

Calibration of Photoemission Spectra and Work Function Determination

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Photoemission spectra are usually displayed in binding energies relative to the Fermi edge of the sample. However, what is really measured are the kinetic energies of electrons photoemitted from the sample. This tutorial will explain how photoemission spectroscopy (PES) data are calibrated, and how the work function of samples can be determined from such data.

Photoemission is usually assumed to occur in a three-step process. First, the incoming photon is absorbed by an electron, which is transferred from its initial state into an excited final state at the location of absorption. Second the electron travels to the sample surface, and third the electron is ejected into the vacuum. During the travel to the surface the majority of generated electrons suffer inelastic collision, which result in a reduction of their kinetic energy. Hence PE-spectra consist of two principal components: (1) primary electrons which did not suffer inelastic collisions, and (2) secondary electrons (primary electrons, which lost varying amounts of energy). The primary electrons result in distinct spectral features (peaks) mirroring (in first order approximation) the density of states (DOS) of the sample, while secondary electrons have a more or less continuous energy spectrum down to zero kinetic energy, which is superimposed to the primary electron spectrum. These two types of electrons contain different information: The primary peaks allow the determination of the binding energies of the electronic states in the sample, while the secondary electrons are mainly used for the measurement of the work function of the sample. However, the secondary electrons are typically thought of as “being scattered into conduction bands states above the vacuum level”. Hence, they contain also information about the density of these states, which sometimes leads to distinct features in the secondary electron background (see for example highly oriented pyrolytic graphite (HOPG) ultraviolet photoemission (UPS) spectra, where usually a strong peak is visible at about 13.2 eV).

Fig.1 shows the PES process schematically. The (external) photoelectric effect generates free electrons with a certain kinetic energy depending on the exciting photon energy $h\nu$, the work function of the sample Φ_s , the binding energy E_b of the excited electron, and inelastic scattering processes in the sample. This is shown on the left side where electrons in a metallic sample are excited into the vacuum by $h\nu$. The resulting spectrum is a superposition of the primary electrons with a kinetic energy (E_{kin}) distribution $E_{kin} = h\nu - E_b - \Phi_s$, and the secondary electron continuum. The fastest electrons of this spectrum will be primary electrons emitted directly from the Fermi edge ($E_b=0$) having $E_{kin} = h\nu - \Phi_s$. The slowest electrons will be secondary electrons that just barely made it out of the sample after having lost energy in scattering processes before arriving at the sample surface. These electrons have a kinetic energy of $E_{kin} = 0$ eV.

In order to measure the kinetic energy of these electrons we need to send them through the kinetic energy analyzer into the detector (often a “channeltron”) where they are counted. This is shown to the right of the initial kinetic energy spectrum. Since the channeltron also has a work function (usually called “analyzer work function” Φ_a), a contact potential of $\Phi_s - \Phi_a$ exists

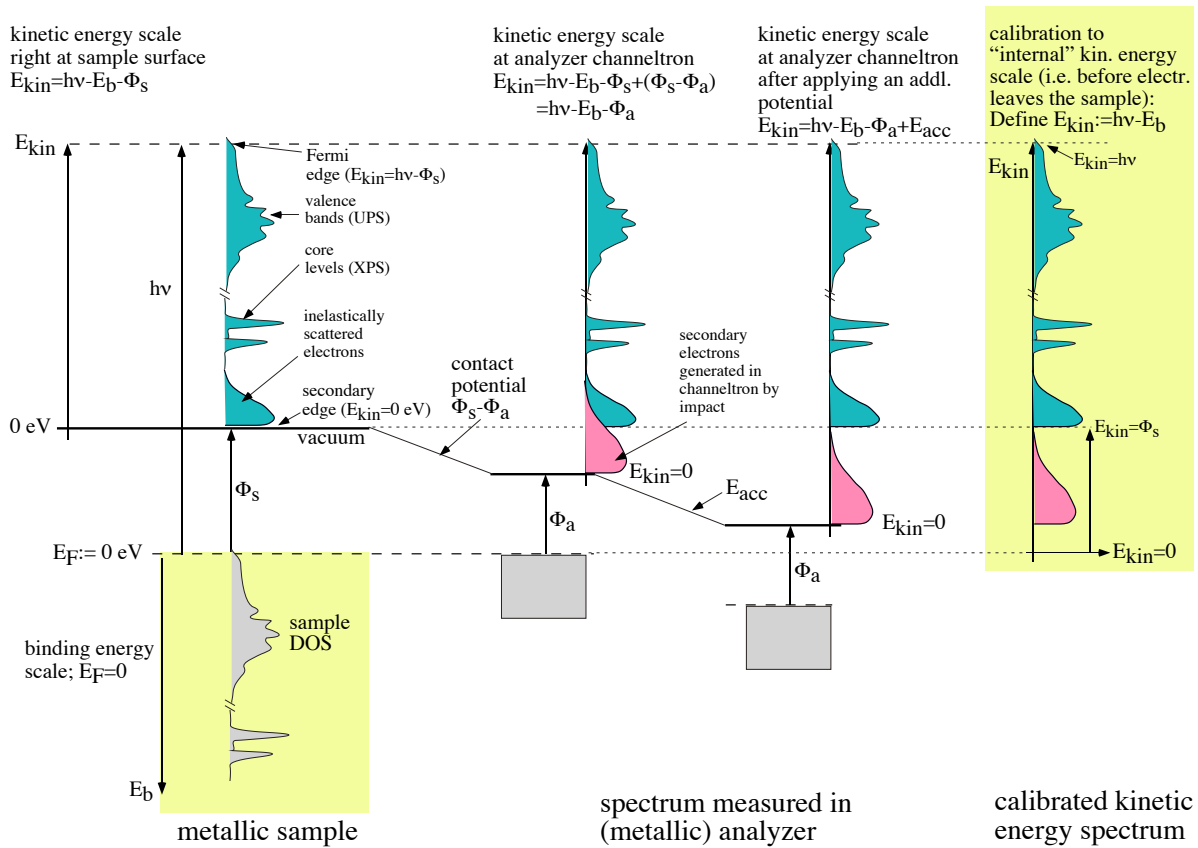


Fig.1: Schematic of photoemission spectroscopy (PES) process on metallic sample.

between sample surface and channeltron once sample and analyzer are connected electrically (through the sample holder and the electronics/cables of the system), and their Fermi levels are equilibrated. Usually the analyzer work function is smaller than the sample work function, i.e. the contact potential results in an acceleration of the electrons as they fly through the analyzer. Consequently, the kinetic energy of all electrons increases by $\Phi_s - \Phi_a$, yielding $E_{kin} = h\nu - E_b - \Phi_s + \Phi_s - \Phi_a = h\nu - E_b - \Phi_a$ for the primary electrons. The secondary electrons also get accelerated, i.e. those right at the secondary edge have now an energy equal to the contact potential. As bottom line we can say the entire spectrum is now shifted by $\Phi_s - \Phi_a$ to higher kinetic energy (if $\Phi_s > \Phi_a$). This is the raw spectrum measured during the PES process.

Note that there is one more feature in a typical spectrum: the secondary electrons of the analyzer itself (shown pink in Fig.1). These electrons are generated as photoelectrons from the sample hit surfaces in the analyzer generating secondary electrons by impact. These are again a continuum, which has electrons with kinetic energies down to 0 eV. Since they are mostly generated in the channeltron/detector itself, they are not influenced by the contact potential, i.e. show up starting at 0 eV kinetic energy. This results in a spectrum superimposed to the secondary

edge of the sample spectrum. This makes it often difficult to determine the position of the secondary edge of the sample.

The “trick” to deal with this issue is to apply an accelerating potential (resulting in additional kinetic energy E_{acc}) between sample and analyzer, which is often said to “separate the secondary edges of sample and analyzer” when measuring the secondary edge, usually during UPS measurements . This is shown schematically to the right of the analyzer kinetic energy spectrum. Again the electrons coming from the sample are accelerated, similar to what happened due to the contact potential. This pushes the spectrum away from the analyzer secondary electrons, which are not accelerated by the potential, and remain close to 0 eV kinetic energy. Hence, sample and analyzer secondary edges are now well separated and can be analyzed individually.

Now we have a kinetic energy spectrum where $E_{kin} = h\nu - E_b - \Phi_a + E_{acc}$ for primary electrons. The expression clearly suggests that the kinetic energies of primary electrons are not influenced by the work function of the sample (which is a result of the contact potential between sample and analyzer that “automatically compensates” for any change of the substrate work function), but they are influenced by the work function of the analyzer.

The problem here is that usually no one really knows the work function of the analyzer. However, one can use the Fermi edge of a metal surface to calibrate the kinetic energy scale relative to the Fermi edge of the sample, i.e. an “internal” kinetic energy scale can be defined giving the energy of the electrons in their final state before they left the sample (this is possible since the work function of the substrate does not affect the measured kinetic energy of the electrons). This is shown in Fig.1 on the right side in the yellow box. We simply define that the fastest electrons of our spectrum (i.e. the Fermi edge feature) have $E_{kin}=h\nu$, and shift the entire spectrum accordingly. Now all features of the spectrum are shown at their kinetic energies before the respective electrons left the sample. Note that this process also shifted the secondary edge cutoff to a kinetic energy corresponding to the work function of the sample, since the cutoff represents the electrons that had just enough energy on arrival at the surface to overcome the work function (i.e. were in an electronic state just above the vacuum level).

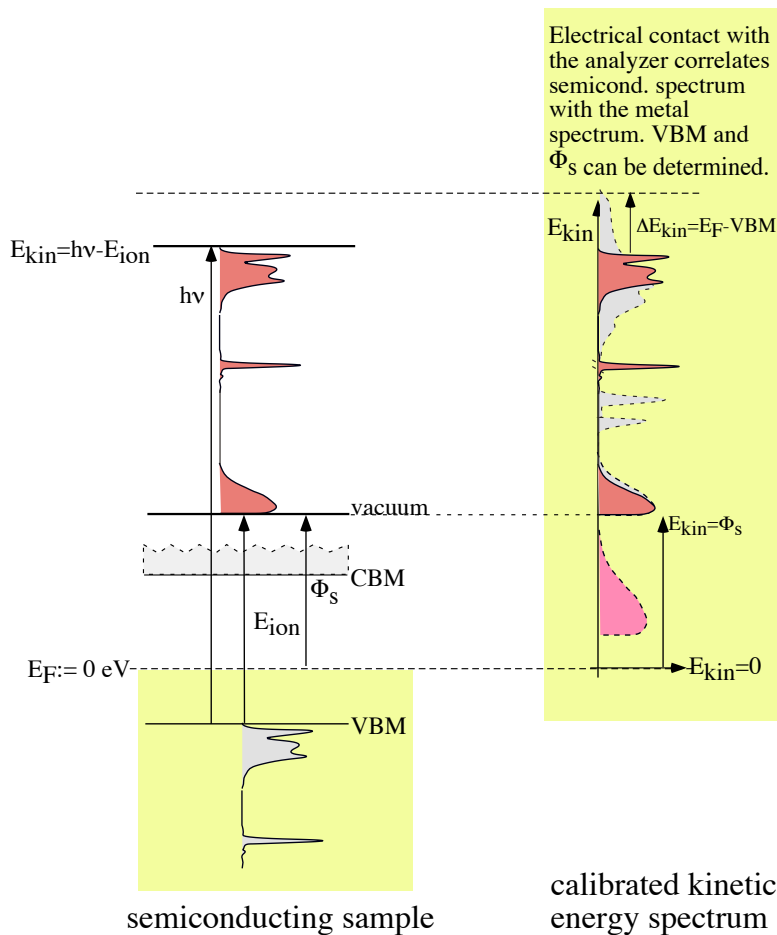
Now that we have a kinetic energy scale referenced to the Fermi level of the sample, it is straight forward to define the usual binding energy scale by defining $E_b=h\nu-E_{kin}(\text{internal})$. This puts E_b of the Fermi edge automatically to $E_b = 0$ eV. On this scale the secondary edge cutoff shows up at a binding energy of $E_b=h\nu-\Phi_s$, i.e. the usual way to determine the work function from spectra shown on the binding energy scale is done by subtracting the binding energy of the cutoff from the photon energy.

Measurements on Semiconductors:

It should be pointed out that most of the secondary cutoff electrons used to measure the work function are not originating from the Fermi edge (they come instead from all primary

electron emissions combined, after losing random amounts of energy during the inelastic scattering processes). The process works well even if there are no electronic states at the Fermi edge at all. This is what makes it possible to measure the work function of semiconductors.

This process is schematically shown in Fig.2, where the initial semiconductor spectrum is shown in relation to the final “internal” kinetic energy spectrum. The transfer to the analyzer was left out in this figure. It would look exactly the same as in Fig.1. It is interesting to note, that, in difference to the above case of a metal, from a semiconductor spectrum alone the work function cannot not be determined. All we get from the initial spectrum is some highest kinetic energy, corresponding to the VBM, whose binding energy we do not know, and a lowest kinetic energy



which is again zero. With these two numbers one can only calculate the ionization energy E_{ion} , as indicated in Fig.1.. This is done by subtracting the width of the entire PE-spectrum from the exciting photon energy.

If the work function of the semiconductor is to be determined, we need to calibrate the analyzer first with a metal as outlined above. This essentially gives us a reference where the analyzer Fermi edge is on the energy scale. Now we can connect the semiconductor sample to the analyzer by mounting it on the sample plate. This immediately equilibrates the semiconductor Fermi level with that of the analyzer, i.e. the “internal” kinetic energy spectrum of the semiconductor becomes calibrated, and absolute values for work function and VBM binding energy can be

Fig.2: Photoemission spectroscopy on a semiconducting sample.

extracted. Note, that this process only yields the VBM energy at the surface of the sample, i.e. if there is surface band bending, the VBM would be shifted relative to the bulk VBM.