1st on-line School on Synchrotron Radiation “Gilberto Vlaic”:
Fundamentals, Methods and Application

Introduction to photoelectron spectroscopy in atoms, molecules and solids

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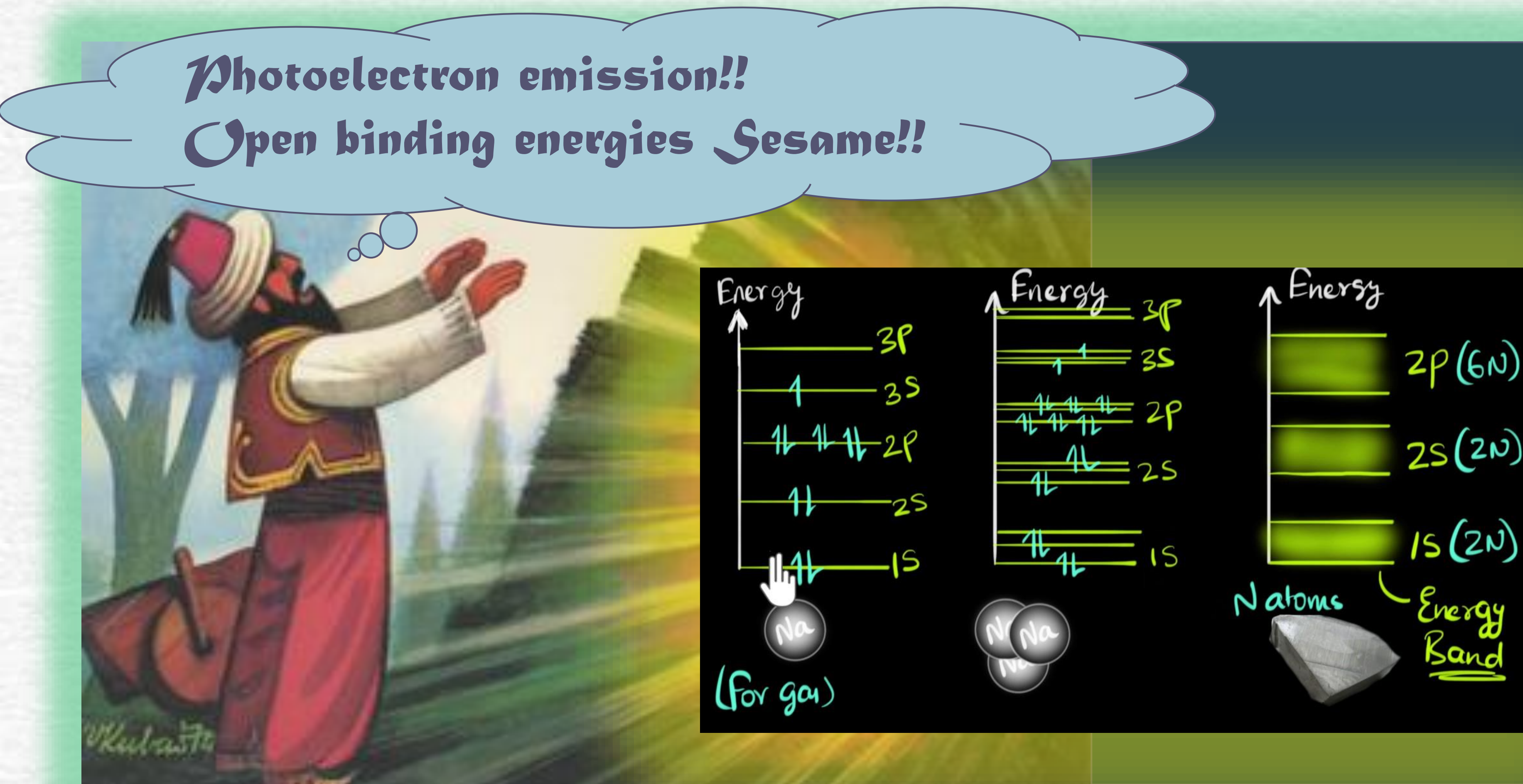
SOCIETA' ITALIANA DI LUCE DI SINCROTRONE

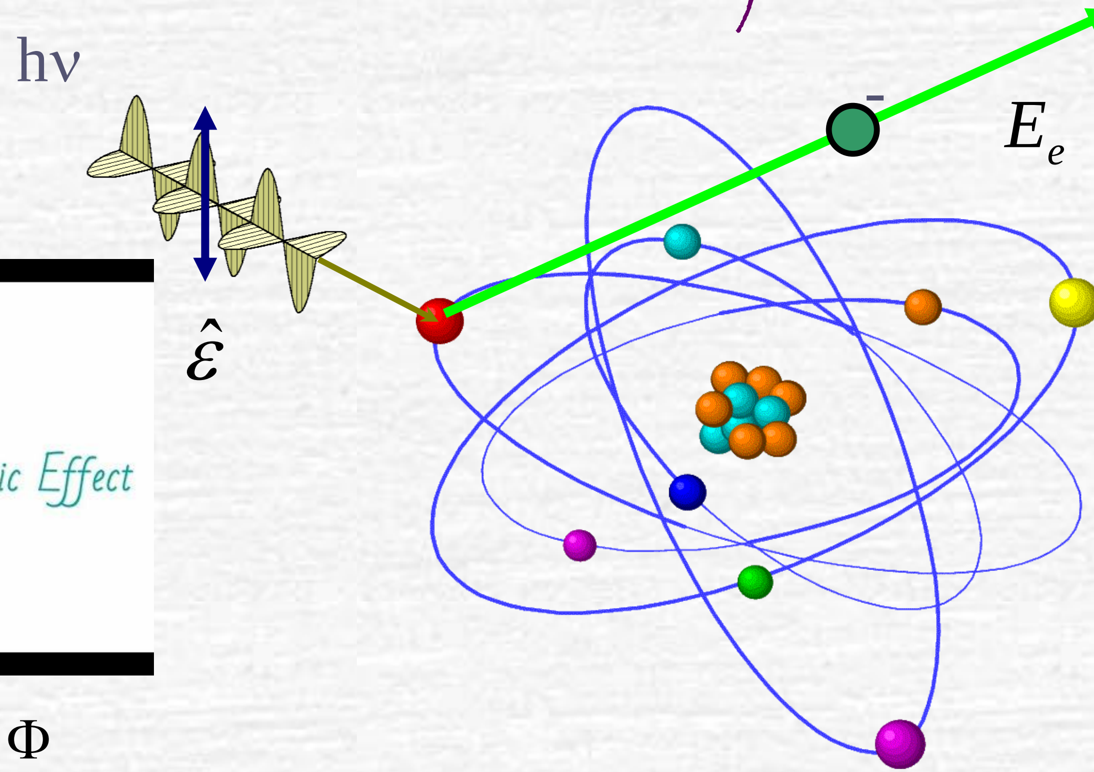
Elettra Sincrotrone Trieste

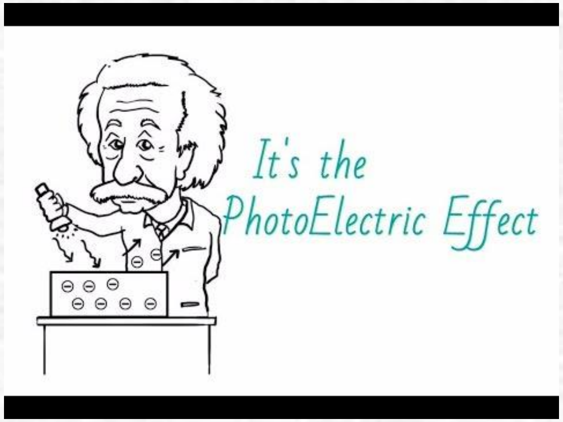
The spectroscopists' dream



The photoelectric effect

Basic Concept



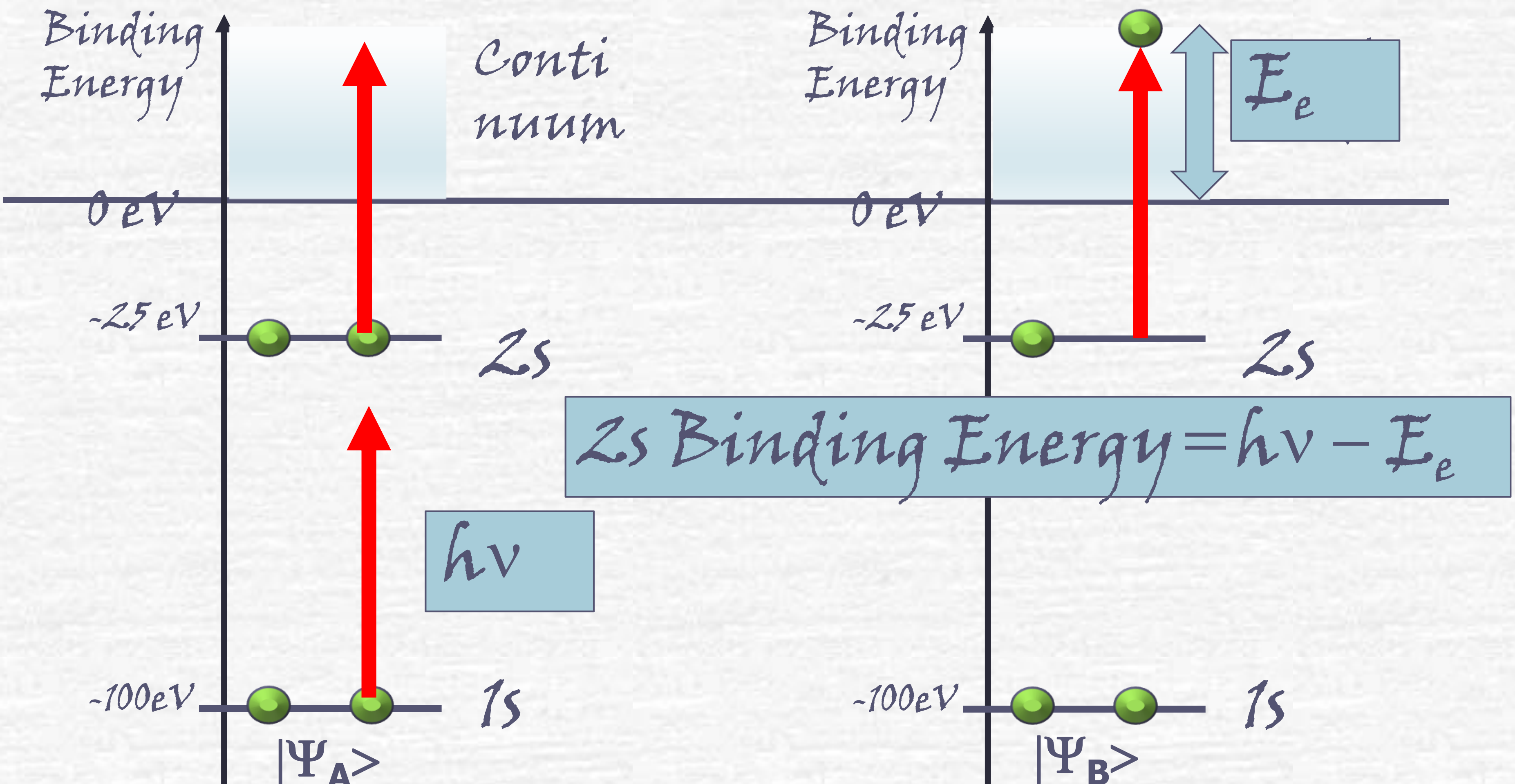



A. Einstein
Nobel prize 1921

$$E_e^{MAX} = h\nu - \Phi$$

$$E_e = h\nu - \Phi - \Delta energy$$

Basic Concept Energy Distribution Curve EDC

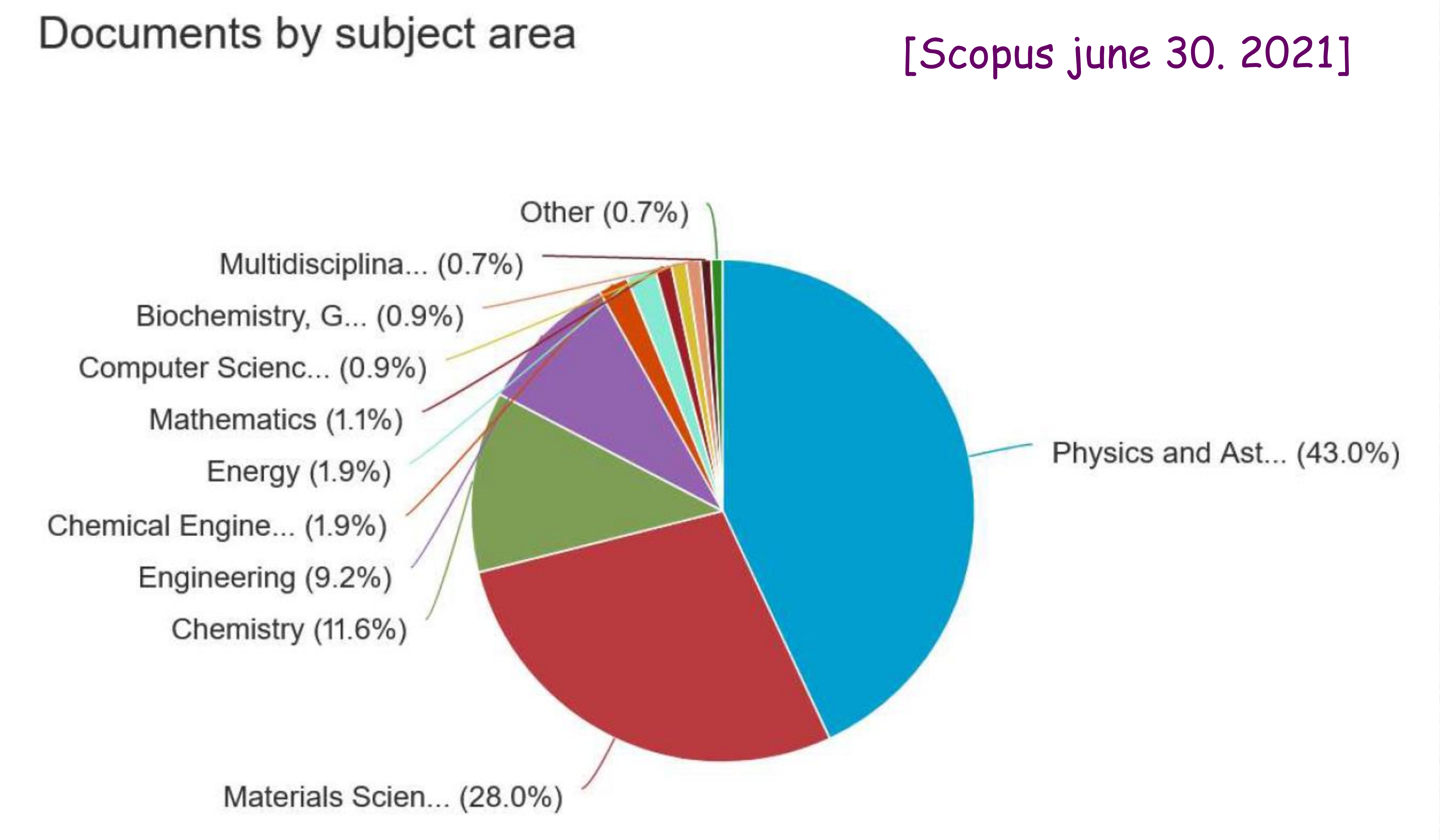


Have forgotten Relaxation and Correlation!

Photoelectron in abstract 37,398 from 1951 to 2020 [Scopus june 30. 2021]

The ubiquitous photoelectron spectroscopy

[Scopus june 30. 2021]



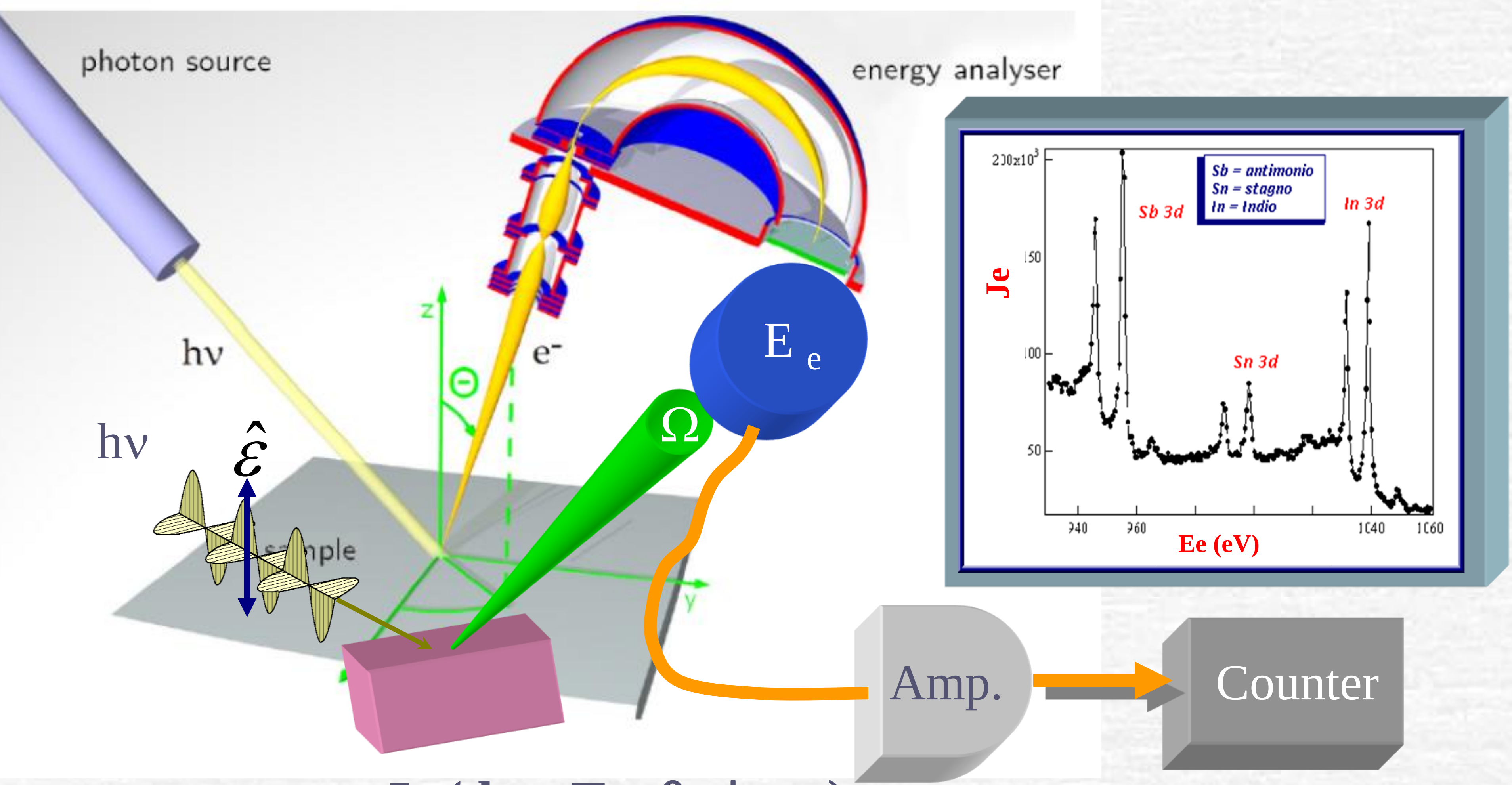
Outline

- Photoelectron energy and bound state energy
- Satellites, multiplet splitting: many-body
- Chemical shift
- Molecular photoelectron spectra
- Photoelectron angular distributions

- Photoelectron emission in solids
- PES EDC and density of states
- Angular resolved PES: electronic band structure
- Spin and time resolved PES: charge dynamics
- High energy photoemission HAXPES

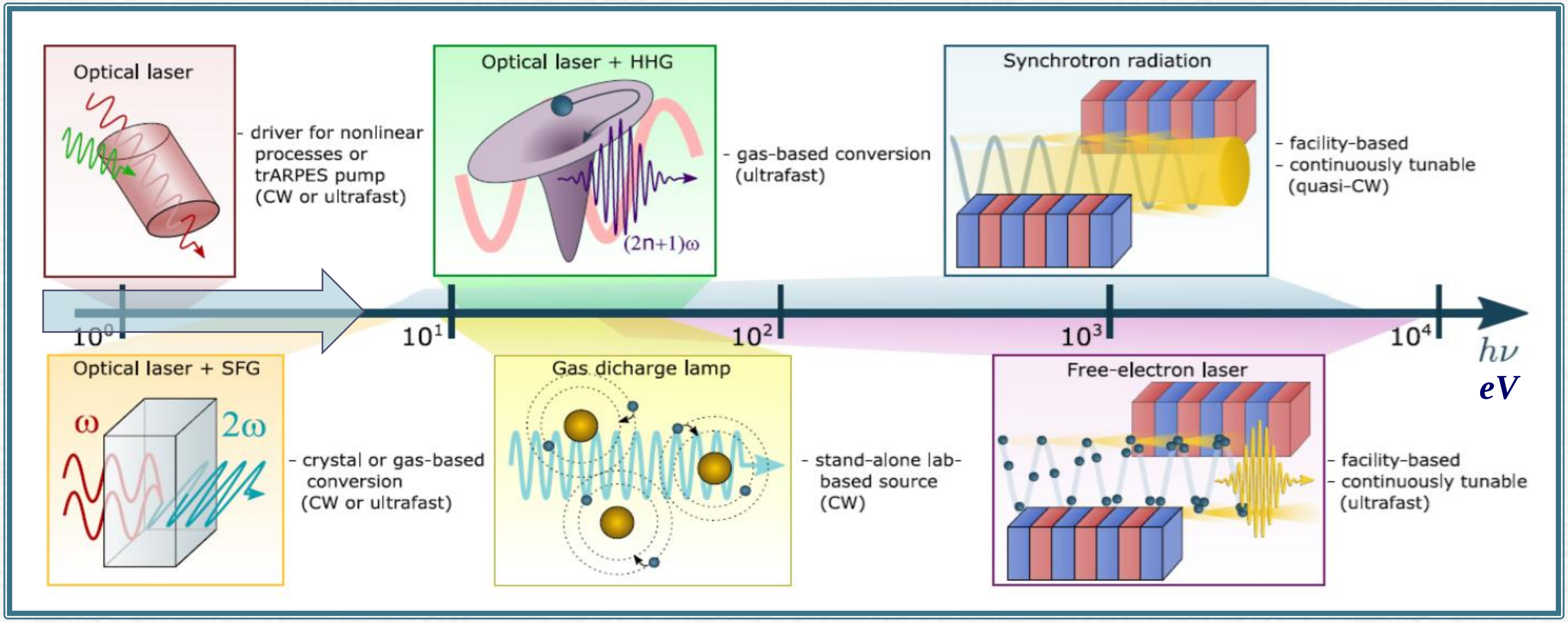
C. Mariani and G. Stefani Chapter 9 in «Synchrotron Radiation Basics, Methods and Applications»

Photoelectron Spectroscopy Schematics:



$$J_e\,(\,h\nu,\,E_e,\,\theta,\,\phi,\,\sigma\,)$$

Available photon sources:

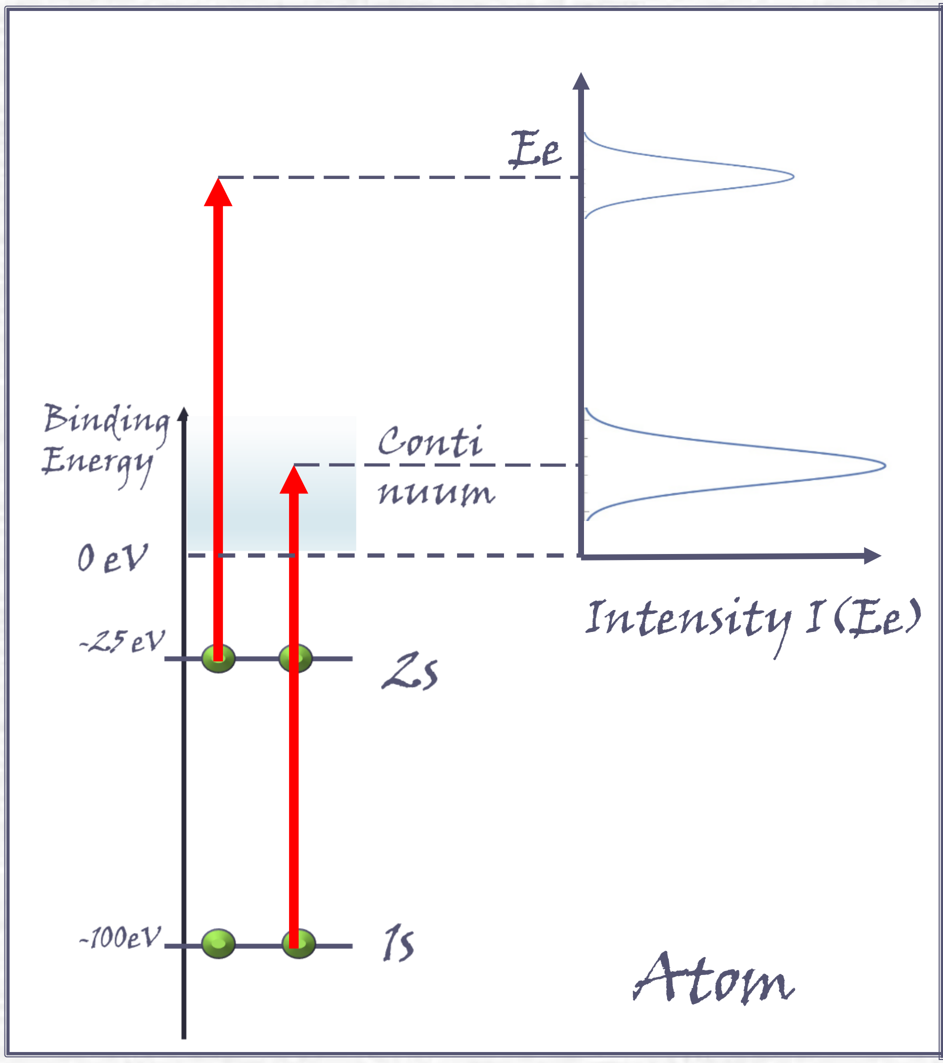


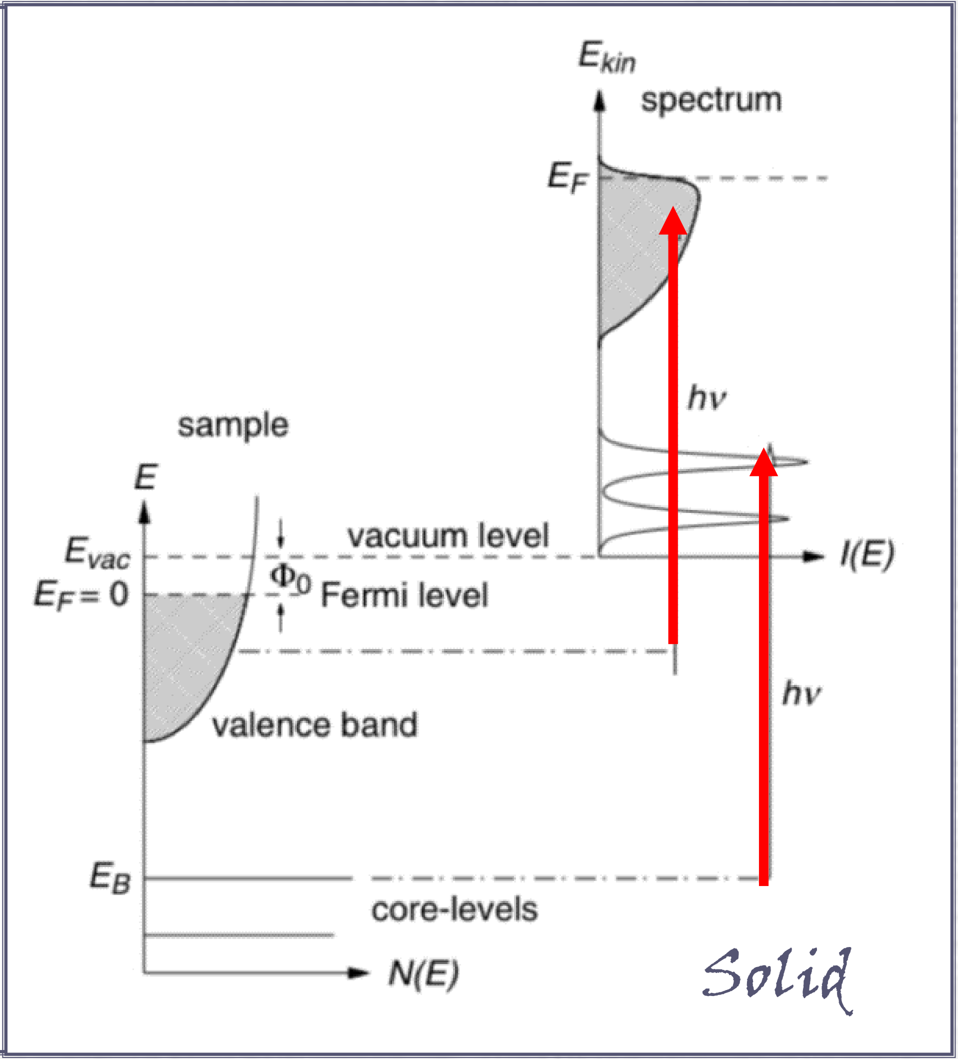
He Iα=21.23eV **He IIα=40.82eV**

Mg Kα1,2 = 1253,6 eV **Al Kα1,2=1486,6eV**

Synchrotron Radiation

Energy Distribution Curve EDC



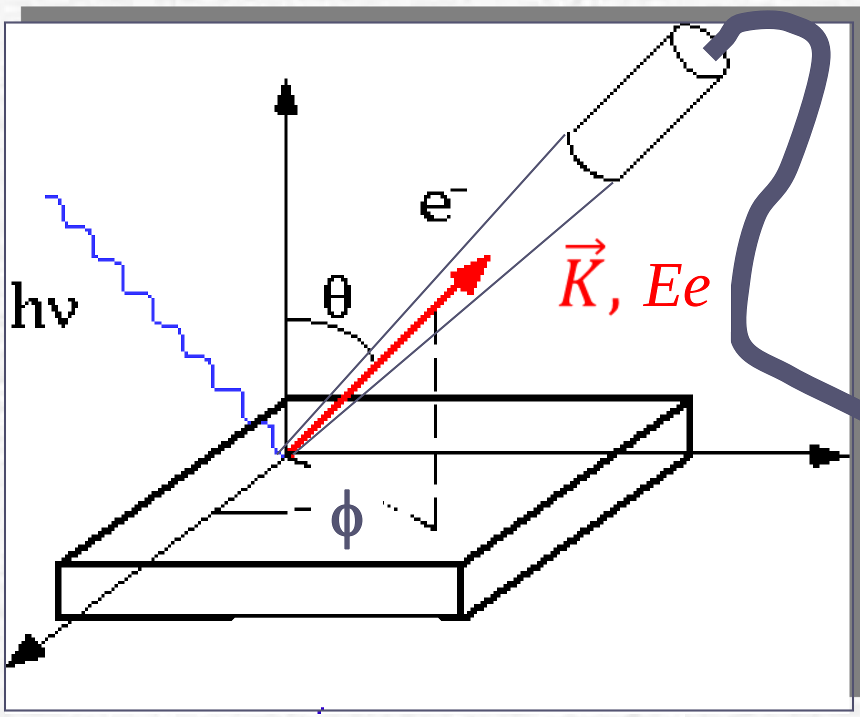


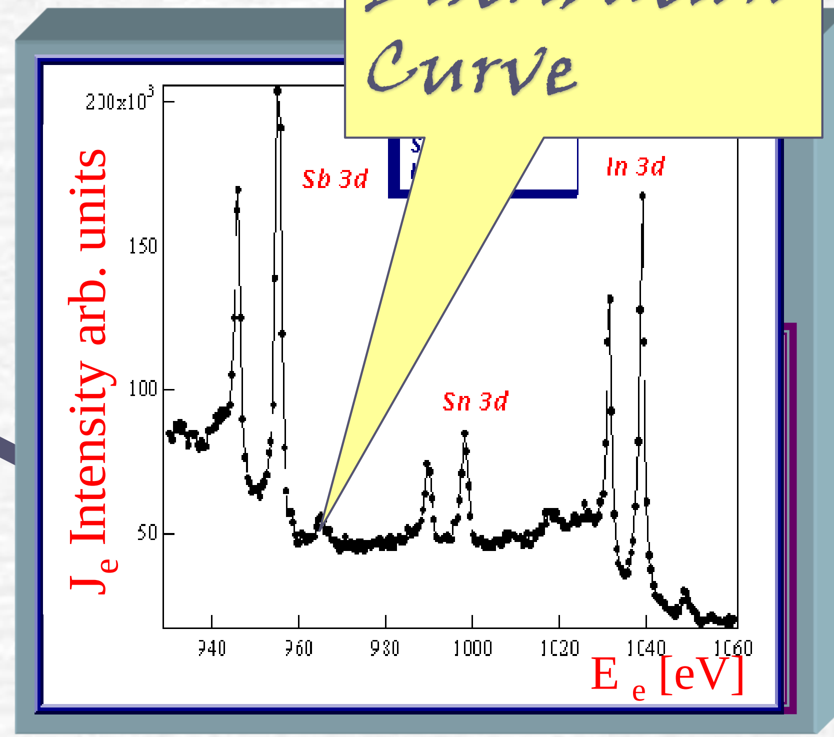
Energy conservation: Photoelectron energy & Binding energy

$$E_e = \frac{K^2}{2m}$$

$$E_e = h\nu - \Phi - |E_b|$$

EDC
Energy
Distribution
Curve





Photon absorption transition probability

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

From Boscherini's lectures at this school

|Ψ$_A$> Initial state A = Neutral ground (excited) st

|Ψ$_B$> Final state B = Residual ion + **free ele**

$$\frac{d\sigma}{dh\nu} = \int_E \int_\Omega \frac{d\sigma}{d\Omega dE} d\Omega dE$$

Finite experiment acceptances

X-section vs. Photoelectric current

$$J_e(h\nu,\vartheta,\phi) = J_{h\nu}(\rho l)\int_{\Delta E}\int_{\Delta\Omega}\frac{d\sigma}{d\Omega dE}F_{an}(E,\Omega)\eta_{\det}(E)d\Omega dE$$

Photoemission peak lineshape

1. *Photon monochromaticity* — *Gaussian*
2. *Electron analyzer resolution* — *Gaussian*
3. *Final state lifetime (uncertainty principle)* — *Lorentian*

Lineshape =Convolution (1,2,3)

Energy balance for 2e atom: He 1s^2

$$E_B = E_A + h\nu$$

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

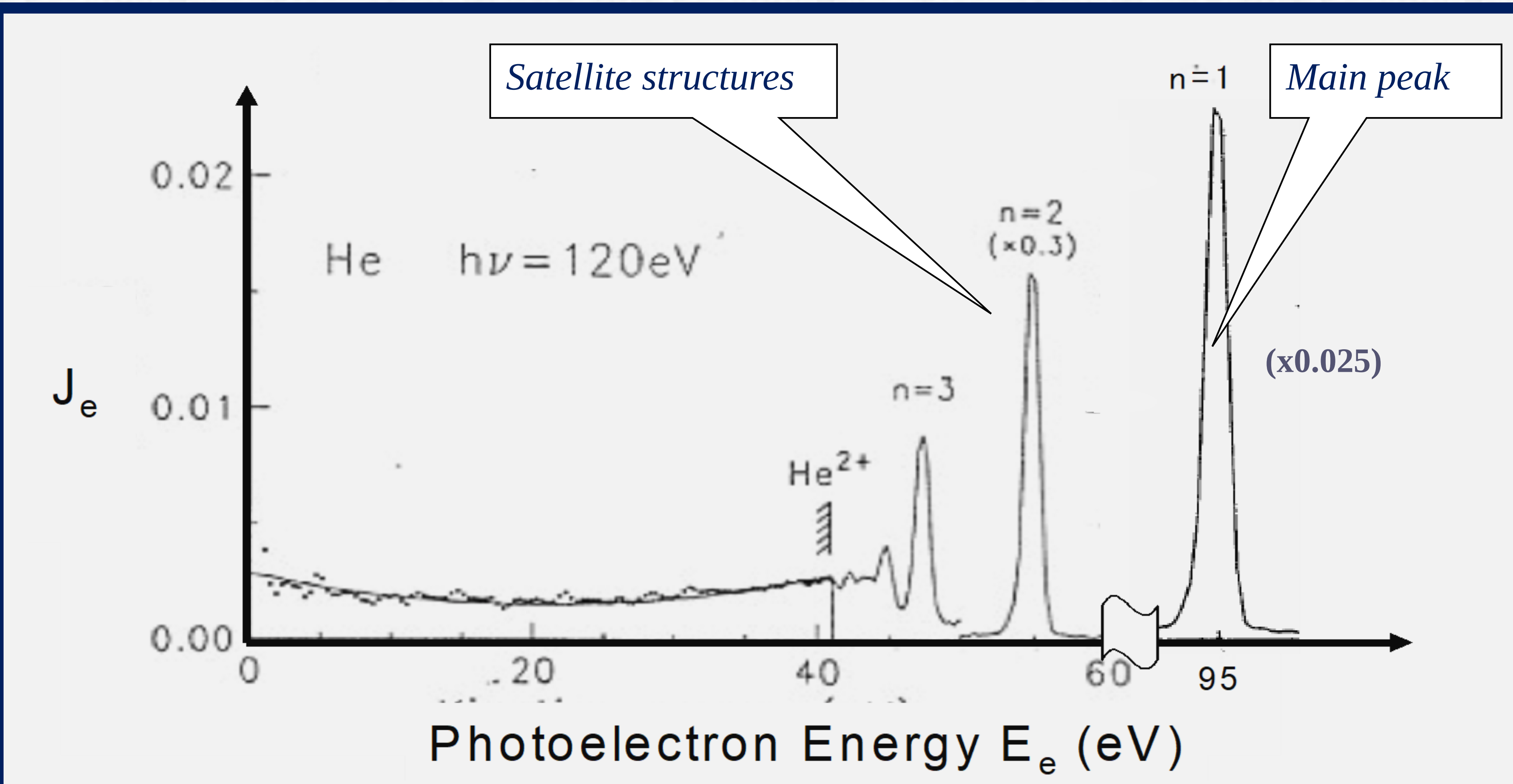
$$\Psi_B = \hat{A}\phi_1\varepsilon_2$$

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

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

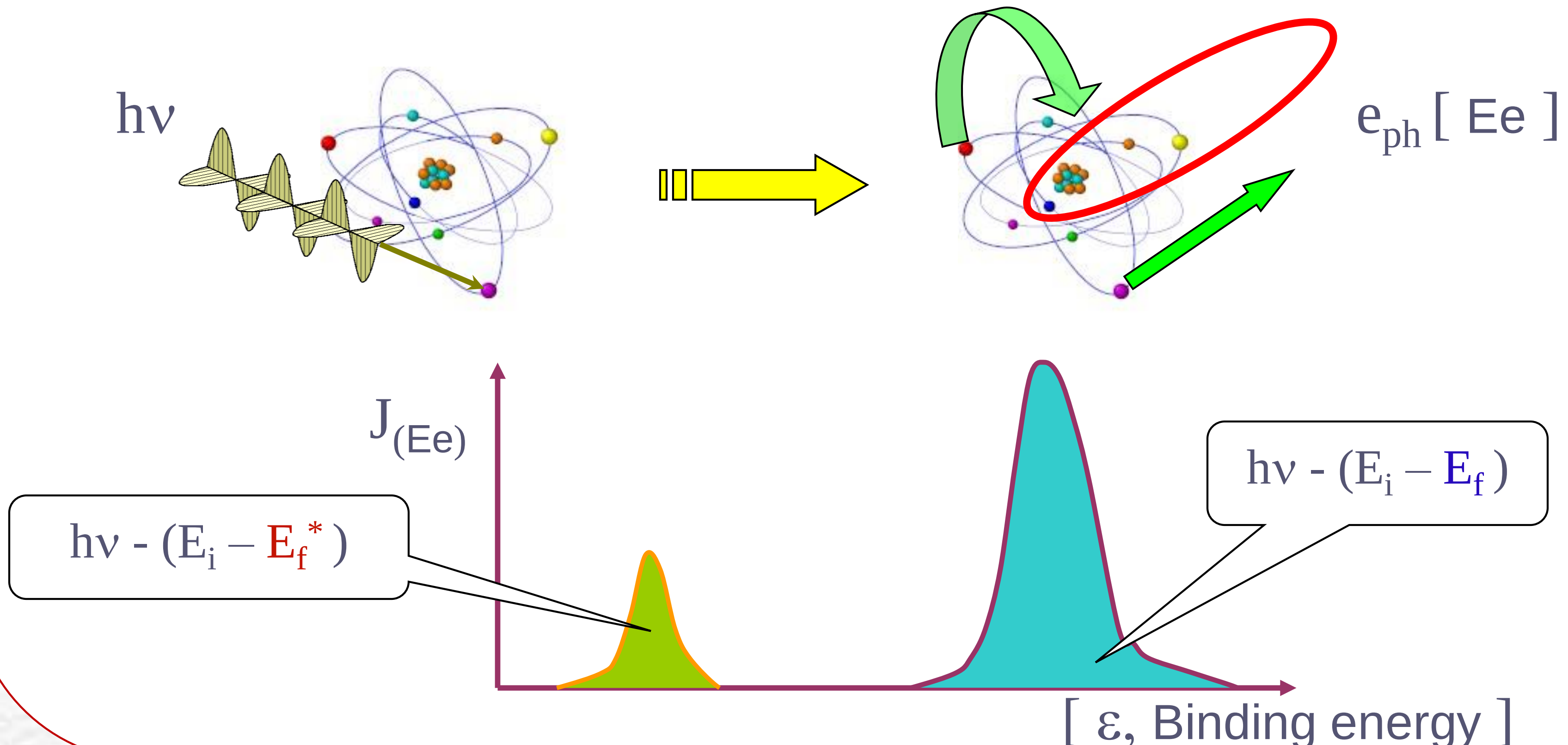
One single photoemission peak is expected
Energy and momentum are conserved

Complexity of the photoelectron spectrum: He 1s²



Primary photoionization processes

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



A many electron atom

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

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

$$\left|\Psi_A^{(N)}\right\rangle = \widehat{A}(\phi_j(\vec{r}_i,\sigma_i);\Psi_{R,A}^{(N-1)})$$

Single particle orbital

$$H_0^{'}\left|\widehat{A}(\varepsilon_j(\vec{r}_i,\sigma_i);\Psi_{R,B}^{(N-1)}\right\rangle = E_B^{(N)}\left|\widehat{A}(\varepsilon_j(\vec{r}_i,\sigma_i);\Psi_{R,B}^{(N-1)}\right\rangle$$

Sudden approximation

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

$$A_{A,B}$$

$$\frac{d\sigma}{d\Omega dE_e} \propto \frac{1}{h\nu}\sum_{A,B}\left|\hat{\varepsilon}\bullet\left\langle\varepsilon_l\left|\vec{r}_j\right|\phi_j(\vec{r}_j,\sigma_j)\right\rangle\left\langle\Psi_{R,B}^{(N-1)}\middle|\Psi_{R,A}^{(N-1)}\right\rangle\right|^2\delta(E_e+E_B^{(N-1)}-E_A-h\nu)$$

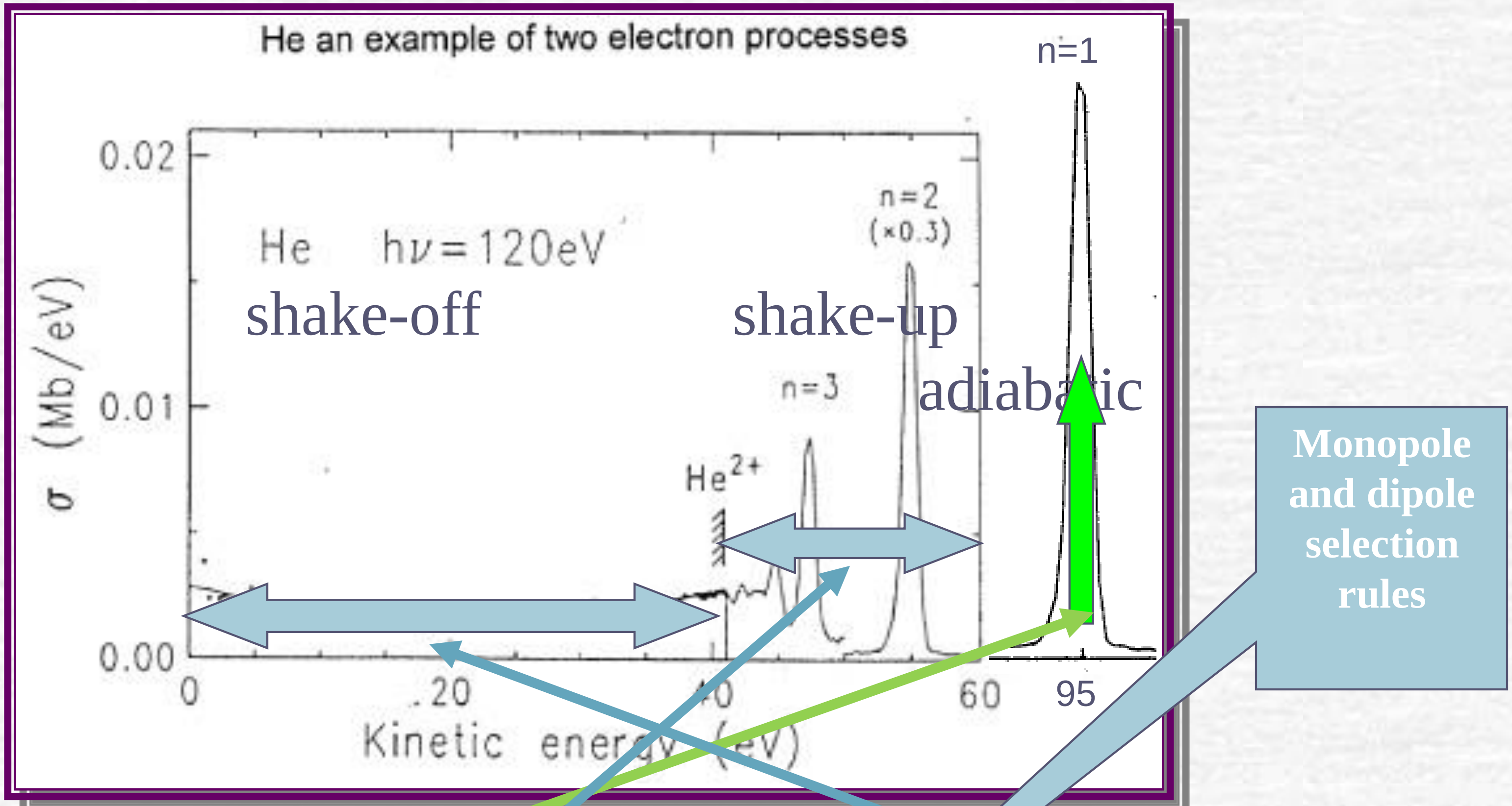
Frozen core approvimation

Neglects relaxation

$$H_0' = H_0$$

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

The full photoemission picture in He (e-e)



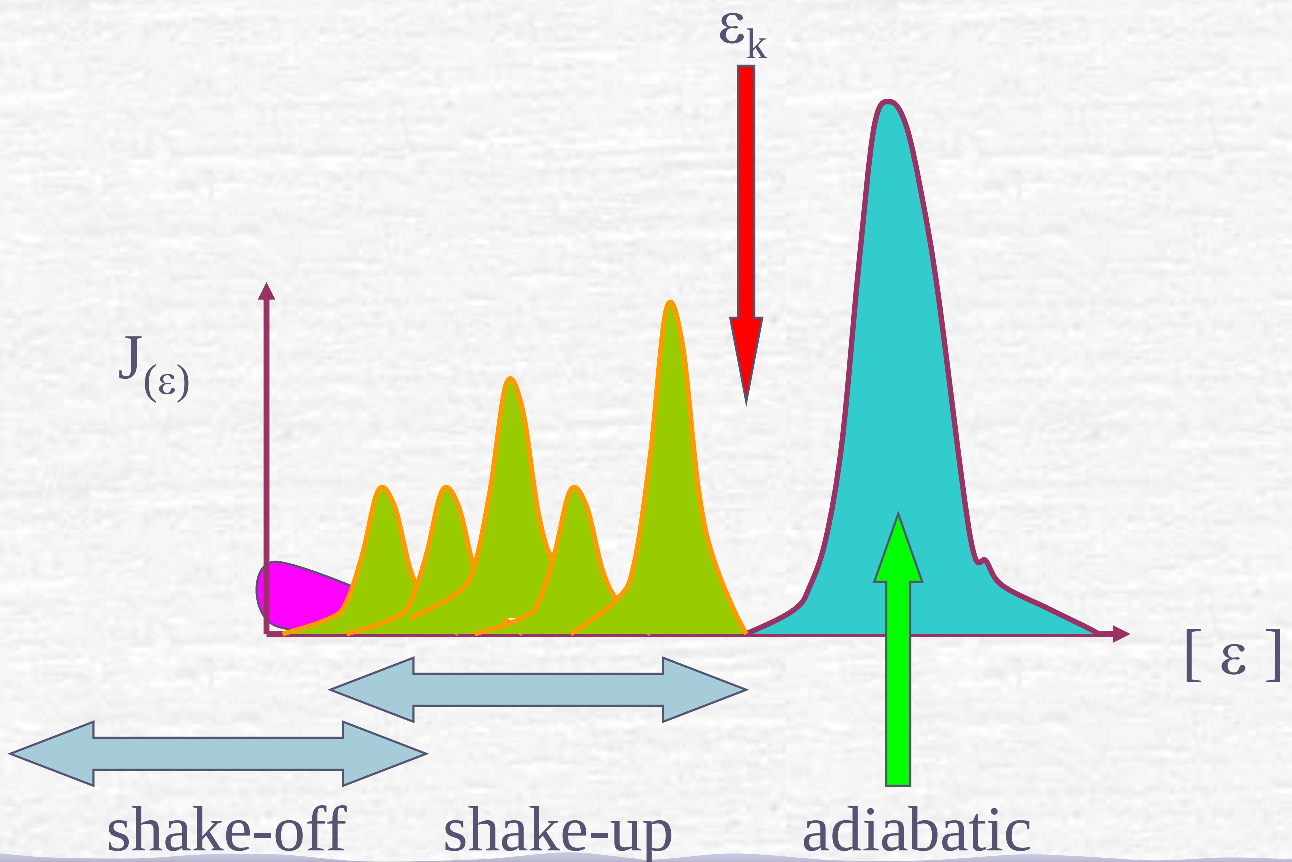
$$h\nu + He(1s^2) \rightarrow He^+(1s^1) + \varepsilon_{\ell=1}$$

$$h\nu + He(1s^2) \rightarrow He^+(2s^1) + \varepsilon_{\ell=1}, He^+(3s^1) + \varepsilon_{\ell=1}, He^+(4s^1) + \varepsilon_{\ell=1}, \ldots\ldots\ldots\ldots He^{++} + \varepsilon_{\ell} + \varepsilon_{\ell'}$$

$$h\nu + He(1s^2) \rightarrow He^+(2p^1) + \varepsilon_{\ell=0}, He^+(3p^1) + \varepsilon_{\ell=0}, He^+(4p^1) + \varepsilon_{\ell=0}, \ldots\ldots\ldots\ldots He^{++} + \varepsilon_{\ell} + \varepsilon_{\ell'}$$

Koopmans energy vs. photoemission peaks

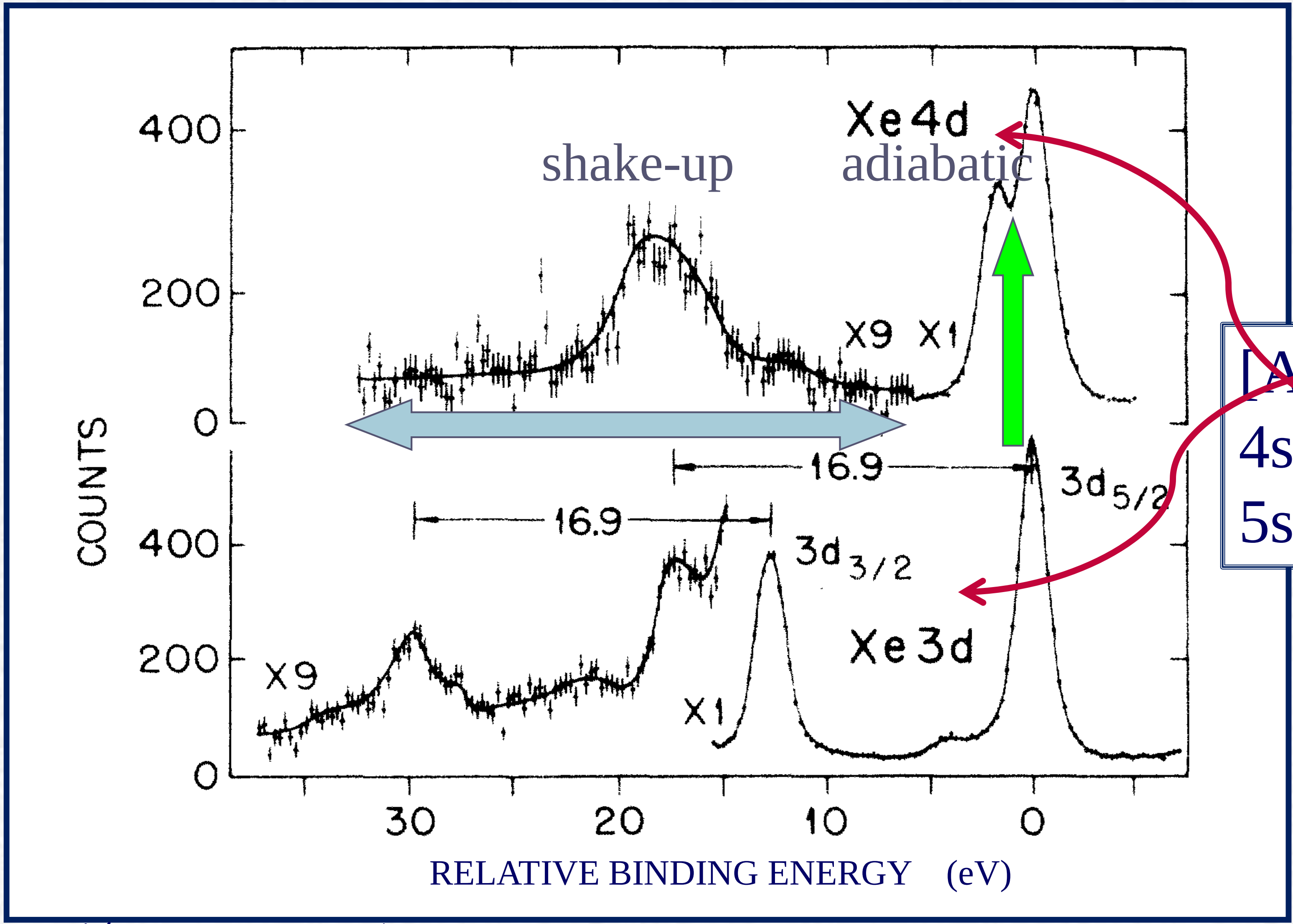
$$\frac{d\sigma}{d\Omega dE_e} \propto \frac{1}{h\nu}\sum_{A,B}\left|\hat{\varepsilon}\bullet\left\langle \varepsilon_l\middle|\vec{r}_j\middle|\phi_j(\vec{r}_j,\sigma_j)\right\rangle\right|^2 A_{A,B}\,\delta(E_e+E_B^{(N-1)}-E_A-h\nu)$$



$$\varepsilon_k = \frac{\sum_i \varepsilon_i I_i}{\sum_i I_i}$$

$$E_{relax} = \varepsilon_{adiab} - \varepsilon_k$$

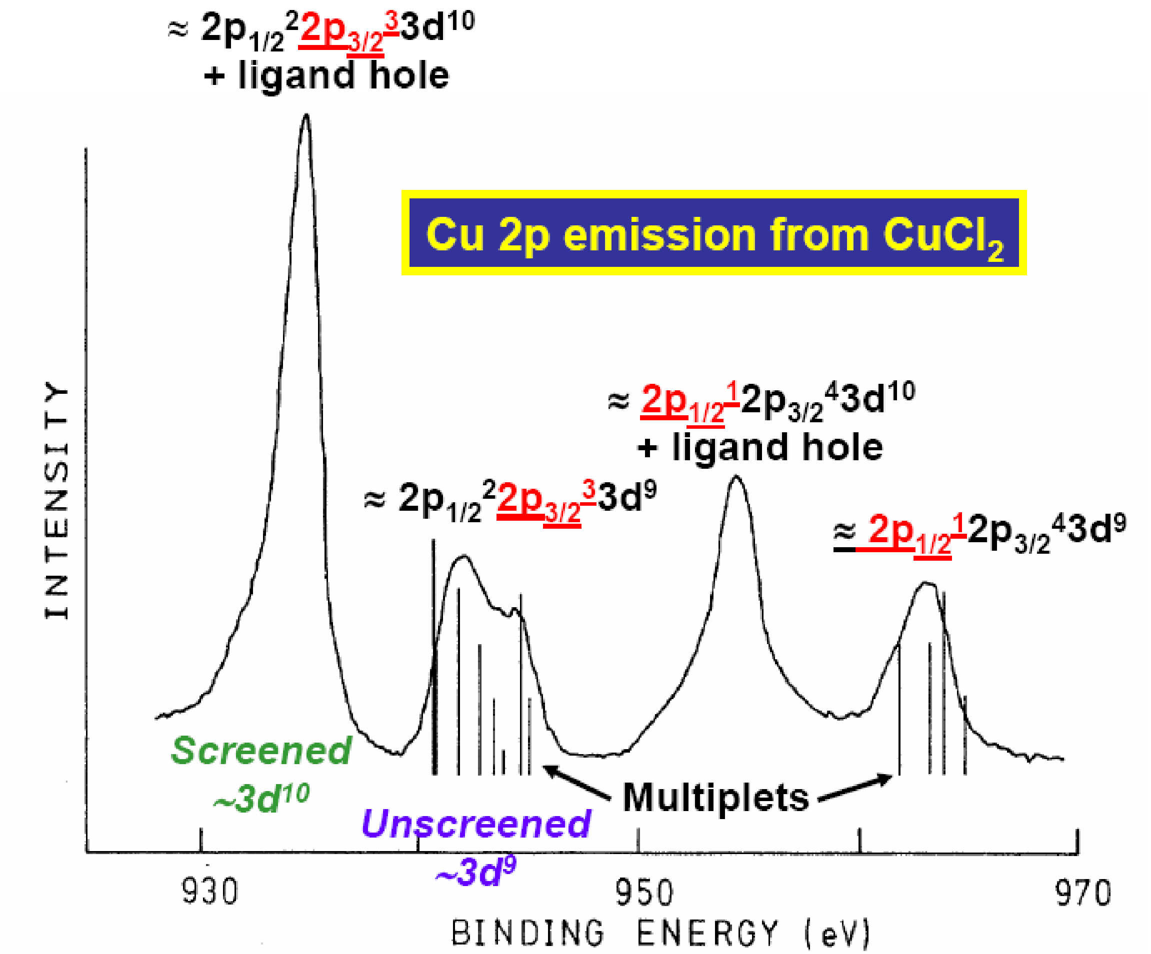
Complexity: is e-e all? Spin-Orbit coupling!!



[Ar] 3d^{10}
4s^2 4p^6 4d^{10}
5s^2 5p^6

PHYSICAL REVIEW A 9 (1974) 1603

$CuCl_2$ multiplet & satellite (l-s) (e-e)

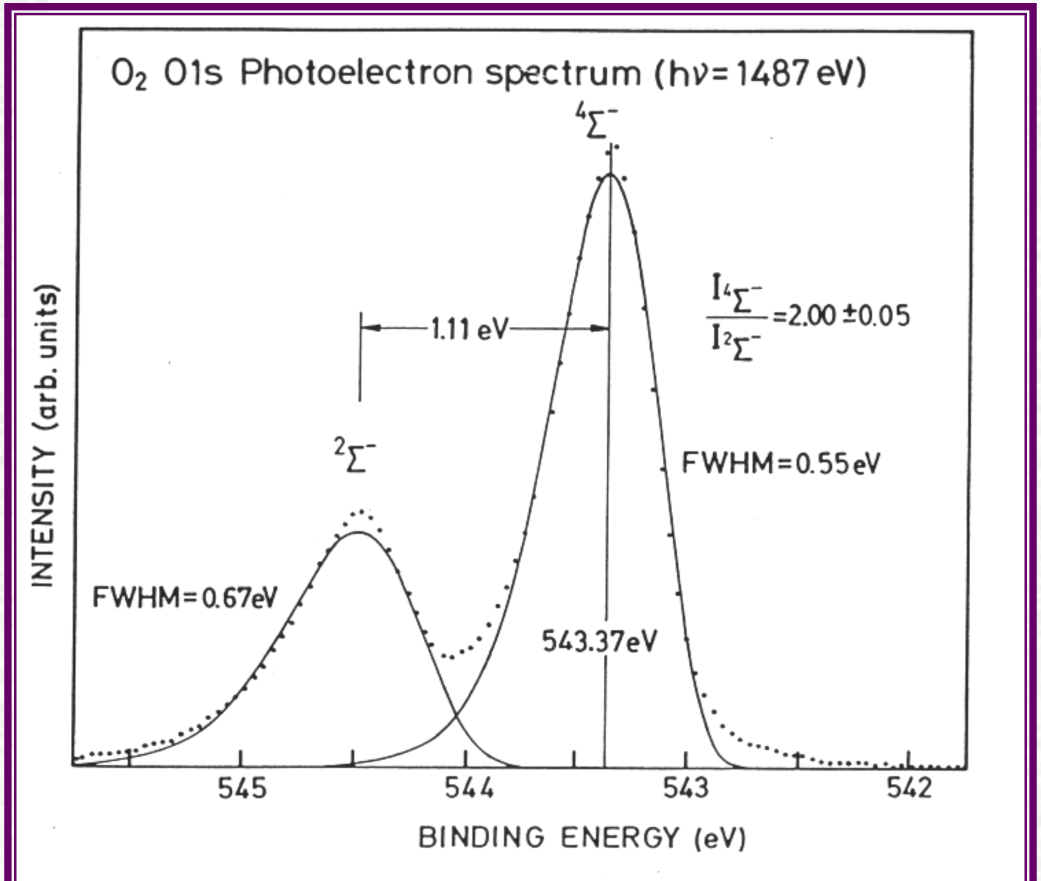


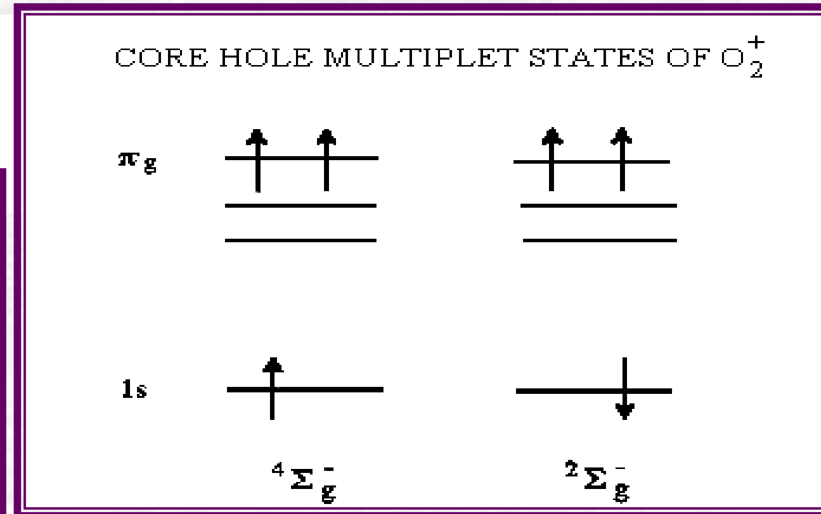
$$\Psi_{final,K}(N-1) = C_{1,K}(2p^{2}_{1/2}2p^{3}_{3/2}3d^{10} + C\ell \text{ hole}) + C_{2,K}(2p^{2}_{1/2}2p^{3}_{3/2}3d^{9})$$

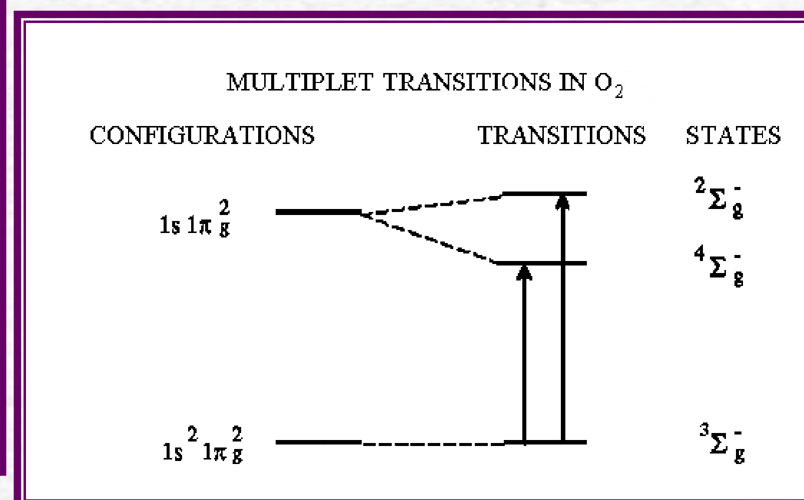
Van der Laan et al., Phys. Rev. B 23 (1981) 4369

Molecular multiplet splitting O_2 (s-s)

$$KK(\sigma_g 2s)^2\,(\sigma_u 2s)^2\,(\sigma_g 2p)^2\,(\pi_u 2p)^4\,(\pi_g 2p)^2\ {}^3\Sigma_g^-$$



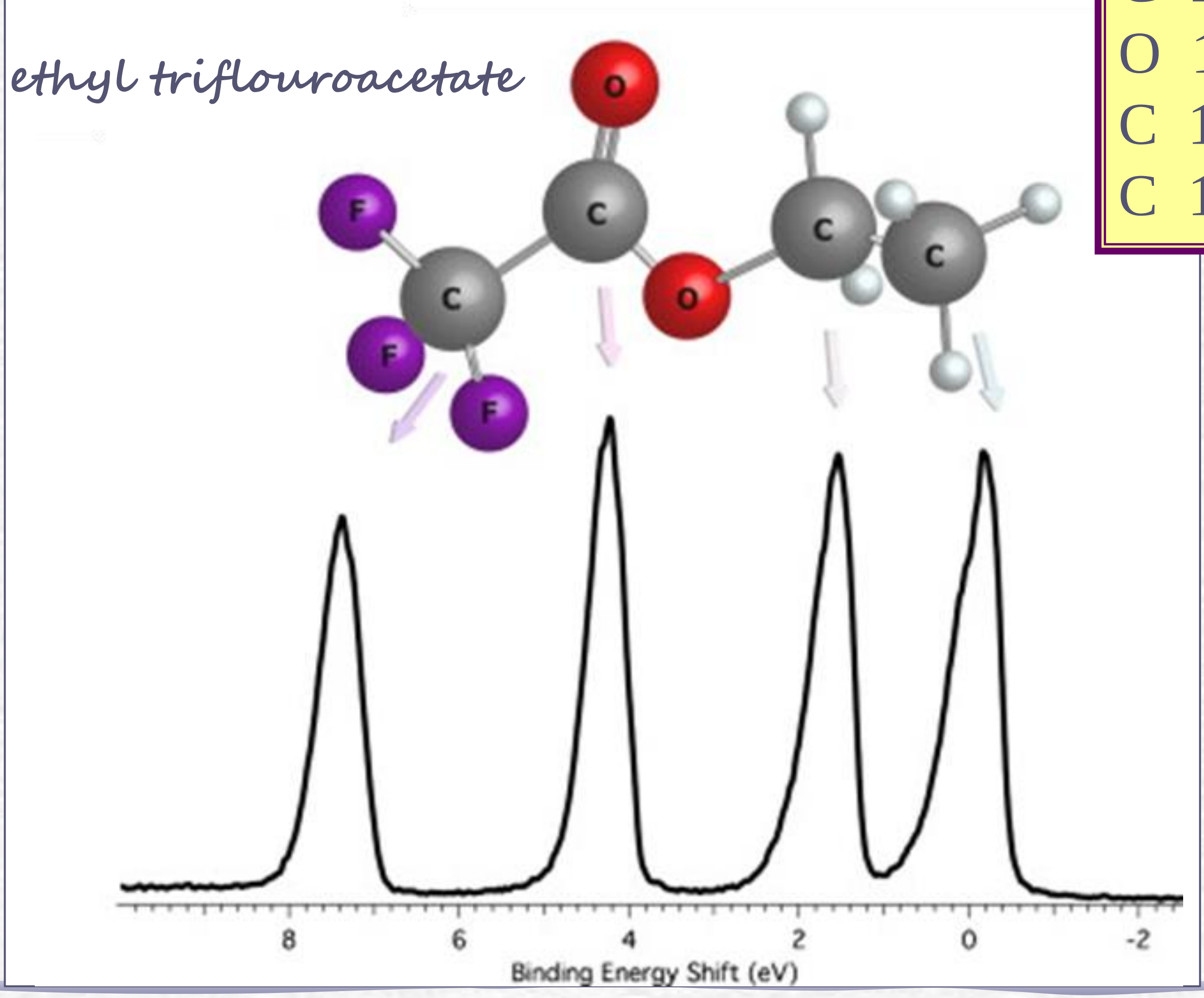




M. Larsson et al. J. Phys. B 23 (1990) 1175

Chemical shift: neighbour interaction

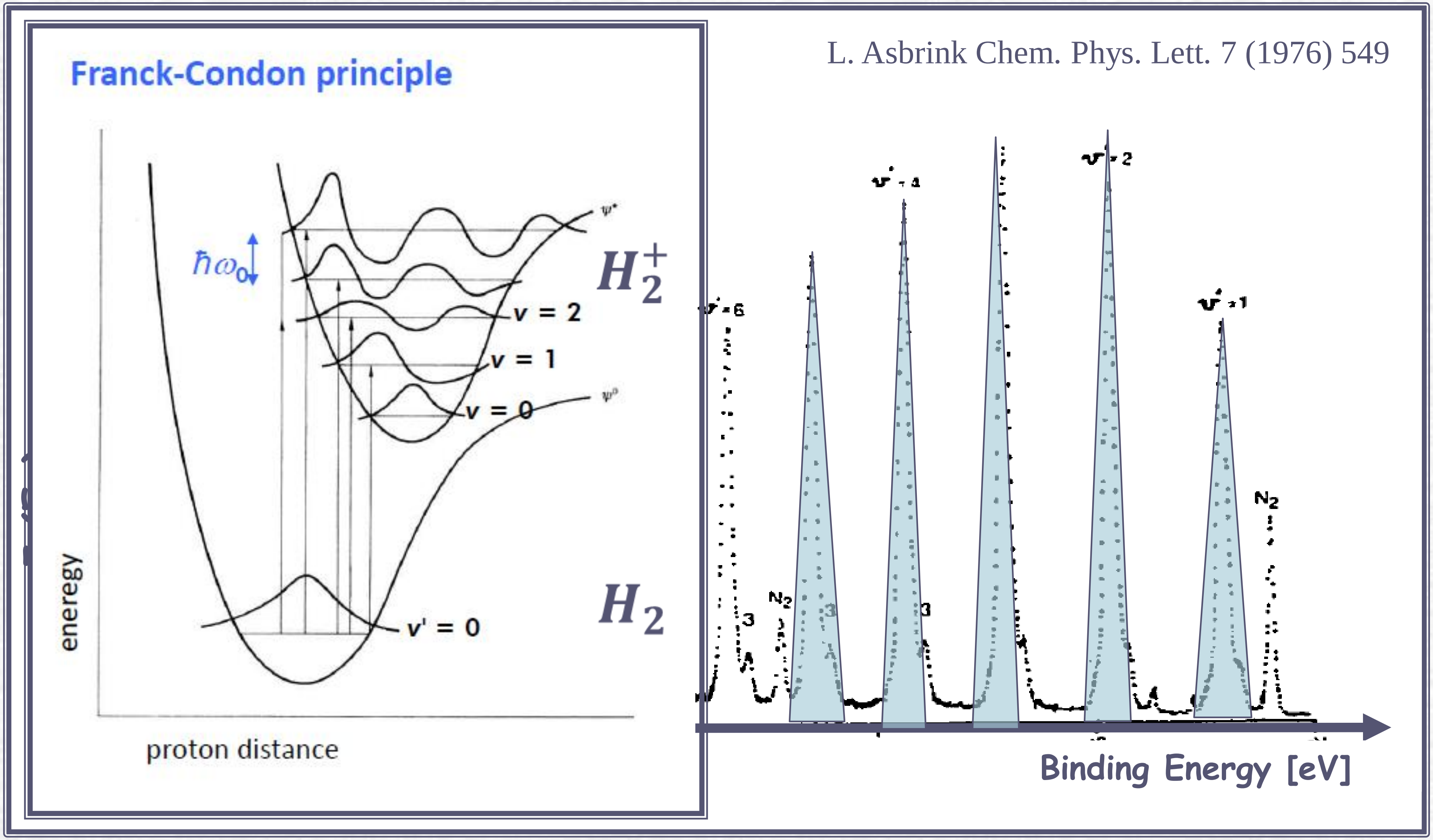
Journal of Electron Spectroscopy and Related Phenomena
Volume 185, Issues 8–9, September 2012, Pages 191–197



C 1s 285-300 eV
O 1s 530-540 eV
C 1s CO_2 298 eV
C 1s CH_4 291 eV

Sensitivity to local chemical Environment

PES spectrum of H_2 (nuclear motion)



Molecular PE x-section: nuclear motion

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

Born Oppenheimer

$$\left|\Psi_{A,B}^{(N)}\right\rangle = \left|\Psi_{A,B}^{(N)}\right\rangle \left|\Psi_{A,B}^{vib}\right\rangle$$

$$\mathrm{A}_{A,B}$$

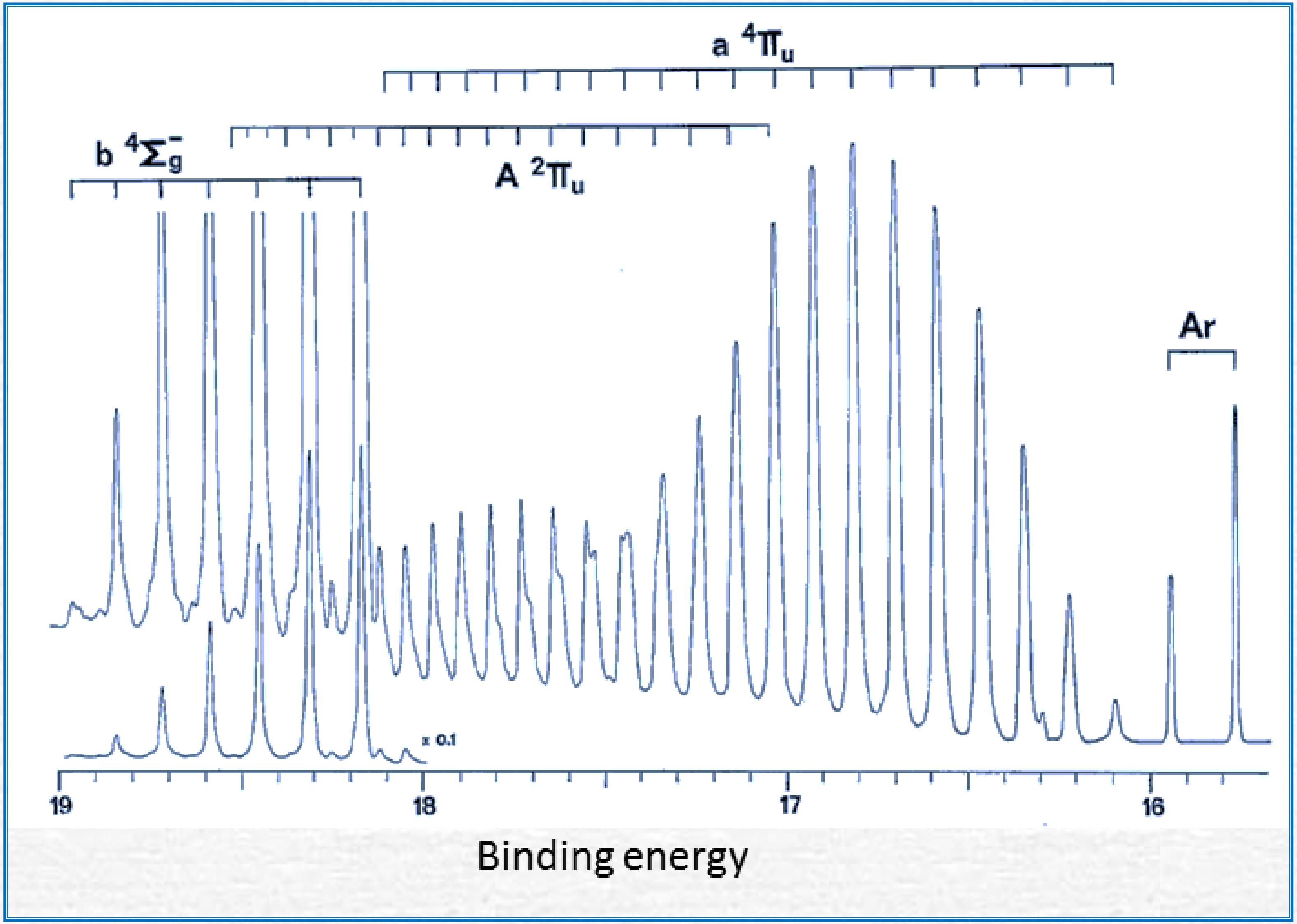
$$\frac{d\sigma}{d\Omega dE_e} \propto \frac{1}{h\nu} \sum_{A,B} \left| \hat{\varepsilon} \bullet \left\langle \varepsilon_l \middle| \vec{r}_j \middle| \sum_{A\lambda} C_{A\lambda}\phi_{A\lambda} \right\rangle \left\langle \Psi_{B,R}^{(N-1)} \middle| \Psi_{A,R}^{(N-1)} \right\rangle \right|^2$$

Frank Condon

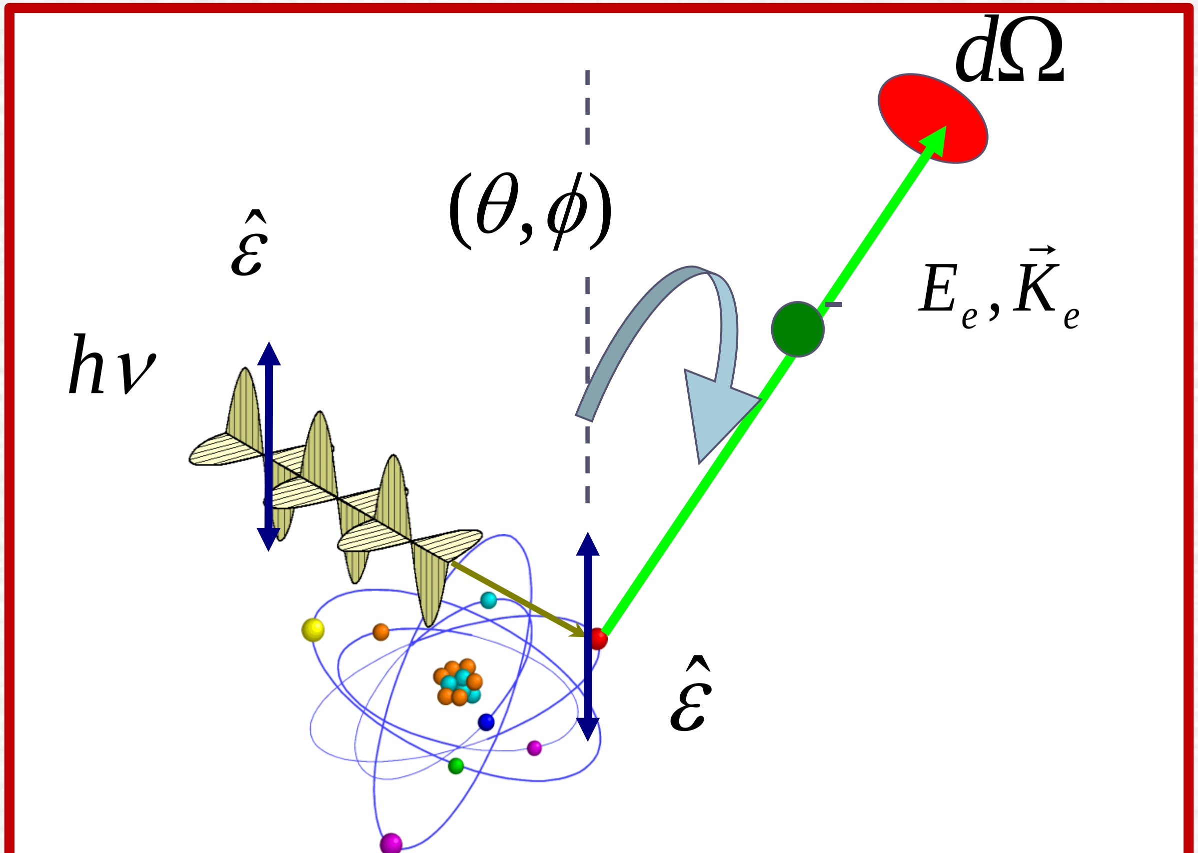
$$\left|\left\langle \Psi_B^{vib} \middle| \Psi_A^{vib} \right\rangle\right|^2 \delta(E_e + E_B^{(N-1)} - E_A - h\nu)$$

PES O_2 vibrational and multiplet splitting

Adapted: Turner Proc. Roy. Soc. A 307 (1968) 1488

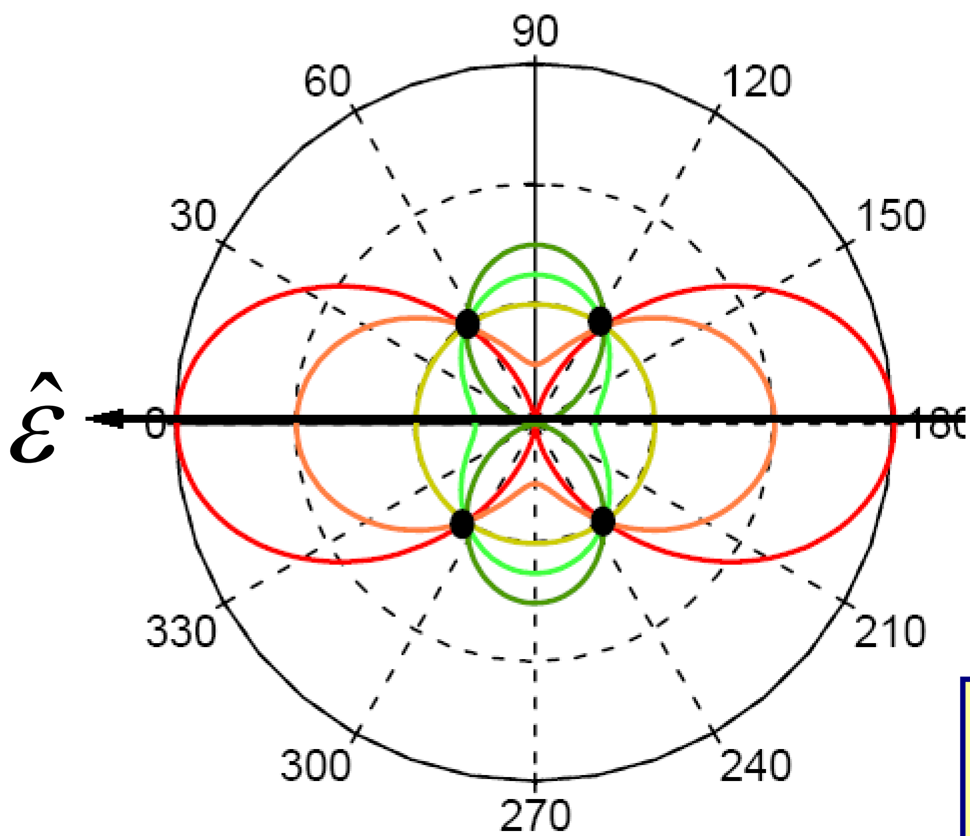


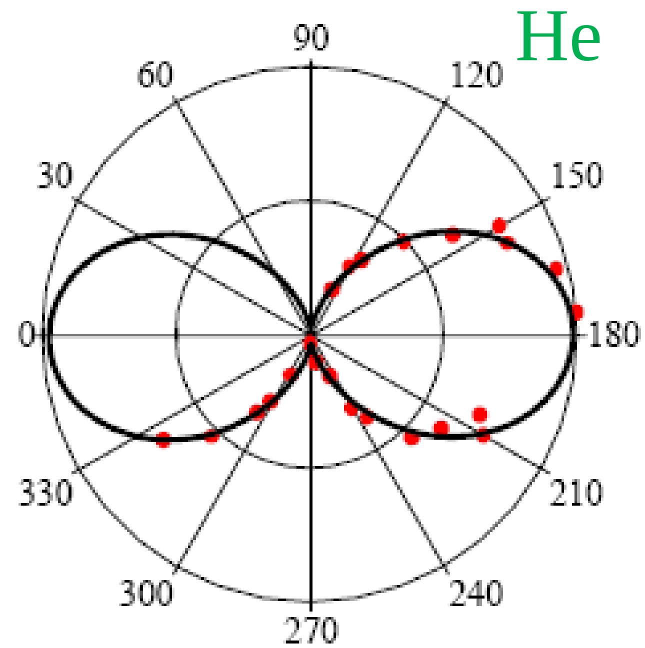
PE angular distribution



$$\frac{d\sigma}{d\Omega} \propto \frac{1}{h\nu} \sum_{A} \left| \hat{\varepsilon} \bullet \left\langle \varepsilon_l \left| \vec{r}_j \right| \phi_j(\vec{r}_j, \sigma_j) \right\rangle \left\langle \Psi_{B,R}^{(N-1)} \middle| \Psi_{A,R}^{(N-1)} \right\rangle \right|^2$$

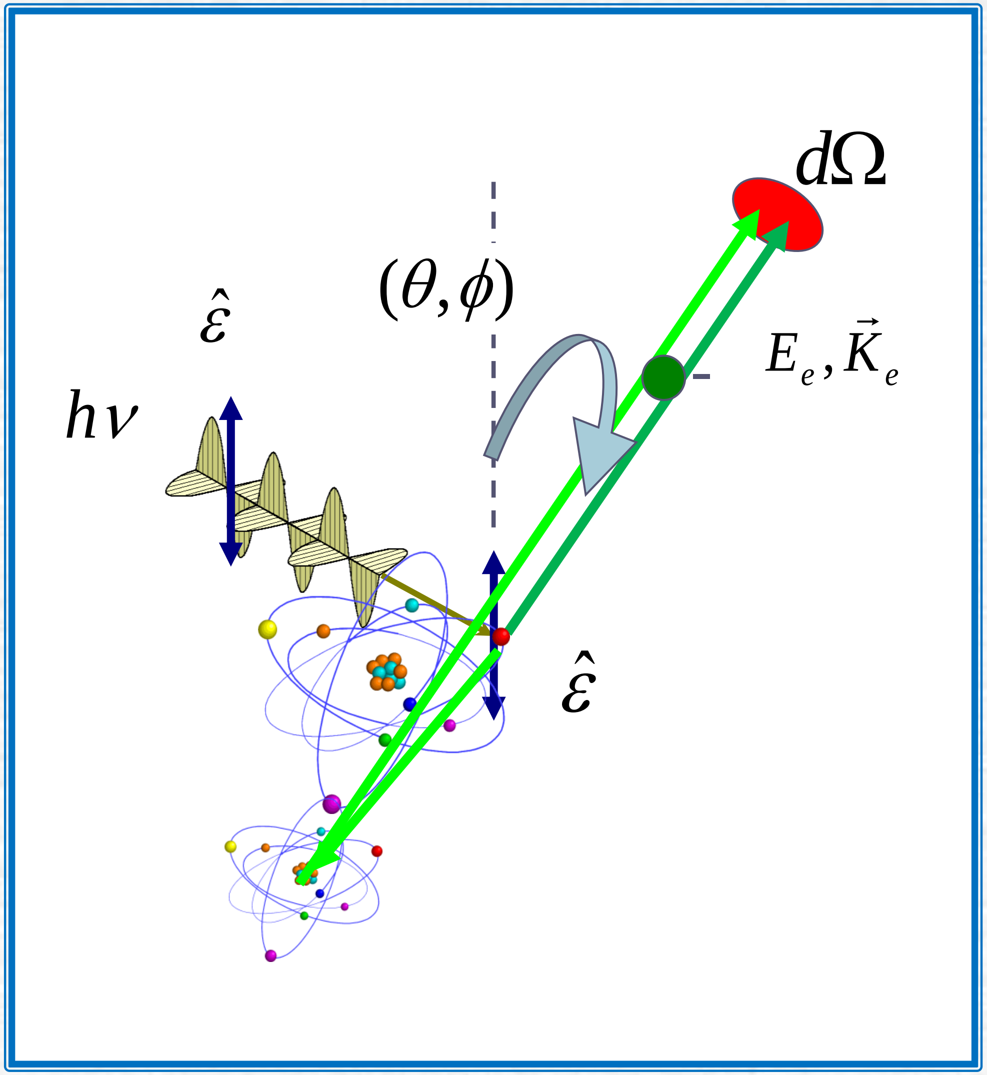
Angular distributions: state symmetry



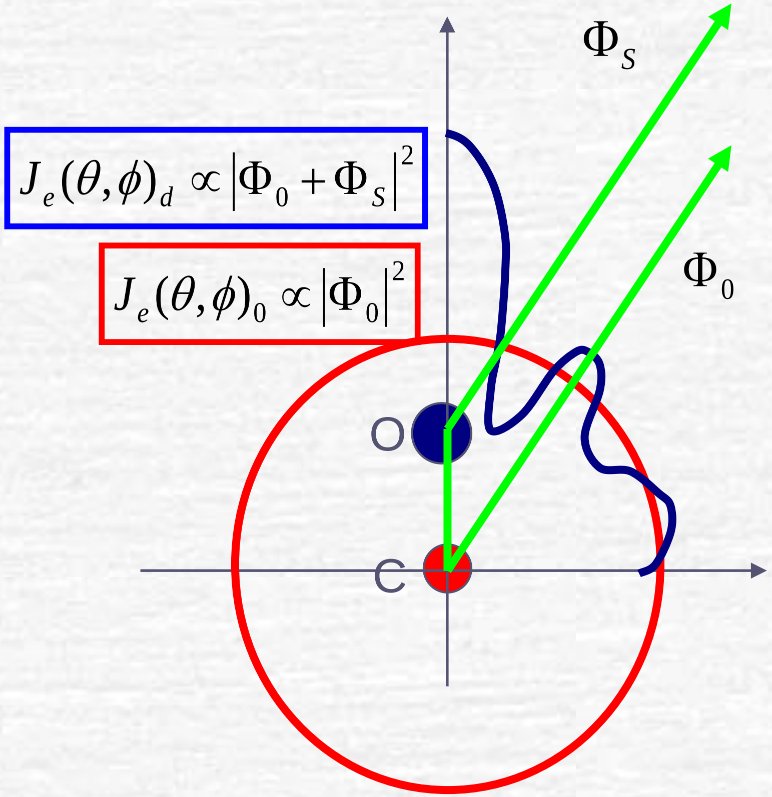


$$\frac{d\sigma}{d\Omega} \propto \frac{\sigma}{4\Pi}\left[1 + \beta P_2 \cos(\vartheta)\right]$$

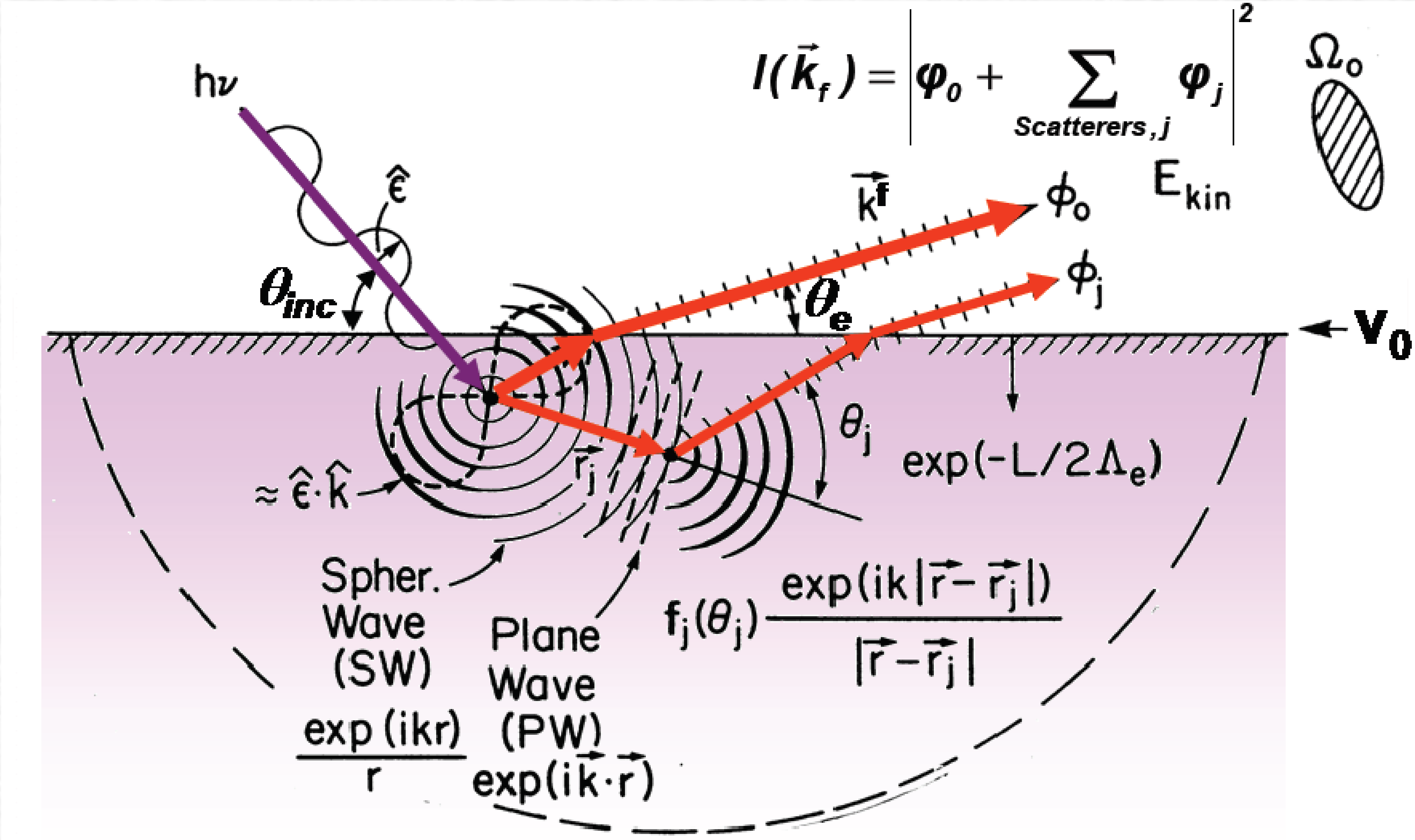
Angular distribution and neighbouring atoms



$$J_e \left| \Phi_{direct} + \sum_i \Phi^i_{scattered} \right|^2$$

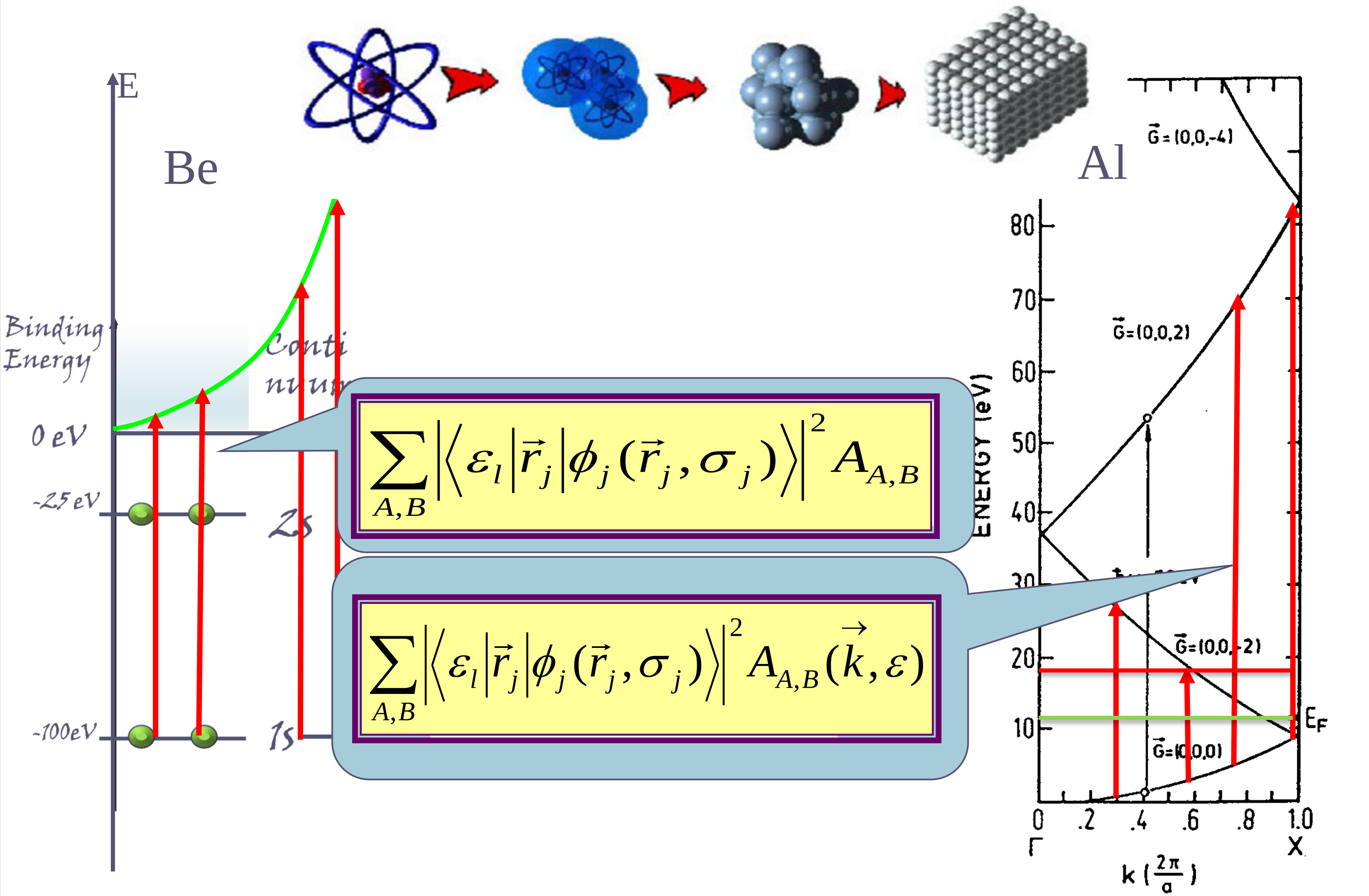


Application to surfaces



Adapted from C S Fadley: *Characterization of Surfaces Interfaces… photoemission*

From central to periodic potential



$$\sum_{A,B}\left|\left\langle \varepsilon_l \left| \vec{r}_j \right| \phi_j(\vec{r}_j,\sigma_j)\right\rangle\right|^2 A_{A,B}$$

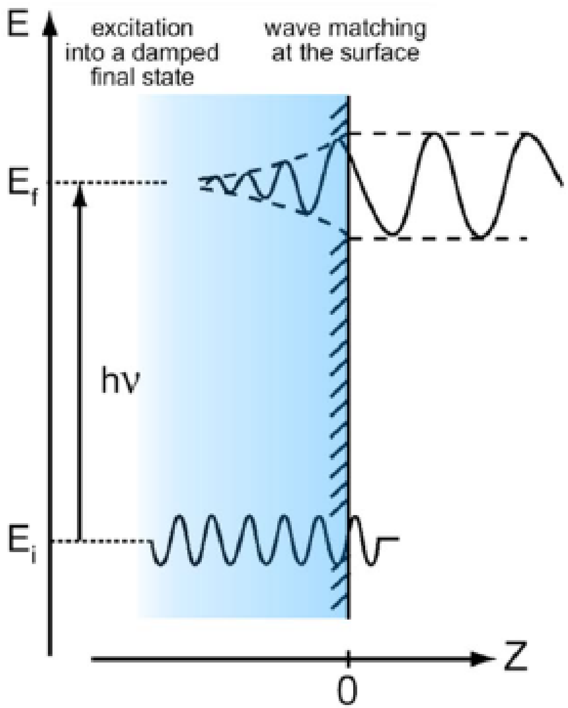
$$\sum_{A,B}\left|\left\langle \varepsilon_l \left| \vec{r}_j \right| \phi_j(\vec{r}_j,\sigma_j)\right\rangle\right|^2 A_{A,B}(\vec{k},\varepsilon)$$

Photoelectron x-section in solids

$$\frac{d\sigma}{d\Omega dE_e} \propto \frac{1}{h\nu} \sum_{A,B} \left| \hat{\varepsilon} \bullet \left\langle \phi_f(\vec{k}) \middle| \vec{r}_{if} \middle| \phi_i(\vec{k}) \right\rangle \right|^2 \cdot A_{A,B}(\vec{k}.\varepsilon) \cdot \delta(E_e + E_B^{(N-1)} - E_A - h\nu)$$

1

One step model



final states: "time-inverted LEED state"

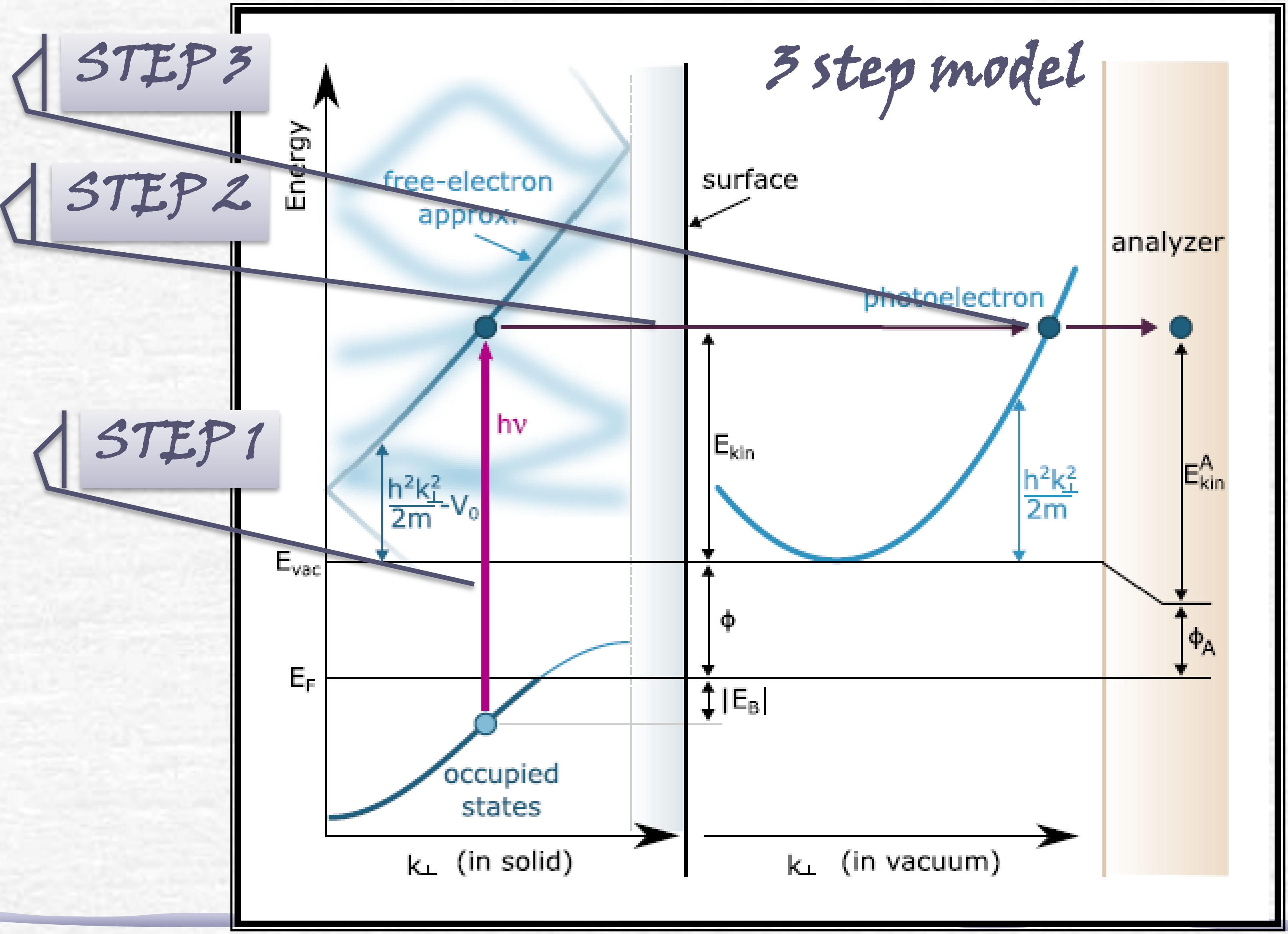
- in vacuum: free electron wave $e^{i\vec{k}_f \cdot \vec{r}}$
- in the solid: matched to high lying Bloch waves, damped by e-e scattering
- energy E_f and wavevector $\vec{k}_f$

initial states in the solid:

- bulk Bloch waves $u_{n\vec{k}_i}(\vec{r})e^{i\vec{k}_i \cdot \vec{r}}$
- energy E_i and wavevector $\vec{k}_i$

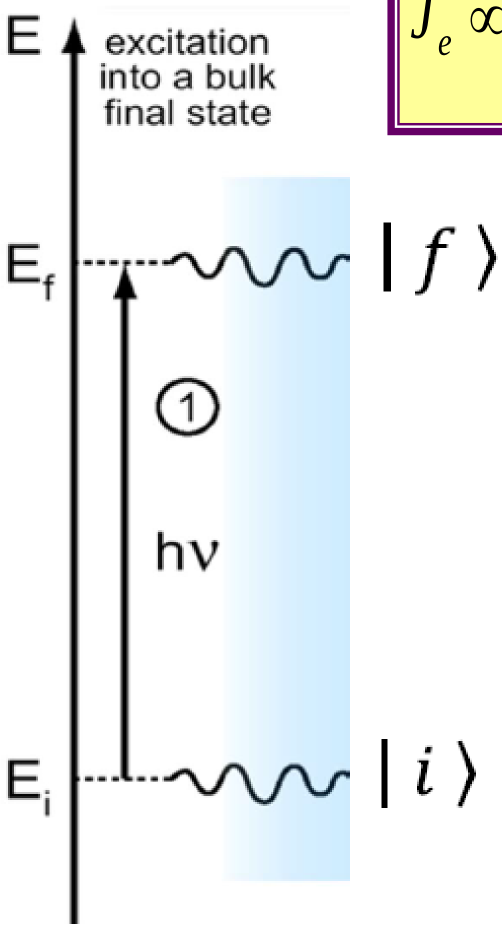
NON inter acting e⁻.

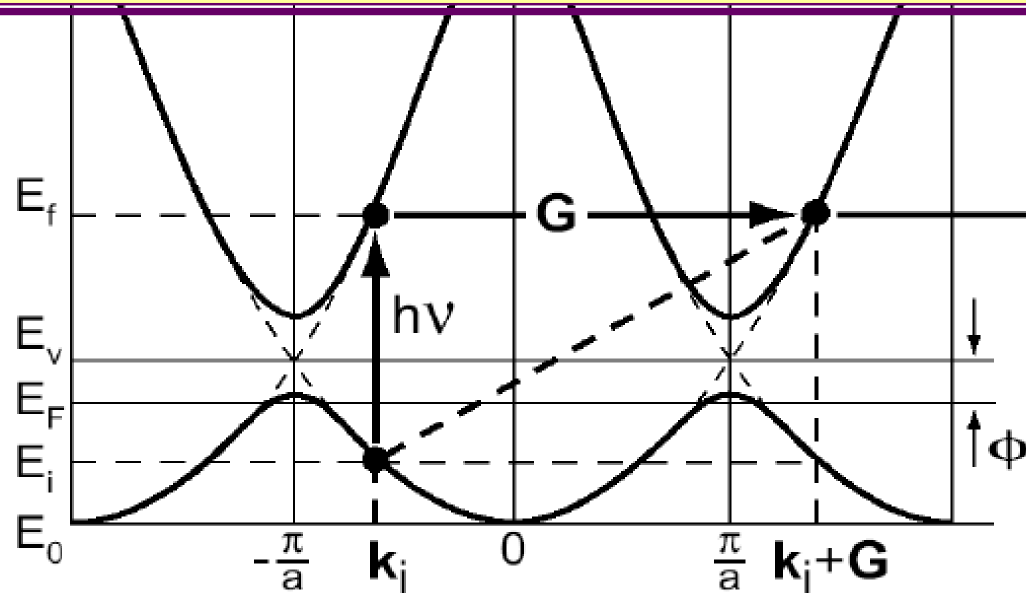
Photoelectron must escape from solid



Step 1: optical excitation in the solid

$$J_e \propto \sum_{i,f} \left\{ \left(f(E_i) \right) \left[1 - f(E_f) \right] \right\} \cdot \left| M_{i,f} \right|^2 \delta(E_f - E_i - h\nu) \cdot \delta(K_i - K_f + G)$$





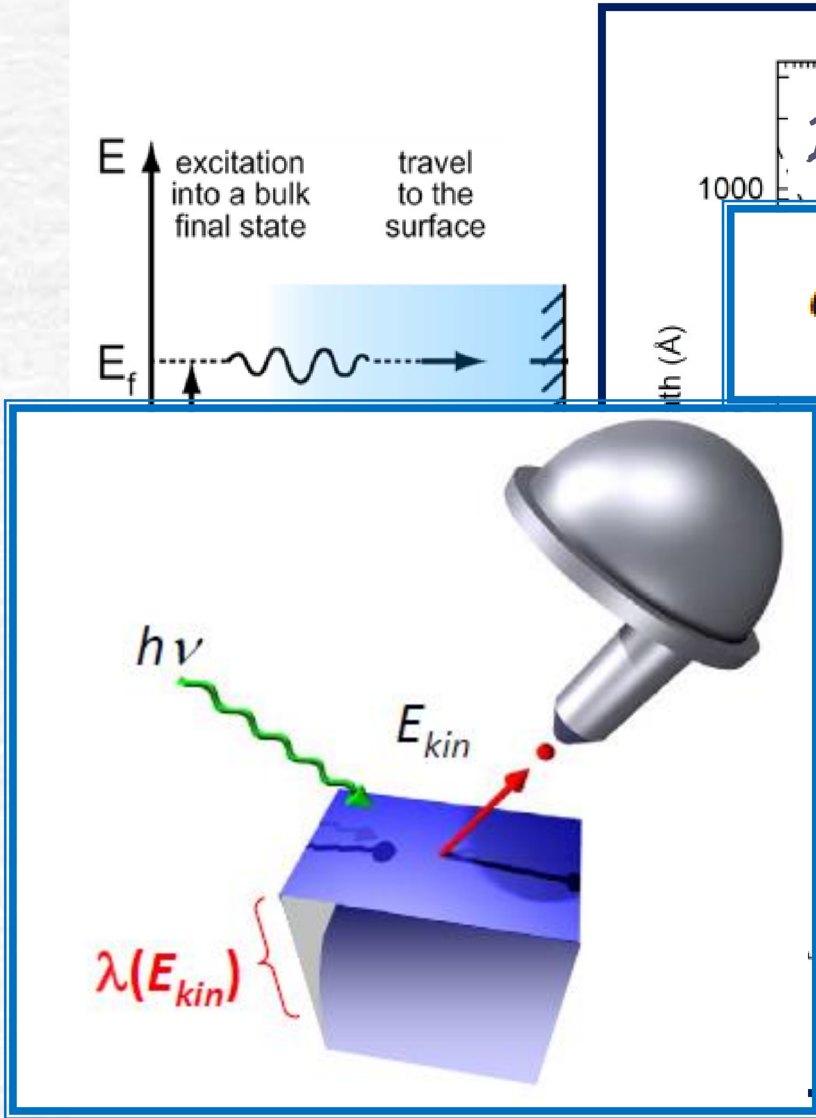
momentum conservation:

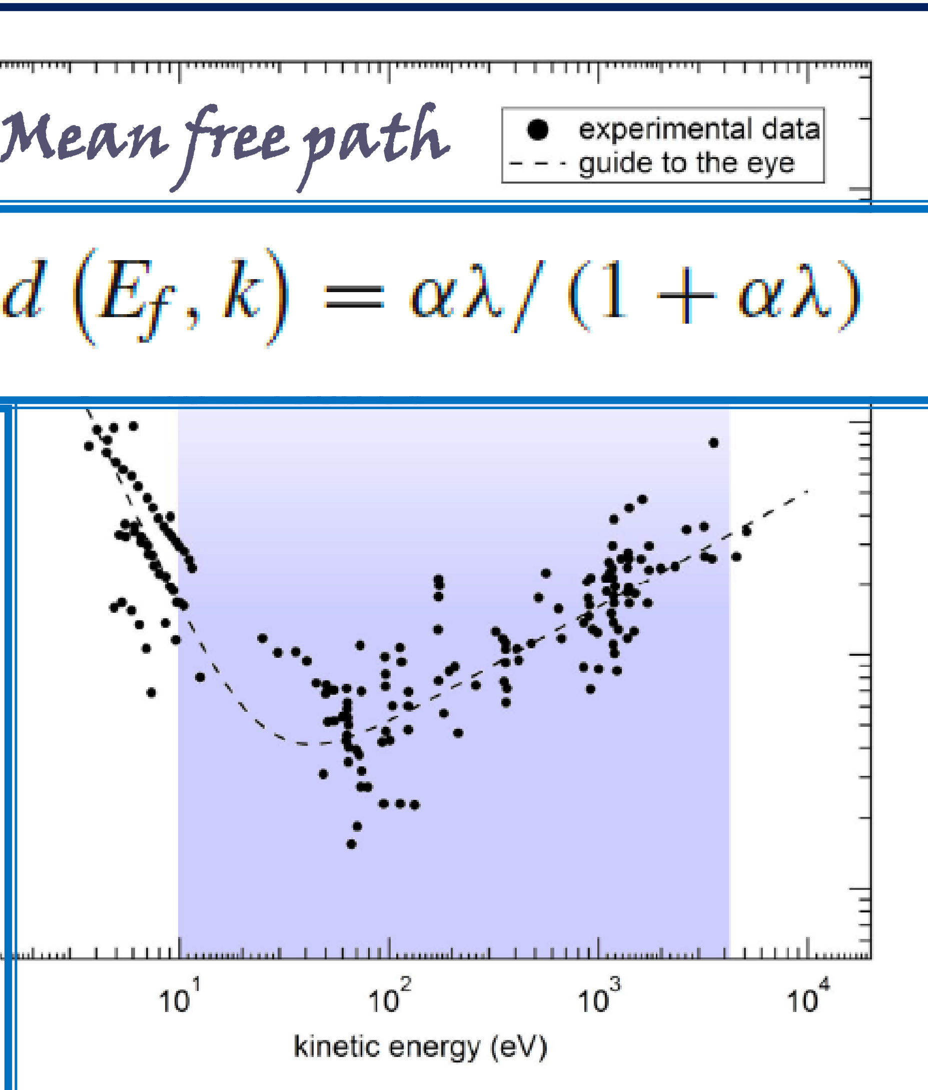
$$\vec{k}_f = \vec{k}_i + \vec{G} + \vec{k}_{photon}$$

only "vertical" transitions

for VUV excitation

Step 2: Transport to the surface

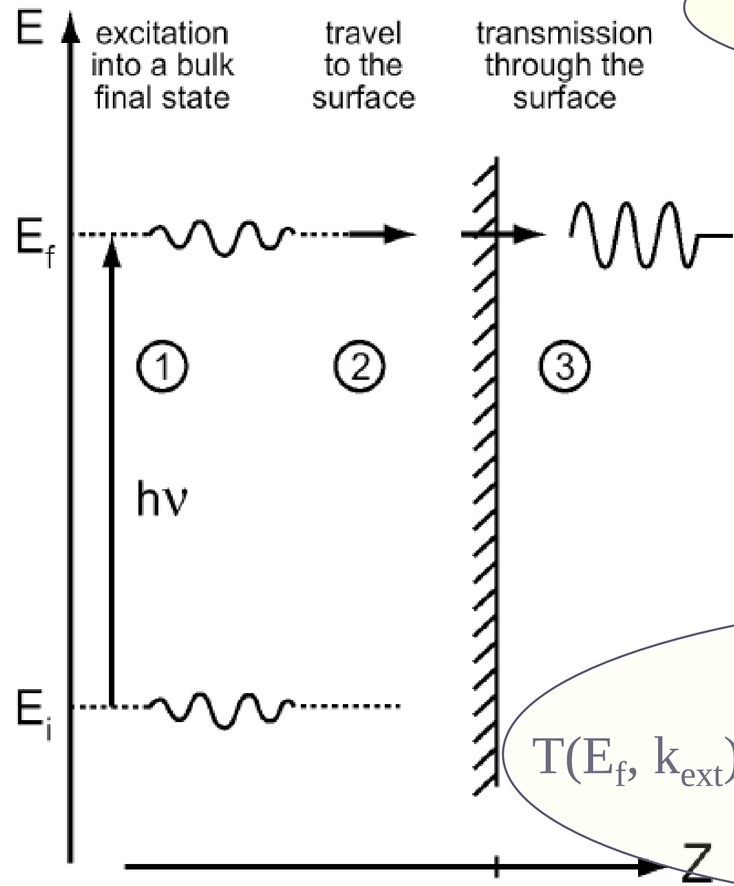


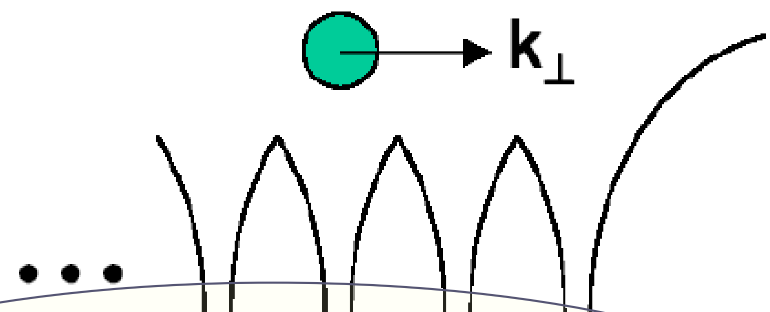


$$d\left(E_f, k\right) = \alpha\lambda / \left(1 + \alpha\lambda\right)$$

Step 3: Transition to vacuum

- conservation of wavevector component parallel to surface, $\vec{k}_{\parallel}$
- **BUT** $k_{\perp}$ changes due to **electron diffraction at surface barrier**

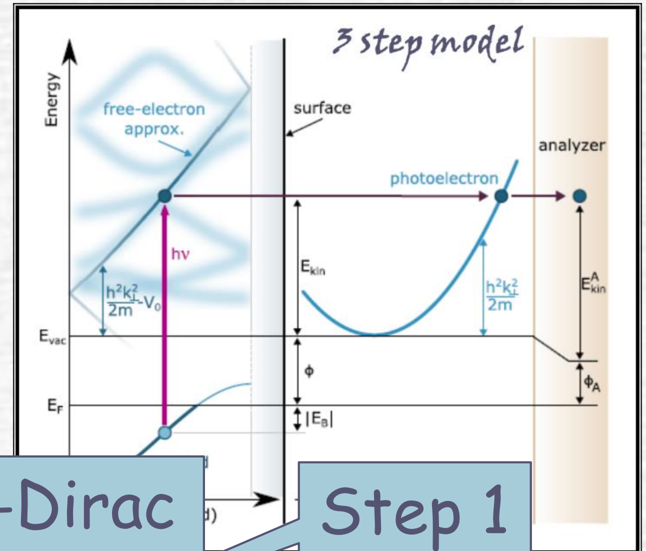




$$T(E_f, k_{ext}) = \begin{cases} 0 \text{ if } E_f < E_F + \Phi \\ 1/2 \sqrt{[1-(E_F+\Phi)/E_f]} \text{ if } E_f > E_F + \Phi \end{cases}$$

J_e in the 3 step model

1. Dipole transition
2. Elastic transport
3. Exit to vacuum



Initial-final states Fermi-Dirac

Step 1

$$J_e \propto \sum_{i,f} \{ (f(E_i)) [1 - f(E_f)] \} \cdot |M_{i,f}|^2 \delta(E_f - E_i - h\nu) \cdot \delta(K_i - K_f + G) \cdot$$

$$d(E_f, k) \cdot$$

Step 2

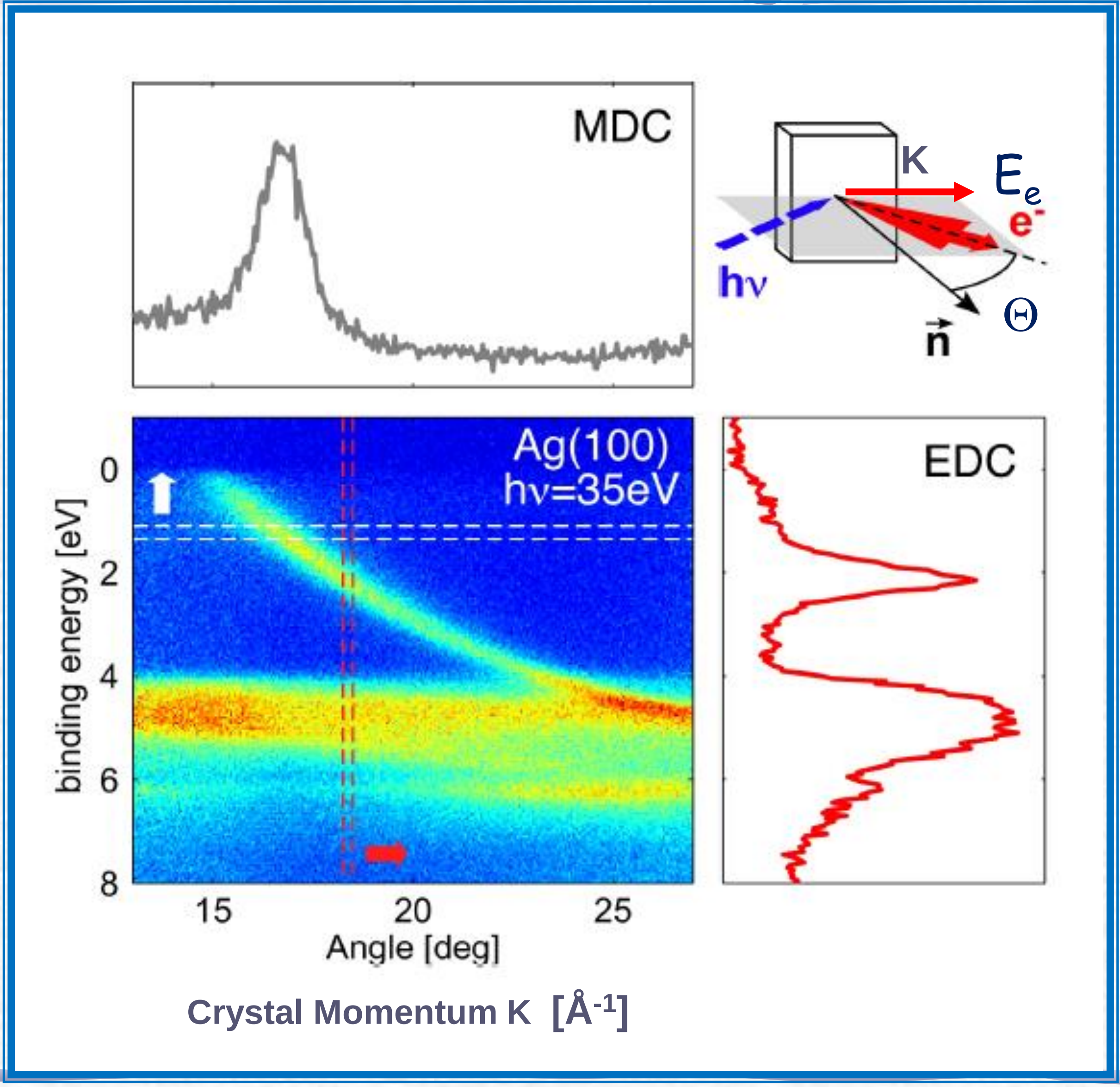
$$T(E_f, k) \cdot \delta(K_i^{//} - K_f^{//} + G^{//}) \cdot \delta(E_{kin} - E_f - \Phi)$$

Step 3

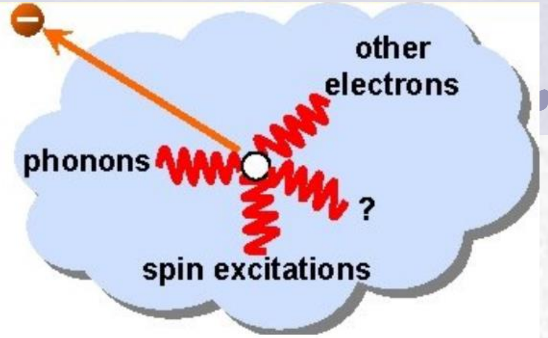
Energy & momentum conservation at surface

Typical J_e (E_e, Θ) distribution in solids

From: Photoelectron Emission Spectroscopy
Claus M. Schneider

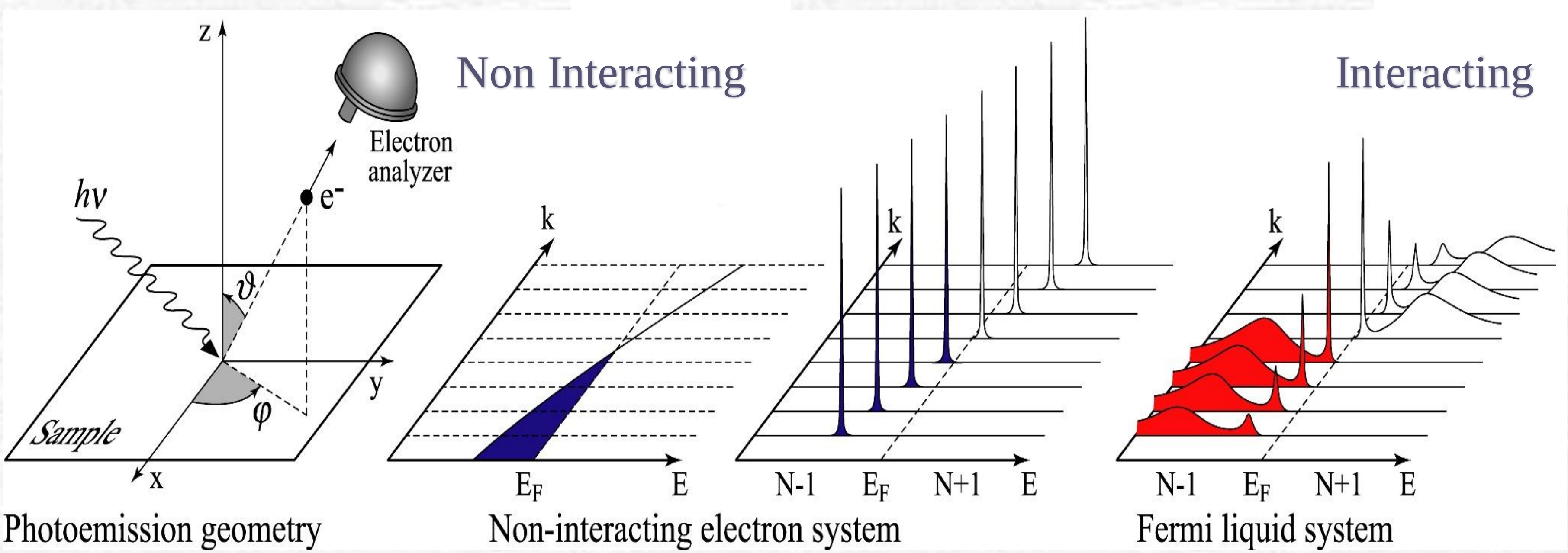


EDC for Interacting Electrons



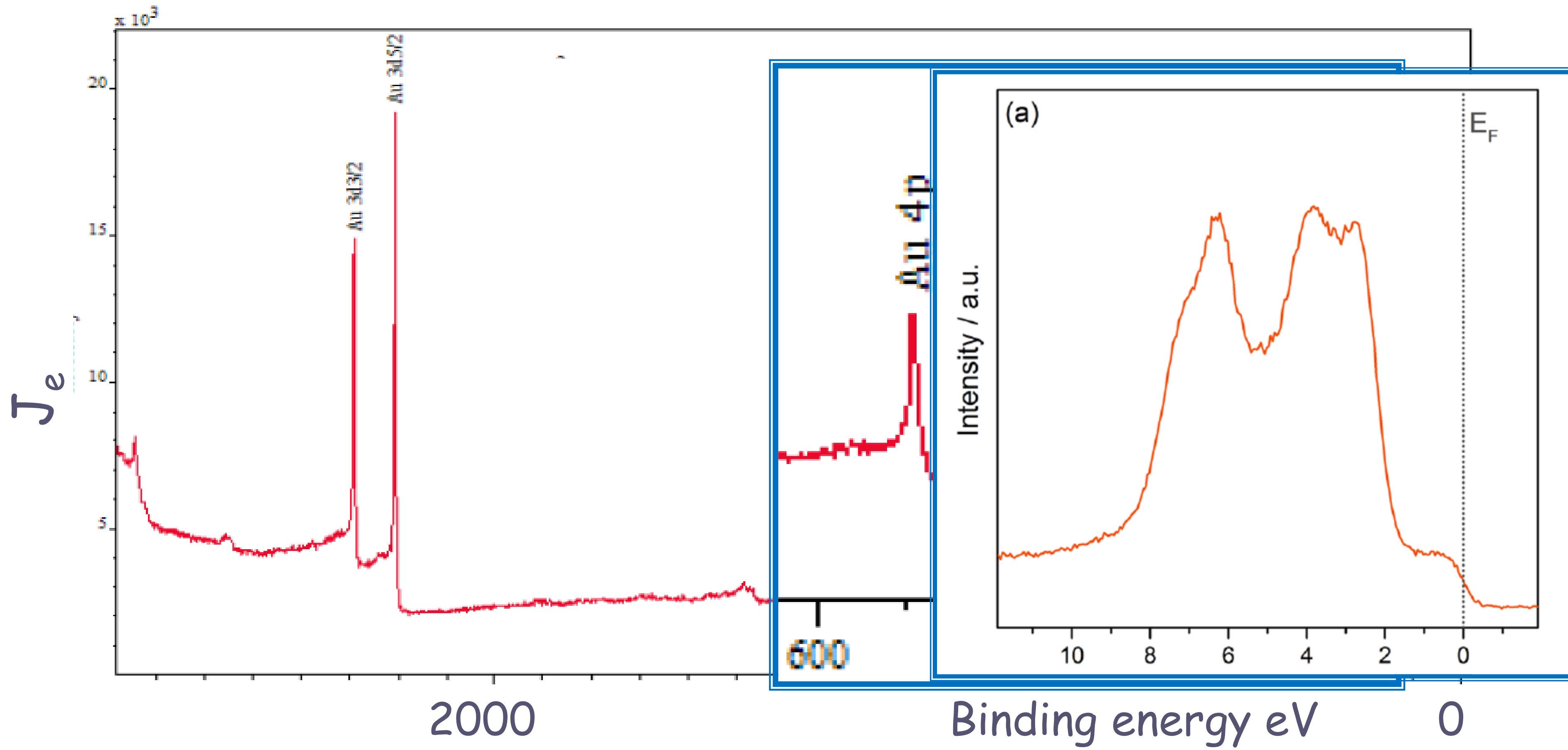
$$\Psi^{N}_{f,i} = \hat{A}\Psi^{N-1}_{f,i}\phi_{f,i}(\varepsilon,\vec{k})$$

$$A(\vec{k},\varepsilon) = \left|\left\langle \Psi^{N-1}_{f} \middle| \Psi^{N-1}_{i} \right\rangle\right|^2 \cdot \delta(\varepsilon + E^{N-1}_{f} - E^{N}_{i})$$



From Kyle Shen Stanford University «High Resolution UPS»

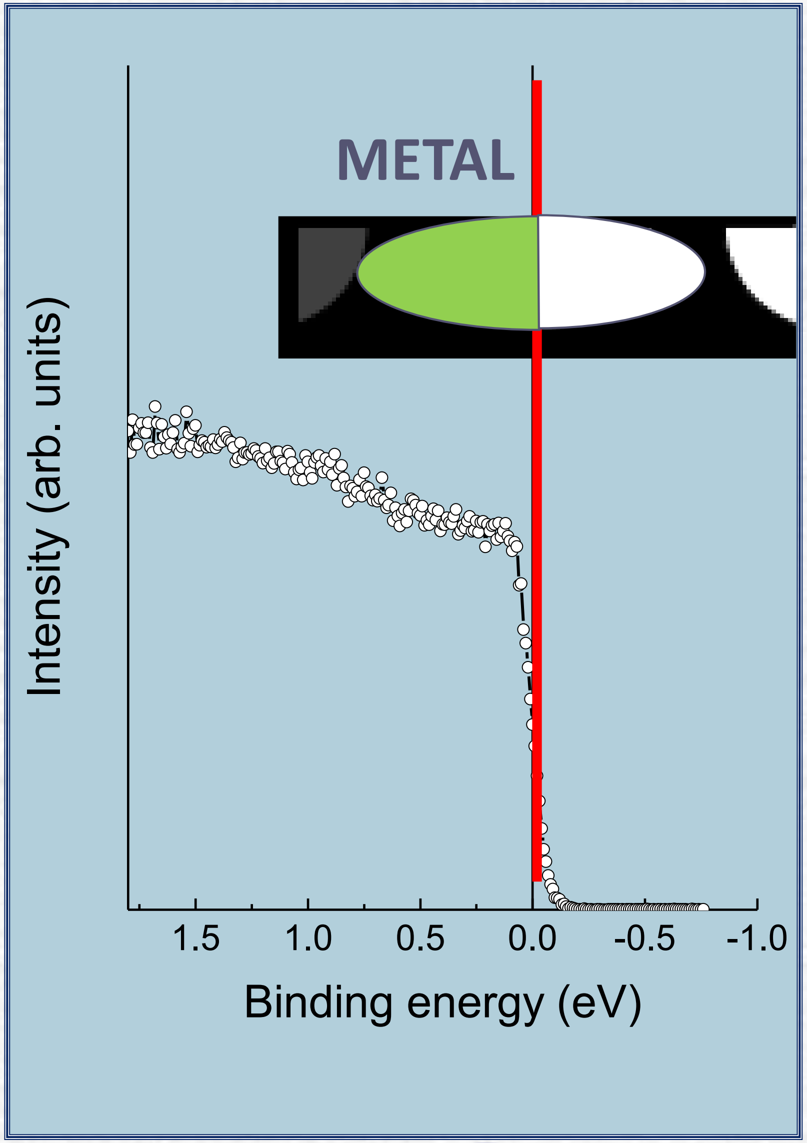
It really works on solids: i.e. Au

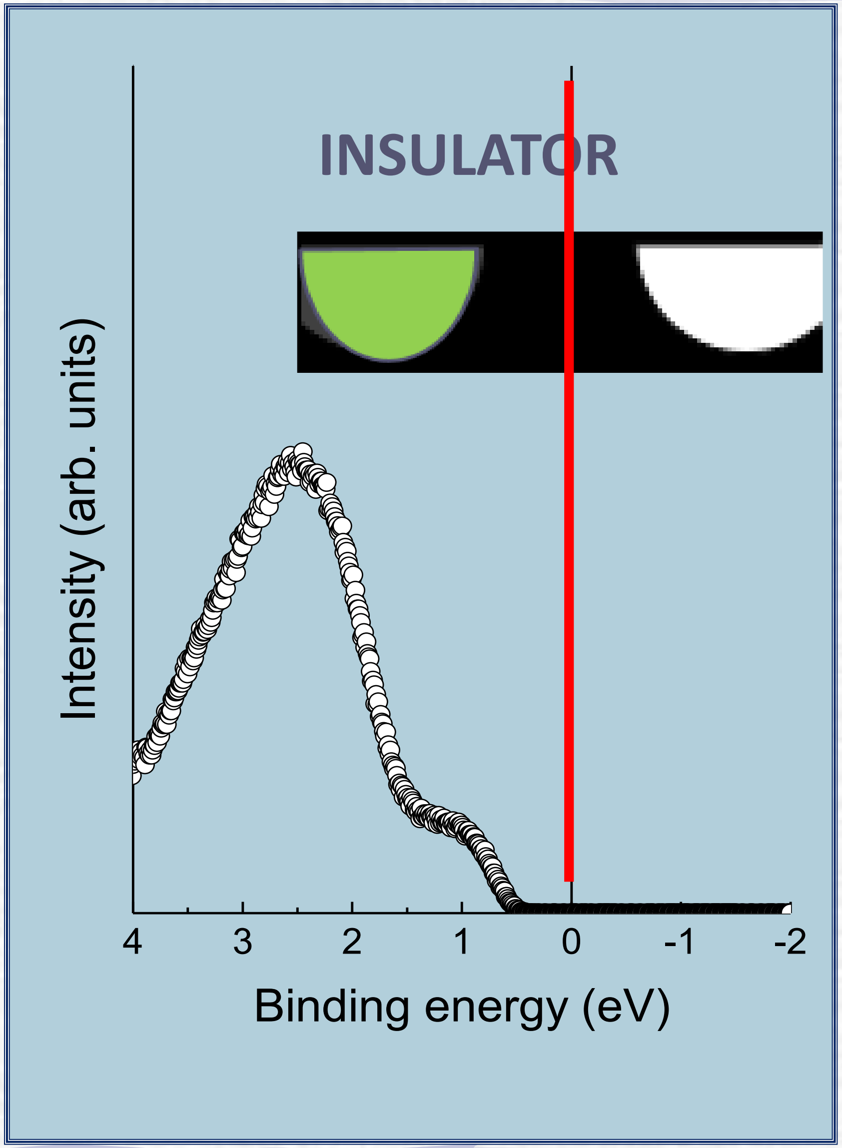


Gold Photoelectron spectrum EDC

Rev. Sci. Instr. 89, 073105 (2018);

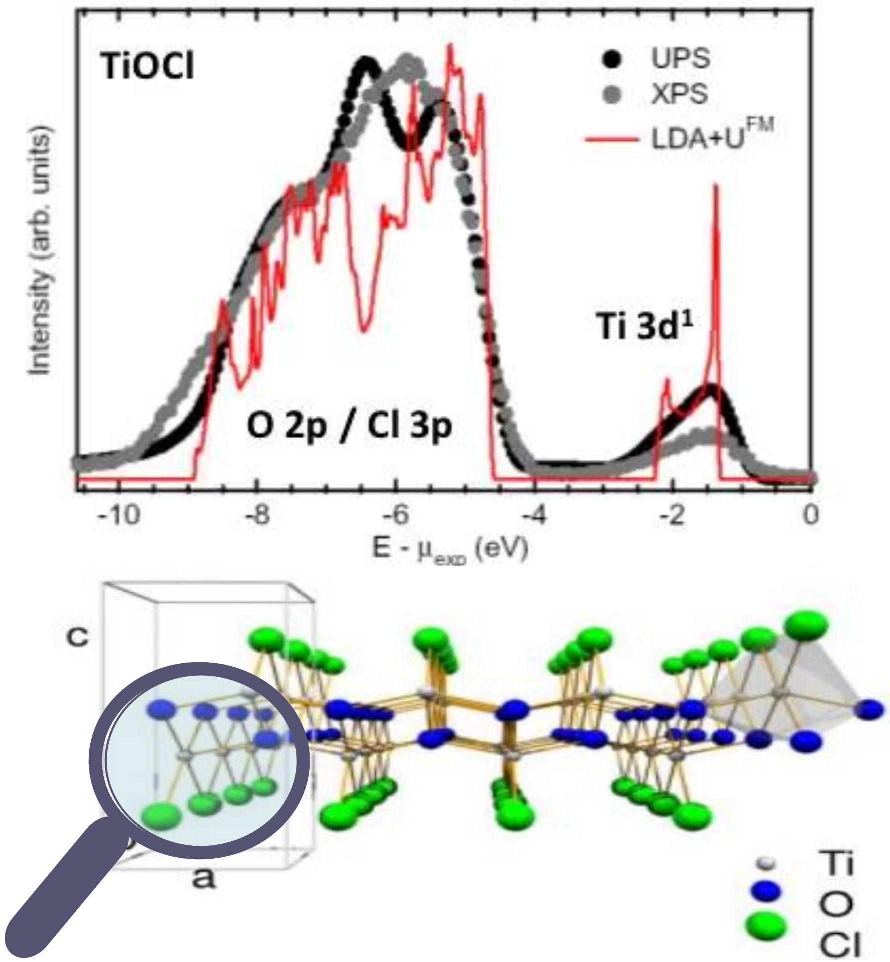
Photoemission spectrum at Fermi Edge



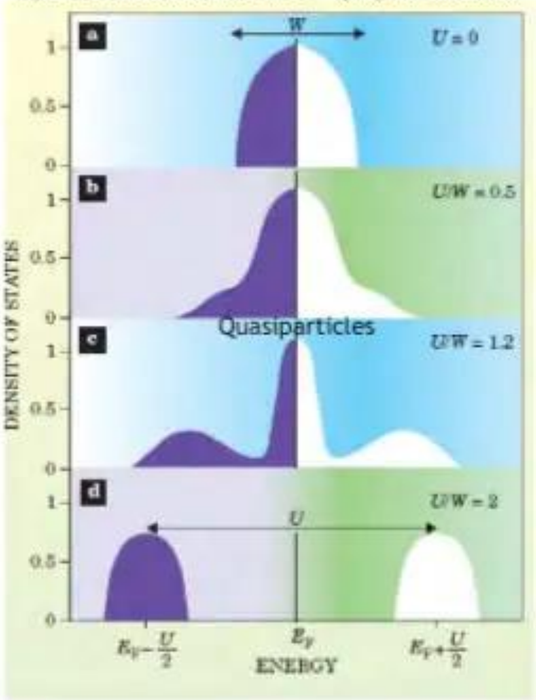


PES of the Mott insulator TiOCl: e-e correlation

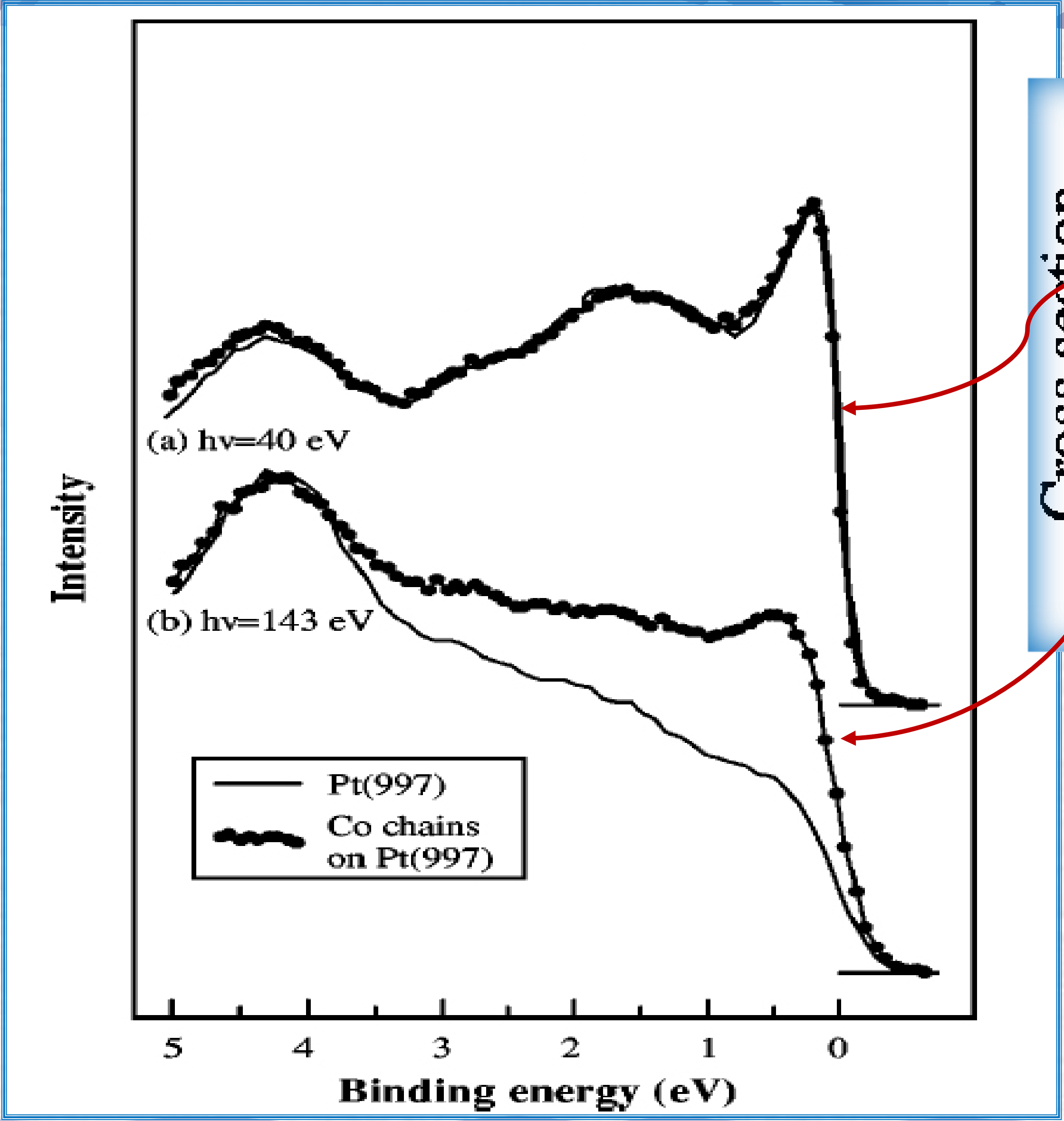
M. Hoinkis et al. PHYSICAL REVIEW B 72, 125127 2005

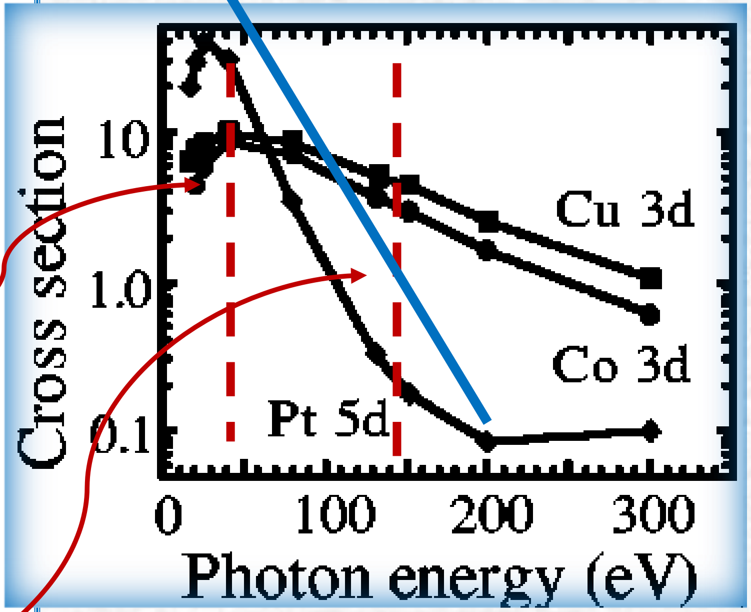


spectral function $A^{<}(\omega)$ (DMFT)



Valence band Energy Distribution Curves at Cooper minimum

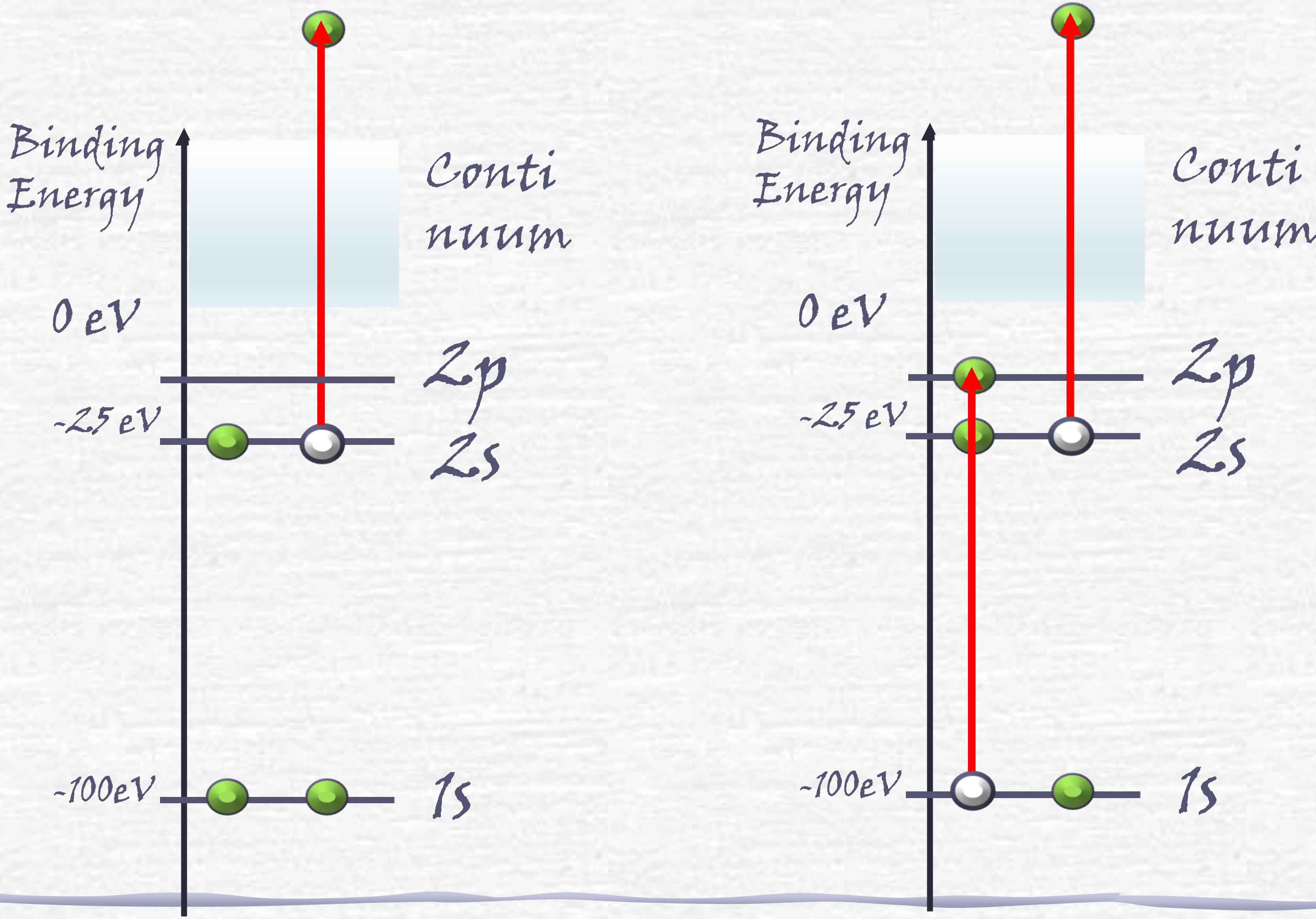




Valence Band EDCs of the clean Pt(997) surface (thin lines) and of **Co-nanowires** grown on Pt(997) (dots and thick lines), taken at different photon energies

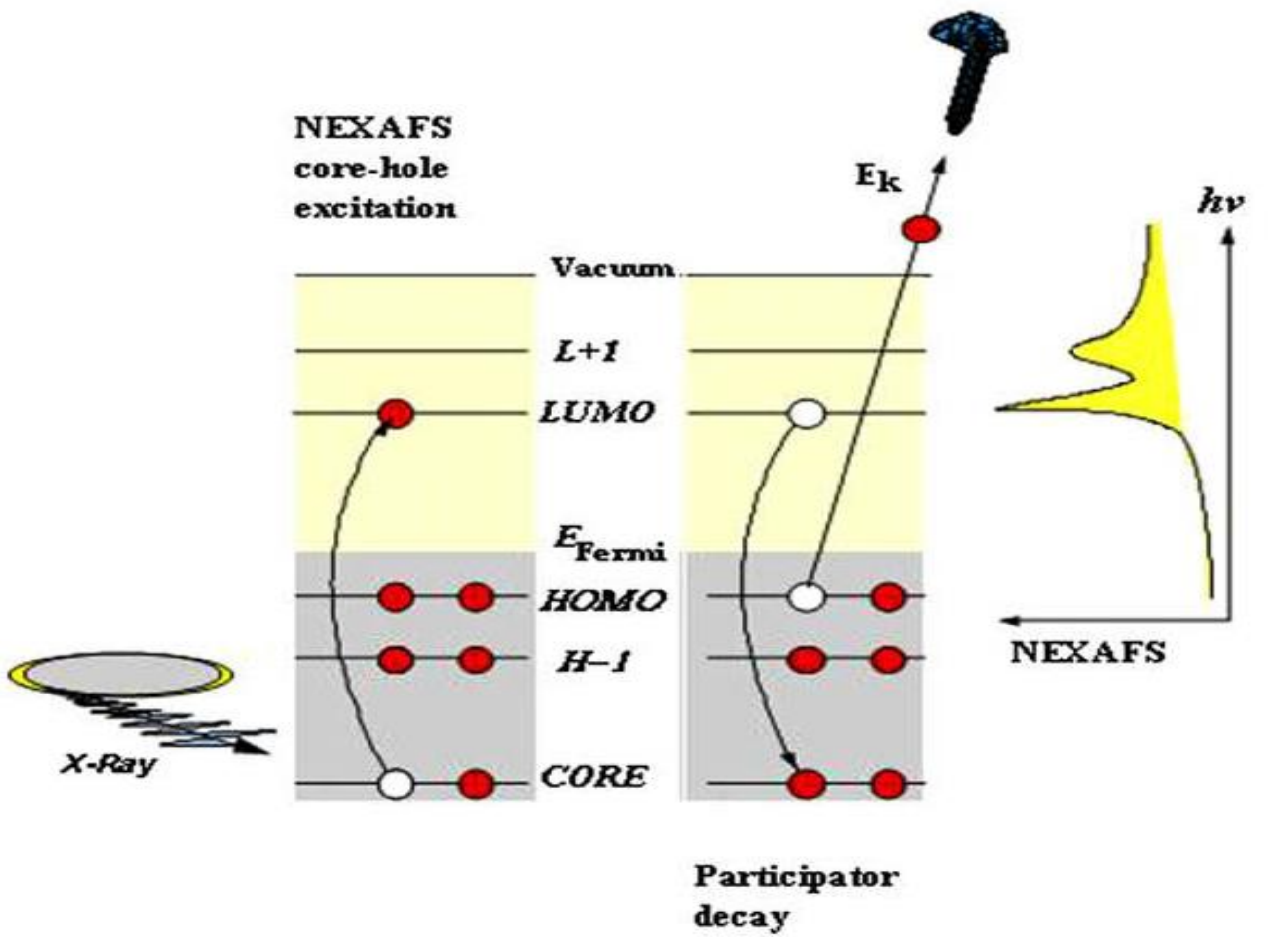
PRB 61, R5133

Direct and Resonant Photoemission

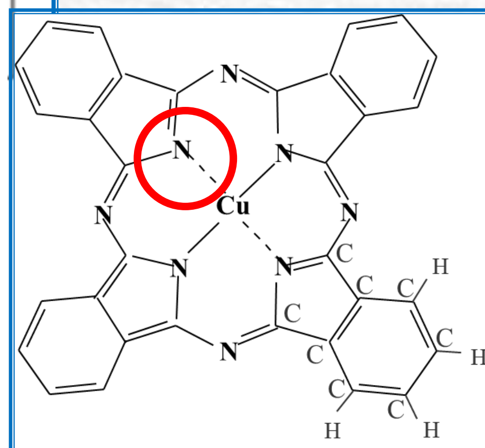


Resonant photoelectron EDC: CuPC/Au(100)

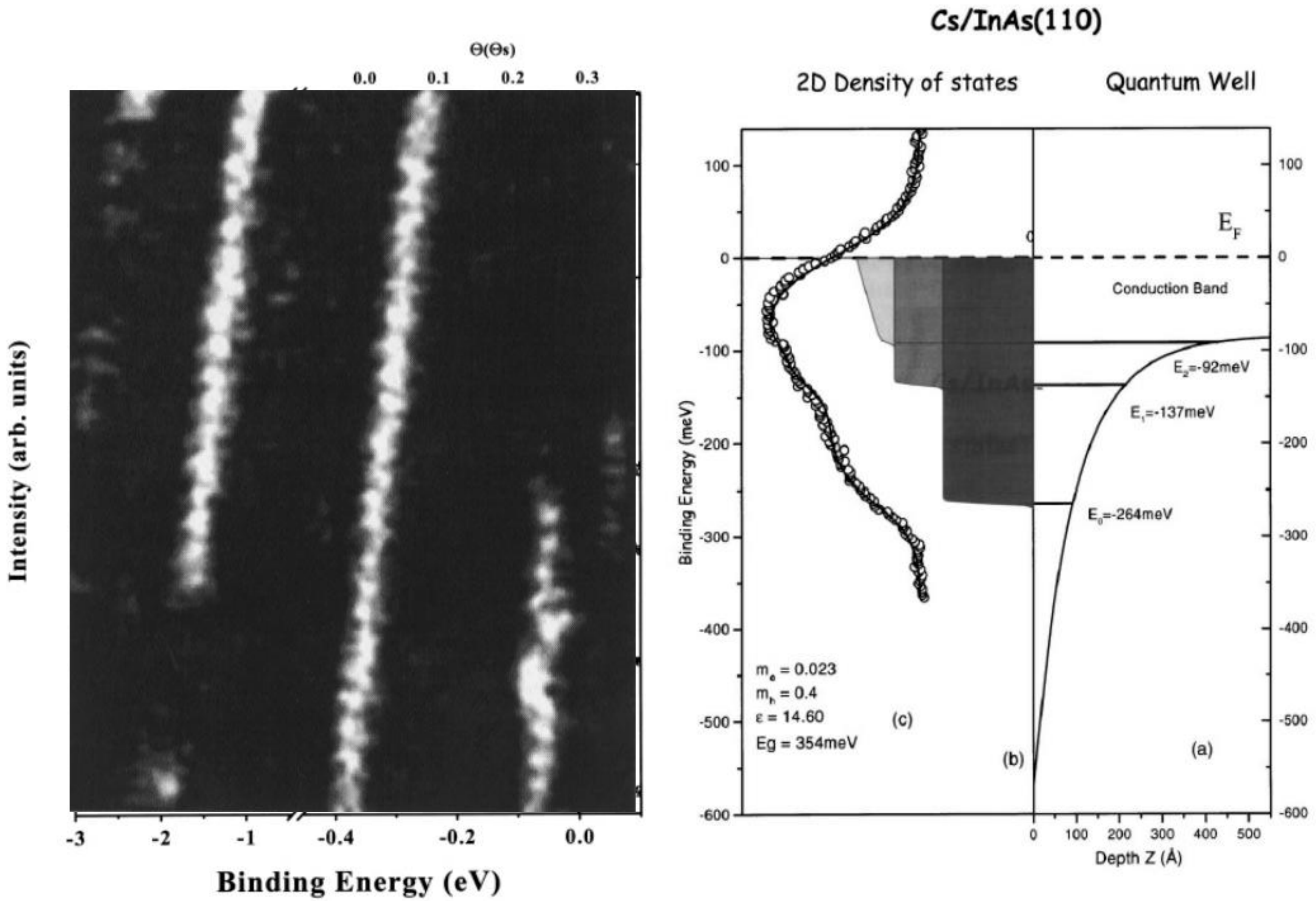
Vilmercati et al. Surface Science 603 (2009) 1542–1556



Valence Band EDCs of a **CuPc** thin-film taken at different photon energies and X-ray Absorption Spectroscopy (XAS) from the same CuPc across the **N K-edge**

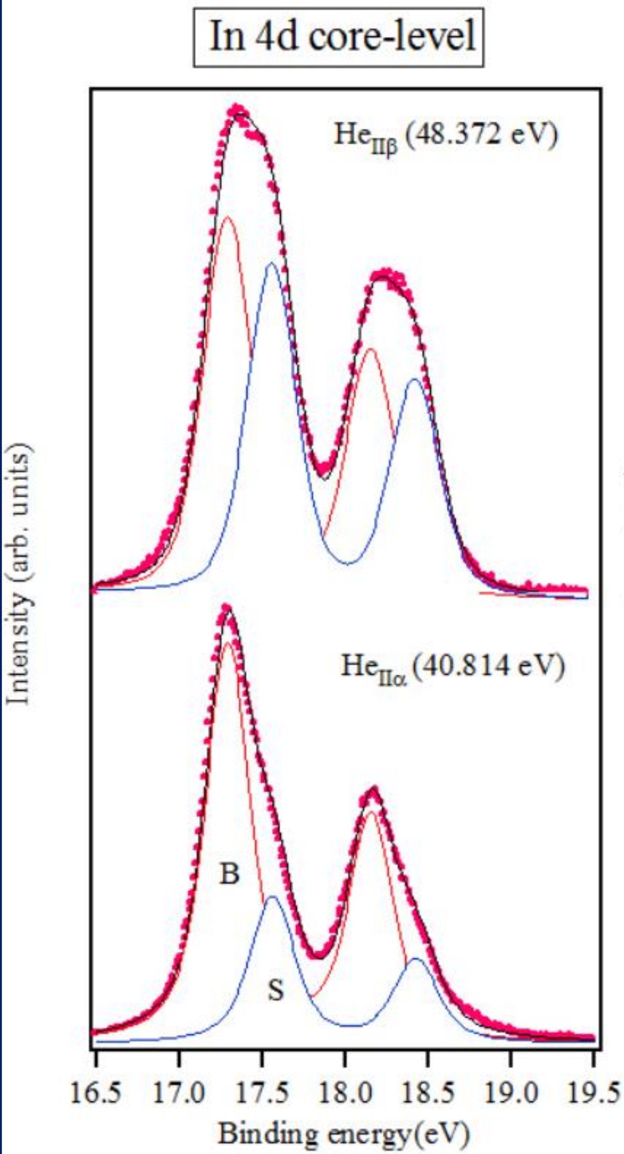


2D electron gas spatially confined Cs/InAs(110)

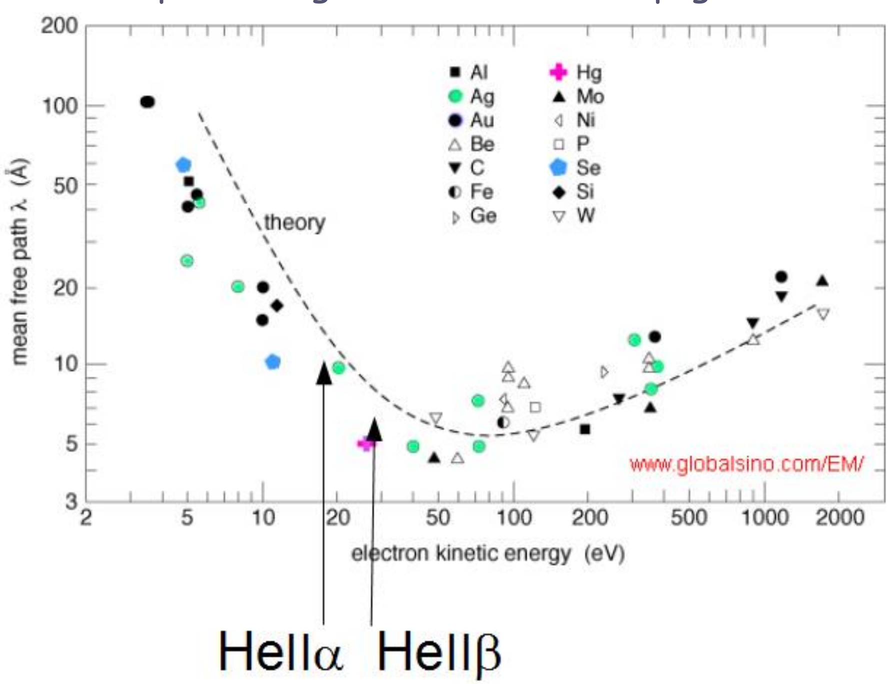


C. Mariani Surf. Sci. 454-456 (2000) 417

Surface core level shift vs. mean free path In 4d

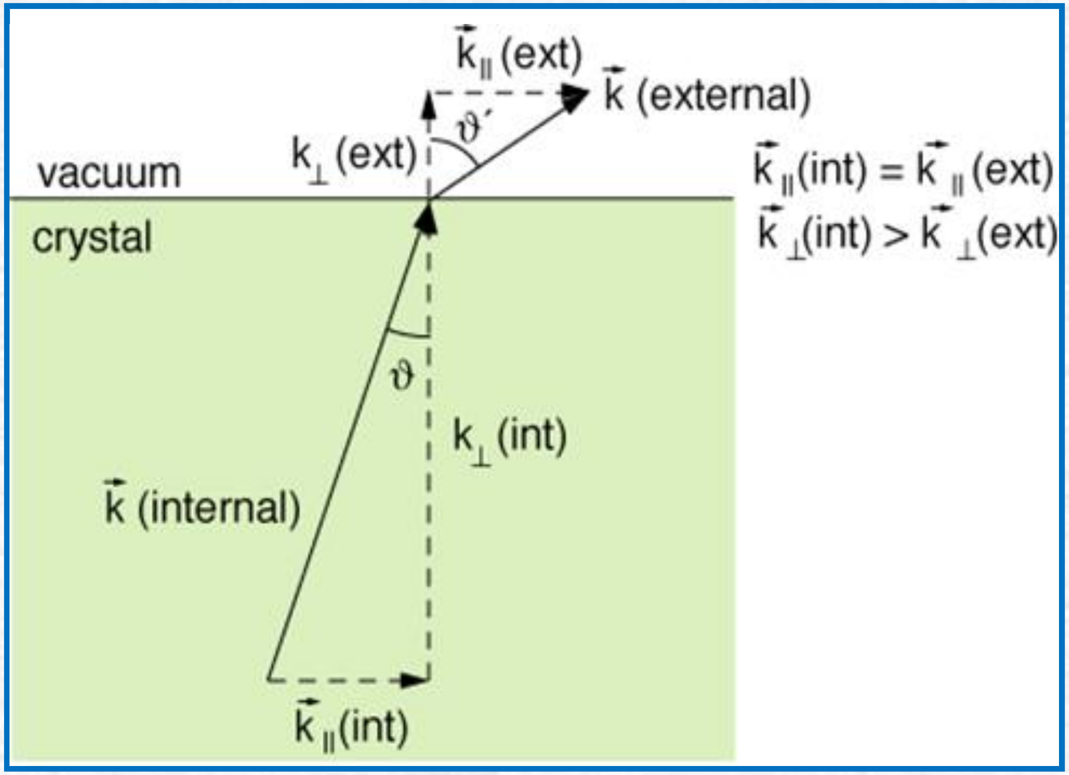


http://www.globalsino.com/EM/page4809.html



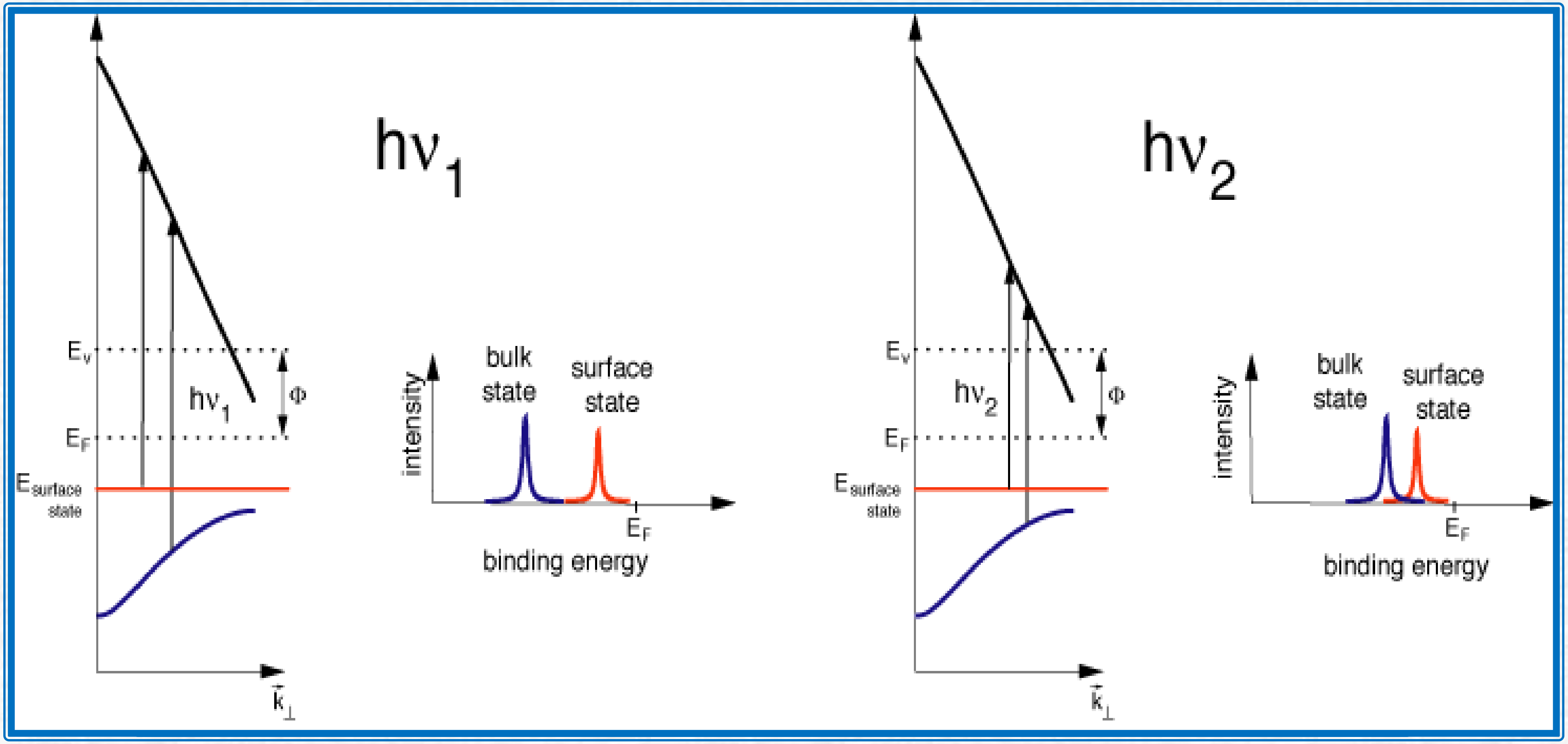
High-resolution **In-4d** core-levels at freshly cleaved **InAs(110),** taken with He_{IIa} and He_{IIb} radiation; Voigt-profiled fit with surface (S, blu lines) and bulk (B, red lines) doublet components (3/2, 5/2)

Angular resolved photoemission



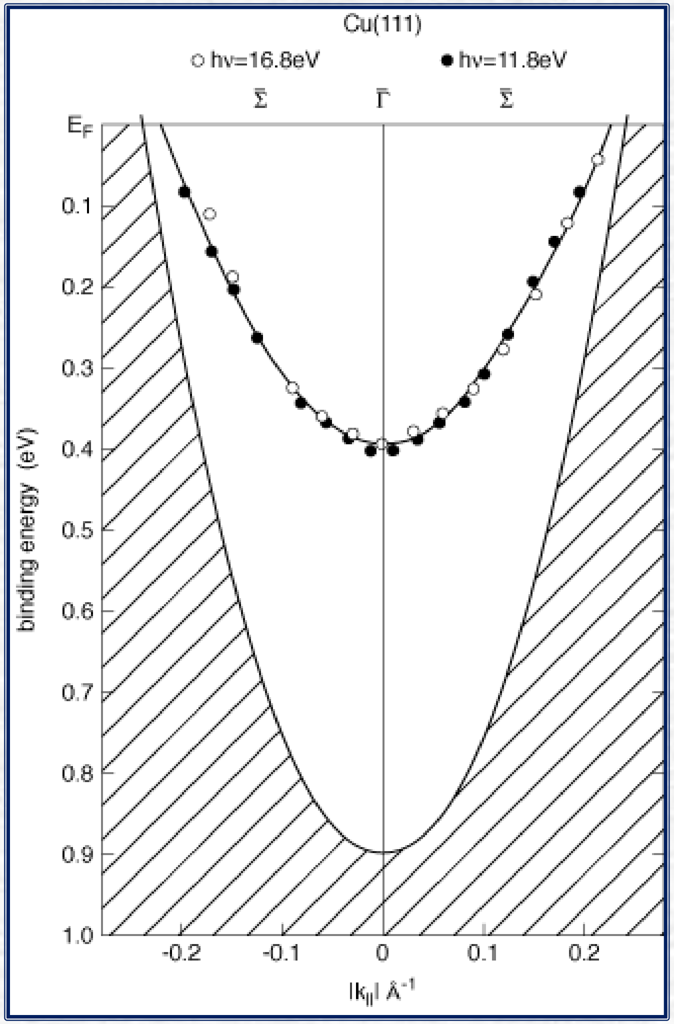
$$J_e \propto \sum_{i,f} \{ (f(E_i) [1 - f(E_f)] \} \cdot |M_{i,f}|^2 \delta(E_f - E_i - h\nu) \cdot \delta(K_i - K_f + G) \cdot \delta(K_i^{//} - K_f^{//} + G^{//})$$

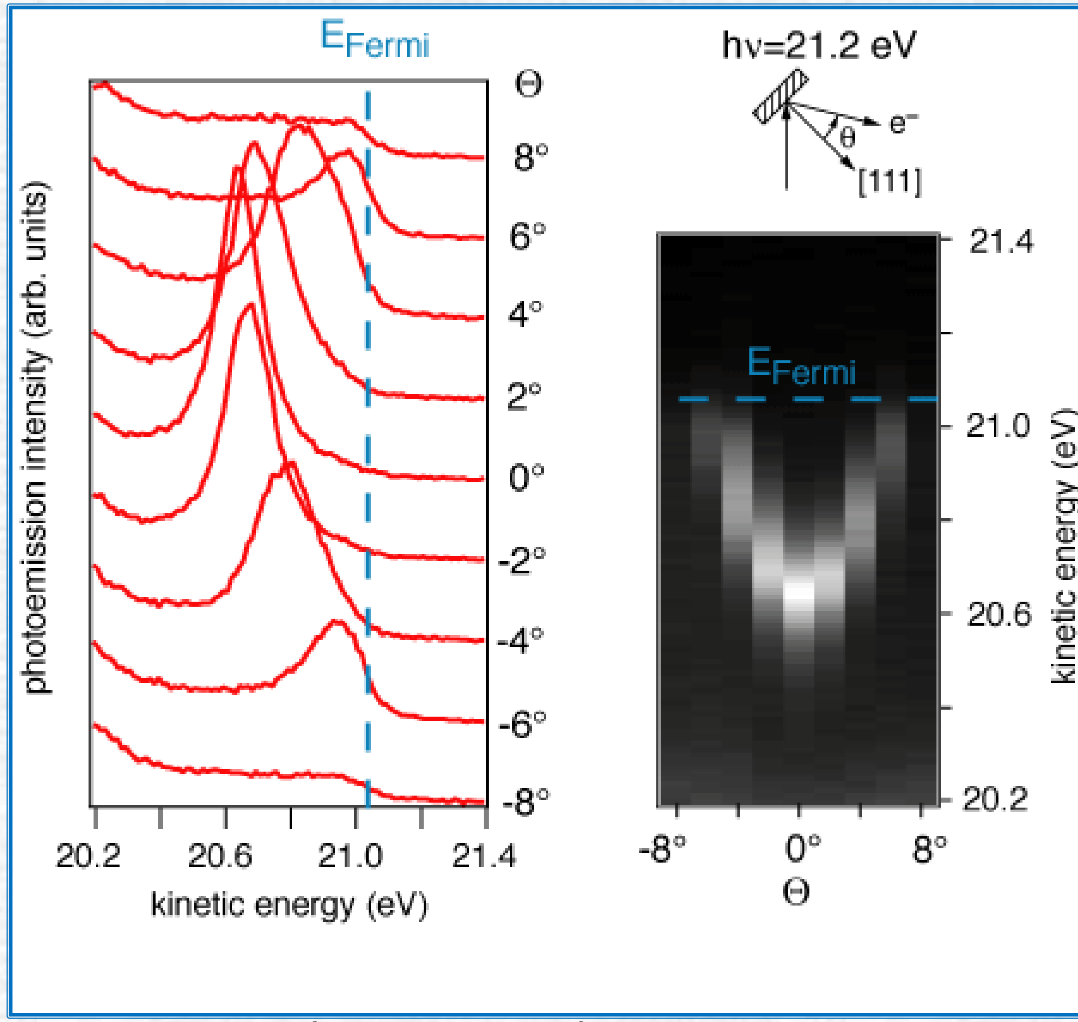
Angle resolved PES: K, $\mathcal{E}$



graphs from Ph. Hoffmann

Electronic surface states at Cu(111)

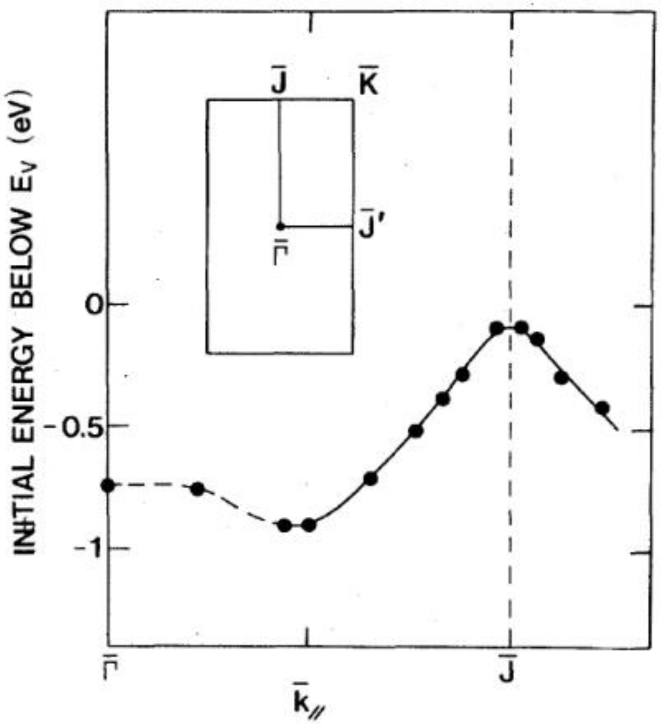


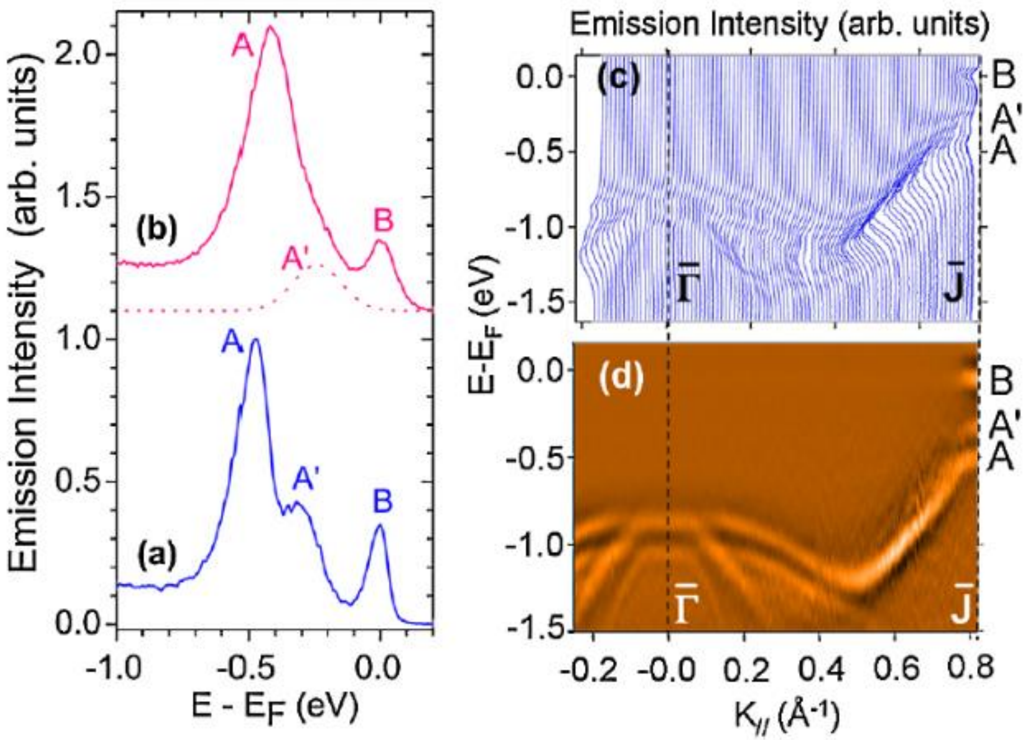


quasi-free electron surface state on Cu (111), Schockley state, s-like

S.D. Kevan, Phys. Rev. Lett. 50,526 (1983).

Dangling bonds Si(111)-(2x1)

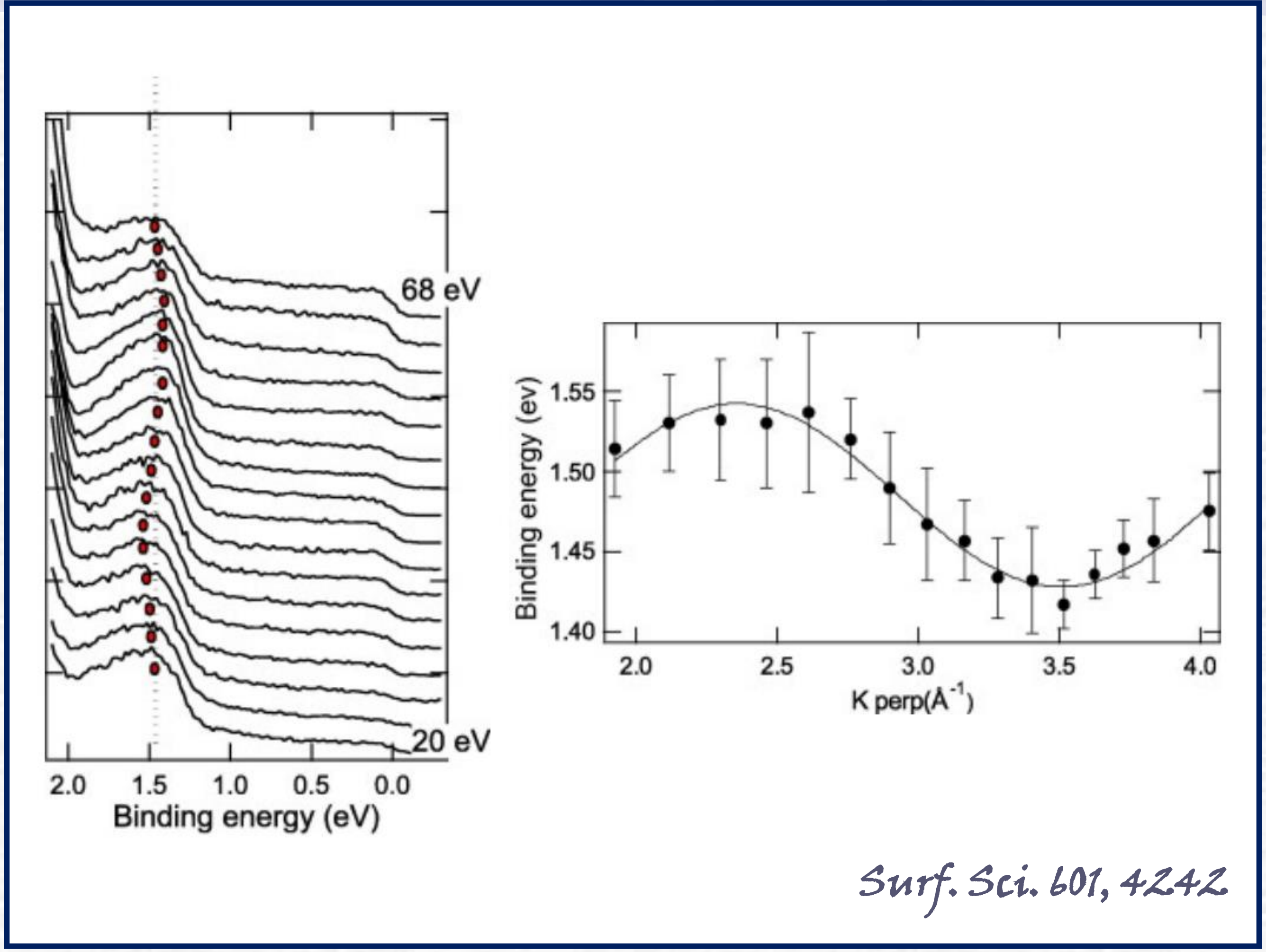




Phys Rev Lett 48, 1032   *Phys Rev Lett 106, 067601*

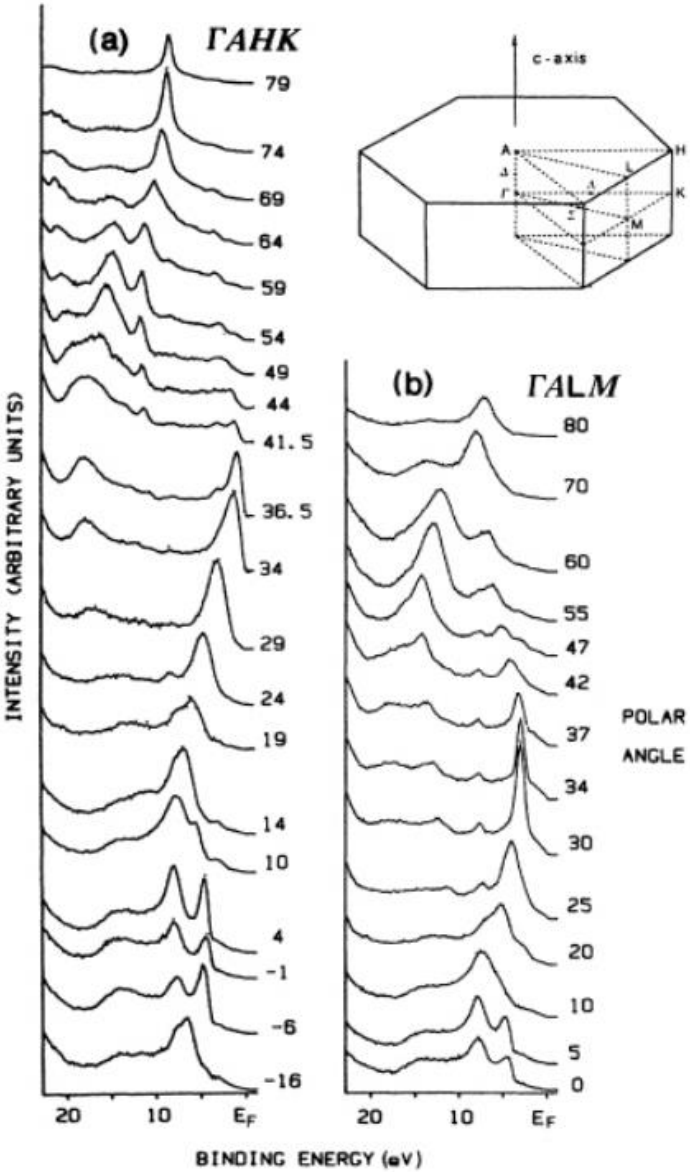
Dangling-bond surface state dispersion at the Si(111)-(2x1) reconstructed surface along the GJ direction of the Surface Brillouin Zone (SBZ). One of the first experimental ARPES dangling-bond dispersion (left panel); recent high-resolution ARPES dangling-bond dispersion.

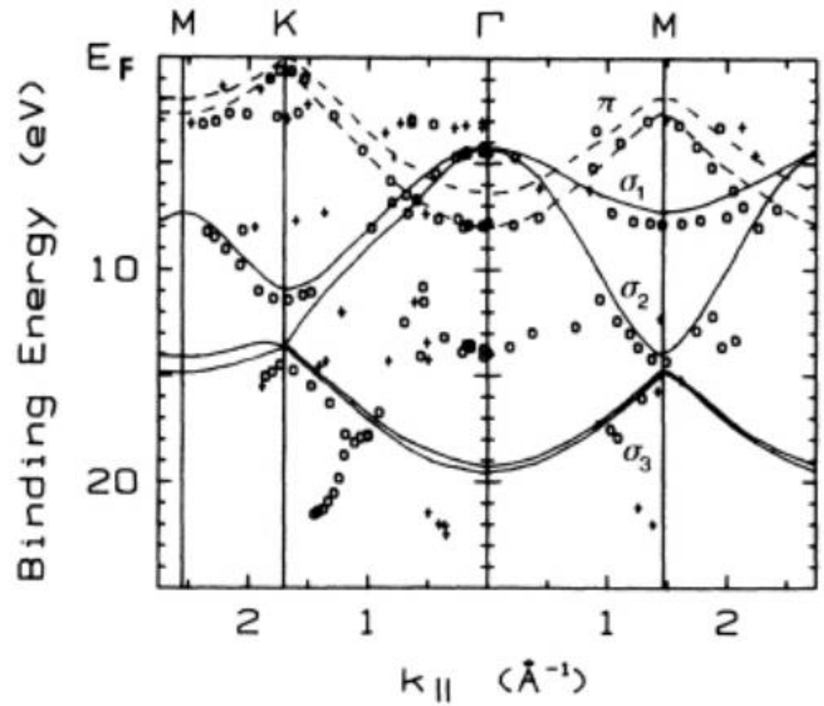
Pentacene on Cu(119): HOMO(ε,K) dispersion



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 $k_{\perp}$ (right). **E. Annese et al. Surf. Sci. 601 (2007) 4242**

ARPES graphite (HOPG)

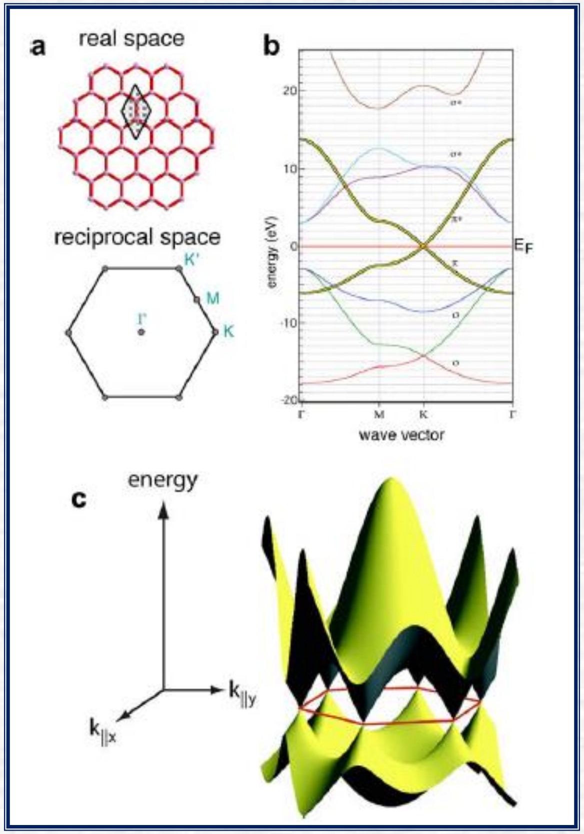


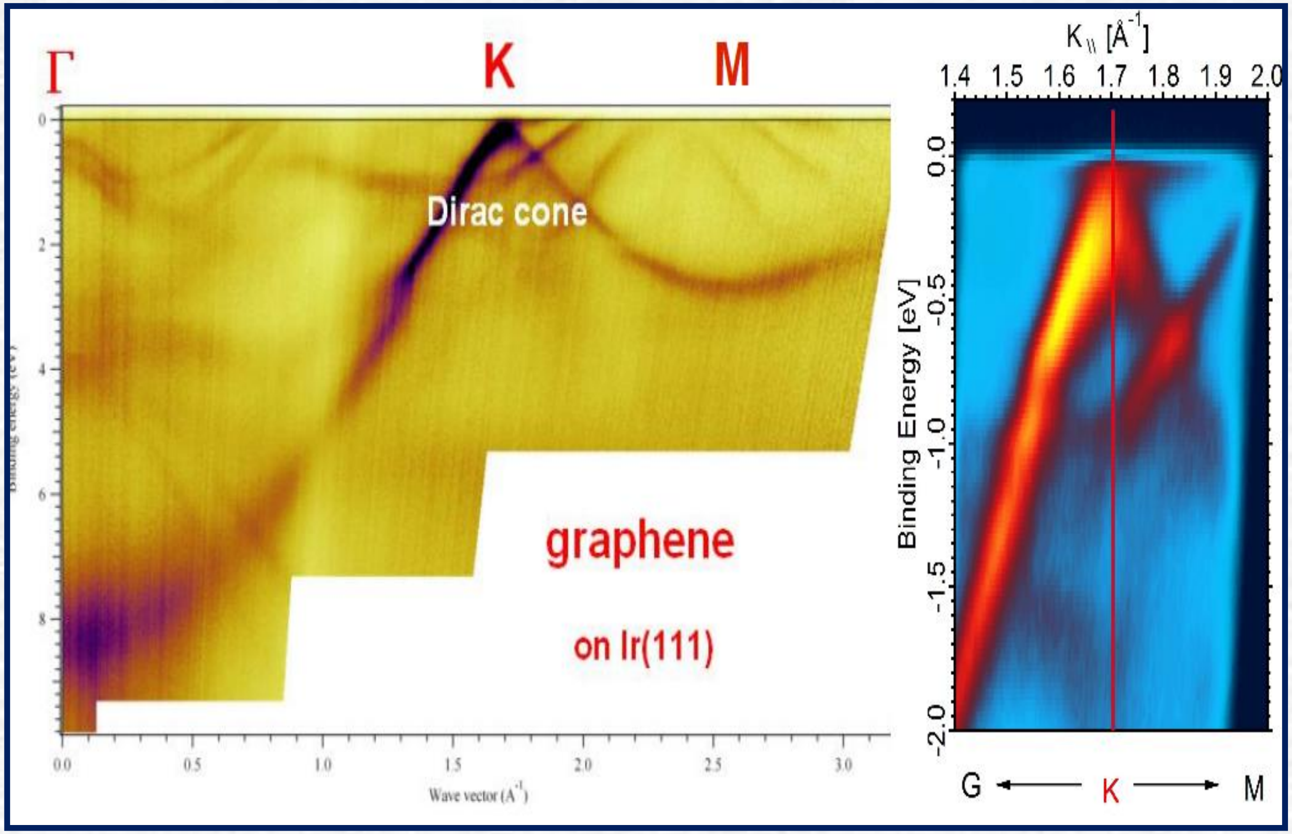


Valence band of graphite (HOPG), stacking of the ARPES spectra as a function of polar angle (left) and experimental band structure (right).

A. R. Law et al. Phys Rev B 34 (1986) 4289

Graphene band structure

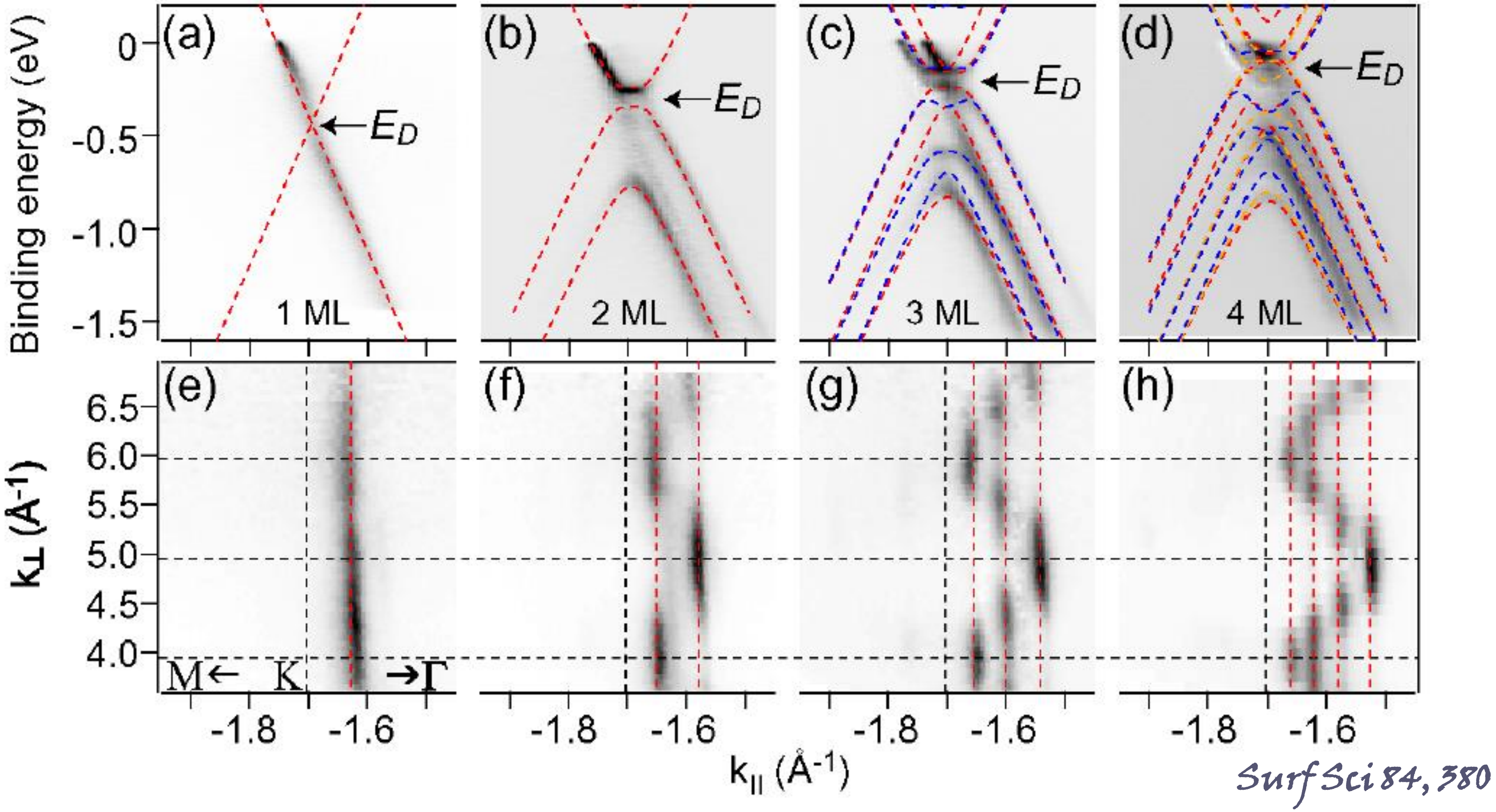




Surf Sci 84, 380 *"Synchrotron Radiation Basics, Methods and Applications» pg. 275)*

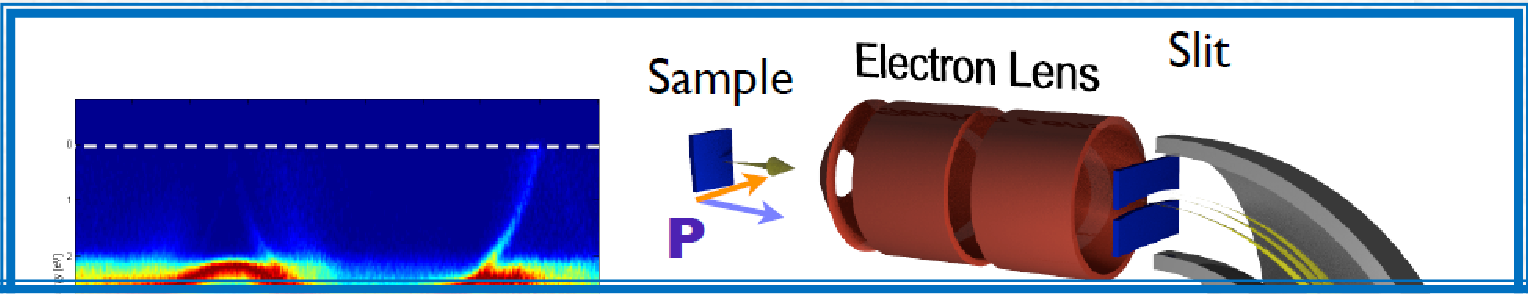
Graphene band structure along GKM and zoom of the Dirac cone around the K point of the SBZ. ARPES data taken with high-resolution ARPES and a He discharge source

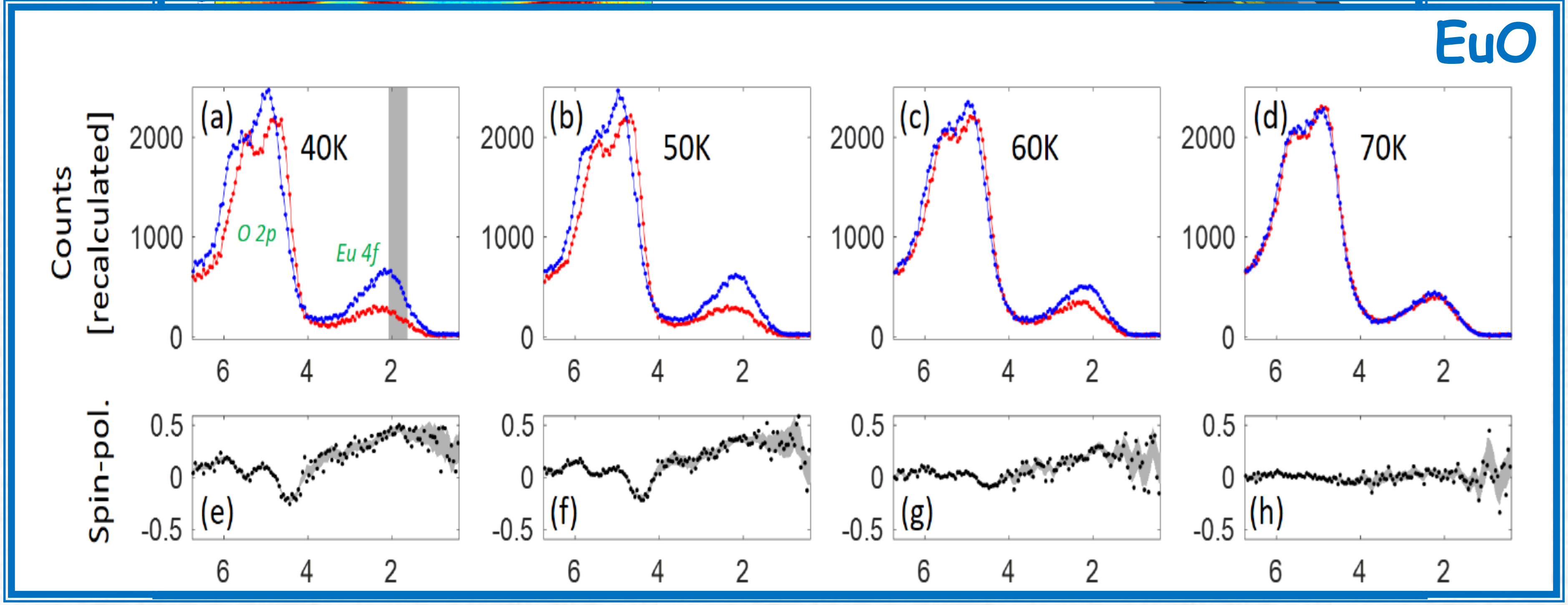
Band formation in graphene multilayers



Formation of graphene electronic band from 1-layer (extreme left) to 4-layer (extreme right) **Ohta et al. Phys Rev. Lett. 98 (2007) 206802.**

Spin Resolved Photoelectron Spectroscopy: EuO

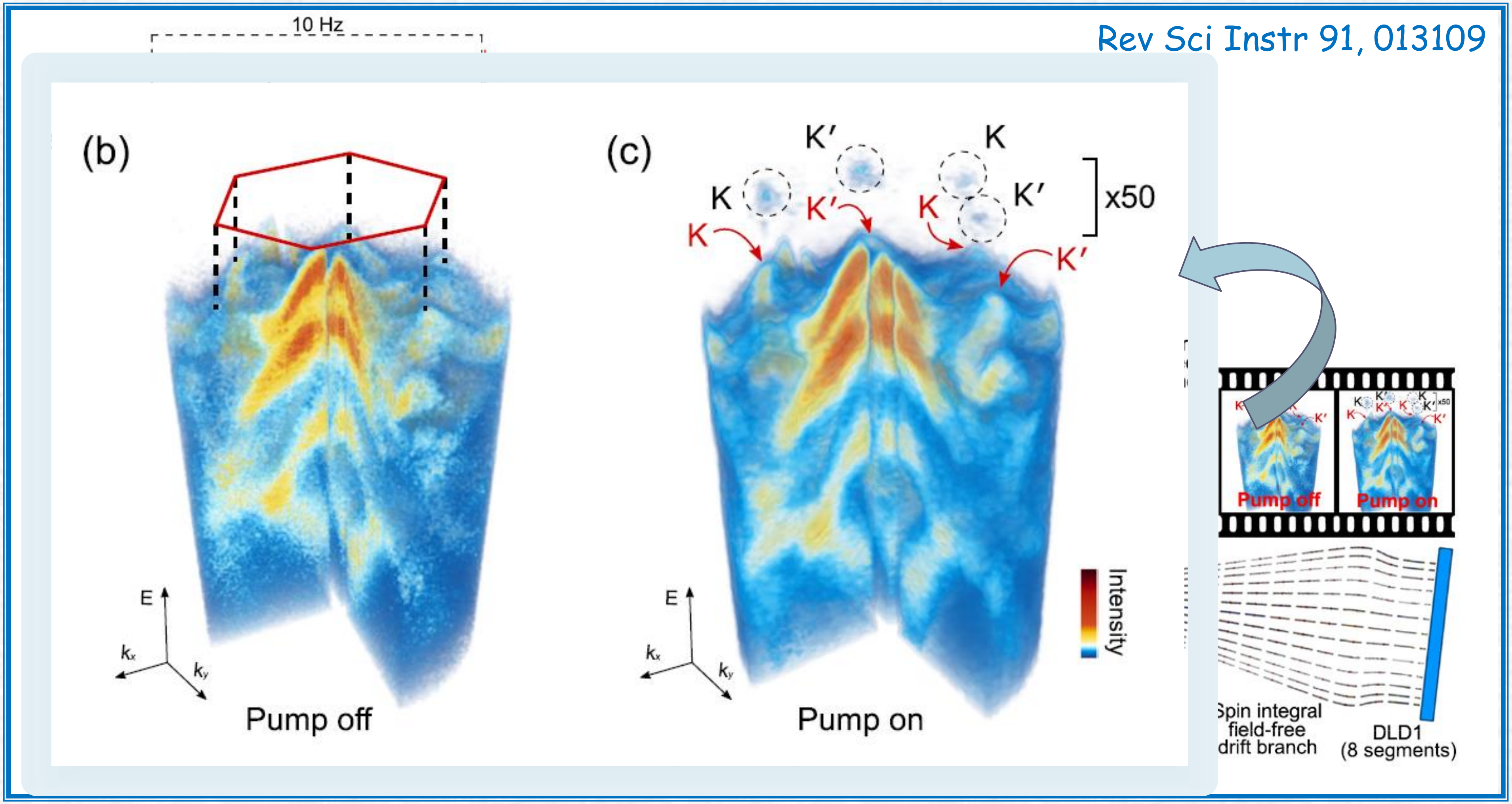




Schneider arXiv:1809.00631v2 [cond-mat.mtrl-sci] 30 Nov 2020

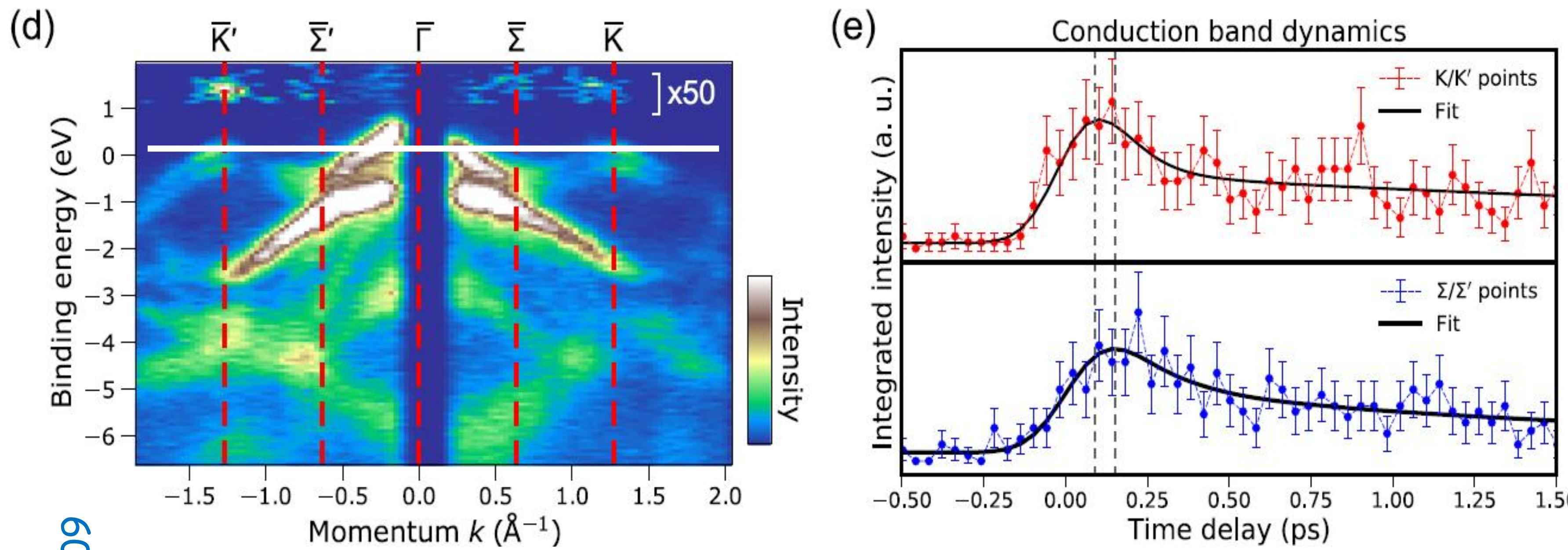
Time Resolved Photoelectron Spectroscopy: WSe_2

Rev Sci Instr 91, 013109

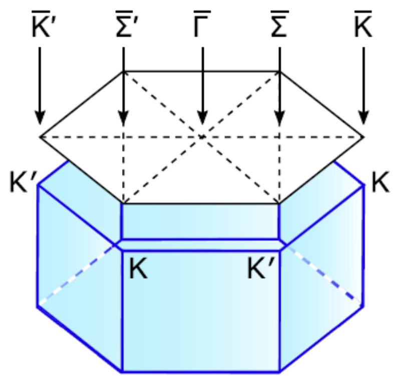


Simplified overview of the FLASH time-resolved momentum microscopy.
It acquire band-mapping movies

Time Resolved Photoelectron Spectroscopy : WSe_2

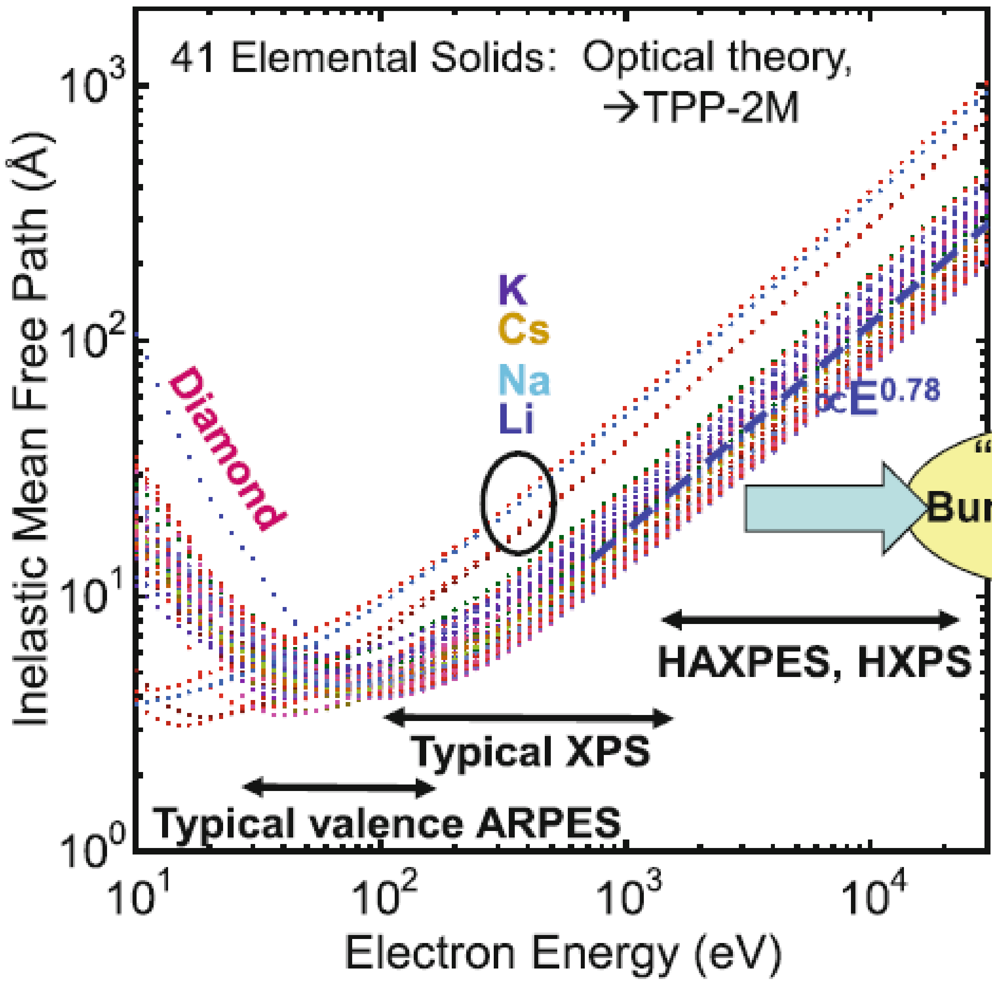


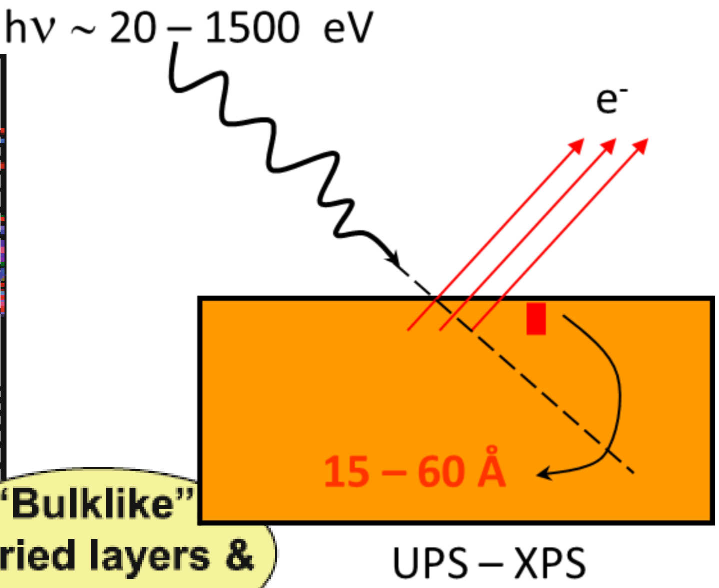
Rev Sci Instr 91, 013109



- *Momentum path sampled through the K′–Γ–K.*
- *Temporal evolution of the excited state signal integrated over a region around the K/K′ and Σ/Σ′ points in the first conduction band.*
- *The signals in the conduction band K/K′ and Σ/Σ′ valleys reach their respective maxima with a delay of ~60 fs.*

Why Hard X-ray PES (HAXPES) ?

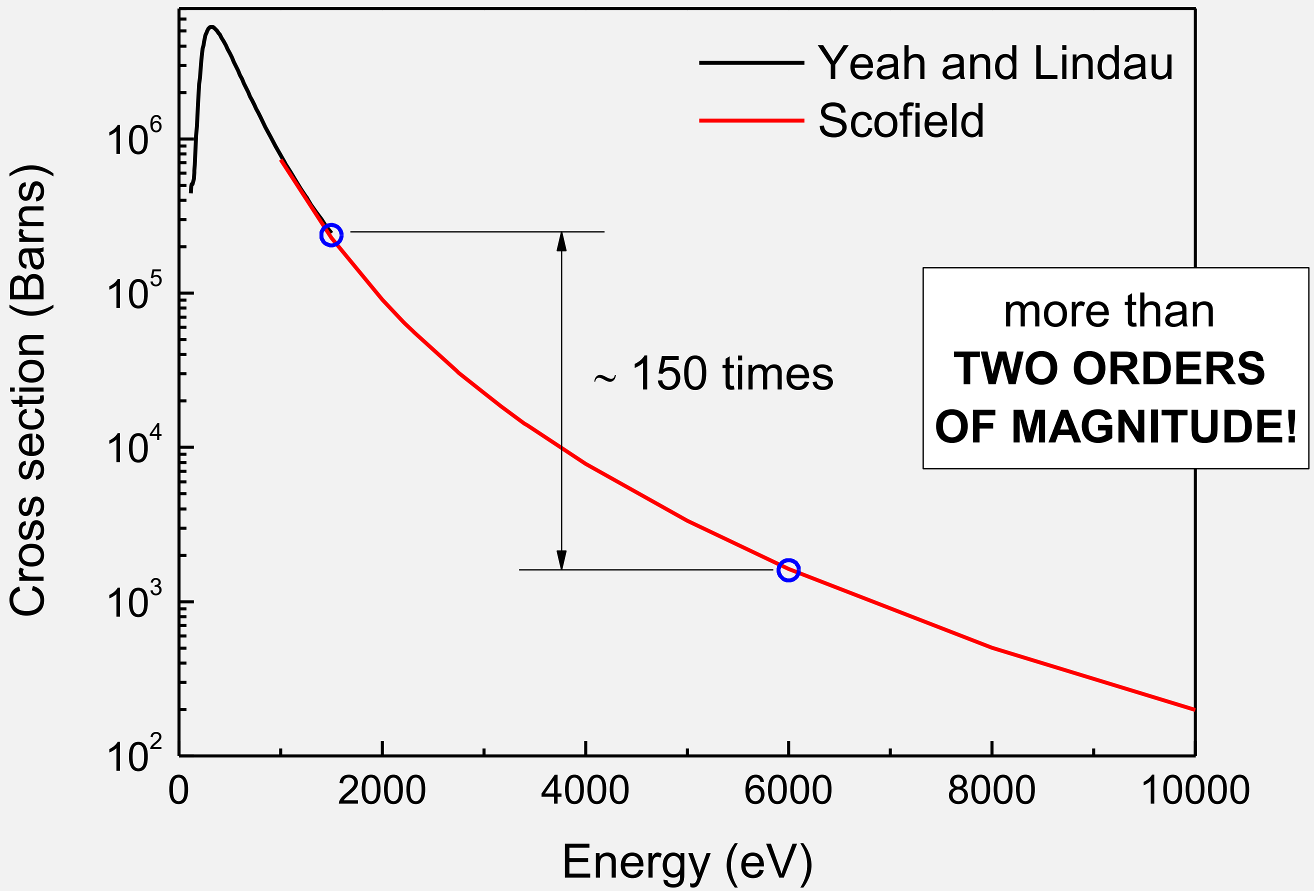




PES is extremely ***surface sensitive****: typically information is retrieved from the topmost ~ 10 – 50 Å.*

C.S. Fadley in: J.C. Woicik ed., «Hard X-ray photoelectron spectroscopy (HAXPES), Springer series in Surface Science

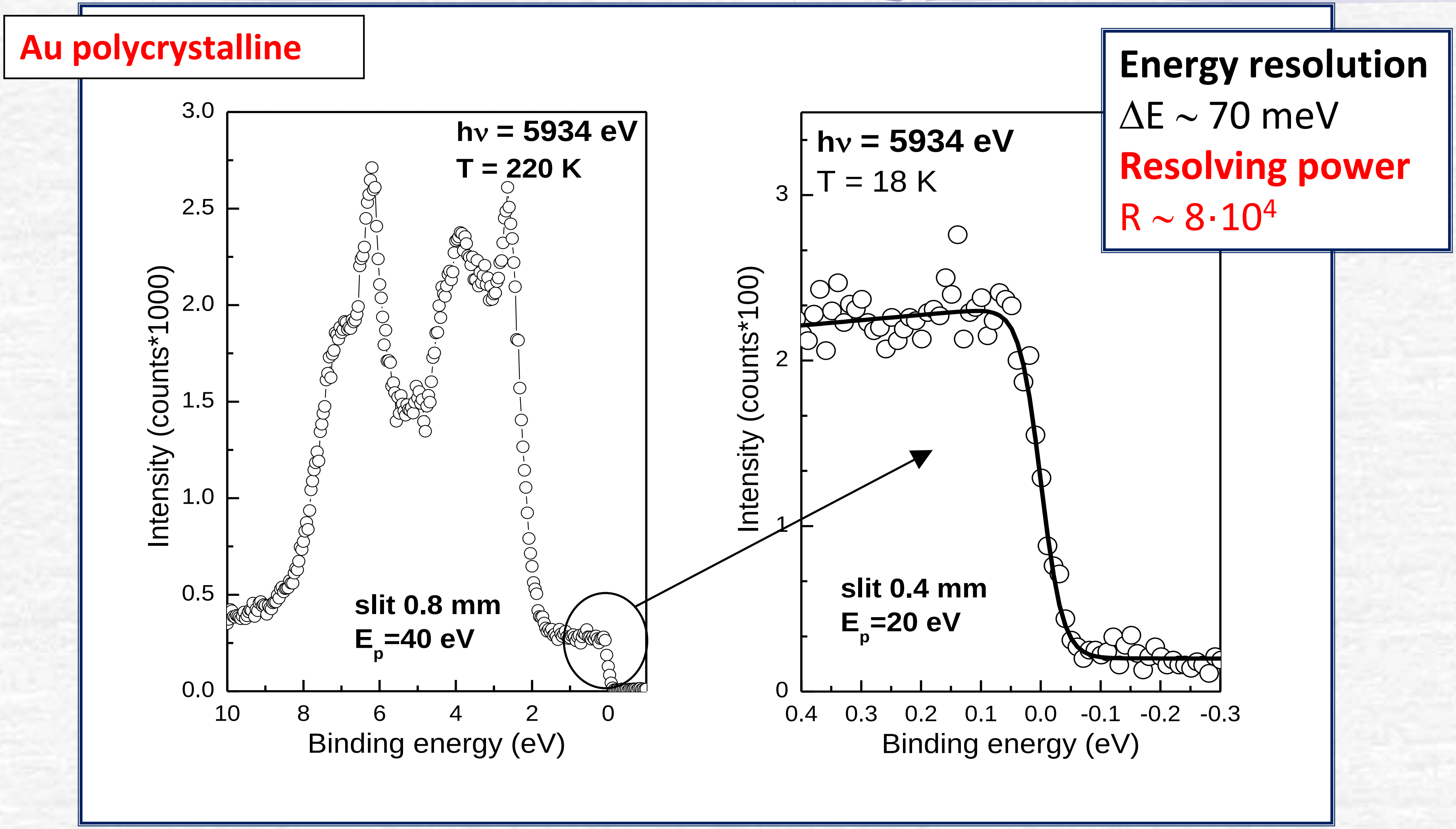
Main difficulty with HAXPES



J. J. Yeh and I. Lindau, At. Data Nucl. Data Tables **32**, 1 (1985)
J. H. Scofield, LLNL Report, UCRL-51326 (1973)

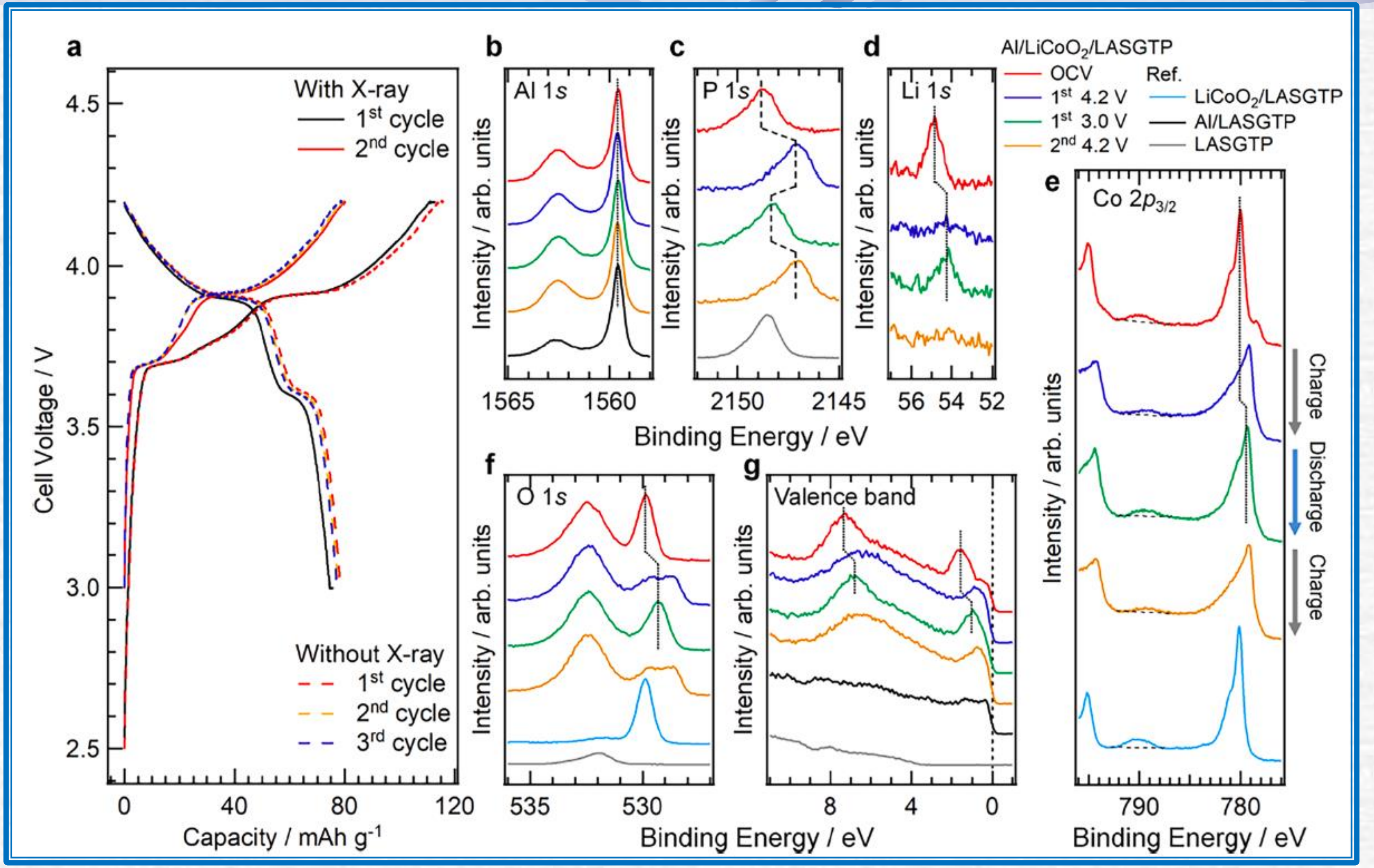
Courtesy of F. Offi

First HAXPES on valence band EDC



G. Paolicelli *et al.*, Journal of Electron Spectroscopy and Related Phenomena **144-147**, 963 (2005)

Operando HAXPES: $LiCoO_2$ battery electrode



H. Kiuchi et al. Electrochemistry Communications 118 (2020) 106790


THANK YOU
FOR YOUR ATTENTION

References

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❖S. Hufner "Photoelectron Spectroscopy, principle and applications" (Berlin Springer 2003) 3rd Edition

❖V. Schmidt "Photoionization of atoms using synchrotron radiation" Report on Progress in Physics 55(1992)1482

❖C.M. Bertoni in "Synchrotron Radiation Basics, Methods and Applications (Springer Verlag Berlin Heidelberg 2015, pg. 145)

❖C. Mariani and G. Stefani in "Synchrotron Radiation Basics, Methods and Applications (Springer Verlag Berlin Heidelberg 2015, pg. 275)

❖J.C. Woicik ed., «Hard X-ray photoelectron spectroscopy (HAXPES), Springer series in Surface Science

❖Campuzano, Norman, Randeria. Photoemission in the high-Tc superconductors. https://arxiv.org/pdf/cond-mat/0209476.pdf

❖Damascelli, Hussain, Shen. Angle-resolved photoemission studies of the cuprate superconductors. Rev. Mod. Phys. 75 473 (2003)

❖Damascelli. Probing the Electronic Structure of Complex Systems by ARPES. Physica Scripta. Vol. T109, 61–74, 2004 (https://www.cuso.ch/fileadmin/physique/document/Damascelli_ARPES_CUSO_2011_Lecture_Notes.pdf)