Introduction to Photoemission Spectroscopy

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Outline:
• Basics
• PES theory I: (mainly) independent electrons
• PES theory II: many-body picture
• Case studies – towards higher photon energies
Photoemission basics
The photoelectric effect

quantitative experiment:
(H. Hertz 1886, W. Hallwachs 1888,
P. Lenard 1902)
measure kinetic energy of photoelectrons in retarding field

experimental observations:
• light intensity increases $I_{phot}$, but not $E_{kin}^{max}$
  (contrary to classical expectation)
• instead: $E_{kin}^{max}$ depends on light frequency $\nu$

$E_{kin}^{max} \propto \nu - const$
The photoelectric effect

Theoretical explanation by A. Einstein (1905):

QUANTIZATION OF LIGHT


Die kinetische Energie solcher Elektronen ist

\[ \frac{R}{N} \beta \nu - P. \]

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

Planck’s constant
photocathode workfunction

A. Einstein
Nobel prize 1921
energy conservation: \[ E_{\text{kin}} = h \nu - E_B - \Phi \]
energy conservation: \[ E_{\text{kin}} = h\nu - E_B - \Phi \]

→ Electron Spectroscopy for Chemical Analysis

K.M. Siegbahn
Nobel prize 1981

Fe\textsubscript{3}O\textsubscript{4} (magnetite)

chemical composition
energy conservation: \[ E_{\text{kin}} = h\nu - E_B - \Phi \]

→ Electron Spectroscopy for Chemical Analysis

chemical shifts in C 1s spectrum of ethylfluoroacetate
Photoelectron spectroscopy: valence bands

Intensity (arb. units)

O 2p / Cl 3p

Ti 3d

E - $\mu_{\text{exp}}$ (eV)

-10 -8 -6 -4 -2 0

TiOCl

UPS
XPS
LDA+$U^{\text{FM}}$

electron analyzer

single crystal

hv

$E_{\text{kin}}, \vec{k}$
Angle-resolved photoemission (ARPES)

measure energy and momentum of the photoelectrons:

\[ E_{kin}, \theta, \varphi \rightarrow \vec{K} \]

with

\[ |\vec{K}| = \frac{1}{\hbar} \sqrt{2mE_{kin}} \]

\[ K_x = |\vec{K}| \sin \theta \cos \phi \]

\[ K_y = |\vec{K}| \sin \theta \sin \phi \]

\[ K_z = |\vec{K}| \cos \theta \]

vacuum

\[ E_{kin}, \vec{K} \]

conservation laws

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

\[ \vec{K} = \vec{k} (+\vec{k}_{photon}) \]

solid

\[ E_B, \vec{k} \]
Angle-resolved photoemission (ARPES)

measure energy and momentum of the photoelectrons:

→ k-space band structure mapping: band dispersions, Fermi surface, ...
Angle-resolved photoemission (ARPES)

Example: Cuprate-High Tc superconductor - 2D Pb-BSCCO (Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$)

- EDC: Energy distribution curves
- MDC: Momentum distribution curves

$\rho(k, \omega)$

PES theory I:
(mainly) independent electrons
Fermi's Golden Rule

starting point for theoretical description of PE process:

effect of photon field is **weak perturbation**

→ Hamiltonian: \[ \hat{H} = \hat{H}_0 + \hat{H}_{\text{int}} e^{-i\omega t} \]

unperturbed system (electrons in atom, solid):

\[ \hat{H}_0 |n\rangle = E_n |n\rangle \] with known eigenstates \( |n\rangle \) and eigenenergies \( E_n \)

perturbation (photon field):

\[ \hat{H}_{\text{int}} e^{-i\omega t} \]
Fermi's Golden Rule

time-dependent perturbation theory

transition rate from initial state $|i\rangle$ to final state $|f\rangle$ of the unperturbed system $\hat{H}_0$ due to perturbation $\hat{H}_{int}e^{-i\omega t}$ is:

$$w_{i\rightarrow f} = \frac{2\pi}{\hbar} \left| \langle f | \hat{H}_{int} | i \rangle \right|^2 \delta(E_f - E_i - \hbar\omega)$$

transition matrix element:
- $k$ conservation
- symmetry

energy conservation!
Fermi's Golden Rule

**Perturbing radiation field: What is \( \hat{H}_{\text{int}} \)?**

described by vector potential of a **classical** electromagnetic plane wave:

\[
\vec{A}(\vec{r}, t) = \vec{A}_0 e^{i(\vec{q} \cdot \vec{r} - \omega t)}
\]

\[ \Rightarrow \text{electric field: } \vec{E}(\vec{r}, t) = -\frac{\partial}{\partial t} \vec{A}(\vec{r}, t) \]

\[ \Rightarrow \text{magnetic field: } \vec{B}(\vec{r}, t) = \nabla \times \vec{A}(\vec{r}, t) \]

**N.B.:** \( \nabla \cdot \vec{A}(\vec{r}, t) = \text{div} \vec{A}(\vec{r}, t) = 0 \), if photon wavevector \( \vec{q} \perp \vec{A}_0 \)

true in vacuum and deep in the solid (transverse wave), but not necessarily at the surface due to discontinuity in dielectric constant \( \varepsilon \)

\[ \Rightarrow \text{surface photoemission} \quad \text{see, e.g., Miller et al., PRL 77, 1167 (1996)} \]

*classical description ignores quantum nature of photon, justified for sufficiently low photon intensities (\( \Rightarrow \) VUV-laser, FEL ?)
Fermi's Golden Rule

Perturbed electronic system (consider only single electron: independent particle picture!):

canonical replacement in unperturbed Hamiltonian: \( \hat{p} \rightarrow \hat{p} - e\hat{A} \)

\[
\hat{H} = \frac{1}{2m} \left( \hat{p} - e\hat{A} \right)^2 + V(\vec{r})
\]

\[
= \frac{1}{2m} \left( -i\hbar\vec{V} - e\hat{A}(\vec{r}, t) \right)^2 + V(\vec{r})
\]

\[
= \frac{\hat{p}^2}{2m} + V(\vec{r}) - \frac{e}{2m} \hat{p} \cdot \hat{A} - \frac{e}{2m} \hat{A} \cdot \hat{p} + \frac{e^2}{2m} \hat{A}^2
\]

\[
= \hat{H}_0 - \frac{e}{m} \hat{A} \cdot \hat{p} - \frac{e}{2m} \left( -i\hbar\vec{V} \cdot \hat{A} \right)
\]

\[
\approx \hat{H}_0 - \frac{e}{m} \hat{A} \cdot \hat{p} = \hat{H}_0 - \frac{e}{m} (\hat{A}_0 e^{i(\vec{q} \cdot \vec{r} - \omega t)} \cdot \hat{p})
\]

\[
\approx \hat{H} - \frac{e}{m} e^{i\vec{q} \cdot \vec{r}} (\hat{A}_0 \cdot \hat{p}) e^{-i\omega t}
\]

describes two-photon processes, can be neglected for weak radiation fields

\[= 0, \text{ except possibly at surface!}\]

of the form \( \hat{H}_{\text{int}} e^{-i\omega t} \) to be used in Fermi's Golden Rule!
back to Fermi’s Golden Rule

\[ w_{i\rightarrow f} = \frac{2\pi}{\hbar} \left| \langle f | \hat{H}_{\text{int}} | i \rangle \right|^2 \delta (E_f - E_i - \hbar \omega) \]

for the transition matrix element we now obtain:

\[ M_{if} = \langle f | \hat{H}_{\text{int}} | i \rangle = -\frac{e}{m} \langle f | e^{i \vec{q} \cdot \vec{r}} \hat{A}_0 \cdot \hat{p} | i \rangle \], or expressed in "real" wave functions:

\[ M_{if} = -\frac{e}{m} \int d^3r \; \psi^*_f (\vec{r}) \; e^{i \vec{q} \cdot \vec{r}} \; (\hat{A}_0 \cdot \hat{p}) \; \psi_i (\vec{r}) \]
Matrix element and dipole approximation

$$M_{if} = -\frac{e}{m} \int d^3r \; \psi_f^*(\vec{r}) \; e^{i\vec{q} \cdot \vec{r}} (\hat{A}_0 \cdot \hat{p}) \; \psi_i(\vec{r})$$

length scales:

• the matrix element can be viewed as spatial Fourier transform ($e^{i\vec{q} \cdot \vec{r}}$)

• the wavefunctions (atomic orbitals or Bloch waves) oscillate rapidly on atomic dimensions ($\sim \text{Å}$)

• the photon wave $e^{i\vec{q} \cdot \vec{r}}$ probes length scales of order $\lambda = \frac{2\pi}{|\vec{q}|}$ which for VUV radiation is large compared to atomic dimensions, e.g.: 

  \[
  \begin{align*}
  h\nu &= 21.2 \text{ eV} \quad \rightarrow \lambda = 584 \text{ Å} \quad \text{(VUV)} \\
  1.486 \text{ keV} &\rightarrow \quad = 8.3 \text{ Å} \quad \text{(XPS)} \\
  6 \text{ keV} &\rightarrow \quad = 2.0 \text{ Å} \quad \text{(HAXPES)}
  \end{align*}
  \]

→ expansion of the plane wave (generates el./magn. multipole moments):

$$e^{i\vec{q} \cdot \vec{r}} = 1 + i\vec{q} \cdot \vec{r} + \cdots \approx 1,$$

with $\vec{q} \cdot \vec{r} \sim 2\pi \frac{a_0}{\lambda} \ll 1$ for VUV radiation
Matrix element and dipole approximation

→ simplified matrix element:

\[ M_{if} = -\frac{e}{m} \int d^3r \, \psi_f^*(\vec{r}) (\hat{A}_0 \cdot \hat{p}) \, \psi_i(\vec{r}) \]

Using the quantum-mechanical identity \( \langle f | \hat{p} | i \rangle = \text{i} m \frac{E_f - E_i}{\hbar} \langle f | \vec{r} | i \rangle \)
the matrix element can be further transformed into:

\[ M_{if} = -\text{i} \frac{E_f - E_i}{\hbar} \hat{A}_0 \cdot \int d^3r \, \psi_f^*(\vec{r}) [e\vec{r}] \, \psi_i(\vec{r}) \]  

← electrical dipole operator

→ selection rules, polarization dependence

→ dipole approximation valid only up to VUV energies

→ at higher photon energies (XPS, HAXPES):
  el. quadrupole/magn. dipole contributions increasingly important!
Fermi’s Golden rule and the one-step model

Photoemission intensity determined by transition rate:

\[ w_{i\rightarrow f} = \frac{2\pi}{\hbar} |\langle f | \hat{A}_0 \cdot \hat{p} | i \rangle|^2 \delta(E_f - E_i - \hbar \omega) \]

What are the initial and final states?

One-step model:

**Final states:** "time-inverted LEED state"
- In vacuum: free electron wave \( e^{i \vec{k}_f \cdot \vec{r}} \)
- In the solid: matched to high lying Bloch waves, damped by e-e scattering
- Energy \( E_f \) and wavevector \( \vec{k}_f \)

**Initial states in the solid:**
- Bulk Bloch waves \( u_{n\vec{k}_i}(\vec{r})e^{i \vec{k}_i \cdot \vec{r}} \)
- Energy \( E_i \) and wavevector \( \vec{k}_i \)
Fermi’s Golden rule and the one-step model

photoemission intensity determined by transition rate:

\[ w_{i\rightarrow f} = \frac{2\pi}{\hbar} |(f|\hat{A}_0 \cdot \hat{p}|i)|^2 \delta(E_f - E_i - \hbar \omega) \]

What are the initial and final states?

One-step model:

- initial states in the solid:
  - bulk Bloch waves \( u_n \vec{k}_i(r) e^{i\vec{k}_i \cdot \vec{r}} \)
  - energy \( E_i \) and wavevector \( \vec{k}_i \)

- final states:
  - free electron wave \( e^{i\vec{k}_f \cdot \vec{r}} \)
  - damped by \( \hbar \cdot e - e \) scattering
  - energy \( E_f \) and wavevector \( \vec{k}_f \)

more on one-step theory of PES

lecture by Jan Minar
One-step model vs. three-step model

courtesy of A. Damascelli
Step 1: Excitation in the solid

\[ w_{i \rightarrow f} = \frac{2\pi}{\hbar} \left| \langle f | \hat{A} \cdot \hat{p} | i \rangle \right|^2 \delta(E_f - E_i - \hbar\omega) \]

momentum conservation:
\[ \vec{k}_f = \vec{k}_i + \vec{G} + \vec{k}_{\text{photon}} \]

only "vertical" transitions

for VUV excitation
Step 2: Transport to the surface

**inelastic scattering** of the photoelectron with

- other electrons
  (excitation of e-h-pairs, plasmons)
- phonons

→ generation of secondary electrons
"inelastic background"

![Diagram showing inelastic scattering and generation of secondary electrons](image-url)
Shirley background

background at energy $E$ proportional to intrinsic spectrum integrated over all energies $E' > E$:

$$I_{BG}(E) = \int_{E}^{E_F} dE' \ I_0(E')$$

can be viewed as convolution with step-like loss function $L(E) = Im \frac{-1}{\varepsilon(E)}$:

$$I_{BG}(E) = \int_{-\infty}^{+\infty} dE' \ I_0(E')L(E - E')$$

Tougaard background

loss function will generally have structure due to interband transitions, plasmons, etc.

use phenomenological model or determine loss function experimentally (EELS)
Step 2: Transport to the surface

**inelastic scattering** of the photoelectron with

- other electrons  
  (excitation of e-h-pairs, plasmons)
- phonons

→ generation of secondary electrons  
*"inelastic background"*

![Diagram showing energy levels and inelastic scattering](image)
Step 2: Transport to the surface

**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** $\lambda$
Mean free path and PES probing depth

"universal curve"

- experimental data
- guide to the eye

<table>
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<th>mean free electron path (Å)</th>
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<tr>
<td>10</td>
</tr>
<tr>
<td>1</td>
</tr>
</tbody>
</table>

typical PES energies
10 ... 1500 eV

\[ h \nu \]

\[ E_{kin} \]

\[ \lambda(E_{kin}) \]

\[ \lambda = 2 \ldots 20 \text{ Å} \]

\[ \text{PES probing depth: } \sim 3\lambda \]

(95% of the signal)

PES is surface-sensitive on atomic length scales!
Step 3: transition to vacuum

- conservation of wavevector component parallel to surface, $k_\parallel$
- **But**: change of $k_\perp$ changes due to electron diffraction at surface barrier

source: E. Rotenberg
The $k_\perp$ problem

electron wave matching at the surface

$E \sim K^2$

final state dispersion generally not known
pragmatic solution: free-electron final state model

**The $k_{\perp}$ problem**

Surface potential step

"inner potential" $V_0$

**Diagram:**
- $E_{\text{kin}}$ vs. $E_V$
- $E \sim K^2$
- $K_{\perp}$ (fixed $K_{||}$)
- $V_0$
- $k_{\perp}$ (fixed $k_{||} = K_{||}$)
The $k_\perp$ problem

pragmatic solution: free-electron final state model

\[ E_{kin} = \frac{\hbar^2 K_{out}^2}{2m} = \frac{\hbar^2 k_{in}^2}{2m} - V_0 \]

\[ \Rightarrow \begin{cases} k_{in,\parallel} = K_{out,\parallel} = \sqrt{\frac{2m}{\hbar^2}} E_{kin} \sin \theta_{out} \\ k_{in,\perp} = \sqrt{\frac{2m}{\hbar^2}} \left( E_{kin} \cos^2 \theta_{out} + V_0 \right) \end{cases} \]

\( k_\perp \) uniquely determined from measured data: \( E_{kin}, \theta_{out} \), but need to know inner potential \( V_0 \) (from band theory, \( k \)-periodicity)
Summary: ARPES in the indep. electron approx.

measure **energy** and **escape angle** of the photoelectrons:

get **bandstructure** (dispersions, Fermi surface,...) from conservation laws:

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

**momentum:** \[ \hbar k_{||} = \hbar K_{||} = \sqrt{2mE_{\text{kin}}} \sin \theta \]

\[ \hbar k_{\perp} \] not so straightforward ...
PES theory II:
many-body picture
Non-interacting electrons

ARPES
↓
band structure $\varepsilon_0(\vec{k})$

Interacting electrons

ARPES
↓
spectral function

$$A(\vec{k}, \varepsilon) = -\frac{1}{\pi} \text{Im} \ G(\vec{k}, \varepsilon)$$

interacting electrons
(Coulomb repulsion)

Photoemission: sudden removal of an electron from $N$-particle system

$E_{\text{kin}}$
interacting electrons
(Coulomb repulsion)

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

Photoemission process:

sudden removal of an electron from \( N \)-particle system

"loss" of kinetic energy due to interaction-related excitation energy stored in the remaining \( N-1 \) electron system!
Photoemission: many-body effects

electron-phonon coupling

\[ h\nu \]

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

**photoemission process:**

**sudden removal** of an electron from \( N \)-particle system

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Photoemission: many-body effects

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

photoemission process:

sudden removal of an electron from \( N \)-particle system

"loss" of kinetic energy due to interaction-related excitation energy stored in the remaining \( N-1 \) electron system!
Fermi's Golden Rule for an $N$-electron system

$$\omega_{i\rightarrow f} = \frac{2\pi}{\hbar} \left| \langle f | \hat{H}_{\text{int}} | i \rangle \right|^2 \delta(E_f - E_i - \hbar \omega)$$

initial state

$$|i\rangle = |N, 0\rangle \quad \text{$N$-electron ground state with energy $E_i = E_{N,0}$ \quad (T=0)}$$

final states

$$|f\rangle = |N - 1, s; \vec{k}\rangle \quad \text{$N$-electron excited state of quantum number $s$ and energy $E_f = E_{N,s}$,}$

$$\text{consisting of } N - 1 \text{ electrons in the solid and one free}$

$$\text{photoelectron with wavevector } \vec{k} \text{ and energy } \varepsilon$$

transition operator

$$\hat{H}_{\text{int}} \propto \sum_{i=1}^{N} \hat{A}(\vec{r}_i) \cdot \hat{p}_i \quad \text{in second quantization} = M_{if} \ c_{\vec{k}_f}^+ c_{\vec{k}_i}$$

one-electron matrix element,

conserves wavevector: $\vec{k}_f = \vec{k}_i$
Fermi's Golden Rule for an $N$-electron system

\[
I(\vec{k}, \varepsilon) \propto \sum_s \left| \langle N - 1, s; \vec{k} | \hat{H}_{\text{int}} | N, 0 \rangle \right|^2 \delta(E_{N,S} - E_{N,0} - \hbar \omega)
\]

**initial state**

\[|i\rangle = |N, 0\rangle \quad \text{\textit{N}-electron ground state} \text{ with energy } E_i = E_{N,0} \quad (T=0)

**final states**

\[|f\rangle = |N - 1, s; \vec{k}\rangle \quad \text{\textit{N}-electron excited state} \text{ of quantum number } s \text{ and energy } E_f = E_{N,s},

consisting of \(N - 1\) electrons in the solid and one free photoelectron with wavevector \(\vec{k}\) and energy \(\varepsilon\)

**transition operator**

\[
\hat{H}_{\text{int}} \propto \sum_{i=1}^N \hat{A}(\vec{r}_i) \cdot \hat{p}_i \quad \text{in second quantization} = M_{if} \ c_{\vec{k}_f}^{+} c_{\vec{k}_i}
\]

one-electron matrix element, conserves wavevector: \(\vec{k}_f = \vec{k}_i\)
Fermi's Golden Rule for an \( N \)-electron system

\[
I(\vec{k}, \varepsilon) \propto \sum_s |\langle N - 1, s; \vec{k} | \hat{H}_{\text{int}} | N, 0 \rangle|^2 \delta(E_{N,s} - E_{N,0} - \hbar \omega)
\]

Sudden Approximation:

\[
|f\rangle = |N - 1, s; \vec{k}\rangle
\]
Fermi's Golden Rule for an $N$-electron system

$$I(\vec{k}, \varepsilon) \propto \sum_s |\langle N - 1, s; \vec{k} | \hat{H}_{\text{int}} | N, 0 \rangle|^2 \delta(E_{N,S} - E_{N,0} - \hbar \omega)$$

Sudden Approximation:

$$|f\rangle = |N - 1, s; \vec{k}\rangle = c_k^+ |N - 1, s\rangle \quad \text{factorization!}$$

- photoelectron
- $s^{th}$ eigenstate of remaining $N - 1$ electron system

Physical meaning:

photoelectron decouples from remaining system immediately after photoexcitation, before relaxation sets in
Fermi's Golden Rule for an $N$-electron system

\[ I(\vec{k}, \varepsilon) \propto \sum_s \left| \langle N - 1, s | c_{\vec{k}} \hat{H}_{\text{int}} | N, 0 \rangle \right|^2 \delta(E_{N-1,s} + \varepsilon - E_{N,0} - \hbar \omega) \]

Sudden Approximation:

\[ |f\rangle = |N - 1, s; \vec{k}\rangle = c_{\vec{k}}^+ |N - 1, s\rangle \quad \text{factorization!} \]

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Sudden Approximation:

\[ |f\rangle = |N - 1, s; \vec{k}\rangle = c_{\vec{k}}^+ |N - 1, s\rangle \quad \text{factorization!} \]

- photoelectron
- $s^{th}$ eigenstate of remaining $N - 1$ electron system

Physical meaning:

- photoelectron decouples from remaining system immediately after photoexcitation, \textit{before} relaxation sets in
after some algebra (using the momentum conservation in $M_{if}$ and assuming that $M_{if} \sim \text{const}$ in the energy and k-range of interest) one obtains:

$$I(\vec{k}, \varepsilon) \propto \sum_s \left| \langle N - 1, s \mid c_{\vec{k}} \mid N, 0 \rangle \right|^2 \delta(E_{N-1,s} + \varepsilon - E_{N,0} - \hbar\omega)$$
Sudden Approximation

after some algebra (using the momentum conservation in $M_{if}$ and assuming that $M_{if} \sim const$ in the energy and k-range of interest) one obtains:

$$I(\vec{k}, \varepsilon) \propto \sum_s |\langle N-1, s | c_{\vec{k}} | N, 0 \rangle|^2 \delta(E_{N-1,s} + \varepsilon - E_{N,0} - \hbar \omega)$$

$$= A(\vec{k}, \varepsilon - \hbar \omega) \cdot f(\varepsilon - \hbar \omega)$$

spectral function

The ARPES signal $I(\vec{k}, \varepsilon)$ directly proportional to the removal part of the spectral function $A(\vec{k}, \omega) = -\frac{1}{\pi} \text{Im} \ G(\vec{k}, \omega)$

probability of removing (or adding) an electron at energy $\omega$ and momentum $\vec{k}$ from (to) the system
after some algebra (using the momentum conservation in $M_{if}$ and assuming that $M_{if} \sim const$ in the energy and $k$-range of interest) one obtains:

$$I(\vec{k}, \varepsilon) \propto \sum_s |\langle N-1, s | c_{\vec{k}} | N, 0 \rangle|^2 \delta(E_{N-1,s} + \varepsilon - E_{N,0} - \hbar \omega)$$

$$= A(\vec{k}, \varepsilon - \hbar \omega) \cdot f(\varepsilon - \hbar \omega)$$

The ARPES signal $I(\vec{k}, \varepsilon)$ directly proportional to the removal part of the spectral function $A(\vec{k}, \omega) = -\frac{1}{\pi} \text{Im} G(\vec{k}, \omega)$
\[ A(\vec{k},\omega) = -\frac{1}{\pi} \text{Im} \ G(\vec{k},\omega) = -\frac{1}{\pi} \text{Im} \frac{1}{\hbar \omega - \varepsilon_{\vec{k}} - \Sigma(\vec{k},\omega)} = \frac{1}{\pi} \frac{|\Sigma''(\vec{k},\omega)|}{\left[ \hbar \omega - \varepsilon_{\vec{k}} - \Sigma'(\vec{k},\omega) \right]^2 + \Sigma''(\vec{k},\omega)^2} \]
example: photoemission of the $\text{H}_2$ molecule

$E_{\text{kin}}$
Many-body effects in photoemission

example: photoemission of the $H_2$ molecule

\begin{align*}
E_{\text{kin}} & \quad \text{electrons couple to proton dynamics!} \\
\text{photoemission intensity:} & \quad I(\omega) \propto \sum_s \left| \langle H_2^+, s | \hat{c} | H_2, 0 \rangle \right|^2 \delta(\omega + E_{H_2^+, s} - E_{H_2, 0}) \\
\text{electronic-vibrational eigenstates of } H_2^+: & \quad \left| H_2^+, s \right\rangle = \left| \sigma^1, v = 0 \right\rangle \\
& \quad = \left| \sigma^1, v = 1 \right\rangle \\
& \quad = \left| \sigma^1, v = 2 \right\rangle \\
& \quad \vdots
\end{align*}
Many-body effects in photoemission

example: photoemission of the H$_2$ molecule

Franck-Condon principle
The $k_\perp$-problem again: photoelectron damping

ARPES signal is actually a convolution of photohole and photoelectron spectral function

$$I(k_{||}, \varepsilon) \propto \int dk_\perp A_h^<(k_{||}, k_\perp, \varepsilon - h\nu) A_e^>(k_{||}, k_\perp, \varepsilon)$$

**total width** assuming lifetime-broadened Lorentzian lineshapes

$$\Gamma_{tot} \approx \Gamma_h + \frac{v_{h\perp}}{v_{e\perp}} \Gamma_e$$

spectrum dominated by photo-electron linewidth unless $v_{h\perp}/v_{e\perp} << 1$

$\Rightarrow$ low-dim systems (e.g., surfaces)

$\Rightarrow$ k-vector in high-symmetry planes
• Photoelectron spectroscopy is ideal tool for the study of **many-body effects** in the electronic structure

• **photohole probes interactions**
  between electrons and with other dynamical degrees of freedom
  → energy shifts
  → shake-up satellites
  → line broadening
  → line shape
  
  (*generalized Franck-Condon effect*)

• ARPES signal proportional to **single-particle spectrum** $A^\leq (\vec{k}, \omega)$
  *(if photohole is localized $\perp$ surface!)*

• facilitates **direct comparison** to many-body theoretical description of interacting system
Low-energy photoemission:
Doping a one-dimensional Mott insulator
TiOCl: a low-dimensional Mott insulator

configuration: Ti $3d^1$

$\rightarrow 1\text{e}^-/\text{atom}: \text{Mott insulator}$

$\rightarrow \text{local spin } s=1/2$

$\rightarrow \text{frustrated magnetism, resonating valence bond (RVB) physics?}$
Doping a Mott insulator

**Hubbard model description:**

- non-interacting bandwidth $W$
- local Coulomb energy $U$
- band-filling $n$

$$n = 1$$

$U \gg W$

- lower Hubbard band (LHB)
- upper Hubbard band (UHB)

**Electron removal** (PES)

**Electron addition** (IPES)
Doping a Mott insulator

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- non-interacting bandwidth $W$
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$U > W$

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$n = 1 + x$
quasi-particle

bandfilling-controlled Mott transition?
here: $n$-doping
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quasi-particle

band-filling-controlled Mott transition?
here: $n$-doping
TiOCl: doping by intercalation

n: alkali metals
p: organic acceptors (e.g., TCNQ)

letters to nature

Superconductivity at 25.5 K in electron-doped layered hafnium nitride
Shoji Yamanaka*+, Ken-ichi Hotehama* & Hitoshi Kawaji*+  

**XPS: in situ Na intercalation and n-doping**

- electron transfer $\text{Na} \rightarrow \text{Ti}$
- doping $x$ from relative $\text{Ti}^{2+}$ and $\text{Ti}^{3+}$ weight

*PRL 106, 056403 (2011)*

![Graph showing Ti2p and Na1s binding energies with intensity and Na1s doping x (%) and Ti2p intensity (arb. units).](image)
UPS: doping effects in valence band

- rigid band shift
- new spectral weight in gap

PRL 106, 056403 (2011)
• new peak in the Mott gap: UHB?
• absence of metallic quasiparticle (QP)?
Spectral weight transfer from LHB to UHB

- **Undoped:**
  - \( w = 1 \)
  - Remove \( \epsilon \) from LHB
  - \( \epsilon \) to UHB

- **Doped:**
  - \( w = 2x \)
  - Remove \( \epsilon + U \) from UHB
  - \( \epsilon \) to LHB

*PRL 106, 056403 (2011)*
Spectral weight transfer from LHB to UHB

undoped:

\[ \text{remove } \varepsilon \]

\[ \text{LHB } w = 1 \]

\[ \text{UHB} \]

\[ \text{LHB } w = 1-x \]

\[ \text{UHB } w = 2x \]

\[ \varepsilon + U \]

doped:

\[ \text{remove } \varepsilon \]

\[ \text{LHB } w = 1-x \]

\[ \text{UHB } w = 2x \]

\[ \varepsilon \]

\[ \text{LHB } w = 1 \]

\[ \text{UHB} \]

\[ \sim 1 + x \]

\[ \sim 1 - x \]

\[ \sim 2x \]

\[ \text{total weight} \]

\[ \text{original weight} \]

\[ \text{additional weight} \]

\[ 0.0 \quad 0.1 \quad 0.2 \quad 0.3 \quad 0.4 \quad 0.5 \]

doping \( x \)

\[ PRL \text{ 106, 056403 (2011)} \]
Absence of metallic QP

Molecular dynamics:

GGA+U - DOS:

- Na ions occupy specific sites close to one Ti-O layer
- in-gap states due to Ti sites closest to Na ions
- local doping into „alloy band“ (AB)
- transfer of spectral weight LHB → AB
- AB: all sites always doubly occupied
- fundamental gap between AB and UHB → insulating for all doping levels

![Graph showing DOS and band structures](image-url)
Hard x-ray photoemission: 
Profiling the buried two-dimensional electron system in an oxide heterostructure
Oxide heterostructures in a nutshell

General idea:
combine interface functionalities with intrinsic functionalities of oxides → novel phases, tunability of interactions

Paradigm material: LAO/STO
• both oxides: wide gap band insulators
• LAO thickness ≥ 4 unit cells (uc): formation of a high-mobility interface

2D electron system (2DES)

Oxide heterostructures in a nutshell

2DES properties:
- tunable conductivity by electric gate field
- superconducting below 200 mK
- magnetoresistance
- coexistence of superconductivity and ferromagnetism

Origin of 2DES (and its critical behavior)?
- O-vacancies @ interface
- cation intermixing (La$_x$Sr$_{1-x}$TiO$_3$)
- electronic reconstruction

see also:
*D.G. Schlom and J. Mannhart,*
*Nature Materials* 10, 168 (2011)
Polar catastrophe and how to avoid it

charge:

\[\begin{array}{c}
\text{AlO}_2 \quad -1 \\
\text{LaO} \quad +1 \\
\text{AlO}_2 \quad -1 \\
\text{LaO} \quad +1 \\
\text{AlO}_2 \quad -1 \\
\text{LaO} \quad +1 \\
\text{TiO}_2 \quad 0 \\
\text{SrO} \quad 0 \\
\text{TiO}_2 \quad 0 \\
\text{SrO} \quad 0 \\
\end{array}\]

\[\Delta q = -1/2\]

\[\begin{array}{c}
\text{AlO}_2 \quad -1/2 \\
\text{LaO} \quad +1 \\
\text{AlO}_2 \quad -1 \\
\text{LaO} \quad +1 \\
\text{AlO}_2 \quad -1 \\
\text{LaO} \quad +1 \\
\text{TiO}_2 \quad 0 \\
\text{SrO} \quad 0 \\
\text{TiO}_2 \quad 0 \\
\text{SrO} \quad 0 \\
\end{array}\]

electrostatic energy increases with thickness of polar film

polar catastrophe

electronic reconstruction

\[0.5e^- \text{ per layer unit cell} \rightarrow n_{2D} = 3.5 \times 10^{14} \text{ cm}^{-2}\]

partial Ti 3d occupation

\[\rightarrow \text{Ti}^{3.5} (d^{0.5}) = \text{Ti}^{3+}/\text{Ti}^{4+}\]

Nakagawa et al., Nature Mat. 5, 204 (2006)
El. reconstruction: The view from band theory

\[ \Delta q = -1/2e \]

Yun Li et al., PRB 84, 245307 (2011)
Pentcheva and Pickett, PRL 102, 107602 (2009)
**LAO/STO: Electronic reconstruction**

\[ \Delta q = -\frac{1}{2}e \]

<table>
<thead>
<tr>
<th>Layer</th>
<th>Charge State</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlO(_2)</td>
<td>-1/2</td>
</tr>
<tr>
<td>LaO</td>
<td>+1</td>
</tr>
<tr>
<td>AlO(_2)</td>
<td>-1</td>
</tr>
<tr>
<td>LaO</td>
<td>+1</td>
</tr>
<tr>
<td>AlO(_2)</td>
<td>-1</td>
</tr>
<tr>
<td>LaO</td>
<td>+1</td>
</tr>
<tr>
<td>TiO(_2)</td>
<td>-1/2</td>
</tr>
<tr>
<td>SrO</td>
<td>0</td>
</tr>
<tr>
<td>SrO</td>
<td>0</td>
</tr>
<tr>
<td>TiO(_2)</td>
<td>0</td>
</tr>
</tbody>
</table>

**ideal el. reconstruction scenario**
Challenges and requirements:

- suitable probing depth:
  - photons (10 nm ... microns)
  - electrons (0.3 ... 10 nm)
- interface signal vs. background intensity from bulk
- spectroscopic contrast:
  - symmetry
  - element specificity
  - chemical shift
  - electronic configuration
- sufficiently high count rates

Methods presented here:

- hard x-ray photoelectron spectroscopy (HAXPES)
- resonant soft x-ray angle-resolved PES (SX-ARPES)
HAXPES of LAO/STO: core levels

- Ti$^{3+}$ weight evidence for 2DES
- Ti$^{3+}$/Ti$^{4+}$ ratio $\rightarrow$ sheet carrier density
- angle dependence $\rightarrow$ thickness

PRL 102, 176805 (2009)
Model and quantitative analysis

Exponential damping:

\[ I \sim e^{-z/\lambda \cos \theta} \]

Intensity ratio:

\[ \frac{I(3+)}{I(4+)} = \frac{p(1 - \exp(-d/\lambda \cos \theta))}{1 - p(1 - \exp(-d/\lambda \cos \theta))} \]

Accessible parameters:

- \( d \) : 2DEG thickness
- \( p \) : Ti\(^{3+}\) fraction
- \( n_{2D} \) : sheet carrier density (= \( p d/\alpha_{STO}^2 \))

Angle dependence

\[ d \ll \lambda \]
\[ d \gg \lambda \]

\( \lambda = 40\text{Å} \)

\( \text{PRL 102, 176805 (2009)} \)
Quantitative analysis

**Graphical Data:**
- **Graph Title:** Plot of intensity versus binding energy for different emission angles.
  - Data points for Ti 2p, hν = 3keV.
  - Intensity (arb. units) vs. binding energy (eV).
- **Data Points:**
  - 5uc LAO, PSI:
    - θ = 05° off NE
    - θ = 35°
    - θ = 50°
    - θ = 60°
- **Graph Details:**
  - **x-axis:** Binding energy (eV).
  - **y-axis:** Intensity (arb. units).
  - **Peak:** Ti^3+.

**Additional Information:**
- **Figure Details:**
  - Scatter plot with a best fit line.
  - Emission angle (degree) versus (3+)/4+.
  - Data points and error bars.

**Table of Data:**
- **5uc LAO, PSI**
  - (p=0.28, d=1uc)
  - p=0.10...0.28
  - d=1uc...3uc

**References:**
- PRL 102, 176805 (2009)
Quantitative analysis: 2DEG thickness

<table>
<thead>
<tr>
<th>Sample</th>
<th>2 uc</th>
<th>4 uc</th>
<th>5 uc</th>
<th>6 uc</th>
</tr>
</thead>
<tbody>
<tr>
<td>(d) (uc*)</td>
<td>3 ± 1</td>
<td>1 ± 0.5</td>
<td>6 ± 2</td>
<td>8 ± 2</td>
</tr>
</tbody>
</table>

*lattice constant of STO unit cell (uc) = 3.8 Å*

\[ \text{interface thickness < 3 nm} \] *

consistent with

- CT-AFM \(\text{Basletic et al. (2008)}\)
- TEM-EELS \(\text{Nakagawa et al. (2006)}\)
- density functional theory \(\text{Pentcheva et al. (2009)}\)
- 2D superconductivity \(\text{Reyren et al. (2007)}\)
- ellipsometry \(\text{Dubroka et al. (2010)}\)

* HAXPES data taken at 300K! \(\text{PRL 102, 176805 (2009)}\)
Quantitative analysis: sheet carrier density

<table>
<thead>
<tr>
<th>Sample</th>
<th>2 uc</th>
<th>4 uc</th>
<th>5 uc</th>
<th>6 uc</th>
<th>el. reconstr.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(p)</td>
<td>0.01</td>
<td>0.05</td>
<td>0.02</td>
<td>0.02</td>
<td>0.5</td>
</tr>
<tr>
<td>(n_{2D} \times 10^{13} \text{ cm}^{-2})</td>
<td>2.1</td>
<td>3.9</td>
<td>8.1</td>
<td>11.1</td>
<td>35</td>
</tr>
</tbody>
</table>

- \(n_{2D}\) much smaller than for purely electronic reconstruction
- \(n_{2D}\) higher than Hall effect data
- Photogeneration of extra Ti 3d electrons
- Remaining excess due to additional localized Ti 3d electrons?

(cf. Li et al. and Bert et al., Nature Phys. (2011): coexistence of superconductivity (free carriers) and magnetism (local moments))
Resonant angle-resolved soft x-ray photoemission: Direct k-space mapping of the electronic structure in an oxide-oxide interface
Soft x-ray ResPES of the valence band

HAXPES ($h\nu = 3.5$ keV)

$O_2p$

SX-ResPES ($h\nu \sim 460$ eV)

resonance enhancement at Ti L edge

*PRB 88, 115111 (2013)*
Soft x-ray ResPES of the valence band

ResPES process

SX-ResPES ($h\nu \sim 460$ eV)

Resonance enhancement at Ti L edge

cf.: 
Drera et al., APL 98, 052907 (2011)
Koitzsch et al., PRB 84, 245121 (2011)
LAO/STO: resonant photoemission at Ti L-edge

- two Ti 3d resonance features below (A) and at $E_F$ (B)
LAO/STO: resonant photoemission at Ti L-edge

- two Ti 3d resonance features below (A) and at $E_F$ (B)

**feature A:**
- max enhancement at Ti$^{3+}$ $e_g$ resonance (cf. LaTiO$_3$)
two Ti 3d resonance features below (A) and at $E_F$ (B)

**feature A:**
max enhancement at $\text{Ti}^{3+} e_g$
resonance (cf. LaTiO$_3$)

**feature B:**
max enhancement **delayed**
→ characteristic for localized (A) and **delocalized** (B) resonating states
LAO/STO: resonant photoemission at Ti L-edge

- two Ti 3d resonance features below (A) and at $E_F$ (B)

**feature A:**
max enhancement at Ti$^{3+}$ $e_g$ resonance (cf. LaTiO$_3$)

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max enhancement *delayed*
→ characteristic for localized (A) and delocalized (B) resonating states

- features A and B also seen in O-deficient STO (e.g., Aiura et al., Surf. Sci. 515, 61 (2002))
LAO/STO: resonant photoemission at Ti L-edge

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- features A and B also seen in O-deficient STO (e.g., Aiura et al., Surf. Sci. **515**, 61 (2002))

⇒ A: charge carriers trapped in d-orbitals of Ti ions surrounding oxygen vacancies

B: mobile interface charge carriers (2DES)
Photoemission of bare STO surface


O-vacancies at surface cause n-doping of Ti 3d states

- Itinerant carriers in conduction band
- In gap weight: localized electrons trapped next to oxygen vacancies
LAO/STO: k-space mapping by SX-ARPES

Schematic Ti 3d-derived Fermi surface

*Popovic et al., PRL 101, 256801*
LAO/STO: k-space mapping by SX-ARPES

- good agreement with DFT band calculations
- individual quantum well states not resolved
- O 2p surface band not observed
LAO/STO: k-space mapping by SX-ARPES

larger \( k_F \)-values along \( \Gamma X \) than \( \Gamma M \) also seen in experiment
LAO/STO: Fermi surface mapping

cf. also: Cancellieri et al., arXiv:1307.6943

experiment does not show LAO-surface hole pockets predicted by band theory!
BL23SU, SPring-8

\[ h\nu = 460.35 \text{eV} \]

Ti 3d \( xz/yz \) bands

Ti 3d \( xy \) bands

O 2p surface band

\( k_x (\text{Å}^{-1}) \)

\( k_y (\text{Å}^{-1}) \)

max

min

but:

- 2uc samples charge up
- no variation on changing photon flux
- band bending seen in other systems, e.g., LaCrO\(_3\)/STO

dynamical equilibrium?


cf. also: Cancellieri et al., \textit{arXiv}:1307.6943
Oxygen vacancies at LAO surface?

O vacancies induce localized hole states above $E_F$

Yun Li et al., PRB 84, 245307 (2011)

cf. also: Zhong et al., PRB 82, 165127 (2010)
Bristowe et al., PRB 83, 205405 (2011)
Pavlenko et al., PRB 86, 064431 (2012)
Yu and Zunger, arXiv:1402.0895

• modified el. reconstruction scenario
• critical thickness, if for each $O_{\text{vac}}$ formation energy < discharge energy
Most of the first part has been taken from the following sources:

**Internet**

**Books**

**Review articles**

For the second part look up references in the lecture notes “DMFT at 25: Infinite Dimensions”.