Overview of spectroscopies IV

Simo Huotari

University of Helsinki, Finland

TDDFT school, Benasque, Spain, January 2012

Outline

Part 1 – Absorption techniques

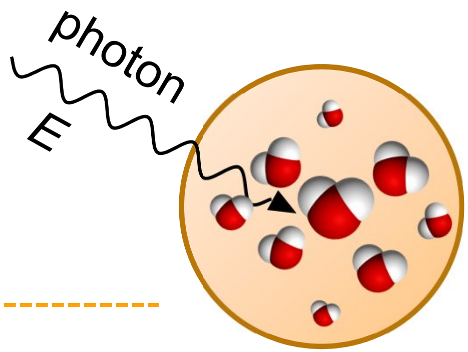
Part 2 – Scattering techniques

Part 3 – Photoemission

Part 4 – Optical techniques

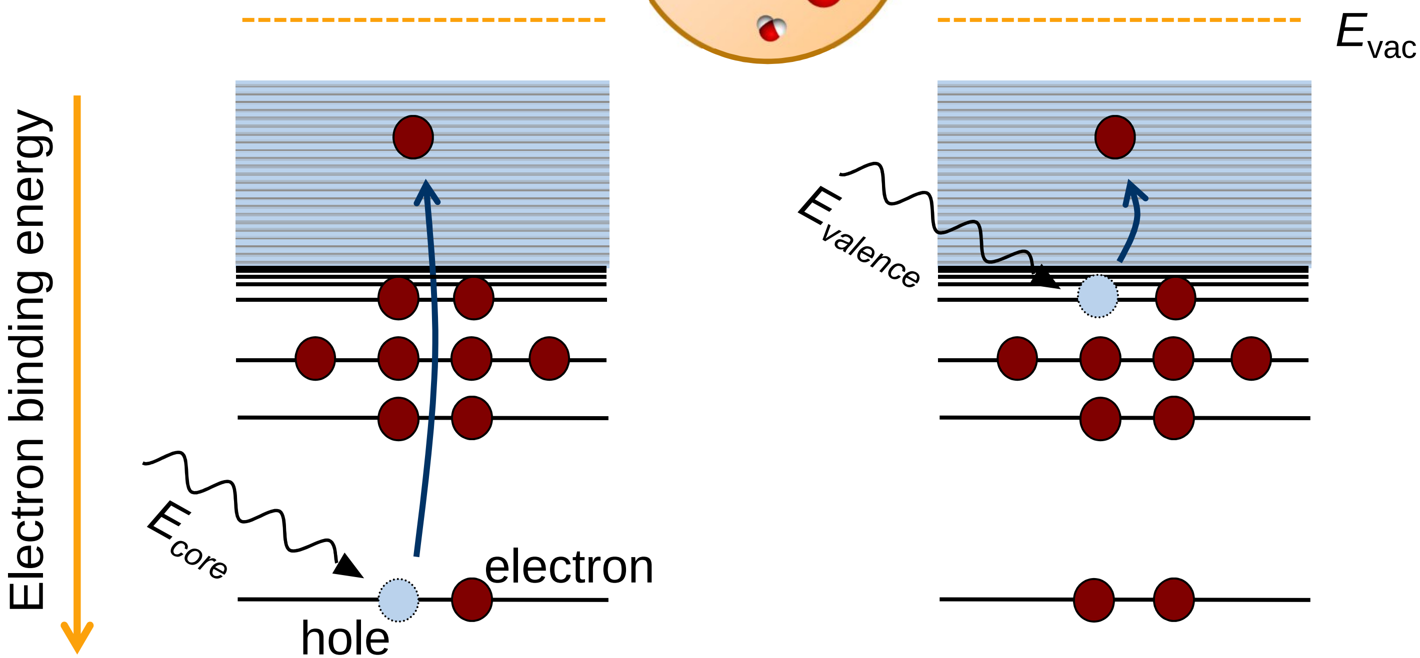
Photon absorption

$\mathbf{p} \cdot \mathbf{A}$ term in first order



Probability for absorption process $1 - \exp\left(-\frac{\mu}{\rho}\rho d\right)$

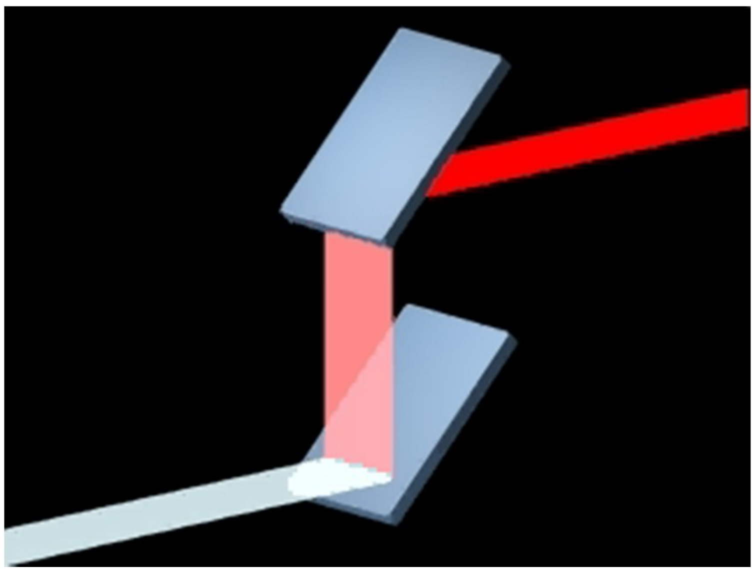
μ/ρ [cm^2/g] = mass absorption coefficient

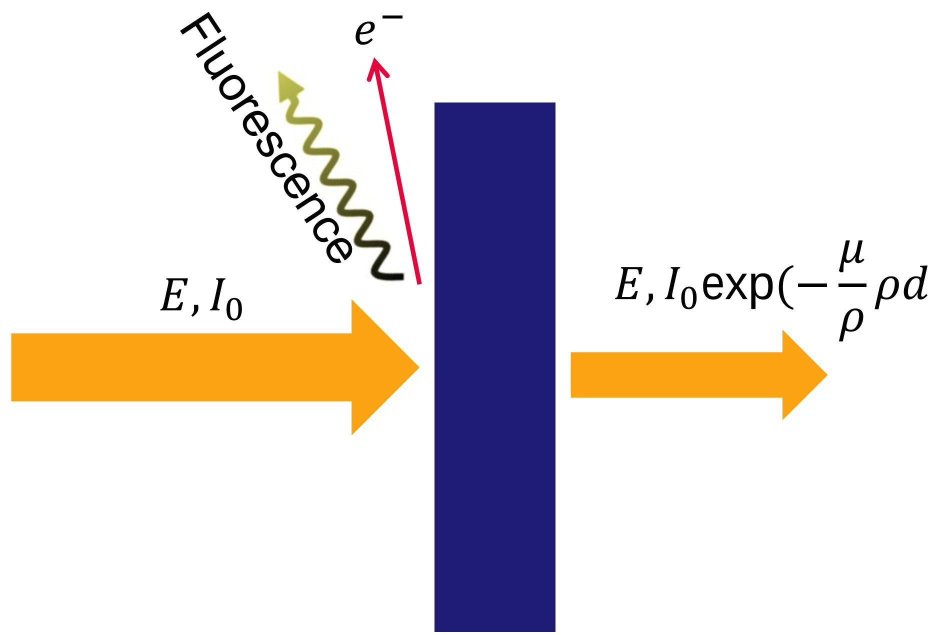


Photon energy E, polarisation

Absorption spectroscopy

A double-crystal x-ray monochromator: perfect Si crystals

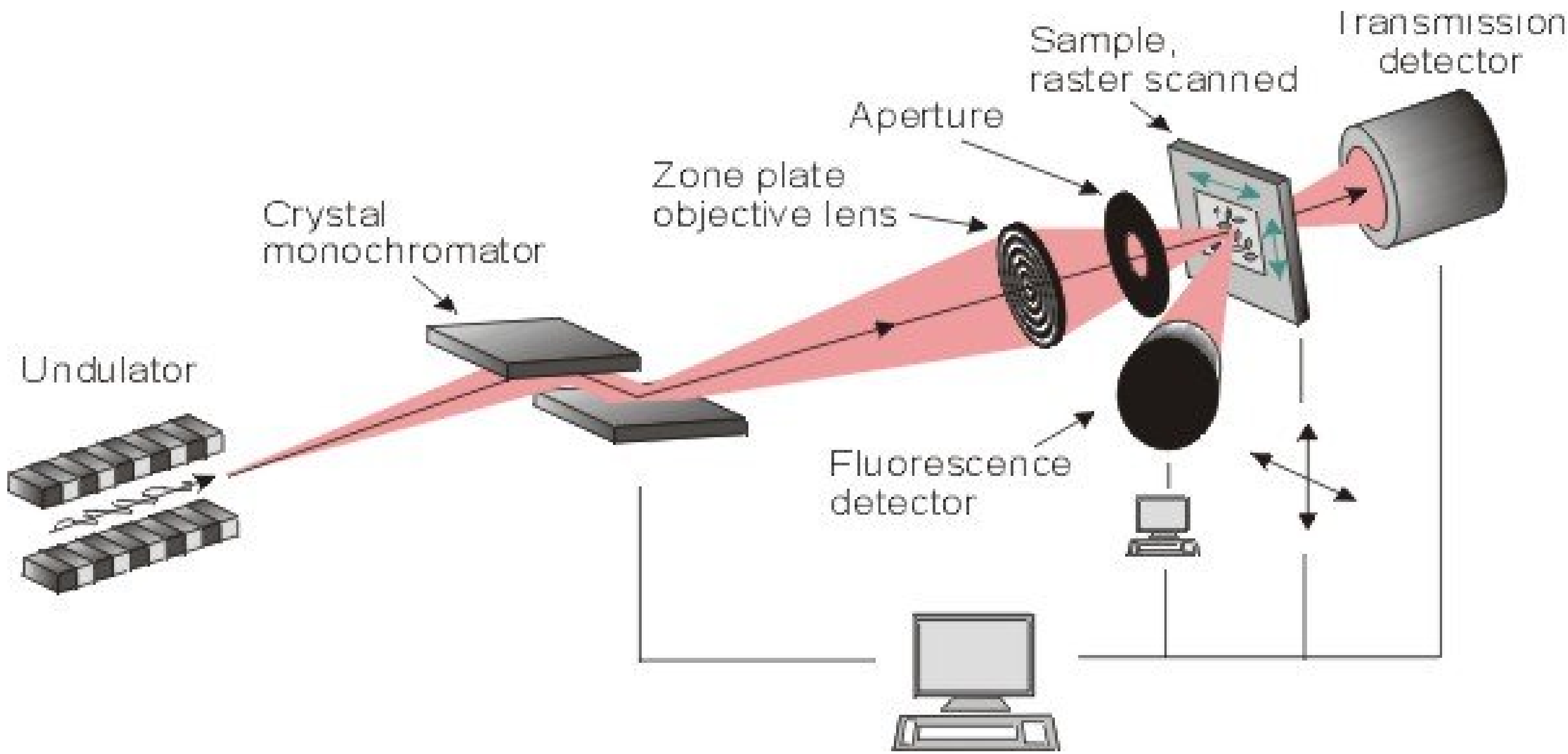




Bragg's law: $\lambda = 2d \sin\theta$

Measure at least one of:
- transmission
- fluorescence yield
- electron yield

Vacuum ultraviolet + x-ray absorption



Scanning x-ray microscope, ESRF ID21
http://www.esrf.eu/UsersAndScience/Experiments/Imaging/ID21/Sxm/Sxm

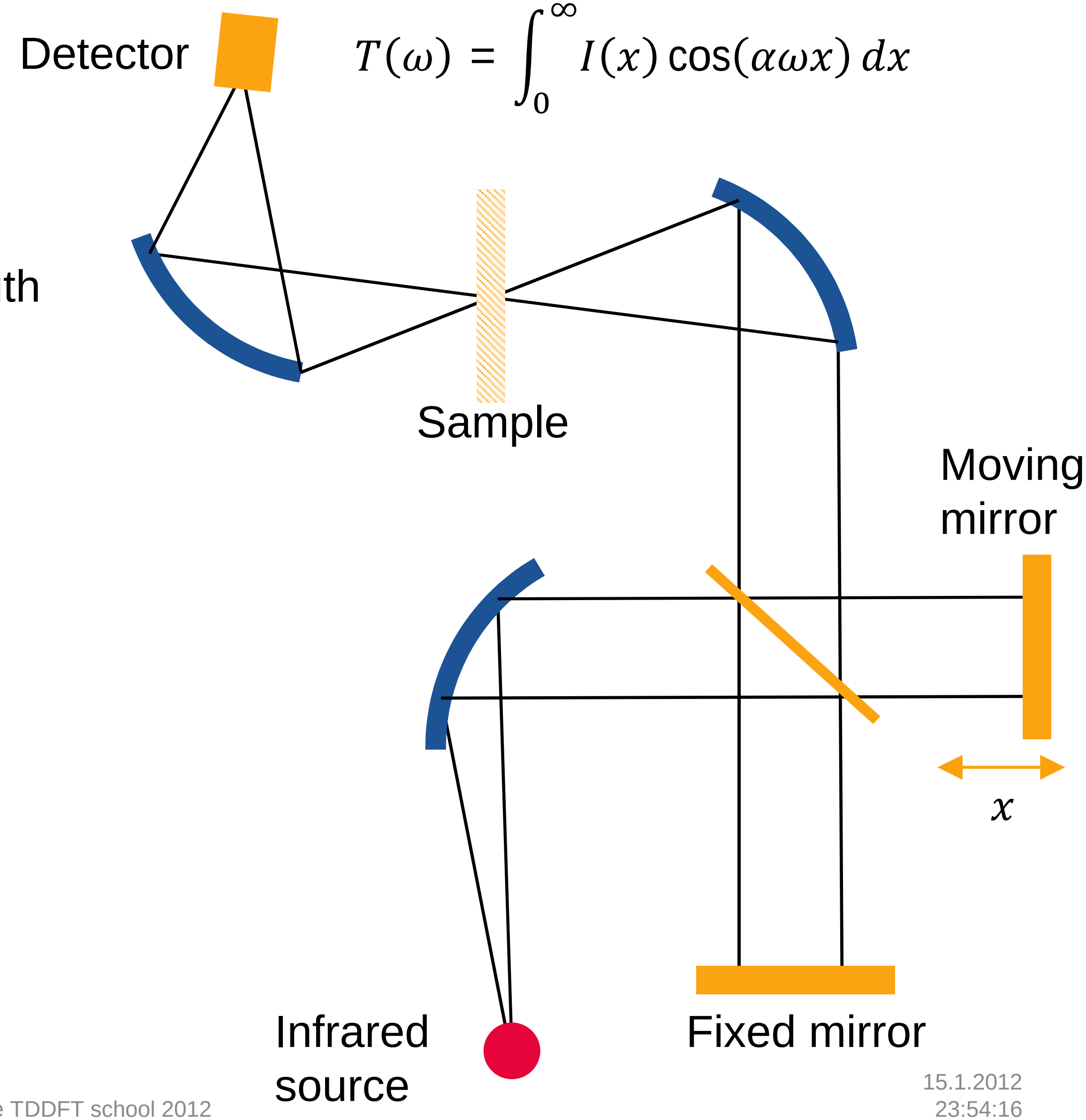
Fourier transform IR

$$T(\omega) = \int_0^\infty I(x)\cos(\alpha\omega x)\,dx$$

Transmission spectra obtained from a Fourier transform of signal as a function of wave path length difference

Infrared region of the excitations:

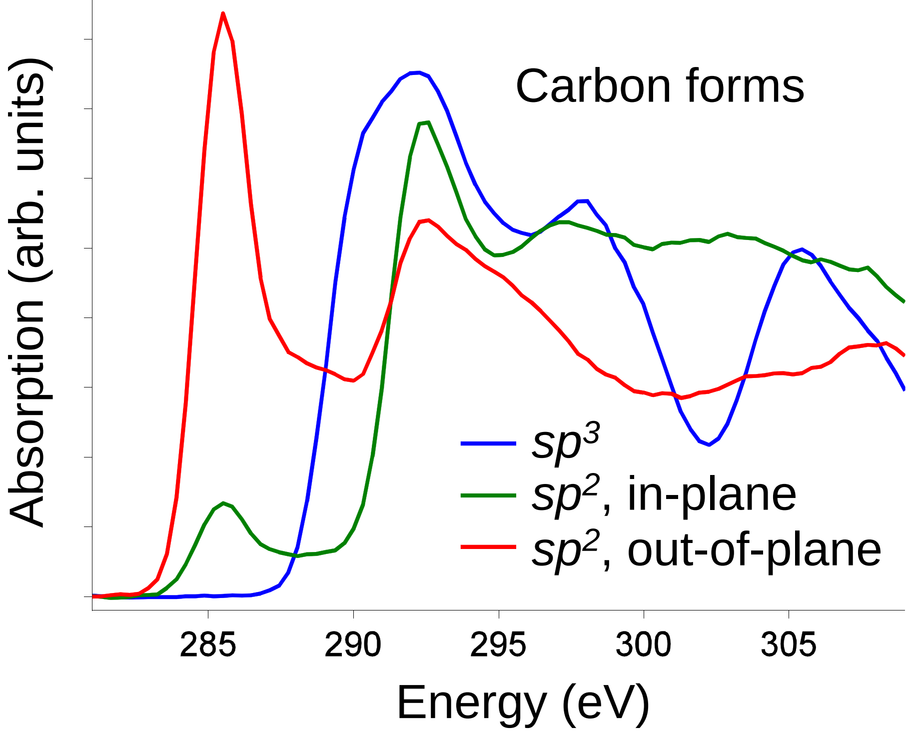
- Molecular dynamics
- Force fields
- Identification of compounds and their environment

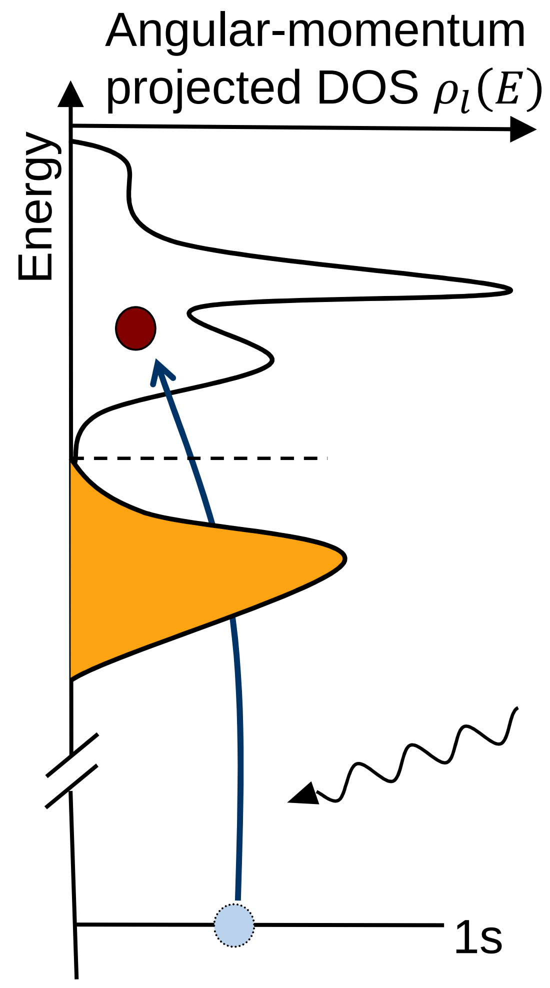


X-ray absorption

$\mathbf{p} \cdot \mathbf{A}$ term in first order

$\mu(E) = M(E)\rho_l(E)$
$M(E)$ is the matrix element
(depends weakly on E)



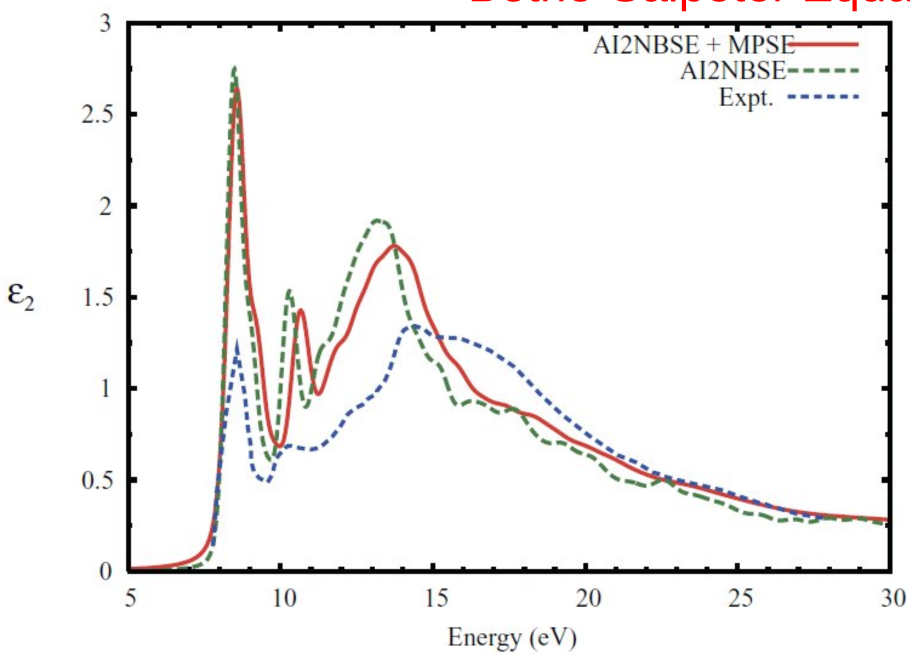


PHYSICAL REVIEW B **85**, 045101 (2012)

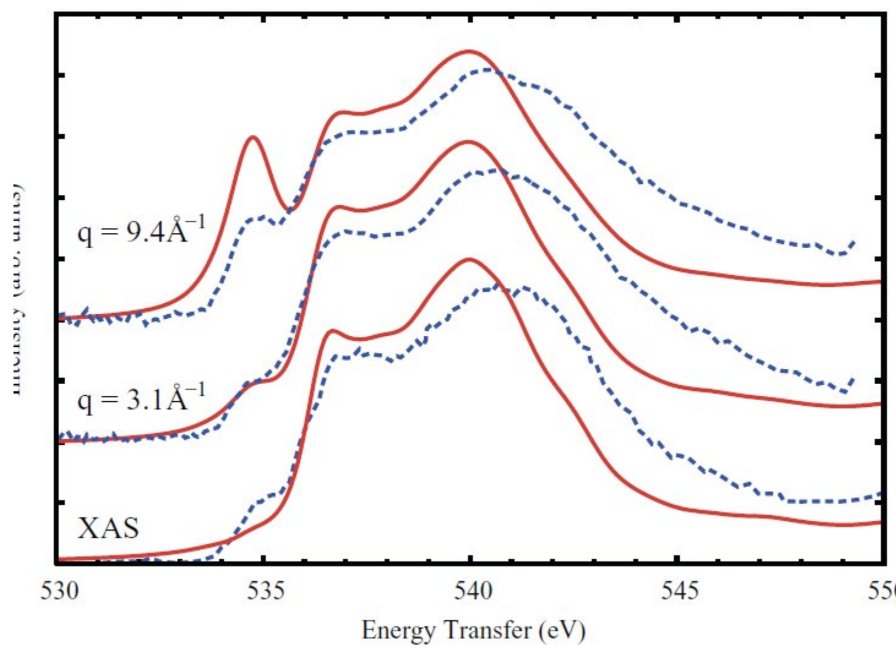
Theoretical optical and x-ray spectra of liquid and solid H_2O

J. Vinson,[1] J. J. Kas,[1] F. D. Vila,[1] J. J. Rehr,[1] and E. L. Shirley[2]
[1]*Department of Physics, University of Washington, Seattle, Washington 98195, USA*
[2]*National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA*
(Received 17 October 2011; revised manuscript received 13 December 2011; published 3 January 2012)

Bethe-Salpeter Equation with GW self energies



Optical (Q=0) valence spectra



1s-to-valence –spectra (Q=0 and Q>0)

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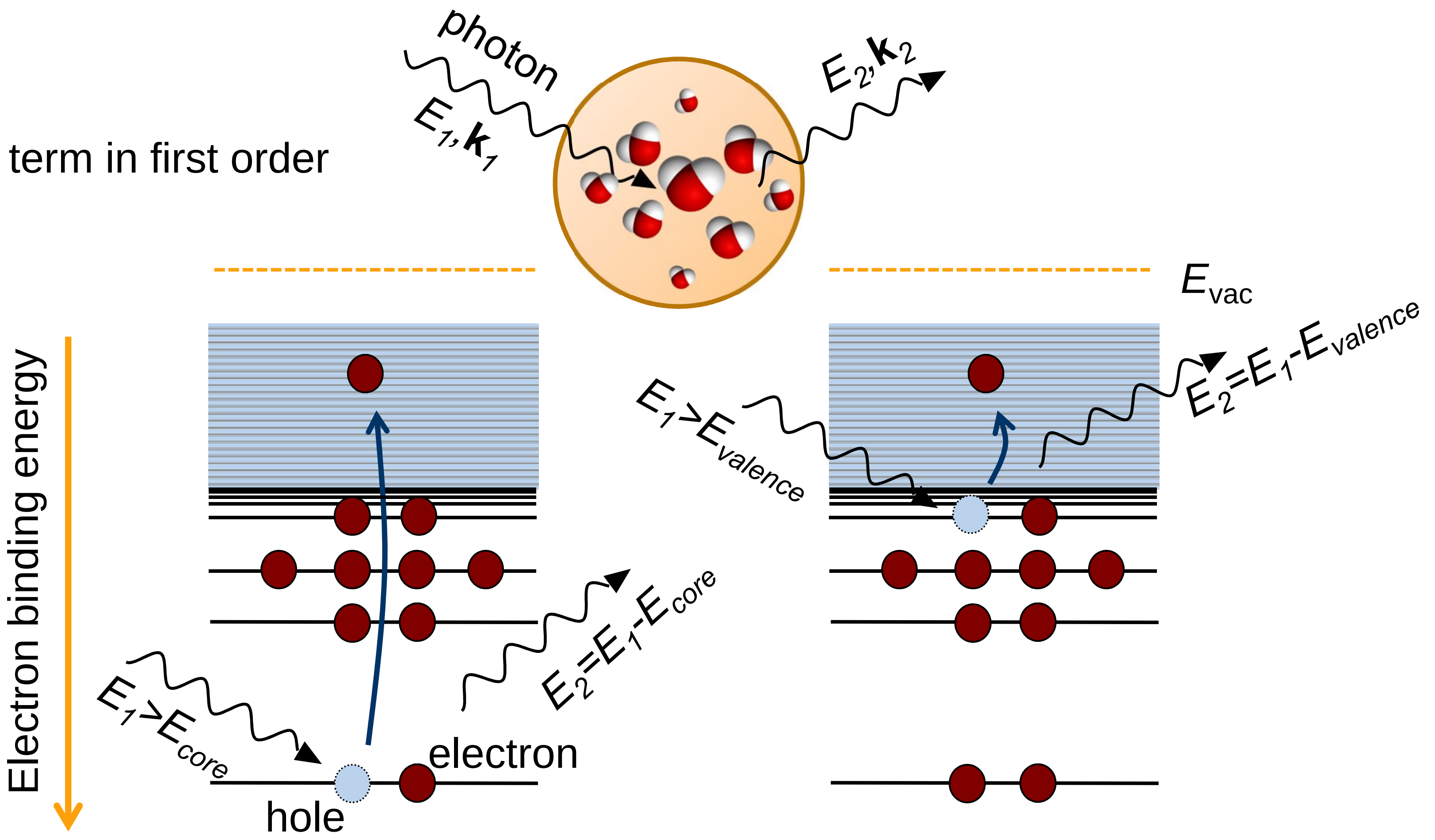
Inelastic scattering

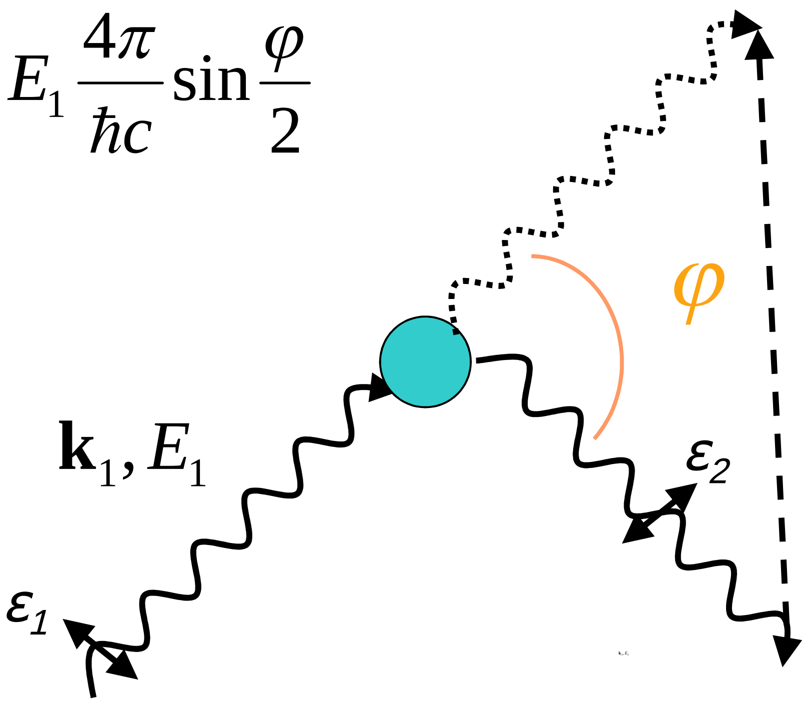
$\mathbf{A} \cdot \mathbf{A}$ term in first order



Energy transfer $E=E_1-E_2$
Momentum transfer $q=k_1-k_2$

Non-resonant x-ray scattering

$$Q \approx E_1 \frac{4\pi}{\hbar c} \sin\frac{\varphi}{2}$$



$$\boxed{\mathbf{Q} = \mathbf{k}_1 - \mathbf{k}_2}$$

$$\frac{d^2\sigma}{dE\,d\Omega} = r_e^2 (\boldsymbol{\epsilon}_1 \cdot \boldsymbol{\epsilon}_2)^2\, S(\mathbf{Q}, E)$$

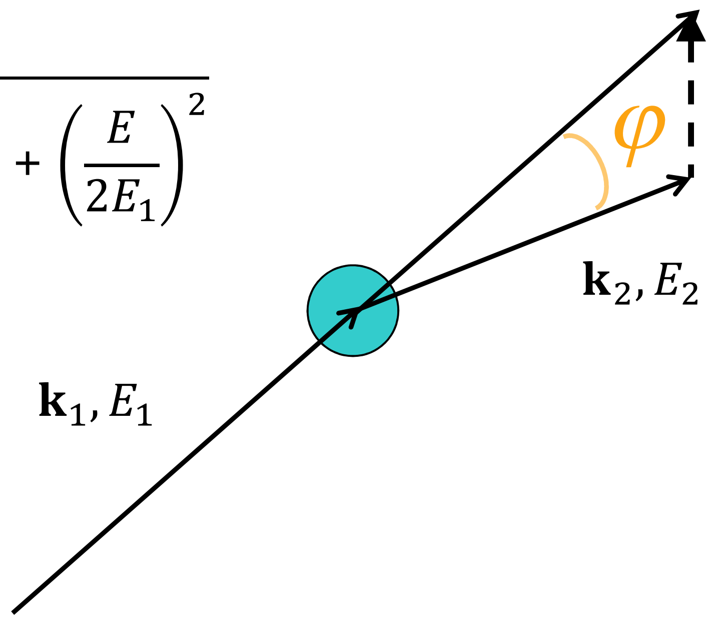
Momentum transfer	$\mathbf{Q} = \mathbf{k}_1 - \mathbf{k}_2$
Energy transfer	$E = E_1 - E_2$

Dynamic structure factor S(Q,E)

$$S(\mathbf{Q}, E) = \frac{Q^2}{4\pi^2 n} \mathrm{Im}\left[\frac{-1}{\varepsilon(\mathbf{Q}, E)}\right]$$

Electron scattering

$$Q = k_1 \sqrt{\varphi^2 + \left(\frac{E}{2E_1}\right)^2}$$



$$\mathbf{Q} = \mathbf{k}_1 - \mathbf{k}_2$$

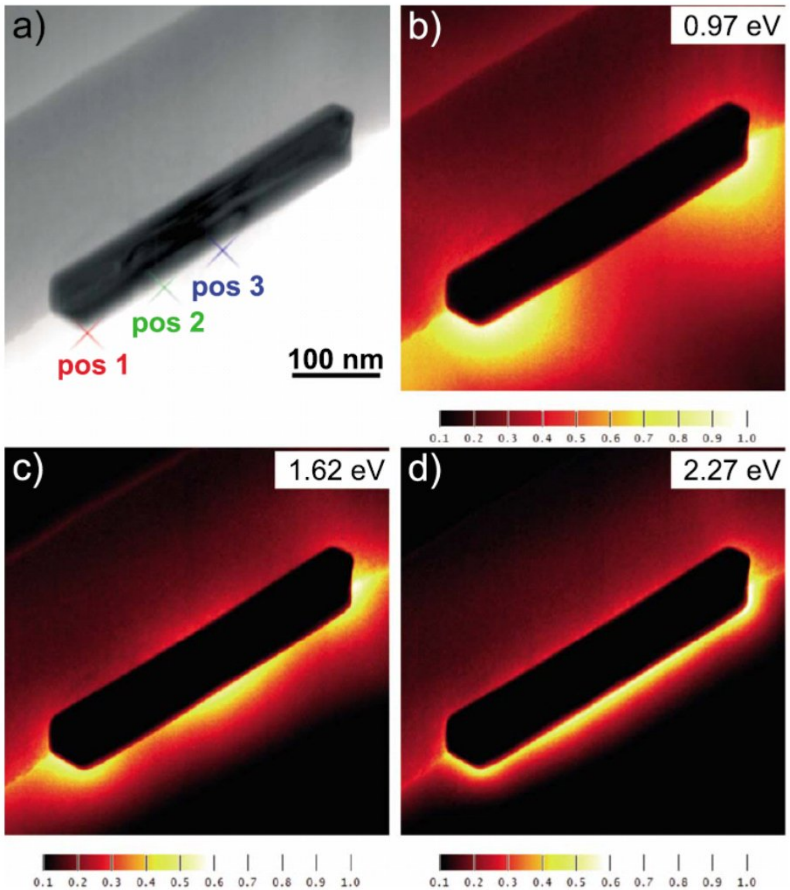
$$\frac{d^2\sigma}{dE\,d\Omega} = \frac{4\hbar\gamma^2}{a_0^2 q^4} S(\mathbf{Q}, E)$$

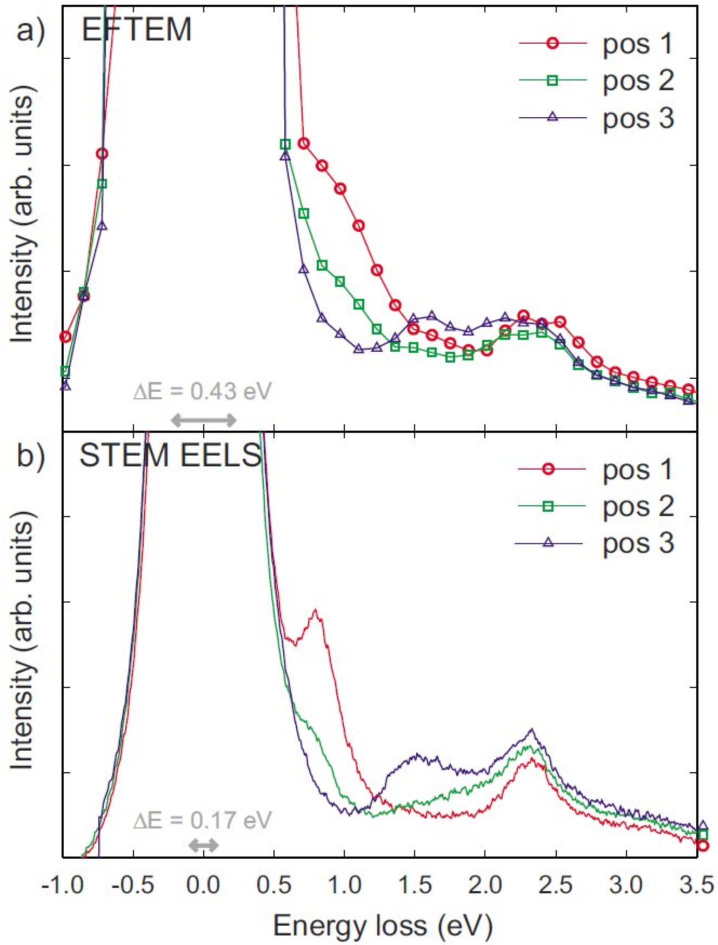
*Dynamic structure factor S(*Q*,E)*

$$S(\mathbf{Q}, E) = \frac{Q^2}{4\pi^2 n} \mathrm{Im}\left[\frac{-1}{\varepsilon(\mathbf{Q}, E)}\right]$$

Momentum transfer	$\mathbf{Q} = \mathbf{k}_1 - \mathbf{k}_2$
Energy transfer	$E = (\hbar^2/2m)(k_1 - k_2)$

Electron microscopy





Plasmon eigenmodes of a gold nanoparticle

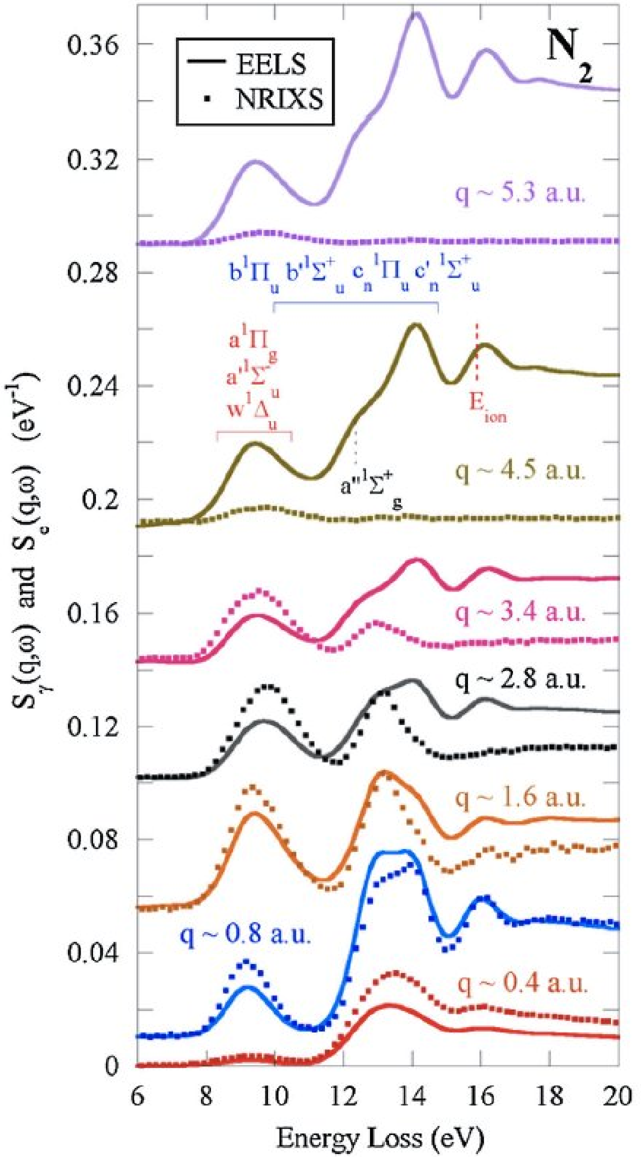
B. Schaffer et al. PRB 79, 041401(R) (2009)

First Born approximation

J. A. Bradley et al.,
PRL 105, 053202 (2010)

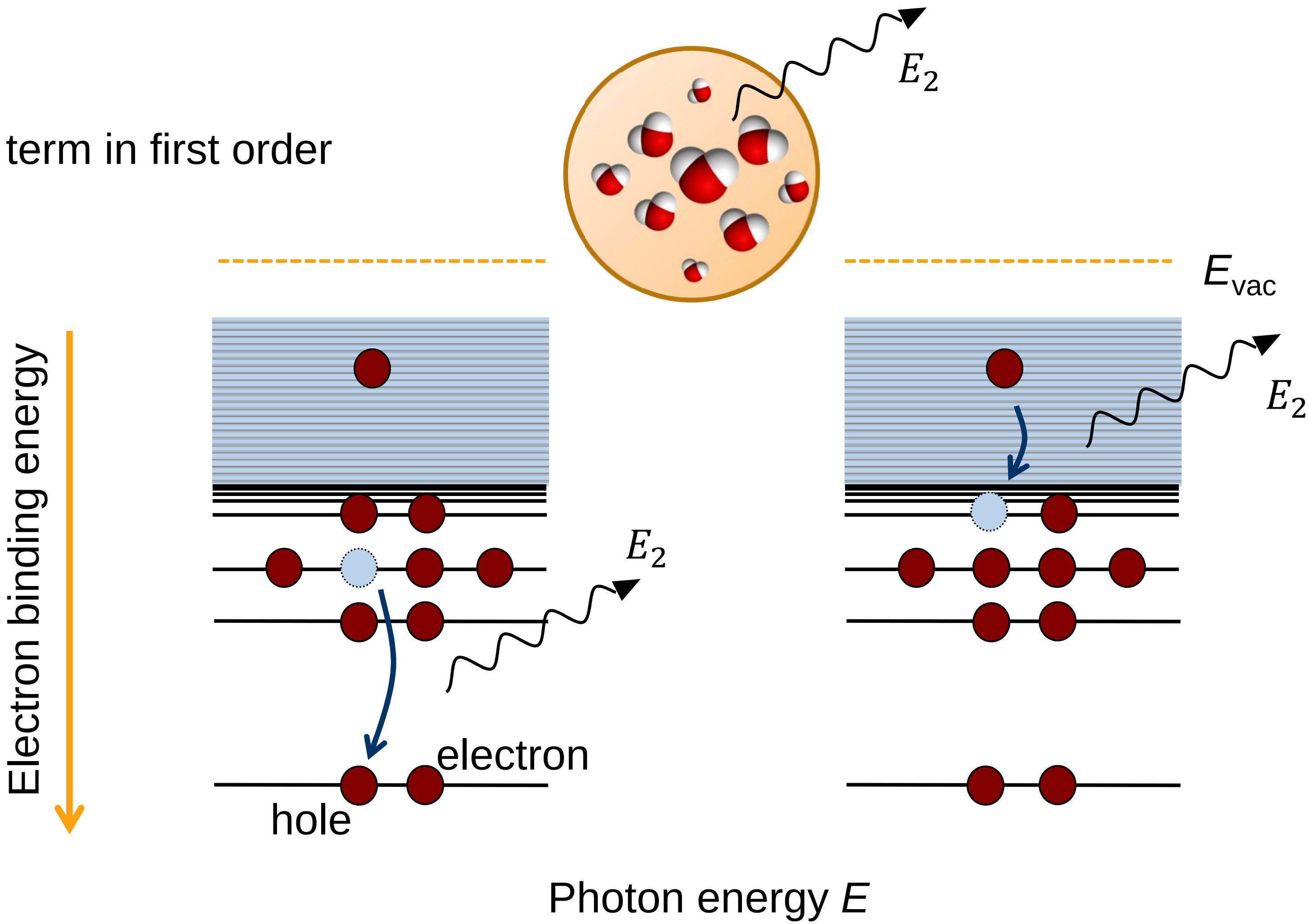
$$\left(\frac{d^2\sigma}{d\Omega d\omega}\right)_{\gamma,e} = \left(\frac{d\sigma}{d\omega}\right)_{\mathrm{Th,Ru}} S(\mathbf{q},\omega)$$

In principle..
But true for all dynamic range?



Photon emission

$\mathbf{p} \cdot \mathbf{A}$ term in first order

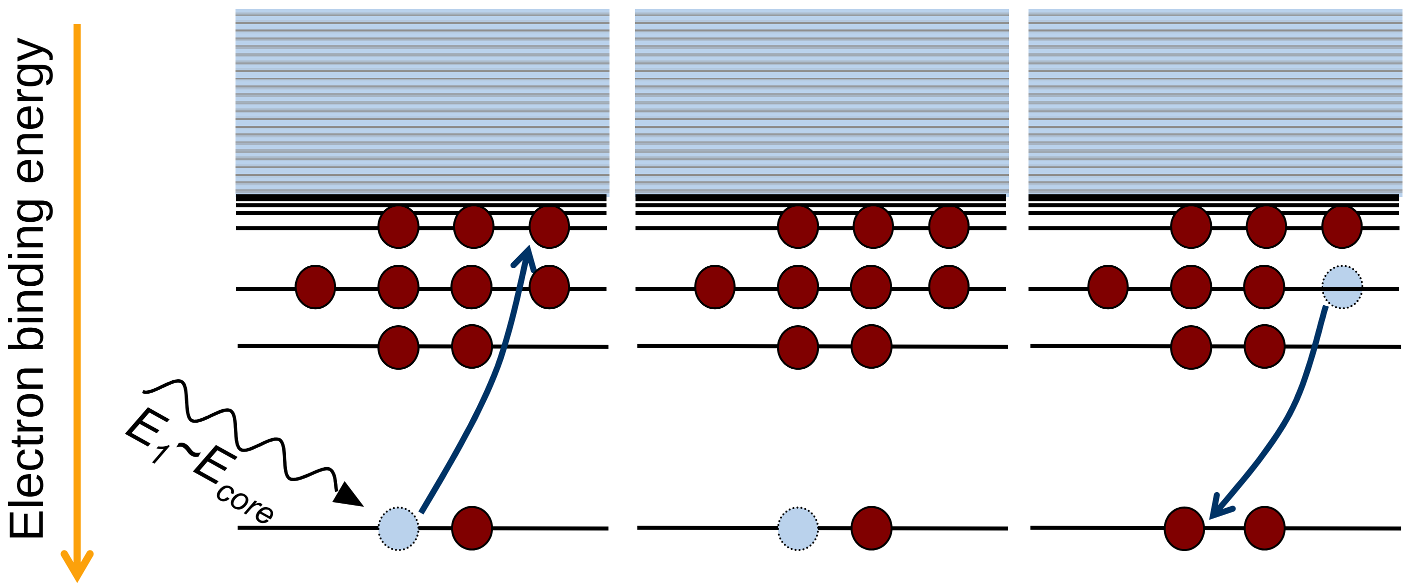


Resonant inelastic scattering

$\mathbf{p} \cdot \mathbf{A}$ term in second order

Ground state → Intermediate state → Final state

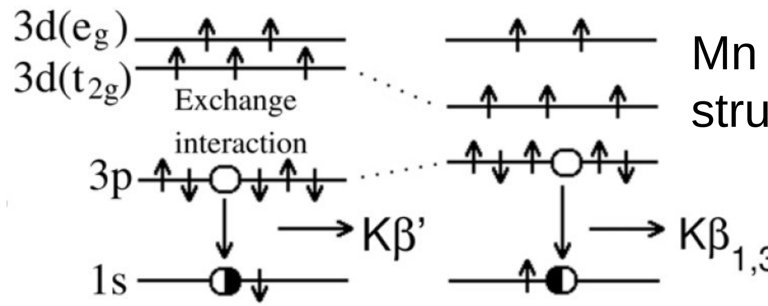
$$\frac{\langle \Psi_n \mid \boldsymbol{\epsilon}_1 \cdot \mathbf{p}\, e^{i\mathbf{k}_1 \cdot \mathbf{r}} \mid \Psi_i \rangle}{E_i - E_n + \omega_1 + i\Gamma_n} \qquad \mid \Psi_n \rangle \qquad \frac{\langle \Psi_f \mid \boldsymbol{\epsilon}_2 \cdot \mathbf{p}\, e^{-i\mathbf{k}_2 \cdot \mathbf{r}} \mid \Psi_n \rangle}{E_i - E_n + \omega_1 + i\Gamma_n}$$



Photon energies E_1, E_2, polarisation, momentum

X-ray emission spectrum

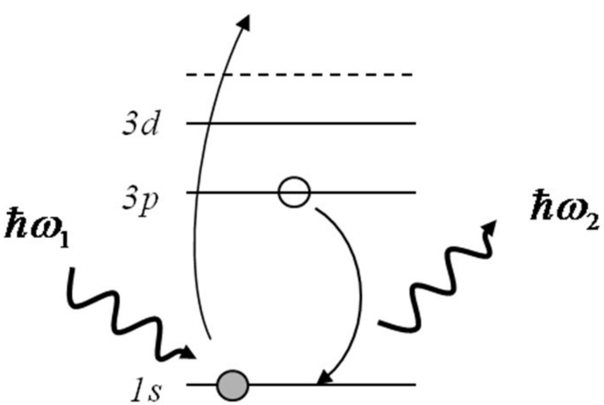
A. Mattila, PhD thesis,
University of Helsinki (2007)



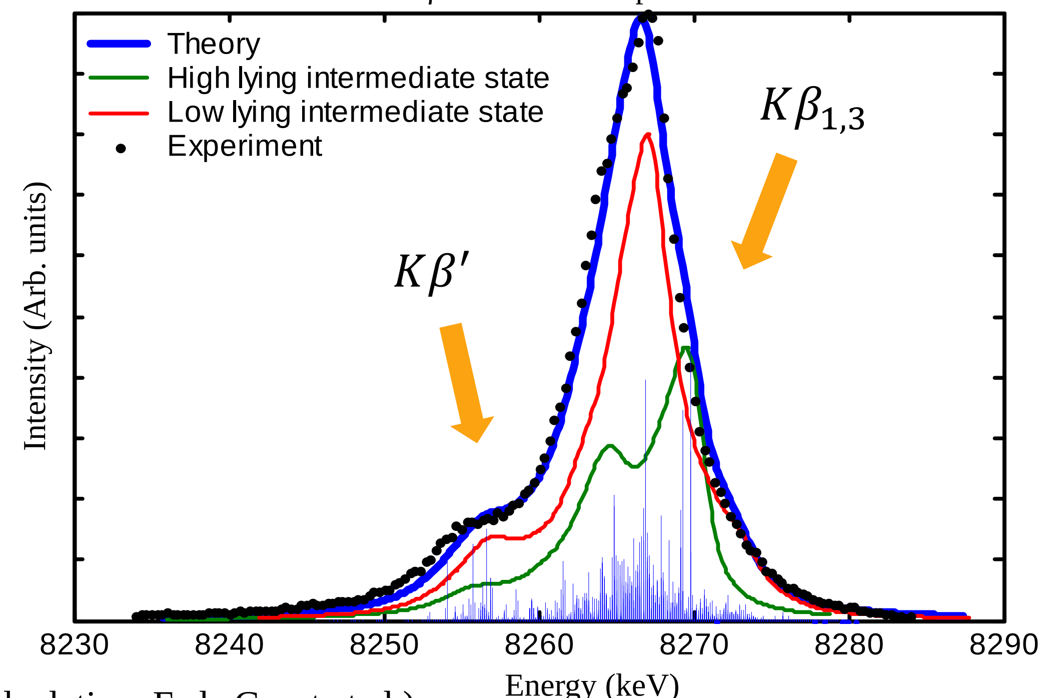
Mn electron structure

$\mathbf{p}\cdot\mathbf{A}$ term in second order

Kβ emission process



NiO Kβ fluorescence spectrum



(CTM calculation, F. de Groot et al.)

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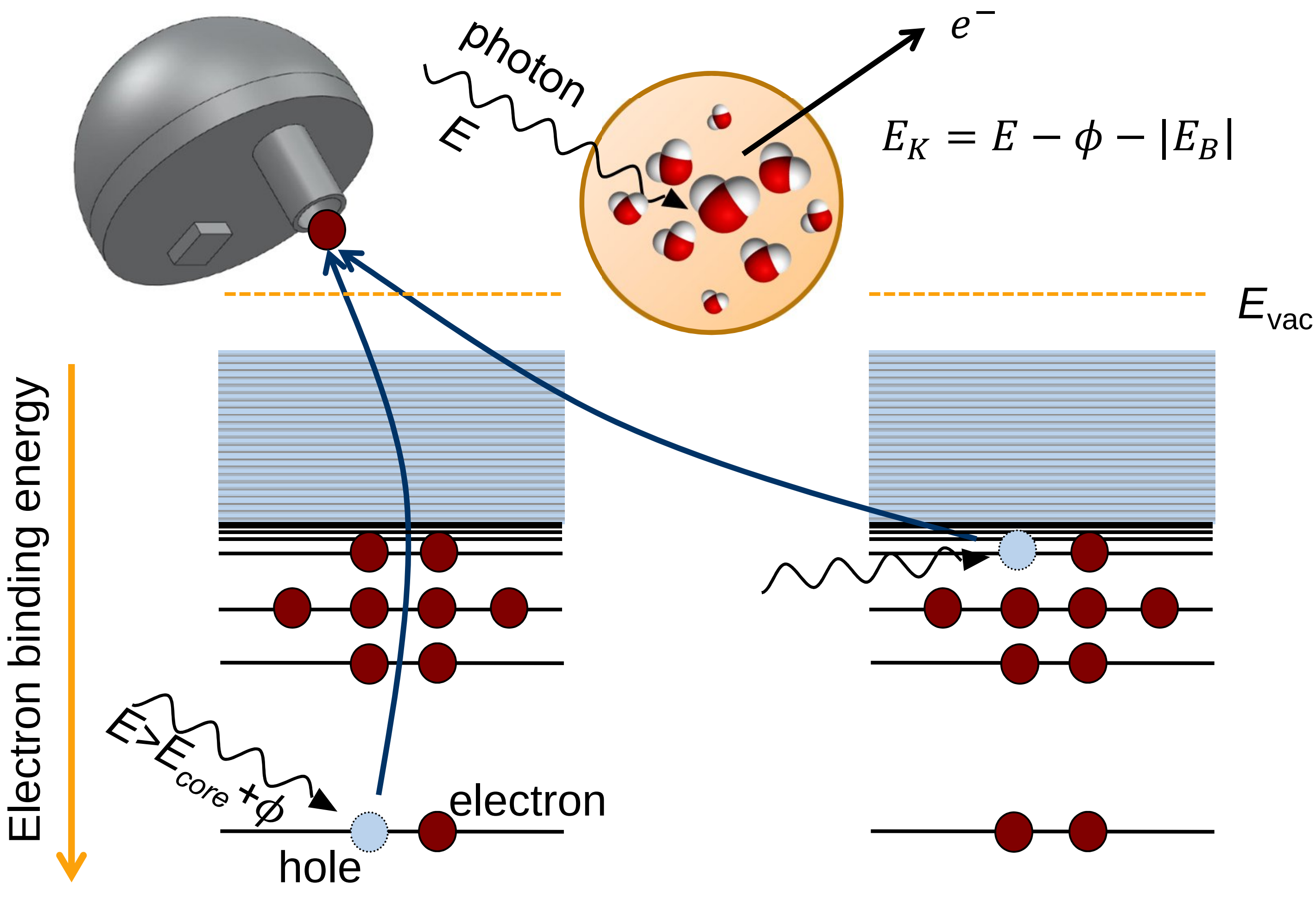
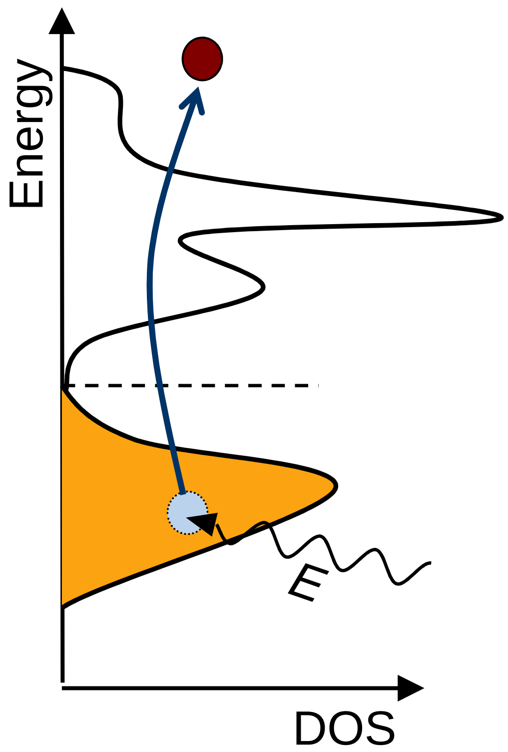
Photoemission

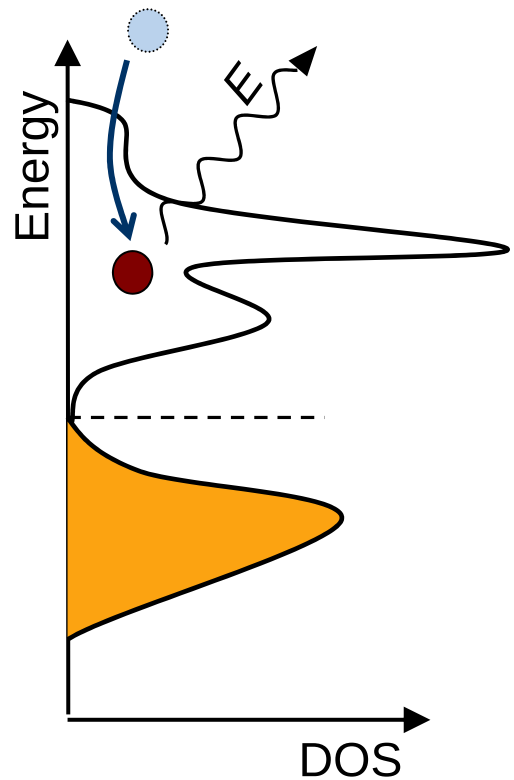


Photon energy *E*, polarisation, momentum...

Inverse photoemission

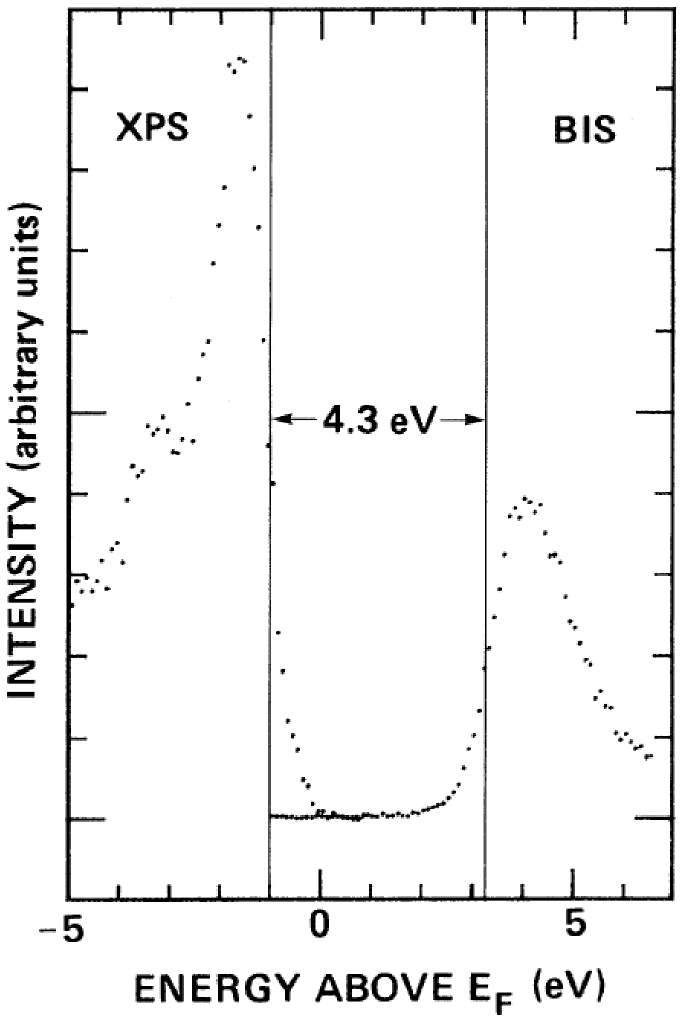


Photoemission



Inverse photoemission (IPES or BIS)

Band gap of NiO

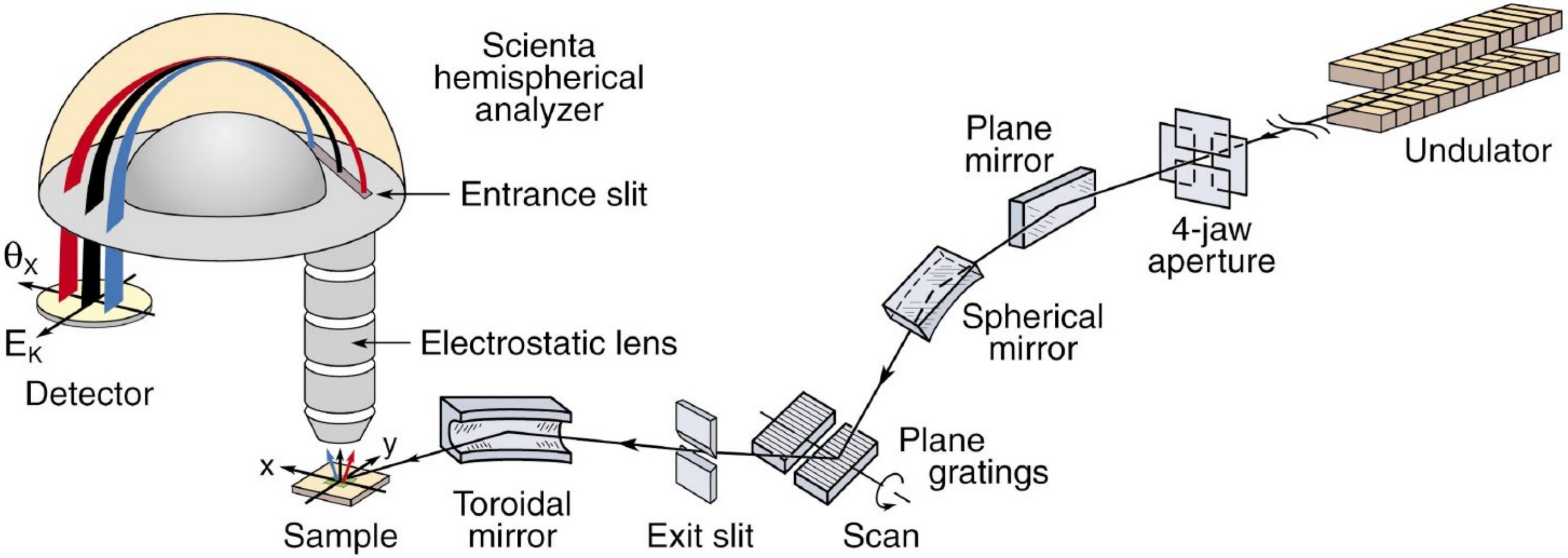


Sawatzky, Allen, PRL 53, 2339

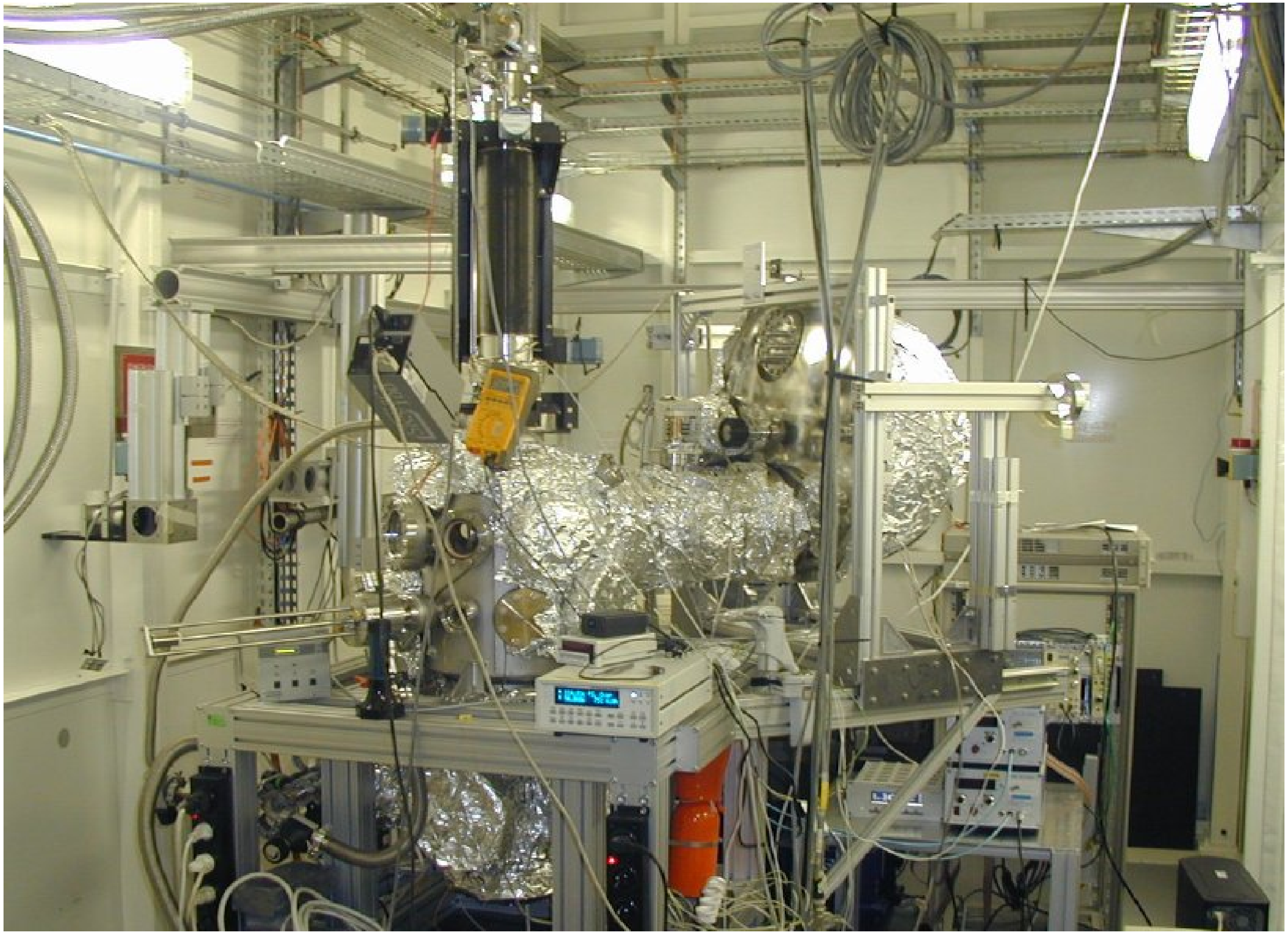
BIS = Bremsstrahlung isochromat spectroscopy

Photoemission

A. Damascelli et al., Rev. Mod. Phys 75, 473 (2003)



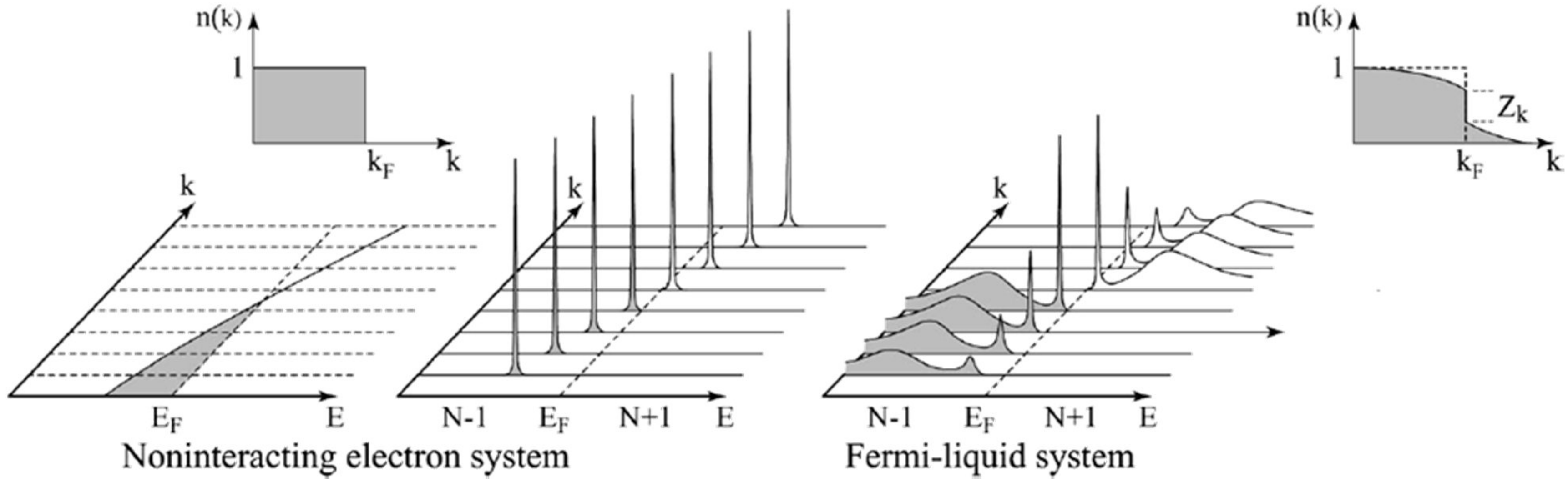
Powerful tool for
- ESCA (electron spectroscopy for chemical analysis): identification of core levels, shifts, shape
- Valence PES for band mapping (ARPES)
- Circular dichroism



The Volume Photoemission (VOLPE) spectrometer at ESRF
(G. Panaccione, M. Sacchi, et al.)

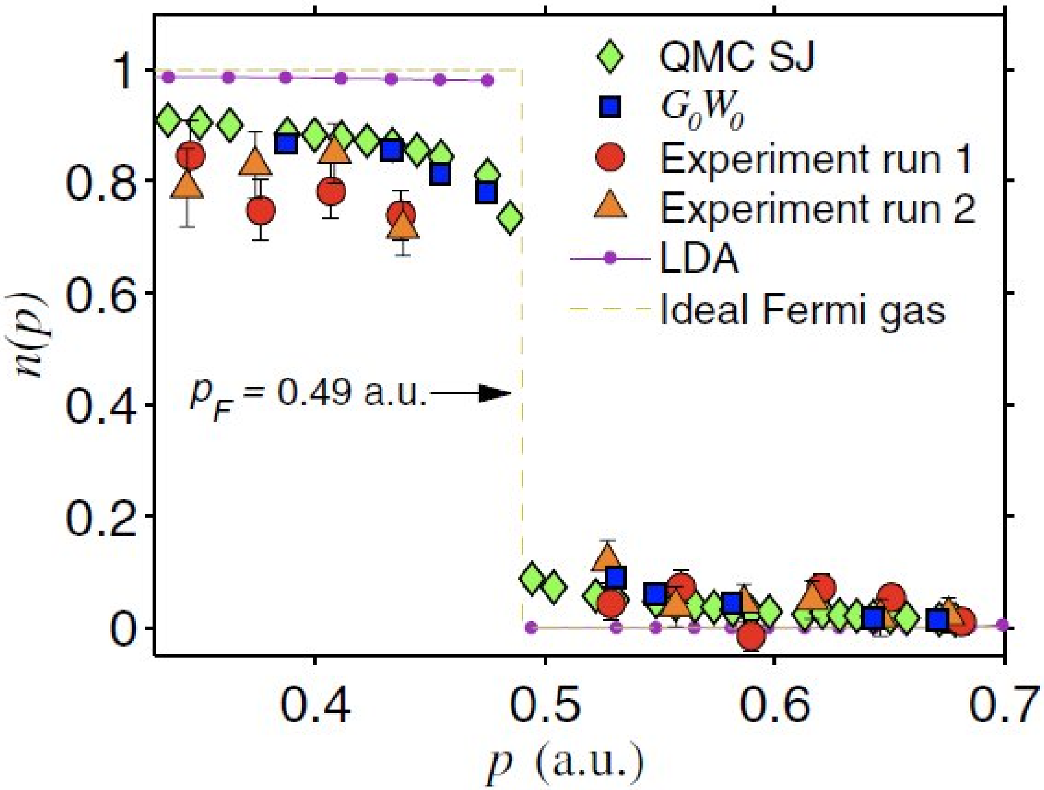
Photoemission

A. Damascelli et al., Rev. Mod. Phys 75, 473 (2003)



$$\mathrm{PES} \propto \sum_{f,i} \left| M_{f,i}^{\mathbf{p}} \right|^2 A(\mathbf{p}, E) \delta \left(E_K + E_m^{N-1} - E_i^N - \omega_1 \right)$$

Quasiparticle renormalisation factor



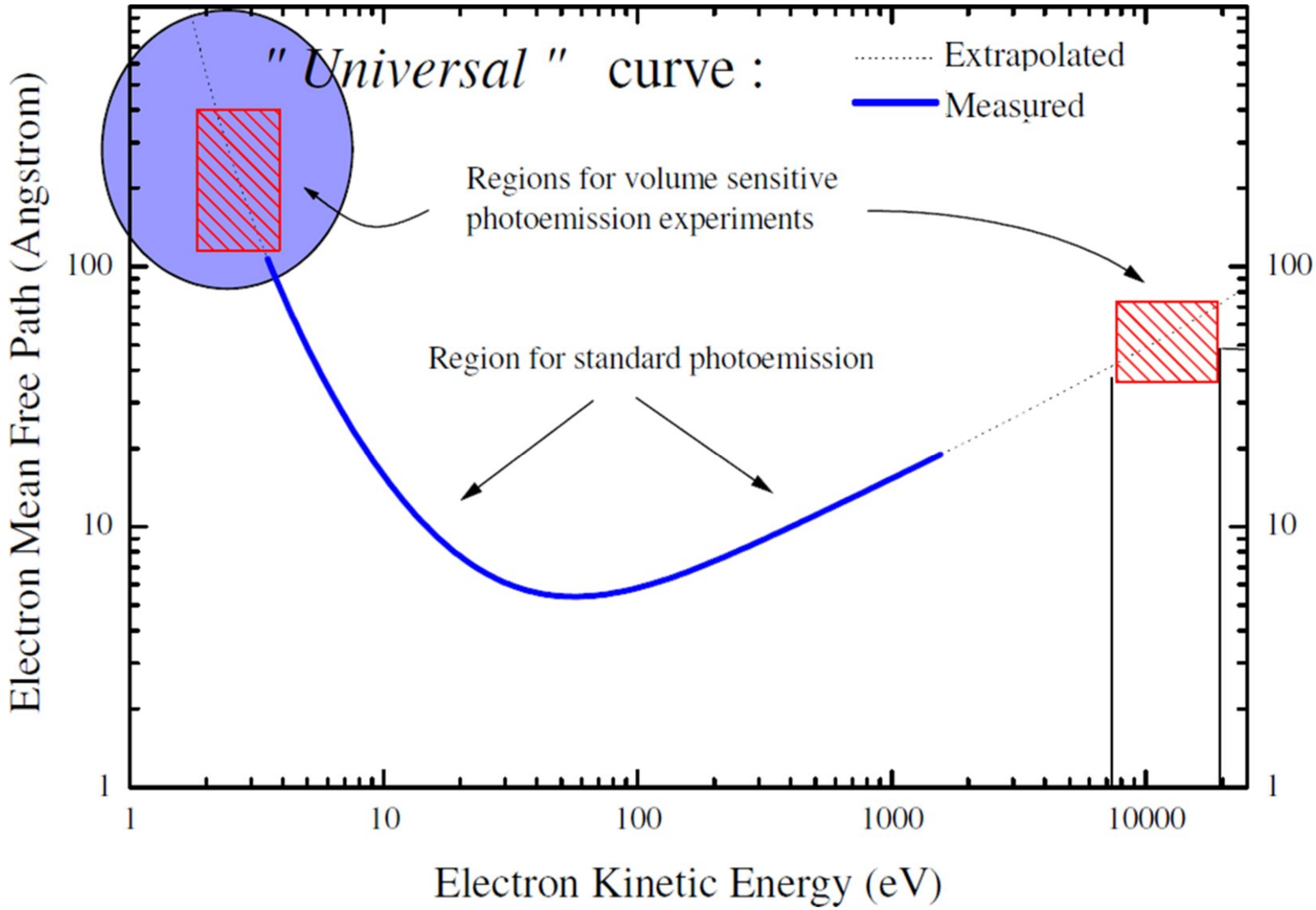
For Na (r_s = 3.99), experimental

$$Z_{k_F} = 0.58 \pm 0.07$$

Method: Compton spectroscopy

S. Huotari, J. A. Soininen, T. Pylkkänen, K. Hämäläinen, A. Issolah, A. Titov, J. McMinis, J. Kim, K. Esler, D. M. Ceperley, M. Holzmann, V. Olevano, Phys. Rev. Lett. 105, 086403 (2010)

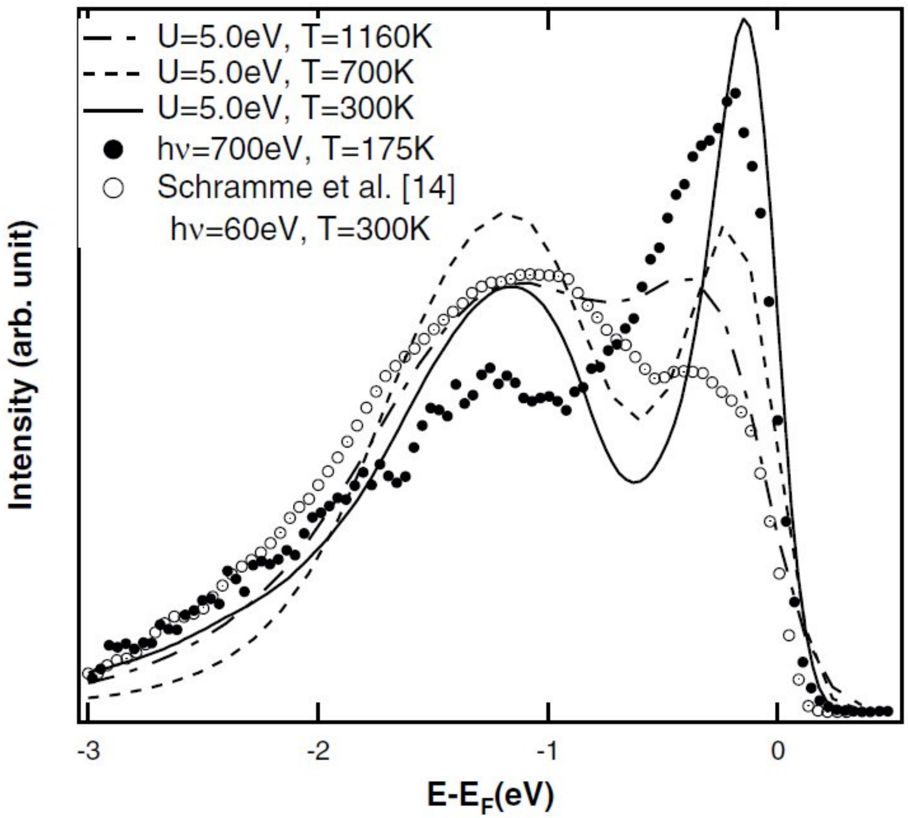
Bulk-sensitive photoemission

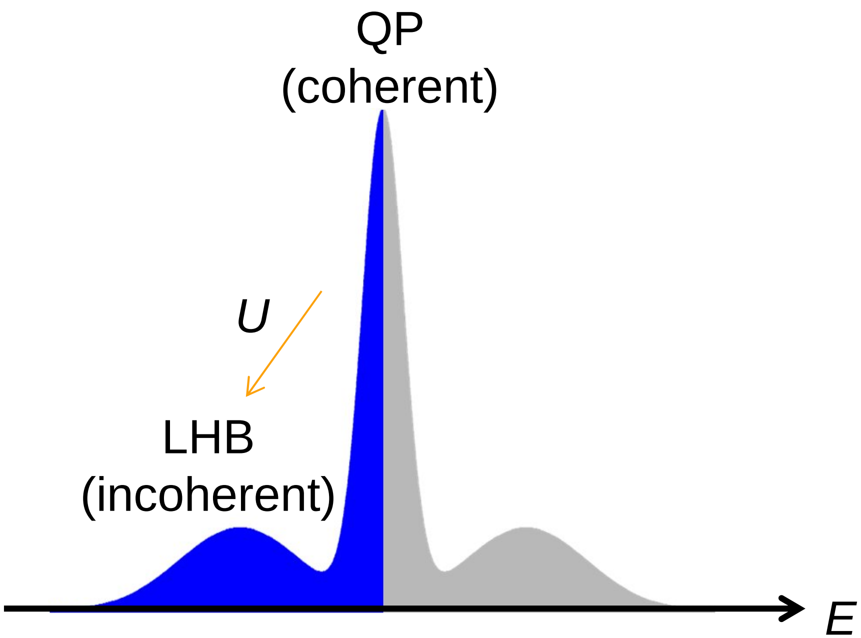


Bulk-sensitive photoemission

The Mott-Hubbard insulator V_2O_3

S.K. Mo et al., PRL 90, 186403 (2003)



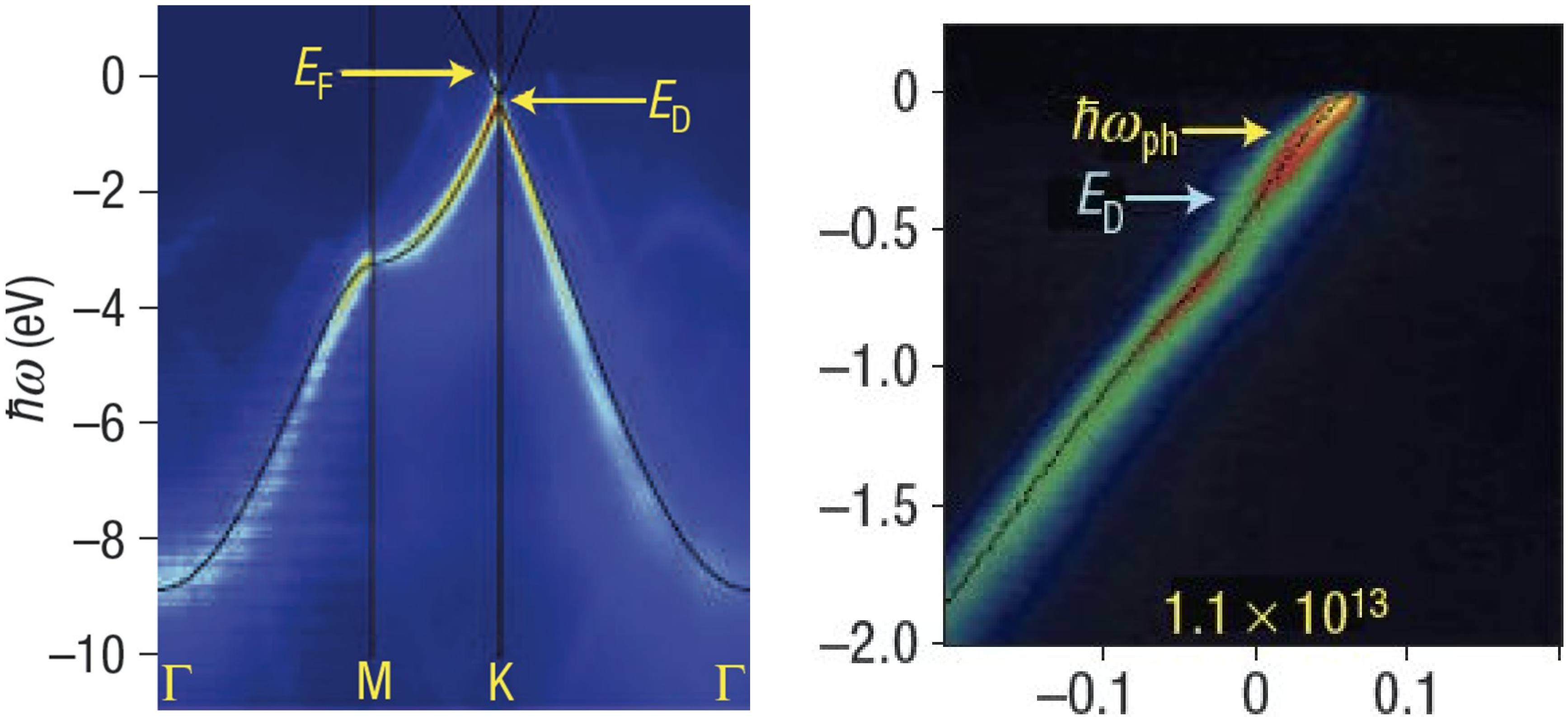


Half-filled one-band Hubbard model

U = on-site Coulomb repulsion

Band mapping by ARPES

Example: Graphene



A. Bostwick et al., Nature Phys. 3, 36 (2007)

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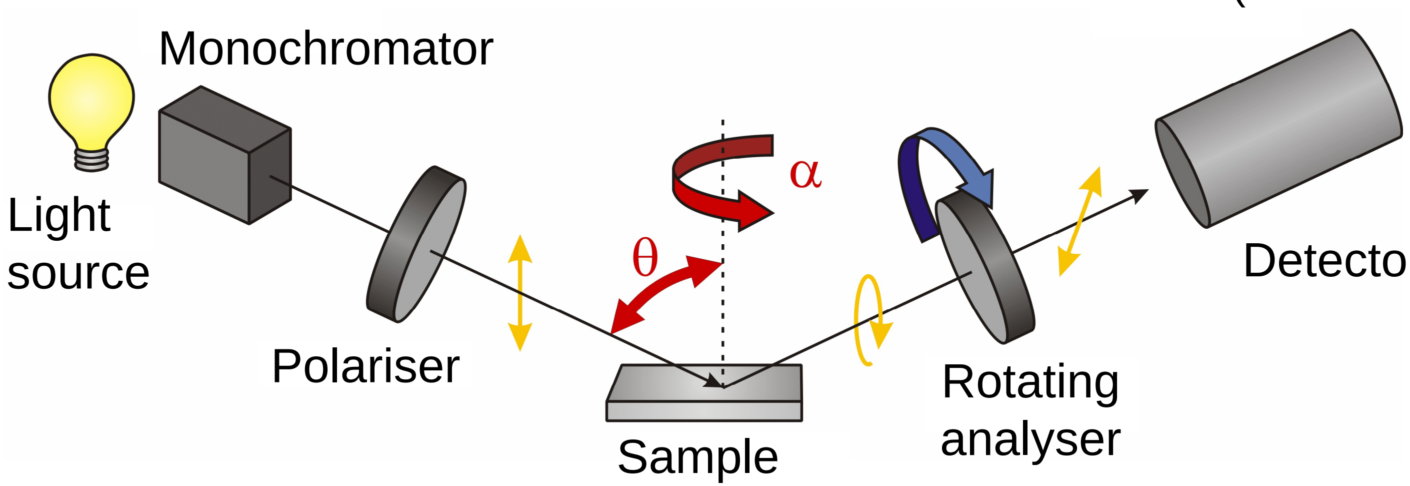
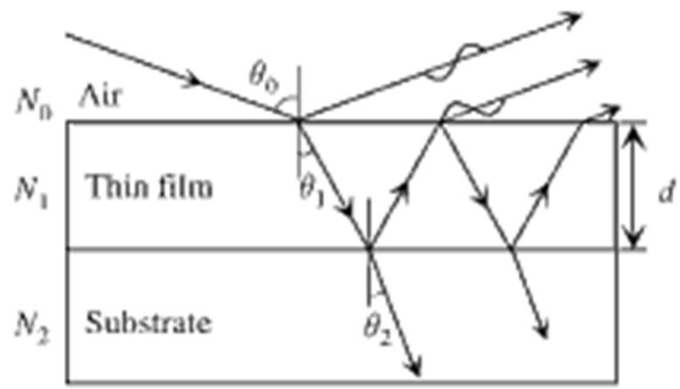
Ellipsometry

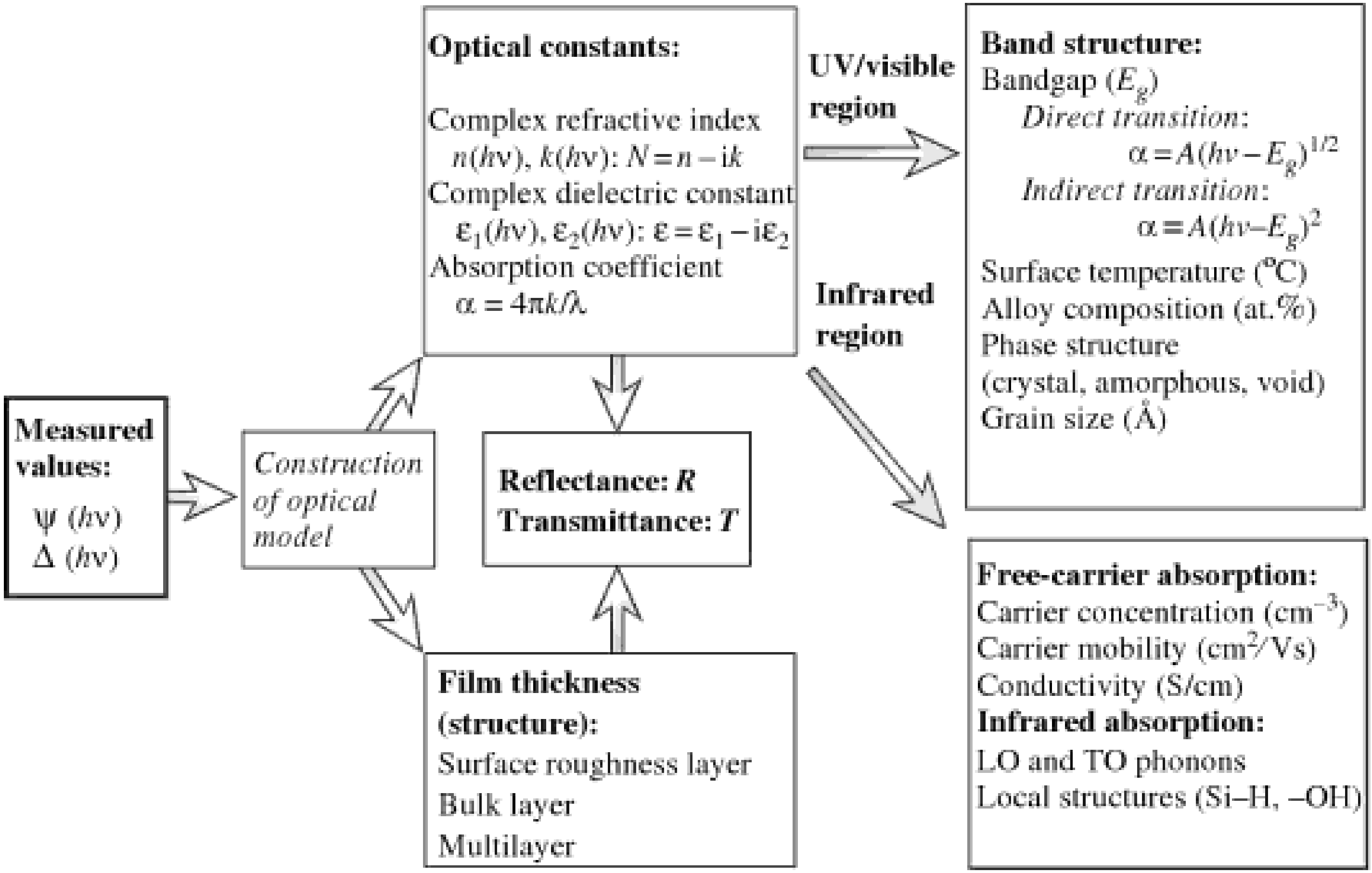
http://www.pi1.uni-stuttgart.de/research/Methoden/Ellipsometrie_e.php
(from Univ. Stuttgart)



Have to solve the Fresnel equations for s- and p-polarized light, in non-normal incidence, from an interface between two media



Ellipsometry

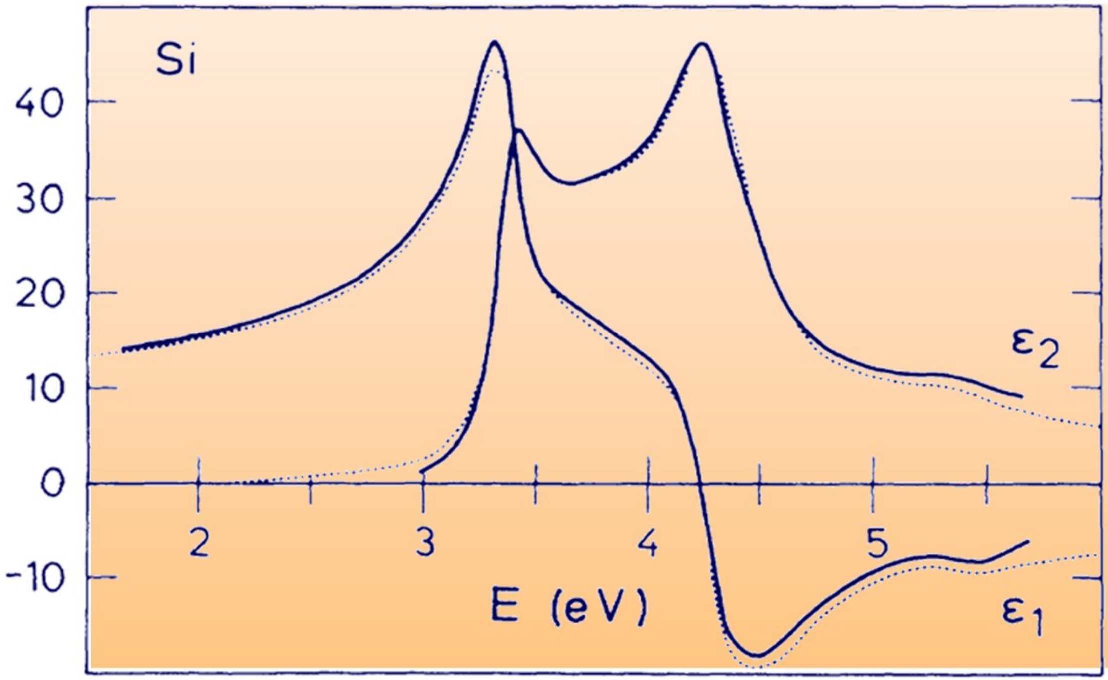


H. Fujiwara, Spectroscopic ellipsometry: Principles and applications, Wiley, 2009

Ellipsometry

Measure both real and imaginary parts of the dielectric function at Q=0 simultenously – no Kramers-Kronig analysis needed!

University of Stuttgart



P. Lautenschlager et al., PRB 36, 4821 (1987)

Thank you!

Valentina Giordano (ESRF and CNRS/Univ. Lyon, France)
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Pieter Glatzel (ESRF)

Keijo Hämäläinen (Univ. Helsinki)
Tuomas Pylkkänen (ESRF and Univ. Helsinki)
Arto Sakko (Univ. Helsinki and Aalto University)
J. Aleksi Soininen, Mikko Hakala (Univ. Helsinki)

G. Panaccione, M. Grioni, et al., (VOLPE collaboration)