

Chapter 4

Electron spectroscopy

- UPS - Ultraviolet Photoelectron Spectroscopy, VUV radiation, especially using synchrotron radiation;
- XPS - X-ray Photoelectron Spectroscopy (ESCA - Electron Spectroscopy for Chemical Analysis), soft X-rays;
- AES - Auger Electron Spectroscopy
- ELS or EELS - Electron Energy Loss Spectroscopy, used in the case of internal excitation of electron levels, also known as IS - Ionization Spectroscopy;
- INS - Ion Neutralization Spectroscopy
- FES - Field Electron Spectroscopy, energy distribution measurements of field-emitted electrons

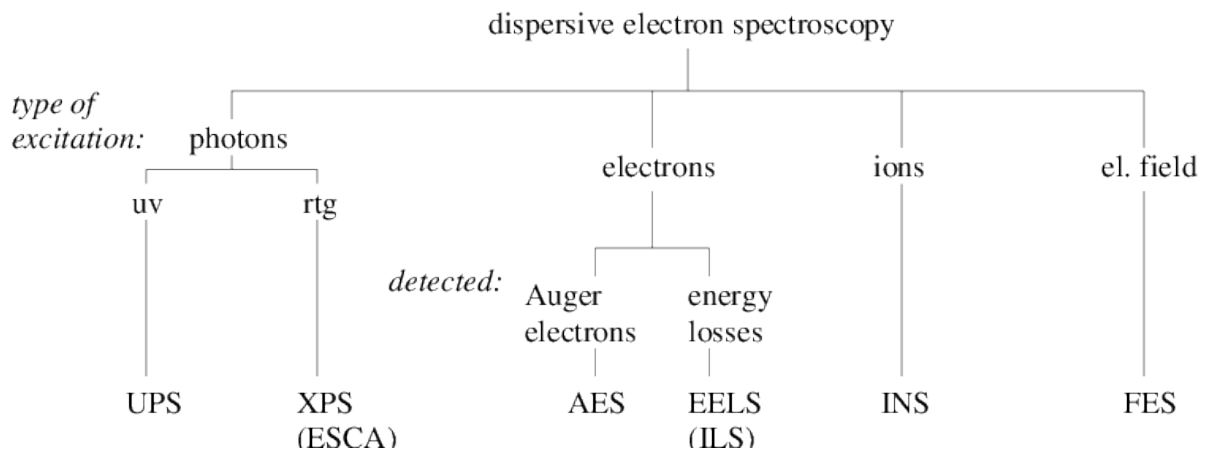


Figure 4.1: Overview of different dispersive electron spectroscopy methods

- XXAPS, XEAPS - X-ray X-ray Appearance Potential Spectroscopy, X-ray Electron Appearance Potential Spectroscopy. Methods in which X-rays are generated from the sample. They are practically not used since electron generation is much easier.
- SXAPS - Soft X-ray APS, electrons impact the sample and emitted X-rays are detected.
- DAPS - Disappearance Potential Spectroscopy, used to measure the surface electrons current.
- AEAPS - Auger Electron APS, records the secondary electrons current.

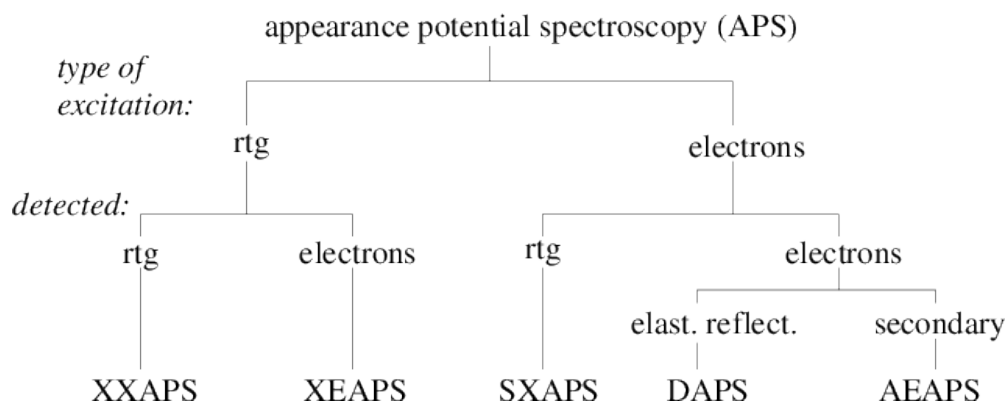


Figure 4.2: Overview of different APS methods

4.1 Electron spectroscopy conditions

All methods except FES require a **monochromatic source** - more or less focused, a **analyser** and a **detector** (electron multiplier). All this system must be kept under high vacuum conditions ($\leq 10^{-7}$ Pa). The surface sensitivity is greater so the depth profile is small. The most stringent conditions for surface are for UPS and not so for XPS. The device is equipped with a surface cleaning systems (Ar^+ sputtering and baking) or for preparation of clean surfaces in situ (cleaving or applying of layers).

4.2 Sources of primary particles

X-rays: soft X-rays are generated by bombardment of a suitable material (Al, Mg, Mo, Co, W) with sufficient e^- energy \Rightarrow characteristic X-rays.

- when beam width may limit the resolution ($E_k = h\nu - E_B - e\phi$). The best e^- energy is ≈ 1.0 eV \Rightarrow characteristic X-ray width s narrower.
- The energy must be high enough in order to obtain emission of photoelectrons from the bulk of material.

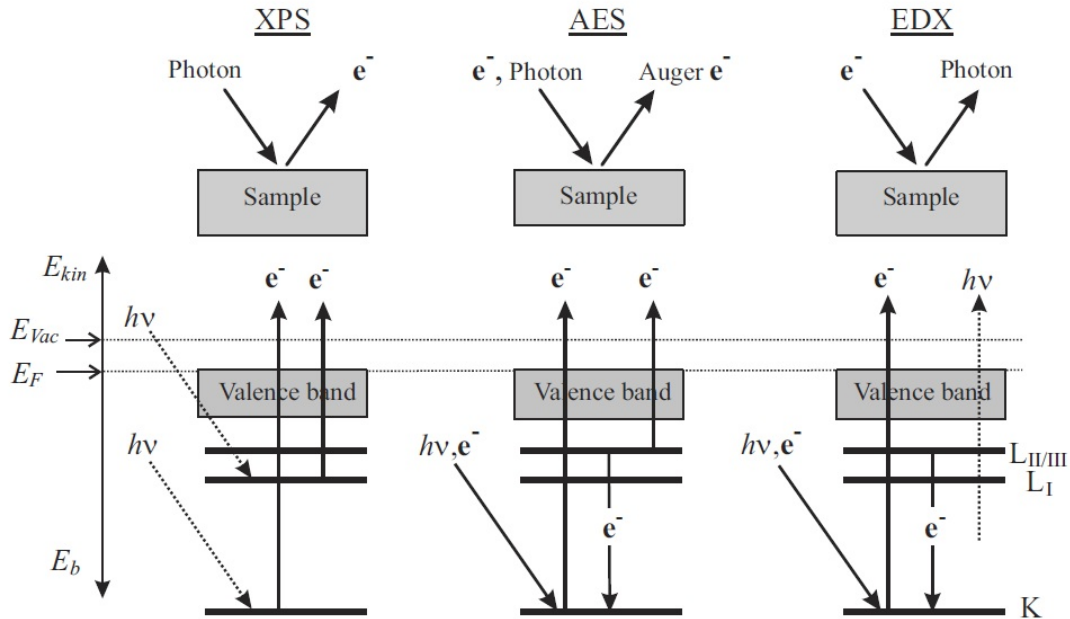


Figure 4.3: Schematic drawing of method's differences.

- In addition, the anode material needs to be capable of working even under e^- bombardment.

\Rightarrow Mg $K\alpha$ ($E = 1253.6$ eV, $\delta E = 0.7$ eV), Al $K\alpha$ ($E = 1486.6$ eV, $\delta E = 0.85$ eV).

Photoemission starts at e^- energies equal with electron ionization threshold for the inner shell and growing rapidly with increasing energy. Therefore, devices allow e^- acceleration up to 15 keV.

The e^- source is the closest to the anode, which is often composed of two anodes. For continuous operation at 1–8 kW, a rotating anode is required. Beside the characteristic lines ($K\alpha$ for Mg and Al), satellite, $K\beta$ and continuous spectrum (Bremsstrahlung) lines exists \Rightarrow sometime monochromatic radiation is used: Bragg diffraction from crystal. Rowland focusing is approximated by aligning the platform of the multi-crystal segmented analyser at a tangent to the Rowland circle (0.5 m).

Synchrotron radiation if the charged particles are accelerated, they radiate energy which covers an area of electromagnetic radiation from hard X-rays up to IR. The synchrotron is a particular type of cyclic particle accelerator in which the magnetic field (to turn the particles so they circulate) and the electric field (to accelerate the particles) are carefully synchronised with the travelling particle beam. Synchrotron radiation has many advantages: a broad spectrum, natural collimation, high intensity, coherence, the source is under vacuum. Maximum intensity is at the critical wavelength (0,1–0,4 nm), which is the curving path of the e^- . The intensity decreases rapidly for lower wavelengths.

Sources of electrons thermionic or field-emission guns. AES monochromatic e^- source. Only the electrons with sufficient energy are able to ionize the inner layer. Beam size is important for EELS max. 0,3–0,5 eV, which is to large for HREELS which requires special monochromatic

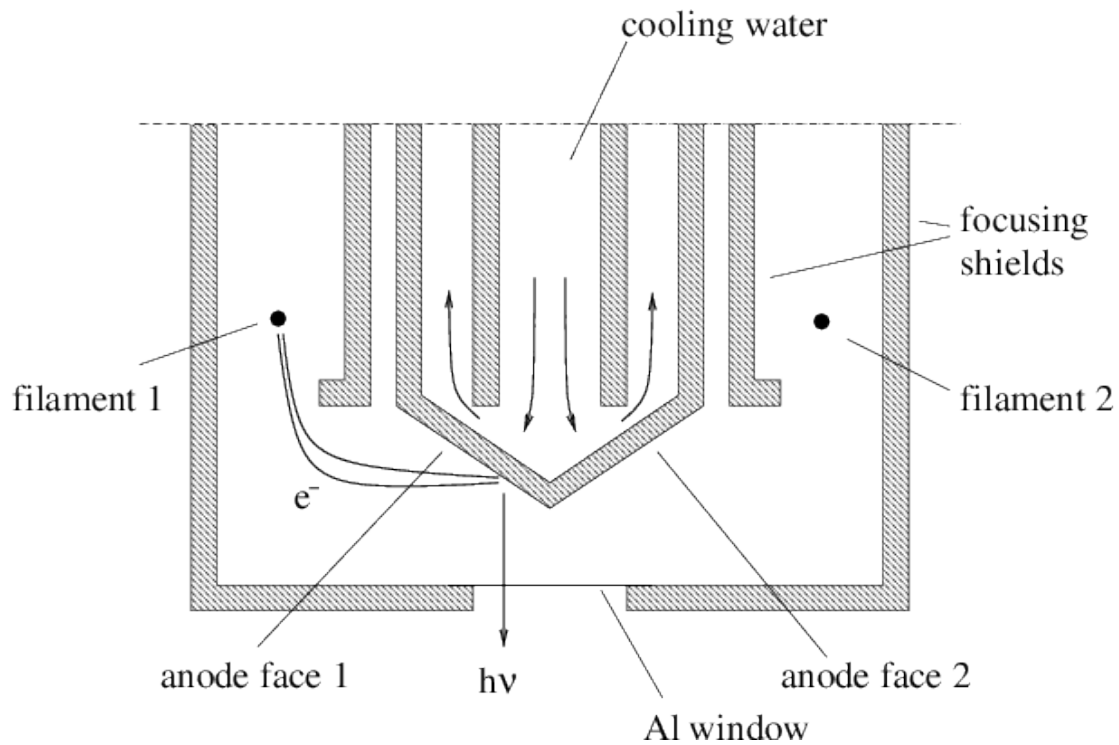


Figure 4.4: Scheme of X - ray source.

electron sources.

4.3 Electron energy analysers

The electron spectroscopy uses electrostatic analysers. The measured values can be divided into

- analysers with retarding field - recording of the total current of particles,
- dispersion analysers - select only certain e^- energies by changing the trajectories.

When choosing the analyser some parameters are assessed:

- resolution $R = E/\Delta E$ - indicates the energy;
- intensity (brightness) - affects the intensity of the output signal;
- analyser size - needs to be under vacuum;
- complexity - economic factor

The final solution is a compromise because the individual requirements have a contradictory character.

4.3.1 Analysers with retarding field

The operation principle is based on potential barrier high V_b . The flow of particles over the barrier is divided in fast and slow components. Only the faster ones are usually recorded:

$$J(E) = \int_E^{\infty} N(E') dE', \quad (4.1)$$

where $N(E')$ is the energy distribution of particles, $E = eV_b$ is the lower energy limit and the symbol ∞ upper limit (maximum energy of particles). The energy distribution function can be obtained from the derivative of the above equation.

Planar analyser

The analysed beam, which is crucial for the accuracy of measurement is usually selected by modifying the slit. Around the threshold energy $E = eV_b$, the resolution is:

$$R_{r_0} = \frac{16d^2}{r_0^2}. \quad (4.2)$$

The basic parameter is the diameter of the solid angle Ω , under which the beam enters the detector (effective area). Impute increases with the slit and Ω .

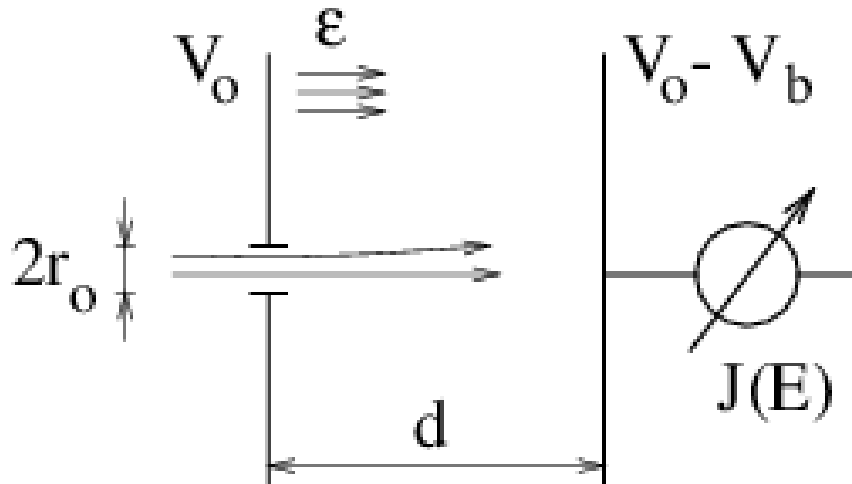


Figure 4.5: Scheme of planar analyser

Spherical analysers

Compact electrode system often use a system of 3 or 4 grids (collectors). Total energy analysis is carried out in a radial trajectory of the particles. It can be used for LEED if the system is equipped with a fluorescent screen or a small movable detector. Retarding fields are generated between the 1st and 2nd (or 3rd and 4th) grids. The resolution is given by the field inhomogeneity (mesh size, number of grids). Analyser throughput is high because it can detect

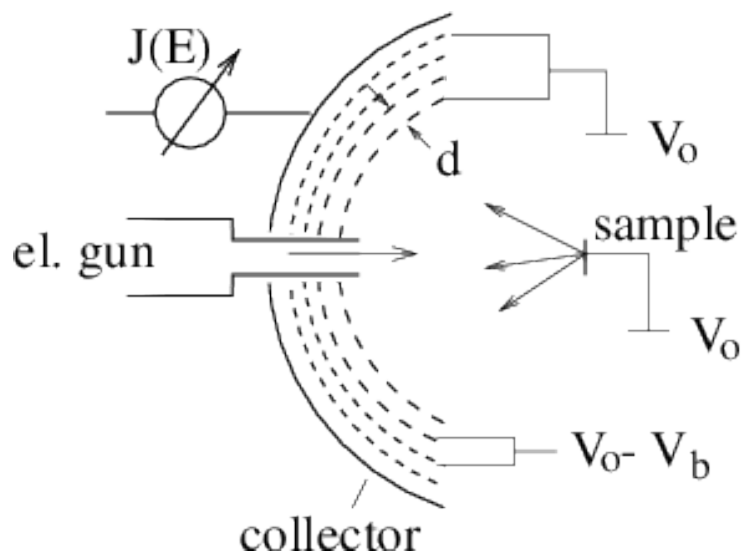


Figure 4.6: Scheme of spherical analyser

particles from a large solid angles (120° or 180°).

4.3.2 Dispersion analyser (deflectors)

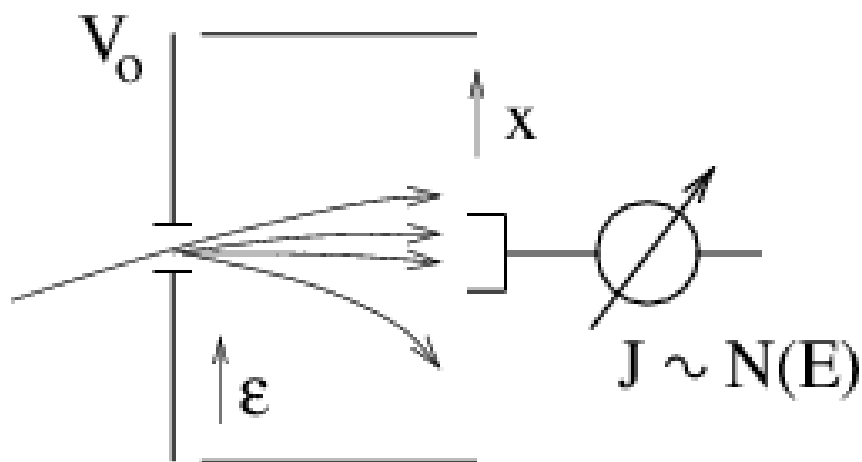


Figure 4.7: Scheme of dispersion analyzer

The parallel beam entering the analyzer is divided into different trajectories (Fig. 4.7) depending on the energy. The detector is either able to monitor signals at different positions (channel plate, screen) or it is tuned to detect particles with a certain energy E_0 (multiplier, Faraday cup). In the latter, a characteristic parameter is the main trajectory, i.e. the trajectory between the

input and output slits. Properties of the analyzer are given by the *dispersion*

$$D(E) = E \partial x / \partial E,$$

i. e. by the quantity expressing the difference in the position in the dependence on the energy. The dispersion with other parameters covering field focustion properties and some construction parts determines energy resolution of the analyzer.

Energy resolution can be estimated by detail analysis of particle trajectories in dependence on their input parameters: energy, coordinates of input slit, input angle. In most cases it is enough to use a rough estimate of the resolution as made below.

Let us irradiate the entrance slit s_1 by monoenergetic parallel beam that is imaged at the output slit with the magnification M . If the beam will be slightly divergent, each point of the entrance slit will be imaged by a line in each directions in which the focustion takes place. The length of this line is approximately

$$\Sigma \doteq a_1\alpha + a_2\alpha^2 + a_3\alpha^3 + \dots + b_1\beta + b_2\beta^2 + b_3\beta^3 + \dots \quad (4.3)$$

The angle 2α is divergence of the beam in the plane of the main trajectory, 2β in the plane perpendicular. The focustion order expresses how many coefficients a_1, a_2, \dots, a_n or b_1, b_2, \dots, b_n are equal to zero.

During analyzer tuning the image in output plane is moving. It is detected if some part of it falls into the output slit s_2 . Its geometrical width is

$$\Delta x_s = M s_1 + s_2 + \Sigma \quad (4.4)$$

and Δx_B is connected with energy width of the image in the vicinity of E_0 by

$$\Delta x_B = \frac{\partial x}{\partial E} \Delta E_B, \quad \frac{\partial x}{\partial E}. \quad (4.5)$$

It means that image of monoenergetic beam source is the peak with final width. If we have two such sources with close energies, they will be imaged with similar sensitivity as two close peaks (Fig. 4.8). They are expected as resolved if the minimum valey inbetween them is at 20% of their maximum, i. e. they intersect at 40% of their height. Their distance in energies ΔE will be approximately half of their energy base ΔE_B and we can write for the resolution ($E_0/\Delta E \doteq 2E_0/\Delta E_B = 2D/\Delta x_B$)

$$R \doteq \frac{2D}{M s_1 + s_2 + \Sigma}, \quad (4.6)$$

where s_1 and s_2 are the slit sizes for input and output, M is the magnification (~ 1) and Σ is the blur due to the input divergence. From this expression is observed the decrease of R with the increase of slit size directly ($M s_1 + s_2$), and indirectly with Σ .

Dispersion analysers are divided into mirror and sector analyzers.

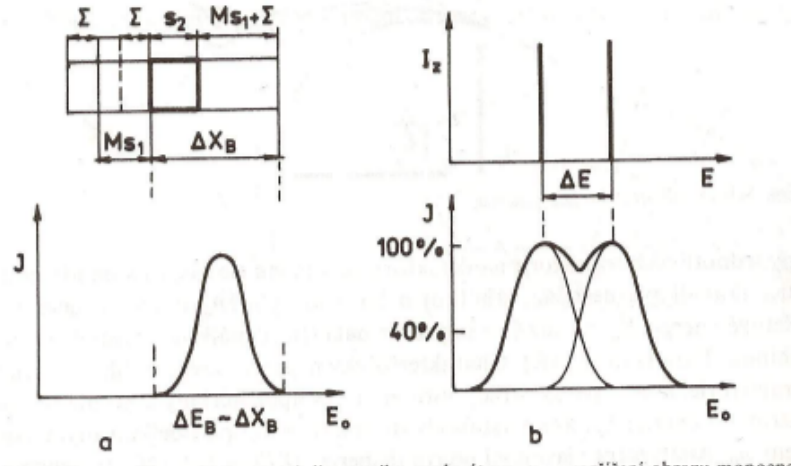


Figure 4.8: Understanding the energy resolution.

Mirror analyser

The beam enters through field lines at an different angle than $\pi/2$; the velocity component perpendicular to the field direction is maintained, v_{\parallel} is gradually changed to the opposite direction \Rightarrow symmetrical axis trajectory \parallel to the field. The input and output slits are places in the positive potential electrode. The entrance angle is chosen with regard to the position of the source and the detector.

- planar - two parallel electrodes focusing only the deflection plane a. Two arrangements (a) $\phi_0 = \pi/4$, source and detector in the entrance and exit slits, (b) $\phi_0 = 30^\circ$, source and detector tangent to field.
- cylindrical (CMA) - it is frequently used because allows the construction of high resolution systems. It consists of two concentric cylinders, with a positive potential between.

Sectors analyzer

The beam enters \perp to the field. The main trajectory is a circle, where the centrifugal force associated with the kinetic energy compensates the centripetal force. The incident and reflected angles is determined by the focus and position of the source and detector. It is mainly used in the differentiated angular spectroscopy:

- cylindrical - two cylindrical sector analyser and two pairs of planar electrodes (in front and lateral); in the frontal one are located the slits. Deflection potential $V_1 - V_2$ is inserted between the cylinders (inner potential is positive), both planar electrodes are isolated and maintained on the potential $V_0 = (V_1 + V_2)/2$. The analyser is focusing only in one direction. Sector angle is $\Phi = \pi/\sqrt{2} = 127,3^\circ$ therefore \Rightarrow the name of 127° analyser.

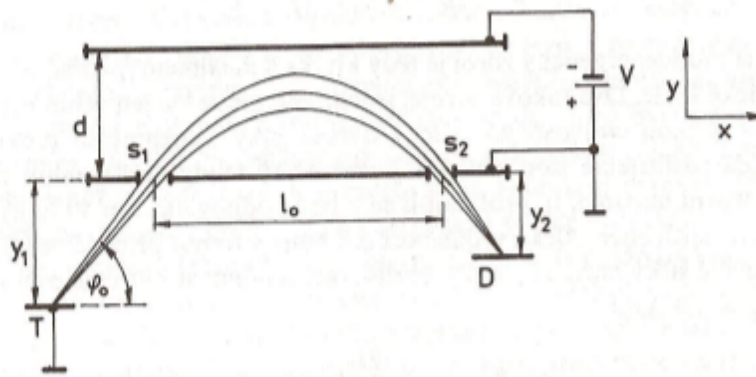


Figure 4.9: Scheme of planar mirror analyzer, T is sample, D is detector.

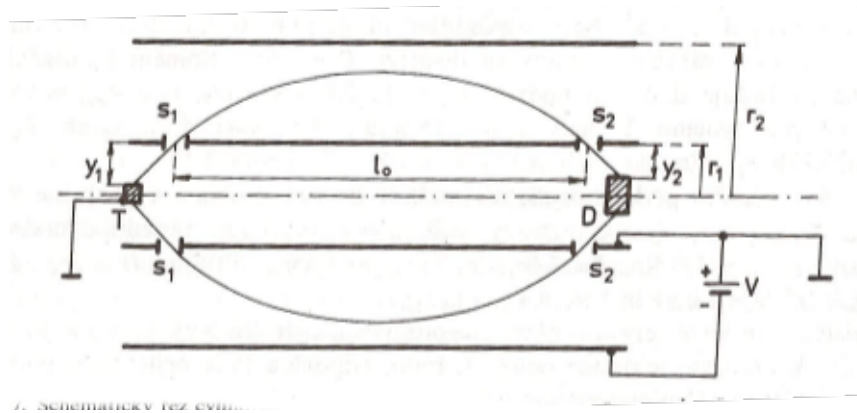


Figure 4.10: Scheme of CMA analyzer

- spherical (CHA - concentric hemispherical analyser) - two concentric spherical segments; input and output electrodes are radial slices are maintained at median surface potential V_0 . The spherical deflector is capable of spatial focusing. Angle or the sector is usually $\Phi = 180^\circ$.

Conclusion

Analysing the energy of electrons has some other associated phenomena such as reflection and secondary emission. It is advantageous to use electron optics in order to increase the input angle, to obtain the image in a suitable place in the optimal regime area of the analyser, finely tune the input angle for slow electrons. The relative resolution of the analyser is constant \Rightarrow absolute intensity will decrease with the decrease of energy.

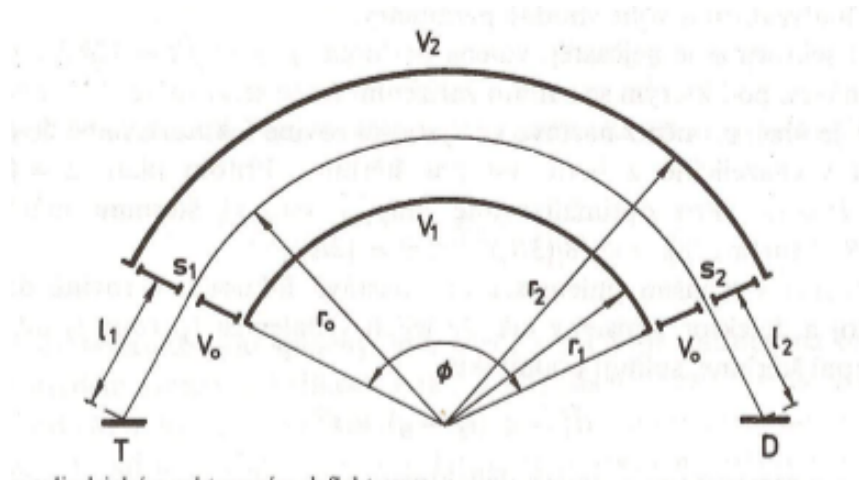


Figure 4.11: Scheme of cylindrical deflector.

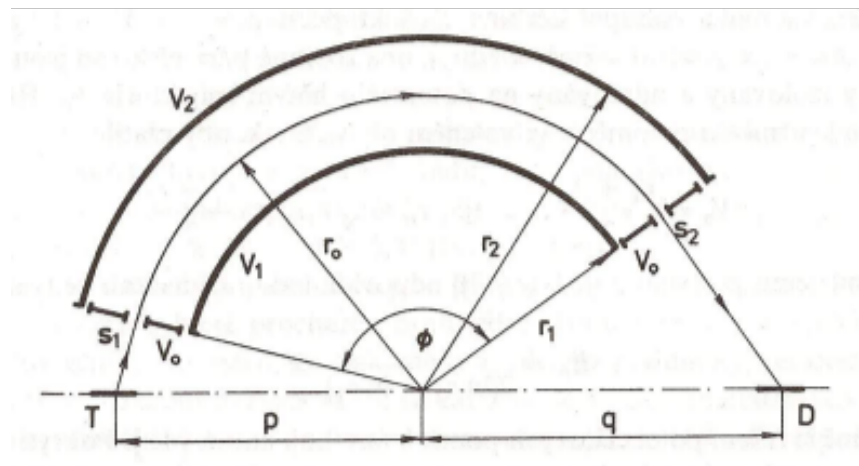


Figure 4.12: Scheme of spherical deflector.

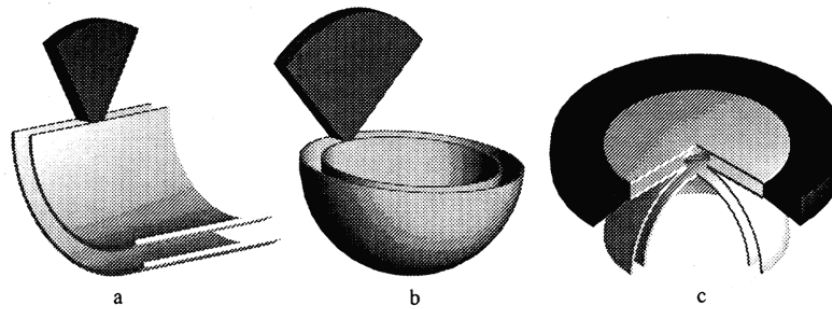


Fig. 1. Evolution of the electrostatic analyzer used in space plasma diagnostics: (a) cylindrical analyzer, (b) spherical analyzer, and (c) top-hat analyzer. The dark regions illustrate the field of view.

Figure 4.13: 3D view of sector analyzers.

4.4 Ultraviolet photoelectron spectroscopy

- If the photon energy is < 3 eV (VIS radiation), photoemission can occur only for substances with very low ϕ and the energy spectrum is narrow because e^- are emitted only from the highest occupied level \Rightarrow information only about ϕ .
- If the photon energy is higher (UV radiation) electrons from the valence band can be emitted (UPS) \Rightarrow distribution of densities of states in valence band can be obtained.
- In addition to energy distribution is possible to measure the angular distribution (ARUPS). In an isolated atom, the electrons occupy certain energy levels. In a solid, the levels involved in bonding 'the valence states', become blurred, and electrons can occupy a range of energies called bands. The energy of an electron in the solid depends on its momentum. Hence, by detecting photoelectrons emitted from a surface at different emission angles, the energy of the electrons as a function of the momentum vector may be determined. This process is known as "band mapping" and is a powerful probe of the electronic structure of crystalline materials.
- The mean free path in the case of UPS is only 0.5–2 nm \Rightarrow surface characterization method.

Photoemission

The first paper of Burglund and Spicer (1964) worked out what is called the three-step model for photoemission, and the second applied it to new data on Cu and Ag. The three-step model uses this picture in considerable detail to predict the spectrum of photoelectrons from a given band structure. This spectrum sometimes resembles the density of occupied electronic states weighted by a function that varies smoothly with energy. This model assumes the photoemission process can be described by three sequential processes:

- photoexcitation of an electron (photoabsorbtion) - general theory based on Fermi's golden rule, which determines the transition probability between two electron states of the same Hamiltonian H^N , if the disturbance Δ is small.

$$w = \frac{2\pi}{\hbar} |\langle \psi_f^N | \Delta | \psi_i^N \rangle|^2 \delta(E_f^N - E_i^N - \hbar\omega) \quad (4.7)$$

- transport of that electron to the surface without inelastic scattering
- scape of the electron into the vacuum

The law of energy conservation must be applied ($E_{\text{kin}} = E_f^u - e\Phi = E_i^u + \hbar\omega - e\Phi$) and the wavelength vector. Overall, the wave-vector is not maintained because the emitted electron escapes into vacuum, and the system achieve three-dimensional symmetry. The surface has only two-dimensional translation symmetry of the surface reciprocal lattice vector \vec{G}_S :

$$\vec{k}_{\parallel}^{\text{vn}} = \vec{k}_{\parallel}^{\text{u}} + \vec{G}_S \quad (4.8)$$

Inside the crystal the wave-vector is preserved:

$$\vec{k}_f^u = \vec{k}_i^u + \vec{G}_B, \quad (4.9)$$

where \vec{G}_B is the reciprocal lattice volume vector. Dispersion relation for free e^- :

$$E_{\text{kin}} = \frac{\hbar^2}{2m}(k_{\parallel}^2 + k_{\perp}^2). \quad (4.10)$$

If we don't know the dispersion relation within the crystal we are able to directly measure the band structure, but if we know the initial dispersion or the final states, we can limit the dispersion or the initial conditions. For surface conditions these restrictions do not apply \Rightarrow layered materials with two-dimensions periodicity exists: TaS₂, GeS or graphite, where the bulk band structure $E(k_{\parallel})$ will be explored.

$$k_{\parallel} = \sqrt{\frac{2m}{\hbar^2} E_{\text{kin}}} \sin \theta, \quad (4.11)$$

where θ is the angle between the surface normal and the axis of the detector. The UPS method can be applied to absorb on substrate system like CO on Ni

Several modes exist for the evaluation of the emitted electrons:

- the number of emitted electrons is measured as the function of the final-state energy E_f (kinetic energy $E_k = E_f - E_{\text{surf-barrier}} = E_f - e\Phi$ is measured) for a fixed photon energy and a fixed mutual position of the source and the surface elementary cell - energy distribution curve (EDC). EDC can be measured as integral or differential function of the emission angle. The latter is called angular resolved UPS (ARUPS).
- By scanning photon energy $h\nu$ and holding fixed the energy windows of the electron spectrometer, one measures the constant final-state spectra (CFS), $N(h\nu, E_f \text{ fixed})$. Unlike in EDC, the energy and wave vector are the same in every point of the spectra.
- By synchronously scanning $h\nu$ and E_f , so that $h\nu - E_f$, is held fixed, one measures the constant-initial-state spectra (CIS), $N(h\nu, h\nu - E_f \text{ fixed})$.

EDC

Přenesení počáteční hustoty stavů na hustotu prázdných konečných stavů vzdálených o $\hbar\omega$. Hlavní obtíž spočívá v oddělení příspěvků počátečních a koncových stavů. Tuto eliminaci je možné dostatečnou energií budící energie, aby e^- byly excitovány do oblasti, kde hustota tvoří prakticky kontinuum. Při energiích nad 100 eV to však vede ke ztrátě informací o impulzu e^- . Pro energie 30–100 eV jde o spektra zobrazující hustotu počátečních stavů a zachovávající možnost určení disperzních relací \Rightarrow synchrotronové záření. Musíme znát pásovou strukturu konečných stavů \Rightarrow aproximace model téměř volných e^- ; kritické je umístění dna paraboly na energetické stupnici.

CFS

Elektrony jsou excitovány do jednoho zvoleného stavu \Rightarrow dává užitečné informace o výběrových pravidlech a symetrii stavů; pokud je okénko nastaveno tak, že leží mimo dovolené přechody

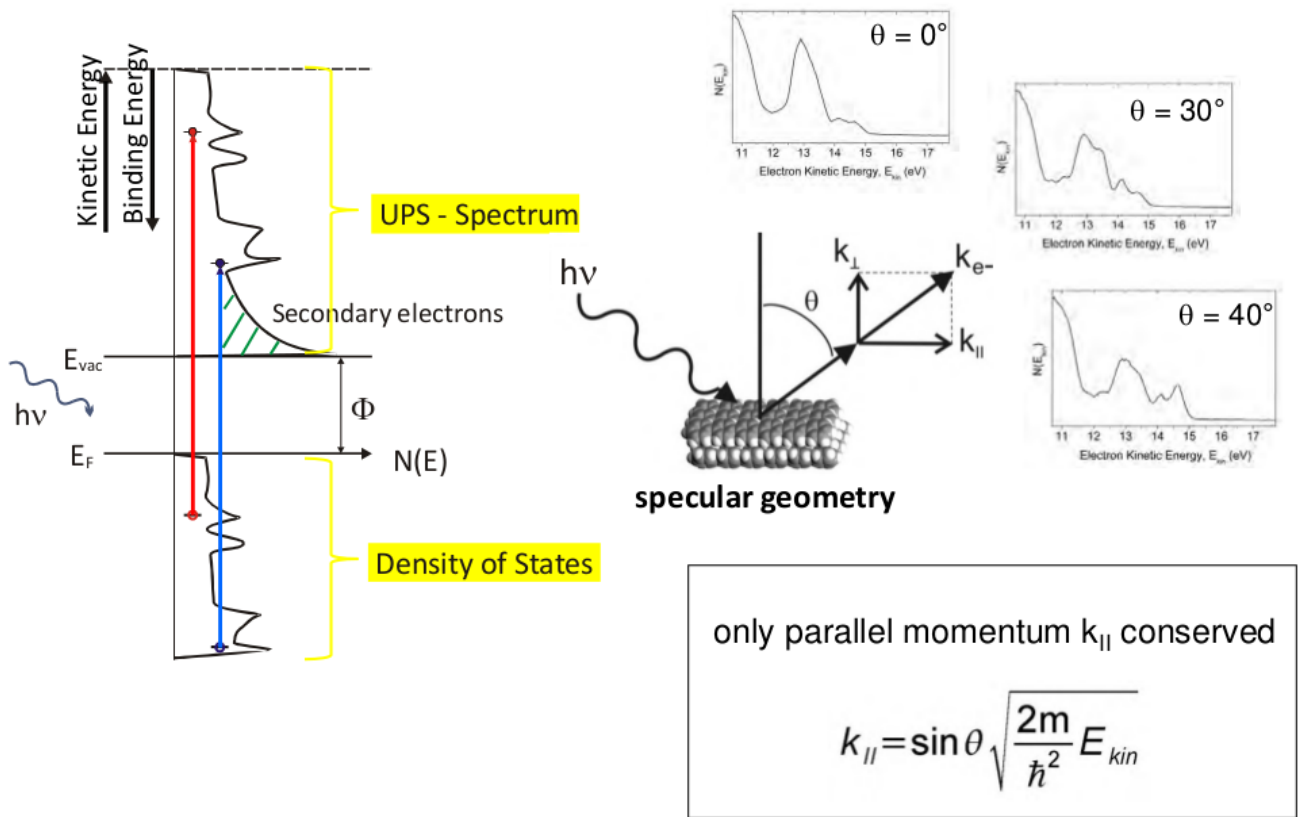


Figure 4.14: Angular resolved UPS.

v objemu, dominuje ve spektru příspěvek od povrchových stavů. Technika CFS je pro studium pásové struktury výhodnější než postup EDC, protože dovoluje snímat spektra s $\vec{k}_{\parallel} = \text{konst}$ i mimo normálu. Opět je nutné určit \vec{k}_{\perp} vně PL a dát ji do souvislosti s odpovídající složkou vl. vektoru e^{-} v konečném stavu uvnitř PL \Rightarrow postup obdobný jako u EDC.

CIS

Není tak rozšířena jako předchozí dvě techniky, protože byly vyvinuty jiné metody umožňující spektroskopii prázdných stavů v oblasti těsně nad dnem vodivostního pásu. U fotoemisních měření totiž nemohou e^{-} excitované do energetických pásů pod hladinou vakua přispívat k fotoproudu. Navíc se zvyšující se energií se zvětšuje energetické rozmazání pásů, a tím je velice obtížné získat informace o momentu e^{-} z úhlově rozlišených měření.

4.5 Spectroscopic photoemission of electronic states

Molecules can possess several types of angular momentum. Electrons possess orbital and spin angular momenta, rotation of the molecule generates angular momentum, degenerate vibrations may give rise to vibrational angular momentum, and nuclei may also have spin angular momentum. Interactions (coupling) between these various types of angular momentum can have important implications for interpreting spectra, particularly high resolution spectra, and so it is important to be familiar with some basic results from the quantum theory of angular momentum.

The angular momentum is a vector quantity and a simple vector model provides a useful visual recipe for assessing how different angular momenta interact. There are more powerful and rigorous mathematical approaches to angular momentum coupling than that described here. These more comprehensive treatments deal explicitly with the angular momenta as mathematical operators, and the coupling behaviour then follows from the properties of these operators when added vectorially. The simple vector picture is used to emphasize the physical principles underlying the coupling of angular momenta, focussing on electronic angular momentum.

The magnitude of the orbital angular momentum for a single electron in an atom is given by the expression $\hbar\sqrt{l(l+1)}$ where l is the orbital angular momentum quantum number with allowed values 0, 1, 2, . . . Similarly, the magnitude of the spin angular momentum vector is given by $\hbar\sqrt{s(s+1)}$ where s is the spin quantum number which, for a single electron, can only take the value 1/2. For an electron with both orbital and spin angular momenta, the total angular momentum vector j will be the sum of the two constituent vectors $j = l + s$. The magnitude of this vector is $\hbar\sqrt{j(j+1)}$, where j is the corresponding quantum number, and according to the quantum theory of angular momentum this can only take on the values $j = l + s, l + s - 1, \dots, |l - s|$. Series such as this are called Clebsch – Gordan series and arise when the total angular momentum results from a system composed of any two sources of quantized angular momentum. In the general case, if two angular momenta, say j_1 and j_2 , can interact then the allowed values for the angular momentum quantum number for the resultant total angular momentum will be given by the Clebsch – Gordan series $j = j_1 + j_2, j_1 + j_2 - 1, \dots, |j_1 - j_2|$

4.5.1 L-S (Russell-Saunders) coupling

In the Russell – Saunders limit the coupling between the orbital angular momenta is strong. The source of the coupling is the electrostatic interaction between two electrons. Electron spins can also couple together, although spin is a magnetic phenomenon and therefore the coupling is via magnetic fields, which tends to be a weaker effect than electric field coupling. In Russell – Saunders coupling the interaction between the orbital and spin angular momenta of a given electron is assumed to be small compared with the coupling between orbital angular momenta. In this limit the principal torque causes the orbital angular momenta to precess about a common direction, the axis of the total orbital angular momentum of all electrons. The spin angular momenta also couple together through the magnetic interaction of electron spins.

The vector model described above can be employed to see the effect of coupling on atoms.

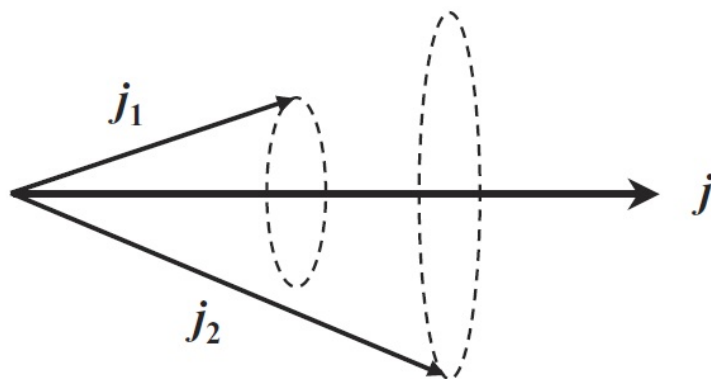


Figure 4.15: Forming the total angular momentum.

For illustration, consider an atom with two electrons outside its closed shell. The orbital angular momenta of these electrons are represented by l_1 and l_2 , and the corresponding spin momenta by s_1 and s_2 . The coupling of orbital angular momenta dominates and they form a resultant total orbital angular momentum $L = l_1 + l_2$. In the same way, the spin momenta also couple to form $S = s_1 + s_2$. When this coupling case is valid, the individual orbital angular momenta l_1 and l_2 precess rapidly around L , and s_1 and s_2 precess rapidly around S . L and S can themselves couple with each other, but this coupling, known as spin – orbit coupling, is assumed to be relatively weak. As a result, L and S precess slowly around the resultant total angular momentum $J = (L + S)$.

4.5.2 *jj* coupling

The Russell–Saunders scheme describes the electronic states of light atoms rather well but breaks down for heavier atoms, particularly for the lanthanides and actinides. This is due to increasing coupling between the orbital and spin angular momenta of individual electrons to the point where it is no longer negligible, as was assumed in the Russell – Saunders case. In the limit of very strong coupling between orbital and spin angular momenta, the appropriate coupling scheme is known as *jj coupling*. A dominant spin – orbit torque will first couple the spin and orbital momenta of each electron to form resultants, $j_1 = l_1 + s_1$ and $j_2 = l_2 + s_2$. The vectors j_1 and j_2 interact more weakly, forming the total angular momentum $J = j_1 + j_2$. In *jj* coupling, $l_1(l_2)$ and $s_1(s_2)$ precess rapidly around $j_1(j_2)$, while j_1 and j_2 precess slowly around their resultant J . As a result, only j_1, j_2, J and the projection of $J(M_J)$ are good quantum numbers, i.e. the quantum numbers L and S in the Russell – Saunders scheme have no significance in *jj* coupling. Of course it is also possible that the spin–orbit coupling is neither weak enough for Russell–Saunders to be applicable, nor strong enough for true *jj* coupling.

4.6 Auger electron spectroscopy

4.6.1 Auger effect

Auger electrons were named after Pierre Auger who, together with Lise Meitner, discovered Auger electron emission in 1920s. When a high-energy electron (or X-ray photon) strikes an inner shell electron of an atom, the energy of the incident particle can be high enough to knock out the inner shell electron. Thus, the atom becomes ionized and in an excited state. The atom will quickly return to its normal state after refilling the inner electron vacancy with an outer shell electron. In the meantime, the energy difference between the outer shell electron and the inner shell may cause emission of either an Auger electron from an electron shell or a characteristic X-ray photon. The kinetic energy of an Auger electron is approximately equal to the energy difference between binding energies in the electron shells involved in the Auger process. For example, the kinetic energy of an Auger electron is approximated by the following equation:

$$E_{KL_1L_2,3} = E_K - E_{L_1} - E_{L_2,3}^* \quad (4.12)$$

where E_i is the binding energy and $E_{L_2,3}^*$ is marked with asterisk because the energy levels $L_{2,3}^*$ differs slightly from the energy levels of $L_{2,3}$.

The notation for kinetic energy of Auger electron describes its origin, but the nomenclature is rather complicated. For example, the kinetic energy of an Auger electron is from a following process: an incident electron knocks out a K shell electron, a L_1 shell electron refills the K shell vacancy, and a $L_{2,3}$ shell electron is ejected as the Auger electron. Auger electron spectroscopy (AES) identifies chemical elements by measuring the kinetic energies of Auger electrons. In an AES spectrum, an individual kinetic energy peak from an Auger electron is marked with an elemental symbol and subscripts indicating the electron shells or sub shells involved, for example, in aluminium oxide case, Al_{KLL} , O_{KLL} . . .

A typical AES spectrum is a plot of intensity versus kinetic energy; most commonly, it is a plot of the first derivative of intensity versus the kinetic energy. The primary electrons ejected from a solid surface by inelastic scattering comprise the background of an AES spectrum in the region of high kinetic energies while the secondary electrons comprise the background in the region of low kinetic energies. The number of Auger electrons ejected from a sample is much less than that of scattered primary electrons and secondary electrons. Thus, the direct-mode spectrum is not favoured except for quantitative analysis.

4.6.2 Fine Auger structure

A recent interest is concerned with the fine structures in the neighbourhood of Auger lines, denoted by EXAFS (extended X-ray absorption fine structure). It is a powerful nondestructive technique that provides structural information on metal or metal oxide phases highly dispersed on inorganic supports under reaction conditions. Bond lengths and coordination numbers of X-ray absorbing material can be determined. When single crystals are employed as supports, characterization of metal sites on them can be achieved separately in two different bonds parallel

and normal to the surface by polarized X-ray radiation.

In transmission mode, the EXAFS signal of surface species on solid substrates can not be detected because of the large adsorption by the substrate. To determine surface structures, it is possible to measure EXAFS spectra by detecting the reflected X-rays from sample, but usually the sensitivity is worse.

4.6.3 Quantitative analysis

Quantitative elemental analysis in electron spectroscopy is similar to that in X-ray spectroscopy. Analysis quantifies the concentrations of chemical elements on a sample surface from the peak intensities of the spectra. In theory, the quantitative relationship between the intensities of electron signals and atomic fractions of elements can be calculated. In practice, for quantification in both XPS and AES, most parameters for calculations are not available.

Sensitivity factor method: the Auger current is described by

$$I_{\alpha,XYZ} = I_p \gamma_{\alpha,XYZ} T(E_{\alpha,XYZ}) D(E_{\alpha,XYZ}) \int_{E_{\alpha,X}}^{E_p} \sigma_{\alpha,X}^{\text{total}}(E) dE \int_0^{\infty} n_{\alpha}(z) e^{\left(-\frac{z}{\lambda^M(E_{\alpha}) \cos \theta}\right)} dz \quad (4.13)$$

where I_p is the excitation current, $\gamma_{\alpha,XYZ}$ is the Auger efficiency, $\sigma_{\alpha,X}^{\text{total}}(E)$ is the ionization cross section X the element α , E_p is the energy of the primary electron $n_{\alpha}(z)$ is the density of element α at depth z . The transmittance of the spectrometer is $T(E_{\alpha,XYZ})$ and the sensitivity of the detector is $D(E_{\alpha,XYZ})$.

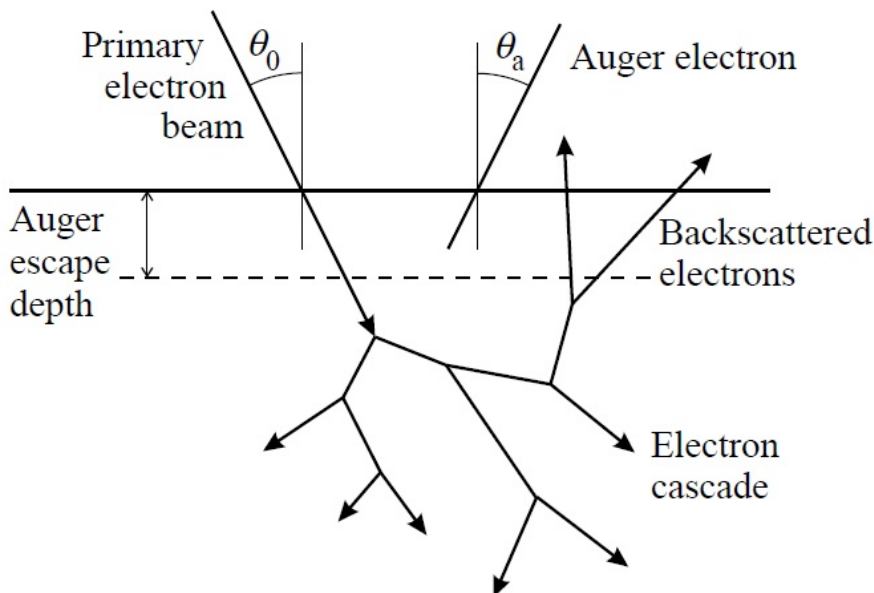


Figure 4.16: The physical processes occurring when an electron strikes a solid surface.

Ionization is caused not only by the electrons but also by the backscattered energy which has the distribution $n(E)$

$$\sigma_{\alpha,X}^{\text{total}} = \sigma_{\alpha,X}(E_p) + \int_{E_{\alpha,X}}^{E_p} \sigma_{\alpha,X}(E)n(E)dE \quad (4.14)$$

This relation can be approximated as:

$$\sigma_{\alpha,X}^{\text{total}} = \sigma_{\alpha,X}(E)[1 + r^M(E_{\alpha,XYZ}, \psi)] \quad (4.15)$$

which can be simplified for homogeneous material

$$I_{\alpha,XYZ} = I_p \gamma_{\alpha,XYZ} T(E_{\alpha,XYZ}) D(E_{\alpha,XYZ}) \sigma_{\alpha,X}(E) [1 + r^M(E_{\alpha,XYZ}, \psi)] n_{\alpha} \lambda^M(E_{\alpha}) \cos \theta \quad (4.16)$$

The sensitivity factor $S_{\alpha,XYZ}$ is defined as:

$$I_{\alpha,XYZ} = I_p n_{\alpha} \cos \theta S_{\alpha,XYZ} \quad (4.17)$$

and the atomic concentration α in the M matrix

$$c_{\alpha} = \frac{n_{\alpha}}{\sum_{\alpha'} n_{\alpha'}} = \frac{I_{\alpha,XYZ}}{S_{\alpha,XYZ}} \sum_{\alpha'} \frac{I_{\alpha',XYZ}}{S_{\alpha',XYZ}} \quad (4.18)$$

The sensitivity factor must be determined either theoretically or directly experimentally. Common practice is to use the sensitivity factors from published handbooks with certain corrections according to the instrument characteristics, because it is not feasible to compile a set of in-house sensitivity factors.

Standard method: For simplicity, a binary alloy $\alpha\beta$ is selected. No contamination on the surface or segregation phenomena exists:

$$\frac{I_{\alpha} I_{\beta}^s}{I_{\alpha}^s I_{\beta}} = \frac{n_{\alpha}}{n_{\beta}} \left(\frac{n_{\alpha}^s}{n_{\beta}^s} \frac{\lambda_{\alpha} \lambda_{\beta}^s}{\lambda_{\beta} \lambda_{\alpha}^s} \frac{(1+r_{\alpha})(1+r_{\beta}^s)}{(1+r_{\beta})(1+r_{\alpha}^s)} \right) = \frac{n_{\alpha}}{n_{\beta}} K \quad (4.19)$$

and the elemental concentration α is

$$c_{\alpha} = \left(1 + \frac{I_{\beta} I_{\alpha}^s}{I_{\alpha} I_{\beta}^s} \frac{1}{K} \right)^{-1}. \quad (4.20)$$

The matrix correction factor K describes the influence of the $\alpha\beta$ alloy. When $K = 1$, we assume that the influence on matrix is negligible.

4.7 X-ray photoelectron spectroscopy

The X-ray photoelectron is an electron ejected from an electron shell of an atom when the atom absorbs an X-ray photon. An incident X-ray photon can have sufficient energy (a value of $h\nu$) to knock out an inner shell electron, for example from the atom's K shell. In such a case, the K -shell electron would be ejected from the surface as a photoelectron with kinetic energy E_K . Knowing the kinetic energy E_K , we can calculate the binding energy of the atom's photoelectron (E_B) based on the following relationship:

$$E_B = h\nu - E_K - \phi \quad (4.21)$$

The value of ϕ depends on both the sample material and the spectrometer. The binding energies (E_B) of atomic electrons have characteristic values, and these values are used to identify elements, similar to the way that characteristic X-ray energy is used in X-ray spectroscopy. X-ray photoelectron spectroscopy (XPS) identifies chemical elements from the binding energy spectra of X-ray photoelectrons.

Inner shell

- depending on how deep is, we obtain atomic number and the energy of X-rays
- doublet separations in photoelectron lines \Leftarrow spin-orbital coupling jj . Splitting distance is directly proportional with $\langle 1/r^3 \rangle$ for a given orbit, so it increases for higher Z or lower l (at constant n).

subshell	value of j	area ratio
s	$\frac{1}{2}$	—
p	$\frac{1}{2}, \frac{3}{2}$	1:2
d	$\frac{3}{2}, \frac{5}{2}$	2:3
f	$\frac{5}{2}, \frac{7}{2}$	4:4

- Relative intensities are given by the photoemission cross section, analyser transmission and very little by the X-ray energy
- peak width (FWHM) is determined by

$$\Delta E = (\Delta E_n^2 + \Delta E_p^2 + \Delta E_a^2)^{1/2}, \quad (4.22)$$

where ΔE_n is the natural width of the inner surface, ΔE_p is the width of the X-rays ΔE_a is the analyser resolution (in all cases Gaussian distribution).

- ΔE_n associated with the lifetime τ

$$\Gamma = \frac{h}{\tau}. \quad (4.23)$$

where τ is related with the photoemission of X-rays, emission of Auger electrons or special type Auger electron (Coster-Kronig transition), which prefers l and is very fast. Width for light elements ($1s, 2p$) increases with the atomic number.

- ΔE_a is constant for all peaks in "constant analyser energy" (CAE) mode, but changes in "constant retard ratio" (CRR), because $\Delta E/E$ ratio remains constant.

Valence shell

Electrons with low binding energy (0–20 eV). They are very close to each other \Rightarrow band structure. At high resolution spectrum scanning can show the band structure and a sharp decrease of intensity for E_F .

Auger series

Kinetic e^- energy from Coster-Kronig transition is very low; four basic series exists:

- KLL - from boron to magnesium (with Mg $K\alpha$) or aluminium (with Al $K\alpha$),
- LMM - from sulphur to germanium (with Mg $K\alpha$) or selenium (with Al $K\alpha$),
- $M_{4,5}N_{4,5}N_{4,5}$ - from molybdenum to neodymium (with Mg $K\alpha$),
- $M_{4,5}N_{6,7}N_{6,7}$ - only for high energy X-rays (e.g. Ag $L\alpha$, 2984 eV).

4.7.1 Energy scale calibration

For meaningful measurements it is important to ensure the instrument is calibrated. For example, to identify chemical constituents from the peak energy correctly, the energy scale needs to be calibrated. To provide quantitative information, use sensitivity factors and compare with other instruments, while the intensity scale needs to be linear and also corrected for the intensity response function. The intensity response function (IRF) includes the angular acceptance of the analyser to electrons, the transmission efficiency of electrons and the detection efficiency.

- for metals is possible to observe directly the Fermi level in the valence lines;
- the semiconductors are sufficiently conductive in order to offset the E_F . It is yet difficult to determine the exact location of line since the Fermi level depends on doping, surface states and defects;
- in the analysis of dielectrics the surface charge and energy shift occurs. The most commonly used method is called internal standard - a reference line from photoemission with a known binding energy from other measurements. It is based on the fact that often the sample is contaminated with hydrocarbons ($C1s = 284,6\text{--}285,2$ eV).

Cu and Au samples set with their angle of emission $\leq 56^\circ$ are sputtered clean, and the measured energies of the peaks are compared with the energy values given in the table. As for AES, the peak energy for the calibration is evaluated from the top of the peak without background subtraction. For gold line $4f_{7/2}$ the energy is 83.95 eV. The lineshapes and energies of the $K_{\alpha 1}$ and $K_{\alpha 2}$ X-rays that characterize $h\nu$ appear to be the same in all unmonochromated instruments. However, the lineshapes and energies of the K_α X-rays, when monochromated vary significantly and depend on the set-up of the monochromator and its thermal stability. By

altering the monochromator settings, the measured energies of the peak may be moved over a kinetic energy range of 0.4 eV without too much loss of intensity.

Use of the standard with a modern, well-maintained spectrometer should result in calibration within tolerance limits of ± 0.2 eV over four months or ± 0.1 eV over one month before recalibration is required. For many purposes ± 0.2 eV is satisfactory.

4.7.2 Primary structure information

Inner shell line

The binding energy is influenced by interactions with other electrons \rightarrow chemical shift. The exact calculation of the binding energy is very difficult and limited to small molecules \rightarrow approximate methods, such as electrostatic model - the model potentials (charge Potential model)

$$E_B = E_B^0 + kq_i + \sum_{i \neq j} \frac{q_j}{4\pi\epsilon_0 r_{ij}}, \quad (4.24)$$

where E_B^0 has significant calibration factor, k is a constant indicating an average repulsion between inner shell and valence e^- , q_i is the atom i charge and sum of potentials of neighbouring atoms j , also called Madelung potential, where r_{ij} are the internuclear distances.

Valence band peak

The valence electrons are directly involved in bond formation and molecular interactions, so the intensity and energy of the valence band peaks depend on their bonding environment. Thus, quantitative interpretation of the valence band spectrum for most materials requires a full molecular orbital calculation. For multi-component materials or those containing a large number of atoms per structural unit (e.g. polymers) this requires computer calculations.

Valence band analysis is worth pursuing because it can provide electronic structure information that cannot be obtained from typical core level analysis. Also, it is sometimes possible to extract useful structural information from valence band spectra.

In metals the information about the valence band and the Fermi energy give the opportunity to observe the transformation of the material from dielectric to metal (VO_2 non-conductor \times metal at 65° , Na_xWO_3 non-conductor \times metal when changing x).

Auger chemical shift

To identify the oxidation state of an element is often preferable to use the Auger parameter:

$$\alpha = E_K(jkl) - E_K(i) = E_K(jkl) + E_B(i) - h\nu, \quad (4.25)$$

where $E_K(jkl)$ and $E_K(i)$ is the kinetic Auger energy. α does not depend on the reference surface or the sample charge. The Auger parameter is modified

$$\alpha' = \alpha + h\nu = E_K(jkl) + E_B(i). \quad (4.26)$$

Auger line shapes

Auger lines can be readily distinguished from photoemission lines by changing X-ray sources (e.g.

using a Mg K_{α} source instead of an Al K_{α} source). If the Auger process causes the formation of at least one hole, then the distribution of Auger lines intensities strongly depends on the type of molecule.

4.7.3 Final state effects

X-ray satellites and ghost peaks

Satellites appear together with the less intensive X-ray characteristic peaks. The main peak $K_{\alpha_{1,2}}$ corresponding to the $2p_{3/2,1/2} \rightarrow 1s$ transition, satellites are $K\beta$, valence bands $\rightarrow 1s$ or multi ionized atoms.

Ghosts appear due to excitation of surface contaminants. Often, Al $K_{\alpha_{1,2}}$ from the Mg K_{α} (due to the aluminium window), followed by Cu L_{α} and O K_{α} .

Multiplet splitting

A requirement for this splitting of the s photoemission peak into a doublet is that there be unpaired orbitals in the valence shells. Complex peak splitting can be observed in transition metal ions and rare earth ions when multiplet splitting occurs in p and d levels.

$$\Delta E = (2S^v + 1)K_{sd} \quad \text{a} \quad \frac{I(S^v + 1/2)}{I(S^v - 1/2)} = \frac{S^v + 1}{S^v}, \quad (4.27)$$

where S^v is the total spin of a unpaired valence electron and K_{sd} is the s-d exchange integral.

Shake-up satellites

It represents photoelectrons that have lost energy through promotion of valence electrons from an occupied energy level (e.g. a π level) to an unoccupied higher level (e.g. a π^* level). Shake-up peaks (also called "loss peaks" because intensity is lost from the primary photoemission peak) are most apparent for systems with aromatic structures, unsaturated bonds or transition metal ions. In contrast to the continuum of reduced energies seen in the inelastic scattering tail, shake-up peaks have discrete energies ($\sim 6.6\text{eV}$ higher binding energy than the primary peak in C_{1s} spectra of aromatic-containing molecules) because the energy loss is equivalent to a specific quantized energy transition (i.e., the $\pi \rightarrow \pi^*$ transition).

Asymmetric metal lines

The metal lines may change with the degree of surface charging during data acquisition. With asymmetric metal lines as encountered with many transition metals, this effect may mimic the presence of metal ions, The line broadening is, most likely, due to varying degree of differential charging, since it is paralleled in the widths of the support elements.

Asymmetric non-metal lines

Appears only at high resolution. The asymmetry occurs due to fine vibrational structure of molecules. After ionization there is a change in interatomic distances and narrowing the potential curves of the molecule.

Shake-off satellites

If the departing photoelectron transfers sufficient energy into the valence electron to ionize it into the continuum, the photoemission loss peak is called a "shake-off" peak. The shake-off satellite peaks of the photoemission peak can have a wide range of possible energies (of course, always with a lower KE than the photoemission peak). This energetically broad feature is typically hidden within the background signal and is usually not detected or used analytically.

4.7.4 Quantitative analysis

The intensity of the photoemission line i

$$I_A^i \sim Q \mathcal{A} c_A \sigma_A^i \lambda^i T^i L_A^i f(\phi, \theta), \quad (4.28)$$

where Q is the photon flux [$\text{cm}^{-1}\text{s}^{-1}$], \mathcal{A} effective area of the sample, c_A concentration of A, σ_A^i is the partial ionization cross section, λ^i mean free path, T^i the transmission, L_A^i angular asymmetry coefficient and $f(\phi, \theta)$ function, depending on the geometry of the experiment. The above equation does not detect the absolute concentration of elements. The intensities of the lines for individual measured elements under the same conditions can determine the relative atomic composition. When a solid is homogeneous within the analysed depth for all elements of interest (A and B for example), the uncertainties can be partially cancelled by considering relative atomic values. We obtain:

$$\frac{I_A^i}{I_B^j} = \frac{c_A \sigma_A^i \lambda^i T^i L_A^i}{c_B \sigma_B^j \lambda^j T^j L_B^j} = \frac{c_A \sigma_A^i L_A^i}{c_B \sigma_B^j L_B^j} R. \quad (4.29)$$

If the kinetic energy differs by more than ~ 400 eV, correction of T and λ should be performed. the correction used for transmission:

$$T \sim 1/E_k \quad \text{for constant energy (CAE)} \quad (4.30)$$

and

$$T \sim E_k \quad \text{for constant resolution (CRR)}. \quad (4.31)$$

To calculate the mean free path, the typically used equation is

$$\lambda = aE_k^{-2} + bE_k^{1/2}. \quad (4.32)$$

One of the major problem in quantitative analysis is the integral of photoemission intensity lines. When using the theoretical values σ we have determine the overall intensity of lines including the contributions of all satellites and inelastic electron scattering. For practical purposes we can use the equation:

$$\frac{I_A^i}{I_B^j} = \frac{c_A S_A^i}{c_B S_B^j}. \quad (4.33)$$

4.7.5 Angular effects

1. Enhancement of system sensitivity and depth profile

Almost all electrons (95 %) come on a path equal with 3λ . If e^- are detected at angle θ different from normal, the thickness of the analysed layer is:

$$d = 3\lambda \sin \theta \quad (4.34)$$

For the substrate (s) with homogeneous layer (v), the change of intensity in the ideal case is:

$$I^s(d) = I_0^s e^{-d/\lambda \sin \theta} \quad \text{and} \quad I^v(d) = I_0^v (1 - e^{-d/\lambda \sin \theta}). \quad (4.35)$$

In practice, however, the geometry of the system also exhibits a angular response dependence function \Rightarrow measured values for I^v/I^s

2. Single-crystal studies

Measuring the absolute core electron intensity from a single-crystal surface, depending on the angle θ gives modulated intensity. Similar modulation is observed for fixed θ and rotation of surface plane. \Rightarrow **X-ray photoelectron diffraction XPD**

4.7.6 Numerical data analysis

Simple operation with data:

(a) integration and determination of area, (b) noise removal, (c) satellites removal, (d) background subtraction, (e) addition and subtraction of spectra, (f) search for lines maxima, (g) conversion to the binding energy after calibration.

background subtraction

- linear background: straight line between the first and last point of the spectrum
- integral background: the integral is calculated over the hole line area and a calibrated curve thus obtained is subtracted from the peak area
- background based on the elastic and inelastic processes

Signal to noise ratio

The noise is characterised in three different ways: peak-to-peak (p.t.p.), root-mean-square (r.m.s.), standard deviation. If the spectrometer is limited to statistical noise, the signal to noise ratio (S/N) can be defined like:

$$S/N = \sqrt{\frac{S+B}{F}}, \quad (4.36)$$

where S is the height of the line above background B , is the background B and F is the intensity factor

$$F = \frac{(S/B + 1)(S/B + 2)}{(S/B)^2}. \quad (4.37)$$

If we desire S/N constant

$$t_2/t_1 = F_2/F_1. \quad (4.38)$$

Smoothing

- fitting the data with a suitable smooth function (polynomial, fractional polynomial, exponential, Fourier and splines)
- convolution data using a suitable algorithm, which leads to a smoothing

$$y_r^{\text{sm}} = \sum_{r=-m}^m \frac{C_r y_r}{\text{NORM}}, \quad (4.39)$$

where C_r is the convolution number and NORM is the normalizing factor. Savitsky-Golay convolution is recursive. the convolution function represented by least squares fitting of an polynomial(cubic-quadratic) to m points on either side of each data point.

- frequency filter for Fourier transformation (mathematical equivalent of convolution algorithm).

Analysis of overlapping spectral lined

- spectra derivation (background removal, separation of overlapping lines), negative lines in the second derivative correspond to approximately the position of overlapping lines \Rightarrow noise problems \Rightarrow smoothing with derivation
- deconvolution, mostly for the shape of the line

$$y_j^{\text{m}} = \sum_{i=1}^N y_i^{\text{t}} g_{j-1} + n_j, \quad (4.40)$$

where n_j is the noise. The instrument function g can be determined by line measurement of Ag 4 eV from the Fermi level with a monochromatic X-ray source.

- fitting with Gaussian or Lorentz function. It can either be used the Voigt convolution or a mix Gauss-Lorentz function

$$f(E) = \frac{A}{[1 + M(E - E_0)^2/\beta^2] \exp([1 - M][\ln 2(E - E_0)^2/\beta^2])}, \quad (4.41)$$

where M is mixing ration (1 for pure Lorentz shape) and β is a parameter, which is nearly 0.5 FWHM.

4.8 Electron energy loss spectroscopy

Metoda EELS je založena na **nepružném rozptylu primárních e^-** pevnou látkou, při níž dochází k vybuzení e^- nebo skupiny e^- (vybuzení plazmonů) pevné látky do vyššího stavu.

Hodnoty **energie primárních e^-** jsou několik **desítek eV** \Rightarrow povrchová metoda.

Elektrony přecházejí do vyšších hladin téhož pásu (vnitropásové přechody), do jiného pásu (mezipásové přechody) nebo do povrchových stavů. \Rightarrow Měřením ztrát získáme představu o elektronové struktuře PL - neobsazených stavech. Musíme mít ovšem nezávislou informaci o rozdělení a polohách zaplněných stavů, např. z fotoelektronové spektroskopie.

Hodnoty **energetických ztrát jsou 1–20 eV**.

The laws of energy and impulse conservation forms

$$E'(\vec{k}') = E_0(\vec{k}) - \hbar\omega, \quad (4.42)$$

$$\vec{k}'_{\parallel} = \vec{k}_{\parallel} - \vec{q}_{\parallel} \pm \vec{g}_{\parallel}, \quad (4.43)$$

where $E_0(\vec{k})$ is the incident e^- -energy with momentum $\hbar\vec{k}$, $E'(\vec{k}')$ is the backscattered e^- -energy with momentum $\hbar\vec{k}'$, $\hbar\omega$ is e^- -energy loss in the transmission, \vec{q} is the transferred momentum \vec{g} is the lattice reciprocal vector. EELS modifications: AREELS - Angle Resolved EELS, HREELS - High Resolution EELS.

Experimental

If we consider the experimental requirements for EELS or HREELS, low energy electrons, single crystal substrates (usually), then it is clear that this is a high vacuum technique. In practice the working pressure limit for most EELS instruments is 10^{-6} mbar due to a gas-phase scattering processes.

Usually at least one unit, the monochromator or analyzer, has some ability to rotate about an axis perpendicular to the plane of the experiment while the sample may also rotate. In this way it is possible to vary the angle of incidence over a wide angular range and still maintain the ability to detect at angles away from the specular position. The monochromators and analysers are electrostatic selection units based upon either 127-degree cylindrical capacitors or hemispherical capacitors. The potentials applied to these capacitors are such that only electrons having specific pass energies may reach first the sample surface and second the detector. The working surfaces of the spectrometer are coated with an inert material such as graphite in order to minimize changes in spectrometer work function that may occur upon exposure to various gases.

The design of an EEL spectrometer is such that the energy spread of the incident low-energy electron beam is minimized while maintaining a reasonable electron flux. This primary consideration means that the area of surface sampled by the beam is of secondary importance.

Three independent ways for measuring spectra can be used:

1. measurements at constant angle θ , θ' and constant energy loss value $\hbar\omega$ depending on the incident energy loss profile
2. measurement of the loss energy $\hbar\omega$ at constant \vec{k} in accordance with the scattering angle θ' .
3. measurements at constant \vec{k}' electron dispersion direction depending on the energy loss spectrum.

The basic problem of the measurements is the assignment scattering mechanism for measured energy loss. First the plasma loss should be determined and then distinguish between the remaining peak volume and the surface processes. They are often represented as the corresponding maximum ionization of deeper levels.

4.9 Threshold techniques

An alternative form of core level spectroscopy is based on the detection of the onset on ionization as the exciting beam energy passes through such a threshold (equal to the binding energy of the core level relative to the Fermi level of the solid). A technique of this kind involves sweeping the exciting energy beam and detecting the onset of emission of photons or Auger electrons associated with the refilling of the core hole thus created. These different modes of detection form a group under the general heading of APS (Appearance Potential Spectroscopy). In principle, either incident electrons or photons could be used but the photon calls for a tunable light source in the 50–2000 eV range, only possible using synchrotron radiation.

All three modes of the incident electron technique have been used, however, the thresholds either being detected by fall in the elastically scattered electron flux (Disappearance Potential Spectroscopy - DAPS), by the onset of photons emission (Soft X-ray Appearance Potential Spectroscopy - SXAPS) or by the onset of the new Auger electron emission channel (Auger Electron Appearance Potential Spectroscopy - AEAPS). Note that in all of these techniques the surface sensitivity is guaranteed by inelastic scattering of the incident electron beam.

Primary energy E_p is determined by:

$$E_p = eV_p + \phi + kT. \quad (4.44)$$

By applying the conservation of energy

$$E_p - E_1 = E_B + E_2, \quad (4.45)$$

where E_1 is the primary electron energy level, E_B is the binding energy of the electron on the surface E_2 . At the threshold energy can be captures just above the Fermi level i.e. $E_1 = E_2 = 0$ and $E_p = E_B$. If instead of thermionic cathode we have tunnel cathode, the $eV_p = E_B$. The probability of excitation of the inner layers is:

$$W(E_p) \approx \int_0^{E_p} \psi(E' - E_B) \int_0^{E_p + E'} \quad (4.46)$$