A Study of Topological Insulator States of Half-Heusler Materials and the Momentum Density of Overdoped Cuprates

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ABSTRACT OF DISSERTATION

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Abstract

We have applied first-principles calculations to investigate the topological insulator state of half-Heusler materials and the momentum density for overdoped cuprates. The specific topics addressed in this thesis are as follows.

1. Topological insulators are materials exhibiting a novel quantum state of matter; these insulators are characterized by a bulk excitation generated by the spin orbit interaction, and protected conducting states on their edge or surface. In this work we investigate in detail the electronic structure of a series of ternary half-Heusler compounds MM’X of MgAgAS-type with M = (Lu, La, Sc, Y) and M’X=(PtBi,AuPb,PdBi,PtSb,AuSn,NiBi,PdSb). The characteristic features of all half-Heusler compounds considered here are topological nontrivial semimetal, or nontrivial metal, or trivial insulator. The analysis of the relation among the band inversion strength (distance from the critical line), atomic number of constituents, and lattice constant could provide a methodology (a rule of thumb) to predict the topological order of hypothetical nonmagnetic half-Heusler compound more generally.

2. The bulk Fermi surface (FS) is observed in an overdoped ($x=0.3$) single crystal of La$_{2-x}$Sr$_x$CuO$_4$ by using Compton scattering. A 2-D momentum density recon-
struction from measured Compton profiles yields a clear FS signature in the third Brillouin zone along [100]. The quantitative agreement between density functional theory calculations and momentum density experiment suggests that Fermi-liquid physics is restored in the overdoped regime. The FS shows signs of a change topological of the FS found at lower doping. We find similar quantitative agreement between the measured 2D angular correlation of positron annihilation radiation (2D-ACAR) spectra and DFT simulations. However, 2D-ACAR does not give such a clear signature of the FS in the extended momentum space in either theory or experiment.
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List of Articles

During the duration of the author’s time at Northeastern several articles were published and prepared for publication. These are listed below, but only the first and fifth article will be discussed in this thesis.


5. Study of bulk Fermi surface and momentum density in heavily doped $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($x=0.3$) using high resolution Compton scattering and positron annihilation spectroscopies. W. Al-Sawai, Y. Sakurai, M. Itou, B. Barbiellini, P. E. Mijnarends, R. S. Markiewicz, S. Kaprzyk, S. Wakimoto, M. Fujita, S. Basak, H. Lin, H. Schut, K. Yamada, and A. Bansil, (In preparation to be submitted to PRB).


Chapter 1

Introduction

The discovery of electrons, over a century ago, was a turning point in the study of condensed matter physics. It was obvious at the time that electrons in solids give rise to electrical conductivity. But questions then arose, since all solids contain electrons, why do some conduct electricity and other do not?

The theory of electrons in matter ranks among the great challenges of theoretical physics, to develop theoretical approaches and computational methods that can accurately treat the interacting system of many electrons and nuclei found in condensed matter and molecules. Ultimately, the principles of understanding the materials and phenomena depend upon the understanding of electronic structure.

The most widely used theory to study the electronic structure is the density functional theory (DFT), which provides a huge simplification to the original many body problem. Because of the approach suggested by Kohn and Sham [1], to replace the many-body problem by an auxiliary independent particle problem, it became remarkably successful. As a self-consistent method, the Kohn-Sham approach in-
volves interaction densities, an appreciation of which clarifies the way the method is used.

In crystalline materials, another important simplification comes from Bloch’s theorem, which enables us to separate the problem into two parts: the first that is the same in every unit cell and the second that describes global behavior. This theory takes advantage of the translation symmetry of the crystal to classify the electronic states in terms of their crystal momentum. The electronic states are eigenstates of the Bloch Hamiltonian within a single unit cell of the crystal. The eigenvalues define the energy bands that collectively form the band structure. In more simple terms, band structure of a solid defines ranges of energy that an electron is “forbidden” or “allowed” to have. It is a function of the diffraction of the quantum mechanical electron waves in the periodic crystal lattice. The presence of allowed and forbidden bands of energy explains the behavior of materials like metals, semiconductors and insulators.

These band structures are often determined by solving the Schrödinger equation for a crystal potential $V(\mathbf{r})$, where the crystal potential is approximated by using Slater’s approximation, the muffintin potential. Many modern electronic structure methods employ this approximation. Among them are the augmented plane wave (APW) method and Green’s function methods (KKR) [2]. However, the linear augmented plane wave (LAPW) method [3] facilitates the construction of a full-potential with no shape approximation and it adapts a basis that is suitable for calculation of all states in an energy “window”. The LAPW method is particularly adapted for compounds involving transition metals and rare earth elements. Understanding many properties of these interesting materials often involves small energy differences due to magnetic order and/or lattice distortion. For such compounds,
we have employed the LAPW to study the topological insulator state for a series of Half-Huesler compounds that have attracted a lot of attention recently.

On the other hand, the Green function method has proved to be a very successful method to study metals. We have employed this method to study the momentum density of the metallic phase in an overdoped ($x=0.3$) single crystal of La$_{2-x}$Sr$_x$CuO$_4$ (LSCO). The momentum density can be measured by using two experimental techniques namely, Compton scattering and Positron annihilation, both can determine the ground state electronic structure of the system under consideration.

The study of momentum density is of interest to most subjects in physics, for example for systems of atoms in solid and liquid phases as well as interacting electron systems, such as conduction electrons. In the latter case a calculated band structure and Fermi surface would be employed with corresponding wavefunctions to calculate the complete shape of momentum density and then compare to experimental spectra. Measurement of Fermi surfaces is crucial for testing any electronic structure model and the Fermi liquid picture. In this context, we have performed calculations for both positron annihilation and Compton scattering of overdoped LSCO.
Chapter 2

Density Functional Theory

2.1 Introduction

The purpose of this chapter is to introduce the theory that has been used throughout this work to calculate the electronic states in crystals. One of the most powerful theories to solve many body problems is the so called Density Functional Theory (DFT). This theory can be applied not only to the electron gas as we use it here, but also to the proton-neutron gas in order to construct nuclear models, or to the nucleus-electron gas without the Born-Oppenheimer approximation to describe solids with light elements [4]. The Hamiltonian for a system of interacting electrons at sites $\mathbf{r}_i$ and nuclei with charges $Z_I$ and masses $M_I$ at sites $R_I$ can be written as [5]

$$H = -\frac{\hbar^2}{2} \sum_i \frac{\nabla^2 R_i}{M_i} - \frac{\hbar^2}{2} \sum_i \frac{\nabla^2 r_i}{m_e} - \frac{1}{4\pi\epsilon_o} \sum_{i,j} \frac{e^2 Z_i}{|\mathbf{R}_i - \mathbf{r}_j|} + \frac{1}{8\pi\epsilon_o} \sum_{i\neq j} \frac{e^2 Z_i Z_j}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{1}{8\pi\epsilon_o} \sum_{i\neq j} \frac{e^2 Z_i Z_j}{|\mathbf{R}_i - \mathbf{R}_j|}. \quad (2.1)$$
Under normal conditions some of the electrons will be bound more tightly to the nuclei as in free atoms, and as a result ions will be formed which are perturbed only very weakly by the motion of the residual electrons. Because of the large difference between electron and ion masses, the ionic motion measured on an electronic time scale is very slow, i.e. quasi static. Therefore, the electronic system remains in the same quantum state with respect to the wavefunction that depends parameterically on the ionic position. This is called Born-Oppenheimer (or adiabatic) approximation [4]. The effective Hamiltonian for the electronic system is given by

\[ H = -\frac{\hbar^2}{2 m_e} \sum_i \nabla^2 r_i - \frac{1}{4\pi\epsilon_0} \sum_{i,j} \frac{e^2 Z_i}{|R_i - r_j|} + \frac{1}{8\pi\epsilon_0} \sum_{i\neq j} \frac{e^2}{|r_i - r_j|} \]  

(2.2)

It is interesting to note here that the kinetic and electron-electron terms of eqn. 2.2 depend only on the fact that we are dealing with a many-electron system. They are independent of the particular kind of many-electron system. This part is universal. However, even after using the Born-Oppenheimer, the Hamiltonian still far too difficult to solve exactly. Therefore, we need a theory to deal with such a large number of electrons. Since DFT provides us with the stationary states of a single electron, it is preferable first to explain why such a theory can be used to describe the properties of real metals and semi-conductors.

### 2.2 DFT foundations

In the DFT due to Hohenberg and Kohn [6], instead of dealing with the many-body Schrödinger equation eqn. 2.2, which involves the many-body wavefunction, one deals with a formulation of the problem that involves the total density of elec-
trons \( \rho(\mathbf{r}) \). This is a huge simplification, since the many-body wavefunction need never be specified. The traditional formulation of the two theorems of Hohenberg and Kohn is as follows. First Theorem: The relation between the density of electrons and the wavefunction can be reversed, i.e. for a given ground-state density \( \rho(\mathbf{r}) \) it is possible, in principle, to calculate the corresponding ground-state wavefunction \( \Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N) \). Therefore, there is a one-to-one correspondence between the ground-state density \( \rho(\mathbf{r}) \) of a many-electron system (atom, molecule, solid) and the external potential \( V_{\text{ext}} \). The consequence is that the ground-state expectation value of any observable \( \hat{O} \) is a unique functional of the exact ground-state electron density.

\[
< \Psi | \hat{O} | \Psi > = O[\rho] \quad (2.3)
\]

The second theorem: For \( \hat{O} \) being the Hamiltonian \( \hat{H} \), the ground-state total energy functional \( H[\rho] \equiv E_{\text{ext}}[\rho] \) is of the form:

\[
E_{\text{ext}}[\rho] = \frac{< \Psi | \hat{T} + \hat{V} | \Psi >}{F_{\text{HK}}[\rho]} + < \Psi | V_{\text{ext}} | \Psi >
\]

\[= F_{\text{HK}}[\rho] + \int n(\mathbf{r}) V_{\text{ext}}(\mathbf{r}) d\mathbf{r} \quad (2.5)\]

where the functional \( F_{\text{HK}}[\rho] \) is a universal functional for any many-electron system and \( V_{\text{ext}}[\rho] \) is called the non-universal functional, as it depends on the system under study.

### 2.2.1 Kohn-Sham single particle equations

The approach proposed by Kohn and Sham [1] turns DFT into a practical tool to obtain the ground state density. The essence of this approach is to replace the
many-body problem by an auxiliary independent particle problem, which involves independent particles but an interacting density. Therefore, they replace the difficult interacting many-body system described in the Hamiltonian 2.2, with a different auxiliary system, a one particle system, that can be solved more easily.

The fundamental theorems, stated in the previous section show that in principle the ground state can be represented by the ground state of an auxiliary system of non-interacting particles. The second assumption is the auxiliary Hamiltonian is chosen to have the usual kinetic operator and effective local potential $V_{eff}$. Let us rewrite the Hohenberg-Kohn functional. The correlation energy is defined as that part of the total energy which is present in the exact solution, but absent in the Hartree-Fock solution. The total energy functionals $E_e[\rho]$ and $E_{HF}[\rho]$ corresponding to the exact and Hartree-Fock Hamiltonian respectively, are:

\begin{align*}
E_e[\rho] & = T[\rho] + V[\rho] \quad (2.6) \\
E_{HF}[\rho] & = T_0[\rho] + \left( V_x[\rho] + V_H[\rho] \right). \quad (2.7)
\end{align*}

Here $T$ and $V$ are the exact kinetic and electron-electron potential energy functionals, $T_0$ is the functional for the kinetic energy of a non-interacting electron gas, $V_H$ stands for the Hartree contribution and $V_x$ for the exchange contribution. By subtracting 2.6 from 2.7, the functional for the correlation contribution is

$$V_c[\rho] = T[\rho] - T_0[\rho].$$

The exchange contribution to the total energy is defined as the part which is present in the Hartree-Fock solution, but absent in the Hartree solution. Obviously,
with the Hartree functional given by:

\[
E_H[\rho] = T[\rho] + V_H[\rho].
\]  
(2.9)

The exchange potential it can be defined as:

\[
V_x[\rho] = V[\rho] - V_H[\rho],
\]  
(2.10)

with this knowledge, we can rewrite the Hohenberg-Kohn functional in the following way:

\[
F_{HK} = T + V + T_0 - T_0
= T_0 + V + \left( T - T_0 \right)_{V_c}
= T_0 + V + V_c + V_H - V_H
= T_0 + V_H + V_c + \left( V - V_H \right)_{V_x}
F_{HK}[\rho] = T_0[\rho] + V_H[\rho] + (V_x[\rho] + V_c[\rho]).
\]  
(2.11)

Here \( V_{xc} \) is the exchange-correlation energy functional. We don’t know it formally, as it contains the difficult exchange and correlation contributions. If we assume for a while that we do know \( V_{xc} \), we can write explicitly the energy functional:

\[
E_{V_{ext}}[\rho] = T_0[\rho] + V_H[\rho] + V_{xc}[\rho] + V_{ext}[\rho],
\]  
(2.12)

where \( V_{ext} \) is the external potential due to the nuclei and any other external fields. We can interpret the above expression also as the energy functional of a non-interacting classical electron gas, subject to two external potentials: one due to
Figure 2.1: Flow chart for the $n^{th}$ iteration of the self-consistency procedure for the Kohn-Sham equation

The density of the auxiliary system is given by the sum of the squares of the nuclei, and one due to exchange and correlation effects. Then the Kohn-Sham approach to the full interacting many-body problem is to rewrite eqn. 2.12 in the form

$$E_{KS} = T_0[\rho] + \int d\mathbf{r} V_{ext}(\mathbf{r})\rho(\mathbf{r}) + V_H[\rho] + V_{xc}[\rho].$$  \hspace{1cm} (2.13)

The density of the auxiliary system is given by the sum of the squares of the
orbitals for each spin.

\[ \rho(r) = \sum_\sigma \rho(r, \sigma) = \sum_\sigma \sum_i |\psi_i^\sigma|^2 \quad (2.14) \]

and the independent-particle kinetic energy \( T_0 \) is given by

\[ T_0 = -\frac{1}{2} \sum_\sigma \sum_i <\psi_i^\sigma | \nabla^2 | \psi_i^\sigma > \quad (2.15) \]

and we define the classical Coulomb interaction energy of the electron density \( \rho(r) \) interacting with itself

\[ V_H[\rho] = \frac{1}{2} \int d^3r d^3r' \rho(r) \rho(r') / |r - r'|. \quad (2.16) \]

A successful minimization of the energy functional will yield the ground-state density \( \rho_0 \) and thus all other ground-state observables. The variational problems of minimizing the energy functional \( E_{KS}[\rho] \) can be solved by applying the Lagrangian method of undetermined multipliers.

\[ \frac{\delta}{\delta \rho} [E_{KS}[\rho] + \varepsilon(\int d^3r \rho - N)]_{\rho_0} = 0, \quad (2.17) \]

subject to the constraint \( N=\int d^3r \rho(r) \), where \( N \) is the number of electrons in the system. By using:

\[ \frac{\delta T_0}{\delta \rho_i^\sigma} = -\frac{1}{2} \nabla^2 \rho_i^\sigma; \quad \frac{\delta \rho_i^\sigma(r)}{\delta \rho_i^\sigma} = \psi_i^\sigma(r), \quad (2.18) \]

this leads to Kohn-Sham equations:

\[ (H_{KS}^\sigma - \varepsilon_i) \psi_i^\sigma(r) = 0, \quad (2.19) \]

where the \( \varepsilon_i \) are the eigenvalues, and \( H_{KS} \) is the Kohn-Sham Hamiltonian in Hartree
units, and is given by:

\[
\hat{H}_{KS} = \hat{T}_0 + \hat{V}_H + \hat{V}_{xc} + \hat{V}_{ext}
\]

(2.20)

\[
= \frac{-1}{2} \nabla^2 \psi_i + \int \frac{\rho(r')}{|r - r'|} dr' + V_{xc} + V_{ext}
\]

(2.21)

\[
= \frac{-1}{2} \nabla^2 + V_{eff}(r).
\]

(2.22)

To find the ground-state density, we can rely on solving familiar Schrödinger-like non-interacting single-electron equations. The single-electron wave functions \(\psi_i\) are not the wave functions of electrons. They describe mathematical quasi-particles, without a direct physical meaning. Only the overall density of these quasi-particles is guaranteed to be equal to the true electron density. Also the single-particle energies \(\epsilon_i\) are not single-electron energies. Both the Hartree operator \(V_H\) and the exchange-correlation operator \(V_{xc}\) depend on the density \(\rho(r)\), which in turn depends on the \(\psi_i\) which must be calculated. This means that we are dealing with a self-consistency problem: the solutions \(\psi_i\) determine the original \(V_H\) and \(V_{xc}\) in \(H_{KS}\), and the equation cannot be written down and solved before its solution is known.

An iterative procedure is needed to escape from this paradox. Some starting density \(\rho_0\) is guessed, and a Hamiltonian \(H_{KS}\) is constructed with it. The eigenvalue problem is solved, and results in a set of \(\psi_1\) from which a density \(\rho_1\) can be derived. Most probably \(\rho_0\) will differ from \(\rho_1\). Now \(\rho_1\) is used to construct \(H_{KS}\), which will yield a \(\rho_2\), etc. The procedure can be set up in such a way that this series will converge to a density \(\rho_f\) which generates a \(H_{KSf}\) which yields as solution again \(\rho_f\). This final density is then consistent with the Hamiltonian. Fig. 8.1 explains the self-consistency procedure.
2.3 The exchange correlation energy*

So far we have neglected the fact that we do not know the exchange-correlation functional. Since $E_{xc}[\rho]$ is small compared to the kinetic and Hartree energies, a good approximation might be sufficient. Once a suitable approximation for $E_{xc}[\rho]$ can be found we can calculate the ground state energy, the ground state density, and any observable that is known as an explicit functional of the density. A widely used approximation is the Local Density Approximation (LDA)[1].

In this approximation the exchange-correlation energy, due to a particular density $\rho(\mathbf{r})$, is found by dividing the material into infinitesimally small volumes with a constant density in each. Each volume element contributes to the total exchange correlation energy by an amount equal to the exchange correlation energy of an identical volume filled with a homogeneous electron gas, that has the same overall density as the original material has in this volume.

The significance of this model is the assumption that we can write the exchange-correlation functional in the form:

$$E_{xc}^{LDA}(\rho) = \int d\mathbf{r} \rho(\mathbf{r}) \epsilon_{xc}(\rho(\mathbf{r})), \quad (2.23)$$

the quantity $\epsilon_{xc}(\rho)$ is the exchange-correlation energy density of a homogeneous electron gas with density $\rho(\mathbf{r})$, and can be split into exchange and correlation contributions,

$$\epsilon_{xc}[\rho] = \epsilon_x[\rho] + \epsilon_c[\rho]. \quad (2.24)$$

---

The exchange part, $\epsilon_x[\rho]$, which represents the exchange energy of an electron in a uniform electron gas of a particular density is equal to

$$\epsilon_x[\rho(r)] = -\frac{3}{4} \left( \frac{3\rho(r)}{\pi} \right)^{1/3},$$  \hspace{1cm} (2.25)

the correlation part $\epsilon_c[\rho]$ has no known mathematical formula. However, it is accurately calculated by using quantum Monte-Carlo simulations\(^\dagger\). LDA is expected to perform well for systems with a slowly varying density. Surprisingly, it works very well in many other (realistic) cases.

A step to improve the LDA is making the exchange-correlation contribution of every infinitesimal volume not only dependent on the local density $\rho(r)$ at a particular point $r$, but also on the density in the neighboring volumes. In other words, the gradient of the charge density, $\nabla \rho(r)$ will play a role, in order to account for the inhomogeneity of the true electron density. This approximation is therefore called the Generalized Gradient Approximation (GGA)[11].

There are a few drawbacks. There is only one LDA exchange-correlation functional, because there is a unique definition for $\epsilon_{xc}$. But there is some freedom to incorporate the density gradient, and therefore several versions of GGA exist (First drawback). Moreover, in practice one often fits a candidate GGA-functional with (hopefully only a few) free parameters to a large set of experimental data on atoms and molecules. The best values for these parameters are fixed then, and the functional is ready to be used routinely in solids. Therefore such a GGA-calculation is strictly speaking not an ab initio calculation, as some experimental information is

\(^\dagger\)The best approximation for XC part follows from the quantum Monte Carlo calculations of Ceperley and Alder[7] by means of an appropriate interpolation or parametrization, see Refs. [8, 9, 10]. Then C part can be deduced from XC and X (see eqn. 2.25) parts.
used (Second drawback). Nevertheless, there exist GGA’s that are parameter free.

### 2.3.1 MBJLDA

The DFT band structure calculations within the LDA or GGA approximation have been successfully employed to determine the ground-state electronic properties of a large class of materials [12]. However, if DFT-(LDA,GGA) is used to determine the quasiparticle spectra of many-electron systems in most cases results are in disagreement with experiments. For instance, in the case of bulk semiconductors, the assumption of the Kohn-Sham eigenvalues as electronic quasiparticle energies leads to a systematic underestimate of the electronic transition energies with respect to experiment (band-gap problem) [12, 13, 14, 15, 16, 17, 18].

The self-energy operator is treated usually in the GW approximation (screened electrons) by starting from DFT-LDA basis used to compute the one-particle Green function and the screened Coulomb interaction [15]. So far, the numerical effort required to calculate the dynamical screened interaction for the GW self-energy has restricted the systematic solution of the quasiparticle problem mainly to simple structures [16, 17].

Fabien Tran and Peter Blaha suggest a simple modification of the original Becke and Johnson (BJ) exchange potential which yields band gaps with an accuracy comparable to approaches which are orders of magnitude more expensive [19]. The modified BJ potential (MBJ) proposed is:

\[
v_{x,\sigma}^{MBJ} = cv_{x,\sigma}^{BR}(r) + (3c - 2) \frac{1}{\pi \sqrt{\frac{5}{12}}} \sqrt{\frac{2t_\sigma(r)}{\rho_\sigma(r)}},
\]  

(2.26)
where $\rho_\sigma = \sum_{i=1}^{N_\sigma} |\psi_{i,\sigma}|^2$ is the electron density, $t_\sigma = \frac{1}{2} \sum_i^{N_\sigma} \hat{\nabla} \psi_{i,\sigma}^* \cdot \hat{\nabla} \psi_{i,\sigma}$ is the kinetic energy density and

$$v_{x,\sigma}^{BR} = -\frac{1}{b_\sigma(r)} \left( 1 - e^{-x_\sigma r} - \frac{1}{2} v_\sigma(r) e^{-x_\sigma r} \right)$$

(2.27)

is the Beck-Roussel [20] potential, $x_\sigma$ is determined from an equation involving $\rho_\sigma$, $\hat{\nabla} \rho_\sigma$, $\hat{\nabla}^2 \rho_\sigma$ and $t_\sigma$, $b_\sigma = \left[ x_\sigma^3 e^{-x_\sigma} / (8\pi \rho_\sigma) \right]^{1/3}$, and $c$ was chosen to depend linearly on the square root of the average of $\frac{\nabla^2 \rho}{\rho}$:

$$c = \alpha + \beta \left( \frac{1}{V_{\text{cell}}} \int_{\text{cell}} \frac{|\hat{\nabla} \rho(r)|}{\rho(r)} \right)^{1/2}$$

(2.28)

here $\alpha$ and $\beta$ are two free parameters and $V_{\text{cell}}$ is the unit cell volume. Where $\alpha$ and $\beta$ are determined by minimization of the mean absolute relative error for the band gap of several solids, and take the values $\alpha=-0.0012$ and $\beta=1.023$ bohr$^{1/2}$. Using this potential instead of LDA or GGA, MBJLDA offers an improvement over LDA or GGA for the description of the band gap of many materials.
Chapter 3

LAPW Method

Regardless whether one has used HF or DFT, one ends up with an infinite set of one-electron equations of the following type:

\[
\begin{aligned}
\left(-\frac{\hbar^2}{2m_e} \nabla^2 + \frac{e^2}{4\pi\epsilon_0} \int \frac{\rho(r')dr'}{|r-r'|} + V_\alpha + V_{ext}\right) \phi_m = \epsilon_m \phi_m,
\end{aligned}
\]

(3.1)

where \(\hat{H}_{sp}\) is the single-particle Hamiltonian, \(V_\alpha\) is the exchange-correlation operator, and \(m\) is an integer. The \(\phi_m(r)\) are mathematical single particle, KS, orbitals. The various methods for solving the Schrödinger equation 3.1 differ in the form chosen for the single-particle orbitals \(\phi_m(r)\). Here solving means finding the coefficients \(c^m_p\) needed to express \(\phi_m(r)\) in terms of a given basis set \(\phi^b_p\),

\[
\phi_m = \sum_{p=1}^{P} c^m_p \phi^b_p.
\]

(3.2)
The wave functions $\phi_m$ belong to a Hilbert space which has an infinite dimension, therefore $P$ in principle is infinite. In practice, one works with a limited set of basis functions, such that the number of basis states is enough to describe a function close to $\phi_m$. Having chosen a basis number $P$, then we can handle the eqn 3.1 as an eigenvalue problem. For a given $m$, we substitute eqn 3.2 into 3.1 and left-multiply with $<\phi_i^b|i = 1...P>$. Then we get:

\[
\begin{bmatrix}
\vdots & \cdots & \cdots & \cdots \\
<\phi_i^b|\hat{H}_{sp}|\phi_j^b> - \epsilon_j <\phi_i^b|\phi_j^b> & \vdots & \vdots & \vdots \\
\vdots & \cdots & \cdots & \cdots \\
\end{bmatrix}
\begin{bmatrix}
\epsilon_1^m \\
\vdots \\
\epsilon_P^m \\
\end{bmatrix}
= 
\begin{bmatrix}
0 \\
0 \\
0 \\
\end{bmatrix}
\] (3.3)

We recognize here the matrix elements of the single-particle Hamiltonian in the basis states, and the overlap matrix elements. The overlap matrix is a unit matrix if the basis set is orthonormal. Diagonalization of the Hamiltonian matrix will lead to $P$ eigenvalues and $P$ sets of coefficients that express each of the $P$ eigenfunctions in the given basis (if more eigenfunctions are needed, $P$ must be increased). The larger the $P$, the better the approximation of the eigenfunction, but the more time-consuming the diagonalization of the matrix in eqn. 3.3.

It is very important in theoretical condensed matter physics to find a basis set that is efficient and unbiased. In this chapter, we will discuss the framework to solve the many-body problem by linear augmented plane wave (LAPW), and later we will do the Green function method (KKR). We start by introducing the Augmented Plane Wave (APW) method and the motivation for its modification to the LAPW method.
3.1 APW

The object of each band structure calculation is to solve the Schrödinger eqn 3.1. A simple-minded solution would be to expand \( \phi_m \) into an infinite set of plane waves which have the Bloch form. In the region far away from the nuclei the electrons are more or less ‘free’, and free electrons are described by plane waves. However, close to the nuclei, the electrons behave quite as if they were in a free atom, and they could be described more efficiently by atomic-like functions. As a result, the plane wave expansion converges very slowly, since the oscillations of the electrons wave functions near the nucleus require the presence of high momenta. Therefore, one would have to solve a secular equation of a very large order. Hence for practical computations of electron wave functions an expansion into plane waves is unsuitable.

As a solution, one can divide the space into two regions: around each atom a sphere with radius \( R_\alpha \) is drawn (call it \( S_\alpha \)). Such a sphere is often called a muffin tin sphere, and the part of space occupied by the spheres is the muffin tin region. The remaining space outside the spheres is called the interstitial region (I).

One augmented plane wave (APW) is used in the expansion of \( \psi^n_k \)

\[
\phi^k_K(r, E) = \begin{cases} 
\frac{1}{\sqrt{\tau}} e^{i(k+K) \cdot r}, & r \in I \\
\sum_{l,m} A^\alpha_{l,m} u^\alpha_l(r', E) Y^l_m(\hat{r'}), & r \in S_\alpha,
\end{cases}
\tag{3.4}
\]

where \( k \) is the wave vector, \( K \) is the reciprocal vector, \( \tau \) is the volume of the unit cell, and \( u^\alpha_l \) is the regular solution of

\[
[-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + V(r) - E_l] r u_l(r) = 0. \tag{3.5}
\]
Figure 3.1: Division of a unit cell into muffin tin regions and the interstitial region, for a case with two atoms per unit cell. The black dot is the origin of the axis system (which may but need not coincide with the nucleus of an atom).

The position inside the spheres is given with respect to the center of each sphere by \( \mathbf{r}' = \mathbf{r} - \mathbf{r}_\alpha \) (see Fig. 3.1). The length of \( \mathbf{r}' \) is \( r' \), and the angles \( \theta' \) and \( \phi' \) specify the direction of \( \mathbf{r}' \) in spherical coordinates, indicated as \( \hat{\mathbf{r}}' \). The \( Y_{l}^{m} \) are spherical harmonics. The \( A_{lm}^{\alpha,k+K} \) are unknown constants, as well as \( E \). The latter has the dimension of energy. The \( u_{l}^{\alpha} \) are solutions to the radial part of the Schrödinger equation for an approximate free atom \( \alpha \), at the energy \( E \). For a true free atom, the boundary condition that \( u_{l}^{\alpha}(r, E) \) should vanish for \( r \to \infty \), limits the number of energies \( E \) for which a solution \( u_{l}^{\alpha} \) can be found. But as this boundary condition does not apply here, we can find a numerical solution for any \( E \). Hence, the \( u_{l}^{\alpha} \) themselves do not correspond to something physical, they are only part of basis
functions, not of the search eigenfunction itself. Since they are close to how the actual eigenfunction will look in that region of the crystal, they will work as basis functions.

Figure 3.2: Flowchart of the APW method.

If an eigenfunction is discontinuous, its kinetic energy would not be well-defined. Such a situation is not physical, and we have to enforce that the plane wave outside the sphere matches the wavefunction inside the sphere over the entire surface of the
sphere (in value, not in slope). A plane wave is expanded in spherical harmonics and imposed to match the wavefunction at the muffin tin surface of atom $\alpha$:

$$
\frac{e^{i(k+K)\cdot r}}{\sqrt{\tau}} = \frac{4\pi}{\sqrt{\tau}} e^{i(k+K)\cdot r_0} \sum_{l,m} j_l(|k+K||r|) Y_m^l(k+K) Y_m^l(r'),
$$

(3.6)

where $j_l(r)$ is spherical Bessel function of order $l$. The two terms in eqn. 3.4 must be equal at the boundary ($r' = R_\alpha$). We get:

$$
A_{lm}^{\alpha,k+K} = \frac{4\pi j_l(|k+K||r_0|)}{\sqrt{\tau}} \frac{\sqrt{\tau}}{u_l^l(\alpha,E)} j_l(|k+K||r_0|) Y_m^l(k+K).
$$

(3.7)

This uniquely defines the $A_{lm}^{\alpha,k+K}$, apart from the still undetermined $E$. In principle there are an infinite number of terms in eqn.3.5, which would force us to use an infinite number of $A_{lm}^{\alpha,k+K}$.

We match the two wavefunction approximately by truncating at angular momenta cutoffs $l_{\text{max}}$ for a sphere representation in terms of the plane waves cutoff, $K_{\text{max}}$. A good approach is to tune these cutoffs so that the two truncations will be well matched, thereby avoiding Gibbs-like oscillations [3]. $Y_m^{l_{\text{max}}}$ can have at most up to $2l_{\text{max}}$ nodes (roots) along the circle, $\theta \in [0, 2\pi]$. Thus the number of nodes per unit length for the $\alpha$-circle (see Fig. 3.1) is $\frac{2l_{\text{max}}}{2\pi R_\alpha}$. To match between the wave in the interstitial region and the plane wave inside the sphere the number of nodes must be equal. The plane wave with the shortest length is $\frac{2\pi}{K_{\text{max}}}$, where $K_{\text{max}}$ corresponds to a sphere with radius $K_{\text{max}}$ centered at the origin of reciprocal space \(^\ast\) and has $\frac{2\pi}{K_{\text{max}}}$ nodes per unit length. This provides the condition $R_\alpha K_{\text{max}} = l_{\text{max}}$, and hence allows us to pick a good $l_{\text{max}}$ for a given $K_{\text{max}}$.

\(^\ast\)All reciprocal lattice vectors that are inside this sphere are taken into the basis set.
For the coefficient $c_{n,k}^n$ to describe the eigenstate $\psi_{n,k}^n(r)$ accurately with APW’s, one has to set $E$ equal to the eigenvalue (or band energy) $\epsilon_{k}^n$ of that state. Therefore, we start with a guessed value $E$ for the band energy $\epsilon_{k}^n$ to find the AWP’s, and then construct the Hamiltonian matrix elements and overlap matrix (the APW’s are not orthogonal). The secular equation is determined, and our guessed $\epsilon_{k}^n$ should be a root of it. Usually it is not, hence we have to try a second guess and so fourth until we find a root. This procedure is summarized in Fig. 3.2.

### 3.2 The LAPW method

The APW method requires $u_l^\alpha(E, r)$ to be constructed at eigenvalues that are not known yet, $\epsilon_{k}^n$. LAPW is a modification to APW that can provide the $u_l^\alpha(\epsilon_{k}^n, r)$ directly from known quantities. If we calculate the $u_l^\alpha$ at some energy $E_0$, then we can use a Taylor expansion to find the energy not far from it,

$$u_l^\alpha(r', \epsilon_{k}^n) = u_l^\alpha(r', E_0) + (E_0 - \epsilon_{k}^n) \left( \frac{\partial u_l^\alpha(r', E)}{\partial E} \right)|_{E=E_0} + O(\epsilon_{k}^n - E_0)^2,$$

where $O(\epsilon_{k}^n - E_0)^2$ is the error quadratic in this energy difference. Then the LAPW method basis functions or LAPW’s, in terms of this basis, are

$$\phi_{k}^{\alpha}(r, E) = \begin{cases} \frac{1}{\sqrt{V}}e^{i(k+K)\cdot r}, & r \in \mathbb{I} \\ \sum_{l,m} [A_{l,m}^{\alpha,k+K} u_l^\alpha(r', E) + B_{l,m}^{\alpha,k+K} \dot{u}_l^\alpha(r', E)] Y_l m (\hat{r}'), & r \in S_{\alpha}, \end{cases}$$

22
where the energy derivative $\dot{u}_l^\alpha(r', E)$ satisfies:

$$\left[-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + V(r) - E_l\right]r\dot{u}_l(r, E_l) = 0. \quad (3.10)$$

To determine the coefficients $A^\alpha_{l,m}^{a,k+K}$ and $B^\alpha_{l,m}^{a,k+K}$, we require that the function in the sphere matches the plane wave both in value and in slope at the sphere boundary. This can be done by using an expression similar to eqn. 3.6 and its radial derivative. This results in a 2x2 system from which both coefficients can be solved. It is advantageous to choose $E_0$ close to the center of the $l$-band to reduce the error resulting from the linearization. In this way, the term $O((\epsilon_0^a - E_0)^2)$ in eqn. 3.8 will remain small. We do the same thing for every orbital $l$ (s, p, d, and f orbital) and every atom. Therefore we should select a well chosen set of $E_0$’s, and let us call them $E_{1,l}^a$’s ($l$ taking values up to 3),

$$\phi^K_k(r) = \begin{cases} \frac{1}{\sqrt{r}}e^{i(k+K) \cdot r} & \text{r } \in I \\ \sum_{l,m}[A^\alpha_{l,m}^{a,k+K}u_l^\alpha(r', E_{1,l}^a) + B^\alpha_{l,m}^{a,k+K}\dot{u}_l^\alpha(r', E_{1,l}^a)]Y_l^m(\hat{r}') & \text{r } \in S_a. \end{cases} \quad (3.11)$$

With the $E_{1,l}^a$ being fixed, the basis functions can be calculated. The same procedure used for the plane wave basis set can now be applied. Each diagonalization will produce P different band energies for this $k$. The accuracy of a plane wave basis set is determined by $K_{max}$. For the APW or LAPW basis set, it is fine to use the same criterion. However, the quantity $R^{min}_a K_{max}$ may provide a better accuracy, where $R^{min}_a$ is the smallest muffin tin radius.

In general we need to choose the muffin tin radii as large as possible, in such a way that the spheres touch but do not overlap. The wavefunction is better rep-
resented if muffin tin spheres occupy the largest volume possible in the crystal. However this is not necessarily the optimal choice. For instance, $R_{\alpha}^{\text{min}}$ can not be too large as the spherical harmonics are not suited to describe the wave functions in the region far away from the nuclei. And $K_{\text{max}}$ must be large enough so the number of plain waves is sufficient to represent the wavefunction. Therefore, a balance between $R_{\alpha}^{\text{min}}$ and $K_{\text{max}}$ will give the optimal choice for the muffin tin radii. Compared to a plane wave basis set, the LAPW basis set can be much smaller than APW.

The calculation time, mainly determined by matrix diagonalization, scales with the third power of the basis set size, which makes LAPW in this respect about 2 to 3 times faster than APW. There are other aspects however that slow down LAPW, such that in the end it is comparable in speed with plane waves.

### 3.3 LAPW with Local Orbitals

When a conduction electron approaches the nucleus of a positively charged ion, its wave function which was rather smooth in the outer region of the muffin-tin begins to oscillate in order to build up sufficient kinetic energy to compensate the strongly attractive potential energy term. These oscillations require the presence of high momenta in the Bloch wave and cause the plane-wave expansion to converge very slowly. Therefore, we need to define the limit of the momenta in which we can treat electrons as valence or core electrons. The limiting of the $K$ set, with $K \leq K_{\text{max}}$ defines the separation between the core states and valence states. Often the free energy corresponding to $K_{\text{max}}$ is called the energy cutoff $E_{\text{cut}} = \frac{\hbar^2 K_{\text{max}}^2}{2m_e}$ which separates core and valence electrons.
Generally speaking, a core state is a state that does not participate directly in chemical bonding with other atoms. Therefore, it must be embedded entirely in the muffin tin spheres. The valence states leak outside the muffin tin spheres, and the properties of materials, such as the chemical bonding, are largely determined by those electrons. These are the orbitals which are treated by LAPW. The augmenting functions, $u_l^l Y_{lm}$ and $\hat{u}_l Y_{lm}$, used in LAPW are orthogonal to any core state that is contained in muffin-tin spheres. This condition is satisfied only in the trivial case when there are no core states with the same $l$ \[^\dag\] [3]. For example, the 1s orbital in bcc-Fe is strongly bound to the nucleus and will behave almost as if it were in a free Fe atom (atom which is not in a bulk solid). Such an orbital is a core state. Therefore, it does not make any sense to include 1s orbital in the calculations.

It often happens that states with the same orbital quantum number $l$ but a different principal quantum number $n$ are both valence states. As a result, there can be a false * component of the low lying state contained in the valence wavefunctions as computed by the LAPW method. For instance, due to hybridization Fe in bcc-Fe will have a significant amount of 4p-character in its valence states that lies about 0.2 Ry below the Fermi level. But the 3p-states that are 4.3 Ry below the Fermi level are also not entirely contained in the core. Such low-lying valence states are called semi-core states. It is not clear how $E_{1s,l=1}^{Fe}$, must be chosen: close to 3p, or close to 4p, or at an intermediate value. None of the choices is optimal. This dilemma is solved by adding another type of basis function to the LAPW basis set, called a local orbital (LO). A local orbital is defined as:

\[^\dag\] The augmenting functions and the core states.

*This could result in what is called “Ghost” band.
A local orbital is defined for a particular $l$ and $m$, and for a particular atom $\alpha$. The local orbital is zero in the interstitial region and in the muffin tin spheres of other atoms. In the muffin tin sphere of atom $\alpha$, the same $u_l^\alpha(\mathbf{r'}, E_{1,l}^\alpha)$ and $\dot{u}_l^\alpha(\mathbf{r'}, E_{1,l}^\alpha)$ as in the LAPW basis set are used, with linearization energy $E_{1,l}^\alpha$ value suitable for the higher of the two valence states (4p in our example). The lower valence state that is much more free-atom-like is sharply peaked at an energy $E_{2,l}^\alpha$. A single radial function $u_l^\alpha(\mathbf{r'}, E_{2,l}^\alpha)$ at that same energy will be sufficient to describe it. Local orbitals are not connected to plane waves in the interstitial region i.e., they have no $\mathbf{k}$ or $\mathbf{K}$ dependence.

The three coefficients $A_{lm}^{\alpha,LO}$, $B_{lm}^{\alpha,LO}$, and $C_{lm}^{\alpha,LO}$ are determined by requiring that the LO is normalized, and has zero value and zero slope at the muffin tin boundary, which means that it does not leak out of the muffin tin sphere. Adding local orbitals increases the LAPW basis set size. If for each atom local orbitals for $p$- and $d$-states are added, the basis set increases with $3+5=8$ functions per atom in the unit cell. This number is rather small compared to typical LAPW basis set sizes of a few hundred functions. The accuracy that local orbitals provide makes worthwhile the extra computational time required for using them.
Chapter 4

Topological states for half-Heusler materials

4.1 Introduction

An ideal topological insulator is electrically insulating in its bulk, but has conducting electronic states that are formed on its surface (or edges in a two-dimensional material). The bulk gap is generated because of strong spin-orbit coupling [21, 22, 23, 14, 24, 25] inherent to these systems, and the gapless surface results in metallic surface states, resembling chiral edge modes in quantum Hall systems, but with unconventional spin textures [26, 27, 28]. The recent experimental realization of the quantum spin Hall effect has caused a lot of interest in these topological states of matter [26]. Topological insulators are a new phase of matter that is not characterized by a spontaneously broken symmetry [29, 21]. Instead the materials are characterized by topology of the manifold of the occupied
Bloch states [21]. They have the unique property that the surface states are spin polarized based upon the direction the current is flowing [22]. Like the quantum Hall effect, the resistance of the surface states is quantized with the quantum unit of resistivity [22].

The bulk excitation generated by the spin-orbit interaction is protected conducting states on their edge or surface against scattering by time reversal symmetry [25, 22, 23, 30, 28]. In the Hall state, an external magnetic field perpendicular to a two-dimensional electron gas causes the electrons to rotate in orbits, in quantum Hall state these orbits are quantized. Spin-orbit coupling causes an insulating material to acquire protected edge or surface states that are similar in nature to edge states in the quantum Hall effect.

4.2 Spin-orbit interaction

4.2.1 Introduction

Spin-orbit interaction is a weak coupling between the intrinsic spin and extrinsic orbital degrees of freedom of spinning particles. It implies mutual conversion between a particle’s spin and orbital angular momentum. The quantum spin Hall state can exist without a magnetic field, due to spin-orbit interaction, while Hall states require a magnetic field. The interaction of the electrons in a magnetic field resembles a spin-orbit interaction (see appendix 10.1 and 10.2). The 2D topological insulator is a quantum spin Hall insulator, which is a close cousin of the integer

\[ \text{In the first case we have Zeeman effect in which the perturbative interaction is proportional to } \mathbf{B} \cdot \mathbf{L}, \text{ in the second case we have the hyperfine structure in which the perturbative term is proportional to } \mathbf{S} \cdot \mathbf{L}. \text{ Therefore, the spin in quantum Hall state plays the role of the magnetic field in the Hall state.} \]
quantum Hall state [21, 22, 23, 29]. Therefore, spin-orbit interaction is crucial to understand the underlying physics of topological insulators.

4.2.2 Dirac equation

Our discussion, so far, of the electronic structure avoids spin as a relevant factor in the energy bands; we just use a wavefunction in space, and for each $\psi_k$ assume that we can put two electrons, of opposite spins, into two states with this wavefunction. The frequent occurrence of fine-structure in optical spectra of atoms and Zeeman splitting of the spectral lines, in the presence of magnetic field, provided evidence that two electronic states can exist, where only one would ordinarily be expected, so electrons must have a magnetic moment. The magnetic moment was also associated with an intrinsic angular momentum or spin which gives rise to two internal states. The spin-orbit interaction may split the degeneracy between the two states. Fine-structure occurs as a result of the coupling between the orbital angular momentum $l$ and the spin $1/2$. The theory of intrinsic internal angular momentum follows directly from Dirac theory.

Relativistic effects introduce a coupling of spin and orbital angular momentum. This correction is important only if the velocity of the electron is comparable to the speed of light. The relativistic correction can be neglected in the interstitial region since the velocity is limited by the cutoff in k-space. Within the muffin-tin spheres the importance of relativistic correction increases with increasing quantum number. The Dirac Hamiltonian can be written as (energy measured relative to rest energy):

$$H_D\psi = [c\vec{\alpha} \cdot \vec{p} + \beta mc^2 + V(\mathbf{r})]\psi = E\psi \quad (4.1)$$
where $\bar{\alpha}$ and $\bar{\beta}$ are 4x4 matrices.

$$\bar{\alpha} = \begin{pmatrix} 0 & \tilde{\sigma} \\ \tilde{\sigma} & 0 \end{pmatrix} ; \bar{\beta} = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix}$$  \hspace{1cm} (4.2)

where $\sigma_x, \sigma_y$ and $\sigma_z$ are the Pauli-Spin matrices, and the solution of eqn. 4.1 is:

$$\bar{\psi}(r) = \begin{pmatrix} \phi \\ \chi \end{pmatrix}$$  \hspace{1cm} (4.3)

where $\phi$ and $\chi$ are two-component spinor wavefunctions. $E$ is the total energy of the electron which includes the rest energy $mc^2$ so that we write:

$$E = E' + mc^2.$$  \hspace{1cm} (4.4)

By making use of the fact that both $E'$ and $V(r)$ will be much smaller than $mc^2$ and performing some mathematical manipulation of eqn. 4.1, see appendix A2 for more details, it is possible to show that:

$$\left(\frac{p^2}{2m} + V(r) - \frac{p^4}{4m^2c^2} - \frac{\hbar^2}{4m^2c^2} \nabla V(r) \cdot \nabla + \frac{\hbar^2}{4m^2c^2} \bar{\beta} [\nabla V(r) \times p] \right) \phi(r) = E' \phi(r).$$  \hspace{1cm} (4.5)

In eqn. 4.5, the first and second terms account for the non-relativistic Schrödinger equation. The third is the relativistic correction of mass with velocity. The fourth
has no classical analogue. The last term corresponds to the spin-orbit coupling. In practice, it is possible to solve Dirac equation for an electron in a crystal by making suitable modifications to either of the two methods described for non-relativistic calculations. The form of eqn. 4.5 suggests that it might be profitable as an alternative to solving eqn. 4.1. One way of doing it is to start from the result of non-relativistic band structure calculation and then introduce one or more extra terms in eqn. 4.5, treating them as a perturbation. If we assume $V(r)$ possesses spherical symmetry then,

$$\nabla V(r) = \frac{1}{r} \frac{dV(r)}{dr} r.$$  \hspace{1cm} (4.6)

Therefore the spin-orbit term can be written as:

$$H_{so} = \frac{1}{2m^2c^2} \frac{1}{r} \frac{dV(r)}{dr} S \cdot L,$$  \hspace{1cm} (4.7)

where $L = r \times p$, denotes the orbital angular momentum and $S = \frac{\hbar}{2} \sigma$ denotes the spin angular momentum.

### 4.3 Time reversal symmetry

#### 4.3.1 Introduction

In the special theory of relativity the time is treated on an equal footing with space coordinates. The inversion as a symmetry operation of space-time coordinates suggests the time inversion or time reversal operation $T$, which takes $t$ to $-t$. Classically, the application of $T$ requires reversing velocities and letting the time flow in reverse direction. In general, time reversal symmetry is present in all systems with
no magnetic field. The time reversal operator\(^1\), \(K\), leads to reversal of both spin and momentum. Thus the relation of states at \(k\) and \(-k\) is \(K\psi_{\uparrow,k}(r) = \psi_{\downarrow,-k}(r)\). This is an example of Kramers theorem which requires that all states must occur in degenerate pairs in any system with time reversal symmetry.

### 4.3.2 Time reversal without spin

Since the Hamiltonian represents an energy it is expected to be real. In systems without spin \(T\) simply takes \(\psi\) into \(\psi^*\), which can be seen by taking the complex conjugate of Schrödinger’s equation:

\[
H\psi = i\hbar \frac{\partial \psi}{\partial t}
\]

(4.8)

Then we get

\[
H\psi^* = i\hbar \frac{\partial \psi^*}{\partial (-t)}.
\]

(4.9)

Therefore, the wavefunction \(\psi\) will evolve into -t direction exactly the same way \(\psi^*\) evolve into +t. Obviously, the probability density will not be affected. In a time-independent system such as in eqn. 2.18, the energy is unchanged, since \(H\psi = E\psi\) implies \(H\psi^* = E\psi^*\). The degeneracy associated with this symmetry depends on whether \(\psi^*\) is linearly independent of \(\psi\) or not. The following discussion will be more technical to show how the \(T\) operator affects different physical quantities. If

\(^1\)The difference between \(K\) and \(T\) will be clarified in subsections 4.3.2 and 4.3.3
we have a sequence of events that occurs at $t_1, t_2, t_3, \ldots$ such as $t_1 < t_2 < t_3 \ldots$ then:

$$T(t_1 - t_2) = -(t_1 - t_2)$$

$$t_1 < t_2 < t_3 \ldots \Rightarrow Tt_1 > Tt_2 > Tt_3 \ldots$$

$$T = T^{-1}. \quad (4.10)$$

The transformed wavefunction can be written as:

$$\psi'(\mathbf{r}, t) = \psi(\mathbf{r}, Tt), \quad (4.11)$$

then we can write eqn. 4.8 as $^\dagger$

$$i\hbar \frac{\psi'(\mathbf{r}, t + dt) - \psi'(\mathbf{r}, t)}{dt} = i\hbar \frac{\psi(\mathbf{r}, Tt - dt) - \psi(\mathbf{r}, Tt)}{dt} =$$

$$-i\hbar \frac{\psi(\mathbf{r}, Tt) - \psi(\mathbf{r}, Tt - dt)}{dt} = -H\psi(\mathbf{r}, Tt) = -H\psi'(\mathbf{r}, t). \quad (4.12)$$

Then we can see that

$$-i\hbar \partial_t \psi'(\mathbf{r}, t) = H\psi'(\mathbf{r}, t). \quad (4.13)$$

On the other hand we have

$$-i\hbar \partial_t \psi^*(\mathbf{r}, t) = H\psi^*(\mathbf{r}, t). \quad (4.14)$$

$^\dagger$A discussion can be found in “Group Theory and Quantum Mechanics” by Michael Tinkham, McGraw-Hill (1964).
Now we introduce the Wigner time-reversal operator $\hat{K}_o$ defined as [31]:

$$\psi(r, Tt) = \psi^*(r, t) = \hat{K}_o \psi(r, t). \quad (4.15)$$

It is important to note some of the properties of $\hat{K}_o$ that can be deduced from the discussion above. It is straightforward to see that:

$$\hat{K}_o^2 = 1 \Rightarrow \hat{K}_o^{-1} = \hat{K}_o, \quad (4.16)$$

and then we can find the second property which is the antiunitary [31]:

$$\langle \psi | \phi \rangle = \langle \psi | \hat{K}_o^{-1} \hat{K}_o | \phi \rangle = \langle \hat{K}_o \phi | \hat{K}_o \psi \rangle \quad (4.17)$$

and then

$$\langle \psi | \hat{K}_o \phi \rangle = \langle \hat{K}_o \psi | \phi \rangle = \langle \phi | \hat{K}_o \psi \rangle^*. \quad (4.18)$$

The second property we care about is the non-linearity, which is evident because:

$$\hat{K}_o (c_1 |\phi\rangle + c_2 |\psi\rangle) = c_1^* \hat{K}_o |\phi\rangle + c_2^* \hat{K}_o |\psi\rangle. \quad (4.19)$$

In general $c_1 \neq c_1^*$, therefore $\hat{K}_o$ is a nonlinear operator. The squared operator $\hat{K}_o^2$ is equal to unity; nevertheless $\hat{K}_o$ is not unitary because it is antilinear rather than linear [32]. The $\hat{K}_o$ operator should keep the coordinate unchanged, $\hat{K}_o r \hat{K}_o^{-1} = r$, and change the direction of momentum, $\hat{K}_o p \hat{K}_o^{-1} = -p$. It also changes the
direction of angular momentum $\hat{K}_o \hat{L} \hat{K}_o^{-1} = -\hat{L}$. Then we can write the following:

$$\hat{K}_o(r\psi) = r\hat{K}_o\psi \implies \hat{K}_o r = r\hat{K}_o,$$

$$\hat{K}_o(p\psi) = -p\hat{K}_o\psi \implies \hat{K}_o p = -p\hat{K}_o,$$

$$\hat{K}_o L = \hat{K}_o (r \times p) = r\hat{K}_o \times p = -(r \times p)\hat{K}_o = -L\hat{K}_o. \quad (4.20)$$

### 4.3.3 Time reversal with spin

When we take the spin into account $\hat{K}_o$ is no longer an operation of complex conjugation. We have shown that time reversal leaves $r$ invariant and reverses $p$, and $L$. Since the spin operator is analogous to an angular momentum operator we expect that the Wigner time-reversal operator $\hat{K}$ will be defined by

$$\hat{K} r \hat{K}^{-1} = r, \hat{K} p \hat{K}^{-1} = -p, \hat{K} \sigma \hat{K}^{-1} = -\sigma. \quad (4.21)$$

A Hamiltonian with spin-orbit coupling defined in eqn. 4.5 will commute with time reversal:

$$\hat{K}H = H\hat{K}. \quad (4.22)$$

Let us determine $\hat{K}$ by setting:

$$\hat{K} = \hat{U} \hat{K}_o, \quad (4.23)$$

where $\hat{K}_o$ is Wigner time-reversal without spin and $\hat{U}$ is unknown unitary spin
operator that commutes with \( r \) and \( p \). We want to find

\[
\hat{U} \sigma^* \hat{U}^{-1} = -\sigma. \tag{4.24}
\]

Therefore we can choose \( \hat{U} \) to be:

\[
\hat{U} = -i \exp\left(\frac{i\pi \sigma_y}{2}\right), \tag{4.25}
\]

where \( \sigma_y \) is the y component of spin. Using the identity \( e^{(i\alpha j)} = I \cos(\alpha) + i\sigma_j \sin(\alpha) \), where \( (j = x, y, z) \), and defining:

\[
\hat{K} = \sigma_y \hat{K}_o = -i \exp(i\pi \sigma_y/2) \hat{K}_o, \tag{4.26}
\]

we can easily show that:

\[
\hat{K}^{-1} = \hat{K}_o \sigma_y = \sigma_y^* \hat{K}_o = -\sigma_y \hat{K}_o = -\hat{K}. \tag{4.27}
\]

Therefore it is straightforward to show\(^\dagger\):

\[
\begin{align*}
K^{-1} \sigma_x K &= (-\sigma_y \hat{K}_o) \sigma_x (\sigma_y \hat{K}_o) = \sigma_y \sigma_x \sigma_y = -\sigma_x \\
K^{-1} \sigma_y K &= (-\sigma_y \hat{K}_o) \sigma_y (\sigma_y \hat{K}_o) = -\sigma_y \\
K^{-1} \sigma_z K &= (-\sigma_y \hat{K}_o) \sigma_z (\sigma_y \hat{K}_o) = \sigma_y \sigma_z \sigma_y = -\sigma_z
\end{align*}
\]

Therefore, \( \hat{K} \sigma = -\sigma \hat{K} \). The term \( \frac{k^2}{4m^2c^2} \bar{\sigma} \cdot [\vec{\nabla} V(\mathbf{r}) \times \mathbf{p}] \) in eqn. 4.5 commutes

\(^\dagger\)Using the relation \( \sigma_i \sigma_j = \delta_{ij,k} + i \sum_l \epsilon_{ikl} \sigma_l \), where \( \epsilon_{ikl} \) is the Levi-Civita tensor.
with $K$:

\[
\hat{K}^{-1} \hat{\sigma} [\hat{\nabla} V(r) \times \hat{p}] \hat{K}
\]

\[
\hat{K}^{-1} \hat{\sigma} \hat{K} \hat{K}^{-1} [\hat{\nabla} V(r) \times \hat{p}] \hat{K}
\]

\[-\hat{\sigma} [\hat{\nabla} V(r) \times \hat{K}^{-1} \hat{p} \hat{K}]\]

\[-\hat{\sigma} [\hat{\nabla} V(r) \times -\hat{p}]\]

\[\hat{\sigma} [\hat{\nabla} V(r) \times \hat{p}]\] \hspace{1cm} (4.28)

$\hat{K}$ is an anti-unitary operator, and sometimes called a $Z_2$ symmetry generator. The symmetry of this operator is crucial to understand the behavior of topological insulators.

### 4.3.4 Kramers degeneracy

The Kramers degeneracy theorem states that the energy levels of systems with an odd number of electrons remain at least doubly degenerate in the presence of purely electric fields (i.e., no magnetic fields). It is a consequence of the time reversal invariance of electric fields, and follows from an application of the antiunitary $\hat{K}$ to the wavefunction of an odd number of electrons. The theorem is valid for any configuration of static or time-varying electric fields. Let us consider an eigenfunction $\psi(r_1, s_1, ..., r_N, s_N)$, where $r_1$ and $s_1$ are the position and the spin for the first electron, and $H$ is the Hamiltonian for $N$ electrons,

\[
H \psi = E \psi,
\] \hspace{1cm} (4.29)
where

\[ \hat{K}H\hat{K}^{-1} = H. \quad (4.30) \]

The time-reversed wavefunction, \( \hat{K}\psi \), is then also eigenfunction of \( H \) with the same eigenvalues,

\[ \hat{K}H\hat{K}^{-1}\psi = E\psi \implies H(\hat{K}\psi) = E(\hat{K}\psi), \quad (4.31) \]

where the representation of \( \hat{K} \) is

\[ \hat{K} = \sigma_y^{(1)}...\sigma_y^{(N)}\hat{K}_o = (-1)^N\hat{K}_o\sigma_y^{(1)}...\sigma_y^{(N)}. \quad (4.32) \]

We get \( \hat{K}^2 = (-1)^N \) [33], and by using the anti-unitary relation eqn. 4.18 we get

\[
<\psi|\hat{K}\psi> = \langle\psi|\sigma_y^{(1)}...\sigma_y^{(N)}|\hat{K}_o\psi\rangle = (-1)^N\langle\psi|\hat{K}_o\sigma_y^{(1)}...\sigma_y^{(N)}|\psi\rangle \\
= (-1)^N\langle\sigma_y^{(1)}...\sigma_y^{(N)}\psi|\hat{K}_o|\psi\rangle = (-1)^N\langle\psi|\sigma_y^{(1)}...\sigma_y^{(N)}|\hat{K}_o\psi\rangle \\
= (-1)^N<\psi|\hat{K}\psi> \quad (4.33)
\]

The last equation has a clear meaning: for an odd number of electrons \( \psi \) and \( \hat{K}\psi \) are orthogonal, so the eigenstates of the system are at least two-fold degenerate.
4.3.5 Kramers degeneracy of Bloch states

Let us consider the Hamiltonian derived in eqn. 4.5. This Hamiltonian is invariant with respect to time-reversal as shown in section (4.3.3),

\[ \hat{K}H\hat{K}^{-1} = H. \] (4.34)

From the previous section it follows that the eigenstates are at least two-fold degenerate:

\[ H\psi = \epsilon\psi \]
\[ H\hat{K}\psi = \epsilon\hat{K}\psi. \] (4.35)

If \( \psi_k(\mathbf{r}) \) satisfies the Bloch condition then \( \psi_k(\mathbf{r}) = u_k(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}} \). Substituting in eqn. 4.5 we get

\[ H_k = \frac{(p + \hbar k)^2}{2m} + V(\mathbf{r}) - \frac{(p + \hbar k)^4}{8m^3c^2} + \frac{\hbar^2}{8m^2c^2}\hat{\nabla}^2V(\mathbf{r}) + \frac{\hbar}{4m^2c^2}(\hat{\nabla}V(\mathbf{r}) \times (p + \hbar k)) \cdot \hat{\sigma}. \]

It is straightforward to show that (see appendix 10.3 for proof)

\[ \hat{K}H_k\hat{K}^{-1} = H_{-k}. \] (4.36)
Therefore\(^\dagger\)

\[
\hat{K} H_k \psi_k (\mathbf{r}) = \varepsilon_k \hat{K} \psi_k (\mathbf{r}) \\
H_{-k} (\hat{K} \psi_k (\mathbf{r})) = \varepsilon_k (\hat{K} \psi_k (\mathbf{r}))
\]

\[\varepsilon_{-k} = \varepsilon_k.\]  \(\text{(4.37)}\)

Since the operator \(\hat{K}\) contains \(y\)-component of Pauli matrices \(\sigma_y\), and this matrix flips the spin of any component. Thus, by applying the \(\hat{K}\) operator in the wavefunction \(\psi_{k,\sigma}(\mathbf{r})\), taking into account that \(\hat{K}^2 = -1\), we find:

\[
\hat{K} \psi_{k,\sigma}(\mathbf{r}) = K_o \exp(i \mathbf{k} \cdot \mathbf{r}) (\sigma_y) u_{k,\sigma}(\mathbf{r}) = i e^{(-i \mathbf{k} \cdot \mathbf{r})} u_{k,-\sigma}^*(\mathbf{r}) = \psi_{-k}^{(t)}(\mathbf{r}), \quad \text{(4.38)}
\]

and then, the two degenerate wavefunctions are

\[
\psi_k (\mathbf{r}) = e^{i \mathbf{k} \cdot \mathbf{r}} \begin{pmatrix} u_{k\uparrow}(\mathbf{r}) \\ u_{k\downarrow}(\mathbf{r}) \end{pmatrix}; \psi_{-k}^{(t)}(\mathbf{r}) = e^{-i \mathbf{k} \cdot \mathbf{r}} \begin{pmatrix} i u_{k\uparrow}^*(\mathbf{r}) \\ -i u_{k\downarrow}^*(\mathbf{r}) \end{pmatrix}, \quad \text{(4.39)}
\]

both solutions of the Schrödinger equation with the same energy. So \(\varepsilon_{k,\sigma} = \varepsilon_{-k,-\sigma}\).

The second function differs from first through a simultaneous reversal of wave vector and electron spin, among other things the Kramers degeneracy remains unaffected when including the spin-orbit interaction term in the Hamiltonian. Note that \(\uparrow\) and \(\downarrow\) do not necessarily denote eigenfunctions of the spin operator \(\sigma_z\), but correspond to the two quantum numbers denoting eigenstates for a given Bloch vector.

The time reversal symmetry operator changes the sign of the wave vector and also reverses the spin. For a system with time reversal symmetry, that is nonmagnetic

\^Note that \(\hat{K} H_k = H_{-k} \hat{K}\)

40
materials in the absence of an external magnetic field, application of the time reversal operator to an eigenstate of the Hamiltonian generates a second eigenstate of the Hamiltonian with the same energy eigenvalue, all spins reversed, and the sign of the wave vector reversed. If we label the original eigenstate by \((n, k)\), where \(n\) is a band label that includes the spin labels of the components of the wave function (the state may not be a spin eigenstate), and label the transformed state by \((-n, -k)\), where \(-n\) implies that the signs of all spin components have been reversed, the eigenvalues satisfy \(\varepsilon_n(k) = \varepsilon_{-n}(-k)\).

### 4.4 Inversion Symmetry

Let us consider the case when also space inversion applies:

\[
V(Ir) = V(-r) = V(r)
\]

\[
IH_{-k}I = H_k.
\]  
(4.40)

This implies that \(\varepsilon_k = \varepsilon_{-k}\) with the corresponding wavefunction for \(-k\). If we apply the inversion operator \(I\) on \(\psi_{k,\sigma}(r)\)

\[
I\psi_{k,\sigma}(r) = \exp(-ik \cdot r)u_{k,\sigma}(-r) = \psi_{-k,\sigma}(-r),
\]  
(4.41)

or we can write:

\[
\psi^{(I)}_{-k}(r) = e^{-ik \cdot r} \begin{pmatrix} u_{k \uparrow}(-r) \\ u_{k \downarrow}(-r) \end{pmatrix}.
\]  
(4.42)

In case of both time-reversal and inversion symmetry, the two eigenfunctions for
-k with the same energy \( \varepsilon_{-k}(= \varepsilon_k) \) are orthogonal:

\[
\int \psi_{-k}^{(l)}(r) \psi_{-k}^{(l)}(r) = -i \int [u_k \downarrow(r) u_k \uparrow(-r) - u_k \uparrow(r) u_k \downarrow(-r)] d^3r = 0.
\] (4.43)

Thus, the Bloch-states, \((n, k)\), of a nonmagnetic centro-symmetric crystal are at least twofold degenerate. For a system with inversion symmetry, the Hamiltonian eigenvalues satisfy \( \varepsilon_n(k) = \varepsilon_n(-k) \). The inversion symmetry operator changes the sign of the wave vector but does not influence spin. For a system with both time reversal and inversion symmetry, sequential application of the two operators implies \( \varepsilon_n(k) = \varepsilon_{-n}(k) \). In this case because \((n, k)\) and \((-n, k)\) label two distinct states with the same wave vector, all bands are at least two-fold degenerate. For the case with inversion symmetry, the bands are two-fold degenerate. In effect, reversing the spin in the state \( \psi_k(r) \) is equivalent to looking at \( \psi_k(-r) \), which has the same energy. For the case without inversion symmetry, the bands are non-degenerate. In other words, the energy can not depend on the electron spin. Consequently, for crystals which have inversion symmetry (like fcc, hcp), spin splitting is not allowed in the bulk, and these solids keep their spin degeneracy.

### 4.5 Crystal symmetry and spin-orbit interaction in cubic structure

So far we have discussed the effect of time-reversal and inversion symmetry on energy levels and wavefunctions. However, the symmetry of the crystal structure, related to the point group, is very important in electronic structure calculations. Basically, the energy, \( \varepsilon(k) \), in the Brillouin zone has the full point group symmetry
of the crystal. Any operation, such as rotating the crystal around an axis, that leaves it invariant, also transforms the function $\varepsilon(k)$ into itself. This can be used to categorize and simplify the energy levels and wavefunctions corresponding to various points in the Brillouin zone, and determine at what points we may expect to have degeneracy between the levels. There are special points in the Brillouin zone where the spin-orbit effect may be quite important. The most interesting case is at the center of the zone or $\Gamma$-point, a point of cubic symmetry.

In a tight-binding model we could use $p$-orbitals to construct a 'p-band'. There are three degenerate $p$-states of an atom, so that we have three such bands corresponding to $p_x$, $p_y$ and $p_z$ orbitals of the atom. These 3 bands are degenerate at the $\Gamma$-point as shown in Fig. 4.1; they are simply transformed into each other by cubic symmetry operations at that point. Each band state is doubly spin-degenerate, so that there is six-fold degeneracy altogether, Fig. 4.1(a). When we apply the spin-orbit interaction these spatial states are coupled with spin. The Clebsch-Gordon coefficients for coupling in the zone center point group are the same as those for coupling $l=1$ and $s=1/2$ angular momentum states and it is convenient to label the states in analogy with angular momentum states. The four states at the top of the valence band are:

\[
\begin{align*}
\left| \frac{3}{2}, \frac{3}{2} \right\rangle &= \frac{1}{\sqrt{2}} |(p_x + ip_y) \uparrow \rangle \\
\left| \frac{3}{2}, -\frac{3}{2} \right\rangle &= \frac{1}{\sqrt{2}} |(p_x - ip_y) \downarrow \rangle \\
\left| \frac{3}{2}, \frac{1}{2} \right\rangle &= \frac{1}{\sqrt{6}} |2p_z \uparrow + (p_x + ip_y) \downarrow \rangle \\
\left| \frac{3}{2}, -\frac{1}{2} \right\rangle &= \frac{1}{\sqrt{6}} |2p_z \downarrow + (p_x - ip_y) \uparrow \rangle
\end{align*}
\]

and the two states split to lower energy are:

\[4.44\]
Figure 4.1: Effect of spin-orbit interaction on the p-levels at the center of the Brillouin zone: (a) Without spin-orbit interaction, six degenerate levels are observed at the Γ-point (b) Spin-orbit interaction leads to a splitting into $p_{3/2}$ and $p_{1/2}$ levels, but leaves the spin degeneracy in lattices with inversion symmetry; (c) in a lattice without inversion symmetry, the spin degeneracy is fully removed, except for the Γ-point [34].

\[
\begin{align*}
\left| \frac{1}{2}, \frac{1}{2} \right> &= \frac{1}{\sqrt{3}} \left( -p_z \uparrow + (p_x + ip_y) \downarrow \right) \\
\left| \frac{1}{2}, -\frac{1}{2} \right> &= \frac{1}{\sqrt{3}} \left( p_z \downarrow - (p_x - ip_y) \uparrow \right)
\end{align*}
\]

(see appendix 10.4 for proof). The four-fold orbitals, grouped by eqn. 4.44, can be labeled as $(p_{3/2})$ and the remaining two, grouped by eqn. 10.39, as $(p_{1/2})$. If there is inversion symmetry, then each level is still doubly degenerate as shown in Fig. 4.1(b). Away from the Γ-point each level is still doubly degenerate. If there is no inversion, these would again split by the spin-orbit coupling, and the electron spin becomes sensitive to the amount of ‘screw$^\dagger$’ in the crystal potential along the direction of propagation as displayed in Fig. 4.1(c). Semiconductors, such as Germanium and

\[\text{\textsuperscript{†}It comprises a structure in which a helical path is traced around the linear defect by the atomic planes in the crystal lattice.}\]
Silicon, have tetrahedral bonds that have $sp^3$ hybridization. In this case the states formed from coupling the antibonding $s$-type with spin:

$$\left| \frac{1}{2},\frac{1}{2} \right\rangle = |s \uparrow\rangle$$

$$\left| \frac{1}{2},-\frac{1}{2} \right\rangle = |s \downarrow\rangle.$$  \tag{4.46}$$

The fourfold degenerate zone center states ($p_{3/2}$) describe the top of the valence band and the two fold $s$, eqn. 4.47 describes the the bottom of the conduction band. The character of the valence and conduction bands is of great importance to the study of topological insulators, namely the $p$-bonding and $s$-antibonding state as we shall see. The normal order, in the trivial topological insulator and semiconductor is $s$-type in the bottom of the conduction band and $p$-type in the top valence band. However, in the case of HgTe compounds the order is reversed as a result of strong spin-orbit coupling[35]. In the compounds that have inversion symmetry, topological insulators can be identified by the number of band inversions realized as a result of spin-orbit coupling [36]. In a non-trivial topological insulator the $s$-like orbital at the $\Gamma$ point is below the fourfold-degenerate $j=3/2$ multiplet. Band symmetries for trivial and non-trivial orderings in the HgTe class are schematically shown in Fig. 4.2(a-c). In the trivial case the $s$-like orbital lies above at the bottom of the conduction band.

### 4.6 $Z_2$ topological insulators

Despite the fact that the band inversion near $\Gamma$ is a strong indication that a system is in a topological insulator state, it is not definite proof, simply because
the topological insulator is a global behavior in the entire Brillouin zone. There are several criteria that have been proposed to identify the topological insulator state. Fu and Kane [36] have proposed a parity criterion to identify topological insulators in systems with both time-reversal and spatial inversion symmetry. For crystals that do not have inversion symmetry the topological invariants can be calculated directly from the bulk band structure. For simplicity, we will consider the formalism for a 2D system. In the presence of time-reversal symmetry, Kramers theorem states that the energy eigenstates must be, at least, doubly degenerate. This allows us to enforce a time reversal constraint on the Bloch functions 4.38, so we only need to obtain Bloch functions in half of the Brillouin zone, denoted by $B^+$, as those in the other half are fixed by the constraint. The band topology is characterized by the $Z_2$ invariant, given by [36],

$$Z_2 = \frac{1}{2\pi} \left( \int_{\partial B^+} \mathbf{A}(k) \cdot \mathbf{A}(k) - \int_{B^+} \mathbf{d}^2 \mathbf{k} \mathbf{F}(k) \right) \mod (2), \quad (4.47)$$

where $\mathbf{A}(k) = i \sum_n < u_n(k) \nabla u_n(k) >$ is the Berry connection and $\mathbf{F}(k) = \nabla_k \times \mathbf{A}(k)|_z$ is the Berry curvature; the sum is over all occupied bands. A topological insulator will have a value $Z_2 = 1$ for a trivial and -1 for a nontrivial insulator, while ordinary insulators have $Z_2 = 0$. The nonzero $Z_2$ invariant is an obstruction to smoothly defining the Bloch functions in $B^+$ under the time reversal constraint.

### 4.7 Surface states

In the absence of external or internal magnetic fields, spin-orbit splitting is the only possible cause for a splitting of spin degenerate levels at the surface [38], except at particular high-symmetry points, the Kramers points on the Brillouin zone.
Figure 4.2: Schematic band structures near the Γ point for trivial insulator, non-trivial semi-metal and non-trivial insulator cases, respectively. Red dots denote the s-like states near the Γ point. Band inversion occurs in the non-trivial case where the s-like states at the Γ point are below the fourfold degenerate $J=3/2$ states. The degeneracy of the $J=3/2$ states (in c) is lifted by the lattice distortion in the non-trivial case.

The surface states are invariant under time reversal and variant under inversion symmetry because of the termination of the crystal by a surface. This makes them robust against perturbations that are time reversal invariant such as spin-orbit coupling. In this way, it permits electron surface states with the same parallel wave vector, $k_\parallel$, opposite spins to have different energies, $\varepsilon_{k_\parallel,\uparrow} \neq \varepsilon_{k_\parallel,\downarrow}$, which can be explained by Rashba scattering. It is now generally accepted that the spin-orbit interaction in a narrow-gap systems is governed by the Rashba Hamiltonian [40]. In order to understand the basic origin of spin-orbit coupling at the surface
of a crystal, it is a natural starting point to consider a 2D free-electron model, applicable to surface states that are localized in the near surface plane [41]. The model Hamiltonian including the Rashba spin-orbit scattering will be written as

$$H = \frac{p^2}{2m} + \alpha E_z (\hat{e}_z \times \mathbf{k}) \cdot \vec{\sigma}$$

(4.48)
with $\alpha$ is an effective mass parameter, $E_z$ is the electric field, and $\vec{\sigma}$ is the vector of Pauli spin matrices. The solutions of the above Hamiltonian can be found analytically. We choose a Cartesian coordinate system with the $z$-axis perpendicular to the 2D plane of electron motion. It can be shown (see appendix 10.5) that the free-electron quadratic dispersion will now be split into two parabolas, shifted in the $\mathbf{k}$ direction with energies:

$$\varepsilon_{1,2} = \frac{\hbar^2 k^2}{2m} \pm \alpha \hbar k$$  \hspace{1cm} (4.49)

The corresponding eigenfunction are:

$$\psi_1(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}}(|\uparrow> + ie^{i\vartheta_k}|\downarrow>)$$ \hspace{1cm} (4.50)

$$\psi_2(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}}(ie^{-i\vartheta_k}|\uparrow> + |\downarrow>)$$

The spin vectors $|\uparrow>, |\downarrow>$ denote the spin-up and spin-down states respectively, with respect to $z$ direction; $\vartheta_k$ is the angle between $\mathbf{k}$ and $x$-axis. The eigenfunctions 4.50 describe a spin polarization within the xy-plane (see the appendix 10.5), which is oriented perpendicular to the direction of electron motion. This means that, the electrons with the same $\mathbf{k}$ vector and opposite spins will have different energies. The most important results of the model are, it correctly describes the nature of the splitting and, it shows that Rashba type spin-orbit interaction will orient the spins of propagating electrons. Therefore, spin-half particle cannot scatter within a time-reversed pair (a Kramers pair) if the Hamiltonian is time-reversal invariant, then by using eqn. 4.33 and 4.18 one can show

$$\langle \hat{K}\psi|H'|\hat{K}\phi \rangle = \langle \phi|H'|\hat{K}^2\psi \rangle = -\langle \phi|H'|\psi \rangle,$$

where $H'$ is Rashba Hamiltonian. Consequently, time-reversal symmetry is sufficient to prevent backscattering [42]. Another theoretical point of view: the surface states in topological insulator sit on a massless Dirac cone, a relativistic energy-momentum dispersion in reciprocal space.
Dirac cones also appear in graphene, but there are significant differences between topological insulators and graphene [43]. In a topological insulator, as in contrast to the case for graphene, the surface states display a remarkable robustness against any type of disorder or perturbation that is invariant under time-reversal symmetry, even though the surface states in both of these systems are Dirac fermions. The reason for that is the Brillouin zone in topological insulators features a single Dirac cone, an odd number, however in graphene the number of Dirac cones is even. This can be probed experimentally, e.g., via photoemission spectroscopy [26, 44] to reveal how many Dirac cones exist in the Brillouin zone. In a regime with a single Dirac cone, Kramers theorem of degeneracy guarantees that the energy bands of the surface states in topological insulators must cross at the time-reversal invariant at Γ-point (k=0). Therefore, no disorder or perturbation that preserve the time-reversal invariance can generate a gap in the surface-state spectrum [43].

4.8 Half Heusler compounds*

The half-Heusler compounds have complex crystal structures that exhibit unusual electronic properties. They have recently attracted considerable experimental and theoretical attention with a vision to harness these unconventional properties into possible device applications based on the unique interplay between spin and charge. While the first 3D topological insulators were the binary compounds such as Bi$_{1-x}$Sb$_x$ [26] and Bi$_2$Se$_3$ [44], the search for topological insulator behavior has recently been extended to ternary compounds [45, 46, 47, 48, 49, 50]. In particular,

band computations [46, 45] have predicted that many of the ternary half-Heusler (THH) compounds are topologically non-trivial with topological order $Z_2 = -1$. Their electronic band structures have been shown to be similar to those of the well known topological material HgTe with zinc-blende structure. Here, we have investigated a series of 28 nonmagnetic THH compounds of the form $MM'X$ with $M = \text{Lu, La, Sc, Y; } M' = \text{Pt, Pd, Au, Ni, and } X = \text{Sb, Bi, Sn}$. We find that the topology of the electronic band structures can be characterized by band inversion between the $\Gamma_6$ and $\Gamma_8$ energy levels at the $\Gamma$ symmetry point in the Brillouin zone. We define the band inversion strength (BIS), $\Delta$, as the energy difference between these two states, i.e. $\Delta = [E_{\Gamma_8} - E_{\Gamma_6}]$. The half-Heusler compounds with positive values of $\Delta$ are predicted to be topologically non-trivial, while those with negative $\Delta$ values are topologically trivial.

However, the earlier computations of Refs. [45] and [46] on the THHs suffer from the well known problem of underestimation of the band gap for semiconductors in the density functional theory (DFT) using the local density approximation (LDA) or the generalized gradient approximation (GGA), which results in a systematically larger estimate of the BIS value. An efficient way to correct this error is to utilize a semilocal exchange-correlation potential. With this motivation, in this study we use the modified Becke and Johnson potentials (MBJLDA) [19] instead of LDA or GGA. MBJLDA offers an improvement over LDA or GGA for the description of the band gap of many materials, including semiconductors with zinc-blende structure. We find similar improvements for BIS values. For example, in HgTe, LDA or GGA yields too low an energy for $\Gamma_6$, leading to a GGA-derived BIS value of 1.04 eV, which is considerably larger than the experimental value of 0.302 eV [51]. In contrast, the
computed BIS value from MBJLDA is 0.415 eV, which is comparable to GW values in the range 0.37 eV to 0.57 eV [52, 53], and is thus a considerable improvement over LDA or GGA. Our analysis also reveals a relatively simple relationship for predicting TI behavior in the present series of compounds by correlating the value of the BIS parameter with the lattice constants of the compounds and the atomic numbers of their constituent atoms.

4.8.1 Structure and compounds

The THH compounds have a face-centered cubic structure described by the space group F4/3m (No 216). Crystalline compounds of this structure can be described by the chemical formula MM’X, where M’ is transition element and X is an sp-valent element. M, M’, and X are atomic occupied Wyckoff 4b, 4c and 4a positions respectively [54], leaving 4d empty. The M’ and X positions form a zinc-blende structure when taken alone. Atoms M fill empty spaces within the zinc-blende structure and form a rock-salt structure arrangement together with the X atoms. M’X atoms have the fourfold tetrahedral coordination characteristic of the zinc-blende structure. The absence of inversion symmetry due to an empty M site in the half-Heusler compounds could lead to novel electronic properties in these materials. Fig. 4.3 shows the crystal structure of the LuBtSb half-Heusler compound. The total number of valence electrons of each compound in the this series is 18. Thus, this set is characterized as an 18-electron configuration. The 18-electrons are required to fill 5 d-orbitals (M’), 1 s-orbital (M) and 3 p-orbitals (X) of a transition metal. The combination of these nine atomic orbitals with ligand orbitals gives rise to nine molecular orbitals which are either metal-ligand bonding or non-bonding. The sum of all the valence electrons with ligands would assume a noble gas configuration of
Ar. All elements in THH have Ar core forms a closed shell (each atom by itself has 18 core electrons), the total spin and angular momentum are zero and this applies to the molecular orbitals as well. Therefore the series of THH is nonmagnetic. However, the last two compounds namely, GdPtBi and YbPtBi are not an 18-electron
configuration. One can construct the entire group by combining \( M = (\text{Lu, Sc, La, Y}) \) with \( M'X = (\text{PtBi, AuPb, PdBi, PtSb, AuSn, NiBi, PdSb}) \). The group can be divided into 7 subgroups, where each subgroup is labeled by a particular binary \( M'X \). The series is listed in table 1 and constructed based on an 18-electron configuration, by adding the \( M \) atom to the binary atoms \( M'X \).

Figure 4.5: (a) MBJLDA band structure of non-trivial HgTe, (b)-(g) nontrivial THH compounds with a zero gap at the Fermi level near the \( \Gamma \)-point. Size of red dots indicates the degree of \( s \)-like occupancy.
4.8.2 Computation

In the light of the issues discussed in this and previous chapters, we have studied a family of half-Heusler compounds within the framework of the LAPW method. First-principles electronic structure calculations are proving to be a useful tool in sorting out the mechanisms that lead to useful properties in complex materials such as half-Heusler (HH) compounds. Due to the presence of a single particle energy gap, electron-electron interactions do not modify the state in an essential way. Thus, the phenomenology of topological insulators can be understood in the framework of the band theory of solids. The topology of the electronic band structures can be characterized by the band inversion between $\Gamma_6$ and $\Gamma_8$ at the $\Gamma$-point. We define the band inversion strength (BIS) as the energy difference between these two states, $E_{\Gamma_8} - E_{\Gamma_6}$. The half-Heusler compounds with positive (negative) values of BIS are predicted to be topologically non-trivial (trivial). The crystal structure inputs for these compounds have been taken from the literature except for the compounds labeled by one or more star symbols in Table 4.1 (page 69) in which case the compounds are hypothetical, where the lattice constants are obtained by minimizing the total energy using the GGA of Perdew, Burke, and Ernzerhof [11]. These hypothetical compounds either do not exist naturally or have a different crystal structure. We have included these hypothetical compounds in our study for the sake of comparison and completeness. We have performed DFT based electronic structure calculations. A full potential linearized augmented plane wave (LAPW) method is used. We use MBJLDA for the exchange-correlation potentials [19] to get accurate values for the BIS. The WIEN2K package [55] has been employed to perform self-consistent band structure calculations. The band structures have been computed along high symmetry lines in the Brillouin zone, as shown in Fig. 4.5, for
a series of 28 nonmagnetic and 2 magnetic half-Heusler compounds listed in Table 4.1. The details of the 28+2 studied compounds, their crystal structures and the computed $\Delta$ values obtained using GGA and MBJLDA, are summarized in Table 4.1. Also shown for each compound is the value of the quantity $t$, which will be introduced in the following section.

4.8.3 Results and Discussion

We have calculated the DFT-GGA as well as DFT-MBJLDA based band structures along high symmetry lines in Brillouin zone as shown in Fig. 4.4 for the 28+2 THH compounds and HgTe. A comparison between the band structures of Hg$_{1-x}$Cd$_x$Te and the half-Heusler series simplifies the determination of possible topological order in the half-Heusler compounds. Hg$_{1-x}$Cd$_x$Te is a family of 3D materials with strong spin-orbit coupling\cite{62}. The topologically nontrivial HgTe \cite{63} and the trivial CdTe possess zinc-blende structure, and can be considered as being half-Heusler if one assigns a vacancy to the M site, i.e. these compounds can be written as [Hg]Te and [Cd]Te, where the symbol [ ] denotes a vacancy at the M-site and M’=(Hg,Cd) and X=Te. Recall now that bulk HgTe is a zero gap semiconductor (topologically nontrivial semimetal) in which valence and conduction bands touch at the $\Gamma$ point\cite{64}. The $\Gamma_8$ states at the Fermi level have $p$-like symmetry with 4-fold degeneracy ($j=3/2$), while the valence level $\Gamma_6$ has $s$-like symmetry below the 4-fold degenerate band. In contrast, the trivial bulk CdTe has a direct band gap at $\Gamma$ between the $s$-like level $\Gamma_6$ and the 4-fold ($j=3/2$) $p$-like $\Gamma_8$ level and the $s$-like band is the conduction band\cite{64}. This difference between the ordering of the bands at $\Gamma$ is shown schematically in Figs. 4.2(a,c), where the red dots indicate the degree of $s$-like occupancy with larger dots representing larger $s$-like occupancy.
Figure 4.6: MBJLDA band structures of the nontrivial THH compounds which display a metallic band. The size of red dots indicates the degree of s-like occupancy as in Fig. 4.5.
Since all topologically nontrivial compounds are characterized by a similar band inversion of $\Gamma_8$ and $\Gamma_6$ levels, we may define the quantity $\Delta = [E_{\Gamma_8} - E_{\Gamma_6}]$ as the band inversion strength (BIS), which would be positive for topologically nontrivial cases and negative for topologically trivial systems. $\Delta$ values for the half-Heusler series are listed in Table 1, and separate these compounds into topologically nontrivial semimetals/metals or trivial insulators.

The nontrivial semimetal group along with HgTe is shown in Fig. 4.5, where the 6 half-Heusler compounds, namely, YPtBi, ScPtBi, LaPtBi, YAuPb, LaAuPb and LuPdBi, possess positive values of $\Delta$. [Note that LaAuPb and ScPtBi here are hypothetical [61] compounds.] The band structures of these compounds are very similar to the band structure of HgTe shown in Fig. 4.5(a). In Figs. 4.5(a-h) the four-fold degenerate states at $\Gamma$ have $p$-type orbital symmetry with a total angular momentum eigenvalue of $j=3/2$, while the $s$-type state, labeled by red dots, lies below the $p$-type orbital. This inversion of the natural order of $s$- and $p$-type orbitals characterizes the topologically ordered material. The four nontrivial metallic band structures are shown in Fig. 4.6. Here band inversion occurs as it does in Fig. 4.5, but these compounds are not zero-gap semiconductors because finite band overlap occurs, leading to pockets at either $\Gamma$ or with a second band near X. Finally, Fig. 4.7 shows the 20 remaining compounds, which are all seen to be trivial insulators. Here the band structures are similar to that of CdTe with natural band ordering [$s$-type (red dots) band lies higher than the $p$-type band] and an open direct gap. Obviously, the $s/p$ inversion which is responsible for topological order is absent in these compounds. Notably, LuPtSb is close to the topological critical point since the gap in LuPtSb is close to zero.
Figure 4.7: MBJLDA band structures of 20 trivial THH compounds which display a direct gap. Figure (a) shows the schematic band structure of this THH series.

The electronic structure of Fig. 4.6 reveals that the orbital-angular-momentum symmetries of the ternary half-Heusler LuPtbi is similar to those in either HgTe or CdTe except that, the low-energy electronic properties are dominated by an
additional set of conduction bands that drop below the Fermi level to form a bulk electrons pocket near $\Gamma$ making the system bulk metallic. And an inversion relative to the natural order of s- and p-type-orbital-derived band structure. We consider the rhombohedral structure to investigate the distortion effect in $[111]$ direction on the band structure, see Fig. 4.8.

We apply a uniaxial strain along a $[111]$ direction that reduces the lattice constants $a$ by 3% and $c$ by 4%. As a result, the reduction of the crystal symmetry breaks the fourfold degeneracy of the $\Gamma_8$, $p_{3/2}$, states. Therefore, the lattice distortion causes a gap to open at $E_F$, generating a topological insulator state where surface bands span the bulk band gap and consist of an odd number of Dirac cones.

The distortion has been applied on the compound LuPtBi where the resulting band structure is shown in Fig. 4.9. Obviously, the effect of the uniaxial distortion has transformed the metallic phase to an insulator for LuPtBi. We notice that the band structure still has the inversion of the natural order of s- and p-type orbitals, which characterizes the topologically non-trivial ordered material. Similar behavior has been noticed in the compound LaPtBi [36]. Uniaxial distortion in [001] direction is expected to produce similar results.

Fig. 4.10 summarizes the results of Table 4.1 and Figs. 4.5-4.7. It shows the relationship between $\Delta$ and the quantity $t=(Z_{M'}+Z_X)V$ for the entire group, where $V$ is the unit cell volume and $Z_{M'}$ and $Z_X$ are the atomic numbers of the $M'$ and $X$ atoms in the binary $M'X$. The value of $t$ captures the effects on $\Delta$ of the $M'X$ unit, which forms the backbone of the THH compounds, and also of the overall volume of the crystalline unit cell. The critical line, $\Delta=0$, divides the figure into two parts.

†In particular, $\Delta$ increases as $V$ increases in the THH compounds, and the band gap decreases in the group III-V zinc-blende semiconductors with increasing atomic number.
where the compound is nontrivial for $\Delta > 0$ and is trivial for $\Delta < 0$. The figure shows a systematic increase of $\Delta$ with increasing $t$ values. Insight into the TI behavior of the 28 investigated THH compounds is gained by framing with a triangle the four
Figure 4.9: MBJLDA band structures of nontrivial THH LuPtBi under uniaxial strain along [111]-direction, which decreases the lattice constants $a$ by 3% and $c$ by 4%. A gap opens and an insulating phase results from the distortion. The size of the red dots indicates the degree of $s$-like occupancy as in Fig. 4.5.

compounds in each of the seven subgroups labeled by the same binary unit $M'X$. It is striking that for all seven subgroups, Sc, La, and Lu form the corners of the triangle while $Y$ lies inside. In fact, the 'orientation' of all seven triangles is the same in the sense that it runs counterclockwise going from La to Lu to Sc, where
the element with the highest binding energy, Lu, occupies the corner with highest Δ. Moreover, the volume of the compounds in each subgroup is ordered as ScM’X< LuM’X< YM’X< LaM’X, except for the MAuPb subgroup. The center of gravity for each triangle is seen to increase with t for all subgroups. All compounds, whether physically realized or hypothetical, follow the aforementioned trends independent of the sign of Δ. The preceding observations suggest that the relationships between Δ and t may be valid more generally and could be useful in ascertaining the nature of topological order and the value of the BIS in other non-magnetic half-Heusler alloys.
Figure 4.10: Band inversion strength (BIS), $\Delta = [\Gamma_8 - \Gamma_6]$ for various THH compounds versus $t = (Z_{M'} + Z_X)V$, where $Z_{M'}$ and $Z_X$ are atomic numbers $M'$ and $X$ atoms and $V$ is the unit cell volume. The 28 THH compounds investigated are divided into 7 subgroups of 4 compounds each (marked by shaded triangles of different colors), where each subgroup corresponds to the same binary unit $M'X$. The schematic illustration of the components in each of the 7 subgroups is given in the top left corner.
Table 4.1: Lattice constants, parameter $t=(Z_{M'} + Z_X)V$, and band inversion strengths (BIS), $\Delta$, based on GGA and MBJLDA for the 28 THH compounds and HgTe in the FCC structure described in the text.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Lattice Constant (Å)</th>
<th>$\Delta$ (GGA) (eV)</th>
<th>$\Delta$ (MBJLDA) (eV)</th>
<th>$t$ (nm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LuPtBi</td>
<td>6.57 [56]</td>
<td>1.58</td>
<td>1.44</td>
<td>45.74</td>
</tr>
<tr>
<td>ScPtBi</td>
<td>6.56</td>
<td>0.96</td>
<td>0.70</td>
<td>45.46</td>
</tr>
<tr>
<td>LaPtBi</td>
<td>6.83 [56]</td>
<td>0.86</td>
<td>0.65</td>
<td>51.27</td>
</tr>
<tr>
<td>YPtBi</td>
<td>6.64 [56]</td>
<td>1.10</td>
<td>0.87</td>
<td>47.13</td>
</tr>
<tr>
<td>LuAuPb</td>
<td>6.79</td>
<td>1.17</td>
<td>1.11</td>
<td>50.05</td>
</tr>
<tr>
<td>ScAuPb</td>
<td>6.64</td>
<td>0.06</td>
<td>-0.15</td>
<td>46.29</td>
</tr>
<tr>
<td>LaAuPb</td>
<td>7.11 **</td>
<td>1.05</td>
<td>0.96</td>
<td>57.91</td>
</tr>
<tr>
<td>YAuPb</td>
<td>6.73 [57]</td>
<td>0.70</td>
<td>0.54</td>
<td>49.05</td>
</tr>
<tr>
<td>LuPdBi</td>
<td>6.57 [56]</td>
<td>0.72</td>
<td>0.47</td>
<td>36.52</td>
</tr>
<tr>
<td>ScPdBi</td>
<td>6.43 [56]</td>
<td>-0.30</td>
<td>-0.74</td>
<td>34.34</td>
</tr>
<tr>
<td>LaPdBi</td>
<td>6.82 [56]</td>
<td>-0.41</td>
<td>-0.76</td>
<td>41.01</td>
</tr>
<tr>
<td>YPdBi</td>
<td>6.64 [56]</td>
<td>0.08</td>
<td>-0.29</td>
<td>37.76</td>
</tr>
<tr>
<td>LuPtSb</td>
<td>6.46 [56]</td>
<td>0.23</td>
<td>-0.01</td>
<td>34.73</td>
</tr>
<tr>
<td>ScPtSb</td>
<td>6.31 [58]</td>
<td>-0.74</td>
<td>-1.12</td>
<td>32.44</td>
</tr>
<tr>
<td>LaPtSb</td>
<td>6.88 ***</td>
<td>0.244</td>
<td>-0.03</td>
<td>41.96</td>
</tr>
<tr>
<td>YPtSb</td>
<td>6.53 [58]</td>
<td>1.10</td>
<td>-0.45</td>
<td>34.73</td>
</tr>
<tr>
<td>LuAuSn</td>
<td>6.56 [59]</td>
<td>-0.70</td>
<td>-0.89</td>
<td>36.05</td>
</tr>
<tr>
<td>ScAuSn</td>
<td>6.42 [59]</td>
<td>-1.67</td>
<td>-1.98</td>
<td>34.12</td>
</tr>
<tr>
<td>LaAuSn</td>
<td>7.01 **</td>
<td>-0.04</td>
<td>-0.11</td>
<td>44.41</td>
</tr>
<tr>
<td>YAuSn</td>
<td>6.74 ***</td>
<td>-0.58</td>
<td>-0.75</td>
<td>39.51</td>
</tr>
<tr>
<td>LuNiBi</td>
<td>6.34 [56]</td>
<td>-0.17</td>
<td>-0.47</td>
<td>28.29</td>
</tr>
<tr>
<td>ScNiBi</td>
<td>6.19 [56]</td>
<td>-1.20</td>
<td>-1.68</td>
<td>26.34</td>
</tr>
<tr>
<td>LaNiBi</td>
<td>6.72 **</td>
<td>-0.47</td>
<td>-0.92</td>
<td>33.73</td>
</tr>
<tr>
<td>YNiBi</td>
<td>6.41 [56]</td>
<td>-0.66</td>
<td>-1.11</td>
<td>29.25</td>
</tr>
<tr>
<td>LuPdSb</td>
<td>6.51</td>
<td>-0.42</td>
<td>-0.76</td>
<td>26.72</td>
</tr>
<tr>
<td>ScPdSb</td>
<td>6.05 [60]</td>
<td>-1.67</td>
<td>-2.17</td>
<td>24.39</td>
</tr>
<tr>
<td>LaPdSb</td>
<td>6.84 **</td>
<td>-1.14</td>
<td>-1.44</td>
<td>31.09</td>
</tr>
<tr>
<td>YPdSb</td>
<td>6.53 *</td>
<td>-1.18</td>
<td>-1.60</td>
<td>27.05</td>
</tr>
<tr>
<td>HgTe</td>
<td>6.46</td>
<td>1.04</td>
<td>0.41</td>
<td>35.58</td>
</tr>
<tr>
<td>YbPtBi</td>
<td>6.58 [56]</td>
<td>2.13</td>
<td>2.06</td>
<td>45.87</td>
</tr>
<tr>
<td>GdPtBi</td>
<td>6.68 [56]</td>
<td>1.86</td>
<td>1.04</td>
<td>47.99</td>
</tr>
</tbody>
</table>

* These compounds do not occur in nature. We have obtained the FCC lattice constants via a constrained minimization of the DFT-GGA total energy.

** Naturally occurring compound possesses hexagonal structure[61].

*** Naturally occurring compound possesses space group $P6_3/mmc$[56].
Chapter 5

Green Function Method

5.1 Introduction

The second method we are going to employ to solve the Kohn-Sham eqn. 2.24 is the Green function method. The Green (multiple-scattering) method of Korringa, Kohn and Rostoker (KKR) for the calculation of the electronic structure of materials was introduced in 1947 by Korringa [65] and in 1954 by Kohn and Rostoker [2]. The technique looks different from APW in principle but it provides similar results. Most electronic structure methods calculate eigenfunctions $\psi_i$ and eigenvalues $\epsilon_i$. However, the calculation of $\psi_i$ and $\epsilon_i$ can be avoided, if instead the single-particle Green function $G(\mathbf{r}, \mathbf{r}'; E)$ of the Kohn-Sham equation is determined based on multiple scattering theory. Hence, all observables can be calculated for the ground state.

In this framework, the scattering properties of each scattering center (atom, scatterer) are determined and described by a scattering matrix, then the multiple scattering by all atoms in the lattice is determined by requiring that the incident
wave at each center is the sum of the outgoing waves from all other centers. In this way, a separation between the potential and structure of the lattice is achieved. Here we consider only muffin-tin potentials, where each site can be viewed as a spherical scatterer and electrons propagate between sites with the free propagator or Green function.

5.2 Definition and General Properties of Green Function

One may define the (time-independent) Green function as the resolvent of the time-independent Schrodinger equation, via the operator equation

$$G(E) = (E - H)^{-1}.$$ \hfill (5.1)

In terms of a complete set of eigenfunctions of $H$, $|\psi_i\rangle$, corresponding to eigenvalues $\varepsilon_i$, the following spectral representation can be obtained:

$$G(E) = \sum_i \frac{|\psi_i\rangle\langle\psi_i|}{E - \varepsilon_i}.$$ \hfill (5.2)

In real space, the above equation becomes

$$G(r, r'; E) = \sum_i \frac{\psi_i(r)\psi_i^*(r')}{E - \varepsilon_i},$$ \hfill (5.3)

representing, in the limit of $ImE = \varepsilon \to 0^+$, an outgoing wave at $r$ with a source term at $r'$. From the above equation one can see that the imaginary part of $G$ is
directly related to the spectrally- and space-resolved density of states \( n(\mathbf{r}; E) \) for real \( E \):
\[
n(\mathbf{r}; E) = -\frac{1}{\pi} \text{Im} G(\mathbf{r}, \mathbf{r}; E).
\]

(5.4)

### 5.3 Relation between Perturbed and Unperturbed System

If we introduce a reference system \( G^{-1}_o(E) = E - H_o \), while for the perturbed system \( G^{-1}(E) = E - H = E - (H_o + V) \), we conclude that the two Green functions are connected via
\[
G^{-1}(E) = G^{-1}_o(E) - V.
\]

(5.5)

The Dyson equation can be rewritten in the following forms:
\[
G(E) = [1 - G_o(E)V]^{-1}G_o(E) = G_o(E)[1 - VG_o(E)]^{-1} = G_o(E) + G_o(E)VG_o(E).
\]

(5.6)

If we expand \( G \) in the right-hand side:
\[
G(E) = G_o(E) + G_o(E)VG_o(E) + G_o(E)VG_o(E)VG_o(E) + \ldots
\]

(5.7)

Observing that the Schrödinger equation for the perturbed system can be written as:
\[
(E - H)|\psi\rangle = V|\psi\rangle,
\]

(5.8)
we can write $|\psi\rangle$ in terms of the unperturbed eigenstates $|\psi_o\rangle$ as

$$|\psi\rangle = |\psi_o\rangle + G_o(E)V|\psi\rangle. \quad (5.9)$$

Expanding the right-hand side of this Lippmann-Schwinger equation leads to the Born series

$$|\psi\rangle = |\psi_o\rangle + G_o(E)V|\psi_o\rangle + G_o(E)V|\psi_o\rangle G_o(E)V|\psi_o\rangle + ... \quad (5.10)$$

We now introduce the transition matrix, or T-matrix, of a scattering system. It relates the states $|\psi\rangle$ of the perturbed Hamiltonian to the states $|\psi_o\rangle$ of the unperturbed system via the defining equation

$$V|\psi\rangle = T(E)|\psi_o\rangle. \quad (5.11)$$

In terms of the T-matrix the Lippmann-Schwinger eqn. 5.10 is written as

$$|\psi\rangle = |\psi_o\rangle + G_o(E)T(E)|\psi_o\rangle. \quad (5.12)$$

The Dyson eqn. 5.7 becomes

$$G(E) = G_o(E) + G_o(E)T(E)G_o(E), \quad (5.13)$$
where $T(E)$ is given by

\[
T(E) = V[1 - G_o V]^{-1}
= [1 - VG_o]^{-1}V
= V + VG_o T(E).
\] (5.14)

The right-hand side of the last equation leads once more to a Born series:

\[
T(E) = V + VG_o(E)V + VG_o(E)VG_o(E)V + ..., \tag{5.15}
\]

while for small perturbations we are led to the first-order Born approximation, $T = V$. If $V$ has a spherically symmetric potential of finite range in free space, then we have a single site scattering problem, and we denote $T$ as $t$. In angular-momentum representation it is diagonal and its elements are related to the scattering phase shifts $\eta_l(E)$ (see appendix 10.6 and 10.7 for proof and more discussion) via:

\[
t_l(E) = -\frac{1}{\sqrt{E}} \sin(\eta_l(E)) e^{i\eta_l(E)}. \tag{5.16}
\]

### 5.4 Scattering from multiple potentials

In this section we are going to study the scattering of waves (particles) by several scatterers. We have two basic equations in the multiple scattering theory:

\[
\psi(r) = \zeta(r) + \sum_n \psi_n^s(r), \tag{5.17}
\]
and
\[ \psi_n^i(r) = \zeta(r) + \sum_{p \neq n} \psi_p^s(r). \]  

Eqn. 5.17 implies that the total wavefunction \( \psi(r) \) is given by the unperturbed wavefunction \( \zeta(r) \) in the absence of the scatterers added to the sum of the scattered waves \( \psi_n^s(r) \) propagating outward from all other scatterers. In eqn. 5.18, \( \psi_n^s(r) \) is the incident wave to the \( n^{th} \) scatterer which is given by the sum of the unperturbed wavefunction in the absence of the scatterers plus the scattered waves from all scatters except the \( n^{th} \) scatterer [66]. These two equations summarize the multiple scattering theory which is based upon the principle proposed originally by Huygens in 1678 [67] to determine the position of an advancing wavefront at time \( t + \delta t \), from its position at previous time \( t \). In a solid the crystal field can be approximated by the muffin-tin potentials, which in turn are the scattering potentials. These potentials are spherically symmetric around each scattering center, within a sphere of radius \( R_{MT} \), and constant otherwise; the spheres can be touching each other but can not overlap. The procedure leads to the KKR equations for the band structure of periodic crystals. The quasi-particle wavefunctions can be described by the Kohn-Sham equation eqn. 2.24, in atomic units this can be written in the form:

\[ (\nabla^2 + k^2)\psi(r) = V(r)\psi(r), \]  

where \( k = \sqrt{E} \). Then, we introduce the Green function:

\[ (\nabla^2 + \kappa^2)G(r, r') = \delta(r - r'), \]
where the solution of eqn. 5.20 gives the Green function which has to be written in the form:

$$G(r - r') = -\frac{1}{\tau} \sum_n \frac{\exp(i k_n \cdot (r - r'))}{k_n^2 - E}.$$  \hspace{1cm} (5.21)

where \(\tau\) is the size of the atomic polyhedron.

This Green function has, obviously, the properties:

$$G(r, r') = G(r - r') = G^*(r' - r),$$  \hspace{1cm} (5.22)

and satisfies the Bloch’s condition

$$G(r, r' + R) = e^{i k_n \cdot R} G(r - r'),$$  \hspace{1cm} (5.23)

Where \(k_n\) is the Bloch wave vector and \(R\) is the Bravais lattice vector. Following the theory of partial homogeneous differential equation one can write:

$$\psi(r) = \int G(r - r')V(r')\psi(r')dr',$$  \hspace{1cm} (5.24)

eqn. 5.24 gives the meaning of the Green function \(G(r - r')\), which is defined as quantity transmitting the wave \(\psi(r')\) at all different positions \(r'\) to the wavefunction \(\psi(r)\) at the position \(r\) through the scattering due to the potential \(V(r - r')\). If we make the the substitution \(\psi(r) \rightarrow G(r - r')\psi(r')\) in both sides of eqn. 5.19 the integration over a whole space\(^\dagger\)

$$\int \{\nabla^2 + k^2\}G(r - r')\psi(r')dr' = \int G(r - r')V(r')\psi(r')dr',$$  \hspace{1cm} (5.25)

\(^\dagger\)This step was done to prove that the integral equation, eqn. 5.24, is indeed a solution for Schrödinger equation, the differential form, and to provide an insight in the Green function role.
this immediately will give eqn. 5.22, since the left hand side obviously reduces to the wavefunction $\psi(r)$. We confirm in this way that the eqn. 5.22 is indeed the Schrödinger equation in integral form.

The discussion above is limited to the scattering due to one scatterers [5.17-5.25]. It is easy to extend the previous result to a more general periodic muffin-tin potentials (scatterers) given by

$$V(r) = \sum_{r_s} v(r - r_s). \tag{5.26}$$

The wave function characterized by the wave vector $k$ eqn. 5.21 is therefore extended to the case of a crystal:

$$\psi_k(r) = \sum_{r_s} \int G(r - r') v(r' - r_s) \psi_k(r') dr' = \sum_{r_s} \int G(r - r') v(r' - r_s) \exp(i k \cdot r_s) \psi_k(r' - r_s) dr', \tag{5.27}$$

where the second equation is obtained by using the Bloch condition $\psi_k(r + r_s) = \exp(i k \cdot r_s) \psi_k(r)$. Eqn. 5.27 means that the wavefunction at the position $r$ is determined by the sum of the contribution from wavelets scattered from all equivalent muffin-tin potentials with lattice vectors $r_s$. Note that the whole dependence on $k$ and on the crystal structure is completely included in the Green function. In a periodic lattice one can write $k_n = k + K_n$, where $K_n$ is the reciprocal lattice vector, and if we make the substitution $r'' = r' - r_s$ and plug into eqn. 5.21 we get:

$$G(r - r'') = -\frac{1}{\tau} \sum_n \frac{\exp(i(K_n + k) \cdot (r - r'' - r_s))}{(K_n + k)^2 - E}, \tag{5.28}$$
this is called the structural Green function, and it is convenient to describe the 
motion of electrons in a periodic crystal and works as propagator to all the wavelets 
at the position \( \mathbf{r}'' \) scattered from periodic potential with lattice vector \( \mathbf{r}_s \) to the 
position \( \mathbf{r} \). The Bloch wave function \( \psi_k(\mathbf{r}) \) can be obtained as a solution of the 
Kohn-Sham equation in a periodic potential \( V(\mathbf{r}) \). The following step is to construct 
a functional which gives the integral eqn. 5.26 upon variation:

\[
5.4.1 \quad \text{The variational principle of KKR}
\]

Kohn and Rostoker in their paper [2] set up a proper variational \textit{ansatz} by 
defining the function:

\[
\Lambda = \int \psi_k^*(\mathbf{r})(\mathbf{H} - E)\psi_k(\mathbf{r})\,d\mathbf{r}, \tag{5.29}
\]

Using \( \mathbf{H} = -\vec{\nabla}^2 + V(\mathbf{r}) \), one gets

\[
\Lambda = \int d^3\mathbf{r}\psi_k^*(\mathbf{r})V(\mathbf{r})\psi_k(\mathbf{r}) - \int d^3\mathbf{r}\psi_k^*(\mathbf{r})[\vec{\nabla}^2 + E]\psi_k(\mathbf{r}) \tag{5.30}
\]

with \( \tau \) as the volume of the unit cell of the crystal. Making use of eqn. 5.24, 5.19, 
and the second term of eqn. 5.30 we get:

\[
\Lambda = \int d^3\mathbf{r}\psi_k^*(\mathbf{r})V(\mathbf{r})\psi_k(\mathbf{r}) - \int d^3\mathbf{r}d^3\mathbf{r}'G^*(\mathbf{r} - \mathbf{r}')\psi_k^*(\mathbf{r}')V(\mathbf{r}')\psi_k(\mathbf{r})V(\mathbf{r})\psi_k(\mathbf{r}) \tag{5.31}
\]

and by interchanging \( \mathbf{r} \) with \( \mathbf{r}' \)

\[
\Lambda = \int d^3\mathbf{r}\psi_k^*(\mathbf{r})V(\mathbf{r})\psi_k(\mathbf{r}) - \int d^3\mathbf{r}d^3\mathbf{r}'\psi_k^*(\mathbf{r})V(\mathbf{r})G(\mathbf{r} - \mathbf{r}')V(\mathbf{r}')\psi_k(\mathbf{r}). \tag{5.32}
\]
The solution of the variational equation

\[ \delta \Lambda = 0 \]  

will provide the solution of the integral equation eqn. 5.22.

### 5.4.2 The Spherical potential secular equation

The muffin-tin potential approximation is a significant simplification of the real crystal potential complexity for KKR method

\[ V(r) = \begin{cases} V(|r|) & |r| \leq r_{MT} \\ 0 & |r| > r_{MT}. \end{cases} \]  

Thus, all integrals over the unit cell \( \tau \) can be replaced by integrals over the muffin-tin sphere (MTS) with radius \( r_{MT} \),

\[ \Lambda = \int_{MTS} d^3r \psi^*_k(r)V(r)\psi_k(r) - \int_{MTS} \int_{MTS'} d^3rd^3r' \psi^*_k(r)V(r)G(r - r')V(r')\psi_k(r'). \]

As a result, the trial function for the required wavefunction is defined only inside and on the MTS. In that region the potential is spherically symmetric as stated in eqn. 5.35, and we can write

\[ \psi_k(r) = \sum_{lm} c_{lm}(k)\phi_{lm}(r; E) = \sum_{lm} c_{lm}(k)R_l(r; E)Y_{lm}(\theta, \varphi). \]
By plugging eqn. 5.36 into eqn. 5.35, we get

\[ \Lambda = \sum_{l,m} c^*_l(k)c_{l',m'}(k) \times \left[ \int_{MTS} d^3r \phi^*_lm(r,E)V(r)\phi_{l',m'}(r,E) \right. \]

\[ - \int_{MTS} \int_{MTS'} d^3r d^3r' \phi^*_lm(r;E)V(r)G(r - r')V(r')\phi_{l',m'}(r';E). \]  

(5.37)

where the expression inside the brackets defines the components of the KKR secular equation \( \Lambda \) for the row \((l, m)\) and the column \((l', m')\)

\[ \Lambda = \sum_{l,m} c^*_l(k)c_{l',m'}(k)\Lambda_{l,m,l',m'}(k). \]  

(5.38)

Taking the derivative of \( \Lambda \) with respect to the parameters \( c^*_lm(k) \) leads to

\[ \frac{\delta \Lambda}{\delta c^*_lm(k)} = \sum_{l',m'} \Lambda_{l,m,l',m'}(k)c_{l',m'}(k) = 0 \]  

(5.39)

and, accordingly, to the system of homogenous linear equations

\[ \sum_{l',m'} \Lambda_{l,m,l',m'}(k)c_{l',m'}(k) = 0, \]  

(5.40)

then, the components of the corresponding secular equation are

\[ \Lambda_{l,m,l',m'}(k) = \int_{MTS} d^3r \phi^*_lm(r;E)V(r)\phi_{l',m'}(r;E) \]

\[ - \int_{MTS} \int_{MTS'} d^3r d^3r' \phi^*_lm(r;E)V(r)G(r - r')V(r')\phi_{l',m'}(r';E). \]  

(5.41)

For numerical calculations, one has to take into account that the secular equation \( \Lambda \) has to be restricted to a matrix of finite order. By limiting the angular momentum
to \( l \leq l_{\text{max}} \), one gets a KKR matrix of order \((l_{\text{max}} + 1)^2\). \( \Lambda_{l_m,l_m'}(k) \) contains the basis functions \( \phi_{l_m}(r,E) \), and the radial functions \( R_l(r;E) \) that are solutions of the differential equation

\[
\left[ \left( \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right) + \frac{l(l+1)}{r^2} + V(r) - E \right] R_l(r;E) = 0. \tag{5.42}
\]

That means that these radial functions include implicitly the information about the crystal potential \( V(r) \). From the theoretical point of view, it would be desirable that \( \Lambda \) could be transformed such that the potential would explicitly disappear in eqn. 5.20. Such a transformation is possible, as it is demonstrated in appendix 10.8. The result is as follows:

\[
\Lambda_{l_m,l_m'}(k) = \lim_{\epsilon \to 0} \int_{S_{\text{MTS}-\epsilon}} ds \int_{S_{\text{MTS}-2\epsilon}} ds' \left[ \frac{\partial \phi^{*}_{l_m}(r;E)}{\partial r} - \phi^{*}_{l_m}(r;E) \frac{\partial}{\partial r} \right] \times \left[ \phi_{l_m'}(r';E) \frac{\partial}{\partial r'} G(r-r') - G(r-r') \frac{\partial}{\partial r'} \phi_{l_m'}(r';E) \right], \tag{5.43}
\]

where \( S_{\text{MTS}-\epsilon} \) and \( S_{\text{MTS}-2\epsilon} \) mean that the integration goes over to the two surfaces of muffin-tin spheres with radii \( r_{\text{MT}} - \epsilon \) and \( r_{\text{MT}} - 2\epsilon \) (\( \epsilon > 0 \) is infinitely small), by this trick, singularities of the Green function for \(|r-r'|\) are avoided. Inserting the relation \( \phi_{l_m}(r,E) = R_l(r,E)Y_{l_m}(\theta,\varphi) \) into eqn. 5.43, then the KKR matrix elements are

\[
\Lambda_{l_m,l_m'}(k) = \lim_{\epsilon \to 0} r_{\text{MT}}^4 \int d\Omega d\Omega' Y^{*}_{l_m}(\theta,\varphi)Y^{*}_{l_m'}(\theta',\varphi') \times \left[ R'(r_{\text{MT}};E) - R_l(r_{\text{MT}};E) \frac{\partial}{\partial r} \right] \times \left[ R'_l(r_{\text{MT}};E) \frac{\partial}{\partial r'} G(r-r') - G(r-r') R'_l(r_{\text{MT}};E) \right], \tag{5.44}
\]

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with $|\mathbf{r}| = r_{MT} - 2\epsilon$, $|\mathbf{r}'| = r_{MT} - \epsilon$, $R'_l(r_{MT}; E) = \left[ \frac{d}{dE} R_l(r; E) \right]$, $d\Omega = \sin \vartheta d\vartheta d\varphi$, and $d\Omega' = \sin \vartheta' d\vartheta' d\varphi'$. In order to facilitate the integration over $d\Omega$ and $d\Omega'$ in eqn. 5.44, it is useful to expand the Green’s function eqn. 5.21.

The expansion of the plane wave in spherical harmonics and spherical Bessel’s functions is give by

$$e^{i\mathbf{k} \cdot \mathbf{r}} = 4\pi \sum_{l,m} \hat{j}_l(|\mathbf{k}| |\mathbf{r}|) Y_{lm}(\vartheta, \varphi) Y_{lm}^*(\vartheta_k, \varphi_k),$$

(5.45)

where $j_l$ is the spherical bessel function which is given by

$$j_l(x) = \left( \frac{\pi}{2x} \right)^{1/2} J_{l+1/2}(x),$$

(5.46)

and $J$ is the Bessel function. Then we substitute into eqn. 5.21

$$G(\mathbf{r} - \mathbf{r}') = \frac{(4\pi)^2}{\tau} \sum_{l,m} \sum_{l',m'} \sum_{n} \hat{j}_l(|\mathbf{k}_n||\mathbf{r}|) j_{l'}(|\mathbf{k}_n||\mathbf{r}'|) j_{l'}(kr) j_l(kr_0) E - |\mathbf{k}_n|^2$$

$$\times Y_{lm}(\vartheta, \varphi) Y_{lm}^*(\vartheta', \varphi') Y_{lm}^*(\vartheta_k, \varphi_k) Y_{lm}^*(\vartheta_k, \varphi_k)$$

(5.47)

where $\vartheta_k$ and $\varphi_k$ mean the angle that belongs to the vector $\mathbf{k}_n = \mathbf{k} + \mathbf{K}_n$. Kohn-Rostoker expand the Green function in eqn. 5.28 in the form, see appendix 10.9,

$$G(\mathbf{r} - \mathbf{r}') = \sum_{l,m} [A_{lm,l'm'}(\mathbf{k}; E) j_l(kr) j_{l'}(kr')]$$

$$+ k \delta_{l,l'} \delta_{m,m'} j_l(kr) n_l(kr') Y_{lm}(\vartheta, \varphi) Y_{lm}^*(\vartheta', \varphi'),$$

(5.48)

where $k^2 = E$, and the function $n_l(x)$ mean the Neumann functions

$$n_l(x) = \left( \frac{\pi}{2x} \right)^{1/2} J_{l-1/2}(x).$$

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The equivalence of the expressions eqn. 5.47 and 5.48 is obtained by determination of the coefficients $A_{lm;l_0m_0}$ in eqn. 5.48 by comparison of coefficients with respect of the terms $Y_{lm}(\theta, \varphi)Y_{l_0m_0}(\theta', \varphi')$:

$$A_{lm;l_0m_0} = \frac{(4\pi)^2}{\tau} \frac{i^{l-l'}}{j_l(kr)j_{l'}(kr')} \sum_n \frac{j_l(|k_n|r)j_{l'}(|k_n|r')}{E - |k_n|} \times Y_{lm}^*(\theta_k, \varphi_k)Y_{l_0m_0}^*(\theta_{k'}, \varphi_{k'}) - \frac{kn_l(kr')}{j_l(kr')} \delta_{l,l'} \delta_{m,m'}.$$  \hspace{1cm} (5.49)

These parameters are exclusively determined by the structure of the lattice and are completely independent of the crystal potential. Substituting eqn. 5.49 into eqn. 5.44 and taking account of the well-known orthogonality relations between the spherical harmonics, one obtains

$$\Lambda_{lm;l_0m_0}(k) = r_{MT}^4 R_l(r_{MT}; E) R_{l'}(r_{MT}; E) [L_l j_l(kr_{MT}) - j_l'(kr_{MT})] \times \{[A_{lm;l_0m_0}j_{l'}(kr_{MT}) + k \delta_{m,m'} \delta_{l,l'} n_{l'}(kr_{MT})] - [A_{lm;l_0m_0}j_{l'}(kr_{MT}) + k \delta_{m,m'} \delta_{l,l'} n_{l'}(kr_{MT})] L_l\},$$  \hspace{1cm} (5.50)

with the definitions

$$L_l = \frac{1}{R_l(r_{MT}; E)} \frac{dR_l(r; E)}{dr} \bigg|_{r=r_{MT}},$$  \hspace{1cm} (5.51)

$$j'(kr_{MT}) = \frac{d j_l(kr)}{dr} \bigg|_{r=r_{MT}},$$  \hspace{1cm} (5.52)

$$n_{l'}'(kr_{MT}) = \frac{d n_{l'}(kr)}{dr} \bigg|_{r=r_{MT}}.$$  \hspace{1cm} (5.53)

For the calculation of the eigenvalues of the secular matrix 5.50, only the zeroes of the corresponding determinant are of interest, not the values of the determinant.
themselves. After rearranging the terms, it is straightforward to get the relation as

\[
\det \{ A_{lm;l'm'} + k \frac{n_i(k \rho_{MT}) L_i - n_i'(k \rho_{MT})}{j_i(k \rho_{MT}) L_i - j_i'(k \rho_{MT})} \delta_{ll'} \delta_{mm'} \} = 0.
\] (5.54)

The above equation can be connected to the equation suggested by Korringa which has more compact form, see appendix 10.10 for proof, as:

\[
\det \{ A_{lm;l'm'} + k \cot \eta_i \delta_{ll'} \delta_{mm'} \} = 0
\] (5.55)

where \( \eta_i \) is given by:

\[
\tan(\eta_i) = \frac{j_i(k \rho_{MT}) L_i - j_i'(k \rho_{MT})}{n_i(k \rho_{MT}) L_i - n_i'(k \rho_{MT})}.
\] (5.56)

In KKR we sum over reciprocal lattice vectors and we have a secular determinant in the contributions from different spherical harmonics. Eqn. 5.54 and 5.55 demonstrate the advantage of KKR: the coefficient of the secular matrix consist of two terms, where the first one is only determined by the geometry of the lattice, and the second by the crystal potential. The disadvantage of this method is that it leads to a non-linear eigenvalue problem, because the energy \( E \) not only appears linearly in the secular equation, but also in a non-trivial manner in coefficients \( A_{lm;l'm'} \) and \( L_i \), and within the functions \( j_i(k \rho_{MT}) \) and \( n_i(k \rho_{MT}) \). KKR is very similar to the APW method. In the APW method we expand as far as we like in spherical harmonics, and then have to solve a secular determinant for contributions from different reciprocal lattice vectors. The advantage of APW is that it gives a better picture of the wavefunction outside the atomic spheres.
Chapter 6

Compton Scattering

6.1 Introduction

Compton discovered in 1923 that x-rays scattered from elements like graphite have a wavelength longer than that of the incident beam [68]. This effect usually called Compton scattering, is the well known type of inelastic x-ray scattering (IXS) that is widely used to determine electron a momentum distribution. IXS is a useful probe of a wide variety of electronic excitations [69]. The various physical phenomena existing within the concept of IXS can be classified in a meaningful way according to the associated energy and momentum transfers relative to the characteristic energies or structural dimensions.

In an IXS experiment, a beam of photons that have been monochromatized to a definite wavevector $k_1$, frequency $\omega_1$, polarization $e_1$ shines on a sample and scatters into some final state specified, far from the sample, by $k_2$, $\omega_2$ and $e_2$. The momentum and the energy transferred to the matter are $\hbar k = \hbar (k_2 - k_1)$ and
\[ h\omega = h(\omega_2 - \omega_1), \] respectively. The theory of IXS is often based on relativistic treatment of the interaction between electromagnetic waves and quasi free electron. However, since the energy transfers is much smaller than the energy itself then the non-relativistic limit is a good approximation. For an x-ray of energy \(10\text{KeV} < h\omega < 100\text{KeV}\) that interacts weakly with bulk samples, the inelastic scattering can be treated in Born approximation and the scattering cross section is specified by \(k,\) energy transfer \(h\omega,\) and incoming (outcoming) polarization \(e_1(e_2) \] [70].

In experiments with hard X-rays, the large transfer conditions\(^\dagger\) are typically true for the majority of the electrons. In most cases, only the innermost shells fail to fulfill this approximation. In particular, the Compton scattering technique is most sensitive to the spatially extended valence electron (delocalized) states as their contribution is largely confined to the peak area of the Compton profile due to the lower average momentum. Depending on the energy transfer, the inner shells might not even participate in the IXS process.

Compton scattering is a powerful technique for probing the ground-state electronic structure of materials, leading to directional Compton profiles which are closely related to momentum density. The 1D Fourier transform of the directional Compton profiles does not give any direct structural information of the target in a general case. However, a definite correlation between the electronic structure and the features found in the profiles, or their anisotropies, does exist. The anisotropies can taking differences between the given directional profiles. The contributions from the isotropic core states and any residual background are thus subtracted out. What remains is dominated by the electron wave function phase coherence among the neighboring atoms. The Compton scattering technique is also quite insensitive

\(^\dagger2\pi/q \ll a\) where \(q\) is the momentum transfer and \(a\) is the average spacing between electrons
to the crystal quality, unlike methods utilizing electrons or positrons.

6.2 IXS Cross section

We restrict ourselves to the non-relativistic scheme. It is important to know that the spin dependence and the polarization are absent from our formalism since we are not interested in spin information. Moreover, the interaction between hole\(^\dagger\) and surroundings is not included as well. The total Hamiltonian that describes the interaction of the photons with electrons can be written as:

\[
H = H_{\text{photon}} + H_{\text{one-electron}} + H_{\text{interaction}}.
\]  \hspace{1cm} (6.1)

The interaction part of the Hamiltonian consists of interaction processes coupling the electromagnetic vector field \(A\) with the electron and its spin \(\sigma\), and we can write the interaction part of the Hamiltonian as:

\[
H_{\text{interaction}} = \frac{e^2}{2mc} \mathbf{A} \cdot \mathbf{A} + \frac{e}{mc} \mathbf{p} \cdot \mathbf{A} + \frac{e\hbar}{2mc} \mathbf{\sigma} \cdot \nabla \times \mathbf{A}.
\]  \hspace{1cm} (6.2)

As far as charge scattering is concerned, the Compton limit of inelastic scattering is based only on the first term in the interaction Hamiltonian \(A^2\). We shall assume that we are far enough from resonance. Therefore, the non-relativistic double differential scattering cross section for X-ray scattering consists of two parts and

\(^\dagger\)Electrons excited to the conduction band leave behind electron holes, or unoccupied states in the valence band. The holes don’t move, but a neighboring electron can move to fill the hole, in this way the holes appear to move and behave as if they were actual positively charged particles. The Coulomb interaction between holes and electrons can, in some cases, results into a bound state called exciton.

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is given by:

\[
\frac{d^2 \sigma}{d \Omega d \omega_2} = \left( \frac{d \sigma}{d \Omega} \right)_{Th} S(q, \omega) .
\]  

(6.3)

The cross section is proportional to the so-called dynamic structure factor \(S(q, \omega)\) which reflects the properties of the target in the absence of perturbation due to the probe. The second term, \(\left( \frac{d \sigma}{d \Omega} \right)_{Th}\), is the Thomson cross section which represents the photon-electron coupling and is given by,

\[
\left( \frac{d \sigma}{d \Omega} \right)_{Th} = r_o^2 \left( \frac{\omega_2}{\omega_1} \right) (e_1, e_2).
\]  

(6.4)

We assume that this is weak enough to be treated in the lowest Born approximation (first order perturbation). \(r_o\) is the classical electron radius. The response of the electrons to the probe is included in the dynamic structure factor, which is given by

\[
S(q, \omega) = \sum_F \langle F | \Sigma_j \exp(iq \cdot r_j) | I \rangle^2 \delta(\omega + \epsilon_I - \epsilon_F),
\]  

(6.5)

where the summation runs over all final states \(F\). We can transform eqn. 6.5 into a representation of \(S(q, \omega)\), which reveals much better the information about the correlated motion of the scattering particles inherent in the dynamic structure factor, using the the well known representation of the \(\delta\)-function

\[
\delta(\epsilon_F - \epsilon_I - \hbar \omega) = (1/2\pi) \int_{-\infty}^{\infty} \exp(-i(\epsilon_F - \epsilon_I - \hbar \omega)t) dt,
\]  

(6.6)

we obtain the following expression [71] for \(S(q, \omega)\)

\[
S(q, \omega) = (1/2\pi) \int_{-\infty}^{\infty} \langle I | \sum_{i,j} \exp[iq \cdot r_i(0)] \exp[iq \cdot r_j(t)] | I \rangle e^{i\omega t} dt,
\]  

(6.7)
this expression demonstrates the role of interference phenomena, when probing multiple-particle system with certain momentum and energy transfer [72]. The response of the system will depend on the $\frac{2\pi}{q}$ compared with the typical inter-particle distance, and how $\omega$ compares with characteristic $\omega_c^\dagger$ of the system. If $qa$ is small compared to $2\pi$, and $\omega$ is nearly equal to $\omega_c$, interference between waves scattered from many particles at different times is of importance. In this situation, we can probe mainly the collective behavior of the multiple-particle system. This domain of energy and momentum transfer is called “regime of characteristic energy losses” [72].

On the other hand, if $aq$ is large compared with $2\pi$ and $\omega$ is large compared to $\omega_c$, the waves scattered from different particles do not interfere, so that we are probing the position of one particle at different times. In this scenario, the measurement of $S(q, \omega)$ will yield information about the single particle momenta provided $\omega \gg \omega_c$ guaranteeing that the timescale of probing is small enough to prevent the remaining system from rearranging itself. This domain is called the “Compton domain” [72, 73]. The condition $\omega \gg \omega_c$ is the requirement for treating the scattering process within the limits of the so-called impulse approximation.

### 6.2.1 Compton scattering regime

Compton scattering is the regime of IXS in which we are looking at scattering events with high momentum transfer $q$ and high energy transfer $\hbar\omega$. In this respect, high momentum transfer means that $\frac{2\pi}{q} \ll a$. According to eqn. 6.7, with such a large momentum transfer, we can neglect all interference effects between waves scattered from different particles at different times. Therefore one is probing the

$\dagger$The frequency corresponding to binding energies for core electrons, Fermi-energy for quasi-free electrons in metals
positions of one particle in different times, so that we are mainly looking at the single-particle properties. After the scattering process the electron is in a continuum state, not exerting influence to the state of the parent atom, nor to the band structure of the electronic system. The purely atomic excited states which are created decay locally by emitting fluorescence radiation.

### 6.2.2 Impulse approximation

This approximation consists in replacing the final electronic states by plane-wave states and substituting the energy difference between final and initial states by the corresponding kinetic-energy differences of independent particles. This means the potential energy of the scattered electron is assumed not to change during the scattering process due to the very short time interval. Following the formal justification provided by Eisenberger and Platzman [74] the dynamic structure factor eqn. 6.5 is given by

\[
S(q,\omega) \simeq \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp(i\omega t) \sum_{I \in \text{occ}} \sum_{F \in \text{unocc}} \langle I | e^{-iq \cdot r} | F \rangle \langle F | e^{i(H_e+V)t} e^{iq \cdot r} e^{-i(H_e+V)t} | I \rangle dt.
\]

(6.8)

Due to the instantaneous nature of the scattering process, the target has no time to relax; thus the potential cancels between initial and final states. Consequently the scattered photons carry no information about the latter states. The essence of impulse approximation can be stated as follows. For large energy transfers ($\hbar \omega \gg \langle [H_e V] \rangle^{1/2}$) only a short interval of time ($t \lesssim \omega^{-1}$) contribute to the above time integration.

---

†The Compton scattering data in this work is interpreted within the impulse approximation.
integral, justifying the approximation

\[ e^{i(H_0 + V)t} = e^{iH_0 t} e^{iV t} e^{-|H_0 V|^2 / 2} \cdots \simeq e^{iH_0 t} e^{iV t}, \]  

(6.9)

since \( V \) and \( r \) commute, the eqn. 6.8 can be written as:

\[ S(q, \omega) \simeq (1/2\pi) \int_{-\infty}^{\infty} \exp(i\omega t) \sum_{\text{occ}} \sum_{\text{unocc}} \langle I | e^{-iqr} | F \rangle \langle F | e^{iH_0 t} e^{iqr} e^{-iH_0 t} | I \rangle dt. \]  

(6.10)

Assuming the recoil electron to be free in its final state, i.e, we insert a complete set of eigenfunction \( |p_f\rangle \) of the kinetic energy part \( H_0 \) of the Hamiltonian into eqn. 6.8 and using

\[ \exp(iH_0 t/\hbar)|p_f\rangle = \exp(i\varepsilon(p_f)t/\hbar)|p_f\rangle \]  

(6.11)

where

\[ \varepsilon(p_f) = p_f^2/2m, \]  

(6.12)

then eqn. 6.10 becomes

\[ S(q, \omega) \simeq \sum_{p_f} |\langle I | \exp(iq\cdot r) | p_f \rangle|^2 \delta[\varepsilon(p_f) - \varepsilon(p_f - \hbar q) - \hbar \omega], \]  

(6.13)

where we make use of the integral representation of the \( \delta \)-function. Finally we use the substitution

\[ p = p_f - \hbar q. \]  

(6.14)
Substituting eqn. 6.14 and changing the sum from $\mathbf{p}_f$ to a $p$ integration, we end up with

$$S(\mathbf{q}, \omega) \simeq \int |\langle I | p \rangle|^2 \delta_h q^2 / 2m + \mathbf{h q} / m - h\omega) d\mathbf{p}, \quad (6.15)$$

where $\langle I | p \rangle = \chi(\mathbf{p})$ is the projection of the initial state in the momentum space which is nothing but the initial state in the momentum space. Let $\psi(\mathbf{r})$ be the single-particle wavefunction in the coordinate representation, representing the initial state $|I >$, in other words it is the projection of the initial state in the position space. Then we can write the momentum density as

$$\rho(\mathbf{p}) = 1/(2\pi \hbar)^3 |\langle I | p \rangle|^2 = 1/(2\pi \hbar)^3 |\chi(\mathbf{p})|^2 = 1/(2\pi \hbar)^3 \int \psi(\mathbf{r}) \exp(-i\mathbf{r} \cdot \mathbf{p}/\hbar) d\mathbf{r}^2. \quad (6.16)$$

The quantity under the integral of eqn. 6.15 represents the momentum density of the scattering system in the ground state $|I >$ and gives the probability of finding the initial electron with a given momentum $\mathbf{p}$. Due to the $\delta$-function, the $\mathbf{p}$-space integral in eqn. 6.15 extends over a plane in momentum space perpendicular to $\mathbf{q}$, where $\mathbf{q} = \mathbf{k}_1 - \mathbf{k}_2$. Choosing $\mathbf{q}$ to lie in the $z$-direction so that $p_q = p_z$, we can write eqn. 6.15 in the convenient form:

$$\frac{d^2\sigma}{d\Omega d\omega_2} = \frac{d\sigma}{d\Omega}_{TH}(m/hq) \int \int \rho(p_x, p_y, p_z = p_q) dp_x dp_y \int \psi(\mathbf{r}) \exp(-i\mathbf{r} \cdot \mathbf{p}/\hbar) d\mathbf{r}^2, \quad (6.17)$$

where we have introduced the so-called (directional) Compton profile

$$J(p_q) \equiv \int \int \rho(p_x, p_y, p_z = p_q) dp_x dp_y. \quad (6.18)$$
Let us consider scattering from a many-electron system. If we assume that the system is composed of independent particles described by single-particle wavefunctions $\psi_i(r_j)$, then, within the limits of the impulse approximation, each scattering process will involve only one particle of the system. We can then rewrite eqn. 6.16 for the momentum density by summing over all occupied single-electron states of the system,

$$
\rho(p) = (1/2\pi\hbar)^3 = \sum_{occ} |\chi(p)|^2
= (1/2\pi\hbar)^3 \sum_{occ} \left| \int \psi_i(r) \exp(-i\mathbf{p} \cdot \mathbf{r}/\hbar) d^3r \right|^2.
$$

Therefore, a system of independent bound electrons, investigated by inelastic X-ray scattering under the conditions of the impulse approximation, is considered to consist of free particles with a certain momentum distribution, where both energy and momentum are conserved during the collision. The momentum density for any particular momentum in this free-electron system is obtained from the square of the Fourier transform of its single-particle wavefunction. Kaplan et al. have shown that in the high-energy transfer regime one can recover from a general formalism the standard impulse approximation based formula for the cross section [75]. The Compton profile is strictly symmetric in $p_z$ within the impulse approximation, but the experiments (e.g. on low-Z targets) clearly show appreciable deviations from this picture [76]. The peak of the atomic Compton profile is shifted in the $h\omega_2$-scale (the direction of the shift depends on which is the outermost electron shell) and the profiles are clearly asymmetric. Among the several schemes to explain these Compton defects the most widely used approaches are the operator series-expansion
methods but this will not be discussed in the present work [77].

6.3 Momentum Density and Band Structure

We will discuss the momentum density computations based on band theory. In the valence electron system of a crystalline solid, the electron charge density distribution function \( \rho(\mathbf{r}) \) in the real \( \mathbf{r} \)-space is given by:

\[
\rho(\mathbf{r}) = 2 \sum_{n,k} |\psi_{nk}(\mathbf{r})|^2
\]  

(6.20)

where \( \psi_{nk} \) is the Bloch wavefunction of an electron with wave vector \( \mathbf{k} \) in the \( n \)th energy band and the summations on \( n \) and \( k \) should be taken over all occupied electronic states. Here, the solid is supposed to be nonmagnetic, so that the spin summation gives only the factor of 2 in eqn. 6.20. On the other hand, since the momentum density distribution function \( \rho(\mathbf{p}) \) for the valence electron system is the electron density in the momentum \( \mathbf{p} \)-space described by the Fourier-transformed wavefunction.

\[
\psi_{nk} = \frac{1}{\sqrt{\tau}} \int \psi_{nk}(\mathbf{r}) \exp(-i\mathbf{p} \cdot \mathbf{r}) d^3\mathbf{r},
\]

(6.21)

it is given by:

\[
\rho(\mathbf{p}) = 2 \sum_{n,k} |\psi_{nk}(\mathbf{p})|^2 = \sum_{n,k} \left| \int \psi_{nk}(\mathbf{r}) \times \exp(-i\mathbf{p} \cdot \mathbf{r}) \frac{d^3\mathbf{r}}{\sqrt{\tau}} \right|^2
\]

(6.22)

where \( \tau \) is the unit cell volume of the solid. The electrons distribute in the crystal according to the electronic potential field and distribute in momentum space according to their energy dispersion structure.

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6.3.1 KKR formalism for the Momentum density

There are several methods to calculate the band structure, and in this work we discuss two of them, namely the LAPW and KKR. For momentum density, we shall tie ourselves to the framework of the KKR method, and consider a compound with more than one atom per unit cell. By inserting eqns. 5.27 and 5.28 into eqn. 5.36, we get

\[ \psi_{n,k}(\mathbf{r}) = \frac{4\pi}{\tau} \sum_{n,k} \sum_{\ell} \exp[i \mathbf{k}_n \cdot (\mathbf{r} - \mathbf{b}_\ell)] \sum_L \mathcal{C}_{L\mu} S_{L\ell}(\mathbf{k}_n, E) \cdot \frac{E - |\mathbf{k}_n|^2}{E - |\mathbf{k}_n|^2} \sum_{LL'} C_{L\mu}^* \tilde{C}_{L'}^{\mu} \mathcal{S}_{L\ell}(\mathbf{k}_n, E). \] (6.23)

Here, \( L \) is \((lm)\) and the \( C_L \) are coefficients of expansion as in eqn. 5.36, and the summation with respect to \( \mu \) runs over all atoms at positions \( \mathbf{b}_\mu \) in the unit cell. The \( S_{L\mu} \) are fourier transforms of \( R_{\mu} \) given by:

\[ S_{L\mu}(\mathbf{p}, E) = -\kappa \cot(\eta_\mu) Y_L(\mathbf{p}) \int_0^{R_{MT\mu}} j_l(p r_{MT\mu}) V_\mu(r) R_{\mu}(r, E) r^2 dr. \] (6.24)

If the wavefunctions are used to calculate observables such as momentum density, they must be properly normalized. The normalization of the wave function belonging to the eigenvalue \( E_j \) is given by [78]

\[ \int_{\tau} |\psi(\mathbf{r})|^2 d^3 \mathbf{r} = \frac{d\Lambda}{dE} \bigg|_{E=E_j} \] (6.25)

and hence

\[ \int_{\tau} |\psi(\mathbf{r})|^2 d^3 \mathbf{r} = N \int_{\tau} |\psi(\mathbf{r})|^2 d^3 \mathbf{r} = -\tau^{-1} \sum_{LL'} \sum_{\mu\nu} \tilde{C}_{L\mu}^* \tilde{M}_{L\ell L'}^{\mu\nu} \tilde{C}_{L'}. \] (6.26)
Here, $C_L = (\kappa \cot(\eta_l))^{-1}C_L$, $\eta_l$ is the phase shift, $N$ is the number of unit cells per unit volume, and $\dot{M} \equiv \frac{dM}{dE}$ is the energy derivative of the matrix $M$ evaluated at $E = E_j$. It is straightforward to derive the expression for the momentum density by plugging eqn. 6.23 into eqn. 6.22 and using eqn. 6.26 for the normalization. One finds [79]

$$\rho(p) = \frac{(4\pi)^2}{\tau} \sum_j \left( \frac{f(E)}{(E - p^2)^2} \times \left| \sum_\mu \exp[-i\mathbf{p} \cdot \mathbf{b}_\mu] \sum_L C_L^{\mu}(\mathbf{k}) S_{L\mu}(\mathbf{p}, E) \right|^2 \right) \sum_{LL'} \sum_{\mu \nu} C_{L\mu}^{\nu} \dot{M}_{LL'}^{\mu \nu} C_{L'}^{L}.$$ \hspace{1cm} (6.27)

The distribution function $\rho(p)$ represents the probability density in momentum space or momentum density of the electrons in the solid. This quantity is measurable by means of a Compton scattering experiment as discussed here and in other works [72].
Chapter 7

Positron Annihilation

7.1 Introduction

One of the important methods for investigating the electronic structure of solids is angular correlation of positron annihilation radiation (2D-ACAR). When a high energy positron emitted by radioactive source enters a solid, it is rapidly slowed down in a time of the order of a picosecond by atomic ionization, electron-positron collisions, and finally the electron-positron interaction. After thermalization the positron is in a delocalized Bloch state in its own conduction band. In this work, the DFT has been employed to the calculation of gamma spectra of positron annihilation. The KKR formalism is employed to obtain a formula for momentum density in a perfect crystal in muffin-tin potential. The multi-atom unit cell is considered. Experimentally, the three-dimensional electron-positron momentum distribution is reconstructed from measurements of the two-dimensional angular correlation of (2D-ACAR).
7.2 The annihilation process and momentum density

The main purpose here is to develop a many-body theory approach to the calculation of the gamma-spectra from positron-electron annihilation. Due to the conservation of momentum, annihilation of an electron-positron pair must lead to the emission of at least two photons. When this process occurs in an external field, e.g., when the electron is bound to an atom, annihilation into a single photon is also possible. However, its probability is small [80]. According to quantum electrodynamics (QED), annihilation into two photons is possible only if the total spin $S$ of the pair is zero [81]. For $S = 0$ annihilation into 2, 4, \ldots photons is possible, while for $S = 1$ the number of photons must be odd (3, 5, \ldots). In both cases the process with the smallest number of photons has a higher probability to occur.

We limit the discussion to the two-photon mode of decay, since it, in principle, contains all the information so far obtained from the physical systems, lifetime and angular correlation. In QED the process of electron–positron annihilation is described by the second- or third order diagram, depending on the number of photons emitted [81]. The photons carry away the energy of the particles, $\sim 2mc^2$, and have large momenta $\sim mc$, where $m$ is the electron mass, and $c$ is the speed of light. In positron annihilation with matter, even if the initial positron is fast, it quickly loses energy due to inelastic ionizing collisions, and most of the annihilation events involve slow positrons. As a result, the annihilation amplitude is independent of the electron and positron momenta. Hence most positrons in condensed matter annihilate with the emission of two $\gamma$-photons. In the center of mass frame of reference the two photons are emitted in opposite directions and carry off the total
energy of the electron-positron pair; in the laboratory frame the momentum of the particle pair results in a small deviation from collinearity of the two photons. The angular correlation between the photons, measured in a 2D ACAR experiment, is essentially the two-dimensional projection of the momentum density distribution $\rho^{2\gamma}(p)$ of the photon pairs

$$N(p_y, p_z) = \text{const.} \int_{-\infty}^{\infty} \rho^{2\gamma}(p) dp_z. \quad (7.1)$$

The matrix element for the transition for the slow electrons and positrons in which we shall be interested is to a good approximation independent of the initial momentum. Therefore, the part of the second order Hamiltonian that produces the two $\gamma$-photon final state of total momentum $\hbar p$ is proportional to

$$H' = \sum_{p_1} \sum_{p_2} \hat{a}_{p_1} \hat{b}_{p_2} \delta_{p_1+p_2,p} \quad (7.2)$$

where $\hat{a}_{p_1}$ and $\hat{b}_{p_2}$ are the destruction operators of the electron and positron respectively with momentum $p_1$ and $p_2$, and the $\delta$-function ensures momentum conservation, $p = p_1 + p_2$ [82]. Using electron and positron creation (destruction) field operators $\hat{\psi}_+(x_1)$ and $\hat{\psi}_-(x_2)$ in the coordinate representation one can define

$$\hat{a}(p_1) = \frac{1}{\sqrt{V}} \int \exp[-ip_1 \cdot x_1] \psi_-(x_1),$$

$$\hat{b}(p_2) = \frac{1}{\sqrt{V}} \int \exp[-ip_2 \cdot x_2] \psi_+(x_2), \quad (7.3)$$

where $V$ is the quantization volume [83]. Substituting into eqn. 7.2 and simplifying, one obtains

$$H'(p) = \int \exp[-ip \cdot x] \psi_-(x) \psi_+(x) d^3x. \quad (7.4)$$
The probability for annihilation with emission of two photons with total momentum $\mathbf{p}$ from an initial state $|i\rangle$ consisting of the one positron $n$ electron system (including Coulomb interactions) to final state $|f\rangle$ consisting of $n-1$ electrons and two photons is then given by

$$
\rho_f^{2\gamma}(\mathbf{p}) = \text{const.} \left| <f| \int \exp[-i\mathbf{p} \cdot \mathbf{x}]\psi_-(\mathbf{x})\psi_+(\mathbf{x})d\mathbf{x}|i\rangle \right|^2.
$$

(7.5)

If the final state is not measured, as is the case in an ACAR experiment, one obtains the total annihilation probability by summing over all final states by closure:

$$
\rho^{2\gamma}(\mathbf{p}) = \sum \rho_f^{2\gamma} = \text{const.} \left| <i| \int \exp[-i\mathbf{p} \cdot \mathbf{x}]\psi_-(\mathbf{x})\psi_+(\mathbf{x})|i\rangle \right|^2 d\mathbf{x}.
$$

(7.6)

The reduction of the annihilation process in an $n$-electron system, described by Slater determinant, to a one-electron problem is equivalent to neglecting the possibility that one annihilation of an electron from a specific state is followed by filling the annihilated electron state by the transition of another electron into this state; in other words, the wavefunction of the system is not allowed to change in the annihilation process which is similar is to Compton scattering. Hence, in this approximation, the annihilation probability of a specific electron and a positron into pair of photons with total momentum $\mathbf{p}$ can shown to be given by

$$
\rho^{2\gamma}(\mathbf{p}) = \text{const.} \left| \int \exp[-i\mathbf{p} \cdot \mathbf{r}]\psi_-(\mathbf{r})\psi_+(\mathbf{r}) \right|^2.
$$

(7.7)

We have ignored correlation effects*, and this is usually referred to as the

---

*The positron-electron interaction requires the two particle wavefunction to be written as $\psi_-(\mathbf{x})\psi_+(\mathbf{x})\sqrt{\gamma_1(\mathbf{r})}$, where $\sqrt{\gamma_1(\mathbf{r})}$ is the enhancement factor [84]. It is important when we consider the positron lifetime.
independent-particle model. The total annihilation probability is found by sum-
ing eqn. 7.7 over all occupied electron states [83],

$$\rho^{\gamma\gamma}(p) = \text{const.} \sum_{\text{occ}} \left| \int \exp[-i p \cdot r] \psi_-(r) \psi_+(r) \right|^2.$$  \hspace{1cm} (7.8)

This equation forms the starting point for independent-particle model calculations and it is similar to the electron momentum density relations eqn. 6.27. It is now straightforward to derive the formula for the electron-positron momentum density \(\rho^{\gamma\gamma}(p)\) relevant for two-photon annihilation [83]:

$$\rho^{\gamma\gamma}(p) = \frac{(4\pi)^4}{\pi^2} \sum_{k_+} f_+(E_+) \sum_j f(E) \times \left| \sum_n \sum_{\mu} \exp[-i(p - k_+ - K_n) \cdot b_\mu] \sum_L \overline{C}_{L\mu}(k) \frac{S_{L\mu}(p - k_+ - K_n, E)}{E - |p - k_+ - K_n|^2} \times \sum_{\nu} \exp[-i(k_+ + K_n) \cdot b_\nu] \sum_{L'} \frac{S_{L'\nu}^+(k_+ + K_n, E)}{E_+ - |k_+ + K_n|^2} \times (\sum_{LL'} \sum_{\mu\nu} \overline{C}_{LL'}^\mu(k) \overline{M}_{LL'}^{\mu\nu}(k) \sum_{L'} \sum_{\sigma\tau} \overline{C}_{L\sigma}(k_+) \overline{M}_{L\sigma}^{+\sigma\tau}(k_+))^{-1} |_{E=E_+}. \right.$$  \hspace{1cm} (7.9)

In this formula all positron related quantities have been distinguished by the superscript +, and \(f_+\) represents the Maxwell-Boltzmann distribution for the low density positron state. The expression looks like a convolution in momentum space. Despite the fact that the convergence of the summation over all reciprocal vectors \(K_n\) of the electron wavefunction is slow, the plane-wave expansion of the positron wavefunction converges relatively rapidly, and then limits the number of reciprocal vectors in the summation. On the other hand, eqn. 7.9 allows inclusion of terms with \(l > 0\) into \(e^+\) wavefunction, which is of importance in crystal structures of low symmetry. Hence, one is not limited to the assumption of a spherically symmetric
positron wavefunction inside the muffin-tin sphere [83].
Chapter 8

LSCO*

8.1 Introduction

Since their discovery over two decades ago, high temperature cuprate superconductors have continued to be the subject of intense research activity.[85, 86] The parent undoped compounds in these fascinating materials are antiferromagnetic (AFM) insulators with complex phase diagrams in which the addition of electrons or holes yields a metallic state with high superconducting transition temperatures. The pathways by which the strongly correlated insulating state, i.e. the Mott insulator, turns itself into a superconductor are of fundamental interest in unraveling the mechanism of high-temperature superconductivity, but details of these pathways are not well understood.[87, 88] The search for answers is complicated by the presence of inhomogeneities such as stripes and charge density waves [89] in the underdoped

*This chapter is adapted from the paper: Study of bulk Fermi surface and momentum density in heavily doped La_{2-x}Sr_xCuO_4 (x=0.3) using high resolution Compton scattering and positron annihilation spectroscopies, by W. Al-Sawai, Y. Sakurai, M. Itou, B. Barbiellini, P. E. Mijnarends, R. S. Markiewicz, S. Kaprzyk, S. Wakimoto, M. Fujita, S. Basak, H. Lin, H. Schut, K. Yamada, and A. Bansil. In preparation to be submitted to PRB.
system and possible clustering of dopants in the overdoped regime [90].

Insight into the evolution of electronic states can be obtained via Fermi surface (FS) measurements, which can establish first the possible existence of the FS, and when it is found to exist, determine the size and shape of the FS in various doping regimes. Experimental FS work on the cuprates has to date been limited mainly to angle-resolved photoemission (ARPES),[85, 86] quantum oscillations (QO)[91, 92, 93], and scanning tunneling spectroscopies (STS).[94] However, ARPES and STS are surface sensitive probes. While QO measurements probe the bulk, they provide only FS areas without giving information on the location of the FSs in the momentum space. Furthermore QO require long mean free paths, and large magnetic fields which could alter the ground state. For underdoped samples there is evidence of FSs strongly distorted from LDA predictions, involving arcs or pockets, but as doping is increased it appears that a large, LDA-like FS becomes manifest as the pseudogap collapses near optimal doping. For an overdoped Tl-cuprate, the FS has been found to be large and closed around \((\pi, \pi)\), suggesting that the Van Hove singularity still lies below the Fermi energy \(E_F^{}\) [95].

These considerations provide motivation for deploying genuinely bulk sensitive spectoscopies for FS measurements in the cuprates. Two such spectoscopies, which have been used extensively for this purpose, are high resolution Compton scattering and two-dimensional angular-correlation of positron annihilation radiation (2D-ACAR). Compton scattering probes the momentum density of the many-body electronic ground state of the system and is insensitive to the presence of defects or surfaces in the sample [96]. 2D-ACAR also probes the bulk momentum density, but its interpretation can be complicated by the positron spatial distribution effects.[97, 98, 99] On the other hand, the Compton scattering technique requires
large single crystals, and in materials involving atoms with high Z values, which is the case for all cuprates, it suffers from the problem of a relatively low signal from valence electrons sitting on the large background contribution from the core electrons.

In this context, the present work reports a study of the FS and electron momentum density (EMD) of an overdoped single crystal of La$_{2-x}$Sr$_x$CuO$_4$ (LSCO) for the hole doping level $x=0.3$. Compton scattering and 2D-ACAR experiments have been carried out on the same LSCO sample, and the results are analyzed through parallel computations of the FS, the EMD and the electron-positron momentum density within the framework of the density functional theory (DFT). The conventional picture of the metallic state based on the Landau Fermi liquid theory is expected to become increasingly viable with doping as the system becomes more weakly correlated, even though the physics of the cuprates is generally dominated by deviations from such a simple picture of the electronic states. For this reason, overdoped LSCO provides a good starting system for investigating the fermiology of the cuprates. [95, 100]. To our knowledge, this is the first attempt to study the FS of LSCO using high-resolution Compton scattering experiments. The 2D-ACAR experiments, on the other hand, have been deployed successfully by several groups in the past for delineating the FSs of the cuprates in a number of favorable cases [97].

Here, by measuring a series of high resolution Compton profiles, we have reconstructed the 2D momentum density in overdoped LSCO and identified a clear signature of the FS in the third Brillouin zone. Moreover, the DFT based theoretical EMD is found to be in quantitative accord with the Compton scattering results, indicating that the ground state wavefunction in the overdoped system is well-described
by the weakly correlated DFT picture. We have also found a quantitative level of agreement between the measured and computed 2D-ACAR spectra. However, the 2D-ACAR spectra do not reveal clear FS signatures due to the well-known positron spatial distribution effects, which can make the positron insensitive to electrons in the Cu-O planes.

Figure 8.1: Crystalline structure of representative hole-doped cuprates: La$_{2-x}$Sr$_x$CuO$_4$ (LSCO). We note the presence of CuO$_6$ octahedron. The figure is made by XCrysden program [37].
Figure 8.2: Energy bands for La$_2$CuO$_4$ along the high symmetry directions of the Brillouin zone, with $E_F$ taken as the zero of energy. These bands also apply to the hole-doped compound which contains fewer electrons by shifting the Fermi level down to accommodate the proper number of holes.

### 8.2 LSCO crystal structure

The compound La$_2$CuO$_4$ is body-centered tetragonal with space group $I4/mmm$ (139) and lattice parameters $a=3.7817$ Å and $c=13.2487$ Å as in Freeman et al. [101]. We show the crystal structure in Fig. 8.1. It consists of a repetition of the rock salt-type La$_2$O$_2$ block layer and the CuO$_2$ plane equally spaced with their oxygens stacked one above the other, the copper ions alternating between the (0,0,0) and (1/2,1/2,1/2) sites in adjacent planes. These planes are body-centered images of each other, and are perfectly flat because they are reflection planes. Half of the oxygens, O(1), are in the planes, and the other half, O(2), between the planes.
Copper is octahedrally coordinated with oxygen. The geometry of the Brillouin zone is somewhat complicated because the crystallographic structure is body centered.

8.3 LSCO Electronic Structure

The one-electron, paramagnetic, band calculations have been performed for LSCO. An all-electron fully charge-self-consistent semi-relativistic (KKR) method in combination with local density approximation functional have been employed to calculate the electronic structure for the undoped La$_2$CuO$_4$[102]. A non-spinpolarized calculation was performed and the magnetic structure was neglected. Self-consistency was obtained for $x = 0$ and the effect of doping $x$ was treated within a rigid band model by shifting the Fermi energy to accommodate the proper number of electrons. The results are reproduced in Fig. 8.2 along several high-symmetry lines in the Brillouin zone ($\Gamma \rightarrow X \rightarrow M \rightarrow \Gamma$) as shown in Fig. 8.3. An important note is that this compound contains an odd number of electrons in the unit cell, so a paramagnetic band structure must be metallic. The DOS shows that the five Cu $d$ states and the three O $p$ states for each of the four oxygen atoms form a complex of 14 hybridized $p - d$ valence bands. The total band width is 8 eV.
Figure 8.3: Symmetry lines in Berllouin zone for tetragonal structure starting form $\Gamma \to X \to M \to \Gamma$.

Figure 8.4: Total Density of state of LSCO. The blue (dashed-pink) line is the integration of total (spin up or down) DOS which is the number of electrons below a certain energy.
Figure 8.5: La Partial Density of states (PDOSs) of LSCO.

Figure 8.6: Cu PDOSs of LSCO.
Figure 8.7: $O_1$ PDOSs of LSCO.

Figure 8.8: $O_2$ PDOSs of LSCO.
Despite the complex nature of the valence bands, the band structure near $E_f$ is rather simple. A single band of anitbonding character crosses $E_f$, which is obtained by all methods of calculation [103]. The total and atom-projected densities of states (DOS) in Figs. 8.4, 8.6, 8.15 and 8.16 show that the centroid of Cu $d$ and O $p$ states are more or less coincident. Therefore the valence-band extreme, which occur occurs at the zone corner $X$ point, are directly related to the bonding and anitbonding combinations of Cu $d(x^2 - y^2)$ and O $p(x,y)$ orbitals.

A large hole Fermi surface is centered at $X$. This clearly indicates the formation of a metal. However this undoped compound is, experimentally, an antiferromagnetic insulator. This is indeed a demonstration of the failure of the ordinary band theory even though the electron-electron interaction is taken into account at some level through the use of the LDA. The electron-correlation in LSCO plays an important role in its electronic properties. Thus we may say that undoped cuprates are governed by Mott physics. In the undoped parent compound, the electronic states of the Cu on the plane are in the $d^{9}$ configuration.

If the electron-electron interaction is neglected, the hybridization of these three orbitals gives rise to the bonding, non-bonding and half-filled anti-bonding bands and predicts a good metal, in contrast to the large gap observed in the undoped compounds. The failure of the band theory, and hence that of the conventional Fermi liquid approach to high $T_c$ problem, stems from the existence of a large on-site Coulomb interaction that well exceeds the bandwidth of the tight-binding anti-bonding band. If a charge carrier were to hop onto a partially filled Cu $d_{x^2-y^2}$ orbital, the two Cu $d_{x^2-y^2}$ carriers would experience a large energy penalty, and, hence, it is energetically more favorable to localize the electrons. Electronic systems with half-filled states and strong localization are known as Mott insulators. The strong
on-site Coulomb repulsion suppresses charge fluctuations, splits the half-filled anti-bonding band into an empty upper-Hubbard band and a filled lower-Hubbard band, thereby turning a band metal into a Mott insulator with an optical gap of a few $eV$. However, upon doping LSCO undergoes phase transition to several phases [85]. In the following section will discuss the behavior of LSCO with doping.

8.4 Phase Diagram

In the specific case of La$_2$SrCuO$_4$ (LSCO), the subject of this study, the CuO$_2$ plane per cell is charged to -2, since Cu and O atoms are ionized to +2 and -2, respectively. Substituting Sr for La has the effect of changing the electron content of the unit cell through the addition of holes; this lowers the Fermi level strongly affects the superconducting properties. The phase diagram of Fig. 8.17 illustrates the resulting behavior as a function of the hole-doping parameter $p \sim x$. At half filling LSCO is an AFM insulator. When holes are doped into the CuO$_2$ planes, the Neel temperature of the system decreases rapidly. The long-range coherent AFM order disappears completely around $x = 0.02$ and is replaced by a ‘pseudogap’ phase, and superconductivity sets in at $x \sim 0.05$ and lasts up to $x \sim 0.25$. Near optimal doping, the pseudogap phase changes into an anomalous non-Fermi liquid regime. With further doping, the more conventional Fermi-liquid physics seems eventually to be recovered [104, 90, 85, 105]. The pattern seen with LSCO is repeated with essentially every cuprate superconductor.
Figure 8.9: Schematic phase diagram of superconductor as a function of doping $p$. The Mott insulator at $p = 0$ shows antiferromagnetic order below $T_N$ which vanishes rapidly with doping. At high doping, the metallic state shows all signs of a conventional Fermi liquid [104].

8.5 Experiments

The heavily overdoped single crystal ($x = 0.30$) was grown by the traveling solvent floating method. For this purpose, a powder sample was first synthesized by the conventional solid state reaction method. It was then shaped into feed rods under hydrostatic pressure and sintered at 1173 K for 12 hours, and at 1423 K for an additional 10 hours. In this process, excess CuO of 2 mol% was added to the feed rods to compensate for the evaporation of CuO during the high temperature process. The grown crystal was subsequently annealed under an oxygen pressure of 3 atm at 1173 K for 100 hours. SQUID measurements showed no superconductivity
down to 2 K. Neutron diffraction studies indicated that the crystal is tetragonal (I4/mmm) down to the lowest temperature.

We have measured 10 Compton profiles with scattering vectors equally spaced between the [100] and [110] directions using the Cauchois-type X-ray spectrometer at the BL08W beamline of SPring-8 [106, 107, 108, 109]. All measurements were carried out at room temperature. The overall momentum resolution is estimated to be 0.13 a.u. full-width-at-half-maximum (FWHM). The incident X-ray energy was 115 keV and the scattering angle was 165°. Approximately $5 \times 10^5$ counts in total were collected at the Compton peak channel, and two independent measurements were performed in order to check the results. Each Compton profile was corrected for absorption, analyzer and detector efficiencies, scattering cross section, possible double scattering contributions and X-ray background. The core-electron contributions were subtracted from each Compton profile. A two-dimensional momentum density, representing a projection of the three-dimensional momentum density onto the (ab)-plane, was reconstructed from each set of ten Compton profiles using the direct Fourier transform method [110].

The 2D-ACAR was measured using the Delft University 2D-ACAR spectrometer [111] with a conventional $^{22}$Na positron source. The data were taken at a temperature of about $T=70$K. To correct for the sample shape ($5.7 \times 3.5 \times 4.5$ mm$^3$) the data were convoluted with a gaussian of FWHM of 0.1 channel in the $x$ direction and 1.7 channels in the $y$ direction, where 1 channel corresponds to 0.184 mrad. The total resolution is $1.0 \times 1.0$ mrad$^2$ FWHM (1 mrad = 0.137 a.u.). The total number of coincidences collected is $76.3 \times 10^6$ and the maximum number of coincidences is $16.7 \times 10^3$ counts.


8.6 Calculations

Our electronic structure calculations are based on LDA within the framework of the DFT. An all-electron fully charge-self-consistent semi-relativistic KKR methodology was used [102]. A non-spinpolarized calculation neglecting the magnetic structure was performed. Self-consistency was obtained for $x = 0$ and the effect of doping $x$ was treated within a rigid band model by shifting the Fermi energy to accommodate the proper number of electrons. The formalism for computing momentum density, $\rho(p)$, has been discussed in Chapter 5 in eqns. 6.21-6.23 and in Refs. [112, 113, 114, 115, 116]. In the $\rho^{2d}(p)$ calculation, we have neglected the enhancement factor for the annihilation rate [117, 118]. The inclusion of enhancement effects is crucial for the calculation of lifetimes but is well-known to be not too important for discussing questions of bonding and FS signals in momentum density. The momentum densities are calculated on a momentum mesh with step $(\delta p_x, \delta p_y, \delta p_z) = 2\pi(1/32a, 1/32a, 1/4c)$. The calculations were done for the undistorted body-centered tetragonal lattice, and include contributions from both the filled valence bands and the conduction-band which gives rise to the FS in LSCO. To study the electronic structure of the system, we consider two quantities of interest: 2D-EMD and 1D-EMD which are the projection of EMD in 2D and 1D respectively and given by:

\[
\rho^{2d}(p_y, p_z) = \int \rho(p) dp_x
\]

(8.1)

and

\[
\rho^{1d}(p_z) = \int \int \rho(p) dp_x dp_y.
\]

(8.2)

Positron annihilation and Compton scattering both probe all the electrons in the system, but the core and semi-core electrons give inertially isotropic distributions
8.7 Momentum Density Anisotropy

We start our discussion of the EMD by comparing the experimental and theoretical 1D-EMD for Compton scattering and ACAR calculated by eqn. 8.2. Fig. 8.10 shows that these two quantities are in reasonable quantitative agreement with experiment. However we are mainly interested in the conduction band contribution. Therefore, in order to facilitate comparison between experiment and theory, we

\[ A^{2d}_{C_{4v}}(p_y, p_z) = \rho(p_y, p_z) - \rho\left(\frac{(p_y + p_z)}{\sqrt{2}}, \frac{(p_y - p_z)}{\sqrt{2}}\right). \]  

(8.3)

\[ C_{4v} \] is the Schoenflies notation for a group containing a \( \sigma_v \) reflection in addition to \( C_4 \), a single 4-fold axis symmetry. See e.g. M. Tinkham, *Group Theory and Quantum Mechanics*, (McGraw-Hill, 1964)
analyze experimental as well as theoretical distributions using the $C_{4v}$ anisotropy plots defined by eqn. 8.3. $C_{4v}$ anisotropy distributions for positron annihilation and Compton scattering spectra are shown in Fig. 8.11 and Fig. 8.12 respectively. Our ACAR measurements are in reasonable accord with earlier studies [98, 99]. Fig. 8.11 (a) reveals a highly anisotropic covalency structure which can be modeled by a simple molecular orbital method [119] involving the overlap of the positron wavefunction with Cu $3d$ states hybridized with O $p$ states. The Compton scattering anisotropy map in Fig. 8.12 (a) is very similar overall, but it is seen to extend to significantly higher momenta as expected since in the ACAR case the tendency of the positron to avoid positively charged ionic cores in the solid has the effect of suppressing higher momentum components of the EMD.

Figs. 8.11 (b) and 8.12 (b) show that theoretical calculations reproduce all of the major features of the measured Compton as well as positron-annihilation distributions including the momenta at which the dominant high and low amplitude
features are found. The fourfold symmetry of the computed and measured spectra is a consequence of the body-centered tetragonal symmetry. To examine the spectra more closely, we consider the 1D-projection of the anisotropy of Eq. 8.3 as:

$$A^{1d}(p_z) = \frac{1}{\Delta p_y} \int_{p_{y_i}}^{p_{y_f}} A^{2d}_{C_{4v}}(p_y, p_z) dp_y,$$  \hspace{1cm} (8.4)

where the integral represents an average over one of the momentum components, and $\Delta p_y = p_{y_f} - p_{y_i}$ is the difference between the integration limits or the momentum range in which the average is taken. The results are shown in Fig. 8.13 (a) for ACAR and Fig. 8.13 (b) for the Compton spectra. In both cases, the agreement between theory and experiment is quite remarkable in that the theory reproduces not only the positions of various dips and peaks in the measured anisotropic spectrum, but that this agreement also extends to the amplitudes of these features, despite some

\[^{\dagger}\text{The limits of integration for experimental Compton spectra are defined in the interval } p \in [-2.5, 2.5] \text{ a.u., all others in the interval } p \in [-3, 3] \text{ a.u.}\]
Figure 8.13: Theoretical and experimental $A^{1d}(p_z)$ for (a) ACAR and (b) EMD for $x=0.3$ LSCO.

discrepancies – particularly for the Compton results in Fig. 8.13 (b). We emphasize that this result is in sharp contrast to the earlier positron studies on the cuprates and the Compton studies in complex materials such as the manganites and magnetite where the amplitudes of the LDA-based computed anisotropies are usually found to differ substantially from experiments, an effect attributed to the shortcomings of the LDA in describing electronic correlations. The good agreement seen in Fig. 8.13 suggests that correlation effects in highly overdoped LSCO may be weak.

### 8.8 Positron Wavefunction

For the understanding of the electron-positron momentum density distributions, insight into the way the positron samples the unit cell is important. Knowing the parts of the unit cell which are most probably visited by the positron, one can determine whether or not positron annihilation spectroscopy will be sensitive to the properties of the electrons associated with specific atoms in the cell. Since the positron has a positive charge, it is pushed away by the atomic cores. Hence its
distribution is mostly governed by the available free volume. Such a behavior can
be seen in Fig. 8.14 where the positron apparently avoids the Cu-O planes and stays
longer in La-O planes.

### 8.9 Fermi surface results

We comment briefly on the positron results first. Although the electron-positron
momentum density measured in a positron-annihilation experiment contains FS
signatures, the amplitude of such signatures is controlled by the extent to which
the positron wavefunction overlaps with the states at the Fermi energy. Fig. 8.6
shows that the positron density in the Cu-O planes is fairly small so that this factor
is not favorable in LSCO. Moreover, positron-annihilation favors FSs involving s or p
states because the positron wavefunction generally overlaps more with such extended
states compared to the more tightly bound orbitals of higher l values.[120] Indeed,
we see little evidence of FS signatures in either the computed or the measured ACAR
distributions of Fig. 8.4 (a). A more favorable case for the 2D-ACAR distribution
is provided by the YBa$_2$Cu$_3$O$_7$ cuprate superconductor, where the 1-dimensional
ridge FS has a two-fold symmetry which distinguishes it from important four-fold
symmetry wave function effects [121, 122].

The Lock-Crisp-West (LCW) theorem can be used to study the non isotopic
features of the momentum density by folding the data into a single central Brillouin
zone. This technique can enhance FS discontinuities (‘breaks’) by coherently su-
perposing the umklapp terms [98]. However, the LCW folding can also artificially
enhance errors in the experimental data.

To more clearly expose structure in the data, a radially isotropic and smooth dis-
tribution was subtracted. Here we are considering the cylindrical average anisotropy,

$$A^{2d}(p_y, p_z) = \rho(p_y, p_z) - S \left( \sqrt{p_x^2 + p_y^2} \right), \quad (8.5)$$

where $S$ is a smoothed cylindrical average of $\rho$, in which the original spectrum is
averaged over rotation angles from $0^\circ$ to $45^\circ$ in steps of $1^\circ$. Since the subtracted
function is smooth this procedure does not contribute to, nor create, new structures
in the data remaining after subtraction.

Fig. 8.15 (a) shows the cylindrical anisotropy of the theoretical spectrum. The
momentum density is plotted in the extended zone scheme. Because the FS is
periodic, a complete FS in each Brillouin zone must exist, but with its intensity
modulated by matrix element (ME) effects. For a predominantly $d$-wave FS, these
MEs will strongly suppress spectral weight near $\Gamma$, so the FS breaks are most clearly
seen in higher Brillouin zones. These FS breaks appear superimposed on the mo-
Figure 8.15: (color online) Top: Cylindrical anisotropy for theoretical Compton scattering momentum density. The white lines define the Brillouin zones, while blue squares indicate a family of zones where the FS features are particularly strong. (b) Bottom: The blue squared regions are isolated from the rest of the spectra and folded back to the central region.

momentum density in the form of discontinuities which can occur in any Brillouin zone. In Fig. 8.15 (a), the Fermi breaks are the regions where the contours run closely together. This means that the electron momentum density varies rapidly at these locations. Fig. 8.15 (a) shows the calculated Fermi breaks in several Brillouin zones. In particular, in the 3rd zones framed with blue squares, the arc-like features are theoretically predicted FS associated with Cu-O planes. Due to the BCT symmetry, a rotation of the spectrum by $\pi/2$ will generate symmetry-related regions (blue squares) with equivalent strong FS features. These regions are isolated
in Fig. 8.15 (b). By forming a ‘limited LCW folding’, that is, folding only these regions back in the first Brillouin zone, we produce a “full” FS, with the strong MEs removed. The resulting FS map is shown in the center of Fig. 8.15 (b), and again on a larger scale in Fig. 8.16 (a). Applying the same procedure on other Brillouin zone regions produces similar results. For instance, the four regions along the diagonal neighboring the central region can also yield full FS information, but here it is superimposed on strong momentum density features. To minimize experimental error when we compare experiment and theory, we will apply the restricted LCW folding to only four squares (regions) at a time. Here the central region corresponds to a weight of unity (fully occupied) and the outer regions to zero (unoccupied). The sets of contours along the $x$- and $y$- directions of the FS are due to partial occupancy associated with interlayer coupling – i.e., dispersion in the direction perpendicular to the layers. In Fig. 8.16 we compare the ‘restricted LCW’ FS to experiment. Fig. 8.16 (a) shows that the restricted backfolding procedure has restored the FS with the correct size and topology. The same procedure has been carried out on the experimental spectrum, i.e. the folding back of the corresponding Brillouin zone in the experiment spectra to the first Brillouin zone as shown in Fig. 8.16 (d).

To compare with theory, we have convoluted the data in Fig. 8.16(a) with 0.07 a.u and 0.15 a.u† experimental resolutions, leading to the spectrum of Fig. 8.16 (b) and (c) respectively -the latter is the actual experimental resolution used in this work-. By comparing the four frames in Fig. 8.16 we find a good agreement between the theoretical prediction and experimental results. The data in the regions of densely-spaced contours (along the edges in Fig. 8.16 (c)) are consistent with the hypothesis of an underlying discontinuity in momentum space, i.e., Fermi surface, when ac-

---

†0.15 a.u is the actual experimental resolution, 0.07 a.u shows how the enhancement of the resolution by ‘almost’ a factor of 2 can provide a sharper features of the FS.
counting for the instrumental resolution. This confirms that a large FS exists in the bulk of this material.

To further investigate the effect of the experimental resolution on the FS, cuts have been taken in the nodal direction from Fig. 8.16 [a-d] and plotted in Fig. 8.17. The discontinuity associated with the FS in the theory is smeared as we add the experimental resolution of 0.07 and 0.15 a.u. However, the FS break is still visible. Based in our analysis, the enhancement of the experimental resolution by a factor of 2, can largely improve the sharpness of the FS features as we can see in Fig. 8.16 (b) and Fig. 8.17. Some additional smearing effects of the FS could be signatures of [intrinsic or extrinsic] inhomogeneity effects (such as the appearance of local ferromagnetic clusters about concentrated regions of dopant atoms [90]) which have been neglected in the present simulations. Our conclusion based on Fig. 8.16 [a-d] is that the FS is closed at \( x = 0.30 \) in agreement with surface-sensitive ARPES results[123].
Figure 8.16: Top: (a) Back folding of the 3rd Brillouin zone, the region in the center of Fig. 8.15; (b) Theory convoluted with simulated resolution of 0.07. Bottom: (c) Theory convoluted with experimental resolution of 0.15; (d) experiment.

Figure 8.17: Cuts through distributions in Fig. 8.16 [a-d] along the nodal direction, compared to an unbroadened theoretical cut. The amplitudes of theory and experiment are compared on the same scale.
Chapter 9

Conclusions

DFT has proven to be an accurate and reliable basis for the understanding and prediction of a wide range of materials properties from the first principles of quantum mechanics (ab initio), without any experimental input. We have employed the DFT to study the topological insulator state for a series of half-Heusler compounds and the momentum density for overdoped cuprate LSCO. The agreement between DFT calculations and experimental results provide an insight about the power of DFT and its limitations.

In this thesis, we have applied the LAPW method to compute the band structures of 28 THH compounds listed in Table 4.1. The calculations have been performed within the GGA and MBJLDA exchange-correlation functional for the purpose of delineating their topologically interesting behavior. Six compounds of Fig. 4.5 are found to be topologically nontrivial with a zero band gap, 2 compounds of Fig. 4.6 are nontrivial with small electron pockets, and 20 compounds of Fig. 4.7 are trivial band insulators. We introduce the quantities $BIS$, $\Delta$, and $t=(Z_{M'} + Z_X)V$, and show that the 28 THH compounds naturally divide into seven subgroups in
terms of $\Delta$ and $t$, characterized by the binary unit $M'X$. Based on our analysis, we suggest that $\Delta$ and $t$ may prove to be useful measures more generally for identifying other topologically interesting non-magnetic half-Heusler compounds. The search for new materials that have topological order is an important area of research. While in this study we focus on non-magnetic 18-electron configuration, a future work may include the magnetic compounds.

We also present theoretical calculations and experimental measurements of positron annihilation and Compton scattering. Theoretical calculations have been performed by using the KKR method within the LDA. The quantitative agreement between the calculations and the experiment for both ACAR and EMD anisotropies suggests that overdoped LSCO recovers conventional Fermi-liquid physics at the doping $x = 0.3$. Nevertheless, the FS was only clearly observed by Compton scattering in the third Brillouin zone along [100] but with a different topology from that previously found in Tl-cuprates. While the FS topology is correctly predicted in both materials by LDA, the result suggests a complicated, material-dependent relationship between optimal doping and the Van Hove Singularity. The methodology and technique adapted in this work can be easily applied to other cuprates such as NCCO. If the DFT is successful in predicting the behaviour of the overdoped regime for other cuprates, this will highlight some outstanding and interesting issues in the field of high temperature superconductivity.
Chapter 10

Appendix

10.1 An atom in a magnetic field

Classically, if we view the electron spin as a vector, $\vec{\sigma}$, because it has direction, just as normal angular momentum does, then we would expect an associated magnetic moment

$$\vec{\mu}_s = g\mu_B \vec{\sigma}$$

(10.1)

The Hamiltonian for a spin $1/2$ system subjected to a magnetic field $\mathbf{B}$ is given by

$$H = \mu \vec{\sigma} \cdot \mathbf{B}$$

(10.2)

and the quantum mechanical Hamiltonian associated with that magnetic moment in the field $\mathbf{B}$ is given by

$$H_s = \frac{1}{2} g\mu_B \vec{\sigma} \cdot \mathbf{B}.$$  

(10.3)

From the theory of electromagnetism, the vector potential corresponding to a
uniform magnetic field may be written as \( \mathbf{A} = \frac{1}{2}(\mathbf{B} \times \mathbf{r}) \) since using the vector identity \( \vec{\nabla} \times (\mathbf{C} \times \mathbf{D}) = \mathbf{C}(\vec{\nabla} \cdot \mathbf{D}) - \mathbf{D}(\vec{\nabla} \cdot \mathbf{C}) + (\mathbf{D} \cdot \vec{\nabla})\mathbf{C} - (\mathbf{C} \cdot \vec{\nabla})\mathbf{D} \), then we have

\[
\vec{\nabla} \times \mathbf{A} = \frac{1}{2}[\mathbf{B}(\vec{\nabla} \cdot \mathbf{r}) - (\mathbf{B} \cdot \vec{\nabla})\mathbf{r}] = \frac{1}{2}[3\mathbf{B} - \mathbf{B}] = \mathbf{B}, \tag{10.4}
\]

where we have used \( \vec{\nabla} \cdot \mathbf{B} = 0 \), \( (\mathbf{r} \cdot \vec{\nabla})\mathbf{B} = 0 \), \( \vec{\nabla} \cdot \mathbf{r} = 3 \), \( (\mathbf{B} \cdot \vec{\nabla})\mathbf{r} = \mathbf{B} \). When the charge, with no magnetic moment (spin), is placed in a magnetic field \( \mathbf{B} \), its linear momentum becomes (canonical momentum) \( \mathbf{p} \rightarrow \mathbf{p} - (q/c\mathbf{A}) \), where \( c \) is the speed of light. The Hamiltonian of the particle is given by

\[
H = \frac{1}{2m}(\mathbf{p}^2 - \frac{q}{c}\mathbf{A})^2 + V = H_o - \frac{q}{2mc}(\mathbf{p} \cdot \mathbf{A} + \mathbf{A} \cdot \mathbf{p}) + \frac{q^2}{2mc^2}\mathbf{A}^2, \tag{10.5}
\]

where \( H_o = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}) \) is the Hamiltonian of the particle when the magnetic field \( \mathbf{B} \) is not present. The term \( \mathbf{p} \cdot \mathbf{A} \) can be calculated by analogy with the commutator \([\hat{\mathbf{p}}, \hat{\mathbf{F}}] = -i\hbar \frac{d\hat{\mathbf{F}}}{dx} \):

\[
(\mathbf{p} \cdot \mathbf{A})|\psi > = -i\hbar(\vec{\nabla} \cdot \mathbf{A})|\psi > -i\hbar(\mathbf{A} \cdot \vec{\nabla})|\psi > = -i\hbar(\vec{\nabla} \cdot \mathbf{A})|\psi > + (\mathbf{A} \cdot \mathbf{p})|\psi > . \tag{10.6}
\]

By using the Coulomb gauge \( \vec{\nabla} \cdot \mathbf{A} = 0 \), one can show

\[
\mathbf{p} \cdot \mathbf{A} - \mathbf{A} \cdot \mathbf{p} = -i\hbar(\vec{\nabla} \cdot \mathbf{A}) = 0. \tag{10.7}
\]

Since \( \mathbf{A} = \frac{1}{2}(\mathbf{B} \times \mathbf{r}) \), we have

\[
\mathbf{A} \cdot \mathbf{p} = \frac{1}{2}(\mathbf{B} \times \mathbf{r}) \cdot \mathbf{p} = \frac{1}{2}\mathbf{B} \cdot (\mathbf{r} \times \mathbf{p}) = \frac{1}{2}\mathbf{B} \cdot \mathbf{L} \tag{10.8}
\]
where $\mathbf{L}$ is the orbital angular momentum operator of the particle. Then one gets

$$H = H_o - \frac{q}{2mc}(\mathbf{L} \cdot \mathbf{B}) + \frac{q^2}{2mc^2}A^2. \quad (10.9)$$

### 10.2 Spin-orbit interaction

The Dirac equation for a particle with energy eigenvalue $E$ in the presence of a radial potential $V(r)$ is given by:

$$[E - \vec{\alpha} \cdot \mathbf{p} - \vec{\beta}m - V(r)]\vec{\psi}(r) = 0 \quad (10.10)$$

where $\vec{\alpha}$ and $\vec{\beta}$ are 4x4 matrices.

$$\vec{\alpha} = \begin{pmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{pmatrix}; \quad \vec{\beta} = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix} \quad (10.11)$$

and

$$\vec{\psi}(r) = \begin{pmatrix} \phi \\ \chi \end{pmatrix}$$

$$\begin{pmatrix} E - m - V & -\vec{\sigma} \cdot \mathbf{p} \\ -\vec{\sigma} \cdot \mathbf{p} & E + m - V \end{pmatrix} \begin{pmatrix} \phi \\ \chi \end{pmatrix} = 0 \quad (10.13)$$

$$(E - m - V)\phi - (\vec{\sigma} \cdot \mathbf{p})\chi = 0 \quad (10.14)$$

$$(-\vec{\sigma} \cdot \mathbf{p})\phi + (E + m - V)\chi = 0. \quad (10.15)$$

With $E - m = E_T$, $E_T$ is the kinetic energy. One can get easily from eqn. 10.15
the relation
\[ \chi = \frac{1}{(2m + E_T - V)} \mathbf{\sigma} \cdot \mathbf{p} \phi \] (10.16)

If we substitute into eqn. 10.14 we get:
\[ E_T\phi = -V\phi + \frac{(\mathbf{\sigma} \cdot \mathbf{p})(\mathbf{\sigma} \cdot \mathbf{p})}{E_T - V + 2m} \phi \] (10.17)

But
\[ \frac{1}{(2m + E_T - V)} \simeq \frac{1}{2m} \left[ 1 - \left( \frac{E_T - V}{2m} \right) \right] \]
\[ = \left[ \frac{1}{2m} - \left( \frac{E_T - V}{4m^2} \right) \right], \] (10.18)

substituting in eqn. 10.19 we get
\[ E_T\phi = -V\phi + (\mathbf{\sigma} \cdot \mathbf{p})(\mathbf{\sigma} \cdot \mathbf{p}) \left[ \frac{1}{2m} - \left( \frac{E_T - V}{4m^2} \right) \right] \phi \] (10.19)

Using the general result
\[ (\mathbf{\sigma} \cdot \mathbf{A})(\mathbf{\sigma} \cdot \mathbf{B}) = \mathbf{A} \cdot \mathbf{B} + i\mathbf{\sigma} \cdot (\mathbf{A} \times \mathbf{B}), \] (10.20)

we get the equation
\[ E_T\phi = \left[ V + \left( 1 - \frac{E_T - V}{2m} \right) \frac{p^2}{2m} \right] \phi - \frac{1}{4m^2}(\nabla V \cdot \nabla \phi) + \frac{1}{4m^2} \mathbf{\sigma} \cdot (\nabla V \times \mathbf{p} \phi) \] (10.21)
In the non-relativistic limit, \( E_T - V \approx \frac{p^2}{2m} \), and \( (E_T - V)p^2 \approx \frac{p^4}{2m} \), yielding

\[
E_T \phi = \left[ \frac{p^2}{2m} - \frac{p^4}{8m^2c^2} + V - \frac{\hbar^2}{4m^2c^2} \frac{\partial V}{\partial r} \frac{\partial}{\partial r} + \frac{1}{2m^2c^2} \frac{1}{r} \frac{\partial V}{\partial r} \frac{\mathbf{S} \cdot \mathbf{L}}{r} \right] \phi,
\]

where \( \mathbf{S} = \hbar/2\sigma \) is the spin and \( \mathbf{L} = \mathbf{r} \times \mathbf{p} \) is the angular momentum.

### 10.3 Effect of the time reversal operator on the Hamiltonian

We discuss the effect of time reversal operator \( \hat{K} = \sigma_y \hat{K}_o \) on the Hamiltonian \( H_k \). We have

\[
\hat{K} H_k \hat{K}^{-1} = \hat{K} \left[ \frac{(p + \hbar k)^2}{2m} + \frac{V(r)}{2} - \frac{(p + \hbar k)^4}{8m^3c^2} \right]
+ \frac{\hbar^2}{8m^2c^2} \nabla^2 V(r) + \frac{\hbar}{4m^2c^2} \left( \nabla V(r) \times (p + \hbar k) \right) \cdot \vec{\sigma} \hat{K}^{-1}.
\]

To simplify the discussion, we are going to study the effect of \( \hat{K} \) on each term separately from left to right. The first term will give rise to

\[
\hat{K} \left[ \frac{(p + \hbar k)^2}{2m} \right] \hat{K}^{-1} = \frac{2m}{2m} \left[ \frac{-p + \hbar k}{2m} \right] \left[ \frac{-p + \hbar k}{2m} \right] = (-1)^2 \left[ \frac{(p - \hbar k)^2}{2m} \right] = \left[ \frac{(p - \hbar k)^2}{2m} \right].
\]
Similarly, the third will give \( \frac{(p - \hbar k)^4}{8m^4c^2} . \) \( \hat{K} \) has no effect on \( V(r) \) nor \( \frac{\hbar^2}{8m^4c^2} \hat{\nabla}^2 V(r) \). The last term will produce

\[
\hat{K}[\frac{\hbar}{4m^2c^2}(\hat{\nabla} V(r) \times (p + \hbar k)) \cdot \sigma] \hat{K}^{-1} = \\
\frac{\hbar}{4m^2c^2}(\hat{\nabla} V(r) \cdot \hat{K}(p + \hbar k) \hat{K}^{-1}) \cdot \hat{K} \sigma \hat{K}^{-1} = \\
\frac{\hbar}{4m^2c^2}(\hat{\nabla} V(r) \times (-p + \hbar k)) \cdot -\sigma = \\
\frac{\hbar}{4m^2c^2}(\hat{\nabla} V(r) \times (p - \hbar k)) \cdot \sigma,
\]

thus, the Hamiltonian \( \hat{K} \hat{H}_k \hat{K}^{-1} \) can be written as

\[
\hat{K} \hat{H}_k \hat{K}^{-1} = \frac{(p - \hbar k)^2}{2m} + V(r) - \frac{(p - \hbar k)^4}{8m^4c^2} + \frac{\hbar^2}{8m^2c^2} \hat{\nabla}^2 V(r) + \frac{\hbar}{4m^2c^2}(\hat{\nabla} V(r) \times (p - \hbar k)) \cdot \sigma = \hat{H}_{-k}.
\]

### 10.4 Clebsh-Gordan coefficients for \( S=1 \) and \( S=1/2 \)

We illustrate the derivation of the Clebsch-Gordan coefficients (the eigenstates of \( J \) and \( J_z \)) of a system with \( j_1 = 1 \) coupled to another system with \( j_2 = 1/2 \). According to the theory of angular momentum coupling, the possible values of the total angular momentum are \( j = 3/2 \) and \( j = 1/2 \)

\[
j = \begin{cases} 
3/2, & m = \pm 3/2, \pm 1/2 \\
1/2, & m = \pm 1/2.
\end{cases}
\]

Starting with the maximum value of \( j(=3/2) \) and maximum value of \( m(=3/2) \),

\[
|jm\rangle = \begin{pmatrix} 3 \\ 2 \\ 2 \end{pmatrix} = |j_1 = 1, j_2 = 1/2; m_1 = 1, m_2 = 1/2\rangle.
\]

130
Operating on $|\frac{3}{2} \frac{3}{2}\rangle$ with $j-1|j, m\rangle = \sqrt{(j + m)(j - m + 1)}|j, m - 1\rangle$ until one reaches the smallest allowed $m(-3/2)$, we get

\[
\begin{align*}
|\frac{3}{2} \frac{3}{2}\rangle &= |1, 1; 1/2, 1/2\rangle, \\
|\frac{3}{2} \frac{1}{2}\rangle &= \sqrt{\frac{2}{3}}|1, 0; 1/2, 1/2\rangle + \sqrt{\frac{1}{3}}|1, 1; 1/2, -1/2\rangle, \\
|\frac{3}{2} \frac{-1}{2}\rangle &= \sqrt{\frac{1}{3}}|1, -1; 1/2, 1/2\rangle + \sqrt{\frac{2}{3}}|1, 0; 1/2, -1/2\rangle, \\
|\frac{3}{2} \frac{-3}{2}\rangle &= |1, -1; 1/2, -1/2\rangle.
\end{align*}
\]  
(10.29)

For $j = 1/2$ let

\[
|\frac{1}{2} \frac{1}{2}\rangle = a|1, 1/2; 1/2, 1/2\rangle + b|1, 1/2; 1/2, -1/2\rangle.
\]  
(10.30)

The orthonormality of the eigenvectors gives

\[
\begin{align*}
\langle \frac{3}{2} \frac{1}{2} | \frac{1}{2} \frac{1}{2}\rangle &= 0, \\
\langle \frac{1}{2} \frac{1}{2} | \frac{1}{2} \frac{1}{2}\rangle &= 1.
\end{align*}
\]  
(10.31)

Using the result of eqn. 10.29 one can show

\[a\sqrt{\frac{2}{3}} + b\sqrt{\frac{1}{3}} = 0.\]  
(10.32)

Similarly, eqn. 10.31 can be written as

\[a^2 + b^2 = 1.\]  
(10.33)

The last two equations show that $a$ and $b$ are real and can be taken as $a = -\sqrt{1/3}$.
and \( b = \sqrt{2/3} \). Hence

\[
\begin{align*}
\frac{1}{2}, \frac{1}{2} \rangle &= -\sqrt{\frac{1}{3}} \left| 1,0; \frac{1}{2}, \frac{1}{2} \right\rangle + \sqrt{\frac{2}{3}} \left| 1,1; \frac{1}{2}, -\frac{1}{2} \right\rangle.
\end{align*}
\] (10.34)

Using a similar procedure, used above, operating on \( \frac{1}{2}, \frac{1}{2} \) by \( j_- \) one gets

\[
\begin{align*}
\left| \frac{1}{2}, -\frac{1}{2} \right\rangle &= \sqrt{\frac{1}{3}} \left| 1,0; \frac{1}{2}, -\frac{1}{2} \right\rangle - \sqrt{\frac{2}{3}} \left| 1,-1; \frac{1}{2}, \frac{1}{2} \right\rangle.
\end{align*}
\] (10.35)

Taking the \((\theta, \varphi)\) system and taking into account the fact that the state \( |j_1, j_2; m_1, m_2\rangle \) is the product state \( |j_1, m_1\rangle |j_2, m_2\rangle \), we have

\[
\langle \theta, \varphi | j_1, j_2; m_1, m_2 \rangle = \langle \theta, \varphi | j_1, m_1 \rangle |j_2, m_2 \rangle = Y_{j_1, m_1}(\theta, \varphi) |j_2, m_2 \rangle,
\] (10.36)

where \( Y_{lm}(\theta, \varphi) \) is the spherical harmonic function, and for \( j_2 = 1/2 \) we denote \( |j_2, m_2\rangle \) by

\[
\begin{align*}
\left| \frac{1}{2}, m_2 \right\rangle &= \begin{cases} 
|\uparrow \rangle, & m_2 = +\frac{1}{2}, \\
|\downarrow \rangle, & m_2 = -\frac{1}{2}.
\end{cases}
\end{align*}
\] (10.37)

The spherical harmonics can be written as:

\[
\begin{align*}
|1, \pm 1 \rangle &= Y_{1, \pm 1} = \pm \sqrt{\frac{3}{8\pi}} \sin \varphi e^{\pm i\varphi} = \frac{1}{\sqrt{2}}(p_x \pm ip_y), \\
|1, 0 \rangle &= Y_{1, 0} = \sqrt{\frac{3}{4\pi}} \cos \varphi = p_z.
\end{align*}
\] (10.38)

Therefore the orthonormal set of equations. 10.29, 10.34 and 10.35 can be written
\[
\begin{align*}
\begin{pmatrix} 3 \ 3 \ 2 \ 2 \end{pmatrix} &= \frac{1}{\sqrt{2}} |(p_x + ip_y) \uparrow\rangle, \\
\begin{pmatrix} 3 \ 3 \ 2 \ 2 \end{pmatrix} &= \frac{1}{\sqrt{2}} |(p_x - ip_y) \downarrow\rangle, \\
\begin{pmatrix} 3 \ 1 \ 2 \ 2 \end{pmatrix} &= \frac{1}{\sqrt{6}} |2p_z \uparrow + (p_x + ip_y) \downarrow\rangle, \\
\begin{pmatrix} 3 \ -3 \ 2 \ 2 \end{pmatrix} &= \frac{1}{\sqrt{6}} |2p_z \downarrow + (p_x - ip_y) \uparrow\rangle, \\
\begin{pmatrix} 1 \ 1 \ 2 \ 2 \end{pmatrix} &= \frac{1}{\sqrt{3}} |p_z \uparrow + (p_x + ip_y) \downarrow\rangle, \\
\begin{pmatrix} 1 \ -1 \ 2 \ 2 \end{pmatrix} &= \frac{1}{\sqrt{3}} |p_z \downarrow - (p_x - ip_y) \uparrow\rangle.
\end{align*}
\]

\[10.39\]

### 10.5 Rashba Hamiltonian

The Rashba Hamiltonian describes the splitting of the conduction band as a result of spin-orbit coupling in an external field and is used to model the electronic structure of confined narrowgap semiconductors [40]. It provides a visual demonstration of the effect that Rashba spin-orbit interaction has on the electron energy and the spin. In this model electrons with the same wave vector and different spins will have different energies, and that Rashba spin-orbit interaction leads to ordered spins that point perpendicular to the direction of electron propagation. The one-electron Hamiltonian is written as [40]

\[
H = -\frac{\hbar^2 \nabla^2}{2m} + \alpha (\mathbf{\nabla} \times \mathbf{E}) \cdot \mathbf{\sigma},
\]

where \(\alpha\) is an effective mass parameter, \(\mathbf{\sigma} = (\sigma_x, \sigma_y, \sigma_z)\) is the vector of Pauli spin matrices, and for a 2D electron gas with a confining electric field normal to the
interface \( \mathbf{E} = (0, 0, E_z) \). The Rashba Hamiltonian can be written in the form

\[
H_R = iE_z \alpha (\hat{e}_z \times \mathbf{k}) \cdot \vec{\sigma}
\]

(10.41)

with \(-i\hbar \vec{\nabla} = \mathbf{p} = \hbar \mathbf{k}\), then

\[
H_R = iE_z \alpha (\hat{e}_z \times \mathbf{k}) \cdot \vec{\sigma} = iE_z \alpha \begin{vmatrix}
0 & 0 & e_z \\
k_x & k_y & k_z \\
\sigma_x & \sigma_y & \sigma_z
\end{vmatrix} = iE_z \alpha (k_x \sigma_y - \sigma_x k_y),
\]

(10.42)

and

\[
\sigma_x = \begin{pmatrix}
0 & 1 \\
1 & 0
\end{pmatrix}, \quad \sigma_y = \begin{pmatrix}
0 & -i \\
i & 0
\end{pmatrix}, \quad \sigma_z = \begin{pmatrix}
1 & 0 \\
0 & -1
\end{pmatrix}.
\]

(10.43)

We obtain a 2x2 Hamiltonian matrix for the 2D problem

\[
H = \begin{pmatrix}
-\frac{\hbar^2}{2m} (\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}) & E_z \alpha \hbar \frac{\partial}{\partial x} - iE_z \hbar \frac{\partial}{\partial y} \\
-E_z \alpha \hbar \frac{\partial}{\partial x} - iE_z \hbar \frac{\partial}{\partial y} & -\frac{\hbar^2}{2m} (\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2})
\end{pmatrix}.
\]

(10.44)

The vectors \( \begin{pmatrix} 1 \\ 0 \end{pmatrix} \) and \( \begin{pmatrix} 0 \\ 1 \end{pmatrix} \) are the eigenfunctions of the spin operator \( \sigma \). It is important to note that superposition of two spin states in opposite directions, with equal amplitudes, and constant phase difference, does not result in a cancelation of spins, but in a spin in different direction. This physics is similar to what we see in the coherent superposition of right- and left-circularly polarized light waves, which does not result in an unpolarized wave, but in a linearly polarized light. The spin part of an electron wave function \( \chi \) describes an electron with an arbitrary spin

\footnote{Note that, on the surface the system loses its periodicity, and as a result the states on the surface are not Bloch states. Therefore, \( \mathbf{k} \) is no longer a good quantum number and we make use of the momentum operator, \(-i\hbar \vec{\nabla} = \mathbf{p} = \hbar \mathbf{k}\), which is not correct in the bulk.}
direction, which can be written (in the non-relativistic limit) as a linear combination of spin-up and spin-down

\[ \chi = \begin{pmatrix} a_1 \\ a_2 \end{pmatrix}. \tag{10.45} \]

For a spin function that describes a spin in the direction \( \vartheta, \varphi \) we get

\[ \frac{a_2}{a_1} = \tan\left( \frac{\vartheta}{2} \right) e^{i\varphi}, \tag{10.46} \]

\[ a_1 = \cos\left( \frac{\vartheta}{2} \right), \quad a_2 = \sin\left( \frac{\vartheta}{2} \right) e^{i\varphi}. \tag{10.47} \]

The full wave function of an electron can hence be written as:

\[ \psi = e^{i(k_x x + k_y y)} \begin{pmatrix} a_1 \\ a_2 \end{pmatrix}. \tag{10.48} \]

To determine the eigenvalues of the Hamiltonian, one has to solve the system of homogeneous equations. For non-trivial solutions, the determinant of the coefficients has to be zero:

\[
\det(H - \varepsilon \mathbf{I}) = \left| \begin{array}{cc}
\frac{\hbar^2}{2m}(k_x^2 + k_y^2) - \varepsilon & E_z \alpha \hbar (ik_x + k_y) \\
E_z \alpha \hbar (-ik_x + k_y) & \frac{\hbar^2}{2m}(k_x^2 + k_y^2) - \varepsilon
\end{array} \right| = 0. \tag{10.49}
\]

Hence, the eigenvalues are

\[ \varepsilon_{1,2} = \frac{\hbar^2}{2m}(k_x^2 + k_y^2) \pm E_z \alpha \sqrt{k_x^2 + k_y^2}. \tag{10.50} \]
We choose spherical coordinates with the z-axis perpendicular to the 2D electron plane, so that the components of the unit vector $\hat{e} = e_x, e_y, e_z$ becomes

$$e_x = \sin \vartheta_k \cos \varphi_k, \quad e_y = \sin \vartheta_k \sin \varphi_k, \quad e_z = \cos \vartheta_k.$$ \hspace{1cm} (10.51)

We can find the spin direction corresponding to each eigenvalue $\varepsilon_{1,2}$ as

$$\varepsilon_1 : \frac{a_2}{a_1} = \frac{\sqrt{k_x^2 + k_y^2}}{ik_x - ik_y} = i(\cos(\vartheta_k) - i \sin(\vartheta_k))^{-1} = i e^{i \vartheta_k}$$ \hspace{1cm} (10.52)

$$\varepsilon_2 : \frac{a_2}{a_1} = \frac{i(k_x - ik_y)}{\sqrt{k_x^2 + k_y^2}} = i(\cos(\vartheta_k) - i \sin(\vartheta_k)) = i e^{-i \vartheta_k},$$ \hspace{1cm} (10.53)

where $\vartheta_k$ is the angle between the x axis and the vector $k$. The wavefunction is then

$$\psi_1(\mathbf{r}) = e^{i \mathbf{k} \cdot \mathbf{r}} (|\uparrow\rangle + i e^{i \vartheta_k} |\downarrow\rangle),$$

$$\psi_2(\mathbf{r}) = e^{i \mathbf{k} \cdot \mathbf{r}} (i e^{-i \vartheta_k} |\uparrow\rangle + |\downarrow\rangle).$$ \hspace{1cm} (10.54)

In summary, we found that a parabolic dispersion, typical for the free-electron Hamiltonian, splits into two branches with energies $\varepsilon_{1,2}$ when the Rashba Hamiltonian is added to the free-electron Hamiltonian. The eigenfunctions correspond to electrons with spins oriented in two opposite directions perpendicular to the vector $k$. 

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10.6 Green Function and the Asymptotic Solution of the Schrödinger Equation

There is a particularly important operator in three dimensions, namely Helmholtz equation (time independent wave equation), which yields readily to the Fourier transform method. The operator in question is

\[ H_\circ = \nabla^2 + \lambda. \]  \hspace{1cm} (10.55)

We shall employ the Fourier transform method to solve

\[ H_\circ \psi(r) = F(r). \]  \hspace{1cm} (10.56)

If we assume that \( \psi(r) \) and \( F(r) \) are Fourier transformed. Then

\[ \tilde{F}(k) = \frac{1}{(2\pi)^{3/2}} \int e^{-ik \cdot r} F(r) d^3r, \]  \hspace{1cm} (10.57)

and,

\[ \tilde{\psi}(k) = \frac{1}{(2\pi)^{3/2}} \int e^{-ik \cdot r} \psi(r) d^3r. \]  \hspace{1cm} (10.58)

By taking the Fourier transform of eqn. 10.56 we get

\[ (-k^2 + \lambda) \tilde{\psi}(k) = \tilde{F}(k). \]  \hspace{1cm} (10.59)

The Helmholtz operator is now algebraic, so we can write eqn. 10.59 as

\[ \tilde{\psi}(k) = \frac{\tilde{F}(k)}{k^2 - \lambda}. \]  \hspace{1cm} (10.60)
when $\lambda > 0$, the denominator has zeroes at $k = \pm \sqrt{\lambda}$. If we assume that $\lambda = (q \pm i \epsilon)$, where $\epsilon > 0$ then we can write

$$\tilde{\psi}_\pm(k) = -\frac{\tilde{F}(k)}{k^2 - (q \pm i \epsilon)^2}. \quad (10.61)$$

Let us for the moment neglect the homogenous solution and focus on the particular one. We find the solution of eqn. 10.56 by inverse transform eqn. 10.61, writting

$$\psi_\pm(r) = -\frac{1}{(2\pi)^{3/2}} \int d{k} \frac{\tilde{F}(k)e^{ik \cdot r}}{k^2 - (q \pm i \epsilon)^2} = -\frac{1}{(2\pi)^3} \int dr' \int d{k} \frac{F(r')e^{ik \cdot (r-r')}}{k^2 - (q \pm i \epsilon)^2}. \quad (10.62)$$

Then the Green function can be written as

$$G_\pm(r, r') = -\frac{1}{(2\pi)^{3/2}} \int d{k} \frac{e^{ik \cdot (r-r')}}{k^2 - (q \pm i \epsilon)^2}. \quad (10.63)$$

If the spherical coordinates are chosen for the variables in $k$-space, then we have $dk = k^2 \sin \vartheta d\vartheta dk d\varphi = -k^2 d\cos \vartheta d\varphi dk$, with respect to polar axis direction $r - r' = \tilde{r}$. Taking into that account the integral is on even function of $k$, it is straightforward to show,

$$G_\pm(r, r') = -\frac{1}{2(2\pi)^2 i \rho} \int_{-\infty}^{+\infty} dk \frac{(e^{ik \rho} - e^{-ik \rho})k}{(k - (q \pm i \epsilon))(k + (q \pm i \epsilon))}. \quad (10.64)$$

To solve this integral, we extend the variable $k$ analytically into the complex
plane. We divide the integral in eqn. 10.64 into two parts, with the first part

\[ I_\pm = \int_{-\infty}^{+\infty} dk \frac{e^{ik\rho}k}{(k - (q \pm i\epsilon))(k + (q \pm i\epsilon))}. \] (10.65)

We choose the contour in the upper half plane, then we have the pole at \( q + i\epsilon \) and the value of the residue is

\[ \text{Res}_{q+i\epsilon}(I_\pm) = \lim_{k \to q+i\epsilon} \frac{k e^{ik\rho}}{(k - (q \pm i\epsilon))(k + (q \pm i\epsilon))} = \frac{e^{i\rho(q+i\epsilon)}}{2q}(q + i\epsilon), \] (10.66)

and the value of the integral \( I_\pm \) is given by

\[ I_\pm = 2\pi i \text{Res}_{q+i\epsilon}(I_\pm) = 2\pi i \frac{e^{i\rho(q+i\epsilon)}}{2q}(q + i\epsilon). \] (10.67)

The second integral in eqn. 10.65 gives \( 2\pi i \frac{e^{i\rho(q+i\epsilon)}}{2q}(q + i\epsilon) \), we can write

\[ G_\pm (r, r') = -\frac{e^{\pm iq(r-r')}}{4\pi |r-r'|}. \] (10.68)

Hence the solution of Helmhotz eqn. 10.56 is given by

\[ \psi_\pm (r) = \psi_{\text{inc}}(r) - \frac{1}{(4\pi)^{3/2}} \int dr' F(r') e^{\pm i(q+i\epsilon)|r-r'|} \frac{1}{|r-r'|}. \] (10.69)

In almost all scattering experiment, detectors are located at a distance from the target that is much larger than the size of the target, thus we are interested in the asymptotic behavior of the Green function in eqn. 10.123. If we write

\[ |r - r'| = \sqrt{r^2 - 2r \cdot r' + r'^2} = r[1 - \frac{2r \cdot r'}{r^2} + \frac{r'^2}{r^2}]^{1/2}, \] (10.70)
and assume \( r \) is very large, then a binomial expansion yields

\[
|r - r'| = r - n \cdot r' + O(1/r), \tag{10.71}
\]

where \( O(1/r) \) represents terms which vanish at least as fast as \( 1/r \) for large \( r \) and \( n \) is a unit vector in the radial direction. Thus, for large \( r \), eqn. 10.69 becomes:

\[
\psi_{\pm}(r) = \psi^{inc}(r) - \frac{e^{\pm iqr}}{r} \int e^{\mp iqn \cdot r'} F(r') dr'. \tag{10.72}
\]

In quantum mechanics the boundary condition can be put in the form of behavior of the solutions at large distances. The choice \( q + i\epsilon \) and \( q - i\epsilon \) correspond to application of particular boundary conditions at all points of a two-dimensional surface.

### 10.7 Single slit scattering, Partial wave amplitude, Phase shift, and T-matrix

We discuss in this section the scattering problem of a spherical atomic potential embedded in free space, in an environment of constant potential. Thus the reference system is a free-electron system where the Hamiltonian contains only the kinetic energy term, and the eigenfunctions are plain waves. Here we are considering the scattering of a wave from one scatterer. The Korringa approach tells us that the total wave after scattering is given by eqn. 5.1:

\[
\psi(r) = \psi^{inc}(r) + \psi^{sc}(r), \tag{10.73}
\]

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where $\psi^{inc}(r)$ is the incident wave and $\psi^{sc}(r)$ is the scattered wave. We are going to assume that the incident particle is coming from very far away, so the wave packet is uniform and can be represented by a plane wave. Furthermore, in the case of scattering by a central potential, it is useful to work in angular-momentum representation. We therefore represent an incoming plane wave as:

$$e^{i k r} = 4\pi \sum_{l,m} i^l j_l(|k||r|) Y_{lm}(\theta, \varphi) Y^*_{lm}(\theta, \varphi).$$  \hfill (10.74)

where $k = \sqrt{E}$. On the other hand, the scattered wave\footnote{Here we consider the outgoing wave.} is given by:

$$\psi^{sc}(r) = \int G(r, r') V(r') \psi(r') dr',$$  \hfill (10.75)

where $G(r, r')$ is the Green function, $V(r')$ is the potential, and $\psi(r')$ is the wavefunction. The Green function is given by eqn. 10.123, the total solution is given by:

$$\psi(r) = \psi^{inc}(r) + \int G(r, r') V(r') \psi(r') dr.$$  \hfill (10.76)

Using eqn. 10.72, and setting $k_f = k n$, we get:

$$\psi(r) = \psi^{inc}(r) + f(k_f) e^{i k r},$$  \hfill (10.77)

where

$$f(k_f) = -\int e^{i k_f r'} V(r') \psi(r') dr'.$$  \hfill (10.78)
\[ f(\mathbf{k}_f) \] is called the scattering amplitude. The radial wavefunction eqn. 5.42 has two possible solutions, the spherical Bessel function \( j_l(kr) \) and spherical Neumann function \( n_l(kr) \). For spherical symmetric potential \( Y_{lm}(\theta, \varphi) \) will be reduced to \( P_l(\theta) \) (Legendre Polynomial) and if we choose \( \mathbf{k} \) the in \( z \) direction, then we can write

\[
\psi(r) = 4\pi \sum_l i^l(2l+1)j_l(kr)P_l(\cos \vartheta) + f(\vartheta) \frac{e^{ikr}}{r}. \tag{10.79}
\]

The asymptotic behavior of \( j_l(kr) \) is given by

\[
j_l(kr) \to \frac{\sin(kr - l\pi/2)}{kr} \quad (r \to \infty). \tag{10.80}
\]

Using the Euler identity \( \sin(kr - l\pi/2) = \frac{(-i)^l e^{ikr} - i^l e^{-ikr}}{2i} \) we can write

\[
\psi(r, \vartheta) \to \sum_l i^l \left( \frac{(-i)^l e^{ikr} - i^l e^{-ikr}}{2i} \right) P_l(\cos \vartheta) + f(\vartheta) \frac{e^{ikr}}{r}, \tag{10.81}
\]

and rearranging the terms we get

\[
\psi(r, \vartheta) \to -\frac{e^{-ikr}}{2ikr} \sum_l i^{2l}(2l+1)P_l(\cos \vartheta) + \frac{e^{ikr}}{r} \left[ f(\vartheta) + \frac{1}{2ikr} \sum_l i^l(-i)^l(2l+1)P_l(\cos \vartheta) \right]. \tag{10.82}
\]

The general solution for a free particle radial equation 5.42 (in a region that excludes the origin) is given by a linear combination of \( j_l(kr) \) and \( n_l(kr) \)

\[
R_l(r, k) = A_l j_l(kr) + B_l n_l(kr), \tag{10.83}
\]
and asymptotic behavior of \( n_l(kr) \) is given by

\[
n_l(kr) \to -\frac{\cos(kr - l\pi/2)}{kr} \quad (r \to \infty).
\] (10.84)

Substituting in eqn. 10.83 one gets

\[
R_l(r;k) \to A_l \frac{\sin(rk - l\pi/2)}{kr} - B_l \frac{\cos(kr - l\pi/2)}{kr} \quad (r \to \infty).
\] (10.85)

By making the substitution \( A_l = C_l \cos \delta_l \) and \( B_l = C_l \sin \delta_l \) one can get

\[
R_l(r;k) \to \frac{\sin(rk - l\pi/2 + \delta_l)}{kr}.
\] (10.86)

The most general solution of the Schrödinger eqn. 5.42 reads

\[
\psi(r) = \sum_{lm} C_{lm} R_l(r;k) Y_{lm}(\theta, \varphi).
\] (10.87)

Since \( V(r) \) is spherically symmetric (around the z-axis), then we can write

\[
\psi(r) = \sum_l a_l R_l(r;k) P_l(\cos \theta).
\] (10.88)

If we substitute eqn. 10.86 into eqn. 10.88 we get

\[
\psi(r) \to \sum_l a_l \frac{\sin(rk - l\pi/2 + \delta_l)}{kr} P_l(\cos \theta) \quad (r \to \infty),
\] (10.89)

and by substituting \( \sin(kr - l\pi/2 + \delta_l) = [(-i)^l e^{ikr} e^{i\delta_l} - i^l e^{-ikr} e^{-i\delta_l}] \) into eqns. 10.89 we get

\[
\psi(r, \theta) \to -\frac{e^{-ikr}}{2i kr} \sum_l a_l^l e^{-i\delta_l} P_l(\cos \theta) + \frac{e^{ikr}}{2i kr} \sum_l a_l^l (-i)^l e^{i\delta_l} P_l(\cos \theta).
\] (10.90)
By equating the coefficient of $e^{-ikr/r}$ in eqn. 10.90 and 10.82, we find that

$$a_l = (2l + 1)i^l e^{i\delta_l}. \quad (10.91)$$

Substituting eqn. 10.91 into 10.90 and equating the coefficient of $e^{ikr/r}$ we have

$$f(\vartheta) + \frac{1}{2ik} \sum_l i^l (-i)^l (2l + 1)P_l(\cos \vartheta) = \frac{1}{k} \sum_l (2l + 1)i^l (-i)^l e^{2i\delta_l} P_l(\cos \vartheta). \quad (10.92)$$

It is straightforward to show that

$$f(\vartheta) = \sum_l f_l(\vartheta) = \frac{1}{2ik} \sum_l i^l (-i)^l (2l + 1)P_l(\cos \vartheta)(e^{2i\delta_l} - 1) = \frac{1}{k} \sum_l (2l + 1)e^{i\delta_l} \sin \delta_l P_l(\cos \vartheta), \quad (10.93)$$

where $f_l(\vartheta)$ is the partial wave amplitude. We are interested in the quantity $t_l = e^{i\delta_l} \sin \delta_l / k$. Now our goal is to establish a relation between the partial wave amplitude and the t-matrix. Let us consider again eqn. 10.83 and using similar substitution to what we used to get eqn. 10.85, we can write

$$R_l(r, k) = A_l(j_l(kr) \cos \delta_l - n_l(kr) \sin \delta_l). \quad (10.94)$$

On the other hand, the radial part of eqn. 10.77 reads

$$R_l(r, k) = j_l(kr) + \int g_l(r, r')V(r')R_l(r', k)dr'. \quad (10.95)$$

where $g_l(r, r')$ is the radial Green function and is given by eqn. 10.120 below. Thus
eqn. 10.95 can be written as

\[ R_l(r, k) = j_l(kr) - ik h_l(kr) \int j_l(kr') V(r') R_l(r', k) dr'. \] (10.96)

The integral is just the \( t \)-matrix element in angular-momentum representation (see eqn. 5.11),

\[ t_l(k) = \int j_l(kr') V(r') R_l(r', k) dr', \] (10.97)

so that we obtain

\[ R_l(r, k) = j_l(kr) - i k t_l(k) h_l(kr). \] (10.98)

From eqn. 10.94 and 10.96 it is straightforward to show that

\[ t_l(k) = -\frac{1}{k} \sin \delta_l e^{i\delta_l}. \] (10.99)

An incoming wave can be expanded in Bessel functions and spherical harmonics as

\[ \psi^{inc}(r) = \sum_{lm} a_{lm}^o R_l(r, k) Y_{lm}(\theta, \varphi). \] (10.100)

The scattered wave can be expanded analogously as:

\[ \psi^{sc}(r) = \sum_{lm} a_{lm}^{sc} R_l(r, k) Y_{lm}(\theta, \varphi). \] (10.101)

Within the range where \( r \leq r_{MT} \) we have

\[ \psi(r) = \sum_{lm} a_{lm} R_l(r, k) Y_{lm}(\theta, \varphi). \] (10.102)

Using eqns. 10.101 and 10.102 for incident and scattered waves respectively and
from the continuity of the wavefunction eqn. 10.73 at $r = r_{MT}$, we obtain

$$a_{lm}^{sc} = -ikt(k)a_{lm}^0.$$  \hspace{1cm} (10.103)

Thus, we have established the relation between the partial wave amplitude and the t-matrix. In this simple example we established a connection between the Korringa approach (Multiple scattering in the first part of the discussion) and Kohn-Rostoker approach (Green function method in the second part of the discussion).

10.8 Potential independent KKR secular equation

Following Kohn and Rostoker [2], to deal properly with the singularities of the Green function we must use a limiting procedure in calculating $\Lambda$. Then we will have demonstrated that eqn. 5.41 can be rewritten in the form:

$$\Lambda_{lm,l'm'}(k) = \lim_{\epsilon \rightarrow 0} \int_{r < r_{MT} - 2\epsilon} d^3r \phi_{lm}^{*}(r, E)V(r)$$

$$\times \{ \phi_{l'm'}(r, E) - \int_{r' < r_{MT} - \epsilon} d^3r' G(r - r')V(r')\phi_{l'm'}(r'; E) \}. \hspace{1cm} (10.104)$$
First, if we consider the integral inside the bracket, and we make substitution

\[-V(r') = \vec{\nabla}^2 + E\]

we can write:

\[I_1 = \int_{r' < r_{MT-\epsilon}} d^3r' G(r - r') \left[ \vec{\nabla}^2 + E \right] \phi_{l'm'}(r'; E) + \int_{r' < r_{MT-\epsilon}} d^3r' \left[ \phi_{l'm'}(r'; E) \right] \left( \vec{\nabla}^2 + E \right) G(r - r') - \int_{r' < r_{MT-\epsilon}} d^3r' \phi_{l'm'}(r'; E) \left( \vec{\nabla}^2 + E \right) G(r - r') \]

(10.105)

Note that \( \phi_{lm}(r; E) = \int_{r' < r_{MT-\epsilon}} d^3r' G(r - r') \left[ \vec{\nabla}^2 + E \right] \phi_{l'm'}(r'; E) \). Obviously, the first and the second terms will give rise to \( \int_{r' < r_{MT-\epsilon}} d^3r' \left[ G(r - r') \vec{\nabla}^2 \phi_{l'm'}(r'; E) - \phi_{l'm'}(r'; E) \vec{\nabla}^2 G(r - r') \right] \). Therefore, the integral \( I_1 \) can be written as

\[I_1 = \phi_{lm}(r; E) + \int_{r' < r_{MT-\epsilon}} d^3r' \left[ G(r - r') \vec{\nabla}^2 \phi_{l'm'}(r'; E) - \phi_{l'm'}(r'; E) \vec{\nabla}^2 G(r - r') \right] \]

(10.106)

By using the second form of Green’s theorem

\[\oint_s (\phi_1 \vec{\nabla} \phi_2 - \phi_2 \vec{\nabla} \phi_1) \cdot ds = \int_\tau (\phi_1 \vec{\nabla}^2 \phi_2 - \phi_2 \vec{\nabla}^2 \phi_1) d\tau, \]

(10.107)

one can rewrite \( I_1 \) in the form

\[I_1 = \phi_{l'm'}(r; E) + \int_{r' < r_{MT-\epsilon}} dS' \left[ G(r - r') \frac{\partial}{\partial r'} \phi_{l'm'}(r'; E) - \phi_{l'm'}(r'; E) \frac{\partial}{\partial r'} G(r - r') \right]. \]

(10.108)

Then we get:

\[\Lambda_{lm,l'm'}(k) = \lim_{\epsilon \to 0} \int_{r' < r_{MT-\epsilon}} dS' \left[ \frac{\partial}{\partial r'} \phi_{l'm'}(r'; E) - \phi_{l'm'}(r'; E) \frac{\partial}{\partial r'} \right] \times \int_{r' < r_{MT-\epsilon}} d^3r G(r' - r) \phi_{lm}^*(r; E) V(r). \]

(10.109)
Let us consider the integral $I_2$, and similar to what we did for $I_1$ one can show

$$I_2 = \int_{r<r_{MT}-2\epsilon} d^3r G(r' - r) \phi_{lm}^*(r; E) V(r) = \int_{r<r_{MT}-2\epsilon} d^3r \phi_{lm}^*(r; E) \delta(r - r') + \int_{r<r_{MT}-2\epsilon} d^3r \left[ G(r - r') \nabla^2 \phi_{lm}(r'; E) - \phi_{lm}(r'; E) \nabla^2 G(r - r') \right].$$

(10.110)

Notice that the integral $I_2$ goes over a sphere of radius $r_{MT}-2\epsilon$ that is, in the integral $I_2$, $r$ and $r'$ can never be equal. Therefore, the first term in eqn. 10.110 vanishes. In a similar way, by using the second form of the Green Theorem we get:

$$I_2 = \int_{r<r_{MT}-2\epsilon} dS \left[ G(r' - r) \frac{\partial}{\partial r} \phi_{lm}^*(r; E) - \phi_{lm}^*(r; E) \frac{\partial}{\partial r} G(r' - r) \right].$$

(10.111)

Finally, one can easily show that

$$\Lambda_{lm,lm'}(k) = \lim_{\epsilon \to 0} \int_{r<r_{MT}-\epsilon} dS \int_{r>r_{MT}-2\epsilon} dS' \left[ \phi_{lm}^*(r; E) - \frac{\partial}{\partial r} \phi_{lm}(r; E) \frac{\partial}{\partial r} G(r' - r) - \phi_{lm}(r; E) \frac{\partial}{\partial r} \phi_{lm'}(r'; E) \right].$$

(10.112)

10.9 Expansion of Green function in spherical harmonics

We start with the expansion of the Green function in spherical Bessel functions and spherical harmonics. The inhomogeneous Helmholtz equation which $G(r, r')$ satisfies is:

$$(\nabla^2 + k^2) G(r, r') = -\delta(r - r')$$

(10.113)
The solution of this equation, subject to the Sommerfeld radiation condition, which ensures that the sources radiate waves instead of absorbing them, is written [2]:

\[ G(r, r') = \frac{\exp(ik|r - r'|)}{4\pi|r - r'|}. \] (10.114)

The spherical harmonics satisfy the completeness relation:

\[ \sum_{l=0}^{\infty} \sum_{m=-l}^{l} Y_{lm}^*(\hat{r})Y_{lm}(\hat{r'}) = \delta(\theta - \theta')\delta(\phi - \phi'). \] (10.115)

Now the three dimensional delta function can be written:

\[ \delta(r - r') = \frac{\delta(r - r')}{r}\delta(\theta - \theta')\delta(\phi - \phi'). \] (10.116)

It follows that

\[ \delta(r - r') = \frac{\delta(r - r')}{r} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} Y_{lm}^*(\hat{r})Y_{lm}(\hat{r'}). \] (10.117)

Let us expand the Green function in the form

\[ G(r, r') = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} g_l(r, r')Y_{lm}^*(\hat{r})Y_{lm}(\hat{r'}). \] (10.118)

Substitution of this expression into eqn. 10.113 yields

\[ \left( \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} - \frac{l(l+1)}{r^2} \right) g_l = -\frac{\delta(r - r')}{r^2}. \] (10.119)

The appropriate boundary conditions are that \( g_l \) is finite at the origin and
corresponds to an outgoing wave at infinity (i.e. \( g_l \propto e^{ikr} \) in the limit \( r \to \infty \)). The solution of the above equation which satisfies these boundary conditions is [124]:

\[
g_l(r, r') = A j_l(kr_<) h_l^{(1)}(kr_>) ,
\]

(10.120)

where \( r_<, r_> \) are the greater and the lesser of \( r, r' \) respectively, \( j_l \) is the spherical Bessel function and \( h_l^{(1)} \) is spherical Hankel functions of the first kind. The correct discontinuity in slope at \( r = r' \) is assured if \( A = ik \), since:

\[
\frac{dh_l^{(1)}(r)}{dr} j_l(r) - h_l^{(1)}(r) \frac{dj_l(r)}{dr} = \frac{i}{r^2}.
\]

(10.121)

Therefore, the Green function for the problem of scattering by a central potential can be written as a product of two linearly independent solutions, the regular \( j_l(kr) \) converges as \( r \to 0 \), and irregular \( h_l^{(1)}(kr) \) diverges as \( r \to 0 \). The expansion of the Green function is:

\[
-\exp(ik|\mathbf{r} - \mathbf{r}'|) \frac{4\pi}{4\pi|\mathbf{r} - \mathbf{r}'|} = -ik \sum_{l=0}^{\infty} j_l(kr_<) h_l^{(1)}(kr_>) \sum_{m=-l}^{l} \ Y_l^m(\hat{r}) Y_l^m(\hat{r}')
\]

(10.122)

where \( h_l^{(1)}(x) = j_l(x) + in_l(x) \), and finally:

\[
-\exp(ik|\mathbf{r} - \mathbf{r}'|) \frac{4\pi}{4\pi|\mathbf{r} - \mathbf{r}'|} = -ik \sum_{l,m} j_l(kr_<) j_l(kr_>) + in_l(kr_>) \ Y_l^m(\hat{r}) Y_l^m(\hat{r}')
\]

(10.123)

Kohn and Rostoker [2] expand the \( G(\mathbf{r} - \mathbf{r}') \) in eqn. 5.28 in the form

\[
G(\mathbf{r}, \mathbf{r}') = D(\mathbf{r}, \mathbf{r}') + G_o(\mathbf{r}, \mathbf{r}').
\]

(10.124)

Other authors such as Nemoshkalenko and Antonov [125], call the first part regular.
(converges as $r \to 0$) and the second singular (diverges as $r \to 0$). However, Kohn and Rostoker did not use this terminology. By using this trick Kohn and Rostoker [2] were able to separate the structure part and the potential (phase shift) part. Expanding eqn. 10.123 in imaginary and real parts, the real part reads

$$G_o(r, r') = -\frac{1}{4\pi r} \cos(k|r - r'|) = k \sum_{l,m} j_l(kr) n_l(kr') Y^*_l m(\hat{r}) Y_{l m}(\hat{r}').$$

(10.125)

The above equation satisfies the inhomogeneous wave equation as $G(r, r')$ for $r, r'$ lie inside the atomic polyhedron [2] and usually called the irregular solution. Accordingly, $D$, regular, satisfies the homogeneous wave equation in $r$ and $r'$, and has a solution inside the muffin-tin sphere of the form:

$$D(r, r') = \sum_{l,m} \sum_{l',m'} A_{lm;lm'} j_l(kr) j_{l'}(kr') Y_{lm}(\hat{r}) Y^*_{l'm'}(\hat{r}).$$

(10.126)

Therefore, we can write the expansion of the Green function in the form

$$G(r, r') = \sum_{l,m} \sum_{l',m'} \left[ A_{lm;lm'} j_l(kr) j_{l'}(kr') + k \delta_{ll'} \delta_{mm'} j_l(kr) n_l(kr) \right] Y_{lm}(\hat{r}) Y^*_{l'm'}(\hat{r}).$$

(10.127)

A comparison between eqns. 5.47 and the above equation with respect to $Y_{lm}(\hat{r}) Y^*_{l'm'}(\hat{r})$ will lead to

$$A_{lm;lm'} = \frac{(4\pi)^2}{\tau} \frac{j_l(|k_n|r) j_{l'}(|k_n|r')}{j_l(kr) j_{l'}(kr)} \sum_n \frac{j_l(|k_n|r) j_{l'}(|k_n|r')}{E - |k_n|}$$

$$\times Y_{lm}^*(\phi_k, \varphi_k) Y_{l'm'}(\phi_k, \varphi_k) - \frac{kn_l(kr')}{j_l(kr')} \delta_{l,l'} \delta_{m,m'}$$

(10.128)
10.10 Connection with Korringa’s work

When the incident wave interacts with a spherical and isotropic potential, the total wavefunction is the superposition of the incident and scattered waves, given by

\[ \psi \propto e^{ikr} + f(\vartheta) \frac{e^{ikr}}{r} \]  \hspace{1cm} (10.129)

The plane wave can be expanded as in eqn. 5.45 as

\[ e^{ikr} = 4\pi \sum_{l,m} j_l(|k||r|)Y_{lm}(\vartheta, \varphi)Y^*_{lm}(\vartheta_k, \varphi_k). \]  \hspace{1cm} (10.130)

The asymptotic form of the radial function is:

\[ R_l(kr) \to \frac{c_l}{kr} \sin(kr - \frac{l\pi}{2} + \eta_l) \quad (r \to \infty). \]  \hspace{1cm} (10.131)

By using trigonometric identities, we can write:

\[ \sin(kr - \frac{l\pi}{2} + \eta_l) = \cos(\eta_l) \left[ \sin(kr - \frac{l\pi}{2}) + \tan(\eta_l) \cos(kr - \frac{l\pi}{2}) \right]. \]  \hspace{1cm} (10.132)

Thus, we can write eqn. 10.131 as

\[ R_l(kr) \to c_l \left[ j_l(kr) + \tan(\eta_l) \frac{1}{kr} \cos(kr - \frac{l\pi}{2}) \right]. \]  \hspace{1cm} (10.133)

Substituting the Neumann and spherical Bessel functions instead of their asymptotic forms given in eqns. 10.80 and 10.84, we can write the following relations:
\[ R_l(kr) \propto c_l[j_l(kr) - \tan(\eta_l)n_l(kr)] \]
\[ R'_l(kr) \propto c_l[j'_l(kr) - \tan(\eta_l)n'_l(kr)] \] \hspace{1cm} (10.134)

Following the definition of \( L_l \) in eqn. 5.53

\[ L_l = \frac{R'(r_{MT}; E)}{R_l(r_{MT}; E)} = \frac{j'_l(kr_{MT}) - \tan \eta_l j'_l(kr_{MT})}{n'_l(kr_{MT}) - \tan \eta_l n'_l(kr_{MT})}. \] \hspace{1cm} (10.135)

Rearranging terms, one gets

\[ \tan \eta_l = \frac{j_l(kr_{MT})L_l - j'_l(kr_{MT})}{n_l(kr_{MT})L_l - n'_l(kr_{MT})}. \] \hspace{1cm} (10.136)

Then, we get

\[ \det\{A_{lm'; m'} + k \cot \eta_{l'} \delta_{l,m'}\} = 0 \] \hspace{1cm} (10.137)

In this way, Rostoker and Kohn [2] were able to prove that the Green function and multiple scattering method (Korringa’s approach [65]) are equivalent.
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