Introduction to Photoemission Spectroscopy

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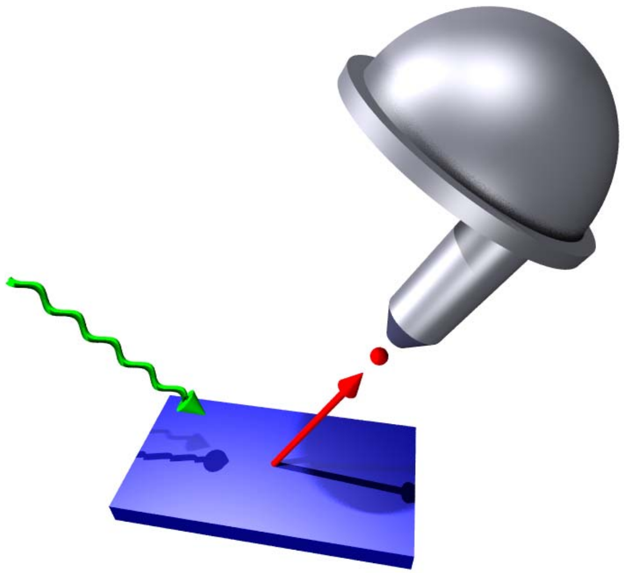
Outline:

- Basics
- PES theory I: (mainly) independent electrons
- PES theory II: many-body picture
- Case studies – towards higher photon energies

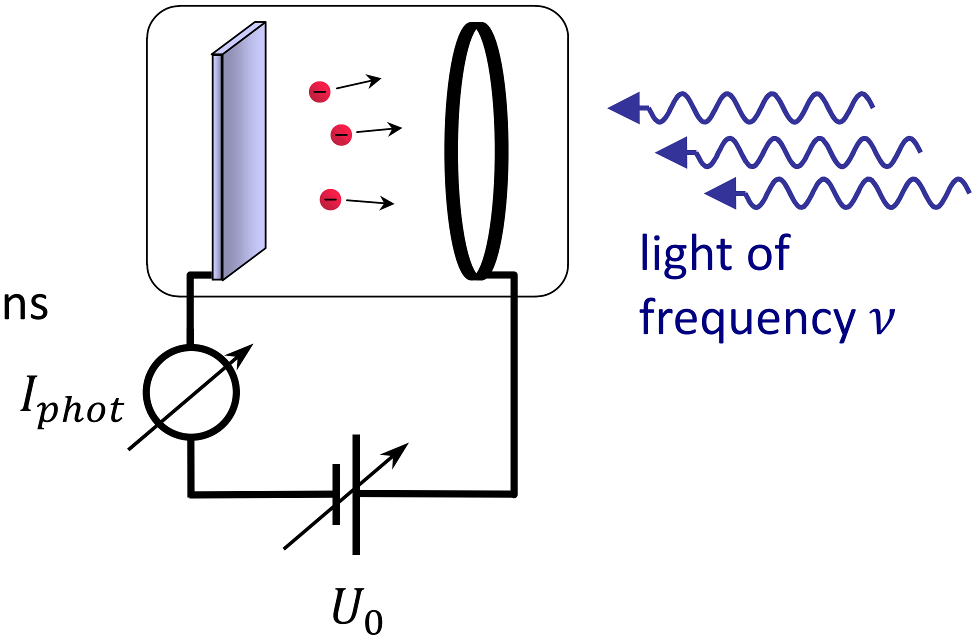


Photoemission basics

The photoelectric effect

quantitative experiment:
(H. Hertz 1886, W. Hallwachs 1888,
P. Lenard 1902)

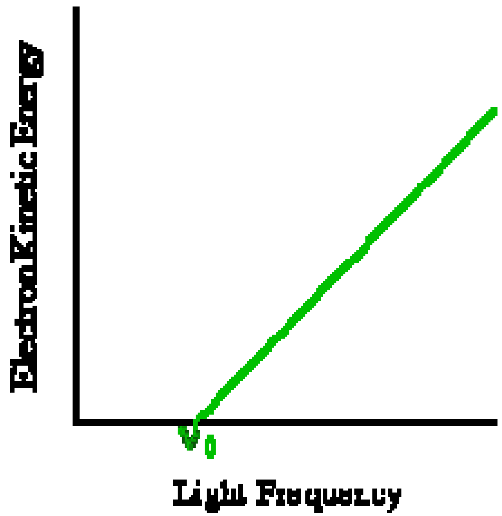
measure kinetic energy of photoelectrons in retarding field



experimental observations:

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

$$\boldsymbol{E_{kin}^{max} \propto \nu - const}$$



The photoelectric effect

A. Einstein
Nobel prize 1921

Theoretical explanation by A. Einstein (1905):
QUANTIZATION OF LIGHT

Ann. d. Phys. 17, 132 (1905):

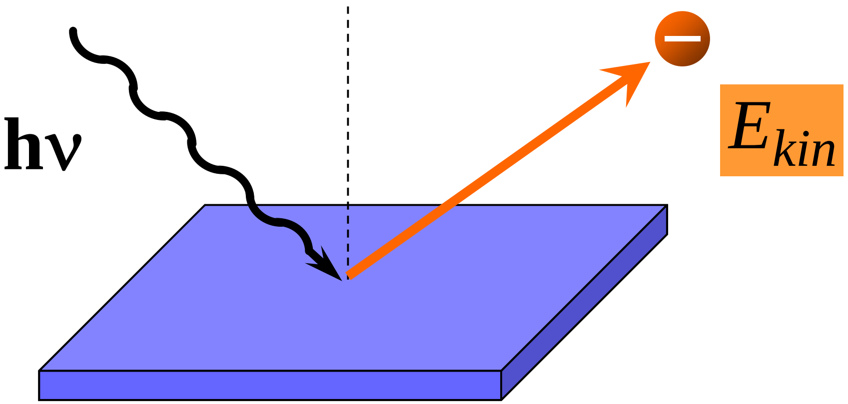
Die kinetische Energie solcher Elektronen ist

$$\frac{R}{N}\beta\nu - P.$$

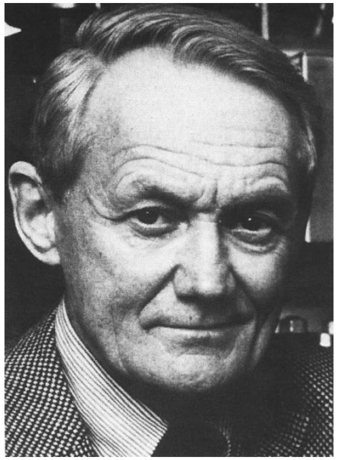
$$E_{kin}^{max} = h\nu - \Phi$$

Planck´s constant

photocathode workfunction



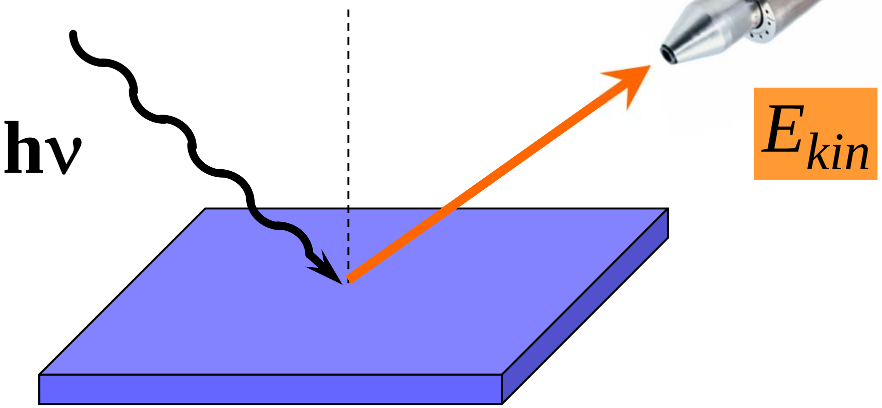
Photoelectron spectroscopy

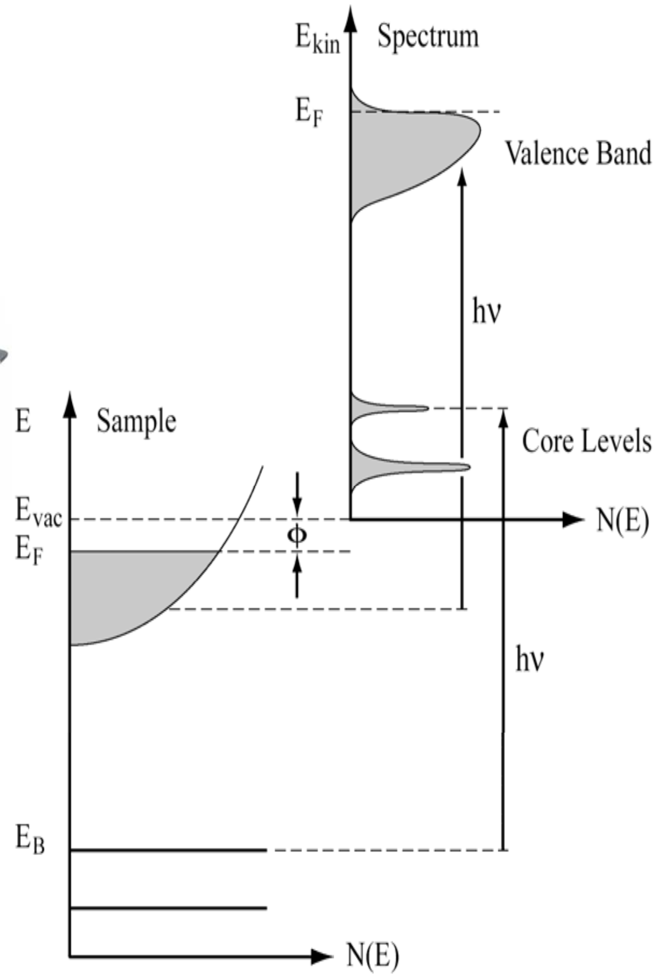


K.M. Siegbahn
Nobel prize 1981

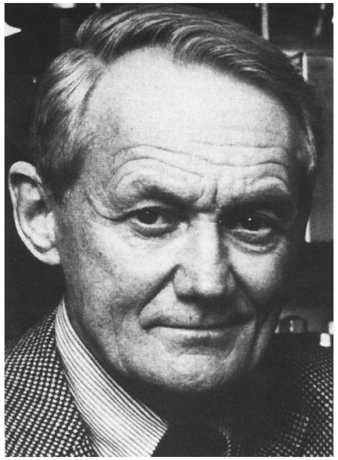
energy conservation: $E_{kin} = h\nu - E_B - \Phi$

electron analyzer





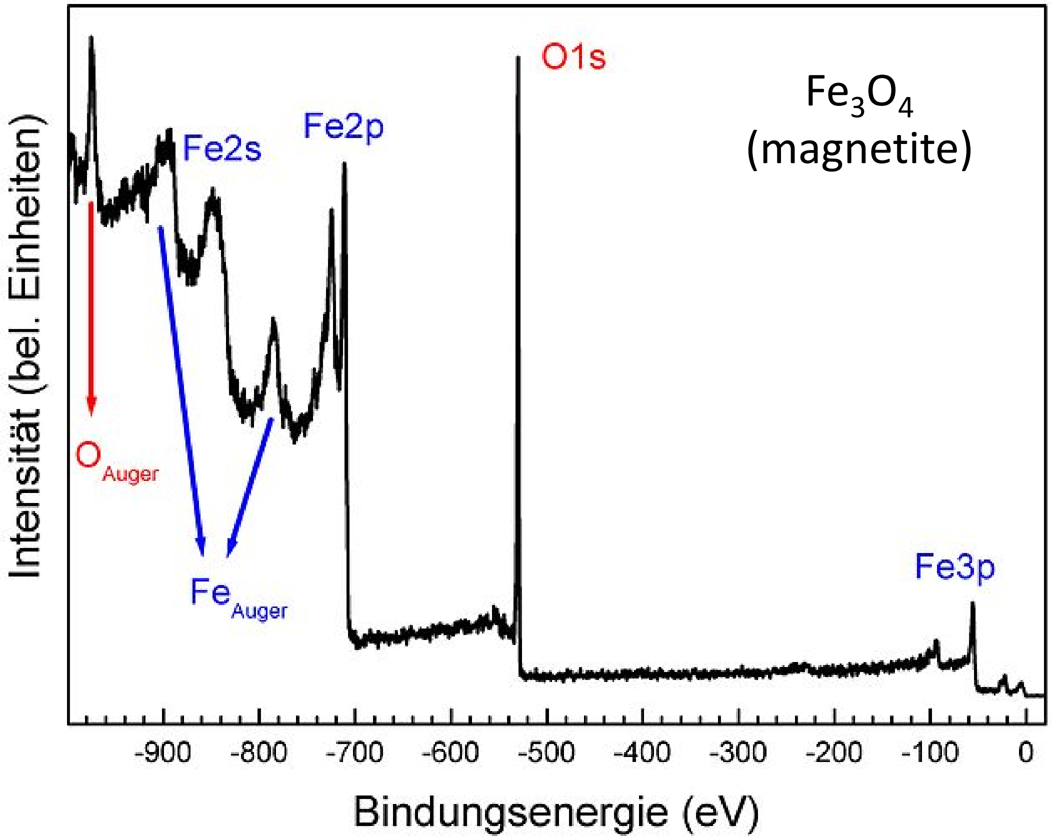
Photoelectron spectroscopy: ESCA



K.M. Siegbahn
Nobel prize 1981

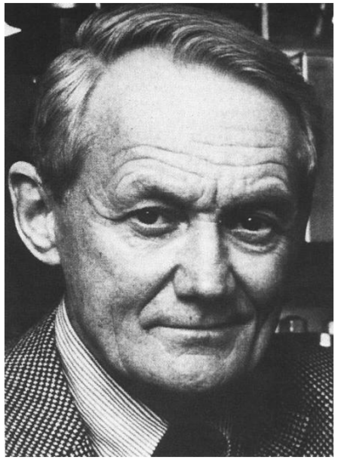
energy conservation: $$E_{kin} = h\nu - E_B - \Phi$$

→ **Electron Spectroscopy for Chemical Analysis**



chemical composition

Photoelectron spectroscopy: ESCA



K.M. Siegbahn
Nobel prize 1981

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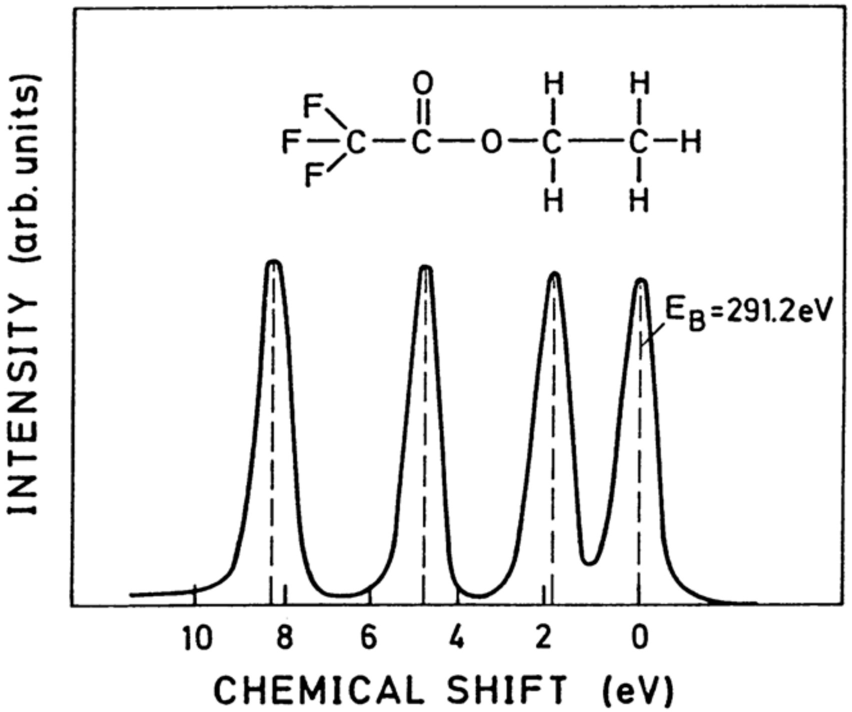
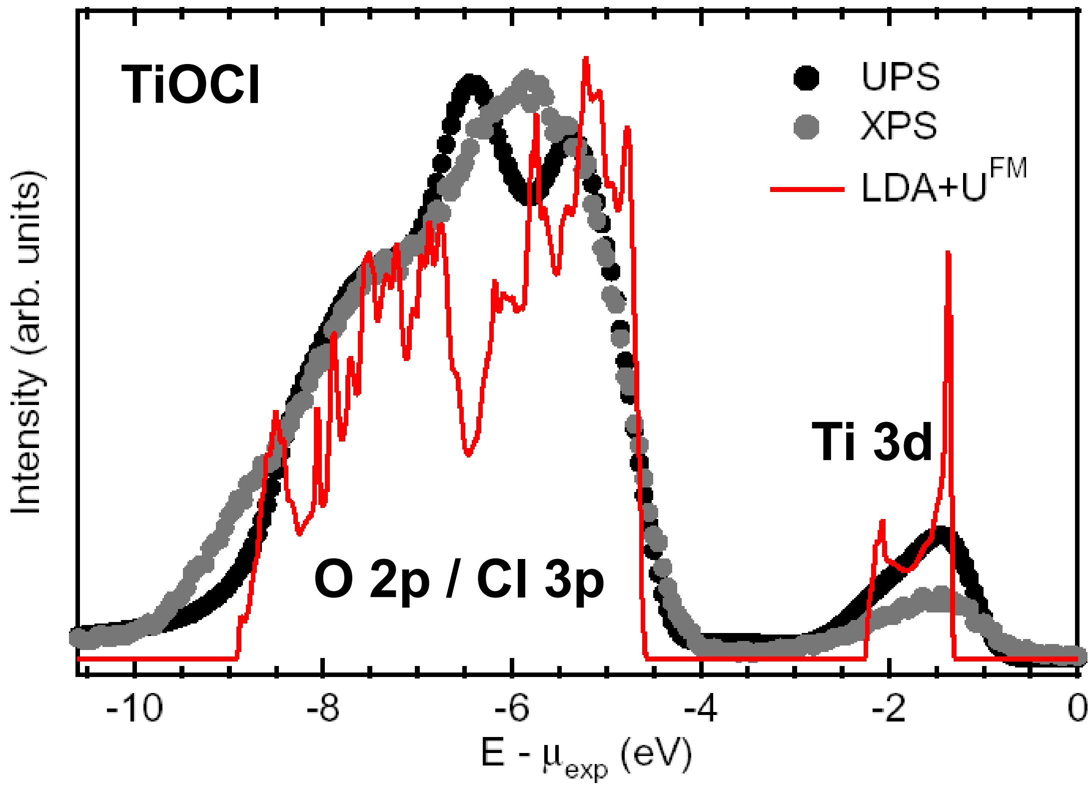
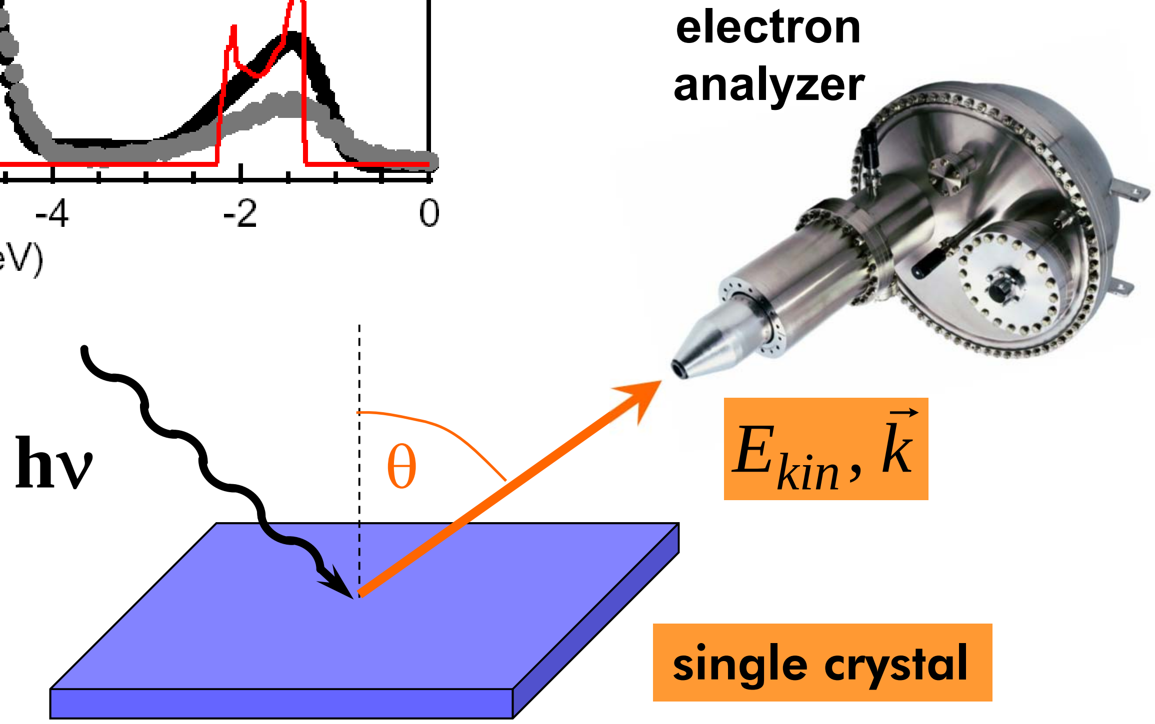
→ **Electron Spectroscopy for Chemical Analysis**



chemical shifts
in C 1s spectrum of
ethylfluoroacetate

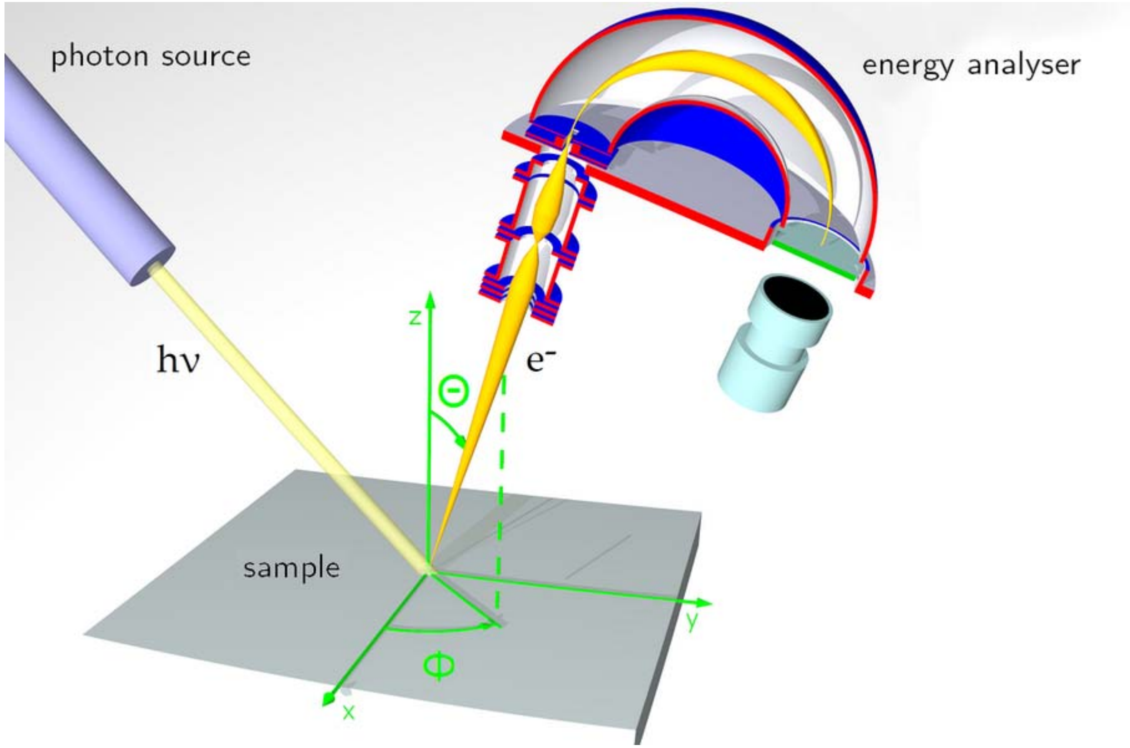
Photoelectron spectroscopy: valence bands





Angle-resolved photoemission (ARPES)

measure energy **and momentum** of the photoelectrons:



$\boldsymbol{E_{kin}, \theta, \varphi} \longrightarrow \boldsymbol{\vec{K}}$

with

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

$$K_x = |\vec{K}|\, sin\theta\; cos\phi$$

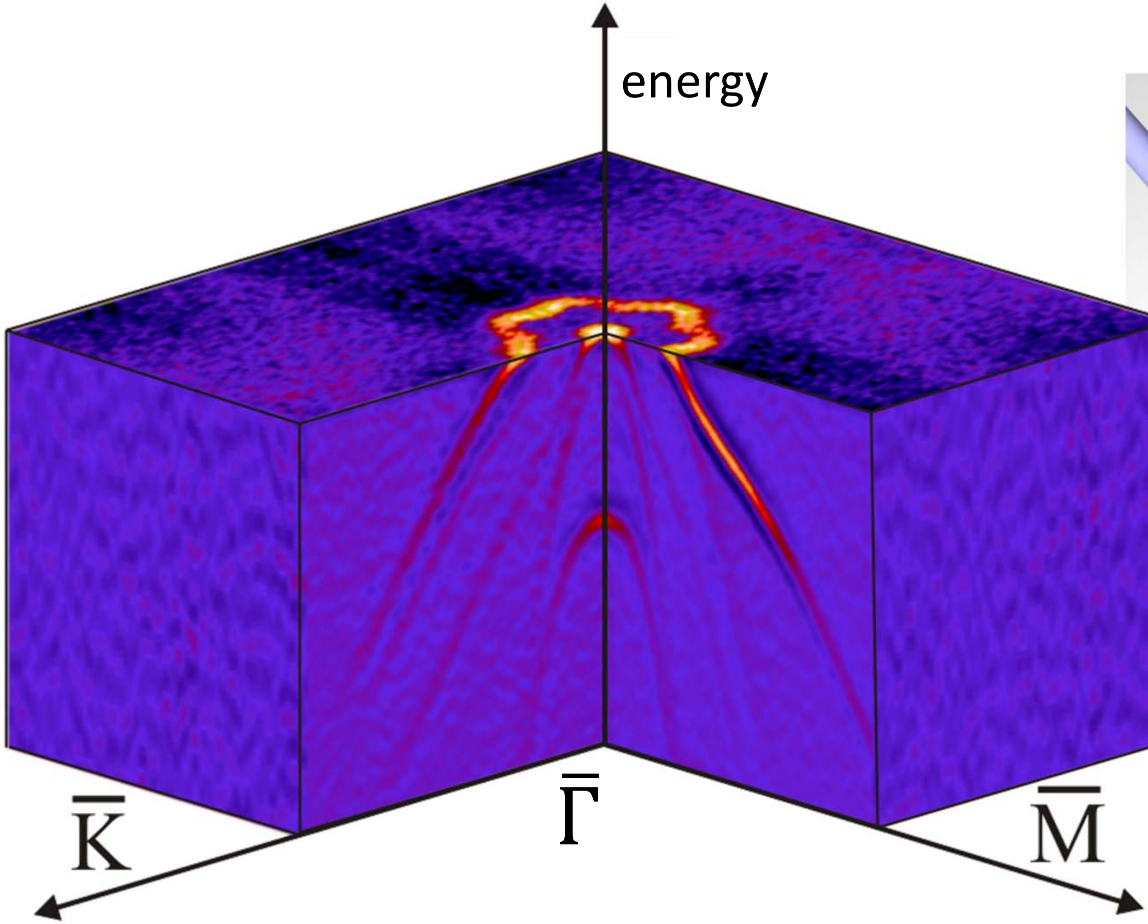
$$K_y = |\vec{K}|\, sin\theta\; sin\phi$$

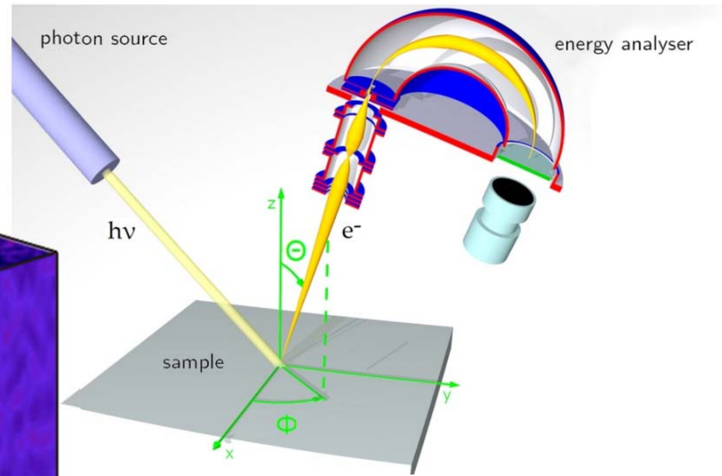
$$K_z = |\vec{K}|\, cos\theta$$

vacuum	**conservation laws**	**solid**
E_{kin}, $\vec{K}$	$E_{kin} = h\nu - \lvert E_B\rvert - \phi$ $\vec{K} = \vec{k}\;\; (+\vec{k}_{photon})$	E_B, $\vec{k}$

Angle-resolved photoemission (ARPES)

measure energy **and momentum** of the photoelectrons:





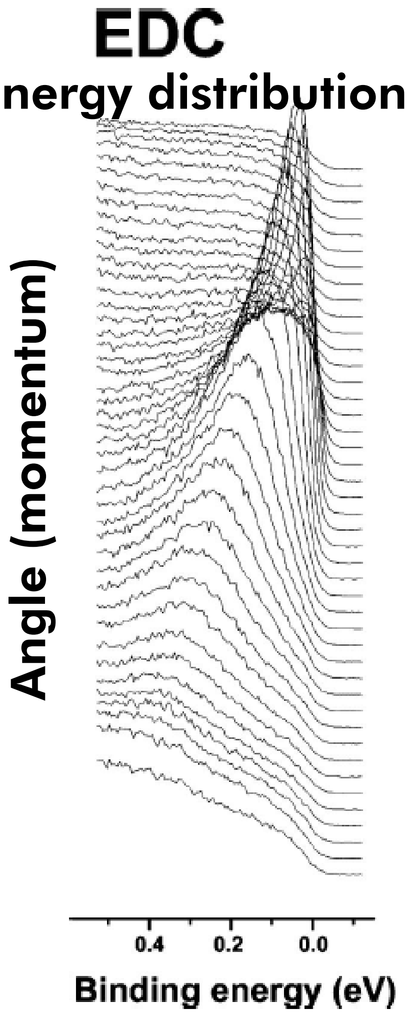
example:
Au/Ge(111)

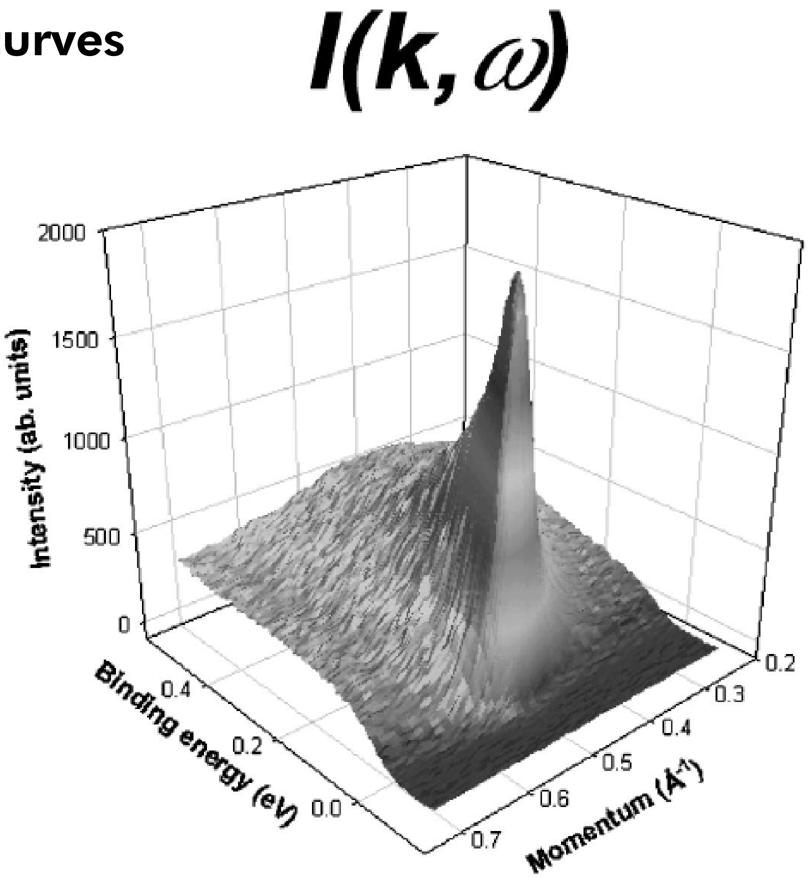
→ k-space band structure mapping: band dispersions, Fermi surface, …

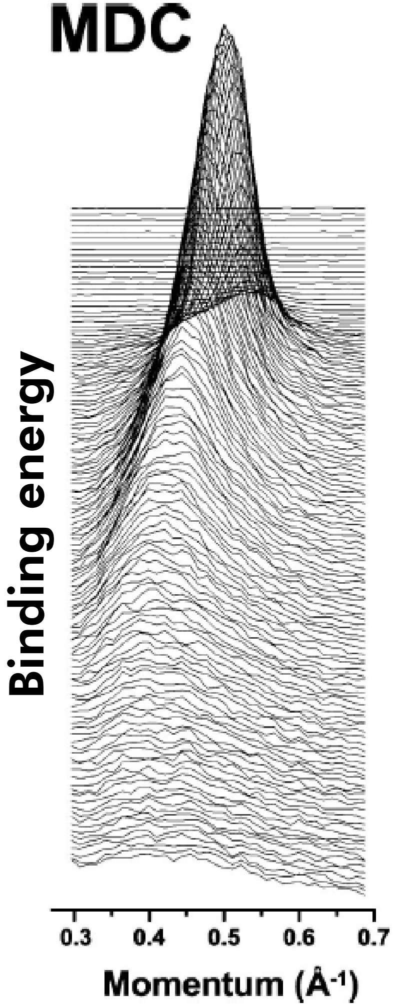
Angle-resolved photoemission (ARPES)

Example: Cuprate-High Tc superconductor - 2D Pb-BSCCO ($Bi_2Sr_2CaCu_2O_{8+\delta}$)

momentum distr. curves







*Borisenko et al., Phys. Rev B **64**, 094513 (2001)*

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: $\hat{H} = \hat{H}_0 + \hat{H}_{int} e^{-i\omega t}$

unperturbed system

operator of time-dependent perturbation (radiation field)

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):

$\hat{H}_{int} e^{-i\omega t}$

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:

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

transition matrix element:

- **k conservation**
- **symmetry**

energy conservation!

Fermi's Golden Rule

Perturbing radiation field: What is $\hat{H}_{int}$?

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

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

→ electric field: $\vec{E}(\vec{r},t) = -\frac{\partial}{\partial t}\vec{A}(\vec{r},t)$

→ magnetic field: $\vec{B}(\vec{r},t) = \nabla \times \vec{A}(\vec{r},t)$

N.B.: $\nabla \cdot \vec{A}(\vec{r},t) = \mathrm{div}\,\vec{A}(\vec{r},t) = 0$, 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 ε
→ **surface photoemission** *see, e.g., Miller et al., PRL **77**, 1167 (1996)*

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*classical description ignores quantum nature of photon,
justified for sufficiently low photon intensities (→ VUV-laser, FEL ?)

Fermi's Golden Rule

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

canonical replacement in unperturbed Hamiltonian: $\hat{\vec{p}} \rightarrow \hat{\vec{p}} - e\vec{A}$

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

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

$$= \underbrace{\frac{\hat{\vec{p}}^2}{2m} + V(\vec{r})}_{=\hat{H}_0} \underbrace{- \frac{e}{2m}\hat{\vec{p}}\cdot\vec{A} - \frac{e}{2m}\vec{A}\cdot\hat{\vec{p}}}_{-\frac{e}{m}\vec{A}\cdot\hat{\vec{p}} - \frac{e}{2m}\left(-i\hbar\cancel{\vec{\nabla}\cdot\vec{A}}\right)} + \overbrace{\frac{e^2}{2m}\vec{A}^2}^{\text{describes two-photon processes, can be neglected for weak radiation fields}}$$

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

= 0, except possibly at surface !

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

$$\rightarrow \boxed{\hat{H} \approx \hat{H}_0 - \frac{e}{m}e^{i\vec{q}\cdot\vec{r}}\left(\vec{A}_0\cdot\hat{\vec{p}}\right)\, e^{-i\omega t}}$$

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

back to Fermi´s Golden Rule

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

for the **transition matrix element** we now obtain:

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

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

Matrix element and dipole approximation

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

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

$h\nu$ =	21.2 eV	$\rightarrow \lambda$	= 584 Å	(VUV)
	1.486 keV	$\rightarrow$	= 8.3 Å	(XPS)
	6 keV	$\rightarrow$	= 2.0 Å	(HAXPES)

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

$$e^{i\vec{q}\cdot\vec{r}} = 1 + i\vec{q}\cdot\vec{r} + \cdots \approx 1, \quad \text{with } \vec{q}\cdot\vec{r} \sim 2\pi\frac{a_0}{\lambda} \ll 1 \quad \text{for VUV radiation}$$

dipole approximation

Matrix element and dipole approximation

→ simplified matrix element:

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

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

$$M_{if} = -i\frac{E_f - E_i}{\hbar}\vec{A}_0 \cdot \int d^3r\, \psi_f^*(\vec{r})\, \underbrace{[e\vec{r}]}_{\text{electrical dipole operator}}\; \psi_i(\vec{r})$$

→ 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 !

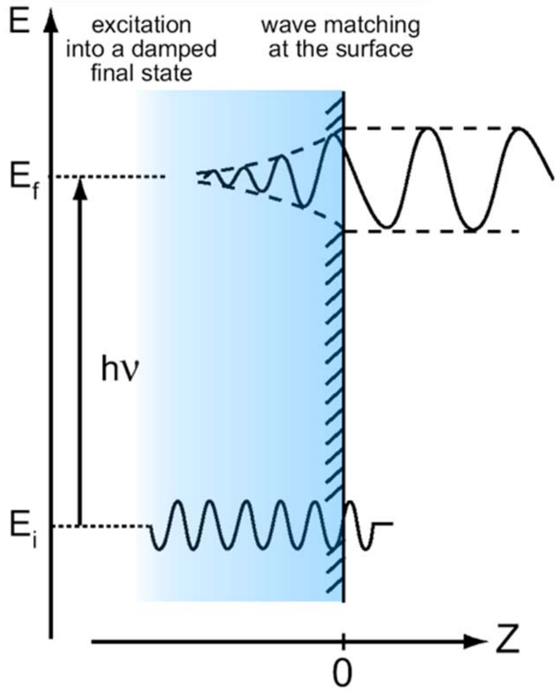
Fermi´s Golden rule and the one-step model

photoemission intensity determined by transition rate:

$$w_{i\to f} = \frac{2\pi}{\hbar} \left|\langle f|\vec{A}_0 \cdot \hat{\vec{p}}|i\rangle\right|^2 \delta(E_f - E_i - \hbar\omega)$$

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 $\vec{k}_i$

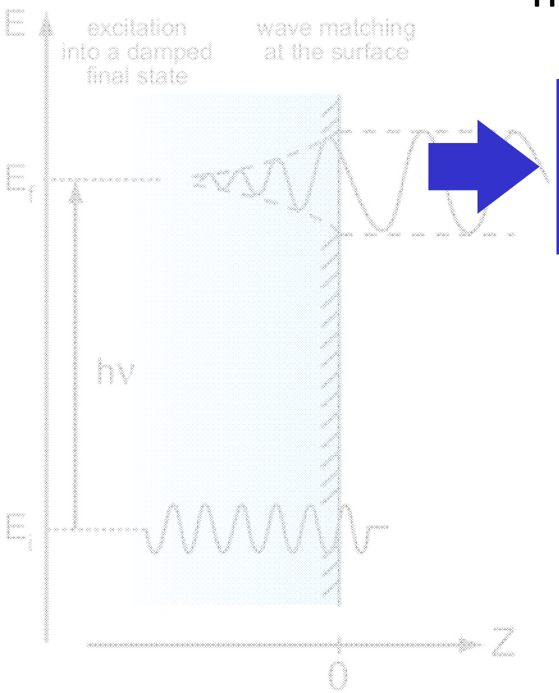
Fermi´s Golden rule and the one-step model

photoemission intensity determined by transition rate:

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

What are the initial and final states?

One-step model:



more on one-step theory of PES

lecture
by Jan Minar

final states: "time-inverted LEED state"

- in vacuum: free electron wave $e^{i\vec{k}_f\cdot\vec{r}}$

to high lying Bloch waves,

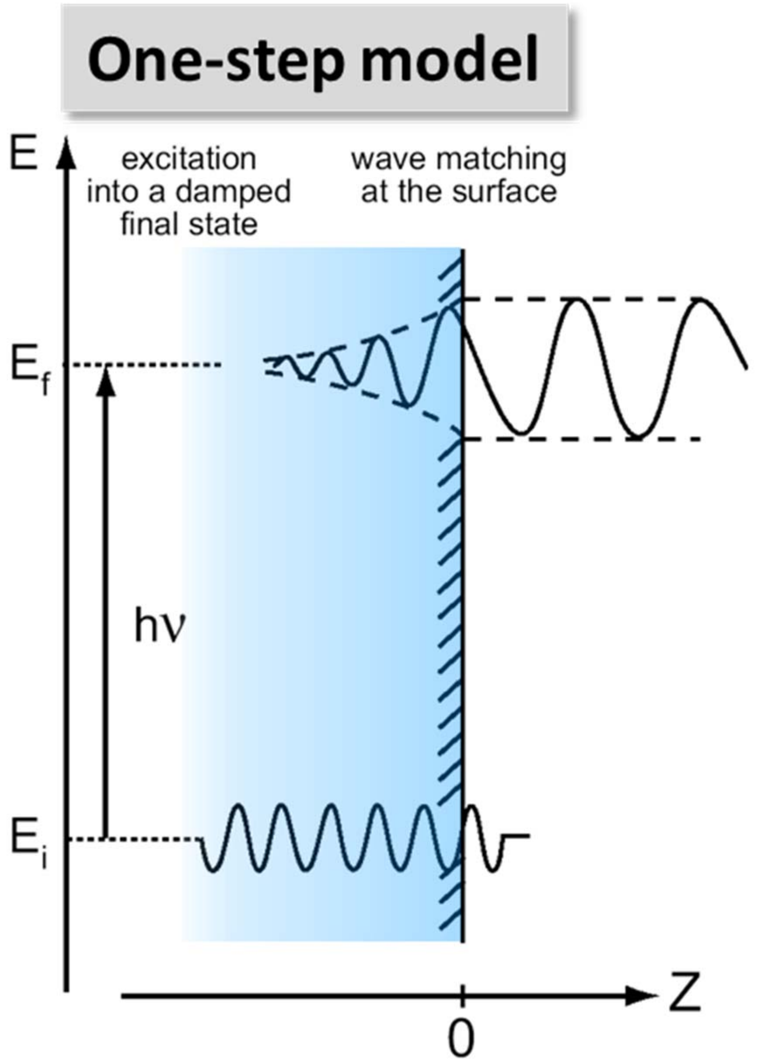
by e-e scattering

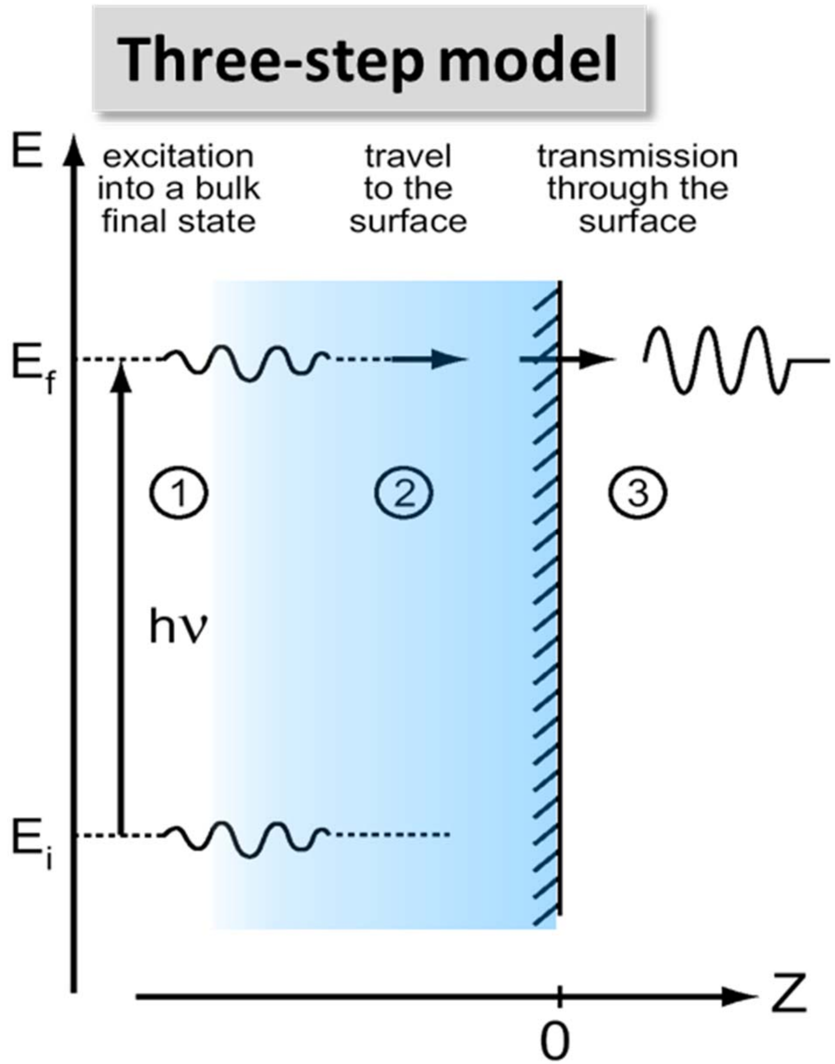
- energy E_f and wavevector $\vec{k}_f$

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 $\vec{k}_i$

One-step model vs. three-step model

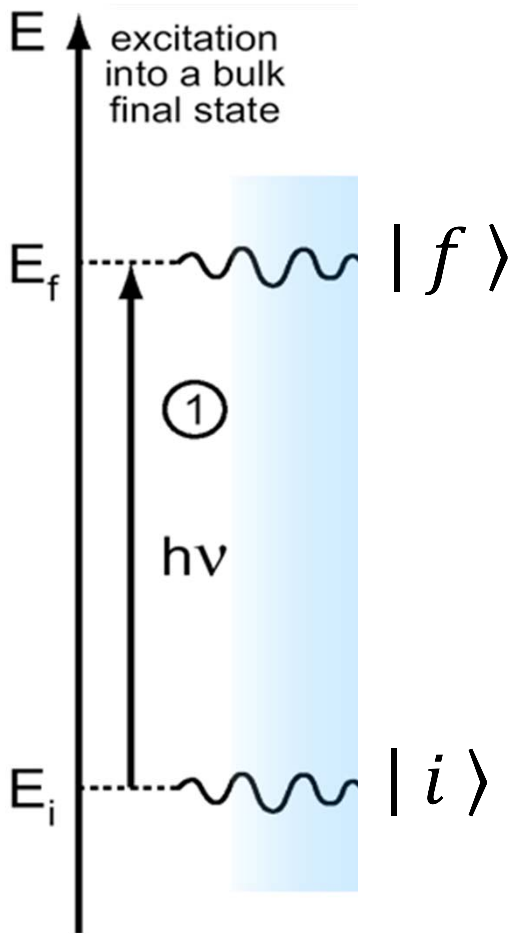


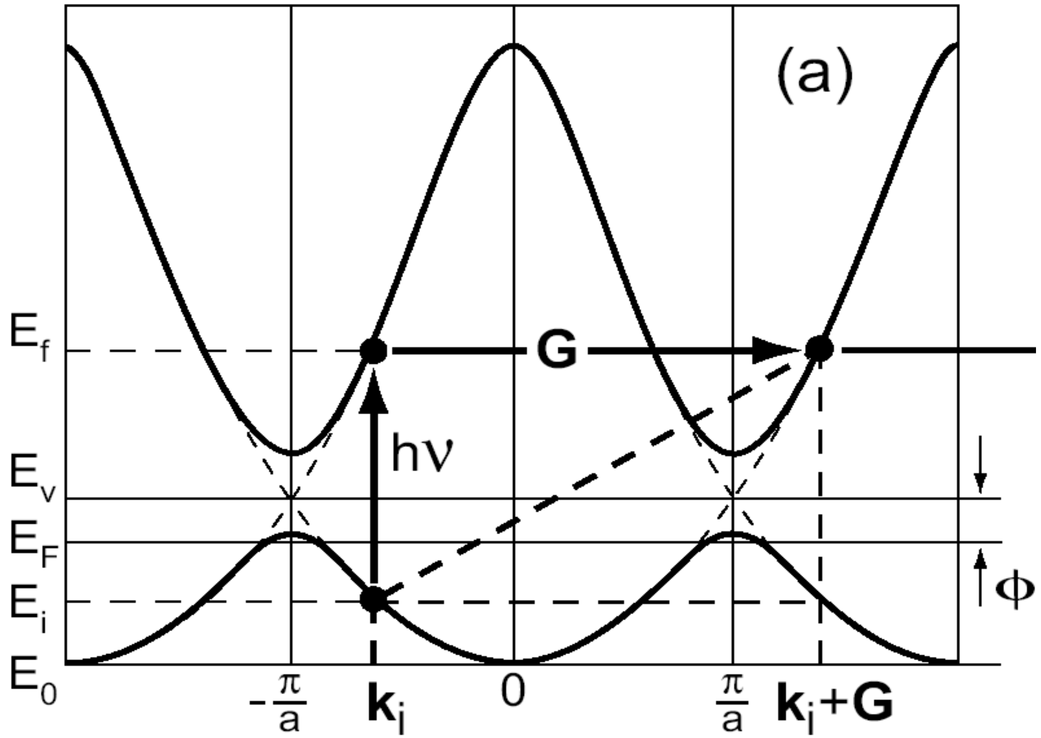


courtesy of A. Damascelli

Step 1: Excitation in the solid

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





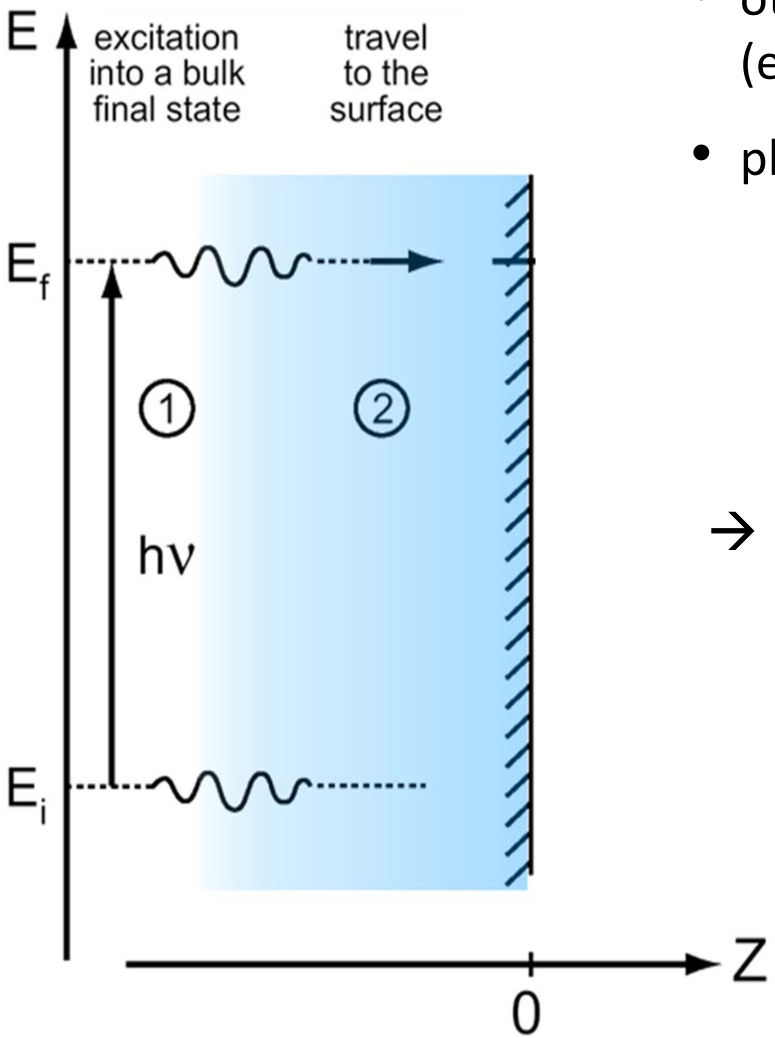
momentum conservation:

$$\vec{k}_f = \vec{k}_i + \vec{G} + \cancel{\vec{k}_{photon}}$$

only "vertical" transitions

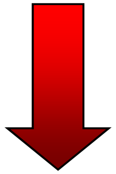
for VUV excitation

Step 2: Transport to the surface

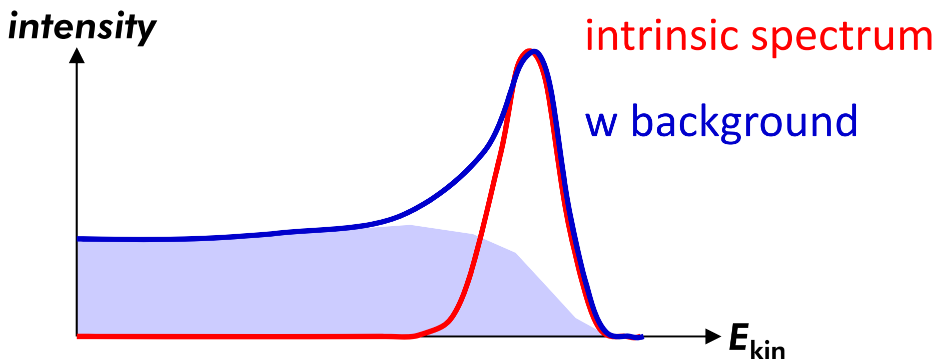


inelastic scattering of the photoelectron with

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

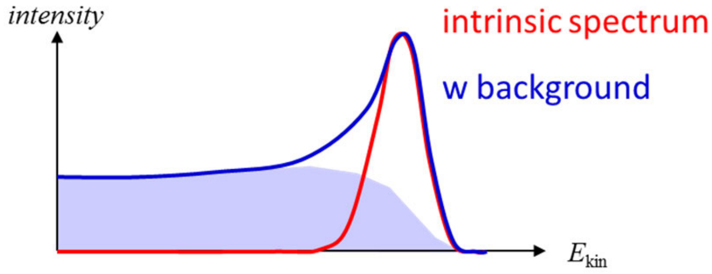


→ generation of secondary electrons
"inelastic background"



Inelastic background

Shirley background

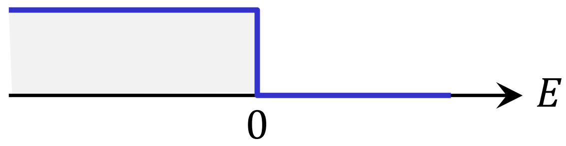


background at energy E proportional to intrinsic spectrum integrated over all energies $E' > E$:

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

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

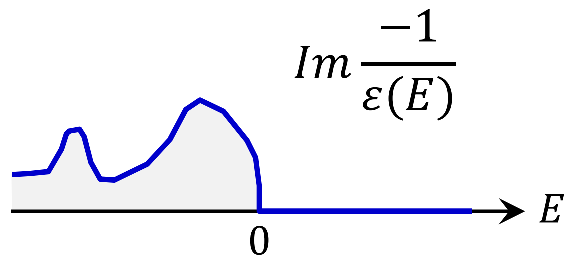
$$I_{BG}(E) = \int_{-\infty}^{+\infty} dE' \, I_0(E') L(E - E')$$



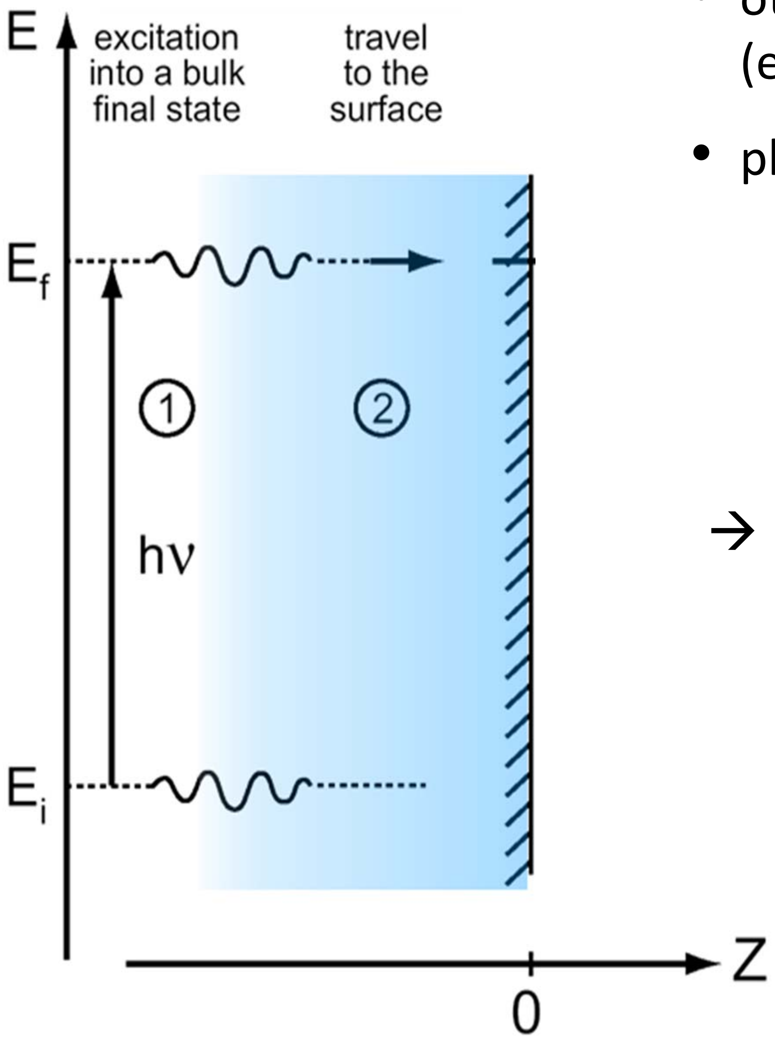
Tougaard background

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

use phenomenological model or determine loss function experimentally (EELS)



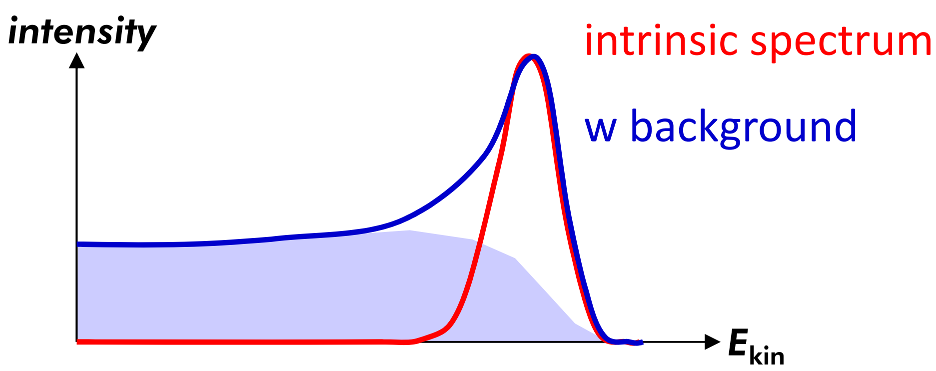
Step 2: Transport to the surface



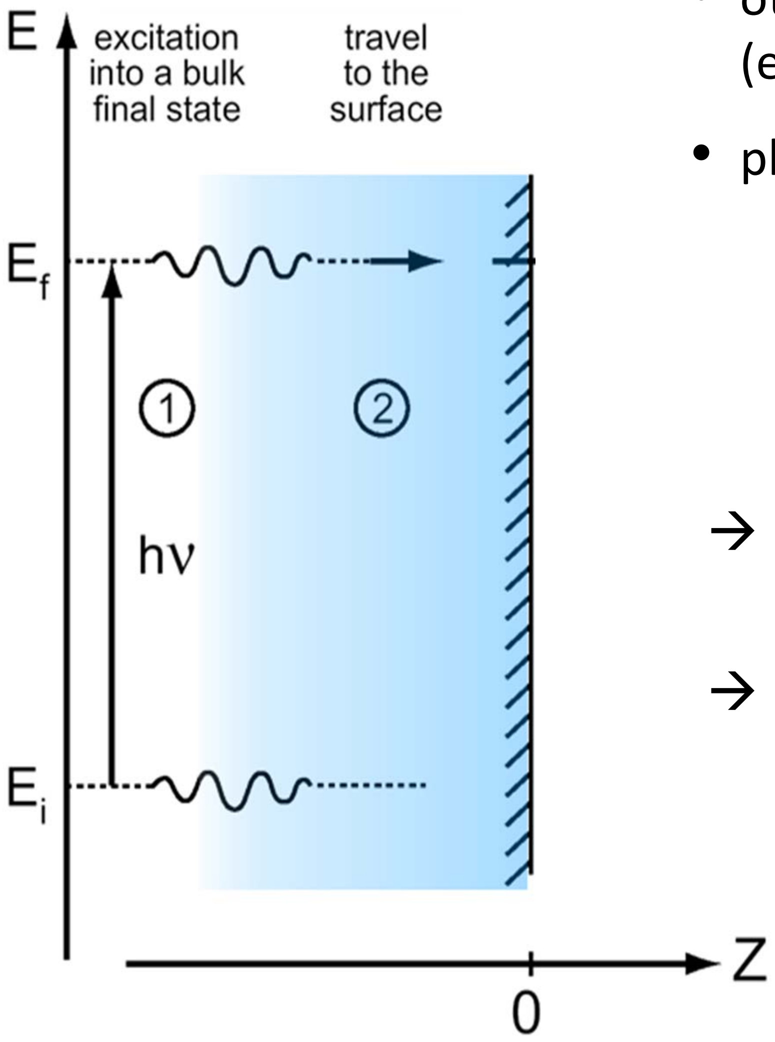
inelastic scattering of the photoelectron with

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

→ generation of secondary electrons
"**inelastic background**"



Step 2: Transport to the surface



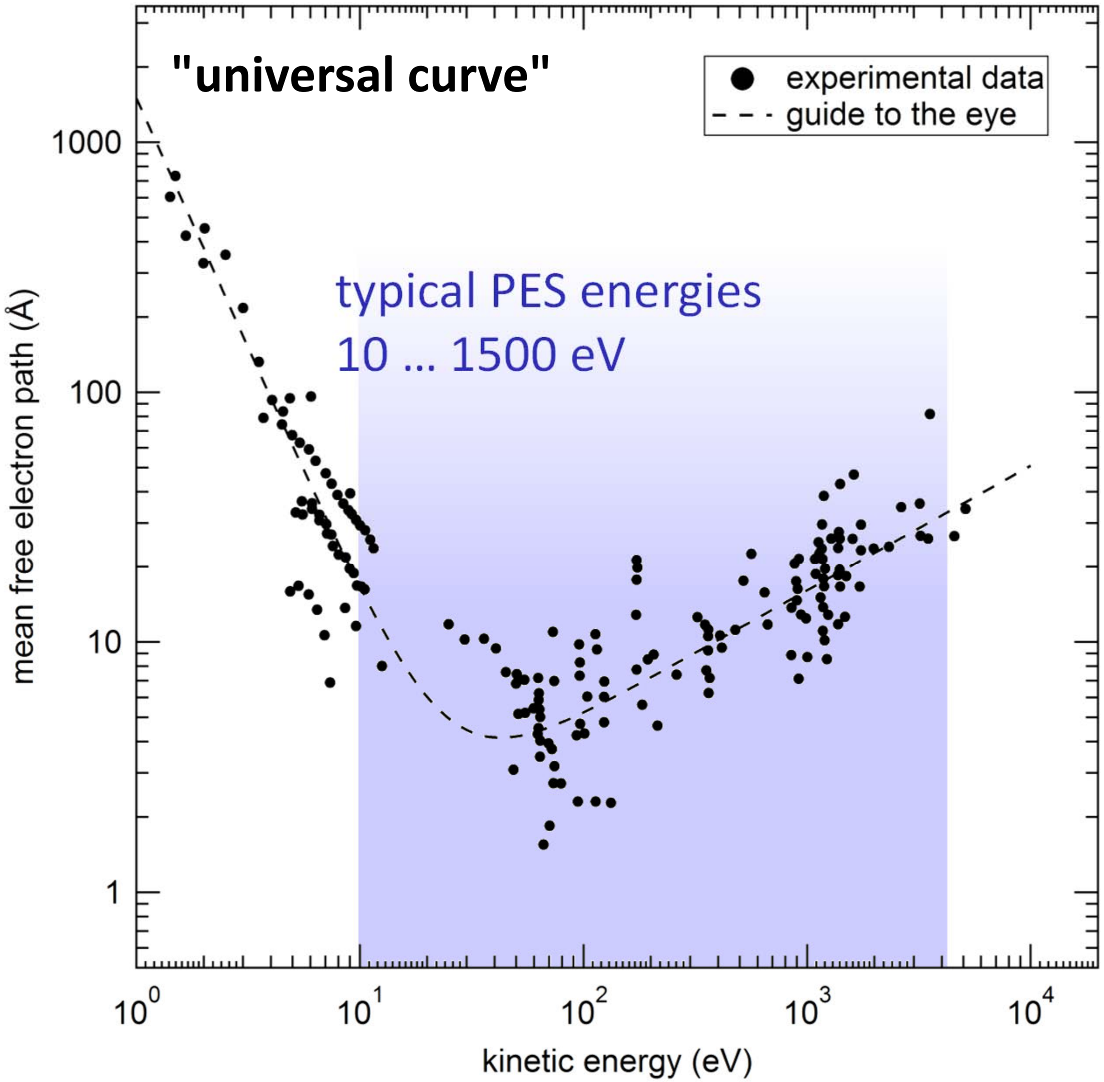
inelastic scattering of the photoelectron with

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

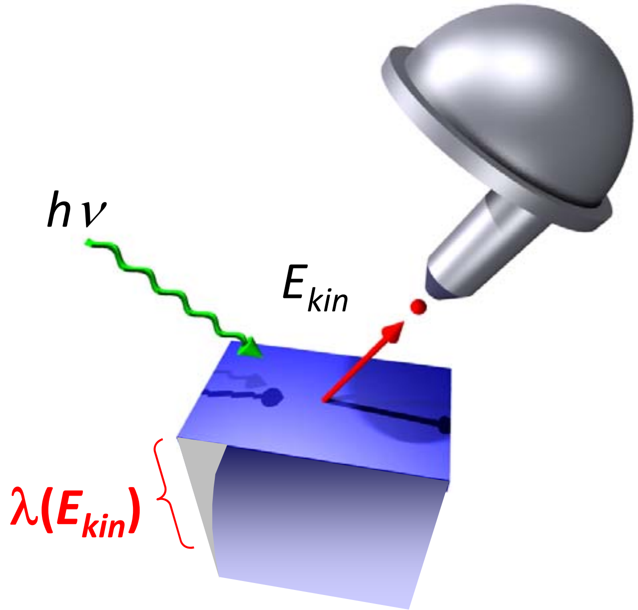
→ generation of secondary electrons
"inelastic background"

→ loss of energy and momentum information in the photoelectron current:
inelastic mean free path λ

Mean free path and PES probing depth



data taken from: M. P. Seah and W. A. Dench, Surface and Interface Analysis, Vol. 1, No. 1, 1979

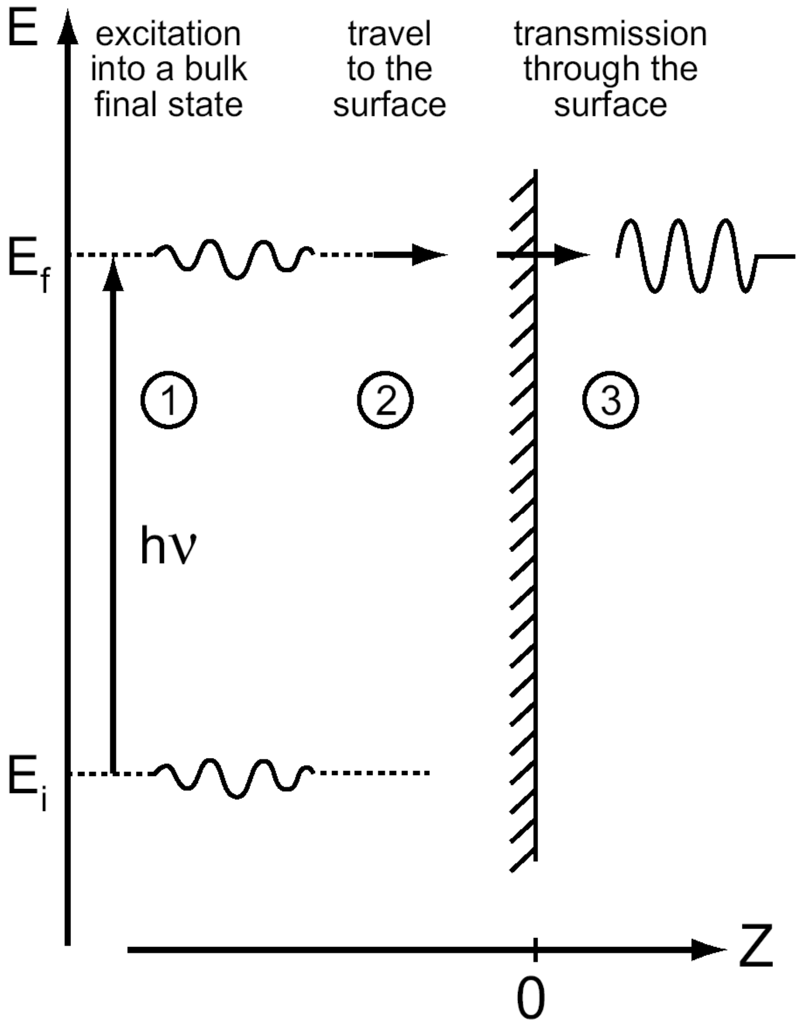


→ λ = 2 … 20 Å

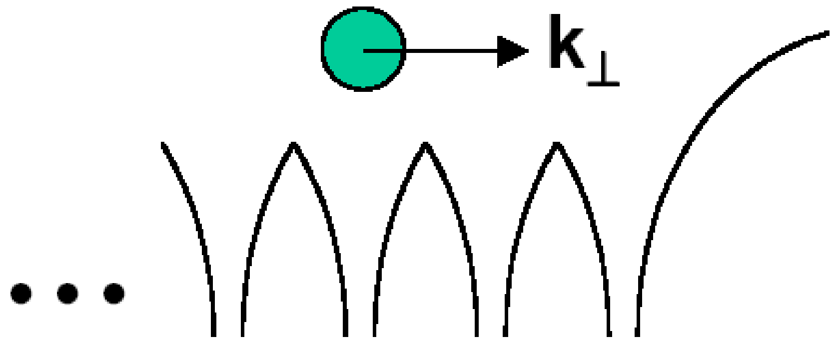
→ PES probing depth: $\sim 3\lambda$
(95% of the signal)

PES is surface-sensitive on atomic length scales !

Step 3: transition to vacuum



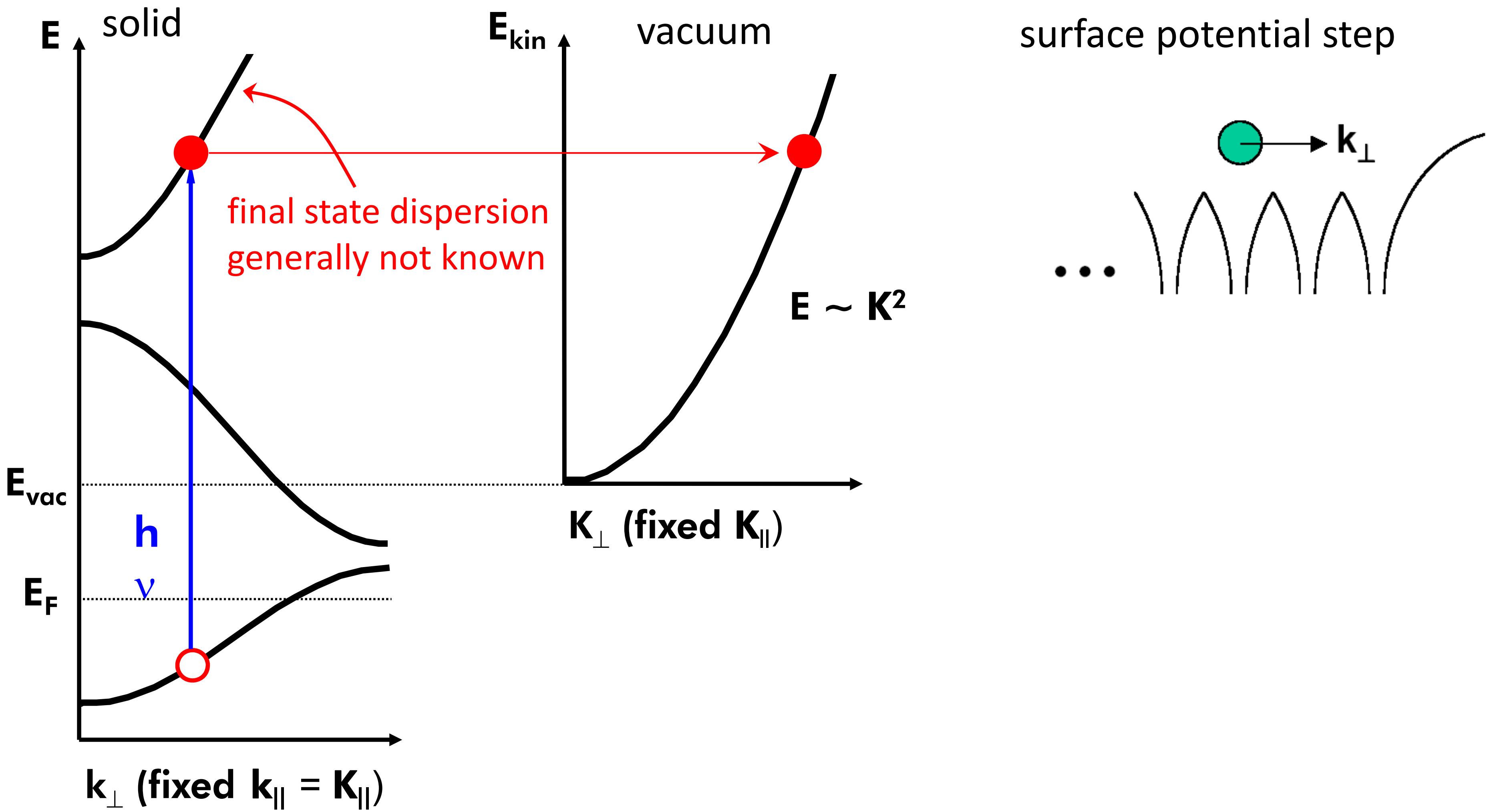
- conservation of wavevector component parallel to surface, $\vec{k}_{\parallel}$
- **But:** change of $k_{\perp}$ changes due to **electron diffraction at surface barrier**



source: E. Rotenberg

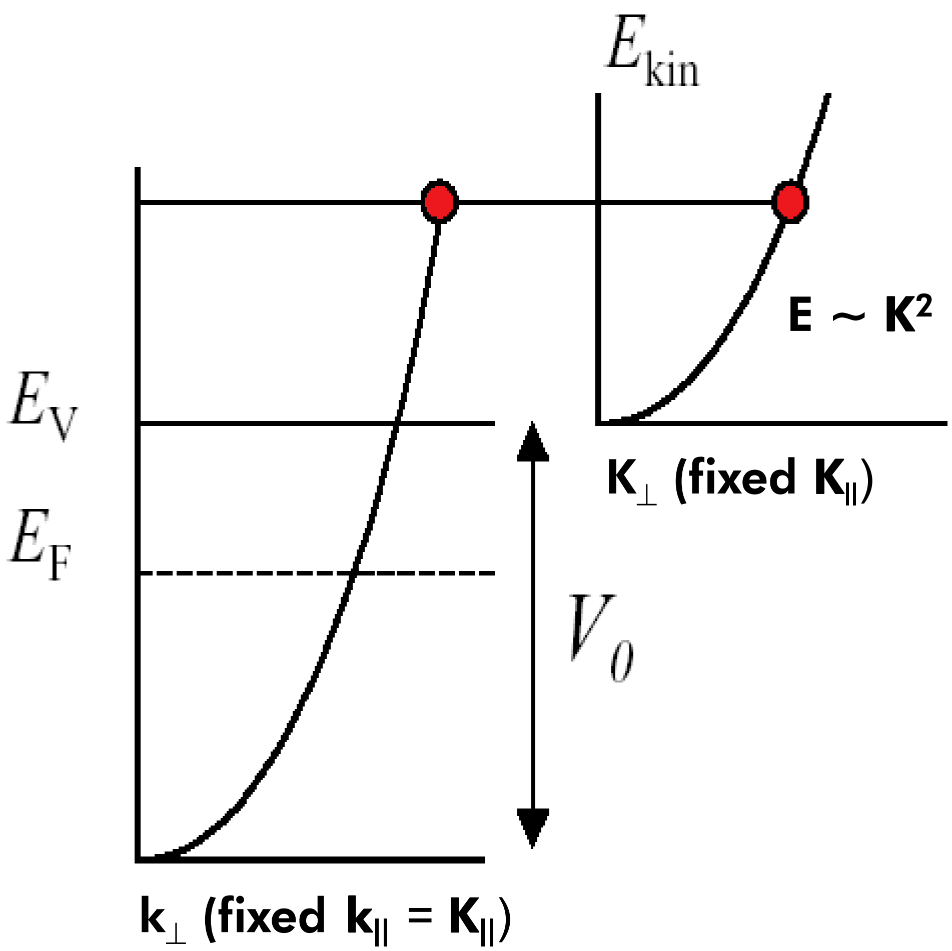
The $k_\perp$ problem

electron wave matching at the surface

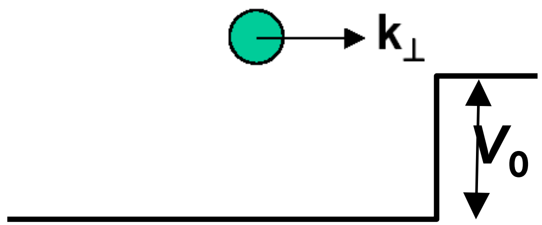


The $k_\perp$ problem

pragmatic solution: free-electron final state model



surface potential step



"inner potential" V_0

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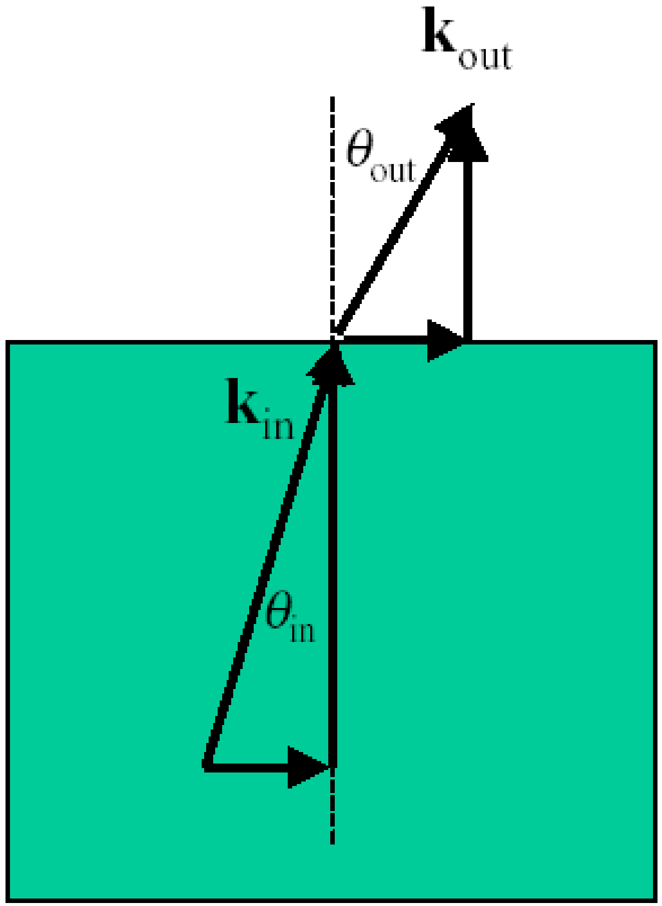


kinematic relations

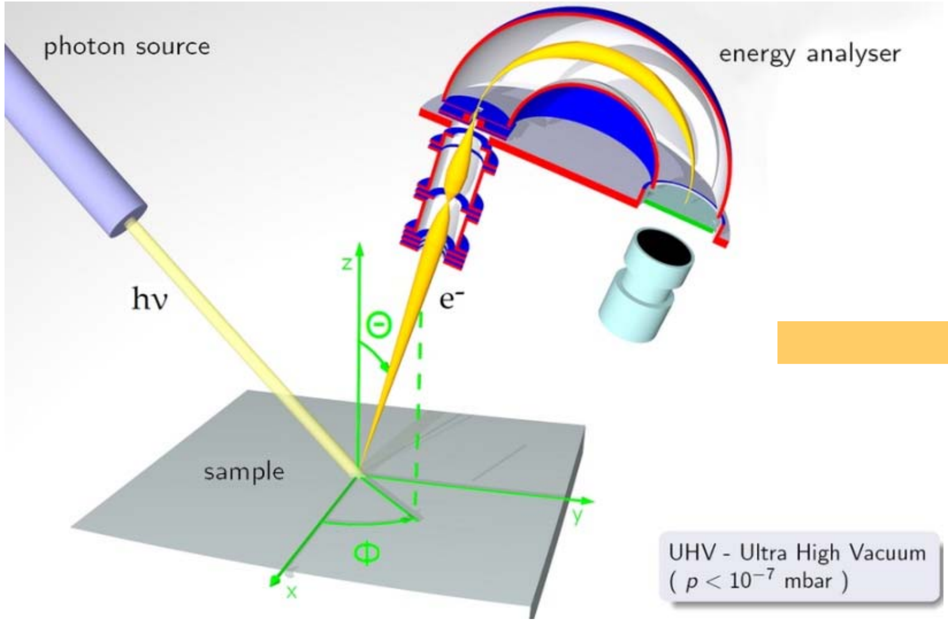
$$E_{kin} = \frac{\hbar^2 \vec{K}_{out}^2}{2m} = \frac{\hbar^2 \vec{k}_{in}^2}{2m} - V_0$$

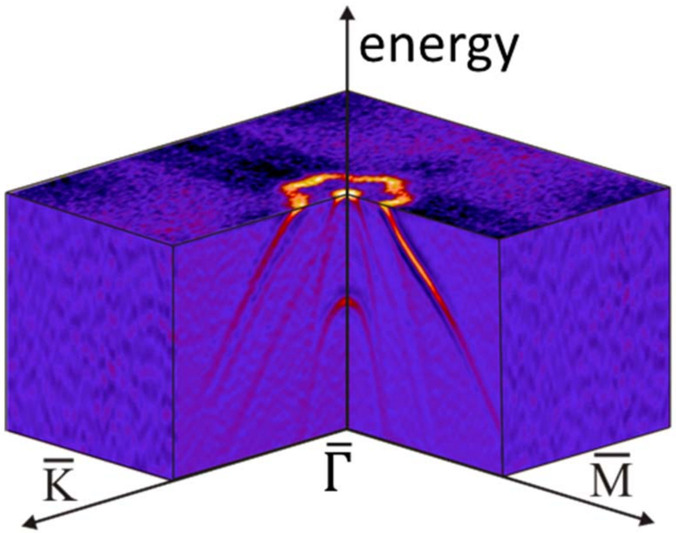
$$\Rightarrow \begin{cases} k_{in,\parallel} = K_{out,\parallel} = \sqrt{\frac{2m}{\hbar^2} E_{kin}} \sin\theta_{out} \\ k_{in,\perp} = \sqrt{\frac{2m}{\hbar^2} (E_{kin}\cos^2\theta_{out} + V_0)} \end{cases}$$

→ $k_\perp$ uniquely determined from measured data: E_{kin}, θ_{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:

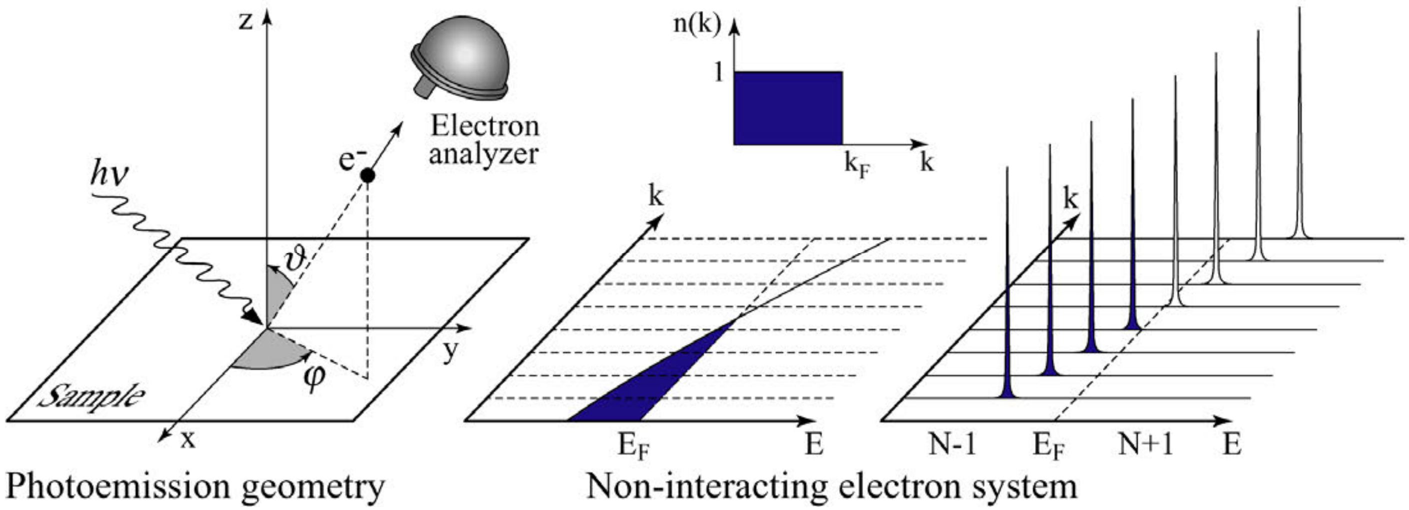
energy: $E_{kin} = h\nu - \phi - |E_B|$

momentum: $\hbar k_{\parallel} = \hbar K_{\parallel} = \sqrt{2mE_{kin}} \sin\theta$

$\hbar k_{\perp}$ not so straightforward …

PES theory II:
many-body picture

Photoemission: many-body effects



Damascelli et al., Rev. Mod. Phys. ***75****, 473 (2003)*

non-interacting electrons

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

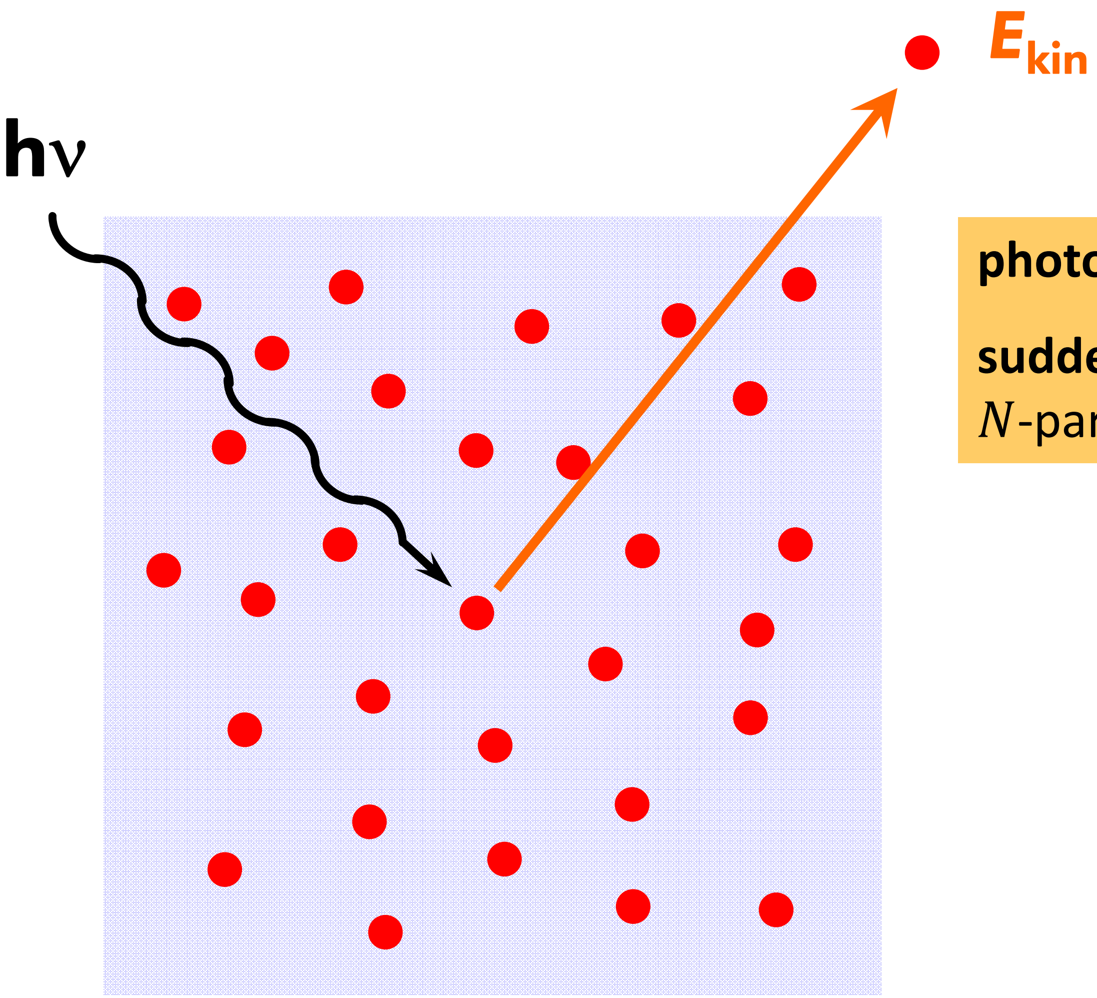
interacting electrons

ARPES
↓
spectral function

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

Photoemission: many-body effects

interacting electrons
(Coulomb repulsion)



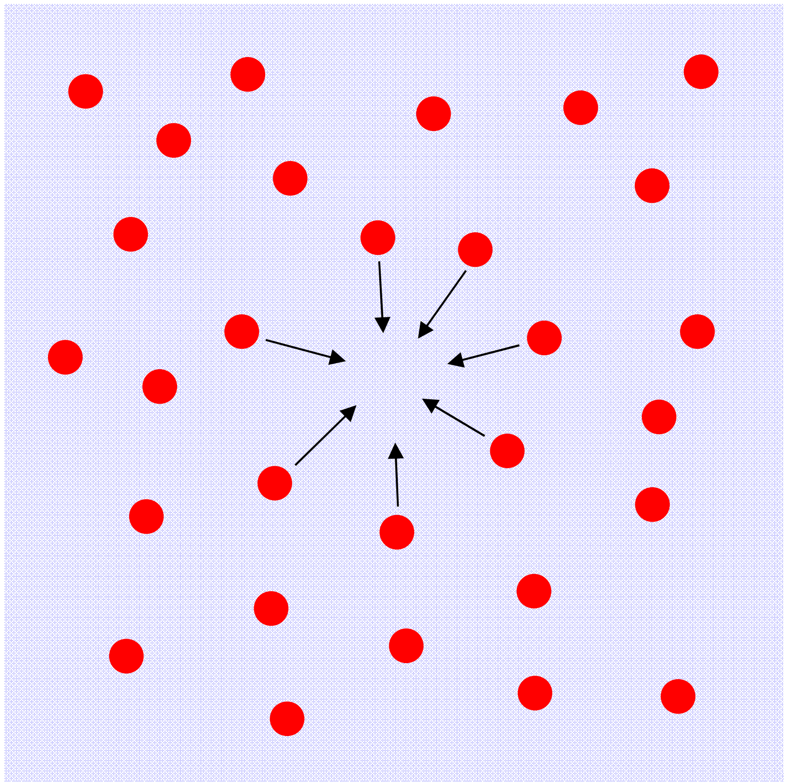
photoemission process:

sudden removal of an electron from N-particle system

Photoemission: many-body effects

interacting electrons
(Coulomb repulsion)

E_{kin}



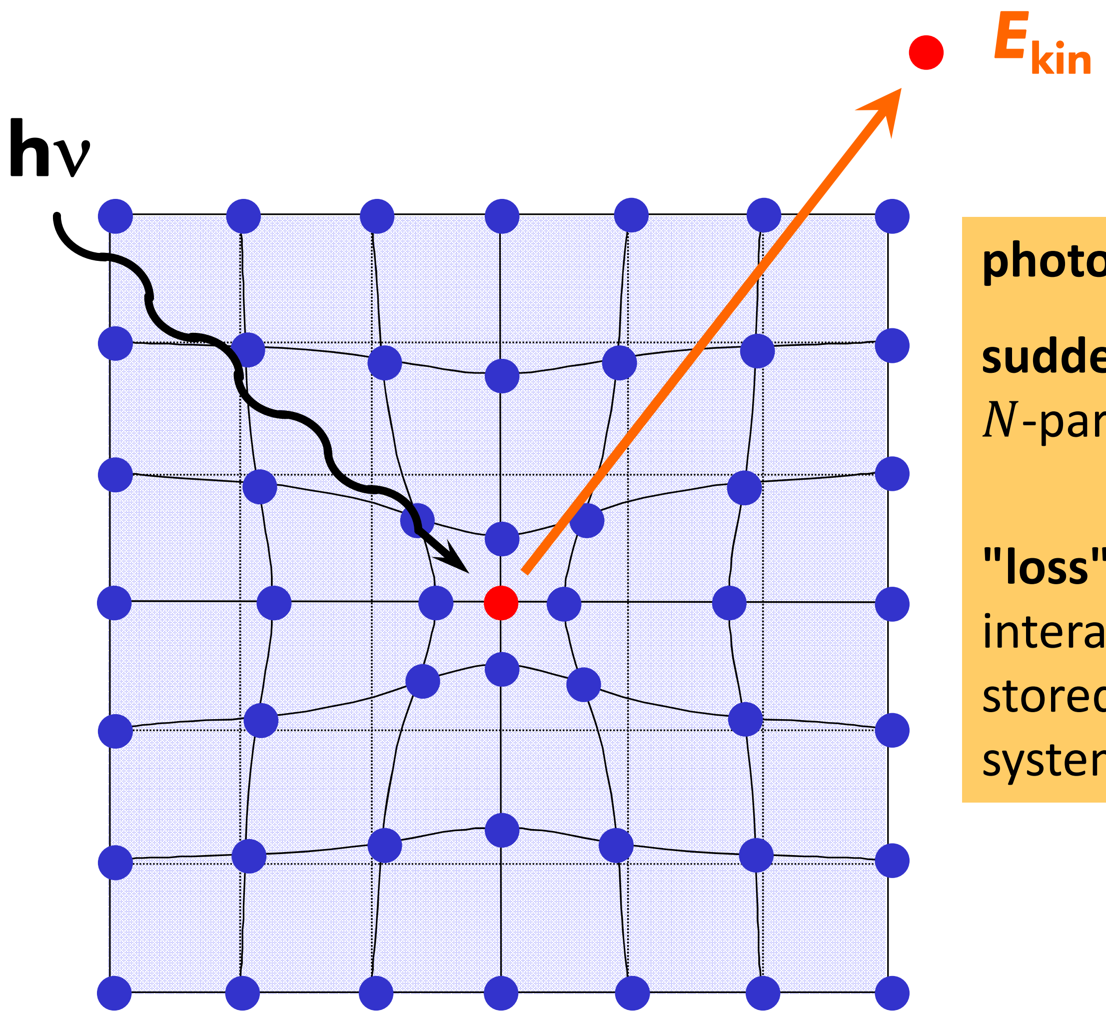
photoemission process:

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



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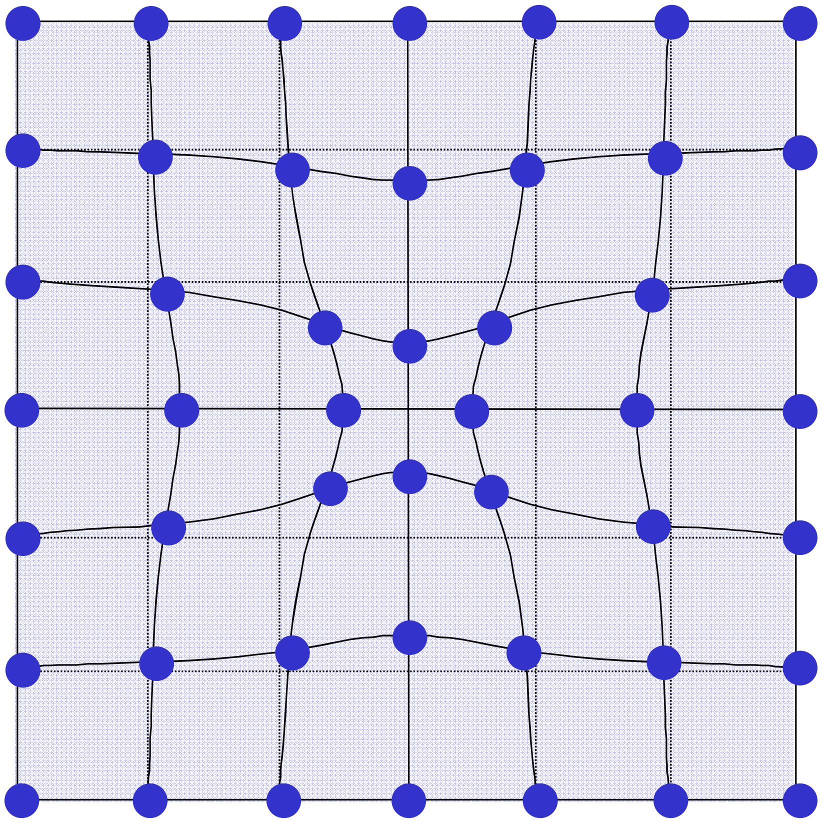

photoemission process:

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

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

initial state

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

final states

$|f\rangle = \left|N-1, s; \vec{k}\right\rangle$ — N-electron **excited state** of quantum number s 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 ε

transition operator

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

one-electron matrix element, conserves wavevector: $\vec{k}_f = \vec{k}_i$

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

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$$|f\rangle = \left|N-1,s;\vec{k}\right\rangle = c_{\vec{k}}{}^{+}|N-1,s\rangle$$ 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

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Fermi's Golden Rule for an N-electron system

$$I(\vec{k},\varepsilon) \propto \sum_s \left|\langle N-1, s \mid \underbrace{c_{\vec{k}} \hat{H}_{int}}_{\sum_{if} M_{if} c_{\vec{k}} c_f{}^{+} c_i} |N,0\rangle\right|^2 \delta\left(E_{N-1,s} + \varepsilon - E_{N,0} - \hbar\omega\right)$$

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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:

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$$= \underbrace{A(\vec{k},\varepsilon-\hbar\omega)}_{\textbf{spectral function}} \cdot f(\varepsilon-\hbar\omega)$$

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

probability of removing (or adding) an electron at energy ω and momentum $\vec{k}$ from (to) the system

single-particle Green´s function

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:

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

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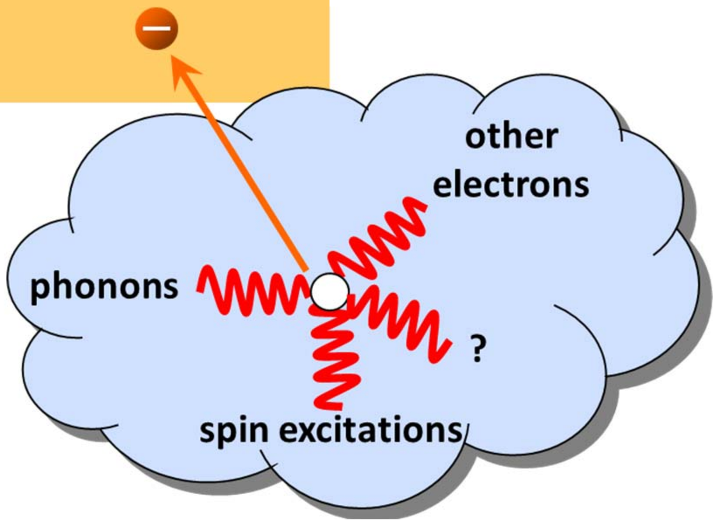
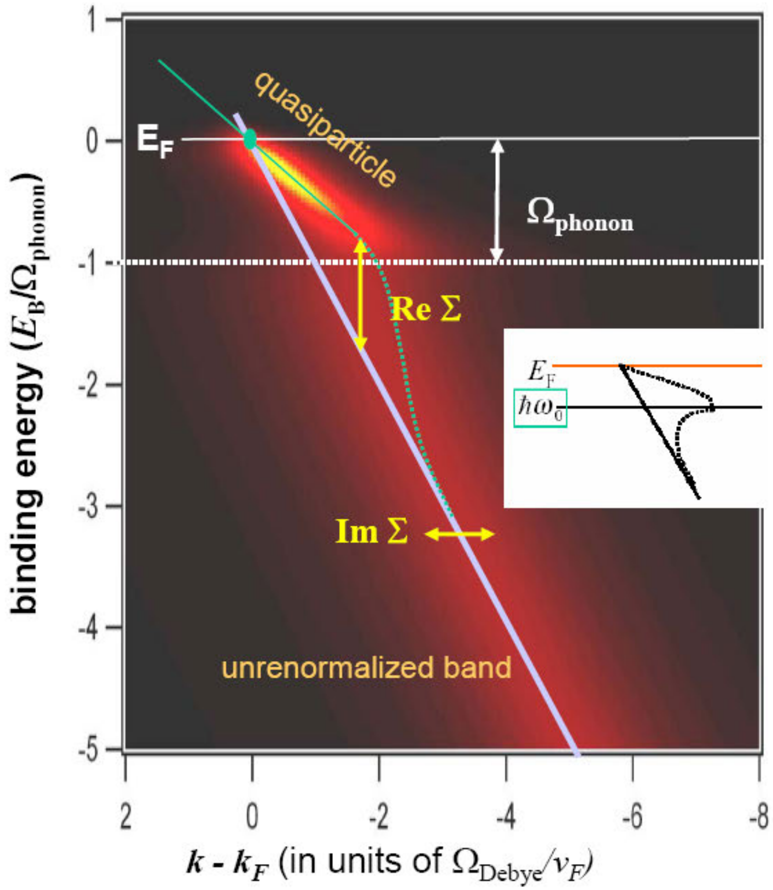
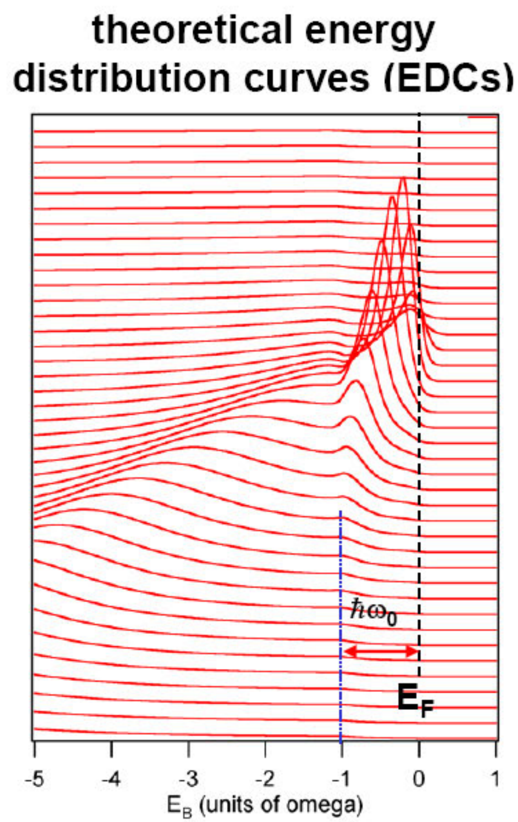


Spectral function

$$A(\vec{k},\omega) = -\frac{1}{\pi} Im\, G\,(\vec{k},\omega) = -\frac{1}{\pi} Im \frac{1}{\hbar\omega - \varepsilon_{\vec{k}} - \Sigma(\vec{k},\omega\,)} = \frac{1}{\pi} \frac{|\Sigma''(\vec{k},\omega\,)|}{\left[\hbar\omega - \varepsilon_{\vec{k}} - \Sigma'(\vec{k},\omega\,)\right]^2 + \Sigma''(\vec{k},\omega\,)^2}$$

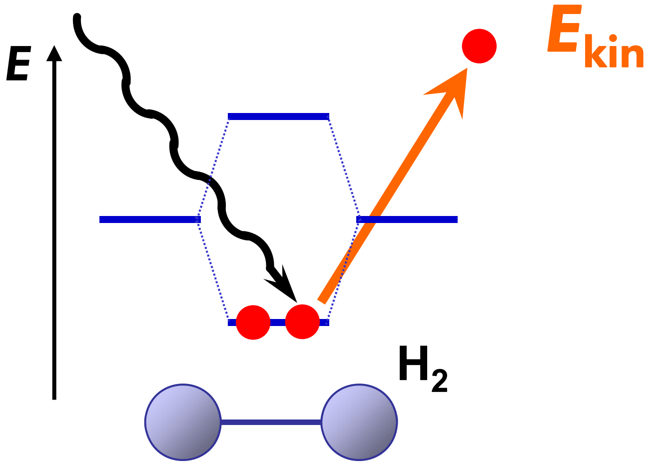
Debye Model (λ = 1)



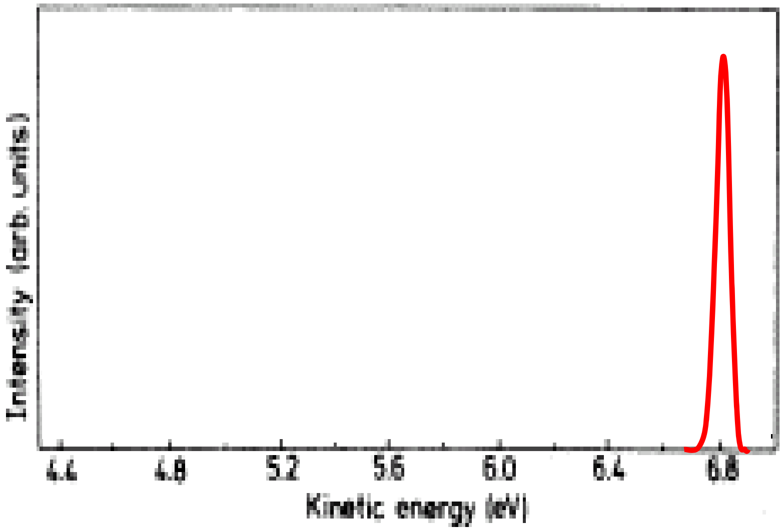


Many-body effects in photoemission

example: photoemission of the H_2 molecule



electrons couple to proton dynamics !



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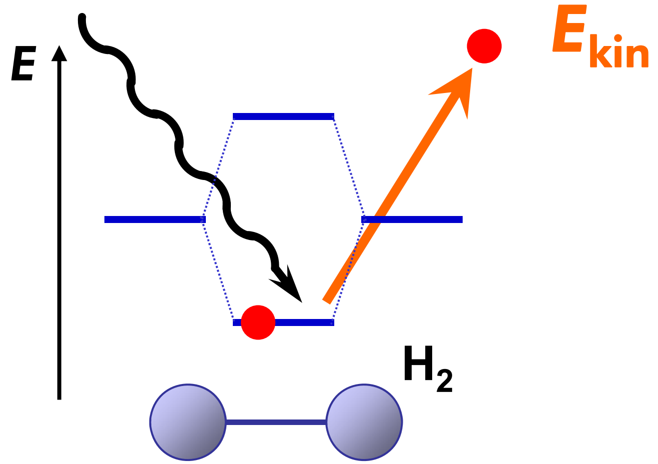


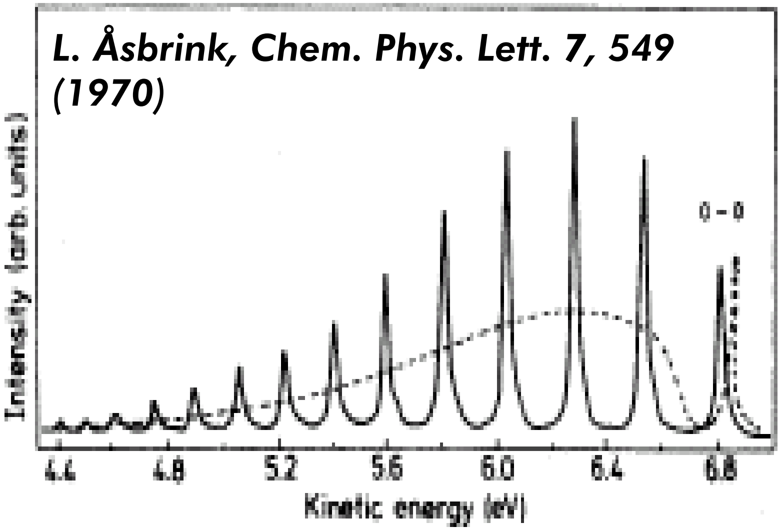
electrons couple to proton dynamics !

photoemission intensity:

$$I(\omega) \propto \sum_s \left| \left\langle H_2^+, s \middle| \hat{c} \middle| H_2, 0 \right\rangle \right|^2 \delta(\omega + E_{H_2^+,s} - E_{H_2,0})$$

electronic-vibrational eigenstates of H_2^+:

$$\left| H_2^+, s \right\rangle = \left| \sigma^1, v = 0 \right\rangle$$
$$= \left| \sigma^1, v = 1 \right\rangle$$
$$= \left| \sigma^1, v = 2 \right\rangle$$
$$\vdots$$



L. Åsbrink, Chem. Phys. Lett. 7, 549 (1970)

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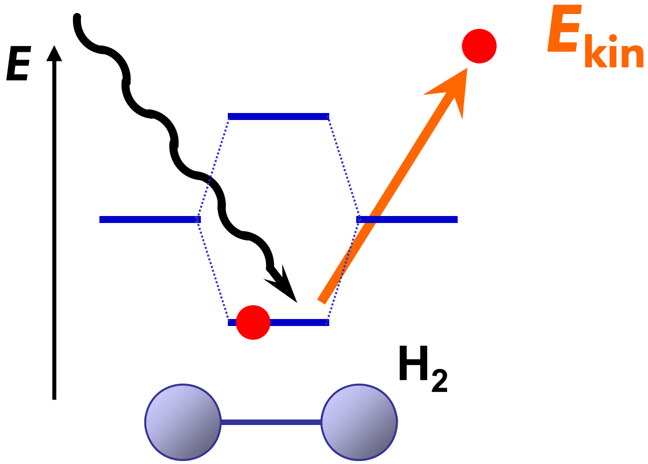
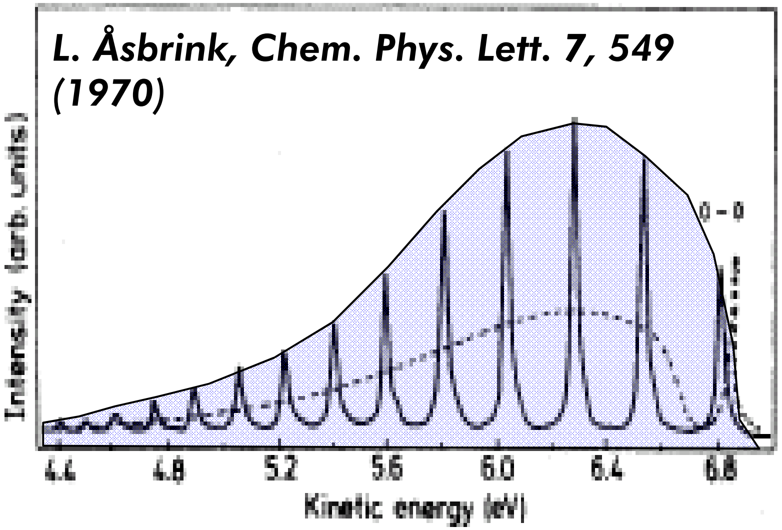
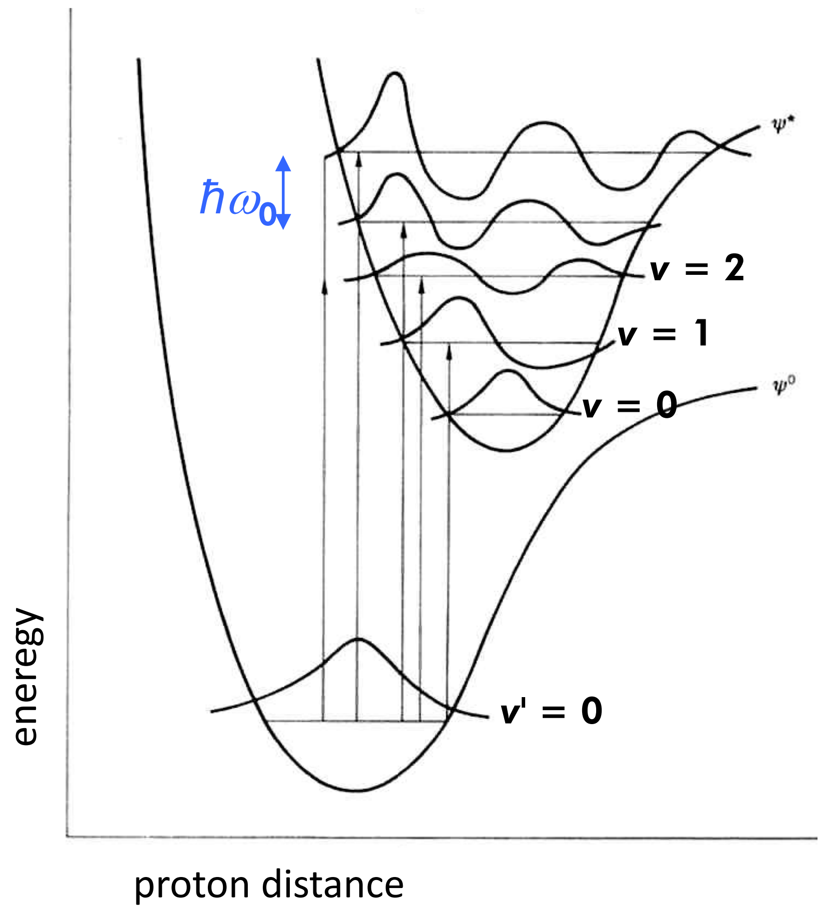




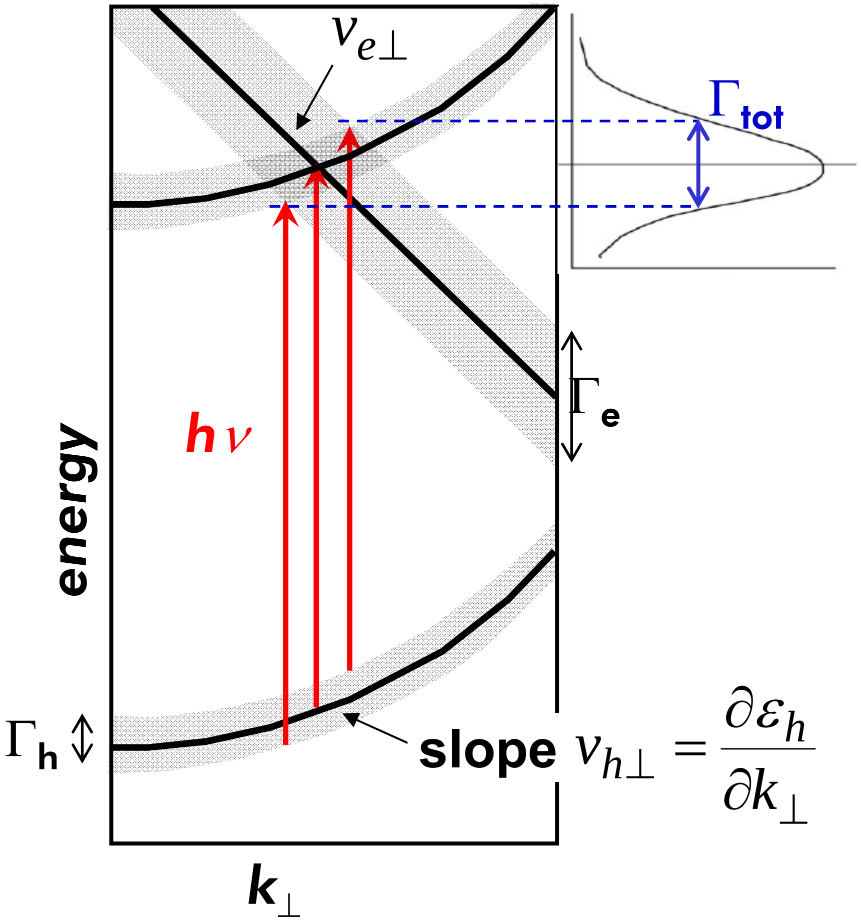
Franck-Condon principle



The $k_\perp$- problem again: photoelectron damping

ARPES signal is actually a **convolution** of photo*hole* and photo*electron* 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

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

~ meV ~ eV

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

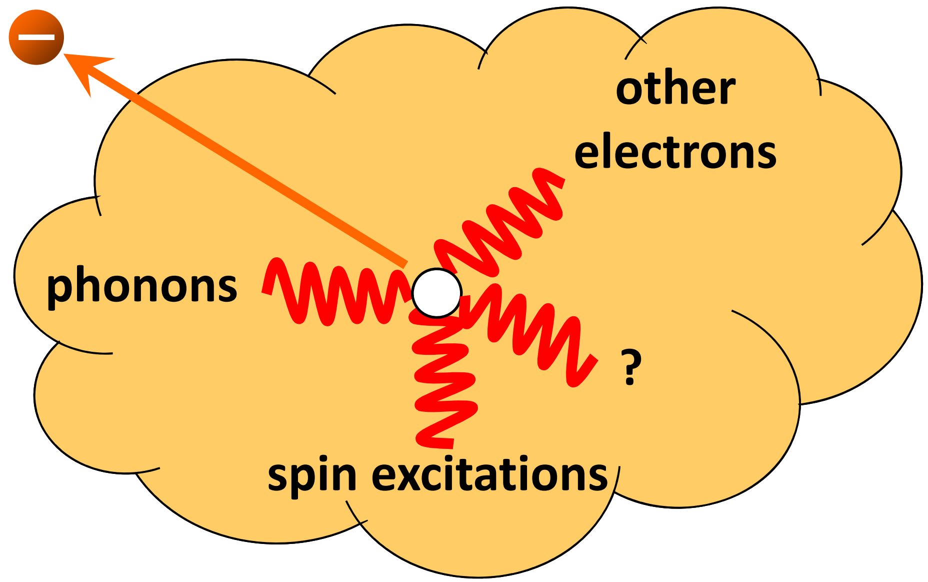
$\Rightarrow$ **low-dim systems (*e.g.*, surfaces)**

$\Rightarrow$ **k-vector in high-symmetry planes**

Summary: The view from many-body physics

- 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
  $\rightarrow$ energy shifts
  $\rightarrow$ shake-up satellites
  $\rightarrow$ line broadening
  $\rightarrow$ line shape
  (generalized Franck-Condon effect)



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

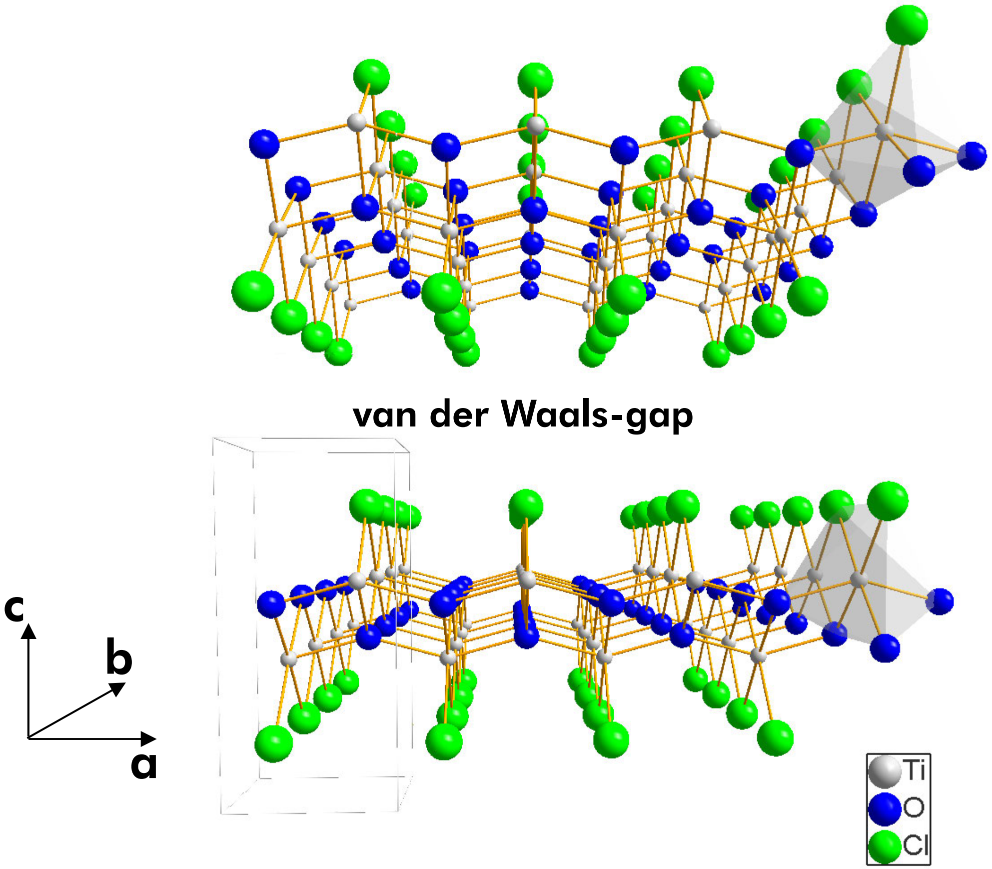
- facilitates **direct comparison** to many-body theoretical description of interacting system

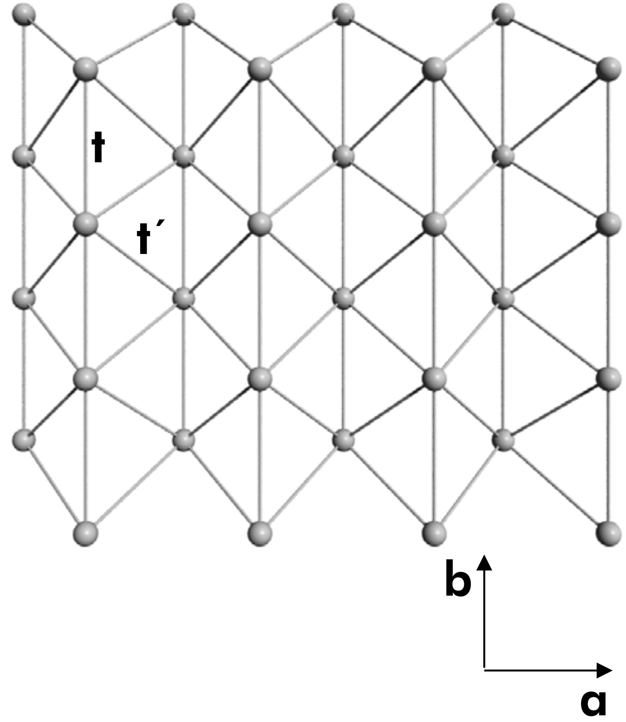
Julius-Maximilians-UNIVERSITÄT WÜRZBURG

ep4

Low-energy photoemission:
Doping a one-dimensional Mott insulator

TiOCl: a low-dimensional Mott insulator



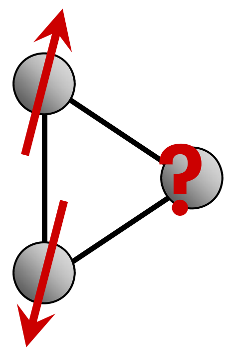


configuration: Ti $3d^1$

→ $1e^-$/atom: Mott insulator

→ local spin s=1/2

→ frustrated magnetism,
resonating valence bond (RVB) physics?



Doping a Mott insulator

<u>Hubbard model description</u>:

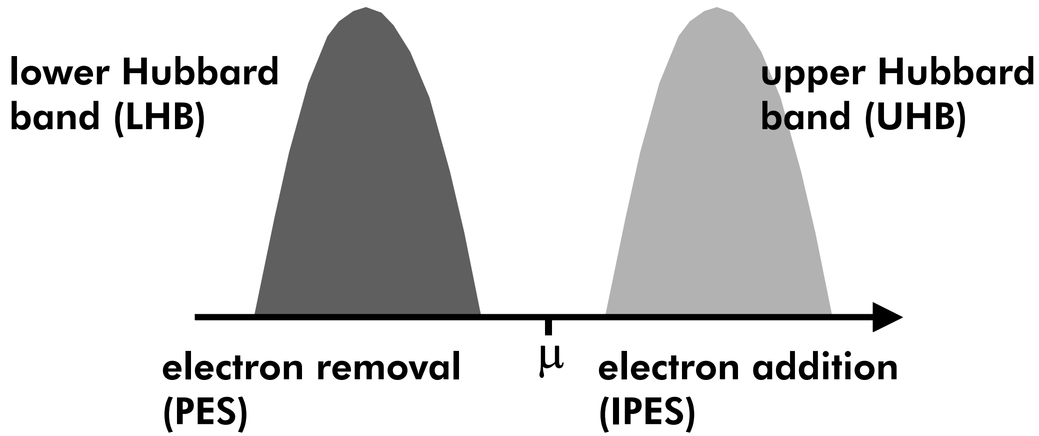
non-interacting bandwidth W

local Coulomb energy U

band-filling n

n = 1

U > W



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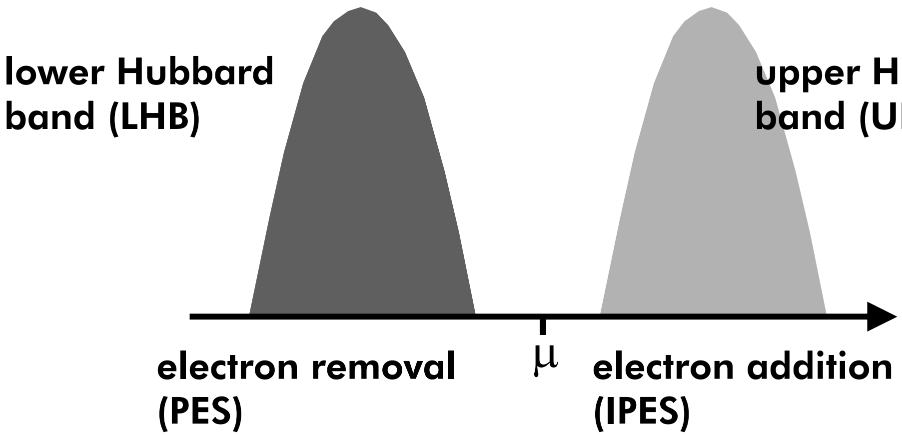
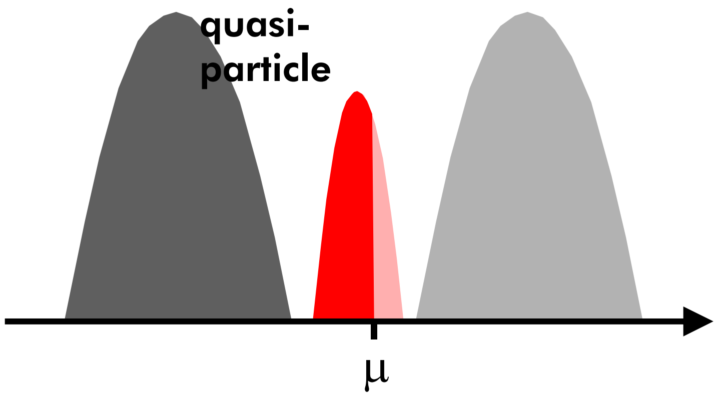


n = 1+x



bandfilling-controlled Mott transition?

here: n-doping

Doping a Mott insulator

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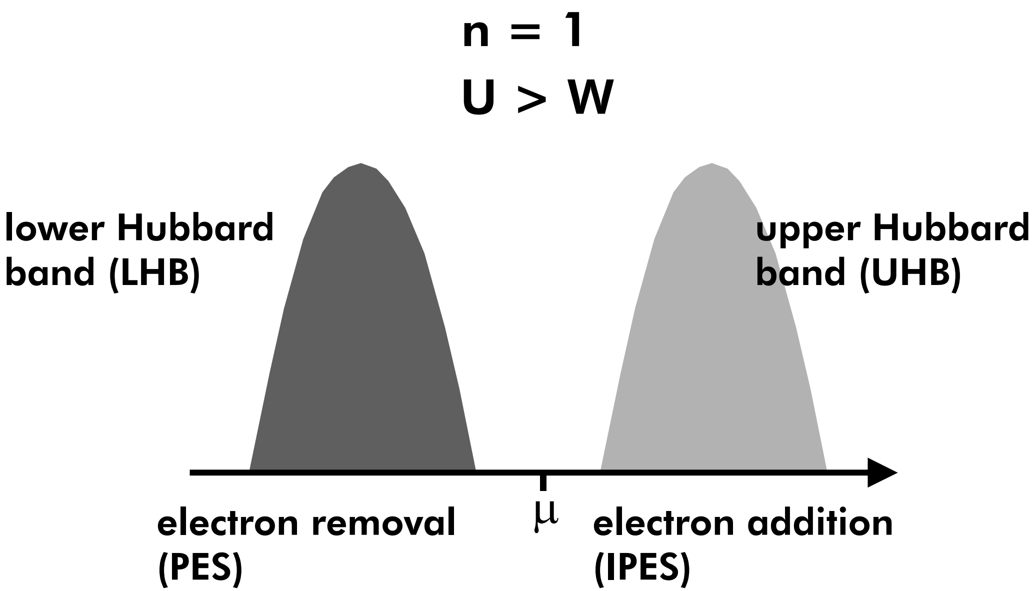

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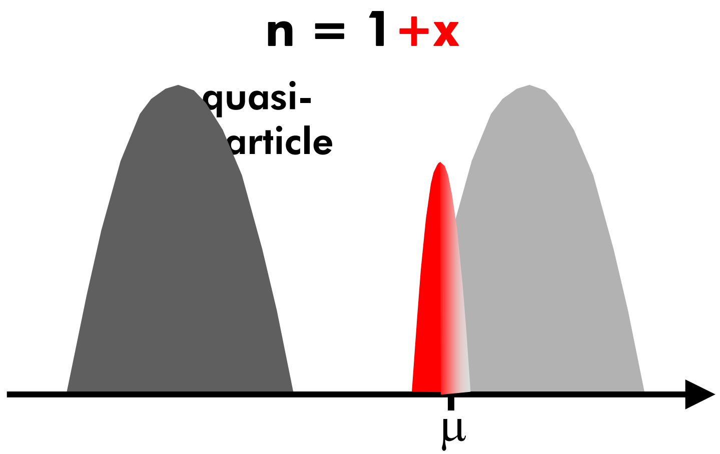
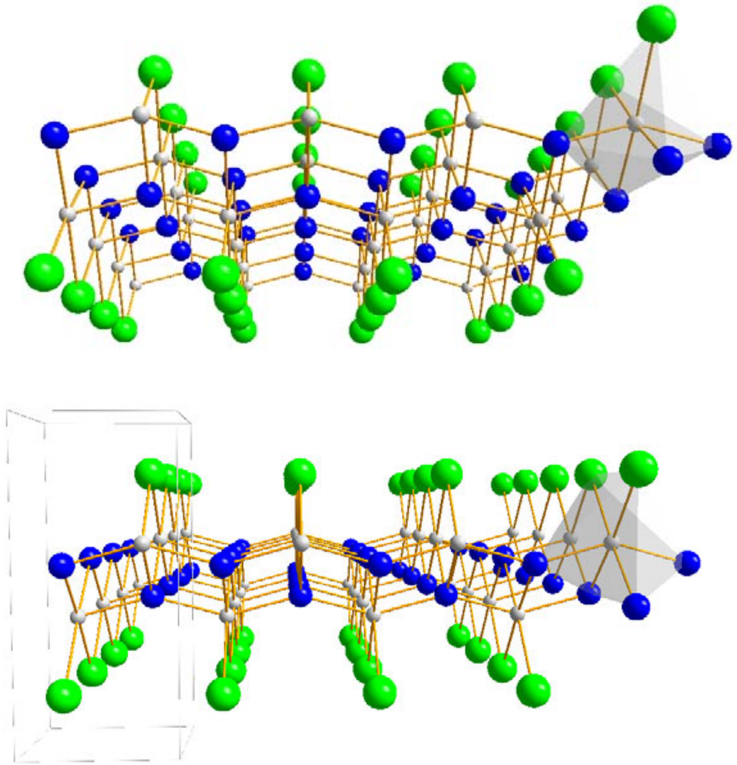


TiOCl: doping by intercalation

donors
acceptors

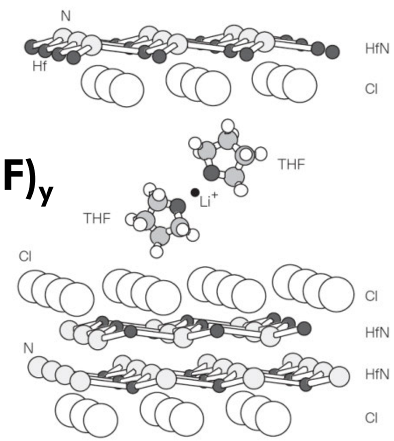


n: alkali metals

p: organic acceptors
(e.g., TCNQ)

$Li_x(THF)_y$

HfNCl



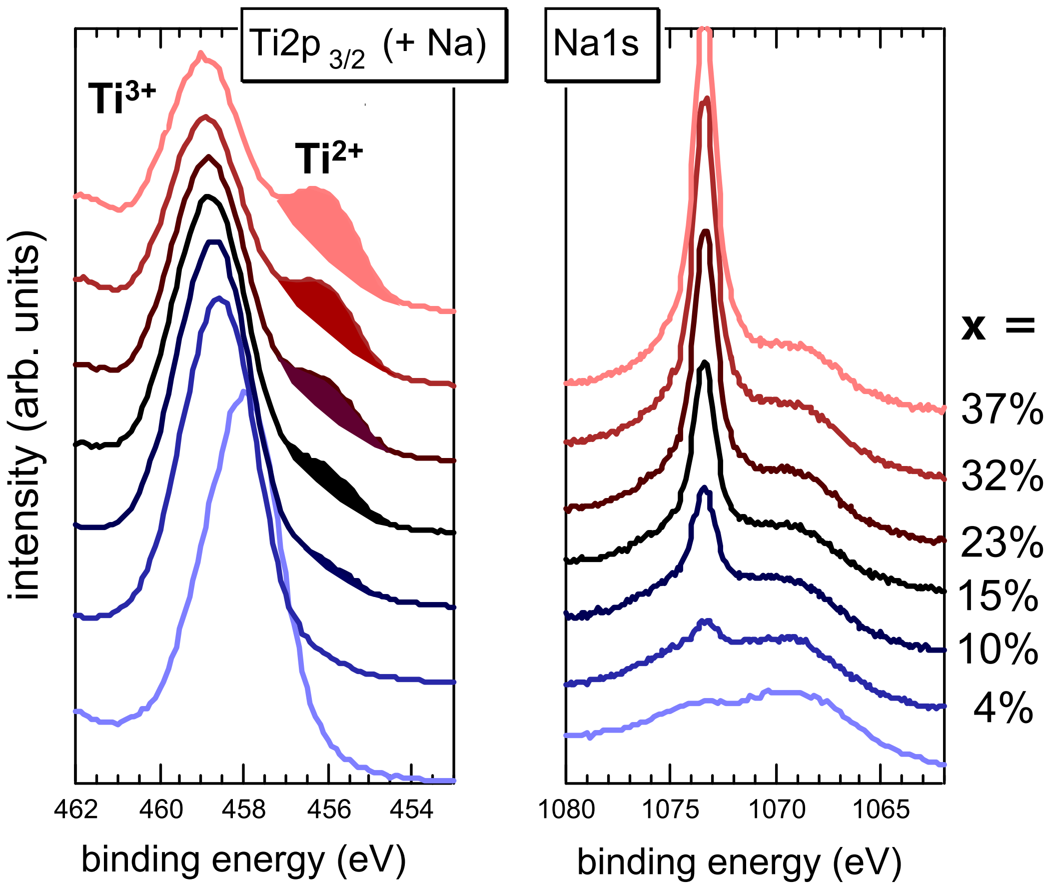
letters to nature

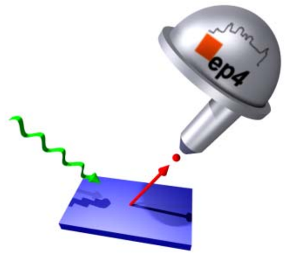
Superconductivity at 25.5 K in electron-doped layered hafnium nitride

Shoji Yamanaka*†, Ken-ichi Hotehama* & Hitoshi Kawaji*

Nature **392**, 580 (1998)

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

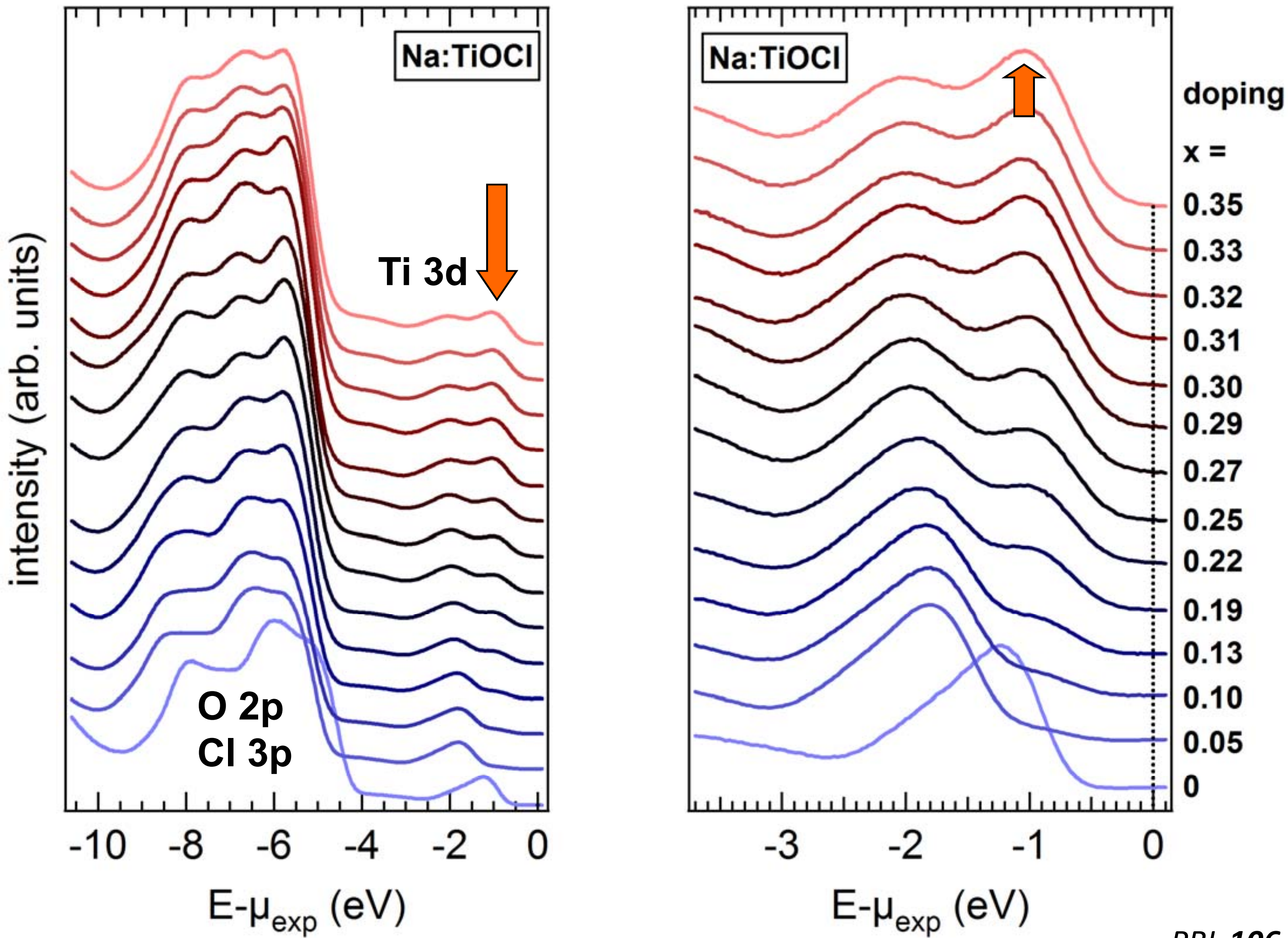


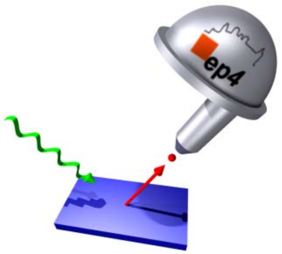


PRL ***106****, 056403 (2011)*

- **electron transfer Na → Ti**
- **doping x from relative Ti^{2+} and Ti^{3+} weight**

UPS: doping effects in valence band

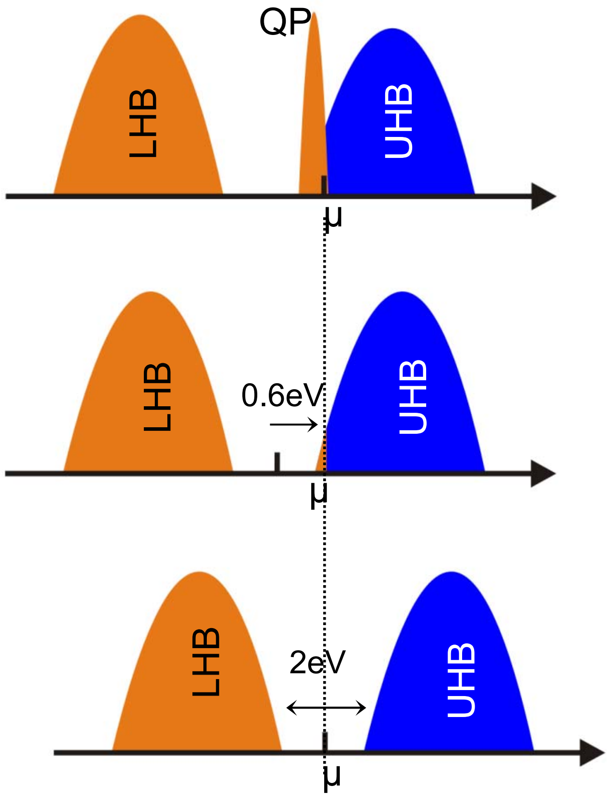


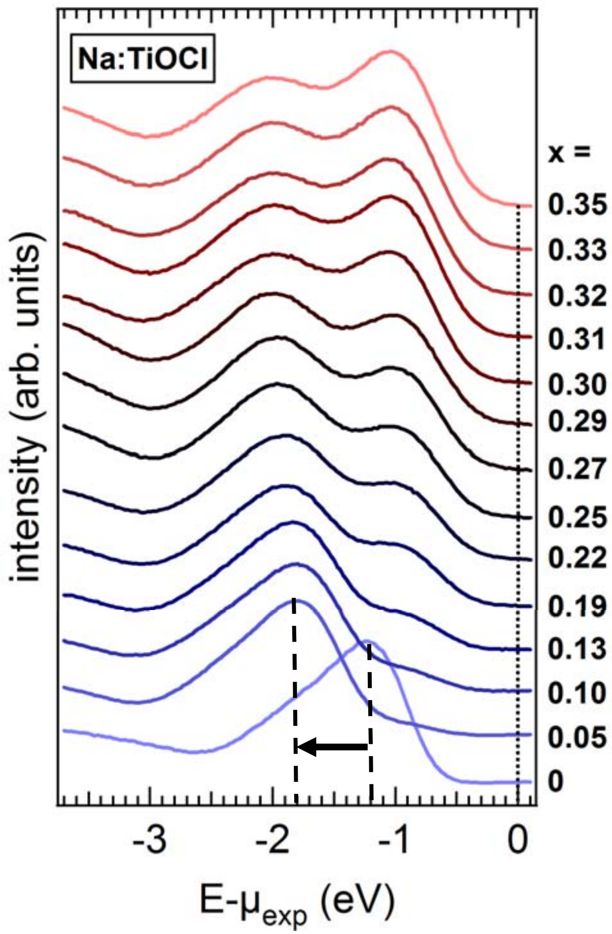


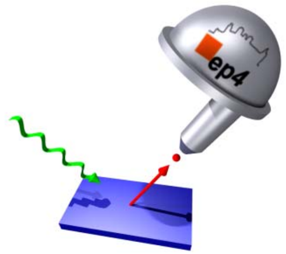
*PRL **106**, 056403 (2011)*

- rigid band shift
- new spectral weight in gap

Doping a Mott insulator

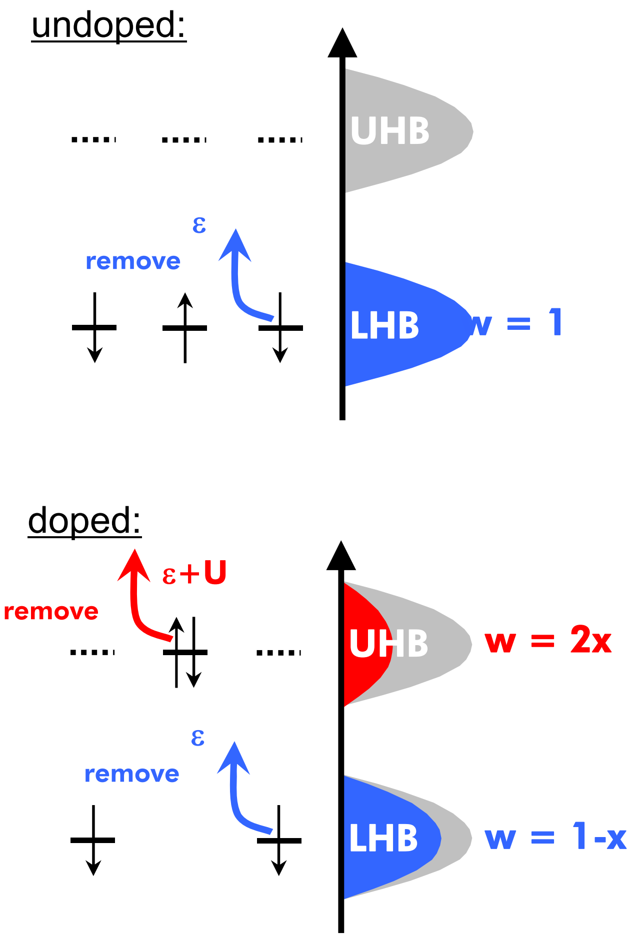






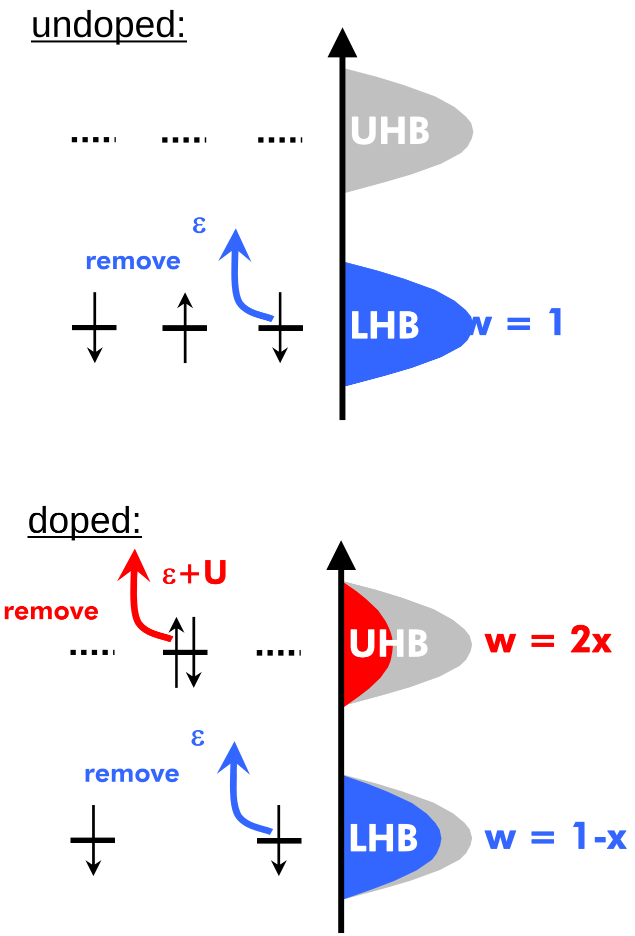
- new peak in the Mott gap: UHB?
- absence of metallic quasiparticle (QP)?

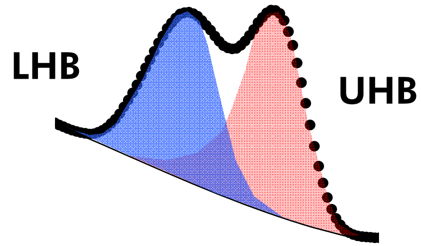
Spectral weight transfer from LHB to UHB

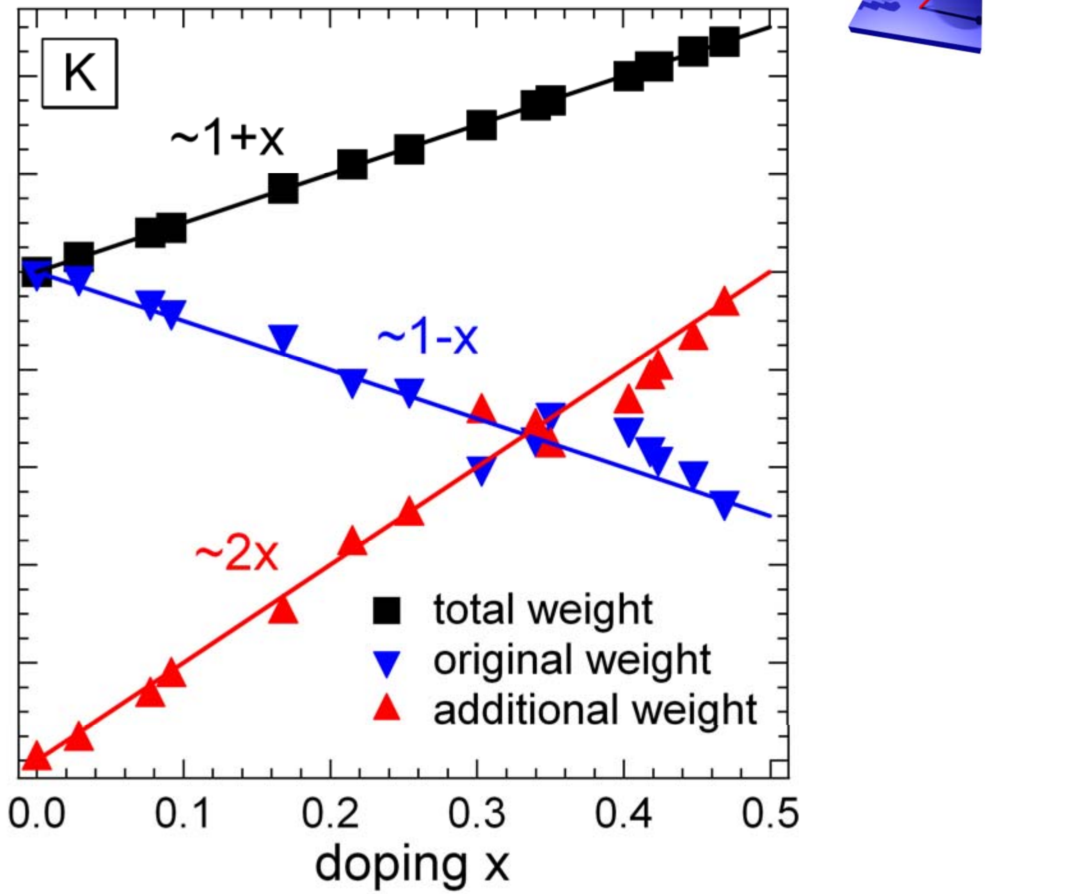


*PRL **106**, 056403 (2011)*

Spectral weight transfer from LHB to UHB





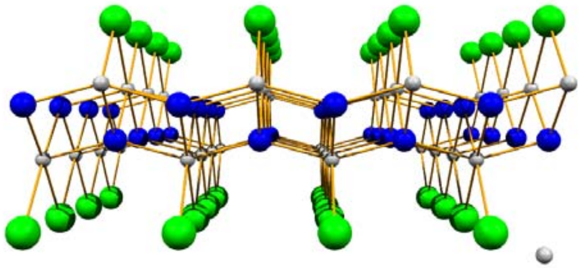


PRL ***106****, 056403 (2011)*

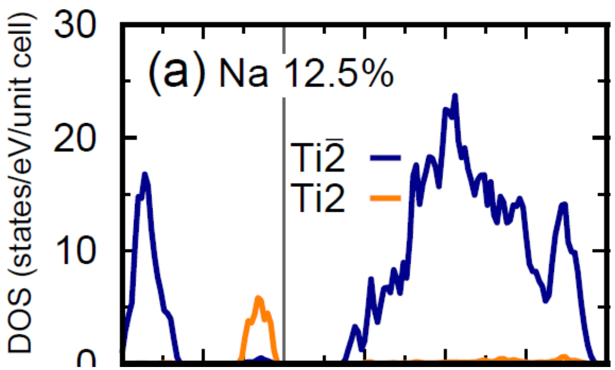
Absence of metallic QP

Molecular dynamics:

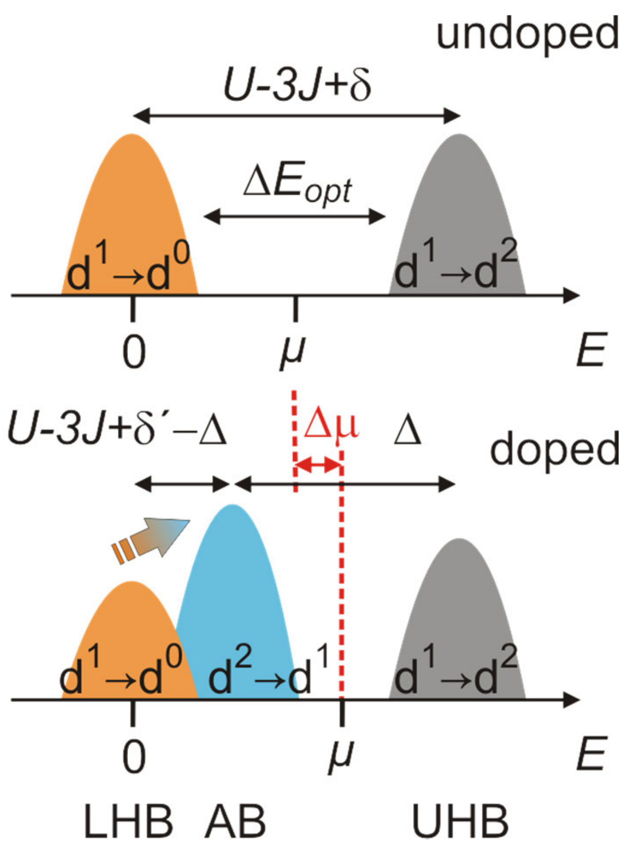
Y.-Z. Zhang, Phys. Rev. Lett. ***104****, 146402 (2010)*



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

Hard x-ray photoemission:
Profiling the buried two-dimensional electron system in an oxide heterostructure

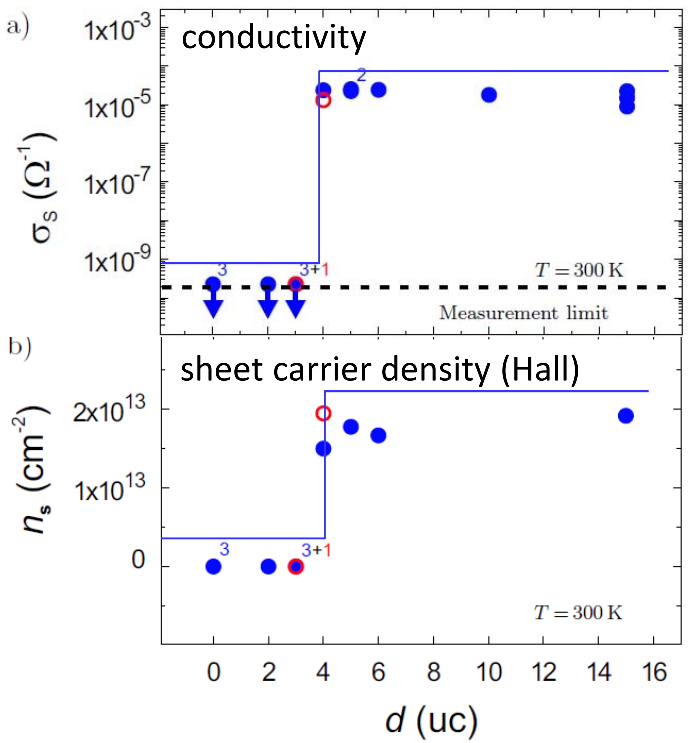
Oxide heterostructures in a nutshell

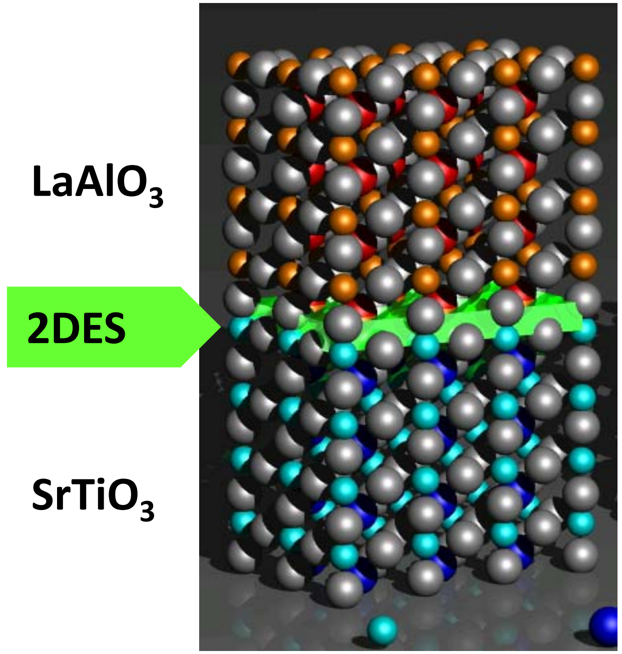
General idea:

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

Paradigm material: LAO/STO

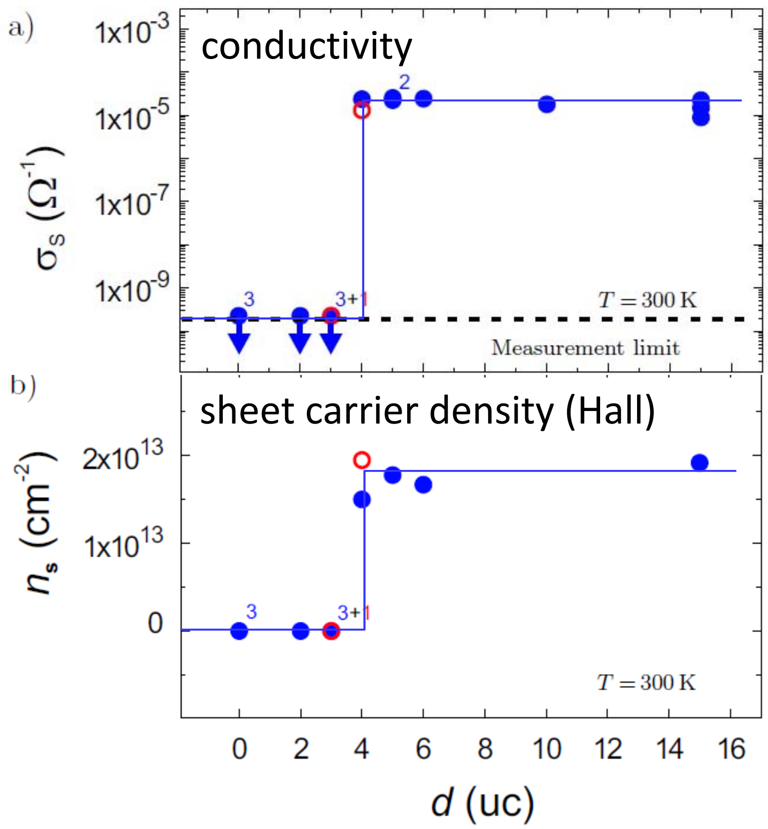
- both oxides: wide gap band insulators
- LAO thickness ≥ 4 unit cells (uc): formation of a high-mobility interface **2D electron system (2DES)**





A. Ohtomo et al., Nature ***427****, 423 (2004)*
S. Thiel et al., Science ***313****, 1942 (2006)*

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)?

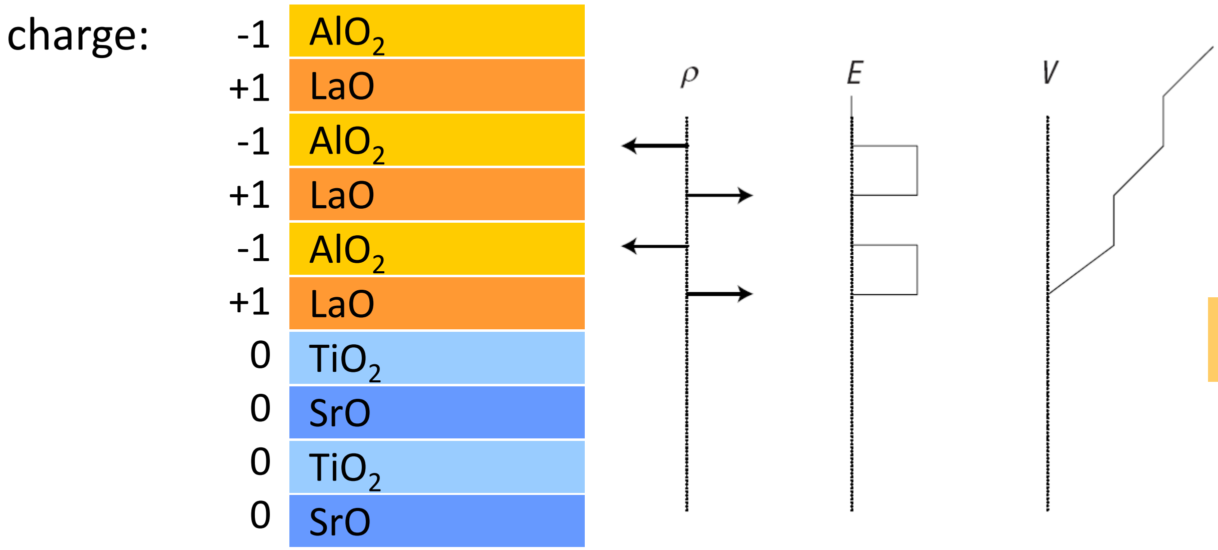
→ O-vacancies @ interface

→ cation intermixing ($La_xSr_{1-x}TiO_3$)

→ **electronic reconstruction**

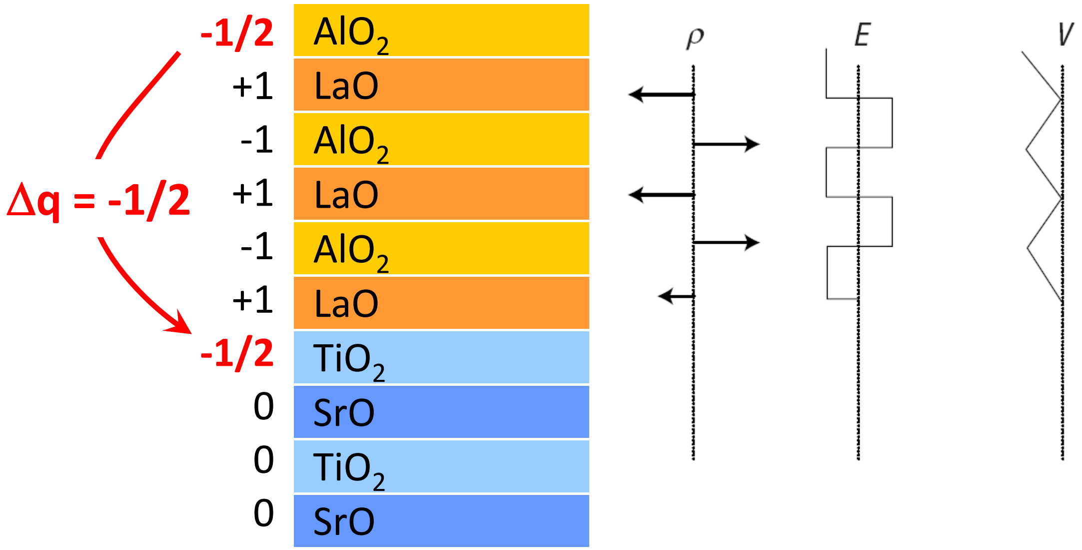
see also:
D.G. Schlom and J. Mannhart, Nature Materials ***10****, 168 (2011)*

Polar catastrophe and how to avoid it



electrostatic energy increases with thickness of polar film

polar catastrophe



electronic reconstruction

0.5e^- per layer unit cell

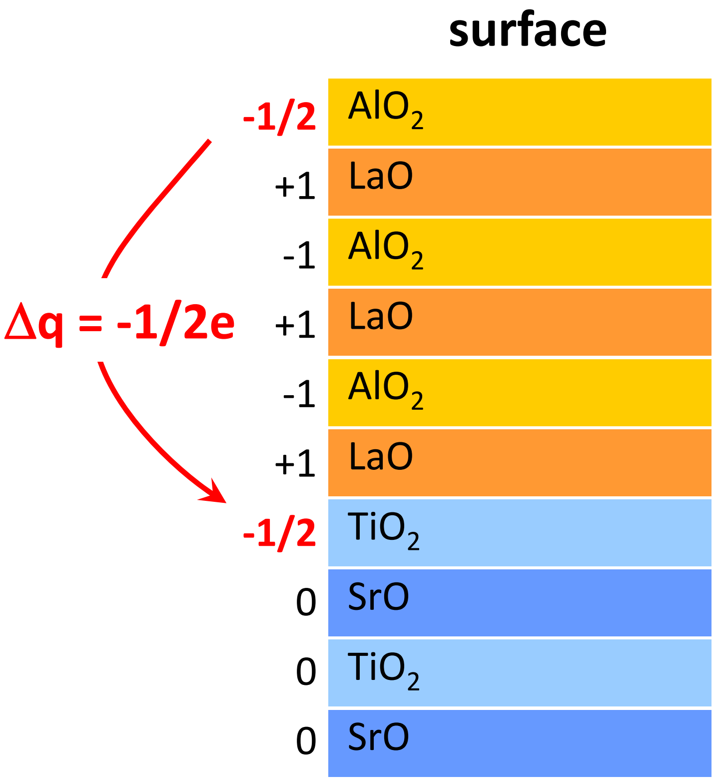
$\rightarrow$ $\boldsymbol{n_{2D} = 3.5\times10^{14}\ \mathrm{cm}^{-2}}$

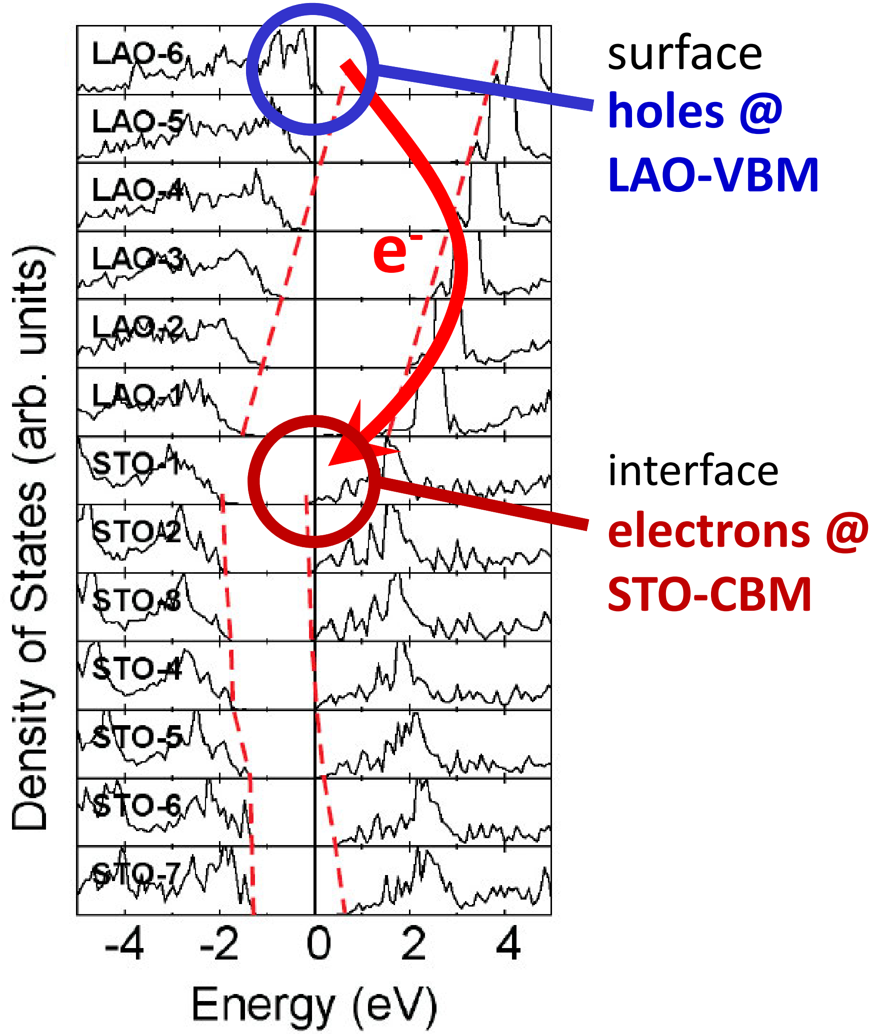
partial Ti 3d occupation

$\rightarrow$ $\mathbf{Ti^{3.5}\ (d^{0.5}) = Ti^{3+}/Ti^{4+}}$

Nakagawa et al., Nature Mat. ***5****, 204 (2006)*

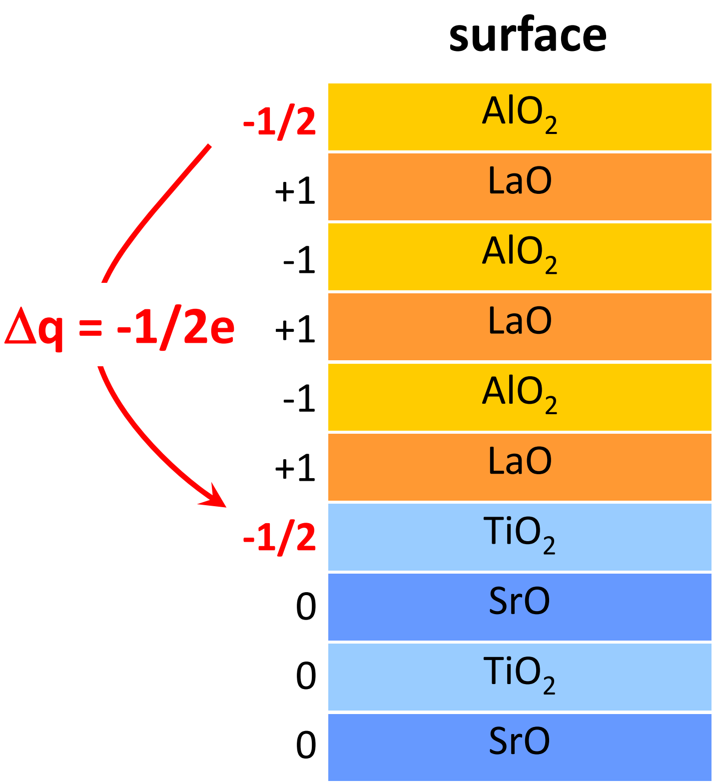
El. reconstruction: The view from band theory

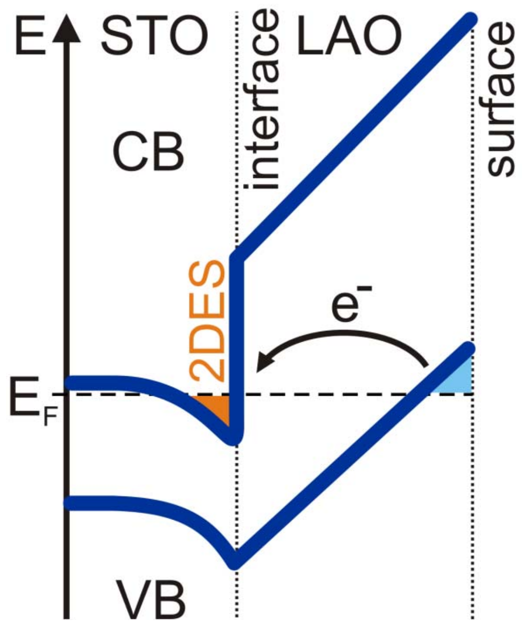




*Yun Li et al., PRB **84**, 245307 (2011)*
*Pentcheva and Pickett, PRL **102**, 107602 (2009)*

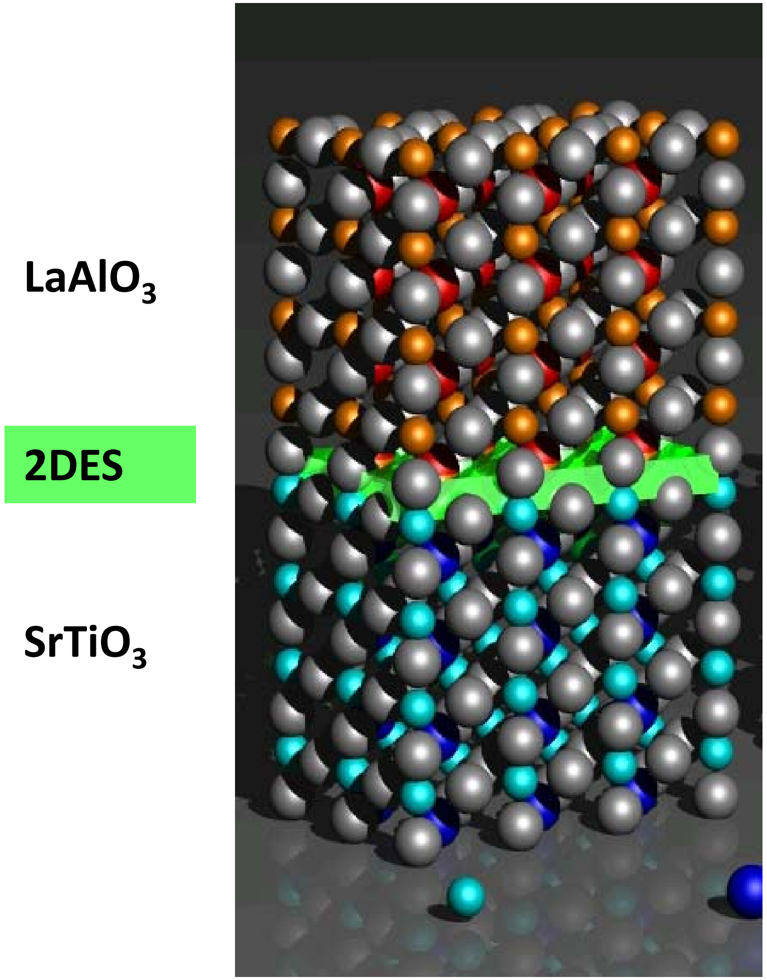
LAO/STO: Electronic reconstruction





ideal el. reconstruction scenario

Spectroscocpy of buried interfaces



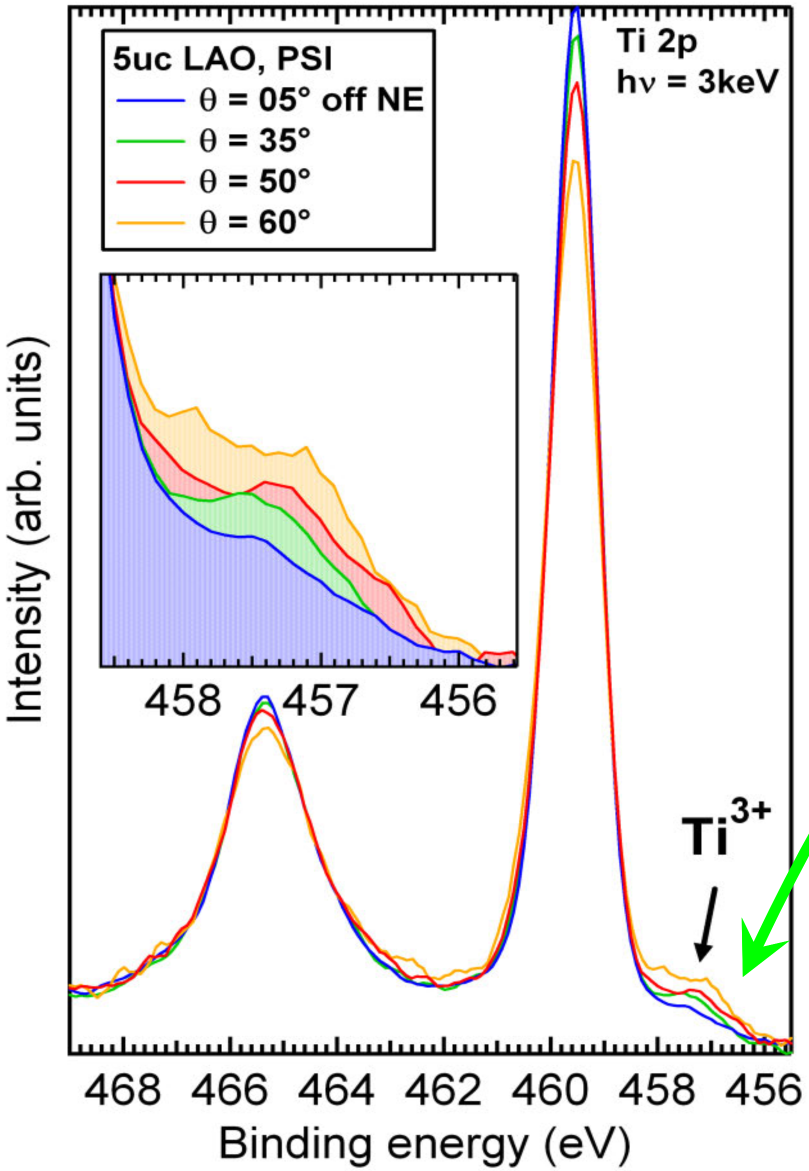
Challenges and requirements:

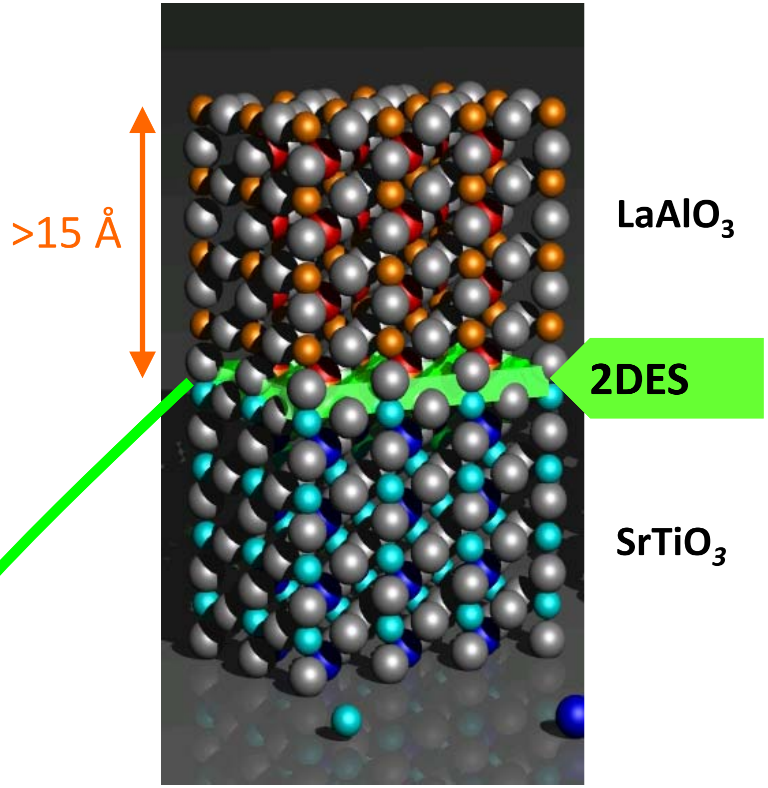
- suitable probing depth:
  - photons (10 nm … microns)
  - electrons (0.3 … 10 nm)
- interface signal *vs.* background intensity from bulk
- spectroscopic contrast:
  - symmetry
  - element specificity
  - chemical shift
  - electronic configuration
- sufficiently high count rates

Methods presented here:

- hard x-ray photoelectron spectroscopy (HAXPES)
- resonant soft x-ray angle-resolved PES (SX-ARPES)

HAXPES of LAO/STO: core levels

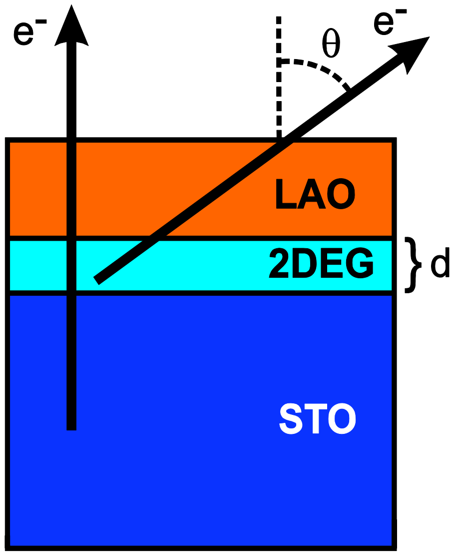




- Ti^{3+} weight evidence for 2DES
- Ti^{3+}/Ti^{4+} ratio → sheet carrier density
- angle dependence → thickness

*PRL **102**, 176805 (2009)*

Model and quantitative analysis



Exponential damping:

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

Intensity ratio:

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

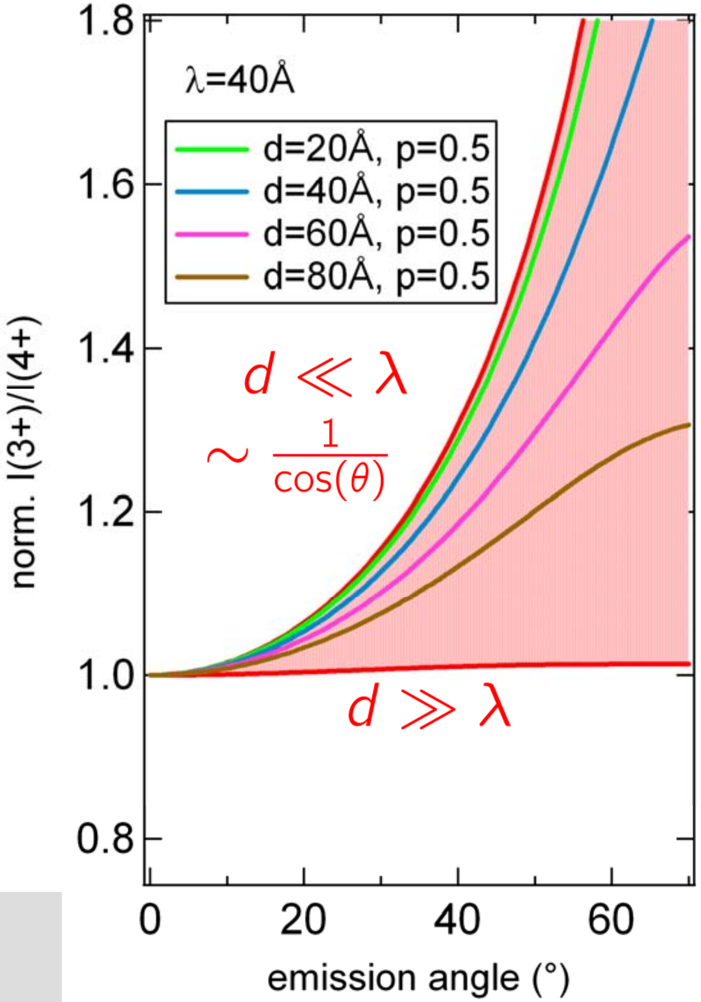
Accessible parameters:

d : 2DEG thickness

p : Ti^{3+} fraction

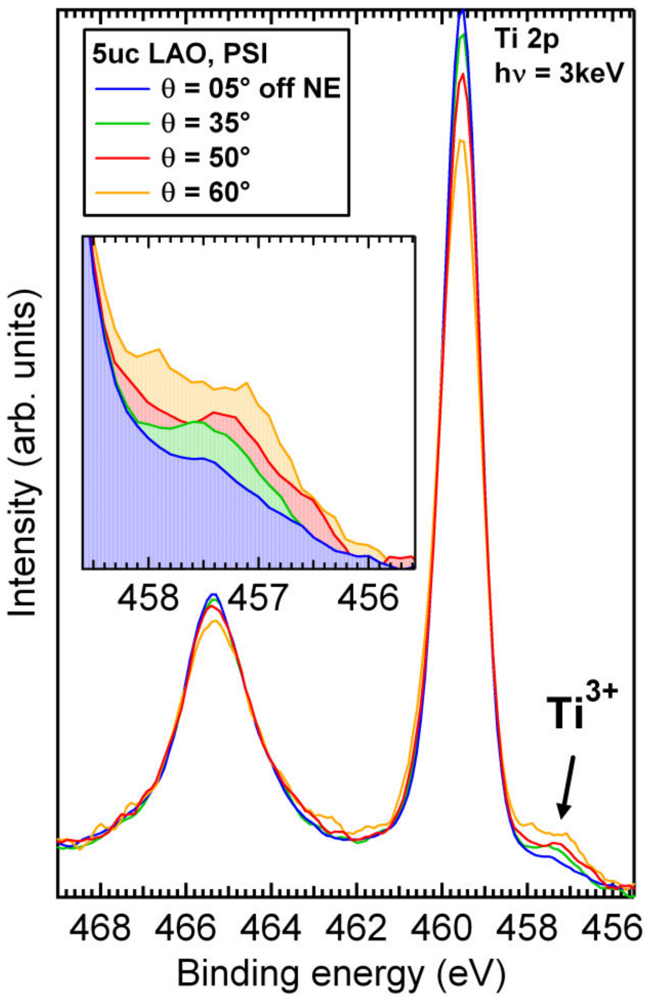
n_{2D} : sheet carrier density $(= pd/a_{STO}^2)$

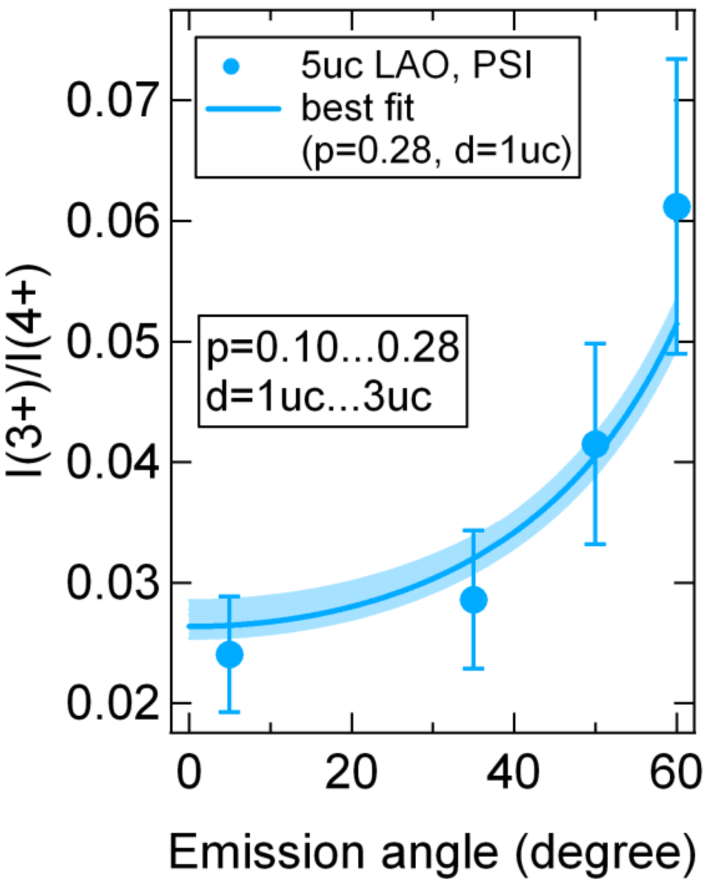
Angle dependence

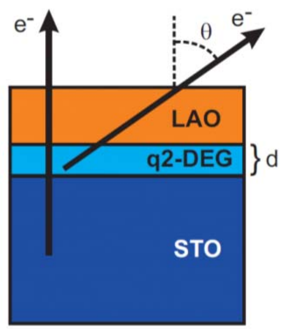


PRL ***102,*** *176805 (2009)*

Quantitative analysis

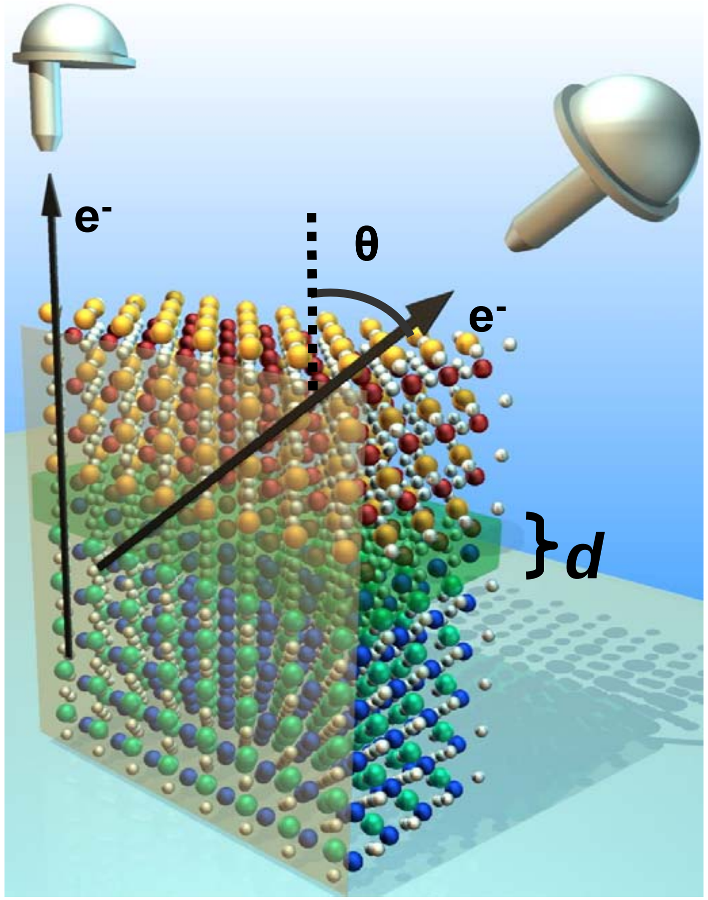






*PRL **102,** 176805 (2009)*

Quantitative analysis: 2DEG thickness



Sample	2 uc	4 uc	5 uc	6 uc
d **(uc*)**	3 ± 1	1 ± 0.5	6 ± 2	8 ± 2

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

→ interface thickness < 3 nm *

consistent with

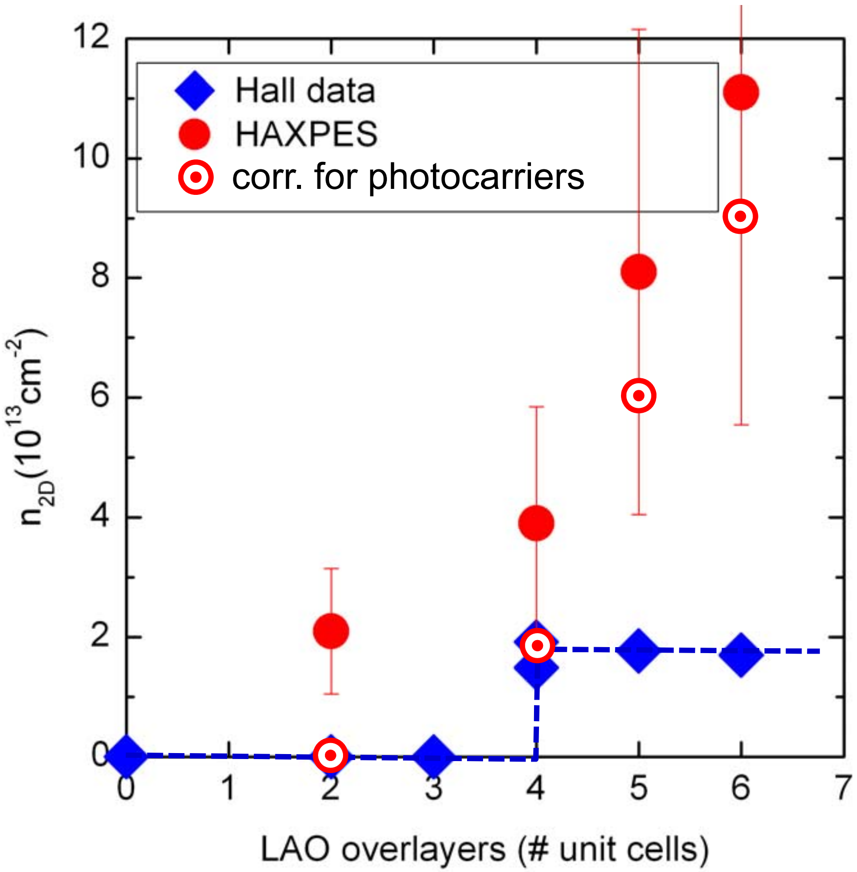
- CT-AFM *Basletic et al. (2008)*
- TEM-EELS *Nakagawa et al. (2006)*
- density functional theory *Pentcheva et al. (2009)*
- 2D superconductivity *Reyren et al. (2007)*
- ellipsometry *Dubroka et al. (2010)*

* HAXPES data taken at 300K!

PRL ***102,*** *176805 (2009)*

Quantitative analysis: sheet carrier density

Sample	2 uc	4 uc	5 uc	6 uc	el. reconstr.
p	0.01	0.05	0.02	0.02	0.5
n_{2D} **(10^{13} cm^{-2})**	2.1	3.9	8.1	11.1	35



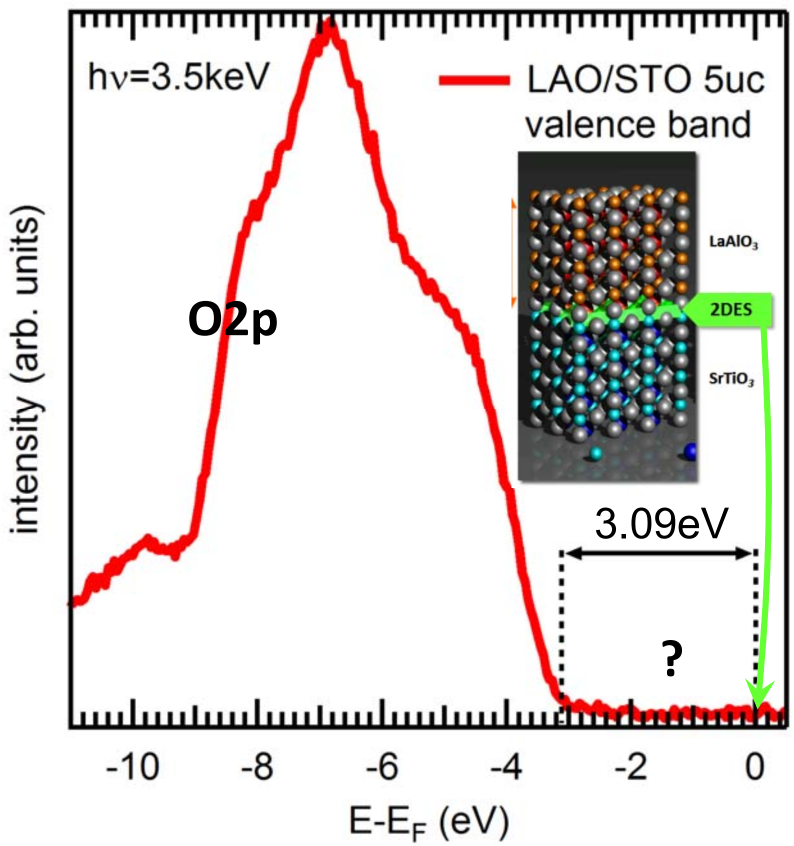
- n_{2D} much smaller than for purely electronic reconstruction
- n_{2D} higher than Hall effect data
- photogeneration of extra Ti 3d electrons
- remaining excess due to **additional localized** Ti 3d electrons?

  (cf. Li *et al.* and Bert *et al.,* Nature Phys. (2011): coexistence of superconductivity (free carriers) and magnetism (local moments))

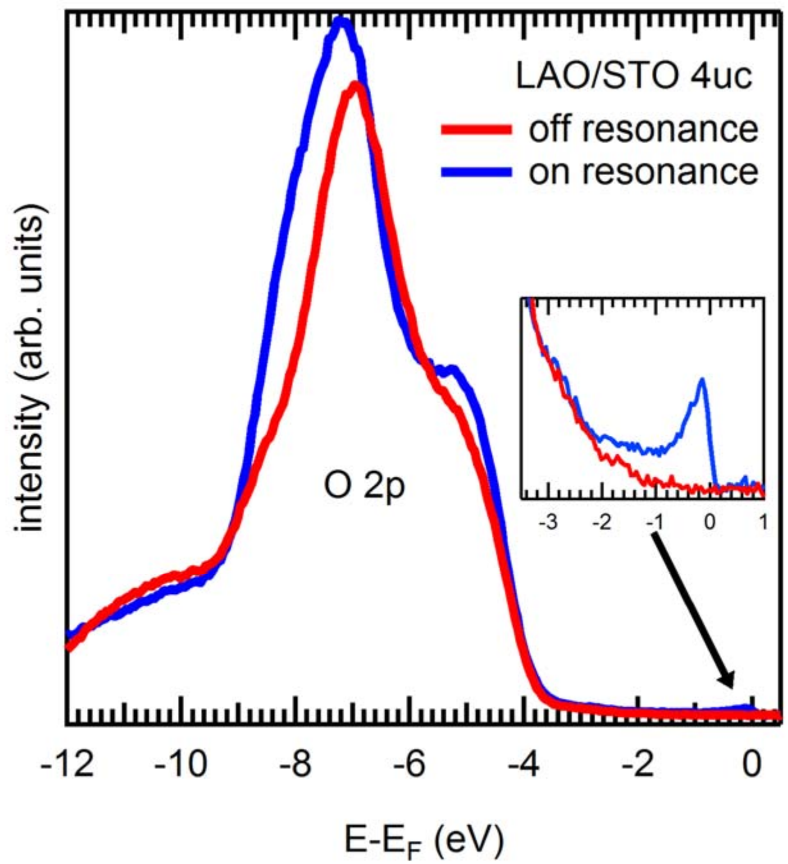
Resonant angle-resolved soft x-ray photoemission: Direct k-space mapping of the electronic structure in an oxide-oxide interface

Soft x-ray ResPES of the valence band

HAXPES (hν = 3.5 keV)



SX-ResPES (hν ~ 460 eV)

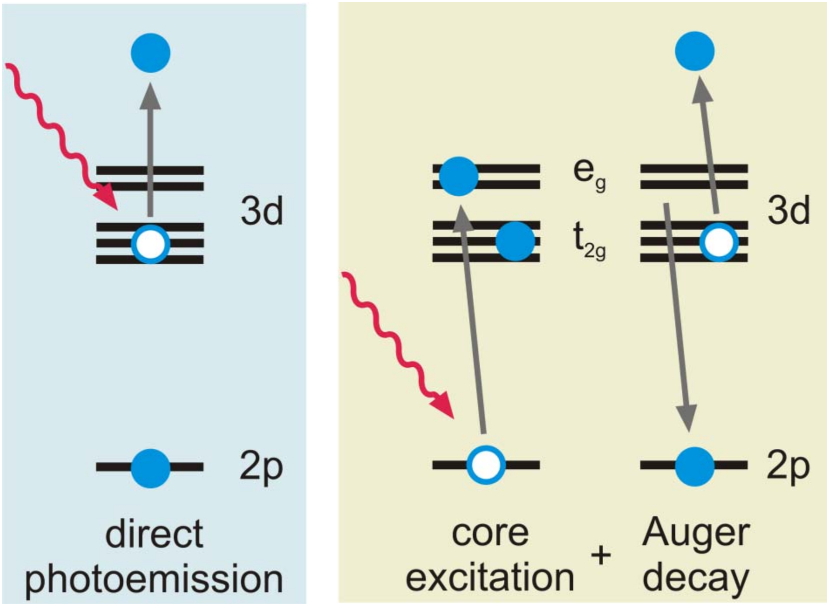


resonance enhancement at Ti L edge

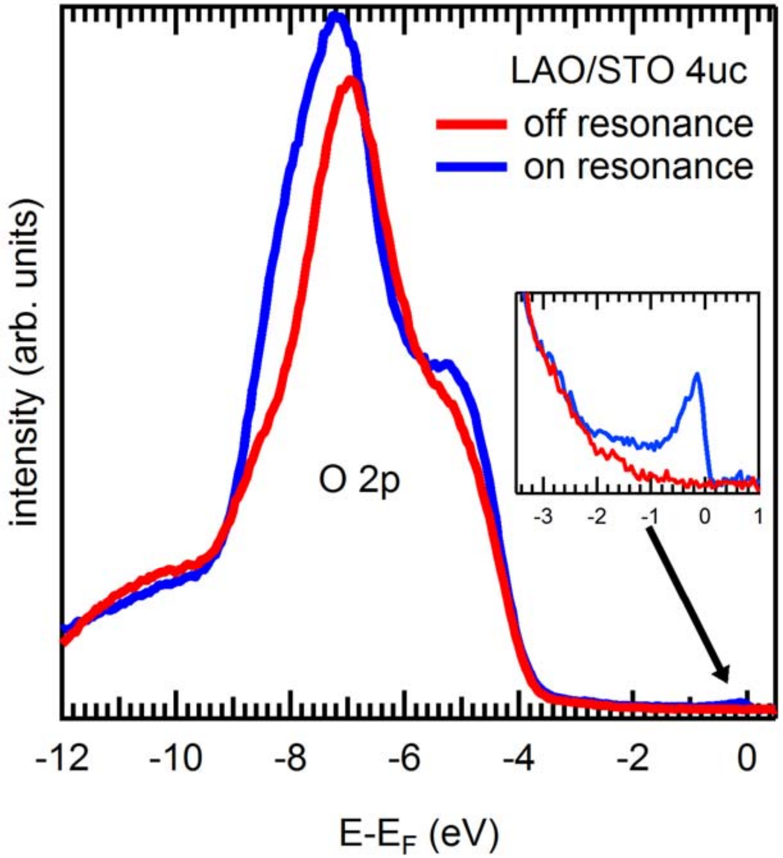
PRB ***88,*** *115111 (2013)*

Soft x-ray ResPES of the valence band

ResPES process



SX-ResPES (hν ~ 460 eV)

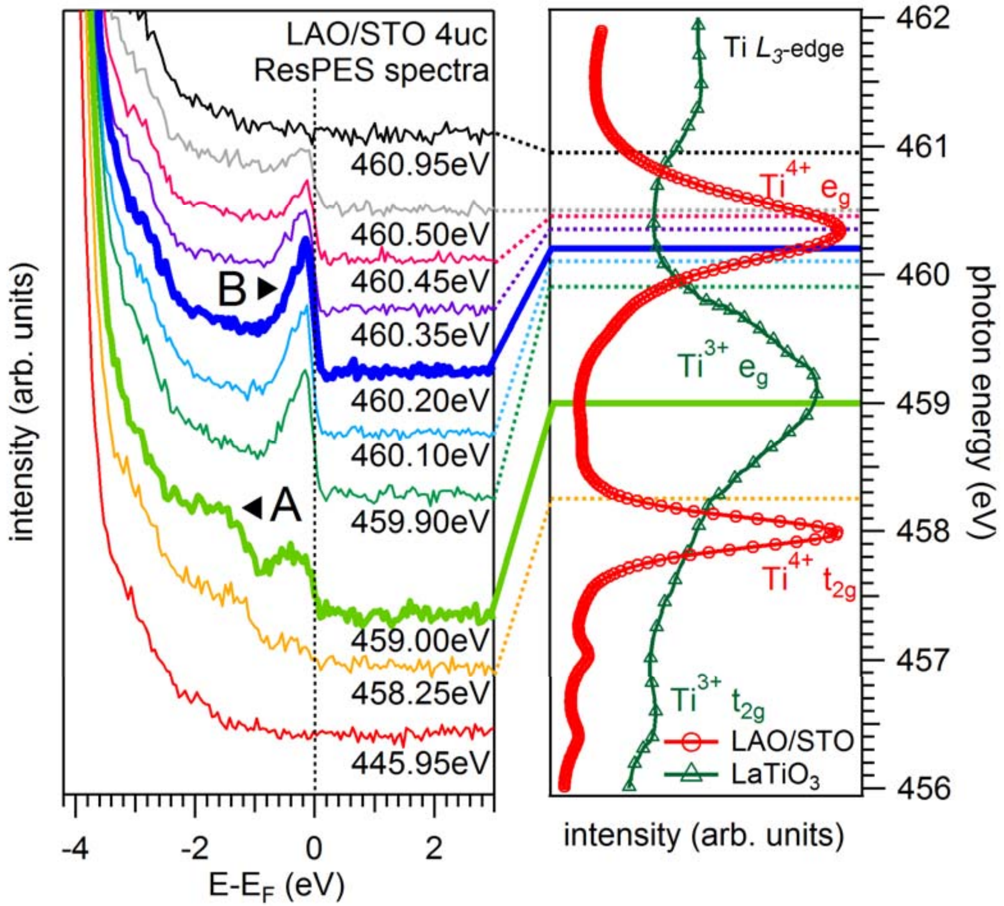


resonance enhancement at Ti L edge

cf.:
*Drera et al., APL **98**, 052907 (2011)*
*Koitzsch et al., PRB **84**, 245121 (2011)*

LAO/STO: resonant photoemission at Ti L-edge

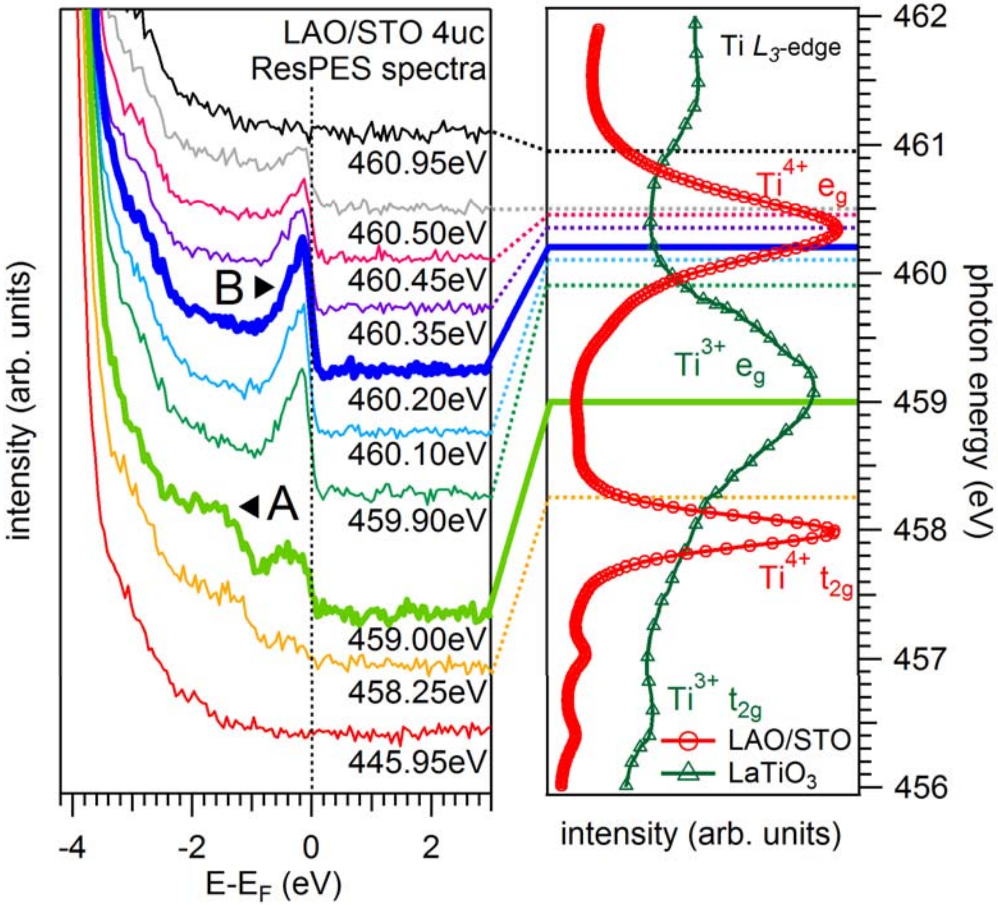
ResPES **XAS**



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

LAO/STO: resonant photoemission at Ti L-edge

ResPES **XAS**



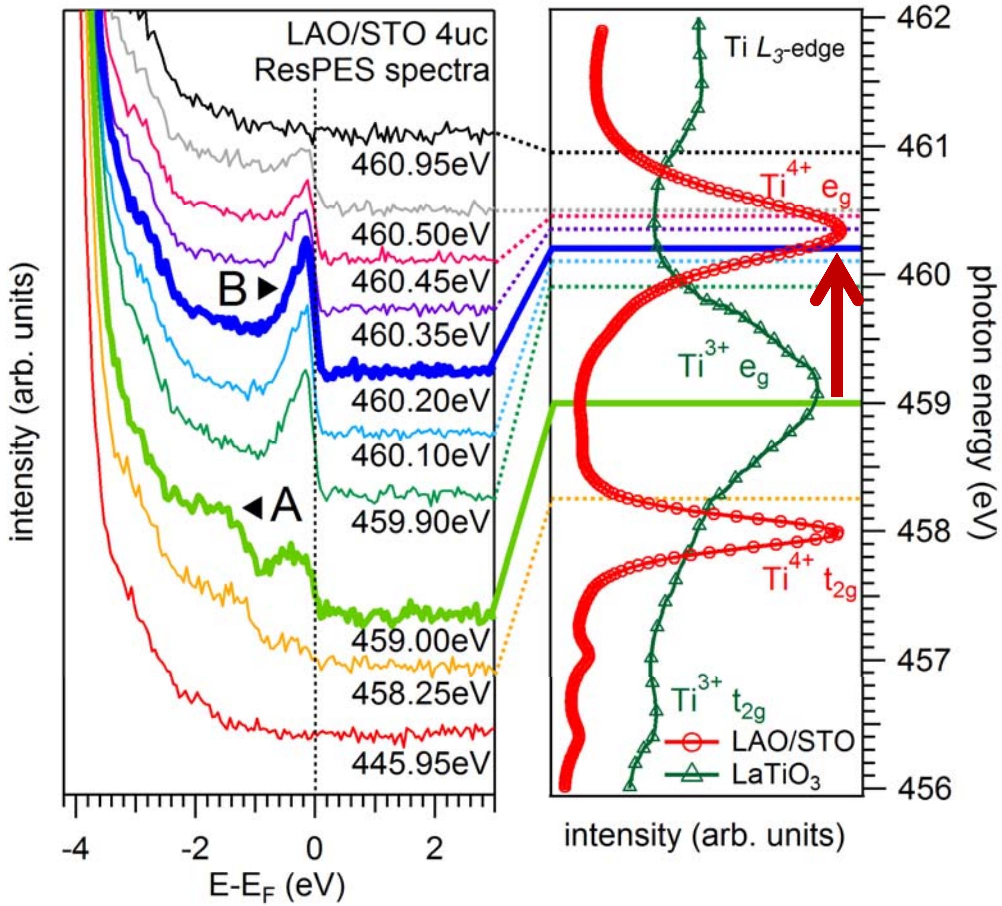
- two Ti 3d resonance features below (**A**) and at E_F (**B**)

feature A:

max enhancement at **Ti^{3+} e_g** resonance (cf. $LaTiO_3$)

LAO/STO: resonant photoemission at Ti L-edge

ResPES **XAS**



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

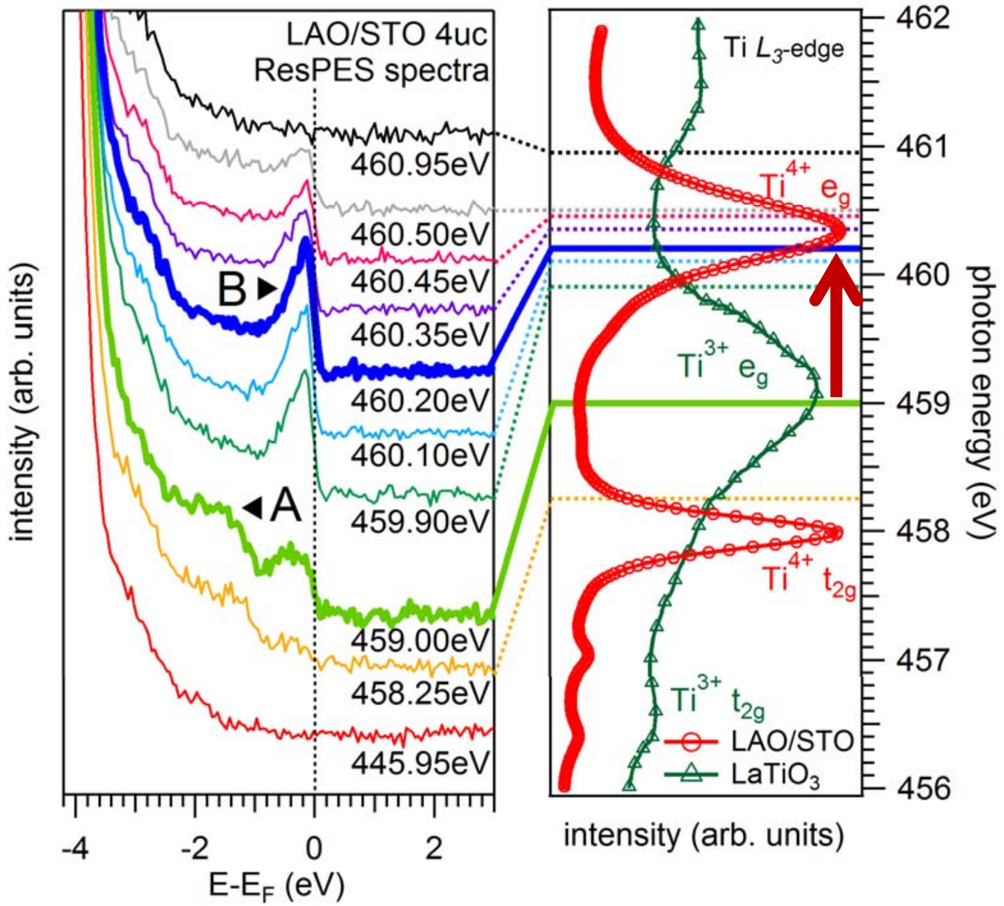
  feature A:
  max enhancement at **Ti^{3+} e_g** resonance (cf. $LaTiO_3$)

  feature B:
  max enhancement ***delayed***

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

LAO/STO: resonant photoemission at Ti L-edge

ResPES **XAS**



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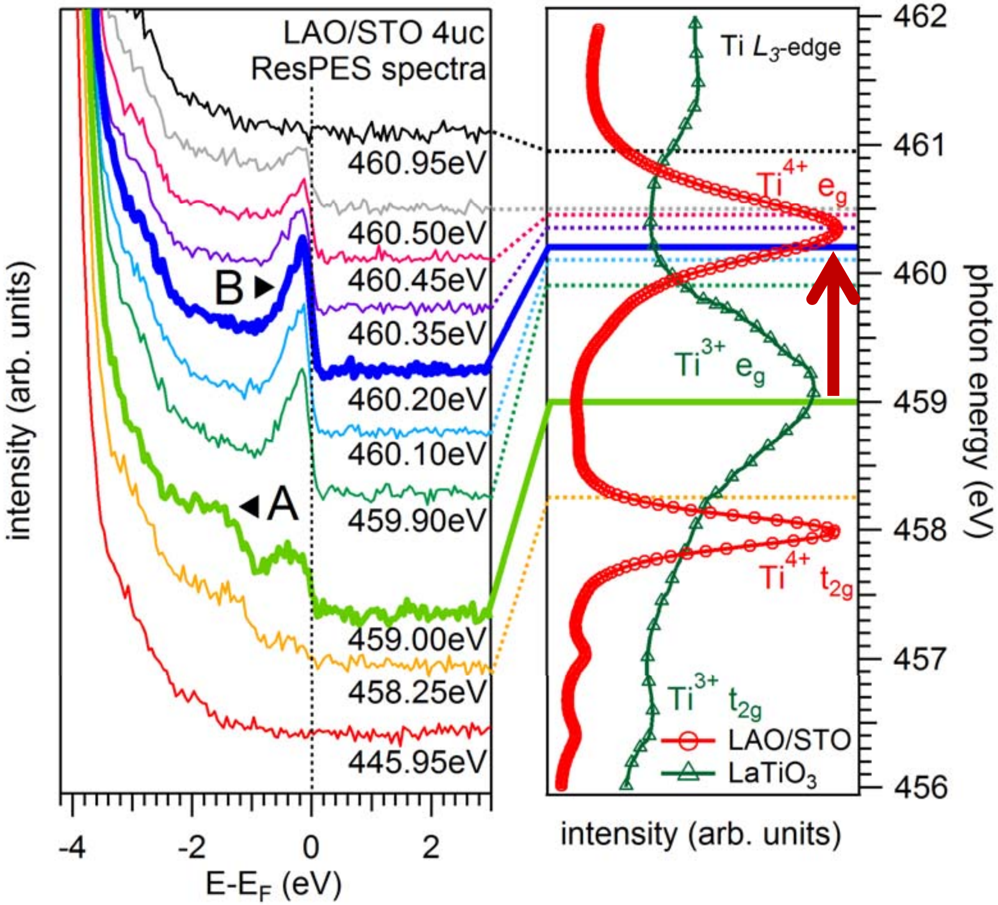
  → characteristic for **localized (A)** and **delocalized (B)** resonating states

- 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

ResPES **XAS**



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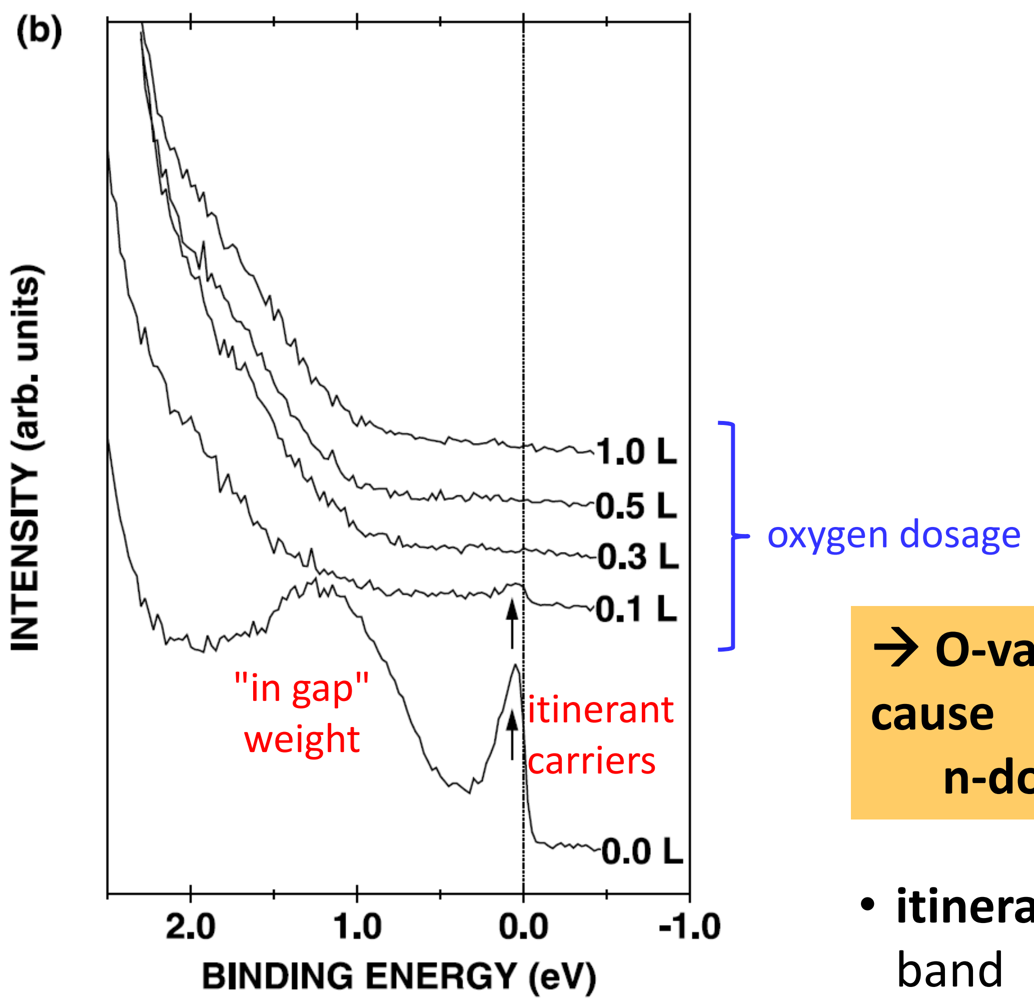
  → characteristic for **localized (A)** and **delocalized (B)** resonating states

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

⇒ **A:** charge carriers trapped in d-orbitals of Ti ions surrounding oxygen vacancies
B: mobile interface charge carriers (2DES)

Photoemission of bare STO surface

photoemission of fractured STO

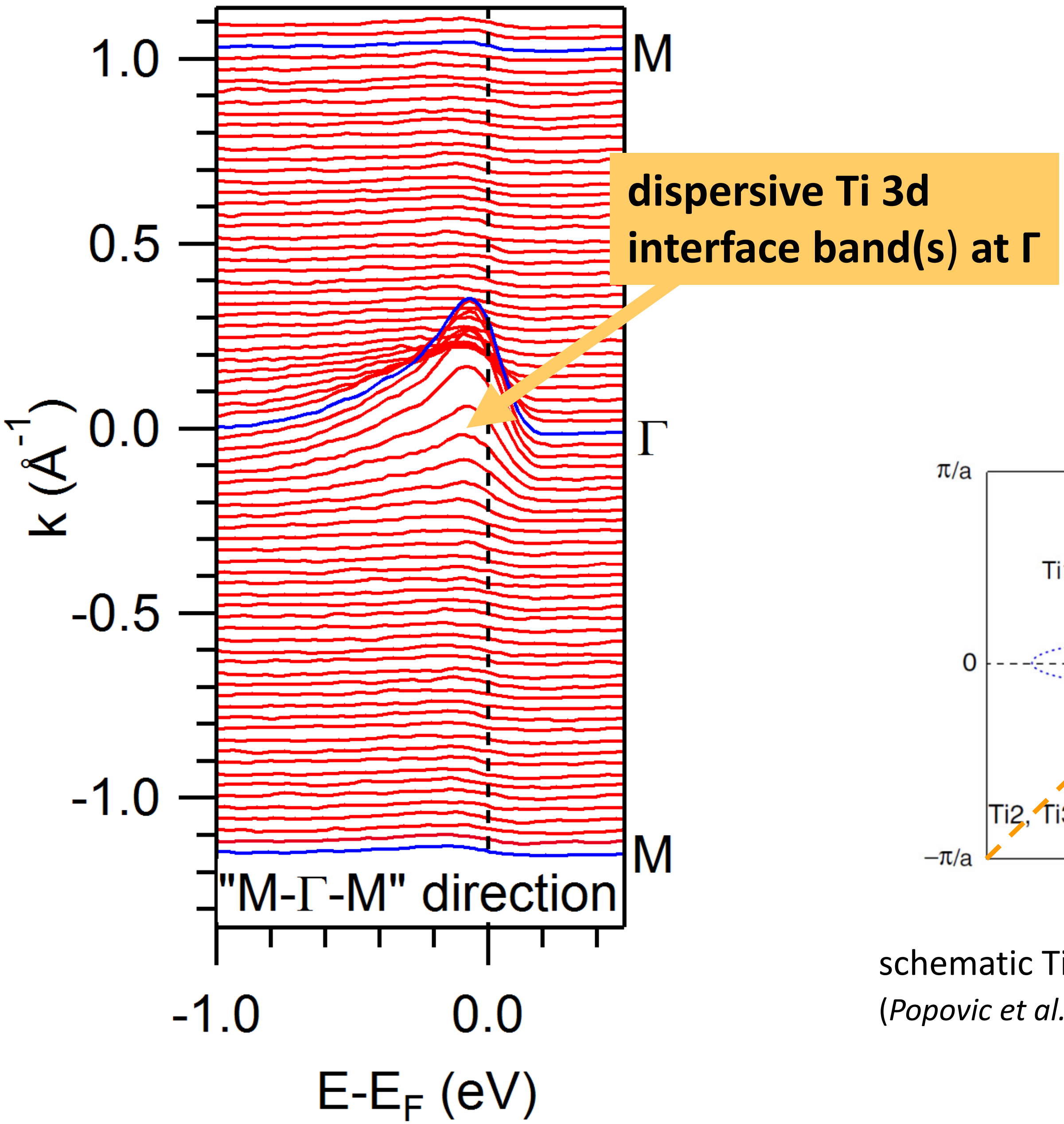


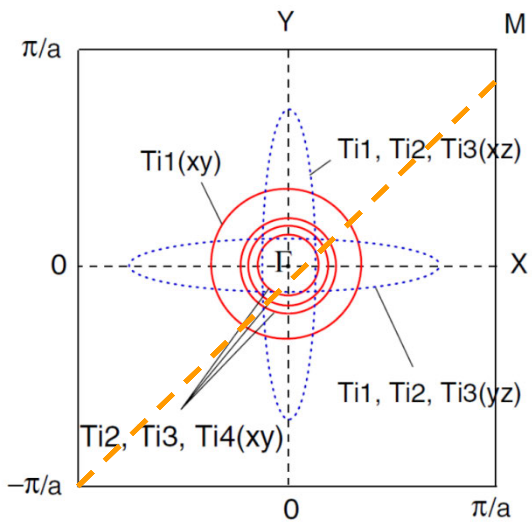
Aiura et al., Surf. Sci. 515, 61 (2002)

→ 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

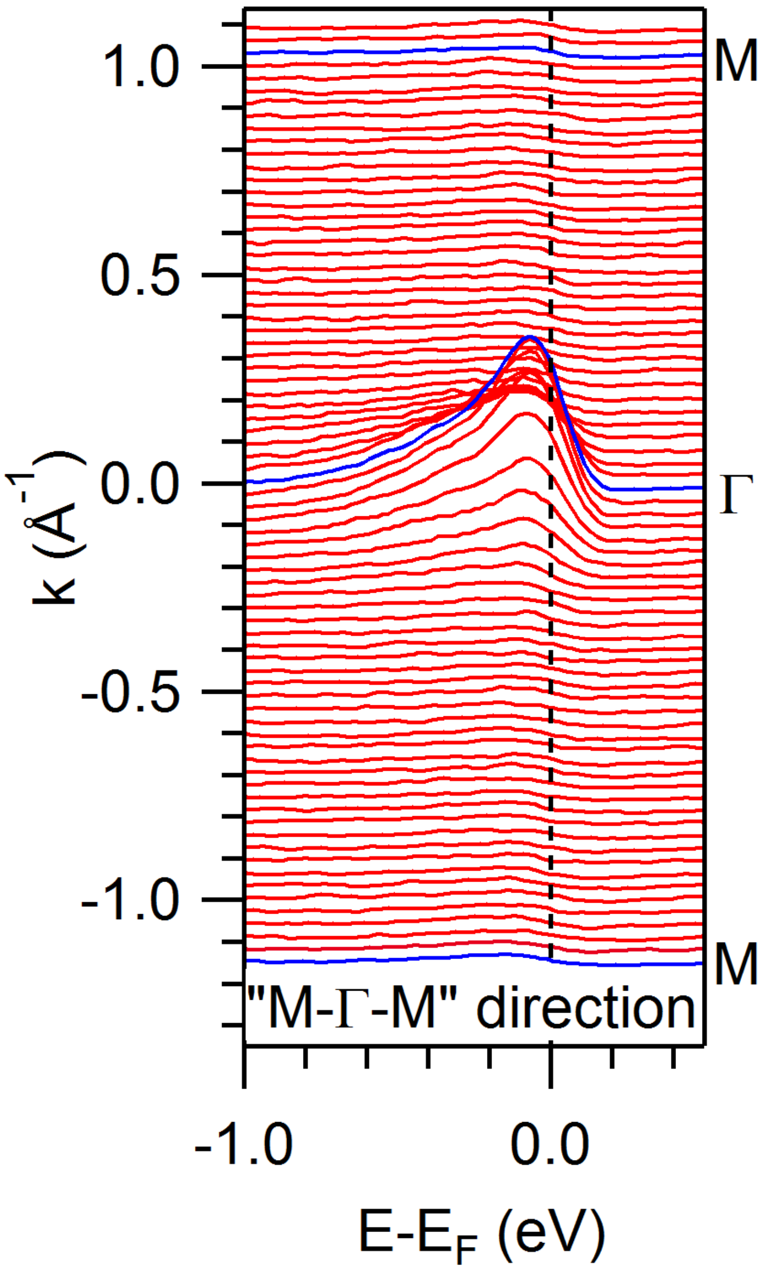
LAO/STO: k-space mapping by SX-ARPES

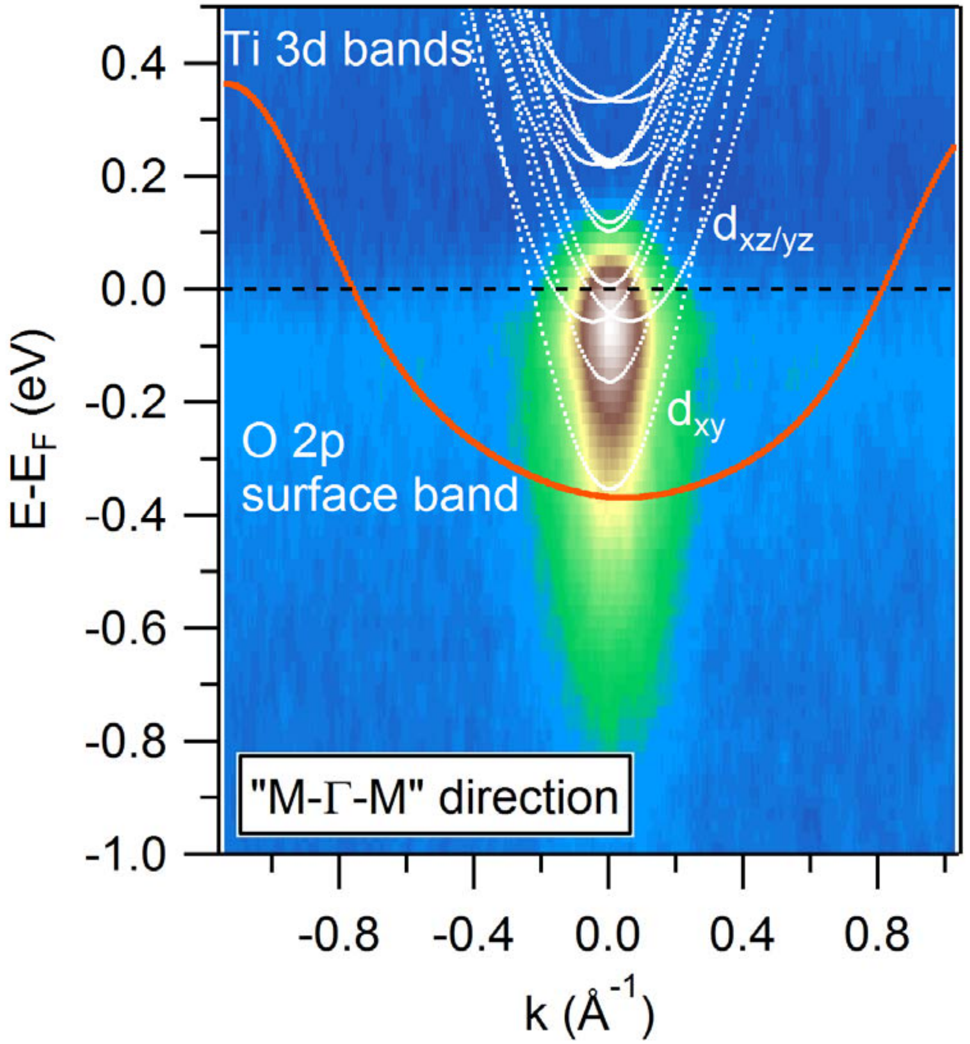




schematic Ti 3d-derived Fermi surface
(*Popovic et al., PRL **101**, 256801*)

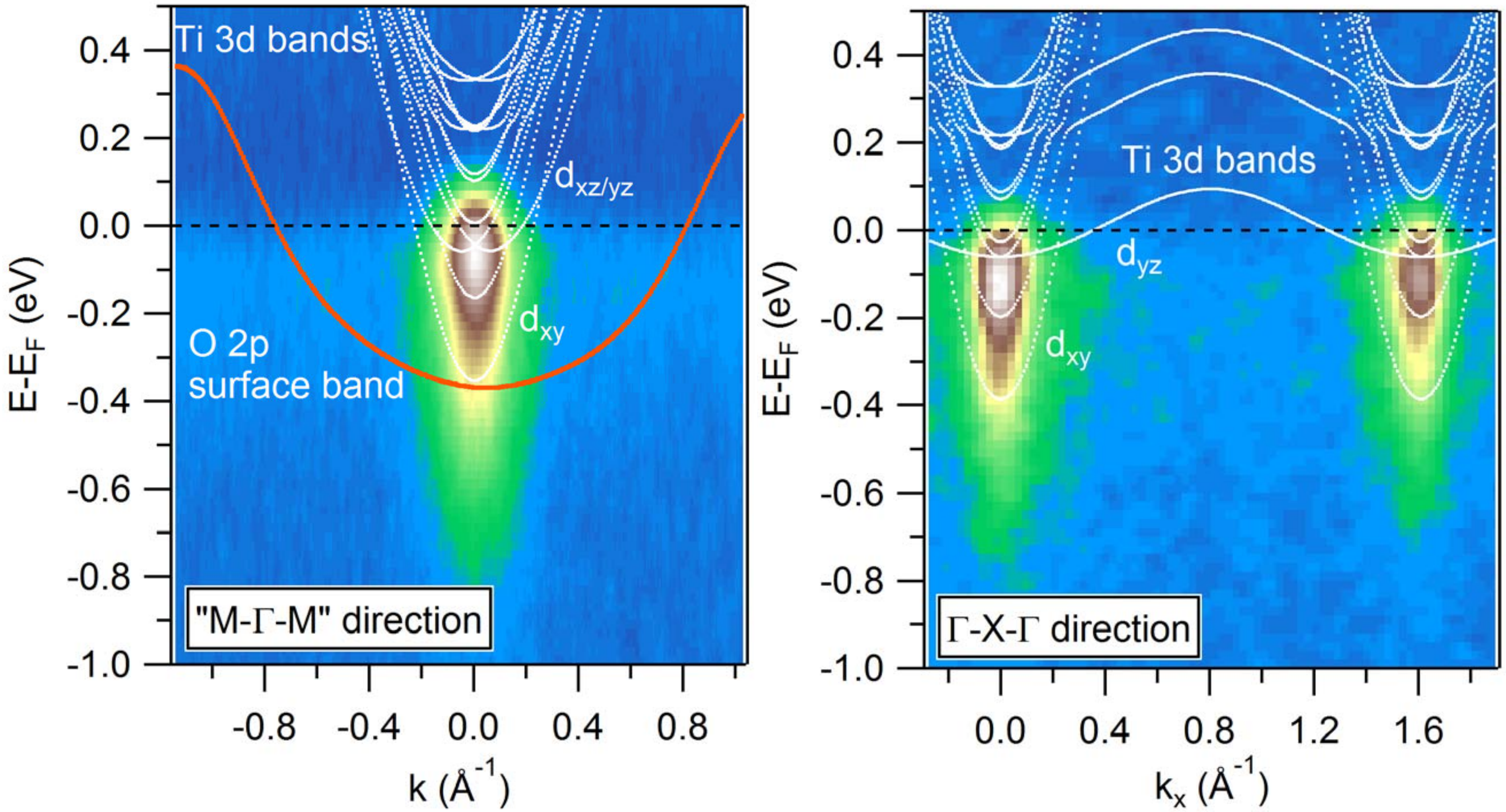
LAO/STO: k-space mapping by SX-ARPES





- 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

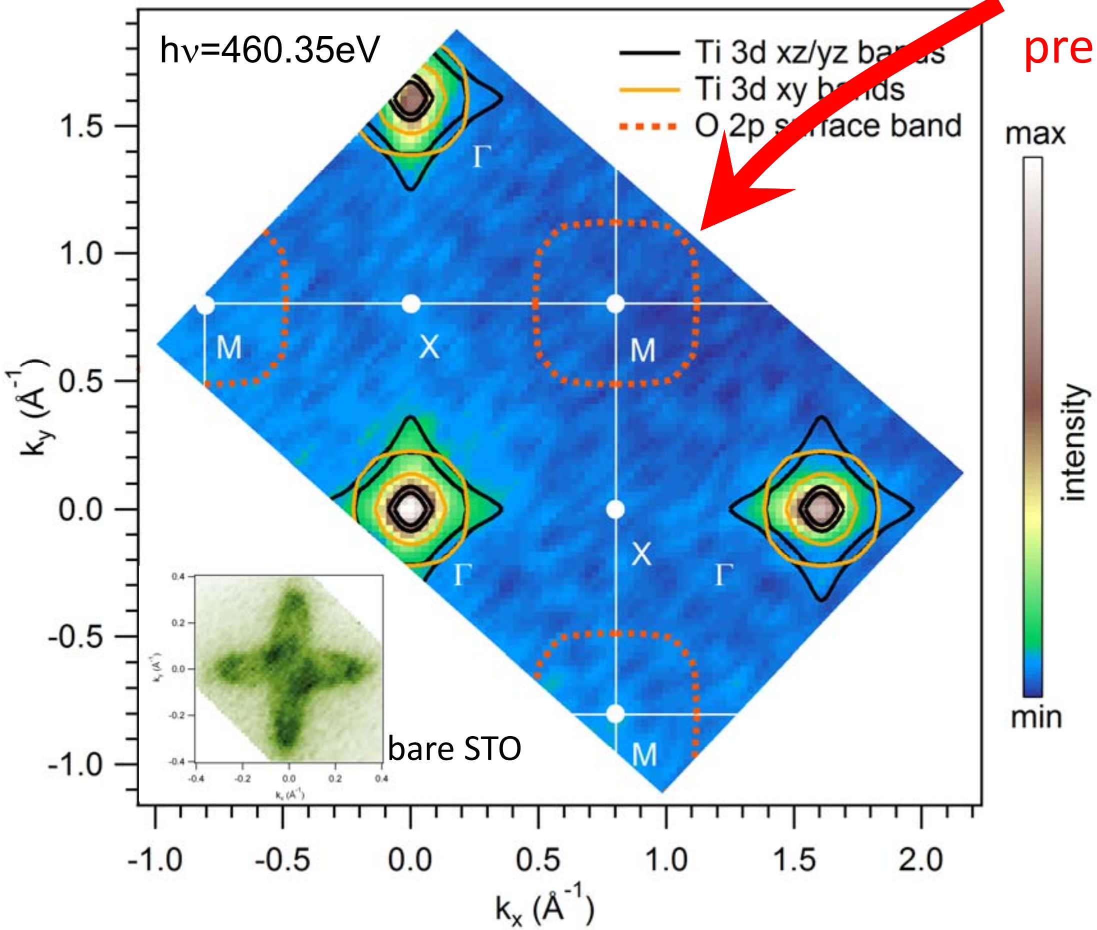


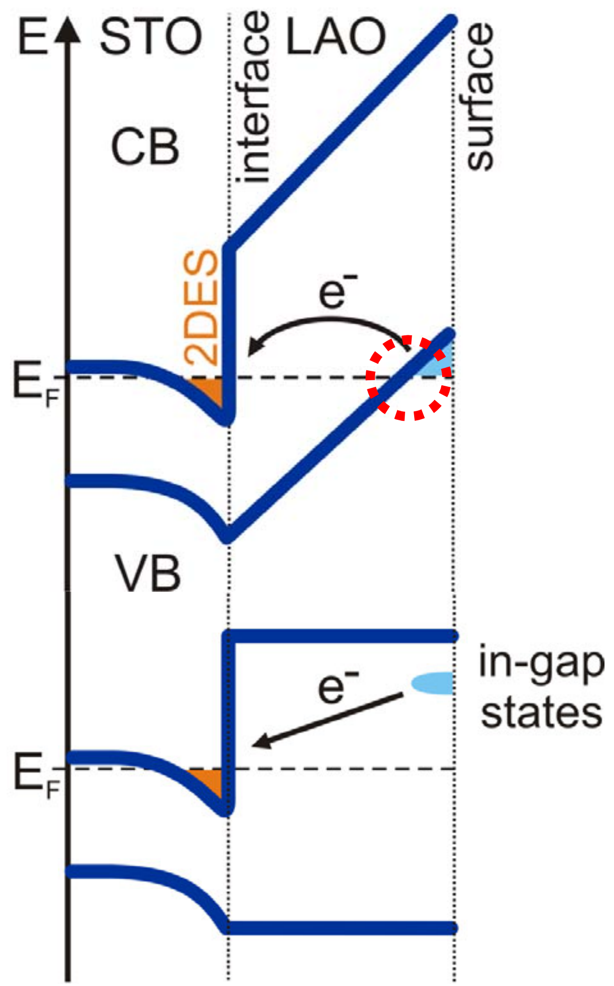
larger k_F-values along ΓX than ΓM also seen in experiment

LAO/STO: Fermi surface mapping

BL23SU, SPring-8

experiment **does not** show
LAO-surface hole pockets
predicted by band theory!

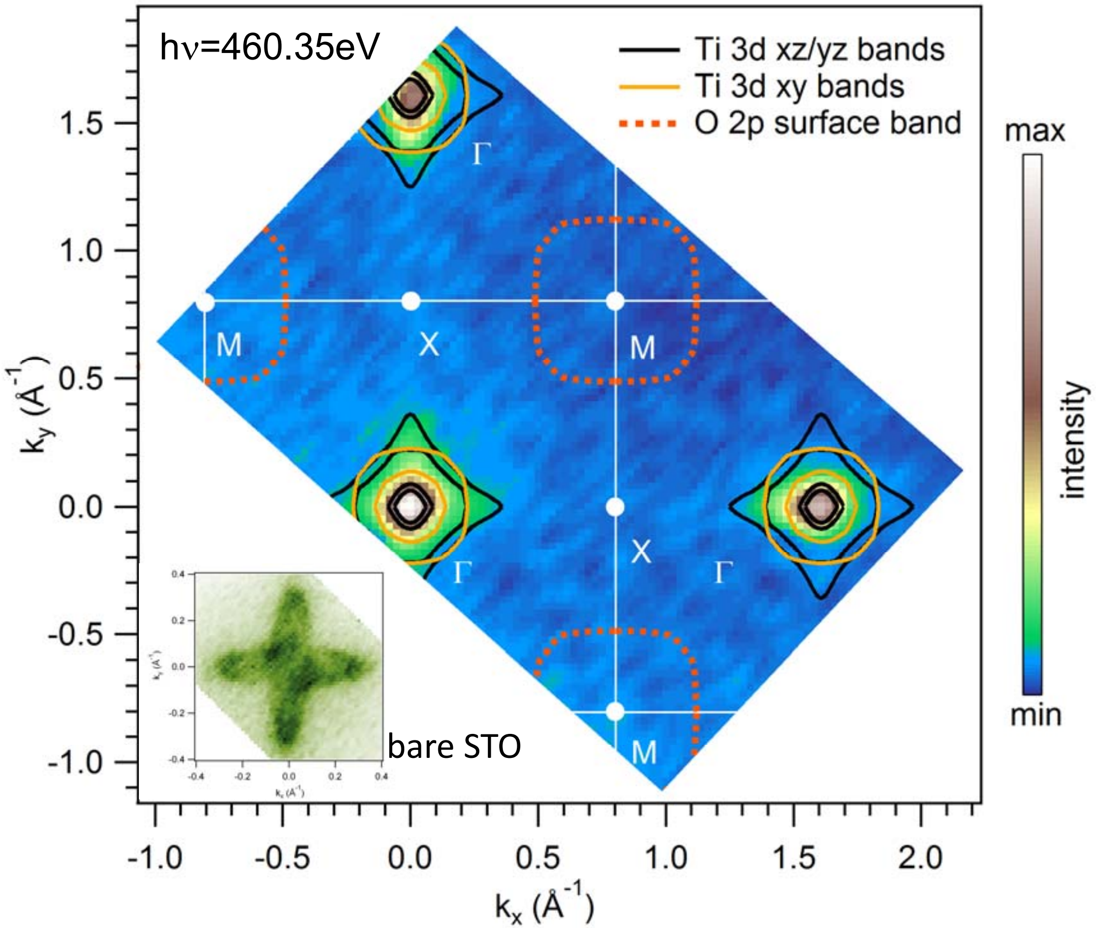




Phys. Rev. Lett. ***110****, 247601 (2013)*
cf. also: Cancellieri et al., arXiv:1307.6943

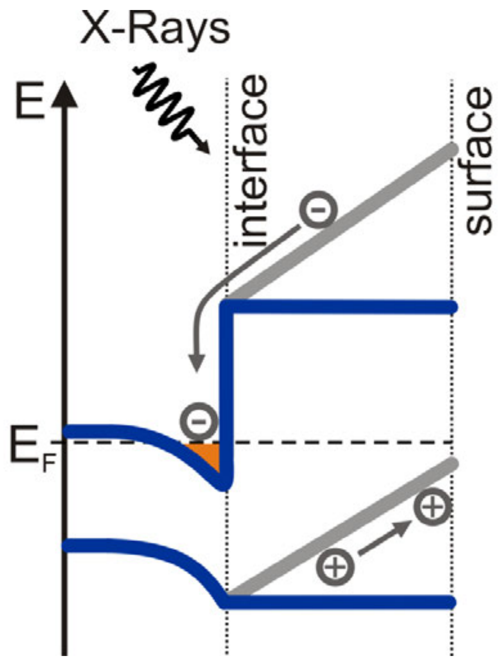
LAO/STO: Fermi surface mapping

BL23SU, SPring-8



Phys. Rev. Lett. ***110****, 247601 (2013)*
cf. also: Cancellieri et al., arXiv:1307.6943

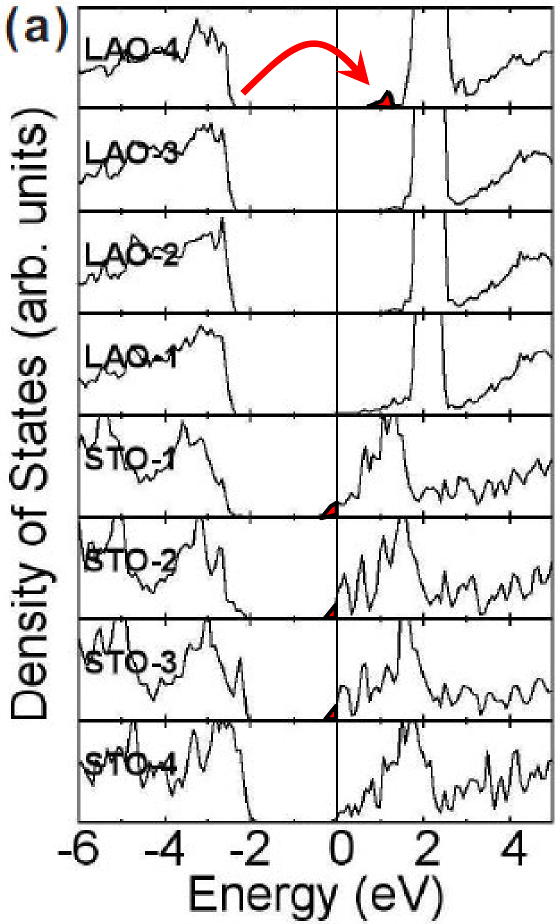
dynamical equilibrium?



but:

- 2uc samples charge up
- no variation on changing photon flux
- band bending seen in other systems, e.g., $LaCrO_3$/STO

Oxygen vacancies at LAO surface?

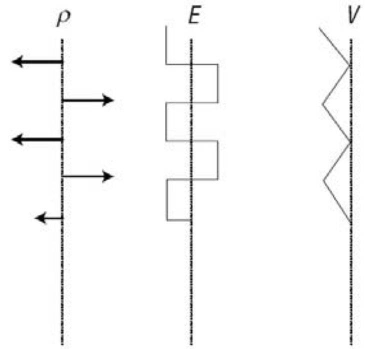


Yun Li et al., PRB **84**, 245307 (2011)

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

O vacancies induce localized hole states above E_F

$AlO_{1.75}$	**-0.5**
LaO	+1
AlO_2	-1
LaO	+1
AlO_2	-1
LaO	+1
AlO_2	-1
LaO	+1
TiO_2	**-0.5**
SrO	0
TiO_2	0
SrO	0
TiO_2	0
SrO	0



- ***modified*** **el. reconstruction scenario**
- **critical thickness, if for each O_{vac} formation energy < discharge energy**

Sources and further reading

Most of the first part has been taken from the following sources:

Internet

- **www.physik.uni-wuerzburg.de/EP4/teaching/Cargese2005/cargese.php and LesHouches2014 (coming soon)**
  (by R. Claessen, U Würzburg)
- **www-bl7.lbl.gov/BL7/who/eli/SRSchoolER.pdf**
  (by E. Rotenberg, Advanced Light Source)
- **www.physics.ubc.ca/~quantmat/ARPES/PRESENTATIONS/Lectures/CIAR2003.pdf**
  (by A. Damascelli, U British Columbia)

Books

- S. Hüfner, *Photoelectron Spectroscopy – Principles and Applications, 3rd ed.* (Berlin, Springer, 2003)
- W. Schattke, M.A. van Hove (eds.), *Solid-State Photoemission and Related Methods – Theory and Experiment* (Weinheim, Wiley-VCH, 2003)
- S. Suga, A. Sekiyama, *Photoelectron Spectroscopy – Bulk and Surface Electronic Structures* (Berlin, Springer, 2014)

Review articles

- F. Reinert and S. Hüfner, New Journal of Physics **7**, 97 (2005)
- A. Damascelli, Physica Scripta **T109**, 61 (2004)
- S. Hüfner *et al.*, J. Electron Spectrosc. Rel. Phen. **100**, 191 (1999)

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