In 1905 Albert Einstein proposed the concept of light quanta (photons) to explain the photoelectric effect, which was pivotal in establishing the quantum theory in physics. In 1921 he was awarded the Nobel Prize in Physics "for his services to theoretical physics, and especially for his discovery of the law of the photoelectric effect."

Since the late 1940’s Kai Siegbahn has been working on the Electron Spectroscopy for Chemical Analysis (ESCA) also termed the X-ray Photoelectron Spectroscopy (XPS). In 1981 he was awarded the Nobel Prize in Physics "for his contribution to the development of high-resolution electron spectroscopy."

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

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

Reference books:
What are the samples and probed states?

- **Atoms**
  - atomic orbitals (states)
- **Molecules**
  - molecular orbitals
- **Nanoparticles**
  - valence bands/states
- **Solids**
  - valence bands
  - core level states (atomic like)

Single particle description of energy levels (Density of States) (most convenient in PE)

- **Na atom**
- **Na metal**

Energetics in PES

**Conservation of energy**

Density of States (DOS)

**E_k = hν – E_B – ε**

- **E_v**: vacuum (energy) level
- **E_F**: Fermi (energy) level
- **ε = 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

Energy Distribution Curve (EDC)

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)

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

\( \lambda(E) \): IMFP depending on KINETIC ENERGY inside solid or 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

X-Ray Data Booklet

http://xdb.lbl.gov/

Core level photoemission: chemical analysis of elements

ESCA (XPS)

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

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

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

\( E_s \sim 45-74 \text{ eV}, \text{ most surface sensitive} \)

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

Chemical Analysis of C1s core levels

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)

http://xdb.lbl.gov/
Handbook of XPS

Photoemission Process

Explicitly responsible for IMFP
Implicitly responsible for IMFP

Conceptually intuitive, Simple calculation works
Rigorous, requires sophisticated calculation
Schematic wave functions of initial and final states (valence band initial states)

(a) Surface resonance  (d) Surface resonance
(b) Surface state      (e) In-gap evanescent state
(c) Bulk Bloch 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 (ARPES)

Conservation of linear momentum parallel to the surface

$$k = \frac{2m}{\hbar^2} E_k \sin \theta$$

$k_{||}(\text{inside solid}) = k_{||}(\text{outside in vacuum})$

$k_{||}$ is not conserved, obtained by changing photon energy

Electron emission angle $\theta$ with respect to the crystalline surface normal and symmetry planes is also measured

$\Rightarrow$ Electronic band dispersion $E(k_{||}, k_{L})$

inside (ordered) crystalline solids

Band Mapping (3D) $E(k_{||}, k_{L}=0)$

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 $E(k_{||})$
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.

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

Ag(111) thin films epitaxially grown on Au(111) substrate

Gap below \( E_F \) at L-point

\( \frac{L}{g} \)/42/g3/X

\((111) \rightarrow (001)\)

Nearly free electron like in xy-plane

Quantized discretely along z-direction
Energy levels depend on film thickness \( L \)

Ag QWS can exist within Au gap

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

2D Int. plots

\( k_{||} = 0 \)

EDCs

Luh et al.
PRL 2008
NSRRC BL21B1

Clean Au(111) surface state
Deposit 22 ML Ag at 37 K disordered form
Anneal to 258 K Atomically flat 22 ML thin film

Proposed growth model

Annealing Temp

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

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

Ag S.S.

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

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

$\epsilon_k$: 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 = $2\Sigma''$

ARPES for valence band PE uses primarily VUV light because of

1. Better absolute photon energy resolution for most BLs designed as nearly const $\Delta E/E$.
2. Better photoionization cross section at low photon energy.
3. Better momentum resolution for a given angular resolution.

$$\Delta k_{\parallel}/(\AA) = 0.5123 \sqrt{E_k/(eV)} \cos(\theta) \Delta \theta$$

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.
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.

Buried interface is mostly undetectable by PE using VUV/SX photons because IMFP is too small compared to thickness of outermost thin layer.

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.

Resonance photoemission

(near-edge absorption followed by Auger like electron emission)

- e.g. Ce$^{3+}$ (4f$^1$)
- Intensity enhanced by absorption
- Predominantly 4f DOS

Direct PE

- Absorption +
- Auger like emission

Resonance PE

- Intermediate state
- 4f mixed with other DOS
By using Ce 3d $\rightarrow$ 4f Res. PE near 880 eV surface 4f component becomes greatly reduced compared to 4d $\rightarrow$ 4f Res. PE near 120 eV, the resulting spectra are closer to true bulk 4f DOS.

HAXPES example: Hard x-ray photoemission on Si-high k insulator buried interface

$\nu_h = 6$ keV, $\Delta \nu \approx 0.24$ eV
Take-off angle dependence $\Rightarrow$ non-destructive depth profile
Can probe buried interface at 35 nm! (achievable only by hard x-ray PE)
World wide efforts on SR based HAXPES

- SPring-8 BL29XU (RIKEN, HAXPES end station can move in, pioneer in HAXPES)
- SPring-8 BL15XU (National Institute Materials Science (NIMS) WE Brom, fixed installation)
- SPring-8 BL19LXU (RIKEN long undulator BL, HAXPES end station can move in)
- SPring-8 BL46XU (JASRI Engineering Science Reseach, fixed installation)
- SPring-8 BL47XU (JASRI HX PES, fixed installation)
- SPring-8 BL12XU-SL (NSRRC, fixed installation) unique with dual analyzers
- *SPring-8 ID16 (mainly for IXS, used by VOLPE)
- *SPring-8 ID32 (fixed installation, shared with XRD)
- *SPring-8 BM32 SpLine (fixed installation, PXD/XAS/SRD/HAXPES+SXRD)
- BESSY II KMC-1 BM (HIKE and XUV diffraction, fixed installation)
- *NSLS X24A BM (fixed installation)
- *DESY BW2 Wiggler (fixed installation)
- *DLS I09 (Surface and Interface Analysis (SISA))
- *SOLEIL Galaxies (under construction, RIXS and HAXPES)
- *CLS SX RMB BM (wide range 1.7-10 keV)
- *APS (?)

Why Hard X-rays?
Electron IMFP (probing depth) and Cross section

Higher E_k for deeper probing depth or more bulk sensitivity, for strongly correlated systems and interface properties
Photoemission signal (\sigma_\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_2O and ZnO
band-insulators, no electron-correlation effects – LDA should do (+U_{d\sigma}+U_{p\pi})

Cu_2O – valence band
ZnO – valence band

HAXPES: TM-4s overwhelms TM-3d and O-2p

Tjeng et al.
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 $\beta$-asymmetry parameter

$$\frac{d\sigma}{d\Omega} = \frac{\sigma_0}{4\pi} [1 + \beta P_2(\cos \theta)] + ...$$

$\beta$-parameters @ $h\nu = 5-10$ 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

$\theta$: angle between electron emission and polarization vector
$\beta$: electron emission asymmetry parameter
$\beta \approx 2$ for s-orbitals, strong emission near $\theta = 0^\circ$ (horiz.) while suppressed near $\theta = 90^\circ$ (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

DM: horizontal dispersion
HRM: vertical dispersion

Diamond (111) reflection
6-12 keV

6-12 keV using diamond (111) reflection
Designed for HAXPES

Layout of the side beamline of BL12XU
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\textsuperscript{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\textsubscript{N}=523 K

NiO: a prototypical strongly correlated electron system

NiO above Neel temperature at 523 K

How important is long range AF ordering?

• Ni 2p\textsubscript{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)

Implications:
1. First ionization state is \textsuperscript{2}E (compensated spin, (photo)hole in the mixed state made of \textit{e}\textsubscript{g} (d\textsuperscript{2}) and O 2p\textsubscript{\textit{g}} (d\textsuperscript{4}L) (ZR-doublet), instead of \textsuperscript{4}T\textsubscript{1} (atomic-like Hund’s rule high spin, d\textsuperscript{7}, quasi-core) as previously suggested.
2. Peak B due to non-local (neighboring sites) effect.
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.

Nakagawa et al., Nature Mater. 5, 204 (2006)

Hard X-ray Photoemission Spectroscopy (HAXPES)

Conducting interface due to electronic reconstruction

2DEG confined to only ~ 1 or at most a few u.c. thick

total Ti$^{3+}$ 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

Sing et al., PRL 102, 176805 (2009)
LaAlO$_3$/SrTiO$_3$ (001) grown with PLD, $10^4$ 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)

LaAlO$_3$ (Ti$^{4+}$)SrTiO$_3$

Measure intensity ratio Ti$^{3+}$/Ti$^{4+}$ as a function of incident angle

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