Reading and Problem Assignments for Physics 243A
Surface Physics of Materials: Spectroscopy, Fall, 2016
(In order of coverage in lecture)

Reading:

  Chapter 1
  Chapter 2: Sections 2.1, pp.22 (bottom)-23(top) on Wood notation for surface structures,
  2.4, and 2.5 (pp. 31-37), 2.9.6 on standing waves
  Chapter 6: 6.9, 6.10, 6.11
  Chapter 3: Sections 3.1, 3.2, 3.3, 3.5

- Zangwill, “Physics at Surfaces”, downloadable Chapters 1-5 (see course website)--
  Chapter 1: Everything except "The roughening transition"
  Chapter 3: pp. 28-34, pp. 49-52 on STM
  Pages 85-86, 192-196, 204-212
  Chapter 2: All
  Chapter 4: Introduction, with lighter reading of The jellium model, One-dimensional band
  theory, and Three-dimensional band theory, and detailed reading of Photoelectron
  spectroscopy, Metals, and Alloys

- Ibach, “Physics of Surfaces and Interfaces”, downloadable book (see course website)---
  Chapter 2: 2.1, 2.2
  Chapter 8: 8.2

- Desjonqueres and Spanjaard, “Concepts of Surface Physics”, excerpts downloadable from
  Course website: On STM current calculation, equilibrium shapes of surfaces, thermodynamics,
  kinetics and adsorption isotherms. No need to follow every step, but this fills in the line of
  arguments in Zangwill and lecture

- Fadley, “Basic Concepts of XPS”, to be handed out, but also downloadable—
  Sections I, II, and III. A-C, with remaining sections by the end of the course

- Attwood, Downloadable excerpt on synchrotron radiation from the book
  “Soft X-Rays and Extreme Ultraviolet Radiation” (see course website)

Problem assignments:
Problem Asst. 1— all of PS 1. Due Thursday, October 13th
Problem Asst. 2— all of PS 2, plus 3.1 and 3.2. Due Thursday, October 27th
Problem Asst. 3— finish PS 3, plus 4.1-4.4,4.6. Due Monday, November 21st
Problem Asst. 4— 4.5, 4.7(a) only, 5.1, 5.2, 5.3, 5.4, 5.7, 5.8, 5.9, 5.10, due Friday, December 2nd
The Soft X-Ray Spectroscopies

Valence PE  e^-

Core PE  e^-

hν  CB  VB

Electron-out: surface sensitive

PE = photoemission = photoelectron spectroscopy
XAS = x-ray absorption spectroscopy
AES = Auger electron spectroscopy
XES = x-ray emission spectroscopy
REXS/RIXS = resonant elastic/inelastic x-ray scattering
Matrix elements in the soft X-ray spectroscopies: Dipole limit

- Photoelectron spectroscopy/photoemission:

\[ I \propto |\hat{e} \cdot \langle \varphi_f(1) | r | \varphi_i(1) \rangle|^2 \]

\( \varphi_i(\text{bound}) \)

\( \varphi_f(\text{free}) \)

Vacuum
PHOTOELECTRON SPECTROSCOPY

Energy analyzer

Sample

Detector

a) RIGHT, LEFT CIRCULAR

b) NO. OF e\textsuperscript{-} STATES = DOS.

BOUND \leftrightarrow FREE

h\nu

CORE (CHEMICAL, MAGNETIC STATE)

VALENCE

E\textsubscript{F} \quad E\textsubscript{Vac}

\phi = WORK FUNCTION

N(E\textsubscript{kin})

INELASTIC

Kinetic energy \(E\textsubscript{kin}\)

h\nu = E\textsubscript{kin} + E\textsubscript{binding} + \phi

Binding energy

E\textsubscript{F}
Typical Photoelectron Spectra: Oxidized Aluminum

Figure 1

"Basic Concepts of XPS"
Figure 1
**Photoelectron Spectroscopy**

**The Photoelectric Effect (Einstein, 1905):**

\[
\text{Photon Energy} = (\text{e}^- \text{ Binding Energy in System Absorbed}) + (\text{Photoelectron Kinetic Energy Emitted})
\]

**Example - CO Molecule:**

- **Photoelectrons:**
  - \(5\sigma\)
  - \(1\pi\)
  - \(4\sigma\)
  - \(3\sigma\)

- **Vacuum Level:**
  - \(15\text{ eV}\)
  - \(17\text{ eV}\)
  - \(21\text{ eV}\)
  - \(41\text{ eV}\)

- **Core:**
  - \(1\text{ s}\)
  - \(2\text{ s}\)
  - \(1\text{ s}\)

- **Valence MO's (Band Structure):**
  - \(5\sigma\)
  - \(1\pi\)
  - \(4\sigma\)
  - \(3\sigma\)

- **Photoe- Spectrum:**
  - \(5\sigma\)
  - \(1\pi\)
  - \(4\sigma\)
  - \(3\sigma\)

- **No. Photo e-**

- **C1s**
  - \(290\text{ eV}\)
  - \(535\text{ eV}\)
X-ray Photoelectron Spectrum of CO

NO. ATOMS → QUANTITATIVE SURFACE ANALYSIS

Intensity

∝ Area

∝ Photoelectric Cross Section × NO. ATOMS → QUANTITATIVE SURFACE ANALYSIS
The LCAO or tight-binding picture for CO:

Chemist’s picture (no core):

\[ x\text{C}_x\text{::O}^x \]
Valence-level Photoelectron spectra of CO adsorbed on various transition metal surfaces.
Theoretical Calculations of charge density for CO bound to Ni(001)- "on-top":

\[ \text{CO } 5\sigma \]
\[ \text{Ni } 3d_{z^2} \sigma \text{ bond} \]

\[ \text{CO } 2\pi = \pi^* \]

\[ \text{Density gain} \]

\[ \text{Ni } 3d_{xy} \pi \text{ "back bond"} \]

Zangwill, p. 307, plus PRL 55, 2618 ('85)


**Vibrational fine structure**

Kimura et al., "Handbook of Hel Photoelectron Spectra"
**Intensities in Photoelectron Spectra:**

- **General:** Final state $K$ (K-subshell + all other design)

  \[
  \text{Int.}_K \left| \hat{e} \cdot \Psi_{N,K} \right|^2 \frac{2\pi}{\hbar} \frac{\epsilon_0}{\epsilon} \left( \Psi^i_{N}(N) \right) \leq 1^2 \quad \text{(Dipole Approx.)}
  \]

- **Born-Oppenheimer:** $e^m$'s Fast, Vibrations Slow

  \[
  \text{Int.} \leq \left| \left< \Psi_{N,K}^i \right| \frac{2\pi}{\hbar} \frac{\epsilon_0}{\epsilon} \left( \Psi^i_{N}(N) \right) \right|^2 \quad \text{Franck-Condon Factor}
  \]
VIBRATIONAL STRUCTURE IN VALENCE-LEVEL (MO) SPECTRA

Diatomic A-B example

(Also applies to core-level emission if equilibrium distance changes on forming core hole)
VIBRATIONAL STRUCTURE IN VALENCE-LEVEL (MO) SPECTRA

H₂ Hydrogen

\[ E_p (K) = \text{Ionization Energy (eV)} \]

\[ I_v (eV) \]

Exptl. a)

I \[ \begin{array}{c}
15.98
\end{array} \]
**INTENSITIES IN PHOTOELECTRON SPECTRA:**

- **GENERAL.** Final state \( K \) (K-subshell + all other design).
  \[
  \text{Int.}_K \propto | \hat{\mathbf{E}} \cdot \langle \Phi^e_{\text{tot}}(N, K) | \sum_{i=1}^{N} \hat{\mathbf{r}}_i \hat{\mathbf{r}}_i^* \rangle |^2 \] (Dipole approx.)

- **BORN-OPPENHEIMER:** \( e^{-}\)'s fast, vibrations slow
  \[
  \text{Int.}_K \propto | \langle \Phi^e_{\text{vib}, \nu} | \mathbf{v}_{\text{vib}, \nu}_i \rangle |^2 \langle \Phi^e_{(N, K)} | \hat{\mathbf{r}}_i \hat{\mathbf{r}}_i^* \rangle |^2
  \]
  Franck-Condon factor

- **SUDDEN APPROXIMATION:** \( \Phi^e_K \rightarrow \Phi^f = \text{photo}^{-} \) (fast)
  \[
  \Phi^i \rightarrow \Phi^i',
  \Phi_{K-1} \rightarrow \Phi_{K-1}^{'},
  \Phi_{K+1} \rightarrow \Phi_{K+1}^{'},
  \Phi_N \rightarrow \Phi_N^{'},
  \]
  (Slow)

- **K-HOLE**

- **SLATER DETS.** For \( \Phi^e_K = \det \left( \Phi \right)
  \[
  \Phi^e_K = \det \left( \Phi \right)
  \]

- **SAME SUBSHELL COUPLING + TOTAL L,S:**
  \[
  \text{Int.}_K \propto | \langle \Phi^e_{\text{vib}, \nu} | \mathbf{v}_{\text{vib}, \nu}_i \rangle |^2 \langle \Phi^e_{(N-1, K)} | \hat{\mathbf{r}}_i \hat{\mathbf{r}}_i^* \rangle |^2
  \]
  \[
  \leq \text{normal} \frac{\Delta K}{\Delta \Omega}
  \]

- **SPIN-ORBIT +**
  \[
  \left| \hat{\mathbf{E}} \cdot \langle \Phi^e_{\text{tot}} | \sum_{i=1}^{N} \hat{\mathbf{r}}_i \hat{\mathbf{r}}_i^* \rangle \right|^2
  \]
  \[1 \text{e}^{-} \rightarrow \text{DIPOLE} \rightarrow \frac{d\sigma}{d\Omega}
  \]

- **SHAKE-UP/SHAKE-OFF**
  \[
  \text{Int.}_K \propto | \langle \Phi^e_{\text{vib}, \nu} | \mathbf{v}_{\text{vib}, \nu}_i \rangle |^2 \langle \Phi^e_{(N-1, K)} | \hat{\mathbf{r}}_i \hat{\mathbf{r}}_i^* \rangle |^2
  \]

- **MONOPOLE**
  \[
  \text{Int.}_K \propto | \langle \Phi^e_{\text{vib}, \nu} | \mathbf{v}_{\text{vib}, \nu}_i \rangle |^2 \langle \Phi^e_{(N-1, K)} | \hat{\mathbf{r}}_i \hat{\mathbf{r}}_i^* \rangle |^2
  \]

- **PLUS DIFFRACTION EFFECTS IN \( \Phi^e_K \) ESCAPE**

"Basic Concepts of XPS"
Chapter 3.D.
Magnetic Circular Dichroism in X-Ray Absorption (XMCD): Only happens because of the spin-orbit effect

**Spin-orbit splitting of levels:**

\[ \Rightarrow \text{Effective } \vec{B} (\text{nucleus around } e^-) \propto \vec{L} \]

\[ \vec{L}_{S=0} = \xi(r) \vec{L} \]

- Splits all \( n \ell \) levels
  \[ \frac{2(2\ell+1)}{2\ell+2} \]
  \[ n\ell_j = \ell + \frac{1}{2} \rightarrow 2\ell+2 \]
  \[ n\ell_j = \ell - \frac{1}{2} \rightarrow 2\ell \]

- Mixes spin and orbital angular momentum:

\[ \psi_{n\ell j m_j} = c_1 \psi_{n\ell,j-m_j-\frac{1}{2}} (\frac{1}{0}) + c_2 \psi_{n\ell,j+m_j+\frac{1}{2}} (0 \frac{1}{0}) \]

\[ m_s = \pm \frac{1}{2} \]

- **WITH C1 AND C2 TABULATED CLEBSCH-GORDAN OR WIGNER 3j SYMBOLS**
Example: **Photoelectron spin polarization from spin-orbit coupling and circularly-polarized radiation**—The Fano Effect

Photoelectrons $E_{\text{kin}}$'s
(Neglect $E_{\text{kin,d}}$)

Degenerate

Spin externally referenced to $\vec{k}_h v$ and $\vec{M}$ of sample
Photoelectron spin polarization from spin-orbit coupling and circularly-polarized radiation—The Fano Effect

\[ P = \frac{l_{\text{up}} - l_{\text{down}}}{l_{\text{up}} + l_{\text{down}}} = \frac{1^2 - \sqrt{1/3}^2}{1^2 + \sqrt{1/3}^2} \times 100 \]

\[ P = \frac{2/3}{4/3} \times 100 = +50\% \]

\( m_e = 0 \)
\( m_j = m_s = -1/2 \)

Degenerate np\(_{3/2}\)

\( m_j = m_s = -3/2 \)

Spin externally referenced to \( k_{hv} \) and \( \tilde{M} \) of sample
Measuring Electron Binding Energies

Figure 3 -- Energy level diagram for a metallic specimen in electrical equilibrium with an electron spectrometer. The closely spaced levels near the Fermi level $E_F$ represent the filled portions of the valence bands in specimen and spectrometer. The deeper levels are core levels. An analogous diagram also applies to semiconducting or insulating specimens, with the only difference being that $E_F$ lies somewhere between the filled valence bands and the empty conduction bands above.
Figure 4 -- Full XPS spectral scan for a polycrystalline Au specimen, showing both the cutoff of the secondary electron peak at zero kinetic energy and the high-energy cutoff for emission from levels at the metal Fermi level. The measurable distance $\Delta E$ thus equals $h\nu - \phi_s$, provided that suitable specimen biasing has been utilized. For this case, $h\nu$ was 1253.6 eV and $\phi_s$ was 5.1 eV. (From Baer, reference 56).
<table>
<thead>
<tr>
<th>1</th>
<th>H</th>
<th>Low</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>Li</td>
<td>Be</td>
</tr>
<tr>
<td>2.4</td>
<td>Be</td>
<td>1.5</td>
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<tr>
<td>11</td>
<td>Na</td>
<td>Mg</td>
</tr>
<tr>
<td>12</td>
<td>Mg</td>
<td>3.6</td>
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<tr>
<td>19</td>
<td>K</td>
<td>Ca</td>
</tr>
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<td>Ca</td>
<td>2.8</td>
</tr>
<tr>
<td>37</td>
<td>Rb</td>
<td>Sr</td>
</tr>
<tr>
<td>2.2</td>
<td>Sr</td>
<td>2.35</td>
</tr>
<tr>
<td>55</td>
<td>Cs</td>
<td>Ba</td>
</tr>
<tr>
<td>1.8</td>
<td>Ba</td>
<td>2.5</td>
</tr>
<tr>
<td>87</td>
<td>Fr</td>
<td>Ra</td>
</tr>
</tbody>
</table>

**Work functions of the Elements [eV]**


- **Low**
- **High**
# Electron Work Functions of the Elements


<table>
<thead>
<tr>
<th>Element</th>
<th>Surface crystallographic orientation</th>
<th>Work function (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>polycrystalline</td>
<td>4.26</td>
</tr>
<tr>
<td></td>
<td>(100) 4.64</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(110) 4.52</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(111) 4.74</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>polycrystalline</td>
<td>4.28</td>
</tr>
<tr>
<td></td>
<td>(100) 4.41</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(110) 4.06</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(111) 4.24</td>
<td></td>
</tr>
<tr>
<td>As</td>
<td>polycrystalline</td>
<td>3.75</td>
</tr>
<tr>
<td>Au</td>
<td>polycrystalline</td>
<td>5.1</td>
</tr>
<tr>
<td></td>
<td>(100) 5.47</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(110) 5.37</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(111) 5.31</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>polycrystalline</td>
<td>4.45</td>
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<tr>
<td>Ba</td>
<td></td>
<td>2.7</td>
</tr>
<tr>
<td>Be</td>
<td></td>
<td>4.98</td>
</tr>
<tr>
<td>Bi</td>
<td></td>
<td>4.22</td>
</tr>
<tr>
<td>C</td>
<td></td>
<td>5.0</td>
</tr>
</tbody>
</table>

Depends on surface orientation
Measuring Electron Binding Energies: Charging Effects For Insulators

Figure 3 -- Energy level diagram for a metallic specimen in electrical equilibrium with an electron spectrometer. The closely spaced levels near the Fermi level $E_F$ represent the filled portions of the valence bands in specimen and spectrometer. The deeper levels are core levels. An analogous diagram also applies to semiconducting or insulating specimens, with the only difference being that $E_F$ lies somewhere between the filled valence bands and the empty conduction bands above.

"Basic Concepts of XPS" Figure 3
BEST CURRENT SOLUTION TO AN OLD PROBLEM: CHARGING IN INSULATORS

(a) 100 μm x 800 μm Scanned Line

New Neutralizer

FWHM (eV)
CH 0.99
C-O 0.98
O=C-O 0.76

O=C-O, C-O

Binding Energy (eV)

298 288 278

(b) 20μm static point

New Neutralizer

FWHM (eV)
O=C-O 0.88

Binding Energy (eV)

298 288 278

c) 20μm static point

Conventional Flood Gun + Ion Source

Binding Energy (eV)

298 288 278

d) 20 μm Static Point

Conventional Flood Gun

Binding Energy (eV)

298 288 278

E− only, shifted completely to higher BE!

One-Electron Picture of Photoemission from a Surface

\[ \psi \propto e^{ikz} \]

\[ \lambda_e = \frac{h}{p} = \frac{2\pi}{k} \]

\[ \lambda_e \quad \text{E} \quad (\AA) \quad (\text{eV}) \]

\[ 3.9 \quad 10 \]

\[ 1.2 \quad 100 \]

\[ 0.4 \quad 3000 \]

Potential energy

Vacuum level

Image potential in vacuum

Potential step

Muffin-fil constant in adlayer

Potential step

Spherical atoms

Muffin-tin zero

Adatom ion core

Adlayer

Substrate
One-Electron Picture of Photoemission from a Surface

\[ \phi^f(\vec{r}) \approx \exp(i\vec{k}^f \cdot \vec{r}) \quad \phi^i(\vec{r}) = \exp(i\vec{k}^i \cdot \vec{r}) \]

\[ h\nu - \phi_s = E_{\text{kin}} \text{ (before entry into analyzer)} \]

(1) \[ E_{\text{kin},i} = h\nu - E^F_b(k) + V_0 - \phi_s \approx \frac{\hbar^2 (k^f)^2}{2m} \]

(2) \[ E_{\text{kin}} = E_{\text{kin},i} - V_0 = \frac{\hbar^2 (K^f)^2}{2m} \]

(3) \[ \vec{k} + \vec{k}_{\text{photon}} + \vec{g} = \vec{k}^f \]
Basic energetics

\[ h\nu = E_{\text{Vacuum binding}} + E_{\text{kinetic}} = E_{\text{Fermi binding}} + \phi_{\text{spectrometer}} + E_{\text{kinetic}} \]
CALCULATION OF $V_0$ FOR AN IDEAL METAL

Fig. 4.2. Electron density profile at a jellium surface for two choices of the background density, $r_s$ (Lang & Kohn, 1970).

![Electron density profile diagram]

Fig. 4.3. Electrostatic potential, $v(z)$, and total effective one-electron potential, $v_{\text{eff}}(z)$, near a jellium surface (Lang & Kohn, 1970).

![Electrostatic potential diagram]

$Q = CV_{\text{retard}}$

WITH IMAGE POTENTIAL

ZANGWILL, "SURFACE PHYSICS"
Electron Spectroscopy—A typical configuration

Energy resolution:

\[ \frac{\delta E}{E_0} \approx \frac{\delta R_{\text{ent}}}{2R_0} + \frac{\delta R_{\text{det}}}{2R_0} + C_r \alpha_r^2 + \text{higher order terms} \]

\[ C_r \approx 1.0 \]

Not focussed in \( \alpha_r \)

Focussed in \( \alpha_r \)
With proper lens imaging in vertical angle—
an energy vs angle image at detector

\[ \alpha_z = \text{vertical angle} \]

Distance along lens (mm)

\[ E, \tilde{k} \text{ band mapping} \]
The Nobel Prize in Physics 2010
Andre Geim, Konstantin Novoselov
"for groundbreaking experiments regarding the two-dimensional material graphene"

MULTICHANNEL DETECTION GEOMETRIES

Multiple channeltrons: brute force

$10^6 - 10^8$ $e^-$

Up to $\sim$ 1-5 MHz per channel

Crossed-wires—2D

Up to $\sim$ 1 MHz

Microchannel plates (MCPs) and

Channel

$x = \frac{(A+B)-(C+D)}{A+B+C+D}$

Resistive Anode—2D:

Up to $\sim$ 1 MHz

$y = \frac{(B+D)-(A+C)}{A+B+C+D}$

Individual Collectors—1D (Elettra and the ALS):

Up to $\sim$ 1 GHz

To IC channel
MULTICHANNEL DETECTION GEOMETRIES

Multiple channeltrons: brute force

$10^6$-$10^8$ e$^-$ Up to $\sim$ 1-5 MHz per channel

Crossed-wires—2D
Up to $\sim$ 1MHz

Microchannel plates (MCPs) and

To IC channel

$x = \frac{(A+B)-(C+D)}{A+B+C+D}$

$y = \frac{(B+D)-(A+C)}{A+B+C+D}$

Phosphor + Video Camera

Individual Collectors—1D
(Elettra and the ALS): Up to $\sim$ 1GHz
The Microchannel Plate Electron (and Photon) Multiplier

Diam. Down to 5 microns

Pb-DOPED GLASS

INPUT ELECTRON

INPUT SIDE ELECTRODE

CHANNEL WALL

OUTPUT ELECTRODE

OUTPUT ELECTRONS

$\sim 10^6 - 10^8$

E.g.- 10 collisions with 4-5 $e^-$ each
The MicroMott Electron Spin Detector


Soft X-Ray Emission Spectroscopy—A typical configuration

Grating no. | Radius | Groove density. | Incid. angle | Operating range
---|---|---|---|---
#1 | 5 m | 1200 l/mm | 1.9 | 300-1500 eV
#2 | 5 m | 400 l/mm | 2.6 | 100-450 eV
#3 | 3 m | 300 l/mm | 5.4 | 20-200 eV

Difference of path lengths =
\[
d[\sin(\theta_{inc} = +no.) + \sin(\theta_{refl} = -no.)] = m\lambda_x
\]

\[
\sin \theta_{inc} + \sin \theta_{refl} = \frac{m\lambda_x}{d}
\]
The (Focusing) Rowland Circle
X-Ray Monochromator/Spectrometer Geometry

$R_g = \text{the grating (crystal) radius}$

$R_f = \frac{R_g}{2} = \text{Rowland circle radius}$

Source

Curved grating (soft x-rays) or single crystal (hard x-rays)

Detector

$m = -1$

$m = 0$

$m < 0$

$m > 0$

Specular
One commercial soft x-ray spectrometer—Scienta XES 300
Hard X-ray Photoemission at the Advanced Light Source: The Multi-Technique Spectrometer/Diffractometer (MTSD)

Scienta soft x-ray spectrometer: XES 300

Sample prep. chamber: LEED, Knudsen cells, electromagnet,...

5-axis sample manipulator

Chamber rotation

Scienta electron spectrometer (hidden)

ALS
BL 9.3.1
hν = 2-5 keV

Permits using all relevant spectroscopies on a single sample: XPS (incl. Al and Mg Kα), HXPS, XPD; XAS (e⁻ or photon detection), soft XES/RIXS
Hard X-ray Photoemission at the Advanced Light Source: The Multi-Technique Spectrometer/Diffractometer (MTSD)

Sample prep. chamber: LEED, Knudsen cells, QCM, electromagnet, ...

Loadlock for sample introduction

5-axis automated sample manipulator

Soft x-ray spectrometer: Scienta XES 300

Diff. seal

Chamber rotation

XPS: Al/Mg Kα

Electron spectrometer: Scienta SES 2002
Basic energetics

\[ h\nu = E_{\text{Vacuum}}^{\text{binding}} + E_{\text{kinetic}} = E_{\text{Fermi}}^{\text{binding}} + \phi_{\text{spectrometer}} + E_{\text{kinetic}} \]
Complete Reading and Problem Assignments for Physics 243A
Surface Physics of Materials: Spectroscopy, Fall, 2016

READING:
- WOODRUFF AND DELCHAR, "MODERN TECHNIQUES OF SURFACE SCIENCE", 2ND EDITION--
  Chapter 1
  Chapter 2: Sections 2.1, pp.22 (bottom)-23(top) on Wood notation for surface structures,
  2.4, and 2.5 (pp. 31-37), 2.9.6 on standing waves
  Chapter 6: 6.9, 6.10, 6.11
  Chapter 3: Sections 3.1, 3.2, 3.3, 3.5
- ZANGWILL, "PHYSICS AT SURFACES", DOWNLOADABLE CHAPTERS 1-5 (SEE COURSE WEBSITE)--
  Chapter 1: Everything except "The roughening transition"
  Chapter 3: pp. 28-34, pp. 49-52 on STM, Pages 85-8, 192-196, 204-212
  Chapter 2: All
  Chapter 4: Introduction, with lighter reading of The jellium model, One-dimensional band
  theory, and Three-dimensional band theory, and detailed reading of Photoelectron
  spectroscopy, Metals, and Alloys.
- IBACH, "PHYSICS OF SURFACES AND INTERFACES", DOWNLOADABLE BOOK (SEE COURSE WEBSITE)—
  Chapter 2: 2.1, 2.2
  Chapter 8: 8.2
- DESJONQUERES AND SPANJAARD, "CONCEPTS OF SURFACE PHYSICS", EXCERPTS DOWNLOADABLE FROM
  COURSE WEBSITE:
  On equilibrium shapes of surfaces, thermodynamics, kinetics and adsorption isotherms,STM current calculation, photoelectron diffraction
  and Dollye-Waller factors. No need to follow every step, but as needed to fill in the line of arguments in lecture and Zangwill
- FADLEY, "BASIC CONCEPTS OF XPS", HANDED OUT, BUT ALSO DOWNLOADABLE—
  Read all of it
- FADLEY, “THE STUDY OF SURFACE STRUCTURES BY PHOTOELECTRON DIFFRACTION AND AUGER ELECTRON DIFFRACTION”,
  PAGES 421-450 only, DOWNLOADABLE FROM COURSE WEBSITE
  with other examples and exercises using the EDAC web program introduced in lecture
- ATTWOOD, DOWNLOADABLE EXCERPT ON SYNCHROTRON RADIATION FROM THE BOOK
  “Soft X-Rays and Extreme Ultraviolet Radiation” (see course website)
- SIX READING DOWNLOADS FROM THE COURSE WEBSITE: If needed for comprehension at level of lectures or to use programs
  1) Molecular orbital basics
  2) Tight-binding basics
  3) Core-Hole Multiplets with Charge Transfer--Basic Theory, or similar pages from Book by de Groot and Kotani
  4) Brief Manual for SESSA spectral simulation program
  5) Brief Manual for CTM4XAS20 charge-transfer multiplet simulation program
  [ 7) Optional only for physics students: Basic theory for the Hubbard Model of bonding ]

PROBLEM ASSIGNMENT 4-FINAL: Not all problems assigned
Problem Asst. 4—4.5, 4.7(a) only, 5.1, 5.2, 5.3, 5.4, 5.7, 5.8, 5.9, 5.10, due Friday, December 2nd

REMAINING LECTURE SCHEDULE:
22 November, Happy Thanksgiving!, 29 November and 1 December

FINAL EXAMINATION: TUESDAY, DECEMBER 6TH, 10:30-12:30 PM, PHYSICS 185
Open book: You may use lecture notes, copies of lecture slides, textbooks, and laptops, with signed
affirmation as follows:
I will not make use of any hardcopy or online material from prior versions of this course
that is not posted at the current course website.
Copying from such material will be considered as cheating.
CALCULATION OF PHOTOELECTRON INTENSITIES—THE 3-STEP MODEL

3-STEP MODEL

1. EXCITATION:
   DIFF. CROSS SECTION

2. TRANSPORT TO SURF.:  
   INELASTIC ATTENUATION

3. ESCAPE FROM SURF.:  
   ELASTIC SCATTERING:
   DIFFRACTION, G, K, ...

E profound spectrometer geometry for calculating angular-dependent
 Photoelectron peak intensities, with various important parameters and
 variables indicated.
CALCULATING INTENSITIES IN PHOTOELECTRON SPECTRA

**Diagram:**
- Broad hv source
- Active vol. $\propto \frac{A_0}{\sin \theta}$
- $\Omega_0 = \text{solid angle}$
- $\Delta \Phi (\text{photoe}) \sin \theta$
- Very deep penetration (except for $\theta$; very small!)

**Equations:**
- Intensity $\propto \left[ \text{incident exciting flux} \right] \cdot \left[ \text{density of atoms excited} \right] \cdot \left[ \text{active volume} \right]$
  - Flux: No. atoms/cm$^2$-sec
  - Density: No. atoms/ cm$^3$
  - Volume: cm$^3$

- "Cross section" per atom for excitation into analyzer (cm$^2$)
- Probability for no-loss escape
- Probability for detection in analyzer

- $\sigma = e^{-Z / \Delta \Phi \sin \theta}$
- $\varepsilon \Delta \Phi_0$
$I(Qn\ell j) = C \int_{0}^{\infty} I_{hv}(x,y,z,\hat{\varepsilon}) \rho_{Q}(x,y,z) \frac{d\sigma_{Qn\ell j}(hv,\hat{\varepsilon})}{d\Omega} \exp \left[ -\frac{z}{\Lambda_{e}(E_{\text{kin}}) \sin \theta} \right] \Omega(E_{\text{kin}}, x, y) dx dy dz$

$I_{hv}(x,y,z,\hat{\varepsilon}) = x$-ray flux, $\hat{\varepsilon} = $ polarization

$\rho_{Q}(x,y,z) = $ density of atoms $Q \rightarrow $ quantitative analysis

$\frac{d\sigma_{Qn\ell j}(hv,\hat{\varepsilon})}{d\Omega} = $ energy-dependent differential photoelectric cross section for subshell $Qn\ell j$

$\Lambda_{e}(E_{\text{kin}}) = $ energy-dependent inelastic attenuation length + elastic scattering: $f(\theta_{\text{scat}})$

$\rightarrow $ Effective Attenuation Length (EAD) $\rightarrow$ Mean Emission Depth (MED)

$\Omega(E_{\text{kin}}, x, y) = $ energy-dependent spectrometer acceptance solid angle

$\iint \Omega(E_{\text{kin}}, x, y) dx dy = T(E_{\text{kin}}) = $ transmission function

$V_{0} = $ inner potential

E.g.-Eqns. (113) and (114) of Basic Concepts of XPS
For a given subshell:

\[
I(E_{\text{kin}}, Qn_{\ell} j) =
\]

\[
C' \int_0^\infty I_{hv}(x,y,z,\hat{\epsilon}) \rho_{Qn_{\ell}}(E_b,x,y,z) \frac{d\sigma_{Qn_{\ell}}(hv,\hat{\epsilon})}{d\Omega} \exp \left[ -\frac{z}{\Lambda_e(E_{\text{kin}}) \sin \theta} \right] \Omega(E_{\text{kin}}, x, y ) dxdydz
\]

\[
I_{hv}(x,y,z) = \text{x-ray flux, } \hat{\epsilon} = \text{x-ray polarization}
\]

\[
\rho_{Qn_{\ell}}(E_b,x,y,z) = \text{density of states, projected onto } Qn_{\ell} \text{ character}
\]

\[
\frac{d\sigma_{Qn_{\ell} j}(hv,\hat{\epsilon})}{d\Omega} = \text{energy-dependent differential photoelectric cross section for subshell } Qn_{\ell} j
\]

\[
\Lambda_e(E_{\text{kin}}) = \text{energy-dependent inelastic attenuation length}
\]

\[
\rightarrow \text{Mean Emission Depth}
\]

\[
\Omega(E_{\text{kin}}, x, y ) = \text{energy-dependent spectrometer acceptance solid angle}
\]

For the total VB intensity:

\[
I_{\text{total}}(E_{\text{kin}}) = \sum_{Qn_{\ell}} I(E_{\text{kin}}, Qn_{\ell} j)
\]

E.g.-Pages 56-57 of Basic Concepts of XPS
Copper densities of states—total and projected onto orbital type

- ~Bonding
- ~Anti-Bonding

- More localized 3d-like
- Delocalized free electron-like
SrTiO$_3$ and La$_{0.67}$Sr$_{0.33}$MnO$_3$ band structures and DOS

**SrTiO$_3$-band insulator**

Expt'l. bandgap 3.3 eV

Expt'l. band offset 3.0 eV

Plucinski, TBP with expt'l. band offset

**La$_{0.67}$Sr$_{0.33}$MnO$_3$- Half-Metallic Ferromagnet**

Projected DOSs

Spin-up

Spin-down

No spin down!

**SrTiO$_3$ -band insulator**

Mn $e_g$

Mn $t_{2g}$

$d_{xz} + d_{yz}$

$d_{xy}$

$d_{z^2}$

$d_{x^2-y^2}$

O 2p

---

Plucinski, TBP

Chikamatsu et al., PRB 73, 195105 (2006);
Plucinski, TBP
PHOTOELECTRON INTENSITIES FOR SOME USEFUL CASES

(a) Semi-infinite specimen, atomically clean surface, peak $k$ with $E_{\text{kin}} \equiv E_k$:

$$N_k(\theta) = I_0 \Omega_0(E_k) A_0(E_k) D_0(E_k) \rho \frac{d\sigma_k}{d\Omega} \Lambda_e(E_k)$$ (115)

This case corresponds to an optimal measurement on a homogeneous specimen for which no surface contaminant layer is present.

Yeh & Lindau cross section table

http://ulisse.elettra.trieste.it/services/elements/Webelements.html

+ SESSA Program (more later)

http://www.quases.com/products/quases-imfp-tpp2m/

NIST Database and TPP-2M Formula (Powell et al.) E.g.-
http://www.ss.teen.setsunan.ac.jp/e-imfp2.html
(b) Specimen of thickness $t$, atomically clean surface, peak $k$ with $E_{\text{kin}} = E_k$:

$$N_k(\theta) = I_0 \Omega_0(E_k) A_0(E_k) D_0(E_k) \rho \, d\sigma_k / d\Omega \, \Lambda_e(E_k)$$

$$\times [1 - \exp \left( -t / \Lambda_e(E_k) \sin \theta \right)]$$

(116)

Here, the intensity of a peak originating in a specimen of finite thickness is predicted to increase with decreasing $\theta$. 

Diagram:
- $I_0$ and $E_k$
- Incident angle $\theta$
- $k^{th}$ subshell, $\rho$, $\Lambda_e$
- Specimen thickness $t$
(c) Semi-infinite substrate with uniform overlayer of thickness $t$.

Peak $k$ from substrate with $E_{\text{kin}} = E_k$:

$$N_k(\theta) = I_0 \Omega_0(E_k) A_0(E_k) D_0(E_k) \rho \frac{d\sigma_k}{d\Omega} \Lambda_e(E_k)$$

$$\times \exp \left( -\frac{t}{\Lambda_e'(E_k) \sin \theta} \right) \tag{117}$$

Peak $l$ from overlayer with $E_{\text{kin}} = E_l$:

$$N_l(\theta) = I_0 \Omega_0(E_l) A_0(E_l) D_0(E_l) \rho' \frac{d\sigma_l}{d\Omega} \Lambda_e'(E_l)$$

$$\times \left[ 1 - \exp \left( -\frac{t}{\Lambda_e'(E_l) \sin \theta} \right) \right] \tag{118}$$

where

$\Lambda_e(E_k)$ = an attenuation length in the substrate

$\Lambda_e'(E_k)$ = an attenuation length in the overlayer

$\rho$ = an atomic density in the substrate

$\rho'$ = an atomic density in the overlayer.
(d) Semi-infinite substrate with a non-attenuating overlayer at fractional monolayer coverage—Peak \( k \) from substrate: Eq. (115).

Peak \( l \) from overlayer:

\[
N_l(\theta) = I_0 \Omega_0(E_l) A_0(E_l) D_0(E_l) s'(d\sigma_l/d\Omega)(\sin \theta)^{-1} \tag{120a}
\]

Overlap/substrate ratio:

\[
\frac{N_l(\theta)}{N_k(\theta)} = \frac{\Omega_0(E_l) A_0(E_l) D_0(E_l) s'(d\sigma_l/d\Omega)}{\Omega_0(E_k) A_0(E_k) D_0(E_k) s d\sigma_k/d\Omega (\Lambda_e(E_k) \sin \theta/d)}
= \left[ \frac{s'}{s} \right] \cdot \frac{D_0(E_l) \Omega_0(E_l) A_0(E_l) (d\sigma_l/d\Omega)d}{D_0(E_k) \Omega_0(E_k) A_0(E_k) d\sigma_k/d\Omega \Lambda_e \sin \theta} \tag{120b}
\]

with:

\( s' \) = the mean surface density of atoms in which peak \( l \) originates in \( \text{cm}^{-2} \)

\( s \) = the mean surface density of substrate atoms in \( \text{cm}^{-2} \)

\( s'/s \) = the fractional monolayer coverage of the atomic species in which peak \( l \) originates

\( d \) = the mean separation between layers of density \( s \) in the substrate (calculable from \( s/\rho \)).
Surface sensitivity enhancement for grazing exit angles

Fig. 5. Illustration of the basic mechanism producing surface sensitivity enhancement for low electron exit angles $\theta$. The average depth for no-loss emission as measured perpendicular to the surface is $\Lambda_0 \sin \theta$.

E.g., $\Lambda_0 = 28\,\AA$ in Au(s) at 1400 eV

<table>
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<th>$\theta$</th>
<th>Mean Depth</th>
<th>No. Layers</th>
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<tr>
<td>&quot;BULK&quot; $\rightarrow$ 90°</td>
<td>28,\AA</td>
<td>~9</td>
</tr>
<tr>
<td>&quot;SURFACE&quot; $\rightarrow$ 10°</td>
<td>~4.4,\AA</td>
<td>~1.5</td>
</tr>
</tbody>
</table>

... but refraction at surface and elastic scattering can reduce surface enhancement, esp. at low $\theta \lesssim 30°$
Surface sensitivity enhancement for grazing exit angles

Fig. 7. Si2p spectra at three electron exit angles for a Si specimen with a 15Å thick oxide overlayer. Note the complete reversal of the relative intensities of oxide and element between high and low θ. (From Hill et al., ref. (19).)
Surface sensitivity enhancement for grazing exit angles

Figure 44 — Broad-scan core spectra at low and high exit angles for a Si specimen with a thin oxide overlayer (~ 6 Å) and an outermost carbon contaminant overlayer approximately 1-2 monolayers in thickness. The C1s and O1s signals are markedly enhanced in relative intensity at low θ due to the general effect presented in Figure 43. (From Bailey, reference 17.)
CALCULATION OF PHOTOELECTRON INTENSITIES—THE 3-STEP MODEL

1. Excitation: \( \frac{d\sigma}{d\Omega} \)
2. Diff. Cross Section
3. Transport to Surf.: Inelastic Attenuation
4. Elastic Scattering: \( \Delta \theta' \), Diffraction
5. Escape from Surf.: \( \phi \) Elastic Scattering, Diffraction, Exit
6. \( V_0 \) Refraction: \( \Theta' \rightarrow \Theta \)

Fig. 1: Idealized spectrometer geometry for calculating angular-dependent photoelectron peak intensities, with various important parameters and variables indicated.
FOR ATOMIC-LIKE EMISSION:

LIN.
Polarized: \( \frac{d\sigma_{nl}(E_f)}{d\alpha} = \frac{\sigma_{nl}(E_f)}{4\pi} \left[ 1 + \beta_{nl}(E_f) \left( \frac{3}{2} \cos^2 \theta - \frac{1}{2} \right) \right] \)

Unpolarized: \( \frac{d\sigma_{nl}(E_f)}{d\alpha} = \frac{\sigma_{nl}(E_f)}{4\pi} \left[ 1 + \frac{3}{2} \beta_{nl}(E_f) \left( \frac{3}{2} \sin^2 \alpha - 1 \right) \right] \)

Figure 7 -- General geometry for defining the differential cross section \( d\sigma/d\alpha \), showing both polarized and unpolarized incident radiation. The polarization vector \( \vec{e} \) is parallel to the electric field \( \vec{E} \) of the radiation. In order for the dipole approximation to be valid, the radiation wave length \( \lambda \) should be much larger than typical target dimensions (that is, the opposite of what is shown here).

WITH:

\( \sigma_{nl} \) = TOTAL CROSS SECTION

\( \beta_{nl} \) = ASYMMETRY PARAMETER

\( \sigma_{nl}, \beta_{nl} \) TABULATIONS IN: GOLDBEAG ET AL., J. ELECT. SPECT.

TOTAL SUBSHELL CROSS SECTION:  \[ \int \frac{d\sigma_{nl}}{d\Omega} = \int \frac{4\pi\alpha_0^2}{3} (hv)[lR_{l-1}^2(E') + (l+1)R_{l+1}^2(E')] \]

= SUM OVER ALL \( m_L, m_s \) IN SUBSHELL \( nl \)

RADIAL MATRIX ELEMENTS TO \( \pm1 \) CHANNELS:

\[ R_{l\pm 1}(E') = \int R_{nl}(r)R_{E'}r\, dr = \int P_{nl}(r)P_{E'}r\, dr \]

DIFFERENTIAL CROSS SECTION: UNPOLARIZED

\[ \frac{d\sigma_{nl}}{d\Omega} (E') = \frac{\sigma_{nl}}{4\pi} [1 - \frac{1}{2}\beta_{nl}(E')P_2(\cos \alpha)] \]

= \[ \frac{\sigma_{nl}}{4\pi} [1 - \frac{1}{2}\beta_{nl}(E')(\frac{3}{2} \sin^2 \alpha - 1)] \]

= A + B \sin^2 \alpha

ASYMMETRY PARAMETER:

\[ \beta_{nl}(E') = \frac{-6l(l+1)R_{l+1}(E')R_{l-1}(E') \cos \left[ \delta_{l+1}(E') - \delta_{l-1}(E') \right]}{(2l+1)[lR_{l-1}^2(E') + (l+1)R_{l+1}^2(E')]} \]

\( \delta_{2\pm 1}(E') = \text{CONTINUUM ORBITAL PHASE SHIFTS IN ATOMIC POTENTIAL } V(r) \)
Range of shapes of $\frac{d\sigma}{d\Omega}$
Intraatomic electron screening in many-electron atoms—a self-consistent Q.M. calculation

Plus radial one-electron functions:

\[ P_{n\ell}(r) = rR_{n\ell}(r) \]
The one-electron wave functions $P_{n\ell}(r)$ and $P_{E',\ell\pm1}(r)$ for 2p emission from Carbon

RADIAL MATRIX ELEMENTS TO $\ell \pm 1 = s$ and $d$ CHANNELS:

$$R_{s(d)}(E^f) = \int_{0}^{\infty} R_{2p}(r) R_{E',s(d)}(r) r^2 dr$$

$$= \int_{0}^{\infty} P_{2p}(r) P_{E',s(d)}(r) dr$$

“Basic Concepts of XPS” Figure 9
GRAPH 1. Atomic Subshell Photoionization Cross Sections for 0−1500 eV, 1 ≤ Z ≤ 103
See page 6 for Explanation of Graphs

C 1s edge

C binding energies (eV) are:
1s(2) 2.90860
2s(2) 17.5409
2p(2) 8.98202

Plus other Examples from Yeh and Lindau in Sec. 1.5 of X-Ray Data Booklet, and plots for all elements at: http://ulisse.elettra.trieste.it/elements/WebElements.html
The five ways in which x-rays Interact with Matter:

Fig. 3-1. Total photon cross section $\sigma_{\text{tot}}$ in carbon, as a function of energy, showing the contributions of different processes: $\tau$, atomic photo-effect (electron ejection, photon absorption); $\sigma_{\text{coh}}$, coherent scattering (Rayleigh scattering—atom neither ionized nor excited); $\sigma_{\text{inc}}$, incoherent scattering (Compton scattering off an electron); $\sigma_n$, pair production, nuclear field; $\kappa_e$, pair production, electron field; $\sigma_{\text{ph}}$, photonuclear absorption (nuclear absorption, usually followed by emission of a neutron or other particle). (From Ref. 1; figure courtesy of J. H. Hubbell.)
Graphite - NEXAFS

$\pi^*$ Out-of-plane bonds in the $sp^2$ bonding configuration

Exciton

$\sim 4.5 \text{ eV} = \text{work function of graphite}$

The usual free-atom tabulations (e.g. CXRO)

Electron can escape

Energy (eV)

280 290 300 310 320

Intensity (Arb.)

Ethane: C 1s NEXAFS

COMPARISON OF SCANNED-ENERGY PD TO EXTENDED X-RAY ABSORPTION FINE STRUCTURE

"NEAR-EDGE" = XAS, XANES, NEXAFS
"EXTENDED" = EXAFS

---

Figure 1.1. The x-ray absorption coefficient for the K-edge of copper metal.

Also scanned-energy, but integrates over all electron emission directions
Atomic Calculation of Photoionization Cross-Sections and Asymmetry Parameters

This periodic table interface was developed to easily access the calculated atomic cross sections for photoionization and the related asymmetry parameters. The data are taken from: J.J. Yeh, Atomic Calculation of Photoionization Cross-Sections and Asymmetry Parameters, Gordon and Breach Science Publishers, Langhorne, PE (USA), 1993 and from J.J. Yeh and I.Lindau, Atomic Data and Nuclear Data Tables, 32, 1-155 (1985). The data shown here are those calculated in the dipole length approximation.

This is a beta version: comments are welcome.

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Elements:
- He
- Be
- Mg
- Ca
- Sc
- Ti
- V
- Cr
- Mn
- Fe
- Co
- Ni
- Cu
- Zn
- Ga
- Ge
- As
- Se
- Br
- Kr
GRAPH I. Atomic Subshell Photoionization Cross Sections for 0-1500 eV, 1 \leq Z \leq 103

See page 6 for Explanation of Graphs

H binding energies(eV) are:

13.6 eV = THRESHOLD FOR C^- EMISSION

1s(1) 13.6050
GRAPH 1. Atomic Subshell Photoionization Cross Sections for 0–1500 eV, 1 ≤ Z ≤ 103
See page 6 for Explanation of Graphs
GRAPH I. Atomic Subshell Photoionization Cross Sections for 0–1500 eV, 1 ≤ Z ≤ 103

See page 6 for Explanation of Graphs

Ag binding energies(eV) are:

1s(2) 24693.5 2s(2) 3591.17 2p(6) 3352.94
3s(2) 665.102 3p(6) 567.205 4s(2) 94.2146
3d(10) 384.360 4p(6) 62.9041 4d(10) 12.6499
5s(1) 6.42700

hv ~ 130 eV
FIG. 5. Partial photoionization cross section for 4d electrons of Ag in logarithmic scale. Our experimental data for the Ag/Si interface (squares) are compared with the Hartree-Fock results for atomic Ag by Yeh and Lindau (solid line). Note that our experimental data are normalized at the minimum to the theoretical value.

FIG. 6. Asymmetry parameter for 4d electrons of Ag. Our experimental data for the Ag/Si interface (squares) are compared with the data for atomic Ag (circles), the RRPA prediction for atomic Pd by Radojevic and Johnson (solid line, velocity form; short-dashed line, length form), and the HS calculations for atomic Ag by Manson (long-dashed line).

If either $R_{\ell+1}$ or $R_{\ell-1}$ goes to zero, get a Cooper minimum

**TOTAL SUBSHELL CROSS SECTION:**

$$\int \frac{d\sigma_{nl}}{d\Omega} = \frac{4\pi \alpha_0 a_0^2}{3} (hv)[lR_{l-1}^2(E_f) + (l+1)R_{l+1}^2(E_f)]$$

= sum over all $m_\ell, m_s$ in subshell $\ell$.

**RADIAL MATRIX ELEMENTS TO $\ell \pm 1$ CHANNELS:**

$$R_{l\pm 1}(E_f) = \int_0^\infty R_{ni}(r) R_{Ef}, \, i_{\pm 1}(r) \, dr = \int_0^\infty P_{ni}(r) P_{Ef}, \, i_{\pm 1}(r) \, dr$$

**DIFFERENTIAL CROSS SECTION: UNPOLARIZED**

$$\frac{d\sigma_{nl}}{d\Omega} (E_f) = \frac{\sigma_{nl}}{4\pi} [1 - \frac{1}{2} \beta_{nl}(E_f) P_2(\cos \alpha)]$$

$$= \frac{\sigma_{nl}}{4\pi} [1 + \frac{1}{2} \beta_{nl}(E_f)(\frac{3}{2} \sin^2 \alpha - 1)]$$

= $A + B \sin^2 \alpha$

**ASYMMETRY PARAMETER:**

$$\beta_{nl}(E_f) = \frac{-6l(l+1)R_{l+1}(E_f)R_{l-1}(E_f) \cos [\delta_{l+1}(E_f) - \delta_{l-1}(E_f)]}{(2l+1)[lR_{l-1}^2(E_f) + (l+1)R_{l+1}^2(E_f)]}$$

$\delta_{\ell \pm 1}(E_f) =$ CONTINUUM ORBITAL PHASEhiftS

IN ATOMIC POTENTIAL $V(r)$
COOPER MINIMUM IN In 4d ($Z = 49$) CROSS SECTION—Radial Matrix Element Variation

$R_{1s} = R_{3s}$
$R_{1d} = R_{2p}$

$\hbar \nu \approx 115$ eV

$\hbar \nu \approx 135$ eV

Goldberg, Kono, Fadley
J. Elect. Spect. 21, 285 ('81)

In binding energies (eV) are:

- $1s(2) \ 26971.5$
- $2s(2) \ 3983.01$
- $2p(6) \ 3731.41$
- $3s(2) \ 764.232$
- $3p(6) \ 659.286$
- $4s(2) \ 118.953$
- $3d(10) \ 462.909$
- $4p(6) \ 84.0558$
- $5s(2) \ 10.1384$
- $4d(10) \ 26.2168$
- $5p(1) \ 4.69781$
An additional many-electron effect: **Resonant photoemission**
Single-atom resonant photoemission:

Ex. - Mn atom: Mn3d emission, resonance with Mn3p

\[ \text{Photo } e^-, E \approx 50 \text{ eV} \]
\[ \ell = p + f \]

\[ h\nu_{3p} = 50 \text{ eV} \]

\[ \langle Ef | \hat{e} \cdot \hat{r} | \text{Mn3d} \rangle \]

\[ \langle Ef, \text{Mn3p} | \hat{e} \cdot \hat{r} | \text{Mn3d, Mn3d} \rangle \]

\[ \text{Strong} \]
\[ \langle \text{Mn3d} | \hat{e} \cdot \hat{r} | \text{Mn3p} \rangle \]

\[ \text{Mn3d} \]

\[ \text{Mn3p} \]

---

**Experimental (Krause et al.)**

- 3d

**Theoretical (Garvin et al.)**

- MBPT
- HF

\[ h\nu_{3p} \]

\[ \text{Resonant } (\pm) = 0.63 \]

\[ \text{Non-Resonant} = 1.0 \]

---

**Atomic Mn(g)**

**Photon Energy, \( h\nu \) (eV)**

\[ I_{\text{Mn3d}} \]

---

55
SINGLE-ATOM RESONANT PHOTOOEMISSION:

**Experimental Setup:**

- **Mn Vapor**
- **Angular Distribution Parameter** \( \beta \) of 3d photoelectrons (upper panel)
- **Partial Cross Section** (left panel)

**Theoretical Models:**

- **HOMOELCTRON SPECTROMETRY OF MANGANESE VAPOR...**
- **Expt. (This Work)**
  - 3d
  - 4s
  - 3d Satellites
  - Theory (Garvin et al.)
  - MBPT
  - HF = SIMPLE
  - Hartree-Fock Theory

**Figure 2:** Angular distribution parameter \( \beta \) of 3d photoelectrons (upper panel) and partial cross sections of 4s, 3d and satellite peaks (lower panel). Crosses (×) are from Ref. 3, theory from Ref. 4. The resonance near 50 eV is due to the 3p → 3d excitation into the partially filled 3d subshell of Mn.

**Resonant Process:**

- **If** \( h\nu = E_b \) of Mn subshell inside of Mn subshell of interest (e.g., 3p for 3d), two “channels” couple:
  - Usual 3d: \( Mn^0 \rightarrow 3s^2 3p^6 3d^5 4s^2 \rightarrow h\nu \rightarrow Mn^+ 3s^2 3p^6 3d^4 4s^2 \)
  - Resonant 3p: \( Mn^0 \rightarrow 3s^2 3p^4 3d^5 4s^2 \rightarrow h\nu \rightarrow Mn^0 3s^2 3p^6 3d^4 4s^2 \)

- **Coupling Much Enhances Cross Section**
- **Auger Electron** + Electron @ Same Ekin as Photoelectron
SrTiO$_3$ and La$_{0.67}$Sr$_{0.33}$MnO$_3$ band structures and DOS

SrTiO$_3$-band insulator

La$_{0.67}$Sr$_{0.33}$MnO$_3$- Half-Metallic Ferromagnet

Projected DOSs

Spin-up
Spin-down

No spin down!

O 2p

Chikamatsu et al., PRB 73, 195105 (2006);
Plucinski, TBP

Plucinski, TBP

SrTiO$_3$-band insulator

Expt’l. bandgap 3.3 eV
Expt’l. band offset 3.0 eV

Plucinski, TBP with expt’l. band offset

Mn $e_g$
Mn $t_{2g}$

Spin-up
Spin-down

$\text{d}_{xz} + \text{d}_{yz}$
$\text{d}_{xy}$

$d_{x^2-y^2}$
$d_{xy}$

$d_{xz} + d_{yz}$
$d_{z^2}$

Plucinski, TBP

Plucinski, TBP

SrTiO$_3$ and La$_{0.67}$Sr$_{0.33}$MnO$_3$ band structures and DOS
Resonant Photoemission—La_{0.6}Sr_{0.4}MnO_3, Mn 3d with Mn 2p

Valence spectrum

Mn 2p absorption spectrum


MATRIX ELEMENTS IN THE SOFT X-RAY SPECTROSCopies: DIPOLE LIMIT

- **Photoelectron spectroscopy/photoemission:**
  \[ I \propto \hat{e} \cdot \langle \phi_f (1) | \vec{r} | \phi_i (1) \rangle^2 \]

- **Near-edge x-ray absorption:**
  \[ I \propto \hat{e} \cdot \langle \phi_f (1) | \vec{r} | \phi_i (1) \rangle^2 \]

- **Auger electron emission:**
  \[ I \propto \langle \phi_f (1) \phi_1 (2) | \frac{e^2}{r_{12}} | \phi_3 (1) \phi_2 (2) \rangle - \langle \phi_1 (1) \phi_f (2) | \frac{e^2}{r_{12}} | \phi_3 (1) \phi_2 (2) \rangle^2 \]

- **X-ray emission:**
  \[ I \propto \hat{e} \cdot \langle \phi_f (1) | \vec{r} | \phi_i (1) \rangle^2 \]
CALCULATION OF PHOTOELECTRON INTENSITIES—THE 3-STEP MODEL

1. **Excitation:**
   - Diff. Cross Section
   - \( \Delta \theta' \), Diffraction

2. **Transport to Surf.:**
   - Inelastic Attenuation
   - \( f(\theta) \)
   - Elastic Scattering

3. **Escape from Surf.:**
   - \( f(\theta) \)
   - Elastic Scattering, Diffraction, \( \theta' \)
   - \( V_0 \)
   - Refraction: \( \theta' \rightarrow \theta \)

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Fig. 1: Shown is an actualized spectrometer geometry for calculating angular-dependent photoelectron peak intensities, with various important parameters and variables indicated.
Electron inelastic mean free paths for 41 elements-theory

41 Elemental Solids: TPP-2M theory

Inelastic Mean Free Path (Å)

Electron Energy (eV)

Diamond

K Cs Na Li

“Bulklike” prop., Buried layers & interfaces

HAXPES, HXPS

Typical XPS

Typical valence ARPES

Tanuma, Powell, Penn, Surf. Interface Anal. 37, 1 (2005) and TBP
Inelastic mean free paths in solids

Estimation from the **TPP-2M** formula: any compound

\[ \Lambda_c \approx \lambda = \frac{E}{E_p^2[\beta \ln(\gamma E) - (C/E) + (D/E^2)]} \]

where

\[ \beta = -0.10 + 0.944/(E_p^2 + E_g^2)^{1/2} + 0.069 \rho^{0.1} \]

\[ \gamma = 0.191 \rho^{-0.50} \]

\[ C = 1.97 - 0.91 U \]

\[ D = 53.4 - 20.8 U \]

\[ U = N_v \rho / M = E_p^2 / 829.4 \]

and \( E_p = 28.8 \ (N_v \rho / M)^{1/2} \) is the free-electron plasmon energy (in eV), \( \rho \) is the density (in g cm\(^{-3}\)), \( N_v \) is the number of valence electrons per atom (for an element) or molecule (for a compound), \( M \) is the atomic or molecular weight, and \( E_g \) is the bandgap energy (in eV). These equations are collectively known as the **TPP-2M** equation.

Tanuma, Powell, Penn, Surf. Interface Anal. 21, 165 (1994)
Inelastic mean free paths for many materials

Downloadable program:
http://www.quases.com/products/quases-imfp-tpp2m/
CALCULATION OF PHOTOELECTRON INTENSITIES—THE 3-STEP MODEL

1. EXCITATION:
   - Diff. cross section

2. TRANSPORT TO SURF.:
   - Inelastic attenuation
   - \( f(\Theta) \) - Elastic scattering;
   - \( \Delta \Theta' \), diffraction

3. ESCAPE FROM SURF.:
   - Elastic scattering, diffraction, \( 90^\circ \)
   - \( f(\Theta) \) - Elastically scattered, \( \Theta' \rightarrow \Theta \)

Fig. 1. Idealized spectrometer geometry for calculating angular-dependent photoelectron peak intensities, with various important parameters and variables as indicated.
Switching from bulk to surface sensitivity for lower electron takeoff angles

Simplest interpretation:
Average emission depth = \( \Lambda_{\text{inelastic}} \sin \theta_{\text{takeoff}} \)
How valid?

\( E_{\text{kin}} \approx 500\text{-}1000 \text{ eV} \)

\( f(\theta_{\text{scat}}) \)

\( V_0 = \text{inner pot.} \)
\( \theta_{\text{takeoff}} > 20\text{-}30^\circ \)

EFFECTS OF ELASTIC SCATTERING ON ANGULAR DISTRIBUTIONS: POLYCRYSTALLINE OR AMORPHOUS SAMPLE

Figure 4. Dependence of the photoelectron intensity emitted normal to the surface on the angle of Al Kα x-rays with respect to the direction of analysis. Curves and solid line: Monte Carlo calculations accounting for elastic collisions of photoelectrons; dashed line: result of common simple formalism of XPS in which elastic collisions are neglected. (a) Silicon 2s photoelectrons; (b) copper 3s photoelectrons; (c) palladium 4s photoelectrons. (Taken from Ref. 20.)

Intensity increased by elastic scattering

Intensity decreased by elastic scattering

Up to this point, included in the SESSA program

Sablonski, Pinwell, Surf. Int. Anal. 20, 799 (19)
Surface sensitivity enhancement for grazing exit angles

\[ \Lambda_e \geq 5\text{Å} \geq \Lambda_e \leq 80\text{Å} \]

Fig. 5. Illustration of the basic mechanism producing surface sensitivity enhancement for low electron exit angles \( \theta \). The average depth for no-loss emission as measured perpendicular to the surface is \( \Lambda_e \sin \theta \).

\[
\begin{array}{|c|c|c|}
\hline
\text{Mean Depth} & \text{No. Layers} \\
\text{"Bulk"} \rightarrow 90^\circ & 28\text{Å} & \sim 9 \\
\text{"Surface"} \rightarrow 10^\circ & \sim 4.4\text{Å} & \sim 1.5 \\
\hline
\end{array}
\]

\[ \therefore \text{BEST QUANTITATIVE ANALYSIS FOR RANGE} \]
\[ 20-30^\circ \leq \theta \leq 90^\circ \]

\[ \cdots \text{BUT REFRACTION AT SURFACE AND ELASTIC SCATTERING CAN REDUCE} \]
\[ \text{SURFACE ENHANCEMENT, ESP. AT LOW } \theta \leq 30^\circ \]
CALCULATION OF PHOTOELECTRON INTENSITIES—THE 3-STEP MODEL

→ The SESSA program calculates this for arbitrary multilayer samples, but neglecting x-ray optics and electron refraction.
The SESSA program for XPS simulations

https://drive.google.com/drive/folders/0B-VeL-nROIxaME41T2dEb1d2MFk?usp=sharing
CALCULATION OF PHOTON ELECTRON INTENSITIES—THE 3-STEP MODEL

Fig. 4: Idealized spectrometer geometry for calculating angular-dependent photoelectron peak intensities, with various important parameters and variables indicated.

1. EXCITATION: DIFF. CROSS SECTION
2. TRANSPORT TO SURF.: INELASTIC ATTENUATION
3. ELASTIC SCATTERING: Δθ', DIFFRACTION

V_o ← REFRACTION: θ' ← θ
Electron Refraction at the Surface Due to the Inner Potential

\[ \theta = \cos^{-1}\left[ \left( 1 + \frac{V_0}{E_{\text{kin}}} \right)^{1/2} \cos \theta' \right] \] or \[ \theta = \tan^{-1} \left[ \sqrt{\frac{\sin^2 \theta' - \frac{V_0}{E_{\text{kin}}}}}{\cos \theta'} \right] \]

**Observed Low-Index Directions Above W(110)**

- **E_{\text{kin}} = 1455eV**
- **V_0 = 13.75eV**
- \[ \theta'_{\text{IR}} = \theta_{\text{IR}} \approx 6^\circ \]

- **E_{\text{kin}} = 40eV**
- **V_0 = 13.75eV**
- \[ \theta'_{\text{IR}} = \theta_{\text{IR}} \approx 39^\circ \]
Fig. 14. Calculation of electron refraction effects for different electron kinetic energies and a typical $V_0$ value of 15eV. The degree of refraction is indicated by the difference $\theta'$ (internal) - $\theta$ (external). Contours of equal probability of internal reflection are also shown. (From ref. (5).)
CALCULATION OF PHOTOELECTRON INTENSITIES—THE 3-STEP MODEL

1. Excitation:
   - Diff. cross section
   - Transport to surf.
   - Inelastic attenuation

2. Elastic scattering:
   - $\Delta \theta'$, diffraction

3. Escape from surf.:
   - Elastic scattering, diffraction, 9keV
   - Refraction: $\theta' \rightarrow \theta$

Penetrate deeply ($10^{-3} - 10^{-5} \text{A}$)

Unless $\theta_{hv} \leq 1^\circ$

Or $hv = E_{b,m}$: Core absorption threshold

Simplified spectrometer geometry for calculating angular-dependent electron peak intensities, with various important parameters and variables indicated.
X-Ray Interactions with Matter

Contents

- Introduction
- Access the atomic scattering factor files.
- Look up x-ray properties of the elements.
- The index of refraction for a compound material.
- The x-ray attenuation length of a solid.
- X-ray transmission
  - Of a solid.
  - Of a gas.
- X-ray reflectivity
  - Of a thick mirror.
  - Of a single layer.
  - Of a bilayer.
  - Of a multilayer.
- The diffraction efficiency of a transmission grating.
- Related calculations:
  - Synchrotron bend magnet radiation.

NEW! What's New?

Other x-ray web resources.

These pages utilize JavaScript, but the decaffeinated versions are still available.

Reference


http://www-cxro.lbl.gov/optical_constants/
SOME X-RAY OPTICAL EFFECTS: REDUCED PENETRATION DEPTHS AND INCREASED REFLECTIVITY AT GRAZING INCIDENCE ANGLES

$\theta_{\text{crit}} = $ Grazing angle at which reflectivity begins ($R \approx 0.20$)

$= [2 \delta]^{0.5}$
X-ray Optical Effects in Photoemission: The Beginning

B.L. Henke, Phys. Rev. A 6, 94 (1972)

- Enhanced surface sensitivity as critical angle approached
- Effects on average depth and intensity in photoemission (x-ray emission also)
- Determination of optical constants from data
X-ray Optical Effects in Photoemission: Reduced inelastic backgrounds in total x-ray reflection

Kawai et al., Spectrochim. Acta B 47, 983 (’92)
Chester & Jach, Phys. Rev. B 48, 17262 (’93)
Jach & Landree, Surf. & Int. Anal. 31, 768 (’01)