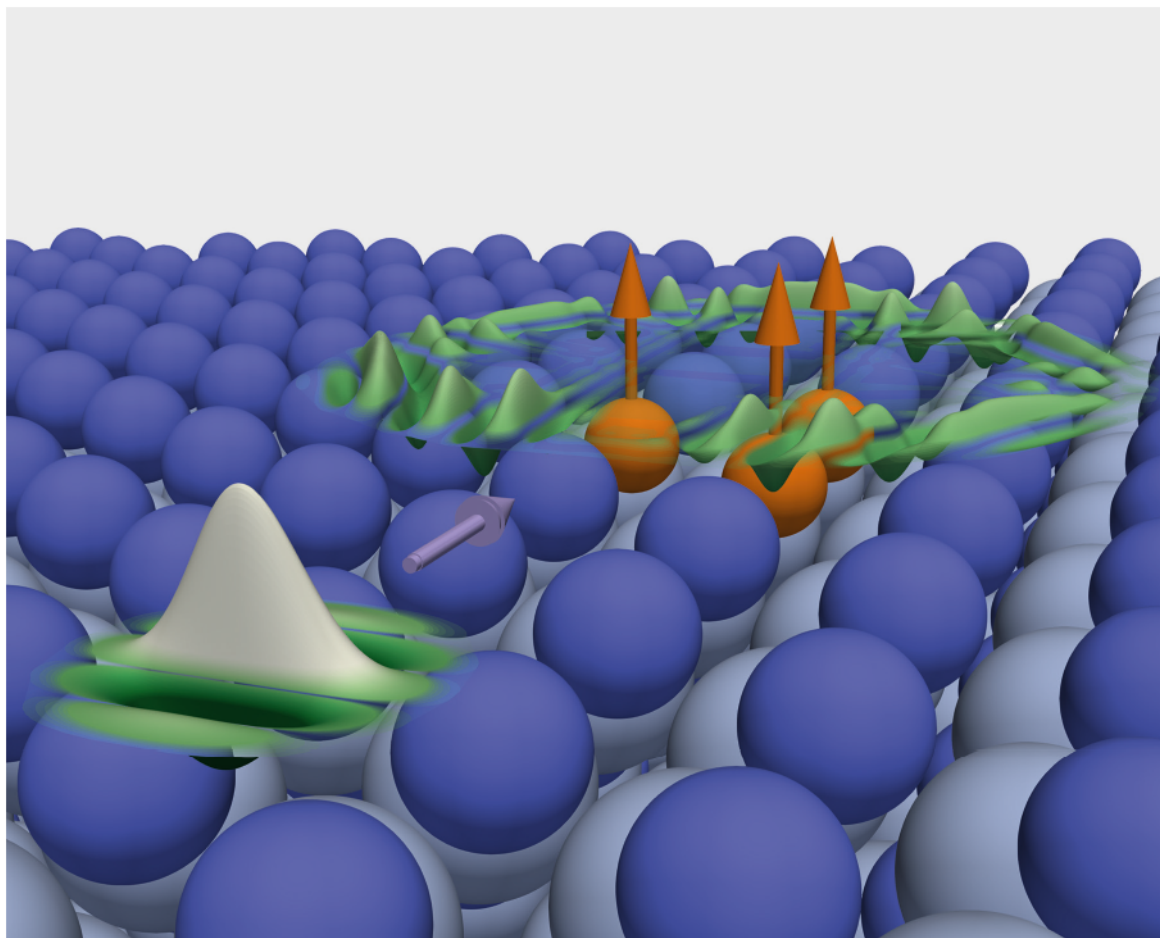




Spin scattering of topologically protected electrons at defects

Philipp Rüßmann

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Abstract

This thesis provides a detailed microscopic understanding of the impurity scattering of topologically protected electrons, which are studied within the example of strong three-dimensional topological insulators (TIs) and type-II Weyl semimetals. The immense research interest in the recent past in topological materials is to a large extent due to the fact that their unconventional electronic surface states are robust against perturbations, such as surface structural relaxations or defects. One of the most intriguing physical properties of topological surface states in TIs is the forbidden backscattering off time-reversal invariant defects, which makes TI materials very promising candidates for future low-power electronics or quantum information technology.

In a theoretical and computational study, we were able to verify the predicted protection against backscattering off non-magnetic defects and reveal the strong suppression of, on the one hand, formally allowed near-backscattering processes, and, on the other hand, backscattering off small time-reversal-breaking defects, e.g. single Mn atoms embedded in the surface of Bi_2Te_3 . Furthermore, we demonstrated that suitable band structure and defect engineering can lead to a focusing effect in charge density oscillations in form of standing waves around impurities. These oscillations, commonly named *quasiparticle interference* (QPI), allow to extract scattering information of defects at the surface, and form a very important tool in the research concerning topological materials. We investigated the effect that scattering of topologically protected electrons has on distance-dependent oscillatory exchange interactions between magnetic impurities, and explained experimentally observed trends in the collective magnetization at different transition metal coverages on Bi_2Te_3 . Finally, we explored the scattering signatures of Fermi arcs in the type-II Weyl semimetal candidates WTe_2 and MoTe_2 , where, moreover, a universal response to impurities across the topological phase transition was uncovered.

For the very first time the scattering properties of topologically protected electrons were investigated on the basis of ab-initio calculations, employing the relativistic full-potential Korringa-Kohn-Rostoker Green function method. The simulations were made possible by improving the available methods in terms of an efficient parallelization of existing computer codes and by developing new tools to compute QPI images from first principles. The results of this thesis underline the importance of a realistic description of the impurities embedded into the clean topological surfaces and thus the need for ab-initio calculations. The very good agreement between our results and several different experiments such as scanning tunneling microscopy, X-ray magnetic circular dichroism, or angular-resolved photo-emission spectroscopy highlight the extremely high accuracy we were able to achieve in our calculations and provides confidence in the predictive power of our method.

Throughout our investigation the importance of resonances in the scattering potential became evident, giving a unified view on QPI, quantum coherence, and magnetic interactions in both TIs as well as Weyl semimetals. These fundamental new insights set the foundations of tuning transport properties and controlling the magnetization in the fascinating class of topological materials in the future. Our results are thus of importance in overcoming the material science challenges on the way to topological-materials-based technology.

Conventions and abbreviations

The following conventions and frequently used abbreviations occur in this thesis:

Symbol	Explanation
$\mathbf{r}$	general vector
$\hat{A}$	quantum mechanical operator
$\underline{A}$	general matrix
X_Y	substitutional defect (atom X replaces atom Y)

Abbreviation	Explanation
AFM	antiferromagnetic
ARPES	angular-resolved photo-emission spectroscopy
CEC	constant-energy contour
DFT	density functional theory
exJDOS	extended joint density of states
FM	ferromagnetic
FT-QPI	Fourier-transformed QPI
GF	Green function
HPC	high performance computing
JDOS	joint density of states
KKR	Korringa Kohn Rostoker
KKRQPI	fully ab-initio FT-QPI images computed with the KKR method
ML	monolayer
QL	quintuple layer, unit cell of the Bi_2Te_3 class of materials
QPI	quasiparticle interference
RKKY	Ruderman-Kittel-Kasuya-Yosida
STM	scanning tunneling microscopy
STS	scanning tunneling spectroscopy
TI	topological insulator
TL	trilayer, building block of MoTe_2 and WTe_2
TRS	time-reversal symmetry
TSS	topological surface state
XAS	X-ray absorption spectroscopy
XMCD	X-ray magnetic circular dichroism

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Introduction

The recent success of the concepts of topology entering condensed matter physics marks a revolution in our understanding of solids. Instead of a description in terms of local order parameters topological nontrivial phases of matter are described with global, non-locally measured, topological numbers. In solid state physics the classification of the Hamiltonian describing a certain state of matter in terms of its, in the mathematical sense, geometrical properties describes the topology of the physical system. The importance of nontrivial band structures of solids lies in its inherent connection to quantization, which is tied to the discovery of new, very robust and highly unconventional states of matter. The recent hype around topologically nontrivial phases is not only based on the fundamental interest in their properties but especially on the robustness of certain physical observables.

The concept of topology entered solid state research with the description of the Kosterlitz-Thouless transition in 1972 [1]. Among the first systems where the importance of topology was realized were the integer quantum Hall effect [2] and spin chains [3]. Recently, the success of a description in terms of topology was even celebrated with the Nobel Prize of 2016, which was awarded to J. M. Kosterlitz, D. J. Thouless and F. D. M. Haldane [4]. Topological insulators (TIs) are among the most prominent examples for topological matter and their discovery [5–7] led to the finding of a plethora of other nontrivial phases such as topological crystalline insulators, weak topological insulators, topological superconductors, Weyl semimetals or Dirac semimetals. TIs are examples realizing the quantum spin Hall effect [5], where the nature of a nontrivial insulator's band structure leads to the existence of robust, spin-momentum-locked metallic states on the surface [6, 7]. These unconventional states have the possibility to revolutionize information processing due to the availability for pure spin-currents. Also, they could be used to realize low-power spintronics, and, if interfaced with a superconductor, are predicted to show the existence of Majorana zero modes, which might open up ways towards topological, and therefore fault tolerant, quantum computing.

Strong 3D topological insulators of the Bi_2Te_3 family of compounds are a prime example for this new class of materials. The defining topological protection of their surface states

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can be associated with three aspects of these states [8]; (i) their robust existence, (ii) the spin-momentum locking leading together with time-reversal symmetry to the absence of backscattering and (iii) the Dirac nature of the surface state which leads to distinguished transport properties.

The so-called bulk-boundary correspondence captures the connection between the robust existence of the surface state and the nontrivial topological invariant in the bulk. A change in the $\mathbb{Z}_2$ topological invariant at the interface between topologically nontrivial and trivial insulators (or vacuum), results in the fact that there has to exist a non-degenerate surface state crossing the bulk band gap. The topological surface state (TSS) can only be destroyed if the nontrivial topology in the band structure is reversed and this robustness is one of the main reasons for the ongoing large research interest which similarly holds in other topological materials, for example in the field of Skyrmions.

Typical TI materials exhibit strong spin-orbit coupling which, together with the non-degenerate nature of the nontrivial surface state, necessarily leads to spin-momentum locking in the surface state with the spin-polarization being usually oriented perpendicular to the velocity. The TSS can thus be called helical and is characterized by a spin-texture reminiscent of the Rashba-effect [9, 10]. Together with time-reversal symmetry, which protects the topological nature of the bulk band structure, this nontrivial spin-texture results in the absence of backscattering. The protection against backscattering results in one of the very exciting properties of TI materials, namely very long surface-state lifetimes, which made the observation of the quantum Hall effect possible in TI materials [11]. The intrinsic locking of spin and charge degrees of freedom of the TSS also opens up new perspectives for the control of surface transport properties, for example, via optical irradiation with polarized light, where it was demonstrated that photocurrents with high fidelity can be generated in TI systems [12].

Furthermore, the emergent field of the interface between magnetism and topologically nontrivial systems is of fundamental importance. For instance, in the Cr-doped 3D strong TI $(\text{Bi,Sb})_2\text{Te}_3$ the experimental discovery of the quantum anomalous Hall effect (QAHE) was recently achieved at low temperature [13]. Also, the Edelstein or inverse Edelstein effect [14] was used for spin-to-charge conversion and vice-versa, where a charge current leading to a spin accumulation interacts with the magnetization in the ferromagnet via the spin-transfer torque [15–18]. The helical and non-degenerate nature of the TSS therefore hosts great potential of bringing this technology to a new level, where recently, for example, in spin-pumping [19] or tunneling spin injection [18] experiments much larger efficiencies could be demonstrated in TI-based systems than using the so-far state of the art technique of inverse spin Hall effect in metals like Pt or W [20].

Apart from the possibility of reduced energy dissipation due to suppressed backscattering, the TSS electrons further implicate interesting transport phenomena based on the Dirac nature of the carriers. The topologically nontrivial nature associates with them a π -Berry phase, that has the consequence that an electron traveling clockwise or anti-clockwise on a closed loop has a phase difference of π , which leads to destructive interference. TI systems therefore exhibit weak antilocalization in their magnetotransport properties and an unusual nature of the quantum oscillations is measured in the unconventional quantization of Landau levels and Shubnikov-de-Haas oscillations [8, 21].

Overall, we can say that future topological insulator based technology hosts great potential for spintronics and low-power nanoelectronics. The size of the band gap in typical materials

like Bi_2Te_3 even suggest applications at room temperature and radical new technology like spin transistors using topological p - n -junctions [22], spin-orbit torque magnetoresistive random access memory (SOT-MRAM) devices with much higher energy-efficiency [15] than those used in heavy metal devices [23], unprecedented high efficiency in spin-to-charge conversion [20], microwave-driven spin batteries [24] or even opto-spintronics applications [12, 25, 26] could become reality.

The topological protection and robustness of the surface state, that are the driving force behind the ongoing high interest in this field of research, in particular with respect to inevitably occurring defects in real materials is one of the key issues that have to be addressed. While the robust existence of the surface state, given by the topological nature of the bulk band structure, is understood in principle, microscopic details on the scattering properties of topological surface state electrons are less clear. The importance of impurities on transport properties has been known for a long time, leading, for example, to the residual resistivity in metals or important contributions to the spin Hall or anomalous Hall effect via impurity scattering [27–31]. Even ten years after the first experimental discovery of topological insulators [7], a lot of fundamental material challenges have to be overcome on the way towards TI-based technology, among which are control over surface and bulk contributions to the transport [32, 33] or the issue of lifetimes and coherence lengths [34] leading to the observation that typically the interesting transport properties associated to the TSS are only seen at very low temperatures [13]. To be able to understand and in the future manipulate possible impurity-scattering-related properties, the fundamental scattering features of TSS electrons have to be studied in detail. Clearly, very accurate calculations revealing on a quantitative level in realistic settings are needed to be able to reveal the relevant scattering signatures of topologically protected electrons off impurities.

One way of probing scattering phenomena on surfaces is the quasiparticle interference (QPI) technique. Experimentally, the scanning tunneling spectroscopy provides a tool that can image the charge and spin density oscillations around defects on the surface, which act as scattering centers in particular for surface state electrons. The resulting standing wave pattern, known as Friedel oscillations [35], is a result of scattering off the impurities and, if Fourier transformed, it allows to extract scattering signatures of Bloch electrons carrying information of the crystal's properties. Already in 2004 Pascual et al. [36] identified that in systems with strong spin-orbit coupling the spin can strongly affect quasiparticle interference signatures on the surface, which is obviously of utmost importance for the QPI signatures in the helical TSS. Recently, the QPI technique was successfully applied to 3D topological insulators, where the absence of backscattering signatures [37, 38] provided experimental evidence for the topologically nontrivial nature of the surface state in $\text{Bi}_{1-x}\text{Sb}_x$. The introduction of time-reversal-symmetry-breaking magnetic impurities then leads to a reopening of the backscattering channel, which was also recently observed in Fe bulk-doped [39] and Mn surface-doped [40] samples of Bi_2Te_3 .

Within this thesis the scattering properties of topologically protected electrons, in particular coming from the surface state in the strong topological insulators Bi_2Te_3 and Bi_2Se_3 as well as the Fermi arcs in the type-II Weyl semimetal MoTe_2 , off different defects are addressed based on ab-initio calculations. A realistic description of impurities that act as scattering centers is of paramount importance, since we find that resonances in the scattering potential strongly

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affect quasiparticle interference, quantum coherence and magnetic exchange interactions. Here, impurities were embedded self-consistently in the crystalline host using a Green function formalism, which allows to accurately account for the charge relaxation around impurities very efficiently. Historically the first generation of 3D topological insulator materials was found in $\text{Bi}_x\text{Sb}_{1-x}$ alloys [41], where, however, the disordered nature of the alloy leads to finite lifetimes of the quasiparticle in the solid. Later the second generation of materials was discovered in the Bi_2Te_3 family of compounds, which are a prime example of a strong TI with a single Dirac cone found around the center of the Brillouin zone [42] and are thus an ideal testbed to explore the properties of TIs. Additionally, the dispersion of the TSS shows an interesting energy-dependent warping behavior, that allows to tailor properties of the nontrivial surface state electrons via shifting the Fermi level. The next generation of topological insulator materials studied today are for example ternary or quaternary compounds of the BSTS (alloys of Bi, Sb, Te and Se) class or p - n -junctions often also consisting of Bi_2Te_3 [43]. These new materials make it possible to improve the tuning properties of the band structure, for example, by controlling the position of Fermi level. Thus also in the next generation of materials Bi_2Te_3 is a major ingredient and the insights we are gaining within this thesis are expected to be transferable and of general importance.

Our studies of non-magnetic defects on the surface of Bi_2Te_3 and Bi_2Se_3 confirm the absence of backscattering and additionally shed light on the importance of formally allowed near-backscattering processes, that we find to be strongly suppressed leading to a very strong directionality in forward (i.e. small angle) scattering. Surprisingly, scattering off magnetic defects, that break time-reversal symmetry, does not automatically lead to a re-opening of the backscattering channel. For instance, single magnetic impurities of Mn still show a very strong forward scattering and a backscattering amplitude that is several orders of magnitude weaker. This can be traced back to the spin-momentum locking in the TSS which is a very robust signature of the topologically protected electrons.

Throughout our analysis of the scattering properties of topologically protected electrons the importance of resonant scattering centers became apparent. We found that resonances have a strong influence on the scattering phase shift that determines fundamental properties such as the lifetime of the surface state and the strength of the backscattering amplitude off magnetic centers. Furthermore, we showed that quantum coherence, visible over mesoscopic distances in charge density oscillations around Mn defects on Bi_2Te_3 , can be achieved by tuning the band structure to be conform with the focusing (i.e. nesting) condition in the TSS and combine this with atomic control over the backscattering signal via defect engineering. In this context, only strong resonance or strong magnetic impurity potentials, in this particular example formed by macro-spins as a result of ferromagnetically coupled individual spins, lead to a reopening of the backscattering channel. These results motivated the study of magnetic exchange interactions in transition metal doped Bi_2Te_3 , where the mechanism of the distance-dependent exchange interaction was uncovered and new ways of tuning the TSS-mediated exchange interactions were found.

The study of impurity-induced resonances in the type-II Weyl semimetal candidates MoTe_2 and WTe_2 further enhanced the analysis of scattering properties of topologically protected electrons in TI systems. In collaboration and in mutual agreement of different experimental techniques on the one hand, and the ab-initio calculations of this work on the other hand, the importance of impurity resonances was demonstrated and scattering signature associated to protection against backscattering due to spin-momentum locking was also found in these

newly emerging materials.

The thesis is structured as follows:

In *chapter 2* the basic theory supporting the remainder of this thesis is reviewed. This consists of a short introduction to density functional theory in general and the Korringa-Kohn-Rostoker (KKR) Green function method in particular. Additionally, a brief introduction to the concept of topology with an emphasis of the topological surface state in topological insulators is presented.

Then, *chapter 3* describes the developments achieved in the parallelization of the *KKRcode*, which is the basis of the following ab-initio calculations. It is explained how the hybrid OpenMP/MPI version of the code is implemented and the excellent parallel performance in terms of weak and strong scaling characteristics is demonstrated. These developments are the basis of the time-efficient usage of the architectures available in today's high-performance computing and form the backbone for the results obtained within this thesis.

Chapter 4 introduces the scattering theory of topologically protected electrons after which a discussion of first principles calculations of the scattering probability off different non-magnetic and magnetic (time-reversal symmetry breaking) impurities is presented. The importance of the TSS's spin-momentum locking is highlighted which results in the incredibly strong directionality in small-angle (forward) scattering and a spin-selection rule is found for scattering off magnetic scattering centers. This rule states that, for large angle scattering (i.e backwards direction), the direction that provides an alignment of the final state's spin with the impurity moment is favored. Then the experimentally accessible signature of scattering processes, namely the quasiparticle interference around single defects in real and reciprocal space, is discussed. The limits of the widely used joint density of states approach are highlighted and the significantly improved newly developed extended joint density of states is introduced that takes into account a realistic description of the scattering matrix elements. Furthermore, the formally exact treatment of the Fourier-transformed QPI images directly calculated in reciprocal space is developed going beyond the ad-hoc approaches of the joint density of states-based calculations, which is demonstrated for selected examples.

In *chapter 5* the results of a collaborative study between experimentalist groups performing scanning tunneling microscopy (STM) and X-ray magnetic circular dichroism (XMCD) measurements, on the one hand, and the theoretical calculations for Mn-doped Bi_2Te_3 performed within this thesis, on the other hand, are discussed. It is shown that band structure engineering in Bi_2Te_3 can lead to the focusing effect, which, if combined with sufficiently strong magnetic scattering centers, supports coherent and directional transfer of spin information over mesoscopic distances. These findings demonstrate how the backscattering signatures in magnetically doped Bi_2Te_3 can be controlled on the atomic scale and reveal the importance of strong magnetic scattering centers, realized here by small groups of ferromagnetically coupled individual spins forming a macro-spin.

Chapter 6 highlights the importance of resonances to the scattering properties of topologically protected electrons. The energy-dependence of the surface state's lifetime and scattering

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rates on Bi_2Te_3 and Bi_2Se_3 are analyzed, where the focus is on intrinsic (surface vacancy) defects. In the energy-dependent lifetimes we found a strong signature of the impurity's properties, which manifest in a one-to-one correspondence of impurity density of states and TSS lifetime. This signature of resonant scattering has severe consequences and changes the surface state lifetime by three orders of magnitude. At energies where the TSS coexists with bulk states, the scattering rates are decomposed into surface-to-surface and surface-to-bulk contributions and the TSS's localization on the surface is found to protect the surface state from scattering into the bulk. Predominantly intra-band scattering happens, as long as the phase space of available bulk final states is not much larger than the number of possible final states within the TSS.

In *chapter 7* the concentration-dependent exchange coupling strength for different transition metal adatom doped Bi_2Te_3 surfaces is studied in collaboration with a experimentalist group doing XMCD measurements. The detailed analysis reveals different contributions, which dominate the exchange interaction at different distances. The short-range behavior in the impurity-impurity distance is governed by the competition between superexchange (favoring antiferromagnetic coupling) and double exchange (favoring ferromagnetic coupling) contributions, that were traced back to the relative position of impurity resonances to the Fermi level, i.e. is a signature of the impurity density of states. In the dilute limit (i.e. for long impurity-impurity distances) the exchange coupling is found to be of RKKY-type [44] where also a strong signature of the impurity phase shift is seen, which is related to the peak structure of the impurity density of states. The scattering properties related to impurity resonances in combination with the possibility to fine-tune the distance-dependent exchange coupling strength with a shift of the Fermi level give important insights into the mechanism of exchange interactions mediated by topologically protected electrons, which might open up new ways to tune the magnetic properties in topological insulator systems and could therefore help making room-temperature QAHE applications possible.

Chapter 8 extends the discussion on scattering related properties of topologically protected electrons to the topologically nontrivial metals of the type-II Weyl semimetal class. Here topologically protected Fermi arcs coexist on the surface with trivial bulk-derived states. In a collaboration with experimentalist groups providing STM and angular-resolved photo-emission results together with the ab-initio calculations of this work the functional response of WTe_2 and MoTe_2 to impurities could be demonstrated, where robust signatures across the topological phase transition in terms of impurity resonances and spin-polarized surface states are found. The scattering features of suppressed backscattering are visualized with simulations of Fourier-transformed quasiparticle interference images and the calculation of scattering rates. Additionally, the importance of impurity resonances, which appear close to the energy where the topologically nontrivial Weyl points emerge, is highlighted. These properties have important implications for the fascinating transport properties in this new class of Weyl-II materials.

The thesis concludes in *chapter 9* where the results of the different parts are summarized and an outlook is given.

Basic theory

In this chapter the basic theory needed in the remainder of this thesis is reviewed. First, a short introduction to density functional theory (DFT), that allows to solve quantum mechanical problems in solid state physics very accurately, is given. Nowadays DFT is the workhorse of computational solid state physics due to its predictive power. Next, the Korringa-Kohn-Rostoker Green function formalism is introduced. Therefore the basics of Green functions in general and then the KKR-specific form of the Green function is briefly reviewed. Having access to the Green function of solids in the framework of DFT gives one the advantage, amongst other things, to efficiently embed impurities in the crystalline solid. Finally a short introduction to topology in solid state physics is given with an emphasis on topological insulators. Here the surface state of TIs is introduced and discussed in terms of topological protection. The introduction, which is presented in this chapter is only intended to give a short overview, without a claim to being comprehensive or mathematically rigorous. It is, however, meant to introduce the basic concepts and give references for further reading.

2.1. A short introduction to density functional theory

One of the challenges in solid state physics is to find a solution of the principal problem of quantum mechanics, which is to solve the Schrödinger equation [45]. If we are interested in ground state properties we have to deal with the *stationary* Schrödinger equation

$$\hat{H}\psi = E_0\psi, \quad (2.1)$$

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where the Hamiltonian $\hat{H}$ determines the many body wavefunction¹ $\psi \equiv \psi(r_1, r_2, \dots, r_N)$ that has the ground state energy E_0 . The Hamiltonian² $\hat{H}$ contains the kinetic energy of the electrons, the Coulomb potential of the electron-electron interaction and the interaction of the electrons with external fields that is for example given by Coulomb potential between electrons and the atomic nuclei in the crystal lattice³ and possible externally applied fields.

The Schrödinger equation given in Eq. (2.1) poses a very hard problem and is actually impossible to solve exactly for realistic systems⁴ as the following simple example of an Fe atom (atomic charge $Z = 26$) illustrates: if we would chose to solve the Schrödinger equation in the naive way of having a real space grid and we are very optimistic to assume that 10 grid points per spacial direction (x, y, z) are enough to achieve the desired accuracy, then already storing the wavefunction would need saving the information of $10^{3 \cdot 26} = 10^{78}$ grid points, which is of the order of the total number of atoms that exist in the universe and thus by far too large to treat.

Fortunately, the ingenious idea of density functional theory (DFT) (see for example Refs. [47–50]) is to treat the electron density instead of the wavefunction which reduces the number of degrees of freedom from $3N$ to 3, i.e. three spacial coordinates of $\mathbf{r} = (x, y, z)^T$ instead three degrees of freedom *per electron*. The foundation for this approach was given by Hohenberg and Kohn [51] who proved that (i) the total energy can be uniquely determined by the ground state density and (ii) the functional of the total energy is minimized by the ground state density.

The breakthrough came with the work of Kohn and Sham [52] who came up with the idea of separating all the parts of the Schrödinger equation that are known and that can be treated exactly from the rest and to find a reasonable approximation for everything that is unknown. This is done by expressing the problem in terms of the Schrödinger equation of *non-interacting* electrons in an *effective* potential which gives the single-particle Kohn-Sham equation

$$\left[-\nabla^2 + \int d^3r' \frac{n(r')}{|\mathbf{r} - \mathbf{r}'|} + V_{\text{ext}}(\mathbf{r}) + V_{\text{xc}}(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}) \quad (2.2)$$

for the auxiliary Kohn-Sham orbitals ϕ_i with Kohn-Sham eigenvalues ϵ_i that give the electron density as $n(\mathbf{r}) = \sum_i |\phi_i(\mathbf{r})|^2$ where the sum is over the N lowest eigenstates. Here V_{ext} is the external potential (amongst other things the potential of the nuclei) and everything that is missing to go back to Eq. (2.1) is put in V_{xc} . Rewriting this has the advantage, that a big part of the electron's kinetic energy (first term in Eq. (2.2)), the *Hartree* term of the electron-electron interaction (second term in Eq. (2.2)) as well as interactions with external potentials such as the electrostatic interaction with the nuclei of the atoms in the

¹The inclusion of relativistic effects, such as spin orbit coupling, generalizes the Schrödinger equation to the Dirac equation, where the wavefunctions are 4-component spinors (spin up/down and large/small components). However, for the sake of simplicity of the notation we stick in this general introduction to the Schrödinger equation and drop all spin indices.

²Note that we are using Rydberg atomic units here. This means that $\hbar = 2m_e = e^2/2 = 1$, which gives the physical units that are defined as: angular momentum $[l] = \hbar$, mass $[m] = 2m_e$, charge $[q] = e/\sqrt{2}$, length $[r] = \hbar^2/(me^2) \equiv a_B \approx 0.529\text{\AA}$ and energy $[E] = Ry \approx 13.6\text{eV}$.

³Throughout this thesis the atomic nuclei are always assumed to be at fixed positions as it is mostly, e.g. not in superconductivity, true for systems close to 0 K and which also holds for higher temperatures as the electron, which is orders of magnitude lighter than the nucleus and therefore moves much faster than the nucleus. This approximation is referred to as adiabatic or Born-Oppenheimer approximation [46].

⁴Heavy elements with a large number of electrons, several types of atoms in the unit cell, etc.

crystal or external electric or magnetic fields (third term in Eq. (2.2)) are treated exactly. Everything that is beyond these terms⁵ is put into the so-called *exchange-correlation* potential (fourth term in Eq. (2.2)) that can formally be written as $V_{xc}(\mathbf{r}) = \delta E_{xc}[n]/\delta n(\mathbf{r})$, which is a functional derivative of the exchange-correlation energy functional that depends on the electron density. While the formal equation for this Ansatz can be written down exactly, the solution to the problem is still not accessible. However, very successful approximations have been found for the exchange-correlation part such as the so-called local density approximation (LDA) or the generalized gradient approximation (GGA). This is the reason for the great success of DFT up to now. Throughout this thesis the LDA approach was used [53].

These local approximations for the exchange-correlation potential are incredibly successful as they allow to have a method with *predictive power*, that can give quantitative predictions for a number of physical properties with reasonable computational cost. The Kohn-Sham wavefunctions (ϕ_i) and the band structures that follow from the Kohn-Sham eigenenergies [$\epsilon_i = \epsilon_i(\mathbf{k})$, for crystal momentum $\mathbf{k}$] on the other hand are – strictly speaking – only a mathematical tool that give an approximation to the real quasiparticle wavefunctions in a crystal. This can for example be seen in the *band gap problem* of DFT which is reflected in band gaps of insulators that are often underestimated in LDA or GGA as compared to experiment. Close to the Fermi level the Kohn-Sham approximation is nevertheless often in very good agreement with the real quasiparticle band structure, which is the regime where the calculations of this thesis are aiming at. In this thesis we will therefore not distinguish between the real band structure and our calculation of the Kohn-Sham approximation to it.

In the following section the Korringa-Kohn-Rostoker Green function (KKR-GF) method – a special implementation of the DFT framework, which was used within this thesis – is introduced in some detail.

2.2. The Korringa-Kohn-Rostoker Green function method

Today many implementations and a full zoo of methods to solve the Kohn-Sham equation of DFT are on the market with comparable accuracy that allows to make quantitative predictions for experimentally observable quantities in solid state physics and quantum chemistry [54]. As the gold standard one could see the *all-electron* methods, that treat core as well as valence electrons on the same footing. The *KKRcode* developed in Jülich is a full-potential relativistic implementation [55–63] of the Korringa-Kohn-Rostoker Green function (KKR-GF)⁶ method, that was used for all first-principles calculations throughout this thesis.

The Green function formulation of the KKR-GF method makes it a very powerful tool which has certain non-standard features, some of which (the ones used within this thesis) will be mentioned below, as compared to wavefunction based methods [59, 64, 65]. For example, having the Green function at hand allows to embed impurities into the host system without the need for large supercells [61]. Based on the self-consistent impurity embedding, scattering of host electrons off the impurity can be calculated from first principles. Also, more elaborate quantities like non-local response functions of magnetic coupling parameters (the exchange

⁵These are complicated things like exchange and correlation effects among the electrons.

⁶Also simply referred to as *KKR* (omitting the addition *GF* in the acronym) within this thesis

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coupling J_{ij} or Dzyaloshinskii-Moriya interaction $\mathbf{D}_{ij}$) are accessible. Calculations with these different steps were done within this thesis and will now be introduced shortly.

There follows a short introduction to the basic properties of Green functions in solid state physics in general, and the multiple scattering theory of the KKR-GF formalism in particular. We will only give a very short review of the theory and refer for a deeper going introduction to standard literature for example found in the book by Gonis [66] or to the KKR specific literature, for example given in the introductions of Refs. [60, 61, 63].

Generally the KKR-GF method is still under ongoing conceptual development and a very powerful technique, e.g. being able to perform $\mathcal{O}(N)$ calculations for extremely large systems [67], DMFT and CPA calculations for disorder, compute response functions [64] or transport properties [68, 69].

2.2.1. Green functions in solid state physics

The Green function (GF) is formally defined as the resolvent of the Schrödinger equation [cf. Eq. (2.1)]

$$(E - \hat{H}) \hat{G} = \mathbb{1} \quad (2.3)$$

which can be rewritten as $\hat{G}(E) = (E - \hat{H} + i0)^{-1}$, with $i0$ being a positive⁷ infinitesimal imaginary part, which ensures convergence of the calculation and that is set to zero in the end. Here we used the convention that $\hat{}$ stands for a quantum mechanical operator that can be evaluated in a suitable basis. The GF is equivalent to the set of wavefunctions ψ_i that diagonalize the Hamiltonian with eigenenergies ϵ_i (i.e. $\hat{H}|\psi_i\rangle = \epsilon_i|\psi_i\rangle$), as can be seen from the spectral representation of the GF

$$\hat{G}(E) = \sum_i \frac{|\psi_i\rangle\langle\psi_i|}{E - \epsilon_i + i0}. \quad (2.4)$$

Multiplying with $|r'\rangle$ from the right and $\langle r|$ from the left gives the real-space representation of the Green function that makes it obvious that the Green function $\langle r|\hat{G}|r'\rangle = G(\mathbf{r}, \mathbf{r}'; E)$ describes the propagation of an electron from a point $\mathbf{r}$ in space to $\mathbf{r}'$. The expectation value A of an observable operator $\hat{A}$ can in general be computed from the Green function

$$A = \langle \hat{A} \rangle = -\frac{1}{\pi} \text{Im} \int_{-\infty}^{E_F} dE \text{Tr}[\hat{A}\hat{G}(E)], \quad (2.5)$$

where the trace is taken in any convenient basis, where the integration sums over all occupied states and therefore goes up to the Fermi energy E_F (for $T = 0$). This leads to the fundamental quantity of density functional theory, which is the electron density

$$\rho(\mathbf{r}) = -\frac{1}{\pi} \text{Im} \int_{-\infty}^{E_F} dE \text{Tr}[G(\mathbf{r}, \mathbf{r}; E)]. \quad (2.6)$$

The above introduced equations showed the equivalence of the wavefunctions (which in the context of DFT are Kohn-Sham orbitals) and Green functions, however the complexity of

⁷The positive sign means that we are dealing with the *retarded* Green function that is used throughout this thesis. If a negative sign is chosen, then the *advanced* Green function is dealt with.

the problem was not reduced. The multiple scattering Ansatz by Korringa [70], Kohn and Rostoker [71] gives a formalism that allows the efficient computation of the Green function without explicitly computing all wavefunctions in the sum of Eq. (2.4). Furthermore, the analytical properties of the Green function allow to perform the energy integration in Eq. (2.6) over a complex energy contour [59], which reduces the number of energy points and k -points needed for the numerical evaluation of the integration significantly.

2.2.2. Ab-initio computation of the Green function within the KKR-GF formalism

The idea behind the Korringa-Kohn-Rostoker method is a multiple scattering Ansatz allowing to separate the solution of the Schrödinger equation into two steps; (i) first the problem of an isolated atom in free space is solved and (ii) then the multiple scattering step is performed, where the solution of the single atom in free space is connected to the crystalline lattice.

The Green function in the KKR formalism is expanded in site-centered coordinates where a general position in the crystal is written as $\mathbf{r} = \mathbf{X}_n + \mathbf{x} = \mathbf{R}_i + \boldsymbol{\chi}_\mu + \mathbf{x}$, with $n = (i, \mu)$ being the combined site index defining the lattice site $\mathbf{X}_n$ by a lattice vector $\mathbf{R}_i$ and a sub-lattice vector $\boldsymbol{\chi}_\mu$ and $\mathbf{x}$ gives the position within the atomic cell with respect to the site center $\mathbf{X}_n$. Following the multiple scattering idea, the GF can be decomposed into a single site term (G_S dealing with the single atomic potential on site n in free space) and the multiple scattering contribution (G_M) that describes scattering between different sites and is expressed using the structural Green function coefficients $\mathcal{G}_{LL'}^{nn'}(E)$. The Green function in the KKR language then reads

$$\begin{aligned} G(\mathbf{X}_n + \mathbf{x}, \mathbf{X}_{n'} + \mathbf{x}'; E) &= \sum_L G_{SL}^n(\mathbf{x}, \mathbf{x}'; E) \delta_{nn'} + \sum_{LL'} G_{MLL'}^{nn'}(\mathbf{x}, \mathbf{x}'; E) \\ &= -i\sqrt{E} \sum_L \left[\mathcal{R}_L^n(\mathbf{x}; E) \bar{\mathcal{H}}_L^n(\mathbf{x}'; E) \theta(\mathbf{x}' - \mathbf{x}) \right. \\ &\quad \left. + \mathcal{H}_L^n(\mathbf{x}; E) \bar{\mathcal{R}}_L^n(\mathbf{x}'; E) \theta(\mathbf{x} - \mathbf{x}') \right] \delta_{nn'} \\ &\quad + \sum_{LL'} \mathcal{R}_L^n(\mathbf{x}; E) \mathcal{G}_{LL'}^{nn'}(E) \bar{\mathcal{R}}_{L'}^{n'}(\mathbf{x}'; E). \end{aligned} \quad (2.7)$$

The second line give the expansion of single site and multiple scattering part in site-dependent (n labels the site) regular $\mathcal{R}_L^n(\mathbf{x}; E)$ and irregular $\mathcal{H}_L^n(\mathbf{x}; E)$ wavefunctions, where $L = (\ell, m, s)$ is the combined index of spin and angular momentum indices. We would like to point out that the regular $\mathcal{R}_L$ and irregular $\mathcal{H}_L$ right-hand solutions are (2×1) or (4×1) column-vectors (spinors) in Pauli- or Dirac-theory and the corresponding left-hand⁸ solutions $\bar{\mathcal{R}}_L$ and $\bar{\mathcal{H}}_L$ are row-vectors.

In the following first the single site problem will be addressed where the site-dependent wavefunctions are introduced and afterwards the multiple scattering problem that relies on the computation of the structural Green function coefficients will be discussed.

⁸The complex energies in the energy integration lead to a non-hermitian set of equations, which has the consequence that left and right solutions of the eigenvector problem posed by Eq. (2.2) are not equivalent.

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The single site problem: scattering solutions and atomic t -matrix

The single site problem of the KKR formalism breaks down to finding the site-dependent wavefunctions. These wavefunctions are the eigenfunctions to the Hamiltonian of a single atom [of site n with potential $V^n(\mathbf{x})$] embedded into a reference system, that was traditionally the potential free space⁹ (where the solutions are analytically known) but for technical reasons is nowadays an auxiliary system of repulsive potentials called V^{ref} [72, 73].

All wavefunctions ($\mathcal{R}$, $\mathcal{H}$, $\bar{\mathcal{R}}$ and $\bar{\mathcal{H}}$) are further expanded in real spherical harmonics $Y_L(\hat{\mathbf{x}})$ which gives the expansion for the regular right solution

$$\mathcal{R}_L^n(\mathbf{x}) = \sum_{L'} \frac{1}{x} \mathcal{R}_{L'L}^n(x) Y_{L'}(\hat{\mathbf{x}}) \quad (2.8)$$

where $x = |\mathbf{x}|$ and $\hat{\mathbf{x}} = \mathbf{x}/|\mathbf{x}|$ and the irregular, regular left and irregular left solutions are expanded in the same way.

The basic scattering problem of the potential embedded into free space that can be solved if the solution, i.e. the site-dependent wavefunctions, of the potential in free space is known. This precondition is given and the regular and irregular solutions corresponding to the potential are called $J_L^n(x; E)$ and $H_L^n(x; E)$ and are analytically known to be spherical Bessel and Hankel functions of the first kind. The solution for a potential embedded into free space [given by $g^{\text{free}}(\mathbf{r}, \mathbf{r}'; E) = -\frac{1}{4\pi} \frac{e^{i\sqrt{E}|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}$] is now given by the Lippmann-Schwinger equation [66, 74] (dropping the obvious site indices n of $\mathcal{R}_{L'L}$ etc.), that for the regular right solution reads

$$\mathcal{R}_{L'L}(x; E) = J_L(x; E) \delta_{LL'} + \sum_{L''} \int dx'' g_L^{\text{free}}(x, x''; E) V_{L'L''}(x'') \mathcal{R}_{L''L}(x''; E) \quad (2.9)$$

where $V_{L'L''}(x'')$ is the expansion coefficients in real spherical harmonics corresponding to the atomic potential. The corresponding Lippmann-Schwinger equation for the irregular solution is [61]

$$\mathcal{H}_{L'L}(x; E) = H_L(x; E) \beta_{L'L}(E) + \sum_{L''} \int dx'' g_L^{\text{free}}(x, x''; E) V_{L'L''}(x'') \mathcal{H}_{L''L}(x''; E) \quad (2.10)$$

with

$$\beta_{L'L} = \delta_{L'L} - \sqrt{E} \int dx' J_L(x'; E) \sum_{L''} V_{L'L''}(x') \mathcal{H}_{L''L}(x'; E) \quad (2.11)$$

defining the appropriate boundary conditions in the second (i.e. L') index [61, 63]. Analogously the left solutions are given by

$$\bar{\mathcal{R}}_{LL'}(x; E) = \bar{J}_L(x; E) \delta_{LL'} + \sum_{L''} \int dx'' \bar{\mathcal{R}}_{LL''}(x''; E) V_{L''L'}(x'') g_L^{\text{free}}(x'', x; E) \quad (2.12)$$

and

$$\mathcal{H}_{LL'}(x; E) = \bar{\beta}_{LL'}(E) H_{L'}(x; E) + \sum_{L''} \int dx'' \mathcal{H}_{LL''}(x''; E) V_{L''L'}(x'') g_L^{\text{free}}(x'', x; E) \quad (2.13)$$

⁹Also simply referred to as "free space" or vacuum.

where

$$\bar{\beta}_{LL'} = \delta_{LL'} - \sqrt{E} \sum_{L''} \int dx' \bar{\mathcal{R}}_{LL''}(x'; E) V_{L''L'}(x') H_{L'}(x'; E) \quad (2.14)$$

is used. Note that the quantum numbers corresponding to the boundary condition are now written as first index of $\bar{\mathcal{R}}_{LL'}$ and $\bar{\mathcal{H}}_{LL'}$ [61, 63]. The algorithm that is used to solve the Lippmann-Schwinger equation is based on rewriting it with the help of Chebychev polynomials, which finally allows to perform a direct inversion of the integral equations. For further details we refer to the work of Bauer [61].

With the definition of the wavefunctions the atomic Δt -matrix, corresponding to the potential difference $\Delta \hat{V}(x) = V^n(x) - V^{\text{ref}}(x)$ between atomic and reference potential, can be written down in the expression

$$\Delta t_{LL'}(E) = \sum_{L''} \int dr \bar{\mathcal{J}}_L^{\text{ref}}(x; E) \Delta \hat{V}_{LL''}(r) \mathcal{R}_{L''L'}(x; E). \quad (2.15)$$

that contains all the scattering properties of the atom embedded into the reference system with $\bar{\mathcal{J}}_L^{\text{ref}}$ being the left solution to the reference potential in free space. This quantity will be used in the next step to combine the scattering properties of the single atoms at sites n to the multiple scattering part.

The multiple scattering step: structure constants and the Dyson equation

The multiple scattering part is captured by the algebraic Dyson equation (reintroducing the site indices n)

$$\mathcal{G}_{LL'}^{nn'}(E) = \mathcal{G}_{LL'}^{\text{ref}nn'}(E) + \sum_{n''L''L'''} \mathcal{G}_{LL''}^{\text{ref}nn''}(E) \Delta t_{L''L'''}^{n''n'}(E) \mathcal{G}_{L'''L'}^{n''n'}(E) \quad (2.16)$$

where the structural Green function coefficients of the reference system enter. $\mathcal{G}^{\text{ref}}$ can be computed in the same way from the analytically known structure constants of the free space (i.e. replacing $\mathcal{G}^{\text{ref}}$ by $\mathcal{G}^{\text{free}}$) and the expression for t^{ref} which is also known analytically and that replaces Δt in the above expression. Via $\mathcal{G}$ the systems geometry enters and the scattering solutions of the individual atomic sites are interconnected in the multiple scattering part of the Green function. We have therefore collected all ingredients to construct the Green function of a crystalline solid within the framework of density functional theory.

2.2.3. Beyond the crystalline solid: Impurity embedding and elastic scattering off impurities

So far we have seen the basic equations that allow the computation of the Green function within the framework of density functional theory. Now we want to highlight two benefits this approach has. On the one hand this is the possibility to use the Dyson equation to compute the Green functions of a host system into which an impurity is embedded, given that the Green function of the host system is known. And on the other hand the knowledge of the impurity Green function allows to compute scattering properties off the impurity that is embedded via the Dyson equation into the host system.

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The calculations that are presented in this thesis are based on these steps, which can be summarized in the following recipe: (i) the self-consistent density functional theory calculation is performed to find the host Green function, i.e. the Green function of the crystalline solid, (ii) the Dyson equation is used to self-consistently embed impurities into the system and finally (iii) scattering properties of host electrons scattered off the embedded impurity are computed. The discussion above enables us to perform the first step of finding the Green function of the crystalline solid and in the following steps (ii) and (iii) will be reviewed quickly, where the interested reader is referred to the works of Heers [60], Bauer [61] and Zimmermann [75] for more detailed discussions.

Impurity embedding

The Dyson equation [66, 74] connects the system of an impurity embedded into the host system, i.e. it is described by the Hamiltonian $\hat{H}^{\text{imp}} = \hat{H}^{\text{host}} + \Delta V$. Here the system without impurity is described by $\hat{H}^{\text{host}}$, which is assumed to be known, and $\Delta V = V^{\text{imp}} - V^{\text{host}}$ gives the potential difference between host system and the perturbation by the impurity, which can be assumed to be nonzero only in a small region surrounding the defect. In terms of the corresponding Green functions G^{imp} and G^{host} the impurity Green function is obtained from the Dyson equation

$$G^{\text{imp}} = G^{\text{host}} + G^{\text{host}} \Delta V G^{\text{imp}} \quad (2.17)$$

$$= G^{\text{host}} + G^{\text{host}} \Delta V G^{\text{host}} + G^{\text{host}} \Delta V G^{\text{host}} \Delta V G^{\text{host}} + \dots \quad (2.18)$$

$$= G^{\text{host}} + G^{\text{host}} \mathcal{T} G^{\text{host}}, \quad (2.19)$$

which follows from the definition of the GF (Eq. (2.3)) and where in the last step the $\mathcal{T}$ -matrix has been introduced. Note that we used a short hand notation dropping all indices and dependencies of space coordinates and energies in writing $G^{\text{host}} = G^{\text{host}}(\mathbf{r}, \mathbf{r}'; E)$ which is done analogously for ΔV , G^{imp} and $\mathcal{T}$. Similar to the atomic $\Delta \hat{t}$ -matrix the $\mathcal{T}$ -matrix contains the scattering corresponding to the change in the potential that is induced by the presence of the impurity

$$\mathcal{T} = \Delta V + \Delta V G^{\text{imp}} \Delta V \quad (2.20)$$

$$= \Delta V + \Delta V G^{\text{host}} \Delta V + \Delta V G^{\text{host}} \Delta V G^{\text{host}} \Delta V + \dots \quad (2.21)$$

$$= \Delta V + \Delta V G^{\text{host}} \mathcal{T}, \quad (2.22)$$

where the middle line is the so-called Born series expansion. It is clear that the $\mathcal{T}$ -matrix does not vanish only in the vicinity of the defect, i.e. where $\Delta V \neq 0$. These equations allow the efficient embedding of impurities into the host system for which the host Green function has to be known only in a region around the impurity where $\Delta V \neq 0$. The self-consistent impurity embedding is then the iterative procedure of starting with a guess for the impurity potential which finally gives G^{imp} from the solution of Eq. (2.17). Using the density (given via Eq. (2.6)) and the Poisson equation the output potential can be computed, which is then used with appropriate mixing (e.g. Broyden [76] or Anderson mixing [77]) together with the old input potential for the new input in the succeeding iteration. As typically done in DFT calculations, this iterative procedure is repeated until convergence of the potential is reached. More details on the algorithm and the specific implementation in the *KKRimp* code, which was used in the impurity calculations, can be found in the work of Bauer [61].

Secular equation, KKR wavefunctions and scattering probability rate

The structural Green function coefficients that were introduced in Eq. (2.7) and Eq. (2.16) can be used together with the Δt matrix containing the atomic scattering properties to write down the *secular equation* [60, 63]

$$\sum_{L'} [\delta_{LL'} - \sum_{L''} G_{LL''}^{\text{ref}\mu\mu'}(\mathbf{k}; E) \Delta t_{L''L'}^{\mu'}(E)] c_{kL'}^{\mu'} = 0 \quad (2.23)$$

where the Fourier-transform $G_{LL''}^{\text{ref}\mu\mu'}(\mathbf{k}; E) = \sum_i G_{LL''}^{\text{ref}i\mu;i'\mu'}(E) e^{i\mathbf{k} \cdot (\mathbf{R}_i - \mathbf{R}_{i'})}$ of the structure constants has been introduced, which is only over lattice vectors (index i of the combined index $n = (i, \mu)$ and therefore the sub-lattice indices survive). This defines an eigenvalue problem that can be solved for fixed energy E , e.g. $E = E_F$ to find the $\mathbf{k}$ -points of the Fermi surface very efficiently and to extreme accuracy [63]. The importance of the coefficient vector c_{kL}^{μ} (i.e. the eigenvectors) is given by the relation [75]

$$\Psi_{\mathbf{k}}(\mathbf{x} + \mathbf{X}_n) = \sum_L c_{kL}^{\mu} \mathcal{R}_L^{\mu}(\mathbf{x}; E) e^{i\mathbf{k} \cdot \mathbf{R}_i} \quad (2.24)$$

that connects the vector of coefficients c_{kL}^{μ} to the Bloch wavefunctions $\Psi_{\mathbf{k}}$ together with the radial solutions of the Lippmann-Schwinger equation [Eq. (2.9)]. The scattering formalism incorporated by the Lippmann-Schwinger equation can now be used to relate this to the scattered wave off an impurity in the crystal. The expansion of the scattered wave can be written analogously to Eq. (2.24)

$$\Psi_{\mathbf{k}}^{\text{imp}}(\mathbf{x} + \mathbf{X}_n) = \sum_L \mathcal{R}_L^{\text{imp},\mu}(\mathbf{x}; E) c_{kL}^{\text{imp},\mu} e^{i\mathbf{k} \cdot \mathbf{R}_i} \quad (2.25)$$

and its solution is connected to the already known solutions of the impurity-free case via the Lippmann-Schwinger equation

$$\Psi_{\mathbf{k}}^{\text{imp}}(\mathbf{x} + \mathbf{X}_n) = \Psi_{\mathbf{k}}(\mathbf{x} + \mathbf{X}_n) + \int d\mathbf{x}' G^{\text{imp}}(\mathbf{x}, \mathbf{x}') \Delta V(\mathbf{x}') \Psi_{\mathbf{k}}(\mathbf{x}' + \mathbf{X}_n) \quad (2.26)$$

$$\mathcal{R}_L^{\text{imp}}(\mathbf{x}) = \mathcal{R}_L(\mathbf{x}) + \int d\mathbf{x}' G^{\text{imp}}(\mathbf{x}, \mathbf{x}') \Delta V(\mathbf{x}') \mathcal{R}_L(\mathbf{x}') \quad (2.27)$$

which finally also give $c_{\mathbf{k}}^{\text{imp}} = (\mathbb{1} + G^{\text{imp}} \Delta t^{\text{imp}}) c_{\mathbf{k}}$, where we have dropped the obvious site and angular momentum indices [63] for the simplicity of the notation.

The knowledge of host and scattered (impurity) wavefunctions let us now evaluate the matrix elements of the $\mathcal{T}$ -matrix, which was introduced above. These transition matrix elements describe the scattering from a Bloch state $\mathbf{k}$ (e.g. being from the Fermi surface defined by $E_{\mathbf{k}} = E_F$) to another state $\mathbf{k}'$ on the Fermi surface

$$\mathcal{T}_{\mathbf{k}\mathbf{k}'} = \langle \Psi_{\mathbf{k}} | \mathcal{T} | \Psi_{\mathbf{k}'} \rangle \quad (2.28)$$

$$= \langle \Psi_{\mathbf{k}} | \Delta V | \Psi_{\mathbf{k}'}^{\text{imp}} \rangle \quad (2.29)$$

where the second line expresses the problem in terms of incoming and scattered, i.e. changed due to the scattering off the impurity, wavefunctions. These matrix elements are the basic ingredients for the scattering probability rate that can be computed from Fermi's Golden rule

$$P_{\mathbf{k}\mathbf{k}'} = 2\pi |\mathcal{T}_{\mathbf{k}\mathbf{k}'}|^2 \delta(E_{\mathbf{k}} - E_{\mathbf{k}'}) \quad (2.30)$$

that describes the transition rate to scatter elastically (i.e. conserving energy) from an initial state $\mathbf{k}$ to a final state $\mathbf{k}'$. The last two equations give the fundamental properties that will be the basis of a large part of the discussion in the remainder of this thesis.

2.2.4. Summary of the KKR-GF method

To sum up, the KKR-GF method allows to compute the Green function of the density functional theory problem within a multiple scattering Ansatz. The availability of the Green function allows to embed impurities into the system and to compute scattering properties of Bloch electrons off these embedded impurities. These different steps are the basis of the calculations which were done in this thesis for topologically protected electrons mainly of the surface state in 3D topological insulators and for the topologically nontrivial Fermi arcs in Weyl semimetals. The concept of topology in solid state physics and topological protection in particular will be introduced in the next section.

2.3. Introduction to topology in solid state physics at the example topological insulators

In this section the terminology of topology in the electronic structure is introduced and its important implications are derived, in particular in terms of the physical properties of topological insulators are discussed. This introduction is however only very brief and non-mathematical. For a deeper going introduction we refer to the excellent reviews [8, 78–80] and textbooks [81–84].

2.3.1. Topology in band structures

In general, the term *topology* means the mathematical classification of certain geometrical properties of (mathematically defined) spaces. Geometrical shapes are called topologically equivalent, if they can be transformed smoothly into each other. This means, in a popular example, that a smooth deformation, e.g. of a European football (i.e. a round “soccer” ball) to an American football (“egg-shaped”), is allowed without destroying it (i.e. tearing apart or creating holes) to bring one shape to the other. An intuitive meaning of different topologies can be seen from the following analogy, where the topological *in*-equality of two distinct shapes (an *orange*, i.e. a closed ball, and a *doughnut*, i.e. a torus with one hole) is discussed. Obviously, the orange is a closed surface without any holes going through,¹⁰ therefore no smooth transformation (meaning without pinching holes into the shape) of the orange can be done to bring it into the shape of a doughnut, which has exactly one hole. In this case the number of holes in a shape can be understood as the *topological invariant* that classifies the different shapes. Different members of a topological invariance class in this context are characterized by their number of holes which makes for example a coffee mug (closed shape with one hole at the handle) topologically equivalent to the doughnut.

In the context of solid state physics the mathematically defined space we are dealing with is the Hilbert space of Bloch electrons¹¹ in a solid, that can be characterized by their crystal momentum $\mathbf{k}$ and a band index which discriminates between different bands and possible

¹⁰The small dents on the surface, making the orange not perfectly round are not holes and we can easily imagine that a smooth transition to a perfect sphere or a football.

¹¹Here we restrict our discussion to topology relevant to topological insulators. Entire other fields of topological matter exist, such as the topology in magnetic structures of Skyrmions etc. The discussion of these would however go beyond the scope of this thesis.

2.3. Introduction to topology in solid state physics at the example topological insulators

degeneracies. The analogon to the presence or absence of holes in the example of orange and doughnut is the appearance or absence of so called band inversions¹² in band structures. In Figure 2.1 the bulk band structure of topologically trivial and nontrivial insulators is depicted. The typically strong spin-orbit coupling¹³ of topological insulator materials leads to a shift in valence and conduction bands, which first closes the gap and, if further increased, shifts the (in Fig. 2.1 red and blue colored) bands across each other. If no special symmetries protect crossing of bands, the hybridization between the red and blue bands will generally lead to avoided crossings and open up the band gap again. On first sight one might think that we are back to the starting point with a valence and a conduction band separated by a band gap. However this is not the case, as is highlighted by the red and blue colors. To follow the blue band from the left to the right of the schematic band structure in the topological insulator (right panel of Fig. 2.1), we start in the conduction band and when approaching the region of band inversion have to “jump” over to the valence band before “jumping back” to the conduction band when going further to the right. This jump is topologically distinct from the case of the normal insulator (left in Fig. 2.1) where, by following the blue band we can stay within the conduction band and never touch the valence band. In band structures of solids the colors of Fig. 2.1 correspond to their parity and in the time-reversal and inversion symmetric three-dimensional topological insulators (3DTIs), of which the Bi_2Te_3 family is a prime example, the topological invariant can be computed easily by looking at the time-reversal invariant momenta (TRIM points) of the Brillouin zone. In this context the topological $\mathbb{Z}_2$ invariants classify topological and trivial insulators. They can be computed based on *spin Chern number* integrals over planes in the Brillouin zone that can be computed from the band structure via the *Berry curvature*. Here we will not go into much details of Chern numbers and the Berry curvature and the interested reader is referred to the work of Mookrousov [87] for a more detailed introduction. Recently, Schnyder et al. [88] worked out the *periodic table of topological insulators*, where based on the symmetries of the Hamiltonian the mathematical equivalence classes were tabulated.

2.3.2. Connection between topology and physical observables

After the concise reference to topology in the electronic structure of TIs, we briefly review the history of the quantum Hall effect [89] and quantum anomalous Hall effect [13] (QAHE), where the first connection from topology to measurable physical observables (here the quantized Hall conductivity) was developed in condensed matter physics. This finally led to the discovery of topological insulators, that can be understood as a doubled version of the quantum anomalous Hall effect.

The understanding of the quantum Hall effect in terms of topology goes back to the pioneering work of Haldane [3] who introduced Chern insulators, which are insulators with nontrivial Chern number, that capture the topological nature of the band structure of solids. The connection to the quantized Hall conductivity was done for the intrinsic anomalous Hall effect by Thouless, Kohmoto, Nightingale and den Nijs [2] who derived that the Hall

¹²Generally also touchings of bands can be topological in nature, which will be discussed in the Chapter about Weyl semimetals. In this introduction we will restrict ourselves to the topological insulators with a band gap.

¹³In the Bi_2Te_3 class of materials this is certainly the case [85]. However also other possibilities like strain could lead to a band inversion as demonstrated in Sb under strain [86].

2. Basic theory

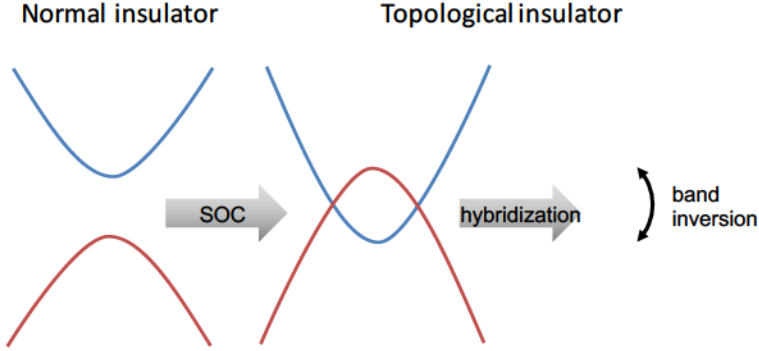


Figure 2.1.: Schematic image of the spin orbit coupling (SOC) induced transition from the (topologically trivial) normal insulator (left) to the topologically non-trivial topological insulator (right). SOC leads to a closing of the bulk band gap between valence and conduction band. Hybridization between the shifted bands leads to avoided crossings and a reopening of the band gap. This leads to a band inversion in the topological insulator (right) as indicated by the blue and red colors.

conductivity in two-dimensional systems with broken time-reversal symmetry can be written as

$$\sigma_{xy} = \frac{j_y}{E_x} = \frac{e^2}{h} \int_{\text{BZ}} dk_x dk_y \frac{1}{2\pi} (\Omega_k)_z \quad (2.31)$$

where j_y is the current in y -direction for an applied electrical field in x -direction E_x , e^2/h is the conductance quantum computed from the electron's charge and Planck's constant and the topology of the system enters via the Berry curvature $\Omega_k = \nabla_k \times \mathbf{A}_k$, derived from the Berry connection $\mathbf{A}_k$. The Berry connection can be computed from the band structure in terms of derivatives of the wavefunction and involves complicated summations over all occupied states [87]. For the discussion presented in this thesis these technical details are not of importance and no topological invariance is computed explicitly. The integral of the Berry curvature in Eq. (2.31) gives the (first) Chern number

$$\mathcal{C} = \frac{1}{2\pi} \int_{S \in \Omega_{\text{BZ}}} \Omega_k \cdot d\mathbf{S} \quad (2.32)$$

where the surface integration goes over a closed surface in the Brillouin zone and takes only integer values ($\mathcal{C} \in \mathbb{Z}$), which makes the distinction between trivial and nontrivial (Chern) insulator.

The story of topological insulators started with the considerations of spin orbit coupling in graphene by Kane and Mele [5]. The Kane-Mele model can be seen as two copies of the Haldane model [3] – one copy for each spin channel – giving the quantum spin Hall effect (QSHE) as two pairs of the Chern insulator. This system is essentially the first prediction of a topological insulator in graphene, which, however, has an incredibly small band gap of only a few μeV , which makes the physics associated to its topological nature, that is typically seen

for E_F in the bulk band gap, practically inaccessible. Nowadays there are however attempts to increase the effective spin orbit coupling in graphene via doping with heavy adatoms [90, 91], by proximity [92] or in analogous honeycomb structures like stanene [93], which is essentially a heavier version of graphene. Later on, the first realization of a two-dimensional topological insulator (2DTI) was discovered theoretically [6] and then experimentally [7] in semiconductor of HgTe/CdTe quantum wells. Here the necessary band inversion occurs for quantum well thicknesses below a certain threshold and a quantized conductance of $\sigma_{xy} = \frac{2e^2}{h}$ was measured in a Hall bar geometry [7]. The factor 2 is a result of the two spin channels in the QSHE (as opposed to the QAHE), where each one-dimensional spin channel contributes a factor $\sigma_{xy}^{(\downarrow)} = e^2/h$.

The examples that were given here show that topology in the bulk band structure relates to physical observables. More generally, the so called bulk-boundary correspondence, that will be discussed in the following, relates the topological nature of the band structure to the existence of robust surface states, to which the quantized conductance seen in the above examples can be related.

2.3.3. Bulk-boundary correspondence and topological protection

So far we have seen that the topologically nontrivial Chern and quantum spin Hall insulator exhibit quantized conductance. Since we are dealing with insulators the conductance cannot come from bulk states, because E_F lies within the gap. As we will discuss here, these contributions come from the surface and we introduce the bulk-boundary correspondence that generally connects the topologically nontrivial nature of the bulk band structure to properties, i.e. surface states, on the surface.

For simplicity, we first consider the 2DTI and deal with the generalization to three dimensions later on. If we have a boundary between trivial (i.e. Chern number is zero) and nontrivial (non-zero Chern number) insulator, then the bulk-boundary correspondence dictates the existence of a number of gapless modes which correspond exactly to the difference in Chern numbers of the two insulators. An exact mathematical proof for this is quite cumbersome [94], so that we will only discuss a hand-waving justification. For the following example we consider a topologically trivial insulator (CdTe, GaAs, or other trivial insulators or vacuum) and a 2D topological insulator with a single point of inverted bands in the Brillouin zone. The band inversion shall now be characterized by a parameter that we call the mass M , which varies at the boundary (which we assume to be oriented along the y -direction at $x = x_0$) from positive (i.e. in the trivial insulator) to negative (topological insulator with a band inversion). Intuitively the mass varies smoothly over the boundary, so that at the interface we find $M(x_0) = 0$. This however means nothing else than the existence of a massless (i.e. gapless) excitation in the quasiparticle band structure. We therefore find a surface state crossing the band gap at the interface of trivial and topological insulator. This is illustrated in Figure 2.2 (a), where the crossing for both spin channels (i.e. red-to red and blue to blue) from trivial to topological insulator leads to two crossing in opposite directions, i.e. the two states have opposite group velocities and are therefore counter-propagating.

In experiments one has samples, e.g. in transport measurements in a Hall bar structure, with boundaries all around. The discussion on the existence of an edge channel now holds for all boundaries so that in the 2DTI two counter-propagating, spin-momentum-locked metallic and one-dimensional edge channels must exist. This situation is illustrated in Fig. 2.2

2. Basic theory

(b). Since E_F lies within the bulk bandgap, the quantized conductance of the 2DTI can be understood from the existence of the edge channels since a one-dimensional conductance channel exactly contributes e^2/h to the conductance. A generalization to three dimensions is straightforward and the additional degree of freedom leads to the existence of *two-dimensional* helical (i.e. spin-momentum locked) electron liquid on the surface as shown in Fig. 2.2 (c).

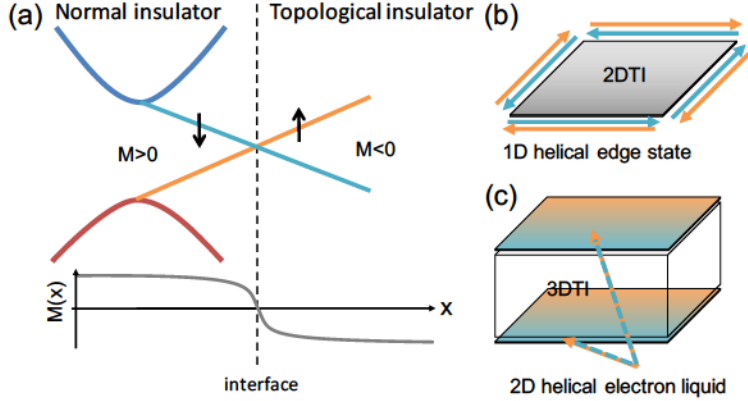


Figure 2.2.: Illustration of the bulk-boundary correspondence. (a) At the interface of topologically trivial (normal) insulator and topological (nontrivial) insulator the bulk-boundary correspondence forces the band character to re-invert. This leads to the helical, topologically protected metallic surface states (indicated in light-blue and orange for spin-up and -down). (b) At the boundary of a two-dimensional topological insulator (2DTI) two counterpropagating, spin-momentum locked surface states appear. (c) On the surface of a three-dimensional topological insulator (3DTI) on the surfaces a two-dimensional electron liquid which is spin-momentum-locked is the consequence of the bulk-boundary correspondence. Here only the top and bottom surfaces are shown and periodicity is assumed in the in-plane directions.

We have seen that the topologically nontrivial nature of the band structure in the bulk leads to helical edge states. This is typically referred to as *topological protection* of the metallic surface state on topological insulators. There are different aspects to the topological protection of the surface states on topological insulators; (i) the existence of surface states is topologically protected making them robust against surface perturbations (reconstructions, defects, etc.) that do not break time-reversal symmetry and (ii) the topology of the system is inherited by the topological surface states protecting them against backscattering. The first point is easy to understand because in the discussion above we only assumed that a change to another insulator with different Chern number is present. This does not make any assumptions on the nature of the interface, in particular with respect to its cleanliness or surface roughness, which makes the existence of the gapless edge channels very robust. Indeed the surface state in topological insulators is found to exist on strongly disordered surfaces [95]. Generally one can only get rid of the topological surface state if the band inversion in the topological insulator is reversed. The second point is associated to the helicity, i.e. the

spin-momentum locking, of the surface states. Our discussion of the “poor-man’s” picture motivated that the helicity of the surface state and in fact the spin-momentum locking is inherited from the topology of the band structure. In general the non-degenerate nature and spin-momentum locking of the topological surface state [96] together with time-reversal symmetry leads to protection against backscattering, since spin-flip scattering is forbidden.¹⁴ In the 1D edge channel of 2DTIs, this has dissipationless transport as a result, no matter if defects are present, resulting in the quantized conductance that has been measured [7]. The technique of a scanning SQUID¹⁵ was successfully used to prove, that the current distribution in the transport experiment of the 2DTI HgTe/CdTe in fact follows the edges and does not penetrate into the bulk [97]. In 3DTIs on the other hand the 2D nature of the surface state only forbids *exact* backscattering, while *near* backscattering is formally allowed. This holds in the case of non-magnetic impurities that do not break time-reversal symmetry but the presence of magnetic impurities can effectively break the protection against backscattering. The question of recurring backscattering and the robustness of the backscattering signature is one of the major points of this thesis and will be addressed in detail in chapters 4 and 5.

2.3.4. Other topologically nontrivial solids apart from topological insulators

So far, we have discussed topology in solid state physics for two- and three-dimensional topological insulators, which are typically referred to as *strong* TIs. The discovery of the QSHE systems however lead to the discovery of a plethora of related topological systems. These are for example the *weak* topological insulators, that host topologically protected surface states only on certain surfaces (sometimes called “bright”) while others are “dark” surfaces without topologically protected electrons. The $\text{Bi}_{14}\text{Rh}_3\text{I}_9$ material is a realization of 3D weak TIs [98, 99] that consists of stacks of 2DTIs, where on the side facets topologically protected surface states exist, while the top surface is trivial. Furthermore, while in the topological insulators, that were discussed so far, time-reversal symmetry protects the existence of the band inversion and therefore the existence of the surface states, in topological *crystalline* insulators the surface states are protected by mirror symmetries in the crystal [100, 101]. Even more exotic phases like topologically nontrivial superconductors are getting more and more attention in the literature, due to their potential of realizing Majorana Fermions that could be used in topological quantum computing in future technological applications.¹⁶

Additionally, apart from the gapped systems of topological *insulators*, ungapped systems (i.e. metals or semimetals) of topological nature exist, such as Dirac, nodal line or Weyl semimetals. These will, however, not be introduced at this point and we refer for example to Murakami’s work [105] for a detailed discussion. The major part of this thesis will deal with the scattering properties of topologically protected electrons coming from the surface state of 3DTIs. Only in the last chapter of this thesis the class of topological Weyl semimetals are introduced and studied.

¹⁴A detailed discussion will be presented in chapter 4.

¹⁵A SQUID is a superconducting quantum interference device that uses the breakdown of its superconducting properties to measure the $\mathbf{B}$ -field that is induced by the local current distribution.

¹⁶An introduction to Majorana Fermions, topological superconductors and topological quantum computing can for example be found in the works of Hassler [102], Ando [103], and Roy and DiVincenzo [104].

Parallelization of the *KKRcode*

In this chapter the parallelization efforts that were made to improve the KKRcode are presented. We review the three level parallelism, that consists of two levels (over atoms and energies) of distributed memory parallelization with MPI and a third level of shared memory parallelization with OpenMP, which have been implemented within this thesis. This approach was very successful and delivered a program that is parallelized very well, which is demonstrated by the excellent strong and weak scaling characteristics of the parallel application. In particular, a speedup of more than 2100 was demonstrated in concrete tests.

The discussion in this chapter begins with an introduction of the state of the art of high performance computing and the programming models that are currently being used. Afterwards the algorithm of parallelization is discussed and the three levels of parallelism are explained. The different levels of parallelism are analyzed in detail and the performance of the implementation is demonstrated. The chapter finishes with the weak and strong scaling characteristics and an outlook.

3.1. Introduction

In modern day solid state physics, computational science plays an increasingly important role. Accurate calculations with predictive power are key to the understanding of the physical phenomena that drive the interest on fundamental research possibly leading to breakthroughs in future generations of technology. The workhorse of these calculations is density functional theory, which allows to solve the quantum mechanical problem encoded in the Schrödinger or Dirac equation to very high accuracy at competitive computing cost. The physical problems of interest nowadays demand extreme numerical accuracy at increasingly large system sizes in a calculation. This, for example, is the case in topological insulator research, where this thesis is thematically placed. Here small energies play an important role, namely because

3. Parallelization of the KKRcode

all the interesting phenomena arise due to spin orbit coupling, which in general is a small effect that nevertheless can have drastic impact. Additionally, surfaces have to be treated for the interesting surface physics to appear. This requires a modeling by thick films, typically containing of the order of 100 inequivalent atoms.

Fortunately, the evolution of computer power comes to the rescue by delivering faster architectures every year. This development was first stated by Moore who observed a doubling of the number of transistors on a chip roughly every two years [106], which is often referred to as *Moore's law*. As Dennard explained [107], the reduction in size of MOSFETs¹ allows for higher frequencies at constant power density, which in turn leads to higher computer power in CPUs. This so-called *Dennard's law* inevitably breaks down if the size of transistors reaches the atomic scale. By now, the atomic scale has become reality in devices – the latest smartphone models are the first commercially available devices using transistors fabricated with the 10 nm technology² [108]. Thus *Dennard's law* started to break down in the early 21st century [109]. This is mostly due to the so called power threshold that is crossed. With smaller transistors that operate at lower voltages and higher frequencies at some point power dissipation plays a major role since leakage currents become important [110, 111]. This raises the question of *energy-to-solution*³ in contrast to the *time-to-solution*⁴ that was initially the only bottleneck in high performance computing (HPC).

Empirical evidence for these trends show up in the *Top 500 list* that collects the performance data of the fastest 500 supercomputers in the world [112]. Figure 3.1 (a) shows the evolution of the peak performance⁵ from June 2005 to November 2016 for the fastest (#1) and slowest (#500) machine in the list as well as the sum of all listed HPC systems. An extrapolation of the performance of the fastest machine promises that at least from the hardware side the next milestone of the *exa-scale* era, i.e. machines that are capable of doing 10^{18} floating point operations per second, will be reached around the year 2020.

Figure 3.1 (b) shows some details of the supercomputer architectures that comprise the *Top 500 list*. Shown is the number of cores per node⁶ averaged over all 500 systems in the list between 2006 and 2016. While in 2006 almost all of the systems consisted of single or double core CPUs (cf. pie chart inset in Fig. 3.1 (b)), by 2016 the average HPC system had 13.1 cores per node and, as the pie chart inset shows, a large diversity among the systems in the *Top 500 list* exist.

It is clear that, although computing power still increases and roughly doubles every 1.8 years, this can only be achieved by increasing parallelism in the HPC architecture and not by a doubling of frequency or more generally performance of a single core. In fact the clock speed of the single cores on modern CPUs did not increase significantly over the last decade [111]. Therefore after Dennard's law broke down the speedup in computer power can almost solely be achieved through parallelism. But this challenges us to evolve our methods and our

¹metal–oxide–semiconductor field-effect transistor: typical transistor technology.

²Note that for a lattice constant of Si (5.5 Å) this means that less than $\frac{10 \text{ nm}}{5.5 \text{ Å}} \times 4 \approx 73$ (the factor 4 comes from 4 atomic layers per unit cell) atomic sites are needed to cover a length of 10 nm.

³i.e. the amount of energy that is needed to operate a supercomputer for the time needed to finish a specific calculation

⁴i.e. the wall-clock time, which the user has to wait until a specific calculation is finished.

⁵The peak performance is measured with the LINPACK benchmark which gives the number of floating point operations done per second (flop/s).

⁶A detailed description of cores, nodes etc. follows in section 3.1.1.

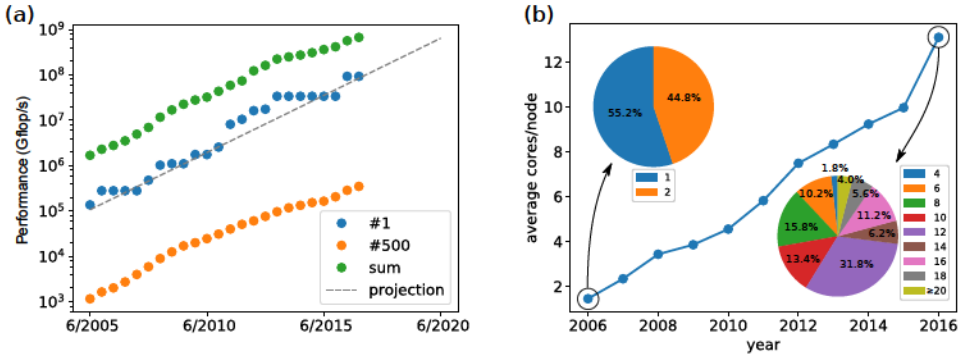


Figure 3.1.: Peak performance (a) and average number of cores per node (b) of the high performance systems listed in the *Top500* list between July 2005 and November 2016. The next milestone of the exaflop/s regime will be reached around the year 2020 which is due to an increase in parallelism in the computer architectures. The pie chart insets in (b) show a detailed view of the system's cores per node for the years 2006 and 2016. Whereas in 2006 only one and two core systems were available, in 2016 the systems in the *Top500* list comprised of nodes with 4 to more than 20 cores per node. Data taken from [112].

software to keep up with the developments on the hardware side.

3.1.1. The state of the art in HPC architecture and parallel programming models

To discuss the details of the parallelization and the challenges that arise in practice we shortly review the state of the art architecture of HPC systems and discuss programming models for parallel computers. In this section we generally follow the good overview given in Refs. [110] and [113].

Modern high performance computers are massively parallel systems that offer the possibility to use thousands or even millions of processors in parallel in one single application. A schematic image of such a cluster architecture is given in Fig. 3.2. It shows the hybrid distributed-shared memory setup. Typically clusters mostly consist of general purpose CPUs⁷. Several CPUs, in this context also called *processors* or *cores*, that share the same memory are grouped together into a common *node*. These nodes are typically of the *cache-coherent non uniform memory access* (cc-NUMA) type which means that the different cores can access all of the memory within one node without losing coherence of the data. Within one node this is the so called *shared memory* architecture. Then several of such nodes are linked together with specially designed high performance *interconnects*. Via the interconnect a process that is physically located on one node can communicate data to another process that is located on a different node. This procedure is a realization of the so-called *distributed memory* architecture.

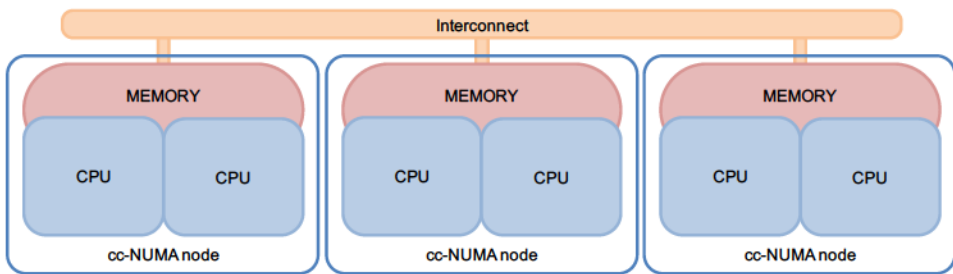


Figure 3.2.: Sketch of a typical hybrid distributed and shared memory architecture. In this example each cc-NUMA node consists of two CPUs (cores) that can access the same memory within the node. Communication between nodes is done via a network interconnect.

This architecture supports several levels of parallelism [110]. The different levels can be classified in the following hierarchical order:

1. **Instruction-level parallelism (ILP):** Multiple instructions can be executed in parallel by a single core. A good compiler can exploit this (architecture dependent) level of parallelism.
2. **Data-level parallelism (DLP):** Single cores can treat not only single numbers but whole vectors to do an operation on the full vector in parallel using the *single instruction*

⁷Accelerators like cards from Intel's Knight's landing series or graphics cards will not be discussed in detail but are a possible field for future developments.

multiple data (SIMD) approach [110]. This is getting more and more important since the SIMD vector length increases with the most recent generation of CPUs. The compiler can detect parts of the code that vectorize well but additionally this can be tuned on the level of the source code.

3. **Thread-level parallelism (TLP):** Multiple *threads* are executed on a single node to make better use of the cc-NUMA nodes. *OpenMP* [114] is a well established programming model to make use of this level of parallelism.
4. **Process-level parallelism (PLP):** The highest level of parallelism where several processes, often called *ranks*, are executed in parallel. These can reside on the same node with shared memory or on different nodes with distributed memory since each process works on its own address space (i.e. own part of the memory) and communication between the processes has to be done explicitly. The *message passing interface* (MPI) [115] implements this programming model.

In this thesis only the last two levels are considered because the first two are very hardware-specific and optimization in this direction is less portable than developments on the higher levels. Furthermore, the higher levels of parallelism have the biggest impact if compared to a serial version of a program. Note that here we defined threads and ranks that will from now on stand synonymic, respectively, for the OpenMP and MPI level in the here implemented hybrid OpenMP/MPI parallelization scheme.

The MPI programming model for distributed memory parallelization

Before continuing with the sections on parallel performance and the implementation in the *KKRcode* we take a side note to review the MPI programming model for distributed memory parallelization. This shall serve as a definition for the MPI related terminology that will be used in the remainder of this chapter. Also, possible caveats for parallel performance are briefly discussed.

The message passing interface was designed for distributed memory parallelization. The idea behind it is that several processes execute the same code⁸ within their private address space. The processes are called *ranks* that can be distributed over one or several nodes of a compute cluster. After initialization the ranks are numbered starting from 0 to $N_{ranks} - 1$ and can be identified unambiguously. Then the distribution of work as well as communication of data between ranks has to be implemented explicitly. Ranks can be grouped into so-called *communicators*⁹. With these communicators *collective communication* routines like the *all-to-all* communication that transfers data between ranks can be used. For instance, this is used where all ranks of one communicator fill different parts of an array that has to be available in a second step to all ranks to continue the calculation. Typically such routines are *blocking*, which means that a *barrier* is implied for the ranks until all ranks successfully exit the communication routine.

Barriers force ranks to wait for others. If the workload of one or more ranks of the communicator differs from the rest of the ranks, then at some point some ranks have to

⁸The ranks are assumed to to very similar jobs in the sense that in a loop that is parallelized the different iterations of the loop are executed by the different ranks.

⁹The communicator over all ranks is called *MPI_COMM_WORLD*.

3. Parallelization of the KKRcode

wait for the ones with the highest workload¹⁰. This is a problem called *load imbalance* that poses a common challenge in parallel programs. It leads to increased overhead of the parallel program which reduces the parallel efficiency¹¹.

The OpenMP programming model for shared memory parallelization

After introducing the MPI programming model we briefly review the OpenMP programming model for shared memory parallelization and define the OpenMP related terminology for the rest of this chapter. The OpenMP programming model was designed for shared memory parallelism and gains importance in today's HPC computing since the nodes in modern computer architectures have an increasing number of cores per node. This can be seen in Fig. 3.1, for example.

OpenMP is a directive based programming model that is designed to minimize the programming and development overhead as compared to the explicit MPI parallelism. It is based on *threads* that are basically lightweight versions of processes [113]. A number of threads that can be controlled easily by environment variables when running the program are spawned when an *OpenMP parallel region* is encountered, which is defined by *directives* in the source code. Every thread can access the same memory locations as the other threads if no private copies of variables have been defined. *Synchronization* between the memory locations that were accessed by different threads is done automatically which implies that *barriers* are implicitly included here as well.

Typical problems with OpenMP parallelized programs occur when *race conditions* appear. This is the case when a thread changes the memory that is then accessed by a second thread. If the second thread retrieves some information from the memory location that is previously supposed to have been changed by the first thread, which might not have arrived at this point yet, then the wrong data is processed by the second thread. This is called a race condition that can lead to wrong outcomes. To ensure that no race conditions are present in the hybrid OpenMP/MPI version of the KKRcode we checked the program with the *Intel Inspector* [116] that allows to find race conditions and other OpenMP related issues.

3.1.2. Parallel performance and scaling laws

Next we are taking a look at how the performance of a parallel application can be measured and what the central caveats and challenges are in achieving a well parallelized application with scalable performance. It is worthwhile to focus the comparison on the time it takes for a computer code to finish a calculation. In the context of this thesis a representative computation is a single iteration in the self-consistency cycle of a DFT calculation. The time $T_p(n)$ needed to finish this step in the parallel version using a certain number n of processors can be compared to the time T_0 using only a single processor. Then the *speedup* can be defined as the ratio

$$S(n) = \frac{T_0}{T_p(n)}. \quad (3.1)$$

¹⁰This is assuming that all ranks, i.e. processes executed possibly on different nodes, are equally fast so that the time needed to finish a certain task of certain size is proportional to the workload of the task. This assumption is valid on today's HPC architectures.

¹¹Cf. section 3.1.2

The scaling, i.e. evolution of the speedup with the number of used processors, is theoretically determined by Amdahl's law, which is introduced in the following side note.

Amdahl's law and strong scaling

Generally not 100% of a code can be parallelized because typically some initialization, e.g. read-in of data, and some overhead, e.g. due to communication between ranks or threads, have to be done. If f is the fraction of code that can run perfectly in parallel so that the time needed to finish the parallelized part with n processors is reduced by a factor $1/n$ as compared to running in serial, then the total time needed for the parallel execution can be split into serial and parallelized parts. This can be written as

$$T_p(n) = \left(\underbrace{1-f}_{\text{serial part}} + \frac{f}{n} \right) T_0 \quad (3.2)$$

which assumes that overhead can be neglected [117]. From here the speedup is given by *Amdahl's law* [118]:

$$S(n) = \left(\frac{f}{n} + 1 - f \right)^{-1}. \quad (3.3)$$

It is obvious that even in perfect conditions where no overhead comes into play when parallelizing a program the maximal speedup can only be as high as $S_{\max} = \lim_{n \rightarrow \infty} S(n) = (1-f)^{-1}$. Thus, when $f = 98\%$ of the code is running in parallel, still only a maximal speedup of 50 can be expected if compared to serial execution^a. Amdahl's law gives the limit for the so called *strong scaling* of the parallel application. The strong scaling is an upper bound of how fast a problem of a certain size can be solved, if only enough resources, i.e. computing power in terms of number of nodes and cores, are available. It gives important performance characteristics with major consequences for the scalability of an applications. In section 3.4.1 this is investigated for the parallelization of the *KKRcode*.

^aThe value $f = 98\%$ is the fraction of parallelism that the *KKRcode* had before this work started [119]. This was achieved in an OpenMP only parallelization and gave a maximal *measured* speedup of ≈ 9 for 12 threads.

Related to the speedup of a parallel executed code is the *parallel efficiency*

$$E(n) = \frac{S(n)}{n} \quad (3.4)$$

which is given as the quotient of speedup and number of used processors. The parallel efficiency goes to zero for large n because of the maximal speedup in the strong scaling characteristics dictated by Amdahl's law.

In 1988 Gustafson pointed out that the strong scaling behavior is not the ultimate measure of a parallel program [120]. Rather the possibility to use more resources to solve larger problems in the same time-frame should be considered. This was based on the empirical observation that the serial part of a parallelized application typically is a constant with respect to the system size. It refers to the assumption that only some small read-in of parameters and

3. Parallelization of the KKRcode

initializations has to be done before the actual calculation, which can still be done in parallel, can start. A description of Gustafson's law which introduces the weak scaling is given below.

Gustafson's law and weak scaling

Let us assume to have two systems; (i) a reference system with a certain workload, where the time to solve the problem with p processors is given as in Eq. (3.2) and (ii) a system with scaled workload^a which for n' processors can be done in the time $\hat{T}_p(n')$. Furthermore the time needed for a serial execution for the scaled workload shall be $\hat{T}_0$ so that we get following Eq. (3.2): $\hat{T}_p(n') = (1 - f)\hat{T}_0 + \frac{f}{n'}\hat{T}_0$. The serial part for the scaled workload is now assumed to stay constant and the parallelized part is assumed to scale proportional to the workload so that $f\hat{T}_0 = n'fT_0$. The execution time for the scaled workload can then be written as

$$\hat{T}_p(n') = \underbrace{(1 - f)\hat{T}_0}_{(1-f)T_0} + \underbrace{\frac{1}{n'} f \hat{T}_0}_{f n' T_0} = (1 - f)T_0 + fT_0 \quad (3.5)$$

from where it can be seen that the total execution time can be kept constant with a scaled workload. This in turn leads to a constant scaled speedup. This is referred to as the *weak scaling* characteristic of a parallel application. The weak scaling of the parallelized *KKRcode* is further elaborated on in section 3.4.1.

^aNote that the scaling behavior between system size and actual workload, i.e. number of floating point operation needed to solve a problem, depends on the algorithm. If for example a matrix has to be inverted then the workload typically increases with the cube of the system size so that for a system twice as large, eight times as many processors have to be used.

3.2. Implementation of hybrid parallelism in KKR

In this section the details of the parallelization of the *KKRcode* are explained. We point out where the parallelization can be introduced in the basic steps in the KKR formalism and explicate the parallel algorithm that is implemented here. First the *two level MPI* implementation is discussed on top of which the *OpenMP level* for hybrid OpenMP/MPI parallelism is reviewed. Finally, several performance characteristics of the implementation are shown and the weak and strong scaling behavior is discussed.

3.2.1. Parallelization scheme - levels 1 and 2: parallelization with MPI

To understand the two levels of the MPI parallelism implemented in the *KKRcode* we have to revisit the basic equations of the KKR formalism.¹² In a DFT calculation we are interested in the electron density which can be computed within the KKR formalism following three steps: (i) solve the single site problem, (ii) solve the Dyson equation for the structural green function and (iii) construct the Green function out of single site and multiple scattering parts

¹²Cf. chapter 2

to compute the density. These three steps typically consume 99.99% of the time of a single iteration¹³ as is indicated in Fig. 3.3. In the following equations, where the same notation as introduced in the previous chapter is used, the two levels of MPI parallelization are highlighted in **orange** for the atom/ k -point and **green** for the energy parallelization level, respectively.

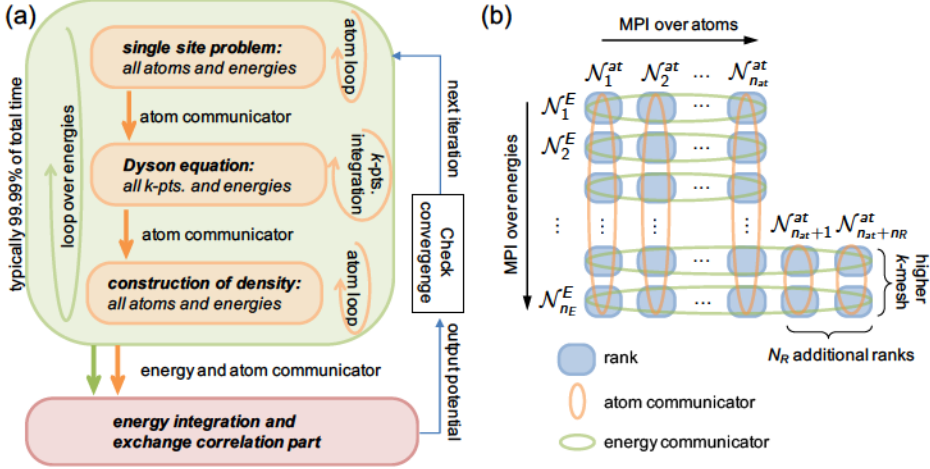


Figure 3.3.: Schematic view of the parallelism employed in the *KKRcode*. The major steps of a self-consistency iteration in the KKR formalism are shown in (a) together with the two MPI levels of parallelism (loops over energies or atoms(k -points) are indicated by green and orange arrows, respectively). Typically $\sim 99.99\%$ of the total time per iteration is spent in the part that can be parallelized straightforward. A detailed view on the *two-level MPI communication* scheme is shown in (b). Included are some additional ranks that are used to tackle the load imbalance problem in typical calculations.

Figure 3.3 (a) shows a schematic representation of the three steps in the KKR formalism where the two levels of MPI parallelism are indicated. The MPI standard also allows to define subgroups of ranks that are grouped together in so called communicators. Apart from the global communicator where all ranks can communicate to all other ranks we defined two *sub-communicators*; (i) the *energy communicator* where all ranks that work on a single or one group of energies can communicate and (ii) the *atom communicator* where all ranks that work on a single atom or a group of atoms can communicate the information of all energies. These sub-communicators allow the usage of collective communication routines of the MPI standard [115] that are very convenient in the usage and that are typically very well implemented and optimized on HPC systems, even taking some specifics of the design of the hardware into account. The choice for these communicators will now be discussed in detail.

The single site problem breaks down to the computation of wavefunctions or *scattering*

¹³The remaining 0.01% is the time needed for initialization etc. The timings for this example were taken from the test system T3 where 60 ranks were used to execute the test run. A detailed analysis of this test will be presented in section 3.3.3.

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solutions¹⁴ $\underline{\mathcal{R}}$ that can be computed from the analytically known reference Green function $\underline{g}^{\text{ref}}$ and the potential difference between atomic and reference potentials $\underline{\Delta V} = \underline{V} - \underline{V}^{\text{ref}}$ via the Lippmann-Schwinger equation:

$$\underline{\mathcal{R}}^\mu(x; E) = \underline{\mathcal{J}}^\mu(x; E) + \int dx' \underline{g}^{\text{ref}, \mu}(x, x'; E) \underline{\Delta V}^\mu(x'; E) \underline{\mathcal{R}}^\mu(x'; E) \quad (3.6)$$

where $\underline{\cdot}$ is a short hand notation indicating that $\underline{\mathcal{R}}$, $\underline{g}^{\text{ref}}$, the potential difference $\underline{\Delta V}$ [72, 73] and the Bessel functions $\underline{\mathcal{J}}$ are matrices in angular momentum and spin indices, typically of size 32×32 or 50×50 . This allows to compute the *atomic Δt -matrices*

$$\underline{\Delta t}^\mu(E) = \int dx \underline{\mathcal{J}}^\mu(x; E) \underline{\Delta V}^\mu(x) \underline{\mathcal{R}}^\mu(x; E). \quad (3.7)$$

It is clear that the wavefunction for each atom in the unit cell (μ) and energy point (E) in the complex energy contour can be computed independently from one another. The single site problem can therefore be independently parallelized over atoms *and* energies. Typically this step does not introduce a load imbalance in the computation because, firstly, all atoms in the unit cell have the same energy mesh, and thus the same number of energy points, and secondly the radial mesh usually differs only very little between different atom types.¹⁵

Once the atomic t -matrices are computed, the second step in the KKR formalism is the multiple scattering part. The goal is to compute the energy and atom dependent structural Green function that is given by the equation

$$\underline{G}_{i\gamma}^{\mu\mu'}(E) = \frac{1}{V_{\text{BZ}}} \sum_j w_j^k \underline{G}^{\mu\mu'}(\mathbf{k}_j; E) e^{-i\mathbf{k}_j \cdot (\mathbf{R}_i - \mathbf{R}_\gamma)} \quad (3.8)$$

where a k -point integration (written here in terms of the discrete sum $\sum_j$ with integration weights w_j^k), with typically $N_k = 20 - 40$ k -points per dimension in reciprocal space¹⁶ has to be performed for all energy points. The quantity $\underline{G}^{\mu\mu'}(\mathbf{k})$ satisfies the *Dyson equation* (where the atom indices μ were absorbed in the short hand matrix notation $\underline{\cdot}$ for simplicity of the notation)

$$[\underline{1} - \underline{g}(\mathbf{k}_j; E) \underline{\Delta t}(E)] \underline{G}(\mathbf{k}_j; E) = \underline{g}^{\text{ref}}(\mathbf{k}_j; E) \quad (3.9)$$

which is solved numerically for each pair $(\mathbf{k}_j; E)$ of k - and energy points. Note that all energy points can still be treated independently, which implies that the energy level of parallelism can be used here in the same way as it is done in the single site part. However, the Dyson equation couples the atomic Δt -matrices of different atoms. This implies that for a given energy point an *all-to-all communication* has to be performed within the energy communicator so that all ranks that work on the same energy point (or group of energy points) have access to all atomic Δt -matrices (i.e. for all μ) at this particular energy.

The structure of Eq. (3.8) suggests that the second parallelization level (over atoms) in the single site part can be used to parallelize the k -point integration highlighted in orange colors

¹⁴Here only the equation for the regular right solution is shown. The irregular solution and the left solutions for regular and irregular wavefunctions can be computed analogously as is discussed in section 2

¹⁵As a worst case example the test system *T3* (cf. Tab. 3.1) could be considered where in the slab geometry large elements such as Bi together with empty cells in the vacuum region have to be treated. This finally leads to negligible load imbalance as can be seen in the trace analysis presented in section 3.3.3.

¹⁶i.e. typically N_k^2 in 2D and N_k^3 in 3D.

in Eq. (3.8) in the computation of the structural Green function. Of course, the integration over k -points is discretized so that the integral becomes a discrete sum which finally needs another collective communication over the energy communicator. This is indicated in Fig. 3.3 (a). Here it is worthwhile noting that, in order to achieve the same accuracy in each energy point, the k -integration for different energies demand different densities of k -points. The complex energy contour¹⁷ that is used in the energy integration in the KKR-GF formalism starts at $E = E_B$ on the real axis, then goes up into the imaginary plane and parallel along the real axis along $E = \epsilon + i\eta$ for $\epsilon, \eta \in \mathbb{R}$ where a large majority of the total number of energy points have the same imaginary part, and then comes down to the real axis at the Fermi energy [121]. The Green function $G^{\mu\mu'}(\mathbf{k})$ now consists of poles on the real axis which become smeared-out Lorentzians away from the real axis [121]. The width of each Lorentzian is proportional to the imaginary part of the energy which implies that that a lower density in the k -point integration mesh is needed for all points on the energy contour that are far away from the real axis. Only the very few energy points that are close to the real axis, i.e. at $E = E_F + i\eta$ with small η , need a fine k -mesh. In a typical calculation 3 – 6 different k -meshes are used that may differ by an order of magnitude in the number of k -points, between the least and most dense integration mesh. This introduces a load imbalance between different energy points. The actual significance of this load imbalance depends strongly on the system as the ratio of the time needed for the Dyson equation and the time needed to compute wavefunctions and Δt -matrix from the single site problem are system dependent.

For systems where the load imbalance due to the k -point integration becomes a problem, the possibility to use a number of ranks that is incommensurate to the number of atoms and energies is implemented. Suppose that the number of ranks used for the calculation is N_{ranks} which are divided into n_E energy groups and n_{at} atom groups. If N_{ranks} is larger than the product of energy and atom groups then $N_{rest} = N_{ranks} - n_E \cdot n_{at} > 0$ ranks are freely available. These ranks are added to the groups of energies that have a higher k -mesh to speed up the calculation in the part where the structural Green function is computed via k -integration. This is depicted in Fig. 3.3 (b). In practice, most energy points will have the same coarse k -mesh and only the last one or two points have a significantly finer k -mesh. The quality of the approach that was implemented here to tackle the load imbalance problem is further analyzed in section 3.3.3.

The last step within the energy-loop of the KKR-GF formalism is the construction of the density from single site and multiple scattering parts of the Green function $\underline{G}(\mathbf{x} + \mathbf{X}_n, \mathbf{x} + \mathbf{X}_n; E)$ [$\mathbf{X}_n = \mathbf{R}_i + \mathbf{x}_\mu$ with lattice vector $\mathbf{R}_i$, sublattice vector $\mathbf{x}_\mu$ and the combined index $n = (i, \mu)$]:

$$\underline{\rho}^\mu = -\frac{\text{Im}}{\pi} \text{Tr} \sum_j w_j^E \overbrace{\left[\underbrace{\sqrt{E_j} \int d\mathbf{x} \underline{R}^\mu(\mathbf{x}; E_j) \underline{H}^\mu(\mathbf{x}; E_j)}_{\text{single site}} + \underbrace{\int d\mathbf{x} \underline{R}^\mu(\mathbf{x}; E_j) \underline{G}_{ii}^{\mu\mu}(E_j) \underline{R}^\mu(\mathbf{x}; E_j)}_{\text{multiple scattering}} \right]}^{\underline{G}(\mathbf{x} + \mathbf{X}_n, \mathbf{x} + \mathbf{X}_n; E_j)}. \quad (3.10)$$

where the energy integration is written as a discrete sum ($\sum_j w_j^E$ with integration weights w_j^E) over typically 30-50 energies and the trace sums over the large and small components of

¹⁷A more detailed description of the energy integration and the complex energy contour used within the KKR-GF formalism can be found in section 2.2.

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the Dirac 4-vector. The wavefunctions of the single site problem together with the structural Green function can be collected for each pair (μ, E) of atoms and energies independently which implies that this step can be done in the same parallelization as the single site part. For the energy integration and further post processing, e.g. creating the output potential from the density and check for convergence of the self-consistency iteration, all of the results have to be collected. Thus two calls of MPI communication routines are needed; first to perform the communication over the atom communicator for the energy integration and secondly over the energy communicator to have the information of all pairs of atoms and energies available.

In earlier versions¹⁸ of the *KKRcode* all of the wavefunctions that were computed in the single site part to compute the t -matrix were not stored, but recalculated in the construction of the density because of memory storage demands.¹⁹ Due to the two-level MPI parallelism that was introduced, the total memory that is available in a calculation is distributed over several ranks and nodes so that the wavefunctions can indeed be stored and reused. This gives an additional speedup up to 40% as compared to the old version.²⁰ The current version that will be discussed in the following is *KKRcode* v2.2.

3.2.2. Parallelization scheme - level 3: parallelization with OpenMP

The two-level MPI scheme of parallelization allows us to maximally use the number of atoms times the number of energies as MPI ranks in the calculation.²¹ For typical small to large system sizes of 1 – 200 atoms in the unit cell and 20 – 60 energy points this means that 20 – 12000 ranks can be used in the MPI levels to speed up the calculation. As we have seen from the analysis of HPC systems in the *Top500* list the way to go is to increase the parallelism in the applications. To further increase parallelism – exceeding this two-level MPI specific threshold – hybrid parallelism via shared memory OpenMP on top of the distributed memory MPI levels is needed. A sketch for this hybrid three-level parallelism scheme is given in Fig. 3.4. Suppose a HPC system is a cluster of nodes where a single node consists of N_{proc} processors per node. Each MPI rank has the possibility to spawn OpenMP threads to speedup the calculation. Then it is possible to divide the MPI ranks in such a way that only a single rank is allocated to one node. Compute intense parts can then be accelerated on this node by using the *fork-join* model of OpenMP as shown in Fig.3.4 (b) and (c). If for example a loop has to be executed where each iteration in the loop is independent of the other iterations, then this loop can be parallelized and the time needed to finish this specific part of the work can be diminished. This can lead to an additional speedup on top of the one given by the

¹⁸Before v2.0-38-g6593f48. Note that the version number consists of the version tag (v2.0 in this case), and a serial number indicating uniquely which specific commit is referred to. In the following only the version tag will be referred to, since with an increment of the tag only the major steps in the development are indicated.

¹⁹Typically a single wavefunction needs 15-20MB per atom in the unit cell and energy point to be stored. This quickly blows up to 75-100GB for typical values of 50 energy points and 100 atoms.

²⁰For the t -matrix two wavefunctions (regular and irregular right) whereas for the recalculation of the density three wavefunctions (regular, regular left and irregular left) per energy and atom are computed. Thus the speedup can be as high as $\frac{3}{2+3} = 40\%$ if the k -integration part is much faster than the computation of the wavefunctions.

²¹Here we neglect the load imbalance by the k -point mesh and that a small number ranks are beneficial to solve this problem. This additional number is typically much smaller than $N_E \cdot N_{at}$.

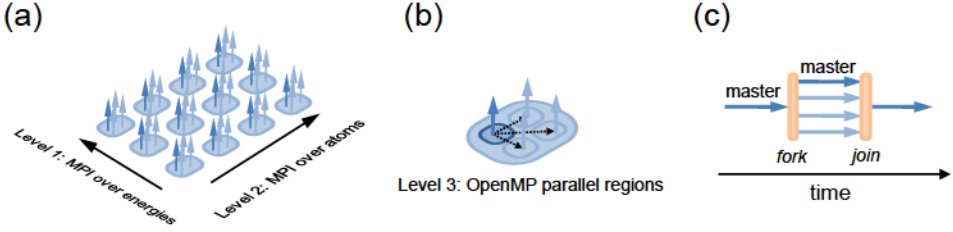


Figure 3.4.: Sketch of the hybrid OpenMP/MPI implementation. The two levels of MPI are shown in (a) as a grid of nodes in the xy -plane with the third level (OpenMP) indicated by the arrows pointing in z -direction. A closeup of a single node showing the OpenMP level of parallelism (level 3) is displayed in (b). Panel (c) shows the *fork-join* programming model of parallel computation as it was introduced with the OpenMP standard.

MPI level of parallelism. For the same setup as discussed above ($N_E = 60$, $N_{at.} = 200$) and 2-12 threads that can be used efficiently²² by each rank, up to $N_{ranks} \cdot N_{threads} = 144000$ processors can be used which brings the code to a *massively parallel* level.

The OpenMP level of parallelism that was introduced in the *KKRcode* is sketched in Fig. 3.5. As it is depicted here, most of the time needed to one iteration is typically spent in the part that calculates the wavefunctions (routine called `r11s11`). This typically sums up to 70-80% of the total time. This routine was first parallelized by Sachin Nanavati with whom I collaborated on the OpenMP parallelization discussed in this part of the work. In this older version of the *KKRcode* other parts of the code – especially the routines `g1113` and `kkrm1` – an automatic OpenMP parallelization was used for the LU-decomposition in the Dyson equation by linking the threaded LAPACK library²³ which allows to automatically speed up all matrix-matrix operations.

However, the typical matrix size for matrix-matrix multiplications as they appear for example in the Dyson equation²⁴ is quite small; for a typical ℓ_{max} cutoff value of 3 and one atom per unit cell, square matrices of size 32 have to be handled, but the matrix-matrix multiplications of these small matrices have to be done thousands or even millions of times. Even in the case of films with tens or hundreds of inequivalent atomic layers, the principle layer technique [72, 73, 122, 123] breaks down the problem to typically not more than 10 atoms per principal layer, resulting in small matrices of the order of 320×320 in size. This makes the automatic parallelization by threaded LAPACK libraries not very efficient since they cannot reach peak performance at such small matrices. Thus, by automatic parallelization only, effectively not more than 70-80% of the code is therefore running in parallel on the OpenMP level which according to Amdahl's law gives a maximal speedup of 3-5.

The fraction of code that can run in parallel has been improved further during this thesis. In the current version the missing parts, namely `g1113` and `kkrm1`, were parallelized explicitly with OpenMP directives. This increases the fraction of parallel code so that a 60% higher

²²Cf. Fig. 3.11 and the discussion on the OpenMP speedup

²³Using the option `-lmkl_intel_thread` instead of `-lmkl_sequential`

²⁴Cf. equation 3.9

3. Parallelization of the *KKRcode*

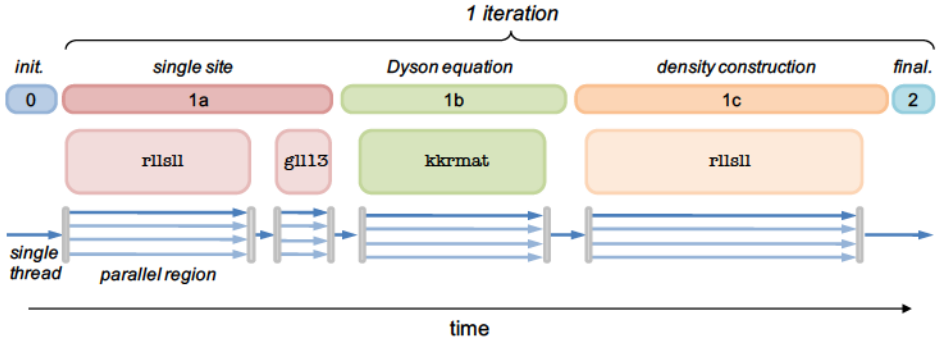


Figure 3.5.: Detailed view on the OpenMP parallelized regions of the *KKRcode*. A single iteration is shown schematically for a single MPI rank which represents the workload every single MPI rank has to do within the three level parallelism scheme. In the single site problem (1a) two parts are done; the calculation of the wavefunctions in `rllsll` and the construction of the reference green function in `glll3`. The Dyson equation is solved in `kkrmatt`. This schematic image assumes that the wavefunctions are recalculated and not stored so that in the construction of the density (1c) again `rllsll` is executed. The parts that are explicitly parallelized using OpenMP are indicated in the lower row.

performance²⁵ of the OpenMP level could be achieved.

A detailed analysis of the performance of the two levels of MPI as well as the third level of OpenMP parallelization will be done in the following sections.

3.3. Performance of the two-level MPI parallel implementation in the *KKRcode*

Before we delve into details of the performance analysis we quickly mention the methods used to evaluate the performance of the parallel program. First, we discuss a trace analysis of the different MPI level. Using tools like *Score-P* [124, 125] and *Vampir* [126, 127] a parallel program can be executed for a test system while performance data such as the time spent in a certain routine or the time needed for MPI communication is tracked. Such a trace gives valuable information about the internals of a parallel program and allows to identify bottlenecks of the parallelization such as load imbalances. Using these tracing tools always come at the price of some overhead so that this analysis is limited to small and medium sized systems.

Secondly, execution times measured for realistic systems are compared and the strong- as well as the weak-scaling behavior is discussed. The test systems used in this part are described in Table 3.1 where the most important parameters of the calculation as well as

²⁵Cf. section 3.4.2 on the OpenMP speedup of the `rllsll`-parallelized-only version as compared to the new hybrid version.

information of the system's hardware, where the test was executed, are collected.

Table 3.1.: Description of the test systems that were used to generate the data shown in Figures 3.6 to 3.11. $T1$ and $T2$ are small test systems that represent ideal cases for energy and atom parallelization, respectively. The systems $T3$, $S1$ and $S2$ consist of realistic parameter sets for typical calculations and H is a system chosen to demonstrate the hybrid OpenMP MPI parallelization with an emphasis on the OpenMP level - thus only with two energy points are used. ℓ_{max} is the angular momentum cutoff, N_{at} the number of inequivalent atoms in the unit cell, N_E the number of point in the energy contour, N_k the density of the maximal k -mesh [121], N_{at}^{cls} the number of sites in the cluster for the reference Green function [73], N_{pan} the number of panels and N_{cheb} the degree of the Chebychev polynomials used in the radial mesh [61].

ID	System description	Calculation parameter						
		ℓ_{max}	N_{at}	N_E	N_k	N_{at}^{cls}	N_{pan}	N_{cheb}
$T1$	NbP thin film	2	24	24	5x5	149	20	12
$T2$	NbP thin film	2	24	24	30x30	83	20	12
$T3$	Bi ₂ Te ₃ 6QL thin film	3	72	58	20x20	65-77	20	12
$S1$	Bi ₂ Te ₃ 6QL thin film	3	72	50	30x30	65-77	20	12
$S2$	Au(111) thin film	3	1-16	32	30x30	79	24	17
H	NbP thin film	3	10	2	30x30	149	20	12

System ID	N_{ranks}	$N_{threads}$	execution host
$T1$	24	-	RWTH-CLX ²⁶
$T2$	24	-	RWTH-CLX ²⁶
$T3$	58-72	-	RWTH-CLX ²⁶
$S1$	1-3650	-	RWTH ²⁷
$S2$	16-1024	-	RWTH ²⁷
H	1-20	1-10	viti-node ²⁸

3.3.1. Trace analysis of level 1 - MPI: parallelization over energies

We start by analyzing the parallelization of the first MPI level – the parallelization over energies. As a test case for the trace analysis a NbP thin film with 24 energy points in the

²⁶CLAIX partition of the RWTH compute cluster: Intel Broadwell EP E5-2650v4 CPUs running at a clock speed of 2.2Ghz with 24 cores per node and 128GB memory. Further information: <https://doc.itc.rwth-aachen.de/display/CC/Hardware+of+the+RWTH+Compute+Cluster>

²⁷MPI-S and MPI-L partition of the RWTH compute cluster: Intel Westmere X5675 CPUs, 12 cores per node, 3.07Ghz clock speed and 24GB or 96GB memory, respectively. Further information: <https://doc.itc.rwth-aachen.de/display/CC/Hardware+of+the+RWTH+Compute+Cluster>

²⁸viti_node partition of the PGI-inhouse cluster iff003: Intel Xeon E5-2680v2 CPUs, 20 cores per node, 2.80 Ghz clock speed and 128GB memory. Further information: <https://pgi-jcns.fz-juelich.de/portal/pages/clusterview.html>

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complex energy contour and 24 atoms in the unit cell was chosen (system *T1* of Tab. 3.1). The system was selected to have a representative case where the energy parallelization is supposed to work well, i.e. a system with negligible load imbalance due to the small number of k -points.²⁹

Figure 3.6 shows the result of this analysis. In panel (a) the trace data of all ranks is shown over execution time. The different steps in the calculation can be identified; in the beginning the initialization step is done by the master rank alone and the other ranks wait for this step to complete. As can be seen from (e) where the total time for the different parts is shown, this takes only 1.3 seconds. Then the information that the master rank has read in and prepared is communicated to all other ranks and the single site part (*1a*) starts. Here mostly the wavefunctions are computed which is done in the routine `tmat_newsolver`. This can be seen from the close up view of the trace data of the master rank and the last rank in (b) and (c) and the corresponding total times for the different parts of the code in (f) and (g), respectively. Then the Dyson equation is solved in the *1b* part. Only a negligible load imbalance is introduced which is reflected by the short red region at around 19 seconds where most ranks wait for a short time of less than 1 second for the last rank to finish the k -integration with the most dense k -mesh. The time spent for the construction of the density (*1c*) in this example is dominated by the (re)calculation of the wavefunctions.³⁰ The finalization step that is done in serial can also be spotted at the end of the trace and takes 1.3 seconds.

The trace analysis of the energy parallelization is summarized in panel (d) of Figure 3.6. The serial parts in initialization and finalization as well as the load imbalance in the Dyson equation only play a minor role. Note that the fraction of the total time that is spent in serial parts in realistic calculations is typically much smaller than for this small test system with $\ell_{max} = 2$. Especially when more self-consistent iterations are performed, the initialization procedure (here, the first 1.3 seconds by Thread 0) is only done in the first iteration and avoided in the others. Furthermore, we can identify the communication that is needed for the energy integration in the *1c* part. Between 20 and 42 seconds the `rhovalnew` part is clearly divided into 24 (this is the number of atoms in the system) segments and after each some communication has to be done. This leads to the red spikes seen in (d).

Overall, we can state that the implementation of the MPI level over energies works well. This can be seen in the ratio between green and red areas in the trace data which shows that only very little overhead (red regions) is introduced and the compute intensive parts (green/yellow regions) dominate. Also, we already identified the problem of load imbalance in the energy dependent k -integration that will be addressed later on.

²⁹The case of important load imbalance is discussed in section 3.3.3

³⁰In this example the option to save the wavefunctions pre-calculated in *1a* was not used.

3.3. Performance of the two-level MPI parallel implementation in the KKRcode

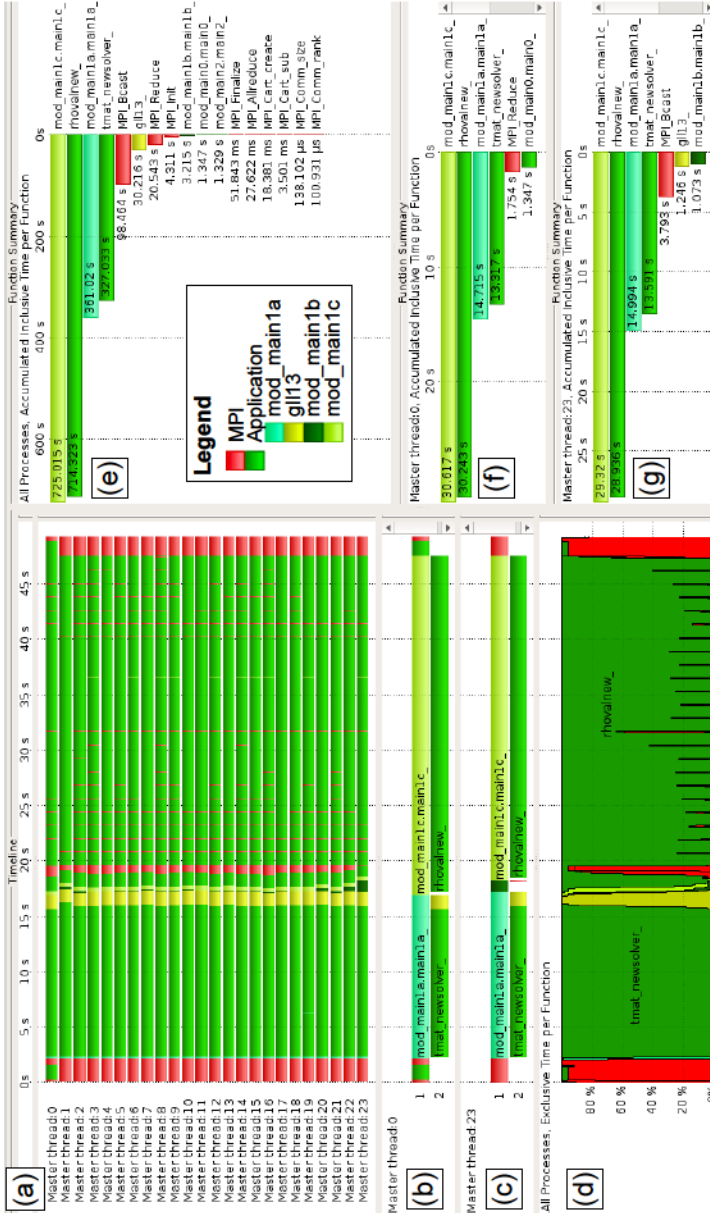


Figure 3.6.: Trace analysis, obtained with the *Score-P* [124, 125] and *Vampir* [126, 127] tools, of the distributed memory parallelization called level 1: MPI over energies. The test was run for the test system 71 as specified in Tab. 3.1. Shown is the trace data of all 24 ranks in (a), with more details on the time spent in the different parts of the code for master rank in (b) and last rank in (c). A summary for all ranks is shown in (d). The total inclusive time for all routines is shown in (e) as well as the contributions from the master (f) and last rank (g). The serial parts (red regions at beginning and end of trace, seen in the first and last 2 seconds) that come from unparallelized regions of the code (*main0*, *main2*) are clearly visible as well a small load imbalance (around 18 seconds runtime) in the solution of the Dyson equation (*main1b*). Green and yellow regions correspond to computation, red regions correspond to the idle time due to communication or waiting.

3.3.2. Trace analysis of level 2 - MPI: parallelization over atoms

After analyzing the energy level of parallelism we focus our attention on the second level of MPI parallelism that deals with parallelization over atoms (in *1a* and *1c*, single-site and construction of the density, respectively) or k -points (in *1b*, Dyson equation), respectively. Note that in this particular test the energy level of parallelization was deactivated to analyze the second MPI level of parallelism alone. Again, we performed a trace analysis that tracks the behavior of all ranks over the total execution time of a single iteration. Here, another test system (*T2* from Tab. 3.1) was used to highlight the atom level parallelism. For this test we chose a significantly higher number of k -points and a slightly smaller cluster radius for the screening cluster that mainly affects the time needed for the `g1113` part of the calculation. This is intended to highlight the load imbalance that we already saw in the discussion of the energy parallelization in the previous section. We can compare the time a test run takes with the same number of ranks when using atom or energy parallelization.³¹ In the case of the energy parallelization the total execution time of the parallelization over energies takes 77 seconds (not shown) whereas for the very same input using the parallelization over atoms one iteration finishes in 55 seconds. This is primarily due to the severe load imbalance that is reflected in the different time the first and the last rank need to complete the Dyson equation part in *1b*. For the energy parallelization the first rank needs 3.8 seconds and then has to wait for the last rank to finish this part which takes 29.5 seconds. This is not the case for parallelization over atoms where all ranks need exactly the same time of 7.6 seconds.

A detailed analysis of the trace data for the atom parallelization is presented in Figure 3.7. The same panels (a-g) as in Fig. 3.6 are shown in Fig. 3.7 that contain the trace of all ranks, details on the first and last ranks in a time resolved view as well as the total timings for the different parts. As before we can identify the serial parts in the initialization step and finalization step and the parallel code in between. We see a small load imbalance in the `g1113` part where only 4 out of 24 ranks are active. For this particular test system 4 inequivalent cells instead of 24 individual cells are found which is why 20 out of 24 ranks are idle while the reference Green function for the 4 inequivalent cells is being computed. Obviously, the number of inequivalent cells is system dependent and the parallelization over energies would work better for this part. However, the time spent in the `g1113`-routine is small compared to the total execution time. Especially if a mixture of atom and energy parallelization is used this load imbalance is further reduced. Thus, the load imbalance problem in the `g1113`-routine can be assumed to be small.

The most important change as compared to the energy parallelization is the behavior in the *1b*-part (solution of the Dyson equation). We see that all ranks need the same time to finish which comes at the cost of slightly increased MPI overhead because for each pair of atom and energies one communication over the energy communicator needs to be done to finalize the k -point integration. This overhead turns out to be negligible and the time that is saved due to better load balance is far bigger.

Overall, the trace analysis shows that the parallelization over atoms is comparable in performance to the parallelization over energies. This can again be seen in the ratio of red to green areas in the trace data which shows that only little overhead is introduced in the second level of MPI parallelization. Thus both levels of the MPI parallelization are well equipped for

³¹Note that the number of energy points and the number of atoms was chosen to be the same for this comparison to work well.

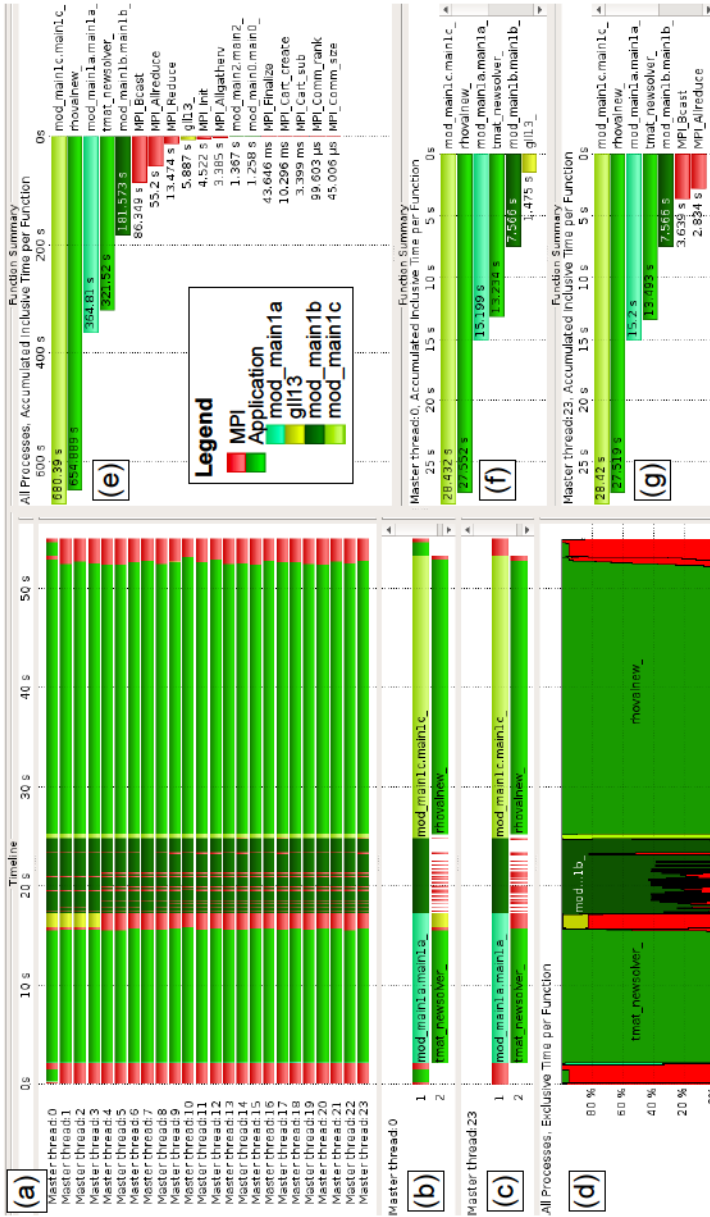


Figure 3.7.: Trace analysis of the second level of distributed memory parallelization called level 2: MPI over atoms. Panels are given in the same order as in Fig. 3.6. Details on the test system T2 are shown in Tab. 3.1. Here the only load imbalance is coming from the calculation of the reference Green function that has to be done for the non-equivalent clusters only and is therefore only parallelized over the number of clusters that is always less or equal to the number of atoms.

a joint two-level MPI parallelization including parallelization in both directions – atoms and energies. Only the problem of load imbalance because of the different types of k -mesh seen in previous section, needs to be addressed further.

3.3.3. The load imbalance problem

So far we have seen how the different MPI levels are implemented and how they perform for certain test cases. Now we want to move towards a more realistic case. Test system³² *T3* is a thin film system of 6 quintuple layers of the topological Insulator Bi_2Te_3 . This system has been studied in the main part of this thesis and poses a realistic challenge to the parallel implementation in the *KKRcode*. The load imbalance problem that comes about from the different k -mesh densities, used in the energy dependent k -point integration can be the main bottleneck for sufficiently high speedup in the parallel code version if the k -loop is performed in a serial way. Following Amdahl's law [118] we have to reduce the size of serial parts in the algorithm to get a program that scales well with the number of ranks that are used for the computation in parallel.

To examine this issue and show strategies to resolve it, we are considering the energy parallelization only because, as we argued in the previous section, the atom level of parallelization does not pose the same problem. The test system has 58 energy points (N_E) in the energy contour with 4 different k -meshes that differ in size by a factor 7.5 between the one with the highest and the one with the lowest number of k -points. In Figure 3.8 we compare the trace data of running a single iteration of the scf-cycle with 58 ranks shown in (a) and 60 ranks shown in (b), i.e. where $N_{\text{ranks}} = N_E + 2$ are used to reduce the load imbalance.

For both cases we see that the overhead in the initialization step and the finalization steps, seen as red vertical stripes in the trace data, are negligible. The execution with two additional ranks is $\Delta T \approx 71$ seconds faster than the original calculation with $N_{\text{ranks}} = N_E$. As can be seen by comparing Fig. 3.8 (a) and (b), this is coming from a reduction of the load imbalance in *1b*. The reduction of the load imbalance comes at the negligible cost that is introduced by the load imbalance in the additional ranks in the *1c* part where the groups of more ranks per energy point have to wait for those ranks that deal with this part by themselves. This can be seen at around 200 and around 550 seconds runtime. However, this additional overhead is negligible if compared to the total time saved by adding two ranks.

The efficiency of this approach and the trade off that has to be paid can be evaluated by looking at the total runtime needed (i.e. wall clock time) to complete the calculation and compare the time spent in the application (T_{App}) (green parts in the trace plots) with the time spent in MPI routines (T_{MPI} , overhead due to MPI, red parts in the trace data). This is presented in the inset Fig. 3.8 (c) for 0 to 14 additional ranks. The efficiency of the implementation that we measure with the ratio $T_{\text{App}}/T_{\text{MPI}}$ is initially, i.e. for $N_{\text{ranks}} = N_E$, at a value of 12.5 which can be increased to ~ 30 by taking $N_{\text{ranks}} = N_E + 2$. If more and more ranks are additionally used then the overhead due to the ranks that finish faster than the majority of ranks in part *1c* reduces the efficiency.

We have seen that taking a few additional ranks can speedup the calculation effectively by reducing the load imbalance problem. This allows to use available computational resources efficiently in terms of time-to-solution as well as energy-to-solution since no resources are

³²Cf. Tab. 3.1

3.3. Performance of the two-level MPI parallel implementation in the KKRcode

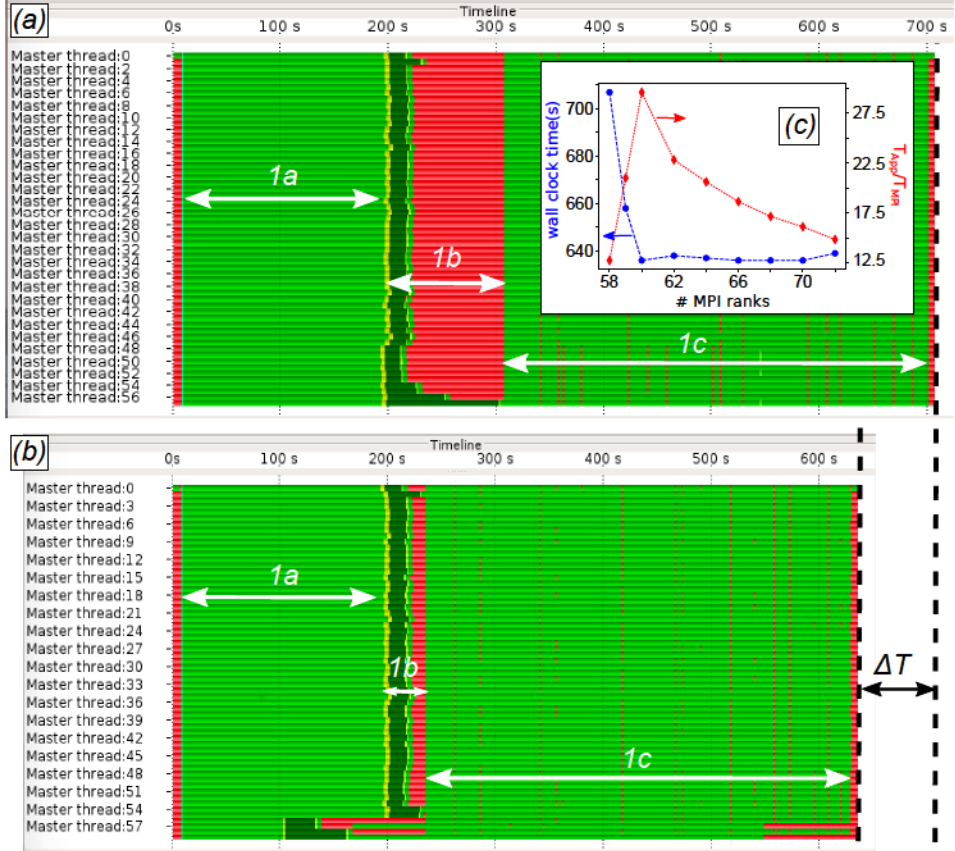


Figure 3.8.: Comparison of the load imbalance introduced by the non-equivalent k -meshes at different energy points of the complex energy contour for $N_{ranks} = N_E$ in (a) and $N_{ranks} = N_E + 2$ in (b). Test system $T3$ was used here and is specified in Tab. 3.1. The additional ranks used in (b) are automatically distributed to the last two energy points so that the load imbalance entering via the Dyson equation (1b) is reduced significantly. In inset (c) a comparison of wall clock time and MPI overhead is shown for N_{rest} ranging from 0 to 14. The trace data plotted in (a) and (b) correspond to 58 and 60 MPI ranks of the plot in (c), respectively.

3. *Parallelization of the KKRcode*

wasted by an inefficient implementation.

3.4. Strong and weak scaling behavior of the hybrid MPI/OpenMP parallelization

We conclude the chapter on the parallelization with a discussion of the strong and weak scaling characteristics of the parallelization in the *KKRcode*. For this, benchmark calculations have been performed with the systems *S1* for strong scaling, *S2* for weak scaling and *H* for the strong scaling behavior of the OpenMP parallelization level in the hybrid parallelization scheme. The systems are described in Table 3.1.

We compare this to the parallelism that preexisted in the old version of the *KKRcode* [119]. Previously a theoretical maximal speedup of ~ 50 was reached with an OpenMP level of parallelizing the computation over energy points. This parallelization was limited to shared memory architectures and the best *measured* speedup was ~ 9 on up to 12 threads.

As we will discuss in this section the measured maximal speedup that was achieved for the new implementation was ~ 2100 using 3600 MPI ranks which gives a good parallel efficiency of $\sim 60\%$ even at the highest possible level of MPI parallelism which shows the excellent performance. We would like to stress that this many processors could only be used with energy- and atom-parallelization simultaneously.

3.4.1. Parallel performance of the two level MPI: strong and weak scaling

First we discuss the strong scaling behavior. Figure 3.9 shows runtime (a) and speedup (b) for system *S1* which is a realistic test case of a Bi_2Te_3 film with 72 atoms in the unit cell and 50 energy points in the contour. The data was acquired for 1-3645 ranks, where N_{rest} was chosen such that the load imbalance is minimal. The blue and orange curves show the data for the scf-iteration part (called *iter.* in the plot which is the total time without the time for initialization that in a calculation with several iterations only has to be done a single time in the beginning) and the parallelized part (called *par.* that is the scf-iteration part without finalizing part that was not parallelized, i.e. only the parallelized parts of the code).

One iteration in serial mode runs for more than 17.5h. Keeping in mind that for such a system typically a number of iterations of the order of 100 are needed to reach convergence, the need for efficient parallelization is obvious, as waiting for 100 iterations would correspond to 73 days. With the two level MPI parallelization that is implemented here the runtime for a single iteration can be reduced below one minute if ~ 1800 ranks³³ or more are used in the parallel execution, reducing the total time to a little more than one hour. The benefit with respect to obtaining timely research results cannot be overstated.

Around $N_{\text{ranks}} = 1200$ several data points corresponding to $N_{\text{rest}} = 0$ to $N_{\text{rest}} = 45$ are plotted to illustrate the importance of dealing with the load imbalance problem. This is highlighted in the insets in the runtime and speedup plots. The data for $N_{\text{rest}} = 1 \dots 45$ additional ranks show that the speedup can be increased from ~ 700 to a value above 800 which means that a 15% speedup is gained at an additional cost of 1.5% additional processors.

The overall speedup curves in Figure 3.9 (b) show the very good strong scaling behavior of

³³For 50 energies and 72 atoms this means that each rank has to deal with two atoms and a single energy point which almost maxes out the capabilities of the two MPI parallelization levels.

3. Parallelization of the KKRcode

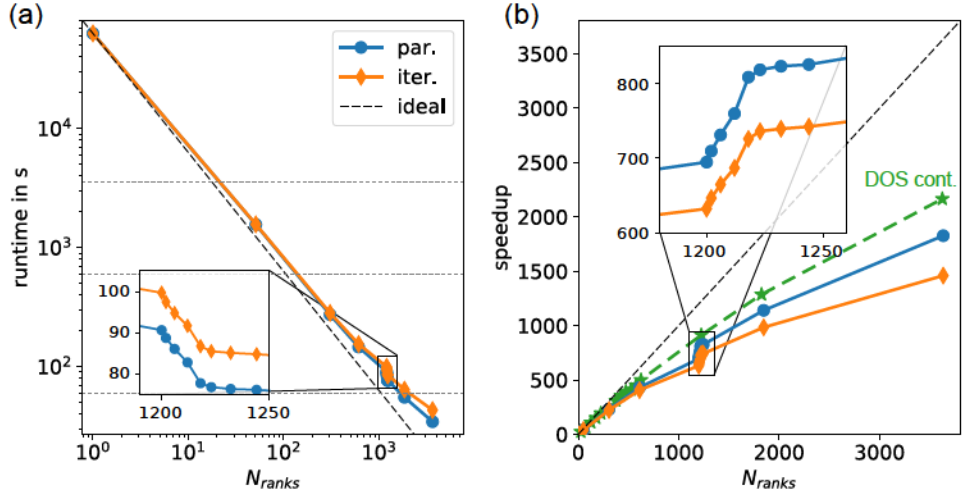


Figure 3.9.: Strong scaling characteristics of KKRcode v2.2. The test system used for this calculation was *S1* with energy contour as specified in Tab. 3.1. In (a) the runtime of the self-consistency iteration part (iter.) and parallelized part (par.) and, in (b) the corresponding speedup are shown. The gray horizontal lines in (a) show the threshold of 1 minute, 10 minutes and 1 hour of runtime. The insets in (a) and (b) show runtime and speedup obtained by taking 1-45 additional ranks for the N_{rest} -parallelization that tackles the load imbalance problem for a base parallelization around $N_{ranks} = 1200$. The load imbalance that occurs in the calculation using the energy contour is effectively reduced by taking 18 additional ranks. As a comparison, the green dashed line gives the speedup for a DOS contour where the load imbalance is absent by construction.

the implementation. The speedup curves only flatten very slowly as it follows from Amdahl's law with a very small proportion of the code that still runs in serial. The flatter curve for the total self-consistency iteration part that includes the serial part of the finalization steps highlights that for extreme parallelism every single bottleneck plays an important role. However, we should not forget that for that many ranks the regime where the time per iteration was reduced from 17.5 hours below 1 minute was already reached so that every second that is spent in a serial part reduces the possible speedup. The parallel efficiency is well above 40% even for the highest possible number of ranks which speaks for the quality of the implementation.

Additionally to the strong scaling with a *self-consistency energy contour*, i.e. the energy contour used in a self-consistency iteration with different k -meshes for different energy points, we can study a *DOS (density of states) contour*. The DOS contour is characterized by a straight line parallel and close to, but not exactly on, the real axis. This means that all energy points in the DOS contour have the same imaginary part of the energy which leads to a constant k -mesh in all energy points so that no load imbalance is coming from the Dyson equation. The green dashed line in Figure 3.9 (b) show the speedup as a comparison to the usual (self-consistency) contour. This is an improvement to the blue (par.) curve coming from the load imbalance problem alone. For less than 1200 ranks the different curves almost fall on top of each other, which highlights that the remaining load imbalance problem only plays a role for the extreme scaling case.

The very good performance in the strong scaling regime suggests that only very little overhead is introduced in the implementation which implies that a good weak scaling characteristics can also be expected. This is confirmed by the plot shown in Fig. 3.10 where the weak scaling characteristics are shown.

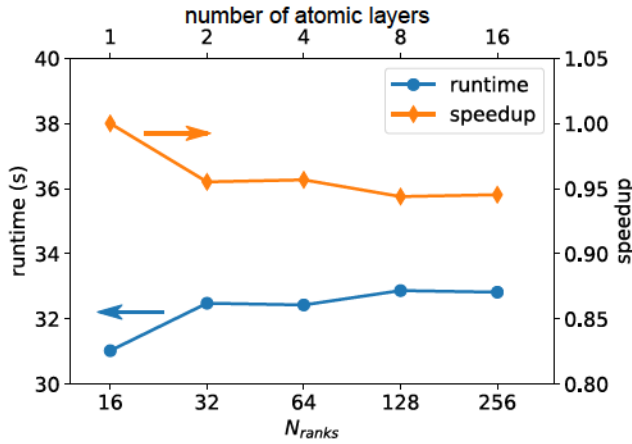


Figure 3.10.: Weak scaling characteristics of the two-level MPI version for test system S2 as specified in Tab. 3.1. A doubling of the system size (number of atomic layers in the film) and a simultaneous doubling of the number of ranks leads to an almost constant execution time (blue) and a speedup (orange) very close to the ideal value of 1.

3. Parallelization of the *KKRcode*

The KKR formalism is implemented in the *screened-KKR* version [73]. This offers the feature that in a film setup the computational cost only scales linearly with the number of layers that are included in a film. This is the ideal setup to test the weak scaling characteristics of the *KKRcode* as the workload in an iteration scales linearly with the number of layers. The weak scaling benchmark was performed for the test system *S2* that consists of a Au(111) film with an increasing number of layers. Linearly with the number of layers the number of ranks that were used in the computation was increased from 16 to 256 for 1 to 16 layers.

It can be seen that the time needed to finish one iteration stays almost constant if the system size is scaled with the number of layers in the thin film. Consequently the speedup stays almost constant with values above 95% which is an excellent performance. In conclusion we showed the excellent strong and weak scaling behavior of the new two level MPI implementation in the *KKRcode*.

3.4.2. The scaling behavior of the OpenMP level in the hybrid implementation

The last section of this chapter deals with the scaling behavior of the OpenMP level of parallelization. The test calculations were performed for the system *H* which consists of 2 energy points without load imbalance induced by the *k*-integration and for 10 atoms.³⁴ Note that this is not a physically meaningful calculation but it mimics the amount of work that is typically done by a single rank using the two-level MPI implementation. The node on which the test was executed contains 20 cores so that for 1, 2, 5, and 10 MPI ranks can be used without introducing a load imbalance due to non-commensurate division of work in the two levels of MPI. On the side of the OpenMP level 1 to 10 OpenMP threads were spawned by each rank. The results in terms of runtime and speedup are presented in Figure 3.11. Two versions of the code are compared; (i) the version *KKRcode* v2.0 where OpenMP was only included in the `r11s11` routine³⁵ in (a) and (b) and (ii) the improved version *KKRcode* v2.2 that include *explicit* parallelization in the `g1113` and `kkrm13` routines³⁶ in (c) and (d), respectively. The speedup is measured with respect to the calculation with a single OpenMP thread *per MPI rank* which is why we call it the *OpenMP speedup*.

While the speedup of the old version already starts to deviate from the ideal if more than two threads per rank are used, the improved version shows a linear scaling behavior up to four threads. This holds for one rank on the node and likewise for several MPI ranks on the same node that spawn OpenMP threads. We also see that in contrast to the version v2.0 in (b), the OpenMP speedup for one and two MPI ranks, plotted in (d), show an almost identical scaling. Overall the OpenMP scaling was improved by up to 40% so that now $\gtrsim 8$ threads per MPI rank can be used efficiently.

³⁴Cf. Tab. 3.1

³⁵Done by Sachin Nanavati in the `r11s11`-routine with automatic parallelization due to threaded MKL libraries in the rest.

³⁶Cf. section 3.2.2 and Fig. 3.5

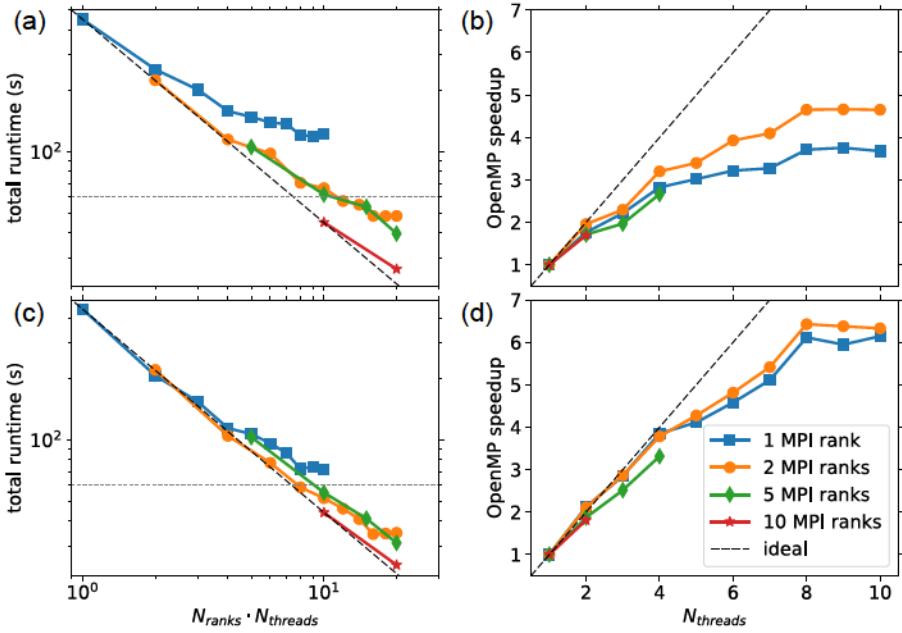


Figure 3.11.: Parallel performance of the hybrid two-level MPI+OpenMP code version for test system H as specified in Tab. 3.1. (a) and (b): runtime and OpenMP speedup, defined as $\frac{T_p(N_{\text{threads}})}{T_p(N_{\text{threads}}=1)} \Big|_{N_{\text{ranks}}=\text{const.}}$, of the version *KKRcode* v2.0, i.e. with OpenMP only in the `r11s11` routine. Panels (c) and (d) show the runtime and OpenMP speedup as (a) and (b) but for the improved hybrid version of *KKRcode* v2.2. An improvement of 20-40% was achieved by including more OpenMP parallel regions in 1a and 1b. Details can be found in the text.

3.5. Conclusions and outlook

In this chapter we first introduced the modern concepts in HPC architectures and parallel programming models. We showed that the continuous increase in parallelism on the hardware side in combination with the demand for ever larger systems demands increasingly parallel applications. In the main part the three levels of parallelism, that were introduced in the *KKRcode*, were explained and analyzed in depth. A trace analysis was performed for the different MPI levels of parallelism independently. Excellent strong and weak scaling could be demonstrated in both MPI levels as well as a significant improvement in the OpenMP level was achieved. It should be stressed that the test calculations in this chapter use the different levels of parallelism simultaneously, showing that the different MPI and OpenMP levels of parallelism work well together. Now the *KKRcode* is equipped for the age of massive parallelism. Instead of a single node with typically 12-24 cores, now theoretically more than 100000 processors could be used. This allows to compute the solutions to interesting physical problems faster and make the calculation of much larger systems than before possible.

In the future, further improvements of the parallelism could go in the direction to totally removing the load imbalance by restructuring the energy and k -loops that appear in the calculation of the structural Green function. Moreover, the strictly serial parts in the initialization- and the finalization step could be parallelized. Here the data input and output could also be parallelized with the use of parallel I/O as for example possible with MPI-I/O. Then new hardware concepts, for example the use of accelerators such as Intel's Xeon Phi co-processors or graphics cards, might be advantageous. The in this chapter developed three level parallelism should also be extended to the other codes of the *JuKKR* family of computer programs such as the *KKRimp* code [61] that allows to embed impurities into crystalline systems. Here, also an improvement of the algorithms that go beyond standard LAPACK routines and that are especially designed for parallel systems can be beneficial [128] as in the case of the impurity code the solution to the Dyson equation consists of large matrices.

Revealing scattering properties of topologically protected electrons off defects from first principles

During this thesis, scattering properties of surface state electrons off impurities embedded into the surface of the strong topological insulator Bi_2Te_3 have been studied for the first time from first principles. The analysis presented here gives valuable insights into the protection against backscattering for scattering off non-magnetic defects, and the mechanism of recurring backscattering for time-reversal breaking (i.e. magnetic) defects.

The quasiparticle interference (QPI) phenomenon allows to visualize scattering processes off impurities at surfaces and is experimentally accessible via scanning tunneling microscopy. Here, we present the theory of QPI images and compare different approaches to the computational treatment based on ab-initio calculations, which have either been used in the literature so far, or were new developments within this thesis. We find that the widely used joint density of states (JDOS) approach can be qualitatively wrong and improve the scheme by introducing the scattering rates, calculated for realistic impurities, into the picture. Additionally, the formally exact treatment of QPI images from first principles is developed and its importance is pointed out in comparison to the ad-hoc (JDOS-based) approach.

The results presented here led to the lecture notes published in Ref. [129], a submitted manuscript [130] and a collaboration (published in Ref. [131]) with the experimentalists group of Matthias Bode (Würzburg University). These results will be discussed in detail in the next chapter. Here, the general theory of impurity scattering and first applications of the newly developed tools are introduced and discussed.

4.1. Introduction

The visualization of standing waves around intrinsic defects on the (111) surfaces of Cu [132] and Au [133] was a groundbreaking achievement as it demonstrated that with the *scanning tunneling microscope* (STM), an experimental technique, that has atomic resolution, can give access to quantum oscillations in the electron density on a surface. For the first time the so-called *Friedel oscillations* [35] around defects, that are the result of interference of electrons traveling to and electrons that were reflected due to scattering off the impurity, could be seen directly.

The idea that a more intuitive access to the scattering phenomena of electrons off defects can be gained by taking the Fourier transform of the quantum oscillations on a surface as measured with STM, that was first presented by Petersen et al. [134], was the next major step forward. In the high- T_c superconductor research of Cuprates, the understanding of the *Fourier-transformed scanning tunneling spectroscopy* (FT-STs) was pushed forward with the development of the *T-matrix* approach [135] and the phenomenological *joint density of states* (JDOS) [136] interpretation of the experimentally accessible FT-STs data. This line of research is nowadays known as the *quasiparticle interference*¹ (QPI) and is a widely used tool in different areas of modern solid state research. Often the term quasiparticle interference synonymically stands for the oscillations in real space and their Fourier-transform in reciprocal space. Both quantities will be used and computed in the following. The importance of QPI in the last decades of solid state research is for example reflected in the number of citations to publications that can be found for on the topic “quasiparticle interference” [137], that shows an exponential increase as depicted in Figure 4.1.

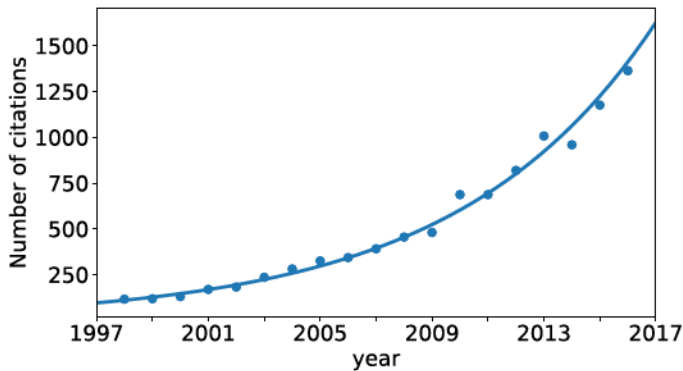


Figure 4.1.: Number of citations to publications on the topic “*quasiparticle interference*” in the field of solid state research for the past 20 years according to the ISI Web of Science [137]. An exponential fit (solid line) to the data points shows the exponential increase in the citations per year highlighting the increasing importance of the QPI technique in solid state physics.

¹In general this term refers to the interference effects of single-electron quasiparticle waves that occur in crystal due to elastic scattering off defects. In this thesis the term quasiparticle interference will refer to the electron density waves formed around impurities as probed with the STM.

In the surface state of topological insulators the spin is locked to its momentum, which has severe consequences on its scattering properties. Already in 2004 Pascual et al. [36] noticed that in such situations the quasiparticle interference is strongly affected and not connected in a simple way to the bandstructure of the system. In topological insulators, the spin-momentum locking frequently leads to the absence of backscattering, that was for the first time directly² seen in a QPI measurement on the dual strong 3D topological insulator $\text{Bi}_{1-x}\text{Sb}_x$ [37]. Complementary to the experimental observation, a number of theoretical calculations based on the T -matrix formalism were published (see for example Refs. [138–140]) that model the QPI features in TIs. The Bi_2Te_3 class of 3D strong TI materials obeys time-reversal symmetry (TRS), which leads to topological protection without backscattering being possible. The recurrent backscattering in the topological surface state if TRS is broken was then observed using FT-STs in Fe bulk-doped Bi_2Te_3 [39] and Mn surface-doped samples [40, 131]. The so-called *warping* term [141] in the band structure of Bi_2Te_3 , that deforms the Dirac cone having circular constant-energy contours in its simplest models to a hexagonal-like shape, leads to characteristic QPI signatures in $\overline{\Gamma K}$ -direction of the crystal occur if TRS is broken which can be related to the backscattering channel being activated due to the presence of magnetic scattering centers.

So far the understanding of scattering processes based on QPI data from experiment and model calculations only allows *qualitative* insights. For example, the strength of a magnetic moment needed to observably break time-reversal symmetry is not clear yet. This needs to be understood to interpret different seemingly contradicting experimental observations. Often the backscattering signal in the QPI images is very weak³ [39, 40] or even absent although the material was doped with magnetic impurities [143]. Only very recently, we could show⁴ that a large magnetic moment, as achieved by ferromagnetic coupling of a few impurities forming a *super spin*, is needed in addition to effective focusing by the Fermi surface to observe clear backscattering signals [131].

These examples make it clear that *ab-initio* calculations are needed, since only then a realistic description of the electronic structure of the surface and more importantly of the impurity embedded into the host system can be achieved. The importance of a correct self-consistent description of the charge density relaxations at the impurity site cannot be overstressed as it affects the impurity's scattering phase shifts⁵ and spin-orbit strength.

The outline of this chapter is as follows. As scattering off defects is the basic ingredient of the calculations presented in this thesis, the scattering theory of electrons off defects is introduced first. Then the scattering properties off different defects in the strong topological insulator Bi_2Te_3 is studied. Based on this knowledge, we implemented for the first time an *ab-initio* approach for the simulation of quasiparticle interference images in reciprocal space having predictive power, which especially allows to distinguish the scattering signatures of different impurities. Therefore we derive the formulas of the Fourier-transformed charge density in terms of Green functions and T -matrices. This allows us to formulate the computation of QPI in reciprocal space in the language of the Korringa-Kohn-Rostoker Green function

²meaning not in an indirect way via transport measurements

³In the experiment the signal quality is often enhanced by symmetrization of the data. This procedure can however be problematic [142] and might even lead to misinterpretations.

⁴A detailed discussion of the focusing effect and the engineering of backscattering will be presented in the next chapter. Here only the single impurity case showing low backscattering rates is analyzed in detail.

⁵An introduction to the scattering phase shift can be found in chapter 7

(KKR-GF) method [58], that is used throughout this thesis. Our calculations are therefore realistic and we gain a *quantitative* understanding of the scattering off non-magnetic and magnetic impurities in topological insulators. First, we study the FT-STs images in a model calculation to get qualitative understanding of the visible distinct scattering features seen on Bi₂Te₃. Then, the phenomenological approach of the joint density of states (JDOS) is presented and the *extended* joint density of states (exJDOS) that includes the scattering properties of *real* defects as computed from ab-initio is introduced. Finally the calculation of the Fourier-transformed charge density from first principles is presented and compared to the theoretical approaches of model calculations and (ex)JDOS approaches.

4.2. Electron scattering off defects and standing waves around impurities on topological insulators

We start our discussion with a short introduction into scattering of electrons off defects in general and introduce the $\mathcal{T}$ -matrix that contains the scattering information of the impurity. During the work that led to this thesis several impurities on the surface of the strong topological insulator Bi₂Te₃ have been considered. We review our ab-initio results and summarize the general scattering properties of individual defects that will be the basis of the discussion on the quasiparticle interference that follows. Then the calculation of the standing wave pattern forming around single defects will be presented. Some parts of this introduction have been discussed in [129].

4.2.1. Scattering of topologically protected surface state electrons off defects at the surface of Bi₂Te₃

Electron states in crystals can be written as a two-component spinor $\Psi_k = (\Psi_k^\uparrow, \Psi_k^\downarrow)^T$ that contains both spin channels. In the presence of an impurity or defect, an electron that is described by the above spinor can interact with it if the electron comes close to the impurity. The wavefunction will be scattered so that after the scattering event we have to rewrite the wavefunction as Ψ_k^{imp} which is a superposition of incoming and scattered waves. The Lippmann-Schwinger equation captures this superposition

$$\Psi_k^{\text{imp}}(r) = \Psi_k(r) + \int d^3r' G^{\text{host}}(r, r'; E) \Delta V(r') \Psi_k^{\text{imp}}(r') \quad (4.1)$$

$$= \Psi_k(r) + \int d^3r' G^{\text{imp}}(r, r'; E) \Delta V(r') \Psi_k(r') \quad (4.2)$$

where we have introduced the retarded Green functions⁶ of the host system G^{host} in the first expression. We call the *host system* the system without, i.e. far from, the impurity that defines the incoming wavefunction of the electron. Here we should note that the incoming wave obeys Bloch's theorem according to the crystal's periodicity. The scattered wave on the other hand is not a Bloch state as the defect is localized in space and breaks translational invariance. Nevertheless, Ψ_k^{imp} inherits the k -index as the Lippmann-Schwinger equation

⁶Here we will always work with the retarded Green functions, which is why we drop the prefix "retarded" in the text.

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relates Ψ_k^{imp} to the incoming Bloch wave which poses the boundary condition for this problem. The second formulation of the Lippmann-Schwinger equation given in Eq. (4.2) introduces the Green function G^{imp} of the perturbed system, i.e. the impurity described by V^{imp} embedded into the host system that is determined by V^{host} . The two Green functions are connected by the difference in the potential $\Delta V = V^{\text{imp}} - V^{\text{host}}$ that only differs from 0 in the vicinity of the impurity. Formally, the Green function can be written as $G(E) = (E - H + i0)^{-1}$, with $i0$ being an infinitesimal imaginary part that is set to zero at the end of the calculation. This allows to derive the Dyson equation

$$G^{\text{imp}} = G^{\text{host}} + G^{\text{host}} \Delta V G^{\text{imp}} \quad (4.3)$$

$$= G^{\text{host}} + G^{\text{host}} \mathcal{T} G^{\text{host}} \quad (4.4)$$

where in the last step we have introduced the $\mathcal{T}$ -matrix

$$\mathcal{T} = \Delta V + \Delta V G^{\text{imp}} \Delta V \quad (4.5)$$

$$= \Delta V + \Delta V G^{\text{host}} \Delta V + \Delta V G^{\text{host}} \Delta V G^{\text{host}} \Delta V + \dots \quad (4.6)$$

$$= \Delta V + \Delta V G^{\text{imp}} \mathcal{T} \quad (4.7)$$

which describes the scattering properties of the impurity. It is clear that the $\mathcal{T}$ -matrix is non-vanishing only in the vicinity of the defect where $\Delta V \neq 0$. The importance of the $\mathcal{T}$ -matrix can be seen from the matrix elements $\mathcal{T}_{kk'} = \langle \Psi_k | \mathcal{T} | \Psi_{k'} \rangle$ that express the transition rate between an initial Bloch state $\Psi_{k'}$ that is scattered elastically (thus scattering between states of the same energy) to a final state Ψ_k (with $k \neq k'$) through *Fermi's Golden Rule*

$$P_{kk'} = 2\pi |\mathcal{T}_{kk'}|^2 \delta(E_k - E_{k'}) \quad (4.8)$$

In a practical calculation we approximate $\mathcal{T} \rightarrow Nc\mathcal{T}^{\text{single}}$ where the prefactor Nc describes the number of equivalent impurities (where the $\mathcal{T}$ -matrix of the single impurity is denoted $\mathcal{T}^{\text{single}}$) in the system from the impurity concentration c and the total number of atoms in the crystal N . This approximation is certainly justified for small impurity concentrations and will be used in the following where for convenience we drop the superscript "single" and write $\mathcal{T} \equiv \mathcal{T}^{\text{single}}$ from now on.

The transition rate, that we will also call *scattering probability* or *k-resolved scattering rate*, gives valuable insights into the scattering processes of electrons off defects. Within the KKR formalism the density functional calculations are performed with the help of Green functions. This allows to use the Dyson equation to embed impurities into the system [61] and then compute the scattering probability [60, 62, 63] from first principles. This feature distinguishes the KKR-GF approach from wavefunction-based, supercell approaches and results in realistic treatment of impurities in particular taking into account the correct charge screening of the impurity embedded in the host system with much smaller computational effort.

Integrating the expression Eq. (4.8) over the Fermi surface allows to compute the inverse *relaxation time* of each state

$$\tau_k^{-1} = 2\pi Nc \frac{1}{\Omega_{\text{BZ}}} \int_{FS} dk' |\mathcal{T}_{k'k}|^2 \quad (4.9)$$

that is the integrated scattering probability of scattering from initial state to all possible final states. The integration over the line segments dk instead of a surface element dk^2 implies

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that two-dimensional systems are treated and the Fermi surface therefore consists of lines. It can also be beneficial to look at the *total* scattering rate [averaged over the density of surface states $n(E)$] which we get from a second integration over all possible initial states so that

$$\tau^{-1} = \frac{2\pi Nc}{n(E)} \frac{1}{\Omega_{\text{BZ}}^2} \int_{FS} dk' \int_{FS} dk |\mathcal{T}_{k'k}|^2 \quad (4.10)$$

can be computed to compare scattering rates between different impurities. These quantities will be discussed in chapter 6.

Computational details and description of the scattering centers

The density functional calculations of this chapter are done assuming the local density approximation for the exchange-correlation potential [53] and an angular momentum cutoff of $\ell_{\text{max}} = 3$. After the self-consistent calculation of the host system (6 quintuple layer thick film of Bi_2Te_3) the Fermi level was shifted into the middle of the band gap to correct for the truncation error due to the finite angular momentum cutoff. A comparison to a calculation that includes corrections from *Lloyd's formula*⁷ [144] gave reasonable agreement. The following calculations are based on several steps: (i) the self consistent calculation of a 6 quintuple layer (QL) thick Bi_2Te_3 film, (ii) the self-consistent impurity embedding including a real space cluster around the impurity in solving the Dyson equation and finally (iii) the calculation of scattering properties based on *real* impurities. In this chapter only single impurities are considered where a screening cluster including the first nearest neighbors was chosen to account for correct charge screening of the impurity in the self-consistent embedding. This approximation was checked against a calculation using a larger (taking up to the third shell of neighbors) and smaller (i.e. single-site approximation, taking no neighbors into account in the single-site approach) screening cluster which reveals that the single-site limit is not enough⁸ while the impurity properties quickly converge so that taking the first shell of neighbors is enough.

Within this thesis several defects at different positions at the surface (e.g. adatoms, substitutional or interstitial impurities at different positions) have been considered. We find similar scattering trends on the different impurity positions and present here a detailed analysis of substitutional impurities on the position of the first Bi atom (cf. Fig. 4.2) which summarizes the general trends. In particular we discuss the intrinsic Te_{Bi} anti-site defect as a non-magnetic scattering center and Mn_{Bi} and Fe_{Bi} defects as magnetic scattering centers with magnetic moments pointing in the out-of-plane direction. The self-consistent impurity embedding gave spin moments of $m^s = 4.48\mu_B$ for Mn and $m^s = 3.54\mu_B$ for the Fe defect. Lattice relaxations around the impurity positions were neglected in this work. In Figure 4.2 the impurity position and the density of states of the different defects are shown together with

⁷Lloyd's formula can be used to correct for the truncation error arising from the finite angular momentum cutoff in practical calculations [144]. In particular in gapped systems this can lead to a wrong position of the Fermi level, while the bandstructure itself is in good agreement. Here we shifted the Fermi level by hand and continued in the calculation. As a crosscheck the self-consistent correction using Lloyd's Formula gave impurity properties (DOS, scattering) that were in good agreement with the approach of shifting the Fermi level "by hand".

⁸This result also implies that the CPA approach for small concentrations will not be a good approximations, since CPA is a single-site theory. For larger concentrations the treatment of the multiple scattering (i.e. between the single-site impurities) part of the Green function could, however, be more important.

the bandstructure and spin-polarization of the topological surface state in the Bi_2Te_3 -host material.

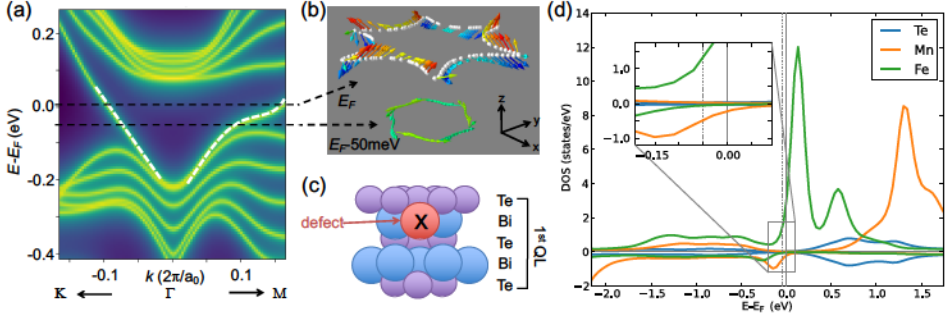


Figure 4.2.: Host properties and setup of the impurity calculations that serve as input for the calculation of the scattering probability. Shown is the bandstructure of Bi_2Te_3 in (a) where the topological surface state is highlighted with a white dashed line. The spin-polarization of the surface state is shown in (b) where the z-component is highlighted in the blue-green-red color scale applied to the arrows indicating the spin direction. The substitutional position of the defects replacing the first Bi atom is shown in (c) and the density of states of the three impurities that are discussed in detail in this chapter are shown in (d). The vertical lines in (d) show the position of the Fermi level (full line) and indicate the position of $E = E_F - 50\text{meV}$ (dotted line).

The scattering probability, that is the focus of the discussion in this chapter, will be analyzed for the above mentioned defects in the following. It relies on an accurate calculation of the Fermi surface. A highly parallelized code developed by Bernd Zimmermann [63] was used to chart the Fermi-surface with an accuracy equivalent to a uniform mesh of ~ 70 million k -points in the Brillouin zone. This Fermi surface was used to compute scattering properties. The existing code was improved with the implementation for the calculation of JDOS, SJDOS and exJDOS images that will be discussed in the second part of this chapter.

4.2.2. Ab-initio calculation of scattering probabilities for non-magnetic defects

The scattering analysis for scattering of electrons coming from the topological surface state off non-magnetic defects will be analyzed. First, the general theory will be introduced and afterwards the ab-initio results are discussed and compared to a model based on the spin-conserving scattering.

General aspects of time-reversal scattering off non-magnetic defects

As a consequence of strong spin-orbit coupling and time-reversal symmetry the topological surface state in Bi_2Te_3 has its spin locked to the momentum which is shown for the two energies that we study here in Fig. 4.2(b). Obviously the spin-polarization of the topological

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surface state in Bi_2Te_3 will affect the scattering properties of the TSS. Backscattering would now require spin-flip. In the presence of spin-orbit coupling in either the impurity or in the host band structure, spin-flip scattering is generally possible but typically weak compared to non-spin-flip scattering. Of special importance is scattering between two time-reversal points⁹ $\Psi \rightarrow \mathcal{K}\Psi$ which is always impossible even including spin-orbit coupling because it violates time-reversal symmetry. This can in fact be shown in a straight forward calculation using the properties of the time-reversal operator acting on the Hamiltonian [145]. For the following discussion the pair of Bloch electrons $\Psi_{\alpha,k}$ and $\Psi_{\bar{\alpha},-k}$ represent time-reversal partners where α is a general band index. For the magnetization $\mathbf{m}(\mathbf{r})$ we therefore find in a straight forward calculation

$$\mathbf{m}_{\bar{\alpha},-k}(\mathbf{r}) \equiv \Psi_{\bar{\alpha},-k}^\dagger(\mathbf{r}) \frac{1}{2} \boldsymbol{\sigma} \Psi_{\alpha,k}(\mathbf{r}) = -\Psi_{\bar{\alpha},-k}^\dagger(\mathbf{r}) \frac{1}{2} \boldsymbol{\sigma} \Psi_{\alpha,k}(\mathbf{r}) \equiv -\mathbf{m}_{\alpha,k}(\mathbf{r}) \quad (4.11)$$

where it is seen that the time-reversal partners have exactly opposite spin, point-by-point in space. This property makes the time-reversal point special. We can thus find a reference spin frame (that will also be called local spin frame) in which $\Psi_{\alpha,k}$ is diagonal, i.e.

$\Psi_{\alpha,k}(\mathbf{r}) = \begin{pmatrix} u_{\alpha}(\mathbf{r}) \\ 0 \end{pmatrix} e^{ik \cdot \mathbf{r}}$. The exact opposite spin of the time-reversal partner now allows

to write $\Psi_{\bar{\alpha},-k}(\mathbf{r}) = \begin{pmatrix} 0 \\ u_{\bar{\alpha}}^*(\mathbf{r}) \end{pmatrix} e^{-ik \cdot \mathbf{r}}$ in the same spin frame. Obviously the interference $\langle \Psi_{\alpha,k} | \Psi_{\bar{\alpha},-k} \rangle = 0$ vanishes.

The exactly opposite nature of the spin only holds for time-reversal partners. This motivate that near-backscattering can indeed be possible, is however expected to be strongly suppressed. It can indeed be shown [145] that the matrix element around the point of forbidden backscattering behaves as $\mathcal{T}_{\bar{\alpha},-k+\delta k;\alpha,k} \propto \delta k$. The special nature with respect to backscattering in TIs is now given by the non-degenerate nature of the topological surface state, a case very much different than, for example, in the Rashba surface state of $\text{Au}(111)$, where a similar spin-polarization as in the TI surface state is seen but additionally a second state (distinguished by the α index) exists close by in the Brillouin zone. Thus in Au exact backscattering between time-reversal partners is absent but near-backscattering is possible [119]. On the other hand, the fact that the surface state in Bi_2Te_3 is non-degenerate gives the theorem of forbidden backscattering its importance in the field of topological insulators.

The above discussed protection against backscattering that was associated to the spin-momentum locking in the TI let's us write a qualitative model for the scattering one expects to see in topological insulators. We can thus assume that the spin-conservation plays the dominant role in the scattering process of a non-magnetic defect so that we write the widely used approximation

$$|\mathcal{T}_{kk'}|^2 \propto 1 + \cos(\mathbf{s}_k, \mathbf{s}_{k'}). \quad (4.12)$$

This form of the scattering has previously been used in model calculations for the quasiparticle interference [37] based on the argumentation of spin-momentum locking and time reversal symmetry as given above.

⁹Formally time-reversal can be written in form of the anti-unitary operator $\mathcal{K} = -i\sigma_y \mathcal{K}_0 = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} \mathcal{K}_0$

with the complex conjugation $\mathcal{K}_0$. A Bloch state then is transformed as $\mathcal{K}\Psi_{\mathbf{k}}^\sigma = \Psi_{-\mathbf{k}}^{-\sigma}$ where the change in the propagation direction and a spin-flip is obvious.

First principles results and comparison to ad-hoc model

Now the ab-initio discussion of the scattering rates off non-magnetic defects will be discussed and compared to the model given in Eq. (4.12). During the work that led to this thesis several non-magnetic defects have been considered, including the intrinsic Te_{Bi} defect which is shown in Fig. 4.3 and that will be discussed in detail. Generally, other considered non-magnetic (single) defects show very similar features and we expect that the here discussed results are of general importance in TIs.

From the density of states at the Fermi energy and at $E_F - 50\text{meV}$, highlighted in the inset of Fig. 4.2(d), we can see that only a very low density of states is present close to the Fermi level. Therefore we expect the anti-site defect to result in a small scattering probability as follows from the Breit-Wigner formula¹⁰ for the total scattering rate that can be related to the difference in the density of states between host and impurity. In TI materials the host density of states is however very low since E_F lies within the bulk band gap. Some basic scattering properties can therefore be accessed from the density of states of the impurity.¹¹ This is indeed the case as can be seen for the scattering probability shown for $E = E_F$ and $E = E_F - 50\text{meV}$ in Fig. 4.3, where a scattering probability of only up to $10^{-7}\text{fs}^{-1}/\text{at.}\%$ per line segment¹² dL is found.

Next the angle-dependence of the scattering process will be discussed. We see that generally forward scattering, i.e. small-angle scattering with respect to the initial wave $\mathbf{k}_0$ (for which $\mathbf{k}' \approx \mathbf{k}$), dominates the scattering probability. Note that here we often abbreviate $\mathbf{k} \equiv \Psi_{\mathbf{k}}$. This statement does not only hold for the two pairs of energies and initial waves presented in Fig. 4.3 but it is a general feature that we also observed for other non-magnetic impurities (not shown explicitly) at different positions at the surface of Bi_2Te_3 .

Especially for the case in Fig. 4.3(a) and (c) where scattering from the middle of the valleys in $\bar{\Gamma}\bar{K}$ -direction we see that only for angles deviating by more than 20° from the exact backscattering direction (180°) a scattering probability of more than $10^{-13}\text{fs}^{-1}/\text{at.}\%$ (non-black region) is found. A comparison to scattering from an initial state located at the tips of the constant-energy contours in (b) and (d) on the other hand shows that this only holds in a very small range from 180° scattering as indicated by the scattering probability that quickly goes up by several orders of magnitude reflected by the lighter colors. The suppression against backscattering is also contained in the model of Eq. (4.12) and plotted in panels (e,f), shows much weakened directionality, as highlighted by the difference in the color scales (logarithmic scale in ab-initio results and linear scale in model results).

A comparison of this model to the scattering rate off the Te defect can be done with the plots shown in (e,f). We see that qualitatively the main features are reproduced. However it should be noted that the color scale in (e,f) is linear whereas the scattering probabilities in (a-d) are shown on a logarithmic scale. The strong focusing of the scattering probability in forward direction is less pronounced in the model which shows that the model only fits qualitatively but is quantitatively wrong.

¹⁰This will be discussed in chapter 7.

¹¹In chapter 6 the relation between impurity DOS and scattering rates will be discussed in detail. Here scattering symmetries and the protection against backscattering is addressed.

¹²This line segment of the constant-energy contour comes from the fact that the integrated quantity $\tau_{\mathbf{k}}^{-1} = \frac{1}{\Omega_{\text{BZ}}} \int_{FS} \frac{d\mathbf{k}'}{v_{\mathbf{k}'}} P_{\mathbf{k}\mathbf{k}'}$ which is the total scattering rate or inverse lifetime has units of $\text{fs}^{-1}/\text{at.}\%$ as it scales linearly with the impurity concentration.

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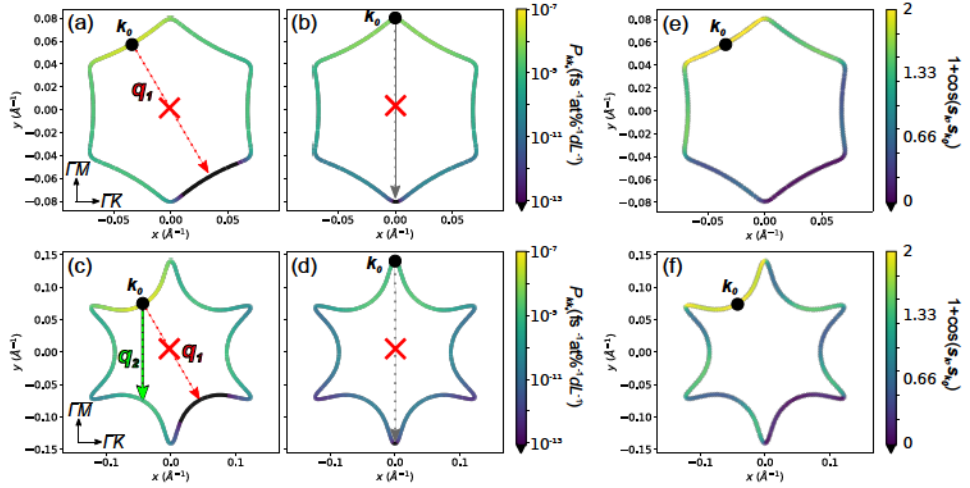


Figure 4.3.: Scattering probability P_{kk_0} off a TeBi -impurity for two different incoming waves labeled k_0 , respectively, in (a, b) for $E = E_F - 50 \text{ meV}$ and (c, d) for $E = E_F$. The scattering probability from k_0 to all possible final states on the Fermi surface is given in a logarithmic color scale. Generally, the TeBi antisite-defect only poses a weak scattering center with low scattering probability. In all four cases of initial waves k_0 the forward (small angle) scattering dominates and the (by TRS forbidden) backscattering is highlighted [q_1 in (a,c)]. In (c) the non-vanishing scattering in $\bar{\Gamma M}$ is pointed out by a green dashed arrow (q_2). In (e,f) the approximation $P_{kk_0} \propto 1 + \cos(s_k, s_{k'})$ is shown for $E = E_F - 50 \text{ meV}$ and $E = E_F$. Generally similar features can be seen but in particular the forward scattering is more pronounced in the real scattering probabilities as indicated by the linear color scale in (e,f) as compared to the logarithmic scale in (a-d).

Furthermore, we should point out that so far only those energies were considered where the scattering is dominated by the topological surface state alone, i.e. for the Fermi energy lying within the bulk band gap. If trivial bulk states coexist with the surface state then this situation of strongly suppressed backscattering might be more complex and other scattering channels could open up in the direction of 180° -scattering (however for $|\mathbf{k}| \neq |\mathbf{k}'|$) that do not correspond to exact $\mathbf{k} \rightarrow -\mathbf{k}$ transitions. Those transitions are therefore generally allowed by time-reversal and spin-conservation.

4.2.3. Ab-initio calculation of scattering probabilities for magnetic defects

Next the scattering properties off magnetic defects, i.e. defects that break time-reversal symmetry will be analyzed. Again first general aspects of time-reversal scattering in particular will be introduced before the ab-initio results for MnBi and FeBi are shown and compared.

Theory of time-reversal breaking scattering

In contrast to the non-magnetic defects discussed in the previous chapter, a magnetic impurity breaks time-reversal symmetry. This can be seen from the properties of the time-reversal operator $\mathcal{K}$ that acting on a potential consisting of time-reversal symmetric ($\Delta V_0 = \mathcal{K} \Delta V_0 \mathcal{K}^{-1}$) and antisymmetric (i.e. magnetic, $\mathbf{B} \cdot \boldsymbol{\sigma}$) parts as shown by the relation

$$\mathcal{K} \Delta V \mathcal{K}^{-1} = \mathcal{K} (\Delta V_0 \sigma_0 + \mathbf{B} \cdot \boldsymbol{\sigma}) \mathcal{K}^{-1} = \underbrace{\mathcal{K} \Delta V_0 \sigma_0 \mathcal{K}^{-1}}_{\Delta V_0 \sigma_0} + \underbrace{\mathcal{K} \mathbf{B} \cdot \boldsymbol{\sigma} \mathcal{K}^{-1}}_{-\mathbf{B} \cdot \boldsymbol{\sigma}} = \Delta V_0 \sigma_0 - \mathbf{B} \cdot \boldsymbol{\sigma} \quad (4.13)$$

where it is seen that a magnetic scattering potential does not preserve time-reversal symmetry since $\mathbf{B} = \mathbf{B}(\mathbf{r})$ is assumed to be only a real function of the position and thus $\mathcal{K} \mathbf{B}(\mathbf{r}) \mathcal{K}^{-1} = \mathbf{B}(\mathbf{r})$. Note that $\boldsymbol{\sigma}$ is the vector of Pauli matrices, σ_0 denotes the unity matrix in spin space and ΔV is then a two-by-two matrix in spin space. Therefore backscattering cannot be exactly forbidden anymore. Indeed it can be shown [145] that for small B (neglecting $\mathcal{O}(B^2)$ -terms) in a potential as described in Eq. (4.13) the transition rate only grows quadratically with the strength of the magnetic part of the scattering potential. This result is derived using the Born series expansion of the Dyson equation $G_B(E) = G_0(E) + \mathbf{B} \cdot \boldsymbol{\sigma} G_0(E) \mathbf{B} \cdot \boldsymbol{\sigma} + \dots$ for the Green function corresponding to the magnetic scattering potential with respect to the Green function G_0 corresponding to ΔV_0 alone. Truncating this series after the first order finally leads to the matrix elements

$$\mathcal{T}_{\mathbf{k}\mathbf{k}'} \approx \langle \mathbf{k} | \mathcal{T}_0 + \mathbf{B} \cdot \boldsymbol{\sigma} + \Delta V_0 G^{\text{host}}(E) \mathbf{B} \cdot \boldsymbol{\sigma} + \mathbf{B} \cdot \boldsymbol{\sigma} G^{\text{host}}(E) \Delta V_0 | \mathbf{k}' \rangle \underset{\mathbf{k}' \rightarrow -\mathbf{k}}{\propto} B \quad (4.14)$$

where $\mathcal{T}_0$ corresponds to the non-magnetic part (ΔV_0) alone, that vanishes for $\mathbf{k}' \rightarrow -\mathbf{k}$ due to TRS in the host. This finally leads to $P_{\mathbf{k} \rightarrow -\mathbf{k}} \propto B^2$ [145] which was verified for the scattering process of the Rashba surface state in $\text{Au}(111)$ [119].

The analysis of the first principle results for scattering off single Mn defects are shown in Figure 4.4. The following discussion starts for scattering at $E = E_F$ which will be decomposed in two regions; first the small angle scattering (region I, blue background) will be analyzed and afterwards large angle scattering (region II, red background) will be analyzed, where the

4. Revealing scattering properties of topologically protected electrons

backscattering signal is visible and a spin-selection rule is found. Afterwards scattering at other energies will be discussed revealing the warping dependence of the transition rates and the scattering rates for Mn will be compared to Fe impurities to study the importance of resonant scattering.

Region I: small angle scattering

First we look at the scattering probability for scattering off a substitutional Mn_{Bi} -impurity for $E = E_F$ where we show the transition rate for three different incoming waves in Figure 4.4(a-c). The black arrows in (a) indicate the in-plane spin-direction of the topological surface state and the symbols highlight the out-of-plane component. We find that the overall amplitude of the transition rates is two orders of magnitude larger (in particular if compared to the region of backscattering, highlighted with the red dotted line marked q_1) than the scattering probabilities seen for the Te_{Bi} defect studied above. This is understood from the density of states at the Fermi energy shown in Fig. 4.2(d) where the larger DOS for the Mn impurity as compared to the Te defect is seen.

In contrast to non-magnetic impurities, we see that scattering from the tip of the hexagonal shapes in $\bar{\Gamma}\bar{M}$ is not symmetric as seen in (a). This is a consequence of the magnetic moment pointing in the $\odot$ -direction (i.e. $+z$ -direction). The alternating out-of-plane component of the spin now breaks the left-right symmetry observed previously in the case of non-magnetic defects. Obviously switching the direction of the impurity spin would lead to the reversed picture which was verified explicitly (not shown here).

Apart from the general scattering asymmetry, the dominant feature is actually a generally strong forward scattering with a scattering rate within region I, i.e. for small angle scattering, that is several orders of magnitude (note the logarithmic color scale in Fig. 4.4) larger than scattering to region II. This observation suggests that the non-magnetic, i.e. ΔV_0 , part in the scattering potential plays the dominant role over the magnetic, i.e. $\mathbf{B} \cdot \boldsymbol{\sigma}$, part.

Spin-selection rule in scattering off magnetic defect: region II (large angle scattering)

The analysis of region II (large angle scattering) shows that, although the magnetic impurity breaks time-reversal symmetry, the backscattering (q_1) is still surprisingly weak. We can interpret this also from the density of states of the impurity (Fig. 4.2) where the off-resonant behavior of the impurity is seen. In terms of the scattering phase shift,¹³ that captures the scattering properties of the impurity and corresponding Wigner time-delay that will for such a case be small, we can qualitatively understand this behavior. For a small time-delay, that we expect for this kind of impurity, an electron that is scattered off the impurity only stays for a short time at the impurity. During this time the spin of the incoming wave can precess around the impurity moment enlarging the overlap with a possible final state of opposite spin. The off-resonant behavior of the Mn impurity therefore only leads to an effectively small magnetic part of the scattering potential. Therefore the scattering features are dominated by small angle scattering into region I over large angle scattering into region II.

¹³A detailed introduction of the scattering phase shift and the time-delay will be given later on in chapter 7 on pages 144ff.

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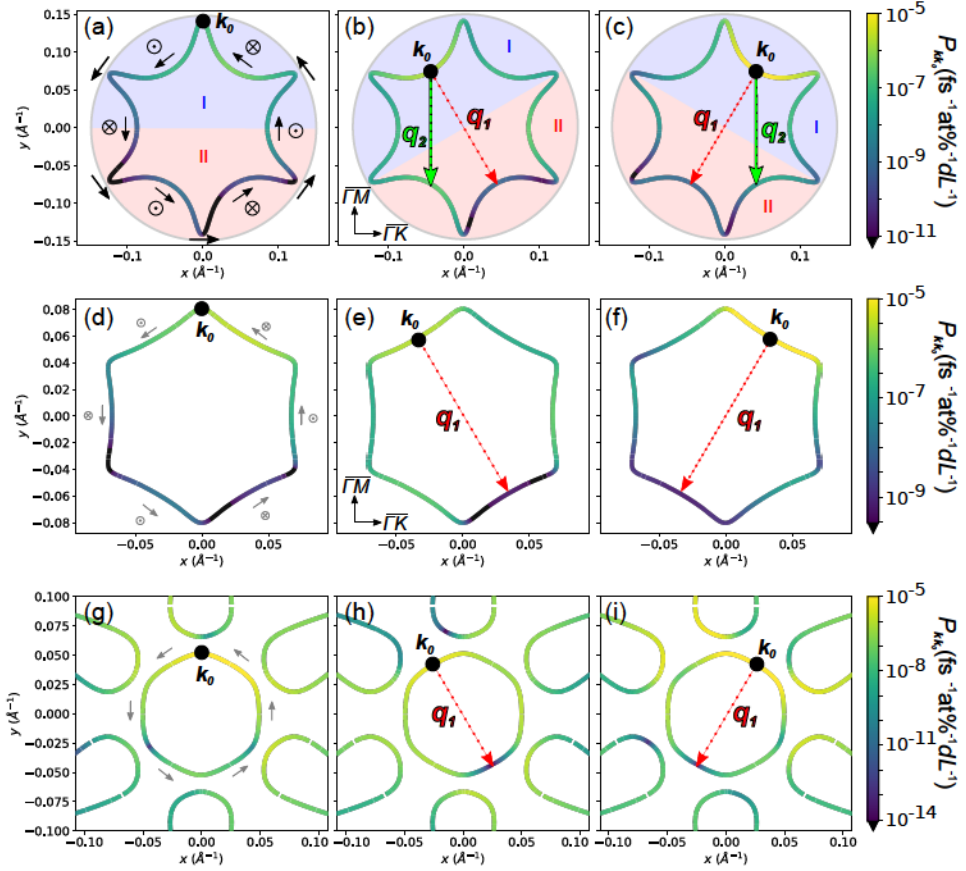


Figure 4.4.: Scattering probability P_{kk_0} off a MnBi -impurity for three different incoming waves labeled k_0 for $E = E_F$ in (a-c), $E = E_F - 50\text{meV}$ in (d-f) and $E = E_F - 100\text{meV}$ in (g-i) where the inner ring is the topological surface state and the outer lobes are bulk states from the valence band. The scattering probability from k_0 to all possible final states on the constant-energy contour is given in a logarithmic color scale. The black and gray arrows in (a), (d) and (g) indicate the in-plane direction of the spin polarization and the symbols $(\odot, \otimes)$ show the alternating out-of-plane component of the spin present in the six valleys in $\overline{\Gamma K}$ -direction that vanishes for decreasing energy. The red/green arrows in (b) and (c) highlight the importance of the relative alignment of spin of the final state and the direction of the magnetic moment of the impurity that points in the out-of-plane $(\odot)$ direction in this calculation: Backscattering (q_1) is possible due to the broken time-reversal symmetry but is quite weak (logarithmic color scale). The misalignment between the initial and final state's out-of-plane spin component, on the one hand, and the direction of the impurity's magnetic moment, on the other hand, lead to a strong suppression of the scattering amplitude in $\overline{\Gamma M}$ -direction (q_2) in (c) as opposed to the reversed situation in (b).

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The asymmetry seen between (b) and (c) was previously discussed in terms of the direction of the impurity moment. A detailed comparison of the q_1 and q_2 rates for the different incoming waves reveals that q_1 is stronger in (c) than in (b) and q_2 is stronger in (b) than in (c). We refer to this as a *spin-selection rule* in the large angle scattering off magnetic impurities which will be explained in the following. The impurity moment in this particular case is aligned in the $\odot$ -direction. Therefore comparing the q_1 and q_2 scattering rates from (b) and (c) reveals that scattering in the direction aligning the final state's spin with the impurity moment is favored over the opposite case. This can indeed be understood with a larger overlap of the wavefunctions with the spin-polarized impurity potential, leading to the observed asymmetric scattering pattern.

The relatively small effect of this asymmetry can be understood from the off-resonant behavior of this impurity and time-delay argument given above. For resonant scattering centers we would therefore expect to see a stronger effect of this spin-selection rule. This rule is intrinsically tied to the warping in Bi_2Te_3 , because the warping results in an opposite out-of-plane component of the spin-polarization.

Energy and warping dependence of the transition rates

Strictly speaking, the qualitative discussion of the magnitudes of the scattering rates for different angles only holds for strong warping where the out-of-plane spin plays a dominant role. At lower energies the warping is less pronounced and the closer the energy comes to the Dirac point the more circular the constant-energy contours (CEC) of the topological surface state becomes. With the smaller warping of the CEC the out-of-plane component of the spin vanishes and the approximations we used in the discussion above that allowed us to assume a certain matrix structure in the scattering potential for small and large scattering angles do not apply anymore. Instead, we expect the clear features of the asymmetry to vanish¹⁴ for a magnetic moment pointing perpendicular to the spin-direction in the surface state. This is indeed the case as can be seen in the scattering amplitudes presented in (d-f) for $E = E_F - 50$ meV and in (g-i) for $E = E_F - 100$ meV of Fig. 4.4. While the spin asymmetry is very strong at $E = E_F$ a gradual decrease between $E = E_F - 50$ meV and $E = E_F - 100$ meV is visible. Note that in Fig. 4.4 within each energy presented here the same logarithmic color scale has been used but different ranges are shown for the three different energies. At the same time the backscattering amplitude (q_1) decreases. For $E = E_F - 100$ meV we also see that scattering from the surface state to bulk states (outer lobes of the CEC in $\overline{\Gamma M}$) cannot be neglected over the scattering within the surface state alone. The problem of surface to bulk scattering will be the subject of a later chapter. For the remainder of this chapter we will focus on the first two energies that lie within the bulk band gap so that the Fermi surface (or CEC if $E \neq E_F$) consists of the topological surface state alone.

Importance of resonant scattering - comparison of Mn and Fe impurities

After the detailed scattering features of scattering of the magnetic Mn_{Bi} impurity have been understood we want to compare the previously discussed case with another magnetic impurity;

¹⁴Note that this is certainly only true for weak magnetic scatterers as we find for the Mn impurities discussed here. For strong scattering potentials, i.e. resonant scattering the Born approximation that we used for the T -matrix breaks down and the infinite sum in Eq. (4.7) has to be taken into account.

4.2. Electron scattering off defects and standing waves around impurities on TIs

an Fe atom residing at the same substitutional Bi site in the first quintuple layer. In contrast to the half-filled d -shell, that one expects for the Mn impurity, the density of states for an Fe atom is expected to be much higher close to the Fermi level since the minority d -states will be partly occupied. This can be seen in the density of states presented in Fig. 4.2(d) which is one order of magnitude higher for Fe as compared to Mn. In Figure 4.5 the scattering rates off the Fe and Mn impurities are compared for $E = E_F$ and two different incident waves.

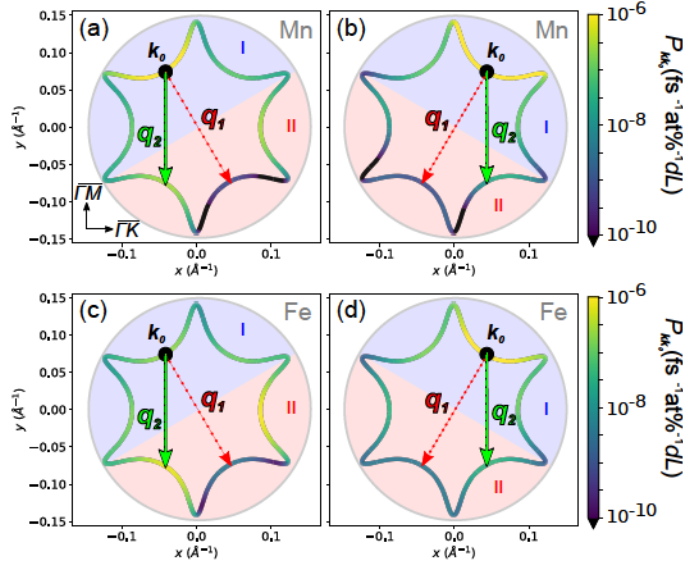


Figure 4.5.: Scattering probability P_{kk_0} off a Mn_{Bi} (a,b) and Fe_{Bi} -impurities (c,d) for $E = E_F$ for two non-equivalent incoming waves. The transition rates are shown in a logarithmic color scale where the range was adapted in comparison to Fig. 4.4 to highlight the differences between Mn and Fe impurities. The scattering amplitudes in ΓK and ΓM are highlighted, respectively, with red (q_1) and green (q_2) arrows. The regions I and II indicate the limits of small and large angle scattering as in the discussion of Fig. 4.4(a-c).

Overall similar features can be seen; the left-right asymmetry in the scattering for the inequivalent incident waves in (a,c) and (b,d) is present for both magnetic impurities as well as the relatively low scattering amplitude in backscattering direction. However, the detailed features of the scattering process depend on the electronic structure of the impurity. With the resonance on one spin channel, the spin-dependent part of the scattering is more pronounced for Fe as compared to Mn. This can be understood from the Wigner time delay,¹⁵ which gives the time an electron spends on the impurity during the scattering process before it leaves the impurity again. In the case of resonant scattering the delay time is long so that the electron spends a longer period of time in the potential well of the impurity. During this time the impurity moment causes the spin to precess and increase the matching the spin of the final state (which is opposite to the initial spin in the case of backscattering). This enhances the

¹⁵This is introduced together with the phase shift in chapter 7 on page 145.

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transition rate compared to the non-resonant case where the contact of the in-state with the impurity is short in time, causing only a small precession and therefore only a small overlap with the final state that has opposite spin. Consequently, the features in region II (large angle scattering), that were associated to a spin-selection rule in the scattering process, are more pronounced for the Fe impurity than for Mn. While the scattering in $\bar{\Gamma}M$ (q_2) off the Mn impurity shown in (a) is smaller than scattering in forward-direction, the same incident wave on an Fe impurity will be scattered more in 120° -direction (q_2) as seen in (c). The second type of incoming wave shown in (b) for the Mn and (d) for the Fe impurity generally look rather similar but the backscattering ($\mathbf{k} \rightarrow -\mathbf{k}$) amplitude marked q_1 is two orders of magnitude higher for Fe as compared to Mn.

Summary of the scattering features for single impurities in Bi_2Te_3

Before the discussion in this chapter is continued, we summarize the results of the analysis of the scattering rates, that we presented so far.

Non-magnetic defects

We verified that backscattering (180° or $\mathbf{k} \rightarrow -\mathbf{k}$ scattering) vanishes for non-magnetic impurities. This even holds for larger segments of the Fermi surface or CEC (for $E \neq E_F$) in the vicinity of the exact time reversal scattering partner of the incoming wave. Generally, single non-magnetic impurities in TI's show a strong tendency to forward scattering, however, scattering at 120° is possible and can lead to near-backscattering (at small deviations from the exact backscattering) [146] if two impurities are close by, in which case multiple scattering effects can become important. We furthermore showed that the scattering rate can be understood qualitatively from spin-conservation at non-magnetic defects which leads to the phenomenological description of the form $|\mathcal{T}_{\mathbf{k}\mathbf{k}'}|^2 \propto 1 + \cos(\mathbf{s}_{\mathbf{k}}, \mathbf{s}_{\mathbf{k}'})$. However, taking into account the real scattering probabilities is important to explain significant deviations, in particular the much stronger focus of the scattering in forward direction for the non-magnetic Te_{Bi} impurity as compared to the phenomenological model.

Magnetic defects

For scattering off single magnetic impurities we found that the non-magnetic part of the scattering potential still has a dominant effect with the backscattering, that is formally allowed due to broken time-reversal symmetry, being rather weak. We furthermore found a *spin-selection rule* that relates the asymmetric scattering off the magnetic defects to the direction of the magnetic moment of the scatterer.

We can summarize that the transition rates for scattering off magnetic and non-magnetic impurities can vary immensely depending on whether or not the case of *resonant scattering* is met. A priori the detailed scattering features off impurities in Bi_2Te_3 cannot be predicted, which highlights the need for first-principles calculations as done in this thesis.

4.2.4. Seeing scattering processes in real-space: QPI images

The scattering probabilities that have been discussed so far are not easily observable. What can be seen is the *result* of scattering off defects. The wave of an electron hitting an impurity in a crystal can be reflected so that incoming and outgoing waves can interfere forming a standing wave pattern in the electron density around the impurity. These so called *Friedel oscillations* [35] therefore contain information of the scattering process as the following example illustrates. Let us consider two systems where one is dominated by the topological surface state having spin-momentum locking and therefore no backscattering off non-magnetic impurities and a second system having a trivial surface state that is doubly degenerate as for example seen on a Cu(111) surface. The scattering of the trivial surface state has fundamentally different properties and scattering from $\mathbf{k}$ to $-\mathbf{k}$ is possible¹⁶ so that the strong focusing in forward direction that we saw in the topological insulator does not happen. Therefore much stronger oscillations in the charge density are expected around defects on Cu as compared to defects on Bi₂Te₃. From the fact that a state $|\sigma, \mathbf{k}\rangle$ and its time-reversal partner $|\bar{\sigma}, \mathbf{k}\rangle$ have exactly opposite spin as seen in Eq. (4.11), the absence of a signal in the charge density oscillations can be understood [129]. The exact orthogonality in spin-space allows us to define a local reference spin frame at $\mathbf{r}$ that makes $\Psi_{\sigma, \mathbf{k}}(\mathbf{r}) = \langle \mathbf{r} | \sigma, \mathbf{k} \rangle$ spin-diagonal and we thus obtain $\Psi_{\sigma, \mathbf{k}}(\mathbf{r}) = (u_{\sigma}(\mathbf{r}), 0)^T e^{i\mathbf{k} \cdot \mathbf{r}}$ and similarly for the time-reversal partner TRS partner $\Psi_{-\sigma, -\mathbf{k}}(\mathbf{r}) = (0, u_{-\sigma}^*(\mathbf{r}))^T e^{-i\mathbf{k} \cdot \mathbf{r}}$. The interference in the charge density can then be written as

$$n(\mathbf{r}) = [\Psi_{\sigma, \mathbf{k}} + S_{\mathbf{k}, -\mathbf{k}}^{\sigma, -\sigma} \Psi_{-\sigma, -\mathbf{k}}]^{\dagger} [\Psi_{\sigma, \mathbf{k}} + S_{\mathbf{k}, -\mathbf{k}}^{\sigma, -\sigma} \Psi_{-\sigma, -\mathbf{k}}] \quad (4.15)$$

where $S_{\mathbf{k}, -\mathbf{k}}^{\sigma, -\sigma}$ is an amplitude of the S-matrix.¹⁷ Obviously no cross terms of the form $\Psi_{\sigma, \mathbf{k}}^{\dagger} \Psi_{-\sigma, -\mathbf{k}}$ appear and therefore no modulation of the charge density occurs in the interference of time-reversal partner states. This is also seen in comparing the calculated scattering results presented for defects on Au(111) [119] with the scattering results presented here.¹⁸

In section 4.2.1 the language of Green functions and $\mathcal{T}$ -matrices was introduced to describe the scattering process of Bloch waves. The knowledge of the Green function generally allows to compute the fundamental properties of the physical system that it describes. The electron density is then given from the Green function as

$$n(\mathbf{r}; E) = -\frac{1}{\pi} \text{ImTr} G(\mathbf{r}, \mathbf{r}; E). \quad (4.16)$$

The use of the $\mathcal{T}$ -matrix in Eq. (4.4) allows to compute the charge density via

$$G(\mathbf{r}, \mathbf{r}; E) = G^{\text{host}}(\mathbf{r}, \mathbf{r}; E) + \int d^3 r' d^3 r'' G^{\text{host}}(\mathbf{r}, \mathbf{r}'; E) \mathcal{T}(\mathbf{r}', \mathbf{r}'') G^{\text{host}}(\mathbf{r}'', \mathbf{r}; E) \quad (4.17)$$

¹⁶Note that in both systems time-reversal symmetry is preserved which generally forbids exact backscattering between time-reversal partner. In contrast to the non-degenerate topological surface state the trivial surface state is doubly degenerate so that indeed scattering between $|\sigma, \mathbf{k}\rangle$ and $|\bar{\sigma}, -\mathbf{k}\rangle$ is forbidden but a state $|\sigma, -\mathbf{k}\rangle$ exists. Here σ is the spin-index that distinguishes the two degenerate bands.

¹⁷The S-matrix is the scattering matrix which is related to the scattering phase shift and can be connected to the $\mathcal{T}$ -matrix in general.

¹⁸The surface states in Au(111) and Cu(111) are very closely related and the (almost) degeneracy of Cu(111) is further lifted in Au(111) due to the stronger spin-orbit coupling strength.

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around an impurity very efficiently – even for large distances from the impurity – by using the translational invariance of the host Green function that describes the propagation of electrons in the clean crystal. This can be seen from the fact that the $\mathcal{T}$ -matrix is short ranged, i.e. it acts only in the small range around the impurity where $\Delta V \neq 0$. Similar to the charge density, a magnetization density in the non-magnetic host system is induced in the surrounding of a magnetic impurity given by

$$m(\mathbf{r}; E) = -\frac{1}{\pi} \text{ImTr}[\boldsymbol{\sigma} \cdot G(\mathbf{r}, \mathbf{r}; E)]. \quad (4.18)$$

The short-ranged property of the $\mathcal{T}$ -matrix has been used to compute the charge density oscillations around the Mn_{Bi} defect as well as the induced magnetization in its surrounding in a large area of $\sim 50 \times 50 \text{ \AA}^2$. This is only possible in the Green-function-based approach of the KKR formalism that we apply here as for the same calculation in a wavefunction-based supercell method a unit cell with at least $32 \times 32 \times 30 = 30720$ atoms¹⁹ would be needed which is hardly possible. The result of the calculation can be seen in 4.6 for $E = E_F$. The corresponding Fermi surface is given as an inset in Fig. 4.6(c).

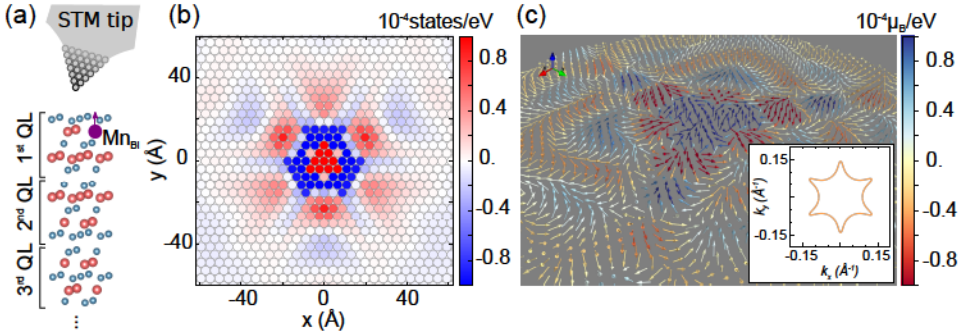


Figure 4.6.: Real-space image of the standing wave forming around a Mn_{Bi} -impurity with magnetic moment pointing in out-of-plane direction as indicated in (a). The oscillations in the charge channel are shown in (b), where the colored points give the difference in the charge density (Eq. (4.19)) integrated in the atomic cell, and the complex non-collinear oscillations in the induced spin in (c). The color code of the vectors in (c) give the out-of-plane component of the magnetization density (i.e. $m_z(\mathbf{r}; E)$) and the data shown in (b,c) was simulated at a distance of $\approx 1.4 \text{ \AA}$, i.e. in the first vacuum layer above the surface. The inset in (c) displays the corresponding Fermi-surface that determines the long range behavior of the oscillations.

The data plotted in (b) show the difference between the system without and with the impurity

$$\Delta n(\mathbf{r}; E) = n^{\text{imp}}(\mathbf{r}; E) - n^{\text{host}}(\mathbf{r}; E) \quad (4.19)$$

so that a white color indicates no change in the charge density as compared to the case of the pristine surface. We can see trigonal features that are typically found in this class of

¹⁹Here a 6QL thick film consisting of 6×5 atoms was assumed.

materials [38, 42, 147–151]. The details of the charge density oscillations measured on the surface depend on the electronic properties and on the local environment of the impurity at hand [150, 152, 153]. We find similar looking QPI images in real space for other defects (not shown here) that are in agreement with previously published data [153].

The charge density oscillations are always rather short ranged if compared to, for example, the Friedel oscillations around defects on Au(111) [119]. This can be understood from the fundamental difference in the topological surface state as compared to the Rashba surface state found on Au. Very long ranged oscillations (even up to hundreds of Ångströms from the impurity) can be seen if efficient scattering between states with opposite group velocity is present as seen in the stationary phase approximation [154]. This stands in contrast to TI surfaces where even for magnetic impurities backscattering is – in principle – possible the spin-momentum locking in the topological surface state does not allow the incoming and scattered waves to interfere in the charge channel [129] because the time-reversal partners, that govern the interference pattern assuming a circular shape of the Fermi surface in the long-range limit, necessarily have opposite spin directions. On the other hand, the Rashba surface state in Au(111) where in addition to the exact time-reversal partner with exactly anti-parallel spin a second state with the same group velocity direction but parallel spin exist to which spin-conserving scattering is possible. Therefore, electron wavefunctions having the same spin direction interfere and form long-range oscillations in the charge channel. As a consequence, magnetic and non-magnetic impurities show almost indistinguishable oscillations in the charge density around the impurity as the additional spin-flip scattering does not give a charge signal. In fact, it can be shown that in the Fourier-transformed quasiparticle interference of the charge channel the magnetic part of a scattering potential only enters in second order [140] leading to much smaller signals than those coming from the non-magnetic part of the scattering potential.

The spin channel on the other hand shows the difference between non-magnetic and magnetic impurity, as oscillations in the induced magnetization are only present for magnetic impurities. The oscillations shown in Fig. 4.6(c) are in good agreement with theoretical predictions [155] of a complex spin rotation with the distance from the magnetic impurity. These induced spin-density oscillations can mediate long-ranged magnetic (RKKY) interaction between individual magnetic impurities which can eventually lead to collective behavior. This will be studied later on in chapter 7.

In the previous discussion of the scattering properties and transition rates we have seen that the warping in the dispersion of the surface state of Bi_2Te_3 depends on the energy. As the Friedel oscillations around impurities depend crucially on the shape of the Fermi surface, it is obvious that tuning the Fermi level can significantly change the strength and directionality of charge density oscillations around impurities. A detailed analysis of this energy dependence in combination with the *focusing effect*, that was recently demonstrated in Bi_2Te_3 [131], will be discussed in the next chapter. Here, we will focus on introducing the methods that were developed and that are being used in the following chapters.

Experimentally the quasiparticle interference is accessible via scanning tunneling microscopy (STM). A very short introduction to the STM technique is given in the side note below, meant for the reader who might not be familiar with it. On a realistic surface, typically several defects are present and their charge density oscillations interfere with each other. It is therefore not a straight-forward task to deduce scattering information directly from the overlapping real space oscillations around defects. One way to go is to study more extended

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and well defined defects such as step edges in certain directions giving a better signal-to-noise ratio [149]. The drawback is however that only certain directions in the long-range limit are visible and in addition they give no information on the single impurities that one might actually want to study. An alternative approach is to study an ensemble of several single point defects on the surface. The STM image can be acquired over a large area containing several defects. The scattering information can then be extracted using a Fourier transformation of the charge density map. This is typically referred to as quasiparticle interference (QPI) images in reciprocal space or Fourier-transformed scanning tunneling spectroscopy (FT-STs) if done at several bias voltages, i.e. changing the scanning energy called E in Eq. (4.19). The large extent in the STM scan allows a good signal-to-noise ratio and therefore is well suited for the study of complex phenomena such as the scattering phenomena in topological insulators.

In the following, the theory of Fourier-transformed quasiparticle interference (FT-QPI) maps will be derived and an ab-initio formalism will be developed that allows to compute the Fourier-transformed images for realistic defects. Although in principle Fourier-transformed images could be obtained from the above discussed real-space images, in practice the calculation is too costly to be done as very large areas around the impurities – with in principle a Fourier summation up to infinity – have to be taken into account. The formalism we develop is the more efficient way and allows to directly relate scattering processes at the impurity to experimental observables.

Measuring quasiparticle interference with STM

The principle of the *scanning tunneling microscope* (STM) [156–158] is to measure the tunneling current between a tip, that approaches the sample up to a few Ångströms, and the sample that is to be studied. At constant applied voltage U between tip and sample, the decay of the tunneling current between the sample the tip at a distance z can be written as $I \propto \exp(-z/d_0)$ with a constant d_0 that comes from the exponential decay of the sample's wavefunctions into the vacuum. This exponential localization of the wavefunctions on the surface allows to have atomic resolution in the study of effects on surfaces. Since a tunneling current has to be measured for the STM technique to work, in principle every sample that is not perfectly insulating can be probed which makes the STM a very versatile tool in modern solid state research. The topological surface state in Bi_2Te_3 and related materials is metallic and therefore studying topological insulators with the STM brought important insights that could not have been measured with other techniques such as transport measurements alone. The lateral position of the tip relative to the surface can be controlled in the experiment and allows to measure extended effects on surfaces such as the previously discussed Friedel oscillations that might be long-ranged.

According to the Tersoff-Hamann model [159] the STM signal can be directly related to the local density of states

$$n(\mathbf{r}; E_F + eU) \propto \frac{dI}{dU}(U) \quad (4.20)$$

where U is the applied voltage and $\mathbf{r}$ the position on the surface where the STM tip is positioned. The Tersoff-Hamann model neglects special features of the tip's

wavefunctions and especially its geometry but it is usually in good agreement at not too large applied voltages. A more comprehensive introduction to the theory of STM where also the theory going beyond the Tersoff-Hamann approximation is given in [160] which will not be discussed in detail here. It should however be mentioned that also inelastic effects can be important as the actual measured STM signal can contain contributions going beyond the simple local density of states of the surface [161, 162] but also can contain artifacts such as set-point effects [163, 164] or interactions with plasmons [165, 166]. For the discussion presented in this chapter we can however neglect the above mentioned effects and work within the Tersoff-Hamann approximation.

In contrast to techniques like *angle-resolved photo-emission spectroscopy* (ARPES) that measure the occupied states only, the QPI measurement with STM can also be obtained for energies both above and below the Fermi level by applying the appropriate (positive or negative) voltage. This is called the *scanning tunneling spectroscopy* (STS) that can also be Fourier-transformed giving quasiparticle interference (i.e. FT-STs) maps in reciprocal space at different energies. This was for example used in topological insulators to reconstruct the dispersion of the surface bands and show how the surface states merges with bulk states at higher energies [167].

4.3. Green function and $\mathcal{T}$ -matrix approach to the quasiparticle interference on surfaces

4.3.1. The general formalism

Here, an expression for the Fourier-transformed charge density²⁰ in the language of Green functions and $\mathcal{T}$ -matrix is introduced. Starting point is the difference in the charge density given in Eq. (4.19) that we rewrite in terms of Green functions as

$$\Delta n(\mathbf{r}; E) = -\frac{1}{\pi} \text{Im} \text{Tr} \left[\underbrace{G^{\text{imp}}(\mathbf{r}, \mathbf{r}; E) - G^{\text{host}}(\mathbf{r}, \mathbf{r}; E)}_{\Delta G} \right]. \quad (4.21)$$

where G^{imp} is the single-electron Green function of the system with impurity, G^{host} the one of the pristine surface and the trace is with respect to the spin degree of freedom where also a summation over large and small components is implied in case of the Dirac formalism. Using the Dyson equation [Eq. (4.4)], the difference in the Green function between host and impurity system can be expressed as

$$\Delta G(\mathbf{r}, \mathbf{r}; E) = \int d^3 r' \int d^3 r'' G^{\text{host}}(\mathbf{r}, \mathbf{r}'; E) \mathcal{T}(\mathbf{r}', \mathbf{r}''; E) G^{\text{host}}(\mathbf{r}'', \mathbf{r}; E) \quad (4.22)$$

where the $\mathcal{T}$ -matrix, as defined in Eq. (4.7), enters in its real-space formulation

$$\mathcal{T}(\mathbf{r}', \mathbf{r}''; E) = \Delta V(\mathbf{r}') \delta(\mathbf{r}' - \mathbf{r}'') + \Delta V(\mathbf{r}') G^{\text{imp}}(\mathbf{r}', \mathbf{r}''; E) \Delta V(\mathbf{r}''). \quad (4.23)$$

²⁰We will restrict our discussion to the charge density oscillations as observed with conventional STM. A generalization to the case observable with a spin-polarized STM is straight forward. This is, however, not done routinely in experiment.

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We introduce cell-centered coordinates $\mathbf{r} = \mathbf{R} + \mathbf{x}$, where $\mathbf{R}$ is a discrete lattice vector parallel to the surface and $\mathbf{x}$ is a continuous position vector confined in the unit cell.

To change to reciprocal space it is convenient to use the Bloch theorem for the host Green function of the crystal with translational invariance which allows us to write

$$G^{\text{host}}(\mathbf{R} + \mathbf{x}, \mathbf{R}' + \mathbf{x}'; E) = \frac{1}{\Omega_{\text{rec}}} \int d^2k G_k^{\text{host}}(\mathbf{x}, \mathbf{x}'; E) e^{ik \cdot (\mathbf{R} - \mathbf{R}')} \quad (4.24)$$

where the Fourier-transformed Green function obeys the spectral representation

$$G_k^{\text{host}}(\mathbf{x}, \mathbf{x}'; E) = \sum_{\alpha} \frac{\Psi_{\alpha k}(\mathbf{x}) \Psi_{\alpha k}^{\dagger}(\mathbf{x}')}{E - E_{\alpha k} + i0} \quad (4.25)$$

from which the equivalence of Green function and wavefunctions $\Psi_{\alpha k}$, with a general band index α and $\Omega_{\text{rec}} = (2\pi)^2/\Omega_{\text{cryst}}$ that is connected to the total crystal surface Ω_{cryst} , is evident. The difference in the Green functions of Eq. (4.22) then becomes

$$\begin{aligned} \Delta G(\mathbf{R} + \mathbf{x}, \mathbf{R} + \mathbf{x}; E) &= \frac{1}{\Omega_{\text{rec}}^2} \int d^2k \int d^2k' e^{i(k-k') \cdot \mathbf{R}} \sum_{\mathbf{R}', \mathbf{R}''} \int_{\mathbf{R}'} d^3x' \int_{\mathbf{R}''} d^3x'' e^{-ik \cdot \mathbf{R}'} e^{ik' \cdot \mathbf{R}''} \\ &\quad \times G_k^{\text{host}}(\mathbf{x}, \mathbf{x}'; E) \mathcal{T}(\mathbf{R}' + \mathbf{x}', \mathbf{R}'' + \mathbf{x}''; E) G_{k'}^{\text{host}}(\mathbf{x}'', \mathbf{x}; E) \quad (4.26) \\ &= \frac{1}{\Omega_{\text{rec}}^2} \int d^2k \int d^2k' \sum_{\alpha \alpha'} e^{i(k-k') \cdot \mathbf{R}} \\ &\quad \times \frac{\Psi_{\alpha k}(\mathbf{x}) \mathcal{T}_{\alpha k \alpha' k'}(E) \Psi_{\alpha' k'}^{\dagger}(\mathbf{x})}{(E - E_{\alpha k} + i0)(E - E_{\alpha' k'} + i0)} \quad (4.27) \end{aligned}$$

where the sums over $\mathbf{R}'$, $\mathbf{R}''$ and the integration over d^3x' , d^3x'' are confined to the region where ΔV and consequently the $\mathcal{T}$ -matrix does not vanish. The first form of the last equation [Eq. (4.26)] explicitly contain the phase factors $e^{-ik \cdot \mathbf{R}'} e^{ik' \cdot \mathbf{R}''}$ that describes the propagation between lattice sites if the impurity extends over several lattice positions as it is typically the case if neighboring cells have to be considered for correct charge screening²¹ of the impurity. The second form of the equation [Eq. (4.27)] is a more compact form where the matrix elements $\mathcal{T}_{\alpha k \alpha' k'}(E) = (\Psi_{\alpha k}, \mathcal{T}(E) \Psi_{\alpha' k'})$ have been introduced. This form leads in the stationary phase approximation [154] to a simplified form for the long-range limit ($|\mathbf{R}| \rightarrow \infty$).

The Fourier-transformed QPI (FT-QPI) images are obtained for two-dimensional maps for fixed distance z from the surface that can be written as

$$\begin{aligned} \Delta G(z; \mathbf{q}; E) &= \int_{(z)} d^2r \Delta G(\mathbf{r}, \mathbf{r}; E) e^{-iq \cdot \mathbf{r}} \quad (4.28) \\ &= \frac{\Omega_{\text{BZ}}}{\Omega_{\text{rec}}^2} \int_{(z)} d^2x e^{-iq \cdot \mathbf{x}} \int d^2k \sum_{\mathbf{R}' \mathbf{R}''} e^{-ik \cdot \mathbf{R}'} e^{i(k-\mathbf{q}) \cdot \mathbf{R}''} \int_{\mathbf{R}'} d^3x' \int_{\mathbf{R}''} d^3x'' \\ &\quad \times G_k^{\text{host}}(\mathbf{x}, \mathbf{x}'; E) \mathcal{T}(\mathbf{R}' + \mathbf{x}', \mathbf{R}'' + \mathbf{x}''; E) G_{k-\mathbf{q}}^{\text{host}}(\mathbf{x}'', \mathbf{x}; E). \quad (4.29) \end{aligned}$$

In going from Eq. (4.28) to Eq. (4.29) the expression of Eq. (4.26) has been used together with the identity $\sum_{\mathbf{R}} e^{i(k-k'-\mathbf{q}) \cdot \mathbf{R}} = \Omega_{\text{BZ}} \delta(\mathbf{k} - \mathbf{k}' - \mathbf{q})$ with Ω_{BZ} being the surface Brillouin

²¹Cf. section on computational details on page 56.

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zone area. It can be seen that the Fourier-transformed difference in the Green function – given in real space²² as a product of two Green functions – is a convolution of two Green functions. Using this expression in Eq. (4.21), we arrive at the final expression for the FT-QPI

$$\begin{aligned}\Delta n(\mathbf{z}; \mathbf{q}; E) &= \int_{(\mathbf{z})} d^2r n(\mathbf{r}; E) e^{-i\mathbf{q}\cdot\mathbf{r}} \\ &= -\frac{1}{2\pi i} \text{Tr} [\Delta G(\mathbf{z}; \mathbf{q}; E) - [\Delta G(\mathbf{z}; -\mathbf{q}; E)]^*] \end{aligned} \quad (4.30)$$

where the complex conjugation in ΔG^* is implied to be done after the Fourier transformation. The straight forward extension for the spin density is obtained by replacing ΔG with $\boldsymbol{\sigma} \Delta G$, where $\boldsymbol{\sigma}$ is the vector of Pauli matrices.

The dominant scattering signatures that can be seen in the FT-QPI images can be understood from the stationary phase approximation (i.e. in the long-range limit) of the real-space change of the charge density which generally, i.e. so far not taking into account the protection against backscattering in the TSS, result in the asymptotic form (assuming that a single pair $(\mathbf{k}, \mathbf{k}')$ of stationary points is dominating) off a point defect²³ [129]

$$\Delta n(\mathbf{r}; E) = |A_{\mathbf{k}\mathbf{k}'}| \frac{\sin[(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r} + \phi_{\mathbf{k}\mathbf{k}'}]}{r} \quad (4.31)$$

where $|A_{\mathbf{k}\mathbf{k}'}|$ contains all the prefactors for example including a factor for the curvature, i.e. the flatness of the CEC in the sense of the focusing effect [154], and $\phi_{\mathbf{k}\mathbf{k}'}$ collects all phase factors in particular coming from the phase of the $\mathcal{T}$ -matrix, r is the distance of from the point-like impurity and a two-dimensional system was assumed giving the $1/r$ envelope. Obviously the scattering vector $\mathbf{q} = \mathbf{k}' - \mathbf{k}$ dominates the behavior. A number of observations concerning the form of the real space oscillations in Eq. (4.31) are noteworthy: Firstly, the result assumes a single stationary point and if multiple stationary points are present, e.g. if the focusing condition is met, the decay behavior, will generally be slower [154]. Secondly, if the $\mathcal{T}$ -matrix vanishes as in the case of the TSS in topological insulators the decay is faster with an envelope of $1/r^2$, as for example shown by Liu et al. [155]. Lastly, the Fourier transform of $\sin(\mathbf{q} \cdot \mathbf{r})/r$ gives a strong peak at $\mathbf{q}$, which is significantly sharper than the corresponding peak for the faster decaying envelope of $1/r^2$ [129]. This explains the most prominent feature of the FT-QPI images seen on topological insulators: If backscattering is present, then a clear signature corresponding to the backscattering $\mathbf{q}$ -vector can be seen. On the other hand, if backscattering is absent (signaling topological protection) this feature will not be visible. This is in particular the case since in experiment external perturbations such as temperature effects blur weaker signals corresponding to a faster decaying envelope of the charge density oscillations as in Eq. (4.31). In other words the FT-QPI image of the long range oscillations reveal the presence or absence of backscattering.²⁴

Typically the strongest change in the electron density is found directly above the impurity, i.e. at $z > 0$ in vertical distance from the position of the position on the surface where $\Delta V \neq 0$. Often this region is excluded in the Fourier transformation of STM images [168] to

²²Cf. Eq. (4.22).

²³If line defects are considered the decay is generally slower [155] but the bottom line of the following discussion holds analogously.

²⁴As long as the long-range limit is considered.

4. Revealing scattering properties of topologically protected electrons

reduce the influence of the shape of the impurity [37] and highlight the scattering vectors being responsible for the long-range oscillations. This exclusion of the short range behavior around impurities (indicated by a region called Ω_{excl} in the following) can be subtracted explicitly²⁵ via

$$\Delta \tilde{n}(z; \mathbf{q}; E) := \Delta n(z; \mathbf{q}; E) - \int_{\Omega_{\text{excl}}} d^2r n(z; \mathbf{q}; E) e^{-i\mathbf{q} \cdot \mathbf{r}} \quad (4.32)$$

$$= \Delta n(z; \mathbf{q}; E) + \frac{1}{\pi} \text{ImTr} \int_{\Omega_{\text{excl}}} d^2r \Delta G(\mathbf{r}, \mathbf{r}; E) e^{-i\mathbf{q} \cdot \mathbf{r}}. \quad (4.33)$$

where Ω_{excl} is a straight forward integration over a finite sized area in real space.

The expressions derived in Eq. (4.30) and Eq. (4.33) are the basis of the discussion that follows. They are valid for a single impurity, i.e. can be directly used for cases where only a dilute concentration of impurities is present and the distance between individual impurities is very large. Less obvious is that this form based on the single impurity can actually be applied to systems with higher defect concentrations. We turn now to a discussion of this question.

Validity of the single impurity approximation and importance of multiple scattering

In a typical QPI experiment a large area that is scanned with the STM that includes many individual impurities in a random configuration. This means that multiple scattering between different impurities can be present. A rigorous theoretical description would require to take this into account and compute the full $\mathcal{T}$ -matrix for a large area consisting of a statistical distribution of impurities. While this is in principle possible with the method presented here, it would be numerically far too expensive in practice. Luckily considering the single impurity is a very good approximation to the random distribution of multiple impurities. As Fang et al. [169] showed, the single impurity approximation agrees with the multiple impurity case exactly in first order of the potential difference around the single impurity (ΔV). Here we extend this argument also to strong scattering centers where ΔV is not necessarily small (i.e. in the case of resonant scattering centers) and considering the full $\mathcal{T}$ -matrix instead of ΔV is necessary.

The full $\mathcal{T}$ -matrix of several impurities at a surface that includes multiple scattering between individual scattering centers can be expressed as

$$\mathcal{T}_{nn'} = t_n \delta_{nn'} + t_n G_{nn'}^{\text{host}} (1 - \delta_{nn'}) t_{n'} + \sum_{m \neq n, n'} t_n G_{nm}^{\text{host}} t_m G_{mn'}^{\text{host}} t_{n'} + \dots \quad (4.34)$$

$$= t_n \delta_{nn'} + t_n \sum_m \check{G}_{nm} \mathcal{T}_{mn'}. \quad (4.35)$$

where $t_n(E)$ is the $\mathcal{T}$ -matrix of the single impurity at site n expressed in matrix form of a localized basis set and the matrix $\check{G}_{nm} = G_{nm}^{\text{host}} (1 - \delta_{nm})$ contains the site-off-diagonal part of the Green function.²⁶ The form of the equation above includes multiple scattering between impurities while separating it from sequential scattering events off the same impurity.²⁷

²⁵Note that the summation over lattice sites in Eq. (4.29) implicitly includes Ω_{excl} .

²⁶A proof of this relation can be found in Appendix of [130].

²⁷All orders of the single-site ΔV are contained in t_n .

4.3. Green function and $\mathcal{T}$ -matrix approach to the quasiparticle interference on surfaces

Next we assume the impurities to be non-overlapping which is reasonable for low impurity concentrations and that only one type of impurity (i.e. all individual impurities are described by the same matrix $t_n = t \forall n$) is present. Next we apply the stationary phase approximation [154] for the host Green function which allows us to write for large distances $G^{\text{host}}(\mathbf{R}_n + \mathbf{x}, \mathbf{R}_{n'} + \mathbf{x}'; E) \approx K_{nn'}(\mathbf{x}, \mathbf{x}'; E) e^{i\mathbf{k}_{nn'} \cdot \mathbf{R}_{nn'}}$, where $\mathbf{k}_{nn'}$ is a stationary point of the constant-energy contour $E_{\mathbf{k}_{nn'}} = E$ and is defined by the group velocity at this point being parallel to the vector $\mathbf{R}_{nn'} = \mathbf{R}_n - \mathbf{R}_{n'}$. This approximation is valid for low impurity concentrations as the largest part of the surface, on which the Fourier transform is performed, is covered by host atoms that are far from the impurities. The quantity $K_{nn'}$ contains the rest²⁸ of the Green function and includes a power-law decay with the distance which is $|\mathbf{R}_{nn'}|^{-1/2}$ in two dimensions. The phase factor $e^{i\mathbf{k}_{nn'} \cdot \mathbf{R}_{nn'}}$ is now the important quantity in the argumentation that follows, where we will see based on Eq. (4.35) that in the Fourier transform the first term (t_n) on the right hand side, which gives the single impurity contribution, is dominant and that the second term ($t\check{G}\mathcal{T}$) can be neglected.

To see this, Eq. (4.35) is used to decompose the difference of the Green functions (cf. Eq. (4.22)) as

$$\Delta G_{nn} = \Delta G_{nn}^{(1)} + \Delta G_{nn}^{(2)} \quad (4.36)$$

$$= \sum_m G_{nm}^{\text{host}} t_m G_{mn}^{\text{host}} + \sum_m G_{nm}^{\text{host}} t_m \sum_{n''} \check{G}_{mn''} \mathcal{T}_{n''n'} G_{n'n}^{\text{host}}. \quad (4.37)$$

The first-order terms ($G_{nm}^{\text{host}} t_m G_{mn}^{\text{host}}$) give identical contributions to the Fourier transform $\Delta G(\mathbf{q})$ because both G_{nm}^{host} and G_{mn}^{host} depend on n and m only via the difference $\mathbf{R}_{nm}$. This can be seen explicitly for the example discussed in the following. If N is the number of identical impurities and setting one impurity at $m = 0$, then the first order term becomes

$$\Delta G_{nn}^{(1)} = \sum_n \int_n d^2x e^{-i\mathbf{q}(\mathbf{x} + \mathbf{R}_n)} \sum_m G_{nm}^{\text{host}} t_m G_{mn}^{\text{host}} = N \sum_n \int_n d^2x e^{-i\mathbf{q}(\mathbf{x} + \mathbf{R}_n)} G_{n0}^{\text{host}} t_0 G_{0n}^{\text{host}}. \quad (4.38)$$

The higher order terms on the other hand cannot be simplified like this. We use the stationary phase approximation for G^{host} and get

$$\Delta G_{nn}^{(2)} \approx \sum_m G_{nm}^{\text{host}} t_m \sum_{n''} \check{G}_{mn''} \mathcal{T}_{n''n'} K_{n''n} e^{i\mathbf{k}_{n''n} \cdot \mathbf{R}_{n''n}}. \quad (4.39)$$

The Fourier-transform of the sum over the phase factors $e^{i\mathbf{k}_{n''n} \cdot \mathbf{R}_{n''n}}$ in the latter expression will now cancel in practice for randomly distributed impurities. Of course this cancellation only holds for infinitely large sums which is not done in practice but if the scan area in the experiment is large enough then this approximation holds nevertheless. With this form we can in particular see that the single impurity contribution ($\Delta G^{(1)}$) will in practice have the dominant contribution. This hypothesis was tested numerically in a model system of s -wave point defects randomly placed on a free-electron surface where it was shown that the multiple scattering part is an order of magnitude smaller than the single-site term [130].

For the remainder of this thesis we will therefore consider single defects only and derive the resulting QPI images in reciprocal space based on this approximation.

²⁸i.e. everything that is not the phase factor $e^{i\mathbf{k}_{nn'} \cdot \mathbf{R}_{nn'}}$.

4.3.2. Model calculations for the QPI on Bi_2Te_3

After having established the theoretical basis of the calculation of FT-QPI images we want to first get a qualitative understanding of the features that can be seen in the strong 3D-TI Bi_2Te_3 . We apply Eq. (4.30) to a model containing the host's bandstructure based on a $\mathbf{k} \cdot \mathbf{p}$ theory and identify signatures of backscattering that are absent (for non-magnetic defects) or present (for magnetic defects) within this model. Here the scattering potential takes a very simplified form of an s -wave point defect (so-called δ -scatterer) that has no structure except for its time-reversal breaking (modeling magnetic defects) or conserving (for non-magnetic impurities) nature.

In the following first the model that is based on the description presented by Lee et al. [139] is introduced which is then enhanced by magnetic scattering centers to study FT-QPI images for different defects and at different energies, effectively modeling the situation as it occurs in typical FT-STs experiment of the prototypical topological insulator Bi_2Te_3 .

Description of the model

Routinely, a model Hamiltonian from $\mathbf{k} \cdot \mathbf{p}$ theory [138, 139], where only the surface state electrons are considered via a Dirac-like term which is modified by a cubic warping term [141], is used in model-based studies of the surface state on topological insulators. Here, we followed the work of Lee et al. [139] for the surface state electrons and write the Hamiltonian of the host system as $\hat{H}_0 = \int d^2k \Psi_k^\dagger H_0(\mathbf{k}) \Psi_k$ with $\Psi_k = (c_{k\uparrow}^\dagger, c_{k\downarrow}^\dagger)$ and

$$H_0(\mathbf{k}) = \left[v(\mathbf{k} \times \boldsymbol{\sigma}) \cdot \hat{\mathbf{e}}_z + \lambda k^3 \cos(3\phi_k) \sigma_z \right]. \quad (4.40)$$

where the parameters $v = 2.55 \text{ eV} \cdot \text{\AA}$ and $\lambda = 250 \text{ eV} \cdot \text{\AA}^3$ depend on the dispersion of the surface state and the strength of the hexagonal warping, and were taken from Ref. [141]. This Hamiltonian can be diagonalized using a transformation from local to global spin frame which can be expressed by the unitary matrix

$$\hat{U}_k = \begin{pmatrix} \cos(\theta_k/2) & ie^{-i\phi_k} \sin(\theta_k/2) \\ ie^{i\phi_k} \sin(\theta_k/2) & \cos(\theta_k/2) \end{pmatrix} \quad (4.41)$$

Here we have introduced the angle $\phi_k = \tan^{-1} \frac{k_y}{k_x}$ between the $\mathbf{k}$ -vector and the $\hat{x}$ -axis, that is defined as the $\overline{\Gamma K}$ -direction, and the angle $\theta_k = \tan^{-1} \frac{k_0^2}{k^2 \cos 3\phi_k}$ describing the C_{3v} symmetry in Bi_2Te_3 leading to the hexagonal warping. The wavevectors and energies are given in units of $k_0 = \sqrt{v/\lambda}$ and $E_0 = vk_0$ and the eigenenergies are [139] $E_{\pm}(\mathbf{k}) = \pm \sqrt{(vk)^2 + (\lambda k^3 \cos 3\phi_k)^2}$ which allows to construct the Green function (which is 2×2 in spin space and expressed in the local frame of reference defined by the local spin frame) of the pristine surface as

$$G^{\text{host}}(\mathbf{k}; E) = \begin{pmatrix} (E + i0 - E_+(\mathbf{k}))^{-1} & 0 \\ 0 & (E + i0 - E_-(\mathbf{k}))^{-1} \end{pmatrix} \quad (4.42)$$

which follows from the spectral representation of the Green function [Eq. (4.25)]. Because of particle-hole symmetry we can concentrate on $E > 0$ in the rest of the discussion.

4.3. Green function and $\mathcal{T}$ -matrix approach to the quasiparticle interference on surfaces

Scattering off an impurity is modeled with a δ -scatterer having a scalar part (V_0), a spin-orbit part ($\propto c$) that is important for larger $\mathbf{k}$ -vectors, and a magnetic part ($-\mathbf{m} \cdot \boldsymbol{\sigma}$) in the impurity potential:

$$H_{\text{imp}}(\mathbf{k}, \mathbf{k}') = \hat{U}_{\mathbf{k}'}^\dagger V_0 [\mathbb{1} + ic \mathbf{k} \times \mathbf{k}' \cdot \boldsymbol{\sigma} - \mathbf{m} \cdot \boldsymbol{\sigma}] \hat{U}_{\mathbf{k}}. \quad (4.43)$$

that is transformed into the local spin frame of the host's electrons by applying $\hat{U}^\dagger$ and $\hat{U}$. Note that the magnetic part of the potential was not included in the work of Lee et al. [139]. The importance of the spin orbit part was recently pointed out in the model-based studies of the QPI in the Rashba material BiTeI [164] as it tends to change the relative intensities between different signatures seen in the QPI images. The parameters V_0 , c and $\mathbf{m} = |\mathbf{m}|$ give the scattering strength of the scattering center, the relative strength of spin orbit coupling as compare to the scalar part, and the relative strength of the impurity's magnetic moment, respectively.

Using the $\mathcal{T}$ -matrix formalism explained above, namely by virtue of the Dyson equation seen in Eq. (4.22) and the $\mathcal{T}$ -matrix in Eq. (4.23), the Green function of the system ΔG with impurity can be computed. Then the Fourier transform of the charge density around the impurity $\Delta n(\mathbf{q}; E)$ can be calculated via [139]

$$\Delta n(\mathbf{q}) = \frac{1}{2i} \int d^2k \text{Tr} \left\{ \hat{U}_{\mathbf{k}} \Delta G(\mathbf{k}, \mathbf{k} + \mathbf{q}) \hat{U}_{\mathbf{k}+\mathbf{q}}^\dagger - [\hat{U}_{\mathbf{k}} \Delta G(\mathbf{k}, \mathbf{k} - \mathbf{q}) \hat{U}_{\mathbf{k}-\mathbf{q}}^\dagger]^* \right\} \quad (4.44)$$

where the energy dependence in $\Delta G(\mathbf{k}, \mathbf{k}') \equiv \Delta G(\mathbf{k}, \mathbf{k}'; E)$ and thus in $\Delta n(\mathbf{q}) \equiv \Delta n(\mathbf{q}; E)$ is implied. The Green function difference is computed from $\Delta G = G^{\text{host}} \mathcal{T} G^{\text{host}}$ where the $\mathcal{T}$ -matrix is computed in the iterative approach of a Born series $\mathcal{T} = V_{\text{imp}} + V_{\text{imp}} G^{\text{host}} V_{\text{imp}} + V_{\text{imp}} G^{\text{host}} V_{\text{imp}} G^{\text{host}} V_{\text{imp}} + \dots$ which starts from the impurity potential given by Eq. (4.43) and successive iterations are performed until convergence is reached. Note the strong resemblance to the formulation presented in Eq. (4.30).

In the following, this equation is solved numerically and the resulting FT-QPI images are discussed.

Numerical results

We performed our model calculations with the following set of parameters:²⁹ $E/E_0 = 0.75$ and $E/E_0 = 1.5$, $V_0/E_0 = 0.1$, a 101×101 $\mathbf{k}$ -point mesh in the interval $[-3k_0, 3k_0]^2$, $c = 0.5$ and various strengths of the impurity moment ranging from a non-magnetic impurity ($m = 0$) to a strong magnetic scatterer with $m = 2$. A finite broadening ($i0$ in Eq. (4.42) of $0.05E_0$) has been used in the calculations. The results are shown in Figure 4.7 for $E/E_0 = 0.75$ in (a-c) and $E/E_0 = 1.5$ in (d-f) representing the previously discussed cases $E = E_F - 50\text{meV}$ and $E = E_F$, respectively.

In (a) and (d) the constant-energy contours (CECs) are given, demonstrating the increasing effect of the warping term leading to a deformation of the CEC from a hexagon at $E/E_0 = 0.75$ to a snowflake shape for $E/E_0 = 1.5$. The corresponding FT-QPI images are shown in (b) and (e) for a non-magnetic defect with $m = 0$ and in (c) and (f) for a strong magnetic defect

²⁹We also performed calculations for various sets of parameters at $E/E_0 = 0.25$ which are not shown here but are in agreement with the previously published data [138, 139].

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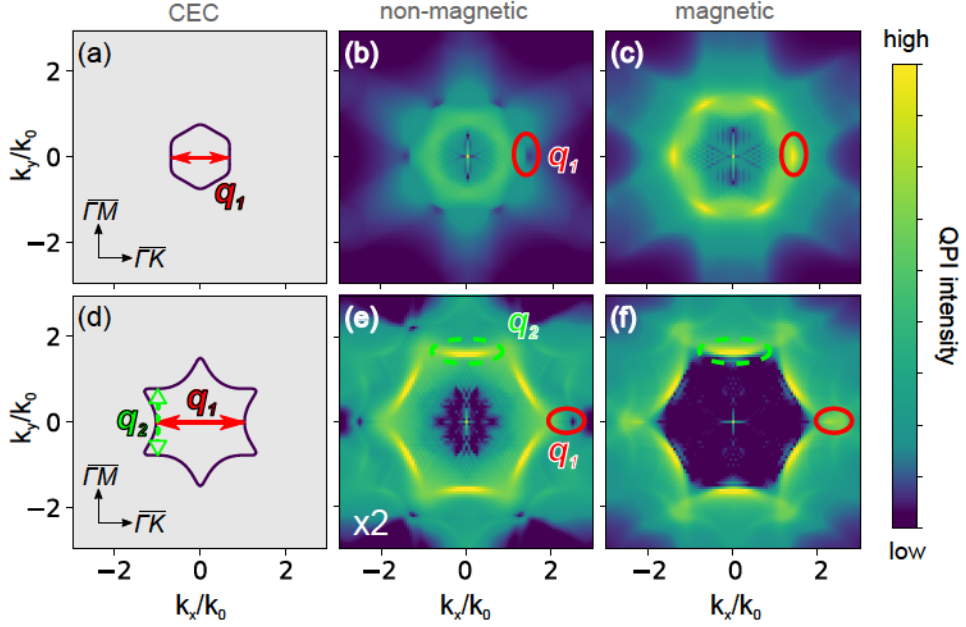


Figure 4.7.: Model calculation of the Fourier-transformed quasiparticle interference in Bi_2Te_3 at two different energies. Shown are in (a) the constant-energy contour (CEC) for $E/E_0 = 0.75$ with corresponding FT-QPI image for scalar impurity ($m = 0$) in (b) and magnetic impurity with $m = 2$ in (c). Indicated is the backscattering direction q_1 with a red arrow in (a) and corresponding red ellipses in (b, c) highlighting the absence (b) and reoccurrence (c) of backscattering for non-magnetic and magnetic defect. Panels (d-f) show Fermi surface and FT-QPI images like (a-c) but for higher energy ($E/E_0 = 1.5$) where the constant-energy contour is warped. In addition to the backscattering signal (q_1) the trivial scattering channel q_2 , that opens up with the deformation in the constant-energy contour, is shown in green. Note that within each energy the same color scale has been used for comparability but the data for $m = 0$ at $E/E_0 = 1.5$ (e) has been scaled up by a factor 2.

with $m = 2$. Generally, a 6-fold symmetry is found as a result of the C_{3v} symmetry in the crystal. Overall the point-like structure of the defect does not lead to small angle scattering (i.e. forward or near forward scattering with small $\mathbf{q}$), which results in the absence of any structure in the FT-QPI images for small $\mathbf{q}$. Only a bright spot at $\mathbf{q} = 0$ is visible that comes from the total difference in the density of states (i.e. $\int n(\mathbf{r})d^2r$).

The backscattering direction in $\overline{\Gamma K}$ is indicated by the red arrows [in (a) and (d)] and ellipses [in (b,c) and (e,f)] labeled q_1 . We can see that the QPI image of a non-magnetic defect at the lower energy, shown in (b), is essentially featureless. This can be understood as a result of the forbidden backscattering that does not lead to long range oscillations in the charge channel, which consequently does not lead to a prominent signature in the FT-QPI image. If a strong magnetic defect is present a signature at q_1 becomes visible, which is shown in (c). As we will discuss at a later point³⁰ this can be associated to the strong magnetic defect together with the nesting condition that is fulfilled in the hexagon of the CEC. For now, it is only important to see a strong signal in $\overline{\Gamma K}$ if backscattering is present while no such spot in the QPI images are seen for cases where time-reversal symmetry is preserved.

At higher energies the constant-energy contour becomes warped, as seen in panel (d), and other scattering channels emerge. Especially the trivial scattering channel in $\overline{\Gamma M}$ – which is labeled q_2 and is indicated in green in (d-f) – that was absent in the QPI images presented for $E/E_0 = 0.75$, now emerges for both non-magnetic and magnetic scattering centers. In the backscattering direction (q_1), no intensity in the QPI is found for the non-magnetic defect whereas this scattering channel opens up for the strong magnetic scatterer shown in (f). However the trivial scattering channel is dominating the image and leads to a stronger intensity in $\overline{\Gamma M}$ (q_2 highlighted in green), as compared to the orthogonal $\overline{\Gamma K}$ -direction (q_1 highlighted in red).

In conclusion, we have established the essential scattering channels that one expects to see in the quasiparticle interference images in reciprocal space and have seen their energy dependence as it can be measured with FT-STIS imaging. In the following, different approaches to a first-principles calculation of these quantities will be introduced and discussed for the same example (non-magnetic and magnetic impurity coupled to the surface state of Bi_2Te_3) that has been introduced in this section in the context of simplified model calculations.

4.3.3. An *ad-hoc* approach: The joint density of states and beyond

Typically, the direct interpretation of Fourier-transformed quasiparticle interference images, that are measured in the experiment, is quite cumbersome and practically impossible by looking at the resulting image alone. Especially if the constant-energy contour that in analogy to the previous section is responsible for the FT-QPI image is unknown, the task of extracting scattering information from FT-QPI images is pointless. A widely used, simplified approach to understanding the FT-QPI images rests on the so called *joint density of states* (JDOS) [37–39, 164, 167, 169–173]. Its phenomenological introduction can for example be found in the works of Simon et al. [170, 171]. Here, we take a descriptive approach and introduce the JDOS as a phenomenological model and compare the results of the ab-initio based calculations to

³⁰Cf. next chapter 5.

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the model calculations for the QPI presented above. Within this thesis the extension that includes the scattering phenomena of real defects for the first time from first principles called *exJDOS* is also introduced. Finally, the formal connection to the (formally exact) FT-QPI is done at a later point on page 87ff. and in section 4.4.

The (extended) joint density of states, (*ex*)JDOS can be computed from the knowledge of the constant-energy contour (CEC) at energy E when the full Green function G^{host} or the full T -matrix of the system with embedded impurity are not known. Typically, the CEC is obtained from first principles calculations or angle-resolved photoemission experiments. In close analogy to Eq. (4.29) it is written as

$$\text{exJDOS}(\mathbf{q}; E) = \int_{E_k=E} d\mathbf{k} n_{\text{surf}}(\mathbf{k}; E) M_{\mathbf{k}, \mathbf{k}-\mathbf{q}} \gamma_{\mathbf{k}, \mathbf{k}-\mathbf{q}}^{\text{STM}} n_{\text{surf}}(\mathbf{k}-\mathbf{q}; E) \quad (4.45)$$

which is a convolution of the spectral density on the pristine surface $n_{\text{surf}}(\mathbf{k}; E) = \int_{\text{surf}} |\Psi_{\mathbf{k}}(\mathbf{r})|^2 d^3r$ (the integration over r is bounded between the sample and the tip position). The wavevectors $\mathbf{k}$ and $\mathbf{k}-\mathbf{q}$ are assumed to be confined to the constant-energy contour and the matrix element $M_{\mathbf{k}, \mathbf{k}-\mathbf{q}}$ contains information on the scattering process off the impurity and will be discussed in detail in the following. The Ansatz of elastic scattering (constant energy) can be justified from Lindhard's theory of screening in metals [171]. The Lindhard susceptibility connects the change in the density in linear response to the original density via $\Delta n(\mathbf{q}) = \chi(\mathbf{q}) n(\mathbf{q})$ with $\chi(\mathbf{q}) = \sum_{\mathbf{k}} \frac{f(\mathbf{k}) - f(\mathbf{k}+\mathbf{q})}{E_{\mathbf{k}} - E_{\mathbf{k}+\mathbf{q}}}$ and where $f(\mathbf{k})$ is the Fermi function [174]. It can be seen that by far the largest contribution will be given by terms for which $E_{\mathbf{k}} = E_{\mathbf{k}+\mathbf{q}}$. It is therefore sufficient to consider a single energy alone. The factor $\gamma_{\mathbf{k}, \mathbf{k}-\mathbf{q}}^{\text{STM}} = 1 - \cos(\mathbf{v}_{\mathbf{k}}, \mathbf{v}_{\mathbf{k}-\mathbf{q}})$ in Eq. (4.45) has been introduced recently [131] to account for the sensitivity to backscattering in an STM experiment in the spirit of the stationary phase approximation.

The different factors that enter Eq. (4.45) will be discussed in detail in the following.

The standard way - simple JDOS to SJDOS calculations

A standard way to analyze QPI data is the usual JDOS approach which is obtained from Eq. (4.45) by setting $M_{\mathbf{k}\mathbf{k}'} = 1$ and $\gamma_{\mathbf{k}\mathbf{k}'}^{\text{STM}} = 1$. It can be qualitatively understood as follows. Assuming no special scattering structure, all possible connections of initial to final states will be relevant to the standing wave that forms as a consequence of scattering off an impurity. This is reflected in the auto-convolution of the surface spectral density than effectively counts³¹ the number of possibilities of initial and final states for scattering within the constant-energy contour. All possible structure of the impurity scattering is neglected and the resulting JDOS image for the surface state on Bi₂Te₃ at the energy $E = E_F$ can be seen in Figure 4.8. The Fermi surface is shown in (a) and the resulting JDOS image in (b) where the previously discussed scattering channels q_1 and q_2 in $\bar{\Gamma}\bar{K}$ and $\bar{\Gamma}\bar{M}$ are highlighted.

The central star-like feature, oriented in $\bar{\Gamma}\bar{K}$ and visible for $|\mathbf{q}| < 0.1\text{\AA}^{-1}$, is associated to small scattering vectors and can be understood as a signature of small angle scattering. The scattering features q_1 and q_2 are reproduced qualitatively in the JDOS approach, however, they are comparable in intensity. This can be understood with the missing protection against backscattering, as no scattering information is used, leading to unrealistically high intensity

³¹This includes $\mathbf{k}$ -dependent weights in the spirit of the Fermi surface integration $\int_{\text{FS}} dS = \int \frac{d^2\mathbf{k}}{v_{\mathbf{k}}}$ which gives the density of states as $n = \int \frac{d^2\mathbf{k}}{v_{\mathbf{k}}} [75]$.

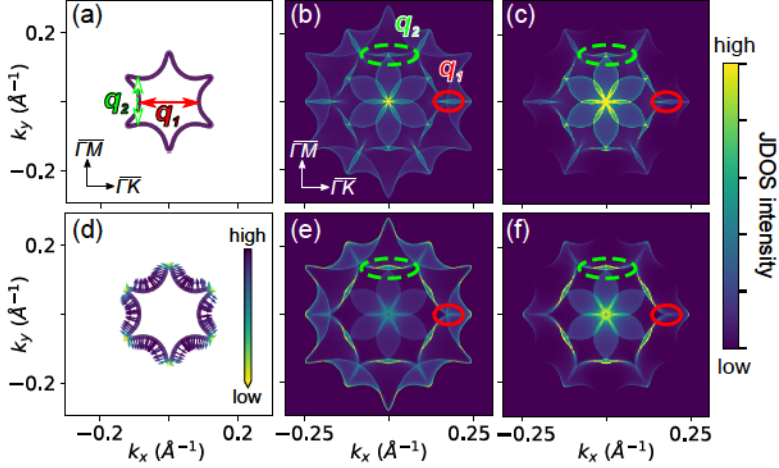


Figure 4.8.: The (S)JDOS and approach: Panel (a) shows the Fermi surface where the time-reverse backscattering (q_1) and trivial (q_2) (back) scattering directions are highlighted, (b) the simple JDOS approach that does not include any scattering information and (c) the SJDOS that takes the forbidden backscattering by spin-conservation in the transition matrix elements into account. In (d) the Fermi velocity on the Fermi surface, that is basic ingredient for the STM sensitivity factor, are shown where the magnitude is indicated by the color scale. In (e,f) the JDOS and SJDOS images [cf. (b,c)] are shown where the STM sensitivity factor $\gamma_{kk'}^{\text{STM}} = 1 + \cos(\mathbf{v}_k, \mathbf{v}_{k'})$ was used. The features associated to q_1 and q_2 are highlighted in the (S)JDOS images with solid red and dashed green ellipses, respectively.

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at q_1 . Usually this is interpreted as how the QPI image should look like for magnetic defects, assuming that the backscattering channel opens up. This is however only partly true since the exact backscattering contribution does not give a signal in the charge channel. However, also additional features like the w-shape at the outer edge for example seen at $k_x \approx 0.25\text{\AA}^{-1}$, that are absent in the QPI calculations discussed in Fig. 4.7, turn up which shows that the description of QPI images with the help of the simple JDOS approach only holds is problematic.

The forbidden backscattering can be taken into account by setting $M_{kk'} = 1 + \cos(\mathbf{s}_k, \mathbf{s}_{k'})$ which was first seen by Pascual et al. on Bi(110) [36] and later introduced by Roushan et al. [37] for the interpretation of FT-QPI images in the field of topological insulators. If the knowledge of the spin-momentum locking in TIs is used this can be further simplified to $M_{kk'} \approx 1 + \cos(\mathbf{k}, \mathbf{k}')$, which – strictly speaking – only holds for the circular CEC but is nevertheless used as an approximation for the warped contour as well [37, 38, 175]. This approach is known as the *spin-conserving* joint density of states (SJDOS) which also goes under the name *spin-selective scattering probability* (SSP). The SJDOS image for this system is shown in (c). It can be seen that the outermost w-like features disappear and only the star-like feature in the center as well as features at q_1 and q_2 survive. The relative intensities of the trivial (q_2) and forbidden backscattering (q_1) channels change from being comparable in (b) to a significantly stronger intensity for the trivial scattering channel in (c). We want to point out that the SJDOS feature at q_1 does not vanish completely as scattering for $\mathbf{q}$ -vectors parallel to q_1 but connecting points on the Fermi surface that are at $k_y = k'_y \neq 0$, $k_x = -k'_x$ are still possible.

A comparison of the above discussed JDOS and SJDOS with the model QPI results shown in Fig. 4.7 reveals that the main features, namely the presence and suppression of the backscattering peak for magnetic and non-magnetic impurities, can be reproduced qualitatively. Especially the appearance of additional features as well as the ratio of (S)JDOS intensities at certain $\mathbf{q}$ -vectors does however not fit the real QPI images yet.

To improve the description, we introduce the factor $\gamma_{kk'}^{\text{STM}}$ that was set to 1 in the JDOS and SJDOS approaches. The need for this additional factor can be understood from looking at the process of how QPI images are being measured. The quasiparticle interference images are the result of standing waves formed around impurities. As we have discussed above, especially the long range behavior in the charge density oscillations will be important in the Fourier transformed images. It is now intuitively clear (and can also be shown within the stationary phase approximation that captures this) that the STM measurement is essentially blind to forward scattering and promotes backscattering. Note that this does not necessarily mean exact backscattering for which time-reversal protection occurs but generally scattering under angles larger than 90° . The closer the scattering angle is to 180° the longer ranged the visible standing wave in the charge density oscillation will be. This is captured by setting $\gamma_{kk'}^{\text{STM}} = 1 - \cos(\mathbf{v}_k, \mathbf{v}_{k'})$ that acts as an *STM-sensitivity factor* so that states with opposite group velocities are favored – in the spirit of the stationary phase approximation. The Fermi velocities for this example are shown in Fig 4.8(d).

Including this improvement leads to the QPI images shown in (e) and (f) for the JDOS ($M_{kk'} = 1$) and SJDOS [$M_{kk'} \approx 1 + \cos(\mathbf{k}, \mathbf{k}')$]. It can be seen that the star-like central feature is suppressed and that also the intensity at q_1 drops. Especially for the SJDOS this is a significant improvement over the simple (S)JDOS shown in (b) and (c).

So far, we have seen that the (S)JDOS can be used qualitatively to understand where some

features of the QPI images come from. However, no sensitivity to the impurity, especially with respect to its specific scattering properties, is contained within this approach. In the previous discussion of the scattering rates we have seen already that the scattering properties depend strongly on the impurity that is embedded into the system. The JDOS and SJDOS calculations presented so far cannot capture this and, for example, also cannot explain why typically the QPI intensity found for magnetically doped TIs is either absent or strongly suppressed [39, 40] in contradiction to the expectation that this scattering channel opens up with the broken time-reversal symmetry due to magnetic defects, which should lead to enhanced (near³²) backscattering and therefore charge density oscillations.

Including impurity specific scattering channels - the exJDOS approach

An improved description, that can include the realistic treatment of the scattering properties of different impurities, was developed within this thesis. We call this approach the *extended joint density of states* [exJDOS, Eq. (4.45)] that, instead of using a model based approach to the transition matrix M (as in the SJDOS) or even neglecting it completely (as in the JDOS), uses the transition rate $P_{kk'}(E)$ based on ab-initio calculations. This approach suppresses the time-reverse scattering automatically as it relies of a realistic description of the impurity in the host system. We have seen above that it is beneficial to use the STM-sensitivity factor. Therefore this is applied for all the exJDOS results that follow.

The exJDOS results for the different impurities, for which the scattering rates were discussed previously (namely the Te_{Bi} , Mn_{Bi} and Fe_{Bi} impurities) are presented in Figure 4.9 for $E = E_F$ and in Figure 4.10 for $E = E_F - 50\text{meV}$ where the corresponding Fermi surfaces are shown in panels (a) of the respective figures.

We start the discussion by looking at the Te impurity shown in Fig. 4.9(b). The corresponding scattering results have been discussed in Fig. 4.3, where the strong forward scattering and vanishing backscattering that holds essentially for all final states within the valley around 180° scattering, i.e. near-backscattering, has been seen. This can explain the structure seen in the exJDOS image of Fig. 4.9(b). The intensity of the star-like feature in the center in comparison to the q_2 -feature is higher for the exJDOS images than in the SJDOS approach. This can be understood from the analysis of the scattering rate in the first part of this chapter where the inequivalence of the scattering probability and the phenomenological approach of $1 + \cos(\mathbf{s}_k, \mathbf{s}_{k'})$ was shown. The higher ratio of exJDOS intensity at q_2 compared to q_1 , in contrast to the previously discussed SJDOS results, is a result of the strong suppression of near-backscattering in addition to the strictly forbidden exact time-reversal scattering. This already showed up in the discussion of Fig. 4.3 where the limits of the approximation setting $P_{kk'} \propto 1 + \cos(\mathbf{s}_k, \mathbf{s}_{k'})$ were pointed out. The comparison to model QPI calculations shown in Fig. 4.7, shows that the exJDOS calculation indeed gives a much better description than the SJDOS approach without the impurity specific scattering information. Especially the strong suppression of the w-like features around $k_x \approx 0.25$ is in better agreement.

The apparently missing small-angle scattering signature (star-like feature around $|\mathbf{q}| = 0$) in the model QPI images can be understood with the missing near-impurity structure of the δ -scatterer in the model. A point-like scatterer without any structure looks “infinitely far away” for all waves that are being scattered. Therefore the δ -scatterer only reveals the

³²The exact backscattering transition does not give a signal to the charge density.

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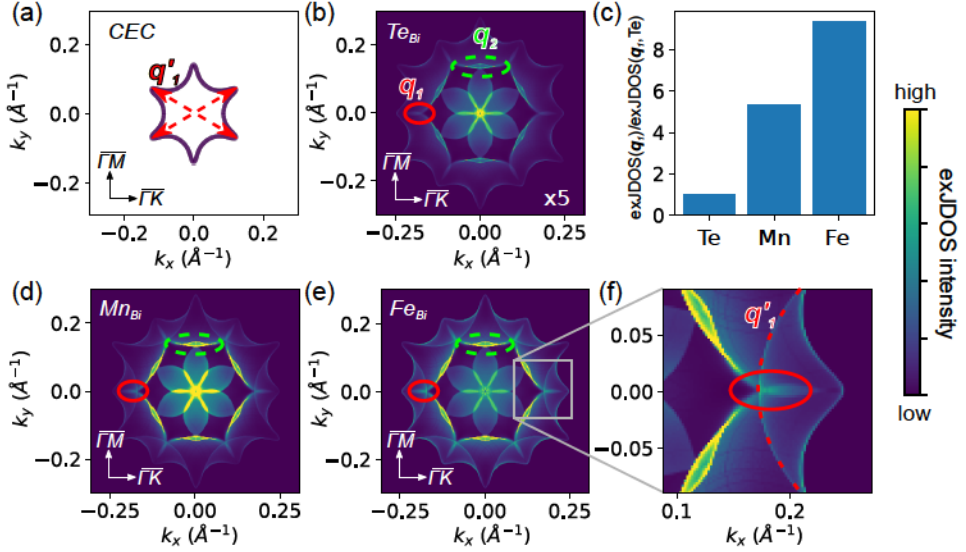


Figure 4.9.: exJDOS results for different impurities at $E = E_F$. Shown is the constant-energy contour in (a), the exJDOS image for the Te_{Bi} impurity in (b). Panels (d,e) show the exJDOS of Mn_{Bi} and Fe_{Bi} impurities and (f) highlights with a zoom around q_1 , the backscattering feature visible for magnetic defects. The magnetic near-backscattering feature, that shows up in addition to the time-reverse backscattering (q_1) and trivial scattering channels (q_2) of Fig. 4.8(a), is the bow like feature marked q'_1 in (f) coming from scattering from the k -points of one valley in the CEC to k -points from the valey on the opposite side. The end-points marking of the bow are indicated with red dashed arrows in (a). The histogram in (c) shows the comparison of the intensity at the q_1 feature for the different impurities (b,d,e) with respect to the intensity of the Te_{Bi} impurity shown in (b).

long-range limit of the oscillations. The JDOS-based approaches on the other hand take (almost) every scattering vector connecting points on the constant energy contours into account. This also includes small $\mathbf{q}$ connections which would only lead to a change in the charge density very close to the impurity site. This can be understood as follows. Consider a wave packet having a certain spatial extend that hits the impurity. For small $\mathbf{q}$ -vectors the incoming wavepacket and the scattered wavepacket only overlap in a very small region very close to the impurity. The small $\mathbf{q}$ vectors in the JDOS-based approaches can therefore only contribute to the near-impurity structure of the charge density oscillations.

The exJDOS image for a Mn impurity is shown in Fig. 4.9(d). In agreement with the scattering results (Fig. 4.4) only a very small enhancement in the backscattering signal at q_1 is found. Dominant is on the one hand the strong forward scattering leading to the star like feature around the origin (which is only partly suppressed³³ by γ^{STM}) and on the other hand the trivial scattering channel (q_2). Overall, no clear signature of time-reversal breaking can be seen in the exJDOS image at $E = E_F$.

The scattering analysis for the Fe impurity (section 4.2.3 and Fig. 4.5) showed a case closer to the resonant scattering case which led to an enhancement of the backscattering amplitude. This is also reflected in the higher intensity ratio of the area around q_1 compared to the area at q_2 showed in Fig. 4.9(e). The increasing exJDOS intensity for the backscattering (q_1) channel with the near resonance behavior of Fe is shown in panel (c) containing a comparison of the exJDOS signals at q_1 for the three different impurities. The zoom shown in (f) highlights the difference to the nonmagnetic impurity shown in (b) where the bow shaped q'_1 feature is completely absent. This new scattering channels called q'_1 comes from near backscattering from $\mathbf{k}$ -points within one valley of the CEC to $\mathbf{k}$ -points on the opposite valley which forms a bow-like shape. The end-points of the bow are indicated by dashed red arrows in the Fermi surface in (a). The bow-like shape can also be seen faintly in the exJDOS image of the Mn defect but is completely absent in the exJDOS image of the non-magnetic Te defect shown in (c) in agreement with the observation in the scattering rate that showed a very strong suppression also for near backscattering (cf. Fig. 4.3). This feature is, however, relatively small in intensity which might make it hard to detect experimentally.

Overall, we have seen that for all the defects, non-magnetic and magnetic, a time-reverse backscattering signature (q_1 and q'_1) is much lower in intensity for $E = E_F$ as compared to the trivial scattering channel (q_2). The energy dependence of the warping of the constant-energy contour allows to reduce the trivial scattering channel as in the spirit of the stationary phase approximation no long range oscillations will be possible in $\Gamma\bar{M}$ -direction since the group velocities will have an angle of 120° and not 180° . This is achieved by going to $E = E_F - 50 \text{ meV}$ as in the previous examples. The exJDOS images for the three different defects at this energy are shown in Figure 4.10 where the CEC, that now is a hexagon, and also the corresponding JDOS and SJDOS images are shown in addition. All images use the STM-sensitivity factor $\gamma_{\mathbf{k}\mathbf{k}'}^{\text{STM}} = 1 - \cos(\mathbf{v}_{\mathbf{k}}, \mathbf{v}_{\mathbf{k}'})$ but different transition matrix elements as discussed above. For the hexagonal contour the trivial scattering channel (formerly q_2) reduces to the short-range scattering feature showing up as a star-shaped area oriented in $\Gamma\bar{M}$. This feature can be seen in different intensities in (b-f) and is called q_3 (highlighted with

³³Exact suppression is only given for $\mathbf{v}_{\mathbf{k}'} = -\mathbf{v}_{\mathbf{k}}$ but small deviations from this are only strongly suppressed. The very strong focusing in forward scattering direction seen in the analysis of the scattering rates however counteracts this trend so that for small (but non-zero) angles between $\mathbf{v}_{\mathbf{k}'}$ and $\mathbf{v}_{\mathbf{k}}$ the forward scattering in the scattering rates win.

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cyan dotted lines). The comparison of the simplified models leading to the JDOS image in (b) and the SJDOS image in (c) show that the backscattering signature around q_1 is strongly suppressed [note that the intensity in (c) has been scaled up by a factor 5], if forbidden backscattering is accounted for, but still present. This is a result of the nesting condition that is met in the CEC which will be discussed in detail in the next chapter.

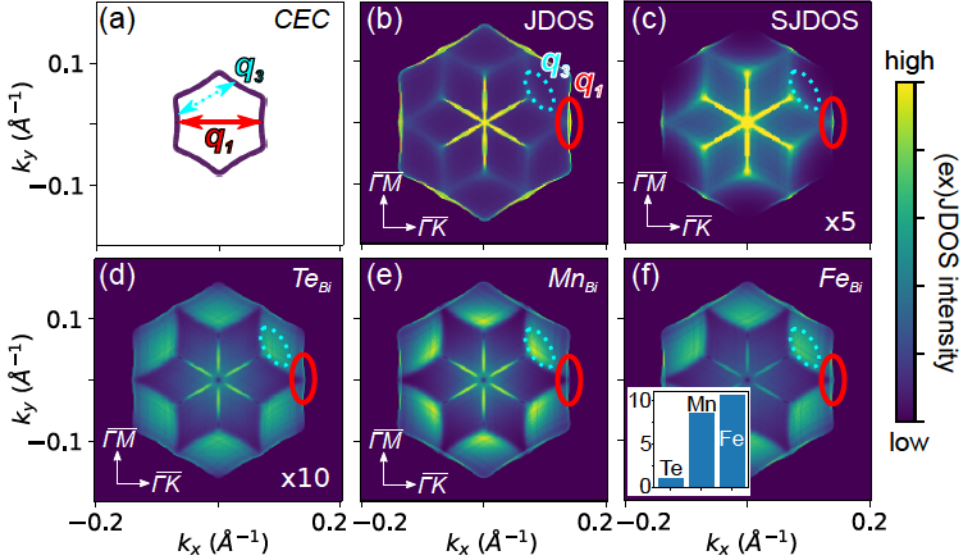


Figure 4.10.: JDOS, SJDOS and exJDOS results for different impurities on Bi_2Te_3 for $E = E_F - 50\text{meV}$. Panel (a) shows the constant-energy contour with two distinct scattering vectors (q_1 and q_3) highlighted in red and cyan. The corresponding calculations of JDOS, and SJDOS, that depend on the host properties alone, are shown in (b) and (c). The improved exJDOS calculations for three different impurities are presented in (d-f) where only a vanishingly small backscattering signal (q_1) can be detected for both magnetic and non-magnetic impurities, in agreement with the scattering rates shown in Fig. 4.5. The inset in (f) shows $\text{exJDOS}(q_1)/\text{exJDOS}(q_1, \text{Te})$, i.e. the relative exJDOS intensities at q_1 of the three defects in (d-f) with respect to the non-magnetic Te_{Bi} defect.

A comparison of the exJDOS images shows that the strong focus to forward scattering in the Te impurity leads to the image seen in the exJDOS. Especially no signature at q_1 is visible which is in agreement with the model QPI calculations for a non-magnetic point defect presented above. Additionally we observe a small feature which we call q_3 that can be associated to 120° -scattering that was also observed in the discussion of the scattering rates in Fig. 4.3. We distinguish q_2 and q_3 explicitly because q_2 satisfies the conditions for a couple of stationary points but q_3 not. The feature in real space associated to q_2 will therefore be much longer ranged than for q_3 .

At first sight it comes as a surprise that the magnetic scattering centers, shown in (e) and (f) of Fig. 4.10, essentially show no clear signature of backscattering that has been seen in

the model calculations and that would be expected at q_1 . However this is traced back to the scattering properties of the impurities that showed also for time-reversal breaking scattering centers only small scattering rates in the "back"-direction. Indeed the stronger back-scattering rate of the Fe impurity (cf. Fig. 4.5) can be seen as a slightly increasing exJDOS intensity at q_1 in (f) compared to the Mn impurity in (e). This is seen from the histogram shown as an inset in (f), where the relative exJDOS intensities at q_1 of the three defects with respect to the non-magnetic Te_{Bi} defect are plotted. The stronger overall scattering rates of the Mn and Fe defects lead to the large difference in replacing the Te impurity by Mn in the q_1 intensity (seen in the inset) but without drastically changing the overall exJDOS images shown in (d) and (e). Replacing Mn by Fe then only leads to a slight increase in the q_1 intensity which is highlighted in the histogram inset in (f). A detailed analysis of the backscattering rate compared to experimental signatures of focused standing waves in the charge density on mesoscopic length scales has been achieved recently [131] and will be the subject of a detailed discussion in the next chapter.

Comparison of exact QPI and Joint density of states: model or approximation?

So far we have seen that the widely used JDOS and SJDOS approaches only give a qualitative idea of how the quasiparticle interference images can be interpreted and are in particular not impurity specific. The exJDOS approach that has been developed within this thesis is a significant improvement which leads to results that are consistent with scattering rates and explain most of the features seen in model QPI calculations or experiments.

They remains the question how good the exJDOS is compared to real QPI. In particular, are the features seen in the exJDOS, that are at first sight in disagreement with the model calculations of the QPI, an artifact of the exJDOS approach or is there actually an underlying physical mechanism that goes beyond the description included in the model calculations? The open questions are especially important with respect to the only very small backscattering signal visible for $E = E_F - 50\text{meV}$.

Here, the exJDOS approach will be analyzed theoretically by comparing it to the equations giving the QPI images in reciprocal space.

The exJDOS approach has been introduced based on a phenomenological idea as an ad-hoc model. Here the question whether or not this model is also an approximation to the theory leading to equations (4.26), (4.29) and (4.30) will be addressed. As we will discuss in the following the relation $\text{exJDOS} \propto |\Delta n(\mathbf{q}; E)|^2$ can be derived under a number of assumptions. We can see from equations (4.29) and (4.30) that

$$\begin{aligned} |\Delta n(\mathbf{q})|^2 &= \Delta n(\mathbf{q}) \Delta n(-\mathbf{q}) \\ &= -\frac{1}{4\pi^2} \text{Tr}[\Delta G(\mathbf{q}) - \Delta G(-\mathbf{q})^*] \text{Tr}[\Delta G(-\mathbf{q}) - \Delta G(\mathbf{q})^*] \end{aligned} \quad (4.46)$$

where the variables E and z have been dropped for simplicity. Using the stationary phase

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approximation we get

$$\Delta G(\mathbf{r}, \mathbf{r}; E) \approx -\frac{4\pi^3}{\Omega_{\text{rec}}^2 \hbar^2} \sum_{\mathbf{k}(\mathbf{r}), \bar{\mathbf{k}}(\mathbf{r})} u_{\mathbf{k}}(\mathbf{r}) \mathcal{T}_{\mathbf{k}, \bar{\mathbf{k}}} u_{\bar{\mathbf{k}}}^\dagger(\mathbf{r}) \exp \left\{ -\frac{i\pi}{4} \left[\text{sign} \left(\frac{\partial^2 E_{\mathbf{k}}}{\partial k_{\parallel}^2} \right) + \text{sign} \left(\frac{\partial^2 E_{\bar{\mathbf{k}}}}{\partial \bar{k}_{\parallel}^2} \right) \right] \right\} \\ \times (|\mathbf{v}_{\mathbf{k}}| |\mathbf{v}_{\bar{\mathbf{k}}}|)^{-1/2} \left| \frac{\partial^2 E_{\mathbf{k}}}{\partial k_{\parallel}^2} \frac{\partial^2 E_{\bar{\mathbf{k}}}}{\partial \bar{k}_{\parallel}^2} \right|^{-1/2} \frac{e^{i(\mathbf{k}-\bar{\mathbf{k}}) \cdot \mathbf{r}}}{|\mathbf{r}|} \quad (4.47)$$

$$:= \sum_{\mathbf{k} \bar{\mathbf{k}}} a_{\mathbf{k}} a_{\bar{\mathbf{k}}} u_{\mathbf{k}}(\mathbf{r}) \mathcal{T}_{\mathbf{k}, \bar{\mathbf{k}}} u_{\bar{\mathbf{k}}}^\dagger(\mathbf{r}) e^{i(\mathbf{k}-\bar{\mathbf{k}}) \cdot \mathbf{r}} / |\mathbf{r}| \quad (4.48)$$

for the Green function at large distances $|\mathbf{r}|$ from the impurity that is assumed to be placed at $\mathbf{r} = 0$. The band index α has been dropped for simplicity of the notation. The sum in Eq. (4.47) runs over stationary $\mathbf{k}$ -points so that they are pinned to the CEC ($E = E_{\mathbf{k}} = E_{\bar{\mathbf{k}}}$) with their corresponding group velocities $\mathbf{v}_{\mathbf{k}}$ ($\mathbf{v}_{\bar{\mathbf{k}}}$) pointing in the direction of $\mathbf{r}$ ($-\mathbf{r}$) for $\mathbf{k}$ ($\bar{\mathbf{k}}$). The symbols $u_{\mathbf{k}}$ and $u_{\bar{\mathbf{k}}}$ describe the lattice periodic part of the wavefunction and $k_{\parallel}$ and $\bar{k}_{\parallel}$ are coordinates in the tangential direction to the CEC and therefore in the orthogonal direction of $\mathbf{v}_{\mathbf{k}}$ and $\mathbf{v}_{\bar{\mathbf{k}}}$, respectively. The latter expression [Eq. (4.48)] is a short hand notation for the expression discussed above with $a_{\mathbf{k}}$, $a_{\bar{\mathbf{k}}}$ being the obvious shorthand notations. The Fourier transformation of the expression above reads as

$$\Delta G(\mathbf{q}; E) = \int d^2 r \sum_{\mathbf{k} \bar{\mathbf{k}}} a_{\mathbf{k}} a_{\bar{\mathbf{k}}} u_{\mathbf{k}}(\mathbf{r}) \mathcal{T}_{\mathbf{k}, \bar{\mathbf{k}}} u_{\bar{\mathbf{k}}}^\dagger(\mathbf{r}) e^{i(\mathbf{k}-\bar{\mathbf{k}}-\mathbf{q}) \cdot \mathbf{r}} / |\mathbf{r}| \quad (4.49)$$

$$= \int_0^\infty dr \int_{\text{CEC}} d\ell \mathcal{D}(\ell) \sum_{\mathbf{k}} a_{\mathbf{k}} a_{\bar{\mathbf{k}}} u_{\mathbf{k}}(\mathbf{r}) \mathcal{T}_{\mathbf{k}, \bar{\mathbf{k}}} u_{\bar{\mathbf{k}}}^\dagger(\mathbf{r}) e^{i(\mathbf{k}-\bar{\mathbf{k}}-\mathbf{q}) \cdot \mathbf{r}}. \quad (4.50)$$

where in the last step the integration has been changed from $d^2 r$ to $\mathcal{D}(\ell) d\ell$ with ℓ running along the CEC forming a closed loop (in an isotropic model, $\mathcal{D}(\ell) d\ell$ would be equivalent to $d\theta$ in polar coordinates). Note that the exact form of $\mathcal{D}(\ell)$ depends on the exact shape of the CEC and that the stationary points $\mathbf{k}$ and $\bar{\mathbf{k}}$ are now functions of ℓ .

In order to arrive at the exJDOS expression in addition to the stationary phase approximation additional assumptions have to be made. First, $\mathcal{D}(\ell)$ has to be dropped. Then, in the spirit of the stationary phase approximation the dominant contribution to the integral in Eq. (4.50) is assumed to come from the stationary points where the phase vanishes, i.e. where $\mathbf{k} - \bar{\mathbf{k}} - \mathbf{q} = 0$, so that the r -integration can be dropped and the ℓ -integration reduces to a finite number of stationary points on the CEC. Additionally, the mixed products of the type $G(\mathbf{q}; E) G^*(\mathbf{q}; E)$ as well as products of wavefunctions $u_{\mathbf{k}}^\dagger u_{\bar{\mathbf{k}}}$ and products of $\mathcal{T}$ -matrix elements are neglected. Those assumptions make it clear that interference effects arising from these kind of pairs will not be taken into account in the exJDOS approach which might change what is seen in the exJDOS as compared to the real QPI images. Finally, to comply with the exJDOS form $\gamma_{\mathbf{k}\mathbf{k}'}^{\text{STM}} = \delta(\mathbf{k} - \mathbf{q} - \bar{\mathbf{k}})$ should be set which comes from the stationary phase approximation in the long distance limit that results in the disappearance of mixed- $\mathbf{k}$ terms in the density.

In conclusion, the above formulated exJDOS approach to the QPI can be understood as a qualitative model but not as an approximation so that the real calculation of QPI images fully from first principles is desirable. This will be the subject of the final section of this chapter.

4.4. QPI calculations within the KKR formalism: the “real thing”

We have seen that the exJDOS model is a reasonable approach to the calculation of QPI images from first principles, and it is especially powerful in combination with the calculation of individual scattering rates presented in the first part of this chapter. We have, however, seen that some contribution is missing which, in principle, can alter the real QPI images as compared to the exJDOS approach. Therefore, in this section a fully ab-initio formalism is derived that allows the computation of QPI images within the KKR method.

The long range nature of oscillations around impurities, that becomes most evident by the stationary phase approximation of anisotropic Fermi surfaces [154, 176], makes supercell methods not suitable for the purpose as the computational demand would be far too high. Instead, the KKR method expressed in its Green function formulation allows a straight forward application of the T -matrix formalism described above in a first-principle’s method. The power of the KKR-approach to this kind of problem has been demonstrated for example for the long ranged focusing effect seen for buried impurities under the surface of Cu(100) and Cu(111) [154].

Here, we formulate equations Eq. (4.30) and Eq. (4.33) explicitly in the language of the KKR-GF method which avoids the explicit calculation of the QPI in real space over a possibly very large area. This implementation is then applied to the systems discussed above, i.e. non-magnetic and magnetic defects at the surface of Bi_2Te_3 , in terms of scattering rates, model calculations and exJDOS simulations and the quality of the exJDOS approach is discussed.

4.4.1. Theoretical description of the QPI in reciprocal space within the language of the KKR method

In the introductory chapter (section 2.2.2) the notation of the Green function in the language of the KKR method has been introduced. For convenience we reprint [cf. Eq. (2.7) on page 11] the equations for the Green function that breaks down into single-site and multiple scattering terms:

$$\begin{aligned}
 G(\mathbf{X}_n + \mathbf{x}, \mathbf{X}_{n'} + \mathbf{x}'; E) &= \sum_L G_{SL}^n(\mathbf{x}, \mathbf{x}'; E) \delta_{nn'} + \sum_{LL'} G_{MLL'}^{nn'}(\mathbf{x}, \mathbf{x}'; E) \\
 &= -i \frac{\sqrt{2mE}}{\hbar} \sum_L \left[\mathcal{R}_L^n(\mathbf{x}; E) \tilde{\mathcal{H}}_L^n(\mathbf{x}'; E) \theta(\mathbf{x}' - \mathbf{x}) \right. \\
 &\quad \left. + \mathcal{H}_L^n(\mathbf{x}; E) \tilde{\mathcal{R}}_L^n(\mathbf{x}'; E) \theta(\mathbf{x} - \mathbf{x}') \right] \delta_{nn'} \\
 &\quad + \sum_{LL'} \mathcal{R}_L^n(\mathbf{x}; E) \mathcal{G}_{LL'}^{nn'}(E) \tilde{\mathcal{R}}_L^{n'}(\mathbf{x}'; E) \quad (4.51)
 \end{aligned}$$

For our purpose, it is important that the lattice Fourier transform only affects the structural Green functions

$$\mathcal{G}_{LL'}^{\text{host}\mu\mu'}(\mathbf{k}; E) = \sum_i \mathcal{G}_{LL'}^{\text{host}ii';\mu\mu'}(E) e^{-ik \cdot \mathbf{R}_i}. \quad (4.52)$$

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and not the $\mathcal{T}$ -matrix and the local scattering solutions. Within the language of the KKR formalism the analogon to the $\mathcal{T}$ -matrix is the *scattering path operator* of the impurity $[\tau(E)]$ which connects the single-site $\mathcal{T}$ -matrices $\Delta t_{LL'}^{nn'}(E) = t_{LL'}^{\text{imp};n}(E) - t_{LL'}^{\text{host};n}(E)$ and the structural Green function of the host via the Dyson-like equation $[\tau] = [\Delta t] + [\Delta t][\mathcal{G}^{\text{host}}][\tau]$. This quantity is not site-diagonal and has non-vanishing elements $\tau_{LL'}^{nn'}(E)$ only for pairs of (n, n') for which $\Delta t^n \neq 0$ and simultaneously $\Delta t^{n'} \neq 0$. The structural Green function of the impurity embedded into the host system is then given by

$$\mathcal{G}_{LL'}^{\text{imp};nn'}(E) = \mathcal{G}_{LL'}^{\text{host};nn'}(E) + \sum_{n''} \sum_{L''L'''} \mathcal{G}_{LL''}^{\text{host};nn''}(E) \tau_{L''L'''}^{n''n'''}(E) \mathcal{G}_{L''L'}^{\text{host};n''n'}(E) \quad (4.53)$$

in close analogy to Eq. (4.22).

As mentioned above and in detail in the introductory chapter of this thesis, the KKR method is based on the site-centered expansion of the wavefunctions. In this basis the vacuum is described by fictitious empty cells, i.e. cells without nuclear charge but with non-vanishing electron density, parallel to the surface, in continuation of the lattice describing the crystal geometry. One thus has “vacuum layers” in the sense of “atomic layers” but with empty cells. It is therefore convenient to approximate the Fourier-transformation over a surface at distance z by an integration over a vacuum layer of volume Ω_{scan} , centered at a vertical distance z from the surface by substituting $\int_{(z)} d^2r \rightarrow \sum_{n \in \Omega_{\text{scan}}} \int_n d^3r$. Using the above introduced notation, Eq. (4.29) becomes

$$\begin{aligned} \Delta G(\mathbf{q}; E) &= \Delta G_S(\mathbf{q}; E) + \Delta G_M(\mathbf{q}; E), & \text{with} & \quad (4.54) \\ \Delta G_S(\mathbf{q}; E) &= \sum_{\nu}^{\Omega_{\text{scan}} \cap \Omega_{\text{imp}}} e^{-i\mathbf{q} \cdot (\mathbf{R}_j + \mathbf{x}_{\nu})} \int_{j\nu} d^3x e^{-i\mathbf{q} \cdot \mathbf{x}} \sum_L \Delta G_{S;L}^{j\nu}(\mathbf{x}, \mathbf{x}; E) \\ \Delta G_M(\mathbf{q}; E) &= \frac{\Omega_{\text{BZ}}}{\Omega_{\text{rec}}^2} \sum_{\nu} e^{i\mathbf{q} \cdot \mathbf{x}_{\nu}} \int d^2k \sum_{i\mu, i'\mu'}^{\Omega_{\text{imp}}} e^{-i\mathbf{k} \cdot \mathbf{R}_i} e^{-i(\mathbf{k} - \mathbf{q}) \cdot \mathbf{R}_{i'}} \\ &\quad \times \sum_{LL'L''L'''} \mathcal{G}_{LL''}^{\text{host}\nu\mu'}(\mathbf{k}; E) \tau_{L''L'''}^{i\mu; i'\mu'}(E) \mathcal{G}_{L''L'}^{\text{host}\mu'\nu}(\mathbf{k} - \mathbf{q}; E) \\ &\quad \times \int_{\nu} d^3x e^{-i\mathbf{q} \cdot \mathbf{x}} [\mathcal{R}_L^{\nu}(\mathbf{x}; E) \bar{\mathcal{R}}_{L'}^{\nu}(\mathbf{x}; E)] \end{aligned}$$

where $\Delta G_{S;L}^{j\nu}(\mathbf{x}, \mathbf{x}; E) = G_{S;L}^{\text{imp};j\nu}(\mathbf{x}, \mathbf{x}; E) - G_{S;L}^{\text{host};j\nu}(\mathbf{x}, \mathbf{x}; E)$ is the difference in the single-site parts of the Green functions with and without impurity and is only taken in the impurity region as it vanishes with vanishing ΔV outside. Note that the terms $[\mathcal{R}_L^{\nu}(\mathbf{x}; E) \bar{\mathcal{R}}_{L'}^{\nu}(\mathbf{x}; E)]$ and $\Delta G_{S;L}^{j\nu}(\mathbf{x}, \mathbf{x}; E)$ are 2×2 or 4×4 matrices in Pauli- or Dirac-theory and have to be traced over the spin as well as large and small components. It shall however be noted that no $\mathbf{k}$ -dependence occurs in ΔG so that only the structural Green function (given by Eq. 4.52) has to be computed on a dense $\mathbf{k}$ -mesh. Also the matrix elements of the scattering path operator $\tau_{L'L''}^{i\mu; i'\mu'}(E)$ depend only on the energy. By virtue of the principal-layer and decimation technique [73, 122, 123] the structural Green function can be computed efficiently even for a very large number of layers (hundreds of atomic layers) and even in the case of semi-infinite boundary condition to a bulk crystal.

To arrive at the FT-QPI image in Fourier space where the short range behavior is taken out ($\Delta \tilde{n}(\mathbf{z}; \mathbf{q}; E)$ as described in Eq. 4.33) the form of Eq. (4.54) changes. Outside of Ω_{imp} the

4.4. QPI calculations within the KKR formalism: the “real thing”

single-site contribution automatically vanishes. In the multiple scattering part on the other hand the same region has to be excluded explicitly, which is done by replacing $\Delta G_S(\mathbf{q}; E)$ in Eq. (4.54) by the following correction to the multiple scattering part

$$\begin{aligned} \mathcal{C}_M(\mathbf{q}; E) = & \sum_{j\nu}^{\Omega_{\text{excl}}} e^{-i\mathbf{q} \cdot (\mathbf{R}_j + \mathbf{x}_\nu)} \sum_{i\mu, i'\mu'}^{\Omega_{\text{imp}}} \sum_{LL'L''L'''} \mathcal{G}_{LL''}^{\text{host}j\nu; i\mu}(E) \tau_{LL''L'''}^{i\mu, i'\mu'} \mathcal{G}_{L''L'''}^{\text{host}i'\mu'; j\nu}(E) \\ & \times \int_{\nu} d^3x e^{-i\mathbf{q} \cdot \mathbf{x}} [\mathcal{R}_L^\nu(\mathbf{x}; E) \bar{\mathcal{R}}_{L'}^\nu(\mathbf{x}; E)] \end{aligned} \quad (4.55)$$

Here we used the notation Ω_{imp} and Ω_{excl} indicating the full region where $\Delta V \neq 0$ and the region of the impurity cluster that is excluded from the summation, respectively. These regions may overlap but are not necessarily identical.

The integrals $\int_{\nu} d^3x e^{-i\mathbf{q} \cdot \mathbf{x}} [\mathcal{R}_L^\nu(\mathbf{x}; E) \bar{\mathcal{R}}_{L'}^\nu(\mathbf{x}; E)]$ can be computed by employing the usual expansion of the scattering solutions in the KKR formalism [58] together with the identity $e^{-i\mathbf{q} \cdot \mathbf{x}} = \sum_{\ell m} i^\ell j_\ell(qr) Y_{\ell m}(\mathbf{q}) Y_{\ell m}^*(\mathbf{r})$, where spherical harmonics $Y_{\ell m}$ are used.³⁴ In this way the integral splits in a radial part to be calculated numerically and angular parts to be calculated semi-analytically. The integrals with similar contributions in the expression for $\Delta G_{S_L}(\mathbf{q}; E)$ can be treated in the same way.

In summary, within the KKR formalism the QPI images in real space can be computed via

$$\Delta n(\mathbf{q}; E) = -\frac{1}{2\pi i} \text{Tr} [\Delta G_M(\mathbf{q}; E) - \Delta G_M^*(-\mathbf{q}; E) + \Delta G_S(\mathbf{q}; E) - \Delta G_S^*(-\mathbf{q}; E)] \quad (4.56)$$

$$\Delta \tilde{n}(\mathbf{q}; E) = \Delta n(\mathbf{q}; E) + \frac{1}{2\pi i} \text{Tr} [\mathcal{C}_M(\mathbf{q}; E) - \mathcal{C}_M^*(-\mathbf{q}; E)] \quad (4.57)$$

giving the expressions for $\Delta n(\mathbf{q}; E)$ as introduced in general in Eq. (4.30) and $\Delta \tilde{n}(\mathbf{q}; E)$ in 4.33.³⁵

4.4.2. Results of QPI calculations for different defects in Bi_2Te_3 within the ab-initio KKR formalism

Finally the results of the newly implemented first-principles approach to the direct QPI calculation in reciprocal space, that was introduced above are discussed. For this purpose, based on some input from the *KKRcode*, a new module has been developed that implements the effective calculation of QPI images in reciprocal space with the KKR method. The dense $\mathbf{k}$ - and $\mathbf{q}$ -meshes that are needed for high-quality images, as seen from Eq. (4.54) and Eq. (4.56), were parallelized using a straight forward hybrid OpenMP/MPI scheme over the $\mathbf{k}$ and $\mathbf{q}$ -loops.

Figure 4.11 summarizes the results of the simulation by showing the FT-QPI images (absolute value, $|\Delta n(\mathbf{q})|$) for three defects; Te_{Bi} (non-magnetic), Mn_{Bi} and Fe_{Bi} are shown for $E = E_F$ in (a-c) and $E = E_F - 50\text{meV}$ in (d-f), respectively. For the comparison with previous results (model FT-QPI and exJDOS) we will now refer to the FT-QPI images computed from first principles as *KKRQPI* images to highlight the difference to the model calculations also semantically.

³⁴More details on the implementation are given in Appendix A.1

³⁵Note that Eq. (4.57) assumes that Ω_{excl} and Ω_{imp} have no overlap. Otherwise the corresponding part in the single site part has to be subtracted in analogy to the multiple scattering part.

4. Revealing scattering properties of topologically protected electrons

The results presented here were computed with a 301×301 k -point mesh in the surface Brillouin zone and the converged potentials of the host system and the impurities, that were used in the scattering and exJDOS calculations, were reused.

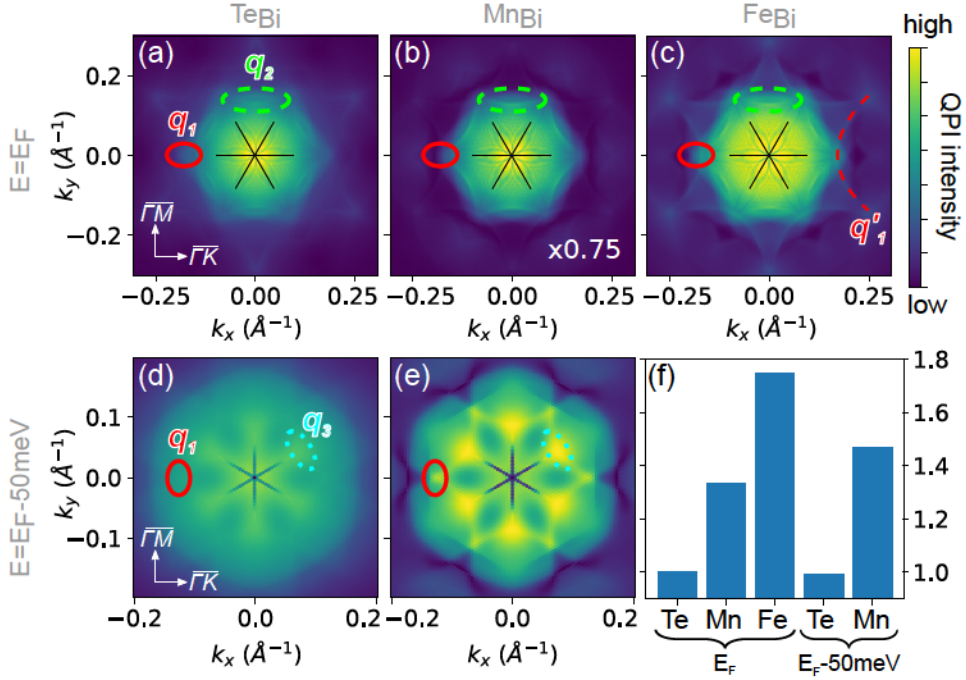


Figure 4.11.: Fourier-transformed QPI images fully from first principles [$|\Delta n(\mathbf{q}; E)|$ given in Eq. (4.56)]. Panels (a-c) show the simulations for Te, Mn and Fe impurities at $E = E_F$ and in (d,e) the corresponding images for $E = E_F - 50 \text{ meV}$ for the Te and Mn impurities are shown. For each energy the same linear color scale has been used for the three defects for comparability but the data for Mn at $E = E_F$ shown in (b) has been scaled by a factor 0.75. The $\mathbf{q}$ -vectors $\mathbf{q}_1$ (red ellipse), $\mathbf{q}'_1$ (red dashed line) and $\mathbf{q}_2$ (green dashed ellipse), $\mathbf{q}_3$ (cyan dotted ellipse) highlight the time-reverse backscattering features, trivial scattering and (near) backscattering channels, respectively, as discussed previously in Figs. 4.7-4.10. In (f) the relative intensities $|\Delta n(\mathbf{q}_1)|/|\Delta n(\mathbf{q}_1)|[\text{Te}]$ at $\mathbf{q}_1$ is shown, highlighting the increase in the backscattering signal with the magnetic moments of Mn (and Fe for E_F). The data was taken within the vacuum layer at a vertical distance from the surface of $\approx 3.4 \text{ \AA}$.

At the Fermi energy ($E = E_F$), in the KKRQPI images for all three defects show a high intensity centered around the origin that decays with increasing $|\mathbf{q}|$. This dominating feature that is absent in the exJDOS and model QPI calculations can be understood as a result of the near-impurity behavior³⁶ in the charge density that was shown in real space for the

³⁶Cf. discussion on the star-like near-impurity features on page 83.

MnBi impurity in Fig. 4.6(b). This can be proven with a direct Fourier transform of the real space data [Fig. 4.6(b)] that is presented in Figure 4.12 where in (a) the Fourier transform of the full image, in (b) the Fourier transform of the long-range behavior only and in (c) the dominating contribution of the near-impurity region only is shown. The near-impurity region was chosen as all positions within a radius of $R_0 = 28 \text{ \AA}$ around the impurity position at (0,0), which excludes the first 6 shells of in-plane neighbors where the signal in the charge density is much higher than the oscillation seen in the long-range limit. The low resolution in the images are a result of the limited size in the real space data that have been calculated. This highlights the importance of the approach followed here instead of a direct Fourier transform of real space images that would become numerically far too expensive to be done in sufficient accuracy for practical cases.

The difference between the KKRQPI and model and exJDOS images is therefore easy to understand: In the model calculations (Fig. 4.7) the impurity was assumed to be of point-like nature which does therefore not include the extended nature of the defect that comes from the near-impurity region. Therefore in the model FT-QPI results no significant small q feature is seen. The exJDOS includes only the scattered waves and gives them by the STM sensitivity factor γ^{STM} an ad-hoc weight, certainly neglecting the near-field effects.

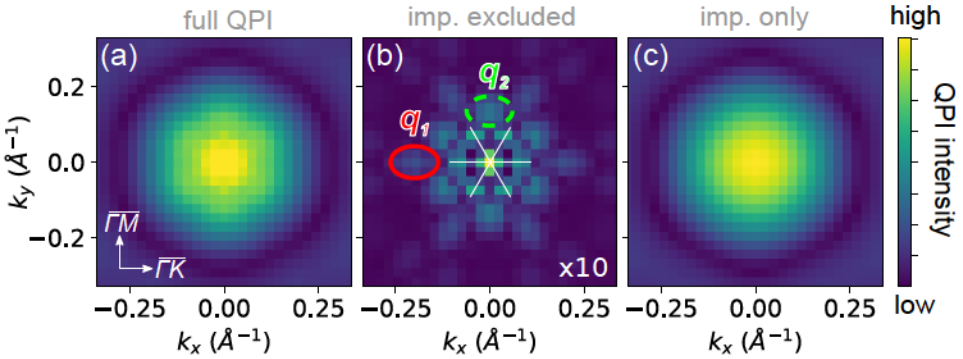


Figure 4.12.: QPI images in reciprocal space based on a direct Fourier transform of the real space image shown in Fig. 4.6(b) shown in a linear color scale. Panel (a) shows the Fourier transform of the full image, (b) the QPI image, but with the signal within a radius of $R_0 = 28 \text{ \AA}$ around the impurity at (0,0) taken out and (c) the QPI image for the impurity region only, i.e. the region within the radius R_0 without the long range oscillations. The Fourier transform of the short range around the impurity is dominating the full QPI image, which is why the important scattering channels (q_1 and q_2) are only hardly visible in (a) but clearly there if the impurity region is excluded as shown in (b). The thin white lines in (b) indicate short range scattering feature as in Fig. 4.11(a-c). The low resolution in the images is due to the small area of real space positions that is available from the calculation in real space shown in Fig. 4.6(b) and the intensity in (b) has been scaled up by a factor 10 as compared to the other panels.

Nevertheless, the KKRQPI images of Fig. 4.11 have common signatures with the typical QPI images on Bi_2Te_3 seen in the previous model cases. For one, as in the previous discussions

4. Revealing scattering properties of topologically protected electrons

of the exJDOS images and in agreement with the scattering rates computed in the first part of this chapter, the backscattering signal (q_1) for non-magnetic *and* magnetic single impurities is rather weak at $E = E_F$. In (a) a depression at q_1 can be seen which is lifted in (b) for the Mn impurity and is even stronger visible in (c) for the case of the Fe impurity, where due to the resonant scattering behavior the backscattering rate was found to be larger than for Mn. This is highlighted in the comparison of the KKRQPI intensities at q_1 shown in (f). Additionally, the bow-like q_1' -feature that we associated to the stronger backscattering rates is visible for the Fe impurity as it was the case in the exJDOS images. The trivial scattering channel (q_2) on the other hand can be seen for all three defects although the dominant near-impurity contribution makes it hard to detect. In the exJDOS images a star-like feature was seen around the origin that was assigned to small angle scattering. This feature can also be seen in the ab-initio KKRQPI data (highlighted with thin black lines in (a-c)).

At $E = E_F - 50\text{meV}$ we find essentially the same features in the KKRQPI images as seen previously in the exJDOS calculations. No signature of backscattering (q_1) is found for the non-magnetic Te impurity shown in Fig. 4.11(d) and the dominant feature is the star-like shape ending in spots at q_3 indicating 120° -scattering. With the magnetic moments of the Mn impurity shown in (e), the backscattering signal re-appears but is still relatively small in comparison to the trivial q_3 feature. This is in agreement with the result that was obtained from the exJDOS images in Fig. 4.10. We can therefore say that, although the constant energy contour supports good nesting, single magnetic impurities which formally break time-reversal symmetry only show very weak signatures if increasing backscattering. In particular the time-reverse backscattering associated q_1 -intensity only increases moderately [cf. panel (f)] and small angle scattering signatures coming from the near-impurity region in real-space hide this interesting feature. This can be explained with the observation of quite low back-scattering probabilities for the magnetic impurities, that was discussed in the first part of this chapter together with the theoretical result of vanishing QPI in the charge channel at the exact time-reversal point. We can therefore understand why the backscattering signature in the QPI experiments of magnetically doped topological insulators was very weak [39] or even absent [40, 143]. In the next chapter we will come back to this question and apply the here introduced methods to find a mechanism of tuning the backscattering rate in Bi_2Te_3 leading focused oscillations visible on mesoscopic length scales [131].

In conclusion, the KKRQPI is a powerful tool that is able to compute impurity specific QPI images from first principles with no further approximations than those inherent in any DFT calculations (exchange-correlation potential and the Tersoff-Hamann model).

4.5. Conclusion and outlook

In this chapter we have investigated the scattering properties of electrons coming from the topological surface state in the prototypical 3D topological insulator Bi_2Te_3 . The theory of scattering was introduced and scattering off different non-magnetic and magnetic defects at the surface of a Bi_2Te_3 thin-film was studied within this thesis for the first time from first principles. Our analysis improved the understanding of scattering processes in the topological surface state and provided deeper insights into the physics of topologically protected electrons.

The chapter was divided in two parts; (i) the introduction and analysis of scattering processes off different defects and (ii) the experimentally observed result of scattering processes, namely

the quasiparticle interference around single defects in real- and reciprocal space.

Scattering

Through the analysis of time-reversal preserving (non-magnetic) and time-reversal breaking scattering process off defects in the strong topological insulator Bi_2Te_3 from first principles we found strong signatures of topological protection in the scattering processes. We verified that exact backscattering in TIs for non-magnetic defects is absent and showed that also an extended region in the vicinity of the exact point of time-reversal scattering shows very low scattering probabilities. In other words, we always find strong forward scattering for time-reversal preserving impurities. Even for single magnetic impurities the backscattering rate was found to be relatively small. The calculated scattering rates were understood in terms of a model for spin-conservation for non-magnetic impurities and with a spin-selection rule for magnetic impurities, stating that for large angle scattering the direction of an alignment of the final state's spin with the impurity spin moment is favored.

Quasiparticle interference

Quasiparticle interference images were computed in real space and also in their Fourier-transformed (FT-QPI) versions, which was the focus of the work presented here. Several approaches to the simulation of FT-QPI images have been discussed in terms of model calculations, phenomenological approaches and fully ab-initio calculations. The typical features seen in QPI experiments have been discussed and explanations based on our calculations were given.

We pointed out the limits of the widely used (spin-conserving) joint density of states, (S)JDOS, approaches, and developed a significant improvement with the extended joint density of states, exJDOS, that takes into account a realistic description of the scattering properties off impurities by promoting back-scattering interference and accounting for the full scattering rate. Also the ab-initio FT-QPI calculation has been developed making it possible to compute realistic FT-QPI images fully from first principles, that are impurity specific providing us with predictive power in the calculations.

Overall, the importance of ab-initio calculations for a quantitative and not only qualitative description of scattering processes in the fascinating class of topological materials has been demonstrated. The methods developed here will further be used to study the focusing effect in topological insulators that will be discussed in the following chapter. In the future the computational methods could be improved further and applied to more complex systems, for example larger impurities on topological insulators, metals or other topological systems, for example the recently emerging field of type-II Weyl semimetals.

Superparamagnetism-induced mesoscopic electron focusing in topological insulators

In this chapter the scattering properties in topological insulators, in particular with respect to backscattering signatures in magnetically doped Bi_2Te_3 , and how they can be controlled at the atomic scale, will be analyzed. The here presented work is the result of a collaboration between an STM group (Paolo Sessi, Matthias Bode et al. from Würzburg University), an XMCD group (Alessandro Barla, Carlo Carbone et al. from Trieste University) and our theoretical support based on first principles calculations. The results have been published in Ref. [131], from which most of the figures have been taken and on which the discussion in this chapter is based.

In the previous chapter we have seen that backscattering, which is usually prohibited in topological insulators by time-reversal symmetry, can be induced by magnetic dopants [39, 40]. Here, we were able to engineer the – in the previously discussion always very low – backscattering rates to be large enough that it can even be seen in the charge channel with conventional STM. Our combined study of quasiparticle interference measurements and density-functional-theory-based simulations showed that – by appropriate Fermi level tuning – strongly focused interference patterns can be observed on the surface of Bi_2Te_3 . This proves that coherent transfer of information over mesoscopic length scales can be achieved using the topological protected surface state of TIs.

With the help of our ab-initio as well as model-based calculations we could unveil that two conditions have to be fulfilled to see a strong backscattering signal in charge density oscillations around impurities: (i) the Fermi surface has to support good nesting with large parallel segments in its shape and (ii) a few magnetic dopants have to couple ferromagnetically (FM) forming a larger defect with a macro-spin, that exceeds the magnetic moment of the single impurity. Indeed, the X-ray magnetic circular dichroism (XMCD) measurements of the Trieste group showed superparamagnetism even at

very dilute Mn concentrations with groups of Mn atoms aligned in ferromagnetic configuration.

The chapter is organized as follows. After an introduction, the STM measurements of the Würzburg group are reviewed, then the observations are analyzed in detail with the help of our first principles calculation and finally a comparison to the XMCD measurements by the Trieste group is done.

5.1. Introduction

Coherence of waves in general, describing the capability of keeping a well-defined phase relation while propagating in space and time, sets the limit on how far information can be transmitted and processed with high fidelity. The quantum mechanical nature of quasiparticles in solids, for example realized by charge excitations in the topological surface state of strong topological insulators, are examples where phase coherence plays an important role. The STM technique allows to visualize coherent phenomena in real space by imaging the long-range standing wave pattern around defects on surfaces [132]. As introduced in the previous chapter, these are produced by scattering events around atomic-scale defects that can even be engineered on the level of single atoms to tailor quantum mechanical interference phenomena, which was for example demonstrated by the creation of quantum mirages [177]. In the past even the phase of electron wavefunctions was successfully extracted [178] and indirect coupling mechanisms [179], which will be studied in detail for transition-metal-doped Bi_2Te_3 in chapter 7, were measured. Recently, the measurement of quasiparticle interference images (QPI) allowed to show that quasiparticle waves propagate anisotropically on a surface, if the constant-energy contour (CEC) deviates from an isotropic contour. In analogy to optics, focusing and defocusing leads to enhanced intensity along certain crystallographic directions and suppression along others [180]. In the context of the present study this can be observed in the undamped magnitude of charge density oscillations in certain directions with the distance from a scattering center.

Despite its relevance for possible future applications based on the quantum nature of quasiparticles, still much has to be revealed about the role played by the spin-degree of freedom for QPI phenomena in particular. The topological surface state (TSS) of topological insulators (TIs) is a prime example for materials where the spin plays a major role. The strong spin-orbit coupling locks the spin and momentum degrees of freedom forming the helicity in the TSS, so that the motion of electrons from the TSS is always connected to a certain spin-polarization. As we have discussed in the introductory chapter to scattering in topological insulators (chapter 4), the spin-momentum locking leads to the suppression of backscattering [37, 42], as long as time-reversal symmetry is not broken, and even ties spin currents intrinsically to charge currents [7]. Most of the discussion in topological insulators deals with the vicinity of the Dirac point where the CEC is circular. However in Bi_2Te_3 the electronic structure of the TSS shows an evolution from an almost circular, and therefore convex, shape of the CEC to a snowflake-like (concave) shape at higher energies [141, 181]. A specific energy can therefore be found where the CEC is hexagonal, consisting of straight parallel edges facing each other. This energy region has already been seen in the discussion of the previous chapter and it obviously supports good nesting vectors, which can strongly

enhance the long-range susceptibility to external perturbations. In pristine TIs, these nesting – or focusing – scattering vectors are suppressed by time-reversal symmetry [37, 42]. In bulk [39] and surface-doped TIs [40], magnetic impurities break time-reversal symmetry opening up the backscattering channel. However, the experimentally accessible backscattering signal along the $\bar{\Gamma}K$ -direction, was found to be either very weak [39] or comparable to other, i.e. trivial, scattering channels [40].

In a combined experimental (STM measurements performed at Würzburg University, XMCD measurements at University of Trieste) and theoretical work, consisting of our ab-initio and model based calculations, we could now show that carefully tuning the Fermi level and the type of defect in a magnetically doped TI can maximize the backscattering intensity such that it leads to highly focused interference patterns in real space. We demonstrate that these can even be seen in the charge channel on topological insulators, which intrinsically is strongly suppressed due to the opposite spin-direction of the wavefunctions on opposite sides of the Fermi surface in the helical TSS. This is supported by the good nesting condition that is met in the hexagonally deformed CEC of Bi_2Te_3 . The resulting coherent quantum oscillations are observed in QPI signals that can be detected experimentally over tens of nanometers without significant loss of intensity. With the help of our first principles calculations we have been able to show that the long coherence lengths require two conditions to be fulfilled: (i) the Fermi surface (FS) must exhibit large parallel segments (support good nesting) *and* (ii) the magnetic dopants must couple ferromagnetically to create a high-spin state forming a larger defect with a strong magnetic moment that increases the backscattering probability. The existence of superparamagnetic coupling, leading to groups of ferromagnetically coupled Mn atoms, that already emerges at very dilute concentrations for Mn on Bi_2Te_3 , has been proven to exist with X-ray magnetic circular dichroism (XMCD) measurements.

Our study provides an indication of strongly anisotropic Dirac fermion-mediated interactions and demonstrates that spin information¹ can indeed be transmitted over long distances. This might help to design future experiments and devices based on coherent quantum effects, which could possibly be realized in topological insulators.

5.2. Seeing electron focusing and backscattering in real and reciprocal space: STM experiments on Mn surface-doped Bi_2Te_3

We start the discussion with a review of the experimental setup² and the STM measurements by the Würzburg group, that were initially discussed in [131]. The experiments were performed at a controlled sample temperature of $T < 5$ K. The cleaved Bi_2Te_3 crystal has been put into the vacuum chamber and afterwards a small amount³ of Mn was deposited in-situ by e-beam evaporation onto the cold sample surface ($T \leq 7$ K). The nominal amount of Mn on the

¹The observed charge density oscillations also contain the spin information, since the oscillations are on the one hand the result of propagating spin polarized states due to the spin-momentum locking in the TSS of Bi_2Te_3 , and on the other hand reflect the existence of strong *spin* scattering potentials. This aspect will be the central point of this chapter.

²The STM technique has been introduced in the previous chapter.

³A coverage of much less than a monolayer.

5. Superparamagnetism-induced mesoscopic electron focusing in topological insulators

surface was measured to be 1% of a monolayer (0.01 ML). In Figure 5.1(a) the topographic image (taken in constant-current mode) of the Bi_2Te_3 surface after Mn evaporation can be seen, where the small dots, that are found all over the surface, are individual Mn atoms. Keeping the temperature low during adatom evaporation is important to prevent the Mn atoms to diffuse deeper into the Bi_2Te_3 surface. This experimental setup allows to have microscopic control over the defects and makes sure that the TSS, that is exponentially localized at the surface, couples to the defects. The distribution of Mn atoms on the surface has been analyzed with the help of STM images, where a statistical distribution of nearest-neighbor Mn-Mn distances was found (cf. supplemental material of Ref. [131]) with a peak in the distribution at an interatomic distance between 1 and 3 nm. Before deposition of the impurities, the Bi_2Te_3 crystal was intrinsically n-doped and the introduction of Mn atoms results a negative shift of ≈ 120 meV of the Fermi level [40]. This results in a position of the Fermi level that – after Mn evaporation – lies within the bulk band gap (see supplementary information in Ref. [131]).

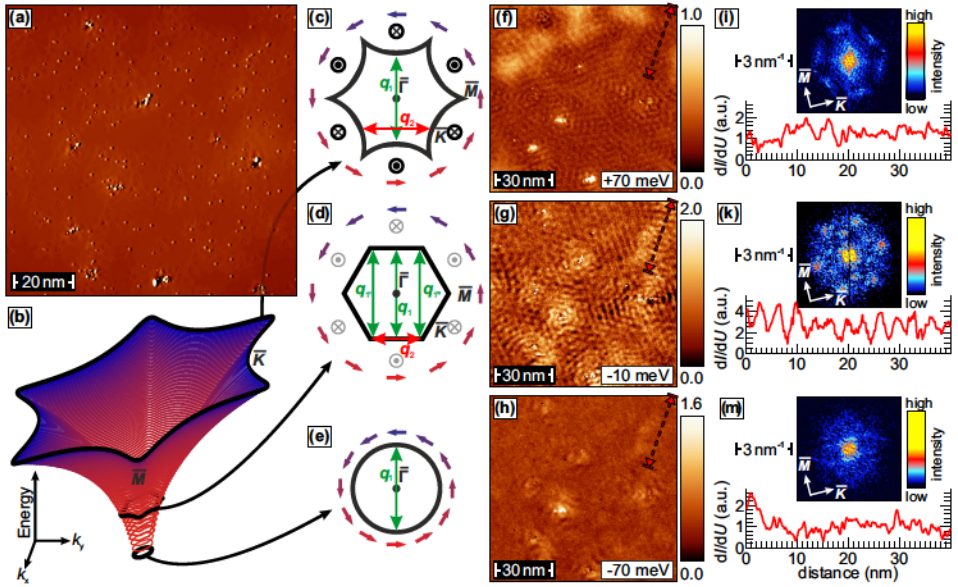


Figure 5.1.: (a) Topographic STM image of 0.01 ML Mn on Bi_2Te_3 ($I = 35$ pA; $U = 150$ mV). (b) Schematic dispersion above the Dirac point and (c-e) constant-energy contours with in-plane/out-of-plane spin polarization at selected energies. Green and red arrows indicate preferred scattering vectors q_1 and q_2 along $\bar{\Gamma}\bar{K}$ and $\bar{\Gamma}\bar{M}$ directions, respectively. Corresponding quasiparticle interference maps measured at energies that mark the transition from convex to concave constant energy cuts are shown in (f) $E - E_F = +70$ meV, (g) -10 meV, and (h) -70 meV. Line sections measured between the arrows are plotted in panels (i-m). Insets show the corresponding Fourier-transformed dI/dU maps (top, raw data). Experiments were performed by the Würzburg group and the image including caption was taken from Ref. [131].

In Fig. 5.1(b) a sketch of the dispersion of the surface state in Bi_2Te_3 is shown, where the CECs relevant for the following discussion are highlighted by black lines and shown in detail (not to scale with respect to each other) in Fig. 5.1(c-e). Just above the Dirac point the CEC has a circular shape with a spin that is perpendicularly locked to the momentum (see also discussion in the previous chapter). It leads to a helical spin structure indicated by colorized arrows. With the strong warping in Bi_2Te_3 , further away from the Dirac point, the CEC becomes hexagonal and eventually turns into a snowflake-like shape. As we have computed in the previous chapter (cf. Fig. 5.2), this goes along with the development of an alternating out-of-plane component of the spin polarization within the valleys of the CEC oriented in $\overline{\Gamma K}$ direction of the surface Brillouin zone. This has previously been shown theoretically [141] as well as experimentally [181]. The symbols ($\otimes$, $\odot$) in Fig. 5.1(c) and (d) indicate the developing out-of-plane component with higher energy. The previous discussion (chapter 4) of the scattering rates showed that this leads to changes in the scattering properties of magnetic defects. In the following chapter the energy dependence of the scattering rates will be discussed in detail. Here we focus on the three representative energies, depicted in Fig. 5.1(c-e), and in particular on the backscattering strength for scattering off time-reversal breaking impurities.

The STS scans, showing the QPI at three representative energies ($E - E_F = +70$ meV, -10 meV, and -70 meV) which mark the transition from convex to concave shape of the CEC, are shown in panels (f-h). We would like to highlight that the case presented in (d,g) represents the perfect nesting region with flat parts on opposite sides in the CEC. Green and red arrows in Fig. 5.1(c-e) depict the scattering vectors $\mathbf{q}_1$ and $\mathbf{q}_2$, that were introduced in the previous chapter (Figs. 4.8 and 4.10) and that are specific for each energy. These scattering vectors determine the long range limit of the oscillations in the spirit of the stationary phase approximation [155]. At $E - E_F = -70$ meV, the CEC is almost circular and consequently only one⁴ (we count only the inequivalent vectors and not the 5 other copies associated to the hexagonal symmetry) scattering vector ($\mathbf{q}_1$) together with only very weak QPI modulations are observed in Fig. 5.1(h). The line scan, taken along the red line in Fig. 5.1(h), and Fourier-transformed (FT-)QPI map, show in (m), confirm the very low intensity of scattering events. This can be understood by arguments given in the introduction of scattering processes in topological insulators (cf. chapter 4.), where it was explained that the time-reversal partners cannot interfere to give a signal in the charge channel and a spin-polarized measurement would be needed to detect this. In contrast, very strong scattering is observed in the QPI map at $E - E_F = -10$ meV, shown in panel (g), with intense modulations of the dI/dU signal seen in the line scan profile, that is shown in (k). The corresponding FT-QPI map reveals the simultaneous existence of two (inequivalent) scattering vectors: due to the hexagonal symmetry, six (very weak) inner spots in $\overline{\Gamma M}$ -directions and six (dominating) outer spots along the $\overline{\Gamma K}$ -directions are visible. As we have discussed in the previous chapter, the scattering channel along $\overline{\Gamma M}$ ($\mathbf{q}_2$, weak intensity) is routinely found on TIs [39, 42, 167] and can be associated to what we called the trivial scattering channel. Its appearance was understood based on the parallel out-of-plane spin polarization in next-nearest

⁴Here we neglect – for now, more will follow in the next chapter – that bulk states are actually coexisting with the topological surface state at this energy (seen in the previous chapter in Fig. 4.4). This might open up new scattering channels, including ones with $\mathbf{q}$ in backscattering direction. However, the delocalized nature of bulk states will lead to scattering away from the surface so that no significant long-range signature in the standing wave images seen by STM on the surface is expected from them.

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sections of the CEC that favors the previously discussed 120° (between $\mathbf{k}$ and $\mathbf{k}'$) scattering events. The high-intensity spots, visible along $\overline{\Gamma K}$, are not found on pristine TIs which implies that, here, time-reversal symmetry is broken [182] due to the presence of the Mn adatoms. This conjecture will on the one hand be tested with our ab-initio calculations in the main part of this chapter and furthermore experimentally verified by XMCD measurements⁵ for Mn doped Bi_2Te_3 that are presented at the end of this chapter.

At even higher energies ($E - E_F = +70$ meV) again a weaker⁶ modulation of dI/dU signal is found. The corresponding FT-QPI map, shown in (i), only shows six weak spots along the $\overline{\Gamma M}$ direction corresponding to $\mathbf{q}_2$. In particular no backscattering signal ($\mathbf{q}_1$) can be detected although magnetic impurities are present, which fits the discussion of FT-QPI images for the warped CEC, presented in the previous chapter.

A closer inspection of the real space images reveals that, with the opening of the backscattering channel [cf. (g,k)], coherent waves can propagate over distances larger than 30 nm without any significant intensity loss. This is seen in the line scan along the red line indicated in (g). The absence of a clear decay within this range prohibits a quantification of the relaxation length by fitting with an exponential function as done previously in Ref. [183]. However the experimental results indicate that the lower bound exceeds hundreds of nanometers and furthermore show that the charge density oscillations are highly focused⁷ over mesoscopic distances well beyond the atomic scale. This suggests that Dirac fermion-mediated interactions in TIs will be highly anisotropic, as theoretically predicted [184]. A detailed discussion of the anisotropic, distance-dependent interaction strength between magnetic impurities as well as their mechanism will be presented later on in chapter 7.

In the remainder of this chapter we focus on the explanation of the STM results, which have been discussed so far. The Fermi surface, seen in Fig. 5.1(d), supports good nesting, which is known to be a prerequisite for the focusing effect [154, 180]. The additional scattering vectors, seen in Fig. 5.1(d), for which $\mathbf{v}_k \approx -\mathbf{v}_{k'}$ ($\mathbf{v}_k$ is the group velocity), e.g. $\mathbf{q}'_1$ or $\mathbf{q}''_1$, are never strictly forbidden by time reversal symmetry, but are expected to be strongly suppressed by the almost opposite spin projection of initial and final states. The analysis of single defects, shown in the previous chapter, revealed that this is even true for single magnetic defects. A priori, different scenarios could be invoked to explain the the backscattering signature seen in the experiment at $E - E_F = -10$ meV: (i) the existence of time-reversal symmetry breaking perturbations is sufficient; (ii) both conditions, FS nesting *and* the presence of magnetic scatterers, are required; (iii) the Mn adatoms effectively polarize the topological-state spins, so that after the overall breaking of time-reversal symmetry any larger scattering center leads to the observed signature of backscattering. The experimental finding that only the nesting condition supporting CEC (Panels (d,g,k) in Fig. 5.1) leads to a clear backscattering signal, indicates that hypothesis (i) can be ruled out – in agreement with the QPI simulations for the warped CEC (cf. previous chapter).

Additionally, the discussion on single magnetic and non-magnetic scattering centers in the previous chapter showed that indeed the scattering rate for near-backscattering is rather

⁵X-ray magnetic circular dichroism allows to measure the magnetic moments of the adatoms. A detailed discussion of the XMCD technique in comparison with our ab-initio calculations of magnetic exchange interactions for adatoms on Bi_2Te_3 will be the subject of a chapter 7.

⁶Cf. the scale bars of Fig. 5.1(f,g,h).

⁷In the STS image and its Fourier-transform, shown in (g,k) a strong signature is only seen in $\overline{\Gamma K}$ but not in $\overline{\Gamma M}$.

low, even when time-reversal symmetry is formally broken by single magnetic impurities. At first sight it is therefore puzzling that the strong focused oscillations have been observed in experiment. However, by means of our theoretical ab-initio and model-based study we were able to show that case (iii) can also be ruled out and that strong focusing as well as a *strong* magnetic scattering center, with an magnetic moment that exceeds the moment of a single impurity, is needed to achieve backscattering rates that are sufficient for the observations in the STM-based experiments that were presented so far.

5.3. Explanation of the observations: calculations and discussion

Here we discuss our theoretical analysis, consisting of model calculations based on the T -matrix formalism, (introduced in the previous chapter) and first principles calculations of scattering rates as well as simulated FT-QPI images. The results are analyzed in detail to understand the physical mechanism that governs the experimental observations, which have been discussed in the first part of this chapter. First, the details of the calculations are reviewed before the importance of magnetic order and the tailoring of the backscattering amplitude are analyzed.

5.3.1. Details of the calculations

The ab-initio based calculations of this chapter are based on the local spin density approximation as parametrized by Vosko et al. [53], where in our calculations we used the relativistic full-potential Korringa-Kohn-Rostoker Green function method. As mentioned in more detail in the previous chapter, the pristine Bi_2Te_3 surface is modeled by a 6 quintuple layer thick film, into which defects have been embedded self-consistently [61]. A number of different impurities were examined, namely non-magnetic Te-vacancies (single vacancy site Vac_{Te} or three neighboring cells Vac_{Te}^3 representing a larger defect). As will be discussed later, the important scattering processes arise from small clusters of Mn atoms, e.g. trimers, residing on the surface [bright spots in Fig. 5.1(a,f-h)]. However, their exact geometry is experimentally unknown. We chose to simulate such trimers by three Mn impurities substituting 3 Te atoms in the topmost Te layer, in a triangular geometry. We compared with the properties of isolated Mn atoms at the same lattice position and, as we find, important is the total spin moment and not the exact position (comparing also with the results of the Mn_{Bi} impurity of the previous chapter). It is known [148, 185, 186] that the Bi substitution site (that has been considered in the previous chapter) is a fact the thermodynamically stable position. However the experimental setup of depositing Mn atoms at very low temperatures does not allow the Mn atoms to relax to their stable position. Instead they stay on the surface, where they land upon e-beam evaporation, and do not relax deeper into the crystal. The defects under consideration consist of single atom defects or extend over three neighboring sites (indicated by superscript 3) in triangular configuration. A perturbed surrounding shell of host atoms was included in the calculation in order to account for the charge screening by the metallic surface state and throughout the calculation an angular momentum cutoff of $\ell_{\text{max}} = 3$ was used. The scattering amplitudes were calculated by the Golden Rule from the T -matrix of the impurity,

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obtained by a calculation of the impurity Green function as described in Refs. [62, 75] as well in the previous chapter. Structural relaxations around the impurities were neglected and in the calculation of FT-QPI images the previously introduced extension of the widely used joint density of states approach [37, 172], i.e. the exJDOS, was used.

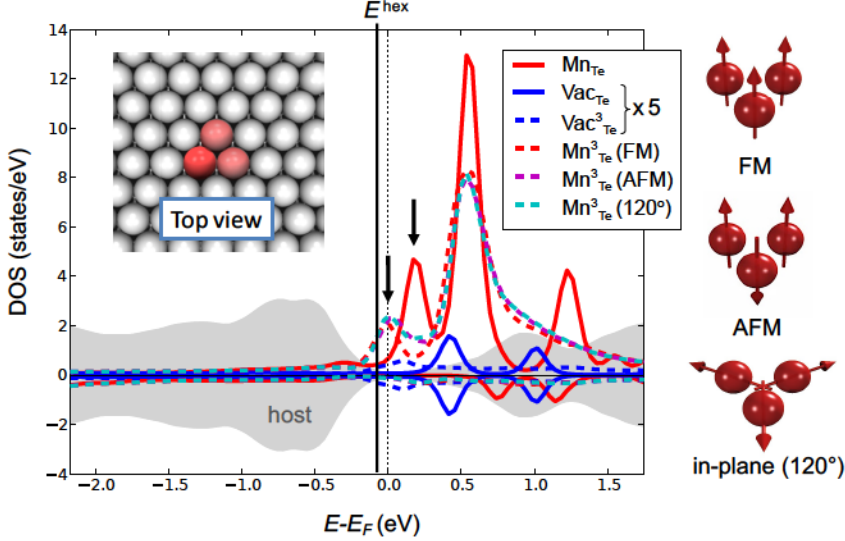


Figure 5.2.: Impurity density of states for different impurities embedded into the first Te layer on the surface of Bi_2Te_3 , replacing one (or three) Te atoms in the surface. The DOS of the first quintuple layer (host) is shown in gray, the DOS on the Mn_{Te} impurities with red and for the Vac_{Te} impurities in blue lines (scaled up by a factor 5). Full lines correspond to the single-atom impurities (Mn_{Te} , Vac_{Te}) and dashed lines to the trimer defects (Mn^3_{Te} , Vac^3_{Te}). For the Mn trimer, in addition to the ferromagnetic alignment of the spins (FM), also the DOS for the in-plane oriented (120°) and antiferromagnetic (AFM) alignment is shown spin-projected in the local frame of reference of each atom. The relative alignment of the moments is depicted on the right and the positions of the impurities within the surface is shown in the inset, where red atoms correspond to the impurity and gray atoms represent the first Te layer in Bi_2Te_3 as seen from above. E^{hex} is the energy at which the CEC becomes hexagonal and the black arrows highlight the shift of the lowest-lying peak in the unoccupied DOS of the Mn^3_{Te} defects as compared to the Mn_{Te} impurity.

The density of states on the impurity site for the different defects under consideration is shown in Figure 5.2. Note that the Fermi level in the calculations is different to the Fermi level found in experiment after Mn-deposition. Here E_F corresponds to a situation where the CEC is snowflake-like in shape and the region, where it becomes hexagonal, is at $E = E_F - 50 \text{ meV}$, which is denoted E^{hex} in Fig. 5.2. We find that the Mn d-shell is close to half-filling with a magnetic moment of $4.4 \mu_B$ (here only the minority peak can be seen while

the majority peak lies below -2 eV . We see that the unoccupied states of Mn substituting the first Te atom⁸ lie closer to the Fermi level than the unoccupied states on Mn substituting Bi (cf. previous chapter). This can be understood from the different hybridization with neighboring atoms, in other words the crystal field at the two positions is different. In the discussion that follows this situation (Mn_{Te}) will be compared to the case where three Mn atoms occupy neighboring sites (dashed lines in the DOS). The calculated ground state for such a configuration is the ferromagnetic alignment, that is shown on the top right of Fig. 5.2. In this defect the individual moments of the Mn atoms add up forming an effective magnetic moment of $13.1\mu_B$. From the impurity DOS we see that the hybridization with neighboring Mn atoms leads to a broadening of the unoccupied states and a shift of the first peak (located at $E - E_F \approx 200\text{ meV}$ in the case of a single Mn atom) very close to the Fermi level. This is highlighted with the black arrows in Fig. 5.2. From the discussion in the previous chapter we would therefore expect to see much larger scattering rates for the Mn trimer than for the single Mn atom at energies close to E_F . In order to study the influence of the total magnetic moment on the scattering rate we compare the FM alignment of the Mn trimer to the case where the moments have been rotated artificially so that in the AFM alignment two out of the three moments cancel each other leaving the effective magnetic moment of a single Mn defect (shown on the middle right in Fig. 5.2), and to the case of the in-plane alignment ("120", bottom right) all three moment are directed in-plane with an effective total magnetic moment that cancels out. The DOS curves for these different trimer defects show very similar peak structures, especially in the position of the resonances so that differences in the scattering properties, that we will analyze within this chapter, can be associated to the size of the effective magnetic moment of the extended defect.

5.3.2. On the importance of magnetic order: uniform background magnetization

We continue the discussion by analyzing the possibility of a uniform magnetic field, that breaks time-reversal symmetry globally,⁹ so that in principle backscattering is possible and any (larger) defect could lead to a sufficiently strong backscattering amplitude. For this purpose on the one hand we extended the model by Lee et al. [139], that was introduced in the previous chapter, by a term describing a global exchange-field $\mathbf{J}$ in the of the host system ($\hat{H}_0 \rightarrow \hat{H}_0 - \mathbf{J} \cdot \boldsymbol{\sigma}$). We can imagine that this situation could be induced by ferromagnetically ordered magnetic impurities on the surface, or by a homogeneous external magnetic field, so that time-reversal symmetry is broken globally in the electron liquid of the topological surface state. Such a situation would lead to an opening of a gap at the Dirac-point, if the magnetization points perpendicular to the surface [187]. However, the TSS, which we study far above the Dirac point would not vanish but would only be deformed, as explained below.

We performed a number of model based calculations for the FT-QPI images (some of which have been discussed in the previous chapter) varying the values of the global exchange coupling strength between $J/E_0 = 0$ and $J/E_0 = 0.2$, where the CECs are strongly deformed, in agreement with the calculations by Henk et al. [187]. The numerical details have already

⁸This is a rather good approximation to the more realistic treatment of the adatom site done in chapter 7 as a comparison to the DOS in Fig. 7.7 (g) shows.

⁹i.e. all over the surface in the TSS and not only locally in the immediate vicinity on the Mn defect.

been introduced in the previous chapter and can also be found in the supplemental information of Ref. [131]. We checked different energies that correspond to the cases of circular, hexagonal and snowflake-shaped CECs, shown in Fig. 5.1(c-e), and varied the strength of the local moment from zero over $m = 0.5$ to $m = 2.0$, corresponding to a non-magnetic defect, a defect with a magnetic moment of $\sim 4\mu_B$ and a stronger defect with a moment of $\sim 16\mu_B$, respectively. The variation of the global exchange coupling strength did not lead to a strong backscattering signal. *Only* for the very strong magnetic moment ($m = 2$, cf. previous chapter) at the energy, that corresponds to the good nesting case [shown in Fig. 5.1(d,g,k)], did we see a significant signature of backscattering in the FT-QPI image.

By means of ab-initio calculations we could furthermore confirm the absence of significant backscattering rates for a uniformly polarized electron liquid on the surface of Bi_2Te_3 . For this purpose, we artificially applied an uniform exchange coupling field in the out-of-plane direction in the host system (6 QL thick slab of Bi_2Te_3). The strength of the external field was tuned so that an opening of the gap at the Dirac point of 16 meV – which was reported in Ref. [187] for 18% impurity concentration of Mn bulk-doped Bi_2Te_3 with ferromagnetic order directed in out-of-plane direction – was produced. With this modified host system the different impurity potentials were re-converged and CECs as well as scattering rates computed.

We observe that the two surface states, initially located on the opposite sides of the Bi_2Te_3 slab and were degenerate in k -space, split off with the external field forming an inner and an outer hexagon (or snowflake-shaped CEC at higher energies). The splitting between the two rings is, however, very small ($< 0.01 \text{ \AA}^{-1}$ at $E = E^{\text{hex}}$). This response to the uniform external field can be understood from the out-of-plane component of the spin, as it develops with the increasing deformation from circular over hexagonal to snowflake-shaped CEC. Subsequent valleys in $\overline{\Gamma K}$ have opposite s_z -components and therefore the external field $-J\sigma_z$ will favor one over the other, effectively breaking the sixfold symmetry. Because the surface states on opposite sides have opposite spin directions, the splitting will be opposite on the bottom surface as compared to the top surface. If we follow the contour going around of one of the two rings that develop at the CEC, then we find that, due to the alternating out-of-plane component of the spin, subsequent segments are localized on opposite surfaces of the crystal. The surface state of one surface is therefore located in the inner ring in one segment and then goes over to the outer ring in the next segment. At the tips in $\overline{\Gamma M}$ between subsequent segments, we find that in the wavefunction of the one surface goes over from the inner to outer ring and in this crossover region we find that the wavefunction becomes delocalized.

This situation reminds us of the Fermi arcs seen in Weyl semimetals, that also form open contours; towards the contour endpoints (at the projections of the bulk Weyl points), the states become delocalized, penetrating into the bulk and touching the opposite surface. Generally, it is known¹⁰ that a strong TI such as Bi_2Te_3 can be tuned into a Weyl phase by breaking either inversion symmetry or time-reversal symmetry [105, 188–190]. However, here we will not continue to look for the Weyl nature in time-reversal broken Bi_2Te_3 since this is a very artificial situation and serves only as a numerical experiment to study the effect of a uniform exchange split TSS.

Although the assumed external field is very strong, as it was applied for values representing

¹⁰A more detailed discussion of Weyl semimetals will be presented in the last chapter where the scattering properties of the type-II Weyl semimetal candidates MoTe_2 and WTe_2 are discussed.

a very high¹¹ concentration of magnetic doping, no significant enhancement in the (near) backscattering rates for neither single Te-vacancy nor single Mn impurity were found. Even for the considerably larger defect of a Te vacancy trimer (i.e. three neighboring Te atoms that are missing in the surface forming a trigonal hole as indicated in the inset of Fig. 5.2) only a vanishing backscattering probability was seen.

We can therefore conclude, that the hypothesis of a uniform exchange splitting, generated by ferromagnetic order between different impurities that collectively polarize the topological surface state, has to be ruled out as an explanation of the experimental results. In the following the impurity-dependent backscattering strength will therefore be analyzed further.

5.3.3. Tailoring the backscattering amplitude: strong magnetic scattering centers

We were able to gain a better insight into the physical mechanism that governs the (near) backscattering rates by a number of KKR-based numerical experiments, that will be presented in this section. Since we ruled out the possibility of a uniform magnetic exchange splitting induced in the topological surface state of Bi_2Te_3 as the reason for the recurring backscattering channel, we come back to the pristine (i.e. without artificial external field) Bi_2Te_3 surface into which the different impurities (introduced in the DOS image in Fig. 5.2) have been embedded. In Figure 5.3 [131] the results of the numerical experiments on the exJDOS are depicted at different energies (corresponding to the warped and hexagonal CEC in the left and right column, respectively) and for different defects (top row: single Te vacancy, middle row: single Mn_{Te} impurity, lower row: $\text{Mn}_{\text{Te}}^{(3)}$ defect filling three neighboring Te vacancies in FM configuration).

In our analysis we concentrate on a signature at q_1 and q_2 and set aside the feature that was in the previous chapter associated to 120° -scattering (in particular visible in the exJDOS image in (f) for $|q| \approx 1 \text{ nm}^{-1}$ in $\overline{\Gamma M}$). If backscattering (green arrows) is present – which was experimentally seen in Fig. 5.1(g) – we expect to see a high exJDOS($q; E$) intensity along the $\overline{\Gamma K}$ -directions. This can only be seen in Fig. 5.3(f) – highlighted by a green ellipse – which corresponds to the case when the Fermi surface [seen in the inset of (d)] supports good nesting *and* a large magnetic moment [$m_{\text{spin}}(\text{Mn}_3) \approx 13.1 \mu_B \gg m_{\text{spin}}(\text{Mn})$] is present. In particular, even in the case of good nesting but with a single magnetic impurity, shown in (d), no considerable intensity in backscattering direction is found. This is in agreement with the discussion presented in the previous chapter where different single magnetic impurities substituting the first Bi atom in the Bi_2Te_3 slab only showed a very small (near) backscattering rate and, correspondingly, no clear signature of backscattering in the simulated FT-QPI images.

The scattering rates off the single Mn impurity and the Mn trimer (FM) are explicitly shown in Figure 5.4, where it can be seen that by coupling three Mn atoms ferromagnetically – i.e. forming a macro-spin – the magnetic part in the scattering potential can indeed be tuned, giving a scattering amplitude in near backscattering amplitude (q'_1) that increases by an order of magnitude. The importance of the magnetic part in the scattering potential was

¹¹In Ref.[187] a concentration of 18% of Mn atoms substituting Bi atoms was assumed in a calculation based on the coherent potential approximation. It is however questionable if this would be possible experimentally, possibly a structural phase transition would occur [191].

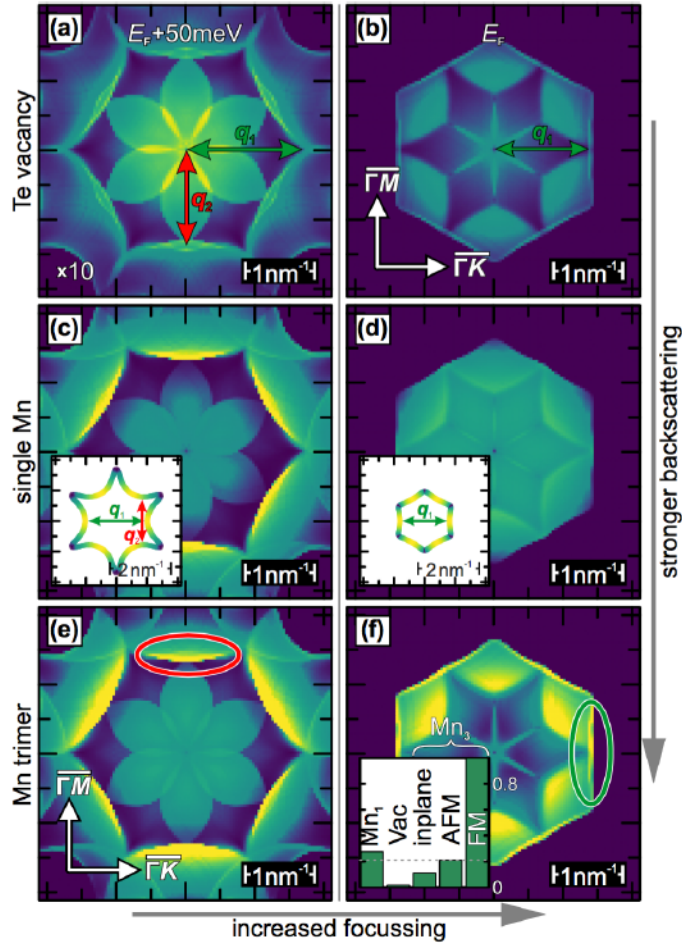


Figure 5.3.: Simulated exJDOS images for energies $E = E_F + 50 \text{ meV}$ (a, c, e) and $E = E_F$ (b, d, f) as generated by a Te vacancy (top row), a single Mn atom at a Te vacancy site (middle), and a Mn trimer (bottom). With the exception of (a) (contrast 10-fold magnified) the color scale is the same in all panels. Red ($\bar{\Gamma}M$ direction) and green ($\bar{\Gamma}K$) ellipses highlight exJDOS features associated to conventional scattering and backscattering, respectively. Insets in (c) and (d) show iso-energy contours for the different energies color-coded by the states' surface localization (yellow: $> 80\%$ in first QL, dark blue: $\sim 60\%$ in first QL). In the inset in (f) the relative magnitude of the backscattering signal is compared for 5 different impurity and spin configurations. Image including caption taken from Ref. [131].

checked by rotating the spins in the Mn trimer forming the AFM and in-plane alignment as introduced in Fig. 5.2. Although the DOS at $E = E^{\text{hex}}$ showed no significant change, the scattering rates for q'_1 in AFM and in-plane alignment results in a significant reduction of the (near) backscattering amplitudes. Consequently, only for the large joint magnetic moment a significant backscattering amplitude at q_1 seen in the FM trimer of Mn atoms is seen in the exJDOS image. This is highlighted in the inset in Fig. 5.3(f) where the relative exJDOS intensity at q_1 of the single Mn atom (Mn_1), and Mn trimers with different spin configurations (in-plane 120° , with $0 \mu_B$ effective moment, antiferromagnetic, $\uparrow\uparrow\downarrow$, with $4.4 \mu_B$ effective moment, and FM alignment with $13.1 \mu_B$ effective moment) is shown in a histogram.

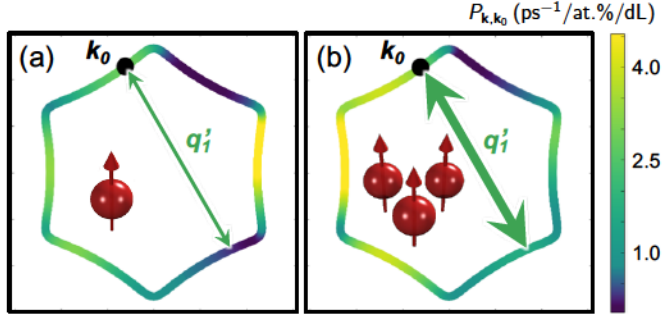


Figure 5.4.: Scattering probability off a single Mn impurity (a) and a FM coupled Mn trimer forming a macro-spin (b). The incoming wave is denoted by k_0 and the scattering probability to all possible final states on the CEC is shown in a linear color scale. The near backscattering amplitude, highlighted with the green arrows marked q'_1 , shows that the scattering amplitude for the Mn trimer defect increases by an order of magnitude over the scattering off a single Mn impurity.

The need for a large magnetic moment can be understood from the spin-momentum locking in the TI surface state. As it was discussed in the previous chapter, a non-vanishing interference in the charge density can only be realized for (near) backscattering processes, where the interfering waves have a non-vanishing overlap. Additionally, following the idea of the stationary phase approximation, only the parallel, nested parts on opposite sides of the constant energy contour contribute to the dominating long range behavior. The (near) backscattering amplitude now grows as $P_{k,-k+\delta} \propto |\delta|^2$ with the distance from the time-reversal scattering pair $(k, -k)$ and additionally increases with the impurity moment m as $P_{k,-k} \propto |m|^2$ [145]. It is therefore clear, that only a sufficiently large magnetic moment can lead to a large enough scattering amplitude in the vicinity of exact backscattering. Thus, only scattering centers with large moments, realized by ferromagnetically coupled magnetic impurities, can significantly contribute to form standing waves in the charge density modulations, which are visible in the (FT-)STM measurements.

Our ab-initio calculations performed for the Mn trimer also indicate, that the FM state has the lowest energy [$\Delta E(\text{AFM} - \text{FM}) = 87 \text{ meV}$ and $\Delta E(\text{in-plane} - \text{FM}) = 117 \text{ meV}$] as compared to the other configurations discussed above. In the experiment we can speculate that a ferromagnetic alignment of several Mn atoms is the result of indirect RKKY-type coupling mediated by the Dirac fermions. For the average Mn-Mn spacing of about 3 nm (see

supplemental material in Ref. [131]) indeed a ferromagnetic exchange coupling strength for $\sim 20 - 30 \text{ \AA}$ Mn-Mn distance has been observed.¹² In the topographic STM data, shown in Fig. 5.1(g), we can indeed see that the long ranged, focused charge density oscillations arise mainly around the larger defects and not around individual atoms. These larger defects are experimentally unidentified, but our calculations indicate that the scenario of neighboring Mn atoms in ferromagnetic coupling is justified. Since these “clustered” Mn atoms do not show evidence for long-range FM coupling with far-away atoms or other clusters, we conclude that they are in the superparamagnetic regime, i.e., behaving as a single macro-spin, decoupled magnetically from other spins or macro-spins. Therefore we refer to the observed effect as “superparamagnetism induced electron focusing”.

Additional information on the magnetic interactions between the Mn atoms on the Bi_2Te_3 surface were obtained by comparison with XMCD measurements, that allow to study the (collective) magnetic behavior of the Mn dopants. In the following a short description of the XMCD results, presented in [131], will be given and related to the in this chapter discussed mechanism of backscattering by FM coupled Mn atoms. A more in-depth analysis of the exchange interactions on magnetically doped TIs, the exchange mechanism and the coverage dependence of the magnetic properties of different impurities will be done at a later point in chapter 7 on page 125ff.

5.4. Experimental signatures of magnetism in Mn-doped Bi_2Te_3 : comparison to XMCD measurements

The above discussed signature of ferromagnetism in Mn doped samples comes on the first sight as a surprise since usually bulk Mn [192] and Mn nanostructures [193] are known to exhibit an antiferromagnetic or non-collinear ground-state. Experimentally, the magnetic properties are accessible by XMCD measurements, which, in this project, were performed at the BOREAS beamline of the Alba synchrotron facility by the Trieste group [131]. The XMCD method, which will be described in brief later on (in chapter 7), allows by measuring the photo-induced sample drain current the X-ray absorption spectrum (XAS), which was done in the total electron yield mode with left (I^-) and right (I^+) circularly polarized photons. The results are shown in Fig. 5.5(a) (top panel) where the XAS signal at the Mn $L_{2,3}$ edges with normal and grazing X-rays incidence are shown. The data was taken for a Mn coverage of about 0.016 ML, at $T = 2.5 \text{ K}$ and in a magnetic field of 6 T applied along the photon beam direction. The obtained spectra are characteristic of Mn atoms in a configuration close to d^5 (cf. in-depth discussion in chapter 7), which would result in a maximum magnetic moment of $5 \mu_B$ per Mn atom. This is in agreement with previous studies in Mn bulk-doped Bi_2Te_3 [185].

The XMCD signal, calculated as $I^- - I^+$, gives information on the magnetization in the sample. It is shown in the bottom panel of Fig. 5.5(a), where a considerable magnetic polarization of the Mn surface dopants is seen. Fig. 5.5(b) shows the result of the magnetization cycles at $T = 2.5 \text{ K}$, at normal (green) and grazing incidence (yellow), following the XMCD

¹²Cf. discussion about Fig.7.7 in chapter 7 where indeed for a distance of $20 - 30 \text{ \AA}$ FM coupling is seen.

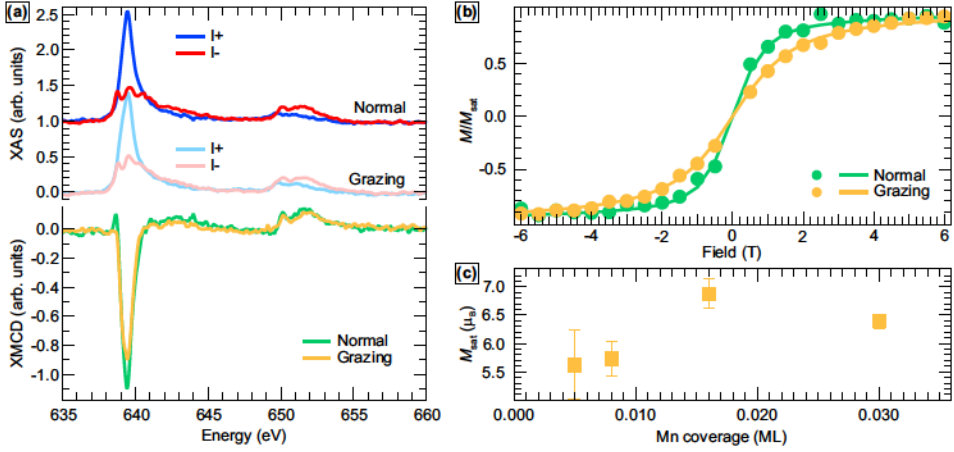


Figure 5.5.: (a) Mn $L_{2,3}$ -edges x-ray absorption spectra (XAS; top panel) and x-ray magnetic circular dichroism (XMCD; bottom panel) signal of 0.016 ML Mn on Bi_2Te_3 , obtained at normal and grazing incidence, with $B = 6$ T and $T = 2.5$ K. (b) Corresponding magnetization cycles, recorded at the XMCD maximum at the Mn L_3 -edge. (c) Mn-coverage dependence of the saturation magnetization extracted from the recorded magnetization cycles. Experiments were performed by the Trieste group and the image including caption was taken from Ref. [131].

magnitude at the Mn L_3 -edge as a function of the applied magnetic field. As we will discuss later on¹³ in detail, this gives the effective magnetic moments (i.e the collective behavior) of the Mn atoms. The larger slope in $M(H)$ at small fields and the saturation at large fields in normal incidence geometry indicate an out-of-plane magnetic anisotropy for Mn on Bi_2Te_3 . This direction was also used in our model and ab-initio calculations. The analysis of the effective magnetization [called M_{sat} in Fig. 5.5(c) by the Trieste group] shows that, already at low coverages of 0.008 ML, a significant enhancement of the effective magnetic moment becomes evident which, with increasing the coverage to 0.016 ML, leads to an effective moment of almost $7 \mu_B$. This large value is certainly larger than what would be expected for a single Mn atom. It implies the existence of FM interactions among neighboring Mn atoms, as we have suspected in the discussion above. At this point we can only speculate that the exchange coupling between Mn adatoms may be mediated by the surface electrons of Bi_2Te_3 and that – although FM correlations are present – thermal fluctuations and disorder are too strong to establish stable FM order. Nevertheless, some groups of Mn atoms with small enough Mn–Mn separation will exhibit sufficiently strong magnetic interactions to couple their individual moments to a macro-spin, that enhances the susceptibility characteristic for superparamagnets [cf. Fig 5.5(b)]. This interaction may be mediated by the topological surface state and its mechanism will be analyzed in detail in a comparison between XMCD measurements and ab-initio calculations, presented in chapter 7 for different transition metal impurities on Bi_2Te_3 .

For now we can conclude that the XMCD measurement averages spatially over a macroscopic

¹³Cf. Chapter 7

sample area and that the large effective magnetization of $7\mu_B$ therefore implies the existence of assemblies of Mn atoms with considerably larger magnetic moments in parallel to single Mn atoms with $4 - 5\mu_B$. This is in agreement with our theoretical finding that, units composed of at least three ferromagnetically coupled Mn atoms, are required to activate the scattering channel along the $\bar{\Gamma}K$ direction, seen clearly in the STM experiments.

5.5. Conclusions and outlook

In this chapter the results of a collaborative experimental study (STM by the Würzburg group, XMCD by the Trieste group) and our theoretical contribution (first principles and model calculations) have been presented. We found evidence that, through electron focusing, long-ranged coherent quantum oscillations in the charge density can be observed, which paves the way to the design of new experiments and possibly devices based on spin coherent phenomena in the fascinating class of topological insulator materials. More generally, we exemplified the concept that, through appropriate band engineering, e.g. in this system the position of the Fermi level, materials with spin-split states can host interesting quantum coherent phenomena with important implications for example in the field of spintronics.

In particular we identified that highly focused charge density oscillations, coherent over mesoscopic distances, are possible in magnetically doped topological insulators. We found that two conditions have to be fulfilled simultaneously: (i) the constant-energy contour has to support good nesting, which in Bi_2Te_3 is achieved by tuning the Fermi level to obtain a hexagonal shape with large parallel segments facing each other, and (ii) a *strong* magnetic scattering center has to be present, which was realized by a group of Mn atoms coupled ferromagnetically to form a macro-spin. The importance of the magnetic, i.e. time-reversal-breaking part in the scattering potential, was pointed out, giving a new knob to tune scattering properties in the topologically protected surface state of TIs.

These new insights solve a puzzle left unsolved in the previous chapter, namely the low backscattering amplitudes seen for single time-reversal breaking impurities, and gives a quantitative understanding of the mechanism of time-reversal protection in the TSS in contact with magnetic impurities. The XMCD measurements indicated an interesting behavior in the magnetic interactions between magnetic impurities that are coupled to the topological surface state in Bi_2Te_3 . This motivates the detailed analysis of the coverage-dependent exchange coupling mechanism, which will be discussed in chapter 7.

One way of intensifying time-reverse scattering is to group a number of magnetic impurities such that they act as a superparamagnetic entity, as done here with three Mn impurities. Another way could be to use resonant magnetic impurities, e.g. Fe impurities as discussed in chapter 4, where the resonance intensifies the backscattering not because of a stronger exchange field, but because the interaction of the electron with the impurity field is longer in time. This latter possibility has, however, not been examined experimentally so far.

Lifetime and surface-to-bulk scattering of the topological surface state in the 3D topological insulators Bi_2Te_3 and Bi_2Se_3

The energy dependence of the lifetimes and scattering rates of the topologically protected electrons in the surface state of Bi_2Te_3 and Bi_2Se_3 are analyzed in this chapter. The scattering rates are decomposed into surface-to-surface and surface-to-bulk scattering rates, which allows us to gain new fundamental insights into the scattering properties of the topological surface states (TSS). In particular the relation to topological protection^a by spin-momentum locking and time-reversal scattering are discussed.

We find that impurity resonances have a significant impact on the scattering properties of the TSS. They can strongly change the lifetime of the surface state to vary between tens of femto- to picoseconds. We uncovered that the response of the TSS electrons to resonances in the scattering potential can explain the calculated trends, which highlights the need for quantitatively correct description of scattering properties and consequently the need for ab-initio calculations in the prediction of scattering properties. Additionally, we found predominantly intra-band scattering within the TSS (i.e. mostly scattering for pairs of initial and final states both coming from the TSS). Only if the number of possible final states from bulk states is much larger than the number of surface states, the surface-to-bulk scattering rate is of importance, otherwise the surface-to-surface scattering rate will dominate.

^aHere meaning the robust existence of the TSS and its non-degenerate nature and helicity.

6.1. Introduction

Typical samples of the binary topological insulators like Bi_2Te_3 and Bi_2Se_3 are full of native defects so that the Fermi level is at a position where bulk states coexist with the topological surface states [194]. This raises the question how large the lifetime of surface state electrons is in the presence of bulk states or, more generally, what the energy-dependence of the scattering rate going from the conduction band through the bulk band gap to the valence band is. The importance of these questions is obvious as the scattering features of the TSS will play a major role in surface transport properties and also in the long coherence lengths that were demonstrated for E_F within the bulk band gap of Bi_2Te_3 in the previous chapter.

Nowadays, different strategies exist to tune the position of the Fermi level into the band gap in order to suppress the number of bulk states at the Fermi level. The task can be achieved by compositional tuning (see for example Refs. [195, 196]) or by compensating individual doping trends in forming topological p - n -junctions [43]. Nevertheless, typical transport measurements in this class of materials still fight against contributions from bulk states, as opposed to the desired surface-dominated transport, and a cumbersome disentanglement of surface and bulk contributions is needed (e.g. Refs. [195, 197, 198]).

In addition to transport measurements, the two-photon photo-emission spectroscopy¹ allows to extract information about the dynamics of excited electrons in topological insulators [199–203]. In the strong topological insulator Bi_2Se_3 , a persisting population for longer than 10 ps [199] has been found lately, which was attributed to a dominant contribution to the relaxation dynamics from elastic scattering of excited electrons between surface and bulk states. Even long lifetimes of the surface state exceeding 4 ps were reported [201]. However, these lifetimes are the result of a complicated interplay between elastic and inelastic scattering and only recently in Sb_2Te_3 elastic² lifetimes of 300 fs–2.5 ps were found using mid-IR pump pulses, that allow to excite direct transitions from occupied to unoccupied parts within the topological surface state [202, 203].

So far, the question of surface-to-bulk scattering has, at least from a theoretical point of view, only been treated based on simple models [204]. Here, the first ab-initio treatment will be presented, that gives valuable insights into the energy-dependence of the scattering properties of the TSS in strong topological insulators and allows to draw conclusions about their topological protection.

The work presented in this chapter aims at answering the following questions: what is the energy-dependence of the scattering rates and how is it related to the impurity properties, e.g. the impurity density of states? Furthermore, if the TSS coexists with bulk states, what are surface-to-bulk scattering rates and how do they relate to the surface-to-surface scattering rates? We find that three factors are of major importance for the understanding the scattering rates in the prototypical topological insulators Bi_2Te_3 and Bi_2Se_3 : (i) the impurity density of states, (ii) the number of available final states in the scattering process and (iii) the localization of the wavefunctions, in particular their spatial overlap with the perturbation introduced by the impurity in the system and the spin-polarization in the surface states. The

¹Essentially a two-step ARPES measurement where a pump pulse is irradiated onto the sample exciting electrons into unoccupied states and after a time delay an ARPES measurement is performed. This allows to access the unoccupied part of the band structure as well and can be performed to get the time evolution of the out-of-equilibrium states measured with different time-delays after the pump pulse.

²Meaning the lifetime corresponding to the elastic scattering rate.

comparison of Bi_2Te_3 with Bi_2Se_3 allows to draw the conclusion that the warping of the constant energy contour, which is stronger in Bi_2Te_3 than in Bi_2Se_3 , does not significantly alter the total scattering rate off impurities. This result suggests that our findings are of general importance for strong 3D topological insulators, irrespective of the exact shape of the Fermi surface.

6.2. Energy dependent lifetime and scattering rates of the topological surface state in Bi_2Te_3

To study the lifetime of the TSS in Bi_2Te_3 and Bi_2Se_3 we considered a single defect localized at the surface, i.e. a Te (Se) vacancy in the first layer on the surface of a 6 quintuple layer thick slab. The position of the impurity is shown in Figure 6.1(c). This particular defect has been chosen because of its very frequent occurrence in this class of materials [40]. Additionally this defect is suspected to be the reason for n-type doping in Bi_2Te_3 [153, 205]. Within this work only the elastic scattering, i.e. with $E_{k,\text{in}} = E_{k,\text{out}}$, leading to scattering between states on the constant energy contours at different energies will be studied; in particular we neglect the electron-phonon coupling which is assumed to be small for low temperatures. In fact, ab-initio calculations of the electron phonon coupling constant for Bi_2Te_3 and Bi_2Se_3 [206] showed that the coupling strength is quite weak, which highlights the importance of our calculations.

6.2.1. Numerical details of the calculation

The Bi_2Te_3 and Bi_2Se_3 surfaces were simulated by 6 quintuple layer thick films as described in detail in the chapter 4. The main difference in the bandstructure between Bi_2Te_3 and Bi_2Se_3 is, that the warping term in Bi_2Te_3 is more pronounced. A comparison between these systems will therefore give information on the importance of the warping term in the topological surface state's scattering properties. As in the precious chapter, the Te-vacancy (Se-vacancy for the Bi_2Se_3 -surface) have been embedded self-consistently with a screening cluster that includes the first shell of neighboring atoms using the Dyson equation. Lattice relaxations have been neglected. The vacancy can cause a significant shift if the surrounding atoms, which would be important in the calculation of the vacancy-formation energy. However, concerning the trends of the scattering rate, lattice relaxations should only play a minor role.

We start the detailed discussion of the surface state's lifetime with the Bi_2Te_3 system. The Bi_2Te_3 bandstructure (a,b), the position of the Te-vacancy in the film (c) and the density of states of the impurity (d) are shown in Fig. 6.1.

The DOS of the impurity shows a small resonance, which has its maximum around $E - E_F \approx 75 \text{ meV}$. Its contribution was neglected in the previous chapter since the scattering off Mn atoms was found to be much stronger. An analysis of the contributions coming from the different positions in the impurity cluster reveal that the vacancy, is partly filled by electrons coming from the adjacent Bi_1 positions: Some charge leaks into the empty cell, filling it partly, which finally leads to the impurity resonance seen in the total DOS. We find that the adjacent Te atoms around the vacancy only play a minor role and associate the peak to dangling bonds from the Bi_1 atoms. This is supported by the observation that no such

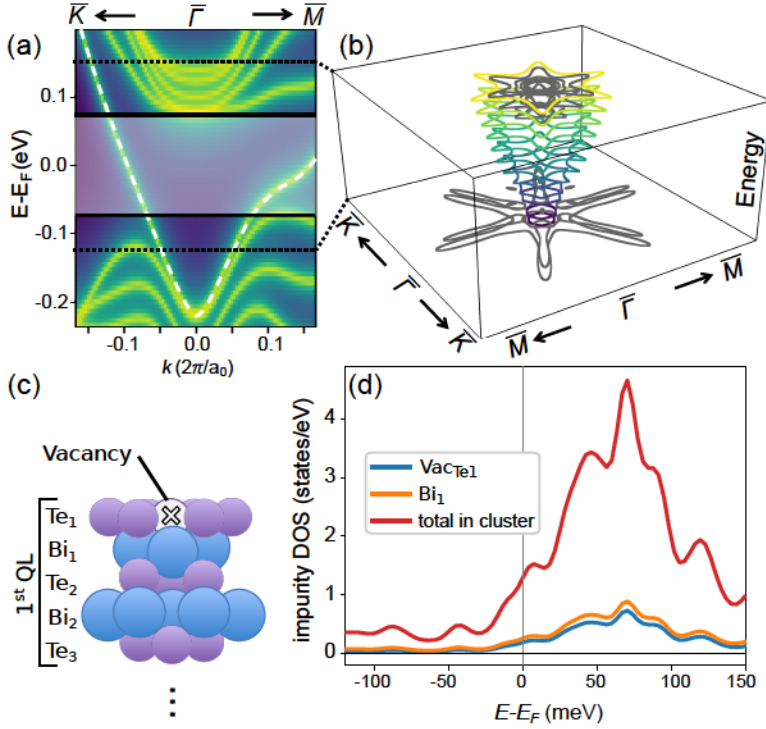


Figure 6.1.: Setup of the calculation. (a) Bandstructure of a 6QL Bi_2Te_3 thin film, where the shaded area between the two horizontal black lines highlight the region of the bulk band gap and the black dotted lines indicate the energy range for which the scattering rates are analyzed. (b) 3D plot of the dispersion where the bulk bands are shown in gray and the TSS [white dashed line in (a)] in color representing the energy (c) Side view of the vacancy position in the first quintuple layer. (d) Density of states of the vacancy defect in the first Te-layer of Bi_2Te_3 , where the total DOS (sum over full impurity cluster containing the vacancy and the surrounding atoms, red), as well as the contributions from the vacancy position ($\text{Vac}_{\text{Te}1}$, blue) and the neighboring Bi-atoms (Bi_1 , orange) are shown. The resonance seen in Bi_1 is mainly due to d -states in Bi and is absent without the impurity and is therefore associated to dangling bonds which then leaks into the vacancy site.

peak is present in the density of states without the vacancy defect, i.e. where no dangling bonds are present. This impurity resonance will become important in the energy dependent scattering rates, that will be analyzed in the following.

6.2.2. Anisotropic lifetime of the surface state in Bi_2Te_3

To answer the question how the presence of native defects affect the lifetime of the topological surface state, we computed the scattering probability³ $[P_{k',k} = 2\pi Nc |\mathcal{T}_{k',k}|^2 \delta(E_k - E_{k'})]$ for an incoming wave $\mathbf{k}$ that is scattered off the impurity into a final state $\mathbf{k}'$ at different energies from the valence band over the band gap to the conduction band. For the non-magnetic Vac_{Te} defects, that were considered here, we find the same trends in terms of forward scattering and forbidden backscattering as for the Te_{Bi} defect discussed in detail in chapter 4. This statement even holds at higher (and lower) energies where – outside of the bulk band gap – the TSS coexists with bulk states from the valence and conduction band, respectively. In the remainder of this chapter the directionality in the scattering process, i.e. the strong focusing in forward direction, will not be of importance, because we are mainly interested in the total scattering rates of surface state electrons.

We start by looking at the relaxation rate $\tau_k^{-1}(E) = \frac{1}{\Omega_{\text{BZ}}} \int_{\text{FS}} \frac{dk'}{v_{k'}} |\mathcal{T}_{k',k}|^2$ [introduced in Eq. (4.9)]. It is shown in Figure 6.2(a) for $E = E_F + 150 \text{ meV}$, where a number of bulk states from the conduction band coexist with the topological surface state.

In the presence of the Vac_{Te} -impurity, mostly the TSS is scattered (visible as yellow colored areas) whereas the bulk states are mainly unaffected. This can be understood from the position of the impurity and the localization of the wavefunctions in space. The TSS is strongly localized at the surface and consequently has a large overlap with impurity with which it interacts, i.e. from which it is strongly scattered. It lies in the nature of the bulk states that they are delocalized and only a small portion of the wavefunction is located at the surface. Therefore, the bulk states have only a small overlap with the impurity and are much less susceptible to scattering off the surface vacancy. Furthermore, the $\mathbf{k}$ -dependent scattering rates of the states from the TSS show an anisotropy with higher values for states from the valleys in $\overline{\Gamma K}$ and strongly reduced values for states from the tips of the constant energy contour (CEC) in $\overline{\Gamma M}$. This anisotropy was also seen in angular-resolved photo emission experiments [207] where the line-width of the spectral features can be related to the scattering rate of the states. This anisotropy associated with the warping of the topological surface states in Bi_2Te_3 , indicates that the widely used constant relaxation time approximation (eg. as for example in [197] for Sb_2Te_3) might not always be sufficient to describe the scattering properties off impurities in this class of materials. The wavefunctions of states at the tips of the warped contour are more delocalized, while those in the valleys are more localized. This can explain the observed anisotropy. We should however keep in mind, that the calculations presented here only consider a single defect which is localized directly at the surface, while in experiments other intrinsic sub-surface or bulk defects are likely to occur.

³The scattering probability was introduced in chapter 4.

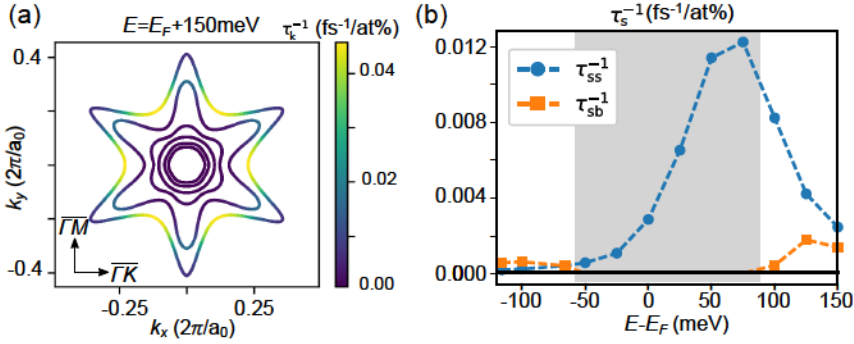


Figure 6.2.: Scattering rates of topological surface state electrons. (a) Inverse relaxation time, τ_k^{-1} , of the states on the constant energy contour (all $\mathbf{k}$ with $E_k = E_F + 150$ meV) for scattering off the Te-vacancy defect on top of Bi_2Te_3 . The topological surface states (outermost, star-like line) is scattered more effectively (yellow regions) than the bulk-derived states (inner lines) of the conduction band. A strong anisotropy in the scattering rates is seen that leads to smaller relaxation times of states in the valleys in $\overline{\Gamma K}$ as opposed to the states at the tips of the star in $\overline{\Gamma M}$. (b) Total scattering rate of the TSS decomposed into surface-to-surface (τ_{ss}) and surface-to-bulk (τ_{sb}) contributions. The gray shaded area highlights the position of the bulk band gap. The resonant scattering off the Vac_{Te} impurity [cf. DOS in Fig. 6.1(b)] leads to strong surface-to-surface scattering rates with a maximum around $E - E_F \approx 75$ meV.

6.2.3. Resonant scattering of the topological surface state in Bi_2Te_3

Next, the total scattering rate (averaged over the whole surface state with density n_s)

$$\begin{aligned} \tau_s^{-1}(E) &= n_s^{-1}(E) \left[\sum_{k \in \text{surf}} \sum_{k' \in \text{surf}} P_{k,k'} + \sum_{k \in \text{surf}} \sum_{k' \in \text{bulk}} P_{k,k'} \right] \quad (6.1) \\ &= \underbrace{\frac{2\pi Nc}{n_s(E)\Omega_{\text{BZ}}^2} \int_{k \in \text{surf}} \frac{dk}{v_k} \int_{k' \in \text{surf}} \frac{dk'}{v_{k'}} |\mathcal{T}_{k,k'}|^2}_{\tau_{ss}^{-1}} + \underbrace{\frac{2\pi Nc}{n_s(E)\Omega_{\text{BZ}}^2} \int_{k \in \text{bulk}} \frac{dk}{v_k} \int_{k' \in \text{surf}} \frac{dk'}{v_{k'}} |\mathcal{T}_{k,k'}|^2}_{\tau_{sb}^{-1}} \quad (6.2) \end{aligned}$$

decomposed in surface-to-surface (τ_{ss}^{-1}) and surface-to-bulk (τ_{sb}^{-1}) contributions will be analyzed, where the prefactors $2\pi Nc$ and $1/\Omega_{\text{BZ}}$ come from the definition of the scattering probability and the relation $\sum_k \rightarrow \frac{1}{\Omega_{\text{BZ}}} \int_{FS} \frac{dk}{v_k}$. The integrations compared to the definition [Eq. (4.10)] of chapter 4 are restricted to the lines of the constant energy contour that belong to the TSS ($k', k \in \text{surf}$) or those lines derived from bulk states ($k \in \text{bulk}$). The scattering rates were normalized with respect to the density of states of the topological surface state [$n_s(E)$] and thus also with respect to the phase space of possible initial states (i.e. the length of the line corresponding to the TSS in the CEC) that varies with the energy. In this way we take all the complexity of directionality and anisotropy of the scattering out of the discussion and focus on the total scattering rates instead.

The energy-dependence of the surface-to-surface and surface-to-bulk scattering rate is shown in Figure 6.2(b). Overall, the surface-to-bulk scattering rate is lower than (in the conduction band), or of the same order of magnitude (for E in the valence band) as, the surface-to-surface scattering rates. This observation seemingly agrees with the interpretation that the scattering rate is high if the localization of initial and final states have a high overlap with the position of the scattering defect. However the number of available bulk end-states is also larger than the number of available surface end-states. The two contributions, τ_{ss} and τ_{sb} , should therefore be comparable, if only the qualitative overlap argument is taken into account. Thus the stark contrast of the two contributions is a highly nontrivial result [208]. The dominant feature in Fig. 6.2(b) is the very strong variation in the surface-to-surface scattering rate with energies, that leads to a strong variation of the surface state's lifetime⁴ between $\tau_s \approx 66$ fs at% for $E \approx E_F + 75$ meV and $\tau_s \approx 3.3$ ps at% around $E \approx E_F - 100$ meV. This energy-dependence can be understood from the density of states on the scattering defect [cf. Fig. 6.1(b)]. The energy-dependent scattering rate exactly follows the resonance seen in the density of states of the impurity, which highlights the importance of resonant scattering. Resonant scattering is generally known to be important for the scattering behavior in metals. Here we have demonstrated that also in the topologically protected surface state of Bi_2Te_3 this is the case.

We can conclude that the electrons of the TSS are just as susceptible to scattering off defects as are trivial surface states, e.g. the Cu or Au(111) surface states [119, 208, 209]. The total scattering rate is strongly enhanced if resonances in the scattering potential are met. This is the behavior one would expect for normal metallic states and the only difference to

⁴The lifetime scales in inverse proportionality with the impurity concentration, i.e. for a defect density of 2 at% the here obtained lifetimes (then given in fs = 10^{-15} s) would have to be multiplied by 1/2.

topologically protected states is that the scattering is directed (scattering mostly in forward scattering direction) and exact or near backscattering, respectively, is absent or strongly suppressed.

6.2.4. On the importance of the scattering phase space end-states: understanding the surface-to-bulk scattering rates

We have witnessed the dominating feature of the surface-to-surface scattering rates of the TSS. Next, the coexistence of surface and bulk states that leads to surface-to-bulk scattering will be discussed in detail. Therefore the scattering rates are shown in a semi-logarithmic plot in Figure 6.3(a) making the bulk contribution better visible.

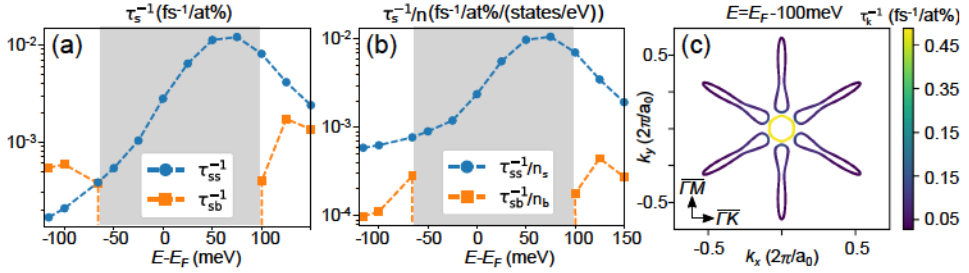


Figure 6.3.: Surface to bulk scattering rates of the topological surface state in Bi₂Te₃. (a) Energy-dependence of the surface-to-surface (τ_{ss}^{-1}) and surface-to-bulk (τ_{sb}^{-1}) scattering rates off a Te-vacancy, where the different behavior ($\tau_{ss}^{-1} < \tau_{sb}^{-1}$ for E in the valence band as compared to $\tau_{ss}^{-1} > \tau_{sb}^{-1}$ for E in the conduction band is observed. (b) Rescaled scattering rates showing the importance of the number of possible final states for the scattering of the TSS to bulk states. The gray shaded areas in (a,b) highlight the position of the bulk band gap. (c) Inverse relaxation time (τ_k^{-1}) for $E = E_F - 100$ meV, where the TSS is the innermost ring. On the one hand the TSS is scattered more intensely (yellow color) and on the other hand a very large number of final states leading to increasing surface-to-bulk scattering rates in the valence band are seen.

We see that the surface and bulk decomposed scattering rate shows a qualitatively different ($\tau_{ss}^{-1} < \tau_{sb}^{-1}$) behavior in the valence band than in the conduction band ($\tau_{ss}^{-1} > \tau_{sb}^{-1}$). With decreasing energy, the constant energy contour of the TSS becomes smaller and smaller until it reduces to a single point at the Dirac point. It is therefore clear that the ratio between the number of surface states [$n_s(E)$] and the number of bulk states [$n_b(E)$] will differ largely in valence and conduction band. The available phase-space ratio $n_b(E)/n_s(E)$, of bulk final states to surface final states, is consequently larger in the valence band as compared to the onset of the conduction band. The large number of bulk states can for example be seen in (c) where the k -dependent scattering rates for $E - E_F = -100$ meV are shown. Again, mostly the surface state (innermost ring) is scattered most and the large areas of bulk states (extended shapes in ΓM) are largely unaffected by the presence of surface impurities. The

effect of a larger scattering phase space in the final states can therefore be factored out by renormalizing the surface-to-surface and surface-to-bulk scattering rates to the number of final states [$n_s(E)$ and $n_b(E)$, respectively]. This is shown in Fig. 6.3(b), where in both cases of coexistence of the topological surface state with valence and conduction bands the renormalized surface-to-bulk scattering rate is significantly smaller than the renormalized surface-to-surface scattering rate. Our calculations thus show the importance of the final states' phase space, which was shown to significantly impact the surface-to-bulk scattering rate. This observation is in agreement with the model-based calculations by Saha et al. [204].

In conclusion, we have understood the energy-dependence of the surface state's scattering process off a Te-vacancy in Bi_2Te_3 . We found that the scattering rate is dominated by scattering between states where both initial *and* final state are coming from the TSS. The localization at the surface therefore has crucial implications for the scattering properties of topologically protected electrons. Scattering to bulk states only becomes important, if the total number of bulk states is much larger than the number of surface states, i.e when the phase space of possible final scattering states is dominated by bulk states. This observation certainly holds true for the energy range that was studied here, however it could be different if surface resonances occur. In Bi_2Se_3 spin-polarized surface resonances were recently found in the unoccupied band structure far above the Dirac point [201]. The surface-localization of these states and their spin-polarization can then have a significant impact on possible scattering event between the TSS and the topologically trivial resonance states.

6.3. The influence of the warping strength: comparison to Bi_2Se_3

Finally, the influence of the warping strength in the surface states of Bi_2Te_3 will be analyzed further in comparison with calculations for the energy dependent scattering rates off the analogous case of a Se-vacancy in Bi_2Se_3 . The results are summarized in Figure 6.4. The smaller warping strength in Bi_2Se_3 can be seen in the bandstructure shown in (a) and (b). The density of states of the Se-vacancy defect embedded into the surface shows a similar behavior as the Te-vacancy in Bi_2Te_3 with a resonance lying within the bulk band gap [cf. Fig. 6.4(c)]. A priori, we would therefore expect to see a resonance in the scattering rates around $E - E_D \approx 150$ meV. This follows also from the generalized Friedel sum rule that relates the change in the charge density due to the impurity to the energy dependence of the $\mathcal{T}$ -matrix via $n^{\text{imp}}(E) - n^{\text{host}}(E) = \pi^{-1} \text{ImTr} \ln \mathcal{T}(E)$. In Bi_2Se_3 the warping becomes important only very close to the conduction band [cf. Fig. 6.4(b)]. A resonance in the scattering rates that deviates from the generalized Friedel sum rule would then indicate an unexpected influence of the warping on the scattering rate. Especially if the resonance lies significantly higher in energy than the peak seen in the impurity DOS, the hypothesis, formulated in the previous section and stating that the warping is negligible, would be contradicted.

The energy-dependence of τ_{ss}^{-1} and τ_{sb}^{-1} for the Se-vacancy are shown in Fig. 6.4(c) in a semi-logarithmic plot. A very sharp resonance in the surface-to-surface scattering rate is found which exactly coincides with the impurity DOS of the vacancy defect. Thus the effect of the warping is found to be negligible. As previously seen for the case of Bi_2Te_3 , within the valence band a stronger surface-to-bulk scattering rate is found over the surface-to-surface scattering

6. Lifetime and surface-to-bulk scattering of the TSS in 3D TIs

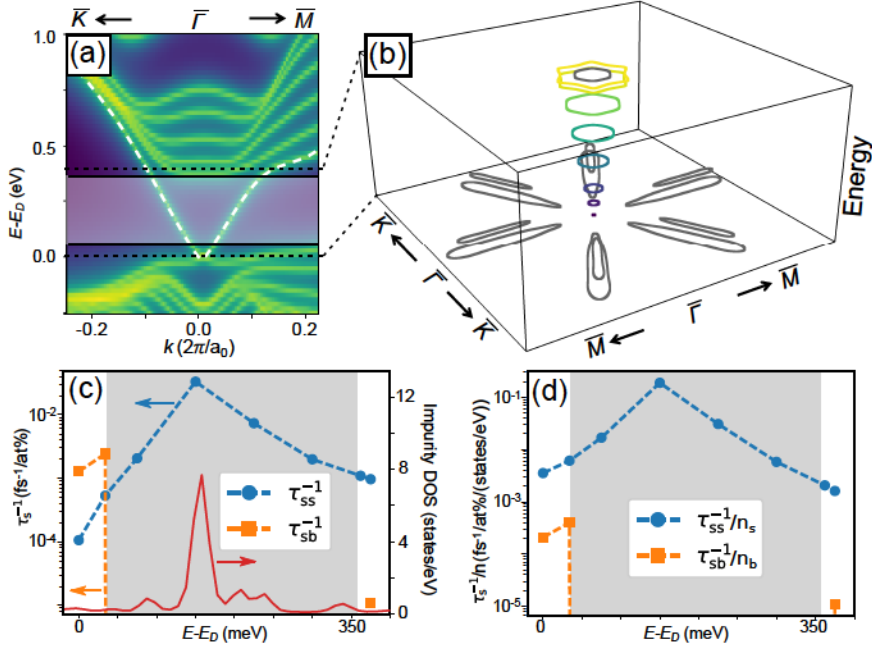


Figure 6.4.: Scattering rates off a Se-vacancy in Bi_2Se_3 . (a) Plot of the bandstructure where the dispersion of the topological surface state is highlighted with white dashed lines. The light shaded area (between the black horizontal lines) denotes the bulk band gap and the black dotted lines indicate the range in which the scattering rate and lifetimes have been analyzed. (b) Dispersion of the TSS (colored with the energy) showing the small warping in Bi_2Se_3 and the position of the valence and conduction bands that are plotted in gray. (c) Total density of states of the Se-vacancy (red, full line) and energy-dependence of the surface-to-surface (τ_{ss}^{-1}) and surface-to-bulk (τ_{sb}^{-1}) scattering rates for a Se-vacancy defect. (d) The scattering rates renormalized to the density of final states, showing the importance of the available scattering phase space. The gray shaded areas in (c,d) highlight the position of the bulk band gap and the energies are measured with respect to the Dirac point energy E_D .

rate, while the reversed situation occurs for the onset of the conduction band. To highlight the influence of the final state phase space we again renormalize with respect to the final state's density of states, shown in (d). This reveals that the renormalized surface-to-surface scattering rates are an order of magnitude higher than the surface-to-bulk scattering rates. The strong variation of the scattering rates due to resonant scattering off the impurity leads to lifetimes that vary between $\tau_s \approx 165 \text{ fs at } \% \text{ at } E - E_D \approx 150 \text{ meV}$ and $\tau_s \approx 6.5 \text{ ps at } \% \text{ at } E = E_D$.

We can thus summarize, that the scattering rates in Bi_2Se_3 show an analogous behavior as the scattering rates in Bi_2Te_3 . The impurity resonance plays a dominant role in the energy dependence of the scattering rates and the TSS mainly scatters to other states within the TSS. Only when a large number of bulk states is available does the scattering rate from the TSS to bulk states become important. In conclusion, the stronger warping in Bi_2Te_3 as compared to Bi_2Se_3 only plays a minor role in the scattering properties.

The scattering resonances of the topologically protected surface state in 3D strong topological insulators can therefore be connected to the peak in the impurity DOS. In chapter 7 (pages 144ff.) the scattering properties of specific impurities are further interpreted in terms of the scattering phase shift, which can be connected to the density of states of the impurity⁵ via the Breit-Wigner formula [cf. Eq. (7.5) on page 145].

6.4. Conclusion and outlook

In this chapter, the energy-dependence of scattering rates (and lifetimes) of topological surface state electrons have been studied from first principles. The analysis was concentrated on single (non-magnetic) vacancy defects located in the first layer on the (111) surfaces of Bi_2Te_3 and Bi_2Se_3 . These defects occur frequently and are important for their intrinsic doping as well as transport properties.

In the scattering rates of the TSS, we found a strong signature of the impurity's properties, namely the resonances in its density of states. For a quantitatively correct description it is therefore of paramount importance to describe impurities embedded in the system realistically, which makes the need for our ab-initio approach to the scattering rates evident. In the presence of bulk states that coexist with the TSS, we find higher surface-to-surface scattering rates than surface-to-bulk scattering rates. An electron that has potentially been prepared in the TSS (e.g. in a surface state dominated transport experiment) stays within the TSS, even if bulk states as possible final states coexist with the TSS. This is consistent with the recent quantum transport measurements Bi_2Se_3 , where the phase coherence length and a strong focusing in forward scattering direction was even seen for strongly disordered samples [210, 211]. We expect that this behavior will hold quite generally, if the density of bulk states is not much larger than the density of states of the topological surface state.

The warped contour of the surface state in Bi_2Te_3 was found to have a large impact on the anisotropy of the relaxation rate [207]. This was understood with the localization of the wavefunction for different states on the constant energy contour. The widely used constant relaxation time approximation might therefore not be sufficient to capture the interesting

⁵More precisely the difference in the DOS between host and impurity matters. For topological insulators with E_F within the gap the DOS is very small (only contributions from the surface state are there) and therefore the interpretation in terms of the impurity DOS is valid in this context.

6. Lifetime and surface-to-bulk scattering of the TSS in 3D TIs

scattering properties of the topological surface state in 3D strong topological insulators but our approach of k -dependent relaxation rates is important. The comparison of the strongly warped Bi_2Te_3 and the much less warped Bi_2Se_3 systems showcased, that the total scattering rates do not depend on the strength of the warping. The scattering results off magnetic defects, that showed an anisotropy favoring certain segments in the warped CEC due to the developing out-of-plane component (cf. chapter 4), would however indicate that magnetic impurities might behave differently. An extension to other defects, including not only defects in the first surface layer but throughout the whole system, would be important in the future.

Recently, scanning tunneling potentiometry, that allows the measurement of transport properties on the atomic scale using a multi-tip STM approach, has been demonstrated on topological insulators [212, 213]. This technique could give access to the spacial distribution of electron transport around individual defects. The here presented calculation of lifetimes and scattering rates could be compared and a deeper understanding of transport properties, that can be computed based on a semi-classical Boltzmann formalism [75], would be of interest.

Exchange interactions on magnetically doped topological Insulators

In this chapter the interplay between the topologically protected surface states of TIs and magnetism, introduced via surface-doping with transition metal impurities, is studied. The work presented here is the result of a collaboration between theory and experiment and gives valuable insights into the the complicated competition between different exchange coupling mechanisms that determines the magnetic order in these interesting materials.

In particular the double and superexchange mechanisms that favor, respectively, ferro- or antiferromagnetism at short distances and the long-range Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction that is mediated by the electrons of the topological surface state can be distinguished and understood in terms of the scattering properties of the different magnetic impurities. We highlight the importance of the RKKY interaction for dilute concentrations of magnetic impurities that in Bi_2Te_3 is furthermore strongly anisotropic in space due to a focusing effect coming from a strong warping in the Fermi surface.

We uncovered different mechanisms and especially point out the importance of the scattering properties of the magnetic impurities for the exchange coupling strength that can be observed in this material. The distance-dependence of the oscillatory exchange coupling of magnetic impurities on the surface of topological insulators was studied for Mn, Fe and Co adatoms in different concentrations and a mechanisms that allows tuning the exchange interactions and therefore the magnetic properties of transition metal doped topological insulators was found. We could demonstrate that the density of states of a single impurity can in fact be analyzed to predict magnetic properties in this system. Furthermore, microscopic control of the distance-dependent exchange interactions can be achieved by tuning of the Fermi level position which allows to tailor magnetic properties of transition metals on the surface of a strong TI.

7.1. Introduction

The interplay between topological non-trivial states and magnetism is a fascinating new emerging field in solid state physics. One of the most prominent examples is the quantum anomalous Hall effect (QAHE), that realizes a hallmark of topological states of matter in magnetic topological insulators [214, 215]. A precondition for the QAHE is the existence of a gap in the bandstructure. In the helical surface state of the topological insulator (TI) this can be achieved by ferromagnetic ordering with out-of plane magnetic anisotropy [187]. The mechanism of gap opening in topological insulators is still under debate since impurity resonances are predicted to occur close to the Dirac point [184, 216] and which might form impurity bands that hybridize with the surface state in the topological insulator. This hybridization could be responsible for the gap opening that can be still be seen far above the Curie temperature (T_C) that was measured in Ref. [217].

Apart from the mechanism of gap opening and despite numerous research on magnetically doped topological insulators [148, 152, 181, 182, 185, 191, 218–236] also the mechanism of how to achieve ferromagnetism (FM) in TIs is not clear yet. As it turns out, a distinction has to be made between surface and bulk doped samples. In bulk doped TIs a competition between the carrier concentration independent *van Vleck* mechanism¹ and the carrier mediated *Ruderman-Kittel-Kasuya-Yosida* mechanism [44] has been found in different magnetically doped binary and ternary topological insulators of the Bi_2Te_3 -family of materials [215, 220, 231, 232]. On the other hand, a comparison of bulk sensitive muon-spin rotation measurements with surface sensitive *X-ray circular magnetic dichroism* (XMCD) measurements [185] show an increase of the Curie temperature at the surface as compared to the bulk. This is in line with theoretical calculations [219] that state that the topological surface state in TIs can break the common rule, stating that the Curie temperature in lower dimensions is typically smaller, i.e. $T_C^{3D} > T_C^{2D}$, and that $T_C^{\text{bulk}} < T_C^{\text{surface}}$ can be possible in topological insulators, which suggest that the magnetism of surface-doped topological insulators does not simply follow the bulk one. Additionally, in recent experiments [225] ferromagnetism at room temperature was observed at the interface of a $\text{EuS}/\text{Bi}_2\text{Se}_3$ heterostructure that consists of the topological insulator and the ferromagnetic insulator EuS. This comes as a surprise since the Curie temperature of pure EuS is only 17 K. Obviously the interplay of magnetism and the surface states of topological insulators is very fascinating and needs a more detailed analysis.

So far, surface-doped samples were studied mainly with respect to the geometry (absorption site, relaxation to thermodynamically stable position) and basic properties (magnetic moment of the impurity, hybridization with TI states, magnetocrystalline anisotropy) of individual adatoms [152, 227–230, 234–236]. *In this work* a study of the exchange interactions of purely *surface-doped* topological insulators is presented, which is an important contribution to the emerging field of magnetically doped topological matter. Our approach is based on the interaction of an ensemble of magnetic impurities which is captured by the classical

¹The van Vleck paramagnetism can occur in band insulators as it is the case in the bulk of Bi_2Te_3 . For a concentration c_{imp} the response to an external field is given in second order perturbation theory by the van Vleck susceptibility that in materials like Bi_2Te_3 and Bi_2Se_3 can be written as $\chi = 4\mu_B^2 c_{\text{imp}} \sum_{E_{nk} < \mu, E_{mk} > \mu} \frac{\langle nk|S_z|mk\rangle \langle mk|S_z|nk\rangle}{E_n - E_0}$, with $|nk\rangle$ in the valence band ($E_{nk} < \mu$) and $|mk\rangle$ in the conduction band ($E_{mk} > \mu$). The matrix elements $\langle nk|S_z|mk\rangle$ can be rather large due to the inverted-band nature of the band gap in topological insulators [214].

Heisenberg Hamiltonian

$$\hat{H} = -\frac{1}{2} \sum_{ij} J_{ij} \hat{\mathbf{e}}_i \cdot \hat{\mathbf{e}}_j - \sum_i K_i (\hat{\mathbf{e}}_{z,i})^2, \quad (7.1)$$

that describes the interaction between two magnetic moments i and j , sitting at positions $\mathbf{R}_i$ and $\mathbf{R}_j$. The *classical* description of the spins is appropriate for our case because of the usually large spin values of $S = 3/2$ to $S = 5/2$, which is inferred by a magnetic moment of the impurity that, for example, reaches $\sim 5\mu_B$ in Mn. Also, the non-integer spin-values found for the different transition metal impurities justify the usage of the classical spin model. The direction of the magnetic moments at site i and j is given by the unit vectors $\hat{\mathbf{e}}_{i,j}$ and the second term in Eq. (7.1) is the *uniaxial anisotropy* that either favors out-of-plane ($K_i > 0$) or in-plane ($K_i < 0$) orientation of the magnetization direction of the individual impurity. The exchange coupling is given by the *exchange coupling constants* J_{ij} that are the focus of the study presented in this chapter. The sign determines if ferromagnetic ($J_{ij} > 0$) or antiferromagnetic coupling ($J_{ij} < 0$) between two magnetic impurities is favored.

In the following, the theoretical aspects of the different exchange mechanisms that play a role and which can compete are explained. Then the XMCD measurements, that guide this combined theoretical and experimental study, are described. The main part of this chapter is the detailed explanation and discussion of the experimental findings with respect to the results of our ab-initio calculations where different competing mechanisms that govern the exchange interactions in surface-doped topological insulators are analyzed. The microscopic understanding that is gained eventually opens up new ways in tailoring the exchange interactions in magnetically doped topological insulators in the future.

7.1.1. Competing mechanisms of the exchange interaction

The band structure of topological insulators contains on the one hand the insulating bulk states but on the other hand also the topologically protected metallic surface states. Thus, the mechanisms of the exchange interactions on the one hand have a close resemblance to the mechanisms known from the field of diluted magnetic semiconductors (DMS) [237] but on the other hand also from magnetically doped metals or two dimensional electron liquid² (2DEL). Here, we review the mechanism that dictate the exchange interactions in surface-doped Bi_2Te_3 that are studied here.

Following the discussions presented in [238] and [239] we distinguish between the following mechanisms: (i) *superexchange* mechanism also known as kinetic exchange due to level repulsion between occupied and unoccupied d -states, (ii) *double exchange* due to broadening associated to bonding-antibonding formation and (iii) the free-carrier mediated long-ranged *Ruderman-Kittel-Kasuya-Yosida* (RKKY) interaction due to polarization of the electron liquid in the presence of magnetic impurities. It should be noted that the superexchange mechanism usually favors antiferromagnetism whereas double exchange usually favors ferromagnetic coupling. Both mechanisms decay strongly with the distance R between impurities, since

²In the literature often the term two-dimensional electron *gas* (2DEG) is used, which seem however inappropriate, since the density of states is much higher as for example in the conduction band of semiconductors filled by temperature, where the term 2DEG is correctly used due to the very small fraction of occupied states.

they rely on hopping between orbitals on different impurities that decreases exponentially with R . This is a consequence of the localization of the impurity wavefunctions. The RKKY interaction on the other hand oscillates with the distance between the magnetic atoms. Additionally, the decay of this interaction is only polynomial (in two dimensions usually with $1/R^2$ in the asymptotic limit) and the interaction is thus long-ranged.

The different mechanisms and especially how they can be tested in a first principles calculation – as done in the main part of the text – are explained in the following.

Superexchange mechanism for short-range AFM coupling

The superexchange mechanism, also known as *kinetic exchange*, stabilizes antiferromagnetic coupling between two magnetic atoms. It is simplest to explain if the density of state assumes a special form for the magnetic impurities where the Fermi energy lies in between the majority and minority resonances. For two atoms in antiferromagnetic alignment, the occupied level of atom 1 and the unoccupied level of atom 2 interact since they are of the same spin. This leads to level repulsion between the orbitals of the two spins which is shown in Figure 7.1.

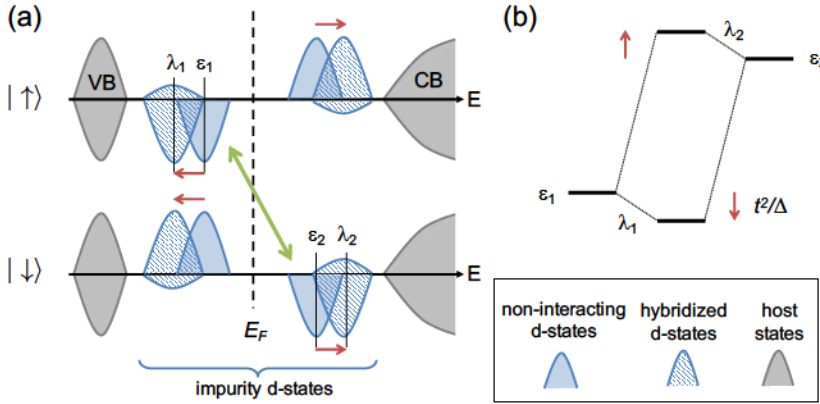


Figure 7.1.: Illustration of the superexchange mechanism that favors antiferromagnetism due to level repulsion. (a) Schematic image of the hybridization of the impurity orbitals and the resulting energy level shifts. The interaction between levels is highlighted with a green double arrow and the resulting energy shift with red horizontal arrows. The corresponding image of the energy levels is shown in (b). VB and CB denote valence and conduction band, that do not play an important role for this mechanism. Figure modified after [238].

In a simple tight binding picture this situation can be captured by a two-band model that is described by the Hamiltonian

$$\hat{H} = \begin{pmatrix} \epsilon_1 & t \\ t & \epsilon_2 \end{pmatrix} \quad (7.2)$$

where $\epsilon_{1,2}$ is the energy of occupied and unoccupied levels and t is the hopping strength between the two levels. A straightforward diagonalization of this matrix gives the eigenenergies in the toy model. Due to the interaction described by t , the original levels shift and form the

levels $\lambda_{1,2} = E_0 \pm \sqrt{\Delta^2 + t^2}$ with $E_0 = (\epsilon_1 + \epsilon_2)/2$ and $\Delta = (\epsilon_2 - \epsilon_1)/2$. Assuming $t \ll \Delta$, the energy gain due to level repulsion (coming from the shift of the occupied states) can be written as $2(\epsilon_1 - \lambda_1) \approx t^2/\Delta$, where the factor 2 comes from the two electrons of the two atoms. This is depicted in Fig. 7.1 (b).

From the energy gain due to level repulsion it is obvious that by artificially increasing the exchange splitting Δ the superexchange mechanism is weakened. This can be done in a numerical experiment which we performed for the systems under study to gain insight into the importance of the superexchange mechanism. A small shift of the Fermi level will not affect the superexchange mechanism as long as the Fermi energy lies still in the gap, or more precisely that the density of states at the Fermi energy stays low.

Double exchange for short-range FM coupling

The double exchange mechanism is stabilizing ferromagnetic order. This mechanism dominates the exchange interaction if either majority or minority states, called $\epsilon_{1,2}$ as in the previous section on the superexchange mechanism, are close to the Fermi level. This situation is schematically shown in Figure 7.2.

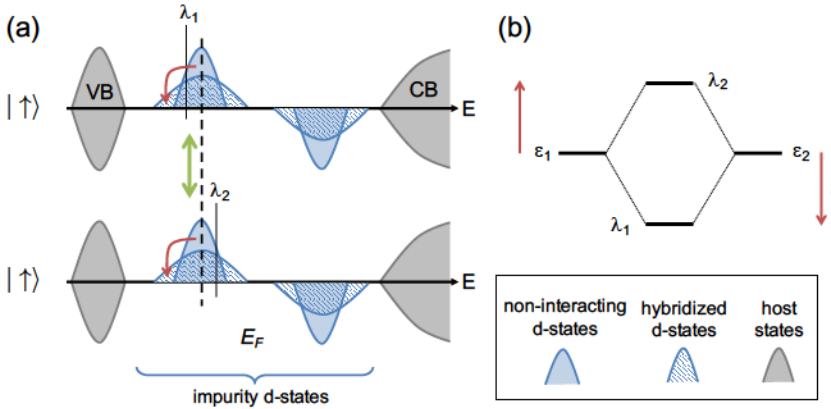


Figure 7.2.: Illustration of the double exchange mechanism that favors ferromagnetic alignment. (a) The hybridizations of the orbitals (indicated by a green double arrow) that results in a broadening of the orbital and a redistribution of the electrons that gain energy (red arrows). This energy gain is depicted in (b) where the formation bonding-antibonding pairs is shown. VB and CB denote valence and conduction band. Figure modified after [238].

In a ferromagnetic alignment of the two atoms, the states close to the Fermi level have the same spin and can therefore interact. Following the same toy model as written down in Eq. (7.2), the shifted energy levels due to the formation of bonding and antibonding levels is $\lambda_{1,2} = \pm t$ because of $E_0 = \Delta = 0$. Thus, the hybridization leads to a broadening of the energy levels and electrons close to the Fermi level are redistributed into lower lying states which means that energy is gained.

7. Exchange interactions on magnetically doped topological Insulators

A small shift of the Fermi level can tune the resonance out of half filling and therefore significantly change the number of electrons that are redistributed which reduces the energy gain and therefore the strength of the double exchange mechanism. This can be done in a calculation where the Fermi level is varied.

So far we have seen the two mechanisms that determine the short-range interactions. In real systems these two mechanism occur simultaneously and can compete. In general the ratio Δ/t , together with the position of the Fermi level (if E_F lies within the resonance, $|t/\Delta| \lesssim 1$ determines which of the above discussed mechanisms wins), determines whether the energy gain by super- or double exchange dominates which will result in antiferro- or ferromagnetic coupling between two magnetic impurities. In a realistic system also effects like crystal field splittings and more generally the strength of the hybridization with the host states can have significant impact on the impurity states. This can lead to multiple peaks within the minority and majority resonances so that a complicated balance between competing interactions is to be expected.

RKKY interaction and long-range coupling

The Ruderman-Kittel-Kasuya-Yosida interaction [44] is a result of the polarization that the exchange-split impurity states induce on the free carriers of the host system [237]. In topological insulators this is the electron liquid of the topological surface state. This effect is also related to the *Friedel oscillations* [35] that – as a result of scattering of free electrons off the impurity – manifests as standing waves in the charge (spin) density around (magnetic) impurities. These polarized electrons can then transport the information of the magnetism at one impurity to other locations which leads to an exchange coupling over long distances. The idea of a carrier mediated interaction goes back to Zener [240] and is depicted in Figure 7.3 (a). The polarization effect is indicated by green double arrows whereas the resulting shift in the host states is indicated by the red horizontal arrows.

It is intuitively clear that the exact form of the Friedel oscillations around an impurity depends on the one hand on the impurity and on the other hand on the host crystal that engraves its physical properties, such as topology, into the wavefunctions of the polarized electrons. The host plays a major role in the (an)isotropy of the interactions due to (an)isotropies in the Fermi surface, in the spirit of the stationary phase approximation [154]. The impurity, by its spin direction or orbital ordering, may however also play an important role. The paramount importance of the host's properties, that are reflected in the Fermi surface, is sketched in Figure 7.3 (b). Assuming isotropic scattering properties (for example by a point-like δ -scattering potential), an isotropic Fermi surface (left) will lead to universal Friedel oscillations in all directions that oscillate radially with a common phase and decay. Typically these oscillations are of the form $\cos(q_1 R + \phi)/R^2$ in two dimensions depending on the distance from the impurity R , a phase shift ϕ and $q_1 = 2k_F$ coming from backscattering of states on the Fermi surface (k_F is the Fermi wave number). This directly translates into an oscillating decay of the RKKY interaction with increasing impurity-impurity distance. This situation is shown on the left in Fig. 7.3 (b). In the case of an anisotropic Fermi surface (here depicted by a hexagon) more stationary points than the scattering vector q_1 , here called q'_1 , appear that connect different pairs of k -points which have the same Fermi velocity. This leads to a focusing in the Friedel oscillations that can be translated into *focused RKKY* interactions with a much slower decay in certain crystallographic directions as compared to

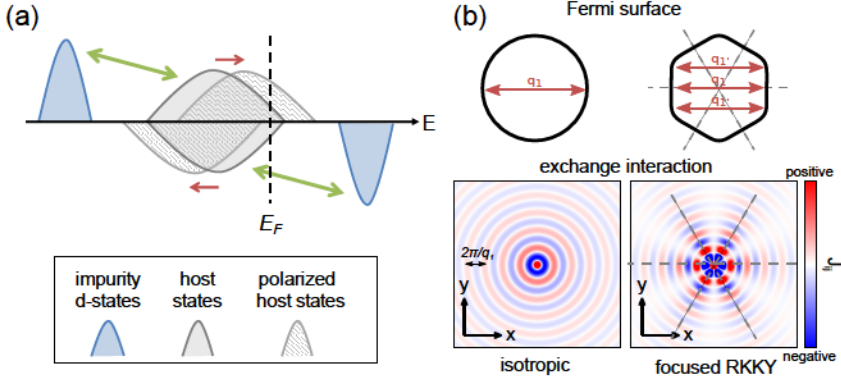


Figure 7.3.: Sketch of the induced polarization in the host states by an exchange-split impurity (a). The polarizing interaction is depicted with green double arrow that leads to an induced polarization in the host states (indicated with red arrows). The correspondence of host properties (Fermi surface) and the directionality of the RKKY interaction is shown in (b). Flat parts in the Fermi surface (b, top right) lead to strongly focused exchange interactions (lower right) highlighted with dashed lines. VB and CB denote valence and conduction band. Figure modified after [238].

others [154, 179, 180]. This is sketched on the bottom right of Fig. 7.3 (b).

Because of the close relation between the RKKY interaction and Friedel oscillations, insights into the importance of this mechanism is given by a comparison of the Friedel oscillations around a single impurity with the decay and oscillations of the distance-dependent exchange interactions. This can be done easily within the framework of the KKR method that was used in the calculations presented below.

7.2. Experimental observation of magnetism in surface-doped Bi_2Te_3

The work presented in this chapter is the result of a very fruitful collaboration with an experimental group at Trieste performing X-ray magnetic circular dichroism (XMCD) measurements [242]. Highlighted should be the work done by Alessandro Barla with whom I collaborated most. In this section, the experimental results of the Trieste group are briefly reviewed. A quick side note on the XMCD technique is given below before the setup of the experiment and the results of the Trieste group are presented.

Here, we can only take a quick look at the technique of X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism to introduce the reader who might not be familiar with this technique to the topic. A more complete introduction to the XMCD technique can for example be found in the work of Baumgarten [241] whose manuscript is being followed here.

The XAS and XMCD technique

As the name X-ray absorption spectroscopy suggests, in this technique X-rays are being shot at the sample that is studied. The X-ray photons have a high enough energy to excite transitions from core electrons to possible final states near the Fermi level. This results in an absorption spectrum that is element specific. The setup is depicted in Figure 7.4.

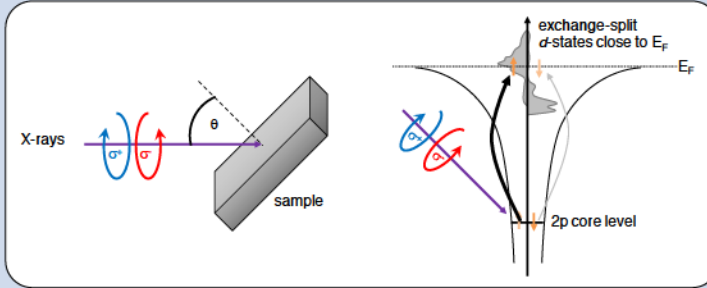


Figure 7.4.: Schematic image of the XAS/XMCD measurement. The incident angle is depicted on the left while the schematic excitation of 2p electrons to the d-states at the Fermi level for left and right polarized X-rays is shown on the right hand side.

To study magnetism typically circular polarized light is being used in an energy range around the $L_{2,3}$ edges which stands for electrons being excited from the 2p core level to the states at the Fermi level. The orbital selection rules dictate that the orbital quantum numbers of initial and final states have to differ by one. This means that for example 2p electrons are absorbed by the d-orbitals at the Fermi level which makes this technique sensitive to the magnetism coming from the d-states as it is the case in transition metals. Left and right circular polarized light gives different weighting on the excitation of core electrons depending on their total angular momentum (orbital plus spin moment).

The X-ray magnetic circular dichroism is the difference of the Intensity of the XAS obtained from right and left circular polarized light. As depicted on the right on Fig. 7.4, the XAS signal differs due to the difference in the final states density of states that is different for the two spin channels. The XMCD signal can be measured for different incident angles and the difference between normal and grazing incidence gives information about the favored direction of the magnetization, i.e. the magnetocrystalline anisotropy. The integrated XMCD intensity allows to use *sum rules* to get information about the average magnetic- and orbital moments in the sample. The finite penetration depth of X-rays makes XAS and XMCD a surface sensitive technique, in contrast to other approaches like muon-spin rotation experiments.

7.2.1. Experimental setup

To have a controlled experiment of surface-doped Bi_2Te_3 , Mn and Co was deposited by the experimental group at very low temperatures ($\sim 4\text{ K}$) in varying concentrations of 0.5-8% of a monolayer for Mn and 0.4-28% of a monolayer for Co onto the clean Bi_2Te_3 surface. Transition metals deposited at low temperatures on Bi_2Te_3 are known to occupy two different positions – the fcc and hcp hollow sites [152, 227, 228, 230, 234]. At higher temperatures adatoms diffuse into the material and occupy the thermodynamically stable position substituting Bi [229, 236] or going deeper into the van der Waals gap [185, 224, 233]. Therefore, keeping the temperature as low as possible is a central ingredient in having experimental control over the absorption position. XAS and XMCD measurements were then performed applying an external field of 6 T and under different incident angles. Further details on the experimental setup can be found in [242].

7.2.2. Experimental results

Figure 7.5 summarizes the experimental results of the Trieste group for Mn and Co deposited at low temperatures and for different coverages. A more in-depth analysis of the experimental data can be found in [242]. An analysis of the line shape and spectral features in the XAS and XMCD spectra of Mn and Co shown in (a) and (b) gives information about the d -filling of the 3d transition metals. For Mn a state between d^5 and d^6 and for Co close to d^8 can be extracted. The magnetocrystalline anisotropy is found to be out-of-plane for Mn as well as Co where a value of the anisotropy constant K at the lowest coverage takes values of 1-1.2 meV for Mn and 1.7-3.6 meV for Co.

Figures 7.5 (c) and (d) show the results of the sum-rule analysis that gives access to the average spin- and orbital moments of Mn and Co at different coverages, respectively. The measurement of the spin moment also contains the dipole term (m_D) [243, 244], that is not included in the calculations. With increasing coverage a clear decrease of the average moments can be seen for both Mn as well as Co. While at very dilute concentrations the average spin moment of the Mn atoms is close to $5\mu_B$ a decrease to less than $3\mu_B$ is found at higher coverage of 0.08 monolayers (ML). In Co the average spin moment of roughly $3\mu_B$ decreases to $1\mu_B$ for coverages exceeding 0.04 ML. We should point out that the sum-rule analysis involves the total integrated XMCD intensities and therefore includes monomers at different distances as well as dimers and other small clusters that are more and more likely to occur with increasing coverage. This was for example seen in Mn surface-doped Bi_2Te_3 , which is shown in Fig. S2 of the supplemental material in Ref. [131]. This results in an averaged value for the spin and orbital moments that is effectively decreased if neighbors at short distances couple antiferromagnetically. For Mn the guide to the eye (black dashed line) highlights that on top of the general decrease in m_s with higher coverage one data point at 0.018 ML coverage breaks this trend and forms a shoulder. This is an indication, that for this concentration some contribution of ferromagnetic coupling is competing with the predominant antiferromagnetic coupling in small clusters. This behavior is further studied with an analysis of the effective magnetization presented below.

The effective magnetization is derived from the intensity of the main spectral feature in the XMCD signal at varying field and not from the integrated intensities used in the sum rule analysis. This intensity allows to study the magnetization curves at different coverages which

7. Exchange interactions on magnetically doped topological Insulators

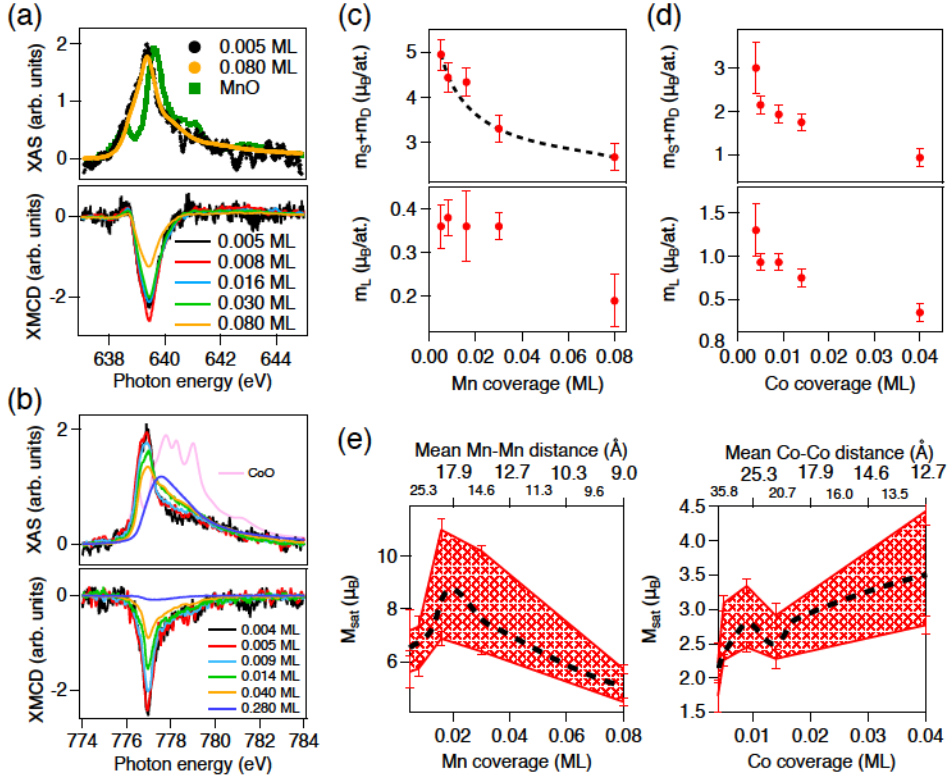


Figure 7.5.: Experimental results for Mn and Co deposited in different coverages at low temperatures on Bi_2Te_3 . The XAS and XMCD spectra are shown, respectively, for Mn and Co in (a) and (b). (c) and (d) show the spin and orbital moments depending on the coverage of 3d adatoms determined from the XMCD sum rules. The measurements were performed below 5 K in a field of $B^{\text{ext}} = 6$ T. Panel (e) shows the effective magnetization (sometimes called saturation magnetization M_{sat}) obtained by fitting the magnetization curves for the external field sweeping a range of $B^{\text{ext}} = \pm 5$ T of Mn and Co for different coverages. The shaded area indicates the a range of possible values due to uncertainties in the measurement apparatus. Image taken and modified from [242].

7.3. Microscopic origin of the exchange mechanism in Bi_2Te_3 and comparison to experiment

are then fitted to the magnetization curve of a model of coupled spins with superparamagnetic behavior to extract the effective magnetization. Choosing only the main spectral feature allows to neglect contributions from dimers and other small clusters since these are expected to change the shape of the XAS spectra. This can for example be seen in Figure 7.5 (b) where a shoulder at higher photon energies arises at high coverages. Thus, the data presented in (e) gives information about the monomers and especially the collective behavior of single magnetic impurities.

The high effective magnetization of $6\text{--}10\ \mu_B$ – that clearly exceeds the magnetization of a single Mn atom – for Mn indicates short-range magnetic order of ferromagnetically coupled spins. The black dotted lines provide a guide to the eye that highlights a maximum in the effective magnetization around 0.02 ML coverage while for higher coverages the effective magnetization decreases monotonically. The general trend of decreasing magnetization with higher coverages, i.e. smaller average Mn-Mn distances, indicates an increase in antiferromagnetic coupling in the short-range regime while around 0.02 ML coverage (roughly 18Å mean distance) a sign change in the exchange coupling could explain the increase in the effective magnetization.

For Co, the effective magnetization shows the general trend of increasing moment with coverage. This suggests ferromagnetic coupling in the short-range regime. Around 0.015 ML coverage (roughly 20Å mean Co-Co distance) a dip in the general trend can be seen that suggests a sign change in the exchange coupling.

In conclusion, the experimental observations by the Trieste group show different trends of competing mechanisms in Mn and Co. While the sum rule analysis indicates a tendency to antiferromagnetic coupling for both Mn and Co probably at short distances or in clustered atoms, the effective magnetization of long-distance coupled monomers clearly shows different trends for Mn and Co impurities. It reveals a range of mean impurity-impurity distances where the interaction can be tuned from antiferromagnetic to ferromagnetic and back to antiferromagnetic coupling in Mn and vice-versa for Co. With the following analysis based on *ab-initio* calculations we are able to demystify the nature of the exchange coupling of transition metal surface-doped topological insulators.

7.3. Microscopic origin of the exchange mechanism in Bi_2Te_3 and comparison to experiment

The experimental data presented so far give indication of competing mechanisms that act in different strengths at different concentration regimes. To shed some light into the microscopic details of the exchange interactions and to get a better understanding we performed an extensive *ab-initio* study of Mn, Fe and Co surface-doped Bi_2Te_3 . The results are presented in the following and compared to the experiment outlined above.

7.3.1. Setup of calculation and computation details

We start by discussing the setup of the calculation. The density functional theory based calculations for the Bi_2Te_3 host system and the impurity embedding were performed within the

7. Exchange interactions on magnetically doped topological Insulators

framework of the relativistic³ full-potential Korringa-Kohn-Rostoker Green function (KKR-GF) method [60–63] that is described in the first chapter. The local spin density approximation [53] for the exchange correlation potential and an angular momentum cutoff of $\ell_{max} = 3$ was used. The pristine surface of Bi_2Te_3 was simulated using a 6 quintuple layer (QL) thick film with the experimental lattice constant [245] into which a single impurity was embedded self-consistently by solving the Dyson equation. This simulates the dilute limit of impurity concentrations where single impurities can be treated independently. An impurity cluster that consists of the impurity itself and the first shell of neighboring atoms was included in the calculation to account for correct charge screening by the metallic surface state in the topological insulator. The calculation was checked for convergence against a larger cluster consisting of three times as many neighboring atoms within a larger radius. The presence of the metallic surface state leads to an efficient charge screening which results in the small cluster being enough to converge the calculation.

Transition metal adatoms deposited on the surface of strong topological insulators such as Bi_2Te_3 have been studied in the literature already. It is known that two different absorption⁴ sites – the hcf and fcc hollow sites – are possible [230, 234, 236]. Bi as well as Te are large atoms so that the smaller transition metal adatoms relax considerably into the first quintuple layer [152, 230, 234, 236]. This is especially pronounced in the fcc hollow site without a Bi atom directly beneath, as it occurs for the hcp site. This is shown in Figure 7.6 where the impurity position in the fcc hollow site is shown from a side view (left) and in a top view (middle).

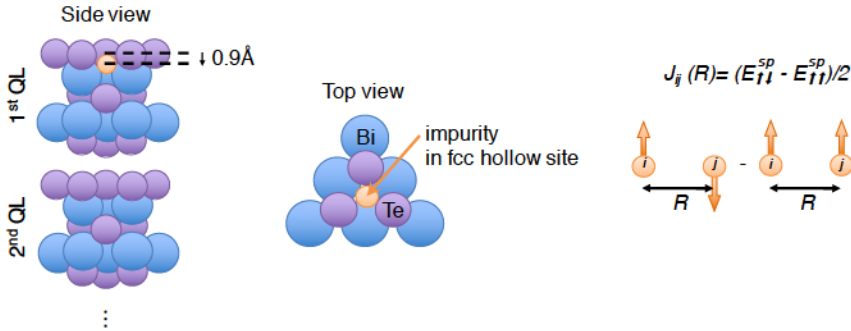


Figure 7.6.: Setup of the DFT-based calculation of the exchange interactions for dilute impurity concentrations. The position of the impurity at the fcc hollow site position (taken from Ref. [234]) within the first quintuple layer is shown in a side view (left) and from a top view (middle). On the right hand side the calculation scheme of the exchange interaction strength using the magnetic force theorem is depicted.

The sister compound Bi_2Se_3 of Bi_2Te_3 has been studied in the past mainly with Fe doping

³Meaning that spin-orbit coupling and other relativistic effects are included in all steps of the calculation of the self-consistent density.

⁴We use the term *absorption* instead of *adsorption* because the position of the impurity is significantly relaxed into the first QL of the Bi_2Te_3 film.

[152, 227–230]. Surface doping in Bi_2Te_3 on the other hand was so far only studied for Fe [234, 236], Co and Ti [235] adatoms. As it turns out, the relaxations into the first QL are larger in Bi_2Te_3 as compared to Bi_2Se_3 because of the larger in-plane lattice constant.

Due to the lack of data for the relaxations we chose the relaxed position of Fe in Bi_2Te_3 [234] to model the absorption sites for Mn, Fe and Co at the fcc hollow site position.⁵ The hcp hollow site was not considered because of the more complex relaxations due to the presence of the neighboring atoms – especially the underlying Bi atom – that in Bi_2Se_3 can lead to a change of the adatom height of 0.06–0.027 Å if Mn and Co are compared [152]. However, the topological surface state is rather delocalized within the first quintuple layer [246] and only then decays quickly over the next quintuple layers. We can therefore assume that the surface state couples efficiently to the transition metal impurity no matter where exactly it resides. Only if the transition metal impurity is effectively decoupled from the surface state a strongly weakened electron-mediated exchange interaction can be expected. This is for example the case in MnPc molecules deposited on the surface of Bi_2Te_3 the case where no interaction between the magnetic moment of Mn and the surface state was found [247].

Additionally, the *Friedel sum rule*⁶ connects the change in the valence charge due to an impurity to the basic scattering properties, namely the phase shift,⁷ of the impurities. The charge of the impurity however will not change significantly for small changes in the relaxed positions and neither will the overall Fermi level. Also, Eelbo et al. [234] showed that, while the electronic structure of Fe impurities in the fcc and hcp sites differs slightly, the magnetic moment on the other hand is very similar ($2.7 \mu_B$ in fcc and $2.5 \mu_B$ in hcp site). This implies that the long-range RKKY interaction that is determined by these three quantities⁸ will not be affected by small relaxations around the position that we assumed for our calculation. Thus, we can assume that the coupling to the surface state that mediates long-range RKKY interaction is similar for both absorption sites. In conclusion, we can assume that the exchange coupling mechanism only depends very little on the absorption site so that considering the fcc hollow site alone is sufficient.

The calculations of the exchange interactions were performed in an approximation applying the *magnetic force theorem* [248, 249] that avoids time-consuming self-consistency for each pair of impurities at different distances. This involves taking the energy difference of a system with 2 impurities that are once aligned ferromagnetically and once antiferromagnetically. However, the two states are not calculated self-consistently. One uses instead the self-

⁵Note that this is an improvement over the substitutional site in the first Te layer, that was considered in chapter 5. However a comparison of the Mn impurity DOS that is shown here and the DOS shown in Fig. 5.2 indicates that the substitutional Te position of chapter 5 was a good approximation to the more realistic case studied in this chapter.

⁶See for example the appendix D8 (p. 899ff) of Ref. [66] where the relation $\delta N(E) = \frac{1}{\pi} \sum_{\ell} (2\ell + 1) \delta_{\ell}(E)$ is given that describes the change in the integrated up to energy E (local) density of states $\delta N(E)$ due to the energy dependent scattering phase shifts $\delta_{\ell}(E)$ which are a signature of the scatterer, i.e. the impurity embedded into the system. In the case of substitutional impurities this results in the relation $Z^{\text{imp}} - Z^{\text{host}} = \frac{2}{\pi} \sum_{\ell} (2\ell + 1) \delta_{\ell}(E_F)$ where Z^{imp} and Z^{host} are the valence charge of impurity and substituted host atom, respectively, and the factor two is coming from the spin degree of freedom. Here the situation is more complex because of the lack of spherical symmetry around the impurity, but a generalized Friedel sum rule still holds, with $Z^{\text{host}} = 0$ in the case of an interstitial impurity or adatom.

⁷A detailed discussion on the phase shifts and the relation to impurity scattering is presented on pages 144ff.

⁸For a detailed discussion see Eq. (7.9) on page 147.

7. Exchange interactions on magnetically doped topological Insulators

consistent potential of a single impurity twice, placing it at the two distant sites, once aligned parallel and once antiparallel in spin space. These should be considered as trial potentials, not very far from the true self-consistent potentials. According to the force theorem, the sum of eigenvalues $\sum_i \epsilon_i$ of occupied Kohn-Sham states is taken in each trial potential, and the difference $\Delta E = \sum_i \epsilon_i(FM) - \sum_i \epsilon_i(AM)$ is calculated as a good approximation to the difference in self-consistent total energies. It is safe to assume that this holds for large enough distances between the two impurities because of the efficient screening of the single impurities by the surface state electrons, as discussed above.

Thus, based on the single impurity calculations, in a one-shot manner the single particle energies of two impurities at distance at positions $\mathbf{R}_i$ and $\mathbf{R}_j$ were computed for the ferromagnetic and the antiferromagnetic alignment of the moments. The difference of the single particle energies of this pair of atoms at a distance $R = |\mathbf{R}_i - \mathbf{R}_j|$ then gives the exchange coupling strength⁹ $J_{ij}(R) = (E_{\uparrow\downarrow}^{sp} - E_{\uparrow\uparrow}^{sp})/2$. A positive sign of the exchange interaction signals ferromagnetic coupling whereas a negative sign means antiferromagnetic coupling which corresponds to the Heisenberg model that is described by the Hamiltonian given in Eq. (7.1). Note that the plots of Figures 7.7, 7.8, 7.10, 7.12 and 7.13 show the energy difference $\Delta E = 2J_{ij}$ that differs by a factor two to the definition of the exchange coupling constants of the Hamiltonian defined in Eq. (7.1).

This procedure is shown on the right in Fig. 7.6. Because in the screening cluster of a single impurity only the first shell of neighbors have to be taken into account the force theorem is best for two impurities having a larger distance than two times the in-plane lattice constant, i.e. impurities at second nearest-neighbor positions or further apart. Here, we only considered pairs of atoms having the same local environment, i.e. they both occupy the fcc hollow site position so that the vector connecting the two sites is a 2D lattice vector.

The strong relaxation of the transition metal atomic states into the Bi_2Te_3 film lets the atoms hybridize with the surrounding states from the host which influences the size of the moments that differ from the free atomic configuration. We find spin and orbital moments ranging from $1.2 - 3.6 \mu_B$ and $0.17 - 0.37 \mu_B$, respectively. The corresponding filling of the d -orbitals, the spin- and orbital moments as well as the magnetocrystalline anisotropies are summarized in Table 7.1.

Table 7.1.: Spin and orbital moments, the spin resolved number of electrons N_e in the d -orbitals and magnetocrystalline anisotropy constants K of Mn, Fe and Co adatoms in the fcc hollow site position on Bi_2Te_3 . Non-integer values of N_e are the result of hybridization with the host states.

	$m^{spin} (\mu_B)$	$m^{orb} (\mu_B)$	$d_{\downarrow} (N_e)$	$d_{\uparrow} (N_e)$	total d -filling (N_e)	K (meV)
Mn	3.57	0.19	1.24	4.69	5.93	6.73
Fe	2.55	0.37	2.28	4.75	7.03	4.73
Co	1.20	0.17	3.51	4.67	8.18	-3.43

⁹More generally the full exchange tensor can be computed that – in addition to the so called *isotropic exchange* which we deal with in the main part of this work – also contain the *Dzyaloshinskii-Moriya interaction*. In the dilute limit of concentrations that we study here, this should however be not important due to the single-ion anisotropy. A more detailed discussion can be found in section 7.3.6 at the end of this chapter.

We find a strong out-of plane anisotropy for Mn as well as Fe which is well in line with previous calculations of Fe on Bi_2Te_3 [234] where a value of 12 meV was found within the LDA+U method. In contrast to the XMCD experiment presented above, where for Mn and Co an out-of-plane anisotropy is found, we find an in-plane anisotropy for Co atoms. One reason for this discrepancy could be that the two absorption sites might favor different directions. This is for example seen in Bi_2Se_3 where for the Co doped surface an in-plane anisotropy is found for the fcc hollow site while the hcp hollow site favors an out-of-plane anisotropy [230]. This trend was also seen for other transition metals on Bi_2Se_3 [152]. An influence of different Fermi level positions, as discussed in detail in section 7.3.5, shows that the anisotropy in Mn varies only a little and stays out-of-plane, in Fe a strong decrease from $K = 4.7$ meV to $K = 1$ meV for shifts of the Fermi level of up to 425 meV is observed and in Co the in-plane anisotropy varies between $K = -4$ meV and $K = -2.5$ meV. Additionally, an influence of small clusters as discussed in section 7.3.6 cannot be excluded. There, an increasing trend towards out-of-plane anisotropy is reported for Co clusters of increasing size. For the interpretation of the data representing the dilute limit the experimental out-of-plane anisotropy was assumed for Co as well, but the exchange coupling constants were derived from theory, since we believe that the mechanisms that determine the exchange interaction are rather stable and only small quantitative changes would arise.

In addition to the dilute limit, clusters of dimers and trimers at the next nearest positions were also computed but with a self-consistent calculation that takes the changes in the local electronic structure into account. These results and the changes that arise as compared to the case of dilute concentrations are presented in the end of this chapter.

7.3.2. Spatially anisotropic exchange coupling in transition metal doped Bi_2Te_3

We start the discussion of the distance-dependent exchange interactions between magnetic impurities by looking at the exchange coupling strength $J_{ij}(R) = \Delta E/2$ between a pair of impurities i and j sitting at positions $\mathbf{R}_i = (0, 0)$ and $\mathbf{R}_j = (R, 0)$. This means that we will first analyse the coupling strength in one crystallographic direction ($\overline{\Gamma K}$) which we set as the x -direction. This is presented in Figure 7.7 (a) where the three curves show the coupling strength for Mn-Mn, Fe-Fe and Co-Co pairs at increasing distances. The shortest distance considered here is the second nearest-neighbor in $\overline{\Gamma K}$ -direction around $x = 8 \text{ \AA}$.

It is worthwhile to take a closer look at the order of magnitude we find for the strength of the exchange coupling. A pair of Mn atoms at a distance of $x \approx 8 \text{ \AA}$ couples antiferromagnetically with an exchange energy of ~ 4.2 meV. Together with the size of the spin moment of $3.57 \mu_B$ reported in Table 7.1 we can estimate that an external field of roughly 20 T would have to be applied to force the two atoms into a ferromagnetic alignment.¹⁰ This would be possible in modern high-field laboratories.¹¹ For Co at the same distance we find a ferromagnetic exchange coupling strength of 3.8 meV which would correspond, hypothetically, to a magnetic field of approximately 55 T acting only locally and opposite in direction on the two spins to force them into an antiferromagnetic alignment. This strong coupling strength at short

¹⁰ 1 meV = $17.276 \mu_B \text{ T}$

¹¹ Such as the high-field laboratory of the Radboud University in Nijmegen where experiments with magnetic fields up to 37.5 T can be performed. (cf. <http://www.ru.nl/hfml/facility/experimental/>)

7. Exchange interactions on magnetically doped topological Insulators

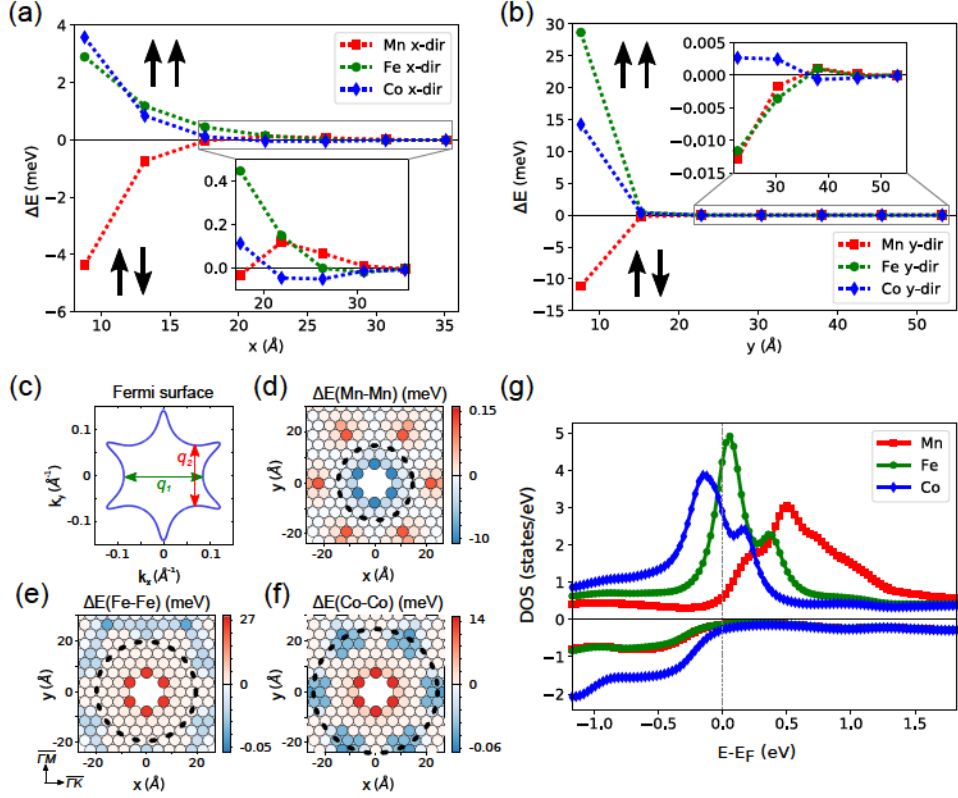


Figure 7.7.: Spatial anisotropy and distance dependence of the exchange interaction for Mn, Fe and Co adatoms in the fcc hollow site of Bi_2Te_3 . The distance dependent exchange coupling in x- and y-directions is shown in (a) and (b) starting from the second nearest-neighbor. The interaction strength shows a different decay in x- (a) and y-direction (b) and an oscillation in the sign of the exchange coupling is found. This can be related to the shape of the Fermi surface (c) which results in the anisotropic behavior of the exchange interaction shown in the exchange interaction maps in (d-f) for Mn, Fe and Co, respectively. The scattering vectors q_1 and q_2 indicate the backscattering and trivial scattering channels. The first impurity is located at (0,0) and the strength of the exchange coupling is given as a color code. The dashed black line indicate the critical radius R_c that corresponds to the Zeeman energy in an external field of 6 T as it happens in the XMCD experiment. (g) shows the density of states around the Fermi level for Mn, Fe and Co.

7.3. Microscopic origin of the exchange mechanism in Bi_2Te_3 and comparison to experiment

distances is a typical value for transition metal atoms and clusters as it was for example studied on Cu(001) and Cu(111) surfaces by Mavropoulos et al. [239] where coupling strengths exceeding 100 meV for first nearest-neighbors of Fe and Cr were found.

If the order of magnitude of the distance-dependent coupling strength is compared to values of Co on Pt(111) [179], we find the coupling strength¹² to be almost an order of magnitude larger in the here studied transition metal doped topological insulator system. We suspect that a reason for the stronger magnetic coupling of the spins in the TI is related to the fact that (at least at E_F) no scattering to bulk states can occur because no other states except for the topological surface state exist (for E_F in the bulk band gap). In Pt on the other hand such scattering channels from surface states to bulk states are always present, which might reduce the coupling strength.

At lower impurity concentrations, i.e. larger distance between impurities, we find a decrease in the coupling strength and for all of the transition metal adatoms a sign change in the exchange coupling constants around $x = 25 \text{ \AA}$. This can be seen in the inset of Figure 7.7 and it is the typical RKKY-type behavior of an oscillation in the carrier mediated long-range exchange coupling coming from the Friedel oscillations in the spin density around impurities. For Mn the maximal amplitude of ferromagnetic coupling is found to be $\sim 0.15 \text{ meV}$. This magnitude is still reasonably large to be of use as this corresponds to a (local) magnetic field of 0.7 T.

The distance dependent strength of the exchange coupling in the orthogonal crystallographic direction ($\overline{\Gamma M}$), which we set as the y -direction, is shown in Fig. 7.7 (b). The general trend of ferromagnetic coupling for Fe and Co and antiferromagnetic coupling for Mn with a decay at larger distances and an RKKY-type sign change is also seen here. The larger exchange coupling strength at the first data point can be understood from the fact that the first position in y -direction is the second nearest-neighbor whereas the first data point in x -direction is the third nearest-neighbor¹³ so that the impurity distance is smaller. Obviously the decay of the exchange coupling is strongly anisotropic as the magnitude of the exchange coupling constants decay much faster in y - as compared to the x -direction. This becomes evident in looking at the magnitude of the sign change that happens in y -direction around $y = 40 \text{ \AA}$ that is two orders of magnitude smaller than the corresponding sign change in x -direction.

This spatial anisotropy can be understood from the Fermi surface seen in Fig. 7.7 (c). Since the long-range oscillations are suspected to occur due to the RKKY interaction, the shape of the Fermi surface plays a major role as focusing can occur. In the spirit of the stationary phase approximation, the relatively flat valleys in $\overline{\Gamma K}$ -direction (i.e. in k_x -direction) support the condition for good nesting. The Fermi velocity of a larger number of k -points is focused in the x -direction so that the RKKY interaction shows a weaker decay in x - (i.e. $\overline{\Gamma K}$) as compared to y -direction ($\overline{\Gamma M}$). Theoretical predictions on the scattering signatures of the topological surface state [138, 139, 155, 218], based on a low energy model for the warped Dirac surface state that describes the topological surface state of Bi_2Te_3 [141], showed the appearance of these scattering vectors (q_1 and q_2) which are in agreement with the stationary points being derived within the stationary phase approximation. Recently, in combination with STM experiments we could show the focusing effect in the real space oscillations of the

¹²Note that the plot in Fig. 7.7 shows ΔE while Fig. 2a of Ref. 7.7 gives $J = \frac{\Delta E}{2}$.

¹³The first nearest-neighbor will be discussed later in section 7.3.6 where small compact clusters are considered, in which case the isolated impurity potential is not a good approximation and a full self-consistent calculation is needed.

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charge density on the topological insulator [131]. This work is discussed in detail in chapter 5. The panels (d-f) of Fig. 7.7 highlight the anisotropic exchange interactions in showing a map of the exchange coupling constants in a color code at the position of the second impurity with the first impurity sitting at (0, 0).

The different behavior of Mn as compared to Fe and Co (AFM vs. FM at short distances) can already qualitatively be understood from the competing mechanisms discussed in section 7.1.1. This can be seen from the density of states around the Fermi level for the different impurities that is shown in Fig. 7.7 (g). For Mn one observes a state close to half filling which results in the Fermi energy lying in between the fully occupied majority peak and the unoccupied minority peak coming from the exchange split d -states. Fe (Co) then has one (two) electrons more occupying the d -states so that the relative position of the peak in the DOS to the Fermi energy shifts downwards. This suggests that in the different cases the details of the competition between double and superexchange mechanisms play a different role. The relatively broad and multiple peak features in the DOS indicate a complicated influence of the crystal field splitting due to the surrounding atoms in the host Bi_2Te_3 crystal. In the next section the features of the DOS are further analyzed with respect to their implications for the exchange mechanism.

7.3.3. Competing exchange mechanisms in Mn, Fe and Co surface-doped Bi_2Te_3

We have seen that the three different transition metal adatoms deposited on Bi_2Te_3 in general show a decay in the exchange coupling strength with distance and a signature of the RKKY interaction that comes with a sign change at large impurity-impurity distances. However, Mn tends to couple antiferromagnetically whereas Co and Fe tend to couple ferromagnetically. These differences are analyzed in detail here. Three different test calculations were performed to study the nature of the exchange mechanism in surface-doped Bi_2Te_3 ; (i) for a single impurity the Friedel oscillations in the induced spin density around a single magnetic impurity are studied and compared to the long-range behavior of the exchange interactions, (ii) the distance dependent exchange interactions are compared for small shifts of the Fermi level and (iii) the exchange interactions are analyzed with a numerical experiment where the occupied d -level is shifted further down in energy to artificially increase the exchange splitting. The results of this analysis are presented in Figure 7.8. Note that we only study the x -direction in the following as this is the dominant direction compared to the y -direction and the nature of the exchange mechanism qualitatively will be the same.¹⁴

Exchange mechanisms in Mn doped Bi_2Te_3

First we study the origin of the exchange mechanism in Mn doped Bi_2Te_3 . For a single Mn atom in the fcc hollow site at (0, 0) the induced spin moment shown in Fig. 7.8 (a) is

¹⁴In principle the exchange interaction can also be spatially anisotropic due to different orbitals that contribute and which extend in different directions. The (111) surface of Bi_2Te_3 however has a relatively high symmetry (C_{3v}) where x - and y -directions are not exactly equivalent, but as can be seen in Figure 7.14, only the out-of-plane oriented d_{z^2} -orbital differ significantly from the other in-plane oriented orbitals. This will result in a very robust mechanism as long as the d_{z^2} peak does not dominate the DOS at the Fermi energy. More details can be found in section 7.3.5.

7.3. Microscopic origin of the exchange mechanism in Bi_2Te_3 and comparison to experiment

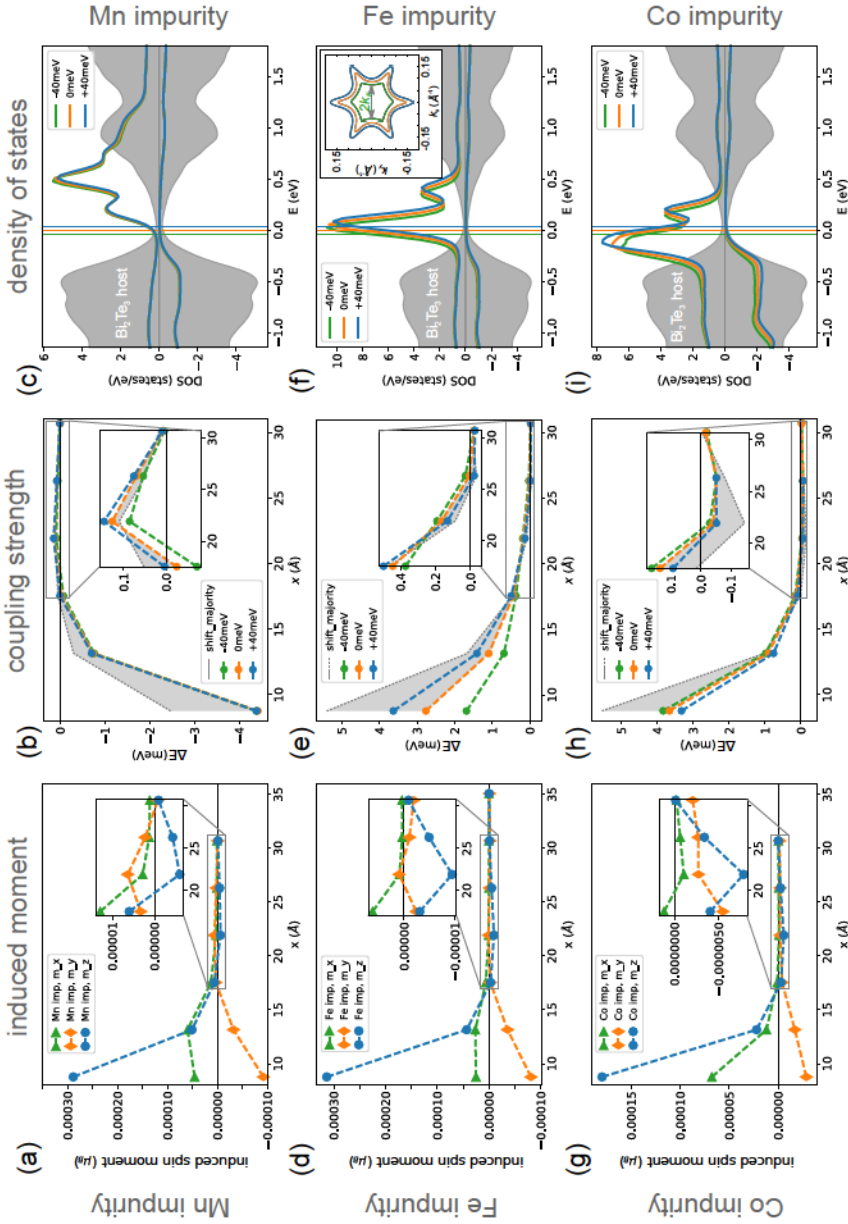


Figure 7.8.: Disentanglement of the competing mechanisms playing a role in the distance-dependent exchange coupling in Mn, Fe and Co doped Bi_2Te_3 . (a) shows the induced spin moment away from a single Mn impurity at (0,0), (b) the changing exchange coupling strength by slightly varying the Fermi level and by shifting the occupied (having their peak originally around -2 eV) d -states down (to ≈ -7 eV) in energy and (c) shows the corresponding density of states. The inset in (c) shows the evolution of the Fermi energy at the three energies. Plots in (d-i) like (a-c) but for Fe and Co, respectively.

7. Exchange interactions on magnetically doped topological Insulators

computed within the fcc hollow site at distance x , i.e. at position $(x, 0)$, where in the calculation of the exchange interaction the second atom is residing. The x -, y - and z -components of the spin are plotted in green, orange and blue, respectively. The non-vanishing x - and y -components indicate that a complex rotation of the spin with the distance of the impurity is present. This leads to a complex interference pattern as it also occurs in the induced magnetization around an Fe atom on Au(111) [119, 209, 250]. At large distances, the easy-axis single-ion anisotropy energy prevails over the in-plane part of the exchange, so that the impurity spin moment is forced to the $\pm z$ direction. The calculation of the exchange coupling therefore assumes that both impurities are pointing in the z -direction (i.e. out-of-plane moment $\mathbf{M} = M\hat{e}_z$) so that the surface state electron-mediated RKKY interaction is of the form $J_{ij}(R) \propto \mathbf{m}^{ind}(R) \cdot \mathbf{M} = m_z M$ with the induced moment $\mathbf{m} = (m_x, m_y, m_z)^T$ that decays from the first impurity as seen in Fig. 7.8 (a). Therefore, in the comparison of induced moment by a single impurity with the exchange coupling shown in (b), we can neglect the in-plane components and deal with the m_z -component only. We see that m_z decays from the impurity and a sign change can be seen at a distance of $\sim 20\text{\AA}$ from the impurity. This fits very well to the sign change in the exchange interaction shown in the Fig. 7.8 (b). Generally the RKKY interaction in a two dimensional electron liquid has the asymptotic form $J_{ij}^{RKKY}(R) \propto \frac{\cos(2k_F R + 2\phi + \delta)}{R^2}$ for large distances R where the phase shift δ is a scattering property of the impurity and ϕ as well as k_F are determined by the Fermi surface. Note that we discuss the x -direction here which means that k_F is given by the k -vector as indicated in the inset of (f). A comparison of the structure of the density of states given in (c), the induced Friedel oscillations (a) and the resulting exchange interaction given in (b) is explained in the following. For this discussion the phase shift and it's relation to the RKKY interaction is needed which is introduced in the short degression presented below.

Scattering phase shifts and the RKKY interaction

In this side note we introduce the scattering phase shifts that determine essential properties of the scattering off impurities. A general introduction to the scattering problem in quantum mechanics can for example be found in [251] where the basic equations that are being used here are explained in detail.

For simplicity we assume that the scattering potential is spherically symmetric $V(\mathbf{r}) = V(r)$, that it decays quickly, i.e. $r^2 V(r) \xrightarrow{r \rightarrow \infty} 0$ and that the electrons far away from the potential behave as free particles with $E = \frac{\hbar^2 k^2}{2m}$. Then the angular part of the Schrödinger equation is decoupled from the *radial Schrödinger equation* that reads

$$\left(-\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + \frac{\ell(\ell+1)}{2mr^2} + V(r) \right) u_\ell(r) = E u_\ell(r) \quad (7.3)$$

by using an expansion in partial waves $P_\ell(\cos \theta)$ that are given by Legendre polynomials and ℓ indicates the angular momentum quantum number. In this basis the full wave function is given as $\Psi(\mathbf{r}) = \Psi(r, \theta) = \sum_{\ell=0}^{\infty} \frac{u_\ell(r)}{r} P_\ell(\cos \theta)$. The solutions of the radial Schrödinger equation have the asymptotic behavior $u_\ell(r) \xrightarrow{r \rightarrow \infty} \sin(kr - \ell\frac{\pi}{2} + \delta_\ell)$ which defines the *scattering phase shifts* $\delta_\ell(E)$. Generally, the phase shifts are given by the eigenvalues of the S -matrix or scattering matrix $S_\ell(E) = e^{2i\delta_\ell(E)}$ that can be related to the t -matrix of the scattering potential which in 2D reads $t_\ell(E) = \sin \delta_\ell(E) e^{i\delta_\ell(E)}$

[252].

The scattering center now can be assumed to have a single resonance in a single channel $\ell = \ell_0$ so that the ℓ -subscript will be dropped from now on. We assume that the resonance occurs at the energy E_R and has a full width at half maximum of Γ so that the density of states for this impurity in a 2DEL is a Lorentzian of the form

$$\text{DOS}(E) = \frac{1}{\pi} \frac{\Gamma/2}{(E - E_R)^2 + (\Gamma/2)^2}. \quad (7.4)$$

This situation is depicted in orange in Figure 7.9 (a). In the case of resonant scattering the phase shifts read as $\delta(E) = -\arctan\left(\frac{\Gamma/2}{E - E_R}\right)$. This energy-dependence of the scattering phase is shown in blue in Figure 7.9 (a). With this expression for the phase shift the *Breit-Wigner formula* for the scattering cross section

$$\sigma(E) = \frac{2\pi}{k} \frac{(2\ell_0 + 1)(\Gamma/2)^2}{(E - E_R)^2 + (\Gamma/2)^2} \quad (7.5)$$

can be derived. Here we find – up a a constant – the same Lorentzian as in Eq. (7.4) which directly relates the density of states to the scattering properties of the impurity. Additionally the phase shift can be interpreted in terms of the *Wigner time delay* that reads as

$$\Delta t = 2\hbar \frac{d\delta(E)}{dE} = \frac{\hbar\Gamma}{(E - E_R)^2 + (\Gamma/2)^2}. \quad (7.6)$$

The time delay has the physical interpretation that an electron which encounters the scattering potential with a resonance at E_R is trapped at the impurity and stays there for the time given by the Wigner timer delay. After a long time and at a large distance after the scattering event the initial wave has traveled further and picked up the phase shift δ because the electron stayed for the time delay at the impurity before continuing.

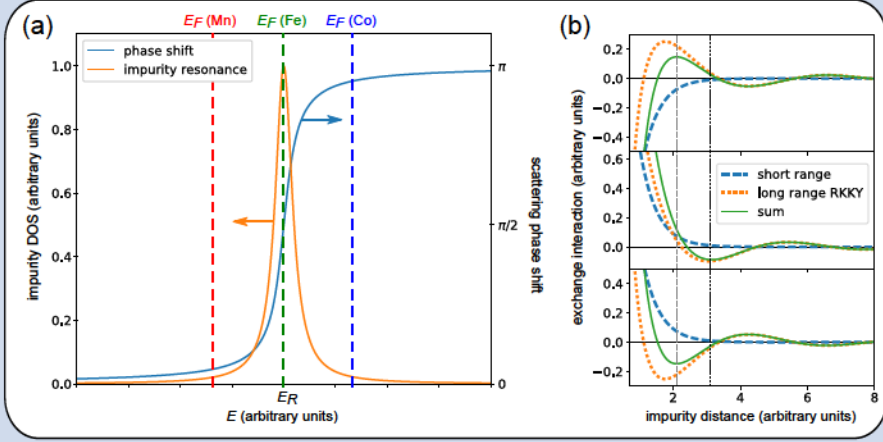


Figure 7.9.: Relation between the scattering phase shifts due to impurity resonances and the competing mechanisms for $\Gamma = E_R/10$. (a) shows phase shift and density of states of the impurity resonance. The Fermi level positions of Mn, Fe and Co are schematically indicated on top in red, green and blue dashed lines, respectively. The resulting competition of the short-range and long-range RKKY mechanism is shown in (b) where the gray dashed and black dotted line indicate the first maximum (or minimum) after the sign changes in the exchange interactions for Mn and Co as well as Fe, respectively.

The general discussion of the phase shifts given above can now directly be connected to the RKKY interaction. The RKKY interaction is the interaction of the induced magnetization by a spin residing at the origin with a second spin at distance R

$$J^{RKKY} \propto -\mu_B \mathbf{m} \cdot \mathbf{S} = -\mu_B S m_z \quad (7.7)$$

where the spins are assumed to point along the z-direction $\mathbf{S}_i = S_i(0, 0, 1)^T$ with $S_i = \pm|S_i|$. Following the stationary phase approximation [154] we can compute the asymptotic form of the induced magnetization for large distances R with

$$\begin{aligned} m_z(R; E) &= -\frac{\text{Im}}{\pi} \text{Tr}_s \left(\underline{\sigma}_z \cdot \underline{\Delta G}(R, R; E) \right) \\ &\propto \text{Tr}_s \sum_{jj'} \underline{\sigma}_z \cdot \underline{\psi}_{k_j}(E) \underline{t}_{k_j, k_{j'}}(E) \underline{\psi}_{k_{j'}}^\dagger(E) \frac{\exp(i(k_{\perp, j} - k_{\perp, j'})R + i(\phi_j - \phi_{j'}))}{R \left| \frac{\partial^2 E}{\partial k_{\parallel}^2} \right|} \\ &\approx \sum_j \left| \underline{\psi}_{k_j}^\dagger \right|^2 \left| \underline{t}_{k_j, k_{j'}}^\dagger \right|^2 \frac{\sin(2k_{\perp, j}R + 2\phi_j + \delta_{k_j})}{R \left| \frac{\partial^2 E}{\partial k_{\parallel}^2} \right|} \end{aligned} \quad (7.8)$$

where $\underline{\cdot}$ and $\underline{\cdot}$ denote a matrix and vector in spin space, Tr_s the trace over spins and ΔG is the difference in the Green function between the system without and with impurity. The vector $\mathbf{k}_j = k_{\perp, j} \hat{\mathbf{e}}_{\perp} + k_{\parallel, j} \hat{\mathbf{e}}_{\parallel}$ is the point on the Fermi surface where the phase of

the contributions $e^{ik \cdot R}$ to ΔG , as k is varied through the band structure, is stationary, decomposed into parallel and perpendicular components with respect to the Fermi surface. This point gives rise to the phase ϕ_j which takes the values $\pi/2$, $-\pi/2$ or 0, if the stationary point is a minimum, maximum or saddle point, respectively. In the case we study here the Fermi surface has a minimum at the intersection with the k_x -axis [cf. inset in Fig. 7.8 (f)], which gives $\phi_j = \pi/2$. For the discussion in the main text only a single pair of stationary points $k_{\perp,j}$ for the x -direction is important. We will refer to the difference between these points as $2k_F$. This is shown in the inset (f) of Fig. 7.8. The denominator in the final expression measures the curvature of the Fermi surface and gives rise to the focusing effect.

In the last step the approximation $\underline{\sigma}_z \cdot \underline{\psi}_{k_j}(E) t_{k_j, k_{j'}}(E) \underline{\psi}_{k_{j'}}^\dagger(E) \approx \psi^\dagger t^{\uparrow\uparrow} \psi^{\uparrow\upagger}$ that assumes the majority spin channel ($\downarrow$) to be fully occupied and the minority ($\uparrow$) peak to be close to the Fermi level which is the only energy of importance in the long-range limit. Thus we used $\underline{\psi}(E) = (\psi^\dagger(E), \psi^\downarrow(E))^T \approx (\psi^\dagger(E_F), 0)^T$. Equation (7.8) is the expression for the Friedel oscillations that mediate the indirect interactions.

Finally, to get from the magnetization density to the magnetization, the energy integration $m_z(R) = \int_{-\infty}^{E_F} dE m(R; E)$ has to be performed to arrive at the final expression for the RKKY interaction

$$J^{RKKY}(R) \propto \frac{\cos(2k_{\perp,j}R + 2\phi_j + \delta_{k_j})}{R^2 \left| \frac{\partial E}{\partial k_{\parallel}} \right|}. \quad (7.9)$$

We can see that the scattering phase shift that entered via the t -matrix directly translates into the RKKY interaction. To understand the competition between short-range interaction and long-range RKKY interaction, we show in Fig. 7.9 (b) the different contributions from short- and long-range interactions for Mn (top), Fe (middle) and Co (bottom), respectively. The short-range exchange interaction is modeled with an exponential decay $J^{short}(R) = A e^{-R/R_0}$ with $-A^{Mn} = A^{Fe} = A^{Co} = 5$ and $R_0 = 0.5$ that is shown with a dashed blue line. The RKKY interaction is plotted with an orange dotted line that is given by $J^{RKKY}(R) = \cos(2k_F R + 2\phi + \delta)/R^2$, where $k_F = 0.7$, $\phi = \pi/2$ and the phase shift depends on the impurity; $\delta^{Mn} = 0$, $\delta^{Fe} = \pi/2$ and $\delta^{Co} = \pi$.

The model that we used here makes several simplifications. First of all, we have assumed an effective potential that scatters for the sake of simplicity only via a single scattering channel. Secondly the interaction with the host system is neglected in the sense that the surface state electrons are simply modeled by free electrons of the 2DEL. This is certainly not true and in reality also the simple relation between t -matrix and phase shifts does not hold anymore. Furthermore due to strong spin-orbit coupling the Green function acquires off-diagonal elements [250, 252] which we neglect here. However, Bouaziz et al. [253] showed, that the induced magnetization around impurities can also in systems with non-spherical symmetry be connected to the eigenvalues of the generalized⁹ S -matrix, which connects the above presented discussion of the phase shifts for the here considered spherical symmetric case to the general situation.

Overall we can conclude, that the simple model presented here does give a reasonable agreement to our calculations and offers valuable insights into the mechanism under investigation.

^aNote that the t -matrix and S -matrix for non-spherical scattering problems are not necessarily diagonal in the same basis.

Mn in the fcc hollow site of Bi_2Te_3 is close to a half filled d -state so that the Fermi energy lies in-between the d -resonances as can be seen in Fig. 7.8 (c). In other words, the minority spin resonance is above the Fermi energy which is the same situation as sketched in Figure 7.9 (a). Thus, the scattering off the Mn defect is *off-resonant* which means that the scattering phase shift δ is close to zero. This determines only the long-range limit of the exchange interaction. To analyze the short-range coupling, the following two numerical experiments are performed.

The first numerical experiment is done to test for the contribution of the double exchange mechanism at short distances. A priori, we expect the double exchange to be negligible for Mn since the density of states at the Fermi level is very low. This is shown in the Fig. 7.8 (c). This conjecture is tested by the following set of calculations. The position of the Fermi level was shifted by $\pm 40 \text{ meV}$ from the original value which we call E_F^0 . The impurity was re-converged self-consistently with the shifted Fermi level which results in a changed density of states at the Fermi energy as shown in (c) and the exchange coupling curves were analyzed. The resulting distance dependence of the exchange coupling is shown in Fig. 7.8 (b) in green ($E_F = E_F^0 - 40 \text{ meV}$), orange ($E_F \equiv E_F^0$) and blue ($E_F = E_F^0 + 40 \text{ meV}$). With a shift of the Fermi level also the relative position of the d -level peaks with respect to E_F can change. For Mn impurities a small shift of the Fermi level only leads to negligible changes in the density of states at E_F [cf. Fig. 7.8 (c)]. In principle, the shift of the Fermi level has two effects (i) the double exchange mechanism is varied if the relative position of the partially occupied d -levels to the Fermi level changes and (ii) with a change of the Fermi level also the Fermi surface and therefore k_F changes and the oscillation period in the Friedel oscillations and consequently also the RKKY interaction changes. In the case of Mn, the short-range behavior does not change with varying Fermi level [the three curves in Fig. 7.8 (b) coincide for the first few data points] but the exact position of the sign change highlighted in the inset moves with increasing Fermi level closer to the origin which comes from the larger k_F at higher energies. The change in k_F can be seen in the inset in (f).

Since the contribution of the double exchange mechanism is vanishingly small, the superexchange mechanism that leads to antiferromagnetic coupling dominates at small distances. This conjecture explains the sign of the short-range interaction and was verified by the following test. As introduced in section 7.1.1, the strength of the superexchange mechanism is inversely proportional to the exchange splitting. Since for Mn, Fe and Co at least 5 electrons occupy the d -levels, this means that – following Hund's rule – the majority spin channel is to a very good approximation fully occupied and the minority spin channel empty. Thus, the splitting between spin up and spin down states can be increased artificially by shifting the occupied d -states down in energy. The gray dotted curve in Fig. 7.8 (b) shows the resulting exchange coupling when the majority d -states are shifted down by 5.44 eV . The gray shaded area between the original ΔE -curve for $E_F = E_F^0$ in orange and the modified coupling strength highlights that a sizable reduction of the exchange coupling strength can be

seen only for short distances (up to $\sim 18 \text{ \AA}$). This confirms that the short-range interaction is governed by the superexchange mechanism and that the long-range exchange coupling that explains the sign change around $x = 20 \text{ \AA}$ is due to a different mechanism – the RKKY interaction.

In summary, the short-range interaction for Mn impurities can be modeled as $J^{\text{short}} \propto -e^{-R/R_0}$ due to the exponential decay of the tight binding hopping parameter that enters the qualitative description of the double- and superexchange mechanisms. The negative sign indicates that in Mn the superexchange mechanism is dominating, which leads to short-range antiferromagnetic coupling. The long-range RKKY behavior is given by a term that can be described as $J^{\text{RKKY}} \propto \cos(2k_F R + 2\phi + \delta) = -\cos(2k_F R)$, because the geometry of the Fermi surface gives $\phi = \pi/2$ [154] and the off-resonant scattering in Mn leads to $\delta \approx 0$. The resulting exchange mechanism, shown in Fig. 7.8 (b), can therefore be modeled with the sum of these two contributions as schematically plotted in the top panel of Fig. 7.9 (b).

Exchange mechanisms in Fe doped Bi_2Te_3

In contrast to Mn doped Bi_2Te_3 , the exchange mechanism in Fe turns out to be dominated by the double exchange mechanism at short distances. The same analysis as in the detailed discussion for Mn, presented above, is carried out for Fe impurities. These results are given in Figure 7.8 (d-f).

The induced spin moment shown in (d) qualitatively has the same behavior as in Mn. However the sign change, seen in the inset occurs at a shorter distance. This indicates a different scattering phase shift as compared to Mn as one would have expected because in Fe the DOS shows an impurity resonance right at the Fermi level as shown in (e). This makes the Fe impurities a *resonant* scattering center in contrast to Mn, leading to a scattering phase shift of $\delta \approx \pi/2$. The comparison of the oscillations in the induced spin in Figure 7.8 (d) and the exchange coupling (e) suggest a more challenging comparison as compared to Mn, since the sign change for Fe occurs only around $x \approx 27 \text{ \AA}$, which is barely seen due to the very small amplitude as compared to the case of Mn. The reduced amplitude is a result of the overall decay of the Friedel oscillations and consequently the long-range interactions mediated by conduction electrons. Before this behavior can be understood we have to analyze the short-range interactions in Fe in detail.

The resonance of the minority d -states in Fe suggested already a dominant double exchange mechanism for Fe impurities in Bi_2Te_3 . The analysis of shifting the Fermi level by $\pm 40 \text{ meV}$ shows the consequences of the Fermi level being tuned closer to the peak of the resonance as seen in Figure 7.8 (f). This strongly modifies the exchange interaction strength presented in (e). A very strong influence of the double exchange mechanism can therefore be deduced. The superexchange mechanism on the other hand cannot be neglected entirely as the numerical experiment of shifting the occupied d -states reveals that the ratio between the competing double- (J^{DX}) and superexchange (J^{SX}) mechanisms in Fe is estimated to be $|J^{\text{SX}}|/J^{\text{DX}} = (J^{\text{DX}} + J^{\text{SX}})/J^{\text{DX}} = (J^{\text{DX}} - |J^{\text{SX}}|)/J^{\text{DX}} = 1 - J/\tilde{J} \approx 0.5$ with J standing for the original¹⁵ $J_{ij}(x = x_0)$ at unshifted Fermi energy, with $x_0 \approx 8 \text{ \AA}$ being the first data point in the plot (i.e. $J = J^{\text{DX}} - |J^{\text{SX}}|$, since $J^{\text{SX}} < 0$ and $J^{\text{DX}} > 0$), and $\tilde{J}$ standing for $J_{ij}(x = x_0)$ after shifting the occupied d -states downwards to increase the energy level

¹⁵Note that $J_{ij} = \frac{\Delta E}{2}$, i.e. J s and ΔE only differ by a constant which drops out in the ratio $|J^{\text{SX}}|/J^{\text{DX}}$.

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splitting and diminish the superexchange (thus $\tilde{J} = J^{DX}$). The double exchange mechanism is twice as important as the contribution from superexchange which reduces the overall coupling strength.

Overall, the short-range exchange mechanism behaves as $J^{short} \propto e^{-R/R_0}$ and the long-range RKKY interaction as $J^{RKKY} \propto \cos(2k_F R + 2\phi + \delta) = -\sin(2k_F R)$, since $\phi = \pi/2$ as discussed above and the resonant scattering for Fe gives a scattering phase shift of $\delta \approx \pi/2$. The competition between the short- and long-range interactions is depicted in the middle panel of Fig. 7.9 (b) from where it can be seen that the first oscillation that is visible for Mn occurs at shorter distances and therefore with a higher amplitude as compared to the case of Fe.

Exchange mechanisms in Co doped Bi_2Te_3

Finally, we analyze the competing exchange mechanisms for Co adatoms on Bi_2Te_3 . The trend we saw by comparing the induced moments by Mn and Fe impurities continues with a further increased phase shift that manifests itself in the position of the first sign change that moves towards smaller distances R between the impurities. This is highlighted with the inset in Fig. 7.8 (g). The resonance in the density of states of Co adatoms is shown in (i) and lies below E_F . Consequently, the scattering phase shift approaches $\delta \approx \pi$. The second peak in the DOS can be neglected for now because it arises from the d_{z^2} -orbital that is directed out-of-plane.¹⁶ A comparison to the distance-dependent exchange coupling in Fig. 7.8 (h) shows that the complicated competition of short- and long-range (RKKY) behavior is obvious as the sign change in Fig. 7.8 (h) does not coincide with the sign change in (g), but is close to the position of the sign change observed for Mn. This indicates that the position of the sign change, that is due to the oscillations in the RKKY interaction, is modified by the competition with the ferromagnetic short-range coupling that shifts the position of the onset of AFM coupling towards larger distances.

The analysis of competing double- and superexchange mechanisms presented in Fig. 7.8 (h) shows that a shift of the Fermi level has some effect on the double exchange mechanism which is however much less pronounced than in Fe. A comparison with the numerical experiment [grey line in (h)] that decreases the superexchange part reveals that the double exchange mechanism in Co is dominating with an even smaller ratio of $|J^{SX}|/J^{DX} = 1 - J/\tilde{J} \approx 0.2$.

Overall, the competition of short and long-range interactions can be written as $J^{short} \propto e^{-R/R_0}$ and $J^{RKKY} \propto \cos(2k_F R + 2\phi + \delta) = \cos(2k_F R)$ with $\phi = \pi/2$ and a scattering phase shift of $\delta \approx \pi$ which is depicted in the bottom panel of Fig. 7.9 (b). From here, we also understand why the position of the sign change, respectively from AFM to FM and FM to AFM coupling, in the exchange coupling constants of Mn and Co, occurs at similar distances whereas in Fe the position of the sign change in the exchange coupling only happens at much larger distances.

7.3.4. Comparison to experiment

For the moment, experimental XMCD results are only available for Mn and Co. Therefore we leave Fe out of the comparison presented in this section. So far, we have seen in experiment

¹⁶Cf. Fig. 7.14 and discussion in section 7.3.5 for details.

that in Mn and Co different mechanism contribute and understood the competition between different mechanisms in the different transition metal adatoms on Bi_2Te_3 at varying distances. Now we want to compare the results of the calculations presented in section 7.3.2 to the experimental observables discussed in section 7.2.2.

Comparison between experiment and theory for very low coverages

First, the properties of single adatoms are compared which in the experiment are extracted from the lowest adatom coverage of 0.005 ML in Mn and 0.004 ML in the Co doped system. While the d -orbital filling in experiment (d^5 - d^6 for Mn and d^8 for Co) is in good agreement with experiment,¹⁷ the resulting spin- and orbital moments are slightly smaller in the simulation as compared to the experiment. We should point out that the dipolar term m_D is not included in the simulation but it is contained in the results from the sum rule analysis. However, the spin moment should be the dominating contribution. Nevertheless the dipolar term can be as large as 20% of the spin moment [242] which will make a quantitative comparison difficult. In the XMCD experiments the impurity does not occupy only the fcc hollow site but the hcp site as well. DFT calculations within LDA are furthermore known to systematically underestimate the orbital moment [254, 255]. A comparison of the values obtained here for the Fe impurity with the LDA+U calculations presented by Eelbo et al. [234] shows that the spin moment is in very good agreement but the orbital moment is larger if corrections due to correlation effects, as it is done within LDA+U, are accounted for. The simulation results for spin and orbital moments certainly only considers *single* impurities whereas the sum-rule and effective magnetization analysis from XMCD give average moments and the collective behavior. Another reason for the higher moments in the experiment as compared to our simulation could therefore be the influence of collective behavior between multiple impurities. If short-range magnetic order is present already at very dilute concentrations (due to long-ranger magnetic interactions), the averaging done implicitly in the sum rule analysis will give a higher effective moment than that of a single atom. The effective magnetization fitting gives a moment of roughly $6\mu_B$ for Mn and $2\mu_B$ for Co whereas the sum rules give $5\mu_B$ for Mn and $3\mu_B$ for Co. The high values (certainly higher than the maximal value of $5\mu_B$) for Mn can be understood in the sense that at dilute concentrations the effect of antiferromagnetic coupling is only very weak and more pairs of Mn atoms are present at a distance where they couple ferromagnetically than at shorter distances where they couple antiferromagnetically. For Co the higher moment in the sum-rule analysis indicates that – in contrast to Mn – the short-range ferromagnetic coupling seems to be more important than the long-range antiferromagnetic contributions for pairs at larger impurity-impurity distances.

Comparison for Mn doped Bi_2Te_3 at different coverages

The averaging over the statistical distribution of adatoms that is inherently done within the XMCD measurement does not allow to distinguish between different coupling strength in different crystallographic directions. We have seen already that the exchange interactions are strongly anisotropic with the x -direction being much more important than the y -direction. Therefore, in the long-range limit we can restrict our analysis to the dominant exchange

¹⁷Cf. Table 7.1 on page 138

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coupling constants of the x-direction (i.e. $\overline{\Gamma K}$) in the following discussion and comparison to experiment. The much smaller contributions in y-direction (i.e. $\overline{\Gamma M}$) will be neglected.

Next, we compare the coverage dependence of the average spin moments and effective magnetization for Mn shown in Fig. 7.5 (c,e) with the results of the ΔE -simulations presented in Fig. 7.7. The strong decrease of the *average moment* for Mn with higher coverage can be understood from the fact that at short distances Mn tends to couple antiferromagnetically. With the increasing concentration of Mn atoms on the surface the presence of pairs of atoms at a short distance is increasing. These pairs couple antiferromagnetically so that on average the moment is reduced. We should point out that the XMCD measurements for Fig. 7.5 (c) are performed with an external field of $B^{\text{ext}} = 6$ T. Together with the spin moment of Mn and the overall decay of the exchange coupling constants we can estimate that only of positions within a critical radius of $R_c \approx 15$ Å have to be considered. This radius is found by looking for $\Delta E(R_c) = m^{\text{spin}} B^{\text{ext}}$ where $B^{\text{ext}} = 6$ T and m^{spin} is taken from the values of our calculation shown in Tab. 7.1. This radius is shown in Fig. 7.7 (d) with a dashed black circle. The exchange coupling to all other positions outside of this circle is too small to counteract the Zeeman energy the individual spin gains by aligning with the external field. We see that in Mn doped Bi_2Te_3 all the positions within the dashed circle are colored in blue which means that the interaction is antiferromagnetic. This explains the large decrease with increasing coverage which will result in shorter Mn-Mn distances on average so that more and more pairs are within the radius of AFM coupling.

This is well in line with the *effective magnetization* measurements that shows overall antiferromagnetic coupling (general trend of decreasing moment) for increasing coverage on Mn atoms on the surface. Additionally, a sign change to ferromagnetic coupling for average Mn-Mn distances of 15-20 Å is observed. Since the effective magnetization effectively excludes short-range clusters and is performed at varying external fields between $B^{\text{ext}} = -5$ T and $B^{\text{ext}} = +5$ T, the measurement can be compared straightaway with the simulated ΔE curves assuming the dilute limit. Especially it is not restricted to the positions within the circle given by R_c at 6T. The observed change to FM coupling that occurs around 15-20 Å in experiment [peak in Fig. 7.7 (e)], is well reproduced by the calculated oscillation around 20 Å shown in Fig. 7.7 (a).

Comparison for Co doped Bi_2Te_3 at different coverages

The *average moments* for Co at different coverages in Fig. 7.5 (d) show a decrease with higher coverages while, according to the ab-initio calculations, the short-range mechanism favors ferromagnetic coupling. The critical radius for Co with a spin moment of $1.2\mu_B$ corresponding to the external field of $B^{\text{ext}} = 6$ T is $R_c \approx 22$ Å. If this is taken into account [cf. black dashed circle in Fig. 7.7 (f)], then we see that the sign change at distances of ~ 20 Å plays a role for the average moments as antiferromagnetically coupled Co atoms can be present. It is however unlikely that this is the only mechanism leading to the observed decrease in the average Co-moment because the reduction is large, reaching a factor 3. The magnitude of the sign change to antiferromagnetic coupling is only small compared to the size of the ferromagnetic coupling at shorter distances that is supposed to be more and more important with increasing coverages. Therefore it is unlikely that the small antiferromagnetic coupling strength can lead to this strong decrease. The effect of doping, that we have neglected so far, should be taken into account. This will be studied in detail in the next

7.3. Microscopic origin of the exchange mechanism in Bi_2Te_3 and comparison to experiment

section.

The *effective magnetization* of Co on the other hand fits very well the distance dependence of the exchange coupling constants in Co doped Bi_2Te_3 . The clear trend to ferromagnetism that increases with increasing coverage is observed with a sign change in the exchange mechanism that manifests itself as a dip in the magnetization curve around a mean impurity-impurity distance of 20 Å. The calculations show the same trends with a sign change in the RKKY interaction to antiferromagnetic coupling around 25 Å. This slightly larger distance could also be due to doping that changes the Fermi level.

An intermediate summary

In summary, we can understand the majority of the features seen in experiment from the calculations we have analyzed so far. The overall behavior in the average moments of Mn and effective magnetization fit well between theory and experiment. However the feature that deviates from the guide to the eye in Fig. 7.5 (c) at a coverage of 0.018, where the decrease in the average spin moment shows a shoulder, cannot be understood from the discussion so far.

Also for Co – at least to some extent – the decrease in the average moment and the effective magnetization fit to the calculated ΔE -curves. Also the surprisingly small influence of ferromagnetic coupling at short Co-Co distances that seems to decrease further with higher coverages is not fully understood at this point. Additionally, the exact location of the sign changes in the for Mn as well as Co occurs at larger distances in the calculation as compared to experiment. The discrepancies that occur between theory and experiment will be discussed in the following where the effect of doping that is introduced by the increasing amount of adatoms on the surface will be analyzed.

7.3.5. Tailoring the exchange interaction: doping dependence

Introducing impurities to the surface of topological insulators results in a shifted Fermi level. The effect can for example be seen by ARPES and STS measurements of Fe doped Bi_2Se_3 [228, 229] or Co doped Bi_2Se_3 [230] where a shift of ~ 50 meV for 1% doping concentration is observed. Similar trends for Mn and Co adatoms were seen with a Fermi level shift of ~ 100 meV in Bi_2Te_3 [40]. Additionally the pristine surfaces of topological insulators already show inhomogeneities in the local position of the Fermi level that are known as *charge puddles*. They can be attributed to specially varying concentrations of different intrinsic defects [38]. The size of the charge puddles typically extends over tens of nanometers. Thus the XMCD measurements may average over several areas with locally varying Fermi levels. This can even be controlled to form topological *p-n* junctions [153] by changing the growth conditions in preparing single crystals of topological insulators. The concentration of different intrinsic defects, such as vacancies or anti-site impurities, can therefore be controlled to vary in space.

The influence of doping that we suspect to increase with increasing impurity concentration will be discussed in the following. The change in the impurity density with varying Fermi levels and the resulting distance-dependent exchange coupling strength is calculated and related to the observations in the XMCD experiment.

Influence of a changing Fermi level for Mn doped Bi_2Te_3

In Figure 7.10 the doping dependence of the Mn-Mn interactions is presented. The Fermi level was varied in a range of -20 meV to $+425\text{ meV}$ with respect to the initial Fermi level position. In (a) the distance dependent exchange coupling strength is shown. With increasing Fermi level the short-range antiferromagnetic coupling in x-direction decreases monotonically from -4.5 meV to -0.5 meV . This can be understood from the change in the density of states that is shown in (b) as follows in the discussion below.

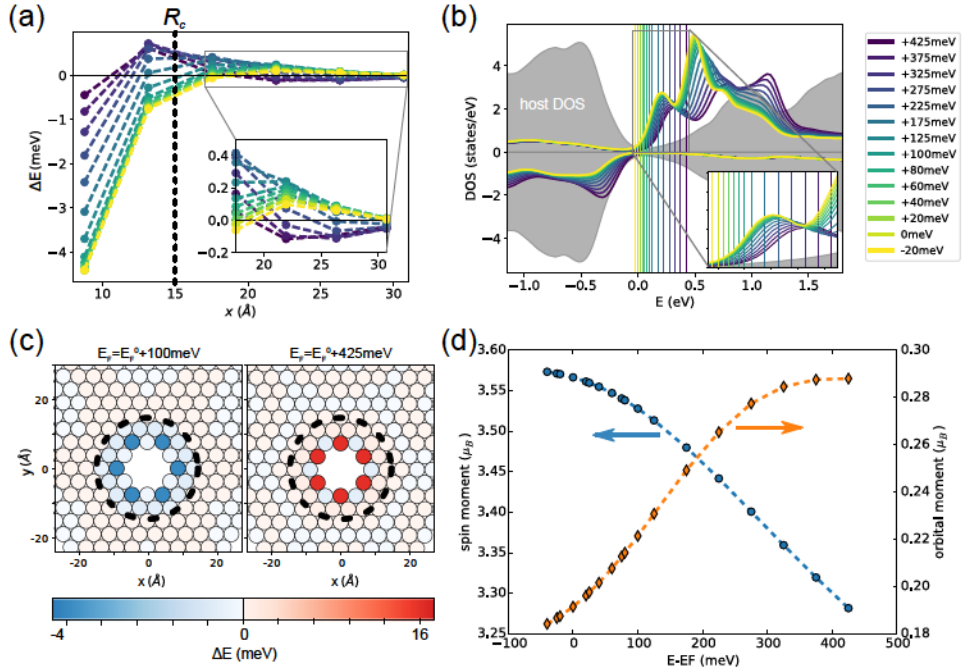


Figure 7.10.: Doping dependence of the Mn-Mn exchange interaction. (a) and (b) show the exchange interaction strength in x-direction and corresponding DOS for a Fermi level shifted in the range -40 meV to $+425\text{ meV}$ with respect to the original Fermi level (cf. Fig. 7.7). The position of the Fermi level is marked with a vertical line in the color corresponding to the Fermi energy shift. (c) shows the anisotropy and directionality of the interaction and (d) the change in spin- and orbital moment with a shift in the Fermi level in blue and orange, respectively. Strongly shifting the Fermi level leads to a strong change in the exchange mechanism because the relative alignment of the peaks in the DOS to the Fermi level can be tuned.

Charge neutrality dictates that the peaks in the Mn density of states have to move up in energy with a shift in the Fermi level. However, the strong hybridization of the impurity states with the surrounding lets the Mn d -states 'pin' to the host states which results in the relative position of the Fermi level to the impurity states to shift up. The Fermi energy

gets tuned through the first peak in the crystal field split minority DOS of the impurity. Thus, with a Fermi level that moves slowly through the DOS the complex competition between super- and double exchange mechanisms is changed in favor of the double exchange mechanism. Consequently the sign change in the exchange coupling constants occurs at smaller impurity-impurity distances. On the one hand this is due to the competition between RKKY and short-range interaction where the RKKY part takes over at shorter distances. On the other hand the wavelength of the oscillating RKKY interaction decreases with the increase in the Fermi wavevector when the Fermi energy increases. This can be seen from the Fermi surfaces which are shown in Figure 7.11 for Fermi levels at +100 meV, +275 meV and +425 meV with respect to the original Fermi level position.

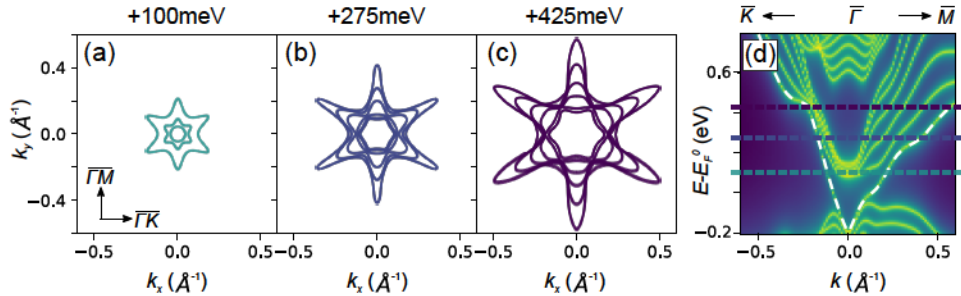


Figure 7.11.: Evolution of the Fermi surface with shifted Fermi energy from +100 meV (a) over +275 meV (b) to +425 meV (c) with respect to the original Fermi level. The topological surface state is the outer-most line while the other lines are projections of the bulk states. The corresponding dispersion in $\bar{\Gamma}\bar{K}$ and $\bar{\Gamma}\bar{M}$ -directions is shown in (d) where the topological surface state is highlighted with a white dashed line.

The full maps of the Mn-Mn interaction at strong doping of +100 meV and +425 meV is shown in Fig. 7.10 (c). It can be seen that at short distances even a change to ferromagnetic coupling can occur due to the changing double- vs. superexchange ratio discussed above. Therefore, with very high doping and small average Mn-Mn distances ferromagnetism could be possible even with Mn impurities.

The spin and orbital moments as they vary with changing Fermi level position are shown in (d). It can be seen that the spin moment decreases slightly by roughly 9% with the increasing occupation of the d -states at higher Fermi level. The orbital moment on the other hand increases by 50% reaching a value of $0.29\mu_B$.

Now that we know what happens with shifting Fermi level that progressively occurs for increasing coverages in the experiment we can understand the so far unclear shoulder that was observed in the decreasing average spin moment curve at 0.018 ML coverage presented in Fig. 7.5 (c). With increasing coverage the Fermi level shifts and for a shift of more than 175 meV the sign change in the exchange interactions lies within the radius R_c that is dictated by the external field applied in the experiment.¹⁸ This value is well in line with the experimentally known Fermi level shift in Mn doped Bi_2Te_3 [40]; if we extrapolate the values

¹⁸Cf. discussion in section 7.3.4 and Figure 7.7

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obtained for 1% doping to 1.8% where we see the anomaly in the XMCD measurements we obtain a Fermi level shift of $\Delta E_F \approx 1.8 \cdot 100 \text{ meV} = 180 \text{ meV}$ which is well in line with the value obtained from the sign change in the exchange coupling constants from first principles.

Also the trend in the measured orbital moment [lower panel in Fig. 7.5 (c)], which shows a very flat curve up to $\sim 3\%$ Mn-doping, can be understood. With increasing coverage the average orbital moment is expected to decrease due to antiferromagnetically coupled Mn atoms that effectively cancel the total orbital moment of this arrangement of atoms. The trends of an orbital moment that increases, as the Fermi level progressively shifts into the Mn *d*-resonance, counteracts this trend – at least partially – which might give an explanation for the experimental observation an an almost constant orbital moment for Mn coverages between 0 and 0.04 ML.

In conclusion, we have seen that the Fermi level shift due to doping can explain the last remaining discrepancies between experiment and theoretical simulations. Control over the position of the Fermi level opens up the way to a new mechanism for microscopic control over the exchange interactions in Mn doped Bi_2Te_3 . This may lead to new possibilities for future experiments.

Influence of a changing Fermi level for Fe doped Bi_2Te_3

The Fermi level dependence of Fe surface-doped Bi_2Te_3 is presented in Figure 7.12. With increasing position of the Fermi level the strength of the short-range exchange coupling first increases from $\sim 2.2 \text{ meV}$ to $\sim 4.5 \text{ meV}$ with a shifted Fermi level position going from 0 to $+125 \text{ meV}$. Afterwards, up to a Fermi level of $+425 \text{ meV}$ the short-range exchange decreases to less than 2 meV at $\sim 8 \text{ \AA}$ Fe-Fe distance. This behavior can be understood from the corresponding density of states shown in (b) where it can be seen that the position of the Fermi level relative to the *d*-resonances is tuned through the maximum, that is reached at a Fermi level position of $+125 \text{ meV}$. This is highlighted in the zoomed inset. Consequently the double exchange mechanism that favors ferromagnetism at short distances is strengthened when the position of the Fermi level approaches the maximum of the *d*-level resonance.

The position of the sign change – that comes from the competition of oscillating RKKY interaction and the short-range interaction discussed above – on the other hand decreases monotonically with a shift in the Fermi level. This is due to the decreasing wavelength of the oscillations that shifts the position of the first sign change to lower distances. Additionally the phase shift is tuned from slightly below $\delta = \pi/2$ to slightly above which also shifts the position of the phase shift closer to the origin.

The resulting ΔE -maps at $+100 \text{ meV}$ and $+425 \text{ meV}$ are shown in (c). Only for a strong shift of the Fermi level does the oscillation in the exchange coupling approach small enough distances so that positions where antiferromagnetic coupling lie in the circle given by the critical radius $R_c \approx 20 \text{ \AA}$ that is determined by the external field of 6 T in the measurement.

The spin- and orbital moment depending on the Fermi level position are shown in (d). In the spirit of Hund's rule, as the Fermi level scans through the resonance, the spin moment decreases monotonically by $\sim 20\%$ and the orbital moment first increases by $\sim 13\%$, has its maximum where the maximum in the DOS peak is hit exactly by the Fermi energy and then decreases by $\sim 25\%$ up to a Fermi level position of $+425 \text{ meV}$.

Overall we can say that the strong ferromagnetic coupling in Fe doped Bi_2Te_3 up to large distances is rather stable which makes Fe a good candidate for achieving ferromagnetism in

7.3. Microscopic origin of the exchange mechanism in Bi_2Te_3 and comparison to experiment

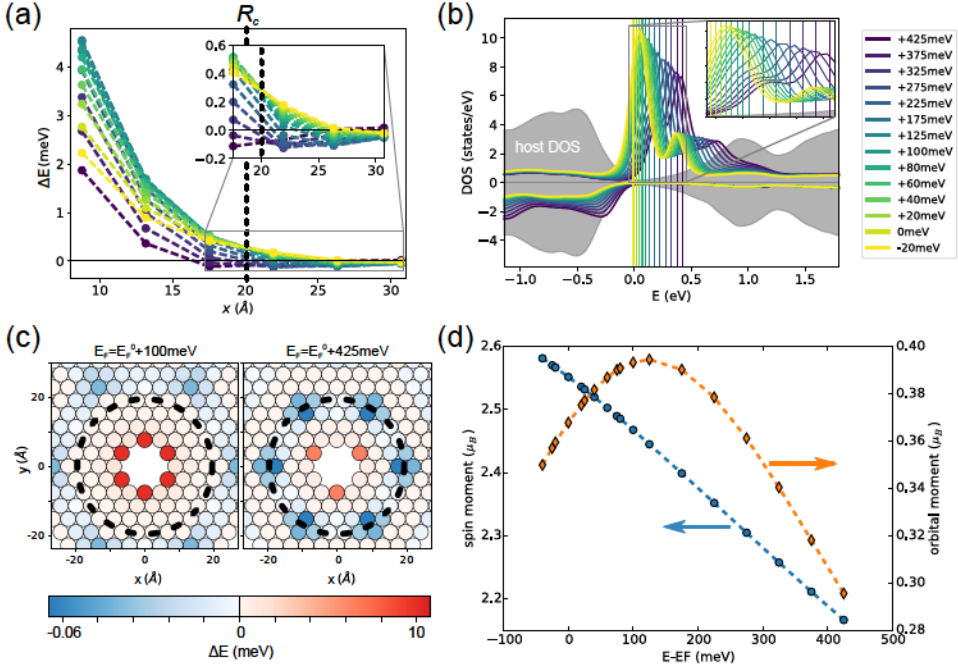


Figure 7.12.: Doping dependence of the Fe-Fe exchange interaction. Panels as described in Fig. 7.10. The strong shift in the Fermi level tunes the peak position into the d -level resonance and further out of resonance. This leads to an initial increase and a succeeding decrease in the exchange coupling strength at short distances due to changes in the double exchange mechanism.

surface-doped three dimensional topological insulators.

Influence of a changing Fermi level for Co doped Bi_2Te_3

The doping, i.e. Fermi level, dependence of the exchange coupling at varying distances for Co surface-doped Bi_2Te_3 is presented in Figure 7.13. In (a) the exchange coupling strength in x -direction is shown for a variation of the Fermi level position between -20 and $+425$ meV. We see that the short-range interaction strength decreases drastically by 80% with increasing Fermi level. This can be related to the relative position of the Fermi energy to the peaks in the d -resonances of the impurity due to the 'pinning-effect' discussed in the analogous case of Mn doped Bi_2Te_3 . While the Fermi level sits at the right shoulder of the first peak in the minority spin channel, the Fermi levels gradually shifts into the second peak that is split off from the first one due to the crystal field. This seems to be counter intuitive as the superexchange mechanism should increase and the double exchange mechanism should be strongest at the peak position. However, we can see from an orbital analysis of the density of states, that is presented in Figure 7.14, that the second peak in the DOS consists of the d_{z^2} -orbital which is oriented in the out-of-plane direction and thus only plays a minor role for the in-plane directed exchange interaction. Consequently, for the exchange interactions studied here only the first peak is important and the contribution from *both* the double exchange *and* the superexchange mechanisms is getting smaller with increasing Fermi level.

In the sign change of the exchange interactions, highlighted in the inset of Fig. 7.13(a), we still see a monotonic decrease in the position of the zero-crossing with increasing Fermi level as in the case of Mn and Fe. However, also the amplitude of the RKKY interaction is reduced due to the orbital character of the d -electrons in the impurity, since the spin polarization of the in-plane oriented orbitals play a major role in the exchange interaction within the plane of fcc hollow site absorption positions of the impurities and since the impurity spin moments drops with increasing E_F [Fig. 7.14 (d)].

In total, the interaction strength of Co impurities in the whole range between short- and long-range limits – that are governed by different exchange mechanisms – shows a decrease in the coupling strength. The resulting ΔE -curve at $E_F = E_F^0 + 425$ meV in x -direction is very flat. This is true for all crystallographic directions as can be seen in Figure 7.13 (c) where for Fermi levels of $+100$ meV and $+425$ meV the full maps of exchange coupling interactions is shown. For moderate doping, resulting in a Fermi level shift of $+100$ meV, the antiferromagnetically coupled (blue) positions lie well within the circle of R_c that depends on the external field applied in the experiment. The ratio of the AFM to FM interaction moves in favor of the AFM interaction with an increasing position of the Fermi energy and gives an additional explanation for the strong decrease seen in the measured average magnetic moments presented in Fig. 7.5 (d).

The dependence of the spin- and orbital moments on the position of the Fermi energy shown in Figure 7.13 (d) strengthen this trend. The spin moment is found to decrease by more than 40% with increasing doping which is another reason for the decreasing average spin moment in experiment. The orbital moment also has a drastic decrease by 75% with varying the position of the Fermi level in a range of -20 meV and $+425$ meV which goes in line with experimental observations of the average orbital moments in Co with increasing coverage.

The calculated trends that occur when increasing doping of Co in surface-doped Bi_2Te_3 help

7.3. Microscopic origin of the exchange mechanism in Bi_2Te_3 and comparison to experiment

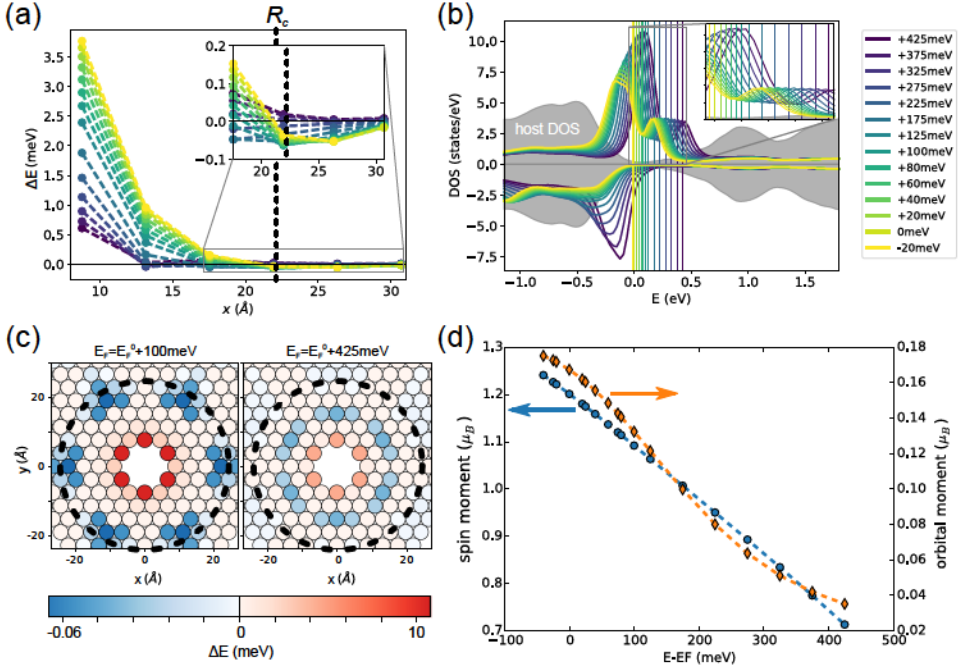


Figure 7.13.: Doping dependence of the Co-Co exchange interaction. Panels as described in Fig. 7.10. With increasing Fermi level shift the peak at higher energies arising from crystal field splitting becomes resonant, i.e. lies at the Fermi level. This leads to a decrease in the overall exchange coupling strength as seen in (a) and (c) because of the orbital character discussed in Fig. 7.14.

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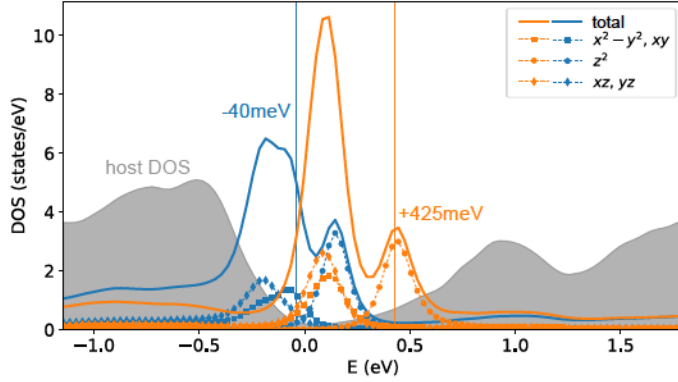


Figure 7.14.: Density of states of the Co impurity with shifted Fermi level by -40 meV and +425 meV with respect to the original Fermi energy. The corresponding Fermi energy is shown with a vertical line in the respective color. Shown is only the minority spin channel and a decomposition into the different orbitals of the d -level is shown. The crystal field splitting resulting from the crystal symmetries gives a degeneracy of $d_{x^2-y^2}$ and d_{xy} orbitals as well as the d_{xz} and d_{yz} orbitals. At higher Fermi energy the position of the Fermi level moves into the peak formed by the d_{z^2} orbital of Co that is split off due to crystal field splitting.

us to understand the trends in the XMCD experiment. We can claim that we do understand the mechanisms that happen when a strong topological insulator is magnetically doped at the surface. This newly gained knowledge allows us to have more control over the magnetic properties in this fascinating class of materials.

7.3.6. The high concentration limit: nearest-neighbor dimer and trimer

So far we have assumed that the impurities interact magnetically but do not change the local electronic structure of each other. This allowed us to do “one-shot” calculations using the magnetic force theorem where the self-consistently calculated impurity potential of the single impurity case was reused. This was motivated with the efficient screening by the surface state electrons that we find for adatoms in the fcc hollow site on Bi_2Te_3 . However, for atoms occupying nearest-neighbor positions this approximation breaks down. Therefore we studied dimers and trimers of atoms that still occupy the fcc-hollow site position but that only have a distance of a single lattice constant. The calculation of the ground state electronic and magnetic structure for these small clusters was done fully self-consistently. In Figure 7.15 (a-c) the total (i.e. sum of minority and majority spin channel) density of states for Mn, Fe and Co is shown with a solid red line for the single impurity case, with a solid and a dashed green line for the two atoms of the dimer and with a solid blue, dashed lighter blue and dotted sky blue line for the three atoms of the trimer. The corresponding alignments of the spins is shown in (d) for the dimers and in (e) for the trimers of Mn, Fe and Co.

The density of states curves in (a-c) show that the basic shape of the resonances is kept

7.3. Microscopic origin of the exchange mechanism in Bi_2Te_3 and comparison to experiment

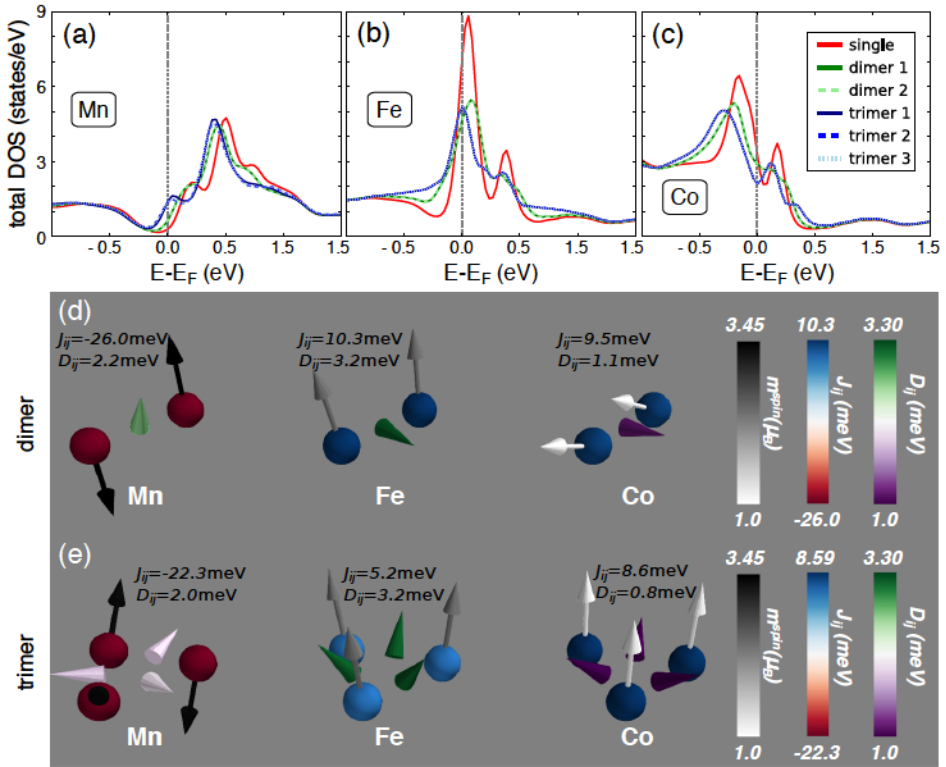


Figure 7.15.: Total density of states (a-c) and exchange interactions in dimers (d) and trimers (e) on nearest-neighbor positions. The positions of the atoms (showing only the transition metal atoms and not the surrounding host atoms) is indicated by balls in (d,e) which are colored according to the strength of the exchange interaction J_{ij} . The arrows show the direction of the relaxed spin moments with the size of the moments given in a white-to-black color scale. The cones give size and direction of the Dzyaloshinskii-Moriya interaction D_{ij} colored in a purple-white-green. The direction of the spins (white grey and black arrows) in the small clusters are a result of J_{ij} , D_{ij} and anisotropy energy. The total density of states (a-c) of the transition metal atoms given for single impurity, dimer and trimer in for Mn, Fe and Co reveal that the self-consistent calculation only introduce small shifts of the position of the peaks as compared to the single impurity case.

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also for dimers and trimers but the curves shift downward in energy and/or are broadened. For Mn (a), the antiferromagnetic alignment of the moments reduces the hybridization between d -orbitals of the same spin at neighboring impurities, thus no significant broadening appears. Sharp features as they appear in the Fe and Co (b,c) DOS are being washed out into broader peaks due to hybridization with the neighboring atoms. These trends will generally lead to a reduction of the exchange interactions with increasing impurity-cluster as it happens for example in transition metal clusters on Cu [239].

In contrast to the pairs of single atoms that were studied for larger distances, we computed the full exchange coupling tensor $\mathcal{J}_{ij}^{\alpha\alpha'}$ for all pairs of atoms within the dimers and trimers. We used the Liechtenstein formula [248, 249] as extended by Ebert and Mankovsky [256] which it is implemented in the *KKRimp* code [61]. The exchange tensor can be extracted with the energy integral [256, 257]

$$\mathcal{J}_{ij}^{\alpha\alpha'} = -\frac{1}{\pi} \text{Im} \int_{-\infty}^{E_F} dE \text{Tr} \left[\underline{\Delta V}_i^{\alpha} \underline{G}_{ij} \underline{\Delta V}_j^{\alpha'} \underline{G}_{ji} \right] \quad (7.10)$$

where $\underline{\Delta V}_i^{\alpha}$ is the change in the potential due to an infinitesimal rotation of the magnetic moment i in direction $\alpha \in x, y, z$ and $\underline{G}_{ij}$ is the Green function that describes the propagation between sites i and j . Note that $\underline{\Delta V}$ and $\underline{G}$ are matrices in orbital and spin degrees of freedom. The reference state for the $\mathcal{J}$ -matrix calculation was chosen to be the collinear configuration and not the canted alignment of the spins shown in Fig. 7.15 (d,e). The canted directions of the spins were however the results of another self-consistency calculation, where the direction of the moments were allowed to relax. The non-collinear alignment of the spins can rather be seen as the result of the different competing interactions.¹⁹

This gives us on the one hand the exchange coupling constant J_{ij} that we discussed previously but also allows us to compute the Dzyaloshinskii-Moriya vector $\mathbf{D}_{ij}$ as well. The corresponding Hamiltonian containing these two interactions plus the single-ion anisotropy reads as

$$\hat{H} = -\frac{1}{2} \sum_{ij} J_{ij} \hat{\mathbf{e}}_i \cdot \hat{\mathbf{e}}_j - \sum_{ij} \mathbf{D}_{ij} \cdot \hat{\mathbf{e}}_i \times \hat{\mathbf{e}}_j - \sum_i K_i (\hat{\mathbf{e}}_{i,z})^2 \quad (7.11)$$

where the direction of the spins is given by $\hat{\mathbf{e}}_i$ and the uniaxial anisotropy K determines if the easy axis is out-of-plane ($K < 0$) or in-plane ($K > 0$) with respect to the surface is favored with the surface normal pointing in the z -direction. This equation makes it clear that the Dzyaloshinskii-Moriya interaction (DMI) favors a tilting of the spin with a certain chirality, depending on the direction of $\mathbf{D}_{ij}$, whereas the exchange coupling favors parallel or antiparallel alignment. The competition of these interactions is the driving force behind interesting phenomena such as spin-spirals or Skyrmions in magnetic systems with spin-orbit coupling [258–262]. We should point out that a strong out-of-plane anisotropy, as found for transition metal doped Bi_2Te_3 , will reduce the tilting of the moments introduced by the Dzyaloshinskii-Moriya interaction as the spins are forced to point perpendicular to the surface. The J_{ij} -constants then determines if two moments will be aligned in parallel or antiparallel configuration.

¹⁹Note however that in the self-consistent calculation even interactions that might not be include in the model description [cf. Eq. (7.11)] that we used in our interpretation. This could include bi-quadratic or 4-spin interaction terms in addition to the here considered single-ion anisotropy, exchange interaction and Dzyaloshinskii-Moriya interaction.

7.3. Microscopic origin of the exchange mechanism in Bi_2Te_3 and comparison to experiment

In the following the exchange interaction in small clusters, namely dimers and trimers, will be analyzed and the relation to the dilute limit studied in the previous sections and to the experimental findings will be investigated.

Exchange and Dzyaloshinskii-Moriya interaction in nearest-neighbor dimers of Mn, Fe and Co in surface-doped Bi_2Te_3

We continue by looking at the dimers presented in Fig. 7.15 (d). We show only the transition metal atoms and exclude the neighboring atoms as the induced magnetization is two orders of magnitude smaller than on the impurity itself and can therefore be neglected. The spin moments, relaxed self-consistently in amplitude and direction, are given by the arrows where the size of the spin moments is represented with the color in a white-to-black color scale. We see that the moments in the Mn-dimer align antiferromagnetically whereas the moments in Fe- and Co-dimers point in the same direction. The Co dimer is oriented in-plane due to the easy-plane anisotropy of the single atoms. The directions of the spins within the dimers are a result of the competing exchange, Dzyaloshinskii-Moriya and uniaxial anisotropy energies. The corresponding values of exchange coupling constants are given in the color (red-to-blue) of the balls showing the position of the atoms. The direction and strength of the $\mathbf{D}_{ij}$ -vector is given by the cones in a violet-to-green color scale. To get a better understanding the numbers for J_{ij} and D_{ij} , averaged over the two positions of the dimer, are given in Table 7.2.

Table 7.2.: Average strength of exchange and Dzyaloshinskii-Moriya interactions in nearest-neighbor dimers and trimers of Mn, Fe and Co.

	Mn-dimer	Mn-trimer	Fe-dimer	Fe-trimer	Co-dimer	Co-trimer
J_{ij} (meV)	-26.00	-22.26	10.31	5.19	9.53	8.59
D_{ij} (meV)	2.23	1.99	3.24	3.22	1.12	0.82

Obviously the tilting in the Fe-dimer is more pronounced as compared to the Mn dimer which is a result of the relatively large D/J -ratio²⁰ giving a value of 0.31 for Fe but only 0.09 for Mn. Li et al. [227] studied Fe on Bi_2Se_3 and also found a large D/J -ratio of 0.3 that led to canted moments as the consequence of the different terms appearing in Eq. (7.11) where also the importance of the large out-of plane anisotropy of 5.8 meV for the final non-collinear spin-structure in the dimer was stressed. In the Co-dimer both moments are tilting slightly in z-direction. This cannot be understood from the in-plane anisotropy of the Co atoms and the small D/J -ratio of 0.12. However this trend fits the observations made for single Co atoms deposited on Bi_2Se_3 [230] where experimentally an in-plane anisotropy at low coverages that changes to an out-of-plane anisotropy at higher coverages was observed. DFT calculations revealed that Co favors an in-plane direction in the fcc hollow site but an out-of-plane direction of the magnetization in the hcp hollow site [230].

Overall we can say that for dimers the trends seen in the short-range interactions of the dilute limit still hold at nearest neighbor positions. The exchange coupling together with the anisotropy play the major role in the alignment of the spins.

²⁰Neglecting uniaxial anisotropies, the D/J -ratio leads to an opening angle θ between the two spins via $\tan \theta = D/J$.

Nearest-neighbor trimers of Mn, Fe and Co in surface-doped Bi_2Te_3

In Figure 7.15 (e) the nearest-neighbor Mn, Fe and Co trimers are shown. As in the case of Mn-dimers, in the Mn-trimers the exchange coupling between the atoms is antiferromagnetic but the strength decreases slightly. This can be attributed to the small shift seen in the DOS and in combination to the mechanism of the exchange, which was investigated in the dilute limit by shifting the Fermi level. For three atoms the antiferromagnetic coupling cannot be compensated and *frustration* happens. This results in a strong tilting out of the z-direction of two moments that compensate the third moment which points almost entirely in $-z$ -direction. This explains why – in contrast to Fe and Co trimers that align ferromagnetically and are symmetric – the density of states of the three atoms shown in blue (a) is not completely degenerate. The non-collinear alignment of the spins in the Mn-trimer is almost entirely due to frustration and not because of the Dzyaloshinskii-Moriya interaction as the D/J -ratio is only 0.09 – as in the case of the Mn-dimer.

The size of the cluster (three as compared to two atoms discussed above) also plays an important role in the exchange interaction strength in the Fe-trimer. It decreases from 10.3 meV in the dimer to 5.2 meV in the trimer (cf. Tab. 7.2). The interaction is still ferromagnetic but undergoes a strong decrease that can be explained with the overall broadening of the density of states peaks that lead to a significantly smaller density of states at the Fermi level. This directly influences the exchange mechanism and finally reduces the coupling strength. The Dzyaloshinskii-Moriya interaction on the other hand is almost constant which finally leads to an even larger D/J -ratio of 0.62. This explains the large tilting angle seen in Fig. 7.15 (e, middle).

In the case of Co-trimers we see that the trend towards out-of-plane orientation that was seen in the dimer continues and finally leads to an out-of-plane alignment of the three spins. The strength of the ferromagnetic exchange interaction only decreases slightly which is in line with the small change that can be seen in the density of states when going from the dimer to the trimer. The three moments align almost perfectly in parallel since the D/J -ratio even drops below 0.1.

On the influence of nearest-neighbor clusters - comparison to experiment

Finally we want to comment on the implications the results for dimers and trimers have on the interpretation of the data obtained from the XMCD measurements and on the comparison we have done so far. The results for nearest-neighbor clusters suggest that the basic mechanisms that determine the competition between super- and double exchange will not change significantly. Actually clusters of growing size will be less important since the interactions between atoms that are very close by a strong hybridization of the wavefunctions comes hand-in-hand which causes a reduction of the interaction strength. However, the nearest neighbor interactions are still stronger in clusters as for more distant neighbors. In picking only the intensity of the main feature of the XMCD signal to get the effective magnetization the clusters are indeed effectively excluded since the XMCD spectra will change due to the changes in the DOS. Therefore in the effective magnetization measurements in fact the dilute limit – which was the focus of our study – can be tested.

The changes in the distance dependent exchange coupling strength that occur due to a shift of the Fermi level already capture the physics behind a change in the coupling strength

and the complicated interplay between different mechanisms. The approximation in treating the exchange coupling alone and neglecting contributions from the Dzyaloshinskii-Moriya interaction is justified. The reason for this is that only for Fe the DMI can have a significant impact, which was not studied experimentally. In such cases where the D/J -ratio gets as large as 0.3 or higher a long-range influence of the DMI has been found. This is for example the case in Fe on Pt111 where the ratio between D and J does not systematically favor one over the other at larger distances but a complex non-collinear structure arises [263]. In the Liechtenstein formula [Eq. (7.10)] it can be seen that the exchange as well as Dzyaloshinskii-Moriya interaction decay via the decaying propagation between the impurities that enters through the Green functions.²¹ It is therefore clear that the DMI will show a similar decay with the distance as the exchange. In contrast to the Fe/Pt111 case [263], the out-of-plane anisotropy is much stronger for this system. This explains why – at least in the dilute limit – the DMI can be neglected since the magnetocrystalline anisotropy will not depend on the distance but only on the position of the atoms locally. The contribution for the anisotropy will not decay with distance but the DMI does. Hence, a tilting of the magnetic moments will be less and less favored over a collinear orientation and only the exchange interaction alone will play a role.

7.4. Conclusions and outlook

In this chapter we have studied the exchange mechanisms for surface-doped Bi_2Te_3 . Different transition metal impurities – namely Mn, Fe and Co – have been considered and a careful comparison to measurements by the Trieste group was carried out. In combination of XMCD measurements and density functional calculations we successfully understood the mechanisms that govern the exchange interactions in this interesting class of materials.

We found that the nature of the exchange interaction can be decomposed into a short-range and a long-range part. The short-range interactions are determined by a complex competition between contributions of different origin; (i) the superexchange mechanism that favors antiferromagnetism coming from level repulsion between occupied and unoccupied states and (ii) the double exchange mechanism that favors ferromagnetism due to hybridization induced broadening of impurity resonances. For Mn, Fe and Co impurities on Bi_2Te_3 these mechanisms were distinguished and the resulting short-range exchange interaction could be explained.

Additionally, we found that the electrons of the topological surface state in Bi_2Te_3 play a crucial role for the exchange mechanism in the dilute limit. The surface state electrons can mediate the long-range RKKY interaction. The importance of the impurity's scattering properties and the competition between short- and long-range mechanisms was discussed. The scattering phase shift, that depends crucially on the impurity, is a central ingredient that – to our knowledge – has not been studied so far in the discussion of possible long-range RKKY interactions on topological insulators. Taking the impurity phase shifts into account even modifies the case where the Fermi energy approaches the Dirac point. In contrast to what was stated earlier [182] the RKKY interaction does not always have to be ferromagnetic

²¹In the stationary phase approximation [154] the Green functions $G(R, 0)$ decay in 2D with $1/\sqrt{R}$ for large distances R from the impurity (which leads to the known $1/R$ behavior via $G(R, 0)TG(0, R)$) as can for example be seen in Eq. (7.8).

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because of $J^{RKKY}(k_F \rightarrow 0) \propto \lim_{k_F \rightarrow 0} \frac{\cos(2k_F R + \delta)}{R^2} \propto \cos \delta$. Thus for $\delta = \frac{\pi}{2}$ antiferromagnetic order would be expected at all distances.

The influence of surface state electrons can be very crucial in achieving ferromagnetic order in magnetically doped topological insulators. Here we show that for surface doped samples already in concentrations of less than 0.5%, with the long-range magnetic interactions mediated by the surface state electrons, signatures of ferromagnetism can be observed in XMCD experiments.

Furthermore, we studied the Fermi level dependence on the exchange mechanisms in surface-doped Bi_2Te_3 . We showed that the position of the Fermi energy can systematically change long- and short-range interactions which opens up new possibilities to tailor the exchange interactions in magnetically doped topological insulators. Especially in the case of Fe doped Bi_2Te_3 a way to possible long-range ferromagnetic order opens up which could give better control over the magnetic properties that are essential to realize the quantum anomalous Hall effect.

Moreover, the strong doping limit was studied by considering small clusters – dimers and trimers – of transition metal atoms and the changes in the exchange interactions as well as the Dzyaloshinskii-Moriya interaction at very short distances was investigated. Due to the large ratio of DMI to exchange, Fe is a candidate to realize possible non-collinear states such as Skyrmions on the surface of topological insulators, in the high concentration limit.

The strong spatial anisotropy of the exchange interactions that comes along with the focusing effect in Bi_2Te_3 might open a way to engineer novel magnetic storage devices. For a further study, experiments that can measure the spatial anisotropy (for example using the atomic resolution of scanning tunneling microscopy) would be of interest. Recently this technique was used to study exchange interactions [179, 264] and even Dzyaloshinskii-Moriya interactions on the atomic scale [263] which could open up new perspectives on the field of magnetism in combination with topological matter.

Universal response to impurities in the type-II Weyl semimetal phase diagram

In this chapter the study of topologically protected electrons, that was presented in the previous chapters of this thesis for the surface state in topological insulators, is broadened from gapped to metallic systems. In particular we study the new class of type-II Weyl semimetals, where the results of a collaborative experimental and theoretical work, which was recently submitted for publication [265], are reviewed.

In our work, we identify that, in inversion symmetry broken transition metal dichalcogenites (TMDCs), a topological phase transition can be observed in going from WTe_2 , which is found to be topologically trivial, to $MoTe_2$, that is found to be in a stable, topologically nontrivial Weyl phase. Our detailed analysis reveals, that – across the topological phase transition – universal signatures, in particular without a clear on-off behavior in physical observables, is found. This includes the existence of spin-polarized, arc-like features in the surface electronic structure – which might be misinterpreted as topological Fermi arcs – and impurity resonances, that appear close to the position where Weyl points emerge. These resonances were found to be due to intrinsic anti-site defects. Their existence may strongly affect the interesting transport properties in this family of materials, in particular since the intrinsic defects can be expected to occur frequently in TMDCs. Our work is therefore of immense importance for the future research in this new field of topological matter.

The analysis of scattering features, measured by quasiparticle interference, reveals that the topological Fermi arcs in $MoTe_2$ are characterized by strongly suppressed inter-arc scattering. This can be traced back to the opposite spin-texture in arcs on opposite sides of the Brillouin zone.

In this chapter we will first introduce the topic of type-II Weyl semimetals in the $Mo_xW_{1-x}Te_2$ family of TMDCs and then present our detailed characterization of WTe_2 and $MoTe_2$. Our density functional based calculations are compared to ARPES

measurements showing the Fermi surface in these materials. Then scattering signatures in terms of quasiparticle interference measurements by STM and our simulations are compared. Finally, the existence of impurity resonances and their importance for transport properties is discussed in the last part of this chapter.

8.1. Introduction

So far, the work presented in this thesis dealt with topological *insulators* and in particular with their surface state's properties. Here, the discussion is extended to topological *metals* by studying the scattering properties in the (possibly) topologically nontrivial type-II Weyl semimetal candidates WTe_2 and MoTe_2 . After the discovery of topological insulators [266, 267], concentrated research interest was driven by the exciting new physics that comes along with the topological properties in the electronic band structures of solids. Recently, our understanding of topologically non-trivial band structures was enlarged from gapped systems of topological insulators (TIs) to the ungapped family of Weyl semimetals (WSMs) [268, 269].¹ In contrast to TIs, not only the surface but also the bulk hosts topologically nontrivial quasiparticles. These are related to the so called Weyl points, which are band touchings in the three dimensional bulk band structure, that generally occur at generic² k -points in the Brillouin zone and are protected by topology, i.e they cannot vanish by small perturbations. One of the most striking features of Weyl semimetals is, that the well known bulk-boundary correspondence dictates the existence of topologically protected surface states. These non-trivial surface states form unusual, open but finite contours of the constant energy contour, connecting the projections of the bulk Weyl points on the surface [274, 275]. A number of interesting transport phenomena are associated to Weyl semimetals, which include the very high mobility, extremely large magnetoresistance [276], and even more exotic phenomena such as the chiral anomaly [277] or the possibility to tunnel between opposite surfaces through the bulk by going across the Weyl points [278]. The robustness, that is expected from the topologically protected nature of the Weyl points, is a strong driving force behind the currently skyrocketing research interest in this field.

The first observation of Weyl semimetals was reported in the TaAs monopnictide family, known as type-I Weyl semimetals [268, 269, 279–282]. Later on the so called type-II class of Weyl semimetals was discovered, where Lorentz-invariance is broken. This leads to strongly tilted Weyl cones at the boundary of bulk electron and hole pockets [283]. Recently the $\text{Mo}_x\text{W}_{1-x}\text{Te}_2$ family was found to be a promising candidate to realize this new class of topological metal [283–286]. These materials even allow to continuously tune their topological properties by changing the chemical composition [286]. The phase diagram of $\text{Mo}_x\text{W}_{1-x}\text{Te}_2$ is therefore a perfect playground for studying the electronic properties and fundamental properties in the fascinating class of type-II Weyl materials.

¹Weyl semimetals are however not the sole example of topologically nontrivial metals and Dirac (e.g. in Na_3Bi [270, 271]) as well as nodal line semimetals (e.g. in Cu_3PdN [272, 273]) have attracted considerable research interest in the recent past. However, in this thesis we restrict the discussion to the classes of topological insulators and Weyl semimetals.

²Generally not high symmetry points in the Brillouin zone protected by crystal symmetries.

Our combined experimental (STM measurements by the Würzburg group, ARPES measurements by the Lausanne group [A. P. Weber, J. H. Dil et al.]) and theoretical study goes beyond the mere identification of possible Weyl materials but aims at a detailed characterization of their functional³ response, which is certainly a prerequisite for possible future applications based on the topological nature of Weyl semimetals. We explore the extreme cases of the $\text{Mo}_x\text{W}_{1-x}\text{Te}_2$ phase diagram, i.e. WTe_2 and MoTe_2 , and demonstrate the existence of a universal response to perturbations. In particular, we show that impurity-induced scattering properties can be found in the topologically non-trivial MoTe_2 but also for WTe_2 , which we find to be topologically trivial. Fermi arc scattering is analyzed in detail and we find additionally impurity induced resonances, that appear close to the energy where Weyl points are expected to emerge. This can lift the Weyl points locally, which has certainly severe implications for the transport properties in topological metals.

In the following, first the $\text{Mo}_x\text{W}_{1-x}\text{Te}_2$ family of materials is introduced, their topological properties are analyzed and a comparison of our calculated DFT-band structures with angle-resolved photo-emission⁴ experiments (ARPES) is presented. Then, scattering signatures that were computed for intrinsic defects, which can be experimentally accessed via QPI measurements using the STM on the pristine material, will be discussed. Finally, the possibility of impurity resonances, which might even lift the Weyl node, is demonstrated. The reader, who might not be familiar with Weyl semimetals, can find a short introduction to the topic in the side note below. We would like to stress that all experimental STM measurements and the ARPES measurements of Fermi surfaces, shown and discussed in this chapter in comparison to our first-principles calculations, are coming from the Würzburg (STM) and Lausanne (ARPES) groups, respectively.

Weyl semimetals

After the intense study of electronic structure topology in gapped systems (i.e. in topological insulators), recently also topology in *ungapped* systems became a focus of modern condensed matter research, which eventually led to the discovery of Weyl semimetals (WSM) in condensed matter systems.^a In this side note the basics of Weyl physics in solid state research^b are reviewed based on the discussion by Murakami in [105].

In Weyl semimetals, topologically protected crossings in the bulk band structure occur at generic points in the Brillouin zone. These so-called *Weyl points* (WPs) always occur in pairs. One condition for their appearance is that either inversion symmetry or time-reversal symmetry has to be broken.^c The Weyl points are protected by the topology of the band structure and cannot be annihilated by small perturbations, which would only result in shifting the Weyl points in k -space. The WPs are characterized by the topological charge of chirality of Berry curvature, or “Chern number”. They form

³We understand the term functional in a mathematical sense and study the response of the system to some external stimulus, in this case naturally occurring defects.

⁴In ARPES electrons from the occupied states in a sample are excited by irradiating with Laser pulses or synchrotron irradiation. Typically hemispherical analyzers are used which gives a good energy and k resolution and the full (occupied) quasiparticle band structure in solids can be reconstructed. A much deeper going introduction can be found for example in [287].

either sources or drains of Berry curvature, depending on the Chern number [105]. A pair of WPs can only vanish, if pairs of opposite chirality meet.

In analogy to the topologically protected surface state in topological insulators, the bulk-boundary correspondence leads to topologically protected surface states on the surface of Weyl semimetals as well. In contrast to the closed loops of typical Fermi surfaces, the topologically protected surface states are open contours, so called *Fermi arcs*, that connect the projections of the bulk Weyl points of opposite chirality on the surface. As k on a Fermi arc approaches the projections of the WP on the surface, the corresponding surface state becomes delocalized and turns into a bulk state as a singular bulk band structure point (the Weyl point), which results in the open contour shape seen on the surface. The existence of Fermi arcs is topologically protected and they can only vanish if the corresponding pair of Weyl points is annihilated by bringing them together in k -space.

Among the first materials, where – in inversion symmetry broken systems – Weyl points and Fermi arcs were found, was the TaAs-class of materials, where – at the Weyl point energy – the constant-energy surface becomes point like. These materials are known as type-I Weyl semimetals. Additionally, in Lorentz-invariance broken systems,^d so called type-II Weyl semimetals are possible [283]. In type-II WSMs the Weyl points occur at the contact between electron and hole pockets. The corresponding Fermi arcs therefore always coexist with (trivial) electron and/or hole pockets on the constant-energy contours. The materials studied in this chapter, MoTe₂ and WTe₂, are candidates for this new class of Weyl-II topological materials.

^aActually not only Weyl semimetals exist but other topological metals such as Dirac- or nodal line (semi-) metals were found. The interested reader can find an introduction to these in Ref. [105] and in the references therein.

^bIn high-energy physics the Weyl Hamiltonian was long known. However, a physical realization of this fundamental particle in terms of quasiparticles in solids is far easier to achieve.

^cIf both symmetries are present the Weyl points can collapse to a single point forming a Dirac semimetal.

^dThe type-II Weyl physics has not been met in high energy physics because there Lorentz-invariance is necessarily preserved. In the quasiparticle band structures of solids, the corresponding restriction is however not there.

8.2. Mo_xW_{1-x}Te₂: a type-II Weyl semimetal?

The transition metal dichalcogenites (TMDCs) of the Mo_xW_{1-x}Te₂ family are characterized by a layered structure, where the transition metal (TM) atoms (Mo or W) are separated by bilayers of Te, thus forming stacks of Te-TM-Te trilayers (TLs). The TLs are bound to each other via van der Waals forces and this weak bond forms a natural cleaving plane, which is why experimentally always a Te-terminated surface is found. At temperatures below ≈ 250 K MoTe₂ undergoes a phase transition from the high-temperature inversion symmetric, monoclinic 1T' structure to the low-temperature inversion symmetry breaking, octahedral T_d structure (space group $Pmn2_1$) [288–291]. The low-temperature crystal structure of MoTe₂ is shown in Figure 8.1a, which is the same crystal structure WTe₂ can be crystallized in [292].

These inversion symmetry breaking materials can therefore, at least in principle, host the unconventional Weyl physics. As shown in Fig. 8.1a, the TMDC trilayers are buckled so that the Te-atoms in a surface layer occupy two inequivalent positions, which we denote as Te1 and Te2. This structure is also seen in the atom-resolved STM image in **b**, where the pristine surface of WTe_2 is shown and the columns of Te1 and Te2 positions are visible.

Recent density functional theory calculations indicated that, by increasing the Mo concentration in $\text{Mo}_x\text{W}_{1-x}\text{Te}_2$ when starting from WTe_2 , the system enters a progressively more stable Weyl phase with an increasingly large separation between the Weyl points [286]. This is schematically illustrated in Fig. 8.1c, where the transition from – in this case topologically trivial⁵ – WTe_2 over $\text{Mo}_x\text{W}_{1-x}\text{Te}_2$ with 8 Weyl points (WPs) in the Brillouin zone to MoTe_2 having 4 WPs is shown. We would like to point out, that we find MoTe_2 to host 4 WPs, in agreement with Ref. [285]. However, some other calculations on MoTe_2 [293–295] find MoTe_2 to have crossed to a phase hosting 8 WPs. The additional pairs of Weyl points are however very close in reciprocal space and could be annihilated by small lattice distortions, e.g. induced experimentally via strain or temperature [294]. For the following discussion, this will, however, not play an important role as even in the 8 WP phase of MoTe_2 by far the largest part of the observed arc is of topological nontrivial nature and the trivial part will only have a vanishingly small spectral weight.

The topological phase throughout the $\text{Mo}_x\text{W}_{1-x}\text{Te}_2$ phase diagram, which is indicated in Fig. 8.1c, is discussed in the following. With increasing Mo concentration the electron and hole bands (indicated by green and orange colors in Fig. 8.1) come closer (i.e. the orange band moves up and the green band moves down) and finally touch forming pairs of Weyl points (black and white points labeled WP_1 and WP_2), which, due to the crystal symmetry in this materials, happens simultaneously in four regions of the Brillouin zone. This leads to a total number of 8 WPs in the full Brillouin zone. With increasing Mo concentration the orange and green bands move further into each other so that WP_2 moves down in energy and comes closer in $\mathbf{k}$ to its “mirror-symmetry cousin” from the left. The WPs of this pair have opposite chirality due to mirror symmetry [105] in the lattice and can therefore annihilate if they touch. The situation is shown on the right part of Fig. 8.1c, where – after annihilation of WP_2 – only WP_1 is left, representing the case of 4 WPs in the full Brillouin zone.

The increasingly larger separation between pairs of Weyl points,⁶ in going from the left to right in Fig. 8.1c with increasing Mo concentration, makes the Weyl phase successively more stable, since small perturbations in the crystal would only lead to small changes in the band structure and the WPs would only move slightly in reciprocal space [286]. The larger WP separation would also have severe consequences for the topologically nontrivial Fermi arcs on the surface, as indicated in **d**. We have to mention, that the type-II nature of this material, with coexisting electron and hole pockets at some energy, substantially complicates the structure of surface states and bulk pockets seen on the surface of these materials, which is schematically shown in Fig. 8.1d. Generally, surface states can exist, which formally do not form open arcs, i.e. they are not unclosed contours as Fermi arcs are. However, parts of the (closed) contours may overlap with projected bulk bands forming surface resonances (dashed lines in Fig. 8.1d), which have a reduced surface weight, as compared to true surface

⁵Here we indicate WTe_2 to be topologically trivial having no Weyl points. This is in contrast to earlier studies (e.g. Ref. [283]) and will be addressed in the next section in detail.

⁶ WP_1 in the discussion above.

8. Universal response to impurities in the type-II Weyl semimetal phase diagram

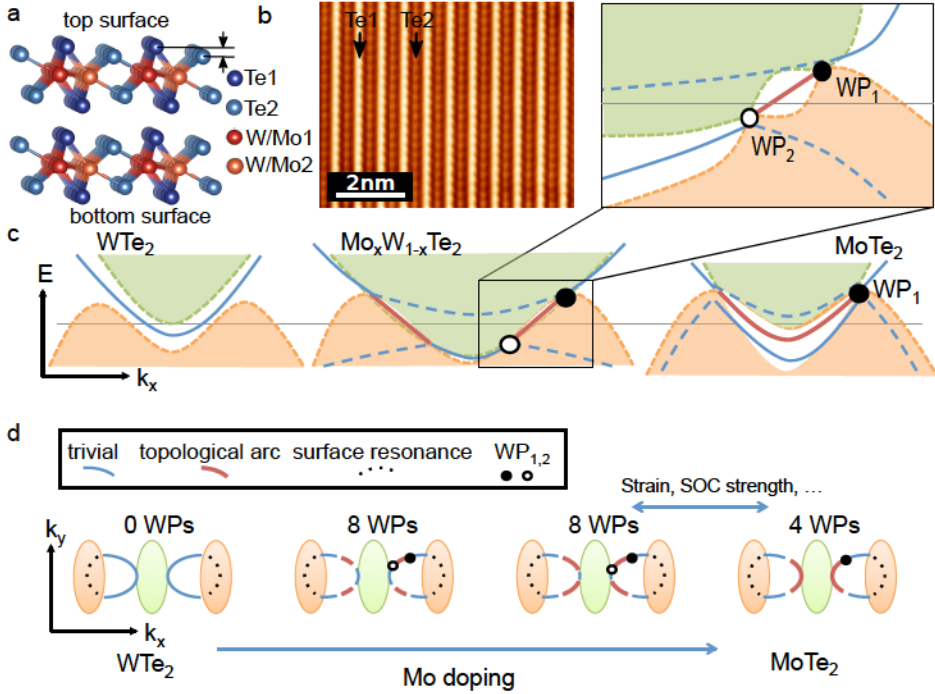


Figure 8.1.: **a** Crystal structure of MoTe_2 and WTe_2 ; **b** Atomically resolved STM topography of the WTe_2 surface. The existence of two inequivalent Te sites labelled Te1 and Te2 with Te1 being slightly higher than Te2 gives rise to the column-like character visible in the STM image. **c** Schematic representation of the type-II Weyl phase diagram. Although being topologically trivial, WTe_2 is found to lie very close to the topological phase transition. Consequently, small lattice distortions can easily drive WTe_2 into a Weyl phase. By starting from WTe_2 and substituting W with Mo, the system enters into a progressively more stable Weyl phase. **d** Evolution of the topological Fermi arcs as a function of the Mo concentration. By increasing the Mo concentration, topological Fermi arcs (red lines) become progressively larger. Image including caption taken from Ref. [265]. STM experiment (panel b) performed by the Würzburg group.

states, which extend in the projected band gap. As we will discuss in detail in the following, this situation is found in WTe_2 , where – without having WPs – (trivial) surface states exist which effectively appear to be open. Therefore, experimentally answering the question of the topological nature of the compounds in this phase diagram proves to be problematic. The discrimination between topologically nontrivial and trivial surface states is very challenging due to the fact that – in contrast to type-I Weyl semimetals – the projections of the WPs lie within the projections of several bulk-derived states [294–301]. Also, the Weyl points in $\text{Mo}_x\text{W}_{1-x}\text{Te}_2$ are expected to appear at energies above the Fermi level [283–286], which makes them inaccessible to conventional photo-emission techniques [294–301]. While a general consensus was reached over the topological nature of the MoTe_2 arcs [294–296], the situation in WTe_2 is highly controversial [297–300]. MoTe_2 is found in a stable Weyl phase,⁷ but WTe_2 on the other hand appears to be very close to a phase transition where WPs can appear [297]. This would however mean that the WPs – if they exist at all – are in close proximity and could easily be annihilated by small lattice distortions, for example introduced by strain or temperature [297]. It is therefore of special importance to understand the two extreme cases of the $\text{Mo}_x\text{W}_{1-x}\text{Te}_2$ phase diagram and study the two materials MoTe_2 and WTe_2 in order to gain important insights into the behavior of the topologically nontrivial type-II Weyl semimetals across the topological phase transition.

In the remainder of this chapter, we present a study visualizing the compositional independence of the response to perturbations and discuss the result in terms of Weyl nodes and Fermi arcs. In contrast to earlier studies [295], we can clearly resolve the open-contour nature of the surface states, discuss their topological nature and demonstrate that topological Fermi arc contributions are strongly suppressed by their spin texture, which protects them from backscattering [295, 302]. In line with theoretical predictions [303, 304], we find in our ab-initio calculations and the Würzburg STS measurements new quasiparticles, stemming from defect resonances, that arise close to the Weyl point energy and lift the density of states minimum associated to Weyl nodes. The insights gained into the topological nature of surface states and resonances in WTe_2 and MoTe_2 , together with the existence of impurity resonances and the scattering signatures of Fermi arcs, is an important extension of the properties of topologically protected electrons, that were so far mainly discussed with the surface states of topological insulators.

8.2.1. Computational details

In this section, we review the computational details of our ab-initio calculations and in particular stress the differences in our calculations, showing no Weyl phase in WTe_2 , as compared to earlier studies (e.g. Ref.[283]), where WTe_2 was predicted to be in a Weyl phase.

⁷Note that the possible phase transition between 4 and 8 WPs will not play an important role, since in the case of 8 WPs only the “tips” of the surface state arcs will be cut off as indicated in Fig. 8.1d. The topologically trivial part of the arc will also not play an important role since it is very short and thus its spectral weight can be assumed to be much smaller than that of the topologically nontrivial part of the arc.

Bulk and thin film calculations

Our first principles calculations are performed using the full-potential relativistic Korringa-Kohn-Rostoker Green function method (KKR) [60, 62, 63, 144], where the experimental low-temperature lattice constants for MoTe_2 [288] and WTe_2 [305] have been used. The local spin density approximation (LSDA) for the exchange correlation functional [53] was used and the truncation error due to the finite angular momentum cutoff in the expansion of the wavefunctions of $\ell_{\text{max}} = 3$ was corrected by using Lloyd's formula [144]. The full-potential treatment includes corrections for the exact shape of the atomic cells [56, 57] and the convergence of the calculation was checked with respect to k -point grid and energy contour. The band structures along high symmetry lines (not shown explicitly) and Fermi surfaces are in good agreement with previously published data on MoTe_2 (e.g. found in Ref. [285]) and WTe_2 (e.g. Ref. [283]).

Even though the DFT calculations of the dispersion along high symmetry lines is in good agreement, in contrast to the calculations in Ref. [283] we do not find Weyl points in WTe_2 . We see, globally in the Brillouin zone, a direct energy gap varying in energy but of at least ~ 15 meV, although an indirect gap does not exist.⁸ It is known that the exact location of the transition to the type-II Weyl phase can be tuned with the lattice constant, spin-orbit coupling strength, or doping between MoTe_2 and WTe_2 in $\text{Mo}_x\text{W}_{1-x}\text{Te}_2$ [286, 294]. It is therefore easy to foresee that all the details of the approximations, that enter the different calculations, can play an important role in the accurate description of the location of the phase transition. In most of the literature [283–286, 294, 295, 297, 301, 302, 306], the calculations of the topological nature of materials are based on Wannier functions, with tight-binding parameters extracted from on first principles calculations using the *pseudopotential* package VASP. In our calculations on the other hand we used the *all-electron* KKR method and computed the band structure in the full Brillouin zone without a detour via Wannier functions and interpolation. Calculations by Irene Aguilera [307] with the all-electron full-potential augmented plane wave (FLAPW) method as implemented in the FLEUR code [308], and using the generalized gradient approximation GGA [309] for the exchange correlation functional, confirm the absence of Weyl points in WTe_2 . We can therefore conclude that the choice of exchange-correlation functional (LSDA vs. GGA) only plays a minor role and does not significantly change the outcome of the calculations. The differences (WPs found or not in WTe_2) are therefore suspected to be due to the details in the Wannier interpolation or due to small differences in the all-electron vs. pseudopotential description.

In Figure 8.2 the bulk Fermi surface of MoTe_2 is shown, where the color code indicates the spin-polarization (s_x in **a,b**, s_y in **c,d** and s_z in **e,f**) of the states on the Fermi surface. We would like to point out that no touching points of electron and hole pockets (large central shape and smaller outer wedges, respectively) can be seen in the Fermi surface, because the Weyl points do not lie at the Fermi level. With increasing energy – i.e. coming closer to the Weyl point energy – electron and hole sheets come closer together and finally touch, forming 4 Weyl points, as discussed later on in Fig. 8.4b. Because inversion symmetry is broken in the T_d crystal structure, already in the bulk band structure the two-fold conjugation degeneracy is broken and each Fermi surface sheet is singly degenerate. The right column of Fig. 8.2 (panels **b,d,f**) highlights this fact by showing a cut of the Fermi surface along $k_y = 0$, where also the inner parts of the Fermi surface can be seen. This shows that each Fermi surface

⁸cf. Fig. 8.4a, which will be discussed in the next section.

sheet is split in two and each pocket also contains a second, inner pocket with opposite spin direction (highlighted by the black arrows in **d**). The strong SOC leads to a reduction of the spin polarization to magnitude of the order of 80% (in units of $\hbar/2$) which is further significantly reduced along lines of crystal-symmetry-enforced band crossings (e.g. along $k_x = 0$). The Fermi surface of WTe_2 shows very similar behavior where the main difference is the size of the inner pocket (not shown explicitly). We can therefore deduce that *any* surface state – being of topologically nontrivial or trivial origin – will be spin-polarized and that the mere observation of spin polarized surface states, that due to overlap with bulk states only seem to be open, does not automatically mean that the observed state is a Fermi arc, as for example recently concluded for the arc-like feature seen in WTe_2 [306].

The thin film calculations, with which the surfaces of WTe_2 and MoTe_2 were simulated, were performed for a thickness of 8 triple layers (TL). The buckling of the structure led to a total size of the unit cell that consists of 74 atoms including empty cells, computed fully self-consistently including spin orbit coupling.⁹ The large thickness was chosen to ensure that the top and bottom surfaces decouple,¹⁰ which was checked by comparing the band structures with increasing thicknesses between 1TL ($\sim 4\text{\AA}$ thin film) and 8TL ($\sim 53\text{\AA}$ thick film) thicknesses. The orientation of the film, which was used in the calculation, is shown in Tab. 8.1 to define uniquely the inequivalent – due to lacking inversion symmetry – “top” and “bottom” surfaces.

Table 8.1.: Positions of the first layer in MoTe_2 in units of the in-plane lattice constant ($3.477\text{\AA}$) [288]. In between two TMTe_2 layers lies a layer with empty spheres (ES) that is needed for convergence in the angular momentum expansion. The “top” surface layer is the first line. In total, the unit cell consists of 16 layers (including empty spheres to account for the larger separation in the van der Waals gap), that contain two triple layers (columns 2-4 and 6-8, respectively), where the buckling leads to the need of two positions per Te and TM layer, respectively. The buckled positions can be seen in Fig. 8.1a. The calculated WTe_2 film was oriented in the same way with only slight changes in the lattice constant and positions [305].

	x	y	z		x	y	z
Te	0.50	-1.29	1.63	Te	0.50	0.54	1.61
Te	0.00	-0.39	1.45	Te	0.00	-0.37	1.43
TM	0.00	-1.10	1.06	TM	0.0	-1.08	1.04
TM	0.50	-1.77	1.00	TM	0.50	0.07	0.98
Te	0.50	-0.66	0.61	Te	0.50	1.16	0.60
Te	0.00	-1.57	0.44	Te	0.00	-1.54	0.42
ES	0.50	-1.06	0.05	ES	0.50	0.75	0.02
ES	0.50	-0.15	0.02	ES	0.50	1.65	0.00

The top and bottom surface localization of the electronic states in the thin film calculations of MoTe_2 and WTe_2 in the T_d -structure are shown in Fig.8.3, where the slightly different

⁹This results in a problem size of considerable computational demand. Only the parallelization efforts, described in chapter 3, made a timely computation of this system feasible.

¹⁰Except for possible Fermi arcs, that necessarily connect through the bulk near their end-points (at the Weyl points), no matter how thick the film becomes.

8. Universal response to impurities in the type-II Weyl semimetal phase diagram

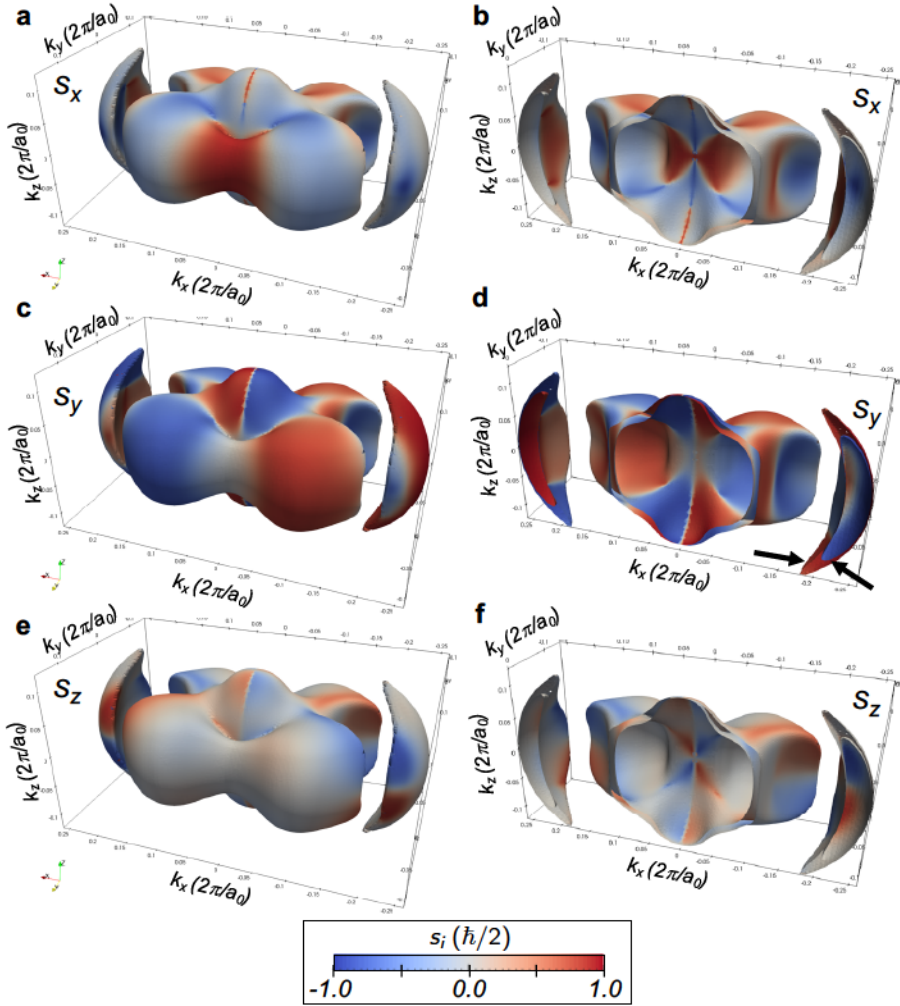


Figure 8.2.: Bulk spin polarization of MoTe₂ at $E = E_F$. **a,c,e** Fermi surface of MoTe₂ where the color code gives the value of s_x -, s_y - and s_z -component of the spin, respectively, from top to down. **b,d,f** Fermi surface with components of the bulk spin-polarization but cut along $k_y = 0$ to reveal the inner lying Fermi surface sheets. The arrows in **d** highlight the opposite spin-direction (red, blue colors) of the inner and outer Fermi surface sheet.

shape of the surface states on the two surfaces can be seen. The localization of the states is indicated by blue (localized on top surface) and red (bottom surface) color. The measure of localization, that was used here, is defined as $X = \frac{A-B}{A+B}$, where A (B) are the integrated densities within the first (last) MoTe_2 and WTe_2 trilayers (TLs) in the film. The detailed comparison of ARPES measurements of the Fermi surface, done by the Lausanne group, QPI images from the Würzburg group and the here reported ab-initio calculations of the surface electronic structure, let us come to the conclusion that in MoTe_2 the top surface (blue states in Fig. 8.3) were probed experimentally whereas in WTe_2 the 'bottom' surface (red states) have been studied.

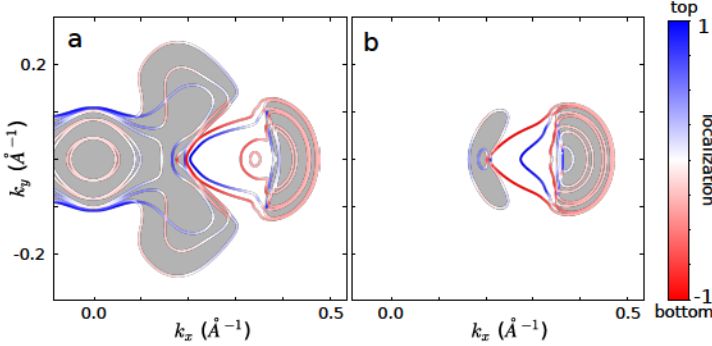


Figure 8.3.: **a,b** Localization of the states on the Fermi surface in MoTe_2 and WTe_2 thin films. The color code indicates the localization on top (blue) and bottom (red) surfaces that are inequivalent due to the lack of inversion symmetry. The projections of bulk bands are highlighted with a gray background. Image including caption modified from the supplemental material of Ref. [265].

Based on the converged potentials of the thin films of WTe_2 and MoTe_2 , the two-dimensional Fermi surfaces (e.g. seen in the localization plots of Fig. 8.3) were computed with very high accuracy [60, 63]. The high accuracy, with a dense k -mesh of $\sim 10^6$ points in the surface Brillouin zone, is necessary for the accurate exJDOS images, which are used to simulate the experimental Fourier-transformed quasiparticle interference (FT-QPI) images, that will be discussed in main part of this chapter.

Calculations of impurity properties and scattering rates

The calculation of scattering rates and Fourier-transformed quasiparticle interference images was done for single substitutional impurities representing intrinsic defects. The computation was done self-consistently using the embedding technique via the Dyson equation for the impurity Green function [61]. In our calculations we neglected structural relaxations around the impurities and assumed non-magnetic defects. The calculations included impurity clusters consisting of the neighboring atoms up to, and including, the third shell of neighbors for a correct screening of the change in the charge density around the impurity. A number of substitutional intrinsic defects in the outermost TL of MoTe_2 and WTe_2 films have been considered. The surface buckling in the T_d structure leads to two distinct positions in each layer ($\text{Te}1/2$ and $\text{TM}1/2$), which – due to the lack of inversion symmetry – also differ on top

8. Universal response to impurities in the type-II Weyl semimetal phase diagram

and bottom surfaces. The defects that were considered are vacancies in the outermost Te layer ($V_{\text{Te}1/2}$), the substitution of a Te atom by an intrinsic transition metal atom ($W_{\text{Te}1/2}$ in WTe_2 and $\text{Mo}_{\text{Te}1/2}$ in MoTe_2) and the reversed situation of a Te atom in the outermost TM layer ($\text{Te}_{\text{TM}1/2}$). Both top and bottom surfaces were considered, which is indicated by a subscript “t” or “b” in the following. A detailed analysis of the local density of states on the different impurities and the comparison to experimental STS spectra on observed defects¹¹ shows that only the $\text{TM}_{\text{Te}1/2\text{t}}$ and $\text{TM}_{\text{Te}1\text{b}}$ impurities have a resonance in the local density of states that lies within the energy range, where resonances are measured experimentally.¹² The total energy calculations additionally revealed that the $\text{Te}1\text{t}/\text{Te}1\text{b}$ positions are 1.0 – 1.5eV more stable than the $\text{Te}2\text{t}/\text{Te}2\text{b}$ positions (cf. Tab. 8.2).

Table 8.2.: Total energies of different $\text{TM}_{\text{Te}2}$ substitutional defects with respect to the $\text{TM}_{\text{Te}1}$ defect at top and bottom surfaces, respectively. Values are given in eV.

system\impurity	$\text{TM}_{\text{Te}2\text{t}}$	$\text{TM}_{\text{Te}2\text{b}}$
WTe_2	1.41	1.24
MoTe_2	1.45	1.04

The comparison of LDOS spectra, total energies of the defects, and a comparison of simulated quasiparticle interference (QPI) spectra (using the exJDOS) with experimental observations let us conclude, that on MoTe_2 the $\text{Mo}_{\text{Te}1\text{t}}$ defect and the top surface and on WTe_2 the $W_{\text{Te}1\text{b}}$ defect on the bottom surface have been probed in the experiments. For the remainder of this chapter we will use these impurities. In the following discussion and comparison to experimental observations, we will – for simplicity of the notation – drop the indices “t” and “b”.

The calculations of impurity scattering are based on the computation of the $\mathcal{T}$ -matrix and Fermi's Golden rule [62], as discussed extensively in the previous chapters. For the analysis that we present here, the exJDOS images as well as the scattering rates (inverse of the lifetime) of the states at different energies were used. As introduced previously, the scattering rate of a state k at energy E is defined as $\tau_k^{-1} = \frac{1}{\Omega_{\text{BZ}}} \int dk' v_{k'}^{-1} \tilde{P}_{k',k}$ where $P_{k',k}(E) = \tilde{P}_{k',k} \delta(E_{k'} - E_k)$ is the transition rate from state k to state k' and the integral is performed over a constant-energy contour $E_k = E_{k'} = E$ and the exJDOS [131] is computed via Eq. (4.45) defined in chapter 4.

8.2.2. Ab-initio surface band structures of WTe_2 and MoTe_2 in comparison to ARPES measurements

Our DFT-calculated band structures of bulk WTe_2 and MoTe_2 are shown for $k_z = 0$ in Figure 8.4a,b, where, due to crystal symmetry, the Weyl points are expected to emerge [283]. However, as the band structures in a,b show, in WTe_2 no Weyl points are found in our calculation, whereas in MoTe_2 4 WPs emerge.¹³ Red and green dots indicate the Weyl points in MoTe_2 , where the color refers to the different chirality. We would like to stress again that

¹¹These are shown in the last section of this chapter.

¹²Cf. Fig. 8.8 and corresponding discussion in the text.

¹³Note that only the $k_y > 0$ half of the Brillouin zone is shown which contains one pair of WPs. A second pair of WPs exist by mirror symmetry at the corresponding $k_y \rightarrow -k_y$ locations with interchanged chirality.

the electronic structure of WTe_2 in particular, is very delicate and, as discussed in Ref. [286], already small changes of the lattice constants can drive the system into a non-trivial phase hosting 8 WPs. The differences in the calculation methods showing contradicting results of WTe_2 with 8 Weyl points were already discussed in detail in the previous section.

Although we find WTe_2 to be trivial and MoTe_2 to be topologically nontrivial, the surface electronic structure, shown in c,d, that is based on the thin film calculations, indicate that in both WTe_2 (a,c) and MoTe_2 (b,d) surface states are found, which end in the pockets around $|k_x| = 0.4 \text{ \AA}^{-1}$, so that the hybridization with bulk states leads to surface resonances and effectively a seemingly open arc contour. The overlap with the bulk-derived pockets (cf. gray regions in Fig. 8.3) can then reduce the surface-weight of the surface state contours, effectively mimicking an open arc even for WTe_2 . The ARPES measurements of the Lausanne group (Fig. 8.4e,f) show an overall excellent agreement with our calculations and prove the existence of arc-like features in the Fermi surface of both materials. An open contour is, however, not very clear, in particular for MoTe_2 (f), where closed loops are actually seen. This can be attributed to the considerable bulk sensitivity of the APRES technique, that effectively measures the first few atomic layers, so that distinguishing surface resonances and surface states is very difficult.

The observations of arc-like features could be misinterpreted as a signature of Fermi arcs. However, with the detailed comparison to our calculations, we could show, that the situation is more complicated and that not every feature that looks like an open arc is automatically of topological nature. Indeed, in our ab-initio calculations we observe several electronic features within a small part of the Brillouin zone, that cannot be resolved with the ARPES measurements of the Fermi surface. The analysis of our calculated band structures actually shows that most of the observed arc-like features are of trivial origin and that only for MoTe_2 topologically nontrivial Fermi arcs can exist. The topological arcs are, however, not located directly at the Fermi level but $\sim 60 \text{ meV}$ above.

From this comparison, we can thus conclude that the analysis presented in this section proves the existence of arc-like features in the surface band structure of inversion symmetry broken crystals of the $\text{Mo}_x\text{W}_{1-x}\text{Te}_2$ family. This is however merely a *necessary*, but not a *sufficient* condition for the existence of bulk Weyl points. The disentanglement of surface and bulk contributions and a discussion on their trivial and nontrivial nature will be given in the following section.

8.3. QPI signature of the scattering properties of topologically trivial and nontrivial surface states in WTe_2 and MoTe_2

Now we focus on the comparison of scattering rates and quasiparticle interference signatures between our first principles based calculations and experimentally measured QPI images from the Würzburg group. The quasiparticle interference approach is known to be a powerful tool in accessing the properties of surface states in topological matter [37, 40, 42, 310–312]. In contrast to the previously discussed ARPES approach to the Fermi surface, also the unoccupied electronic structure can be probed experimentally. This makes the energy, where the Weyl points are expected to emerge, accessible [283–286]. After comparing the QPI

8. Universal response to impurities in the type-II Weyl semimetal phase diagram

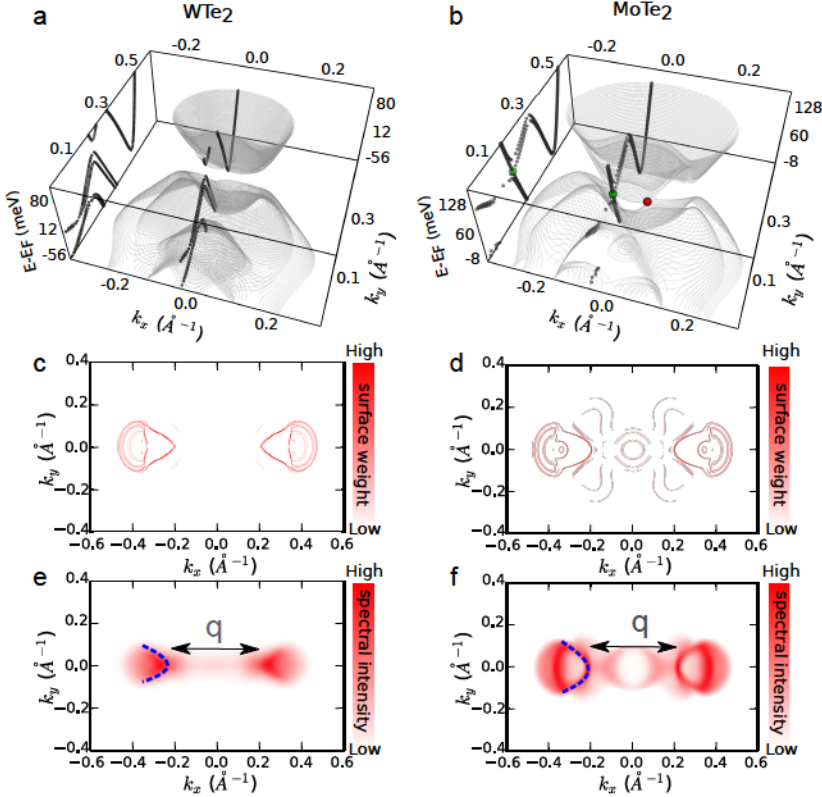


Figure 8.4.: **a,b** Calculated bulk band structure at $k_z = 0$, **c,d** theoretical and **e,f** experimental Fermi surface for WTe₂ and MoTe₂, respectively. For MoTe₂ the calculation for the “top” surface and for WTe₂ for the “bottom” surface are presented in **c,d** (see notation in Tab. 8.1). In **a**, the dotted lines show the band structure along k_y at the particular k_x where the electron and hole pockets approach each other closest. In **b**, the dotted lines show the band structure along k_y at the specific k_x where Weyl points appear (green and red circles, reflection-symmetric around $k_x = 0$). The experimental Fermi surfaces have been obtained by angle-resolved photoemission spectroscopy at a temperature $T < 60$ K using photon energies of 20 and 24 eV for MoTe₂ and WTe₂, respectively. Image including caption taken from Ref. [265]. Experiments in **e,f** performed by the Lausanne group.

images for WTe_2 and MoTe_2 between experiment and theory and relating the results to the observations made in ARPES experiments, we will analyze the energy dependence of the scattering signature in MoTe_2 and comment on the observations with respect to the topological nature of the surface states.

8.3.1. Quasiparticle interference on the surface of type-II Weyl semimetal candidates WTe_2 and MoTe_2

In Figure 8.5a,d, the differential conductance maps, measured by the Würzburg group, close to the Fermi energy ($E - E_F = 10$ meV) are shown, respectively, for WTe_2 and MoTe_2 . The Fourier-transformed images (b,e) allow the analysis of scattering properties off intrinsic defects on the pristine material in reciprocal space. We observe arc-like features for both WTe_2 and MoTe_2 , highlighted by blue dashed lines, which develop around $q_x = 0.4 \text{ \AA}^{-1}$ in q_x -direction and which, contrary to the ARPES results, give a signature for *open* arcs in WTe_2 as well as MoTe_2 .

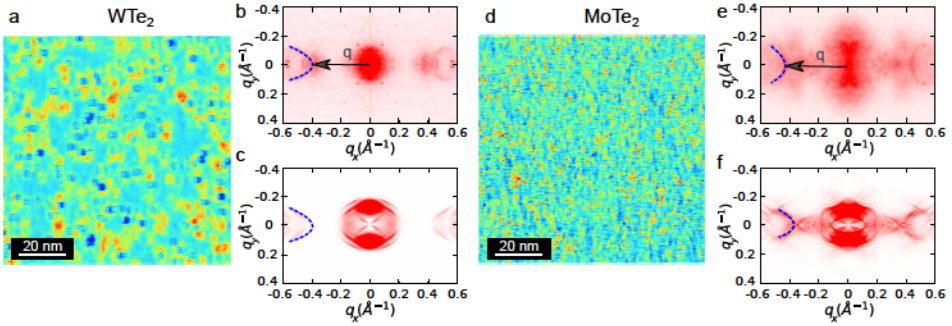


Figure 8.5.: **a** Differential conductance dI/dU map close to the Fermi ($E - E_F = 10$ meV); **b** Fourier-transformed dI/dU map and **c** theoretically calculated quasi-particle interference pattern obtained on WTe_2 ; **d** Differential conductance dI/dU map close to the Fermi ($E - E_F = 10$ meV); **e** Fourier-transformed dI/dU map and **f** theoretically calculated quasi-particle interference pattern obtained on MoTe_2 . The quasi-particle interference pattern is dominated by scattering events between opposite Fermi arcs. Image including caption taken from Ref. [265]. Experiment (**a,b,d,e**) performed by the Würzburg group.

To understand their origin we computed the FT-QPI images using the exJDOS approach [131], where the scattering properties of the impurities, that were identified as described in sec. 8.2.1, enter. The exJDOS results are shown in c,f for WTe_2 and MoTe_2 , respectively. We see that, in agreement with FT-QPI images from experiment (b,e), (open) arc-like features are visible in our exJDOS calculations. The features at small $|q|$ will not be analyzed in detail since, as discussed in a previous chapter, they concern only short range scattering signatures. We are, however, mostly interested in the intra-arc scattering, on which the focus of the following analysis is put. The observation of an arc-like feature is supported by the previously discussed photo-emission data (cf. Fig. 8.1e,f). If we write the initial and final states as k_i and k_f , then the scattering vector is governed by momentum conservation to be

$\mathbf{q} = \mathbf{k}_f - \mathbf{k}_i$. The quantitative agreement between ARPES results (scattering vector $\mathbf{q}$ in **e,f** of Fig. 8.4), and the scattering signatures in FT-QPI images from STM and exJDOS images is remarkable. We can thus relate the open-arc feature in the QPI images to intra-arc scattering between the arc-like features on the Fermi surface on opposite sides of the Brillouin zone. The higher surface sensitivity of the STM technique as compared to ARPES measurements¹⁴ demonstrates the open-contour nature of the surface states and explains, in particular for MoTe₂, the seemingly closed contours, observed in the Fermi surface by ARPES measurements with the higher sensitivity also to surface resonances in ARPES as compared to STM experiments.

We can thus state that indeed arc-like features are clearly observed at the Fermi energy in different experimental (STM and ARPES) measurements and our DFT calculations. This is found in both WTe₂ and MoTe₂, which comes as a surprise if the observed absence of Weyl points in WTe₂ is considered. Thus we have an indication that the nature of the states is trivial. The close proximity of WTe₂ to a topological phase transition, but lying on the trivial side of the phase diagram, lets us additionally exclude any significant contribution of topological nontrivial Fermi arcs in the observation of WTe₂. Even if a slight distortion of the structure results in the appearance of Weyl points and contributions from topological arcs the expected very small separation of the WPs in reciprocal space would give rise to only a vanishingly small contribution to the total signal. In MoTe₂ on the other hand, the topological Fermi arcs are expected to be much larger giving a robust signature. The position of the Weyl points in energy is, however, above the Fermi level and the arc-like feature in the surface states of MoTe₂ is therefore likely to be of the same (trivial) nature as the arc-like feature in WTe₂.

8.3.2. Energy dependence of Fermi arc scattering in MoTe₂

To gain a deeper insight into the scattering properties of trivial and topological (Fermi) arcs and to reveal signatures of their topological protection, we focus in the following investigation on MoTe₂, where the bulk band structure clearly showed the stable existence of Weyl points. The energy dependence of the scattering properties, which can be accessed experimentally via FT-STIS images for different bias voltages, will be analyzed to scan a range of energies which is far below the WP energy, and then progressively comes closer to the position in energy where WPs emerge.

In Figure 8.6a a schematic representation of the energy-dependence of the scattering events among surface arcs is shown, which is derived from our theoretical calculations of the constant energy cuts, that are displayed in **b** for three representative energies ($E_F - 50$ meV, $E_F + 10$ meV and $E_F + 60$ meV). With increasing energy, i.e. in going from top to bottom in Fig. 8.6, the trivial part of the arc-like feature first splits off from the bulk-derived bands¹⁵ and the (trivial, V-shaped) arc-like surface state (which has previously been discussed close to E_F) emerges. The nature of this state can be concluded to be the same as the one seen for WTe₂. We can conclude that it is a topologically trivial state, because it is present for

¹⁴In ARPES the photons have a finite penetration depth into the sample and electrons from the first couple of layers can leave the sample which results in an effective measurements of the first few atomic layers.

The tunneling current that is measured with STM on the other hand probes the tail of the wavefunctions that extends out of the surface.

¹⁵At the highest energy the state is a surface resonance, that lies within the projected bulk bands.

8.3. QPI signature of the scattering properties of Fermi arcs in WTe_2 and MoTe_2

both WTe_2 and MoTe_2 , irrespective of the existence of Weyl points, and additionally it lies well below the position in energy, where the Weyl points are found. This observation is in agreement with recent studies in the literature, where in MoTe_2 [294] and WTe_2 [297], with changing number of Weyl points – including no WPs at all – the same structure of surface states has been seen.

The experimental FT-STs images, shown in c, reveal that at the lowest energy (top panel) only very weak QPI signatures are found. This can be understood as a consequence of the small surface character found for the surface resonances, that lie completely within the projection of bulk-derived bands. When coming closer to the position of the Weyl points (middle panel) the surface states emerges and scattering between the V-shaped, arc-like features occur. This is visible as the clear open arc, that can be seen around $q_x = 0.4 \text{ \AA}^{-1}$ in the middle panel of Fig. 8.6c.

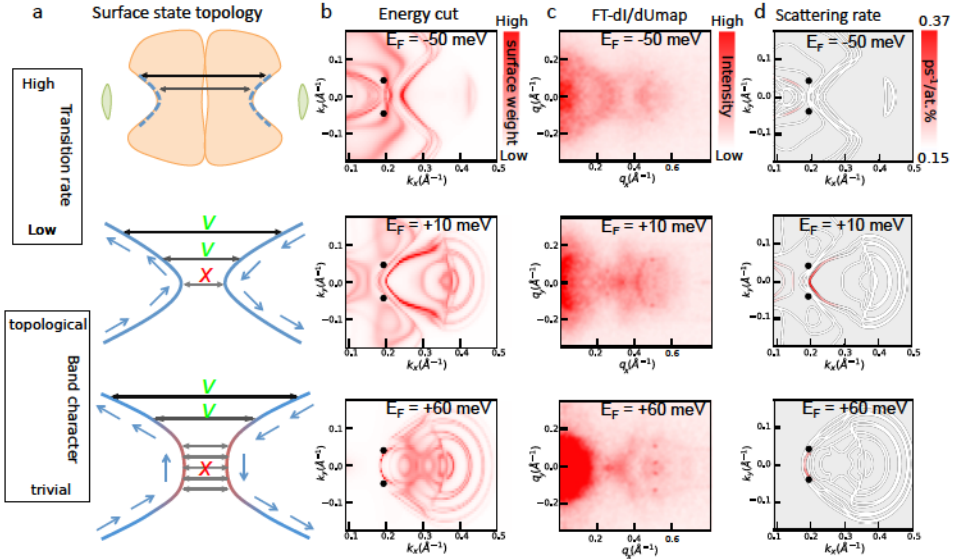


Figure 8.6.: **a** Schematic representation of the scattering events among Fermi arcs in MoTe_2 , **b** theoretically calculated surface-projected constant energy cuts, **c** experimentally obtained Fourier transformed quasi particle interference patterns and **d** theoretically calculated scattering rate. In (b-d) the black dots identify the Weyl points. All results are given for three representative energies; below the Fermi (top panels), close to the Fermi (middle panels), close to the position of the Weyl points, where the extension of the topologically non-trivial arcs is maximized (bottom panels). Image including caption taken from Ref. [265]. Experiment (c) performed by the Würzburg group.

When going further up in energy (lowest row in Fig. 8.6) we see that the arc-like surface state is progressively absorbed into the bulk pocket, that develops around $q_x = 0.4 \text{ \AA}^{-1}$, while the central pocket shrinks,¹⁶ as seen in b. This is accompanied by a flattening of the arc,

¹⁶Cf. Fig. 8.4b

which is indicated in **a**. We would like to stress that the center of the Fermi arc, which is visible close to the energy of the WPs (bottom panel), does not hybridize with projections of the bulk states, even though it lies completely within the projection of bulk bands. Instead it is strongly localized on the surface and – as expected for Fermi arcs – becomes delocalized only very close to the projections of the WPs. This can be seen from the surface weight, shows in the lower panel of **b**. We would like to point out that the topologically nontrivial Fermi arc in MoTe_2 develops out of the tip of the topologically trivial surface state, which was also seen in WTe_2 . When coming closer to the energy of the Weyl points the topologically protected Fermi arc shows up and the topological protection prevents it from being absorbed by the projected bulk pocket.

In Figure 8.7 the surface state localization, together with the spin polarization is shown for $E_F + 60 \text{ meV}$. The topological surface state, located on the top surface (**a**) is highlighted with the black arrow. From the spin polarization it can be seen, that the arc is mainly polarized in y -direction, where by mirror symmetry the arc on the opposite side of the Brillouin zone shows a polarization in opposite direction. The flattening of the arcs, together with the spin-polarization (indicated in **a** with the blue arrows) leads to the considerably weaker QPI signatures, that are measured experimentally (cf. lowest panel in **c**) close to the energy of the Weyl points. The clear arc seen in **c** (middle) disappears almost completely (bottom).

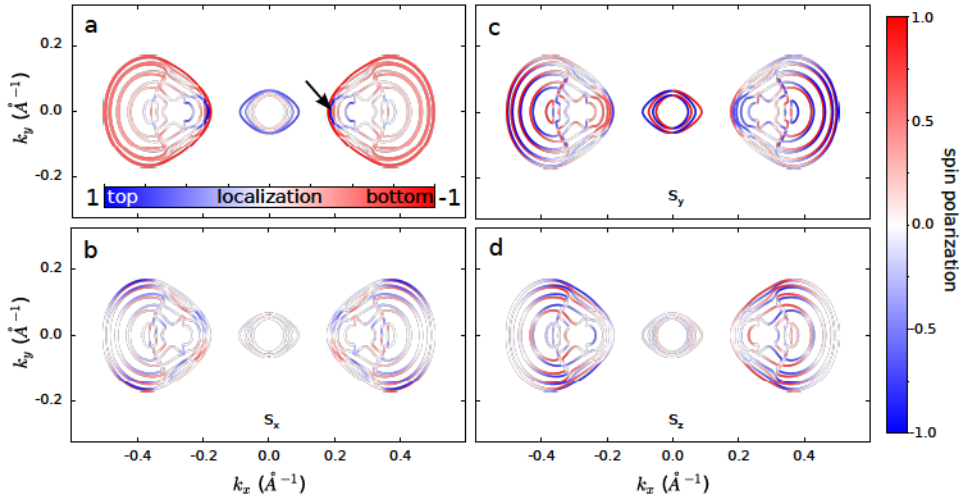


Figure 8.7.: Localization **a** and spin polarization for the surface projected states in MoTe_2 for $E = E_F + 60 \text{ meV}$. Given are x , y and z components of the spin polarization (in units of $\hbar/2$) in **b,c,d**. The topological Fermi arc, localized at the “top” surface is marked by a black arrow in **a**. Image including caption taken from supplemental material of Ref. [265].

This mechanism of protection against backscattering, originally discussed in Rashba materials [36] or recently in topological insulators [42], extends in the present case over large parallel segments of the constant-energy contour, well beyond individual pairs of time-reversal partners. Essentially the full length of the topological Fermi arc fulfills the nesting condition but has opposite spin polarization on opposite sides of the surface Brillouin zone. The

discussion of the scattering rates in the topological surface state, that was presented in the previous chapters, showed that the strong spin-momentum locking led to protection against backscattering, which even holds for near backscattering and in the presence of (not too strong) magnetic defects. The intra-arc scattering of the topological Fermi arcs in MoTe_2 is also close to time-reversal symmetry, which results in forbidden exact backscattering. The opposite spin character of the Fermi arcs on opposite sides therefore leads – in analogy to near backscattering in TIs – to a strong suppression of near backscattering. Consequently, intra-arc scattering among topologically nontrivial Fermi arcs in MoTe_2 is strongly suppressed.

This mechanism of forbidden backscattering is further supported by the calculated scattering rates, that are presented in panel **d** of Fig. 8.6. In going closer to the energy of the Weyl point (from top to bottom), first the scattering rate increases due to the better localization at the surface and the increasingly larger extend of the arc-like surface states. With the closer proximity to the Weyl point (bottom panel) the scattering rate decreases again, which is a result of the discussed spin-texture protection mechanism. This observation means, that long lifetimes and relaxation lengths are expected for these states which means that these states are well suited for coherent transport.

8.4. Impurity resonances in MoTe_2 and WTe_2

Finally, the effect impurities have on the Weyl nodes, that are characterized by a minimum in the density of states, is discussed. Recent theoretical studies showed that Dirac-like materials commonly host impurity induced resonances, which can lift the Dirac-node [304]. In topological insulators this was recently confirmed, where magnetic dopants have been found to effectively fill the gap, that opens up at the Dirac point with magnetic order [216]. In Weyl semimetals scattering off impurities is expected to lift the Weyl node and introduce new quasiparticles close to the energy of the Weyl point [303, 304].

The experimental and ab-initio investigation of this prediction is summarized in Figure 8.8, where, respectively, in **a,b** high resolution images of the topography around defects in WTe_2 and MoTe_2 , measured by the Würzburg group, are shown. Two characteristic intrinsic defects, highlighted by the white arrows, were identified as anti-site defects, that commonly occur in transition metal dichalcogenites [302, 313, 314]. The identification was based on a comparison of the local density of states, computed for different intrinsic defects (anti-sites, vacancies, adatoms), with the LDOS spectra from the STS measurement. In experiment only a single type of impurities is found, so that a comparison with the exJDOS images for different types of impurities will reveal differences in the scattering signatures, that dominate the experimental FT-QPI image. The best match of impurity density of states, local density of states measured in the STS curves on the defect, as well as FT-QPI and exJDOS images for individual impurities, in particular without statistical average of different impurity types, let us conclude that anti-site TM_{Te} defects are observed in experiment.

The STS scans on the impurities, which were performed by the Würzburg group, were acquired on two positions; (i) directly above of the defect (red line) and (ii) far away from the defect (blue line). The existence of a low minimum, seen in the blue curves for the unperturbed material, suggests a semi-metallic character of WTe_2 and MoTe_2 . In contrast, on top of the defects a strong peak is seen, which lifts the minimum seen in the local density of states of the defect-free material. The position of the impurity resonances lies very close

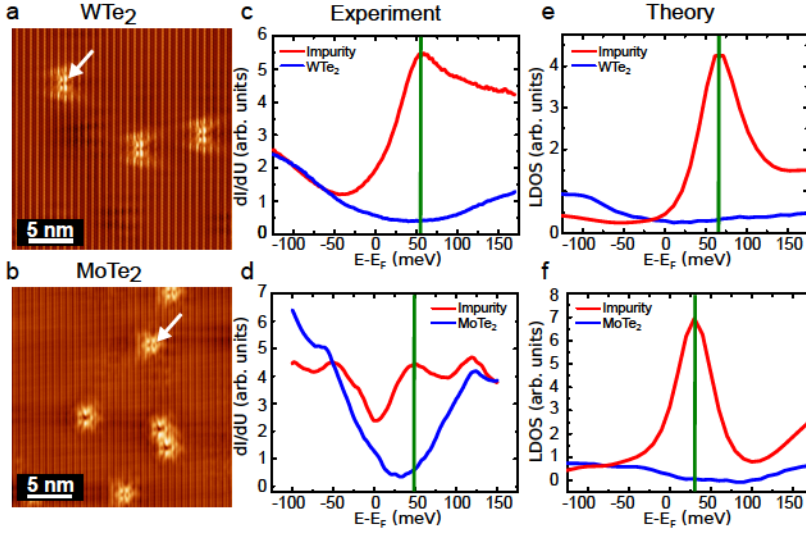


Figure 8.8.: **a,b** Topographic images acquired on WTe₂ and MoTe₂. In both cases, intrinsic defects are present on the surface. **c,d** Comparison of scanning tunneling spectroscopy data taken on a defect-free area (blue line) and by positioning the tip on top of antisites defects (W and Mo substituting Te) revealing the emergence of quasiparticle resonances close the Weyl point energy (see discussion in the text). **e,f** Ab-initio calculated local density of states on the pristine surface (blue line) and on top of an antisite defect (red line) confirm the experimental findings. Green vertical lines are used as marker to identify the position of the peak maximum. Image including caption taken from Ref. [265]. Experiment (**a-d**) performed by the Würzburg group.

to the position in energy where Weyl points are expected to emerge, i.e. at the energy where the Weyl points are found in MoTe_2 or where the minimum in the gap in WTe_2 is seen, which is in agreement with the energy, where other works find Weyl points in WTe_2 [283, 297, 300]. The impurity resonances calculated from first principles for the TM_{Te} impurities are shown in e,f. The calculated position of the impurity resonance peak is in excellent agreement¹⁷ with the experimental observations. We can thus conclude that similar behavior in term of transition metal anti-site defects induced resonances close to the energy of the Weyl points are common in WTe_2 and MoTe_2 . In particular the topological nature of the bulk band structure, i.e. the fact if a topological phase transition was passed or not, does not play an important role in the existence of resonances close to the position where Weyl points emerge.

The relevance of our observations goes well beyond the identification of topological aspects in the band structure. It is well known that disorder, in particular resonant impurities, significantly affect transport properties. In the field of topological semimetals both positive as well as negative magnetoresistance effects were reported with impurities being claimed to be the explanation [315, 316]. Our combined experimental and theoretical observations now serve as an important contribution by providing a detailed microscopic picture of resonant scattering off impurities in type-II Weyl semimetals.

8.5. Conclusions and outlook

The results of this chapter were the collaborative outcome of different experiments (STM, ARPES) and our ab-initio calculations. With the help of our first principles based analysis, we were able to shed light on the topological nature of observed surface states and clarify their response to scattering off naturally occurring defects. We studied the newly discovered type-II Weyl semimetals of the transition metal dichalcogenites in the $\text{Mo}_x\text{W}_{1-x}\text{Te}_2$ family. In particular, by a thorough characterization of WTe_2 and MoTe_2 we were able to show that, while MoTe_2 is in a stable Weyl phase, WTe_2 is close to a topological phase transition and we find it to be topologically trivial. Irrespective if the topological phase transition has taken place or not, we find common characteristics in both topologically trivial (WTe_2) and topologically nontrivial (MoTe_2) phases; (i) we clearly resolve arc-like features at E_F , which are, however, identified to be topologically trivial in nature, and (ii) impurity resonances show up close to the position in energy (~ 50 meV above E_F), where Weyl points are found (in MoTe_2) or expected to emerge (by closing the gap seen in WTe_2 e.g. through tuning the lattice constant).

We demonstrated, that the observation of an seemingly open, arc-like feature in the surface electronic structure is only a *necessary* but not a *sufficient* signature for the existence of Weyl points in the bulk, because topologically trivial surface states and surface resonances may simply look similar to nontrivial Fermi arcs. The broken inversion symmetry, together with the strong spin-orbit coupling in these materials, necessarily result in spin-polarized states. The observation of spin-polarized arc-like features is therefore not enough to deduce the topological nature of a system, i.e. to tell if Weyl points are present in the bulk band structure.

¹⁷Note that in the theoretical calculations we show the LDOS directly on the impurity while the STM experiment measures at some distance from the impurity.

8. Universal response to impurities in the type-II Weyl semimetal phase diagram

Furthermore, we identified scattering signatures of both the topologically trivial surface states (e.g. in WTe_2 and MoTe_2 at E_F) and nontrivial Fermi arcs (in MoTe_2 at $E \approx E_F + 60 \text{ meV}$). We find that the flat shape of the Fermi arc in MoTe_2 , in combination with the inversion symmetry and spin-orbit coupling induced spin-momentum locking leads to a spin-texture protection mechanism, which strongly suppresses inter-arc scattering in between Fermi arcs. This behavior has previously¹⁸ also been observed in the protection against backscattering in the surface state of topological insulators. We can thus conclude that such a signature is a common scattering feature of topologically protected electrons, that are typically characterized by strong spin orbit coupling and therefore spin-momentum locked, topologically protected surface states. Moreover, also states arising in the proximity of the topological phase transition, that will inherit topological properties when the phase transition to a topologically nontrivial phase occurs, were found to show similar behavior.

The study of intrinsic anti-site defects, which naturally occur in these materials, showed the existence of strong impurity resonances close to the Fermi energy. We could demonstrate that these defects are responsible for strong changes in the local density of states close to the Weyl point energy. Even in WTe_2 , where no Weyl points are seen in the calculations, we observe the same signature in the local density of states in the defective systems. Since impurity resonances are important for transport properties in general, we can conclude that the importance of defects for the fascinating transport properties in this new class of materials cannot be overstressed [317, 318]. Recently, the importance of resonant impurity states was also demonstrated in half-Heusler Dirac semimetals [319] which highlights the generic importance of resonant states for the transport properties of topologically nontrivial systems and stresses the importance of our results beyond the specific systems of type-II Weyl semimetals.

Overall we have seen *universal* signatures in both topologically trivial WTe_2 and nontrivial MoTe_2 , no matter if the transition to the Weyl phase was passed or not. In particular we showed that – even though the topological invariant changes discontinuously at the phase transition – a smooth behavior is found in physical observables, such as impurity resonances and the existence of spin-polarized surface states, that only seem to be arc-like at the Fermi energy. Especially no *on-off* behavior can be seen in the studied responses (impurity resonances and seemingly open contours via quasiparticle interference) across the phase diagram of the type-II Weyl material family of $\text{Mo}_x\text{W}_{1-x}\text{Te}_2$. Recently, a similar behavior was found in topological insulators, where – by approaching the critical point (i.e. the point of inversion in bulk band structure) – spin polarized states progressively emerge [320]. We can therefore claim that the fascinating new physics connected to the topological nature of topologically protected electrons show common characteristics in both nontrivial insulators (i.e. TIs) and metals (Weyl semimetals).

¹⁸i.e. in the chapters 4 to 6

Conclusions and outlook

This thesis has dealt with the first principles calculation of the scattering processes of topologically protected electrons off defects on topological insulators and type-II Weyl semimetals. Despite the ongoing high research interest in this relatively new field of condensed matter physics, the microscopic scattering properties of topologically protected electrons off impurities have so far not been studied in detail on the high level of accuracy possible with *ab-initio* calculations. Several parts of this work benefited immensely from fruitful collaborations with experimentalist groups from Würzburg (STM experiments), Trieste (XMCD) and Lausanne (ARPES) and an overall very good agreement between their high precision measurements and the calculations presented in this thesis was found. This mutual agreement speaks for the quality of the first-principles approach followed here and in particular highlights the importance of impurity resonances in topologically nontrivial systems. The work that was presented in this thesis is composed of two parts; (i) technical improvements to the existing computer codes and developments of new functionalities that made the calculations of this thesis possible and (ii) in-depth studies of different aspects related to impurity scattering in the prototypical topological insulator Bi_2Te_3 and the newly discovered type-II Weyl semimetals of the transition metal dichalcogenite family of materials, giving a unifying picture of the response of topologically protected electrons to defects.

Method development

The very interesting surface physics that was studied in this work in topologically nontrivial systems rest on the accurate calculation of, at least from the point of view of a computational scientist, large systems. The parallelization efforts, described in chapter 3, resulted in the new implementation of a hybrid (OpenMP/MPI) three-level parallelization scheme in the Jülich *KKRcode* for density functional theory based calculations of solid state properties. It was demonstrated that the parallel version of the code works very well and in particular exhibits excellent weak and strong scaling characteristics. The benefit of this new development for the time-efficient availability of future scientific results based on the Jülich *KKRcode* is immeasurable.

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In addition, a new functionality related to the computation of scattering signatures, as accessed experimentally via quasiparticle interference measurements, was developed. This was presented in chapter 4, where different approaches to the computation of Fourier transformed quasiparticle interference images, measured with scanning tunneling spectroscopy (FT-STs), were compared and in particular the limits of the “standard way” of modeling FT-STs results with the so-called joint-density-of-states-based approaches were criticized. Only if the newly proposed *extended* joint density of states model, that takes into account a realistic description of the scattering matrix off impurities together with the necessary weighting of large-angle scattering in STs, is used, can the physical nature of the fascinating scattering processes in topological insulators be reproduced accurately enough and understood on the level of the single impurity scattering properties. Additionally, the, within the approximations of density functional theory, very first implementation of the formally exact ab-initio computation of Fourier-transformed quasiparticle interference images was developed, which is a significant improvement over the ad-hoc models of the based on joint density of states approaches. The availability of these new tools offers great potential for future applications to interesting physical problems and allows to uncover captivating scattering signatures observed in experiments.

Scattering-related physical properties of topologically protected electrons

The fundamental scattering properties of topologically protected electrons were introduced in chapter 4. We verified the absence of time-reverse backscattering off non-magnetic single atom defects, which even extends over a wide region of electronic states on the constant energy contour in the vicinity of the exact backscattering point of time-reversal partners. A very strong suppression of the (near) backscattering rate is found within this region that is accompanied by a very strong directionality in forward (small angle) scattering direction of the overall scattering response to single non-magnetic defects. Even more surprising was that for single magnetic defects the backscattering strength was found to be still very low although time-reversal symmetry is broken in the presence of the magnetic defect. This behavior could be understood with the off-resonant nature of the defects by employing Wigners picture of a time-delay in the scattering process. Asymmetric scattering signatures were furthermore seen and associated to a spin-selection rule, stating that for large scattering angles (i.e. in backscattering direction) the direction aligning the final state’s spin with the impurity moment is favored. This was found to be the consequence of the strong warping of the Bi_2Te_3 surface state together with the associated complex spin-texture, promoting this material to a paradigmatic TI with promising properties.

The results presented in chapter 5 demonstrated how the fundamental scattering signatures in the metallic surface state in a strong topological insulator can be tailored via Fermi level tuning and defect engineering. The warping of the Bi_2Te_3 surface state allows to tune the Fermi level into a regime of hexagonally-shaped Fermi surface that supports good nesting. Together with an increased backscattering rate, very long-ranged and real-space focused charge density oscillations were observed in agreement with STM experiments demonstrating the possibility for coherent transfer of spin-information in topological insulator systems over mesoscopic distances, relevant for possible future device applications. The backscattering strength was shown to rely crucially on the magnitude of the spin-moment of the defect (i.e. the magnetic part in the scattering potential) and only for a group of several magnetic

impurities coupled together ferromagnetically, i.e. forming a macro-spin with a much larger moment than the single impurity, was the backscattering strength found to be sufficiently large to explain the experimental observations. This led to the fundamental new insight on the opening of a very directional backscattering channel for scattering off magnetic defects in topological insulators.

Furthermore, the energy-dependence of lifetime and scattering rates of the topological surface state (TSS) were discussed in chapter 6, where intrinsic impurities (in particular surface vacancies) showed resonances that lead to strong signatures in the corresponding scattering rates. Namely, evidence of resonant scattering was found that could be connected to the density of states of the impurity. A strong influence on the lifetime of the surface state that can vary between tens of femtoseconds to picoseconds is the result of these impurity resonances. Moreover, we find that intra-band scattering in the TSS is promoted over scattering into bulk states as long as the phase space of available final states in the bulk is not much larger than that of the surface state. This was associated to the localization of the TSS at the surface and this rule was found to hold as long as the Fermi energy lies in the vicinity of the bulk band gap.

The importance of resonant scattering was additionally seen in the distance-dependent exchange interactions on magnetically doped Bi_2Te_3 , studied in chapter 7. The nature of the exchange interaction could in fact be decomposed into a short-range and a long-range part that, respectively, dominate the behavior at moderate and dilute concentration of the magnetic dopants. These calculations helped understanding the trends seen in XMCD experiments and, the short-range behavior was found to depend crucially on the location of impurity resonances with respect to the Fermi level, which can lead to either ferromagnetic or antiferromagnetic coupling. The TSS electrons were furthermore found to mediate long-ranged RKKY-type interactions, where the phase shift of the corresponding oscillations in the distance-dependent exchange coupling strength could also be traced back to the impurities scattering properties and the position with respect to the Fermi energy of resonances in the impurity density of states. A thorough investigation showed that the nature of the exchange coupling between magnetic impurities can indeed be changed with different impurities and even fine-tuned with a shift in the Fermi level, i.e. engineered for instance by doping. Also, interesting non-collinear magnetic structures were found in the high concentration limit of Fe impurities on Bi_2Te_3 opening the possibility to realize non-collinear states such as Skyrmions on the surface of a topological insulator.

Finally, the discussion of scattering properties of topologically protected electrons was complemented with an ab-initio investigation of impurity resonances and the corresponding scattering properties off surface anti-site defects in materials realizing the type-II Weyl semimetal phase diagram. In particular the low-temperature structures of MoTe_2 and WTe_2 were studied, where MoTe_2 was found to host Weyl points and a corresponding nontrivial Fermi arcs but WTe_2 was found to be topologically trivial. As discussed in detail in chapter 8, and in agreement between experiments (STM and ARPES) and theory (this thesis), universal signatures in terms of impurity resonances and spin-polarized surface states were shown to exist no matter if the topological phase transition in these transition metal dichalcogenites has been passed or not. Complementary to the findings in the strong topological insulators Bi_2Te_3 and Bi_2Se_3 , the type-II Weyl semimetal candidates of the $\text{Mo}_x\text{W}_{1-x}\text{Te}_2$ family also show a spin-texture protection mechanism in the time-reversal scattering properties and moreover impurity resonances, that are due to intrinsic non-magnetic defects. These new insights have

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important implications for the promising transport properties in this new class of materials.

Throughout the studies presented here, the benefit of ab-initio calculations for the correct description of impurities, and in particular for their scattering properties, was pointed out. It is long known that resonant scattering of electrons is of great importance, especially with respect to electronic transport. The work of this thesis demonstrated, based on first principles calculations, the immense importance of impurity resonances on the scattering properties also for topologically protected electrons. The fundamental understanding of the scattering properties that were gained within this thesis has therefore great potential in guiding future experiments. The understanding of different ingredients determining the microscopic scattering signature of topologically protected electrons opens up new ways to tune these properties and could even be used to strongly influence coherence lengths and collective magnetic behavior of magnetic impurities on the surface of topological insulators on the brink of the emerging fields of interfaces between magnetism and topological insulators.

In conclusion, the relevance of resonant impurities cannot be overstated, in particular with respect to transport properties of time-reversal protected electrons.

Outlook

Based on the microscopic understanding of scattering properties in topologically nontrivial systems achieved while working on this thesis, the next step is the simulation of transport properties in surface doped topological insulators. In this work, among other things, we demonstrated the possibility to achieve ferromagnetism from impurities coupled to the topological surface state in Bi_2Te_3 . This system therefore has the prospect for a realization of the quantum anomalous Hall effect, which could be explored in the future. Additionally, after achieving a ferromagnetic state of magnetic defects on the surface, simulations of spin-pumping experiments via the Edelstein effect is a natural extension of this work. The need for currents flowing through the surface states in TI systems also raises the demand for real-space simulations of the potential landscape on TI surfaces around defects, which is experimentally accessible by scanning tunneling potentiometry. The visualization of currents around defects (in the spirit of the Landauer dipole) as well as the spin and charge redistribution of the standing waves due to the presence of external currents should furthermore be part of such an analysis. All of the above mentioned possibilities for future directions need a careful tuning of the resonant properties of intentionally induced, and naturally occurring, impurities in topological insulator systems. The present thesis shows that such a targeted design is indeed a realistic possibility in the near future.

Appendix

A.1. Implementation details of the FT-QPI calculation within KKR

Here some details on the implementation of Eq. (4.55) and Eq. (4.56) are given. Throughout this appendix the short hand notation $\underline{\cdot}$ indicates a matrix in combined angular momentum and spin indices $L = (\ell, m, s)$. Three ingredients are needed which are (i) the construction of the Fourier coefficients of the structure constants entering the multiple scattering part of the Green function $\underline{\underline{G}}^{\text{host}}(\mathbf{k})$ which is computed from the scattering path operator $\underline{\underline{T}}^{\text{host}}(\mathbf{k})$, (ii) the construction of the impurity scattering path operator $\underline{\underline{T}}$ and (iii) the computation of the prefactor containing the radial integration. In the following expressions we drop the lattice vector indices i and j that are treated explicitly in the lattice sum presented in the main text and keep the sub-lattice indices only. The notation used here is the same as in chapter 2.

A.1.1. Construction of $\underline{\underline{G}}^{\text{host}}$

In the routine `kkrmatrix` of the *KKRcode* the scattering path operator $\underline{\underline{T}}^{\text{host}}(\mathbf{k})$, which is the KKR equivalent of the $\mathcal{T}$ -matrix, is used to construct the multiple scattering part of the Green function. The scattering path operator used in the screened-KKR formalism is defined with respect to the difference $\underline{\underline{t}} - \underline{\underline{t}}^{\text{ref}}$ in the single-site $\mathcal{T}$ -matrices of the atomic potential and the auxiliary repulsive reference potential, needed to achieve N -scaling in the number of atomic layers in the structure constants. Therefore, $\underline{\underline{G}}^{\text{host}}(\mathbf{k})$ needs to be computed from the knowledge of $\underline{\underline{T}}^{\text{host}}(\mathbf{k})$, which can be done using the relation

$$\underline{\underline{G}}_{\nu\mu}^{\text{host}}(\mathbf{k}) = -(\underline{\underline{t}}^{\mu} - \underline{\underline{t}}^{\text{ref},\mu})^{-1} \delta_{\nu\mu} + (\underline{\underline{t}}^{\nu} - \underline{\underline{t}}^{\text{ref},\nu})^{-1} \underline{\underline{T}}_{\nu\mu}^{\text{host}}(\mathbf{k}) (\underline{\underline{t}}^{\mu} - \underline{\underline{t}}^{\text{ref},\mu})^{-1} \quad (\text{A.1})$$

where the single-site $\mathcal{T}$ -matrices $\underline{\underline{t}}$ and $\underline{\underline{t}}^{\text{ref}}$ are computed in the routines `tmatrix_newsolver` and `tbref` of the *KKRcode*. The matrix inversion $(\underline{\underline{t}}^{\mu} - \underline{\underline{t}}^{\text{ref},\mu})^{-1}$ is computed efficiently via LU-decomposition using the LAPACK-routines.

A.1.2. Impurity scattering path operator

In the KKR language the scattering off an impurity is captured by the impurity scattering path operator, that can be constructed from $\underline{\underline{\Delta}}_t^{\text{imp}}$ and $\underline{\underline{G}}^{\text{imp}}$, which were defined in chapter 2 and that also enter the calculation of scattering rates. These quantities are matrices in angular momentum indices and atomic position in the real space cluster around the impurity.¹

From the knowledge of $\underline{\underline{\Delta}}_t^{\text{imp}}$ and $\underline{\underline{G}}^{\text{imp}}$ the impurity scattering path operator is given as

$$\tau_{\mu\mu'} = \underline{\underline{\Delta}}_{\mu}^{\text{imp}} \delta_{\mu\mu'} + \underline{\underline{\Delta}}_{\mu}^{\text{imp}} \underline{\underline{G}}_{\mu\mu'}^{\text{imp}} \underline{\underline{\Delta}}_{\mu'}^{\text{imp}}. \quad (\text{A.2})$$

A.1.3. Calculation of the prefactor

Finally some computational details of the integral prefactor

$$\int_{\nu} d^3x e^{-iq \cdot x} \underbrace{[\mathcal{R}_{\nu}^{\nu}(x; E) \bar{\mathcal{R}}_{\nu}^{\nu}(x; E)]}_{\equiv \tilde{\underline{\underline{Q}}}^{\nu}(x)}, \quad (\text{A.3})$$

which is a matrix in angular momentum indices, will be addressed. This integral is evaluated in analogy to the construction of the density in the full-potential KKR-formalism and some important details are briefly reviewed.

We start with the expansion in the angular momentum basis of the term in square brackets containing the site-dependent scattering solutions. This expansion reads

$$\tilde{\underline{\underline{Q}}}^{\nu}(x) = \sum_L \tilde{\underline{\underline{Q}}}_L^{\nu}(x) Y_L(\hat{x}) \quad (\text{A.4})$$

where $\tilde{\underline{\underline{Q}}}_L^{\nu}(x)$ are the expansion coefficients containing the radial dependence and for which we can write

$$\mathcal{R}_L^{\nu}(x; E) \bar{\mathcal{R}}_{L'}^{\nu}(x; E) = \sum_{L'' L'''} \mathcal{R}_{L'' L}^{\nu}(x; E) \bar{\mathcal{R}}_{L'' L'}^{\nu}(x; E) C_{L' L'' L'''} \quad (\text{A.5})$$

Here $\mathcal{R}$ and $\bar{\mathcal{R}}$ are the scattering solutions defined in Eq. (2.9), Eq. (2.12) in chapter 2 and the Gaunt coefficients $C_{L' L'' L'''}$ enter due to the cutoff at the cell boundaries in analogy to the single-site expansion of Green function as for example explained by Drittler [55] and Bauer [61]. The summations over L'' and L''' are truncated with the cutoff ℓ_{max} in the angular momentum expansion of the scattering solutions because the Gaunt coefficients obey the relation

$$C_{L' L'' L'''} = 0 \text{ if } \ell' > |\ell'' + \ell'''| \quad (\text{A.6})$$

which leads to an upper cutoff of $L^{\text{cut}} = (4\ell_{\text{max}} + 1)^2$.

The second step is to use the identity

$$e^{-iq \cdot x} = \sum_L 4\pi i^{\ell} j_{\ell}(qx) Y_L(\hat{q}) Y_L(\hat{x}) \quad (\text{A.7})$$

¹The files DTMRX and GMATLL_GES written out by the *KKRscatter*-tool contain this information.

where the real spherical harmonics Y_L and spherical Bessel function of the first kind j_ℓ are used. We can therefore separate the angular (giving Gaunt coefficients) and radial parts of the integration prefactor which reads

$$\begin{aligned} \int_{\nu} d^3x e^{-i\mathbf{q}\cdot\mathbf{x}} \tilde{\underline{\underline{Q}}}^{\nu}(\mathbf{x}) &= \sum_{LL'L''} \int_{\nu} d\mathbf{x} j_\ell(xq) 4\pi i^\ell Y_L(\hat{\mathbf{q}}) \tilde{\underline{\underline{Q}}}_{L'}^{\nu}(\mathbf{x}) \Theta_{L''}^{\nu}(\mathbf{x}) \\ &\times \underbrace{\int_{\nu} d\Omega Y_L(\hat{\mathbf{x}}) Y_{L'}(\hat{\mathbf{x}}) Y_{L''}(\hat{\mathbf{x}})}_{=C_{LL'L''}} \end{aligned} \quad (\text{A.8})$$

where $x = |\mathbf{x}|$, $q = |\mathbf{q}|$, and the shape function $\Theta_{L''}^{\nu}(\mathbf{x})$ take care of a truncation of the radial integration to the boundaries of the cells. It should be mentioned that the Gaunt coefficients $C_{LL'L''}$ that arise here have a maximal cutoff depending on the ℓ -cutoff used for expansion of exponential $e^{-i\mathbf{q}\cdot\mathbf{x}}$. In practice we found a value of $\ell_{\text{max,exp}} = 18$ suitable for sufficiently high accuracy without too much computational cost.

A.2. Used Software packages

The plots and diagrams of this thesis were produced using the software packages *VESTA* [321], *Paraview* [322], and *matplotlib* [323].

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