

Chapter 2

The Photoemission Technique

2.1 Introduction

Angle resolved photoemission spectroscopy (ARPES) (Hüfner, 2003; Cardona & Ley, 1978) is the most direct way to observe the quantum-mechanical structure of electrons in solids, and is one of the key tools used to study the complex electronic interactions that lead to high T_c superconductivity (Damascelli, Hussain, & Shen, 2003). The technique is based on the photoelectric effect, for which Einstein won the 1921 Nobel prize in physics (Einstein & Stachel, 1987). Einstein said that when an electron in a solid absorbs a photon with enough energy to overcome the work function (a constant, Φ , typically 4 - 5 eV for most materials), that electron can escape from the surface of the solid with a kinetic energy gain equal to the photon energy minus the work function ($E_{final} = h\nu - E_{initial} - \Phi$). Since the electron momentum is also conserved in this process, the angular distribution of photoelectrons from a single domain crystal is representative of the initial momentum distribution of electrons in the solid. By measuring this photoelectron distribution, we are directly imaging the electrons of the solid in momentum space. This chapter discusses the details of photoemission and the ARPES technique.

2.2 Angle-integrated photoemission

It is easiest to begin the discussion of ARPES with the most basic form of photoemission spectroscopy, angle-integrated photoemission. In this type of experiment, one simply counts the total number of electrons emitted from the sample as a function of kinetic energy. Since energy is conserved in the photoemission process, electrons with an initial energy E_i in the solid will have a final kinetic energy given by $E_f = h\nu - E_i - \Phi_a$, where $h\nu$ is the photon energy.¹ In free space, the photoelectron kinetic energy depends on the sample work function Φ_s . However, if the sample shares the same ground as the electron analyzer, then the measured energy will instead depend on the work function of the analyzer Φ_a .² In a typical photoemission experiment, $h\nu$ is held constant, and the analyzer work function Φ_a is known, so the measured photoelectron spectrum E_f is directly proportional to the spectrum of initial electric density of states in the solid E_i . Figure 2.1 shows a simplified cartoon of this process where the density of states in the sample (red) is reproduced above the vacuum level (blue). Not shown in the figure is the featureless background of electrons that scatter inelastically on their way out of the solid, which will be discussed in sections 2.4.1 and 3.2.3.

¹ In this equation E_f is measured relative to the vacuum level, and E_i is measured relative to the Fermi level. I always find it easiest to use a diagram like figure 2.1.

² This can be easily seen if you draw an energy diagram in which the Fermi energy of the sample and analyzer are aligned since they are in electrical contact.

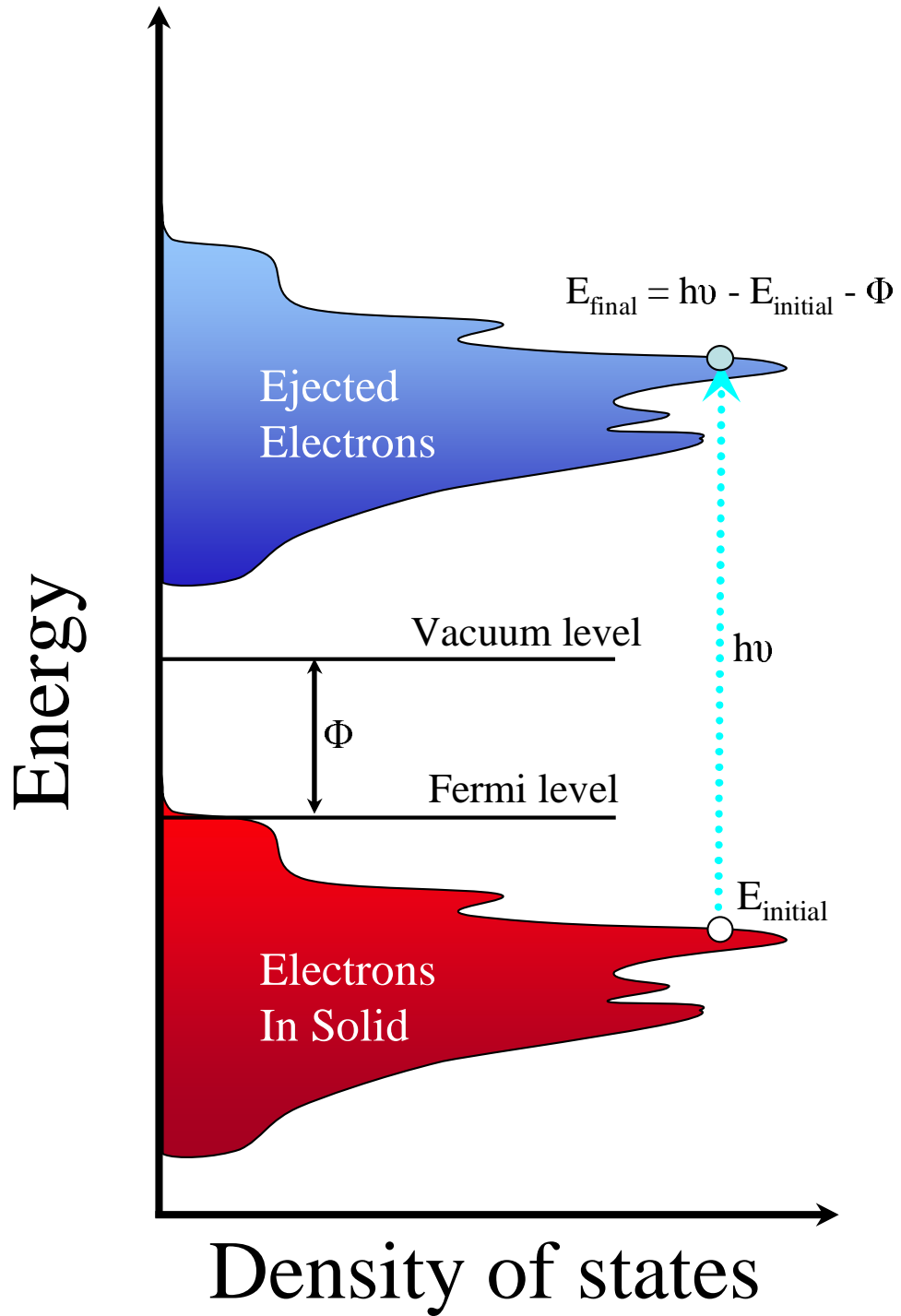


Figure 2.1: (color) In the photoelectric effect, a photon ($h\nu$) is absorbed by an electron inside the solid. If the photon has sufficient energy to overcome the work function Φ , then the electron will be ejected from the solid (above the vacuum level). In this way, the spectrum of ejected electrons represents the spectrum of occupied states in the solid.

2.3 Angle-resolved photoemission

Angle-resolved photoemission takes advantage of the fact that as electrons escape from the face of a single-crystal sample, the components of their momenta parallel to that crystal face are conserved (figure 2.2). Since the photon momentum is essentially zero, the electrons fly away from the sample surface at an angle governed only by their initial momentum in the crystal (the photon energy and sample work function also affect emission angle, but these are both constant in most experiments). This means that if we count the number of photoelectrons as a function of energy and emission angle, we will be directly observing their distribution in momentum space as illustrated in figure 2.3. Modern electron spectrometers can analyze electrons from many emission angles at once, generating a 1-D snapshot of the electronic structure in momentum space.

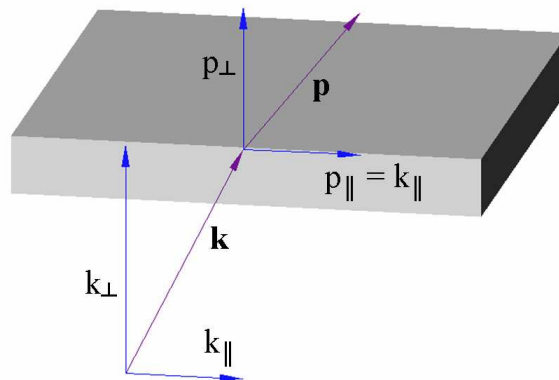


Figure 2.2: (color) This illustration shows how conservation of the parallel component of the crystal momentum determines the photoelectron emission angle. Here, \mathbf{k} is the electron's initial crystal momentum, and \mathbf{p} is the final photoelectron momentum.

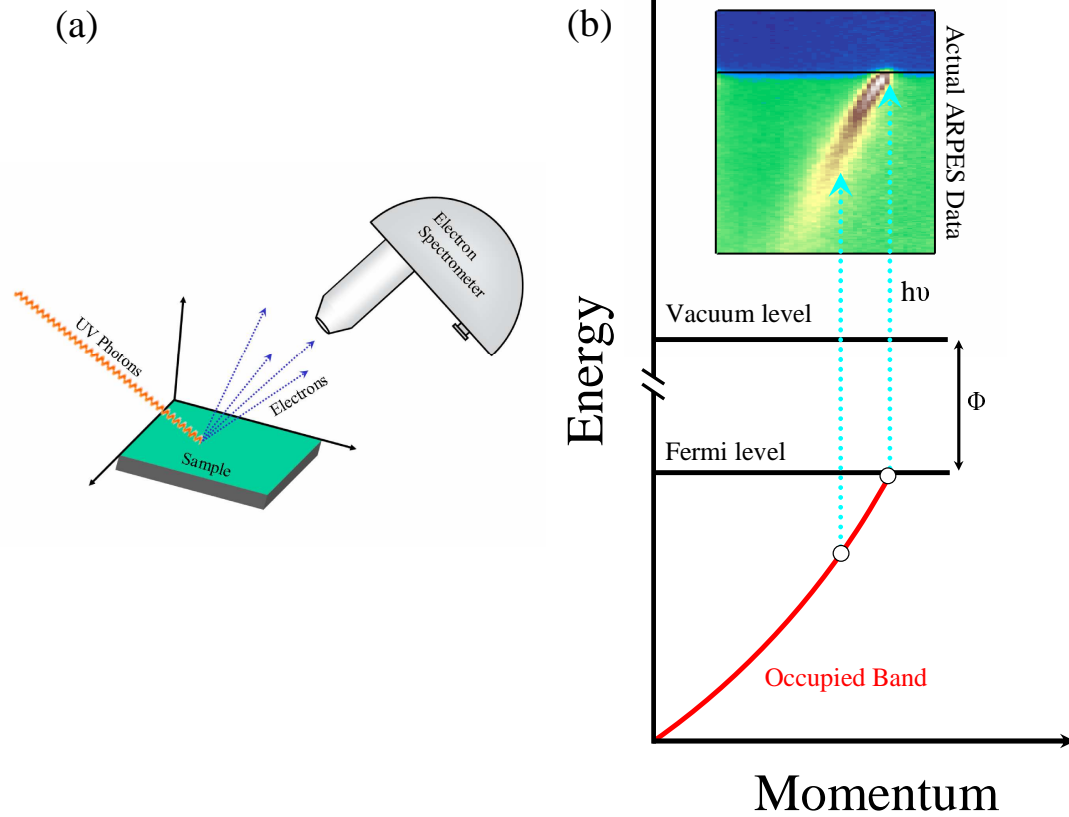


Figure 2.3: (color) (a) Cartoon of an ARPES experiment. UV photons eject electrons from the sample. By moving the angle of the sample relative to the electron spectrometer, we can map out the electronic structure in momentum space. (b) Schematic of the ARPES process. Electrons, initially occupying the red band, are ejected from the sample in a momentum conserving process. Electrons with different initial momentum are emitted at different angles, allowing us to directly measure the initial band structure. The color image is actual ARPES data, showing a 1-dimensional slice of \mathbf{k} -space as viewed by the electron spectrometer.

2.4 Photoemission theory

2.4.1 The three-step model

The most intuitive theoretical approach to the photoemission process in solids is the three step model (Burglund & Spicer, 1964). In this model, the optical excitation, the transport of photoexcited electrons to the sample surface, and their escape to the vacuum are treated separately in order to relate the ARPES intensity to the fundamental properties of the sample. The resulting expression for the ARPES intensity $I(E, \mathbf{p}_{\parallel}, h\nu)$ is,

$$I(E, \mathbf{p}_{\parallel}, h\nu) \propto \sum_{i,f} |\langle f | \mathbf{p} \cdot \mathbf{A} | i \rangle|^2 \times \delta(E_f - E_i - h\nu) \times \delta(E - (E_f - \phi)) \times \delta(\mathbf{k}_i + \mathbf{G} - \mathbf{K}) \times \delta(\mathbf{K}_{\parallel} - \mathbf{p}_{\parallel}) \quad (2.1)$$

where i and f denote the initial and final states, \mathbf{k} is crystal momentum, \mathbf{K} is the momentum of the photoexcited electron in the crystal, \mathbf{p} is the electron's final momentum outside of the crystal, and \mathbf{G} is a reciprocal lattice vector.

In the first step, an electron in the solid absorbs a photon. Energy and momentum are conserved during this optical excitation, leading to the $\delta(E_f - E_i - h\nu)$ and $\delta(\mathbf{k}_i + \mathbf{G} - \mathbf{K})$. We can ignore the momentum of the photon since it is small compared to other momenta in the problem. The optical excitation step also gives rise to the $\langle f | \mathbf{p} \cdot \mathbf{A} | i \rangle$ term which connects the initial and final states of the electron system through the photon interaction operator. It is from this important term that we will eventually be able to extract the sought after electronic physics of the solid $|i\rangle$.

The second step is the transport of excited electrons to the surface of the solid. Photoelectrons created within one mean free path of the surface will escape without scattering, and so will still carry information about the physics of the solid. The other electrons can scatter inelastically, appearing at a lower final

kinetic energy than expected from their E_i . This inelastic background is present in all photoemission experiments, and typically decreases with kinetic energy. The surface sensitivity of ARPES is also determined by the electron mean free path, since electrons that scatter while escaping the solid will no longer carry information about the initial state $|i\rangle$. Surface sensitivity has been a major concern for the application of ARPES to bulk physics such as superconductivity, and will be discussed more later in this thesis.

The third step, escape to the vacuum, tells us how the electrons initial crystal momentum \mathbf{k} is related to its emission angle from the sample surface. Due to the translational symmetry of the crystal lattice, the component of momentum parallel to the sample surface is conserved, giving rise to the $\delta(\mathbf{k}_{\parallel} - \mathbf{p}_{\parallel})$ in equation 2.1. This process is illustrated graphically in figure 2.2. For a free electron final state, the crystal momentum \mathbf{k} is related to the photoelectron final momentum \mathbf{p} by,

$$E_k = \frac{\hbar^2}{2m} (\mathbf{p}_{\parallel}^2 + \mathbf{p}_{\perp}^2) = \frac{\hbar^2}{2m} (\mathbf{k}_{\parallel}^2 + \mathbf{p}_{\perp}^2) \quad (2.2)$$

where E_k is the photoelectron kinetic energy measure relative to the vacuum level. If we measure the angle θ of the outgoing electron from the surface normal, for the parallel component of the crystal momentum we have,

$$\mathbf{k}_{\parallel} = \left(\frac{2m}{\hbar^2} E_k \right)^{1/2} \sin \theta = \left(\frac{2m}{\hbar^2} [E_i + h\nu - \Phi_s] \right)^{1/2} \sin \theta \quad (2.3)$$

This is the important relation between emission angle and crystal momentum that describes how ARPES directly measures momentum space electronic structure. Note that the measured emission angle depends on the sample work function Φ_s , unlike the measured energy which depends on the analyzer work function Φ_a .

2.4.2 The sudden approximation and spectral function

The sudden approximation (Hüfner, 2003; Damascelli et al., 2003) is central to the interpretation of ARPES data, allowing a direct connection between the ARPES spectrum and the single electron spectra function $A(\mathbf{k}, E)$ containing all of the electronic physics of the solid. In this approximation we assume that photoemission process is fast enough that we are measuring the electrons before the sample has had a chance to relax from their removal. This approximation becomes less appropriate as we move to lower photon energy, and therefore slower photoelectrons. The details of how the sudden approximation breaks down is not currently well understood, and will be discussed more in chapter 6.

If we assume the photoemission process to be instantaneous, then the initial and final states of the entire N electron system, $|i\rangle$ and $\langle f|$, can be broken up into the states of the photoelectron ϕ and those of the remaining $N-1$ electron system. The matrix element in 2.1 can then be written as,

$$|\langle f | \mathbf{A} \cdot \mathbf{p} | i \rangle|^2 \propto |\langle \phi_f | \mathbf{A} \cdot \mathbf{p} | \phi_i \rangle|^2 \sum_s |\langle N-1, s | c_{\mathbf{k}} | N \rangle|^2 \quad (2.4)$$

where the sum is over the entire set of excited states s of the $N-1$ electron system (with the photoelectron final state now described by $\langle \phi_f |$), $c_{\mathbf{k}}$ is the electron annihilation operator, and $|N\rangle$ is the initial state of the N electron system. All of the electronic physics of the solid is now consolidated in $\sum_s |\langle N-1, s | c_{\mathbf{k}} | N \rangle|^2 = A(\mathbf{k}, E)$, which is the single particle spectral function (Fetter & Walecka, 1971; Mahan, 2000). The ARPES intensity can now be written in a compact form.

$$I(\mathbf{k}, E) \propto A(\mathbf{k}, E) \times f(E) \sum_{f,i} |M_{f,i}|^2 \quad (2.5)$$

Here, $f(E)$ is the Fermi-Dirac function, indicating that we can only remove electrons from occupied states. The left over matrix element $M_{f,i} = \langle \phi_f | \mathbf{A} \cdot \mathbf{p} | \phi_i \rangle$ will make the overall ARPES intensity depend on the relationship between the photo-

electron final momentum \mathbf{p} and the photon energy and polarization \mathbf{A} (Bansil & Lindroos, 1998; Bansil, Markiewicz, Kusko, Lindroos, & Sahrakorpi, 2004). The spectral function is just the imaginary part of the Green function of the electron system,

$$A(\mathbf{k}, E) = -\frac{1}{\pi} \text{Im} \{G(\mathbf{k}, E)\} \quad (2.6)$$

which is simply the amplitude for removal of an electron from the system described by $G(\mathbf{k}, E)$ (Fetter & Walecka, 1971; Hüfner, 2003; Mattuck, 1967).

2.4.3 The self-energy

For a system of non-interacting electrons, the Green function has poles at the electron energies $\varepsilon_{\mathbf{k}}$, and the spectral function is simply,

$$A(\mathbf{k}, E) = -\delta(E - \varepsilon_{\mathbf{k}}) \quad (2.7)$$

An ideal ARPES experiment on such a system would yield infinitely sharp peaks where the states $\varepsilon_{\mathbf{k}}$ exist, and zero everywhere else (figure 2.4 (b)). In real systems with electron-electron interactions, the spectral function will differ from equation 2.7 by the self-energy $\Sigma(\mathbf{k}, E)$, with which it becomes,

$$A(\mathbf{k}, E) = -\frac{1}{\pi} \frac{|\text{Im}\Sigma(\mathbf{k}, E)|}{[E - \varepsilon_{\mathbf{k}} - \text{Re}\Sigma(\mathbf{k}, E)]^2 + [\text{Im}\Sigma(\mathbf{k}, E)]^2} \quad (2.8)$$

where $\text{Re}\Sigma(\mathbf{k}, E)$ determines how the interacting electronic bands differ from the non-interacting ones, and $\frac{1}{2|\text{Im}\Sigma(\mathbf{k}, E)|}$ is the finite lifetime due to the interactions. Both of these quantities can, in principle, be measured with ARPES (notice that with constant Σ equation 2.8 is simply a Lorentzian). By measuring the detailed energy, momentum, and temperature dependence of the self energy, we can gain insight into the electronic interactions that cause these effects. Figure 2.4 shows drawings of ARPES spectra from an ideal non-interacting electron system, and from a weakly interacting Fermi liquid system (Damascelli et al., 2003; Landau,

1957; Ashcroft & Mermin, 1976; Mattuck, 1967) (also see section 6.8.1 for more on Fermi liquid theory).

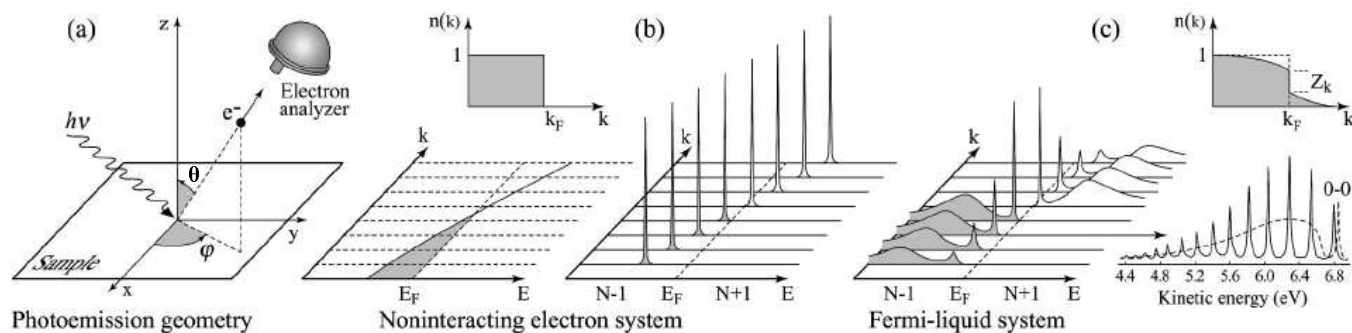


Figure 2.4: Angle-resolved photoemission spectroscopy: (a) shows the geometry of an ARPES experiment in which the emission direction of the photoelectron is specified by the polar (θ) and azimuthal (φ) angles; (b) momentum-resolved one-electron removal and addition spectra for a noninteracting electron system with a single energy band dispersing across E_F . The spectral function for the non-interacting case is simply a series of delta functions. (c) the same spectra for an interacting Fermi-liquid system (Sawatzky, 1989). For both noninteracting and interacting systems the corresponding ground state ($T = 0$ K) momentum distribution function $n(\mathbf{k})$ is also shown. With interactions, the step in $n(\mathbf{k})$ is smeared out due to renormalization of the electronic dispersion. The peaks in the removal and addition spectra are now shifted in position by $\text{Re}\Sigma$, and now have a finite width, or lifetime, due to the $\text{Im}\Sigma$. The interacting spectra also exhibit a broad, incoherent background. (c) Lower right, photoelectron spectrum of gaseous hydrogen (solid line) and the ARPES spectrum of solid hydrogen (dashed line) developed from the gaseous one (Sawatzky, 1989). Figure adapted from Damascelli *et al.* (Damascelli *et al.*, 2003).

2.5 Energy and momentum distribution curves

With modern electron spectrometers capable of multichannel detection, like the Scienta SES2002 discussed in section 3.5, ARPES data is acquired in 2D images showing the photoelectron intensity as a function of energy and momentum along a certain direction. The two most useful ways of slicing these images up for analysis are shown in figure 2.5. Energy distribution curves (EDCs) are cuts through the data at constant \mathbf{k} , and momentum distribution curves (MDCs) are cuts at constant E . Of the two, MDCs usually have the simpler lineshape, partly because the Fermi function and inelastic background depend strongly on energy, but only weakly on momentum. Furthermore, the self-energy Σ typically depends so weakly on momentum that it is essentially constant on the scale of an MDC peak, leading to a Lorentzian lineshape (equation 2.8 with constant Σ). In this case, the Lorentzian centroid gives the position of the renormalized state, making MDCs ideal for tracking band dispersion and $\text{Re}\Sigma$. Extracting $\text{Im}\Sigma$ from MDCs is less straightforward as it requires multiplication of the widths by the bare (non-interacting) velocity, which is not directly measurable. However, with proper handling of the Fermi function and background, the EDC half-width directly gives $\text{Im}\Sigma$.

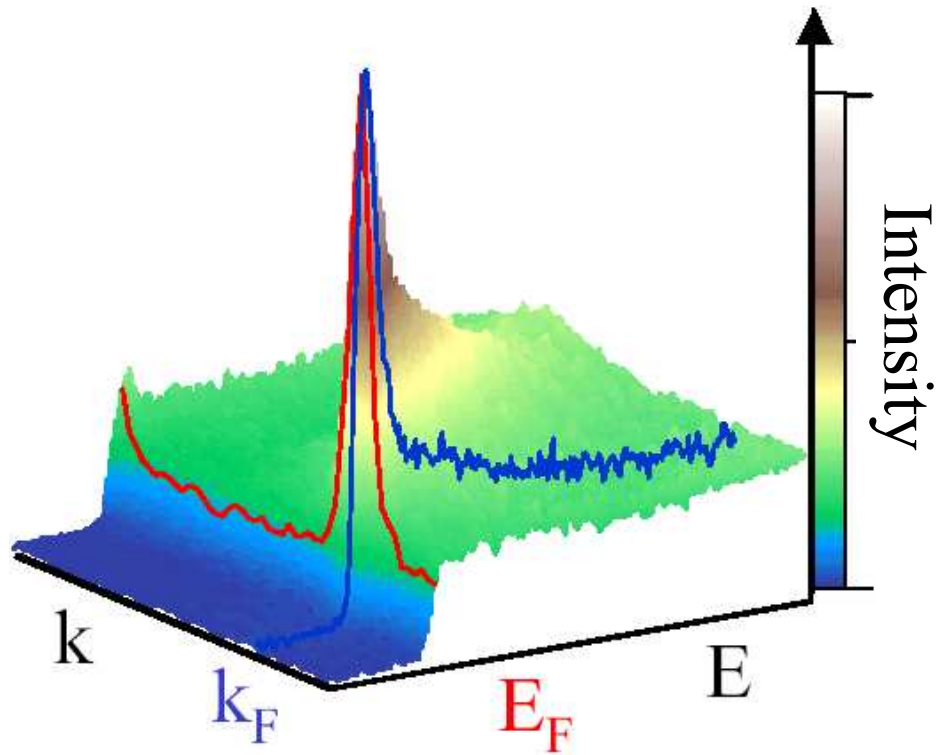


Figure 2.5: (color) A two-dimensional surface plot of $A(\mathbf{k}, E)$ measured on Bi2212 with a Scienta spectrometer, showing an electronic band dispersing through the Fermi energy. The red curve is the momentum distribution curve (MDC) at E_F . The blue curve is the energy distribution curve (EDC) at \mathbf{k}_F . The MDC has a simple Lorentzian lineshape, while the EDC is complicated by energy dependence of the self-energy, Fermi function, and background. Figure adapted from Gromko (Gromko, 2001)