given \( V_{ext} \). The electron density which minimizes the functional is the ground state electron density \( n_0(r) \).

The first theorem is proofed by contradiction to the initial assumption that two external potentials differing in more than a constant can lead to the same ground state electron density, which is not the case. The proof can be found for instance in chapter 6 of [17, 28]. The case of a degenerated ground state is included in an alternative formulation by Levy [26].

The proof of the second theorem (as for example in [17, 28]) compares the realisation of the functional \( E_{HK} \) as \( E_{HK} = \langle \psi|\hat{H}|\psi \rangle \) with the one of the unique ground state \( \psi_0 \). Its energy \( E_0 = \langle \psi_0|\hat{H}|\psi_0 \rangle \) is per definition the lowest, so the density \( n_0 \), corresponding to \( \psi_0 \), represents the density of the ground state. Any other density will result in a higher energy, apart from the case of degenerated ground states.

The pair density is formed in such a way that the corresponding single electron density minimizes \( E_{HK}[n] \).

### 3.1.2 Kohn-Sham equations

The previous section showed that the electronic ground state density, only depending on \( r \), contains equivalent information about the ground state as the wavefunction \( \psi_0 \). So far the electron density is not of much use. But with
The explanation of the Kohn-Sham equations given in this section, the importance of the electron density should become more evident\(^1\).

Kohn and Sham made the ansatz [21] that it is possible to replace the interacting many body system with an auxiliary system which contains only non-interacting particles which obey solvable independent particle equations but result in the same ground state density \(n_0(r)\). The interactions of the original system are covered by the so called exchange-correlation functional \(E_{xc}[n]\) of the density.

The Hamiltonian \(\hat{H}^{\sigma}_{KS}\) of the auxiliary system therefore consists only of a single particle kinetic operator and a spatial and spin dependent, effective local potential \(V^{\sigma}_{\text{eff}}(r)\), expressed in atomic units:

\[
\hat{H}^{\sigma}_{KS} = -\frac{1}{2} \nabla^2 + V^{\sigma}_{\text{eff}}(r),
\]

(3.10)

\[
\hat{H}^{\sigma}_{KS} \psi^{\sigma}_i(r) = \epsilon^{\sigma}_i \psi^{\sigma}_i(r).
\]

The ground state density (3.7) can now be written as a sum including each orbital \(i\) and spin \(\sigma\),

\[
n(r) = \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} |\psi^{\sigma}_i(r)|^2,
\]

(3.11)

here already the DFT extension to spin polarized systems by Barth and Hedin [38] are incorporated. The internal energy of the electrons \(E_{\text{int}}\) causing problems in the original system is now easily evaluated, because under the assumption of having independent particle the single particle densities are independent from each other and the corresponding pair density separates into a product of its two single densities:

\[
E_{\text{int}}^{\text{nonint}}[n] = \int dr_1 dr_2 n(r_1)n(r_2) \frac{n(r_1)n(r_2)}{|r_1 - r_2|}
\]

\[
= E_{\text{Hartree}}[n],
\]

(3.12)

which is nothing else than the classical Coulomb interaction energy \(E_{\text{Hartree}}\) of the electron density \(n(r)\) interacting with itself assuming that there are only local correlations in the density.

In the next step towards an expression for the effective potential \(V^{\sigma}_{\text{eff}}(r)\) the original functional \(F_{HK}\) is divided into an interacting and a non-interacting part and called \(F_{KS}\):

\[
F_{HK}[n] = T[n] + E_{\text{int}}[n],
\]

\[
F_{KS}[n] = T_s[n] + E_{\text{Hartree}}[n] + E_{xc}[n],
\]

\[
E_{KS}[n] = F_{KS}[n] + \int dr V_{\text{ext}}(r)n(r) + E_{nn}.
\]

(3.13)

\(^1\)A more detailed discussion can be found in [28].
\( T_s[n] \) represents the kinetic energy functional in the same way as \( T[n] \) does in (3.8). All kinds of many body effects are put into the term \( E_{xc} \). Subtracting \( F_{HK} \) from \( F_{KS} \) gives

\[
E_{xc}[n] = (T[n] - T_s[n]) + (E_{int}[n] - E_{Hartree}[n]).
\] (3.14)

This equations shows that \( E_{xc} \) is just the energy difference between the original interacting system and the auxiliary system of independent particles. Only if \( E_{xc} \) is known the exact ground state energy and ground state electron density can be determined. Unfortunately that is almost always not the case. But nevertheless many good approximations for \( E_{xc} \) have been found, for instance the local density approximation (LDA) and its extension the generalized gradient approximation (GGA), which will be introduced in the next section.

As in the original system, the density of the auxiliary system can only be pinned for the ground state. The energy variation of the functional with respect to the density (or the wavefunction) has to be zero

\[
\frac{\delta E_{KS}}{\delta \psi_i^{\sigma \ast}(r)} = 0,
\] (3.15)

in order for \( E_{KS} \) to be the energy minimum. The orthonormalization constraint for the wavefunction is incorporated in Lagrange multipliers, \( \varepsilon_i^{\sigma} \). The result is a Schrödinger-like equation for the effective Hamiltonian \( \hat{H}_{KS}^{\sigma} \) (3.10) from above

\[
\hat{H}_{KS}^{\sigma}\psi_i^{\sigma}(r) = \varepsilon_i^{\sigma}\psi_i^{\sigma}(r).
\] (3.16)

The potential \( V_{eff}^{\sigma}(r) \) in the Hamiltonian has the form

\[
V_{eff}^{\sigma}(r) = V_{ext}^{\sigma}(r) + V_{Hartree}^{\sigma}(r) + V_{xc}^{\sigma}(r),
\]

\[
V_{Hartree}^{\sigma}(r) = \int d\mathbf{r}_2 n^{\sigma}(\mathbf{r}_1) \frac{n^{\sigma}(\mathbf{r}_1)}{||\mathbf{r} - \mathbf{r}_1||},
\]

\[
V_{xc}^{\sigma}(r) = \frac{\delta E_{xc}}{\delta n^{\sigma}(r)}.
\] (3.17)

The potentials \( V_{Hartree} \) and \( V_{xc} \) are just the variations of the respective energy functionals with respect to the density.

Finally, the self-consistent cycle to compute the electron density is sketched. Starting from an initial guess for the electron density, one calculates the effective potential of (3.17) which is a functional of the density. Than one solves the independent particle Kohn-Sham equations (3.16), resulting in a new electron density (3.11) which is compared with the input density. If they differ one can in the simplest case use the new density as an input and run the cycle again. The procedure is repeated until input and output density coincide sufficiently.
Due to the successful ansatz of Kohn and Sham the obtained density of the independent particle system is equal to the one of an equivalent system but for interacting particles. The Hohenberg-Kohn theorems guarantee that the density is equal to the ground state density from which one can extract the ground state properties.

3.1.3 Approximations of the exchange-correlation potential

The previous sections illustrated the steps necessary to find a solution of the many body problem expressed by the Hamiltonian (3.3). The explanations ended with the Schrödinger-like Kohn-Sham equations (3.16) describing independent electrons moving in an effective potential, mimicking among others things, the interaction effects with the other electrons.

The solution of (3.16) would give the exact ground state density and energy, if the effective potential could be expressed exactly. But this is not the case. Somewhere one has to pay a tribute for the remarkable simplifications done so far. All the problems raised in the beginning of the chapter are hidden in the exchange-correlation potential $V_{xc}$. But due to the intuitive approach to the nature of the interactions it is now much easier to find approximations.

First let us take a look back to the origin of the exchange-correlation functional (3.9). The occurring pair density expresses the probability of finding one out of the $N$ electron at $r_1$ and at the same time an additional electron out of the left $N-1$ electrons at $r_2$ and is defined as in [20] as

$$n(r_1, r_2) = N(N-1) \int dr_3 \ldots dr_N |\Psi(r_1, r_2, \ldots, r_N)|^2. \quad (3.18)$$

A simple generalization of the pair density is the reduced density matrix $\gamma_2$ which necessity becomes clear in the next step,

$$\gamma_2(r_1, r_2, r'_1, r'_2) = N(N-1)/2 \int dr_3 \ldots dr_N \Psi^*(r_1, r_2, \ldots, r_N) \Psi(r'_1, r'_2, \ldots, r'_N). \quad (3.19)$$

Note, that it is not integrated over the primed arguments, nevertheless the diagonal matrix elements, where $r_i = r'_i$, should result in the pair density again. But what happens if one interchanges the unprimed arguments? Since the particles are indistinguishable, nothing should happen, but as soon spins are included, the wave functions $\Psi$ are antisymmetric and therefore will change sign under this operation. That means first of all, electrons with the same spin can not be at the same place instantaneously. But more important is that electrons of the same spin must have non-local correlations in order to obey the above result and "stay" away from each other. This effect is called the exchange or Fermi correlation.

A bit different is the influence of the charge in the pair correlation. It enters spin independent and is simply the electrostatic force which keeps the electrons away from each other. It is called the Coulomb interaction.
With the correlation effects from above in mind the pair density can be written as a product of single particle densities and a so-called correlation function \( f(\mathbf{r}_1, \mathbf{r}_2) \) including the different types of correlations and right normalization

\[
n(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2} n(\mathbf{r}_1)n(\mathbf{r}_2) \left( 1 + f(\mathbf{r}_1, \mathbf{r}_2) \right).
\] (3.20)

Single particle densities are said to be strongly correlated at points \( \mathbf{r}_i \), if \( f \to 1 \) and vice versa, they are weakly correlated or almost independent, if \( f \to 0 \). In case of non-local correlations \( f > 0 \) even for a longer distances between the \( \mathbf{r}_i \), but for local correlations \( f \approx 0 \) even if the \( \mathbf{r}_i \) are very close.

Comparing now the probability of finding an electron at \( \mathbf{r}_2 \), if there is already one at \( \mathbf{r}_2 \), \( \frac{n(\mathbf{r}_1, \mathbf{r}_2)}{n(\mathbf{r}_1)} \), with the probability of just finding one at \( \mathbf{r}_2 \) without knowing about probability at \( \mathbf{r}_1 \) gives

\[
\frac{n(\mathbf{r}_1, \mathbf{r}_2)}{n(\mathbf{r}_1)} - n(\mathbf{r}_2) = n(\mathbf{r}_2)f(\mathbf{r}_1, \mathbf{r}_2) = h_{xc}(\mathbf{r}_1, \mathbf{r}_2).
\] (3.21)

Usually, like the Fermi correlation effect shown above, the correlations reduce the electron density around \( \mathbf{r}_2 \), that is why the \( h_{xc} \) is called exchange-correlation hole. And specifically in numbers, the sum rule condition, the integration of \( h_{xc} \) over the volume, results in a charge of an electron hole,

\[
\int d\mathbf{r}_2 h_{xc}(\mathbf{r}_1, \mathbf{r}_2) = -1.
\] (3.22)

Now that we know the "origin" of the pair density one has to find an expression for the exchange correlation function. This has not been successful, apart for the uniform electron gas. That is why approximations are applied. The requirement for the approximated exchange potential is that the original density must be reproduced.

The uniform electron gas is similar to the electronic environment in a perfect metallic crystal: (almost) free electrons move in a positive ionic background. And, as already said, the exchange correlation functional is the only one available so far. So why not using it? The key features are, that the electron density and the exchange-correlation hole, which is assumed to be spherical symmetric, are varying smoothly in order to be integrable. Then one can approximate (3.14) in the local density approximations as

\[
E_{xc}^{LDA}[n] = \int d\mathbf{r} n(\mathbf{r}) \varepsilon_{xc}(n(\mathbf{r})).
\] (3.23)

The quantity \( \varepsilon_{xc}(n(\mathbf{r})) \) is the exchange-correlation energy per electron of a uniform electron gas density \( n \) at point \( \mathbf{r} \), motivated by \( h_{xc} \). The exchange correlation potential \( V_{xc}^{\sigma} \) follows from (3.23) as a variational derivative, as already mentioned above.
The GGA now extends the approximation by including the magnitude of the gradient of the local density into $\varepsilon_{xc} = \varepsilon_{xc}([n], |\nabla n|, r)$. The advantage of GGA over LDA is that it takes varying densities better into account. Among others, it corrects the LDA over-binding by lowering the exchange energy especially in atoms, but less in molecules or solids. Anyhow the GGA is used in our calculations because there is no measurable performance difference between LDA and GGA. So why not using a method which proposes improved results? There are several approaches to generalized gradient approximations. The code used in this work has the GGA of Perdew and Wang implemented [35].

3.2 Computation on solids

This section is dedicated to a brief outline of the numerical issues solving the Kohn-Sham (KS) equations (3.16) for solids. For instance the use of the translational symmetry properties of the periodic lattice, which give raise to the Bloch theorem, help to reduce the problem of solving the KS equations for the electrons in the periodic potential of the lattice ions. An implication of the Bloch theorem is the concept of eigenvalue bands (band structure) which are important for the explanation of the conductivity in the Boltzmann theory presented in chapter 4.

3.2.1 Bloch states

Although the KS equations (3.10) represent an immense simplification compared to (3.4) a further reduction is needed because the computational resources are still limiting the size of the problem.

Therefore, especially in condensed matter theory, one uses extensively all kinds of symmetries which allow to focus only on the irreducible part, that is usually much smaller than the original system under consideration.

The problem to solve in this section is the further simplification of the KS equations for the eigenstates normalized to a volume $V_0$, the spin index is suppressed for the moment,

\[
\hat{H}_{\text{eff}}(r) \psi_i(r) = \left[ -\frac{\hbar^2}{2m_e} \nabla^2 + V_{\text{eff}}(r) \right] \psi_i(r) = \epsilon_i \psi_i(r). \tag{3.24}
\]

In such a system each function can be expanded in a complete set of orthogonal plane waves by a Fourier expansion. Let us write the expansion of the eigenfunctions of (3.24) as

\[
\psi_i(r) = \sum_q c_{i,q} \frac{1}{\sqrt{V_0}} e^{iqr}, \tag{3.25}
\]

with the expansion coefficients $c_{i,q}$ dependent on the energy level $i$ and wave vector $q$. 

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The effective potential of (3.24) can be expanded in the same way. But due to the translational invariance of the lattice potential only components with wave vectors $G_m$ corresponding to sites $m$ in the reciprocal lattice give raise to a non-vanishing contribution,
\[
V_{\text{eff}}(G_m) = \frac{1}{V_{\text{cell}}} \int_{V_{\text{cell}}} d\mathbf{r} V_{\text{eff}}(\mathbf{r}) e^{-iG_m\mathbf{r}}. \tag{3.26}
\]
Note, that the volume $V_{\text{cell}}$ is that of the primitive cell, which is the smallest and not further reducible elementary unit of the lattice. A derivation of this expression can be found for instance in [1] or [28]. In the same manner the whole Hamiltonian of equation (3.24) can be expanded, if one substitutes the plane wave vectors $\mathbf{q}$ by $\mathbf{q} = \mathbf{k} + G_m$ and $\mathbf{q}' = \mathbf{k} + G_{m'}$, with $G_m$ and $G_{m'}$ being reciprocal lattice vectors representing reciprocal lattice sites $m$ and $m'$, then $\mathbf{q}$ and $\mathbf{q}'$ differ always by a reciprocal lattice vector and the Hamiltonian becomes
\[
\sum_{m'} \left[ \frac{\hbar^2}{2m_e} |\mathbf{k} + G_m|^2 \delta_{m,m'} + V_{\text{eff}}(G_m - G_{m'}) \right] c_{i,m'}(\mathbf{k}) = \varepsilon_i(\mathbf{k}) c_{i,m}(\mathbf{k}). \tag{3.27}
\]
The index $i$ labels the eigenvalues as in (3.24) but specified for a certain $\mathbf{k}$.
In equation (3.27) the Fourier expansion of the potential contains the lattice periodicity. This has consequences for the eigenfunctions which can be represented by (3.25). Because they are now restricted to wave vectors $\mathbf{q} = \mathbf{k} + G_m$, the sum is running over the reciprocal lattice sites $m$ only,
\[
\psi_{i,k}(\mathbf{r}) = \sum_m c_{i,m}(\mathbf{k}) \frac{1}{\sqrt{V_0}} e^{i(\mathbf{k}+G_m)\mathbf{r}}. \tag{3.28}
\]
If one splits the exponent and rearranges the equation one arrives at an expression that shows that the eigenfunctions of a periodic system are a product of a plane wave and a periodic lattice function:
\[
\psi_{i,k}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} \times \left[ \frac{1}{\sqrt{V_0}} \sum_m c_{i,m}(\mathbf{k}) e^{iG_m\mathbf{r}} \right]. \tag{3.29}
\]
Equation (3.28) is a representation of the Bloch theorem which maps the crystal problem with its periodic lattice onto the primitive cell of the crystal.
Nevertheless, the sums are still running over all reciprocal lattices sites $G_m$. The computational efforts can be further reduced by the following observations. At first, the plane wave states with large kinetic energy $\frac{\hbar^2}{2m_e} |\mathbf{k} + G_m|$ usually contribute less the total energy. Therefore in equations (3.27) and (3.28) the sum can be truncated beyond a sufficiently large cutoff energy. The cutoff energy depends on the system under consideration. Secondly the volume per $\mathbf{k}$-point is inverse proportional to the real space volume. Which means when the considered real space volumes become large the $\mathbf{k}$-points will be

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very close to each other. It is reasonable to assume, that the wavefunctions and eigenvalues of neighbored $k$-points will only slightly differ. That is why one can reduce the number of $k$-points in the mesh without losing too much precision. The weight coefficients $c_{i,m}$ change of course.

3.2.2 Projector augmented waves

The Bloch representation of states introduced in the last section in solids helps to reduce the computational effort for instance by setting a cutoff energy neglecting terms of high kinetic energy. A low cutoff energy can be chosen, if the periodic potential is weak and does not fluctuate too much. But as soon as the potential has deep wells or high peaks a lot of plane waves are needed to properly represent the potential in the reciprocal space. The potential curvature around an ionic core is such an example.

On the other hand, the properties of a state, scattered on a localized spherical potential, are outside the scattering region determined by an energy dependent phase shift modulo $2n\pi$. Furthermore only the valence electrons can be scattered in a solid. The electrons on lower atomic energy levels are bound closely to the core. Because of their high spatial probability distribution in the near vicinity of the core they produce an effective negative potential, which diminishes the positive core potential experienced by the electrons being more remote from the core than the inner ones. Therefore an electron, a distance $r$ away from the core, does not only experiences an potential reduced by $1/r$ but also an additional reduction due to the screening by the inner electrons.

That motivates at first to treat the weakly bound valence electrons separately from the tightly bound core electrons. The latter are considered as inert and do not influence the properties of the solid nor changed itself, which is also known as frozen core approximation. The core electrons contribute to the ionic potential and weakening it. Furthermore one can exploit the ambiguity in the scattering phase and replace the real potential by a weaker potential but with the same scattering properties.

This ideas are implemented in pseudopotential methods which treat the core and valence electrons separately and introduce smooth potentials. In this work the projector augmented waves (PAW) method developed by Blöchl and others [5, 4] has been used, which is a rather new method compared to the first pseudopotential approaches from the 1940’s. It enhances the orthogonalized plane wave (OPW) method and uses projectors and auxiliary localized functions.

Just to illustrate the principle of the PAW-method the orthogonalized plane wave (OPW) method introduced by Herring [16] is briefly presented. At first, basis functions are composed out of yet unknown functions $u_j(r)$ localized around each core $j$, where their overlap with plane wave states are subtracted
from the plane wave states itself,

\[ \chi_{q}(r) = \frac{1}{V_{\text{cell}}} \left\{ e^{i(q)(r)} - \sum_{j} \langle u_{j} | q \rangle u_{j}(r) \right\}; \quad \langle u_{j} | q \rangle = -\int d\mathbf{r} u_{j}(\mathbf{r}) e^{i\mathbf{q}\mathbf{r}}. \tag{3.30} \]

The resulting basis functions are therefore orthogonal to the localized functions. Valence states \( \psi_{lm}^{v} \) with angular momentum \( lm \) expanded in such a basis will have a smooth part \( \tilde{\psi}_{lm}^{v}(r) \) due to the plane waves in the basis and part projected onto the localized functions,

\[ \psi_{lm}^{v}(r) = \tilde{\psi}_{lm}^{v}(r) + \sum_{j} B_{lmj} u_{lmj}(r) \]

\[ B_{lmj} u_{lmj}(r) = \int d\mathbf{q} c_{lm}(\mathbf{q}) \langle u_{j} | \mathbf{q} \rangle \]

\[ |\psi_{lm}^{v}\rangle = T |\tilde{\psi}_{lm}^{v}\rangle. \tag{3.31} \]

The last equation gives the connection to the PAW method. The transformation \( T \) makes it possible to recover the full valence function \( \psi_{lm}^{v} \) from the smooth function \( \tilde{\psi}_{lm}^{v} \). Therefore a solution for the smooth wave function is sufficient. The localized functions are often assumed equal to the core states of the atom. Unfortunately the basis functions are not orthonormal.

The formalism to get the solution for the smooth function is nicely explained by the Phillips-Kleinman method \[36\]. The valence wavefunction expressed in (3.31) is placed in a Schrödinger equation with a Hamiltonian from above (3.16). Then the smooth and the local part are separated and rearranged. The result is a Schrödinger equation for the smooth valence wavefunctions \( \tilde{\psi}_{i}^{v} \)

\[ \left\{ \hat{H}_{\text{KS}} + \sum_{j} (\varepsilon_{i}^{v} - \varepsilon_{j}^{c}) |\psi_{j}^{v}\rangle \langle \psi_{j}^{c}| \right\} \tilde{\psi}_{i}^{v} = \varepsilon_{i}^{v} \tilde{\psi}_{i}^{v}. \tag{3.32} \]

The index \( i \) is a combined index and the localized core states \( \psi_{j}^{c} \) are the realisation of the localized functions \( u_{j} \) from above. The equation shows that the effective potential in the KS-Hamiltonian (3.10) is extended to a non-local potential

\[ V_{\text{PSP}} = V_{\text{eff}} + \sum_{j} (\varepsilon_{j}^{v} - \varepsilon_{j}^{c}) |\psi_{j}^{v}\rangle \langle \psi_{j}^{c}| \] \tag{3.33} \]

for the smooth valence state functions \( \tilde{\psi}_{i}^{v} \). The second term on the right hand side of (3.33) is repulsive because the difference between valence and core state energies is always positive. A stronger attractive nuclear potential leads to deeper core states so that the second term in (3.33) becomes even more repulsive\(^2\). This leads to much weaker overall pseudo-potential \( V_{\text{psp}} \) but having the drawback of being a non-local operator.

So far there is no improvement of the smooth wavefunction. But what the Phillips-Kleinman method shows is, how to write the potential. The potential

\(^2\)The effect is covered by the “cancellation theorem” of Cohen and Heine \[8\]
can now be replaced by one that causes the same scattering phase but is much smoother.

The constraints for pseudopotentials, in order to be reliably accurate and transferable on to different problems, have been defined in [15] and cited in [28] for so called norm-conserving pseudopotentials which are widely used in ab-initio codes:

- All-electron and pseudo-valence wavefunctions agree for the chosen core radius \( R_c \).
- All-electron and pseudo-valence wavefunctions agree beyond the core radius \( R_c \).
- The logarithmic derivatives of the all-electron and pseudo wavefunctions agree at \( R_c \).
- The integrated charge inside \( R_c \) for each wavefunction agrees (the actual norm conservation).
- The first energy derivative of the logarithmic derivative of the all-electron and pseudo-wavefunction agrees at \( R_c \).

The PAW method is an advanced pseudopotential method because it keeps the full all-electron wavefunction [3]. First each valence state wavefunction \( \psi \) is expanded in a basis which contains a smooth part and one which is based on muffin tin spheres. Further on, as in other pseudopotential approaches, the all electron valence state functions \( \psi \) can be expressed by a linear transformation \( T \) of the smooth wavefunction \( \tilde{\psi} \), originally seen in the OPW method,

\[
|\psi\rangle = T |\tilde{\psi}\rangle .
\]  

(3.34)

After an expansion of the all-electron valence state wavefunction \( \psi \) and the smooth wavefunction \( \tilde{\psi} \) in partial waves \( \psi_m \) respective \( \tilde{\psi}_m \) projected on the muffin tin spheres the linear transformation \( T \) of the all electron wavefunction can be expressed as

\[
|\psi\rangle = |\tilde{\psi}\rangle + \sum_m c_m \{|\psi_m\rangle - |\tilde{\psi}_m\rangle\} .
\]  

(3.35)

The linearity constraints the expansion coefficients \( c_m \) to be a projection in each sphere labeled with \( m \),

\[
c_m = \langle \tilde{p}_m |\tilde{\psi}\rangle .
\]  

(3.36)

The projections \( \langle \tilde{p}_m | \) are not uniquely defined, but if they are dual \( |\tilde{\psi}_m\rangle \), \( \langle \tilde{p}_m | \tilde{\psi}_{m'} \rangle = \delta_{mm'} \) then the expansion of the smooth function \( \sum_m |\psi_m\rangle \langle \tilde{p}_m | \tilde{\psi} \rangle \) is \( \tilde{\psi} \) itself again. Then the linear transformation can be written as

\[
T = 1 + \sum_m \{|\psi_m\rangle - |\tilde{\psi}_m\rangle\} \langle \tilde{p}_m | .
\]  

(3.37)

With the help of the linear transformation \( T \) any operator can be transformed to act on the smooth wavefunction only. From there one can derive the desired physical quantities.
3.3 VASP

For the band structure calculations the ab-initio code "Vienna Ab-initio Simulation Package" has been used. The basic methods are explained in [22, 23, 9]. It is a plane wave basis density functional theory code which allows different types of pseudopotentials. All the calculations done in this work have been conducted with PAW-potentials in the GGA-approximation.

The default cutoff energy provided with the PAW-potential data was usually used. For relaxations the cutoff energy was increased to 150% of the default value. The generation of the K-point mesh in irreducible part of the Brillouin Zone for the self consistent calculations was done according to the Monkhorst-Pack scheme [32].

The partial occupancies in the structure relaxation calculations have been set with a Gaussian smearing method. Whereas the selfconsistent runs used a tetrahedron method with Blöchl corrections [6]. The principle is similar to the modified tetrahedron method explained in 4.6.

The band structures have been calculated in non-selfconsistent runs based on electron densities obtained in self consistent runs before. The k-point mesh was generated by the code used for the conductivity calculations (see section 4.6).
4. Transport theory

4.1 Introduction
The relation between an applied constant voltage $V$ and the induced current $I$ in a conductor is expressed by Ohms law

$$I = G \cdot V .$$

(4.1)

The conductance $G$ is an extensive observable dependent on the conductors geometry. Nevertheless, the intrinsic material properties are described by the version of Ohms law which relates the current density $j$ and the electrical field $E$ linearly by the conductivity tensor $\hat{\sigma}$,

$$j = \hat{\sigma} \cdot E .$$

(4.2)

There are different ways to calculate the conductivity. The very first approach is to regard electrons as free particles moving with a velocity $v$ driven by the force of the applied electrical field through the lattice as in the Drude theory. The Sommerfeld theory extends it further by regarding the velocities energy dependent with a Fermi distribution function. In the limit of the free electron gas, the conductivity is expressed as

$$\sigma = \frac{n e^2 \tau}{m},$$

(4.3)

where $n$ is the free electron density, $e$ the elementary electronic charge and $\tau$ the averaged relaxation time. In the Drude model the relaxation time stands for the average time between two subsequent collisions of an electron with the lattice ions or with defects. This collision picture is a rather simple approach and needs to be specified further for periodic structures. In the next section the relaxation time is approximated by the rate of change of the electron distribution function and through that gives a measure of how strong the electronic transport is influenced by any scattering process.

4.2 Scattering probability and relaxation time
In this section follows a short review based on [1] and [41] about the theory which leads to the equations used to calculate the conductivities in this work.

In a metallic conductor the charge carriers are the nearly free electrons in a lattice of ionic cores. In an ideal, unperturbed crystal the influence of external
fields would lead to an infinite electronic current. That is not the case in a real crystal, there the electrons are scattered at crystal defects or collective lattice excitations as phonons. So the transport properties in a crystal are greatly influenced by such perturbations.

The evolution of these perturbations compared to the equilibrium distribution of the electrons is expressed by the Boltzmann equation. The starting point is the classical distribution function \( f_k(r, t) \) for electrons in a crystal being in a Bloch state \( k \) for a given wave vector \( \mathbf{k} \) and band index \( n \). Because the next steps are using quasi classical, statistical arguments the spin index is omitted. Nevertheless, the arguments are valid if one thinks in terms of suppressed spin flip effects and considers the spin channels as independent from each other.

A further quasi classical approximation is to consider electrons as point-like objects moving on trajectories with momentum \( \hbar \mathbf{k} \). Because the electrons can be represented in Bloch states the information is obtained from the band structure \( E(k) \) (see section 3.2.1). \( \mathbf{v}_k \) defines the group velocity and \( e \) is the unsigned elementary electron charge,

\[
\mathbf{v}_k = \frac{\hbar}{\partial \mathbf{k}} \frac{\partial E(k)}{\partial \mathbf{k}} = \mathbf{v}_k,
\]

\[
\mathbf{h} \mathbf{k} = -e \mathbf{E}(r) = \mathbf{F}(r, \mathbf{k}).
\]

Magnetic fields are not included, since the presented investigations in this work have been conducted without external magnetic fields. In addition only homogeneous, non-oscillating electric fields \( \mathbf{E}(r) = \text{const} \) have been considered.

The phase space volume is constant under the time evolution of the system according to Liouville’s theorem. In addition in a steady state the distribution function will not change in time therefore the net rate of change of the single particle distribution function is zero, but not necessarily the individual contributions

\[
\frac{d \mathbf{r}}{dt} \frac{\partial f_k}{\partial \mathbf{r}} + \frac{d \mathbf{k}}{dt} \frac{\partial f_k}{\partial \mathbf{k}} - \frac{\partial f_k}{\partial t} \bigg|_{\text{scatt}} = 0.
\]

This is a master equation which describes how diffusion, external fields and scattering processes influence the distribution function. The first term describes the diffusion due to the group velocity of the particles. This term can be neglected for electric fields, homogeneous on the length scale of the mean free path and if the mean free path is larger than the period of the crystal structure, which is the case for weak scattering. The change of the distribution function due to the external electric field \( \mathbf{E} \) is covered by the second term through \( \mathbf{k} = -\frac{e}{\hbar} \mathbf{E} \).

All contributions of scattering effects are collected in the third term. The probability of a scattering event between two \( k \)-states is given by the microscopic transition probability \( P_{kk'} \), explained in section 4.3, which allows to set
up a balance equation
\[ \left. \frac{\partial f_k}{\partial t} \right|_{\text{scatt}} = \sum_{k'} f_{k'} (1 - f_k) P_{k'k} - f_k (1 - f_{k'}) P_{kk'}. \] (4.6)

The first term on the right-hand side gives the number of particles scattered from state \( k' \) into a state \( k \), where the second term gives a measure for the reverse process. The influence of all kind of scattering processes, like defects and phonons, is parametrized by the transition probability.

The distribution function \( f_k \) of the steady state can be seen as a sum of the equilibrium distribution function \( \tilde{f}_k \) and a perturbation \( g_k \), \( f_k = \tilde{f}_k + g_k \). It is reasonable to assume that the electron distribution at equilibrium is given by the Fermi-Dirac distribution \( \tilde{f}_k = \frac{1}{\exp(\frac{E_k - \mu}{k_B T} + 1)} \). If one assumes a small perturbation of the equilibrium distribution, one can neglect the terms of quadratic and higher order in the expansion of \( f_k \). The remaining linear term is just \( g_k \) which is coupled with the external field by the vector mean free path \( \Lambda_k \),

\[ g_k = -\frac{e}{\hbar} \frac{\partial \tilde{f}_k}{\partial E} \Lambda_k E. \] (4.7)

Using the microscopic reversibility, \( P_{kk'} = P_{k'k} \), and the assumption that only elastic scattering processes occur, \( E_k = E_{k'} \), the expression for the change due to scattering (4.6) can be simplified to

\[ \left. \frac{\partial f_k}{\partial t} \right|_{\text{scatt}} = \sum_{k'} P_{kk'} (g_{k'} - g_k). \] (4.8)

Placing this expression back in the master equation (4.5) under the assumption of weak scattering, which canceled the first term in the master equation and neglecting high order terms in \( E \), one obtains the linearized Boltzmann equation

\[ v_k = \sum_{k'} P_{kk'} (\Lambda_k - \Lambda_{k'}). \] (4.9)

If one now introduces the relaxation time \( \tau_k \) as

\[ \tau_k = \left( \sum_{k'} P_{kk'} \right)^{-1}, \] (4.10)

one can write (4.9) as a coupled integral equation in order to find the mean free path,

\[ \Lambda_k = \tau_k \left( v_k + \sum_{k'} P_{kk'} \Lambda_{k'} \right). \] (4.11)

The term \( \tau_k v_k \) describes the scattering transition from state \( k \) into \( k' \) and the other term on the right hand side the reverse, the so-called ”scattering-in” to state \( k \).
The relaxation time approximation assumes that this scattering-in term can be neglected. A closer investigation of the microscopic transition probability (see section 4.3) shows that then only the symmetric part of the transition probability contributes. The neglected scattering-in term contains the so-called vertex corrections, which are represented by the antisymmetric part of the transition probability.

The relaxation time approximation is appropriate in the case of isotropic scattering. If one further neglects the \( k \)-state dependence of \( \tau \) by averaging the relaxation time over all states relaxation times \( \tau_k \) one obtains the constant relaxation time \( \tau \).

### 4.3 Microscopic transition probability

The estimation of the relaxation time requires knowledge about the transition probability \( P_{kk'} \) between the unperturbed state \( k \) and the perturbed state \( k' \). In the case of spin conserving, elastic scattering the microscopic transition probability is given by Fermi’s Golden rule

\[
P_{kk'} = 2\pi |T_{kk'}|^2 \delta (E_k - E_{k'}),
\]

(4.12)

where the scattering matrix elements \( T_{kk'} \) are the folds of the states \( k \) and \( k' \) with the perturbation potential. \( T_{kk'} \) includes all scattering processes of the whole volume. The perturbed state is in general no longer translational invariant. Under the assumption that only one type of defect exists in the system and that in a low concentration, the defect itself can be regarded as independent, a superposition of single scattering probabilities can be done

\[
P_{kk'} = 2\pi cN |T_{kk'}|^2 \delta (E_k - E_{k'}),
\]

(4.13)

where \( c \) represents the concentration of the defects in the unit cell.

It is obvious that \( P_{kk'} \) has a dependence on the angle between \( k \) and \( k' \). The influence of such dependency has been intensively studied in [41]. Because of the more qualitative character of the investigations done in the presented articles we have considered anisotropic scattering as negligible.

### 4.4 Semiclassical model and conductivity

As already mentioned in the introduction, the current density is linearly related to the applied external field by (4.2). In a quasi classical picture (4.4) the current density \( \mathbf{j} \) can be written as

\[
\mathbf{j} = \frac{e}{V} \sum_k f_k \mathbf{v}_k
\]

(4.14)
The notation of the band structure entities was introduced in section 4.2 and $V$ is the considered volume. Again the spin is omitted for simplicity but the equations are valid for each spin channel independently.

The distribution function $f_k$ of the steady state can be written as a equilibrium distribution $\hat{f}_k$ plus a perturbation $g_k$ as shown in section 4.2. There is no resulting current in the equilibrium state due to the inversion symmetry $\hat{f}_k = \hat{f}_{-k}$, that is why the equilibrium distribution term does not contribute to the current density.

In section 4.2 an explicit expression for $g_k$ has been derived (4.7). In the limit of low temperature the energy derivation of $\hat{f}_k$ becomes a delta function centered at the Fermi energy $E_F = \mu$. With that in mind and applying the constant relaxation time approximation, equation (4.14) leads to

$$ j = \frac{\tau e^2}{V} \sum_k \delta(E_k - E_F) \mathbf{v}_k \mathbf{v}_k^T. $$

(4.15)

In order to find the conductivity tensor $\hat{\sigma}$, one compares equation (4.15) with the general expression of equation (4.2). After rewriting the vector $\mathbf{v}_k(\mathbf{v}_k^T \mathbf{E})$ in a tensor form so that $\mathbf{E}$ can be plugged in as a vector into the matrix $\mathbf{v}_k \circ \mathbf{v}_k$, the conductivity tensor is given by

$$ \hat{\sigma} = \frac{\tau e^2}{V} \sum_k \delta(E_k - E_F) \mathbf{v}_k \circ \mathbf{v}_k. $$

(4.16)

Because of the zero temperature approximation the inverse of the conductivity tensor

$$ \hat{\rho} = \hat{\sigma}^{-1} $$

(4.17)

is also called the residual resistivity.

4.5 Fermi surface and conductivity tensor

This section summarizes the numerical implementation of the conductivity calculation. The zero temperature approximation introduced a delta function in the expression for the conductivity tensor. That means that only $k$-states with energies in the near vicinity of Fermi surface contribute to the conductivity. That is why the volume summation of $k$ states in (4.16) can be reduced
to an integral in the Brillouin zone over a constant energy surface $E_k = E_F$,

$$
\sum_k \delta(E_k - E_F) \rightarrow \frac{V}{8\pi^3} \int_{BZ} d^3k \delta(E_k - E_F)
$$

$$
= \frac{V}{8\pi^3} \int_{E_k = \text{const}} dS_k \int d\mathbf{k}_\perp \delta(E_k - E_F)
$$

$$
= \frac{V}{8\pi^3} \int_{E_k = \text{const}} dS_k \int dE_k \left( \frac{\partial \mathbf{k}_\perp}{\partial E_k} \right) \delta(E_k - E_F)
$$

$$
= \frac{V}{8\pi^3} \int_{E_k = E_F} dS_k \left( \frac{\partial \mathbf{k}_\perp}{\partial E_k} \right). \tag{4.18}
$$

The integral was performed over surface elements $dS_k$ where the $k$ component perpendicular to them was labeled with $k_\perp$. After replacing the $k_\perp$-energy gradient by the inverse of the absolute value of the group velocity $v_k$, the conductivity tensor looks like

$$
\hat{\sigma} = \tau \frac{e^2}{8\pi^3 \hbar} \oint_{E_k = E_F} dS_k \frac{v_k}{v_k} \circ \mathbf{v}_k. \tag{4.19}
$$

So far everything has been explained for an index $k$. But as defined in the beginning $k$ represents a state with wave vector $\mathbf{k}$ and a band index $n$. Because interband scattering was not allowed the conductivity of each band is calculated independently from each other and the overall conductivity tensor is just the sum of each band contribution. In the same manner the spin channels have been regarded as independent, in equation (4.19) the Fermi surface and the group velocities are spin dependent.

In the cases considered in this work, like the tetragonal strained cells, the matrix of the conductivity tensor has only diagonal elements, all off diagonal elements are zero. The non-diagonal elements of sigma vanish due to the symmetry and absence of a $\mathbf{B}$ field. The so-called conductivity in plane (CIP) is given by $\hat{\sigma}_{xx} = \hat{\sigma}_{yy}$ and the conductivity perpendicular to the plane (CPP) by $\hat{\sigma}_{zz}$. The directional dependence comes from the tensor form of the integrand,

$$
\hat{\sigma}_{xx} = \tau \frac{e^2}{8\pi^3 \hbar} \oint_{E_k = E_F} dS_k \frac{(\mathbf{e}_x v_k)^2}{v_k}. \tag{4.20}
$$

For $\hat{\sigma}_{zz}$ the integrand just changes to $(\mathbf{e}_z v_k)^2$, where $\mathbf{e}_i$ is the unit vector pointing along either $i = x$ or $i = z$ axis.
The density of states at the Fermi surface $n(E_F)$ is another observable which influences the conductivity, defined as

$$n(E_F) = \frac{1}{V} \sum_k \delta(E_k - E_F)$$

$$= \frac{1}{8\pi^3} \oint_{E_k = E_F} dS_k \frac{v_k}{v_k}.$$  (4.21)

The density at the Fermi surface more or less complements the Fermi velocity $v_k, E_k = E_F$, what becomes clear when defining the root mean square of $v_k e_i$ as

$$\langle v_i^2 \rangle = \left( \sum_k \delta(E_k - E_F) \right)^{-1} \sum_k \delta(E_k - E_F) (v_k e_i)^2$$

$$= \frac{1}{8\pi^3 \hbar} \oint_{E_k = E_F} dS_k (e_i v_k)^2.$$  (4.22)

$$= n(E_F)^{-1} \frac{\hat{\sigma}_{ii}}{e^2}. (4.23)$$

From the above equation one can see that the diagonal elements of the conductivity tensor $\hat{\sigma}_{ii}$ are proportional to both the density of states at the Fermi energy $n(E_F)$ and the root mean square of the $i$-component of the Fermi velocity $\langle v_i^2 \rangle$,

$$\hat{\sigma}_{ii} \propto n(E_F) \langle v_i^2 \rangle.$$  (4.23)

### 4.6 Tetrahedron method

Finally, the numerical interpolation of the Fermi surface in the numerical code is explained. It utilizes a modified tetrahedron method [25, 31, 40] which interpolates the Fermi surface linearly by triangles or tetragons spanned in tetrahedrons of nearest neighbor $k$-points with energies $E(k)$. In the discussion the band index is suppressed because all bands are treated independently and it is assumed that the states belong to the same band. Also the spin index is suppressed.

To each $k$-point of the Brillouin zone there is an energy $E(k)$ assigned. Four neighbored $k$-points at a time are combined to form a tetrahedron as illustrated in figure 4.1. Then the energy within the tetrahedron can be linearly interpolated with the help of the four corner energies $E(k_i), i = 1, \ldots, 4$. The
following parametrization is used

\[
\varepsilon = \begin{bmatrix}
E(k_1) - E(k_0) \\
E(k_2) - E(k_0) \\
E(k_3) - E(k_0)
\end{bmatrix} \\
K = \begin{bmatrix}
k_1 - k_0, k_2 - k_0, k_3 - k_0
\end{bmatrix}^T \\
\kappa = k_0 + K\alpha; \quad 0 \leq \alpha_i \leq 1; \quad |\alpha| \leq 1.
\] (4.24)

The last equation parametrizes all points \(\kappa(\alpha)\) within the tetrahedron through \(\alpha\). If the Fermi energy \(E_F\) can be found in the energy interval between the two corner energies, then the point \(\kappa_j(\alpha_j) \leftrightarrow E_F = E(\kappa_j)\) on edge line \(j\) is found through a linear interpolation of the energy \(E(\kappa)\) along the edge line \(j\) between its corner energies. The parametrization vectors \(\alpha_j\) along the six edge lines are, according to the labels in figure 4.1,

\[
\alpha_j \in \{ (\alpha_j, 0, 0), (0, \alpha_j, 0), (0, 0, \alpha_j) , \\
(1 - \alpha_j, \alpha_j, 0), (1 - \alpha_j, 0, \alpha_j), (0, 1 - \alpha_j, \alpha_j); 0 \leq \alpha_j \leq 1 \}.
\]

Then the linear interpolated Fermi energy on each edge line is given by

\[
E(k_0) + \alpha_j \varepsilon = E_F.\] (4.25)

The obtained three (four) \(\alpha_j\) set the \(\kappa_j\) which span the approximated Fermi surface triangle (trapezoid) within the tetrahedron.
Now it is straightforward to compute the area of the surface element $\Delta S_Q$, its center of mass $Q$ and the Fermi velocity $v_Q$. The conductivity integrals (4.20) are numerically evaluated as the following sums

$$\hat{\sigma}_{xx} = \frac{1}{8\pi^3 \hbar} \sum_Q \frac{\Delta S_Q}{v_Q} (e_x v_Q)^2.$$  \hspace{1cm} (4.26)

Again as done before in (4.20) $e_x$ changes to $e_z$ for $\hat{\sigma}_{zz}$.

It is to mention that the tetrahedron method works fine for reasonable smooth Fermi surfaces. If its topology becomes too complex the error of approximation can become large, for instance if two Fermi surface sheets cut the tetrahedron or if the surface bending, due to band hybridization, is too strong.
5. Results

The chapter presents the investigated problems and the interesting answers found so far.

First in focus is the anomalous low conductivity of the half-filled transition metals which is in contradiction to the conductivity trend of the other elements across the transition metal series. As an successor of this project the influence of strain on the conductivity of the 4d series elements is presented.

After these papers follows a representation on conductivity behavior of strained Si. Silicon is an exemplary representative of the group of semiconductors. It is explained first here, even so this work was done before the transition metal project. The wider range of c/a deformations investigated in the transition metal papers makes it more illustrative to show the general trends first. It turns out that the semiconductor Si follows the same trends in the vicinity of the fcc point as the metals. The increase in conductivity upon tensile strain is used in order to manufacture high mobility semiconductor devices like MOSFETs.

In the second part also strain induced conductivity changes are presented. This time the strain was caused by hydrogen loading which in addition can supply rather delocalized electrons which influence the global band structure. It is interesting to see how the different multilayer configurations (either Fe, Cr or Mo) interact with vanadium. The multilayer behavior is quite different to that of a bulk model mimicking the single layers in the multilayer system which is also presented.

In the papers the method used to calculate the conductivity is based on the semi-classical Boltzmann approach explained in section 4.2. It was chosen because it allows among other reasons interesting insights into the conducting mechanisms due to the separation of the electronic band structure effects and its related quantities like Fermi velocity and density of states, and effects from scattering events.

We have restricted ourselves to statements about trends because the scattering mechanism influencing the conductivity are approximated by a constant relaxation time, compare eq. (4.10). That is why absolute numbers for the conductivity cannot be expected. But as long as the systems are in conditions in which the scattering mechanisms can be considered to be more or less isotropic and lattice vibrations small can provide reliable statements about the observed trends. These are explained in terms of the electronic band struc-
ture. The obtained results which will be shown in the next sections justify the assumed approximations.

5.1 Materials under strain/deformation

In this section first the conductivity trends of the transition metals series are in focus. Later results about the conductivity behavior of silicon under lattice distortions are presented.

5.1.1 Transition metal conductivity

It is known since a long time, that bulk Mn has an unusually high resistivity [14]. The corresponding conductivity values for the transition metal series are compiled in figure 5.1. The resistivity of Mn at room temperature is about $145 \mu \Omega \text{cm}$ in comparison to $13 \mu \Omega \text{cm}$ of Cr.

The experimental data from [24] shown in figure 5.1 reveal a characteristic change of maxima and minima across each series. First there is an increase of the conductivity across the series until a first maximum for Cr/Mo/W, thereafter follows directly a minimum at the middle of the series (Mn/Tc/Re) then the conductivity increases again up to a maximum (Co, Rh, Ir) after that the conductivity drops again (Ni, Pd, Pt). The dip in the middle of the series is especially pronounced for the 3d-series and low temperatures. In 4d and 5d the corresponding dip becomes smaller. The conductivities differ by order of magnitudes depending on the temperature. Nevertheless, the conductivity trend is preserved between $10K$ and $1000K$. Below $10K$ defect scattering dominates the resistivity and the earlier mentioned phonon scattering disappears resulting in drastic change of trends.

The Boltzmann conductivity was calculated for the elements across the entire 3d, 4d and 5d series. The lattice types used for each element in the calculations are summarized in 5.1. Mn has a complex structure labeled A12 but we used a bcc structure for Mn. The nearest neighbor distance $D$ is based on experimental values. The self-consistent potential was calculated with VASP a ab-initio package explained in section 3.3. $12 \times 12 \times 12$ special k-points were used for the Brillouin zone integration. The conductivity was computed according to equation (4.26) with about 50000 k-points in the whole Brillouin zone. The discussion about the approximation of the relaxation time follows below.

In order to compare the experiment with our calculated conductivity the approximation of the relaxation time has to be done carefully. Due to the variety of defects in the metals the scattering strength in diffusive transport can be expressed as a superposition of the transmission probabilities and caused phase shift are neglected. Furthermore, at a constant temperature the defect concentration is assumed to be constant. This includes especially the scatter-
### Table 5.1: The experimental structures of 3d, 4d, and 5d transition metals.

<table>
<thead>
<tr>
<th>3d</th>
<th>Structure</th>
<th>4d</th>
<th>Structure</th>
<th>5d</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc</td>
<td>HCP</td>
<td>Y</td>
<td>HCP</td>
<td>Lu</td>
<td>HCP</td>
</tr>
<tr>
<td>Ti</td>
<td>HCP</td>
<td>Zr</td>
<td>HCP</td>
<td>Hf</td>
<td>HCP</td>
</tr>
<tr>
<td>V</td>
<td>BCC</td>
<td>Nb</td>
<td>BCC</td>
<td>Ta</td>
<td>BCC</td>
</tr>
<tr>
<td>Cr</td>
<td>BCC</td>
<td>Mo</td>
<td>BCC</td>
<td>W</td>
<td>BCC</td>
</tr>
<tr>
<td>Mn</td>
<td>A12</td>
<td>Tc</td>
<td>HCP</td>
<td>Re</td>
<td>HCP</td>
</tr>
<tr>
<td>Fe</td>
<td>BCC</td>
<td>Ru</td>
<td>HCP</td>
<td>Os</td>
<td>HCP</td>
</tr>
<tr>
<td>Co</td>
<td>HCP</td>
<td>Rh</td>
<td>FCC</td>
<td>Ir</td>
<td>FCC</td>
</tr>
<tr>
<td>Ni</td>
<td>FCC</td>
<td>Pd</td>
<td>FCC</td>
<td>Pt</td>
<td>FCC</td>
</tr>
</tbody>
</table>

*Note: BCC: body centered cubic, FCC: face centered cubic, HCP: hexagonal closed packed, see also the text.*

### Figure 5.1: The experimental conductivity of transition metals in the temperature range between 20K and 300K (data from [24])

![Conductivity Graph](image)

The constant $C$ covers the scattering cross section and the defect concentration which has been chosen to minimize the deviation of the calculated values from the experimental values for 3d, 4d, and 5d metals at the same time. The experimental room temperature results were chosen as reference.

In figure 5.2 for each series experimental and calculated results are plotted. One can see, the assumptions lead to fairly good agreement. In difference the maxima in the second half of the series are shifted downwards one element for the 4d and 5d series.

The approximation time can be related to the density of final states:

$$\frac{1}{\tau} \propto n(E_F) \cdot C . \quad (5.1)$$
Figure 5.2: The conductivity of the transition metals series. Experimental conductivities at room temperature from [39] are given for comparison. The panels present the results for the 3d series (top), 4d series (middle) and 5d series (bottom). In addition, in the lower part of each panel the used n-n distance is given.

Furthermore, the nearest neighbor distances in the lower parts of the panels of figure 5.2 let deduce that the anomalous low conductivity of Mn is caused by a volume effect. The corresponding elements in the 4d and 5d series (Tc,Re) do not show such a pronounced dip but they do neither have an especially large nearest neighbor distance compared to the elements close by. The effect can be explained by the stronger localization of the d-electrons leading to a reduced conductivity.

It was found by co-workers in earlier work [30] that the Fermi velocity has a dominant impact.

The approximation made in equation (5.1) expresses the relaxation time by the density of states (DOS) at the Fermi level. A high DOS means a short relaxation time or many scatterers. At the same time the DOS at the Fermi level in the conductivity equation is canceled out by this approximation. Therefore, under approximation (5.1), the DOS does not influence the conductivity anymore, instead it can gives some information about the scattering events. In figure 5.3 the DOS’s at the Fermi level for the elements are
Figure 5.3: DOS at E_F for 3d, 4d and 5d transition metals

plotted. Cr/Mo/W have the maximum conductivity in their corresponding series, but a DOS which is in a local minimum. The DOS for the elements at the end of each series is high but the conductivity belonging to them is comparatively small.

5.1.2 Piezoresistivity in transition metals

In paper II we have focused on the 4d and 5sp metals and their dependence on tetragonal unit cell deformation. All elements have been initially placed in a bcc lattice which has a ratio of c/a = 1. Then the c/a ratio of the lattice has been changed from values around 0.8 to about 1.6, at \( c/a = \sqrt{2} \) one arrives at the fcc lattice symmetry. It is to note that the change of the c/a ratio affects only the shape of the unit cell/supercell, the relative positions of the ions in the cell are fixed. Therefore only volume relaxations have been conducted. The assumption could be confirmed, that under ambient strain or stress, the electron gas density will only change slightly in metals, and therefore prevents strong volume changes when changing the shape. The maximal volume change considering the deformation between bcc and fcc was less than a few percent in our calculations.

To characterize the unidirectional anisotropy the ratio of the conductivity along the basal plane (current-in-plane, CIP) and perpendicular to the basal plane (current-perpendicular-to-plane, CPP) was considered. In our calculation of the conductivity we only include the effect of the coherent electronic structure and assume that concentration of scattering centres and their scattering strength is independent of the crystal distortion.
The obvious fact that in both symmetry points, bcc and fcc, the CIP should be equal to CPP could be reproduced. Nevertheless, due to some symmetry mismatch in the calculation setup the equality was not always reached directly in the fcc point. Further, considerations about the evolution of the CIP and CPP on the path from the zero limit for c/a-ratio to infinity show that there must be a third crossing point of the CIP and CPP curves. As an example the conductivity curve for vanadium is shown in figure 5.4.

![CIP and CPP conductivities for vanadium as function of c/a at the experimental atomic volume.](image)

**Figure 5.4:** CIP and CPP conductivities for vanadium as function of c/a at the experimental atomic volume.

We have not seen the third point in the c/a-range investigated. If one comes to more extreme values for c/a one has to have in mind that the potentials used in the calculation may not be designed for such extreme anisotropies and give misleading results.

The anisotropy of the conductivity varies on wide range as function of c/a-ratio with the orbitals at the Fermi level determining the principal behavior. Filling the d levels up to Pd elements with the same number of electrons and holes in the 4d band show a similar behavior. In the figures 5.5 and 5.6 one can see that for most of the elements the ratio \( \sigma' = \sigma_{CIP}/\sigma_{CPP} \) increases for c/a increasing from 1 (bcc structure) and approaching again 1 when reaching c/a = \( \sqrt{2} \) (fcc structure).

The variation of the conductivity anisotropy is most pronounced for elements with a partially filled d shell. But for the elements which have the isotropic s and p orbitals dominating no clear trend can be seen. Nevertheless the interesting fact is that in the vicinity of the fcc point for many elements the CIP and CPP show reverse behavior as on would expect from considerations for c/a asymptotic limits.
Figure 5.5: Ratio of CIP and CPP conductivity $\sigma'$ as function of $c/a$ for 4d transition metals

Figure 5.6: Ratio of CIP and CPP conductivity $\sigma'$ as function of $c/a$ for 5sp metals
5.1.3 Strained silicon

In the previous work we have found typical patterns how the CIP and the CPP changes under strain or stress. Because it is already known from experimental work that distortion of just a few tens of a percent gives raise to an increase in conductivity of Si up to 100% [33, 18], it motivated to apply the above methods onto Si in order to see if the conductivity enhancement can be described in a band structure picture.

As already said, the effect itself is known since quite a while [34] and experimental results are available [18]. Whereas others focused on the influence of phonon or defect scattering [12] and used mainly Monte-Carlo methods like in [19] we focused in our work on the influence of the electronic band structure.

The tensile strain is characterized by the relative change of the in-plane lattice constant with respect to the cubic, unstrained value

$$\frac{a - a_0}{a_0} = \frac{\Delta a}{a_0}.$$  \hspace{1cm} (5.2)

The in-plane conductivity enhancement $\hat{\sigma}_x$ gives the ratio of the values with and without strain

$$\hat{\sigma}_x = \sigma_x \left( \frac{\Delta a}{a_0} \right) / \sigma_x \left( \frac{\Delta a}{a_0} = 0 \right).$$  \hspace{1cm} (5.3)

First in figure 5.7 experimental data [18] are plotted together with the conductivity enhancements based on ab-initio calculations. The transport

![Figure 5.7: Conductivity enhancement $\hat{\sigma}_x$ for n-type Si as a function of the in-plane lattice distortion $\frac{\Delta a}{a_0}$ at T=0 depending on the carrier density $\rho$ (in units of 10^{19} cm^{-3}). Experimental data are given for comparison [18].](image-url)
was treated in the zero temperature limit according to equation (5.3) with about 109800 k-points in the irreducible part of the Brillouin zone. The self-consistent calculation was performed with $39 \times 39 \times 39$ k-points. The experimental data are measured at room temperature for a carrier concentration of about $6 \times 10^{18} cm^{-3}$, the numerical values are calculated for carrier densities between 0.6 and $12.5 \cdot 10^{19} cm^{-3}$ which are multiples of $10^{18} cm^{-3}$. Thus the results marked with triangles in figure 5.7 correspond to the carrier concentration of the experimental setup.

We have shown that a remarkable part of the conductivity enhancement comes from the change in the band structure due to strain because we have considered the relaxation time to be constant which is valid at low temperature. At higher temperatures the scattering mechanisms change. It was stated in literature [2, 37] that in the unstrained case optical phonons contribute to the intervalley scattering but when strain is applied and the energy difference between the splitted bands increases the contributions due to optical phonons diminish. This leads to a further increase of the conductivity enhancement which also explains the difference between theory and experiment in figure 5.7. The major role plays the splitting of the sixfold degenerated conduction band minimum due to strain. The increased strain causes a depletion of the lifted band minima illustrated in figure 5.8.

![Figure 5.8: Fermi surfaces dependence on tensile strain: $\Delta a/a_0 = 0$ (left), 0.34% (middle), 1.7% (right) and carrier densities of $2.5 \cdot 10^{19} cm^{-3}$ (top row) and $12.5 \cdot 10^{19} cm^{-3}$ (bottom row).](image)

Figure 5.7 illustrates the enhancement behaviour dependent upon tensile strain as described in paper III. It shows, that the strain dependent conductivity enhancement varies with the carrier density - the higher the carrier density the lower the maximum enhancement. But on the other hand below a certain carrier concentration the conductivity enhancement becomes equal for different carrier concentrations. The almost coinciding graphs for the two lowest
carrier concentration \(0.625 \times 10^{-19} \text{cm}^{-3}, 1.25 \times 10^{-19} \text{cm}^{-3}\) illustrate this behavior. The reason as explained in paper II is the non-parabolicity of the bands which causes higher total conductivities and thus lowers the relative enhancement.

In our numerical approach the tiny Fermi surface pockets in k-space were difficult to resolve, if the charge carrier concentrations was lower than in the upper row of figure 5.8. That is why carrier concentrations smaller than \(0.625 \times 10^{-19} \text{cm}^{-3}\) could not be considered within the tetrahedron method in the zero temperature limit.

Therefore an analytical model was used instead, which exploits the band structure features by parametrization. Paper III explains the construction of the model. With the help of the model we have been able to investigate small carrier concentrations and temperature dependent effects. Nevertheless, the model can be applied only to carrier concentrations less than \(2.5 \times 10^{-19} \text{cm}^{-3}\). For higher concentration the deviation of the band dispersion from parabolic behavior can not be neglected anymore. Non-parabolic bands cause the carrier concentration dependence of the conductivity enhancement already explained above. The maximum conductivity enhancement obtained with the parametrized band model is about \(\hat{\sigma} \approx 1.36\).

The obtained results can be assigned to either a low temperature or a room temperature regime. For low temperatures only the DOS at the Fermi level \(n(E_F)\) and the corresponding Fermi velocity play a role. They change contrary when the applied tensile strain is increased (see figures 5.9 and 5.10.

![Figure 5.9: Evolution of the transport density of states \(n_{\text{eff}}\) under strain at different doping levels (in units of \(10^{19} \text{cm}^{-3}\)) and temperatures](image)

The DOS \(n(E_F)\) shows a strong reduction due to the depletion of the lifted pockets and the occupation of the lowered pockets, right column in figure 5.8 illustrates the effect. But the increase of the Fermi velocities overcompensates
the DOS reduction and an increase of the conductivity enhancement dependent on strain follows (figure 5.11). In Paper III we have shown that in the room temperature regime the latter statements apply as well if one replaces the DOS and the Fermi velocity at $\varepsilon_F$ by the effective transport density of states and the effective Fermi velocity as defined in the paper. The main difference is that the transition area from occupied to unoccupied states in the Fermi-Dirac-distribution is extended. That has the effect that the DOS is smoothly lowered when tensile strain is increased. The DOS of a high carrier concentration sample shows this behavior more pronounced than at low carrier concentrations. Thus, the conductivity enhancement increases smoother the higher the temperature as shown in figure 5.11 but as long as the bands are considered to be parabolic the maximum enhancement of about 1.36 does not change and is completely determined by the effective masses. It is to mention again that the constant relaxation time approximation does not cover the change of the scattering mechanism at room temperature which causes an even stronger enhancement of about 1.7. The tensile strain reduces here the scattering due to optical phonons which are not active at low temperatures [13].

Figure 5.10: Evolution of effective Fermi velocity $\bar{v}_x$ under strain at different doping levels (in units of $10^{19} \text{cm}^{-3}$) and temperatures.
Figure 5.11: Conductivity enhancement $\hat{\sigma}_x$ for n-type Si as a function of $\frac{\Delta a}{a_0}$ for temperatures of 4K and 300K. Carrier densities are given in units of $10^{19} cm^{-3}$. 
5.2 Change of resistivity by H loading

5.2.1 Conductivity variation in Cr/V multilayers

The second part of the result chapter presents the investigations done on multilayer systems which undergo hydrogen loading. The systems have been Fe/V, Cr/V and Mo/V. In a first naive assumption about the conductivity dependency on hydrogen loading, one would consider the hydrogen atoms as defects increasing the disorder and because of that decreasing the conductivity. The conductivity of a system without hydrogen would be rather high but successively diminished with increased hydrogen uptake. The conductivity would reach a minimum for about 50% hydrogen loaded. Beyond that concentration, the conductivity would increase again until an ordered state is reached again for 100% hydrogen load. At a first glance that is indeed the case for the Mo and Cr systems as one can see in figure 5.12. The question which arises first is why not for iron? First of all the band structure based Boltzmann formalism is not suitable to describe disorder scattering. The focus was more on the yet unknown effect which lowers the conductivity in the Cr/V-system more than in the other systems.

The conductivity calculations for the empty and full load system shown in figure 5.13 give a first hint. The figure shows the resistivity which is just the inverse of the conductivity as defined in (4.17). In the further discussion we refer to resistivity rather than conductivity. The resistivity of the Fe or Cr system changes more than it does for the resistivity for Mo/V. The properties of the Mo and Fe system have already been investigated in [29]. There, among others it was pointed out that the different vanadium expansion plays

![Figure 5.12: Schematic diagram showing the measured in-plane resistivity as a function of the relative hydrogen concentration. The measurement data are taken from [10].]
an important role. Fe and Cr have smaller bcc lattice parameters than V. When growing a Fe/V or Cr/V superlattice Fe and Cr are stretched and the Mo sites are compressed compared to the respective bulk lattices. It is vice versa Mo/V. Therefore hydrogen loading causes in the Fe- or Cr-based superlattices are much larger expansion of the vanadium layers in z-direction than in Mo/V. The effect is that vanadium in Fe/V- and Cr/V-systems gets a localized $d$ states due the enlarged interlayer distance.

In paper IV it could be shown that under hydrogen loading only in Cr/V occurs a resonance in the pseudogap of the vanadium $d$ states in such a strength that it strongly influences the resistivity. The peak can be seen clearly in figure 5.14.

Figure 5.15 emphasizes the necessity of hydrogen in the system for the existence of the resonance. The Cr/V system, shown in the figure, does not contain hydrogen but has the same lattice constant as the full loaded system. There the resonance is much weaker. It is to mention that in the paramagnetic Fe setup the $d$-resonance peak can be seen, as in figure 5.16, but located below the Fermi level, not falling in a global pseudogap and overlapping energetically with the Iron $d$ continuum. The Iron $d$-states dominate the Fermi energy such that the $d$-resonance when eventually lying at the Fermi energy will not drastically alter the conductivity behaviour of the paramagnetic Fe/VH superlattice.

We concluded, that the distortion of the V layers in Mo/VH is not sufficient for a localization to appear and the spin-polarization of Fe/VH gives rise to a weakening of the $d$-resonance. In summary the large increase in resistivity for the Cr/VH system at about 50% hydrogen loading does originate from localization at the central vanadium sites along the z direction. We show that the
Figure 5.14: Site projected density of states for Cr/VH. From top to bottom we show the projection on the following layers: Cr interface, V interface, V subinterface, V center, H. The solid line marks the position of the localization.

Figure 5.15: Site projected density of states for Cr/V in the Cr/VH lattice. From top to bottom we show the projection on the following layers: Cr center, Cr interface, V interface, V center. The solid line marks the position of the localization.
hydrogen dissolution gives rise to a resonance. The resonance only exists in Cr/V based superlattices because the vanadium expansion is larger in Cr/VH than in Mo/VH and the spin-polarization of Fe/VH weakens the $d$-resonance.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Fe/VH_paramagnetic.png}
\caption{Site projected density of states for paramagnetic Fe/VH. From top to bottom we show the projection on the following layers: Fe center, Fe interface, V interface, V center. The solid line marks the position of the localization.}
\end{figure}

5.2.2 Influence of vanadium spin-polarization

In paper IV we have performed calculations of the hydrogen dissolution in V. The result is that for small magnetic moments the solubility is decreased. The strength of the reduction depends on the lattice geometry as one can see in figure 5.17 where we have compared bcc-vanadium with vanadium in a tetragonal superlattice geometry based on Fe/VH. For bulk V the hydrogen dissolution is slightly diminished up to a magnetic moment of $0.75\mu_B$. For tetragonally distorted V layers, as found in Fe/V superlattices, the dissolution energy is increased for moments up to $1.25\mu_B$. The reason is the similar density of states at the Fermi energy for both V and VH in the distorted lattice structure, see figure 5.18, which determines the energy cost of spin polarization. For higher magnetic moments of the V host, the hydrogen dissolution becomes favored in all considered cases. The reason is the higher density of
Figure 5.17: Hydrogen dissolution energy of bulk and superlattice vanadium

Figure 5.18: Spin-dependent site projected DOS of V d-states for different magnetic moments: in bulk V, at the V site of VH, and bulk V with the VH-lattice parameter.
at the Fermi energy of VH compared to V. In addition, we have shown that the magnetostriction effect is negligible compared to the hydrogen dissolution energy.

### 5.2.3 Conductivity dependence on extra charge

In conjunction with paper IV we have investigated how extra charge influences the conductivity of bulk materials.

In paper VI we showed that extra charge filling of the bandstructure of Cr and Mo decreases the Fermi velocity and increases the density of states at the Fermi energy. We have obtained a drastic reduction of the conductivity as one can see in figure 5.19. The minimum in both Cr and Mo is obtained for about 0.2 extra electrons.

![Figure 5.19: Calculated conductivity as a function of the number of added electrons for Cr (left) and Mo (right). In the top panel the in plane conductivity for Cr (Mo) with a $c/a$ ratio equal to 0.957 (1.052) is shown, middle panel for Cr (Mo) with a $c/a$ ratio equal to 0.977 (1.027), and in the bottom panel for an undistorted bcc lattice.](image)

It is worth do note that for tetragonal distortions with increasing $c/a$ ratio the minimum flattens out especially for Mo. The change of the orbital overlap of the $d$-states can be the reason for that. In addition the same trend can be seen in the Fermi velocities in figure 5.20.
Figure 5.20: Fermi velocity (left) and DOS (right) at EF of Cr (top) and Mo (bottom) for the undistorted lattice (solid line) and the most distorted lattice (dashed line).
6. Conclusion and outlook

In this thesis we have extensively used the Boltzmann formalism in order to understand conductivity properties of strained materials. This work has shown that the Boltzmann approach using an appropriate relaxation time approximation gives remarkable results when explaining the conductivity trends by means of bandstructure properties.

It has been shown that the 3d, 4d, and 5d transition metal elements behave in a similar way when undergoing strain or stress. Nevertheless there are deviations which we explained by the orbital orientation of for instance the d electrons. We could reproduce the observed conductivity changes in strained Si. Its unstrained lattice, a zinc blend structure, has an c/a ratio of $\sqrt{2}$ and can be considered as a fcc lattice with a basis. Now after having all the results we can conclude that Si for ambient changes of the c/a ratio around $\sqrt{2}$ shows the same behaviour as the transition metals around the fcc point.

For a complete description of the conductivity changes in Cr/V multilayers under Hydrogen loading one has to include disorder. That can not be done in the Boltzmann formalism without quantifying scattering processes and the resulting relaxation time. Nevertheless, we could collect information about the virgin and fully loaded superlattices, which are ordered systems, and therefore we have been able to make statements about the conductivity in Cr/V superlattices. We could pin the occurrence of local resonances in V as the main reason for the conductivity drop in half filled Cr/V systems and could explain why they do not occur and/or do not have such an impact in Mo/V and Fe/V.

The last paper about the influence of extra charge in Cr-bulk and Mo-bulk demonstrates how the Boltzmann formalism gives valuable insight in underlying conductivity mechanisms. Cr and Mo are isovalent. The bandstructure analysis shows that they have the bonding d states almost filled and any additional charge will shift the Fermi level closer to the pseudogap. According to the bandstructure one would assume decreasing conductivity when adding additional charge. This was confirmed by our calculations.

In the future it would be worthwhile to investigate additional semiconductors, such as GaAs, due to the fact that they obey the same lattice type. A wide field of research is to find a good approximation of the relaxation time without loosing the simplicity and the coupling to the band structure. The results of the papers investigating the general trends motivate the assumption that there is a simple relation expressing the conductivity in terms of the number of nearest neighbours and orbital overlaps. This relation could not be proven in our
work yet, but could be an issue of further research. Only a few spin polarised calculations have been conducted so far. The influence of magnetism could be more investigated. Another problem which can be tackled is the influence of surface relaxations on the contribution of surface states and resonances to the conductivity of ultra thin metallic films. Investigations of Cu films with unrelaxed surface structures can already be found in literature [11].

Finally one may conclude that with our straightforward method it is easy to describe the effects which give rise to the conductivity in solids. The strain induced conductivity change can be utilised in many applications, for instance in high mobility semiconductors, strain or stress sensors.
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