Polarization Dependent Angle Resolved Photoemission Spectroscopy for the Determination of Intrinsic Material Symmetries

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by

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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.
In this thesis I investigate the utility of the polarization and angle dependence of the photoemission matrix element in angle resolved photoemission spectroscopy (ARPES). This technique is capable of determining internal symmetries of the electronic wave functions in crystalline solids and has been historically underutilized in the ARPES community. In Chapter 1, I introduce the ARPES technique, the established theory and models behind it, and the experimental considerations in performing the technique. It is my personal belief that the fastest way to build intuition for complex physical phenomena is through simulation, and a good portion of graduate school career was spent developing simulation toolkits for the photoemission process. This work will be covered in detail in chapter 2. The later chapters cover the application of this technique to various materials systems. Chapter 3 focuses on the use of this technique to observe a topological phase transition in the Lanthanum Monopnictides. Chapter 4 contains my work on the Cuprate high temperature superconductors, Bi$_2$Sr$_2$Ca$_1$Cu$_2$O$_{8+x}$ and La$_{2-x}$Sr$_x$CuO$_2$ and the use of tight binding simulations to approximate the single particle wave function in this material.
Dedication

To my family, my friends, and all of those who helped along the way.
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Chapter 1

Introduction to ARPES

Angle resolved photoemission spectroscopy (ARPES) is a spectroscopic technique designed to measure electronic states in solids. ARPES can be thought of as a sophisticated extension of the photoelectric effect first observed by Heinrich Hertz in 1887 and later theoretically described by Albert Einstein; work for which he would go on to receive the Nobel prize in physics in 1921. The spectroscopy is a ”photon in, electron out” (schematically shown in fig 1.1) spectroscopy where a photon ejects an electron from the solid under study. An electron lens coupled to an electron spectrometer captures the ejected electron and records its energy and momentum. Using conservation of energy and momentum, the experimenter can deduce the energy and momentum of the electron when it was inside the solid. For crystalline solids with an ordered Bravais lattice, this technique is a direct measure of the electronic momentum eigenstates inside the solid.

1.1 Photoemission Theory

The physical foundations of ARPES are the conservation laws of energy and momentum. Energy conservation for the $N$ electron system can be described by:

$$ E_f^N - E_i^N = h\nu $$

(1.1)

where $E_f^N$ is the final energy of the $N$ electron system, $E_i^N$ is the initial energy of the $N$ electron system, and $h\nu$ is the energy of the incident photon. Within a model of non-interacting electrons, the $N$ electrons within the solid can be treated as independent of each other and the above equality
can be expressed in terms of the kinetic energy of a single electron which has been emitted from the solid:

\[ E_{\text{kin}} = h\nu - \Phi - |E_B| \]  

(1.2)

where \( E_{\text{kin}} \) is the kinetic energy of the emitted electron outside of the solid, \( \Phi \) is the work function of the solid, and \( E_B \) is the binding energy of the electron within the solid. The binding energy of an electron inside the solid is always referenced to the Fermi energy. Note that this equality cannot be satisfied with a positive kinetic energy if \( h\nu < \Phi \). Physically, this implies that the photon is not energetic enough to overcome the energy barrier of the work function and therefore the electron cannot escape the solid. For most solids, the range of typical work functions is \( 2 \lesssim \Phi \lesssim 6 \text{ eV} \), which limits the photon energies to vacuum ultraviolet ranges and beyond. If the kinetic energy of the emitted electron is measured and both the photon energy and work function are known, it is trivial to determine the initial binding energy of the electron. A visualization of the energy scales within ARPES is provided in fig 1.2.

1.1.1 Models of the Photoemission Process

The absorption of a photon by an electron inside a solid is the genesis of the photoemission process. The full quantum mechanical treatment from absorption to detection is a difficult and complex task which has been researched heavily [2, 3, 4, 5, 6, 7]. In a complete sense, photoemission should be described in terms of an optical transition between initial and final energy eigenstates internal to the solid. These eigenstates are most accurately described by many-body wave functions which extend throughout the solid and are damped beyond the boundaries of the solid. The final state wave function must consist of the ionized solid along with a free electron plane wave which is damped at the surface of the solid but also has some partial overlap with the initial state.

Models which treat the photoemission process as a single coherent process described above are referred to as one-step models. These models most accurately describe the physics but can be intractable by analytic methods for all but the simplest of systems. As with many examples
Figure 1.1: Schematic of a photoemission experiment. The photon source ejects electrons from within the solid and these electrons are captured by an electron lens. The lens sorts the electrons in angle and directs them into a hemispherical spectrometer where they are sorted in angle before detection. Reproduced with permission from: https://upload.wikimedia.org/wikipedia/commons/8/83/ARPESgeneral.png
Figure 1.2: Basic energetics in the photoemission process. Inside the sample the electrons fill the available energy levels according to the Fermi-Dirac distribution up to the Fermi level, \( E_F \). The Fermi energy is below the vacuum energy level by an amount equal to the work function \( \Phi \). Once an electron absorbs a photon with energy \( h \nu \), it is ejected from the sample into vacuum where it has a kinetic energy referenced to the vacuum energy. Taken from \[1\]
in physics, approximations allow for a trade-off of giving up a slight amount of accuracy in order to gain vast amounts of simplification. Two of the most widely used approximations in ARPES analysis are the **sudden approximation** and the **three-step model**.

When a solid containing \( N \) electrons has a single electron removed by absorption of a photon, in principle, the \( N - 1 \) many-body wave function will relax during the photoemission process and interact with the exiting electron. This interaction complicates the interpretation of the of the initial state from the ARPES spectrum. For high kinetic energy electrons, which quickly exit the solid, this interaction is small and can be ignored. The removal of the photo-electron is said to be **sudden**, hence the name **sudden approximation**.

As its name suggests, the **three-step model** takes the photoemission process and divides it into three simpler separate steps: excitation of the the electron from its bulk initial state to a higher energy final state inside the bulk of the solid, travel of the excited electron to the surface of the solid, and finally, transmission through the surface of the solid into vacuum. The total rate of the photoemission process, and hence the strength of the photo-current, in this approximation is then the product of the three separate rates.

The rate of the initial step of excitation can be estimated by Fermi’s golden rule for first order processes:

\[
    w_{fi} = \frac{2\pi}{\hbar} |\langle \Psi_f^N | H_{int} | \Psi_i^N \rangle|^2 \delta(E_f^N - E_i^N - h\nu)
\]  

(1.3)

where \( \Psi_f^N \) and \( \Psi_i^N \) are the final and initial \( N \) electron wave functions respectively, \( E_f^N \) and \( E_i^N \) are the final and initial total energies of the system, \( H_{int} \) is the Hamiltonian describing the light-matter interaction, \( h\nu \) is the photon energy, and \( \hbar \) is the reduced Planck’s constant. The Dirac delta function enforces energy conservation in the system and after the emission of the photo-electron the total energy of the final state can be written as \( E_f^N = E_f^{N-1} - E_{\text{kin}} \).

There are several paths which can be taken to simplify the expression from Fermi’s golden rule for the excitation from the ground state to the final state. First I’ll address the interaction Hamiltonian. The perturbation Hamiltonian for an electron in a electromagnetic field is:
\[ H_{int} = -\frac{e}{2mc} (\vec{A} \cdot \vec{p} + \vec{p} \cdot \vec{A}) + \frac{e^2}{2mc^2} \vec{A}^2 \]  

(1.4)

where \( \vec{A} \) is the operator for the electromagnetic vector potential, \( \vec{p} \) is the momentum operator, \( m \) is the electron mass, \( e \) is the electron charge, and \( c \) is the speed of light. The quadratic term in \( \vec{A} \) is small compared to linear terms under typical experimental conditions of ARPES and can be neglected. The semi-classical treatment of the electromagnetic field is used to write the vector potential as:

\[ \vec{A} = \frac{1}{c} e^{i \vec{k}_p \cdot \vec{r}} \vec{\epsilon} \]  

(1.5)

where \( \vec{\epsilon} \) is the unit polarization vector, \( \vec{k}_p \) is the wave vector of the photon, and \( \vec{r} \) is the position operator. Putting these together, the interaction Hamiltonian can be written as:

\[ H_{int} = \frac{-ihe}{mc} e^{i \vec{k}_p \cdot \vec{r}} \vec{\epsilon} \cdot \nabla \]  

(1.6)

In the form of second quantization, this Hamiltonian can be thought of annihilating an electron in an initial state \( | \psi_n \vec{k}_i \rangle \) with band index \( n \) and crystal momentum \( \vec{k}_i \), with the operator \( \hat{c}_{\vec{k}_f} \) and creating an electron in the final state \( | \psi_m \vec{k}_f \rangle \) with the operator \( \hat{c}_{\vec{k}_i}^\dagger \):

\[ H_{int} = \frac{-ihe}{mc} \sum_{\vec{k}_i, \vec{k}_f} \langle \psi_m \vec{k}_f | e^{i \vec{k}_p \cdot \vec{r}} \vec{\epsilon} | \psi_n \vec{k}_i \rangle \hat{c}_{\vec{k}_f}^\dagger \hat{c}_{\vec{k}_i} = \sum_{\vec{k}_i, \vec{k}_f} M_{\vec{k}_f \vec{k}_i} \hat{c}_{\vec{k}_f}^\dagger \hat{c}_{\vec{k}_i} \]  

(1.7)

where \( M_{\vec{k}_f \vec{k}_i} \) is known as the matrix element.

Using the sudden approximation, the final state in the matrix element of Fermi’s golden rule can be simplified as follows, \( \Psi_f^N \) can be factorized into the \( N-1 \) electron bulk wave function and the outgoing electron wavefunction if there is no interaction between the photo-electron and the photo-hole:

\[ | \Psi_f^N \rangle \propto \hat{A} (| \psi_{\vec{k}_f} \rangle \otimes | \Psi_f^{N-1} \rangle) = \hat{c}_{\vec{k}_f}^\dagger | \Psi_f^{N-1} \rangle \]  

(1.8)
where the operator $\hat{A}$ ensures the proper anti-symmetrization of the wave function to satisfy the Pauli exclusion principle.

Combining these expressions back into the expression for Fermi’s golden rule allows for simplification:

$$w_{fi} = \frac{2\pi}{\hbar} \sum_{\vec{k}_i} |M_{\vec{k}_f\vec{k}_i}|^2 \left| \langle \Psi^N_{N-1} | \hat{c}_{\vec{k}_i} | \Psi^N_i \rangle \right|^2 \delta(E^N_i - E^N_{N-1} + \hbar\nu)$$  \hspace{1cm} (1.9)

If the many body matrix element and the delta function are summed over all possible $|\Psi^N_{N-1}\rangle$, one arrives at the one electron removal spectral function:

$$A^- (\vec{k}_i, \omega) = \sum_{f} \left| \langle \Psi^N_{N-1} | \hat{c}_{\vec{k}_i} | \Psi^N_i \rangle \right|^2 \delta(\omega - E^N_{N-1} + E^N_i)$$  \hspace{1cm} (1.10)

which contains information on the eigenstates of the system under study.

### 1.1.2 Kinematics

The ability to measure the energy of the outgoing electron along with its direction allows for the determination of its momentum, $p$. However, more commonly the wave vector is used instead:

$$\vec{K} = \vec{p}/\hbar = \frac{\sqrt{2mE_{\text{kin}}}}{\hbar}$$  \hspace{1cm} (1.11)

where $m$ is the free electron mass (throughout this thesis I will denote the wave vector of the electron outside of the solid as $\vec{K}$ and the wave vector of the electron inside the solid as $\vec{k}$). Being a vector quantity, one can measure both the in-plane (relative to the surface of the solid) and out-of-plane components:

$$|\vec{K}_i| = |\vec{K}_x + \vec{K}_y| = \frac{\sqrt{2mE_{\text{kin}}}}{\hbar} \sin(\theta) = |\vec{k}_x + \vec{k}_y|$$  \hspace{1cm} (1.12)

$$|\vec{K}_\perp| = |\vec{K}_z| = \frac{\sqrt{2mE_{\text{kin}}}}{\hbar} \cos(\theta) \neq |\vec{k}_z|$$  \hspace{1cm} (1.13)

Here $\theta$ represents the polar angle from the surface normal, $\hat{z}$. It is important to note that the momentum of the incident photon is being neglected in these relations. This is because for the
Figure 1.3: Differences in the *one-step* and *three-step* models of photoemission. (Left) The three step model breaks apart the photoemission process into distinct steps: excitation of the initial to an available final state, travel to the surface of the crystal, and transmission through the surface into vacuum. (Right) The one step model treats the photoemission process as one coherent process consisting of the overlap of a damped wave exiting the crystal to the excited initial state. From [1]
photon energies most commonly used in ARPES ($h\nu < 100$ eV) the photons will have momentum $p_{\text{photon}} < 51$ mÅ$^{-1}$ which is $< 5\%$ of the width of the first Brillouin zones of typical materials. This approximation starts to break down at higher photon energies, especially approaching the soft x-ray regime ($\sim 1$ KeV). In a reduced zone scheme diagram of the electronic bands of a solid, the absorption of a photon by an electron inside the crystal is represented by a vertical transition between initial and final electronic states: $\vec{k}_i - \vec{k}_f = 0$. In the extended zone scheme, $\vec{k}_i - \vec{k}_f = \vec{G}$, where $\vec{G}$ is a reciprocal lattice vector.

Figure 1.4: Conservation of momentum during the photoemission process. (a) Within the solid the photon causes an optical transition which is mediated by a reciprocal lattice vector from an initial state to a final state. (b) Outside of the solid the free electron has a parabolic dispersion. (c) Measured photo-electron spectrum. From [1]

The presence of the surface of the solid creates a potential energy gradient along the surface normal. Due to this fact, there is not a simple conservation of momentum along this direction ($\vec{k}_\perp$ or $k_z$). For 2D materials with dispersion only in the $k_x/k_y$ plane, this is of little concern as $\vec{k}_z$ is not a good quantum number to begin with. However, for 3D materials, more care is required. In general, information about the dispersion of the final state inside the solid is required to extract $\vec{k}_\perp$. This information can be determined experimentally through techniques such as inverse ARPES, but usually is determined via band structure calculations and a priori assumptions [7]. For higher kinetic energies, the potential of the ionic cores of the solid are a small perturbation and therefore
Figure 1.5: Examples of ARPES data from the literature. (Left) A 2D dispersion cut where intensity is plotted as a function of binding energy and in-plane momentum along the analyzer slit. Higher intensity areas are more red. From [8]. (Right) A 3D ARPES map. Here the horizontal axes are the two orthogonal components of in-plane momentum and the vertical axis is binding energy. Maps are constructed by stacking multiple dispersion cuts to form a volume of data. Higher intensity regions are dark blue in this image. From [9].
it is safe to assume a nearly-free electron dispersion for the final state:

\[ E_f(\vec{k}_f) = \frac{\hbar^2 \vec{k}_f^2}{2m} - |E_0| = \frac{\hbar^2 (\vec{k}^2 || + \vec{k}^2 \perp)}{2m} - |E_0| \]  

(1.14)

where \( E_0 \) is the energy of the bottom of the valence band referenced from the Fermi energy, \( E_F \).

Substituting in eqns. 1.1 and 1.2 on the left and eqns 1.12 and 1.13 on the right, \( \vec{k}_\perp \) can be expressed in terms of directly measured observables:

\[ |\vec{k}_\perp| = \frac{1}{\hbar} \sqrt{2m(E_{\text{kin}} \cos^2(\theta) + |E_0| + \Phi)} \]  

(1.15)

Where \( \theta \) is the polar angle of the electron’s momentum relative to normal emission. Although \( E_0 \) is defined as the bottom of the valence band which could in principle be measured at a single photon energy, it is more accurately measured by scanning photon energy and fitting the periodicity of the 3D Brillouin zone with \( E_0 \) as the free parameter.

1.2 Practicalities of Photoemission

1.2.1 Photon Sources

In order to accurately measure the kinetic energy of emitted electrons from the solid, a monochromatic photon source is required as the source’s line width contributes to the overall energy resolution of the experiment (discussed below). As mentioned earlier, the incident photons must have an energy greater than the work function of the material under study in order to eject electrons from the material. These requirements have traditionally lead to the use of synchrotron radiation and gas discharge lamps in ARPES. However, in 2007, the Dessau group at University of Colorado Boulder demonstrated the use of ARPES with a laser photon source [10]. The different sources should be viewed as complementary with differing advantages and disadvantages.
1.2.1.1 Synchrotron Based Sources

Synchrotron based light sources have been used for ARPES experiments for decades [7]. These sources operate by the acceleration of charged particles; typically, electrons in storage rings. Third generation synchrotron light sources have been in use since the early 1990’s and typically have storage rings several hundred meters in diameter with electron energies of 1-4 GeV. These facilities mainly utilize undulator insertion devices in straight segments of the storage ring to produce synchrotron radiation. These sources are capable of achieving brilliances several orders of magnitude above conventional x-ray sources such as vacuum tubes.

Brilliance = \frac{\text{(Number of photons produced per second)}}{\text{(angular divergence)(cross-sectional area)(photons within 0.1\% of central frequency)}}

(1.16)

Generation of light by highly relativistic electrons in undulators has several advantages. The far field angular distribution of power radiated by an accelerating charge is given by:

\frac{dP}{d\Omega} \propto \frac{\sin^2(\theta)}{(1 - \beta \cos(\theta))^5}

(1.17)

where $\theta$ is the polar angle measured from the velocity vector of the charge and $\beta = v/c$. As $\beta$ approaches 1, the angular distribution of the emitted electromagnetic radiation becomes highly peaked in the forward direction. The angle at which the maximum in intensity occurs, $\theta_{\text{max}}$, is:

$$\cos(\theta_{\text{max}}) = \frac{1}{3\beta} (\sqrt{1 + 15\beta^2} - 1) \rightarrow \frac{1}{2\gamma}$$

(1.18)

where gamma is the Lorentz factor $\gamma = 1/\sqrt{1 - \beta^2}$. Therefore, the relativistic nature of the electron tightly focuses the emitted radiation into a usable beam.

The beam of light produced in the undulator must then be monochromated before it can be used for ARPES. For photon energies above $\sim 20$ eV, this is done using a plane grating monochromator apparatus (fig 1.7). The light is collimated onto a diffraction grating which disperses the light in angle. The desired wavelength is then selected using exit slits and then refocused onto the sample.
Figure 1.6: (Left) Schematic of a synchrotron light source. Electrons start in the center of the larger storage ring and are accelerated into a booster ring where they are accelerated further to highly relativistic speeds before entering the storage ring. Throughout the storage ring insertion devices, such as undulators, produce UV to x-ray light which is fed into tangentially oriented beam lines. Image credit: Copyright EPSIM 3D/JF Santarelli, Synchrotron Soleil. (Right) Angular distribution of radiated power from a relativistic accelerating charge. $\theta_{\text{max}}$ is the peak of the power distribution. Reproduced from [11].
Figure 1.7: Schematic layout of the ‘I-05’ beamline at the Diamond light source synchrotron in Didcot, Oxfordshire, UK. The undulator insertion device oscillates the relativistic electrons to produce light. The light is then monochromated by passing through a plane grating monochromator apparatus (Primary slits, M1, M2, Diffraction Grating, M3, and exit slits) which disperses the light in the vertical direction. Upon exiting the monochromator, the beam is refocused using the last elliptical toroidal mirror (M4). Reproduced from http://www.diamond.ac.uk/
1.2.1.2 Laser Sources

Laser-based sources for ARPES rely on the upconversion of photon energies via non-linear processes. This is due to the fact that photons with energies large enough to overcome the work function of most materials are readily absorbed by most materials. Therefore, choices for gain media are limited. The upconversion process starts with lower energy photons produced at high intensities by continuous wave, quasi-continuous wave, or pulsed lasers. These photons are directed into a non-linear medium, such as Barium Borate crystals or gas jets, where two low energy photons are converted to a higher energy photon. The rate of upconversion is proportional to the magnitude of the incident electric field squared.

This approach struggles to produce photons with energies in the range of most synchrotron beamlines, however. Each non-linear upconversion process requires high intensities, yet each successive upconversion is accompanied by an exponential decay of intensity. Currently, pulsed laser sources are needed to reach $\sim 15$ eV and higher, as these sources compress their average power output into a ultrafast pulse with large peak intensity. The lower photon energies offer better energy and momentum resolution, as the spectral intensity is confined to a narrower bandwidth.

1.2.2 Measurement of Photo-Electrons

In ARPES experiments an apparatus to resolve both the energy and momentum of the photo-electron is required. Typically this apparatus is a commercial package with these combined features, referred to as an analyzer. Energy sorting is performed by an electron spectrometer while angle sorting is performed by an electron lens.

1.2.2.1 Electron Spectrometers

Electron spectrometers can take many forms depending on their desired measurement capabilities. Modern electron analyzers use a hemispherical geometry, where the electrons enter tangentially through an entrance slit between two hemispherical plates and impact a detector is placed symmetrically on the opposing side (See Fig. 1.8). An electrostatic potential is used to
filter the incoming electrons to the desired energy. This is achieved by applying voltages to inner and outer hemispheres which the electrons travel between. These voltages are chosen to mimic the electric field of a point charge at the shared origin of these hemispheres. The resulting potential in free space is $\sim 1/r$, where $r$ is the radial distance from the origin. This familiar potential is both a conservative potential and supportive of closed orbits about the origin.

The stability of a given orbit is determined by an electron’s initial velocity and position upon entering the potential. Electrons with too high of a kinetic energy will collide into the outer hemispherical wall before completing the necessary half orbit to enter the detector. Electrons with too low of a kinetic energy will suffer a similar fate and collide with the inner hemisphere without reaching the detector. Some electrons will have a kinetic energy such that upon completing one half-orbit will return to the same radial distance as they entered the spectrometer with. This unique energy value is known as the pass energy and is chosen by the experimenter. All the voltages in the hemisphere scale with this energy value. Kinetic energies which slightly vary from the pass energy will map to smaller or larger radial distances for lower and higher kinetic energies respectively. Furthermore, the window of acceptable energies by the detector also scales with the pass energy. Depending on the photon energy and material under investigation, the pass energy is not necessarily equal to the vacuum kinetic energy of the electrons. To match these two energies, an electric field is applied in the electron lens system before the electrons enter the spectrometer to either retard or accelerate the electrons to the desired pass energy. The ratio of $E_{\text{kin}}/E_{\text{pass}}$ is called the retarding ratio.

The width of the energy distribution of electrons which reach the detector sets the energy resolution of the spectrometer. This energy distribution width is directly proportional to the pass energy and the width of the entrance slit.

$$\delta E_{\text{analyzer}} = \left( \frac{w}{R_0} + \frac{\alpha^2}{4} \right) E_{\text{pass}}$$

(1.19)

$w$ is the entrance slit width, $R_0$ is the radius of the analyzer hemisphere, and $\alpha$ is the acceptance
angle along the slit length. State of the art analyzers have $R_0 \sim 200\text{mm}$ and variable slit widths ranging from $50 - 3000\mu\text{m}$. The $\alpha$ term is much smaller in comparison and is therefore usually ignored. Typical energy resolution floors of modern electron analyzers are around $1\text{meV}$.

1.2.2.2 Electron Detection

For detection of the electrons a micro-channel plate (MCP) detector with a phosphor screen, is used. This detection stack can detect a single low-energy electron by amplifying it into a cluster of a large number of electrons. This cluster is then accelerated into the phosphor screen creating a "blob" of light which is in turn imaged by a camera.

This detection scheme does not guarantee the equal amplification of each electron event uniformly, nor is it linear in count rate. These aspects make the quantification of electron counts difficult to determine purely from the intensity of the light emanating from Phosphor screen. Our group has developed a graphics processing unit (GPU) based pulse counting algorithm which corrects for the variance in event amplification along with non-linearities by treating all events which are a local maximum in pixel brightness and above a user-defined threshold as binary events (see Fig 1.10). Due to the ability of GPUs to run highly parallelized algorithms, this peak finding algorithm can be run at 100’s of frames/sec at resolutions comparable to 2000x1200 pixels.

The sole condition of a local maximum with regard to a pixel’s 8 nearest neighbors is not sufficient for accurate event discrimination. Camera or Phosphor noise can produce low-level pulses which would pass a local max test. These can be rejected via a floor threshold for peak height. Cosmic rays can also produce spurious events on the detector which have a pulse height much higher than the distribution of real electron events. These are rejected via a ceiling threshold. Lastly, the CMOS camera can have "hot pixel" errors where a single pixel value is stuck at a random high value. These are rejected via a limit on how high a true event can be relative to the average of its nearest neighbors. See fig 1.10 for a visualization of this algorithm. Optimization of these various thresholds is required in order to maximize counting efficiency while still rejecting false positive events. This optimization was performed using statistical methods to isolate the pulse
Figure 1.8: Schematic of the principles behind the momentum sorting, energy filtering, and detection of photo-electrons. (A) The overall orientation of the electron source and the components of the analyzer. (B) Angular mode of the electron lens. This mode maps electrons with different angles entering the lens to different positions along the entrance slit of the spectrometer. (C) The hemispherical spectrometer with voltages applied between the concentric hemispheres. Electrons enter through the slit at a common radial distance. The trajectories for different energies are shown as different colors. (D) Schematic of the detection stack. The MCP, phosphor screen, and camera are shown. Reproduced from [12].

Figure 1.9: PHOIBOS 225 commercial electron analyzer from SPECS. Image Credit: http://www.specs.de/cms/
Figure 1.10: (a) Discrimination regions for the pulse counting algorithm as a function of a pixel height and the average of its closest 8 neighbors. Pixels too low are regarded as noise and too large are cosmic ray events, regardless of their neighbor’s values. Hot pixel events are pixels whose value is twice that of the average of their neighbors and are not counted. Valid event pixels are pixels whose value is above the value of all of its 8 nearest neighbors but still within the above thresholds. (b) Bar graph of a Gaussian-shaped event where the height represents pixel intensity. The inset shows the event on the camera pixels. (c) The local max is colored in red and its nearest neighbors are colored green. (d) Example of a pixel which would fail the local max test and be rejected as an event by the algorithm. Reproduced from [13].
height distributions of the various count types.

### 1.2.2.3 Electron Lenses

The electron lens system is a stack of cylindrically symmetric electrodes which is used to sort the incoming electrons by their angle. Different voltages are applied to each element along the stack. Inside each cylindrical element there exists no electric field, by Gauss’s law, but near the boundary of each element a cylindrically symmetric electric field bends the electron paths. As mentioned earlier, the lens stack also applies an overall accelerating or decelerating electric field along the symmetry axis in order to adjust a specific vacuum kinetic energy to match the pass energy of the hemispherical spectrometer. At the end of the lens stack is the entrance slit to the hemispherical spectrometer. The slit is placed at the Fourier plane of the lens stack where the angle at which the electrons enter the lens has been mapped to distance from the symmetry axis; analogous to optical lenses and light (see fig. 1.8). Typical angular resolutions of commercial electron lenses used for ARPES are $\sim 0.1^\circ$.

### 1.2.3 Surface Sensitivity and Ultra High Vacuum Requirements

As an excited electron travels towards the surface there is a chance it will inelastically scatter before exiting the solid. The mean free path of the electron is dependent only on its kinetic energy and as shown in fig. 1.11 which is often referred to as the ”universal curve”. For the typical photon energies used in ARPES ($\sim 10 – 1000$ eV), the mean free path is smaller than $10\;\text{Å}$. This implies that ARPES is a surface sensitive technique. The majority of the signal is from photo-electrons that were ejected within the first one or two unit cells to the surface.

Because the mean free path is so small inside the solid, it is crucial that the surface of the crystal be as free from contaminants as possible on the atomic scale. Even elastic scattering events obfuscate the features in the momentum dimension. This is due to a key assumption in the gathering of ARPES data: the in-plane momentum is conserved and the out-of-plane momentum follows the simple assumption in eqn 1.15. An elastic scattering event between the initial state and
the detector would invalidate these relations and preclude the determination of the internal initial without intimate knowledge of the intermediate scattering event.

Furthermore, contaminants from the vacuum can chemically react with the surface atoms of the crystal. These surface reactions can change the measured band structure of the underlying material. This can occur via a rigid shift of the chemical potential (i.e. the contaminants dope the material with electrons or holes), by altering the crystal potential field near the surface, or both.

The requirement of a pristine crystal surface places an upper bound on the pressures under which ARPES experiments can be performed. To calculate this bound it is useful to work with the concept of Langmuirs (L): a unit of or dosage of molecules to the surface of the crystal. One L is defined as 1 second of exposure to a gas at a pressure of $10^{-6}$ Torr. Assuming a sticking coefficient of 1, 1 L represents the dosage required to deposit one monolayer. Therefore, at a pressure of $10^{-6}$ Torr, one monolayer of atoms per second is deposited onto an exposed crystal surface; hardly enough time to perform an ARPES experiment. At a pressure of $10^{-11}$ Torr, it would take slightly over 25 hours for a monolayer to be deposited. This is the typical vacuum regime which ARPES measurements are performed.

1.2.3.1 Resolution

The resolution of an ARPES experiment is a tunable parameter in both energy and momentum with several input parameters. Both of these resolutions define the limit of detail that can be resolved in either dimension due to broadening. It should be noted that broadening can come from extrinsic as well as intrinsic effects of the material. I will refer to resolution as the sum of the extrinsic broadening sources.

Energy resolution can be broken into two categories depending on the source: instrumental and photon source. Photon source resolution results from the non-monochromaticity of the light being used. For non-pulsed laser-based sources, the photon bandwidth is $\lesssim 1$ meV. For synchrotron sources which use monochromators to select the desired center frequency from the distribution of frequencies emitted by the undulator, the bandwidth of the light being used is a linear function
Figure 1.11: The universal curve of inelastic mean free paths of photo-electrons as a function of their kinetic energy. The lower photon energies of laser sources in ARPES probe further into the bulk than the higher energies of synchrotron sources. Taken from [14]
of photon energy. The figure of merit for these sources is therefore quoted as the resolving power which is defined as \( RP = \frac{E}{\Delta E} \). Typical values for resolving power for a synchrotron beamline are \( \sim 20,000 \). However, this is the upper bound for performance. Energy resolution is often traded for higher flux by opening monochromator slits.

Instrumental contributions to the energy resolution are instrument specific, however, they usually arise due to electrical noise or analyzer misalignment. Electrical noise on the vacuum chamber or in the electron analyzer itself will modify the energy distribution of the photoelectrons before they reach the detector. Analyzer misalignment negatively affects energy resolution due to misfocusing of the electrons on the analyzer slit from lens aberrations.

1.2.3.2 Data Analysis

Modern ARPES experimental setups utilize 2D imaging detectors, as mentioned earlier, which can simultaneously collect electron counts along the energy and slit momentum direction. This produces a 2D image of intensity referred to as a dispersion cut. An example cut is shown in fig 1.5 left panel. Electrons fill the bands according to the Fermi-Dirac distribution, which at low temperatures is well approximated by step function at the Fermi energy. Below the Fermi energy electronic bands can be observed which disperse in energy as a function of \( k: \epsilon(\vec{k}) \). Historically, these bands have been analyzed by plotting their profiles in momentum (momentum distribution curve or MDC) and energy (energy distribution curve of EDC), where the peak values correspond to the dispersion function (see fig 1.12). Band mapping of a crystal relies on one’s ability to resolve these peaks above an experimental background.

In addition to peak locations, these profiles have widths that correspond to intrinsic material physics. These bands are the electronic eigenstates of the periodic crystal lattice (Bloch states) which in theory are infinitely long-lived and therefore, according to the Heisenberg relations, should be delta functions energy. However, interactions such as impurity scattering, electron-phonon, and electron-electron coupling cause these states to broaden intrinsically (these states can also be broadened by poor resolution, however that is an extrinsic effect). Because the dispersion relation
connects $\epsilon$ and $\vec{k}$, broadening is either dimensional profile translates into the other dimension via the derivative or electron velocity: $\delta \epsilon \propto (\partial \epsilon / \partial \vec{k}) \cdot \vec{k} = \vec{v} \cdot \vec{k}$.

This correspondence of broadening to various types of electron interaction is established through the spectral function (eqn. 1.10) via the Green’s function for an interacting system, given by:

$$G(\omega, \vec{k}) = \frac{1}{\omega - \epsilon(\vec{k}) - \Sigma(\omega, \vec{k})}$$

where $\Sigma(\omega, \vec{k})$ is the complex electronic self energy: $\Sigma = \Sigma' + i \Sigma''$. The self-energy describes the effect of coupling the electronic eigenstates to perturbations via interactions. One can easily see how experimentally determining this function is of great importance for understanding these interactions. Thankfully, the directly measurable spectral function encodes this information:

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

The poles of $G$ (the eigenstates) are manifested in the data as peaks in the spectral function which depend on the non-interacting dispersion and the real part of the self energy. The broadness of the peaks is controlled by the imaginary part of the self-energy.

### 1.3 Polarization Dependent ARPES

A great deal of information about the internal symmetries of a material can be directly measured by modulating the polarization of an ARPES experiment (also referred to as dichroism experiments). This information can be used to determine qualities such as topological classification, atomic orbital composition of bands, as well as the relative phases of these orbitals [8, 16, 17]. A good deal of my research at CU has centered around this topic which is commonly overlooked by the ARPES community. This section summarizes the general principles and assumptions in the technique. A later Chapter on the simulation of ARPES matrix elements goes into a more mathematical description of the process with a visualization of the angular dependence of the
Figure 1.12: An example ARPES spectrum with example EDC and MDC. (a) The $\epsilon$ vs $\vec{k}$ 2D dispersion cut of intensity from an electronic band. (b) Momentum profile (MDC) along the horizontal teal line in (a). (c) Energy profile (EDC) along the vertical teal line in (a). From [15]
photoemission matrix element.

The polarization dependence of the entire photoemission process of a single electron inside the crystal absorbing a photon and subsequently escaping the crystal, can be described by the semi-classical matrix element in eqn 1.6:

\[
M_{\vec{k}_f\vec{k}_i} = -\frac{i\hbar e}{mc} \langle \psi_{m\vec{k}_f} | e^{i\vec{k}_p \cdot \vec{r}} \vec{\epsilon} \cdot \vec{p} | \psi_{n\vec{k}_i} \rangle
\]

(1.22)

where \( \langle \psi_{n\vec{k}_i} | \) is the initial state of the electron in the crystal with crystal momentum \( \vec{k}_i \) and band index \( n \), \( \vec{k}_p \) is the wave vector of the photon, \( \vec{\epsilon} \) is the polarization vector of the electromagnetic radiation, and \( \langle \psi_{m\vec{k}_f} | \) is the excited final state of the electron inside the solid [7, 2]. In considering a typical ARPES experiment the matrix element can be simplified greatly by making the dipole approximation, to arrive at the following expression:

\[
M_{\vec{k}_f\vec{k}_i} = -\vec{\epsilon} \cdot \langle \psi_{m\vec{k}_f} | i\hbar \nabla | \psi_{n\vec{k}_i} \rangle \propto -i\hbar \langle \psi_{m\vec{k}_f} | \vec{\epsilon} \cdot \vec{r} | \psi_{n\vec{k}_i} \rangle
\]

(1.23)

This approximation is justified when the wavelength of the photon, \( \lambda_p \), satisfies \( \lambda_p >> a \), where \( a \) is the lattice constant of the crystal. For typical ARPES experiments with photons of energy less than 1 KeV, corresponding to wavelengths \( > 1.3 \) nm, this approximation holds in materials without supercell-like structure.

The dipole approximation can be intuitively understood by considering the expressing the matrix element in a position basis:

\[
M_{\vec{k}_f\vec{k}_i} = -i\hbar \int d^3\vec{r} \psi_{m\vec{k}_f}(\vec{r})\vec{\epsilon}(\vec{r}) \nabla \cdot \psi_{n\vec{k}_i}(\vec{r})
\]

(1.24)

The Bloch states can be expanded into its localized Fourier components (Wannier States) as such:

\[
|\psi_{n\vec{k}_i}\rangle = \sum_{\vec{R}} e^{ik_{\vec{R}} \cdot \vec{R}} |\vec{R}, n\rangle
\]

(1.25)

where \( |\vec{R}, n\rangle \) are the Wannier states which are localized to lattice sites within the crystal. The lattice constants of most crystals are a few Angstroms, much smaller than \( 1/k_p \). Beyond this length
scale the Wannier states are nearly zero. Therefore the exponential in eqn 1.24 can be replaced with a constant, \( e^{i\mathbf{k}_p \cdot \mathbf{r}} \approx 1 \), and we arrive at eqn 1.23.

In conjunction with the dipole approximation, a plane wave final state is assumed. After absorbing a photon, the electron is excited into a higher energy final state within the crystal. The final state energy is much higher than the Fermi energy and the energy difference is exactly equal to the photon energy. Physically the use of the plane wave final state approximation is justified due to the high kinetic energies of photo-electrons after absorbing a photon. After it has been excited into the final state, the lattice potential from the ionic cores is a small perturbation to the electron eigenstate.

1.3.1 Linear Dichroism

Once the preceding approximations have been made, symmetry arguments can be applied to determine internal symmetries of the material under study. These arguments rely on an experimental setup which ensures the coincidence of the experimental mirror plane and a crystal high symmetry plane. The experimental mirror plane is the scattering plane of the incoming light and is used to define the polarization configuration of an experiment (\( p \) or \( \pi \) is in the scattering plane, \( s \) or \( \sigma \) is normal to it). A crystal high symmetry plane is defined using the sample surface normal and one of the high symmetry directions of the crystal. Consider now the behaviors of reflection in this mirror plane of components in eqn 1.23. The final state wave function is a plane wave which must always be even under reflections in the experimental mirror plane. The dipole operator’s character under reflection is dependent upon the polarization of light chosen by the experimenter: odd for \( s \), even for \( p \). The initial state parity is \textit{a priori} unknown. Therefore, the overall parity of the matrix element is known up to the parity of the initial state. Because the function which describes this matrix element must be integrated over all space, only functions with even reflection parities in the experimental mirror plane will be non-zero. An experimenter can change the overall parity of this function by changing the polarization. Therefore, if the experimenter was to perform the same ARPES measurement of an initial state twice using \( s \) and \( p \) polarizations and compared
the intensity of the results, the initial state reflection parity in the experimental mirror plane can be determined. This type of experiment is referred to as a "linear dichroism" experiment.

### 1.3.2 Circular Dichroism

Experiments that modulate the polarization of light between right and left circularly polarized light, instead of the linear polarizations $s$ and $p$, are known as "circular dichroism" (CD) experiments. CD experiments rely on different symmetry arguments in order to understand the initial state symmetries but also provide different information about the initial state; most notably the existence of chiral orbital angular momentum (OAM) [19], but also the relative phases of the wave function components [20] [16].

Experimentally, the normalized CD signal as a function of $\vec{k}$ is given by:

$$I_{CD}(\vec{k}) = \frac{I_{C^+}(\vec{k}) - I_{C^-}(\vec{k})}{I_{C^+}(\vec{k}) + I_{C^-}(\vec{k})}$$

(1.26)

where $I_{C^+}(\vec{k})$ and $I_{C^-}(\vec{k})$ are the ARPES intensities produced at $\vec{k}$ with $C^+$ (RHCP) and $C^-$ (LHCP) polarizations, respectively. From eqn 1.9 we know the intensities should be directly proportional to the square of the matrix element. Because the matrix element is the only factor of the ARPES intensity which is dependent upon the experimental polarization, eqn. 1.26 can be expressed in terms of the appropriate matrix elements instead:

$$I_{CD}(\vec{k}) = \frac{|M_{\mu_0}^{+1} |^{2} - |M_{\mu_0}^{-1} |^{2}}{|M_{\mu_0}^{+1} |^{2} + |M_{\mu_0}^{-1} |^{2}}$$

(1.27)

where $M_{\mu_0}^{\mu_0}$ is the matrix element for photoemission with a photo-electron with momentum $\vec{k}$. $\mu_0$ is the polarization index which is 0 for linear polarizations and $\pm1$ for right and left circular polarizations. $\vec{n}$ is the polarization direction for linearly polarized light and the direction of propagation for circularly polarized light.

For linear dichroism, the dipole and plane wave final state approximations were both employed to simplify the end expression. However, only the dipole approximation can be used in the interpretation of the CD signal. This can be easily seen by applying both of these approximations to $|M_{\mu_0}^{-1} |^{2}$:
Figure 1.13: The Mirror Plane in ARPES. (Top) Schematic of an ARPES mirror plane defined by the Poynting vector of the light and the surface normal. This plane is aligned along a high symmetry direction in the sample. A $d_{x^2-y^2}$ orbital is shown as an example. From [18] (Bottom) An example of the configuration of a symmetry-allowed photoemission process. The purple plane is the light scattering plane with impinging electric field and its polarization vector indicated by the blue curve and black arrows respectively. The gray and teal planes are high symmetry planes of the crystal and a $p$ orbital is the initial state from which photoemission will occur. The dipole operator is even under reflections in the gray plane and so is the $p$ orbital initial state, therefore photoemission is symmetry allowed.
\[ |M_{k,n}^{-1}|^2 = |\langle f | \vec{\nabla} \cdot \vec{e} | i \rangle|^2 = |\vec{e} \cdot \vec{k}_f|^2 |\langle e^{ikr} | e^{ikr} | i \rangle|^2 = |M_{k,n}^{+1}|^2 \] (1.28)

which forces the numerator in eqn 1.27 and therefore the CD signal, to be zero. Therefore, it is instructive to think about CD relying on the non-plane wave nature of the final state and mathematically it should be described as an expansion in partial waves.

To intuitively understand the dichroism signal it is useful to look at how the individual components of the dipole operator transfer the angular momentum of the photon to the photoelectron. For simplicity, consider an atomic initial state wave function:

\[ \psi_{n\ell m}(r, \theta, \phi) = f_\ell(r) Y_{\ell m}(\theta, \phi) \] (1.29)

where \( Y_{\ell m}(\theta, \varphi) \) are the spherical harmonics, and \( f_\ell \) contains the radial dependence of the wave function from the atomic core. All of the angular dependence is contained within \( Y_{\ell m}(\theta, \varphi) \) and when evaluating each term in \( M_{k,n}^{\mu_0} \), integrals of the form of:

\[ \int d^3r \psi_f^*(r) \vec{r} \psi_i(r) \propto \sum_{\mu, \ell_f, \ell_i, m_f, m_i} \int d\Omega Y_{\ell_f}^{m_f}(\Omega)^* c_\mu Y_\mu(\Omega) Y_{\ell_i}^{m_i}(\Omega) \] (1.30)

will be encountered, where vector dipole operator, \( \vec{r} \), has been expanded into its spherical harmonic components : \( \vec{r} = \sum_\mu c_\mu Y_\mu(\Omega) \). Because these transitions must conserve angular momentum, only some transitions are allowed from the orbitals of an initial state to final state orbitals after the addition of angular momentum from the photon. These constraints on transitions are known as the dipole selection rules which can be summarized by the following:

\[ |\ell_f - \ell_i| = 1 \] (1.31)

\[ m_f - m_i = \mu \] (1.32)

For \( C^+ (C^-) \) polarized light \( \mu = +1(-1) \) therefore when calculating the square of each matrix element, the CD angular distribution will be determined by the interference between the allowed \( \ell_f = \pm 1 \) and \( m_f = \pm 1 \) channels for each polarization. The interference pattern depends on the
relative phases of the initial state orbitals. More details of the CD angular distribution will be covered in chapter 2.
Figure 1.14: ARPES circular dichroism signal from the 111 surface of Au. (a) Experimental geometry. (b) The Fermi surface measured with 55 eV photons. (c) Panels showing the dispersion cuts near Γ with (from left to right) right circular polarization (RCP), left circular polarization (LCP), and their difference (circular dichroism). From [17]
Figure 1.15: ARPES dispersion cuts from the surface of PrTe$_3$ using (panel a) linear horizontal ($s$) polarization, (panel b) linear vertical ($p$) polarization, and (panel c) the difference of the two signals. From [21]
Chapter 2

ARPES Simulation via Tight Binding Models

The goal of the calculation of the ARPES Matrix element is to compute the angular, experimental geometry, and photon energy dependencies in eqn. 1.9 in order to discern the intrinsic (material specific) features of the material from the extrinsic (experimental condition specific) features. In general, these two classes of features can be of the same order of magnitude in ARPES data which makes misinterpretation easy without an accurate model. The process can be thought of as two distinct parts: calculation of the initial states of the material system and use of these initial states as input to a numerical calculation of the interaction Hamiltonian in eqn. 1.7.

This chapter will be split into two parts which address each of these steps. The first is a burgeoning field of research in condensed matter physics where state-of-the-art techniques such as density functional calculations play a central role. These calculation methods can accurately calculate the electronic ground states in many complicated systems, but come at the cost of enormous complexity and high computational cost. Here I will focus the tight binding model which is a much simpler and faster technique of calculating the electronic eigenstates of a crystal while still being reasonably accurate.

The second part of the simulation pipeline, calculation of photoemission processes, is an area with much less attention in terms of active research but nonetheless contains its own cutting-edge techniques. Here one-step calculations are considered the most accurate, but also come with high costs in terms of complexity and computation requirements. My work in this area has been focused on making appropriate simplifications in the calculation that drastically reduce the complexity and
computation time while still maintaining fidelity to the results. This includes the use of the dipole approximation and the plane wave final state approximation.

2.1 Tight Binding

The tight binding approximation is a calculational model for determining the electronic eigenfunctions of a solid. In general, it can be performed for crystalline or non-crystalline solids where the positions of ionic cores are fixed in space. However, in practice, it is most useful for describing crystalline solids with periodic structure. The tight binding Hamiltonian is as given by:

\[
H_0 = \sum_{ij} t^{\alpha\beta}_{ab} (\mathbf{R}_i - \mathbf{R}_j) |R_i\rangle \langle R_j| + \text{h.c.} + \sum_i \epsilon_i |R_i\rangle \langle R_i| \tag{2.1}
\]

where \(\mathbf{R}\) is a real space lattice vector. The sum is to be taken over each pair of lattice sites in the solid where each term of the sum represents magnitude and phase associated with an electron hopping from the state \(|R_i\rangle\) localized to site \(R_i\) and \(|R_j\rangle\). \(t^{\alpha\beta}_{ab} (\mathbf{R}_i - \mathbf{R}_j)\) is a function which depends on the lattice geometry as well as the vector between the two sites: \(\mathbf{R}_i - \mathbf{R}_j\). The last term represents the potential energy of an electron located on site \(|R_i\rangle\).

The implicit assumption already made is that the eigenstates of this Hamiltonian will be linear combinations of basis states which are localized to a lattice site. The next question is what should one use for these basis states? Wannier states would be the most suitable for the job as they are localized Fourier components of a Bloch state \(|\psi_{kn}\rangle\); the true eigenstate of a periodic potential.

\[
|\bar{R}_n\rangle = \frac{V}{(2\pi)^3} \int_{BZ} d^3k e^{-i\mathbf{k} \cdot \bar{R}} |\psi_{\mathbf{k}}\rangle \tag{2.2}
\]

where the integral is taken over the first Brillouin zone. This can be a tedious task in complex systems and is often best approximated by atomic orbital wave functions centered on each atomic site \([22]\). Atomic orbitals are the eigenfunctions of an isolated atom outside of a lattice but are a good approximation to the eigenfunctions of a solid if the overlap of the atomic orbitals from two sites is low. Hence the name for this model: ”tight binding”.
Using this information the general tight binding Hamiltonian can be simplified to the following:

\[
H_0 = \sum_{i,j,\alpha\beta} t^{\alpha\beta}_{ab} (\vec{R}_i - \vec{R}_j) |\beta b\rangle \langle \alpha a| + h.c. + \sum_{a,\alpha} \epsilon_{a,\alpha} |a,\alpha\rangle \langle a,\alpha|
\]

\[
= \sum_{i,j,\alpha\beta} t^{\alpha\beta}_{ij} c^\dagger_{i,\beta} c_{j,\alpha} + h.c. + \sum_{a,\alpha} \epsilon_{a,\alpha} c^\dagger_{a,\alpha} c_{a,\alpha}
\]

where the Greek letters \(\alpha, \beta\) represent atomic specie indices and the Roman letters \(a, b\) and \(i, j\) represent orbital types and lattice positions respectively and the second line is expressed in second quantization notation of creation and annihilation operators. The sum is now only carried over nearest-neighbor or next-nearest-neighbor sites in the lattice given that the condition of localization of atomic orbitals is being asserted.

Solving this Hamiltonian is done by exploiting the periodicity of the lattice and moving to Fourier space via Bloch states. The creation and annihilation operators can be transformed as such:

\[
c_{k,\alpha} = \frac{1}{\sqrt{N}} \sum_i c_{i,\alpha} e^{i\vec{k} \cdot \vec{r}}
\]

\[
c_{i,\alpha} = \frac{1}{\sqrt{N}} \sum_k c_{k,\alpha} e^{-i\vec{k} \cdot \vec{r}}
\]

where \(N\) is the number of lattice sites. Substitution of these Fourier transforms into the second quantization Hamiltonian followed by use of their completeness and orthogonality relations diagonalizes the Hamiltonian readily in \(k\) space. The eigenvalues of the system will give the band dispersions as a function of \(k\) which also depend on the hopping parameters \(t^{\alpha\beta}_{ij}\). The hopping parameters are proportional to the bandwidth of the various energy bands. As two orbitals on neighboring sites physically overlap more the hopping parameter, and therefore the bandwidth, increases.

The hopping parameters are the input parameters to the model. In general, these are geometry dependent functions which depend on the initial hopping orbital, the final hopping orbital,
the relative orientation of these orbitals, and the distance between them. In most cases these parameters are determined from experiment or by comparison to local density approximation (LDA) calculations. Slater and Koster developed a formalism in an effort to simplify the determination of these hopping parameters by deriving expressions for the angular dependence based on which types of orbitals were involved in the bonding. Because molecular bonds have some degree of symmetry about the axis of the molecular bond, one can classify bonds into types, \(\sigma, \pi, \delta\), by the orbitals involved and their relative orientations. Fig. 2.1 shows the classification scheme for \(s, p, d\) orbitals. This can reduce the number of free hopping parameters in a model while allowing for the retention of atomic orbitals. This is achieved by replacing a separate hopping parameter for each hopping type \((i \rightarrow j, \alpha \rightarrow \beta)\), with hopping parameters for each specific orbital combination \((\alpha \rightarrow \beta)\), if the distance dependence is known. For large unit cell calculations, this can drastically reduce the number of parameters in the model.

### 2.2 Simulation of ARPES Matrix Elements Using Atomic Orbitals

The ARPES intensity as a function of \(\omega\) and \(\vec{k}\) is given by:

\[
I(\vec{k}, \omega) = \left| \langle f | \vec{A} \cdot \vec{p} | i \rangle \right|^2 A(\vec{k}, \omega) f(\omega) + \text{BG} \right|^2 \ast R(\vec{k}, \omega) \tag{2.7}
\]

where \(\langle f | \vec{A} \cdot \vec{p} | i \rangle\) is the matrix element (symbolized as \(M_{\vec{k}_f,\vec{k}_i}\)), \(A(\vec{k}, \omega)\) is the spectral function, \(f(\omega)\) is the Fermi-Dirac distribution, BG represents a background signal, and \(R(\vec{k}, \omega)\) is the experimental resolution function. If one ignores the background function and either assumes or measures the point spread function for the experimental apparatus, the full ARPES intensity can be calculated by knowing both \(A(\vec{k}, \omega)\) and \(M_{\vec{k}_f,\vec{k}_i}\). Both of these functions require information about the initial state eigenfunctions of a material and will, in most cases, be calculated given some \textit{a priori} assumptions.

#### 2.2.1 Photoemission Matrix Element

The initial and final state eigenfunctions of a material are the only input required to calculate the photoemission matrix element for any given experimental geometry. However, if the plane wave
Figure 2.1: Representations of the various geometries of the Slater-Koster bond integrals. There is an axial symmetry about the axis of the molecular bond and therefore the bond types can be classified into either $\sigma, \pi, \delta$ bonds. From [23].
final state approximation is used, the only requirement is the initial states. As described in the previous section, tight binding models are a low-cost solution to determining this input and the eigenfunctions from these models can be straightforwardly projected into an atomic orbital basis. This projection allows for a simpler process of calculating the ARPES intensity as well as increasing the ease of interpreting the results of the model.

In an atomic orbital basis the ARPES matrix element becomes:

\[ M_{\vec{k}_f\vec{k}_i} = \frac{-i\hbar e}{mc} \sum_{\mu,\ell_f,\ell_i, m_f, m_i} \left\langle \phi_{\ell_f}^{m_f}(\vec{k}_f) \middle| \epsilon_{\mu}, r_{\mu} \middle| \phi_{\ell_i}^{m_i}(\vec{k}_i) \right\rangle \]  

(2.8)

When this sum is squared, the interference between the different orbital transition terms determine the overall matrix element as a function of \( \vec{k} \) and \( \omega \). Because both the free particle wave function of the final state and the atomic orbital wave function of the initial state arise from the solution of spherically symmetric Hamiltonians, they are separable functions into radial and angular parts:

\[ \left\langle \vec{r} \middle| \phi_{\ell_i}^{m_i}(\vec{k}_i) \right\rangle = R_{\ell_i}^{m_i}(r)Y_{m_i}^{\ell_i}(\Omega). \]  

In turn, this implies that each of the terms in the matrix element sum is also separable into an angular and a dynamical factor. This can be seen by inserting a complete set of position basis states and integrating:

\[ \left\langle \phi_{\ell_f}^{m_f}(\vec{k}_f) \middle| \epsilon_{\mu}, r_{\mu} \middle| \phi_{\ell_i}^{m_i}(\vec{k}_i) \right\rangle = \int d^3 r R_{\ell_f}^{m_f}(r) r R_{\ell_i}^{m_i}(r) Y_{1}^{m_f}(\Omega) * Y_{1}^{m_p}(\Omega) Y_{m_i}^{\ell_i}(\Omega) \]  

(2.9)

\[ = \int d^3 r R_{\ell_f}^{m_f}(r) r R_{\ell_i}^{m_i}(r) \int d\Omega Y_{1}^{m_f}(\Omega) * Y_{1}^{m_p}(\Omega) Y_{m_i}^{\ell_i}(\Omega) \]  

(2.10)

\[ = R \times A \]  

(2.11)

The evaluation of these two factors will be addressed in the following subsections.

### 2.2.1.1 The Angular Integral

The angular integral contains all of the dependence of the experimental geometry in the matrix element sum. Each of these integrals is proportional to Clebsch-Gordon coefficients. Furthermore, the angular integral is zero for many of the terms in the sum which do not conserve angular momentum. To determine which terms are zero, one projects the initial electronic state into a linear combination of atomic orbitals and the final electronic state as a free electron. This
leads to a set angular momentum conserving dipole selection rules for the photoemission process (outlined in Chapter 1): \( \Delta l = \pm 1 \) and \( \Delta m = m_{\text{initial}} - m_{\text{photon}} \), where \( \Delta l \) is the change in total angular momentum from initial and final state, \( \Delta m \) is the change in the \( z \) component of angular momentum between initial and final state, \( m_{\text{initial}} \) is the \( z \) component of the angular momentum of the initial state, and \( m_{\text{photon}} \) is the \( z \) component of the electromagnetic radiation which can take values of \(-1, 0, +1\). This is schematically shown in figure 2.2.

To determine \( m_{\text{photon}} \), one must project the polarization unit vector into a spherical harmonic basis (with \( \ell = 1 \)). The global coordinate system of the calculation used for this transformation is shown in fig 2.3 where the sample surface normal facing the incoming light defines \( \hat{z} \) and \( \hat{x} \) is chosen along with a crystal plane of one’s choosing. The projection can then easily be done using the following relations:

\[
\hat{x} = \sin(\theta) \cos \phi \quad \rightarrow \quad p_x = \sqrt{\frac{1}{2}} (Y_{1}^{-1} - Y_{1}^{1}) = \sqrt{\frac{3}{4\pi}} \cdot \frac{x}{r} \tag{2.12}
\]

\[
\hat{y} = \sin(\theta) \sin \phi \quad \rightarrow \quad p_y = i \sqrt{\frac{1}{2}} (Y_{1}^{-1} + Y_{1}^{1}) = \sqrt{\frac{3}{4\pi}} \cdot \frac{y}{r} \tag{2.13}
\]

\[
\hat{z} = \cos(\theta) \quad \rightarrow \quad p_z = Y_{0}^{0} = \sqrt{\frac{3}{4\pi}} \cdot \frac{z}{r} \tag{2.14}
\]

It is important to note that in this global coordinate system the Cartesian components of the polarization vector depend not only on whether the polarization is \( s, p, C^+ \), etc., but also on the Poynting vector relative to the sample, henceforth referred to as \( \Omega \).

Throughout the calculation, one will be computing many angular integrals of the same form. Therefore it is computationally advantageous to calculate once and store a "look-up" tensor of all possible combinations of initial state, final state, and light spherical harmonics. Especially, due to the dipole selection rules, because this matrix is sparse. As mentioned earlier, information about the initial state orbital composition can be extracted by applying these selection rules to the analysis of the ARPES intensity on varying experimental geometries.
Figure 2.2: Illustration of dipole-allowed angular transitions with linear polarized light. The top panel shows the non-zero partial wave terms in the final state expansion (orange) if the initial state is a $p_z$ orbital (blue) and the light is polarized along the $\hat{z}$ axis ($m_{\text{photon}} = 0$). The bottom panel illustrates the allowed transitions from a $p_y$ orbital using $\hat{y}$ polarized light.
Figure 2.3: The coordinate system of the ARPES simulation. The sample surface normal is defined by \( \hat{z} \). \( \hat{x} \) is chosen to be along a crystal symmetry direction. The red arrow indicates the incident photon beam at an angle \( \Omega \) with the surface normal.
2.2.2 The Dynamic Integral

The dynamic integral is given by:

\[ R = \int dr R^f_\ell (r) r R^i_\ell (r) \]  

(2.16)

where \( R^f_\ell (r) \) and \( R^i_\ell (r) \) represent the dependence on the wave functions from the radial distance from the atomic site for the final and initial state respectively. The initial state is assumed to be a hydrogenic wave function given by:

\[ \psi_{n\ell m}(r, \theta, \phi) = \sqrt{\left( \frac{2}{na^*_0} \right)^3 \frac{(n - \ell - 1)!}{2n(n + \ell)!}} e^{-\rho/2} \rho^\ell L^L_{n-\ell-1}(\rho) Y^m(\theta, \phi) \]  

(2.17)

where \( \rho = 2r/na^*_0, \ a^*_0 = 4\pi \epsilon_0 h^2/\mu e^2, \ L^L_{n-\ell-1}(\rho) \) are the generalized Laguerre polynomials, and \( Y^m(\theta, \varphi) \) are the spherical harmonics. Therefore, we can identify \( R^i_\ell (r) \) as:

\[ R^i_\ell (r) = \sqrt{\left( \frac{2}{na^*_0} \right)^3 \frac{(n - \ell - 1)!}{2n(n + \ell)!}} e^{-\rho/2} \rho^\ell L^L_{n-\ell-1}(\rho) \]  

(2.18)

For the free electron final state, a partial wave expansion is used:

\[ R^f_\ell (r) = 4\pi \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} i^\ell j_\ell(k fr) \]  

(2.19)

where \( j_\ell(k r) \) is the spherical Bessel function of the first kind. From this equation’s dependence on \( k_f \) (and hence \( E_{kin} \)), one can see how the dynamic integral gets its name.

The dynamic integral contains all of the photon energy dependence in the photoemission matrix element sum. It is a weighting function for the \( \ell_f = \ell_i + 1 \) and \( \ell_f = \ell_i - 1 \) channels which interfere with each other and can drastically change the overall strength of the angular distribution of photoemission intensity at a given angle. However, the functions in the dynamic integral are not a function of \( m_i, m_f, \) or \( m_{photon} \). Therefore, this factor is unaffected by the geometry which is consistent with the assumption of a separable wave function. Consider the case of photoemission from the \( p_z \) orbital with \( \hat{\epsilon} = \hat{z} \), as illustrated in fig 2.2 (top). Fig 2.4 shows the weighting factors from the dynamic integral for each of the allowed outgoing partial waves, \( s \) and \( d_z \). At low photon energies (low \( E_{kin} \)) the terms have opposite signs and destructively interfere. \( |I_s + I_d|^2 \) is
proportional to the total photoemission cross-section and is shown as the green curve. It has a sharp minimum where the two terms strongly destructively interfere. This minimum is referred to as a Cooper minimum. Fig 2.5 shows the cross section for various initial state orbitals. Fig 2.6 shows the angular distribution of photoemission intensity as a function of $E_{\text{kin}}$ from the previously discussed geometry ($p_z$ initial state, $\hat{\epsilon} = \hat{z}$). The overall shape of the angular distribution of intensity changes drastically on either side of the Cooper minimum.

Destructive interference is not the only cause of Cooper minimum, however. If it were, $s$ orbitals would be forbidden to have a Cooper minimum as they only photoemit into a single final state $p$ channel. The radial part of the atomic wave function has $n - \ell - 1$ nodes, which occur on the length scale of the Bohr radius $a_0$. If the final state wavefunction (proportional to $j_{\ell}(kr)$) oscillates on the same length scale, there will be a strong suppression of the dynamic integral [22]. Note that, in general, all of the cross sections decrease with increasing photon energy (fig 2.5). Albeit, not at equal rates. This implies that one can increase their experimental sensitivity for a given state by tuning to a favorable photon energy, even in a non-resonant case.

### 2.2.3 Spectral Function

The spectral function in eqn. [2.7] contains the information on the dispersion of the energy eigenstates of the system. It is independent of extrinsic factors such as geometry and photon energy. Therefore it can be calculated using any applicable method (tight binding, Density Functional, etc..) and dropped into the simulation. In this thesis, I focus only on the use of tight binding calculational methods as they are fast and widely applicable.

The form of the spectral function is given by eqn. [1.10]. The Green’s function has poles at momentum and energy of the eigenstates of the system, which can be seen by examining the denominator. For infinitely-long lived states in the non-interacting limit, where tight binding is performed, these poles are Dirac delta functions. However, in realistic systems measured with realistic resolution, these peaks are broadened. In order to more closely match experiments a small imaginary part is added to the tight binding dispersion to broaden the intensity peaks. An example
Figure 2.4: Numerical weights of the final state partial waves from the dynamic integral as a function of $E_{kin}$ for the case of fig 2.2 top. The initial state is a $p_z$ orbital and the polarization vector is $\hat{z}$. The allowed partial waves are $s$ and $d_{z2}$. The relative phase of the two partial waves flips sign as a function of photon energy and can create destructive interference of the outgoing free electron wave function.
Figure 2.5: Evaluation of the dynamic integral (proportional to the total photoemission cross-section) as a function of $E_{\text{kin}}$ of the photo-electron for various initial state atomic orbitals. The sharp minima are known as Cooper minima. The dynamic integral decreases at higher photon energies which is consistent with the lower count rates observed in ARPES at high photon energies.
Figure 2.6: Angular dependence of the photoemission intensity as a function of $E_{kin}$. Because the interference of final state partial wave terms is strongly dependent on the kinetic energy, the angular distribution of the photoemission intensity can change drastically near a Cooper minimum. Note: the data have been rescaled as to normalize out the overall decreasing cross section as a function of $E_{kin}$. 

<table>
<thead>
<tr>
<th>$E_{kin}$ (eV)</th>
<th>1</th>
<th>5</th>
<th>10</th>
<th>20</th>
<th>40</th>
</tr>
</thead>
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dispersion and spectral function for a fictitious two dimensional material, whose dispersion is given by $E(\mathbf{k}) = \sin^2(k_x) + \sin^2(k_y) - 0.75$, is shown in fig 2.7. The left panel shows the dispersion at a low, but finite, temperature which broadens the edge of the Fermi distribution at $E = E_F$ slightly. The imaginary part of the dispersion is a constant 0.1 eV everywhere. The right panel shows the 2D Fermi surface as a function of $k_x, k_y$.

### 2.2.4 Angular Dependence of the Photoemission Intensity

The photoemission intensity is given in eqn 2.7. As discussed earlier, one must compute the square of the sum of terms in the matrix element and, in general, will end up with a complicated interference pattern resulting from matrix elements of all of the initial state orbitals present and all of their allowed final state channels. Angular intensity patterns have been shown in figs 2.4 and 2.6. In actual ARPES experiments, the angle between the detector and the sample defines which $k_i$ will be measured by in-plane momentum conservation and, in general, the orbital composition of the wave function also varies with $k_i$. Therefore, one cannot simply move the detector to maximize the intensity from a specific orbital because they would also change which initial state orbitals they are measuring. However, because $k_i$ is only unique up to a reciprocal lattice vector $G$, one can move to a higher Brillouin zone and measure the photoemission intensity from $k_i + G$ while maintaining the constancy of the initial state. Experimentally, this is observed as a change in intensity between Brillouin zones.

Another implication of photoemission from solids is that the work function severely limits the angular window of photoelectrons sampled. $k_z$ must be high enough so that the electron escapes the sample work function and can be measured at all. Therefore, most photoelectrons measured in ARPES experiments are within the first Brillouin zone for the in-plane momentum components, but from the second or higher Brillouin zone along the $k_z$ direction; near-normal emission. Furthermore, the photoemission matrix element is, in general, higher along the axis of polarization. This implies that when matrix element effects are not the focus of investigation, $p$ polarized light will give higher photoemission intensity than $s$ polarization.
Figure 2.7: Example of a simulated spectral function of the dispersion \( E(\vec{k}) = \sin^2(k_x) + \sin^2(k_y) - 0.75 \). Left panel: dispersion cut \((E \text{ vs } k)\) along the \( k_y = 0 \) plane. Right panel: constant energy cut taken at \( E = E_F \).
Figure 2.8: Example of simulated ARPES spectra using the same example spectral function presented in Fig 2.7. Top Row, Left (Right) panel: dispersion cut ($E$ vs $k$) along the $k_y = 0$ plane using $p$ ($s$) polarized light. The $s$ polarized transition is dipole forbidden and the signal is zero. Bottom Row, Left (Right) panel: Constant energy surface at $E = E_F$ as measured with $p$ ($s$) polarization.
An example simulated ARPES spectra are shown in fig 2.8. This simulation uses the same spectral function as the example in fig 2.7 but now modulated by the square of the photoemission matrix element assuming a pure s orbital composition throughout k space. In this simulation, the Poynting vector of the light is in the x/z plane and forms a 45° angle with the surface normal (typical for most ARPES experiments). The top row is the same dispersion of fig 2.7 measured with p polarized light (left panel) and s polarized light (right panel). Note, the intensity color scales are equal and the bands are unobservable with s polarization as a simple symmetry analysis would predict. The p polarized measurement of the dispersion is asymmetric about $k_y = 0$. This asymmetry arises from the angle of incidence of the light. The bottom row shows the Fermi surface measured with both linear polarizations (p left panel, s right). Again, the p polarized light shows the same asymmetry about $k_x = 0$, while the s polarized light is 2-fold symmetric. This is due to the fact that the polarization vector always lies in the plane of the sample surface, regardless of angle of incidence.

The symmetry rules used in linear dichroism experiments, presented in the section 1.3.1, can be connected to the dipole selection rules. Consider again the case of an initial state consisting of a pure $p_z$ orbital. Fig 2.6 shows the angular distribution of the intensity using $\hat{\epsilon} = \hat{z}$ for a linear polarization ($\pi$ polarization in the simulation coordinate frame). If the experiment were repeated with $\sigma$ polarization ($\hat{\epsilon} = \hat{y}$) the dipole selection rules state that the photoemission intensity will be proportional to $|d_{yz}|^2$, which goes to zero in the x/z plane. This is precisely what the symmetry analysis would conclude. However, if one measures off the high symmetry plane slightly, there will be a non-zero intensity from this orbital. Experimentalists should keep this fact in mind while performing dichroism experiments.

Circular dichroism is also readily simulated using this technique. The polarization Jones vector is expressed as $\hat{\epsilon}_\pm = (1/\sqrt{2}, \pm i/\sqrt{2})$ and then is rotated to account for the incident angle $\Omega$. An example simulation using the same spectral function as for linear dichroism is shown in fig 2.9. However, in this simulation, the orbital composition has been changed from a pure s orbital to a coherent angular momentum state of p orbitals with $J = 1$. The reasoning behind this change
is that CD-ARPES measures the emergence of chiral orbital angular momentum in an electronic band [28]. By symmetry, a pure $s$ orbital state, used in the previous linear dichroism figure, cannot give a CD signal.

The coherent state chosen for this simulation is comprised solely of $p$ orbitals and therefore has a total angular momentum of $J = 1$ (electron spin is ignored here). The state is defined by an angular parameterization on the unit sphere given by the common polar and azimuthal coordinates: $\theta, \phi$. The definition for such a state is:

$$|\hat{n}\rangle = \frac{1}{2} e^{-i\phi} |\ell = 1, m = +1\rangle + \frac{1}{\sqrt{2}} |\ell = 0, m = 0\rangle + \frac{1}{2} e^{i\phi} |\ell = 1, m = -1\rangle$$

This is an eigenstate of a 2D square lattice consisting of $p$ orbitals with an inversion symmetry breaking electric field applied along the normal direction [28]. Because the gradient in potential due to the work function is largest at the surface of a material, an electric field oriented along the surface normal is commonplace in ARPES experiments. States with different $\hat{n}$ have different dipole moments as well as different energy costs dependent on the relative alignment of their dipole moments to this external field. It can be shown that to minimize electrostatic energy, $\hat{n}$ must be parallel to $\vec{k} \times \hat{z}$ [28]. This gives a chiral structure for $\hat{n}$ as one moves around the Brillouin zone as shown in fig 2.9. Without the inversion symmetry breaking field, different $|\hat{n}\rangle$ would be degenerate, and therefore unresolvable by CD-ARPES. Much like circular dichroism, which manifests in absorption spectroscopy for chiral molecules, CD-ARPES detects the existence of chiral symmetry breaking in electronic structure.
Figure 2.9: Example of simulated circular dichroism ARPES spectra using the same example spectral function presented in fig 2.7. The orbital composition of the bands is \( \cos(\theta) |p_x\rangle + i \sin(\theta) |p_y\rangle \), where \( \theta \) is defined as \( \arctan(k_y/k_x) \).
Chapter 3

Extreme Magnetoresistance and Topology in the Lanthanum Monopnictides

3.1 Introduction to XMR

The binary compounds containing lanthanum and a single pnictogen element in a rock salt crystal structure have recently drawn attention in the literature for both demonstrating Extreme Magnetoresistance (XMR) as well as possible topological states and surface Dirac Fermions [29, 30, 31, 32, 33, 34]. Here magnetoresistance (MR) is defined by the ratio $R(H)/R(0)$, where $R$ is the electrical resistance and $H$ is the applied magnetic field. In transition metal oxides, both Giant and Colossal Magnetoresistance have been observed [35, 36] and implemented in non-volatile magnetic memory [37], as magnetic sensors [38], as well as proposed spin valves in spintronics [39]. Extreme magnetoresistance (XMR) is distinct from these well-understood phenomena in that it is exhibited in materials where $R(0)$ is small, i.e., good metals [40]. The effect also spans several classes of materials including Dirac semimetals [41, 42], Weyl semimetals [43, 44, 45], and layered semimetals [46, 47, 48].

The complete physical description of the mechanism responsible for XMR is currently not understood. Quantum oscillation studies in the partially electron-hole compensated LaSb and LaBi have shown that the electrical transport at low temperature and applied magnetic field is dominated by ellipsoidal electron pockets [40]. Due to the spin-orbit coupling in both of these materials, electronic structure calculations predict mixing between the La $d$ orbital and the pnictogen $p$ orbital bands, which compose the pocket [30, 40]. The mixing of these two bands, in turn, creates an orbital composition crossover at $E_F$ on this pocket. The existence of this crossover is found in
many of the materials which exhibit XMR \cite{40}. Furthermore, topological surface states have been suggested as a necessary ingredient for XMR \cite{49, 50}. Several of the materials which demonstrate XMR have been confirmed or predicted to be, topologically non-trivial \cite{43, 44, 45, 49} indicating, at minimum, a correlation between the two phenomena.

Electronic structure calculations on the lanthanum Monopnictides indicate that these materials may also be topologically non-trivial. In these calculations, the $d$ and $p$ bands cross only once along the $\Gamma - X$ direction and therefore will be inverted at $X$ \cite{30}. This inversion, along with the existence of inversion and time reversal symmetries in these systems, would result in a non-trivial $Z_2$ invariant for the lanthanum Monopnictides which would classify them as topological semi-metals (TSM). TSMs are extensions of topological insulators (TIs) where degenerate crossings between several bulk bands are protected by a fundamental symmetry of the material \cite{51}. These same calculations show the degree of band inversion in a given lanthanum Monopnictide compound is dependent on the pnictogen species present. Furthermore, these results predict that the inversion magnitude decreases with a smaller atomic number, but is present in all compounds in the family except LaN \cite{30}.

Strengthening the connection between topology and XMR is the fact that the $\rho(T)$ profile of XMR in TSMs looks similar to the $\rho(T)$ profile of topological insulators (TI) whereby decreasing temperature, resistivity shows an upturn followed by a plateau \cite{52, 53}. In TIs, the upturn is assigned to a metal-insulator transition and the plateau is assigned to topological surface states. This similarity between the XMR profile and the TI profile opened a debate over the possibility of XMR profile being rooted in the topological properties of TSMs \cite{54, 55, 56, 57}.

However, there have been several studies in the literature that suggest XMR is a semi-classical transport effect of nearly compensated semi-metals \cite{58, 59, 60, 61, 62, 63, 64}. Semi-metals are characterized by small and often compensated electron and hole carrier densities ($n_e/n_h \approx 1$) \cite{65}. In elemental semi-metals, such as bismuth, compensation between high mobility electron and hole carriers reduces the Hall field and produces a large magnetoresistance \cite{66, 67, 68, 69, 70}. A reduced Hall field fails to counteract the Lorentz force that bends the trajectory of charge carriers
in a magnetic field, resulting in a large MR \[65\].

This chapter begins with a presentation of ARPES measurements as well as bulk electronic structure calculations for LaSb, LaBi, and LaAs. Three-dimensional mapping of \(k\) space is performed and shows good but not complete agreement with the Density Functional electronic structure calculations, with the most important differences concerning the inversion of the bands at the X point, which impacts the topological order of these materials. A full mapping of \(k_z\) using ARPES over several Brillouin zones (BZ) shows the presence of several surface effects in the spectra from both LaBi and LaSb, including unique surface states in LaBi. We make a comparative study of the surface states in both materials with a discussion on the topological nature of these surface states. Furthermore, we utilize the selection rules of the photoemission matrix element to directly extract the orbital composition of the electron pockets found in the bulk of these materials. We report a clear band inversion in LaBi, while LaSb is near a band inversion, and LaAs is clearly non-inverted. Previous ARPES studies have been carried out on LaBi\[34, 50, 49\] and LaSb\[49, 30\] focusing on their surface states and corresponding topological classification. However, the topological class of these materials is inferred from calculations and the existence of "Dirac-like" dispersions in each of these reports. The consensus reached by refs. \[50, 49, 34\] is that LaBi is topologically nontrivial. Reference \[32\] claims LaSb to be topologically trivial while ref. \[49\] argues that LaSb is non-trivial.

Lastly, I will present transport measurements from LaAs, including quantum oscillations, magnetoresistance, and Hall effect. Using DFT calculations, I predicted that the topological phase transition would exist between LaBi and LaAs. Our collaborators, the group of Fazel Tafti at Boston College, synthesized single crystal samples of this material in which they performed the transport measurements. My analysis of their quantum oscillation measurements showed that LaAs is an almost perfectly compensated semi-metal, contrary to what was previously believed. A multi-band fit was used to show that the larger Hall field and the smaller magnetoresistance in LaAs, when compared to LaBi and LaSb, are due to the electron-hole mobility mismatch instead of a lack of compensation. This supports the idea that XMR is driven by semi-classical transport.

From direct measurement, we show that LaBi has a band inversion, LaSb is on the verge
Figure 3.1: The top left panel is a schematic of the XMR experimental geometry. The magnetic field is applied perpendicular to the electric field and the magnetoresistance is measured along the electric field $\rho_{xx}$. The remaining panels are resistivity vs. temperature profiles published in the literature for various materials. Their profiles are characteristic XMR resistivity profiles. This indicates that the effect is more widespread than just in the lanthanum monopnictides.
Figure 3.2: Density functional calculations on the lanthanum monopnictide family. These calculations predict a persistent band inversion from LaBi to LaP, indicating non-trivial topology in most of the family. LaN is predicted to be a Dirac semi-metal with a much different lattice constant than the larger family members. Reproduced from: [30]
of inversion, and LaAs is non-inverted. This demonstrates a topological phase transition within
the family of lanthanum Monopnictides. As for implications to XMR, we note that only LaBi is
topologically non-trivial. From these facts, we conclude the possibility that topology is an essential
ingredient for XMR is unlikely.

3.2 Results

Single crystals of LaBi, LaSb, and LaAs were cleaved in-situ along a 100 crystal face. The
presence of a surface termination allows for the possibility of surface states which follow the sym-
metries of a surface Brillouin zone (SBZ) that is different from the bulk Brillouin zone, as shown in
black (bulk) and blue (surface) in Fig. 3.3(C). Note that when cleaved on the 100 surface, Γ and
one of the three bulk X points are located at \( k_{\parallel} = 0 \). Therefore, when projected along the \( k_{\perp} \) (\( k_z \))
direction, they both end up at the same high symmetry point in the SBZ: \( \Gamma \). Similarly, the bulk
\( X_2 \) and \( W \) points both project to the surface \( M \) point. These projections to the SBZ require an
in-plane back folding of states in the SBZ relative to bulk states, as will be discussed in more detail
later in the paper, with these surface states or surface resonances needing to be distinguished from
topologically induced surface states.

Results of Density Functional calculations for LaBi and LaSb materials are presented in
Fig. 3.3(A), showing the bulk Fermi surface to have two hole pockets centered on the Γ point
and ellipsoidal electron pockets centered on the \( X \) points. These reduced dimensionality electron
pockets have been indicated to dominate the transport signal in quantum oscillation experiments
at low temperature and high magnetic field, the same regime of phase space as XMR [40].

The experimental Fermi surfaces as captured by our ARPES measurements are very similar
to the calculations, as shown in panels B and D. Starting from the stacked three-dimensional bulk
Brillouin zones shown in Fig. 3.3(E), we may take in-plane experimental cuts (panel B), or we
may hold an in-plane value such as \( k_y \) fixed, and take a "vertical" slice in \( k_z \) such as is shown in
panel D. The vertical slices in which \( k_z \) is varied allow us to accurately select the high symmetry
in-plane cuts (for example, the cuts of panel B were taken at \( k_z = 6 \ast (2\pi/a) \), equivalent to \( k_z = 0 \)).
Furthermore, these cuts allow us to distinguish between true bulk states, which disperse in \( k_z \) and states localized near the surface, which do not. More details of this will be discussed in a later section, including in the Supplementary Materials, which shows the conversion from photon energies to \( k_z \) values.

Visible in panel B are the "jack-shaped" hole pockets on the Fermi surface, centered at the \( \Gamma \) points \((k_x, k_y, k_z) = (0, 0, 6), (0, 2, 6), (2, 0, 6), (2, 2, 6)\) in units of \( 2\pi/a \), as well as the many in-plane ellipsoidal electron pockets on the Fermi surface at the bulk \( X_1 \) and \( X_2 \) points \((k_x, k_y, k_z) = (0, 1, 6), (1, 0, 6), (1, 2, 6), \) etc. These are exactly as expected from the bulk calculations. The out-of-plane ellipsoids are visible at the \( X_3 \) point, i.e.: \((k_x, k_y, k_z) = (1, 1, 6), (1, -1, 6), \) etc. These in-plane momenta correspond to \( \Gamma \) in the SBZ, as do \((1, 1, 6)\) and \((1, -1, 6)\) and a superposition of spectral weight can be seen around the circular cross-section of the ellipsoid at \( X_3 \) from \( \Gamma \), resulting in a faint jack-shape. This weight in panel B should be considered as originating from the surface which back-folds spectral weight to the smaller SBZ and/or projects weight to surface states and surface resonances, as will be discussed later.

Understanding the orbital character of the bands is a powerful method to determine the topological classification of a material with inversion and time reversal symmetries[71][72]. Projecting our Density Functional calculations to an atomic orbital basis, we see that for both LaBi and LaSb, the X-point ellipsoidal bands near the Fermi energy are composed of both La \( d \) orbitals and pnictogen \( p \) orbitals, as shown in Fig. 3.5(E). The tips of the ellipsoidal electron pockets are majority composed of \( d \) orbitals, while the midsections of the ellipsoids are of a dominant \( p \) orbital character. This is consistent with other calculations on the lanthanum monopnictides [40][30].

We employ polarization dependent ARPES to confirm the orbital character determined by density functional theory (DFT) calculations. Applying symmetry arguments to the photoemission matrix element [8][73], in conjunction with dipole selection rules, allows us to extract the parity and atomic orbital composition of the electronic wavefunction. This is achieved by comparing the photoemission intensity when the perturbing electric field is even versus odd in the plane of light incidence.
Figure 3.3: Determination of the Fermi surface by k space mapping. (A) Calculated Fermi surface for LaBi (top) and LaSb (bottom). Both compounds have ellipsoidal electron pockets centered on the X points and two hole pockets centered on the Gamma point. (B) Fermi surfaces measured in the $k_x$, $k_y$ plane at $k_z = 6.0 (\pi/a)$. (C) Schematic of the Brillouin Zone projected to the surface Brillouin Zone. (D) Measured Fermi surfaces from ARPES in the $k_x$, $k_z$ plane covering two Brillouin zones in the $k_z$ direction with $k_y$ fixed at 0. (E) Planes of fixed $k_y = 0$ (yellow) and $k_z = 6 (\pi/a)$ (green) illustrate the location of the constant energy surfaces in B and C which cut through the tessellated truncated octahedra.
Figure 3.4: $k_z$ dispersions that are consistent with our bulk DFT calculations. (A) Electronic dispersions of the $\Gamma X$ high symmetry direction measured in out of plane momentum (left panel) and in-plane momentum (right panel). The two directions agree nicely as expected for the measurement of bulk states in a cubic crystal. Measuring the MDC widths of the bands along the $k_x$ direction, and assuming they are dominated by intrinsic broadening, we can estimate our $K_z$ resolution to $\sim 0.2 \text{ Å}$. (B) Fermi energy cut in the $k_x/k_z$ plane. The red (purple) line indicates where the dispersion in the left (right) panel of (A) is located. (C) Electronic dispersion over 2 zones of the $X - W - X$ high symmetry direction measured along the $k_z$ momentum axis. We again observe dispersive features over several zones. (D) Fermi surface in $k_x/k_z$ plane. The red line indicates the location of the cut is shown in (C) along the $k_z$ momentum axis.
Fig. 3.5(B) and (C) show the ARPES results for different polarizations and experimental geometries, focusing on the ellipsoidal pockets at the X points. To change the relative orientation of the electron pockets to the Poynting vector of the light, we change the photon energy to move between different $k_z$ planes, namely the $X_2$ point at $k_z = 5(2\pi/a)$ (3.5B and 3.5C, left panel) and the $X_1$ point at $k_z = 6(2\pi/a)$ (3.5B and 3.5C, right panel). This allows us to minimize tilting away from the high symmetry plane of the crystals, keeping the symmetry analysis as pure as possible.

For $\sigma$ polarized light (Fig 3.5B), the central regions of the ellipses are not visible, for either orientation. Via the dipole selection rules, these results imply a lack of in-plane $p$ orbitals along the midsection of the ellipse (see Supplemental Materials for more details). The tips of the ellipses give non zero intensity at $X_1$, and very faint intensity at $X_2$. We attribute this faint intensity at $X_2$ to be from impure $\sigma$ polarization due to the nearly $10^\circ$ tilting of the sample relative to the Poynting vector at this $k_y$ value. These results for the tips of the ellipsoids require a $d$ orbital odd under reflection in the $k_z/k_x$ plane. To determine the specific $d$ orbital we note that crystal symmetry requires each ellipsoidal tip to transform into each other under rotations. The only $d$ orbital consistent with this constraint for an ellipsoidal pocket pointing in the x-direction is $d_{yz}$ (Fig. 3.5D).

When using $\pi$ polarized light (Fig 3.5C), a higher intensity signal from the central region of the ellipse is measured, regardless of the relative in-plane orientation of the ellipse to the polarization vector (i.e. both left and right plots of panel C). Using dipole selection rules we conclude the $p$ orbitals along the midsection of the ellipse must be out of plane (see Supplemental Materials). This is consistent with our previous conclusion from the $\sigma$ polarization measurement. Using $\pi$ polarization at $X_1$, again we see that the zero in intensity at the tip of the ellipse implies that the $d$ orbital there must be odd under reflection in the $k_z,k_x$ plane which is consistent with the $d_{yz}$ orbital.

From these two measurements, subsequent symmetry arguments, and our simulation we can extract the full orbital content of the electron pockets at the X points. For the ellipsoids pointing along the x-direction, the tips of the ellipsoids are composed of La $d_{yz}$ orbitals while the equators are
composed of tangential pnictogen $p$ orbitals as shown in Fig. 3.5(D). A more detailed description of this analysis is given in the supplemental materials.

Fig. 3.8 shows a detailed view of the measured dispersions along the high symmetry directions for both materials along with the surface (blue) and bulk (black) Brillouin zones. Panels A (B) and C (D) shows the raw data from the $\Gamma - X$ and $X - W$ cuts respectively for LaBi (LaSb). The second derivative of the data (panels E and F) is used to highlight the dispersive features of the raw data and is shown overlaid with a trace of the dispersions. Blue dashed lines indicate a dominant $p$ orbital character of the band as determined from the polarization-dependent ARPES experiments of Fig. 3.5, as well as from orbital-projections of our DFT calculations. Red dashes indicate a dominant $d$ orbital character, green and yellow dashes indicate different electronic states that arise due to the presence of the crystal surface and will be described in more detail later.

Panels G and H compile the measured band dispersions (dashed lines, reproduced from panels E and F) with calculated dispersions from DFT (solid red and blue lines). The calculated bands we show are nearly identical to the results from other works [30, 40], and while they have many close similarities to our experimental bulk bands, they also have some clear differences. In particular, we see that many of the calculated $p$-bands from both LaBi and LaSb are shallower in energy and have less dispersion than the experiment, and the calculated $d$ bands are deeper in energy than the experiment. Most important are the energies of the states at the $X$ point, as these determine whether these materials lie in the $\nu = 1$ topological class or not. As shown in Fig. 3.8(G), the actual agreement between experiment and theory for the LaBi bands at the $X$ point is very good, with the $d$ band, at 0.55eV, underneath the $p$ band, at 0.1eV, (inverted) by about 450 meV. This 450 meV inversion gap will be seen to host topological Dirac-like states at the surface (yellow dashed), which are presumably directly related to this band inversion.

In LaSb, the disagreements between the calculations and the experiments become much more important, as shown in panel H. The bulk bands from the Density Functional calculation (solid) show the $d$ band at 0.5 eV at $X$ to be about 300 meV below the $p$ band at 0.2 eV at $X$ (inverted), the experimental result of this inversion (dashed lines) is approximately $0 \pm 50$ meV, i.e. it is not
clear whether the bulk bands are inverted or not, therefore we describe LaSb as being on the verge of a topological transition. This will be discussed in more detail in Fig. 3.10 below.

Compared to LaBi and LaSb, LaAs is the lightest compound of the three materials. Fig 3.9 shows the ARPES results from LaAs. Panels (B) and (C) show the $\Gamma - X$ and $X - W$ cuts respectively. The bands of LaAs are clearly non-inverted and therefore LaAs belongs to the topologically trivial ($\nu = 0$) class of materials. In Fig. 3.10 we compile the evidence for the existence of a topological transition in the lanthanum monopnictides. The top row shows our density functional calculations for (from left to right) LaBi, LaSb, and LaAs along the $\Gamma - X$ direction. The calculations show a trend of a decreasing magnitude of the La $d$ band inversion over the pnictogen $p$ band as both the lattice constant and spin-orbit coupling decrease in the lighter pnictogen species, though the inversion is still present in LaAs in these calculations and others [30]. However, our measurements (bottom row) show that in moving from LaBi (left) to LaAs (right) in the pnictogen family the bands are already non-inverted.

3.3 Discussion

Due to the band inversions that are present at the 3 $X$ points, LaBi can be classified as a 3D topological semi-metal and should host Dirac-like surface states. However, different surface effects can manifest similarly in ARPES. Therefore, it is important to confirm topologically driven origins. We start with a discussion on the differing nature of surface states in ARPES, followed by the comparison of the different dominant surface states in LaSb and LaBi. Later, we discuss the results of LaAs and show it is topologically trivial. This progression between the two classes of $Z_2$ topology demonstrates a topological phase transition in the lanthanum monopnictides.

Surface states are well-defined bands in terms of in-plane momentum only and localized at the surface while obeying the symmetries of the Surface Brillouin Zone (SBZ). To be localized at the surface requires an imaginary $k_z$ component which can only be achieved if the state exists within a gap in the bulk band structure when projected along the crystal normal direction [7]. Otherwise, it will have the correct energy and in-plane component of $k$ to propagate into the crystal with a real
Figure 3.5: Determination of atomic orbitals by linear dichroism. (A) Schematic of the 3D Fermi surface relative to the constant energy in-plane momentum cuts shown below in the polarization dependent ARPES results from the electron pockets at $X$. The measurement plane through $X_3$ and $X_2$ on the zone edge ($k_z = 5 \ (2\pi/a)$) is shown in the left panel. The measurement plane through $\Gamma$ and $X_1$ ($k_z = 6 \ (2\pi/a)$) is shown in the right panel. (B) ARPES measurements of the Fermi surface using $\pi$ polarized light incident from the left and (C) $(\sigma)$ polarized light incident from the left. $\pi$ polarization produces a strong signal from the center of the ellipse, while $\sigma$ polarization gives a stronger signal from the ends. We conclude that dominant orbital composition of the ellipsoid pocket is that of the schematic shown in (D). Tangentially ordered $p$ orbitals compose the central region of the prolate ellipsoid with $d_{yz}$ orbitals composing the ends. (E) Total $p$ vs. total $d$ orbital contribution to the electron pocket shown at $E_F$. (F) Relative contributions from different $p$ orbitals to the highest energy occupied band along the X-W direction. $k_F$ is indicated in the diagram to show where the ARPES measurements were performed. The $p_z$ orbital is the dominant contributor to the wavefunction at $E_F$ along this $k$ direction.
Figure 3.6: Tabulation of experimental geometries and ARPES spectra used to determine the orbital texture of the electron pockets near X. Each quadrant contains a schematic of the experimental geometry, ARPES spectra in the $k_x/k_y$ plane, and symmetry arguments used to determine which orbitals are present. In the schematics, the cyan planes are the $k_x/k_y$ plane where the iso-energy ARPES cuts are measured. The grey planes are the photoemission mirror plane ($k_z/k_x$ plane). The purple planes are the plane formed by the Poynting and polarization vectors. The ARPES results are of the $k_x/k_y$ plane at the Fermi energy of the electron pockets near $X_1$ (right column) and $X_2$ (left column). The top row presents the configuration for sigma polarization and the bottom row for $\pi$. The left column corresponds to measurements taken near $X_1$ while the right corresponds to $X_2$. Each set of symmetry arguments are given for the ellipsoidal body (where $p$ orbitals are dominant) and the ellipsoidal tip (where $d$ orbitals dominate). Note that the final state wavefunction of the photoemitted electron is always even with respect to reflections in the photoemission mirror plane, $P$. 

Final state always even w.r.t $P$
value for $k_z$ and will no longer be damped and localized to the surface. In contrast to this, bulk states are well-defined bands in all three $k$ dimensions and respect the symmetries of the truncated octahedron shaped BZ.

Surface resonances are states formed from a mixing due to a degeneracy of a surface state and a bulk state. These states propagate into the crystal while maintaining an increased amplitude near the surface. Because of the different symmetry of the SBZ to the bulk BZ, these states will be back-folded relative to the bulk BZ (both in-plane and along the $k_z$ direction), which will give them the correct symmetry of the SBZ when viewed in-plane.

Because of the differences in real space localization of these three states, surface states are often differentiated from bulk states by considering $k_z$ dispersions. Bulk states will follow the full 3D symmetry of the lattice (FCC) which, due to cubic symmetry, will have identical in-plane and out of plane dispersions. Surface states will be seen to not disperse over a large range of $k_z$ values; a consequence of the uncertainty principle. Surface resonances may show a slight $k_z$ dispersion due to their partial bulk state composition.

Complicating the analysis of $k_z$ dispersions to delineate between bulk states and surface resonances, is the photon energy dependence of the photoemission matrix element. This effect can drastically change the signal to background contrast of a given band as a function of photon energy. This manifests in the data as states that seem to appear and disappear in $k_z$ which can look similar to a true $k_z$ dispersion. Furthermore, along the $\Gamma - X$ direction, bulk states and surface resonances can have similar in-plane dispersions, making discrimination more difficult. A bulk state must have $k_z$ dispersion while following the periodicity of the BZ along $k_z$, while a surface state with varying intensity due a matrix element effect does not. Therefore, with a careful mapping of $k_z$ over several zones, states which have a similar in-plane dispersion as expected for a bulk state but appear at the incorrect value or periodicity in $k_z$ can be labeled as surface resonances. A demonstration of these surface resonances coexisting with bulk states can be seen in the main text figure 1B at $k_x = 1(2\pi/a), k_y = 1(2\pi/a)$ for both LaBi (top panel) and LaSb (bottom panel). Here the hole pocket which should be centered on $\Gamma$ is visible at $X = X_3$. The SBZ has a smaller area in the
For LaSb, there exist unique surface states at the $X$ point that are not due to a back-folding of bulk states. Figure 3.7 shows a spectrum taken along the $W - X - W$ direction where there are clear Dirac-like states with linear dispersion and, to within experimental energy resolution, a gap-less crossing. The surface nature of the states can be established by considering two pieces of evidence from the data.

1. The linearly dispersing states below the crossing point exist in a bulk band gap for projections to the surface along that direction, i.e., along the $W - X - W$ direction.

2. The centroids of the bands above (fig. 3.7 C) and below (fig 3.7 D) the crossing point are constant in $k_z$ to within $+/-.04\ \AA^{-1}$ over a range of $\sim0.65\ \AA^{-1}$ (roughly $2/3$ of the Brillouin zone in the $k_z$ direction).

As will be discussed below the effective $k_z$ resolution is significantly worse than $.04\ \AA^{-1}$, so these states should be considered non-dispersive.

To confirm the second point, we must first determine the $k_z$ resolution of the experiment. This is achieved by utilizing the symmetry of the FCC crystal structure and measuring the MDC width of bands dispersing in the $\Gamma - X$ direction both along the $k_z$ and $k_x$ axes. The in-plane momentum resolution of the electron analyzer at 120 eV photon energy ($0.01\ \AA^{-1}$) is negligible compared to the MDC line width of the bands ($\sim0.1\ \AA^{-1}$). Therefore we proceed with the assumption that the line width is determined purely by intrinsic broadening. Remeasuring the MDC widths of the same bands in the $k_z$ direction, returns widths of $\sim0.2\ \AA^{-1}$. From this line of reasoning, we estimate that the $k_z$ resolution of our experiment is approximately $0.17\ \AA^{-1}$, which is a reasonable amount considering the finite probe depth of an ARPES experiment. We can conclusively rule out a finite $k_z$ resolution effect from a bulk state as being the cause of the large $k_z$ range over which these surface states do not disperse.
After establishing that this Dirac-like state is localized to the surface, the question of its topology remains. Given that there are two band inversions along the projection of the $X$ point to $\bar{M}$ in the SBZ there can not be a single Dirac cone at this $k$ point. However, there still exists the possibility of two degenerate Dirac cones that have an unresolvable mixing gap given our finite experimental energy resolution of $\sim 15$ meV. Evidence for such a double degeneracy has been shown in [49].

Fig 3.8(C) shows clear evidence of a Dirac-like dispersion in LaBi centered at the $X$ point ($\bar{M}$ point in the SBZ), which is not present in the bulk Density Functional calculations. To prove that this state is, in fact, a topological surface state (TSS) one must demonstrate the correct number of band inversions exist in the bulk band structure in addition to confirming the state in question is localized to the surface. Projecting the bulk density of states of LaBi along the $W - X$ direction to $\bar{M}$ in the [001] SBZ, one can see that there will be a 450 meV direct gap in which only a pure surface state can reside. These states exist within the bulk band gap and also do not disperse in $k_z$ from the top of the cone down to the valence band. Therefore this state must be localized to the surface.

This information, together with the existence of the band inversion, produce the conclusion that this is a TSS, consistent with previous reports [49, 50]. We label these by the yellow dashed lines in Fig 3.8E. The bulk conduction band near $X$ (shown with blue dashed lines) is still present in the ARPES data but is overlapped with the TSS at this location in Fig 3.8 panels E and G. The superposition of bulk and surface states is confirmed by considering the $k_z$ behavior. In Fig 3.3 panel D we show the Fermi surface in the $k_z/k_x$ plane. There is clear periodicity at the $X$ points, indicating bulk states (for a view of the dispersion along the $X - W - X$ direction in $k_z$ see figure 3.4 panels C and D). The existence of the superimposed TSS is made clear in figure 3.7 which shows a Dirac cone that is non-dispersive in $k_z$ and overlaps with the bulk $X$ point. Note that because the $X_3$ point will project to the $\Gamma$ surface point of the [001] surface, one also should expect a very low-intensity topological surface state there at the same energy, though the matrix element for observing this state is strongly suppressed in our data, which emphasize the states at
In LaSb the states observed in ARPES that are not present in DFT calculations are of a separate nature. The same band inversion found in LaBi along the $\Gamma - X$ direction is predicted to exist in our own DFT calculations (Shown in fig 3.10). However, there are conflicting DFT and ARPES studies in the literature that claim the existence of, or lack thereof, a TSS in LaSb. Experimental results (Fig. 3.8 F)) show that LaSb is very near the critical point of a band inversion at $X$, however, we observe no obvious TSS. Although Fig. 3.8 B and Fig. 3.8 D) appear to show Dirac-like states at $X$, we find that these are instead replica bands of the bulk dispersion back-folded due to the presence of the crystal surface (which has a smaller, and therefore back-folded Brillouin zone compared to the bulk), which are shown as green dashed lines in Fig 3.8 F. These back-folded states explain all of the “extra” observed spectral features not predicted by bulk DFT calculations. The assignment of all bands in LaSb to either bulk or surface-back-folded bands means there is no evidence of a separate Dirac-like TSS observed in LaSb, in contrast to the case of LaBi which does have the additional TSS.

An important consequence of the LaAs measurements is that the bands can be non-inverted and still preserve the mass anisotropy and orbital texture of the ellipsoidal electron pockets at $X$. If the occurrence of XMR in the LaBi and LaSb were due to the topological non-triviality of these compounds and not the orbital crossover on the electron pockets, then LaAs is an ideal test case for determining the role of topology in the mechanism for XMR in the lanthanum monopnictides. At this time we are unaware of any studies of ARPES or XMR in the lighter siblings LaP, or LaN.

3.4 Transport on LaAs

Figure 3.11 shows $\rho(T)$ in LaAs measured at different magnetic fields. At $B = 9$ T, with decreasing temperature, $\rho(T)$ decreases initially, then shows a minimum followed by an upturn, and eventually plateaus. With decreasing magnetic field, the resistivity upturn gradually disappears. Such behavior is a generic XMR profile. The resistivity minimum at fields above 5 T in Fig 3.11 (left panel) can be understood by comparing the energy scale of cyclotron frequency $X_1$. 
Figure 3.7: The lack of $k_z$ dispersion from the topological surface states observed at $\overline{M}$ in LaBi demonstrate surface nature of these states. (A) Fermi Surface in the $k_x/k_z$ plane over several zones. The red rectangle indicates the location where the dispersion was measured in (B). The entire range of the vertical axis corresponds to a range of photon energies from 30 eV to 180 eV. (B) Electronic dispersions along the $W - X - W$ direction show a clear Dirac cone with a Dirac point at 200 meV binding energy. (C) Constant energy cut in the $k_x/k_z$ plane corresponding to the upper red line in (B): the upper half of the Dirac cone. The circles are the peak locations from a double Lorentzian fit of the MDC’s indicating the band position. (D) Constant energy cut in the $k_x/k_z$ plane corresponding to the lower red line in (B): the lower half of the Dirac cone. For both (C) and (D), we measure no appreciable dispersion in the $k_z$ direction over nearly half of the zone width.
Figure 3.8: ARPES dispersions along the Γ - X direction for LaBi (A) and LaSb (B) as well as the X-W direction for LaBi (C) and LaSb (D). (E) and (F): 2nd derivatives of the ARPES data along Γ-X-W for LaBi and LaSb respectively. The dotted lines are traces of the band dispersions. Blue (Red) denotes p (d) orbital dominated bands. Green dashed lines denote bands which arise due to the presence of the crystal surface (SS). Yellow dashed lines indicate a TSS. In LaBi, projecting the bulk density of states to the 001 surface produces a gap at $\overline{M}$ in which the surface state resides, i.e., a true surface state. In LaSb, there is no gap at $\overline{M}$ when projecting to the 001 surface. Instead, the bands marked by green are back folded along the $k_z$ direction by $\pi/a$ by the surface. (G) and (H): Comparisons between calculated band dispersions (solid lines) and measured band dispersions (dashed lines). In LaBi (G) the band inversion at X is predicted correctly. In LaSb (H), the calculation predicts a band inversion at X, however, the experimental results suggest LaSb is at, or very near, a critical point of band inversion. (I) In-plane projection of the bulk BZ (black dashed line) and surface BZ (blue dashed line). The solid red (green) line indicates the location of the cuts in (A) and (B) ((C) and (D))
Figure 3.9: (a) Constant energy surfaces of LaAs taken at $E_F$ in the $k_x - k_y$ plane. The dashed overlay is the first Brillouin zone, the solid lines indicate the respective locations of the dispersion cuts in (B), (C), and (D). Cross-sections of the ellipsoidal electron pockets ($\alpha$) are visible at $X_1$, $X_2$, and $X_3$. Cross-sections of the hole pockets ($\beta$ and $\gamma$) are visible at $\Gamma$. (b) Dispersion along $\Gamma - X_1$, centered on the hole bands. (c) Dispersion along $\Gamma - X_1$ centered on the electron pocket along the major axis of the ellipsoid. There is no band crossing in this direction. (d) Momentum dispersive cuts along the minor axis of the ellipsoid electron pocket ($X_2 - X_3$ direction). (e) Zoomed-in dispersion along $X_2 - X_3$ at $T = 7$ K conforming the absence of a Dirac cone. (f) The Fermi surface of LaAs from DFT calculations in agreement with the ARPES picture. (g) Symmetrized constant energy surfaces taken at $E_F$ of LaAs at $T = 7$ K. (h) The same view at $T = 220$ K.
Figure 3.10: Top Row: Band structure calculations of LaBi (left), LaSb (center), and LaAs (right). Red (Blue) lines indicate bands with a dominant $d$ ($p$) orbital components. A band inversion is predicted in all three materials and therefore all are predicted to be topologically non-trivial. Bottom Row: Measured band structure of LaBi (left), LaSb (center), and LaAs (right). LaBi is still clearly inverted at $X$, while LaSb lies very near the critical point of topological triviality. The right panel shows that the un-inverted band structure in LaAs. This demonstrates a topological transition within the chemical family.
\( \hbar \omega_c = \hbar eB/m^* \) to the thermal energy \( k_B T \). As shown later, from quantum oscillations, the average effective mass on the small Fermi surfaces of LaAs is \( m^* \approx 0.15 m_e \). Therefore, MR appears below \( T^* = \hbar eB/m^* k_B \approx 80 \) K (at \( B = 9 \) T).

The presence of an XMR profile in the absence of a Lifshitz transition in LaAs is similar to LaSb \[76\] and LaBi \[77\]. However, XMR is orders of magnitude smaller in LaAs compared to LaSb and LaBi as shown in Figure 3.11(right panel). It has been shown in prior work \[75\] that the XMR magnitude correlates with the residual resistivity ratio (RRR).

At \( B = 9 \) T, the low temperature resistivity is smaller than the room temperature resistivity \( \rho(2K) < \rho(300K) \) in LaAs whereas \( \rho(2K) > \rho(300K) \) in LaBi/LaSb. Since the large magnitude of XMR in LaSb and LaBi is attributed to perfect compensation between electrons and holes \[78, 76\], we measured the Hall effect to examine the compensation in LaAs. Figure 3.11(e) shows the Hall coefficient \( R_H \) in LaAs acquires a much larger negative magnitude without sign change, different from LaSb and LaBi. This may suggest that LaAs is not compensated. However, our analysis below shows that LaAs is as compensated as LaSb/LaBi, and the difference in \( R_H \) comes from an order of magnitude difference in the relative mobilities of electrons and holes (mobility mismatch) instead of their concentrations.

For a precise measurement of the sizes of electron and hole pockets in LaAs, we studied quantum oscillations in the resistivity channel known as the Shubnikov-de Haas effect. Due to the small size of the Fermi surfaces in semi-metals such as LaAs, it is challenging to reliably extract the Fermi volumes from the ARPES spectra. For example, the electron to hole carrier concentration in YSb is estimated to be \( n_e/n_h = 0.81 \) (moderate compensation) from ARPES \[79\] whereas \( n_e/n_h = 0.95 \) (almost perfect compensation) from quantum oscillations \[80\]. Figure 3.12(a) shows the oscillatory part of resistivity \( \Delta \rho \) after removing a smooth background from the resistivity data at different temperatures. Oscillations are periodic in \( 1/B \) and their amplitudes decrease with increasing temperature. Fig. 3.12(b) shows the Fast Fourier Transform (FFT) spectrum of the oscillations at different temperatures. FFT peaks at \( \alpha_1 = 76 \) T and \( \alpha_2 = 315 \) T correspond to the smaller and the larger areas of the ellipsoidal electron pocket \( (\alpha) \). The peaks at \( \beta = 140 \) T and
Figure 3.11: (Left) Resistivity as a function of temperature at different fields in LaAs. (Center) Magnetoresistance as a function of temperature in LaAs, LaSb, and LaBi on a logarithmic scale. (Right) Hall coefficient as a function of temperature in LaAs, LaSb, and LaBi.
\[ \gamma = 382.5 \, \text{T} \] correspond to the smaller (\( \beta \)) and the larger (\( \gamma \)) hole pockets.

Angular dependence of the FFT peaks is used to assign the frequencies to \( \alpha \), \( \beta \), and \( \gamma \) pockets. Fig. 3.12(c) shows a strong angle dependence for the \( \alpha \) frequencies as expected from the minor (\( \alpha_1 \)) and the major (\( \alpha_2 \)) extremal areas of the ellipsoidal pocket [81]. The \( \beta \) frequency is angle independent as expected from a spherical pocket [81]. The \( \gamma \) frequency with a mild angle dependence corresponds to a jack-shaped pocket as seen in the ARPES results. Solid lines on Fig. 3.12(c) represent calculated frequencies for LaAs from DFT using the SKEAF program [81]. The agreement between calculated and observed frequencies at different angles further confirms the Fermi surface geometry.

Using the Onsager relation \[ F = \frac{\phi_0}{2\pi^2} A_{ext}, \] where \( \phi_0 \) is the quantum of flux, we extracted the extremal orbit areas \( A_{ext} \) for \( \alpha \), \( \beta \), and \( \gamma \), then calculated their volumes to find the number of carriers in each pocket. As a result, \( n_\alpha = 1.55 \times 10^{19} \), \( n_\beta = 0.94 \times 10^{19} \), and \( n_\gamma = 3.66 \times 10^{19} \, \text{cm}^{-3} \), corresponding to \( n_e/n_h = 1.01 \). A similar analysis on LaSb yields \( n_e/n_h = 0.99 \) [76]. Therefore, LaAs is as compensated as LaSb. The effective masses of the carriers on \( \alpha_1 \) and \( \beta \) surfaces are estimated by fitting the FFT amplitudes to the Lifshitz-Kosevich formula [82, 83] in Fig. 3.12(d). The average mass, \( m^* \approx 0.15 \, m_e \), used earlier to estimate \( T^* \) in Fig. 3.11 came from this analysis.

The most striking difference between LaAs and the other members of its chemical family, LaSb and LaBi, is the significant reduction in the XMR magnitude of LaAs (Fig. 3.11). Our goal is to understand this dramatic reduction of XMR magnitude in LaAs through the lens of the various probes presented thus far. The Hall effect data in Fig. 3.11 showed that \( R_H(T) \) had a much larger amplitude in LaAs with no change of sign, different from LaSb/LaBi. This could suggest a lack of compensation in LaAs, a proposed prerequisite for XMR [76]. However, ARPES qualitatively showed comparable electron and hole pockets, and quantum oscillations (Fig. 3.12) quantitatively confirmed their compensated densities in LaAs similar to LaSb/LaBi [76, 84, 78].

Furthermore, we implemented a multi-band fit to the field dependence of \( \rho_{xx} \) and \( \rho_{xy} \) simultaneously, as shown in Fig. 3.12(e). Our model assumed three electron pockets and two hole pockets, analogous to LaSb/LaBi, and supported by both our ARPES and quantum oscillations
Figure 3.12: (a) The oscillatory part of resistivity $\Delta \rho$ plotted as a function of $1/B$ at three representative temperatures. (b) Fast Fourier Transform (FFT) of $\Delta \rho$ data at different temperatures. Four main frequencies ($\alpha_1$, $\alpha_2$, $\beta$, $\gamma$) and their harmonics ($3\alpha_1$, $2\beta$) are identified. (c) The observed angular dependence of the main frequencies (solid symbols) agrees with the calculated results from DFT (solid lines). (d) Lifshitz-Kosevich fit to the temperature dependence of the FFT amplitudes. The effective masses of $\alpha_1$ and $\beta$ are extracted reliably within the resolution of our data. (e) Multi-band fit implemented simultaneously to the resistivity ($\rho_{xx}$) and the Hall effect ($\rho_{xy}$) as a function of field.
measurements. This multi-band fit predicted $n_e/n_h = 1.005$ in LaAs, strengthening the consensus around compensation.

To explain the large discrepancies between $R_H(T)$ in the three compounds, we appeal to the mobility mismatch between electron and hole carriers. From the multi-band fits in Fig. 3.12(e), the average electron to hole mobility ratio $\mu_e/\mu_h \approx 13$ in LaAs. This is an order of magnitude different from $\mu_e/\mu_h \approx 1$ in LaSb/LaBi [76, 77]. For a more intuitive understanding of the impact of such mobility mismatch on $R_H$, we turn to the two-band model expression for the Hall resistivity [85]:

$$\rho_{xy} = \frac{(R_h\rho_e^2 + R_e\rho_h^2)B + (R_hR_e^2 + R_eR_h^2)B^3}{(\rho_h + \rho_e)^2 + (R_h + R_e)^2B^2}$$

(3.1)

where $R_{h(e)}$ and $\rho_{h(e)}$ stand for the Hall coefficient and the resistivity of an isolated hole (electron) band. In the limit of compensation, where $n_e/n_h = 1$, Eq. (3.1) reduces to a simple form for the Hall coefficient ($R_H = \rho_{xy}/B$):

$$R_H = \frac{1}{ne} \frac{\mu_h - \mu_e}{\mu_h + \mu_e}$$

(3.2)

From here, we attribute the larger magnitude of $R_H$ in LaAs to the smaller Fermi surfaces i.e. smaller $n$, and we attribute the lack of sign change in LaAs to the mobility mismatch i.e. $\mu_e \neq \mu_h$.

LaAs, LaSb, and LaBi are all nearly compensated semi-metals which exhibit XMR, albeit to varying magnitudes. Therefore, electron-hole compensation cannot be the cause for the significant reduction of XMR magnitude in LaAs when compared to its siblings. We argue instead that one key quantity for determining XMR magnitude in these compensated materials is the matching of electron and hole mobilities. A mobility mismatch allows for a larger Hall field to develop under applied magnetic fields. This larger Hall field in LaAs counteracts the Lorentz force more effectively and disrupts the field induced cyclotron motion, therefore reduces the XMR magnitude.

3.5 Conclusion

We have presented ARPES measurements in which we successfully extract the dispersions in LaBi, LaSb, and LaAs. In addition to this, we determine the dominant orbital contributions of the bands in LaBi and LaSb. From our extraction of the orbital character of the near Fermi surface
bands and the ARPES dispersions, we show that LaBi has a clear band inversion at $X$ while LaSb appears to be very near a critical point between trivial and nontrivial topological phases, but does not host an obvious TSS. LaAs clearly lies on the other side of this phase transition in the class of trivial topology. For LaSb and LaAs, this differs from both our own DFT calculations and those in the literature. We observe a topological phase transition in the lanthanum monopnictides which, argues against a clean role of the topology to the XMR effect.

By growing and characterizing single crystals of LaAs, we confirmed the qualitative existence of XMR in this material although the magnitude is quantitatively much reduced. Quantum oscillations, multiband fit, and ARPES measurements confirm that LaAs is almost perfectly compensated, similar to LaSb/LaBi. The multi-band fit shows that the larger Hall field and the smaller MR in LaAs are due to the electron-hole mobility mismatch instead of a lack of compensation. The ARPES measurements resolve a non-topological band structure in LaAs, placing it on the other side of a topological transition from LaBi. This is the first presentation of a transition from topological to non-topological band structure in the lanthanum monopnictide family.

### 3.6 Methods

The ARPES measurements were done at the Surface/Interface Spectroscopy (SIS) beamline at the Swiss Light Source and the ‘I-05’ beamline at Diamond Light Source. For both beamlines, a VG-Scienta R4000 electron analyzer was used. The photon energies used were from 20 eV to 240 eV with a total experimental resolution between ~20 and ~150 meV over this range. The angular resolution of the electron lens is 0.2°, corresponding to 0.01 Å$^{-1}$ at 120 eV electron kinetic energy. Both beamlines utilize undulators with polarization control. Preparation of the crystals for the ARPES measurement was done in a nitrogen-purged glove box. A pristine sample surface was obtained by cleaving the crystals in situ in a working vacuum better than $5 \times 10^{-11}$ mbar. Proper alignment of the electron analyzer slit to the crystal axes was achieved to a 0.2 degree precision using 6 axis manipulators by performing maps of the electronic dispersion near $E_F$.

DFT with the projector-augmented wave (PAW) pseudopotential and the generalized gradient
approximation to exchange and correlation of Perdew, Burke and Ernzerhof (PBE) as implemented in the Vienna ab initio package (VASP) was utilized. The plane wave basis set size reflected in energy cutoff is 500 eV, and the total energy minimization was performed with a tolerance of $10^{-5}$ eV. Spin-orbit coupling is calculated self-consistently by a perturbation, $\sum_{i,l,m} V_{i}^{SO} \vec{L} \cdot \vec{S}_{l,m,i} \langle l,m,i | \psi(\vec{k}) \rangle$ to the pseudopotential, where $|l,m,i\rangle$ is the angular momentum eigenstate of $i$-th atomic site. The orbital intensity was calculated by projecting the wave functions, $\psi(\vec{k})$, with a plane-wave expansion on the orbital basis (spherical harmonics) of each atomic site, as written in the following:

$$I_{n}^{(i,l,m)}(\vec{k}) = \langle \psi(\vec{k}) | l,m,i \rangle \langle l,m,i | \psi(\vec{k}) \rangle \langle l,m,i | \psi(\vec{k}) \rangle$$

where $n$, $\vec{k}$ denote band index and crystal momentum, respectively.
Chapter 4

Dichroism in the Cuprate Superconductors

4.1 Introduction

The cuprate family of high-temperature superconductors has been studied extensively since the discovery of La$_{2-x}$Ba$_x$CuO$_4$ in 1986. Much has been learned about these materials and non-conventional superconductivity as a larger field through experiments carried out with many different experimental techniques, yet the underlying pairing mechanism is still unknown. The techniques of ARPES and scanning tunneling microscopy (STM) have traditionally dominated the literature pertaining to the cuprates. However, some aspects of these materials are inconsistent when compared across these probes. For example, scattering rates in the cuprates have been found to be much lower when measured with STM than when measured with ARPES [15, 86, 87, 88, 89]. Furthermore, studies have suggested that STM might be more sensitive to the pseudogap due to the tunneling matrix elements being stronger at the anti-node [89, 90]. Even within the ARPES community, debates have surfaced about interpretations of the polarization dependence in the cuprates and it’s relation to the superconducting pairing mechanism [91, 92].

We have measured the near Fermi energy electronic structure of optimally doped Pb-BSCCO (2201) and La$_{2-x}$Sr$_x$CuO$_2$ ($x = 18\%$) using ARPES with various light polarizations, and incident angles. A strong dependence of the photocurrent for a given crystal momentum on the polarization of light is observed. A minimal model tight binding calculation in a basis of local atomic orbitals is then utilized to determine the orbital composition of the single particle wavefunction as a function of crystal momentum in a single plane of CuO$_2$. Building off of these results, we simulate the relative
ARPES photocurrent throughout the first Brillouin zone in the dipole approximation and compare to our experimental data. These comparisons confirm the presence of changing wavefunction orbital composition throughout the Brillouin zone in both these superconducting cuprate compounds.

4.2 Experimental and Simulation Methods

4.2.1 ARPES Measurements

ARPES measurements on Pb-BSCCO with linear polarization were performed at the Advanced Light Source beamline 10.0.1. The single crystal samples were cleaved in-situ under UHV conditions ($P < 10^{-10}$ Torr) at $T = 20$ K. The beamline is capable of producing photons in the energy range of $17 - 340$ eV. The angle of incidence relative to the sample normal is $83^\circ$, i.e. glancing incidence. The electron spectrometer, an SES R4000 analyzer, is able to rotate about the sample. This unique aspect allows for in-plane momentum mapping using a fixed polarization. Traditionally, one would tilt the sample relative to the fixed analyzer in order to scan over in-plane momenta, resulting in a constantly varying polarization vector with respect to the crystal coordinates during the scan.

Successive constant energy spectra were taken at $E_F$ for varying linear polarizations at glancing incidence with 95 eV photons. Starting with $\alpha = 0^\circ$ (s polarization) and ending with $\alpha = 75^\circ$ (nearly p polarization). The geometry is depicted in fig 4.1 a. The energy and angular resolution of our experiments were determined to be 20 meV and 0.1$^\circ$ respectively.

ARPES measurements on LSCO using circular polarization were performed at the SIS HRPES beamline at the Swiss Light Source. Unlike at ALS, the angle of incidence is fixed at 45$^\circ$ and the sample must be tilted in order to access different regions of $k$ space. Samples of single crystal LSCO doped to 18% were cleaved in situ at $T = 20$ K. The photon energy was varied from 60 to 80 eV in 5 eV steps where the dichroism signal was measured at each step with the $\Gamma - X$ direction along the analyzer slit ($k_x$). The measurements were then repeated with the $\Gamma - M$ direction along the analyzer slit.
4.2.2 Tight Binding Model

Minimalistic tight binding models are used to interpret the ARPES results in the two materials. The calculation uses a 2D CuO$_2$ square lattice with an 8 atomic orbital basis, 5 Cu $d$ orbitals on Cu sites and 3 O $p$ orbitals on O sites (schematically shown in fig 4.2 a). The Hamiltonian is as given by:

$$H_0 = \sum_{ij} t_{\alpha\beta}^{ab}(\vec{R}_i - \vec{R}_j)|\beta b\rangle \langle \alpha a|$$  \hspace{1cm} (4.1)

where the Greek letters $\alpha, \beta$ represent atomic type indices and the Roman letters $a, b$ and $i, j$ represent orbital types and lattice positions respectively. Only nearest and next-nearest neighbor hopping terms, such that $|\vec{R}_i - \vec{R}_j| \leq a/\sqrt{2}$, were kept in the Hamiltonian. This allows $H_0$ to be broken up into 3 sectors: (1) Cu to O hopping, (2) O to O hopping, and (3) on-site atomic orbital energies. The hopping sectors can be parameterized by Slater-Koster bond integrals provided in ref [25].

4.2.2.1 Surface Field

To account for the broken symmetry at the surface of a cleaved crystal, an electric field along the surface normal direction, $\hat{z}$, is applied in addition to the standard hopping terms in $H_0$.

$$H_z = -e \left\langle a a(\vec{R}_j) \right| V_z \left| \beta b(\vec{R}_i) \right\rangle$$

$$= -e \left\langle a a(\vec{R}_j) \right| E_z z \left| \beta b(\vec{R}_i) \right\rangle$$ \hspace{1cm} (4.3)

Physically, this represents the gradient of the surface potential, which is present on the surface of all bulk materials and allows for off-diagonal hopping terms which would otherwise be absent. As we will show later, this field is required to measure any circular dichroism signal. The effect of this term in the atomic orbital basis states is to allow for hopping from orbitals that are even in the $z \rightarrow -z$ to those that are odd, which would ordinarily be forbidden by symmetry. This applies to both $p$
and d orbitals (ie: \(p_x, p_y \leftrightarrow p_z, d_{xz}, d_{yz}\) or \(p_z \leftrightarrow d_{z^2}, d_{x^2-y^2}, d_{xy}\)). The angular dependence of this interaction is parameterized by five numerical constants determined by numerically calculating the matrix element in the basis of Hydrogenic Wannier states using adaptive Monte Carlo integration.

To numerically determine the angular dependence of the work function perturbation matrix elements, adaptive Monte Carlo integration is used. First, we express the initial state and final atomic states as Hydrogenic Wannier functions whose centers are offset by a distance of \(a/2\), where \(a\) is the lattice constant for BSCCO \((a = 5.4\,\text{Å})\). The hydrogenic Wannier functions in spherical coordinates are

\[
\psi_{n\ell m}(r, \theta, \phi) = \left( \frac{2}{na_0^*} \right)^\frac{3}{2} (n-\ell-1)! \frac{\rho}{2n(n+\ell)!} L_{n-\ell-1}^{2\ell+1}(\rho) Y_{\ell m}(\theta, \phi)
\]

where \(\rho = 2r/na_0^*\), \(a_0^* = 4\pi\epsilon_0\hbar^2/\mu e^2\), \(L_{n-\ell-1}^{2\ell+1}(\rho)\) are the generalized Laguerre polynomials, and \(Y_{\ell m}(\vartheta, \varphi)\) are the spherical harmonics. A change of variables can be made in order to offset this function from the origin in the \(x/y\) plane to a point \((a, b)\).

\[
\begin{align*}
  r &\rightarrow r' = \sqrt{r^2 + a^2 + b^2 - 2r\sin(\theta)(a\cos(\phi) + b\sin(\phi))} \\
  \theta &\rightarrow \vartheta = \arctan \left[ r\cos(\theta), \sqrt{(x - r\cos(\phi)\sin(\theta))^2 + (y - r\sin(\theta)\sin(\phi))^2} \right] \\
  \phi &\rightarrow \varphi = \arctan [ -x + r\cos(\phi)\sin(\theta), -y + r\sin(\theta)\sin(\phi) ]
\end{align*}
\]

With this change of variables, the Wannier function centered on the point \((a, b)\) can be expressed as

\[
\psi_{n\ell m}(r, \theta, \phi) \rightarrow \psi_{n\ell m}(r', \vartheta, \varphi, a, b)
\]

The entire integral can then be expressed as

\[
V_z = E_z \sqrt{4\pi/3} \int d^3 x \psi_{n\ell m}^*(r', \vartheta, \varphi, a, b) Y_1^0(\theta, \phi) \psi_{n\ell m}(r', \vartheta, \varphi, 0, 0)
\]

The surface field perturbation strength, \(V_z\), is therefore the only free parameter left in the model. In order to fix the value of \(V_z\), we fit the experimentally measured \(k_F\) around the Fermi
surface assuming identical doping in the model and the crystal measured with ARPES. The fit which produces good agreement between the model and experiment is $V_z = 0.6\text{eV}$ (or $V_z/V_{pd\sigma} = -0.33$).

### 4.2.3 ARPES Matrix Element Simulation

Using the atomic orbital eigenfunctions from the tight binding calculation as input, we simulated the ARPES photocurrent as a function of $\vec{k}$ at the Fermi energy.

The ARPES photocurrent is given by

$$I(\vec{k}, \omega) = \left| \langle f | H_{int} | i \rangle \right|^2 A(\vec{k}, \omega) f(\omega) + BG \right) * R(\vec{k}, \omega)$$

with

$$H_{int} = \frac{e}{2mc} (\vec{A} \cdot \vec{p} + \vec{p} \cdot \vec{A})$$

and where $\langle f | H_{int} | i \rangle \equiv M_{fi}$ is the photoemission matrix element, $A(\vec{k}, \omega)$ is the spectral function, $f(\omega)$ is the Fermi distribution, $BG$ is a background signal, and $R(\vec{k}, \omega)$ is the resolution function of the extrinsic experimental setup. The spectral function contains a plethora of interesting physics intrinsic to the system under study: dispersions, self-energies, gapping, etc. Hence it is the focus of many ARPES studies, with the matrix element factor taking a secondary emphasis. However, the photoemission matrix element also contains useful intrinsic physics which can be extracted, most notable symmetries of the electronic eigenfunctions in the material. These simulations focus on extracting these symmetries of the initial state in the photoemission process.

The simulation is carried out in the semi-classical approximation. The perturbing electromagnetic field is treated as a classical wave, while the position and momentum operators, as well as the initial and final states, are quantum mechanical objects. Because the spatial variation of the electronic wave function is much higher than that of the electromagnetic wave ($k_{light} \ll k_F$) it is convenient to employ the dipole approximation to simplify the operator $H_{int}$. Utilizing $[\vec{p}, \vec{A}] = -i\hbar \vec{\nabla}$ and setting $\vec{\nabla} \cdot \vec{A} = 0$, allows the interaction Hamiltonian to be written as
$H_{\text{int}} = \frac{e}{me} \vec{A} \cdot \vec{p} = -i\hbar \vec{e} A_0 e^{i\vec{q} \cdot \vec{r}} \cdot \vec{\nabla}$. Furthermore, the dipole approximation allows us to neglect the momentum of the photon in the calculation of momentum conservation.

Further simplification to the photoemission matrix element can be made by assuming a plane wave final state, $\langle x | f \rangle = e^{i\vec{k}_f \cdot \vec{r}}$. For high photon energies, the crystal lattice potential can be taken as a small perturbation to the high kinetic energy of the excited final state photoelectron. This allows the gradient operator to be applied to the final state yielding the expression, $M_{fi} = \vec{\epsilon} \cdot \vec{k}_f \left\langle e^{i\vec{k}_f \cdot \vec{r}} | i \rangle \right|$. The initial states used the photoemission matrix element calculation are the atomic orbital eigenfunctions determined from the tight binding calculation. These are taken as an approximation to the true Wannier functions, but simplify the interpretation of the experimentally determined symmetry results from ARPES. With this final piece, the intensity due the photoemission matrix element is modeled as

$$I_M(k, \omega) = |M_{fi}|^2 = |\vec{\epsilon} \cdot \vec{k_f}|^2 \left| \left\langle e^{i\vec{k}_f \cdot \vec{r}} | \vec{k}_i, nlm \right\rangle \right|^2$$

(4.12)

where $\left| \vec{k}_i, nlm \right\rangle$ is the linear combination of atomic orbitals that compose the tight binding wavefunction at the initial state crystal momentum $\vec{k}_i$.

### 4.3 Results

#### 4.3.1 ARPES

In Pb-BSCCO, as the polarization angle, $\alpha$, is varied a strong evolution in the photoemission signal at $E_F$ is observed (fig. 4.1b and c). For $\alpha = 0^\circ$, there is a strong signal from the nodal region, while the anti-nodal region is suppressed. As $\alpha$ is increased to $75^\circ$ there is a transfer of spectral weight from the nodal region to the anti-nodal region characterized by a zero in the photoemission intensity at the node.

These results indicate that the wavefunction at the anti-node contains out-of-plane orbital components while the nodal region is dominated by in-plane orbital components. This can be seen by using dipole selection rules acting on various atomic orbitals. Only atomic orbitals which are
both even under reflections in the $x/z$ plane and also have a component along $\hat{z}$ will photoemit strongly when an out of plane polarization is used for excitation. By similar reasoning, the nodal region must be dominated in-plane orbital components. As $\alpha \to 0$, the dipole matrix elements which produce non-zero photoemission intensity along $\hat{z}$ lie in the plane of the crystal surface.

For the circular dichroism (CD) results in LSCO, a more complex structure is observed. The Fermi surface shows a clear odd-symmetry under reflection in the experimental mirror plane ($k_x/k_z$). This is expected due to the geometry of the experimental setup [93, 28, 17] and is seen in both the $\Gamma - M$ and $\Gamma - X$ orientations. Furthermore, there are zeros in the CD signal located along the bands. At the nodal points, there are ”persistent” zeros for both orientations of the measurement and for all photon energies used. Along the band, there also exist, at some photon energies, ”extra” zeros which change position and number when changing photon energy.

### 4.3.2 Simulation

Figure 4.3 a shows the near-$E_F$ dispersions along the high symmetry directions as calculated from the TB model for optimal doping. Figure 4.2 b shows $k_F$ as calculated from the TB model overlaid with the experimentally measured $k_F$. For the highest energy occupied band, the dominant atomic orbital components can be divided into in-plane orbitals ($p_x$, $p_y$, $d_{x^2-y^2}$) and out of plane orbitals ($d_{z^2}$). The percentage contribution to the wavefunction throughout the BZ is shown in a color map in fig 4.2 c. At the anti-nodal region, the $p$ orbitals constitute $\sim 50\%$ of the wavefunction, while the $d_{x^2-y^2}$ and the $d_{z^2}$ constitute $30\%$ and $20\%$, respectively. For the nodal region, the $d_{z^2}$ component goes to zero, as per symmetry, while the $d_{x^2-y^2}$ and $p$ orbital components are roughly unchanged (the remaining portion is split between several other $d$ orbitals, but their fractions of the total wave function are negligible). It is important to note that without the surface field perturbation, the out-of-plane orbitals are not present in the wave function of the highest occupied band. This is because these hopping elements are forbidden by symmetry in the absence of the perpendicular electric field.

Using these results for the TB wave function, we simulate an ARPES spectrum of the Fermi
Figure 4.1: (a) Experimental geometry. The beam is incident on the sample at a glancing angle of 83° from normal. The polarization vector is then rotated about the Poynting vector by an amount $\alpha$, where $\alpha = 0$ corresponds to $s$ polarization. (b) The measured ARPES intensity at the Fermi surface of Pb-BSCCO for $\alpha = 0^\circ$ (c) and $\alpha = 75^\circ$.
Figure 4.2: (a) Schematic of the CuO$_2$ plane used for the simulation. The red atoms are coppers and the blue atoms are oxygens. (b) The experimentally observed Fermi surface of Pb-BSCCO (green/blue) overlaid with the simulation values of $k_F$ (red crosses). (c) Heat maps showing the percent contribution to the band at $E_F$ from the $d_{z^2}$ and $d_{x^2-y^2}$ orbitals. The $d_{x^2-y^2}$ orbital exists throughout the first zone while the $d_{z^2}$ orbital is present near the anti-nodal region. (d) Tight binding simulation dispersions. $E_F$ is the dashed line at $E - E_F = 0$. (e) Orbital contributions to the wave function at the node (orange bars) vs the anti-node (blue bars). $p_{tn}$ represents $p$ orbitals in the CuO$_2$ plane.
Figure 4.3: (a) Comparison of the Fermi surface from experiment (top row) and simulation (bottom row) for various values of \( \alpha \). (b) Schematic showing the locations in the zone where the spectral weight was measured to quantitatively compare experiment and simulation. (c) The ratio of the nodal to anti-nodal spectral weight at \( E_F \) as a function of \( \alpha \). Both simulation and experiment demonstrate a shift of the weight from the nodal to the anti-nodal region with increasing \( \alpha \). The result of the simulation excluding the \( d_{z^2} \) orbital is also shown, however, the transfer of weight is not observed in this case.
Figure 4.4: CD ARPES of the Fermi surface of LSCO. The top (bottom) row was measured with the analyzer slit, and therefore $\hat{k}_x$, along the $\Gamma - X$ ($\Gamma - M$) direction. The left column was measured with 65 eV photons while the right was measured with 75 eV photons. All color scales are the same and therefore a modulation in the CD intensity with photon energy can be seen.
Figure 4.5: Simulation vs experiment of the Fermi surface of LSCO when measured with CD as a function of photon energy. The zeros of the CD signal are coincident with the nodal positions along the bands in both simulation and experiment. Experimental results show extra cancellations in the CD signal along the band whose locations depend upon the photon energy.
surface in the $k_x/k_y$ plane. From the dipole selection rules, we can intuit that in-plane orbitals will produce higher photoemission signals when the electric field polarization vector is in the same plane than when it is out of the plane. The reverse argument applies to out-of-plane orbitals. Qualitatively, this should indicate a higher photoemission intensity for an out-of-plane polarized electric field in the anti-nodal region and a lower intensity for the nodal region with the same polarization. Furthermore, for in-plane polarized electric fields, the photoemission signal should be higher in the nodal region. These aspects are indeed observed from our simulation results.

4.4 Discussion

For the linear dichroism experiment on Pb-BSCCO, there is a good agreement between our experimental results and our simulation. The presence of a similar evolution of the photoemission intensity from the node to the anti-node is observed as $\alpha$ increases towards $90^\circ$. We believe that this effect is mainly due to the changing magnitude of the $d_{z^2}$ orbital component of the wave function. To clarify this point, the simulation of ARPES intensity is repeated but with the $d_{z^2}$ orbital removed from the wave function. Figure 4.3 c shows the ratio of integrated of spectral weights at the node to the anti-node at the various values of $\alpha$. With the $d_{z^2}$ orbital included, this ratio transitions from above to below 1. Without the $d_{z^2}$ orbital included, this ratio never crosses 1, a behavior which is not represented in the data.

Comparing the circular dichroism results from simulation and experiment show some preliminary agreements. Firstly, the zero in the CD signal at the four nodal points is replicated in the simulation. This feature is persistent in both the simulation and experiment as a function of photon energy. It can be removed from the simulation only by removing the $d_{z^2}$ orbital from the calculation artificially. However, the extra zeros in the CD between the node and the anti-node which move along the band as a function of photon energy are not present.

The existence of the CD signal is dependent upon the addition of the surface field through the $V_z$ parameter in the Hamiltonian. This field breaks the chiral symmetry of the ARPES experiment, allowing one to define a handedness using the Poynting vector, the surface electric field vector, and
the photoelectron’s outgoing momentum vector. Without this field, the photoemission intensity pattern must be identical for $C^+$ and $C^-$ polarizations and the CD signal would be zero. Therefore, the strength of the experimental CD ARPES signal suggests that the electric field from the work function at the surface plays an important factor in the measurement of the electronic states at the Fermi surface.

The interplay of this surface field can have implications for not only the interpretation and quantification of ARPES experiments on the cuprates but for other materials as well. Because of the small ($\sim 2\text{Å}$) mean free path of photoelectrons, ARPES experiments are most sensitive to electronic states near the surface. As noted earlier, the size of the $V_z$ parameter in the simulation was tuned while holding the chemical potential constant in order to best match the experimentally determined Fermi surface. This implies that the strength of the surface field will affect the band velocities of electronic states either fully or partially localized near the surface. Therefore, material parameters measured in transport experiments which depend on the Fermi velocity ($v_F$) may not be in good quantitative agreement with those measured in ARPES if there are surface resonances in the ARPES data.

### 4.5 Conclusion

We have performed both linear and circular dichroism ARPES experiments on the cuprate superconductors: optimally doped Pb-BSCCO (2201) and $\text{La}_{2-x}\text{Sr}_x\text{CuO}_2$ ($x = 18\%$). Furthermore, we implement a tight binding model using Cu $d$ and O $p$ orbitals and an out-of-plane electric field to simulate both of the ARPES dichroism signals. The model predicts some of the qualitative features of the CD signal and is dependent upon the existence of the symmetry breaking surface field. The strong modulation of the intensity at the Fermi surface of Pb-BSSCO consistent with the model’s prediction of out-of-plane orbital components of the wave function, whose composition is increased with the strength of the surface field. The results suggest a careful approach is needed in the extraction of material parameters using ARPES from surface localized electronic states.
In this thesis, I covered the utility of the polarization and angle dependence of the photoemission matrix element in angle resolved photoemission spectroscopy (ARPES). Traditionally, it has played the minor role in the interpretation of ARPES intensity when compared to the spectral function. However, this technique is capable of determining internal symmetries of the electronic wave functions in crystalline solids which cannot be gleaned from the spectral function.

In chapter 1 I introduced the ARPES technique, the established theory and models behind it, and the experimental considerations in performing the technique. ARPES is a "photon in, electron out" spectroscopic technique which measures the energy and momentum of photo-emitted electrons. Conservation rules allow the experimenter to deduce the internal eigenstates of the solid by measuring the photo-current intensity across momentum space. Beyond the conservation rules, the over-arching model for photoemission, the three-step model, allows for powerful simplifications in the modeling of the photoemission process under reasonable assumptions about the experimental parameters. As a result, the photoemission intensity can be described as a product of the quantum mechanical matrix element, the spectral function, and the Fermi-Dirac distribution. Symmetry arguments for interpreting the photoemission matrix element were described as well as the information provided by both linear and circular dichroism ARPES.

It is my personal belief that the fastest way to build intuition for complex physical phenomena is through simulation, and a good portion of graduate school career was spent developing simulation toolkits for the photoemission process. This work was covered in detail in chapter 2. Tight binding
models were the means by which the eigenstates of materials were approximated. These models, carried out in the basis of atomic orbitals, offer the benefits of speed and interpretability. These eigenstates are used as the initial states of a photoemission simulation in the dipole approximation.

The later chapters cover the application of these techniques to various materials systems. Chapter 3 focuses the prediction and observation of a topological phase transition in the Lanthanum Monopnictides and its relation XMR. Topological surface states were thought to play the main role in the unknown mechanism for XMR. However, my work in measuring the prerequisite band inversions for the existence of these states in the Lanthanum monopnictides showed that there exists a topological phase transition in this family of compounds. Furthermore, all of the family members thus far synthesized exhibit XMR. This rules out the proposal of the involvement of topological surface states in XMR.

The final chapter, Chapter 4, contains my work on the Cuprate high-temperature superconductors Bi$_2$Sr$_2$Ca$_1$Cu$_2$O$_{8+x}$ and La$_{2-x}$Sr$_x$CuO$_2$. Tight binding simulations were used to approximate the single particle wave function and subsequent ARPES spectra in an attempt to understand experimental polarization dependence in these materials. In the process of validating this model against the experimental data, I found the inclusion of an electric field, oriented perpendicular to the atomic planes, to be necessary in order to match the shape of the experimentally determined Fermi surface. This electric field exists at all surfaces, due to the presence of the work function, and its strength was the only free parameter in the model used to fit the data. The simulated photoemission intensity as a function of polarization angle quantitatively matched a shifting of intensity from the nodal to the anti-nodal region with increasing angle. This implies that atomic orbitals with components along the surface normal are strongly present in these materials at the surface. This has implications for the interpretation of experimental results from probes which are surface sensitive.
Bibliography


Appendix A

Example code repository and README for the photoemission simulation project

**Project Title:** ARPESim. A Mathematica notebook workflow for solving tight binding Hamiltonians and then calculating ARPES photoemission intensities from the eigenfunctions in an atomic orbital basis.

**Getting Started:** The notebook which I used to calculate the photoemission intensity from LSCO can be cloned from this git repository:

https://github.com/tomNummy/ARPESim.git

The example notebook is example_LSCO.nb. This notebook is annotated and contains a walkthrough from construction of the Bravais lattice to photoemission simulation.

**Prerequisites:** Mathematica 10 or later needs to be installed on the machine you plan to run ARPESim on.

**Installing:** For CU students and staff, a Mathematica installation binary for the latest release can be downloaded from the campus OIT website:

https://oit.colorado.edu/software-hardware/site-licenses/mathematica
Follow the instructions on OIT’s site for information about obtaining a proper license code as required by Wolfram.

**Built With:** Mathematica 10

**Versioning:** git was used for versioning of the example code. See the repo tags for available versions.

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