MODELING ELECTRONIC STRUCTURE AND SPECTROSCOPY IN CORRELATED MATERIALS AND TOPOLOGICAL INSULATORS

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by

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ABSTRACT OF DISSERTATION

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Abstract

Current major topics in condensed matter physics mostly focus on the investigation of materials having exotic quantum phases. For instance, $Z_2$ topological insulators have novel quantum states, which are distinct from ordinary band insulators. Recent developments show that these nontrivial topological phases may provide a platform for creating new types of quasiparticles in real materials, such as Majorana fermions. In correlated systems, high-$T_c$ superconducting cuprates are complicated due to the richness of their phase diagram. Surprisingly, the discovery of iron pnictides demonstrates that high-$T_c$ superconductivity related phenomena are not unique to copper oxide compounds. Many people believe that the better the understanding of the electronic structure of cuprates and iron pnictides, the higher chances to unveil the high temperature superconductivity mystery. Despite the fact that silicon is a fundamental element in modern semiconductor electronics technology, the chemical bonding properties of liquid silicon phase still remain a puzzle.

A popular approach to investigate electronic structure of complex materials is combining the first principles calculation with an experimental light scattering probe. Particularly, Compton scattering probes the many body electronic ground state in the bulk of materials in terms of electron momentum density projected along a certain scattering direction, and inelastic x-ray scattering measures the dynamic structure fac-
tor $S(q, \omega)$ which contains information about electronic density-density correlations.

In this thesis, I study several selected materials based on first principles calculations of their electronic structures, the Compton profiles and the Lindhard susceptibility within the framework of density functional theory. Specifically, I will discuss the prediction of a new type of topological insulators in quaternary chalcogenide compounds of compositions $\text{I}_2\text{II-IV-VI}_4$ and in ternary famatinite compounds of compositions $\text{I}_3\text{V-VI}_4$. I will present the electronic structure, Fermi surface topology and the interlayer coupling strength of the iron-based superconductor $\text{Ca}_{10}(\text{Pt}_3\text{As}_8)(\text{Fe}_2\text{As}_2)_5$. In the study of iron-pnictide $\text{LaOFeAs}$ and cuprate $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, I will discuss the Fermi surface topology and the related orbital characters near the Fermi energy from the aspect of Compton profiles and electron momentum density. The Compton scattering related study also includes the effect of disorder and chemical bonding in liquid silicon. I will describe the extension of the Lindhard susceptibility calculation to multiple Brillouin zones and illustrate the zone dependent susceptibility of the electron doped cuprate $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$. I also extend this study to the time-resolved response function of solids in real space.
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Chapter 1

Introduction

1.1 Motivation

First principles modeling of electronic properties has become an essential tool for handling complex materials. In the microscopic world of solids electrons are governed by the Bloch wave function calculated from the solution of the Schrödinger equation. The Hamiltonian of the Schrödinger equation is built up with the periodic potential associated with the composition of distinct chemical elements consistent with the crystal symmetry. A direct path to simulate electronic structure accurately in materials science research is to perform an ab-initio calculation simply relying on the knowledge of a given crystal structure based on density functional theory (DFT)[1]. Thanks to the great computational power of modern computers, the ability of the ab-initio calculation to solve a typical electronic structure can be scaled very well from a simple atom per crystal unit cell to compounds with multiple atoms of different chemical species and complex geometric structure.

One popular approach to study electronic structure of condensed matter is the combination of the theoretical ab-initio calculation and the experimental light scat-
tering probe. It is quite often that the experimental measurement does not directly lead to the underlying electronic structure of the samples. Part of the reason for this is because one neglects important photon and electron interactions which take place during the measurement. Therefore, it needs a sophisticated simulation to convolute the specific light scattering process with the underlying electronic structure of the samples, to understand how well the underlying model describes both the experimental dispersion and the spectroscopic measurement. The research topics in this thesis cover several interesting materials such as topological insulators, high temperature superconducting iron pnictides and cuprates, and liquid phase silicon.

An enormous revolution in condensed matter research is the discovery of a 3D topological insulator which has a novel quantum state classified by the $Z_2$ topological invariant\[2-4\] associated with the global properties of the Bloch states in the solid. The time-reversal symmetry guarantees the existence of robust surface states connecting the conduction and valence bands in these topological insulators. An important character of the surface states is the helical spin texture such that the spin is locked to the momentum rotating around the Dirac point. The current existing 3D topological materials are mostly binary and ternary compositions of heavy elements ranging from Bi/Sb-based binary systems\[5-14\] to Tl-based ternary compounds\[15\]. The potential technological applications will be greatly enhanced if the topological ground state could be combined with a broken symmetry due to local order. For instance, people are looking for the possibility of elementary excitations that satisfy non-Abelian statistics-the so-called Majorana fermions, important for topological quantum computers, which requires the proximity of superconducting and ferromagnetic insulating phases \[16-18\].

The discovery\[19\] of the iron pnictide high-temperature superconductors broadens the hope to resolve the origins of high-$T_c$ superconductivity. The $T_c$\[20-22\]
obtained in the iron pnictide family is quite remarkable compared to the cuprates. From the aspect of crystal structure, the FeAs layers of iron pnictide compounds play a similar role in the electronic structure as the CuO$_2$ layers do in cuprates. Some analogies in the phase diagram are also shared between iron pnictides and cuprates. The parent compound of a iron pnictide is antiferromagnetic and the superconducting states can be induced by either hole or electron doping[23]. A clear message realized from the iron pnictides is that these high-$T_c$ superconductivity related phenomena are not uniquely occurring in copper oxide compounds. With this finding, people are obviously willing to keep exploring all possible structural and chemical variety of the iron pnictides to pursue higher $T_c$ and also trying to develop a better insight about their underlying electronic structures.

The family of superconducting cuprates has held the record of the highest superconducting transition temperature $T_c$ for several decades. Unlike the conventional superconducting mechanism due to electron-phonon interaction, the high temperature superconductivity of cuprates seems to be driven by a different kind of pairing bosons[24]. In fact, the high $T_c$ superconductivity of cuprates so far is still one of the biggest mysteries in condensed matter research. Even though the cuprate family has all kinds of complex layered crystal structures, most people believe the superconductivity originates from the CuO$_2$ planes in which the electronic structure is dominantly hybridized Cu $d_{x^2−y^2}$ orbital and O $p_x$ and $p_y$ orbitals. In a typical phase diagram of cuprates[24, 25], the parent compound at zero doping behaves as an antiferromagnetic insulator. With increasing doping, the antiferromagnetic phase get suppressed and the system transits into a pseudogap phase which refers to an unknown energy gap appearing in the electronic structure at temperatures above the superconducting transition. Increasing the doping into the optimal doping region, the superconducting states emerge as a dome shaped area.
in the phase diagram below a certain critical temperature. Superconductivity arises in cuprates for both electron and hole doping\cite{24, 25}—for instance, for hole-doped \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4 \) (LSCO) with apical oxygens out of the \( \text{CuO}_2 \) plane and electron-doped \( \text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4 \) (NCCO) without any apical oxygens. Due to these complex crystal structure issues and the richness of the phase diagram, the study of the electronic structure is always extremely important and it serves as a key to unveil the high temperature superconductivity mystery.

As we know, silicon (Si) is a fundamental element in the modern semiconductor electronics technology. It is a semiconducting solid at room temperature, while upon melting at high temperature, Si transforms into a metallic liquid. An interesting topic is to understand the evolution of the metallic and covalent bonding properties during the phase transition.

\section*{1.2 The outline of the chapters}

In this thesis, we describe several selected materials, focusing on the calculation of the ab-initio electronic structure and photon spectroscopy modeling. We successfully address the novel quantum electronic states of the materials either via links to the intrinsic underlying electronic structure or to the effects associated with the matrix elements particular to the photon spectroscopy. Here, we provide an outline of each following chapter contained in this thesis:

In chapter 2, we present first-principles calculations to predict several three-dimensional topological insulators in quaternary chalcogenide compounds of compositions \( \text{I}_2\text{-II-IV-VI}_4 \) and ternary famatinite compounds of compositions \( \text{I}_3\text{-V-VI}_4 \). We show that these materials are candidates for 3D topological insulators or can be tuned to obtain topologically interesting phases by manipulating the atomic number.
of the various cations and anions.

In chapter 3, we study the electronic structure and Fermi surface topology of the new iron-based superconductors \( \text{Ca}_{10}(\text{Pt}_3\text{As}_8)(\text{Fe}_2\text{As}_2)_5 \) denoted as the 10-3-8 phase with superconducting transition temperature, \( T_c \), up to 8 K via first principles calculations and angle resolved photoemission spectroscopy (ARPES) experiment [26–28]. The first principles calculations find very small contributions of the platinum density of states at \( E_F \) for the 10-3-8 phase. We also analyze the Fermi surface topology and the band structure close to \( E_F \). Both first principle calculation and ARPES experiment show the well-defined Fermi surfaces with tetragonal symmetry are similar to those of other iron-based superconductors. This indicates a weak interlayer hopping between the FeAs and the PtAs intermediary layers in this Ca-Fe-Pt-As system.

In chapter 4, we present an electronic structure study via modeling X-ray scattering in the deeply inelastic (Compton) regime which provides a direct probe of the correlated many-body ground state in bulk materials while avoiding the surface sensitivity of ARPES. For the iron pnictides, we carry out first principles all-electron calculations of the 2D electron momentum density and the directional Compton profiles in the Fe-based superconductor LaOFeAs, where we identify Fermi surface features in the 2D electron momentum density and the directional Compton profiles, and discuss issues related to the observation of these features via Compton scattering experiments. Furthermore, we demonstrate that the filling of the hole Fermi surface in La\text{O}_{1-x}\text{F}_x\text{FeAs} produces a distinct signature in the Fourier transformed Compton spectrum. For cuprates, we calculate the difference of the 2D-EMD of the high-temperature superconducting cuprate La\text{$_{2-x}$Sr$_x$CuO}_4 (LSCO) at various hole dopings. By comparing to the Compton experimental results, we propose that the \( d_{z^2} \) state participates in the electronic structure near the Fermi energy in addition
to the $d_{x^2-y^2}$. For the liquid silicon study, we investigate the disorder effects and the chemical bonding of liquid silicon by performing the Korringa-Kohn-Rostoker (KKR) coherent potential approximation (CPA) framework simulation.

In chapter 5, we make an approximation to calculate the Lindhard susceptibility $\chi^L(q, \omega)$ efficiently from one particle spectral functions via Fast Fourier Transform. This is related to the dynamic structure factor $S(q, \omega)$ which contains information about density-density correlations. As an example we consider paramagnetic Nd$_{2-x}$Ce$_x$CuO$_4$ (NCCO), which has a relatively simple, nearly two-dimensional metallic Cu-O band near the Fermi level. We identify important features throughout energy and multi-Brillouin zones in momentum space. We also delineate the specific manner in which $\text{Im}\chi^L(q, \omega)$ decays as a function of $q$. These results enable an assessment of the extent to which $S(q, \omega)$ reproduces the RIXS cross-section in a cuprate via direct comparison of the theory with corresponding experiments in extended regions of the momentum space.

1.3 Ab initio calculations with density functional theory

In the last part of this chapter, we elaborate on the formalism of the ab-initio calculation. DFT is based on the finding that ground state energy of a many-body system can be described by a unique functional of the electronic density. In practice, the Kohn-Sham equation[29] (KS-eqn) assumes the electronic density can be calculated from a set of non-interacting one electron wavefunctions embedded within an effective potential environment and the result is exactly consistent with the ground state of the true many-body interacting electron system. Since the nuclei
in chemical compounds are much heavier than electrons, according to the Born-Oppenheimer approximation, we can take the positions of ions as effectively frozen with regard to the moving electrons when we model the effective potential. The total energy functional includes the kinetic energy, nuclear potential, Hartree energy from electron-electron Coulomb repulsion, and exchange and correlation potential,

\[ E(n) = T(n) + \int v(r)n(r)dr + E^H(n) + E^{xc}(n). \]  

(1.1)

In the local density approximation (LDA)[29], one approximates the last exchange and correlation energy by that of a homogeneous electron gas calculated from quantum Monte Carlo simulations. In another approximation known as the generalized gradient approximation (GGA)[30], the exchange and correlation energy does not depend only on the local density, but it further contains the gradient of the local density information. A more sophisticated approximation is to calculate the exact Fock exchange energy and use it in the hybridized functional formalism[31, 32]. However, these more advanced formalisms will not be discussed in this thesis.

In order to find the ground state density of a periodic solid by solving KS-eqn, we utilize full potential linearized augmented plane wave (FLAPW) method as an example[33]. This method starts by assigning the space of a crystal unit cell into two regions. One part is the space filled by non-overlapping spheres centered at the atomic positions which is also known as muffin-tin spheres due to their shape and the corresponding muffin-tin sphere radius is denoted by \( R_{mt} \). The rest of the space is called an interstitial region. When we take the full potential treatment, different
forms of the potential expansion are applied in the two regions:

\[
V(r) = \begin{cases} 
\sum_{lm} V_{lm}(r) Y_{lm}(r) & \text{inside the } R_{mt} \text{ region,} \\
\sum_{G} V_{G}(r) e^{iG \cdot r} & \text{interstitial region,}
\end{cases}
\]  

(1.2)

where \( Y_{lm}(r) \) are spherical harmonic functions. Similar to the potential expansion in the two types of regions, different wavefunction basis sets are applied to the different areas. Inside each \( R_{mt} \) sphere, the basis set is a linear combination of radial functions with coefficients \( \alpha \) and \( \beta \) times spherical harmonics \( Y_{lm}(r) \):

\[
\phi_{kn} = \sum_{lm} (\alpha_{lm}^{kn} u_{l}(r, E_{l}) + \beta_{lm}^{kn} \dot{u}_{l}(r, E_{l})) Y_{lm}(r),
\]  

(1.3)

where \( k \) and \( n \) label the crystal momentum and the band index, \( u_{l}(r, E_{l}) \) is the solution of the radial Schrödinger equation for energy \( E_{l} \) with the corresponding l-orbital quantum number character and \( \dot{u}_{l}(r, E_{l}) \) is the energy derivative of \( u_{l}(r, E_{l}) \) at the energy equal to \( E_{l} \). In the interstitial region, a plane wave expansion is used:

\[
\phi_{kn} = \frac{1}{\sqrt{\Omega}} e^{i(G_{n}+k) \cdot r},
\]  

(1.4)

where \( \Omega \) is the lattice volume, \( G_{n} \) are the reciprocal lattice vectors and \( k \) is the wave vector inside the first Brillouin zone. The two basis sets inside the \( R_{mt} \) and interstitial region need to be matched (in value and slope at the boundary), by having the appropriate coefficients \( \alpha \) and \( \beta \). With the basis set \( \phi_{kn} \), we begin from a guessed wavefunction and then run a series of iteration steps to modify the wavefunction or the corresponding electron density until the wavefunction converges, thereby generating an electron density which reproduces the ground state of the
system. This procedure can be realized as a variational principle procedure in quantum mechanics[1] to reach the total energy minimum of the system. Finally, by running through the variational process, the wavefunction solutions to the Kohn-Sham equations can be expressed in terms of the combination of the $\phi_{kn}$ with the coefficients $\lambda_n$:

$$\psi_{kn} = \sum_n \lambda_n \phi_{kn}.$$  \hspace{1cm} (1.5)

There are other methods, for example, Projector Augmented-Wave Method (PAW) with psudo-potential[34, 35] and Korringa-Kohn-Rostoker (KKR) method[36, 37].

When we deal with a magnetic system, if the spins are restricted to be aligned in the z direction (collinear system), the many-body wavefunction can be fully decomposed as

$$\psi(r) = \psi_i(r, \uparrow), \psi_j(r, \downarrow),$$  \hspace{1cm} (1.6)

where $\psi_i(r, \uparrow), \psi_j(r, \downarrow)$ are the pure spin-up and spin-down states. Otherwise a general noncollinear system should be assumed such that the wavefunctions become two-component spinors with an arbitrary axis for the spin projection and the corresponding noncollinear magnetization density at the position $r$ in real space can be written as[38]

$$m(r) = \frac{e\hbar}{mc} \sum_{\alpha\beta} n^{\alpha\beta}(r) \sigma^{\alpha\beta},$$  \hspace{1cm} (1.7)

where $n(r)$ is the total-density matrix and $\sigma$ represents the Pauli spin matrices.

The spin orbital interaction (SOI) describes the spin interacting with the magnetic field generated by the angular momentum. The SOI is an intrinsic special
relativistic effect. The SOI effect becomes significant when a compound contains heavy chemical elements. Instead of solving fully the special relativistic Dirac equation, the most common treatment is to include the SOI as a second variational perturbation in the KS-eqn[39],

$$H_{so} = \frac{\hbar^2}{4m^2c^2} \frac{1}{r} \frac{dV}{dr} \sigma l,$$

where $\sigma$ denotes the Pauli spin matrices, $m$ is the electron mass, $c$ is the speed of light, $V$ is the atomic spherical potential and $l$ is the orbital angular momentum quantum number.
Chapter 2

First principles prediction of topological insulator*

2.1 Introduction

Several decades ago, the observation of the integer quantum Hall effect (IQHE)[40] demonstrated that the Hall conductivity $\sigma$ of a two-dimensional (2D) electron system is quantized in a strong magnetic field. The expression of $\sigma$ is given by:

$$\sigma = \nu \frac{e^2}{h},$$

(2.1)

where the $\nu$ is an integer number. Later, Thouless, Kohmoto, Nightingale and den Nijs (TKNN) introduced an aspect of topology which distinguished between the IQHE state and a normal insulator[41]. In an IQHE system, the key topological invariant is characterized by the total Chern number which is calculated by inte-

*This chapter is adapted from the following paper.
grating the curl of the Berry phase[42] over the whole Brillouin zone counting all occupied Bloch states $|u_m\rangle$ with band indices $m$,

$$n = \sum_{m=1}^{N} \frac{1}{2\pi} \int d^2k \nabla \times \langle u_m | \nabla_k | u_m \rangle,$$

(2.2)

where $k$ is a crystal momentum restricted in the first Brillouin zone, $N$ is the total number of occupied Bloch states. The total Chern number $n$ is identical to the integer $\nu$ in quantum Hall conductance[41]. In condensed matter, if systems have the same topological phase as classified by the topological invariant, their Hamiltonian $H(k)$ can be adiabatically changed from one to another without closing any band gap.

Another case of symmetry protected topological order is the quantum spin Hall effect (QSH) in a 2D system, which is composed by two distinct quantum Hall states with one holding spin-up electrons the other one holding spin-down electrons. Since electrons are moving in opposite directions in the two quantum Hall states, the total quantum Hall conductance of the system is zero. [43–46], The QSH effect is protected by time reversal symmetry in the presence of strong-spin orbital interaction[43, 44]. Because of the time reversal symmetry protection, the edge states are chiral and they do not vanish in the presence of non-magnetic disorder[43, 47]. Unlike usual parabolic bands in momentum space, these edge states behave like Dirac fermions with a linear energy dispersion. The time reversal operator has the property that, thus

$$T^2 = -1,$$

(2.3)

which implies that for a spin 1/2 system, there always exists two-fold degeneracy
known as Kramers doublets. For this reason, the spin-orbital interaction of 2D-QSH insulator leaves a band degeneracy except at the time reversal invariant momenta $K$ and $K'=-K$. One can also realize a 2D-QSH insulator by looking at the band dispersion between two time reversal invariant momenta. For instance, Fig. 2.1 shows band dispersion between two boundary Kramers degenerate points, $k_a = 0$ and $k_b = \pi$, with different ways that Kramers doublets at $k_a$ and $k_b$ connect to each other. In Fig. 2.1(a), the number of bands crossing the Fermi energy $E_F$ is even, whereas in Fig. 2.1(b) the number is odd. An odd number of crossings indicates a topologically protected state. [48, 49].

In a 3D topological insulator, the edge states become 2D Dirac-like surface states and the Kramers pairs occur at the opposite (e.g. top and bottom) crystal surfaces. Because of a time reversal symmetry, the chiral surface states have opposite signs of in-plane spin with respect to the two time reversal invariant momenta $K$ and $K'=-K$. Over all, there is helical spin texture surrounding each Dirac point corresponding to a $\pi$ Berry phase[48, 49]. The $\mathbb{Z}_2$ invariant index $v_0$ can be either $+1$ or $-1$. An insulator with $v_0$ equal to $-1$ is classified as a topological insulator with a surface
state that is robust even in the presence of non-magnetic impurities. Since the $v_0$ index is independent of the choice of reciprocal-lattice vectors $[2-4]$, the surface state of a topological insulator should exist on any arbitrary crystal surface. In the rest of this chapter, I simply call the $Z_2$ invariant index $v_0$ as $Z_2$.

The discovery of topological insulators$[3-6, 43, 44, 46, 49-51]$ has realized a long-sought opportunity for implementing exotic quantum phenomena in practical materials$[16, 52-57]$. The two-dimensional (2D) quantum spin-Hall effect$[46]$ or the three-dimensional 3D nontrivial topological insulators require a time-reversal invariant number $Z_2 = -1$. Materials with strong spin-orbit coupling (SOC) can host nontrivial topological phases in two as well as three spatial dimensions when the time-reversal symmetry remains invariant. The 3D topological insulating materials realized to date are based on the binary and ternary combinations of mostly heavy metals ranging from Bi/Sb-based binary systems$[5-14]$ to Tl-based ternary compounds$[15]$. However, the potential of topological insulators for technological applications will be greatly enhanced if the topological ground state can be combined with a broken symmetry local order,$[16, 52-57]$ for instance, by adding correlated electronic, magnetic, superconducting and other local order properties to topologically interesting materials$[58-60]$. Furthermore, the possibility of elementary excitations that satisfy non-Abelian statistics – the so-called Majorana fermions, important for topological quantum computers, requires proximity of superconducting and ferromagnetic insulating phases$[16-18]$. These considerations make it clear that it is important to continue to search for materials which can provide greater chemical and structural flexibility through cross-substitution of elements.

The typical topological phases can be classified as trivial band insulator, a non-trivial topological semimetal (zero-bandgap) and a non-trivial topological insulator (finite-bandgap). The corresponding band symmetries near the $\Gamma$ point are
Figure 2.2: Topological band-inversion. Band structures are illustrated schematically near the time-reversal invariant point $\Gamma$ for a trivial band insulator (a), a non-trivial topological semimetal (b), and a non-trivial topological insulator (c). Dark-blue dots mark the twofold degenerate $s$-like states. In the non-trivial case, band inversion occurs when $s$-like states drop below the four-fold degenerate $p$-like states ($J = 3/2$) (blue lines). Owing to lattice distortion, the degeneracy of the $J = 3/2$ states vanishes in the present non-cubic crystal structures.

expressed schematically in Figs. 2.2(a)-(c), respectively. For a trivial topological phase with the $Z_2$ topological order equal to $+1$ in a zinc-blende crystal such as CdTe, a bandgap exists at the Fermi-level as well as the twofold degenerate $s$-like states marked by dark blue dot lies in the conduction band. In the case of a non-trivial topological phase such as HgTe, band inversion occurs in that the $s$-like states drop below the fourfold degenerate $p$-like states of the $J = 3/2$ multiplet yielding $Z_2 = -1$. The fourfold degeneracy is due to the cubic symmetry of the zinc-blende structure. In order to achieve a topological insulating state, the degeneracy must be lifted to open a band gap at $E_F$ (Fig. 2.2(c)). Since the non-cubic famatinites and quaternary chalcogenides are derived from zinc-blende structures, the non-trivial topological insulating phase could be realized in these materials. Indeed, our first-principles calculations predict that a non-trivial 3D topological insulating phase exists in compounds of the famatinite and quaternary chalcogenides families. Among a large number of members of these two family, we give examples of naturally occurring compounds that are mainly Cu-based chalcogenides. We show
that these materials are candidates for 3D topological insulators or can be tuned to obtain topologically interesting phases by manipulating the atomic number of the various cations and anions. A band inversion can occur at a single point $\Gamma$ with large inversion strength, in addition to the opening of a bulk bandgap throughout the Brillouin zone. We also discuss how the two investigated families of compounds are related to each other by cross-substitution of cations in the underlying tetragonal structure.

### 2.2 Crystal structures of quaternary chalcogenide compounds and ternary famatinite compounds

We begin the discussion with the ternary compounds I$_3$-V-VI$_4$ which are known to crystallize in famatinite, sphalerite-type structures. These materials belong to the
space group $I\bar{4}2m$ in which the group VI atoms are surrounded by three group I and one group V atoms. As a result, they obey the octet rule and form a (I-VI)$_3$(V-VI) superlattice structure, see Fig. 2.3(a) for Cu$_3$SbSe$_4$ as an example. In contrast to the high-symmetry zinc-blende sublattice of ternary compounds[15, 61, 62], famatinite structure naturally achieves a tetragonal lattice distortion along the $c-$axis ($c < 2a$) due to the turning on of a strong interlayer coupling between the two cation planes. This also results in a mismatch between the cation-anion bond lengths in the two zinc-blende formula units of the unit cell which helps lower the total energy of the famatinite ground state phase.

Famatinite compounds I$_3$-V-VI$_4$ evolve to the quaternary chalcogenides I$_2$-II-IV-VI$_4$ when one of the group-I element of the former compounds is replaced by one group-II element and the group-V element is changed to group-IV element as seen in Fig. 2.3(b) for the example of Cu$_2$CdSbSe$_4$. High resolution transmission electron microscopy and X-ray diffraction analysis shows that these materials have tetragonal crystallographic structure which belongs to $I\bar{4}2m$ space group. The structure can be described by a (I-II)$_2$(II-VI)(IV-VI) sublattice of the two zinc-blende formula units.[63] The substitution of larger atoms in the tetragonal basis of these systems helps expand the lattice and thus both the tetragonal distortion and the crystal-field splitting increase considerably. Although these changes are relatively small, quaternary chalcogenides have greater structural freedom and possess more complicated electronic and chemical properties than their binary or ternary counterparts.

2.3 Computation method

The crystal structures of ternary famatinite compounds and quaternary chalcogenide compounds are taken from the literature [64–73]. First-principles band calculations
were performed with the linear augmented-plane-wave (LAPW) method using the WIEN2K package [33] within the framework of the density functional theory (DFT). The generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof [30] was used to describe the exchange-correlation potential. Spin orbital coupling (SOC) was included as a second variational step using a basis of scalar-relativistic eigenfunctions. Here, we report the theoretical prediction of three dimensional topological insulator in the pristine state of existing materials in the quaternary chalcogenide compounds of composition I$_2$-II-IV-VI$_4$ and in ternary famatinite of compositions of I$_3$-V-VI$_4$. These two families of compounds are related by cross-substitution of cations in the underlying tetragonal structure. Quaternary semiconductors particularly exhibit more flexible properties due to their enhanced chemical and structural freedom and provide surface quantum control through substitution with magnetic, non-magnetic and other elements involving correlated electrons.

2.4 Electronic structure of quaternary chalcogenide compounds and ternary famatinite compounds

The bulk band structures along the high symmetry path $M(\pi,\pi) - \Gamma(0,0) - X(\pi,0)$ are shown in Fig. 2.4 for two representative compounds Cu$_3$SbS$_4$ and Cu$_3$SbSe$_4$ which belong to the famatinite family. In the ground state of these compounds, the structural compression along the c-axis (i.e. $c < 2a$) compared to the cubic zinc-blende lattice lifts the four-fold degeneracy of the cation $p$–states at the $\Gamma$–point owing to the crystal-field splitting. In Cu$_3$SbS$_4$, an insulating energy gap between the $p$–states is present at the Fermi level throughout the Brillouin zone as shown in Fig. 2.4(a). However, as the nuclear charge of the anion increases from S to Se, the
Figure 2.4: Bulk band dispersion of famatinite compounds with non-trivial topological phases. (a)-(b) Electronic structure of Cu$_3$SbS$_4$ and Cu$_3$SbSe$_4$. In both figures, the black dots are the $p$-states of the cation sites while the size of the blue dots is proportional to the probability of $s$-orbital occupation on the anion site. Gray shadings highlight the low-energy region near the Γ-point where the band-inversion has occurred.

Conduction band drops below the Fermi level at the X-point, yielding an electron pocket as seen in Fig. 2.4(b). Simultaneously, the valence band maximum gradually moves above the Fermi-level making Cu$_3$SbSe$_4$ a metal. Nevertheless, since a finite direct gap persists throughout the Brillouin zone, the $Z_2$ topological invariant can still be defined for the valence bands in these two materials and the inverted band order is retained at only the Γ-point. Therefore, Cu$_3$SbS$_4$ and Cu$_3$SbSe$_4$ are a topologically non-trivial insulator and a metal, respectively.

The mutation of the crystal structure from the ternary to a quaternary compound is also reflected in the electronic structure of these two families of materials. Due to tetragonal symmetry, all the Cu-based quaternary materials shown in Fig. 2.5 host a gap in the $p$-states close to the Fermi-level, where the magnitude of the gap depends on the extra cation cross-substitutions. With increasing atomic mass from Zn to Cd to Hg, this gap decreases mainly due to the downshift of the $s$-like conduction bands at the Γ-point. The Fermi-level goes through the energy gap
of the $p$--states in most materials, revealing a topological insulating state in these compounds. However, in two compounds, Cu$_2$ZnGeTe$_4$ and Cu$_2$CdGeTe$_4$, the conduction band minimum is shifted to the $M$ point and drops below the Fermi level to form bulk electron pockets (e.g. see Fig. 2.5(g),(m)). Simultaneously, the valence band maximum rises above the Fermi level at the $\Gamma$--point, making these systems intrinsically bulk metallic. We find a very similar nature of the band-inversion across these materials in which the split $p$--states lie in energy above the twofold-degenerate $s$-- states at a single time-reversal momentum $\Gamma$--point, representing a band-inversion relative to the natural order of $s$--and $p$--type orbital derived band structure. Therefore, these materials are intrinsically bulk non-trivial topological insulators or semimetals, except Cu$_2$ZnGeS$_4$, Cu$_2$ZnSnS$_4$, and Cu$_2$HgGeS$_4$, which are ordinary band insulators. Note that one of the predicted topological non-trivial cases in Fig. 2.5, Cu$_2$HgSnS$_4$ has I-4 space group symmetry, which is slightly different from the I-42m symmetry of other quaternary chalcogenide compounds. In Table. I, we list the computed band gap values at the $\Gamma$-point of the ternary famatinite and quaternary chalcogenide compounds. The band inversion strength (BIS), which is defined as the energy difference between the lowest conduction state to the highest $s$-like valence state at the $\Gamma$-point, is also given.

2.5 Topological phase transition

Finally, I show how the band structure can be tuned to generate a non-trivial topological phase from a trivial band insulator. Specifically, we take advantage of the structural freedom in the ternary famatinite and quaternary chalcogenides. In Fig. 2.6, we illustrate this route using the example of going from the quaternary chalcogenide Cu$_2$ZnSnS$_4$ as the starting point to the ternary famatinite Cu$_3$SbS$_4$. 39
Figure 2.5: Electronic structure of quaternary chalcogenide compounds. Bulk electronic structure of several Cu-based quaternary chalcogenides. Black dots, blue dots and gray shading have the same meaning as in Fig. 2.4. Compounds without a gray-shaded area are ordinary band insulators without any inverted band symmetries whereas others are non-trivial topological insulators or semimetals with $Z_2 = -1$ topological order.
Table 2.1: Band gap and band inversion strength (BIS, see text) based on GGA for the 2 ternary famatinite and 13 quaternary chalcogenide compounds investigated. In the column marked ‘Gap’, notation ‘Metal’ indicates that the lowest conduction band drops below the Fermi-level and has no band gap at the Γ-point. In the column marked ‘BIS’, positive values imply topologically nontrivial cases, while a negative value gives the band gap energy for topologically trivial cases.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Gap (eV)</th>
<th>BIS(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$_3$SbS$_4$</td>
<td>0.042</td>
<td>0.198</td>
</tr>
<tr>
<td>Cu$_3$SbSe$_4$</td>
<td>Metal</td>
<td>0.615</td>
</tr>
<tr>
<td>Cu$_2$ZnGeSe$_4$</td>
<td>0.069</td>
<td>0.165</td>
</tr>
<tr>
<td>Cu$_2$ZnSnSe$_4$</td>
<td>0.056</td>
<td>0.315</td>
</tr>
<tr>
<td>Cu$_2$CdGeSe$_4$</td>
<td>0.003</td>
<td>0.131</td>
</tr>
<tr>
<td>Cu$_2$CdSnSe$_4$</td>
<td>0.003</td>
<td>0.254</td>
</tr>
<tr>
<td>Cu$_2$HgGeSe$_4$</td>
<td>0.006</td>
<td>0.385</td>
</tr>
<tr>
<td>Cu$_2$HgSnSe$_4$</td>
<td>0.007</td>
<td>0.543</td>
</tr>
<tr>
<td>Cu$_2$ZnGeTe$_4$</td>
<td>Metal</td>
<td>0.348</td>
</tr>
<tr>
<td>Cu$_2$ZnGeS$_4$</td>
<td>0.481</td>
<td>-0.481</td>
</tr>
<tr>
<td>Cu$_2$ZnSnS$_4$</td>
<td>0.115</td>
<td>-0.115</td>
</tr>
<tr>
<td>Cu$_2$CdSnS$_4$</td>
<td>0.033</td>
<td>0.078</td>
</tr>
<tr>
<td>Cu$_2$HgGeS$_4$</td>
<td>0.016</td>
<td>-0.016</td>
</tr>
<tr>
<td>Cu$_2$HgSnS$_4$</td>
<td>0.060</td>
<td>0.217</td>
</tr>
<tr>
<td>Cu$_2$CdGeTe$_4$</td>
<td>Metal</td>
<td>0.288</td>
</tr>
</tbody>
</table>
Figure 2.6: Topological phase transition between quaternary chalcogenide and famatinite compounds. Bulk electronic structure of the compounds at various stages of the topological phase transition process driven by tuning the atomic number $Z$, the lattice constant and the internal displacement of the anion is shown. (a) and (b) are trivial band insulators, (c) is at the critical point of the topological phase transition, whereas (d) and (e) are non-trivial topological insulators.

Note that the topological phase transition is a generic feature and there exist numerous such routes. In their pristine conditions, Cu$_2$ZnSnS$_4$ is a trivial band insulator whereas Cu$_3$SbS$_4$ is a topological insulator as discussed above in connection with Figs. 2.5(i) and 2.4(b). We systematically manipulate the overall crystal structure of our starting compound by making the atomic number $Z$ of the constituent atoms, the lattice constant and the internal displacement of the anion as variable parameters.

To illustrate this process, we denote the atomic numbers $Z$’s of various elements by $Z_{M1}$, $Z_{M2}$, $Z_{M3}$, and $Z_{M4}$. For our starting element Cu$_2$ZnSnS$_4$, we have $Z_{M1}$=29, $Z_{M2}$=30-$x$, $Z_{M3}$=50+$x$, $Z_{M4}$=16, where $x$ varies between 0 to 1 in the phase transformation process. At each step of changing the parameter $x$, we also change the lattice constant and the internal displacements of the anion by keeping the same ratio of changes corresponding to the change in $x$ of atomic numbers (Z’$s)$.
from Cu$_2$ZnSnS$_4$ to Cu$_3$SbS$_4$. Note that variation of the $Z$'s can also be considered as a doping effect in the spirit of the virtual crystal approximation [74, 75] while the total nuclear charge is kept fixed throughout this process. It will be interesting to examine doping effects using first principles approaches [76–79] for tuning topologically interesting electronic structures.

We monitor the band structure along the high symmetry path $M(\pi, \pi) \rightarrow \Gamma(0, 0) \rightarrow X(\pi, 0)$ at every step of the transition process in Figs. 2.6(a)-(e). While the overall band-structure remains very much the same, the band characters and the band gap vary dramatically. In Fig. 2.6(b), upon increasing $x$ by 0.25, the size of the band gap at $\Gamma$ starts to shrink compared to the parent compound in Fig. 2.6(a), although the $s$–character continues to dominate in the conduction band (blue dots). The critical point is reached when the value of $x$ is increased to 0.5 in Fig. 2.6(c), at which point the bottom of the conduction band and the top of the valence band touch at the single momentum point $\Gamma$ leading to a critical topological point. A full band inversion is achieved in Fig. 2.6(d) which recreates an insulating band gap which is topologically non-trivial in nature and the $s$–like orbital character shifts well below the valence band. Finally, in Fig. 2.6(e), when $x$ equals 1, Cu$_3$SbS$_4$ emerges as a non-trivial topological insulator.

2.6 Summary

We have shown via first-principle calculations that some ternary famatinite and quaternary chalogenide compounds are non-trivial topological insulators in their pristine phase. The large tuning possibilities available in the quaternary compounds add versatility in using topological insulators in multifunctional spin-polarized quantum and optical information processing applications. Notably, the copper-based quater-
nary chalcogenides are known to have non-linear optoelectronic and thermodynamics applications.[63]. There is a similar work done by Chen’s group[80], where they also proposed that some of the multinary chalcogenides are potential candidates for non-trivial topological insulators.
Chapter 3

Iron-based superconductor

Ca\textsubscript{10}(Pt\textsubscript{3}As\textsubscript{8})(Fe\textsubscript{2}As\textsubscript{2})\textsubscript{5} DFT and ARPES study*

In 2008, the Hosono group announced the synthesis of LaFeAsO, an iron pnictide high-temperature superconductor, with $T_c = 26$ K\cite{19}. This discovery immediately triggered a superconductivity revolution of the iron-based superconductor. Just one year after the discovery of LaFeAsO, the record $T_c$ in iron-based superconductors was pushed up to 56 K\cite{20-22}. Unlike a conventional superconductor, the first principles calculation indicates that the electron-phonon interaction is not strong enough to support the $T_c$ measured in iron pnictides\cite{81}. According to the phase diagram, the parent compound of iron pnictides is spin density wave (SDW) type antiferromagnetic metal \cite{82, 83}. Chemical doping suppresses the SDW and brings

*This chapter is adapted from the following paper:
the system into a superconducting state[84, 85]. In the LDA calculation, the electrons near the Fermi energy are mainly in Fe 3d orbitals[86]. The Fe 3d multiband nature of the iron pnictides shown in the LDA calculation quantitatively agrees with angle-resolved photoemission spectroscopy (ARPES) results, which observe hole like bands at Γ and electron bands at X [87, 88]. In this chapter we study the electronic structure and Fermi surface topology of the new iron-based superconductors Ca$_{10}$(Pt$_3$As$_8$)(Fe$_2$As$_2$)$_5$ denoted as the 10-3-8 phase with $T_c = 8$ K[26–28]. The Ca-Fe-Pt-As system has FeAs tetrahedral layers and complex PtAs intermediary layers where both of the layers offer the flexibility for systematically adjusted chemical compositions. The correlation between the number of intermediary layers and the superconducting transition temperature ($T_c$) in high-Tc cuprates can be found in the materials such as the Bi$_2$Sr$_2$Ca$_{n-1}$Cu$_n$O$_{2n+4+x}$ (n = 1-3) series[25]. In iron-pnictides, the Ca-Fe-Pt-As system provides a unique platform to understand the relation between the effect of the intralayer (hopping within the FeAs layers) and interlayer (hopping between the FeAs and Ca-Pt-As layers) physics and the microscopic mechanism of the high-Tc superconductivity in iron-based superconductors. In this study, we perform first principles calculations of the 10-3-8 phase electronic structure and compare to the ARPES experiment. The first principles calculations find a very small contribution of the platinum density of states at $E_F$ for the 10-3-8 phase. We also analyze the Fermi surface topology and the band structure close to $E_F$ and both first principle calculations and ARPES experiment show well-defined Fermi surfaces with tetragonal symmetry similar to those of other iron-based superconductors. This evidence indicates a weak interlayer hopping between the FeAs and the PtAs intermediary layers in this Ca-Fe-Pt-As system.
3.1 Angle-Resolved Photoemission Spectroscopy

Among the various measurement techniques in condensed matter, ARPES serves as a direct probe of the electronic band energy-momentum dispersions of solids. An ARPES experiment starts by shining light onto an aligned crystal; then the incident light kicks an electron out of the solid into the vacuum; finally, the electron enters a detector mounted at a certain angle to record the kinetic energy of the excited electron. According to the conservation of momentum and energy, the photoelectron momentum $k_i$ inside the crystal is:

$$|k_i| = \frac{\hbar}{\sqrt{2mE_{\text{kin}}}}, \quad (3.1)$$

where the kinetic energy $E_{\text{kin}}$ measured in the experiment can be expressed as:

$$E_{\text{kin}} = h\nu - E_B + V_0. \quad (3.2)$$

In this equation, $h\nu$ is the incident photon energy and the binding energy, $E_B$ is measured from Fermi energy, $E_F$, and $V_0$ is the potential barrier that an electron needs to overcome to get out of the crystal. Since the emitted electron can be considered to be in a free electron final state when the incident kinetic energy is large, we can take $V_0$ as a step function.

The photoelectron momentum can be decomposed into the in-plane part, $k_{i||}$, parallel to the crystal surface and the out-of-plane part, $k_{i\perp}$, which is perpendicular to the crystal surface. The parallel components of the electron momentum can be written as:

$$\hbar k_{i||} = \sqrt{2mE_{\text{kin}}} \sin \theta, \quad (3.3)$$
where \( \theta \) is emission angle measured from the normal direction of the crystal surface. Because of the presence of the crystal translational symmetry, the parallel component is conserved. However, the perpendicular momentum \( k_{i\perp} \) is not conserved and it is affected by the potential step:

\[
k_{i\perp} = \frac{1}{\hbar} \sqrt{2m(E_{\text{kin}} \cos^2 \theta + V_0)}
\]  

(3.4)

At a certain photon energy, we can rotate the detector to collect the data from various angles and map the band energy dispersion in the in-plane momentum space. By varying the incident photon energy, we can scan the energy dispersion along the \( k_{i\perp} \) direction known as \( k_z \) dispersion of the band structure. Using these procedures, we construct the energy dispersion and Fermi surface of a solid in momentum space.

To interpret ARPES data, the intensity of the ARPES \( I(\omega,k) \) as function of momentum \( k \) and energy \( \omega \) can be approximated as

\[
I(\omega,k) \sim |M_{f,i}^k|^2 A(\omega,k) f(\omega,k)
\]  

(3.5)

where \( M_{f,i}^k \) denotes a one electron dipole matrix element effects which includes the effect of the photon energy, photon polarization, and the orbital symmetry effect of the initial states and the final state effect, \( A(\omega,k) \) represents a one electron spectral function and \( f(\omega,k) \) is the Fermi function. The spectral weight \( A(\omega,k) \) is given by

\[
A(\omega,k) = -\frac{1}{\pi} \frac{\Sigma''(\omega,k)}{[\omega - E_n(k) + \Sigma'(\omega,k)]^2 + [\Sigma''(\omega,k)]^2},
\]  

(3.6)

where \( \Sigma(\omega,k) = \Sigma'(\omega,k) + i\Sigma''(\omega,k) \) is the self-energy induced by the electron-electron or electron-phonon interaction, and \( E_n(k) \) is the band energy associated with Bloch state characterized by momentum \( k \) and band index \( n \). If \( \Sigma(\omega,k) \) is
Figure 3.1: Crystal structure of the 10-3-8 phase, Ca\(_{10}\)(Pt\(_3\)As\(_8\))(Fe\(_2\)As\(_2\))\(_5\). In the PtAs layer, the atom Pt-1 denotes the in-plane platinum atom and the atom Pt-2 denotes the out-of-plane platinum atom. The figure shows both possible sites for the Pt-2, one above the PtAs plane and the other one below the PtAs plane. For visual clarity, we use the labels Pt-2 and Pt-2’ to denote the Pt sites above and below the plane respectively in this figure. The limited Pt-Pt bond distance prevents both Pt-2 sites from being occupied simultaneously.

neglected, the ARPES intensity be directly mapped to the bandstructure of the occupied states calculated by the first principles calculation. However, the situation is much more complicated once we consider the matrix element term. In the discussion below of the electronic structure of the Ca-Fe-Pt-As iron pnictide, the simplest bandstructure and ARPES comparison has been made.

### 3.2 Crystallographic properties of the Ca\(_{10}\)(Pt\(_3\)As\(_8\))(Fe\(_2\)As\(_2\))\(_5\) single crystal

The Ca\(_{10}\)(Pt\(_3\)As\(_8\))(Fe\(_2\)As\(_2\))\(_5\) crystal has triclinic symmetry. As shown in Fig.3.1 the unit cell has side \(a = b = 8.759\), \(c = 10.641\) Å and the angles of the unit cell...
cell spanned by these lattice vectors are $\alpha = 94.744^\circ$, $\beta = 104.335^\circ$ and $\gamma = 90.044^\circ$. Note that the in-plane angle $\gamma = 90.044$ is very close to $90^\circ$.[28] If we neglect the PtAs layers in the entire unit cell, the Ca atoms and FeAs layers reside in a simpler sublattice of approximately tetragonal symmetry. The corresponding sublattice vector lengths are $a_t = b_t = 3.917$ and $c_t = 20.548$ Å. Actually, the main triclinic atomic arrangement arises in the PtAs layers. The in-plane triclinic unit cell is essentially a $\sqrt{5}$ superlattice that forms along the (210) direction of the tetragonal cell, making an in-plane inclusion angle of $\theta = \arctan(1/2) = 26.56^\circ$ and a length relation $a = \sqrt{5} a_t$ between the triclinic lattices and the FeAs sublattice. On the other hand, the top and bottom surface centers of the triclinic unit cell displace horizontally via an in-plane vector $(a_t/2, a_t/2)$. Note that an out-of-plane Pt atom (denoted as Pt-2 in Fig.3.1) can only occupy one of the two position on either side of the PtAs plane. If two out-of-plane Pt atoms occupy both sites, the Pt-Pt separations will be too small. Therefore, the either sides of below-plane sites are randomly occupied with a 50% probability in an real crystal. There is no experimental evidence that there is any long range order to lift this disorder. [28].

Based on the discussion of FeAs, we suggested that if the interlayer hopping between the PtAs and FeAs layers is weak, the ARPES Fermi surface should reflect a similar topology to the other prototype iron pnictides, with possibly weak FeAs shadow bands associated with superlattice folding and additional features associated with the PtAs layer.

3.3 Orbital character of the electronic structure

Here we present the first-principles calculations of the electronic structure based on the density functional theory (DFT) framework plus the local density approxima-
The exchange-correlation functional proposed by D. M. Ceperley and B. J. Alder and projector augmented wave method are implemented in the VASP package[89, 90]. The experimental crystal structure of the 10-3-8 phase is used[28]. In the calculation, the off-plane Pt atom is assigned to a position above the PtAs plane of the 10-3-8 unit cell. The self-consistency of the bulk calculation is done with $8 \times 8 \times 8$ k-point mesh and $E_F$ is adjusted assuming zero doping. For the in-plane Fermi surface calculation, the k-point mesh is increased to $201 \times 201$ in the kx-ky plane. The total energy convergence with respect to the number of k-points is 0.3 meV per atom. The kinetic energy cutoff is 280 eV[34]. Spin-orbit coupling is not included.

In Fig. 3.2 we show the calculated partial DOS (PDOS) of the 10-3-8 phase for the in-plane and out-of-plane Pt atoms in the left column as well as the total density of states (DOS) of the 10-3-8 phase in the right column. In the left column, both in-plane and out-plane Pt atoms show similar low PDOS behavior near $E_F$. In the right column, the total DOS in the vicinity of $E_F$ is dominated by Fe 3d orbitals, which is similar to other prototype iron pnictides, like $\text{AEFe}_2\text{As}_2$ (122, $\text{AE} = \text{Ca, Sr, Ba, etc.}$). In Fig. 3.3 the calculated LDA band structure along high symmetry
3.3 Bulk band dispersion of Ca$_{10}$(Pt$_3$As$_8$)(Fe$_2$As$_2$)$_5$. Calculated band structure of 10-3-8 in the triclinic Brillouin zone. Red dots indicate the contribution of platinum orbitals.

Directions is shown in the triclinic Brillouin zone. Red dots are used to highlight Pt orbital character. The upper panel shows the band structure at $k_c = 0$ and the lower panel shows the band structure at $k_c = \pi/c$. At the X point, we see a Pt associated band with strong $k_z$ dispersion near $E_F$. Near the $\Gamma$ point, the innermost band has stronger $k_z$ dispersion than the other two hole-like iron bands. This band is hybridized with the Pt d$_{xz}$ orbitals.

3.4 Super-lattice folding Fermi surface of

Ca$_{10}$(Pt$_3$As$_8$)(Fe$_2$As$_2$)$_5$

In Fig. 3.4, we present the Fermi surface maps for four different photon energies. The most important observation from the ARPES signal shown in Figs. 3.4 is that the electronic structure of the 10-3-8 phase reveals tetragonal symmetry and the periodicity of the experimental Brillouin zone is proportional to $\pi/a_t$ of the FeAs layer sublattice rather than $\pi/a$ in the $k_x - k_y$ plane. It turns out that the triclinic
arrangement and larger supercell periodicity of the platinum atoms have very little influence on the electronic structure seen in photoemission. Therefore, we can deduce that the orbital hybridization of band structure from the PtAs intermediary layers has to be weak. Qualitatively, the ARPES electronic structure of the 10-3-8 phase exhibits a similar electronic structure to other prototype pnictides; the shapes, sizes, and Fermi velocities of the $X_0$ Fermi pockets show very little difference from those of the 122 parent compounds [8, 91–98].

Despite the overall similarity, we note that there are some observable differences between the Fermi surface of the 10-3-8 phase and that of the prototype iron pnictides. When we compare explicitly the in-plane ARPES Fermi surfaces of the 10-3-8
phase to BaFe$_2$As$_2$\cite{99}, we first find that the Dirac-cone-like Fermi dots around the X points in BaFe$_2$As$_2$ \cite{99} are absent in the 10-3-8 phase [seen most clearly in the 42 eV panel of Fig. 3.4]. Since these dots are a direct consequence of the long range antiferromagnetic order present in the 122 compound\cite{5, 8, 99, 100}, this is therefore consistent with the absence in 10-3-8 phase of an antiferromagnetic signature in transport measurements up to room temperature\cite{28}.

Since the ARPES experimental data give no sign of the triclinic Fermi surfaces, we assume that the potential from the $\sqrt{5}$ superlattice arising from the PtAs layers is very weak, in which case we can approximately “unfold” the LDA triclinic superlattice band structure shown in Fig. 3.5 left panel into the tetragonal BZ as shown in Fig. 3.5 right panel. The tetragonal, X$_0$, and M$_0$ points form a subset of the supercell X and M points. Therefore, we systematically erase all superlattice FS maps not associated with the tetragonal symmetry points. From Fig. 3.5, we see that this process works well for the Fe Fermi surfaces, reproducing the familiar 122 structure. The fate of the electron like Pt bands (the four petal-like small pockets near $\Gamma$) under this unfolding process is less clear, but it should be noted that these pockets are not clearly distinguished by ARPES.

3.5 Summary

In conclusion, we have presented a systematic ab initio calculation and experimental ARPES study on the electronic structure and Fermi surface topology of the Ca-Fe-Pt-As 10-3-8 superconductors. The calculation demonstrates the triclinic band structure can be unfolded into the tetragonal Brillouin zone as long as the potential from the $\sqrt{5}$ supper-lattice arising from the PtAs layer is weak. This result explains why experimental ARPES data see only the reduced tetragonal electronic structure
Figure 3.5: Calculated Fermi surfaces of Ca$_{10}$(Pt$_3$As$_8$)(Fe$_2$As$_2$)$_5$. Fermi surfaces sketched in the triclinic zone and the corresponding Fermi surfaces unfolded into the tetragonal zone

with little $k_z$ dispersion. This evidence points to the conclusion that the interlayer hopping from the PtAs layer in this system is weak. Also, the Dirac-cone-like Fermi dots around X are absent in the 10-3-8 phase, consistent with the absence of long-range antiferromagnetism in this compound. The Ca-Fe-Pt-As superconductors are ideal systems for the study of interlayer hopping in the iron-based superconductors. The present detailed study of the electronic structure of the 10-3-8 phase serves as an important step in that direction.
Chapter 4

High-resolution Compton scattering and electronic momentum density*

Compton scattering is a fascinating spectroscopy for investigating truly bulk electronic structure of materials by using advanced synchrotron light sources and renewed detector technology [101–104]. Since the X-ray photon energy is so high, *This chapter is adapted from the following papers:

Y.J. Wang et al., 'High Resolution Compton Scattering as a Probe of the Fermi Surface in the Iron-based Superconductor LaO$_{1-x}$F$_x$FeAs', J. Supercond. Nov. Magn. 22 569 (2009);

Yung Jui Wang et al., 'Proposal to determine the Fermi-surface topology of a doped iron-based superconductor using bulk-sensitive Fourier-transform Compton scattering', Phys. Rev. B 81 092501 (2010);

W. Al-Sawai et al., 'Bulk Fermi surface and momentum density in heavily doped La$_{2-x}$Sr$_x$CuO$_4$ using high-resolution Compton scattering and positron annihilation spectroscopies', Phys. Rev. B 85 115109 (2012);

Y. Sakurai et al., 'Imaging Doped Holes in a Cuprate Superconductor with High-Resolution Compton Scattering' Science 332 698 (2011);

Compton scattering determines the many-body ground state of the system. Based on the impulse approximation (sudden approximation), Compton scattering observes the electronic structure of the sample in terms of the electron momentum density, which is the square of the wavefunction represented in the extended momentum space scheme. The Compton profiles generally depend on the scattering direction, requiring the measurement of directional Compton profiles. Moreover, for a metallic system, these directional Compton profiles should capture the fingerprints of Fermi surface topology of the sample. In this chapter, we first review the background of the Compton scattering measurement and the formalism of Compton profile and electron momentum density calculation. In the following four sections, we discuss the Fermi surface topology and the associated orbital characters for the high temperature superconducting iron-pnictides and cuprates obtained by performing Compton profiles and we compare calculated momentum density to the available Compton scattering data. In the last section, we compute Compton profiles of liquid silicon based on the Korringa-Kohn-Rostoker (KKR) coherent potential approximation (CPA) framework to determine the disorder effects on the chemical bonding in liquid silicon. We also compare the KKR-CPA result to the Car-Parrinello molecular dynamics modeling, Wannier function simulations, and the experimental Compton profiles.
4.1 Theory of Compton profiles and electron momentum density

4.1.1 Inelastic x-ray scattering spectrum and Compton profiles

Compton scattering emerges in the inelastic x-ray scattering spectrum when the incident x-ray has a very high energy. For instance, the synchrotron-based inelastic x-ray scattering at the BL08W beam line of SPring-8 produces high energy x-ray photons with energy 116 keV for Compton profile experiments with high momentum resolution of 0.16 a.u.. When we use such a hot x-ray to probe the electrons, it causes high energy and momentum transfer between photon and electron during the experiment, which is called the Compton limit in inelastic x-ray scattering. For this reason, the Compton scattering experiment is well described by the impulse approximation, which says that electron electron interactions can be totally ignored during the inelastic photon-electron scattering. This simplifies the interpretation of Compton scattering compared to the usual inelastic x-ray scattering spectrum. Since there is no need to consider excitation effects, Compton profiles directly connect to the wavefunction of electrons in their ground states, which is an important advantage compared to the other light scattering spectra. Compton scattering is also a truly bulk sensitive probe for the electronic properties of solids, which avoids experimental complications regarding defects, impurities, and surface state issues.

Before looking at the Compton scattering limit, we begin by discussing the standard inelastic x-ray scattering cross-section. In the photon-electron scattering event, the generalized Kramers-Heisenberg formula gives the probability of scattering pho-
tons. If one neglects the resonance effect and the spin of the electron, the cross-section of inelastic x-ray scattering \( \frac{d^2 \sigma}{d \Omega d \hbar \omega} \) can be described by the equation[107]:

\[
\frac{d^2 \sigma}{d \Omega d \hbar \omega} = a_0^2 \left( \frac{\omega_2}{\omega_1} \right) |e_1 \cdot e_2^*|^2 S(q, \omega),
\]

(4.1)

where \( \hbar \omega_1/\hbar \omega_2 \) is energy of the incident/outgoing photon, \( \omega \equiv \omega_1 - \omega_2 \), the energy difference between incident and outgoing photon, \( e_1/e_2 \) the polarization of the incident/outgoing photon, \( S(q, \omega) \) the dynamical structure factor and \( a_0 \) denotes the classical electron radius given by

\[
a_0 = \frac{e^2}{4\pi \varepsilon_0 mc^2},
\]

(4.2)

where \( e \) denotes an electron charge, \( \varepsilon_0 \) the vacuum permittivity, \( c \) the speed of light, \( m \) the mass of an electron. At zero temperature \( T = 0K \), \( S(q, \omega) \) is given by

\[
S(q, \omega) = \sum_{i,f} \sum_{\alpha,\beta} \langle i | e^{-iq \cdot r_\alpha} | f \rangle \langle f | e^{iq \cdot r_\beta} | i \rangle \delta(E_i - E_f + \hbar \omega).
\]

(4.3)

In the expression of \( S(q, \omega) \), the \( |i\rangle, |f\rangle \) denotes initial/final states with their corresponding energy \( E_i, E_f \) and \( r_\alpha/r_\beta \) are the positions at which the electron density, \( \rho(r) \), is measured, where

\[
\rho(r) \equiv \sum_\alpha \delta(r - r_\alpha).
\]

(4.4)

The Fourier transform of electron density, \( \rho(r) \), to momentum space can be written as

\[
\rho(q) = \int d^3r \sum_\alpha e^{-iq \cdot r} \delta(r - r_\alpha) = \sum_\alpha e^{-iq \cdot r_\alpha}.
\]

(4.5)

The \( \delta \)-function in \( S(q, \omega) \) basically determines the conservation of energy in the scattering event and mathematically, we can deal with this \( \delta \)-function in terms of
its Fourier transform:

$$\delta(E_i - E_f + \hbar \omega) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt e^{-i\omega t} e^{i(E_f - E_i)/\hbar}. \quad (4.6)$$

We define the Hamiltonian of the system as $H = H_0 + V$ which contains the kinetic energy $H_0$ and the potential $V$. In order to analyze the expression for $S(q,\omega)$, we recall that the relation between the Hamiltonian of the system $H$ and the corresponding eigenstate $|E\rangle$ can be described by:

$$e^{-i\tilde{E}t/\hbar} |E\rangle = e^{-iHt/\hbar} |E\rangle, \quad (4.7)$$

where $\tilde{E}$ is an eigenenergy with respect to $H$. With the above equations, we can rewrite $S(q,\omega)$ as

$$S(q,\omega) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt e^{-i\omega t} \sum_{i,f} \sum_{\alpha,\beta} \langle i|e^{-iq\cdot r_\alpha}|f\rangle \langle f|e^{iHt/\hbar} e^{iq\cdot r_\beta} e^{-iHt/\hbar}|i\rangle. \quad (4.8)$$

A relatively simple schematic of Compton scattering is given in Fig. 4.1. In the Compton limit, we can apply the impulse approximation to $S(q,\omega)$[107, 108]. For such a high momentum and energy transfer, the scattering time is so fast that the target electron in its ground state has no chance to interact with other electrons. Therefore, the effect of electronic excited states can be entirely neglected. It helps to simplify the derivation of $S(q,\omega)$ in the Compton limit by merely focusing on the diagonal density matrix elements of one electron at position characterized by $r_1 = r_\alpha = r_\beta$. The off diagonal density matrix elements such that $r_\alpha \neq r_\beta$ associated with two electron interactions are neglected. For the same reason of the extremely short scattering time, the potential acting on the moving electron can be treated as constant. That means the initial and final states feel the same instantaneous
constant potential [108], and we set $V$ equal to zero in the equation of $H = H_0 + V$. We assume the final state $|f\rangle$ in $S(q, \omega)$ is the free electron final state $|p_f\rangle$ with respect to $H_0$. Now, the expression of $S(q, \omega)$ in the impulse approximation is:

$$S(q, \omega) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt e^{-i\omega t} \sum_{i, p_f} \langle i|e^{-iq \cdot r_1}|p_f\rangle \langle p_f|e^{iH_0 t/\hbar}e^{iq \cdot r_1}e^{-iH_0 t/\hbar}|i\rangle. \quad (4.9)$$

We can use a many body wavefunction with a number $N$ of electrons $\psi(r_1, r_2, \ldots, r_N)$ to be the initial state $|i\rangle$ in $S(q, \omega)$ such that $|i\rangle = \psi(r_1, r_2, \ldots, r_N)$, where $r_1, r_2, \ldots, r_N$ are the positions associated with the N electrons. Next, we introduce the one electron density matrix $\Gamma_1(r_1|r'_1)$ as:

$$\Gamma_1(r_1|r'_1) \equiv \int \psi(r_1, r_2, \ldots, r_N)^* \psi(r_1', r_2', \ldots, r_N') dr_2 \ldots dr_N dr'_2 \ldots dr'_N, \quad (4.10)$$
and we also define that:

\[ e^{iH_0t/\hbar}|p_f\rangle = e^{ip_f^2t/(2m\hbar)}|p_f\rangle, \tag{4.11} \]

where \( m \) denotes the electron mass. By evaluating \( S(q,\omega) \) in Eq. (4.9) with Eq. (4.10) and Eq. (4.11), we obtain:

\[
S(q,\omega) = \frac{1}{2\pi\hbar} \sum_{p_f} \int_{-\infty}^{\infty} dt e^{-i\omega t + ip_f^2t/(2m\hbar) - i(p_f - \hbar q)^2t/(2m\hbar)}
\times \int dr_1 dr_1' e^{i(p_f/\hbar - q) \cdot r_1} e^{-i(p_f/\hbar - q) \cdot r_1'} \Gamma_1(r_1| r_1'). \tag{4.12} \]

If we define a new momentum variable \( p \) as:

\[ p = p_f - \hbar q, \tag{4.13} \]

we can obtain the one electron density matrix in momentum space \( \Gamma_1(p|p) \) which is calculated by the Fourier transform of \( \Gamma_1(r_1| r_1') \):

\[
\Gamma_1(p|p) = \left(\frac{1}{2\pi\hbar}\right)^3 \int \Gamma_1(r_1| r_1') e^{i(p - p') \cdot r_1/\hbar} dr_1 dr_1'. \tag{4.14} \]

By using the integral definition of the \( \delta \)-function such as Eq. (4.6) and Eq. (4.14) the expression of \( S(q,\omega) \) becomes:

\[
S(q,\omega) = \frac{1}{2\pi\hbar} \int dp \Gamma_1(p|p) \delta(h\omega - \hbar^2q^2/2m - \hbar p \cdot q/m). \tag{4.15} \]

Note that the diagonal matrix \( \Gamma_1(p_1|p_1) \) is just the electron density \( \rho(p) \) in momentum space:

\[ \rho(p) = \Gamma_1(p|p), \tag{4.16} \]
which yields:

\[ S(q, \omega) = \frac{1}{2\pi \hbar} \int dp \rho(p) \delta(\hbar \omega - \hbar^2 q^2 / 2m - \hbar p \cdot q / m). \] (4.17)

For a solid, we can rewrite Eq. (4.16) in terms of the occupied Bloch wavefunction \( \psi_n(r) \) characterized by band index \( n \):

\[ \rho(p) = \left( \frac{1}{2\pi \hbar} \right)^3 \sum_n | \int \psi_n(r) e^{-i p \cdot r / \hbar} dr |^2 . \] (4.18)

Comparing Eq. (4.17) to Eq. (4.1), the cross section of Compton scattering is

\[ \frac{d^2 \sigma}{d\Omega d\hbar \omega} = a_0^2 \left( \frac{\omega_2}{\omega_1} \right) |e_1 \cdot e_2^*|^2 \frac{1}{2\pi \hbar} \int dp \rho(p) \delta(\hbar \omega - \hbar^2 q^2 / 2m - \hbar p \cdot q / m). \] (4.19)

If we choose \( q \) to lie in \( z \)-direction in a Compton experiment, the \( \delta \)-function in Eq. (4.19) describes that at each \( q \) and \( \omega \), the scattered intensity is associated with those electrons having a fixed value of momentum \( p_z \) in the direction of \( q \) (see Fig. 4.1). Therefore, the cross section in Eq. (4.19) is proportional to the Compton profile \( J(p_z) \),

\[ J(q) \equiv \int \rho(p) dp_z dp_y, \] (4.20)

According to Eq. (4.20), the Compton profiles measured in a Compton scattering experiment are the projections of the two dimensional integrated electron momentum density \( \rho(p) \) along the scattering direction as a function of the momentum \( p_z \).*

*The formalism of Compton scattering cross-section can be extended beyond the impulse approximation by using Dyson orbitals, which permits the analysis and interpretation of electronic transitions in correlated electron materials. This can be found in the paper: 'Compton scattering beyond the impulse approximation' I. G. Kaplan, B. Barbiellini and A. Bansil, Phys. Rev. B 68 235104 (2003)
4.1.2 KKR-CPA formalism of momentum density calculation

So far, we have derived the electron momentum density (EMD), $\rho(p)$, contribution to Compton profiles. Indeed, we can rewrite the expression of EMD in terms of a one-particle Green function at $T = 0$:

$$\rho(p) = -\frac{1}{\pi} \int_{-\infty}^{E_F} dE \Im G(p, E),$$  \hspace{1cm} (4.21)

where $E$ is the energy, $p$ the momentum, and the one-particle Green function is given by

$$G(p, E) = \sum_n \frac{|\psi_n(p)|^2}{E - E_n + i\epsilon},$$  \hspace{1cm} (4.22)

where $E_n$ is the band energy of the Bloch state characterized by band index $n$ and $\epsilon$ is an infinitesimal number. The computation of the one-particle Green function is an essential part to solve the Kohn-Sham equation in the KKR method based on multiple scattering theory. In this method, a scattering matrix is constructed based on scattering of electrons based on the individual atoms in a solid; and it further requires a description of the multiple scattering by all of the atoms in the solid such that the incoming wave at each atomic site matches the outgoing waves from all the other atomic sites.[109]. Therefore, it is natural to link the computation of EMD to the electronic structure of materials determined by the KKR method.

Here, we discuss the EMD calculation method based on KKR-CPA formalism[110, 111], which works for either disordered systems or perfect crystals. For a given disordered binary alloy $A_xB_{1-x}$, the one electron Hamiltonian is given by

$$H = H_0 + \sum_{\eta} V^{A,B}_{\eta}(r),$$  \hspace{1cm} (4.23)
where \( H_0 \) is the kinetic energy and the crystal potential in the second term of \( H \) is given by a superposition of spherical muffin-tin potentials \( V_{\eta}^{A,B}(r) \) centered on ionic sites \( \eta \):

\[
V_{\eta}^{A,B}(r) = \begin{cases} 
V_{\eta}^{A}(r) & \text{with probability } x, \text{ for } |r| < R_{mt}, \\
V_{\eta}^{B}(r) & \text{with probability } 1 - x, \text{ for } |r| < R_{mt},
\end{cases}
\]  

(4.24)

\( V_{\eta}^{A}(r) \) and \( V_{\eta}^{B}(r) \) in the above equation denote the lattice sites of the crystal which are randomly occupied by the chemical elements A and B, with relative probabilities given by the ratios, \( x \) and \( 1 - x \) respectively, and \( R_{mt} \) is the muffin radius chosen such that different muffin-tin spheres do not overlap. The interstitial potential outside the muffin-tin spheres is zero:

\[
V_{\eta}^{A,B}(r) = 0 \text{ for } |r| > R_{mt}.
\]  

(4.25)

To calculate the EMD of the alloy, we can use the KKR method within the framework of the single-site approximation to the Hamiltonian \( H \). For instance, in the average t-matrix approximation (ATA) and the coherent potential (CPA) approximation, the disordered alloy is replaced by an ordered crystal of suitably chosen effective atoms. In the ATA scatterer, the effective atom is characterized by the averaged scattering matrix \( t^{\text{ata}}(p,p') \) as function of momentum \( p \) and \( p' \):

\[
t^{\text{ata}}(p,p') = xt^{A}(p,p') + (1-x)t^{B}(p,p'),
\]  

(4.26)

where \( t^{A}(p,p') \) and \( t^{B}(p,p') \) are defined as t-matrices that describe the scattering properties caused by the atom A and the atom B in the system respectively. ATA is a non-selfconsistent approximation. The CPA scatterer is more sophisticated and
needs to be determined self-consistently by the constraint that, on the average, there is no scattering from a single A or B atom in the effective medium. For the binary alloy $A_xB_{1-x}$ case, one can build up the corresponding effective CPA t-matrix $t^{\text{cpa}}(p, p')$ as:

$$
t^{\text{cpa}}(p, p') = t^{\text{ata}}(p, p') - \left[ t^A(p, \xi) - t^{\text{cpa}}(p, \xi) \right] F^{\text{cpa}}(E) \left[ t^B(\xi, p') - t^{\text{cpa}}(\xi, p') \right], \quad (4.27)
$$

where $\xi \equiv \sqrt{E}$ and $F^{\text{cpa}}(E)$ is given by:

$$
F^{\text{cpa}}(E) = \frac{1}{N} \sum_k B(k, E) \left[ 1 - t^{\text{cpa}}(\xi, \xi) B(k, E) \right]^{-1}. \quad (4.28)
$$

Here, $N$ is the number of atoms per unit volume, $k$ the crystal momentum limited in the first Brillouin zone, and $B(k, E)$ is the matrix of the KKR structure function which is the Fourier transform of a function $B^{mj}_{LL'}$. In real space, $B^{mj}_{LL'}$ is related to the free-electron Green function $G_0(r + R_n, r' + R'_n)$:

$$
G_0(r + R_n, r' + R'_n) = \sum_{LL'} Y_L(r) j_l(\xi r) B^{mj}_{LL'} j_{l'}(\xi r') Y_{L'}(r'), \quad (4.29)
$$

where $R_n$ denotes lattice vectors, $Y_L(r)$ the spherical harmonic function with respect to positron $r$, $L \equiv (l, m)$ the composite angular momentum index with the orbital quantum number $l$ and magnetic quantum number $m$, $j_l(\xi r)$ the spherical Bessel function. In the KKR-CPA computation of the EMD with effective atoms, the expression of $\rho(p)$ can be written in terms of $t^{\text{cpa}}$ matrices:

$$
\rho(p) = -\frac{1}{\pi} \int_{-\infty}^{E_F} dE \text{Im} \left[ \frac{1}{E - p^2 + i\epsilon} + \frac{(4\pi)^2 N}{(E - p^2 + i\epsilon)^2} \sum_{LL'} Y_L(p) [F^{1}_{LL'} + F^2_{LL'}] Y_{L'}(p) \right], \quad (4.30)
$$

where $E_F$ denotes Fermi Energy, $\epsilon$ an infinitesimal number, $Y_L(p)$ the spherical
harmonic function with respect to momentum \( p \), the expression of \( F_{LL'}^{1} \):

\[
F_{LL'}^{1} = \left[ t_{l}^{cpa}(p,p) - \frac{t_{l}^{cpa}(\xi,p)t_{l}^{cpa}(\xi,p)}{t_{l}^{cpa}(\xi,\xi)} \right] \delta_{LL'},
\]

(4.31)

and the expression of \( F_{LL'}^{2} \):

\[
F_{LL'}^{2} = \frac{t_{l}^{cpa}(p,\xi)}{t_{l}^{cpa}(\xi,\xi) \left[ t_{l}^{cpa}(\xi,\xi) \right]^{-1} - B(\xi,E)} \left[ \frac{1}{t_{l}^{cpa}(\xi,p)} \right]_{LL'}^{t_{l}^{cpa}(\xi,\xi)}.
\]

(4.32)

Here, \( t_{l}^{cpa}(\xi,\xi) \), \( t_{l}^{cpa}(p,p) \) and \( t_{l}^{cpa}(\xi,p) \) are the matrix elements of \( t^{cpa} \) characterized by the orbital quantum number \( l \).

In a perfect crystal limit, we assume there are only A atoms in the \( A_{x}B_{1-x} \) system with \( x \) equal to 1 and the t-matrices of the system depend only on A atoms. Therefore, we use the new notation \( t_{l}^{A} \) to replace \( t_{l}^{cpa} \) in Eq. (4.31) and (4.32). It means that the matrix elements of \( t^{cpa} \) are now only depending on the \( t^{A} \) matrix. It can be shown that Eq. (4.31) vanishes in a perfect crystal limit.

Next, we want to evaluate Eq. (4.30) in the perfect crystal limit[77]. We can have the \( t_{l}^{A} \) matrix elements in terms of \( l \) and \( \xi \) dependent phase shifts \( \phi_{l}^{A}(\xi) \) caused by the potential of A atoms. The diagonal matrix element of \( t_{l}^{A}(\xi,\xi) \) is given by:

\[
t_{l}^{A}(\xi,\xi) = -\frac{1}{\xi} \sin \left[ \phi_{l}^{A}(\xi) \right] e^{i \left[ \phi_{l}^{A}(\xi) \right]}.
\]

(4.33)

The off-diagonal matrix element of \( t_{l}^{A}(p,\xi) \) is:

\[
t_{l}^{A}(p,\xi) = s_{l}^{A}(p,E) \cot \left[ \phi_{l}^{A}(\xi) \right] t_{l}^{A}(\xi,\xi),
\]

(4.34)

In the above equation, \( s_{l}^{A}(p,E) \) is the Hankel transform of the crystal potential \( V^{A} \).
times $\psi^A_i(r, E)$:

$$s_i^A(p, E) = -\frac{1}{\xi} \int_0^{R_{mi}} r^2 j_l(pr) V^A(r) \psi^A_i(r, E) dr,$$

(4.35)

where $\psi^A_i(r, E)$ is the regular solution of the radial Schrödinger equation with the Hamiltonian $H(x = 1)$ in Eq. (4.23). Here, we define a new coefficient $S_L(p, E)$:

$$S_L(p, E) \equiv s_i^A(p, E) \cot \left[ \phi^A_i(\xi) \right] Y_L(p),$$

(4.36)

and introducing a term $M_{LL'}$:

$$M_{LL'} = \left[ t^A_i(\xi, \xi)^{-1} - B(\xi, E) \right]^{-1}_{LL'}. $$

(4.37)

The secular equation of $[t^A(\xi, \xi)^{-1} - B(\xi, E)]$ is written as:

$$||t^A(\xi, \xi)^{-1} - B(k, E)|| = 0,$$

(4.38)

with solutions associated with the band energies $E_n$ of Bloch states in a crystal. By using Eqs. (4.33)-(4.38), the expression of $\rho(p)$ in a perfect crystal limit can be shown to be:

$$\rho(p) = (4\pi)^2 N \sum_{E_n \leq E_F} \frac{1}{(E_n - p^2)^2} \frac{\sum_{LL'} S_L(p, E) M_{LL'}(k, E) S_{LL'}(p, E)}{dE ||(t^A(\xi, \xi)^{-1} - B(\xi, E)||_{E = E_n}},$$

(4.39)

In the derivation of Eq. (4.39), the identity has been used:

$$\text{Im} \frac{1}{||t^{-1}(\xi, \xi) - B(\xi, E)||} = -\pi \sum_n \delta(||(t^A(\xi, \xi)^{-1} - B(\xi, E)||_{E = E_n})$$

$$= -\pi \sum_n \frac{\delta(E - E_n)}{dE ||t^A(\xi, \xi)^{-1} - B(\xi, E)||_{E = E_n}}$$

(4.40)
In general, the EMD computations base on the KKR-CPA formalism shown in Eq. (4.30) and (4.39) is equivalent Eq. (4.18) in the previous section.

4.2 Probing Fermi surface topology in the iron-based superconductor LaO$_{1-x}$F$_x$FeAs via Compton scattering

In this section, we apply the above formalism to study Compton profiles in iron-based superconductors. In particular, we are interested in whether Compton scattering can be used to probe the Fermi surface of these materials. First principles calculations\[81, 86\] report that the density of states (DOS) near the Fermi level ($E_F$) is predominantly due to Fe-$d$ orbitals. Owing to the approximate $S_4$ symmetry of the FeAs tetrahedra, these Fe-$d$ orbitals split into lower lying $e_g$ ($d_{x^2-y^2},d_{3z^2-r^2}$) and higher lying $t_{2g}$ states ($d_{xy},d_{yz},d_{zx}$)\[86, 112\]. Theoretical calculations\[81, 86\] suggest that superconductivity may not be caused by electron-phonon coupling. The theoretical prediction of a striped anti-ferromagnetic spin-density-wave (SDW) ground state existing in the LaOFeAs\[113\] was confirmed by neutron scattering\[82\].

Superconductivity can appear in LaOFeAs with either hole doping\[114\] or electron doping\[19, 115\]. Just as in the cuprates, the anti-ferromagnetic instability, which is suppressed by doping, is one candidate to explain unconventional superconductivity. The superconducting gap in LaFeAsO$_{1-x}$F$_x$ with $x \approx 10\%$ has been determined from the optical reflectance in the far-infrared region\[115\].

The Fermi surface (FS) topology is a key ingredient for understanding high temperature superconductivity in iron based layered pnictides. The so-called $s_{\pm}$ model \[116–119\] predicts superconducting gaps of one sign on the FS cylindrical
hole sheets near $\Gamma(0, 0)$ and of another sign on cylindrical electron sheets at $M(\pi, \pi)$. Doping $x$ is needed to move the system away from the magnetic instabilities due to FS nesting [86, 120, 121]. In the superconducting material, spin fluctuations (related to residual FS nesting) may provide a glue for the Cooper pairs [116]. However, a complete filling of the hole FS at a certain electron doping will eventually lead to the suppression of the spin fluctuation glue. The exact value $x_c$ of this critical doping might be affected by subtle correlation effects [122].

Experimental information regarding the FS topology comes mostly from angle resolved photoemission spectroscopy (ARPES) which is a surface sensitive probe. [121, 123–126] There are indications however that suitable LaO$_{1-x}$F$_x$FeAs samples for ARPES on a large doping $x$ range are difficult to obtain. Moreover, since the doping level in the bulk could be different from that at the surface [117], the FS signal should be checked with bulk probes. Since the FS information from quantum oscillation studies[127, 128] can be distorted because of the required high magnetic fields, we suggest determination of the FS topology via Compton scattering measurements. Positron annihilation would provide another bulk-sensitive probe [101].

Below, we present the results of first-principles computations of the 2D-projected electron momentum density (2D-EMD) and Compton profiles (CPs) in the iron-based superconductor LaOFeAs. We discuss Fermi surface (FS) images in the 2D-EMD and the EMD anisotropy defined by subtracting a smooth isotropic function from the spectrum. Our analysis of the CPs reveals that FS features related to hole- as well as electron-pockets are more prominent in the CP when the momentum transfer vector lies along the [100] rather than the [110] direction.
4.2.1 Methods

The electronic structure calculations are based on the local density approximation (LDA) of density functional theory. An all-electron fully charge self-consistent semi-relativistic KKR method is used\[76\]. The compound LaO$_{1-x}$F$_x$FeAs has a simple tetragonal structure (space-group P4/nmm) as shown in Fig. 4.2. We use the experimental lattice parameters[129] of LaO$_{0.87}$F$_{0.13}$FeAs in which no spin-density-wave order was observed in neutron-scattering. A non-spin-polarized calculation was performed and the magnetic structure was neglected. Self-consistency was obtained for $x=0$ and the effects of doping $x$ were treated within a rigid band model by shifting the Fermi energy to accommodate the proper number of electrons. The convergence of the crystal potential was approximately $10^{-4}$ Ry. The electron momentum density (EMD) $\rho(p_x, p_y, p_z)$ was calculated on a momentum mesh with step $(\Delta p_x, \Delta p_y, \Delta p_z) = (1/16a, 1/16a, 1/16c)2\pi$. The total number of points was $14.58 \times 10^6$ within a sphere of radius 12.8 a.u. in momentum space. The 2D-EMD

Figure 4.2: Crystal structure and the tetragonal unit cell of LaOFeAs composed by LaO and FeAs tetrahedron layers.
\( \rho^{2d}(p_x, p_y) \) was calculated by the KKR formalism as

\[
\rho^{2d}(p_x, p_y) = \int \rho(p_x, p_y, p_z) dp_z \tag{4.41}
\]

while the Compton profile \( J(p_z) \) is given by

\[
J(p_z) = \int \int \rho(p_x, p_y, p_z) dp_x dp_y. \tag{4.42}
\]

Recall that in a Compton scattering experiment, one measures a directional Compton profile (CP), \( J(p_z) \), which is related to the twice integrated ground-state electron momentum density \( \rho(p_x, p_y, p_z) \) for high momentum and energy transfer\[130\]. The exploration of FS topology with the aid of Compton scattering is complicated by the double integral in Eq. 4.41. As a result, FS breaks in \( \rho(p_x, p_y, p_z) \) do not usually induce rapid variations in \( J(p_z) \). A possible approach to deal with this problem is to measure CPs along many different directions and use state-of-the-art reconstruction methods based on the autocorrelation function \( B(x, y, z) \) to obtain \( \rho(p_x, p_y, p_z) \) \[131\].

In Fig. 4.3(a), we show the LDA band structure of LaOFeAs. For \( x=0 \), three bands cross \( E_F \) near the \( \Gamma \) point, forming hole-like FSs [marked by green dots in (c)] while two bands cross \( E_F \) near \( M(\pi, \pi) \), forming electron-like FSs [marked by blue dots in (c)]. As electrons are added, the \( \Gamma \) centered FSs shrink and completely disappear around \( x=0.13 \). The bands near \( E_F \) are dominated by the Fe \( d \) orbitals. The FeAs layers are separated by insulating LaO layers, with the result that the dispersion of these bands along \( \Gamma - Z \) is small and, apart from a small \( \Gamma \)-centered 3D hole pocket, the FSs are quasi two-dimensional. Based on the fully three-dimensional computations, we take advantage of this quasi two-dimensionality and investigate
quantities in the $k_x - k_y$ plane by integrating out the $k_z$ component.

Figure 4.3: (a) LDA band structure of LaOFeAs at $k_z=0$. (b) Theoretical 2D-EMD $\rho^{2d}(p_x, p_y)$ of LaOFeAs projected onto the (001) plane, normalized to $\rho^{2d}(0, 0)$. (c) 2D-LCW folded momentum density. Computed hole-like (green dots) and electron-like (blue dots) Fermi surfaces are marked. Note momentum is given in (c) in units of $2\pi/a$, where $a=7.6052$ a.u.

Figure 4.3(b) shows a map of the theoretical 2D-EMD[131]. This distribution can be described by an inverted bell shape with fourfold symmetry. The peak is at the zone center with tails extending over several unit cells. The dense contours around high symmetry points are signatures of the FS discontinuities. All these features are hidden behind the large inverted bell shaped signal. In order to investigate the Fermi surface topology in detail, we have employed both the 2D Lock-Crisp-West (LCW) folding[131, 132] and the 2D-EMD anisotropy.

The 2D-LCW folding of the projected 2D-EMD $\rho^{2d}(p_x, p_y)$ is defined by

$$n(k_x, k_y) = \sum_{G_x, G_y} \rho^{2d}(k_x + G_x, k_y + G_y),$$

where $n(k_x, k_y)$ gives the number of occupied states at the point $(k_x, k_y)$ in the first Brillouin zone by summing over all projected reciprocal lattice vectors $(G_x, G_y)$. 

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The effect of the matrix element can be eliminated via the 2D-LCW folding process of Eq. (3), which thus provides a tool for focusing on the FS features. The theoretical 2D-LCW folding shown in Fig. 4.3(c) has been smoothed using a Gaussian function with $\Delta \rho = 0.17$ a.u., which is typical of the resolution available in high resolution Compton scattering experiments. The positions and sizes of the FS pockets of LaOFeAs found by the KKR band calculation are shown as green dots for hole pockets and as blue dots for electron pockets. Before the application of the aforementioned Gaussian broadening, $n(k_x, k_y)$ shows a maximum $n_{\text{max}}=29.4$ and a minimum $n_{\text{min}}=24.5$. The maximum of $n(k_x, k_y)$ at $M(\pi, \pi)$ is associated with the electron pockets; the minimum at $\Gamma (0,0)$ is related to the hole pockets. The difference $n_{\text{max}} - n_{\text{min}}=4.9$ is consistent with five bands crossing the Fermi level in the LDA calculation. Even after including experimental resolution, the FS features are still quite visible as seen in Fig. 4.3(c).

Figure 4.4: Calculated 2D-EMD anisotropy in the parent compound LaOFeAs. Letters A and B label $\Gamma$ points for odd and even $k$-space sublattices of the hole-pockets as discussed in the text. The red lines are centered at $M$ points. The rapid changes in the momentum density along these lines are FS signatures of the electron-pockets.
4.2.2 2D-EMD anisotropy and Fermi surface break

Figure 4.4 shows the 2D-EMD anisotropy, found by subtracting a smooth isotropic function from the 2D-EMD. FS features show up as closely spaced contours around the Γ(0,0) and M(π,π) points. The momentum density around the Γ(or M) points in the higher zones is seen to be lower (or higher) than the average due to the presence of hole pockets (or electron pockets). The zone-to-zone variation of intensity of these features can be understood as a matrix element effect associated with the symmetry of the hole pockets at Γ and electron pockets at M. For instance, the weak signal at the origin (0,0) can be understood since the bands crossing the Fermi level are predominantly d orbitals, whereas only an s orbital yields a significant contribution to the momentum density at the origin. Owing to interference effects, the FS features display a marked modulation from zone to zone. The Fe atoms in the unit cell are located at high symmetry positions, Fe1 (0,0,0) and Fe2 (0.5,0.5,0) (in units of lattice constants). The wavefunctions of these two Fe atoms show a constructive and destructive interference in momentum space, which can be represented by the structure factor $S_G = 1 + e^{-i\pi(m+n)/a}$, where $G = (m\hat{x} + n\hat{y})[2\pi/a]$ is a reciprocal lattice vector. Whereas $S_G$ is largest when $(m+n)$ is even, $S_G$ vanishes when $(m+n)$ is odd. Therefore, the FS features show the alternating pattern seen in Fig. 4.4. For the FS hole-pockets centered at Γ, the FS features at B for odd $(m+n)$ are much weaker than those at A for even $(m+n)$. Deviations from this rule are an indication of hybridization of the Fe orbitals with other orbitals. For the FS electron-pockets centered at M, a similar pattern is found. In Fig. 4.4 we show red lines crossing the B sites. The change of the momentum density along the direction in which $\Delta m = \Delta n$ is more rapid than changes along a direction for which $\Delta m = -\Delta n$. 

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4.2.3 Directional Compton profiles and Fermi surface break

The theoretical CPs along [100], [110] and [001] are shown in Fig. 4.5(a). The CP along [001] is a smooth curve, since there are no Fermi breaks along this direction. Thus, we can use this profile for highlighting FS features from the other profiles.

![Diagram showing directional Compton profiles and Fermi surface break](image)

Figure 4.5: (a) Directional Compton profiles (CPs) $J(p)$ along [100], [001] and [110] for $x=0$. (b)-(e) Differences $\Delta J(p)$ between various pairs of CPs for undoped ($x = 0$) and doped ($x = 0.15$) cases as indicated in the figures. Vertical arrows mark FS crossings with the electron pockets centered at $M$ (blue) and the hole pockets at $\Gamma$ (green) as discussed in the text.
In Fig. 4.5(b), we subtract the [001] from the [100] CP. The resulting periodic patterns occur at the Γ and M points and are associated with hole pockets (green arrows) and electron pockets (blue arrows) respectively. The CP has a dip within the hole pocket regions and a hump within the electron pocket regions. The FS breaks are clearly visible and should be amenable to exploration via high resolution Compton scattering experiments with statistics high enough to numerically differentiate the difference profiles.

The same strategy is applied to the [110] CP in Fig. 4.5(c); however, the FS features are not as clear as in the [100] direction. The main reason is that the contributions of the hole- and electron-like FSs projected on [110] overlap each other and tend to cancel out. The interference pattern acts to amplify this effect as follows. When the EMD is projected to form the CP, the projections of A and B are distinct points along [110]. For hole pockets (centered at Γ), A (B) has strong (weak) signal associated with FS breaks. For electron pockets [centered at \((\pi, \pi)\)], the red lines in the EMD are parallel to [110] at the projection of A, while they are perpendicular to [110] at the projection of B. We notice that the FS signals are strong only along the red lines. Therefore, at the projection of A (B), the FS signals are strong (weak) for both hole and electron pockets. In simple terms, at A, strong hole pocket signals cancel strong electron pocket signals, while at B weak hole pocket signals cancel weak electron pocket signals. Thus [110] is not a suitable direction for studying the Fermi breaks.

Next, we discuss how FS breaks disappear with electron doping. The Fermi level for \(x=0.15\) shown in Fig. 1(a) at 0.075eV is obtained by a rigid band shift. At this doping level, all hole pockets around Γ are removed. As indicated by blue arrows in Fig. 4.5(d), the FS breaks associated with the FS electron pockets remain in the [100] CP. Compared to Fig. 4.5(b), the dips associated with the hole pockets have
completely disappeared (green arrows). In Fig. 4.5(e), we subtract the [100] CP with 15% doping from the [100] CP with 0% doping. An interesting pattern of periodic maxima and minima appears around the Γ and $M$ points which are identical with the positions of the hole and electron pockets, respectively. This may prove the most promising method of detecting FS signatures.

4.2.4 Conclusion

In this section, we have identified FS signatures in the momentum density of LaOFeAs, finding alternating intensity patterns in the 2D-EMD due to the crystal symmetry. FS signatures for both hole- and electron pockets are shown to be relatively strong in the [100] CP in comparison to the [110] CP. We thus suggest that the [100] direction is the most favorable one for detecting FS signatures. Our analysis also indicates that a doping-dependent experimental study should be able to determine at which doping level the hole-like FS’s disappear. The work sets a baseline for future experimental Compton scattering studies in the iron-pnictides.

4.3 A bulk-sensitive method for determining Fermi surface topology of doped iron-based superconductors through Fourier transform Compton Scattering

In this section, we use first-principles calculations of the Compton scattering spectra to demonstrate that the filling of the hole Fermi surface in LaO$_{1-x}$F$_x$FeAs produces a distinct signature in the Fourier transformed EMDs and Compton spectrum. We
thus show how the critical concentration $x_c$, where hole Fermi surface pieces are filled up and the superconductivity mediated by antiferromagnetic spin fluctuations is expected to be suppressed, can be obtained in a bulk-sensitive manner. In the previous section, we have discussed the Fermi surface features of LaOFeAs in EMDs and Compton profiles in momentum space. Here, we will present a much simpler and more robust method to analyze the Fermi surface features in real space.

### 4.3.1 Fourier transform of 2D-EMD in real space

In experiments, one adopts the so-called direct Fourier-transform method [131] to reconstruct $\rho^{2D}(p_x, p_y)$ (e.g. see Eq. (4.41)) from several directional CPs $J(p_z)$ measured in the $(001)$ plane. This method uses the autocorrelation function $B(x, y, z)$ which is straightforwardly defined as the Fourier transformation of the momentum density

$$B(x, y, z) = \int \int \int dp_x dp_y dp_z \times \rho(p_x, p_y, p_z) \exp[i(p_x x + p_y y + p_z z)].$$

Since $\rho(p_x, p_y, p_z)$ can be expressed as a sum over the momentum density of the wavefunctions $\psi_j(x, y, z)$ by using the convolution theorem, it can be shown that $B(x, y, z)$ is the autocorrelation of the wavefunctions

$$B(x, y, z) = \sum_j n_j \int \int \int dudvdw \times \psi_j(x + u, y + v, z + w)\psi_j^*(u, v, w),$$

where $n_j$ is the occupation number of the natural orbital $\psi_j(x, y, z)$. In the experiments $B(x, y, z)$ is obtained directly along a given direction by taking the 1D-Fourier
transform of the CP along that direction. Then, once a set of $B$’s has been calculated, a fine mesh is set up in real space and $B(x, y, z)$ is obtained at every mesh point by interpolation. Finally, if desired, an inverse Fourier transform of $B(x, y, 0)$ yields the distribution $\rho^{2D}(p_x, p_y)$.

### 4.3.2 Doping dependence of 2D-EMD in real space

We can get more precise information on wave function symmetry near the Fermi surface (FS) by taking difference maps between two nearby dopings,

$$
\Delta \rho_{x_2}(p_x, p_y) = \rho_{x_2}^{2D}(p_x, p_y) - \rho_{x_1}^{2D}(p_x, p_y),
$$

(4.46)

where $x_2$ and $x_1$ are two different doping levels such that $x_2 > x_1$. The subtraction in Eq. 4.46 acts as a projector on the Fermi level subspace with the advantage of eliminating the large isotropic contribution of the core and some irrelevant valence electrons. The interpretation of Eq. 4.46 may become more complicated when the

![Figure 4.6: $\Delta \rho_{x_2}(p_x, p_y)$ for $x_2 = 0.15$ and $x_1 = 0.10$. The yellow labels indicate the high symmetry positions $\Gamma$ and $M$ in momentum space.](image)

in Eq. 4.46 acts as a projector on the Fermi level subspace with the advantage of eliminating the large isotropic contribution of the core and some irrelevant valence electrons. The interpretation of Eq. 4.46 may become more complicated when the

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system contains strong electronic correlations, or some magnetic or charge density wave order. The difference for \( x_2 = 0.15 \) and \( x_1 = 0.10 \) shown in Fig. 4.6 displays interesting FS effects strongly modulated by Fe d wave function effects. The corresponding Fourier transform \( \Delta B|_{x_1}^{x_2}(x, y) \), Fig. 4.7, separates the different length scales in real space, which contribute to the oscillations in \( \Delta \rho|_{x_1}^{x_2}(p_x, p_y) \). Thus, the peaks in the autocorrelation function \( \Delta B \) indicate characteristic distances over which wave functions at the Fermi level are coherent. The peaks in Fig. 4.7 mostly stem from the Fe d orbitals since these largely dominate at the Fermi level [86]. In fact, from Fig. 4.7 one can see that the main peaks correlate very well with the iron sublattice. However, note that there are weaker features, marked ”As”, which correlate with the positions of the As atoms. Since the bands near the Fermi level mostly consist of Fe \( d_{xz}, d_{yz} \) and \( d_{x^2-y^2} \) orbitals[133] , Fig. 4.7 reveals these characters in real space. To facilitate comparisons we normalize \( \Delta B \) to unity at the origin.

Figure 4.7: \( \Delta B|_{x_1}^{x_2}(x, y) \) for \( x_2 = 0.15 \) and \( x_1 = 0.10 \). The yellow labels Fe indicate the atoms in the iron sublattice; green labels As indicate the \((x, y)\)-projection of the atoms in the arsenic sublattice. Atomic assignments are based on the assumption that Fe is at the origin.
We employ filtering techniques to enhance the sensitivity of the $\Delta B$-maps to particular FS cylinders. Thus, in Fig. 4.8 we artificially remove the FS around M by applying a filter cutting out the Bloch states near M. As a result some Fe peaks essentially disappear, revealing the wavefunction characters of the $\Gamma$ cylinders. In the same way, Fig. 4.9 shows the corresponding maps for the electron cylinders, generated by filtering out the cylinders at $\Gamma$. This filtering procedure can be tested by calculating $\Delta B|_{x_2}^{x_2}(x, y)$ at higher doping for $x_2$ and $x_1$, where the number of added electrons is sufficient to remove the hole cylinders at $\Gamma$ without any filtering needed. Note that the exact value of $x_2$ is sensitive to the assumption of rigid band filling and to the exchange-correlation functional used.[120, 122, 125] The result is very similar to Fig. 4.9, confirming that the present filter is an efficient way of sorting out contributions from different FS cylinders and this filtering procedure can also be applied to experimental Compton data. By comparing Fig. 4.8 and Fig. 4.9, it is clear that the hole FSs and the electron FSs give strikingly different contributions

![Figure 4.8: $\Delta B|_{x_2}^{x_2}(x, y)$ for $x_2 = 0.15$ and $x_1 = 0.10$, after artificially removing all the Bloch states around M. Atomic assignments are based on the assumption that Fe is at the origin.](image)
to $\Delta B|_{x_1}(x, y)$.

In Fig. 4.8 [hole FSs], there is a peak at every Fe site, with a corresponding weaker network of peaks at As sites. In contrast, for the electron contribution in Fig. 4.9, there are dips at some Fe sites and the As sites signatures are not visible. Some of these features can be readily understood with the phase factor $\exp(i\mathbf{k} \cdot \mathbf{r})$ of the Bloch wave function. At the band bottom, $\Gamma$, $\mathbf{k} = 0$ and all atoms are in phase (bonding). At the top of the band, $(\pi, \pi)$, the phase factor is $(-1)^{m+n}$ i.e., perfectly antibonding. Since the FSs are small cylinders near $\Gamma$ and $(\pi, \pi)$ respectively, their $\Delta B$-maps are dominated by this interference term.

Figure 4.9: $\Delta B|_{x_2}(x, y)$ for $x_2 = 0.15$ and $x_1 = 0.10$, after artificially removing all the Bloch states around $\Gamma$. Atomic assignments are based on the assumption that Fe is at origin.

Interestingly, in Fig. 4.10, we show the contrasting behavior of the autocorrelation function $\Delta B$ near the second neighbor Fe, at a distance about 7.6 a.u. from the origin along the [100]-direction. Here, we point out again that the cut of $\Delta B$ with $\Gamma$ FS is derived from $\Delta B|_{x_1}(x, y)$ for $x_2 = 0.15$ and $x_1 = 0.10$ (e.g. see Fig. 4.7), while the cut of $\Delta B$ without $\Gamma$ FS is obtained from $\Delta B|_{x_1}(x, y)$ for $x_2 = 0.15$ and
We can interpret that the minimum is produced by anti-bonding states belonging to the M FSs while the maximum is the result of bonding states belonging to the Γ FSs. Since this last analysis needs only one FT of the experimental Compton profile along [100], it clearly provides particularly robust Fermi surface related discontinuity information in real space. In contrast, the $\rho^{2D}$ reconstruction requires many more numerical manipulations[131] and therefore it can be less reliable. Our $\Delta B$ methodology thus is a more reliable way to detect when the FS signal at Γ vanishes.

![Graph showing $\Delta B(r)$ vs. $r$ for different FSs configurations.](image)

Figure 4.10: Cut of $\Delta B$ along the [100] direction.

### 4.3.3 Conclusion

The shape of the theoretical spectrum after it is transformed into real space for momentum transfer along the [100] direction contains a remarkable signature of the FS evolution with doping. These results indicate that Compton scattering can provide a powerful new spectroscopic window for investigating FSs compatible with the $s_{\pm}$ model for the description of the superconducting order parameter in Fe-based superconductors.
4.4  Momentum density and orbital character of LSCO in various doping regions

The nature of the doped carriers is important for understanding the physics of the cuprates and the mechanism of high-temperature superconductivity. In this section, we try to determine the possible orbital channels which accommodate hole doped carriers in LSCO as the doping evolves from the underdoped to the overdoped region. Below optimal doping, the earlier experimental evidence shows that doped holes are primarily injected into the O-2p orbitals [134–137]. Even though some x-ray absorption[136, 138] and optical reflectivity[139] data propose a change in the oxygen 2p orbital character with overdoping, the actual orbital character of overdoped cuprates still remains an open question. To answer this question, we need to probe a physical quantity which is directly linked to wave functions, such as the electron momentum density (EMD). In this section, we analyze the hole doping dependence of LSCO EMD measured by high-resolution Compton scattering at room temperature.

4.4.1  Methods

The room temperature Compton scattering experiment has been done using a beam-line in SPring-8[105, 140, 141]. The momentum resolution is 0.13 a.u. The core-electron contributions are usually irrelevant to the Fermi surface topology and they are subtracted from each Compton profile. There are a total of ten Compton profiles taken at equal steps between the [100] and [110] directions. The ten Compton profiles can be used to reconstruct a 2D-EMD which represents a projection of the three-dimensional momentum density onto the a-b plane by using the direct Fourier
Figure 4.11: Crystal structure of La$_{2-x}$Sr$_x$CuO$_4$ with CuO planes. The Cu atoms are enclosed by apical oxygen octahedron.

Transform method[142]. The Compton scattering experiments in LSCO are taken to obtain the two-dimensional electron momentum densities (2D-EMDs) for four different single crystalline samples of La$_{2-x}$Sr$_x$CuO$_4$ (LSCO) with hole dopings, $x = 0.0, 0.08, 0.15$ and $0.30$. In the theoretical calculation, the crystal structure of La$_{2-x}$Sr$_x$CuO$_4$ is given in Fig. 4.11. It has body centered tetragonal (I4/mmm) crystal symmetry composed of CuO$_2$ planes and each Cu atom is enclosed by an oxygen octahedron. The underlying KKR self-consistent potential used in the theoretical 2D-EMD calculation is able to produce Fermi surface properties in agreement with angle-resolved photoemission spectroscopy (ARPES) experiments[126].

4.4.2 Matrix element effect of Cu-$d_{x^2-y^2}$ orbitals and 2D-EMD

In this discussion, matrix elements associated with the Cu-$d_{x^2-y^2}$ orbitals are important. The calculated band structure of LSCO ($x = 0.3$) near the Fermi level
is illustrated in Fig. 4.12(a). The band closest to the Fermi level, shown by the red dotted curve, is dominated by copper-oxygen $d_{x^2-y^2}-p_{x/y}$ orbitals. The present calculation for $x = 0.3$ predicts that the van Hove singularity lies above the Fermi energy, so the FS has a diamond shape closed around the point $(\pi,0)$. Fig. 4.12(b) shows the 2D momentum density contribution of the $d_{x^2-y^2}$ band, $\rho_{d_{x^2-y^2}}(p_x,p_y)$, together with the FS sections at $(k_z = 0)$ for the doping level $x = 0.3$ mapped periodically throughout momentum space. The Brillouin zones are visualized in the figure by a grid of $2\pi/a$, where $a$ is the lattice constant. The momentum density
acts as a matrix element on the FS map. Since $\rho_{d_{x^2-y^2}}(p_x,p_y)$ has a large amplitude in the third Brillouin zones, the FS can be more easily detected there. However, the asymmetric intensity of the momentum density due to Cu-$d_{x^2-y^2}$ orbital only highlights parts of the underlying FS. Therefore, the FS shape shown in $\rho_{d_{x^2-y^2}}(p_x,p_y)$ is not identical to the underlying FS.

4.4.3 Nature of the hole carriers

![Figure 4.13: Experimental difference 2D-EMDs in LSCO between hole doping concentrations at nondoped ($x = 0.0$) and heavily overdoped ($x = 0.30$). They are: (A) the difference of 2D-EMD between $x=0$ and $x=0.08$, (B) the difference between $x=0$ and $x=0.15$ (C) the difference between $x=0.15$ and $x=0.3$.](image)

Here, we use the subtraction technique to get the differences in 2D-EMDs between two different hole doped samples. In Fig. 4.13, we show the experimental difference of LSCO 2D-EMD between hole doping levels at nondoped ($x = 0.0$) and heavily overdoped ($x = 0.30$) An important advantage of the subtraction technique is the elimination of the large isotropic contribution of the semi-core and irrelevant valence electrons. It works like a filter which is very similar to the anisotropic method which we applied to the 2D-EMD in the last section. More important, this method allows us to only monitor the orbital character of the added hole carriers[143]. Because EMD is the squared modulus of the momentum-space wave-
function, it possesses the same point symmetry as the corresponding charge density. This phenomenon is known in molecular states[144] and should be equally applicable to the wave functions in solids[145]. We know the intensity of the spherical Bessel function is proportional to $p^l$ at small momenta $p$, where $l$ is the orbital quantum number[146]. When the total wavefunction is made up of atomic orbitals, we can expect oxygen 2p to bands to contribute to the EMD at low momenta, whereas the contribution of the Cu 3d bands is more likely to appear in higher Brillouin zones.

4.4.4 Orbital dependent 2D-EMD

To analyze the orbital characters seen in Fig. 4.13, we first investigate the electronic band structure of LSCO. The band diagram in Fig. 4.12(a) shows the two main bands near the Fermi level. The Cu-d$_{x^2-y^2}$ band is higher in energy than the Cu-d$_{z^2}$ band. Fig. 4.13 shows that by taking difference spectra over appropriate energy intervals, one can determine the patterns associated with particular orbitals. To compare,

![Figure 4.14](image)

Figure 4.14: (A) 2D-EMD contribution between -0.4 eV and +0.1 eV; (B) 2D-EMD contribution between -0.8 eV and -0.4 eV and (C) 2D-EMD contribution between -0.8 eV and +1.3 eV.

we take the difference of theoretical 2D-EMD spectra at three energy intervals. Fig. 4.14(a) shows the contribution of the 2D-EMDs between -0.4 eV and +0.1 eV.
from the Cu-3d$_{xy}$ band; Fig. 4.14(b) is between -0.8 eV and -0.4 eV from the Cu-3d$_{z^2}$ band; and Fig. 4.14(c) is between -0.8 eV and +1.3 eV from both bands. These calculations reproduce trends related to the Cu-O states. Notably, in Fig. 4.14(b) the two diagonal features at the momentum about 1 a.u. approximately agree with the experimental Fig. 4.13(c) despite some discrepancies regarding the position of the Cu-d features along px and py. Interestingly, other small experimental features along these directions, which are related to Cu-d$_{xz}$ and Cu-d$_{yz}$ orbitals, could be found at lower energy in the theory. Overall, the present 2D-EMD result in the energy range between -0.8 eV and +1.3 eV captures the dominant experimental features.

The LDA computations tend to underestimate the Cu-d$_{z^2}$ character of states at the Fermi energy[147], which accounts for part of the disagreement between theory and experiment. Our result suggests that for low Sr concentrations, the doped hole carriers exhibit a substantially greater O-p character than predicted by band theory. These effects seems to imply that the system favors stronger electron correlations at the low doping region suggestive of Zhang-Rice physics which cannot be explained by the conventional Fermi liquid picture. Additional calculations, using the linear combination of atomic orbital molecular orbital model with Cu-d$_{z^2}$ support the present result[148].

### 4.4.5 Conclusion

In short, this is an important study of the doping evolution of the orbital character in the high-T$_c$ cuprate LSCO crossing a wide doping range from the underdoped to the overdoped case. The result is that the LDA seems to underestimate the effect of Cu-d$_{z^2}$ states near Fermi energy. This study also suggests that the bulk-sensitive high-resolution Compton scattering is an ideal spectroscopy to probe the orbital
character of doped carriers in the ground state of complex materials.

4.5 Chemical bonding properties in liquid silicon

When silicon heats up above the melting temperature, 1683 K, the system turns into a metallic liquid phase with the resistivity equal to $0.75 \mu \Omega m$. The density of liquid Si is about 10% higher than solid Si (s-Si) and the coordination number of the first neighbor in liquid Si (l-Si) is 5.56\cite{149}. Because this is only about half of the first neighbor coordination number expected for a normal liquid metal like Al, it suggests that there are extra covalent bonds even in the metallic state. In earlier molecular dynamics simulations of Si, the system was found to contain about 30% of the covalent bonds at 1800 K; however, they are forming and breaking up rapidly on a time scale of 20 fs\cite{150}. In this study, calculated Compton profiles of solid and liquid silicon are compared to Compton scattering experiments. By introducing a number of different first principles approaches to simulate silicon in both solid and liquid state and comparing to the experimental results, we show the persistence of the covalent bond in the liquid silicon phase. It proves that Compton scattering spectroscopy is a sensitive probe of bonding effects even in the presence of disorder induced broadening of the spectrum in the liquid state.

4.5.1 Molecular dynamics and disorder effects in liquid Si

The valence-electron Compton profiles of polycrystalline Si and molten Si were measured at 300 K and 1787 K respectively. The difference between the experimental Compton profiles for the solid and liquid phases [$\delta J(p_z) = J_{\text{solid}} - J_{\text{liquid}}$] is presented in Fig. 4.15. First, we try to estimate disorder effects in the liquid. The effect of disorder on momentum density is very different from the temperature dependence of
the Compton profile in solids; the latter is mainly dominated by the variation of the lattice constant. We perform the Korringa-Kohn-Rostoker (KKR) coherent potential approximation (CPA) simulation\cite{110,111} to mimic liquid silicon as a disordered system. In the simulations, we adopt the lattice model for l-Si given in Ref.\cite{151}. We use a body centered cubic structure with lattice constant 5.13 a.u. in which lattice sites are occupied by a random distribution 50\% Si atoms and 50\% empty spheres. The difference between the KKR-CPA results for l-Si and the spherically averaged s-Si is also shown in Fig. 4.15. The effect of disorder in the KKR-CPA calculation yields a momentum density smearing near $p_z = 1$ a.u.\cite{110,111} and generates a dip of $\delta J(p_z)$ at this same location. However, the experimental $\delta J(p_z)$ shows a peak near $p_z = 1$ a.u.. We therefore conclude that the features induced by the Si site disorder are overshadowed by competing effects due to the covalent bond breaking.

Next, we compare the Car-Parrinello molecular dynamics (CPMD) simulation result to the experiment. In this case, we find a nice agreement between the two $\delta J(p_z)$, which suggests that the CPMD simulation is able to describe the chemical
bonding properties of liquid silicon[152].

4.5.2 Maximally-localized Wannier functions of liquid Si

Base on the CPMD simulation result, we continue to analyze the chemical bonding character in liquid silicon by constructing the maximally-localized Wannier functions (MLWFs)[153]. The MLWFs method projects the Kohn-Sham wave functions onto the local Wannier orbitals by building up an appropriate unitary transform matrix which minimizes the average spatial spread (variance) of the Wannier functions. In solid Si, the spreads of MLWF are all smaller than 1.84 Å² and the corresponding Wannier centers are located half way between two Si atoms. These two results indicate at all electron pairs in solid Si form covalent bonds. Yet, the liquid Si case shows a majority of MLWFs have spreads larger than 1.84 Å² and even up to over 7.8 Å². We refer to such electron pairs as diffuse pairs. In a metallic system, valence electrons are less bound to atoms, so the wavefunction of valence electrons are more extended in real space compared to an insulating system. Therefore, the metallic system also tends to have large spatial spreads in MLWFs. Thus our finding of MLWF with large spatial spreads in liquid Si agrees with the general metallic properties. Interestingly, there is also a special type of MLWF whose spread is comparable to that of the covalent electron pairs but the Wannier center is not shared by any two Si atoms. The MLWFs for this case have a spread of 2.21 Å². This kind of electron pair may be called a lone pair. We confirm this result by doing similar MLWFs calculation for an isolated Si₄H₉ cluster, which is a simple model for a Si-based system containing a lone pair. To provide a summary of the possible chemical bonding in liquid silicon, Fig. 4.16 presents a snapshot of the liquid Si configuration from the CPMD simulation. We sort the total MLWFs of
liquid silicon into three different types of chemical bonding, checking the robustness by varying the cutoff Si-Si bond distance carefully. We conclude that there are 17%, 83% and less than 1% of covalent bond pairs, diffuse pairs, and lone pairs, respectively.

Figure 4.16: Snapshot from the CPMD simulation of liquid Si at 1787 K. We draw Si atoms in yellow, covalent bond pairs in green, lone pairs in red and diffuse pairs in blue. In the plot, the bonds connecting Si atoms are guides to the eye, which do not correspond to the chosen cutoff bond length of 3.1 Å.

4.5.3 Liquid-liquid phase transition in liquid silicon

This picture of the coexistence of metallic bonds and covalent bonds in liquid-silicon brings out another interesting topic called liquid-liquid phase transitions (LLPT)[154–156] involving a possible phase separation between the high-density metallic liquid and a low-density semi-metallic liquid[156]. Since the temperature of l-Si in this study is 1787 K which is much higher than the predicted LLPT onset temperature of 1232 K[156], the chemical bonding data presented here can be considered as a precondition for LLPT. The temperature dependence of the density of l-Si is taken from the temperature between 1350 K and 1850 K[157]. Above the
melting temperature, the curve has linear behavior; as the temperature deceases, the curve becomes more quadratic. We can connect the linear behavior to the majority of metallic bonds in liquid silicon, which is confirmed in this study, while the quadratic behavior can be due to the increasing ratio of covalent bonds as the temperature decreases[158].

4.5.4 Conclusion

In summary, we demonstrate that high resolution Compton scattering retains a high sensitivity to bonding properties in both solid and liquid silicon phases despite the possible smearing effect in the momentum density coming from the disorder in the liquid state. We further use MLWF analysis to resolve a long standing problem of the coexistence of minor covalent bonds and major metallic bonds in the liquid state. This discovery is important for the study of the liquid-liquid phase transition of liquid silicon.
Chapter 5

Lindhard and RPA susceptibility computations of the electron doped cuprate Nd$_{2-x}$Ce$_x$CuO$_4$ in extended momentum space

5.1 Introduction

The dynamic structure factor $S(q, \omega)$ is a useful function of momentum and energy introduced by Leon Van Hove [159], which contains information about density-density correlations and their time evolution. Experimentally, $S(q, \omega)$ can be accessed most directly by inelastic x-ray scattering (IXS), which has acquired greater importance with the advent of powerful synchrotron sources [160]. However, since

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*This chapter is adapted from the following paper:
x-rays are strongly absorbed in materials with high density, IXS may be suitable mostly for low-Z systems. Nevertheless, in the case of heavier elements, recent studies have shown that if the photon incident energy is near an x-ray absorption edge the cross section can be enhanced, and the resulting resonant inelastic x-ray scattering (RIXS) offers a new window for probing both empty and filled electronic states [107, 161–163]. Recent efforts to develop a first-principles formulation of the RIXS spectrum explore an interesting hypothesis [164–166] that the RIXS cross-section is directly related to $S(q, \omega)$, complicating effects of the core hole notwithstanding. However, this claim remains controversial [167] and must be checked by testing the theory against accurate experimental results [168]. Cu-K-edge RIXS for cuprates [107, 169–171] probes the spectrum throughout momentum space encompassing many Brillouin zones. Therefore an important theoretical task is to produce realistic calculations of the dynamic structure factor within the framework of either many-body perturbation theory or time-dependent density functional theory [172] starting from a Lindhard susceptibility representing the response of an unperturbed Kohn-Sham system. In particular, local field effects [173–176] are known to modify the spectral weight of both collective and single-particle excitations in the dynamic structure factor of solids.

In this study we focus on an approximation to efficiently calculate from one particle spectral functions the Lindhard susceptibility $\chi^L(q, \omega)$. This approximation has successfully described the susceptibility of heavy rare earth elements [177] and can also reliably describe the x-ray inelastic scattering momentum dependency in higher Brillouin zones for an energy transfer $\omega$ where the single-particle excitations dominate. As an example we consider paramagnetic Nd$_{2-x}$Ce$_x$CuO$_4$ (NCCO), which has a relatively simple, nearly two-dimensional metallic Cu-O band near the Fermi level. We identify important features throughout energy-momentum space and we
delineate the specific manner in which $\text{Im}\chi^L(q,\omega)$ decays as a function of $q$. These results enable an assessment of the extent to which $S(q,\omega)$ reproduces the RIXS cross-section in a cuprate via direct comparison of the theory with corresponding experiments in extended regions of the momentum space.

5.2 Formalism

In a periodic solid, the susceptibility becomes a tensor in the reciprocal lattice vector space $G$. The fluctuation-dissipation theorem relates the dynamical structure factor $S(q,\omega)$ to the susceptibility $\chi_{G,G}(k,\omega)$ via

$$S(q,\omega) = -\frac{1}{\pi} \sum_{k,G} \text{Im}\{\chi_{G,G}(k,\omega)\} \frac{1}{1 - e^{-\hbar\omega/kT}} \delta(q - k - G),$$

(5.1)

where the crystal momentum $k$ is restricted in the first Brillouin zone. Thus, IXS experiments do not probe all matrix elements of the response $\chi_{G,G'}(k,\omega)$, but only the diagonal elements $\chi_{G,G}(k,\omega)$ [178]. If we approximate the susceptibility by the bare susceptibility $\chi^0_{G,G'}(k,\omega)$ then [174–176, 179]

$$\text{Im}\{\chi^0_{G,G}(k,\omega)\} = -\sum_{\nu,\mu} |M^\nu_\mu|^2 \int_{-\omega}^{0} d\epsilon A_\nu(\epsilon) A_\mu(\epsilon + \omega).$$

(5.2)

The matrix elements $M^\nu_\mu$ can be expressed in the Dyson orbital basis set $g_\nu$ as [130, 180]

$$M^\nu_\mu = \langle g_\nu | e^{i(k+G)r} | g_\mu \rangle.$$

(5.3)

The spectral functions associated with the Dyson orbitals are

$$A(p,\omega) = \sum_\nu |g_\nu(p)|^2 A_\nu(\epsilon),$$

(5.4)
Aν(ω) = \frac{\gamma}{\pi[(\hbar \omega - \epsilon_\nu)^2 + \gamma^2]}, \hspace{1cm} (5.5)

where \(\epsilon_\nu\) is the excitation energy associated with the Dyson orbital \(g_\nu\) and \(\gamma\) is infinitesimally small. The label \(\nu = (k, n)\) is a composite index that codes the Bloch wave vector \(k\) and the energy band index \(n\). The Dyson orbitals can often be approximated reasonably by Bloch orbitals as

\[ g_{k,n}(r) = \exp(i k \cdot r) \sum_G C_{k,n}^G \exp(-i G \cdot r), \hspace{1cm} (5.6) \]

with the momentum density given by

\[ |g_{k,n}(p)|^2 = \sum_G \delta(p-k+G) |C_{G,n}^{k,m}|^2. \hspace{1cm} (5.7) \]

The Fourier coefficients \(C_{G,n}^{k,m}\) of the periodic part of the Bloch function are labeled by the reciprocal vectors \(G\). In this case, the dynamical structure factor at \(T = 0\) becomes

\[ \text{Im} \chi^L(q, \omega) = -\sum_{n,m,k,k',G',G''} (C_{G'}^{k,m})^* C_{G'+G}^{k',m} C_{G''}^{k,n} (C_{G''+G}^{k',m})^* \]

\[ \times \delta(q + k - k' - G) \int_{-\omega}^{0} d\epsilon A_n(k, \epsilon) A_m(k', \epsilon + \omega). \hspace{1cm} (5.8) \]

The dominant part of \(S(q, \omega)\) is given by the partial sum of the real positive terms \(G' = G''\). Next, following the derivation from Wen’s book[181], we neglect the remaining complex terms because the randomness of their phases produces destructive
interferences. A few straightforward algebraic simplifications then yield [107, 182]

\[ \text{Im} \chi^L(q, \omega) = - \int_{-\omega}^{0} \frac{d\epsilon}{2\pi} \int \frac{d^3p}{(2\pi)^3} A(p, \epsilon) A(p + q, \epsilon + \omega). \] 

(5.9)

Thus, our approximation scheme leads to an expression for \( \text{Im} \chi^L(q, \omega) \) similar to the free fermion form [183] but with the spectral function \( A(p, \epsilon) \) expressed in terms of the Bloch wave functions instead of plane waves. The approximation becomes exact when \( q \) is large (e.g. see Ref. [107], p. 137). As already noted above, the asymptotic decay of the imaginary part of the Lindhard susceptibility as a function of \( q \) is well described within the present framework. When \( q \) is small, the most significant features of the susceptibility are produced by band structure effects, which are fully included in our approach. Notably, the origin of major peaks in the imaginary part of the susceptibility lies in FS nesting[184, 185]. Therefore, we expect our scheme to produce a reasonable approximation to the dynamical structure factor in materials.

### 5.3 Computational methods

The Dyson orbitals \( g_{\nu} \) needed for the calculation of the spectral function \( A(p, \epsilon) \), as already noted, can be reasonably replaced by the Kohn Sham orbitals obtained within the Density Functional Theory (DFT) [180]. For this purpose, DFT band structure calculations in NCCO were performed within the Local Density Approximation (LDA) using an all-electron, fully charge self-consistent semi-relativistic (KKR) method [76, 186]. The crystal structure used for NCCO was body centered tetragonal (space-group I4/mmm) with lattice parameters given by Massidda et al. [187]. A self-consistent solution was obtained for \( x = 0 \) with a convergence of the crystal potential to about \( 10^{-4} \) Ry.
To demonstrate our approach in a relatively simple but interesting case, we restrict the calculation to a single band, namely the copper-oxygen band near the Fermi level in NCCO. In particular, the possible contribution of the Nd f-electrons is neglected by removing the f orbital from the basis set after the Nd self-consistent potential has been obtained. In our LDA calculations, we found a paramagnetic copper layer and a half-metallic ferromagnetic ground state of Nd. To remove the Nd levels from the vicinity of the Fermi level, we simply used the minority spin potential. For a large unit cell, LDA does recover the correct rare earth antiferromagnetic ground state\[188]. The doping effects were treated within a rigid band model by shifting the Fermi energy to accommodate the proper number $x$ of electrons \[189\]. The rigid band model is expected to be a good approximation for doping away from the cuprate layers. In the electron momentum density (EMD) calculations, the momentum mesh was given by a momentum step $(\Delta p_x, \Delta p_y, \Delta p_z) = (1/128a, 1/128a, 1/2c)/(2\pi)$. The total number of momentum points is $1.54 \times 10^8$ within a sphere of radius 17.6 a.u.

We show in Fig. 5.1(a) the calculated band structure of NCCO near the Fermi level. The band closest to the Fermi level is shown by the red dotted curve and is well isolated from other bands. This band ranges from $-1.4$ eV to $1.9$ eV and the integral of the spectral function in this energy interval, evaluated with an energy resolution of 40 meV, is shown in Fig. 5.1(b). The two-dimensional spectral function $A(p, \omega)$ is calculated by neglecting the small $k_z$ dispersion in the three dimensional electronic band structure \[190\]. Similar EMD results for NCCO have been obtained within the LMTO\[191, 192\]. The resulting momentum density has the same symmetry as the copper-oxygen $d_{x^2-y^2}-p_{x,y}$ states in real space which form this energy band since the wave function in momentum space is the Fourier transform of the wave function in real space. Fig. 5.1(b) shows that the low intensity along the $x-y$ diagonal direction.
in the 2D-EMD map is a signature of $d_{x^2-y^2}$ symmetry. Moreover, since the radial momentum dependence of an atomic state of angular momentum $\ell$ behaves as $p^\ell$ at small momenta [146], the 2D-EMD intensity at low momenta is from the O-2$p$ orbitals, while the Cu-3$d_{x^2-y^2}$ orbitals contribute at higher momenta. Similar matrix element effects are seen in angle-resolved photoemission spectra of the cuprates [193–196]. This implies that the signal coming from the O-2$p$ states is more visible in the first Brillouin Zone while the Cu-3$d$ states are better seen in higher Brillouin zones.

We can see from Fig. 5.1(b) that the 2D-EMD intensity is strongly modulated by wave function effects, which suggests that the behavior of $\text{Im} \chi^L(q, \omega)$ in NCCO in different zones will also be modified by these effects; however, our approximation neglects some interference effects produced by the phases of the Fourier coefficients of the Bloch wave functions.

At zero temperature $T = 0$ K, $\text{Im} \chi^L(q, \omega)$ can be written as a convolution of two spectral functions. This $\text{Im} \chi^L(q, \omega)$ captures electron-hole excitations described by Dyson orbitals [130, 180] but does not include collective excitations such as plasmons or phonons. For efficient $\text{Im} \chi^L(q, \omega)$ calculations, we replace the momentum space convolution of $A(p, \omega)$ by a simple product of spectral functions $B(r, \omega)$ in real space given by

$$B(r, \omega) = \int \frac{d^3p}{(2\pi)^3} A(p, \omega) \exp(ip \cdot r).$$

This enables us to take advantage of the fast Fourier transform (FFT) efficiency using the convolution theorem [197]. The advantage of our FFT based method can be seen by comparing the computation time of the FFT method with the time needed to directly compute $\text{Im} \chi^L(q, \omega)$ using two matrices of size $2049 \times 2049$. The CPU time for the FFT method is 12 seconds, while the direct computation takes 24 minutes on the same Intel Core i7-920 machine.
Figure 5.1: (a) Band structure of NCCO near the Fermi level. The CuO$_2$ band is shown by the red dotted line. (b) Calculated integrated spectral function $A(p)$ for an isolated CuO$_2$ layer in NCCO. The zone boundaries (for a simple tetragonal approximation) are marked by black lines. Whites denote large values of $A(p)$, blues small values. The $A(p)$ shown here contain contributions only from the CuO$_2$ band.

Figure 5.2: (a) Calculated $-\text{Im}\chi^L(q,\omega)$ of NCCO along high symmetry lines as a function of transition energy. Whites denote the largest $-\text{Im}\chi^L(q,\omega)$, blacks the smallest. (b) The integrated value of $-\text{Im}\chi^L(q,\omega)$ over $q$ vs transition energy $\omega$. 
Figure 5.3: Calculated $-\text{Im} \chi_L(q, \omega)$ of NCCO at $\omega = 1.04$ eV plotted over several Brillouin zones. Black circles near the $\Gamma$-points indicate regions of zero intensity, as in Fig. 5.2. Index I labels the first zone, indices II, III mark zones along the $(\pi, 0)$ direction, and IV and V the zones along the $(\pi, \pi)$ direction.

5.4 Results of zone dependent susceptibility

We discuss our results with reference to Fig. 5.2-Fig. 5.5. In Fig. 5.2a, we show $-\text{Im} \chi_L(q, \omega)$ along high symmetry lines as a function of $\omega$. The black part of this figure marks the region of zero intensity where no electron hole transitions are available. Strong intensity seen near 1 eV around $(\pi, 0)$ is due to a sort of a Van Hove singularity in $\text{Im} \chi_L(q, \omega)$, which is associated with the high energy kink or the waterfall effect in the electronic spectrum[198]. When we compare our Fig. 5.2a to the experimental RIXS spectrum of overdoped NCCO presented in Ref. [199], we find that the experiment is well described by the $k$ resolved joint density of states despite the complicating effects of the core-hole[166]. In particular, the features in the lowest experimental RIXS band within the energy range of $\omega = 0.5$ to $\omega = 2$eV
Figure 5.4: (a-d) Contour maps of $-\text{Im} \chi^L(q, \omega = 1.04 \text{ eV})$ of NCCO in four different Brillouin zones. The symmetry of the maps in zone II and zone III is very similar.

are well reproduced by our calculations. The integrated value of $-\text{Im} \chi^L(q, \omega)$ over $q$, plotted in Fig. 5.2b, yields the total number of electron-hole transitions at a given energy. Since the highest peak in Fig. 5.2b is located at 1.04 eV, we focus on analyzing $-\text{Im} \chi^L(q, \omega)$ at this particular energy in the remainder of this chapter. $-\text{Im} \chi^L(q, \omega)$ is shown in Fig. 5.3 for $\omega = 1.04 \text{ eV}$ over several Brillouin zones marked by yellow lines. The first Brillouin zone, located at the center of the figure, has the highest intensity. The intensity is seen to decrease slowly as $q$ increases, and interesting patterns due to d electron wavefunction effects appear in higher zones. In the first zone, Fig. 5.3, some strong peaks are present surrounding the zero-intensity hole centered at $\Gamma$ with a relatively low intensity appearing at the zone corners $M$.

Further details of $-\text{Im} \chi^L(q, \omega)$ are shown in Figs. 5.4(a)-(d), which are blow ups of the four Brillouin zones marked by II, III, IV, and V in Fig. 5.3. The Brillouin
zones displayed in Figs. 5.4(a)-(d) show a similar overall pattern but modulated with subtle matrix element effects. For instance, regions of strong intensity spread towards (−π, 0) in zone II (Fig. 5.4a), but towards (−π, ±π) in zone III (Fig. 5.4b). The intense (bright) peaks point along one diagonal direction in zone IV in Fig. 5.4c, but are rotated by 90 degrees in zone V in Fig. 5.4d.

Figure 5.5 presents a cut through −Imχ^L(q, ω = 1.04 eV) along the [100] direction in order to illustrate the decay of −Imχ^L(q, ω) as a function of momentum transfer q. The highest intensity has been normalized to unity for ease of comparison. Surprisingly, at momenta as large as 6 a.u. one can still see features with amplitude exceeding 10 % of the highest intensity (located in the first Brillouin zone). This effect can be explained by the fact that d electron particle-hole transitions can involve particularly high momentum transfers. We can fit the envelope of −Imχ^L(q, ω) by using a simple Lorentzian shape \[ \frac{1}{1 + (\frac{q - k_0}{\Delta q})^2} \] with k_0 = 1.89 a.u. We would like to point out that this fit has no direct consequences for the f-sum rule since it involves only the energy slice.
ω = 1.04eV while the f-sum rule is the result of an integration on all the energies. The f-sum rule is automatically fulfilled by our approximation if one neglects self energy corrections and one considers the linear response Lindhard susceptibility (used in this study) as shown in Ref. [200]. Moreover we have numerically checked that \( \int \text{Im}\chi^L(q, \omega = 0) d\omega \) is zero (below \( 10^{-17} \)) as a direct consequence of the f-sum rule. Since RIXS has often been thought to be related to \( S(q, \omega) \), it is an interesting question whether a similar decay factor \( k_0 \) is found in RIXS experiments. Our results thus provide a new way to test the hypothesis that the RIXS cross-section is directly related to \( S(q, \omega) \).

![Figure 5.6: Cuts of \(-\text{Im}\chi^{RPA}(q, \omega = 1.04 \text{ eV})\) (in red dashed line) and \(-\text{Im}\chi^L(q, \omega)\) (in blue solid line) taken along (\( \pi, 0 \)) in Fig. 5.3 (extended to higher BZs). The highest intensity of each curve has been scaled by taking the highest intensity of \(-\text{Im}\chi^L(q, \omega)\) as unity. Labels I, II and III correspond to the zone indices in Fig. 5.3. No plasmon peak is present in this energy slice \( \omega = 1.04 \text{ eV} \).](image)

We have also obtained the real part of the Lindhard susceptibility \( \chi^L \) by applying Kramers-Kronig relation. However, the Lindhard susceptibility gives only the response of the independent electrons to the external potential. In order to estimate the effect of screening, I consider the susceptibility within the random phase approximation (RPA) given by \( \chi^{RPA} = \chi^L/(1 - Vq\chi^L) \), where \( V \) is the Coulomb interaction decaying as \( \sim 1/q^2 \). In this approach, the sharp singularities of \( \chi^{RPA} \) due to the de-
nominate give the plasmon modes. Figure 5.6 illustrates that corrections are more important when the external perturbation is of very long wavelength (i.e. $q$ small). Particularly, when $q$ is of the order of $k_0 = 1.89$ a.u., $-\text{Im} \chi^{RPA}(q, \omega)$ reverts back to $-\text{Im} \chi^L(q, \omega)$. Interestingly, a full matrix treatment of the susceptibility $\chi^{RPA}$ shows that plasmons from the first Brillouin zone can couple with excitations at large momentum transfer[201].

5.5 Dynamical charge density of NCCO

In the presence of a charged impurity in a system, the electrons tend to form a charge density cloud in order to screen out the Coulomb potential of the impurity. If the external perturbation is weak, the electronic interaction in the system can be described by linear response theory:

$$\rho_{in}(q, \omega) = -eV_q \chi(q, \omega)$$  \hspace{1cm} (5.11)

where $\rho_{in}(q, \omega)$ is the induced charge density cloud, $q$ and $\omega$ are momentum and frequency respectively, $e$ denotes the electron charge, $V_q$ is the potential associated with the perturbation, $\chi(q, \omega)$ is susceptibility which describes the charge response due to $V_q$. Once we have the $\rho_{in}(q, \omega)$ of a system, it is possible to visualize the charge density cloud evolution with time and space by using Fourier transform techniques[202, 203].

We present an example in NCCO to observe the reaction of the system to a point charge with bare potential $V_q = \frac{4\pi e}{q^2}$. We take Eq. (5.11) and write it as:

$$\rho_{in}(q, \omega) = \frac{4\pi e^2}{q^2} \chi(q, \omega)n_{ex}(q, \omega).$$  \hspace{1cm} (5.12)
First, we calculate \( \rho_{\text{in}}(\mathbf{q}, \omega) \) and then determine the dynamics of the induced charge density Fourier transforming \( \rho_{\text{in}}(\mathbf{q}, \omega) \) to \( \rho_{\text{in}}(\mathbf{r}, t); t > 0 \), where \( \mathbf{r} \) is position in real space and \( t \) is time. It can be shown\(^{[178]} \) that the calculation of \( \rho_{\text{in}}(\mathbf{r}, t); t > 0 \) only needs the imaginary part of \( \chi(\mathbf{q}, \omega) \) by using a sine Fourier transform:

\[
\rho_{\text{in}}(\mathbf{r}, t) = \frac{1}{4\pi^3} \int_{-\infty}^{\infty} \int_{0}^{\infty} \text{Im}[\chi(\mathbf{q}, \omega)] \sin\left(\frac{\omega t}{\hbar}\right)e^{i\mathbf{q} \cdot \mathbf{r}} d\omega d\mathbf{q}.
\] (5.13)

The dynamical result of \( \rho_{\text{in}}(\mathbf{r}, t) \) is presented in Fig. 5.7 as a series of time frames. We notice that the shape of the electron cloud retains the four-fold symmetry of the crystal structure. We see a strong oscillation near the origin and the electron cloud displays complex structures in the further region as time evolves. It is interesting that most neighboring peaks or bumps are separated by the lattice constant of the
Figure 5.8: The static charge density cloud $\rho_{in}(r, t = \infty)$ screens out the point charge at the origin.

CuO$_2$ plane in NCCO. Overall, the major electron cloud reaction seems to happen within 20 a.u. As time $t$ goes to infinity, the steady state distribution of the electron cloud $\rho_{in}(r, t = \infty)$ can be obtained by taking the Fourier transform of the induced charge density with only a zero frequency component $\rho_{in}(q, \omega = 0)$:

$$\rho_{in}(r, t = \infty) = \frac{1}{4\pi^2} \int_0^\infty \chi(q, \omega = 0)e^{iqr} dq,$$  \hspace{1cm} (5.14)

as shown in Fig. 5.8. A clear cone shaped electron cloud is built up at the center, which implies the point charge is well screened when the system relaxes to the steady state. This result is consistent with the underlying metallic state of NCCO obtained from the LDA calculation.

To have a better understanding of the electron cloud, we calculate the effective charge $C_{eff}$ of the cloud $\rho_{in}(r, t = \infty)$ enclosed in a circular area of radius $r_c$ from $r_c = 0$ a.u. to $r_c = 30$ a.u.:

$$C_{eff}(r_c) = \int_0^{r_c} \int_0^{2\pi} r dr d\theta \rho_{in}(r, t = \infty).$$  \hspace{1cm} (5.15)
Figure 5.9: The integrated effective charge $C_{\text{eff}}$ of the static electron cloud as a function of cutoff radius.

Fig. 5.9 shows the result for $C_{\text{eff}}(r_c)$. The curve of $C_{\text{eff}}(r_c)$ raises up almost linearly from $r_c = 0$ to $r_c = 5$ a.u.. After a small oscillation, the curve reaches a plateau $C_{\text{eff}} = 1$ at $r_c = 12$ a.u. Since the electron cloud screens out a point charge within such a short distance, it again indicates the metallic nature of NCCO within the LDA.

5.6 Susceptibility and the spatial average induced charge density

In the previous section, we have discussed the induced charge density cloud of NCCO. However, in inhomogeneous systems including a crystal with periodic potential, the susceptibility depends on two different spatial coordinates, which can be written as:

$$\chi(r_1, r_2, t) = -\frac{i}{\hbar}\langle m|n(r_1, t), n(r_2, 0)|m\rangle\theta(t), \quad (5.16)$$

where $n(r_1, t)$ and $n(r_2, t)$ are density operators at different locations $r_1$ and $r_2$ at time $t$ and $|m\rangle$ is the ground state of a system, and $\theta(t)$ is a step function with respect to time $t$. Eq. (5.16) describes how the charge density at $r_2$ at time $t = 0$
will propagate to $r_1$ at time $t$. Here, we want to address the difference between the calculation of induced charge density with a single $r$ dependent susceptibility and a full susceptibility[178].

We can convolve an $r_1, r_2$ dependent susceptibility with a delta function $f(r_1, r_2) = \delta(r_1 - r_2)$ which works as a filter:

$$
\chi(r_1 - r_2) = \int dr_1 dr_2 f(r_1', r_2') \chi(r_1 - r_1', r_2 - r_2'),
$$

and rewrite Eq. (5.17) by introducing a variable $r$ defined as $r = r_1 - r_2$:

$$
\chi(r) = \int dr_2 \chi(r + r_2, r_2).
$$

In Eq. (5.18), the full susceptibility reduces to a single $r$ dependent susceptibility by averaging over all possible perturbation source positions at $r_2$. Therefore, when we calculate the induced charge density with a single $r$ dependent susceptibility, the position information of the perturbation source is lost.

### 5.7 Conclusions

We have presented a formalism for a first principles computation of the Lindhard susceptibility $\chi^L(q, \omega)$ in extended momentum space. We have demonstrated a tremendous improvement in performance by calculating $\text{Im} \chi^L(q, \omega)$ through an approximation involving products of real space spectral functions $B(r, \omega)$ and FFTs instead of using the standard approach involving costly matrix multiplications. Our theoretical $\text{Im} \chi^L(q, \omega)$ results for the doped cuprate NCCO will allow a detailed
comparison with the RIXS experiments, and hence an assessment of the extent to which $\text{Im} \chi^L(q, \omega)$ represents a good approximation to the RIXS cross section. The present work also provides a realistic linear response based starting point for developing a many-body perturbation theory of particle-hole excitations within the DFT framework. The dynamical induced charge density of NCCO has been demonstrated by inverting the susceptibility into real space and time domain. Because only a single $r$ dependent susceptibility is involved in the calculation, we interpret this as an average over all the possible positions of the perturbation source.
Chapter 6

Conclusion and discussion

In this thesis, I have used a variety of theoretical approaches, including first principles calculations within the framework of density functional theory, and theoretical modeling of Compton profiles and electron momentum density (EMD), to investigate the novel electronic structure in a variety of materials.

By using first principles calculation with GGA exchange-correlation potential, I predicted several non-trivial topological insulators in ternary famatinite and quaternary chalcogenide compounds. I also use Cu$_2$ZnSnS$_4$ and Cu$_3$SbS$_4$ to demonstrate a topological phase transition from a trivial band insulator to a nontrivial topological phase, which displays the advantage of the structural freedom for device design in the ternary famatinite and the quaternary chalcogenides. The large tuning possibilities available in this class of compounds can add more flexibility in using topological insulators in multifunctional spin-polarized quantum and optical information processing applications.

In the study of the high T$_c$ iron pnictide superconductor Ca$_{10}$(Pt$_3$As$_8$)(Fe$_2$As$_2$)$_5$, I presented theoretical electronic structure simulations of the density of state (DOS) and band structure. Near the Fermi energy, the DOS shows a small amount of Pt orbital contribution. The angle resolved photoemission (ARPES) experiment reveals that the Fermi surface topology follows the tetragonal periodicity of the FeAs layer.
sublattice at least near the surface. In order to explain the ARPES result, I needed to unfold the Fermi surface by neglecting the potential from the $\sqrt{5}$ super-lattice due to the presence of the PtAs layers. These results indicate that the interlayer hopping between the PtAs and FeAs layers is very weak.

I presented first principles calculations of Compton profiles and EMD via the KKR-CPA method in the iron-pnictide LaOFeAs, the cuprate La$_{2-x}$Sr$_x$CuO$_4$ (LSCO) and the liquid phase of silicon. These simulations provided a basis for a detailed comparison between theory and experiment. In the study of LaOFeAs, I investigated the Fermi surface break in momentum space by analyzing both the anisotropy of directional Compton profile and two dimensional EMD (2D-EMD). The result suggests that the [100] directional Compton profiles is the most favorable one for studying the Fermi surface evolution with doping. Moreover, I proposed a real space technique using either a 2D-EMD or a Compton profile to determine the critical doping level associated with the disappearance of the electron Fermi surface in LaOFeAs. Since the $s_{\pm}$ model requires the coexistence of hole and electron Fermi surfaces to describe the superconducting order parameter in iron superconductors, I expect Compton scattering can be a powerful tool to identify the condition for the $s_{\pm}$ model via this real space method. I calculated the 2D-EMD of LSCO considering only the Cu-d$_{x^2-y^2}$ state contribution. This 2D-EMD map indicates that four particular zones in higher momentum are much less influenced by matrix element effects of Cu-d$_{x^2-y^2}$ orbitals. To understand the nature of the hole carriers in LSCO, a series of experimental LSCO 2D-EMDs were taken from underdoped LSCO to overdoped LSCO. By performing the theoretical 2D-EMD of LSCO for comparison, I indicated that the well known Cu-d$_{x^2-y^2}$ orbital alone is insufficient to explain the experimental spectrum, but the contribution of the Cu-d$_{z^2}$ orbital needs to be included. In the study of liquid silicon (Si), the KKR-CPA simulation
suggests the the smearing effect in the EMD from the disorder in liquid Si is suppressed. The molecular dynamic simulation and the maximally-localized Wannier function analysis of the electronic structure of liquid Si reproduced the experimental Compton spectrum of liquid Si, which illustrates the coexistence of the metallic bond and covalent bond in the liquid Si phase. This condition is also a key for the liquid-liquid phase transition in Si.

In the last study, I presented an efficient formalism to calculate the Lindhard and RPA susceptibilities of Nd_{2-x}Ce_xCuO_4 in multiple Brillouin zones by using the Fast Fourier transform based convolution of the spectral function. The susceptibility map varies from zone to zone due to the presence of the Cu-d_{x^2−y^2} matrix element effects. Since resonant inelastic x-ray scattering (RIXS) can detect the electron structure of materials in higher Brillouin zones, it will be interesting to see if the RIXS spectrum has a similar zone dependent behavior. An even more exciting outcome from the susceptibility calculation in a multiple-zone scheme is to enable the possibility to visualize electron-electron response in a solid as a function of particular time and position in real space. Because only the diagonal elements of susceptibility are calculated in this method, the current study only provides the information of spatial averaged induced charge density. To overcome this shortcoming, the full susceptibility including the off diagonal elements needs to be calculated. With this extension, I can study different electronic excitation modes with respect to the particular positions of impurity in real space and time domain. For the same NCCO system, I will be able to monitor the response of the system with respect to an impurity located on the either Cu site or O site in the CuO_2 plane.
Chapter 7

Appendix

7.1 Resonant inelastic x-ray scattering

Resonant inelastic x-ray scattering (RIXS) is one kind of x-ray scattering spectroscopy which is performed by tuning the energy of an incident photon to match a certain atomic transition so that the cross section of RIXS can be remarkably enhanced by the resonance. This kind of atomic transition is called absorption edge. When an atomic transition excites a core electron from an atomic shell, n = 1, the absorption edge is called K-edge, n=2 is called L-edge and n=3 is called M-edge. RIXS can couple to many types of excitation in solids, including plasmons, charge transfer excitation, orbital excitations, magnons and phonons.

There are two types of RIXS scattering[163]: one is called direct RIXS and the other is indirect RIXS. Fig. 7.1 describes the mechanism of direct RIXS. In a first step, the incident photon excites a core electron to an unoccupied valence state and creates a core-hole in the core states. After that, a valence electron drops to fill the core-hole and create another hole in the valence states, emitting a photon in the process. In direct RIXS, the change of momentum and energy between the incident
photon and the outgoing photon is associated with the excited electron-hole pairs in the valence states. Fig. 7.2 shows an indirect RIXS process, where an incident photon excites a core electron to an empty state with much higher energy and leaves a core-hole. A so-called shake-up process will occur in the intermediate state such that the valence electrons tend to screen the strong Coulomb potential $U$ produced by the core-hole. This screening effect can cause a valence electron-hole excitation. Finally, the excited electron at the higher empty state will come back to fill the core-hole and emit a photon.

To obtain the cross-section of RIXS at zero temperature $T = 0$, one can consider a Hamiltonian $H$ including the interaction between the incident light and the electrons in a sample in the nonrelativistic limit[163, 204, 205]:

$$
H = \sum_{i=1}^{N} \left[ \frac{e}{m} A(r_i) \cdot p_i + \frac{e^2}{2m} A^2(r_i) - \frac{e^2 \hbar}{(2mc)^2} \sigma \cdot \frac{\partial A(r_i)}{\partial t} \times A(r_i) + \frac{e \hbar^2 \rho(r_i)}{8(mc)^2 \varepsilon_0} + H_{\text{Coulomb}} + \sum_{k, \epsilon} \hbar \omega_k (a_{k \epsilon}^{\dagger} a_{k \epsilon} + 1/2) \right], \tag{7.1}
$$

where $p_i$, $r_i$ and $\sigma_i$ are the momentum operator, position operator and Pauli matrix acting an electron $i$, $m$ is the mass of an electron, $\rho(r_i)$ the electron density, $\varepsilon_0$
Figure 7.2: An indirect RIXS process. A strong Coulomb potential $U$ produced by the core-hole can induce an electron-hole excitation in the valence band. This is called a shake-up process in the intermediate state.

The vacuum permittivity, $\varepsilon$, the speed of light, $c$, $H_{\text{Coulomb}}$ represents electron-electron interactions, $a_{k\epsilon}$ and $a_{k\epsilon}^\dagger$ are a photon annihilating operator and a photon creating operator associated with an wave vector $k$, a frequency $\omega$ and a polarization $\epsilon$, and $A(r_i)$ is the vector potential of a photon. Note that Eq. (7.1) is obtained by choosing a gauge $\nabla \times A(r_i) = 0$. The Hamiltonian $H$ can be written as $H = H_{\text{ep}} + H_0$, where $H_{\text{ep}}$ denotes the electron-photon interaction and $H_0$ contains the rest of $H$. The expression $A(r_i)$ can be written in terms of plane waves as:

$$A(r_i) = \sum_{k,\epsilon} \sqrt{\frac{\hbar}{2\Omega \varepsilon \omega_k}} (\epsilon a_{k\epsilon} e^{i k \cdot r_i} + \epsilon^* a_{k\epsilon}^\dagger e^{-i k \cdot r_i}), \quad (7.2)$$

where $\Omega$ denotes the volume of the sample. In this system, the incident photon carries momentum $\hbar k$ and energy $\hbar \omega_k$ with polarization $\epsilon$ and the outgoing photon is characterized by $\hbar k'$, $\hbar \omega_{k'}$ and $\epsilon'$. The change of momentum $\hbar q$ and energy $\hbar \omega$ between the incident photon and the outgoing photon are given by $\hbar q = \hbar k - \hbar k'$ and $\hbar \omega = \hbar \omega_k - \hbar \omega_{k'}$. After the photon scattering, the sample evolves from a ground
state $|g\rangle$ to a final state $|f\rangle$ with the corresponding energies $E_g$ and $E_f$ and the intermediate state $|n\rangle$ has the corresponding energy $E_n$.

One can analyze the scattering amplitude of RIXS by using Fermi’s golden rule, where the quadratic term in $A(r_i)^2$ mainly contributes to nonresonant scattering while the linear term in $A(r_i)$ dominates the resonant contribution. Since the resonant scattering amplitude is significantly larger than the nonresonant part in RIXS, one can focus on the resonant scattering amplitude $F_{fg}$, which can shown to be[206]

$$F_{fg} = \frac{e^2\hbar}{2m^2\Omega E_0 \sqrt{\omega_k \omega_{k'}}} \sum_n \sum_{i,j=1}^N \frac{\langle f | e^{-i k' \cdot r_i} (\epsilon' \cdot p_i - \frac{i \hbar}{2} \sigma_i \cdot k' \times \epsilon') | n \rangle}{E_g + \hbar \omega_k - E_n + i \Gamma_n} \times \langle n | e^{i k \cdot r_j} (\epsilon \cdot p_j + \frac{i \hbar}{2} \sigma_j \cdot k \times \epsilon) | g \rangle,$$

(7.3)

where $i \Gamma_n$ is a broadening associated with the core hole excitation in the intermediate state. Eq. (7.3) can be simplified by neglecting the magnetic terms. For example, in some copper-oxide systems, the magnetic contribution is about 100 times smaller than the nonmagnetic contribution. With this simplification, one can introduce a transition operator $D$ associated with a photon to be:

$$D = \frac{1}{i m \omega_k} \sum_{i=1}^N e^{i k \cdot r_i} \epsilon \cdot p_i,$$

(7.4)

and use the subscript ”out” and ”in” for $D$ to denotes the transition operators associated with the outgoing photon ($D_{out}$) and the incident photon ($D_{in}$). The expression of $F_{fg}$ can be rewritten as:

$$F_{fg} = \sum_n \frac{\langle f | D_{out}^\dagger | n \rangle \langle n | D_{in} | g \rangle}{E_g + \hbar \omega_k - E_n + i \Gamma_n}.$$

(7.5)

To have an even more compact form of Eq. (7.5), an intermediate state propagator
\( G_t \) in terms of a Green function can be defined as:

\[
G_t = \frac{1}{t - H} = \sum_n \frac{|n\rangle\langle n|}{t - E_n},
\]

(7.6)

where \( t \) denotes:

\[
t = E_g + \hbar \omega_k + i \Gamma_n.
\]

(7.7)

Therefore, \( F_{fg} \) can be re-written as:

\[
F_{fg} = \langle f | D^\dagger_{\text{out}} G_t D_{\text{in}} | g \rangle.
\]

(7.8)

The cross-section of RIXS, \( I_R \), is proportional to \( F_{fg}^2 \)[107, 163, 205, 206]:

\[
I_R = r_e^2 m^2 \omega_k \omega_{k'}^3 \sum_f |F_{fg}|^2 \times \delta(E_f + \hbar \omega_{k'} - E_g - \hbar \omega_k),
\]

(7.9)

where the delta function ensures energy conservation and the classical electron radius \( r_e \) is given by

\[
r_e = \frac{e^2}{4\pi \varepsilon_0 mc^2}
\]

(7.10)

### 7.2 Susceptibility in a periodic solid

In a real crystal, the calculation of the susceptibility includes the matrix elements associated with reciprocal lattice vectors \( G \) and \( G' \)[173, 207]. For a system with a weak perturbation, one can write down an Hamiltonian \( H \) as:

\[
H = H_0 + V^{\text{scf}}(r, t),
\]

(7.11)
where $H_0$ is the unperturbed Hamiltonian containing the kinetic energy and the periodic lattice potential of the system and $V^{scf}(r, t)$ is a total self consistent potential[208] containing the external potential $V^{ex}(r, t)$ and the induced screening potential $V^s(r, t)$ associated with position $r$ in space at time $t$. The Fourier transform of $V^{scf}(r, t)$ in momentum can be written as:

$$V^{scf}(r, t) = \sum_{q,G} V^{scf}_G(q, \omega) e^{i(q+G) \cdot r}, \quad (7.12)$$

where $q$ is the crystal momentum in the first Brillouin zone and the $G$ is a reciprocal lattice vector. The Bloch state $|k, i\rangle$ related to $H_0$ characterized by the crystal momentum $k$ and band index $i$ can be written as:

$$|k, i\rangle = \frac{1}{\sqrt{\Omega}} e^{i k \cdot r} u^i_k(r), \quad (7.13)$$

and the corresponding eigenenergy $E^i_k$ is given by:

$$H_0 |k, i\rangle = E^i_k |k, i\rangle, \quad (7.14)$$

The density operator $\rho$ can be described by:

$$\rho = \rho_0 + \rho_1, \quad (7.15)$$

where $\rho_0$ denotes an unperturbed density operator which is related to $|k, i\rangle$ with a Fermi function $f_0(E^i_k)$ at the energy $E^i_k$:

$$\rho_0 |k, i\rangle = f_0(E^i_k) |k, i\rangle, \quad (7.16)$$
and \( \rho_1 \) is the change of density associated with the perturbation.

To consider the density response of the system due to \( V^{scf}(r, t) \), one can introduce the Liouville equation:

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

which can be linearized by neglecting \( V^{scf}(r, t) \rho_1 \) and \( i \hbar \frac{\partial \rho_0}{\partial t} \) terms:

\[
i \hbar \frac{\partial \rho_1}{\partial t} = [H_0, \rho_1] + [V^{scf}(r, t), \rho_0].
\]

(7.18)

The matrix elements of Eq. (7.18) calculated in terms of the Bloch states \( |k, i\rangle \) and \( |k + q, j\rangle \) are:

\[
\frac{i \hbar}{\partial t} \langle k, i | \rho_1 | k + q, j \rangle = \langle k, i | [H_0, \rho_1] | k + q, j \rangle + \langle k, i | [V^{scf}(r, t), \rho_0] | k + q, j \rangle + (f_0(E^j_{k+q}) - f_0(E^i_k)) \langle k, i | V^{scf}(r, t) | k + q, j \rangle.
\]

(7.19)

If the weak perturbation is turned on adiabatically, all \( V^{ex}(r, t) \), \( V^s(r, t) \) and \( V^{scf}(r, t) \) should have the same time dependence. Therefore, the expression of \( \langle k, i | \rho_1 | k + q, j \rangle \) can be obtained:

\[
\langle k, i | \rho_1 | k + q, j \rangle = \frac{f_0(E^j_{k+q}) - f_0(E^i_k)}{E^j_{k+q} - E^i_k - \hbar \omega} \sum_G M_G V^{scf}_G(q, \omega),
\]

(7.20)

where the matrix element \( M_G \) is calculated by:

\[
M_G = \frac{1}{\Omega_c} \int_{cell} d^3r u^*_k e^{-i(q+G) \cdot r} u^i_{k+q}(r),
\]

(7.21)

in which \( \int_{cell} \) indicates the integration over a unit cell with volume \( \Omega_c \). The induced
charge density $n(r, t)$ due to $V^s(r, t)$ is:

$$n(r, t) = Tr[\delta(r - r_e)\rho_1] = \frac{1}{\Omega} \sum_{q,G} e^{-i(q+G) \cdot r} \sum_{k,i,j} u_{k+q}^i(r) u_k^i(r) \langle k, i | \rho_1 | k + q, j \rangle,$$ (7.22)

Note that $n(r, t)$ and $V^s(r, t)$ can be connected via Poisson’s equation:

$$\nabla^2 V^s(r, t) = -4\pi e^2 n(r, t).$$ (7.23)

By inserting Eq. (7.20) into the expression for $n(r, t)$ and taking a Fourier transform of Eq. (7.23), we can obtain the linear response relation between the induced potential $V_G^s(q, \omega)$ and the total self consistent potential $V_{G'}^{scf}(q, \omega)$ with the susceptibility $\chi_{G,G'}(q, \omega)$:

$$V_G^s(q, \omega) = -\frac{4\pi e^2}{(q + K')^2} \sum_{G'} \chi_{G,G'}(q, \omega) V_{G'}^{scf}(q, \omega),$$ (7.24)

where $\chi_{G,G'}(q, \omega)$ is written as:

$$\chi_{G,G'}(q, \omega) = \sum_{k,i,j} \frac{f_0(E_{k+q}^j) - f_0(E_k^i)}{E_{k+q}^j - E_k^i - \hbar \omega} M_G^* M_{G'}$$

$$= \sum_{k,i,j} \frac{f_0(E_{k+q}^j) - f_0(E_k^i)}{E_{k+q}^j - E_k^i - \hbar \omega} \times \langle k, i | e^{-i(q+G) \cdot r} | k + q, j \rangle \langle k + q, j | e^{i(q+G') \cdot r} | k, i \rangle.$$ (7.25)
References


REFERENCES


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