

# Photoemission for layered oxides

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## **Abstract:**

The study of electronic structure of complex systems has been intensely prompted since the cuprate has been considered as potential breakthrough in high  $T_c$  superconductivity. Angle-resolved photoemission spectroscopy (ARPES) is one of the most direct methods of studying the electronic structure of solids. By measuring the kinetic energy and angular distribution of the electrons photoemitted from a sample illuminated with sufficiently high-energy radiation, one can gain information on both the energy and momentum of the electrons propagating inside a material. This is of vital importance in elucidating the connection between electronic, magnetic, and chemical structure of solids, in particular for those complex systems which cannot be appropriately described within the independent-particle picture. [1] In this article, I will first give an introduction about ARPES, then provide more detailed description and finally introduce the State-of-the-art photoemission.

## **1 Introduction**

The discovery of superconductivity at 30 K in the LaBaCuO ceramics by Bednorz and Muller in 1986 opened the era of high- $T_c$  superconductivity, changing the history of a phenomenon that had before been confined to very low temperatures. This unexpected result prompted intense activity in the field of ceramic oxides and has led to the synthesis of compounds with increasingly higher  $T_c$ , all characterized by a layered crystal structure with one or more  $\text{CuO}_2$  planes per unit cell, and a quasi-two-dimensional (2D) electronic structure. [2] In this context, angle-resolved photoemission spectroscopy (ARPES) plays a major role because it is the most direct method of studying the electronic structure of solids.

To establish a general idea about ARPES, let's start from photoelectron spectroscopy. Photoelectron spectroscopy is a general term that refers to all those techniques based on the application of the photoelectric effect originally observed by Hertz and later

explained as a manifestation of the quantum nature of light by Einstein, who recognized that when light is incident on a sample an electron can absorb a photon and escape from the material with a maximum kinetic energy  $E_{kin} = h\nu - \phi$  (where  $\nu$  is the photon frequency and  $\phi$ , the material work function, is a measure of the potential barrier at the surface that prevents the valence electrons from escaping, and is typically 4 – 5 eV in metals). [1] So, ARPES is a highly advanced spectroscopic method that allows the direct experimental study of the momentum-dependent electronic band structure of solids.

As we will see, the photoemission process in solids and the quantitative analysis is complicated. Several assumptions have always been made as being discussed in the follows.

## 2 Kinematics of photoemission

The energetics of the photoemission process and of the geometry of an ARPES experiment is sketched in Fig.1 and 2(a). A beam of monochromatized radiation supplied either by a gas-discharge lamp or a synchrotron beamline is incident on a sample (which has to be a properly aligned single crystal, in order to perform momentum-resolved measurements). As a result, electrons are emitted by the photoelectric effect and escape into the vacuum in all directions. By collecting the photoelectrons with an electron energy analyzer characterized by a finite acceptance angle, one measures the kinetic energy  $E_{kin}$  of the photoelectrons for a given emission angle. This way, the photoelectron momentum  $p$  is also completely determined: its modulus is given by  $p = \sqrt{2mE_{kin}}$  and its components parallel and perpendicular to the sample surface are obtained from the polar ( $\theta$ ) and azimuthal ( $\theta$ ) emission angles.

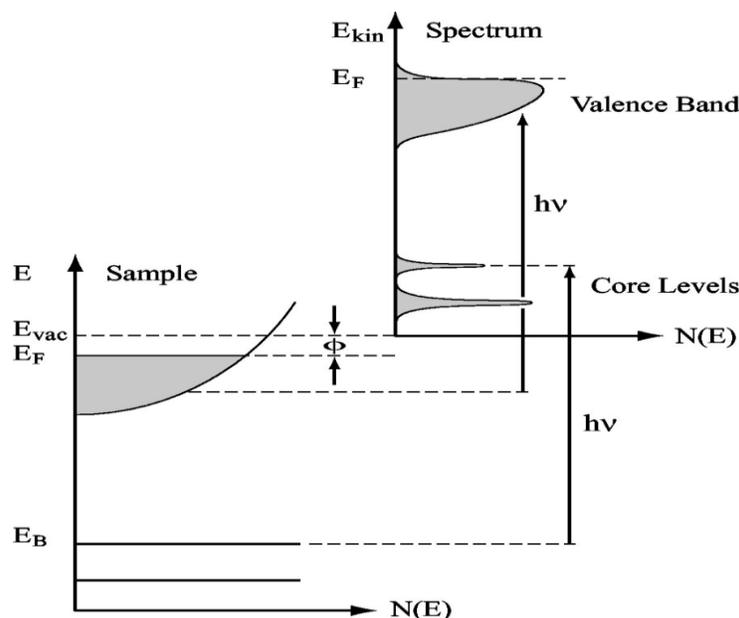


Fig.1: Energetics of the photoemission process. The electron energy distribution produced by incoming photons and measured as a function of the kinetic energy  $E_{kin}$  of the photoelectrons (right) is more conveniently expressed in terms of the binding energy  $E_B$  (left) when one refers to the density of states inside the solid ( $E_B=0$  at  $E_F$ ). [3]

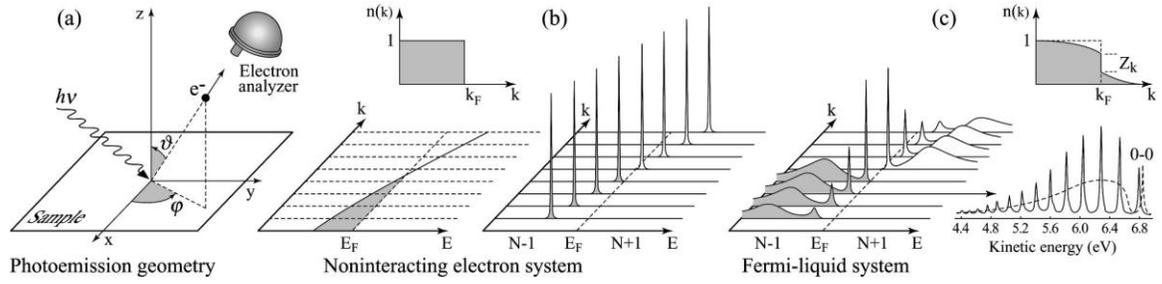


Fig. 2: (a) Geometry of an ARPES experiment; the emission direction of the photoelectron is specified by the polar ( $\theta$ ) and azimuthal ( $\phi$ ) angles. Momentum resolved one-electron removal and addition spectra for: (b) a non-interacting electron system (with a single energy band dispersing across the Fermi level); (c) an interacting Fermi liquid system.

Within the non-interacting electron picture, and by taking advantage of total energy and momentum conservation laws (note that the photon momentum can be neglected at the low photon energies typically used in ARPES experiments), one can relate the kinetic energy and momentum of the photoelectron to the binding energy  $E_B$  and crystal momentum  $\hbar\mathbf{k}$  inside the solid:

$$E_{kin} = h\nu - \Phi - |E_B| \quad (1)$$

$$\mathbf{p}_{||} = \hbar\mathbf{k}_{||} = \sqrt{2mE_{kin}} \sin \theta \quad (2)$$

Here  $\hbar\mathbf{k}_{||}$  is the component parallel to the surface of the electron crystal momentum in the extended zone scheme. Upon going to larger  $q$  angles, one actually probes electrons with  $\mathbf{k}$  lying in higher-order Brillouin zones. By subtracting the corresponding reciprocal lattice vector  $\mathbf{G}$ , one obtains the reduced electron crystal momentum in the first Brillouin zone. Note that the perpendicular component of the wave vector is not conserved across the sample surface due to the lack of translational symmetry along the surface normal.

In addition, most ARPES experiments are performed at photon energies in the ultraviolet (in particular for  $h\nu < 100$  eV). The main reason is that by working at lower photon energies it is possible to achieve higher energy and momentum resolution. This is easy to see for the case of the momentum resolution  $\Delta\mathbf{k}_{||}$  which, from Eq. (2) and neglecting the contribution due to the finite energy resolution, is:

$$\Delta k_{||} \cong \sqrt{2mE_{kin} / \hbar^2} \cos \theta \Delta \theta \quad (3)$$

where  $\Delta \theta$  corresponds to the finite acceptance angle of the electron analyzer. From Eq. (3) it is clear that the momentum resolution will be better at lower photon energy. By working at low photon energies there are also some additional advantages [2]: First, for a typical beamline it is easier to achieve high energy resolution; Second, one can completely disregard the photon momentum in Eq. (2), as for 100-eV photons the momentum is 3% ( $0.05 \text{ \AA}^{-1}$ ) of the typical Brillouin-zone size of the cuprates ( $2\pi/a \cong 1.6 \text{ \AA}^{-1}$ ), and at 21.2 eV (the HeI $\alpha$  line typically used on ARPES systems equipped with a gas discharge lamp) it is only 0.5% ( $0.008 \text{ \AA}^{-1}$ ).

### 3 Three-step model and sudden approximation

In photoemission spectroscopy, one so called “three-step model” is widely used. [1] In such a picture the photoemission event is decomposed in three independent steps:

- (1) Optical excitation between the initial and final bulk Bloch eigenstates;
- (2) Travel of the excited electron to the surface;
- (3) Escape of the photoelectron into vacuum after transmission through the surface potential barrier.

This is the most common approach, in particular when photoemission spectroscopy is used as a tool to map the electronic band structure of solids. (Fig. 3)

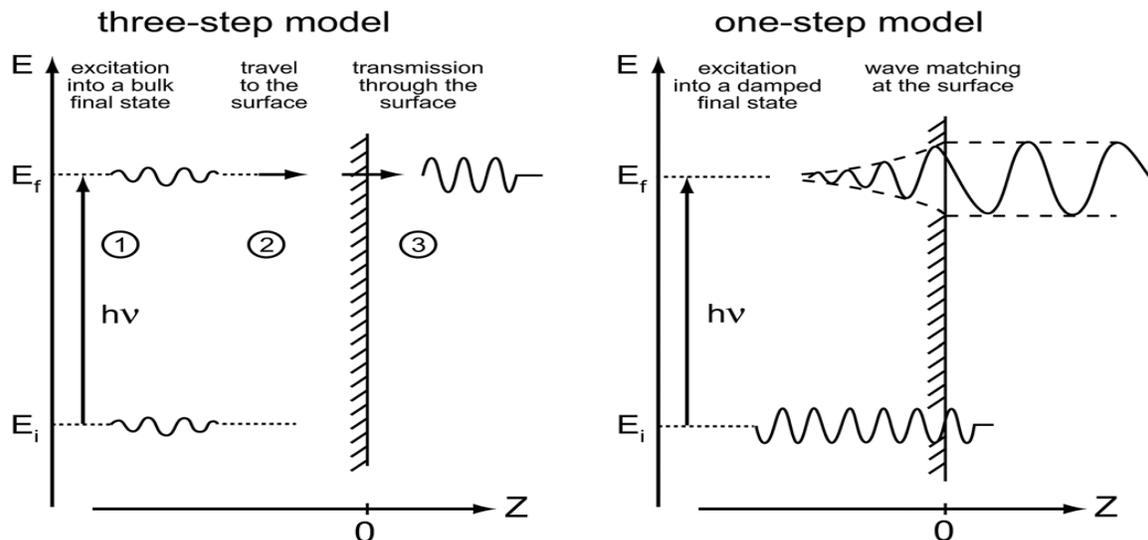


Fig. 3: Pictorial representation of three-step and one-step model descriptions of the photoemission process. [3]

To develop a formal description of the photoemission process, one has to calculate the transition probability  $w_{fi}$  for an optical excitation between the N-electron ground state

$\psi_i^N$  and one of the possible final states  $\psi_f^N$ . This can be approximated by Fermi's golden rule:

$$w_{fi} = \frac{2\pi}{\hbar} | \langle \psi_f^N | H_{int} | \psi_i^N \rangle |^2 \delta(E_f^N - E_i^N - h\nu) \quad (4)$$

Where  $H_{int} = -\frac{e}{mc} \mathbf{A} \cdot \mathbf{p}$  is the interaction with the photon treated as a perturbation. (P is the electronic momentum operator and  $\mathbf{A}$  is the electromagnetic vector potential)

Here, however, using the three-step model: The total photoemission intensity is then given by the product of three independent terms: the total probability for the optical transition, the scattering probability for the traveling electrons, and the transmission probability through the surface potential barrier. Step (1) contains all the information about the intrinsic electronic structure of the material; Step (2) can be described in terms of an effective mean free path, proportional to the probability that the excited electron will reach the surface without scattering. Step (3) is described by a transmission probability through the surface, which depends on the energy of the excited electron as well as the material work function  $\phi$ .

In evaluating step (1), and therefore the photoemission intensity in terms of the transition probability  $w_{fi}$ , it would be convenient to factorize the wave functions in Eq. (4) into photoelectron and (N-1)-electron terms, as we have done for the corresponding energies. This, however, is far from trivial because during the photoemission process itself the system will relax. [2] The problem simplifies within the sudden approximation, which is extensively used in many-body calculations of photoemission spectra from interacting electron systems and which is in principle applicable only to electrons with high kinetic energy. In this limit, the photoemission process is assumed to be sudden, with no post-collisional interaction between the photoelectron and the system left behind (in other words, an electron is instantaneously removed and the effective potential of the system changes discontinuously at that instant). The N-particle final state  $\psi_f^N$  can then be written as

$$\psi_f^N = A \phi_f^k \psi_f^{N-1} \quad (5)$$

where A is an anti-symmetric operator that properly antisymmetrizes the N-electron wave function so that the Pauli principle is satisfied,  $\phi_f^k$  is the wave function of the photoelectron with momentum k, and  $\psi_f^{N-1}$  is the final state wave function of the (N-1)-electron system left behind, which can be chosen as an excited state with eigenfunction  $\psi_m^{N-1}$  and energy  $E_m^{N-1}$ . The total transition probability is then given by the sum over all possible excited states m. [2]

For the initial state, let us assume for simplicity that  $\psi_i^N$  is a single Slater determinant (i.e., Hartree-Fock formalism), so that we can write it as the product of a one electron orbital  $\phi_i^k$  and an (N-1)-particle term:

$$\psi_i^N = A\phi_i^k\psi_i^{N-1} \quad (6)$$

At this point, we can write the matrix elements in Eq. (4) as

$$\langle \psi_f^N | H_{int} | \psi_i^N \rangle = \langle \phi_f^k | H_{int} | \phi_i^k \rangle \langle \psi_m^{N-1} | \psi_i^{N-1} \rangle \quad (7)$$

Where  $\langle \phi_f^k | H_{int} | \phi_i^k \rangle \equiv M_{f,i}^k$  is the one-electron dipole matrix element, and the second term is the (N-1)-electron overlap integral.

Then, The total photoemission intensity measured as a function of  $E_{kin}$  at a momentum  $k$ , namely,  $I(\mathbf{k}, E_{kin}) = \sum_{f,i} w_{f,i}$ , is then proportional to

$$\sum_{f,i} |M_{f,i}^k|^2 \sum_m |C_{m,i}|^2 \delta(E_{kin} + E_m^{N-1} - E_i^N - h\nu) \quad (8)$$

Where  $|C_{m,i}|^2 = |\langle \psi_m^{N-1} | \psi_i^{N-1} \rangle|^2$  is the probability that the removal of an electron from state  $i$  will leave the (N-1)-particle system in the excited state  $m$ . [2] From this we can see that, if  $\psi_i^{N-1} | \psi_{m_0}^{N-1}$  for one particular state  $m = m_0$ , then the corresponding  $|C_{m,i}|^2$  will be unity and all the other  $C_{m,i}$  zero; in this case, if  $M_{f,i}^k \neq 0$ , the ARPES spectra will be given by a delta function at the Hartree-Fock orbital energy  $E_B^k = -\epsilon_k$ , as shown in Fig. 2(b) (i.e., the noninteracting particle picture). In strongly correlated systems, however, many of the  $|C_{m,i}|^2$  will be different from zero because the removal of the photoelectron results in a strong change of the systems effective potential and, in turn,  $\psi_i^{N-1}$  will overlap with many of the eigenstates  $\psi_m^{N-1}$ . Thus the ARPES spectra will not consist of single delta functions but will show a main line and several satellites according to the number of excited states  $m$  created in the process [Fig. 2(c)].

## 4 State-of-the-art photoemission

Now let's move on to the experimental description of photoemission process. The configuration of a generic angle-resolved photoemission beamline is shown in Fig. 4. A beam of white radiation is produced in a wiggler or an undulator (these so-called "insertion devices" are the straight sections of the electron storage ring where radiation is produced): the light is then mono-chromatized at the desired photon energy by a grating mono-chromator, and is focused on the sample. Alternatively, a gas-discharge

lamp can be used as a radiation source (once properly mono-chromatized, to avoid complications due to the presence of different satellites and refocused to a small spot size, essential for high angular resolution). However, synchrotron radiation offers important advantages: it covers a wide spectral range (from the visible to the X-ray region) with an intense and highly polarized continuous spectrum, while a discharge lamp provides only a few resonance lines at discrete energies. Photoemitted electrons are then collected by the analyzer, where kinetic energy and emission angle are determined (the whole system is in ultra-high vacuum at pressures lower than  $5 \times 10^{-11}$  torr).

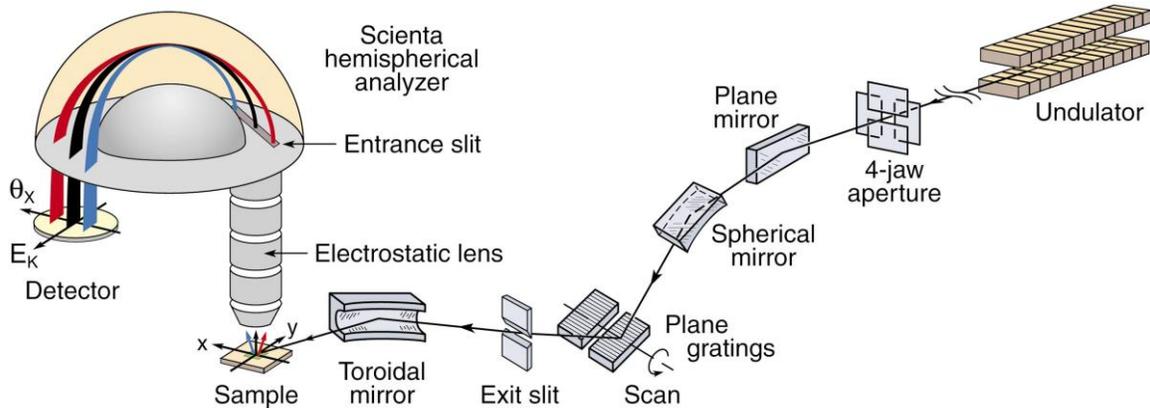


Fig.4: Generic beamline equipped with a plane grating mono-chromator and a Scienta electron spectrometer (Color).

A conventional hemispherical analyzer consists of a multi-element electrostatic input lens, a hemispherical deflector with entrance and exit slits, and an electron detector (i.e., a channeltron or a multichannel detector). The heart of the analyzer is the deflector, which consists of two concentric hemispheres of radius  $R_1$  and  $R_2$ . These are kept at a potential difference  $\Delta V$ , so that only those electrons reaching the entrance slit with kinetic energy within a narrow range centered at the value  $E_{pass} = e\Delta V / (R_1/R_2 - R_2/R_1)$  will pass through this hemispherical capacitor, thus reaching the exit slit and then the detector. In this way it is possible to measure the kinetic energy of the photoelectrons with an energy resolution given by  $\Delta E_a = E_{pass} (w/R_0 + \alpha^2/4)$  where  $R_0 = (R_1 + R_2)/2$ ,  $w$  is the width of the entrance slit, and  $\alpha$  is the acceptance angle. The role of the electrostatic lens is to decelerate and focus the photoelectrons onto the entrance slit. By scanning the lens retarding potential one can effectively record the photoemission intensity versus the photoelectron kinetic energy. One of the innovative characteristics of the Scienta analyzer is the two-dimensional position-sensitive detector consisting of two micro-channel plates and a phosphor plate in series, followed by a charge-coupled device (CCD) camera. In this case, no exit slit is required: the electrons, which are spread apart along the Y axis of the detector (Fig. 4) as a function of their kinetic energy due to the travel through the hemispherical capacitor, are detected simultaneously. In other words, a range of electron energies is dispersed over one dimension of the detector and can be measured in parallel; scanning the lens voltage is in principle no longer necessary, at least for narrow energy windows (a few percent of

$E_{pass}$ ). Furthermore, in contrast to a conventional electron analyzer in which the momentum information is averaged over all the photoelectrons within the acceptance angle (typically  $\pm 1^\circ$ ), the Scienta system can be operated in angle-resolved mode, which provides energy-momentum information not only at a single k-point but along an extended cut in k space. In particular, the photoelectrons within an angular window of  $\sim 14^\circ$  along the direction defined by the analyzer entrance slit are focused on different X positions on the detector (Fig. 4). It is thus possible to measure multiple energy distribution curves simultaneously for different photoelectron angles, obtaining a 2D snapshot of energy versus momentum. (Fig. 5) In the picture, Energy ( $\omega$ ) vs momentum ( $k_{||}$ ) image plot of the photoemission intensity can be clearly seen. This k-space cut was taken across the Fermi surface (see sketch of the 2D Brillouin zone upper left) and allows a direct visualization of the photohole spectral function. The quasi-particle dispersion can be clearly followed up to  $E_F$ , as emphasized by the white circles.

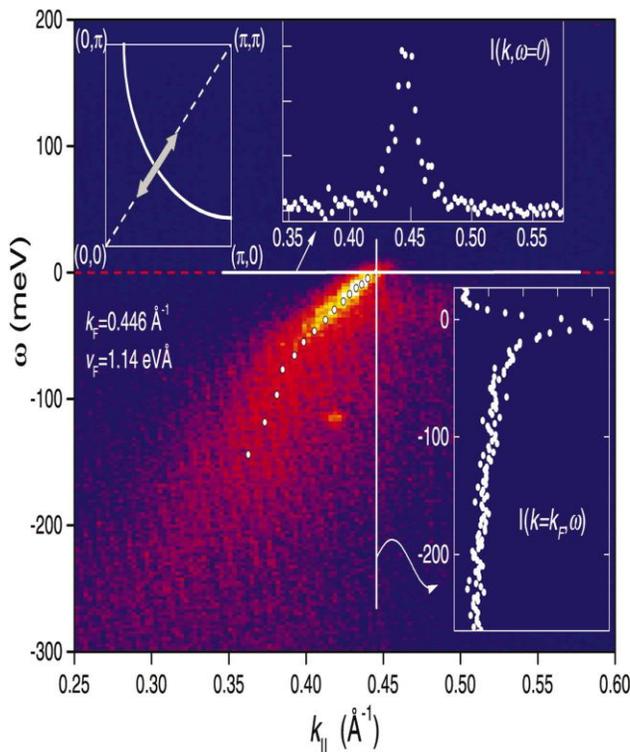


Fig. 5: Energy ( $\omega$ ) vs momentum ( $k_{||}$ ) image plot of the photoemission intensity from  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8.1d}$  along  $(0,0)-(\pi, \pi)$ . This k-space cut was taken across the Fermi surface (see sketch of the 2D Brillouin zone upper left) and allows a direct visualization of the photohole spectral function  $A(k, \omega)$  (although weighted by Fermi distribution and matrix elements). The quasiparticle dispersion can be clearly followed up to  $E_F$ , as emphasized by the white circles. Energy scans at constant momentum (right) and momentum scans at constant energy (upper right) define energy distribution curves (EDC's) and momentum distribution curves (MDC's), respectively. [4]

By taking full advantage of the momentum and energy resolution as well as of the photon energy range nowadays available, state-of-the-art ARPES is a unique tool for momentum space microscopy.

## 5 Summary

Photoemission is an excellent method to study the electronic structure of complex systems such as cuprates. Angle-resolved photoemission spectroscopy is one of the most powerful methods for this study purpose. The last decade witnessed significant progress in this technique and its application. Of course, it has a promising future and may cause revolutionary progress in physics.

## Reference:

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