

X-Ray Photoelectron Spectroscopy (XPS)

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Fulmer 261A

**Electron Spectroscopy for
Chemical Analysis (ESCA)**

- The basic principle of the photoelectric effect was enunciated by Einstein [1] in 1905

$$\mathbf{E = h\nu}$$

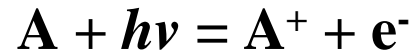
There is a threshold in frequency below which light, regardless of intensity, fails to eject electrons from a metallic surface. $h\nu_c > e\Phi_m$

Where h - Planck constant (6.62×10^{-34} J s), ν - frequency (Hz) of the radiation and Φ_m work function

- In photoelectron spectroscopy techniques such XPS, Auger and UPS, the photon energies range from 20 -1500 eV (even higher in the case of Auger, up to 10,000eV) much greater than any typical work function values (2-5 eV).
- In these techniques, the kinetic energy distribution of the emitted photoelectrons (i.e. the number of emitted electrons as a function of their kinetic energy) can be measured using any appropriate electron energy analyzer and a photoelectron spectrum can thus be recorded.

- By using photo-ionization and energy-dispersive analysis of the emitted photoelectrons the composition and electronic state of the surface region of a sample can be studied.
- Traditionally, these techniques have been subdivided according to the source of exciting radiation into :
- X-ray Photoelectron Spectroscopy (XPS or ESCA) - using soft x-ray (200 - 1500 eV) radiation to examine core-levels.
- Ultraviolet Photoelectron Spectroscopy (UPS) - using vacuum UV (10 - 45 eV) radiation to examine valence levels.
- Auger Electron Spectroscopy (AES or SAM) – using energetic electron (1000 – 10,000 eV) to examine core-levels.
- Synchrotron radiation sources have enabled high resolution studies to be carried out with radiation spanning a much wider and more complete energy range (5 - 5000+ eV) but such work will remain, a very small minority of all photoelectron studies due to the expense, complexity and limited availability of such sources (Berkeley, Stanford, New York (2), Baton Rouge, Argonne in the US).

One way to look at the overall photoelectron process is as follows:



1. Conservation of energy then requires that :

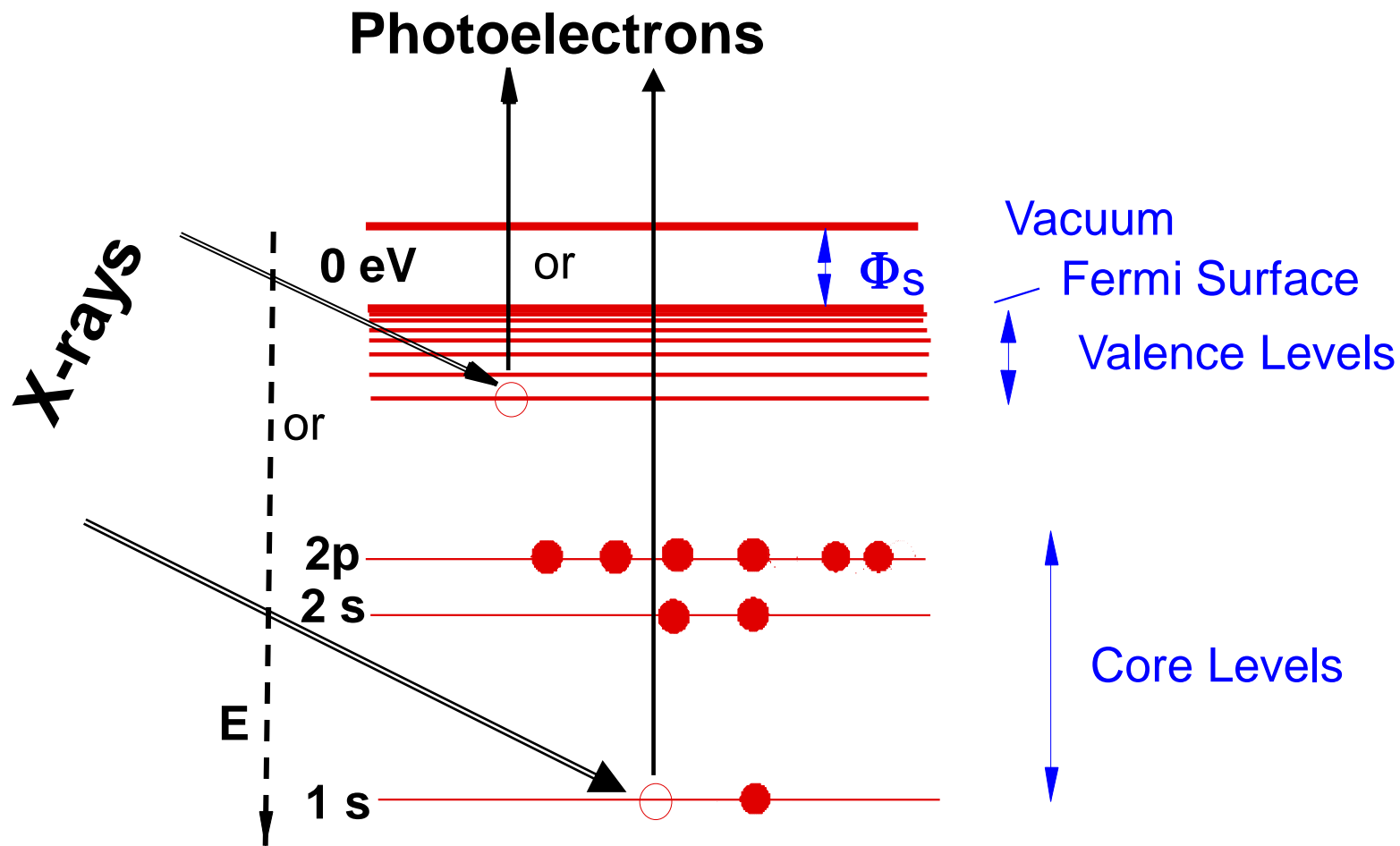
$$E(A) + h\nu = E(A^+) + E(e^-) \quad (\text{energy is conserved})$$

2. Since the energy of the electron is present solely as kinetic energy (KE) this can be rearranged to give the following expression for the KE of the photoelectron :

$$E(e^-) = \text{KE}(e^-) = h\nu - [E(A^+) - E(A)]$$

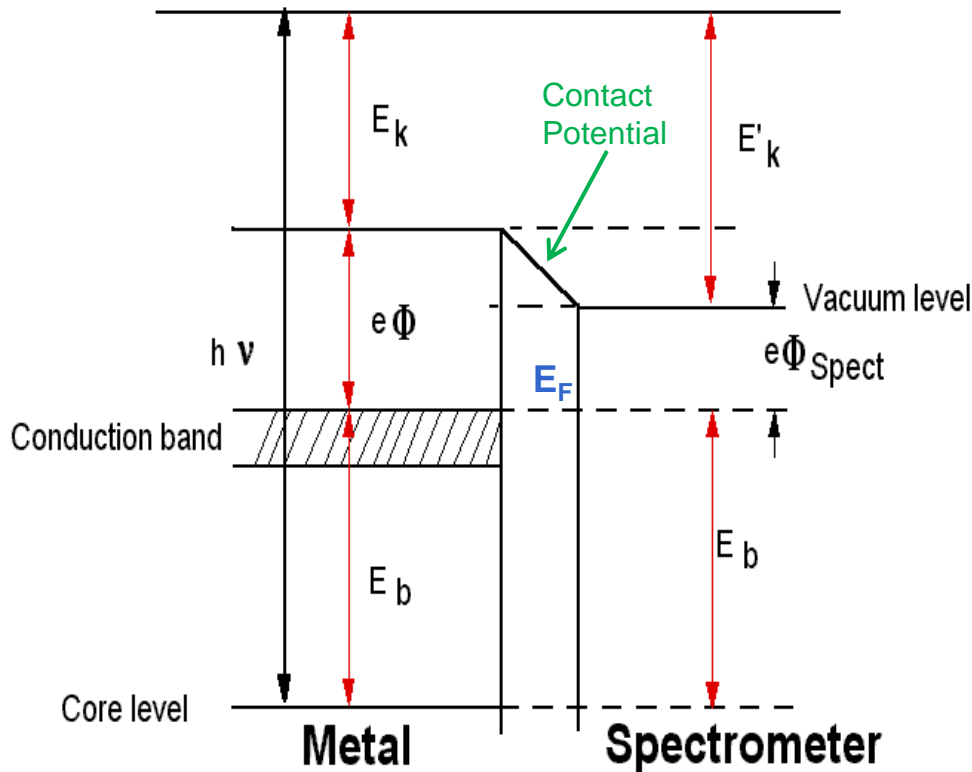
3. The final term in brackets represents the difference in energy between the ionized and neutral atoms, and is generally called the *binding energy* (BE) of the electron - this then leads to the following commonly quoted equation :

$$\text{KE} = h\nu - \text{BE}$$



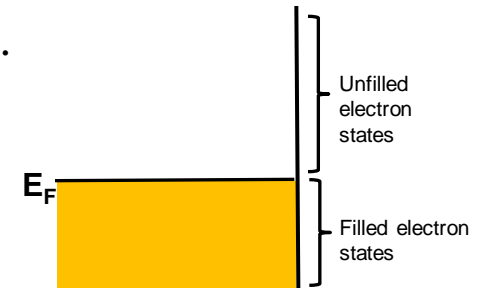
Photoelectron: $BE = h\nu - KE - \Phi_s$

Energy Diagram



- E_b (binding energy) is below the conduction band edge.

- Fermi energies of metal and spectrometer coincide (electrons transfer between metal and spectrometer until the E_F align).



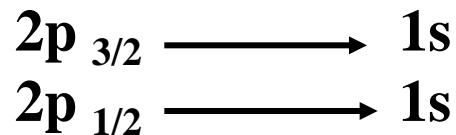
- Contact potential; $e(\phi - \phi_{sp})$.

- E'_k : measured kinetic energy.

- $E_b = h\nu - E'_k - e\phi_{sp}$ (no need to know the work function of the sample)

X-ray Sources

- Their choice is determined by the energy resolution. Typical materials are Mg and Al.
- A heated filament (cathode) emits electrons which are accelerated toward a solid anode (water cooled) over a potential of the order of 5 -20 kV.
- Holes are formed in the inner levels of the anode atoms by the electron bombardment and are then radioactively filled by transitions from higher-lying levels:



Resulting in the emission of X-rays

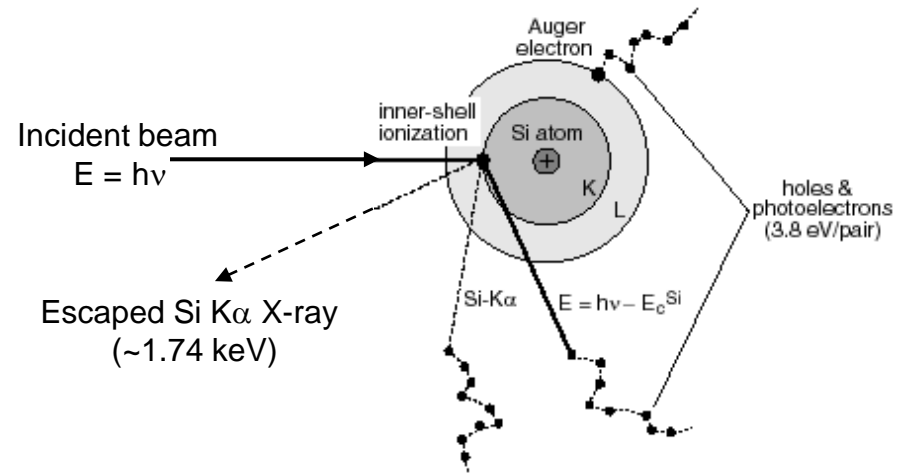
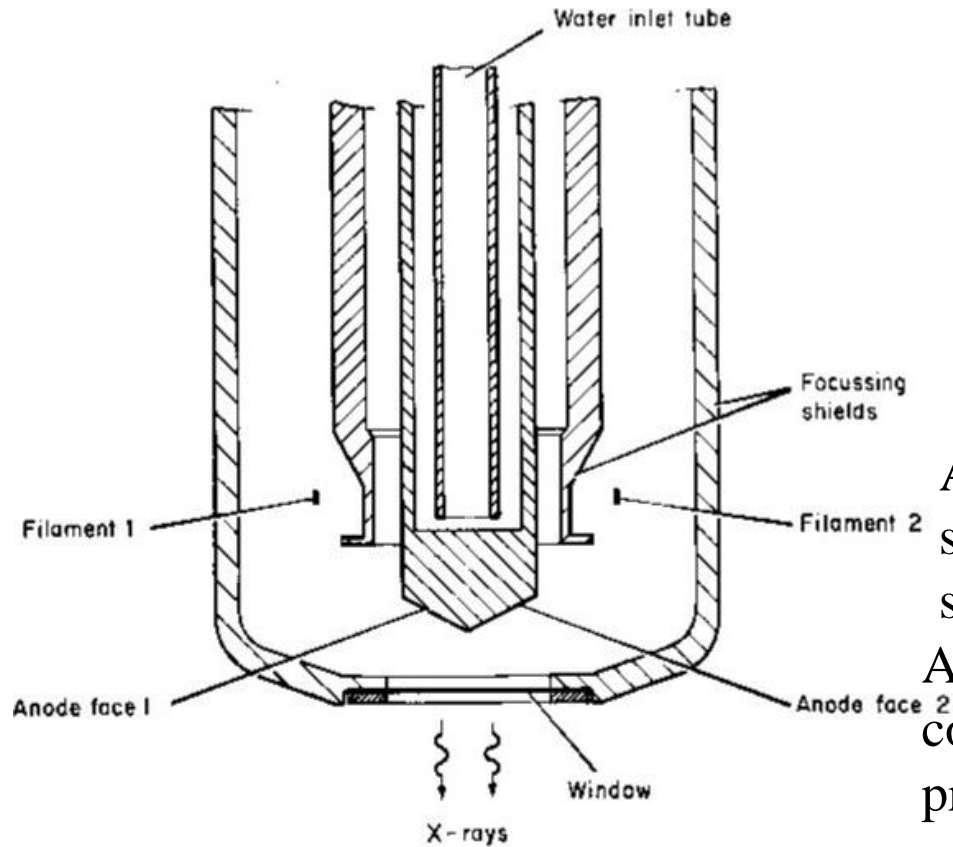
Mg $K\alpha_{1,2}$ at 1253.6 eV

Al $K\alpha_{1,2}$ at 1486.6 eV



Typical emission of X-rays

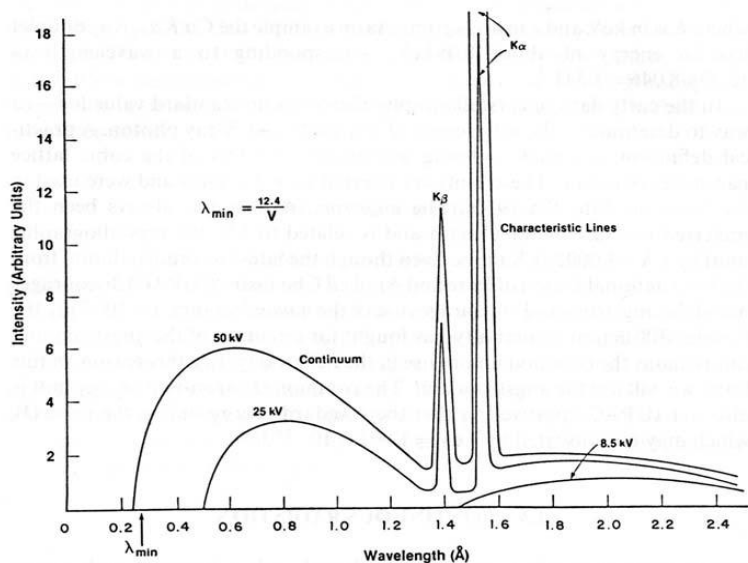
Typical geometry of an X-ray gun



Aluminum windows of 10-30 μm thick separate the excitation region from the specimen.

Additional x-ray lines ($K\alpha_3$ and $K\alpha_4$) and a continuous spectrum (Bremsstrahlung) are produced. Peaks 10 eV above the $K\alpha_{1,2}$ with intensities of 8 % and 4 % of $K\alpha_{1,2}$ and a continuous spectrum contribute to the BG.

X-ray Sources Available

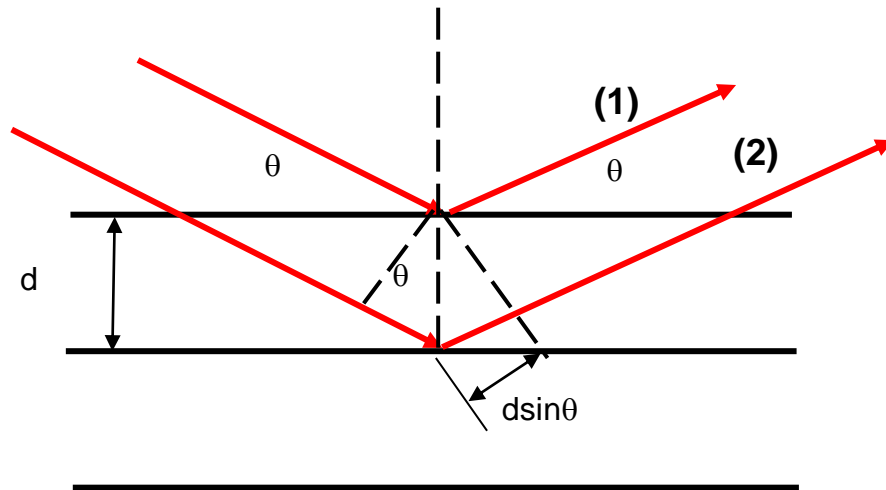


Continuous and characteristic radiation for copper.

X-rays	Energy (eV)	Natural Width (eV)
Cu $K\alpha$	8048	2.5
Ti $K\alpha$	4511	1.4
Al $K\alpha$	1487	0.9
Mg $K\alpha$	1254	0.8
Na $K\alpha$	1041	0.7

Kratos and PHI commonly use Al $K\alpha$ and Mg $K\alpha$

- To remove the unwanted radiation and increase the energy resolution the $\text{AlK}\alpha$ is often monochromatized (cut a “slice” from the x-ray energy spectrum, removing both satellites and Bremstrahlung (which increases the BG level)).
- Crystal used = quartz because can be obtained in near perfect form and can be elastically bent (bending does not affect resolution or reflectivity).

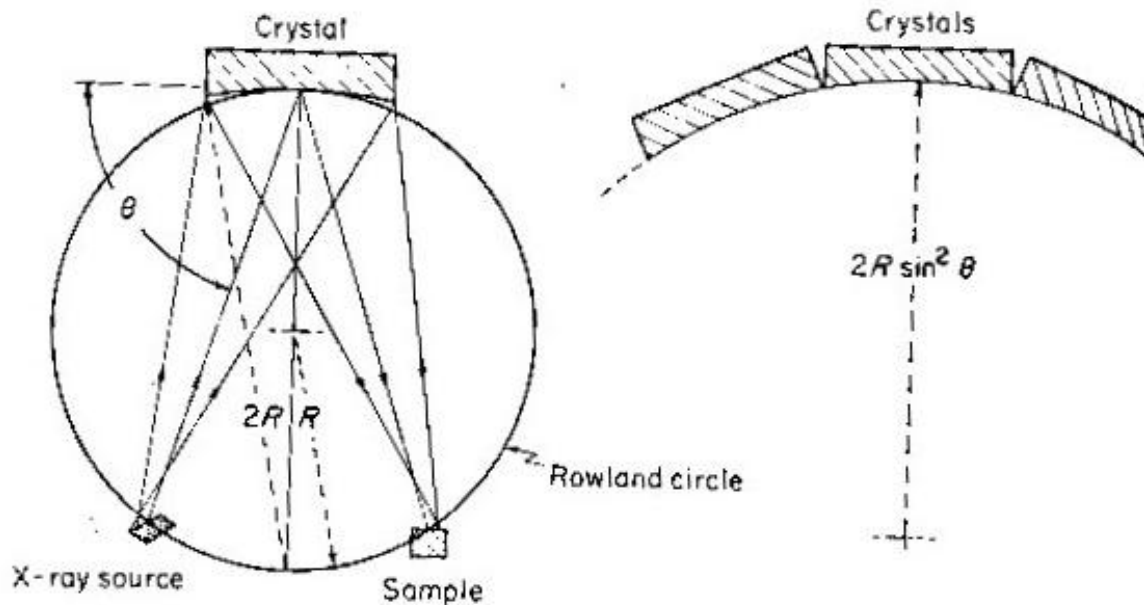


Beam (2) travels an extra $d\sin\theta$ before reaching the surface and beam (1)

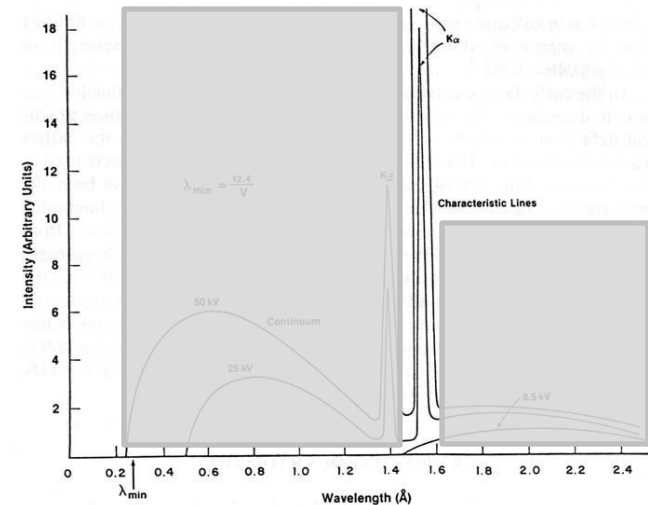
Parallel Atomic Planes
 $n\lambda = 2d\sin(\theta)$

For first order ($n = 1$) diffraction and $\text{Al K}\alpha$ X-rays, $\lambda = 8.3 \text{ \AA}$ for a distance d between planes of about 4 \AA and a Bragg angle, θ of 78.5°

Rowland circle



For Cu $K\alpha$ ($\lambda \sim 1.55 \text{ \AA}$)



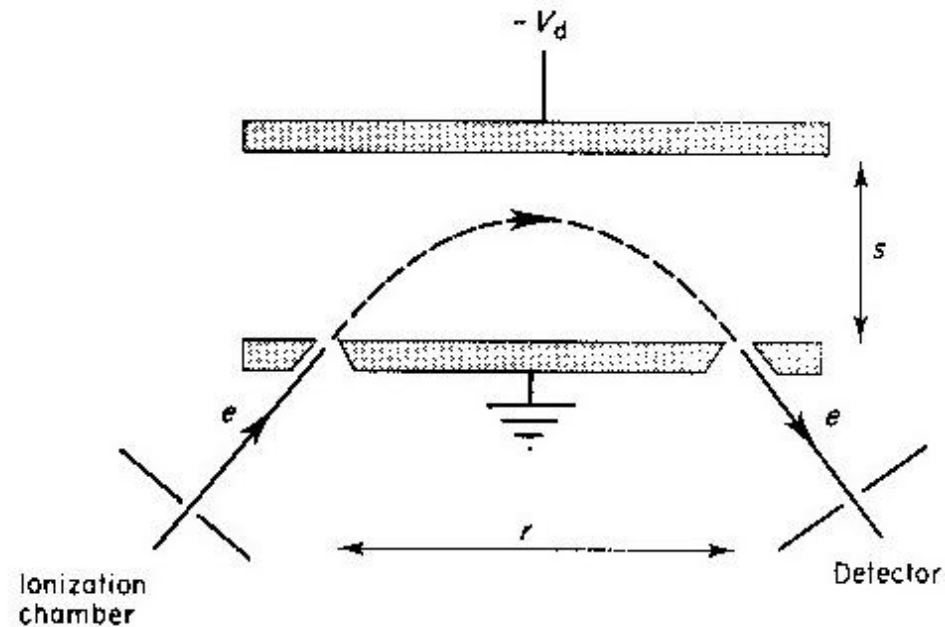
The crystal must lie along the circumference of the Rowland circle (focusing circle), Johann focusing geometry.

Analyzers

Dispersive analysis of the kinetic energy spectrum $n(KE)$

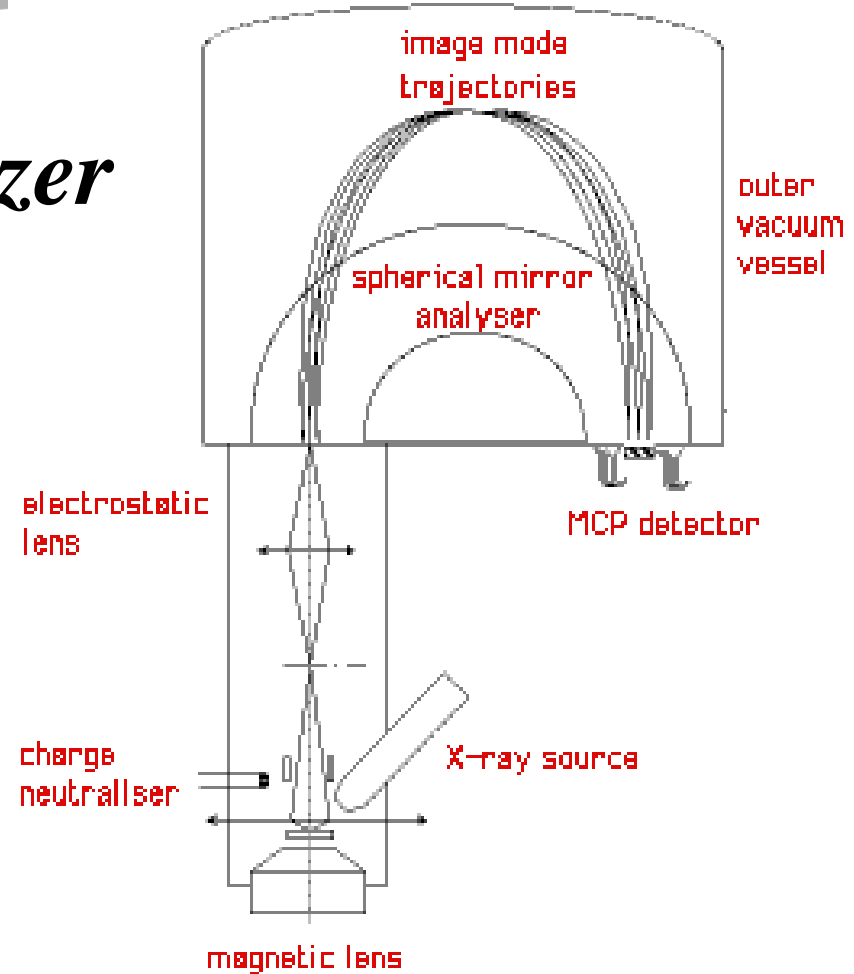
- A field is applied between 2 parallel plates, s apart. The lower plate has slits, entrance and exit r apart. The photoelectrons with kinetic energy KE are transmitted to the detector.
- By varying V_d the spectrum of electron kinetic energies can thus be obtained.
- KE is proportional to V_d therefore the photoemission spectrum is the plot of electron flux against V at the detector.

The parallel plate electrostatic analyzer



$$V_d = \frac{2sKE}{er}$$

Spherical mirror analyzer



www.Kratos.com

The alternative to dispersive analysis is to discriminate the electron KE by a retarding electric field applied between the target region and the detector. Electrons with $KE > eV_r$ will reach the detector (a kind of filtration process).

Spectrometer

Photo ionization process has a rather low absolute probability (10^4 electrons per second, or 10^{-15} A) therefore electron multiplier (gain of 10^6) are used to obtain an accurately measurable current. Newer instruments use channel plates.

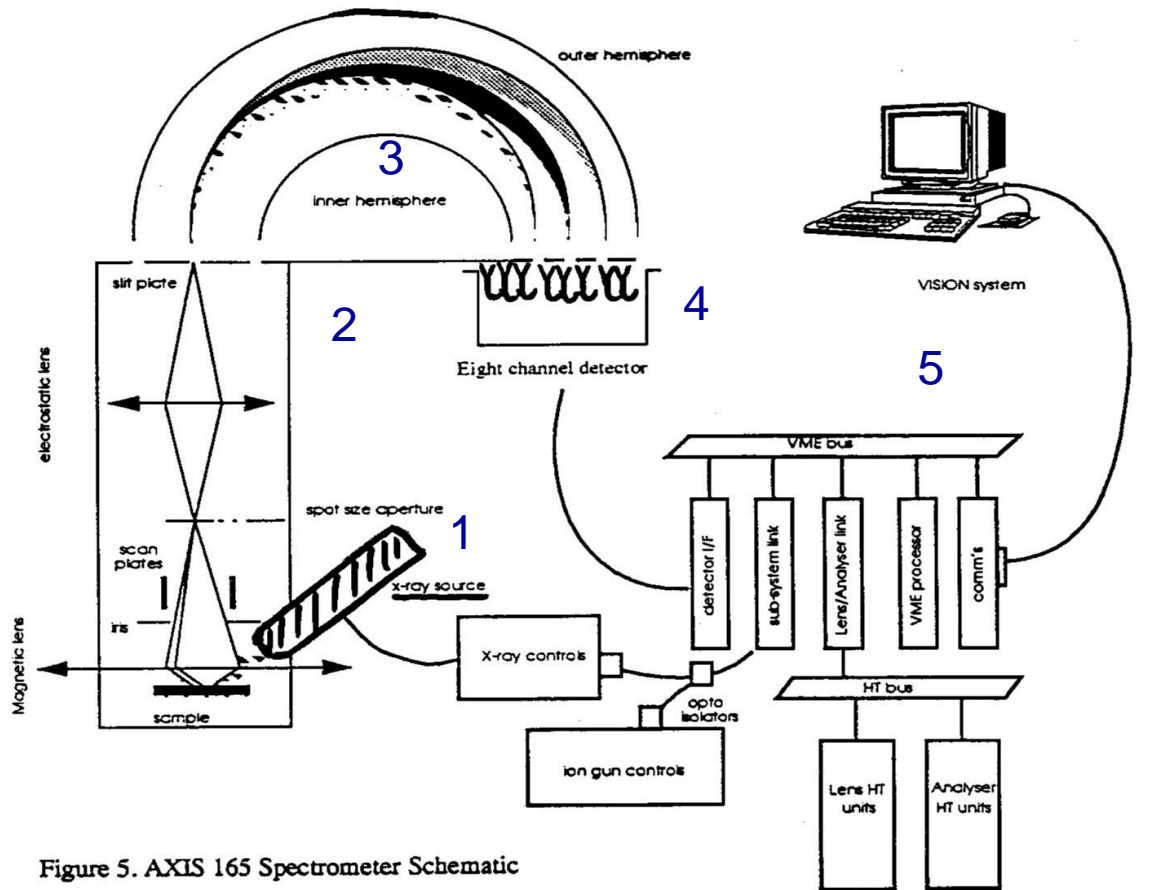


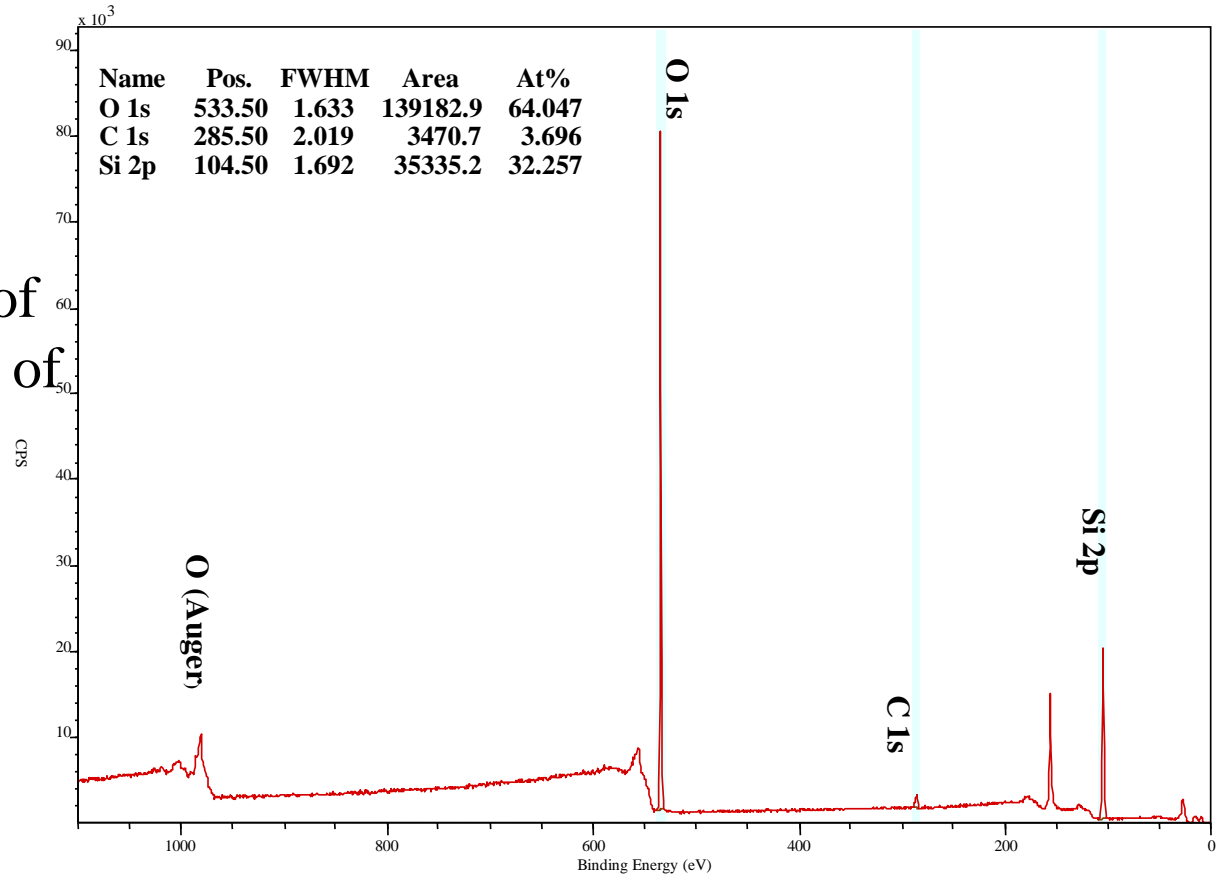
Figure 5. AXIS 165 Spectrometer Schematic

Components:

1. Source of radiation
2. Ionization Chamber
3. Electron energy analyzer
4. Electron detector
5. High vacuum system software and computer

Typical Wide Energy Scan

Immediate identification of the chemical composition of the surface.



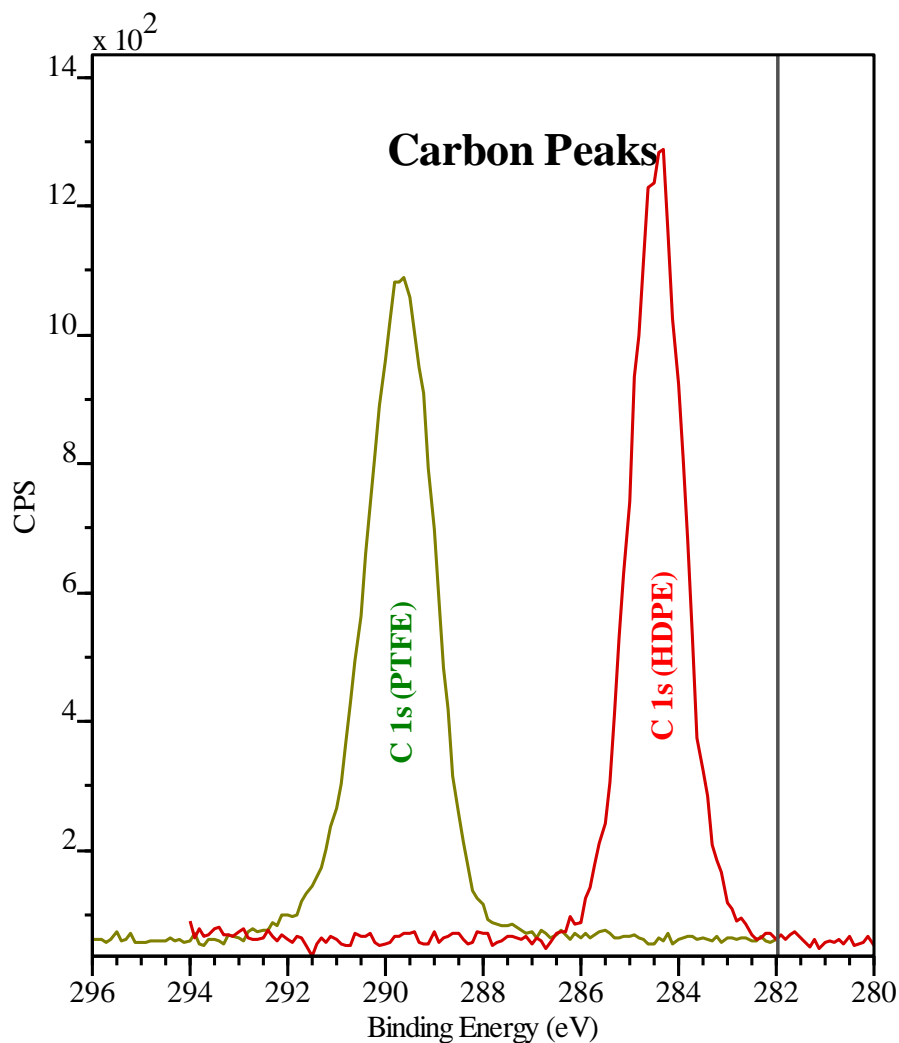
Washington State University--Pullman, WA

The core electron binding energies (BE) of the elements are distinctive

Typical High Resolution Spectra

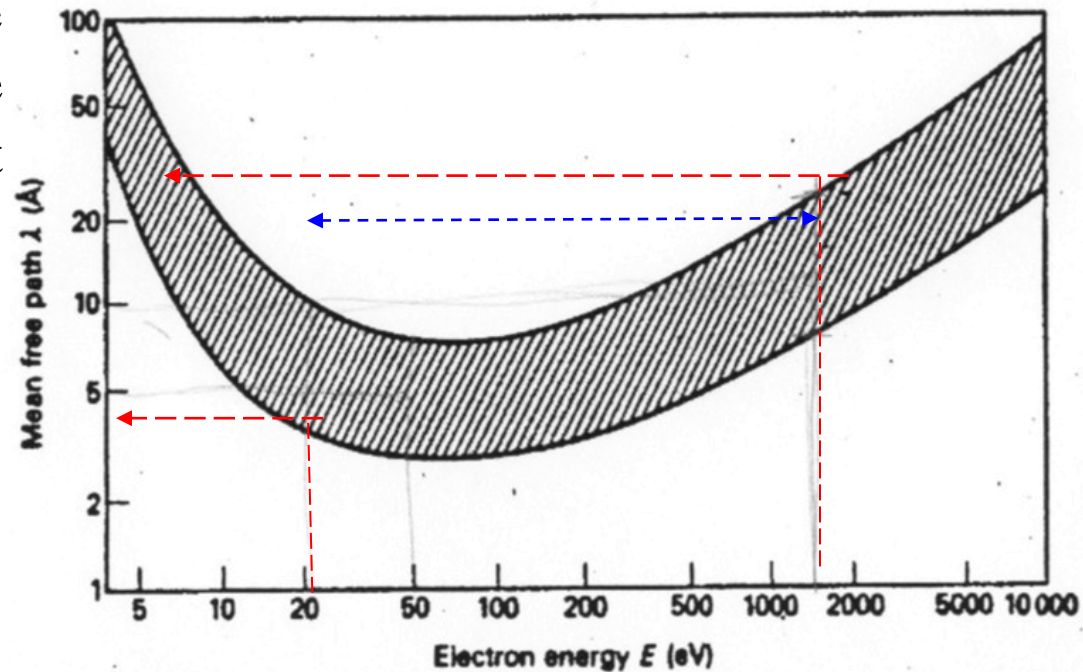
High-resolution acquisition scans
yield information such as

- *Chemical shifts*
- *Multiplet structure*
- *Satellites*
- *Chemical bonding*



Surface Sensitive Technique

- XPS is very surface sensitive because only electrons from the top few atomic layers (mean free path ~ 1.5 nm) can escape without loss of energy.

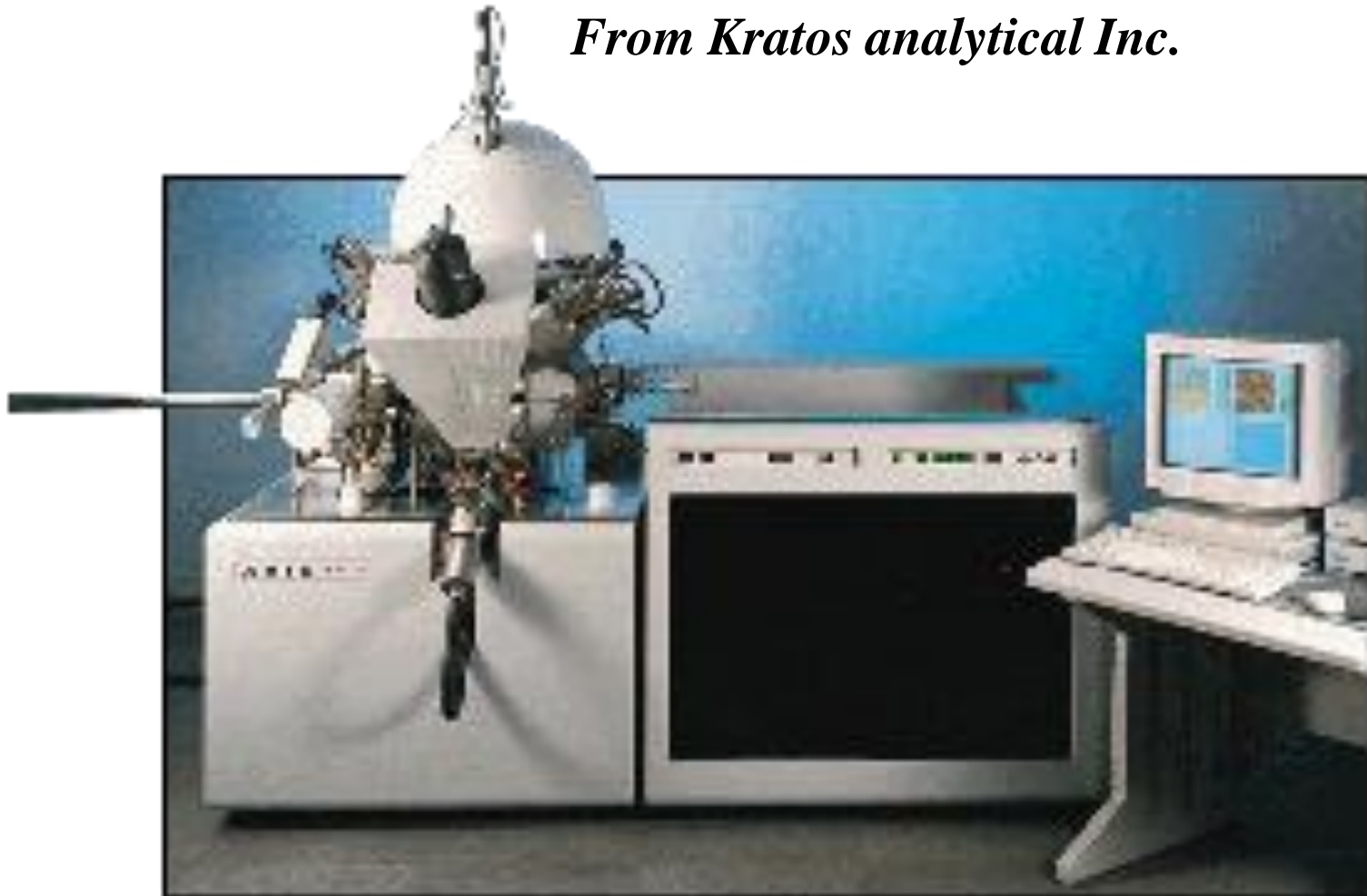


Universal Curve

- The absorption length of the X-rays is about 100 nm to 1000 nm.

AXIS-165 multi-electron spectrometer

From Kratos analytical Inc.



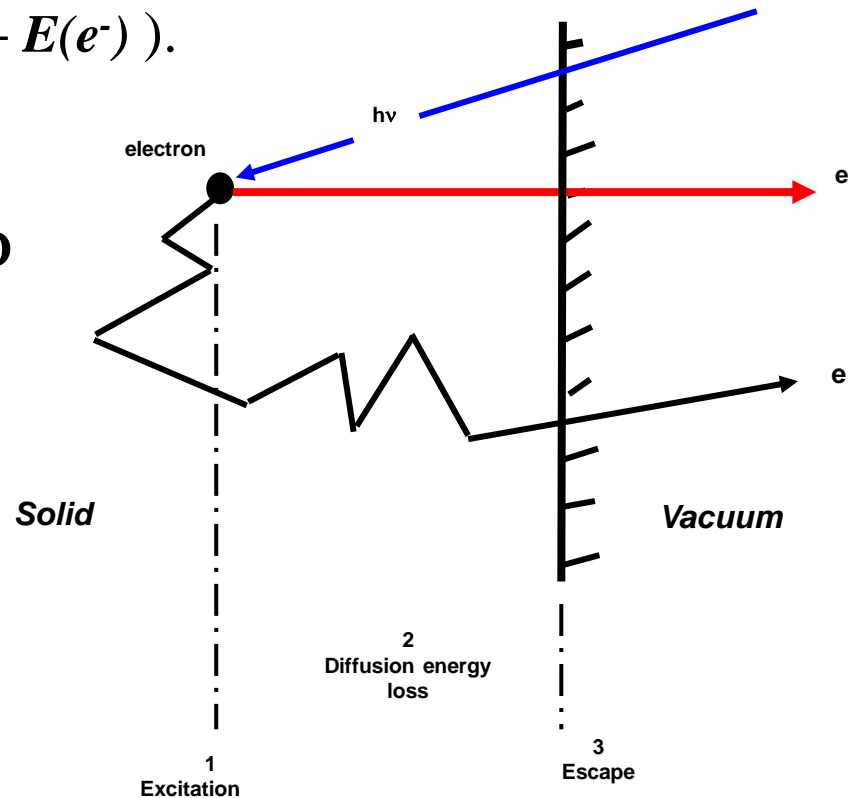
Summary

A *clean* sample is placed in ultra-high vacuum and irradiated with photons of energy ($h\nu$); soft x-rays. Photons are absorbed and energy transferred to atoms on the surface which are ionized and emit electrons (called photoelectrons) (conservation of E: $E(A) + h\nu = E(A^+) + E(e^-)$).

Photoelectric effect: $E = h\nu - \phi$

The 3 –step model:

1. Optical excitation
2. Transport of electron to the surface (diffusion energy loss)
3. Escape into the vacuum



The optical excitation probability is given by the photoionization cross-section $\sigma(E)$

In quantum mechanics $\sigma(E)$ in a subshell; nl (*principal and orbital quantum numbers*) is given by

$$\sigma_{n,l}(E) = \frac{4}{3} \pi^2 a_0^2 \alpha [N_{n,l} [E - E_{n,l}] \frac{1}{2l+1}] [lR^2_{E,l-1} + (l+1)R^2_{E,l+1}]$$

α : fine structure constant 1/137, a_0 Bohr radius (0.05 nm), $N_{n,l}$: number of e in the subshell, $E_{n,l}$ the energy of the nl electrons, E : KE of the ejected electrons.

For $n=1$ and $l=0$

$$\sigma_{1,0}(E) = \frac{4}{3} \pi^2 a_0^2 \alpha N_{1,0} [E - E_{1,0}] R^2_{E,0+1}$$

The radial dipole matrix element is given by $R_{E,l\pm 1} = \int_0^\infty P_{n,l}(r) r P_{E,l\pm 1}(r) dr$

$P_{nl}(r)l/r$ and $P_{E,l\pm 1}(r)l/r$ are the radial parts of the single-particle wave functions of the initial (discrete) and final (continuum) states, respectively. For H: $P_{10}(r) \sim (1/a_0)^{3/2} \exp(-r/a_0)$.

Cooper Minimum: $R_{E,l-1} \ll R_{E,l+1}$, thus $R_{E,l+1}$ will give the basic features and the energy dependence of the cross-sections. For a radial wavefunction with nodes, $R_{E,l+1}$ will go through 0 at a particular energy, giving rise to a minimum in the cross-section σ .

Near photoionization threshold: $R_{E,l+1}$ goes through 0 because

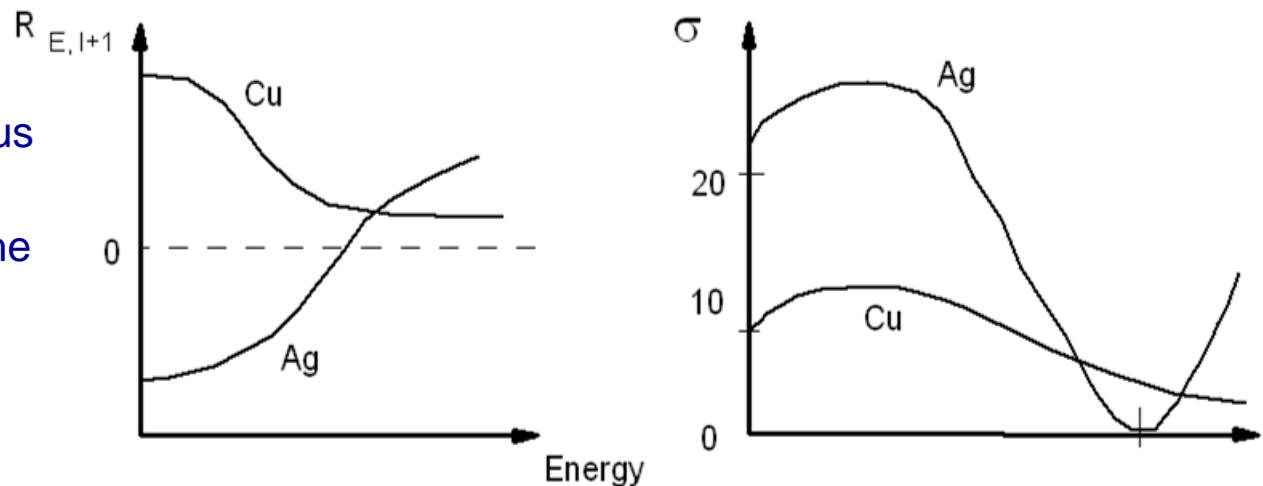
1. Final state (emitted) electron wavefunction is largely excluded from the core region
2. Initial state electron wavefunction has most strength, after it goes through a node.

As the photon energy increases the final state electron wavefunction begins to “penetrate” the core and the overlap goes to 0 due to the node in the initial state wavefunction.

Reference: Cooper Minima in the Photoemission Spectra of Solids, S.L. Molodtsov et al.

Example: Copper (Cu+) versus Silver (Ag+)

→ Increase or decrease of the PE signal of certain states



Photoemission intensity

$$I(\theta) \propto \frac{\sigma_{total}}{4} \left[1 - \frac{\beta}{4\pi} (3 \cos \theta - 1) \right]$$

(β : asymmetry parameter, θ : take off angle and σ_{total} the total cross-section)

Cooper Minima in the Photoemission Spectra of Solids

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The energy dependence of photoionization cross sections is a tool frequently used to identify contributions from different atomic states to valence-band photoemission (PE) spectra. Particularly useful is the appearance of phenomena such as Fano resonances [1] or Cooper minima (CM) [2] providing a strong enhancement or decrease of the PE signal from certain states. While the Fano resonance is a many-body effect caused by coupling of the direct PE channel with photoexcitations into localized intermediate states and subsequent autoionization, the CM represents a simple matrix element effect: Due to a node of the initial-state wave functions the transition matrix element into final states with oscillating free-electron-like wave functions becomes canceled. The behavior of the cross section around the CM depends strongly on the shape of the initial-state waves. Atomic calculations by Yeh and Lindau [3] (denoted YL in the following) provide the photoionization cross sections for all elements of the periodic table in a wide range of photon energies. Thereby, not more than one CM is found for any atomic shell considered.

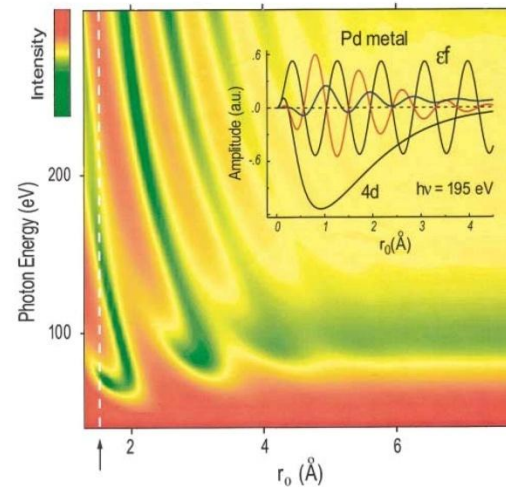


FIG. 2 (color). $|M_{4d \rightarrow (ef+\epsilon p)}^r|^2$ of Pd calculated with our atomic approach for different $h\nu$ and distances r_0 . The CM are represented by green color (see intensity scale). The white broken line and vertical arrow mark a cut at $r_0 = 1.52 \text{ \AA}$ corresponding to the curve presented at the top of Fig. 1. Results of our atomic approach for $r_0 > 5 \text{ \AA}$ are almost equivalent to those of the atomic YL calculations. The inset shows the radial parts of wave functions for the final (ϵf , multiplied with r) and initial ($4d$, multiplied with r^2) states as well as the integrand (red curve) and the integral (blue curve) of Eq. (2).

References

- Surface Analysis, The Principal Techniques Edited by John C. Vickerman, John Wiley & Sons (1997).
- Handbook X-ray and ultraviolet photoelectron spectroscopy, Briggs, Heyden & Son Ltd (1977).
- Solid State Chemistry: Techniques, A. K. Cheetham and Peter Day, Oxford Science Publication (1987).
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Websites:

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<http://www.eaglabs.com>