Photoemission spectroscopy—from early days to recent applications

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Abstract. In this review we describe the development of photoemission spectroscopy (PES) from the first historic observations of the photoelectric effect by Hertz and Hallwachs to state-of-the-art experiments. We present several examples for the application of PES for chemical analysis of solids (ESCA), the determination of the valence band structure by angle-resolved photoemission (ARUPS), and the investigation of many-body effects, in particular by high-resolution PES on the meV-scale. Furthermore, we give a brief overview about the wide spectrum of experimental methods based on PES.

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1. Introduction

Photoemission spectroscopy (PES) has been established as one of the most important methods to study the electronic structure of molecules, solids and surfaces [1, 2]. Furthermore, PES has widespread practical implications in various fields like surface chemistry or material science, and has significantly contributed to the understanding of fundamental principles in solid state physics.

With this overview, we hope to convey an impression about the broad expanse of the field of photoemission applications. For additional information, the reader is referred to the review books in [1]–[5] and, in particular, to the contributions in this focus issue of New Journal of Physics.

2. Historical developments

Historically the first experiments that revealed the interaction of light with solids, which is known today as the photoelectric effect, were performed by Heinrich Hertz (Karlsruhe) and Wilhelm Hallwachs (Dresden) in 1887 [6, 7]. These experiments (see figure 1) demonstrated that negative
Figure 1. Typical experimental setup for the demonstration of the photoelectric effect as used by Hallwachs [8]. Light from a spark gap, with the option of being screened (Schirm) or filtered (Gips), impinges on a charged gold-leaf electroscope with a grounded body (Erde). A negatively charged electroscope could be discharged by ultraviolet light, whereas positive charge could not be removed.

charge—the electron had not yet been discovered—can be removed from a solid when its surface is irradiated by ultraviolet light, whereas no discharge was observed for positive charge. At that time, nobody was able to satisfactorily explain these observations.

Among the many experiments that followed the observations of Hertz and Hallwachs, there were in particular the results by Lenard (Heidelberg) on cathode rays [9], that confirmed Albert Einstein’s revolutionary hypothesis of the localized nature of light quanta. In one of the four famous publications in 1905—Einstein’s annus mirabilis—he introduced [10] the concept of the photon and deduced the relation between the photon energy $h\nu$ and the maximum kinetic energy $E_{\text{kin}}^{\text{max}}$ of the emitted electrons, i.e. the fundamental photoelectric equation

$$E_{\text{kin}}^{\text{max}} = h\nu - \Phi_0,$$

where $\Phi_0$ is a characteristic constant of the sample surface and is known today as the work function.

At that time, the maximum kinetic energy of the photoelectrons could be determined under vacuum conditions by the retarding-field technique. However, it took several years until Einstein’s formula was experimentally confirmed by observing a linear dependence between kinetic energy and $h\nu$ (a review about the history of photoemission can be found in [11]).

Today, a photoemission experiment for spectroscopic purposes is basically performed in the same way as more than 100 years ago (see figure 2). Photons from a monochromatized light source, which can be a laboratory source—for vacuum ultraviolet (VUV) or soft x-ray radiation—or a synchrotron radiation facility, are directed on a sample and the photoelectrons, liberated by the photoelectric effect, are analysed with respect to emission angle and kinetic energy by an electrostatic analyser.

The fundamental principle of the photoemission process is sketched in figure 3. This simplified picture shows the attractiveness of PES, because in that view, which will be refined later, the properties of the photoelectrons basically reflect the electronic eigenstates.
Figure 2. Principle of a modern photoemission spectrometer. Monochromatic photons with energy \( h\nu \) and polarization (\( A \) is the vector potential of the electromagnetic field) are produced by a light source, e.g. an Al-K\(_\alpha\) x-ray anode for XPS or a helium discharge lamp for UPS, and hit the sample surface under an angle \( \Psi_1 \) with respect to the surface normal. The kinetic energy \( E_{kin} \) of the photoelectrons can be analysed by use of electrostatic analysers (usually by an additional retarding field) as a function of the experimental parameters, e.g. emission angle \( (\theta, \phi) \), the electron spin orientation \( \sigma \), or the photon energy or polarization. The whole setup is evacuated to ultra high vacuum (UHV, typically \( p \lesssim 10^{-10} \) mbar).

of the investigated system. Basically, one distinguishes between ultraviolet photoemission (UPS), mainly for the (angle-resolved) investigation of valence band states (ARUPS) and x-ray photoemission spectroscopy (XPS), providing the investigation of core-level states at higher binding energies. This separation is mainly based on the two different types of quasi-monochromatic excitation sources that are available under laboratory conditions, namely VUV line spectra of discharge lamps for energies in the range of approximately 10–50 eV, e.g. with rare gases like helium (He I\(_\alpha\) : 21.23 eV and He II\(_\alpha\) : 40.82 eV), and the characteristic lines from the x-ray source, for which the most commonly used anode materials are aluminium (Al-K\(_{\alpha1,2}\) : 1486.6 eV) and magnesium (Mg-K\(_{\alpha1,2}\) : 1253.6 eV). Although the line width is usually small enough for many applications, i.e. a few meV for the discharge lamp and slightly below 1 eV for x-ray anodes, the use of an additional monochromator can be advantageous for the energy resolution and, more importantly, for the suppression of background and satellites intensities.

2.1. UPS and XPS in the early days

The field of photoemission was pioneered in the early 1960s by several groups, in particular by the group of Spicer (Stanford), who measured the first UPS valence band spectrum on copper [12] and developed the three-step model [13]; the group of Turner, who performed UPS on gases [14] using a novel type of VUV excitation source, namely the differentially pumped gas discharge lamp [15] that is still common in UPS setups today; and the group of Siegbahn in Uppsala, who developed a high-resolution XPS analyser that allowed the detailed study of core-level binding energies of solids [16] (see below).
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A typical XPS spectrum of those days is shown in figure 4, namely the result of an Al-Kα measurement on gold. One can clearly see the (5d6s) valence band close to the Fermi level and the 5d and 4f core-levels at higher binding energies. The Au-4f core-levels have a small intrinsic line width of $\approx 400$ meV and are still very often used for the energy calibration of an XPS spectrometer. The background intensity, increasing towards higher binding energies, is due to secondary electrons, i.e. photoelectrons that are inelastically scattered in the sample before escaping into the vacuum.

Meanwhile, there exist tabulated values for the core-level binding energies and photoemission cross-sections of most elements [1, 2, 17]. With this knowledge, it is relatively easy to analyse an XPS spectrum quantitatively and determine the element composition of a sample with an accuracy of a few percent. Furthermore, there is a dependence of the exact binding energy of a core-level on the chemical environment and the valence state of the emitting atom, the so-called chemical shift. These two aspects, observed and systematically studied by Siegbahn et al [18, 19], together with the high surface sensitivity, make XPS an ideal tool for the chemical investigation of surfaces and thin film, expressed in the famous acronym created by Siegbahn: ESCA (electron spectroscopy for chemical analysis).

Figure 3. Schematic view of the photoemission process in the single-particle picture. Electrons with binding energy $E_B$ can be excited above the vacuum level $E_{vac}$ by photons with energy $h\nu > E_B + \Phi_0$. The photoelectron distribution $I(E_{kin})$ can be measured by the analyser and is—in first order—an image of the occupied density of electronic states $N(E_B)$ in the sample.

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Core -levels
Au-5p

Figure 4. XPS overview spectrum of a polycrystalline Au sample for 100 ≤ E_B ≤ 0 eV, measured with Al-Kα radiation (hν = 1486.6 eV). The Au 5d valence band near the Fermi level E_F (E_B = 0) and the narrow Au4f core-levels are clearly resolved with an experimental line width of Γ = 0.8 eV (from [20]). The background intensity, increasing with the binding energy, is due to secondary electrons.

3. Synchrotron light

The use of synchrotron radiation for the excitation of photoelectrons has become increasingly important because it allows measurements that cannot be performed with usual VUV or x-ray sources in the laboratory. Many dedicated synchrotron facilities have been installed worldwide, e.g. BESSY in Germany (Berlin), Maxlab in Sweden (Lund), the Advanced Light Source in the USA (Berkeley), the NSRRC in Taiwan (Hsinchu), the Australian Synchrotron in Melbourne, or SPring8 in Japan (Osaka), among many others appropriate for PES experiments. The main difference compared to laboratory sources is that the photon energy can be selected by use of a monochromator from a continuous spectrum over a wide energy range. Other important advantages of the synchrotron light are, e.g., high intensity and brightness, variable polarization, small photon spots, or the possibility of time-resolved measurements on a very short timescale in the nanosecond range or even below. However, for many applications the use of the comparatively simple and cheap laboratory sources is still advantageous.

4. Theory of photoemission in a nutshell

The excitation of a photoelectron is actually a much more complicated process than illustrated by the simple picture above (figure 3). The sample represents always a many-body system that is involved as a whole in the photoemission process. However, the simplified single-particle picture is a good starting point for the understanding of many photoemission applications, as long as the spectrum is not significantly influenced by electronic correlation effects or one is interested in features like line shapes, satellites, or details in the band dispersion on the meV-scale.
Over the decades in which photoemission has been applied for the spectroscopic investigation of matter, there have been many important theoretical studies to describe and analyse the spectral features in photoemission data [3, 21, 22]. The most general and widely applied theoretical description of the photoemission spectrum is based on using Fermi’s golden rule as a result of perturbation theory in first order. In this approach, the photocurrent $J$ is the result of a photon-induced excitation of a system in the ground state $|\Psi_i\rangle$ to a final state $|\Psi_f\rangle = |\Psi_{\kappa,s}\rangle$, resulting in a photoelectron with momentum $\kappa$ and kinetic energy $E_{\text{kin}} = \epsilon_\kappa = \hbar^2 \kappa^2 / 2m_e$ and the remaining $(N-1)$-electron system:

$$J_\kappa(h\nu) = \frac{2\pi}{\hbar} \sum_s |\langle \Psi_{\kappa,s} | H_{\text{PE}} | \Psi_i \rangle|^2 \delta(\epsilon_\kappa - \epsilon_s - h\nu). \quad (2)$$

The index $s$ refers to a set of quantum numbers that contains all possible excitations of the final state, including phonons, plasmons, electron–hole pairs and multiple excitations.

The perturbation operator $H_{\text{PE}}$ describes the interaction of a (spin-less) electron in the system with the electromagnetic field $A$ and is given by the transformation $p \rightarrow p - eA$ of the generalized momentum operator $p = -i\hbar \nabla$ in the unperturbed Hamiltonian $H_0 = p^2 / 2m_e + eV(r)$ (the scalar potential can be omitted by choosing an appropriate gauge of the electromagnetic field):

$$H = \frac{1}{2m_e} \left[ p - \frac{e}{c} A \right]^2 + eV(r)$$

$$= \frac{p^2}{2m_e} + \frac{e}{2mc} (A \cdot p + p \cdot A) + \frac{e^2}{2m_e c^2} A^2 + eV(r)$$

$$= H_0 + H_{\text{PE}}, \quad (3)$$

with the photoemission perturbation operator

$$H_{\text{PE}} = \frac{e}{2mc} (A \cdot p + p \cdot A) + \frac{e^2}{2m_e c^2} A^2. \quad (4)$$

The quadratic term in $A$ becomes relevant only for extremely high photon intensities, that are usually not produced by standard light sources in the laboratory. Furthermore, equation (4) can be simplified when particular surface effects (i.e. surface photoemission, see e.g. [23]–[27]) are neglected and one gets

$$H_{\text{PE}}^{\text{vol}} = \frac{e}{mc} A \cdot p. \quad (5)$$

which is an appropriate basis for the theoretical description of most photoemission studies.

However, for the calculation of the spectrum, a very central simplification has to be made, which is known as the ‘sudden approximation’. It decouples in the final state $|\Psi_f\rangle = |\Psi_{\kappa,s}\rangle$, the photoelectron from the remaining solid, so that all extrinsic interactions are neglected. In other words, the final state in equation (2) has to be replaced by

$$|\Psi_{\kappa,s}\rangle = |\kappa; N-1, s\rangle \xrightarrow{\text{SA.}} c_{\kappa,s}^\dagger |N-1, s\rangle, \quad (6)$$
with the creation operator for the photoelectron \( c_{\kappa,s}^\dagger \). With this one can easily transform equation (2) and get

\[
J_k(h\nu) = \frac{2\pi}{\hbar} \sum_k |\Delta_{kk}|^2 A_k^-(\epsilon_k - h\nu),
\]

with the one-electron spectral function \( A_k^-(h\nu) = \sum_s |\langle N-1,s|c_k|N\rangle|^2 \cdot \delta(h\nu - \epsilon_s) \) and the photoemission matrix element \( \Delta_{kk} = \langle \Psi_k | H_{PE} | \Psi_k \rangle \), describing the transition probability of a single electron from state |\( \Psi_k \rangle \) into the final state |\( \Psi_k \rangle \) (the spectral function \( A^- \) should not be confused with the vector potential \( A \)). For most photoemission applications, this matrix element is assumed to be constant over the investigated energy range [2].

By definition, the spectral function \( A_k^-(h\nu) \) is connected to the one-particle Green’s function by

\[
A_k^-(\omega) = -\frac{1}{\pi} \text{Im} \{ G_k(\omega - i0^+) \} \cdot f(\omega, T),
\]

with the Fermi–Dirac distribution (FDD) \( f(\omega, T) \) and we have for the Green’s function

\[
G_k(\omega) = \frac{1}{\omega - \epsilon_k - \Sigma_k(\omega)},
\]

with the complex self-energy \( \Sigma_k(\omega) = \text{Re}\Sigma_k(\omega) + i \text{Im}\Sigma_k(\omega) \), which contains all contributions from many-body processes like electron–electron or electron–phonon interaction that determine the intrinsic quasi-particle spectrum or photoemission line shape. For core-levels of metals for example, the spectral function for the description of low-energy electron–hole excitations in the conduction band gives an asymmetric quasi-particle peak with a power-law singularity (the Mahan–Doniach–Šunjić (MDS) line shape [28]–[30]).

At high electron kinetic energies, the sudden approximation is a well-suited ansatz for the description of finite systems such as free or adsorbed atoms or molecules, but for solids one has to always take extrinsic losses into account [31]. In the three-step model by Berglund and Spicer [13], this is accomplished simply by a convolution of the spectral function with a loss function [32]. However, the exact treatment of extrinsic losses—e.g. for a detailed investigation of lifetime effects [33, 34]—requires more complicated theories because there is a quantum mechanical interference between the intrinsic spectral function and the extrinsic losses.

More detailed information about the theory of photoemission can be found for example in [3, 4, 21, 22].

5. XPS, core-levels and satellites

The simplest photoemission process consists of the photoexcitation of an electron from the K-shell, i.e. the 1s core-level, of an atom. Typical results of such XPS experiments are shown in figure 5, where the 1s core-level lines of Li, Be, B, C, N, O and F are given on a common energy scale. As expected, the individual spectra consist of a single line with a binding energy that increases with the atomic number [18].
Figure 5. XPS spectra on the 1s core-levels of different elements from the second period, measured in the solid state (from [18]). The binding energy increases with the atomic number.

Figure 6. Oxygen 1s core-level of O$_2$ and H$_2$O as free molecules [19]. In paramagnetic O$_2$, the spin of the photo-hole can be parallel or antiparallel to the spin of the valence orbital. The two final-state configurations have an energy difference of $\Delta E_s = 1.1$ eV; the relative intensity is given by the spin multiplicity. In the case of diamagnetic water molecules, the two final states are degenerate.
Figure 7. High-resolution photoemission spectra of the Si2p core-level, measured on an Si(1 1 1)\(7 \times 7\) surface with \(h\nu = 140\) eV in normal emission (from [37]). The spectrum can be decomposed in one bulk line (B) and different surface contributions (C\(_1\)–C\(_5\)). Due to spin–orbit coupling, each contribution appears as a line pair \(2p_{1/2}\) (left) and \(2p_{3/2}\) (right), with an intensity ratio of 1:2 given by the spin multiplicities of the two states.

This is, however, not always the case. In order to demonstrate that core-level spectra can be more complicated, we show in figure 6 a photoemission experiment of the 1s core-level of oxygen in O in the gas phase [19]. H\(_2\)O has a closed-shell configuration and the total spin of the molecule is zero (diamagnetic). Therefore, the energy of the O1s photo-hole is degenerate with respect to spin, i.e. the energy of the spin-up and the spin-down state is identical and no splitting \(O_2\) and \(H_2\) is observed for the O1s line of this molecule. On the other hand, \(O_2\) is paramagnetic because it has one unpaired electron in each of the two \(\pi^2p\) valence orbitals, resulting in a total spin of 1. Thus, the spin 1/2 of the photo-hole can couple to the spin 1 of the unpaired outer electrons, and due to exchange interaction the energy of spin-up and spin-down is different. This is called the spin splitting of core-levels that can be observed for many systems, including the s-levels of anti-ferromagnetic transition metal oxides [35, 36] (see below).

5.1. Core-levels measured with high energy resolution

Figure 7 shows an example for high-resolution core-level XPS that reveals the high data quality that can be obtained by the currently used synchrotron radiation [37]. The spectrum shows the Si 2p core-level from the Si(1 1 1)\(7 \times 7\) surface of silicon that consists of contributions from photoemission from the bulk B and from five different surface configurations (C\(_1\)–C\(_5\)), i.e. five inequivalent types of adatoms, that appear at different binding energies. The line width of the individual contribution is determined by the intrinsic line width of the core-level, the experimental broadening is smaller than 70 meV.
Another example for high-resolution core-level measurements with synchrotron radiation is given in figure 8. It shows the O1s and the C1s core levels from an ordered structure of adsorbed CO molecules on Ni(1 0 0) [38]. One can clearly see that the vibrational fine structure, here due to the intramolecular stretch mode, can easily be resolved and separated from electronic contributions to the line shape. The experimental resolution amounts to 50 and 30 meV for the O1s and the C1s spectrum, respectively, much less than the intrinsic line-width.

It should be mentioned that high-energy resolution at high photon energies is an important field for further development of PES, because it combines the analysis of detailed spectral structures—often related to many-body effects—with an increased sampling depth, resulting in an increased bulk sensitivity [39, 40].

5.2. Valence-band spectra of anti-ferromagnetic NiO

In this section, we shall discuss XPS results on the 3d valence band of the anti-ferromagnetic insulator NiO. These XPS measurements are closely connected to core-level data because the 3d electrons are, like core-states, localized on the emitting Ni atoms. As first suggested by Mott [44], NiO is an example of a solid system whose physical properties, and photoemission spectra, are significantly influenced by strong electronic correlations [45] of the electrons in the localized Ni3d states.

Figure 9 shows the combination of an XPS (Al-Kα) spectrum of NiO and an inverse photoemission spectrum (bremsstrahlung isochromate spectroscopy: BIS) taken at the same photon energy. Note that inverse photoemission can be regarded as the time-inversion of the photoemission process leading, however, to a (N + 1)-final state. It probes the unoccupied...
density of states of a material in the same way as photoemission measures the occupied density of states. Combined XPS/BIS data give some useful help for the interpretation of the optical gap of NiO [46], which was under discussion for a very long period [47, 48]. There are basically two peaks in the occupied density of states below $E_F$ [41, 42]: The first one with a doublet fine structure at a binding energy of 2–4 eV originates from photoemission out of the $d^8$ ground state configuration of NiO, for which the photo-hole is screened by a charge transfer from the ligand $O_2p$ electrons towards the Ni (labelled by $d^8 \rightarrow d^8 L$ in figure 9, with $L$ meaning the hole in the $O_2p$ ligand states $L$ [49]). The second one appears at about 9 eV and represents the unscreened $d^8 \rightarrow d^7$ excitation.

The first peak in the inverse photoemission spectrum at approximately $-4$ eV is a result of the excitation of the $d^8$ ground state configuration into a $d^9$ configuration. From the energy position of these features, one can immediately deduce the two main excitation parameters in NiO, namely the correlation energy $U$ and the charge transfer energy $\Delta$. $U$ is the integral Coulomb repulsion energy of two electrons in the 3d orbital of the same Ni atom (therefore sometimes labelled $U_{dd}$), and is identical to the energy required to transfer one 3d electron from a Ni atom with the ground state configuration $3d^8$ into the 3d states of another Ni atom: $3d^8 \rightarrow 3d^73d^9$ [50, 51]. The charge transfer energy $\Delta$ is the net energy difference between $O_2p$ states and $Ni3d$ states, or more precisely, the energy to transfer one electron from a ligand state $L$ to a neighbouring Ni atom in the ground state: $3d^8L \rightarrow 3d^73d^9L$. From these data it can be seen that—contrary to a long held belief—the lowest charge-neutral excitation in NiO, which is seen by optical spectroscopy at an energy of about 4 eV [52], is of the charge transfer type ($p \rightarrow d$ transition) and not of the Coulomb-gap type ($d \rightarrow d$ transition) (see [53]).

The energy distribution of valence-band states above and below the Fermi level reveals the strong interaction of d electrons in this compound and is an example for many-body effects in solids, which also determine the photoemission spectra and physical properties of systems that we shall discuss below.
Figure 10. Dispersion relations for phonons (top) and electrons (bottom) in copper [54]–[56]. The phonon dispersion has been determined by neutron scattering, the electronic dispersion by ARUPS. The capitals refer to high-symmetry points in the Brillouin zone (see [2]).

6. Valence-band spectra

ARUPS has played an important role in obtaining the valence band structure of a large number of solids and surfaces, much the same way as neutron diffraction has given information about the dispersion of phonons in solids. Figure 10 displays both the phonon dispersions of copper as measured by neutron diffraction [54] and electron dispersion relations as measured by PES
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Figure 11. (A) Fermi surface of copper with the famous belly-neck shape. (B) PES yields spherical cuts through the Fermi surface, when the intensity at the Fermi level is plotted versus the emission angle (FSM [57, 58]); the cut depends on sample orientation and photon energy. (C) FSMs on three low-indexed surfaces on Cu, measured with He I, compared to the results of LDA calculations [59].

[56]. Phonons and electrons are the main elementary excitations of a system, which determine its two essential physical properties, namely the elastic and the electronic properties.

From the electronic dispersion curves, one can see certain points where in $k$-space the bands cross the Fermi level, e.g. along $\Gamma - X$ and $K - \Gamma$ in figure 10. An integration of all $k$-points, where the bands cross the Fermi level, defines the Fermi surface of a metal. Semi-automated methods—also used for the mapping [60] of x-ray photoelectron diffraction (XPD) [61] patterns—allow an efficient measurement of spherical cuts through the Fermi surface, usually called Fermi surface maps (FSM) [57, 58, 62], where the photoemission intensity at $E_F$ is mapped as a function of the electron emission angles $\theta$ and $\phi$ (cf figure 2). The right panel of figure 11(C) shows such cuts through the belly-neck-shaped Fermi surface of copper (figure 11(A)), measured on three different low-indexed surfaces. One can easily assign the observed structures and symmetries (4-, 3- and 2-fold for (0 0 1), (1 1 1), and (1 1 0), respectively) to the features of the three-dimensional (3D) Fermi surface. The bright ring in the centre of the FSM on the (1 1 1) surface is due to the Shockley-type surface state, which we shall discuss in detail in section 7.1. The FSM method has certain advantages in comparison to other established experimental methods for the determination of Fermi surfaces, like de Haas–van Alphen effect, anomalous skin effect or ultrasonic attenuation [63]–[65]. In particular, the demands on sample quality and experimental temperature are less stringent in the photoemission experiments and the FSM gives immediately an impression of the Fermi surface shape without making the detour to extremal areas, an appropriate model, and parameter fitting.

The solid lines in the electron dispersion part of figure 10 and the right side of figure 11(C) are the result of band structure calculations based on the density functional theory (DFT) [66]–[68], which has proven to be very successful for the description and interpretation of photoemission results on valence bands. However, photoemission involves a complex excitation of the whole system, which is generically not described by DFT. If many-body effects have a significant

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influence on the quasi-particle—i.e. the excitation state including the photo-hole interacting with the electrons and phonons of the solid—other, usually more complicated, theoretical concepts have to be used for the interpretation of the data [45, 69].

In general, the interplay of PES experiments and theory has been very fruitful for the investigation of many solid-state properties, including valence-band dispersions, magnetism, Fermi surfaces, and—beyond the single-particle picture—the details of the quasi-particle line shape.

7. High-resolution photoemission in the VUV range

Whereas for band-structure measurements or FSM, an energy resolution of the order of 50 meV is sufficient, the influence of many-body effects on the photoemission spectra close to the Fermi level can be—in contrast to the example of NiO and related systems—on the scale of a few meV and requires an energy resolution of at least one order of magnitude better. In this context, the technical improvement in the field of high-resolution spectrometers during the last few years is remarkable. Figure 12 shows a typical Fermi edge at low temperature, which can be measured with present day commercially available instruments with a standard laboratory VUV source. The energy resolution can be determined from such a measurement by numerical least-squares method, using a convolution of the FDD at the experimental temperature with a Gaussian, describing the energy broadening of the instrument. For the given instrument [70],

Figure 12. Characterizing photoemission experiments for the determination of the energy resolution of a spectrometer. The main panel gives a Fermi edge of polycrystalline silver, measured at $T = 8 \text{ K}$ with He I ($h\nu = 21.23 \text{ eV}$). Fitting the data with a Gaussian broadened FDD by using the least-squares method yields a Gaussian FWHM of 3 meV. The inset shows another measurement on xenon in the gaseous phase. The total line width, fitted by a Gaussian, is 4.3 meV, consisting of intrinsic and experimental broadenings.
the experimental resolution, i.e. the full-width at half-maximum (FWHM) of the Gaussian, was determined as $\Delta E = 2.9$ meV, including contributions from the finite line width of the photons and the finite resolution of the analyser. Another standard method for the determination of the energy resolution is the measurement of a narrow rare-gas core-level in the gas phase (see inset). Meanwhile, there are first experiments with an energy resolution even below 1 meV by use of a laser for the photoexcitation [71].

It should be noted that high performance in energy and angular resolution is closely connected with a high efficiency of the photoelectron detection, e.g. by the use of 2D MCP-CCD detector systems that allow a simultaneous measurement of photoelectrons with different angles and kinetic energies, and intense light sources. The improved resolution in energy and angle reduces the phase space volume and therewith the photoelectron count of one data point—even more if another parameter of the photoemission process is resolved, as e.g. the sample position, the photoelectron spin, or the time.

In the following, we give three examples for many-body features on the meV-scale in the UPS photoemission spectra of solid systems, namely the (1 1 1) Shockley-type surface state on Cu(1 1 1), the superconducting gap of a conventional superconductor (V$_3$Si), and the Kondo resonance in a heavy fermion system (CeCu$_2$Si$_2$). These examples represent model systems for the understanding of more complex questions in solid state physics, including high-temperature superconductivity (HTSC) and heavy fermions.

### 7.1. Narrow lines of surface states

The Shockley-type surface state [73, 74], observed on noble metal faces in (1 1 1) orientation, has been a classical example for extremely narrow photoemission features since the first observation more than 20 years ago [75, 76]. These particular quasi-2D electronic states appear on many metal surfaces and are suitable as model systems for the experimental investigation of fundamental solid state and surface properties, including band dispersion, lifetime effects, the influence of surface modifications and many-body band renormalization, essentially by angle-resolved PES [77]–[87]. In addition, the interest on surface states has been increased recently by the development of spectroscopy with the scanning tunnelling microscope (STM), which produces spectral information on surface electronic states above and below the Fermi level with additional local information [88]–[93].

In the following, we present the example of the Shockley-state on Cu(1 1 1) [72, 75, 77, 94, 95], which appears in the $L$-gap of the projected bulk band structure. Figure 13 shows the result of a photoemission measurement on the Shockley-state of Cu(1 1 1) as a colour plot of the intensity at the Fermi level versus parallel momentum $k_{\parallel} = (k_x, k_y)$ in the FSM in the top panel, and the intensity distribution $I(E_B, k_{\parallel})$ in the lower panel. The cut through the cylindrical Fermi surface of the Shockley-state appears as a circle that lies within the projected neck (dark blue area) of the bulk Fermi surface shown in figure 11. The dispersion, given in the lower panel, is a nearly perfect parabola, with a maximum binding energy of 435 meV and an effective band mass of $m^*/m_e = 0.412$ [72]. By cutting the intensity distribution along vertical or horizontal lines, one gets the so-called energy distribution curves (EDC) or momentum distribution curves (MDC), from which one can analyse the line shape of the Shockley-state in detail.

Figure 14 shows an EDC measured in normal emission, i.e. at $|k_{\parallel}| = 0$. The line is nearly perfectly symmetric with a maximum at a binding energy of 435 meV. By use of the least-squares method, one can fit the line shape of the EDC, when one assumes that the line consists merely
Figure 13. Photoemission intensity from the Shockley-state of Cu(1 1 1) is displayed as a colour plot (ARUPS: He I, T = 30 K) [72]. The lower panel shows $I(E_B, k_x)$ with the nearly parabolic dispersion in below the Fermi level, the upper panel gives the FSM of the Shockley-state, i.e. $I(E_F, k_\parallel)$ with $k_\parallel = (k_x, k_y)$, embedded inside the (1 1 1)-projected neck of the bulk Fermi surface, also called the L-gap (dark blue region).

of an intrinsic Lorentzian contribution and an extrinsic experimental broadening, that can be described by a Gaussian with known FWHM, given by the energy resolution of the spectrometer [96]. The fit gives an intrinsic Lorentzian width of $\Gamma = 23$ meV, only slightly less than the total experimental line width [72]. In the time domain, this value corresponds to a photo-hole lifetime of $\tau = 29$ fs at the band minimum. Here, the lifetime is limited mainly by inter- and intra-band electron–electron scattering events, which are the dominant interaction process at higher binding energies [91, 97].

7.1.1. Electron–phonon coupling in Cu(1 1 1). For states very close to the Fermi level, the contribution from the electron–phonon coupling becomes important. An analysis of the line width as a function of the binding energy is presented in the lower panel of figure 15. At the Fermi level ($E_B = 0$), the intrinsic line width amounts to approximately 5 meV. Here, the contributions from electron–electron and electron–phonon interaction are zero; the remaining line width $\Gamma^{el-imp}$ is due to experimental contributions and the scattering by impurities at the surface [98]. On going to
higher binding energies, the line width increases up to a value of $\Gamma \approx 13$ meV at $E_B = 35$ meV. A comparison with the approximation by the Debye model (with model parameters from the literature [94, 99]) demonstrates that the observed energy dependence of the line width can be explained by the electron–phonon contribution to the imaginary part of the self-energy (equation (9)). Even quantitatively, the theory describes the observed energy dependence reasonably well.

The Debye model describes also the real part of the self-energy $\Re \Sigma$ that determines the band renormalization close to the Fermi level. This band renormalization leads to a reduced slope of the quasi-particle band at $E_F$ by a factor of $1/(1 + \lambda)$ [101]. This $\lambda$ is identical to the value that can be determined from the temperature dependence of the line width [94, 100, 102]. Although the band renormalization for the Shockley-state on Cu(1 1 1)—with $\lambda = 0.137$—is small compared to other surface states [103]–[105], it can be observed by high-resolution photoemission. The upper panel of figure 15 shows $\Re \Sigma$, which is equal to the difference between the measured dispersion and its parabolic extrapolation from higher binding energies (dashed line in inset). Again the agreement between experiment and the result of the Debye model is obvious, although the theoretical curve contains several simplifications and is calculated for $T = 0$. Meanwhile, there are much more elaborate theories that take into account explicitly surface phonon modes in the calculation of the photo-hole lifetime of the Shockley-state [81, 106].

**Figure 14.** Line shape analysis of the Shockley-state on Cu(1 1 1) in normal emission (He I, $T = 30$ K, $\Delta E = 3.5$ meV). The profile can be fitted by a Gaussian broadened Lorentzian, but the experimental broadening is nearly negligible in this case [72]. The intrinsic line width (FWHM) amounts to $\Gamma = 23$ meV. The bars at the horizontal axis indicate the residuum of the least-squares result.
Figure 15. Electron–phonon interaction-induced changes of the dispersion (top panel) and the line width (bottom) of the Shockley-state on Cu(1 1 1) ($h\nu = 21.23$ eV, $T = 30$ K, see [100]). The near-$E_F$ changes—compared with the approximative predictions of the Debye model (solid line, $\hbar\omega_D = 27$ meV, $\lambda = 0.137$)—can be determined very precisely [100].

7.2. Superconductors and electron–phonon coupling

One of the most important examples for the influence of many-body effects on solid state properties is superconductivity. As explained by Bardeen, Cooper and Schrieffer (BCS) in [108], the phonon-driven interaction of two electronic states leads to the formation of Cooper pairs at temperatures below a transition temperature $T_c$. This phase transition appears in the electronic density of states as the creation of an energy gap confined by two singularities symmetrically positioned around $E_F$. For conventional superconductors with transition temperatures up to $T_c \approx 20$ K, this gap is very small, typically below 3 meV. However, modern high-resolution spectrometers allow one to investigate the spectral features of the superconducting properties experimentally. Figure 16 shows two near-$E_F$ spectra [107] of polycrystalline V₃Si, one above and one below the transition temperature $T_c = 17.1$ K (for a review about the A15...
Figure 16. High-resolution UPS ($h\nu = 21.23$ eV) spectra of the conventional superconductor $V_3Si$ [70, 107]. Although the superconducting gap $\Delta_0$ has a width of only a few meV, the photoemission spectra close to the Fermi level show a dramatic change of the intensity distribution between spectra above and below the transition temperature of $T_c = 17.1$ K. The density of the states in the gap range is transferred to the singularities at $\pm\Delta(T)$. The inset gives the experimentally determined gap width versus the sample temperature (theoretical temperature dependence is shown by the dashed line).

superconductors, see [109]). At $T = 19$ K, the spectrum looks perfectly metallic, i.e. it can be fitted by a Gaussian broadened FDD. At $T = 11$ K, i.e. approximately 6 K below the transition temperature, the spectrum looks completely different: there appears a prominent peak with a maximum at $\approx 4$ meV, the intensity drops rapidly towards the Fermi energy, much faster than for a metal at the same temperature (dashed line), and a shoulder remains slightly above $E_F$. Note that these spectral features appear in an energy range of less than 10 meV around the Fermi level. The spectrum can be described by the BCS theory that gives two singularities at $\pm\Delta(T)$, which confine the superconducting energy gap [108]. If one takes into account the FDD at finite temperatures and the experimental broadening (by convolution with a Gaussian with FWHM known from characterizing measurements, see above), one gets the model function that perfectly describes the experimental spectrum [70]. An analysis of spectra measured at different temperatures gives the temperature dependence of the energy gap, displayed in the inset of figure 16. Similar results have been obtained on other conventional and unconventional
superconductors, as e.g. lead and niobium [110], or CeRu$_2$ [71], MgB$_2$ [111, 112] and A$_3$C$_{60}$ [113], respectively.

On single-crystalline materials, one can further investigate the angle dependence of the photoemission signal in the gap range; for example, one has observed by ARUPS a sheet-dependent superconductivity in 2H-NbSe$_2$ [114].

Related experiments have been performed on high-temperature superconducting oxides (HTSC) [117] for which PES is the most important experimental tool for the investigation of the electronic structure [118]–[123]. For these systems, the debate about the origin of the electronic coupling mechanisms is still open [124]. There are indications for both spin-fluctuations and BCS-like phonon interactions [125]. As demonstrated above for the Shockley-state on Cu(1 1 1), the influence of the electron–phonon coupling can also be observed in the normal-conducting phase. The parameters which describe the electron–phonon self-energy are closely related to the spectral properties in the superconducting state. This has been proven for model systems like lead [100, 126] for which the coupling mechanism is known [125, 127]. At the moment, the band renormalization in HTSCs and the quasi-particle line width are studied intensively in this context [118, 128, 129].

7.3. The Kondo resonance of Ce-compounds

The strong Coulomb interaction between electrons in a metallic solid leads to the Kondo effect, that appears as a characteristic minimum in the temperature dependence of the electrical resistivity in systems with magnetic impurities, e.g. 3d or 4f elements [130]. Closely related to the involved scattering processes of the conduction electrons at the impurities is the existence of a peculiar many-body feature in the electronic density of states close to the Fermi-level [131]–[133]. This energetically very narrow feature is called the Kondo resonance.

The most simple theoretical description of the Kondo resonance is given by the single impurity Anderson model (SIAM) [134, 135] that we will use for the discussion here. The SIAM model contains the single particle energies of the conduction electrons $\varepsilon_k$ and the localized $f$ (or d) states $\varepsilon_{fm}$, the hybridization $V_{km}$ between conduction band states and localized moments, and, finally, the Coulomb correlation energy $U$ between two electrons in the $f$ (or d) states of the impurity:

$$ H_{SIAM} = \sum_{k \alpha} \varepsilon_k c_{k \alpha}^\dagger c_{k \alpha} + \sum_{m \sigma} \varepsilon_{fm} f_{m \sigma}^\dagger f_{m \sigma} + \sum_{km\sigma} (V_{km} c_{k \alpha}^\dagger f_{m \sigma} + h.c.) + \frac{U}{2} \sum_{(m \sigma) \neq (m' \sigma')} f_{m \sigma}^\dagger f_{m \sigma} f_{m' \sigma'}^\dagger f_{m' \sigma'}. $$

(10)

Although all energies are typically at least of the order of several 100 meV or more (for many calculations $U$ is even set to infinity), the resulting energy eigenvalues are characterized by a small energy scale, expressed by the Kondo temperature $T_K$, that gives the temperature range for the observation of correlation effects in thermodynamic, magnetic or transport measurements (e.g. Kondo minimum in the resistivity). Typical Kondo temperatures found for Ce systems reach from a few Kelvin (for $\gamma$-Ce like systems) up to several 1000 K (a-like) [130]. Spectroscopically, the Kondo temperature characterizes the width and the position of the Kondo resonance at low temperatures.

Numerical methods, like the non-crossing approximation (NCA) [136], allow to calculate the SIAM spectrum for finite temperatures as shown in the inset of figure 17 (using parameters.
Figure 17. High-resolution angle-integrated UPS (hν = 40.8 eV) spectrum of CeCu$_2$Si$_2$ at T = 11 K. If the energy resolution is of the order of the thermal broadening (or better), one can restore the spectral information up to an energy of 5k$_B$T above $E_F$ [115]. This normalization method can be applied here to reveal the Kondo resonance [116]. The inset gives the result of an NCA calculation over an enlarged energy range (corresponding to approximately ±250 meV), including the spin–orbit features A/E, the crystal-field structures B/D, and the Kondo resonance (C) with its maximum positioned slightly above $E_F$.

for a $\gamma$-Ce like compound). In addition to the Kondo resonance with a maximum slightly above $E_F$, the energy range close to $E_F$ shows other features that are due to a spin–orbit splitting (peaks A and E in figure 17) and a crystal-field splitting (peaks B and D in figure 17) of the f-states.

Furthermore, figure 17 shows a high-resolution UPS spectrum on the prototype heavy fermion compound CeCu$_2$Si$_2$ ($T_K = 11$ K) for which the Kondo resonance appears slightly above the Fermi level, where the photoemission intensity is suppressed by the FDD [116]. By normalizing the data to the FDD [115], one can restore the information up to an energy of approximately 5k$_B$T, provided that the energy resolution is of order of thermal broadening or better. The raw photoemission spectrum near $E_F$ shows only the occupied tail of the Kondo resonance and a weak crystal-field satellite. After normalizing the data, the Kondo resonance appears as a narrow line at a few meV above $E_F$ and can be analysed in more detail.

With increasing sample temperature, the accessible energy range above $E_F$ increases linearly, but the intrinsic spectrum itself has also a temperature dependence on the scale given by
Figure 18. Temperature dependence of the 4f-spectra of CeCu$_2$Si$_2$. Top panel: calculations for finite temperatures by NCA based on the SIAM [137]; and bottom panel: photoemission spectra (He II) after application of the normalization procedure. With increasing temperature the features get broader and the spectral weight at $E_F$ decreases.

The Kondo temperature $T_K$. The lower panel of figure 18 shows the normalized spectra at different temperatures. One can see that the Kondo resonance becomes broader and merges with the neighbouring structures, which are due to crystal field excitations. At 200 K, i.e. approximately $10 \times T_K$, there is only one broad structure left, but still with considerable spectral weight at $E_F$. The same behaviour can be observed in the numerically calculated spectra of the SIAM, for which the information about crystal field energies, spin–orbit splitting and one-particle 4f energy of CeCu$_2$Si$_2$ were determined independently [116], [137]–[139]. Obviously, already the simplified picture of a single magnetic impurity reproduces the main features of the 4f density of states, with surprisingly good quantitative agreement. This again is an example where the comparison of the experimentally observed structures with theoretical results allows, on the one hand, the identification of the experimental structures and, on the other hand, the verification of the applicability of the model used.

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Usual high-resolution UPS spectrometers, which are commercially available today, provide an energy resolution of a few meV, consisting of contributions from the hemispherical electrostatic analyser and the light source. First experiments using a laser for the excitation have been published with a resolution of less than 1 meV [71]. The resolution in a particular photoemission experiment, namely PFI-ZEKE (pulsed-field-ionization, zero-kinetic-energy) employing pulsed lasers as light sources and a time-of-flight spectrometer for the electron detection, is several orders of magnitude better [141]. Figure 19 gives the the time-of-flight spectrum of the Ar$^+\,^2P_{3/2} \leftarrow \text{Ar}^1S_0$ transition on gaseous argon [140]. The experimental line width (FWHM) of 0.06 cm$^{-1}$ is equal to an energy broadening of 0.0074 meV, which is about three orders of magnitude better than in the best standard photoemission experiment. It remains to be seen how this kind of technology can be transferred to classical photoemission experiments.

Based on the photoelectric effect, as discovered by Hertz and Hallwachs, there are many other important applications and experimental methods in use today, on which we cannot comment in detail in this overview. Most of these applications add the control or the measurement of another physical parameter in the photoemission process, in addition to the kinetic energy and the emission angle. Very briefly, we give some examples below.

8. Other members of the photoemission family—resonance, dichroism, diffraction, etc
8.1. Resonance photoemission

One of these methods is resonance photoemission spectroscopy (ResPES) for which the photon energy is tuned through a core-level excitation, i.e. through an x-ray absorption edge [142]. This, of course, requires the possibility of a continuous modification of the photon energy as possible only at synchrotron radiation facilities. The possible immediate Auger decay can lead to a final state which is identical to a certain direct photoemission final state. The coherent resonance of the two final states leads to a characteristic variation of the photoemission intensity with the photon energy—known as the Fano line-shape [143]—that can be used for the assignment of valence band states to individual components of the solid or particular final states (for examples on transition metal oxides see [144]–[147]). This method, for example, supplied the evidence for the two-hole final state assignment of the 6 eV satellite [148] in the valence band of Ni metal [149].

8.2. The photoelectron spin and magnetic dichroism

The investigation of the magnetic properties of surfaces and thin films has become increasingly important mainly because of the development in the field of information storage devices. PES as a surface-sensitive experimental technique has played an important role for the understanding and characterization of these 2D systems.

Additional information about the photoexcitation process and the properties of the sample can be obtained by an investigation of the photoelectron spin by spin-polarized photoemission (SPES) (for a recent review see [150]). Here, one measures the spin polarization of the photoelectrons [3], [151]–[155], typically by use of a Mott detector [156, 157] or a LEED detector [158]. Unfortunately, the application of spin-polarization measurement for photoemission suffers from the small detection efficiency of the spin detector, which is three or four orders of magnitude smaller than for spin integrating detectors. However, because of the importance of high detection efficiency mentioned above, new designs were developed to enable a combination of spin detection and ARUPS [159, 160] with a signal-to-noise ratio comparable to that of standard ARUPS.

The Dirac equation, as an extension of the spin-less Hamiltonian in equation (3), shows that spin-polarized photoelectrons can be produced by two different physical principles: (1) by use of unpolarized light when there is a spin polarization in the ground state, as e.g. in magnetic materials; (2) by use of polarized light in combination with spin–orbit split states, even if there is no polarization in the ground state. A recently published example [161] on a non-magnetic material demonstrates the high performance of SPES, namely the characteristic spin–orbit splitting of the Shockley-state on Au(1 1 1) [162, 162]. Although forbidden by symmetry arguments in the volume of the FCC solid, the Au(1 1 1) Shockley-state shows a resolved spin-degeneracy due to the broken translational invariance at the surface [164, 165]—in contrast to other noble metal surfaces [82]. The result of this SPES investigation on the Shockley-state of Au(1 1 1) was a clear separation of two concentric rings in the FSM with counter-rotating spin orientations in the ground state.

Related to the spin-polarization measurements of the photoelectrons is the effect of dichroism on magnetic materials, in particular when the polarization of the incident light can be controlled, e.g. by using appropriate insertion devices at synchrotron facilities. Thus the photons for the excitation can be linearly, elliptically or circularly polarized, which can induce fine but important asymmetries in the photoelectron intensity distribution, for example as caused by the
Figure 20. Real-time images of Bi-decorated grain boundaries of a polycrystalline Cu surface by use of the photoemission intensity close to the Bi4f\(_{7/2}\) core-level (\(h \nu = 600\) eV, BESSY). The core-level spectra (bottom, middle) are measured at three different surface areas, indicated by coloured rectangles in the top image. The black arrows indicate the different binding energies at which the images are taken.

the magnetic circular dichroism in photoemission (MDPE) [166], first observed by Baumgarten et al on Fe2p [167]. Subsequent experiments by other groups have demonstrated that dichroism can be observed also with linearly polarized light on core levels and valence band states [168, 169], or under certain experimental geometries even with unpolarized light [170, 171]. The various combinations of polarization type, photon energy and investigated binding energy range have produced a number of seemingly different methods—e.g. MLD, MCD (magnetic linear/circular dichroism), MDAD (magnetic dichroism in the angular distribution of photoelectrons), UMDAD or MUDAD (magnetic unpolarized dichroism in angular distribution), MCDAD (magnetic circular dichroism asymmetry distribution)—that all, fortunately, are closely akin to each other with respect to the fundamental physical processes [172, 173]. For typical applications of SPES and dichroism in photoemission, the reader is referred to the above-cited literature.

8.3. Photoelectron microscopy with chemical information

There are also applications that combine the spectral photoemission information with a lateral resolution of the sample surface. This can be obtained either by scanning a focused photon beam over the sample surface or by a parallel imaging of the photoelectrons (see e.g. [174, 175]). When the lateral resolution is better than about 1 \(\mu m\), these applications require high-photon flux sources like synchrotron radiation facilities, because the spacial resolution reduces the number of electrons per energy interval and detector channel. Figure 20 shows a typical result of a system
where a photoelectron microscope lens system (PEEM: photoemission electron microscope) is combined with an energy filter that allows ESCA on small surface areas with high energy resolution [176, 177]. With this example, it is demonstrated that even the chemical modification on grain boundaries can be investigated on the lateral scale of 100 nm. More sophisticated concepts reach lateral resolutions in the low-nm range [178, 179].

9. Summary

Today, 100 years after Einstein’s explanation of the photoelectric effect, there are many well-established analysis methods based on photoemission. These methods are used in particular for the investigation of solids and surfaces and have contributed substantially to the understanding of the electronic structure of condensed matter. As a matter of fact, the present state of knowledge about electronic band structures and Fermi surfaces comes to a large extent from experimental data obtained by PES. With the energy resolution of 1 meV available today, the effects of electron–electron and electron–phonon interaction can be observed and investigated in detail (e.g. band renormalization near the Fermi energy, lifetime width, Kondo resonance and gaps in conventional superconductors). Methods like ESCA and photoelectron microscopy are now widespread analytical methods in materials science and chemistry, and gain more and more importance in fields like nanotechnology and biology.

Of course, there is still plenty of room for improvements in this field. In particular, for high energy resolution, the performance realized in atomic ZEKE photoemission experiments of the order of 0.01 meV points the way for spectroscopy on solids and surfaces. Furthermore, one can hope that in the future there will be intense and continuous light sources available for the laboratory, which will end the necessity to move to synchrotron radiation facilities for numerous photoemission applications.

The examples presented in this overview are probably not sufficient to give a realistic impression of the enormous range of different applications and results of PES; the interested reader is referred to the cited literature and the contributions following in this focus issue of New Journal of Physics.

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