From Einstein’s Photoelectric Effect to Band Mapping

Kyle Shen

PARADIM Summer School

July 11, 2019
Overview of ARPES Lectures & Labs

Thursday, July 11

• Lecture #1 : From Einstein’s Photoelectric Effect to Band Mapping
• Lecture #2 : From Particles to Quasiparticles : Understanding & Measuring Interactions by ARPES
• Lab Lecture : Introduction to ARPES Labs

Friday, July 12

• Lecture #3 : ARPES Studies of Quantum Materials
• Lecture #4 : Frontiers in ARPES
• Lab Lecture : Writing a PARADIM proposal

ARPES Labs

• Lab A : ARPES on MBE-grown thin films (Duffield 308)
• Lab B : PARADIM ARPES Lab

BLUE : Kyle Shen      RED : Luca Moreschini
Angle Resolved PhotoElectron Spectroscopy
FIRST EVIDENCE FOR THE QUANTIZATION OF LIGHT!
Velocity and direction of the electrons in the solid

Low-energy Electronic Structure  →  Macroscopic Physical Properties
Superconductivity, Magnetism, Density Waves, ....
• The Brownian motion
  "On the motion of small particles suspended in liquids at rest required by the molecular-kinetic theory of heat."
  Annalen der Physik, 17 (1905), pp. 549-560.

• The photoelectric effect
  "On a heuristic viewpoint concerning the production and transformation of light"

• The special theory of relativity
  "On the electrodynamics of moving bodies"
  Annalen der Physik, 17 (1905), pp. 891-921

• Mass-energy Equivalency $E=mc^2$
  "Does the inertia of a body depend on its energy?"
1905: Einstein’ hypothesis: light quanta with $E = h\nu = \frac{hc}{\lambda}$

The maximum $E_{\text{kin}} = \frac{1}{2}mv^2$ is proportional to the FREQUENCY but depends also on the material work function $W$

The NUMBER of electrons is proportional only to the INTENSITY
In 1913 Einstein was elected to the Prussian Academy of Sciences and appointed to a research position in Berlin. In his nomination speech to the Prussian Academy, Planck says:

"Summing up, we may say that there is hardly one among the great problems in which modern physics is so rich, to which Einstein has not made an important contribution. That he may sometimes have missed the target in his speculations, as for example, in his hypothesis of light quanta, cannot really be held too much against him, for it is not possible to introduce fundamentally new ideas, even in the most exact sciences, without occasionally taking a risk".
a brief history of photoemission spectroscopy

1887: discovery of photoelectric effect by Hertz

1905: quantization of light by Einstein: $E_{\text{max}} = h\nu - \phi$

1957: x-ray photoelectron spectroscopy for chemical analysis (XPS or ESCA) by Siegbahn and others

1960s: ultraviolet photoemission spectroscopy (UPS) by Spicer, Turner, others

1970s: angle-resolved photoemission spectroscopy (ARPES) by Spicer, Smith, others

1980s – present day: widely used as materials characterization tool
Modern applications of photoemission

Measuring quasiparticle band velocities & band masses

\[ \hbar v_k = \frac{\partial \varepsilon}{\partial k} \]

\[ m_k^{-1} = \left( \hbar^{-2} \frac{\partial^2 \varepsilon}{\partial k^2} \right) \]

\[ \varepsilon = \frac{\hbar^2 k^2}{2m^*} \]

Reinert & Hufner NJP 2005

Zhou et al., Nature Physics 2006
Quantum materials investigated by ARPES

Cuprate Superconductors

Fe-based Superconductors

2D Materials

Topological Materials

Superlattices & Interfaces

Complex Oxides


Electron ionization levels are formed from discrete levels in an atom

Energy conservation: \( h\nu - E_I = KE \)

Energy levels of ionized Ne^+:
- 1s
- 2s
- 2p_{1/2}
- 2p_{3/2}

Photoelectron intensity:
- no need to be on resonance or scan photon energies (e.g. NMR, optical measurements).

Just need photons to have high enough energy!
photoemission from solids: an array of atoms

- Deeply bound "core" electrons remain basically unchanged.
- Outermost "valence" electrons hybridize forming continuous "energy bands".

Na metal (Ne + one 3s electron)
Electrons in reciprocal space: momentum states

Wave functions in a 1D lattice

Allowed electronic states
Repeated-zone scheme

1D chain of atoms

First Brillouin zone
Second Brillouin zone

Second Brillouin zone

Courtesy of Andrea Damascelli
Electrons in reciprocal space: momentum states

Many properties of a solid are determined by electrons near $E_F$ (conductivity, magnetoresistance, superconductivity, magnetism).

Only a narrow energy slice around $E_F$ is relevant for these properties ($kT=25$ meV at room temperature).

Courtesy of Andrea Damascelli
Kinematics of the ARPES process

Kinetic energy conservation laws:

\[ K = p / \hbar = \sqrt{2mE_{\text{kin}}} / \hbar \]

- \[ K_x = \frac{1}{\hbar} \sqrt{2mE_{\text{kin}}} \sin \vartheta \cos \varphi \]
- \[ K_y = \frac{1}{\hbar} \sqrt{2mE_{\text{kin}}} \sin \vartheta \sin \varphi \]
- \[ K_z = \frac{1}{\hbar} \sqrt{2mE_{\text{kin}}} \cos \vartheta \]

Vacuum:

- \[ E_{\text{kin}} \]
- \[ K \]

Conservation laws:

- \[ E_f - E_i = \hbar \nu \]
- \[ k_f - k_i = k_{\hbar \nu} \]

Solid:

- \[ E_B \]
- \[ k \]

Courtesy of Andrea Damascelli
Kinematics of the ARPES process: Energy Conservation

Energy Conservation

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

Momentum Conservation

\[ \hbar k_\parallel = \hbar K_\parallel = \sqrt{2mE_{\text{kin}}} \cdot \sin\vartheta \]
Kinematics of the ARPES process: Momentum Conservation

Energy Conservation
\[ E_{\text{kin}} = h\nu - \phi - |E_B| \]

Momentum Conservation
\[ \hbar k_{||} = \hbar |K_{||}| = \sqrt{2mE_{\text{kin}}} \cdot \sin\theta \]

Electrons in Reciprocal Space

Sample

Electron analyzer

Courtesy of Andrea Damascelli
a simple example of ARPES: 2D free electron gas on Cu (111)

\[ E = \frac{\hbar^2 k^2}{2m^*} \]

F. Baumberger et al., PRB 64, 195411 (2001)
Sudden Approximation in ARPES

Photoemission Intensity $I(k, \omega) \quad \left\{ \begin{array}{c} \omega_{fi} \propto \left| \langle \phi_f^k | A \cdot p | \phi_i^k \rangle \right|^2 \left\langle \Psi_m^{N-1} | \Psi_i^{N-1} \right\rangle^2 \delta(\omega - h\nu) \end{array} \right.$

Sudden approximation

One Slater determinant

$\Psi_f^N = A \phi_f^k \Psi_f^{N-1}$

$\Psi_i^N = A \phi_i^k \Psi_i^{N-1}$

Excitation in the solid

Vacuum

Spectrum

Courtesy of Andrea Damascelli
One-step vs. Three-step model of photoemission

Photoemission Intensity $I(k, \omega)$

$$w_{f,i} \propto \left| \langle \Psi_f^N | A \cdot p | \Psi_i^N \rangle \right|^2 \delta(E_f^N - E_i^N - h\nu)$$

One-step model

- Excitation into a damped final state
- Wave matching at the surface

Three-step model

1. Excitation into a bulk final state
2. Travel to the surface
3. Transmission through the surface

Courtesy of Andrea Damascelli
"Universal Curve" of Mean-free path for excited electrons

Seah, Dench et al., SIA 1, 2 (1979)


Courtesy of Andrea Damascelli
Transmission of electrons through the surface

We approximate the surface as a square potential barrier.

\[ V_0 = \text{Surface potential step} \]
\[ \text{“inner potential”} \]

We assume the electrons outside the sample have energy

\[ E = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m} \]

Can think of a analogous “Snell’s Law” for photoemission, where the in-plane momentum is conserved and the out-of-plane momentum changes due to scattering off the potential barrier (work function)

Courtesy of Eli Rotenberg
inner potential and determination of $k_z$

Free-electron final state

$$E_f(k) = \frac{\hbar^2 k^2}{2m} - |E_0| = \frac{\hbar^2 (k_\parallel^2 + k_\perp^2)}{2m} - |E_0|$$

because

$$\frac{\hbar^2 k^2}{2m} = E_{\text{kin}} \sin^2 \vartheta \quad E_f = E_{\text{kin}} + \phi \quad V_0 = |E_0| + \phi$$

$${k_\perp} = \frac{1}{\hbar} \sqrt{2m(E_{\text{kin}} \cos^2 \vartheta + V_0)}$$
Schematic of the ARPES process

- Photon source
- Energy analyser
- Sample

UHV - Ultra High Vacuum
\( p < 10^{-7} \text{ mbar} \)
We know the angle ($\theta$) and energy ($E$) of the outgoing electron. We also know the momentum (~zero) and the energy of the exciting photon.

We can easily work out the relationship between the measured $\theta$ & $E$ and originating $k$ & $E$ of the electrons in the solid.

This is everything we like to know about the internal electronic states of the solid (except spin!)
ARPES data acquisition

A spectrum at a single momentum $k_x$

Accumulate spectra as the momentum $k_x$ is scanned

Courtesy of Eli Rotenberg
Three-dimensional electronic structure mapping

\[ k_\perp = \frac{1}{\hbar} \sqrt{2m \left( E_{kin} \cos^2 \vartheta + V_0 \right)} \]

3D FS
(e.g. FS from bulk state)

2D FS
(e.g. FS from surface state)

\[ E_k = \frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2) \]

Courtesy of Eli Rotenberg
photon sources for photoemission can be…

<table>
<thead>
<tr>
<th>Photon Source</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>X-ray tubes</strong></td>
<td>Most common sources for XPS (Al, Mg anodes), can be used with grating for better energy resolution (1000-10,000 eV, $\Delta E \sim 0.1-1$ eV)</td>
</tr>
<tr>
<td><strong>Plasma Discharge</strong></td>
<td>Narrow bandwidth, high intensity lamps in VUV (10-100 eV, $\Delta E \sim 0.001$ eV); used for ARPES</td>
</tr>
<tr>
<td><strong>Synchrotrons</strong></td>
<td>Complete control over photon beam (energy, polarization, resolution); user facilities</td>
</tr>
<tr>
<td><strong>Lasers</strong></td>
<td>Higher harmonic generation; low energy (&gt; 10 eV). Pump-probe, or high resolution</td>
</tr>
</tbody>
</table>

**Photon source must be:**
1. Monochromatic
2. High intensity ($> 10^9$ s$^{-1}$)
3. Energetic ($h\nu > \phi \sim 5$ eV)
photoemission at different photon energy ranges

<table>
<thead>
<tr>
<th>$h\nu$ (eV)</th>
<th>$\Delta E$ &amp; $\Delta k$</th>
<th>Cross Section</th>
<th>Primarily Used For / Special Capabilities</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 – 100 eV</td>
<td>$10^{-3}$ eV, $10^{-3}$ A$^{-1}$</td>
<td>$10^{-1}$ (Mb / atom)</td>
<td>High-resolution studies of electronic structure &amp; surfaces, Fermi surface &amp; band mapping, low-energy physics</td>
</tr>
<tr>
<td>100 – 1000 eV</td>
<td>$10^{-2}$ eV, $10^{-2}$ A$^{-1}$</td>
<td>$10^{-2}$ – $10^{-4}$ (Mb / atom)</td>
<td>Resonant photoemission X-ray absorption / magnetic dichroism XPS (elemental chemical analysis)</td>
</tr>
<tr>
<td>1000 – 10,000 eV</td>
<td>$10^{-1}$ eV, $10^{-1}$ A$^{-1}$</td>
<td>$10^{-2}$ – $10^{-4}$ (Mb / atom)</td>
<td>Bulk sensitivity Elemental &amp; chemical analysis Changing orbital cross-sections</td>
</tr>
</tbody>
</table>
Evolution of instrumental resolution over time

Heimann, 1977

Kevan, 1987

Paniago, 1995

Nicolay, 2000

F. Reinert et al., PRB (2001)

VG Scienta R4000 Analyzer

\( \Delta E < 0.0008 \text{ eV} \)

T. Kiss et al., PRL 2005

Evolution of instrumental resolution over time

F. Reinert et al., PRB (2001)
a few things to keep in mind about ARPES

• mean free path (mfp) of photoelectrons in solids is \( \sim 1 \) nanometer. Measurements are sensitive to top unit cells & monolayers

• short mfp means sample surfaces must be kept pristine (no adsorbed gases) in ultrahigh vacuum (UHV - \( 10^{-10} \) torr)

• need to reduce stray electromagnetic fields (deflection)

• infeasible to measure samples in vivo or in solution
layout of a synchrotron beamline

- No good windows for “soft” x-ray, VUV range (10-1000 eV)
- Reflectivities of mirrors in VUV, soft x-ray range of ~ 50%
- Typical resolving powers (ΔE / E) of ~ 3000 : 1
Beamtime at synchrotrons is free of charge – granted based on merit of proposal

Considerations to take into account regarding where to apply:

• what photon energy range, resolution, polarization is needed?
• sample handling capabilities and specialization of endstation
• demand on endstation / beamline
• ease of use / productivity of facility
<table>
<thead>
<tr>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>• surface sensitive (nanometer probe depth)</td>
<td>• bulk insensitive (nanometer probe depth)</td>
</tr>
<tr>
<td>• high elemental sensitivity / specificity</td>
<td>• ultrahigh vacuum necessary (can limit types of samples studied)</td>
</tr>
<tr>
<td>• sensitive to oxidation state &amp; chemical bonding</td>
<td>• cannot study materials under high pressures, under magnetic fields, in solution / in vivo</td>
</tr>
<tr>
<td>• uniquely sensitive probe of electronic structure (can determine electron energy &amp; momentum)</td>
<td>• limited biological applications</td>
</tr>
<tr>
<td>• photoemission “cross-section” is usually quite high (strong signals)</td>
<td>• limited spatial resolution (some exceptions)</td>
</tr>
<tr>
<td></td>
<td>• limited temporal resolution (some exceptions)</td>
</tr>
</tbody>
</table>
Good references

Textbooks

• Photoelectron Spectroscopy : Principles & Applications by Stefan Hufner (Springer-Verlag)

Review articles


• ARPES : A Probe of Electronic Correlations (R. Comin and A. Damascelli, arXiv:1303.1438)