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“Gilberto Vlaic”:
Fundamentals, Methods and Applications
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Società
Italiana
Luce di
Sincrotrone



Elettra Sincrotrone Trieste

Introduction to photoelectron spectroscopy in atoms, molecules and solids

Carlo Mariani*

Dipartimento di Fisica, Università di Roma “La Sapienza”

Carlo.Mariani@uniroma1.it

<https://sites.google.com/uniroma1.it/nano-surface-physics/home>

*warmly thanking **Gianni Stefani**; and remembering **Massimo Sancrotti**

outline

- Ultra-short Historical Background
- Electron Energy Level Scheme and Energy Conservation
- Basic Theory of Photoemission
- Photoelectric Effect in Atoms and Molecules
- Core Level Photoemission
- Core Level Chemical Shift and Line Shape Analysis
- Multiplet Structure and Many Body Effects
- Photoelectron Angular Distribution

- Photoemission in Solids
- Three-Step Model
- Primary and Secondary Photoelectrons
- Photoionization Cross Sections
- Atomic Sensitivity Factors and Semi-Quantitative Analysis
- Valence Band Photoemission
- Angular Resolved Photo Electron Spectroscopy (ARPES)
and Band Structures

Photoemission Spectroscopy: basic principles

Annalen der Physik 17, 132 (1905):*

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

...Außerdem wird anzunehmen sein, daß jedes Elektron beim Verlassen des Körpers eine (für den Körper charakteristische) Arbeit P zu leisten hat, wenn es den Körper verläßt. Mit der größten Normalgeschwindigkeit werden die unmittelbar an der Oberfläche normal zu dieser erregten Elektronen den Körper verlassen. Die kinetische Energie solcher Elektronen ist

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

Ist der Körper zum positiven Potential Π geladen und von Leitern vom Potential Null umgeben und ist Π eben imstande, einen Elektrizitätsverlust des Körpers zu verhindern, so muß sein:

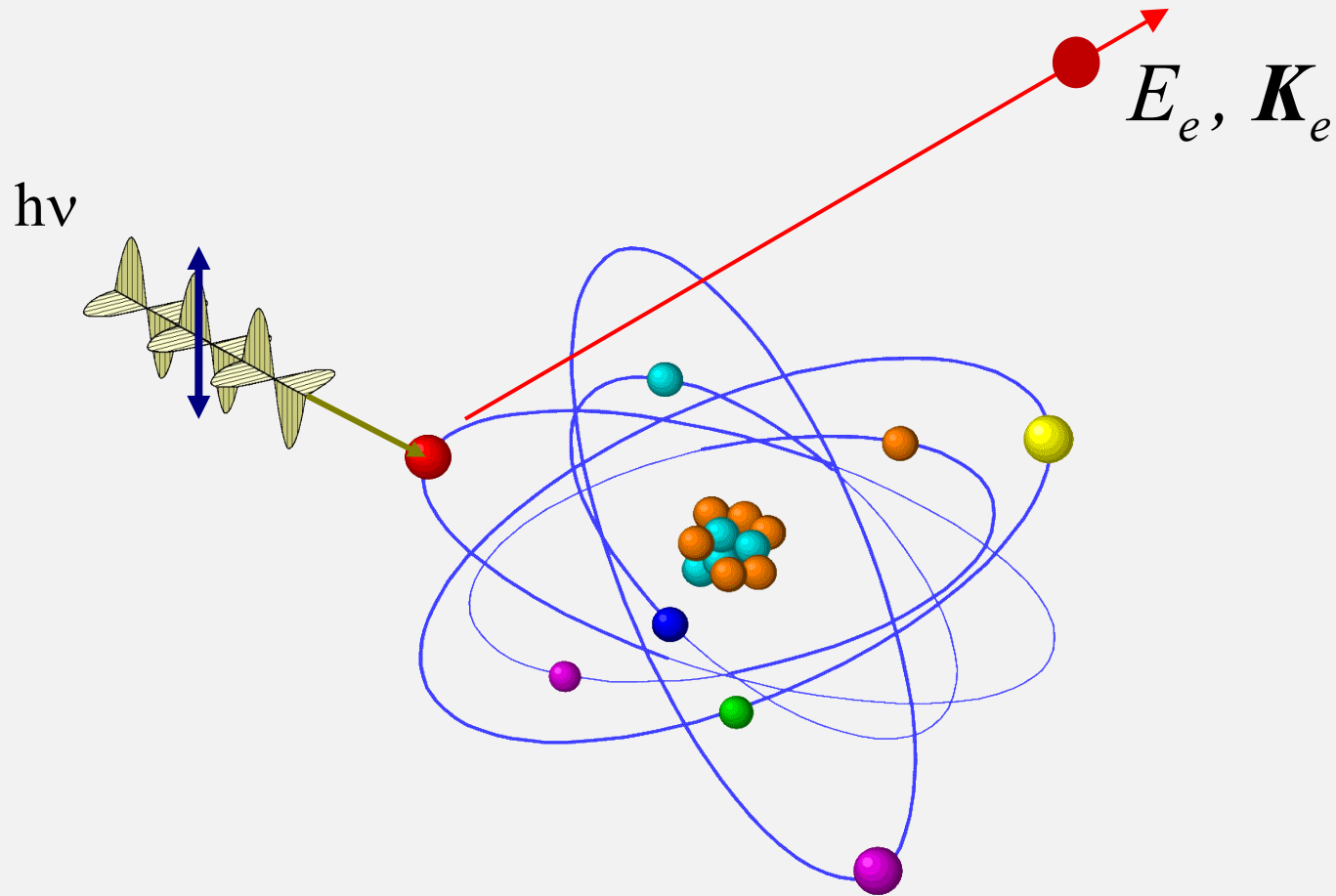
$$\Pi \varepsilon = \frac{R}{N} \beta v - P,$$

wobei ε die elektrische Masse des Elektrons bedeutet...

...in today's formalism... $E_e = h\nu - \Phi$

* <http://myweb.rz.uni-augsburg.de/~eckern/adp/history/Einstein-in-AdP.htm>

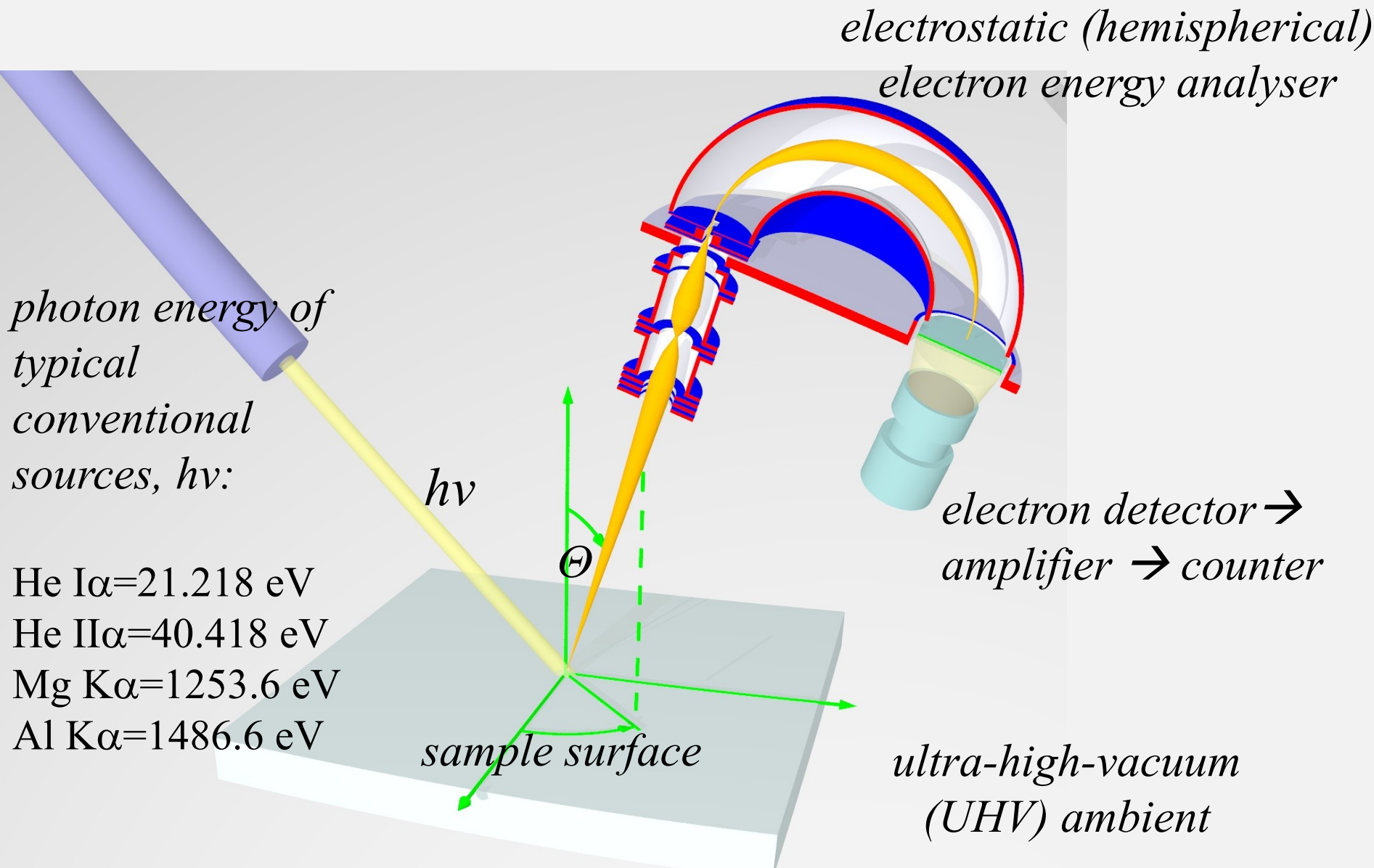
Photoemission Spectroscopy: basic principles



$$E_e^{max} = h\nu - I \text{ for atoms and molecules}$$

$$E_e^{max} = h\nu - \Phi \text{ for solids}$$

Photoemission Spectroscopy: sketch of an experimental set-up



UV photoelectron spectroscopy (UPS) X-Ray Photoemission Spectroscopy (XPS) or Electron Spectroscopy for Chemical Analysis (ESCA)

Single Particle Scheme of Energy Levels Photoelectric Effect in Solids



Photons IN
Electrons OUT

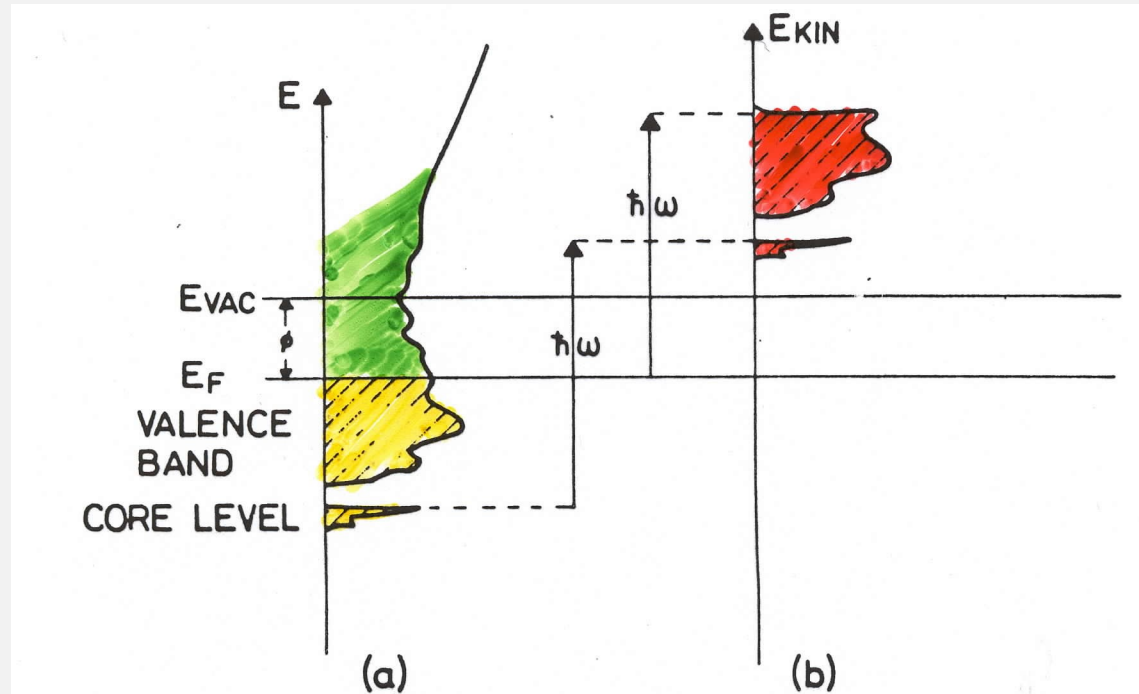


Figure 1.4 Illustrating the fact that the density of electronic states distribution of the emitter, part (a), is reflected in the photoemission spectral fine structure, part (b)

Photoemission Spectroscopy



Single Particle Scheme of Energy Levels

$$E_{kin} = \hbar\omega - E_b^F - \Phi$$

Many Particle Scheme: Total Energies

$$E_f(N-1) + E_k - E_i(N) = \hbar\omega$$

E_{kin} = Final State Kinetic Energy

Φ = Work Function

$E_b^F(k)$ = Binding Energy of the k -th Initial State

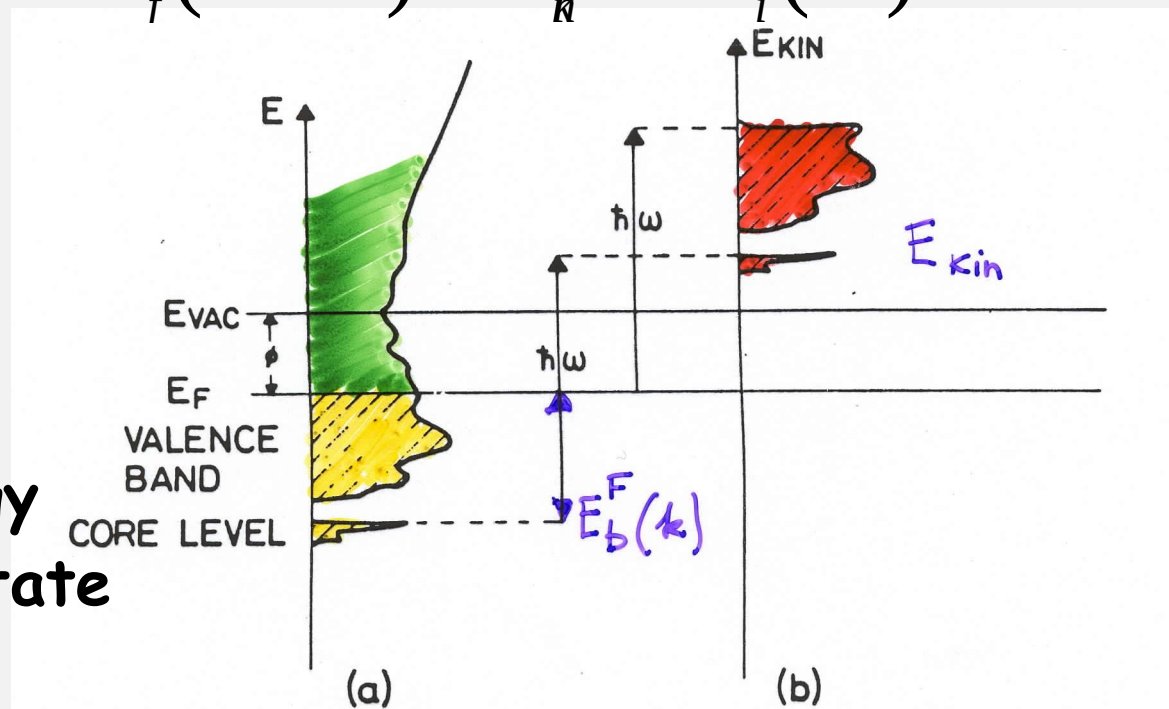
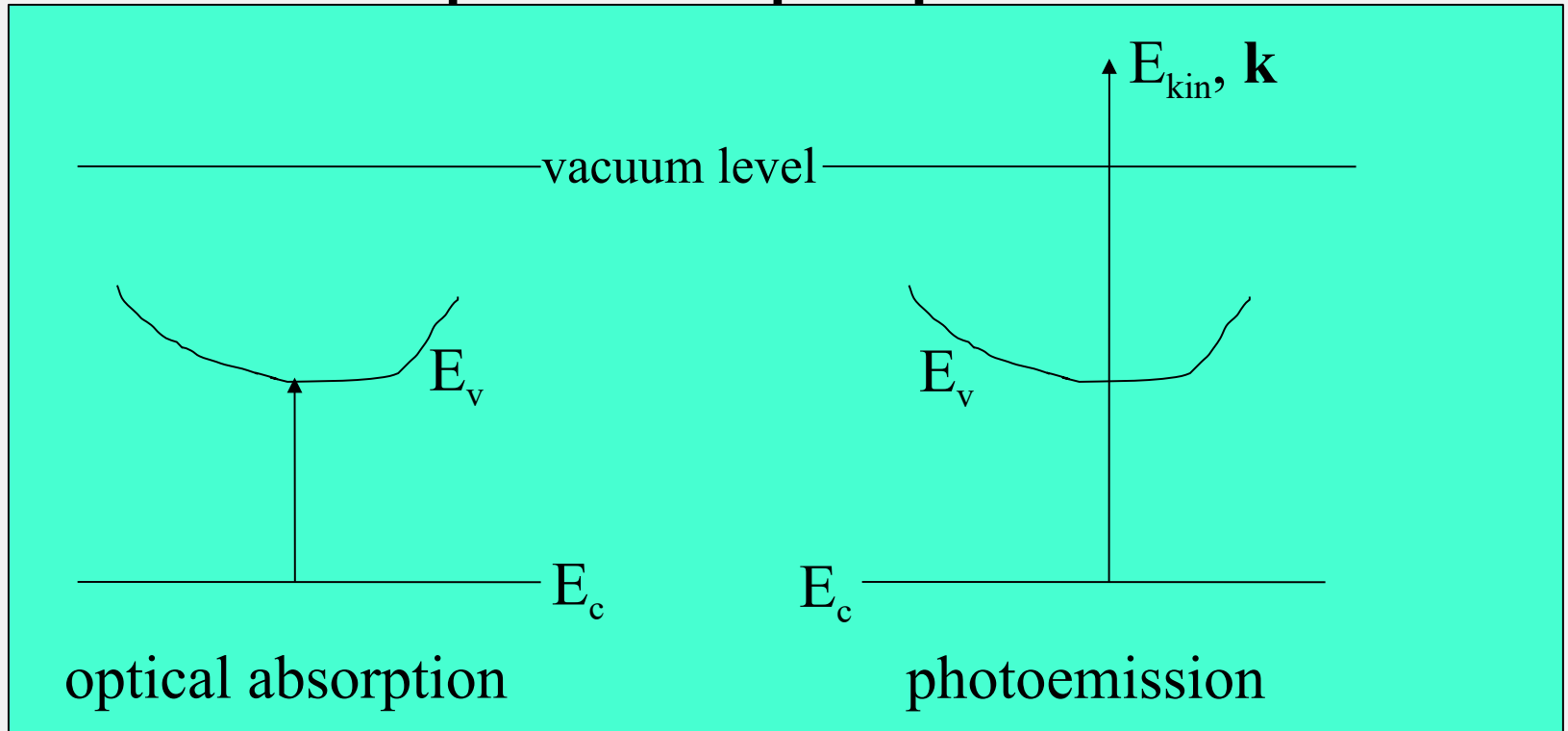


Figure 1.4 Illustrating the fact that the density of electronic states distribution of the emitter, part (a), is reflected in the photoemission spectral fine structure, part (b)

Photoemission Spectroscopy

Basic Theory

the photoabsorption process



optical absorption: $|f\rangle = |N_v + 1 * \rangle |N_c - 1\rangle$

photoemission: $|f\rangle = |N_v * \rangle |N_c - 1\rangle |E_k, \mathbf{k}\rangle$

Photoemission Spectroscopy

Basic Theory *

- One-particle approach
- Electromagnetic Field-Matter Interaction

the photo-excitation cross-section (from the Fermi golden rule):

$$\sigma = 4\pi^2 \alpha h \nu \sum_B \left| \hat{\boldsymbol{\varepsilon}} \cdot \left\langle \Psi_B \left| \sum_i \vec{r}_i \right| \Psi_A \right\rangle \right|^2 \delta(E_B - E_A - h\nu)$$

$\boldsymbol{\varepsilon}$: e.m. field polarisation vector

Ψ_A : neutral ground state

Ψ_B : residual ion + free electron

* see detailed description in F. Boscherini's lectures, this school;

and in Mariani & Stefani, pag. 275-317 in *Synchrotron Radiation: Basics, Methods and Applications*, Eds. Mobilio, Boscherini, Meneghini, Springer 2015; <https://doi.org/10.1007/978-3-642-55315-8>

Photoemission Spectroscopy ~ from an atom

- **by considering N interacting electrons...**

$$H_0 |\Psi_A^{(N)}\rangle = E_A^{(N)} |\Psi_A^{(N)}\rangle$$

$$H_0 = H_0(kin) + H_0(e-n) + H_0(e-e) + H_0(s-o) = \\ = \sum_1^N \frac{p_i^2}{2m} + \sum_1^N -\frac{Ze^2}{r_i} + \sum_{i>j}^N \frac{e^2}{r_{ij}} + \sum_1^N \zeta(r_j) \vec{l}_i \cdot \vec{s}_i$$

initial state Hamiltonian

$$|\Psi_A^{(N)}\rangle = \hat{A}(\phi_j(\vec{r}_j, \sigma_j); \Psi_R^{(N-1)})$$

eigenfunctions described through a Slater determinant

final state Hamiltonian

$$H'_0 |\Psi_B^{(N)}\rangle = E_B^{(N)} |\Psi_B^{(N)}\rangle$$

final N-1 particles state

$$|\Psi_B^{(N)}\rangle = \hat{A}(\varepsilon_l; |\Psi_B^{(N-1)}\rangle)$$

$$\frac{d\sigma}{d\Omega dE_e} \propto \sum_B \left| \hat{\varepsilon} \cdot \langle \varepsilon_l | \vec{r}_j | \phi_j(\vec{r}_j, \sigma_j) \rangle \langle \Psi_B^{(N-1)} | \Psi_R^{(N-1)} \rangle \right|^2 \delta(E_e + E_B^{(N-1)} - E_A^N - h\nu)$$

Photoemission Spectroscopy ~ from an atom

- **by considering N interacting electrons...**

sudden approximation

$$\left| \Psi_B^{(N)} \right\rangle = \hat{A}(\epsilon_l; \left| \Psi_B^{(N-1)} \right\rangle)$$

$$\frac{d\sigma}{d\Omega dE_e} \propto \frac{1}{h\nu} \sum_{A,B} \left| \hat{\epsilon} \cdot \left\langle \epsilon_l \left| \vec{r}_j \right| \phi_j(\vec{r}_j, \sigma_j) \right\rangle \left\langle \Psi_B^{(N-1)} \left| \Psi_R^{(N-1)} \right\rangle \right|^2 \delta(E_e + E_B^{(N-1)} - E_A - h\nu)$$

frozen-core approximation

$$H'_0 = H_0$$

$$\frac{d\sigma}{d\Omega dE_e} \propto \frac{1}{h\nu} \sum_{A,B} \left| \hat{\epsilon} \cdot \left\langle \epsilon_l \left| \vec{r}_j \right| \phi_j(\vec{r}_j, \sigma_j) \right\rangle \right|^2 \delta(E_e + \epsilon_j - h\nu)$$

Photoemission Spectroscopy ~ from an atom

- the example of a He atom

$$E_B = E_A + h\nu$$

$$\Psi_A = \hat{A}\phi_1\phi_2$$

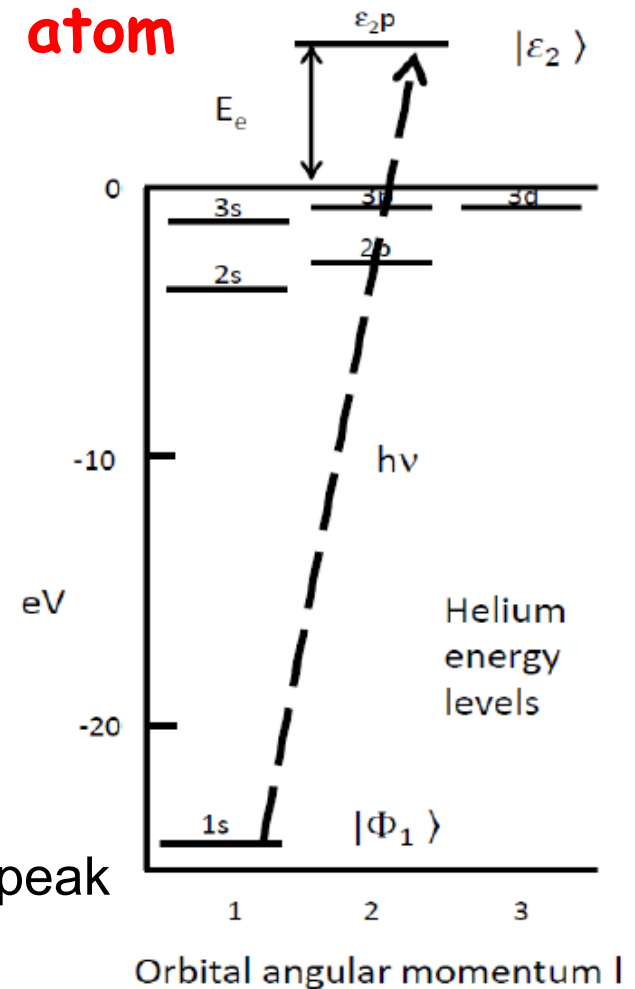
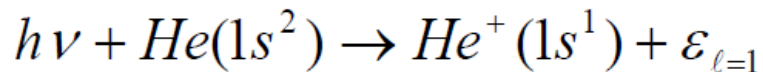
$$\Psi_B = \hat{A}\phi_1\varepsilon_2$$

$$E_e = E_{1s} + h\nu$$

$$E_{1s} + E_e = E_{1s} + E_{1s} + h\nu$$

$$E_e = h\nu - BE_{1s} (24.6eV)$$

the distribution current should produce a single peak associated to the initial state:

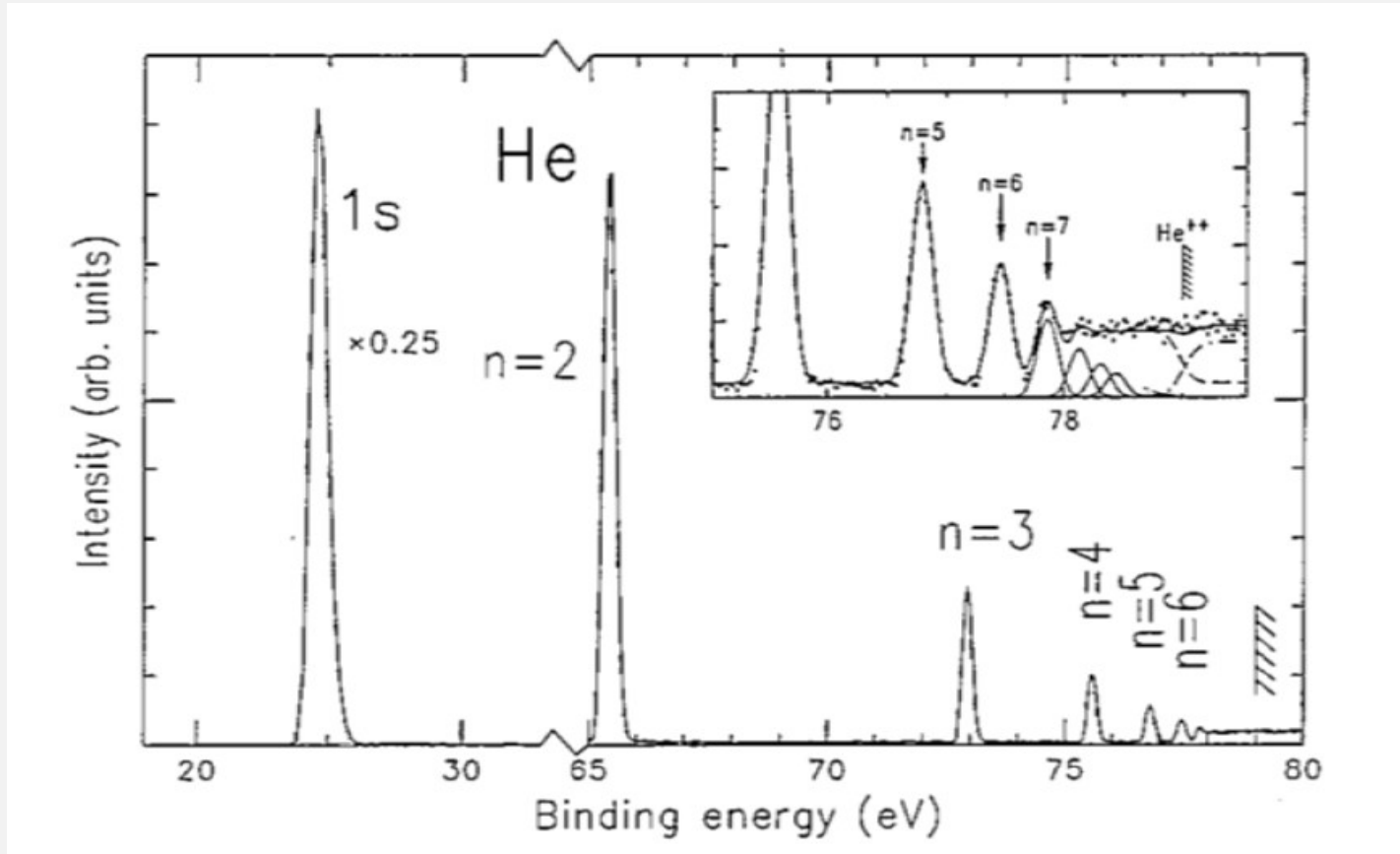


BUT, the independent particle model is not sufficient and ...

Photoemission Spectroscopy ~ from an atom

- the example of a He atom

the real spectrum shows several peaks



where

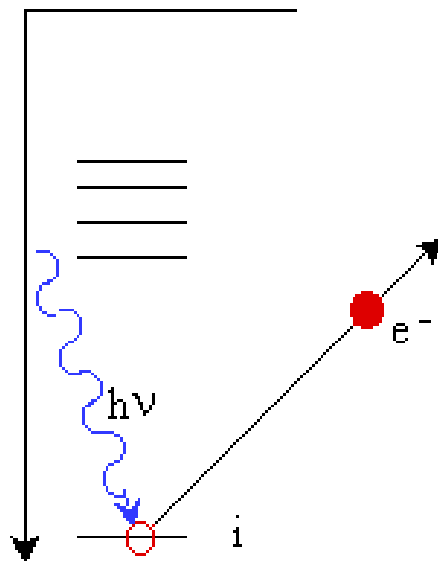
- $n=1$ is the single-particle excitation from the $1s$ core-level;
- $n=2,3,\dots$ are satellite structures in a many-body approach

Photoemission Spectroscopy ~ from an atom

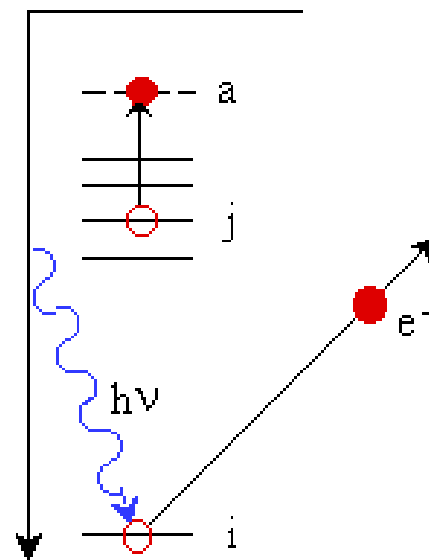
- **Satellite peaks**

PRIMARY PHOTOIONIZATION PROCESSES

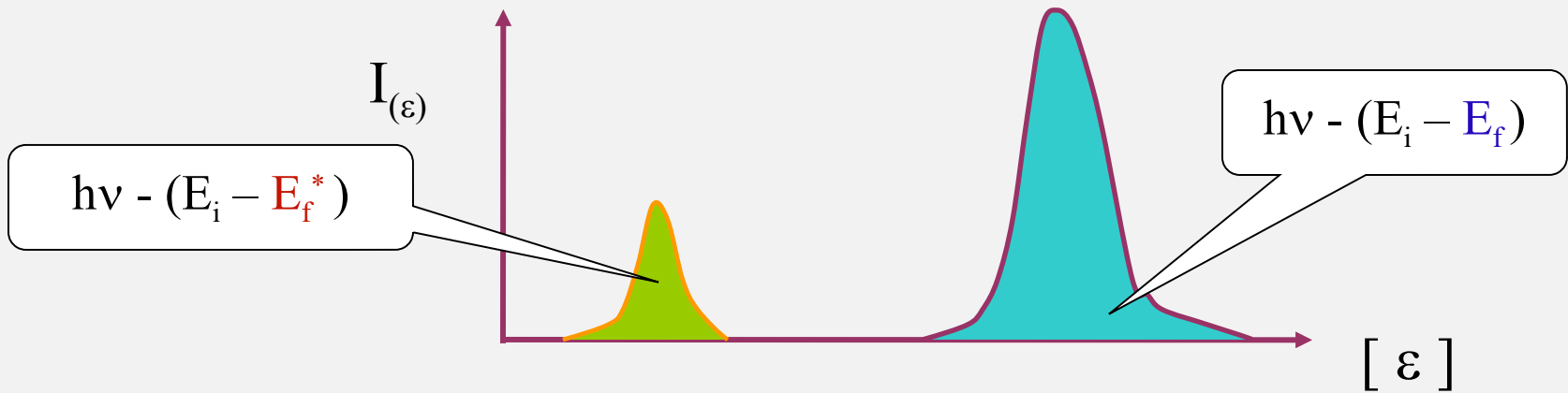
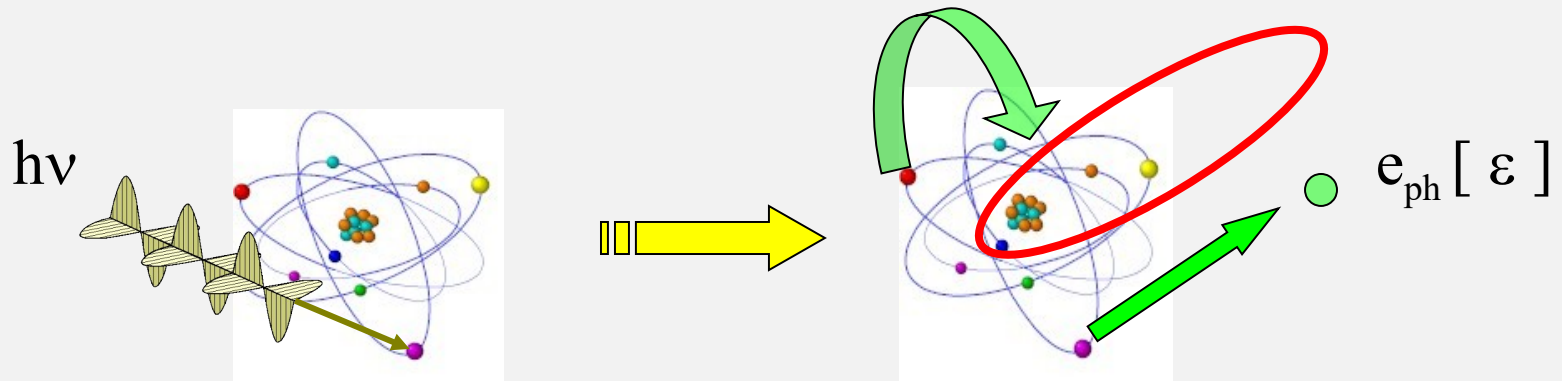
MAIN PROCESS



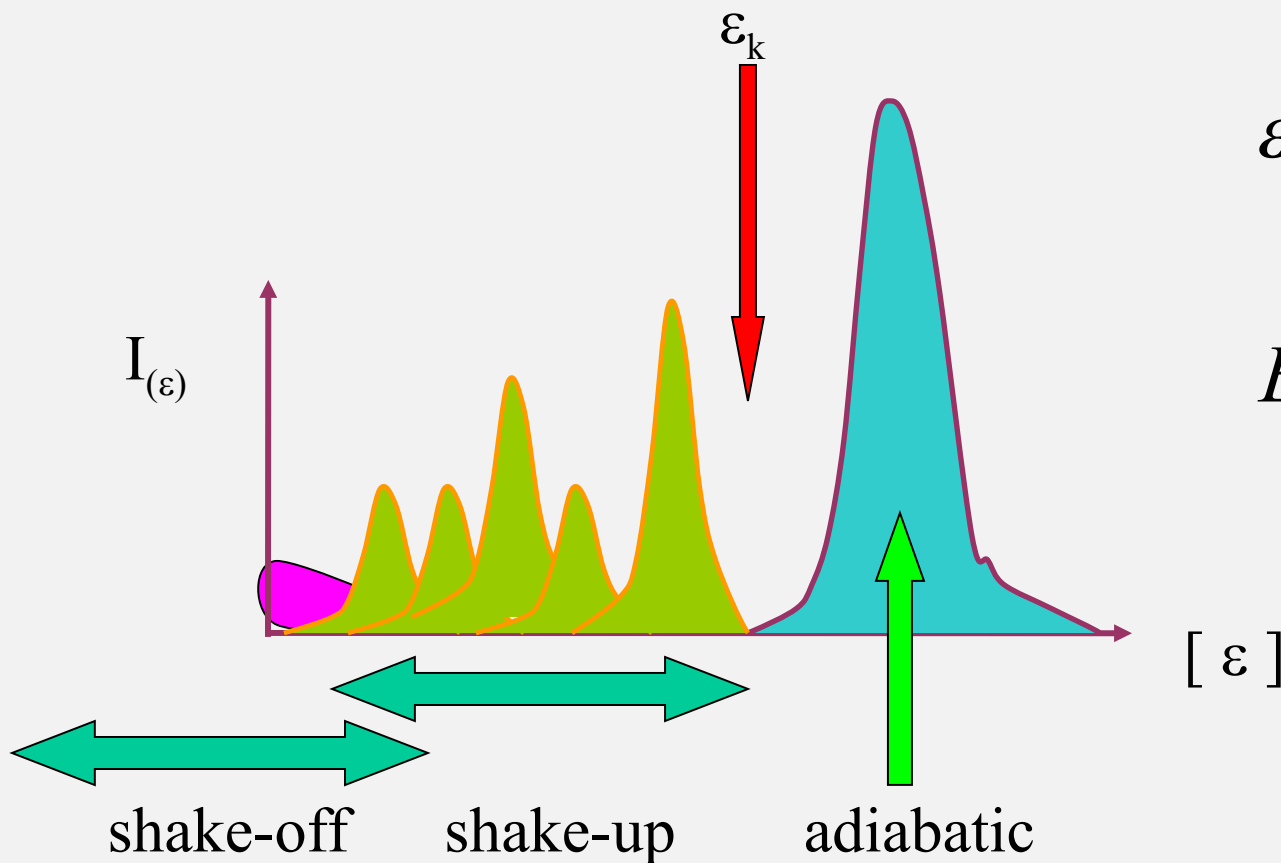
SATELLITE PROCESS



- Photon = single particle operator
- 2 or more particles involved in final state = e-e correlation
- Relaxation & e-e correlation in photoemission = satellite



Koopmans energy vs. photoemission peaks



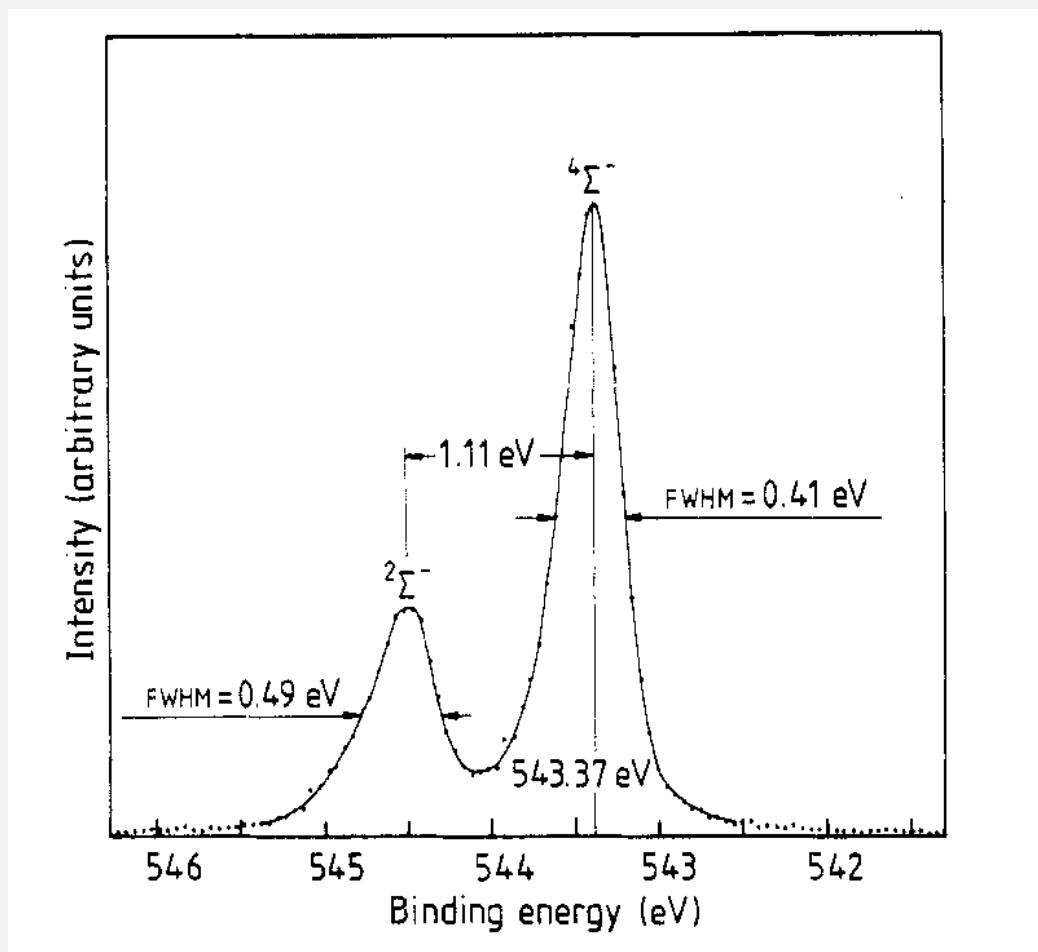
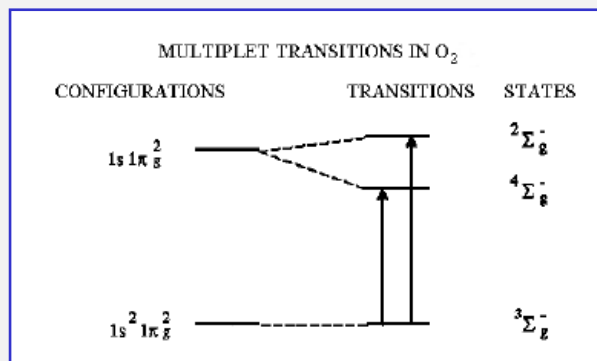
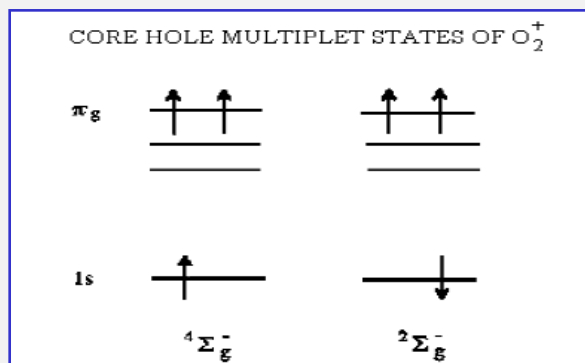
$$\epsilon_k = \frac{\sum_i \epsilon_i I_i}{\sum_i I_i}$$

$$E_{\text{ad}} = \epsilon_{\text{ad}} - \epsilon_k$$

Photoemission Spectroscopy ~ of molecules

multiplet splitting in O_2

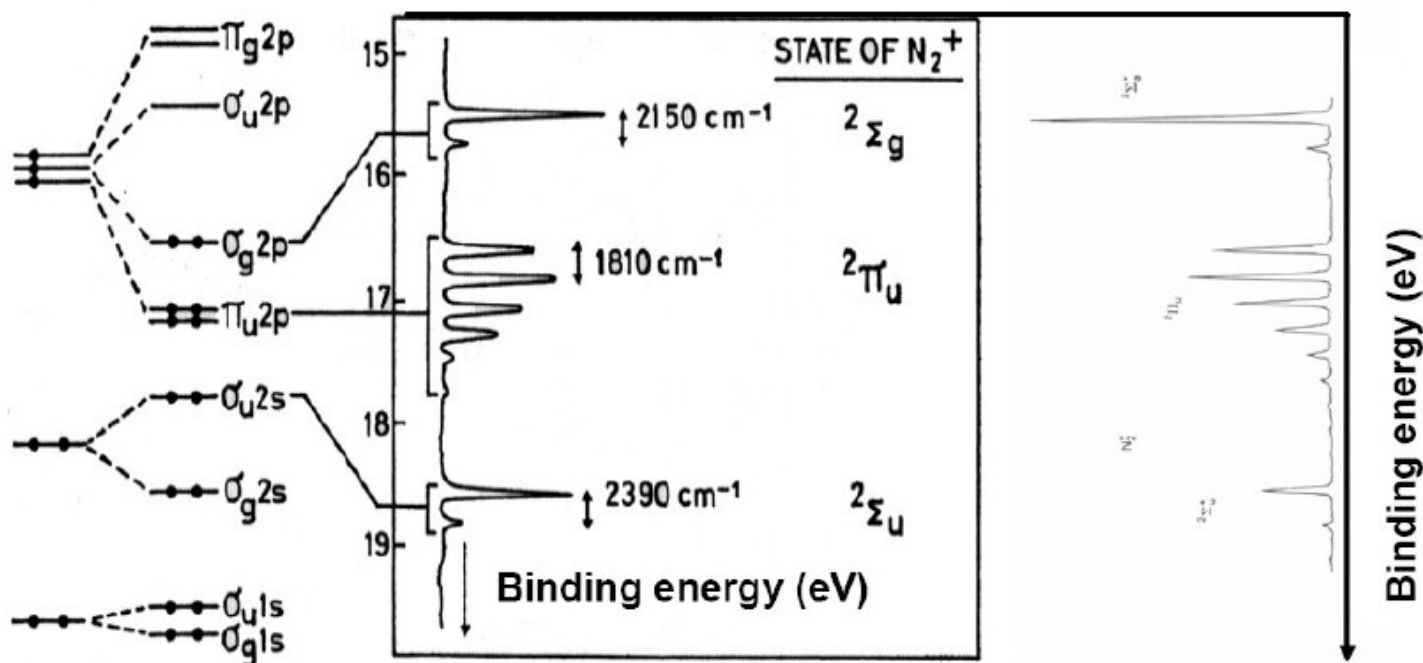
O_2 neutral ground state: $KK(\sigma_g 2s)^2(\sigma_u 2s)^2(\sigma_g 2p)^2(\pi_u 2p)^4(\pi_g 2p)^2^3\Sigma_g^-$



Photoemission Spectroscopy ~ of molecules



Orbital assignment Expected Experimental



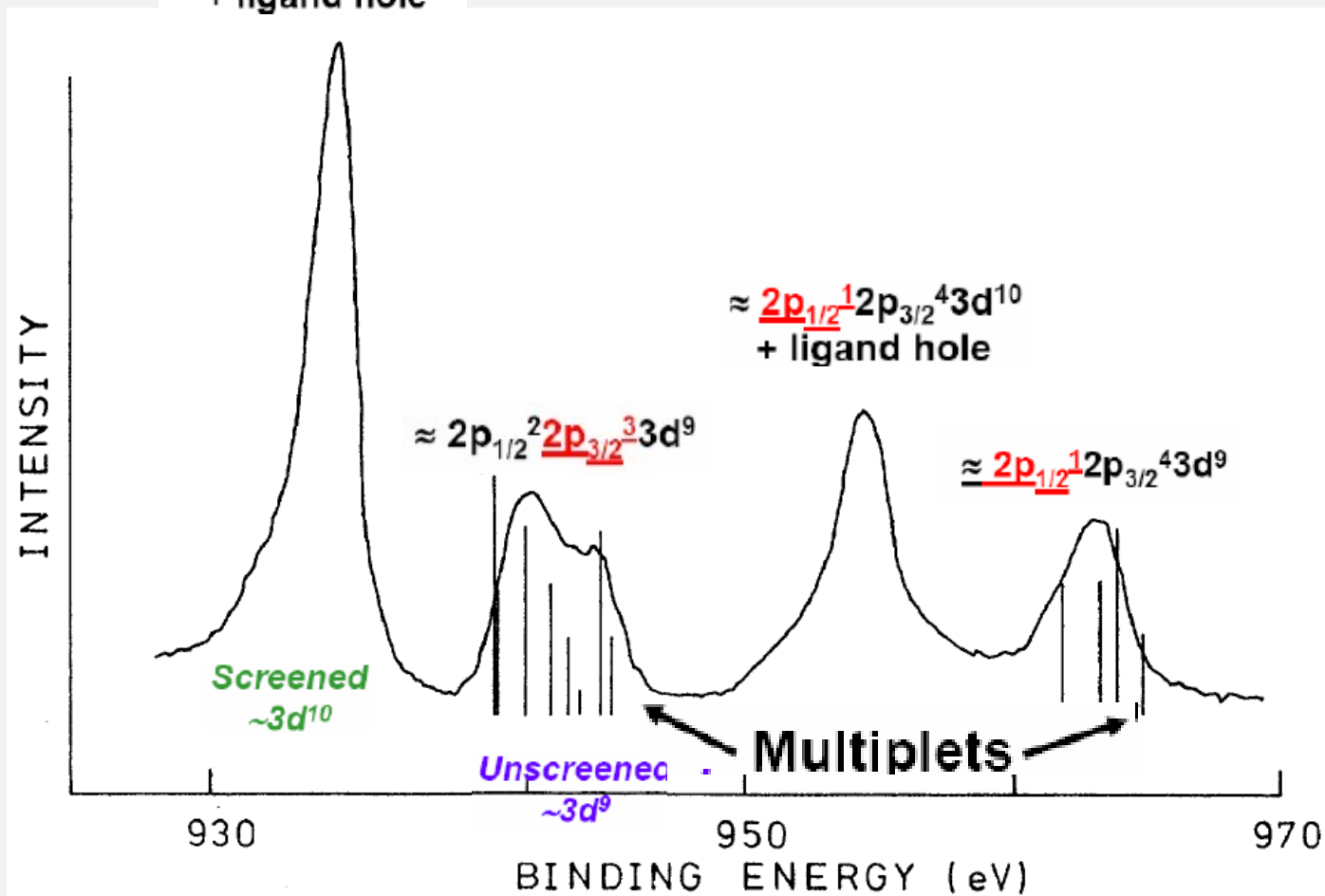
Molecular Nitrogen PES

Photoemission Spectroscopy ~ of molecules

multiplet splitting in CuCl_2

$\approx 2p_{1/2} 2p_{3/2} 3d^{10}$
+ ligand hole

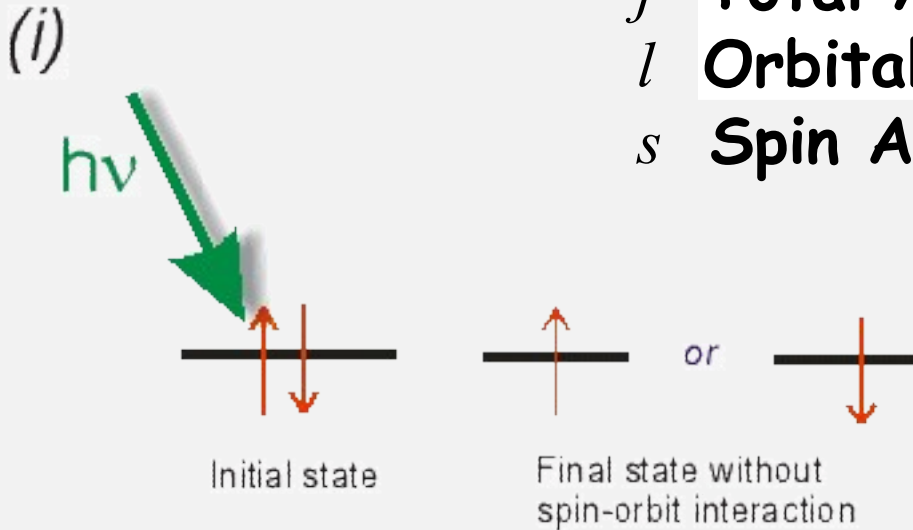
Cu 2p



Photoemission Spectroscopy: Core Levels **Spin-Orbit Splitting**

Quantum Numbers

- j Total Angular Momentum
- l Orbital Angular Momentum
- s Spin Angular Momentum



$$i = l + s$$

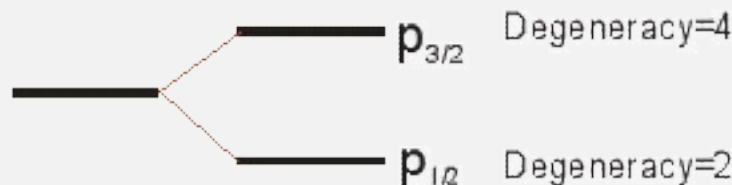
p -symmetry state

$$l = 1$$

$$s = \pm 1/2$$

(ii)

Spin orbit interaction lifts degeneracy



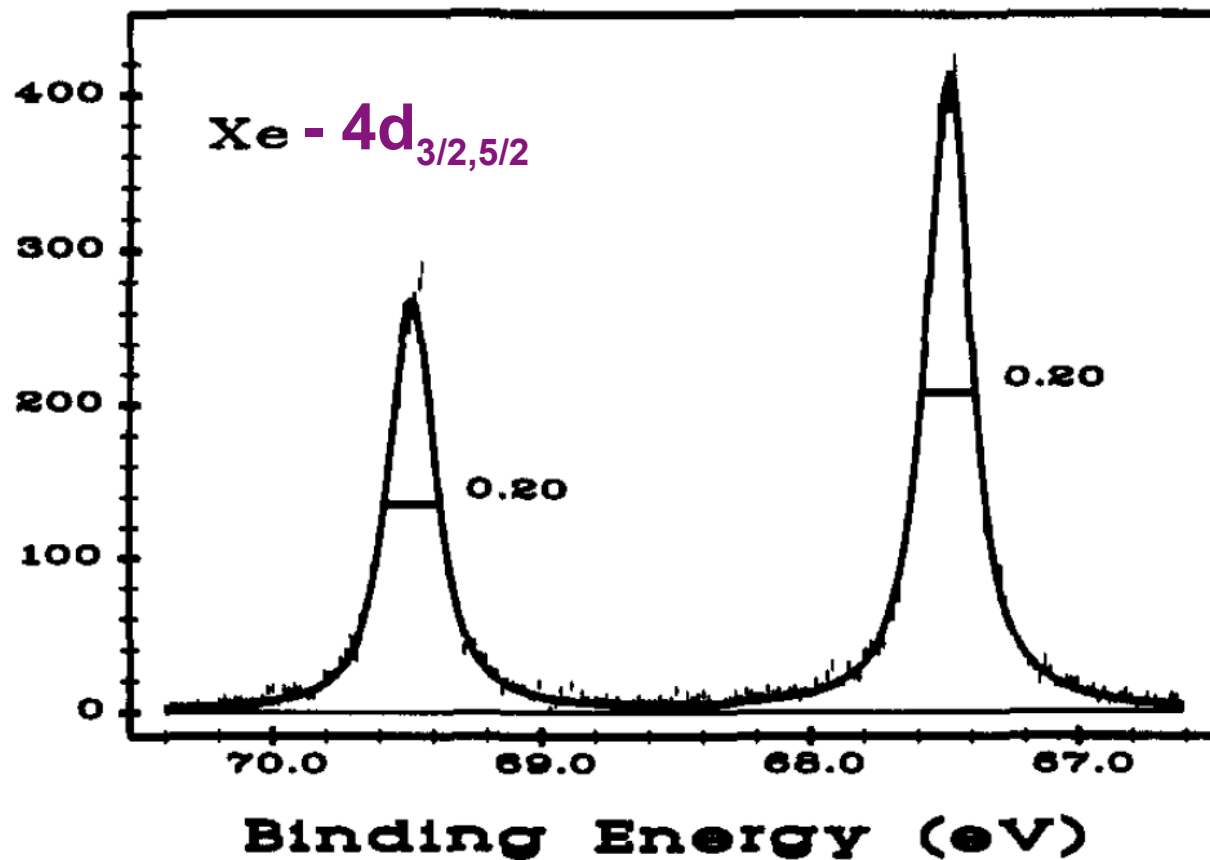
Degeneracy = $|2j+1|$

Photoemission Spectroscopy ~ core-level spin-orbit splitting

Cutler et alii, *J. Am. Chem. Soc.*, Vol. 113, No. 24, 1991 9129

$$\Delta E \propto \vec{l}_i \cdot \vec{s}_i$$

$|2j+1|$ -degeneracy



Binding Energies available at: <https://www.webelements.com/xenon/atoms.html>

Photoemission Spectroscopy

chemical shift in molecules

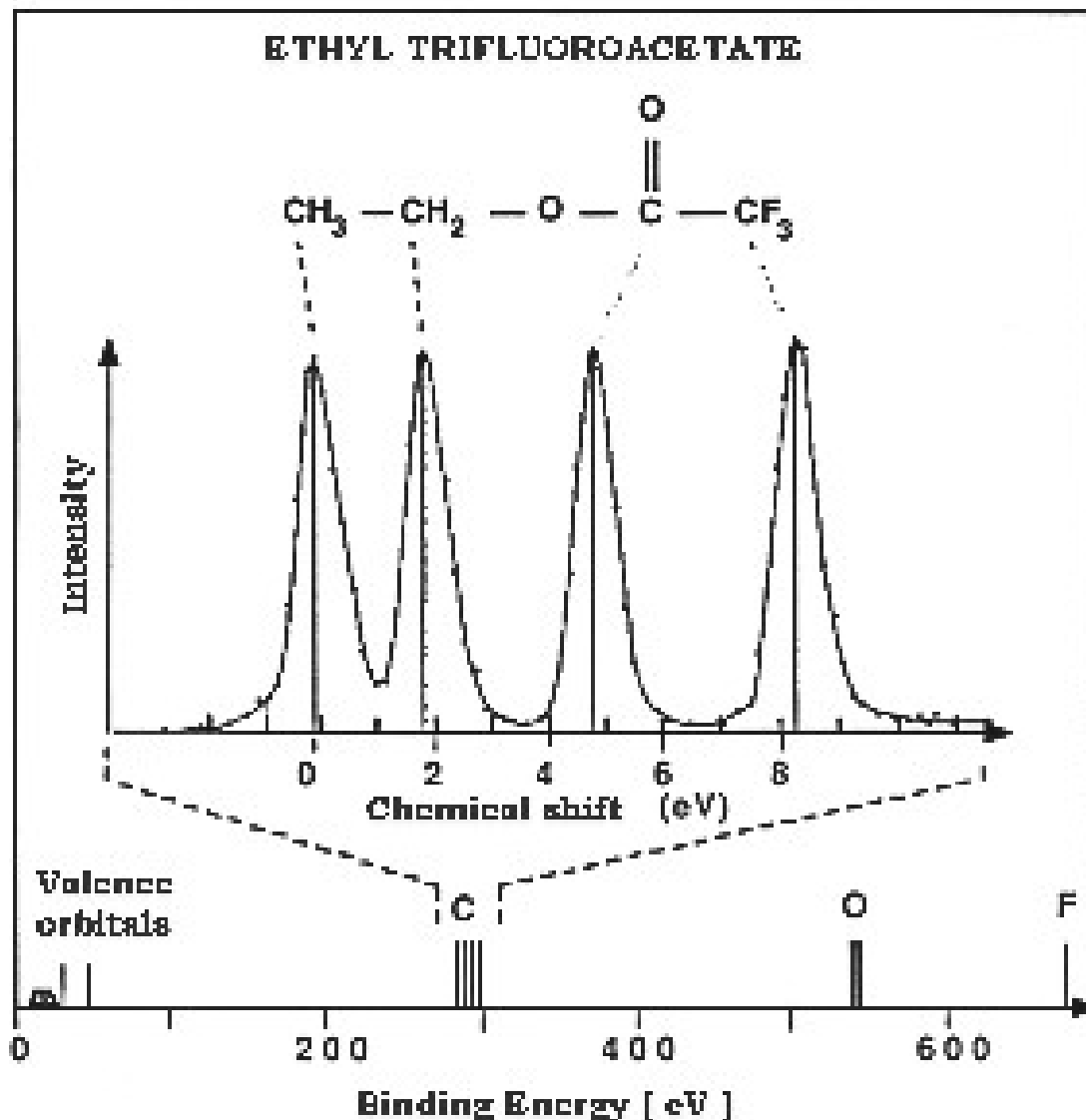
C 1s

C 1s 285-300 eV

C 1s CO₂ 298 eV

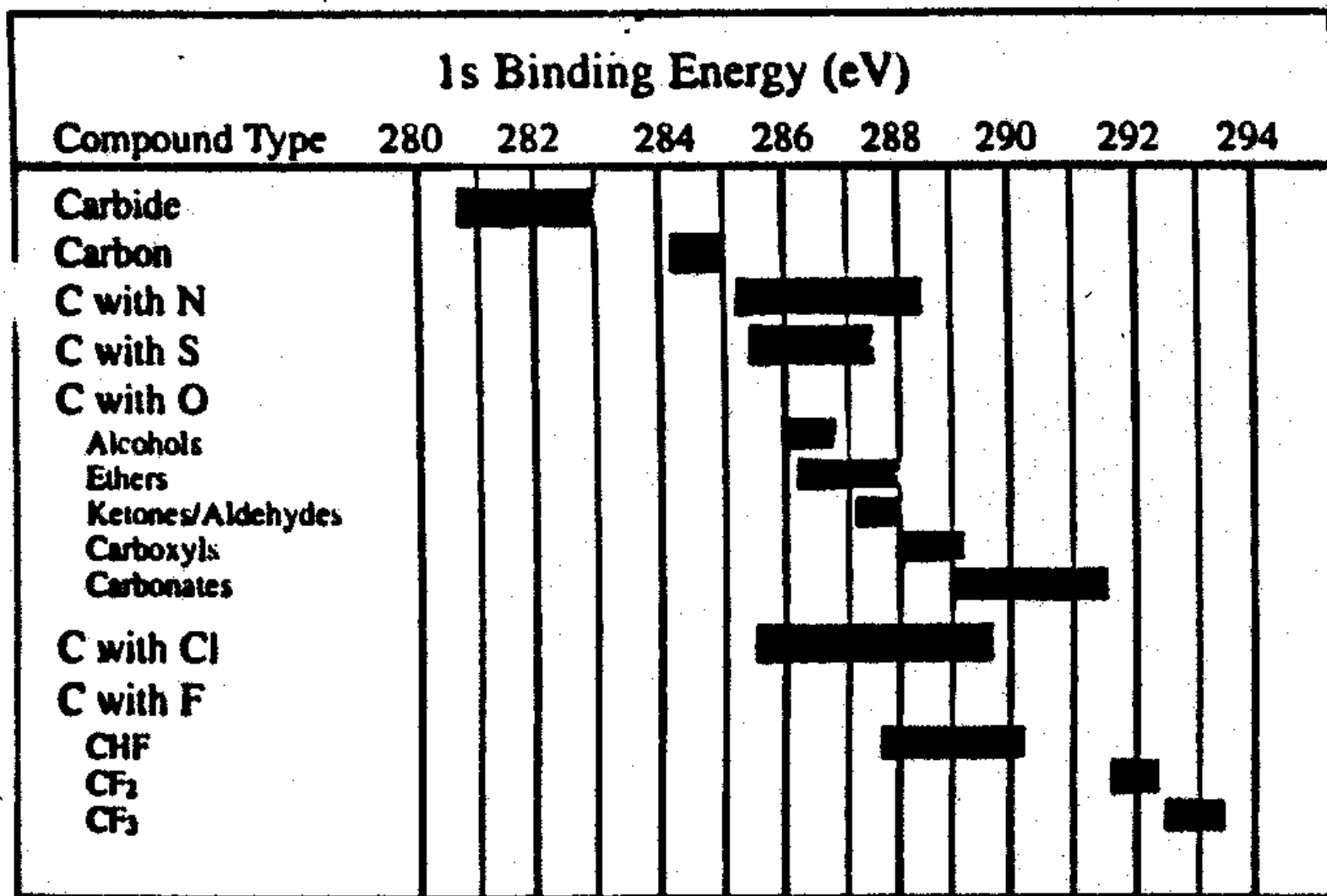
C 1s CH₄ 291 eV

O 1s 530-540 eV



Photoemission Spectroscopy: Chemical Shift (ΔE_b)

How the C 1s binding energy reflects differing chemical environment local to the excited C sites



Photoemission Spectroscopy

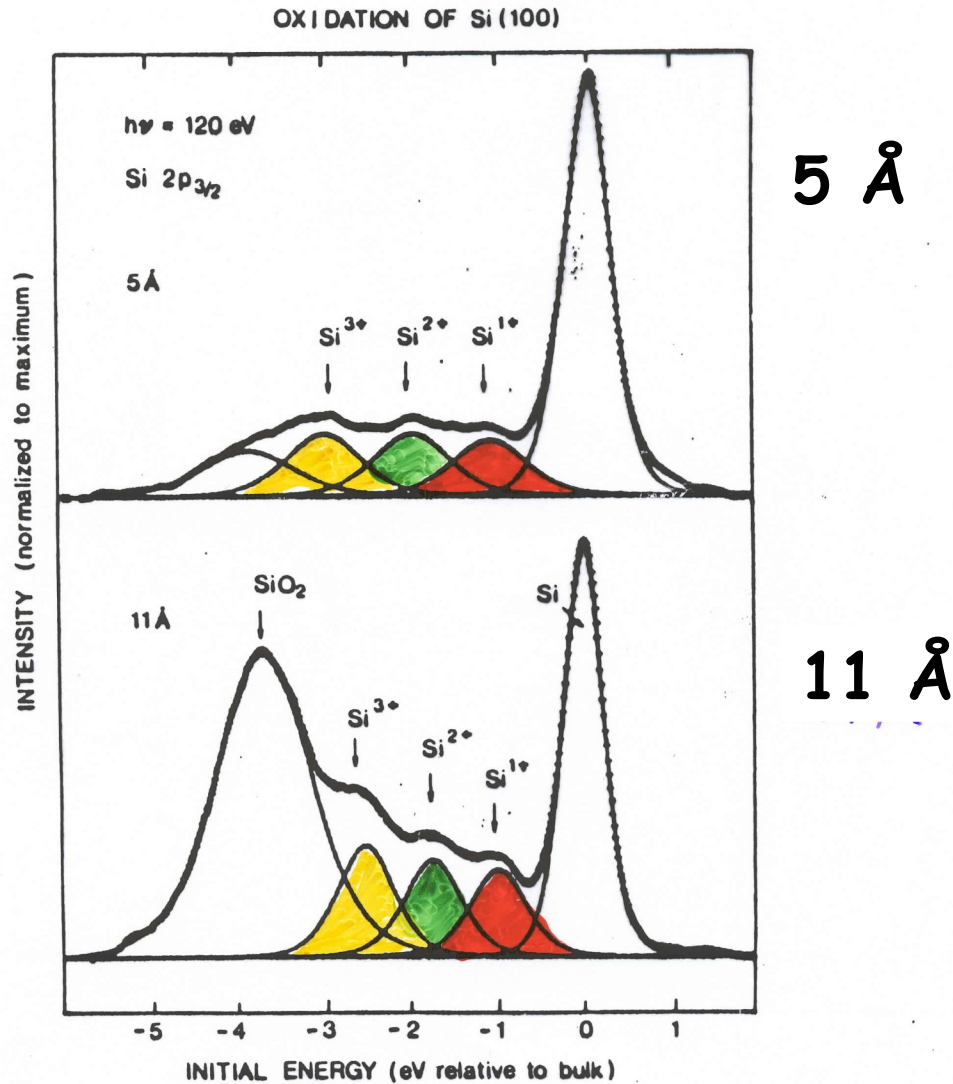


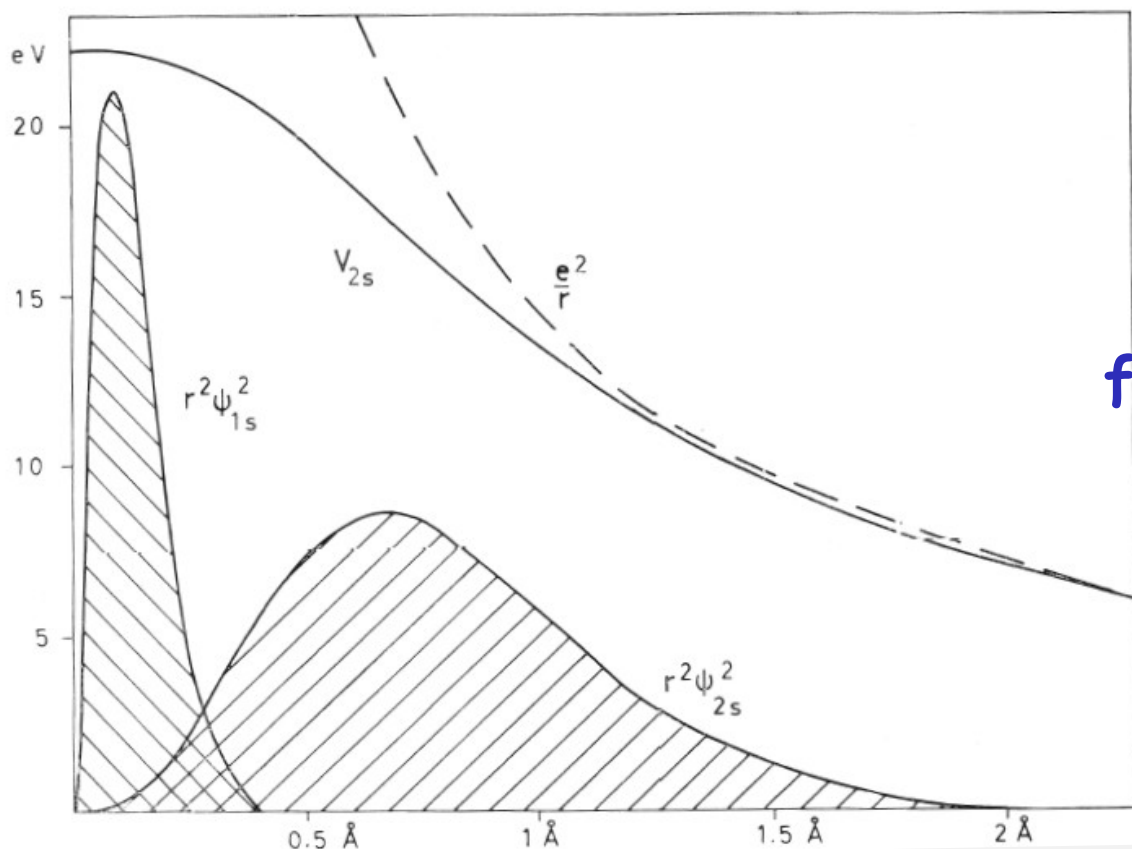
FIG. 3. Si $2p_{3/2}$ core level spectra for 5 and 11-Å-thick oxides decomposed into five components. The black crosses represent the experimental spectra and the solid lines indicate the theoretical functions and the different components.

chemical shift,
in the solid
state

initial phases of
oxidation of a Si
surface

Photoemission Spectroscopy

why chemical shift



spatial extension of external wave-functions down to the core-levels

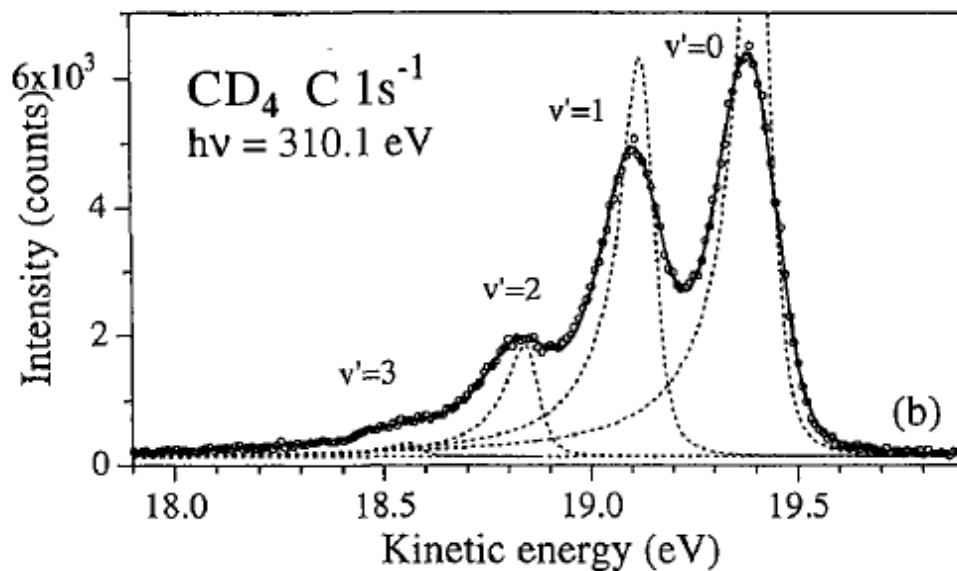
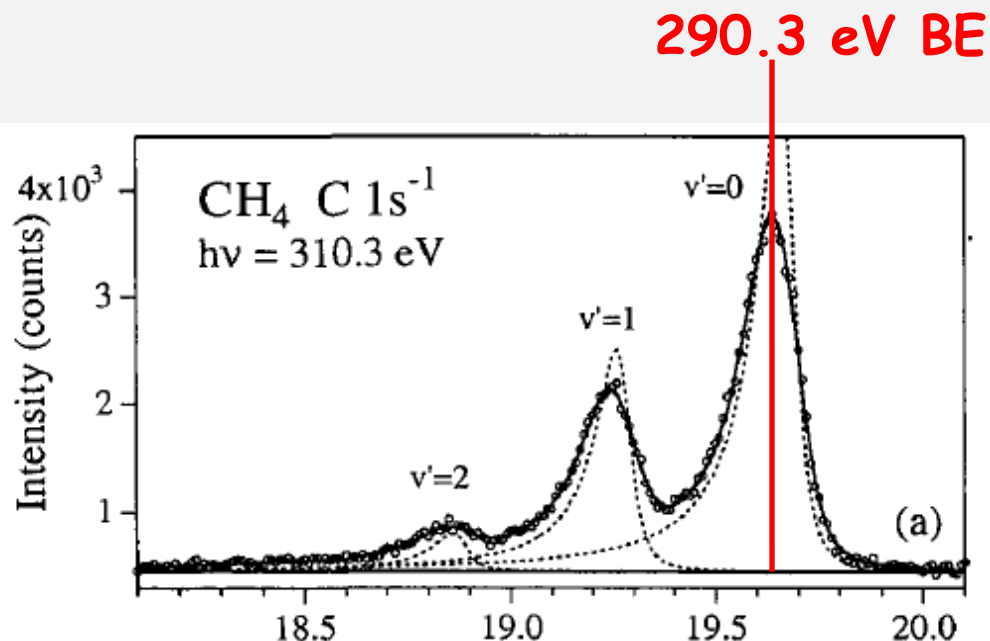
example: calculated electron densities for C

Photoemission Spectroscopy

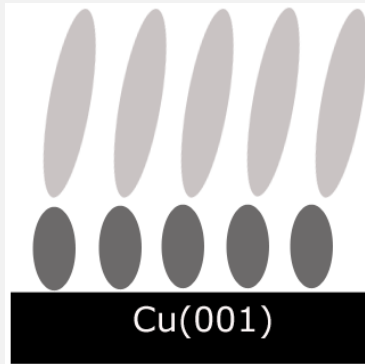
core-level vibrational modes

C 1s in methane
and deuterated
methane

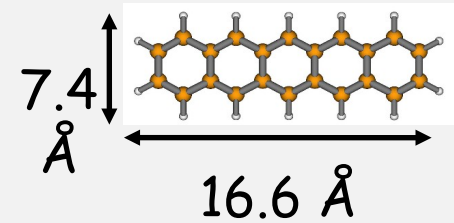
vibrational
overtones



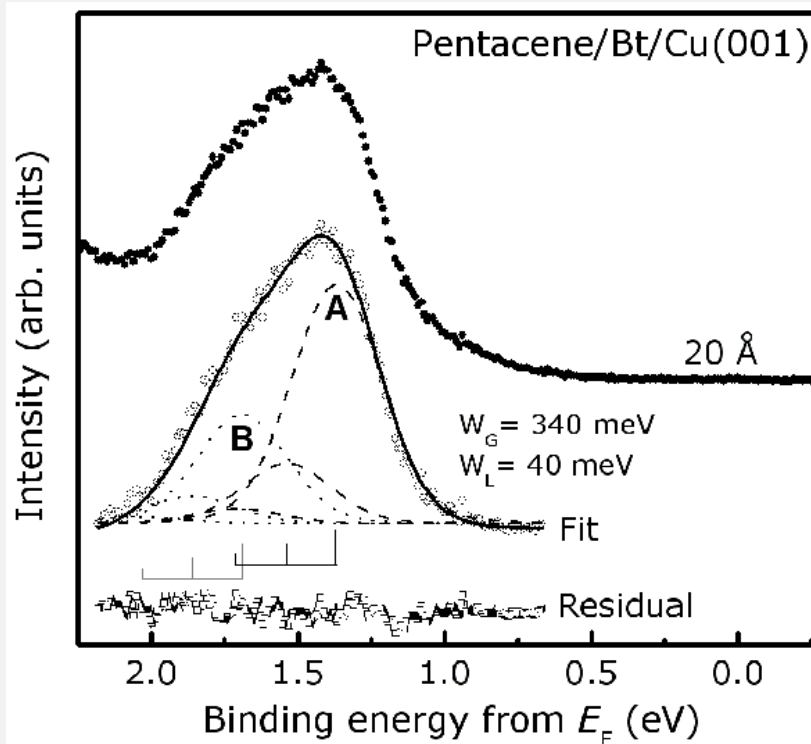
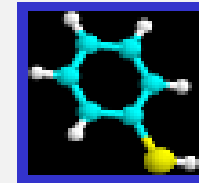
The photo-electron as primary electrons exciting **vibrational modes** also in the **valence band of a molecular solid**



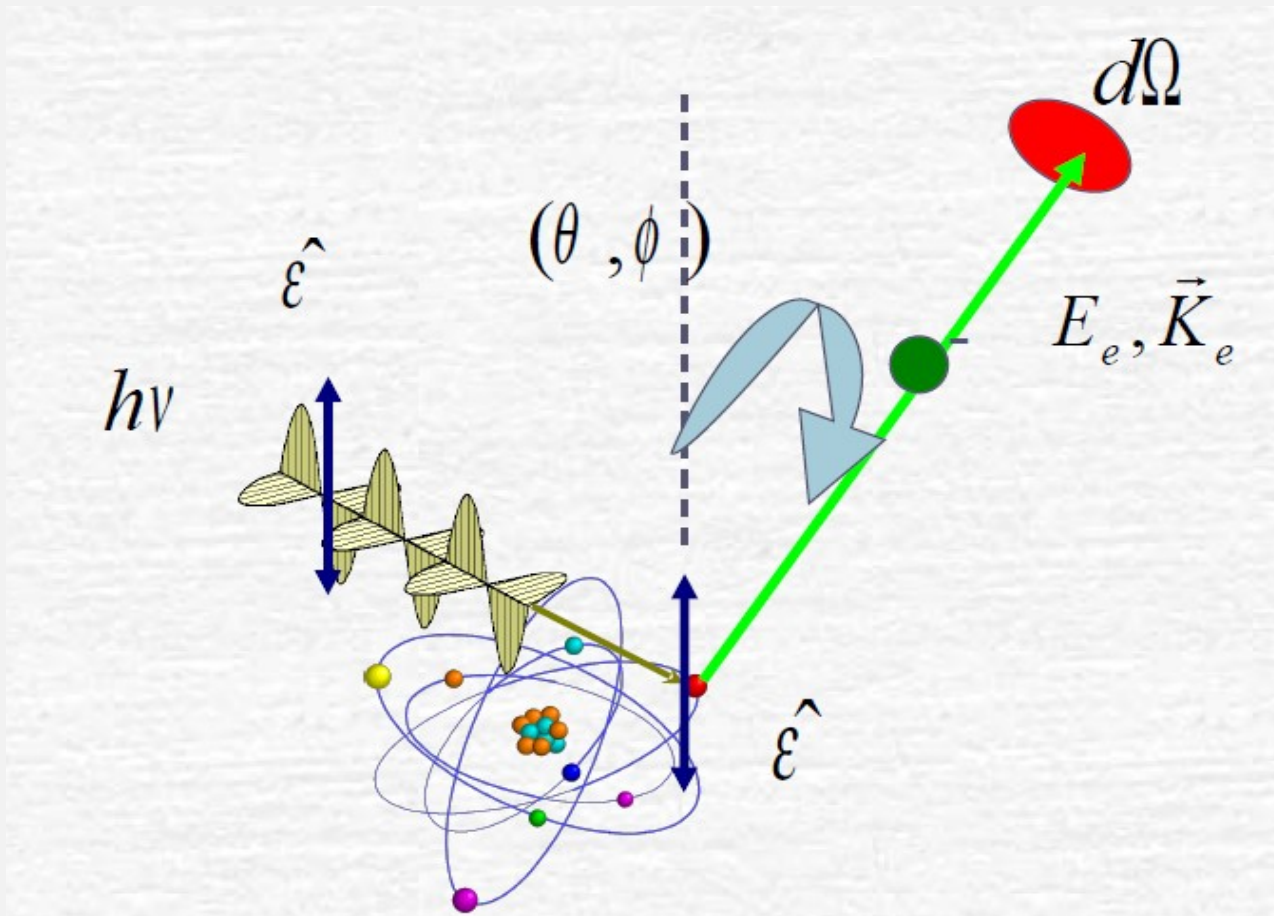
pentacene: $C_{22}H_{14}$



benzene-thiol: C_6H_5-SH

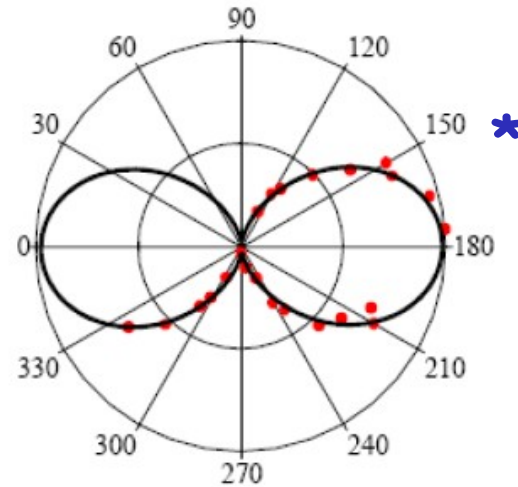
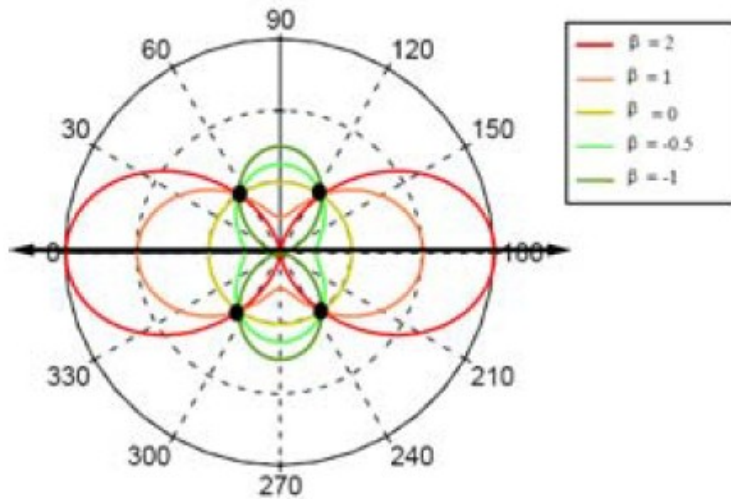


Photoelectron angular distribution



$$\frac{d\sigma}{d\Omega} \propto \sum_B \left| \hat{\epsilon} \cdot \langle \epsilon_l | \vec{r}_j | \phi_j(\vec{r}_j, \sigma_j) \rangle \langle \Psi_B^{(N-1)} | \Psi_R^{(N-1)} \rangle \right|^2$$

Photoelectron angular distribution

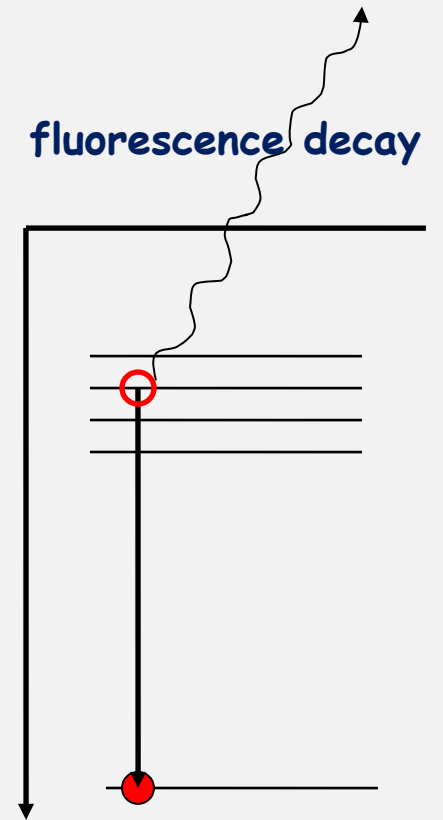
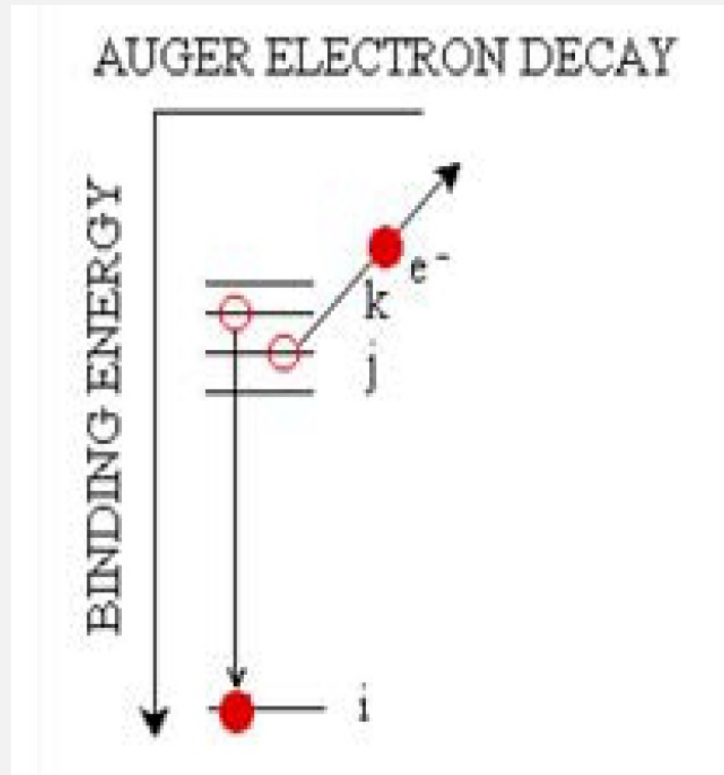
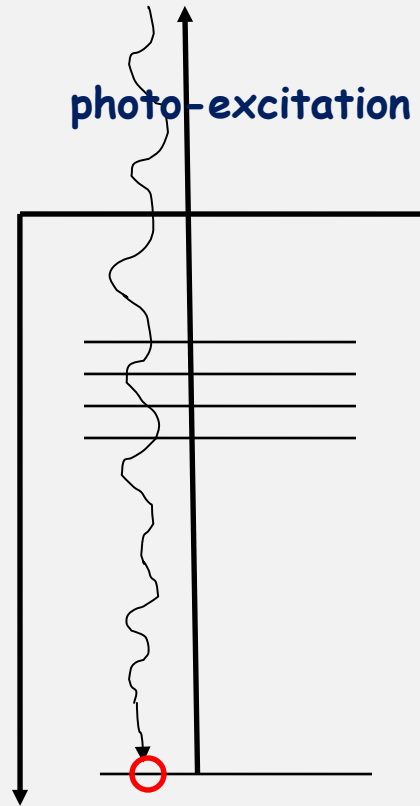


$$\frac{d\sigma}{d\Omega} \propto \frac{\sigma}{4\pi} [1 + \beta P_2 \cos(\vartheta)]$$

- dipolar distribution with asymmetry parameter β
- photoelectrons symmetrically distributed about the polarization direction
- at magic angle (54.74°), intensity independent from β values

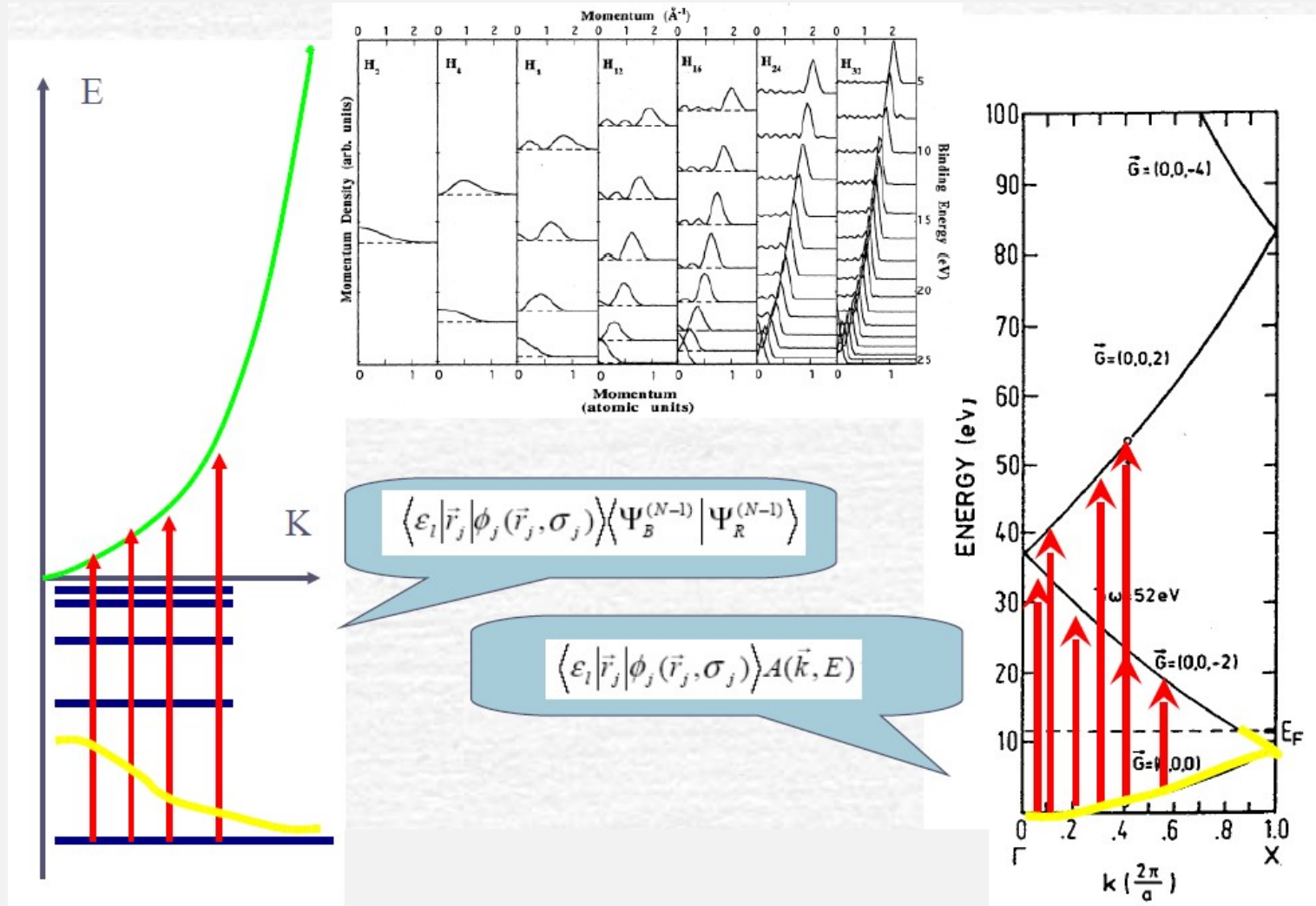
* experimental data for He with best fit $\beta=2$

Core-hole relaxation



Photoemission in Solids

from central to periodic potential



spectral function of interacting electrons in solids

$$J_e \propto \sum_{if} |M_{if}|^2 \left| \sum_m m_{im} \right|^2 \times \delta(E_i^N + h\nu - E_m^{N-1} - E_{kin})$$

M_{if} , matrix element between single-particle Bloch states

m_{im} , overlap integral between states with N-1 electrons, $i=m$ for un-correlated systems

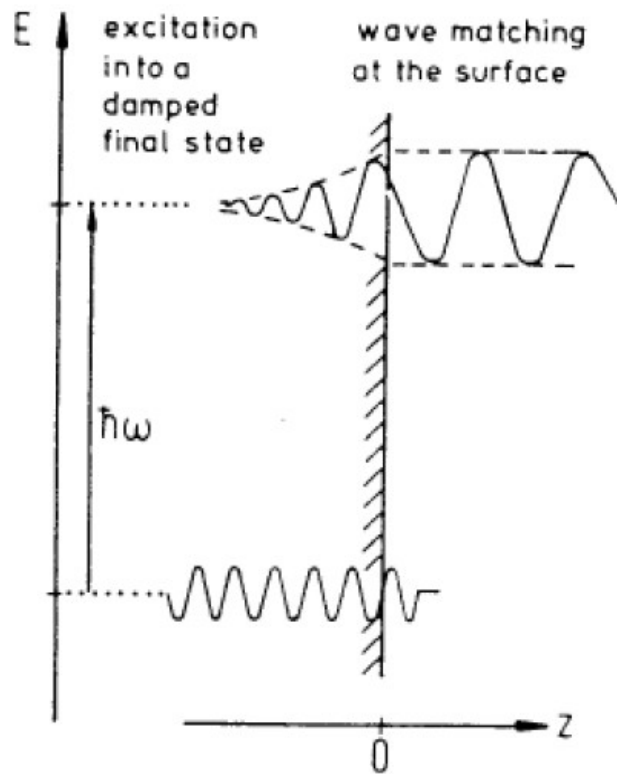
$$A(k, \varepsilon) = \sum_m \left(\left| \langle \Psi_m^{N-1} | c_k | \Psi_i^N \rangle \right|^2 \times \delta(\varepsilon + E_m^{N-1} - E_i^N) \right)$$

$$E_k = E_i^{N-1} - E_i^N$$

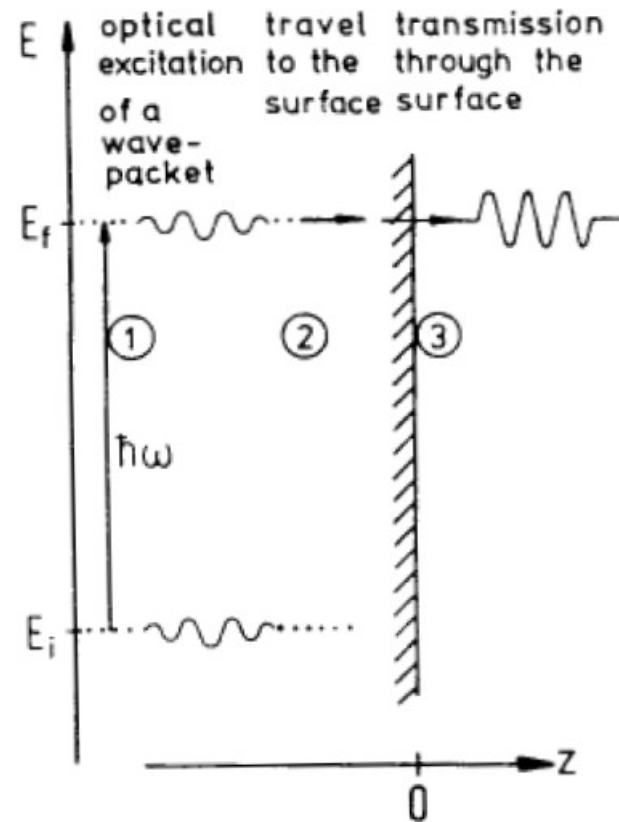
$$A(\varepsilon, k) = \frac{1}{\pi} \frac{\left| \sum''(k, \varepsilon) \right|}{\left| \varepsilon - E_k - \sum'(k, \varepsilon) \right|^2 + \left| \sum''(k, \varepsilon) \right|^2}$$

solids: from the 1-step to the 3-step model

one-step model



three-step model



Photoemission Spectroscopy

Three-Step Model of Photoemission in Solids

- Photon Absorption
 - Optical Absorption Machinery
 - Selection Rules
- Electron Propagation within the Solid
 - Inelastic Mean Free Path [$\lambda(E_{kin})$]
- Electron Escape from the Solid
 - Refractive Effects at the Surface
 - k-parallel vs. k-normal

Photoemission Spectroscopy

Basic Theory

the photoelectron current J

$$J = f(h\nu, \epsilon, \theta, \Phi; E_e, \sigma, \theta_e, \Phi_e)$$

where $h\nu$, ϵ , θ , and Φ are energy, polarization direction and angles defining the incident photon, while E_e , σ , θ_e and Φ_e are energy, spin polarization, polar and azimuthal angle of the emitted electron.

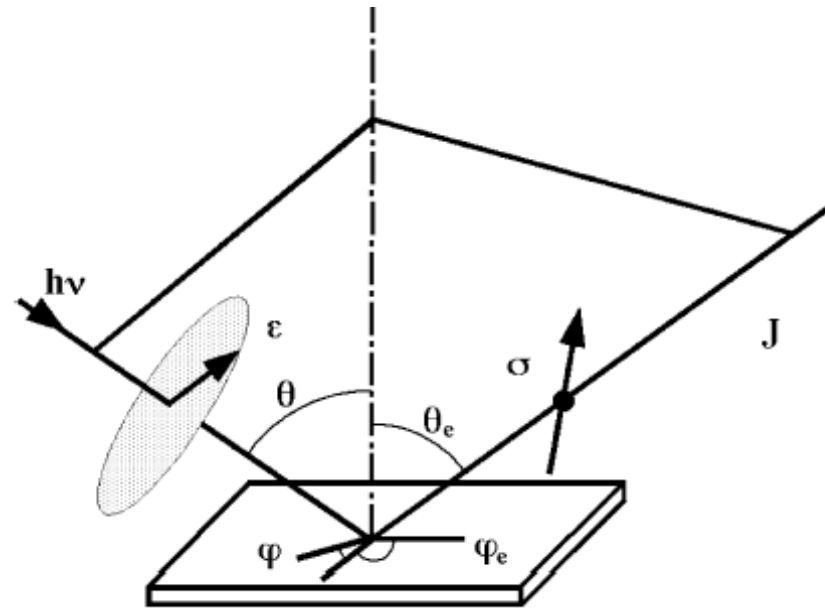


Figure 1: Schematic diagram of the photocurrent J and of all the variables.

Photoemission Spectroscopy

Basic Theory

$$I(E, h\nu) = I_p(E, h\nu) + I_s(E, h\nu)$$

I_p = physical signal, I_s = secondary scattered electrons

the three-step model

$$I_p(E, h\nu) = J(E, h\nu) \times T(E_f, h\nu) \times D(E_f)$$

J = optical transition photoelectron current

T = transmission function, propagation through the solid

D = escape function to the vacuum

Photoemission Spectroscopy

Basic Theory

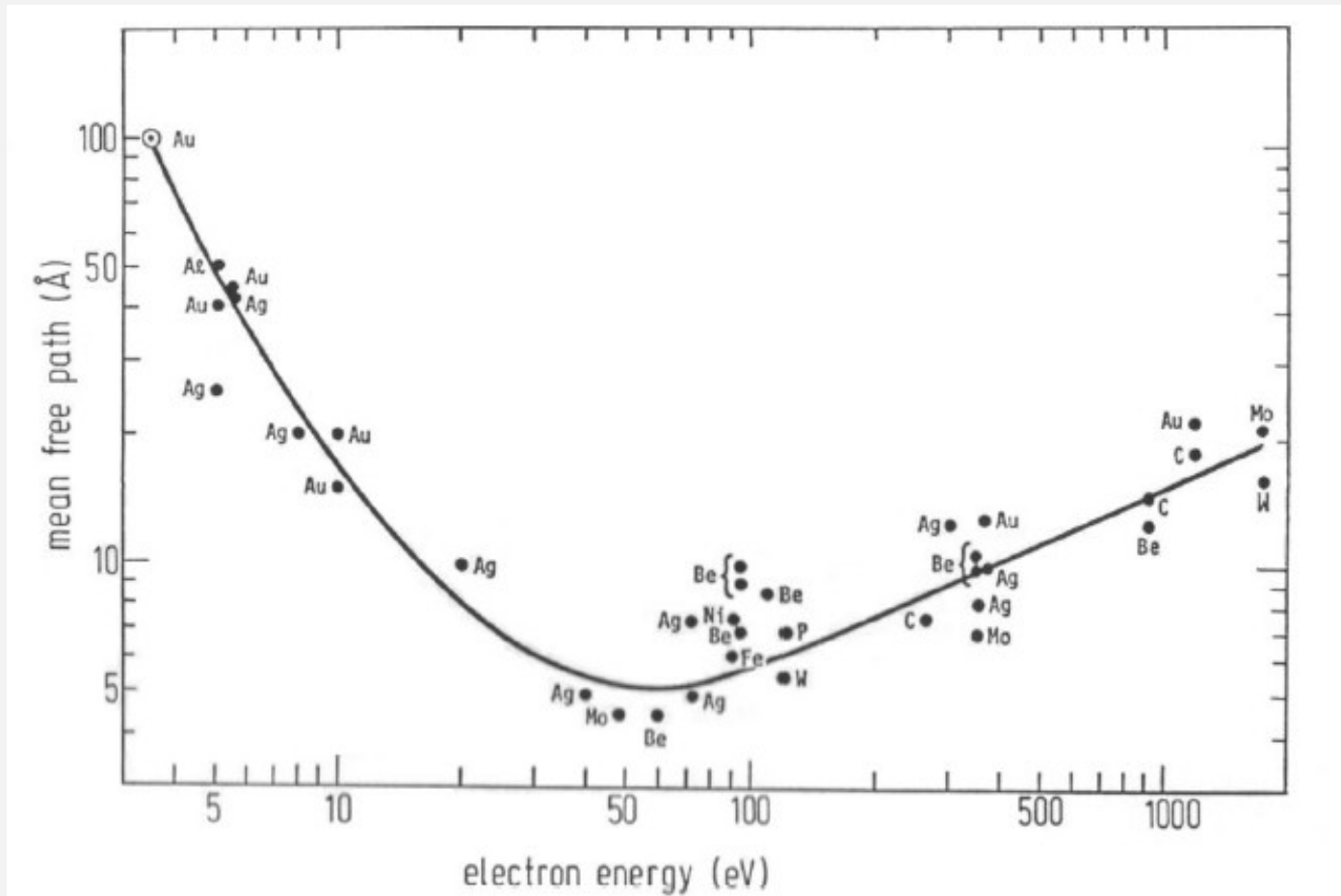
$$T(E_f) = \frac{\lambda_e(E_f)/\lambda_{ph}(h\nu)}{1 + \lambda_e(E_f)/\lambda_{ph}(h\nu)}$$

T = transmission function, propagation through the solid

$$D(E_f) = 1/2 \left[1 - \left(\frac{E_F + \Phi}{E_f} \right)^{1/2} \right]$$

D = escape function to the vacuum

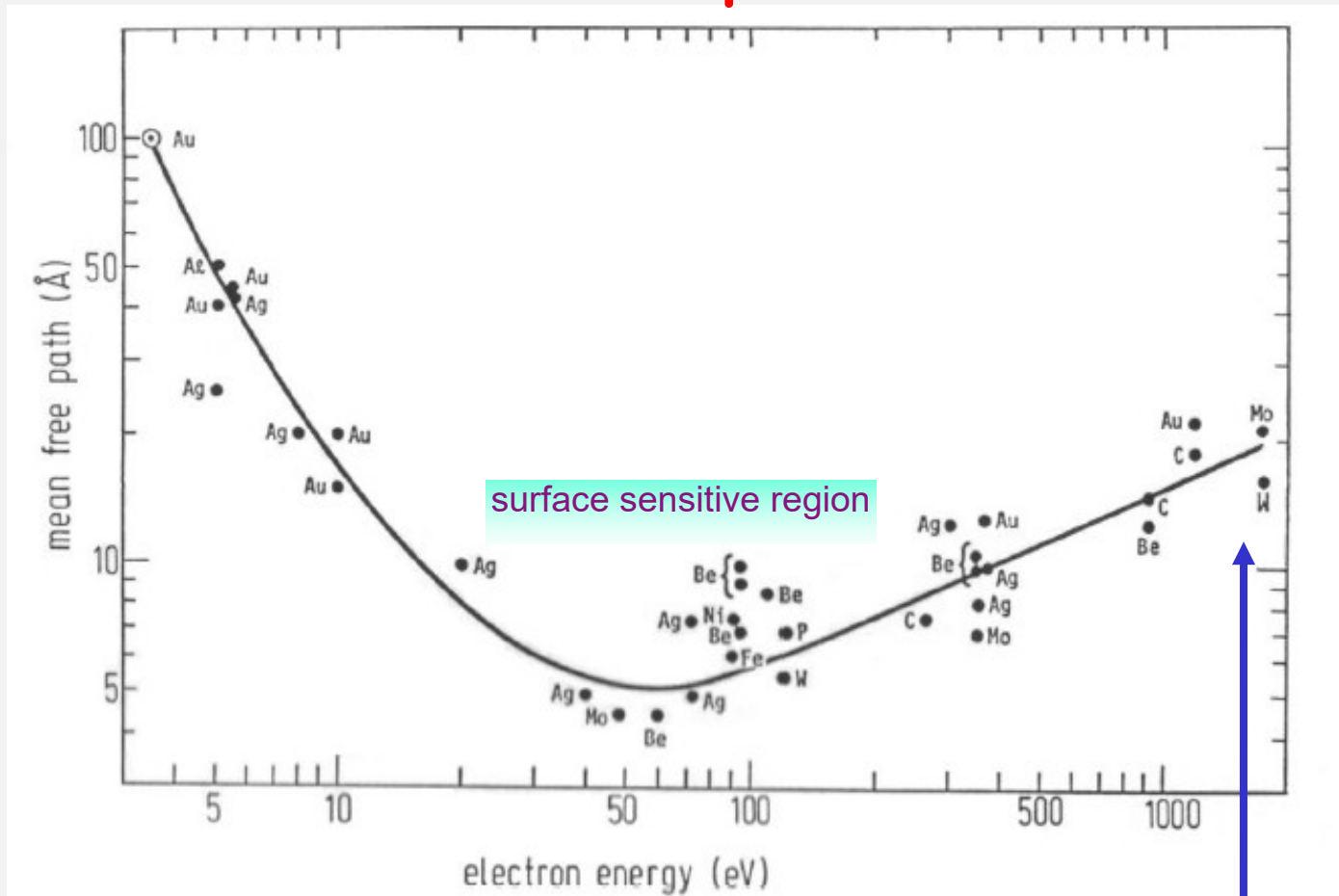
Photoemission Spectroscopy



electron mean free path

Photoemission Spectroscopy

electron mean free path



* see high-energy photoelectron spectroscopy in Torelli's lectures, this school

Photoemission Spectroscopy

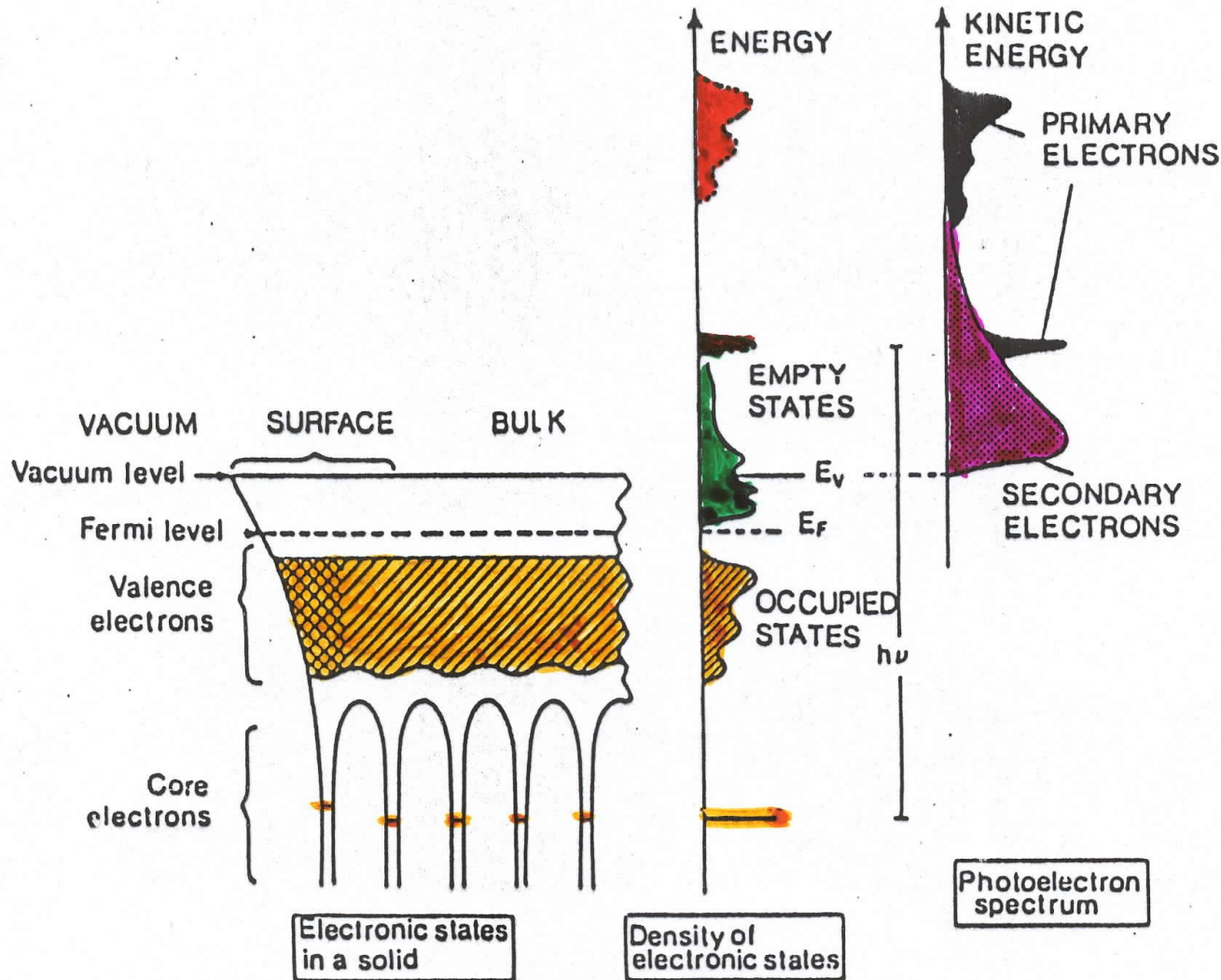
Basic Theory

J = optical transition photoelectron current

$$J_e \propto \sum_{if} f(E_i) [1 - f(E_f)] M_{if}^2 T(E_f, k_{ext}) d(E_f, k) \delta[E_{kin} - (E_f - \Phi)] \\ \times \delta(E_f - E_i - h\nu) \times \delta(k_i + G - k_f) \times \delta(k_i'' + G'' - k_f'')$$

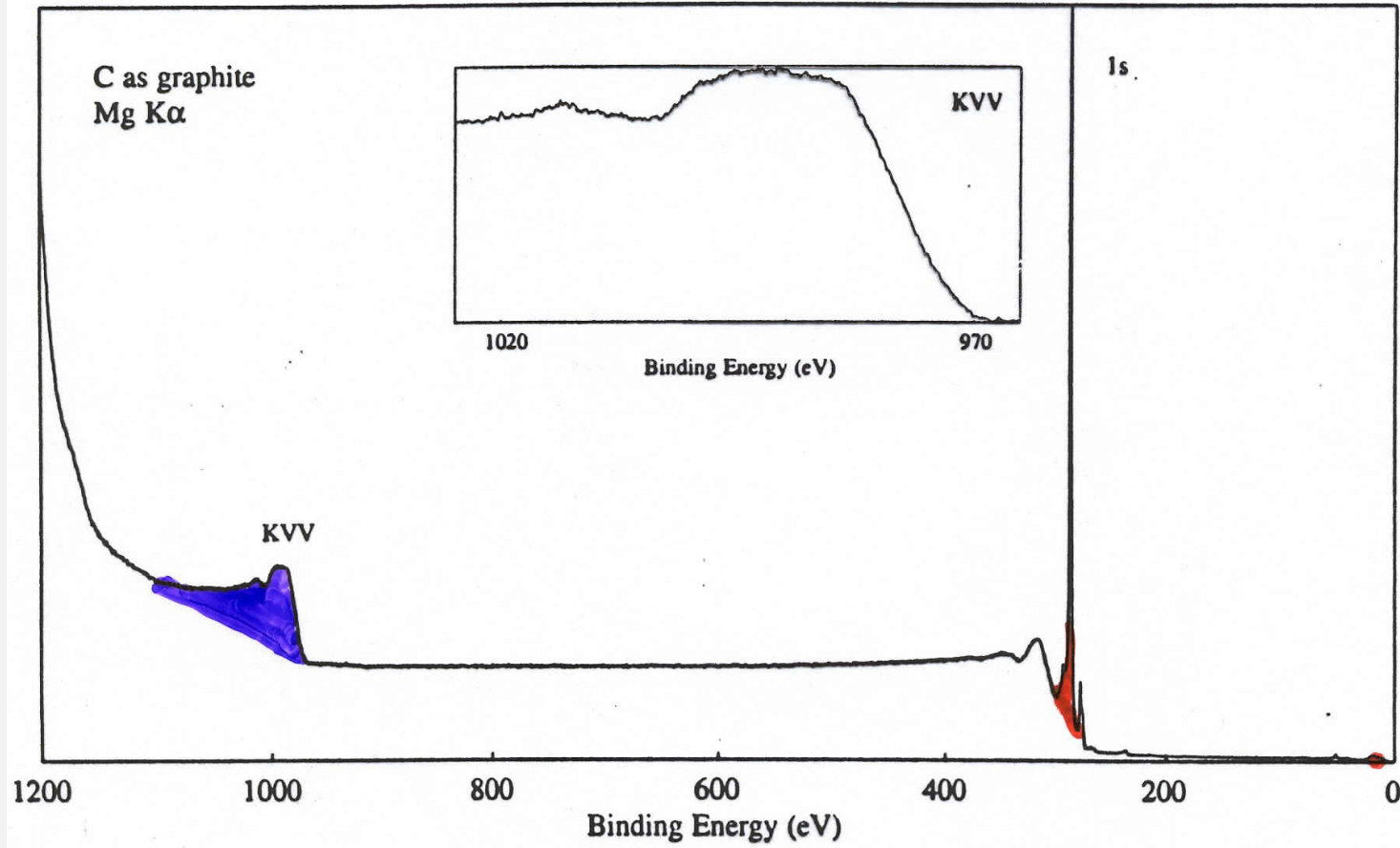
Photoemission Spectroscopy

How real spectra look like:
Primary and Secondary
Electrons

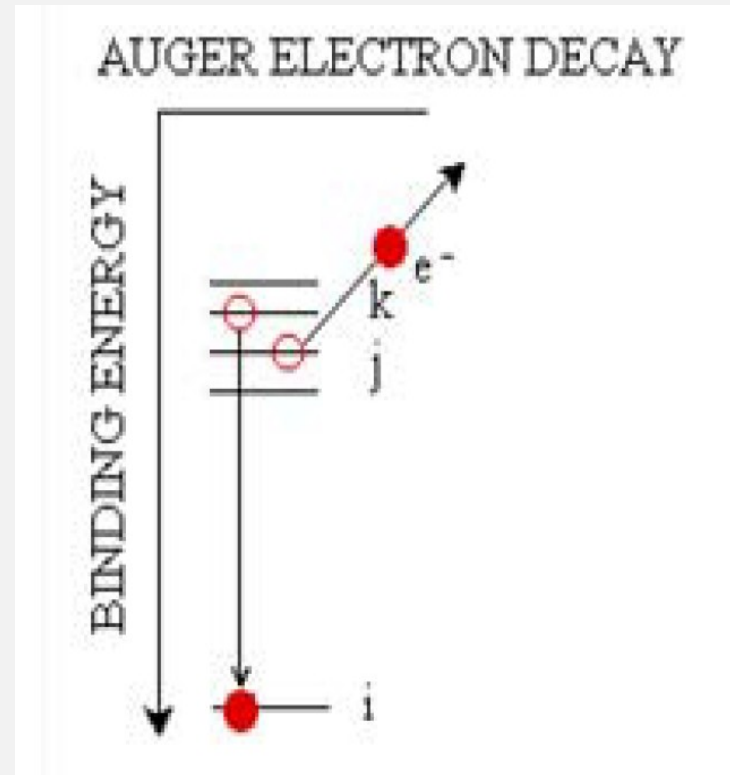
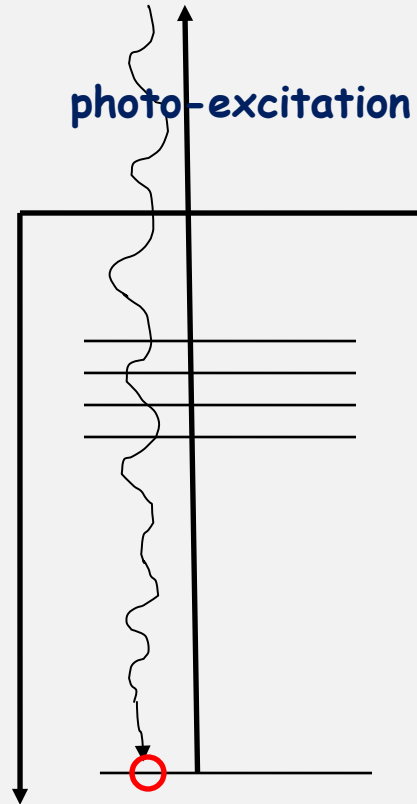


Photoemission - Core Level Spectroscopy

Wide XPS spectrum of graphite (C)

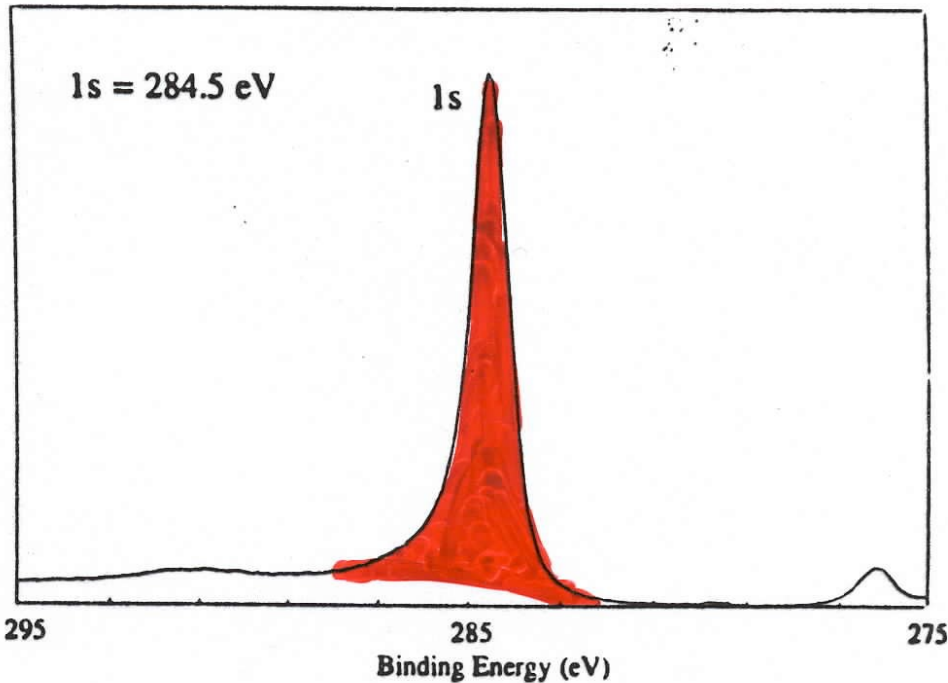


Core-hole relaxation



Photoemission Spectroscopy

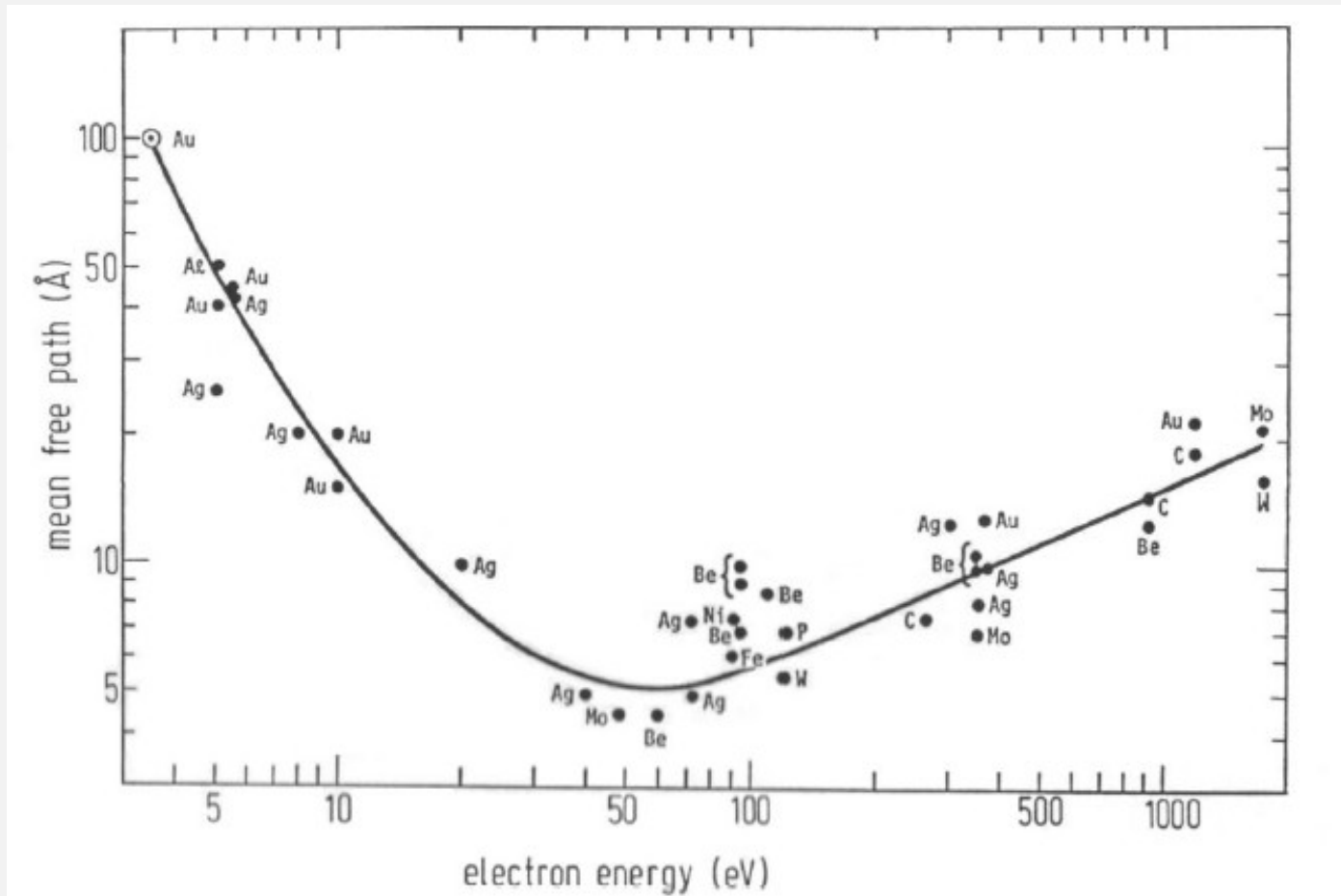
Core level XPS spectrum of graphite (C)



The singlet **C 1s** line is characterized by:

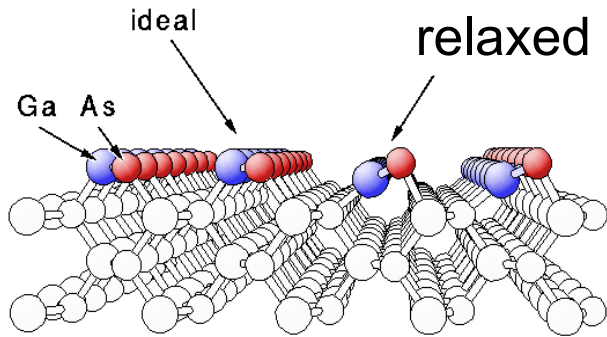
- 1) A specific binding energy which reflects the specific atomic species (C) in a specific chemical environment
- 2) A finite width reflecting the instrumental resolution, lifetime broadening and other many-body effects

Photoemission Spectroscopy



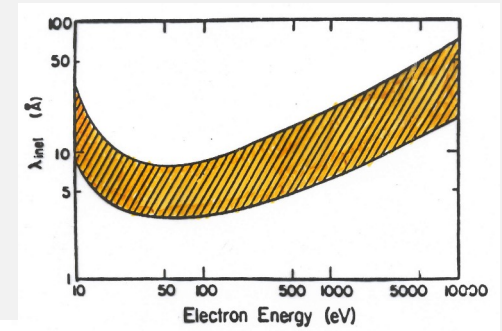
electron mean free path

Photoemission Spectroscopy: Surface Core Level Shifts



The surface sensitivity is achieved by exploiting IMPF vs. $h\nu$

GaAs (110) ideal / reconstructed surface

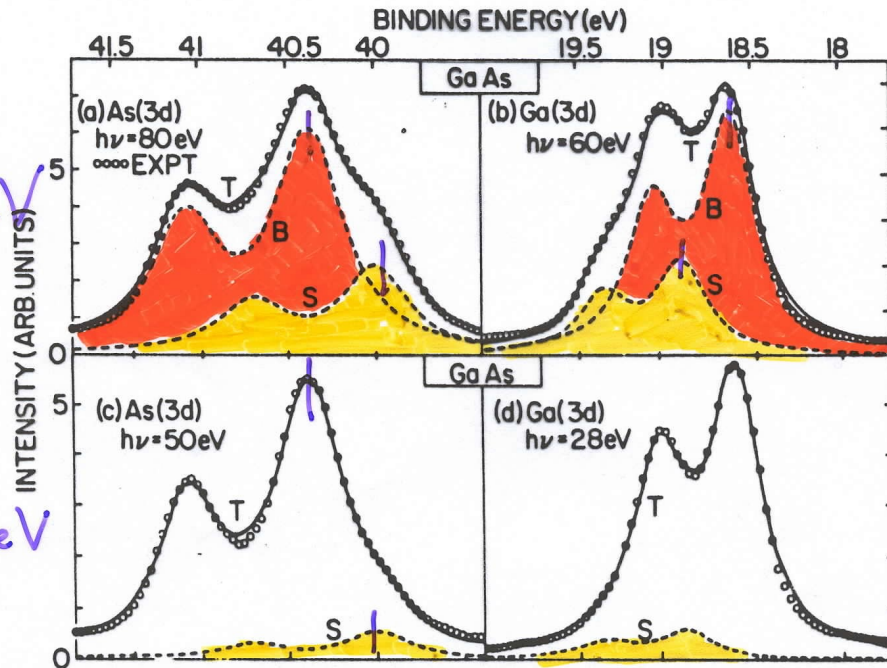


As 3d
 $h\nu = 80\text{eV}$

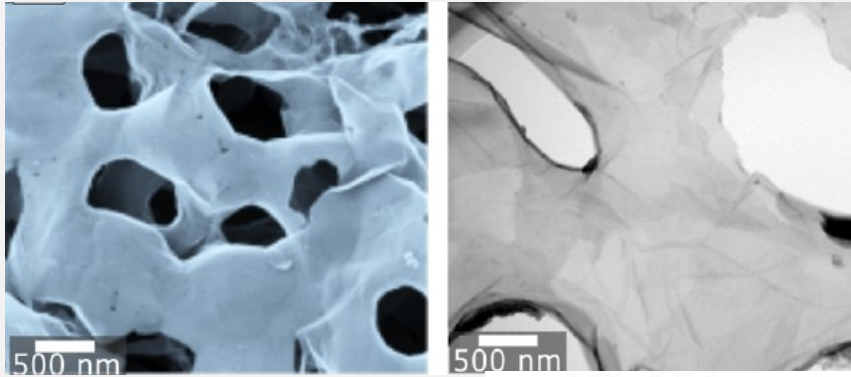
As 3d
 $h\nu = 50\text{eV}$

Ga 3d
 $h\nu = 60\text{eV}$

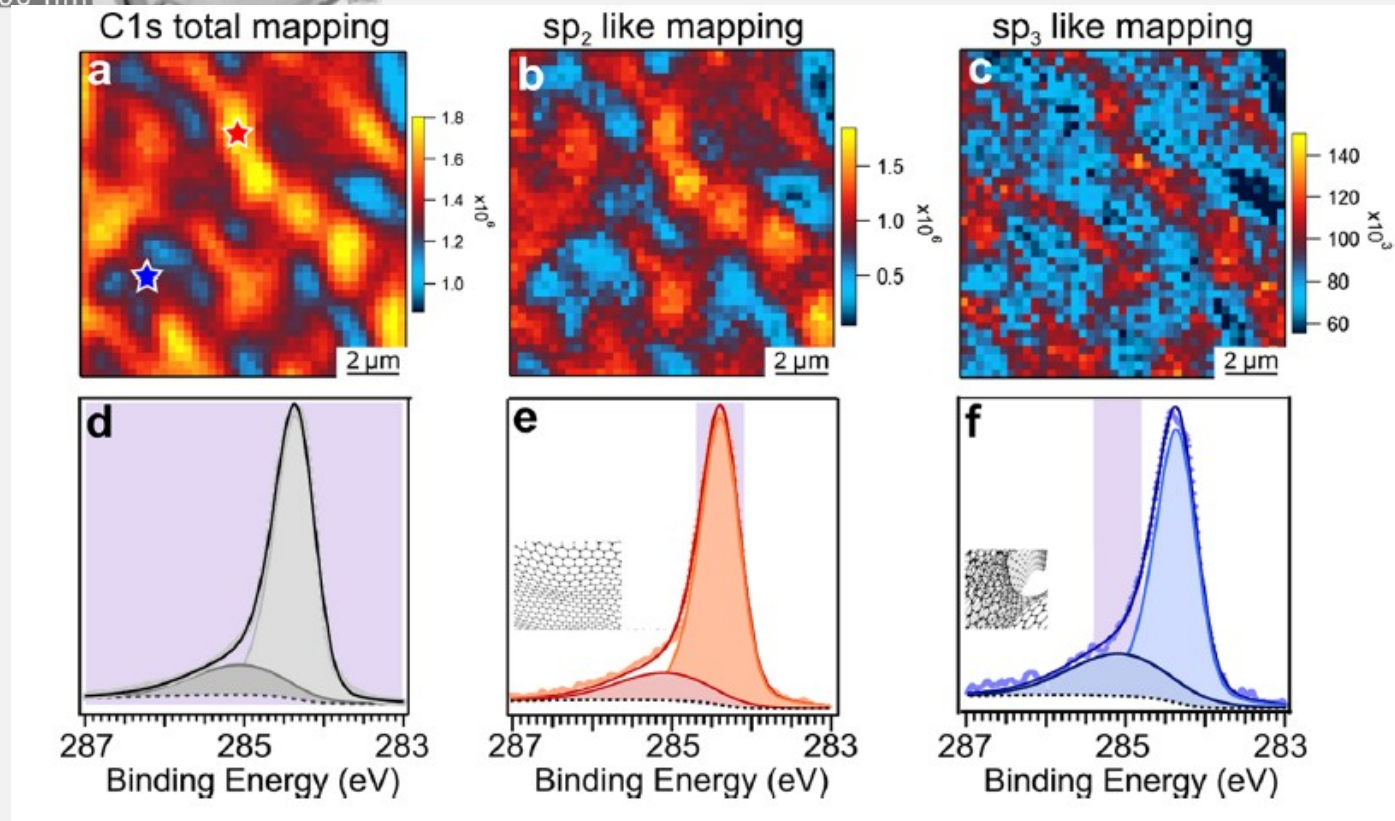
Ga 3d
 $h\nu = 28\text{eV}$



spatially-resolved core-level photoemission C 1s at nano-porous graphene (NPG)



SR-spectromicroscopy



Photoemission Spectroscopy

Semi-Quantitative Analysis

Once the photon flux ϕ is given, the photoelectron current I_i of the (nl) orbital of the i -th atomic species is approximately given by

$$I_i(n) \approx C_i \lambda(E_k) \phi(\hbar\omega) \sigma_n(\hbar\omega) T(E_k)$$

Where

C_i Atomic Concentration of the i -th species

λ Escape Depth

σ_{nl} Orbital Cross Section

T Instrumental Efficiency

Photoemission Spectroscopy

Semi-Quantitative Analysis

Once the **efficiency of detection** of an **atomic species** is calibrated via the **sensitivity factors** one gets

$$C_i = \frac{\frac{I_i}{S_i}}{\sum_i \frac{I_i}{S_i}}$$

Where

C_i Atomic Concentration of the i -th species

s_i Orbital Sensitivity Factor of the i -th species

I_i Spectral Intensity Related to the i -th species

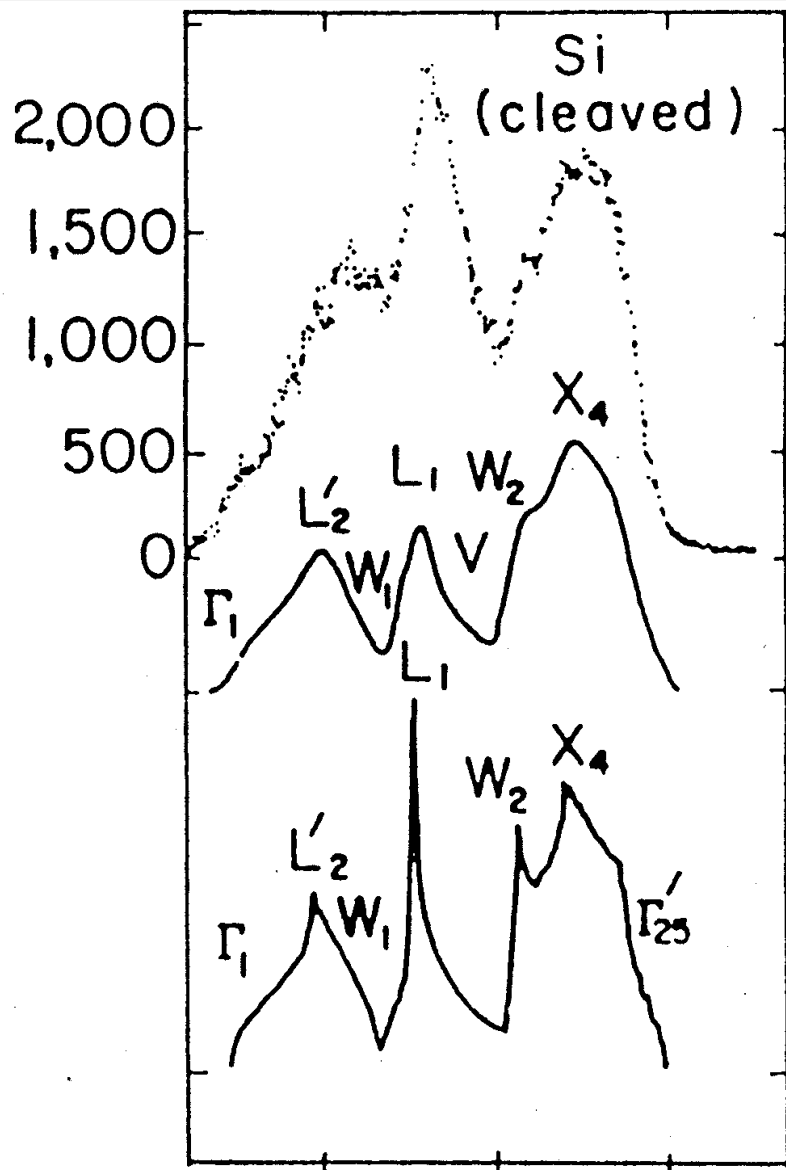
Photoemission Spectroscopy: Valence Band States

Any valence band spectrum brings **altogether** contributions related to **differing atomic sites and orbital symmetry**.

Thereby, one has to properly design **ad hoc experiments** aiming at **disentangling the various spectral components**.

Cooper Minimum Photoemission and **Resonant Photoemission** are two examples of such **ad hoc experiments**.

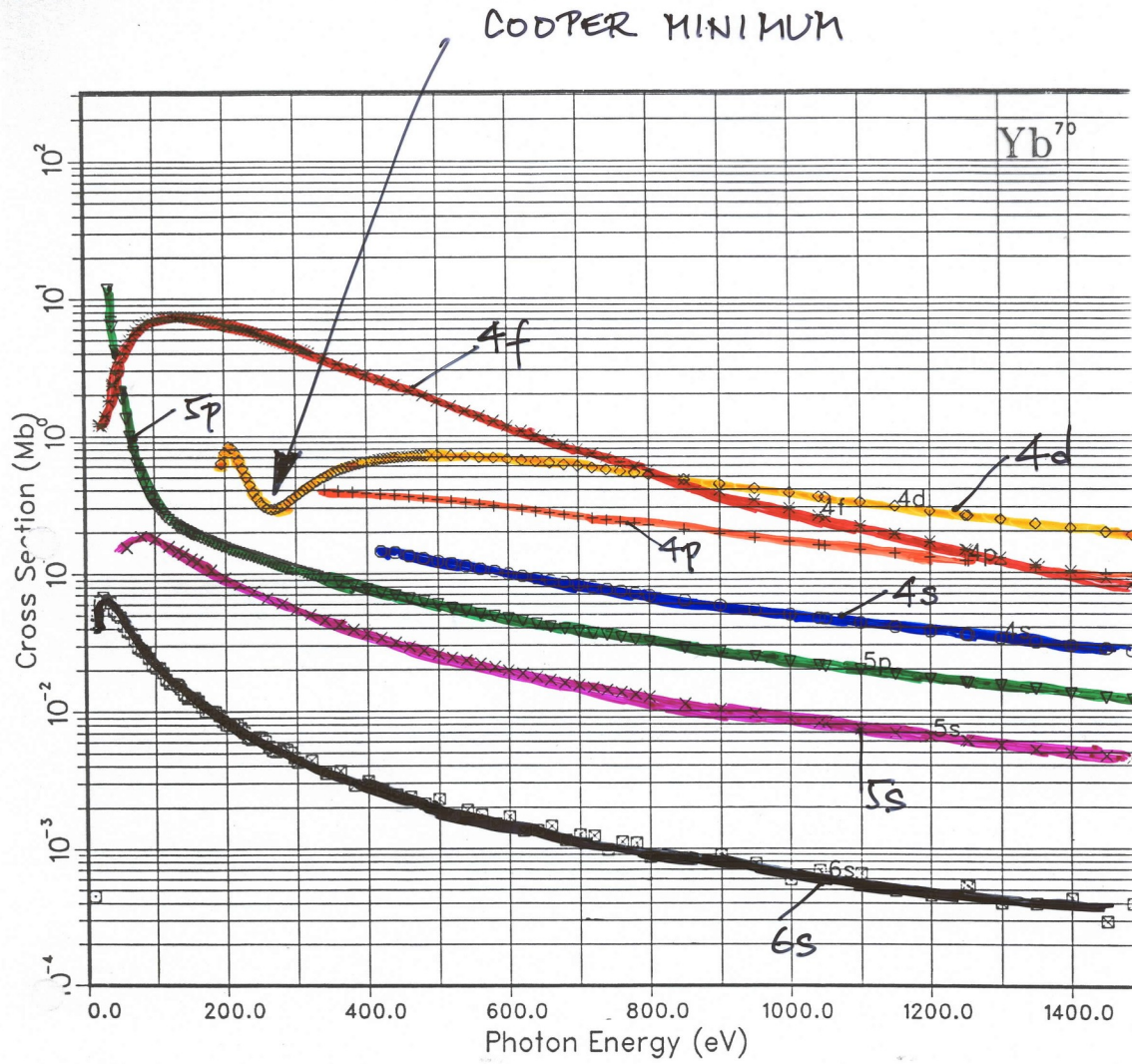
Photoemission Spectroscopy: Valence Band (VB) Energy Distribution Curve (EDC)



In the X-ray regime the VB spectra are expected to mimic the Density of States (DOS)

Fig. 14. XPS valence spectrum for a silicon single crystal cleaved in vacuum (points), together with a calculated total density of states (bottom curve), and a density of states broadened by the instrumental resolution function. Excitation was with monochromatized $AlK\alpha$. The spectrum has been corrected for inelastic scattering. The energy locations of state density primarily due to various high-symmetry points in the reduced Brillouin zone are also indicated. (From Ley *et al.*, ref. 192.)

Photoemission Spectroscopy



Yb binding energies(eV) are:

1s (2) 57009.8	2s (2) 9290.78	2p (6) 8897.20
3s (2) 2086.76	3p (6) 1904.14	4s (2) 402.610
3d(10) 1561.01	4p (6) 327.461	5s (2) 50.8637
4d(10) 190.652	5p (6) 30.7582	6s (2) 5.16038
4f(14) 15.9818		

Calculated
Photoionization Cross
Sections for Free
Atoms
vs. Photon Energy

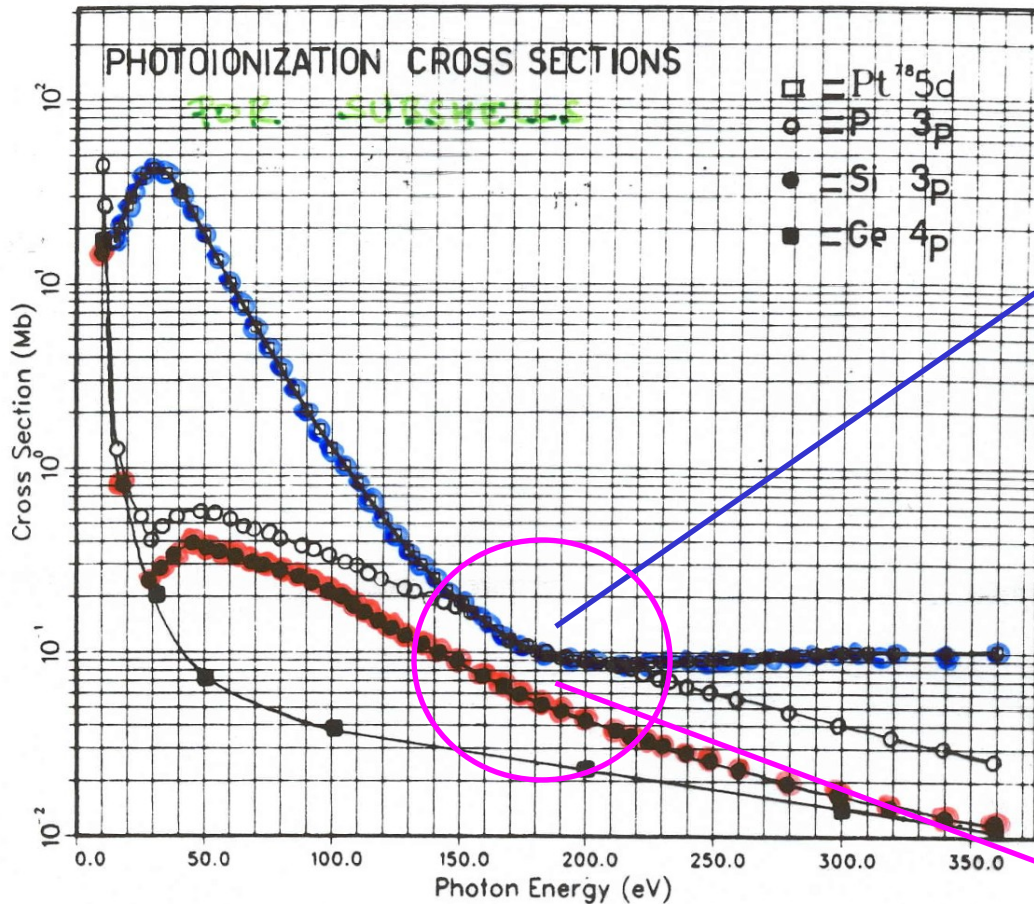
Yeh and Lindau,
Atomic Data and
Nuclear Data Tables
Volume 32, 1-155
(1985)

cross section of all elements available at:

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

Cooper Minimum Photoemission

It is possible when one of the valence band orbital shows a Cooper minimum in the photoionization cross section



Cooper minimum
in the Pt 5d
cross section

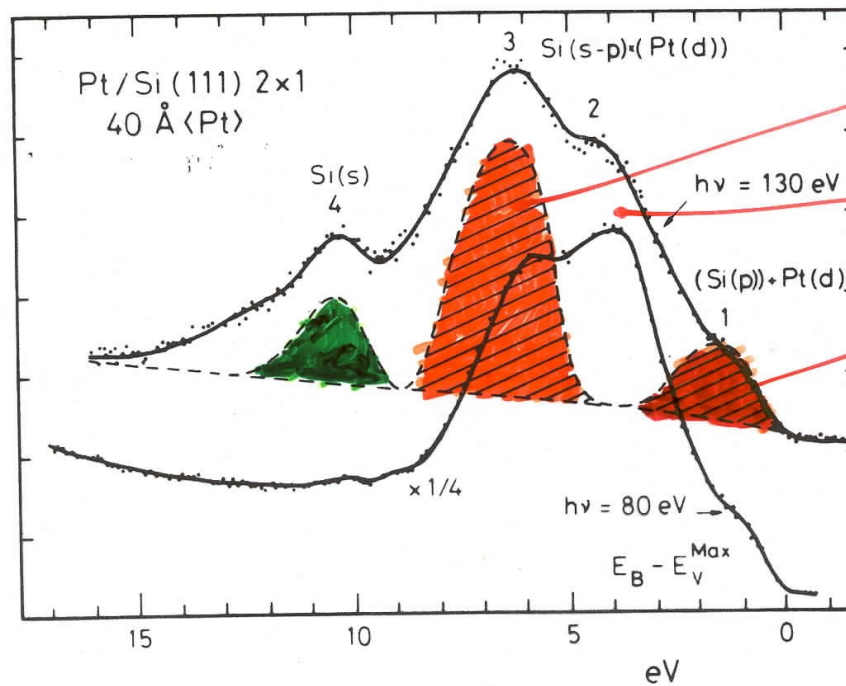
A Cooper minimum
exists when the
radial part of the
orbital wave function
exhibits a node

The Pt 5d and Si 3p cross
sections are comparable

Photoionization cross section for 4d and 5d subshells in the energy range 0–200 eV compared to the cross sections for the 3ps and 4sp valence states of the semiconductors [21].

Cooper Minimum Photoemission

A joint analysis of VB photoemission spectra taken at and off the Cooper minimum enables one to disentangle the differing site- and orbital-specific contributions



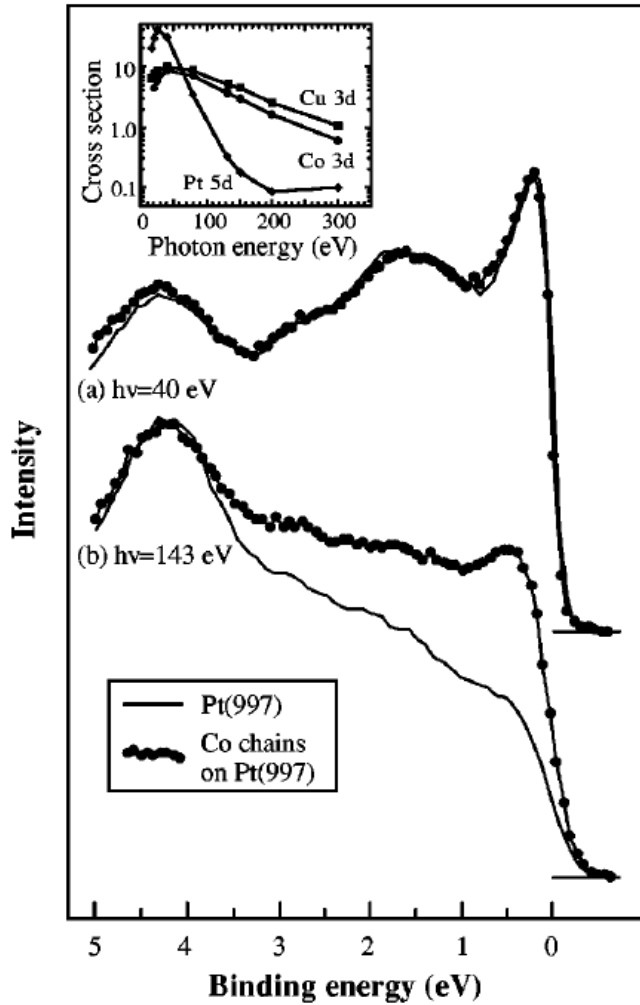
Pt 5d anti-bonding

Pt 5d non-bonding

Pt 5d bonding

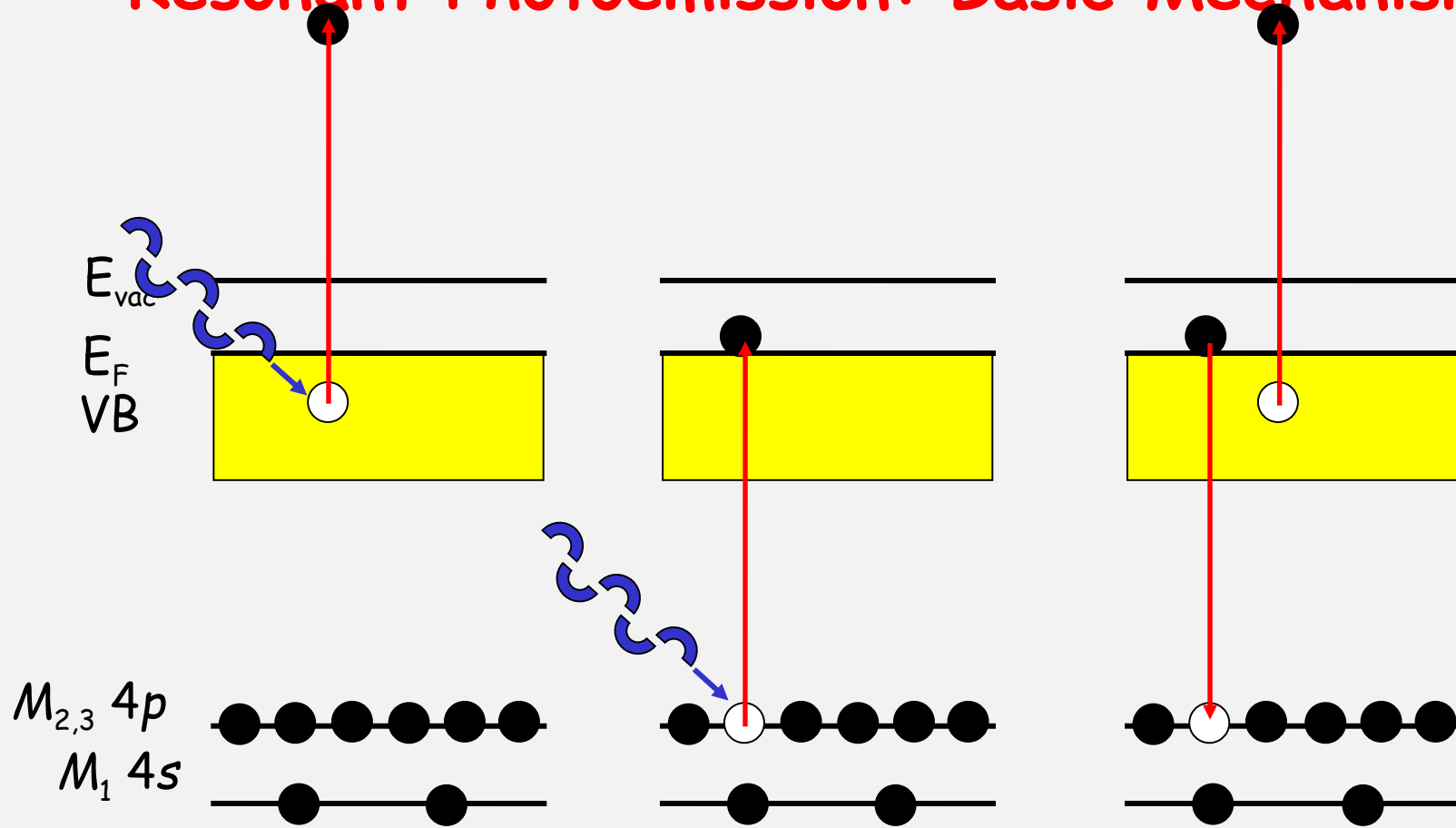
. Analysis of the Si sp partial DOS at the Pt-Si(111) reacted interface (40 Å Pt-Si(111) at room temperature). The top panel displays the CM and the $h\nu = 80$ eV photoemission data, and a three-peak partial DOS that accounts for the Si hybridized 3sp charge at the interface; a gap is present in correspondence to the localized Pt5d states. The same three-peak partial DOS is then self-convoluted and compared to the integrated Si $L_{2,3}$ VV lineshape. The correspondence of all peaks and relative intensities (a part of the known reduction of the Si 3s contribution) confirms the CM derivation of the Si sp partial DOS [159].

Cooper Minimum Photoemission



- clean pristine Pt(997) surface (thin line)
- Co nanowires grown on Pt (dots)

Resonant Photoemission: Basic Mechanisms



- (1) Excitation of a VB hole (2) Threshold excitation of a core hole (3) Recombination Process

The processes (1) & (3) bring the system from the same initial state to the same final state (one hole in VB and one emitted electron) and thus they quantum mechanically interfere giving rise to the **Fano Line Shape**

Resonant Photoemission

Valence band photoemission spectra are taken at selected photon energies while crossing a core level threshold

Example: Pd 4p \rightarrow Pd 4d

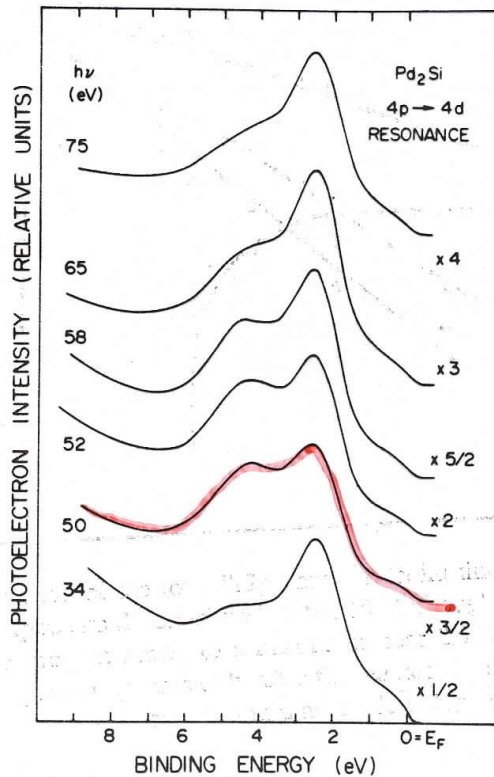
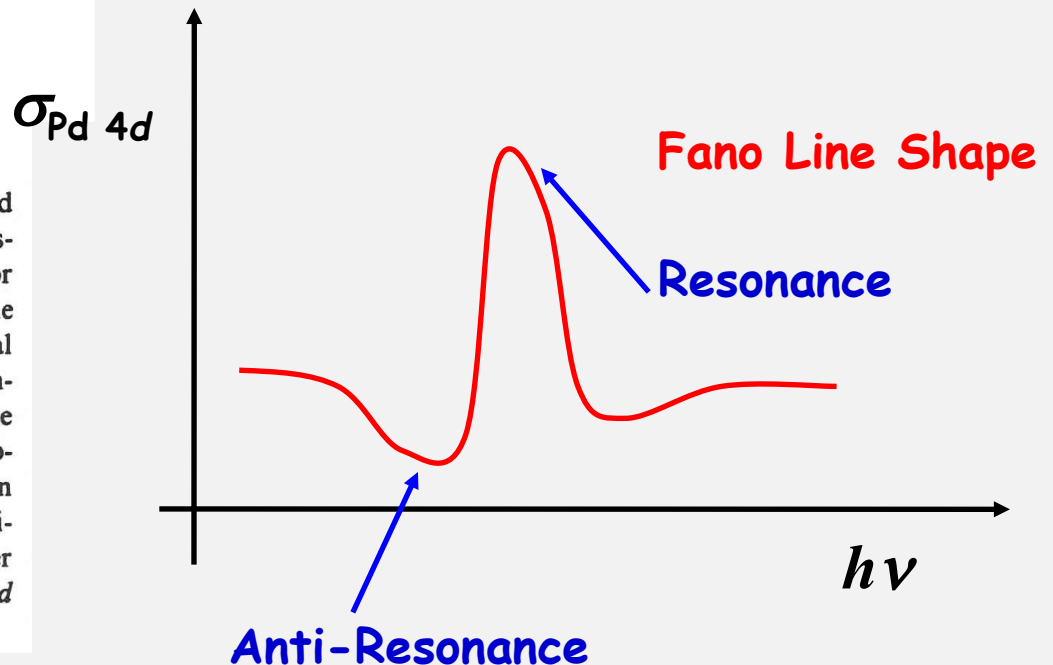


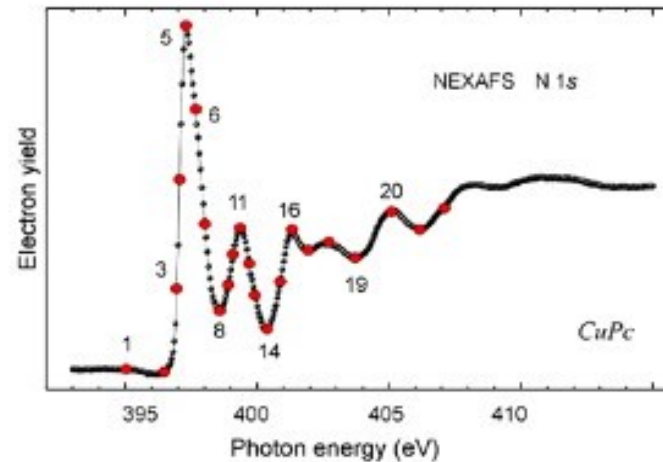
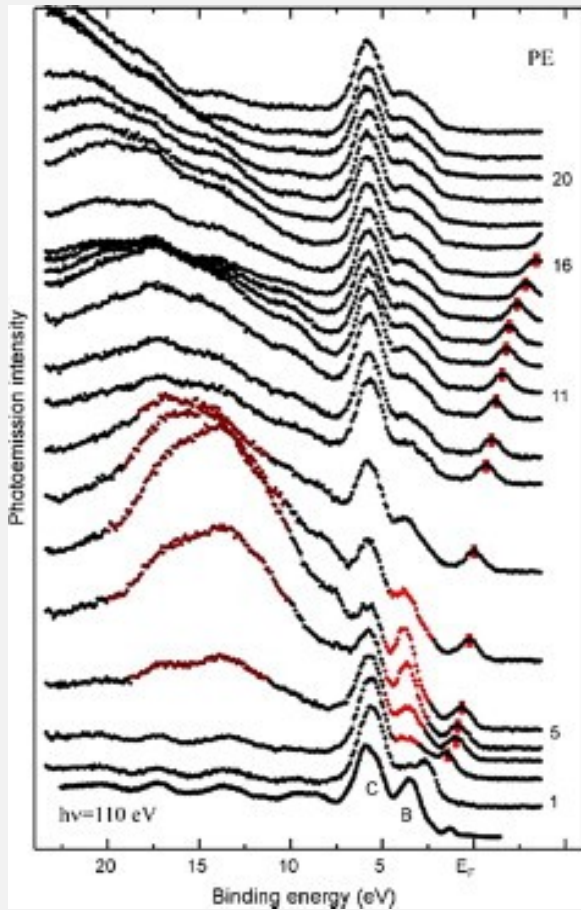
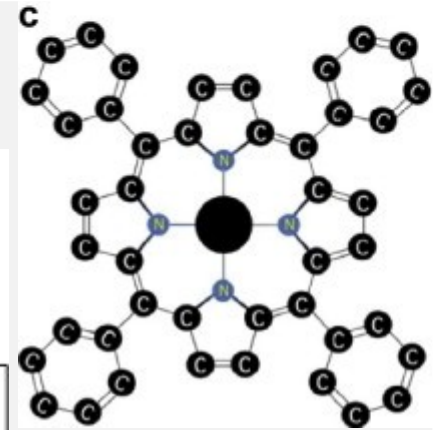
FIG. 4. Representative spectra of the valence-band emission of Pd₂Si for photon energy near the 4p \rightarrow 4d resonance. The spectra were normalized for monochromator output (Ref. 29) and are given in relative units. The modulation of the relative intensity of the experimental features reflects the suppression of the 4d character at antiresonance, where the Si-derived states are more visible ($h\nu \sim 50$ eV), and the following reenhancement at resonance (see Fig. 3). Resonant photoemission represents an important tool for analyzing the different orbital contributions to the valence states and, unlike the Cooper minimum technique, can in principle be applied to all *d* systems.



Resonant Photoemission

Valence band photoemission spectra are taken at selected photon energies while crossing a core level threshold

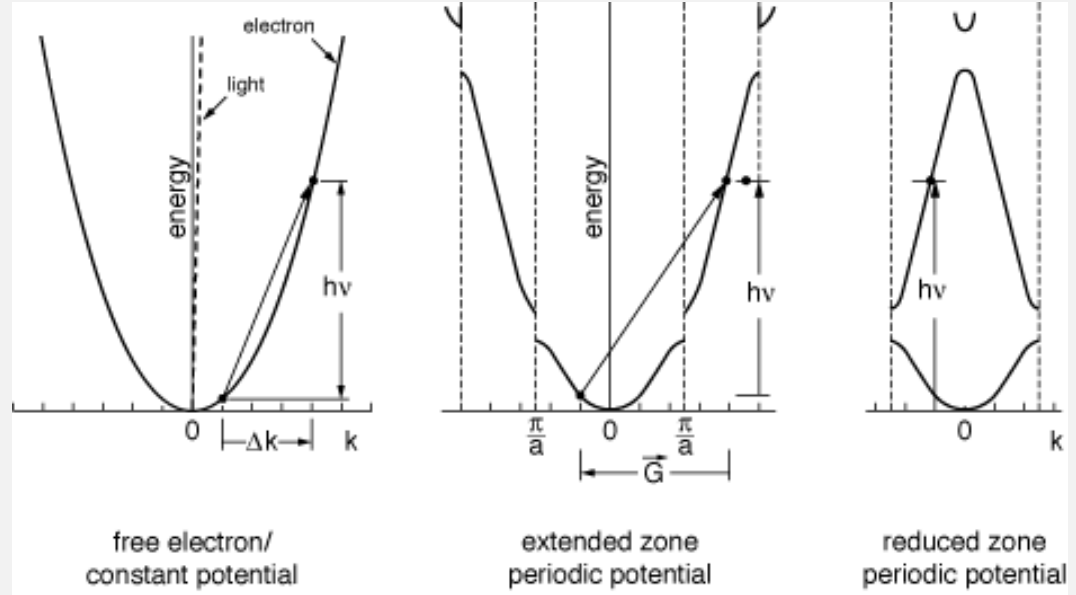
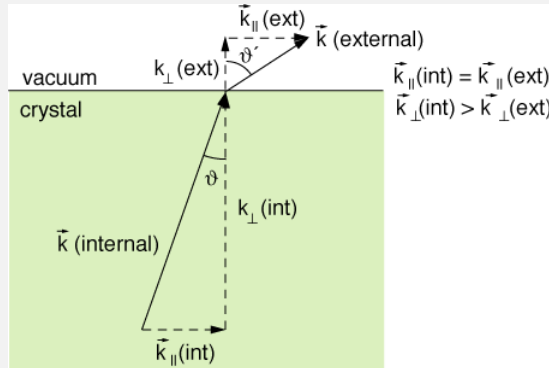
Example: metal-phthalocyanine



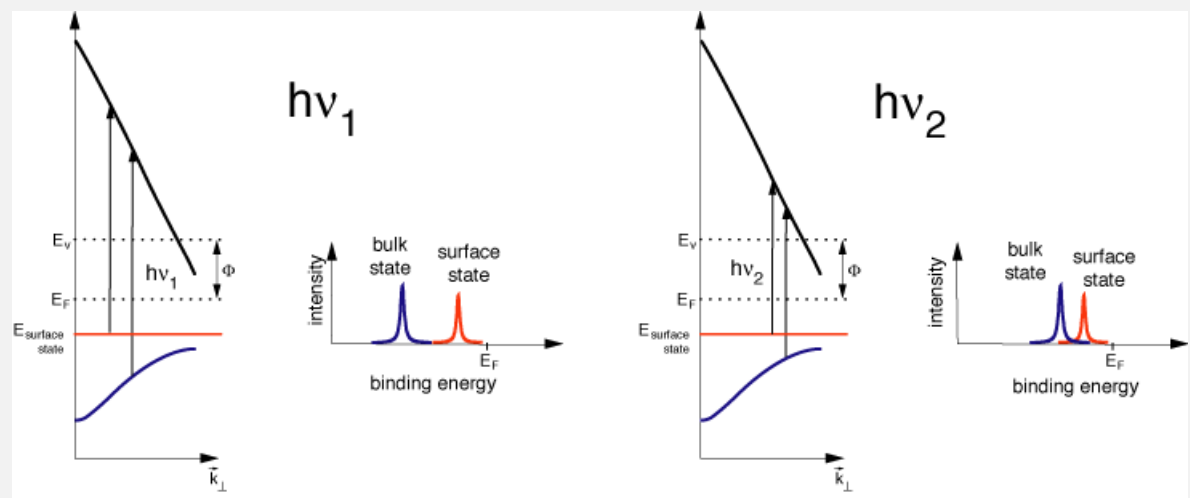
angular resolved photoemission

C. Mariani

How to photo-excite electrons from a crystal in a periodic potential, by photoemission



$$\vec{k}_{\parallel i} = \vec{k}_{\parallel f} = \sin(\Theta) \sqrt{\frac{2m}{\hbar^2}} \sqrt{E_{kin}} = \sin(\Theta) \sqrt{\frac{2m}{\hbar^2}} \sqrt{h\nu - E_{bin} - e\Phi}$$



angular resolved photoemission

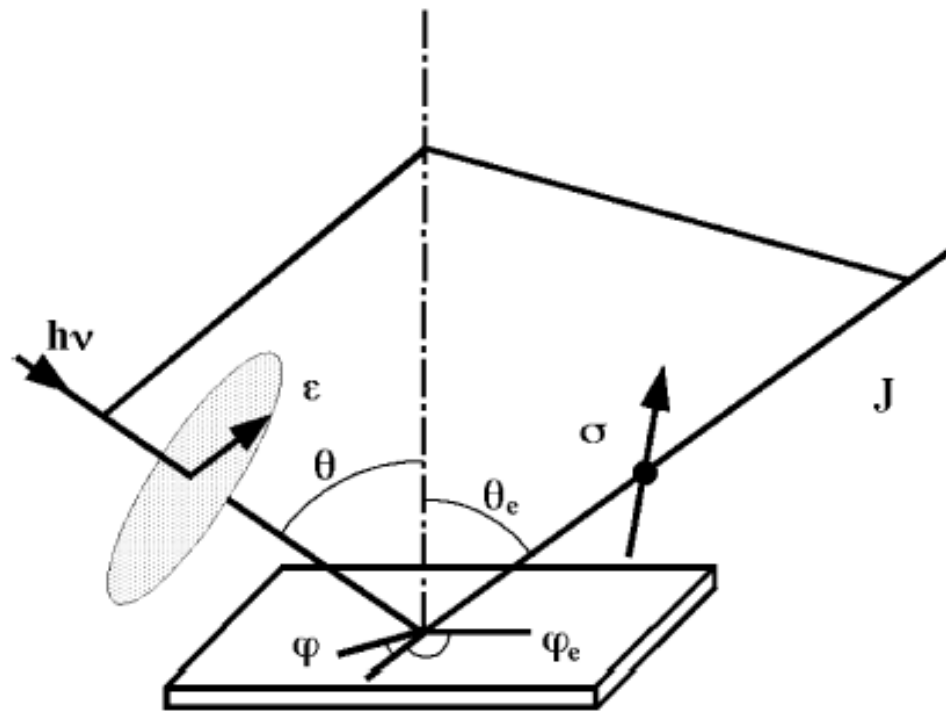
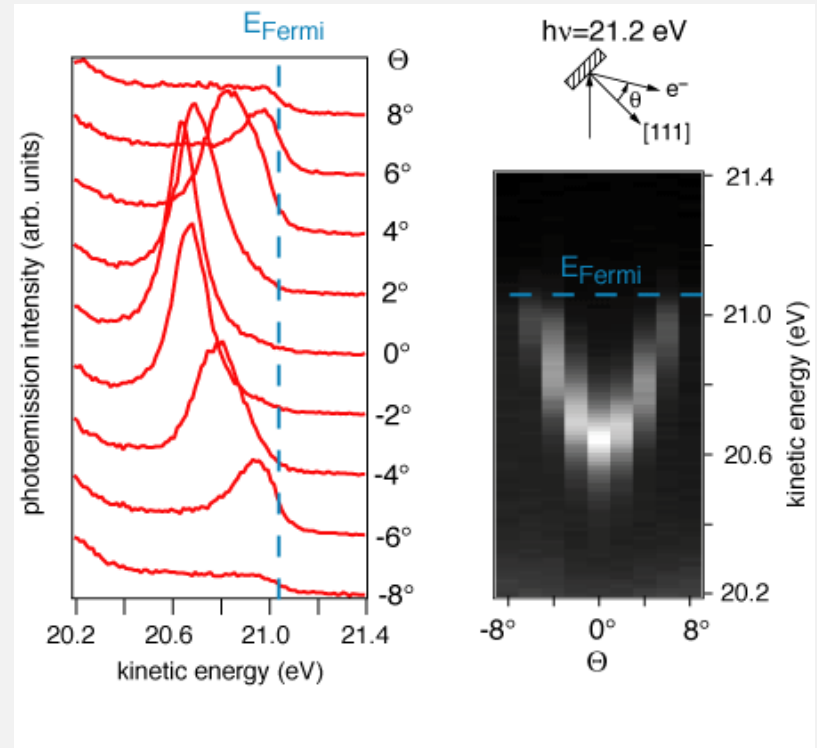
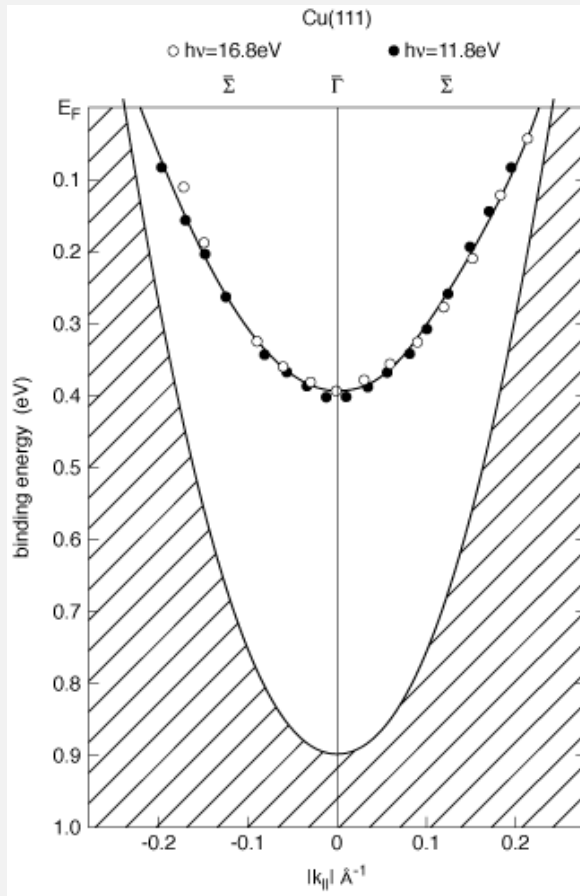


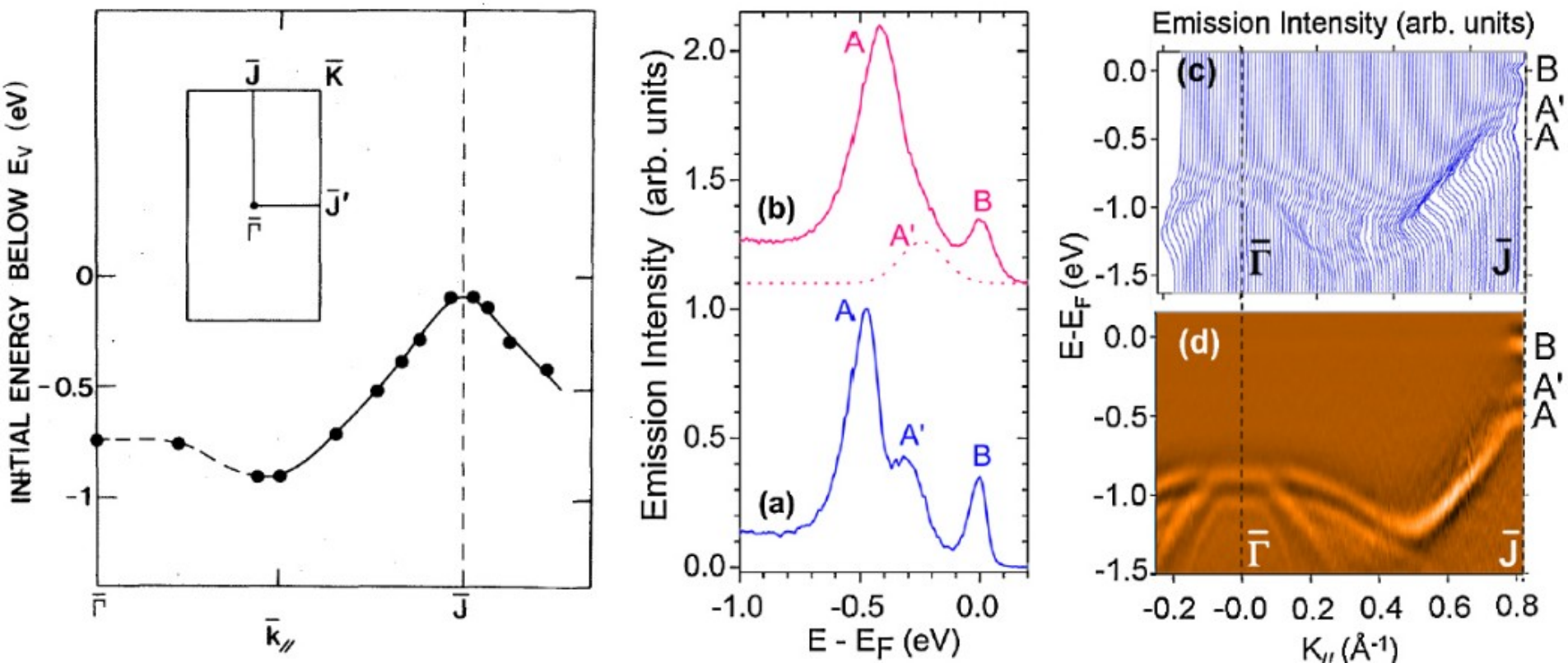
Figure 1: Schematic diagram of the photocurrent J and of all the variables.

electronic surface states at Cu(111)



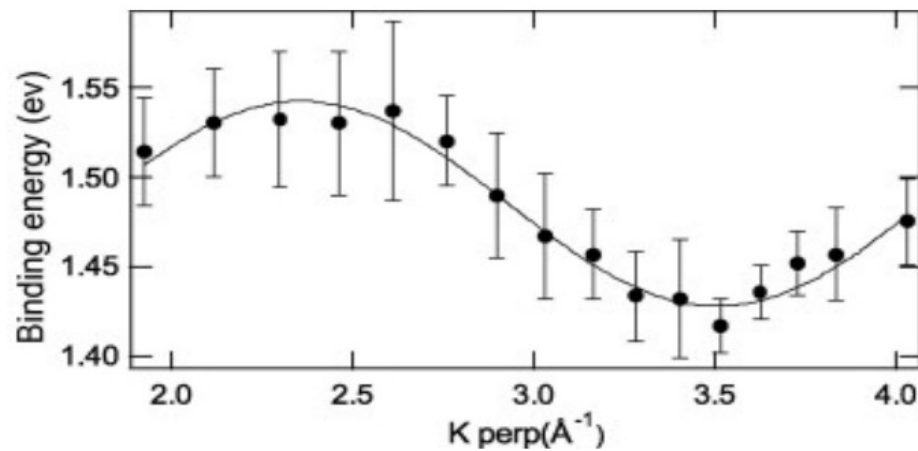
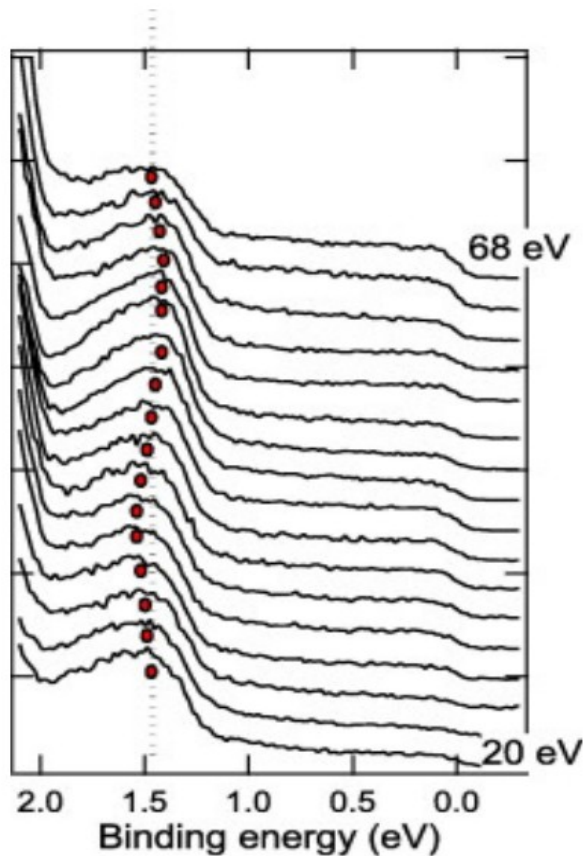
**quasi-free electron surface state on Cu(111),
Schockley state, *s-like***

dangling-bond surface state at Si(111)-(2x1)



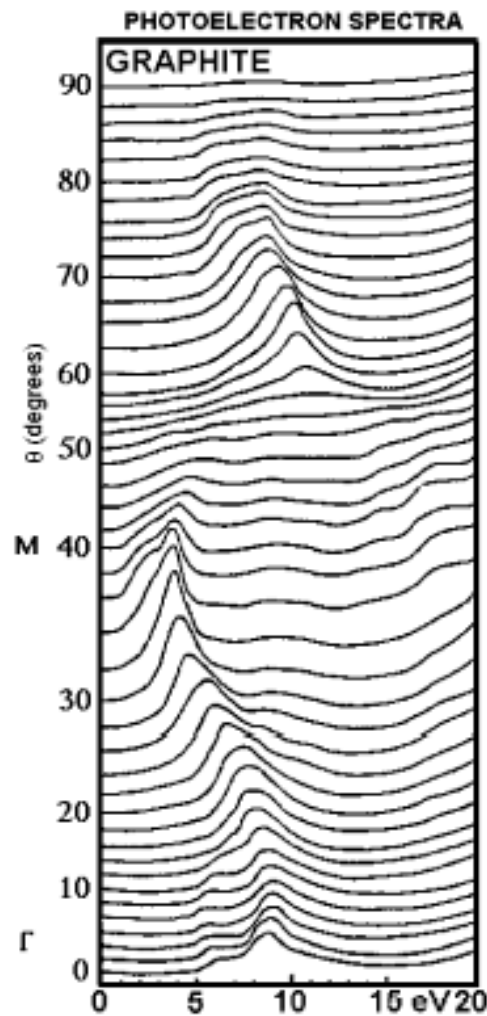
Dangling-bond surface state dispersion at the Si(111)-(2x1) reconstructed surface along the Γ J direction of the Surface Brillouin Zone (SBZ). One of the first experimental ARPES dangling-bond dispersion (left panel); recent high-resolution ARPES dangling-bond dispersion.

pentacene ordered layer on Cu(119)



2-nm thick pentacene film grown on Cu(119). ARPES selection of spectra taken at normal emission and varying the photon energy (left); highest-occupied molecular-orbital (HOMO) band dispersion along k_{\perp}

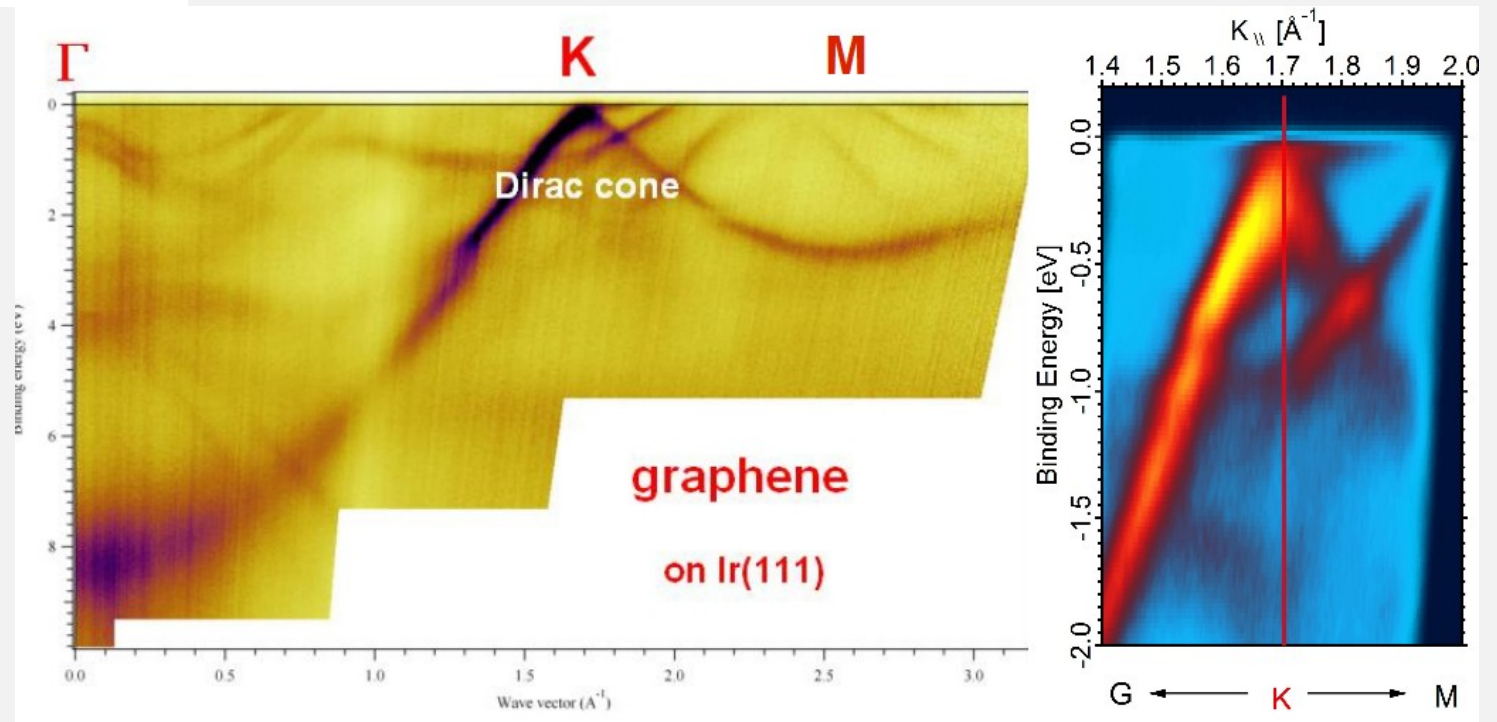
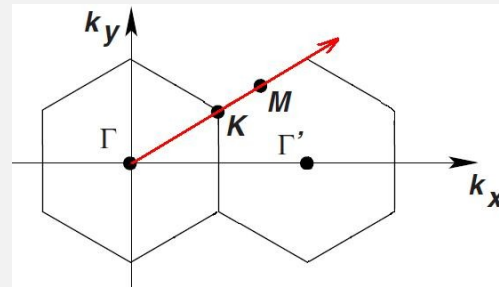
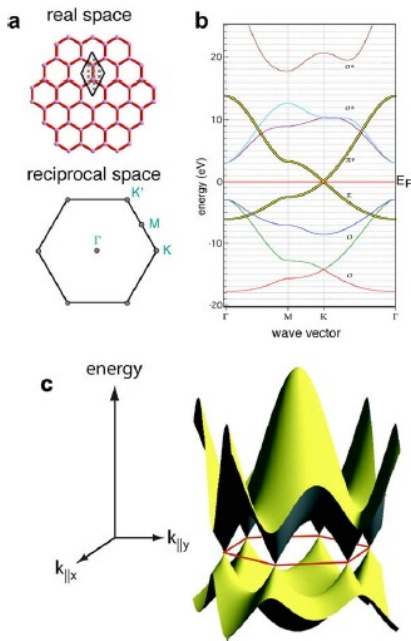
angular resolved photoemission: graphite



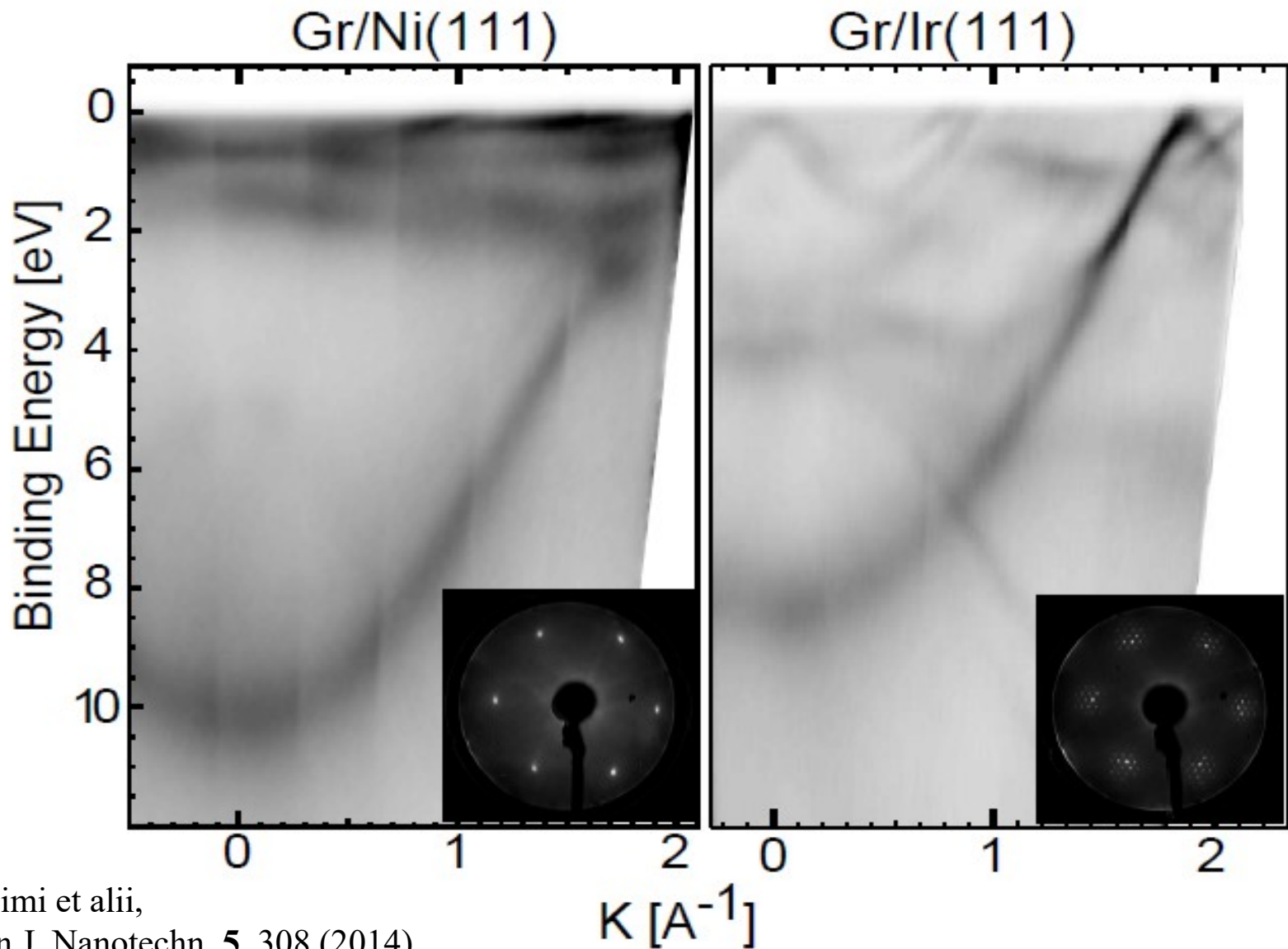
ZONE BOUNDARY CROSSING



angular resolved photoemission: graphene

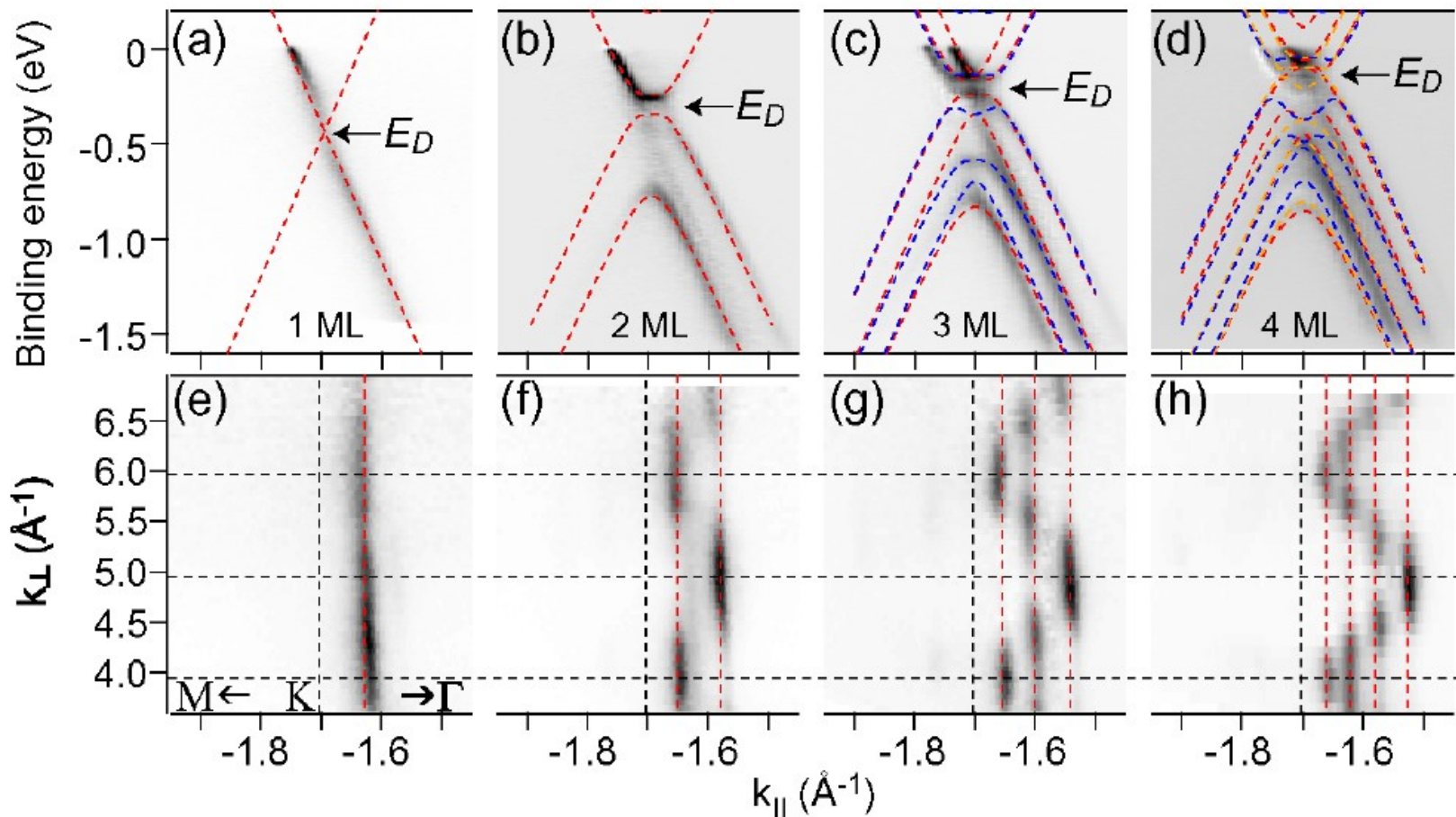


Graphene on metal surfaces: interaction strength

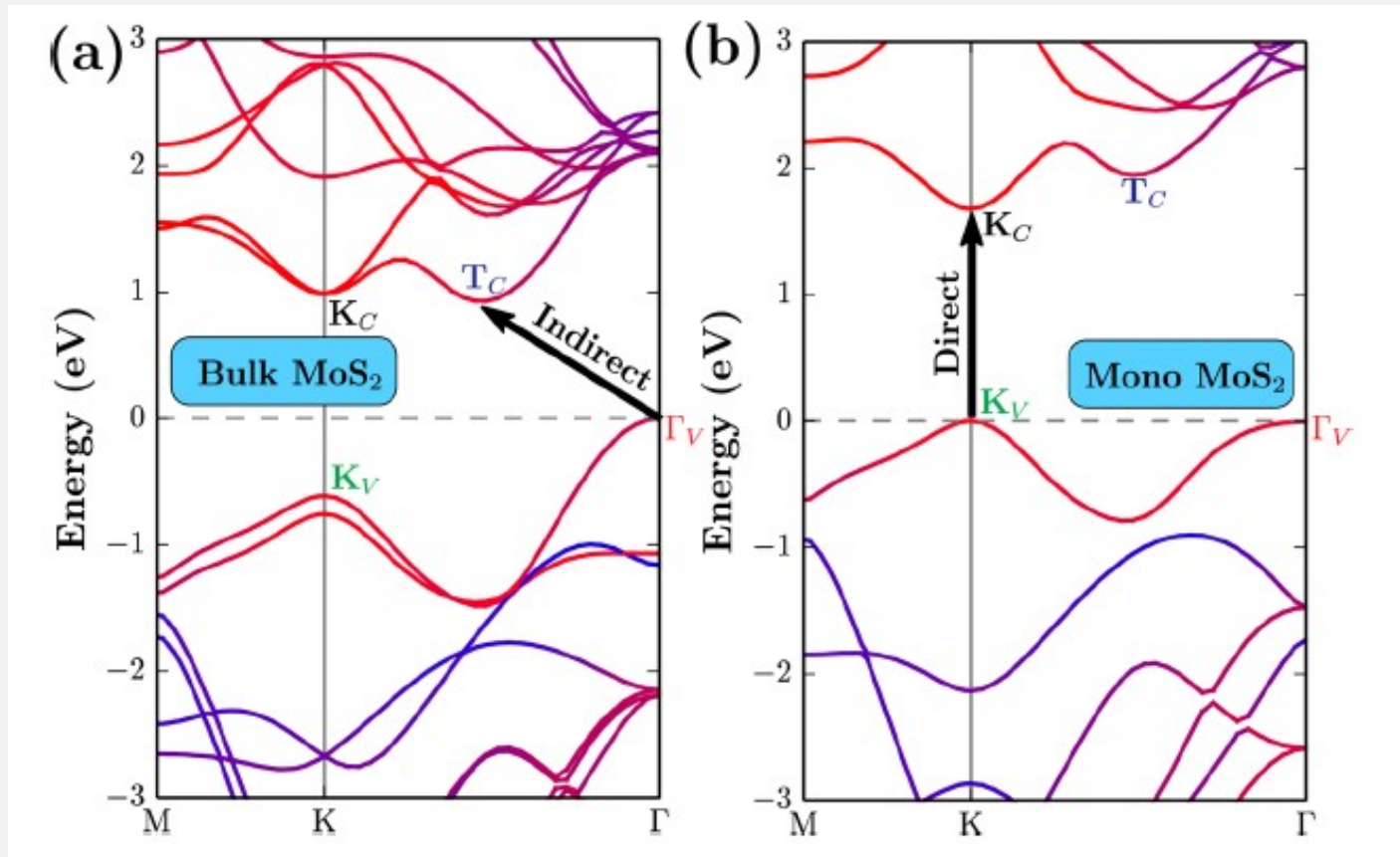


angular resolved photoemission: graphene

how to build-up a 1D electronic band



transition metal dichalcogenides



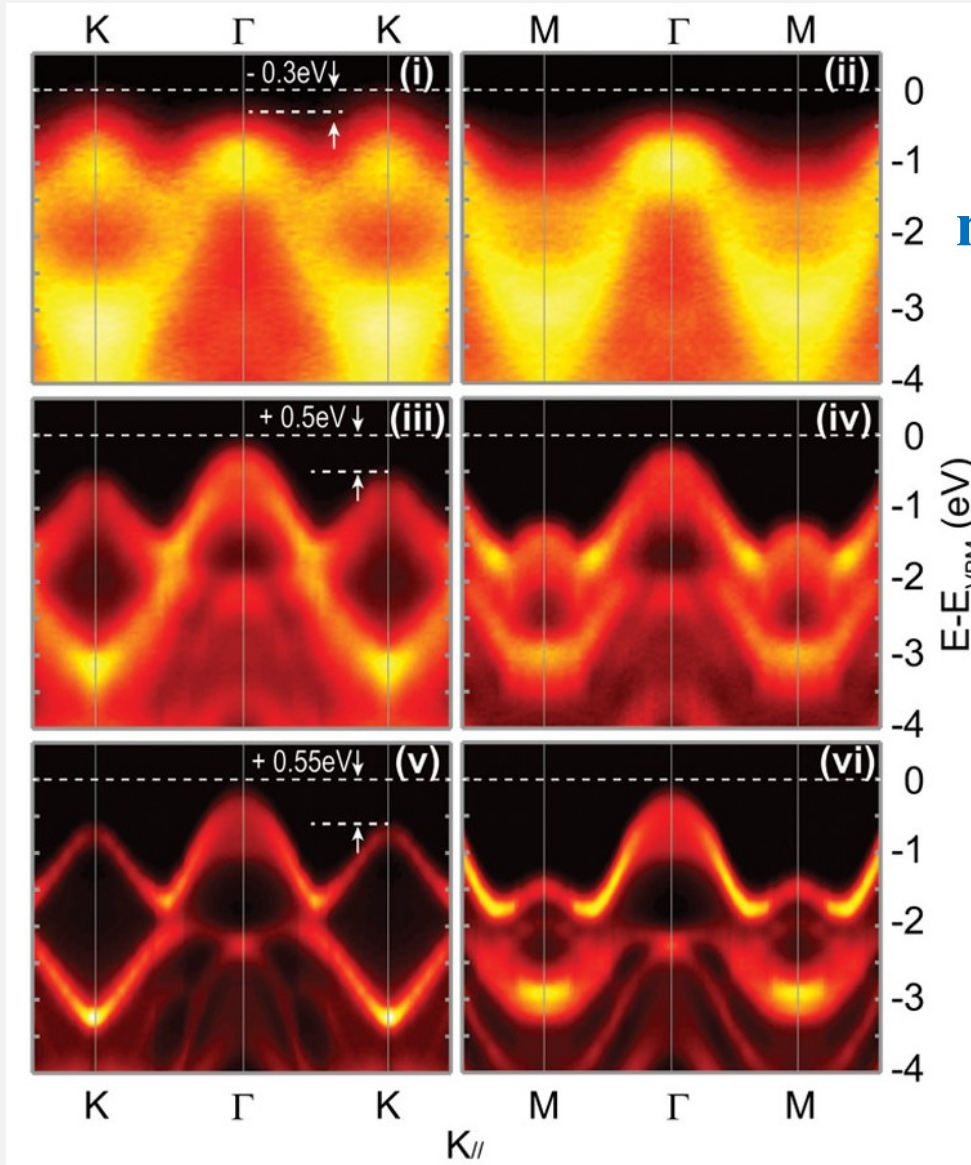
bulk MoS₂ at

Λ_{\min}

mono-layer MoS₂ at

Λ_{\min}

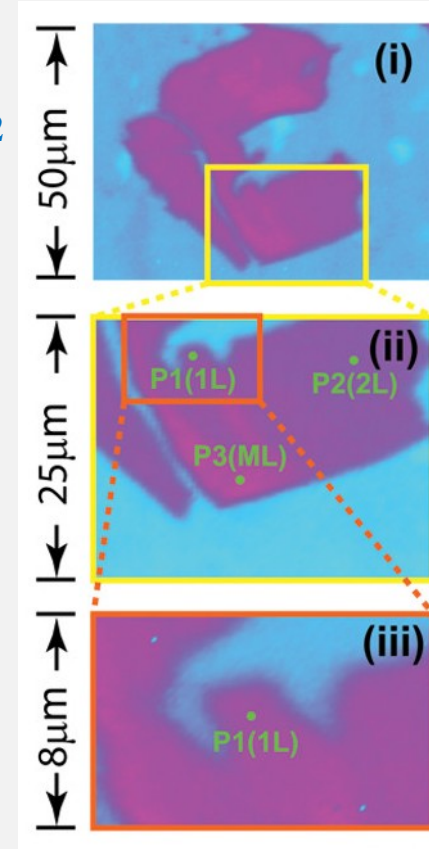
transition metal dichalcogenides



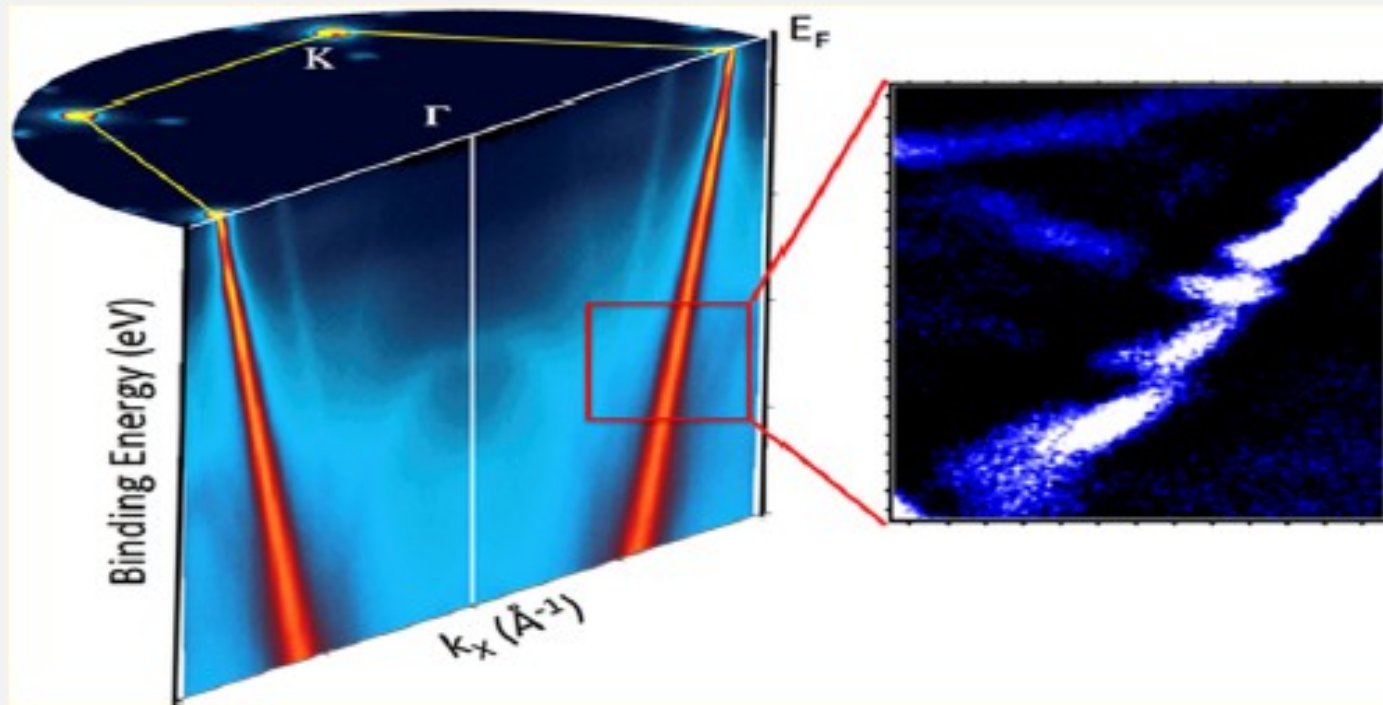
mono-layer MoS₂

bi-layer MoS₂

tri-layer MoS₂



3D Fermi surface

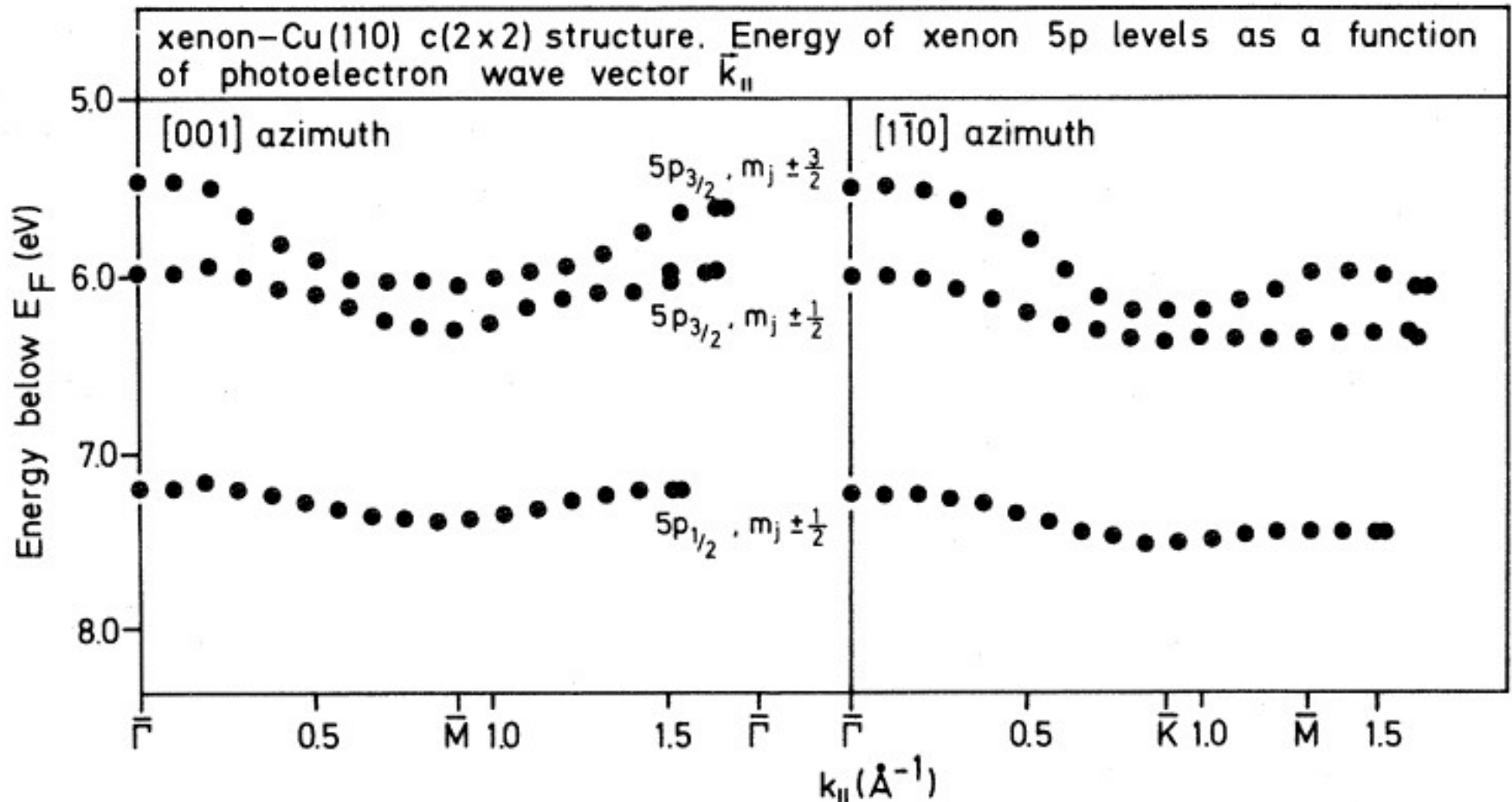


mono-layer MoS₂ / graphene

Λ_{\min}

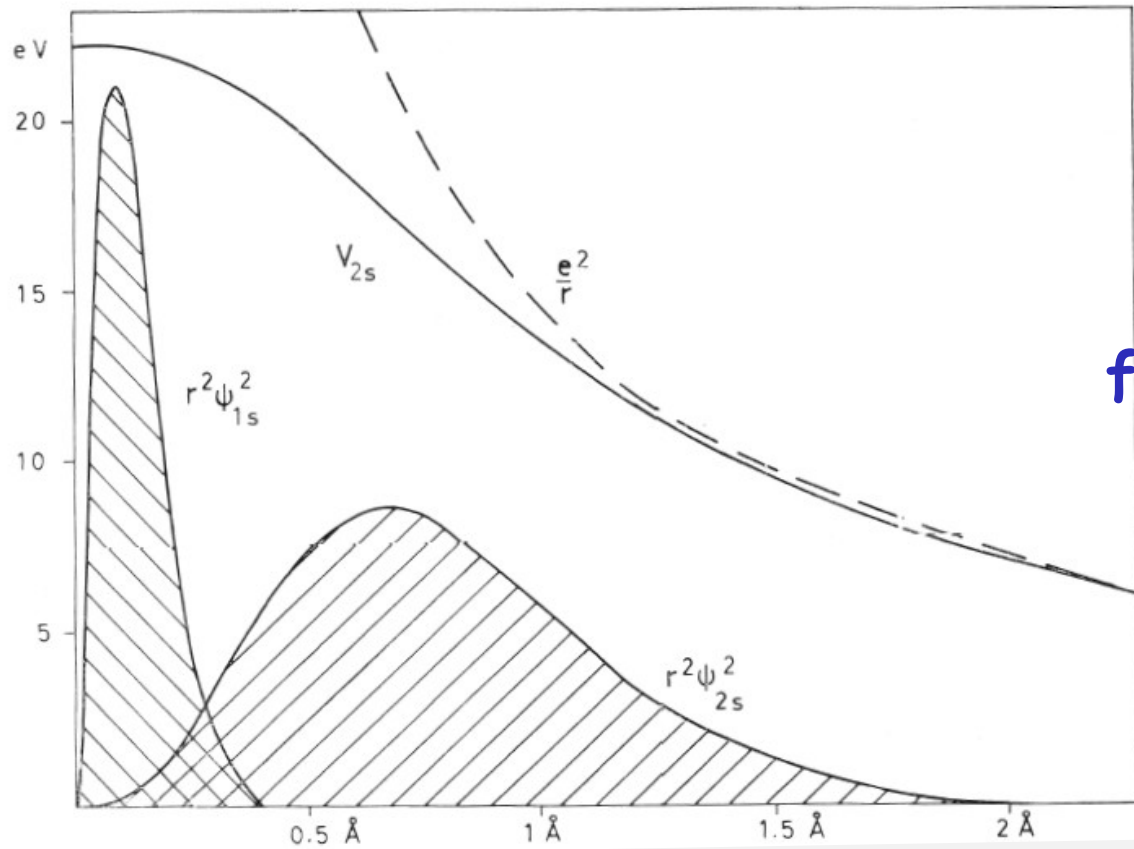
do core-levels present energy dispersion?

the (2x2)-structure of physisorbed Xe on Cu(110)



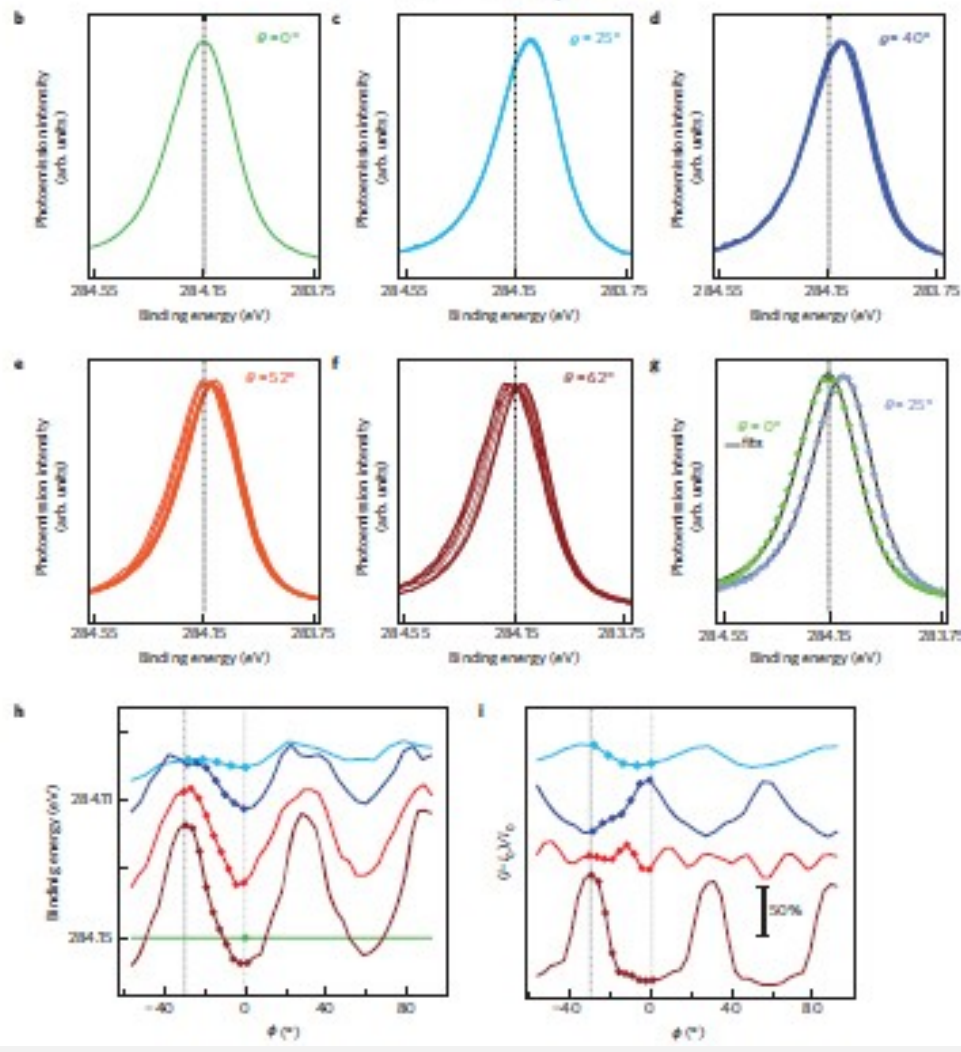
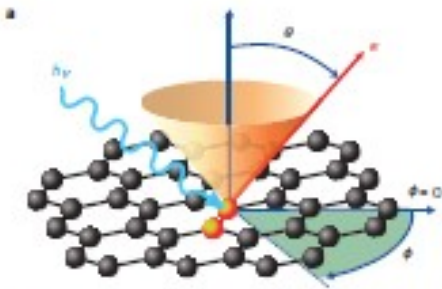
Experimental band structure of the 5p levels of Xe physisorbed in an ordered c(2x2) structure onto the Cu(110) surface. ARPES bands

Photoemission Spectroscopy



spatial extension of
external wave-
functions down to the
core-levels

example: calculated electron densities for C



do core-levels present energy dispersion? *

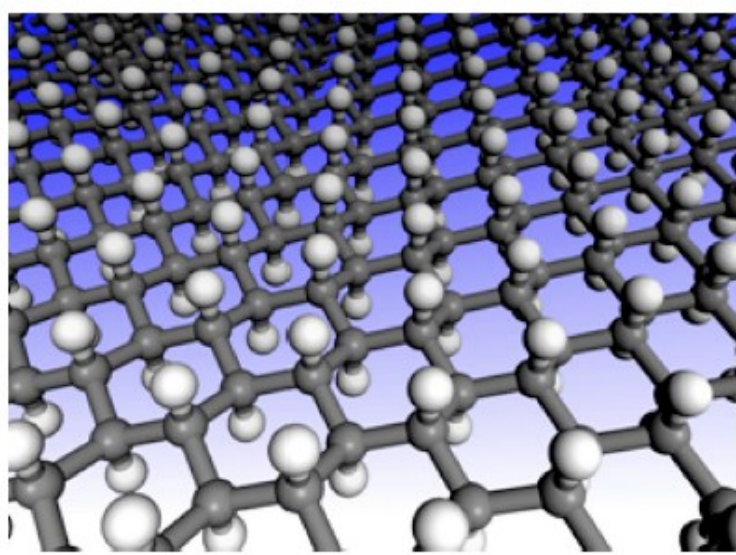
graphene

* see high-resolution core-level photoemission spectroscopy in A. Baraldi's lectures, this school

from graphene to graphane, theory

atomic H as a tool to ‘pinch’ the sp² bonds towards an sp³ configuration while maintaining the planar nature of graphene

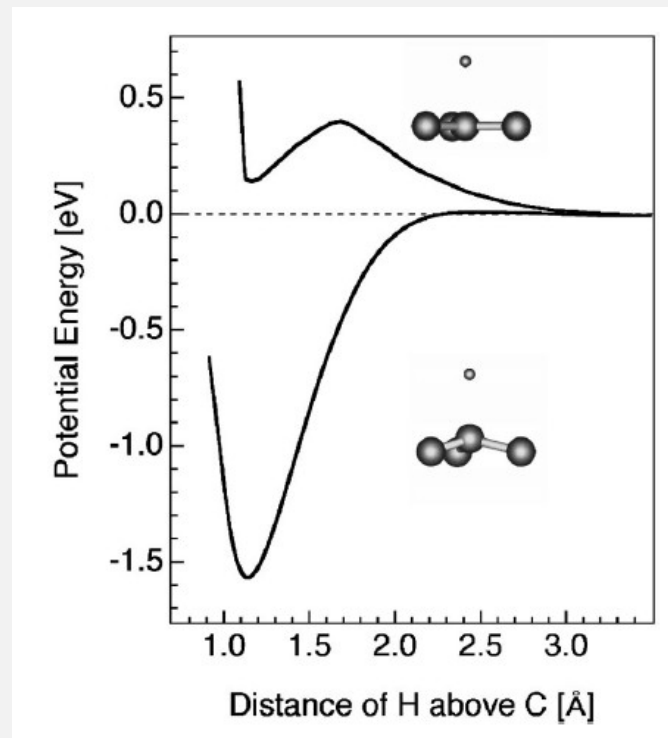
“chair” conformation



Sofu et alii, Phys. Rev. B **75**, 153401 (2007)

covalent bonding, small charge transfer
(~0.003 e)*

Ryu et alii, Nano Lett. **8**, 4597 (2008)

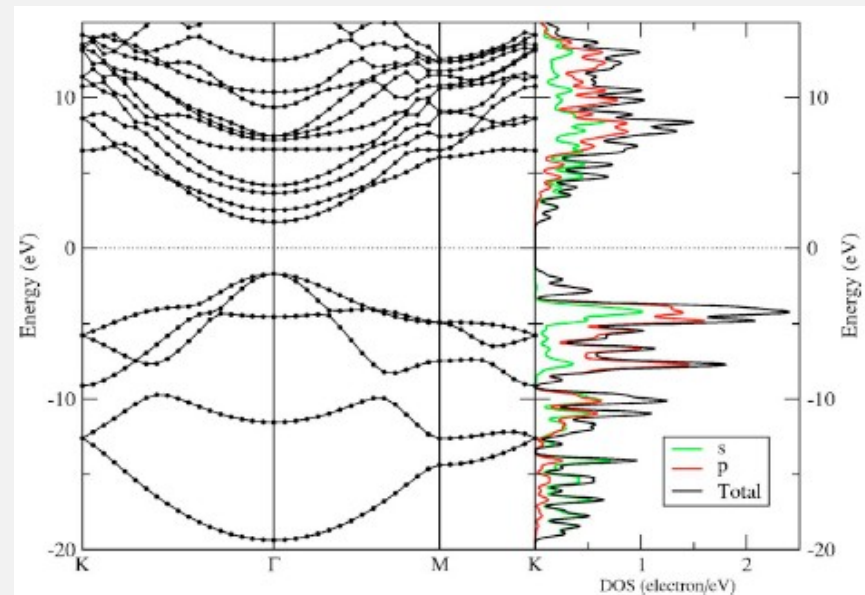
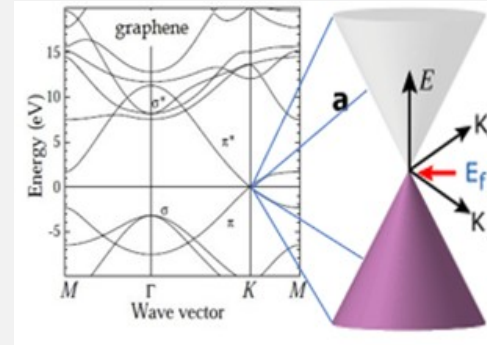
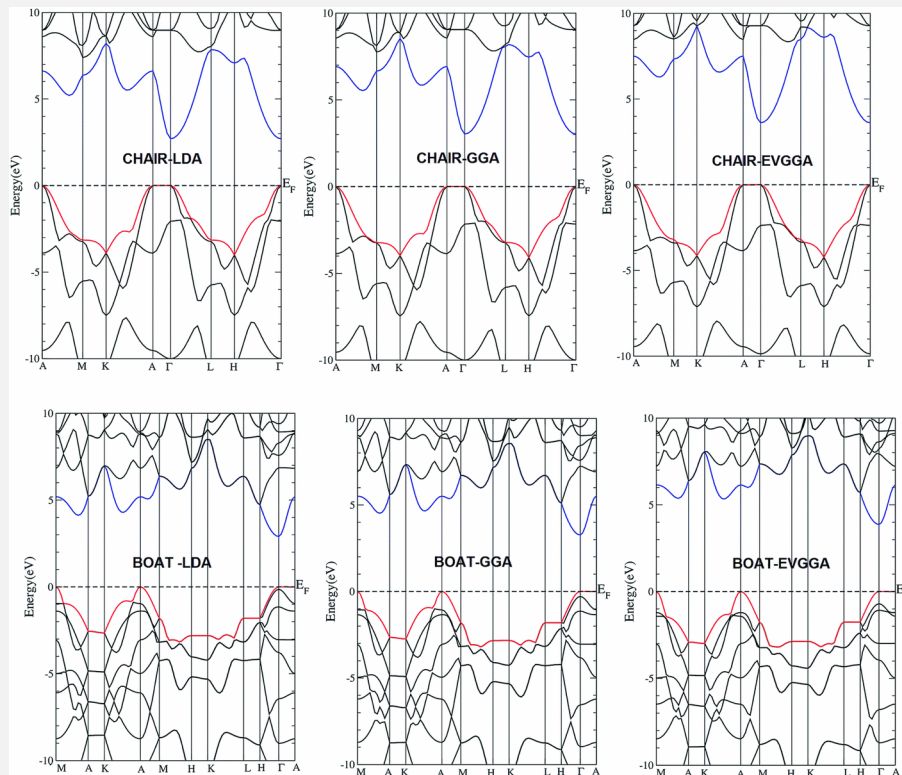


H-to-C potential curve -> favoured sp³ configuration

Ruffieux et alii, Phys. Rev. B **66**, 245416 (2002)

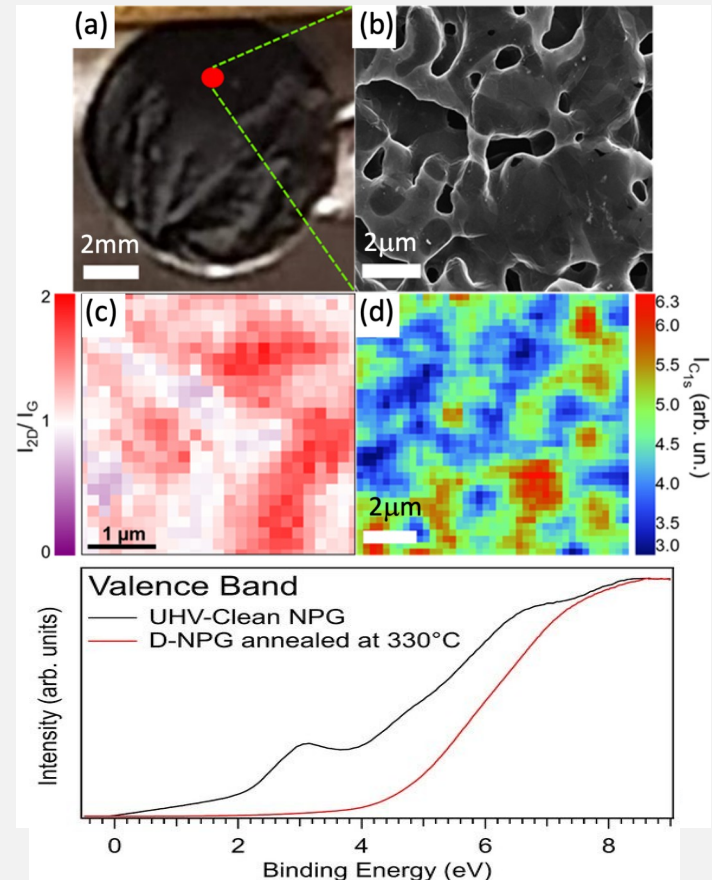
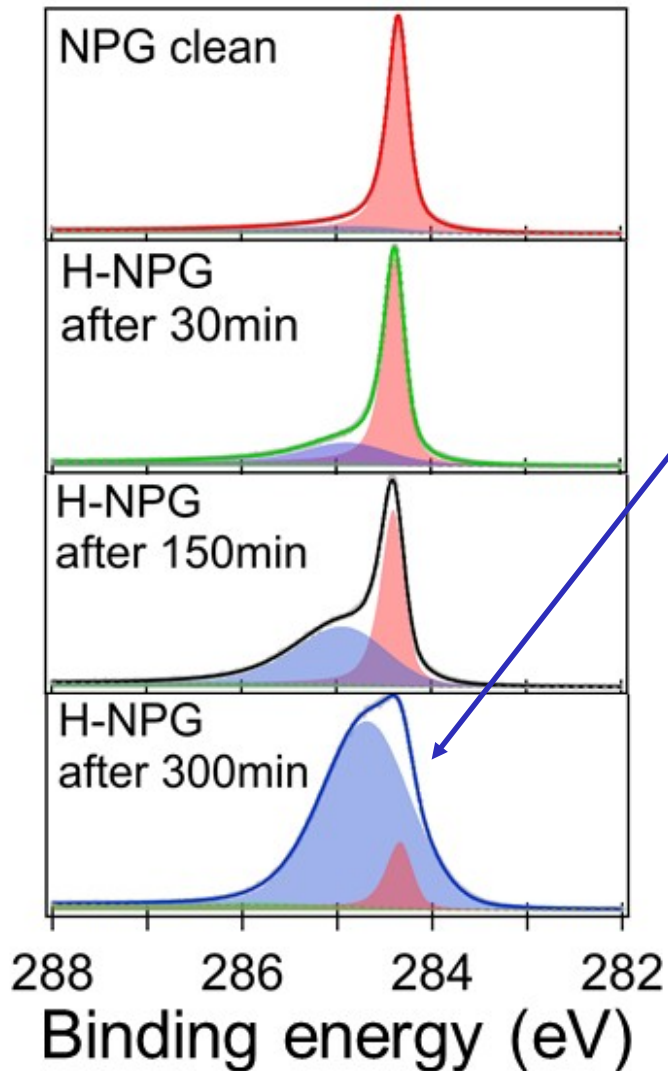
from graphene to graphane, theory

for 100% hydrogenated graphene a semiconductor with ≥ 3.5 eV (depending on the specific configuration) direct energy-gap at Γ is predicted !



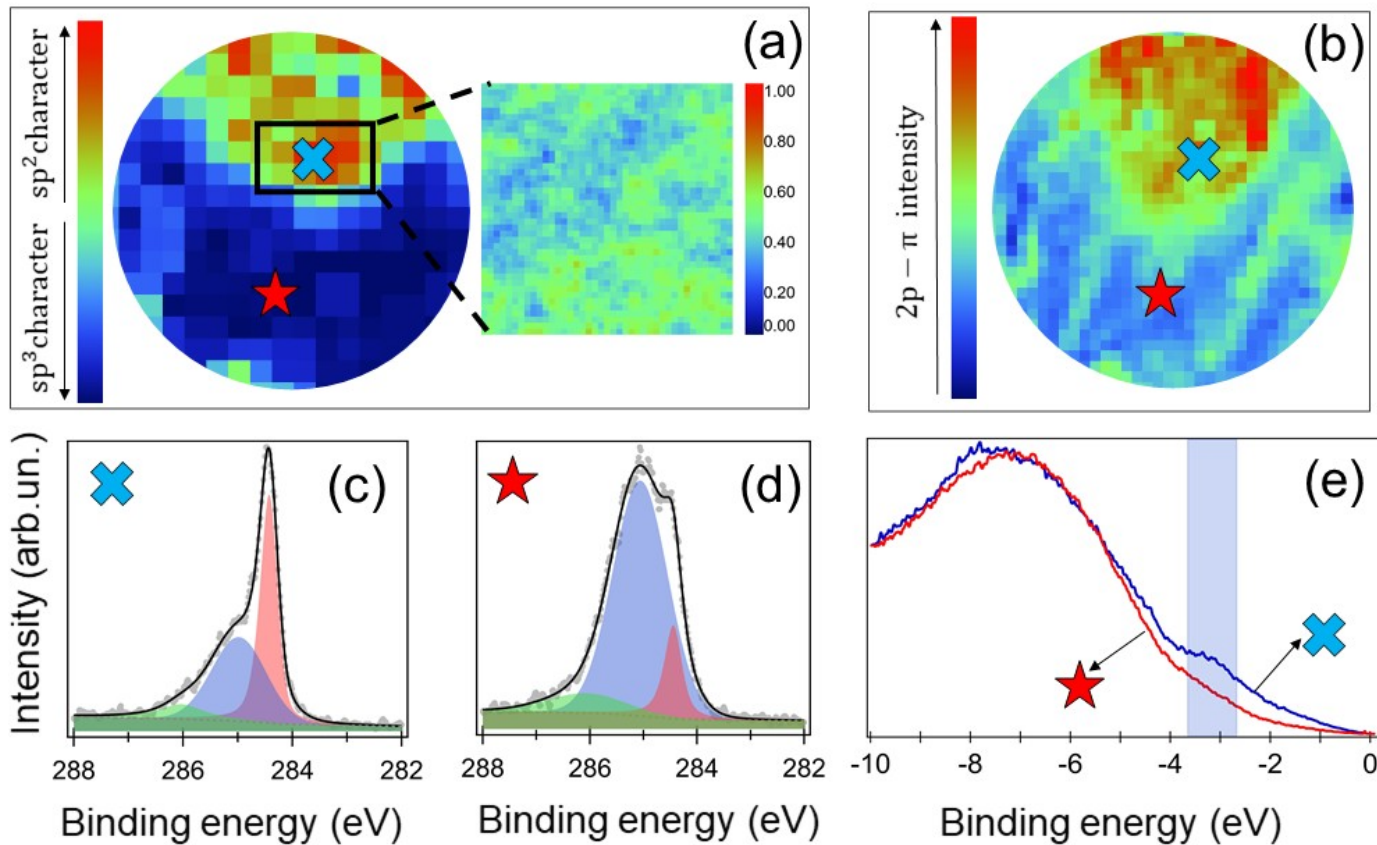
H-NPG photoemission spectromicroscopy

reached ~90%
H-upload!



H-NPG with spatial resolution

H-C spatial distribution: highest sp^3 signal \rightarrow valence band energy gap opening



1-year fellowship (assegno di ricerca) available from ~ Dec 2024 on
"spectromicroscopy of functionalized 2D materials" → contact me:
carlo.mariani@uniroma1.it



1-year fellowship (assegno di ricerca) available from ~ Dec 2024 on
"spectromicroscopy of functionalized 2D materials" → contact me:
carlo.mariani@uniroma1.it

grazie per l'attenzione

