PHOTOELECTRON SPECTROSCOPY (PES)
INTRODUCTION

Law of Photoelectric effect
Albert Einstein, Nobel Prize 1921

Kaiser-Wilhelm-Institut (now Max-Planck-Institut) für Physik Berlin, Germany

High-resolution electron spectroscopy
Kai Siegbahn, Nobel Prize 1981

Uppsala university, Sweden
BASIC CONCEPT

Where,

\[ E_B = \hbar \omega - \phi - E_{kin} \]

- \( E_B \) = Binding energy referred to the Fermi level
- \( \hbar \omega \) = Photon energy
- \( \phi \) = Work function of spectrometer
- \( E_{kin} \) = Kinetic energy of ejected photoelectron
\[ E_{\text{kin}} = \hbar \omega - E_B - \phi_{\text{sample}} \]

\[ E_{\text{kin}} = \hbar \omega - E_B - \phi_{\text{spec.}} \]

\[ E_B = \hbar \omega - E_{\text{kin}} - \phi_{\text{spec.}} \]
BASIC REQUIREMENT OF PES SYSTEM

1. A monochromatic photon source.

2. An electron energy analyser (which can disperse the emitted electrons according to their kinetic energy, and thereby measure the flux of emitted electrons of a particular energy.

3. A high vacuum environment.
LIGHT SOURCES

**X-rays**

- Al K$_\alpha$ 1486 eV
- Mg K$_\alpha$ 1254 eV

\{ XPS, ESCA \}

**UV**

- He-lamp 21.2 eV
  40.8 eV
- Ne-lamp 16.8 eV
  26.9 eV
- H-lamp 4 \( \leq h\nu \leq 12 \) eV

\{ UPS \}

**Synchrotron radiation**

PES
SYNCHROTRON RADIATION

• Unique feature of Synchrotron radiation
  ▶ Ultra-bright light, high polarization
  ▶ Highly directional, collimated beam
  ▶ Wide spectrum of wavelength, stretching from IR to X-rays
• Spot size ~1x3 mm²
• High energy resolution
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ELECTRON ENERGY ANALYSERS
ELECTRON ENERGY ANALYSER

\[ E_k - E_{\text{ret}} = E_{\text{pass}} \]
Schematic view of a spherical deflector analyser. Source and exit slit widths s and w. Sphere radii $R_1$ and $R_2$ and the optical radius $R_m = (R_1 + R_2)/2$. 

ENERGY RESOLUTION
ENERGY RESOLUTION

\[ V_f = \frac{E_{\text{pass}}}{e} \left( \frac{R_2}{R_1} - \frac{R_1}{R_2} \right) \]

Energy resolution

\[ \frac{\Delta E}{E_{\text{pass}}} = \frac{s}{2R_m} + \frac{w}{2R_m} + \alpha^2 \]

\[ \therefore \] Analyser give a broading

Choose:
\[ s, w \text{ and } E_{\text{pass}} \rightarrow \text{small} \]
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WHY ULTRA HIGH VACUUM (UHV) IS NEEDED?

Consider an ideal gas.
The number of gas atoms/molecules striking a unit area of a surface per second is given by:

\[ I_n = \frac{N}{V} \frac{\langle v \rangle}{4} \]

where \( \langle v \rangle = \sqrt{\frac{8RT}{\pi M}} \)

But \( pV = nRT = \frac{N}{N_a} RT \Rightarrow \frac{N}{V} = \frac{N_a}{R} \frac{P}{T} \)

\[ I_n = \frac{N_a}{4R} \sqrt{\frac{8R}{\pi}} \frac{p}{\sqrt{MT}} = 2.6 \times 10^{24} \frac{p}{\sqrt{MT}} \left[ \frac{1}{m^2 s} \right] (p \text{ in } \frac{N}{m^2}) \approx 3.5 \times 10^{22} \frac{p}{\sqrt{MT}} \left[ \frac{1}{m^2 s} \right] (p \text{ in torr}) \]
AN EXAMPLE

Ex. Assume an atom of radius of ca. 3 Å. Then there is room for ca. $10^{15}$ atom on a cm$^2$.

With $p \approx 10^{-6}$ torr

$M = 28$ kg/kmol

$I_n \approx 3 \times 10^{14}$ $(1/\text{cm}^2\text{s})$

$T = 300$ K

If every atom sticks to the surface a monolayer is formed in about 3 sec!.

At $p \approx 10^{-10}$ torr a monolayer is formed in about $3 \times 10^4$ seconds $\approx 8$ hours.

Big differences (in sticking probability) between different materials.

*(From experience at $10^{-10}$ torr Si, Au etc days, Al, Cu etc. hours, Ti, Mo etc. minutes)*
HOW UHV CAN BE OBTAINED?

- Good choice of material selected ex. stainless steel
- Good design of chamber
- Good pumping systems
- Long time baking
On a larger scale, the sample surface is hit with photon flux focused in a small spot. Electrons emitted by the photon are from ca. 10-100Å of the surface layers depending on electron escape depth in the sample investigated.
Electrons: give a high surface sensitivity
Since $\lambda = \text{mean free path}$ is small in solids

$\lambda = \text{average distance an electron travels before it is inelastically scattered, i.e. Suffers energy losses}$

$\lambda(E_k)$ increases monotonically with $E\text{_{kin}}$ (for $E\text{_{kin}} \geq 50 \text{ eV}$)
The flux of electrons of a given energy and momentum decays exponentially with the distance travelled in a material.

\[ I = I_0 e^{-\frac{x}{\lambda}} \]

Small \( \lambda \) gives high surface sensitivity

Electrons that have not been inelastically scattered have been generated close to the surface.

*The surface sensitivity can be enhanced by selecting a larger electron emission angle, \( \theta \). Normal emission, \( \theta = 0^\circ \).*
A SIMPLE LAYER ATTENUATION MODEL

\[ I_{tot} = I_0 \left( 1 + e^{-\frac{d}{\lambda}} + e^{-\frac{2d}{\lambda}} + e^{-\frac{3d}{\lambda}} + \ldots \right) = \]

\[ I_{tot} = I_0 \frac{1}{1 - e^{-\frac{d}{\lambda}}} \quad \text{Normal emission} \]

\[ I_{tot} = I_0 \frac{1}{1 - e^{-\frac{d}{\lambda \cos \theta}}} \quad \text{Angle dependent} \]

\[ I_{Surf} = I_0 \]

\[ I_{bulk} = I_{tot} e^{-\frac{d}{\lambda \cos \theta}} \]

\[ \frac{I_{Surf}}{I_{bulk}} = e^{\frac{d}{\lambda \cos \theta}} - 1 \]
\[ I_{\text{Clean}} \propto \int_{0}^{\infty} ce^{-\frac{z}{\lambda}}dz = c\lambda \quad \text{i.e. with no overlayer} \]

\[ I_{\text{Overlay}} \propto \int_{0}^{d} ce^{-\frac{z}{\lambda}}dz = c\lambda \left(1 - e^{-\frac{d}{\lambda}}\right) \quad \text{from overlayer} \]

The substrate signal is attenuated by \( e^{-\frac{d}{\lambda}} \) when overlayer on top.

Thus, \( \frac{I_{\text{Overlay}}}{I_{\text{Substrate}}} = e^{\frac{d}{\lambda}} - 1 \) with overlayer of thickness \( d \).
Photoelectron Spectroscopy (PES) + Angle resolved photoelectron spectroscopy (ARPES)

**Examine core-level**  \( hv \approx 100-4000 \text{ eV} \)

- Elementals analysis
- Quantitative analysis
  - Thickness
  - Location

**Examine valence levels**  \( hv \approx 10-50 \text{ eV} \)

- Density of state (DOS)
- Surface band structure
ELEMENTALS ANALYSIS

**Aluminum**
- Binding Energy 2s = 117 eV
- Binding Energy 2p = 73 eV

**Silicon**
- Binding Energy 2s = 149 eV
- Binding Energy 2p = 99 eV

KINETIC ENERGY (eV)

![Graph showing kinetic energy distribution for aluminum and silicon elements.](image)
Chemical shifts

\[ E_B^F \text{ exhibits chemical shifts (∼1-10 eV) depending on chemical surrounding } \Rightarrow \]

*Information about the surrounding elements can be obtained.*

Surface shifts

In solids a specific signal from the atoms in the outermost surface layers can be obtained since they feel a different surrounding (potential) than atoms in the bulk.

*Surface shifts < 1 eV.*
QUANTITATIVE ANALYSIS
PHOTOIONIZATION CROSS SECTIONS

Au binding energies (eV) are:

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<table>
<thead>
<tr>
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<tbody>
<tr>
<td>1s (2) 73365.4</td>
<td>2s (2) 12299.4</td>
<td>2p (6) 11842.9</td>
</tr>
<tr>
<td>3s (2) 2895.49</td>
<td>3p (6) 2676.88</td>
<td>4s (2) 619.785</td>
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<td>3d (10) 2265.63</td>
<td>4p (6) 524.392</td>
<td>5s (2) 91.0841</td>
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<td>4d (10) 347.781</td>
<td>5p (6) 60.3581</td>
<td>4f (14) 109.396</td>
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<tr>
<td>5d (10) 12.5152</td>
<td>6s (1) 6.49775</td>
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CHARACTERIZATION

Graphite like carbon

\[ \theta_e = 75^\circ \]

\[ \theta_e < 75^\circ \]

Intensity (relative units)

\[ C = \frac{I(g)}{I(SiC)}; \quad Si = \frac{I(SiO_2)}{I(SiC)} \]
Layers attenuation model

\[ C = \frac{C^C_{\text{SiC}}}{C^C_{\text{Si}}} \cdot e^{\frac{d_{\text{ox}}}{\lambda_{\text{C}} \cos \theta_e}} \cdot \left( e^{\frac{d_{\text{g}}}{\lambda_{\text{C}} \cos \theta_e}} - 1 \right) \]

\[ Si = \frac{C^Si_{\text{SiO}_2}}{C^Si_{\text{SiC}}} \cdot \left( e^{\frac{d_{\text{ox}}}{\lambda_{\text{Si}} \cos \theta_e}} - 1 \right) \]

\[ C = \frac{I(g)}{I(\text{SiC})}; \quad Si = \frac{I(\text{SiO}_2)}{I(\text{SiC})} \]

\[ \text{Oxide} = \lambda \cdot \ln \left( \left( \frac{I_A \cdot \sigma_B \cdot C_B}{I_B} \cdot \frac{C_C}{\sigma_A \cdot C_A} + 1 \right) \right) \]

\[ \text{Graphite} = \lambda \cdot \ln \left( \left( \frac{I_C \cdot \sigma_B \cdot C_B}{I_B} \cdot \frac{-d_{\lambda}}{\lambda} + 1 \right) \right) \]

Thickness

\[ A:=\text{oxide}, \quad B:=\text{bulk SiC}, \quad C:=\text{graphite} \]
PHOTOELECTRON SPECTROSCOPY

ADVANTAGES

• Good energy resolution (chemical shifts & surface shifts)
• Semiquantitative analysis, within a few %, fairly easy

DISADVANTAGE

• Poor spatial resolution (in most cases).