Time-resolved photoelectron spectroscopy: An ultrafast clock to study electron dynamics at surfaces, interfaces and condensed matter

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Outline

Introduction:
Ultrafast phenomena in atoms and solids

Band structure of solids and angle resolved photoemission

Time and Angle Resolved 2 Photon Photoemission:
Lifetime of electrons in condensed matter

Time and Angle Resolved Photoemission:
Optically excited phase transitions in

Outlook:
Challenges and Perspectives of time resolved ARPES
Characteristic Timescales in Matter

- **1 sec (1 s)**: Clock tick
- **1 millisecond (10^{-3} s)**: Camera shutter
- **1 microsecond (10^{-6} s)**: Camera flash
- **1 nanosecond (10^{-9} s)**: Processor speed, Data storage
- **1 picosecond (10^{-12} s)**: Chemical reactions, 1st steps in vision, photosynthesis
- **1 femtosecond (10^{-15} s)**: Electron dynamics in atoms, molecules and materials
- **1 attosecond (10^{-18} s)**
Characteristic Timescales in Matter

- **1 picosecond** ($10^{-12}$ s): Chemical reactions, 1st steps in vision, photosynthesis
- **Femtosecond** ($10^{-15}$ s): Electron dynamics in atoms, molecules and materials
- **Attosecond** ($10^{-18}$ s): Correlation effects between electrons in atoms and molecules

Double ionization of helium

$\frac{1}{\tau} = \omega = \sqrt{\frac{k}{m_r}} \approx \frac{1}{10^{-12} \text{s}}$

Characteristic Timescales in Matter

1 picosecond (10^{-12} s)

Chemical reactions 1st steps in vision, photosynthesis

femtosecond (10^{-15} s)

Electron dynamics in atoms, molecules and materials

attosecond (10^{-18} s)

Correlation effects between electrons in atoms and molecules

Double ionization of helium

\[
\frac{1}{\tau} = \omega = \sqrt{\frac{k}{m_r}} \approx \frac{1}{10^{12} s}
\]

Fundamental phenomena in matter happen on ps to as timescale
Ultrafast phenomena in atoms and molecules

Investigation of isolated, **non-interacting** particles

Atoms in gas phase

Ultrafast Detector:
- Absorption spectroscopy
- High harmonic generation
- Electrons
- Electron diffraction
- ….
Ultrafast phenomena in atoms and molecules

Investigation of isolated, non-interacting particles

Ultrafast electron dynamics in atoms

Atomic wave functions

Why study ultrafast dynamics in condensed matter systems?

Meckel M et al 2008 Science 320 1478–82
On the route to nanoscale devices
Ultrafast phenomena in atoms, molecules and solids

Ultrafast electron dynamics in *atoms* and *molecules*

Ultrafast dynamics in condensed matter

- Isolated systems
- Dynamics of local atomic and molecular wave functions
Ultrafast phenomena in atoms, molecules and solids

Ultrafast electron dynamics in *atoms* and *molecules*

- Isolated systems
- Dynamics of local atomic and molecular wave functions

Ultrafast dynamics in condensed matter

- Coupled system
- Dynamic is determined by ensemble of all electrons and atoms
Ultrafast phenomena in solids

In a condensed matter system:

- Valence electrons can delocalize
- Collective vibrational modes → Phonon modes
- Collective spin-phenomena → Magnetism, Rashba-effect

Periodic arrangement and chemical bonding lead to collective phenomena:
Ultrafast phenomena in solids

In a condensed matter system:

- Valence electrons can delocalize
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Separation into three sub-systems:

- Periodic arrangement and chemical bonding lead to collective phenomena:
Electrons in condensed matter

Electronic wave functions in a solid:
Description as periodic lattice

Electronic band structure

Valence states
Periodic wave functions
Bloch states

Core levels
\( \equiv \)
Atomic levels

Lattice constant

\( a_0 \)

\[ H \Psi_i(r) = E \psi_i(r) \]
Electrons in condensed matter

Electronic wave functions in a solid: Description as periodic lattice

- **Valence states**: Periodic wave functions (Bloch states)
- **Core levels**: $\equiv$ Atomic levels
- **Lattice constant**: $a_0$

Electronic band structure

- **Band gap**: $E_B$ [eV]
- **Brillouin zone**: $k = \frac{2\pi}{a}$

Size of Brillouin zone reflects periodicity in real space

*Electronic band structure* is experimental observable of *electronic wave functions* in momentum space
Angle Resolved Photoemission (ARPES)

Energy conservation

\[ E_f (k_f) = E_B (k_i) + \hbar \nu \]
The “band structure approach”

Angle resolved photoelectron spectroscopy

Excitation in momentum space

Momentum conservation

\[ k_f = k_i + k_{hv} + G \approx 0 \]
Basics of time resolved spectroscopy

Pump-Probe Photoemission Experiment

Probe Pulse
“Sensor”

Pump Pulse
“Trigger”

\[ \Delta t \text{ [fs]} \]

ultrafast clock

Sensor for electron and spin system

Time resolution determined by pulse duration of pump and probe pulse
The Two Limits of Time-Resolved PES

**Single Excitation Limit**
- Low excitation density
- Access to unoccupied states
- Quasi-particle lifetime

**Collective Excitation Limit**
- High excitation density
- Access to occupied/unoccupied states
- Ensemble dynamics

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Tr-2Photon Photoemission

Tr-Pump-Probe ARPES
The Two Limits of Time-Resolved PES

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**Collective Excitation Limit**
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Electron lifetime in metals

Excitation scheme:

1. What are the fundamental scattering mechanisms of electrons in matter?
2. How do these scattering mechanisms change electron dynamics?
Electron lifetime in metals

Excitation scheme:

Fundamental scattering mechanisms:

1. What are the fundamental scattering mechanisms of electrons in matter?

2. How do these scattering mechanisms change electron dynamics?

Cold electrons: inelastic scattering ($\Delta E \approx 0.5*E_i$)

Phonons: quasi-elastic scattering ($\Delta E \approx 10\text{meV}$)

Defect: elastic scattering
Time-resolved 2PPE

Autocorrelation trace

2PPE yield vs. delay $t$ [fs]

FWHM and lifetime

$pump \otimes probe \otimes \exp(-t/\tau)$
Time-resolved 2PPE

Mach-Zehnder Interferometer

Delay-line

30fs, 3.1eV

Δt

Δd

2f

30fs, 1.55eV

Ti:Sa fs-laser
- 800nm
- 80MHz
- nJ/Pulse

Intensity
$I(E_{\text{kin}}, k_{||}, \Delta t)$

Sample

Detector
Electron dynamics in solids

Lifetime of excited electrons in bulk bands

$\tau_0 \approx 20$ fs

Ag thin film

2PPE Data

Electron dynamics in solids

Energy dependent lifetime and *Fermi-Liquid-Behavior*

\[
\frac{1}{\tau} \sim |M|^2 \cdot \rho_s^3 \cdot (E - E_F)^2
\]

Electron dynamics in solids

Electron dynamics at interfaces

The Pb/Cu interface

Lifetime map

- Direct view on electron-electron scattering
- Correlation between band structure and $t_{ee}$

Electron dynamics at interfaces

The Pb/Cu interface

New electronic states at hybrid interface

Electron trapped at interface

Quantum well states

Unoccupied valence band

L. Grad et al., in preparation
Electron dynamics at interfaces

Lifetime Map

Quantum well states @Pb/Cu interface

Larger lifetime at band bottom

Intraband scattering

- Only exchange of energy and momentum
- Lifetime depends on band dispersion

Pure electron-electron scattering

- Only exchange of energy
- Lifetime only depends on energy

Time and Angle Resolved 2PPE

**Summary**

**Bulk states of metals:**
- Lifetime determined by Fermi liquid theory (e-e scattering)
- Lifetime depends on available phase space

**QWS of metal/metal interfaces:**
- Single particle excitation limit
- Quasi particle lifetime of excited electron in unoccupied part of band structure
- Lifetime depends on intraband scattering
- Complex momentum dependent scattering phenomena
The Two Limits of Time-Resolved PES

Single Excitation Limit
- Low excitation density
- Access to unoccupied states
- Quasi-particle lifetime

Collective Excitation Limit
- High excitation density
- Access to occupied/unoccupied states
- Ensemble dynamics
In a condensed matter system:

Separation into three sub-systems

Periodic arrangement and chemical bonding lead to collective phenomena:

- Valence electrons can delocalize
- Collective vibrational modes
  → Phonon modes
- Collective spin-phenomena
  → Magnetism, Rashba-effect
For simple metals/material: Electron wave functions without strong correlations with sub-systems

Separation into three sub-systems

- Electrons
- Spins
- Lattice

Metal

Charge doping level in U/W

Temperature

R(T)
Interactions in condensed matter

For complex materials:
Interactions and correlations result in formation of various phases of matter

Separation into three sub-systems

Fundamental question:
Which interaction/mechanism is driving the formation of a particular phase
Collective excitation limit of tr-ARPES

Strong optical excitation driving condensed matter out of equilibrium

Thermal equilibrium \( R(T) \) → Optical excitation → Non-equilibrium state → Back-relaxation

Dynamics of optical excitation and back relaxation can yield characteristic time scales of coupling mechanisms:

- Electron and Spin coupling: femtosecond time scales
- Coupling to lattice system: high femtosecond to picosecond time scales
Time resolved pump-probe ARPES

- sub 150 meV resolution!
- typical integration time for spectra < 10s
High Harmonic Generation (HHG)

- Coherent x-rays are generated by focusing a femtosecond laser into a gas
- Broad range of harmonics generated simultaneously from UV – keV
- Discovered in 1987, explained in 1993
High Harmonic Generation (HHG)

Photon spectrum

Broad frequency range UV – X-rays

\[ h \nu_{\text{max}} \propto I_{\text{laser}} \lambda_{\text{laser}}^2 \]
**Time resolved pump-probe ARPES**

**Light source:**
- fs-laser amplifier system
- secondary XUV source

**Detected Signal:**
- Transient occupied band structure

**Delay-line**

**Higher Harmonic Generation**

- 30 fs, 1.55 eV
- 30 fs, 22 eV

**fs laser amplifier**

**BBO**

**Transient band structure**
Strong optical excitations in metals

Optical non-equilibrium excitation
Strong IR pulse

R(T)
Optical excitation
Strong optical excitations in metals

Optical non-equilibrium excitation
Strong IR pulse

Non-thermal distribution of excited electrons
Thermalization of electrons by e-e scattering
“Hot” electron distribution

Optical excitation acts on electronic systems

Adapted from M. Wolf et al. Fritz Haber Institute, Berlin
Strong optical excitations in metals

Optical non-equilibrium excitation
Strong IR pulse

Thermalization of non-equilibrium electron distribution

tr-ARPES of Gd(0001)

Energy dissipation of optical excitation

Energy dissipation in coupled systems:

Electron system

Spin system

Phonon system

Optical excitation transfers energy into all sub systems
Optically induced phase transitions in condensed matter

2 examples of optically induced phase transitions in correlated systems:

1. Charge density wave – Metal transition

2. Ferromagnetic – Paramagnetic transition
Optically induced phase transitions in condensed matter

2 examples of optically induced phase transitions in correlated systems:

1. Charge density wave – Metal transition

2. Ferromagnetic – Paramagnetic transition
Charge Density Wave Transition

Metal phase $T>200K$

Charge density wave phase $T<200K$

Charge density lattice

Figure 1, Rohwer et al.

TiSe$_2$
Charge Density Wave Transition

Metal phase $T>200K$

Charge density wave phase $T<200K$

Rohwer et al., Nature 471, 490 (2011)
Static Charge Density Wave Transition

Metal phase $T>200\,\text{K}$

Charge density wave phase $T<200\,\text{K}$

Signature of the charge-density wave state:
back-folding of the Se 4p
bands to the M-point


Wiesenmayer et al., PRB 82, 035422 (2010)
Ultrafast CDW Transition

Typical Tr-ARPES Data Set:

Delay [fs]

Optically induced phase transition

Under investigation:
- Transient changes of **occupied** band structure
- Transient changes of unoccupied band structure very close the $E_F$ of thermal equilibrium

Ultrafast CDW Transition

Typical Tr-ARPES Data Set:

Delay [fs]

Optically induced phase transition

Under investigation:
- Transient changes of **occupied** band structure
- Transient changes of unoccupied band structure very close the $E_F$ of thermal equilibrium

CDW phase transition does not occur instantaneously after optical excitation

Back-relaxation into ground state
Example: CDW System TiSe2

- **Intraband scattering**: Electrons drop down to the bottom of the Ti 3d band.
- **Impact ionization**: More carriers are generated via "impact ionization".

**Graphical Representation**

- **Intraband scattering**:
  - Electrons moving down the energy band.
- **Impact ionization**:
  - Additional carrier generation via impact ionization.

**Data**

- Initial energy level (E_F).
- Transition to lower energy levels (Ti 3d band).

[Graph showing transitions and energy levels]
Optically induced phase transitions in condensed matter

2 examples of optically induced phase transitions in correlated systems:

1. Charge density wave – Metal transition

2. Ferromagnetic – Paramagnetic transition
Band structure view on Ferromagnetic – Paramagnetic transition

The way to ultrafast data storage?

HDD: hard disk drive

Magnetic material
Band structure view on Ferromagnetic – Paramagnetic transition

The way to ultrafast data storage?  

Ultrafast Demagnetization

HDD: hard disk drive

Magnetic material

Band structure view on Ferromagnetic – Paramagnetic transition

The way to ultrafast data storage?

Collective interactions in ferromagnets

Exchange Coupling $J$

Magnetic material

Stroner (Band structure) Model:

Opt. excitation reduces $\Delta_{Ex}$ ?

J leads to $\Delta_{Ex}$

$E_F$
Band structure view on ultrafast demagnetization

Occupied band structure of ferromagnetic Cobalt

SR-XUV photoelectron spectroscopy
Band structure view on ultrafast demagnetization

Occupied band structure of ferromagnetic Cobalt

$$SP = \frac{N^\uparrow - N^\downarrow}{N^\uparrow + N^\downarrow}$$

SR-XUV photoelectron spectroscopy
Band structure view on ultrafast demagnetization

Occupied band structure of ferromagnetic Cobalt

SR-XUV photoelectron spectroscopy

\[ SP = \frac{N^\uparrow - N^\downarrow}{N^\uparrow + N^\downarrow} \]

Haag et al.,
New J. Phys. 18 (2016) 103054
Band structure view on ultrafast demagnetization

Occupied band structure of ferromagnetic Cobalt

SR-XUV photoelectron spectroscopy

fs pump pulse (30fs, 1.55eV)

fs XUV pulse (22eV)

Spin polarization

\[ SP = \frac{N^\uparrow - N^\downarrow}{N^\uparrow + N^\downarrow} \]

Haag et al.,
New J. Phys.18 (2016) 103054
Band structure view on ultrafast demagnetization

Occupied band structure of ferromagnetic Cobalt

Demagnetization trace of Co

\[ SP = \frac{N^\uparrow - N^\downarrow}{N^\uparrow + N^\downarrow} \]

Haag et al.,
New J. Phys. 18 (2016) 103054

Band structure view on ultrafast demagnetization

Ultrafast band renormalization

Transient band structure renormalization

Spin mixing of band structure

Binding energy [eV]

Partial Intensity

Majority $I_{\text{majo}}(\Delta t)$
Minority $I_{\text{mino}}(\Delta t)$
Ultrafast band renormalization

Spin mixing of band structure

Transient band structure renormalization

Partial Intensity

Majority $I_{\text{majo}}(\Delta t)$

Minority $I_{\text{mino}}(\Delta t)$

Binding energy [eV]
Ultrafast band renormalization

Opt. excitation reduces $\Delta E_{\text{ex}}$.

Collapse of exchange splitting

Transient band structure renormalization

Spin mixing of band structure

$E - E_F$ vs. Binding energy [eV]

Majority $I_{\text{majo}}(\Delta t)$
Minority $I_{\text{mino}}(\Delta t)$

Partial Intensity
Ultrafast band renormalization

**Hot electron dynamics**

- Different dynamics for minority and majority electrons
- Dynamics of hot electrons different compared to dynamics of band structure renormalization

**Transient band structure renormalization**

- Spin mixing of band structure

---

**Graphical Elements**

- Intensity [Arb. Units] vs. Delay [fs]
- Partial Intensity vs. Binding energy [eV]
- Schematic representation of spin mixing of band structure
Time resolved pump-probe ARPES

- Collective response after strong optical excitation
- Quasi particle dynamics of occupied and unoccupied part of band structure

Optical excitation $\rightarrow$ Non equilibrium state

Timescale of back relaxation yields information about dominant interactions

Charge density wave transition

Magnetic transition
Outline

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Challenges and Perspectives of time resolved ARPES
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Angle resolved photoelectron spectroscopy

\[ E_{\text{kin}} = \frac{\hbar^2}{2m_e} k^2 \]

Solid

\[ h\nu \]

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

spectrum

\[ h\nu \]

\[ l(E) \]
Outlook: Challenges and Perspectives of time resolved ARPES

Angle resolved photoelectron spectroscopy

$$ E_{\text{kin}} = \frac{\hbar^2}{2m_e} k^2 $$
Perspective: Momentum microscopy

Photoemission electron microscope optics

Time-of-flight energy analyzer

Photoemission electron microscope optics
Perspective: Momentum microscopy

Photoemission electron microscope optics

Time-of-flight energy analyzer

Photoemission electron microscope optics
Perspective: Momentum microscopy

Constant energy maps

Time-of-flight energy analyzer

Photoemission electron microscope optics
Perspective: Momentum microscopy

Constant energy maps

Time-of-flight energy analyzer

Photoemission electron microscope optics
Perspective: Momentum microscopy

Constant energy maps

Momentum space dynamics of hot carriers

Lifetime maps

Time-of-flight energy analyzer

Photoemission electron microscope optics
Perspective: Momentum microscopy

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Momentum space dynamics of hot carriers

Momentum space view on optically induced phase transitions in condensed matter

Time-of-flight energy analyzer

Photoemission electron microscope optics
Perspective: Momentum microscopy

Constant energy maps

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Time-of-flight energy analyzer

Ideal tool to trace ultrafast electron dynamics through momentum, space and time on nm-length and (sub-) fs timescales
The ELI facilities

Extreme Light Infrastructure - Attosecond Light Pulse Source: ELI-ALPS
The ELI facilities

Extreme Light Infrastructure - Attosecond Light Pulse Source: ELI-ALPS

<table>
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<th>Laser system</th>
<th>Peak / average power</th>
<th>Rep-rate</th>
<th>Pulse energy</th>
<th>Pulse duration</th>
<th>Spectral range</th>
<th>UV / XUV</th>
</tr>
</thead>
<tbody>
<tr>
<td>ALPS-HR</td>
<td>&gt; 0.1 TW / 100 W</td>
<td>100 kHz</td>
<td>1 mJ</td>
<td>&lt; 7 fs (CEP stable)</td>
<td>0.3 - 1.3 μm</td>
<td>12-300 nm 4-100 eV/10-1 nJ</td>
</tr>
<tr>
<td>SYLOS</td>
<td>&gt; 2 TW / 20 W</td>
<td>1 kHz</td>
<td>20 mJ</td>
<td>&lt; 10 fs (CEP stable)</td>
<td>0.5 - 1.3 μm</td>
<td>10 - 400 eV, 120 - 3 nm, 0.4 μJ - 4 pJ GHIG</td>
</tr>
</tbody>
</table>

Czech Republic, Prague
Particles and X-ray

Hungary, Szeged
Attosecond

Romania, Bucharest – Magurele
Photonuclear

http://www.eli-hu.hu/
**The ELI facilities**

**Extreme Light Infrastructure - Attosecond Light Pulse Source: ELI-ALPS**

<table>
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<th>PRIMARY SOURCES (lasers)</th>
<th>SECONDARY SOURCES</th>
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| ALPS-HR                  | 12-300 nm         |
| > 0.1 TW / 100 W        | 4-100 eV/10-1 nJ |
| 100 kHz                 |                   |
| 1 mJ                    |                   |
| < 7 fs (CEP stable)     |                   |
| 0.3 - 1.3 μm            |                   |
| Stage 1 (from January 2016 - December 2017) | 80 MHz oscillator |
| SYLOS                    |                   |
| > 2 TW / 20 W           |                   |
| 1 kHz                   |                   |

Vacuum space charge in ARPES: Example: Surface State of Cu(111) surface

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Ultrafast phenomena at surfaces

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Materials in Science

Spin+X
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