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Ab initio Study of Spin-Dependent Transport and Magnetism in Heavy and Superconducting Metals

By

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School of Physics
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A dissertation submitted to the University of Bristol in accordance with the requirements of the degree of DOCTOR OF PHILOSOPHY in the Faculty of Science.

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This thesis is to explore spin-dependent transport current, induced and intrinsic magnetism in bulk uranium as well as in thin films. Uranium, having the largest spin-orbit coupling among naturally existing elements, has potential to achieve high-performance in applications of spin-dependent transport. First, we will calculate the electronic structure for $\gamma$-, hcp- and $\alpha$-U crystal phases using the fully-relativistic Korringa-Kohn-Rostoker (KKR) Green’s function method within the density functional theory (DFT). The intrinsic spin conductivity is described via an integral of the Berry curvature of all occupied states over the Brillouin zone. The extrinsic spin Hall effect (skew scattering) is studied by means of the semi-classical Boltzmann formalism. Comparing the results from these two mechanisms it is found that the hcp-U shows the largest efficiency of charge-to-spin conversion. For practical applications in magnetoresistive random-access memory (MRAM) devices it is crucial to go beyond bulk crystals as the magnetism and spin accumulation at surfaces and interfaces become important.

Considering the spin Hall effect in thin films, there will be spin accumulation at the surfaces and induced magnetism across the thin film. The spin accumulation in light as well as heavy metals is calculated using the semi-classical Boltzmann equation. Comparing the resulting spin accumulation with three different approximations, we identify the contributions to the spin accumulation in the metals with different strengths of spin-orbit coupling. Furthermore, the symmetric and antisymmetric contributions to the spin accumulation will be highlighted for the scenario where impurities break the spatial inversion symmetry of the thin film. The effects of magnetism from impurities on the spin accumulation will be presented.

Using a DFT-KKR solver based on the Bogoliubov-de Gennes equation within the Bardeen–Cooper–Schrieffer (BCS) theory, the superconducting state can be described as well. First, we calculate the electronic structure for the superconducting state of $\gamma$-U and discuss this gap anisotropy of the $f$-electron material. In addition, an in-gap bound state can be induced by magnetic impurities, which is called a Yu-Shiba-Rusinov (YSR) state. We investigate this impurity-induced state by placing a magnetic Mn atom on a Pd thin film and compare our results to experimental observations. The effect of distance between the surface and the Mn impurity on the YSR states will be discussed in detail.
The calculations performed in this thesis were carried out through the Advanced Computing Research Centre at the University of Bristol, with funding provided by the Engineering and Physical Sciences Research Council.

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When asked for advice on doing PhD, I always say 'Have a good supervisor or have a good colleague. Then, stay alive'. Unfortunately, I had both. First of all, I want to thank my supervisor Dr M. Gradhand for providing opportunity and topic for this PhD and for was always making time for my questions or computational issues. I, indeed, gained a great deal of knowledge from his guidance as I conducted scientific research, attended workshops and conferences, and presented findings to people in and out of my field.

Next, I want to thank my colleagues Dr T. Saunderson and O. McHugh who were always optimistic and enthusiastic about sharing fruitful thoughts in discussions and broadening my horizons through their work. Apart from research, they also helped me to become aware with and used to the British culture, which simplified my life.

Thank you to Dr C. Bell and Dr R. Springell for providing experimental perspectives on my work. This helps me to know the distinction between experimental and theoretical work, as well as their connection.

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Last but not least, I want to express my heartfelt gratitude to my parents and brother for always believing in me, showing their love and care, and supporting my every decision.
I declare that the work in this dissertation was carried out in accordance with the requirements of the University's Regulations and Code of Practice for Research Degree Programmes and that it has not been submitted for any other academic award. Except where indicated by specific reference in the text, the work is the candidate's own work. Work done in collaboration with, or with the assistance of, others, is indicated as such. Any views expressed in the dissertation are those of the author.

SIGNED: .................................................... DATE: ..........................................
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In 1879 E. H. Hall discovered the so-called Hall effect [15]. Applying a magnetic field $H_z$ he found that an $x$-direction electric current traveling in a conductor can generate a Hall voltage in $y$-direction perpendicular to the current and the field. The Hall resistivity of this transverse voltage is linearly proportional to the field given by $\rho_{yx} = R_0 H_z$, where $R_0$ is the Hall coefficient determined by the density of carriers (electrons, holes, etc.). Later Hall [16, 17] found the anomalous Hall effect (AHE) that occurs spontaneously in ferromagnetic materials (FMs) without the requirement of applied magnetic fields and its resistivity is established as

$$\rho_{yx} = R_0 H_z + R_s M_z,$$

(1.1)

where $M_z$ is the spontaneous magnetisation and $R_s$ is the specific parameter depending on materials, particularly related to the longitudinal resistivity $\rho_{xx}$. The first term is the original contribution from the external magnetic field driven by the conventional Lorentz force, and the second term is based on the intrinsic property of materials, such as the effect of spin-orbit coupling. The longitudinal charge carriers are asymmetrically deflected into transverse direction perpendicular to the spin direction and applied charge current. In fact, there are two types of current flow in this transverse current, spin and electrical currents. The former one originates from the spin-dependent deflection mechanism where spin-up and spin-down electrons flow in the opposite transverse direction, and it leads to a certain amount of spin-polarised current. The latter is due to the difference between the population of spin-up (majority) and spin-down (minority) electrons. In a magnetic field this leads to a simultaneous flow of transverse charge, the anomalous Hall effect, as well as spin carriers. However, the physical effect of spin dependent scattering induced via spin-orbit coupling happens in nonmagnetic materials as well leading to pure spin currents. M. Dyakonov and V. I. Perel [18, 19] proposed the foundational theory for the spin Hall effect based on the scattering of electrons for localised spin-orbit interaction (Mott...
scattering) in nonmagnetic materials (NMs). This remained unexplored until J. E. Hirsch [20] proposed the conceptual measurement as well as the term "spin Hall effect" in 1999. Figure 1.1 shows the family of Hall effects and the behaviour of the electrons in the different scenarios. The mechanism of the spin Hall effect (SHE) and AHE are the same but the former occurs in nonmagnetic solids, the latter in magnets. Unlike the AHE, containing transverse charge and spin currents, the SHE has only spin currents since the population of spin-up and spin-down electrons are in balance.

Figure 1.1: Illustration of the normal Hall effect, anomalous Hall effect, and spin Hall effect.

In the two current model [21, 22] the electron current \( j^e \) and the spin current \( j^s \) can be obtained by symmetric and antisymmetric combination of the spin-up and spin-down current, expressed as

\[
    j^e = j_\uparrow + j_\downarrow \quad (1.2)
\]

and

\[
    j^s = j_\uparrow - j_\downarrow. \quad (1.3)
\]

In general, the spin-dependent current can be given by the tensor expression under an applied electric field \( \mathbf{E} \),

\[
    \begin{pmatrix}
    j_x \\
    j_y \\
    j_z \\
    \end{pmatrix}
    \begin{pmatrix}
    E_x \\
    E_y \\
    E_z \\
    \end{pmatrix}
    =
    \begin{pmatrix}
    \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\
    \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\
    \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \\
    \end{pmatrix}
    \begin{pmatrix}
    j_\uparrow \\
    j_\downarrow \\
    \end{pmatrix}. \quad (1.4)
\]

The symmetry of the conductivity tensor depends on the lattice structure [23]. Here, for simplicity, we choose the symmetry of a simple cubic crystal for the conductivity tensor and assume the spin
in \( z \)-direction. In that case the spin-dependent conductivity is reduced to
\[
\bar{\sigma}_1 = \begin{pmatrix} a & -d & 0 \\ d & b & 0 \\ 0 & 0 & c \end{pmatrix}, \quad \bar{\sigma}_1 = \begin{pmatrix} a & d & 0 \\ -d & b & 0 \\ 0 & 0 & c \end{pmatrix}.
\] (1.5)

Thus the charge conductivity \( \bar{\sigma}^e \) is given by the form
\[
\bar{\sigma}^e = \bar{\sigma}_1 + \bar{\sigma}_1 = \begin{pmatrix} 2a & 0 & 0 \\ 0 & 2b & 0 \\ 0 & 0 & 2c \end{pmatrix}
\] (1.6)

and the spin Hall conductivity (SHC) \( \bar{\sigma}^s \) current is
\[
\bar{\sigma}^s = \bar{\sigma}_1 - \bar{\sigma}_1 = \begin{pmatrix} 0 & -2d & 0 \\ 2d & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}.
\] (1.7)

These forms show the existence of electron and spin currents where the former one flows along the applied electric field and the latter flows in the transverse direction. In order to quantify the spin Hall effect, the efficiency of charge-to-spin conversion is introduced, which is the so-called spin Hall angle \( \theta_{\text{SH}} \),
\[
\theta_{\text{SH}} = \frac{\vec{j}^s}{\vec{j}^e} = \frac{\sigma_{yx}^s}{\sigma_{xx}^e}.
\] (1.8)

Motivation

In recent years the spin Hall effect has attracted interest due to its potential in spintronic devices such as magnetic random access memory (MRAM), a new storage device [24–27]. For such memory devices, data is stored using the giant magnetoresistance in magnetic tunneling junctions where the structure is composed of ferromagnet/nonmagnet/ferromagnet shown in Fig. 1.2(a). For the parallel and antiparallel magnetisation configuration, the traveling electrons experience different levels of resistance. The channel (or bit) with high resistance is denoted by 0, while the less one is denoted by 1. As shown in Fig. 1.2(b), technological products encode data using binary information of 0-1 array. For writing information into the memory, the bits are able to be switched between 1 and 0, which means that the magnetisation of free magnetic layer [red layer in Fig. 1.2(a)] is able to be switched to be parallel and antiparallel to the fixed layer (blue layer). One way to switch the active magnetic layer is imposing a torque by spin-polarised currents, based on the Landau-Lifshitz-Gilbert equation [28, 29] describing the procession of magnetisation in solid. Therefore, generating spin currents is an important issue. Spin injection is the most established method, however its efficiency to convert charge current to spin current is limited because of scattering process when the spin current travels through the interfaces of multilayer [30, 31]. In contrast, the SHE can create spin currents without the disadvantages of interfaces. This is
a potential way to develop spin-orbit torque (SOT) MRAM. In this device the channel (bit) is constructed of multiple layers as shown in Fig. 1.2(c). When the electron current is applied in the heavy metal with a large spin-orbit coupling (SOC), the spin current is spontaneously generated and flows into the neighboring active magnetic layer. As a result, the magnetisation changes. In addition, in such multilayer systems such as MRAM devices, spin accumulation around interfaces induced by the Rashba-Edelstein effect and SHE can cause additional effects, such as inverse spin galvanic effect [32], on the spin transport and the magnetisation switching process of the active layer. This interfacial effect also has an important influence on the performance of data storage devices [33].

For switching the free-layer magnetisation practically by injecting the spin current generated by the SHE, the experimental study by Yang et al. [34] implies two critical requirements: the spin Hall angle and spin diffusion length. The spin Hall angle should be large to maximise the efficiency of charge-to-spin conversion and save energy. The spin diffusion length specifies the maximum relaxation distance that the induced spin current can survive. It has to be sufficiently large to ensure that the spin current generated by the spin Hall material can reaches the active ferromagnetic layer. These two quantities are closely related to the spin-orbit coupling. The strong spin-orbit coupling is required to induce the large spin Hall effect, while the spin relaxation length becomes small with a significant spin-orbit coupling. Pt with a desirable SOC is the traditional material which has desirable magnitudes in the spin Hall angle (∼0.1) and spin diffusion length (∼10 nm) in balance for the spin Hall devices [35–40]. As technological techniques improve, it is possible to create small devices with a high SOC. For these reasons, the research into spin-dependent transport in materials with a high SOC that are suitable for the aforementioned applications is ongoing.

The majority of research on spin-dependent transport has been mostly focused on d-orbital materials [27, 41–43]. The research of pure f-orbital materials is sparse. Uranium is the heaviest naturally occurring element with a large spin-orbit coupling. Its has various crystalline structures with three bulk phases and one metastable phase in thin films [44–48]. These unique properties widen the avenue to study the electronic structure as well as the spin-dependent transport with not only strong spin-orbit coupling but also f electrons. In this thesis we aim to quantitatively and analytically investigate the spin-dependent transport, spin Hall effect and the spin relaxation process, for uranium and other spin Hall materials such as Pt with varying degrees of spin-orbit coupling using first principles methods. This work will be carried out in both 3-dimensional and reduced dimension systems in order to conduct practical investigation of SHE and its spin accumulation for multilayer systems in real life.
Figure 1.2: (a) Depiction of giant magnetoresistance in ferromagnet/nonmagnet/ferromagnet (F/N/F) structures. The white and orange arrows stand for the direction of magnetisation and charge current density, respectively. The magnetisation of purple and red layer are antiparallel (parallel) in the upper (lower) panel. (b) Depiction of 0-1 binary information in MRAM devices. (c) Depiction of interface spin polarisation induced via the spin Hall effect. Figure(b) is taken from Ref. [1].
1.1 Theory of Spin Hall Effect (SHE)

1.1.1 Spin-orbit coupling

The mechanisms of the SHE and AHE are based on the same concepts of the relativistic spin-orbit coupling generating the spin-dependent asymmetric deflection to the electrons. The following introduction applies equally to the SHE and the AHE.

As discussed in the motivation, the spin-orbit coupling plays an important role for the spin-dependent transport. Therefore, a review of SOC is presented. The relativistic effect of SOC, arising from the Dirac equation, is crucial for the spin dynamics as captured by the electronic band structure. In systems without the SOC the spin $S$ and angular $L$ momentum of electrons are individually good quantum numbers. In the fully relativistic picture the operators $S$ and $L$, however, are no longer good quantum numbers since the interaction between the $L$ and $S$ momentum is critical for the correction of electron kinetic energy. This origin is that the magnetic moment of a traveling electron in an electric field couples with an effective magnetic field. The standard form of the SOC Hamiltonian in a spherical potential is written as

$$H_{\text{SOC}} = \xi(r) \mathbf{L} \cdot \mathbf{S},$$ \hspace{1cm} (1.9)

where $\xi(r)$ is the spin-orbit coupling parameter given by

$$\xi(r) = \frac{1}{2m^2c^2} \frac{dV}{dr} = \frac{1}{2m^2c^2} \frac{1}{r^3} \left( \frac{Ze^2}{4\pi\epsilon_0} \right) \propto Z^4.$$ \hspace{1cm} (1.10)

Here, $Z$ is the atomic number and the expectation value of $\frac{1}{r^3}$ is proportional to $Z^3$ indicating that the SOC energy strongly scales with the atomic number as $Z^4$. Although this expression is based on a spherical model, it suggests the strong SOC in heavy atoms.

In solid systems, the traveling electrons experience two types of potential: periodic and non-periodic potential. The former one, referred as intrinsic SOC, is related to the lattice structure, and the latter, extrinsic SOC, indicates the potential influence of impurities, disorder, interfaces and boundaries. In a clean system, in the absence of disorder, the Hamiltonian of intrinsic SOC can be written as [50–52]

$$H_{\text{intr}}^{\text{SOC}} = -\frac{1}{2} \sigma \cdot \mathbf{B}(\mathbf{k}),$$ \hspace{1cm} (1.11)

where $\sigma$ is the Pauli matrices and $\mathbf{B}(\mathbf{k})$ is the momentum $\mathbf{k}$-dependent effective magnetic field for the electron band depending on the periodic potential of the lattice. On the other hand, the Hamiltonian of extrinsic SOC remains in the original form of Eq. (1.9) with a local potential from impurities or disorder and can be rewritten as

$$H_{\text{extr}}^{\text{SOC}} = \eta_{\text{SOC}} \sigma \cdot [\nabla V(\mathbf{r}) \times \mathbf{k}],$$ \hspace{1cm} (1.12)

where $\eta_{\text{SOC}}$ is the spin-orbit coupling parameter. It differs from the parameter in Eq. (1.9) since the environment here is the solid instead of the vacuum. The atomic number is incorporated in
the potential $V(r)$. The SOC in both the intrinsic and extrinsic contributions are experimentally and theoretically demonstrated critical for the spin-dependent transport [4, 53–57], and it has been shown that the large spin Hall effect is present for heavy metals such as Pt [4, 36] or for systems with heavy impurities such as Cu doped with Bi [58, 59]. Therefore one can suggest heavy metals with large SOC are desirable for the spin-dependent transport.

Illustrating the mechanism of SOC in SHE

![Illustration of SOC in SHE](image)

Figure 1.3: (a) The 2D electronic eigenstates in a Rashba coupled system are labeled by momentum (Green arrows). The two eigenspinors of each momentum point in the azimuthal direction (red arrows). (b) Schematic illustration of displacement of the Fermi surface by an applied electric field. Figure(a) is taken from Ref. [2].

In order to better understand and visualise the mechanism of SOC in SHE, Sinova *et al.* [2] proposed a model describing the SHC in a 2D electron gas (2DEG) system. The Hamiltonian of intrinsic SOC in a 2DEG is known as the Rashba SOC, which is frequently utilised for discussing SOC-related physics in 2D systems such as monolayers, surfaces or interfaces. The Rashba Hamiltonian is written as [60]

$$H = -\lambda \sigma \cdot (\hat{z} \times \mathbf{k}),$$  \hspace{1cm} (1.13)

where $\lambda$, $\sigma$, $\mathbf{p} = \hbar \mathbf{k}$ and $\hat{z}$ is the Rashba coupling constant, Pauli matrices, electron momentum and the direction perpendicular to the 2D plane, respectively. The effective magnetic field in Eq. (1.11) is here given by $\mathbf{B}(\mathbf{k}) = -\lambda (\hat{z} \times \mathbf{k})$ perpendicular to the momentum and this field causes the spin to align perpendicular to the momentum. It also indicates that the spin-up and spin-down states have the same strength of SOC with an opposite sign, which leads to the band splitting as shown in Fig. 1.3(a). In the presence of an applied electric field $E_x$, see Fig. 1.3(b), the Fermi surface of electrons is displaced in $\mathbf{k}$-space by $\delta \mathbf{k}$ from the original position (pink circle) to the new site (grey circle). This leads to the change of the effective magnetic field from initial $\mathbf{B}(\mathbf{k})$ to final $\mathbf{B}(\mathbf{k} + \delta \mathbf{k})$ and consequently induces a torque tilting the electrons out of alignment with
initial field \( \mathbf{B}(\mathbf{K}) \). When moving in momentum space electrons experience an effective torque which tilts the spins up for \( k_y > 0 \) and down for \( k_y < 0 \) according to the simple torque expression \( \tau = s_{\uparrow}(\downarrow) \times \mathbf{B}(\mathbf{k}) \). The spins up and down are tilted in the opposite direction creating a net spin current generated in the \( y \) direction perpendicular to the applied electric field.

### 1.1.2 Intrinsic SHE

In this section I will discuss the theory for the intrinsic SHE. Although the initial theory focuses on the AHE, the SHE is based on the same origin as well. The analytical theory for the AHE was first proposed by R. Karplus and J. M. Luttinger [61] in 1954. They considered the contribution of SOC in ferromagnetic conductors and reasoned that the AHE is attributed to an “anomalous velocity” perpendicular to both the electric and magnetic fields, which causes the second term in Eq. (1.1). This analysis was valid for the intrinsic mechanism as they focused on a \( d \)-band model without perturbations and scatterings.

Later, based on the proposal of an anomalous velocity, the theory was extended to semiclassical wave-packet centered dynamics [62–65], where the velocity of the Bloch state \( \psi_n(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} u_n(\mathbf{r}) \) with crystal momentum \( \mathbf{k} \) and band index \( n \) was derived as

\[
\dot{\mathbf{r}}_n(\mathbf{k}) = \frac{1}{\hbar} \frac{\partial E_n(\mathbf{k})}{\partial \mathbf{k}} + \frac{e}{\hbar} \mathbf{E} \times \mathbf{\Omega}_n(\mathbf{k}) = \frac{1}{\hbar} \frac{\partial E_n(\mathbf{k})}{\partial \mathbf{k}} - \mathbf{k} \times \mathbf{\Omega}_n(\mathbf{k}). \tag{1.14}
\]

Here, \( \mathbf{\Omega}_n(\mathbf{k}) \) is the Berry curvature of the \( n \)th band given by

\[
\mathbf{\Omega}_n(\mathbf{k}) = i \langle \nabla_{\mathbf{k}} u_n(\mathbf{k}) | \times | \nabla_{\mathbf{k}} u_n(\mathbf{k}) \rangle. \tag{1.15}
\]

The first term in Eq. (1.14) is the standard group velocity derived from the dispersion relation of the band energy \( E_n(\mathbf{k}) \). The second term is the anomalous velocity described by the Berry curvature in \( \mathbf{k} \)-space. By comparing Eq. (1.14) to the classical equation of motion

\[
\hbar \ddot{\mathbf{k}} = -e \mathbf{E} - e \dot{\mathbf{r}} \times \mathbf{B}, \tag{1.16}
\]

we can see that within the semiclassical equation of motion the Berry curvature is analogous to the magnetic field but acts in \( \mathbf{k} \)-space. The analogies between the Berry curvature and magnetic fields are summarised in Table 1.1.

The transverse Hall current originating from the anomalous velocity can be obtained by an integration of the Berry curvature over the Brillouin zone [41, 66],

\[
j^{H,\uparrow(\downarrow)} = -\frac{e^2}{\hbar} \int_{BZ} \frac{d\mathbf{k}}{(2\pi)^3} f^{0,\uparrow(\downarrow)}(\mathbf{k}) \mathbf{E} \times \mathbf{\Omega}_n^{\uparrow(\downarrow)}(\mathbf{k}) = \tilde{\sigma}^{\uparrow(\downarrow)}(\mathbf{k}) \mathbf{E}, \tag{1.17}
\]

where \( f^{0,\uparrow(\downarrow)}(\mathbf{k}) \) is the equilibrium electron distribution function of spin-up (down) electrons without applied field in the clean crystal. This equation shows that applying an \( x \)-direction electric field induces a Hall current along the \( y \) direction

\[
j_{xy}^{H} = \tilde{\sigma}_{yx} \mathbf{E}_x, \tag{1.18}
\]
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### Magnetic field Berry curvature

| Vector potential \( \mathbf{A}(\mathbf{r}) \) | Berry connection \( \mathcal{A}_n(\mathbf{k}) = \langle u_n(\mathbf{k})|i\nabla_{\mathbf{k}}|u_n(\mathbf{k}) \rangle \)
| Magnetic field \( \mathbf{B}(\mathbf{r}) = \nabla \times \mathbf{A}(\mathbf{r}) \) | Berry curvature \( \Omega_n(\mathbf{k}) = \nabla_{\mathbf{k}} \times \mathcal{A}_n(\mathbf{k}) \)
| Aharonov-Bohm geometric phase | Berry geometric phase \( \Delta \psi = \frac{\gamma}{\hbar} \oint \mathbf{A}(\mathbf{r}) \cdot d\mathbf{r} = \oint \mathbf{k} \cdot \langle u_n(\mathbf{k})|i\nabla_{\mathbf{k}}|u_n(\mathbf{k}) \rangle \)

Table 1.1: The analogy between the magnetic field in real space and Berry curvature in reciprocal space.

where the Hall conductivity \( \sigma_{yx} \) is a component of the conductivity tensor \( \bar{\sigma} \) derived in Eq. (1.17) and the spin is in the \( z \) direction. The total contribution to the spin Hall current can be obtained by the difference of spin-up and spin-down currents \( j^H_y = j^H_\uparrow - j^H_\downarrow \). In general, the spin-up and spin-down currents flow in the opposite directions. In magnetic solids, there is a nonzero charge current due to the imbalance of population between spin-up and spin-down electrons. In nonmagnetic systems the charge current vanishes and only the spin current survives.

So far the discussion of Berry phase physics is focused on non-degenerate bands within the limit of an Abelian curvature. In reality materials show a two-fold degeneracy (Kramers degeneracy) at each \( \mathbf{k} \) point if neither the time reversal symmetry nor the inversion symmetry is broken. Therefore, the Berry curvature must be generalised to non-Abelian gauge structures [67]. The starting point is the non-Abelian Berry connection written as

\[
\mathcal{A}_{ij}(\mathbf{k}) = \langle u_i(\mathbf{k})|i\nabla_{\mathbf{k}}|u_j(\mathbf{k}) \rangle, \quad i,j \in \Sigma,
\]  

where the states \( u_i(\mathbf{k}) \) and \( u_j(\mathbf{k}) \) are of the eigenspace \( \Sigma \) of \( N \)-fold degeneracy. This connection (vector potential) forms a \( N \times N \) matrix. By introducing the concept of covariant derivative for \( \nabla_{\mathbf{k}} \) in \( \mathbf{k} \)-space, the Berry curvature tensor in the non-Abelian gauge is redefined as [54, 68, 69]

\[
\Omega_{ij}(\mathbf{k}) = i \langle \nabla_{\mathbf{k}} u_i| \times |\nabla_{\mathbf{k}} u_j \rangle - i \sum_{l \in \Sigma} \langle \nabla_{\mathbf{k}} u_i| u_l \rangle \times \langle u_l| \nabla_{\mathbf{k}} u_j \rangle.
\]

The Berry curvature is the core for the anomalous velocity related to the Hall conductivity in the AHE and SHE. The description in the framework of Bloch wavefunction motivates research within first-principles computational schemes. There are different methods reported [3, 35, 70] for evaluating it. Yao et al. [3] reported the calculated Berry curvature \( \Omega^2(\mathbf{k}) \) as well as the corresponding band structure using the Kubo formalism based on fully-relativistic first-principles calculations (see Fig. 1.4). Their results show the value of Berry curvature to become significant at the \( \mathbf{k} \) points where the bands are very close. This can be associated with the spin-orbit
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Figure 1.4: (a) Band structure near the Fermi level (upper panel) and the corresponding Berry curvature along symmetry lines (lower panel) for bcc-Fe. (b) Fermi surface in (010) plane (solid line) and Berry curvature $\Omega^z(\mathbf{k})$ in atomic units (colour map). These figures are taken from Ref. [3].

coupling inducing the avoided crossings of bands and band splittings [36, 71]. This resulting curvature from the Kubo-formula approach is in agreement with other results calculated via Wannier functions [70] which also show significant enhancement at near degeneracies and avoided crossings. In this thesis the Berry curvature is calculated from Eq. (1.20) with Bloch states via the KKR Green function method, which is discussed in Sec. 2.2.2 [35, 66].

The introduction to the intrinsic mechanism has largely focused on the AHE where an applied electric field generates a transverse current in magnetic materials. However, the underlying mechanism for the AHE and the SHE are equivalent. As the experimental observation of the AHE is much easier the original literature often focused on this effect. Only later, realising the conceptional implementation and industrial relevance, the SHE became the focus of the attention.

1.1.3 Extrinsic SHE

The contributions of the SHE proposed by R. Karplus and J. M. Luttinger [61] for the AHE mainly focus on the intrinsic mechanism in the absence of any disorder potentials. Later J. Smit and L. Berger [72–74] proposed other contributions arising from the electron scattering by disorder potentials (see Fig. 1.5). Smit attributed the AHE current to the asymmetric scattering by impurities, known as skew scattering (or Mott scattering) [19, 73]. Another contribution of the disorder scattering, side jump, was also noticed in Smit’s work, but disregarded. Later Berger [74] described that in this contribution the scattered electrons are instantaneously displaced by $\delta \mathbf{r}$ in the transverse direction. In these two mechanisms the direction of scattering is spin dependent. Thus there is a net spin current $\mathbf{J}^s = \mathbf{J}_\uparrow - \mathbf{J}_\downarrow$ transverse to the applied field.
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Figure 1.5: Schematic illustration for the (a) skew-scattering and (b) side-jump mechanism.

In order to realise the extrinsic mechanisms, the impurity potential is conventionally split in a sum of the scalar impurity potential and the spin-orbit potential, \( V(r) = \hat{V} + V_{\text{SOC}} \). The scattering amplitude (or transition \( T \) matrix) between different momentum and spin states, from state \(|ks\rangle\) to \(|k's\rangle\), is written as

\[
\langle k's' | V | ks \rangle = \hat{V}_{kks} \delta_{s's} + i \eta_{\text{SOC}} \hat{V}_{kks} (s'|\sigma|s) \cdot (k' \times k),
\]

where \( \eta_{\text{SOC}} \) represents the spin-orbit coupling parameter. This matrix element determines the scattering rate via Fermi’s golden rule,

\[
P_{k's'ks} = \frac{2\pi}{\hbar} |\langle k's'|V|ks \rangle|^2 \delta(E_k - E_{k'}) = \frac{2\pi}{\hbar} |T_{k's'ks}|^2 \delta(E_k - E_{k'}). \tag{1.22}
\]

In the microscopic picture, the current induced in a material via an applied electric field can be expressed as

\[
\mathbf{J} = -e \sum_k \mathbf{v}_k f'_k, \tag{1.23}
\]

where the distribution function is given by

\[
f'_k = \hat{f}_k + g_k \tag{1.24}
\]

and the velocity \( \mathbf{v}_k \) is defined in Eq. (1.14).

The first term, \( \hat{f}_k \), is the equilibrium distribution function and \( g_k \) is the perturbation term linear in the external field. Thus the scattering properties of impurities can be described by finding the distribution function via the Boltzmann equation for the steady state [75–77]

\[
\hbar \frac{\partial f_{ks}}{\partial t} = \sum_{k's'} [P_{kks'k's} g_{k's'} - P_{k's'ks} g_{ks}], \tag{1.25}
\]

where the first and second terms on the rhs represent the scattering-in (\( P_{kks'k's} \)) and scattering-out (\( P_{k's'ks} \)), respectively. These two quantities are generally distinct (\( P_{kks'k's} \neq P_{k's'ks} \)) since the asymmetric chiral contribution emerges in the transition probability in the presence of SOC

\[
P^A_{k's'ks} \sim (k \times k') \cdot \langle s|\sigma|s' \rangle. \tag{1.26}
\]
This contribution was previously discussed as skew (asymmetry) scattering in Eq. (1.21).

The side-jump effect refers to the displacement of electrons of SOC Bloch states scattered by an impurity or disorder potential from a state to another. Unlike the skew-scattering effect, the side-jump effect remains difficult to be incorporated in quantitative approaches. Sinitsyn et al. [78–80] studied this contribution within wave-packet centered dynamics. They introduced the side-jump velocity as

$$v_{sj}(k) = \sum_{k's'} P_{k's'k0} \delta r_{k's'k0}, \quad (1.27)$$

where the displacement $\delta r_{k's'k0}$ can be evaluated in terms of the Berry curvature [78],

$$\delta r_{k's'k0} = \Omega \times (k_{s'} - k_s). \quad (1.28)$$

The displacement, while mitigated through scattering, only depends on the electronic structure of the clean crystal structures [78]. Moreover, distinct from the effect of impurity scattering shown above, the displacement simultaneously causes an energy shift proportional to the displacement $\Delta U_{k's'k0} = e \mathbf{E} \cdot \delta r_{k's'k0}$, which can influence the spin or anomalous Hall effect. The total current due to extrinsic contributions is given by

$$J^{\text{ext}} = J^{sj} + J^{ss} = -e \sum_{k} \left( v^{sj}_k + v^{ss}_k \right) g_k = -e \sum_{k} \left( \sum_{k's'} P_{k's'k0} \delta r_{k's'k0} g_k + \frac{\partial E_k}{\partial k} g_k \right). \quad (1.29)$$

Here, we find the non-equilibrium distribution function $g_k$ by solving the Boltzmann equation. More details of specific effects in $g_k$ can be found in Ref. [77, 78].

### 1.1.4 Quantifying the contributions to SHE

So far we have introduced the mechanisms of intrinsic, skew-scattering and side-jump contributions to the spin Hall effect, and the total conductivity is a sum of all these terms,

$$\sigma_{yx}^s = \sigma_{yx}^{s,\text{int}} + \sigma_{yx}^{s,ss} + \sigma_{yx}^{s,sj}. \quad (1.30)$$

In reality it is impossible to grow crystalline structures without any disorder and it indeed influences the transport in the devices. Thus understanding the scaling of the Hall conductivity on the impurity concentration is critical. In the dilute limit, in which there is no coupling between impurities, the scattering rate can be written in terms of the impurity concentration as [76]

$$P_{nn'}^{nn'} = \frac{2\pi}{\hbar} c_0 N |T_{nn'}^{nn'}|^2 \delta(E^n_k - E^{n'}_k), \quad (1.31)$$

where $c_0$ is the impurity concentration and $N$ is the number of host atoms in a cell. So $c_0 N$ is the number of non-interacting impurities in our work. All calculations are performed at zero temperature in which the phonon interaction is not taken into account. The spin Hall effect is dependent on the longitudinal resistivity which can be tuned by adjusting the impurity concentration. As previously discussed, the intrinsic and side-jump contributions are only dependent on the
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Intrinsic electronic structure, which implies their independence of impurity concentration and the first term (side jump) in Eq. (1.29) holds irrelevance of impurity concentration [78, 79]. It leads to that the non-equilibrium distribution $g_{ks}$ is inversely proportional to the impurity concentration $c_0$ since the scattering rate [see Eq. (1.31)] scales linearly with the impurity concentration. The dependence of the different conductivities on the impurity concentration is summarised as

\[
\sigma_{sx,\text{int}} \sim (c_0)^0, \\
\sigma_{sx,\text{ss}} \sim (c_0)^{-1}, \\
\sigma_{sx,j} \sim (c_0)^0. 
\]  

(1.32)

In theoretical studies, the concentration can be adjusted easily. However, it is a difficult task to experimentally observe the relation between the concentration and the Hall conductivity. Instead, in experiments it is the longitudinal resistivity which is explored as a scaling parameter. The corresponding scaling relations are [6, 61, 72, 73]

\[
\rho_{sx,\text{int}} \sim (\rho_{xx})^2, \\
\rho_{sx,\text{ss}} \sim (\rho_{xx})^1, \\
\rho_{sx,j} \sim (\rho_{xx})^2. 
\]  

(1.33)

where the contribution of the intrinsic and side jump mechanism to the Hall resistivity scale quadratically with the longitudinal resistivity while the relation is linear for the skew scattering.

The detail of the scaling relations is discussed in Appendix A.

In experimental findings for bulk systems, the dependence of $\sigma_{xx}$ on $\sigma_{yx}$ can be classified into three regimes: (1) high conductivity regime $\geq 10^6(\Omega\text{cm})^{-1}$ dominated by the skew-scattering contribution [4, 81, 82]; (2) good metal regime $10^4 - 10^6(\Omega\text{cm})^{-1}$, where $\sigma_{yx} \sim \sigma_{xx}^0$ leads to the intrinsic mechanism being dominant [37, 83], and (3) dirty regime (bad conductivity regime) $< 10^4(\Omega\text{cm})^{-1}$ where $\sigma_{yx} \sim \sigma_{xx}^{1.6-1.8}$ [83–87] and the effects of localization or electron interaction cannot be ignored [86].

This classification of $\sigma_{xx}$ dependence on $\sigma_{yx}^4$ can be discussed by focusing on, Pt for example. Pt is a conventional spin Hall material and has attracted considerable attention since it shows a large effect in generating and detecting spin currents with large SOC [4, 37, 40, 88–94], including investigating the dependence of spin Hall resistivity (conductivity) on physical parameters such as charge conductivity and spin diffusion length [37, 92–94]. Tanaka et al. [37] theoretically demonstrated that the intrinsic spin Hall resistivity of Pt is independent of charge resistivity in the low resistivity regime while in high resistivity regime it decreases proportional to $\rho_{xx}^{-2}$. On the other hand, Lijun Zhu et al. experimentally studied the effect of carry lifetime on the intrinsic spin Hall conductivity in the dirty regime in the Pt alloyed with various concentrations of MgO. Their results showed the intrinsic SHC in the clean limit is considerably larger than the theoretical predictions [36, 37].

To quantitatively understand the weight of intrinsic and extrinsic contribution in the wide range of charge resistivity for Pt, Sagasta et al. [4] use the scaling relation first introduced by
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Tian et al. [95] based on the connection in Eq. (1.1) with dropping the side-jump contribution due to the dilute limit, which is written as [4]

\[- \rho_{\text{SH}} = \alpha_{ss} \rho_{xx,0} + \sigma_{\text{intSH}}^2 \rho_{xx}^2, \tag{1.34}\]

where \(\alpha_{ss}, \rho_{xx,0}, \sigma_{\text{intSH}}^2\) and \(\rho_{xx}\) are the skew-scattering angle, residual resistivity, intrinsic spin Hall conductivity and observed resistivity, respectively. All of these quantities can be observed experimentally. This expression takes only into account the skew-scattering and intrinsic effect while the side jump is negligible since it arises only for high impurity concentrations [96, 97] where the dilute limit is no longer applicable. Moreover, the connection between spin Hall conductivity \(\sigma_{\text{SH}}\) and spin Hall resistivity \(\rho_{\text{SH}}\) is \(\rho_{\text{SH}} = -\sigma_{\text{SH}}/(\sigma_{\text{SH}}^2 + \sigma_{xx}^2) \approx -\sigma_{\text{SH}}/\sigma_{xx}^2\) (see Appendix A), and the spin Hall angle can be expressed in terms of either \(\rho_{\text{SH}}\) and \(\sigma_{\text{SH}}\) as \(\theta_{\text{SH}} = \sigma_{\text{SH}}/\sigma_{xx} = -\rho_{\text{SH}}/\rho_{xx}\) [6, 80]. Derived from Eq. (1.34), the spin Hall angle \(\theta_{\text{SH}}\) can be expressed as

\[\theta_{\text{SH}} = \frac{\alpha_{ss} \rho_{xx,0}}{\rho_{xx}} + \frac{\sigma_{\text{intSH}}^2}{\rho_{xx}} \approx \frac{\alpha_{ss} \sigma_{xx}}{\sigma_{xx,0}} + \frac{\sigma_{\text{intSH}}^2}{\sigma_{xx}}, \tag{1.35}\]

a function of longitudinal conductivity (inverse of resistivity). Sagasta et al. [4] analysed the connection between their experimental results and Eq. (1.35) for Pt. As shown in Fig. 1.6, their samples are Pt, grown by magnetron sputtering (sputtered Pt), and by e-beam evaporation (evaporated Pt). The grain sizes grown by these two methods are different and it leads to different level of impurity scattering in the samples. In their work, the sputtered samples have larger scattering inducing the smaller conductivity in the range of \(10^4 - 10^6 (\Omega \text{cm})^{-1}\), where \(\sigma_{yy}(\sigma_{\text{SH}}) \sim \sigma_{xx}^0\) within the moderately dirty (good metal) regime. The solid black line corresponds to the spin Hall angle considering only the intrinsic contribution \(\theta_{\text{SH}} = \sigma_{\text{intSH}}^2 \rho_{xx}\). The trend of data points of the sputtered Pt in the moderately dirty regime suits the intrinsic contribution (black solid line). In contrast in the superclean metal regime the trend (dash line) is no longer linearly dependent on the longitudinal resistivity, which implies the importance of skew-scattering contribution as highlighted by first term in Eq. (1.35).

The contribution of side jump becomes important in the bad metal regime where the charge conductivity is small and the impurity (or defect) concentration is large [96]. In the work published by Tian et al. [95], the contribution from the side-jump mechanism was taken into account in the scaling relation [see Eq. (1.34)] via an additional term \(\beta \rho_{\text{Pt,0}}^2\), where \(\beta\) is in the units of \((\Omega \text{cm})^{-1}\). This additional term alters the Hall resistivity to be no longer dominated by the intrinsic or skew-scattering contribution. Onoda et al. [86] theoretically demonstrated that the scaling is \(\rho_{yx} \sim \rho_{xx}^{1.6}\), which is in good agreement with the experimental observation in Ref. [83]. This value is reasonably placed between the scalings \(\rho_{yx} \sim \rho_{xx}^{-1}\) and \(\rho_{yx} \sim \rho_{xx}^{-2}\), discussed before.

1.2 Experimental Observation of SHE

The first experimental evidence of the SHE was observed in the \(n\)-type semiconductor GaAs and InGaAs by Kato et al. [53]. They utilised Kerr rotation microscopy to detect the spin density,
1.2. EXPERIMENTAL OBSERVATION OF SHE

1.2.1 Nonlocal measurement

The experimental setup of nonlocal measurements was firstly proposed by Johnson et al. [98] and reported by Valenzuela et al. [99] for the SHE. Figure 1.7(a) shows the basic geometry of the device, called ISHE device, where the ferromagnetic material (FM) electrode is on the top of a nonmagnetic material (NM). The magnetisation \( \mathbf{M} \) of the FM points out of plane and corresponding to the spin flow from the SHE, at the opposite edges of the thin film sample. By straining the sample, they found that the observed SHE is attributed to the extrinsic SHE because of the weak dependence on crystal orientation. The direct electrical measurement for the SHE is nontrivial as the net transverse current is zero leading to no measurable Hall voltage (Fig. 1.1). However, measurements based on the so-called inverse spin Hall effect (ISHE) enable the direct measurement as a flowing spin current will induce a transverse voltage. This principle idea for an experimental setup was proposed by Hirsch [20]. Similar to the SHE, where a transverse spin current is generated by a longitudinal charge current, the ISHE is the effect where a spin current induces a transverse voltage. This idea inspired direct measurements of the SHE, namely nonlocal and spin-pumping detection, to be discussed in the following.

Figure 1.6: Relationship between Spin Hall angle and longitudinal conductivity. This figure is taken from Ref. [4].
the electrical current is applied from the FM to NM. Figure 1.7(b) shows the electrochemical potentials of spin up, spin down and the average value with blue, red and green, respectively. As the electrons travel across the interface, the electrochemical potentials of spin-up and spin-down electrons become different as a spin accumulation builds up at the interface. While the electrochemical potentials of spin up and spin down have to be continuous at the interface, there is a discontinuity for the average electrochemical potential (green line) leading to spin-coupled resistance. Moreover similar to the charge current driven by the voltage drop, the difference of electrochemical potentials between spin-up and spin-down electrons drives the spin current in the NM [20].

Figure 1.7: (a) Schematic illustration of the nonlocal spin Hall device composed of a ferromagnetic and a normal metal. (b) Electrochemical potential in the ferromagnetic and normal metal.

In the FM the majority of conduction electrons, say spin-up electron, accumulates at the interface in comparison to the minority of spin-down electrons. These interface spin-up electrons drift into the NM to form a spin-polarised current \( j_s \) along the \( x \) direction. When the spin current flows in the NM, the transverse voltage is induced by the ISHE and the electrons accumulate at an edge. Thus, by detecting the voltage \( V_{SH} \) in the NM electrode at a distance \( L \) from the FM, the spin current is shown to exist. In order to detect the voltage, the distance \( L \) has to be smaller than the spin diffusion length, a characteristic length over which the spin decays.
This process is indicated by the electrochemical potentials of spin-up and spin-down electrons gradually becoming equal moving away from the FM. The quantity measured in the experiment is the nonlocal Hall resistance $R_{\text{SH}} = V_{\text{SH}}/I$ and it can be written as \[ R_{\text{SH}} = \frac{1}{2} P_{\text{eff}} \theta_{\text{SH}} \frac{\rho_N}{d_N} e^{-L/\lambda_N}, \] (1.36)

where $\rho_N$ and $d_N$ are the resistivity and thickness of NM, respectively. $P_{\text{eff}}$ and $\lambda_N$ are the effective spin polarization of the FM/NM interface and the spin diffusion length of the NM, respectively. These two quantities can be measured in the nonlocal spin accumulation device as well. More details about this device can be found in Ref. [99]. As these quantities are known, the spin Hall angle $\theta_{\text{SH}}$ and spin Hall conductivity $\sigma_{xy} = \theta_{\text{SH}} \sigma_{xx}$ can be extracted.

The experimental setup introduced so far is the so-called inverse SHE device. The other approach to observe the SHE in nonlocal geometries is called direct SHE device, where the applied current and observed voltage in Fig. 1.7(a) are swapped. The applied charge current applied in the NM electrode along the $y$ direction generates the spin current flowing in the $x$ direction, and the voltage is detected in the FM/NM circuit. These two devices, inverse and direct SHE, can equally confirm and quantify the SHE [40].

### 1.2.2 Spin-pumping measurement

Here, I briefly introduce another approach for the measurement of the SHE, the spin-pumping measurement, first reported by Saitoh et al. [88]. Unlike applying an electrical voltage for the spin current generation, this experiment drives a spin current by the spin dynamics at a FM/NM interface. Figure 1.8(a) shows the geometry of the experimental setup with the NM and FM layer. The sample is placed at the centre of a cavity where a TE$_{011}$ microwave excitation of fixed frequency is applied, inducing the magnetisation $M(t)$ precession in the FM. An external magnetic field $\mathbf{H}_{\text{ext}}$, a tuning parameter, is applied in the direction parallel to the FM/NM interface. Though a spin current $j_s$ is pumped from the FM to the NM when the external field $\mathbf{H}_{\text{ext}}$ and the microwave fulfill the ferromagnetic resonance (FMR) condition [102]. This spin current traveling in the NM is converted to an electrical voltage $V$ as a result of the ISHE and the spin-pumping ISHE voltage is detected [Fig. 1.8(b)]. The ISHE voltage can be described by [103]

\[ V_{\text{ISHE}} = \frac{w \theta_{\text{SH}} \lambda_N \tanh(d_N/2\lambda_N)}{d_N \sigma_N + d_F \sigma_F} \left( \frac{2e}{\hbar} \right) j_s^0. \] (1.37)

Here $w, \lambda_N, d_F(d_N)$ and $\sigma_F(\sigma_N)$ are the width of FM, spin-diffusion length of NM, thickness of FM(NM) and conductivity of FM(NM), respectively. $j_s^0$ is the spin current density at the interface, which is estimated by measuring other quantities such as the saturation magnetisation of the FM, gyromagnetic ratio of the FM and interfacial spin mixing conductance $G_{\text{HM-FM}}^{[1]}$.

Thus the spin Hall angle $\theta_{\text{SH}}$ and the related properties can be obtained. One needs to be highlighted is the spin mixing conductance $G_{\text{HM-FM}}^{[1]}$ in the generated spin current $j_s^0$. This spin-dependent parameter significantly characterise the efficiency of the interfacial spin transport.
considering the spin transmission, spin backflow and the spin accumulation at the interface. The measured voltage is proportional to \( V_{\text{ISHE}} \sim G_{\text{HM-FM}}^{\uparrow\downarrow} \theta_{\text{SH}} \). Thus, unlike theoretical studies in pure crystal structures, this inevitable quantity in reality can cause the large variation in the value of measured spin Hall effect and leads to the discrepancy between theoretical and experimental results.

![Figure 1.8](image)

**Figure 1.8:** (a) Schematic illustration of spin-pumping inverse spin Hall device. (b) Field \( H \) dependence of the electrical potential \( V \).

### 1.3 Spin accumulation

In 1988 the phenomenon of giant magnetoresistance was firstly discovered by the groups of A. Fert [104] and of P. Grünberg [105]. The basic concept is the application of a charge current through a multilayer system that is composed of alternating ferromagnetic and nonmagnetic materials, see Fig. 1.2(a). When the charge current passes through the first ferromagnetic layer, the electrons become spin polarised in the direction parallel to the magnetisation of the ferromagnetic material. This spin-polarised current will experience a larger interface resistance if the magnetisation of the second ferromagnetic layer is antiparallel to the spin current while the interface resistance is smaller in the case in which the magnetisation is parallel. The contribution to the interface resistance via the spin current is attributed to the imbalance of electrochemical potentials between spin-up and spin-down electrons [106]. In a free-electron model, this imbalance of spin-dependent electrochemical potentials can be written as

\[
|\Delta \mu| = \frac{2 \mu_0 |\Delta M|}{3 n \mu_B}, \quad (1.38)
\]

where \( n \), \( \mu_B \), \( \mu_0 \) and \( \Delta M \) are the electron density, Bohr magneton, constant of electrochemical potential and out-of-equilibrium magnetisation, respectively. In a simple model of a ferromagnet,
1.3. SPIN ACCUMULATION

$\Delta M$ is determined by the difference of spin-up and spin-down DOS at the Fermi level, expressed as

$$\Delta M = \frac{D^\uparrow(\mathcal{E}_F) - D^\downarrow(\mathcal{E}_F)}{D^\uparrow(\mathcal{E}_F) + D^\downarrow(\mathcal{E}_F)}$$

where $D^{\uparrow(\downarrow)}$ stands for the density of states of spin-up (spin-down) electrons. In addition, in Sec. 1.2, the different experimental methods for the observation of the SHE are based on the inverse SHE. The samples were built as bilayer or multilayer systems. When the charge or spin-polarised currents travel across these interfaces, a certain amount of electrons would accumulate at the interfaces due to the difference of chemical potential of these materials [20, 77, 107]. Thus, the spin accumulation is an important aspect in the physics of spin-dependent transport. Spin accumulation at the interfaces between the ferromagnetic and nonmagnetic metals induces an imbalance of chemical potentials, affecting the interface transmission of electrical and spin currents. This phenomenon, mostly ignored in theoretical approximations might cause the disparity between theoretical predictions and experimental observations.

There are several mechanisms to induce spin accumulation. Besides the situation of spin injection which is shown in Fig. 1.2(a), spin accumulation can also be induced by the intrinsic properties in metallic 2-dimensional systems. The key ideas of spin accumulation were theoretically introduced by V. M. Edelstein [108] based on the Rashba spin-orbit coupling in systems breaking inversion symmetry [60]. He showed that the Rashba coupling leads to an additional spin-dependent velocity in the 2-dimensional electron gas and the degenerate electron bands are split, as shown in Fig. 1.3(a). If an external current is applied, the Fermi surfaces are shifted opposing the current direction, see Fig. 1.3(b). Thus it leads to a magneto-electric effect originating from the imbalance between spin-up and spin-down density, which implies spin accumulation takes place. This effect is an intrinsic property in the presence of Rashba coupling at surfaces or interfaces, where spatial inversion symmetry is broken.

Furthermore, the spin accumulation at interfaces or surfaces can also be induced via the SHE, see Fig. 1.2(c). In a multilayer system a charge current is applied in the heavy metal layer with large spin-orbit coupling. In contrast to the Rashba coupling discussed above, the spin-orbit coupling here is considered in the 3-dimensional configuration. The charge-to-spin conversion leads to the transverse spin current flowing in the direction which is perpendicular to the interface. Then the electrons with the specific spin direction accumulate at the interface next to the ferromagnetic layer (red layer). This spin accumulation may originate from the intrinsic mechanism described via the Berry curvature or from the extrinsic contributions of side jump and skew scattering, as discussed in Sec. 1.1.

A well known application of the SHE in technology is to generate the spin-orbit torque (SOT) via the SHE to switch the magnetisation in a ferromagnet in the magnetic random access memory (MRAM) devices [1, 27, 33, 102]. The SOT-MRAM architecture is composed of multiple layers, as shown in Fig 1.2(c). The SOT is described by different contributions: (1) the SHE induced spin current directly flowing into the ferromagnet; (2) the spin galvanic effect [32] driven by
the spin accumulation at the interface. Both contributions apply an external force to rotate the magnetisation in the ferromagnetic layer (red layer) to be parallel or antiparallel to the second ferromagnetic layer (purple layer), which leads to the same configuration as for the giant magnetoresistance.

Figure 1.9: Illustration of spin accumulation induced by the spin Hall effect.

In order to obtain better insight into the experimental observation of SHE using the mechanism of inverse SHE, Zhang [77] investigated the SHE induced spin accumulation by taking into account the spin diffusion length. Fig. 1.9 shows the SHE in a nonmagnetic thin film of width $w_N$. If the electron current $j_e$ is applied in the $x$ direction, the spin Hall current $j^\text{SH}_s$, polarised in $z$-direction, is induced along the $y$ direction and vanishes at the strip edges $y = \pm w_N/2$. The distribution of spin accumulation within the strip can be expressed as

$$\delta \mu_N(y) = 2e\theta_{\text{SH}}\rho_N\lambda_N j_e \frac{\sinh(y/\lambda_N)}{\cosh(w_N/2\lambda_N)} e^z,$$

as a function of $y$, where $\theta_{\text{SH}}$, $\rho_N$ and $\lambda_N$ are the spin Hall angle, resistivity and spin diffusion length, respectively. It shows that the spin accumulation is antisymmetrically distributed and has the largest value near the edges. Similar to the traditional Hall effect, this resulting spin accumulation would generate the counter spin current $j_s$ to satisfy the boundary conditions where the Hall spin current is zero at the edges. In order to understand the spin-orbit-dependent physics of surfaces relevant to the experimental observations of SHE, our work will investigate the spin accumulation induced via the SHE within free-standing thin films.

Moreover, for interpreting the phenomena of spin-dependent transport at interfaces such as spin-orbit torque, Amin et al. [109, 110] used the circuit theory to investigate the interfaces between a ferromagnet and nonmagnetic heavy metal with an applied in-plane electric field. They found that in the presence of interfacial spin-orbit coupling the elements of charge/spin conductivity and torkivity tensors are more important than the modifications of other transport parameters (such as the spin mixing conductance) in transport relevant phenomena such as the Rashba-Edelstein effect, SHE induced spin accumulation, spin pumping. Thus, it supports that the spin-dependent transport based on the charge/spin conductivity tensor, we have introduced and will focus on later, is the critical element for bulk as well as real multilayer systems.
In this chapter, I will discuss the computational methods used in my work, from the electronic structure calculations connecting to the spin-dependent transport as well as the superconducting materials. The details of transport and superconducting computations will be discussed in Section 2.1.5 and 2.2, respectively.

In quantum mechanics the system is described by the Schrödinger equation and all information about the system, such as electronic structure, conductivity, thermal conductivity, superconductivity, etc., can be derived from the wave function. The methods for the electronic structure calculations will be presented in the following order. (1) At the beginning, I will give a brief introduction to the density functional theory (DFT) including the assumptions and the effective potential. (2) The Korringa-Kohn-Rostoker (KKR) Green’s function method will be discussed in detail to solve the Kohn-Sham equation either in the reciprocal or in the real space, for clean and impurity systems, respectively. (3) The details of implementing spin-orbit coupling into DFT leading to the Dirac-Kohn-Sham equations will follow.

If the wave functions of the clean and impurity systems are known, the impurity-scattering can be described via Fermi’s Golden rule based on the transition matrix. Spin-relaxation processes, the spin-dependent transport, will be approached in two limits, the clean intrinsic and the scattering-based extrinsic mechanisms. (1) First, I will present the intrinsic transport based on an integral over the non-Abelian Berry curvature. (2) For the extrinsic mechanism, the derivation of the linearised Boltzmann equation within the quantum-mechanics framework will be given. In this semiclassical approach, the calculation of the extrinsic charge and spin conductivities as well as the spin accumulation is discussed.

In addition, the superconducting density functional theory (SCDFT) will be briefly introduced, which relies on the implementation of the Bogoliubov-de Gennes equations. By combining this with the KKR method we can quantify the influence of an impurity on the superconducting state.
2.1 Electronic structure

2.1.1 Density functional theory (DFT)

Starting from the single-electron Schrödinger equation, a wave function $\Psi(r)$ of one electron moving with a kinetic energy $\hat{T}(r)$ in an arbitrary potential $V(r)$ is described as

$$[\hat{T}(r) + V(r)] \Psi(r) = E \Psi(r). \quad (2.1)$$

In a many-electrons system, there is more than one electron. The multiple-electron Schrödinger equation is written as

$$\sum_{i}^{N} [\hat{T}(r_i) + V(r_i)] \Psi(r_1, \ldots, r_N) = E \Psi(r_1, \ldots, r_N). \quad (2.2)$$

The problem now is to deal with a large number of electrons in a macroscopic sample. To deal with this difficulty, P. Hohenberg and W. Kohn [111] derived two theorems known as Hohenberg-Kohn theorems:

1. The electron density is the basic variable and all quantities can be determined by it such as the energy of the system

$$\langle E \rangle = \langle \Psi | \hat{H} | \Psi \rangle = E[n(r)]. \quad (2.3)$$

2. If the number of particles in a system is fixed, its ground state energy can be obtained by finding the minimum value with respect to the density

$$\begin{cases} E_0 = E[n_0(r)] \leq E[n(r)] \\ \frac{\partial E[n(r)]}{\partial n(r)} = 0 \end{cases}. \quad (2.4)$$

This simplifies the multiple-particles Schrödinger equation to a problem described by a functional of the particle density. In principle the ground state can be determined, but two questions need to be answered first:

1. What is the functional for the kinetic energy $T[n(r)]$?
2. How to correctly describe the electron-electron interaction (the exchange-correlation) $E_{xc}[n(r)]$?

These questions were in detail addressed by the Kohn-Sham equations proposed by W. Kohn and L. J. Sham in 1965 [112]. In the Kohn-Sham formalism, the kinetic energy and exchange-correlation energy are calculated considering effective “noninteracting” electrons moving in an effective potential $V_{\text{eff}}$

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{\text{eff}}(r)\right] \psi_i(r) = \epsilon_i \psi_i(r) \quad (2.5)$$

with

$$V_{\text{eff}}(r) = V_{\text{ext}}(r) + \int \frac{n(r')}{|r - r'|} d r + \frac{\partial E_{xc}[n(r)]}{\partial n(r)}. \quad (2.6)$$

The electron density is given by

$$n(r) = \sum_{i=1}^{N} |\psi_i(r)|^2 \quad (2.7).$$
where $i$ labels all quantum numbers including orbital and spin indices. To describe the interaction between electrons, the exchange-correlation term $E_{xc}[n(r)]$, we use the local density approximation written as

$$E_{xc}^{LDA} = \int e_{xc}^{hom}[n(r)]n(r)dr,$$

(2.8)

where $e_{xc}^{hom}[n(r)]$ is the local exchange-correlation energy of each electron in a noninteracting homogeneous electron gas [$n(r)$ varies slowly enough]. The exchange-correlation energy can be calculated by a linear sum of exchange and correlation energy as $e_{xc}^{hom}[n(r)] = e_{x}^{hom}[n(r)] + e_{c}^{hom}[n(r)]$ [113]. This set of Kohn-Sham equations [Eq. (2.5) to Eq. (2.7)] is practically used for solving many-electron physics in real materials. There are other methods for solving the exchange-correlation functional, such as the generalised gradient approximation (GGA) [114] that consider the exchange-correlation term $E_{xc}[n(r), \Delta n(r)]$ as a function of both the electron density and its gradient. There are more functionals considering other factors beyond these two parameters for accuracy for more complicated electronic structures [115, 116].

2.1.2 Green function method

To solve the Kohn-Sham equation for the charge density a Green function method is used. The Green function of the Schrödinger equation with a source at position $r$

$$[\hat{T}(r) + V(r) - E]G(r, r'; E) = \delta(r - r')$$

(2.9)

can be expressed as

$$G(r, r'; E) = \lim_{\epsilon \to 0} \sum \frac{\psi_i(r)^* \psi_i(r')}{E + i\epsilon - E_i},$$

(2.10)

where $\epsilon$ is an infinitesimal small positive number. The local density of states can be expressed by the imaginary part of $G(r, r'; E)$ as $D(r, E) = -\frac{1}{\pi} \text{Im}G(r, r'; E)$. Further integrating $G(r, r'; E)$ over the energy, the local charge density $n(r)$ is obtained,

$$n(r) = -\frac{2}{\pi} \int_{-\infty}^{E_F} dE \text{Im}G(r, r'; E).$$

(2.11)

For practical applications the Green function is analytically continued into the complex plane and a complex energy contour is used. It begins at a lower energy $E_L$, above the core states, shown in Fig. 2.1. This contour integral represents the integral along the real $E$ axis according to Cauchy’s theorem [117].

As the charge density is thus defined via the Green function, we are left to find the Green function for the relevant systems. The Green function is defined as the solution of the inhomogeneous differential equation with a perturbated Hamiltonian such as $H = H_0 + H_1$, where $H_0$ and $H_1$ are referring to an unperturbed, kown, and a perturbed, unkown, system. The Green functions $\hat{G}_0$ and $\hat{G}$ corresponding to $H_0$ and $H$ are defined as

$$\hat{G}_0 = (E - \hat{H}_0)^{-1}$$

(2.12)
CHAPTER 2. COMPUTATIONAL METHOD

Figure 2.1: Contour integral of $G(r, r'; E)$ in the complex energy plane.

and

$$\hat{G} = (E - \hat{H}_0 - \hat{H}_1)^{-1}.$$  \hspace{1cm} (2.13)

Given these two equations, $\hat{G}$ can be found self-consistently via the following so-called Dyson equation [118, 119]

$$\hat{G} = \hat{G}_0 + \hat{G}_0 \hat{H}_1 \hat{G}_0 + \hat{G}_0 \hat{H}_1 \hat{G}_0 \hat{H}_1 \hat{G}_0 + \cdots.$$  \hspace{1cm} (2.14)

Shown via the Feynman diagram (see Fig. 2.2), this equation intuitively presents multiple scattering of a particle traveling through a successive series of potentials, which underscore the physical interpretation of a Green function as a "propagator".

For an energy $E$, belonging to the continuous spectrum, the wave function can be self-consistently formed via a Dyson-like equation, the so-called Lippman-Schwinger equation [120]

$$\psi(r) = \psi_0(r) + \int dr_1 dr_2 \hat{G}_0(r, r_1; E) \hat{H}_1(r_1, r_2) \psi_2(r),$$  \hspace{1cm} (2.15)

where $\psi_0(r)$ and $\psi(r)$ are wave functions of the known and the unknown system, respectively. In the scattering theory, the transition T-matrix $\hat{T}$ is defined as

$$\hat{T}\psi_0 = \hat{H}_1\psi$$  \hspace{1cm} (2.16)

Figure 2.2: Feynman diagram for the Dyson equation, taken from Ref. [5].
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and the Dyson and Lippman-Schwinger equations can be expressed in terms of $\hat{\mathcal{T}}$ as
\[
\hat{G} = \hat{G}_0 + \hat{G}_0 \hat{\mathcal{T}} \hat{G}_0 \tag{2.17}
\]
and
\[
\psi(\mathbf{r}) = \psi_0(\mathbf{r}) + \int d\mathbf{r}_1 d\mathbf{r}_2 \hat{G}_0(\mathbf{r}, \mathbf{r}_1; E) \hat{\mathcal{T}}(\mathbf{r}_1, \mathbf{r}_2) \psi_0(\mathbf{r}_2). \tag{2.18}
\]

2.1.3 Korringa-Kohn-Rostoker (KKR) method

In reality, ideal materials are periodic, constructed from a large number of atoms. The crystal potential $V(\mathbf{r})$ is a sum of the potentials of all atoms,
\[
V(\mathbf{r}) = \sum_n V^n(|\mathbf{R}^n - \mathbf{r}^n|), \tag{2.19}
\]
where $n$ is the atomic index. In our calculation these on-site atomic potential are approximated as spherical symmetric potentials in the so-called atomic sphere approximation (ASA) [121], expressed as
\[
V^n(|\mathbf{R}^n - \mathbf{r}^n|) = \begin{cases} 
V^n(|\mathbf{R}^n - \mathbf{r}^n|) & \text{for } |\mathbf{R}^n - \mathbf{r}^n| < r_{\text{ASA}} \\
0 & \text{for } |\mathbf{R}^n - \mathbf{r}^n| > r_{\text{ASA}}.
\end{cases} \tag{2.20}
\]
The ASA radius is defined as Wigner–Seitz radius whose spheres entirely fill the volume of the crystal. Unlike the muffin-tin approximation (MTA) [Fig. 2.3(a)], having the interstitial regions between the MTA spheres among the crystal, the ASA spheres [Fig. 2.3(b)] fit reality better. However, overlap area between atoms is generated. This method is valid if the integral over the overlap area makes the same contribution as the interstitial area [122, 123], then the quantity varies slowly. The Green function of the Schrödinger equation for each atomic potential $V^n(\mathbf{r})$ is expressed as [117]
\[
[\hat{\mathcal{T}} + V^n(\mathbf{r}) - E] \hat{G}(\mathbf{R}^n + \mathbf{r}, \mathbf{R}^{n'} + \mathbf{r}'; E) = -\delta_{nn'} \delta(\mathbf{r} - \mathbf{r}'). \tag{2.21}
\]
The full Green function is a combination of on-site scattering solutions (special solution), describing the scattering of single spherical potentials, and multiple-site scattering (general solution), presenting the structural scattering among the atoms of the system
\[
\hat{G}(\mathbf{R}^n + \mathbf{r}, \mathbf{R}^{n'} + \mathbf{r}'; E) = -i\sqrt{E} \sum_L R_L^n(\mathbf{r}_<; E) H_L^n(\mathbf{r}_>; E) \delta_{nn'} + \sum_{LL'} R_{LL'}(\mathbf{r}; E) G_{LL'}^{nn'}(E) R_L^{n'}(\mathbf{r}'; E), \tag{2.22}
\]
where $L \equiv (lm)$, $R_L^n(\mathbf{r}_<; E) = R_L^n(\mathbf{r}; E) Y_L(\hat{\mathbf{r}})$, $H_L^n(\mathbf{r}_>; E) = H_L^n(\mathbf{r}; E) Y_L(\hat{\mathbf{r}})$ are angular-momentum indices, regular solutions and irregular solutions, respectively. Here, $\mathbf{r}_< (\mathbf{r}_>)$ stands for minimum (maximum) $(\mathbf{r}, \mathbf{r}')$. $G_{LL'}^{nn'}$ (homogeneous solution) in the second term is the so-called structural Green function (structure constant) defined by the algebraic Dyson equation as
\[
G_{LL'}^{nn'} = g_{LL'}^{nn}(E) + \sum_{n''} \sum_{L''} g_{LL''}^{nn}(E) t_{L''}^{n''}(E) G_{L''L'}^{n''}(E), \tag{2.23}
\]
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Figure 2.3: Schematic illustration of the 2-dimensional crystal landscape for (a) muffin-tin approximation (MTA) and (b) for atomic-sphere approximation (ASA). These figures are taken from Ref. [6].

where $t_{L,L'}^{n'n''}(E)$ is the on-site scattering $t$-matrix defined as

$$t_{L,L'}^{n'n''}(E) = \int_{|r|=0}^{R_{ASA}} d^3r J_L^{n'n''}(r;E)\tilde{V}^{n''}(r)R_{L'}^{n'n''}(r;E)$$

(2.24)

with the spherical Bessel function $J_L(r;E) = j_l(\sqrt{E}r)Y_L(\hat{r})$, and $\tilde{V}^{n''}(r)$ is the free-space Green function.

So far the structure constants are expressed in real space, which is unpractical in an infinite crystal. However, crystals are periodic. A periodic crystal structure is described by a basis unit cell (index $n$) connected by the lattice vectors and each unit cell has various atomic sites of index $\mu$ ($\mu$ is regarded as 1 in the previous real-space discussion). For example, bcc and fcc have 1 atomic site $\mu$ in the unit cell while hcp has 2. This periodicity allows us to calculate the Green function in the reciprocal $k$-space by the Fourier transformation with respect to the index $n$

$$G_{LL'}^{\mu\mu'}(k;E) = \sum_{n'} G_{LL'}^{n'n'n'}(E) e^{-i(kR^n-R'^n)}.$$  

(2.25)

The structure constants become

$$G_{LL'}^{\mu\mu'}(k;E) = g_{LL'}^{\mu\mu'}(k;E) + \sum_{L''} \sum_{\mu''} g_{LL'}^{n'n'n'}(k;E)t_{L''L''''}(E)G_{L''''L'''''}^{\mu''\mu'''}(k;E).$$

(2.26)

The resulting Green function can be transformed back to the real space by

$$G_{LL'}^{n'n'n'}(k;E) = \frac{1}{V_{BZ}} \int_{V_{BZ}} d\mathbf{k} e^{i(kR^n-R'^n)}G^{\mu\mu'}(k;E),$$

(2.27)

where $V_{BZ}$ is the volume of the Brillouin zone. The real-space structure constants are relevant to solve the impurity problem. In the KKR method the unknown system could be solved via the
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Dyson equation starting from the free-space Green function, \( G_{LL'}^{n_1n_1'} \), in reciprocal space. To solve the problem computationally efficiently a special reference system is introduced leading to the screened KKR method (or tight-binding KKR) [124]. In the screened KKR method the Dyson equation is modified to

\[
G_{LL'}^{n_1n_1'} = G_{LL'}^{\text{ref},nn'}(E) + \sum_{n''} \sum_{L'',L'''} G_{LL'}^{\text{ref},nn''}(E) \Delta t_{L''L'''}^n(E) G_{L''L'''}^{n''n'''}(E),
\]  

(2.28)

where \( G_{LL'}^{n_1n_1'} \) is the unknown system, \( G_{LL'}^{\text{ref},nn'}(E) \) is the Green function of the reference system, a repulsive constant potential at each atomic site, and \( \Delta t_{L''L'''}^n = t_{L''L'''}^{n''} - t_{L''L'''}^{\text{ref},n''} \) is the difference of the t-matrices between the real and the reference system. In the standard formalism the effort of calculating the Green function scales with \( O(N^3) \) where \( N \) is the number of atoms in the cluster. The number of elements of \( G_{LL'}^{\text{ref},nn'} \) is proportional to \( N^2 \) and the sum over \( n'' \) drives the calculation effort to scaling of \( N^3 \), which is a large requirement for computational memory and time. The screened KKR method introduces the scattering path operator (or so-called inverse of the KKR matrix),

\[
\Delta \tau = \left[ (\Delta t)^{-1} - G_{\text{ref}}^{-1} \right],
\]  

(2.29)

to reformulate the Dyson equation in terms of \( \Delta \tau \) as

\[
G(E) = G_{\text{ref}}^\text{ref}(E) + G_{LL'}^{\text{ref}}(E) \Delta t G_{LL'}^{\text{ref}}(E) + G_{LL'}^{\text{ref}}(E) \Delta t G_{LL'}^{\text{ref}}(E) \Delta t G_{LL'}^{\text{ref}}(E) + \cdots
\]

(2.30)

Here, for convenience the Dyson equation [eq. (2.28)] is expressed in matrix notation by \( g(E) = \{ g_{LL'}^{nn'}(E) \} \), \( G(E) = \{ G_{LL'}^{nn'}(E) \} \) and \( \Delta t(E) = \{ \Delta t_{LL'}^{nn'}(E) \} \). This reformulated Dyson equation is comparable to Eq. (2.17) with the replacement \( t \rightarrow \Delta \tau \). The Green function of the screened system decays faster than the Green function of free-space [124], thus the calculation effort can be decreased. For instance, it scales with \( O(N) \) if the interaction from the second nearest site can be neglected [124].

So far I have introduced the whole process of solving the electronic structures via DFT using the KKR Green function method. For clearly exhibiting the process, the self-consistent cycle is shown in Fig. 2.4 in detail. The procedure of the full calculation is following:

1. Using the starting potential \( V_{\text{ins}} \) as well as the reference potential \( V_{\text{ref}} \) to calculate the individual on-site scattering solutions \( R_{L}^{n}(r_-,E) \) and \( H_{L}^{n}(r_+,E) \).

2. Using the on-site scattering solutions \( R_{L}^{n}(r_-,E) \) and \( H_{L}^{n}(r_+,E) \) to calculate the individual t-matrices \( t_{L,L'}^{nn'} \).

3. Using the t-matrices \( t_{L,L'}^{nn'} \) to calculate the difference of the t-matrix \( \Delta t_{L,L'}^{nn'} \).

4. Using the t-matrix \( t_{L,L'}^{\text{ref},nn'} \) of the reference system and the free-space Green function \( g_{LL'}^{nn'} \) to calculate the Green function of the reference system, \( G_{LL'}^{\text{ref},nn'} \), via Eq. (2.28).
5. Using the Green function $G_{LL'}^{\text{ref},n,n'}$ and the difference of t-matrix $\Delta t_{L'L}^{n,n'}$ to calculate the structural Green function $G_{LL'}^{n,n'}$.

6. Calculating the full Green function $G(R^n + r, R^{n'} + r'; E)$ by combining the on-site scattering solutions $R_L^n(r<E), H_L^n(r>E)$ and the structural Green function $G_{LL'}^{n,n'}$.

7. Calculating the charge density $n(r)$ via the energy integral of the imaginary part of the Green function.

8. Using the charge density to calculate the effective potential $V_{\text{eff}} = V_{\text{out}}$ via Eq. (2.6).

9. Checking whether the resulting potential $V_{\text{out}}$ is equal to the starting potential $V_{\text{in}}$.

10. If no, mixing the potentials $V_{\text{in}}$ and $V_{\text{out}}$ to create a new starting potential $V_{\text{in}}$ and repeating the step 1 to 9.

11. If yes, the calculation converged.
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![Diagram showing the self-consistent cycle in the KKR Green method](image)

- $V^{\text{in}}(r)$
- $V^{\text{ref}}(r)$

**KKR method**

- On-site radial wavefunctions $R^n_L(r; E)$, $H^n_L(r; E)$
- On-site radial wavefunctions $R^{\text{ref}, n}_L(r; E)$, $H^{\text{ref}, n}_L(r; E)$

- $t^{n'}_{L''L'''}$
- $t^{\text{ref}, n'''}_{L''L'''}$

- $\Delta t^{n''}_{L''L'''} = t^{n''}_{L''L'''} - t^{\text{ref}, n'''}_{L''L'''}$

- $G^{\text{ref}, n' n''}_{L' L'}(E)$ from $g^{n' n''}_{L' L'}(E)$

**Equation**

\[ G^{n' n''}_{L L'}(E) = G^{\text{ref}, n' n''}_{L L'}(E) + \sum_{n'''} G^{\text{ref}, n' n''}_{L' L'}(E) \Delta t^{n''}_{L''L'''}(E) G^{n'' n'''}_{L'' L'''}(E) \]

\[ G(r^n + r, r^{n'} + r'; E) = -i\sqrt{E} \sum_L R^n_L(r; E) H^n_L(r; E) \delta_{nn'} \]

\[ + \sum_{L, L'} R^n_L(r; E) G^{n' n''}_{L' L'}(E) R^n_{L'}(r'; E), \]

**Green function approach**

\[ n(r) = -\frac{2}{\pi} \int_{-\infty}^{E_F} dE \text{Im} G(r, r'; E) \]

Solving the effective potential Eq. (2.6) to obtain $V^{\text{eff}}(r)$ as $V^{\text{out}}(r)$

**DFT**

No, mixing $V^{\text{out}}(r)$ and $V^{\text{in}}(r)$ to create new $V^{\text{in}}(r)$

Yes

**Calculation converged**

Figure 2.4: Illustration of the self-consistent cycle in the KKR Green method.
2.1.4 Relativistic density functional theory

We have introduced DFT to solve many-electron problems based on the Schrödinger equation. To solve the electronic structure for heavy materials, the relativistic effects and spin-orbit coupling have to be taken into account. Here we have to start with the fully relativistic Dirac equation instead of the Schrödinger equation and the latter will add coupling terms between the orbital and the spin moments of the electron.

Starting with the Dirac equation for an electron with charge $e$ and rest mass $m$ in a potential $V(r)$, the Hamiltonian is written as

$$ \hat{H} = -eV(r) + c\mathbf{a} \cdot (\mathbf{p} + e\mathbf{A}) + \beta mc^2 $$  \hspace{1cm} (2.31)

and simplified into [117]

$$ \hat{H} = c\mathbf{a} \cdot \mathbf{p} + \beta mc^2 + V_{\text{eff}}(r)\mathbf{I}_4 + \beta \Sigma \cdot \mathbf{B}_{\text{eff}}(r). $$  \hspace{1cm} (2.32)

The effective electric and magnetic field are generated from the exchange-correlation potential functional of the charge density $n(r)$ and the magnetisation density $m(r)$, which are written as

$$ V_{\text{eff}}(r) = V_{\text{ext}}(r) + \int \frac{e^2 n(r')}{|r - r'|} d\mathbf{r}' + \frac{\partial E_{\text{xc}}[n(r), m(r)]}{\partial n(r)}, $$  \hspace{1cm} (2.33)

$$ \mathbf{B}_{\text{eff}}(r) = \mathbf{B}_{\text{ext}}(r) + \frac{\partial E_{\text{xc}}[n(r), m(r)]}{\partial m(r)}. $$  \hspace{1cm} (2.34)

Here, $\mathbf{a}$ and $\Sigma$ are a set of matrices $a_k(k=1,2,3)$ and $\Sigma_k(k=1,2,3)$, respectively,

$$ a_k = \begin{pmatrix} 0 & \sigma_k \\ \sigma_k & 0 \end{pmatrix} \quad \text{and} \quad \Sigma_k = \begin{pmatrix} \sigma_k & 0 \\ 0 & \sigma_k \end{pmatrix}, $$  \hspace{1cm} (2.35)

where $\sigma_k(k=1,2,3)$ are the Pauli spin matrices ($\sigma_x, \sigma_y, \sigma_z$), and $\beta$ is a $4 \times 4$ matrix

$$ \beta = \begin{pmatrix} \mathbf{I}_2 & 0 \\ 0 & -\mathbf{I}_2 \end{pmatrix}, $$  \hspace{1cm} (2.36)

with $\mathbf{I}_2$ the $2 \times 2$ unit matrix.

In the Dirac equation, including SOC the spin angular momentum is no longer a good quantum number. The Hamiltonian $\hat{H}$ does not commute with the orbital angular momentum operator $\hat{\mathbf{L}}$ nor the spin angular momentum operator $\hat{\mathbf{S}}$. The new operator formed by $\hat{\mathbf{L}}$ and $\hat{\mathbf{S}}$ is $\hat{\kappa} = \beta \left( \frac{\hat{\mathbf{L}}}{\hbar} + 1 \right)$, and the solutions of the Dirac equation are written in the form

$$ \psi = \sum_{k m_j} \left( g_{k m_j}(r) \chi_{k m_j}(\mathbf{r}) \right). $$  \hspace{1cm} (2.37)

Here, $g_{k m_j}(r)$ and $f_{k m_j}(r)$ are radial functions, and $\chi_{k m_j}(\mathbf{r})$ and $\chi_{-k m_j}(\mathbf{r})$ are two component spin-angle functions related to the operator $\kappa$,

$$ \chi_{k m_j} = \sum_{s = \pm \frac{1}{2}} \langle l, \frac{1}{2}, m_l, m_s = \frac{1}{2} | j m_j \rangle Y_{l, m_l}(|\mathbf{r}|) \psi_{s, m_s}, $$  \hspace{1cm} (2.38)
where \((l, \frac{1}{2}, m_l, m_{s-\frac{1}{2}} | jm_j)\), \(Y_{l,m_l}(\hat{r})\) and \(\psi_{s,m_s}\) are the Clebsch-Gorden coefficients, complex spherical harmonics and spin eigenfunctions, respectively.

The total angular momentum \(\mathbf{J} = \mathbf{L} + \mathbf{S}\) commutes with the Hamiltonian, which is a suitable operator. The eigenfunctions and eigenvalues of \(\mathbf{J}^2\), \(J_z\) and \(\hat{k}\) are written as

\[
\begin{align*}
\mathbf{J}^2 \chi_{km_j} &= j(j+1)\hbar^2 \chi_{km_j}, \\
J_z \chi_{km_j} &= m_j\hbar \chi_{km_j}, \\
\hat{k} \chi_{km_j} &= -\kappa \hbar \chi_{km_j}.
\end{align*}
\]

(2.39)

So far we have focused on the fully-relativistic Dirac equation implemented in the normal state. An often useful simplification ignoring SOC but keeping scalar relativistic corrections is the scalar relativistic approximation (SRA), proposed by Koelling and Harmon [125]. In the SRA screened-KKR method, we first solve the modified Schrödinger equation [117] to obtain the wave functions where \(l\) and \(s\) are good quantum numbers and the basis set of wave function is written as

\[
\begin{pmatrix}
g(s(r)\chi_{km_j}(\hat{r})) \\
i\ell(r)\chi_{-km_j}(\hat{r}) \\
i\ell(r)\chi_{-km_j}(\hat{r}) \\
\end{pmatrix} \rightarrow \begin{pmatrix}P_l(r)Y_{l,m_l}(\hat{r})\chi_{s,m_s} \\
Q_l(r)Y_{l,m_l}(\hat{r})\chi_{s,m_s}\end{pmatrix},
\]

(2.40)

where \(l\) and \(l'\) are corresponding to \(\kappa - 1\) if \(\kappa > 0\) and to \(-\kappa\) if \(\kappa < 0\), respectively. The radial wave functions, \(P_l(r)\) and \(Q_l(r)\) are derived from the radial modified Schrödinger equation and the angular parts in the basis set are decoupled spherical harmonics \(Y_{l,m_l}(\hat{r})\) and the spin eigenvector \(\chi_{s,m_s}\).

### 2.1.5 Superconducting density functional theory (SCDFT)

Density functional theory can be extended to the superconducting state by considering the paring potential of the BCS theory as additional effective potential in the Kohn-Sham equations, as proposed by L. N. Oliveira, E. K. U. Gross and W. Kohn [126]. The implementation of the description of the superconducting state into the existing KKR code was done by Tom G. Saunderson [13] and details can be found in his thesis [127]. All calculations presented in the following will be based on the scalar-relativistic version of the solver.

Using DFT for the superconducting state, the effective potential \(V_{\text{eff}}\) and the pairing interaction \(\Delta V_{\text{eff}}\) are written as

\[
V_{\text{eff}}(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\partial E_{\text{xc}}[n(\mathbf{r}), \chi(\mathbf{r}, \mathbf{r}')]}{\partial n(\mathbf{r})}
\]

(2.41)

and

\[
\Delta_{\text{eff}}(\mathbf{r}, \mathbf{r}') = \frac{\partial E_{\text{xc}}[n(\mathbf{r}), \chi(\mathbf{r}, \mathbf{r}')] }{\partial \chi(\mathbf{r}, \mathbf{r}')} ,
\]

(2.42)

where \(\chi(\mathbf{r}, \mathbf{r}')\) is the anomalous density. The pairing interaction \(\Delta_{\text{eff}}(\mathbf{r}, \mathbf{r}')\) is considered in the exchange-correlation energy [128]

\[
E_{\text{xc}}[n, \chi] = E_{\text{xc}}^0[n] - \int d^3r_1 d^3r_2 d^3r'_1 d^3r'_2 \chi(\mathbf{r}_1, \mathbf{r}_1') \chi(\mathbf{r}_2, \mathbf{r}_2') \chi(\mathbf{r}_1, \mathbf{r}_1') \Lambda[n, \chi](\mathbf{r}_1, \mathbf{r}_1', \mathbf{r}_2, \mathbf{r}_2'),
\]

(2.43)
where \( E_{xc}^0[n] \) is the normal state exchange-correlation energy. \( \Lambda[n, \chi](\mathbf{r}_1, \mathbf{r}_1', \mathbf{r}_2, \mathbf{r}_2') \) is the kernel, pairing two electrons, and in ASA it is approximated as [13]

\[
\Lambda[n, \chi](\mathbf{r}_1, \mathbf{r}_1', \mathbf{r}_2, \mathbf{r}_2') = \Lambda \delta(\mathbf{r}_1 - \mathbf{r}_1') \delta(\mathbf{r}_1 - \mathbf{r}_2) \delta(\mathbf{r}_1 - \mathbf{r}_2')
\]  

(2.44)

inside the ASA spheres and set to zero outside. Here \( \Lambda \) is the so-called interaction parameter. Another simplification following from the form of chosen the kernel is

\[
\begin{align*}
\Delta_{\text{eff}}(\mathbf{r}, \mathbf{r}') &= \Delta_{\text{eff}}(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}') \\
\chi(\mathbf{r}, \mathbf{r}') &= \chi(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}')
\end{align*}
\]

(2.45)

reducing the interaction potential to

\[
\Delta_{\text{eff}}(\mathbf{r}) = \Lambda \chi(\mathbf{r}).
\]

(2.46)

In the ASA approximation the potential \( V_{\text{eff}} \) and \( \Delta_{\text{eff}} \) are analogous to Eq. (2.19) written as

\[
\begin{align*}
V_{\text{eff}}(\mathbf{r}) &= \sum_i V_i(\mathbf{r}) \\
\Delta_{\text{eff}}(\mathbf{r}) &= \sum_i \Delta_i(\mathbf{r})
\end{align*}
\]

(2.47)

a sum overall atomic positions if \( |\mathbf{r}| < r_i^{\text{ASA}} \) and zero outside. All quantities related to the pairing interaction will scale with the tuned interaction parameter \( \Lambda \). The procedure to find suitable values for different superconductors is discussed in detail in Ref. [13].

So far we have introduced the external potential and the anomalous density for the superconducting state. To solve the wave functions using the KKR method the Bogoliubov-de Gennes equations are implemented [129] and the corresponding Green function is a 2×2 matrix defined as

\[
\hat{G}_{\text{BdG}}(z) = \begin{pmatrix} \hat{G}^{ee}(z) & \hat{G}^{eh}(z) \\ \hat{G}^{he}(z) & \hat{G}^{hh}(z) \end{pmatrix} = (z\hat{I} - \hat{\mathcal{H}}_{\text{BdG}})^{-1},
\]

(2.48)

where

\[
\hat{\mathcal{H}}_{\text{BdG}}(\mathbf{r}) = \begin{pmatrix} \hat{H}(\mathbf{r}) & \Delta_{\text{eff}}(\mathbf{r}) \\ \Delta_{\text{eff}}^*(\mathbf{r}) & -\hat{H}(\mathbf{r})^* \end{pmatrix}
\]

(2.49)

\( \hat{H}(\mathbf{r}) \) is the single electron Hamiltonian. \( \hat{G}^{ee}(z) \) and \( \hat{G}^{hh}(z) \) represent the electron and hole Green functions, respectively, and \( \hat{G}^{he}(z) \) and \( \hat{G}^{eh}(z) \) are the Green functions describing the pairing interaction. Here \( z = E + i\epsilon \) is the usual complex energy with positive infinitesimal \( \epsilon - 0^+ \). The normal and anomalous density, \( n(\mathbf{r}) \) and \( \chi(\mathbf{r}) \), can be calculated by the energy integral of the Green functions

\[
n(\mathbf{r}) = -\frac{1}{\pi} \int_{-\infty}^{\infty} dE f(E) \text{Im} \text{Tr} \hat{G}^{ee}(E, \mathbf{r}, \mathbf{r}') - \frac{1}{\pi} \int_{-\infty}^{\infty} dE [1 - f(E)] \text{Im} \text{Tr} \hat{G}^{hh}(E, \mathbf{r}, \mathbf{r}'),
\]

(2.50)

\[
\chi(\mathbf{r}) = -\frac{1}{4\pi} \int_{-\infty}^{\infty} dE [1 - 2f(E)] \text{Im} \text{Tr} \hat{G}^{eh}(E, \mathbf{r}, \mathbf{r}') - \frac{1}{4\pi} \int_{-\infty}^{\infty} dE [1 - 2f(E)] \text{Im} \text{Tr} \hat{G}^{he}(E, \mathbf{r}, \mathbf{r}').
\]

(2.51)

The effective normal and pairing potentials can be calculated from these two densities and the self-consistent cycle is followed as sketched in Fig. 2.4.
2.1.6 Band structure, eigenvalue and Fermi velocity

In the previous sections the theory to find the correct normal and superconducting state potentials has been introduced. In the following I will discuss the numerical procedures to extract the physical observables such as eigenvalues, the band structure and Fermi velocities, which are all relevant input parameters for the next step, the transport calculations.

2.1.6.1 Band structure

By the continuity condition of the single-site scattering wave function [Eq. (2.22)] and its differential at the boundary \( R_{\text{ASA}} \), the so-called KKR secular equation is derived

\[
\sum_{\mu} \sum_{Q} \left( \delta_{\mu} \delta_{Q} - G_{Q}^{\mu} \left( k; E \right) \Delta t_{Q}^{\mu} \left( E \right) \right) c_{Q}^{\mu}(k) = 0. \tag{2.52}
\]

Here the generalised relativistic form is used with \( Q \) the set of angular momentum quantum numbers \( \{ \kappa, m_j \} \). To express it explicitly as an eigenvalue problem, the equation is transformed to

\[
\sum_{\mu} M_{Q}^{\mu} \Delta t_{Q}^{\mu} c_{Q}^{\mu}(k) = 0, \tag{2.53}
\]

where \( M_{Q}^{\mu} \) is the KKR matrix\n
\[
M_{Q}^{\mu} = G_{Q}^{\mu} - \delta_{\mu} \left[ \Delta t^{-1} \right]_{Q}. \tag{2.54}
\]

For convenience the eigenvalue equation is written in matrix form

\[
M(k; E) \Delta t(E) c(E) = \lambda(k; E) \Delta t(E) c(E). \tag{2.55}
\]

and the band structure is defined by the points for which the eigenvalues are zero \( \lambda(k; E) = 0 \).

However, the KKR matrix is a non-Hermitian matrix. The implemented transformation from the non-hermitian to the hermitian matrix is detailed in Peter Zahn's dissertation [130], which is discussed in appendix B.1. The new hermitian eigenvalue equation is reformulated as

\[
\tilde{M}(k; E) c(E, k) = \tilde{\lambda}(k; E) c(E, k), \tag{2.56}
\]

where \( \tilde{M}(k; E) \), \( \tilde{c} \) and \( \tilde{\lambda}(k; E) \) are defined in appendix B.1. The electronic band structure \( E_{k} \) is thus defined by finding the roots of the function \( \lambda(k, E) \).

2.1.6.2 Fermi velocity and surface

For the semiclassical transport theory the Fermi velocity is an essential property. We obtain the Fermi velocity \( v_F \) by the numerical \( k \) derivative written as

\[
v_F(k) = \frac{1}{\hbar} \left. \frac{dE(k)}{dk} \right|_{E_F}. \tag{2.57}
\]
In practice we find the iso energy surfaces slightly above and below the Fermi surface for a given infinitesimal value $\delta E$. To do that we create tetrahedra filling the Brillouin zone as sketched in Fig. 2.5. The $k$ points corresponding to the surfaces above, below, and at the Fermi surface are written as

$$k_1^{+}, k_2^{+}, k_3^{+} : E_F + \delta E,$$

$$k_1^{F}, k_2^{F}, k_3^{F} : E_F,$$

$$k_1^{-}, k_2^{-}, k_3^{-} : E_F - \delta E.$$

Finding the $k$ points, the Fermi velocity can be evaluated by

$$\hbar (k_i^{+} - k_i^{-}) v_F = 2\delta E,$$

where $i = 1, 2, 3$. The accuracy of this numerical method depends on the number of tetrahedra in the Brillouin zone. For a complex Fermi surface such as Pt and U atoms, the number of tetrahedra required is higher than for simple metals such as Cu and Au.

![Figure 2.5: Schematic illustration of a tetrahedron used for the numerical deviation of the Fermi velocity.](image)

Separate from the numerical $k$ derivative method, we utilise a method based on an analytic $k$ derivative, firstly proposed by N. A. Shilkova, V. P. Shirokovskii and N. A. Trubitsina [131, 132], to calculate the Fermi velocity, which is discussed in Appendix B.2.

### 2.1.6.3 Wave functions and transition operator in the impurity systems

In the previous sections we discussed the structural constants, Fermi velocity and band structure calculations. To describe the scattering, the transition probability, in the impurity system, the wave functions of the perturbed system is essential. However, unlike the unperturbed system, where a Bloch wave function can be considered in the reciprocal space, the perturbed wave function is expressed by a Lippman-Schwinger equation, starting from the unperturbed wave of the ideal crystal.
Starting from the eigenvalue equation of the ideal crystal, the single-site wave function at each atom is expressed as a Bloch wave [117, 133]

\[
\psi_{\mathbf{k}}^{n\mu}(\mathbf{r}) = \frac{1}{\sqrt{V}} \sum_{Q} e^{i\mathbf{k}\cdot\mathbf{R}_Q} c_{Q}^{n\mu}(\mathbf{k}) \tilde{R}_Q^{n\mu}(\mathbf{r}),
\]

with \( \tilde{R}_Q^{n\mu}(\mathbf{r}) = \left( \begin{array}{c} g_Q^{R}(r) \chi_Q(r) \\ i f_Q^{R}(r) \chi_Q(\mathbf{r}) \end{array} \right) \) at site \((n, \mu)\).

Here, \( V \) is the normalization volume, the superscript \( R \) stands for the regular solutions, and \( Q = (\kappa, m_j) \) and \( \mathbf{Q} = (-\kappa, m_j) \). The perturbed wave is written as

\[
\psi_{\mathbf{k}}^{n\mu}(\mathbf{r}) = \frac{1}{\sqrt{V}} \sum_{Q} c_{Q}^{n\mu}(\mathbf{k}) \tilde{R}_Q^{n\mu}(\mathbf{r}),
\]

with the expansion coefficient \( c_{Q}^{n\mu}(\mathbf{k}) \) derived from the unperturbed system via the Lippman-Schwinger equation

\[
c_{Q}^{n\mu}(\mathbf{k}) = c_{Q}^{n\mu}(\mathbf{k}) + \sum_{n'Q} G_{QQ'}^{nn'} \Delta_{Q}^{n\mu'} c_{Q'}^{n'\mu'}(\mathbf{k}).
\]

To simplify the notation

\[
c_{Q}^{n\mu}(\mathbf{k}) = \sum_{n'Q'} D_{QQ'}^{nn',\mu\mu'} c_{Q'}^{n'\mu'}(\mathbf{k})
\]

we introduced

\[
D_{QQ'}^{nn',\mu\mu'} = \delta_{nn'} \delta_{\mu\mu'} \delta_{QQ'} + \sum_{Q''} G_{QQ''}^{nn',\mu\mu'} \Delta_{Q''}^{n\mu'}.
\]

Therefore, the transition matrix of the impurity system is obtained in terms of the unperturbed and perturbed states as

\[
T_{kk'} = \sum_{n\mu} \int d^3\mathbf{r} \left( \psi_{\mathbf{k}}^{n\mu}(\mathbf{r}) \right)^* \Delta V^{n\mu}(\mathbf{r}) \psi_{\mathbf{k'}}^{n\mu}(\mathbf{r})
\]

\[
= \frac{1}{V} \sum_{n\mu QQ'} \left( c_{Q}^{n\mu}(\mathbf{k}) \right)^* \Delta_{Q}^{n\mu} c_{Q'}^{n\mu}(\mathbf{k})
\]

\[
= \frac{1}{V} \sum_{n\mu QQ'} \sum_{n'\mu'} D_{QQ'}^{nn',\mu\mu'} \left( c_{Q'}^{n'\mu'}(\mathbf{k}) \right)^* \Delta_{Q'}^{n\mu'} D_{QQ'}^{nn',\mu'\mu'} c_{Q'}^{n'\mu'}(\mathbf{k'}),
\]

where the \( \Delta_{Q}^{n\mu} \) matrix is a radial integral over the perturbed and unperturbed radial solutions,

\[
\Delta_{QQ'}^{nn'} = \int_{0}^{R_{ASA}} d^2 r \left( \tilde{R}_Q^{n\mu}(\mathbf{r}) \right)^* \Delta V^{n\mu}(\mathbf{r}) \tilde{R}_Q^{n\mu}(\mathbf{r}).
\]

Thus, the transition probability is given by Fermi’s golden rule as [6, 56, 130]

\[
P_{kk'} = \frac{2\pi}{\hbar} |T_{kk'}|^2 \delta(E_k - E_{k'}).
\]
2.1.7 Spin expectation value

In spin-dynamic, understanding the spin direction of a state is essential for comparison to experiments. For instance, the spin direction of the spin current in spin-pumping experiments is in plane to the interface. Within the density functional theory using the Kohn-Sham-Dirac equation discussed in Eq. (2.32) [71], the term $\beta \Sigma \cdot \mathbf{B}_{\text{eff}}$ represents the energy of the interaction between the electron spin and the effective magnetic field, thus the spin operator is defined as

$$\beta \Sigma = \begin{pmatrix} \sigma & 0 \\ 0 & -\sigma \end{pmatrix},$$

where $\sigma$ is a set of Pauli matrices $\sigma_k$ ($k = x, y, z$). In the non-relativistic theory the spin angular momentum commutes with the orbital angular momentum, thus the quantisation axis for the spin-up and spin-down states can be in an arbitrary direction independent of the radial wave function. However, in the relativistic case the radial wave function is coupled to the spin-angular momentum as discussed in Section 2.1.4. Assuming time-reversal symmetry and spatial inversion symmetry of the Hamiltonian, the two orthonormal states with opposite spin direction, $|\Psi^+\rangle$ and $|\Psi^-\rangle$, are two-fold degenerate. In order to choose a particular spin direction we can take a linear combination of the two wave functions $|\Psi^+\rangle$ and $|\Psi^-\rangle$. The transformed wave functions can be written as

$$|\Psi^3\rangle = c_1|\Psi^+_k\rangle + c_2|\Psi^-_k\rangle,$$

$$|\Psi^4\rangle = -c_2^*|\Psi^+_k\rangle + c_1^*|\Psi^-_k\rangle,$$

with the normalisation conditions

$$\langle \Psi^3|\Psi^3\rangle = \langle \Psi^4|\Psi^4\rangle = 1,$$

$$\langle \Psi^3|\Psi^4\rangle = 0.$$

The coefficients $c_1$ and $c_2$ are chosen such that the spin orientation may point in any direction. Rotating the spin in the $z$ direction the condition will be that the spin polarisation along the $x$ and $y$ directions are zero

$$\langle \Psi^3|\beta \Sigma_x|\Psi^3\rangle = \langle \Psi^3|\beta \Sigma_y|\Psi^3\rangle = 0,$$

$$\langle \Psi^4|\beta \Sigma_x|\Psi^4\rangle = \langle \Psi^4|\beta \Sigma_y|\Psi^4\rangle = 0.$$

The spin expectation value of the $z$ component of the spin on the Fermi surface, $P^z_k$, can be calculated by

$$P^z_k = \langle \Psi^+_k|\beta \Sigma_z|\Psi^+_k\rangle = -\langle \Psi^-_k|\beta \Sigma_z|\Psi^-_k\rangle,$$

where we label the two spin states $|\Psi^3_k\rangle$ and $|\Psi^4_k\rangle$ as $|\Psi^+_k\rangle$ and $|\Psi^-_k\rangle$ according to their relative spin direction. In the nonrelativistic cases, these two states correspond to the pure spin-up $|\Psi^+_k\rangle = |\Psi^+_k\rangle$ and spin-down $|\Psi^-_k\rangle = |\Psi^-_k\rangle$ states. Further details of the practical implementation are discussed in Appendix B.3.
2.2 Electronic transport

So far I discussed how the various physical observables can be obtained from the electronic structure calculations within the DFT framework. For the transport calculations including the intrinsic and extrinsic mechanisms for the spin Hall effect we use the semiclassical transport theory based on the Berry curvature and the Boltzmann equation. The theoretical framework as well as the computational implementation will be discussed in the following.

2.2.1 Spin relaxation

In reality the spin current can be forced in a certain direction, but without further external force the spin polarisation will decay during transport. Understanding this decay is critical for investigating, for instance, the spin accumulation and the spin currents. In our calculation the spin-relaxation process considered is the Elliott-Yafet mechanism, the dominant effect at zero temperature [134, 135], as the electron-phonon interaction can be ignored. Due to the Kramer degeneracy, the presence of time-reversal symmetry and inversion symmetry in our systems, the relativistic wave functions are twofold degenerate at each \( k \) point. This means the two states with opposite spin direction have the same energy. Expressing the spin flip explicitly, Eq. (2.69) can be re-written as

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

where \( E_k^+ \) and \( E_{k'}^- \) are the same energy with opposite spin direction. \( T_{kk'}^{+-} \) represents the spin-up scattered into spin-down and vice versa. The \( k \)-dependent spin relaxation time can be calculated through a sum over all scattering states as

\[
\frac{1}{\tau_{sf}^k} = \sum_{k'} P_{kk'}^{+-}.
\]

The averaged spin relaxation time on the Fermi surface can be expressed as

\[
\frac{1}{\tau_{sf}} = \frac{V}{(2\pi)^3} \sum_{n} \iint dS_n \frac{1}{|v_{kn}| \tau_{sf}^n},
\]

where \( n \) is the band index. To compare the theoretical and experimental results, the spin-diffusion length, the typically observed quantity in experiments, can be calculated from the spin-relaxation time as [101]

\[
l_{sf} = \sqrt{\frac{3\pi}{2}} \frac{\sigma_{xx}}{k_F^2 G_0} \sqrt{\frac{\tau_{sf}^n}{\tau}}.
\]

Here, \( k_F \), \( G_0 \) and \( \sigma_{xx} \) are the averaged Fermi wave vector, the conductance quantum \( \frac{2e^2}{h} \) and the longitudinal charge conductivity, respectively. Furthermore, the momentum relaxation time \( \tau \) can be calculated by Eq. (2.75) conserving the spin (++) instead of (+-).
2.2.2 Intrinsic transport

The spin conductivity in case of the intrinsic spin Hall effect can be derived from the unperturbed Bloch states via an integral over the Brillouin zone of the non-Abelian Berry curvature \[ \sigma_{yx}^+ = -\frac{e^2}{h} \sum_n \int_{BZ} \frac{d\mathbf{k}}{(2\pi)^3} f_n(E_F, \mathbf{k}) \Omega_n^{z+}(\mathbf{k}) \] (2.79)

where \( f_n(E_F, \mathbf{k}) \) is the distribution function and \( \Omega_n^{z+}(\mathbf{k}) \) is the \( z \) component of the non-Abelian Berry curvature given by

\[
\Omega_{ij}^+(\mathbf{k}) = i \left\langle \nabla_{\mathbf{k}} u_{ik}^+ | \times | \nabla_{\mathbf{k}} u_{jk}^+ \right\rangle - i \sum_{l \in \Sigma} \left\langle \nabla_{\mathbf{k}} u_{ik}^+ | u_{lk}^+ \right\rangle \times \left\langle u_{jk}^+ | \nabla_{\mathbf{k}} u_{lk}^+ \right\rangle .
\] (2.80)

The states \( i \) and \( j \) are from the set of degenerate states \( \Sigma \) of band \( n \) and \( u_{nk}^+ \) is the periodic part of the Bloch states. Here, "+" denotes the spin up in the degenerate Bloch band and \( \Omega_n^{z+}(\mathbf{k}) = -\Omega_n^{z-}(\mathbf{k}) \) is provided by the Kramer degeneracy. Further details of the derivation of the spin conductivity can be found in Ref. [35]

2.2.3 Extrinsic transport

2.2.3.1 Linearised Boltzmann equation

The spin-dependent transport arising from the scattering mechanism is calculated via the semiclassical Boltzmann equation. In the steady state the Boltzmann equation describing the transport of electrons with charge \( -e \) can be written as

\[
\frac{df_{\mathbf{k}}}{dt} = -\left. \frac{\partial f_{\mathbf{k}}}{\partial t} \right|_{\text{scatt}} - \left. \frac{\partial f_{\mathbf{k}}}{\partial \mathbf{r}} \right|_{\text{diff}} - \left. \frac{\partial f_{\mathbf{k}}}{\partial \mathbf{k}} \right|_{\text{force}} = 0 ,
\] (2.81)

where the terms "scatt", "diff" and "force" represent the distribution function \( f_{\mathbf{k}} \) changed by the "scattering", "diffusion" and "external force", respectively. For small deviations from the equilibrium distribution \( \hat{f}_{\mathbf{k}} \) we may write

\[
\hat{f}_{\mathbf{k}} = \hat{f}_{\mathbf{k}} + g_{\mathbf{k}},
\] (2.82)

where \( \hat{f}_{\mathbf{k}} \) is the Fermi Dirac distribution

\[
\hat{f}_{\mathbf{k}} = \frac{1}{e^{(\mathbf{k} - \mu)/T} + 1}
\] (2.83)

and \( g_{\mathbf{k}} \) is the perturbation, out of equilibrium.

In a homogeneous electrical field where electrons are uniformly distributed the diffusion term can be neglected. The scattering term is considered as the elastic scattering (\( E_{\mathbf{k}} = E_{\mathbf{k}'} \))

\[
\left. \frac{\partial f_{\mathbf{k}}}{\partial t} \right|_{\text{scatt}} = \sum_{\mathbf{k}'} f_{\mathbf{k}'} (1 - f_{\mathbf{k}'} P_{\mathbf{k}' \mathbf{k}} - f_{\mathbf{k}} (1 - f_{\mathbf{k}'}) P_{\mathbf{k} \mathbf{k}'},
\] (2.84)

\[
= \sum_{\mathbf{k}'} P_{\mathbf{k}' \mathbf{k}} (g_{\mathbf{k}'} - g_{\mathbf{k}})
\]
assuming the transition probability of scattering-out \( P_{kk'} \) and scattering-in \( P_{kk'} \) are reversible as a result of time reversal [136]. The assumption is correct in first order of the impurity potential whereas the skew scattering contribution discussed in Eq. (1.26) will enter in third order only [78]. The force term is expressed as

\[
\frac{\partial f_k}{\partial k} \frac{dk}{dt} \bigg|_{\text{force}} = -eE \left( \frac{\partial f_k}{\partial E_k} + \frac{\partial g_k}{\partial E_k} \right) \nu_k = -eE \frac{\partial f_k}{\partial E_k} \nu_k,
\]

with \(-eE = \hbar \frac{dk}{dt}\) and \(\nu_k = \frac{1}{\hbar} \frac{\partial E_k}{\partial k}\). (2.85)

The perturbation term \(\frac{\partial g_k}{\partial E_k}\) in the external force can be neglected since it is of second order in electric field \(E\), while \(g_k\) is essential for the scattering term. The Boltzmann equation can be written as

\[
\frac{\partial f_k}{\partial t} + \frac{\partial f_k}{\partial k} \frac{dk}{dt} \bigg|_{\text{scatt}} = P_{kk'} (g_{k'} - g_k) - eE \frac{\partial f_k}{\partial E_k} \nu_k = 0.
\]

(2.87)

In the limit of linear response the proportionality of \(g_k \sim E\) is provided by the Ansatz

\[
g_k = -eE \frac{\partial f_k}{\partial E_k} \Lambda_k,
\]

(2.88)

where \(\Lambda_k\) is the mean free path. The linearised Boltzmann equation becomes

\[
\nu_k = \sum_k P_{kk'} (\Lambda_k - \Lambda_{k'}).
\]

(2.89)

Its solution is eventually expressed as an integral equation for the mean free path, by introducing the band index \(n\) it reads

\[
\Lambda^n_k = \tau^n_k \left( v^n_k + \sum_{n'k'} P^{nn'}_{kk'} \Lambda^n_{k'} \right),
\]

(2.90)

where the relaxation time \(\tau^n_k\) is written as

\[
\tau^n_k = \left[ \sum_{n'k'} P^{nn'}_{kk'} \right]^{-1}.
\]

(2.91)

The transition probability \(P_{kk'}(P_{kk'})\) in Eq. (2.69), in the screened KKR, describes the scattering at a single non-interacting impurity. In Eq. (2.90), the first term with anisotropic relaxation time contains the spin-conserving and spin-flipping contributions. The second term is the so-called scattering-in term that contains the skew scattering which is essential for the extrinsic SHE. It was shown by W. H. Butler [137, 138] that the scattering-in term derived in the Boltzmann equation is equivalent to the vertex correction induced by impurities in the dilute limit in the Kubo formula. Adding all individual scatterers via Matthiesens rule leads to [136, 139]

\[
P^{nn'}_{kk'} = \frac{2\pi}{\hbar} c_0 N |T^{nn'}_{kk'}|^2 \delta(E^n_k - E^n_{k'}),
\]

(2.92)

where \(c_0\) is the nominal impurity concentration and \(N\) is the number of atoms in the unit cell. For all our calculations this is fixed at \(c_0 = 1\) at. \% unless stated otherwise. In the spin-dependent transport \(P_{kk'}\) includes the spin flip marked as "\(P^+_-\)" and "\(P^-+\)" and spin conserving, "\(P^{++}\)" and "\(P^{--}\)" scattering, where the electrons transit in these four channels.
### 2.2.4 Charge and spin conductivity

After obtaining the mean free path from the linearised Boltzmann equation, we proceed to calculate the charge and spin conductivity. Here these conductivities are induced by the skew scattering. The charge conductivity $\sigma$ is derived from the definition of Ohm’s law,

$$j = \sigma E,$$

(2.93)

and from the distribution function $f_k$

$$j = -e \sum_k v_k f_k = -e \sum_k v_k (f_k + g_k) = e^2 \sum_k \frac{\partial f_k}{\partial E_k} v_k \Lambda_k E,$$

(2.94)

dropping the equilibrium distribution as it would be zero order in the electric field. Thus the charge and spin conductivity can be evaluated in tensor form as

$$\sigma = \frac{e^2}{\hbar} \sum_n \frac{1}{(2\pi)^3} \int_{E_k = E_F} dS_n \frac{|v_n|}{|v_k|} v_n \Lambda_n \Lambda_k,$$

(2.95)

and

$$\sigma^s = \frac{e^2}{\hbar} \sum_n \frac{1}{(2\pi)^3} \int_{E_k = E_F} dS_n |s_n^s(k)| v_n \Lambda_n,$$

(2.96)

respectively. The efficiency of charge-to-spin current conversion, the so-called spin Hall angle, can be calculated by

$$\theta = \frac{\sigma^s_{yx}}{\sigma^s_{xx}},$$

(2.97)

where $\sigma^s_{yx}$ and $\sigma^s_{xx}$ are the $yx$ component of $\sigma^s$ and the $xx$ component of $\sigma^s$, respectively. In addition, the connection between the scattering-in term in the Boltzmann equation and skew scattering is more discussed in Appendix C with perspective of calculating conductivity.

### 2.2.5 Spin accumulation

The mean free path from the linearised Boltzmann equation gives access to the skew-scattering induced spin accumulation by a similar integral as for the conductivity, but the host system is 2-dimensional. In our calculations we define the electrons with the spin polarisation in the $y$ direction travel in the $x$ direction, thus the electrons are deflected into the $z$ direction perpendicular to the surface. Here, we calculate the magnetisation $\chi_{xy}^i$ to describe the amount of spin accumulation at different atomic sites (layer index $i$) by [140, 141]

$$\chi_{xy}^i = \frac{e\mu_B}{\hbar} \sum_n \frac{V}{d(2\pi)^2} \int_{E_F} dS_n |v_n^i| s_{y,k} \Lambda_{x,k}^n,$$

(2.98)

where $\Lambda_{x,k}^n$ is the $x$ component of the anisotropic mean free path from Eq. (2.90). More discussions about the different contributions in the formula of the spin accumulation will be detailed in Chapter 4.
In this chapter, the descriptions of electronic structure and the spin-dependent transport for uranium will be presented. First, in Section 3.2 I will discuss the electronic structure of uranium. To highlight the importance of spin-orbit coupling in the $f$-electron heavy material, we calculate the band structure for uranium comparing fully relativistic and scalar relativistic KKR solvers. Uranium exists in several crystalline phases depending on the condition, which partially explains the extensive research into its physics. The electronic structure for the various phases are then calculated and compared. The resulting density of states are in good agreement with early work using other different theoretical methods, which establishes the accuracy of the simulated electronic structure as a basis for the further transport studies. Based on the electronic structure, the Bloch spectral function is calculated in order to estimate the wavelengths of quantum well states in $\alpha$-U. These values are in good agreement with experimental results [142].

For the intrinsic spin Hall effect in the various U phases, the theoretical spin conductivities, described by the Berry curvature, will be presented in Section 3.3 and are comparable to the standard spin Hall material Pt. In order to understand the influence of structure and orbital character of impurities on the extrinsic spin-dependent transport, Section 3.4 is dedicated to investigating the spin conductivities as well as spin Hall angles in the various uranium structures doped with a series of $3d$ impurities. Moreover, the effects of magnetism from conventional magnetic atoms such as Fe, Co, and Ni are discussed.

In Section 3.5 the results for the spin diffusion length for the various dilute alloys are compared to experiments. The total spin Hall angle of the intrinsic and extrinsic mechanisms is evaluated to quantify the charge-to-spin conversion. Some of the results in this chapter have been published in Refs. [142, 143].
3.1 Uranium Crystal Structure

Uranium has various crystalline phases. Below about 930 K it is stable in the $\alpha$ (orthorhombic) phase, transforms to the $\beta$ (bct) structure, and eventually realises the $\gamma$ (bcc) phase beyond about 1050 K [44, 45]. The meta-stable hcp phase has been also observed in a thin film system up to about 100 Å of thickness [46], which can be considered a bulk system. We choose the stable phases, $\alpha$-, $\gamma$- and hcp-U, as the objects for the transport study of this 5$f$ heavy metal. The information of their lattice structure and the definition of directions are shown in Table 3.1 and defined in Fig. 3.1. The lattice parameters in our calculations are all taken from experimental observations [47, 48].

- **Figure 3.1:** Crystal structure of (a) $\gamma$-, (b) hcp- and (c) $\alpha$-U.

<table>
<thead>
<tr>
<th>Phase</th>
<th>a (Å)</th>
<th>b/a</th>
<th>c/a</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma$ (bcc)</td>
<td>3.467</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>hcp</td>
<td>2.983</td>
<td>1.836</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\alpha$ (orthorhombic)</td>
<td>2.836</td>
<td>2.075</td>
<td>1.741</td>
<td>0.1017</td>
</tr>
</tbody>
</table>

Table 3.1: Experimental lattice parameters of $\gamma$-, hcp- and $\alpha$-U used for the calculations.
3.2 Electronic structure in uranium

First, in order to understand the impact of SOC in uranium, we use different solvers, including non-relativistic, scalar-relativistic and full-relativistic methods, to calculate the electronic structure for $\gamma$-U, as shown in Fig. 3.2. Around the semicore level of -15 eV, these three approximations are clearly distinguishable. Between the energy of 0 and 2 eV about the Fermi energy the significant band splittings, for instance around the P high symmetry point, and the high symmetry line between G and H, show the impact of SOC in uranium. This suggests that SOC has to be taken into account in the following transport calculations.

![Figure 3.2: (Color online) The comparison of the band structure of $\gamma$-U calculated via the non-relativistic, scalar-relativistic and fully relativistic solvers.](image)

All phases of bulk uranium are nonmagnetic, which allows us to present the density of states for only one spin. Fig. 3.3 shows our resulting partial density of states (PDOS) of spin up of $\gamma$-U and the PDOS in an earlier theoretical report for comparison [7]. In our calculation the band structure is dominated by the narrow 5f bands in the energy range between -2 and 5 eV demonstrating the f-electron characteristics. As the f-electron declines below -2 eV, the d character emerges. This behaviour is in agreement with Ref. [7] and both theoretical results show a small amount of s and p electrons around the Fermi level as well. In addition, our calculation shows the PDOS of semi-core orbitals at around -15 and -25 eV, which are the spin-orbit split p-orbitals.

For the hcp-U, the results are shown in Fig. 3.4 in comparison to Ref. [8], where the authors reported theoretical predictions as well as experimental result using scanning tunneling spectroscopy. The considered thin film was a 30 ML uranium film. In both cases the band structure
around the Fermi level is dominated by $f$ electrons, similar to $\gamma$-U. Our resulting DOS shows three peaks at about -0.25, 0.25 and 0.50 eV (see dash lines in the inset of the left panel), which are counterparts to the three peaks in the measurement (bold line of STS in right panel) at -0.37, 0.20 and 0.50 eV, respectively. Furthermore a shoulder at 0.8 eV in our DOS is also a feature observed at 1.1 eV in the experiment. According to their discussion [8], their theoretical predictions are also in agreement with the experimental observation. Therefore, the electronic structure of hcp-U in our calculation is in agreement with the previous report, both for the theoretical and experimental results.

Figure 3.4: (Color online) Comparison of total density of states in hcp uranium between (a) our results and (b) the experimental and theoretical results in Ref. [8].
3.2. ELECTRONIC STRUCTURE IN URANIUM

The resulting PDOS of α-U is shown in Fig. 3.5. In comparison to the γ and hcp phases, where the existing investigations are sparse, the α-U attracted more attention as this phase is stable at room temperatures. Therefore, we can compare our calculated DOS to a number of previous results [9, 45, 144]. Similarly, the DOS around the Fermi level is dominated by the $f$ states and broadened by the $d$ states below -2 eV. While the $s$ states are vanishing across the whole energy range, the $p$ states appear as semi-core states below -12 eV. These electronic properties are in agreement with the theoretical results of different computational methods [9, 45, 144].

The devices for the SHE applications are generally composed of multiple layers of different metals, as shown in Fig. 1.2(b). The magnetism of the ferromagnetic layer would couple with features arising from the interfaces such as proximity of heavy metals, interfacial SOC and finite size effects, which play a role for the performance of the devices. Here, we are interested in the coupling between the magnetism of the ferromagnetic layer and the quantum well states in the nearby nonmagnetic layer.

In the measurements for the U/Fe bilayer system [142], a nonmonotonic dependence of the magnetic anisotropy on the U thickness was shown. They observed the energy of the magnetic anisotropy to oscillate as the U thickness increases. This could be attributed to the fact that the quantum well states in the U layer couple to the magnetism in the Fe layer. The thickness of U samples varies from 0 to 8 nm [145]. In order to understand and quantitatively analyse such a coupling in the U/Fe bilayer we calculated the Bloch spectral function for the bulk α-U which is the stable phase at room temperatures for which the experiment was conducted.

In an ideal bulk system, the wave function of the electrons is expressed as a Bloch state with no perturbation or boundary condition. As the boundary condition is taken into account in a slab
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Figure 3.6: Illustration of the Bloch state and quantum well state (taken from Ref. [10]).

of limited size, the quantum well state emerges and generates the envelope wave function with an extra periodicity, as shown in Fig. 3.6 [10, 145]. The oscillation period $P$ for the quantum well state in real space is associated to the wave vector as $1/P$ in reciprocal space. Thus near the boundary of the Brillouin zone the total wave vector is the sum of the Bloch wave vector and the envelope wave vector [145], given by

$$k_{tot} = k_{BZ} \pm k_{env}. \quad (3.1)$$

This expression is true if the layer is thick enough so that the total wave vector $k_{tot}$ can be regarded as a bulklike vector that is equivalent to the Fermi wave vector $k_F$ (wave vector at $E_F$) in the band structure of the bulk system. Equation (3.1) shows that the period of the quantum well state corresponds to the inverse of the reciprocal distance between the Fermi wave vector $k_{tot}$ and the Brillouin zone boundary $k_{BZ}$. Notably, the quantum well state appears with a period of half the wavelength of the envelope functions as $P = n \times \lambda_{env}/2$, as increasing the thickness of the well by $\lambda_{env}/2$, still satisfies the boundary condition. Therefore the period can be estimated by the wave vector of the envelope function given by $P = \lambda_{env}/2 = \pi/k_{env} = \pi/(k_{tot} - k_{BZ})$.

Although the uranium was grown in polycrystalline structure in the U/Fe bilayer [142], the measurement shows that the predominant texture in the uranium is the [001] direction perpendicular to the surface. Therefore, we calculated the Bloch spectral function for the (010) and (100) planes, which include the [001] direction as shown in Fig. 3.7. The reciprocal lattice vectors in the $x$ and $y$ axis are in units of $2\pi/a$, where $a$ is 2.836 Å, the lattice parameter of $\alpha$-U. The resulting Bloch spectral function shows a large density (white arrows) at coordinates $(k_x, k_y, k_z) = (0.24, 0, 0.2), (0.312, 0, 0.222), (0.153, 0, 0.057)$ and $(0, 0.241, 0.057), (0, 0, 0.087)$ in the (010) and (100) planes, respectively. As the points are close to the boundary (gray outline), the period of oscillation is given by $\pi/(k_{001} - k_{BZ})$ where $k_{BZ}^{[001]} = k/c$ with $c = 1.741a$. The resulting periods corresponding to $(k_x, k_y, k_z) = (0.24, 0, 0.2)$ and $(0.312, 0, 0.222)$ are 1.62 and 2.17 nm, respectively. For the points away from the boundary $k_{BZ}^{[001]}$ (or close to the centre $k_{BZ}^{[001]} = 0$), the period is calculated by $\pi/k_{BZ}^{[001]}$. The periods corresponding to the other points are 2.49 and 1.63 nm. Thus these four values are in good quantitative agreement to the experimentally observed period of 2 nm.
3.3 Intrinsic SHE in uranium

The 5f band structure combined with the strong SOC increases the number of near degeneracies generally enhancing the Berry curvature, and can generate considerable intrinsic SHE. Figure 3.8 shows the intrinsic spin Hall conductivity (SHC) $\sigma_{yx}^{\alpha}$ for the three phases, $\alpha$-, $\gamma$- and hcp-U calculated by Eqs. (2.79) and (2.80). These phases have similar energy-dependent

![Image](image.png)

Figure 3.7: Theoretical Bloch spectral functions for $\alpha$-U shown for (a) (010) and (b) (100) planes, respectively. In both images the Brillouin-zone boundary is shown as a gray-outline rectangle and the white arrows indicates connection of wave vector between two large-density areas. The colour scale stands for the magnitude of electron density.
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SHC until $-0.8$ eV. All phases start with the positive SHC at low energies and reach peaks at increasing energies, then transit from positive to negative values at different points. Near the Fermi energy the SHC of hcp-U has the most significant increase, sequentially followed by $\alpha$- and $\gamma$-U. The resulting values at the Fermi energy are summarised in Table 3.2. Noticeably the change of SHC magnitude is over two orders of magnitude ranging from $10^2$ for $\gamma$-U, over $10^3$ for $\alpha$ up to $10^4$ for hcp-U.

![Figure 3.8: The intrinsic spin conductivity of $\gamma$, hcp- and $\alpha$-U.](image)

<table>
<thead>
<tr>
<th>Material</th>
<th>$\sigma_{xx} (\Omega^{-1} \text{cm}^{-1})$</th>
<th>$\sigma_{yx} (\Omega^{-1} \text{cm}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma$</td>
<td>$-4.02 \times 10^2$</td>
<td></td>
</tr>
<tr>
<td>hcp</td>
<td>$-1.00 \times 10^4$</td>
<td></td>
</tr>
<tr>
<td>$\alpha$</td>
<td>$-2.12 \times 10^3$</td>
<td></td>
</tr>
<tr>
<td>Exp. U [11]</td>
<td>$3.50 \times 10^4$</td>
<td>$1.40 \times 10^2$</td>
</tr>
<tr>
<td>Theo. Pt [35–38]</td>
<td>$1.3 - 3.2 \times 10^3$</td>
<td></td>
</tr>
<tr>
<td>Exp. Pt [103, 146–150]</td>
<td>$2.0 - 5.3 \times 10^4$</td>
<td>$0.5 - 3.6 \times 10^3$</td>
</tr>
</tbody>
</table>

Table 3.2: The comparison between our theoretical predictions and the experimental results for the longitudinal charge conductivity $\sigma_{xx}$ and the spin Hall conductivity $\sigma_{yx}$. The theoretical and experimental results of Pt are given from references and all experimental measurements are the spin pumping method.

Experimental results of spin-dependent transport for uranium is sparse. One experimental study [11] reported a SHC of $\sigma_{yx} = 1.40 \times 10^2$ $\Omega^{-1} \text{cm}^{-1}$ with a spin Hall angle (SHA) of $\theta = 0.4\%$
at room temperature. This magnitude is comparable to our result of $\sigma_{yx}^s = -4.02 \times 10^2 \, \Omega^{-1}\text{cm}^{-1}$ for $\gamma$-U instead of the experimentally expected phase of $\alpha$-U. In addition, we found a negative sign of the SHC for all three phases, which appears to be different to the experiment. However, it is not clear whether the sign was considered explicitly in the experiment. By reversing the magnetisation direction of FM in nonlocal measurement and the external magnetic field in spin-pumping measurement, the spin direction of electrons can be reversed, which results in the opposite sign for the measured ISHE voltage. Nevertheless, in high symmetry crystal structure such as bcc ($\gamma$-U), the spin conductivities $\sigma_{yx}$ and $\sigma_{xy}$ are in principle in the same magnitude with opposite sign, thus the magnitude of conductivity is more emphasised.

In the experiment the spin diffusion length crucial for deriving $\sigma_{yx}^s$ was assumed to be 3 nm, the same as Pt, since there no data for U was available. This could potentially explain the discrepancy between the theoretical and experimental finding. Moreover, the structural inhomogeneities as well as the experiment being performed at room temperatures may complicate a direct comparison to the theoretical results. Here, we spotlight the charge and spin conductivity of Pt, the conventional material for SHE study, as reference in Table 3.2. The theoretical value for the spin Hall conductivity of Pt is $10^3 \, \Omega^{-1}\text{cm}^{-1}$, while the experimental observations are in the range from $0.5 \times 10^3$ to $3.6 \times 10^3 \, \Omega^{-1}\text{cm}^{-1}$. This one-order gap in Pt can be attributed to crystal quality and determines the transition between the intrinsic and extrinsic regime for the SHE, which has been studied in detail by Sagasta et al. [4]. The effective influence of temperature on the Pt measurements are discussed in detail by Isasa et al. [151]. For uranium, no further experimental work is available for comparison, implying the transition between the superclean (dominance of the extrinsic mechanism) and moderately dirty (dominance of the intrinsic mechanism) regime is ambiguous and complicates the gap between the theory-experiment comparison. Nevertheless, our computation highlight the SHC in hcp-U is two orders of magnitude larger than for the $\alpha$ and $\gamma$ phases, suggesting that the metastable hcp-U is a feasible option to obtain a maximum charge-to-spin current conversion in uranium-based devices.

### 3.4 Extrinsic SHE in uranium

In order to obtain insight into the full picture of spin-dependent transport in uranium, we move forward to study the extrinsic SHE for all three U phases doped with a series of $3d$ transition metals as well as Ga. For the $\gamma$-U all impurities are nonmagnetic including the traditional magnetic elements such as Fe, Co and Ni. Figure 3.9 shows the SHA for $\gamma$-U doped with the various substitutional impurities. Within the dilute limit, the skew-scattering mechanism dominates the SHE and all conductivities including $\sigma_{yx}^s$ and $\sigma_{xx}$ are inversely proportional to the impurity concentration leading to the SHA being independent of the concentration. The largest $\theta$ is found for the Sc impurity and the transition from negative to positive values appears between V and Cr, where the number of $d$ electron is close to half filling at $Z_d = 4$ for the impurity site.
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given by the self-consistent impurity solver. The SHA shows a positive maximum of 1.5% for the Co impurity ($Z_d = 8$) and reverses back to negative values beyond Cu. It reaches $-1.5\%$ for the Ga impurity ($Z_d = 10.5$). Unexpectedly, this SHA trend is similar to the previous results for Cu doped with 5d transition metals reported by Fert et al. [96]. This demonstrates that the resonant scattering between $j = 5/2$ and $j = 3/2$ in d orbitals is dominant in the transport of doped 5f uranium as well. Similar as for Cu, it is the d-orbital impurity level which determines the change of transport properties across the series as those orbitals drive the scattering of the host electrons. In contrast to Cu, the electrons in U are of f-character and the scattering is driven by the $f$-$d$ hybridisation.

Despite the valance and conduction electron in uranium is mostly in f orbitals, the strong d-f hybridization allows a transform between d and f orbitals, consequently enhancing the coupling between the host atoms and the impurities.

Figure 3.9: The spin Hall angle of $\gamma$-U doped with 3d transition metals. All conventionally magnetic atoms become nonmagnetic as impurity in $\gamma$-U.

For hcp-U, the Cr, Fe and Co impurities are magnetic, showing the antiferromagnetic coupling with the induced moments in the surrounding U atoms, while all other impurities remain nonmagnetic. Figure 3.10 shows the comparison of the SHA for the naturally magnetic and constrained nonmagnetic systems. For the nonmagnetic case, the trend of the SHA is similar to the case of $\gamma$-U and the sign change occurs between the Sc and Ti impurity and reach the maximum around Mn and Fe. When the magnetism is taken into account in Cr, Fe and Co with
moments of 1.99, 2.38 and 0.86 $\mu_B$, respectively, the SHAs decrease and we find that the magnetic Fe impurity causes a significant reduction from 1.5% to 0.2%.

Figure 3.10: The spin Hall angle for various substitutional 3d impurities in the hcp-U. Dashed line: Cr, Fe and Co are magnetic impurities. Solid line: All impurities are forcedly nonmagnetic.

Figure 3.11(a) shows the resulting SHA of $\alpha$-U doped with various 3$d$ impurities. Given the reduced symmetry of $\alpha$-U, the symmetry between $\theta_{xy}$ and $\theta_{yx}$ is broken [23, 152, 153] and both are shown in comparison. Nevertheless, the trends for both are similar. Unlike for hcp-U, we find Cr, Mn and Fe to be magnetic with moments of 1.09, 2.37 and 1.93 $\mu_B$, respectively. Again they are ordering antiferromagnetically with the induced moments in the surrounding U. In comparison to the nonmagnetic systems the magnetism reduces the SHA in a similar way as for hcp-U. The principle structure is similar to the other two phases and the maximum value of the SHA is at Mn.

In order to better understand the implication of the reduced symmetry in $\alpha$-U, we present the symmetric and antisymmetric SHC, $\frac{1}{2}(\sigma_{yx}^s - \sigma_{xy}^s)$ and $\frac{1}{2}(\sigma_{yx}^s + \sigma_{xy}^s)$, respectively, for magnetic and nonmagnetic systems as shown in Fig. 3.11(b). In contrast to the simple phases, $\gamma$ and hcp, $\alpha$-U shows a small but nonvanishing symmetric part for the SHC. The SHA shown in Fig. 3.11(a) is mostly induced by the conventional antisymmetric contribution and shows a very similar trend as the other crystalline phases. Nevertheless, the reduced symmetry of the SHC is still visible enough to be relevant in experimental analysis.

We have presented the extrinsic SHE for a series of 3$d$ impurities in all three crystalline phases and highlighted that the $d$-orbital resonant scattering is dominant in all systems in good

51
agreement to Ref. [96]. Although the skew-scattering induced SHA is sizable, their value do not exceed 1.5%. In some previous work [56] it was shown that large SHAs can be induced in heavy metal hosts by light impurities. In Fig. 3.12, we present the SHA in the case of light impurities in comparison to the 3$d$ impurities as well as Mo. All impurities in $\gamma$-U are nonmagnetic, while for hcp-U the Fe and Ni impurities and for $\alpha$-U the Fe impurities are magnetic. Following the mechanism of $d$-orbital resonant scattering, the SHA for Mo, for which the number of $d$ electron is roughly the same as for Cr ($Z_d=5$), is similar to Cr.

The B and C impurities can induce a large SHA comparable to Fe and Co in $\gamma$ and hcp-U, while for $\alpha$-U the corresponding SHA is suppressed. Evidently, the simple argument of the necessity of a large relative change of the SOC of the host versus the impurities as identified for simple metals [56] does not carry over to the complex electronic structure of U in the various crystalline phases.
3.5 Spin diffusion length and dilute concentration

So far our calculations show an extrinsic SHA which is comparable to the experimental observation for α-U, while the magnitude of the intrinsic SHC is one order too large. To understand the full picture of spin-dependent transport in realistic uranium systems, we calculate the spin diffusion length using Eq. (2.78) with an effective experimental impurity concentration \( c_{\text{expt}} \), inversely proportional to the longitudinal charge conductivity in the dilute limit [79, 154],

\[
c_{\text{expt}} = \frac{\sigma_{\text{cal}}}{\sigma_{\text{expt}}^0} \sigma_{xx}.
\]

Here, \( c_0 \) is the nominal impurity concentration of 1 at. % in all our calculations. The charge conductivity for estimating \( l_{sf} \) and \( c_{\text{expt}} \) is taken from Ref. [11] as \( \sigma_{xx}^{\text{expt}} = 3.5 \times 10^{-2} (\mu\Omega\text{cm})^{-1} \) for nominal α-U and we keep it constant for all U phases since no experimental data is available for γ- and hcp-U.

In principle, each impurity will induce a different spin diffusion length \( l_{sf} \) and charge conductivity \( \sigma_{xx} \). However, as the results are dominated by the strong SOC of the U host only small
variations can be seen for a given crystalline phase. All results are summarised in Table 3.3, illustrating the clear distinction between the crystalline phases. We find that for \( \gamma \)-U, the spin diffusion length to be \( l_{sf} = 3 \) nm is comparable to the experimental assumption \([11]\). For hcp-U and \( \alpha \)-U we predict 5 nm and 6.5 nm, respectively, which is about two times larger. Reevaluating the experiment considering the larger spin diffusion length of \( l_{sf} = 6.5 \)nm we obtain a SHA of \( \theta = 0.38\% \), which is similar to \( \theta = 0.4\% \) derived previously assuming a spin diffusion length comparable to Pt. This slight change could not clearly explain the discrepancy between theory and experiment.

To estimate the effective impurity concentration for reaching the experimental longitudinal charge conductivity, we find a range of \( c_{\text{expt}} = 5 - 8 \) at. % for \( \gamma \)-U, about 1.5 times larger than what is needed for hcp-U and \( \alpha \)-U. The concentrations needed for hcp-U and \( \alpha \)-U similarly vary between 1.8 – 3.5 at. % and 2.5 – 5.0 at. %, respectively, although these two phases have a significantly different electronic structure, trends and magnitudes for the SHA. The large necessary impurity concentration needed for \( \gamma \)-U suggests that it is unlikely that the experimental system is based on an ideal \( \gamma \) structure since unrealistically large impurity concentrations or other major disorder in the system will be needed to recover the experimental resistivity. However, on a large length scale in experiments, thin films are predominately polycrystalline structures that is comprised of many individual grains or crystallites, and each grain can be seen as a single crystal. There is no periodicity across polycrystalline thin films. This is difficult to be described from a theoretical perspective since the sample is considered as a perfect crystal with monotonic periodicity across the whole sample. As a result, the different descriptions for crystal would lead to the discrepancy in charge conductivity. On the other hand, hcp-U and \( \alpha \)-U exhibit a reasonable range for the necessary impurity concentration \( c_{\text{expt}} \) easily present in bilayered structures utilised in spin-pumping experiments.

<table>
<thead>
<tr>
<th>Phase</th>
<th>( l_{sf} ) (nm)</th>
<th>( c_{\text{expt}} ) (at. %)</th>
<th>( k_F ) (nm(^{-1}))</th>
<th>( \tau ) (fs)</th>
<th>( \tau_{sf} ) (10(^{-3})fs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \gamma )</td>
<td>( \sim 3 )</td>
<td>5 – 8</td>
<td>11.06</td>
<td>21.6-42.1</td>
<td>4.87-9.24</td>
</tr>
<tr>
<td>hcp</td>
<td>( \sim 5 )</td>
<td>1.8 - 3.5</td>
<td>8.03</td>
<td>22.7-49.2</td>
<td>5.74-13.9</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>( \sim 6.5 )</td>
<td>2.5 - 5.0</td>
<td>7.79</td>
<td>20.6-42.0</td>
<td>4.41-9.09</td>
</tr>
</tbody>
</table>

Table 3.3: The range of the spin diffusion length \( l_{sf} \), the effective experimental impurity concentration, momentum relaxation time \( \tau \), and spin relaxation time \( \tau_{sf} \) for various impurities in \( \gamma \)-, hcp- and \( \alpha \)-U. \( k_F \) is the Fermi wave vector.

In order to understand the contributions of intrinsic and extrinsic effects to the spin-dependent transport in the U phases, we summarise the calculated extrinsic charge conductivities \( \sigma_{xx}^{\text{ext}} \) and the absolute values of the SHC \( |\sigma_{yx}^{\text{s(ext)}}| \) in Table 3.4 at the impurity concentrations of \( c_0 = 1 \) at. %. For \( \gamma \)-U, we find \( \sigma_{xx} \) to be two times larger than for hcp-U and \( \alpha \)-U, directly linked to the effective impurity concentration that is needed to reach the longitudinal conductivity of the experiment as shown in Table 3.3. Considering those conductivities and concentrations it becomes evident
that we are in the moderately dirty regime where the intrinsic mechanism should dominate [4, 86, 155]. To highlight this point, we estimated the absolute value of the total spin Hall angle $\theta^{\text{tot}}$ in the dilute impurity limit combining the intrinsic and extrinsic contributions

$$
\theta^{\text{tot}} = \left| \frac{c_{\text{ext}} \sigma^{\text{int}}_{yx} + \sigma^{\text{ext}}_{yx}}{\sigma^{\text{ext}}_{xx}} \right|.
$$

The results are summarised in Table 3.4. This expression clearly highlights how in the moderately dirty regime the intrinsic mechanism becomes dominant as the impurity concentration increases. Nevertheless, depending on the size of the individual contributions, the intrinsic and extrinsic contributions may become comparable. This is true for $\gamma$-U, where the extrinsic SHC ranges between $0.8 \times 10^{-4}$ and $48.1 \times 10^{-4}$ $(\mu\Omega\text{cm})^{-1}$ can be larger than the intrinsic SHC of $|\sigma^{\text{int}}_{yx}| = 4.02 \times 10^{-4}$ $(\mu\Omega\text{cm})^{-1}$. Therefore the total SHA, in a range of $\theta^{\text{tot}} = 0.01\% - 2.25\%$, is dominated by extrinsic mechanisms for many of the considered impurities. In contrast, for hcp-U the magnitude of the extrinsic SHC to be two orders smaller than that of the intrinsic SHC and the total SHA of $\theta^{\text{tot}} = 27.5\% - 30.1\%$ is showing the giant SHE is induced via the intrinsic mechanism. For $\alpha$-U, we find a broad range of $\sigma^{\text{ext}}_{yx}$ changing over three orders of magnitude from $2.0 \times 10^{-5}$ to $1.8 \times 10^{-3}$ $(\mu\Omega\text{cm})^{-1}$. However, the largest values are still smaller than that of the intrinsic SHC, leading to a total SHA of $5.6\% - 7.1\%$. This is still considerably larger than the purely extrinsic SHA of about 1%. Summarising the above results, our predictions suggest that in the experimental thin films [11] it is $\gamma$-U which is the predominant phase.

| Phase | $\sigma_{xx}(\mu\Omega \text{ cm})^{-1}$ | $|\sigma_{yx}^{\text{ext}}| (\mu\Omega\text{cm})^{-1}$ | $\theta^{\text{Total}}$ (%) |
|-------|-----------------------------------|--------------------------|-----------------------------|
| $\gamma$ | 17.3 - 30.0 $\times 10^{-2}$ | 0.8-48.1 $\times 10^{-4}$ | 0.01 - 2.3 |
| hcp | 6.2 - 12.4 $\times 10^{-2}$ | 1.1-10.6 $\times 10^{-4}$ | 27.5 - 30.1 |
| $\alpha$ | 8.8 - 17.7 $\times 10^{-2}$ | 0.2-17.9 $\times 10^{-4}$ | 5.6 - 7.1 |

Table 3.4: The range of calculated longitudinal charge conductivities $\sigma_{xx}$, spin Hall conductivities $\sigma_{yx}^{\text{ext}}$ and total spin Hall angles $\theta^{\text{tot}}$.

### 3.6 Conclusions

In summary, we calculated the band structure for bcc $\gamma$-U using non-relativistic, scalar relativistic and fully relativistic approaches, which indicated the important role of spin-orbit coupling for the electronic structure of uranium. This result confirms that SOC has to be taken into account for the following transport calculations or the description of magnetism in uranium based systems. Our calculated DOSs for $\gamma$, $\alpha$, and hcp-U are in agreement to other theoretical results using different first-principles methods. In all considered crystal phases the DOS around the Fermi level is dominated by the $f$ electrons and a small amount of $d$ electrons. It leads to $f$-$d$ hybridisation that can be observed more dominantly in the $d$ resonant scattering in the following transport calculations.
CHAPTER 3. ELECTRONIC STRUCTURE AND SPIN-DEPENDENT TRANSPORT OF URANIUM

We investigated the influence of the quantum well states on the magnetism in the bilayer U/Fe system. By calculating the Bloch spectral function, we estimated the wavelengths of quantum well states in the α-U. These values are in good agreement with the experimental results [11].

Predicting the relevant transport parameters such as the intrinsic SHC, extrinsic SHC, longitudinal charge conductivity, spin-diffusion length and the effective impurity concentrations in the dilute limit, we found significant differences for the various U crystalline structures despite similarly strong SOC in all phases. Using these results we were able to give a possible explanation for the surprisingly low spin Hall angle in the experiments. Our calculations suggest that the experimental phases uranium in the experiment [11] is γ-U instead of α-U since the experimentally found SHA of 0.4% locates in the range of total spin Hall angle of γ-U. In addition, we demonstrated that the largest SHA exists in the hcp-U up to 30%, driven by the intrinsic mechanism.

For the extrinsic SHE, we found that the resonant scattering from d electrons is predominant for the 3d transition impurities. The comparison between magnetic and nonmagnetic systems shows that magnetism, induced by the magnetic impurity, led to a reduction of the SHA in all cases scaling with the magnitude of magnetic moment at the impurity site. Based on the results for the extrinsic contributions and assuming the experimental charge conductivity, we found the spin-diffusion length in a range from 3 nm for γ-U to 6.5 nm for α-U. By combining the extrinsic and intrinsic mechanism, we predict the dominance of the extrinsic contribution in γ-U, while the intrinsic mechanism is dominant in the hcp and α phase.

Combining all computational results for the spin-dependent transport in uranium we found the high efficiency of charge-to-spin conversion of 30% in hcp-U with a spin-diffusion length of 5 nm. Both parameters would imply that hcp-Uranium is a valuable material for charge-to-spin current applications.
The electrical and magnetic properties of multilayer systems used in the applications of magnetoresistance are strongly connected to the physics of spin accumulation at interfaces or surfaces. This chapter is dedicated to the investigation of the spin accumulation in different metallic thin films with varying strengths of spin-orbit coupling based on the Boltzmann formalism. In Section 4.1, I will introduce the different approximations giving access to the various of contributions arising from the scattering term in the Boltzmann equation such as the scattering-in term as well as anisotropic and isotropic relaxation time approximations. The normalised spin accumulation is introduced to quantify the efficiency of charge-to-spin-accumulation conversion. The details of the computational methods, including the determinations of the coordinate systems for different crystalline structures, are provided.

In Section 4.2, I quantitatively analyse the different mechanisms on the spin accumulation in Cu and Pt thin films comparing the different strengths of intrinsic spin-orbit coupling. In order to understand the effect of the impurity position on the spin accumulation, I present the normalised spin accumulation in Sec. 4.3. Furthermore, I will discuss the influence of the orbital character on the scattering by changing the considered impurity. The strength of the spin-dependent transport can be enhanced by the SOC induced by either impurities or hosts. Therefore, in Section 4.4 I will investigate the spin accumulation for Cu doped with a Bi impurity, which has been reported to have a large spin Hall angle. In contrast, I will analyse the effect of the heavy host of γ uranium doped with various substitutional impurities. Finally, the effect of magnetism induced by the impurities on the spin accumulation will be presented in Sec 4.5. Some of the results in this chapter have been published in Refs. [141, 156].
4.1 Computational details

In Sec. 2.2.5 I have briefly introduced the theoretical framework for the description calculation of the spin accumulation. Here, the different contributions to the spin accumulation will be discussed in detail. The starting point is Eq. (2.98) presenting the spin accumulation including all scattering processes

$$\chi^{i}_{yx} = \frac{e\mu_B}{\hbar} \sum_{n} \frac{V}{d(2\pi)^2} \int_{E_F} \frac{dS_n}{|\mathbf{v}_{k}^n|} s^{n,i}_{y,k} \Lambda_{x,k}^{n}$$

where \(\Lambda_{x,k}^{n}\) is the mean free path defining the current in the \(x\) direction, \(s^{n,i}_{y,k}\) is the spin expectation value in the \(y\) direction, and the spin accumulation \(\chi^{i}_{xy}\) is a function of the layer or atom index \(i\). The definitions of the directions and the index are shown in Fig. 4.1. In order to quantitatively understand the individual contributions to the total spin accumulation, we will define 3 distinct approximations. First, we consider only the first term in the linearised Boltzmann equation of Eq. (2.90) by dropping the scattering-in term \(P_{nn'}^{kk'}\). This leads to the anisotropic relaxation time approximation

$$\tilde{\Lambda}_{x,k}^{n}(k) = \tau v_{n,k}^{x}.$$  

The resulting spin accumulation is given by

$$\tilde{\chi}^{i}_{yx} = \frac{e\mu_B}{\hbar} \sum_{n} \frac{V}{d(2\pi)^2} \int_{E_F} \frac{dS_n}{|\mathbf{v}_{k}^n|} s^{n,i}_{y,k} \tilde{\Lambda}_{x,k}^{n}.$$  

Second, we describe the spin accumulation

$$\hat{\chi}^{i}_{yx} = \frac{e\mu_B}{\hbar} \sum_{n} \frac{V}{d(2\pi)^2} \int_{E_F} \frac{dS_n}{|\mathbf{v}_{k}^n|} s^{n,i}_{y,k} \left[ \Lambda_{x,k}^{n} - \tilde{\Lambda}_{x,k}^{n} \right]$$

considering the difference between \(\chi^{i}_{xy}\) and \(\hat{\chi}^{i}_{xy}\) in order to specifically quantify the contribution from the scattering-in term in the spin accumulation. Third, taking into account the contribution from the clean systems only, the isotropic relaxation time approximation \(\Lambda_{yx} = \tau v_{n,k}^{x}\) can be used to calculate the spin accumulation as

$$\bar{\chi}^{i}_{yx} = \frac{e\mu_B}{\hbar} \sum_{n} \frac{V}{d(2\pi)^2} \int_{E_F} \frac{dS_n}{|\mathbf{v}_{k}^n|} s^{n,i}_{y,k} v_{n,k}^{x}.$$  

where \(v_{n,k}^{x}\) is the \(x\) component of the Fermi velocity of the clean system.

In the physics of spin Hall transport, the efficiency of charge-to-spin conversion, the spin Hall angle, is an important quantity in evaluating a material’s performance in spintronic devices as already discussed in Chap. 3. To quantify the performance of charge current-induced spin accumulation in materials, we introduce the normalised spin accumulation \(a^{i}_{yx}\) as an efficiency of charge-current-to-spin-accumulation conversion in a similar way to the spin Hall angle

$$a^{i}_{yx} = \frac{a^{i}_{y}}{j_{x}} = \frac{\chi^{i}_{yx}}{a^{i}_{xx}},$$

58
4.2 Quantifying the different mechanisms in spin accumulation

Figure 4.2 summarises the results for the spin accumulation as calculated from Eq. (4.1) in comparison to the various approximations for a Cu thin film doped with Pt impurities, Cu(Pt), as well as a Pt film doped with Cu, Pt(Cu). The impurities in these cases are placed at the embedded position ($i=5$) breaking the inversion symmetry of the thin films, which implies that both symmetric and antisymmetric contributions are simultaneously present in the spin accumulation. There are some noticeable implications from the presented comparison. First the effect in Pt thin films is an order of magnitude stronger than that in Cu. Second while the effect in Pt(Cu) is almost entirely dominated by the anisotropic relaxation time approximation $\hat{\chi}_{yx}$, the

where $a_y^i$ and $j_x$ are the induced magnetic moments along the $y$ direction and the $x$-direction current density, respectively. They are driven by the electric field $E_x$ in the $x$ direction as $a_y = \chi_{yx}E_x$ and $j_x = \sigma_{xx}E_x$.

The model systems in our calculations focus on the cubic crystals, fcc Cu(100), fcc Pt(100) and bcc U(100). All systems are 9-monolayer films to conserve the inversion symmetry of the clean system. The $x$-$y$ plane of different crystals are defined according to Fig. 4.1(a) and (b). The vacuum layers in the $z$ direction are extended to infinity and the layer index $i$ defined in Fig. 4.1 will be used for the following discussions.
scattering-in contribution $\tilde{\chi}_{yx}$ and $\tilde{\chi}_{yx}$ in Cu(Pt) are of comparable magnitude but with opposite sign, which leads to a partial cancellation of the two individual contributions. Third, for these two systems the induced spin accumulation in isotropic relaxation time approximation $\bar{\chi}_{yx}$ is significantly smaller (scaled by a factor of 5) throughout the entire thin film.

Considering all together it shows that in the Cu thin film the spin accumulation of the surface atoms $i=5$ and $i=11$ is dominated by the extrinsic contributions via the scattering-in term. This finding is in agreement with the previous report [157] where the authors theoretically and experimentally demonstrated that the spin accumulation at the interfaces is dominated by the extrinsic skew-scattering mechanism.

Moreover, the dominant contributions to the spin accumulation in Cu(Pt) are almost perfectly symmetric with respect to the central atom while there is an equally strong antisymmetric contribution for Pt(Cu). The resulting accumulation in isotropic relaxation time approximation $\bar{\chi}_{yx}$ is perfectly antisymmetric with the largest value at the surface atoms indicating the induced magnetisation of clean systems, which is again in agreement with the work in Ref. [141].

By comparing these two cases it shows that the spin accumulation is strongly related to the electronic structure of the host system, which is defining the intrinsic spin-orbit coupling. While the spin-orbit coupling scales with the atomic number and is strong in Pt, this effect is small.
in Cu. It results in a dominance of the scattering effects in the Cu thin film. In contrast for the Pt case most of the contributions arise in the anisotropic relaxation time approximation based on the strong intrinsic spin-orbit coupling and excluding the scattering-in term. Furthermore, while the spin accumulation of Pt is restricted to the side where the impurity is located, in the Cu system the spin accumulation is comparable in magnitude across the film. This difference can be connected to the dramatically different spin-diffusion length in comparison to that of Pt, which leads to the slow decay of the spin accumulation in the Cu thin film [146, 150, 154, 158, 159]. Furthermore, despite the fact that spin-diffusion length in the previous articles is larger than the thickness of thin films in our systems, we still see rapid decay in our Pt. This is reasoned that the spin-diffusion length here considered in all directions instead of only the z direction. When the initial electric field is applied in the x direction [see Eq. (4.1)], the scattered electrons travel with a velocity that is composed of x, y and z components rather than entirely of z components, resulting in spin accumulation not occurring across the entire Pt thin film.

Our resulting spin accumulation of Pt also shows that the length scale of spin-diffusion length is smaller than that of the Valet-Fert theory [106]. This is because the spin-diffusion length discussed in their theory is derived from the spin accumulation at nonmagnetic-magnetic interface, and its long spin-diffusion length is beyond the mean free path. Our spin-diffusion length here is derived solely from the scattering event and calculated using an integral of mean free path. Moreover, in the Valet-Fert model the spin-diffusion length is described in a current perpendicular to plane (CPP) model, whereas in our model we assume the initial electric field is applied in plane in the x direction. As a result, the Valet-Fert model and our calculations have different origins.

### 4.3 Effect of impurity position and atomic character

The next step is to investigate the influence from the impurity position on the spin accumulation. As before we focus on the Pt(Cu) and Cu(Pt) systems and place the impurities across the film, starting with the central position \(i=9\), preserving the inversion symmetry, up to the surface position \(i=5\) and including the adatom position \(i=4\). We calculate the normalised spin accumulation \(\alpha_{yx}^i\) as defined in Eq. (4.6) for each case, which is presented in Fig. 4.3. In order to extract the bare spin accumulation the corresponding longitudinal conductivities are summarised in Table 4.2 for Pt and Table 4.3 for Cu.

As discussed in the last section, the spin accumulation for the Cu thin films is dominated by the extrinsic scattering mechanism, which is dramatically altered by the impurity position. The induced spin accumulation becomes more symmetric as the impurity is placed at the surface, and the sign changes for the impurity buried deeper inside the film at layer index \(i = 6\). The spin accumulation gradually becomes perfectly antisymmetric as the impurity reaches the central layer \((i = 9)\). This considerable effect of the impurity position on the overall spin accumulation
is consistent with the suggestion discussed in Ref. [157]. Moreover, while the largest value of the spin accumulation appears at the centre of the film when the impurity is placed close to the surface \((i = 5, 6)\), the effect is more spread out across the thin film for the impurity near the centre \(i = 7, 8\) and 9. This stems from the fact that the profile becomes more and more antisymmetric. The effect in the Pt thin film is entirely different since the intrinsic spin-orbit coupling is driving the spin accumulation in the heavy Pt host. While overall the magnitude of the spin accumulation decreases as the impurity is buried deeper in the thin film \((i = 8, 9)\), the impurity placed in other layers induces a stronger spin accumulation on the side of the impurity within the thin films. The sign of the maximal spin accumulation stays the same as the impurity is placed across the films. Notably, it was predicted [154] that the spin Hall angle of bulk system Cu(Pt) is larger than that of bulk Pt(Cu), with a value of \(27.0 \times 10^{-3}\) and \(-5.2 \times 10^{-3}\), respectively. However, this is no longer true for the thin film systems where the overall normalised spin accumulation of Cu(Pt) is smaller than the effect in Pt(Cu), which implies a less efficient charge-to-spin conversion. This highlights that the quantitative prediction depends on the consideration of realistic experimental geometries in contrast to the simplified bulk systems.

In order to understand the influence of the atomic character on the spin accumulation, we calculated the normalised spin accumulation in Pt thin films doped with the full 3d series of
4.3. EFFECT OF IMPURITY POSITION AND ATOMIC CHARACTER

Figure 4.4: Normalised spin accumulation induced by a series of 3$d$ impurities doped across Pt thin films. All atoms are nonmagnetic.
transition metals from Sc to Zn. Interestingly, the behaviour of the overall spin accumulation across the 3d impurities is similar to the case of Pt(Cu) and the anisotropic relaxation time approximation $\chi_{yx}$ is always the dominating contribution with a vanishing effect from the scattering-in term. As was expected, this is associated to the intrinsic spin-orbit coupling of the Pt host that plays a dominating role for all 3d impurities. The resulting spin accumulations for all impurities are summarised in Fig. 4.4. We collected the largest values of $\alpha_{yx}$ and the corresponding longitudinal conductivities in Table 4.1 and 4.2, respectively. For the sake of simplicity all conventionally magnetic atoms, such as Mn, Fe, Co and Ni, are enforced to be nonmagnetic. We find that in most cases the largest normalised spin accumulation is present at layer index $i = 5$, while for the rest it occurs at layer index $i = 6$ or 7.

<table>
<thead>
<tr>
<th>Element</th>
<th>Pos. 4</th>
<th>Pos. 5</th>
<th>Pos. 6</th>
<th>Pos. 7</th>
<th>Pos. 8</th>
<th>Pos. 9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc</td>
<td>1.28</td>
<td>2.30</td>
<td>2.02</td>
<td>2.77</td>
<td>1.03</td>
<td>1.07</td>
</tr>
<tr>
<td>Ti</td>
<td>1.37</td>
<td>2.31</td>
<td>2.03</td>
<td>2.66</td>
<td>1.00</td>
<td>1.08</td>
</tr>
<tr>
<td>V</td>
<td>1.45</td>
<td>2.33</td>
<td>2.11</td>
<td>2.54</td>
<td>0.97</td>
<td>1.06</td>
</tr>
<tr>
<td>Cr</td>
<td>1.49</td>
<td>2.40</td>
<td>2.23</td>
<td>2.43</td>
<td>0.96</td>
<td>1.05</td>
</tr>
<tr>
<td>Mn</td>
<td>1.37</td>
<td>2.64</td>
<td>2.33</td>
<td>2.31</td>
<td>0.97</td>
<td>0.99</td>
</tr>
<tr>
<td>Fe</td>
<td>1.23</td>
<td>3.07</td>
<td>2.32</td>
<td>2.19</td>
<td>0.97</td>
<td>0.86</td>
</tr>
<tr>
<td>Co</td>
<td>1.14</td>
<td>3.67</td>
<td>2.68</td>
<td>2.03</td>
<td>0.89</td>
<td>0.86</td>
</tr>
<tr>
<td>Ni</td>
<td>1.15</td>
<td>1.99</td>
<td>2.36</td>
<td>2.95</td>
<td>1.12</td>
<td>0.87</td>
</tr>
<tr>
<td>Cu</td>
<td>2.14</td>
<td>2.24</td>
<td>2.28</td>
<td>2.83</td>
<td>1.11</td>
<td>0.88</td>
</tr>
<tr>
<td>Zn</td>
<td>1.34</td>
<td>2.30</td>
<td>2.14</td>
<td>2.83</td>
<td>1.07</td>
<td>0.96</td>
</tr>
</tbody>
</table>

Table 4.1: The largest value of normalised spin accumulation $\alpha_{yx}$ for the Pt thin film doped with various impurities at different positions. For almost all systems, these values would be taken at the layer index $i = 6$. The unit is in $10^{-12}\mu_B\text{cm}^2\text{A}^{-1}$.

<table>
<thead>
<tr>
<th>Element</th>
<th>Pos. 4</th>
<th>Pos. 5</th>
<th>Pos. 6</th>
<th>Pos. 7</th>
<th>Pos. 8</th>
<th>Pos. 9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc</td>
<td>1.31</td>
<td>0.64</td>
<td>0.37</td>
<td>0.36</td>
<td>0.25</td>
<td>0.33</td>
</tr>
<tr>
<td>Ti</td>
<td>0.74</td>
<td>0.61</td>
<td>0.35</td>
<td>0.34</td>
<td>0.24</td>
<td>0.31</td>
</tr>
<tr>
<td>V</td>
<td>0.54</td>
<td>0.57</td>
<td>0.32</td>
<td>0.31</td>
<td>0.22</td>
<td>0.28</td>
</tr>
<tr>
<td>Cr</td>
<td>0.48</td>
<td>0.62</td>
<td>0.33</td>
<td>0.31</td>
<td>0.21</td>
<td>0.27</td>
</tr>
<tr>
<td>Mn</td>
<td>0.53</td>
<td>0.88</td>
<td>0.48</td>
<td>0.39</td>
<td>0.26</td>
<td>0.33</td>
</tr>
<tr>
<td>Fe</td>
<td>0.60</td>
<td>2.1</td>
<td>1.16</td>
<td>0.80</td>
<td>0.56</td>
<td>0.59</td>
</tr>
<tr>
<td>Co</td>
<td>0.78</td>
<td>9.11</td>
<td>4.06</td>
<td>2.70</td>
<td>1.93</td>
<td>1.91</td>
</tr>
<tr>
<td>Ni</td>
<td>1.65</td>
<td>4.17</td>
<td>1.67</td>
<td>1.40</td>
<td>1.11</td>
<td>1.43</td>
</tr>
<tr>
<td>Cu</td>
<td>17.32</td>
<td>1.09</td>
<td>0.60</td>
<td>0.52</td>
<td>0.40</td>
<td>0.51</td>
</tr>
<tr>
<td>Zn</td>
<td>5.57</td>
<td>0.82</td>
<td>0.47</td>
<td>0.43</td>
<td>0.32</td>
<td>0.41</td>
</tr>
</tbody>
</table>

Table 4.2: Charge conductivity of the Pt thin films doped with various impurities at different positions for the nonmagnetic systems. The unit is in ($\mu\Omega\text{cm}$)$^{-1}$.

While there is a large amount of literature focusing on the theoretical description of the charge and spin Hall conductivity, studies on the spin accumulation are sparse. In Ref. [140] a
4.3. EFFECT OF IMPURITY POSITION AND ATOMIC CHARACTER

theoretical result for the normalised spin accumulation in Pt next to L1_0-FePt was reported as up to $17.2 \times 10^{-13} \mu_B \text{cm}^2 \text{A}^{-1}$. This is comparable to our maximum $\alpha_{yx}$ of Pt of the order of $\sim 10^{-12} \mu_B \text{cm}^2 \text{A}^{-1}$ for the various 3$d$ transition impurities. In comparison to experimental observation, our results are in agreement to $\alpha_{yx} = 5 \times 10^{-12} \mu_B \text{cm}^2 \text{A}^{-1}$ for a film with thickness $t \geq 40$ nm as observed in Ref. [160]. The same group also reported other measurements for a Pt(10 nm)/Cu(10 nm) bilayer system and found the magnetic moments of $\approx 1.5 \times 10^{-6} \mu_B$ in Pt with an injected current density of $2.6 \times 10^6 \text{Acm}^{-2}$ [161]. This would imply a normalised spin accumulation of $\alpha_{yx} = 5.7 \times 10^{-13} \mu_B \text{cm}^2 \text{A}^{-1}$, which is again comparable to our prediction.

For Cu, the observed values of the normalised spin accumulation vary in a wide range between $6 \times 10^{-9} \mu_B \text{cm}^2 \text{A}^{-1}$ and $3 \times 10^{-12} \mu_B \text{cm}^2 \text{A}^{-1}$ depending on the different experimental setup [162, 163]. The numbers are significantly larger than our predictions of the order of $\sim 10^{-13} \mu_B \text{cm}^2 \text{A}^{-1}$. This discrepancy might be partially attributed to the fact that in experiments the detected spin accumulation was for Cu atoms interfaced with ferromagnetic materials where the proximity effect of magnetism could be considerable. Furthermore, the spin current in the experiments is generated by spin-pumping and spin-injection methods and measured with the inverse spin Hall effect of spin-to-charge conversion. Our calculations are based on the direct SHE, where neither any charge current flows in direction perpendicular to the surface nor any additional voltage is applied. Furthermore, we have shown that the effect in Cu is dominated by extrinsic effects, which makes any comparison problematic if no structural details of the thin films are known.

The longitudinal charge conductivity $\sigma_{xx}$ is critical for the charge-to-spin conversion. All longitudinal charge conductivities of the nonmagnetic Pt based systems are summarised in Table 4.2. In general the values of $\sigma_{xx}$ are largest for the impurities placed at the surface ($i = 4, 5$), where they weakly interact with the thin film. The conductivities dramatically drop as the impurities are buried deeper and slightly enhance for the impurity at the central layer $i = 9$, which is caused by the effect of finite size for these thin films. In a simplified picture of a potential wall, every second wave function confined between the two boundaries of the thin film would have a node at the central position and would thus avoid the scattering from the impurity. Thus the slight enhancement can be explained by the model of a quantum well describing the clean host.

To investigate the mechanism causing the massive difference in the conductivities for the various impurities, we calculated the local density of states (LDOS) of the host atom and the doped impurity Sc, Fe, Co and Cu placed at layer index $i = 4$ and 5 for the nonmagnetic systems, as shown in Fig. 4.5. For the case of the adatom position, the host LDOS (an empty sphere) shows a vanishing contributions, while the impurity atoms Co and Fe show significant contributions in the LDOS at the Fermi level. This change of the LDOS causes in general a strong scattering. On the other hand, for the Cu and Sc impurities the small contributions shown in the LDOS at the Fermi energy lead to the weaker scattering. This explains the significant change in the longitudinal conductivity for the impurity Fe and Co in comparison to Sc and Cu.
of placing the impurities at layer index $i = 5$, the surface atom of Pt shows a large $d$-electron peak in the LDOS at the Fermi energy similar to the situation of the Fe and Co impurities, which induces the weak scattering. This is in contrast to the $s$ and $p$ character in the LDOS of Cu and Sc impurities. Thus it leads to the opposite effect for the adatom case where now the large conductivities occur for Fe and Co but they are small for Sc and Cu.

4.4 Effect of strong scattering and $f$ electrons on the spin accumulation

So far we focused on $d$-electron host systems Cu and Pt. While the Pt thin film with strong intrinsic SOC is overall weakly affected by the character of $3d$ impurities as well as the impurity position, the spin accumulation in Cu with small SOC can be significantly altered by varying the impurity position. To better understand the effect of the impurity character on the spin accumulation in Cu thin films, we additionally calculated $\alpha_{yx}$ for Cu doped with Bi impurities. For this system the largest spin Hall angle was found in bulk Cu(Bi) [59, 154]. The results are shown in Fig. 4.6.

Figure 4.5: Comparison of the density of states of Sc, Cu, nonmagnetic Fe, and Co impurities in adatom ($i = 4$) and in surface atom ($i = 5$) position.
4.4. EFFECT OF STRONG SCATTERING AND $f$ ELECTRONS ON THE SPIN ACCUMULATION

Figure 4.6: Caption Comparison of the normalised spin accumulation $\alpha_{yx}$ for the various impurity positions in the Cu(Bi) and U(Cu) thin films.

The situation for the overall normalised spin accumulation $\alpha_{yx}$ in Cu(Bi) is similar to Cu(Pt) where the contributions from the anisotropic relaxation time approximation $\tilde{\chi}_{yx}$ and the scattering-in term $\tilde{\chi}_{yx}$ simultaneously play critical roles in the total spin accumulation. While the spin accumulation is more symmetric for the impurity placed at the layer index $i = 4, 5, 6$ close to the surface, it becomes antisymmetric as the impurity is at the central positions. Unlike the situation in the Cu(Pt) thin film, the sign of the overall spin accumulation in Cu(Bi) does not significantly change as the impurity position is shifted. This shows the strong influence of the scattering from the impurity as expected from the above discussion. Surprisingly, the spin Hall conductivity induced by Bi impurities is reported to be much larger than that of Pt impurities, both experimentally and theoretically [58, 59, 154]. In contrast, the spin accumulation in thin films is suppressed to a similar order of magnitude as for Cu(Pt). This similar quantitative prediction points to the importance of considering realistic geometries in contrast to the treatment of the simplified bulk systems.

Further we investigated the spin accumulation choosing a host system with strong spin-orbit coupling, uranium, the heaviest naturally occurring metal with $5f$ electronic structure [44, 47, 48, 164]. The results of the bcc uranium thin film is shown in Fig. 4.6(b). For almost all impurity positions the resulting spin accumulation is comparable to the magnitude of the Pt thin film.
Interestingly, as the impurities are placed at the surface, the largest effects are induced at the opposing side of the thin film. This is in contrast to the intuitive situation in the Pt thin films.

The resulting longitudinal conductivities of Cu and U thin films doped with a series of impurities are summarised in Table 4.3. In the Cu thin films the charge conductivity when doping with Bi impurities is an order of magnitude smaller than for the Pt impurity despite a similar normalised spin accumulation. For all cases of uranium thin films, the conductivities are of the same order of magnitude with the exception of impurities at the adatom position where we find a wide variation. Table 4.4 shows the summary of the largest values for the normalised spin accumulation for all scenarios in both Cu and U thin films. Interestingly, we find in U that the magnitude of Cu-induced spin accumulation is comparable to that of other impurities. This differs considerably from the results shown in Fig. 3.9 where the Cu impurities induce a vanishing spin Hall angle in the U bulk. This difference might be attributed to the incorporation of intrinsic effects in the normalised spin accumulation of a two-dimensional system, whereas the resulting spin Hall angle of Cu is restricted to the extrinsic skew-scattering mechanism recognised as the scattering-in term.

<table>
<thead>
<tr>
<th>Element</th>
<th>Pos. 4</th>
<th>Pos. 5</th>
<th>Pos. 6</th>
<th>Pos. 7</th>
<th>Pos. 8</th>
<th>Pos. 9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(Pt)</td>
<td>1.054</td>
<td>1.199</td>
<td>0.504</td>
<td>0.261</td>
<td>0.276</td>
<td>0.303</td>
</tr>
<tr>
<td>Cu(Bi)</td>
<td>0.211</td>
<td>0.079</td>
<td>0.045</td>
<td>0.038</td>
<td>0.037</td>
<td>0.043</td>
</tr>
<tr>
<td>U(Li)</td>
<td>0.870</td>
<td>0.108</td>
<td>0.075</td>
<td>0.064</td>
<td>0.062</td>
<td>0.055</td>
</tr>
<tr>
<td>U(B)</td>
<td>0.357</td>
<td>0.089</td>
<td>0.076</td>
<td>0.058</td>
<td>0.056</td>
<td>0.053</td>
</tr>
<tr>
<td>U(Al)</td>
<td>0.291</td>
<td>0.098</td>
<td>0.083</td>
<td>0.064</td>
<td>0.060</td>
<td>0.058</td>
</tr>
<tr>
<td>U(nonmag. Fe)</td>
<td>0.460</td>
<td>0.107</td>
<td>0.083</td>
<td>0.070</td>
<td>0.067</td>
<td>0.062</td>
</tr>
<tr>
<td>U(Cu)</td>
<td>0.726</td>
<td>0.097</td>
<td>0.128</td>
<td>0.094</td>
<td>0.090</td>
<td>0.093</td>
</tr>
</tbody>
</table>

Table 4.3: Charge conductivity of the Cu and U thin film doped with Pt and Bi, and Li, B, nonmag. Fe and Cu, respectively. The unit is in ($\mu$Ωcm)$^{-1}$.

<table>
<thead>
<tr>
<th>Element</th>
<th>Pos. 4</th>
<th>Pos. 5</th>
<th>Pos. 6</th>
<th>Pos. 7</th>
<th>Pos. 8</th>
<th>Pos. 9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(Pt)</td>
<td>0.128</td>
<td>0.124</td>
<td>0.099</td>
<td>0.038</td>
<td>0.055</td>
<td>0.020</td>
</tr>
<tr>
<td>Cu(Bi)</td>
<td>0.065</td>
<td>0.142</td>
<td>0.043</td>
<td>0.039</td>
<td>0.029</td>
<td>0.025</td>
</tr>
<tr>
<td>U(Li)</td>
<td>1.25</td>
<td>1.92</td>
<td>0.70</td>
<td>1.18</td>
<td>0.76</td>
<td>0.87</td>
</tr>
<tr>
<td>U(B)</td>
<td>0.85</td>
<td>1.66</td>
<td>0.68</td>
<td>1.13</td>
<td>0.93</td>
<td>0.87</td>
</tr>
<tr>
<td>U(Al)</td>
<td>1.36</td>
<td>1.70</td>
<td>0.72</td>
<td>1.09</td>
<td>0.90</td>
<td>0.86</td>
</tr>
<tr>
<td>U(nonmag. Fe)</td>
<td>0.75</td>
<td>1.70</td>
<td>0.71</td>
<td>1.47</td>
<td>0.88</td>
<td>1.05</td>
</tr>
<tr>
<td>U(Cu)</td>
<td>1.45</td>
<td>1.99</td>
<td>0.67</td>
<td>1.63</td>
<td>0.82</td>
<td>1.69</td>
</tr>
</tbody>
</table>

Table 4.4: The largest magnitude of normalised spin accumulation $\alpha_{yx}$ of the Cu and U thin film doped with Pt and Bi, and Li, B, nonmag. Fe and Cu, respectively. The unit is in $10^{-12}\mu_B$cmA$^{-1}$.
4.5 Effect of magnetism on spin accumulation

So far the analysis of the spin accumulation has been focused on nonmagnetic systems in order to focus on the effect of the atomic character and the impurity position. In fact, the conventionally magnetic elements, Mn, Fe, Co and Ni, exhibit a magnetic moment across all positions in the Pt thin film. For V the magnetism occurs only at layer index $i = 4, 5$. All these magnetic impurities induce antiferromagnetically coupled moments in the surrounding Pt atoms. Moreover, the magnetic moments of all impurities are assumed to point in the same direction, perpendicular to the thin film surface.

The results for the longitudinal conductivities of all magnetic cases are summarised in Table 4.5. In comparison to the results in Table 4.2, the values for the conductivities are enhanced as the impurities are placed as adatom on the surface ($i = 4$). For Fe, Co and Ni, the conductivities are reduced as the impurities are buried deeper in the thin film while this becomes larger for Mn.

Table 4.6 shows the summary of the maximum normalised spin accumulations. For almost all cases the maximum value is extracted at the layer index $i = 6$. The results are comparable to the nonmagnetic case with the exception of Fe and Co at the surface position ($i = 5$), which are slightly reduced.

<table>
<thead>
<tr>
<th>Element</th>
<th>Pos. 4</th>
<th>Pos. 5</th>
<th>Pos. 6</th>
<th>Pos. 7</th>
<th>Pos. 8</th>
<th>Pos. 9</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>0.80</td>
<td>0.60</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>2.82</td>
<td>0.90</td>
<td>0.54</td>
<td>0.52</td>
<td>0.38</td>
<td>0.48</td>
</tr>
<tr>
<td>Fe</td>
<td>1.12</td>
<td>0.74</td>
<td>0.40</td>
<td>0.39</td>
<td>0.28</td>
<td>0.36</td>
</tr>
<tr>
<td>Co</td>
<td>0.95</td>
<td>0.88</td>
<td>0.46</td>
<td>0.43</td>
<td>0.29</td>
<td>0.38</td>
</tr>
<tr>
<td>Ni</td>
<td>3.32</td>
<td>1.36</td>
<td>1.19</td>
<td>0.98</td>
<td>1.27</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.5: Charge conductivity $\sigma_{xx}$ of the Pt thin film doped with magnetic impurities at different positions in units ($\mu\Omega\text{cm}^{-1}$).

<table>
<thead>
<tr>
<th>Element</th>
<th>Pos. 4</th>
<th>Pos. 5</th>
<th>Pos. 6</th>
<th>Pos. 7</th>
<th>Pos. 8</th>
<th>Pos. 9</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>1.42</td>
<td>2.38</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>1.40</td>
<td>2.36</td>
<td>2.18</td>
<td>2.82</td>
<td>1.05</td>
<td>1.00</td>
</tr>
<tr>
<td>Fe</td>
<td>1.44</td>
<td>2.43</td>
<td>2.17</td>
<td>2.70</td>
<td>1.02</td>
<td>1.00</td>
</tr>
<tr>
<td>Co</td>
<td>1.51</td>
<td>2.50</td>
<td>2.29</td>
<td>2.55</td>
<td>1.00</td>
<td>0.95</td>
</tr>
<tr>
<td>Ni</td>
<td>2.16</td>
<td>2.38</td>
<td>2.85</td>
<td>1.11</td>
<td>0.87</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.6: The largest value of normalised spin accumulation $a_{yx}$ of the Pt thin film doped with magnetic impurities at different positions. The unit is in $10^{-12}\mu_B\text{cm}^2\text{A}^{-1}$.

In Fig. 4.7, I have summarised all normalised spin accumulations for systems showing impurity-induced magnetism. It is interesting to note that the effect of magnetism on the spin accumulation appears to be weak as can be seen in comparison to Fig. 4.4. This is in contrast to the result for U based alloys, where the magnetism leads to a strong reduction for the SHA.
4.6 Conclusions

In summary, we calculated the spin accumulation for 9 ML thin films of Cu(Pt) and Pt(Cu) within various approximations. In the Cu host with weak spin-orbit coupling, the resulting spin accumulation in anisotropic-relaxation time approximation $\tilde{\chi}_{3z}^{i}$ and from the scattering-in terms $\tilde{\chi}_{3z}^{i}$ are symmetric across the thin film with similar strength. However, the signs of these two contributions are opposite and partially cancel each other in the total spin accumulation. For the Pt host, the spin accumulation is dominated by the contributions from the anisotropic-relaxation time approximation and it almost vanishes at the opposite side of thin film relative to the impurity position as a large antisymmetric component is present. Within the isotropic-relaxation time approximation,
approximation the spin accumulation in both cases is vanishingly small with symmetric profiles across the thin films. Moreover, the strength of the spin accumulation in Pt with large spin-orbit coupling is dramatically larger than that in Cu. This highlights the importance of intrinsic spin-orbit coupling in driving the spin accumulation.

We investigated the normalised spin accumulation $\alpha_{yx}^i$, the efficiency of charge-to-spin-accumulation conversion, in the Cu and Pt host with the impurities placed at various positions. For the Cu host, the normalised spin accumulation is significantly affected by the impurity position with changing magnitude or sign, while this change is small in Pt. By doping the full 3$d$ series of impurities into Pt we found the normalised spin accumulation to remain almost constant, which again indicates the importance of strong intrinsic spin-orbit coupling. Moreover, our results for the normalised spin accumulation in Pt is in good agreement to experimental observations [160, 161], while the results for Cu are incompatible with the experimental values [162, 163]. This discrepancy could be attributed to the Cu samples in the experiment in bilayer systems with the ferromagnetic materials which could affect the spin accumulation via proximity effects.

The overall normalised spin accumulation for uranium is quantitatively similar to the Pt thin films and equally shows a strong symmetric component. However, the spin accumulation is largest at the opposite side of the thin film relative to the impurity position. The spin accumulation in both cases of material with large intrinsic spin-orbit coupling is more localised at one side. This can be associated with the reduced spin-diffusion lengths in comparison to Cu.
Investigation of Superconductivity and Impurity-Induced Yu-Shiba-Rusinov States

Superconductivity is a topic in condensed matter physics that has received a lot of interest as on the one hand it holds the potential of lower loss electronics while on the other hand the microscopic understanding is still lacking. Our computational method based on density functional theory was developed to describe superconducting materials by implementing the Bogoliubov-de Gennes equation, as shown in Eqs. (2.48) and (2.49) in Chapter 2 [13]. This KKR Green’s function method has the ability to treat real-space impurity systems. In this chapter I focus on the superconducting properties of a heavy metallic materials in clean systems, as well as the Yu-Shiba-Rusinov (YSR) states in magnetic impurity systems.

In Section 5.1 I will review the BCS theory based on the concept of electron-phonon coupling and how this determines the superconducting gap. This will be followed by the theory of the YSR states, superconducting bound states induced by magnetic impurities. The connection between the YSR states and the Kitaev chain model is briefly discussed in the context of the Majorana zero modes. In Section 5.2, we extend the previous work of uranium to the superconducting state and discuss its interpretation in terms of the BCS theory in f-electron materials. Section 5.3 begins with the discussion of various effects induced at the magnetic impurity, followed by the computational results for the YSR states induced by a Mn impurity on a Pb surface at different heights. The resulting energy levels of the YSR states are discussed in comparison to the experimental observations.
CHAPTER 5. INVESTIGATION OF SUPERCONDUCTIVITY AND IMPURITY-INDUCED YU-SHIBA-RUSINOV STATES

5.1 A brief introduction to superconductivity and Yu-Shiba-Rusinov (YSR) states

5.1.1 Review of BCS theory

Superconductivity, zero electrical resistance, was first discovered by H. K. Onnes [165] below a critical temperature when he was investigating the low-temperature physics of mercury. In the following years the Meissner effect [166] was discovered and the theory of superconductivity was developed over many decades [167–171]. To explain superconductivity at a microscopic level, John Bardeen, Leon Cooper, and John Robert Schrieffer proposed a mechanism based on the concept of electron-phonon interaction suggested by H. Fröhlich [171], which is the so-called BCS theory [172].

In the BCS theory the starting point is the Cooper instability (Cooper pair) where the two electrons are attracted to each other through electron-phonon interaction, while conventionally they would repel each other. However, in the superconducting phase the attraction is effective for the electrons around the Fermi level. The physical picture is as follows. As the first electron with momentum \( k \) in the state \( \psi_k(r) \) pass through a metal, the surrounding crystal lattice is displaced by the electromagnetic field from the electron movement. The resulting deformation potential couples with the second incoming electron in the state \( \psi_{-k} \). Shown as a Feynman diagram in Fig. 5.1, this interaction between electrons with the opposite momentum (zero net momentum) are bridged via a phonon, the atomic displacement. One electron is scattered from state \( \psi_k(r) \) to \( \psi_{k'}(r) \) by the emitted phonon, while the other electron is scattered from \( \psi_{-k}(r) \) to \( \psi_{-k'}(r) \) by the absorbed phonon. Thus the interaction through the phonon bundles these two electrons as the so-called Cooper pair, a bound state existing within the Debye energy \( \hbar \omega_D \) above the Fermi level at zero temperature.

![Feynman diagram of the virtual electron-phonon interaction for the BCS interaction.](image)

Figure 5.1: Feynman diagram of the virtual electron-phonon interaction for the BCS interaction.

After the introduction of the zero-momentum Cooper pair, the mean-field BCS Hamiltonian
5.1. A BRIEF INTRODUCTION TO SUPERCONDUCTIVITY AND YU-SHIBA-RUSINOV (YSR) STATES

describing the kinetic energy and electron-electron interaction can be written as

\[ H = \sum_{k} (c_{k} - \mu) c_{k}^{\dagger} c_{k} - \sum_{k} \left( \Delta^{*} c_{-k} c_{k}^{\dagger} + c_{k}^{\dagger} c_{-k} c_{-k}^{\dagger} \right), \]  

(5.1)

where \( \sigma, \mu \) and \( \epsilon_{k} \) are the spin quantum number, the chemical potential and the kinetic energy within the Debye energy of \( \pm \hbar \omega_{D} \) with respect to the Fermi level, respectively. The quantities \( c_{k}^{\dagger} \) and \( c_{k} \) are creation and annihilation operators, for electrons forming the Cooper pairs. \( \Delta \) is the BCS gap parameter (or BCS gap function) given by

\[ \Delta = |g_{\text{eff}}|^{2} \sum_{k} (c_{-k} c_{k}^{\dagger}), \]  

(5.2)

where \( g_{\text{eff}} \) is a constant related to scattering an electron from \( k \) to \( k' \) via the electron-phonon interaction, see Fig. 5.1. The expectation value of the Cooper pair operator \( c_{-k} c_{k}^{\dagger} \) is the pairing amplitude, or "order parameter". Here, the value is nonzero only when the BCS ground state is a coherent state for Cooper pairs, meaning the wave function has components of different even electron numbers. In addition, in s-wave superconductivity, for a spherical Fermi surface where spin and orbital angular momentum are zero, \( S = L = 0 \), the gap \( \Delta \) is a constant on the Fermi surface at zero temperature.

The electron annihilation operator \( c_{-k} \) coupled to \( c_{k}^{\dagger} \) can be regarded as a hole creation operator of \( a_{k}^{\dagger} \), and \( c_{k}^{\dagger} = h_{-k} \). Thus the first term in the electron-electron interaction Eq. (5.1) is redefined as electron-hole condensate where the electron and hole are time reversed states with the correspondences, \( -e \rightarrow e, k \rightarrow -k \) and \( | \downarrow \rangle \rightarrow | \uparrow \rangle \). This concept of electrons and holes is critical for the Bogoliubov transformation to solve the energy spectrum of quasiparticles for the BCS Hamiltonian.

The quasiparticle excitations are created by adding pairs of electrons (holes) through the pair creation or annihilation operators. The excitation spectrum can be obtained by diagonalising the quadratic mean-field Hamiltonian Eq. (5.1) by a Bogoliubov transformation,

\[ H = \sum_{k} E_{k} \left( a_{k}^{\dagger} a_{k} - a_{-k}^{\dagger} a_{-k} \right), \]  

(5.3)

with the quasiparticle energy

\[ E_{k} = \sqrt{(\epsilon_{k} - \mu)^{2} + |\Delta|^{2}}, \]  

(5.4)

where the transformed quantities of \( a_{k}^{(f)} \) are linear combinations of the single particle operators

\[ a_{k} = u_{k}^{*} c_{k}^{\dagger} - v_{k}^{*} c_{-k}^{\dagger}, \]

\[ a_{-k}^{\dagger} = u_{k} c_{k}^{\dagger} + v_{k} c_{-k}^{\dagger}. \]  

(5.5)

The amplitudes, \( u_{k} \) and \( v_{k} \) fulfil the normalisation condition \( |u_{k}|^{2} + |v_{k}|^{2} = 1 \). At finite temperatures the expectation values of the quasiparticle occupation operators are given by the Fermi-Dirac distribution

\[ \langle a_{k}^{\dagger} a_{k} \rangle = f(E_{k}) \]  

(5.6)

75
and
\[ \langle a_{-\mathbf{k}|a_{-\mathbf{k}}^\dagger \rangle = 1 - f(E_{\mathbf{k}}). \] (5.7)

The former represents the distribution of electron occupation below the Fermi energy, while the latter can be regarded as hole distribution. This electron-hole symmetry of the quasiparticle Hamiltonian in Eq. (5.3) is an important property in the description of superconductivity.

The $\Delta$ in the energy $E_{\mathbf{k}}$ implies that there is no state at the Fermi energy and the quasiparticle density of states $N(E)$ is given by
\[ N(E, \Delta) = \begin{cases} N_0 \frac{E}{\sqrt{E^2 - |\Delta|^2}} & \text{for } |E| > \Delta \\ 0 & \text{for } |E| \leq \Delta \end{cases}, \] (5.8)

where $N_0$ is the DOS of the normal state at the Fermi level. Figure 5.2 shows the quasiparticle DOS and the coherence peak occurs at $E = \Delta$.

Figure 5.2: BCS quasiparticle density of states.

Combining Eqs. (5.2), (5.3) and (5.4) together, the BCS gap equation can be derived
\[ 1 = \lambda \int_0^{\hbar \omega_D} dE \frac{1}{E} \tanh \left( \frac{E}{2k_B T} \right), \] (5.9)

where
\[ \lambda = |g_{\text{eff}}|^2 g(E_F) \] (5.10)

with the anomalous density of states $g(E_F)$. Noticeably, $|g_{\text{eff}}|^2$ in this case corresponds to the electron-phonon interaction parameter $\Lambda$ in Eq. (2.46) and it is a tunable parameter in the subsequent calculations. The zero-temperature gap $\Delta_0$ is obtained via
\[ \Delta_0 = 2\omega_D e^{\frac{-1}{\tau}}, \] (5.11)
and the critical temperature $T_c$ is given by the limit $\Delta \to 0$ as
\[
k_B T_c = 1.13 \hbar \omega_D e^{\Delta / T_c}.
\] 
(5.12)
The ratio of these two equations is
\[
2\Delta_0 = 3.52k_B T_c
\] 
(5.13)
and one of the most important BCS results as it connects the zero temperature gap to the critical temperature. The discussion is correct in the weak-coupling regime, where the interaction is small, $\lambda \ll 1$.

### 5.1.2 Impurity-induced YSR bound states

So far we have introduced the basic Hamiltonian describing the superconducting state. The physics of Yu-Shiba-Rusinov (YSR) states [173–175], which originate from the interaction between magnetic impurities and a superconductor, is investigated in the so-called Nambu spinor representation (particle-hole spinor) [176]. Unlike the operator of the normal state with two spins
\[
a_k = \begin{pmatrix} a_k^\uparrow \\ a_k^\downarrow \end{pmatrix}, \quad a_k^\dagger = \begin{pmatrix} a_k^\dagger \uparrow \\ a_k^\dagger \downarrow \end{pmatrix},
\]
(5.14)
the operator in Nambu representation for the superconducting state is defined as
\[
a_k = \begin{pmatrix} a_k^\uparrow \\ a_k^\downarrow \\ a_{-k}^\dagger \downarrow \\ a_{-k}^\dagger \uparrow \end{pmatrix}, \quad a_k^\dagger = \begin{pmatrix} a_k^\dagger \uparrow \\ a_k^\dagger \downarrow \\ a_{-k}^\dagger \uparrow \\ a_{-k}^\dagger \downarrow \end{pmatrix}. 
\]
(5.15)
The elements $a_{-k}^\dagger \downarrow$ ($a_{-k}^\dagger \uparrow$) are the hole operator corresponding to the electron operator $a_k^\dagger$ ($a_k^\uparrow$). Thus in a superconductor an spin-up (spin-down) electron is connected to a spin-down (spin-up) hole.

To consider the impact of a magnetic impurity on a superconductor, the exchange interaction Hamiltonian [174]
\[
H_{ex} = -\frac{J}{2N_c} \sum_{k,k'} a_k^\dagger \sigma S a_{k'}
\]
(5.16)
describing the $s-d$ interaction between a local spin of an impurity and the conduction electrons has to be considered. Here, $N_c$ is a constant, $J$ is the interaction strength, $S$ is the spin at the impurity, and $\sigma$ is the spin operator of the incoming electron. In the limit of classical spin with $S \to \infty$ and $J \to 0$, the interaction is finite $JS = \text{constant}$. In this scenario the quantum dynamics of the spin, such as the interaction between spin-up and spin-down states and spin flip, is no longer relevant and the local spin acts as a local magnetic field. The energy $\epsilon_0$ of the YSR local states is below the superconducting energy gap $\Delta_0$ and can be approximated to [173–175]
\[
\epsilon = \Delta_0 \frac{1 - \alpha^2 + \beta^2}{\sqrt{(1 - \alpha^2 + \beta^2)^2 + 4\alpha^2}},
\]
(5.17)
where

\[ \alpha = \pi N_0 JS, \quad (5.18) \]
\[ \beta = \pi N_0 V. \quad (5.19) \]

The quantity \( N_0 \) is the normal state DOS at the Fermi level, \( V \) is the scalar scattering potential, and \( JS \) is the strength of the exchange interaction. A. I. Rusinov [175] rewrote the YSR energy as a function of the scattering phase shift \( \delta^\pm \) describing the scattering of spin-up (+) and spin-down (−) electrons

\[ \epsilon = \Delta \cos(\delta^+ - \delta^-), \quad (5.20) \]

and the phase shifts \( \delta^\pm \) are defined by the scattering potential \( V \) and the exchange coupling \( JS \) as

\[ \tan\delta^\pm = a \pm \beta. \quad (5.21) \]

In a clean system without the local exchange coupling \( JS = 0 \) and scattering \( V = 0 \), the energy of the bound state \( \epsilon_b \) is equal to the superconducting gap \( \Delta_0 \), which means bound states do not exist. If the exchange coupling \( JS > 0 \), the bound state has two DOS resonances at \( \pm \epsilon \) with respect to the Fermi level, consistent to the electron-peak and hole-peak in the superconductor due to the intrinsic electron-hole symmetry.

Here, I briefly introduce the connection between the YSR states and the Majorana fermions, a particle which is its own antiparticle. A. Y. Kitaev [177] proposed a 1-D \( p \)-wave superconductor model generated by a quantum wire on top of a bulk superconductor. The proximity effect induces the superconductivity from the bulk superconductor into the chain. Considering the chain is composed of \( N \) sites, the two Majorana operators of each site are defined by the electron creation and annihilation operators as

\[ c_{2j-1} = a_j + a_j^\dagger, \quad c_{2j} = -i(a_j - a_j^\dagger), \quad j = 1, \ldots, N, \quad (5.22) \]

which satisfy the relations

\[ c_m^\dagger = c_m, \quad \{c_l, c_m\} = c_l c_m + c_m c_l = 2\delta_{lm}, \quad l, m = 1, \ldots, N. \quad (5.23) \]

These Majorana fermions are quasiparticles and, generally speaking, composed of electrons and holes. The Majorana condition \( c_m^\dagger = c_m \) can be satisfied only if the energy is zero. Thus the Majorana state in condensed matter physics is also called Majorana zero mode. In the topological regime the topological edge state of the system can be described by a Hamiltonian in terms of the Majorana operators

\[ H = \frac{i}{2} \sum_j \left[ -\mu c_{2j-1} c_{2j} + (w + |\Delta|) c_{2j} c_{2j+1} + (-w + |\Delta|) c_{2j-1} c_{2j+2} \right] \]
\[ = i w \sum_j c_{2j} c_{2j+1}, \text{ for } |\Delta| = w > 0, \quad \mu = 0, \quad (5.24) \]
5.1. A BRIEF INTRODUCTION TO SUPERCONDUCTIVITY AND YU-SHIBA-RUSINOV (YSR) STATES

where $\mu$ and $w$ are the chemical potential and the hopping amplitude, respectively. This shows that the Majorana operators, $c_{2j}$ and $c_{2j+1}$, from different sites couple together and there is a single Majorana fermion left at each end of a chain, shown in Fig. 5.3.

After Kitaev proposed Majorana fermions in a superconducting system, many publications emerged to realise similar physics [178–181]. For example, it was investigated whether Majorana fermions can exist in other systems as $p$-wave superconductors are rare. In 2008 L. Fu et al. [178] reported that a combination of $s$-wave superconductors and spin-orbit coupling could generate an effective $p$-wave superconductor. As a result, the electrons in the wire interact with either the superconductivity and spin-orbit coupling through the proximity effect, producing the Majorana zero-mode states. Moreover, in Kitaev’s theory the spin degeneracy causes the difficulty to observe Majorana fermions. S. Nadj-Perge et al. [180, 181] reported the experimental observation of Majorana fermions by depositing ferromagnetic Fe atoms on the surface of a Pb superconductor [179]. Thus the realisation of the Kitaev model became analogous to configurations where YSR states are observed.

5.1.3 Experimental observation for superconductivity and YSR states

J. R. Schrieffer [182] suggested that the scattering of $l = 0$ orbitals does not effectively contribute to the YSR states, but the contributions are dominant for the $l = 2$ orbitals. Thus the YSR resonances are predominantly composed from different non-degenerate $d$ states. The first experimental observation of YSR states was reported for single Mn, Gd and Ag impurities deposited on a Nb superconductor using tunneling experiments by A. Yazdani et al. [183]. In the scanning tunneling microscope (STM) experiments a current is passed from a tip to the substrate to measure the differential conductance $g(V) = dI/dV$, which corresponds to the local density of states (LDOS) [184, 185]. Thus the YSR states can be investigated via the impurity induced LDOS. Yazdani and co-workers [183] demonstrated that Mn and Gd are spin-polarised and have a significant LDOS within the superconducting gap, while the nonmagnetic Ag impurity has zero LDOS. Although the bound states can be observed by the STM measurement, the energy resolution was not good enough to precisely distinguish positions of individual resonances in the LDOS.

In order to improve the energy resolution on the small energy scales required, K. J. Franke et al. [12] implemented a tip of superconducting Pb to explore a Pb superconductor assuring the tip

![Schematic illustration of pairings of Majorana fermions.](image)
has the same superconducting property to the bulk. Figure 5.4(a) shows that the tip of normal metals has an electron distribution following the Fermi-Dirac statistics at the Fermi level and its width at half maximum is $3.5 \, k_B T$, corresponding to a broadening of 1.4 meV at 4.5 K for instance. When the tip is in the superconducting state, the DOS at the Fermi level is zero and there are two quasiparticle coherence peaks at the two edges of the superconducting gap [see Fig.5.4(b)]. The broadening corresponding to the electron-like (hole-like) coherence peak is less than 300 $\mu$eV at 4.5 K with small thermal excitations. Thus, when the tip is biased by a voltage of $\Delta$ where the hole-like peak of the tip matches the electron-like peak of the sample, the high resolution for $dI/dV$ is achieved.

M. Ruby et al. [14, 186, 187] from the same group used this modified method to explore the superconductivity of Pb including the clean bulk systems as well as the impurity-induced YSR states. For Pb it was found experimentally that $2\Delta_0/k_B T_c \geq 4.3$ is not in perfect agreement to the BCS prediction of 3.53 [188]. In the strong-coupling limit where $\Delta_0 = 2\omega_D \lambda$ substitutes Eq. (5.11) [189], the ratio can be up to 4, but is still smaller than the experimental finding. This deviation encouraged the authors to seek other reasons beyond the BCS theory. One possibility is to explore superconductivity via the Eliashberg equations that considers the electron-phonon coupling limit [189]. Another possibility is to focus on the electronic structure. The BCS predictions are based on a single isotropic Fermi surface sheet (FSS), however, this is inconsistent with the reality for Pb [13, 186]. For the bulk superconducting Pb Ruby et al. [186] showed experimentally that Pb is a two-band superconductor with one FSS derived from $s$-$p$ and one from $p$-$d$ orbitals [190]. The former FSS is almost spherical while the latter is tubular. The theoretical result is shown in Fig. 5.5 calculated by T. Saunderson et al. [13]. The colour scale indicates the gap size on the Fermi surface sheets and illustrates the gap anisotropy. The effects of the number
5.1. A BRIEF INTRODUCTION TO SUPERCONDUCTIVITY AND YU-SHIBA-RUSINOV (YSR) STATES

5.1.1. FSS Shape and Gap Anisotropy

The Fermi surface sheet of Pb in the normal state covered with color scale of gap size. This figure is taken from Ref. [13].

Figure 5.5: The Fermi surface sheet of Pb in the normal state covered with color scale of gap size. This figure is taken from Ref. [13].

of FSS, the FSS shape, and the gap anisotropy are critical for its superconducting state and cause a deviation from the BCS predictions. Nevertheless, Pb is still a s-wave superconductor with an anisotropic gap $\Delta(k)$. The modified prediction is in agreement with experimental observations such as the superconducting gap and thermodynamic properties [191–193], which suggests that Pb is a BCS superconductor based on the mechanism of electron-phonon interaction.

The YSR states were investigated by depositing individual Mn atoms on different types of surfaces of a Pb superconductor [14]. For the Pb(001) surface the Mn adatom is at a height of 0.15 Å above the surface. Figure 5.6(a) and (b) show the $dI/dV$ spectrum, corresponding to the LDOS for the Mn and the host superconducting Pb. For Pb there are two resonances around 2.7(-2.7) mV represented by a peak and a close shoulder corresponding to the $s$-$p$ and $p$-$d$ band, respectively [186]. The spectrum for the Mn adatom shows three pairs of YSR resonances within the superconducting gap of Pb, $\alpha$ at $\pm 2.47$ mV, $\beta$ at $\pm 2.08$ mV and $\gamma$ at $\pm 1.61$ mV, which originates from the $d$ orbitals. J. R. Schrieffer [182] reported that only $l = 2$ conduction electrons are scattered by the Mn impurity in an isotropic metal. This implies that these YSR resonances can be attributed to the $d$-orbital scattering. In principle, the $d$ orbital is composed of the five, in an isolated atom degenerate, states, $d_{x^2-y^2}$, $d_{z^2}$, $d_{xy}$, $d_{yz}$ and $d_{xz}$. However, combining the magnetic Mn adatom and the surface crystal structure, this degeneracy is broken into different energy levels. Figure 5.6(c) and (d) show the definitions of the direction on the surface and the energy levels of $d$ orbitals, respectively. Ruby et al. [14] demonstrated that the YSR states are orbital dependent, where the $\alpha$ resonance corresponds to the $d_{x^2-y^2}$, $\beta$ to the $d_{z^2}$ and $\gamma$ to the three-fold degenerate $d_{xy}$ and $d_{yz}$ states. Moreover, they reported that the separation between $d_{xy}$ and $d_{yz}$ depends on the ratio of in-plane and z-component bonding distance, which will be a critical parameter in our calculations.
CHAPTER 5. INVESTIGATION OF SUPERCONDUCTIVITY AND IMPURITY-INDUCED YU-SHIBA-RUSINOV STATES

Figure 5.6: (a), (b) The density of states of the Yu-Shiba-Rusinov states experimentally observed by scanning tunneling microscopy. (c) Schematic of \( xy \) in-plane and \( d_{x^2-y^2} \) directions. (d) Crystal field splitting of the \( d \) orbitals. The figures are taken from Ref. [14].

5.2 Superconductivity of uranium

In previous chapters we investigated the physics in uranium based systems. Here, we extend the uranium research to the superconducting state to explore the superconductivity in \( f \)-electron materials. The crystal structure used in the following calculations is \( \gamma \)-U for the sake of simplicity of the cubic crystal structure and the somewhat spherical Fermi surface sheets. In experiments [194] the superconducting state of uranium appears below \( 0.68 \pm 0.02 \) K. According to the BCS gap equation [Eq. (5.13)], this small critical temperature leads to a superconducting gap of \( \Delta_0 = 0.103 \) meV. In addition, the gap size of \( \gamma \)-U was reported be up to around \( 0.318 \) meV corresponding to a critical temperature of \( 2.1 \) K [195]. In our calculations, we tune the interaction parameter \( \Lambda \) in Eq. (2.46) and find the superconducting gap of \( 1.36 \) meV corresponding to the interaction parameter of \( \Lambda = 0.01505 \) Ry. This discrepancy to the experiments is due to the substantial numerical noise with very small \( \Lambda \).

Figure 5.7 shows the resulting DOS in the superconducting state. The band structure of uranium is complicated with multiple Fermi surface sheets, and as a result, there are multiple coherence peaks and shoulders. To identify the gap size, we label the lowest-energy peak at \( \Delta = 0.98 \) meV and the largest-DOS peaks at \( \Delta = 1.36 \) meV and \( \Delta = 1.48 \) meV.

To investigate the gap anisotropy corresponding to the coherence peaks in the such complicated electronic structure, we show in Fig 5.8 the Bloch spectral function for different high-symmetry lines. In the G-H direction, we find a state at \( \Delta_1 = 0.61 \) that is not resolved in the DOS. Further three peaks at \( \Delta_2 = 1.22, \Delta_3 = 1.18, \) and \( \Delta_4 = 1.48 \) meV correspond to visible peaks, and three gaps at \( \Delta_5 = 1.48, \Delta_6 = 0.97, \) and \( \Delta_7 = 1.32 \) meV in the G-P direction are related to coherence peaks in the DOS. All DOS and the coherence peaks are dominated by \( f \) electrons with...
5.2. SUPERCONDUCTIVITY OF URANIUM

Figure 5.7: The electronic density of states of γ uranium in the superconducting states. The inset indicates the superconducting gap around the Fermi level.

A minority of combinations from d-electrons.

In order to better understand the distribution of the gap in k-space, we present the gap size as colour scale on the Fermi surface sheets, as shown in Figure 5.9. The high-symmetry points are indicated for clarity.

For the first band the gap size is below $\Delta = 1.24$ meV for most k-points and larger gaps are reduced to small spots (red spot). Interestingly, on the second sheet we find the regions of small gaps in the G-P direction. On the third sheet the large variations of the gap between $\Delta_3 = 1.48$ meV and $\Delta_1 = 0.98$ meV in the G-H and G-N direction, respectively, are highlighted. The large region where the gap is comparable to $\Delta_3$ which indicates reasonably well the existence of the largest-coherence peak at 1.36 meV. On the forth sheet we observe all gap sizes from $\Delta_1$ to $\Delta_3$ across the Fermi surface sheet.

To better understand the mechanism behind the gap anisotropy we show the Fermi velocity on all Fermi surface sheets as colour scale in Fig. 5.10. The density of states $g(E_F)$ is inversely proportional to the Fermi velocity $v_F$ and, thus, the BCS gap function, Eq. (5.11), can be expressed in terms of the Fermi velocity as

$$\Delta_0 = 2\omega_p \exp \left( - \frac{1}{\Lambda g(E)} \right) \sim \exp \left( - \frac{v_F}{\Lambda} \right).$$  \hspace{1cm} (5.25)

This implies that the gap is inversely exponentially proportional to $v_F$. While the relation holds quantitatively in some regions when comparing Fig. 5.9 and 5.10, it fails visibly in the details.
It was shown [13] that this simple relation holds almost perfectly for Nb but was fulfilled less convincingly for Pb. Here, for the $f$-electron U with a large number of flat bands at the Fermi surface, the relation is even less perfectly fulfilled. This is not at all surprising as the original BCS equations were derived for simple spherical Fermi surfaces.

This connection is visible in the region around the gap $\Delta_3$ and other red areas in the third band, as well as the blue region in the fourth band. This relationship, however, is inconsistent in other regions, such as the area comparable to $\Delta_1$ on the third sheet. This might be attributed to the fact that the BCS theory is valid in the weak-coupling limit. One factor to consider in the uranium is spin-orbit coupling, which is a crucial effect shown in the band structure of the normal state (Fig 3.2) in Chapter 3. The $f$-orbital character and the large atomic number could equally be important.
Figure 5.9: The Fermi surface sheets with colour scale illustrating the size of the superconducting gap of $\gamma$ uranium.
Figure 5.10: The Fermi surface sheets with colour scale showing the Fermi velocity of $\gamma$ uranium.
5.3 Results of YSR states in conventional superconductors

For a better understanding of the YSR states, we first analyse the YSR model of Eqs. (5.17), (5.18) and (5.19) in some more detail. In this model the spin $S$ is considered as the classical moment and $J$ is the exchange coupling with $JS$ the exchange energy in the Stoner model \[196\] and it can be expressed as

$$JS = \frac{N^\uparrow - N^\downarrow}{N} = \frac{1}{2}(P^\uparrow - P^\downarrow),$$ \quad (5.26)

where $N^\uparrow, N^\downarrow$, and $P^\uparrow, P^\downarrow$ are the density of spin-up (spin-down) electrons, total electron density, and energetic position of spin-up (spin-down) peak in the DOS, respectively. The term $\beta$ in Eq. (5.17) is derived from the scattering potential $V$, which is defined as the potential difference between the impurity and the host atoms. Figure 5.11 shows the trend of Eq. (5.17) (normalised to $\Delta_0$) as a function of the parameters $\alpha$ and $\beta$. For the case of varying $\beta$ with fixed $\alpha = 0$, the YSR states vanish as their energy coincides with the coherence peak and this corresponds to the nonmagnetic scenario. In contrast independent of the scattering strength $\beta$, the YSR states exist within the host superconducting gap and move across it with increasing $\alpha$.

![Figure 5.11: The trend of the YSR energy by changing the parameters $\alpha$ or $\beta$ in Eq. (5.17).](image)

To effectively explore the YSR states in comparison to the experimental observations, we focus on Pb thin films with a Mn impurity as adatom. As shown in Fig. 5.13(a), the Mn is placed in the hollow site of the fcc Pb(001) surface at the height $d$. The directions of the $x$-$y$ plane relative to the crystallography axis as well as the $d$-orbitals are specified in Fig. 5.13(b). In order to understand the effect of the distance between the Mn impurity and the Pb surface on the YSR states, we consider multiple different scenarios, such as $d = a/2$, 0, and 0.15 Å. Here, the parameter $a = 4.9508$ Å is the lattice constant of fcc Pb. The value of 0.15 Å corresponds to...
impurity position in the experimental geometry [14]. In all cases, the superconducting interaction parameter $\Lambda$ of Eq. (2.46) is $\Lambda = 0.351$ Ry optimised to the experimental situation [13].

Figure 5.13 summarises the resulting LDOS including the YSR states for the Mn impurities at different impurity heights. Since we are emphasising the energetic positions of the YSR peaks, the spin-up and spin-down LDOS are presented together. As a result of the BCS theory discussed in Sec. 5.1.1, the energy of the YSR states relative to the Fermi level is symmetric for the spin-up and spin-down states. When the Mn atom is at the height of $d = a/2$, all YSR peaks for the different $d$-orbitals are inside the superconducting gap. The $d_{xy}$ orbitals have the highest energy, followed by the $d_{x^2-y^2}$, the $d_{z^2}$ orbitals, and the degenerate $d_{xz}$ and $d_{yz}$ orbitals at the lowest energy. For the in-plane impurity $d = 0$, the order of energy levels is $d_{x^2-y^2}$, $d_{z^2}$, $d_{xz}$, and $d_{yz}$ from highest to lowest. When the Mn atom is at the height of 0.15 Å, the highest energy emerges as the $d_{x^2-y^2}$ orbital, followed by the $d_{z^2}$, $d_{xz}$, $d_{yz}$, and $d_{xy}$ in sequence. This ordering as well as the narrow gap between $d_{xz}, d_{yz}$, and $d_{xy}$ are in very good agreement with the experimental observation referenced in Fig. 5.6 [14].

As the used ASA approximation is not ideal in the treatment of surface, we explored a scenario where we slightly altered the impurity ASA sphere. Interestingly, for the case of $d = 0.15$ Å we find that the energy levels change if the ASA spheres of the Mn atom is assumed larger, as shown in Fig. 5.12(d). The overall energy of orbitals decreases, with the $d_{x^2-y^2}$ and $d_{z^2}$ orbitals affected most significantly.

To analyse all scenarios using the YSR model (see Fig. 5.11), we calculate the magnetic moment and spin-up (spin-down) LDOS of the Mn impurity for the normal states of each case, as shown in Table 5.1. The large magnetic moments provide a large $\alpha \sim JS$ in the case of $d = a/2$. As a consequence, the YSR states of Mn at a height of $d = a/2$ are very close to the superconducting
5.3. RESULTS OF YSR STATES IN CONVENTIONAL SUPERCONDUCTORS

Figure 5.13: The absolute values of DOS of the YSR states of Mn atom placed at (a) position $d = a/2$, (b) $d = 0$, (c) $d = 0.15$ Å, and (d) $d = 0.15$ Å with a larger ASA sphere.

conherence peaks of Pb. For the case of $d = 0.15$ Å with an adjusted ASA radius, the magnitudes of magnetic moments are nearly equal, indicating that the scattering potential in terms of $\beta \sim V$ are dominating the change according to the YSR model. As the LDOS of Mn is two orders of magnitude smaller than that of Pb and the Mn atoms are located at the same height, we may simply scale the scattering potential by the LDOS of Mn. The large magnitude of the LDOS in the smaller ASA sphere indicates that the electrons are more localised, resulting in a larger scattering potential. In addition, the larger overlap of the ASA spheres between the Mn and Pb atoms (see Fig. 2.3) induces less scattering as the change in the electronic structure becomes smooth. According to Fig. 5.11, a small scattering potential, for a fixed exchange $\alpha$, corresponds to YSR states close to the Fermi level. This is in agreement with our findings where for the large ASA spheres the YSR states move deeper into the gap (see Fig. 5.13).

In comparison to the systems at $d = 0.15$, the situation for the $d = 0$ case is more complicated as all parameters change simultaneously. In addition, the symmetry of the impurity position is changed which will predominantly affect the orbitals pointing out of the plane. Evidently, as the hybridisation becomes negligible for the $d = a/2$ impurity the induced pair breaking is weak and
CHAPTER 5. INVESTIGATION OF SUPERCONDUCTIVITY AND IMPURITY-INDUCED YU-SHIBA-RUSINOV STATES

<table>
<thead>
<tr>
<th>Mn position $d$</th>
<th>Mag. moments ($\mu_B$)</th>
<th>DOS$_{E_F,\uparrow}$</th>
<th>DOS$_{E_F,\downarrow}$</th>
</tr>
</thead>
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<tr>
<td>$a/2$</td>
<td>-4.806</td>
<td>2.102</td>
<td>0.228</td>
</tr>
<tr>
<td>0</td>
<td>-2.740</td>
<td>1.003</td>
<td>0.378</td>
</tr>
<tr>
<td>0.15 Å</td>
<td>-2.930</td>
<td>1.134</td>
<td>0.333</td>
</tr>
<tr>
<td>0.15 Å, larger ASA</td>
<td>-2.927</td>
<td>1.053</td>
<td>0.308</td>
</tr>
</tbody>
</table>

Table 5.1: The magnetic moments and the density of states of normal state in the Mn impurity at different height above the Pb surface.

the YSR states accumulate around the coherence peaks. Table 5.2 summarises the order of YSR states for all $d$ orbitals and all scenarios.

<table>
<thead>
<tr>
<th>Mn position $d$</th>
<th>Energy level (high to low)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a/2$</td>
<td>$d_{xy}$ $d_{x^2-y^2}$ $d_z$ $d_{yz} = d_{y^2}$</td>
</tr>
<tr>
<td>0</td>
<td>$d_{x^2-y^2}$ $d_z$ $d_{xy}$ $d_{xz} = d_{y^2}$</td>
</tr>
<tr>
<td>0.15 Å</td>
<td>$d_{x^2-y^2}$ $d_z$ $d_{xz} = d_{y^2}$ $d_{xy}$</td>
</tr>
<tr>
<td>0.15 Å, larger ASA</td>
<td>$d_z$ $d_{x^2-y^2}$ $d_{xy}$ $d_{xz} = d_{y^2}$</td>
</tr>
<tr>
<td>Expt. [14]</td>
<td>$d_{x^2-y^2}$ $d_z$ $d_{xz} = d_{y^2}$ $d_{xy}$</td>
</tr>
</tbody>
</table>

Table 5.2: The order of YSR energies for all $d$ orbitals.

Figure 5.14 shows the corresponding LDOS in the normal state for all considered heights. For the height of $d = a/2$, the LDOS of spin down (negative DOS) is completely below the Fermi level, while the majority of spin-up LDOS remains unoccupied. This leads to the large magnetic moments and a correspondingly large exchange coupling $J_S$ for all $d$ orbitals. When comparing the two cases of $d = 0.15$ Å with different sizes of ASA spheres, the YSR energy of the $d_{x^2-y^2}$ and $d_z$ orbitals are dramatically different in these two cases, in contrast the profiles of the normal state LDOS remain similar. This highlights that the effects of $J_S$ are minor, and the scattering potential $V$ is the major contribution to the YSR energy, in that case.

For the case of $d = 0$, we find a smaller shift between the spin-up and spin-down LDOS in comparison to $d = 0.15$ Å, which suggests the weak $J_S$ term, as shown in Table 5.1. When the embedded Mn impurity is moved to the adatom position, the $d_{x^2-y^2}$ and $d_{xy}$ orbitals without a $z$ component shift slightly. However, those orbitals with a $z$ component substantially move away from the original position.
5.4 Conclusions

In summary, the BCS theory is briefly introduced and the BCS gap equation is presented, connecting the superconducting gap to the critical temperature. In the next step, the theory of the Yu-Shiba-Rusinov (YSR) states, the bound states within the superconducting gap induced by magnetic impurities, is discussed in terms of the scattering potential and magnetic exchange. Moreover, the connection of the YSR states to the Majorana quasiparticles (zero modes) is introduced in order to highlight the relevance of this work.

Experimentally, scanning tunneling microscopy (STM) measurements are used to observe these bound states and the principle setup is discussed briefly. Following this, the results for superconducting Pb are reviewed, both experimentally and theoretically, indicating that Pb can be described within the BCS framework using our computational technique. The experimental observations of YSR states for a Mn impurity on Pb surfaces are introduced, as well as the result of the $d$-orbital decomposition for these in-gap states.

To investigate the superconductivity in heavy materials with complicated orbital character,
we extended the study of $\gamma$ uranium from the previous normal state to the superconducting state. Our results reveal that there are several coherence peaks around the superconducting gap. This can be related to the large number of flat $f$ bands. We visualise the gap anisotropy of $\gamma$ uranium on the Fermi surface sheets and compared it to the results for the Fermi velocity. In some areas of the Fermi sheets, the gap size is inversely related to the Fermi velocity, as indicated by the BCS framework. However, other effects, such as the $f$ electron character and the large atomic number, need to be considered for the superconductivity in uranium.

For the YSR states, we firstly analysed the model focusing on the effects of magnetic exchange and the scattering potential at impurities. The local DOS for the YSR bound states of the Mn impurity on the Pb surface at various heights was calculated. Surprisingly, the order of the resulting energy level is in almost perfect agreement to the experiment. By comparing the cases of changing heights, we found that the energy of the orbital resolved YSR states shift significantly for specific orbitals most affected by the changing position in $z$ direction.
In this dissertation, I have introduced the applications and the industrial relevance in MRAM devices of investigating the spin-dependent transport in heavy metals. In the presence of spin-orbit coupling the intrinsic and extrinsic mechanisms of the spin Hall effect and the spin accumulation were analytically discussed using the semiclassical transport theory based on wave-packet dynamics and the Boltzmann equation. The measurement methods were briefly introduced as well. In Chapter 2, I discussed the computational method employed in my work. The electronic structure calculations, including the normal and the superconducting state, are performed using the Korringa-Kohn-Rostoker Green’s function method within first-principles DFT in the LDA approximation. The transport calculations are described via the Berry curvature and the linearised Boltzmann equation for the intrinsic and extrinsic mechanisms, respectively. Moreover, the spin accumulation in 2D systems derived from the extrinsic mechanism is presented. Thus, the full computational process of investigating spin-dependent transport is discussed in detail.

In Chapter 3, the material we investigated for the spin-dependent transport is uranium, the heaviest naturally occurring metal with f-electrons at the Fermi energy and large spin-orbit coupling. These features are critical in spin-dependent transport and the research of f-electron materials is sparse. We first calculated the electronic structure for the γ-, hcp-, and α-U and found our results are in good agreement to previous theoretical and experimental work. Together with an experimental group we investigated the influence of the quantum well states on the magnetism in the bilayer U/Fe system. By calculating the Bloch spectral function, we estimated the wavelengths of the quantum well states for the α-U crystal structure. These values are in good agreement with the experimental results. For the spin-dependent transport, we calculated the longitudinal and spin conductivities based on the extrinsic mechanism of skew scattering.
by doping 3d substitutional impurities in the γ-, α- and hcp-U. Our results indicate that the resonant scattering from d-orbital electrons is predominant for 3d impurities in the f-electron U host via the d-f hybridisation. The magnetism induced by the conventional magnetic impurities leads to a reduction of the spin Hall effect in all cases across the different crystalline phases. Besides, we calculated the intrinsic spin Hall conductivity described by the Berry curvature in the semiclassical description. By analysing the contributions of extrinsic and intrinsic mechanisms to the total spin Hall angle, we find that hcp-U shows the largest efficiency of charge-to-spin conversion of up to 30%. This is considerably larger than the standard spin Hall material Pt (∼ 10%).

In Chapter 4, we investigated the spin accumulation. The mechanism of this effect is based on the scattering effect from impurities as well as the Edelstein effect. We calculated the spin accumulation for free-standing thin films for various materials based on the semiclassical Boltzmann equation. By using different approximations we found that while the anisotropic relaxation time approximation (scattering-out term) and vertex correction (scattering-in term) are comparable in a light metal like Cu, the effect of the spin accumulation in heavy metals such as Pt is dominated by the anisotropic relaxation time. In addition, we calculated the normalised spin accumulation, the efficiency of charge-to-spin-accumulation conversion, in the Cu and Pt host. By varying the impurity positions, we found that the effect of the impurity position on the normalised spin accumulation is significant in Cu while this is small in Pt. Our results for Pt are in very good agreement with experiments. In contrast, there is a discrepancy between our results for Cu and the experiments. This could be attributed to further extrinsic perturbations not considered in our calculations. As extrinsic effects are far more dominant in Cu than in Pt, a direct comparison to experimental results would require a detailed knowledge of the sample preparations and conditions. On the other hand, the intrinsically dominated effects in Pt are far more consistent across different samples.

In Chapter 5, first I reviewed the BCS theory as well as the in-gap bound states (YSR states) and connected it to the Majorana quasiparticles (zero energy modes). We calculated the electronic structure of the superconducting state in γ-U and found several coherence peaks around the superconducting gap which shows the complexity of the f-electron bands. By visualising the gap anisotropy on the Fermi surface sheets, we found the relation between the superconducting gap and the Fermi velocity within the BCS framework is valid in some areas of the Fermi surface sheets, whereas more effects, such as the large atomic number and f-electron character, have to be considered for a deeper understanding. In addition, we calculated the YSR bound states for a Mn impurity on a Pb surface. By varying the height of Mn position above Pb, we can analyse the effect of the height on the energetic positions of orbital resolved YSR states by studying the magnetic exchange and the scattering properties in the YSR model. Our results are in almost perfect agreement to the experiments.


**APPENDIX A**


dependence of Hall conductivity on charge conductivity in the dilute limit

Unlike the case in the absence of Hall effect physics where the resistivity is inversely proportional to the longitudinal conductivity, the expression for the Hall resistivity in terms of the longitudinal conductivity, for a crystal with cubic symmetry, is written as

\[
\rho = \sigma^{-1} = \begin{pmatrix}
\sigma_{xx} & \sigma_H & 0 \\
-\sigma_H & \sigma_{xx} & 0 \\
0 & 0 & \sigma_{zz}
\end{pmatrix}^{-1}.
\]

(A.1)

Inverting this conductivity gives

\[
\rho = \begin{pmatrix}
\frac{\sigma_{xx}}{\sigma_{xx} + \sigma_H} & -\frac{\sigma_H}{\sigma_{xx} + \sigma_H} & 0 \\
\frac{\sigma_H}{\sigma_{xx} + \sigma_H} & \frac{\sigma_{xx}}{\sigma_{xx} + \sigma_H} & 0 \\
0 & 0 & \frac{1}{\sigma_{zz}}
\end{pmatrix}.
\]

(A.2)

In the dilute limit the longitudinal conductivity is inversely proportional to the impurity concentration \(C_0\), \(\sigma_{xx} \sim c_0^{-1}\), while for the Hall conductivity it is determined by the intrinsic, skew-scattering and side-jump mechanisms, shown as

\[
\sigma_H = \sigma_H^{\text{int}} + \sigma_H^{\text{ss}} + \sigma_H^{\text{sj}}.
\]

(A.3)

In Chapter 1.1.4, we have discussed the relation between the Hall conductivity and impurity concentration for the various mechanism, see Eq. (1.32). Inserting this dependence into Eq. (A.2) yields individually

\[
\rho^{\text{ss}} \propto \begin{pmatrix}
c_0 & -c_0 & 0 \\
c_0 & c_0 & 0 \\
0 & 0 & c_0
\end{pmatrix}.
\]

(A.4)
for the skew-scattering mechanism, and

\[
\rho_{\text{intr/sj}}^{\text{intr/sj}} \propto \begin{pmatrix}
\frac{c_0}{2} & -\frac{c_0^2}{1+c_0^2} & 0 \\
\frac{c_0^2}{1+c_0^2} & \frac{c_0}{2} & 0 \\
0 & 0 & c_0
\end{pmatrix} \approx \begin{pmatrix}
\frac{c_0}{2} & -c_0^2 & 0 \\
c_0^2 & \frac{c_0}{2} & 0 \\
0 & 0 & c_0
\end{pmatrix}
\]

(A.5)

for the intrinsic and side-jump contribution. The concentration is linearly proportional to the longitudinal resistivity, therefore the Hall resistivity for the different mechanisms can be scaled by

\[
\rho_{yx}^{\text{int}} \sim (\rho_{xx})^2,
\rho_{yx}^{\text{ss}} \sim (\rho_{xx})^1,
\rho_{yx}^{\text{sj}} \sim (\rho_{xx})^2.
\]

(A.6)
B.1 Transformation to the hermitian KKR matrix

To obtain the hermitian KKR matrix for the real eigenvalues, Equation (2.55) is applied by the transformations as

\[ P^T I M(k; E) I^{-1} P P^{-1} I \Delta t(E) c(k) = 0, \]  

(B.1)

where \( P \) and \( I \) are abbreviations of unitary matrices \( P_{QQ'} \) and \( I_{QQ'} \) written as

\[ P_{QQ'} = \sum_{s=\pm 1/2} \left( l, \frac{1}{2}, m_l, m_{s-1/2} \right| j m_j) e^{i \bar{\delta}_l} \delta_{ll'} \left( l', \frac{1}{2}, m_{l'}, m_{s-1/2} \right| j' m_{j'}), \]  

(B.2)

and

\[ I_{QQ'} = \sum_{s=\pm 1/2} \left( l, \frac{1}{2}, m_l, m_{s-1/2} \right| j m_j) i^{-1} \delta_{ll'} \left( l', \frac{1}{2}, m_{l'}, m_{s-1/2} \right| j' m_{j'}). \]  

(B.3)

Here, \( i_l \) and \( \bar{\delta}_l \) are the scattering phase factors and phase shifts of the reference system, respectively. The scattering phase shifts in our calculations are appropriately defined in limit of hard spherical potential as

\[ \tan(\bar{\delta}_l) = \frac{j_l(\sqrt{E} r_{ASA})}{n_l(\sqrt{E} r_{ASA})}, \]  

(B.4)

where \( j_l(\sqrt{E} r_{ASA}) \) and \( n_l(\sqrt{E} r_{ASA}) \) are the spherical Bessel and Neumann functions, respectively. Thus the hermitian KKR matrix and the eigenvectors are defined as

\[ \tilde{M}(k; E) = P^T I M(k; E) I^{-1} P \]  

(B.5)

and

\[ \tilde{c}(k) = P^{-1} I \Delta t(E) c(k). \]  

(B.6)
Here the $I$ transformation matrix takes the special definition of the free-space structure constants into account and the $P$ transformation is for the screened KKR formalism. The real eigenvalues can be calculated by the transformed eigenvalue equation

$$
\tilde{M}(k; E)\tilde{c}(E, k) = \tilde{\lambda}(k; E)\tilde{c}(E, k).
$$  \hspace{1cm} (B.7)

More details of the transformation procedure can be found in Peter Zahn’s PhD dissertation [130].

### B.2 The analytic $k$ derivative calculating the Fermi velocity

Proposed by N. A. Shilkova, V. P. Shirokovskii and N. A. Trubitsina [131, 132], the idea based on the $k$ derivative starts from the eigenvalue equation [Eq. (2.55)] with the eigenvalue $\lambda(k, E)$ of zero and the energy $E$ is $k$ dependent within the band structure. The total $k$ derivative of the eigenvalue is

$$
\frac{d\lambda(k, E)}{dk} = -\frac{\partial\lambda(k, E)}{\partial E(k)}\frac{\partial E(k)}{\partial k} + \frac{\partial\lambda(k, E)}{\partial k} = 0
$$  \hspace{1cm} (B.8)

and the Fermi velocity can be expressed by

$$
\hbar v_F(k) = \frac{\partial E_F(k)}{\partial k} = -\frac{\partial E_F(k)}{\partial \lambda(E, k)}\frac{\partial\lambda(E, k)}{\partial k}.
$$  \hspace{1cm} (B.9)

The eigenvalues are linearly dependent on the energy, thus numerically the energy derivative of the eigenvalues can be simply perform [130]. The eigenvalue derivative of the energy is tackled by the Hellmann-Feynman theorem for the non-hermitian eigenvalue equation. In the Hellmann-Feynman theorem for a hermitian operator $M_h(k, E)$ with an parameter $k$, a $k$ derivative of eigenvalue $\lambda$ can be written as

$$
\frac{d\lambda_s(k, E)}{dk} = \frac{d}{dk}\psi^\dagger_s(k)M_h(k, E)\psi_s(k)
$$  \hspace{1cm} (B.10)

where $s$ labels the considered eigenvalue and $\psi_s(k)$ is the corresponding eigenfunction which is conjugate transpose. The situation is different for the non-hermitian operator $M(k; E)$. A analogous formalism for the non-hermitian eigenvalue problem can be written as

$$
\frac{\partial\lambda_s(k, E)}{\partial k} = \frac{1}{\psi_{s,L}(k), \psi_{s,R}(k)}\psi^\dagger_{s,L}(k)\frac{\partial M(k, E)}{\partial k}\psi_{s,R}(k),
$$  \hspace{1cm} (B.11)

where $\psi_{s,L}(k)$ and $\psi_{s,R}(k)$ are the left and right eigenvectors of the matrix $M$, respectively, expressed by

$$
\begin{cases}
M(k; E)\psi_{s,R}(k) = \lambda_s\psi_{s,R}(k) \\
\psi^\dagger_{s,L}(k)M(k; E) = \lambda_s\psi^\dagger_{s,L}(k)
\end{cases}
$$  \hspace{1cm} (B.12)
These two eigenvectors are normalised by \( \psi_{s,R}^\dagger \psi_{s,R} = \psi_{s,L}^\dagger \psi_{s,L} = 1 \). The KKR matrix \( M(k;E) \) can be substituted by Eq. (2.54) and Eq. (2.25), thus the derivative is eventually expressed by the real-space structure constant of the screened reference system as

\[
\frac{\partial M(k;E)}{\partial k} = \frac{\partial G(k;E)}{\partial k} = \sum_{\mu} G_{LL}^{nnj\mu\mu'}(E) \left[ -i(R^n - R'^n) \right] e^{-i(k(R^n - R'^n))}.
\]  

(B.13)

### B.3 Calculation of spin expectation value

In contrast to the solutions of fully relativistic equation discussed in Section 2.1.4, solutions of the Dirac-Kohn-Sham equation are expressed with the single-site scattering \( t_{QQ'}^n \). Thus the solutions of the Dirac equation is given by \( g_{QQ'} \) and \( f_{QQ'} \) [71, 117] as

\[
\psi_{nk}(r) = \sum_{Q} \sum_{Q'} a_{nQ}^n(k) \begin{pmatrix} g_{QQ'}(r)\chi_Q(r) \\ i f_{QQ'}(r)\chi_{\bar{Q}}(r) \end{pmatrix},
\]  

(B.14)

where \( Q \) and \( \bar{Q} \) are a set of \( \{\kappa m_j\} \) and \( \{-\kappa m_j\} \). The spin expectation value of the \( z \) component [Eq.(2.74)] can be calculated via the matrix elements as

\[
\langle \psi_{nk} | \hat{\Sigma}_z | \psi_{n'k} \rangle = -\sum_{k'\mu'} \sum_{\nu} a_{n'k'\mu'}^* (k) a_{n\kappa\mu} (k) \sum_{\kappa'} \left\{ \sqrt{k^2 - 1/4 - \mu(\mu - 1)} \right. \\
\times \left[ \frac{2}{2k + 1} \int g_{k\mu\kappa\mu'}(r)g_{k-\kappa\mu\mu'}(r)r^2 dr \\
+ \frac{2}{2k - 1} \int f_{k\mu\kappa\mu'}(r)f_{k-\kappa\mu\mu'}(r)r^2 dr \\
\right] + \left. \sqrt{(2k + 1 - 2\mu)(2k + 3 - 2\mu)} \right\} \frac{2k + 1}{2k - 1} \\
\times \int g_{k\mu\kappa\mu'}(r)g_{k-1\mu-1\mu\mu'}(r)r^2 dr \\
+ \sqrt{(2k - 1 + 2\mu)(2k - 3 + 2\mu)} \frac{2k - 1}{2k + 1} \\
\times \int f_{k\mu\kappa\mu'}(r)f_{k-1\mu-1\mu\mu'}(r)r^2 dr \right\}.
\]  

(B.15)

Calculating the spin expectation value of the \( x \) and \( y \) component in Eq.(2.73) can be simply approached using the ladder operators \( \Sigma_+ = \Sigma_x + i\Sigma_y \) and \( \Sigma_- = \Sigma_x - i\Sigma_y \) as

\[
\langle \psi_{nk} | \hat{\Sigma}_x | \psi_{n'k} \rangle = -\sum_{k'\mu'} \sum_{\nu} a_{n'k'\mu'}^* (k) a_{n\kappa\mu} (k) \sum_{\kappa'} \left\{ \sqrt{k^2 - 1/4 - \mu(\mu - 1)} \right. \\
\times \left[ \frac{2}{2k + 1} \int g_{k\mu\kappa\mu'}(r)g_{k-\kappa\mu\mu'}(r)r^2 dr \\
+ \frac{2}{2k - 1} \int f_{k\mu\kappa\mu'}(r)f_{k-1\mu-1\mu\mu'}(r)r^2 dr \\
\right] + \left. \sqrt{(2k + 1 - 2\mu)(2k + 3 - 2\mu)} \right\} \frac{2k + 1}{2k - 1} \\
\times \int g_{k\mu\kappa\mu'}(r)g_{k-1\mu-1\mu\mu'}(r)r^2 dr \\
+ \sqrt{(2k - 1 + 2\mu)(2k - 3 + 2\mu)} \frac{2k - 1}{2k + 1} \\
\times \int f_{k\mu\kappa\mu'}(r)f_{k-1\mu-1\mu\mu'}(r)r^2 dr \right\}.
\]  

(B.16)
APPENDIX B. COMPUTATIONAL DETAILS

\[ \langle \Psi_{n_k} | \hat{\Sigma} \psi | \Psi_{n_k} \rangle = - \sum_{k' \mu' \kappa' \mu'} a_{k' \mu'}^{n^*} (k) a_{k' \mu'}^{n'} (k') \sum_{k \mu} \left\{ \sqrt{k^2 - 1/4 - \mu (\mu + 1)} \right. \\
\times \left[ \frac{2}{2k + 1} \int g_{k \mu \kappa' \mu'}^{*}(r) g_{k \mu + 1 \kappa' \mu'}(r) r^2 dr \right.
\left. + \frac{2}{2k - 1} \int f_{k \mu \kappa' \mu'}^{*}(r) f_{k \mu + 1 \kappa' \mu'}(r) r^2 dr \right] \\
- \frac{\sqrt{(2k + 1)(2k + 3 + 2\mu)}}{2k + 1} \left. \right. \\
\times \int g_{k \mu \kappa' \mu'}^{*}(r) g_{-k - 1 \mu - 1 \kappa' \mu'}(r) r^2 dr \\
\left. \right. \\
\left. \right. \\
- \frac{\sqrt{(2k - 1)(2k - 3 - 2\mu)}}{2k - 1} \left. \right. \\
\times \int f_{k \mu \kappa' \mu'}^{*}(r) f_{-k - 1 \mu + 1 \kappa' \mu'}(r) r^2 dr \right\} . \tag{B.17} \]

The coefficients \(c_1\) and \(c_2\) are known in the process fulfilling Eq. (2.73) and (2.74) and expressed as the form

\[ c_1 = \frac{1}{\sqrt{2}} \sqrt{1 + \frac{|a|^2}{\sqrt{|a|^2 + 4|d|^2}}} \tag{B.18} \]

and

\[ c_2 = - \left( \frac{|a|}{a} \right) \frac{d \sqrt{2}}{\sqrt{|a|^2 + 4|d|^2 + |a| \sqrt{|a|^2 + 4|d|^2}}} \tag{B.19} \]

where the parameters \(a\) and \(d\) are

\[ a = 2i \text{Im} \left\{ \langle \Psi_{k}^{1} | \hat{\Sigma}_{y} | \Psi_{k}^{2} \rangle \langle \Psi_{k}^{2} | \hat{\Sigma}_{x} | \Psi_{k}^{1} \rangle \right\} \tag{B.20} \]

and

\[ d = \langle \Psi_{k}^{2} | \hat{\Sigma}_{x} | \Psi_{k}^{1} \rangle \langle \Psi_{k}^{1} | \hat{\Sigma}_{y} | \Psi_{k}^{2} \rangle - \langle \Psi_{k}^{2} | \hat{\Sigma}_{y} | \Psi_{k}^{1} \rangle \langle \Psi_{k}^{1} | \hat{\Sigma}_{x} | \Psi_{k}^{2} \rangle, \tag{B.21} \]

respectively.
Here I would like to highlight the importance of the scattering-in term $P^{n'n''}_{kk'}$ in the linearised Boltzmann equation [Eq. (2.90)] for the skew scattering in the SHE. It was demonstrated by Butler [137, 138] that this term is equivalent to the vertex correction in the Kubo formula. To directly show that the skew-scattering part of the SHE is encoded by the scattering-in term, I drop the scattering-in term to calculate the spin Hall conductivity only in the anisotropic relaxation time approximation, written as

$$
\sigma_{xy}^s = \frac{e^2}{\hbar (2\pi)^3} \int \frac{dS}{|v_k|} |s_z(k)| |(r^+_k - r^-_k)| v^x_k v^y_k.
$$

(C.1)

It obviously shows the connection $\sigma_{xy}^s = \sigma_{yx}^s$. However, as previously discussed in Eq. (1.7) for simple cubic crystal, the reduced symmetry of relativistic description requires an antisymmetric Hall conductivity tensor with $\sigma_{xy}^s = -\sigma_{yx}^s$. Combining these two conditions gives that the Hall conductivity is zero with. It is clear that the scattering-in term is mandatory for the extrinsic SHE.


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