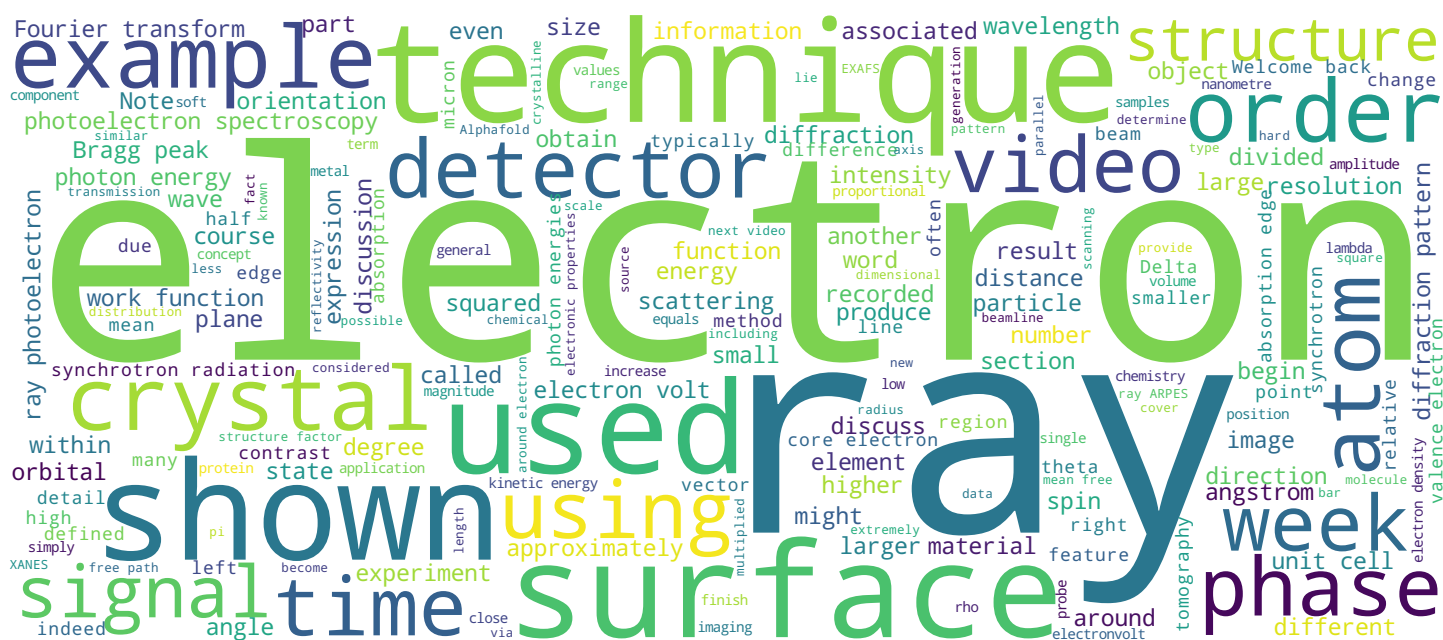


Introduction

Techniques and applications

Prof. Philip Willmott



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Video



Contents and objectives of this video



- The photoelectric effect
- Energy balance and the work function
- Types of photoemission spectroscopy

Welcome back to week 4 of this course on Synchrotron and XFEL Radiation, Techniques and Applications. In this last section of this week, and indeed of our discussions of X-ray spectroscopy, we will cover various types of photoelectron spectroscopies used primarily for either surface chemistry, or electronic structure determination.

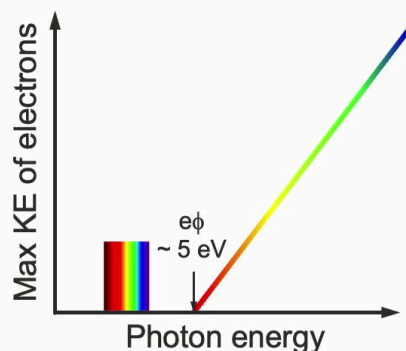
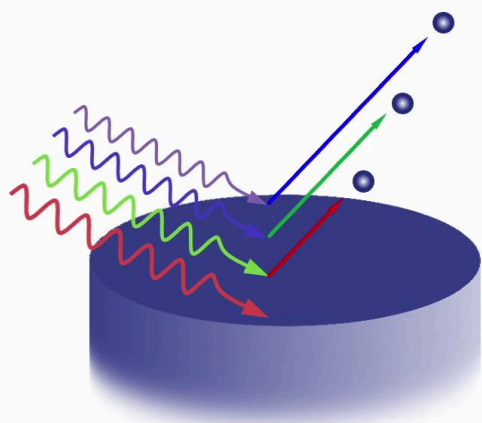
Notes

Summary



0m 05s

The photoelectric effect



- Heinrich Hertz, 1887
 - First to observe PE effect
 - No explanation
- JJ Thomson, 1899
 - PE current varies with colour and intensity
- Albert Einstein, 1905
 - Described PE effect in terms of light quanta (photons) $E = h\nu$
 - Nobel Prize 1921

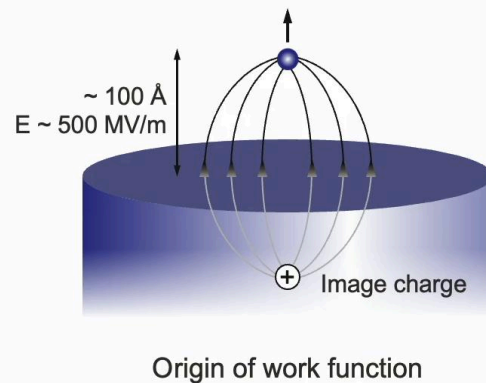
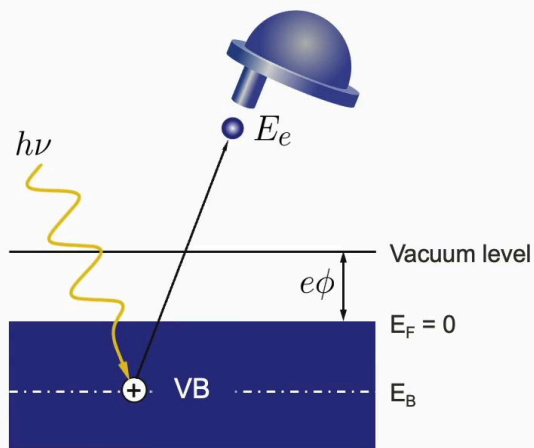
We begin our discussion of photoelectron spectroscopy, with a recap of the physical process, responsible for the generation of photoelectrons, namely the photoelectric effect. This is the phenomenon that electrons can be emitted from the surface of a metal, but only if the wavelength of light used is shorter than a critical value. Light of longer wavelengths than this, fail to eject electrons, even if higher beam intensities are used. Although both Heinrich Hertz and JJ Thompson observed aspects of the photoelectric effect, it would take the insights of Albert Einstein to explain it. Einstein invoked the concept of there being a minimum packet of energy, associated with light of a frequency ν , and that light consisted of these packets, or quanta of light called, nowadays, photons. This paradigm shift in the description of light as consisting of particles, instead of being a wave would earn Einstein a Nobel Prize in physics in 1921. The lowest photon energy required for the case of high-conductivity metals is equal to the work function. The work function has a value of around 5 electron volts. In other words, 2 or 3 electron volts above the blue end of the visible regime.

Notes

Summary



Conservation of energy in the photoelectric effect



$$E_e = h\nu - E_B - e\phi$$

The kinetic energy of the electron is thus equal to the photon energy, minus its binding energy, and this might be zero for a metallic valence electron, and up to hundreds of kiloelectronvolts for the most tightly bound core electrons, of high-Z elements minus the work function. The origin of the work function is the fact that a minimum energy is required to remove an unbound valence electron from the sea of other electrons due to the generation of a positively charged mirror image of itself as it leaves the surface. An electron is sort of considered to be free after about 100 angstroms above the surface. If the work function is around 5 electron volts, this means that one would need an electric field strength of around 500 megavolts per metre, in order to remove an electron simply through electrostatic fields.

Notes

Summary

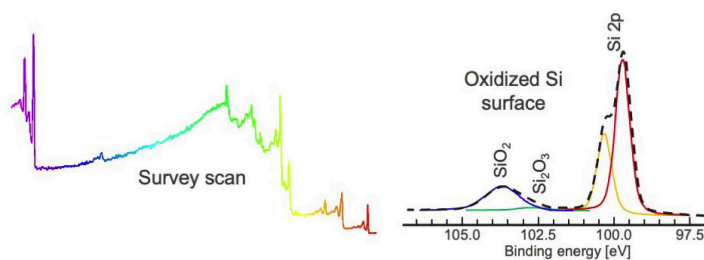


2m 04s

Types of photoemission spectroscopies

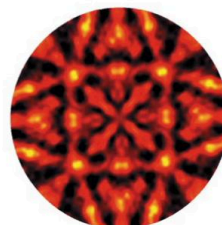
▪ XPS/ESCA

- X-ray photoelectron spectroscopy
- Mainly lab-based sources, ~ 1 keV
- Chemical analysis
- Mainly surface sensitive



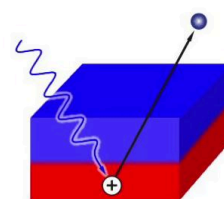
▪ UPD/XPD

- X-ray photoelectron diffraction
- Surface/absorbate structures of crystalline systems
- Mainly but not exclusively lab-based
- Requires 2π sr rotational movement of sample



▪ HAXPES

- XPS using **hard x-rays** up to ca. 15 keV
- Large IMFP \Rightarrow bulk chemistry, buried interfaces
- Low PE cross-section \Rightarrow requires flux provided by SR



There are many variants of photoelectron spectroscopy or PES. The techniques we discuss in this section, are summarised here. At higher photon energies, core electrons can also be accessed, providing information on the sample chemistry in the technique of X-ray photoelectron spectroscopy, originally named Electron Spectroscopy for Chemical Analysis or ESCA. This technique is used commonly in surface-science laboratories, and does not necessarily require synchrotron radiation. Similarly, ultraviolet and X-ray photoelectron diffraction, are often carried out using lab-based light sources. They are used to identify surface species on a crystalline sample via the strong forward scattering of photoelectrons that project the structural and chemical features in a hemispherical manner. Hard X-ray Photoelectron Spectroscopy, or HAXPES, uses high-energy X-rays to access information, of the chemistry via excitation of core electrons to probe the chemistry and via the valence electrons, to determine the electronic properties of the sample. However, because the photon energy is high relative to the electron binding energies, this means that the photoelectron energies will also be high.

Notes

Summary

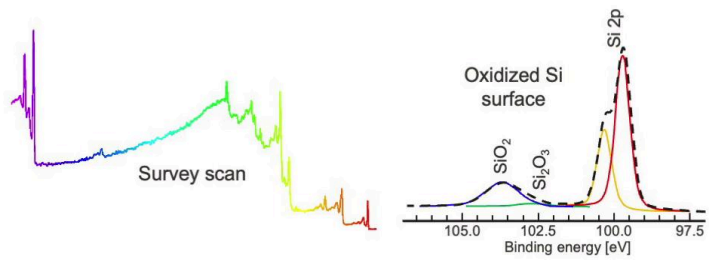


3m 07s

Types of photoemission spectroscopies

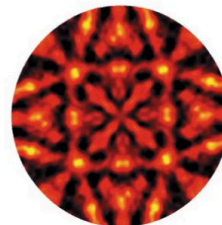
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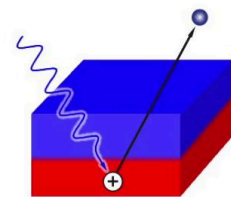
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This brings us towards the high-energy regime of the universal curve, for which the inelastic mean free path is much higher. As a result, HAXPES probes not the surface region, but instead the sample's bulk properties, or indeed, the electronic properties of interfacial regions in thin film heterostructures. Importantly, if photon energies are used far above their resonant energy for photoemission, the photoelectric cross-section, will be very small. HAXPES thus absolutely requires the high flux offered by synchrotron radiation.

Notes

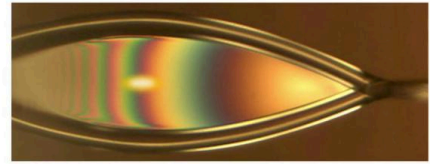
Summary



Types of photoemission spectroscopies

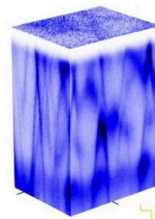
▪ APPEES

- Ambient-pressure photoemission spectroscopy
- Studies of chemistry/dynamics in “real” systems at processing pressures
- Requires extraction of photoelectrons within $1 - 3 \times \Lambda_e$ for conditions used



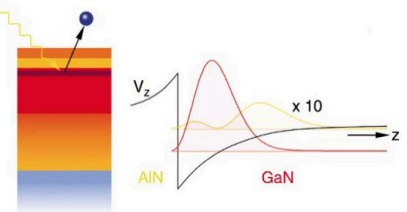
▪ ARPES

- Angle-resolved photoelectron spectroscopy
- Workhorse of electronic-structure determination
- Requires control of sample orientation and polarization of SR



▪ SX-ARPES

- Soft x-ray ARPES up to 2000 eV
- Low signal (see HAXPES) \Rightarrow requires SR
- Electronics of buried interfaces/operando devices



Ambient pressure photoelectron spectroscopy, uses sophisticated differential pumping systems to extract the photoelectrons before they undergo inelastic collision, with the ambient gas surroundings. This technique is used to investigate catalysis, and surface chemistry under real working conditions. Ultraviolet and very soft X-rays probe the most weakly-bound valence electrons of a system, and can provide important information on the material's electronic band structure, particularly when the electron momentum, that is, its emission direction, relative to the crystal lattice from which it emerged, is also recorded. This is the extremely important technique of ARPES or Angle-Resolved Photoelectron Spectroscopy. Although lab-based sources can be used for ARPES, synchrotron radiation has the dual advantage of much higher flux, and tunability of this incident radiation. ARPES requires accurate control of both the sample orientation, and the polarisation of the incident synchrotron light. Soft X-ray ARPES uses photon energies that lie between conventional ARPES, and HAXPES at around 500 electron volts to 2,000 electron volts.

Notes

Summary

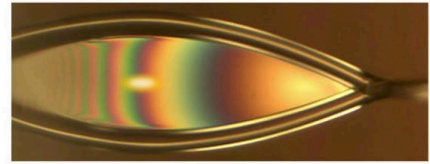


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Types of photoemission spectroscopies

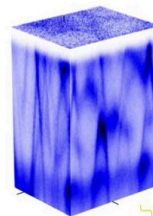
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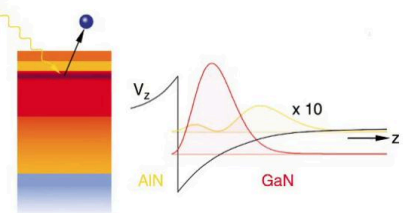
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These energies are more than sufficient to excite high kinetic energy photoelectrons, from the valence band, if not necessarily the core electrons. Soft X-ray ARPES is thus a tool to record bulk or interface electronic properties. The low cross-section of photo-emission in soft X-ray ARPES also means it is a synchrotron-only technique.

Notes

Summary



In the next video...



In the following video, we will discuss X-ray photoelectron spectroscopy, and X-ray photoelectron diffraction.

Notes

Summary



7m 11s