

Photoelectron spectroscopy—An overview

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Abstract

We give an overview about the development of photoelectron spectroscopy (PES) from first historic observations of the photoelectric effect to state-of-the-art experiments. We present selected examples for the application of PES for chemical analysis of solids (ESCA), the determination of the valence band structure by angle resolved photoelectron spectroscopy (ARUPS), and the investigation of many-body effects by high-resolution PES. Furthermore, we give a brief introduction to the possibilities of spatially resolved PES and PES with high photon energies.

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1. Introduction

Photoelectron spectroscopy (PES) is 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.

In this overview, we give several examples to review the present state of the field of PES. For additional information the reader is referred to the review books in Refs. [1–5].

In the laboratory, gas discharge lamps and soft X-ray sources have been used for the photoexcitation with photon energies ranging from 11.8 eV (Ar I) to 1486.6 eV (Al- K_{α}). With synchrotron radiation about the same photon energy range was covered for a long time, however, with the option to tune the energy through resonances or with the aim of k_{\perp} measurements, including other advantages of the synchrotron light. With photon energies in this range, the resulting kinetic energies of the photoelectrons are in the same energy range,

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namely between a few 10 eV and approximately 1.5 keV. A characteristic property of these PES experiments is the *surface sensitivity* due to the fact that the escape depth of the excited electrons is rather small, typically in the range of a few Å, as indicated in Fig. 1. The consequently small information depth of PES can be a drawback if one is interested in studying bulk properties of solids. However it seems that for many materials investigated so far, the observed electron spectra reflect predominantly the bulk properties. On the other hand, there are notable exceptions like e.g. $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ [6,7] or YbInCu_4 [8–11], where recent high photon-energy PES has shown that even at 1486.6 eV the surface contributions can deviate significantly from the bulk spectra and consequently can influence the results. A straightforward way to reduce the surface contributions is, as obvious from Fig. 1, the use of hard X-ray photons (hard X-ray PES: HAXPS) for the photoexcitation, i.e. energies above 2 keV, preferably in the range of 5 keV or even more. This field of HAXPES was first reviewed in the HAXPES 2003 workshop in September 2003 in Grenoble, France. This volume contains the proceedings of this workshop, and since that date a number of

papers have appeared that have demonstrated the usefulness of high photon-energy PES.

One disadvantage of the high photon-energy is the energy resolution, which is at best 100 meV for $h\nu \approx 5$ keV, whereas in the VUV range one reaches values less than 3 meV with He discharge lamps ($h\nu = 21.2$ eV) and even less than 1 meV for excitation with a LASER source at $h\nu \approx 10$ eV [79]. It should also be added that the surface sensitivity of conventional PES can be an advantage in studying surface related properties like electronic surface states, adsorbate structures, or ultra-thin films.

In this introductory paper the field of PES as such will be covered, whereas specialized applications of high photon-energy PES, in particular HAXPS, will be presented in the following contributions.

2. General principles

In one of the four famous publications in 1905—Einstein’s *annus mirabilis*—he introduced [12] 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:

$$E_{\text{kin}}^{\text{max}} = h\nu - \Phi_0. \quad (1)$$

Φ_0 is a characteristic constant of the sample surface and is known as the *work function*. This equation still forms the basis for the interpretation of PE experiments today.

A photoemission experiment consists of two main components (see Fig. 2): (1) 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 (2) the photoelectrons, liberated by the photoelectric effect, are analyzed with respect to emission angle and kinetic energy by an electrostatic analyzer. The fundamental principle of the photoemission process is sketched in Fig. 3. This simplified picture shows the attractiveness of PES, because in that view the properties of the photoelectrons

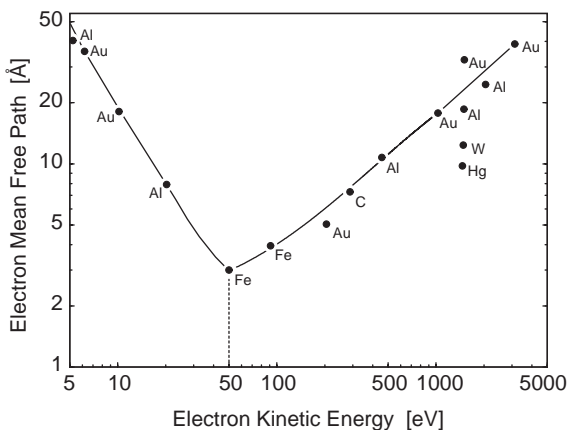


Fig. 1. Electron mean free path λ , measured for various metals, as a function of the kinetic energy. The solid line indicates the “universal curve” with a minimum of 2–5 Å in the kinetic energy range of 50–100 eV. In spite of the universal character of the energy dependence, the different points at $E_{\text{kin}} \approx 1.5$ keV demonstrate the material dependent scatter of the electron mean free path (see e.g. Ref. [2]).

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