Chapter 2

Photoelectron Spectroscopy

Photoelectron spectroscopy (PE) is based on the photoelectric effect originally observed by Hertz (1887). In this process, light is incident on a sample and photons are absorbed while the system changes from the electronic ground state to an excited state. In a solid sample, if the transferred energy is big enough, photoexcited electrons moving in the direction to the sample surface can overcome the surface barrier and escape into the vacuum.

In a typical PE experiment, see Fig. 2.1(a), the sample is irradiated with monochromatic light of energy $h\nu$ and the excited photoelectrons escaping from the surface are collected by an electron-energy analyzer [18]; in this way, kinetic energy and electron emission direction are determined. In a simple picture, the energy distribution of the photoelectrons is an image of the ground-state electron energy distribution shifted by the photon energy (Fig. 2.1(b)). Nevertheless, the PE process produces a final state with one electron lacking as compared to the initial state. Therefore, PE measures always final-state energies that can be related to initial-state energies with the help of theoretical considerations.

2.1   Single-electron picture

In the single-particle picture, the conservation of energy directly relates the kinetic energy E_{kin} of the photoelectron to the photon energy $h\nu$ [19]:

$$E_{kin} = h\nu - E_B - \Phi. \tag{2.1}$$

The kinetic energy of the photoelectron is usually measured with respect to the Fermi energy of the sample, E_F. E_B is the binding energy of the electron and Φ the work function of the solid (equal to the energy difference between the vacuum level and the Fermi energy). Koopman's approximation states that the binding energy measured in PE equals the ground-state energy of the electron that is emitted. This approximation holds only approximately and it is best for itinerant (free-electron band-like) states because it assumes that the excitation does not change any other orbital. In other words, Koopman's approximation neglects the relaxation energy.
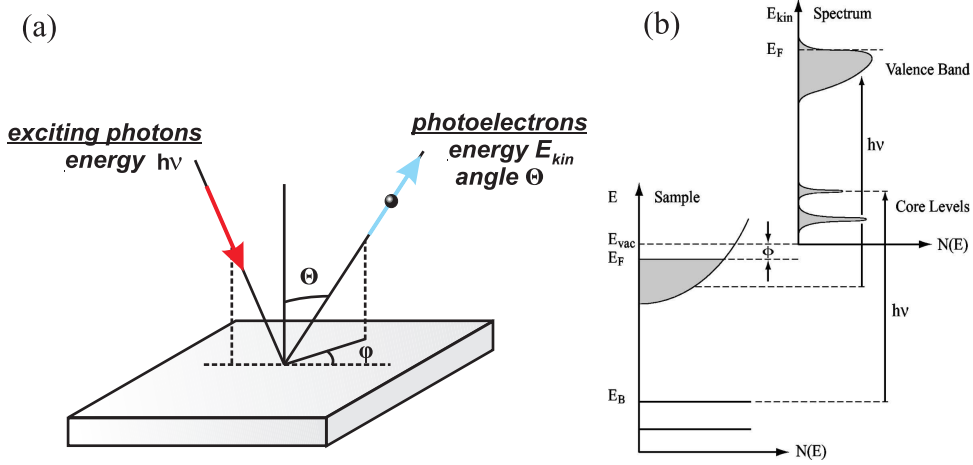
(a)

(b)

Figure 2.1: (a) Experimental geometry and measured parameters of angle-resolved photoemission spectroscopy. (b) Energy relations in the photoemission process. The kinetic energy distribution of excited electrons gives a replica of the electronic band structure of the sample [18].

2.2 Many electron effects

Strictly speaking, the binding energy measured in PE is the difference between the total energy of the initial state with N electrons, E_i^N, and the final state with N-1 electrons E_f^{N-1}:

$$E_B = E_f^{N-1} - E_i^N. \tag{2.2}$$

A disadvantage of this definition is that the total energies are not easy to calculate so that one has to rely on approximations. Quite generally, electrons in a solid must be described by a common N-particle wave function. In addition, the photoexcitation process does not only transfer energy to the excited electron, but it excites the whole N-electron system or, in other words, the photohole changes the potential for the remaining N-1 electrons. The eigenstates of the system in the initial state are not identical with the eigenstates of the system after excitation. To account for this in the equation for the binding energy (Eq. 2.1), we need an additional term that describes relaxation effects:

$$E_B = h\nu - E_{kin} - \Phi - \Delta E_{relax}. \tag{2.3}$$

In the valence band, a hole is almost fully screened by the delocalized electrons so that the relaxation energy is negligibly small. This makes photoemission an especially convenient tool to investigate the valence-band structure. For localized states like core levels, the relaxation energy is substantial, due to the weak screening of the photohole.

The excited electron and the created hole are interacting with other electrons in the solid, giving rise to the so-called final-state effects. The excited electron can generate secondary electrons, plasmons, and phonons. The hole is screened

by the remaining electrons and can decay, e.g. via Auger processes. These multielectron processes are mainly responsible for lifetime broadening, binding energy shifts, and the possible appearance of satellite lines in PE spectra [18].

If the system under investigation has an open shell with corresponding spin and angular momenta, their coupling usually leads to different final states giving rise to an often rich multiplet structure; this is the reason why photoemission is applied to investigate the magnetic properties of materials with open-shell atoms.

Even though photoemission does not probe the ground state directly, it is widely recognized as a powerful tool to study the electronic structure, including modifications caused e.g. by surface adsorption and magnetic ordering.

2.3 Photoemission process

For an interpretation of photoemission experiments, the so-called three-step model, treating the whole PE process in three separate steps, has been proven to be extremely useful [18]. In this model, the photoemission process is divided into three independent and sequential steps that represent different aspects of the problem:

(i) In the first step, photoionization takes place; the photon is absorbed locally and an electron is excited in the bulk of the solid.

(ii) The second step describes the transport of the excited electron inside the crystal to the surface.

(iii) The third step describes the escape of the photoelectron through the surface potential barrier into the vacuum, where it is detected.

This separation is somewhat artificial and, in principle, the whole process of photoexcitation, traveling to the surface, and escape into the vacuum should be treated in one step. But the three-step model certainly provides better insight into the underlying physics.

Excitation: The photoexcitation probability per unit time is described by Fermi's golden rule. Most generally, the excitation process can be described as a transition of the electronic system from the initial to some final state. In the initial state, the electronic system of the solid is described by an N-electron wave function Ψ_i. After photoexcitation, the system is described by another N-electron wave function Ψ_f, comprising the N-1 electrons remaining in the solid plus the emitted photoelectron. The photocurrent per solid angle and energy interval is [20]

$$J(\vec{k}) = \frac{k}{4\pi^2} \sum_i |\langle \Psi_f | \delta H | \Psi_i \rangle|^2 \, \rho(E_i + h\nu). \qquad (2.4)$$

δH represents the perturbation by the electromagnetic field; ρ is the energy density of the final state (and it ensures energy conservation).

The photoexcitation cross section is strongly energy dependent [21]. Near the absorption threshold, it can be strongly modified due to resonant enhancement, i.e. an interference between an indirect excitation channel (in which a

core electron is photoexcited, followed by an Auger decay) and the direct photoemission channel. This resonant enhancement of photoemission lines can be used to identify elements.

In the soft X-ray energy region, the photon transfers negligible momentum to the photoelectron compared to the electron momentum itself; consequently, the momentum of the photoelectron in the final state is approximately the same as in the initial state, modulo a reciprocal lattice vector

$$k_f = k_i + G_B. \tag{2.5}$$

k_f and k_i denote the final-state and initial-state wave vector, respectively; G_B is a reciprocal lattice vector. These excitations are termed direct transitions and, in the reduced zone scheme, they are represented by vertical transitions.

Symmetry: One can determine the initial state symmetry by applying symmetry selection rules. In the case of linearly polarized light, the relative orientation of photon polarization and electron wave function influences the photoexcitation cross section. For normal emission, e.g., the final state continuum wave function should be symmetric with respect to all mirror planes of the surface; otherwise it will have a node at the point of the detector and no photoelectrons will be detected. For the hcp(0001) surface, which has C_{6v} symmetry, only final states with Δ_1 and Δ_2 symmetry satisfy this condition [22]. We have to consider two different cases depending on the light polarization. In case of p-polarized light, δH is even with respect to the mirror plane, defined by the propagation direction of the incident light and the surface normal. Consequently, the initial state must also be even and only electrons from Δ_1 and Δ_2 states can be observed. For s-polarization, by contrast, the light polarization vector is perpendicular to the mirror plane, and δH is odd and the initial state should be odd, so that only states with Δ_5 and Δ_6 symmetry can be observed. In general, to derive symmetry selection rules one has to apply group theory.

Transport: During transport through the solid, the electrons undergo elastic and inelastic scattering owing to the potential of the crystalline solid. The elastically scattered outgoing photoelectron waves are diffracted in the solid. For photoemission from core levels, this effect can be quite strong, and the intensity of a particular line depends on the electron emission direction and the kinetic energy. This effect can be applied as a method to determine the geometrical environment of an emitting atom [23]. It should also be taken into account in any quantitative analysis of PE line intensities, which makes the description of core-level line intensities a relatively complicated task.

Due to inelastic scattering, photoelectrons lose kinetic energy by exciting secondary electrons, plasmons, and phonons. This limits the escape depth of the photoelectrons, described by λ, the so-called inelastic-mean-free path (IMFP). The number of emitted electrons depends on the distance d they have to travel in the solid in order to reach the surface. The intensity $I(d)$ of the emitted electrons is given by

$$I(d) = I_0 e^{-d/\lambda}, \tag{2.6}$$

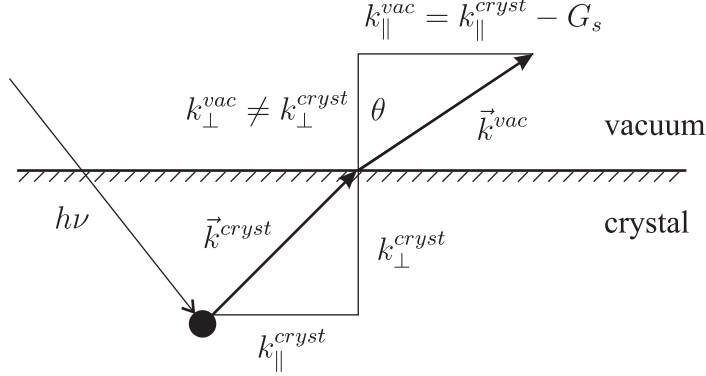where I_0 is proportional to the number of the excited electrons. The energy

Figure 2.2: Momentum relation at the solid-vacuum interface in angle-resolved photoemission. In transmission across the crystal-vacuum interface only the parallel momentum component is conserved, modulo a reciprocal surface lattice vector, but the normal component is altered by the surface potential [18].

dependence of λ is described by the so-called "universal curve", and λ reaches a minimum of about 2..3 monolayers (ML) at 50-100 eV. Because of this rather high surface sensitivity of PE in the VUV, one always has to ask to what extent the experimental spectra represent the bulk or the surface electronic structure.

Escape: During the escape of electrons into the vacuum (see Fig. 2.2), only the parallel component of the wave vector is conserved modulo a reciprocal surface wave vector (due to the periodicity of the lattice potential parallel to the surface). Therefore, we can connect the measured $k_{\parallel}^{vac}$ with the $k_{\parallel}^{cryst}$ by

$$k_{\parallel}^{vac} = k_{\parallel}^{cryst} - G_s, \qquad (2.7)$$

where G_s is a reciprocal lattice vector of the surface Brillouin zone. Photoemission processes, which involve a reciprocal lattice vector, are called "umklapp" processes and can give rise to weak extra final-state bands. Neglecting "umklapp" processes, we can express $k_{\parallel}^{cryst}$ via the kinetic energy and the emission angle θ with respect to the surface normal by

$$k_{\parallel}^{cryst} = sin\theta \sqrt{\frac{2m}{\hbar^2} E_{kin}}. \qquad (2.8)$$

Measuring E_{kin} and θ in the PE experiment fixes $k_{\parallel}^{cryst}$; this is sufficient for surface states but not for bulk bands.

A variable photon energy source is necessary to measure the band dispersion along a direction perpendicular to surface. Due to the discontinuity of the potential at the surface/vacuum interface, the perpendicular component of the electron wave vector is not conserved. The expression for the component of the wave vector perpendicular to the surface is

$$k_{\perp}^{cryst} = cos\theta \sqrt{\frac{2m}{\hbar^2} (E_{kin} - V_0)}, \qquad (2.9)$$
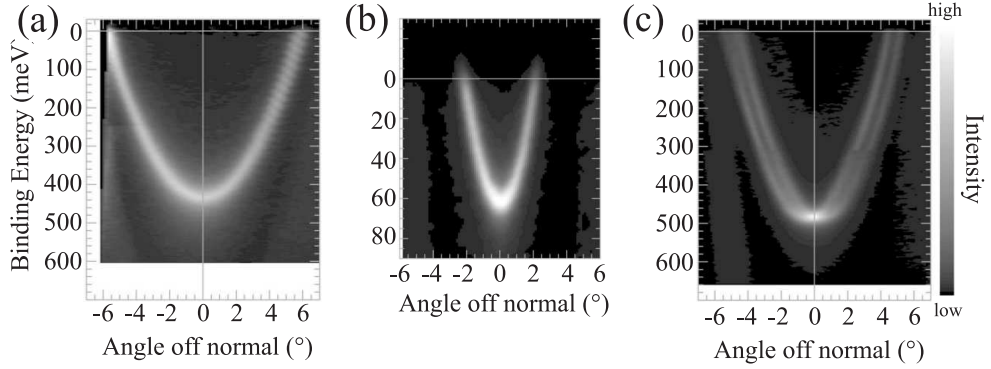
Figure 2.3: Photoemission intensity of Shockley state on noble metal surfaces as a function of energy and momentum (E_b,$k_\parallel$): (a) Cu(111), (b) Ag(111), (c) Au(111); from Ref. [25].

where V_0 is the inner potential of the crystal. There are several methods to determine V_0 ($k_\perp^{cryst}$) in the solid [24]. One can either try to identify the extrema of electron bands at the critical points and compare them with band-structure calculations. If no calculations are available, one can in some cases approximate $k_\perp^{cryst}$ by assuming free-electron-like final states, which are offset from the vacuum potential by the inner potential V_0 of the crystal.

However, the problem of determining $k_\perp^{cryst}$ does not occur for surface and interface electron states which are described in the two-dimensional Brillouin zone. For these bands, the electron momentum is fully defined by the emission angle and the kinetic energy.

A nice example of how PE can be utilized to study the electronic band structure at crystal surfaces is given in Fig. 2.3, showing the surface states of noble metal surfaces. The photoemission intensity of the Shockley surface states on (a) Cu(111), (b) Ag(111) and (c) Au(111) is presented as a function of energy and emission angle [25]. From these images one can directly see the free-electron like dispersion behavior of this type of surface bands, as well as its modification in case of the Au(111) surface, where the spin-orbit splitting of surface state can be clearly seen.

The angular scale is easily converted to electron momentum with help of Eq. 2.8.