8

Electron spectroscopy 1

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Physics of Surfaces and Interfaces
H. Ibach
Springer

Surface Science - An Introduction
K.Oura, V. G. Lifshits, A. A. Saranin, A.V. Zotov, M. Katayama
Springer

Electron spectroscopy

Electronic devices (FET, FGT, ...), created by successive processes (lithography, etching, growth, implantation, ...), are composed of many “layers”

Detection of electron confinement in quantum wells (thin films, heterostructures)

Magnetic tunnel junction (ferromagnet/insulating layers): increased performances by improving the sharpness of interfaces

How to verify composition and cleanliness?

How to verify mixing / alloying at interfaces?

How to determine the density of states?

How to determine the band structure?

How to detect hybridization or bond formation?

Spectroscopy on a macroscopic scale

Electron spectroscopy

Chemical composition	→ XPS, Auger
Valence DOS	→ UPS
Band structure	→ ARUPS (ARPES)

Magnetism	→ XMCD
Bond orientation	→ XLD
Structure modification	→ EXAFS

…

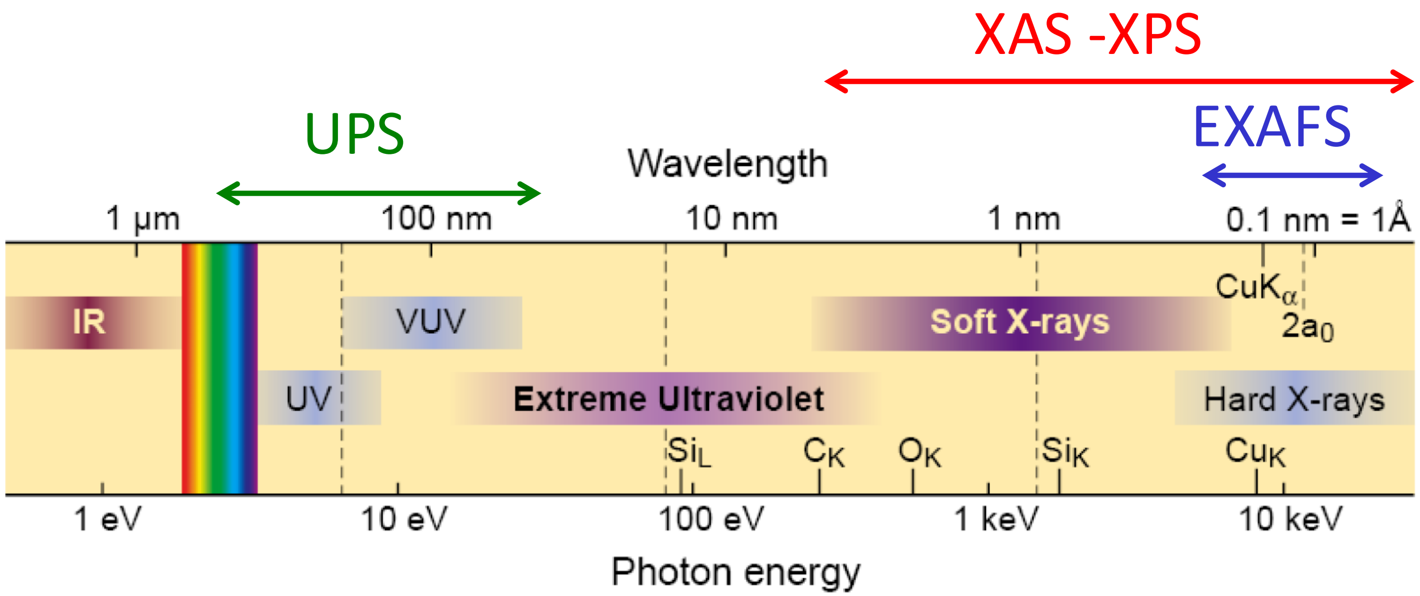
…

Spectroscopy techniques

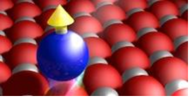
Technique	Probe	Measure
Auger	electron	electron
XPS, UPS, ARPES	photon	electron
XAS, EXAFS	photon	photon / electron

The choice of the technique depends on the information we want to acquire

Electromagnetic spectrum



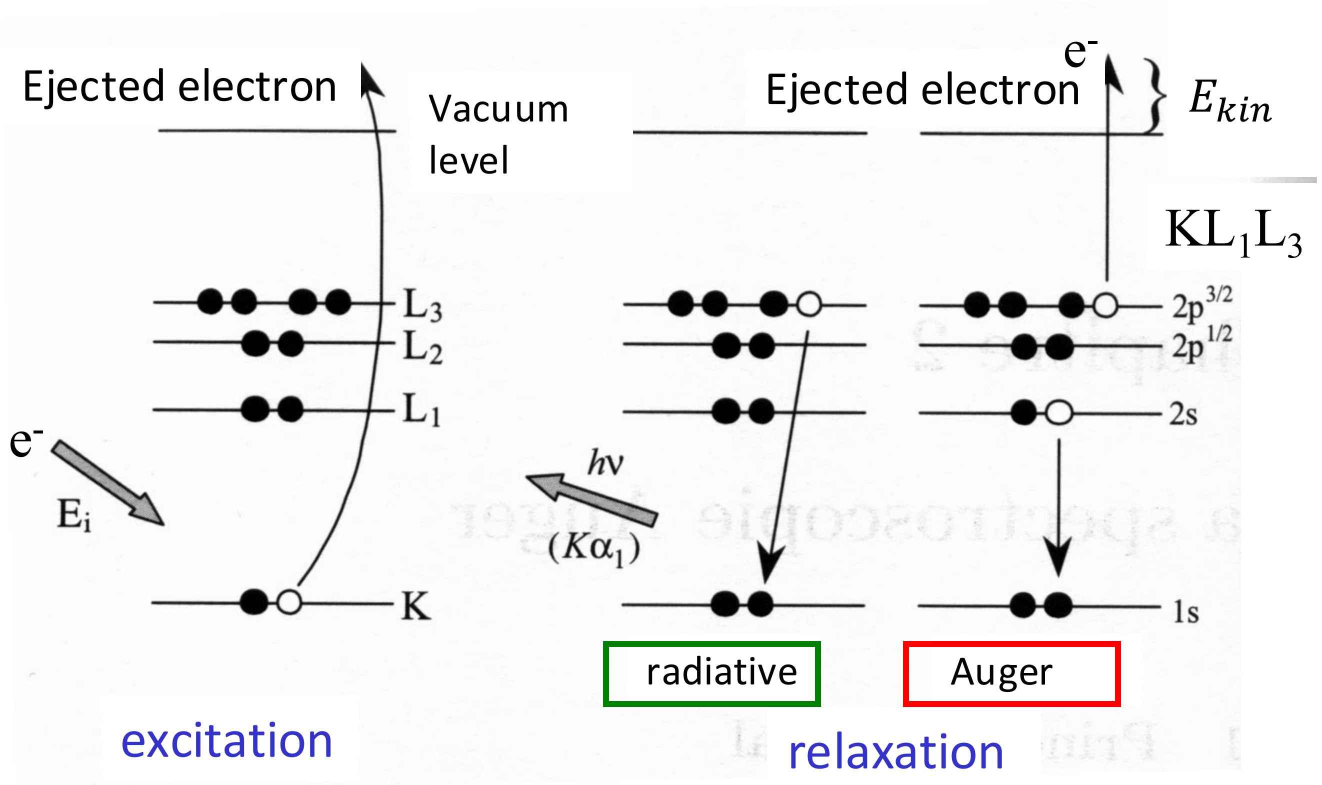
$E = h\nu = hc/\lambda$; $c = 3\ 10^8$ m/s; $h = 6.6\ 10^{-34}$ Js



The Auger process

Exercise 8.1

Auger spectroscopy is based upon an
electron in - electron out process.



E_{bind} : binding energy of the electronic level typically referred to E_F and not to E_{vac} → in principle one needs to consider also the work function Φ (3-5 eV)

$$E_{kin} = E_{bind}(K) - E_{bind}(L_1) - E_{bind}(L_3) - \Phi$$

$E_{bind}(L_i)$ and $E_{bind}(K)$ depend on the element

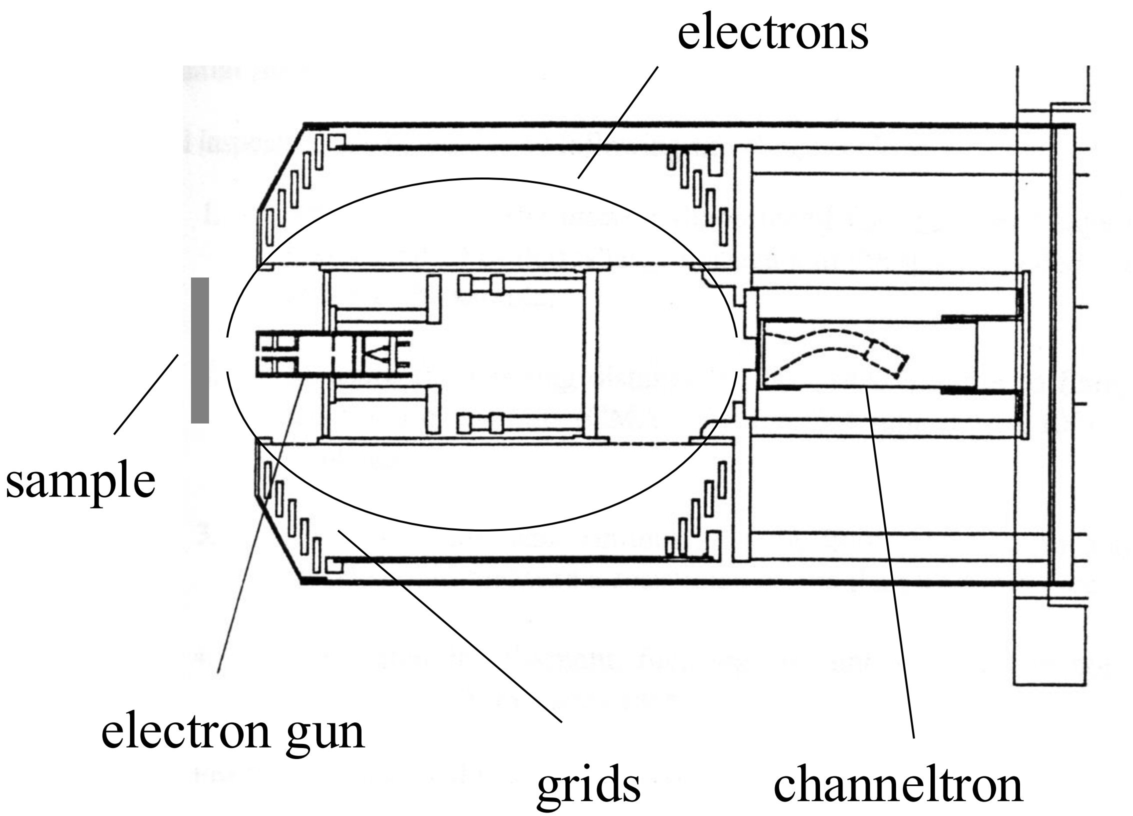
E_{kin} does not depend on $E_{incident}$

↓

chemical sensitivity

simple description neglecting screening and final state effects

Auger experimental setup



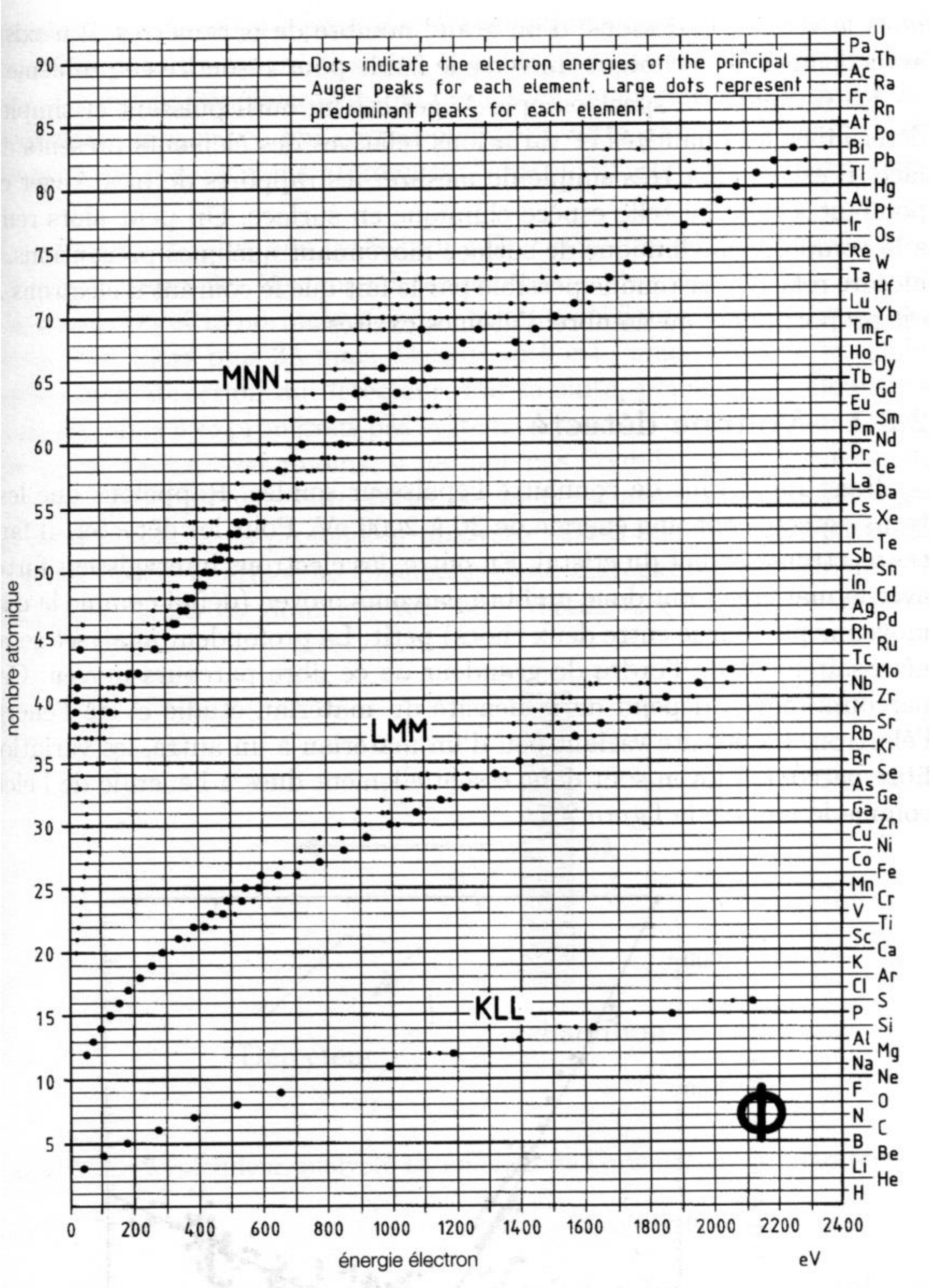
Electron energy:	in	1- 10 keV
	out	0.01 – 2 keV

detection limit ~ 0.5% of a monolayer

Auger spectrum: number of emitted electrons as a function of their kinetic energy

Auger transitions for the different elements

The energy transitions are characteristic of the element
→ chemical sensitivity



Dots indicate the electron energies of the principal Auger peaks for each element. Large dots represent predominant peaks for each element.

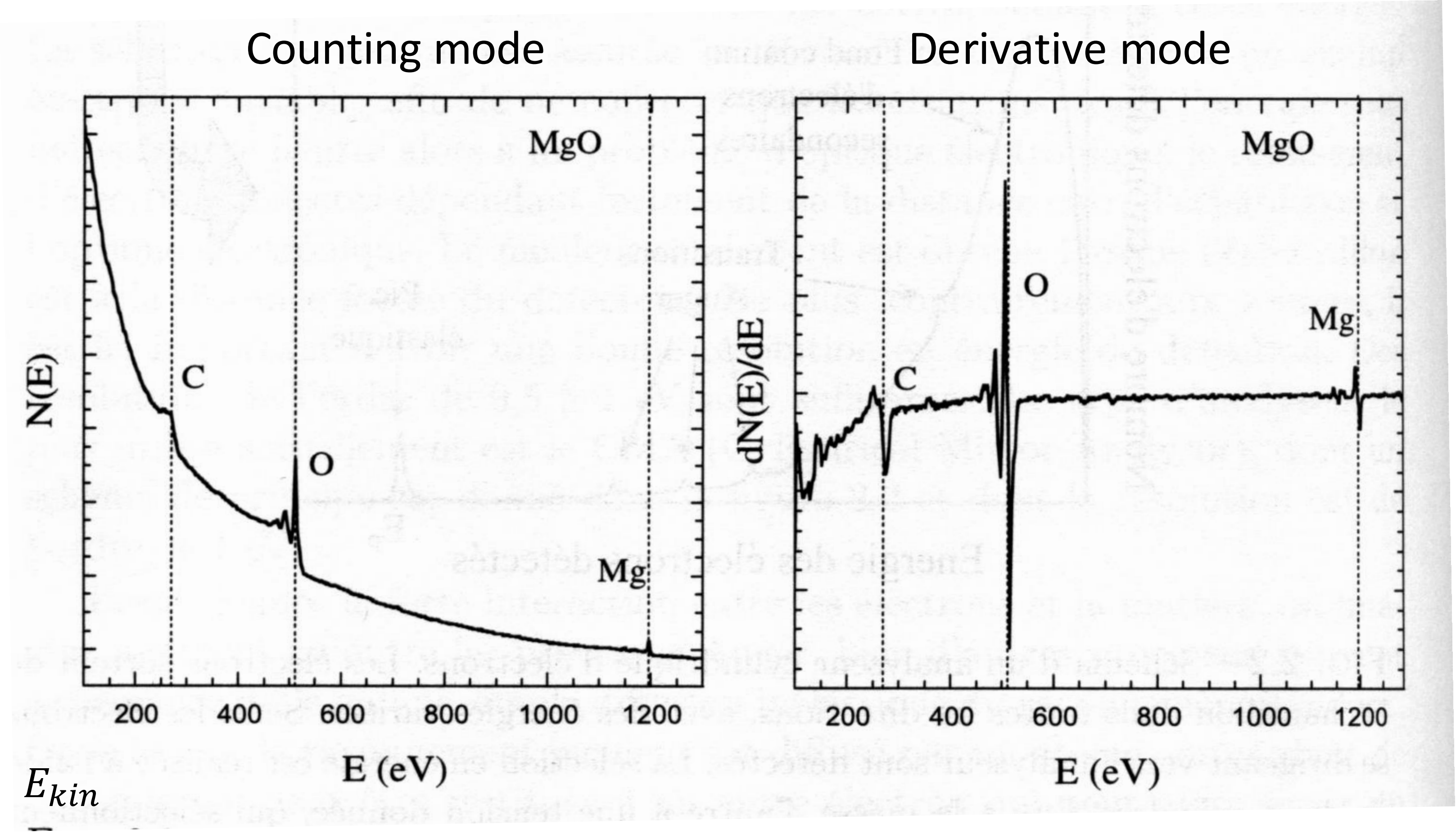
n: principal quantum number

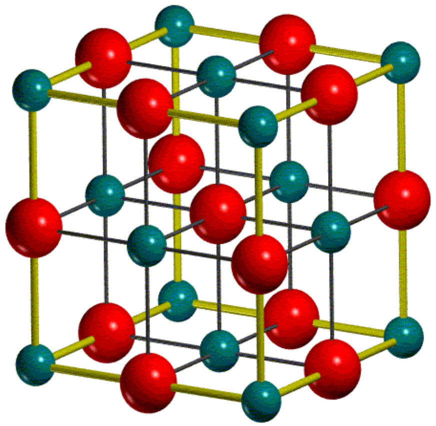
MNN
involved electrons:
n=3 (excitation)
n=4

LMM
involved electrons:
n=2 (excitation)
n=3

KLL
involved electrons:
n=1 (excitation)
n=2

Example: MgO





The monotonic background is due to multi-scattered electrons

Relative sensitivity: correction factors must be considered to obtain the real intensity

Surface sensitivity

Auger electrons (detected at surface) coming from depth z:

$$I(z) = I(0)\ \exp(-z/\lambda)$$

total Auger electron current measured at surface:

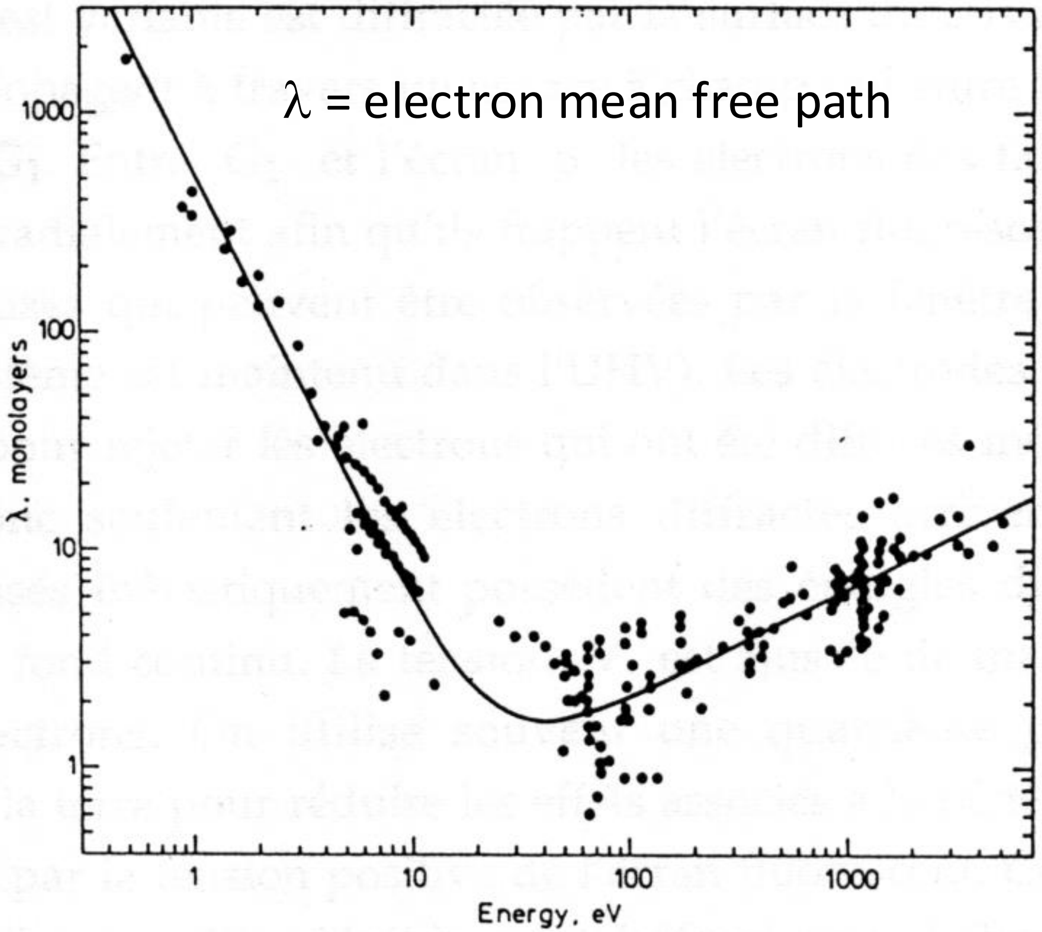
$$I\ =\ \int_0^z I(z)\,dz\ = I(0)\,\lambda\,(1\ - \exp(-z/\lambda))$$

Surface sensitivity results from the limited mean free path of the outcoming electrons

Thickness D from which originates 95% of the signal:

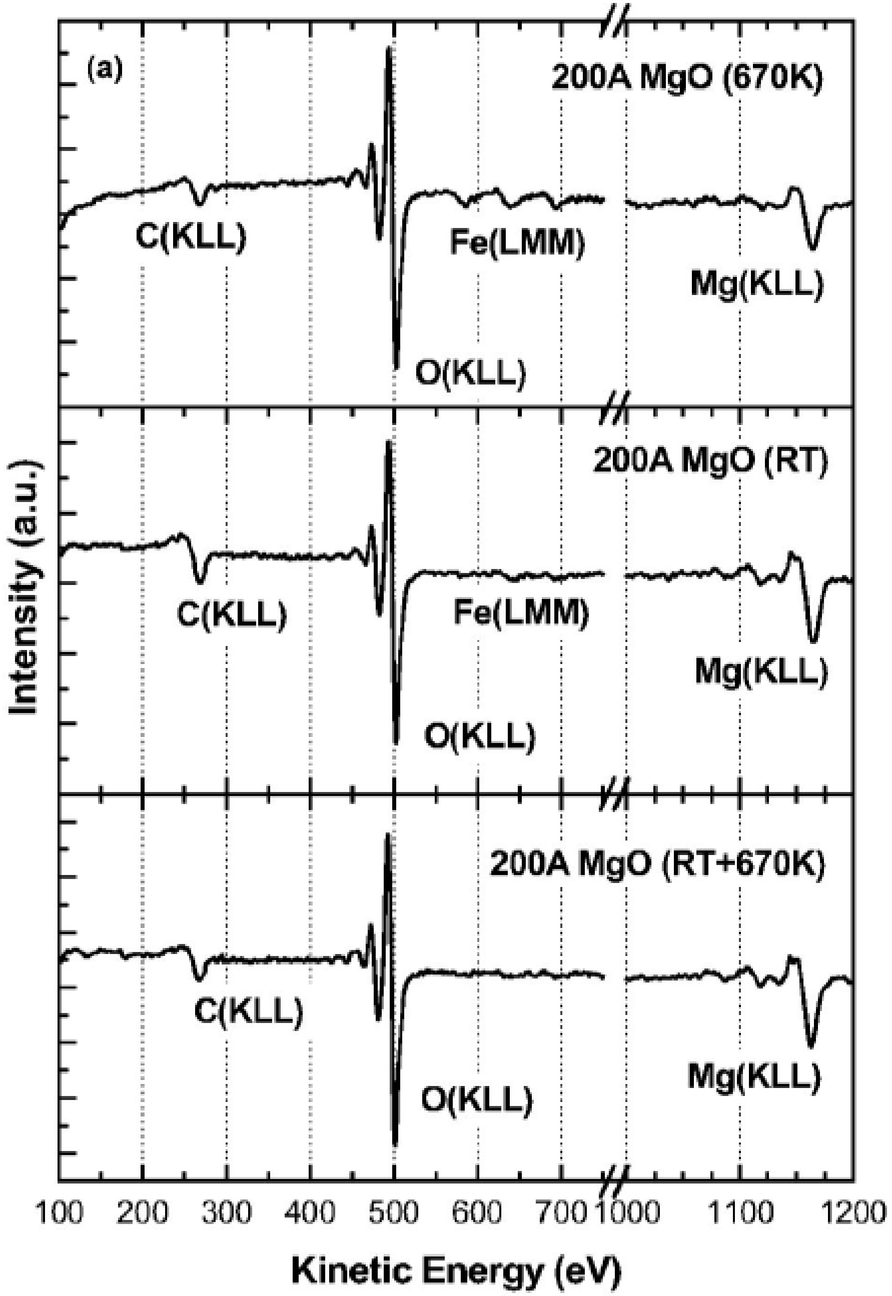
$$I(D) = I(0)\,\lambda\,(1\ - \exp(-D/\lambda)) = I(0)\,\lambda\,0.95$$

$$D\ = -\lambda\ln(0.05) \approx 3\lambda$$



λ = electron mean free path

Example: MgO/Fe(001), information about growth



Visible Fe absorption peaks:
MgO does not wet completely the Fe bottom electrode (columnar growth with pits)

Almost no Fe absorption peaks, but rough MgO layer

No Fe signal:
annealing of the RT grown sample gives rise to a continuous layer (no pits)

J. Appl. Phys. **97**, 036104 (2005)

Photoelectron spectroscopy / Photoemission

Exciting particle: photon

Emitted particle: electron

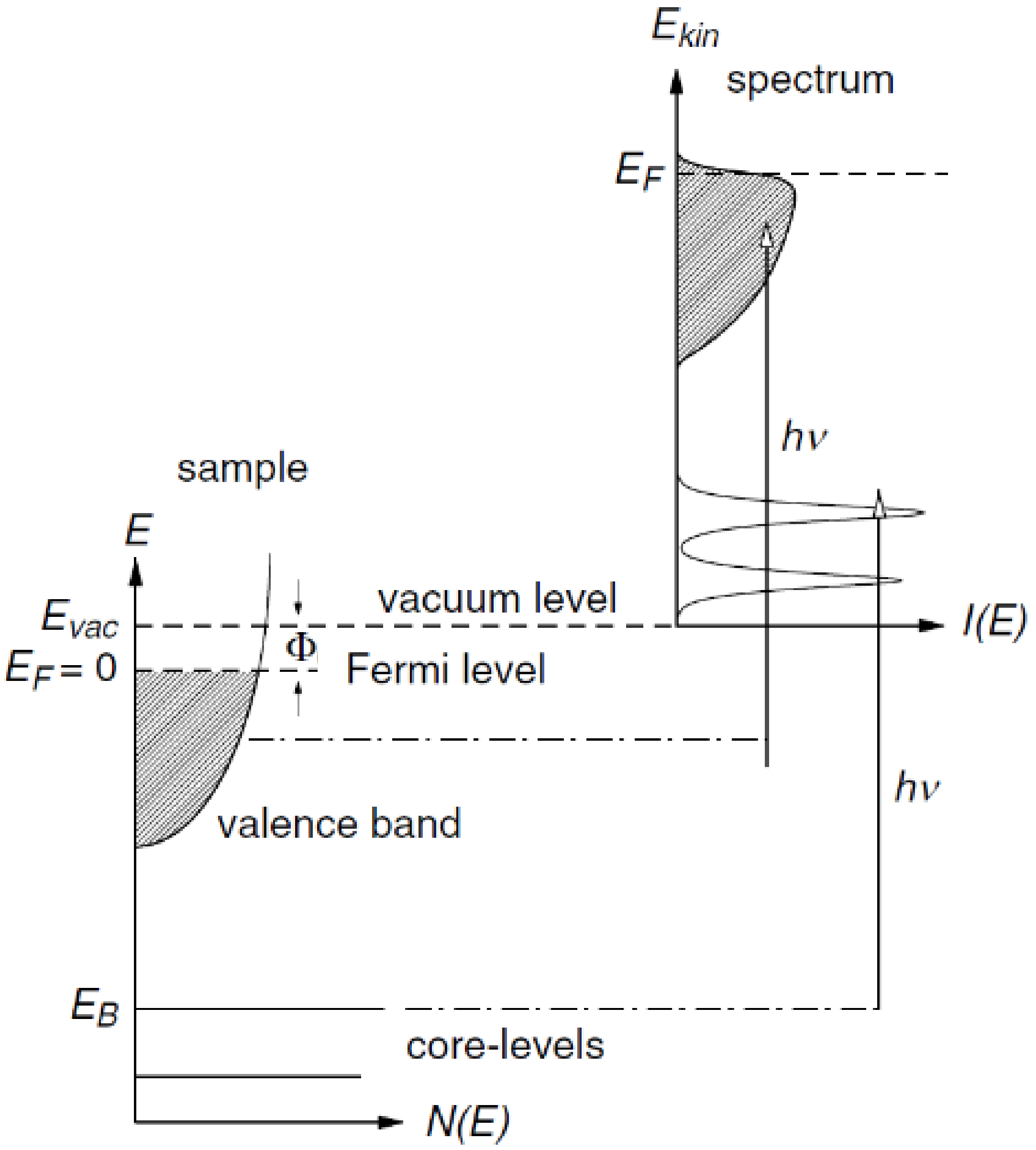
The energy of a photon is given by $E = h\nu$

h Planck constant
ν radiation frequency (Hz)

$$E_{kin} = h\nu - E_{bind} - \Phi$$

E_{kin} is the kinetic energy of the emitted electron

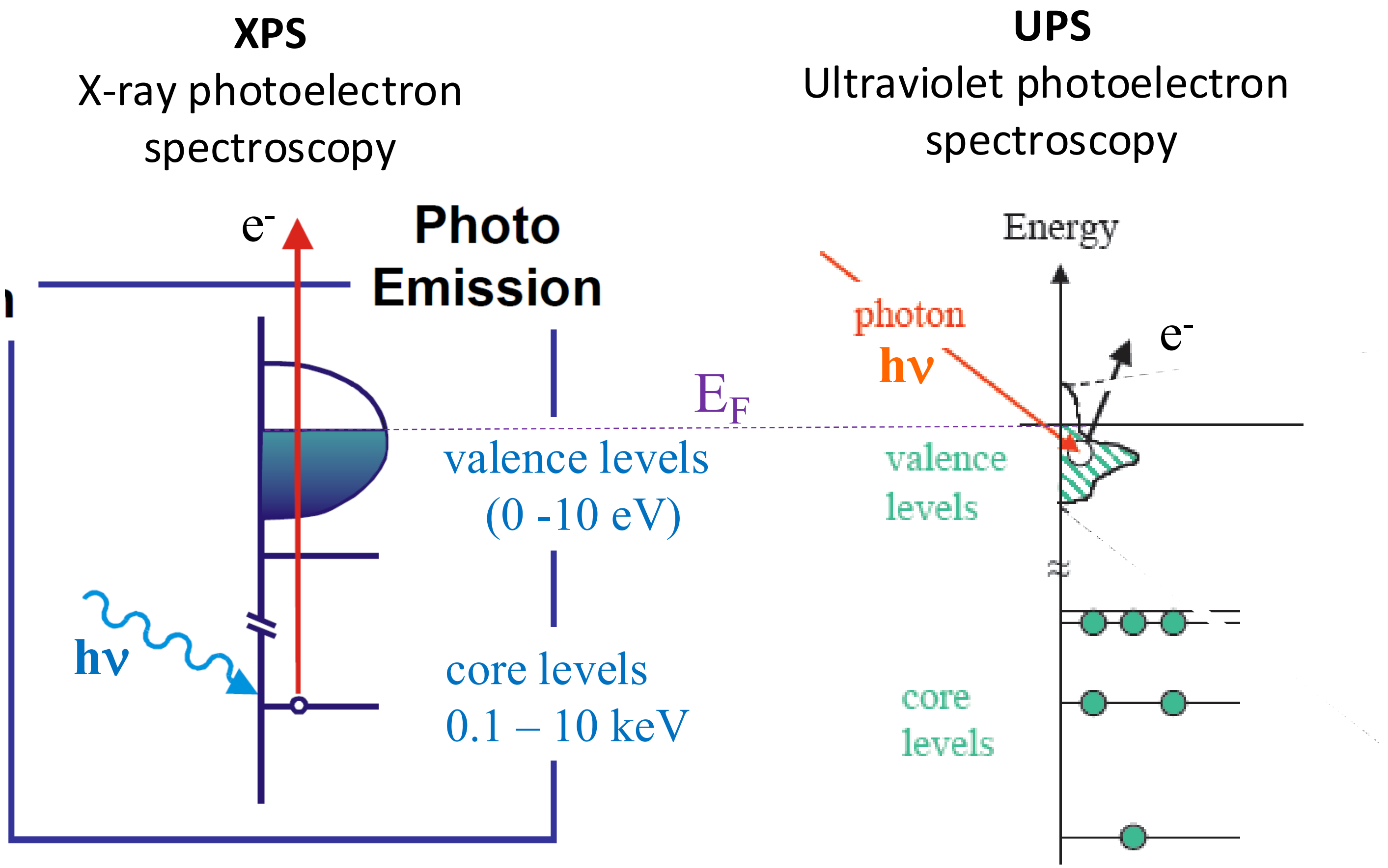
it depends on the level that has been excited



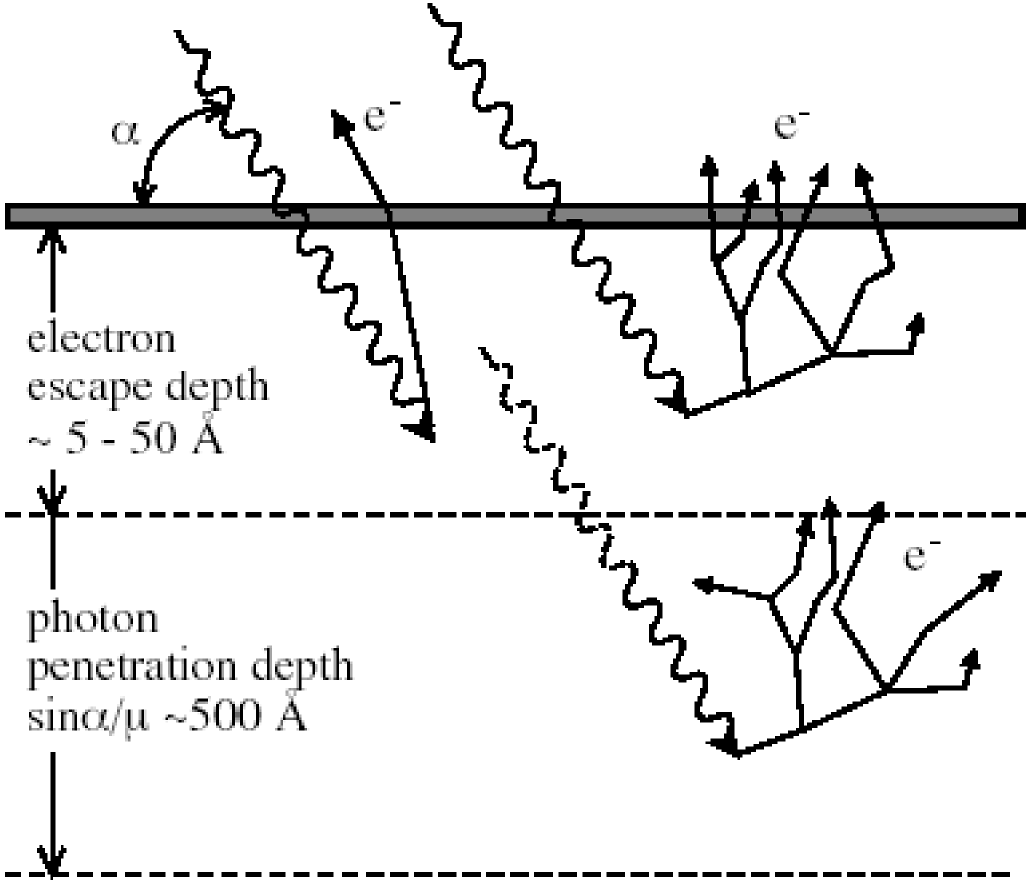
XPS vs. UPS: core vs. valence state excitation

X ray photons (0.2 –10 keV) → to investigate core levels
UV photons (10 - 100 eV) → to investigate valence levels

although energy distinction between core and valence is not strict



Surface sensitivity

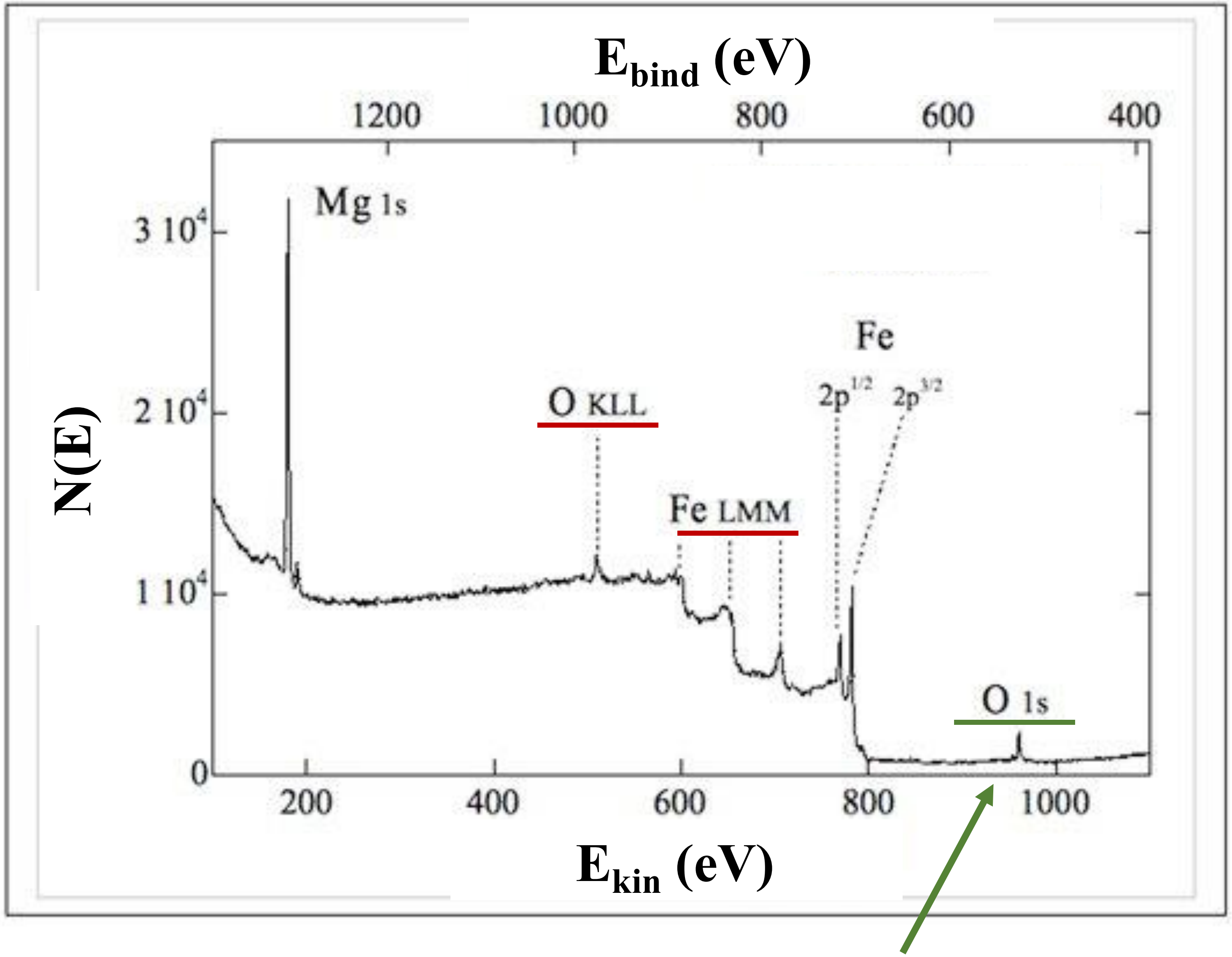


Photon penetration depth > 1-10 mm

→ surface sensitivity given by the reduced mean free path (escape depth) of the outcoming electrons

Example: XPS spectrum of MgO/Fe

Exercise 8.2



$h\nu$ = 1486 eV

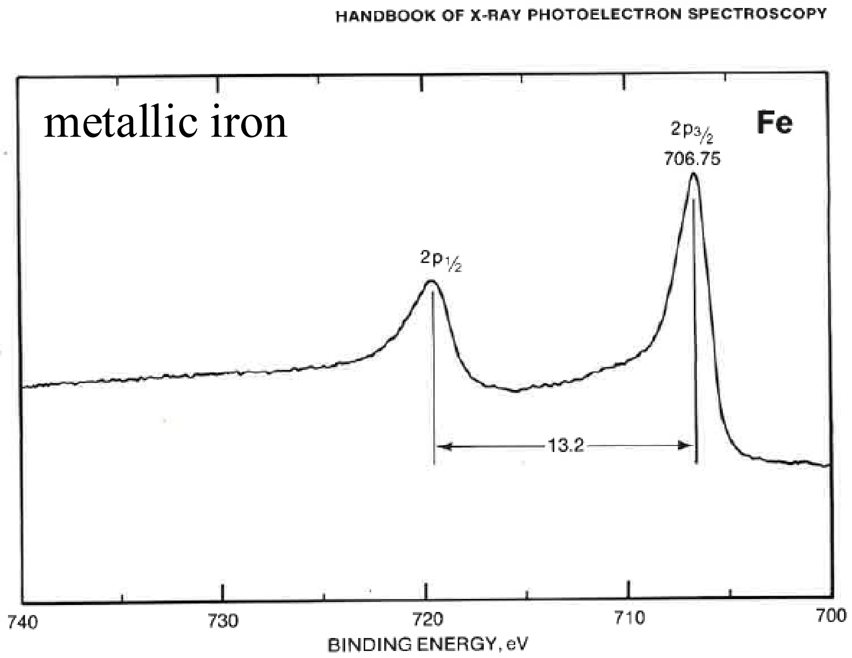
Auger electrons are also detected.

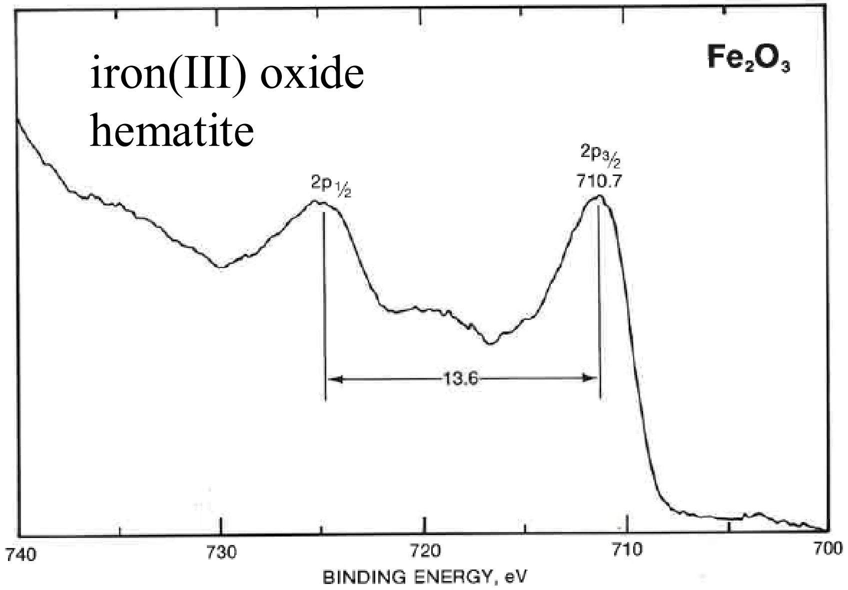
Their energy does not depend on the energy of the photons

energy of O 1s (K edge) : $E_{bind} = h\nu - E_{kin} - \Phi \approx 1486 - 945 \approx 540\text{ eV}$

XPS spectrum: Fe 2p (L_2, L_3), chemical shift

atomic:
[Ar] $3d^6$ $4s^2$





2p levels are split by the spin-orbit coupling

$j = l + s, l - s$

$l = 1$

$s = 1/2$

$j = 3/2, 1/2$

based on degeneracy $(2j + 1)$, intensity ratio: $2p_{1/2}$: $2p_{3/2}$ = 1 : 2
The anti-parallel alignment is more favorable, has a lower energy and therefore appears at higher binding energy

+3 oxidation state:
Fe “loses” the two 4s electrons and one 3d electron

chemical shift correlated with overall charge on atom:
reduced charge → reduced coulomb screening
→ increased binding energy
(mainly an initial state effect)

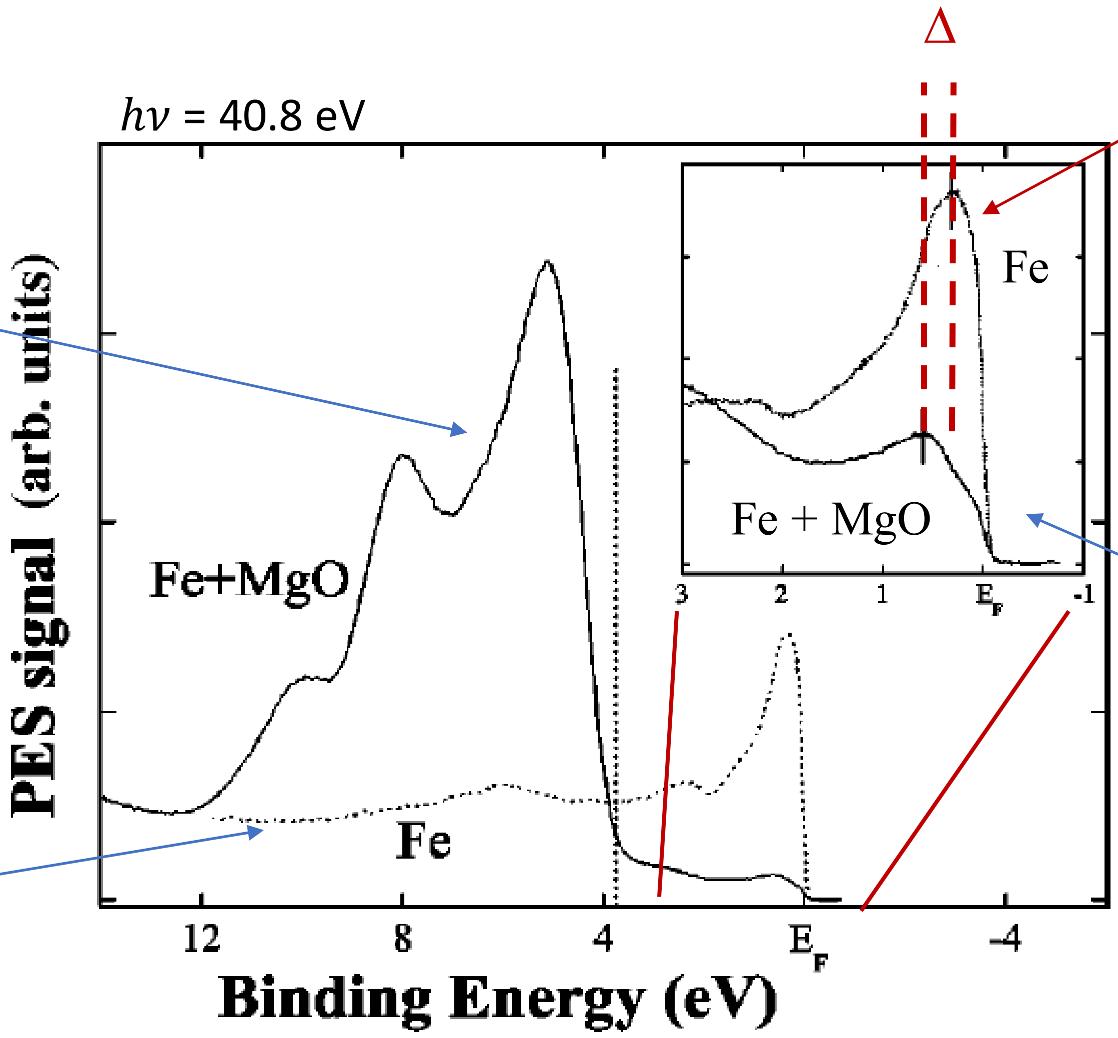
peak energy → oxidation state

Example UPS spectrum: MgO/Fe (interface in MTJ)

Exercises 8.3 – 8.5

MgO is an insulator with a gap of 8 eV

Fe electronic structure: [Ar] $3d^6\ 4s^2$



Weak modification of the Fe DOS

Spectral intensity dominated by the MgO contribution

Spectrum of Fe before MgO growth

Spectral intensity dominated by the Fe contribution (no MgO state in the energy gap)

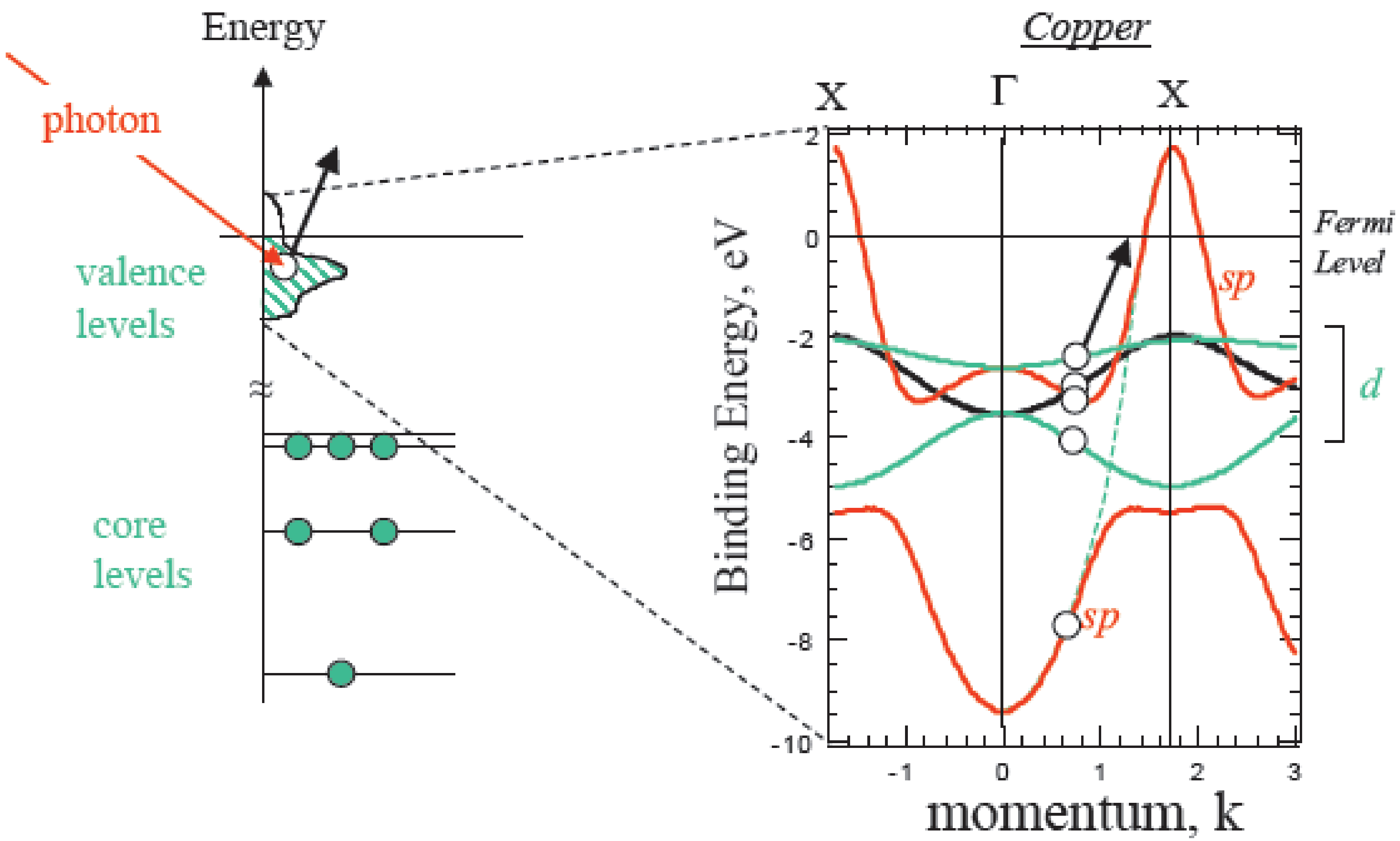
Sicot *et al*. Phys. Rev. B **68**, 184406 (2003)

UPS vs ARUPS (or ARPES)

UV photons (10 - 100 eV) → to investigate valence levels
ARUPS: Angle Resolved UPS
ARPES: Angle Resolved PhotoElectron Spectroscopy

UPS is k-integrated (DOS)

ARPES can measure the wave vector k and the energy at the same time (band structure)

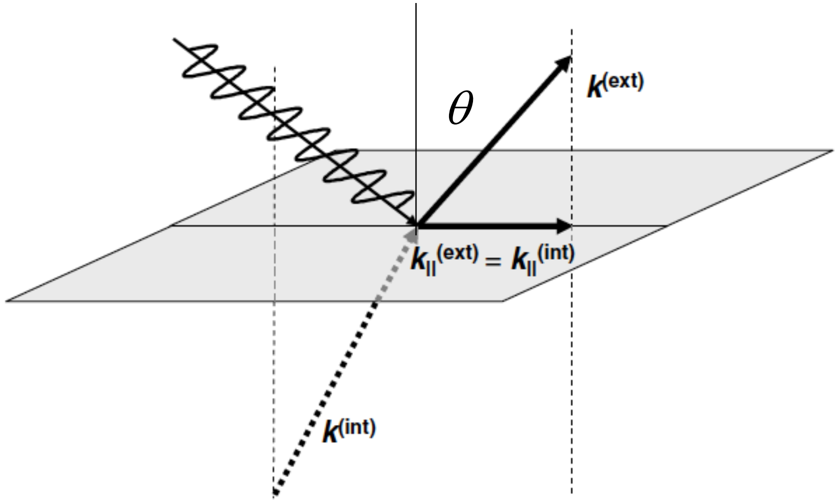


STM gives access to the DOS as a function of energy, but poor information on k (with exceptions, as for example the standing wave of 2D gas at metal surfaces)

ARUPS (or ARPES)

We have already found the condition for energy conservation: $E_{kin} = h\nu - E_{bind} - \Phi$
What about the momentum?

Three-step model (valid also for XPS and UPS):
1) The electron is excited from an initial to a final state within the crystal;
2) The electron travels through the solid towards the surface without scattering;
3) The electron crosses the surface and is emitted into the vacuum with a certain kinetic energy



Momentum conservation: due to symmetry translation breaking at the surface, only the electron momentum component parallel to the surface is conserved, modulo a reciprocal surface vector
(photon momentum is negligible)

$$\hbar \boldsymbol{k}_{/\!/,i} = \hbar \boldsymbol{k}_{/\!/,f} + \boldsymbol{G}$$

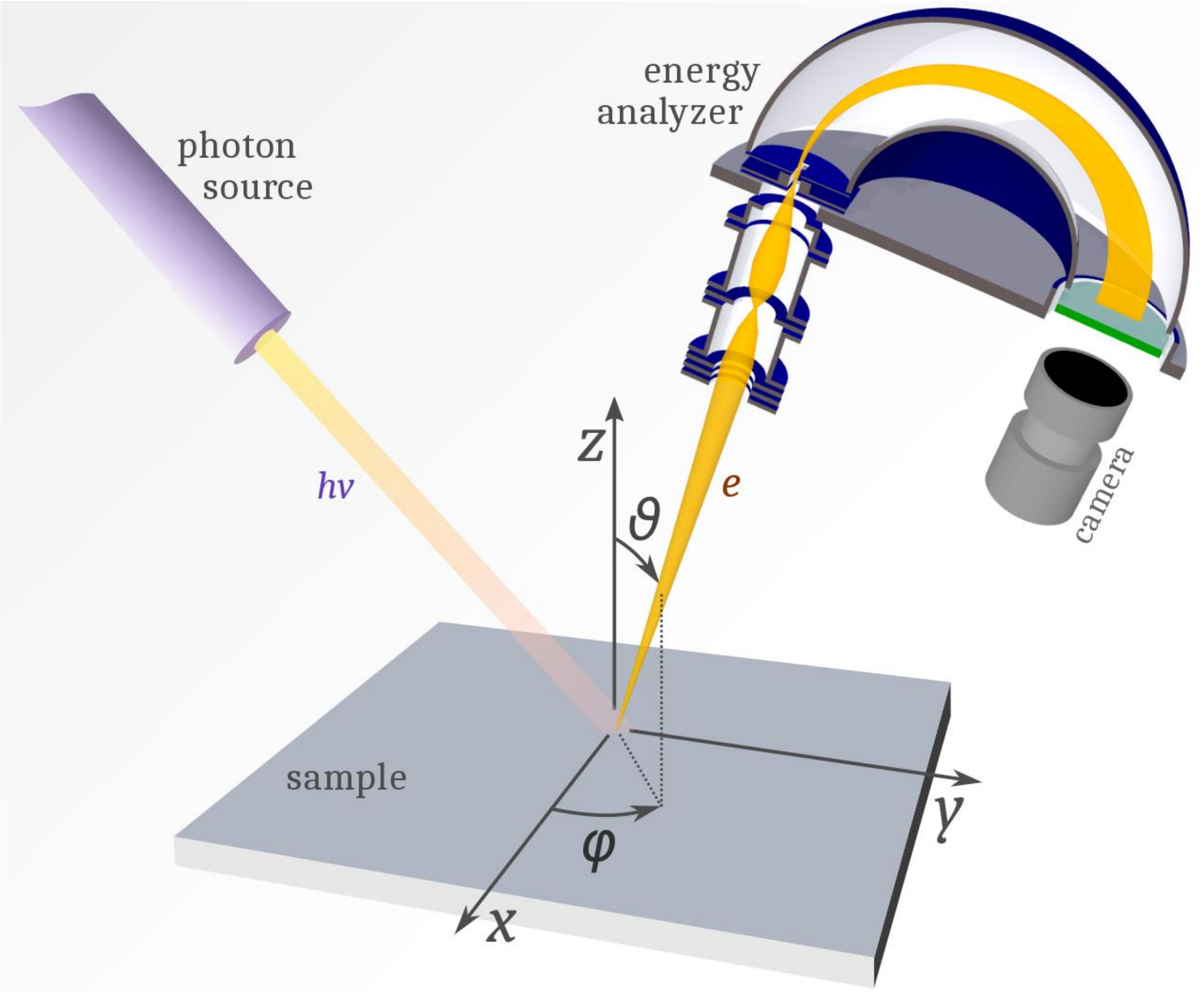
$$\hbar k_{/\!/,f} = \sqrt{2mE_{kin}}\,\sin\theta$$

$$\hbar k_{/\!/,i} = \sqrt{2m(h\nu - E_{bind} - \Phi)}\,\sin\theta$$

Because of their 2D nature, the k-vector of surface states is fully determined by the $k_{/\!/}$ −vector of the photoemitted electron.
The perpendicular component of the k-vector of bulk states remains unknown, but can be established by special techniques

➡ Measurement of E *vs* k
Band structure

ARUPS (or ARPES)

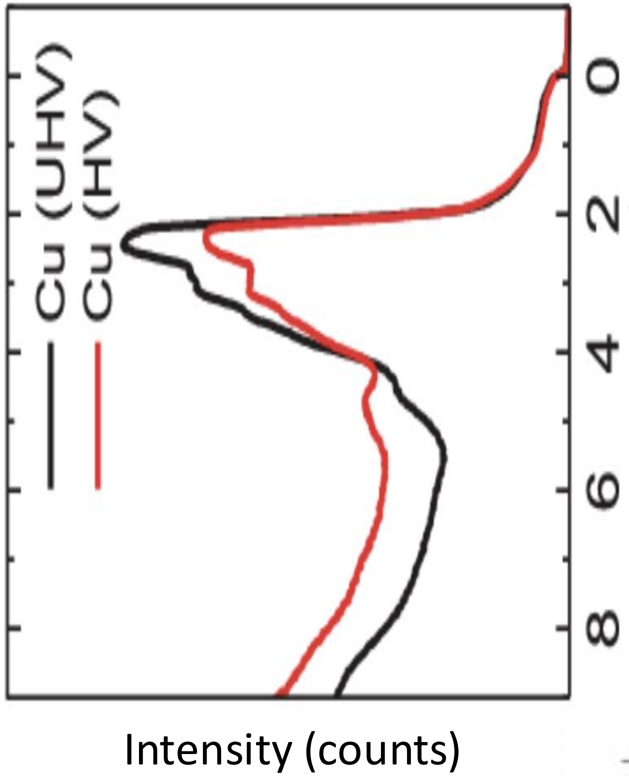


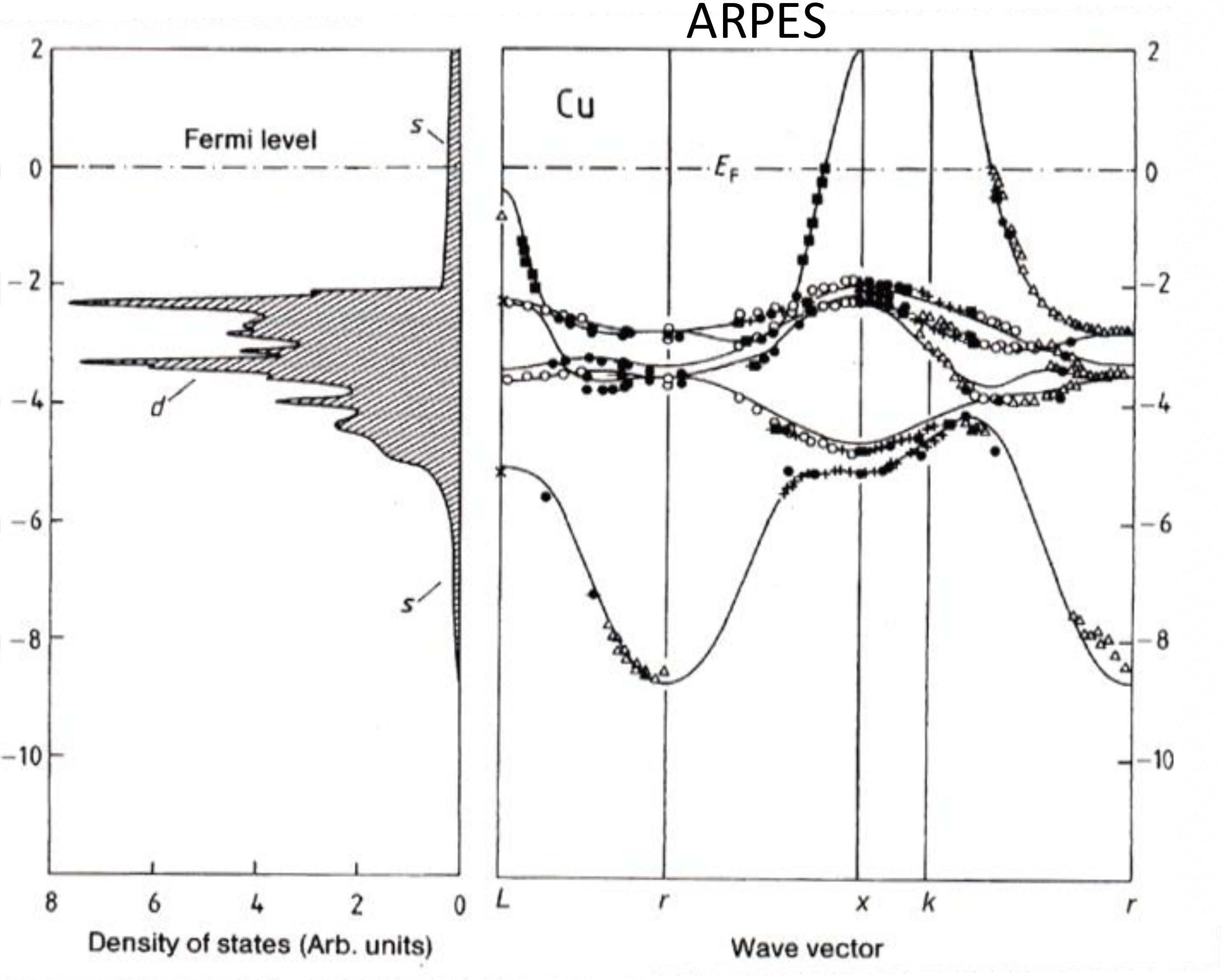
Picture from https://fr.wikipedia.org/wiki/Spectroscopie_photo%C3%A9lectronique_r%C3%A9solue_en_angle

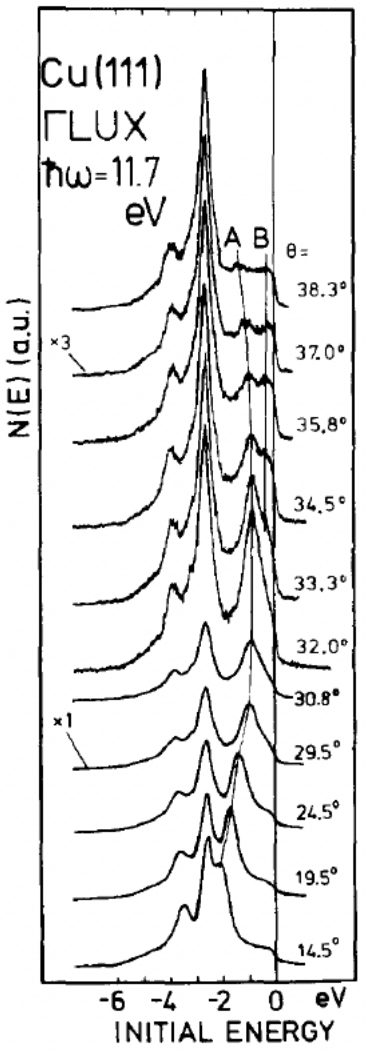
UPS vs ARPES

UPS

ARPES



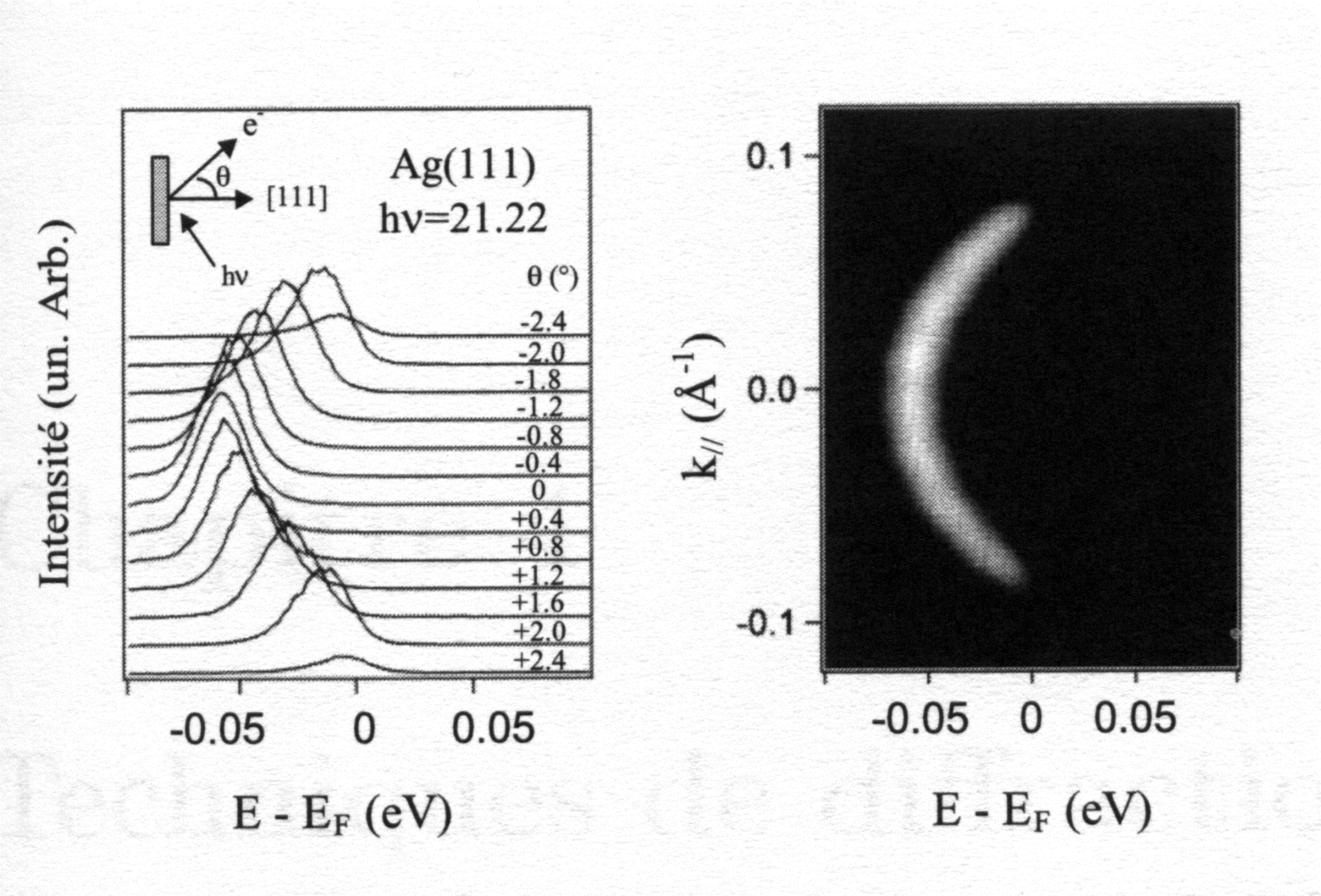




Integrated in k-space

Resolved in k-space:
band structure

Ag(111) surface state



Surface states behave likes a 2D gas of free electrons

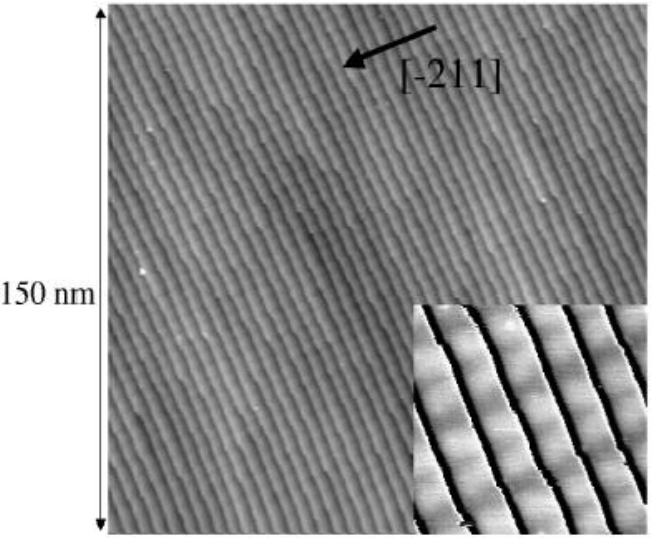
(see lecture on local spectroscopy)

$$E = E_F - E_0 + \frac{\hbar^2 k^2}{2m^*}$$

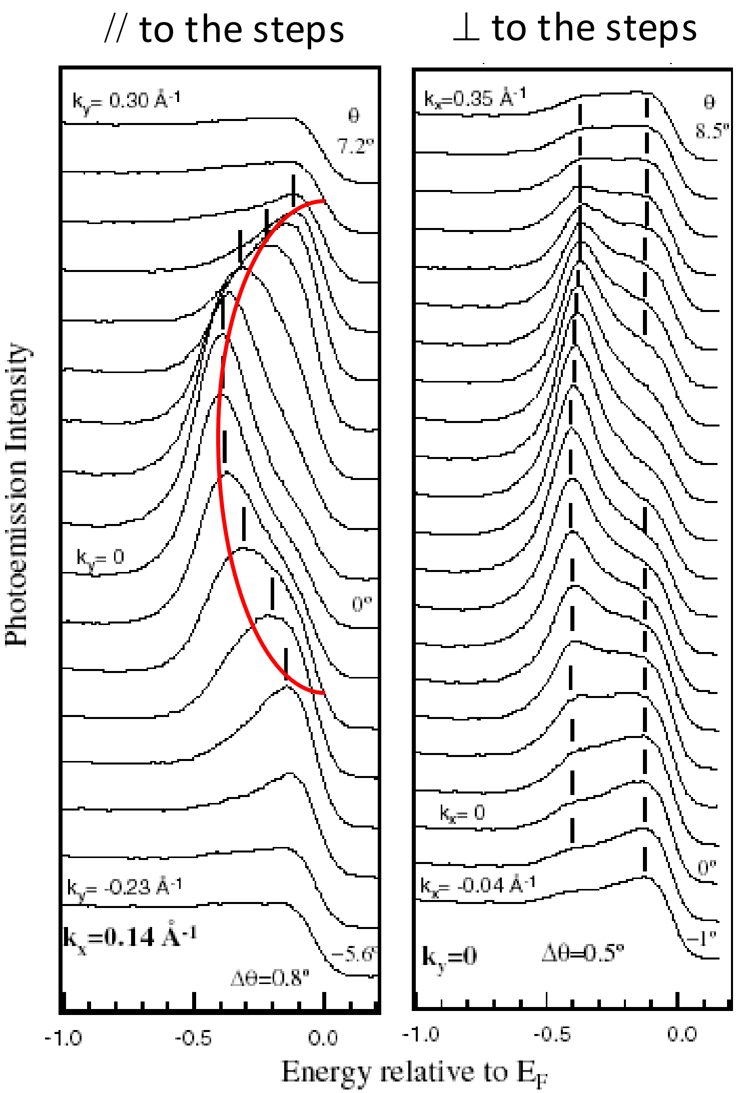
m^* : effective mass of the surface state electron

Example: surface state confinement on Au(788)

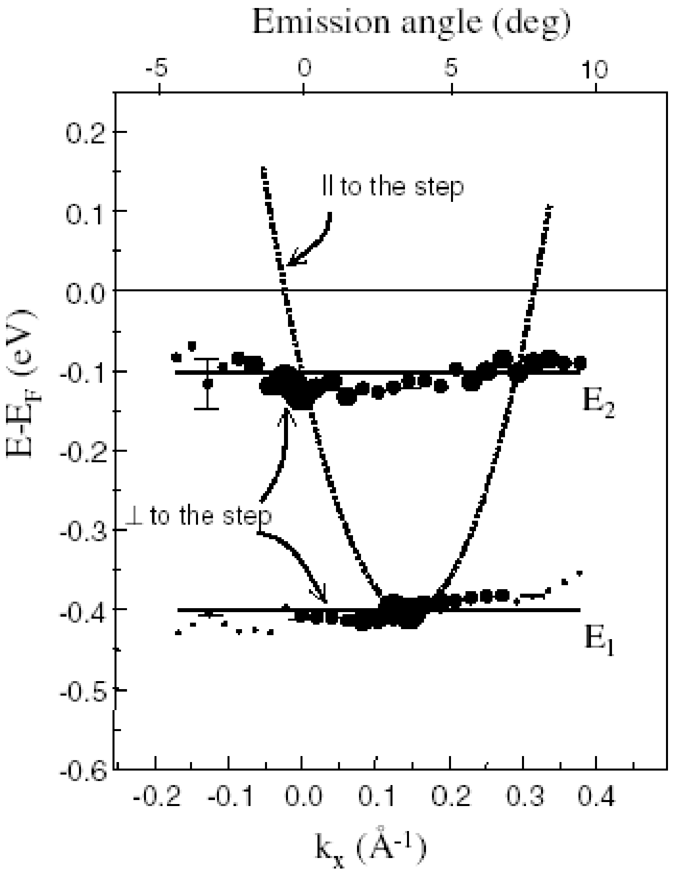
Exercise 8.6



L = terrace width = 3.8 nm



One dimensional quantum well of width L perpendicular to the steps



$$\Psi_{\mathbf{k}}(\mathbf{r}) \propto \exp(ik_{\parallel}y)\,\sin(k_{\perp}x)$$

$$k_{\perp} = \frac{n\pi}{L}$$

$$E_n = E_F - E_0 + \frac{\hbar^2}{2m^*}\frac{\pi^2}{L^2}n^2$$

A. Mugarza et al., Phys. Rev. Lett. **87**, 107601 (2001)

Example: 1D quantum well states

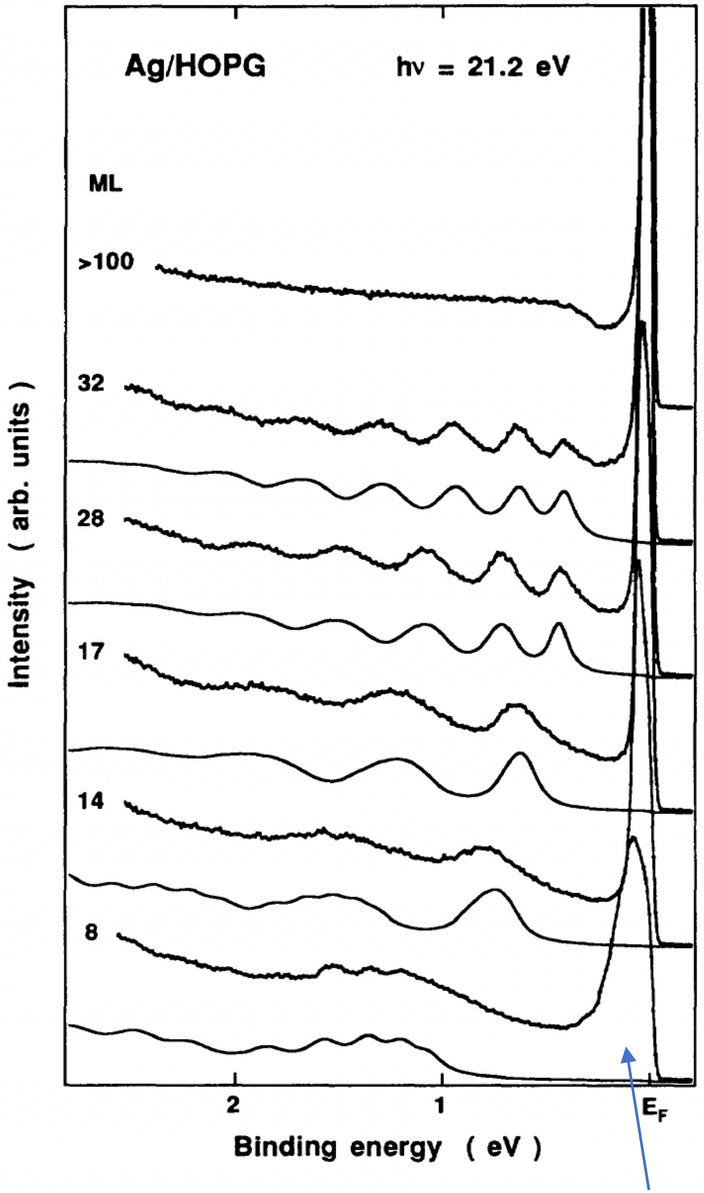
Ag thin films on highly-oriented pyrolytic graphite

Confinement in the direction perpendicular to the surface

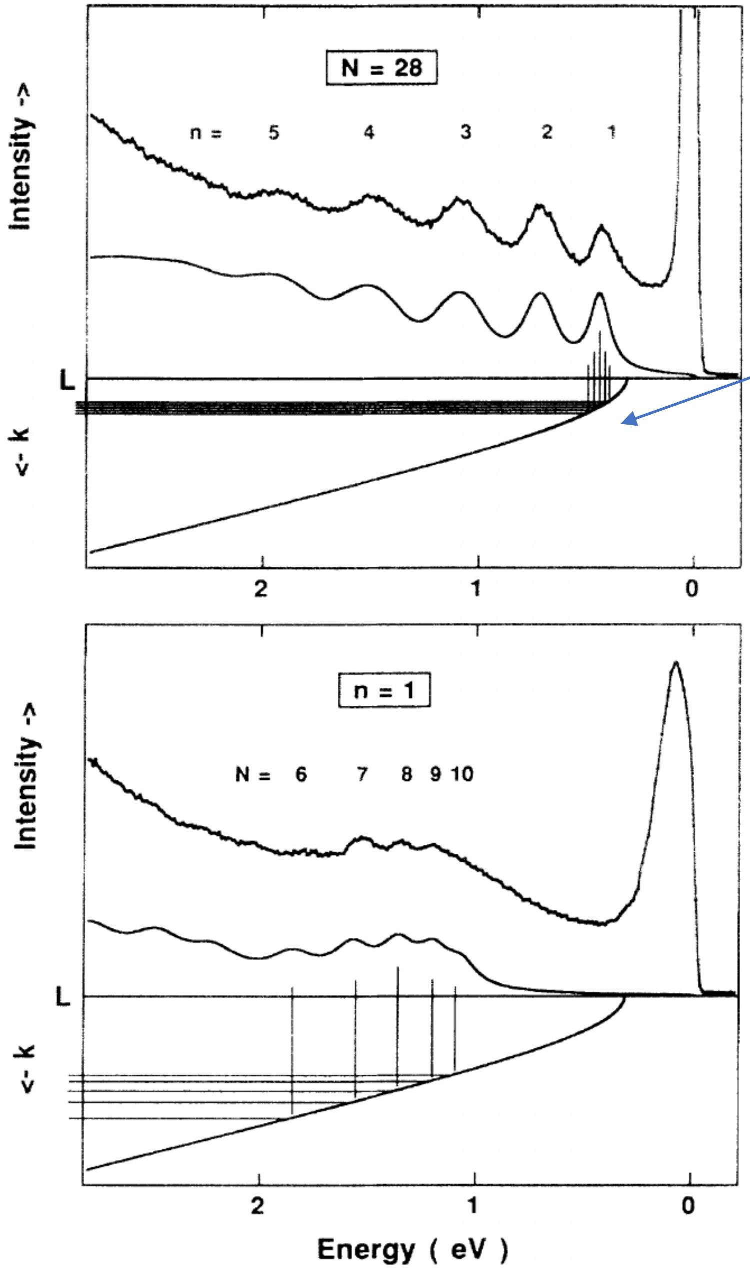
N number of layers

n quantum number

10.1103/PhysRevB.50.17560



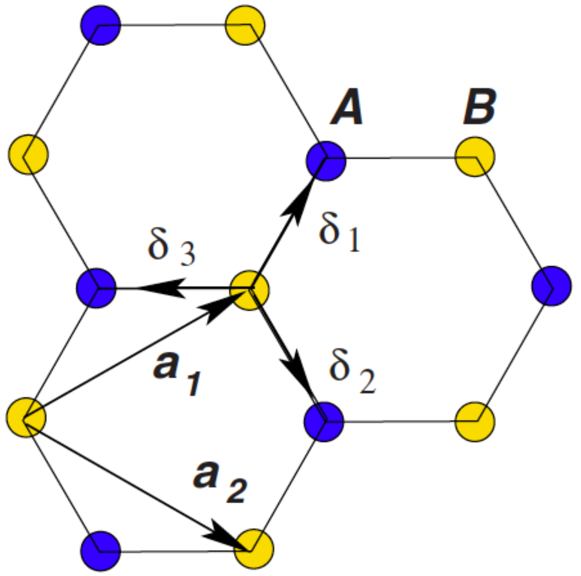
surface state

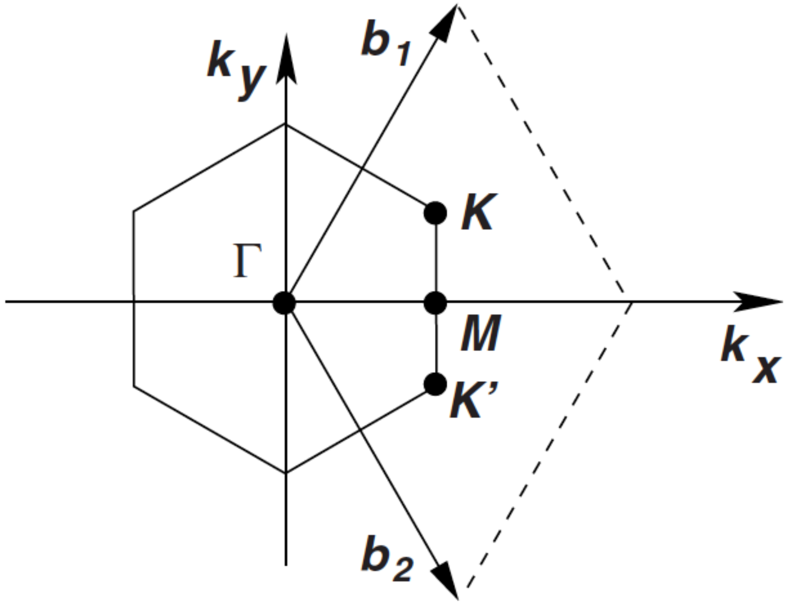


n = 1 for thicknesses around N=28

2D system: Graphene

Tight-binding description of the π bands (originating from p_z)

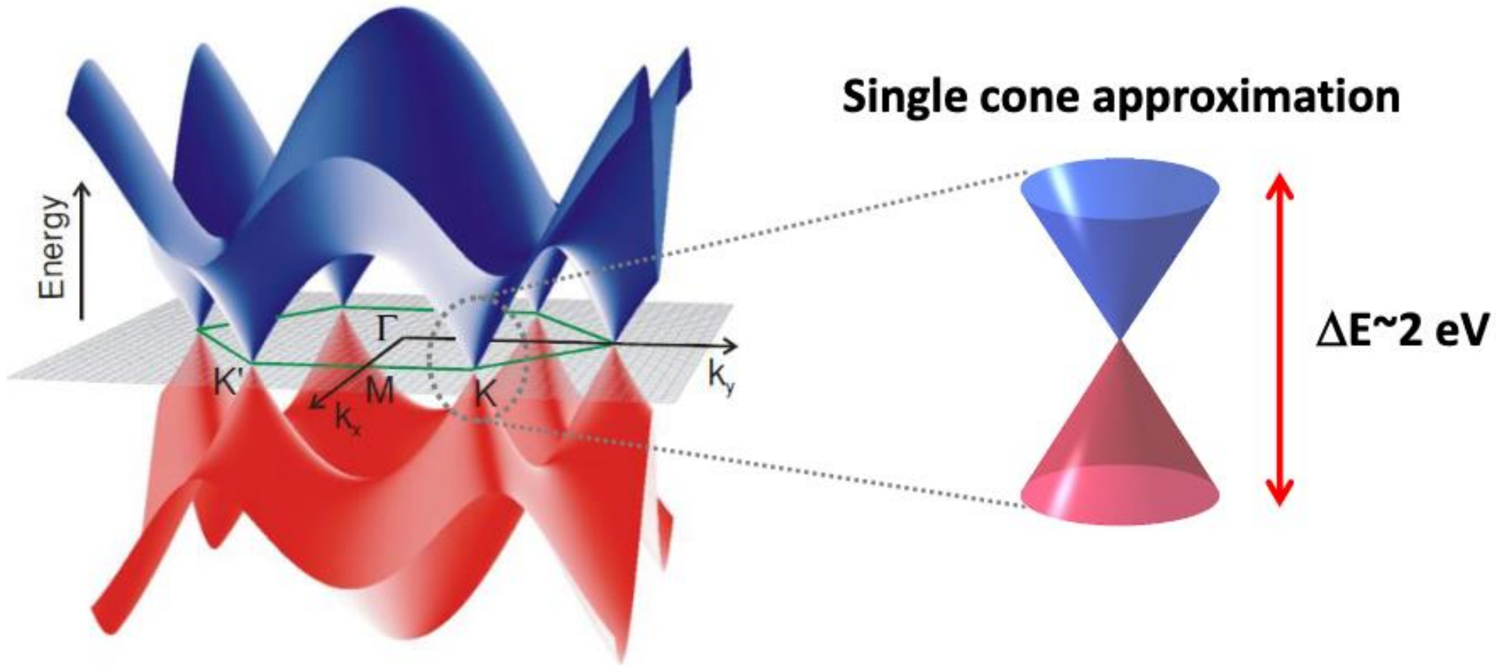




- triangular Bravais lattice with a base formed of two atoms (A and B)
- A and B sublattices
- for each atom, the 3 nearest neighbors belong to the other sublattice
- non-zero hopping parameter only for nn
- starting from Bloch wavefunctions localized on A and B, we build the wavefunctions describing the π bands
- find the expression for their energy vs k in the FBZ

Graphene π bands

Exercises 8.7 – 8.8



Around K and K’ points, the energy dispersion is linear, very different from the usual fee-electron like quadratic dependency (Dirac points)

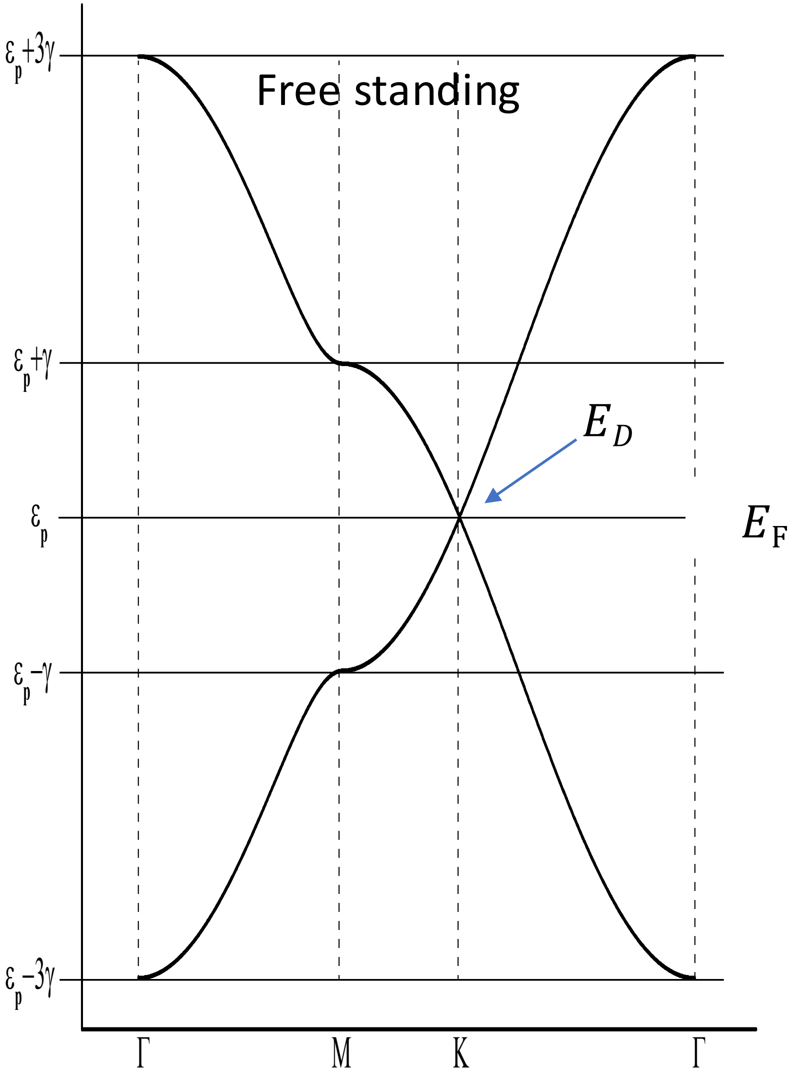
It can be shown that (wavevector k centered on K or K’):

$$E = \pm \hbar v_F k$$

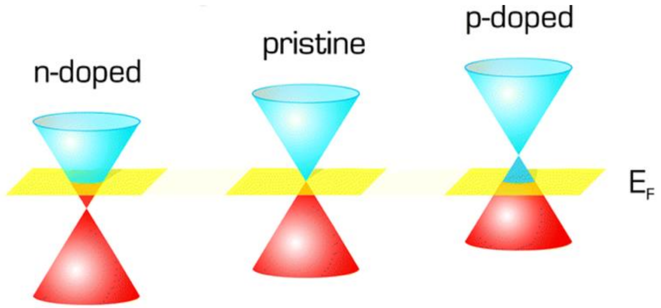
$$v_F = \frac{3|\gamma|a}{2\hbar}$$

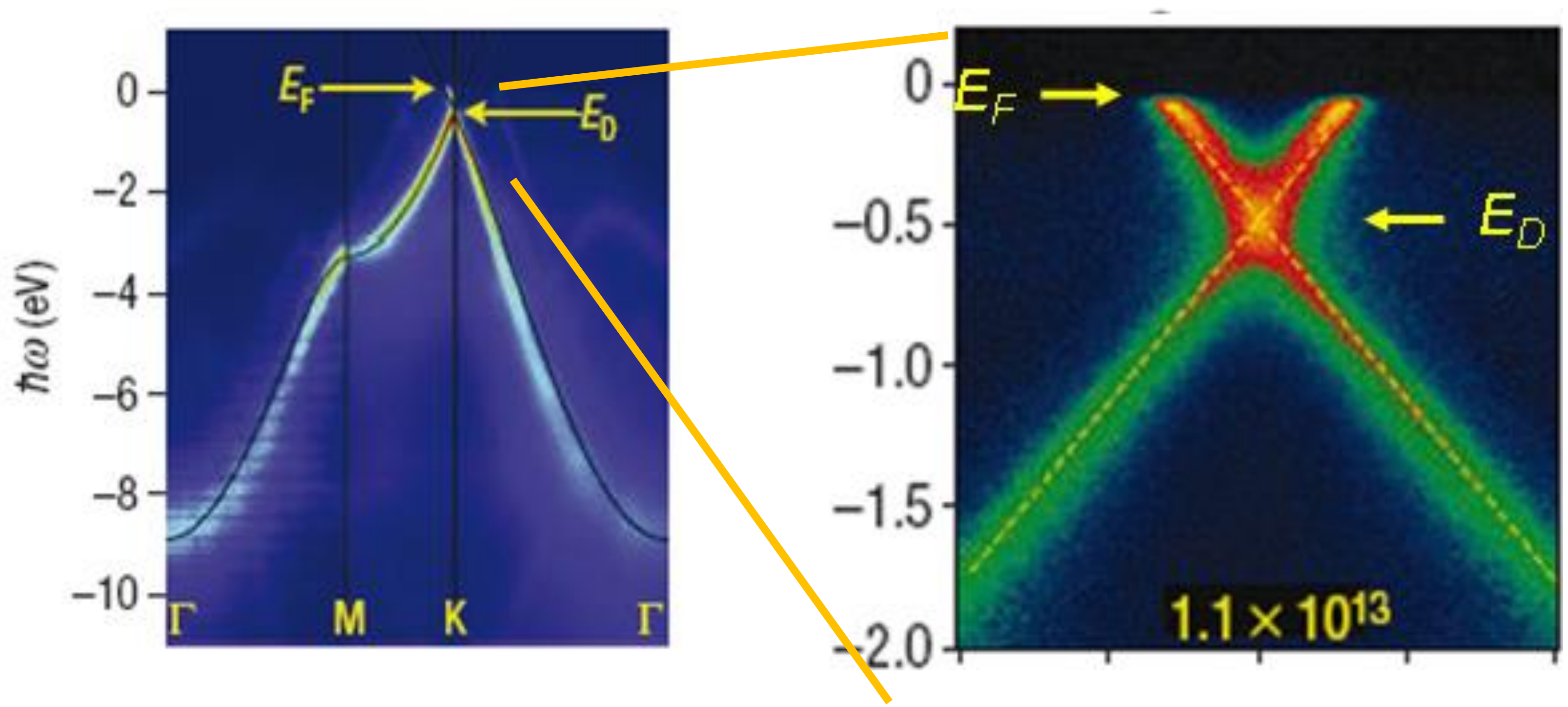
for ideal, free-standing graphene E_F coincides with the Dirac points

Epitaxial graphene



Graphene on SiC





The Dirac point E_D coincides with the Fermi level in free standing graphene

On SiC, E_D = -0.5 eV (below Fermi level) due to graphene-substrate hybridization

Nature Materials **6,** 183–191 (2007)

Gap opening ?

graphene: semimetal or zero-gap semiconductor

technological advantages for graphene to be a semiconductor instead of a semimetal, specifically in electronic applications (transistor)

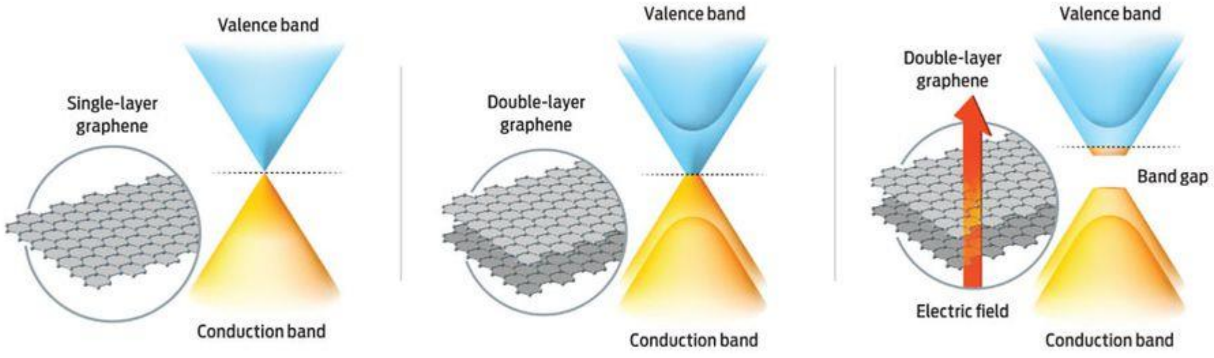
possible paths:

- geometrically confine graphene into nanoribbons or quantum dots
- grow graphene on substrates that induce lattice potentials that open a gap

- bilayer graphene + field effect
- twisted bilayer graphene
- bilayer graphene + strain

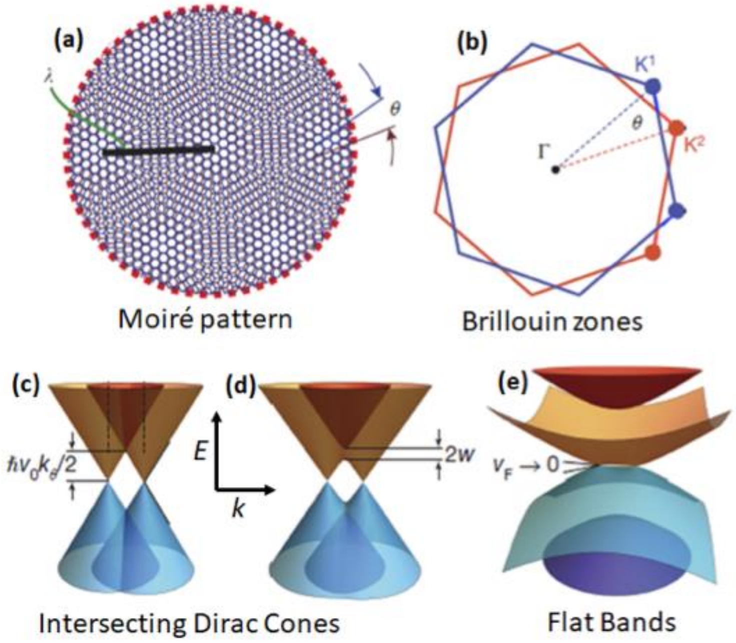
- other 2D materials (h-BN, MoS_2, ...)

Widely tunable bandgap in bilayer graphene



doi.org/10.1038/nature08105

Twisted Bilayer Graphene: Moiré-induced Electronic Structure



Images from Y. Cao, et al., *Nature* 556, 80 (2019)