Photoemission (I) Spectroscopy

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Outline

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

Reference books:
What is photoemission?

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

<table>
<thead>
<tr>
<th>Samples</th>
<th>Probed States</th>
</tr>
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<tr>
<td>Atoms</td>
<td>atomic orbitals (states)</td>
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<tr>
<td>Molecules</td>
<td>molecular orbitals</td>
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<td>Nanoparticles</td>
<td>core level states (atomic like)</td>
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<td>Solids</td>
<td>valence bands/states</td>
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<td>core level states (atomic like)</td>
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</table>
What is photoemission spectroscopy? (photoelectron spectroscopy) (PES)

Monochromatized photons

Initial state: ground (neutral) state

Final state: hole (excited) state

Conservation of energy

\[ E_k = h\nu + E_i - E_f \] (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

Na metal

- 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

\( E_k^{\max} \) 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

Hufner
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)

\[ I(d) = I_0 e^{-d/\lambda(E)} \]

\( \lambda(E) \): 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
Core level photoemission: chemical analysis of elements

ESCA (XPS)

\[ h\nu = \text{Mg } K\alpha = 1253.6 \text{ eV} \]

Synchrotron \[ h\nu = 160 \text{ eV} \]

Different photon energy \( \rightarrow \) different relative cross section for various core levels \( \rightarrow \) 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)
Photoemission Process

Conceptually intuitive,
Simple calculation works

Explicitly responsible for IMFP

Rigorous, requires sophisticated calculation

Hufner, Damascelli
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

Bulk band gap
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)

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

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

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

\( k_\parallel (\text{inside}) = k_\parallel (\text{outside}) \)

Conservation of linear momentum

Important for 3D and 2D band mapping

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

Ultimately to deduce band dispersion \( E(k_\perp) \) or \( E(k_\perp, k_\parallel) \)

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

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

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

Cu

Gap below $E_F(=0)$ at L-point

Small dispersion $d$-band
- more localized state

Large dispersion $sp$-band
- extended state

(nearly free electron like) $sp$-band

Hufner
Quantum well states: manifestation of particle in a box in real materials

- Ag(111) thin films epitaxially grown on Au(111) substrate
- Band gap below $E_F$
- Ag QWS can exist within Au gap
- Bulk projected bands along $\Gamma L$ of Au and Ag, respectively

Quantized discretely along z-direction
Energy levels depend on film thickness $L$
Nearly free electron like in xy-plane
$k_|| = 0$

EDCs

Clean Au(111) surface state

Deposit 22 ML Ag at 37 K disordered form

Anneal to 258 K Atomically flat 22 ML thin film

Luh et al. PRL 2008 NSRRC BL21B1

Ag S.S.

Ag QWS

2D Int. plots
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
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 $\Sigma''$
Peak position

Kink ~25 meV due to electron-phonon scattering

Featureless single particle dispersion curve

Width due to electron-electron scattering \( \sim \omega^2 \)

Width due to electron-phonon scattering

Const bkg width due to impurities

Peak position – single particle curve

Total \( W = W_{e-e} + W_{e-ph} + W_{im} \)
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

U9 undulator
CGM
Scienta SES 200 analyzer
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)

\[ \text{e.g. Ce}^{3+} (4f^1) \]

Intensity enhanced by absorption
Predominantly 4f DOS

4f mixed with other DOS

Direct PE

Resonance PE

Absorption + Auger like emission

Intermediate state
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.
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.
Probing bulk states of correlated electron systems by high-resolution resonance photoemission

Nature 2000

A. Sekiyama*, T. Iwasaki*, K. Matsuda*, Y. Saitoh†, Y. Ōnuki‡ & S. Suga*

Heavy Fermion Kondo systems
Mixed valence Ce $f^0$ & $f^1$
$\Delta E \sim 100$ meV

Drastically diff. electronic structure btn. surface and bulk: $f^0$ vs. $f^1$
No Kondo peak in an itinerant 4f system of CeRu$_2$
Valence Transition of YbInCu$_4$ Observed in Hard X-Ray Photoemission Spectra

Hitoshi Sato,¹,⁸ Kenya Shimada,¹ Masashi Arita,¹ Koichi Hiraoka,² Kenichi Kojima,³ Yukiharu Takeda,¹,⁷ Kunta Yoshikawa,⁴ Masahiro Sawada,¹ Masashi Nakatake,¹ Hirofumi Namatame,¹ Masaki Taniguchi,¹,⁴ Yasutaka Takata,⁵ Eiji Ikenaga,⁶ Shik Shin,⁵,⁷ Keisuke Kobayashi,⁶ Kenji Tamashiki,⁸ Yoshinori Nishino,⁸ Daigo Miwa,⁸ Makina Yabashi,⁶ and Tetsuya Ishikawa⁸

Bulk sensitive HAXPES can determine sharp first order valence band transition
HAXPES example: Hard x-ray photoemission on Si-high k insulator buried interface

Annealed sample
HfSix formation

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!

(except at a grazing incident angle)
A serious issue on going to hard x-rays

Cross sections of 3d TM s-orbitals go down more slowly than d-orbitals which are the needed information on 3d TM strongly correlated electron systems. Hard x-ray PE spectra could be dominated by contribution from less desired s-orbitals
How to cope with this problem?
Unexpected lineshapes in HAXPES compared to XPS

Valence band of simple oxides – e.g. Cu$_2$O and ZnO

band-insulators, no electron-correlation effects – LDA should do (+$U_{dd}$+$U_{pp}$)

Cu$_2$O – valence band

ZnO – valence band

HAXPES: TM-4s overwhelms TM-3d and O-2p
Polarization dependent cross sections in HAXPES

How to suppress the 4s spectral weight?
• photo-ionization cross-section depends on e⁻ emission direction and light polarization
• make use of β-asymmetry parameter

\[
\frac{d\sigma_i}{d\Omega} = \frac{\sigma_i}{4\pi} \left[ 1 + \beta P_2(\cos\theta) \right] + \ldots
\]

β-parameters @ \( h\nu = 5\text{-}10 \text{ keV} \)
Cu 3d 0.48 - 0.32
Cu 4s 1.985
Zn 3d 0.50 - 0.33
Zn 4s 1.987 - 1.986

In general: s orbitals have \( \beta \approx 2 \):
• intensity is enhanced for e⁻ emission || E-vector
• intensity vanishes for e⁻ emission \( \perp \) E-vector

→ choose suitable experimental geometry!
**HAXPES Commissioning: Horizontal vs Vertical geometries**

θ: angle between electron emission and polarization vector

β: electron emission asymmetry parameter

β ~ 2 for s-orbitals, strong emission near θ = 0° (horiz.) while suppressed near θ = 90° (vertical);

can be used to distinguish s-orbital, important in chemical bonding, and d-orbital, important in strongly correlated systems

Zn 4s has relatively larger cross section than 3d at 7.6 keV compared to 1.486 keV, enhanced in horizontal geometry at 7.6 keV, while suppressed in vertical geometry
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
HAXPES Example 1:
NiO at RT and high temp.

Interpretation of XPS valence spectra of NiO against argument of surface effect
First ionization (photohole final) valence state identified as Ni$^{2+}$ low spin state
Indication of non-local screening in valence band of bulk NiO compared to impurity NiO
Peaks splitting due to non-local screening in valence and Ni 2p core level diminishes as temp. approaches $T_N=523$ K
NiO: a prototypical strongly correlated electron system

Peak B is a true bulk feature

Peak B is absent in single NiO$_6$ cluster

Implications:
1. First ionization state is $^2E$ (compensated spin, (photo)hole in the mixed state made of $e_g$ (d$^7$) and O 2$p_\sigma$ (d$^8$L) (ZR-doublet), instead of $^4T_1$ (atomic-like Hund’s rule high spin, d$^7$, quasi-core) as previously suggested.
2. Peak B due to non-local (neighboring sites) effect.
NiO above Neel temperature at 523 K

How important is long range AF ordering?

- Ni 2p$_{3/2}$ splitting due to non-local screening mechanism (Veenendaal and Sawartzky PRL1993)
- Splitting goes smaller with increasing temp.
- Valence band doublet structure also changes w/ temp.

(Why need bulk sensitive HAXPES? Because O decomposes leaving surf. at high T)
HAXPES Example 2:
Interface of LAO/STO

Interface of two band insulators LaAlO$_3$ and SrTiO$_3$ becomes metallic-like. Evidence of charge transfer from LAO to STO is observed but the amount is less than prediction of simplest model.
Polarity discontinuity between LAO and STO plays a crucial role.

Charge transfer balances the polar discontinuity and leads to conducting behavior of the interface.

\[ \frac{1}{2} \text{ e transferred} \]  
Nakagawa et al., Nature Mater. 5, 204 (2006)
Sing et al., PRL 102, 176805 (2009)

\[ h_v = 3 \text{ keV} \]

- Conducting interface due to electronic reconstruction
- 2DEG confined to only ~ 1 or at most a few u.c. thick
- total Ti3+ density < 0.28 e /2D u.c. for 5 u.c. LAO (<0.5 e); sample dependent
Our approach:

* grazing incidence near total external reflection to enhance photon field near the surface and interface region for better detection of Ti$^{3+}$ near the interface

* higher photon energy (6.5 keV) to increase probing depth

\[ h\nu = 6.5 \text{ keV} \]

5 UC (2nm) LAO

STO
LaAlO$_3$/SrTiO$_3$ (001)

grown with PLD, 10^{-5}$ torr O$_2$, 850 C annealed at 100 mtorr of O$_2$

conducting interfaces

5 u.c.
LaAlO$_3$

Ti$^{3+}$?

substrate (TiO$_2$ terminated)

$\text{(AlO}_2)^{0.5-}$

Resistance (Ohm)

<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>0</th>
<th>50</th>
<th>100</th>
<th>150</th>
<th>200</th>
<th>250</th>
<th>300</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistance (Ohm)</td>
<td>0</td>
<td>200</td>
<td>400</td>
<td>600</td>
<td>800</td>
<td>1000</td>
<td>1200</td>
</tr>
</tbody>
</table>

Heating up
Cooling down
Measure intensity ratio $\text{Ti}^{3+}/\text{Ti}^{4+}$ as a function of incident angle.
\[ d_2 = 48.3 \pm 20.3 \text{ Å} \]

\[ \alpha = 0.021 \]

\((\text{Ti}^{3+}/\text{Ti}^{4+} \text{ in } d_2)\)

Total carriers
\[ \sim 0.24 \text{ e} / 2\text{D u.c.} \]

Consistent with electronic reconstruction but only half the amount O vacancies?
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