Electron spectroscopy

Lecture 1-2

Kai M. Siegbahn (1918 - )
Nobel Price 1981 – High resolution Electron Spectroscopy
CY653: Electron Spectroscopy

Course structure

Lecture 1. Introduction to electron spectroscopies

Lecture 2. Ultraviolet photoelectron spectroscopy: introduction

Lecture 3-4. Electron spectroscopies: experimental methods

Lecture 5-7. Interpretation of UPS, complications, computational methods

Lecture 8-12. XPS: spectra, interpretation, basic theory of photoelectron spectroscopy
Lecture 13-15: Complications of photoemission, many body effects

Lecture 16-17: Auger electron spectroscopy

Lecture 18-19: Electron spectroscopy case studies: evolution of metallicity, C60, conductivity

Lecture 20-21: Electron spectroscopy case studies: surfaces

Lecture 22-23: Electron spectroscopy case studies: solids, electronic structure

Lecture 24-25: Electron spectroscopy case studies: catalysis
Lecture 26-27: Electron spectroscopy case studies: monolayers, LBs

Lecture 28-29: Electron energy loss spectroscopy of core levels

Lecture 30-31: Electron energy loss spectroscopy of molecules and surfaces

Lecture 32-33: Bremstrahlung isochromat spectroscopy

Lecture 34: Electron spectroscopy with advanced light sources

Lecture 35: Electron spectroscopy: current research
References


Reviews, papers
• Broad class of spectroscopic techniques, collectively called electron spectroscopy.

• In general terms, electron spectroscopy can be defined as the energy analysis of electrons ejected or reflected from materials.

• All of these spectroscopic techniques yield information on the ELECTRONIC STRUCTURE.
There are, generally five techniques collectively called electron spectroscopy.
X-ray photoelectron spectroscopy (XPS)
Ultraviolet photoelectron spectroscopy (UPS)
Aüger electron spectroscopy (AES)
Electron energy loss spectroscopy (EELS)
Inverse photoemission spectroscopy (IPS)
There are a range of techniques in each of these

<table>
<thead>
<tr>
<th>UPS</th>
<th>Photon source variation</th>
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</thead>
<tbody>
<tr>
<td>He I 21.2 eV</td>
<td>He II 40.8 eV</td>
</tr>
<tr>
<td>Ne I</td>
<td>Synchrotron radiation</td>
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<tr>
<td>.......</td>
<td>.......</td>
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Variations of the same basic technique

- One photon spectroscopy
  - Solids
    - Gases
    - Gas cell
  - Molecular beams

UPS
Photoelectron-photoion coincidence spectroscopy

Zero-kinetic energy photoelectron spectroscopy

Multiphoton photoelectron spectroscopy

Photodetachment spectroscopy
Structure and Properties of Matter

Spectroscopy
Scattering
Physical Properties

Spectroscopy (pre-1965)

Absorption
Magnetic
Mass
Spectroscopy using electrons

\[ e^- + M \rightarrow M^+, M^{2+} \ldots \]

**KE**

**Electron KE**

**Ionization efficiency curves**

**Detector**

\[ I_1, I_2, I_3, I_4 \]
Detector

\[ h\nu \rightarrow I_1 \rightarrow I_2 \rightarrow I_3 \rightarrow I_4 \rightarrow M^+ \]
hv + M → M⁺ + e⁻

hv

(No M²⁺, generally)

Photoelectron Spectroscopy

Photoelectric effect

Early experiments in 1887

hv = KE + φ  1905
Photoion can be excited

\[ M + hv \rightarrow M^+(E_{int}) + e^- \]

\[ \text{elec} \quad \text{vib} \quad \text{rot} \]

\[ hv - I - E_{int} = \text{KE of the electron} \]
Conservation of momentum requires that excess energy is partitioned in inverse proportion to the masses.
Electron and ion separates with equal momenta.

\[ \mu u = MU \]

The relative velocity,

\[ V = u + U \]

\[ = U (1 + \frac{M}{m}) \]

\[ = u (1 + \frac{m}{M}) \]

The kinetic energies,

\[ \frac{1}{2} MU^2 = \frac{1}{2M} \left( \frac{mMV}{m+M} \right)^2 \]

\[ \frac{1}{2} \mu u^2 = \frac{1}{2m} \left( \frac{mMV}{m+M} \right)^2 \]
\[ h\nu - (I_p + E_{int}) \rightarrow KE \]

\[ h\nu - KE \rightarrow I_p + E_{int} \]

\[ E_{int} \rightarrow 0 \]

\[ h\nu - KE_1 \rightarrow IP_1 \]
\[ h\nu - KE_2 \rightarrow IP_2 \]
\[ h\nu - KE_3 \rightarrow IP_3 \ldots .. \]

Vertical 
adiabatic 

- E 

\[ r_e \]
Depth of analysis depends on photon energy.

- **He I**: 21.2 eV, \(2^1P \rightarrow 1^1S\)
- **He II**: 40.8 eV, \(2\ P \rightarrow 1\ S\) of \(\text{He}^+\)
- **Al K\(\alpha_{1,2}\)**: 1486.6 eV, \(2\ P^{3/2,1/2} \rightarrow 1\ S\)
- **Mg K\(\alpha_{1,2}\)**: 1253.6 eV
- **Na K\(\alpha_{1,2}\)**: 1041.0 eV
- **Si K\(\alpha_{1,2}\)**: 1739.5 eV

The diagram illustrates the depth of analysis in terms of photon energy, with different energy levels for core, valence, and soft X-rays.
Photoemission  X-ray fluorescence  Aüger process
$L_2,3^{(Z)}$  
$K(Z)$  
$\text{Neutral atom}$  

$\text{Vac}$  
$\text{Photo emission}$  
$\text{Electronic transition}$  
$\text{Coulomb field redistribution}$  
$\text{Aügur electron emission}$  
$\text{Final state}$
\[ E_{K, L_1, L_2, 3} = E_k - E_{L_1} - E_{L_2, 3} \]

\[ E_{ABC}^{(Z)} = E_A^{(Z)} - \frac{1}{2} \left[ E_B^{(Z)} + E_B^{(Z+1)} \right] - \frac{1}{2} \left[ E_C^{(Z)} + E_C^{(Z+1)} \right] \]

E’s are the binding energies.

\[ E_{ABC} \rightarrow K L_1 L_{2, 3}, K L_1 V, KVV \]

Intense Auger intensities if the valence electron density is high.

Fluorescence efficiency increases with transition energy. Fluorescence and Auger are comparable when \( \Delta E \sim 10,000 \) eV.
VALENCE SHELL
PHOTOELECTRON
SPECTROSCOPY
(A) Counts/sec

(B) Ionization Energy

(M⁺) 

(C) M⁺

M
INTERNUCLEAR DISTANCE
$2 \ P \sigma_g \rightarrow \text{non bonding}$  \hspace{1cm} $2345 \text{ to } 2191 \ cm^{-1}$

$2 \ P \pi_u \rightarrow \text{bonding}$  \hspace{1cm} $2345 \text{ to } 1850 \ cm^{-1}$

$2 \ S \sigma_u \rightarrow \text{weakly antibonding}$  \hspace{1cm} $2345 \text{ to } 2397 \ cm^{-1}$

\[
E_v = E_o + \omega_e (v + \frac{1}{2}) - \omega_e x_e (v + \frac{1}{2})^2
\]

\[
D_e = \omega^2 / 4 \ \omega_e x_e
\]
HeI UPS of $\text{H}_2$ Vibrations and Rotations!

$n$-$\text{H}_2$ 297 K

**Diagram Description:**
- The graph depicts a photoelectron spectrum with peaks labeled from 0 to 25,000 photoelectron counts.
- The x-axis represents kinetic energy in eV, ranging from 3.0 to 6.0.
- The y-axis indicates photoelectron counts, ranging from 0 to 25,000.
- Peaks are labeled with numbers and labeled transitions include $J=0, 1$, and $V=0$.
- Special peaks are marked with 'S'.
XPS-spectra of the 1s core levels of Li, Be, B, C, N, O, F (from S. Hüfner).
The graph shows the binding energy in eV as a function of the counting rate for the molecule CH₃·CH₂·O·CO·Cl. The binding energy peaks at different energies, labeled with letters a, b, and c, and denoted as Cl 1s and Cl 2s peaks.
EB = 291.2 eV

Chemical Shift

Counting Rate
INSTRUMENTATION
Simplest spectrometer
To diffusion pump

μ metal shields

Gas sample

hν (584 Å)

Electron counting system

cps
Layout of the synchrotron radiation laboratory at DORIS.