Fundamental and applications of ARPES: From Einstein's legacy to nowadays state-of-the-art instruments

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SOLEIL SYNCHROTRON

OUTLINE

- **Brief introduction**

  - History of photoemission and angle resolved photoemission
  - Theoretical bases

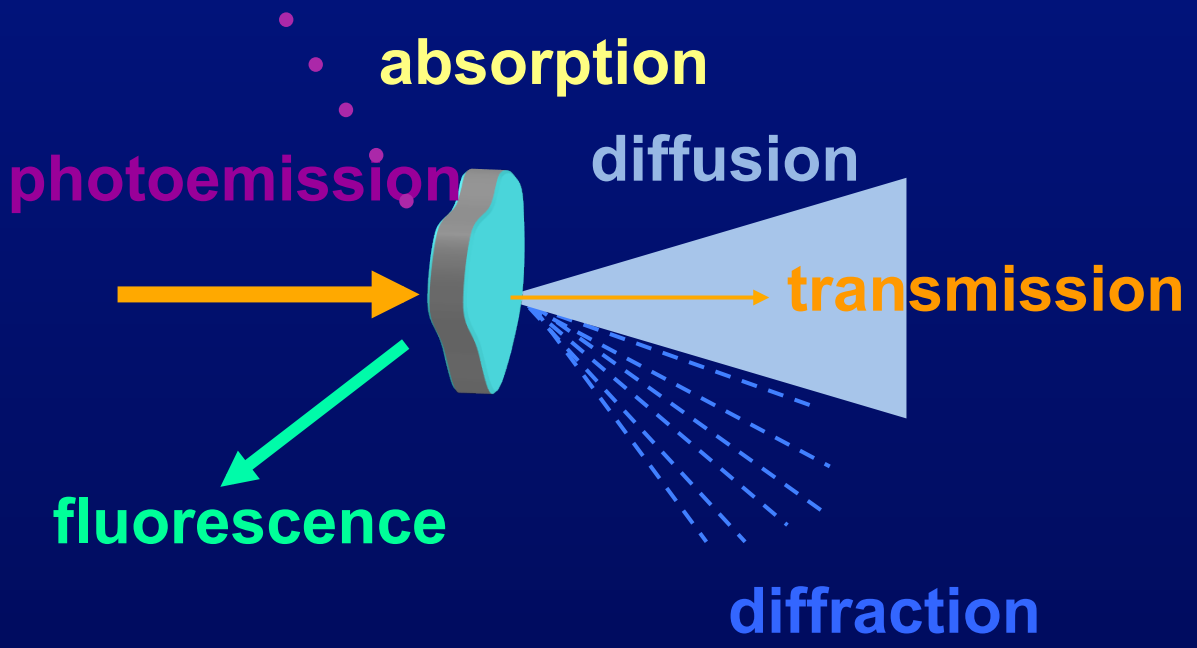
- **Examples and latest results of the electronic structure of complex materials**

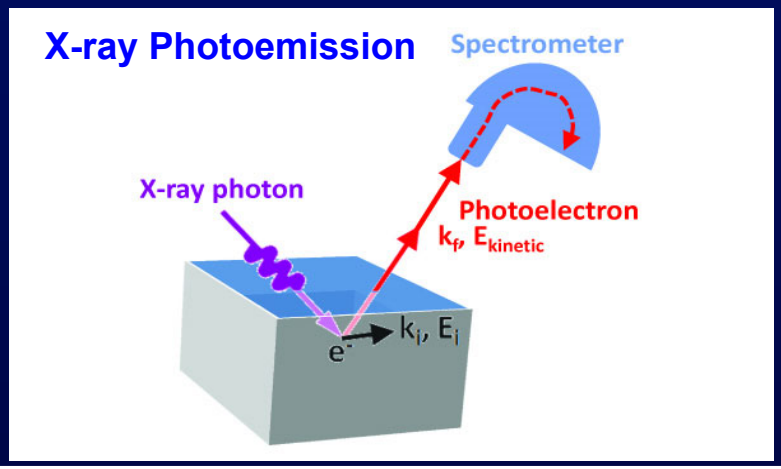
- **Technical developments**

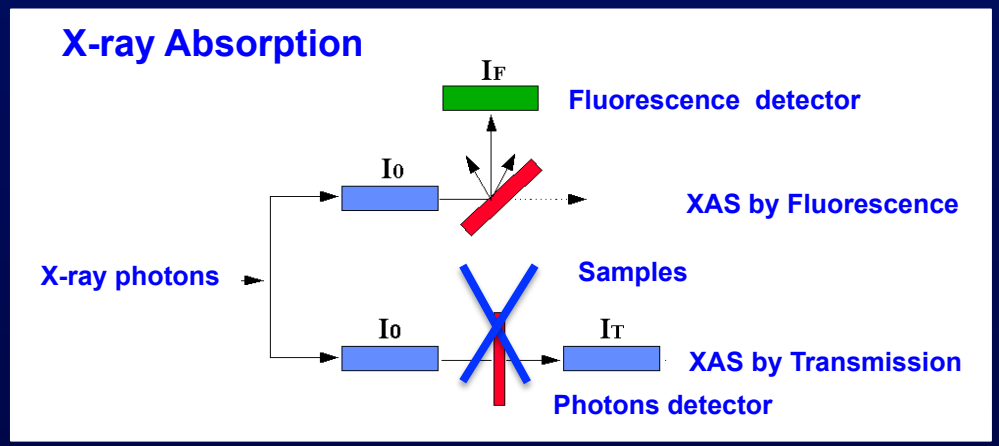
- **Conclusion and perspectives of ARPES Part 1**

SOLEIL SYNCHROTRON

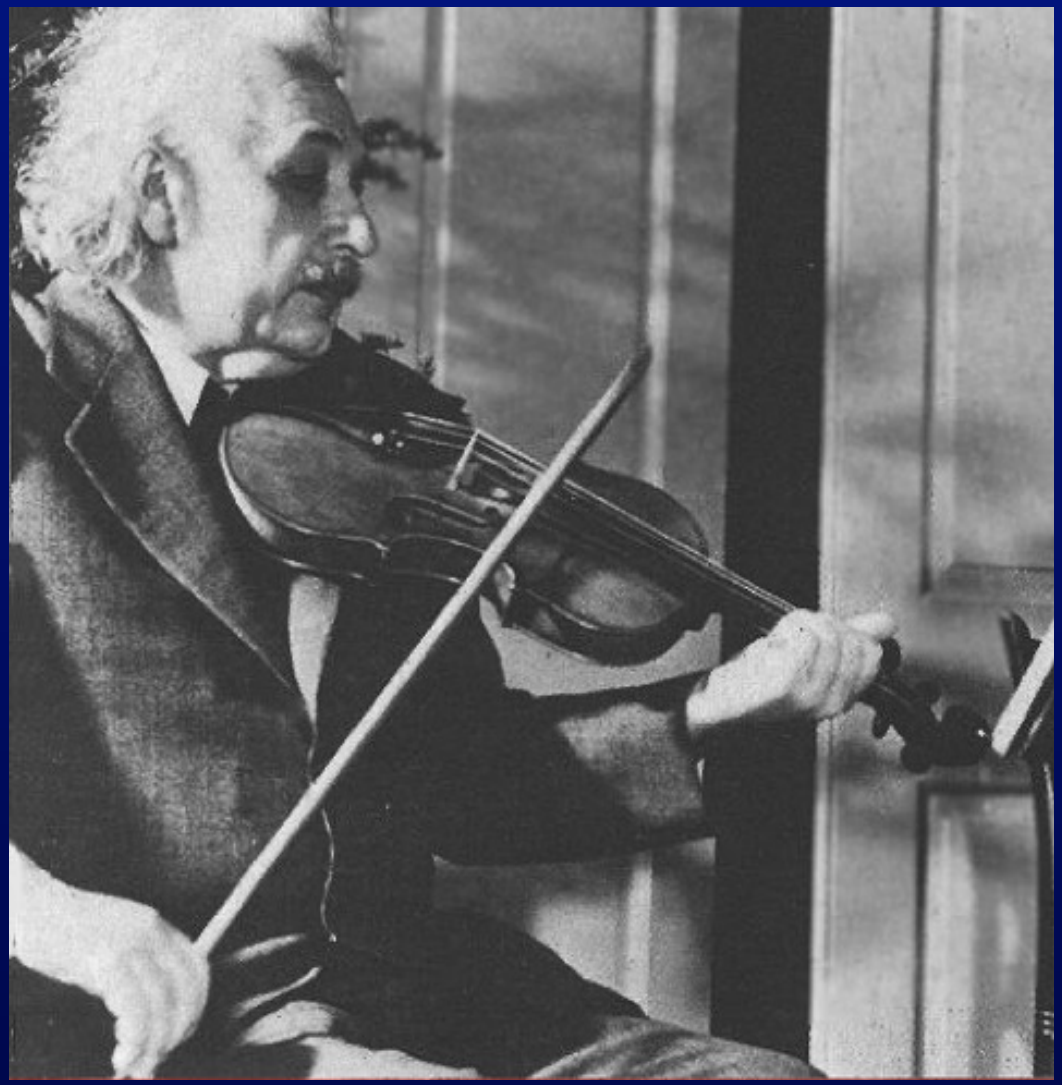
Light interaction with matter







History



Photoemission was first detected by
Hertz 1887
W. Hallwachs (1888)
P. Lenard (1902)

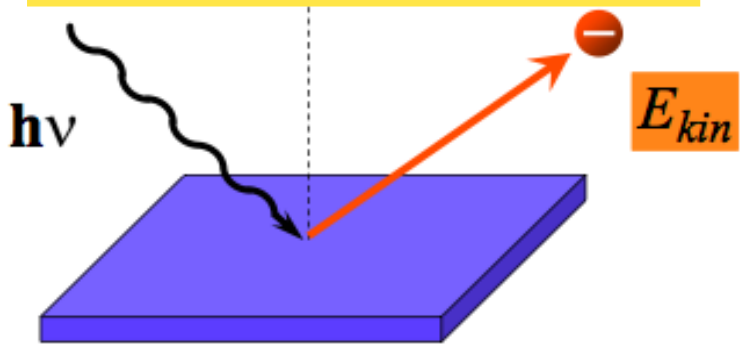
Explained by Einstein in 1905

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

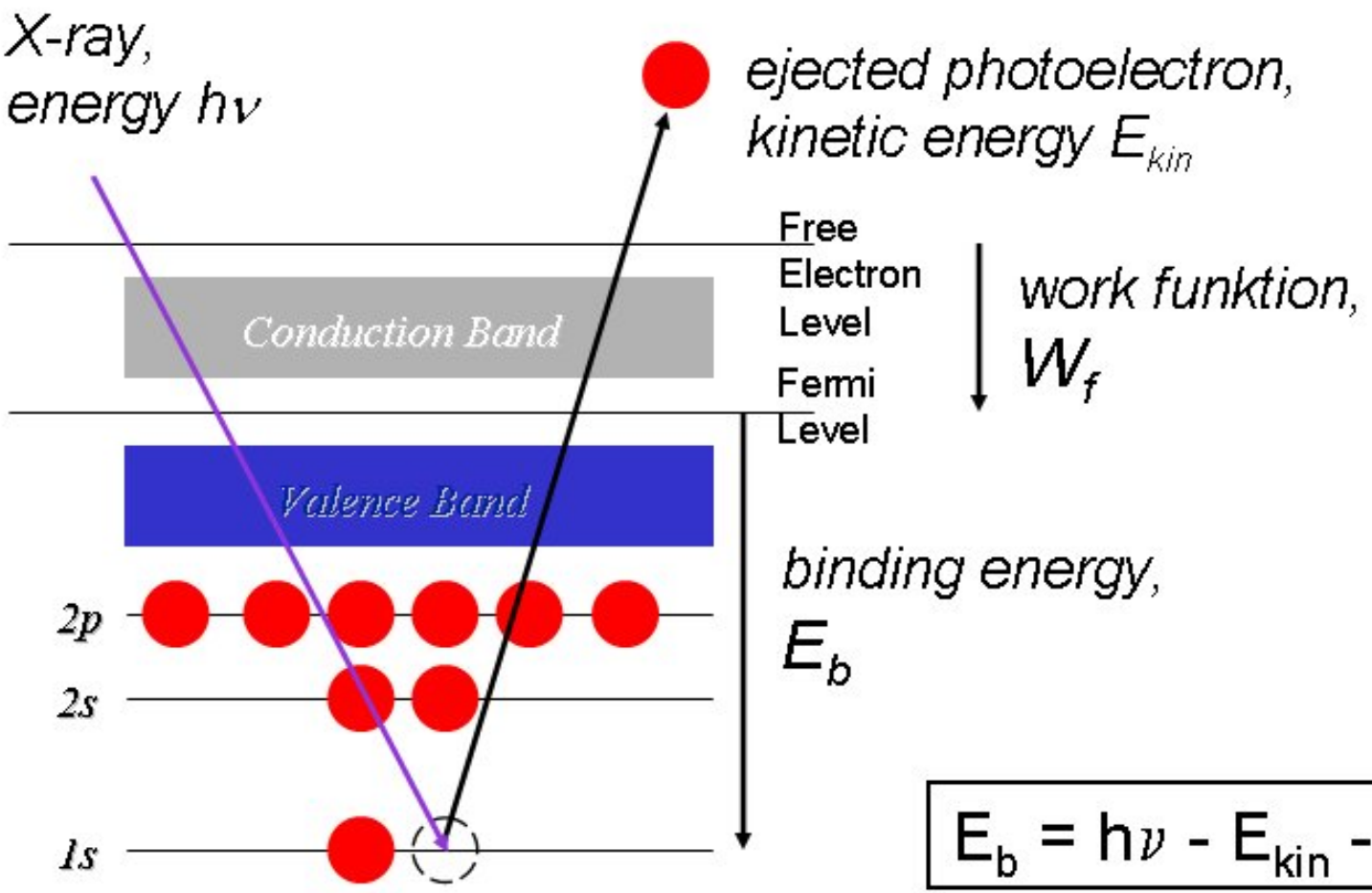
Die kinetische Energie solcher Elektronen ist

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

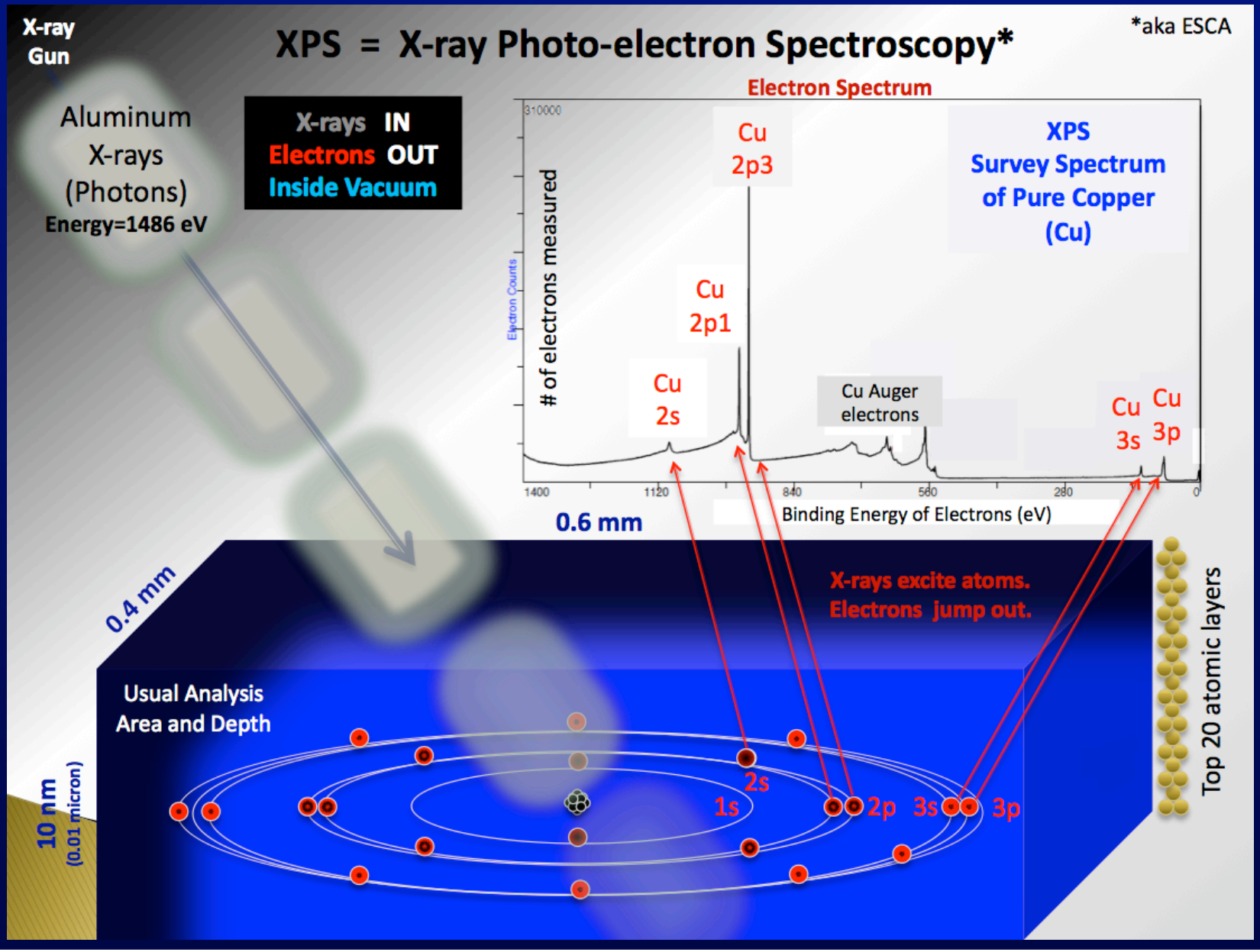
$$E_{kin} = h\upsilon - \varphi - BE$$



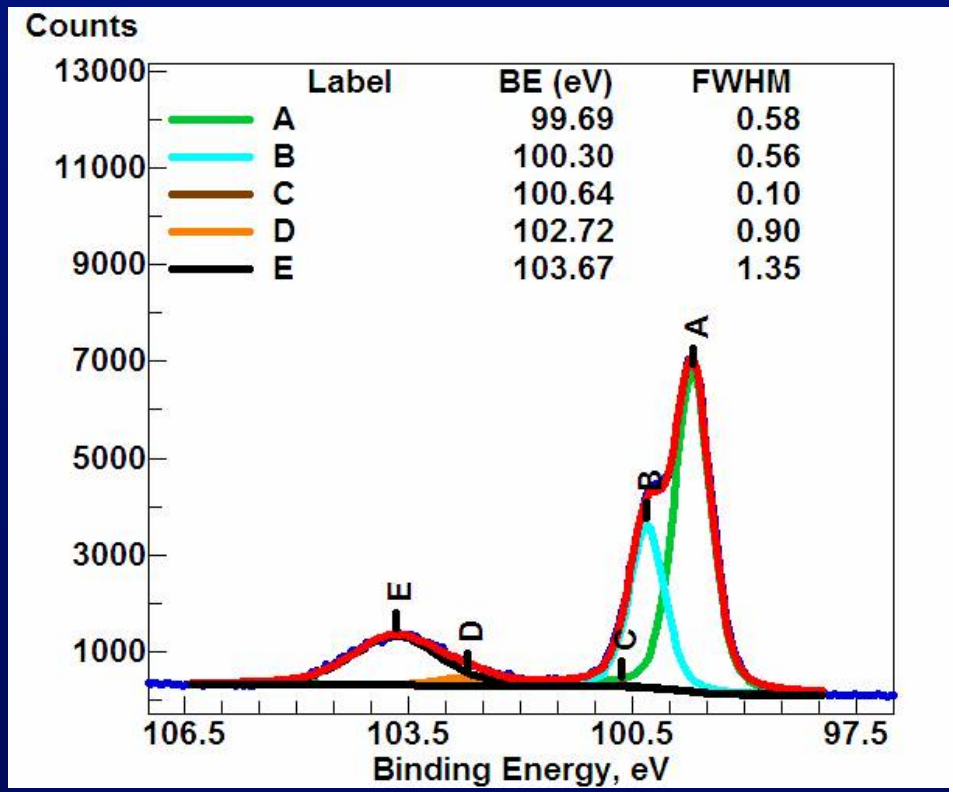
Principle of XPS



$$E_b = h\nu - E_{kin} - W_f$$


X-ray Gun
XPS = X-ray Photo-electron Spectroscopy*
*aka ESCA
Aluminum X-rays (Photons)
Energy=1486 eV
X-rays IN
Electrons OUT
Inside Vacuum
Electron Spectrum
# of electrons measured
Cu 2p3
Cu 2p1
Cu 2s
Cu Auger electrons
Cu 3s
Cu 3p
XPS Survey Spectrum of Pure Copper (Cu)
Binding Energy of Electrons (eV)
0.6 mm
0.4 mm
X-rays excite atoms. Electrons jump out.
Usual Analysis Area and Depth
10 nm
(0.01 micron)
1s
2s
2p
3s
3p
Top 20 atomic layers

Relative binding energies and ionization cross



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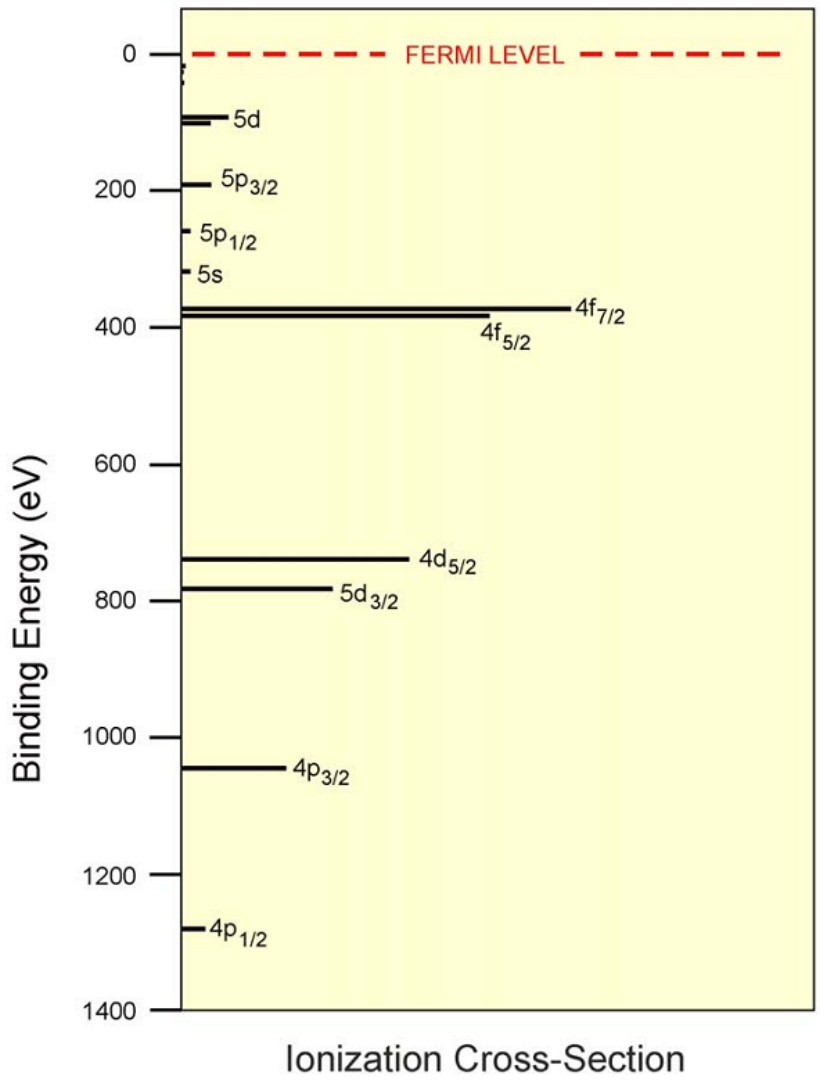


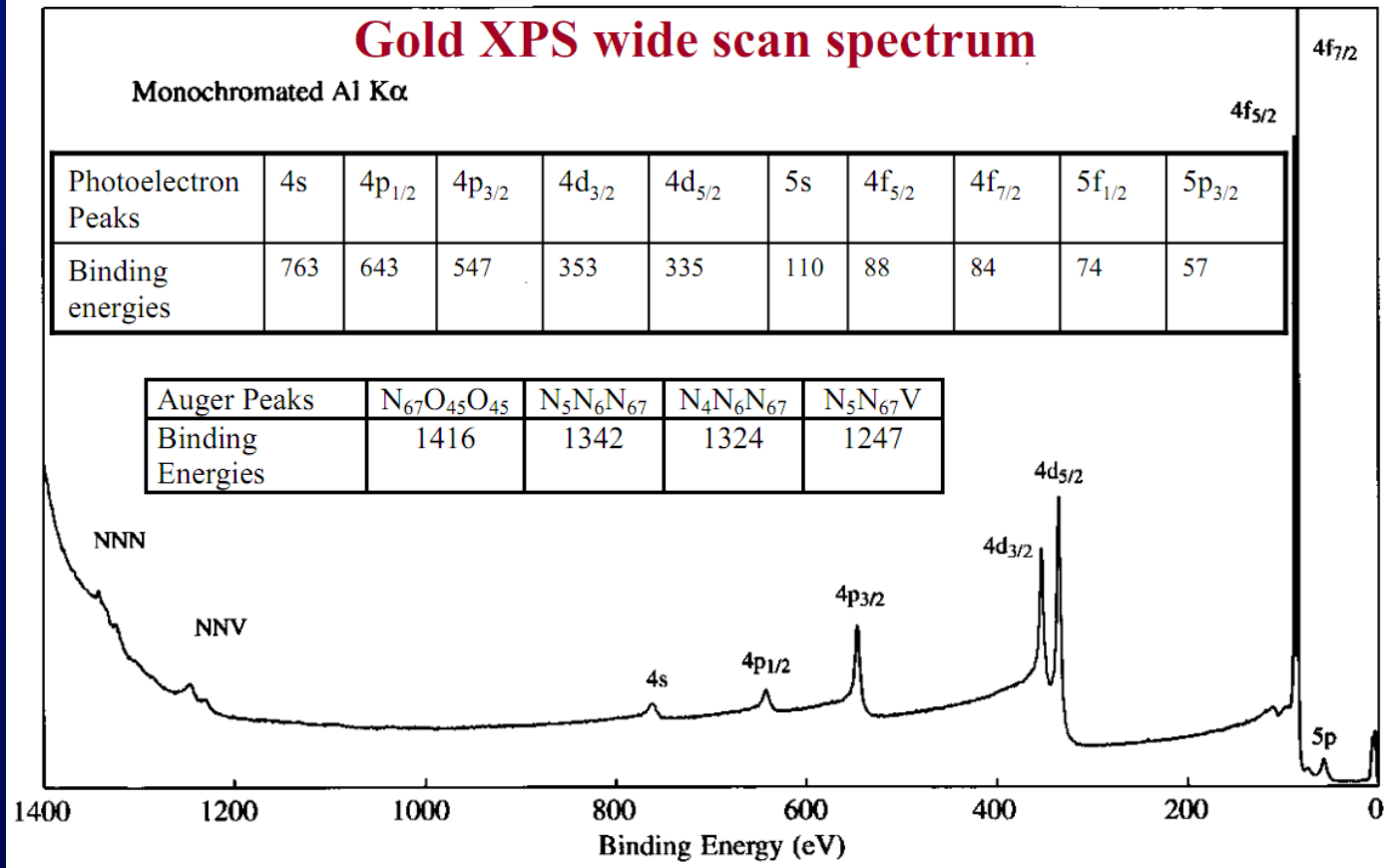
Qualitative analysis

Gold XPS wide scan spectrum

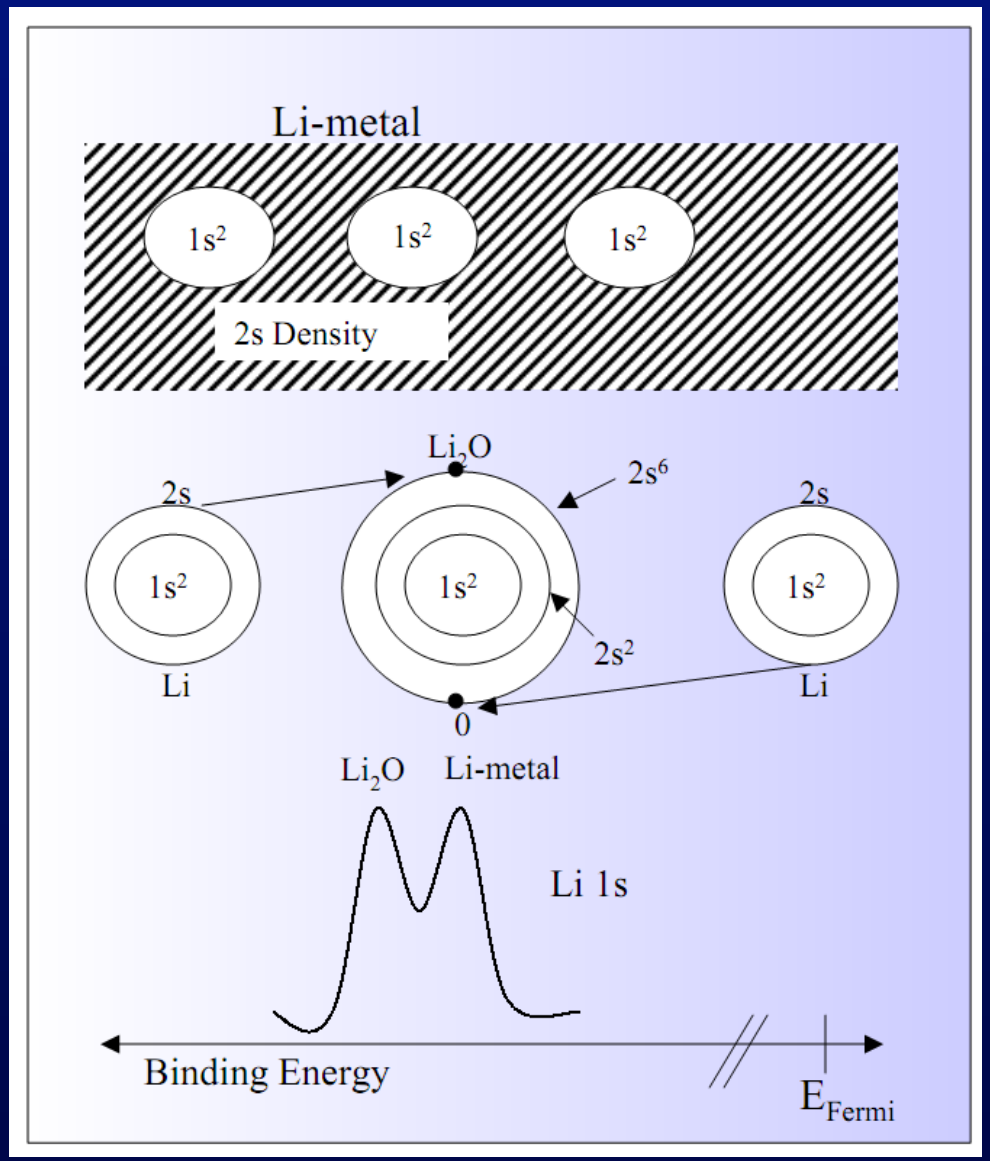
Monochromated Al Kα

Photoelectron Peaks	4s	$4p_{1/2}$	$4p_{3/2}$	$4d_{3/2}$	$4d_{5/2}$	5s	$4f_{5/2}$	$4f_{7/2}$	$5f_{1/2}$	$5p_{3/2}$
Binding energies	763	643	547	353	335	110	88	84	74	57

Auger Peaks	$N_{67}O_{45}O_{45}$	$N_5N_6N_{67}$	$N_4N_6N_{67}$	$N_5N_{67}V$
Binding Energies	1416	1342	1324	1247

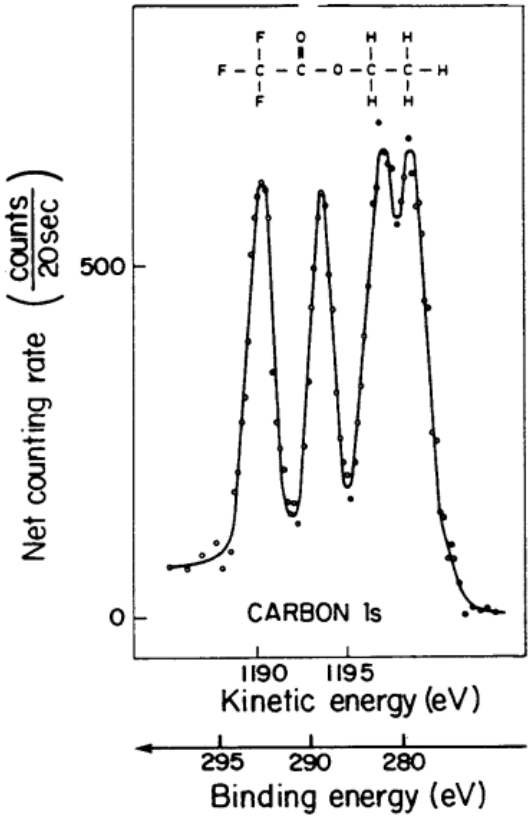


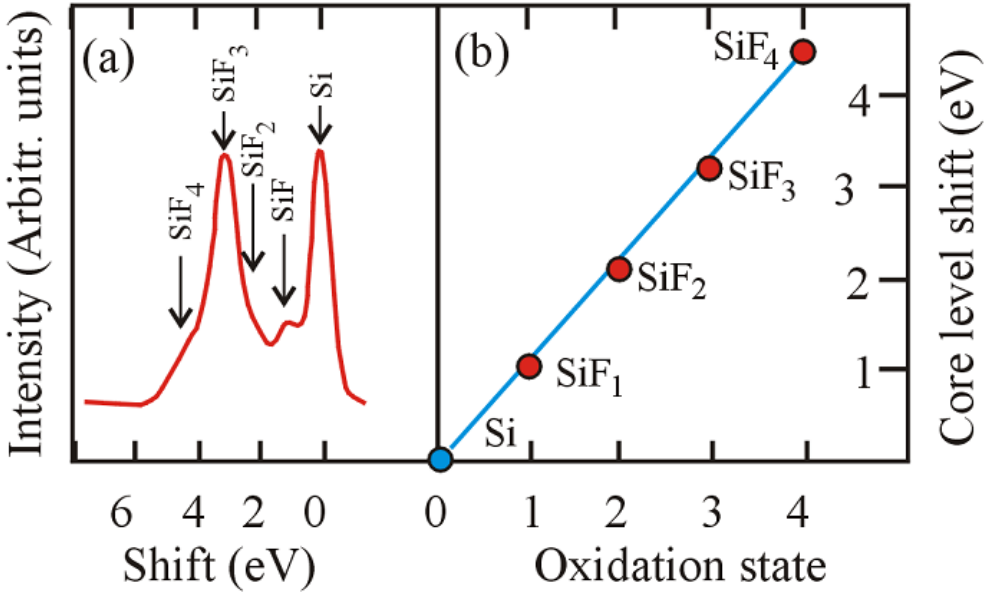
Chemical Shifts: Oxide Compared to Metal

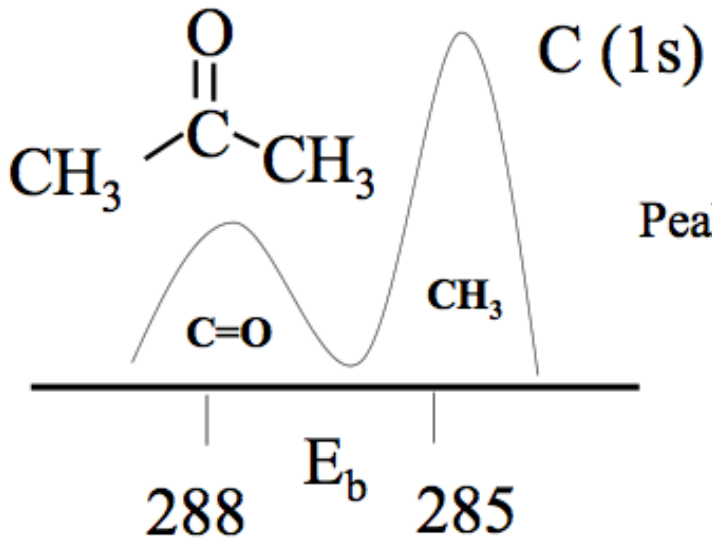


Binding Energy is lower for the metallic Li than the Li oxide, due to increased screening of the nucleus by 2s Conduction

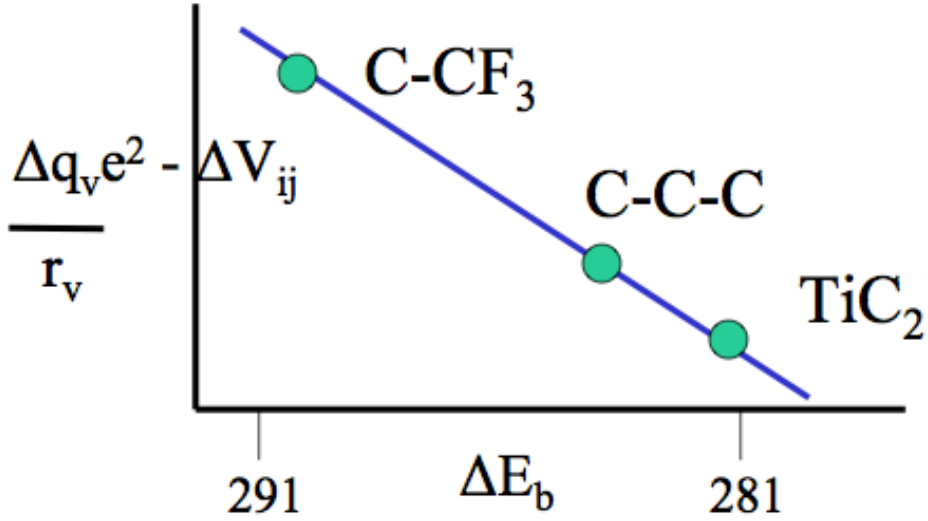
Examples of Chemical Shifts



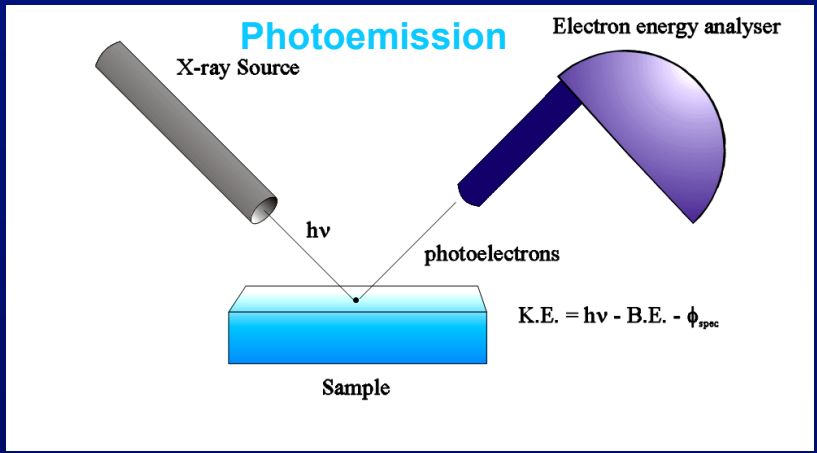


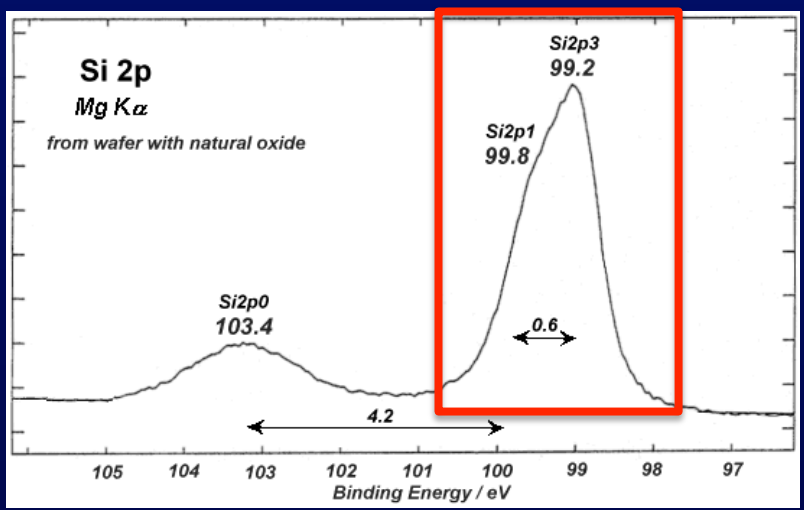


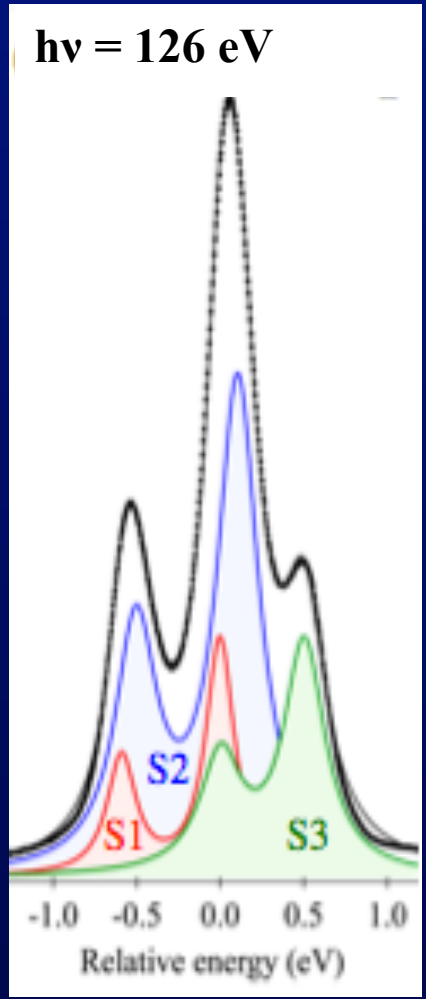
Peak width = 1.1-1.5 eV

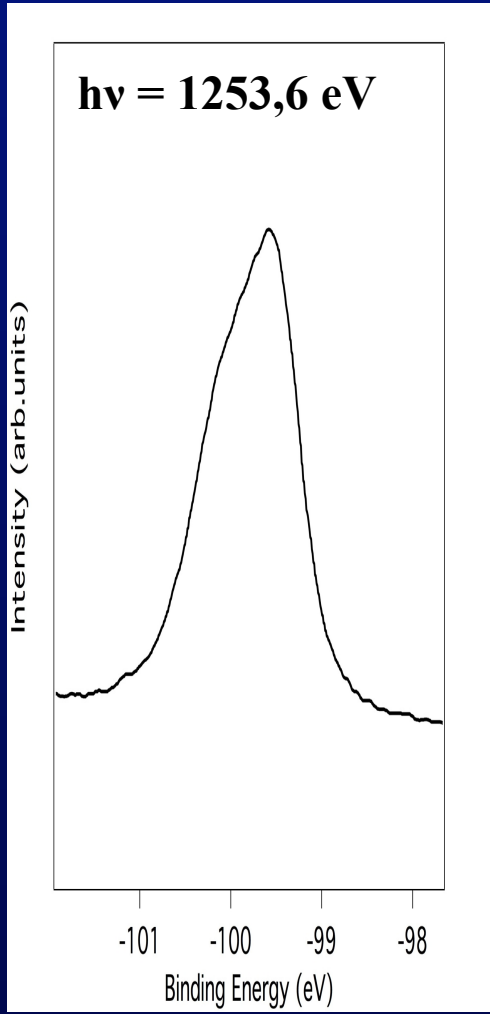


Why do we need Synchrotron radiation photoemission instead XPS?

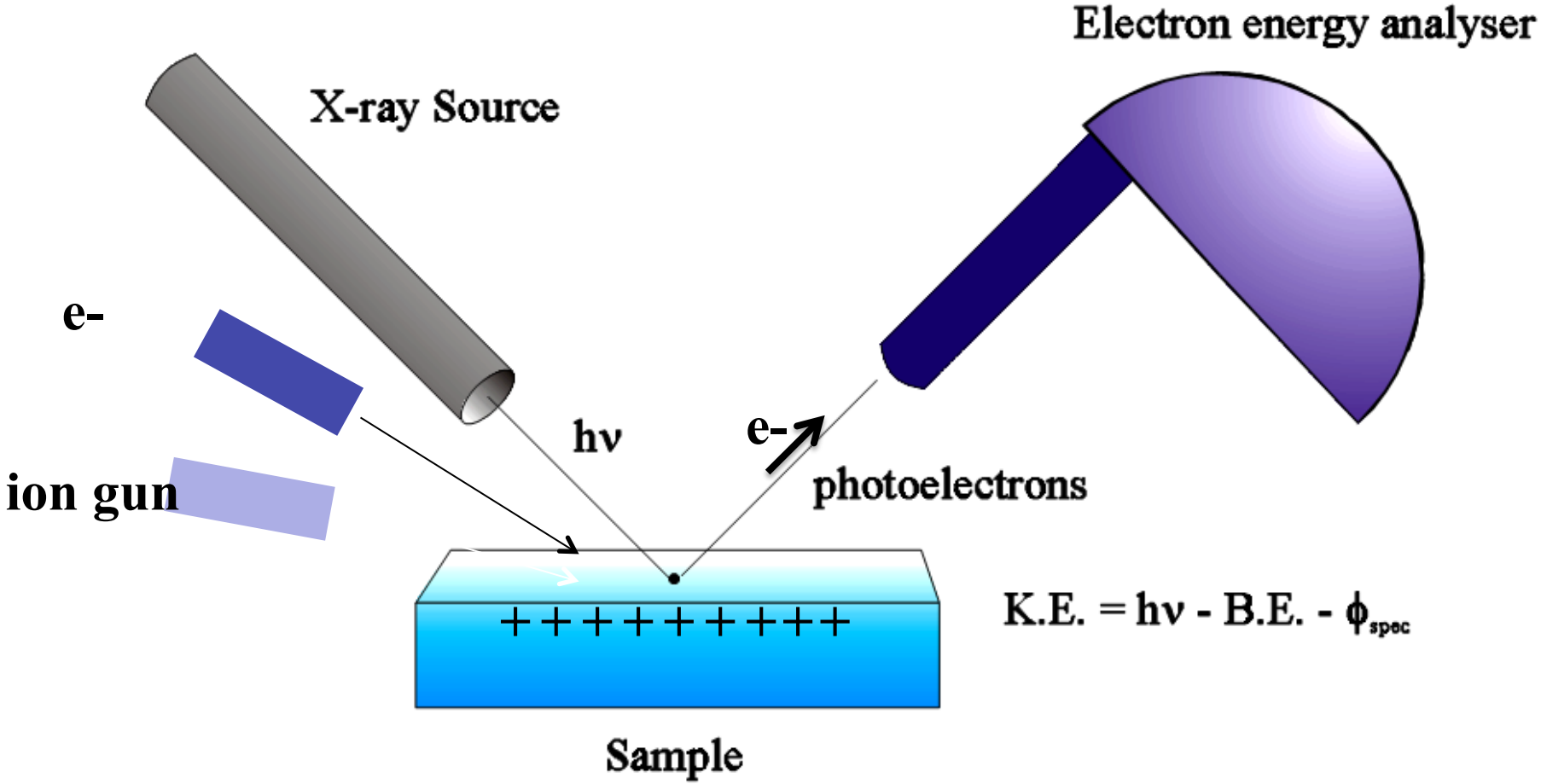








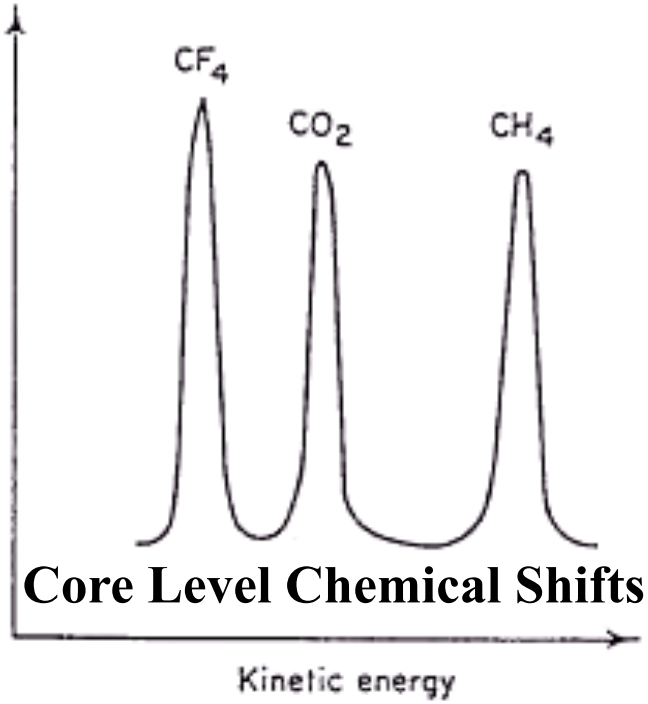
Photoelectron Spectroscopy Using Synchrotron Radiation



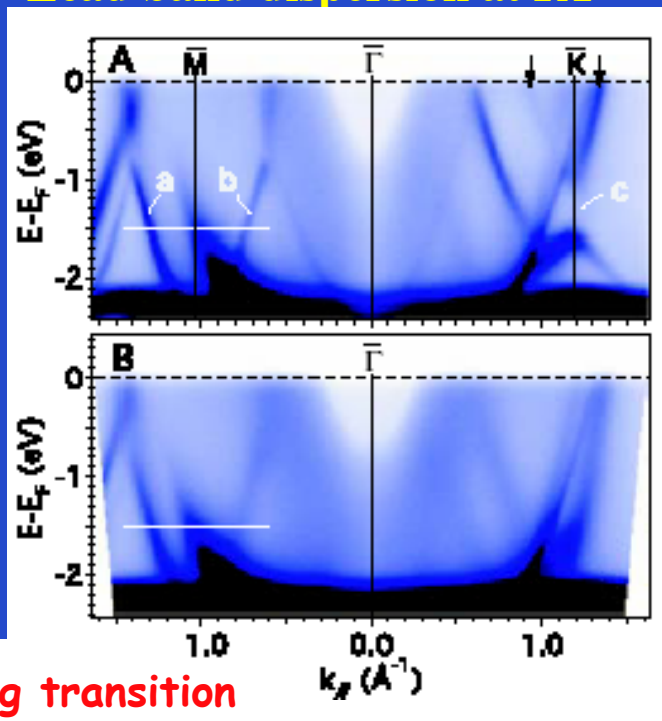
$$K.E. = h\nu - B.E. - \phi_{spec}$$

a qualitative and quantitative analysis …

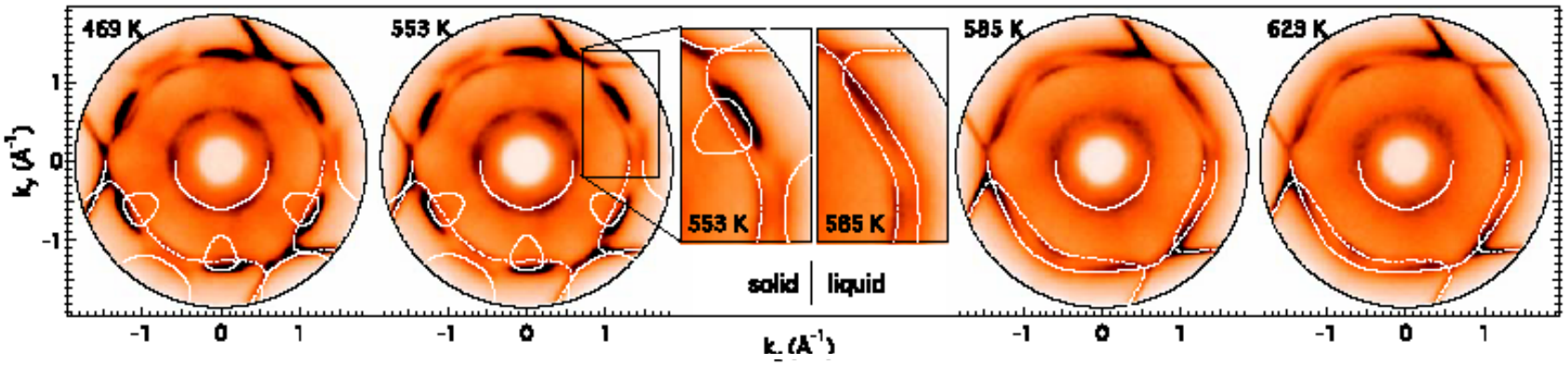
From early days to recent Photoemission results:



Lead band dispersion at RT

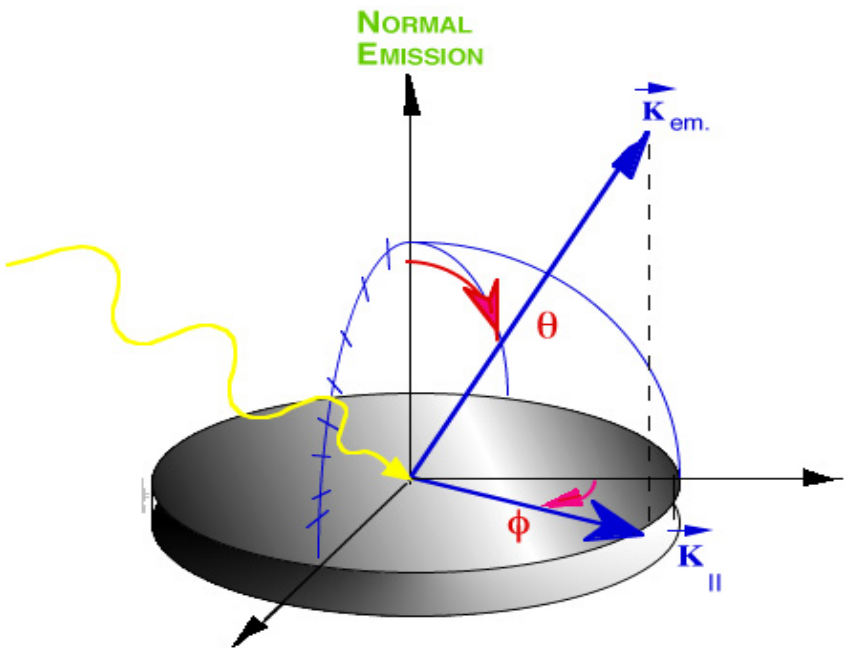


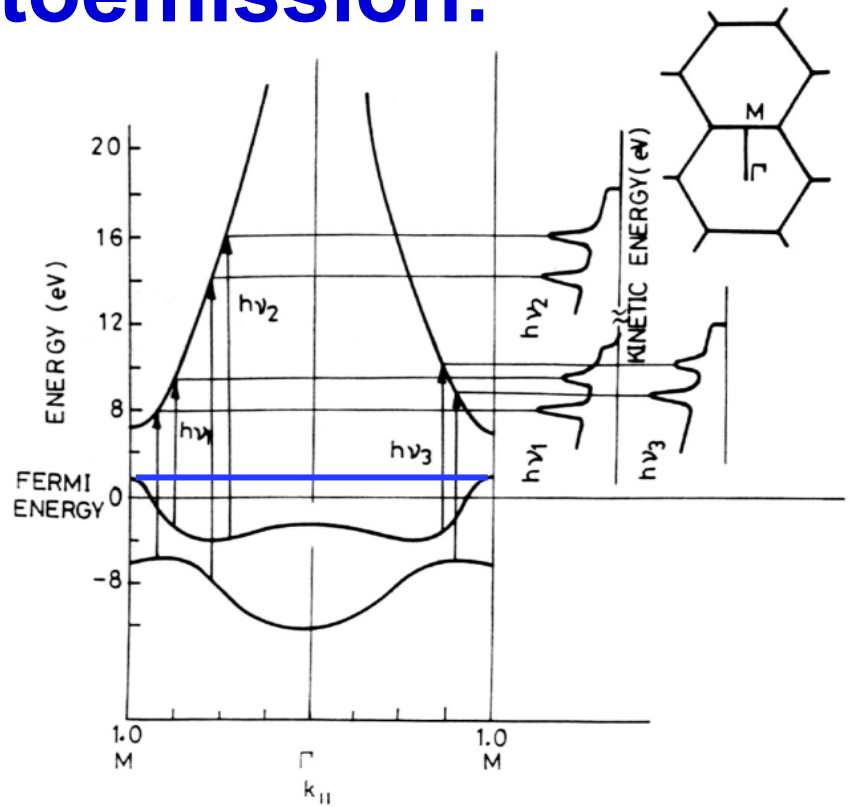
Evolution of the Fermi surface through the melting transition



Angle Resolved Photoemission:

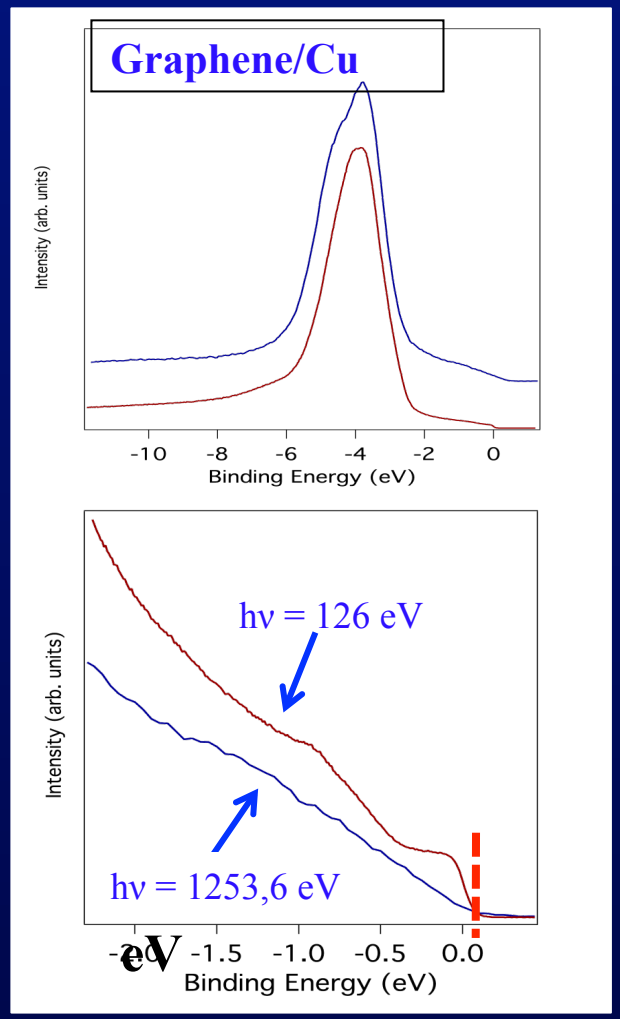
Photon:
- Energy
- Incidence
- Polarization

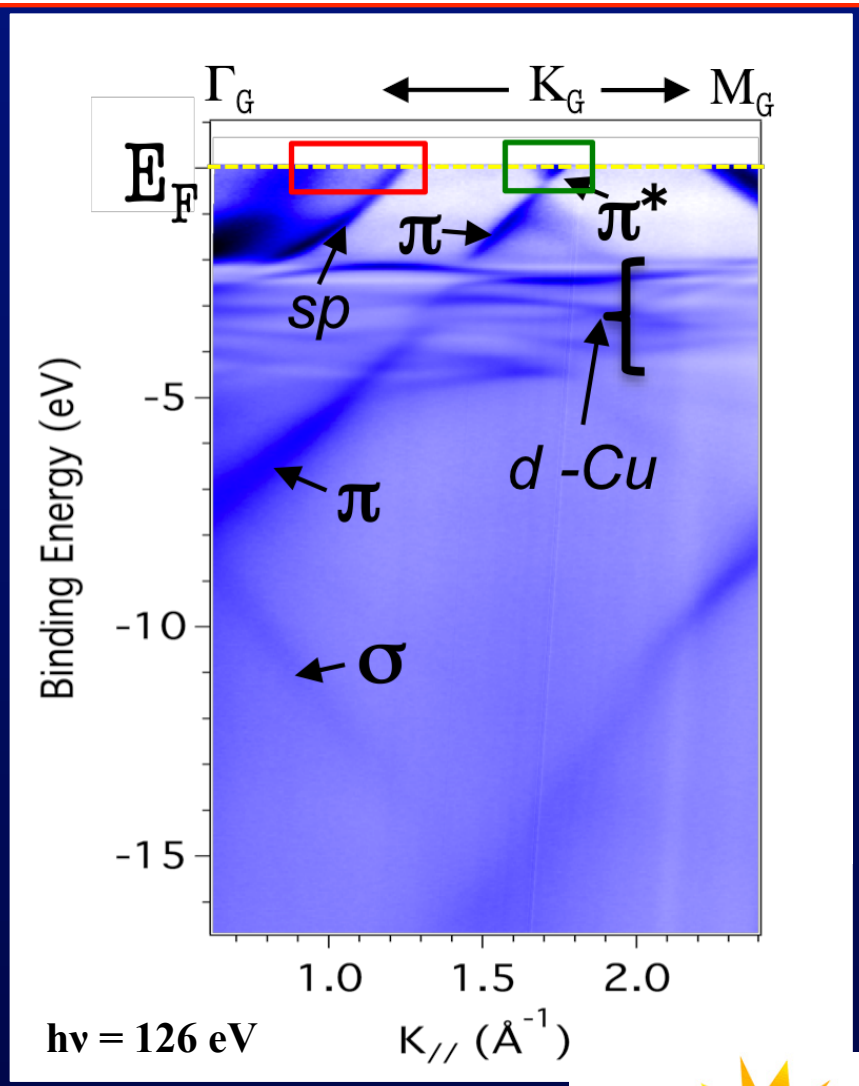




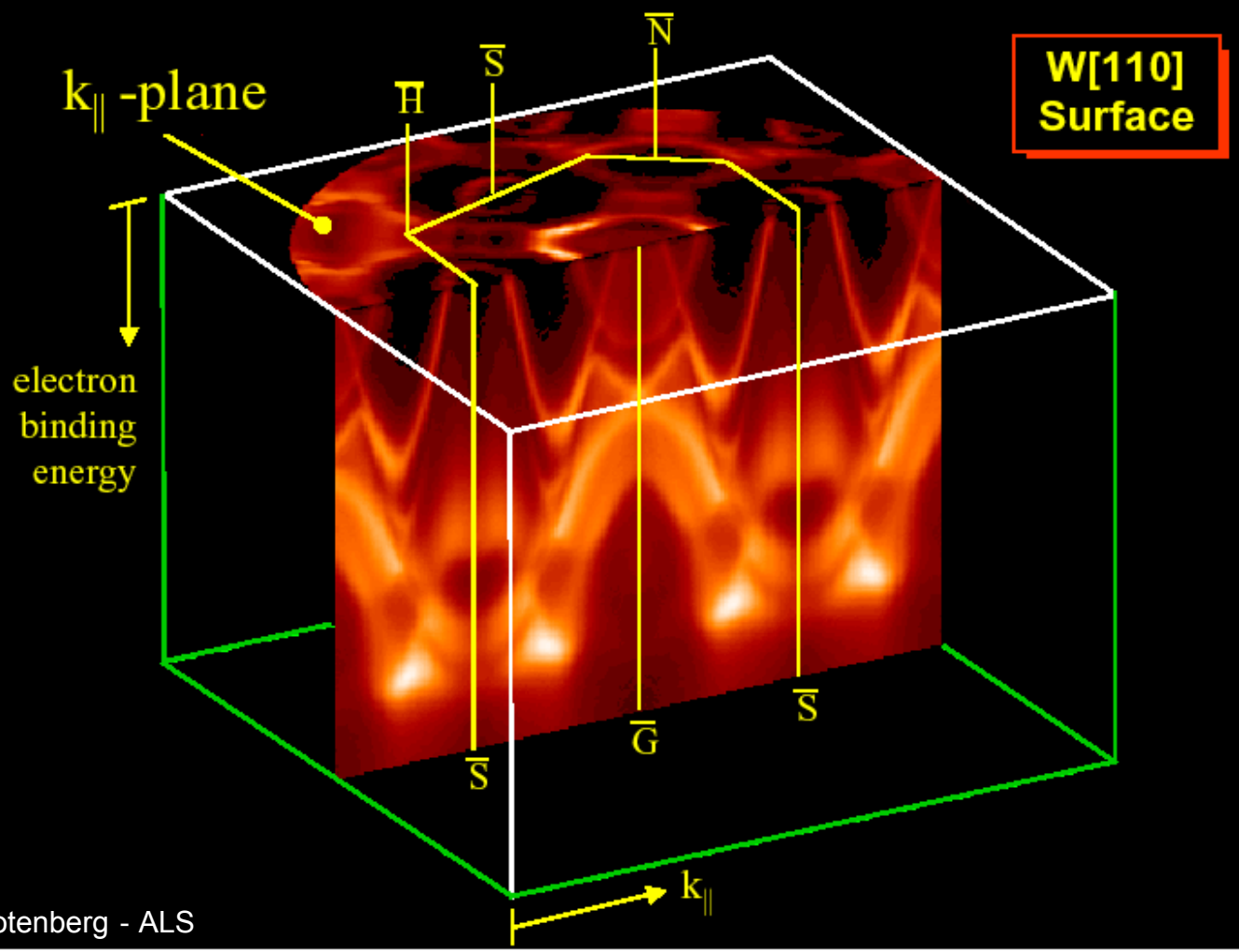
Electron:
- Energy
- Exit angle
- Spin

Valence band Photoemission: chemical bonding information



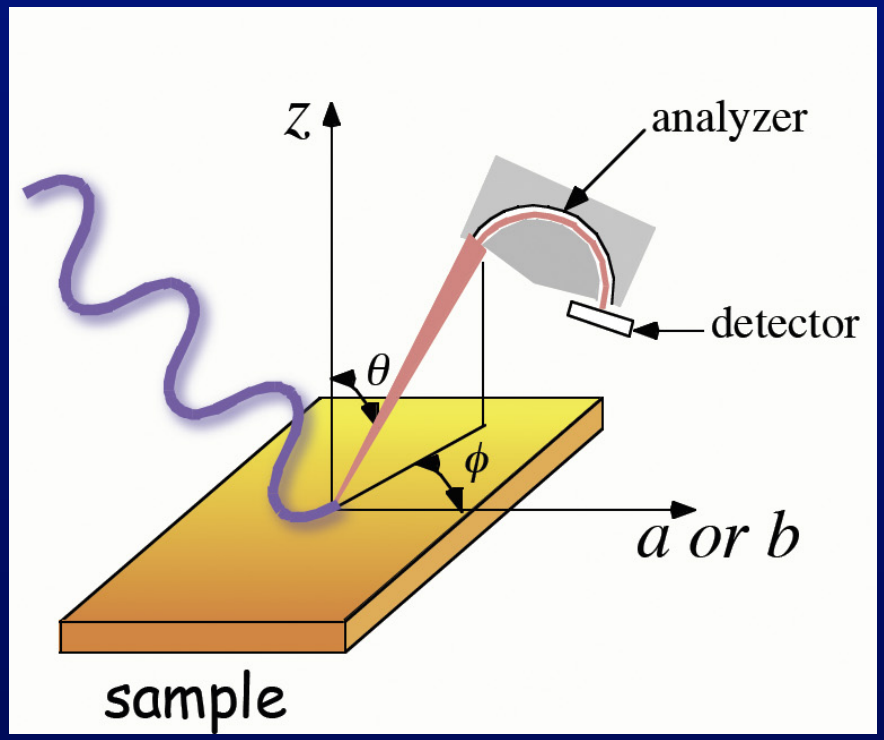


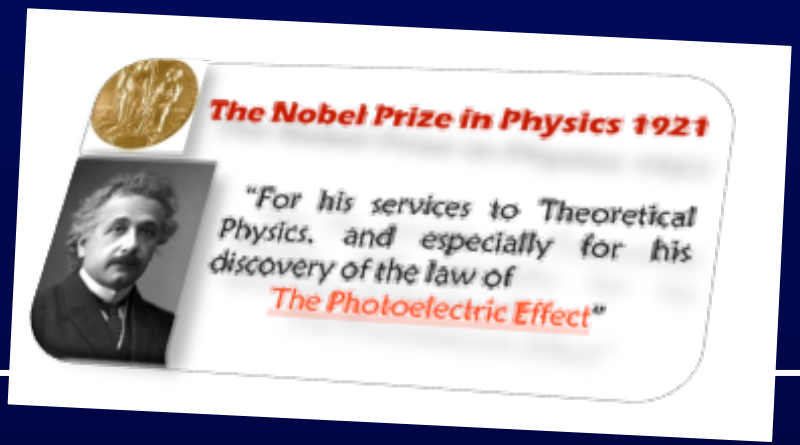
ARUPS FOR NON-INTERACTING SYSTEMS



Courtesy of Eli Rotenberg - ALS

Photoemission Spectroscopy

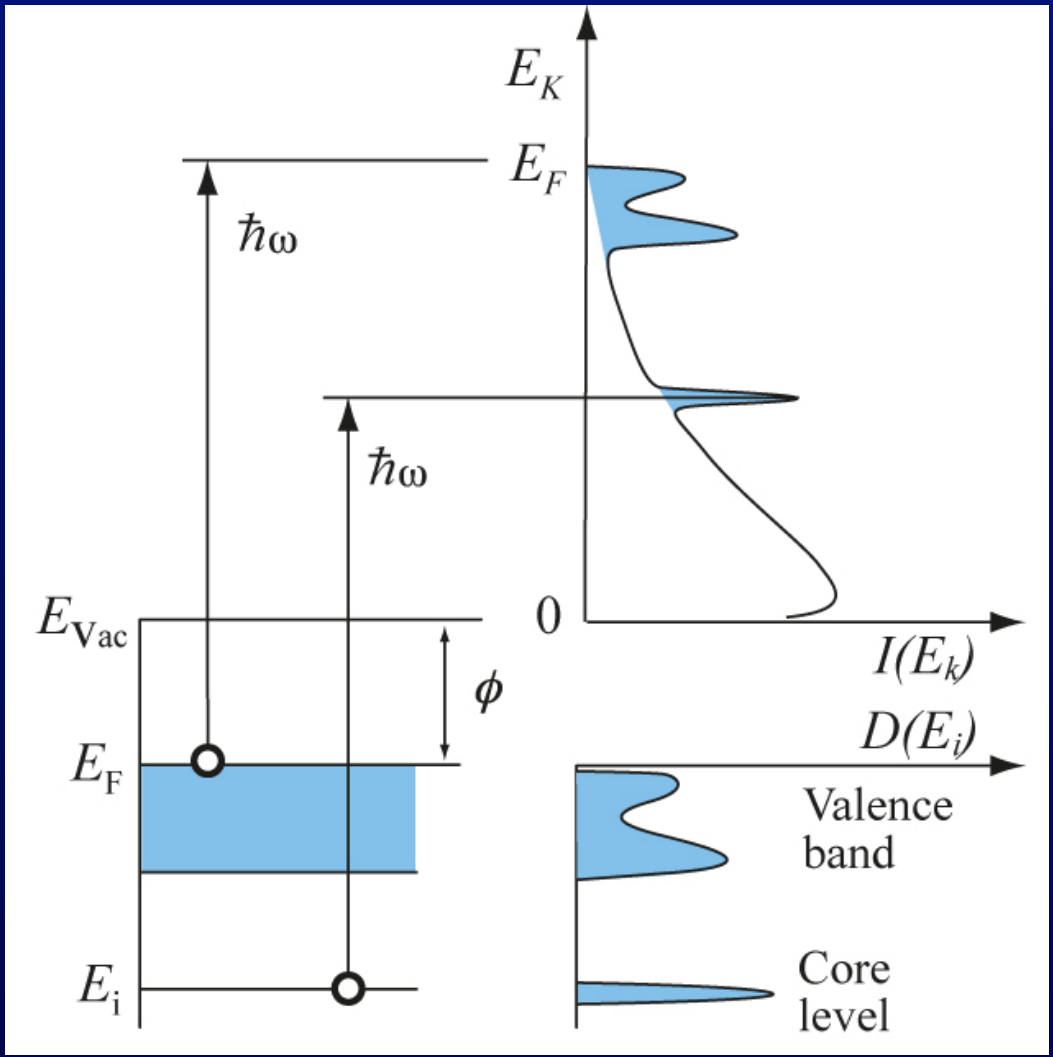


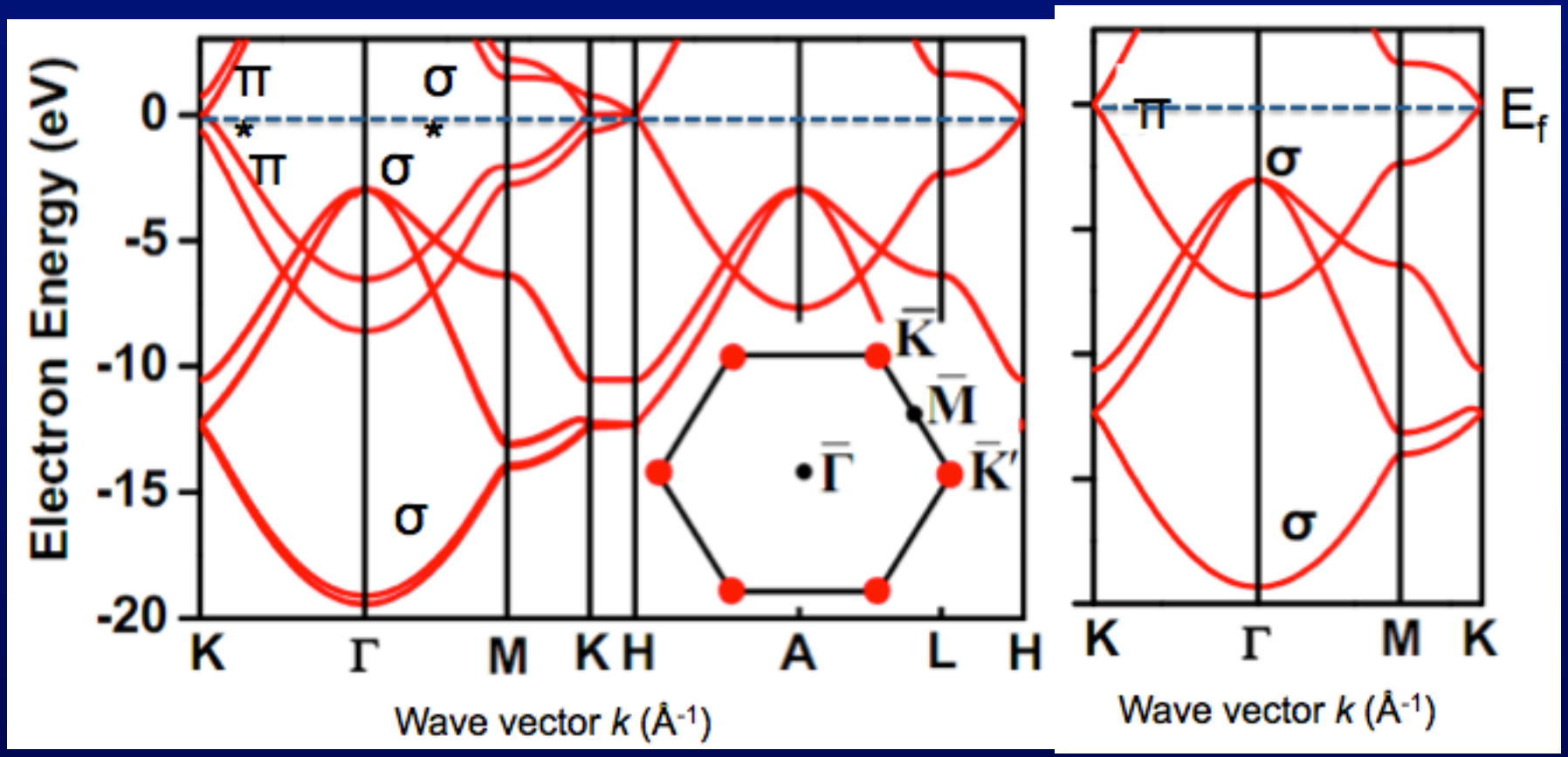


Photoelectrons emitted in real space
E_{kin}, ϑ and $I(E_{kin},\vartheta)$

Energy conservation
$BE = h\nu - \Phi - E_{kin}$
Momentum conservation
$p_{//} = \hbar\, k_{//} = \sqrt{(2m\, E_{kin})} \,.\, \sin\vartheta$

Electronic state in solid:
$\psi(BE, k_{//})$

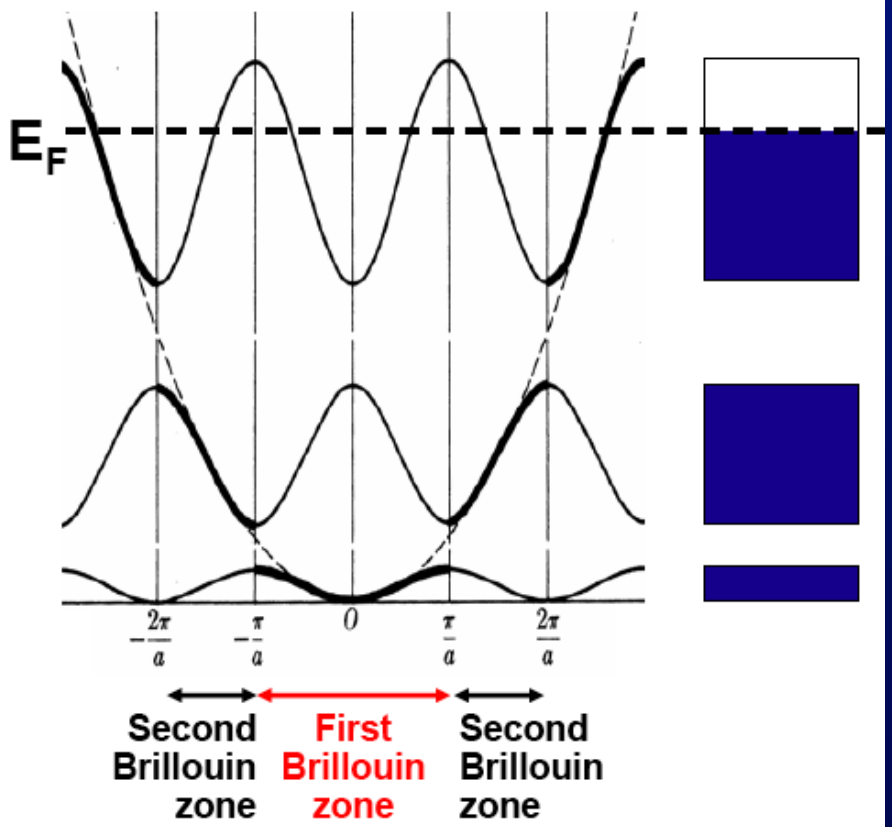

E_K
E_F
$\hbar\omega$
$\hbar\omega$
E_{Vac}
0
ϕ
$I(E_k)$
$D(E_i)$
E_F
Valence band
Core level
E_i


Electron Energy (eV)
0
-5
-10
-15
-20
π
σ
π*
σ*
σ
K̄
M̄
Γ̄
K̄′
K
Γ
M
K
H
A
L
H
Wave vector k (Å-1)
π
σ
σ
Ef
K
Γ
M
K
Wave vector k (Å-1)

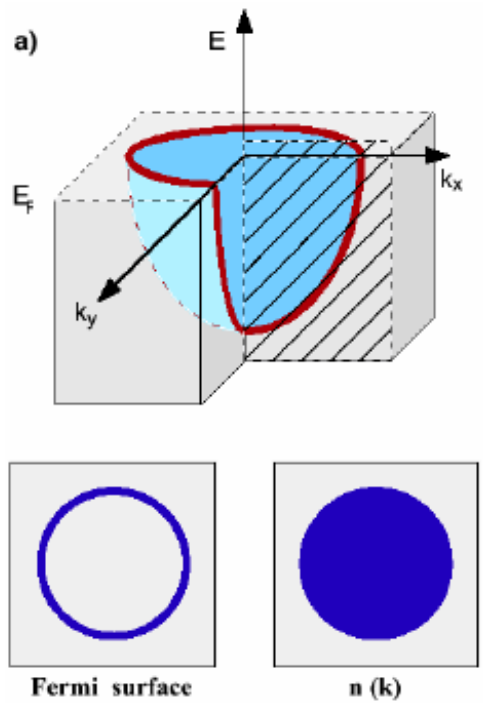
Electronic Properties

Ordered materials

Allowed electronic states
Repeated-zone scheme



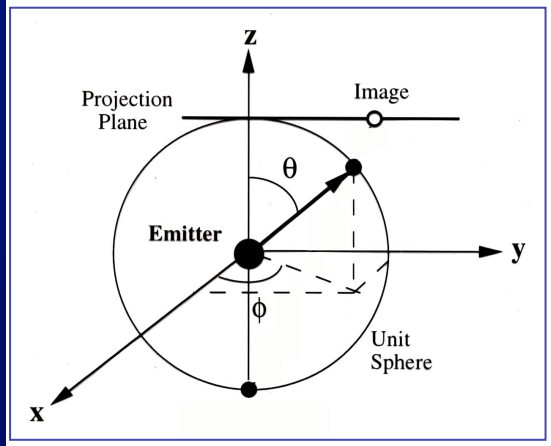
Many properties of a solids are determined by electrons near E_F (conductivity, magnetoresistance, superconductivity, magnetism)

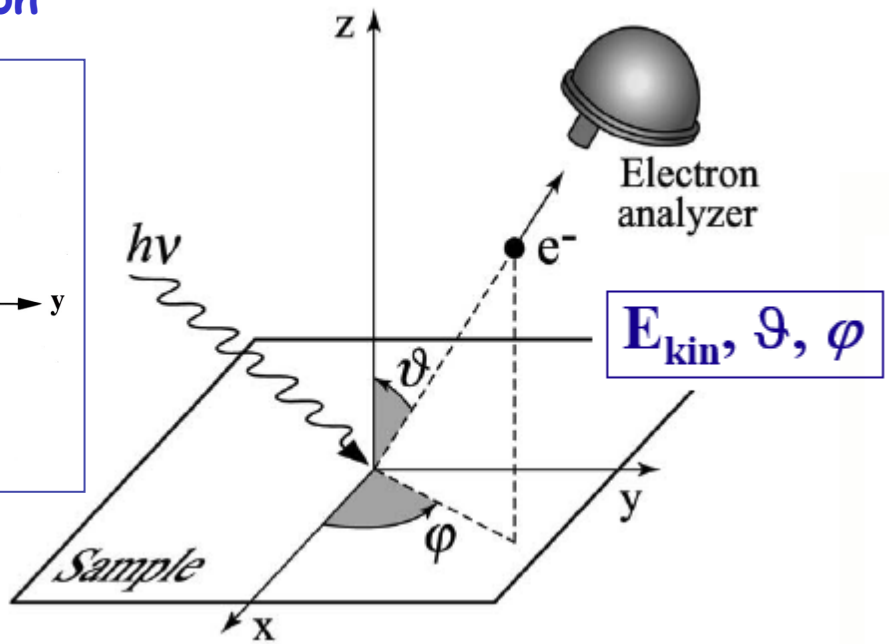


Only a narrow energy slice around E_F is relevant for these properties (kT=25 meV at room temperature)

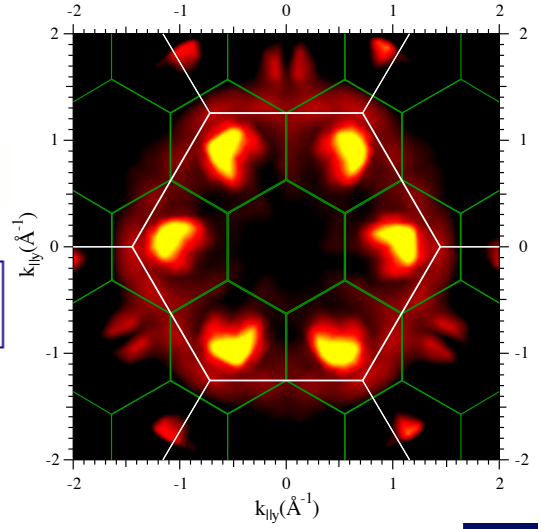
Summary - ARPES non-interacting systems

Prallel projection





Fermi Surface



Vacuum

E_{kin}

$\vec{K}$

Energy Conservation

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

Momentum Conservation

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

Solid

E_B

$\vec{k}$

Interaction Effects between Electrons : “Many-body Physics”

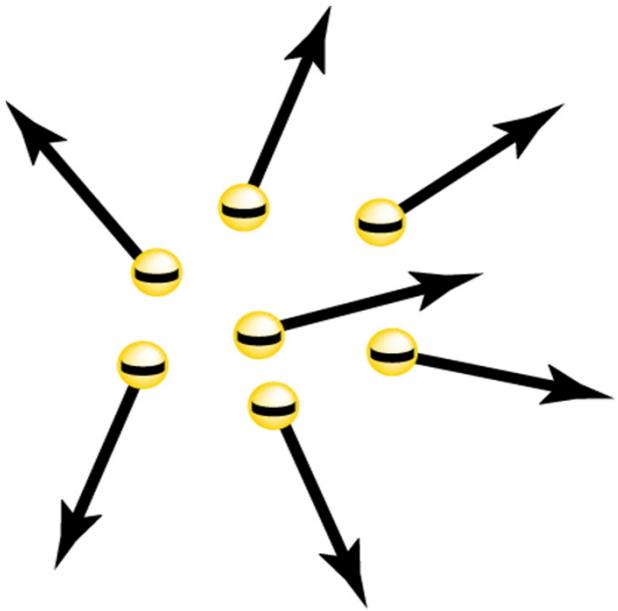
Many-body effects are due to the interactions between the electrons and each other, or with other excitations inside the crystal :

1) A “many-body” problem : intrinsically hard to calculate and understand

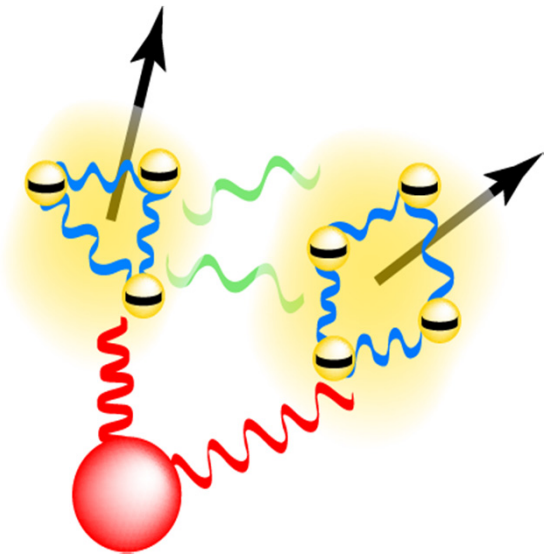
2) Responsible for many surprising phenomena :

Superconductivity, Magnetism, Density Waves, ...

Non-Interacting



Interacting

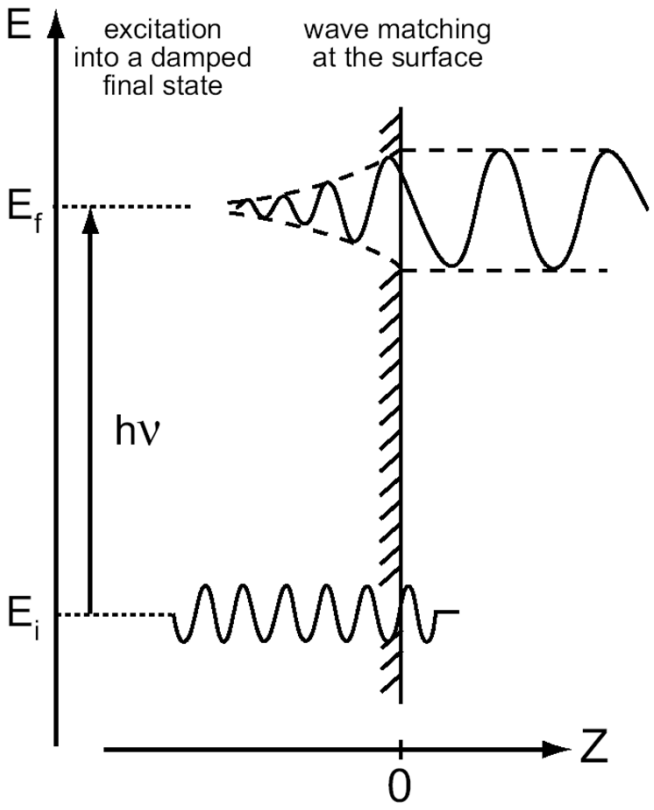


Courtesy of Kyle Shen

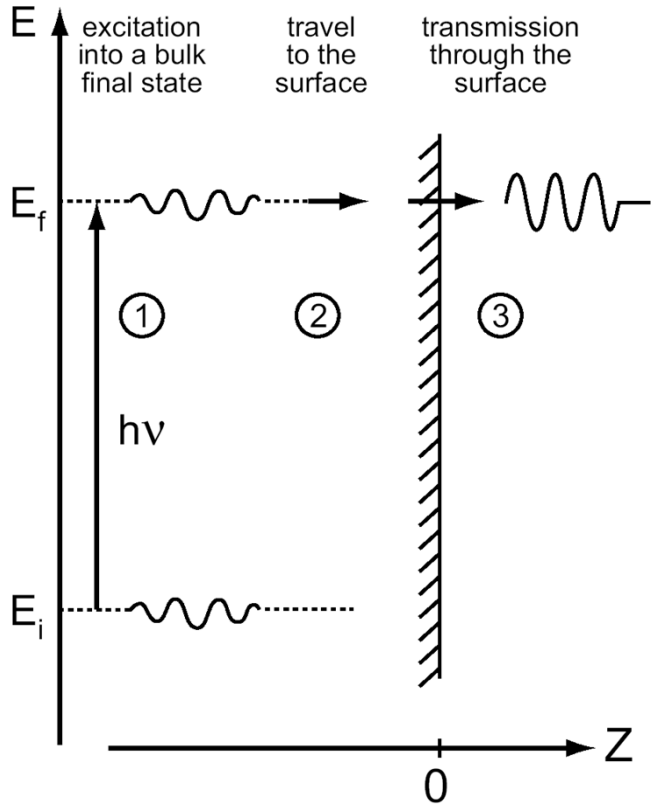
ARPES: One-Step vs Three-Step Model

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

One-step model

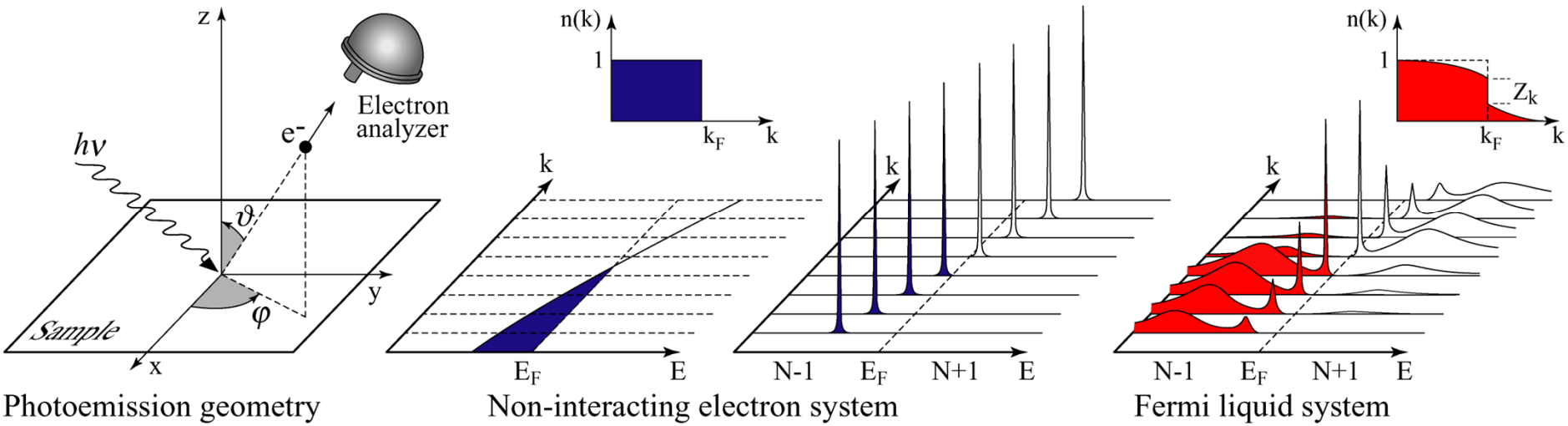


Three-step model



ARPES: The One-Particle Spectral Function

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



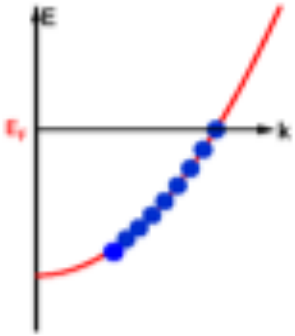
Photoemission intensity: $I(k,\omega)=I_0\,|M(k,\omega)|^2 f(\omega)\,A(k,\omega)$

Single-particle spectral function

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

$\Sigma(k,\omega)$: the "self-energy" captures the effects of interactions

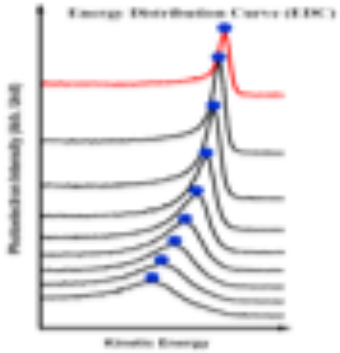
ARPES – Direct tool to measure the electronic structure of solids



E vs k relation

Velocity: $v=dE/dk$

Effective Mass: $1/m^* \sim d^2E/dk^2$

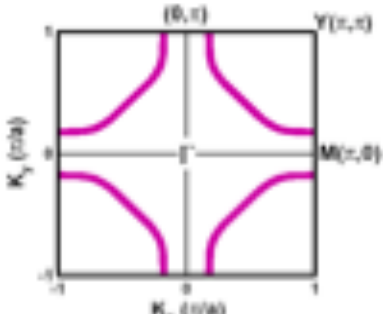


EDC lineshape

Scattering Rate: EDC Linewidth

Superconducting Gap: EDC position

Pseudogap: EDC position



Fermi surface

Carrier Density: Fermi surface volume

Nesting Vector: Fermi surface topology

Microscopic parameters determining the macroscopic properties

OUTLINE: Part I

- Brief introduction

  - History of photoemission and definitions in ARPES

  - Theoretical bases

- Technical developments

- Examples and latest results of the electronic structure

- Conclusion and perspectives of Part I