Spring 1-1-2011

Angle-Resolved Photoemission Spectroscopy Studies on Cuprate and Iron-Pnictide High-Tc Superconductors

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Angle-Resolved Photoemission Spectroscopy Studies on Cuprate and Iron-Pnictide High-$T_c$ Superconductors

by

Qiang Wang

B.S., University of Science and Technology of China, 2003

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A thesis submitted to the
Faculty of the Graduate School of the
University of Colorado in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy
Department of Physics
2011
This thesis entitled:
Angle-Resolved Photoemission Spectroscopy Studies on Cuprate and Iron-Pnictide High-$T_c$
Superconductors
written by Qiang Wang
has been approved for the Department of Physics

Daniel S. Dessau

Assoc. Prof. Dmitry Reznik

The final copy of this thesis has been examined by the signatories, and we find that both the content and the form meet acceptable presentation standards of scholarly work in the above mentioned discipline.
The exotic physics in condensed matter systems, such as High-$T_c$ superconductivity in cuprates and the newly discovered iron-pnictide superconductors, is due to the properties of the elementary excitations and their interactions. The “one-electron removal spectral function” measured by angle-resolved photoemission spectroscopy (ARPES) provides a chance to understand these excitations and reveal the mechanism of the high-$T_c$ superconductivity.

In most cases, ARPES studies focus on the excitations very close to the Fermi level (usually within tens to hundreds of meVs). In this region, by presuming that the correlation effect is not too strong, we usually can describe the correlated electron system in terms of well-defined “quasiparticles”, i.e. electrons dressed with a manifold of excited states. Then the spectral function measured by ARPES can be separated into two parts: a coherent pole part that contains the information about the dispersion relation $E(\vec{k})$ and the lifetime $\tau$ of the quasiparticles, which is usually the main subject of ARPES studies; and an incoherent smooth part without poles which also contains important information about the many-body interactions in the system but is usually overlooked by physicists due to the lack of analysis techniques and theoretical understanding.

In this thesis, we present ARPES measurement on the cuprate High-$T_c$ superconductors Pb$_x$Bi$_{2-x}$Sr$_2$CaCu$_2$O$_{8}$ (Pb-Bi2212) and Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ (Bi2212) and the iron-pnictide High-$T_c$ superconductor’s parent compound CaFe$_2$As$_2$ (Ca122) and BaFe$_2$As$_2$ (Ba122). For Pb-Bi2212 and Bi2212 materials, whose quasiparticle dispersions have already been extensively studied, our work focuses on the incoherent part of the spectral function. By introducing a new ARPES lineshape analysis technique, we separate out the sharp coherent peaks from the higher energy incoherent “background” portions and uncover a new type of scaling behavior of the incoherent portions. In
particular, the fraction of weight that is incoherent is found to be intimately linked to the energy of the dispersive coherent feature through a simple quadratic relationship with no special energy scales. This behavior in concert with strong momentum-dependent matrix element effects gives rise to the heavily studied “waterfall” behavior in cuprate superconductors.

For the newly discovered Ca122 and Ba122 materials, whose intrinsic electronic structure is still missing, our studies aim at understanding its quasiparticle dispersion relation $E(\mathbf{k})$ and the Fermi surface geometry. We observed unequal dispersions and FS geometries along the orthogonal Fe-Fe bond directions. Comparing with the optimized LDA calculations, an orbital-dependent band shifting is introduced to get better agreement, which is consistent with the development of orbital ordering. More interestingly, unidirectional straight and flat FS segments are observed near the zone center, which indicates the existence of a unidirectional charge density wave order. Therefore, our studies indicate that beyond the well-known spin density wave (SDW) order and superconducting state (SC), there are other competing orders in the iron-pnictide materials such as the orbital order (OO), the charge density wave (CDW) order and the possible nematic phase. The coexistence of all these competing orders puts strong constraints on theories for describing the iron-pnictide system.
Dedication

To my family.
Acknowledgements

First and foremost, I would like to thank my advisor, Prof. Dan Dessau. Dan has all the characteristics of a great mentor: successful in career, knowledgeable and still eager to learn more, willing and able to devote time and energy to his students, respect students’ ideas and be able to give constructive feedback, and many others. Under his guidance, I am able to really learn one of the most advanced experimental techniques in modern physical science and to use it to explore the exciting topics in condensed matter physics such as high-Tc superconductivity. Furthermore, Dan is always very kind to me (more accurately, to everyone around him) and willing to share his experiences with me, not only in research, but also in life. This makes him not only my advisor but also my best friend.

I spent the best seven years of my life in Dessau group with the greatest coworkers I have ever met. I joined the group in 2004, within the same year as Nick Plumb and Ted Reber (who are both “Dr.” now). Nick has great research results on the ”Plumb-Kink” in cuprate superconductors and he is a great programmer who wrote the whole computer interface for data taking and sample manipulating of our home system. Ted Reber has been focusing on cuprates, especially the “ATS” type analysis which may be a killer experimental result for understanding the gap function observed in cuprates, and he is also the laser expert in group. We all learned a lot from the older group members: Dr. Jake Koralek, Dr. John Fraser Douglas, and Dr. Zhe Sun. Jake built the first laser-based ARPES system, which put the photoemission technique onto a new level. Fraser
performed the isotope experiments on cuprates which is critical for understanding their superconducting mechanism and he is also the most energetic guy in group. I almost learned everything about synchrotron-based ARPES from Zhe, who is my “inofficial advisor” and a true expert in manganite physics. Furthermore, Zhe is also my best friend in life and taught me driving, so that I could survive on the road from SFO airport to LBNL. I also need to thank Justin Griffith, who is our mechanical designer and is great at machining and drawing things (especially the “Line-Rider”). I also thank the younger group members — Yue Cao, Steve Parham, Sunita Kannan, Justin Waugh, and Daniel Weingarten — for the great time we spent together. I would also like to thank my Comps III and thesis committee members — Dmitry Reznik, Leo Radzihovsky, Minhyea Lee, Kyle McElroy, and Scott Bunch — for their kindness and great advises on my thesis project.

I have also benefited from some excellent outside collaborations and assistances. Most of the data in this thesis came from the Advanced Light Source (ALS) in Berkeley. I would like to thank all the beamline scientists: Yi-De Chuang and Jonathan Denlinger at BL4, Eli Rotenberg and Aaron Bostwick at BL7, Wanli Yang at BL8, Sung-Kwan Mo at BL10, Alexei Fedorov at BL12, and also Donghui Lu and Hashimoto Makoto at Stanford Synchrotron Radiation Lightsourc (SSRL) BL5-4. The cuprate samples come from Prof. Helmuth Berger’s research group at EPFL, Switzerland, and Hiroshi Eisaki and Yoshihiro Aiura’s group at AIST, Japan. The iron-pnictide samples come from Filip Ronning and Eric Bauer’s group at LANL. I also would like to thank Prof. Arun Bansil, Prof. Robert Markiewicz, and Dr. Hsin Lin from Northeastern University for their theoretical calculations on iron-pnictide superconductor’s band structure, and Prof. Alexander Balatsky and Dr. Tanmoy Das from LANL for their calculations on cuprate superconductor’s self-energy.

Special thanks to Sid in machine shop for teaching me the basic machining skills; Jeanne, Jason, Kate, Susan, and all the other stuffs in department for their patience and kindness for doing numerous paperwork for me.

Finally, I have to give my thanks to the most important people in my life — my friends and family. Many thanks to Zhaofeng Liu, who helped me to adapt to this country in the first several years of my PhD study; Xiaoshi, Jin, Mingming, Yun, Jianying, Xibin, Quan, Qing, Lin,
Hua, Xiang, Fang, and many others, who I shared great time with after work. At last but not least, thank my Mom and Dad for everything they have done for me, and thank the girl I love for doubling my happiness and cutting my sadness in half.

*To everyone, thanks!*
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\[ I(k, \omega) = [I_0(k, \nu, A)f(\omega)A(k, \omega)+B(k, \omega)] \otimes R(k, \omega), \]
where \( I_0(k, \nu, A) \) is proportional to the matrix element, \( f(\omega) \) is the Fermi function, 
\[ A(k, \omega) = -\frac{1}{\pi} \frac{\text{Im}_\Sigma(k, \omega)}{(\omega-\epsilon(k)-\text{Re}_\Sigma(k, \omega))^2+(\text{Im}_\Sigma(k, \omega))^2}, \]
is the one-particle spectral function, \( \epsilon(k) \) is the bare-band, \( B(k, \omega) \) is the extrinsic 
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\[ \epsilon(k_x, k_y) = \mu - 2t(cosak_x + cosak_y) - 4t'(cosak_x cosak_y - 2t''(cos2ak_x +
cos2ak_y) - 4t^{(3)}(cosak_x cos2ak_y + cos2ak_x cosak_y) - 4t^{(4)} cos2ak_x cos2ak_y + (...)) \]
Six data points at \( E_F \) as well as the band bottom at -0.55 eV were chosen as constraints, as
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Chapter 1

Introduction

Angle-resolved photoemission spectroscopy (ARPES) is the technique to measure the energy and momentum distribution of the photoelectrons emitted from solids, gases or liquids by the photoelectric effect. Based on the energy and momentum conservation relations, we can relate the measured energy and momentum distributions of the photoelectrons to the band structure of the measured substance, or more generally, the “one-particle spectral function” of the measured system in many-body language. This “one-particle spectral function” contains information about all the complicated many-body interactions in the system. And the many-body interactions in condensed matter systems are the ultimate reasons for all the exotic physics such as superconductivity, colossal magnetoresistance effect, multiferroicity, etc.

In this thesis I will present the latest ARPES studies on the cuprate high-\(T_c\) superconductors \(\text{Pb}_x\text{Bi}_{2-x}\text{Sr}_2\text{CaCu}_2\text{O}_8\) (Pb-Bi2212) and \(\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}\) (Bi2212), and the newly discovered iron-pnictide high-\(T_c\) superconductors’ parent compounds \(\text{CaFe}_2\text{As}_2\) (Ca122) and \(\text{BaFe}_2\text{As}_2\) (Ba122). The purpose of this thesis is to contribute to the understanding of the high-\(T_c\) superconductivity in both cuprate and iron-pnictide superconductors.

Chapter 2 is a general overview of the photoemission theory. In this chapter, the ARPES theory which is the fundamental starting point for explaining ARPES data will be discussed in great detail. The purpose of this part is to give readers a complete picture of the ARPES theory, including what we measure, what the results mean, how the ARPES results relate to the important many-body physics of the system, etc. Several fundamental concepts in many-body theory such as
quasiparticle, Fermi liquid, self-energy are also discussed.

In chapter 3, a review of the modern ARPES experimental setup will be given. The three core components, i.e., the light source, the sample, and the analyzer will be discussed in great detail. A newly developed 6.3-eV laser system will also be presented.

Chapter 4 is an overview of superconductivity with discussion on both conventional BCS superconductivity and high-$T_c$ superconductivity in cuprate and iron-pnictide superconductors. By discussing BCS superconductivity, several important concepts are introduced, such as Cooper pair, gap function, Bogoliubov quasiparticle, which are also very important for high-$T_c$ superconductivity. The cuprate and iron-pnictide superconductors are reviewed in a parallel manner. The crystal structures, general electronic structures, phase diagrams, Cooper pair symmetries, and gap functions are reviewed for both types of materials.

In Chapter 5, I present a systematic ARPES study on the “high energy anomaly”, i.e., the waterfall feature in $\text{Pb}_x\text{Bi}_{2-x}\text{Sr}_2\text{CaCu}_2\text{O}_8$ (Pb-Bi2212) and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ (Bi2212) samples over multiple Brillouin zones (BZ) and with a large variety of ARPES matrix elements. This has allowed us to uncover the intrinsic spectral function over a large energy scale. By empirically separating the spectral function into a sharp coherent part and a broad incoherent part, we uncover an unexpected and universal relationship between the weight of these two components. This indicates that both of these components are intrinsic components of the spectral function, that is, the majority of the incoherent part is not a background of inelastically scattered electrons and is not due to impurities, oxygen bands, or states from separate or unrelated bands. This intrinsic incoherent spectral weight, acting in concert with strongly k-dependent matrix element effects, gives rise to the heavily studied “waterfall” behavior. The possible origins of the intrinsic incoherent spectral weight are also discussed.

In Chapter 6, I will present the ARPES studies on the electronic structure and Fermi surface of the untwinned uniaxial state of $\text{CaFe}_2\text{As}_2$, the parent compound of an iron-based superconductor. We are one of the very first groups to observe unequal dispersions and FS geometries along the orthogonal Fe-Fe bond directions of this material. Comparing with the optimized LDA calcula-
tions, an orbital-dependent band shifting is introduced to get better agreement, which is consistent with the development of orbital ordering. More interestingly, unidirectional straight and flat FS segments are observed near the zone center, which indicates the existence of a unidirectional charge density wave order. Therefore, our studies indicate that beyond the well-known spin density wave (SDW) order and superconducting state (SC), there are other competing orders in the iron pnictide materials such as the orbital order (OO), the charge density wave (CDW) order and the possible nematic phase. The coexistence of all these competing orders puts strong constraints on theories for describing the iron pnictide system.

Finally, Chapter 7 will briefly review the results and conclusions discussed in Chapter 5 and 6. Future experiments are also suggested for further understanding the high-\(T_c\) superconductivity in cuprate and iron-pnictide materials. Several lessons learned during my PhD research are also presented, I hope it will be useful for those fresh PhD students.
Chapter 2

Angle-Resolved Photoemission Spectroscopy (Theory)

2.1 Introduction

In 1887, Heinrich Hertz observed that electric sparks occur more easily when the electrodes are illuminated with ultraviolet light. Inspired by Hertz’s discovery, a series of investigations were performed and people found that when electromagnetic radiation with very short wavelength, such as visible or ultraviolet light, was incident on a material, this material will eject electrons from its surface. This process is the so-called photoelectric effect and electrons emitted in this process may be referred to as “photoelectrons”. The photoelectric effect was theoretically explained by a real genius in 1905. By describing light as composed of discrete quanta rather than continuous waves, Albert Einstein explained the photoelectric effect as the result of quanta absorbing. The quanta are the so-called photons. This amazing discovery led to the quantum revolution in modern physics and also earned Einstein the Nobel Prize in Physics in 1921. The angle-resolved photoemission spectroscopy (ARPES) is the technique to measure the energy and momentum distribution of the photoelectrons emitted from solids, gases or liquids by the photoelectric effect. Based on the energy and momentum conservation relations, we can relate the measured energy and momentum distribution of the photoelectrons to the band structure of the measured substance, or more generally, the “one-particle spectral function” of the measured system in many-body language. In this chapter I will give a detailed discussion on ARPES theory which is the fundamental starting point for explaining ARPES data.
2.2 Photoemission process: three-step model vs. one-step model

Before discussing any detailed photoemission theory, let’s first take a look at what happens in the photoemission process. The most intuitive way to explain the photoemission process in solids is the so-called “three-step model” proposed by [Berglund and Spicer, 1964]. As shown in fig. 2.1, the photoemission process can be simply separated into three independent parts: optical excitation of the electron in the solid, transport of the photoelectron to the surface, and escape of the photoelectron into vacuum. Then the total photoemission intensity is given by the product of these three independent events: the probability of the optical excitation, the probability of the photoelectron reaching the surface without scattering, and the probability of the photoelectron passing through the surface. In principle, almost all the physics we care happens in the first step. In the second step, the photoelectron may suffer from some extrinsic scattering process. And in the third step, the photoelectron’s energy and momentum will be altered when crossing the sample’s surface due to the presence of the work function.

Figure 2.1: Illustration of the three-step model (in independent electron picture). (1) Photoexcitation of the electron, (2) the photoelectron travels to the surface and (3) the photoelectron escapes into vacuum after transmission through the surface potential barrier.
The above “three-step model” looks very plausible except that it neglects all the possible interplay between the electrons in those three steps, e.g., the quantum mechanical interference between the photoelectrons from bulk and surface emission and the interference between the photoelectrons with loss and no-loss transport from the place of optical excitation to the surface. So in principle, to “correctly” calculate the photoemission intensity, one need to treat the three steps mentioned above as a single coherent process by including everything in the photoemission process into a single Hamiltonian, and this is the so-called “one-step model”. So far, the best-found approximation for “one-step calculation” is to use the “inverse LEED function” for the final state, which is based on the idea that the quantum mechanical wavefunction of photoelectron in the solid should match the electron wavefunction in the vacuum. This “one-step model” is way more complicated than the “three-step model” and less intuitive. In most cases, it is just a “theorist’s game” rather than an “experimentalist’s tool”. And we are still using the “three-step model” for discussing most of the experimental results and it has proven to be quite successful.

In the rest of this chapter, I will discuss the photoemission process under the “three-step model” frame and mainly consider “step one”, i.e., the optical excitation step which contains the main physics we care about.

2.3 Photoemission in the independent electron picture

Due to the complexity of the photoemission process in solids, I will start discussing the photoemission procedure in the independent electron picture. In this picture, the electron in a solid is assumed to be independent of the other electrons and can be considered as moving in some effective potential \( V(r) = V_{\text{ion}}(r) + V_{\text{scr}}(r) \), where \( V_{\text{ion}}(r) \) is the potential due to the ions and \( V_{\text{scr}}(r) \) is a screening potential arising from the other electrons. As the result, the electron’s behavior can be given by the solution of the single-particle Schrödinger equation

\[
\left[ -\frac{\hbar^2}{2m} \nabla^2 + V_{\text{ion}}(r) + V_{\text{scr}}(r) \right] \psi_k(r) = \epsilon(k) \psi_k(r)
\] (2.1)
By solving this equation, we can describe the electron’s behavior in the solid by the energy vs. momentum dispersion relationship $\epsilon(k)$. This is just the basic idea for band theory. In this section I will present that in the independent electron picture, the ARPES result just can be interpreted as the observation of the band structure.

### 2.3.1 Photon excitation process

First let’s consider the photon excitation process, i.e., “step one” in the “three-step model”. In the independent electron picture, we can ignore all the other electrons in the system and only consider the electron which gets involved with the photon. Then the initial state of the photon excitation process is an single electron at state $k_i$ with energy $E(k_i)$. After absorbing a photon with energy $h\nu$ and momentum $k_h\nu$, the final state of the process is the electron at state $k_f$ and energy $E(k_f)$. Considering the energy and momentum conservation law, we have

$$E(k_f) = E(k_i) + h\nu$$
$$k_f = k_i + k_h\nu(\sim 0) + G$$

(2.2)

Here we need to note that in ARPES experiment we usually use low photon energies ($h\nu < 200$) and the momentum of the photon can be ignored, i.e., $k_h\nu \sim 0$. Then to make the photon excitation process possible, there must be a “momentum source” in the process. This “momentum source” is actually the periodical crystal potential of the solid. One can think of it as the electron recoiled by the lattice in the photon excitation process. And the momentum provided by the crystal potential is equal to the reciprocal-lattice vector as shown by $G$ in above equations. In the reduced zone scheme, one can just ignore this reciprocal-lattice vector $G$ by folding the band structure back to the first zone, then one have $k_f = k_i$. This is the reason why the photon excitation process is also called “direct transition” of the electron. But in photoemission, since we need to measure the energy and the momentum of the photoelectrons, we might use the extended zone scheme and keep
all the time in our calculation. Then we have

\[ E(k_f) = E(k_i) + h\nu \]  

\[ k_f = k_i + G \]  

where \( E(k_f) \) and \( k_f \) are just the energy and momentum of the photoelectron before its escape into the vacuum.

### 2.3.2 Into space: the energy and momentum relations

In the previous section, I discussed the photon excitation process in the independent electron picture which is the first step of the “three-step model”. As the result, the electron after photon excitation process has the energy \( E(k_f) \) and the momentum \( k_f \). In this section I will discuss the rest two steps.

In the second step of the photoemission process, transport of the electron to the surface, electrons have a certain possibility for losing energy to the system due to the extrinsic scattering process. As a result, there will be a “secondary spectrum” added to the “primary spectrum” of the photoelectron distribution. The probability of this extrinsic scattering process is characterized by the mean free path of the electron in the sample which determines the surface sensitivity of the photoemission experiment. Since now we are discussing the “primary part” I will just ignore this extrinsic scattering process and consider that the electron will move freely to the surface.

In the last step of the three-step model, escape of the electron into the vacuum, the photoelectron will cross a potential barrier between sample and vacuum. This potential barrier is the so-called work function of the sample \( \Phi_s \). The energy relation of the photoelectron in and out of the sample is shown in fig. 2.2. Right now, we need to use the Fermi level of the system as the new energy reference of the photoemission process, then kinetic energy of the photoelectron can be expressed as

\[ E_{kin} = E(k_f) - E_F - \Phi_s \]  

What is the momentum relation of the photoelectron in and out of the sample? First we should note that since the photoelectron out of the sample is a free electron, its momentum and
Figure 2.2: Energy schematic of the photoemission process. Electrons with binding energies $E_i$ are excited by photons of energy $h\nu$. If the photon has sufficient energy to overcome the sample’s work function $\Phi_s$, then the electron will be ejected from the solid. But the photoelectron can only be detected if the photon also has enough energy to overcome the analyzer’s work function $\Phi_a$. Actually, in ARPES experiment the photoelectron’s kinetic energy is measured relative to the analyzer’s work function $\Phi_a$. In the rest of this chapter, we simply ignore this difference and still use sample’s work function $\Phi_s$ in calculations. The example of a core level state with $E_i = E_B$ is highlighted and further details are discussed in the text. Adopted from [Reinert and H"ufner, 2005].
energy must follow the free electron dispersion relationship

\[ E_{\text{kin}} = \frac{\hbar^2 |k_m|^2}{2m} = \frac{\hbar^2 |k_{m\parallel}|^2}{2m} + \frac{\hbar^2 |k_{m\perp}|^2}{2m} \]

(2.5)

where \( k_m \) represents the momentum and can be separated into the component parallel to the surface \( k_{m\parallel} \) and component perpendicular to the surface \( k_{m\perp} \). As the electron leaves the sample, its momentum parallel to the surface is conserved due to the translation symmetry across the surface, then we have

\[ k_{m\parallel} = k_{f\parallel} \]

(2.6)

But due to the presence of the work function, the perpendicular momentum component is not conserved and in general we have

\[ k_{m\perp} < k_{f\perp} \]

(2.7)

The above momentum relations are summarized in fig. 2.3(a).

2.3.3 Interpretation of ARPES data (part I): band mapping

In this section, I will present how to interpret ARPES spectra in the independent electron picture based on the discussion in the previous sections.
Fig. 2.3(b) shows a schematic of the geometry of an ARPES experiment in which the emission direction of the photoelectron is specified by the polar (ϑ) and azimuthal (ϕ) angles. In an ARPES experiment, what we measure is the photoelectron distribution as a function of its kinetic energy and emission direction, i.e., \( I = I(E_{\text{kin}}, \vartheta, \varphi) \). Based on the free electron dispersion relation, the momentum \( \mathbf{k} \) of the photoelectron can be determined as

\[
\begin{align*}
  k_x &= \frac{1}{\hbar} \sqrt{2mE_{\text{kin}}} \cdot \sin \vartheta \cdot \cos \varphi \\
  k_y &= \frac{1}{\hbar} \sqrt{2mE_{\text{kin}}} \cdot \sin \vartheta \cdot \sin \varphi \\
  k_z &= \frac{1}{\hbar} \sqrt{2mE_{\text{kin}}} \cdot \cos \vartheta
\end{align*}
\]  

(2.8)

So after doing some math we can express the photocurrent as a function of the photoelectron’s energy and momentum \( I = I(E_{\text{kin}}, k_x, k_y, k_z) = I(E_{\text{kin}}, k_{m||}, k_{m\perp}) \).

First let’s take a look at the energy relationship. Based on the discussion from previous sections, we have

\[
E(\mathbf{k}_f) = E(\mathbf{k}_i) + \hbar \nu
\]

\[
E_{\text{kin}} = E(\mathbf{k}_f) - E_F - \Phi_s
\]

(2.9)

We can easily get

\[
E_{\text{kin}} = \hbar \nu - \Phi_s - \left[ E_F - E(\mathbf{k}_i) \right]_{E_B}
\]

(2.10)

where \( E_B \) is the so-called binding energy. In general, we should just express \( E_B \) as

\[
E_B = \hbar \nu - \Phi_s - E_{\text{kin}}
\]

(2.11)

which is determined from the experiment without any theory assumption and always serve as the energy coordinate by experimenters. Here we can see that in the independent electron picture, we can just extract the electron’s initial state energy from the measured binding energy. If we just stop here, and ignore the further momentum dependence of the photoelectron current by integrating the spectrum over momentum space, what we get is just the angle-integrated photoemission spectrum and it provides a measure of the single-particle density of states in the independent electron picture. But we can go beyond that in ARPES measurement!
Recall the equations shown in the previous section about the photoelectron’s momentum relation, we have

\[
\vec{k}_m = \vec{k}_f = \vec{k}_i + \vec{G}
\]

\[
\vec{k}_{m\perp} < \vec{k}_{f\perp} = \vec{k}_{i\perp} + \vec{G}_{\perp}
\]

(2.12)

So we can precisely determine the electron’s inplane momentum in its initial state, the offset inplane reciprocal-lattice vector \(\vec{G}_{\parallel}\) can be ignored in the reduced zone scheme. As for the out of plane component, which is not conserved, its value can also be determined by assuming we know the final state dispersion relationship \(E(\vec{k}_f)\). One can either use certain band calculation to approximate \(E(\vec{k}_f)\) or just assume the final states are near-free-electron like:

\[
E(\vec{k}_f) = \left| \frac{\hbar \vec{k}_f}{2m} \right|^2 + E_0 = \left| \frac{\hbar \vec{k}_f}{2m} \right|^2 + \left| \frac{\hbar \vec{k}_{f\perp}}{2m} \right|^2 + E_0
\]

(2.13)

where \(\frac{|\hbar \vec{k}_f|^2}{2m} = E_{\text{kin}}\sin^2\vartheta\) and \(E(\vec{k}_f)\) can also be expressed as \(E(\vec{k}_f) = E_{\text{kin}} + \Phi_s + E_F\). Then we have

\[
\vec{k}_{f\perp} = \frac{1}{\hbar} \left[ 2m(E_{\text{kin}}\cos^2\vartheta - V_0) - \Phi_s - E_F \right]^{\frac{1}{2}}
\]

(2.14)

The inner potential \(V_0\) can be determined by experimentally observed periodicity of the dispersion \(E(\vec{k}_{f\parallel})\) by scanning photon energies.

Finally, let me summarize the energy and momentum relation presented above: in the independent electron picture

\[
E(\vec{k}_i) = E_{\text{kin}} - (h\nu - \Phi_s - E_F)
\]

\[
\vec{k}_i = \vec{k}_m - \vec{G}_{\parallel}
\]

\[
\vec{k}_{i\perp} \approx \frac{1}{\hbar} \sqrt{2m(E_{\text{kin}}\cos^2\vartheta - V_0)} - \vec{G}_{\perp}
\]

(2.15)

So in the independent electron picture, the measured ARPES spectrum \(I = I(E_{\text{kin}}, \vartheta, \varphi)\) can be finally convert into spectrum \(I(E(\vec{k}_i), \vec{k}_{i\parallel}, \vec{k}_{i\perp})\), i.e. the photoelectron distribution can be directly mapped back to system’s band structure\(^1\).

\(^1\) In fig. 2.2, I showed that the kinetic energy of the photoelectron is actually measured against analyzer’s work function. But it will not affect the conclusion we made.
2.4 Photoemission in the interacting electron picture

In the preceding sections we discussed the photoemission procedure in the “independent electron picture”. In that picture, electrons in the system follow the band structure and in the photoemission process we can just remove one electron from its initial state without changing anything else in the system. This picture is illustrated in fig. 2.4(a). But in real many-electron system, as illustrated in fig. 2.4(b), when we remove a electron from the system, the rest of the system will respond to this photoemission process due to the complicated many-body interactions and further modify the photoelectron’s behavior. So for accurately interpreting the ARPES result, we need to consider the more realistic “interacting electron picture” and employ many-body theory to describe the photoemission process. In this section, I will review the photoemission procedure in many-body language.

Here we note that, even if we describe the many-electron system by the very complicated many-body theory, the three-step model is still appropriate for describing the photoemission process. The major difference between the three-step model in the independent electron picture and the interacting electron picture happens in the photon excitation process, while the transport and...
escaping steps of this two pictures are the same in principle.

2.4.1 Initial and final state revisited, sudden approximation

For an interacting electron system, the true initial state of the photoemission procedure is the N-electron ground state (here we assume $T = 0$) which can be described by a N-electron wave function $|\Psi_N^i\rangle (= |\Psi_0^N\rangle)$ with energy $E_N^i (= E_0^N)$ while the final state is the exited state of this N-body system and can be described by the wave function $|\Psi_f^N\rangle$ with energy $E_f^N$. This final state consists of two components: the photoelectron with wavefunction $|\phi_k^f\rangle$ and energy $E_k$, and the (N-1)-body system left behind with wavefunction $|\Psi_{N-1}^f\rangle$ and energy $E_{N-1}^f$. Here we note that the energy $E_k$ is the energy of photoelectron inside the sample, i.e.,

$$E_k = E_{kin} + \Phi_s \quad (2.16)$$

Due to the energy conservation law in photoemission procedure, we express the energy of the photoelectron as

$$E_k = h\nu + E_i^N - E_{N-1}^f$$

$$= h\nu + \left(\frac{E_0^N - E_0^{N-1}}{\mu}\right) - \left(E_{N-1}^f - E_0^{N-1}\right) \quad (2.17)$$

So the kinetic energy of the photoelectron is actually a measure of the energy change of the remaining (N-1)-electron system in the photoemission procedure. Here we note that there are two extreme cases for the photoemission procedure:

1. The photoelectron barely has enough energy to escape through the surface. In this case, the photoelectron may move slowly enough so that the interaction between the photoelectron and the remaining (N-1)-electron system will lead the (N-1)-electron system to relax to the lowest energy state, i.e., $E_{N-1}^f \rightarrow E_0^{N-1}$ in equation 2.17. Then the photoelectron will gain extra energy from the (N-1)-electron system due to the energy conservation law and has the maximum kinetic energy. This is the so-called the “adiabatic limit” in photoemission procedure.

2. The photoelectron has very large kinetic energy. In this case, the photoelectron only stays in the solid for an infinitesimal amount of time before escaping into vacuum and we can ignore
all possible interaction between the photoelectron and the remaining (N-1)-electron system. Then the (N-1)-electron system is left in one of its excitation states (or ground state). If we choose an excited state with eigenfunction $|\Psi_{m}^{N-1}\rangle$ and energy $E_{m}^{N-1}$ as the final state of the (N-1)-electron system, we will get the kinetic energy of the photoelectron $E_{k} = h\nu + \mu - (E_{m}^{N-1} - E_{0}^{N-1})$ and the term in the bracket is just the excitation energy for the (N-1)-electron system. This is the so-called “sudden approximation” in photoemission. Furthermore, recall the expression of the binding energy $E_{B} = h\nu - \Phi - E_{kin}$ and $E_{k} = E_{kin} + \Phi$, we may get

$$E_{B} = h\nu - E_{k} = (E_{m}^{N-1} - E_{0}^{N-1}) - \mu = \varepsilon_{m}^{N-1} - \mu$$

(2.18)

So in the interacting electron picture, the binding energy $E_{B}$ yields a measure of the excitation energies $\varepsilon_{m}^{N-1}$ for the (N-1)-electron system.

The sudden approximation discussed above is actually a core assumption for interpreting the photoemission spectra. Within this approximation, the photoelectron will have a “memory” of the excitation state of the original system. Then by measuring the photoelectron, we may reach an understanding of the complex many-body system. In the following section, I will show that under the “sudden approximation”, the photoelectron current measured in the photoemission experiment can be interpreted as the “one-electron spectral function” in many-body language. In practice, almost all photoemission experiments appear to fall in the sudden regime, not the adiabatic regime. This is true even for the lowest photon energies used in real experiment [Koralek, 2006].

2.4.2 One-electron spectral function

To theoretically calculate the photoelectron current in the photoemission procedure, one can start by calculating the transition probability $w_{fi}$ from $|\Psi_{i}^{N}\rangle \rightarrow |\Psi_{f}^{N}\rangle$ due to the optical excitation (three-step model). This can be approximately calculated by Fermi’s Golden rule as the result of first order perturbation theory:

$$w_{fi} = \frac{2\pi}{\hbar} |\langle \Psi_{f}^{N} | H_{int} | \Psi_{i}^{N} \rangle |^{2} \delta(E_{f}^{N} - E_{i}^{N} - h\nu)$$

(2.19)
where the perturbation Hamiltonian is

\[ H_{\text{int}} = \frac{e}{2mc} [A(r) \cdot \mathbf{p} + \mathbf{p} \cdot A(r)] + \frac{e^2}{2mc^2} |A(r)|^2 \] (2.20)

\( \mathbf{p} \) is the electronic momentum operator and \( A(r) \) is the electromagnetic vector potential. If one chooses the Coulomb gauge \((\nabla \cdot A = 0)\) and also neglects the higher order term \(|A(r)|^2\), then the interaction Hamiltonian is simplified to

\[ H_{\text{int}} = \frac{e}{mc} A(r) \cdot \mathbf{p} \] (2.21)

This Hamiltonian can be further simplified by the so-called dipole approximation which assumes the variation of the external field \( A(r) \) is small in the spatial region where the photoemission procedure happens, i.e.,

\[ A(r) = A_0 \hat{e} e^{ikr} = A_0 \hat{e} (1 + ikr + \ldots) \cong A_0 \hat{e} \] (2.22)

where \( A_0 \) is the amplitude of the field and \( \hat{e} \) is a unit vector in the direction of the light polarization.

To evaluate the transition probability, we need to go back to the “sudden approximation” discussed in the previous section. In this approximation, the \( N \)-electron final state \( |\Psi_N^frangle \) can be factorized into the decoupled single photoelectron state \( |\phi_{k_f}rangle \) and the remaining \((N-1)\)-electron system’s excitation state \( |\Psi_{N-1}^frangle \) which can be expressed as the combination of all the possible eigen-excited states \( |\Psi_{m-1}^{N-1}rangle \) with energy \( E_{m-1}^{N-1} \). While for the initial state, we can also express the initial state wave function as the product of a one-electron orbital \( |\phi_{k_i}rangle \) and an \((N-1)\)-electron wavefunction \( |\Psi_{i-1}^{N-1}rangle \) which actually should be expressed as \( |\Psi_{i-1}^{N-1}rangle = c_k |\Psi_i^Nrangle \) in many body language and \( c_k \) is the annihilation operator for an electron with momentum \( k^2 \). After plugging in all the new expressions of the initial and final states, we could rewrite the equation 2.19 as

\[
W_{fi} = \sum_m w_{mi} = \frac{2\pi}{\hbar} \left| \langle \phi_{k_i}^{N} | H_{\text{int}} | \phi_{k_f}^{N} \rangle \right|^2 \sum_m \left| \langle \Psi_{m-1}^{N-1} | c_k | \Psi_i^N \rangle \right|^2 \delta(E_k + E_{m-1}^{N-1} - E_i^N - \hbar\nu) \] (2.23)

\(^2\) In principle, the initial state can be expressed as a product of a one-electron state with arbitrary momentum and the corresponding \((N-1)\)-electron wavefunction. Here we just choose the one-electron state having the same momentum as the final photoelectron’s momentum, this can be understand as the result of the momentum conservation law in the photoemission procedure.
which is just proportional to the photoelectron current (or the photoemission intensity) $I(E_k, k)$ measured as a function of photoelectron’s energy $E_k$ at momentum $k$.

The term $\text{1}$ in equation 2.23 is just the probability of the single electron transition from $i \to f$ due to photon excitation $H_{\text{int}}$. It is the so-called “ARPES matrix element”. In the dipole approximation discussed above, it can be expressed as

$$M_{f,i}^k \equiv \langle \phi_f^k | H_{\text{int}} | \phi_i^k \rangle \propto \langle \phi_f^k | \hat{e} \cdot \mathbf{p} | \phi_i^k \rangle$$

(2.24)

By using the commutation relation $\hbar \mathbf{p}/m = -i[\mathbf{r}, H]$, we can get

$$M_{f,i}^k \propto \langle \phi_f^k | \hat{e} \cdot \mathbf{r} | \phi_i^k \rangle$$

(2.25)

which is known as the length form of the matrix element and $\hat{e}$ is the unitary vector in the direction of the light polarization.

The term $\text{2}$ in equation 2.23 is the square of the (N-1)-electron system’s overlap integral summed over energy-conserving excited final states. In the next few paragraphs we will show that it is just the one-electron removal spectral function in many body language.

To understand the properties of a many-body system with interactions, the “ideal” way is to know the detailed behavior of each particle in the system, which is impossible and also unnecessary. It turns out that we only need to know the average behavior of one typical particle and the quantities which describe this particle is the time-ordered one-electron Green’s function $G(t - t')$. This one-particle Green’s function can be interpreted as the probability amplitude that a particle added to the system in a Bloch state with momentum $k$ at a time zero will still remain in that state after a time $|t - t'|$. By taking the Fourier-transform, $G(t - t')$ can be expressed in energy-momentum representation and at $T = 0$ it has the form

$$G(k, \omega) = \sum_m \frac{|\langle \Psi_m^{N+1} | c_k^+ | \Psi_i^N \rangle|^2}{\omega - (E_m^{N+1} - E_i^N) + i\eta} + \sum_m \frac{|\langle \Psi_m^{N-1} | c_k | \Psi_i^N \rangle|^2}{\omega - (E_i^N - E_m^{N-1}) - i\eta} \tag{2.26}$$

$\text{3}$ There are also two- or more-particle Green’s function which is out of the scope of this thesis.

$\text{4}$ $\eta$ in followed equation is a positive infinitesimal to make the integration of the Green’s function converge.
where $G^+(k, \omega)$ and $G^-(k, \omega)$ are the one-electron addition and removal Green’s functions, respectively. From equation 2.26, we find that the poles of the one-electron addition and removal Green’s function locate at

$$E_m^{N+1} - E_i^N = (E_m^{N+1} - E_i^{N+1}) + (E_i^{N+1} - E_i^N) = \varepsilon_m^{N+1} + \mu$$

(2.27)

$$E_i^N - E_m^{N-1} = -(E_m^{N-1} - E_i^{N-1}) + (E_i^{N-1} - E_i^N) = -\varepsilon_m^{N-1} + \mu$$

, respectively. They actually represent the possible excitation energies of the one-electron addition and removal processes. This is a very useful argument and has great utility in many-body theory. We can also obtain the one-electron addition and removal spectral functions from the corresponding Green’s function as:

$$A^+(k, \omega) = -\frac{1}{\pi} \text{Im} G^+(k, \omega) = \sum_m |\langle \Psi_m^{N+1} | c_k^+ | \Psi_i^N \rangle|^2 \delta(\omega - E_m^{N+1} + E_i^N)$$

$$A^-(k, \omega) = \frac{1}{\pi} \text{Im} G^-(k, \omega) = \sum_m |\langle \Psi_m^{N-1} | c_k^+ | \Psi_i^N \rangle|^2 \delta(\omega + E_m^{N-1} - E_i^N)$$

(2.28)

Strictly speaking, the spectral function gives the probability that the initial state $|\Psi_i^N\rangle$ with an added/removed electron in state $k$ is an exact eigenstate of the $N+1/N-1$ electron system with energy between $\omega$ and $\omega + d\omega$. They provide information about the nature of the allowed electronic states and can be considered as a generalized density of states.

Comparing the one-electron removal spectral function to term 2 in equation 2.23, one finds that they are just identical by assuming $\omega = E_k - h\nu$. Recall equation 2.18, we have $E_k - h\nu = -E_B$ where $E_B$ is the binding energy of the photoelectron. So they indeed have the same physical meaning and the term 2 in equation 2.23 is just the one-electron removal spectral function after converting the photoelectron’s kinetic energy to binding energy. Then at $T = 0$ we have

$$I(k, \omega) \propto w_{fi} = \frac{2\pi}{\hbar} |M_{fi}^k|^2 A^-(k, \omega),$$

(2.29)

i.e., ARPES is measuring the matrix-element-distorted one-electron removal spectral function.

So far, we haven’t considered any requirement on the energy parameter $\omega$. Actually, for one-electron removal spectral function we always have $\omega < \mu$ since we can only remove an electron from an occupied state. For the similar reason, we always have $\omega > \mu$ for one-electron addition
spectral function. Then the total spectral function can be expressed as

\[
A(k, \omega) = \begin{cases} 
A^+(k, \omega) & \omega > \mu, \\
A^-(k, \omega) & \omega < \mu.
\end{cases} \tag{2.30}
\]

In turn, the one-electron addition and removal spectral function can be expressed as

\[
A^+(k, \omega) = A(k, \omega) \theta(\mu - \omega) \\
A^-(k, \omega) = A(k, \omega) \theta(\omega - \mu)
\tag{2.31}
\]

where \( \theta(x) \) is a step function as

\[
\theta(x) = \begin{cases} 
1 & x < 0, \\
0 & x > 0.
\end{cases} \tag{2.32}
\]

Then we can rewrite equation 2.29 as

\[
I(k, \omega) \propto \frac{2\pi}{\hbar} |M^k_{f,i}|^2 A(k, \omega) \theta(\omega - \mu) \tag{2.33}
\]

The reason we rewrite equation 2.29 in this form is that it is a more general expression and can be extended to the finite temperate \((T \neq 0)\) case (which is the real situation for our experiment) simply by replacing the step function \(\theta(\omega - \mu)\) with the Fermi function \(f(\omega - \mu) = \left( e^{(\omega - \mu)/k_B T} + 1 \right)^{-1} \).

Finally, we have the photoemission intensity at a given \((k, \omega)\) as\(^5\)

\[
I(k, \omega) = I_0(k, \nu, A) f(\omega) A(k, \omega) \tag{2.34}
\]

where \(I_0(k, \nu, A) \propto |M^k_{f,i}|^2\) as shown in equation 2.23 and depends on the electron momentum, photon energy and polarization. \((k, \omega)\) can be obtained from the photoelectron’s momentum and energy due to the conservation law. Again I need to emphasis that in equation 2.34, the spectral function is the total spectral function as defined by equation 3.8. So at finite temperature, ARPES does not only measure the one-electron removal spectral function below the chemical potential but also can extract certain information of the one-electron addition spectral function slightly

\(^5\) Here I replace energy parameter \(\omega - \mu\) with just \(\omega\) in Fermi function by changing the energy origin from zero to chemical potential \(\mu\).
above the chemical potential, but those spectral functions measured around chemical potential are severely distorted by the Fermi function\textsuperscript{6}.

One of the most important properties of the spectral function is the sum rule, for the total spectral function $A(k,\omega)$, we have

$$\int_{-\infty}^{+\infty} d\omega A(k,\omega) = 1 \tag{2.35}$$

which just means that the total probability for modifying a many-body system by adding or removing one particle is 1. For ARPES spectrum which measures the occupied states we have

$$\int_{-\infty}^{+\infty} d\omega f(\omega)A(k,\omega) = n(k) \tag{2.36}$$

where $n(k) = \langle \Psi_f^N | c_k^+ c_k | \Psi_f^N \rangle$ is the momentum distribution function.

So far, all the discussions above are based on the ideal experimental condition. In real-life ARPES experiment, we also need to consider the presence of the background due to the extrinsic\textsuperscript{7} scattering process of the photoelectron, e.g., the inelastic “secondary” photoelectrons; the spectrum broadening due to the system resolution effect; and also other artificial effects from the detector [Plumb, 2011]. As the result, the real-life ARPES intensity may be expressed as:

$$I(k,\omega) = [I_0(k,\nu,A)f(\omega)A(k,\omega) + B(k,\omega)] \bigotimes R(k,\omega) + I_{\text{noise}} \tag{2.37}$$

where $\bigotimes$ denotes convolution, $B(k,\omega)$ is the extrinsic backgrounds, and $R(k,\omega)$ is the resolution effects.

### 2.4.3 Interpretation of ARPES data (part II): self-energy and quasiparticle dispersion

In the previous section, I have shown that the ARPES spectrum represents the one-electron removal spectral function\textsuperscript{8}. If we consider the photoemission procedure as injecting a hole into the many-electron system instead of removing an electron from the system, the one-electron removal

\textsuperscript{6} One may obtain the one-particle spectral function above chemical potential by inverse photoemission technique, which is a complementary technique to photoemission spectroscopy.

\textsuperscript{7} A short discussion about intrinsic and extrinsic process is needed.

\textsuperscript{8} More strictly speaking, it is the total spectral function modified by the Fermi function.
Green’s function can be converted into the one-hole addition Green’s function and can be interpreted as the probability amplitude that a hole added to the system in a Bloch state with momentum $k$ at time zero will still remain in the state at a later time. In this sense, the spectral function measured by the ARPES experiment actually describes the behavior of the hole injected to the system due to the photoemission procedure. This hole is called the photohole, with momentum equal to the momentum of the photoelectron in the same photon excitation process but with different sign (due to the momentum conservation law) and energy equal to the excitation energy of the remaining (N-1)-electron system which can be also determined by measuring the kinetic energy of the photoelectron (due to the energy conservation law). In other words, the photohole is an identical representation for the excitation state of the remaining (N-1)-electron system. In some literature, people just say that the photoemission final state consists of a photohole and a photoelectron, and by measuring the energy and momentum distribution of the photoelectron one can learn the behavior of the photohole which contains the information about the many-body interaction in the many-electron system.

### 2.4.3.1 Self-energy and quasiparticle dispersion

Now assuming that we already have the intrinsic spectral function obtained from the ARPES spectra, to really get the knowledge about the many-body system, we still need to figure out two questions: through what quantities does the spectral function describe the many-body system and how do we extract those quantities from the spectral function.

To answer the first question, we need to recall the fact that the poles of the one-electron addition and removal Green’s function represent the excitation energy of the many-electron system in the one-electron addition and removal processes. First let’s consider the independent electron picture. In this picture, all electrons follow the band structure and stay in the band independently. In the photoemission procedure, we can only remove an electron from an existing state; in other words, add a hole (photohole) to the band. Since there is no interaction between the electrons in

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9 Recall equation 2.17 in sudden approximation.
the band, there is no decay channel for the photohole and the photohole will stay in that specific state for ever. For this reason, the energy vs. momentum dispersion relation of the photohole will just follow electron’s band structure $\epsilon(k)$. $\epsilon(k)$ is also called the “bare-band” due to its non-interacting nature. In other words, the system has the photohole as an excitation, and that energy follows the electron band structure and has an infinite lifetime. In theory one can show that in the independent electron picture the one-particle Green’s function is\textsuperscript{10}:

$$G(k, \omega) = \frac{1}{\omega - \epsilon(k) + i\eta} \quad (2.38)$$

which has a single pole at $\omega_{\text{pole}} = \epsilon(k) - i\eta$. As we expected, the pole of the Green’s function just contains the energy information about the excitation in the system which is $\epsilon(k)$ and the lifetime of this excitation as $\tau = 1/|\eta_{\to 0}| \to \infty$.

The corresponding spectral function in the independent electron picture is

$$A(k, \omega) = \delta(\omega - \epsilon(k)) \quad (2.39)$$

which is a $\delta$-function consisting of a single line at the band energy $\epsilon(k)$. So in the independent electron picture, the spectral function of a photohole measured by ARPES is just a $\delta$-function following the electron bare band. The discussion above can also serve as the general justification for the band mapping argument discussed in section 2.3.3.

Now let’s go to the interacting electron picture. Considering we turn on the electron-electron correlation adiabatically, one\textsuperscript{11} may argue that the ground state of the original independent many-electron system will adiabatically transform into the ground state of the interacting system, i.e., the ground state of the interacting system (also the initial state of the photoemission procedure) can still be described by the electrons filling up the band structure. When we remove an electron from a certain state, i.e., inject a hole to certain state, the interaction between this hole and all the other electrons in the system will strongly affect this hole’s behavior. As the result, there will be a certain amount of energy and momentum transferred from this hole to the other electrons in the system.

\textsuperscript{10} Here I am using the total Green’s function, which contains both the one-electron addition and the one-electron removal parts.

\textsuperscript{11} The very first “one” was Landau.
(by creating electron-hole pairs). Then the hole will not appear at the position where it would be in the independent electron approximation, i.e., there will be an energy renormalization with respect to the bare-band. Furthermore, due to the complication of the interactions, there will be a lot of situations with different amounts of energy and momentum transferred from the hole to the rest of the system that are allowed, i.e., the hole can decay into a lot of different states. Then the spectral function of this hole is not a δ-function anymore, but has a certain width in energy instead.

In other words, the hole state has a certain lifetime. Then the excitations in this many-electron system can be consider as a hole with energy \( E(k) \neq \epsilon(k) \) and finite life \( \tau \). And there is a one-to-one correspondence between the holes \( (E(k), \tau) \) of this interacting many-electron system and the holes \( (\epsilon(k), \tau \rightarrow \infty) \) in the same many-electron system but without interaction. This is just the basic idea of the Fermi liquid theory which is one of the most famous and extensively accepted theories for describing the interacting many-electron system. And the holes with energy \( E(k) \) and life \( \tau \) is the so-called “quasiparticle” which is the elementary excitation of a Fermi liquid\(^{12,13}\).

Following the argument that the poles of the Green’s function represent the excitations, we have the Green’s function and spectral function for the Fermi liquid as

\[
G(k, \omega) = \frac{Z(k)}{\omega - E(k) + i\Gamma(k)} + G_{\text{inch}}
\]

\[
A(k, \omega) = \frac{\Gamma(k)/\pi}{(\omega - E(k))^2 + \Gamma(k)^2} + A_{\text{inch}}
\]

where \( \Gamma(k) = 1/\tau(k) \). Here we note that the Fermi liquid Green’s function contains two parts: a coherent pole part which has a factor \( Z(k) \) and an inherent smooth part without poles. The factor \( Z(k) \) is the so-called coherent factor and one can show that \( Z(k) < 1 \). As the result, the spectral function can also be separated into a coherent part and an incoherent part as shown above. The reason for having this incoherent part in the Green’s function and spectral function is that: unlike free electron, quasiparticles always have finite lifetimes; within their lifetimes the many-electron system can be described through the behavior of quasiparticles; but if the time concerned by us is

\(^{12}\) In our current case, the quasiparticles are holes. There are also electron quasiparticles which can be understood in the similar manner by considering adding an electron to the interacting many-electron system.

\(^{13}\) Beside quasiparticles, there are other types of elementary excitations in the many-electron system which are the so-called collective excitations including phonons, magnons, plasmons, etc.
longer than quasiparticles’ lifetimes, the quasiparticle picture is no longer appropriate for describing
the system and we must have a corresponding term in the Green’s function and spectral function
accounting for that.

Furthermore, we can also separate the sum rule relation of the spectral function into two parts:

\[
\int_{-\infty}^{+\infty} d\omega A(k, \omega) = \int_{-\infty}^{+\infty} d\omega A_{ch}(k, \omega) + \int_{-\infty}^{+\infty} d\omega A_{inch}(k, \omega) = 1
\]  

(2.41)

![Figure 2.5: The one-electron spectral function. The left panels show the electronic dispersion and
spectral function for a noninteracting electron system and the right panel shows an interacting
Fermi-liquid system. For both noninteracting and interacting systems the corresponding ground
state (\(T = 0\) K) momentum distribution function \(n(k)\) is also shown. From [Damascelli et al.,
2003].](image)

Fig. 2.5 shows the spectral function and the momentum distribution function for the non-interacting case and Fermi liquid case as discussed above. Here we note that for the non-interacting case the momentum distribution function is a step function with step at \(k = k_F\); while for the Fermi liquid case, due to the presence of the incoherent part in the Fermi function, the momentum distribution function is not a pure step function but with step size \(Z(k) < 1\).

Although the Fermi liquid theory successfully explained a lot of experimental phenomena and
is almost always chosen as the starting point for treating condensed matter systems, we need to
emphasize that it has its own limitations: first, it is only good for two- or more-dimensional systems,
for pure one-dimensional systems the starting theoretical model is the “Luttinger Liquid”; second, it is valid only if the condition \( \frac{1}{\tau} \ll E(k) - \mu \) is satisfied, based on the phase-space argument, this means it is only valid in proximity to the Fermi surface; third, besides the one-dimensional Luttinger Liquid, there are also some two- or more-dimensional systems whose behaviors cannot be explained by the Fermi liquid theory such as, d- and f-electron metals [Stewart, 2001] and the cuprate superconductors [Varma et al., 1989; Casey et al., 2008].

One can show that for any interacting many-electron system, the Green’s function has the general form\(^{14}\),

\[
G(k, \omega) = \frac{1}{\omega - \epsilon(k) - \Sigma(k, \omega)}
\]

where \( \epsilon(k) \) is the bare-band for non-interacting case, \( \Sigma(k, \omega) = \text{Re}\Sigma(k, \omega) + i\text{Im}\Sigma(k, \omega) \) is the so-called proper self-energy of the particle. To the zeroth order, we can still take the real and imaginary parts of the self-energy as the energy renormalization and the lifetime of the particle, but in general they contain all the information about the many-body interactions even in the case that the quasiparticle concept is no longer appropriate for describing the system. Here I need to emphasize that due to the requirement of causality, the \( \text{Re}\Sigma(k, \omega) \) and \( \text{Im}\Sigma(k, \omega) \) are connected to each other through the Kramers-Kronig relationship\(^{16}\). The corresponding spectral function is

\[
A(k, \omega) = -\frac{1}{\pi} \frac{\text{Im}\Sigma(k, \omega)}{(\omega - \epsilon(k) - \text{Re}\Sigma(k, \omega))^2 + (\text{Im}\Sigma(k, \omega))^2}
\]

### 2.4.3.2 EDC and MDC analysis

In an ARPES experiment, one of the important goals is to extract the self-energy from the measured spectral function. By the properties of the self-energy we can understand the many-body interactions in the system which are the driving force for a lot of exotic physical properties such as high temperature superconductivity, colossal magnetoresistance, etc. In the rest of this section, \(^{14}\) Here we only consider normal state, for superconducting state, there will be a gap opened near the Fermi level and the Green’s function has the form \( G(k, \omega) = \frac{Z(\omega, k)\omega + \epsilon(k)}{[\omega(\omega, k)\omega - \epsilon(k)\omega - (\omega(\omega, k)\Delta(\omega, k))]^2} \), where \( Z(\omega, k) = 1 - \Sigma(k, \omega)/\omega \) is the complex renormalization function and \( \Delta(\omega, k) \) is the complex gap function. \(^{15}\) We always define \( \text{Re}\Sigma(k, \omega) > 0 \) and \( \text{Im}\Sigma(k, \omega) < 0 \) for \( \omega < 0 \). \(^{16}\) To utilize Kramers-Kronig relationship, one needs the real or imaginary parts of the self-energy over the full energy range. But ARPES can only measure the self-energy over limited range below chemical potential. So we need certain approximation, to perform a Kramers-Kronig transform a ARPES data and this will bring more uncertainties.
I will present some basic procedures for extracting the self-energy from the measured spectral function.

![Momentum distribution curves and energy distribution curves](image)

Figure 2.6: Momentum distribution curves (MDC) and energy distribution curves (EDC). The image is ARPES data showing a portion of a band dispersion from Bi2212. The locations of two different MDC slices are indicated by horizontal lines, with the corresponding curves plotted on the top set of axes. Likewise, EDC slices are designated by vertical lines, and the corresponding curves are plotted on the righthand set of axes. Lorentzian fits (black) are overlaid on the MDCs, illustrating their simple form. From [Plumb, 2011].

Fig. 2.6 shows an experimental ARPES data from the Bi2212 high $T_c$ superconductors. Assuming that we have successfully removed the possible matrix element effect, extrinsic background, resolution effect and other artificial noise, it just presents the intrinsic spectral function of the system times a Fermi function at certain temperature. To extract the self-energy from this spectrum,
we can treat it in two different ways: either slice up this 2-D image along lines of constant momentum $k$ which are called energy-distribution-curves or EDCs, or slice it up along lines of constant energy $\omega = E - E_F$ which are called momentum-distribution-curves or MDCs. The two types of slices are illustrated in Fig. 2.6.

First, let’s take a look at a single EDC at specific momentum position $k$:

$$I(k, \omega) = -\frac{1}{\pi} \frac{\text{Im} \Sigma(k, \omega)}{(\omega - \epsilon(k) - \text{Re} \Sigma(k, \omega))^2 + (\text{Im} \Sigma(k, \omega))^2} \times f(\omega) \quad (2.44)$$

We found that the Fermi function brings up the first difficulty for the EDC analysis, which will distort the intrinsic spectral function near the Fermi level and result in an asymmetric lineshape. In principle, people may remove this effect by dividing it out from the measured spectrum to recover the features near the Fermi level (if the sample temperature is known). But due to the resolution effect and other practical difficulties in experiment, the result is not always ideal. But we may also note that the Fermi function will only affect the features in the spectrum which are very close to the Fermi level, for those features far away from the Fermi level, e.g., the blue EDC shown in fig. 2.6, the effect from the Fermi function is minor and can be ignored.

Next, let’s assume we have already corrected the Fermi function effect and only focus on the intrinsic spectral function:

$$\frac{I(k, \omega)}{f(\omega)} = -\frac{1}{\pi} \frac{\text{Im} \Sigma(k, \omega)}{(\omega - \epsilon(k) - \text{Re} \Sigma(k, \omega))^2 + (\text{Im} \Sigma(k, \omega))^2} \quad (2.45)$$

For the fixed momentum $k$, $\epsilon(k)$ is known by assuming we know the bare-band\textsuperscript{17}. The real and imaginary parts of the self-energy are both the functions of energy (and momentum). Here we find that for extracting self-energy from equation 2.45, we usually need to provide extra constrains, i.e., introduce certain theoretical model for the self-energy.

The simplest model for self-energy is “no self-energy”, i.e., Re$\Sigma(k, \omega) \rightarrow 0$ and Im$\Sigma(k, \omega) \rightarrow 0$. Plug them into equation 2.45, the resulted spectral function is the delta function $A(k, \omega) = \delta(\omega - \epsilon(k))$\textsuperscript{18}. Actually, “no self-energy” just means noninteracting, so it’s not surprising that we get

\textsuperscript{17} Actually we can only acquire the bare-band dispersion from the theoretical calculation. In most cases, we either use an empirical dispersion to approximate the bare-band or just set it as a free parameter in the fittings.

\textsuperscript{18} $\delta(x) = \frac{1}{\pi} \lim_{\omega \to 0} \frac{\omega}{x^2 + \omega^2}$. 
the same result as shown in equation 2.39. Apparently, this is not the case for the real system.

Next, let’s consider the Fermi liquid model. For the Fermi liquid theory, the self-energy has the general form\(^{19}\)

\[
\Sigma_{FL}(\omega) = \alpha \omega + i \beta [\omega^2 + (\pi k_B T)^2]
\] (2.46)

By plugging this expression into the spectral function and using the resulted expression to fit the EDCs, one can get the parameters \(\alpha\) and \(\beta\) (and even \(\epsilon(k)\) if it is also set as a free parameter) as the fitting result and further get the self-energy expression in the Fermi liquid model. In equation 2.40, I have shown that if a many-electron system can be described by the Fermi liquid model, its one-particle Green’s function and spectral function can be separated into a coherent pole part with a coherent factor and an incoherent smooth part. The pole of the coherent part describes the quasiparticle’s dispersion \(E(k)\) and inverse lifetime \(\Gamma(k) = 1/\tau(k)\) and the coherent factor \(Z(k)\) describes the quasiparticle’s weight. Suppose we know the self-energy of this Fermi liquid system, then we can extract these quasiparticle parameters from the self-energy. In the next few paragraphs, I will present how it works.

The basic method for extracting the quasiparticle parameters from the self-energy is to extract a function with a pole from the total Green’s function. We start with the one-particle Green’s function

\[
G(k, \omega) = \frac{1}{\omega - \epsilon(k) - \Sigma(k, \omega)} = \frac{1}{\omega - \epsilon(k) - \text{Re}\Sigma(k, \omega) - i\text{Im}\Sigma(k, \omega)}
\] (2.47)

In the zeroth-order approximation, for \(\omega\) very close to \(E_F\) we can neglect the imaginary part and get

\[
\omega - \epsilon(k) - \text{Re}\Sigma(k, \omega) = 0
\] (2.48)

for the zeroth-order pole, which is

\[
E(k) = \epsilon(k) + \text{Re}\Sigma(k, E(k))
\] (2.49)

\(^{19}\) If there are also other interactions in the system, e.g., electron-phonon, electron-magnon, electron-plasmon interactions, there will be extra terms added into this expression.
To obtain the first-order solution, we expand $\Re \Sigma(k, \omega)$ about the zeroth-order solution $E(k)$:

$$\Re \Sigma(k, \omega) \approx \Re \Sigma(k, E(k)) + \frac{\partial \Re \Sigma(k, \omega)}{\partial \omega} \bigg|_{\omega=E(k)} \times (\omega - E(k))$$  \hspace{1cm} (2.50)

and plug it back into the original pole equation:

$$\omega - [\epsilon(k) + \Re \Sigma(k, E(k))] - \frac{\partial \Re \Sigma(k, \omega)}{\partial \omega} \bigg|_{\omega=E(k)} \times (\omega - E(k)) - i \Im \Sigma(k, E(k)) = 0$$ \hspace{1cm} (2.51)

in which we neglect the partial derivative of $\Im \Sigma(k, \omega)$ and simply evaluate it at $E(k)$. Then we will have the complex pole as

$$\omega_{pole} = \epsilon(k) + \Re \Sigma(k, E(k)) + i \frac{\Im \Sigma(k, E(k))}{1 - \frac{\partial \Re \Sigma(k, \omega)}{\partial \omega} \bigg|_{\omega=E(k)}}$$ \hspace{1cm} (2.52)

By defining

$$Z(k) = \frac{1}{1 - \frac{\partial \Re \Sigma(k, \omega)}{\partial \omega} \bigg|_{\omega=E(k)}}$$ \hspace{1cm} (2.53)

we will have the quasiparticle dispersion and inverse lifetime as

$$E(k) = \epsilon(k) + \Re \Sigma(k, E(k))$$ \hspace{1cm} (2.54)

$$\Gamma(k) = -Z(k) \Im \Sigma(k, E(k))$$ \hspace{1cm} (2.55)

Furthermore, we can also get an expression for the Green’s function which is valid near the poles by substituting equation 2.50 into equation 2.47 and also evaluate $\Im \Sigma(k, \omega)$ at $E(k)$ as what we have done in equation 2.51. Then we have

$$G(k, \omega) = \frac{1}{\omega - [\epsilon(k) + \Re \Sigma(k, E(k))] - \frac{\partial \Re \Sigma(k, \omega)}{\partial \omega} \bigg|_{\omega=E(k)} \times (\omega - E(k)) - i \Im \Sigma(k, E(k))} + G_{inch}$$

$$= \frac{Z(k)}{\omega - E(k) + i \Gamma(k)} + G_{inch}$$ \hspace{1cm} (2.56)

$Z(k)$ is just the coherent factor of the quasiparticle.

\[20\text{ Notice this is different from the result in [Damascelli et al., 2003].} \]
Let’s summarize the result above:

$$E(k) = \epsilon(k) + \text{Re}\Sigma(k, E(k))$$

$$\Gamma(k) = -Z(k)\text{Im}\Sigma(k, E(k))$$

$$Z(k) = \frac{1}{1 - \left. \frac{\partial\text{Re}\Sigma(k, \omega)}{\partial\omega} \right|_{\omega=E(k)}}$$

(2.57)

Here we note that we only expand the self-energy about the quasiparticle peak to its first order to get the above result, it is a very coarse approximation. To get a more accurate result, one may need to expand the self-energy to higher order.

If we only consider the range very close to Fermi level, then

$$\text{Re}\Sigma(k, E(k)) \approx \text{Re}\Sigma(k_F, E(k_F) = 0) + \left. \frac{\partial\text{Re}\Sigma(k, \omega)}{\partial\omega} \right|_{\omega=E(k_F)=0} \times (E(k) - E(k_F))$$

$$= \left. \frac{\partial\text{Re}\Sigma(k, \omega)}{\partial\omega} \right|_{\omega=E(k_F)=0} \times E(k)$$

(2.58)

Plug this result into equation 2.57, we have

$$E(k) \approx \frac{\epsilon(k)}{1 - \left. \frac{\partial\text{Re}\Sigma(k, \omega)}{\partial\omega} \right|_{\omega=E(k_F)=0}} = Z(k_F) \times \epsilon(k)$$

(2.59)

This is another expression shown in lots of textbooks and literatures. Note $Z(k_F)$ is a constant, i.e., only evaluated at Fermi level.

People may also define

$$Z(k_F) = \frac{1}{1 + \lambda}$$

where $\lambda = -\left. \frac{\partial\text{Re}\Sigma(k, \omega)}{\partial\omega} \right|_{\omega=0}$. Then we have near Fermi level, $E(k) \approx \epsilon(k)/(1 + \lambda)$. Thus close to the Fermi level the non-interacting bare-band is normalized by a factor of $1 + \lambda$. In other words, due to the interactions the mass of the quasiparticle is $m^* \approx (1 + \lambda)m$, where $m$ is the mass of the non-interacting electron. For this reason, $\lambda$ is also called as the “mass enhancement factor” due to the interaction.

---

21 Here we note that in the above equations, all the parameters are evaluated at $E(k)$, i.e., at the energy of the quasiparticles. There are also review papers and books which expand $\text{Re}\Sigma(k, \omega)$ about $\epsilon(k)$ and then evaluate all the parameters at $\epsilon(k)$. Those expressions are good for simulation since in simulation we know bare-band and self-energy. But it lacks physical significance in interpreting experimental ARPES results since what we are measuring is the quasiparticle peak and the bare-band from the calculation is not always reliable.
Now let’s consider some non-Fermi liquid models for EDC analysis. One of the most extensively studied models is the so-called marginal Fermi liquid model [Varma et al., 1989] for cuprate superconductors which is a phenomenological model based around the requirement of a linear scattering rate. The self-energy of marginal Fermi liquid model is

\[ \Sigma_{MFL}(\omega) = \lambda [\omega \ln \frac{x}{\omega_c} - \frac{i\pi}{2} x] \] (2.61)

where \( x \approx \max(|\omega|, T) \), \( \omega_c \) is an ultraviolet cutoff, and \( \lambda \) is a coupling constant. For a marginal Fermi liquid, if we use equation 2.57 to estimate the quasiparticle weight, we have \( Z(k) \propto 1/\ln \omega \to 0 \), i.e., there is no quasiparticle near the Fermi level and it is a non-Fermi liquid system. Another non-Fermi liquid model for cuprates is the “Anderson lineshape” [Casey et al., 2008], which is based on the basis of a Gutzwiller projection and also gives zero quasiparticle weight at the Fermi surface.

**Note:** In lots of ARPES literatures, a very common statement about EDC analysis is that the EDC peak dispersion presents the quasiparticle dispersion of the system and people may also use “the quasiparticle width does not exceed the quasiparticle energy” as the criterion for testing if an EDC peak could present the quasiparticle. Strictly speaking, the electron/hole quasiparticles should only exist in the system that can be described by the Fermi liquid theory (and its extensions) and has the self-energy as \( \Sigma_{FL}(\omega) = \alpha \omega + i\beta [\omega^2 + (\pi k_B T)^2]^{22, 23} \). The “EDC width vs. binding-energy” criterion for quasiparticle is only a natural output of this self-energy form. One can also show that even in the non-Fermi liquid regime, e.g., the marginal Fermi liquid discussed above, we can also have this criterion satisfied but the excitation in the system is definitely not a quasiparticle. So we need to pay more attention to claiming any sharp EDC peak as quasiparticle, or we can just use the word “quasiparticle-like” EDC before we know if that system can be described by the Fermi liquid theory or not.

So far, I have shown some general results about EDC analysis and also discussed several models for EDC fitting. Before the appearance of the advanced two-dimensional ARPES analyzer, this form can be slightly modified due to the interaction between the quasiparticles and the other elementary excitations, e.g., phonon, magnon, etc.

This definition may be too narrow. There are also elementary excitations which can not be described by the “particle dressed interaction” picture, e.g., the Bogoliubov quasiparticles in superconductors.
EDC spectra were the only result that can be measured, and so the EDC analysis was the only method to treat the old photoemission data. Even after the invention of the two-dimensional analyzer, EDC analysis are still preferred by a lot of physicists due to several reasons: since the momentum of the electron is the good quantum number of the many-body system, the EDC has clear physical meaning which is the probability that the initial state $|\Psi_i^N\rangle$ with an added or removed electron in state $k$ is an exact eigenstate of the N+1 and N-1 electron systems with energy between $\omega$ and $\omega+d\omega$. For a Fermi liquid, the EDC peak dispersion represents the quasiparticle dispersion and the width of the EDC peak has close connections to a quasiparticle’s lifetime. Furthermore, since generally the ARPES matrix element changes slower in energy direction than that in momentum direction and in ARPES measurement we always only care hundreds of meVs energy window close to Fermi level, we may ignore the matrix element effect in EDC analysis to the first order.

But there are also several shortcomings about the EDC analysis. First, we have shown that to get a good understanding of the EDC near the Fermi level, we have to remove the Fermi function from the spectrum which is not easy to do. To extract the self-energy from the EDC, we have to introduce some theoretical model at the beginning and there are always some uncertainties about model selection which makes the EDC fitting result “model-dependent” and may not reflect the true physics. Furthermore, we have shown that in ARPES spectra, there might be some extrinsic backgrounds and most of those extrinsic backgrounds have strong energy dependence. So how to remove those backgrounds from an EDC to get the intrinsic spectral function is a very challenging task. Due to the difficulties of the EDC analysis and also due to the appearance of the modern 2D ARPES analyzer, the MDC analysis has become a more and more popular way to treat the APRES spectrum.

To show the physical significance of the MDC analysis method, let’s take a look at the ARPES spectral function again

$$I(k, \omega) = -\frac{1}{\pi} \frac{\text{Im} \Sigma(k, \omega)}{(\omega - \epsilon(k) - \text{Re} \Sigma(k, \omega))^2 + (\text{Im} \Sigma(k, \omega))^2} \times f(\omega)$$

\(^{24}\) For example, one can use both Fermi liquid and marginal Fermi liquid model to fit one EDC, and the fitting result can be great for both case, but the underlying physics are totally different.
First, we note that at the specific energy $\omega$, the Fermi function is just a constant factor for an MDC. So we can simply ignore the effect of the Fermi function in the MDC analysis except for resolution contribution [Plumb, 2011]. In general the self-energy is a function of both energy and momentum. Following the similar argument we have made for the EDC analysis, for MDC analysis we need to provide extra constraint on the momentum dependence of the self-energy, otherwise the MDC fitting is another “mission impossible”. Other than proposing specific models for MDCs, people usually just assume that the self-energy varies slowly along the momentum direction. Assuming $k_m$ is the zeroth order pole of the spectral function along the momentum direction, i.e., $\omega - \epsilon(k_m) - \text{Re}\Sigma(k_m, \omega) = 0$. Then we can expand the self-energy term about $k_m$ only to its first order Taylor expansion:

$$\text{Re}\Sigma(k, \omega) \approx \text{Re}\Sigma(k_m, \omega) + \left. \frac{\partial \text{Re}\Sigma(k, \omega)}{\partial k} \right|_{k=k_m} (k - k_m)$$

$$\text{Im}\Sigma(k, \omega) \approx \text{Im}\Sigma(k_m, \omega) + \left. \frac{\partial \text{Im}\Sigma(k, \omega)}{\partial k} \right|_{k=k_m} (k - k_m)$$

We can also extract the bare dispersion $\epsilon(k)$ as

$$\epsilon(k) \approx \epsilon(k_m) + \left. \frac{\partial \epsilon(k)}{\partial k} \right|_{k=k_m} (k - k_m) = \epsilon(k_m) + v(k_m) \times (k - k_m)$$

(2.64)

where $v(k_m)$ is the “bare velocity”. Plugging above equations into the general spectral function expression, we get

$$A(k, \omega) \approx -\frac{1}{\pi} \left[ \frac{\text{Im}\Sigma(k_m, \omega)}{v(k_m) + \left. \frac{\partial \text{Re}\Sigma(k, \omega)}{\partial k} \right|_{k=k_m} (k - k_m)} \right]^2 + \left[ \frac{\text{Im}\Sigma(k_m, \omega)}{v(k_m) + \left. \frac{\partial \text{Re}\Sigma(k, \omega)}{\partial k} \right|_{k=k_m} (k - k_m)} \right]^2$$

(2.65)

If we further ignore the momentum-dependent of $\text{Im}\Sigma(k, \omega)$, i.e., $\left. \frac{\partial \text{Im}\Sigma(k, \omega)}{\partial k} \right|_{k=k_m} \approx 0$, then the spectral function follows the Lorentzian lineshape:

$$A(k, \omega) \approx -\frac{1}{\pi} \left[ \frac{\text{Im}\Sigma(k_m, \omega)}{v(k_m) + \left. \frac{\partial \text{Re}\Sigma(k, \omega)}{\partial k} \right|_{k=k_m} (k - k_m)} \right]^2 + \left[ \frac{\text{Im}\Sigma(k_m, \omega)}{v(k_m) + \left. \frac{\partial \text{Re}\Sigma(k, \omega)}{\partial k} \right|_{k=k_m} (k - k_m)} \right]^2$$

(2.66)

$\Gamma_m(\omega)$$

$\Gamma_m(\omega)$

It is the exact form for linear bare-band dispersion.
where $\Gamma_m(\omega) = -\frac{\text{Im}\Sigma(k_m, \omega)}{v(k_m)} + \left. \frac{\partial \text{Re}\Sigma(k, \omega)}{\partial k} \right|_{k=k_m}$.

Based on the result above, if we could fit the MDC by a Lorentzian function with peak at $k_m$ and half-width at half-maximum (HWHM) as $\Gamma_m(\omega)$ and suppose we know the bare-band as $\epsilon(k)$, then the self-energy can be expressed as

\[
\begin{align*}
\text{Re}\Sigma(k_m, \omega) &= \omega - \epsilon(k_m) \\
\text{Im}\Sigma(k_m, \omega) &= -\Gamma_m(\omega) \left[ v(k_m) + \left. \frac{\partial \text{Re}\Sigma(k, \omega)}{\partial k} \right|_{k=k_m} \right]
\end{align*}
\]  

(2.67)

Here let’s review the assumptions that we made in order to get equation 2.67: first we need the real part of the self-energy, $\text{Re}\Sigma$, to be weakly momentum-dependent so that it can be approximated by a linearly momentum-dependent function; the imaginary part of the self-energy, $\text{Im}\Sigma$, is totally momentum independent within the small k-window of the MDC width; the bare band can be approximated by an linear dispersion. The linear bare-band assumption can be satisfied in most cases, especially when we only consider a small energy window. But the first and second assumptions on self-energy part are not obviously satisfied. Actually in real ARPES spectrum, people do observe the symmetric Lorentzian line shape of the MDC, e.g., the MDC taken along the nodal direction of cuprate superconductor, this is always considered as the experimental evidence that the self-energy may be weakly momentum-dependent. So in most cases, people will just assume the self-energy is weakly momentum-dependent or even totally independent (by further assuming $\left. \frac{\partial \text{Re}\Sigma(k, \omega)}{\partial k} \right|_{k=k_m} \sim 0$), then the MDC analysis method discussed above will provide a very convenient way to extract the self-energy from the ARPES spectrum.

Another advantage of MDC analysis over EDC analysis is that the extrinsic backgrounds shown in ARPES spectra are almost always weakly momentum-dependent due to their “local scattering” nature. So for MDC analysis, we do not worry about the background too much and may just have a constant or linear background term in their fitting to get rid of any possible extrinsic backgrounds.

Finally, let’s talk about some limitations of the MDC analysis: first, the self-energy extracted by MDC analysis has strong dependence on bare-band selection. As we discussed before, the bare-band can only be obtained from theoretical calculation. Since theoretical calculations always have
limitations, sometimes it may not be reliable. One can select the bare-band empirically, but this can make this situation even worse. Matrix elements are another potential concern for MDC analysis, since the matrix elements may be strongly momentum-dependent then can severely distort the MDC lineshape. Furthermore, at deeper binding energy the bare dispersion may strongly deviate from the linear dispersion and one may need to consider more complex bare-band form for MDC fitting.

Here I use a table which compares EDC and MDC analysis method to end this section. We can find that to better understand ARPES spectrum, we ideally would use all methods available, including the methods that will be introduced in chapter 5.

Table 2.1: EDC analysis vs. MDC analysis. The ARPES intensity is expressed as $I(k, \omega) = [I_0(k, \nu, A) f(\omega) A(k, \omega) + B(k, \omega)] \otimes R(k, \omega)$, where $I_0(k, \nu, A)$ is proportional to the matrix element, $f(\omega)$ is the Fermi function, $A(k, \omega) = -\frac{1}{\pi} \frac{\text{Im} \Sigma(k, \omega)}{(\omega - \epsilon(k) - \text{Re} \Sigma(k, \omega))^2 + (\text{Im} \Sigma(k, \omega))^2}$ is the one-particle spectral function, $\epsilon(k)$ is the bare-band, $B(k, \omega)$ is the extrinsic backgrounds, and $R(k, \omega)$ is the resolution effect.

<table>
<thead>
<tr>
<th></th>
<th>EDC</th>
<th>MDC</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_0(k, \nu, A)$</td>
<td>Relevant if the matrix element has a strong E-dependence</td>
<td>Relevant if the matrix element has a strong k-dependence</td>
</tr>
<tr>
<td>$f(\omega)$</td>
<td>Strongly distort lineshape near Fermi level, need to be corrected</td>
<td>Can be ignored to first order</td>
</tr>
<tr>
<td>$A(k, \omega)$</td>
<td>Unlikely to be a Lorentzian, since $\Sigma$ is usually E-dependent</td>
<td>Approximated by Lorentzian lineshape by assuming weakly momentum-dependent self-energy and linear bare-band</td>
</tr>
<tr>
<td>$\epsilon(k)$</td>
<td>From calculation or treat as a free parameter in fitting</td>
<td>From calculation or choose empirically</td>
</tr>
<tr>
<td>$B(k, \omega)$</td>
<td>Strongly energy-dependent, need to be treated carefully</td>
<td>Weakly momentum-dependent, can be approximated by constant or linear background</td>
</tr>
<tr>
<td>$R(k, \omega)$</td>
<td>Has effect</td>
<td>Has effect</td>
</tr>
<tr>
<td>Summary</td>
<td>Complicated, model-dependent, but with clear physical meaning good for slowly dispersive bands</td>
<td>Convenient for most of the time, but can be easily affected by matrix element and bare-band selection good for rapidly dispersive bands</td>
</tr>
</tbody>
</table>
2.5 Matrix elements, extrinsic backgrounds, and resolution effects

As shown before, the photoelectron current measured by ARPES can be expressed as:

\[ I(k, \omega) = [I_0(k, \nu, A)f(\omega)A(k, \omega) + B(k, \omega)] \otimes R(k, \omega) \]  

(2.68)

In previous sections, I discussed the intrinsic spectral function part \( f(\omega)A(k, \omega) \) in great detail. In this section I will briefly discuss the artificial and extrinsic term, i.e., the matrix element effect, the extrinsic background and the resolution effect in ARPES spectra.

Figure 2.7: Symmetry considerations of the matrix elements. The mirror plane emission from a \( d_{x^2-y^2} \) orbital is present and details are discussed in the text. From [Damascelli et al., 2003].

The matrix element can be expressed as

\[ I_0(k, \nu, A) \propto |M_{f,i}^k|^2 \propto \langle \phi_f^k | \hat{e} \cdot r | \phi_i^k \rangle, \]  

where \( \hat{e} \) is a unit vector along the polarization direction of the vector potential \( A \). In general, it may be a function of both momentum and kinetic energy of photoelectron (not binding energy). But in most cases we only consider its momentum dependence which may alter the measured spectra, making the interpretation of the data quite difficult. Fig. 2.7 presents an example to show how the matrix element can affect the ARPES result. In this example, a sample is oriented so that the \( d_{x^2-y^2} \) orbital

---

26 Here I drop the noise term \( I_{\text{noise}} \) for simplification.
along its surface is even with respect to the mirror plane. The analyzer’s slit and the photon beam’s incident plane are also in sample’s mirror plane. The final state $|\phi_k^f\rangle$ plane wave is even with respect to this mirror plane. In this example it is also even with respective to the mirror plane. Therefore, to make the total dipole transition to be non-zero, $\hat{e} \cdot \mathbf{r} |\phi_k^i\rangle$ must also be even with respect to the mirror plane. As the result, the electronic states that are even (odd) under reflection with respect to this mirror plane can only be excited by light with the electric field polarization pointing in (out of) the mirror plane. As shown in fig. 2.7, since the initial state is even with respect to the mirror plane, only in-plane p-light has non-zero matrix element and initial state excited by p-light can be detected by the analyzer. This example actually provides us a very convenient method to determine the orbital symmetry properties of ARPES measurement. Another example of using matrix elements to help ARPES experiment is the bilayer splitting selection of Bi2212 materials by tuning the excitation photon energy. One empirically finds that the antibonding portions of the bilayer-split bands of Bi2212 are emphasized with 7 eV [Iwasawa et al., 2008] and 47 eV/55 eV [Chuang et al., 2004] photons.

The extrinsic background $B(k, \omega)$ is mainly due to the secondary electrons due to the extrinsic scattering processes of the photoelectrons on their way to the sample surface. Since it mainly comes from the local scattering of the photoelectron, its momentum dependence may be weak. A well-known theory to model this extrinsic background due to the inelastic scattering of the electrons is the so-called Shirley background [Shirley, 1972] which has the form

$$P(E) = R(E) - B(E) = R(E) - \kappa \int_E^0 P(E')dE' \tag{2.69}$$

where $R(E)$ is the raw EDC, $B(E)$ is the inelastic background term and $P(E)$ is the primary or peak of the EDC after the Shirley background correction. Experimental data suggests that the $\kappa$ is momentum independent and is typically of order of $10^{-2}$ to $10^{-3}$.

The resolution effect mainly broaden the spectral features near the Fermi level. As a second order effect it can also affect the dispersion near Fermi level obtained by the MDC fitting procedure [Plumb, 2011].
Chapter 3

Angle-Resolved Photoemission Spectroscopy (Experiment)

“Good tools are prerequisite to the successful execution of a job.”

- Confucius

3.1 Introduction

In practice, the modern ARPES experimental setup consists of three core components as shown in fig.3.1: the light source, the sample, and the analyzer. In this chapter, a review of the modern APRES experimental setup will be given, all the three core components mentioned above will be discussed in detail.

Figure 3.1: Schematic of the modern ARPES system. Three main components are highlighted: the analyzer (which consists of the electrostatic lens, the hemispherical analyzer, and the MCP-Phosphor-CCD detector), the sample (which is usually affixed to the end of a cryostat manipulator in an ultra-high vacuum (UHV) chamber), and the light source (which must be monochromatic and can supply sufficient energy to the electron so it can overcome the work function and exit from the sample as a photoelectron). Courtesy of SPECS.
3.2 Light source

In general, there are several requirements for the light source used in ARPES system: the light must be monochromatic in order to utilize the energy and momentum conservation relations to obtain the energy and momentum information of the photoelectrons; the photon energy must be high enough to supply sufficient energy to the electron, so it can overcome the work function and exit from the sample as a photoelectron; the photon flux must be high enough in order to generate reasonable photoelectron current that can be detected by the analyzer; the photon beam size need to be small enough on the sample which is essential for high angular resolution in ARPES measurement. It may also be desirable to have a polarized light with a tunable photon energy to get around or utilize the matrix element effects in the photoemission procedure for obtaining more information about the spectral function. Furthermore, the tunable photon energy is also important for obtaining the 3-dimensional electronic structure of the materials.

3.2.1 Synchrotrons

The synchrotron radiation is the electromagnetic radiation emitted by the ultrarelativistic charged particles when they are accelerated transversely. The transverse acceleration of the ultrarelativistic charged particles is usually accomplished by the magnetic forces when they are moving through magnetic fields. For synchrotrons, the magnetic fields are generated by bending magnets, undulators, or wiggler magnets. The radiation generated by the ultrarelativistic electron current when moving through those devices is monochromatized at the desired photon energy by a grating monochromator and focused on the sample by certain optics.

Typically, the ARPES end-stations have photon energies tunable from 20-200 eV with energy resolution as good as several meVs to tens of meVs. Different beamlines may have different photon energy ranges and resolutions due to the design. Further more, the synchrotron radiation light is highly polarized along the direction of acceleration. In principle, fully tunable polarization (linear s/p or circular) is also achievable depending on the beamline’s design.
Based on the discussion above, the synchrotron appears to be the ideal light source for the ARPES experiment since they can provide a very intense, tunable, and polarized beam for use in experiments. The main disadvantage of synchrotrons is the huge costs for constructing, operating, and maintenance. It usually costs tens to hundreds of millions of dollars to construct and tens of millions of dollars to keep normal operation every year. For this reason, there are very limited synchrotron light sources available around the world and there is a great deal of competition for beam time.

3.2.2 Gas-discharge lamps

As an alternative photon source for ARPES, the gas-discharge lamps are intensively used in ARPES experiments for their low costs. In gas-discharge lamps, the gas atoms are ionized and/or excited by colliding with the DC electronic current passing through them (DC discharge) or by absorbing microwave radiation (microwave discharge). Then radiation is emitted by gas atoms that have been excited into electronic levels above the ground state and then lose their energy by radiative decay to lower electronic levels. By virtue of the highly-defined discrete energy levels of the atom, the radiations are sharply peaked at specific energies. By choosing different gases such as He, Ne, Ar, Kr, or H\textsubscript{2}, and selecting different transition lines, various photon energies can be obtained for doing ARPES experiment, e.g., the He-I\textsubscript{α} resonance line \((1s2p - 1s^2)\) at 58.43 nm (21.2 eV), the He-I\textsubscript{β} resonance line \((1s3p - 1s^2)\) at 53.70 nm (23.08 eV), and He-II\textsubscript{α} resonance line \((2p - 1s)\) at 30.38 nm (40.2 eV).

When using gas-discharge lamp as the UV light source for ARPES experiment, the gas discharge is usually confined by a capillary tube which also serves as the light guide to the sample. A focus mirror at the end of the capillary is also desirable for generating a small beam size on samples. The resolution of the gas-discharge lamps is theoretically limited by the Doppler broadening effect which is usually a fraction of one meV to several meVs. This is basically good enough for performing high-resolution ARPES measurement. But there are also possible ancillary transition lines accompanying with the desired main transition line which can worsen the energy resolution.
For this reason, the gas-discharge lamp sometimes is equipped with certain type of monochromator which can yield good separation of the main line and the ancillary lines to achieve better resolution. One disadvantage of the lamps is that the light is generally unpolarized, but polarized light can also be obtained by equipped with certain type of polarizer in the system.

3.2.3 Lasers

Lasers as the light sources which have the advantages of highly stable photon energy and output power, high photon flux in an extremely narrow bandwidth, and fully and easily tunable polarization were first introduced to ARPES experiment by our group [Koralek, 2006] and soon became another major type of light sources for ARPES experiment. Currently, the laser light sources used in APRES are mainly working at low photon energy region which have several intrinsic advantages over the high photon energy synchrotrons and gas-discharge lamps. In this section, these advantages will be discussed and a new 6.3-eV laser system will be introduced.

3.2.3.1 Advantages of low-photon-energy ARPES

◊ More bulk sensitive

In general, the ARPES is a surface sensitive experiment technique and the escape depth of photoelectrons is mainly determined by electron-electron interaction. This escape depth of photoelectrons, i.e., the photoelectron mean free path in the solid mainly depends on the photoelectron’s kinetic energy and roughly follows a “universal curve” as shown in fig. 3.2. Most ARPES experiments are performed in the 20 - 100 eV kinetic energy range, where there is a broad minimum of the mean free path. While with the 6 - 7 eV photons used in laser ARPES, the bulk sensitivity is increased roughly one order of magnitude compared to typical synchrotrons and gas-discharge lamps. Here I need to note that although the escape depth of photoelectrons is greatly improved by using low-photon-energy source, the value of this escape depth is still only about 50Å which is generally just several times of the lattice constant of crystals. In other words, the most photoelectrons still come from the region which is very close to the surface area.
Better momentum resolution

Another main advantage of using low-photon-energy sources is that it is possible to achieve much higher momentum resolution. In previous chapter, I have shown that the measured in-plane momentum of photoelectron can be expressed as

$$ k_m = \frac{1}{\hbar} \sqrt{2mE_{kin} \cdot \sin \theta} \quad (3.1) $$

Then the momentum resolution due to the finite angular resolution ($\Delta \theta$) of the electron spectrometer is given by

$$ \Delta k_m \approx \frac{1}{\hbar} \sqrt{2mE_{kin} \cdot \cos \theta \cdot \Delta \theta} \quad (3.2) $$

which is proportional to the square root of kinetic energy of photoelectrons. Clearly, the low-photon-energy sources will produce photoelectrons with low kinetic energy and give us better momentum resolution. For example, the momentum resolution for ARPES with 6-eV photons is about $(\sqrt{52-1.5} / \sqrt{52-4.5} \sim) 6$ times better than that of the ARPES with 52-eV photons.
Less “final-state” effects

As discussed in the previous chapter, the initial state of photoemission process is the N-electron state while the final state of the photoemission process consists of one photoelectron and the remaining (N-1)-electron system. For Fermi liquid system, the remaining (N-1)-electron system in the photoemission process can be described by a photohole quasiparticle with certain energy vs. momentum dispersion, finite lifetime, and quasiparticle weight. In this picture, the final state of photoemission process consists of one photoelectron and one photohole, and by measuring the energy and momentum distribution of the photoelectrons, the photohole quasiparticle’s dispersion and lifetime can be obtained. This picture is very similar to the “independent electron picture”, in which the initial state is the electron with certain energy and momentum in the band structure and the final state is the photoelectron with different energy and momentum in the band structure. For this reason, many references just call the photoelectron state as the final state while the photohole state as the initial state (this may not be wrong but very confusing).

Based on these definitions about the initial and final states, the photohole/initial state contains the intrinsic information about the electronic structure and many-body interactions in the system, while the photoelectron/final state is strongly affected by extrinsic effects in the photoemission process such as the inelastic scattering of the photoelectron on its way to the sample surface. As the result, certain “final-state” effects are expected in ARPES data such as the inelastic background and the final state broadening. By using low-photon-energy source, these “final-state” effects can be reduced to some extent and we can obtain the spectrum which is more intrinsic.

The longer mean free path of the low-energy photoelectrons indicates smaller inelastic scattering possibility in photoemission process, which in principle will generate less inelastic background in the spectrum. Furthermore, with low-photon-energy source, only electrons from a relatively small region of k-space are excited and therefore able to contribute to the background [Koralek, 2006]. The longer mean free path of the low-energy photoelectrons may also indicate longer lifetime of photoelectrons. It has been shown that the measured ARPES EDC linewidth is actually a combination of the linewidth of both photoelectron and photohole [Smith, 1993], thus the measured
lifetime is also the combination of the lifetime from both photoelectron and photohole. Since the low-energy photoelectron has much longer lifetime, the measured result will be dominated by the photohole’s lifetime, which is just what we want since it contains the intrinsic information about the many-body interactions in the system.

3.2.3.2 The 6.3-eV laser system

Fig. 3.3 shows the schematic of the 6.3-eV laser system proposed by Dessau and developed in our lab. There are three major parts in this laser system: the Lexel Argon-ion laser which generates 244 nm light, the ELS Nd:YAG laser which generates 1030 nm light, and the sum frequency generation system which mixes the 244 nm light with the in-cavity 1030 nm light through a $\beta$-barium borate (BBO) nonlinear crystals and generates the 197 nm ($\sim 6.3 \text{ eV}$) light for direct ARPES experiment.

Figure 3.3: Schematic of the 6.3-eV laser system. The 244 nm light from LEXEL argon ion laser is sent into the 1030 nm ELS solid state laser’s cavity. The two beams mix together in a beta barium borate (BBO) crystal inside the cavity, where the sum-frequency generation (SFG) nonlinear optical process happens. The output 197 nm light (6.3-eV) is sent into the experiment chamber after several reflecting and focusing optics.

The main advantage of the 6.3-eV laser system is that both the Argon-ion laser and the
Nd:YAG laser are working in their continuous modes, as the result, the output 197 nm light is also oscillating continuously, i.e., the pulse length $\Delta t \rightarrow \infty$ and the energy width $\Delta E \rightarrow 0$ due to the uncertainty relation. The experimentally measured energy width of the 6.3-eV laser system is only a small fraction of one meV. The current output power of the 6.3-eV laser system is about 100–120 $\mu$w, which is high enough to get a reasonable counts detected by the analyzer.

![Diagram of BBO crystal geometry and SFG mixing configuration](image)

Figure 3.4: BBO crystal geometry and SFG mixing configuration. The top panel shows the BBO crystal geometry and the relative angles of all the input and output beams. The bottom panel shows the optical axis of the BBO crystal which is labeled as $z$ direction.

Fig. 3.4 shows the BBO crystal geometry and SFG mixing configuration. The type I phase matching condition at 100 $^\circ$C is employed and the output 197 nm light has orthogonal polarization relative to the input 244 nm and 1030 nm light. By using waveplate, different polarizations can be obtained for ARPES measurement.

3.2.3.3 Other low-photon-energy ARPES light sources

◇ **The 6.0-eV laser system** developed by [Koralek, 2006], which is based on a Ti:sapphire oscillator. The output of the Ti:sapphire oscillator is 1.5 eV photons at a repetition rate of 100 MHz and pulse length of 70 fs and energy 6 nJ. The output light from the Ti:sapphire oscillator is doubled twice by sent through two BBO crystals. The resolution of the 6.0-eV laser system is
around 5 meV, mainly due to the very short pulse length. The output power may be as high as mw level.

◊ The 7.0-eV laser system developed by [Douglas, 2008], which is based on a Nd:YVO4 laser that is internally frequency-tripled to output four Watts of 3.5 eV photons at a repetition rate of 80 MHz and pulse length of 15 ps. The output light from the Nd:YVO4 laser is doubled by sent through a KBe$_2$BO$_3$F$_2$ (KBBF) crystal. The resolution of the 7.0-eV laser system is less than one meV since their pulses are longer in duration than those from the 6-eV laser system.

◊ Inspired by the success of the laser-based low-photon-energy ARPES systems, great efforts are also put into developing other low-photon-energy ARPES light sources, such as the low-energy synchrotron beamlines, e.g., the SSRL BL5-4 and HiSOR BL-9A which can generate photons in the sub-10-eV range; and the low-energy gas-discharge lamps, e.g., the xenon lamp developed by [Souma et al., 2007] which can generate the photons with 8.437 eV energy.

Before ending this section, I need to note that since the photoelectrons excited by the low-photon-energy source have very low kinetic energy, there is a big concern about whether or not the sudden approximation remains valid for those low-photon-energy ARPES systems. So far, most of the experimental results suggest that the sudden approximation is still hold for the low-photon-energy ARPES experiment. The detailed discussion about this issue can be found in the thesis of [Plumb, 2011].

3.3 Electron spectrometer

The modern ARPES electron spectrometer consists of three main components: the electrostatic lens, the hemispherical analyzer, and the MCP-Phosphor-CCD detector. The photoelectrons will first be collected by the electrostatic lens, and the photoelectrons with different momentums will be imaged onto different parts of the entrance slit of the hemispherical analyzer; the hemispherical analyzer will further image the photoelectrons onto different parts of its exit slit due to their different energies; finally, those photoelectrons will be detected by the MCP-Phosphor-CCD detector which will record the distribution of the photoelectrons as a function of energy and momentum,
and this distribution can be eventually interpreted as the spectral function of the measured system.

In this section, short reviews will be presented on these three main components.

### 3.3.1 Electrostatic lens

The lens system is a purely electrostatic system which consists of a number of collinear elements. The electrostatic lens mainly serves two purposes: it is used to accelerate or retard the photoelectrons in order to achieve a suitable combination of energy resolution and sensitivity for the subsequent energy analysis; it can distribute the photoelectrons over the hemispherical analyzer’s entrance slit according to their take-off direction (the angular mode), their start position (the imaging or magnification mode), or just to provide the maximum sensitivity of the analyzer (the transmission mode).

The three operation mode mentioned above will adapt the analyzer for different applications: the angular mode is what we use for ARPES experiment since it is a “parallel-to-point” mode and will provide the emission angle information, i.e., the momentum information of the photoelectrons; the imaging or magnification mode can be used for determining the local chemical composition of a sample since it is a “point-to-point” mode and will yield a spectromicroscopic image of the sample over the hemispherical analyzer’s entrance slit and the lateral resolution can be as good as 10-100 μm; the transmission mode maximizes the luminosity of the system, i.e., images as many photoelectrons as possible onto the hemispherical analyzer’s entrance slit for the subsequent energy analysis, thus it is always used for XPS and UPS which does not care the momentum or spatial distribution of the photoelectrons or just for optimizing experimental conditions, e.g., sample alignment.¹

### 3.3.2 Hemispherical analyzer

After passing through the electrostatic lens, photoelectrons will be imaged onto the entrance slit S1 of the hemispherical analyzer. Next, photoelectrons will pass through the entrance slit S1

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¹ When doing ARPES experiment, we usually choose both the transmission mode and the angular mode for sample alignment: transmission mode for optimizing counts and angular mode for searching for the best sample area.
and be focused onto the hemispherical analyzer’s output plane S2. This process is shown in fig. 3.5.

The photoelectron’s radial position on plane S2 depends on its kinetic energy in the hemispherical analyzer. Photoelectrons on the central trajectory (red line in fig. 3.5) possess the nominal pass energy ($E_P$). They are focused to the central radial position at the exit plane S2. Photoelectrons with higher kinetic energy are focused further outside (green line in fig. 3.5), and photoelectrons with lower energy are focused further inside in plane S2 (blue line in fig. 3.5). By setting outer (with radius $r_1$) and inner (with radius $r_2$) hemispheres with potential $V_1$ and $V_2$ respectively, the
electrical field between these two concentric hemispheres is given by

\[ E_r(r) = \frac{(V_1 - V_2) r_1 r_2}{r_1 - r_2} \cdot \frac{1}{r^2} \]  

(3.3)

Here \( V_1 < V_2 \) since the charged particles in the hemisphere are electrons. The photoelectron with nominal pass energy \( E_P \) will follow the central trajectory \( r_0 = (r_1 + r_2)/2 \), then this nominal pass energy \( E_P \) is set by

\[ E_P = (-e) \cdot \frac{r_1 r_2}{2r_0(r_1 - r_2)} \cdot (V_1 - V_2) \]  

(3.4)

where \(-e\) is the charge of electron. In a first order approximation, the radial image position \( r \) for photoelectrons entering the hemispherical analyzer at \( r_0 \) with kinetic energy \( E_k \) is given by

\[ r = r_0(1 + 2 \frac{E_k - E_P}{E_P}) \]  

(3.5)

This is the basic equation for how hemispherical analyzer detects photoelectrons with different kinetic energy.

For **straight entrance slit** S1 shown in fig.3.5’s lower panel, photoelectrons will enter the hemisphere analyzer at different radial position, only those photoelectrons entering through the tangential point\(^2\) between the slit and center circle start at \( r_0 \). In a first order approximation, photoelectrons entering with the pass energy \( E_P \) at a radius \( r_0 + \Delta r \) will be refocused at a radius \( r_0 + \Delta r \) [Wannberg, 2009]. As the result, the photoelectrons with kinetic energy \( E_P \) entering through a straight slit, tangential to the main sphere with radius \( r_0 \) will be refocused along a circular arc inside the main sphere, with a radius \( r_0/2 \), as shown by the red curves in fig.3.5’s lower panel. For other kinetic energies, the photoelectrons will be refocused on the corresponding arcs, e.g., the blue and green curves in fig.3.5’s lower panel. Since the straight entrance slit will give us curved constant-kinetic-energy surface, people also make **curved entrance slit** with the radius \( r_0/2 \) to get straight constant-kinetic-energy surface in experiment. Here I need to note that although the curved entrance slit can give us straight constant-kinetic-energy surface, it deviates from the electrostatic lens mirror plane. Thus in angular mode, this curved entrance slit will give

\(^2\) So far, we ignore the entrance slit’s width along radial direction.
us a curved cut in momentum space. For this reason, both curved slit and straight slit will be used for different experimental purposes: curved slit for straight energy cut and straight slit for straight momentum cut.

Furthermore, as shown in fig.3.5’s lower panel, the image on the detector’s exit plane S2 corresponding to a homogeneous distribution over the entrance slit S1 will be “pie-shaped”. This is a universal behavior due to the hemispherical analyzer’s geometry properties, no matter what slit is chosen. To correct this chromatic aberrations, people usually “de-warp” the raw image by certain program to obtain the corrected spectrum.

### 3.3.3 MCP-Phosphor-CCD detector

After passing through the electrostatic lens and the hemispherical analyzer, the photoelectrons with different energy and takeoff angle (momentum eventually) will be imaged onto different position on the hemispherical analyzer’s exit plane S2. The next step is to detect those photoelectrons and record their distributions on the exit plane. In practice, several types of detectors can be used to detect and record the photoelectrons’ distribution, e.g., Channel Electron Multiplier (or channeltron), MCP-Delayline detector, or MCP-Phosphor-CCD detector. And the MCP-Phosphor-CCD detector is usually the device used for APRES system due to its 2-dimensional detection ability and high detection efficiency. Fig.3.6 shows the schematic of the MCP-Phosphor-CCD detection system, which consists of a micro-channel plate (MCP) pair, a phosphor screen, and a charge-coupled device (CCD).

The MCP consists of millions of very thin, conductive glass capillaries (μm scale in diameter) fused together and sliced into a thin plate. Each capillary works as an independent secondary-electron multiplier, thus forming a two-dimensional secondary electron multiplier. In most ARPES detectors, two MCPs are stacked together for achieving higher amplification efficiency, as shown in fig.3.6. The amplified electron signals are accelerated by the “screen voltage” and hit the phosphor screen, thus electron signals will be converted into light signals. Finally, those light signals will be detected and recorded by the CCD camera. Since the light intensity recorded by CCD is propor-
tional to the electron counts hitting the phosphor and eventually proportional to the electron counts imaged onto the hemispherical analyzer’s exit plane, the photoelectrons’ energy and momentum distribution is finally obtained.

### 3.3.4 Scanning photoelectron kinetic energy

In photoemission process, the photoelectron’s kinetic energy is determined by the photon energy $h\nu$ and the electron’s binding energy $E_B$. Based on the discussion in previous chapter, we have

$$h\nu - E_B = E_{kin} + \Phi_{sample} = E'_{kin} + \Phi_{analyzer}$$

(3.6)

i.e., the photoelectron’s kinetic energy is measured relative to the analyzer’s work function. Then the highest photoelectron kinetic energy (those electrons from Fermi level) is

$$E_{kmax} = h\nu - \Phi_{analyzer}$$

(3.7)
and the lowest photoelectron kinetic energy is

\[ E_{k\text{min}} = \begin{cases} 
0 & \text{if } \Phi_{\text{sample}} \leq \Phi_{\text{analyzer}}, \\
\Phi_{\text{sample}} - \Phi_{\text{analyzer}} & \text{if } \Phi_{\text{sample}} > \Phi_{\text{analyzer}}. 
\end{cases} \]  

(3.8)

In other words, if \( \Phi_{\text{sample}} > \Phi_{\text{analyzer}} \), there will also be a “low-energy-cutoff” of the photoelectrons those can be detected by the analyzer\(^3\).\(^4\). Thus the detected photoelectrons have energy range from a fraction of one eV to several or tens of eVs (depending on photon energy).

In principle, for fixed pass energy \( E_P \), the analyzer’s detected energy range is determined by the size of the inner and outer hemispheres. Based on equation 3.5, we have

\[ \Delta E = \frac{r_1 - r_2}{2r_0} \cdot E_P = \frac{r_1 - r_2}{r_1 + r_2} \cdot E_P \]  

(3.9)

where \( E_P \) is the pass energy, \( r_1 \) and \( r_2 \) are the radii of the outer and inner hemisphere, respectively. If we choose the radii of the outer and inner hemisphere to be 1.25 \( r_0 \) and 0.75 \( r_0 \), we have \( \Delta E = 25\% \cdot E_P \). This number is the “upper limit” for the analyzer’s detected energy range. In real ARPES experimental system, the analyzer’s detected energy range is actually limited by the size of the micro-channel plate (MCP), which is typically chosen to cover an energy range of about \( \Delta E = 10\% \cdot E_P \) due to the practical and economical considerations. Since the \( E_P \) chosen for real ARPES experiments is usually at several to tens of eVs level, then the energy window detected by the analyzer is a fraction of one eV or several eVs, which is usually smaller than the photoelectron’s full energy range.

Based on the discussions above, to obtain the photoelectrons’ energy distribution over a large kinetic energy range, we usually need to scan through the desired kinetic energy range. This is accomplished by changing the electron spectrometer and hemispherical analyzer’s potentials in a combined manner.

\(^3\) This is actually true for most experimental cases.

\(^4\) In general, \( \Phi_{\text{analyzer}} \) is (and should be) very stable in order to provide a stable Fermi level in the experiment. But \( \Phi_{\text{sample}} \) is material-dependent quantity and could also slowly change within hours or days due to the changing of the sample’s surface chemical composition during measurement, i.e., sample aging. By measuring the “low-energy-cutoff”, it actually provides a method to monitor the sample work function changing and further provide information about certain sample aging process.
The most intuitive and extensively used method to scan photoelectron’s kinetic energy is the so-called “\textit{constant pass energy}” mode (CPE). In this mode, the hemispherical analyzer’s inner and outer potentials are fixed to give a constant pass energy $E_P$. To scan photoelectron’s kinetic energy, the system changes the potentials on certain electrostatic lens elements to accelerate or retard the photoelectrons with target kinetic energy to match the pass energy for subsequent energy analysis. One main advantage of the CPE mode is that the energy resolution and the detector energy window are constant throughout an energy scan, which is very important for ARPES measurement since in ARPES we usually care about the detailed energy information and the resolution need to be kinetic energy independent.

Another method to scan photoelectron’s kinetic energy is the so-called “\textit{constant retardation ratio}” mode (CRR). In this mode, the hemisphere’s pass energy is given by $E_P = \frac{E_{\text{kin}}}{R}$, where $R$ is the retardation ratio and is a constant during energy scan. In other words, during energy scan, all photoelectrons are decelerated with the same fixed factor $R$. The main advantage of the CRR mode is that the acceptance at the sample is kept constant during energy scan since all voltages in the lens and analyzer are changed in direct proportion to the kinetic energy [Wannberg, 2009]. This advantage makes the CRR mode the preference for the measurement which need to compare the intensities over large energy ranges. But since in CRR mode the pass energy keeps changing with photoelectron’s kinetic energy, thus the energy resolution will change continuously during energy scan. For this reason, this mode usually will not be chosen for ARPES measurement and sometimes it is even not an option for the “ARPES-specified” commercial analyzer.

3.4 Vacuum chamber, cryostat manipulator and sample preparation

As discussed earlier, ARPES is a “surface sensitive” technique, hence the surface quality and chemical composition will greatly affects the measured spectra. For this reason, the ARPES experiments are typically carried out in an ultrahigh vacuum (UHV) chamber with pressure on the order of $10^{-11}$ Torr and sample is usually cleaved in the vacuum chamber for obtaining the freshest surface.
For study, a sample is affixed to the end of a cryostat manipulator. The sample manipulator controls sample’s both translational and rotational degrees of freedom. Control over translational degrees of freedom is critical for aligning sample to the focus of the electron analyzer and selecting best part of sample to be measured, while control over rotational degrees of freedom allows the scanning over the $k_{\parallel}$ momentum space. An extra sample’s degree of freedom is temperature, which is controlled by a cryostat combined with heater. Two types of cryostats are usually used in ARPES system: the closed-cycle cryostat which uses an electric powered helium compressor and cold head to cool the sample, or the continuous-flow cryostat which is cooled by flowing liquid helium or liquid nitrogen through the heat-sink that is thermally coupled to the sample stage.

Furthermore, because electrons are influenced by stray magnetic fields (including the earth’s magnetic field), it is essential to cancel these fields within the ARPES system, both vacuum chamber where the sample sits at and the analyzer where the electrons pass through. To minimize magnetic fields, only non-magnetic materials is used on the sample manipulator; any possible sources of magnetic field such as pumps and motors are kept away from the sample position and analyzer as far as possible; more important, both analyzer and sample chamber are equipped with the $\mu$-metal shields. By employing above efforts, stray magnetic field can be reduced to as small as 1 mG around the sample position [Koralek, 2006]. Certain analyzer is also equipped with a trim coil around the outer hemisphere of the analyzer, then any residual magnetic field component within the analyzer along the lens axis can be compensated by flowing very small current (tens of mA) through the coil.

3.5 Experimental system imperfection

Is there an ARPES system that consists of a light source which delivers purely monochromatic light with infinitesimal beam spot onto a large, flat, clean, defect-free single crystal surface and an analyzer which collects the photoelectrons, resolves any infinitesimal difference between their energy and momentum, then deflects them onto different part on the detector to be recorded without any artificial distortion? The answer is: yes, but in your dream.
3.5.1 Light source and analyzer imperfection

3.5.1.1 Energy resolution

In real world, no light source is purely monochromatic and there is always certain spectral linewidth $\Delta E_{\text{photo}}$.

For analyzer, since the hemispherical analyzer’s entrance slit always has certain width $s$ along hemisphere radial direction, i.e., the energy dispersion direction, in first order approximation the monochromatic electrons passing through the entrance slit will be imaged onto exit plane as a stripe with the same width $s$. Furthermore, there are also electrons which do not enter tangentially to the equipotential surface, but at an angle against it, i.e., there is a finite acceptance angle $\alpha$ (half angle) along hemisphere radial direction. As the result, the monochromatic electrons can pass through the entrance slit within this acceptance angle and the imaged pattern is further spread. In the first order, the stripe width due to the slit width $s$ and acceptance angle $\alpha$ is $s + 2r_0\alpha^2$, where $r_0$ is the center radius of the hemisphere. Recall euqation 3.5, we have

$$\frac{\Delta E}{E_P} = \frac{s + 2r_0\alpha^2}{2r_0}$$

(3.10)

where $E_P$ is the pass energy of the hemisphere. Here we note that the acceptance angle $\alpha$ is actually controlled by the electrostatic lens element. One way to set the acceptance angle $\alpha$ is to maximize the product $s\alpha$ in order to optimize the sensitivity of the analyzer while keeping the sum $s + 2r_0\alpha^2$ constant. After simple math, we have $2r_0\alpha^2 = s/2$ then the total width is just $3s/2$. In resolution calculation, this electron energy distribution is generally approximated by Gaussian lineshape with full width at half maximum $FWHM \sim s$, then the energy resolution due to the analyzer is

$$\Delta E_{\text{analyzer}} \cong \frac{s}{2r_0} \cdot E_P$$

(3.11)

Based on this equation, we can improve the resolution due to the analyzer by making larger hemisphere, choosing smaller pass energy, and using narrower entrance slit. But in real experimental system, larger hemisphere means much higher cost, smaller pass energy and narrower entrance slit will greatly cut the photoelectron count rates on the exit plane, and very narrow slit (in tens of $\mu m$
level) is usually hard to be manufactured. Due to this reason, people usually choose a compromise combination to achieve a reasonable analyzer resolution.

In real experiment, the system’s energy resolution is usually tested by measuring the width of good metal’s Fermi edge or by measuring the linewidth of inert gas atomic level. For Fermi edge width measurement, the measured Fermi edge at certain temperature $T$ can be approximated by a step function convolved with several Gaussian functions due to the photon energy width, the analyzer energy resolution, and the thermal broadening. Then the measured 12%-88% Fermi edge width can be expressed by

$$\text{Width}_{12\%-88\%} = \sqrt{\Delta E_{\text{photo}}^2 + \Delta E_{\text{analyzer}}^2 + (4k_B T)^2 + \Delta E_{\text{others}}^2}$$  \hspace{1cm} (3.12)

Here we note that there is a $\Delta E_{\text{others}}$ term in above equation which is possibly due to the dirty metal sample’s surface, the unshielded electronic noise in the system, and the mechanical imperfections in the construction. Similarly, for the inert gas atomic level width measurement, the measured total FWHM of the atomic level can be expressed by

$$\text{FWHM} = \sqrt{\Delta E_{\text{photo}}^2 + \Delta E_{\text{analyzer}}^2 + \Delta E_{\text{level}}^2 + \Delta E_{\text{others}}^2}$$  \hspace{1cm} (3.13)

where the $\Delta E_{\text{level}}$ is the inherent line width of the atomic level which is mainly due to the Doppler broadening on the linewidth and can be calculated precisely.

Usually, the Fermi edge width measurement is used by most ARPES groups to test the system’s energy resolution due to its easy accessibility. A very clean metal surface is critical for this measurement, since otherwise the measured resolution may be dominated by the $\Delta E_{\text{others}}$ term.

3.5.1.2 Angular resolution

In principle, the angular resolution of an ARPES system is contributed by two parts: the spatial resolution of the detector and a defocusing due to the finite beam spot size.

Considering an infinitesimal beam spot first, then the angular resolution is mainly determined by the electrostatic lens focusing ability and the pixel size of the CCD. In general, the modern CCD’s
pixel size is about tens of \( \mu m \) and the electrostatic lens can focus the photoelectrons with the same takeoff angle into a spot within several pixels. By defining the size of this spot as \( FWHM_{PSF} \), where PSF stands for the “point spread function”, we have the angular resolution due to the analyzer and detector as

\[
FWMH_{analyzer} = \frac{FWHM_{PSF}}{D}
\]  

(3.14)

where D is the angular dispersion factor of the lens and is defined by

\[
D = \frac{\text{total CCD length along angle direction}}{\text{total acceptance angle of the lens mode}}
\]  

(3.15)

in \( mm/\text{degree} \) unit. Clearly, the wider angular mode is chosen, the worse angular resolution is archived. Usually, the \( FWHM_{PSF} \) is about 0.1mm, and the angular dispersion factor D is about 0.5 \( mm/\text{degree} \) (e.g., \( \pm 10^\circ \) acceptance over a 10 mm CCD) to 5 \( mm/\text{degree} \), thus the angular resolution due to the analyzer and detector is about 0.2 degree to 0.02 degree.

In real ARPES experiment, the photon beam size is not infinitesimal small. Usually, the beam size is about tens to hundreds of \( \mu m \), e.g., 50 (v) \( \times \) 50 (h) \( \mu m \) at ALS BL7, 100 (v) \( \times \) 150 (h) \( \mu m \) at ALS BL10, 80 (v) \( \times \) 100 (h) \( \mu m \) at ALS BL12, 10 (v) \( \times \) 100 (h) \( \mu m \) at ALS BL4, and 500 (v) \( \times \) 600 (h) \( \mu m \) at SSRL BL5-4. The angular resolution due to the finite beam spot size can be expressed as

\[
FWMH_{beam} = \frac{\text{SpotSize} \times \text{LensMagnification}}{D}
\]  

(3.16)

where D is still the angular dispersion factor, \( \text{LensMagnification} \) is the lateral spread factor of rays emitted within the same angular range and is determined by the electrostatic lens elements. Considering \( D = 0.5 mm/\text{degree} \) and \( M = 1 \), the angular resolution due to a 0.1mm beam spot and 1mm beam spot are 0.2 degree and 2 degree, respectively. Clearly, the small beam spot size is critical for achieving good angular resolution.

In real experiment, the system’s angular resolution can be tested by measuring the angular width of an angular calibration device in lens angular mode, then

\[
FWMH_{measured} = \sqrt{FWMH_{beam}^2 + FWMH_{analyzer}^2 + FWMH_{device}^2 + FWMH_{others}^2}
\]  

(3.17)
where $FWHM_{\text{others}}$ is the contribution term due to other possible imperfection of the system. Currently, the best combined angular resolution claimed by commercial analyzer company is about 0.1° for 0.1mm emission spot (SCIENTA R400 and SPECS PHOIBOS225).

### 3.5.2 Sample surface imperfection

For ARPES experiment, which is a “surface sensitive” technique, the sample surface quality and chemical composition will greatly affect the measured spectra. A large, flat, clean, uniform, defect-free single crystal surface is ideal for ARPES measurement but is usually very hard to obtain. The most common problem with sample surface is the **mechanical surface defect** such as flake area, step fracture, and curved surface. These surface defects combined with finite beam spot size will result in an area-averaged spectrum which will smear out the intrinsic feature of the spectrum. This is another key reason why the light source with very small beam spot is desired. And in ARPES experiment, a critical step for sample alignment is to find the best surface area which has as less surface defects as possible.

Beyond those mechanical surface defects, there are also possible surface inhomogeneity due to certain microscopic origin such as **domain formation** and **doping inhomogeneity**. These features are usually in μm or even nm level and will also affect ARPES spectrum.

### 3.5.3 Detector imperfection

Ideally, the MCP-Phosphor-CCD detector will proportionally amplify the photoelectron distribution over the analyzer’s exit plane then record them. In real experiment system, there are several practical issues we need to pay attention to.

◊ **MCP inhomogeneity**

The MCP may deteriorate over time from being bombarded with electrons, and this can result in an inhomogeneous response across the detector. The inhomogeneity along energy direction can be corrected by choosing constant pass energy (CPE) “swept mode” which will average the counts along energy direction and remove the inhomogeneous effect along energy direction. But
for the inhomogeneity along angular direction, we have to correct the spectrum by using certain “renormalization process”, e.g., divide the raw spectrum by gold spectrum taken within the same mode or divide the raw spectrum by background counts (due to the second order synchrotron light) above Fermi level.

◊ **CCD thermal noise and readout noise**

For CCD camera, the thermally excited electrons in the silicon lattice of the CCD chip are counted as a signal, which will generate “dark counts” background in the spectrum. This thermal noise increases linearly with the dwell time $\tau$ and is also temperature dependent: the higher the temperature of the CCD, the higher the thermal noise. Therefore, thermal noise can be reduced by lowering the temperature of the CCD camera. Furthermore, all CCD detectors have an inherent type of noise, i.e., the “readout noise”, which is due to the imperfect operation of physical electronic devices. This readout noise is present in all images and has the same amount regardless of exposure time.

Based on the discussion above, the total noise for CCD detector can be expressed as

$$\sigma_{\text{total}} = \sqrt{\sigma_{\text{readout}}^2 + (D\tau)^2}$$

(3.18)

where $D$ is the thermal noise coefficient and $\tau$ is the dwell time. In general, this noise issue is taken care by data taking software provided by the commercial company.

◊ **CCD non-linearity**

Ideally, the digital signal generated by CCD should be proportional to the amount of incident light. For CCD detectors used in ARPES system, there is usually a very large linearity region except for extremely high or extremely low count rate. By choosing reasonable counts rate, the CCD non-linearity is usually not a problem for most ARPES measurements. Unfortunately, when the area of interest is around the Fermi level, the count rate will decrease dramatically from the region below Fermi level to the region above Fermi level, thus there will be a crossover from the CCD’s linearity region to non-linearity region. This crossover behavior will cause trouble when people try to extract intrinsic information about the spectral function slightly above the Fermi level, e.g., testing the
“electron-hole” symmetry properties. For detailed discussion about this non-linearity behavior and possible correction methods, the reader may refer to work done by [Mannella et al., 2004; Reber et al., 2010].

3.5.4 Space charge effect

At last, since photoelectrons are charge particles, there must be Coulomb interactions between them. Usually, this Coulomb interaction will not introduce noticeable effect in the ARPES spectrum. But when the density of photoelectrons near sample surface becomes too large, the Coulomb interactions between photoelectrons will cause significant broadenings and shifts the energy distributions. This effect is the so called “space charge effect”. Specifically, this effect will broaden the feature along energy direction and shift the Fermi level to higher kinetic energy (since the interaction is repulsive). For detailed discussion, the reader may refer to the work done by [Zhou et al., 2005]. Due to this space charge effect, we usually need to limit the photon flux in ARPES experiment.

Here I also need to note that the reader should not confuse the space charge effect with the sample charging effect. The sample charging effect will happen when the electrons in sample cannot be replenished in time during the photoemission process. As the result, the sample itself will possess positive charges which will attract the outgoing photoelectrons. Thus the energy feature measured by ARPES will be shifted to lower kinetic energy. The sample charging effect may be due to the improper sample preparation or just because the sample is insulating.
Chapter 4

Review of Cuprate and Iron-based High-\(T_c\) Superconductors

4.1 Introduction

Superconductivity is a phenomenon of exactly zero electrical resistance occurring in certain materials below a characteristic temperature. It was first discovered by Heike Kammerlingh Onnes in elemental mercury 100 years ago (1911)\(^1\). Two decades later (1933), Walther Meissner and Robert Ochsenfeld discovered the perfect diamagnetism, or superdiamagnetism in superconductors, i.e., the expulsion of a magnetic field from a superconductor during its transition to the superconducting state. This behavior is the so-called “Meissner effect”. Noticing that the Meissner effect cannot be explained as the result of normal conductor with perfect conductivity, it is another fundamental property of the superconductor. Generally speaking, a superconductor is defined by the **perfect conductivity** and the **Meissner effect**.

Due to the fantastic physical properties of the superconductor, explaining the mechanism of the superconductivity and discovering new superconductors with higher transition temperature became one of the major activities in community in the past 100 years. Fig. 4.1 shows the timeline of major advance in superconductivity research. This chapter presents a brief review of the superconductivity. The conventional superconductivity will be discussed first then the superconductivity in the newly discovered cuprate superconductors and the even more recently discovered iron-based superconductors will be reviewed in a parallel manner.

\(^1\) After he succeeded in liquefying helium in 1908.
4.2 Conventional superconductivity: the BCS theory

In 1957, Bardeen, Cooper, and Schrieffer proposed the first microscopic theory of superconductivity, i.e., the “BCS theory”, which could explain almost all properties of the superconductors discovered by that time [Bardeen et al., 1957]. In turn, materials that display superconductivity as described by BCS theory (or its extensions) are called conventional superconductors. In this section, the basic idea of BCS theory will be described.

In BCS theory, superconductivity arises from the pairing of individual electrons into composite bosons, which are called Cooper pairs. Each Cooper pair consists of two electrons with opposite
momentum and spin, as shown in fig. 4.2(a). Those cooper pairs can take the character of bosons and condense into the ground superfluid state, called the BCS ground state. Then it can be shown that the perfect conductivity and Meissner effect are both the properties of this new BCS ground state.

![Figure 4.2: Schematics of Cooper pair and pair forming via lattice. (a) Schematic of a Cooper pair. (b) Pair forming via lattice by phonon-mediated electron-electron attraction. From [Wang and Lee, 2011].](image)

It’s hard to believe that the electrons will form pairs since in principle they should repel each other through the Coulomb interaction. The net attractive pair-forming interaction between electrons can be explained in the following way: as one electron propagates through the crystal lattice, it causes a local positive polarization of the lattice by attracting the positive ions of the lattice; these excess positive ions in turn attract the second electron, giving an effective attractive interaction between the electrons; if this attraction is strong enough to override the repulsive Coulomb interaction, it gives rise to a net attractive interaction, allowing the electrons to form pairs. Since any lattice distortion can be described as a phonon, the above electron paring interaction through lattice distortion is also called a phonon-mediated attraction. The process discussed above is illustrated in fig. 4.2(b). In many-body language, this process can be described as electrons paring through exchanging phonons.

Then another question is raised: how can this phonon-mediated attraction be strong enough to override the repulsive Coulomb interaction between electrons? The simple answer is that in
conventional superconductors which are usually simple metals and their alloys, the Coulomb interaction between two electrons is actually well screened due to the existence of the other electrons in the system. As the result one can approximate the effective Coulomb repulsion between two electrons as \( V_{eff}(r) = \frac{e^2}{r} e^{-\lambda r} \), which is much weaker than the original Coulomb repulsion when two electrons are far apart. Then even the very small phonon-mediated attraction between electrons could have great chance to override the “screened Coulomb repulsion” and make electrons forming pairs\(^2\).

The detailed BCS theory can be found in countless textbooks, in the next few paragraphs only the main result will be presented. One key approximation made by BCS when considering the phonon-mediated attraction between electrons is that they ignore the detailed information about the electron-phonon coupling and only approximate it by a constant coupling term within an energy window defined by the averaged phonon energy. One can show that the direct result of this approximation is that only the electrons with opposite momentum and spin can form pairs, which is the Cooper pair mentioned above. Considering the BCS ground state consisting of Cooper pairs, the ground state of the superconductor is expressed as

\[
|\Psi_{BCS}\rangle = \prod_k (u_k + v_k b_k^+)|0\rangle, \quad \text{where } b_k^+ = c_{k\uparrow}^+ c_{-k\downarrow} \quad \text{and } u_k = \sqrt{1 - v_k^2} \tag{4.1}
\]

\( |0\rangle \) is the vacuum state, i.e., there is no electrons in the system. \( b_k^+ \) is the paring operator which indicates creating a Cooper pair \((k \uparrow, -k \downarrow)\) in the vacuum state. \( v_k \) is the probability amplitude that the pair state \((k \uparrow, -k \downarrow)\) is occupied. The behavior of the BCS ground state is determined by a reduced Hamiltonian\(^3\) which is expressed as

\[
H = 2 \sum_k \epsilon_k b_k^+ b_k - \sum_{k \neq k'} V_{kk'} b_k^+ b_{k'}^+ b_k b_{k'} \tag{4.2}
\]

\(^2\) The “electrons interacting with each other with the reduced Coulomb repulsion due to the existence of the other electrons” is actually the “quasiparticle” picture in the many-body theory discussed in the previous chapter.

\(^3\) This is the “reduced” Hamiltonian since it only considers the paired electrons, i.e., all the electrons in the system form pairs.
where\[ V_{kk'} \equiv V_{-k',k,-k,k'} = \begin{cases} \begin{array}{ll} V \text{ (constant) for electrons' energy } \epsilon_k, \epsilon_{k'} \in (-\hbar \omega_c, \hbar \omega_c) \\ 0 \text{ otherwise} \end{array} \end{cases} \]

\( \epsilon_k \) and \( \epsilon_{k'} \) are the electrons’ energies relative to the Fermi level and can be understood as the “bare band” discussed in the previous chapter. \( \hbar \omega_c \) is the average photon energy \( \sim 10^{-2} \text{ eV} \). Here \( V \) is defined as a positive number, then \( -V \) represents the effective attraction between electrons.

Ignoring the detailed calculations, it is shown that the \( v_k \) in equation 4.1 can be expressed as

\[ v_k^2 = \frac{1}{2} \left[ 1 - \frac{\epsilon_k}{E_k} \right] \]

\[ E_k = \sqrt{\epsilon_k^2 + \Delta_k^2} \]

(4.3)

where

\[ \Delta_k = \sum_{k'} V_{kk'} u_{k'} v_{k'} = \sum_{k'} V_{kk'} \frac{\Delta_{k'}}{2E_{k'}} \]

(4.4)

Based on equation 4.4 and considering the approximation made by BCS on the effective attraction coupling term \( V_{kk'} \) shown above, one can show that

\[ \Delta_k = \Delta \approx 2\hbar \omega_c \cdot \exp[-\frac{1}{N(0)V}], \text{ for small } V \]

(4.5)

where \( N(0) \) is the density of states at the Fermi surface. For most metal superconductors we have \( \Delta \approx 1 \text{ meV} \). Furthermore, for the ground state energy BCS obtained

\[ E_s - E_n \approx -\frac{1}{2} N(0)\Delta^2 < 0, \text{ for small } V \]

(4.6)

where \( E_s \) is the energy of the BCS ground state and \( E_n \) is the energy of the normal ground state. Clearly the BCS ground state has lower energy and there must be a phase transition from the normal state to the superconducting state if the electrons form Cooper pairs.

All terms in equations 4.3 and 4.4 have great physical significance in describing the superconducting state. First, \( E_k = \sqrt{\epsilon_k^2 + \Delta_k^2} \) represents the excitation energy of the superconducting system. The elementary excitations in the superconducting system are called the “Bogoliubov quasiparticles”. They are not like the “conventional”quasiparticles discussed in the previous chapter, which can be understood as an electron or hole dressed with a manifold of excited states. The
Bogoliubov quasiparticles are actually a linear combination of particle and hole excitations with the coherence factors $u_k$ and $v_k$\(^4\). There is a minimum excitation energy for the system, i.e., $E_k = |\Delta_k| > 0$ when at the Fermi surface with $\epsilon_k = 0$. Then $\Delta_k$ actually represents the “gap” for the elementary excitations. Here we note that if we break a Cooper pair by removing one electron from the occupied state under the Fermi level and adding it to the unoccupied state above the Fermi level, this process actually equals to two quasiparticle excitations in the superconductive system and the minimum energy needed for this process is $2\Delta_k$.

Now let’s consider the gap function $\Delta_k$ specifically. In equation 4.5, it is shown that for a BCS superconductor $\Delta_k = \Delta$, i.e., the gap is isotropic. In the equations above, all the key parameters ($\Delta_k$, $u_k$, $v_k$) are set to be real. In general, they should be complex numbers, e.g., $\Delta_k = |\Delta_k|e^{i\varphi_k}$. For BCS theory, it can be shown that

$$\Delta_k = |\Delta|e^{i\varphi} \quad (4.7)$$

i.e., it has an (isotropic) s-wave gap function. This is actually the direct result of the isotropic effective attraction coupling term $V_{kk'} = V$. In other words, the gap function reflects the properties of the paring mechanism. The phase $\varphi$ of the gap function also has its own physical meaning. In general one can show that

$$v_k = |v_k|e^{i\varphi_k} \quad (4.8)$$

i.e., the phase of the gap function $\varphi_k$ also represents the relative phase of the Cooper pairs. For the BCS ground state $\varphi_k = \varphi$ as a constant, then all the Cooper pairs in the BCS ground state have the same phase $\varphi$. In other words, all the Cooper pairs move coherently. For this reason, one can not treat the BCS ground state just as a pile of independent Cooper pairs. Instead, it is actually a macroscopic quantum state. This picture is very important for understanding the zero resistance in superconductivity: if the BCS ground state is just a pile of independent Cooper pairs, it actually can be treated as a normal metal having charge carrier with $2e$ and $2m$, then it still can be scattered by phonons, impurities and defects and there is no zero conductivity; in the true BCS

\(^4\) By transforming the original particle and hole excitations into the Bogoliubov quasiparticles, we can have a set of nearly independent elementary excitations. This is the reason for calling these combined excitations as quasiparticles.
ground state, since all pairs move coherently, scattering one pair requires destroying the coherence of all pairs and this only can be accomplished until enough energy is introduced, so we have zero conductivity at low temperature.

All the discussions above are held in energy-momentum space. Furthermore, the real space gap function $\Delta(r)$ turned out to be proportional to the superconducting state’s order parameter $\psi(r)$ described by the Ginzburg-Landau (GL) theory. In GL theory, $|\psi(r)|^2$ represents the local density of the superconducting electrons, $n_s(r)$.

Before ending this section, I need to note that the BCS theory discussed above was developed in the weak-coupling approximation, i.e. the electron-phonon interaction is assumed to be weak and the entire model is determined by a single parameter $V_{kk'} = V$. As the result, there are several universal relations for the BCS superconductor:

$$\frac{2\Delta}{k_B T_c} \approx 3.53$$
$$\frac{C_s - C_n}{C_n} \approx 1.43$$

$$T_c M^{\frac{1}{2}} \approx \text{constant}$$

where $T_c$ is the superconducting transition temperature, $C_s$ and $C_n$ are the specific heat of superconducting and normal state, $M$ is the mass of the ion (the last equation represents the famous isotope effect). But in some phonon-mediated superconductors, the electron-phonon coupling is not weak and their behaviors in superconducting state strongly deviate from those universal relations. To describe the behaviors of those materials, the BCS theory needs to be extended into the strong-coupling regime. Materials that display superconductivity as described by BCS theory or its strong-coupling extensions are called conventional superconductors. All conventional superconductors have s-wave gap function\(^5\). By far, the highest critical temperature achieved in a conventional superconductor was 39 K in $MgB_2$ [Nagamatsu et al., 2001] and its properties were explained by standard strong-coupling approach for electron-phonon interactions [Buzea and Yamashita, 2001].

\(^5\) For this reason, the conventional superconductor is also defined as the superconductor with an s-wave gap function.
4.3 High-$T_c$ superconductivity: cuprate vs. iron-based superconductors

Before 1986, BCS theory and conventional superconductors dominated the research on superconductivity. Though a few new types of superconductors were found to be quite unconventional, e.g., the singlet d-wave heavy fermion superconductors ($\text{CeCu}_2\text{Si}_2$, $\text{UBe}_{13}$, $\text{UPt}_3$, $\text{URu}_2\text{Si}_2$, ...) [Stewart, 1984] and the triplet organic superconductors ($[\text{TMTSF}]_2X$ ($X = \text{PF}_6$, $\text{ClO}_4$, ...)) [Jérome and Schulz, 1982], the transition temperatures of those unconventional superconductors are too low to make them applicable. Even for the extensively studied conventional superconductors, the highest $T_c$ found by that time was still only 23.2K in $\text{Nb}_3\text{Ge}$ [Testardi et al., 1974] and the theoretical calculations proposed that the maximum achievable $T_c$ would be $\sim 40$ K in $\text{V}_3\text{Si}$ [McMillan, 1968].

In 1986, Bednorz and Müller reported superconductivity in a lanthanum-based cuprate perovskite material ($\text{La}_{2-x}\text{Ba}_x\text{CuO}_{4+\delta}$) with transition temperature as high as 35 K [Bednorz and Müller, 1986]. This discovery inspired an enormous effort in searching new superconductors with even higher $T_c$ and developing new theories to describe their unconventional behavior. The high-$T_c$ superconductivity in $\text{La}_{2-x}\text{Ba}_x\text{CuO}_{4+\delta}$ was soon confirmed and further improved to over 40K by replacing $\text{Ba}$ with $\text{Sr}$ [Tarascon et al., 1987]. One year later, the superconductivity at 90 K in the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ family was discovered by Wu and Chu [Wu et al., 1987]. This was the first time that $T_c$ reached the liquid nitrogen temperature and really started the “high-$T_c$” superconductivity era. In early 1988, the even higher $T_c$ was reported in $\text{BiSrCaCuO}$ ($T_c \sim 110$K for $\text{Bi2223}$) [Chu et al., 1988] and $\text{TlBaCaCuO}$ ($T_c \sim 125$K for $\text{Ti2223}$) [Sheng and Hermann, 1988] families. Note that all the high-$T_c$ compounds mentioned above are hole-doped compounds, in 1989, Tokura, Takagi, and Uchida discovered the first class of electron-doped high-$T_c$ superconductors, $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ [Tokura et al., 1989]. By now, the highest $T_c$ reached is 164K by $\text{HgBaCaCuO}$ class superconductor $\text{Hg-1223}$ under pressure [Gao et al., 1994]. This incredible soaring in $T_c$ is shown in fig. 4.1. All the superconductors mentioned above have a common point: they all contain planes of copper and oxygen (Cu-O layer). These planes dominate the electronic structures of those materials and
are also the places where the superconductivity is believed to happen. Due to this common point, these materials are referred as “cuprates”.

Before 2008, the “high $T_c$” superconductivity only referred to the cuprate superconductivity mentioned above. Actually, the “high $T_c$” is a very loose definition, sometimes it refers to the superconductivity that happens above liquid nitrogen temperature (77 K), sometimes it refers to the superconductivity with $T_c$ higher than the BCS predictions ($\sim 40$ K). Nevertheless, the cuprate superconductors satisfy the criterions for both cases.

In February 2008, Hideo Hosono and co-workers reported the discovery of 26K superconductivity in fluorine-doped LaFeAsO, which $T_c$ is higher than most of the conventional superconductors [Kamihara et al., 2008]. Unlike cuprates, there are no “Cu-O” planes in this material, instead it is shown that the electronic structure of this material is mainly determined by the “Fe-As” planes which are also critical for its superconductivity. This discovery started a new worldwide effort to investigate the new family of superconductors and soon a series of superconductors based on the Fe-As planes are discovered and the $T_c$ was improved to as high as 55K [Ren et al., 2008] (shown in fig. 4.1). Due to the “Fe-As” planes appearing in all of these materials, they are referred as the “iron-pnictide” superconductors. Since the highest $T_c$ for “iron-pnictide” superconductors is above the BCS limit, they are also referred as the second family of the high-$T_c$ superconductors (criterion 2). It is further found that by replacing pnictogen atoms (P, As) with chalcogen atoms (Se, Te), the materials based on Fe-Se or Fe-Te planes also have superconductivity properties [Hsu et al., 2008]. There materials are referred as “iron-chalcogenide” superconductors and generally have lower $T_c$ than the iron-pnictide superconductors. In general, people may refer the “iron-based” superconductors for both the “iron-pnictide” and the “iron-chalcogenide” superconductors.

Since the cuprate and the iron-based superconductors can not be described by the standard BCS theory (and its extensions), they are all unconventional superconductors. In this section, a brief review on both cuprate superconductors and iron-based superconductors will be presented.
4.3.1 Families and crystal structures of cuprate and iron-based superconductors

4.3.1.1 Cuprate superconductors

Since the discovery of the first cuprate superconductor, there has been hundreds of cuprate superconductors reported. It is almost impossible to give a review on all of them, here I will only focus on several main families of the cuprate superconductors. Actually, in the previous section I almost mentioned all the main cuprate families: the lanthanum family $La_{2-x}(Ba, Sr)_x CuO_4$, the yttrium family $YBa_2Cu_3O_7-\delta$, the (ARPES preferred) bismuth family $Bi_2Sr_2Ca_{n-1}Cu_nO_{4+2n+\delta}$ ($n = 1$, $2$ and $3$), the thallium family $TlBa_2Ca_{n-1}Cu_nO_{2n+3}$ ($n = 1$, $2$, $3$, $4$, and $5$) and $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$ ($n = 1$, $2$, $3$ and $4$), the mercury family $HgBa_2Ca_{n-1}Cu_nO_{2n+2}$ ($n = 1$, $2$ and $3$), and the electron doped neodymium family $Nd_{2-x}Ce_x CuO_4$. Here we note that the lanthanum, yttrium, and neodymium families only contain a single Cu-O layer in unit cell while the other families mentioned above can have $1$, $2$, $3$ or even more layers in a single unit cell. In general, the experiment showed that there is a strong dependence of $T_c$ on the number of Cu-O layers within the same family, i.e., the more Cu-O layers, the higher $T_c$. But interestingly, this trend does not hold for $TlBa_2Ca_{n-1}Cu_nO_{2n+3}$ when $n > 4$ and $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$ when $n > 3$.

In the rest of this chapter, I will mainly focus on the crystal structure and electronic structure of the bismuth family cuprate $Bi_2Sr_2Ca_{n-1}Cu_nO_{4+2n+\delta}$ ($n = 1$, $2$ and $3$), and this thesis will focus on the ARPES studies on $n = 2$ materials. The reason for the bismuth family cuprate (especially $n = 2$ material) to be widely studied by ARPES technique is that their samples can be readily produced and are easily cleaved (between the Bi-O planes) to have a nice surface, which is very important for the surface sensitive ARPES experiments.

Fig. 4.3 shows the unit cells of the Bi-based family of cuprates with different numbers of $CuO_2$ layers. The $CuO_2$ planes are separated by rock-salt layers containing bismuth, strontium and calcium atoms (so-called charge reservoir layers). Strictly speaking, the Bi-cuprates should be described as a base-centered orthorhombic lattice with slightly different a and b axes. For example, the a and b lattice constants of Bi2212 material are 5.415Å and 5.421Å, respectively. Then each
Figure 4.3: Unit cells of the Bi-based family of cuprates. Here the based-centered orthorhombic lattice is approximated by the body-centered tetragonal lattice structures with \( a = b = 3.814 \, \text{Å} \), while the \( c \) axis parameter of the crystallographic cells increases from 24.6 to 30.6 and 37.1 Å for the single-, bi-, and tri-layer systems, respectively. From [Kovaleva et al., 2004].

unit cell has two formula units, i.e., \((\text{Bi}2212) \times 2\). Since \(a_o \approx b_o\), the structure is pseudo-tetragonal, and in most case their crystal structure is approximated by a body-centered tetragonal lattice with \(a_t = b_t = 3.85 \, \text{Å}\) and each unit cell has one formula unit. This is the structure shown in Fig. 4.3 actually. Furthermore, since there is a mismatch between the equilibrium Bi-O bond length and the lattice constant imposed by the \(\text{CuO}_2\) planar net, the Bi2212 crystal has an incommensurate modulation along the \(b\) axis of its orthorhombic lattice. The modulation vector \(\mathbf{q} \approx 0.21 \cdot \mathbf{b}_o\) and it will generate the so-called “superstructure band” in ARPES spectra.

4.3.1.2 Iron-based Superconductors

Compared to the twenty-six-year-old Mr. Cuprate, it is much easier for us to track the history of the three-and-half-year-old Mr. Iron-pnictide and his younger cousin, Mr. Iron-chalcogenide. Currently, there are four main families of the iron-pnictide superconductors and one main family of the iron-chalcogenide superconductors.
Figure 4.4: Crystallographic structures of five iron-based superconductor families. All have the active planar iron layers (Fe-Se or Fe-As). Those layers are either simply stacked together, as in FeSe, or are separated by spacer layers using alkali (for example, Li), alkaline-earth (for example, Ba), rare-earth oxide/fluoride (for example, LaO or SrF) or more complicated perovskite-type combinations (for example, Sr$_3$Sc$_2$O$_5$). Adopted from [Paglione and Greene, 2010].

The four main families for iron-pnictide superconductors are the 1111-type $ReFeAsO$ [$Re$: rare earth elements], e.g., $LaFeAsO_{1-x}F_x$; the 122-type $AEFe_2As_2$ [$AE$: alkali earth elements], e.g., $CaFe_2As_2$; the 111-type $LiFeAs$ and $NaFeAs$; and the 22426-type $(Fe_2Pn_2)(AE_4M_2O_6)$ [$Pn$: pnictogen elements], e.g., $(Fe_2P_2)(Sr_4Sc_2O_6)$ and $(Fe_2As_2)(Sr_4M_2O_6)$ ($M = Sc, Cr$)\(^6\). For the iron-chalcogenide superconductor, there are only one main family, i.e., the 11-type $FeCh$ [$Ch$: chalcogen elements], e.g., FeTe and FeSe.

Fig. 4.4 shows the crystallographic structures of five iron-based superconductor families mentioned above. Similar to the cuprates, the iron-pnictide or iron-chalcogenide materials consist of Fe-As or Fe-Te/Se layers separated by different types of spacer layers. At room temperature, all the two-dimensional Fe-As or Fe-Te/Se layers have the tetragonal structures with about the same

\(^6\) Sometimes the 22426-type is also referred as the 32522-type, e.g., $(Sr_3Sc_2O_5)(Fe_2As_2)$. But they are in general the same case by considering the Fe-As layers separated by complicated perovskite-type layers.
in-plane lattice constant ($\sim 4\text{Å}$). Therefore their physical properties are considered to be highly two-dimensional, which is similar to those of cuprates, and the superconductivity is believed to be associated with the Fe square lattice layers for all iron-based compounds. But it should be noted that unlike cuprates which have almost perfect two-dimensional $CuO_2$ layers, the iron-based superconductors Fe-As and Fe-Te/Se layers are described by the edge-sharing $FeAs_{4/4}$ tetrahedra. In principle, this may indicate the iron-based superconductors have stronger $k_z$ dispersion than cuprates which have very weak dispersion along the $z$ axis.

### 4.3.2 General electronic structures of cuprates and iron-pnictides

#### 4.3.2.1 Cuprate superconductors

Although the cuprate superconductors have very complicated crystal structures with various atoms, it is shown that their near $E_F$ electronic structures are basically determined by the $CuO_2$ planes. It makes a lot of sense since in general the electrons near $E_F$ contribute most strongly to the superconductivity and for cuprates the $CuO_2$ planes are believed to be the place where the superconductivity happens.

Fig. 4.5(a) shows a band calculation result on $La_2CuO_4$ (mother compound with zero doping) as an example. The copper cation in undoped cuprate has 9 d electrons. Considering the copper cation is situated in the center of the oxygen octahedra, its five d-orbitals will split into the lower $t_{2g}$ orbitals and the higher $e_g$ orbitals due to the existence of the crystal field. The $e_g$ orbitals will further split due to the Jahn-Teller distortion of the octahedron. As the result, the $d_{x^2−y^2}$ orbital has the highest energy and only has one electron filled. Similarly, the oxygen anion with the $2p^6$ electron configuration will also split. Considering that the band structure originates from the hybridizations between copper and oxygen orbitals, after hybridizations, the uppermost states, where the Fermi level of cuprates is expected to be, will be composed of the antibonding hybrids of the copper $3d_{x^2−y^2}$ orbital and the oxygen $2p_x$ and $2p_y$ orbitals and this band is half-filled. This indicates that the $La_2CuO_4$ material should be a metal, which is in contradiction to the fact that
Figure 4.5: Electronic structure of cuprate superconductors. (a) The left panel shows the hybridization giving rise to the Cu-O bands. The right panel shows the LDA band calculation of LSCO. From [Feng and Jin, 2005]. The uppermost states around the Fermi level is composed of antibonding hybrids of the Cu 3\textit{d}_{x^2−y^2} states and O 2\textit{p}_x and 2\textit{p}_y states. (b) to (d) show the schematics of the opening of a correlation gap in cuprates. Details are discussed in the text. Adopted from [Damascelli et al., 2003].

Actually, the undoped mother compounds of cuprate superconductors are all excellent insulators with antiferromagnetic long-range order. The reason why their electronic structures can not be described by the traditional band calculations is the strong on-site electron-electron repulsion $U$ of the copper 3\textit{d} electrons, which is much larger than their bandwidth $W$. As the result, in cuprates the conduction band will split into upper and lower Hubbard bands due to the strong electron-electron correlation as indicated in fig. 4.5(b) and (c). Then the cuprates’ mother compounds are better described as the “charge-transfer insulators” since in cuprates the Cu-O charge-transfer energy $\Delta$ is smaller than the on-site Coulomb repulsion $U$.

Due to the “charge-transfer” nature of the cuprates’ mother compounds, we should consider all the copper 3\textit{d}_{x^2−y^2} orbital and the oxygen 2\textit{p}_x, 2\textit{p}_y orbitals which will lead to a three-band
Hubbard model. But this three-band problem was further simplified by Zhang and Rice. They first considered the two linear combinations of the oxygen $p_x$ and $p_y$ orbitals and ignored one of them which will not hybridize with the copper $d_{x^2−y^2}$ orbital since it will not contribute to the low energy excitations. By doing this, the three-band problem is converted into a two-band problem. Furthermore, they considered the hybridization between the remaining combined p orbital and the d orbital, the hybridization will lead to a singlet and a triplet. The triplet is ignored again since it’s away from the Fermi level and will not contribute to the low energy excitations. By doing this, they finally got a single band problem in which the “effective lower Hubbard band” is the remained singlet and the “effective higher Hubbard band” is the primarily Cu $3d^{10}$ derived band. The “Mott gap” is the Cu-O charge-transfer energy $\Delta$ mentioned above. The singlet here is the famous “Zhang-Rice singlet” (ZRS) [Zhang and Rice, 1988] and the process described above is illustrated in fig. 4.5(d).

Now the problem can be described by the single-band Hubbard model and can be further simplified into the so-called “t-J model”, which is the strong correlation limitation ($U \gg t$) of the standard Hubbard model:

$$H = -t_{\text{eff}} \sum_{<ij>,\sigma} (\tilde{c}_{i\sigma}^+ \tilde{c}_{j\sigma} + \text{h.c.}) + J_{\text{eff}} \sum_{<ij>} (\mathbf{S}_i \cdot \mathbf{S}_j - \frac{n_i n_j}{4})$$

(4.10)

where $\tilde{c}_{i\sigma} = c_{i\sigma}(1 - n_{i,-\sigma})$ excludes double occupancy, $t_{\text{eff}} = t_0^2/\Delta$ is the effective hopping amplitude of the ZRS between the nearest Cu-Cu, $J_{\text{eff}} = 4t_{\text{eff}}^2/\Delta$ is the effective antiferromagnetic exchange coupling constant between the nearest Cu-Cu, $\Delta$ is the charge-transfer gap between the nearest Cu and O, and $t_0$ is the hopping amplitude from copper to the nearest oxygen site. In other words, by introducing the ZRS, the three-band problem can be simplified into an effective Cu one-band problem but the parameters of this one-band problem are determined by the properties of the original three bands. In the actual cuprate materials, it is shown that $U \to \Delta \sim 2$ eV and $t_{\text{eff}} \sim 0.35$ eV, so the approximation ($U \gg t$) made above is not unreasonable. This “t-J model” is proposed to be the starting point for understanding the high-$T_c$ superconductivity in cuprates.

In summary, in this section it is shown that the near $E_F$ electronic structure of cuprates is
mainly determined by the copper $d_{x^2-y^2}$ orbital with the oxygen $p_x$ and $p_y$ orbitals, but one need to consider the strong correlation effect to correctly understand their electronic structures.

4.3.2.2 Iron-pnictide superconductors

Similar to cuprates whose near $E_F$ electronic structures are mainly decided by the $CuO_2$ planes, the iron-pnictide superconductors’ near $E_F$ electronic structures are also mainly determined by the $Fe_2As_2$ layers. Fig. 4.6(a) shows a possible electron configuration for the iron cation. Due to the tetrahedral crystal-field splitting, the five Fe $d$ orbitals split into the higher $t_{2g}$ orbitals and the lower $e_g$ orbitals (opposite to the picture for cuprates). Furthermore, due to the irregular tetrahedron geometry of the As atoms, the higher $t_{2g}$ orbitals split into lower $d_{xy}$ and higher degenerate $d_{xz}$ and $d_{yz}$ orbitals. Considering the undoped mother compounds in which the iron cations have 6 $d$ electrons, its electron configuration will be determined by the well-known Hund’s rules combined with those orbital splittings. In the case shown in Fig. 4.6(a), the iron cation is in an $S = 1$ intermediate spin state. Here we note that it is only a possible electron configuration for the iron cations, the slight variation of the environment around the iron cation may change its orbital drastically and lead to totally different electron configurations.

The iron-pnictides’ electronic structure can be considered as originating from the hybridizations between Fe $3d$ and As $4p$ orbitals. Fig. 4.6(b) shows a LDA band calculation of LaFeAsO material in the normal state, which details will not be discussed here. The main point to show here is that for iron-pnictides the electronic structure near $E_F$ is mainly originated from the iron $d$ orbitals and the calculation suggests the mother compounds of iron-pnictides are metals. The iron-pnictides’ mother compounds are indeed metallic but with long range collinear antiferromagnetic order at low temperature.

So far the correlation effect in iron-pnictides has been left out of the discussion. Since the mother compounds of iron-pnictides are metallic which is predicted by the band calculation correctly, one may think the correlation effect in the system is not as important as that in cuprates. Then people tried to describe the iron-pnictides as a system with itinerant Fe electrons and the
long-range magnetic order at low temperature was proposed to be SDW-like due to the Fermi surface nesting. But on the contrary, the transport and optical measurements show a very large resistivity and a small Drude weight, which indicates that they may not be conventional metals and the electron correlations could also play a crucial role, similar to the cuprates. Then the iron-pnictides may be considered in terms of a proximity to a Mott insulator and the long range order magnetism is due to the exchange interactions between the local magnetic moment of iron cations. So far, whether the iron-pnictides should be described by the fully itinerant picture, or by the fully localized picture, or even the mixed local-itinerant picture is still under debate. But the general argument that the near $E_F$ electronic structure of iron-pnictides is mainly the iron $d$ orbitals holds for all iron-pnictides.
4.3.3 Phase diagram

Fig. 4.7 shows a comparison of the phase diagrams between cuprate and iron-pnictide superconductors. First I need to note that these two phase diagrams come from different doping sides. But it has been shown that the phase diagrams from the electron-doping side and the hole-doping side are quite similar for both systems, so the comparison made here holds in general.

Looking at Fig. 4.7 without knowing further details, the first impression is that these two phase diagrams look very similar to each other: they are both characterized by an antiferromagnetic “mother phase” and a superconducting dome. This makes people think of a possible deep connection between these two systems. But after examining these two phase diagrams in detail, one may find that there are also significant differences between these two systems.

4.3.3.1 Cuprate superconductors

The undoped parent compounds of cuprates are antiferromagnetic charge-transfer insulators. By doping holes into the system, cuprates will leave the antiferromagnetic insulator phase and enter into the superconducting phase as shown in fig. 4.7(a). Here we note that the superconducting
phase is “dome-shaped” and the maximum $T_c$ happens at a certain doping level. This doping level is called the “optimal doping” level. Then the phase diagram is always separated by this optimal doping level into the “underdoped” and the “overdoped” regions.

In the underdoped region, there is a very special range between the normal and superconducting state, which is called the “pseudogap” state, as shown in fig. 4.7(a). In this pseudogap region, the low energy excitations near the Fermi level are depressed, i.e., it very much looks like the system opens a gap at the Fermi level but there is no associated superconducting behavior. By now, there is no consensus on the origin of this pseudogap phase. Some argue that it represents the phase-incoherent pairing electrons while there is also evidence that it is a second gap of the system due to a competing order such as charge order or spin density wave.

The phase diagram in the overdoped region seems simpler than that in the underdoped region, there are only normal and superconducting states. As doped further, the system will leave the superconducting dome. It is shown that at the heavily overdoped side of the phase diagram, the cuprates exhibit Fermi liquid behavior. But the “normal state” above the superconducting dome is not really normal since it cannot be described by the conventional Fermi liquid theory, e.g., unlike the Fermi liquid in which the low energy scattering rate varies as $\omega^2$ and $T^2$, in cuprates’ “normal” phase, experiments show a $\omega$ and $T$ dependence on low energy scattering rate instead. This is actually the experimental evidence for the marginal Fermi liquid model discussed in the previous chapter. Other theories were also proposed to explain the strange behavior of this abnormal normal state, e.g., the “Anderson lineshape” mentioned in the previous chapter.

Besides the main features mentioned above, there are also a lot of subtle features in this phase diagram, e.g., the dip in $T_c$ near 1/8 hole doping region, and the possible quantum critical point (QCP) inside the superconducting dome. Actually those subtle features may represent some very important physics happening in cuprates which may directly relate to the superconducting mechanism.
4.3.3.2 Iron-pnictides superconductors

Fig. 4.7(b) shows the phase diagram of iron-pnictide 122 family with Co-doping. Unlike cuprates, the iron-pnictides’ undoped parent compounds are metals. But they are actually “bad metal” and also have long-range collinear antiferromagnetic order. By doping electrons, the system will leave its parent phase and enter into the superconducting dome. For iron-pnictides, it has been shown that the superconductivity and antiferromagnetic phase can coexist within certain doping range as shown in the figure. Whether the antiferromagnetism homogeneously coexists with superconductivity or there is local phase separation between them is still under debate.

Another main feature of the iron-pnictides’ phase diagram is that in their parent phase, the magnetic phase transition is coupled to a weak (1%) tetragonal to orthorhombic crystal structure phase transition, which happens at (un-doped compound) or slightly above (doped compound) the magnetic phase transition temperature. The relation between the structural and magnetic phase transitions is under heavy debate. Recently, more evidences indicate the combined structural and magnetic phase transition may be due to the developing of orbital ordering in the system.

4.3.4 Cooper pair and superconducting gap function

For the BCS superconductor, due to the isotropic phonon-mediated effective attraction between electrons, i.e., $V_{kk'} = V$ (within a thin shell around $E_F$), the electrons will form Cooper pairs which consists of two electrons with opposite momentum and spin. Furthermore, the BCS ground state’s excitation is characterized as a s-wave gap function $\Delta_k = |\Delta|e^{i\phi}$. This is shown in fig. 4.8(a).

This case can be extended to a much more general situation. Considering two electrons with opposite momentum $(k, -k)$ and a general effective coupling term $V_{kk'}$ (within a thin shell around $E_F$ and do not need to be attractive at all) between them. This coupling term will scatter electrons from their original states $(k, -k)$ to new states $(k', -k')$. Since $V_{kk'}$ is only effective near $E_F$, we may just assume $|k| \approx |k'| \approx |k_F|$, then $V_{kk'} = V(\cos\theta_{kk'})$, i.e., it can be expressed as a function
Figure 4.8: Superconducting order parameter. A schematic representation of the superconducting order parameter in different cases: (a) s-wave conventional superconductors, (b) d-wave cuprate superconductors, (c) two-band s-wave MgB$_2$ superconductor and (d) s$_{\pm}$-wave iron-pnictide superconductors. From [Mazin, 2010].

of the relative angle between $k$ and $k'$. Furthermore, this coupling term can be expressed as the Legendre polynomials of $\cos \theta_{kk'}$, i.e.,

$$V_{kk'} = V(\cos \theta_{kk'}) = \sum_l (2l + 1)V_l P_l(\cos \theta_{kk'})$$  \hspace{1cm} (4.11)

It can be shown that if for certain order $l$ we have $V_l < 0$, i.e., is attractive, then the two electrons will form a bound pair with lower energy and the combined wavefunction $\varphi(k) \propto Y_{lm}(\theta_k, \phi_k)$, where $Y_{lm}$ is the spherical harmonic function with $m = -l \rightarrow l$, $\theta_k, \phi_k$ are the polar angles of the momentum $k$. This bound pair is called “generalized Cooper Pair”. From the discussion above, to form a generalized Cooper pair, it is not necessary to have a pure attractive coupling $V_{kk'}$, instead we only need a $V_l$ component from it to be attractive, then the electrons will form pairs with certain momentum distribution according to what $l$ is. By far, the spins of the electrons in the generalized Cooper pair is left out in the discussion. Due to the Pauli exclusion principle, the total wave function of the paired electrons must be antisymmetric. As the result, for even $l(= 0, 2, 4, \ldots)$, electrons will form spin singlets; for odd $l(= 1, 3, 5, \ldots)$, electrons will form spin triplets.

For the BCS superconductor, we actually have $V_{kk'} = V_{l=0} = constant$, the electrons will
form spin singlets and the gap function follows the s-wave symmetry.

For cuprates, the experiment indicated that the electrons in superconducting state also form spin singlets. Furthermore, the ARPES measurement found that its gap function follows a $d_{x^2−y^2}$ symmetry [Shen et al., 1993], i.e., $|\Delta_k| = \frac{\Delta_0}{2}|\cos k_x − \cos k_y|$. Since ARPES can not probe the phase information about the Cooper pair, strictly speaking, the above result only indicates that the superconducting gap in cuprates is anisotropic. The phase information is further obtained by Scanning SQUID microscope [Tsuei et al., 1994] which confirmed the d-wave paring symmetry. Combining all the experimental results above, in cuprates the electrons’ pair wave functions are $d_{x^2−y^2}$-wave singlets as shown in fig. 4.8(b). This result requires that the effective coupling’s $l = 2$ component should be attractive which put strong constrains for the paring mechanism in cuprates.

For iron-pnictide, the Cooper pairs are also confirmed to be the spin singlets by Knight shift measurement [Terasaki et al., 2008], which indicates an even symmetry paring function, i.e., $l = 0, 2, 4 \ldots$. Further more, the ARPES measurement indicated that the gap function is isotropic in these materials [Ding et al., 2008]. And most of the phase sensitive techniques indicated that the paring symmetry is consistent with the $s\pm$ paring proposed by [Mazin et al., 2008]. Here, $s$ refers to the fact that the order parameter is unchanged by the symmetry operations of the crystal, and $\pm$ refers to the sign change of the order parameter between the electron- and hole-like Fermi surface. This proposed paring symmetry is shown in fig. 4.8(d).

Finally, I use the table from [Mazin, 2010] as a summary to end this section and also this chapter.

Table 4.1: Properties of different classes of superconductors. From [Mazin, 2010].

<table>
<thead>
<tr>
<th>Property</th>
<th>Conventional superconductors</th>
<th>Copper oxides</th>
<th>MgB$_2$</th>
<th>Iron-based superconductors</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_c$ (maximum)</td>
<td>$&lt;30,\text{K}$</td>
<td>$134,\text{K}$</td>
<td>$39,\text{K}$</td>
<td>$56,\text{K}$</td>
</tr>
<tr>
<td>Correlation effects</td>
<td>None (nearly-free electrons)</td>
<td>Strong local electronic interaction</td>
<td>None (nearly-free electrons)</td>
<td>Long-range (non-local) magnetic correlations</td>
</tr>
<tr>
<td>Relationship to magnetism</td>
<td>No magnetism</td>
<td>Parent compounds are magnetic insulators</td>
<td>No magnetism</td>
<td>Parent compounds are magnetic metals</td>
</tr>
<tr>
<td>Order parameter</td>
<td>One band, same-sign s wave</td>
<td>One band, same-sign d wave</td>
<td>Two band, same-sign s wave</td>
<td>Two band, presumably changing s wave</td>
</tr>
<tr>
<td>Pairing interaction</td>
<td>Electron-phonon</td>
<td>Probably magnetic (no consensus)</td>
<td>Electron-phonon</td>
<td>Presumably magnetic</td>
</tr>
<tr>
<td>Dimensionality</td>
<td>Three dimensional</td>
<td>Two dimensional</td>
<td>Three dimensional</td>
<td>Variable</td>
</tr>
</tbody>
</table>

In this table, MgB$_2$ is separated out form the conventional superconductors due to its multi-band nature.
5.1 Introduction: low energy kink vs. high energy anomaly/waterfall

The exotic physics in condensed matter systems such as superconductivity is due to the properties of the elementary excitations and their interactions, i.e., the interactions among the quasiparticles and the collective modes such as phonon, magnon, plasmon, and so on. For the well-understood conventional superconductor, the ”glue” holding the electrons together in Cooper pairs is the electron-phonon coupling and can be described by the famous “BCS theory” [Bardeen et al., 1957]. As the result of this electron-phonon coupling, the conventional superconducting ground state is an s-wave paring state with a dispersion relation given by $E_k = \sqrt{\varepsilon_k^2 + \Delta^2}$, where the $\varepsilon_k$ is the normal state quasiparticle dispersion and $\Delta$ is the isotropic gap function. Here we should note that the BCS theory is a “weak coupling theory”, i.e., the electron-phonon coupling is assumed to be weak. In this weak coupling approximation, the detailed information about the electron-phonon coupling, e.g., the lattice properties and the phonon dispersions, is not included in the theory.

More generally, the electron-phonon coupling can be described by the Eliashberg function $\alpha^2 F(\omega; E, k)$ [Grimvall, 1981], which gives the electron’s total transition probability between an initial state $(E, k)$ and all other states which differ in energy from the initial state by the coupled phonon mode energy $\hbar \omega$. In general, it can be calculated as

$$\alpha^2 F(\omega; E, k) \propto \frac{1}{2\pi^3} \sum_{\lambda} \int \frac{dk'}{|v_k'|^2 |g_{\lambda}(k, k')|^2 \delta[\hbar \omega - \hbar \omega_{\lambda}(q)]}$$

(5.1)
where \( \lambda \) is the label of different phonon branch, \( \hbar \omega_\lambda(q) \) is the phonon dispersion for branch \( \lambda \), \( v_{k'} \) is the electron’s velocity at state \( (E', k') \), and \( g_\lambda(k, k') \) is the so-called screened electron-phonon matrix element for phonons in branch \( \lambda \). Here we note that the equation 5.1 contains the energy and momentum conservation relations for electron-phonon interaction implicitly, i.e., one actually need

\[
E' = E + \hbar \omega_\lambda(q) \\
k' = k + q + G
\]

where \( G \) is the reciprocal lattice constant. For this reason, the electron-phonon matrix element sometimes is also expressed as \( g_\lambda(k, q) \) where \( q \) is the momentum transfer of the electron in the electron-phonon interaction process and directly relates to the phonon momentum. Often, people are interested in the average of \( \alpha^2 F(\omega; E, k) \) over all \( k \) in the momentum space and then introduce the \( \alpha^2 F(\omega, E) \) as the momentum averaged Eliashberg function.

Further, it is shown that the self-energy correction of the electron due to this electron-phonon coupling can be expressed as:

\[
Im \Sigma^{el-ph}(E, T) = \pi \int_0^\infty d\omega \ \alpha^2 F(\omega, E) (1 - f(E - \omega) + f(E + \omega) + 2n(\omega)), \tag{5.3}
\]

\[
Re \Sigma^{el-ph}(E, T) = \int_{-\infty}^{\infty} d\nu \int_0^\infty d\omega \ \alpha^2 F(\omega, E) \frac{2\omega}{\nu^2 - \omega^2} f(\nu + E). \tag{5.4}
\]

where \( f \) and \( n \) are the Fermi and Bose distribution functions, respectively\(^1\). By far, only the electron-phonon interaction is considered. Actually, the general interactions between electrons and other bosonic modes, e.g., magnon, plasmon, etc, can also be described by the above Eliashberg function. Then one can obtain the electron’s self-energy correction due to the electron-boson interaction in general. This self-energy correction due to the electron-boson interaction can be observed by ARPES experiment.

\(^1\) If we use \( \alpha^2 F(\omega; E, k) \) instead of its momentum-averaged value \( \alpha^2 F(\omega, E) \) in above equations, the complete self-energy as the function of both energy and momentum is obtained. In the ARPES theory chapter of this thesis, it is shown that in most cases we may ignore the momentum dependence of the self-energy to analysis the spectral function. But if we need to compare two relevant features which are far away in momentum space, we may need to consider the momentum dependence of the self-energy which may directly relate to the difference between these features [Plumb, 2011].
Fig. 5.1 shows several ARPES measurements on the high-$T_c$ cuprate $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi2212) materials. Fig. 5.1(a) was taken along the nodal direction, i.e., the diagonal direction as indicated by the green line in Fig. 5.1(b)’s sub-panel (f). In this spectrum, there is a sizeable dispersion anomaly about $60 \sim 70$ meV below $E_F$. One can find that the black curve, which is the MDC dispersion, apparently deviates from the red dashed line, which is an assumed bare-band dispersion. This feature is referred as the “kink” in Bi2212 materials. The spectra shown in Fig. 5.1(b) were taken along antinodal direction as indicated by the blue lines in its sub-panel (f). In those spectra, another kink is shown at $30 \sim 40$ meV below $E_F$. Currently, both the $60 \sim 70$ meV kink near nodal direction and the $30 \sim 40$ meV kink near antinodal direction are attributed to the interactions between electrons and certain bosonic mode, but whether this bosonic mode is the phonon or the magnon (due to the spin fluctuation interactions) is under heavy debate. Furthermore, another kink at roughly 10 meV below $E_F$ is reported by one of our colleagues recently [Plumb et al., 2010] and this kink is also very likely caused by certain phonon mode.

In 2007, [Graf et al., 2007] reported a “universal high energy anomaly” found in both Bi2212 and Bi2201 materials at different doping levels. Based on their observation, a new energy scale
Figure 5.2: High energy anomaly. ARPES intensity maps of Bi2212 samples with different doping. All spectra show the high energy anomaly at $E_1 \sim 0.4$ eV as indicated by the thick gray arrows. The thin gray arrows at $E_0 \sim 0.06$ eV indicate the low energy kink. From [Graf et al., 2007].

$E \sim 0.3 - 0.4$ eV is proposed and explained as an indication of the spin charge separation in the high $T_c$ cuprates. Fig. 5.2 shows their Bi2212 spectra which were taken along the nodal direction. The 60 $\sim$ 70 meV low energy kink discussed above is labeled as the energy scale $E_0$ in the plot; way below $E_0$, at the energy scale labeled as $E_1 \sim 0.38$ eV, the dispersion suddenly undergoes a steep downturn accompanied by a substantial drop of the ARPES intensity. Due to its appearance, this high energy anomaly is also referred as the “waterfall” in high $T_c$ cuprates.

[Graf et al., 2007]’s observation inspired a huge amount of efforts to study this “high energy anomaly” or “waterfall” feature, both experimentally and theoretically\(^2\). Since the “waterfall” feature looks very much like a “kink in high energy scale”, it’s very straightforward for people to think of it as the result of some many-body effect at a specific high energy scale ($0.3 \sim 0.4$ eV), e.g., the electron coupling to the high-energy spin excitations [Valla et al., 2007], to the phonons [Xie

\(^2\) Actually, as early as 2005, a very similar “anomalous high-energy dispersion” in insulating cuprate $Ca_2CuO_2Cl_2$ was reported by [Ronning et al., 2005] but did not draw too much attention in community.
et al., 2007], or to the plasmons [Markiewicz and Bansil, 2007], the in-gap band-tails [Alexandrov and Reynolds, 2007], the purely electronic mechanism due to strong correlations [Byczuk et al., 2007], the “Mott physics” related mechanism [Meevasana et al., 2007], etc. Additionally, a small number of groups have begun claiming that the “waterfall” dispersion is actually an artificial effect caused by the details of the ARPES matrix elements [Inosov et al., 2007, 2008], or the spectral weight from the valence band [Zhang et al., 2008].

In this chapter, I report a systematic ARPES study on the “high energy anomaly” in Pb$_x$Bi$_{2-x}$Sr$_2$CaCu$_2$O$_{8}$ (Pb-Bi2212) and Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ (Bi2212) samples over multiple Brillouin zones (BZ) and with a large variety of ARPES matrix elements. This has allowed us to uncover the intrinsic spectral function over a large energy scale. By empirically separating the spectral function into a sharp coherent part and broad incoherent part, I uncover an unexpected and universal relationship between the weight of these two components. This indicates that both of these components are intrinsic components of the conduction electron spectral function, that is, the majority of the incoherent part is not a background of inelastically scattered electrons and is not due to impurities, oxygen bands, or states from separate or unrelated bands. This intrinsic incoherent spectral weight, acting in concert with strongly k-dependent matrix element effects, gives rise to the heavily studied “waterfall” behavior. The possible origins of the intrinsic incoherent spectral weight will also be discussed.

5.2 Experimental

High quality single crystals of Pb-Bi2212 (T$_c$~85 K) and optimally doped Bi2212 (T$_c$~91 K) were prepared for the ARPES experiments, with the crystals cleaved in the UHV environments of the spectrometers. The Pb-Bi2212 samples were studied using Beamline 7.0.1 (BL7), 10.0.1 (BL10) and 12.0.1 (BL12) at the Advanced Light Source (ALS), Berkeley. The angular resolution of the experiments was approximately 0.3° and the energy resolution was 20-35 meV (depending upon photon energy). The optimally doped Bi2212 samples were studied using Beamline 5-4 (BL5-4) at Stanford Synchrotron Radiation Lightsource (SSRL) and with the 6eV laser ARPES system at the
University of Colorado at Boulder. The angular resolution of the experiments was approximately 0.3° and the energy resolution was better than 5 meV. All data shown were taken with 7 eV, 52 eV, 90 ∼ 95 eV photons. For these photon energies, the main features probed in Pb-Bi2212 and Bi2212 are their antibonding bands.

5.3 Pb-Bi2212 Fermi surface and electronic structure revisited

5.3.1 Fermi surface and matrix element effect

Fig. 5.3(a) shows an unsymmetrized and unfolded Fermi surface map of a Pb-Bi2212 sample with area more than three BZs. In the plot, the Fermi surface contributions from the main band and the shadow band are clearly resolved. The superstructure band is highly suppressed since Pb substitutes into the Bi-O plane and relaxes the mismatch between the equilibrium Bi-O bond length and the lattice constant imposed by the CuO$_2$ planar net. The intensity maps along cuts C1 and C2 are shown in panels (b) and (c), respectively. These two cuts are along equivalent directions in momentum space while they appear quite different. In fig. 5.3(b) the dispersion starts vertically diving from a binding energy (BE) ∼ 0.4 eV and there is no band minimum observed down to BE = 1.1 eV at which point the main valence band features appear. But in fig. 5.3(c), a band minimum at BE ∼ 0.5 eV is clearly seen. In fig. 5.3(d), which is the intensity map at BE = 0.6 eV, the spectral intensity is highly suppressed along the two zone diagonal directions in the first zone. In the second zone however, the intensity is only suppressed along the horizontal direction. Such a suppression pattern is likely a result of the $d_{x^2-y^2}$ orbital symmetry of the Cu states being probed. The spectrum at cut C3 ($k_y = 0.25\pi/a$) in fig. 5.3(d) is shown in fig. 5.3(e). In this spectrum, the dispersion breaks at $k_x = \pm 0.25\pi/a$ as indicated by the arrows and this broken position just matches the intensity suppression pattern shown in fig. 5.3(d).

In ARPES, the measured spectral intensity can be expressed as $I(k, \omega) = I_0(k, v, A)f(\omega)A(k, \omega)$ where $I_0(k, v, A)$ is proportional to the one-electron matrix element, $f(\omega)$ is the Fermi function and $A(k, \omega)$ is the single-particle spectral function [Damascelli et al., 2003]. The single-particle
Figure 5.3: Fermi surface and matrix element effects. (a) The Fermi surface map of Pb-Bi2212. Black dashed lines show the BZ boundaries. The black and red dashed circles indicate the Fermi surface portion from the main band and the shadow band. (b) and (c) Spectra taken along cut C1 and C2 in panel (a). (d) ARPES intensity map at BE = 0.6 eV. Thin black dashed lines indicate the “spectral weight suppression direction” by the matrix element effect. (e) Spectrum taken along cut C3 in panel (d). All the data were taken at T=52K (superconducting state) using 95 eV photons.

The spectral function should have the same value at all equivalent points in different BZs and the Fermi function does not contain any momentum information, so one must take the matrix element effect as the reason for the difference of the spectra in the first and second zones. Also the matrix element effect may explain why the apparent dispersion at high energy scales is almost perfectly vertical, which in this picture would indicate it is not a real dispersion.
5.3.2 Coherent peak dispersion

Fig. 5.4 (a1) to (d1) show four selected spectra of a Pb-Bi2212 sample over the first and second BZs as indicated in panel (e). I extract the band dispersions by two different methods: the Momentum-Distribution-Curve (MDC) Lorentzian fitting method which will highlight the MDC peak dispersion as indicated by the black curves in figs. 5.4(a1) and (b1), and the Energy-Distribution-Curve (EDC) second derivative method which will highlight the EDC peak dispersion as shown in figs. 5.4(a2) to (d2).

Figure 5.4: Intrinsic quasiparticle dispersion of Pb-Bi2212. (a1)-(d1) ARPES spectra taken along cuts a-d shown in the schematic Fermi surface plot (e). The black curves in panels (a1) and (b1) are the dispersions obtained by MDC Lorentzian fitting. (a2)-(d2) The EDC second derivative images of spectra (a1)-(d1). The red curves are the dispersions obtained by tight-binding fitting. Spectra (a)-(c) were taken at T=25K; (d) was taken at T=50K; all data were taken with 52eV photons.

Fig. 5.4(a1) shows the spectrum along the nodal direction in the first BZ which clearly shows the “waterfall” feature. Correspondingly, in fig. 5.4(a2), the EDC peak dispersion stops at BE ∼ 0.3 eV since the almost “vertical” MDC dispersion does not generate peaks in the EDC second derivative process. For spectra shown in fig. 5.4(b1), which are slightly off the nodal direction in
the second BZ, the spectral weight on the left side band is severely depressed due to an asymmetric matrix element effect. Then we notice that there is a clear discrepancy between the MDC peak dispersion shown in panel (b1) and the EDC peak dispersion shown in panel (b2): the MDC peak dispersion on the strong side shows the “waterfall” feature without band minimum while the EDC peak dispersion clearly shows a band minimum around 0.5 eV and the EDC peak dispersions from weak and strong sides connect to each other smoothly. It has been extensively accepted that as long as the ARPES matrix elements do not vary too severely as a function of momentum, the MDC Lorentzian fitting will give us the correct single-particle dispersion if the self-energy itself is also weakly momentum-dependent. But this is not the case for the spectrum shown in panel (b1) which covers more than half of the BZ with strong asymmetric matrix elements. In this case, the EDC dispersion rather than the MDC dispersion gives us a more realistic dispersion relation.

Fig. 5.4 (c1) shows the spectrum along cut c, which contains a band minimum around BE \( \sim 0.25 \) eV as confirmed by its EDC second derivative image. Finally, in fig. 5.4(d1) which is along the \( \Gamma M \) direction in the second BZ, a band minimum at BE \( \sim 0.55 \) eV is clearly seen and is also confirmed by the corresponding EDC second derivative image (d2).

After fixing the band bottom at the zone center at the measured BE = 0.55 eV (figs. 5.4(a2), (b2)), I use the six-parameter effective tight-binding model to fit the experimental dispersion (details discussed in table 5.1) and find that the fitted tight-binding dispersion matches all of the EDC peak positions extremely well (red curves in lower panels of fig. 5.4). Clearly however, the tight binding analysis ignores the physics of the deeper ”waterfall-like” features shown in the upper panels of fig. 5.4.

As seen from fig. 5.4, there is strong spectral weight beyond the band minimum at each cut no matter if there are strong momentum-dependent matrix element effects or not. In cuts a and b, the strong spectral weights at high binding energy combined with the matrix element effects give out the waterfall feature. It has been argued that the origin of the strong spectral weights at high binding energy could be the disorder-localized in-gap state [Inosov et al., 2007], the inelastic scattering of photoelectrons [Inosov et al., 2007], or due to the interstitial oxygens in the Bi\(_2\)O\(_2\).
Table 5.1: The tight-binding fitting result. A six-parameter tight-binding model was used to fit the dispersion: 
\[ \varepsilon(k_x, k_y) = \mu - 2t(cosak_x + cosak_y) - 4t'(cos2ak_x + cos2ak_y) - 4t^{(3)}(cosak_xcos2ak_y + cos2ak_xcosak_y) - 4t^{(4)}cos2ak_xcos2ak_y + (...) \]
Six data points at \( E_F \) as well as the band bottom at -0.55 eV were chosen as constraints, as represented by the red-yellow circles in the fig. 5.4(e). For the data point in the unoccupied state, we refer to the latest LDA calculation of Bi2212 [Lin et al., 2006] and assume the same renormalization factor for both the unoccupied and occupied states.

<table>
<thead>
<tr>
<th>( \mu ) (eV)</th>
<th>( t ) (eV)</th>
<th>( t' ) (eV)</th>
<th>( t'' ) (eV)</th>
<th>( t^{(3)} ) (eV)</th>
<th>( t^{(4)} ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2130</td>
<td>0.1944</td>
<td>-0.0338</td>
<td>0.0305</td>
<td>0.0028</td>
<td>-0.0060</td>
</tr>
</tbody>
</table>

layers [Zhang et al., 2008]. To examine the validity of these scenarios, I performed detailed EDC analysis to characterize the properties of the spectral weight in the high binding energy region, which will be discussed in the next section.

5.4 Energy-dependent scaling of incoherent spectral weight

Fig. 5.5(a) shows four selected EDCs (EDC1 to 4) as labeled in Fig. 5.4(b1) and EDC0 which is chosen from where no dispersive band is present \( (k>k_F) \). This EDC0 may consist of the spectral weights due to the elastic scattering of the electrons from the occupied \( (k<k_F) \) k point in the dispersive band and the spectral weight from any non-dispersive band in this energy window. This spectrum will be helpful for removing a background term from the other spectra. Fig. 5.5(b) shows the spectra EDC1 to 4 with the spectrum EDC0 subtracted. As seen from Fig. 5.5 (a) and (b), the “background spectrum” EDC0 has very weak spectral weight in the binding energy region. Once we subtracted EDC0 from EDC1 to 4, the remaining EDCs still have very strong spectral weights at high binding energy.

Fig. 5.5(b) shows that as the EDC peak position gets deeper, the spectral weights at high binding energy get stronger. Based on the fact that the strong spectral weight at high binding energy does not vary a lot as a function of binding energy, we introduce a quantitative method to characterize the relation between the strong incoherent spectral weights and the coherent dispersive peak. In our method, the flat tail-like high binding energy spectral weight is separated from the
Figure 5.5: Strong spectral weights at high binding energy range. (a) EDC0 and EDC1-EDC4 extracted from and indicated in fig. 5.4(b1). (b) Elastic background subtracted EDCs by subtracting EDC0 from EDC1-EDC4. (c)-(f) Tail fitting result on EDC0 subtracted EDCs. (g) $\kappa$ factor vs. EDC peak location plot for spectra shown in fig. 5.4.

The total spectral function by the formula

$$P(E) = R(E) - T(E) = R(E) - \kappa \int_{E}^{0} P(E')dE'$$

(5.5)

where $R(E)$ is the raw EDC, $T(E)$ is the tail term and $P(E)$ is the coherent part of the EDC after removing the strong tails. By this equation, we can conveniently separate out the coherent EDC peak from the tail-like incoherent high binding energy spectral weight, with the proportionality factor $\kappa$ telling us the relative strength of the peak and the EDC weight from the waterfalls.

Figs. 5.5(c) to (f) present the fitting performed on EDCs shown in panel (b), the black curves are the raw EDCs, the blue curves are the fitted tails and the red curves are the remaining EDCs after removing the tails. The fitted $\kappa$ factors are also shown for each EDC; it is clearly shown that as the EDC peak position gets deeper, the $\kappa$ value gets larger.

With this method we analyzed all EDCs of fig. 5.4. The fitting results are shown in panel (g) which shows the $\kappa$ factors returned from each of the individual fits, plotted against the EDC peak location.
positions obtained from the same fits. Fig. 5.4(g) indicates an unexpected but quite simple scaling relationship - the $\kappa$ factor scales closely with the EDC peak position, independent of location in momentum space and matrix element. For example, although the spectral weights from the left and right sides of the cut shown in fig. 5.4 (b1) are drastically different, the procedure gives almost the same $\kappa$ vs. EDC energy curve for each side of the cut.

![Figure 5.6: Characterization of the strength of the high binding energy spectral weights. $\kappa$ factor vs. EDC peak location plot for Pb-Bi2212 samples measured at BL07, BL10, and BL12; and Bi2212 samples measured at SSRL BL5-4. The photon energies, polarizations and temperature for each experimental setup are labeled in the plot. The inset shows where we chose the EDCs for fitting.](image)

A more extensive result is shown in fig. 5.6 which contains the fitting results from more positions in momentum space throughout the first and second BZs, and under different experimental conditions (different photon energies, s or p polarizations and different temperature), and also on different materials (Pb-Bi2212 and Bi2212). The similar $\kappa$ vs. EDC peak location curves are
obtained within reasonable errors for different experimental conditions. This more general result indicates that there is a “universal relationship” between the strength of the incoherent high binding energy tail and the coherent EDC peak position: as the coherent EDC peak gets deeper, the $\kappa$ factor keeps rising, i.e. more spectral weights is transferred from the coherent part to the incoherent part. To quantify this relation, we have parameterized the $\kappa$ values as a function of energy based on all EDCs indicated in fig. 5.6, finding that a simple quadratic function ($\kappa = 0.66 - 0.46E + 17.5E^2$) does an adequate job, as shown in fig. 5.6. Additionally, there is no evidence of any breaks or steps at for example the often-cited anomalous energy scale of 300 $\sim$ 500 meV [Valla et al., 2007; Graf et al., 2007; Chang et al., 2007; Xie et al., 2007] in the “$\kappa$ vs. EDC peak position” plot. This is further, more robust, evidence against any new high binding energy scale where the high energy anomaly begins.

5.5 Origin of the waterfall

5.5.1 Ruled out

5.5.1.1 Inelastic scattering

If one takes a close look at equation 5.5 in the previous section, one will find that it is actually identical to the equation developed by Shirley to distinguish un-scattered “primary” photoelectrons from the background of “secondary” electrons which are inelastically scattered while making their way out of the sample [Shirley, 1972]. In the original treatment this was a parameter important for the photoemission process but not for the initial state or Greens function of the electrons. In this case the $\kappa$ factor represents the relative strength of the scattering process, and is expected to be a weak function of the photoelectron kinetic energy (according to the so-called “universal curve” of inelastic mean free paths), but not of the binding energy of the initial excited state.

In our fitting, the $\kappa$ factor represents the relative strength of the coherent EDC peak and the incoherent high binding energy spectral weights which accounts for the waterfall features. Figs 5.5 and 5.6 show that for EDCs with different peak positions $\kappa$ varies by almost an order of magnitude.
This is strong evidence that the origin of the waterfall spectral weights removed here is NOT the inelastically scattered electrons originally considered by Shirley. Additionally, even the smallest $\kappa$ factor we extracted is still more than an order of magnitude larger than the $\kappa$ factor for inelastically scattered electrons obtained from a valence band result on Bi2212 [Liu et al., 1991].

5.5.1.2 Other purely extrinsic feature

Several previous studies argued that the waterfall is not an intrinsic feature of the spectral function, but due to some extrinsic effect in the system such as the disorder-localized in-gap state [Inosov et al., 2007] or the interstitial oxygens in the Bi$_2$O$_2$ layers [Zhang et al., 2008]. Our result argues against these viewpoints. If the spectral weight in the high binding energy region is the result of some extrinsic feature (usually non-dispersive), it is unlikely for us to obtain such a “universal” behavior of this spectral weight determined only by the coherent peak of the spectral function. In other words, our finding strongly suggests that the spectral weight in the high binding energy region is the intrinsic feature of the electron’s spectral function.

5.5.2 Coherent vs. incoherent revisited

Let me summarize the results presented so far: Pb-Bi2212’s (and Bi2212’s) EDC is generally characterized by a coherent peak part which pretty much follows the tight-binding-like dispersion (section 5.3.2), and a smooth/flat incoherent part which strength is found to be intimately linked to the energy of the dispersive coherent feature through a “universal” relationship with no special energy scales (section 5.4); when strongly momentum-dependent matrix effect presents in the spectrum (section 5.3.1), it mainly modifies the spectral weight distribution along the momentum direction and gives the appearance of the heavily studied “waterfall” features. Since the coherent peak and the incoherent tail are both the intrinsic feature of the spectral function, they must be the direct result of a certain type of self-energy.

In this thesis, the concepts of “coherent part” and “incoherent part” of the spectral function were first introduced in the ARPES-theory chapter based on the Fermi liquid theory. Considering a
many-body system with very weak interactions, there will be an one-to-one correspondence between the quasiparticles in the interacting many-electron system and the bare particles in the same many-electron system but without interactions. Then the spectral function of the system can be expressed as

$$A(k, \omega) = Z(k) \frac{\Gamma(k)/\pi}{(\omega - E(k))^2 + \Gamma(k)^2} + A_{\text{inch}}$$  \hspace{1cm} (5.6)

The first part is called the "coherent part" and the second part is called the "incoherent part". The coherent part represents the quasiparticle in the system with quasiparticle's dispersion $E(k)$, inverse lifetime $\Gamma(k) = 1/\tau(k)$, and coherence factor $Z(k)$. These important parameters for quasiparticles can be obtained from system’s self-energy approximately as

$$E(k) = \epsilon(k) + \text{Re}\Sigma(k, E(k))$$

$$\Gamma(k) = -Z(k)\text{Im}\Sigma(k, E(k))$$  \hspace{1cm} (5.7)

$$Z(k) = \frac{1}{1 - \frac{\partial\text{Re}\Sigma(k, \omega)}{\partial\omega}\bigg|_{\omega=E(k)}}$$

In our previous discussions, we claimed that by introducing equation 5.5, the measured spectral function can be separated into a coherent EDC peak and an incoherent EDC tail. Actually, this coherent-to-incoherent separation based on equation 5.5 is very loosely defined. In fig. 5.7, a simulation of the spectral function is presented based on a certain form of self-energy. The “quasiparticle coherent part” was obtained based on equations 5.7, and the “kappa coherent part” was also shown which was obtained based on the kappa fitting equation 5.5.

Here we find that the “quasiparticle coherent part” and the “kappa coherent part” have different lineshape. More interestingly, even the “quasiparticle coherent part” showed abnormal behavior near $E_F$, i.e., it is even stronger than the total spectral function. The reason for this abnormal behavior is that the equations in 5.7 are only valid in the proximity of the Fermi level. In our simulation, the EDC peak happens at $\sim 100$ meV which has already been “too far away from the Fermi level” for the approximation made in equation 5.7 to be valid. For this reason, both the “quasiparticle coherent part” and the “kappa coherent part” are the qualitative representation of
Figure 5.7: Coherent peak vs. incoherent part. Top: Spectral function with the model self-energy given by $\Sigma(\omega) = \frac{G\omega}{(\omega+i\gamma)^2}$ with $G = 0.45$ and $\gamma = 0.6$. Delta function $\delta(\omega - \epsilon(k))$ represents the spectral function without self-energy, where $\epsilon(k)$ is the bare-band. The red curve represents the total spectral function obtained from the bare band and the self-energy. The blue Lorentzian represents the coherent part obtained by using equation 5.7. The green curve represents the “coherent part” obtained by using equation 5.5 to remove the incoherent tail, and the black dashed line represents the fitted tail. Bottom: The Model self-energy. Red curve represents the real part and blue curve represents the imaginary part. The black line represents $\omega - \epsilon(k)$, whose crossing points (the black circle) with the real part of the self-energy gives out the solution of the first equation in 5.7. Following [Okazaki, 2002].

The quasiparticles other than the quantitative expression of their lineshape. Furthermore, in our analysis the EDC peak goes as deep as $\sim 500$ meV, whether those peaks at such a deep binding energy could still represent the “coherent part” of the spectral function or not is an open question.
Based on the discussion above, a more accurate statement based on our observation should be expressed as: due to the many-body interactions in the system, the intrinsic spectral function of Pb-Bi2212 (and Bi2212) is characterized by a “peak-and-tail” structure and the strength of the tail part is intimately linked to the position of the peak through a “universal” relationship with no special energy scales. This special appearance of the spectral function, acting in concert with strongly k-dependent matrix element effects, gives rise to the heavily studied “waterfall” behavior. In the next section, several physical origins which can possibly cause such an appearance of the spectral function will be discussed.

5.5.3 Possible origins

5.5.3.1 Crossover from quasiparticle band (QPB) to lower Hubbard band (LHB)

Fig. 5.8 shows a calculated single-particle spectral function from [Moritz et al., 2009]. In their calculation, an 2D single-band Hubbard Hamiltonian was used as an effective, low energy model of the cuprate’s copper-oxide planes. As shown in the figure, they find that for the hole doped cuprate, the LHB is essentially localized near the Γ point with a weak tail of spectral intensity extending toward the points \((\pi, \pi)\) and \((\pi, 0)\). As the QPB approaches the Γ point, there will be a
spectral weights transfer from the QPB to the LHB. By further including the matrix elements in their calculation, the waterfall feature is successfully reproduced. This “spectral-weight-transfer” picture is consistent with our experimental observation. As the spectral weights transferring from the QPB to the LHB, a strong tail which connects the QPB and LHB will appear in the spectral function. Here we note that in [Moritz et al., 2009]’s picture, the weight transfer is discussed as a function of momentum while in our result the tail is characterized by a universal function in energy. But due to the dispersion relation of the QPB, this weight transfer can be described as a function of QPB’s peak position eventually. To further test the validation of this theory, a more carefully “κ vs. EDC peak position” fitting is needed.

5.5.3.2 Gutzwiller-projected non-Fermi liquid lineshape

One major advantage of laser-based ARPES is that it is more bulk sensitive (according to the “universal curve” of the electron’s inelastic mean free path) and this combined with the much improved resolution leads to a much sharper quasi-particle excitation with reduced background which is believed to be more intrinsic than synchrotron-based ARPES data. This is clearly shown in fig. 5.9(b). But after using equation 5.5 to treat the “much weaker” spectral weights at high binding energy region of the laser data, a κ value was extracted which is very similar to the EDC obtained from the synchrotron. In other words, even in the much shaper laser-ARPES data, the EDC is still characterized by a tail which is not weak. This is another evidence that the strong spectral weight in the high binding energy region is the intrinsic feature in the spectral function.

Recently, the nodal laser-ARPES data were analyzed in terms of a Gutzwiller-projected non-Fermi liquid lineshape [Casey et al., 2008] and a certain level of success was achieved. This theory treats the strong electronic correlation in cuprate on the basis of a Gutzwiller projection, which gives zero quasiparticle weight at the Fermi surface and removes the possibility for double electron occupancy on any one site. As shown in fig. 5.9(a), the near kF EDCs taken by our 6 eV-laser ARPES system [Koralek, 2006] at different temperature are fitted by this Gutzwiller-projected non-Fermi liquid lineshape (or called Anderson-lineshape) reasonably well. This Gutzwiller lineshape is
Figure 5.9: Anderson lineshape and strong tails in laser-excited ARPES EDCs. (a) Near $k_F$ EDCs taken at different temperature and fitted by Anderson lineshape. From [Casey et al., 2008]. (b) $\kappa$ factor fitting on two low temperature (20K) nodal EDCs peaked at 20meV from ALS BL10 on a Pb-Bi2212 sample and 6eV laser system on an optimal doped Bi2212 sample.

Another example of a lineshape which intrinsically has a strong spectral weights at the high binding energy, and the origin of this strong spectral weight is the electronic correlation in the system. A similar “$\kappa$-factor fitting” based on equation 5.5 done on the Gutzwiller lineshape using previously determined parameters and from fits performed only on nodal data [Casey et al., 2008] returns $\kappa$ factors having the similar “$\kappa$ vs. EDC peak position” relation (not shown) which is consistent with our result, although the $\kappa$ values are not quite the same as those extracted directly from the data. But since the available parameters for the Anderson lineshape is very limited, no further investigation has been made recently.
5.5.3.3 Spin fluctuation mechanism

Fig. 5.10(a) shows a specific type of self-energy obtained by our theoretical collaborators in LANL. By introducing an one-band tight binding model Hamiltonian which includes spin and charge fluctuation to the LDA dispersion in addition to pseudogap and superconducting gap competition, the resulted self-energy has a zero crossing at 0.6 ~ 0.8 eV (parameter dependent) in its real part and a corresponding peak in its imaginary part. Figs. 5.10(b) and (c) shows a simulated spectrum and its second derivative image along EDC direction based on this self-energy and a LDA band calculation along nodal direction for Bi2212 [Markiewicz et al., 2005]. Due to the zero crossing of the real part self-energy, when bare-band locates above this energy scale, the self-energy will renormalize the dispersion towards the Fermi level, while the opposite situation will happen when the bare-band locates below the zero-crossing point. This will cause the “waterfall feature” observed

Figure 5.10: Waterfall feature due to the possible spin fluctuation mechanism. (a) Calculated cuprate self-energy based on an intermediate coupling model which includes spin and charge fluctuation in addition to pseudogap and superconducting gap competition. (b) Simulated spectrum based on the calculated self-energy and LDA dispersion. (c) second derivative image of panel (b) which highlights the EDC peaks. (d) \( \kappa \) fitting on simulated spectrum.
Interestingly, when fitting this spectrum with equation 5.5, a “κ vs. EDC peak position” curve was obtained which is very close to our experimental result, as shown in fig. 5.10(d). The consistency between theory and experiment makes this theory to be a potential answer to the waterfall feature in cuprates. Here we note that in this theory, there is a underlying energy scale, i.e., the zero crossing point of the real part self-energy which is about 0.6 ∼ 0.8 eV. But in the experimental data, we can only track EDC peaks down to 0.5 ∼ 0.6 eV without any specific energy scale. This contradiction can be reconciled if one take a look at fig. 5.10(c): although the theoretical band minimum happens at ∼ 1.2 eV, due to the self-energy effect there will be strong spectral weight at 0.4 ∼ 0.5 eV near zone center. If this theory is true, the band bottom at 0.5 ∼ 0.6 eV observed in experiment might be a “fake band bottom”, while the true band bottom could be smeared out by the oxygen valence band then can not be observed experimentally.

5.6 Summary

In this chapter, we presented a systematic ARPES study on the “high energy anomaly” in Pb₂Bi₂₋ₓSr₂CaCu₂O₈ (Pb-Bi2212) and Bi₂Sr₂CaCu₂O₈₊δ (Bi2212) samples over multiple Brillouin zones (BZ) and with a large variety of ARPES matrix elements. This has allowed us to uncover the intrinsic spectral function over a large energy scale. By empirically separating the spectral function into a sharp coherent part and broad incoherent part, we uncover an unexpected and universal relationship between the weight of these two components. This indicates that both of these components are intrinsic components of the spectral function, that is, the majority of the incoherent part is not a background of inelastically scattered electrons and is not due to impurities, oxygen bands, or states from separate or unrelated bands. This intrinsic incoherent spectral weight, acting in concert with strongly k-dependent matrix element effects, gives rise to the heavily studied “waterfall” behavior. The possible origins of the intrinsic incoherent spectral weight are also discussed.
Chapter 6

Symmetry-Broken Electronic Structure and Uniaxial Fermi Surface Nesting of Untwinned CaFe$_2$As$_2$

6.1 Introduction

The recently discovered iron pnictide superconductors [Kamihara et al., 2008] provide a new platform for studying the unconventional superconductivity and have attracted massive attention in the condensed matter community. Similar to the cuprate superconductors [Bednorz and Müller, 1986], the iron pnictides are layered systems with transition metal d-electrons, and have non-superconducting parent compounds exhibiting anti-ferromagnetic (AFM) order. Although, unlike the cuprates whose parent compounds are Mott insulators, the pnictides parent compounds are metals, the transport [Kamihara et al., 2008] and optical [Dong et al., 2008] measurements on iron pnictides show a very large resistivity and a small Drude weight. This indicates that the iron pnictides may not be conventional metals and the electron correlations could also play a crucial role as they do in the cuprates.

It has been proposed that in cuprates the strong electron correlations could lead the system into exotic quantum electronic liquid crystalline phases with translational and rotational symmetries broken (“stripes” or smectic phase) or only rotational symmetry broken (nematic phase) [Fradkin et al., 2010] and cause the strong in-plane anisotropies observed by the transport measurement [Ando et al., 2002], the neutron scattering study [Hinkov et al., 2008] and the scanning tunneling microscope (STM) study Kohsaka et al. [2007]; Lawler et al. [2010]. As for iron pnictides, the recent transport [Chu et al., 2010; Tanatar et al., 2010] and inelastic neutron scattering [Zhao et al., 2009]
measurements also indicate a large in-plane anisotropy. Furthermore, the STM study [Chuang et al., 2010] reveals unidirectional electronic nanostructures, which is explained as the evidence of the existence of the nematic phase. These observations of broken C4 tetragonal symmetry have been proposed to stem from the development of nematic orbital ordering [Lv et al., 2009; Lee and Wu, 2009; Singh, 2009; Krüger et al., 2009; Lee et al., 2009] and could be also explained as the result of pure spin interactions [Chandra et al., 1990].

To examine the validity of the above theories as well as to direct the development of future theories, a comprehensive understanding of the electronic structure of the iron pnictide system is badly needed. ARPES, as the method which allows direct access to the electron dispersion and spectral function in condensed matter systems, is one of the best methods to study the electronic

Figure 6.1: Optical observation of twin domains. First row, high resolution optical image of pure BaFe$_2$As$_2$ above (left) and (below) right the temperature of the coupled structural/magnetic transition, $T_{SM} = 135$ K. The stripes in the right-band image are domain boundaries. Second row, schematics of the domain formation in the orthorhombic phase. From [Tanatar et al., 2009].
structure of the strongly correlated electron system such as cuprates [Damascelli et al., 2003; Shen and Dessau, 1995] and has also been performed on iron pnictides [Lu et al., 2008; Zabolotnyy et al., 2009; Hsieh et al., 2008; Yi et al., 2009a,b]. One difficulty of ARPES measurements on iron pnictides is the formation of a pattern of twin domains [Tanatar et al., 2009], as shown in fig. 6.1. Generally, the domain size is smaller than the photon beam size in the experiment, so that most of the current ARPES studies on iron pnictides presented the domain averaged result and the intrinsic electronic structure is still missing. In our present study, we measured the high quality $CaFe_2As_2$ crystals with a very small photon beam size. This, together with the relatively large single domain area on the crystal surfaces, allowed us to make measurements of monodomain regions of the cleaved sample surfaces. The ability to deconvolve the twinned structure combined with our detailed polarization dependent studies, $k_z$ dependent studies, and Local-Density Approximation (LDA) calculations, enabled us to make the most comprehensive analysis of the electronic structure of a pnictide to date.

6.2 Experimental

The ARPES experiments were performed at Beamline 7.0.1 (BL7) and Beamline 10.0.1 (BL10) at the Advanced Light Source (ALS), Berkeley. The angular resolution of the experiments was approximately 0.3° and the combined energy resolution was about 20 meV. High-quality single crystals of $Ca(Fe_{1-x}Co_x) _{2}As_2$ ($x=0$ and 0.035) with large untwinned regions were grown in a Sn flux as described in [Ronning et al., 2008]. For the undoped sample, the magnetic susceptibility, resistivity, and heat capacity all show a first order phase transition at $T_0=171$ K. For the 3.5% Co-doped sample, the magnetic susceptibility and resistivity measurement show a superconducting phase transition at $T_c=17$ K and the structure and magnetic phase transitions around 60~90 K. The crystals were cleaved in situ and measured in an ultra high vacuum better than $3 \times 10^{-11}$ torr.
6.3 Symmetry-broken electronic structure

6.3.1 From real space lattice to momentum space Brillouin zone

As we discussed before, the parent phase of the iron-pnictide superconductors is AFM metal, and there is a magnetic phase transition from the high temperature paramagnetic phase to the low temperature AFM phase. This AFM phase is characterized by its collinear properties: an AFM arrangement of ferromagnetic (FM) chains. Furthermore, the magnetic phase transition is coupled to a weak (∼1%) tetragonal to orthorhombic crystal structure phase transition, which happens at (un-doped compound) or slightly above (doped compound) the magnetic phase transition temperature. Thus the iron-pnictides have different crystal structures and the corresponding Brillouin zones (BZ) at different phases. Since ARPES is a technique to map the electronic structure in the momentum space, it is very necessary for us to understand the momentum structure of the studied system.

Figs. 6.2 shows the real space crystal structures and the corresponding 3D BZs of $AFe_2As_2$ type ($A=$Ba, Sr, Ca) iron pnictides in the paramagnetic-tetragonal state and the AFM-orthorhombic state, respectively. For $CaFe_2As_2$ which is the main material studied in the thesis, at high temperature tetragonal phase, the inplane lattice constant $a_t = b_t \approx 3.89\,\text{Å}$ and $c \approx 11.7\,\text{Å}$; at low temperature orthorhombic phase, the inplane lattice constant $a_o \approx 5.51\,\text{Å} \neq b_o \approx 5.45\,\text{Å}$ and c axis is about the same as that in the tetragonal phase. It is shown that the longer lattice constant happens along the AFM direction. Here we define that in the AFM-orthorhombic state, the AFM spin ordering happens along the x-direction in the crystal coordination while the FM spin ordering happens along the y-direction. Then In the plots of BZs, the $\Gamma - X/\gamma - x$ is along the AFM order direction and the $\Gamma - Y/\gamma - y$ is along the FM direction. For the 2D BZs plots at $k_z = 0$ and $k_z = 2\pi/c$ planes, the BZs in the tetragonal state and the AFM-orthorhombic state are overlapped for comparison. Here we ignore the tiny lattice constant difference in the AFM-orthorhombic state so that at $k_z = 0$ plane the $\gamma - x - z/\gamma - y - y$ direction in the AFM-orthorhombic state are equivalent to the $\Gamma - X/\Gamma - Y$ direction in the tetragonal state. At $k_z = 2\pi/c$ plane, the $z - \gamma/z - n - z$ direc-
Figure 6.2: Lattices and Brillouin Zones of AFe$_2$As$_2$ type (A=Ba, Sr, Ca) iron pnictides. Top: Crystal structures. From left to right: paramagnetic-tetragonal unit cell, AFM-orthorhombic lattice (simplified by ignoring the As atoms), and the comparison of the inplane unit cell between them. Bottom: BZs. From left to right: paramagnetic-tetragonal phase BZ, AFM-orthorhombic phase BZ, and comparison of the inplane BZs between them at different $k_z$ position, i.e., $k_z = 0$ and $k_z = 2\pi/c$. The red boxes represent the unit cell and BZ for the tetragonal phase and the green boxes represent the unit cell and BZ for the orthorhombic phase. The large red and green arrows in the 3D lattice plots represent the primitive vectors, while the small red arrows on top of iron atoms in the 2D inplane lattice plot represent the magnetic momentums which are aligned to the “collinear-AFM” pattern in the orthorhombic AFM phase.

6.3.2 In-plane electronic structure

6.3.2.1 Asymmetric FS topology

Fig. 6.3(a) shows a typical phase diagram for AFe$_2$As$_2$ type (A=Ba, Sr, or Ca) iron pnictides. The inset is the schematic of the in-plane crystal structure in the magnetic phase. Fig. 6.3(b) shows
an overview of the experimental Fermi surface (FS) of CaFe$_2$As$_2$ in the AFM-orthorhombic state taken with 80 eV photons. The photon energy dependent studies (details discussed later) indicate that the 80 eV photons probe the electronic structure in the Z plane in momentum space. There is
a well-known hole pocket at the zone center highlighted in blue as well as an electron pocket at the zone corners highlighted in green, with the AFM nesting vector $\vec{q}_0$ joining them. This thesis shows that calling these “pockets” is actually a misrepresentation, as there is much detail within each of them and they are far from being simple hole or electron pockets. In particular, we see that the internal structure within the “pockets” does not show a 4-fold symmetry: there are closed small Fermi pockets along one Fe-Fe bond direction while they are absent along the orthogonal direction. By comparing with our LDA calculation (details discussed later), we assign the direction that contains the small Fermi pockets to the $y$-direction (FM direction) and the orthogonal direction to the $x$-direction (AFM direction). Then the $\vec{q}_0$ in the plot indicates the collinear AFM ordering vector.

Panels (c) to (g) show the FS and intensity maps at different binding energies. In this case, we rotated the sample’s in-plane angle by 90 degrees and these small pockets rotate with the sample as it is rotated, indicating that they are an intrinsic aspect of the electronic structure and are not, for example, a result of the photon polarization effect. Furthermore, along the $y$-direction, the small Fermi pockets are electron-like while along the $x$-direction there are only hole-like features, i.e., when going to deeper binding energy the spectral weight spreads further away from the zone center. Hence, the plots shown in fig. 6.3 present a clear uniaxial electronic structure of $\text{CaFe}_2\text{As}_2$ in the AFM-orthorhombic phase.

If one takes a closer look at the small Fermi pockets along the $y$-direction, two long parallel straight FS segments can be found which indicate an incommensurate FS nesting as indicated by $\vec{q}_1$ in the fig. 1(b). We will come back to this unusual FS nesting later and show that it is a very important feature of the electronic structure of the iron pnictide materials.

### 6.3.2.2 Orbital properties of the electronic structure

To further understand the electronic structure of $\text{CaFe}_2\text{As}_2$, a polarization-dependent ARPES study using three different experimental geometries (fig. 6.4 rows a, b and c) has been performed. Figs. 6.4(a1)-(c1) are the schematics of three different experimental configurations. In panels (a1)
Figure 6.4: Orbital properties of the electronic structure. (a1-c1) Schematics of the three different ARPES experimental configurations. Symmetries with respect to the gray-shaded mirror plane are shown. (a2-c2) FSs, and (a3-c3) intensity plots along the high symmetry directions indicated by the white dashed lines in (a2)-(c2), respectively. (a4)-(c4) Dispersions along the high symmetry cuts obtained from (a3)-(b3), with allowable symmetries determined by the experimental geometries indicated. All data were taken with 80 eV photons at T=20K.

and (b1) the incident photon beam’s polarization is in the mirror plane of the sample and the sample is placed so that the x-direction (AFM direction) or y-direction (FM direction) is along the analyzer’s slit direction, respectively. In (c1) the incident photon beam’s polarization is perpendicular to the mirror plane. Here we note that for setup (a1) and (b1), the small beam size gives us a chance to probe the un-twinned electronic structure along different direction in the crystal while for setup (c1) the relatively large beam spot always gives out the twinned result in the experiment.

The polarization-dependent study allows us to emphasize or de-emphasize different states according to their orbital symmetries - for example we turn on the flat portions of FS near the zone center in panel (c2) but turn these off and turn on complementary portions of the FS in panel
Experimental dispersions along high symmetry cuts (white dashed lines in panels (a2), (b2) and (c2)) are shown in (a3), (b3) and (c3), while (a4), (b4) and (c4) show the extracted dispersions along these cuts as well as the allowed orbital symmetries: since the ZX'/ZY' cuts lie in the plane of mirror symmetry (xz/yz plane) in the crystal, the electronic states that are even (odd) under reflection with respect to this mirror plane can only be excited by light with the electric field polarization pointing in (out of) the mirror plane. Then in the setup (a1), the dispersions observed along the high symmetry direction should have $x^2 - y^2/z^2$ symmetry while the dispersions observed along the high symmetry direction in setup (b1) should contain $yz/x^2 - y^2/z^2$ symmetry. For setup (c1), the dispersion should contain $xy/yz$ and/or $xy/xz$ symmetry due to the domain averaging effect.

6.3.2.3 Summary on inplane electronic structure

Fig. 6.5 shows a compilation of the FS data, dispersion data, and orbital data. Figs. 6.5(a1) and (a2) are the experimentally extracted dispersions and FS with symmetry information color-coded. Here we ignore the possible $x^2 - y^2$ and $z^2$ symmetry component for simplification, consistent with the band calculation which indicates that the near $E_F$ states are dominantly the xy and xz/yz states [Boeri et al., 2008]. Figs. 6.5 (b1) and (b2) are raw data taken with mixed polarizations so as to show all symmetry states. Here we utilize the tetragonal Brillouin zone (BZ) so as to be able to utilize standard orbital symmetry labels.

6.3.3 Three dimensionality of electronic structure

By far, only the inplane electronic structure is presented. To further understand the system, we also performed photon energy dependent studies to extract $k_z$ dispersion of the material. Figs. 6.6(a) and (b) show the FS’s in the AFM-orthorhombic phase taken with 80 eV and 99 eV photons, corresponding to $Z$ and $\Gamma$ plane at the zone center, respectively. Figs. 6.6(c)-(d) and (e)-(f) show the dispersions along the AFM (yellow cut) and FM directions (blue cut) taken with 80 eV and 99 eV photons, respectively. Along $\Gamma X/ZX'$ direction, there are three bands with different Fermi
crossings near the zone center while along ΓY/ZY’ direction, there is a clear band folding with both 80 eV and 99 eV data. Figs. 6.6(g) and (h) show the $k_z$ dispersions of the Fermi crossings along ΓX/ZX’ and ΓY/ZY’ directions. Consistent with the uniaxial electronic structure, panels (g) and (h) exhibit different $k_z$ dispersions.

The observation of $k_z$ dispersion have several physical significance. First, unlike cuprates which have very weak $k_z$ dispersion, the iron-pnictide’s electronic structure is more three-dimensional. This will weaken the anisotropy between Fe-As plane and c-axis and cause the “nearly isotropic superconductivity” in iron-pnictides observed in transport measurement [Yuan et al., 2009]. Furthermore, the high-$T_c$ superconductivity in three-dimensional system also indicates that the speculation,
Figure 6.6: Incommensurate FS nesting and asymmetric $k_z$ dispersion. (a,b) FSs taken with 80 eV and 99 eV photons at T=20K. The incommensurate FS nesting vector $\vec{q}_1$ is labeled on both plots. (c-f) ARPES intensity maps along the blue and yellow lines in panels (a) and (b). The Fermi crossings are indicated by the yellow and blue arrows on the plots. (g,h) $k_z$ dispersions of the Fermi crossings along the blue and yellow lines of (a) and (b). The dashed lines are guides for the eyes of the $k_z$ dispersions while the blue solid lines indicate the persistence of the nesting vector $\vec{q}_1$ in momentum space.

that reduced dimensionality is a necessary prerequisite high-$T_c$ for superconductivity, may not be true. Also the theories those try to connect the iron-pnictide’s antiferromagnetic order and/or high-$T_c$ superconductivity to the strong FS nesting between corner-pocket and center-pocket (the green and blue pockets highlighted in fig. 6.3) need to be further investigated.

Another important observation in our data is that, the incommensurate FS nesting with nesting vector $\vec{q}_1$ mentioned in the previous section has minimum $k_z$ variation, as shown in fig. 6.6(h).
This result confirms that the incommensurate FS nesting observed along ΓY/ZY' direction (FM direction) persists through the whole momentum space with an essentially unchanged nesting vector \( \vec{q}_1 = 0.33(-\pi/a, \pi/a) \). The importance and the possible physical origins of the incommensurate FS nesting will be discussed later in this chapter.

Further more, not only in \( \text{CaFe}_2\text{As}_2 \), the strong \( k_z \) dispersion was also observed in \( \text{BaFe}_2\text{As}_2 \) material, as shown in fig. 6.7. This indicates that the “3-dimensionality” is a “universal” property of the iron-pnictide superconductors.

![Image of k_z dispersion](image)

**Figure 6.7:** \( k_z \) dispersion of Ba122 materials. (a) FS near Γ point. The boundary of the first BZ is indicated by the black box and high symmetry points are labeled. (b) Spectrum taken along the direction indicated by the solid red line in panel (a). (c) Second-derivative of MDC at \( E_F \) along cut in panel (a) as a function of excitation energy from 21eV to 111eV. (d) Determination of \( k_z \) for several selected photon energy. The black curve is the schematic Fermi surface in Γ – Z – X plane.
6.3.4 Comparing with the LDA calculation

Looking for consistency (actually it should be inconsistency) between the experimental result and the theoretical prediction is the main way to improve both sides and get better understanding of the studied system. For this reason, the ARPES data is always compared to band theory result to extract further information of the system. And the local-density-approximation (LDA) calculation based on the density functional theory (DFT) is one of the most intensively used methods to calculate the band structure and further be compared to the ARPES result

Fig. 6.8 shows the comparison between the experimental result and the theory calculation. Figs. 6.8 (a1) and (a2) present the proposed FS and dispersion based on the experimental result taken at $k_z = 2\pi/c$ plane. Figs. 6.8 (b1) and (b2) present the FS and dispersions along the high symmetry directions (also at $k_z = 2\pi/c$ plane) from our LDA calculations (based on the KKR methodology for complex crystals [Bansil et al., 1999]). Here we found that with a bandwidth renormalization factor of 2.5, the LDA calculations with magnetic moment of 0.19 $\mu_B$ give us the best match to the experimental dispersions and FS.

First we need to mention that the magnetic moment 0.19 $\mu_B$ is much smaller than the value measured by the neutron scattering experiment [Goldman et al., 2008]. But the recent muon spin-relaxation and and Müssbauer studies on the Fe-based pnictides always give out smaller magnetic moment size comparing to the neutron scattering measurement [Klauss et al., 2008; Aczel et al., 2008], so the true value of the magnetic momentum is still under debate. The renormalization factor of 2.5 which is similar to what has been determined from other experiments [Yi et al., 2009a; Hsieh

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1 Strictly speaking, ARPES experiment measures the “one-electron spectral function” of the system. In quasi-particle picture, it measures the dispersion and lifetime of the quasihole which is the elementary excitation of the many-electron system. But the LDA calculation (or the general “time-independent” DFT) is the method to calculate the ground state electronic structure. Furthermore, unlike Hartree-Fock method which single orbital energy can be understood as the single electron energy (“Koopmans theorem” in frozen-orbit-approximation), the Kohn-Sham eigenvalues in DFT have no clear physical meaning except for the highest occupied which corresponds to the ionization energy [Aryasetiawan and Gunnarsson, 1998]. Although there is no theoretical justification, they are often interpreted as single-particle excitation energies corresponding to excitation spectra of the system upon a removal or addition of an electron. And the discrepancy between the LDA calculation and ARPES result can be understood as due to the many-body interaction in the photon excitation process and is further used to extract the self-energy, i.e., LDA serves as the bare-band in the spectral function. While in theory, the Hartree-Fock orbital energy exactly means the single electron energy and should serve as the bare-band.
Figure 6.8: Comparison between experimental data and theoretical calculations. (a1), (a2) Proposed FS and dispersion along high symmetry direction as shown in fig. 6.5. (b) Calculated FS and dispersion along high symmetry direction. The theory has been optimized for best agreement with the experiment by choosing a magnetic moment of 0.19 $\mu_B$, the bands with the minimal weight due to the structure factor are removed from the image for better comparison, and the curves of (b2) have been renormalized by an overall factor of 2.5. The agreement with experiment is improved by shifting the yz bands up about 0.1 eV (arrows), which is indicative of orbital ordering.

et al., 2008] is one of the aspects that indicate the importance of the electron correlations in the pnictides. To further improve the agreement between the theory and experiment, we shift the two calculated bands with yz symmetry (green dashed lines) up by 0.1 eV (green solid lines) to match the bands $\gamma_1$ and $\gamma_2$ in fig. 3(a2). After this modification, the overall band calculation matches the experimentally determined dispersions reasonably well, though it is certainly not perfect. Here we note that the up-shifting of the bands with specific orbital property may be a sign of the developing of the orbital ordering, which has been advanced by recent theoretical studies [Lv et al., 2009, 2010; Lee et al., 2009; Lee and Wu, 2009; Singh, 2009; Krüger et al., 2009].
Beside the similarities between the experimental and theoretical dispersions and FS after the optimizations mentioned above, there are also some important differences as well. In the experiment, we only observe one electron pocket ($\alpha_1$) at $X'$ point but nothing at $Y'$ point while the calculation indicates a relatively complex dispersion near the zone corner. This may indicate strong matrix element effects in the photoemission data. The symmetry properties obtained from the experiment are also not fully consistent with the calculation: along $ZY'$ direction, the FS contains two electron pockets which are formed by the bands with different symmetry properties ($\gamma_1$, $\gamma_2$ with $xy/xz$ symmetry and $\beta_1$, $\beta_2$ with $yz/x^2-y^2/z^2$ symmetry) while the calculation indicates that both bands should be mainly of $xy$ symmetry for one of these two pockets.

Accompanying this discrepancy in symmetry properties, a more interesting feature is found for the dispersion along the $ZY'$ direction: there is no gap opened between the bands that form the electron pockets. This indicates that the electron pockets along $ZY'$ direction are not formed in the traditional spin-density-wave manner but more like a Dirac cone structure instead, which is consistent with the orthogonal symmetry properties we have observed for the bands that make up these electron pockets. We note that this observation is consistent with the “nodal spin density wave” picture proposed by [Ran et al., 2009], in which a symmetry enforced band degeneracy at high symmetry points causes the existences of the nodes in the SDW gap function and leads to a Dirac-cone-like band structure. Furthermore, recent ARPES studies on $BaFe_2As_2$ [Richard et al., 2010] also suggest that band $\gamma_1$ and $\gamma_2$ along $ZX'$ direction could form a Dirac-cone-like feature and present a tiny pocket at Fermi level, though they have not shown the orthogonal symmetry of the relevant bands. In our case, the un-closed FS segments along $ZX'$ direction in our proposed FS also may be due to the formation of this Dirac cone but the current experimental condition does not allow us to fully resolve this tiny feature to get a conclusive result.

Last, but most important, the unidirectional incommensurate FS nesting observed in the experiment are not present in the theoretical calculations we presented here, which include the effects of the uniaxial spin order and which have been optimized for best agreement with the experimental data. Here we note that the calculations did not include the effect of the very small
(~ 1%) orthorhombicity. However, this distortion is so small that it is not expected to have a significant effect on the electronic structure. Therefore, the very straight FS pieces we observed appear well beyond the results of the structure and/or spin anisotropy of the system.

In the next section, I will focus on this incommensurate FS nesting and also the orbital-dependent band shifting mentioned above. By comparing with other theoretical models and experimental techniques, the possible physical origins behind these features will be discussed.

6.4 Evidence for other competing orders

6.4.1 Anisotropic properties beyond the structural/magnetic origin

One major puzzle of the iron-pnictides physics is the paramagnetic-tetragonal to AFM-orthorhombic phase transition in the parent state. Due to its metallic nature, some argue that these materials are spin-density-waves driven by nesting of FSs and they should be viewed as weakly correlated itinerant magnets. But on the contrary, the transport and optical measurements show a very large resistivity and a small Drude weight, which indicate that they may not be conventional metals and the electron correlations could also play a crucial role as they do in the cuprates. For this reason, others have argued that these materials should be considered in terms of a proximity to a Mott insulator, then the magnetism should be described by Heisenberg type model. In latter approach, the collinear AFM order can be understood as the result of the competition between the nearest neighbor antiferromagnetic exchange $J_1$ and the second neighbor antiferromagnetic exchange $J_2$. It is shown [Yildirim, 2008; Si and Abrahams, 2008] that once $J_2 > |J_1|/2$ this competition will lead to the collinear-AFM order in the system and further cause the crystal distortion, as shown in fig. 6.9. This is the so-called “$J_1 - J_2$” model and can be extended to “$J_1 - J_2 - J_3$” model is one also include the third-nearest-neighbor coupling $J_3$ in the model.

Here we note that in this $J_1 - J_2$ model, the spin interactions between the nearest neighbors along AFM or FM direction are the same, i.e., $J_{1a} = J_{1b} = J_1$. The “anisotropic” spin alignment,
Figure 6.9: $J_1 - J_2$ model. Left-hand panel shows the AFM1 configuration where nearest-neighbor spins are always aligned antiparallel. Right-hand panel shows the AFM2 configuration where the next-nearest-neighbor spins (i.e., $J_2$) are always aligned antiparallel. From [Yildirim, 2008].

i.e., the collinear-AFM order is due to the dominant antiferromagnetic next-nearest-neighbor exchange interaction $J_2$. But the recent neutron scattering measurement on $CaFe_2As_2$ reported a strong anisotropic property of the spin interactions along different directions. As shown in fig. 6.10(a), the measured spin-wave dispersion is better described by a strong anisotropic model, i.e., $J_{1a} >> J_{1b}$. This result indicates the underlying anisotropy in the iron-pnictide materials. Furthermore, the recent transport measurement [Chu et al., 2010] reported a strong in-plane resistivity anisotropy in underdoped $Ba(Fe_{1-x}Co_x)_2As_2$ materials, as shown in fig. 6.10(b). Interestingly, this resistivity anisotropy starts above the structural and magnetic phase transition temperate, and $\rho_b (FM \text{ direction}) > \rho_a (AFM \text{ direction})$ which is counterintuitive, since the longer a-axis lattice constant may cause smaller orbital overlap and lead to larger resistivity; also the scattering from spin fluctuations would ordinarily result in a higher resistivity along the AFM a-axis. So the transport measurement also indicates the underlying anisotropic order beyond the magnetic/structural origin. Another example indicating the strong anisotropic property beyond the magnetic/structural origin was reported in parent phase $Ca(Fe_{1-x}Co_x)_2As_2$ ($x=0.3 \pm 0.5\%$) by [Chuang et al., 2010] using spectroscopic imaging-scanning tunneling microscopy (STM). As shown in fig. 6.10(c), a unidirectional electronic nanostructures is revealed along the AFM direction with
wave vector $\vec{q} = 2\pi/8a_{F_Fe-Fe}$, which is explained as the evidence of the existence of the nematic phase in iron-pnictide materials.

All the experimental results above indicate certain anisotropic order beyond the magnetc/structure origin in the iron-pnictide materials. Actually, our ARPES results on $CaFe_2As_2$ also indicate certain anisotropic competing orders in the system. More specifically, the orbital-dependent band shifting may be a signature of developing orbital ordering in the iron-pnictide system, and the incommensurate FS nesting may indicate a possible charge density wave order and may also have
a connection to the nematic order observed by STM.

### 6.4.2 ARPES signature of orbital ordering

![Ferro-orbital order](image)

Based on the strong in-plane anisotropies discovered in iron-pnictide materials, some have proposed [Lv et al., 2009, 2010; Lee et al., 2009; Lee and Wu, 2009; Singh, 2009; Krüger et al., 2009] that the orbital-ordering physics (of a similar kind as in the manganite transition-metal oxides) may be the answer to this strong in-plane anisotropies, which can also explain the structural-magnetic phase transition in a natural way.

The basic idea behind this orbital ordering picture is that in iron-pnictides some electrons are localized (according to the local moments observed by neutron scattering), e.g., electrons in $e_g$ orbitals, while others are itinerant (for the bad-metal behavior of the parent compound), e.g., electrons in $t_{2g}$ orbitals. The electronic structure of iron-pnictides is determined by the interplay between, (1) the superexchange couplings between local moments, (2) the itinerant electron orbitals, and (3) the ferromagnetic Hund coupling between local moments and itinerant electrons. As the
result, the degeneracy between the iron’s $d_{xz}/d_{yz}$ orbitals can be broken and this will lead to the anisotropies in iron-pnictides materials. A possible orbital ordering configuration is presented in fig. 6.11 [Lv et al., 2010].

The orbital-dependent band shifting observed in our ARPES result, specifically the upshifting of bands with $d_{yz}$ symmetry, is fully consistent with this orbital-ordering picture, since the degeneracy-broken due to the developing of orbital ordering will lead to the orbital-dependent band shifting and result in unequal occupation between $d_{xz}/d_{yz}$ orbitals. Furthermore, recent calculations from [Chen et al., 2010] showed that if the orbital ordering is included in the band calculation, the resulted FS will have drastically orbital-dependent weight distributions, as shown in fig. 6.11(b). This is also consistent with our observation, which shows that the inner and outer pieces of FS near zone center have different orbital properties (fig. 6.5).

### 6.4.3 Uniaxial Fermi surface nesting: CDW or nematic phase?

As discussed in previous sections, the incommensurate FS nesting observed in our ARPES data happens along the FM direction and has a constant nesting vector $\mathbf{q}_1 = 0.33(-\pi/a, \pi/a)$ which persists through the whole momentum with minimum $k_z$ variation. This nesting vector $\mathbf{q}_1 = 0.33(-\pi/a, \pi/a)$, i.e., $|\mathbf{q}_1| = 2\pi/6a_{Fe-Fe}$, corresponds to a unidirectional real-space periodicity with dimension $6a_{Fe-Fe}$. Additionally, we made ARPES measurements on $Ca(Fe_{1-x}Co_x)_2As_2$ ($x = 3.5\%$) sample and also notice a possible nesting instability with $\mathbf{q}_1' = 0.24(-\pi/a, \pi/a)$ or $|\mathbf{q}_1'| = 2\pi/8.3a_{Fe-Fe}$, though the data is less clear than that from the undoped material. These results are presented in fig. 6.12. Furthermore, [Kondo et al., 2010] also reported a similar incommensurate FS nesting in $BaFe_2As_2$ materials\(^2\). These results indicate that the incommensurate FS nesting may be a general feature in iron-pnictides. But such a unusual uniaxial FS nesting could not be quantitatively duplicated by any theoretical calculations by far.

Here we need to note that although there is strong nesting instability shown here, we did not

\(^2\) Unlike the uniaxial FS nesting observed by us, they observed a 4-fold symmetry nesting, which is actually the averaged result due to the sample twinning.
observe any gap opened due to this nesting. For this reason, the gapless incommensurate FS nesting observed at low temperature may be explained as the failed charge density wave order, where the nesting instability gives its way to other orders such as SDW or SC in iron-pnictides. Recently, a “valley density wave” picture was proposed by [Cvetkovic and Tesanovic, 2009]. In this theory, the authors argued that the iron-pnictide physics can be understood as the competition between superconductivity and a combination of spin, charge, and orbital density-waves at the wave vector which connects the valleys (i.e., electron and hole pockets). Based on this theory, it is not surprised if there is ceratin charge order instability in the system.

Furthermore we notice that the nesting vector observed by ARPES experiment, more specifically, the nesting vector of the superconducting sample $Ca(Fe_{1-x}Co_x)_{2}As_2$ ($x = 3.5\%$), $|\vec{q}'_1| = 2\pi/8.3a_{Fe-Fe}$, is quantitatively consistent with the unidirectional nematic-like electronic nanostructures observed in [Chuang et al., 2010]’s STM studies on $Ca(Fe_{1-x}Co_x)_{2}As_2$ ($x = 3\%$) sample, which indicates a wave vector $|\vec{q}'| = 2\pi/8a_{Fe-Fe}$. But we need to note that in [Chuang et al., 2010]’s original paper, the nematic wave vector happens along the AFM direction, while the nest-
ing seen by ARPES happens along the FM direction by comparing with the band calculations. So whether our ARPES observation could be explained as the evidence of the nematic phase still needs to be further investigated.

Figure 6.13: Doping dependence of the nesting vector. Schematic phase diagram of the “122” pnictide system as a function of doping concentration (x) adopted from [Chuang et al., 2010]. The structural ($T_S$), antiferromagnetic ($T_{AF}$), and superconducting ($T_c$) transitions are shown. The two red squares indicate the size of the incommensurate nesting vector at 0 and 3.5% doping obtained from ARPES and the black square indicates the size of the nesting vector at 3% doing obtained from STM [Chuang et al., 2010]. The dashed line through all these three data points indicates the simplest linear fitting, which extrapolates to a possible quantum critical point in the overdoped regime. Although we plot the ARPES nesting vector and the STM nesting vector together, whether these two features have true connection or not still needs to be further investigated.

Finally, the doping dependence of the nesting vector is fully consistent with the doping effect: One can expect that by increasing the doping level, the nesting vector will keep getting smaller while at a specific point this incommensurate FS nesting will disappear due to the absence of the Fermi crossings of the hole-like bands. In real space, this means that the unidirectional nanostructure (if there is) will no longer exist and the system will evolve into a new phase without the possible
charge density wave order. The doping at which the FS nesting disappears would be a quantum critical point in the phase diagram. As shown by the dashed line in fig. 6.13, the simplest linear extrapolation indicates that this quantum critical point may occur near the end the superconducting dome. This therefore may point to a relationship between the different phases such as spin density wave, charge density wave, superconducting state, and possible nematic phase.

6.5 Summary

In this chapter, we presented the ARPES studies on the electronic structure and Fermi surface of the untwinned uniaxial state of \( \text{CaFe}_2\text{As}_2 \), the parent compound of an iron-based superconductor. We observed unequal dispersions and FS geometries along the orthogonal Fe-Fe bond directions. Comparing with the optimized LDA calculations, an orbital-dependent band shifting is introduced to get better agreement, which is consistent with the development of orbital ordering. More interestingly, unidirectional straight and flat FS segments are observed near the zone center, which indicates the existence of a unidirectional charge density wave order and is quantitatively consistent with the unidirectional electronic nanostructures observed recently in parent iron-based superconductors [Chuang et al., 2010]. Therefore, our studies indicate that beyond the well-known spin density wave (SDW) order and superconducting state (SC), there are other competing orders in the iron pnictide materials such as the orbital order (OO), the charge density wave (CDW) order and the possible nematic phase. The coexistence of all these competing orders puts strong constraints on theories for describing the iron pnictide system.
Chapter 7

Summary and Future Directions

7.1 Summary and Conclusions

This thesis presented our new discoveries on both cuprate superconductors and iron-pnictide superconductors. Since the high-\(T_c\) superconductivity in those materials is such a broad field with so many questions needed to be answered, our research mainly focuses on the “high energy anomaly” in slightly overdoped \(\text{Pb}_x\text{Bi}_{2-x}\text{Sr}_2\text{CaCu}_2\text{O}_8\) material and the electronic structure of the iron-pnictide mother compound \(\text{CaFe}_2\text{As}_2\). We hope that our works can add important pieces to the puzzle of high-temperature superconductivity in cuprate and iron-pnictide superconductors.

In chapter 2, a very detailed ARPES theory review is presented. Some very important conceptions are discussed to provide a clear physical picture for ARPES experiment, such as independent electron picture vs. interacting electron picture, three-step model vs. one-step model, sudden approximation vs. adiabatic limit, intrinsic features vs. extrinsic backgrounds, EDC analysis method vs. MDC analysis method, etc. The reason I put so much effort to review the existing ARPES theory is that the better we understand our tools, the more reliable information we can extract from the data.

In chapter 3, I presented a detailed review about experimental ARPES setup. The light source, the electron spectrometer, and the sample system are discussed in great detail. The low-photon-energy ARPES light sources are reviewed and a newly developed 6.3-eV laser system is introduced. The working principle of ARPES experimental system is also presented. Furthermore, the practical issues about ARPES measurement, e.g., the energy and momentum resolution, the
detector's imperfection, the space charge effect are discussed in detail.

In chapter 4, a general review is presented for conventional BCS superconductivity and unconventional high-$T_c$ superconductivity in cuprate and iron-pnictide superconductors. Again, some very important conceptions are discussed even they are not directly related to the research works presented in this thesis, e.g., the strong coupling theory vs. the weak coupling theory, the BCS Cooper pair vs. the generalized Cooper pair. Furthermore, the cuprate superconductors and the iron-pnictide superconductors are reviewed in a parallel manner, by which we can emphasis the similarities and dissimilarities between these two systems and give the readers better overall pictures about them.

Our studies on the “high energy anomaly” in slightly overdoped Pb$_2$Bi$_{2-x}$Sr$_2$CaCu$_2$O$_{8}$ material is presented in chapter 5. By continuing discussing the electron-phonon interaction from BCS theory, the “low energy kink” and the “high energy anomaly” are introduced naturally. By measuring the sample over multiple Brillouin zones and with a large variety of ARPES matrix elements, we uncover the intrinsic spectral function over a large energy scale, which is characterized by a “peak-tail” lineshape. Furthermore, by empirically separating the spectral function into a sharp peak (coherent) part and broad tail (incoherent) part, a universal relationship between the weight of these two components is uncovered. This is a further convincing evidence for proving that the “peak-tail” lineshape represents the intrinsic spectral function of the cuprate superconductors. Then the “high energy anomaly” can be naturally explained as the intrinsic spectral function mediated by the ARPES matrix element. Furthermore, the possible origins of the strong incoherent spectral weight are also discussed.

In chapter 6, I presented the ARPES studies on the iron-pnictide mother compound CaFe$_2$As$_2$. By measuring the high quality CaFe$_2$As$_2$ crystals with a very small photon beam size, we obtained the intrinsic electronic structure on sample’s single domain. This has allowed us to observe the unequal dispersions and FS geometries along the orthogonal Fe-Fe bond directions. The 3-dimensional symmetry-broken electronic structures are obtained. To the zeroth order, the observed electronic structure is consistent with the SDW-included-LDA-calculation. A renormalization factor 2.5 indi-
brates a moderate level electron correlation in the material. Beyond this, two discrepancies between experimental results and theoretical calculations are noticed: the orbital-dependent band shifting and the incommensurate Fermi surface nesting near zone center. Both of these two features have important physical implication: the orbital-dependent band shifting is consistent with the orbital ordering picture, while the incommensurate Fermi surface nesting is quantitatively consistent with the nematic order observed by recent STM studies. Our studies indicate that beyond the well-known spin density wave (SDW) order and superconducting state (SC), there are other competing orders in the iron pnictide materials such as the orbital order (OO), the charge density wave (CDW) order and the possible nematic phase. The coexistence of all these competing orders puts strong constraints on theories for describing the iron-pnictide system. Both they may be the answer to the strong in-plane anisotropies in iron-pnictide superconductors. Furthermore, those features can be the potential answers to the strong anisotropies observed in the iron-pnictide superconductors.

7.2 Future works

For “high energy anomaly” studies, more effort will be put into examining the possible origins for the intrinsic spectral function lineshape observed experimentally, especially the “spin fluctuation mechanism” discussed in chapter chapter 5’s section 5.5.3.3. Furthermore, since our “κ-fitting” procedure is a “self-energy” sensitive method. A more careful momentum-dependent analysis will be performed on the EDCs at different momentum positions and try to find any momentum-dependent self-energy effect beyond the “universal behavior”. We will also apply this EDC analysis technique to different doping level, e.g., the underdoped and overdoped regions since understanding the doping dependence of the spectral function is important for understanding the doing introduced superconductivity. The “κ-fitting” method can be also applied on those non-cuprate materials, e.g., manganite materials. The information extracted from those materials will also be instructive for understanding the many-body interaction in the system.

For iron-pnictide materials, the first thing to do is to confirm the possible orbital ordering and charge density wave vector observed by ARPES. These can be done by using different experimen-
tal techniques. For orbital ordering, a detailed temperature-dependent ARPES studies could be extremely helpful for detecting the possible onsite temperature. Furthermore, the orbital ordering could be detected by x-ray absorption spectroscopy (XAS) through linear dichroism measurement. For possible charge ordering or nematic phase, extensive doping-dependent ARPES studies are badly needed to test our “quantum critical point” scenario. We could also use resonant soft x-ray scattering (RSXS) technique to search further evidence of the nesting vector. One main problem of the x-ray based experiments on iron-pnictide materials is the domain effect. So for obtaining truly intrinsic data, certain sample detwinning techniques are needed to be developed.

7.3 Lessons learned

I end this thesis with several lessons I have learned during my PhD studies (please do not take it as the “fault-list” in my research . . .):

◊ Please take notes when you are learning new instruments, experimental systems, theories.

◊ If you are not sure about how an instrument works, look for someone who knew it.

◊ The three most important things for working in a multi-person research team are: communicating with your colleagues, communicating with your colleagues, and communicating with your colleagues.

◊ If the “check engine” light goes on for your car, check your fuel cap first; if the “interlock” light goes on for your instrument, check all the covers first.

◊ Please backup your files.

◊ Do not try to submit your March Meeting abstract in the afternoon of the deadline. It seems that the APS website can only handle one request at one time.

◊ The very last but the most important one: after choosing the defence date, start writing thesis as early as you can!
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