Outline

1. What is photoemission spectroscopy?
2. Fundamental aspects of photoemission.
3. Examples.
4. Increase bulk sensitivity: HAXPES.

General reference books:

What is photoemission?

Photon in $\rightarrow$ electron out (emission)
### What are the samples and probed states?

<table>
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<tr>
<th>Samples</th>
<th>Probed States</th>
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<td>Atoms</td>
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What is photoemission spectroscopy? (photoelectron spectroscopy) (PES)

hv

Monochromatized photons

sample

Initial state: ground (neutral) state

Final state: hole (excited) state

Conservation of energy

\[ E_k = \hbar v + E_i - E_f \] (most general expression)

- \( E_k \): photoelectron kinetic energy
- \( E_i (N) \): total initial state system energy
- \( E_f (N-1) \): total final state system energy

Energy Distribution Curve (EDC) (Spectrum)
Single particle description of energy levels (Density of States) (most convenient in PE)

Na atom

3p
3s
2p$_{3/2}$
2p$_{1/2}$
2s
1s

Fermi level

$E_F$

$\sqrt{E}$ (nearly free electron like)

Valence (sp) Band (DOS)

Core levels

$N(E)$ (DOS)
Energetics in PES

\[ E_k = h\nu - E_B - \phi \]

Conservation of energy

- \( E_v \): vacuum (energy) level
- \( E_F \): Fermi (energy) level
- \( \phi = E_v - E_F \): work function
- \( E_0 \): bottom of valence band
- \( V_0 = E_v - E_0 \): inner potential

\( E_k^{\text{max}} \) marks \( E_F \) in spectra
\( E_B \) measured relative to \( E_F = 0 \)

Usually fixed photon energy scanning not needed
An XPS Energy Distribution Curve (EDC)

Most spectra expressed this way
Light sources and terminology

**Ultraviolet Photoemission Spectroscopy (UPS)**
- UV He lamp (21.2 eV, 40.8 eV)
- valence band PE, direct electronic state info

**X-ray Photoemission Spectroscopy (XPS)**
- (Electron Spectroscopy for Chemical Analysis) (ESCA)
- x-ray gun (Al: 1486.6 eV, Mg: 1253.6 eV)
- core level PE, indirect electronic state info
- chemical analysis

**Synchrotron radiation:**
- continuous tunable wavelength
- valence band: <100 eV, maybe up to several keV
- core level: 80-1000 eV, maybe up to several keV
- depending on core level binding energies
Inelastic Electron Mean Free Path (IMFP)

\[ I(d) = I_o e^{-d/\lambda(E)} \]

\(\lambda(E)\): IMFP depending on kinetic energy relative to \(E_F\).

Minimum due to electron-electron scattering, mainly plasmons

PE is a surface sensitive technique! (requires UHV)

High energy photoemission: several keV to increase bulk sensitivity
Core level binding energies are characteristic of each orbital of each element

Finger prints

Core level BE independent of photon energy used

Table 1-1. Electron binding energies, in electron volts, for the elements in their natural forms.

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* Note: The asterisk indicates the core level binding energy.
Core level photoemission: chemical analysis of elements

ESCA (XPS)
\[ h \nu = \text{Mg } K\alpha \approx 1253.6 \text{ eV} \]

Synchrotron \( h \nu = 160 \text{ eV} \)

Different photon energy \( \rightarrow \) different relative cross section for various core levels
Relative intensity changes with photon energy

PJW, NSRRC
A case study of IMFP applied to PE of CdSe nano particles with tunable SR
How to choose photon energies for valence and different core levels with the max surface sensitivity?

Actual choices:
Cd 3d_{5/2} : 480 eV
Se 3d: 120 eV
Valence band: 50 eV

E_k ~ 45-74 eV, most surface sensitive

Wu, PRB 2007 NSRRC
Core level photoemission: chemical shift

higher oxidation state => higher BE

higher emission angle → more surface sensitive (IMFP)  
Pi, SS 2001 NSRRC
Auger Electron Spectroscopy

Core electron ionized by photons or high energy electrons
Non-radiative core hole decay → Auger electron emission
Radiative decay → Fluorescent x-ray emission

Comparison between PES and AES
PES: constant BE, Ek shift with changing photon energy
AES: constant Ek, apparent BE shift with changing photon energy (synchrotron)
Conceptually intuitive, Simple calculation works

Explicitly responsible for IMFP

Hufner, Damascelli

Rigorous, requires sophisticated calculation

Implicitly responsible for IMFP
Schematic wave functions of initial and final states (valence band initial states)

(a) Surface resonance
(b) Surface state
(c) Bulk Bloch state

(d) Surface resonance
(e) in-gap evanescent state
(f) Bulk Bloch final state
Electron kinetic energy inside and outside of solids

Inner potential: $E_V - E_0$

Concept of inner potential is used to deduce 3D band structure from PE data assuming free electron like final state inside solids
Angle Resolved Photoemission Spectroscopy (ARPES)

Angular Resolved Photoemission Spectroscopy (ARPES)

Electron emission angle: $\Theta$
Photon incident angle: $\phi$, s- and p-polarization
Conservation of linear momentum parallel to the surface

\[ k// = \sqrt{\frac{2m}{\hbar^2}} E_k \cdot \sin \theta \]

\[ k// (\text{Å}^{-1}) = 0.5123 \sqrt{E_k (eV)} \cdot \sin \theta \]

\[ k_{\|}(\text{inside}) = k_{\|}(\text{outside}) \]

Conservation of linear momentum

*Important for 3D and 2D band mapping*

\[ k_{\perp} (\text{inside}) \neq k_{\perp} (\text{outside}) \text{ because of inner potential} \]

Ultimately to deduce band dispersion \( E(k_{\perp}) \) or \( E(k_{\perp}, k_{\|}) \)

Normal emission: \( \theta = 0 \), or \( k_{\|} = 0 \), most used detection geometry
Band Mapping (3D) \( E(k_\perp, k_{||}=0) \)

Vertical transition (using visible, uv and soft x-rays) at normal emission

For hard x-ray photon momentum cannot be neglected

Using different \( h\nu \) at normal emission to map out \( E(k_\perp) \)
Bulk band structure and Fermi surfaces

Fermi surfaces:

Electron pockets and hole pockets
Related to Hall coefficient
Electric conductivity
Magnetic susceptibility

(nearly free electron like) sp-band
Small dispersion d-band
more localized state
Large dispersion sp-band
extended state

Dispersion of a band can tell how localized or extended a state is in a solid

Gap below $E_F(=0)$ at L-point
Quantum well states: manifestation of particle in a box in real materials

- Ag(111) thin films epitaxially grown on Au(111) substrate
- Nearly free electron like in xy-plane
- Quantized discretely along z-direction
- Energy levels depend on film thickness \( L \)

Bulk projected bands along \( \Gamma L \) of Au and Ag, respectively

Band gap below \( E_F \)

Ag QWS can exist within Au gap
Clean Au(111) surface state

Deposit 22 ML Ag at 37 K disordered form

Anneal to 258 K Atomically flat 22 ML thin film

$2D$ Int. plots

$k_{||} = 0$ EDCs

Luh et al. PRL 2008 NSRRC BL21B1

Ag S.S.

Ag QWS
Anneal to 180 K
QWS appear minimal flat dispersion
Small localized domains within xy-plane

Anneal to 189 K
Coexistence of two kinds of dispersion
Anneal to 258 K
Well developed dispersion
Large, good crystalline domains in xy-plane

Same QWS energies  
Same crystalline film thickness along z even though lateral crystalline domains grow from small to large

Proposed growth model

Annealing Temp
One-particle spectral function near $E_F$ measured by ARPES with many-particle correction (quasi-particle)

$$A(k, \omega) = -\frac{1}{\pi} \frac{\Sigma''(k, \omega)}{[\omega - \varepsilon_k - \Sigma'(k, \omega)]^2 + [\Sigma''(k, \omega)]^2}$$

$\varepsilon_k$: single particle energy without many-particle correction
$\omega = 0 : E_F$

Self energy correction due to interaction with phonons, plasmons and electrons, etc.

$$\Sigma(k, \omega) = \Sigma'(k, \omega) + i\Sigma''(k, \omega)$$

Real part: shift observed peak energy from single particle energy
Imaginary part: peak FWHM = $2 \Sigma''$
Many-Body Effects in Angle-Resolved Photoemission: Quasiparticle Energy and Lifetime of a Mo(110) Surface State

T. Valla, A. V. Fedorov, P. D. Johnson, and S. L. Hulbert

1Department of Physics, Brookhaven National Laboratory, Upton, New York 11973-5000
2National Synchrotron Light Source, Brookhaven National Laboratory, Upton, New York 11973-5000

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In a high-resolution photoemission study of a Mo(110) surface state various contributions to the measured width and energy of the quasiparticle peak are investigated. Electron-phonon coupling, electron-electron interactions, and scattering from defects are all identified mechanisms responsible for the finite lifetime of a valence photohole. The electron-phonon induced mass enhancement and rapid change of the photohole lifetime near the Fermi level are observed for the first time.

- Peak position
- Kink ~25 meV due to electron-phonon scattering
- Featureless single particle dispersion curve
- Width due to electron-electron scattering ~ $\omega^2$
- Width due to electron-phonon scattering
- Const bkg width due to impurities
- Peak position – single particle curve
- Total $W=W_{e-e}+W_{e-ph}+W_{im}$
Photoemission cross section in single particle approximation (1\textsuperscript{st} step in 3-step model, inside bulk)

\[
\frac{d\sigma}{d\Omega} \propto \sum \left| \langle \Psi_f | A \cdot p | \Psi_i \rangle \right|^2 \cdot \delta(E_f - E_i - h\nu)
\]

\[
M_{fi} = \langle \Psi_f | A(r) \cdot p | \Psi_i \rangle \approx A(0) \cdot \langle \Psi_f | p | \Psi_i \rangle \propto A(0) \cdot \langle \Psi_f | r | \Psi_i \rangle
\]

dipole approximation

\(A\) : polarization vector

\(\Psi_i\) : initial state (orbital) wave function (1s, 2p, valence states etc.)

contain orbital symmetry information

\(\Psi_f\) : final state (orbital) wave function \(\sim \exp(ikr)\) for high kinetic energy photoelectrons, no orbital symmetry retains (non-resonance photoemission)

(orbital symmetry in final state is important in near edge absorption measurements (XAS) and in intermediate state in resonance photoemission)

Dipole transition rule: \(\Delta l = \pm 1\)

\textbf{Symmetry selection rule} for initial (valence) state governed by matrix element

e.g. suppose \(A(0) = Ax, \langle e^{ikx} | x | \psi_f(x) \rangle = 0 \) if \(\psi_f(-x) = +\psi_f(x)\)

\textit{Important for crystalline samples}
Symmetry of states in ARPES determined by selection rule example: LiCu$_2$O$_2$

Cu$^{2+}$O$^{2-}$$_2$ chains along b-axis built by edge sharing Cu$^{2+}$O$_4$ plaquettes

Cu$^{2+}$ : 3d$^9$ → spin-1/2

Quasi-1D spin-1/2 chain

Coexistence of spin-spiral long range order with ferroelectricity → multiferronic

Ideal spin-1/2 1D chain system will have spin-charge separation of photo-hole decay
Does it happen on LiCu$_2$O$_2$?
Must be checked by ARPES
(not discussed further)

Will focus on symmetry of states determined by ARPES with polarization
Basic building unit: CuO₄ planar plaquette

Highest energy state: Cu 3dₓᵧ and O 2p antibonding (AB) state

Still keeps dₓᵧ symmetry
Normal emission $|f\rangle = \exp(ikz)$ even to all symmetry operations $|i\rangle$ even to y'z-plane, Ax' odd to y'z-plane

$\langle f| Ax' |i\rangle = <+| - | +> = 0$, forbidden

Off-normal emission $|f\rangle = \exp(ikz+kx')$ even to x'z-plane $|i\rangle$ even to x'z-plane, Ax' even to x'z-plane

$\langle f| Ax' |i\rangle = <+| + | +> \neq 0$, allowed

Normal emission $|f\rangle = \exp(ikz)$ even to all symmetry operations $|i\rangle$ odd to xz-plane, Ax even to xz-plane

$\langle f| Ax |i\rangle = <+| + |-> = 0$, forbidden

Off-normal emission $|f\rangle = \exp(ikz+ikx)$ even to xz-plane $|i\rangle$ odd to xz-plane, Ax even to xz-plane

$\langle f| Ax |i\rangle = <+| + |-> = 0$, forbidden
Focus on B.E. = 0.7 eV peak at Y’

The highest energy peak at 0.7 eV has dxy symmetry!
ARPES for valence band PE uses primarily VUV light because
1. Better absolute photon energy resolution for most BLs designed as const $\Delta E/E$.
2. Better photoionization cross section at low photon energy.
3. Better momentum resolution for a given angular resolution.

$$\Delta k|| = 0.5123 \sqrt{(E_k)} \cos(\theta) \Delta \theta$$

SX ARPES has been tried for increasing bulk sensitivity, more free electron like final states and reduced matrix element effects. The increasing bulk sensitivity will be discussed.
NSRRC U9 BL21B1 BL and high resolution photoemission end station
Hemispherical electron energy analyzer

R1 : radius of inner sphere
R2 : radius of outer sphere
Ro=(R1+R2)/2 : mean radius
and along electron path
V1: inner potential
V2: outer potential
Ep: pass energy = electron kinetic energy along mean radius
Resonance photoemission (near-edge absorption followed by Auger like electron emission)

- Direct PE
- Resonance PE
- Intensity enhanced by absorption
- Predominantly 4f DOS

4f mixed with other DOS

E\text{F}

3d/4d

E\text{F}

4f

4f

4f

4f

4f

4f

4f

Absorption +

Auger like emission

Intermediate state

e^{-}
Comments on photoelectron IMFP

Valence band PE using VUV and SX has IMFP near minimum, very surface sensitive. It is great to probe surface electronic structure such as surface states and surface resonances.

Many strongly correlated systems have electronic structure sensitive to coordination, thus surface contains different electronic structure from that of deeper bulk. Great surface sensitivity posts a serious problem to probe true bulk properties.

Need larger IMFP by using higher energy photons to enhance bulk sensitivity.
By using Ce 3d → 4f Res. PE near 880 eV surface 4f component becomes greatly reduced compared to 4d → 4f Res. PE near 120 eV, the resulting spectra are closer to true bulk 4f DOS.
Drive to go to even higher photon energies into hard x-ray regime

**HArd X-ray PhotoEmission Spectroscopy** *(HAXPES)*

HAXPES not only reach even closer to true bulk properties of strongly correlated systems, but also becomes capable of probing interface electronic structure, Very difficult using conventional VUV/SX.
HAXPES example: Hard x-ray photoemission on Si-high k insulator buried interface

Annealed sample
HfSix formation

Kobayashi, APL 2003 SPring-8

hv = 6 keV, ΔE ~ 0.24 eV
Take-off angle dependence => non-destructive depth profile
Can probe buried interface at 35 nm! (achievable only by hard x-ray PE)
NSRRC HAXPES project at SPring-8
Why Hard X-rays?

Electron IMFP (probing depth) and Cross section

Higher Ek for deeper probing depth or more bulk sensitivity, for strongly correlated systems and interface properties

Photoemission signal \( \sigma \cdot \lambda \) decreases rapidly > 1 keV

Need photon source of higher flux/brightness (modern SR), efficient BL design and good electron analyzers

HAXPES is a low count rate, photon hungry experiment!
Optical design concept

Diamond (111) reflection
6-12 keV

DM: horizontal dispersion

HRM: vertical dispersion
Layout of the side beamline of BL12XU

6-12 keV using diamond (111) reflection
Designed for HAXPES
Commission of SPring-8 BL12XU SL HAXPES end station

KB Focus at sample
Aft HRM Si(333)
7.6 keV
38x38 microns

In collaboration with
Cologne U of Germany

Low resolution w/o HRM
8 keV

Medium resolution
Si(333) HRM, 7.6 keV
Challenging future directions of Photoemission Spectroscopy

1. ARPES at submicron to tens of nanometer scale, using Schwatzchild optics or zone plates. Need brighter light sources.


Thanks for your attention