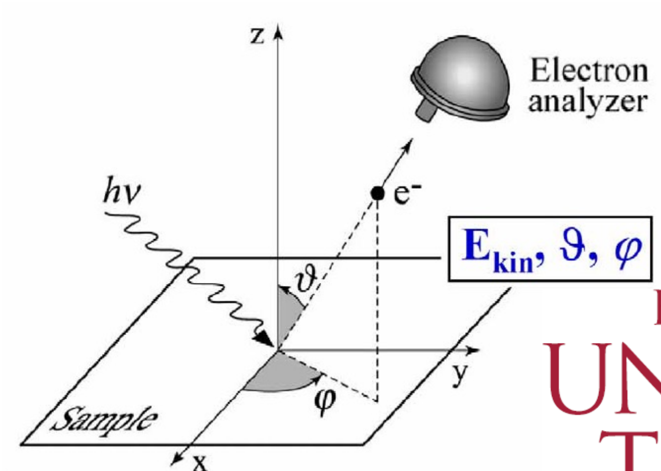
Advanced Topics in Condensed Matter

Lecture 9: Electronic Structure probed with Photoelectrons



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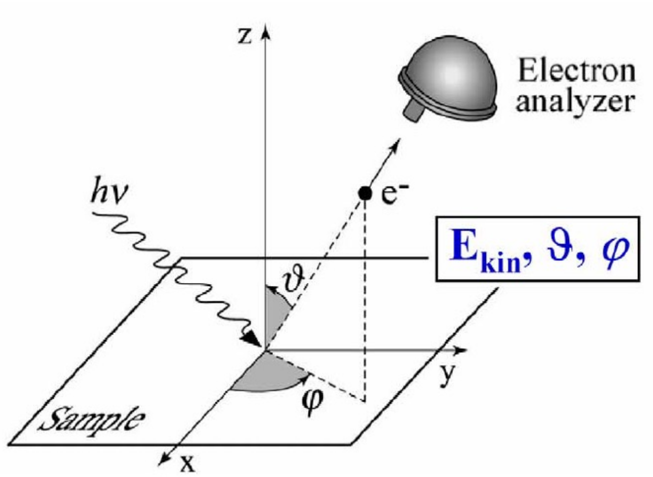
Prof. Dr. Frank Schreiber

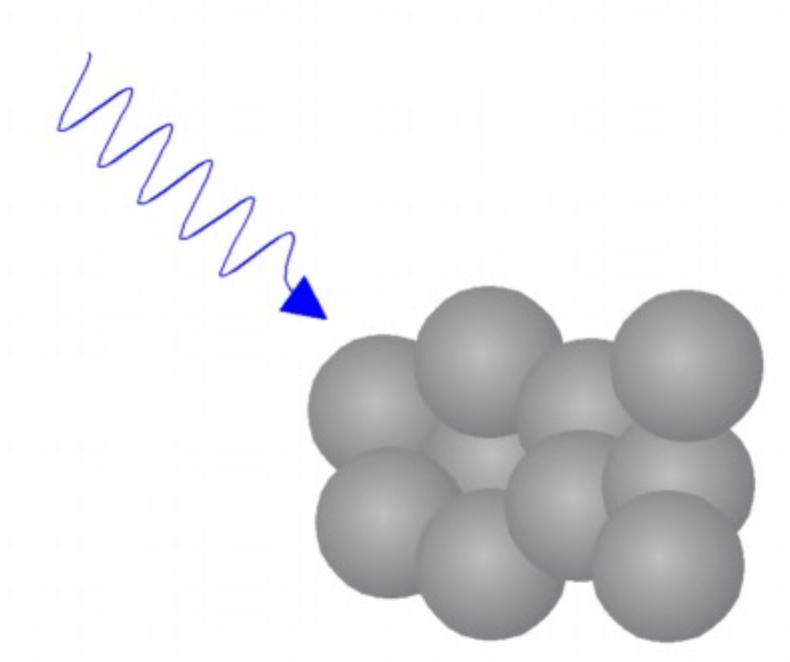
with special thanks to Dr. Alexander Gerlach

EBERHARD KARLS UNIVERSITÄT TÜBINGEN

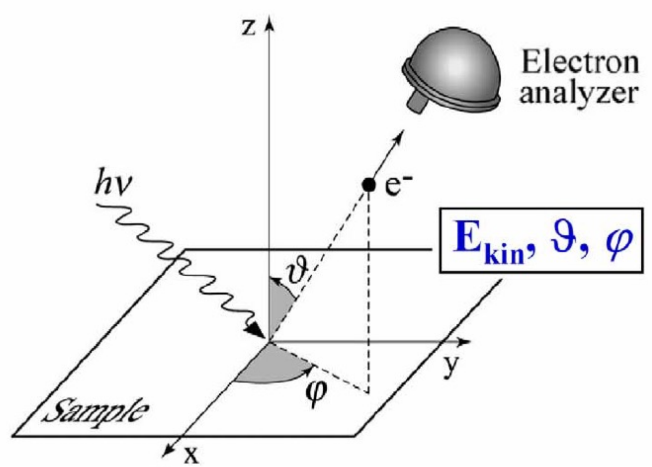
Photoelectrons



Photoelectrons



$$M + h\nu \rightarrow M^{+} + e^{-}$$



- Photoelectron spectroscopy (PES; in general)
- X-ray photoelectron spectroscopy (XPS)
  $h\nu$ = 50 … 5000 eV
- Ultraviolet photoelectron spectroscopy (UPS)
  $h\nu$ = 10 … 50 eV

Photoelectrons: History

6. ***Über einen die Erzeugung und Verwandlung des Lichtes betreffenden heuristischen Gesichtspunkt;***
von A. Einstein.

Zwischen den theoretischen Vorstellungen, welche sich die Physiker über die Gase und andere ponderable Körper gebildet haben, und der Maxwellschen Theorie der elektromagnetischen Prozesse im sogenannten leeren Raume besteht ein tiefgreifender formaler Unterschied. Während wir uns nämlich den Zustand eines Körpers durch die Lagen und Geschwindigkeiten einer zwar sehr großen, jedoch endlichen An-

Raume verteilt sei. Nach der hier ins Auge zu fassenden Annahme ist bei Ausbreitung eines von einem Punkte ausgehenden Lichtstrahles die Energie nicht kontinuierlich auf größer und größer werdende Räume verteilt, sondern es besteht dieselbe aus einer endlichen Zahl von in Raumpunkten lokalisierten Energiequanten, welche sich bewegen, ohne sich zu teilen und nur als Ganze absorbiert und erzeugt werden können.

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

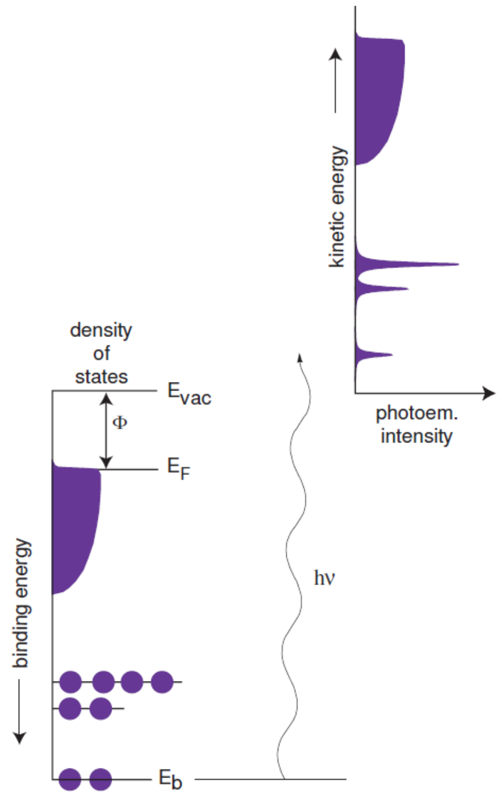
1905 Albert Einstein explains photoelectric effect [1,2]

1921 Nobel prize
“for his services to Theoretical Physics, and especially for his discovery of the law of the photoelectric effect”

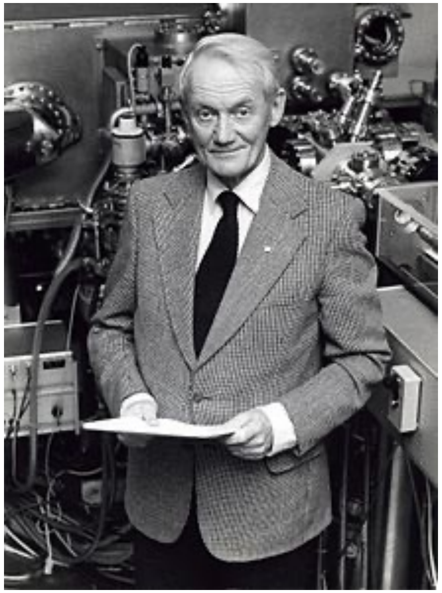
... demonstrates the particle nature of light

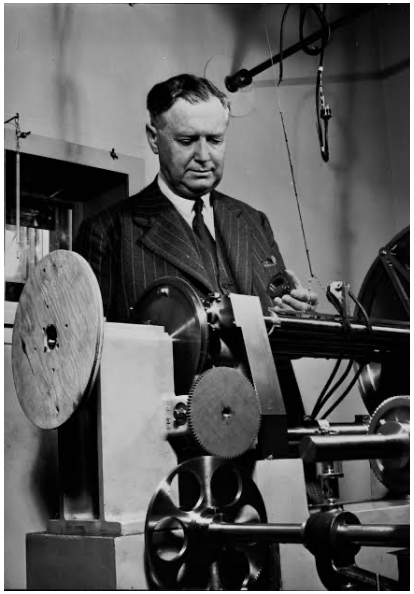
1. H. Hertz, Ann. Physik 31, 983 (1887).
2. A. Einstein, Ann. Physik 17, 132 (1905).

Photoelectrons: History



$$E_{kin} = h\nu - E_{bin} - \Phi,$$ *solid state*





Mid1960s Kai Siegbahn and his group develop photoelectron spectroscopy[1]

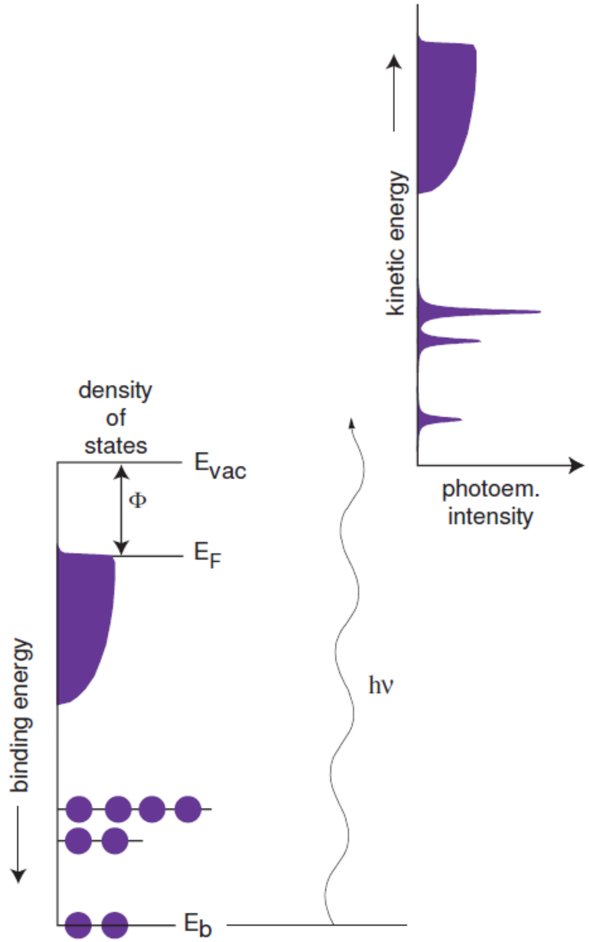
1981 Nobel prize
"for his contribution to the development of high-resolution electron spectroscopy"

Note also Manne Siegbahn (Kai's father) 1924 Nobel prize
"for his discoveries and research in the field of X-ray spectroscopy"

1. *K. Siegbahn et al., Nova Acta Regiae Soc.Sci., Ser. IV, Vol. 20 (1967)*

XPS Basics: Overview

Simple picture (Koopman's theorem):



$$E_{kin} = h\nu - E_{bin} - \Phi,$$

- absorption very fast ~10^{-16} s
- energy conservation (with workfunction ϕ)
  - no photoemission for $h\nu < \phi$
  - no photoemission from levels with $E_{bin} + \phi > h\nu$
  - E_{kin} of photoelectron increases as E_{bin} decreases
- intensity of photoemission ~ intensity of photons
- monochromatic (x-ray) incident beam needed
- since each element has unique set of core levels, E_{kin}'s can be used to fingerprint element

$$I(E_{kin}) = DOS(h\nu - E_{kin} - \Phi)$$

XPS Basics: Element-Specific Energies

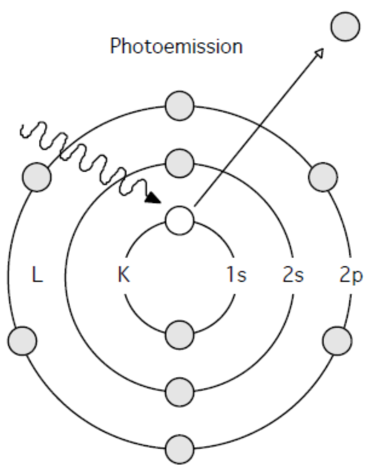
Binding energy (E_{bin}) reflects the interaction strength of electrons

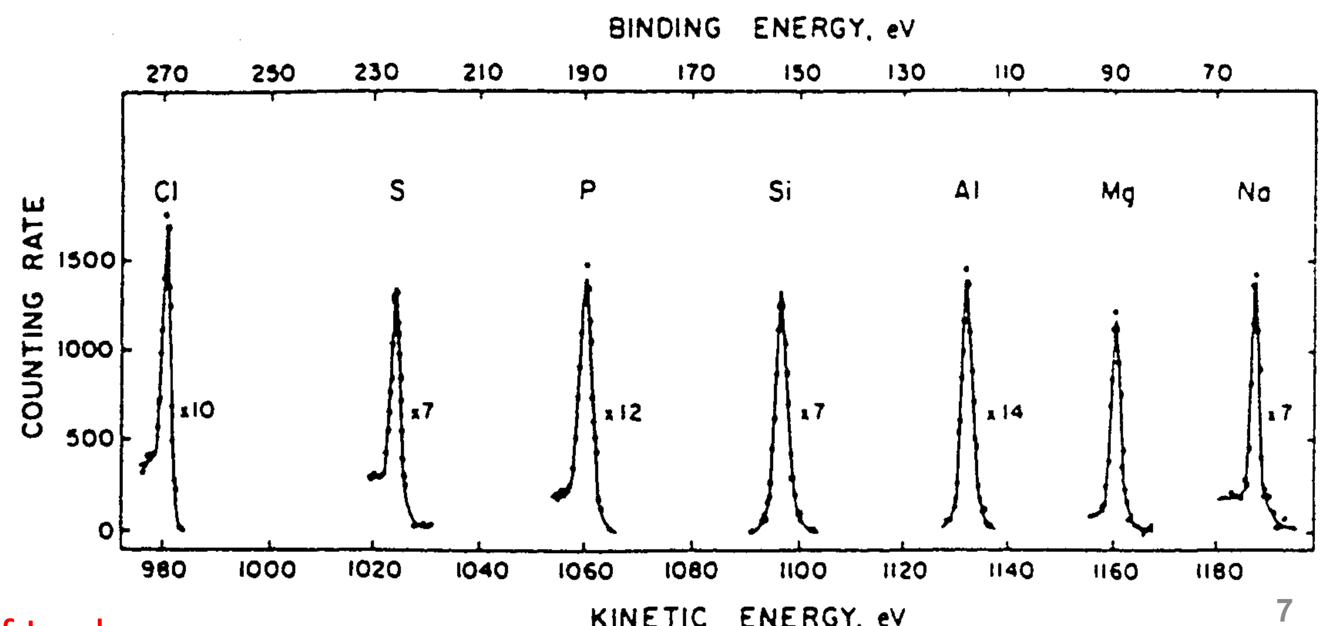
- E_{bin} follows energy of levels

  E_{bin} (1s) > E_{bin} (2s) > E_{bin} (2p) > E_{bin} (3s)

- E_{bin} of orbitals increases with Z

  E_{bin} (Na 2s) < E_{bin} (Mg 2s) < E_{bin} (Al 2s)



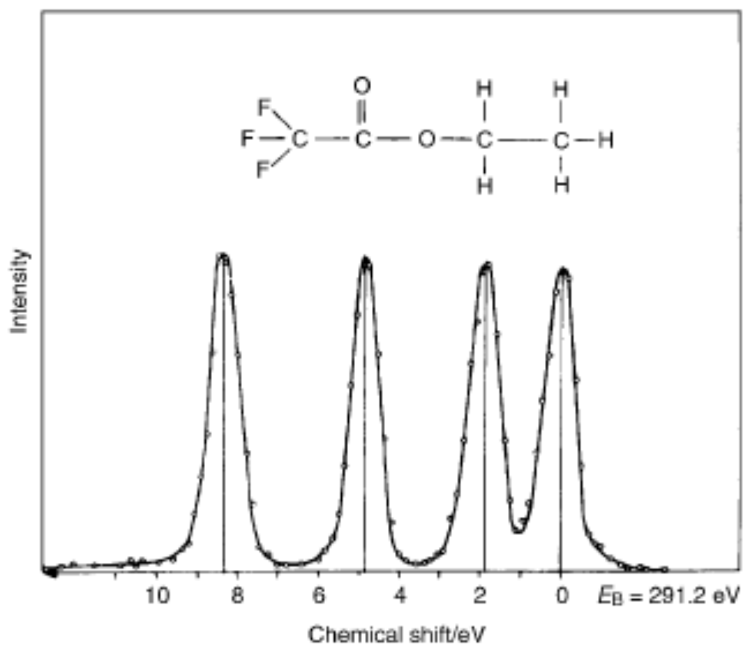


Example: energies of L edges

XPS Basics: Chemical Shifts of Core Levels

Information about chemical environment of the atoms (here C(1s) levels)

- *Core level chemical shifts* caused by overall charge redistribution depending on the bonding partners (*initial state effect*)
- Charge withdrawal increases BE by reducing nuclear shielding



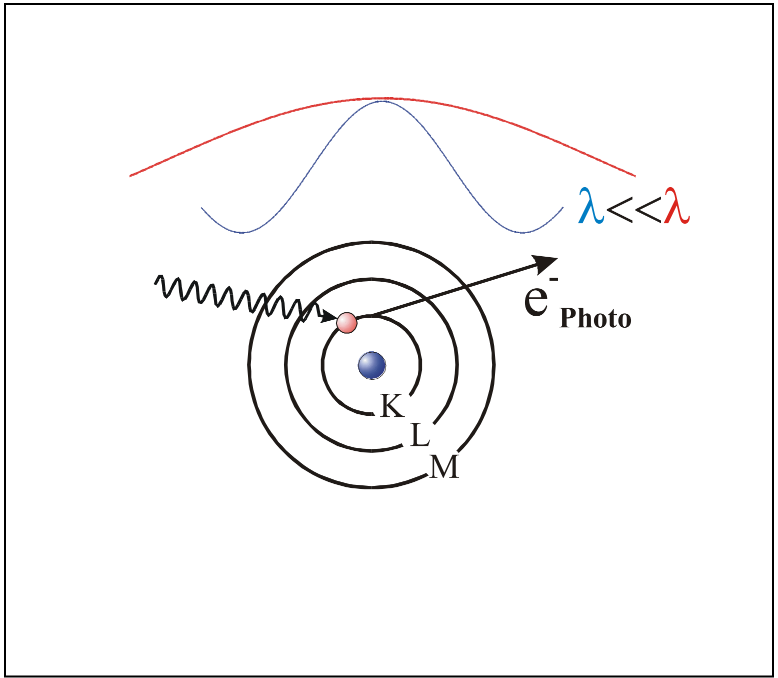
Functional Group		Binding Energy (eV)
hydrocarbon	C-H, C-C	285.0
amine	C-N	286.0
alcohol, ether	C-O-H, C-O-C	286.5
Cl bound to C	C-Cl	286.5
F bound to C	C-F	287.8
carbonyl	C=O	288.0

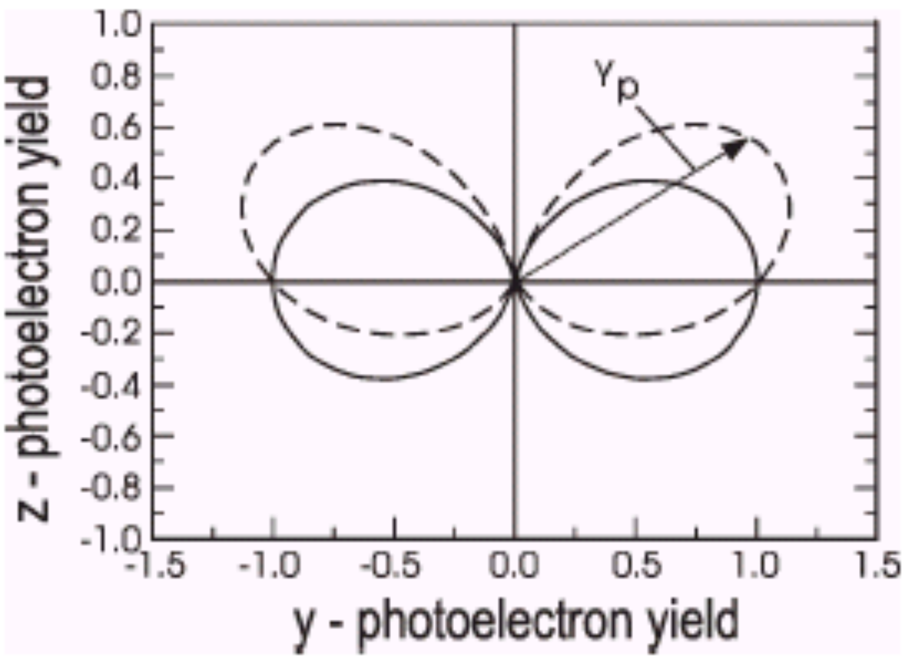
Photoelectrons: Matrix Element for Transitions

Photoelectric scattering

$$M_{fi} = \langle f|\mathbf{A}_0 e^{i\mathbf{k}\cdot\mathbf{r}} \cdot \mathbf{p}|i\rangle \qquad \text{with} \qquad e^{i\mathbf{k}\cdot\mathbf{r}} = 1 + i\mathbf{k}\cdot\mathbf{r} - \tfrac{1}{2}(\mathbf{k}\cdot\mathbf{r})^2 - \ldots$$

	dipole approximation (E1)	nondipolar contribution (E2)
selection rule	$\Delta l = 1$	$\Delta l = 2$
transition from s-state	$s \rightarrow p$	$s \rightarrow d$
matrix element	$M^D = \mathbf{A}_0 \cdot \langle f|\mathbf{p}|i\rangle$	$M^Q = \langle f|(\mathbf{k}\cdot\mathbf{r})(\mathbf{A}_0\cdot\mathbf{p})|i\rangle$





Vartanyants and Zegenhagen phys stat sol b 215 (1999) 819
Schreiber et al., Surf. Sci. Lett. 486 (2001) L519

Photoelectrons

Distinction

- Now consider less localized and less strongly bound electrons “valence levels” --- lower energies

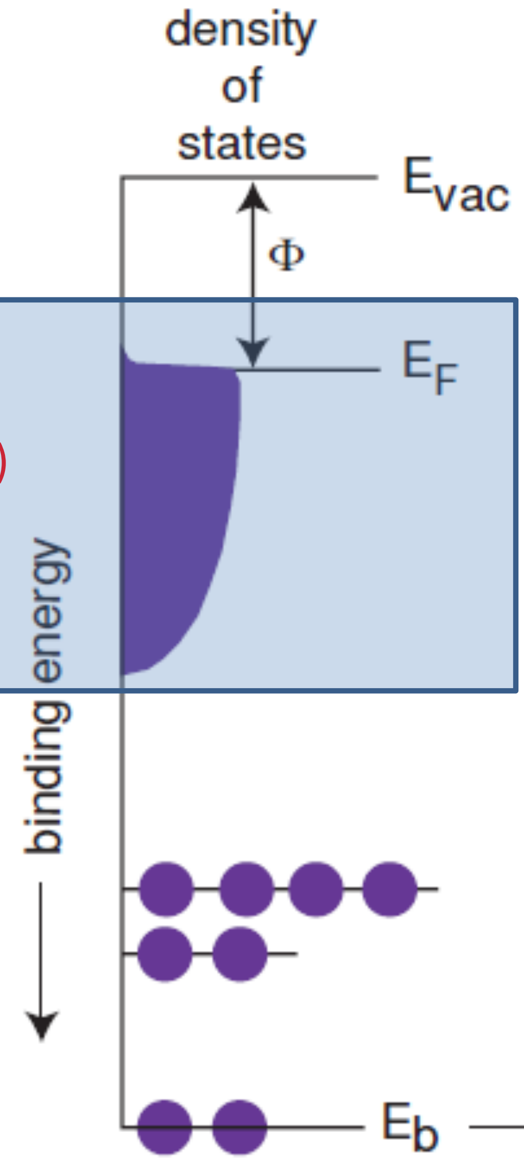
  Ultraviolet photoelectron spectroscopy (UPS)

  hv = 10 … 50 eV

- So far we considered localized and strongly bound electrons “core levels” --- high energies

  X-ray photoelectron spectroscopy (XPS)

  hv = 50 … 5000 eV



Recap of Electronic Structure (Block II of BM KoMa)

... approach from free electrons with weak (periodic) perturbation

... approach from atomic levels broadened by neighboring atoms

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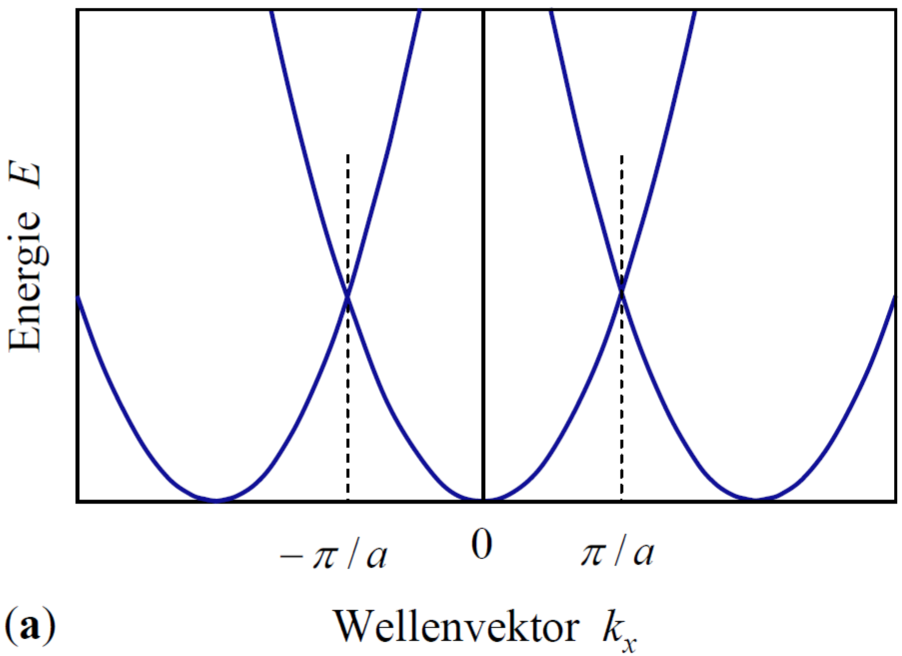
... approach from free electrons with weak (periodic) perturbation



$$E^0_{\boldsymbol{k}} = \frac{\hbar^2 k^2}{2m} \qquad E^0_{\boldsymbol{k}-\boldsymbol{g}} = \frac{\hbar^2 |\boldsymbol{k}-\boldsymbol{g}|^2}{2m}$$

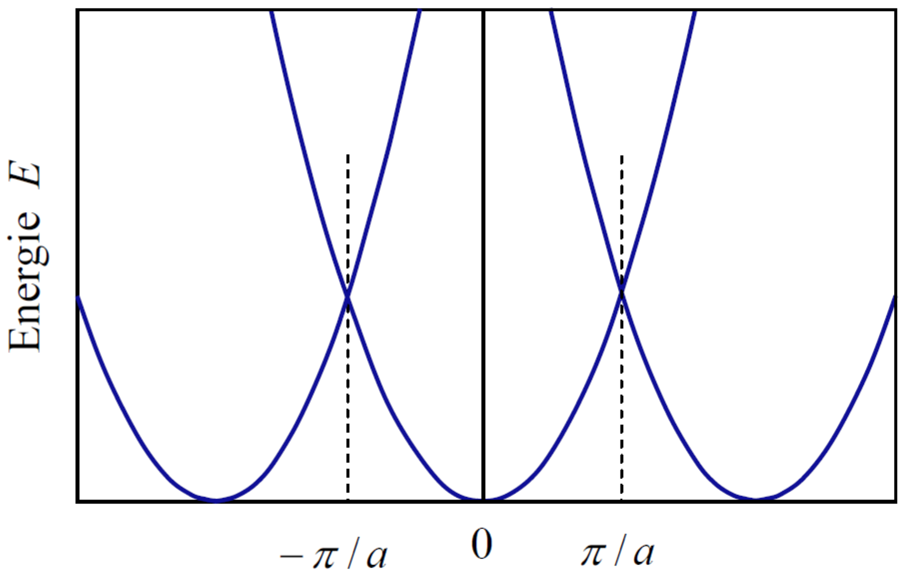
Hunklinger

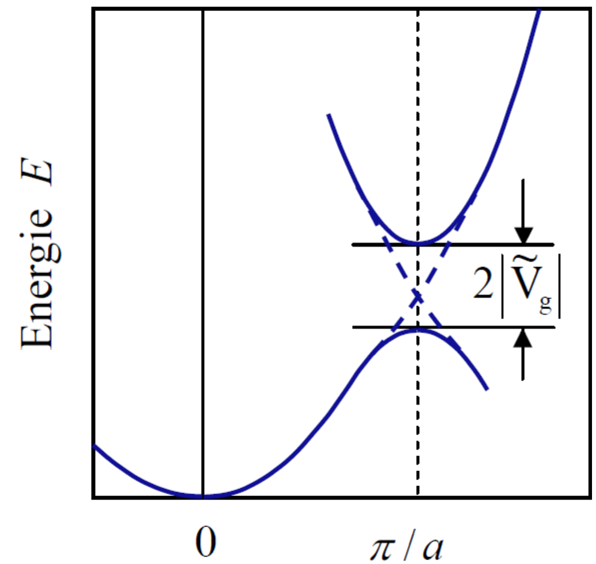
Recap of Electronic Structure (Block II of BM KoMa)

... approach from free electrons with weak (periodic) perturbation

$$\widetilde{V}(\boldsymbol{r}) = \sum \widetilde{V}_{\boldsymbol{G}}\, \mathrm{e}^{\mathrm{i}\boldsymbol{G}\cdot\boldsymbol{r}}$$

$$H\psi(\boldsymbol{r}) = \left[-\frac{\hbar^2}{2m}\Delta + \widetilde{V}(\boldsymbol{r})\right]\psi(\boldsymbol{r}) = E\,\psi(\boldsymbol{r})$$





Periodic perturbation creates gap

$$E_{\mathrm{s,a}} = E^0_{\boldsymbol{k}} \pm |\widetilde{V}_{\boldsymbol{g}}|$$

$$E^0_{\boldsymbol{k}} = \frac{\hbar^2 k^2}{2m} \qquad E^0_{\boldsymbol{k}-\boldsymbol{g}} = \frac{\hbar^2|\boldsymbol{k}-\boldsymbol{g}|^2}{2m}$$

$$E_{\mathrm{s,a}} = \frac{1}{2}(E^0_{\boldsymbol{k}-\boldsymbol{g}} + E^0_{\boldsymbol{k}}) \mp \sqrt{\frac{1}{4}(E^0_{\boldsymbol{k}-\boldsymbol{g}} - E^0_{\boldsymbol{k}})^2 + \widetilde{V}^2_{\boldsymbol{g}}}$$

Hunklinger

Recap of Electronic Structure (Block II of BM KoMa)

... approach from free electrons with weak (periodic) perturbation

... approach from atomic levels broadened by neighboring atoms

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... approach from free electrons with weak (periodic) perturbation

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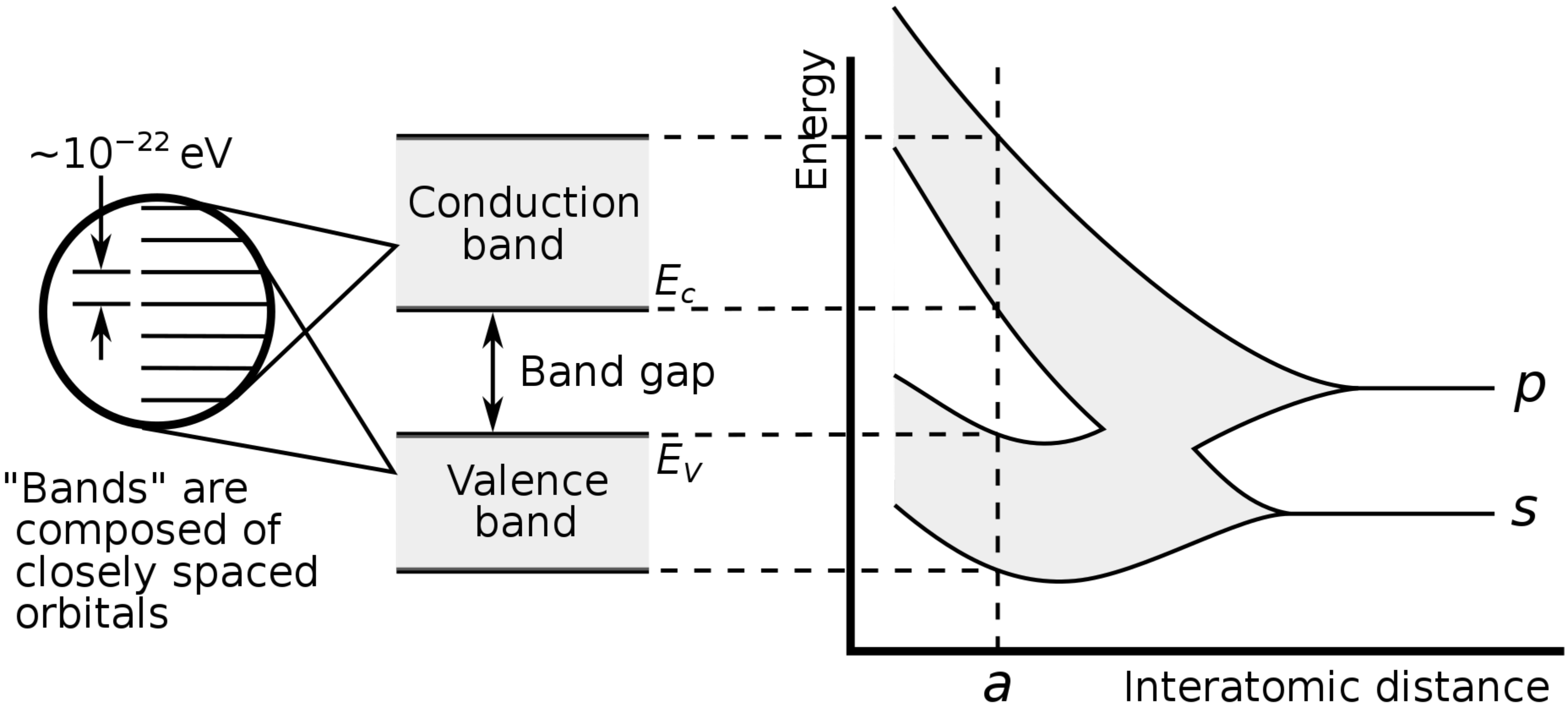
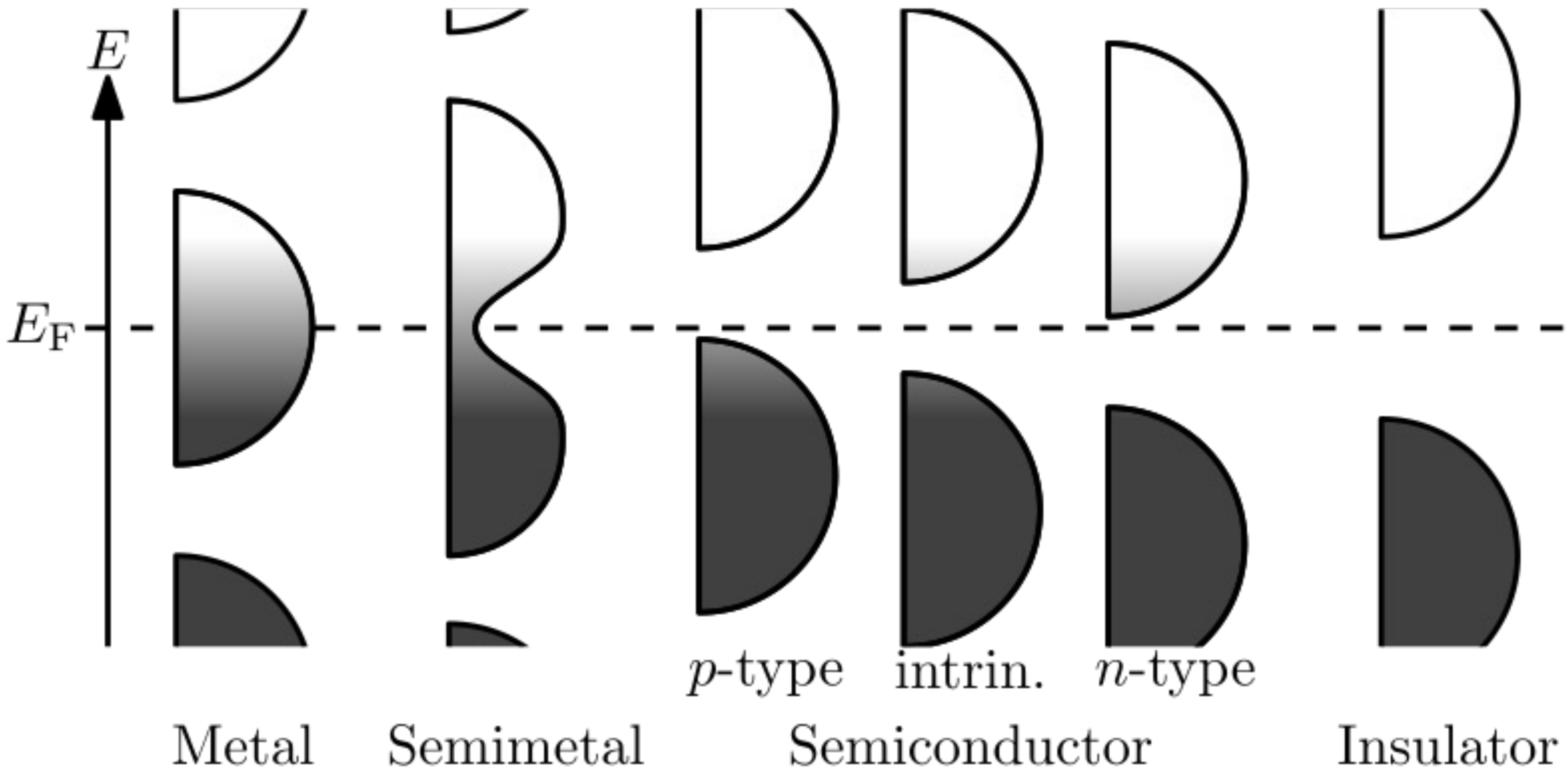


https://en.wikipedia.org/wiki/Electronic_band_structure

Recap of Electronic Structure (Block II of BM KoMa)



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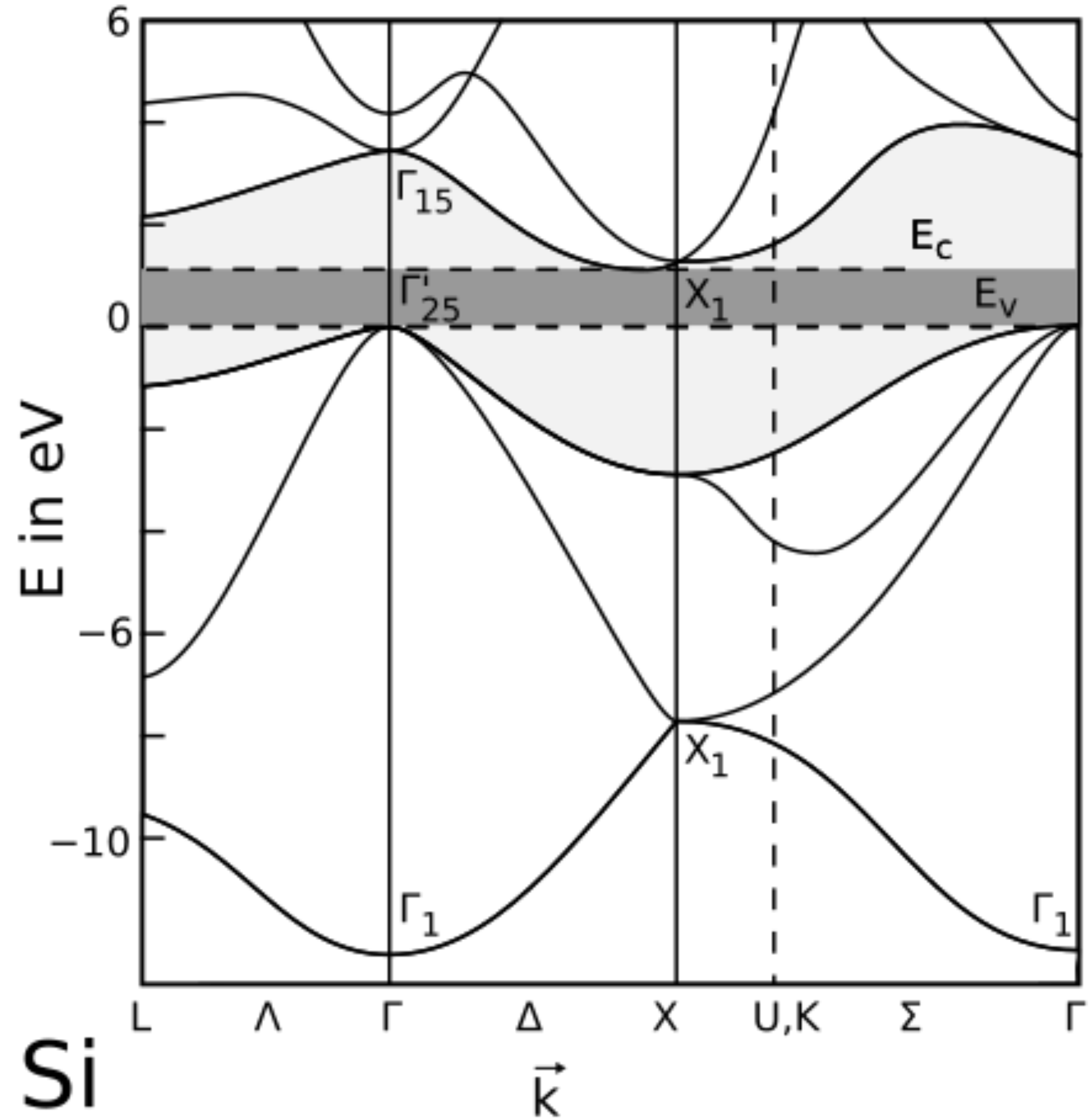
Some Real Electronic Structures E(k)



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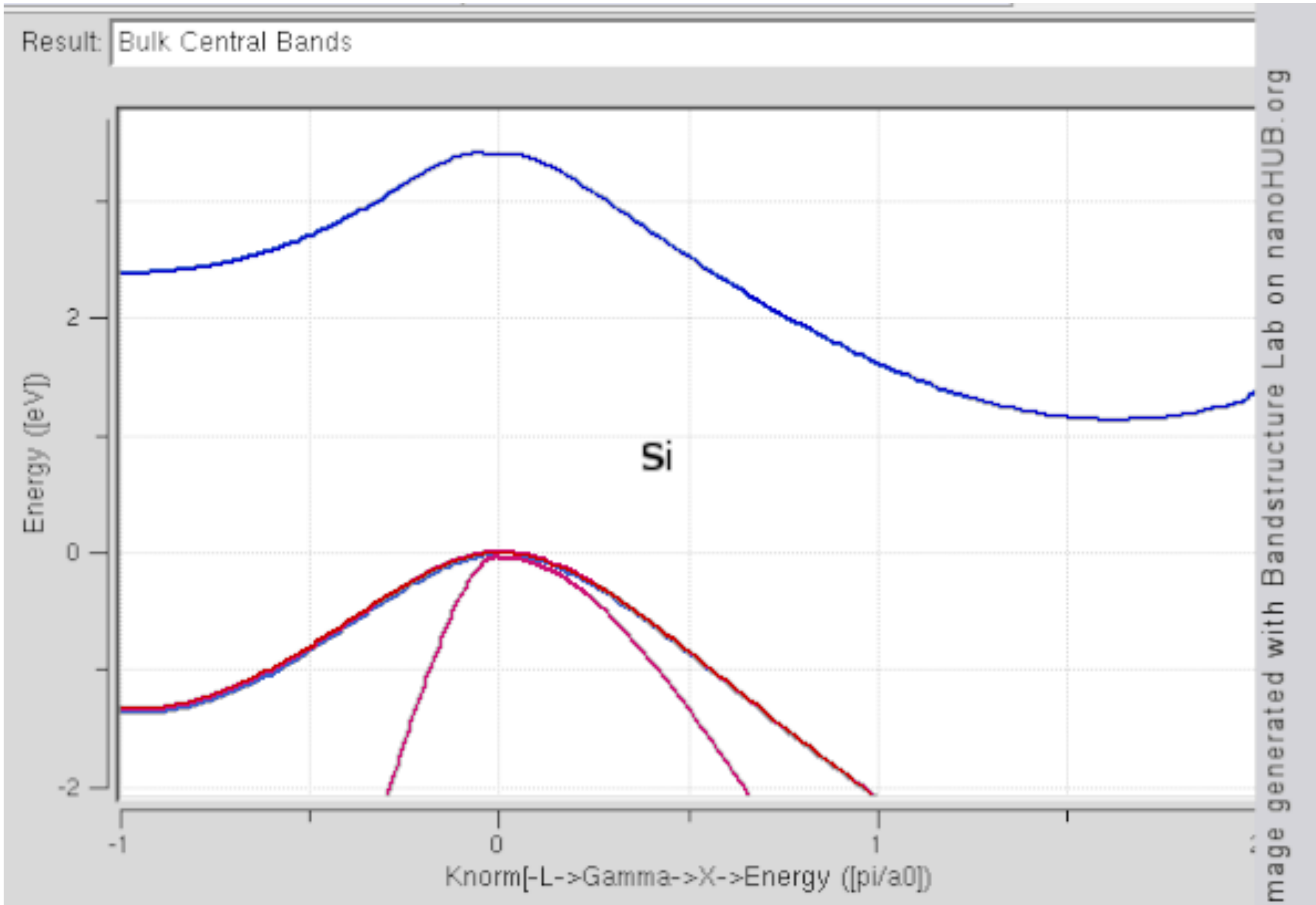

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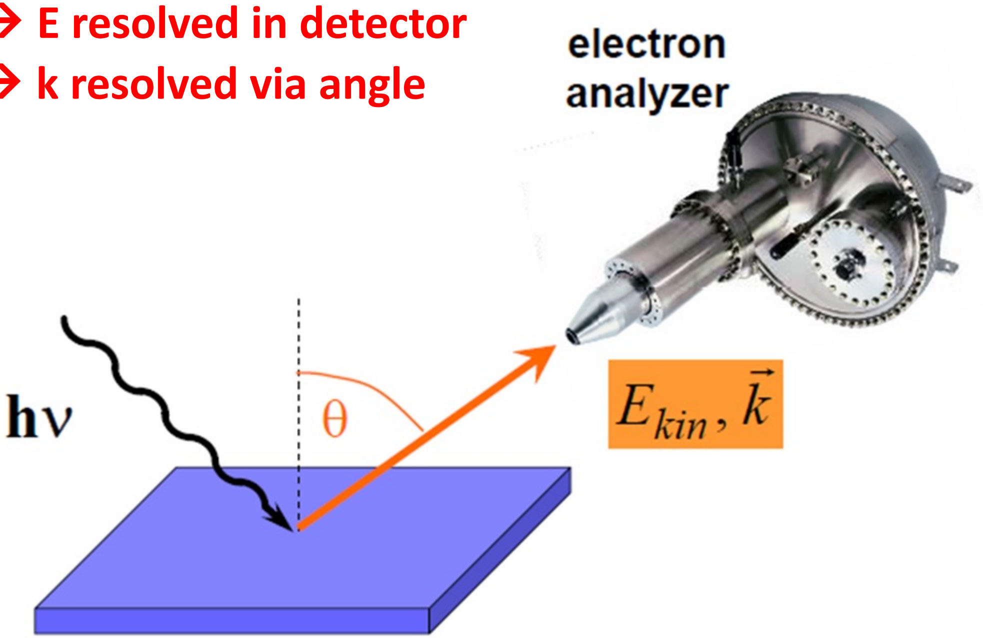
UPS Basics: Measurement of Dispersion E(k)

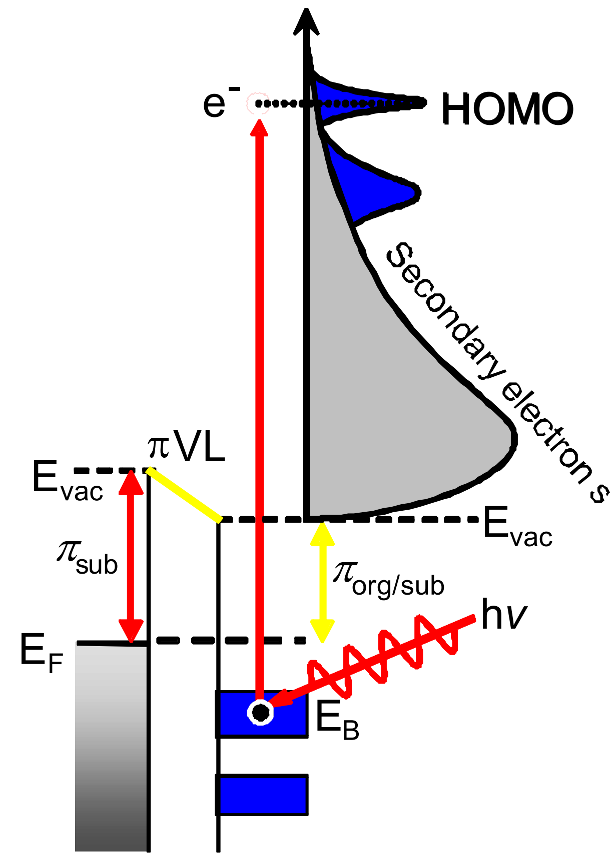
Measurement of energy dispersion E(k)

Angle-resolved photoelectron spectroscopy (ARPES)

→ E resolved in detector

→ k resolved via angle





Energy conservation

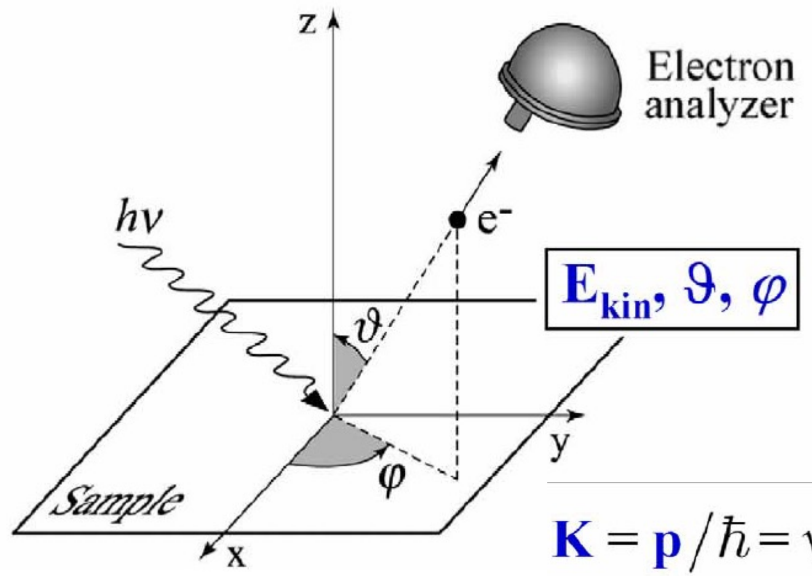
$$E_{kin} = h\nu - \phi - |E_B|$$

UPS Basics

Angle-resolved photoelectron spectroscopy (ARPES)

→ **E resolved in detector**

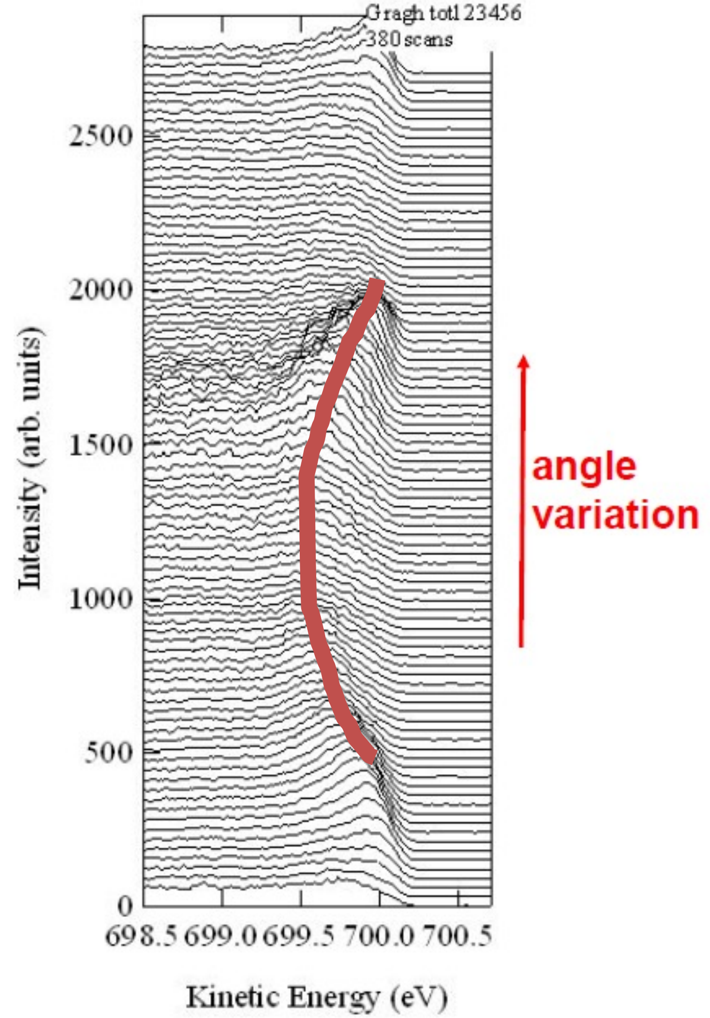
→ **k resolved via angle**



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

Momentum conservation

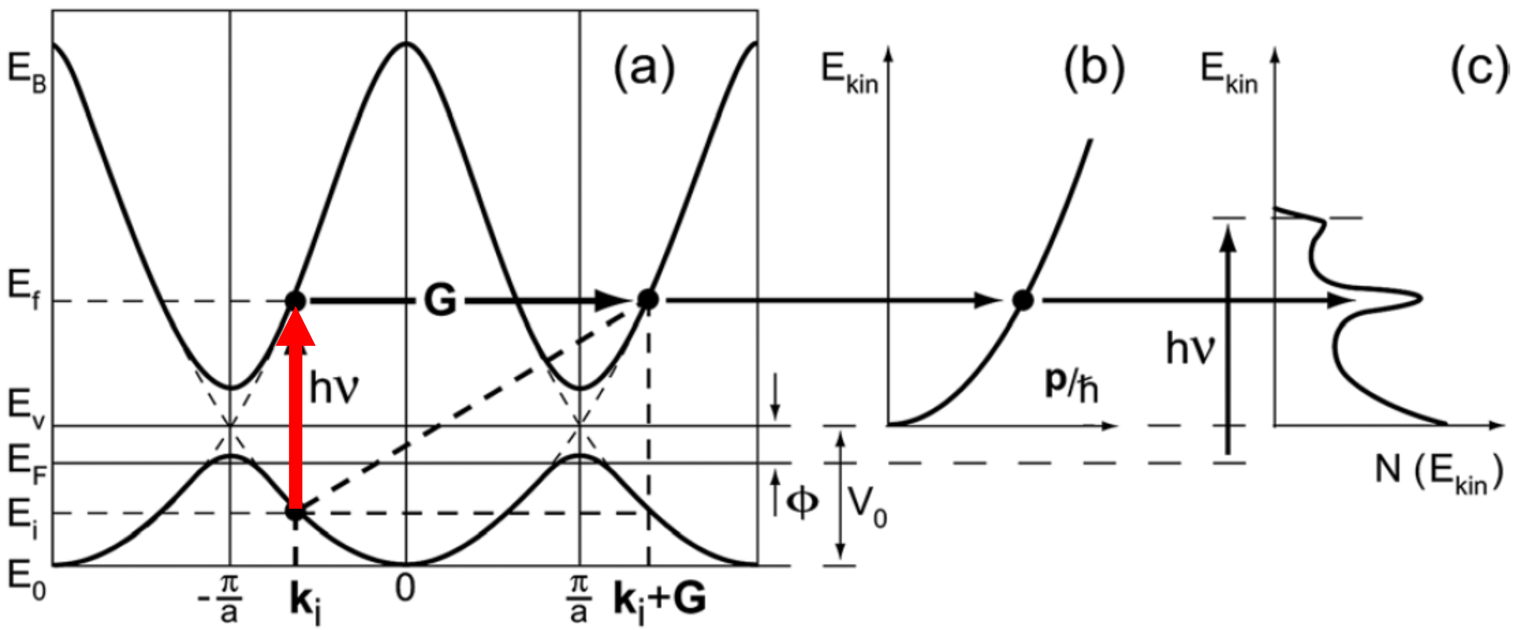
$$\hbar \mathbf{k}_{\|} = \hbar \mathbf{K}_{\|} = \sqrt{2mE_{kin}} \cdot \sin\vartheta$$



example:
soft x-ray ARPES on $Sr_2Ru_{1-x}Ti_xO_4$

UPS Basics

Photo-excitation in a periodic potential



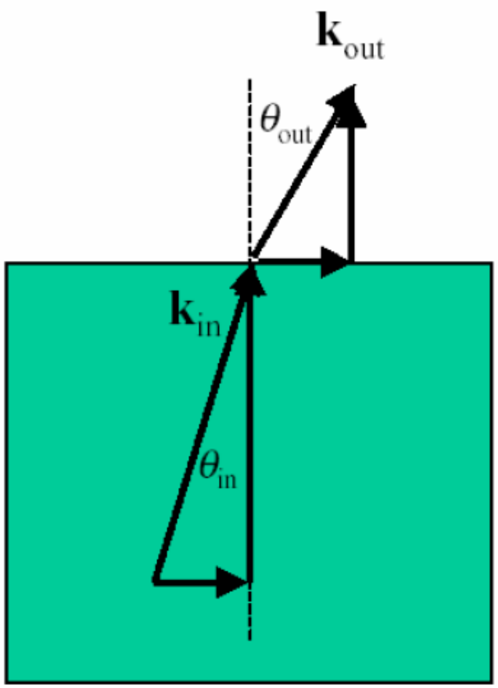
momentum conservation:

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

Example
$h\nu$ = 21.2 eV (He I_α):
k_{photon}= 0.008 $Å^{-1}$ << π / a,
i.e. very small momentum transfer,
essentially vertical transitions

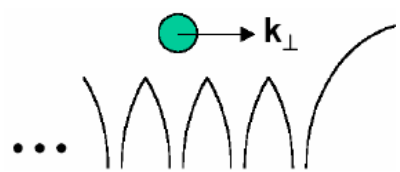
UPS Basics

3D systems ($k_\perp \neq 0$)

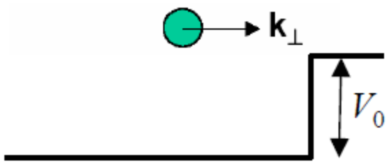


Free-electron final state model

surface potential step



surface potential step



"inner potential" V_0

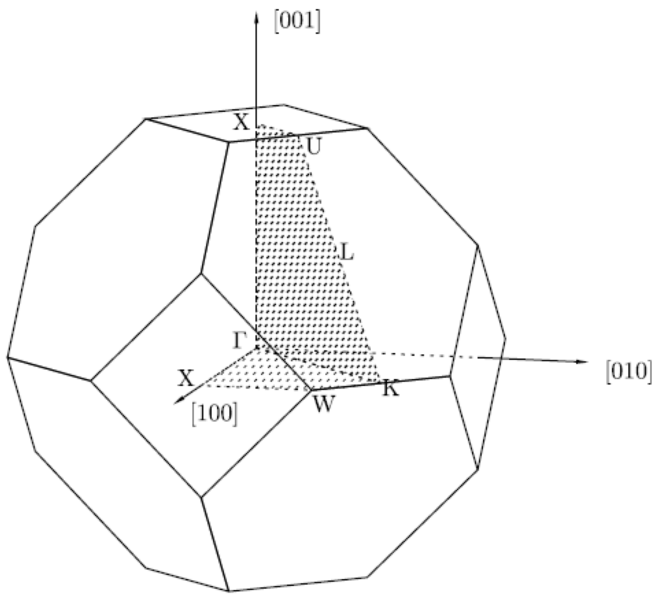
Kinematic relations

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

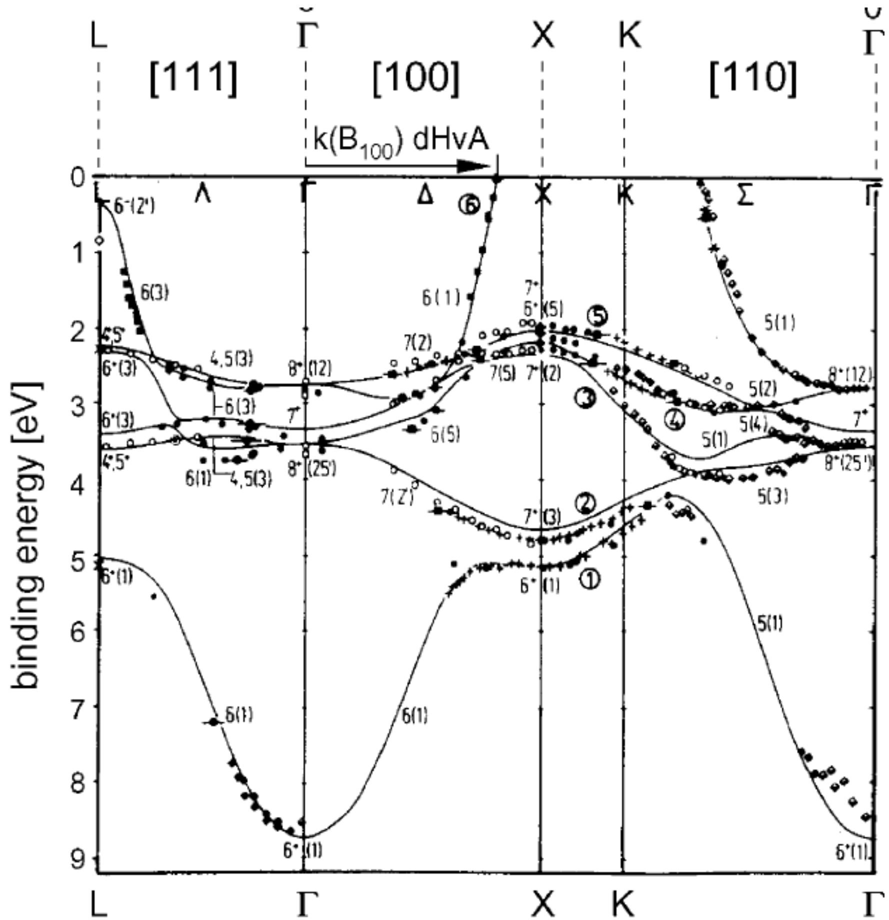
$$\Rightarrow \begin{cases} k_{in,\parallel} = K_{out,\parallel} = \sqrt{\frac{2m}{\hbar^2} E_{kin}} \sin\theta_{out} \\ k_{in,\perp} = \sqrt{\frac{2m}{\hbar^2}(E_{kin}\cos^2\theta_{out} + V_0)} \end{cases}$$

UPS: Electronic Band Structure of Copper

3D band mapping (k⊥ ≠ 0):



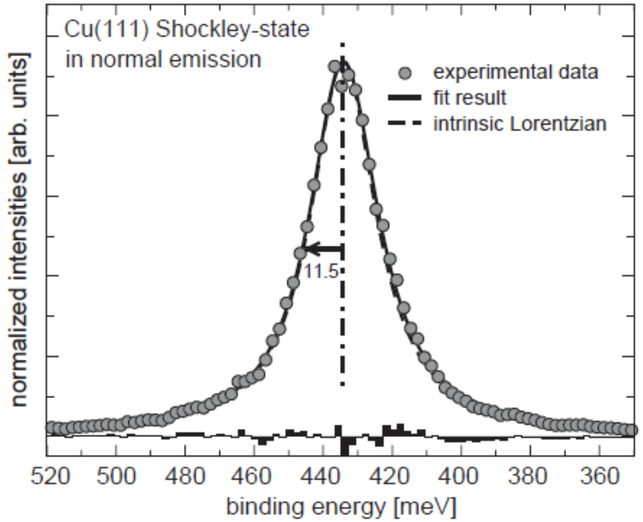
Brillouin zone of Copper



Synchrotron radiation needed

UPS: Electronic Surface States of Cu(111)

2D band mapping ($k_\perp = 0$) here with "free-electron-like" dispersion !

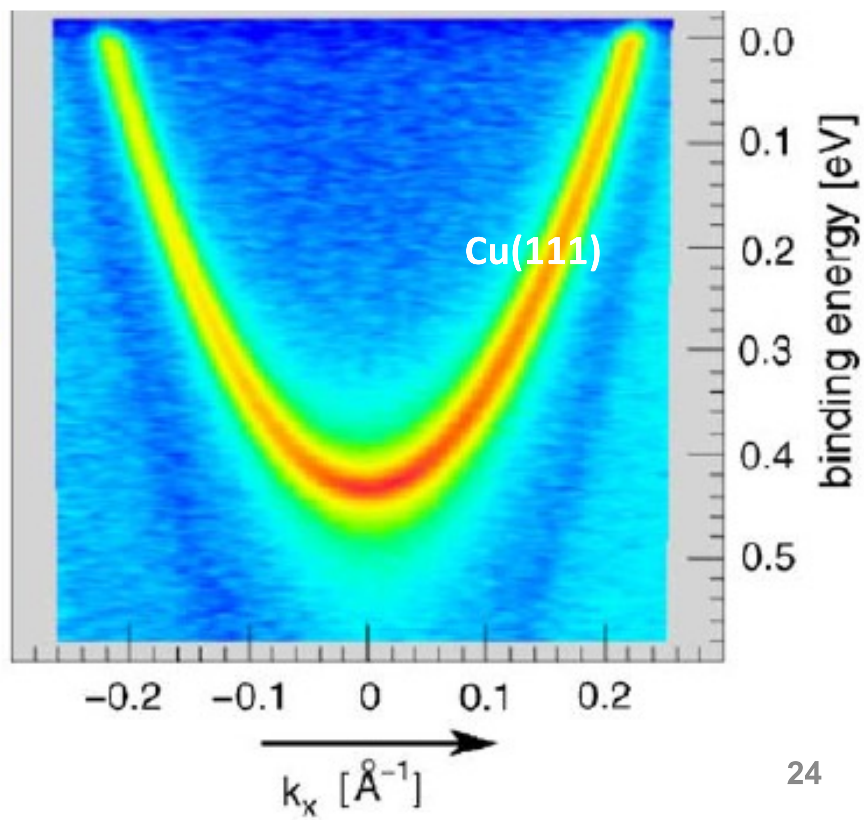


Energy Conservation

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

Momentum Conservation

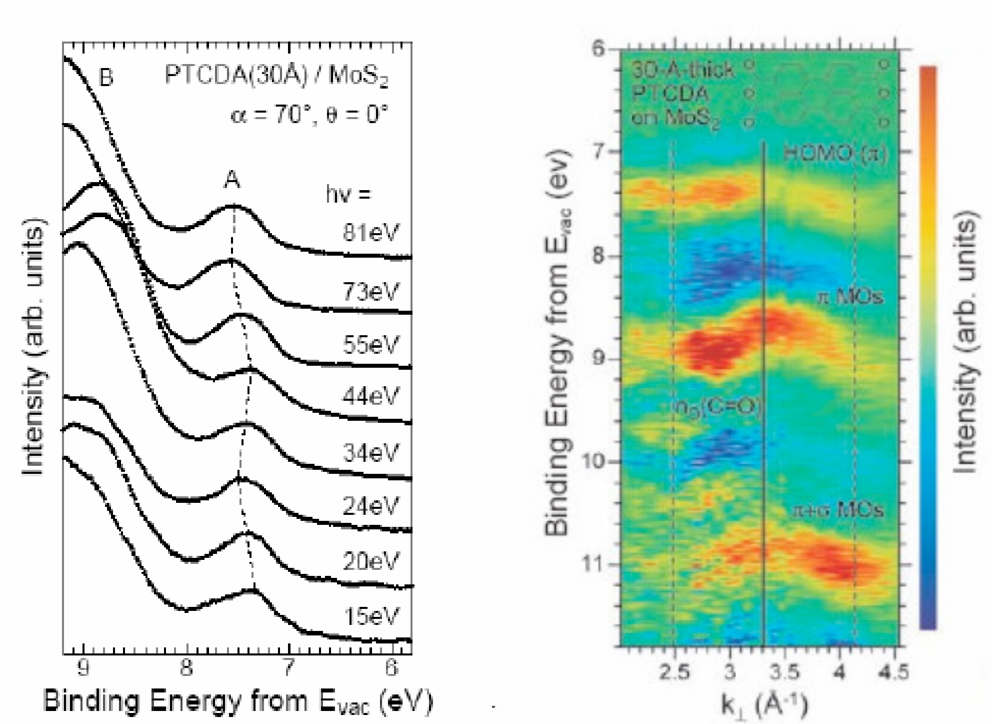
$$\hbar \mathbf{k}_{||} = \hbar \mathbf{K}_{||} = \sqrt{2mE_{kin}} \cdot \sin\vartheta$$

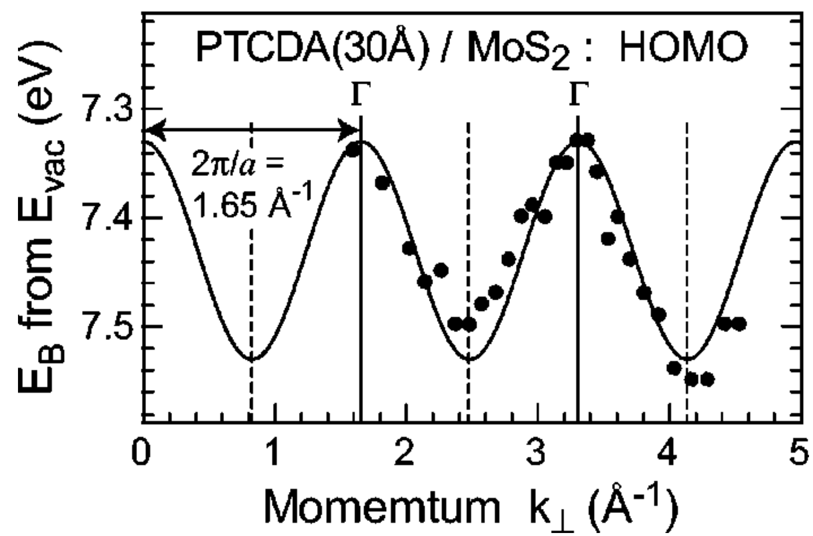


F. Reinert, Phys. Rev. B **63** (2001) 115415

UPS: Electronic Band Structure of Organic Films

Band dispersion in organic thin films (PTCDA)





Dispersion shows intermolecular interactions

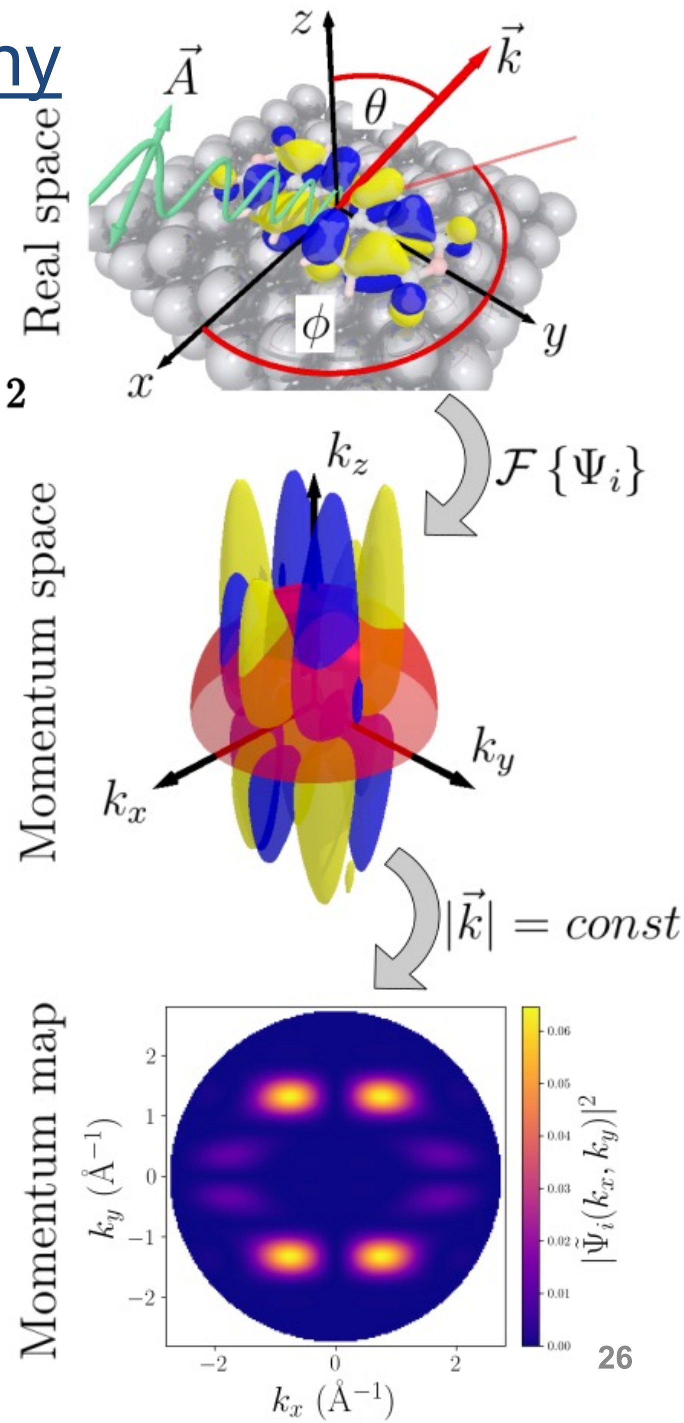
$$E_B(k_\perp) = E_B^0 + 2t\cos(a_\perp * k_\perp)$$

*H. Yamane et al, Phys. Rev. B **68**, 033102 (2003)*

Photoelectrons: Orbital Tomography

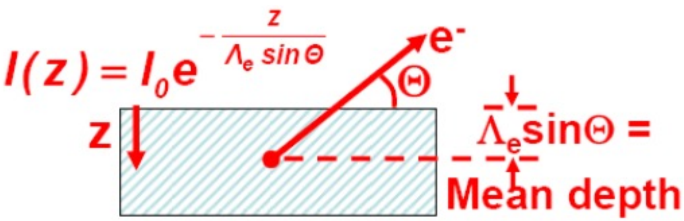
Recording emission in many directions

$$I(k_x, k_y; E_{\text{kin}}) \propto \left| \langle \Psi_f(k_x, k_y; E_{\text{kin}}) | \vec{A} \cdot \vec{p} | \Psi_i \rangle \right|^2$$
$$\times \delta \left(E_i + \Phi + E_{\text{kin}} - \hbar\omega \right)$$



https://en.wikipedia.org/wiki/Photoemission_orbital_tomography

Photoelectrons: Penetration depth and HAXPES

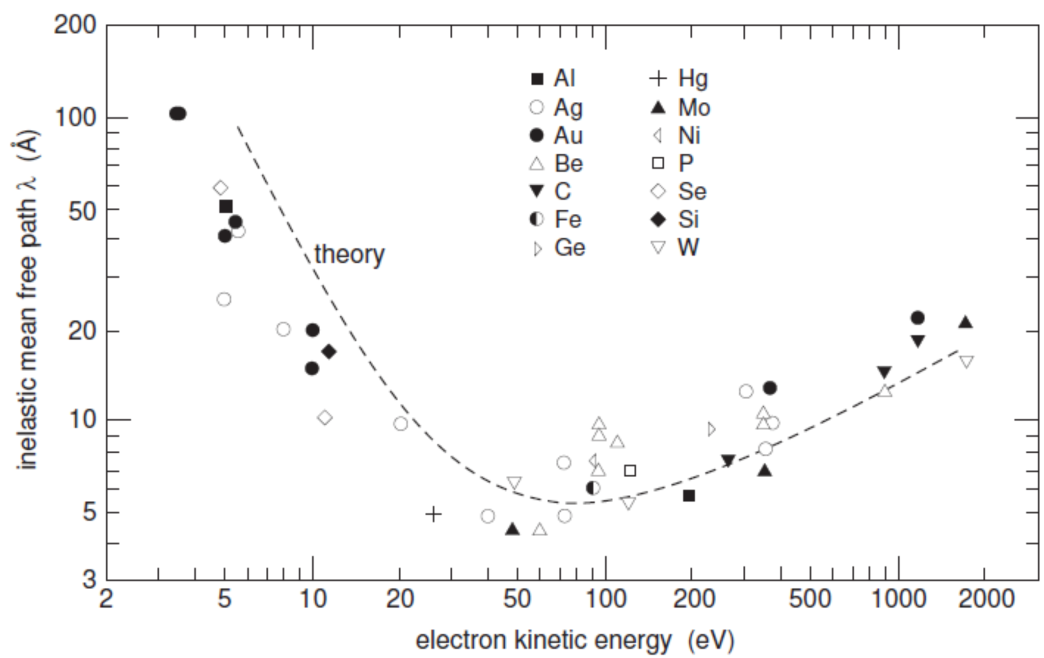


Probability of escape without loss determines *Sampling depth* z of XPS

If we seek information from deeper in the sample, we need high energies (hard X-ray PES, i.e. HAXPES)

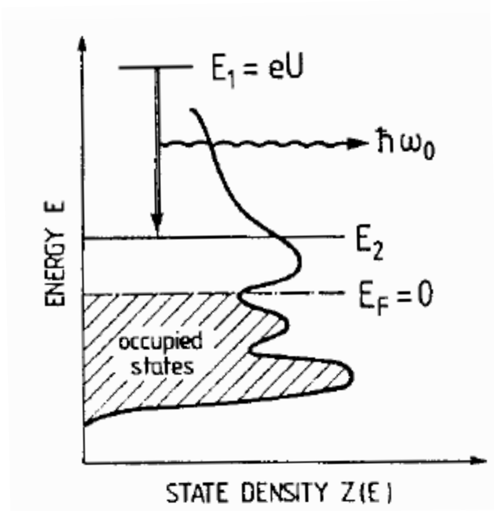
Inelastic mean free path Λ_e

- *IMFP* is the average distance between inelastic collisions
- "*universal curve*" of *IMFP* versus E_{kin}
- Maximum surface sensitivity at 50-100 eV (Λ_e ~ 5 Å)
- 95 % of electrons from $3\Lambda_e$ depth



Photoelectrons: Inverse PES

Inverse photoemission spectroscopy (IPES) probes *unoccupied* states

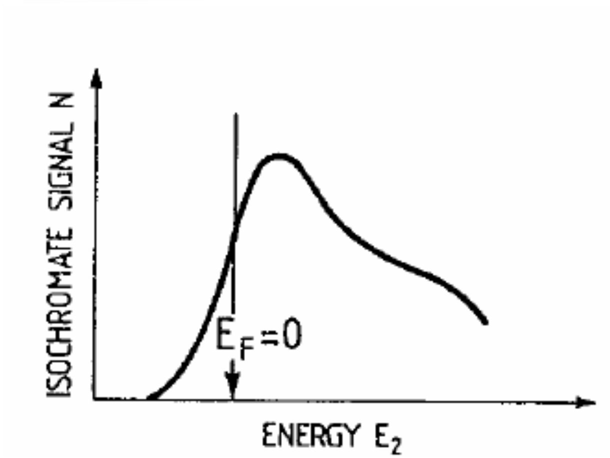


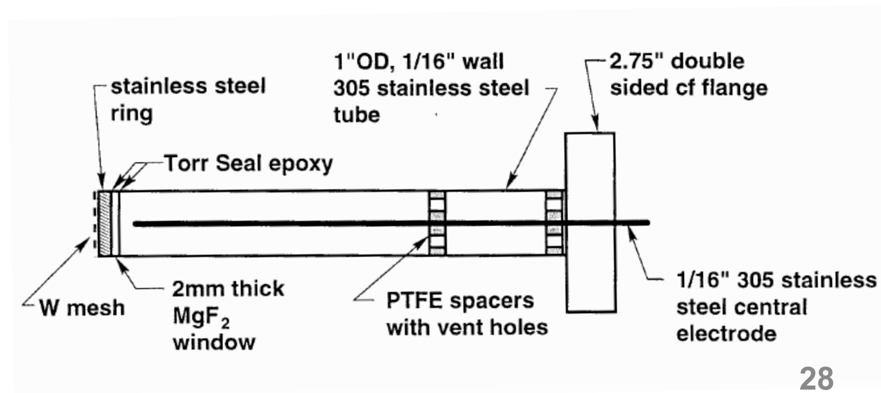
UPS

$$M + h\nu \rightarrow M^{+} + e^{-}$$

IPES

$$M + e^{-} \rightarrow M^{-} + h\nu$$

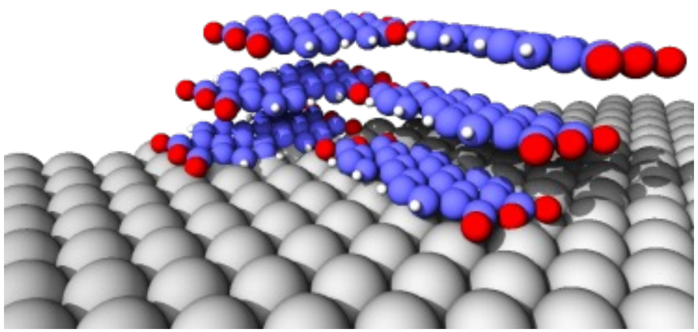


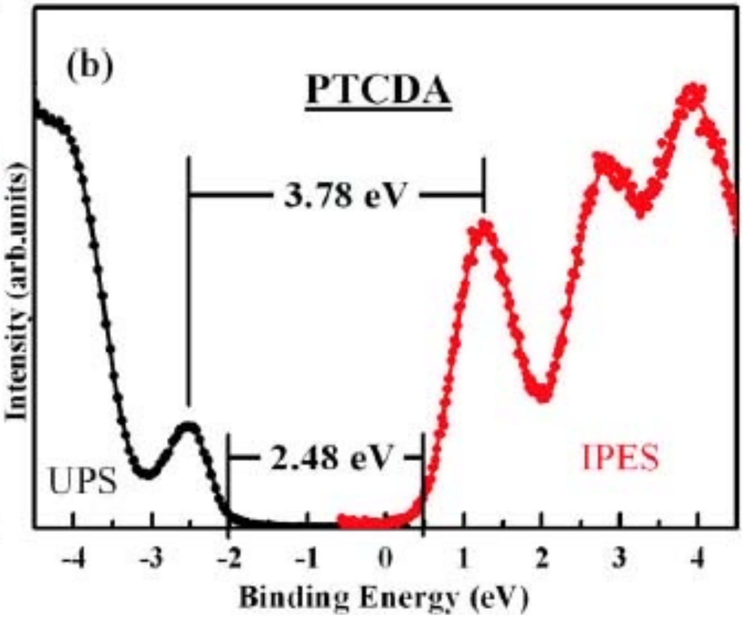


H. Lüth book

Photoelectrons: Inverse PES

PTCDA/Ag(111)





Occupied states	Gap	Unoccupied states

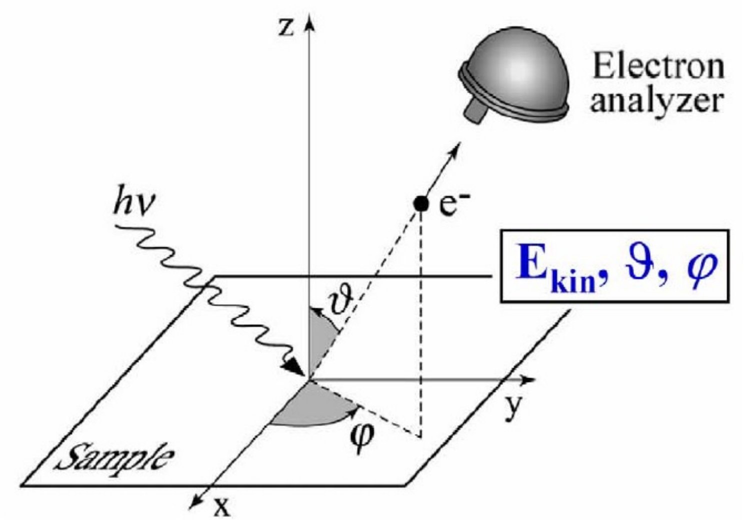
HOMO – LUMO gap 2.5 eV

S. Krause et al, New J. Phys. ***10*** *(2008) 085001*

Photoelectrons: Summary

Advantages of UPS

- Non-destructive
- Very surface sensitive
- Energy and momentum resolution allow band mapping for 2D and 3D systems
- Density of occupied states can be measured
- Orbital symmetry of occupied states
- Some structural information



Literature I

Some general textbooks covering PES are

- *Modern Techniques of Surface Science by T. A. Delchar, and D. P. Woodruff, Cambridge Solid State Science Series, 1994*
- *Solid Surfaces, Interfaces and Thin Films by Hans Lüth, Springer, 2001*

A general comprehensive text on photoelectron spectroscopy including XPS is

- *Photoelectron Spectroscopy: Principles and Applications by S. Hüfner, Springer, 2003*

An excellent collection of XPS binding energies, cross sections and a lot of other information can be found in the

- *X-ray Data Booklet*, that can be downloaded at xdb.lbl.gov

Example spectra as well as cross sections for XPS and APS can be found in

- *Handbook of X Ray Photoelectron Spectroscopy by J. F. Moulder, et al., Physical Electronics, 1995*
- *Handbook of Auger Electron Spectroscopy by , L. E. Davis et al, Physical Electronics, 1978*

Literature II

For (angle-resolved) photoemission spectroscopy

- Photoelectron Spectroscopy: Principles and Applications by S. Hüfner, Springer, 2003.
- Solid-State Photoemission and Related Methods: Theory and Experiment by W. Schattke, M.A. Van Hove (Eds.), Wiley-VCH, Weinheim, 2003.
- Angle-resolved Photoemission by S. D. Kevan (Ed.), Elsevier, 1992.
- Photoelectron spectroscopy - An overview by S. Hüfner, S. Schmidt, F. Reinert, Nuclear Instr. Meth. in Physics Research A 547 (2005) 8–23 and references therein.

More general introduction to surface science

- Concepts in Surface Physics by M. C. Desjonqueres, D. Spanjaard, Springer 2002.
- Modern Techniques of Surface Science by T. A. Delchar, and D. P. Woodruff, Cambridge Solid State Science Series, 1994.
- Solid State Physics by N. Ashcroft and N. D. Mermin, Saunders College, 1976.

Internship at ILL in Grenoble

What to remember

XPS – X-ray photoelectron spectroscopy

- Core levels
- Which elements are in the sample ?
- What is their (local) chemical environment ? (chemical shift)

UPS – ultraviolet photoelectron spectroscopy

- Valence levels
- Band structure E(k) from resolution of E and k (via angle)

Synchrotron sources

- tunable photon energy … new opportunities
- tunable polarization