

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.
- 5. Challenging future directions.

Reference books:

- 1. "Photoelectron Spectroscopy" 3rd Ed. by S. Hufner, Springer-Verlag 2003
- 2. "Angle-Resolved Photoemission: Theory and Current Applications", S. D. Kevan, ed., Amsterdam; Elsevier 1992
- 3. "Very High Resolution Photoelectron Spectroscopy" Ed. by S. Hufner, Springer 2007



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)



Initial state: ground (neutral) state

Conservation of energy

 $E_k = hv + E_i - E_f$ (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 Electron energy analyzer



Final state: hole (excited) state



Energy Distribution Curve (EDC) (Spectrum)

What are the samples and probed states?

Atoms Molecules Nanoprticles Solids atomic orbitals (states) molecular orbitals core level states (atomic like) valence bands/states core level states (atomic like) valence bands core level states (atomic like)

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





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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 inside solid or relative to E_F



Fig.1.9. Electron escape depth as a function of their kinetic energy for various metals. The data indicate a universal curve with a minimum of $2\div 5$ Å for kinetic energies of $50\div 100$ eV. The scatter of the data is evident from the values obtained at $E_{kin} = 1480$ eV

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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

Element	K 1s	L ₁ 2s	L ₂ 2p _{1/2}	L ₃ 2p _{3/2}	M ₁ 3s	M ₂ 3p _{1/2}	M ₃ 3p _{3/2}	M ₄ 3d _{3/2}	M5 3d5/2	N ₁ 4s	N ₂ 4p _{1/2}	N ₃ 4p _{3/2}	
1 H	13.6												
2 He	24.6*								\sim				
3 Li	54.7*								()(n	I A	iel h	inding energies are
4 Be	111.5*												maning chicigies are
5 B	188*												
6 C	284.2*								Ch	ara	ACte	eristi	c of each orbital of
7 N	409.9*	37.3*								are			
8 O	543.1*	41.6*											-1
9 F	696.7*								ea	ICN	ele	eme	nt in the second s
10 Ne	870.2*	48.5*	21.7*	21.6*									
11 Na	1070.8†	63.5†	30.65	30.81									
12 Mg	1303.0†	88.7	49.78	49.50									
13 Al	1559.6	117.8	72.95	72.55									
14 Si	1839	149.7*b	99.82	99.42					• • • • • •			and an Ale	
15 P	2145.5	189*	136*	135*					11	nde	er D	orints	5
16 S	2472	230.9	163.6*	162.5*						.9.			
17 CI	2822.4	270*	202*	200*									
18 Ar	3205.9*	326.3*	250.6†	248.4*	29.3*	15.9*	15.7*						
19 K	3608.4*	378.6*	297.3*	294.6*	34.8*	18.3*	18.3*						
20 Ca	4038.5*	438.4†	349.7†	346.2†	44.3 †	25.4†	25.4*		0				C independent of
23 V	5465	626.7†	519.8†	512.1†	66.3†	37.2†	37.2†			ле	Ie/	ei e	
24 Cr	5989	696.0†	583.8†	574.1†	74.1†	42.2†	42.2*						
25 Mn	6539	769.1†	649.9†	638.7†	82.3†	47.2†	47.2†		nh	oto			avuood
26 Fe	7112	844.6†	719.9†	706.8†	91.3†	52.7†	52.7†			Οι) (ener	av usea
27 Co	7709	925.1†	793.2†	778.1†	101.0^{+}	58.9†	59.9†						57
28 Ni	8333	1008.6^{+}	870.0†	852.7†	110.8^{+}	68.0†	66.2*						
29 Cu	8979	1096.7†	952.3†	932.7	122.5†	77.3†	75.1†						
30 Zn	9659	1196.2*	1044.9*	1021.8*	139.8*	91.4*	88.6*	10.2*	10.1*				
31 Ga	10367	1299.0*b	1143.2†	1116.4†	159.5†	103.5†	100.0^{+}	18.7*	18.7†				
32 Ge	11103	1414.6*b	1248.1*b	1217.0*b	180.1*	124.9*	120.8*	29.8	29.2				
33 As	11867	1527.0*b	1359.1*b	1323.6*b	204.7*	146.2*	141.2*	41.7*	41.7*				
34 Se	12658	1652.0*b	1474.3*b	1433.9*b	229.6*	166.5*	160.7*	55.5*	54.6*				
35 Br	13474	1782*	1596*	1550*	257*	189*	182*	70*	69*				X-Ray Data Booklet
36 Kr	14326	1921	1730.9*	1678.4*	292.8*	222.2*	214.4	95.0*	93.8*	27.5*	14.1*	14.1*	A hay bala bookiet
37 Rb	15200	2065	1864	1804	326.7*	248.7*	239.1*	113.0*	112*	30.5*	16.3*	15.3 *	
38 Sr 20 N	16105	2216	2007	1940	358.77	280.37	270.07	136.07	134.27	38.9 ⁺	21.3	20.1*	
39 Y	17038	2373	2156	2080	392.0*b	310.6*	298.8*	157.77	155.87	43.8*	24.4*	23.1*	
40 Zr 41 Nb	1/998	2552	2307	2225	450.51	276.14	260.64	205.04	202.24	56.44	28.5	27.11	http://ydb.lbl.gov/
41 NO 42 Mo	20000	2090	2403	2571	400.01 506.24	411.64	204.04	205.01	202.51	62.24	32.0	35.5*	
43 Tc	20000	2000	2025	2520	544*	447.6	417.7	251.1	227.91	60.5*	42.3*	30.0*	
44 Ru	221044	3045	2195	2838	586.1*	483.5+	461.4+	237.0	235.9	75.0+	46.3+	43.2+	
45 Rb	22117	3412	3146	2000	628.1+	521.24	401.41	204.21	200.01	81.4*b	50.5+	47.3+	
46 Pd	24350	3604	3330	3173	671.6+	550.0+	532.34	340.5+	335.2+	87.1*b	55.7te	50.9†	
47 A a	25514	3806	3524	3351	710.0+	603.84	573.0+	374.0+	368.3	97.0+	63.7±	58.3+	
., ng	20014	5000	2244	5551	119.0	005.0	515.0	574.0	500.5	51.0	0.5.7	50.5	

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

Core level photoemission: chemical analysis of elements





Surface core level shift (chemical and/or environmental)

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

 $E_k \sim 45-74$ 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

Chemical Analysis of C1s core levels



http://surfaceanalysis.group.shef.ac.uk

Auger Electron Spectroscopy

Handbook of XPS

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/

(a) Photoelectric absorption



(b) Fluorescent X-ray emission



(c) Auger electron emission



Photoemission Process



Conceptually intuitive, Simple calculation works

Rigorous, requires sophisticated calculation

Schematic wave functions of initial and final states (valence band initial states)



(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

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

 k_{\parallel} (inside solid) = k_{\parallel} (outside in vacuum)

 k_{\perp} is not conserved, obtained by changing photon energy

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

 $\Rightarrow \text{Electronic band dispersion } \textit{E}(\textit{k}_{||}, \textit{k}_{\perp})$ inside (ordered) crystalline solids 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 hv 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



Fig. 10-15 Various aspects of the Fermi surface of Cu. (a) The Brillouin zone of an fcc lattice with some special points labeled. (b) A (110) section of the Brillouin zone. See the text for the meaning of the internal curves. (c) The proposed Fermi surface of Cu. (d) The extended zone picture of a (110) section of the Fermi surface showing the dog bone orbits.

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





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



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



Quantized discretely along z-direction Energy levels depend on film thickness *L*

Nearly free electron like in xy-plane

Bulk projected bands along ΓL of Au and Ag, respectively





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
0.2 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)

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

 ε_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 = 2Σ "

Many-Body Effects in Angle-Resolved Photoemission: Quasiparticle Energy and Lifetime of a Mo(110) Surface State

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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.



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. $\Delta k_{\parallel}(1/\text{\AA})=0.5123 \sqrt{(E_k(eV)) \cos(\theta) \Delta \theta}$

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.

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

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. Ce³⁺ (4f¹) Intensity enhanced by absorption Predominantly 4f DOS 4f mixed with other DOS e e intermediate state 4f 4f 4f E_{F} E_{F} 4f 4f 4f Auger like Absorption + emission 3d/4d 3d/4d 3d/4d **Resonance PE** Direct PE

letters to nature

2000

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

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



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.

Valence Transition of YbInCu₄ Observed in Hard X-Ray Photoemission Spectra

Hitoshi Sato,^{1,*} Kenya Shimada,¹ Masashi Arita,¹ Koichi Hiraoka,² Kenichi Kojima,³ Yukiharu Takeda,^{1,†} 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 Tamasaku,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



 $hv = 6 \text{ keV}, \Delta E \sim 0.24 \text{ eV}$ 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

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) WEBRAM, 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 HXPES, fixed installation)
- * SPring-8 BL12XU-SL (NSRRC, fixed installation) unique with dual analyzers
- * ESRF ID16 (mainly for IXS, used by VOLPE)
- * ESRF ID32 (fixed installation, shared with XRD)
- * ESRF 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 SXRMB BM (wide range 1.7-10 keV)
- * APS (?)

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 (σ · λ) 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



Trzhaskovskaya et al., ADNDT 2001,2006

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



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

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

β -parameters @ hv= 5-10 keV

Cu 3*d* 0.48 - 0.32

Cu 4*s* 1.985

Zn 3*d* 0.50 - 0.33

Zn 4*s* 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

 \rightarrow choose suitable experimental geometry !



HAXPES Commissioning: Horizontal vs Vertical geometries



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





Layout of the side beamline of BL12XU



Horizontal geometryVertical geometryFor selecting different orbital symmetries in valence band

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 Ni²⁺ 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 NiO₆ cluster

Implications:

- 1. First ionization state is ²E (compensated spin, (photo)hole in the mixed state made of e_g (d⁷) and O $2p_\sigma$ (d⁸L) (ZR-doublet), instead of ⁴T₁ (atomic-like Hund's rule high spin, d⁷, 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 LaAlO₃ and SrTiO₃ 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.

Electronic reconstruction



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

¹/₂ e transferred Nakagawa et al., Nature Mater. 5, 204 (2006)

Hard X-ray Photoemission Spectroscopy (HAXPES)



 \Rightarrow 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</p>

Our approach:

- * grazing incidence near total external reflection to enhance photon field near the surface and interface region for better detection of Ti³⁺ near the interface
- * higher photon energy (6.5 keV) to increase probing depth



LaAIO₃/SrTiO₃ (001)





Measure intensity ratio Ti³⁺/Ti⁴⁺ as a function of incident angle





Chu et al., Appl. Phys. Lett. 99, 262101 (2011)

 $d_2 = 48.3 \pm 20.3 \text{ A}$ ~ 12 u.c.

 $\alpha = 0.021$ (Ti³⁺/T⁴⁺ in *d*₂)

Total carriers ~ 0.24 e / 2D u.c.

Consistent with electronic reconstruction but only half the amount O vacancies? Challenging future directions of Photoemission Spectroscopy

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

2. Time-resolved PES.

Pump-probe: dynamics.

Need efficient detection and brighter sources. lasers or laser+SR.

Thanks for your attention