Basic principles and applications of ARPES and Spin-ARPES

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Outline

• A brief introduction to photoemission
  • History
  • Theory
  • Experimental requirements

• Valence band photoemission
  • Refreshing solid state physics concepts
  • ARPES
    • Spin ARPES → complete photoemission experiment

• Complete photoemission experiment @ Elettra

• ARPES and Spin-ARPES station: @
1887 - Photoelectric Effect

Observed by Heinrich Hertz 1887
- P. Lenard: measuring kinetic energy of photoelectrons in retarding field

Experimental observations:

- Measured photoelectron current increases with photon intensity

- Maximum energy of the (photo)electrons depends on light frequency (contrary to classical expectation)
1905 – Explained by Albert Einstein

I won the Nobel prize for the Photoelectric Effect

You've probably never heard of it.

The Nobel Prize in Physics 1921

Albert Einstein

Prize share: 1/1

The Nobel Prize in Physics 1921 was awarded to Albert Einstein "for his services to Theoretical Physics, and especially for his discovery of the law of the photoelectric effect".
1905 – Photoelectric effect according to Einstein

- Electrons inside material absorb incoming light quanta - photons

- If their energy is sufficiently high they leave the material carrying info on their properties inside the material

Photoemission
Birth of photoemission 1950s

ideal tool for the chemical investigation of surfaces and thin film, expressed in the famous acronym created by Siegbahn: **ESCA** (electron spectroscopy for chemical analysis) or **XPS** – X-ray Photoelectron/Photoemission Spectroscopy
Atom → Solid Cartoon

Localized core electrons

Localized core electrons
Delocalized valence electrons (energy bands)
What do we learn from photoemitted electrons?

$$E_{\text{kin}} = h\nu - E_B - \Phi$$

Core electrons (XPS):
composition, chemical bonding, valence, density of states, electronic correlations

$\text{Bi}_2\text{Se}_3$ topological insulator

C. Bigi, Master Thesis
Uni. Milano 2016

G. Panaccione et al.
New J Phys 2011
Experimental requirements for XPS (ESCA)

Laboratory
- X-rays - generated by bombarding a metallic anode with high-energy electrons
- UV - noble gas discharge lamps

Synchrotrons
- Tunable and polarized UV \( \rightarrow \) hard X-rays

Whatever you wish as long as sufficiently conductive...

Surface sensitivity - surfaces are an issue...

Hemispherical electron energy analyzer

Channeltron MCP
Experimental requirements – real life

End station of APE – LE beamline at Elettra

Sample manipulator

Sample surface preparation chamber

ARPES chamber

Hemispherical electron energy analyzer

Photons
- Number of electrons reaching the surface is reduced by electron-electron scattering

\[ \rightarrow \text{Only sensitive to first couple of atomic layers}!! \rightarrow \text{Clean surfaces} \text{ and UHV needed} \]

- Scattered electrons with lower kinetic energies form background (secondaries)
Valence electron photoemission

ARPES

Spin-ARPES

Transport properties of a solids are determined by electrons near $E_F$ (conductivity, magnetoresistance, superconductivity, magnetism)
Valence band photoemission
Atom → Solid Cartoon

Localized core electrons

Localized core electrons
Delocalized valence electrons (energy bands)

Energy

Vacuum level
Real vs. reciprocal (momentum or $k$-)space

Free electron vs. electron in a lattice:

Periodic potential $\rightarrow$ electronic bands and band gaps
Classification of materials according to the filling of the electronic bands

...when things get more complicated and electrons interact: **fingerprints of electronic correlations**
The question is...

Can $E$ vs. $k$ (i.e., the electronic band structure of solids) be directly measured?

... and the answer...

Yes!
Valence band photoemission with angular resolution: Angle-Resolved PhotoEmission Spectroscopy - ARPES
What do we learn from photoemitted valence electrons?

Energy conservation

\[ E_{\text{kin}} = h\nu - E_B - \Phi \]

Momentum conservation

Inside the crystal:

\[ \vec{k}_f = \vec{k}_i + \vec{k}_{hv} \]
\[ \vec{k}_f = \vec{k}_i \]

Refraction on the surface (Snell’s law):

\[
\begin{align*}
  k_{\text{out}} &= \sqrt{\frac{2m}{\hbar^2}} E_{\text{kin}} \\
  k_{\text{in}} &= \sqrt{\frac{2m}{\hbar^2}} (E_{\text{kin}} + V_0) \\
  k_{\text{in}} || &= k_{\text{out}} || 
\end{align*}
\]

\[
\begin{align*}
  k_{\text{in}} || &= \sin \theta_{\text{out}} \sqrt{\frac{2m}{\hbar^2}} E_{\text{kin}} = \sin \theta_{\text{in}} \sqrt{\frac{2m}{\hbar^2}} (E_{\text{kin}} + V_0) \\
  E_{\text{kin}} &= E_V - E_F \\
  V_0 &= V_0
\end{align*}
\]
What do we learn from photoemitted *valence* electrons?

Measure:
- **Kinetic energy** of the photoemitted electrons
- **Angle** at which they are emitted

\[ E_{\text{kin}} = h\nu - E_B - \Phi \]

Textbook example – the electronic band structure of copper:

- **Core levels**
- **Valence levels**
- **SP band**
- **D band**
- **Surface state**

Courtesy of H. Dil
How do we handle the angle of the photoemitted electrons?

- Large angular acceptance (~30°)

- Analyzer electronic lenses keep track of the electrons emitted at different angles

- 2d detection (MCP)

→ Dispersion along the analyzer slit directly measured (i.e. dispersion along one line in k space)
Band mapping: 2d surface state on Au(111) surface

- 2d electron gas – parabolic dispersion, circular Fermi contour - expected

- and measured by ARPES

$E_B = \text{const}$

$k_x = \text{const}$

$k_y = \text{const}$
Back to textbooks: 1D $\rightarrow$ 2D $\rightarrow$ 3D

1D: Constant energy points
2D: Constant energy circles
3D: Constant energy spheres
Fermi surface mapping – Fermi surface of copper

- 3d Fermi surface of Cu:
  Almost (but not really) free electrons: the sphere is not perfect – the necks connect the spheres in the subsequent Brillouin zones

- With single photon energy ARPES measures a spherical cut through the 3d Fermi surface

Surface state Fermi contour (perfect circle)
Periodic Table of the Fermi Surfaces of Elemental Solids

Tat-Sang Choy, Jeffery Naset, Selman Hershfield, and Christopher Stanton
Physics Department, University of Florida

Jian Chen
Seagate Technology
(15 March, 2000)

Ferromagnets:

Alternate Structures:


This work is supported by NSF, AFOSR, Research Corporation, and a Sun Microsystems Academic Equipment Grant.
Principal boost to ARPES development

The Nobel Prize in Physics 1987

J. Georg Bednorz, K. Alex Müller

The Nobel Prize in Physics 1987 was awarded jointly to J. Georg Bednorz and K. Alexander Müller "for their important breakthrough in the discovery of superconductivity in ceramic materials"

Searching for the mechanism of high Tc superconductivity → room temperature superconductivity!!!
ARPES – stone age

High Tc cuprates:
Band mapping and Fermi surface mapping... by hand

Superconducting gap:

Energy resolution < 10 meV; angular resolution ~1°
Milestone: Development of two dimensional detectors

→ Images rather than spectra, BUT still composed of spectra!!!

 ARPES evolution

Energy resolution \(\sim 1\) meV; angular resolution \(\sim 0.1^\circ\)
What do we learn from the ARPES SPECTRA?

Intuitive (NOT exact) three-step model of the photoemission process:
Three-step model: step 1

Transition probability from initial to final state under the excitation by the photon with vector potential $\mathbf{A}$

$$w_{fi} = \frac{2\pi}{\hbar} \left| \langle f \left| H_{\text{int}} \right| i \rangle \right|^2 \delta(E_f - E_i - \hbar \nu)$$

$$H_{\text{int}} = \frac{e}{mc} \mathbf{A} \cdot \mathbf{p}$$

Optical transition in the solid:
- Energy is conserved
  $$E_f = E_i + \hbar \nu$$
- Wave vector is conserved modulo $\mathbf{G}$
  $$\mathbf{k}_f = \mathbf{k}_i + \mathbf{G}$$
Inelastic scattering of the photoelectron with
- other electrons
  (excitation of e-h-pairs, plasmons)
- phonons

- Generation of secondary electrons
  "inelastic background"
- Loss of energy and momentum information in the photoelectron current:
  inelastic mean free path
Three-step model: step 3

The lowest energy electrons can’t exceed the work function potential

\[ E_{\text{kin}} = h \nu - E_B - \Phi \]

Surface breaks crystal symmetry \( k_\perp \) is not a good quantum number

\[
k_{\text{out}} = \sqrt{\frac{2m}{\hbar^2}} E_{\text{kin}}
\]

\[
k_{\text{in}} = \sqrt{\frac{2m}{\hbar^2}} (E_{\text{kin}} + V_0)
\]

\[
k_{\text{out}} \parallel = k_{\text{in}} \parallel = k_\parallel = \sin \theta_{\text{out}} \sqrt{\frac{2m}{\hbar^2}} E_{\text{kin}} = \sin \theta_{\text{in}} \sqrt{\frac{2m}{\hbar^2}} (E_{\text{kin}} + V_0)
\]
Exact one-step vs. intuitive three-step model

The three-step model is a strong simplification; quantitative description only possible by matching wave function of initial and final state.
Photoemission intensity is directly related with...

One particle Green’s function

\[ G(x,t,x',t') = -i \langle N,0 | T [ \Psi(x,t) \Psi^+(x',t') ] | N,0 \rangle \]

How?

Starting from the Fermi golden rule

the transition probability from the initial state \( |N,0\rangle \) to a final state \( |N,s\rangle \) with a photoelectron of energy \( \epsilon_\kappa \) and momentum \( \kappa \) is given by

\[ p(\epsilon_\kappa) = \frac{2\pi}{\hbar} \sum_s |\langle N,s | H_{\text{int}} | N,0 \rangle|^2 \delta(E^N_s - E^N_0 - \hbar \omega) = ... \]

Dipole approximation, Sudden approximation - the photoelectron is instantaneously created and decoupled form the remaining N-1 electron system

\[ ... = \frac{2\pi}{\hbar} |M_{kk}|^2 A(\kappa,\omega) = \frac{2\pi}{\hbar} |M_{kk}|^2 \frac{1}{\pi} \text{Im} G^<(\kappa,\omega) \]
Beyond images—spectral line-shape & electronic correlations

\[
I(k, \omega) \propto \left| \langle f | \vec{A} \cdot \vec{p} | i \rangle \right|^2 A(k, \omega) f(\omega)
\]

\[
f(\omega) = \frac{1}{1 + e^{(\omega - \mu)/kT}}
\]

\[
G(\vec{k}, \omega) = \frac{1}{\omega - \varepsilon_k - i\eta}, \eta \rightarrow 0
\]

\[
A(\vec{k}, \omega) = \delta(\omega - \varepsilon_k)
\]

\[
G(\vec{k}, \omega) = \frac{1}{\omega - \varepsilon_k - \Sigma(\vec{k}, \omega)}
\]

\[
A(\vec{k}, \omega) = \frac{1}{\pi} \left| \frac{\text{Im} \Sigma(\vec{k}, \omega)}{\omega - \varepsilon_k - \text{Re} \Sigma(\vec{k}, \omega)} \right|^2 + \left| \text{Im} \Sigma(\vec{k}, \omega) \right|^2
\]
Matrix elements – orbital character of the bands

\[ I(k, \omega) \propto \left| \langle f | \vec{A} \cdot \vec{p} | i \rangle \right|^2 A(k, \omega) f(\omega) \]

\[ H_{int} = A \cdot p \]

The light beam and the analyser define the **scattering plane**.

If to be detected, the photoelectron final state **has to be even** under reflection in the scattering plane.

Access to the **symmetries** (i.e. Orbital character) of the initial state in the solid.
Prevalent s- or p- character of the Be(0001) surface states

I. Vobornik et al., PRB 2005, PRL 2007
ARPES w/ synchrotron radiation: powerful tool in investigation of electronic properties of materials – electronic band structure, orbital character, correlations

**Dirac dispersion and Fermi surface in PbBi₆Te₁₀**
M. Papagno et al., ACS Nano 2016

**PdTe₂**
M. S. Bahramy, Nature Materials 2018

**Au(001) surface states**
S. Bengio et al. PRB 2012

**Te-rich GeTe(111) - Sₜ**
G. Manzoni et al., PRL 2016

**WTe₂**

**ZrTe₅ band structure**
G. Manzoni et al., PRL 2016

**GeTe**
C. Rinaldi et al., Nano Letters 2018
ARPES and 21st century materials

Electronic materials
Spintronic materials
Functional materials
QUANTUM materials!
2004: graphene came into scene

- **The thinnest possible material** - only one atom thick
- **Ballistic conduction** - charge carriers travel for $\mu$m w/o scattering
- **The material with the largest surface area per unit weight** – 1 gram of graphene can cover several football stadiums
- **The strongest material** – 40 N/m, theoretical limit
- **The stiffest known material** - stiffer than diamond
- **The most stretchable crystal** – can be stretched as much as 20%
- **The most thermal conductive material** - $\sim$5000 Wm\(^{-1}\)K\(^{-1}\) at room temperature
- **Impermeable to gases** – even for helium
Application areas of Graphene

- Car interior
- Construction materials
- Interior and wings of aeroplanes
- Antimicrobial materials
- Lubricants
- Wings of wind turbines
- Flame retardants
- Battery and supercapacitors
Dirac electrons enter the condensed matter physics...

Conical (linear) Dirac dispersion and point-like Fermi surface measured by ARPES:


... and not only in graphene: topological insulators

Conical (linear) Dirac dispersion
and
Spin-momentum locking

Characterized with well defined spin texture

The technique of choice: Spin-ARPES!
... more textbooks → beyond Ashcroft-Mermin/Kitell

The concepts of high energy physics within condensed matter!
Quantum Materials in **20th century**

- Metal
- Semimetal
- Semiconductor
- Insulator
- Metal $\rightarrow$ Insulator transition (High $T_c$) superconductivity

Quantum Materials in **21st century**

- Graphene
- Topological insulators
- Quantum materials

Google Scholar hits: "Graphene" vs "Quantum materials" vs "Topological insulators" over the years (2000-2016).
Transition metal dichalcogenides (TMDCs)

- **Layered structure** with strong intra-layer covalent bonding and weak (van der Waals type) inter-layer coupling

- Exhibit **wide variety of physical properties** – semimetals ($\text{WTe}_2$, $\text{TiSe}_2$), metals ($\text{NbS}_2$, $\text{VSe}_2$), semiconductors ($\text{MoS}_2$, $\text{MoSe}_2$), superconductors ($\text{NbSe}_2$, $\text{TaS}_2$)

- Properties often conditioned by the **number of layers**

- Host spin polarized electrons and/or Dirac/Weyl fermions
Quantum Materials in 21st century – High energy physics concepts within condensed matter

- Low-dimensional materials (2D, surfaces, few atomic layers)
- The Bloch wave functions follow Dirac-like or Weyl-like equations at vicinity of some special points of the Brillouin zone
- Envisioned applications: spintronics, quantum computing, etc.

- The materials characterized by particular spin texture → ARPES Milestone: High-resolution Spin-ARPES
What else do we learn from photoemitted electrons?

Spin:

magnetism, spin texture in the systems with strong spin-orbit interaction

Spin - ARPES: $E(k)$, Spin

Complete set of quantum numbers of photoemitted electron

Complete photoemission experiment!
Exchange-split spin-polarized bands in ferromagnetic iron

Detecting electron’s spin: spin-dependent scattering

- **MOTT scattering**
  - spin-orbit interaction
  - left-right asymmetry
  - >25keV
  - commercial
  - Au target
  - FOM $10^{-4}$

- **VLEED scattering**
  - magnetic exchange interaction
  - parallel-antiparallel asymmetry
  - <15eV
  - non-commercial
  - FeO target
  - FOM $10^{-2}$
Target magnetization dependent intensity asymmetry between spin up and spin down electrons

If the target is magnetized Up / Down, the incoming electrons with spin-up/down will be reflected more (top/bottom panel)

If the primary beam is polarized, then non-zero asymmetry value will be measure.

Resulting ARPES spectra →
Spin-integrated vs. spin-resolved ARPES

\[ P = \frac{1}{S} \frac{E D C_{m\uparrow} - E D C_{m\downarrow}}{E D C_{m\uparrow} + E D C_{m\downarrow}}, \]

\[ S E D C_{\uparrow\downarrow} = \frac{(1 + P)(E D C_{m\uparrow} + E D C_{m\downarrow})}{2}. \]

Spin integrated

Au(111) surface state

Spin resolved

Au(111) surface state

Spin integrated

Bi\textsubscript{2}Se\textsubscript{3} topological surface state

Spin resolved

Bi\textsubscript{2}Se\textsubscript{3} topological surface state
VLEED based spin-ARPES scheme

Two scattering chambers

In each two orthogonal directions of spin can be measured

Vectorial (3d) spin analysis
Magnetization coils outside... ... and inside the scattering chamber
VESPA: spin polarimeter @ APE

- **VESPA**: Very Efficient Spin Polarization Analysis
- Designed, built and commissioned in Trieste (CNR-IOM, NFFA)
- Operates from Dec. 2015 at APE beamline @ Elettra
APE: Advanced Photoelectric effect Experiments

Two independent, off-axis, variable polarization (APPLE type) undulators
→ two independent canted beamlines operating simultaneously
→ First users: 2003

- **APE – High Energy (150-1600 eV)**
  - XPS spectroscopy
  - X-ray absorption (XAS, XMCD, XMLD)

- **APE – Low Energy (8-120 eV)**
  - High-resolution ARPES @ Spin-ARPES
  - Electronic band structure
  - Fermi surface mapping
  - Fermi surface instabilities
APE surface science laboratory

Variable polarization photons 150-1600 eV

Users’ docking ports

Load-lock

Sample preparation

MO Kerr effect; LEED/Auger
Sample growth and prep.

Distribution center

APE-LE

Variable polarization photons 8-120 eV

VG Scienta DA30 analyzer + 2 VLEED spin polarimeters

Omicron EA125

APE-HE

S segregation on Fe(100)

Fe(100) Fermi surface

Bc(0001), hv=32.5 eV
Complete Photoemission Experiment @ beamline APE

- **APE – High Energy (150-1600 eV)**
  - XPS spectroscopy
  - X-ray absorption (XAS, XMCD, XMLD)
  - **NEW:** Spectroscopy in-operando and ambient pressure

- **APE – Low Energy (8-120 eV)**
  - High-resolution ARPES
  - Electronic band structure
  - Fermi surface mapping
  - Fermi surface instabilities
  - **NEW:** Spin-resolved ARPES
Spin-resolved ARPES at beamline APE (CNR-IOM, NFFA)

In search for spin polarized electrons for future spintronic materials

- **VESPA:** Very Efficient Spin Polarization Analysis
- Designed, built and commissioned in Trieste (CNR-IOM, NFFA)
- Operates from 2015 at APE beamline @ Elettra
- C. Bigi et al. JSR (2017) 24, 750-756, on the title page of JSR:

**Some recent results:**

Maximizing Rashba-like spin splitting in PtCo$_2$

Surface induced symmetry breaking enhances spin-orbit interaction and induces spin polarized electrons on the surface of PtCo$_2$.

Co-existence of type-I and type-II three dimensional bulk Dirac fermions in PdTe$_2$
M.S. Bahramy *et al*., *Nature Materials*, 2018

Spin-resolved ARPES data confirm the helical spin texture of the two surface states in PdTe$_2$, and therefore their topological nature.

Weyl electrons on the surface of MoTe$_2$
J. Jiang *et al*., *Nature Communications* 8, 13973 (2017)

Measured spin polarization provides evidence of the presence of Weyl electrons in MoTe$_2$. 
Latest result: Spin-Fermi surface mapping

O.J. Clark et al., PRL 2018
After this lecture...

→ feeling of what ARPES and Spin-ARPES can do for you

→ If interested in quantum properties of materials - electronic band structures, Fermi surfaces, electronic correlations, spin polarization:

http://www.elettra.trieste.it/elettra-beamlines/ape.html

http://www.trieste.nffea.eu/
Interested in learning more?

**ARPES:**
- S. Suga, A. Sekiyama, Photoelectron Spectroscopy – Bulk and Surface Electronic Structures (Berlin, Springer, 2014)

**Spin-ARPES:**
- Chiara Bigi et al., J. Synchrotron Rad. 24, 750-756 (2017)
Photoemission relations

\[ E_{\text{kin}} = h \nu - E_B - \Phi \]

\[
\begin{align*}
  w_{fi} &= \frac{2\pi}{\hbar} \left| \langle f \left| H_{\text{int}} \right| i \rangle \right|^2 \delta(E_f - E_i - h\nu) \\
  H_{\text{int}} &= \frac{e}{mc} \vec{A} \cdot \vec{p} \\
  I(\vec{k}, \omega) &\propto \left| \langle f \left| \vec{A} \cdot \vec{p} \right| i \rangle \right|^2 A(\vec{k}, \omega) f(\omega) \\
  A(\vec{k}, \omega) &= \frac{1}{\pi} \frac{|\text{Im} \Sigma(\vec{k}, \omega)|}{\left( \omega - \varepsilon_k - \text{Re} \Sigma(\vec{k}, \omega) \right)^2 + |\text{Im} \Sigma(\vec{k}, \omega)|^2} \\
  f(\omega) &= \frac{1}{1 + e^{(\omega - \mu)/kT}}
\end{align*}
\]

\[
\begin{align*}
  k_{\text{out}} &= \sqrt{\frac{2m}{\hbar^2} E_{\text{kin}}} \\
  k_{\text{in}} &= \sqrt{\frac{2m}{\hbar^2} (E_{\text{kin}} + V_0)} \\
  k_{\text{out}} \parallel = k_{\text{in}} \parallel &\equiv k_{\parallel} = \sin \theta_{\text{out}} \sqrt{\frac{2m}{\hbar^2} E_{\text{kin}}} = \sin \theta_{\text{in}} \sqrt{\frac{2m}{\hbar^2} (E_{\text{kin}} + V_0)}
\end{align*}
\]