Elettra Sincrotrone Trieste

School on Synchrotron and Free-Electron-Laser Based Methods: Multidisciplinary Applications and Perspectives

Angle-Resolved Photoemission Spectroscopy (ARPES)

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Resources

<u>Books</u>

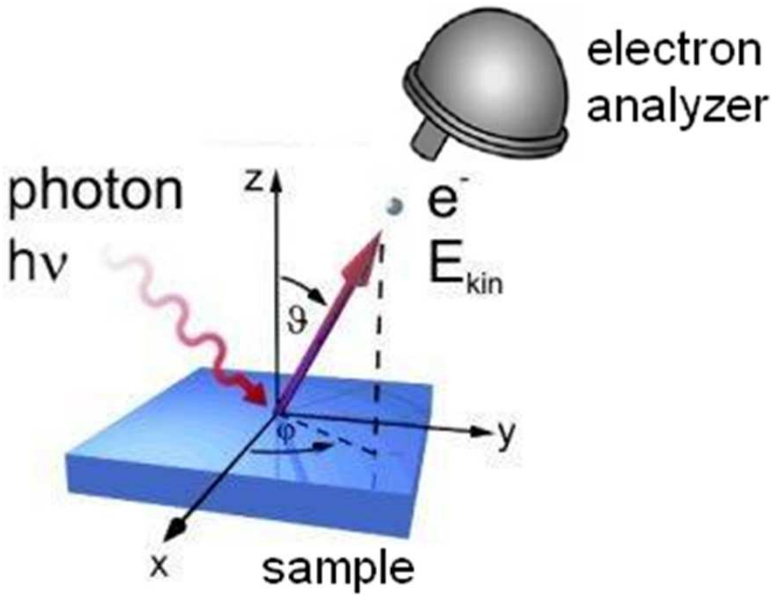
- S. Hüfner, *Photoelectron spectroscopy*, 2nd ed. Springer 1996
- S. Hüfner, *Very high resolution photoelectron spectroscopy*, Springer 2007
- R.D. Mattuk, *A guide to Feynman diagrams in the many-body problem*, 2nd ed. Dover, 1976/1992

<u>Review articles</u>

- F. Reinert et al., *New J. Phys.* **7**, 97 (2005)
- A. Damascelli et al., *Rev. Modern Phys.* **75**, 473 (2003)
- J. Braun, *Rep. Prog. Phys.* **59**, 1267 (1996)

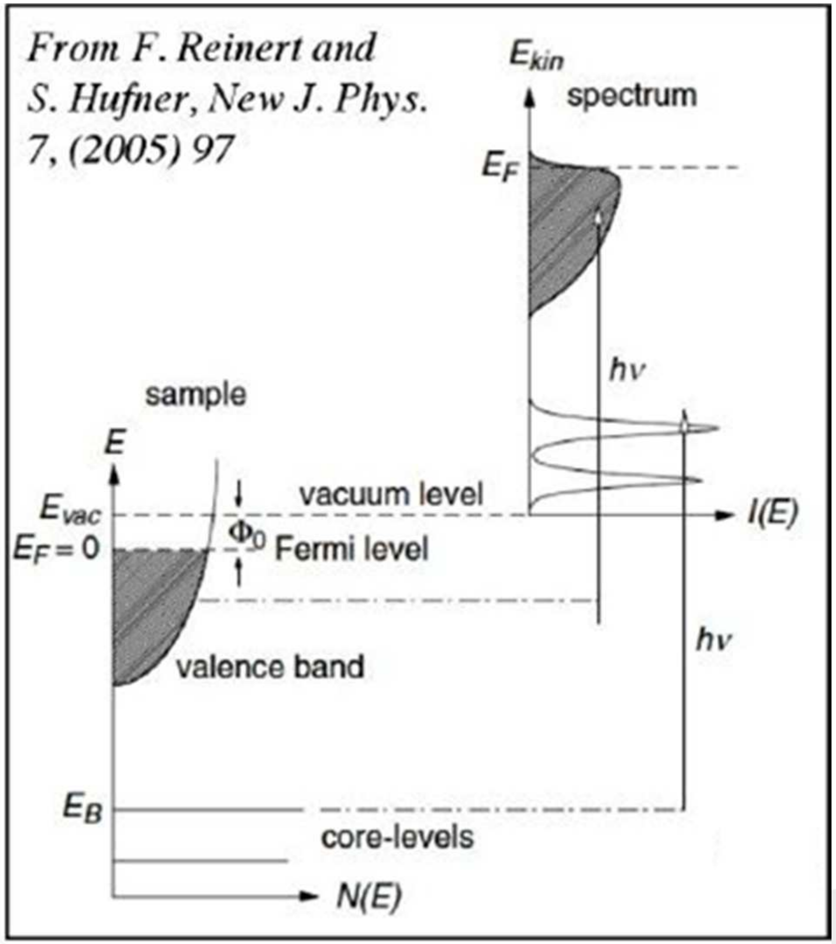
Thanks to A. Damascelli, K. Shen, and E. Rotenberg from which I took and adapted some slides and figures.

Photoelectric effect: Scientific application



K.M. Siegbahn

«for his contribution to the development of high-resolution electron spectroscopy»



Photoelectron Spectroscopy

(ESCA / XPS, PD, **UPS - ARUPS / ARPES**…)

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

$\phi \sim$ **1.5-5.5 eV** $|E_B| \sim$ **0-1/15 eV (valence band)**

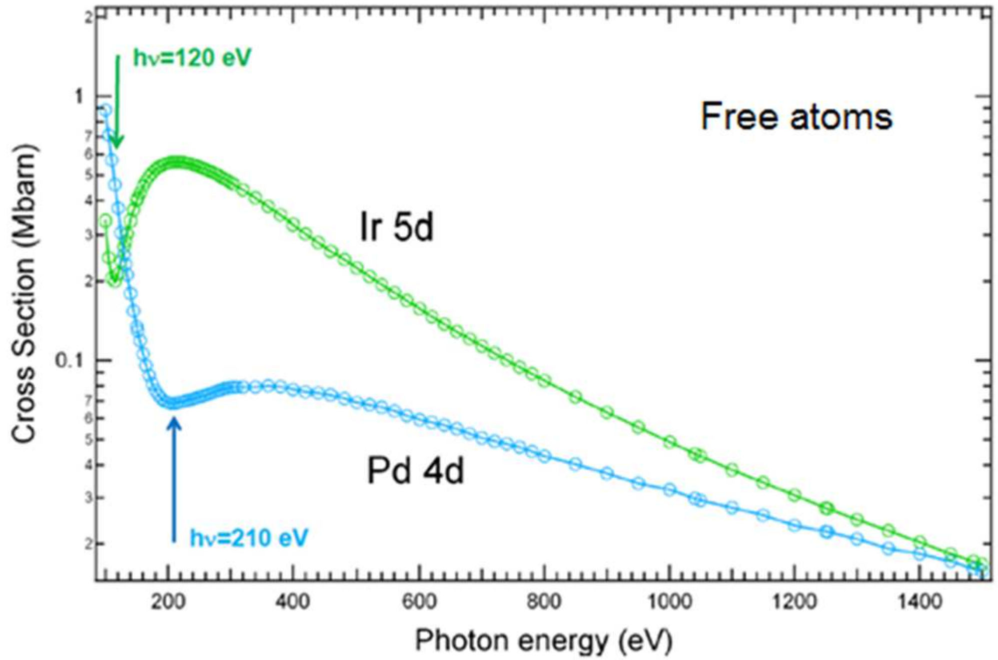
$|E_B| \rightarrow$ 1500 eV (interesting core levels)

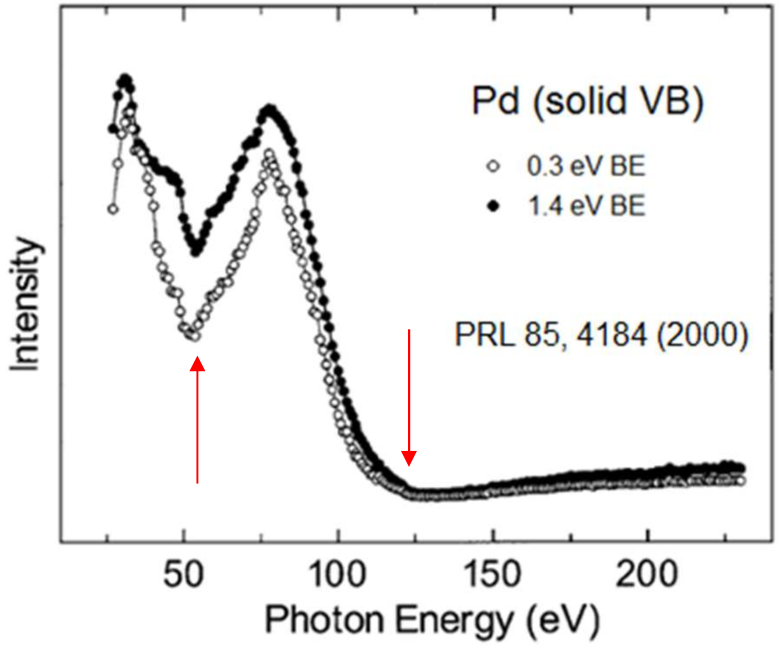
Ultraviolet vs X-ray radiation

Photoemission cross section vs $h\nu$

The **UPS/ARPES** experiment is quite similar to XPS, only that the photon energies are lower and the energy and angular resolution is higher.

The need for lower photon energies stems from the **photoemission cross section for valence band photoemission**. Emission sets in as the photon energy reaches the work function and the cross section then drops quickly, as it does for core levels in figure

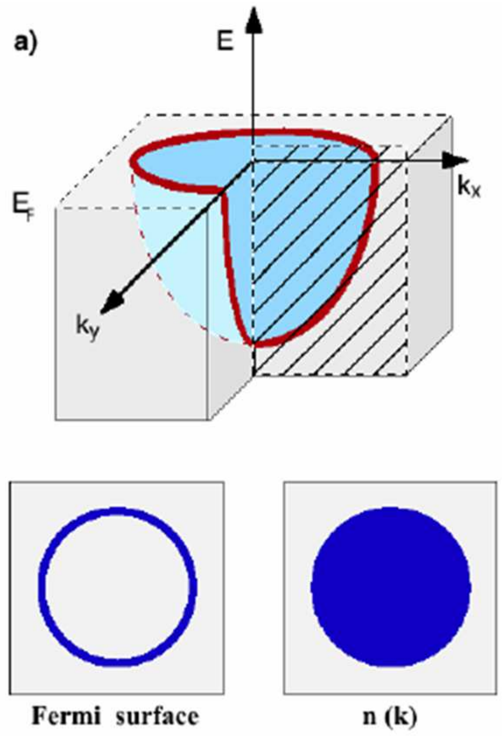




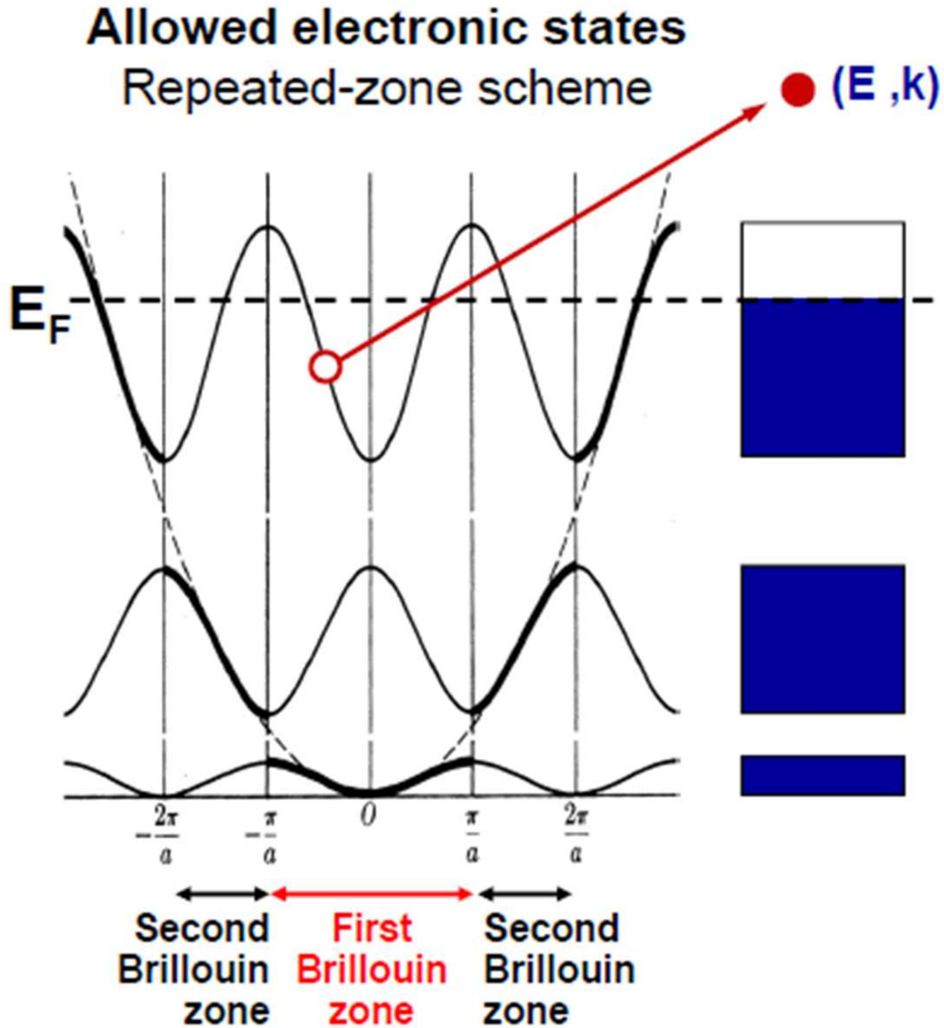
For the high photon energies used in XPS, the cross section for valence band photoemission is very small.

Understanding the Solid State: Electrons in Reciprocal Space

Many properties of solids are determined by valence electrons near E_F (conductivity, superconductivity, magnetoresistance, magnetism …)



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



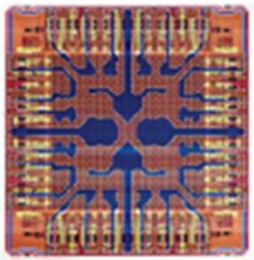
Non-interacting electrons in solids: the band picture

Interactions can give rise to new states of matter

"Conventional Materials"

Diamond

Silicon



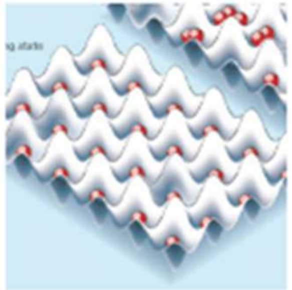
Copper

- Understood physical properties (resistivity, magnetic, thermodynamic)
- Well described by conventional theories of solids (band structure, DFT, etc..)
- Correlations between individual electrons can be essentially neglected

"Correlated Materials"

High-T_c Superconductors

Mott Insulators



Colossal Magnetoresistance

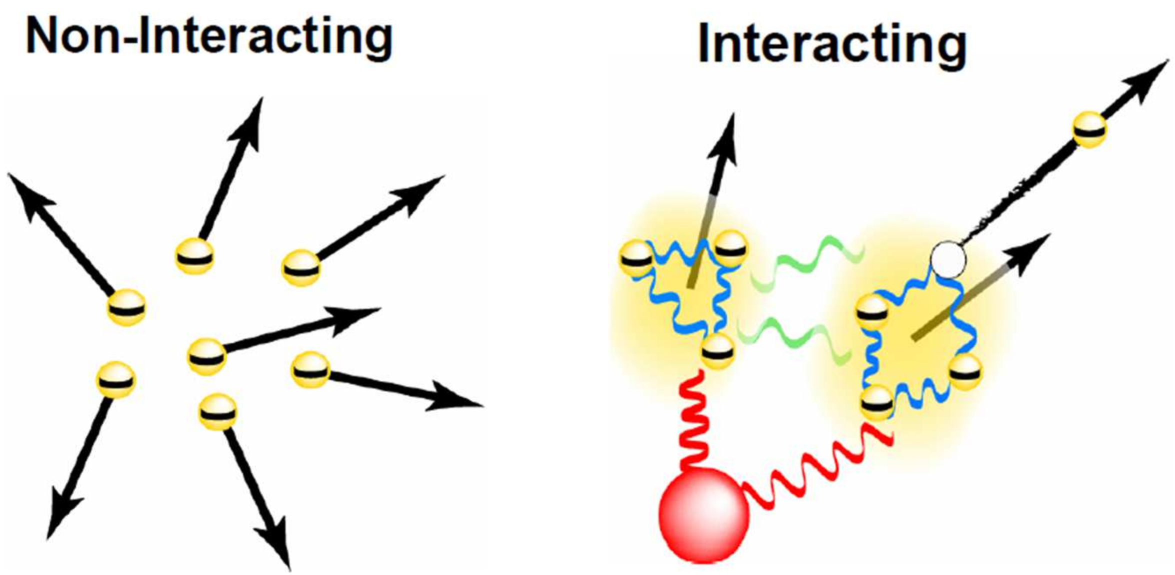
- Correlations between individual electrons are EXTREMELY important
- Failure of conventional theories to explain properties or electronic structure
- Highly exotic and dramatic physical properties

Courtesy of Kyle Shen

Interaction or many-body effects: the whole is greater than the sum of parts

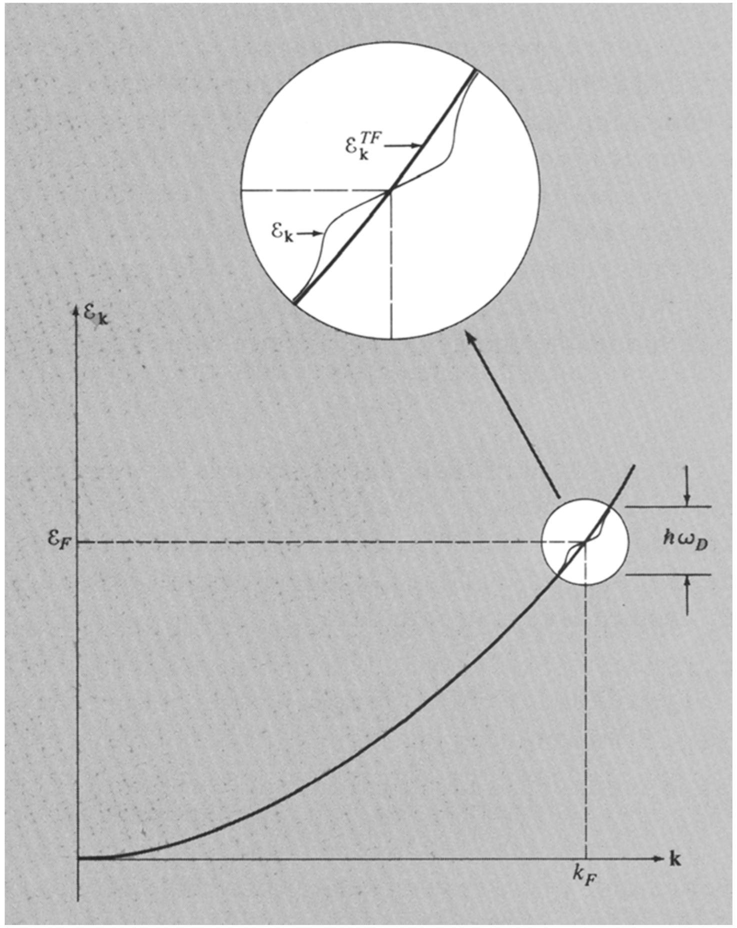
Many-body effects are due to the interactions between electrons and each other, or with other excitations inside the crystal (phonons, plasmons…)

- Interactions: intrinsically hard to calculate
- Responsible for many surprising phenomena: superconductivity, magnetism, density waves…



Quasiparticles

Ashcroft & Mermin

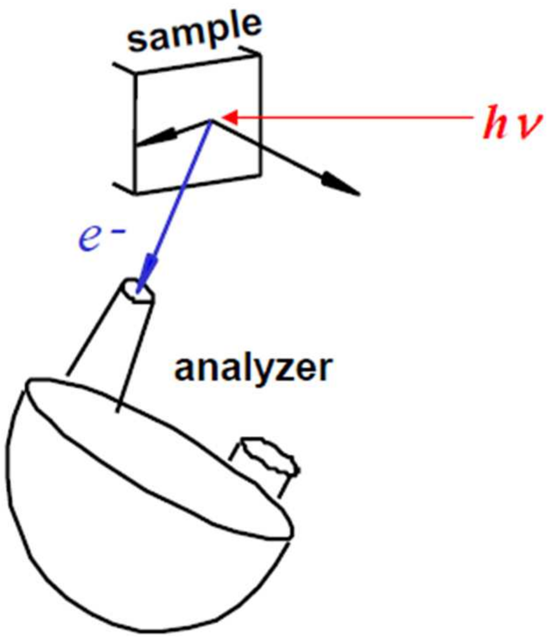


Changes in the carrier mass due to electron-phonon (or other electron-boson) coupling only affects the near-E_F states.

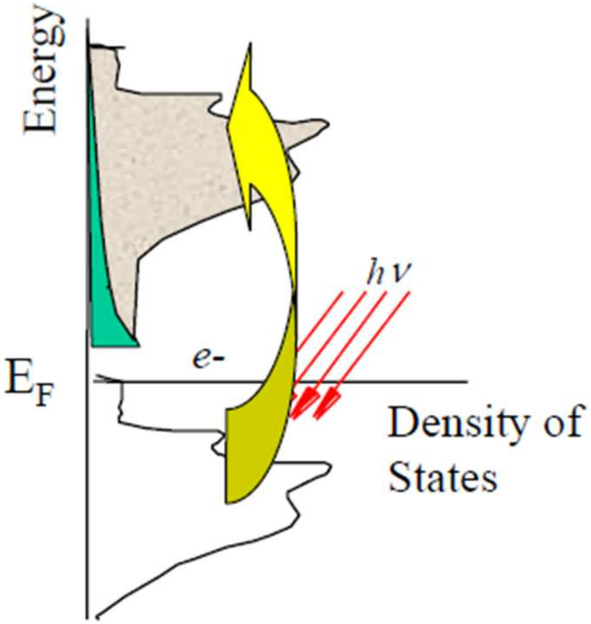
VUV Photoemission Spectroscopy

A specialized technique used in solid state physics and materials science to study the filled electronic structure (density of states and band structure)

and many-body effects [by high resolution (1-10meV, 0.1-1°) and low temperature (<20 K)]

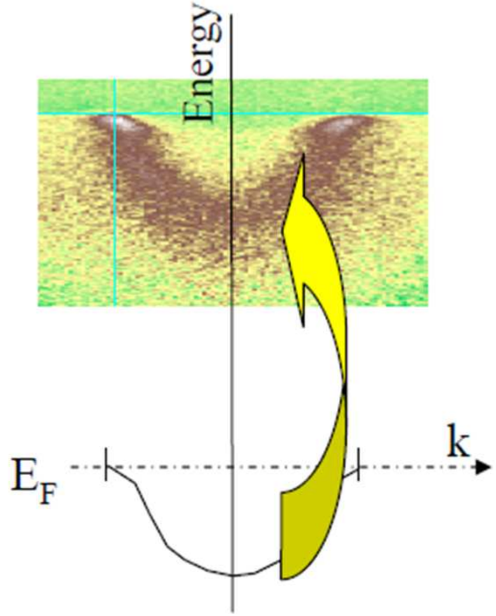


PES



Angle-integrated (UPS)

→ Density of States



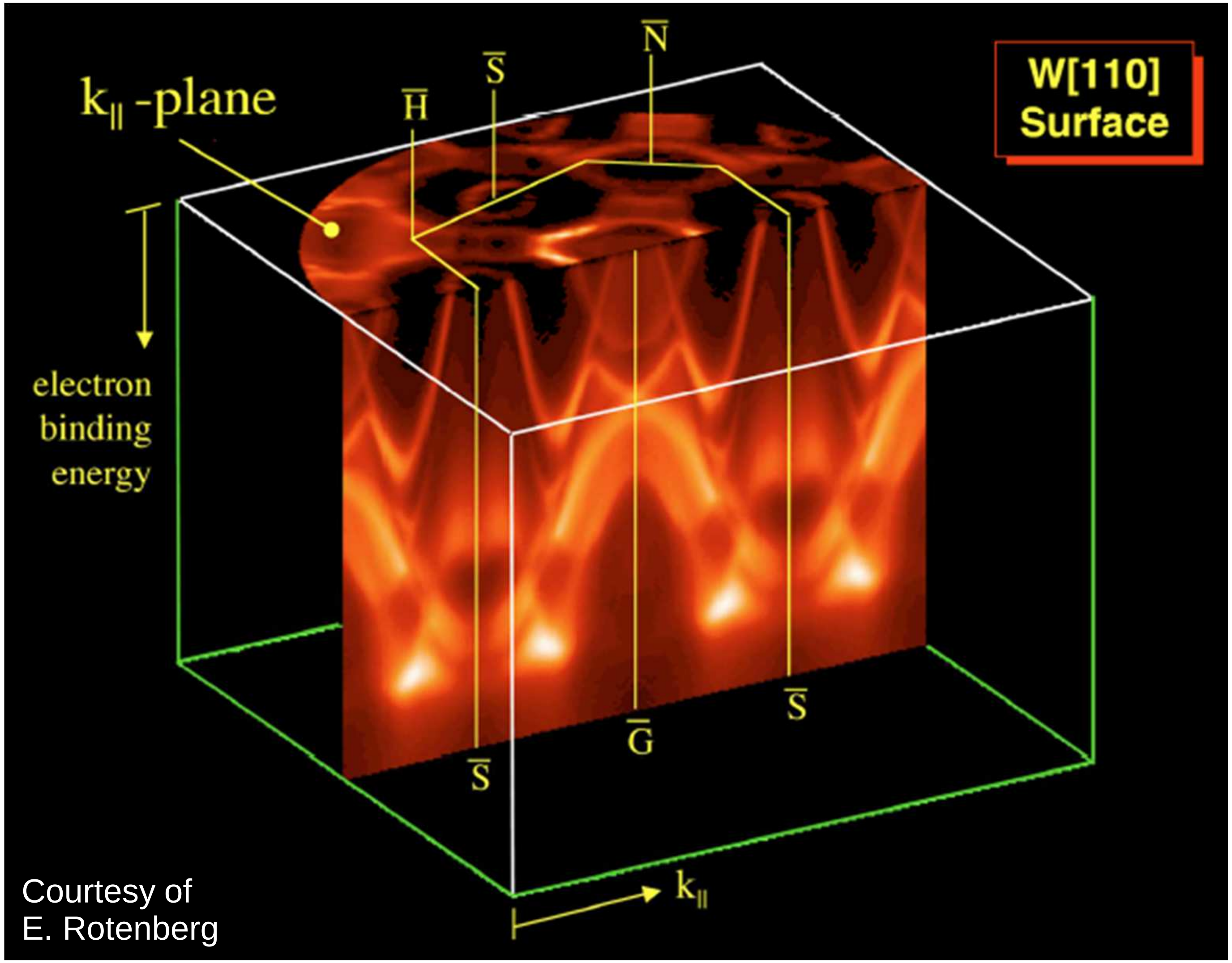
Angle-resolved (ARPES)

→ Electronic Bands $E(\mathbf{k})$

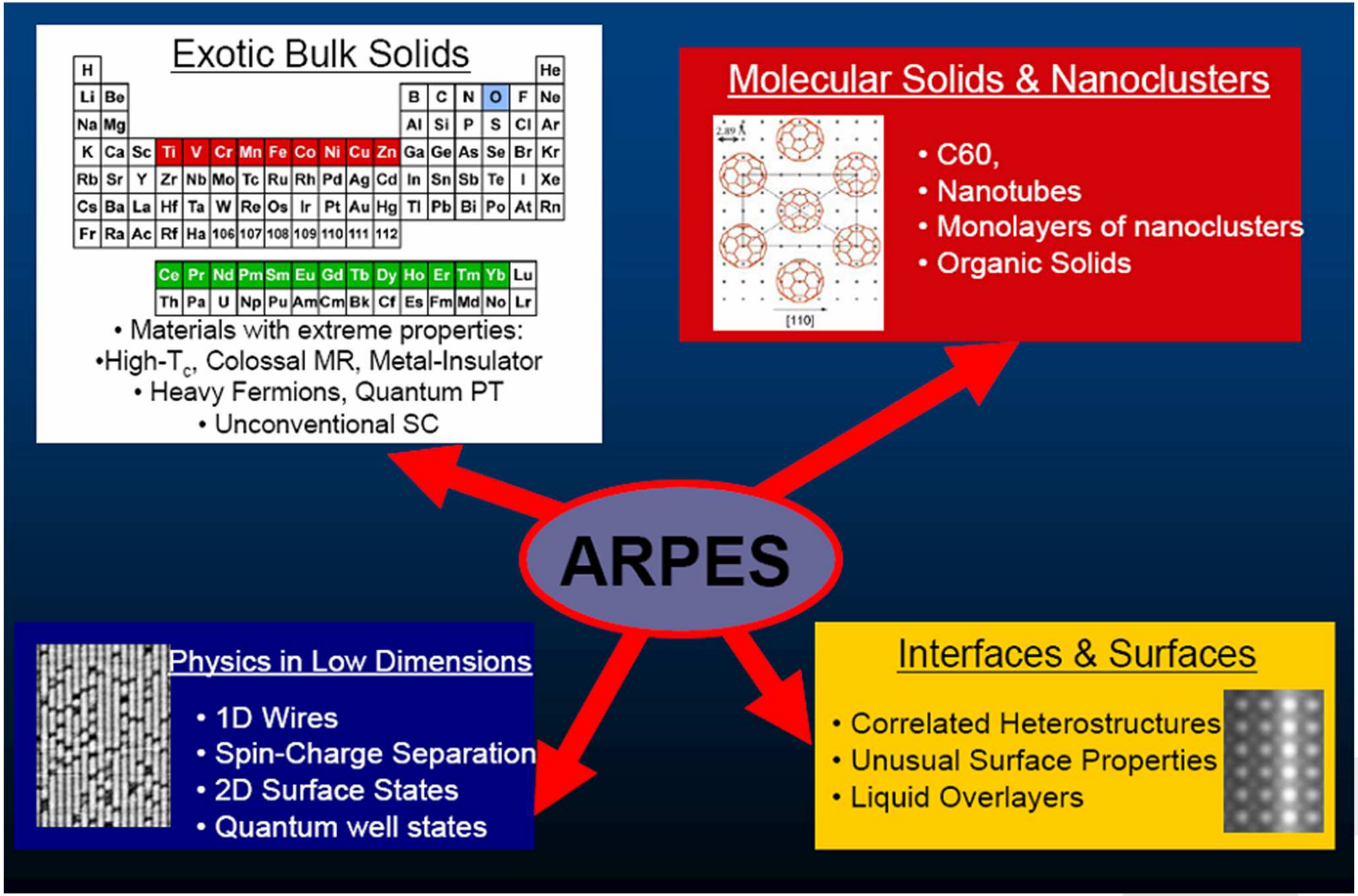
Interested in critical details of the lowest energy interactions near E_F

→ Requirement for the highest spectral resolution and sensitivity

Band mapping and Fermi surface by ARPES



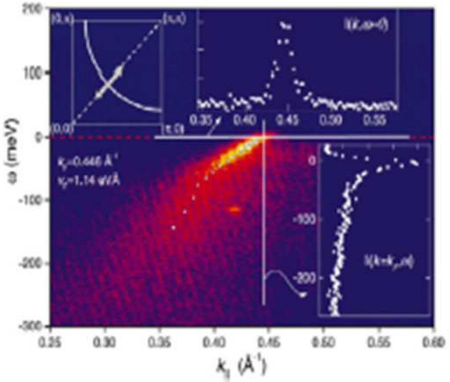
ARPES: Widespread impact in materials



Courtesy of Kyle Shen

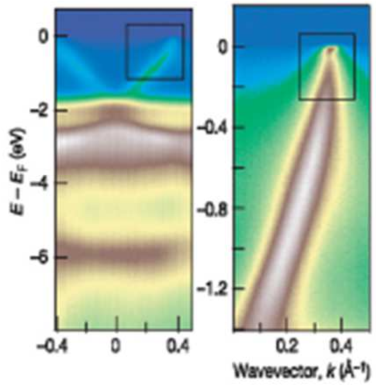
ARPES: Widespread impact in science

HTSC's



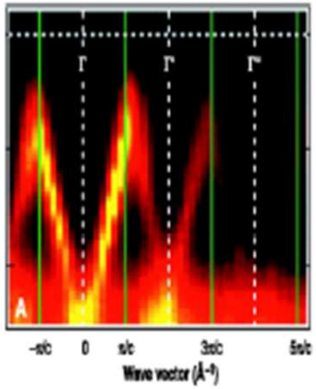
Science 1999

CMR's



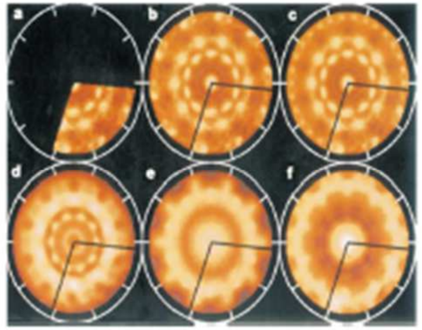
Nature 2005

CDW's



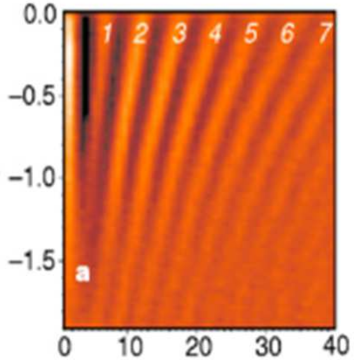
Science 2000

Quasicrystals



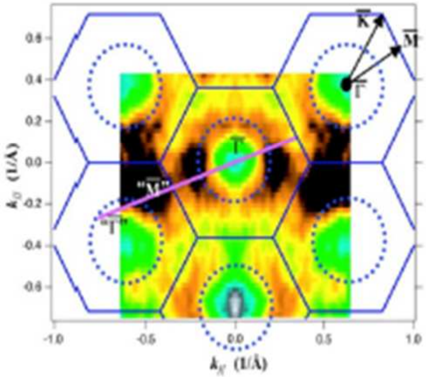
Nature 2000

Quantum Wells



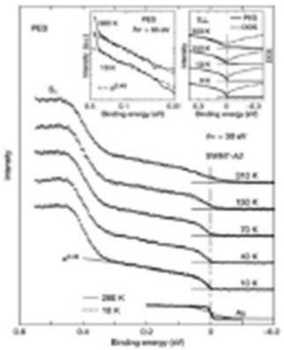
Nature 1999

C_{60}



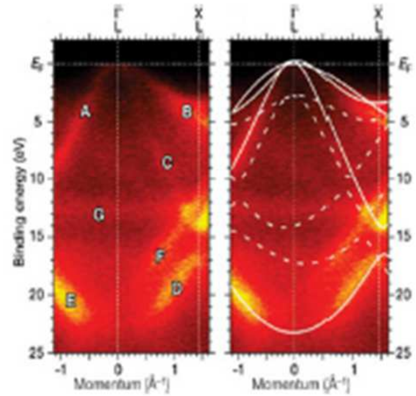
Science 2003

Nanotubes



Nature 2003

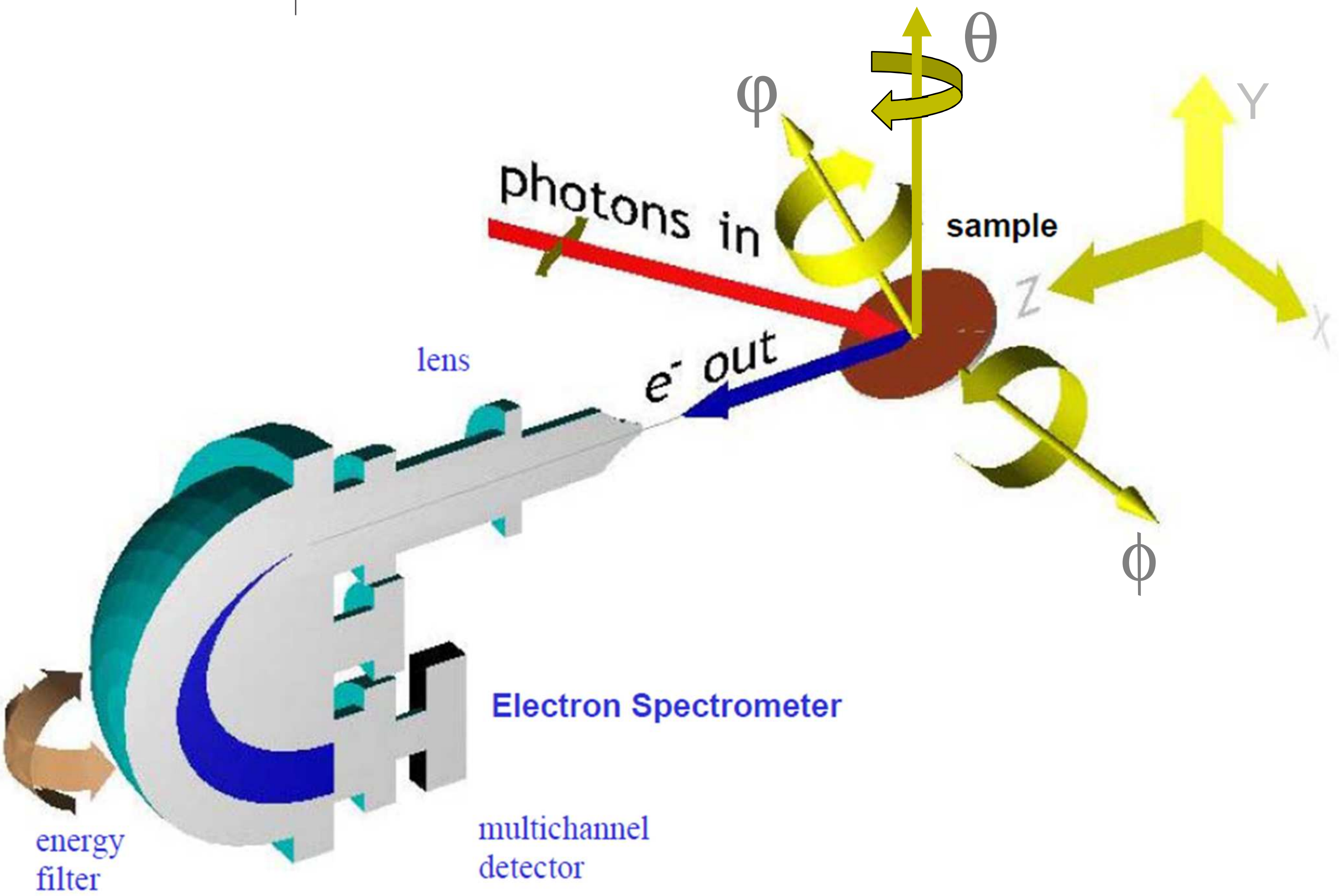
Diamond



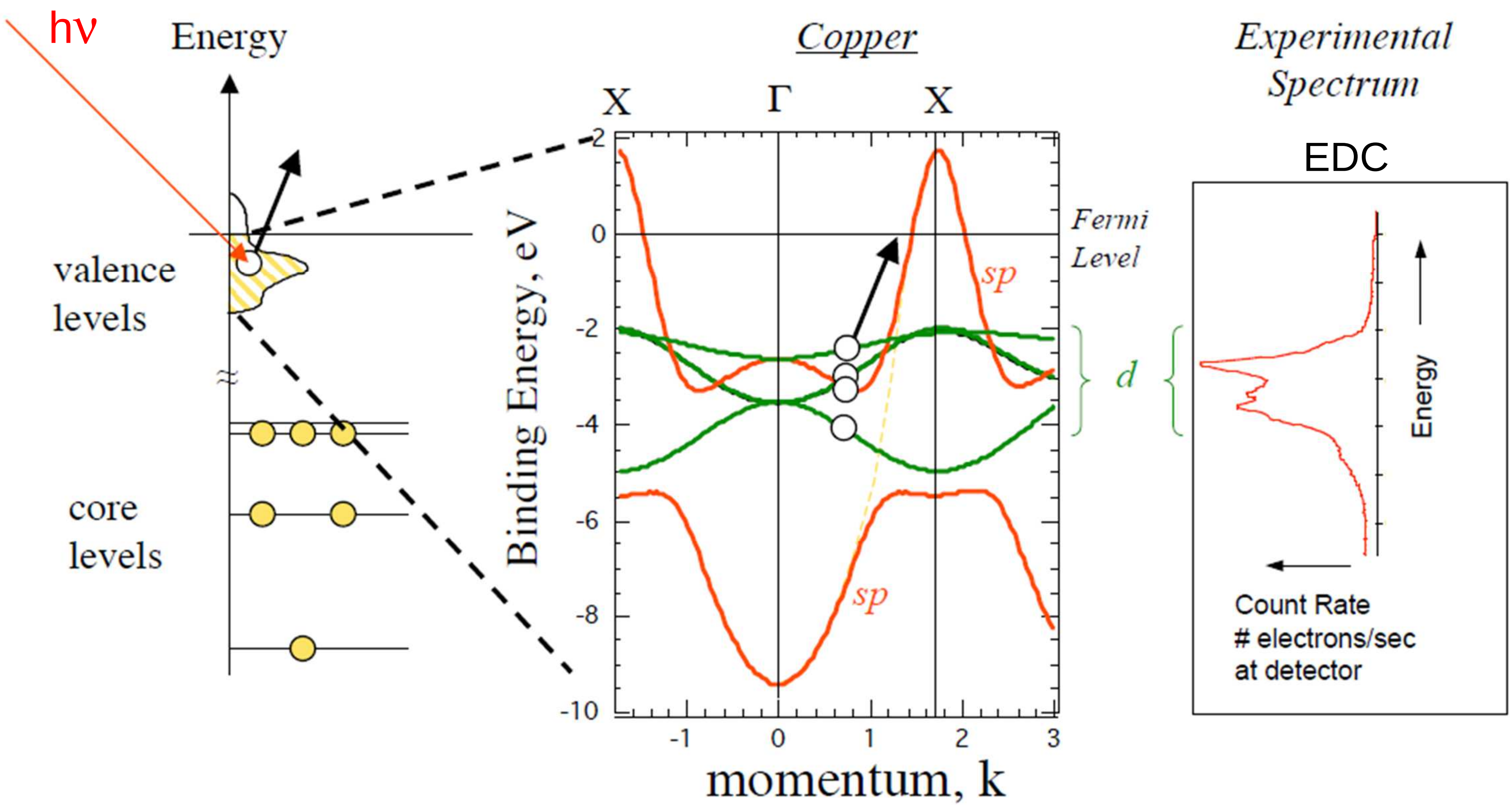
Nature 2005

Courtesy of A. Damascelli

Experimental geometry

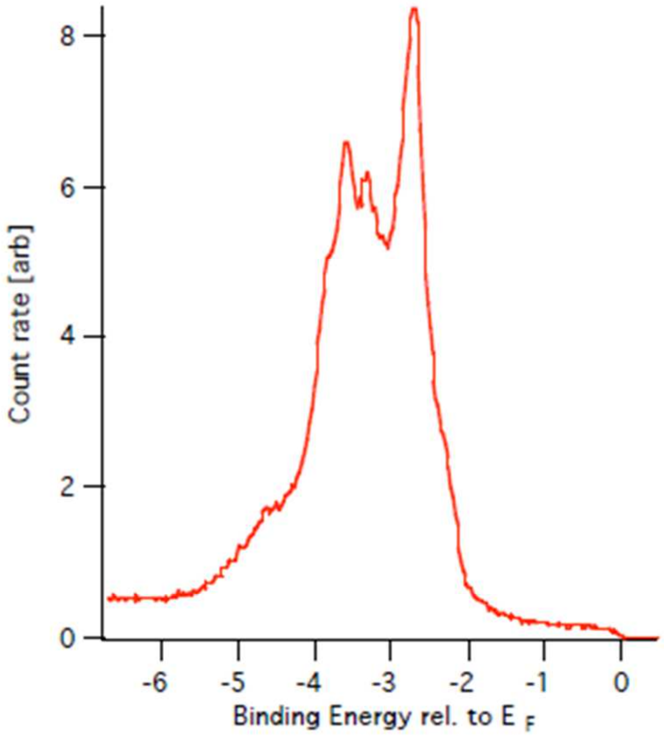


Angle-Resolved Photoemission Spectroscopy

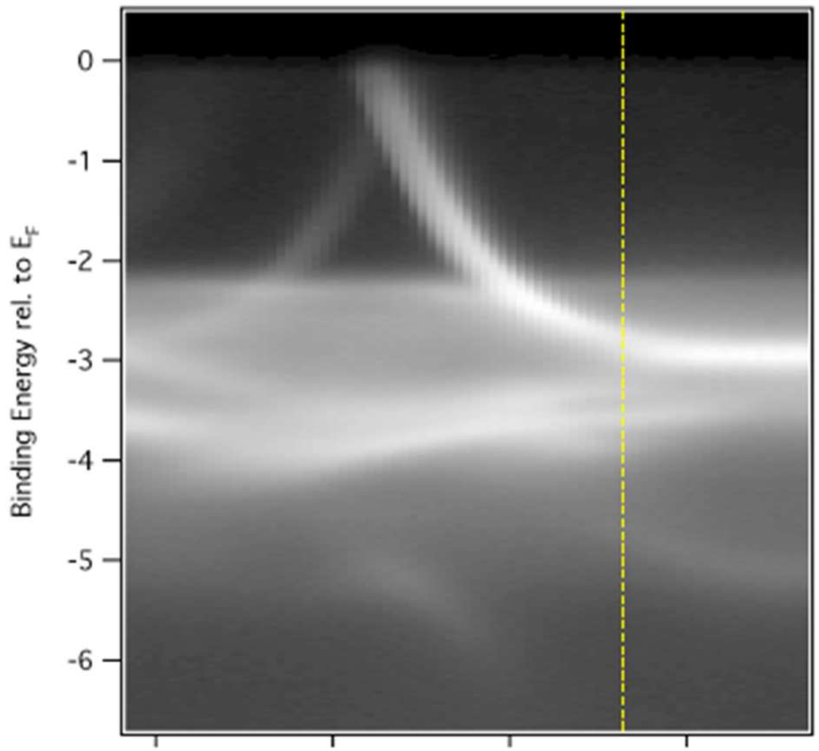


Typical experimental result

Copper



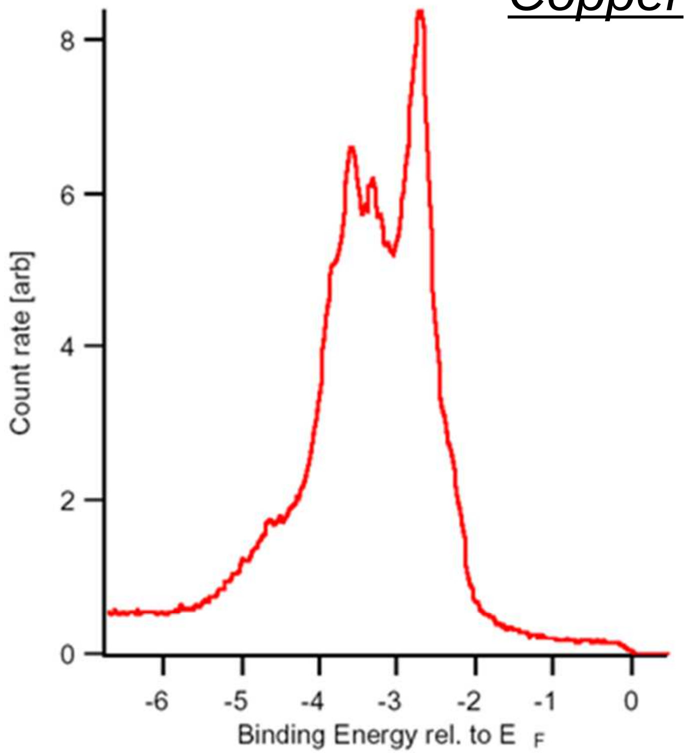
A spectrum at a single momentum k_x



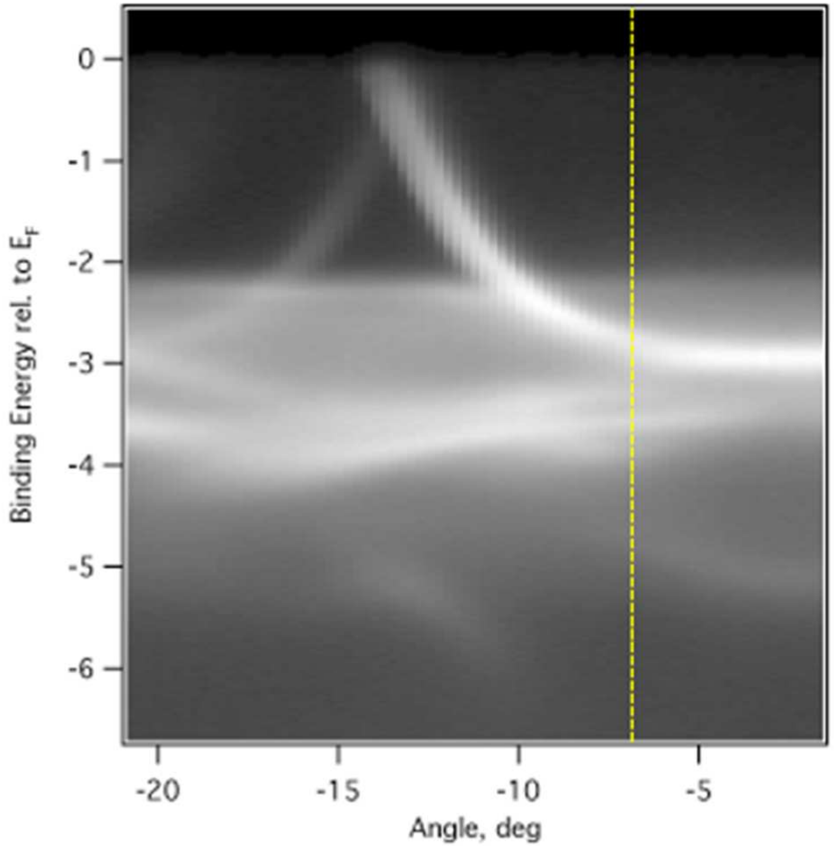
Accumulate spectra as the momentum k_x is scanned

Typical experimental result

Copper

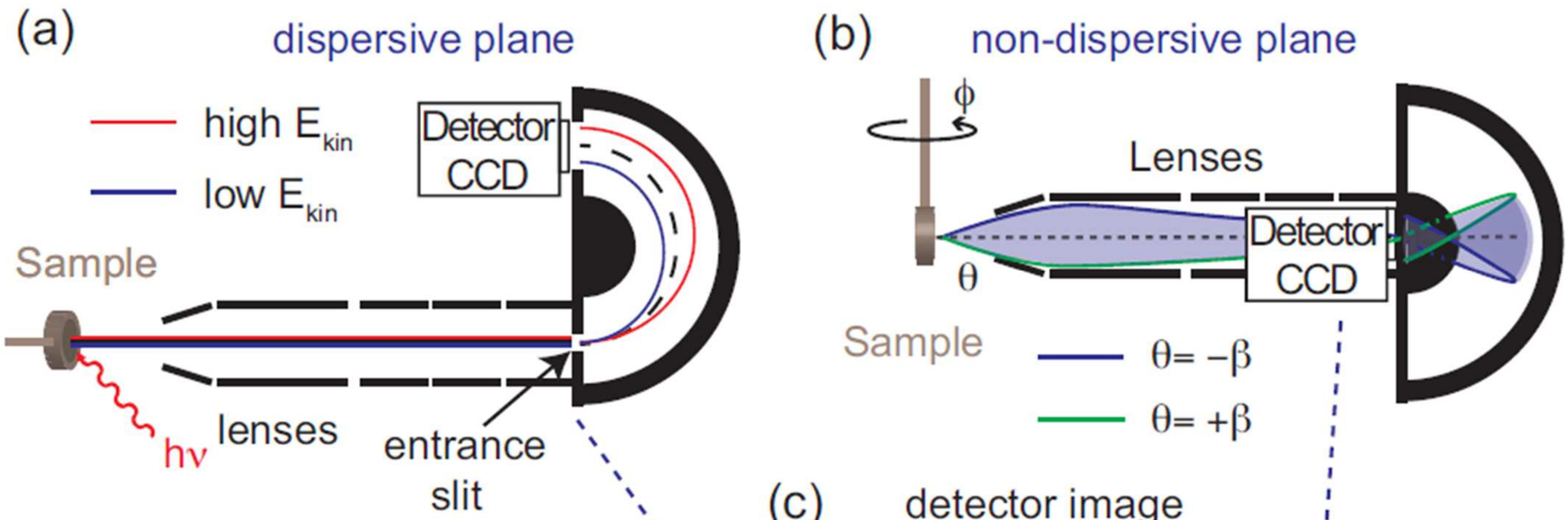


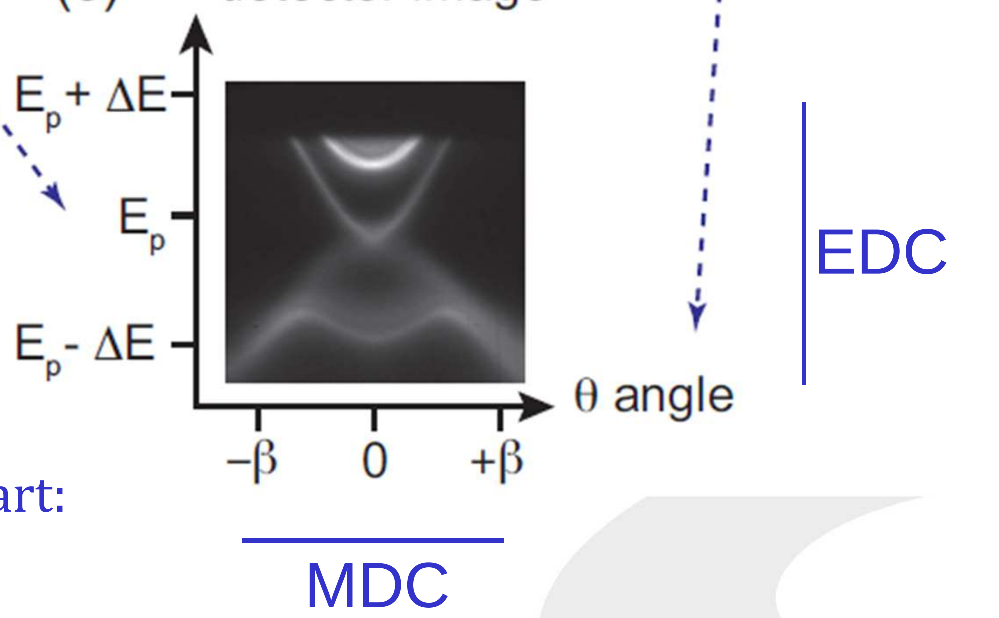
A spectrum at a single polar angle



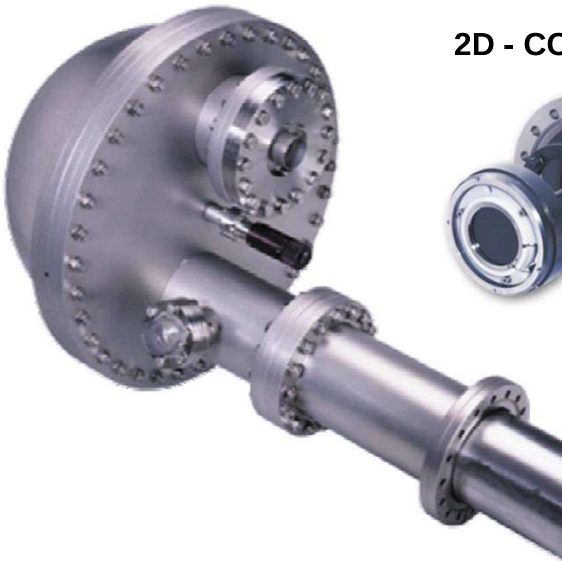
Accumulate spectra as the angle is scanned

3rd generation hemispherical detector





hemispherical energy analyzer



2D - CCD Imaging detector

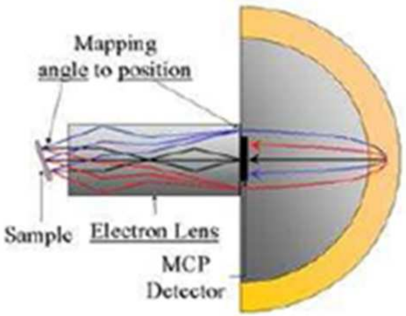
State of the art:

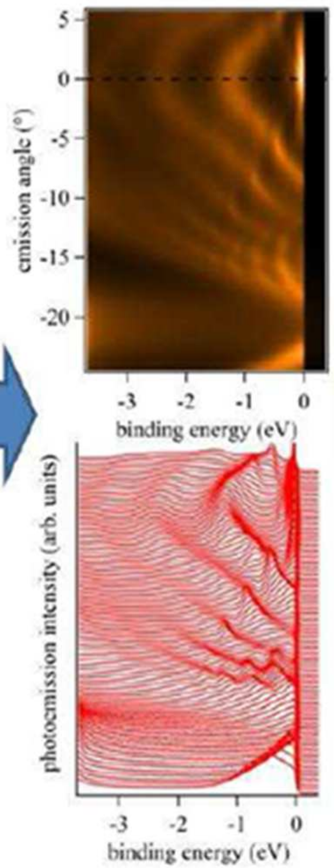
$\Delta E \leq 1$ meV

$\Delta\alpha \leq 0.1°$

Higher dimensional data set

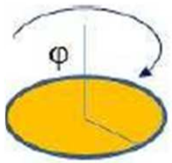
A second angle/momentum coordinate can be scanned to build up a volume data set

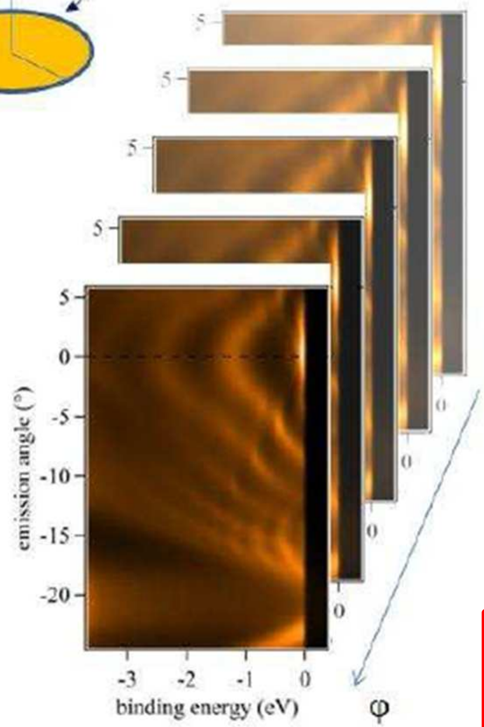




Single photoemission map (~700 spectra) for a fixed φ

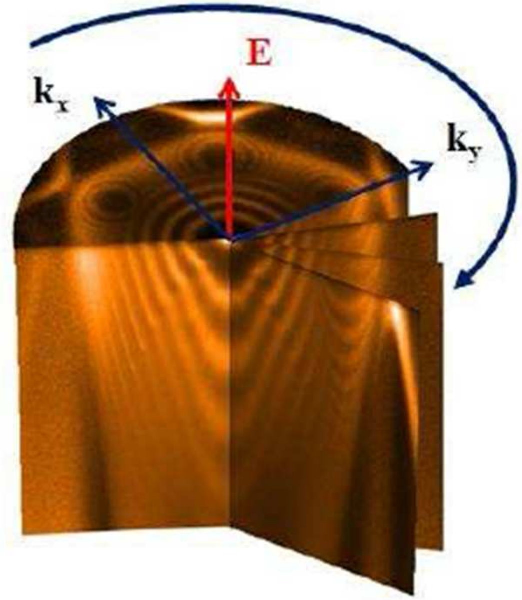
Azimuthal angle





Set of maps for different φ

Building a full (E, $\mathbf{k}_{||}$) set of PES data



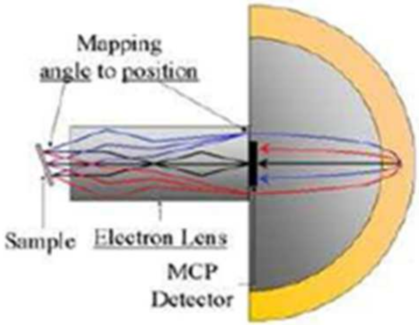
Conversion to 2D k-space of each single map in function of θ and φ

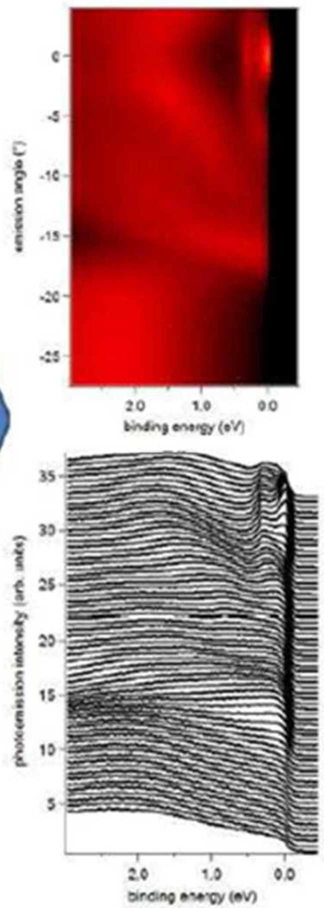
$$k_x = 0.512\sqrt{E_{kin}}\, sin\theta cos\varphi$$

$$k_y = 0.512\sqrt{E_{kin}}\, sin\theta sin\varphi$$

Higher dimensional data set

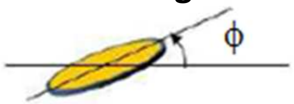
A second angle/momentum coordinate can be scanned to build up a volume data set

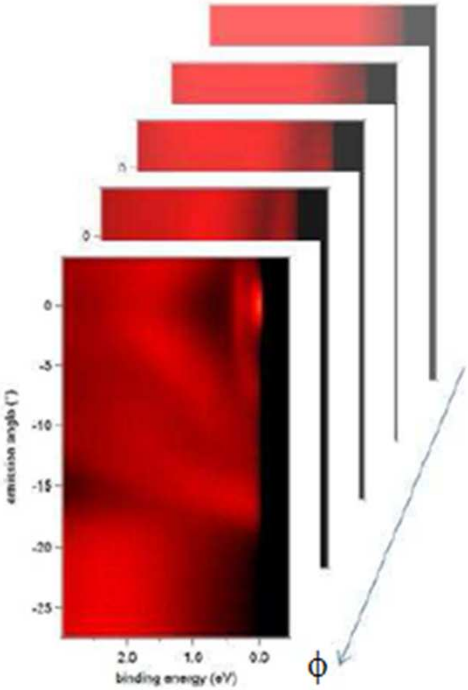




Single photoemission map (~700 spectra) for a fixed ϕ

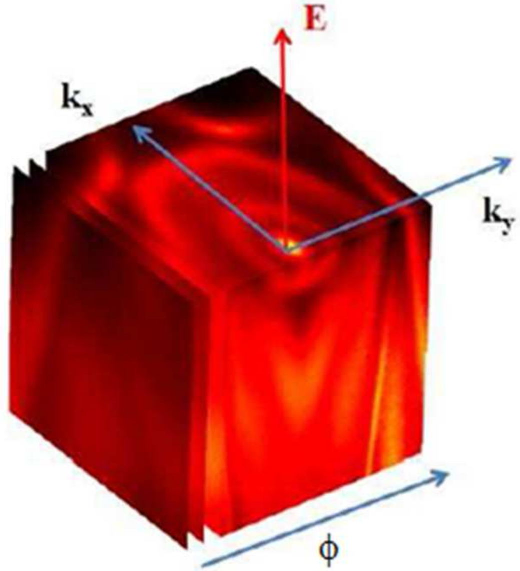
Tilt angle





Set of maps for different ϕ

Building a full (E, $\mathbf{k}_{||}$) set of PES data



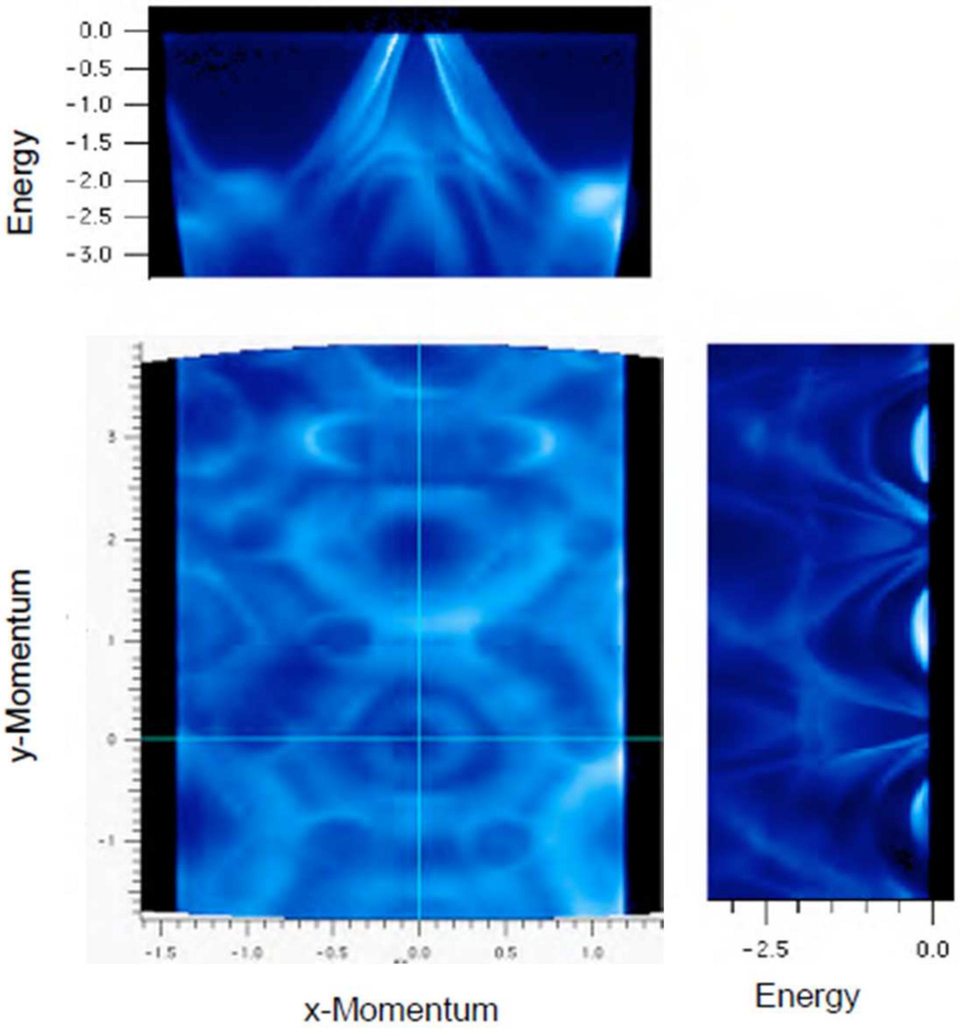
Conversion to 2D k-space of each single map in function of θ and ϕ

$$k_x = 0.512\sqrt{E_{kin}}\, sin\phi$$

$$k_y = 0.512\sqrt{E_{kin}}\, sin\theta$$

Higher dimensional data set

$TiTe_2$



A second momentum coordinate can be scanned to build up a volume data set

3 orthogonal slices
of a volume data set

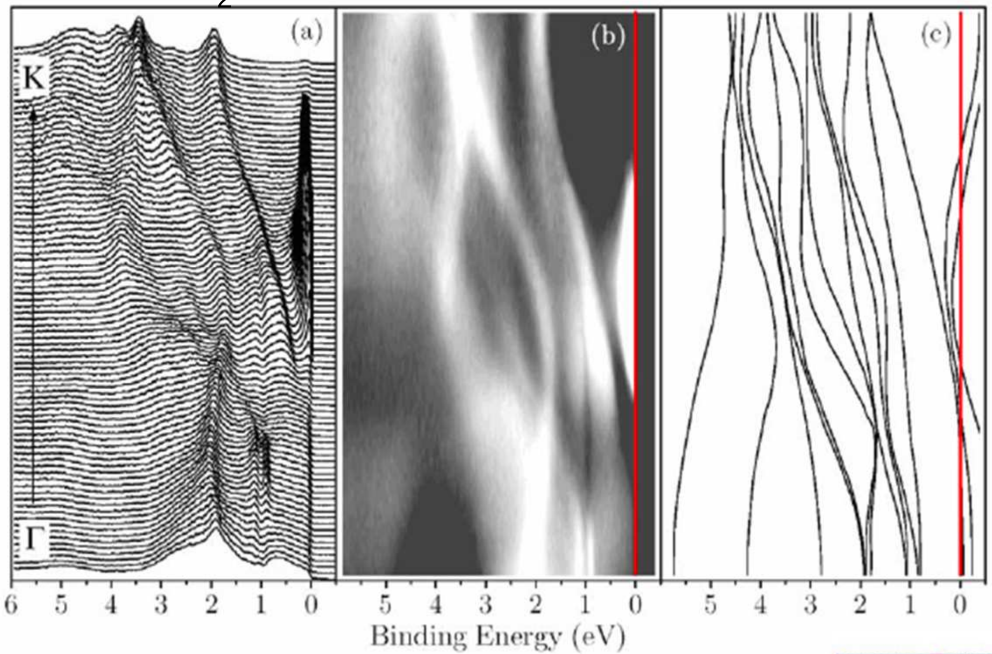
Energy / x-Momentum / y-Momentum

16 minutes total data acquisition time

Courtesy of K. Rossnagel

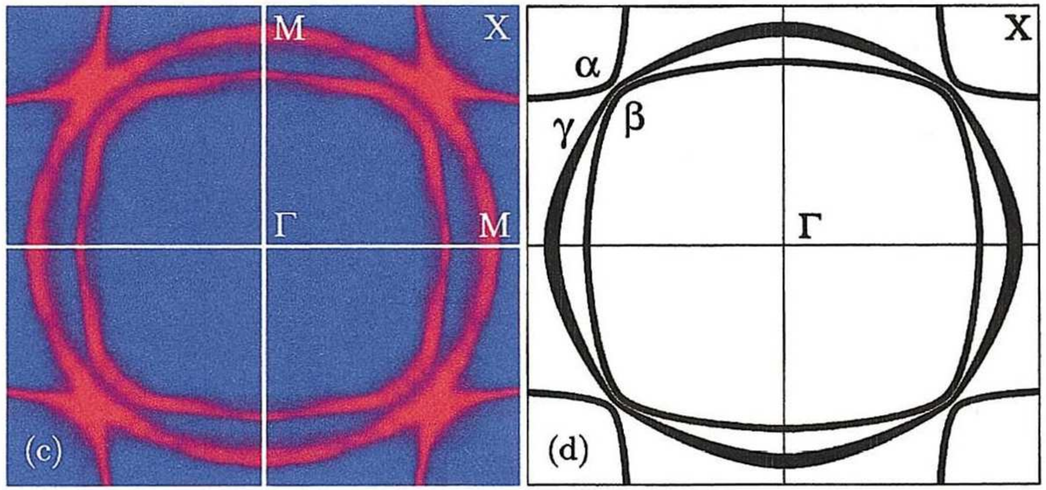
Comparison with theoretical predictions

NbSe$_2$ Damascelli *et al.* (2000)



Band dispersion

Fermi surface



Sr_2RuO_4 cleaved at 180 K
T= 10 K hν=28 eV

Local-density-approximation
band-structure calculation

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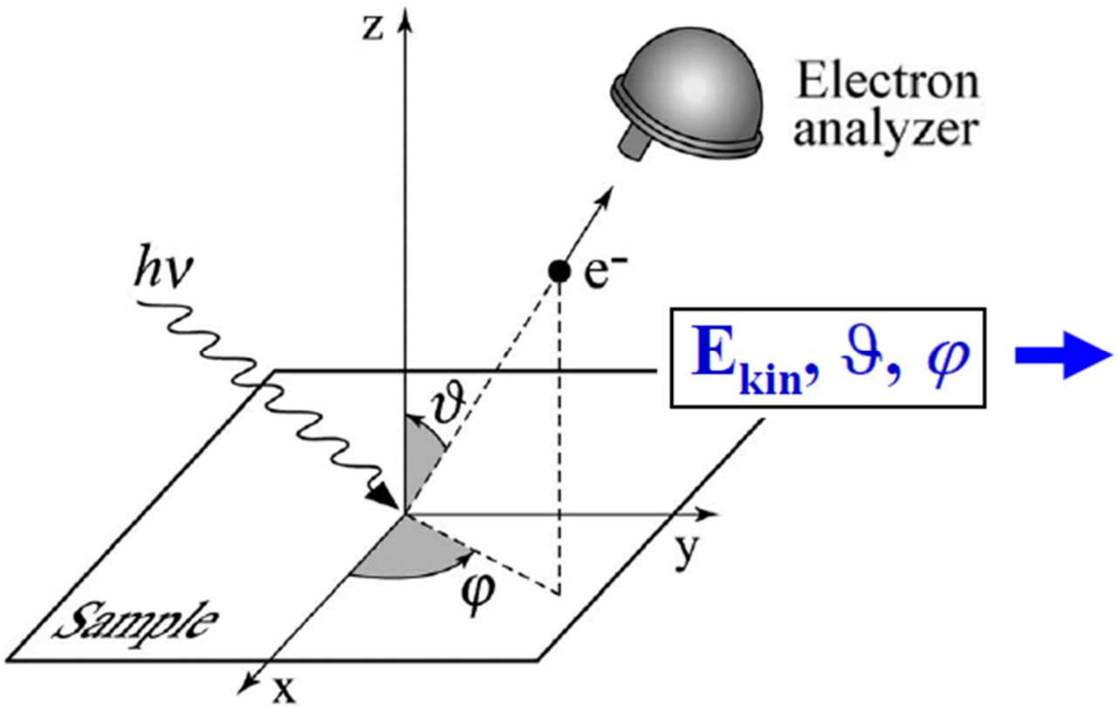
Angle-Resolved Photoemission Spectroscopy (ARPES)



$$\mathbf{K} = \mathbf{p}/\hbar = \sqrt{2m E_{kin}}/\hbar$$

$$K_x = \frac{1}{\hbar}\sqrt{2mE_{kin}}\sin\vartheta\cos\varphi$$

$$K_y = \frac{1}{\hbar}\sqrt{2mE_{kin}}\sin\vartheta\sin\varphi$$

$$K_z = \frac{1}{\hbar}\sqrt{2mE_{kin}}\cos\vartheta$$

Vacuum

E_{kin}

$\mathbf{K}$

Conservation laws

$$E_f^N - E_i^N = h\nu$$

$$\mathbf{k}_f^N - \mathbf{k}_i^N = \cancel{\mathbf{k}_{h\nu}}$$

Solid

E_B

$\mathbf{k}$

Theory of Photoemission

The calculation of the photocurrent starts from *first order time-dependent perturbation theory*. Assuming a small perturbation, the *transition probability per unit time w* for an optical excitation between two N-electron states, *i* and *f*, of the same Hamiltonian H is given by *Fermi's golden rule*:

Photoemission Intensity ***I(k,ω)*** $$w_{fi} \propto |\langle \Psi_f^N | H_{\text{int}} | \Psi_i^N \rangle|^2 \delta(E_f^N - E_i^N - h\nu)$$

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

Sudden approximation
The ejected electron is fast enough to neglect its interaction with the *N-1*-electron system left behind

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

One Slater determinant
Hartree-Fock formalism

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

Photoemission Intensity ***I(k,ω)*** $$w_{fi} \propto |\langle \phi_f^{\mathbf{k}} | \mathbf{A} \cdot \mathbf{p} | \phi_i^{\mathbf{k}} \rangle \langle \Psi_m^{N-1} | \Psi_i^{N-1} \rangle|^2 \delta(\omega - h\nu)$$

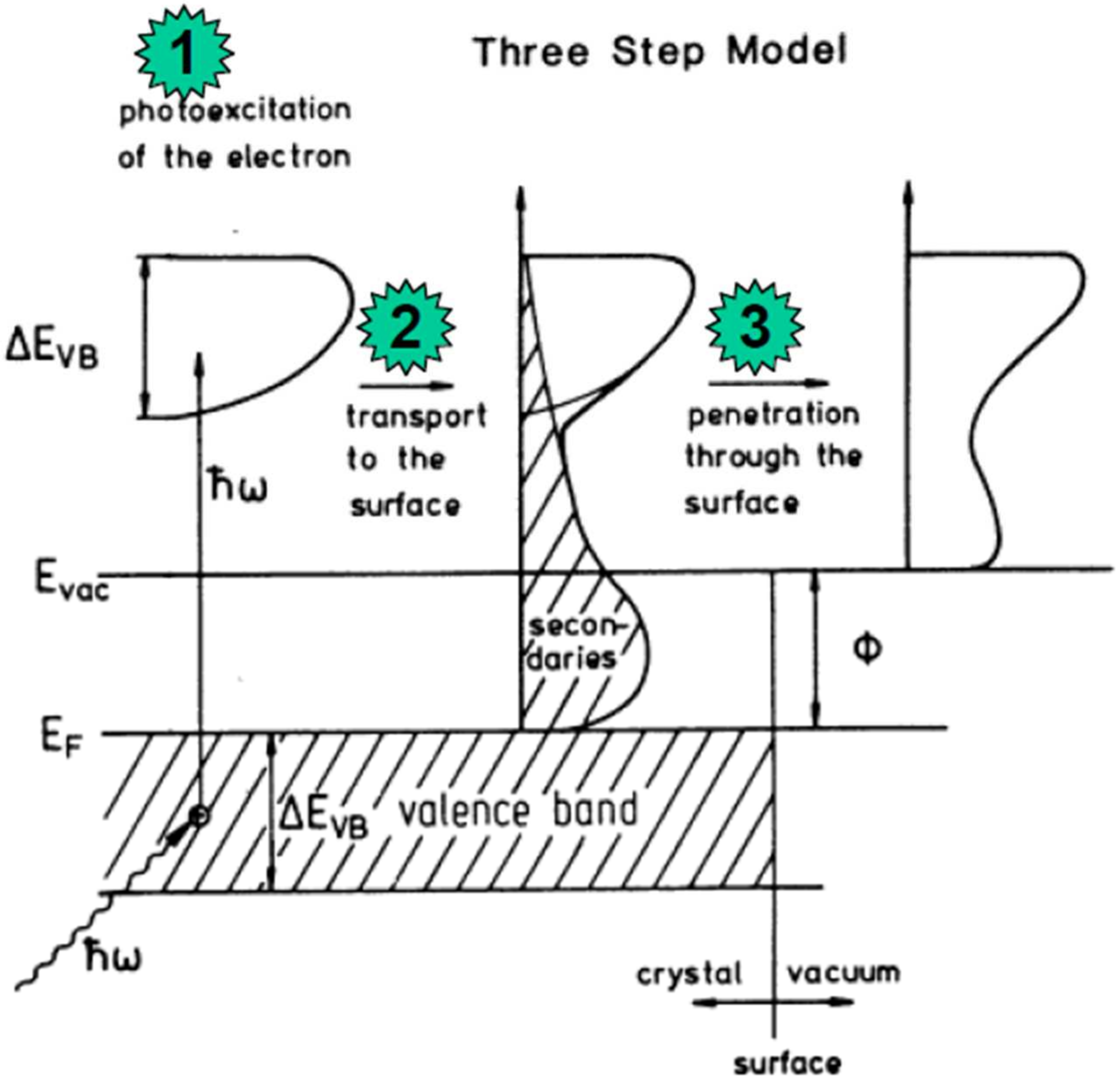
1

Frozen-orbital approximation

$$E_f^N = E_f^{N-1} + E_{kin}$$

$$\omega = E_{kin} + E_m^{N-1} - E_i^N \equiv E_{kin} - |E_B^{vac}|$$

Three-Step Model

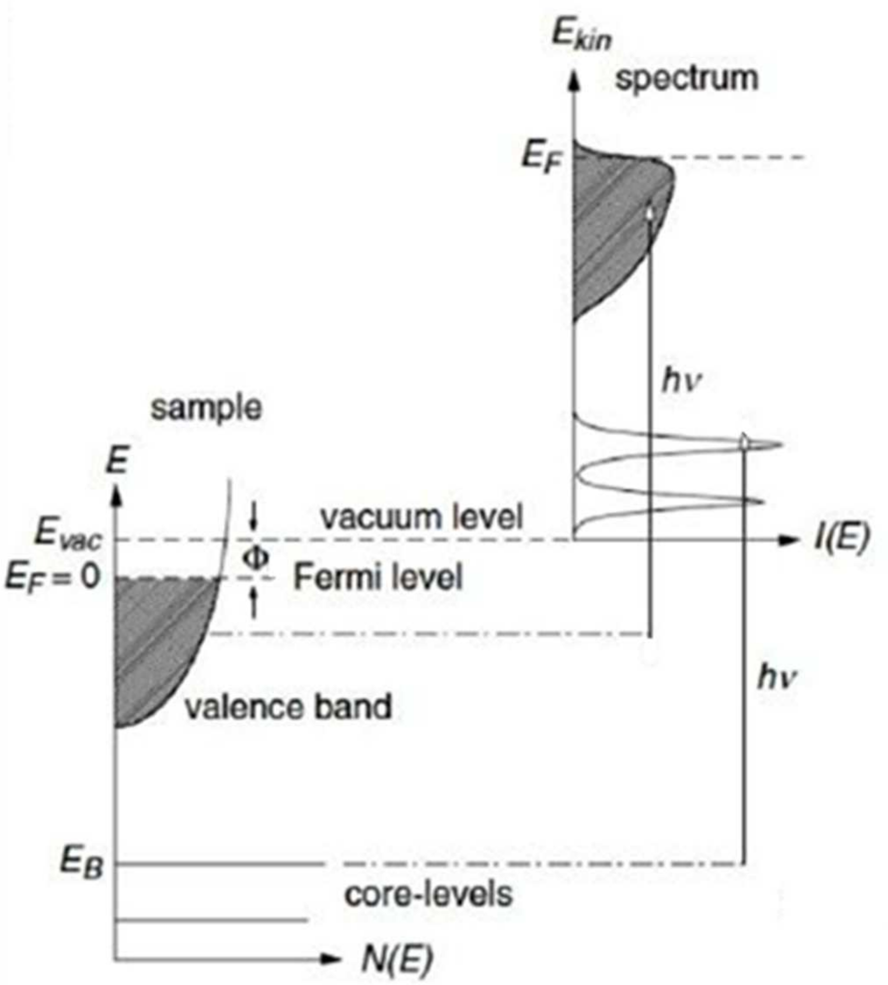


$$I(\boldsymbol{k},\omega) = I_p(\boldsymbol{k},\omega) + I_s(\boldsymbol{k},\omega)$$

Step 1: Energy conservation

1

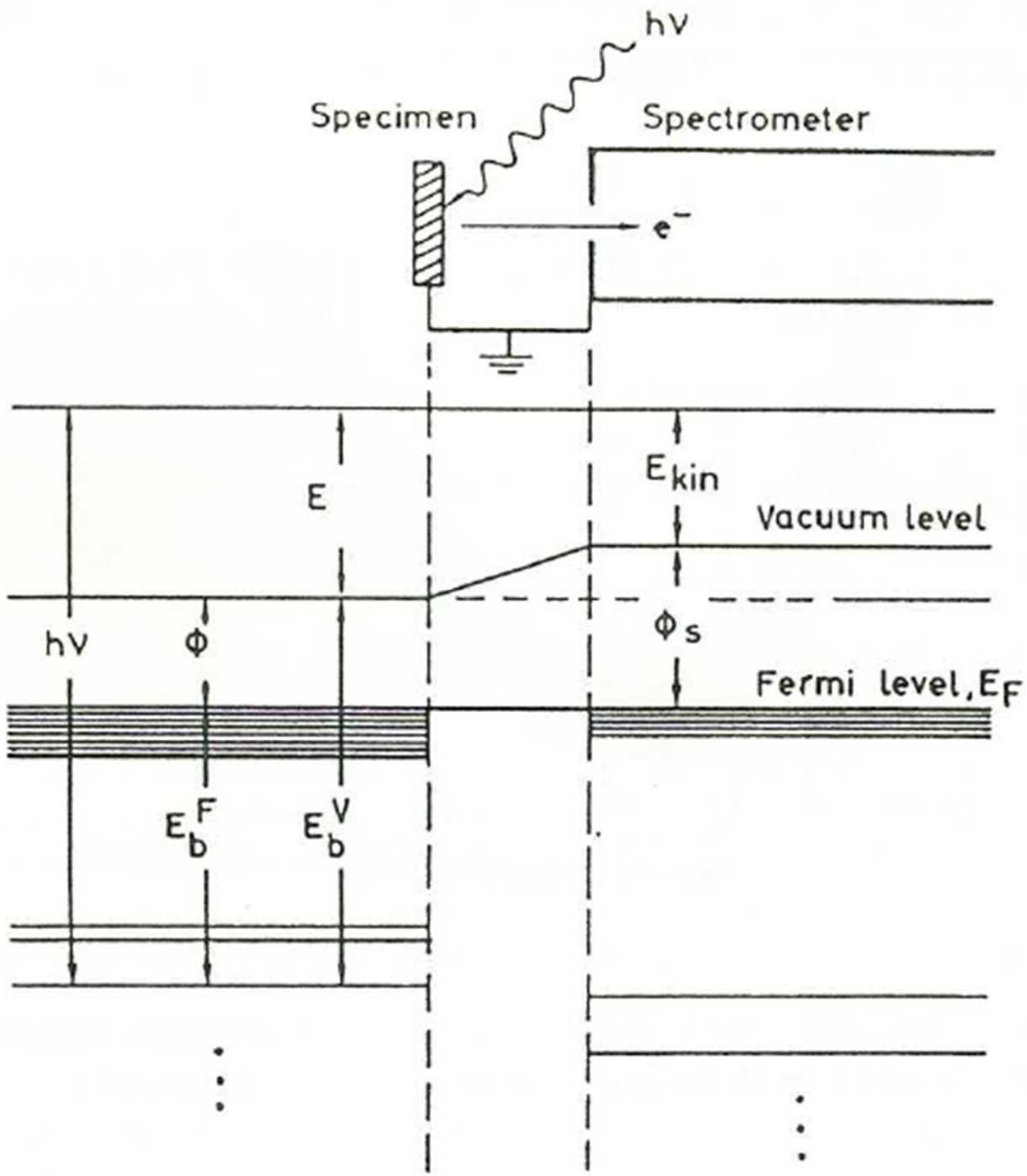
Photoexcitation process



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

- E_{kin}: Measured Kinetic Energy
- $h\nu$: Measured Photon Energy
- Φ: Measured Work Function
- E_B: Electron Binding Energy

Absolute energy scale in PES experiment



In PES experiment, it is not necessary to know Φ as E_{kin} is measured with respect to the Vacuum level of the spectrometer.
If sample and analyzer are in good electric contact, the Fermi levels are aligned and

$$E_{kin} = h\nu - \Phi_s - |E_B|$$

For electrons at E_F (i.e., E_B=0):

$$E_{kin}^{max} = h\nu - \Phi_s$$ **for all samples**

$\rightarrow$ $$|E_B| = E_{kin}^{max} - E_{kin}$$

Step 1: Momentum conservation

1

Photoexcitation process

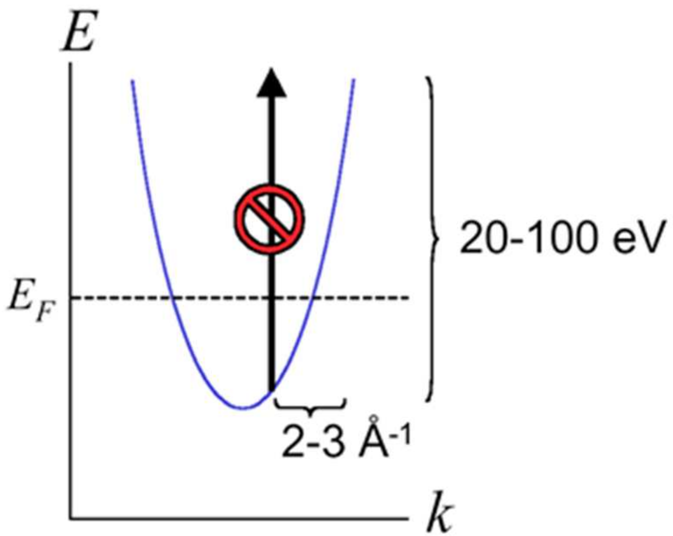
Photon Momentum $p = \hbar q = h / \lambda$

Photon Energy $E = h\nu = hc / \lambda$

Typical photon wavenumber

$$q = 2\pi \frac{E}{hc} = 2\pi \frac{E\,[\mathrm{eV}]}{12400\,[\mathrm{eV}\text{ - }\text{Å}]}$$

$$= .01 \text{ to } .05\ \text{Å}^{-1} \quad (\text{for } E = 20 \text{ to } 100 \text{ eV})$$

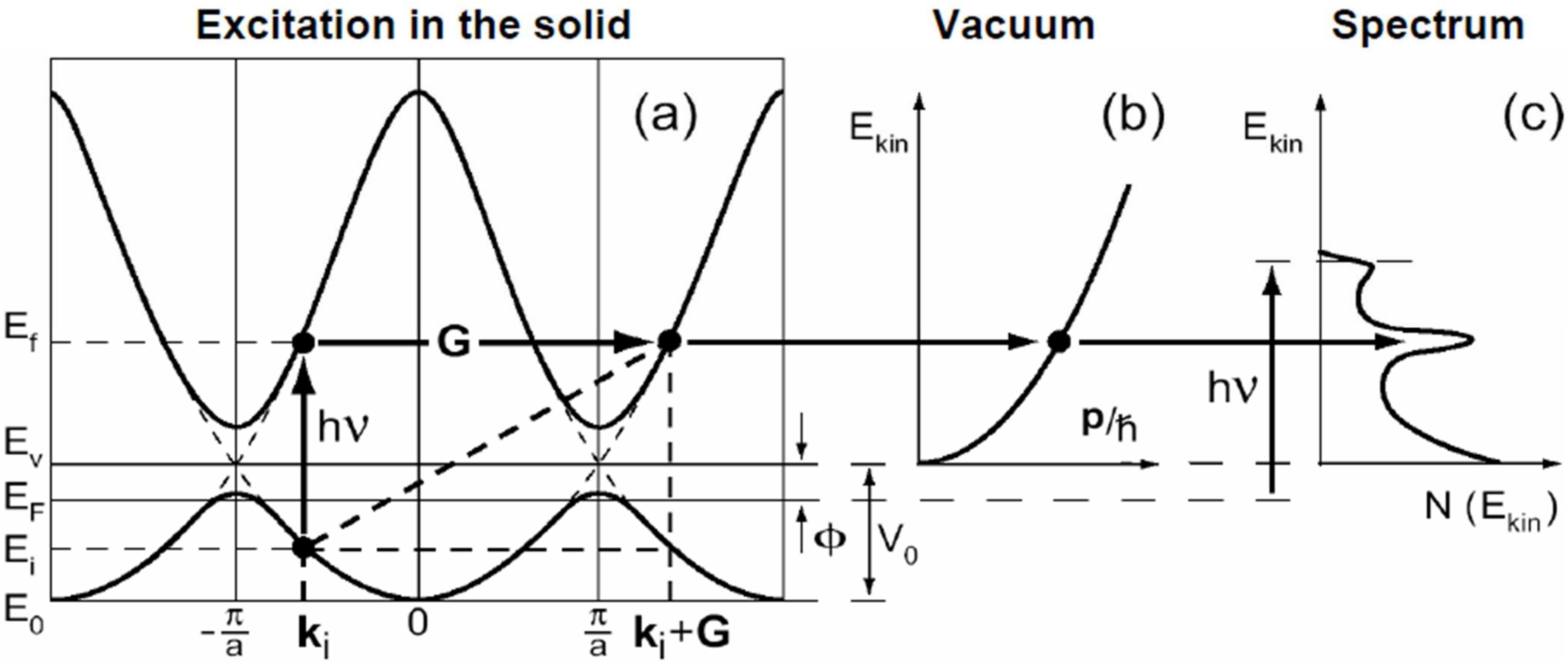


- **The photons impart very little momentum in the photoemission process, i.e. vertical transitions**
- **Therefore photon-stimulated transitions are not allowed for free electrons (energy and momentum conservation laws cannot be satisfied at the same time).**

Step 1: Momentum conservation

In order to satisfy both energy and momentum conservation:

The role of crystal translational symmetry is crucial

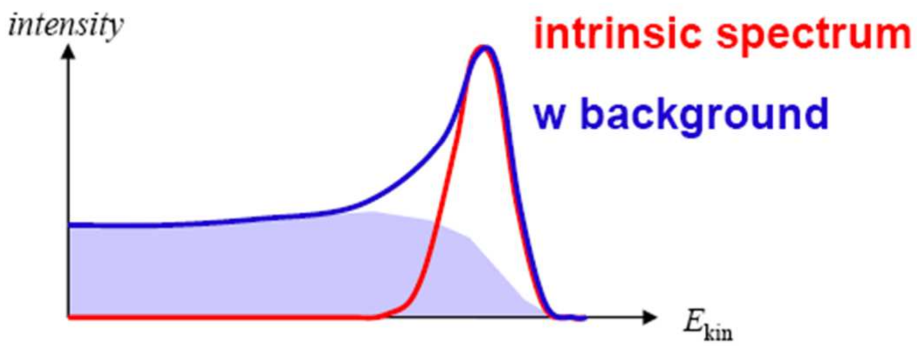


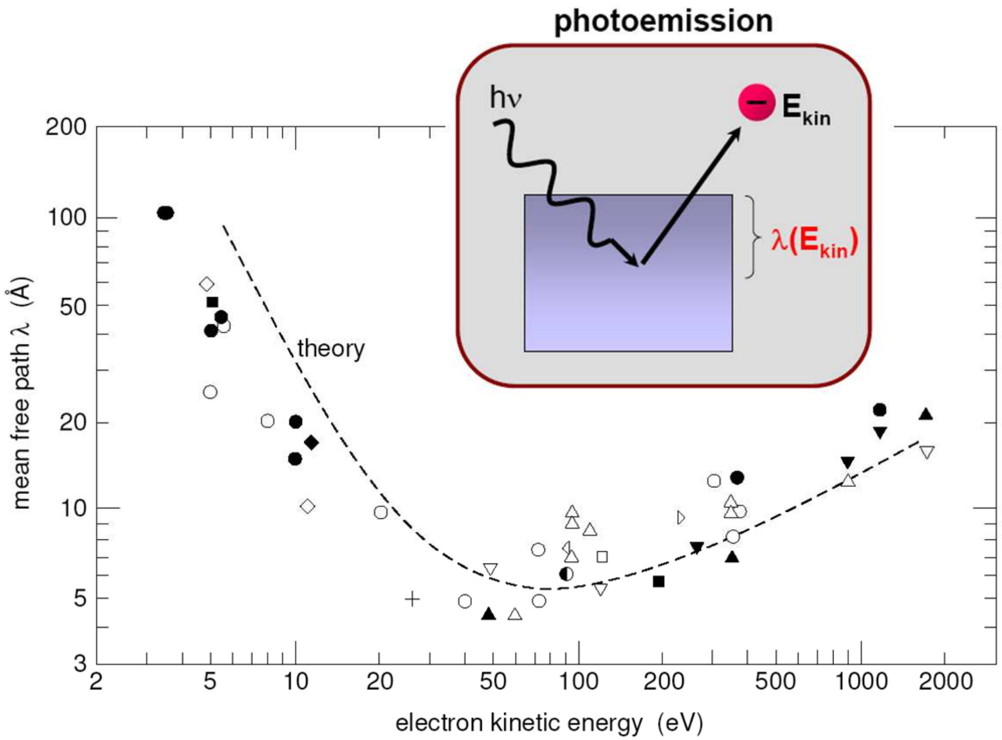
Photoemission Intensity $I(k,\omega)$ $\Big\}$ $w_{fi} \propto |\langle\phi_f^{\mathbf{k}}|\underline{\mathbf{A}\cdot\nabla V}|\phi_i^{\mathbf{k}}\rangle\langle\Psi_m^{N-1}|\Psi_i^{N-1}\rangle|^2\delta(\omega-h\nu)$

Step 2: Transport to the surface

Inelastic scattering by electron-electron interaction, electron-phonon etc. leads to a loss of electrons reaching the surface

- **Valence band measurements are sensitive to only within the first few atomic layers of the material**
- **Spectral peaks have a “loss tail” towards lower kinetic energies**

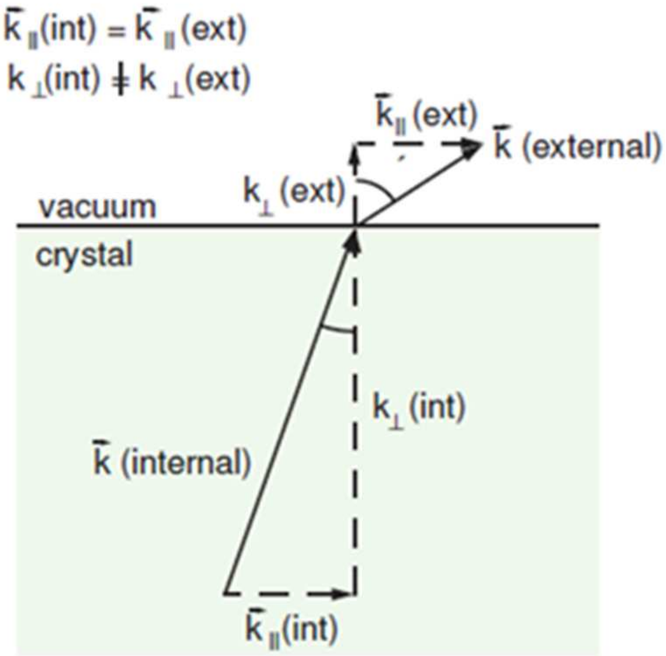




2 Transport to the surface

Step 3: Transmission through the surface

The transmission through the sample surface is obtained by matching the bulk Bloch eigenstates inside the sample to free-electron plane waves in vacuum.

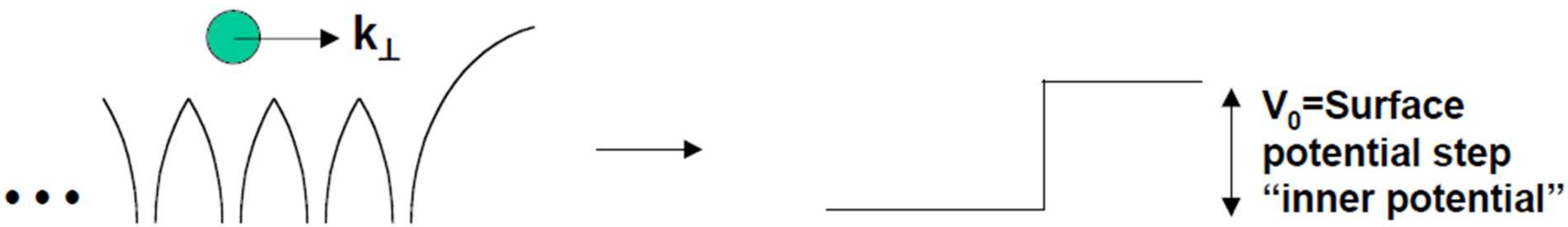


At the surface the crystal translational symmetry is conserved in the (x,y) plane but is broken perpendicularly to the surface: the component of the electron crystal momentum parallel to the surface plane **$k_{\parallel}$** is **conserved**, but **$k_{\perp}$** is **not**

$$|\mathbf{k}_{\parallel}| = |\mathbf{K}_{\parallel}| = \frac{1}{\hbar}\sqrt{2mE_{kin}}\, sin\vartheta$$

$$k_{\perp} \neq K_{\perp} = \frac{1}{\hbar}\sqrt{2mE_{kin}}\, cos\vartheta$$

The potential barrier at the surface slows the electron in the direction normal to the surface.

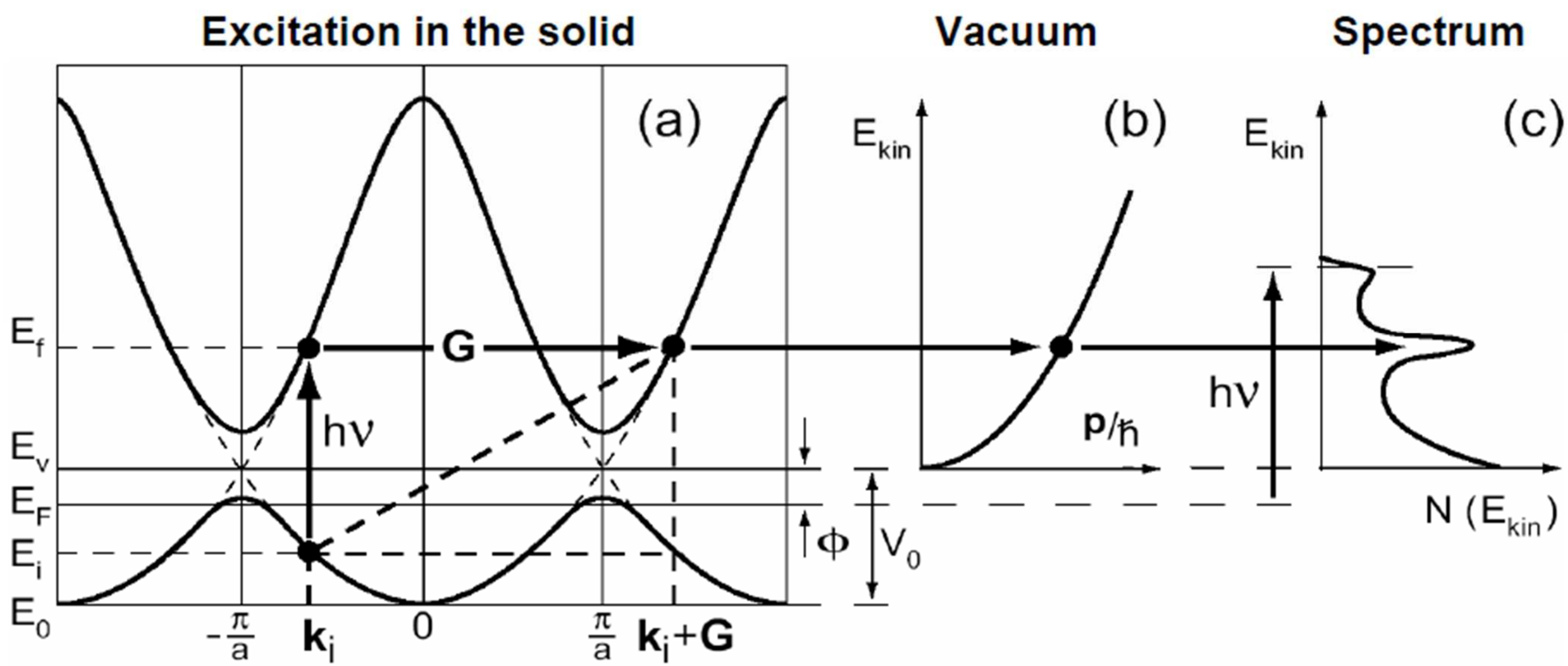


Step 3: Inner potential V_0 and determination of $k_\perp$

Free-electron final state model $$E_f(\mathbf{k}) = \frac{\hbar^2\mathbf{k}^2}{2m} - |E_0| = \frac{\hbar^2({\mathbf{k}_\parallel}^2 + {\mathbf{k}_\perp}^2)}{2m} - |E_0|$$

because $\hbar^2\mathbf{k}_\parallel^2/2m = E_{kin}\sin^2\vartheta$ $\quad E_f = E_{kin} + \phi$ $\quad V_0 = |E_0| + \phi$

$$\mathbf{k}_\perp = \frac{1}{\hbar}\sqrt{2m(E_{kin}\cos^2\vartheta + V_0)}$$



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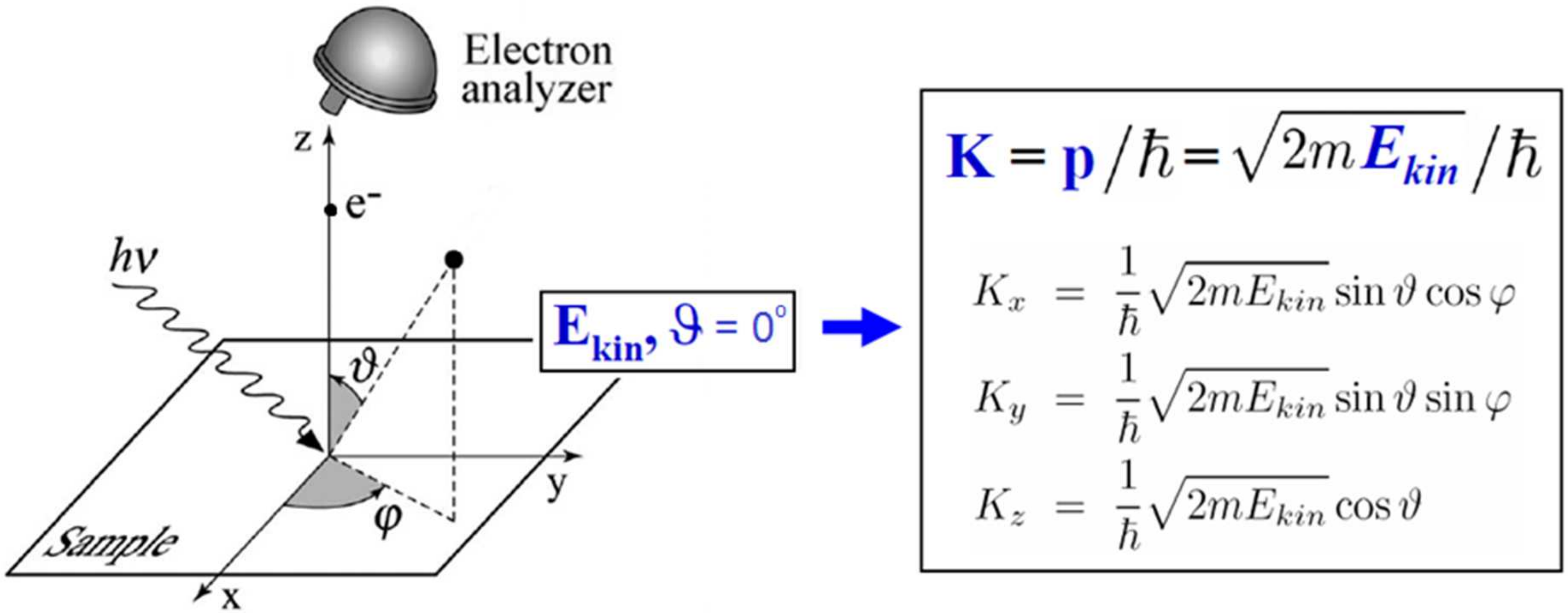
Experimental determination of V_0

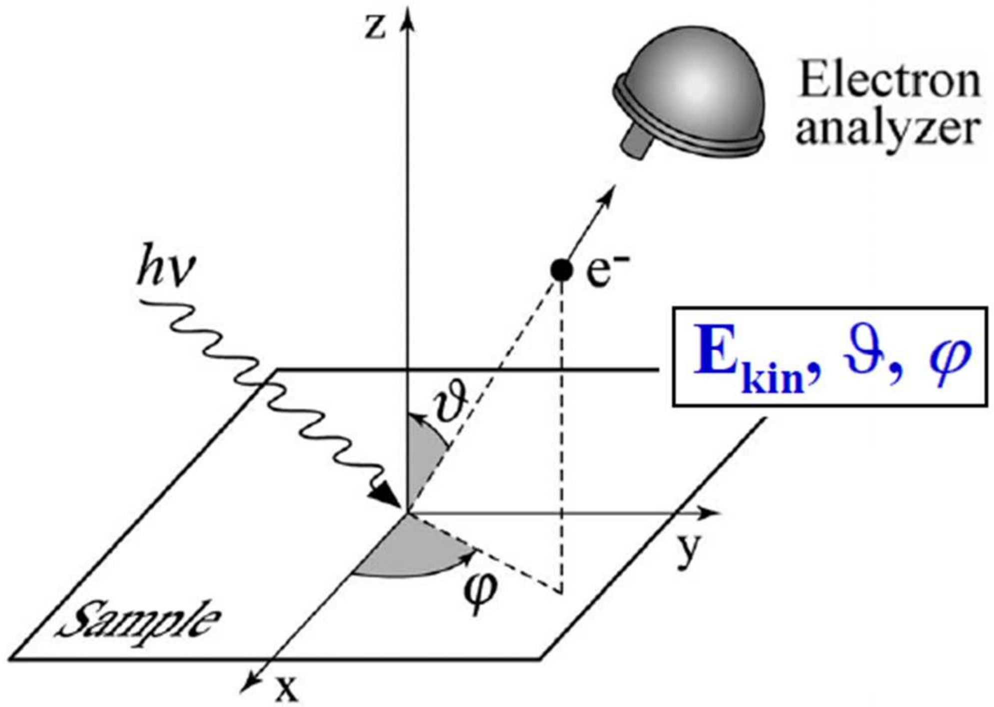
- We don't normally have a priori knowledge of V_0.
- Methods to determine V_0:
  - (i) optimize the agreement between theoretical and experimental band mapping for the occupied electronic state;
  - (ii) infer $\mathbf{V_0}$ from the experimentally observed periodicity of the dispersion $\boldsymbol{E(k_\perp)}$ doing experiment at $\boldsymbol{\vartheta=0°}$ (i.e., $\mathbf{k_{||}}$ = 0) while **varing $h\nu$** (i.e., E_{kin} and K_z).



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

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

ARPES basic equations:
Energetics and kinematics



$$\mathbf{K} = \mathbf{p}/\hbar = \sqrt{2mE_{kin}}/\hbar$$

$$K_x = \frac{1}{\hbar}\sqrt{2mE_{kin}}\sin\vartheta\cos\varphi$$

$$K_y = \frac{1}{\hbar}\sqrt{2mE_{kin}}\sin\vartheta\sin\varphi$$

$$K_z = \frac{1}{\hbar}\sqrt{2mE_{kin}}\cos\vartheta$$

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

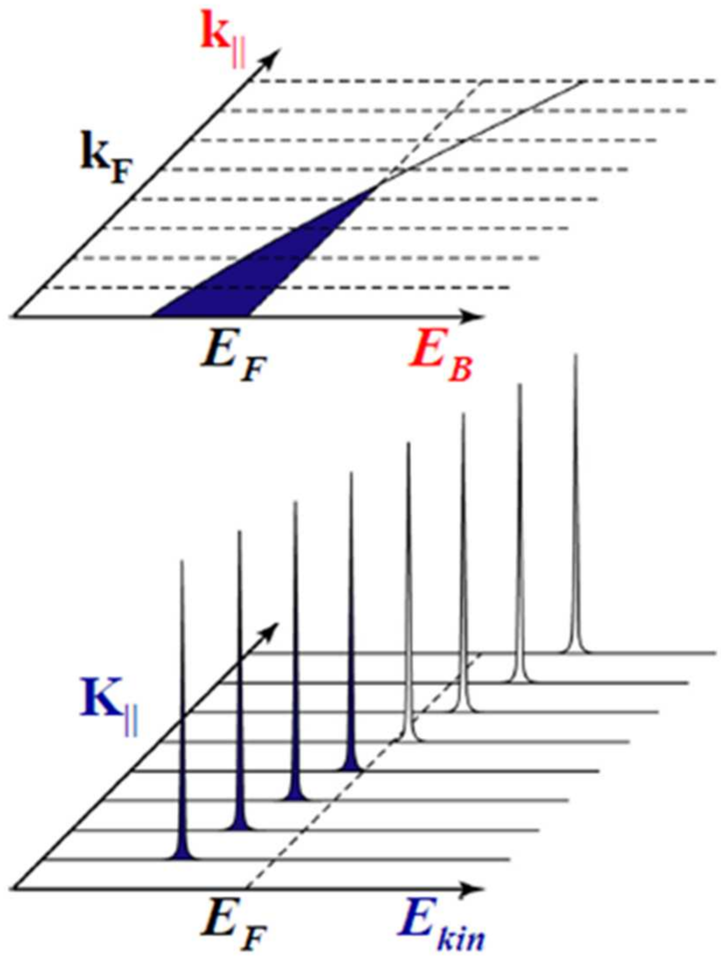
$$k_\perp = \frac{1}{\hbar}\sqrt{2m(E_{kin}cos^2\vartheta + V_0)}$$

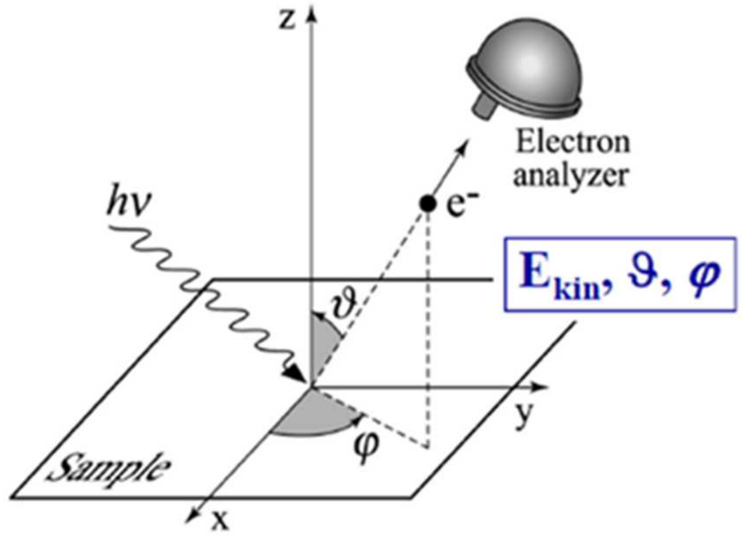
$$|\mathbf{k}_{||}| = |\mathbf{K}_{||}| = \frac{1}{\hbar}\sqrt{2mE_{kin}}\, sin\vartheta \rightarrow k_{||}[\dot{A}^{-1}] = 0.512\sqrt{E_{kin}[eV]}\, sin\vartheta$$

For **2D** or **1D systems** and **Surface States** the **occupied Band Structure $E_B(k_{||})$** is completely determined.

The periodicity of $\boldsymbol{E_B(k_\perp)}$ is determined **varying $h\nu$** at normal emission $\boldsymbol{\vartheta = 0°}$.

ARPES: Non-interacting particle picture





Energy Conservation

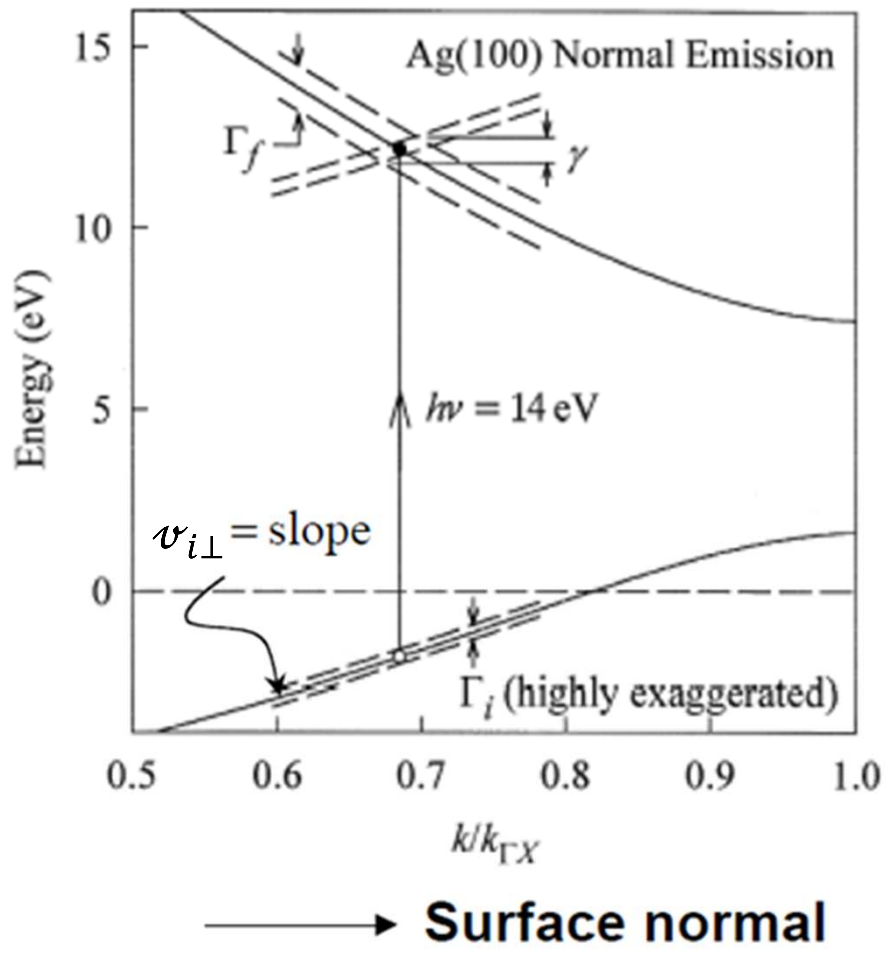
$$E_{kin} = h\nu - \phi - |E_B|$$

Momentum Conservation

$$\hbar \mathbf{k}_{||} = \hbar \mathbf{K}_{||} = \sqrt{2mE_{kin}} \cdot \sin\vartheta$$

The ARPES spectrum consists of a *spike* (δ-function) at E_{kin} , $K_{||}$

Bulk state linewidths and inverse lifetime



- **The total ARPES linewidth has contributions from both initial and final bands**

$$\gamma = \frac{\dfrac{\Gamma_i}{|v_{i\perp}|} + \dfrac{\Gamma_f}{|v_{f\perp}|}}{\left|\dfrac{1}{v_{i\perp}} - \dfrac{1}{v_{f\perp}}\right|}$$

Γ_i = 1 / hole-lifetime in the initial band of photoexcitation, (~meV)

Γ_f = 1 / electron-lifetime in the final band of photoexcitation, (~eV)

Chiang *et al,*, Chem. Phys. 251, 133 (2000)

Implication for surface states

- **Bulk bands may satisfy**

$$v_{i\perp} = v_{f\perp} \;\rightarrow\; \gamma \rightarrow \infty$$

implying artificially large linewidths (''geometrical'' broadening)

- **Surface states bands do not disperse along $k_{\perp}$, i.e.**

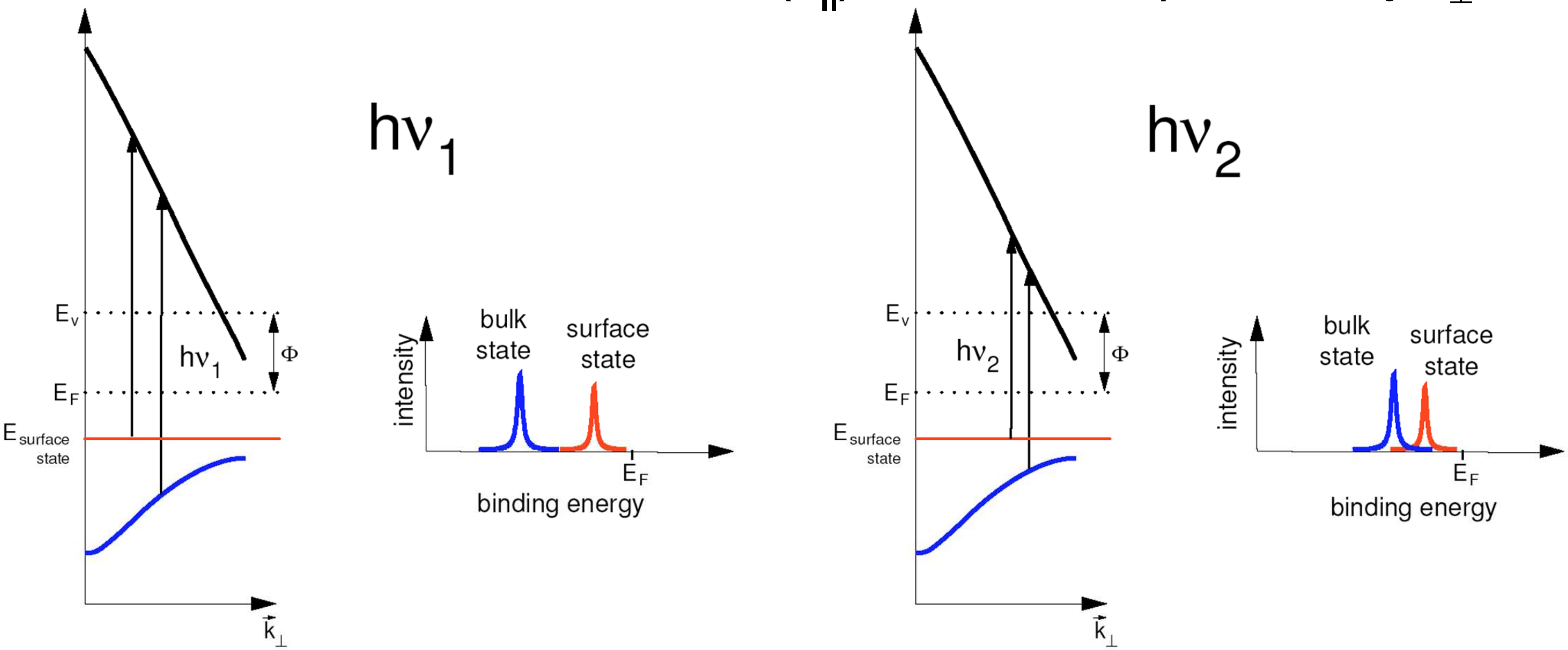
$$v_{i\perp} = 0 \;\rightarrow\; \gamma \rightarrow \Gamma_i$$

So there is no ''geometrical'' broadening for surface states,

2D and 1D states ...

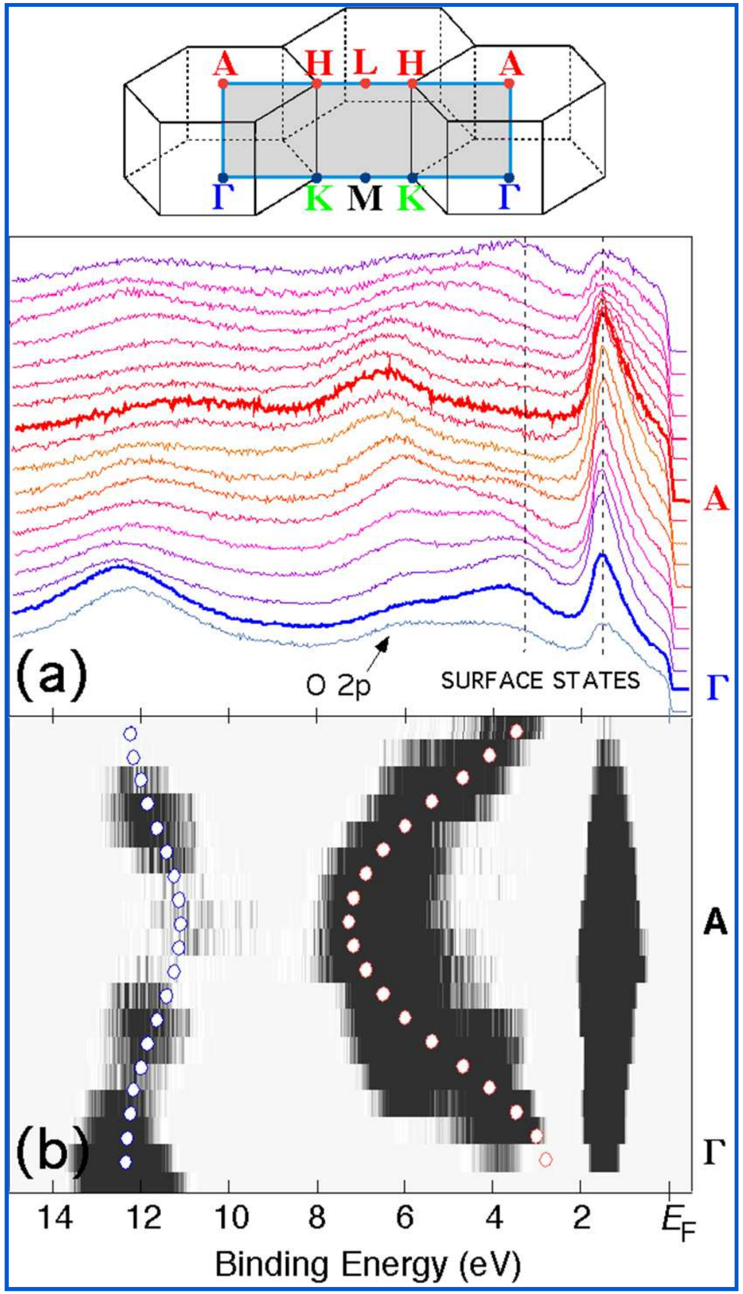
Bulk states vs Surface states

- Bulk state: $E(\mathbf{k}_{||}, k_{\perp})$
- Surface state: $E(\mathbf{k}_{||})$ i.e., independent by $k_{\perp}$



Easiest way: fix $\mathbf{k}_{||} = 0$ (Γ , normal emission $\theta = 0°$) and change $h\nu$ (easy at synchrotron)

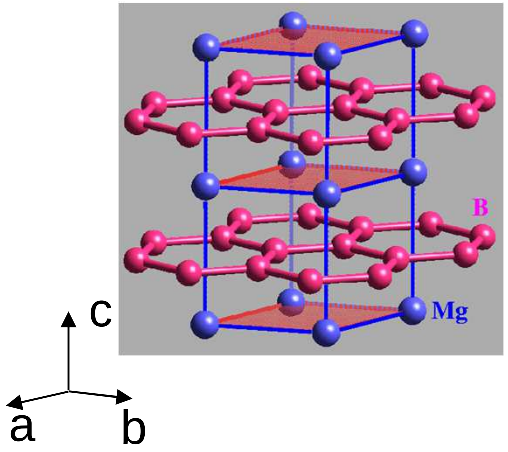
Surface vs Bulk states



$k_\perp$ dispersion along ΓA direction

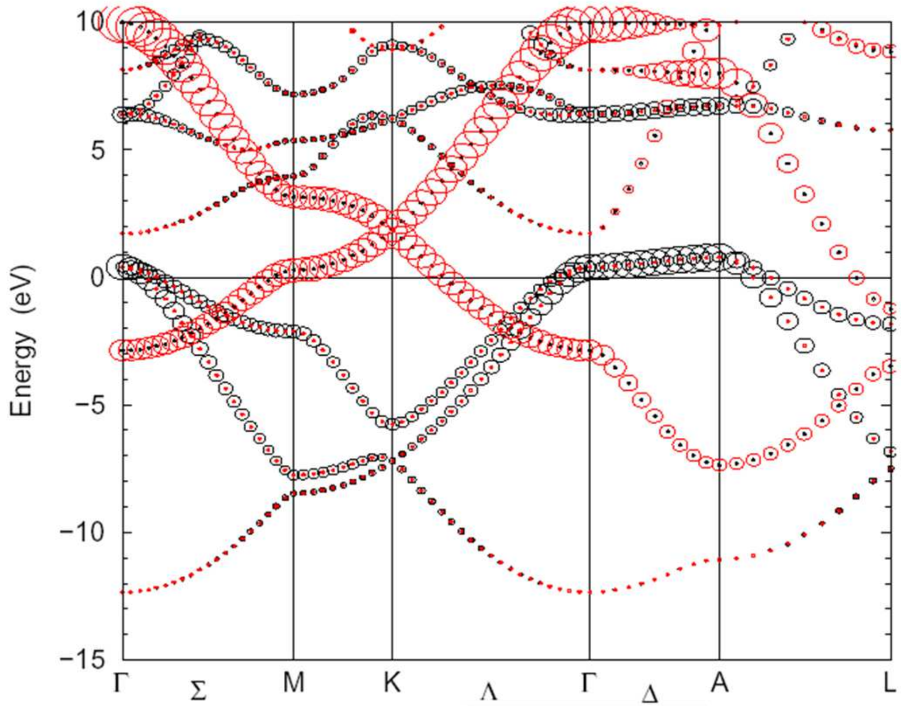
Normal emission geometry θ=0°

***hν* = 95-185eV**



No dispersive peak at 1.65 eV:
Mg terminated MgB_2(0001)
surface state

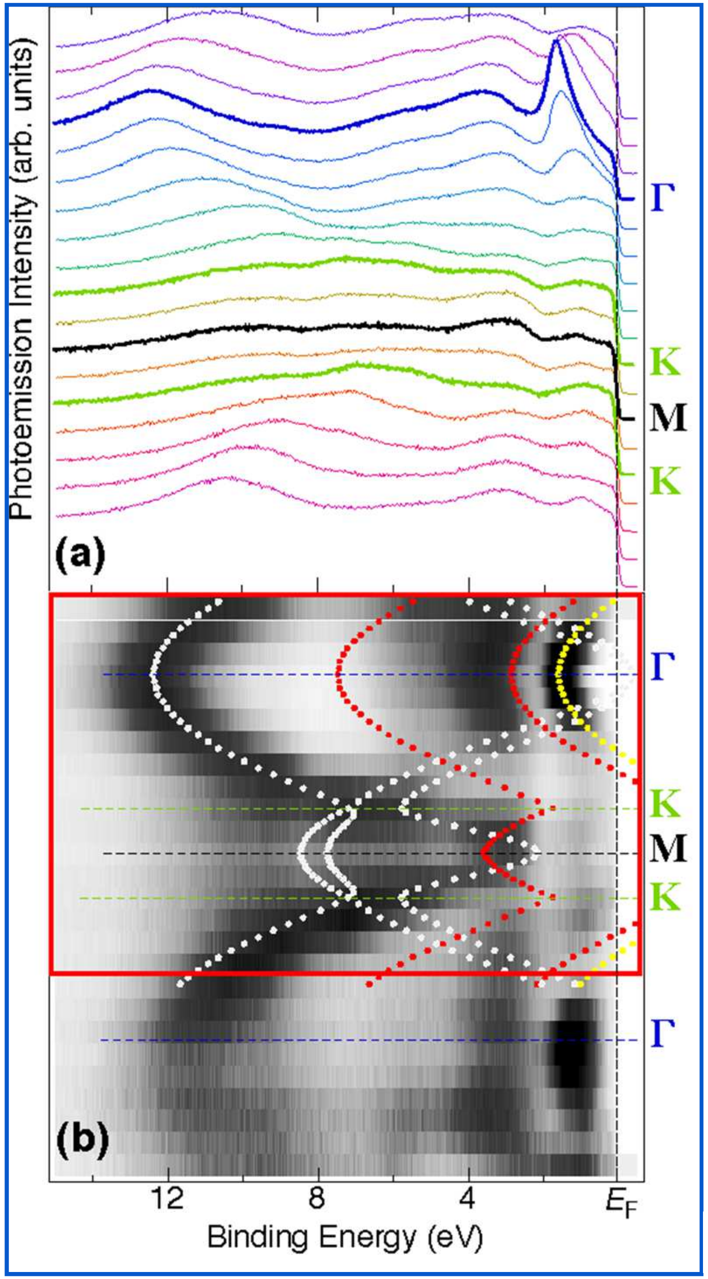
MgB_2

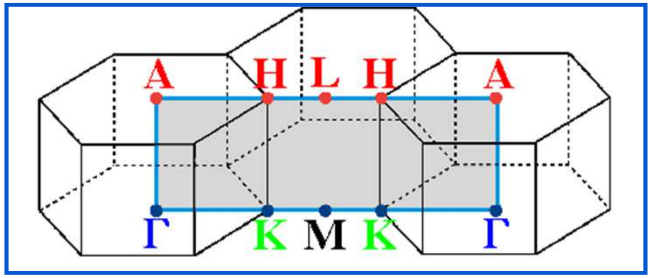


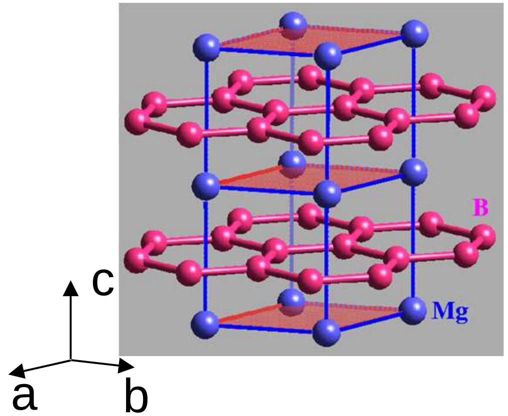
New J. Phys. **8**, 12 (2006)

I.I.Mazin *et al.*, Physica C **385**, 49 (2003)

Surface vs Bulk states





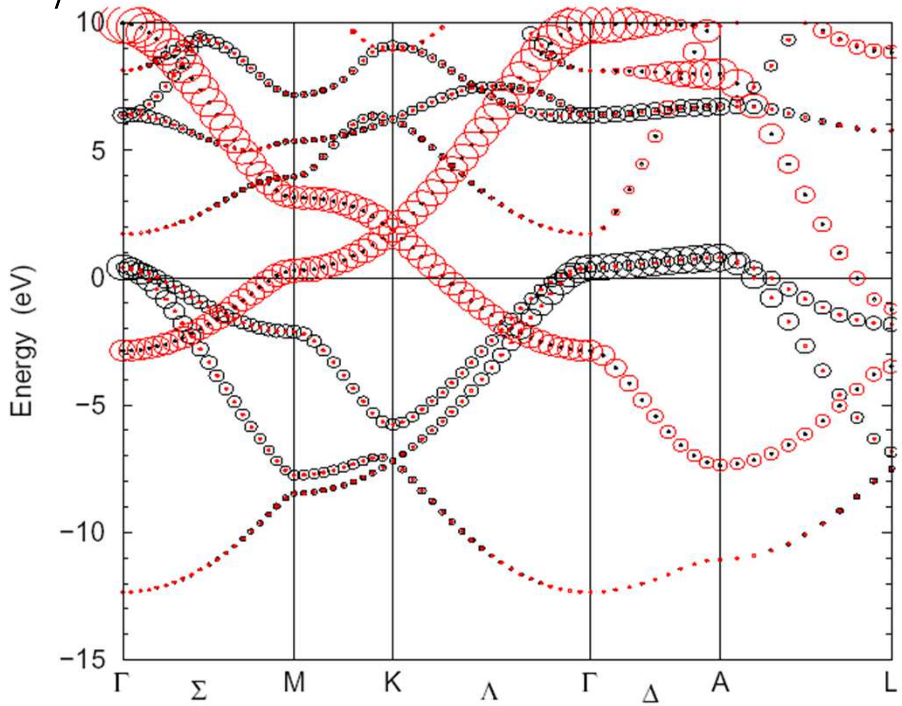


in-plane ($\mathbf{k}_{||}$) dispersion along ΓKMKΓ

$h\nu$ = 105eV (ΔE≈50meV)

changing θ at proper φ

MgB_2



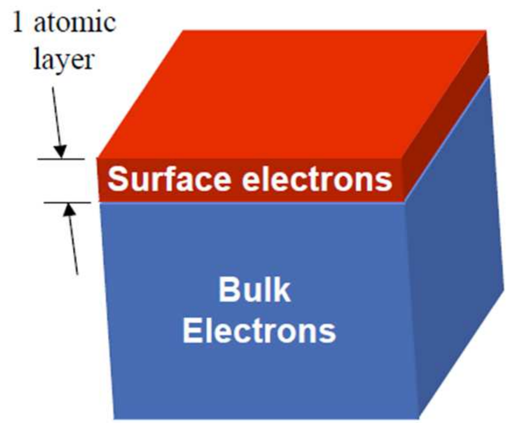
New J. Phys. **8**, 12 (2006)

Surface states vs Bulk states

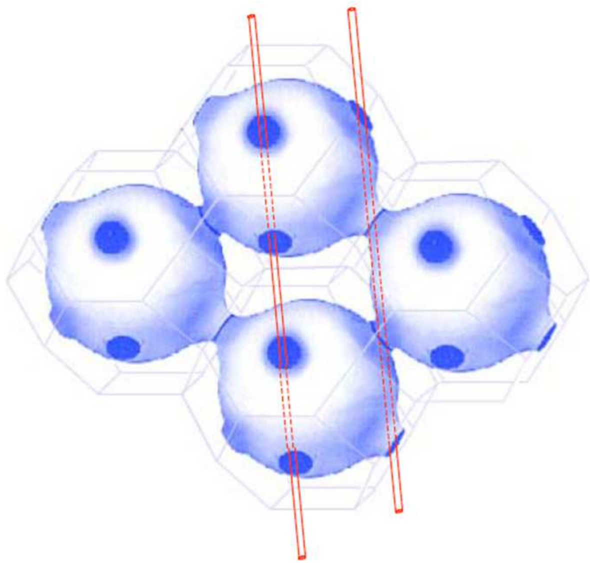
- Surface states are highly localized in real space, therefore completely delocalized in k-space along $k_\perp$
  - No dispersion of surface states in $k_\perp$ direction

- Energy and momenta of surface and bulk states cannot overlap (otherwise why would the states be localized to the surface?):
  - Surface states lie in a gap on the projected bulk band structure

- Surface states have sharper linewidths than bulk states
  - no ''geometrical'' broadening: $\gamma \rightarrow \Gamma_i$



Real Space



Momentum Space

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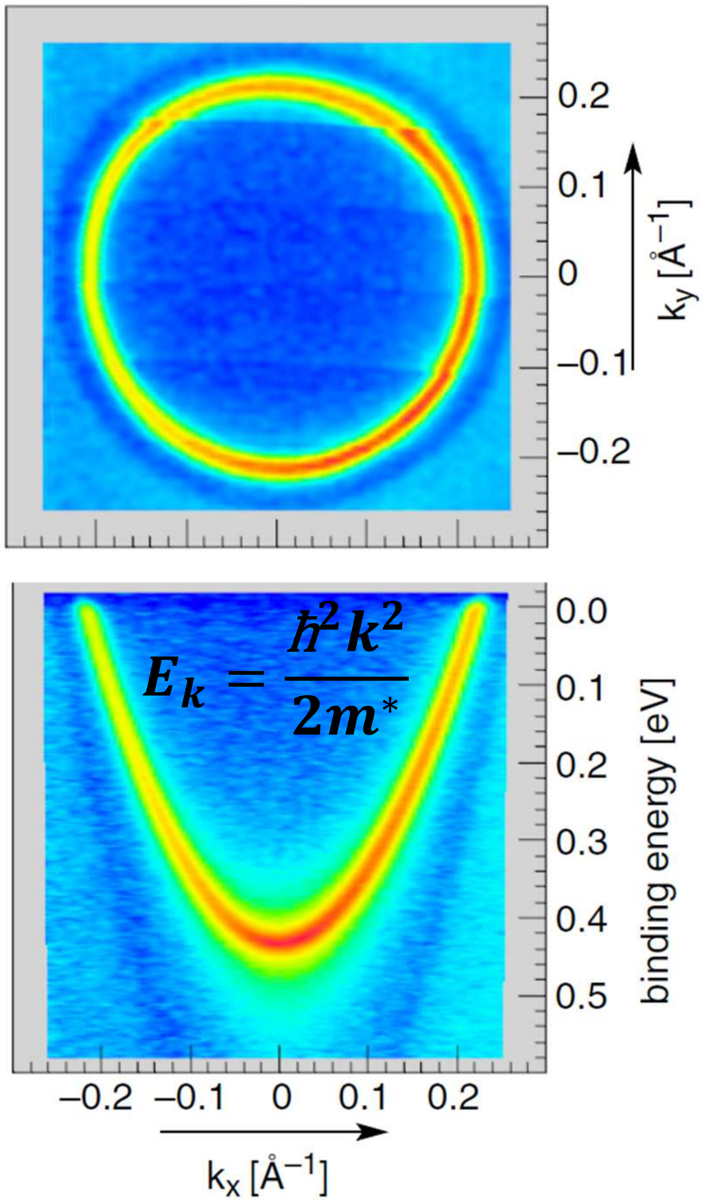
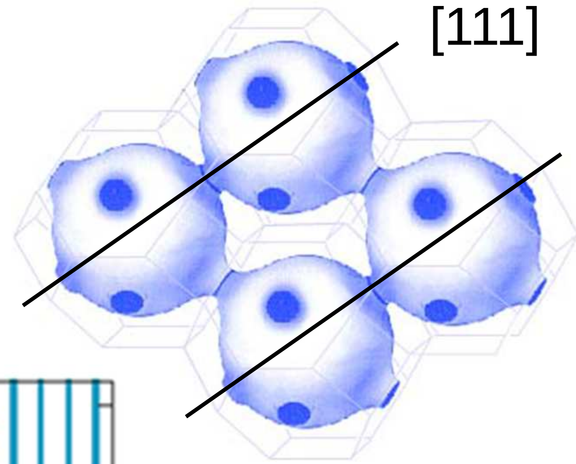
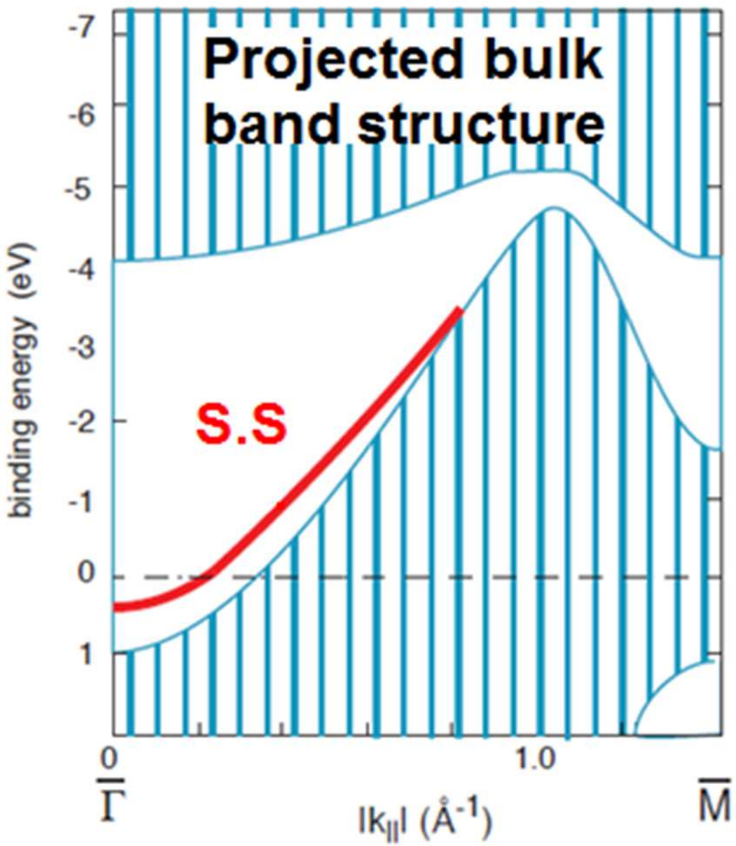
Surface states on clean metal surfaces



Cu(111)

By varying the θ & φ, we can sample states in the k_x-k_y plane (for a fixed hν).





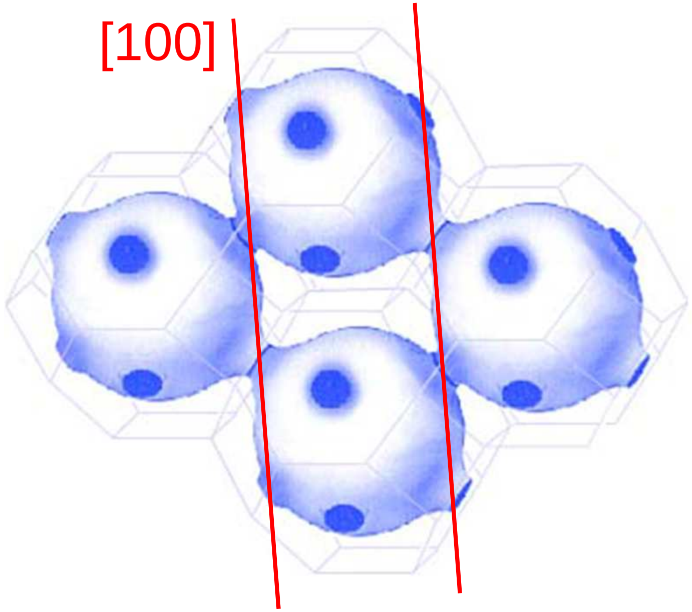
Band Mass

$$\frac{1}{m_k^*} = \frac{1}{\hbar^2}\frac{\partial^2 E_k}{\partial k^2}$$

$$m^* = 0.412m$$

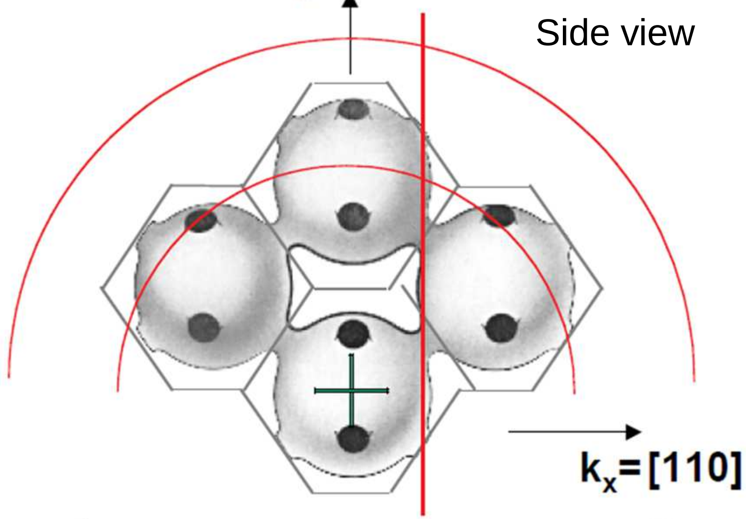
Reinert *et al.*, New J. Phys. 7, 97 (2005)

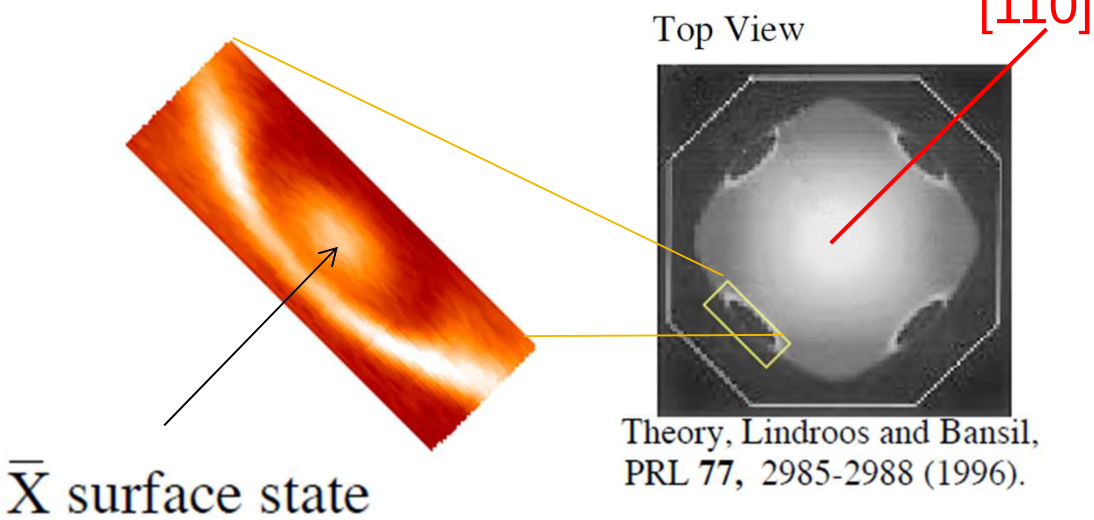
Surface states on clean metal surfaces

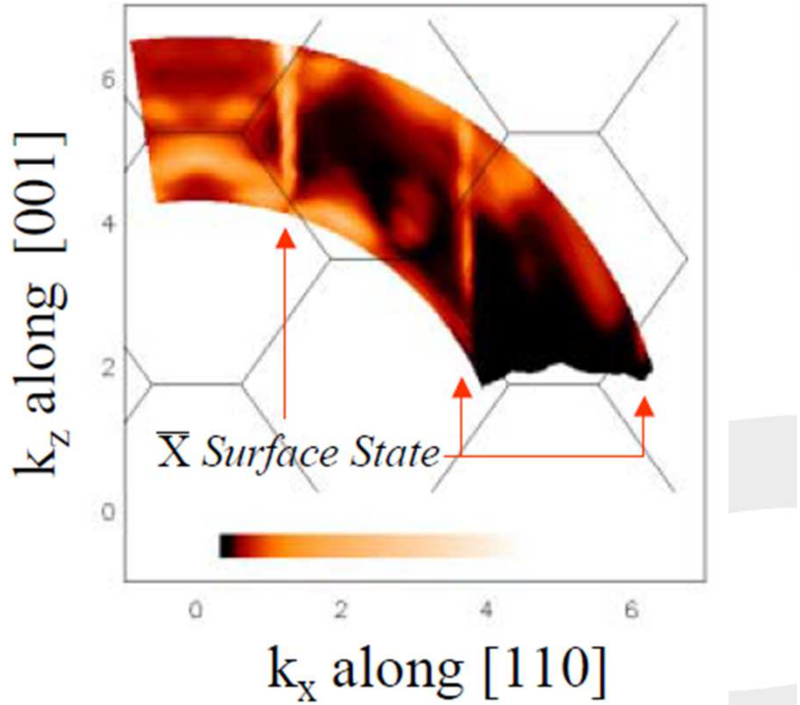


Cu(100)

By varying the hν & θ, we can sample states in the k_x-k_z plane (for a proper φ).



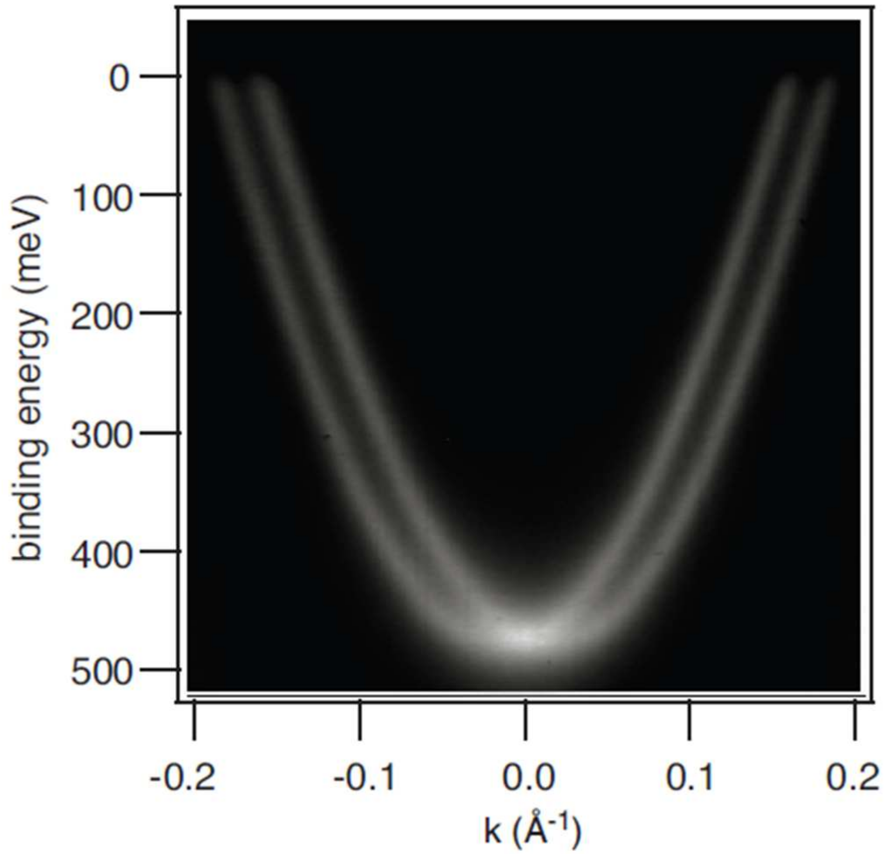


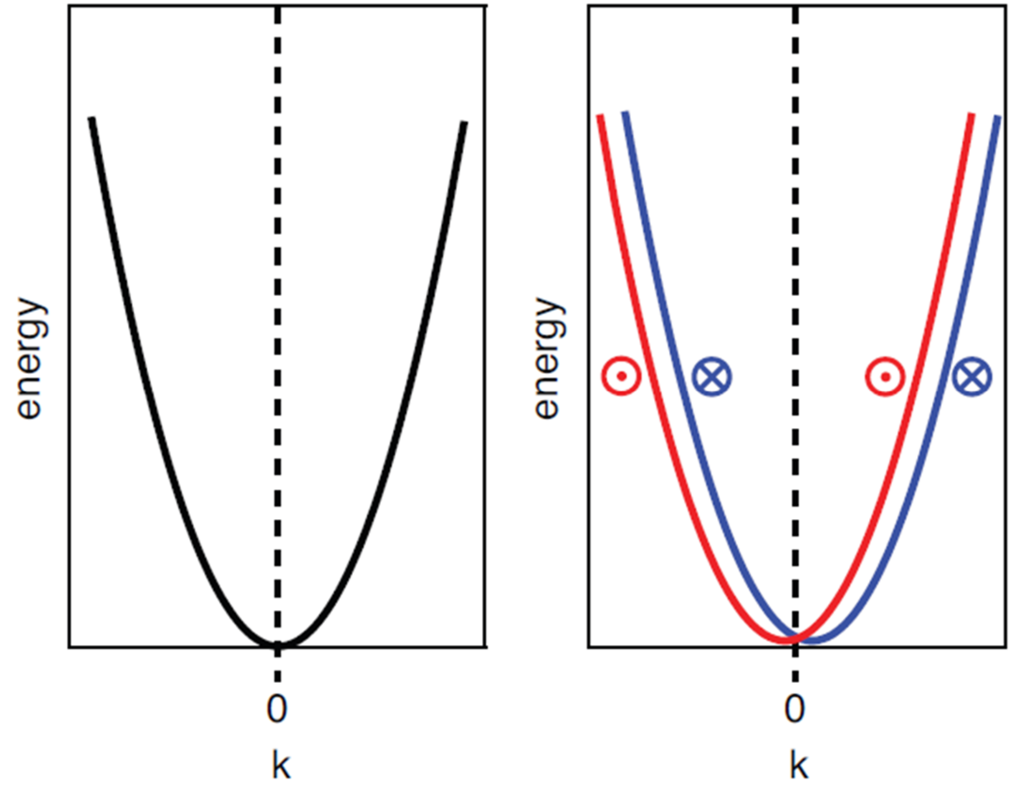


Rotenberg in *X-ray in Nanoscience*, Wiley (2010)

Surface states on clean metal surfaces

Au(111) Two parabolas: spin-orbit splitting





Rasbha model

$$E(k) = \frac{\hbar^2 k^2}{2m_e} \pm \alpha\hbar k = \frac{\hbar^2}{2m_e}\left(k \pm \frac{\alpha m_e}{\hbar^2}\right)^2 - \frac{\alpha^2 m_e}{2\hbar^2}$$

Reinert *et al.*, PRB 63, 115415 (2001)

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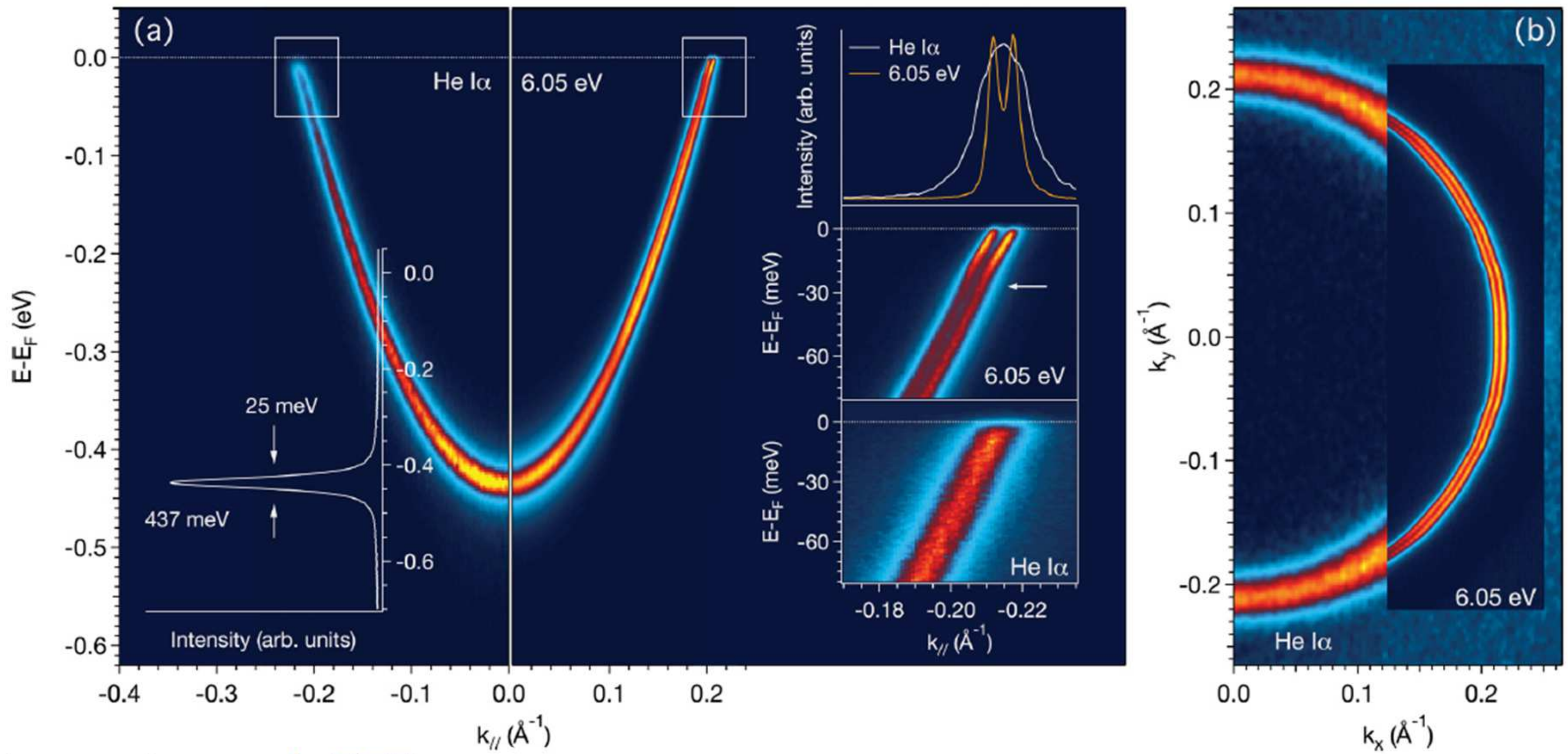
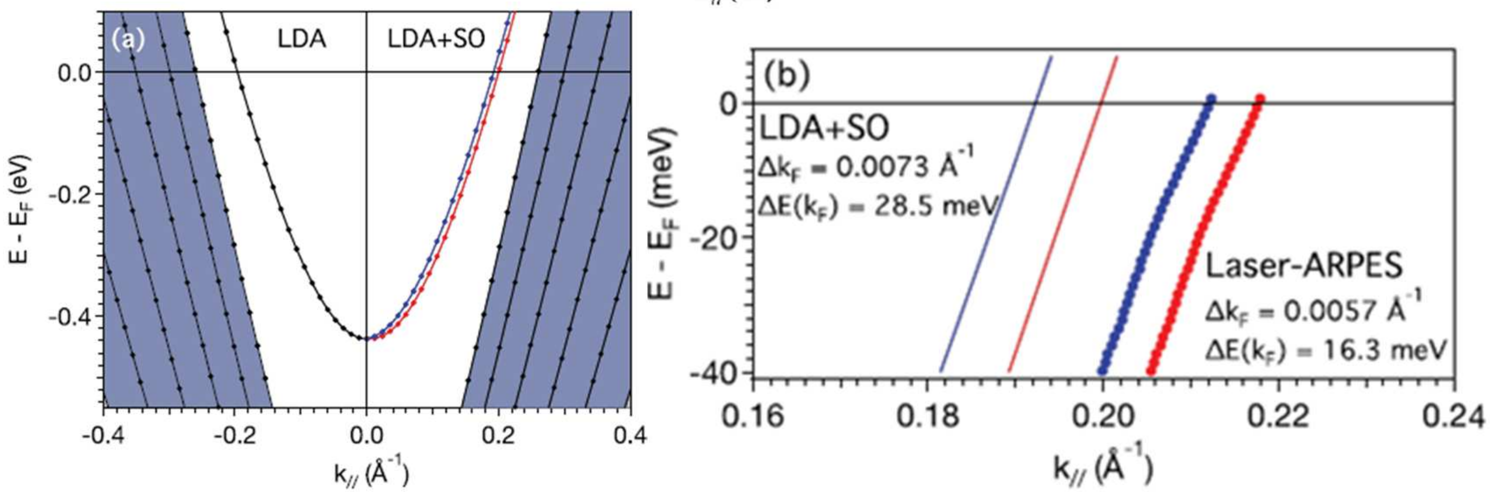
Surface states on clean metal surfaces

Cu(111) using higher resolution

Tamai *et al.*, Phys. Rev. B 87, 075113 (2013)





Two parabolas:
spin-orbit splitting

Low photon energy ARPES

- Improved *k* and *E* resolution
- Improved bulk sensitivity (less k_z broadening)
- Reduced background

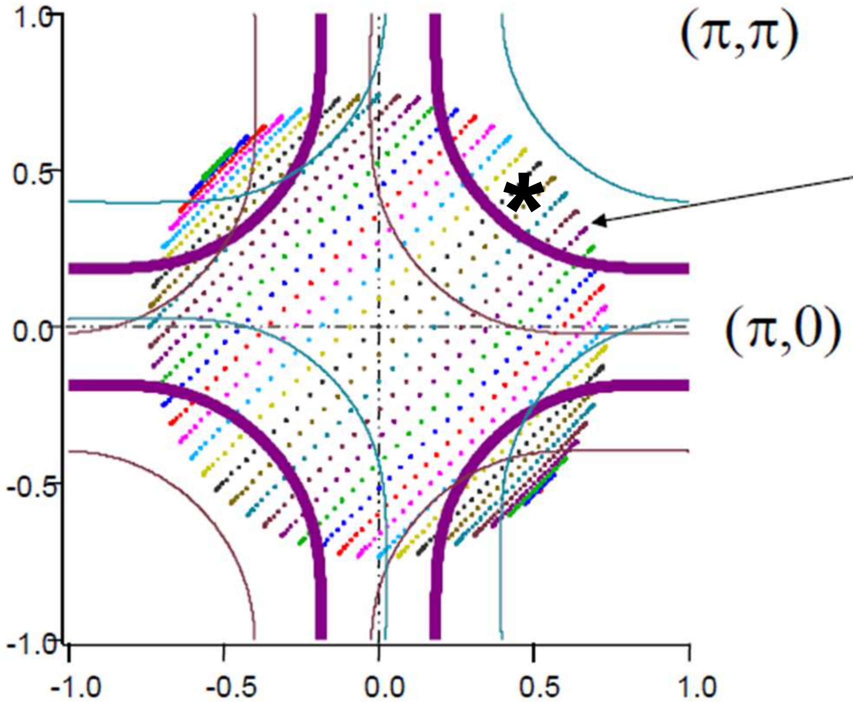
Disadvantages of low-energy ARPES

- Potential issues with breakdown of the sudden-approximation ?
- Technically more challenging (electron analyzers don't like low kinetic energy)
- Often a lack of matrix element/photon energy control
- Not many synchrotron beamlines

BaDElPh @ Elettra, $h\nu$ *= 5 - 40 eV,* ΔE *= 5 meV @ 8 eV*

Low photon energy ARPES

Resolution and *k*-space effect



Range of *k*-space accessible in Bi2212 at $h\nu$=6 eV

$$|\boldsymbol{k}_{||}| = \frac{1}{\hbar}\sqrt{2mE_{kin}}\, sin\vartheta$$

$$\Delta \boldsymbol{k}_{||} \cong \frac{1}{\hbar}\sqrt{2mE_{kin}}\, cos\vartheta\Delta\vartheta$$

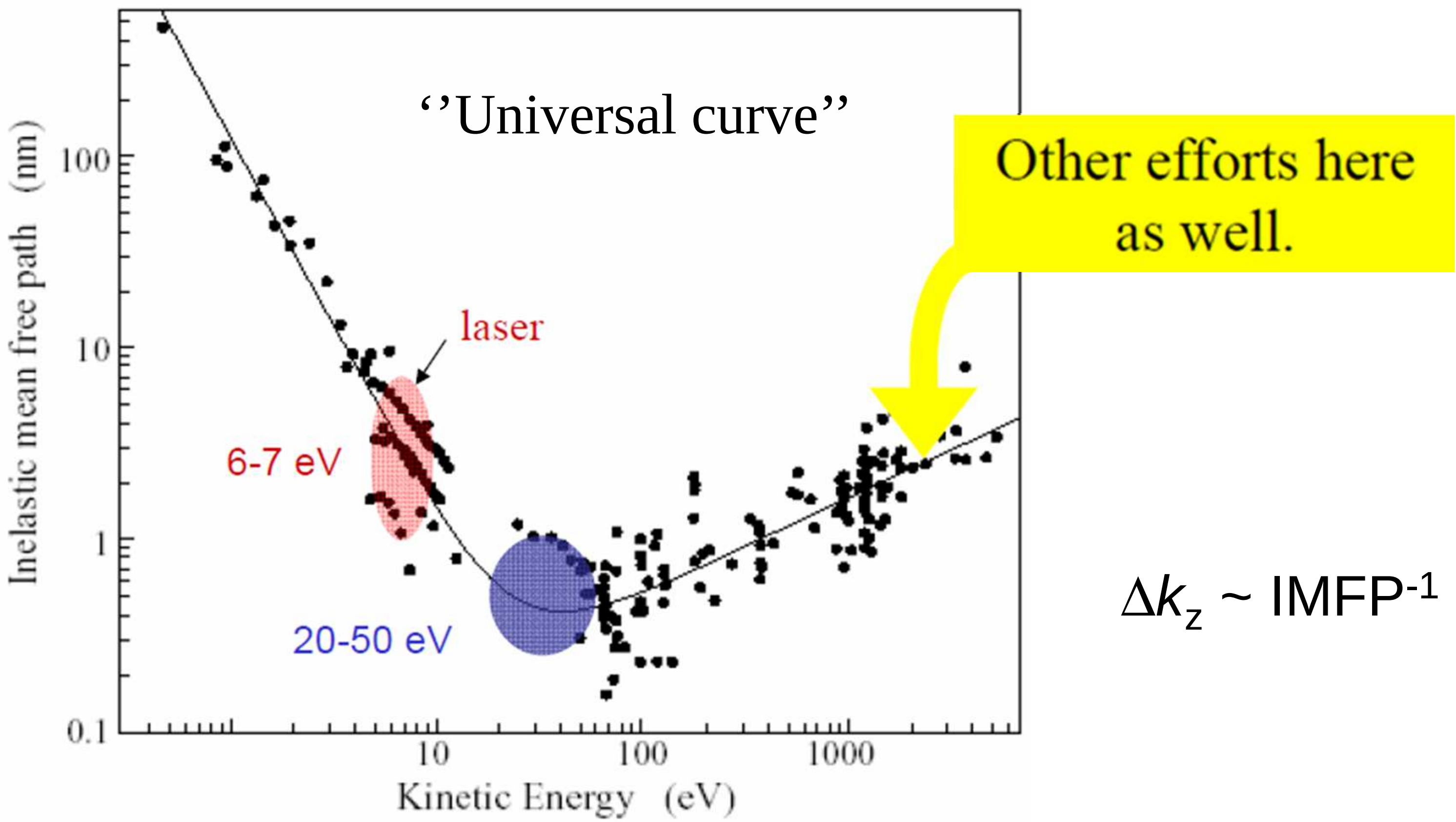
- For the same angular resolution, the ***k*** resolution at low *E* is superior.
- ***k*** resolution translates to *E* widths if the peak is dispersive:

  For nodal states***** and 0.3° angular resolution,

  5 meV broadening for $h\nu$=6 eV, and 38 meV for $h\nu$=52 eV.
- However, relatively small range of ***k***-space accessible.

ARPES: Surface vs Bulk sensitivity

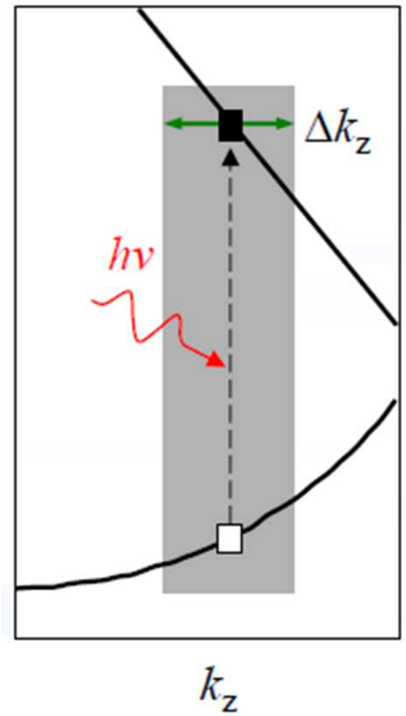
Seah & Dench, Surf. Interf. Anal. 1, 2 (1979)



Decreasing phase space for excitations (plasmons, e-h pairs, etc.)

Decreasing interaction time.

$\Delta k_z \sim \mathrm{IMFP}^{-1}$



PE signal by *averaging* of $E(k_z)$ within Δk_z

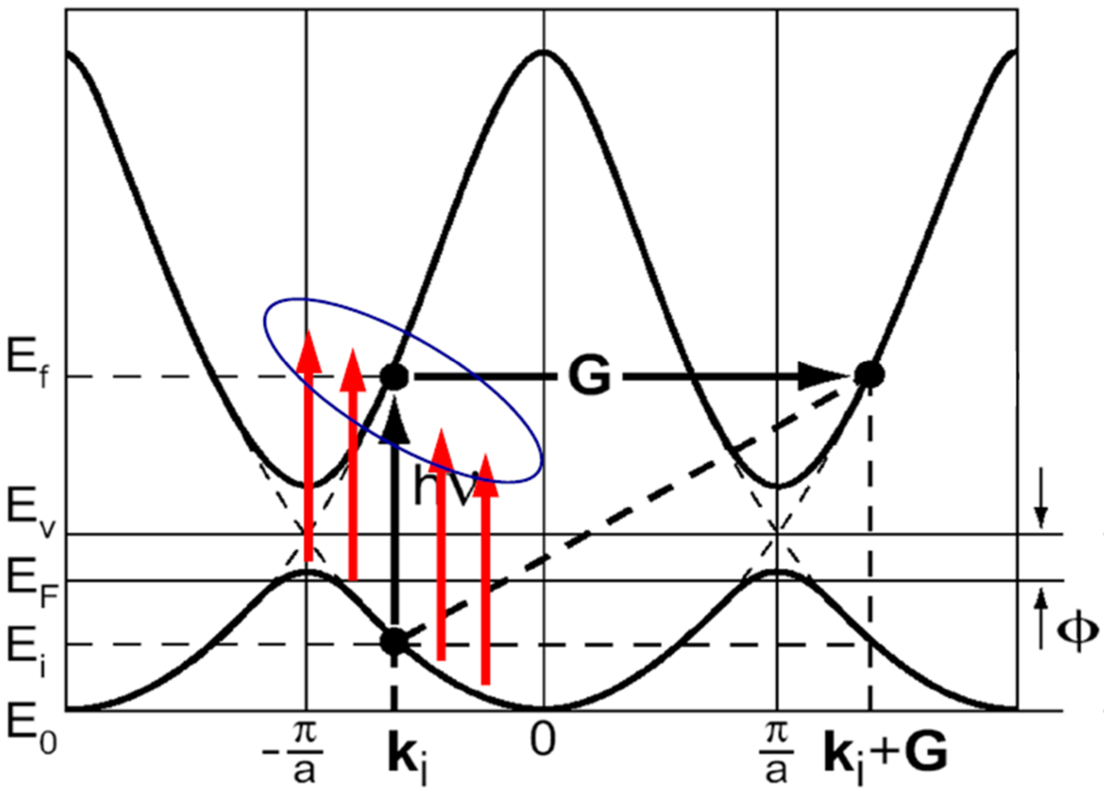
$\Delta k_z \ll k_z^{BZ}$ for ARPES

→ 3-10 times more *bulk* sensitive than ''standard'' ARPES (i.e., $h\nu$ = 20-50 eV)

Low photon energy ARPES and final-state effects

Photoemission Intensity $I(k,\omega)$ $\Big\}$ $w_{fi} \propto |\langle \phi_f^{\mathbf{k}} | \mathbf{A}\cdot\mathbf{p} | \phi_i^{\mathbf{k}} \rangle \langle \Psi_m^{N-1} | \Psi_i^{N-1} \rangle|^2 \delta(\omega - h\nu)$

Excitation in the solid



At **low photon energy** photoemission is affected by the kinematic constrain deriving from energy and momentum conservation, and the *k*-dependent structure of the final states. For some initial state there is no final state that can be reached at a given photon energy and the intensity vanishes.

Working at **high photon energies** the electron is excited in a continuum of high-energy states; a final state is always available and the photoemission process can take place (with intensity still dependent on matrix elements).

Soft-X-ray ARPES

- Improved bulk sensitivity (less k_z broadening)
- Technically less challenging (electron analyzers like high kinetic energy)
- Simplified matrix elements (free-electron final states approximation works better)

Disadvantages of soft-X-ray ARPES

- Worst $k_{||}$ and E resolution [averaging $E(k)$ in Δk]
- Small valence band cross-section vs $h\nu$ (photon flux required!)
- Increased background
- Not many synchrotron beamlines with enough resolution and flux

ADRESS @ SLS, $h\nu = 300 – 1800$ *eV,* $\Delta E = 30$ *meV @ 1keV*

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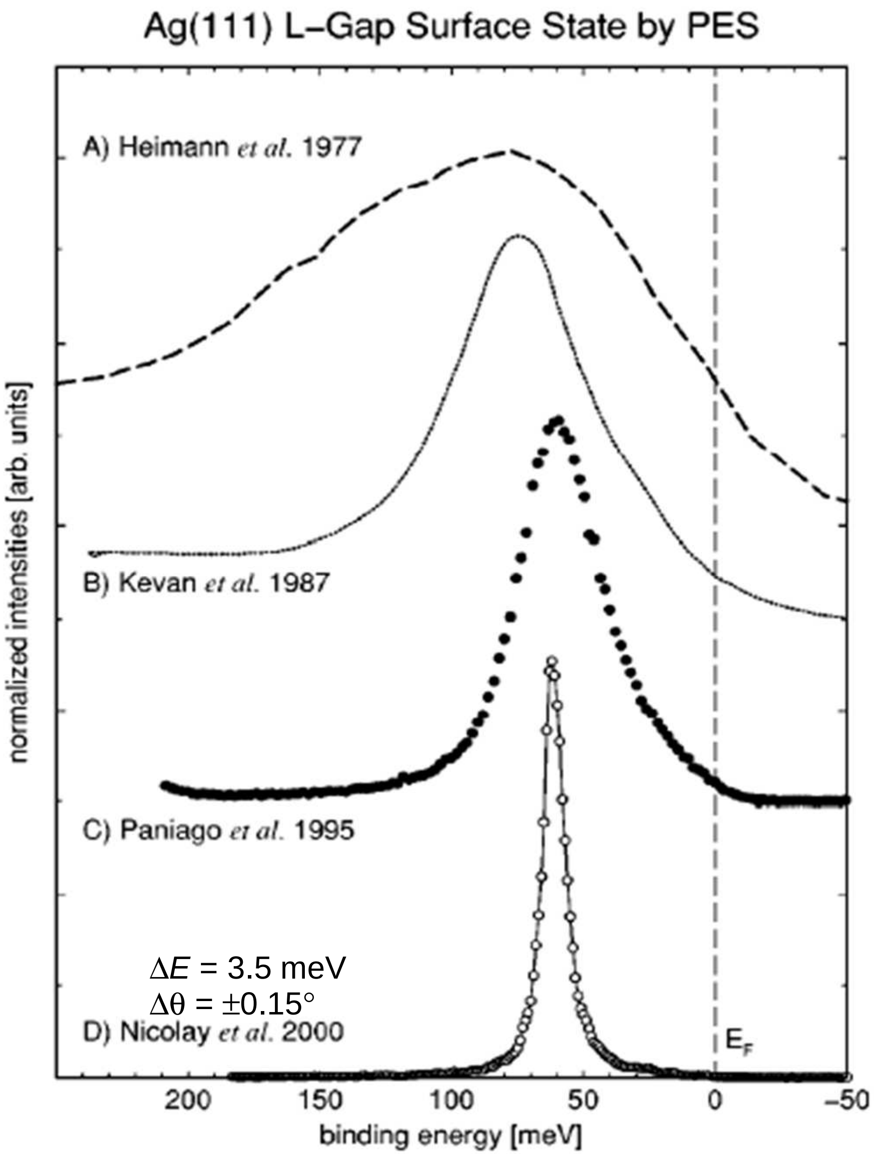
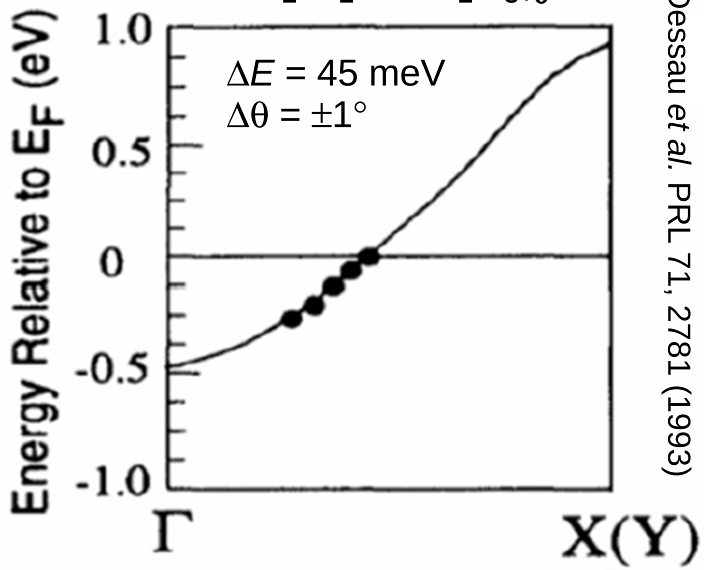
Effect of energy resolution

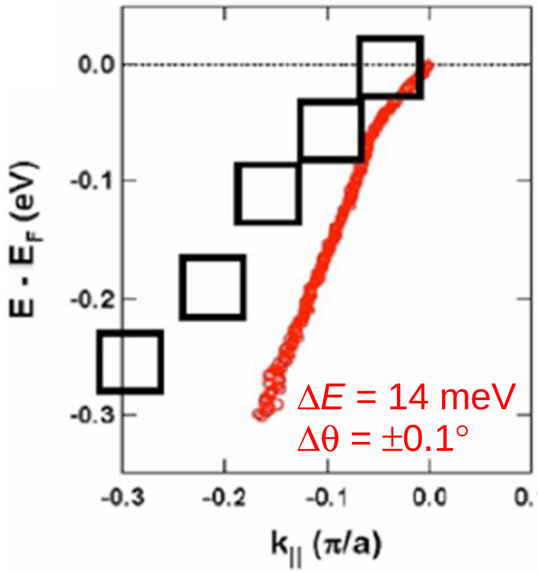
Reinert *et al.* PRB 63, 115415 (2001)



$Bi_2Sr_2CaCu_2O_{8+\delta}$



Dessau *et al.* PRL 71, 2781 (1993)



Bogdanov *et al.* PRL 85, 2581 (2000)

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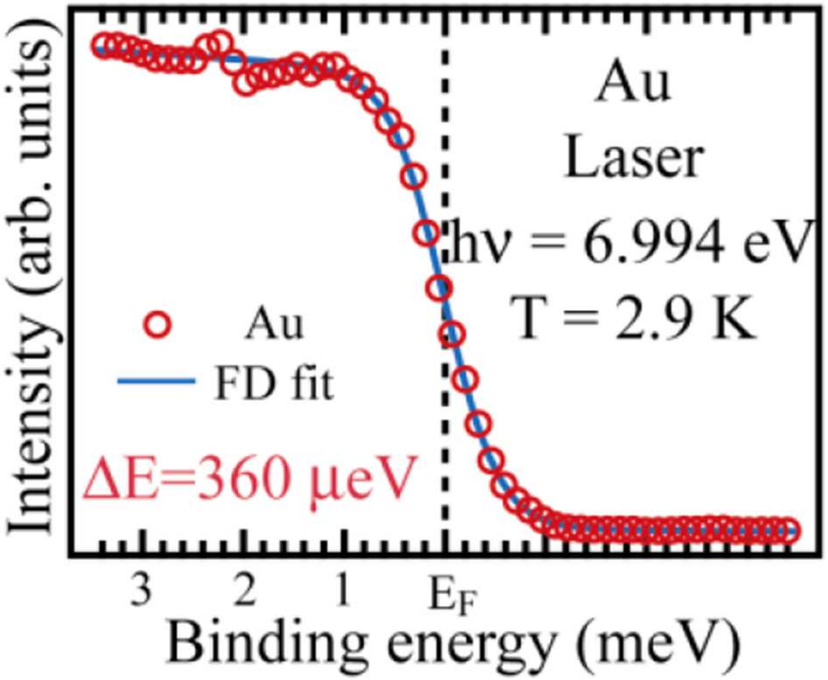
Best energy resolution so far

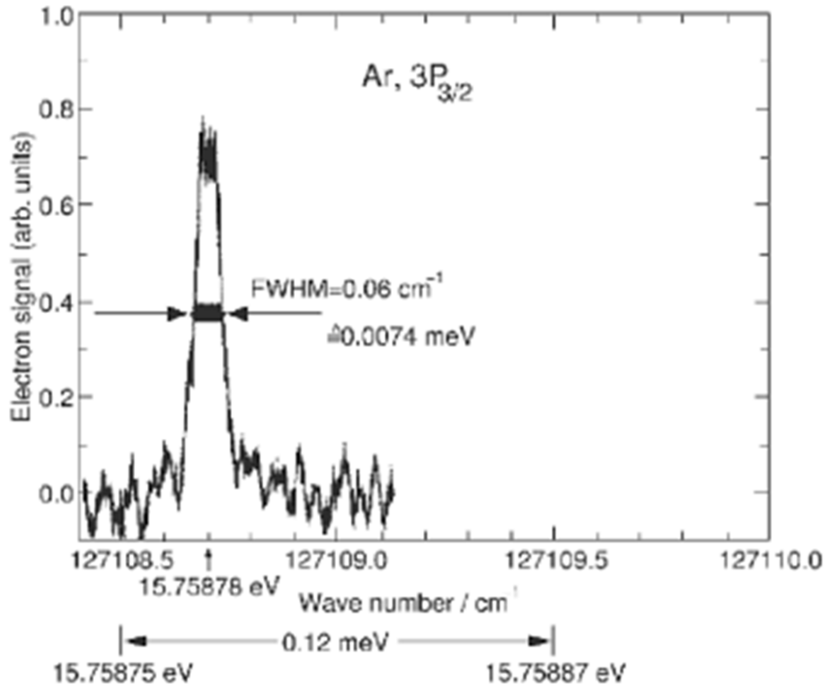
Kiss *et al.*, Phys. Rev. Lett. 94, 057001 (2005)

In solid state on Au-poly



The instrumental energy resolution after subtraction of temperature broadening is **ΔE = 360 μeV**

In gas phase on Ar



Only the $3P_{3/2}$ line is showns with an inherent width of **ΔE = 7.4 μeV**

Hollenstein *et al.*, J. Chem. Phys. 115, 5461 (2001)

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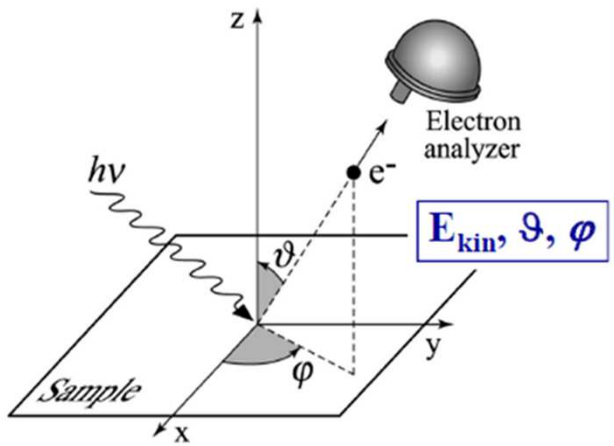
ARPES: Non-interacting particle picture

$$w_{fi} \propto |\langle\phi_f^{\mathbf{k}}|\mathbf{A}\cdot\mathbf{p}|\phi_i^{\mathbf{k}}\rangle\langle\Psi_m^{N-1}|\Psi_i^{N-1}\rangle|^2\delta(\omega-h\nu)$$

1

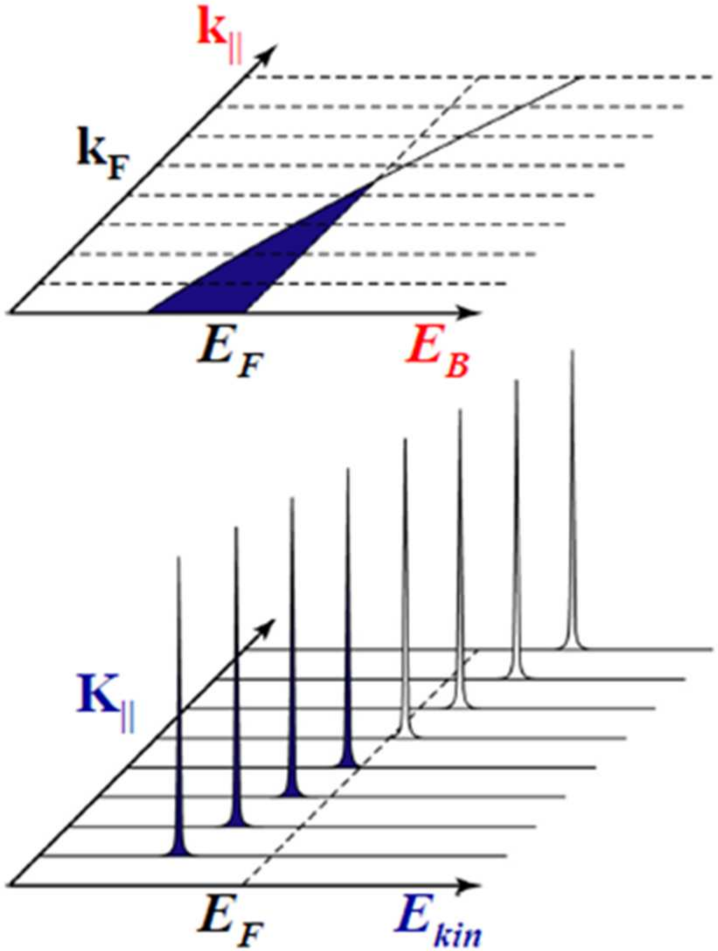


Energy Conservation

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

Momentum Conservation

$$\hbar \mathbf{k}_{||} = \hbar \mathbf{K}_{||} = \sqrt{2mE_{kin}} \cdot \sin\vartheta$$

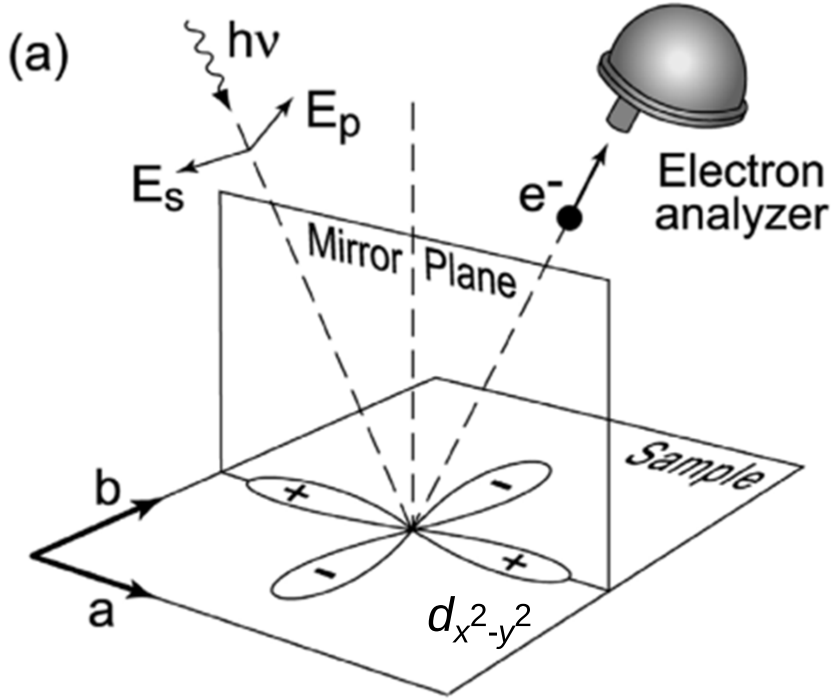


The ARPES spectrum consists of a *spike* (δ-function) at E_{kin}, $K_{||}$

The intensity is modulated by the one-electron matrix element $M_{f,i}^{\mathbf{k}}$

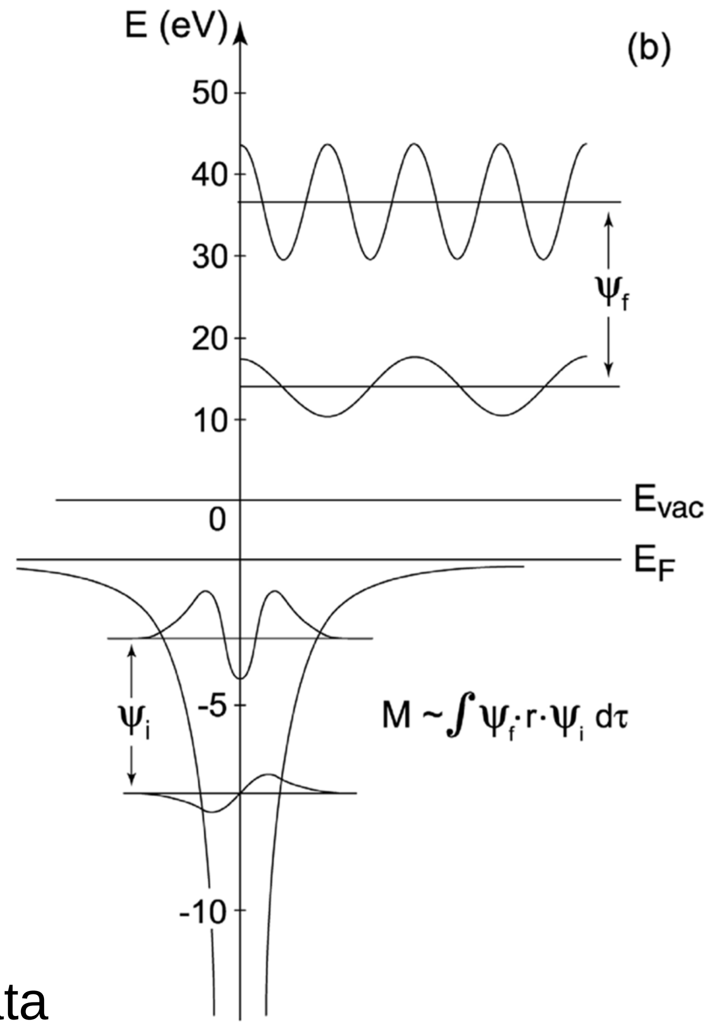
ARPES: Matrix elements effects

Photon polarization



$$|M_{f,i}^{\mathbf{k}}|^2 \equiv |\langle \phi_f^{\mathbf{k}} | \mathbf{A} \cdot \mathbf{p} | \phi_i^{\mathbf{k}} \rangle|^2$$

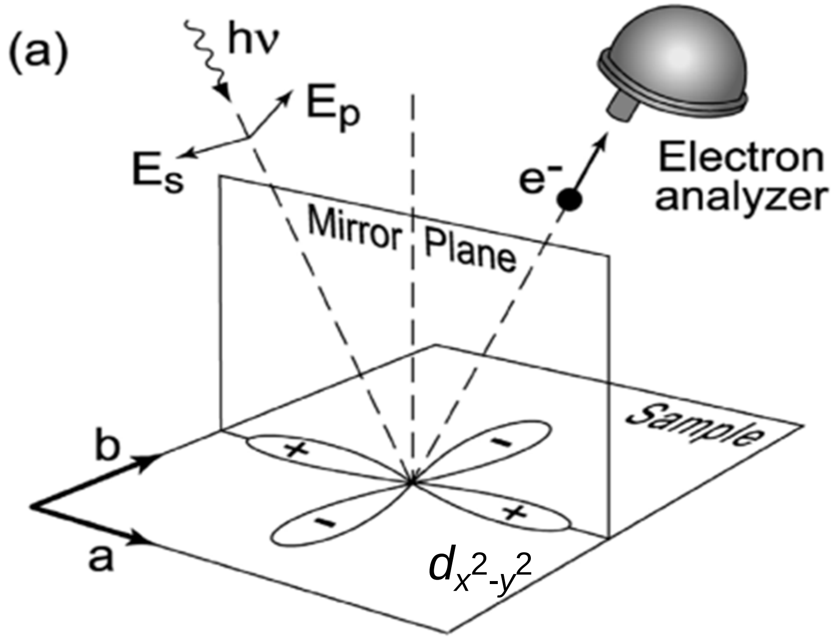
Photon energy



This is responsible for the dependence of the PES data on photon energy and experimental geometry, and may even result in complete suppression of the intensity.

ARPES: Matrix elements effects

Photon polarization



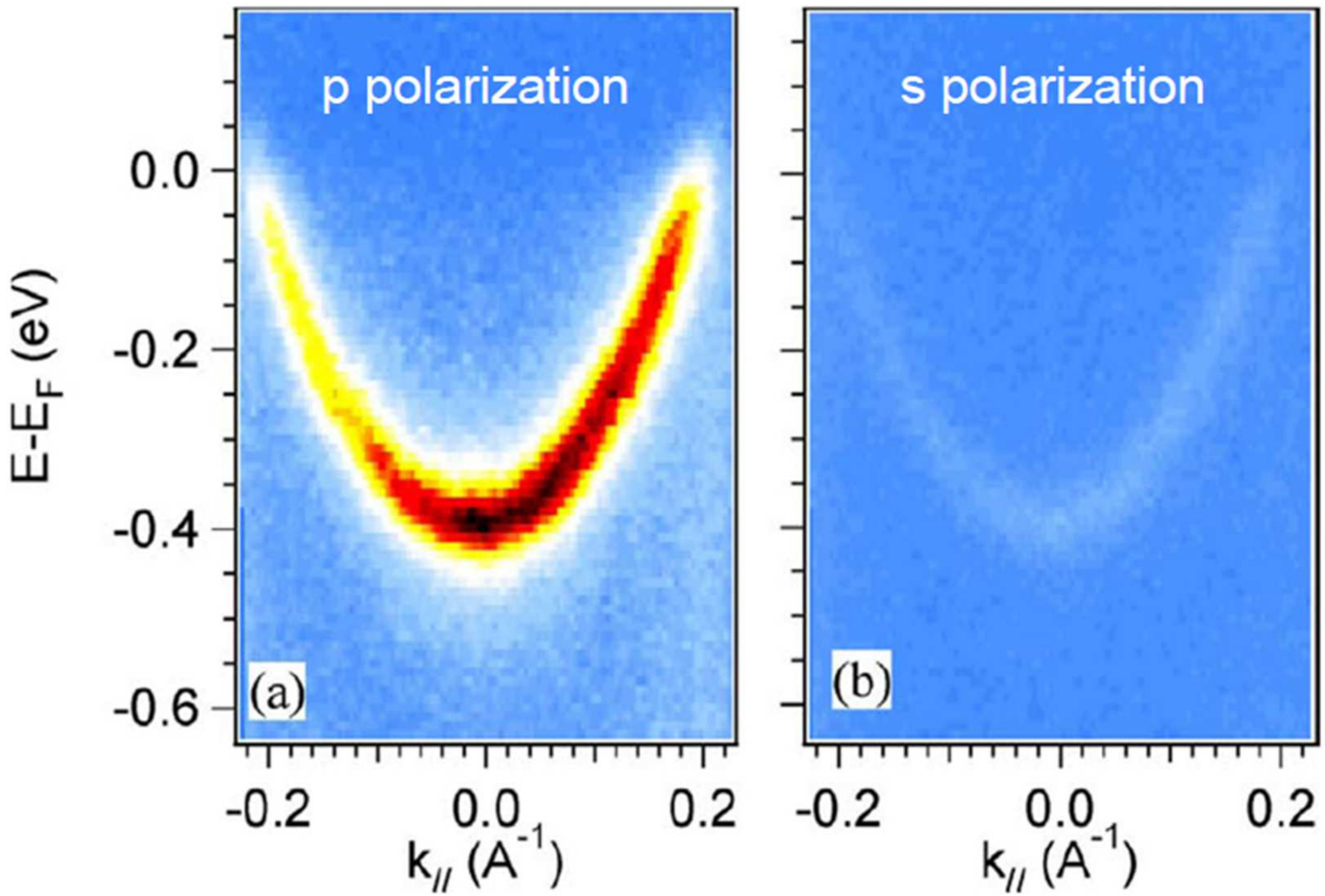
- The sample has mirror-plane symmetries.
- Each part of the matrix element has its own possible symmetry with respect to the sample plane.
- Whether a transition is allowed or forbidden depends on a combination of experimental geometry and the details of the wavefunctions

$$\left\langle \phi_f^k | \boldsymbol{A} \cdot \boldsymbol{p} | \phi_i^k \right\rangle \begin{cases} \phi_i^k \text{ even } \langle + | + | + \rangle \Rightarrow \boldsymbol{A} \text{ even} \\ \phi_i^k \text{ odd } \langle + | - | - \rangle \Rightarrow \boldsymbol{A} \text{ odd} \end{cases}$$

Symmetry selection rules

ARPES: Polarization dependence

Cu(111) surface state



Mulazzi *et al.*, Phys. Rev. B 79, 165421 (2009)

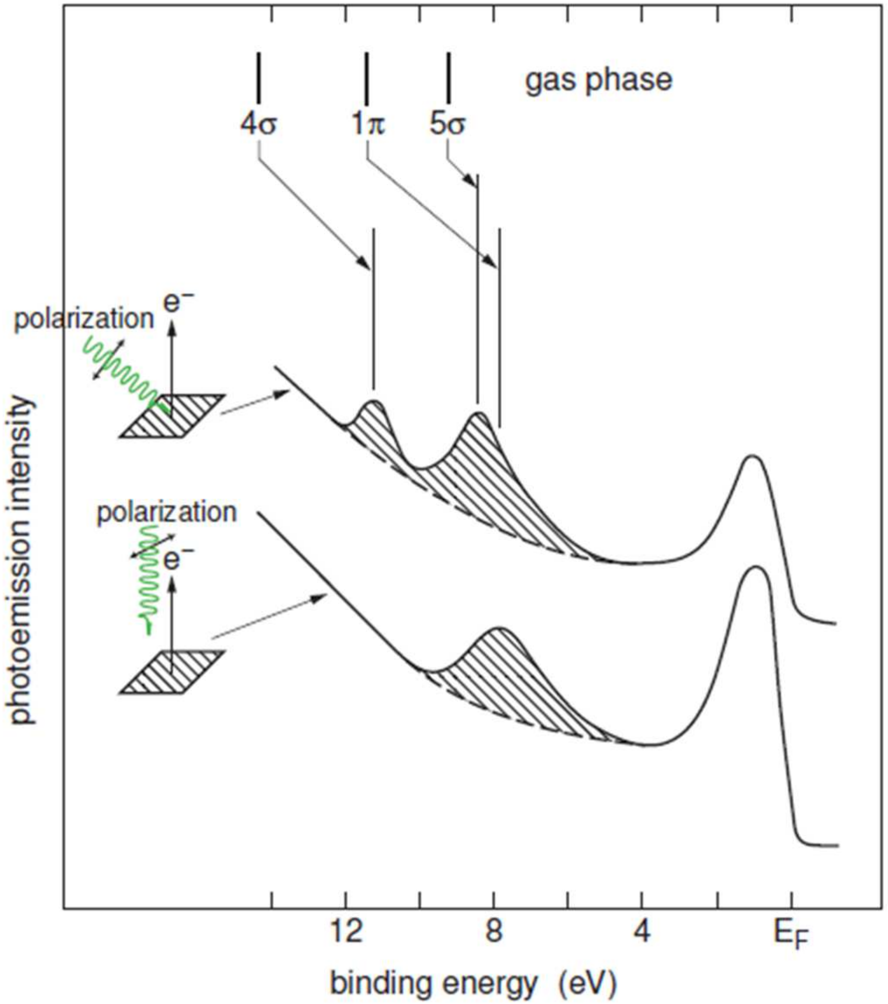
Adsorbate orientation by polarization-dependent ARPES

CO on Ni(001)

NE geometry

Polarization ⊥ surface ≠ 0

Polarization || surface

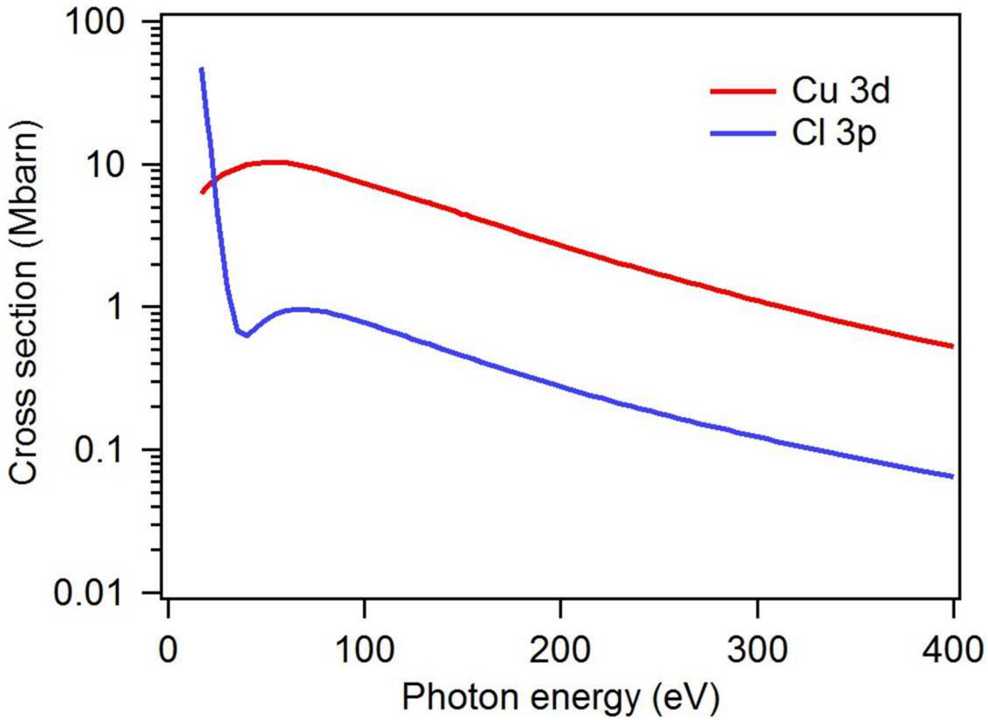


R.J. Smith et al, PRL 37, 1081 (1976)

→ CO molecular axis perpendicular to the surface

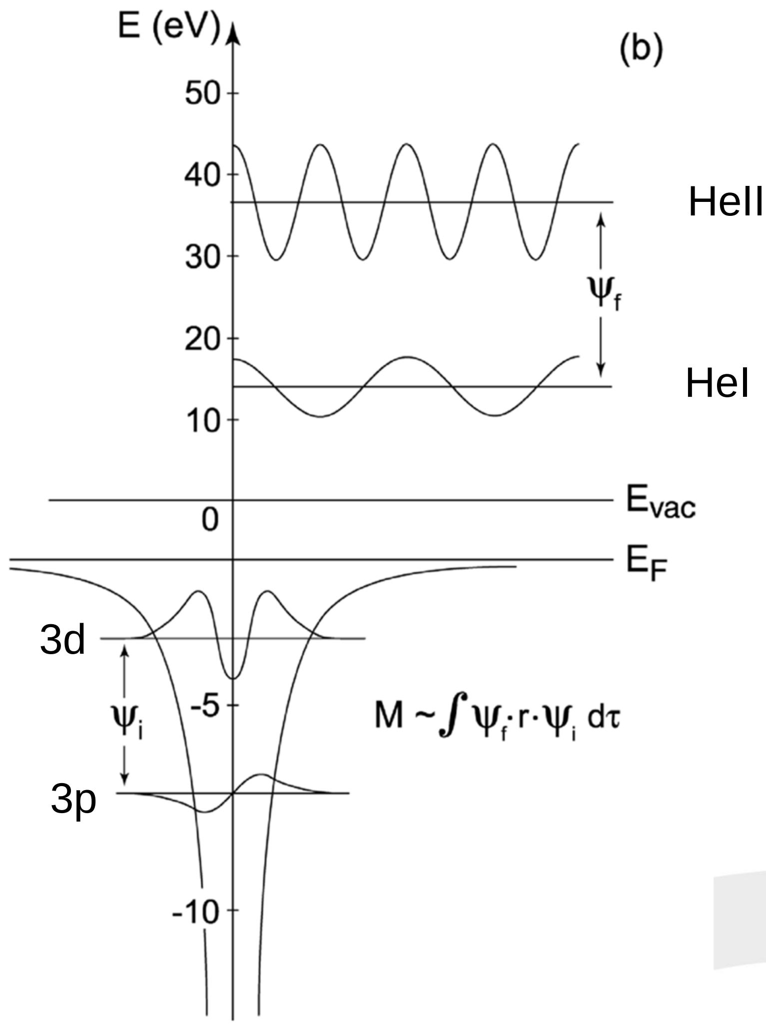
ARPES: Matrix elements effects

$$\left\langle \phi_f^k | \boldsymbol{A} \cdot \boldsymbol{p} | \phi_i^k \right\rangle^2 \propto |(\varepsilon \cdot \boldsymbol{k}) \langle \phi_i^k | e^{i\boldsymbol{k}\boldsymbol{r}} \rangle|^2$$



Cross-section & **Cooper minimum**

Photon energy

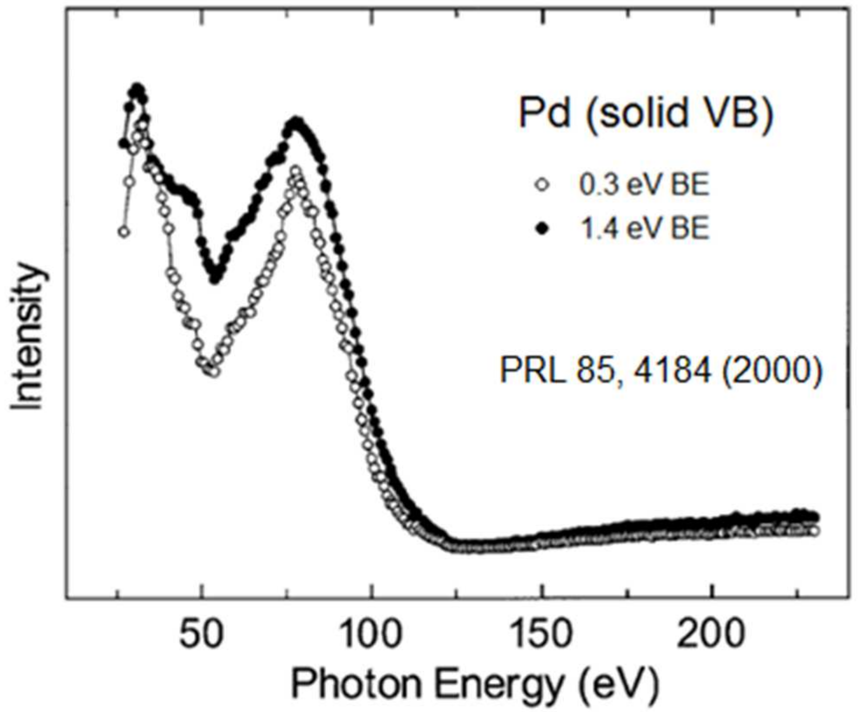


https://vuo.elettra.eu/services/elements/WebElements.html

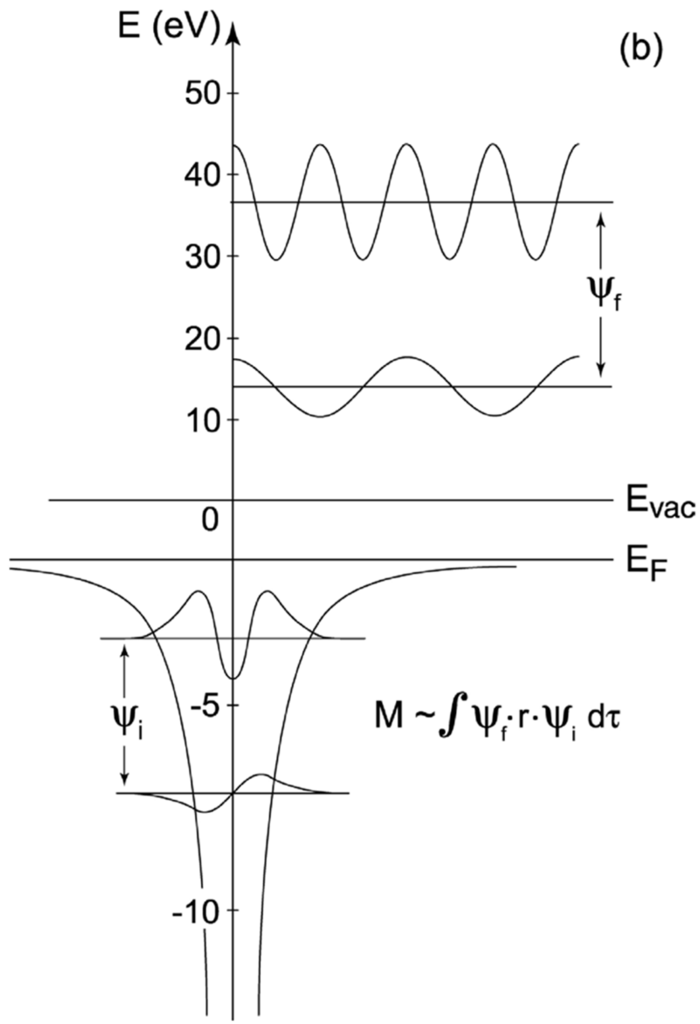
Elettra Sincrotrone Trieste

ARPES: Matrix elements effects

$$\left\langle \phi_f^k | A \cdot p | \phi_i^k \right\rangle^2 \propto |(\varepsilon \cdot k)\langle \phi_i^k | e^{ikr} \rangle|^2$$



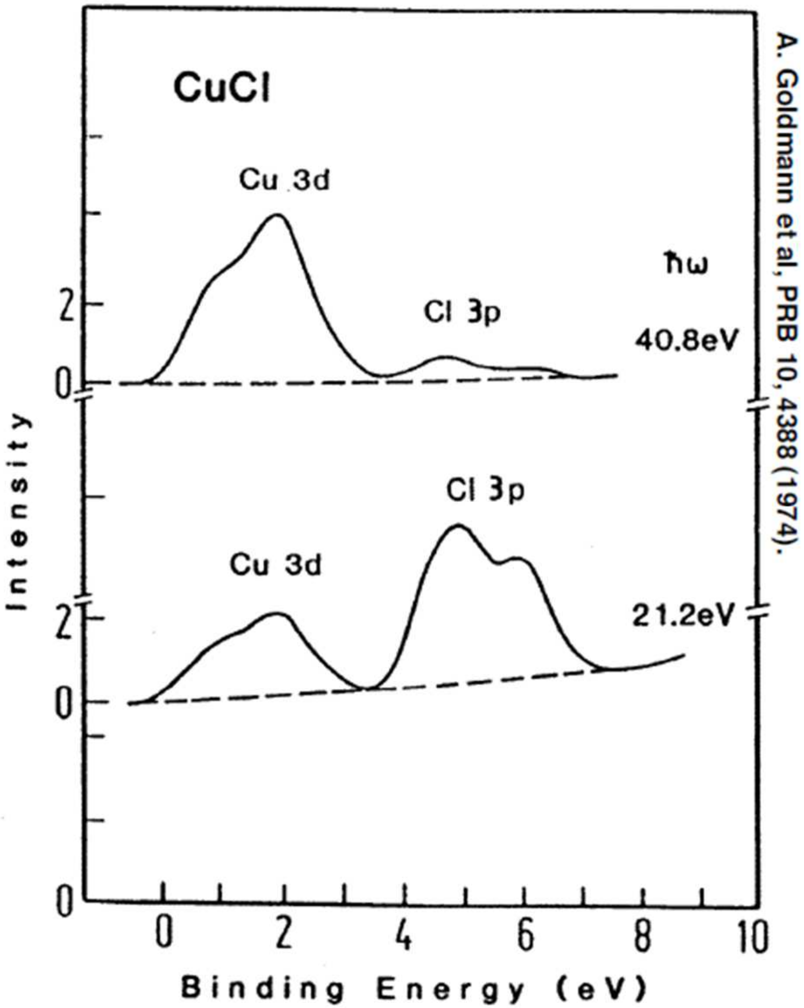
Photon energy

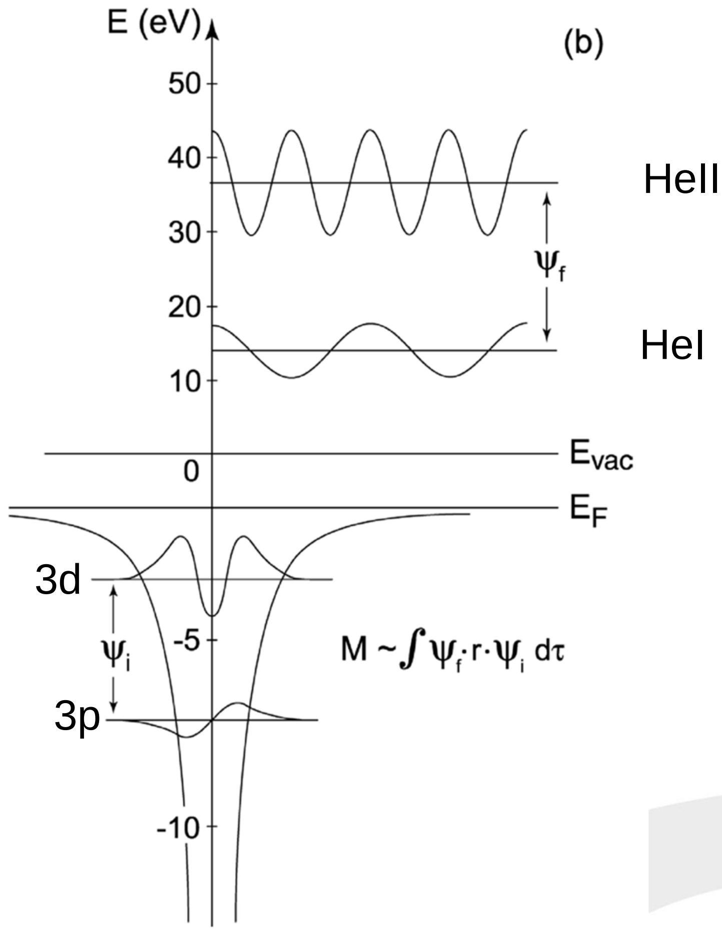


Cross-section & **Cooper minima**

ARPES: Photon energy dependence

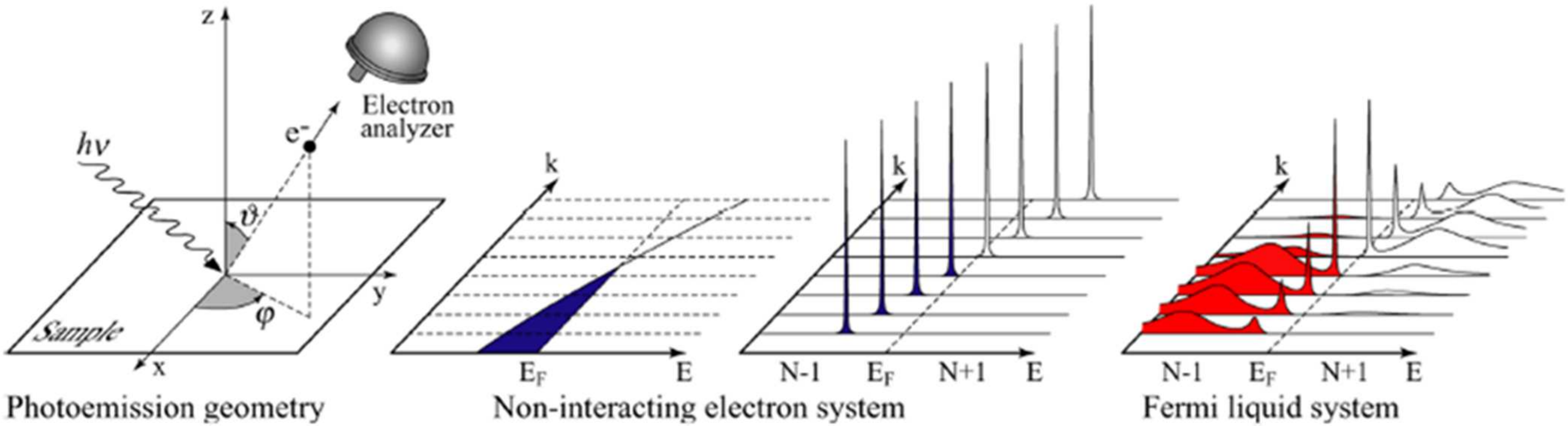
As a tool to identify contributions from different atomic states
to valence-band photoemission spectra





ARPES: Interacting systems

A. Damascelli, Z. Hussain, Z.-X Shen, Rev. Mod. Phys. **75**, 473 (2003)



Photoemission intensity: $I(\mathbf{k}, E_{kin}) = \sum_{f,i} w_{f,i}$

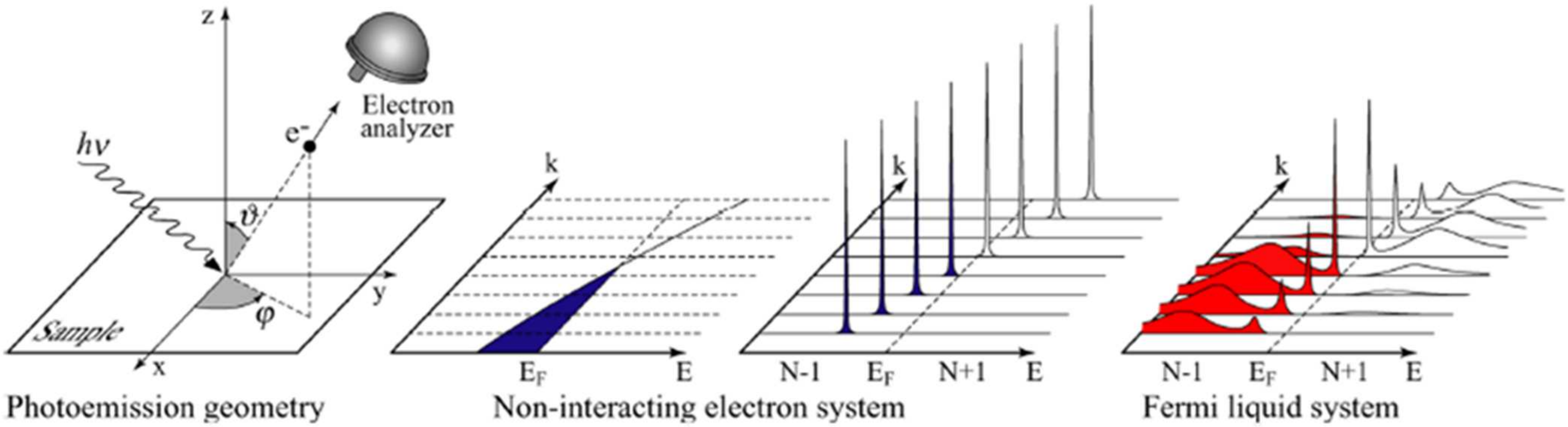
$$I(\mathbf{k}, E_{kin}) \propto \sum_{f,i} |M^{\mathbf{k}}_{f,i}|^2 \sum_m |c_{m,i}|^2 \delta(E_{kin} + E^{N-1}_m - E^N_i - h\nu)$$

$$|M^{\mathbf{k}}_{f,i}|^2 \equiv |\langle \phi^{\mathbf{k}}_f | \mathbf{A} \cdot \mathbf{p} | \phi^{\mathbf{k}}_i \rangle|^2 \qquad |c_{m,i}|^2 = |\langle \Psi^{N-1}_m | \Psi^{N-1}_i \rangle|^2$$

''Like removing a stone from a water bucket''

ARPES: Interacting systems

A. Damascelli, Z. Hussain, Z.-X Shen, Rev. Mod. Phys. **75**, 473 (2003)



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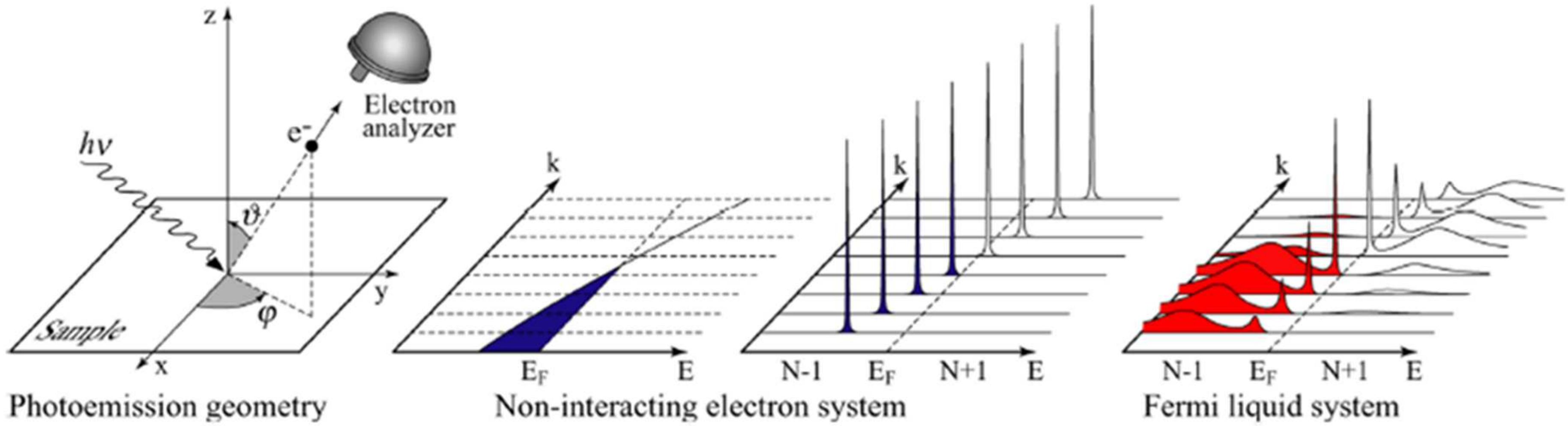
$$|M^{\mathbf{k}}_{f,i}|^2 \equiv |\langle \phi^{\mathbf{k}}_f | \mathbf{A}\cdot\mathbf{p} | \phi^{\mathbf{k}}_i \rangle|^2 \qquad |c_{m,i}|^2 = |\langle \Psi^{N-1}_m | \Psi^{N-1}_i \rangle|^2$$

In general $\Psi^{N-1}_i = c_{\mathbf{k}} \Psi^N_i$ **NOT orthogonal** Ψ^{N-1}_m

ARPES: The single-particle spectral function

A. Damascelli, Z. Hussain, Z.-X Shen, Rev. Mod. Phys. **75**, 473 (2003)



Photoemission intensity: $I(k,\omega)=I_0\,|M(k,\omega)|^2 f(\omega)\,A(k,\omega)$

Single-particle spectral function

$$A(\mathbf{k},\omega)=-\frac{1}{\pi}\frac{\Sigma''(\mathbf{k},\omega)}{[\omega-\epsilon_{\mathbf{k}}-\Sigma'(\mathbf{k},\omega)]^2+[\Sigma''(\mathbf{k},\omega)]^2}$$

$A(\boldsymbol{k},\boldsymbol{\omega})$= Probability of adding or removing one electron at (**k**,$\boldsymbol{\omega}$); Lorentzian shape.

$\boldsymbol{f}(\boldsymbol{\omega})$= Fermi-Dirac distribution.

$\boldsymbol{\Sigma}(\mathbf{k},\boldsymbol{\omega}) = \boldsymbol{\Sigma}'(\mathbf{k},\boldsymbol{\omega}) + \boldsymbol{i}\,\boldsymbol{\Sigma}''(\mathbf{k},\boldsymbol{\omega})$**: the ''self-energy'' captures the effects of interactions**, i.e., electron-electron interaction, electron-phonon coupling, electron-impurity scattering… that determine the *intrinsic* quasiparticle spectrum or PES line shape

Interaction effects on ARPES spectra

Photoemission intensity: $I(k,\omega)=I_0\,|M(k,\omega)|^2 f(\omega)\,A(k,\omega)$

Single-particle spectral function

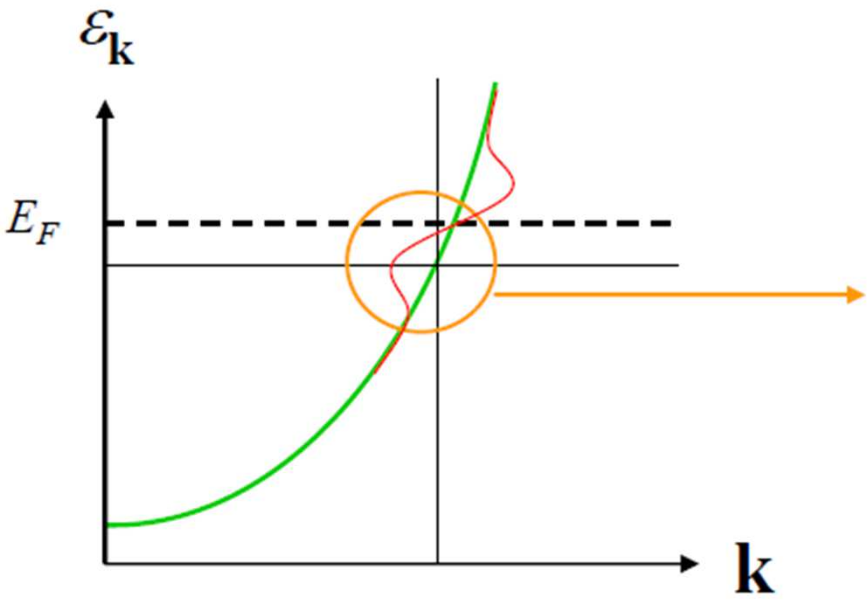
$$A(\mathbf{k},\omega) = -\frac{1}{\pi}\frac{\Sigma''(\mathbf{k},\omega)}{[\omega-\epsilon_{\mathbf{k}}-\Sigma'(\mathbf{k},\omega)]^2+[\Sigma''(\mathbf{k},\omega)]^2}$$

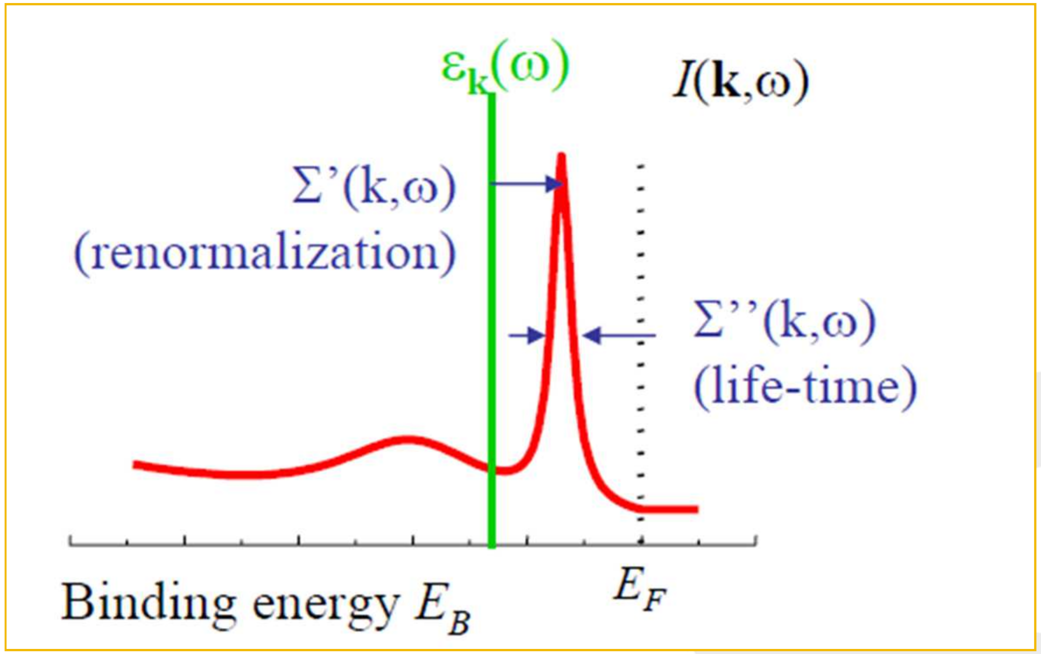
$$|E_B| \equiv \hbar\omega,\ \hbar = 1$$

Σ' ⟶ Energy renormalization

Σ'' ⟶ Inverse life-time of dressed particle (quasiparticle)

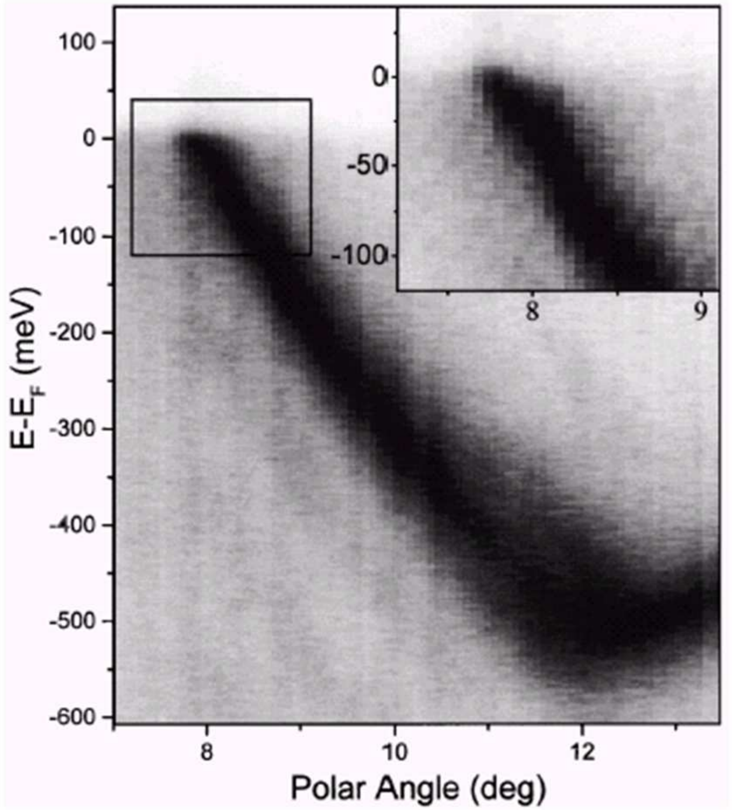
➡ **Many-body physics**

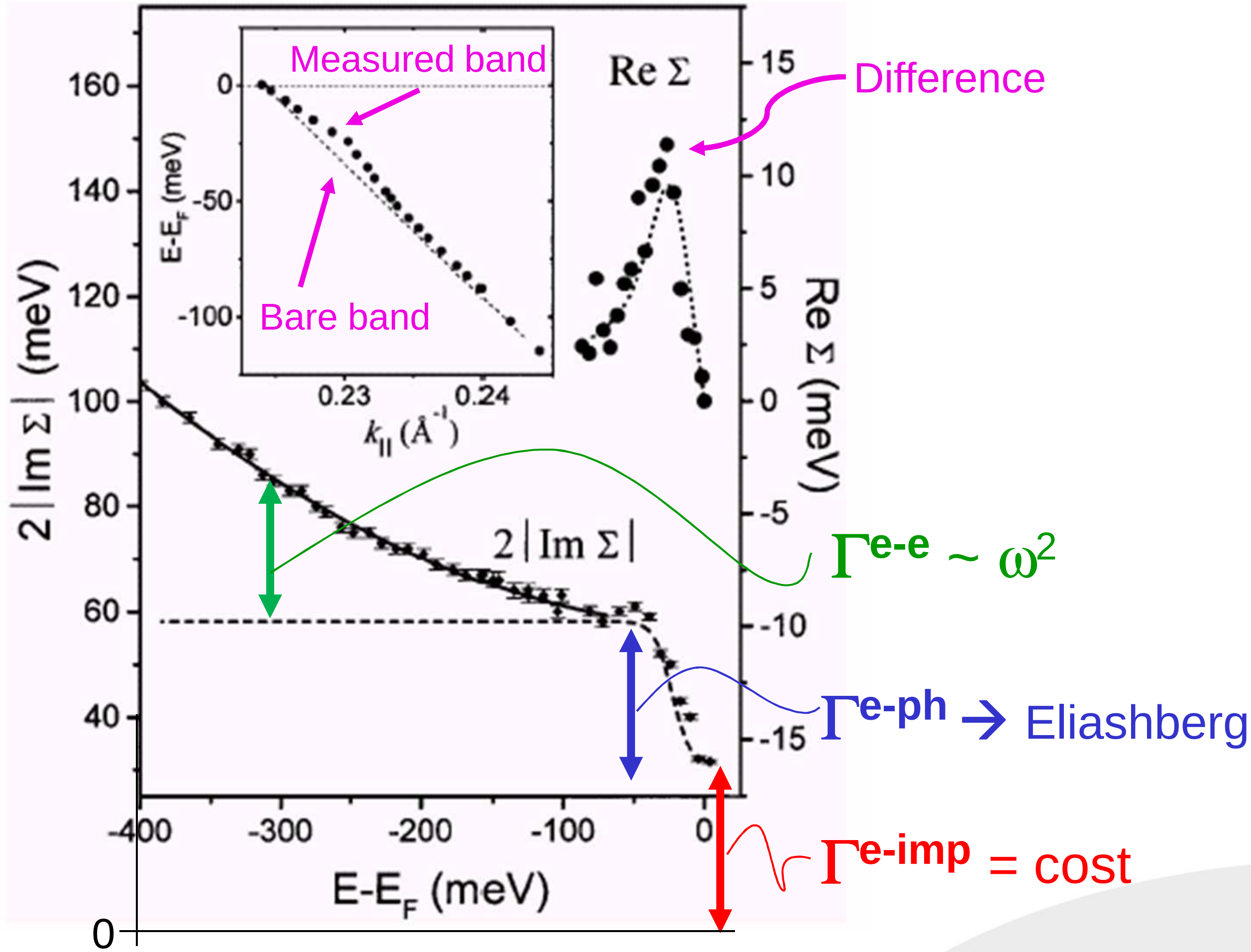




Many-body effects in ARPES

Surface state of Mo(110)





Bare band: ReΣ = 0

Measured band: ReΣ = finite

2|ImΣ| = FWHM of spectral peak, measurable in the same spectra

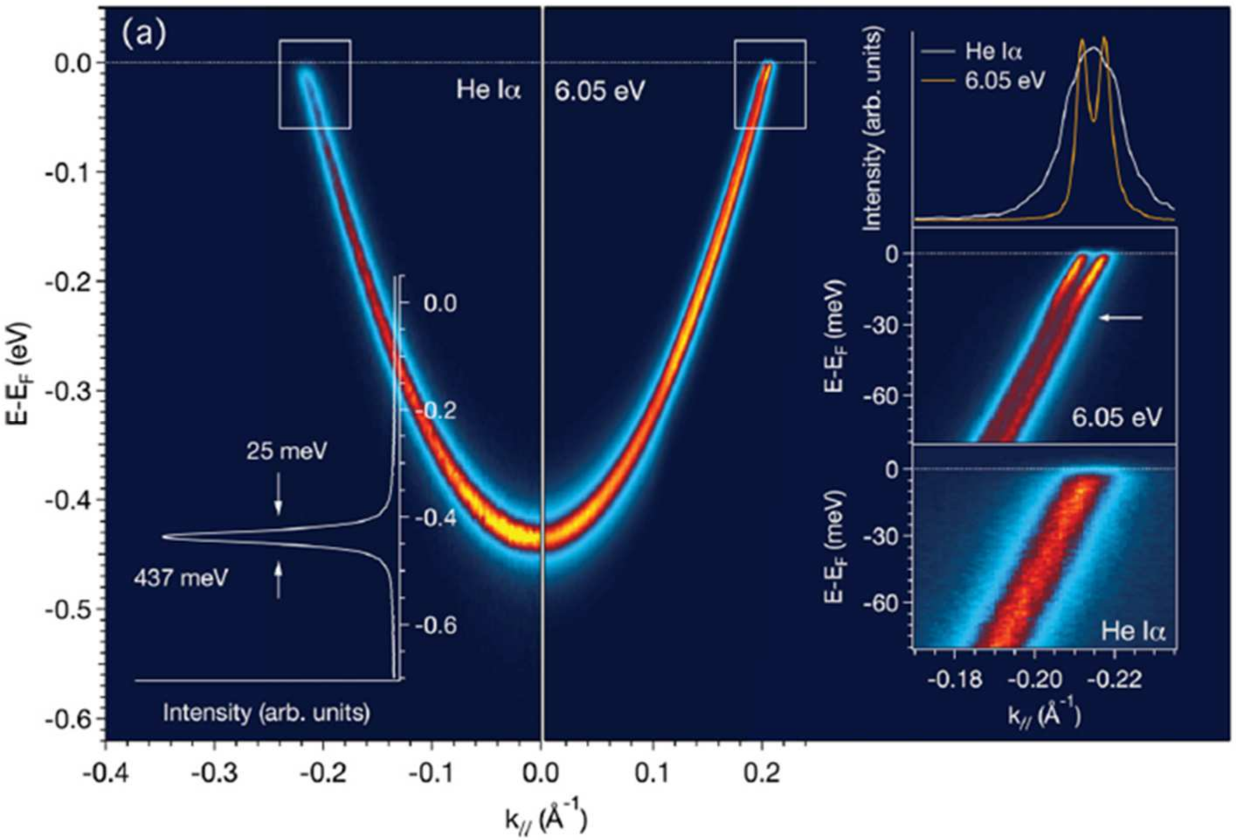
ImΣ and **ReΣ** related through **Kramers-Kronig** relations

Valla *et al.*, Phys. Rev. Lett. 83, 2085 (1999)

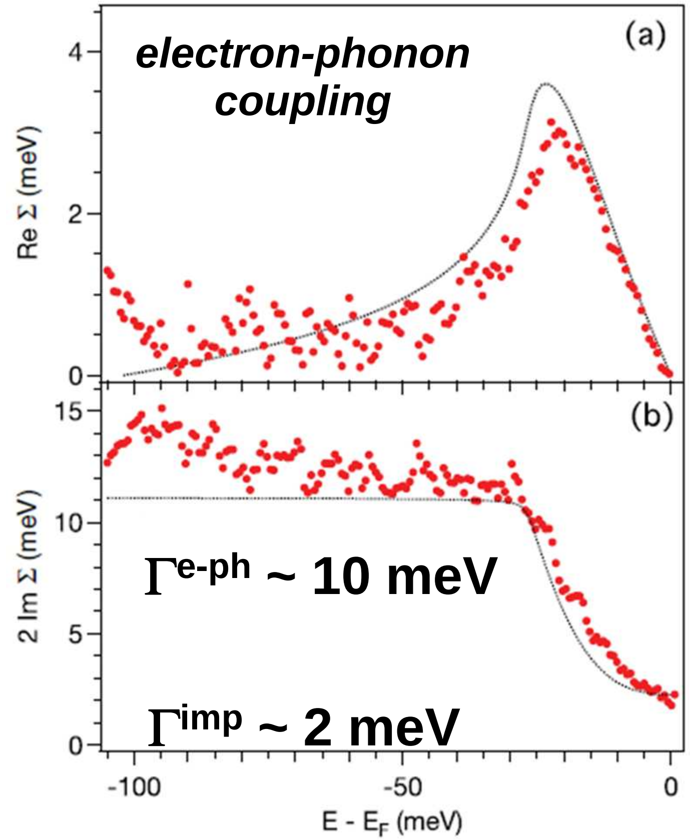
Many-body effects in ARPES

Surface state of Cu(111)

Tamai *et al.*, Phys. Rev. B 87, 075113 (2013)



''kink'' analysis close to E_F



$$m^* = 0.412\, m$$

E_0 = 437 meV, Γ_i = 25 meV → τ_i = 31 fs at $k_{||}$=0

limited mainly by electron–electron scattering events

ω_D **= 27 meV**

λ = 0.16

$$m'^* = (1 + \lambda)\, m$$

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ARPES: The single-particle spectral function

Photoemission intensity: $I(k,\omega)=I_0\,|M(k,\omega)|^2 f(\omega)\,A(k,\omega)$

Single-particle spectral function

$$A(\mathbf{k},\omega) = -\frac{1}{\pi}\frac{\Sigma''(\mathbf{k},\omega)}{[\omega-\epsilon_{\mathbf{k}}-\Sigma'(\mathbf{k},\omega)]^2+[\Sigma''(\mathbf{k},\omega)]^2}$$

Σ’ and **Σ’’** related through **Kramers-Kronig** relations

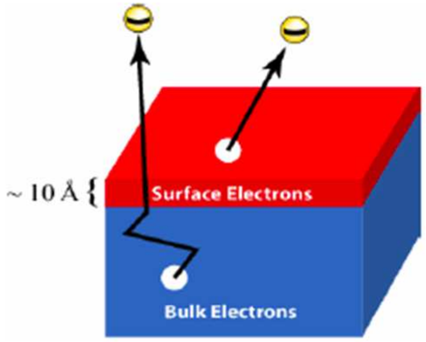
- **In practise, an experimentalist does not have to be an expert in the many-body physics.**
- **One can often look up the self-energy function and use it to simulate spectra.**
- **Theorists can easily look up experimental self-energies and compare to their models.**

ARPES

Advantages

- **Direct information about the electronic states!**
- Straightforward comparison with theory - little or no modeling.
- High-resolution information about **BOTH energy** and **momentum**
  $\rightarrow$ band structure $E(\mathbf{k})$
  $\rightarrow$ Fermi surface $\mathbf{k}(E_F)$
- Sensitive to "**many-body**" effects
  $\rightarrow$ spectral function $A^{<}(\mathbf{k},E)$
  (if photohole localized $\perp$ surface)
- **Surface-sensitive probe**

Limitations



- **Not bulk sensitive**
- 3dim k-space information difficult to obtain
- Requires clean, atomically flat surfaces in **ultra-high vacuum**
- Cannot be studied as a function of pressure (or magnetic field)

Adapted from Kyle Shen

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Thanks for your attention!

www.elettra.eu