

Chemical Information in X-ray Spectroscopy

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G. Bunker:

“Introduction to XAFS”

Cambridge Press, 2010

F.M.F. de Groot and A. Kotani:

“Core level spectroscopy of solids”

Taylor and Francis, 2008

J. J. Sakurai:

“Advanced Quantum Mechanics”

Addison Wesley, 1967

M. Newville:

“Fundamentals of XAFS”

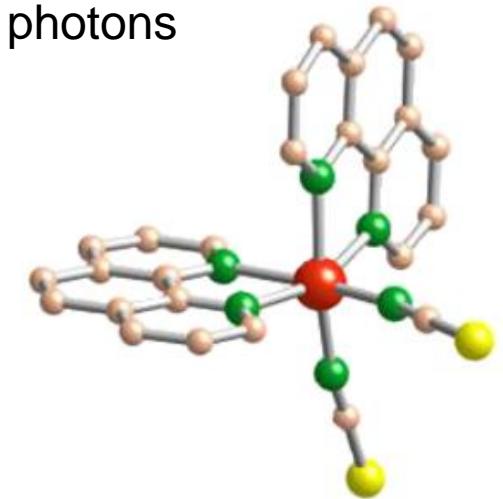
IXAS portal

M. Van Veenendaal

“Inelastic scattering and absorption of X-rays”

Cambridge University Pres

The response of the system that is probed by photons depends on the photon energy.



Infrared

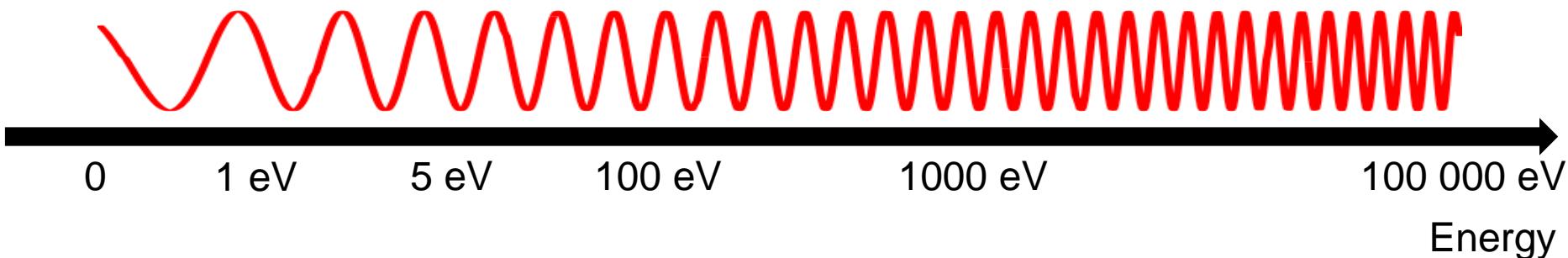
Raman

UV-Vis

VUV

Soft X-ray

Hard X-ray



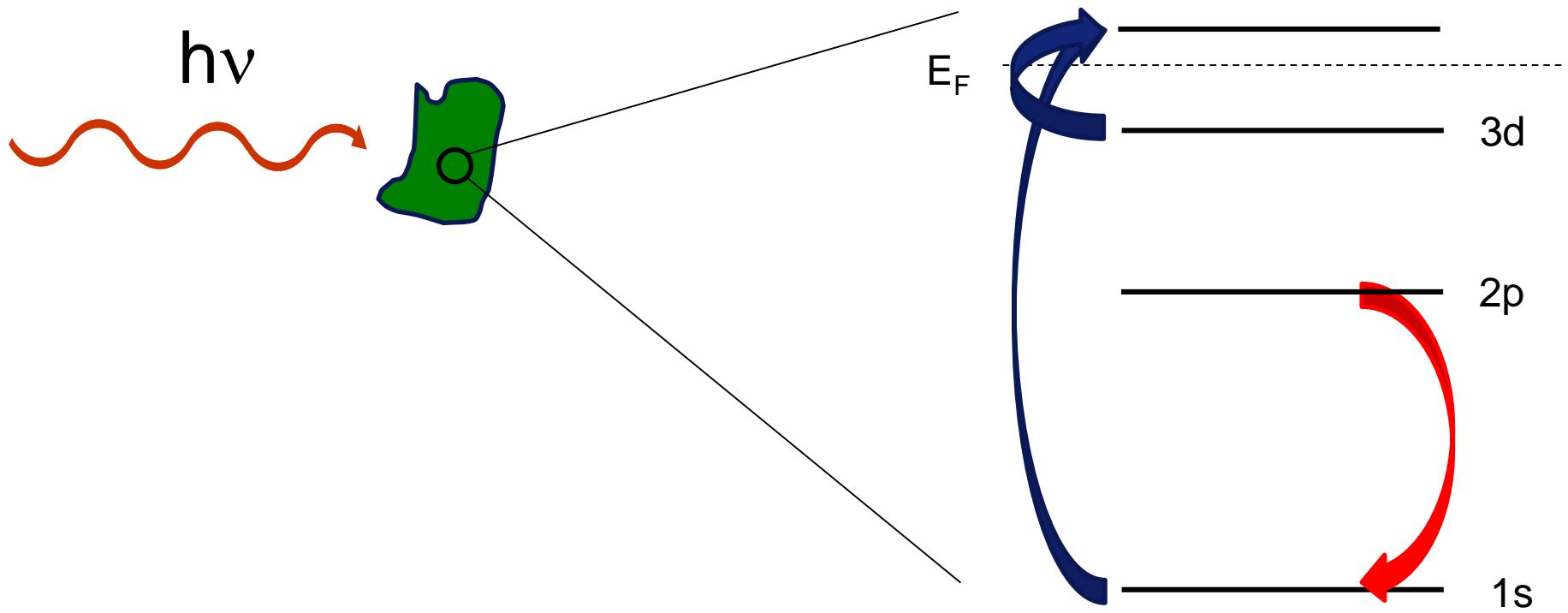
Vibration

Valence shell

Core levels

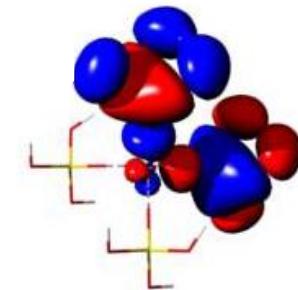
What may happen in the sample?

A simplified view: An electron is excited to an unoccupied orbital.

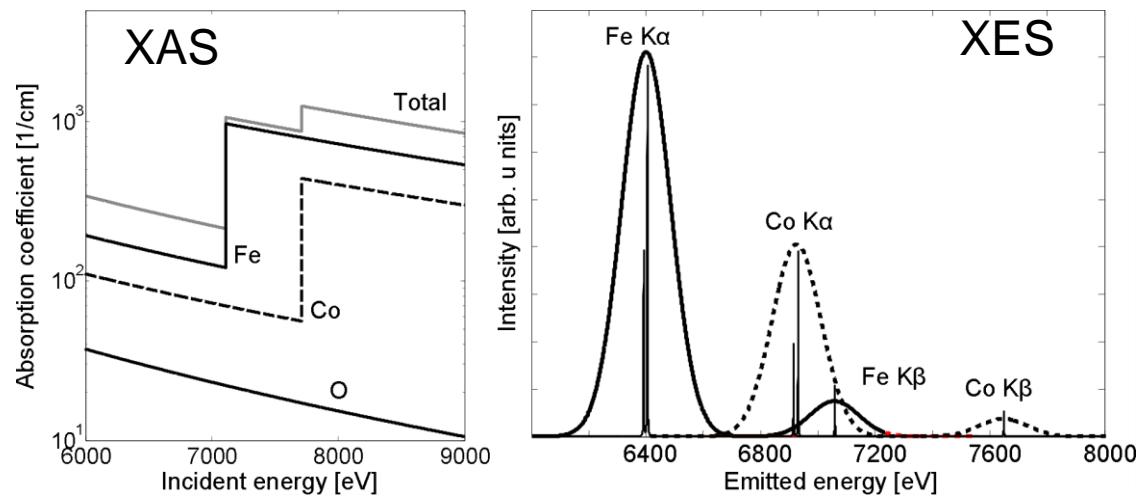


A single electron energy diagram is simple and qualitative.

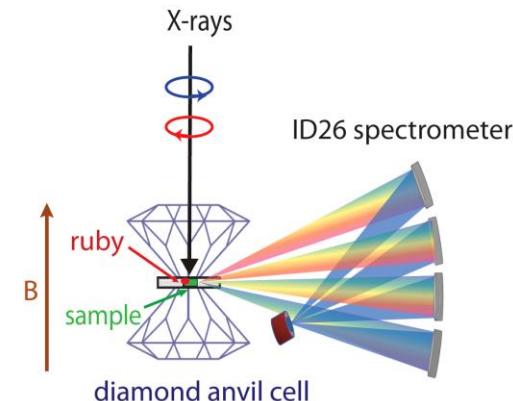
Electronic and atomic structural information



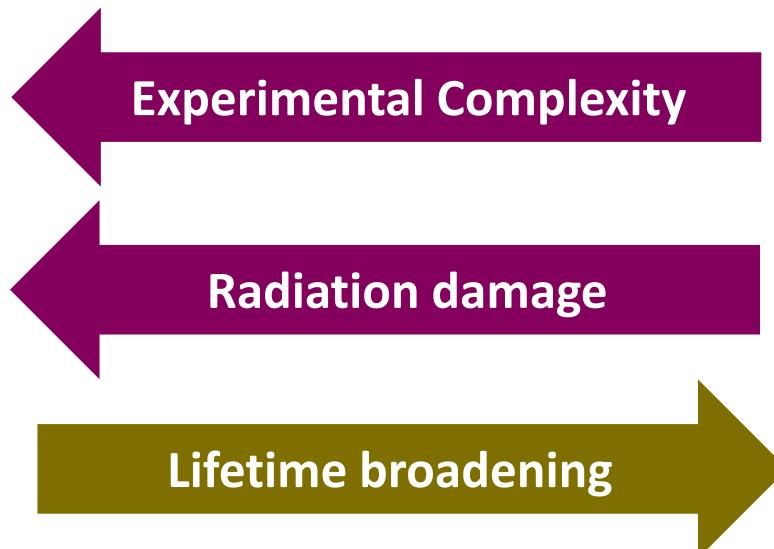
Element specific



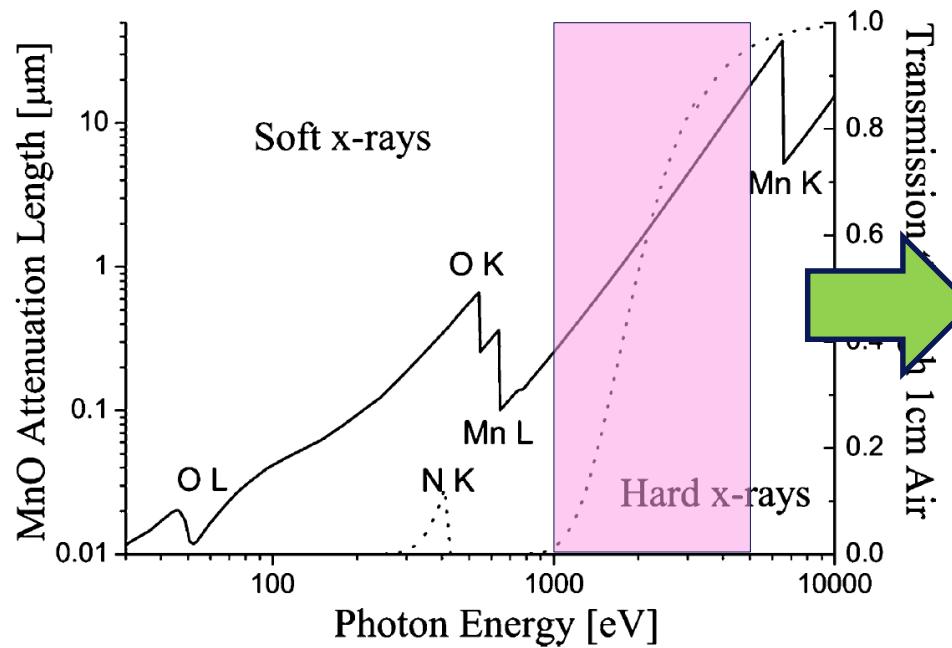
Bulk sensitive; compatible with *in-situ* and extreme conditions



Soft
X-rays



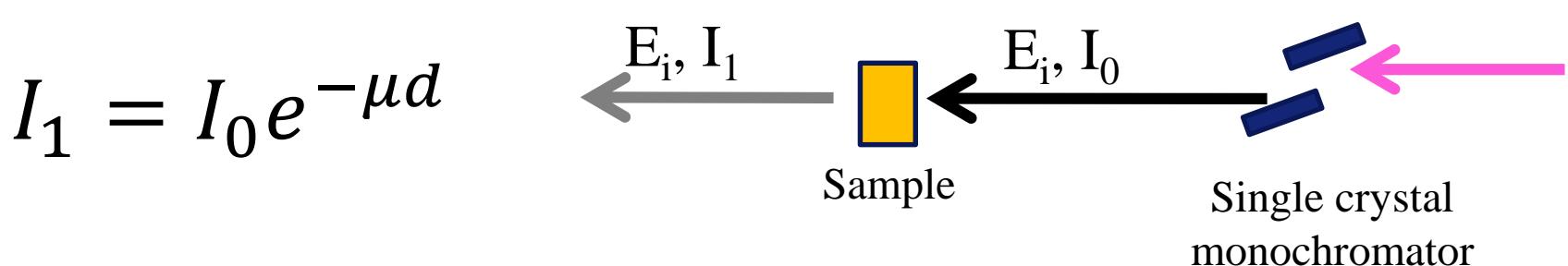
Hard
X-rays



Tender X-rays



THE ABSORPTION CROSS SECTION



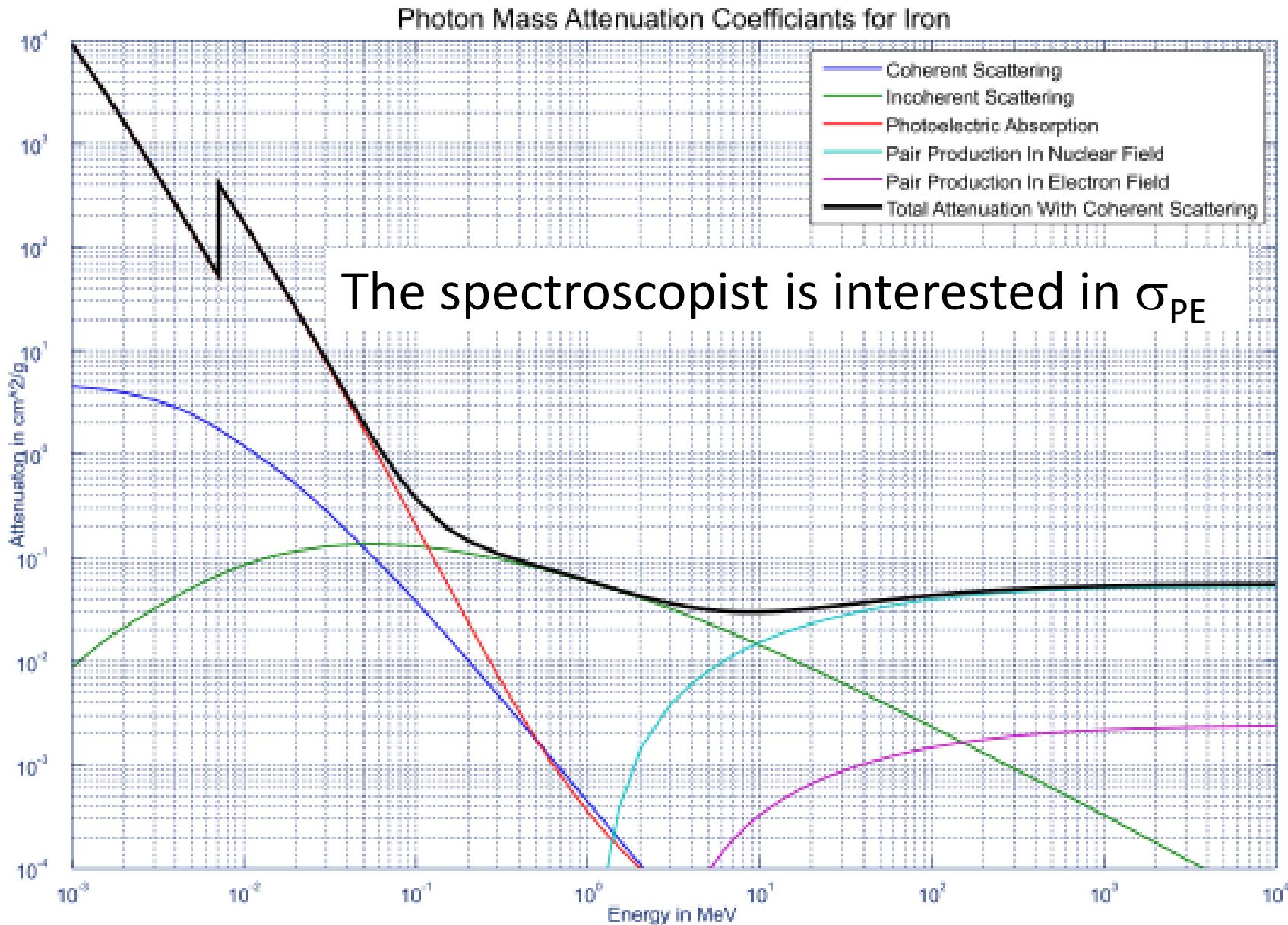
For homogeneous sample of one element:

$$n\sigma_a = \mu$$

$$\left[\frac{1}{m^3} m^2 \right] = \left[\frac{1}{m} \right]$$

$1/\mu$ is attenuation length, i.e. where $I(x)=I_0/e$

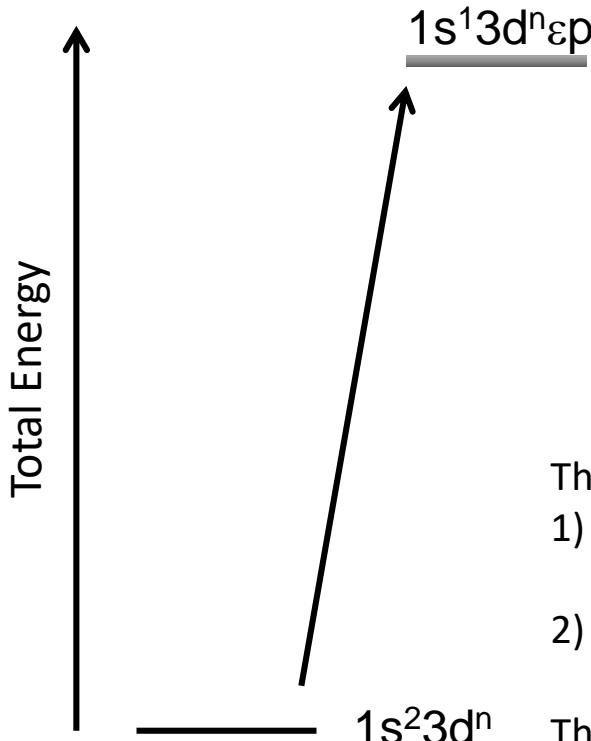
CROSS SECTIONS



TRANSITION MATRIX ELEMENT

How does one calculate the intensity of an absorption line?

It is given by the probability of the atom to go from one state to another when interacting with a photon (Golden Rule).



$$\begin{aligned} & |\langle \Psi_{ground} | \hat{O}_{photon} | \Psi_{excited} \rangle|^2 \\ & \approx S^2 |\langle \varphi_{1s} | \hat{\varepsilon} \cdot \vec{r} | \varphi_p \rangle|^2 \\ & = S^2 \left| \int \varphi_{1s}(\vec{r}) \hat{\varepsilon} \cdot \vec{r} \varphi_p(\vec{r}) d\vec{r} \right|^2 \end{aligned}$$

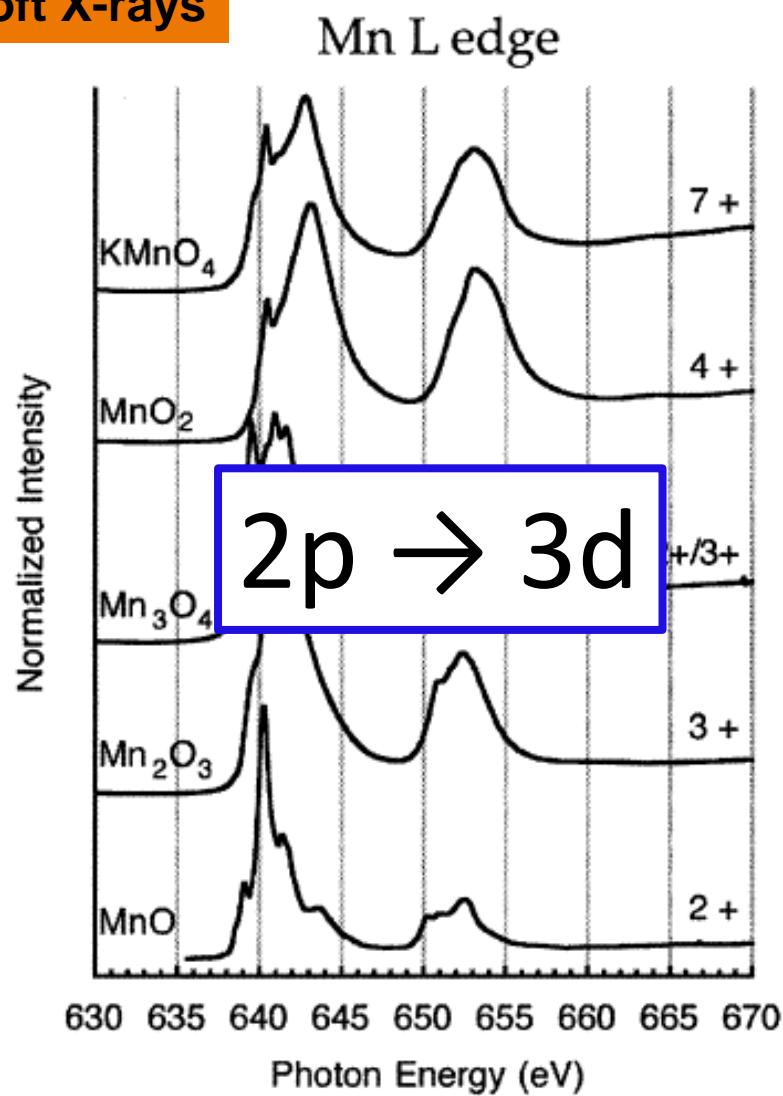
The steps assume:

- 1) One-electron approximation: The response of all other electrons is lumped together in S^2
- 2) Dipole approximation

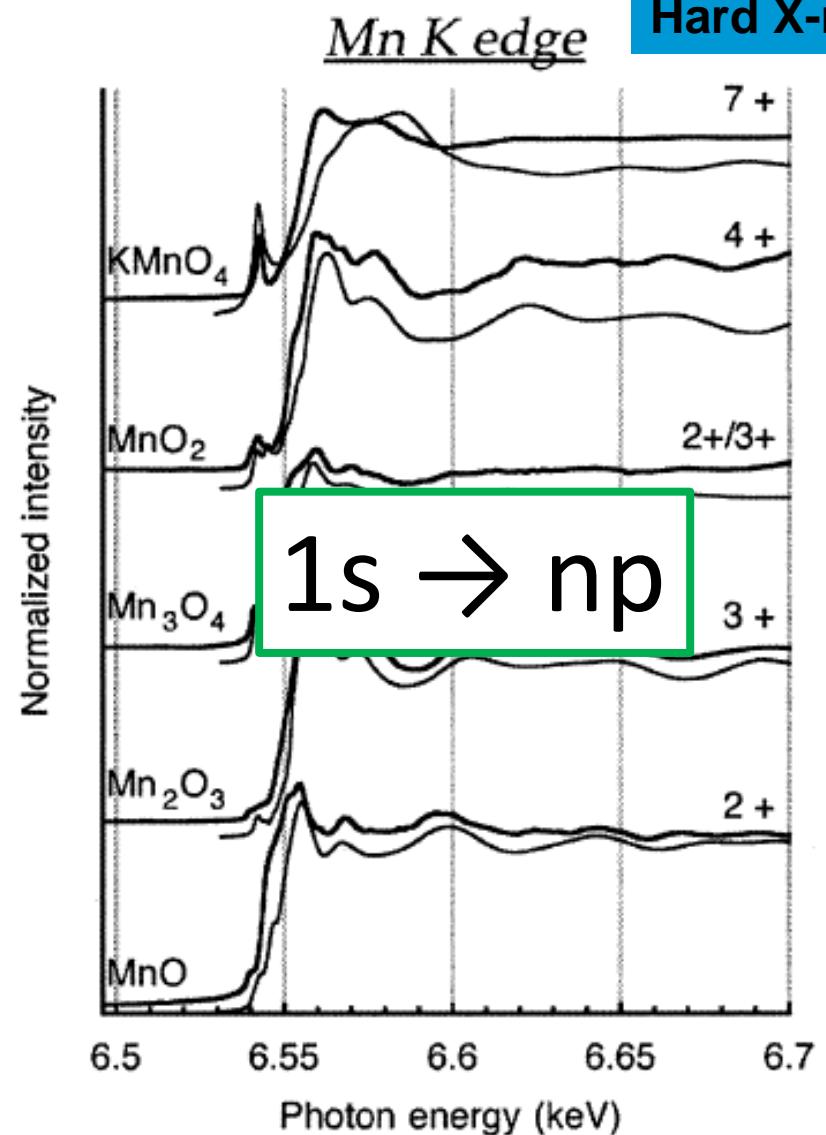
The one-electron approximation is frequently used. Whether or not this approximation is good depends on the observed transition.

L- AND K-EDGES IN 3D TRANSITION METALS

Soft X-rays

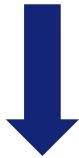


Hard X-rays



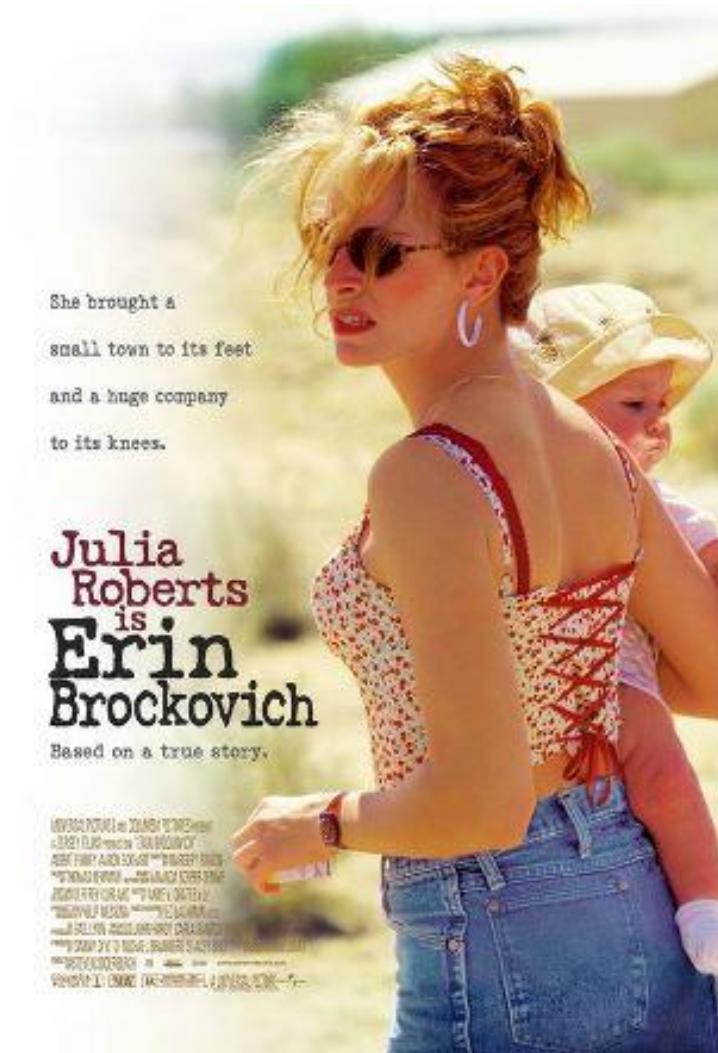
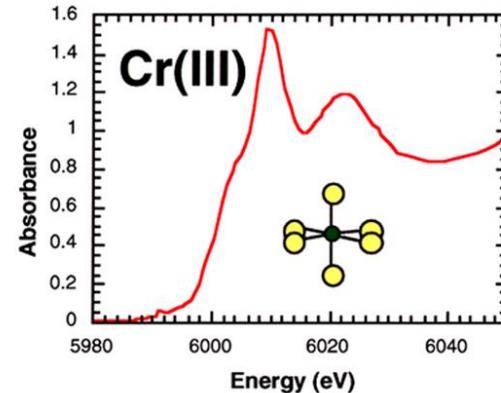
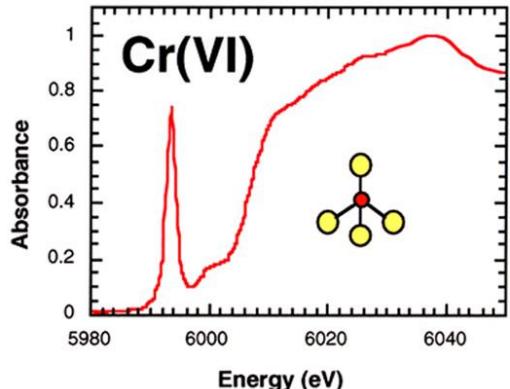
WHY X-RAY SPECTROSCOPY?

Spectroscopy does not require long range order.



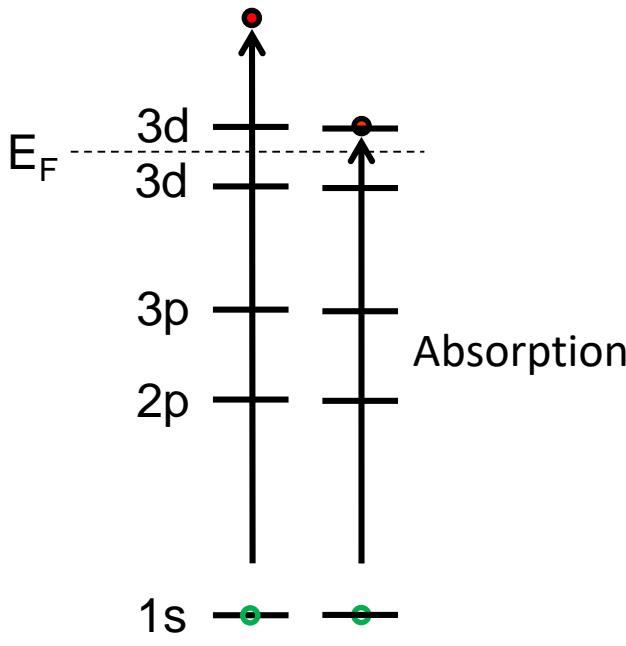
Ideal tool for e.g. catalysis, environmental sciences, biology, ...

Identify Cr(VI)...

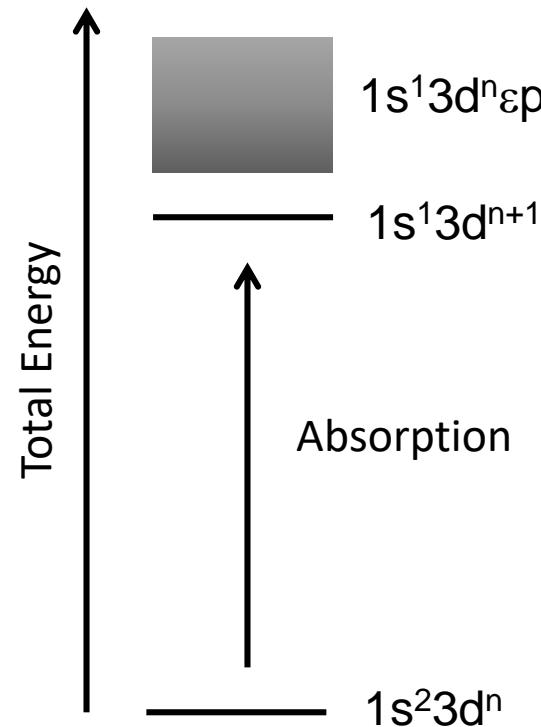


TRANSITION SCHEMES

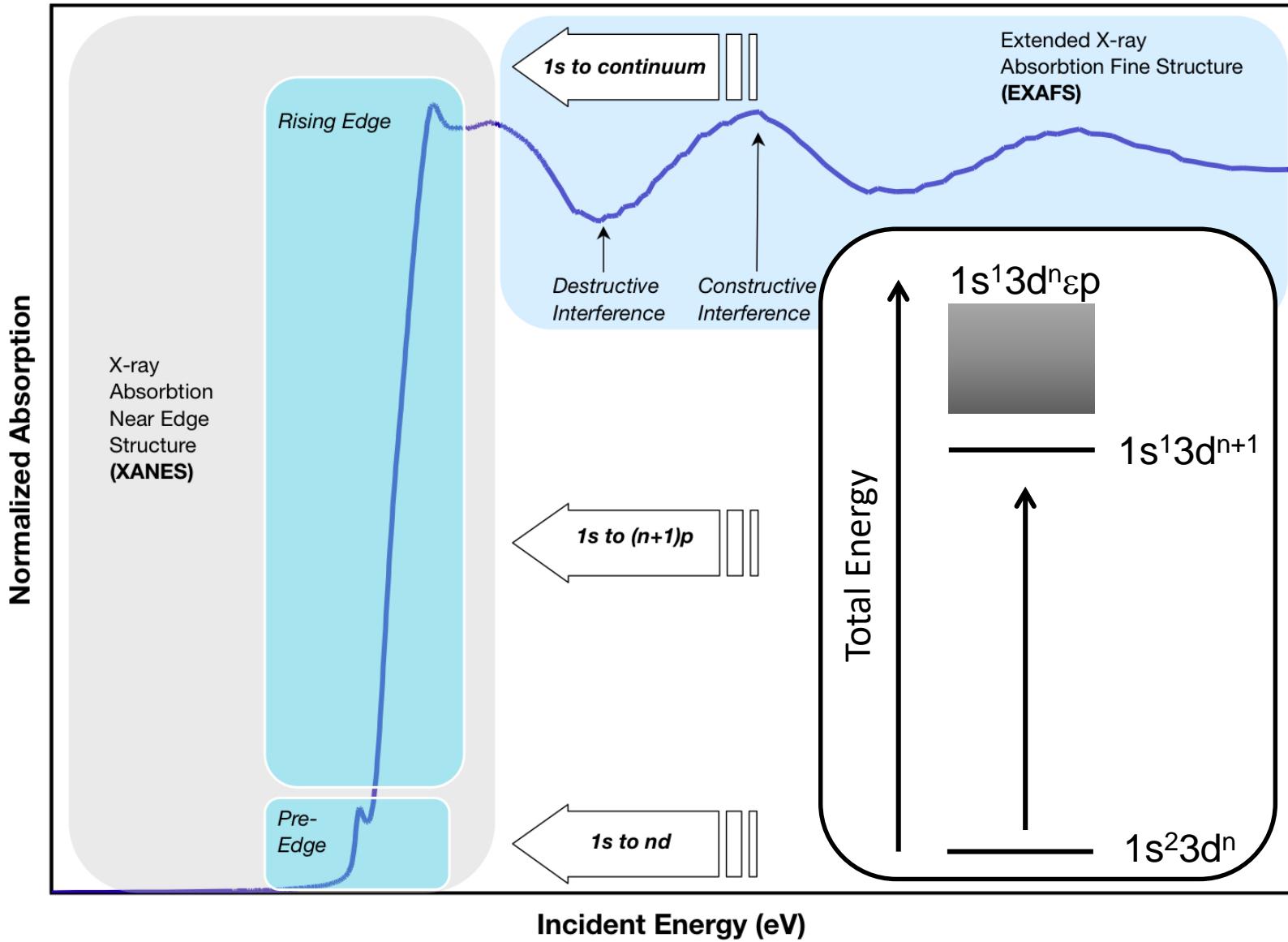
Two ways of describing the same process.



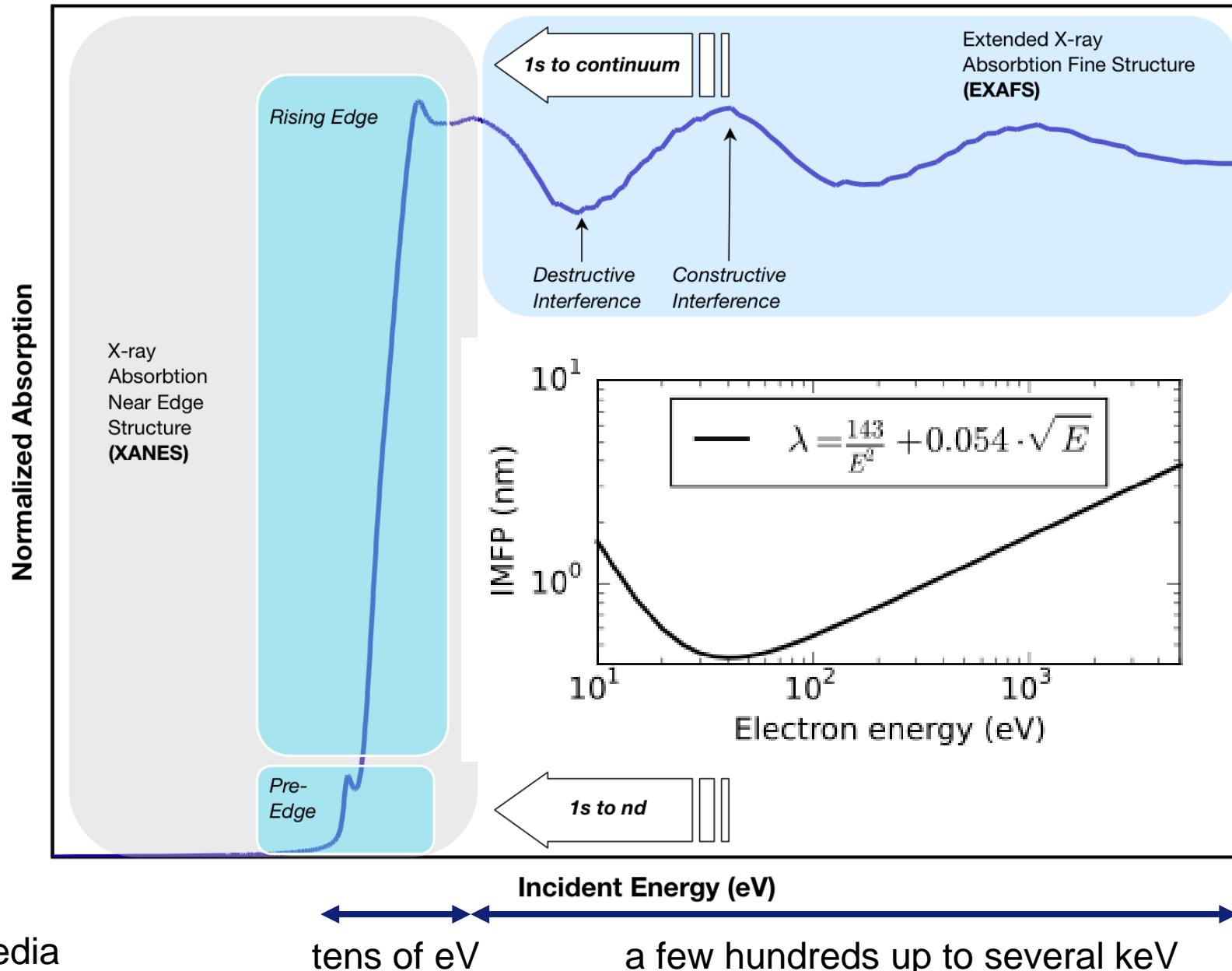
One-electron diagram



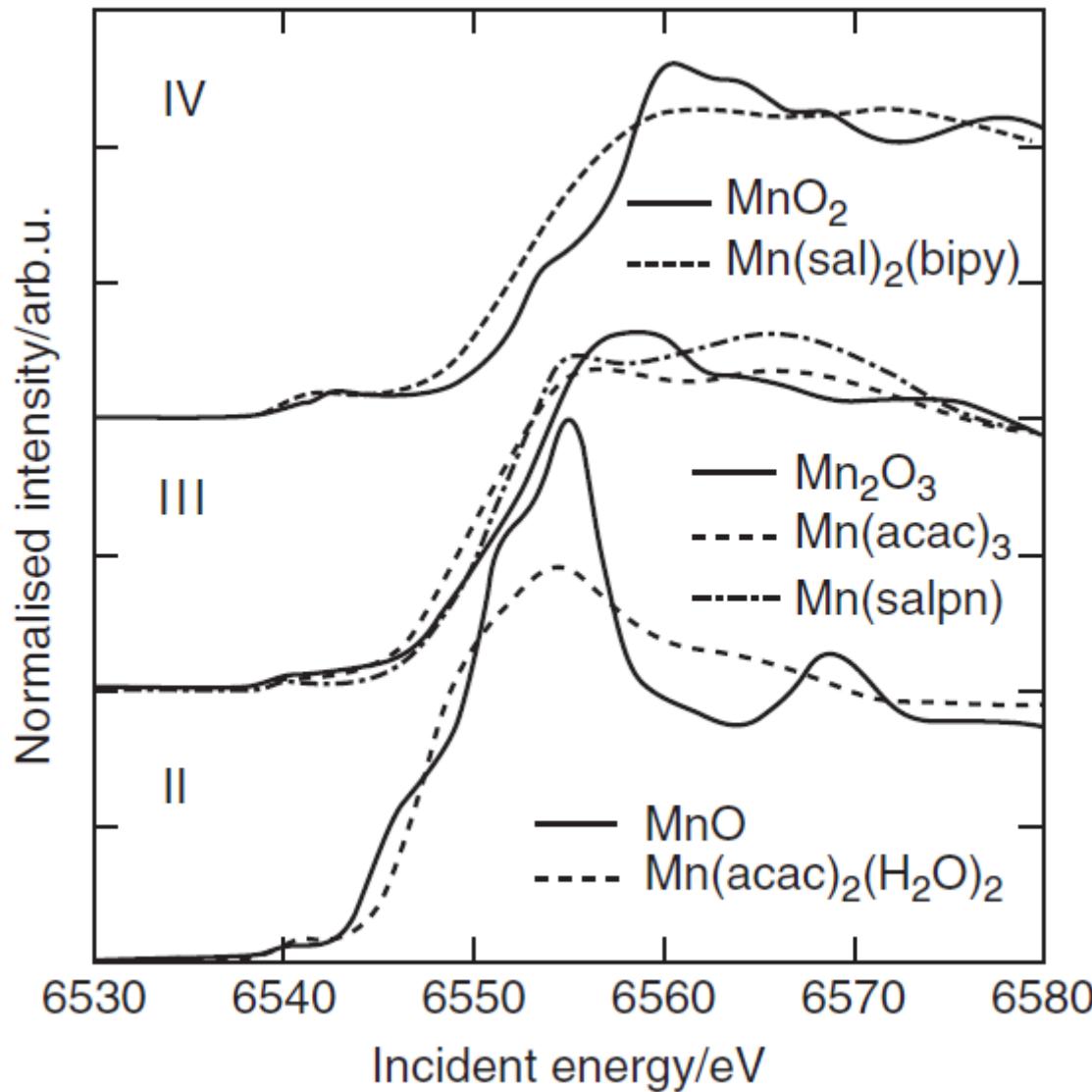
Many body diagram:
Observes energy conservation



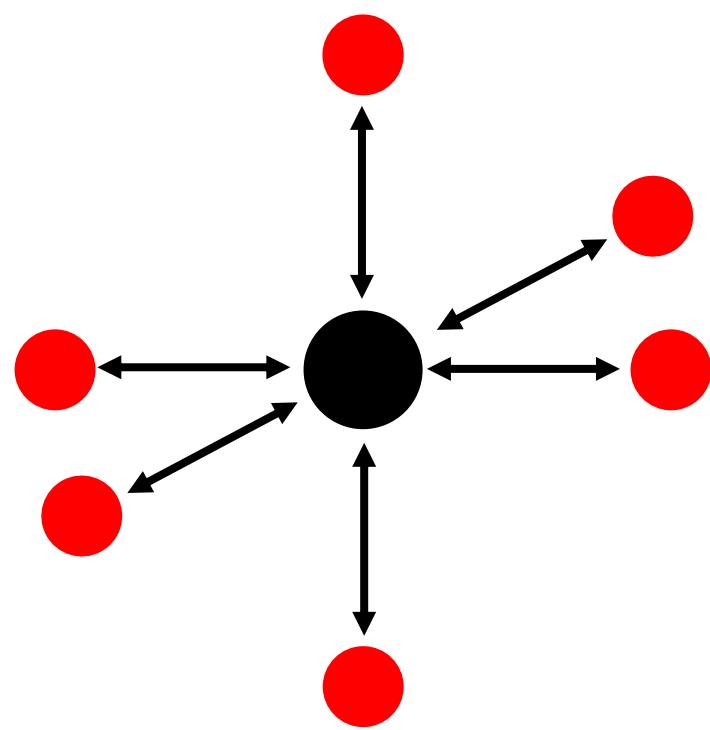
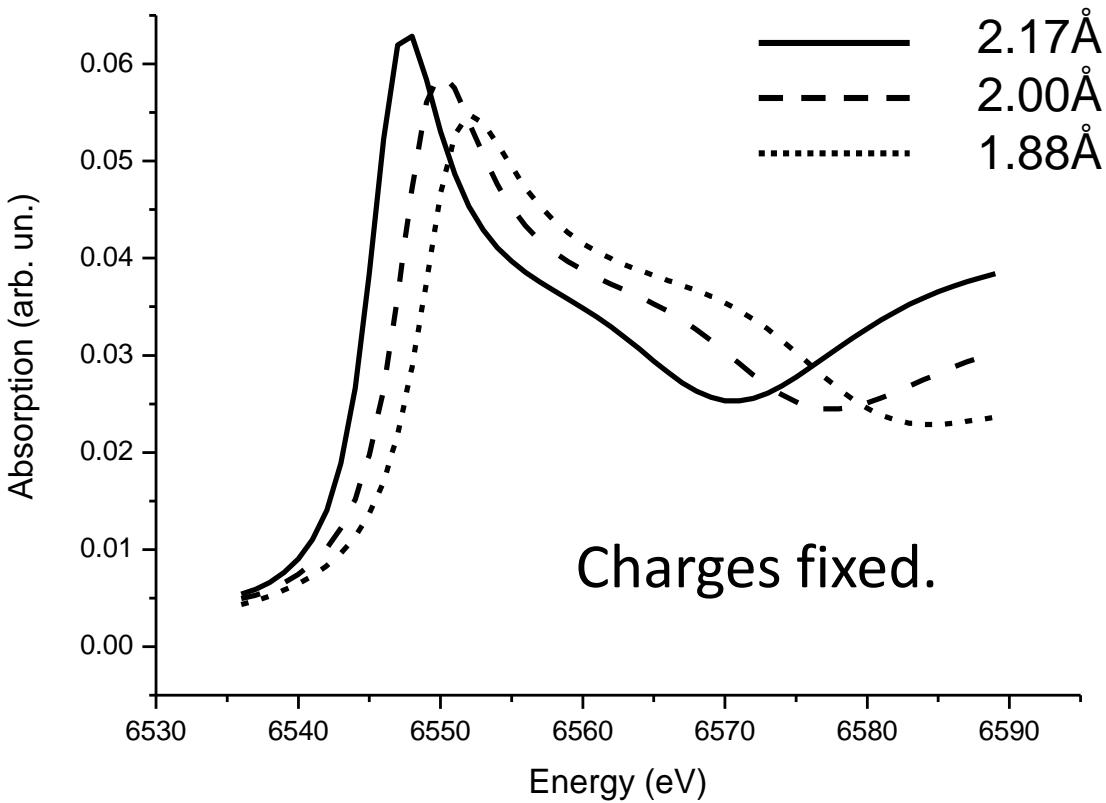
X-ray absorption fine structure



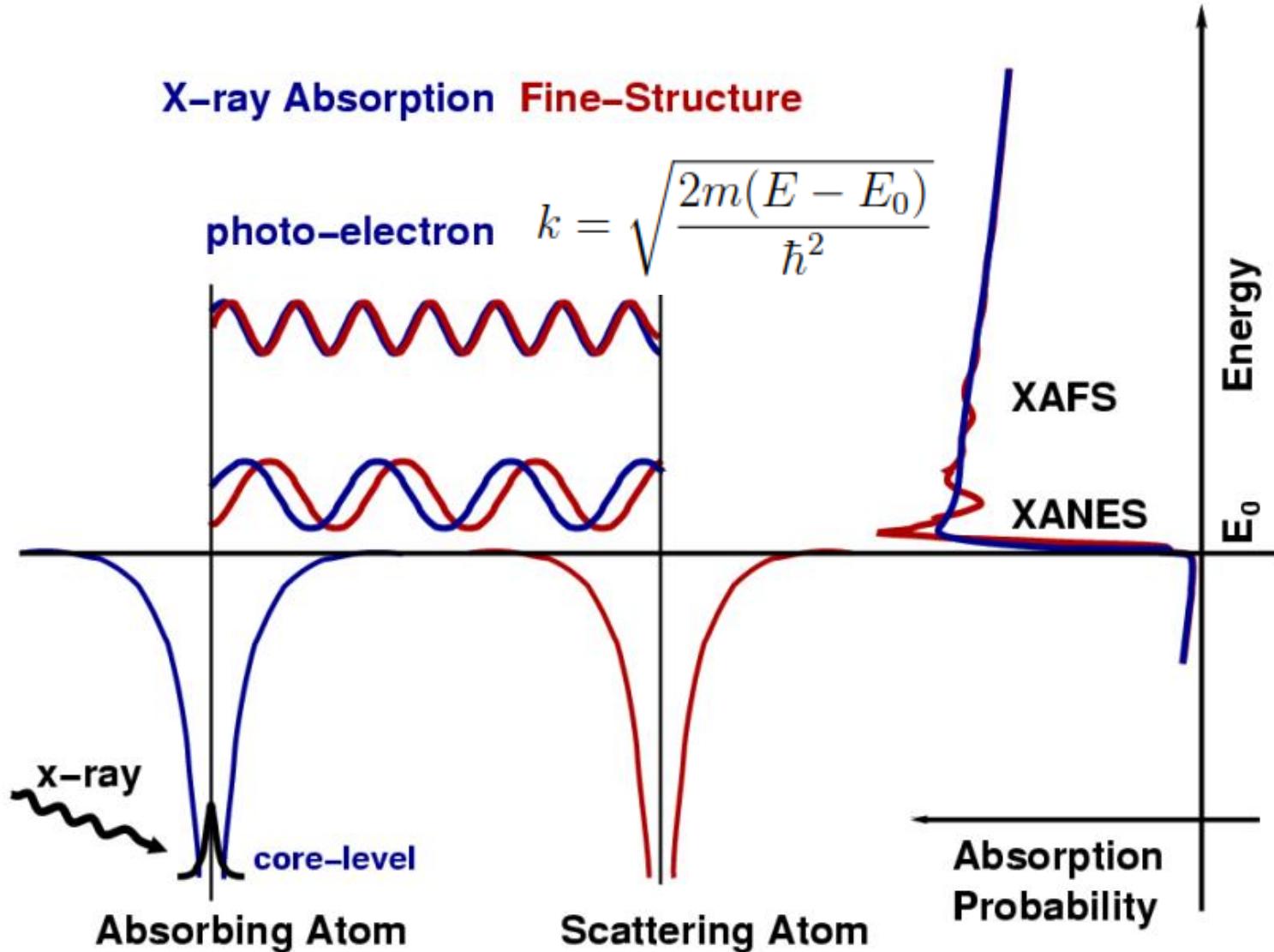
The spectral shape depends on oxidation state and local coordination.



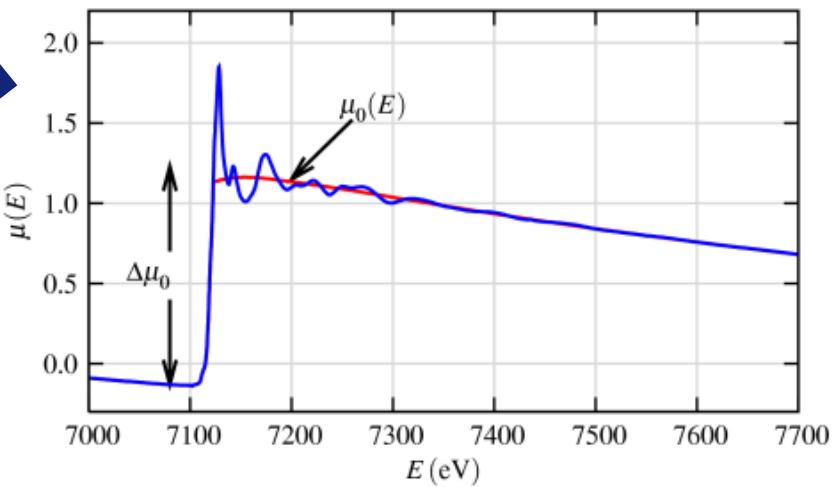
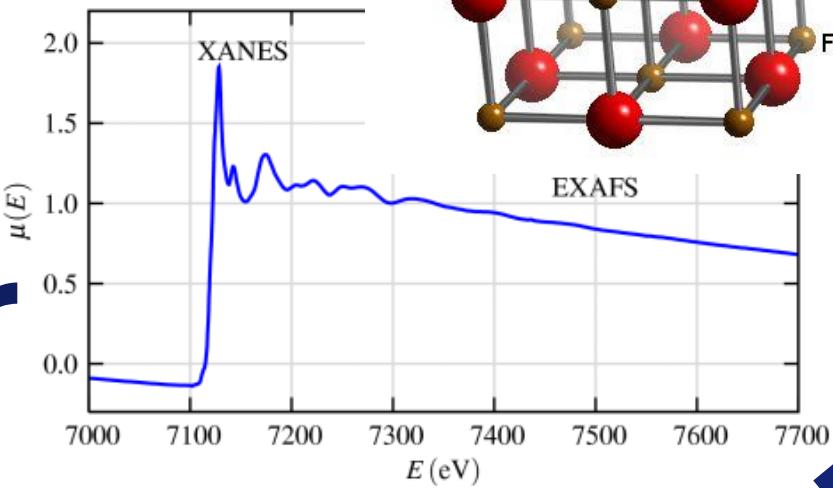
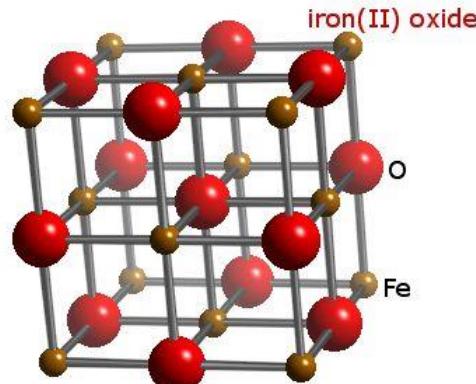
Theoretical XANES spectroscopy on MnO_6



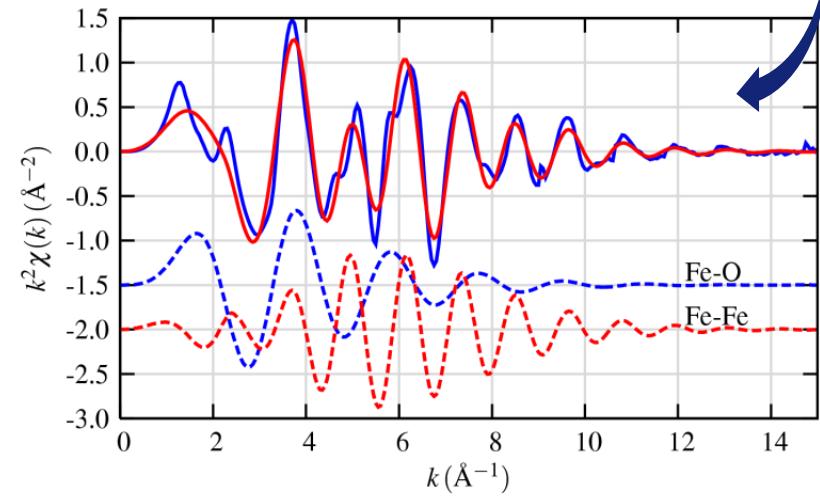
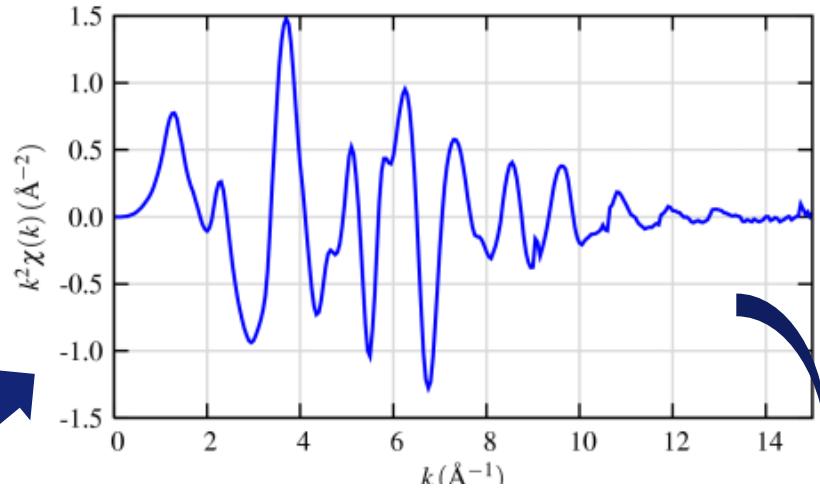
→ XANES is sensitive to electronic *and* atomic structure.



EXAFS data analysis



M. Newville, B. Ravel
XAFS software packages

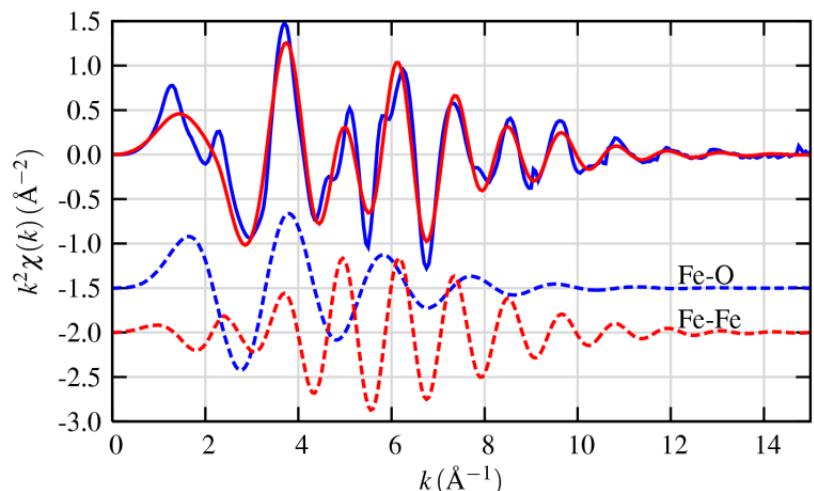
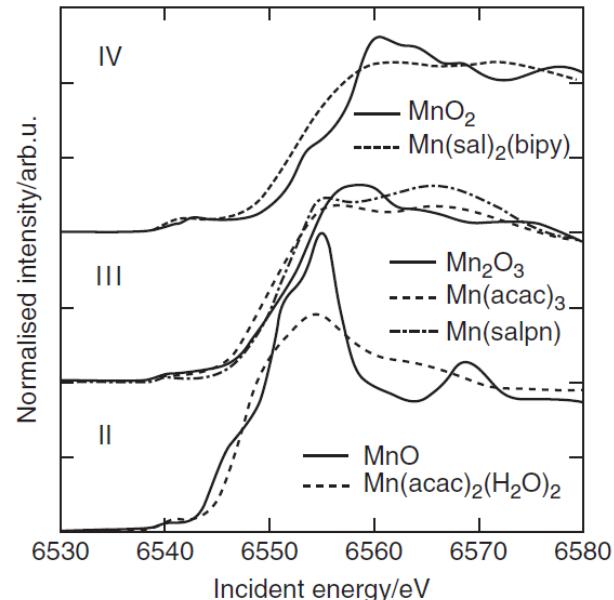


X-ray absorption spectroscopy

The X-ray absorption fine structure (XAFS: XANES, EXAFS) is shaped by the local electronic structure, i.e. the chemical environment.

Commonly, scientists attempt to extract:

- Absorber ion oxidation state
- Interatomic distances
- Coordination numbers
- Type of ligands



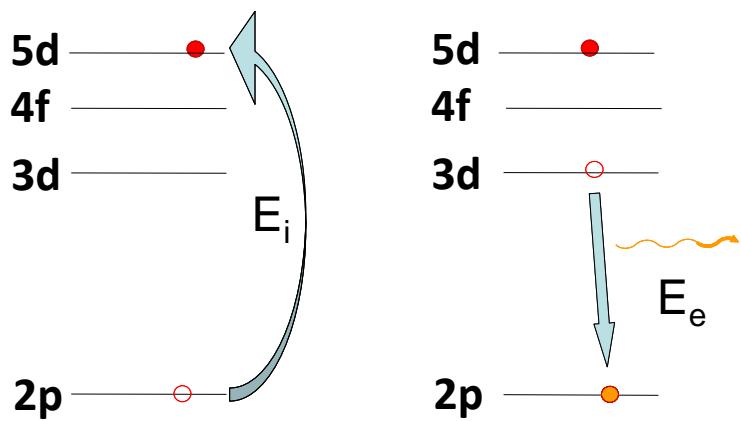
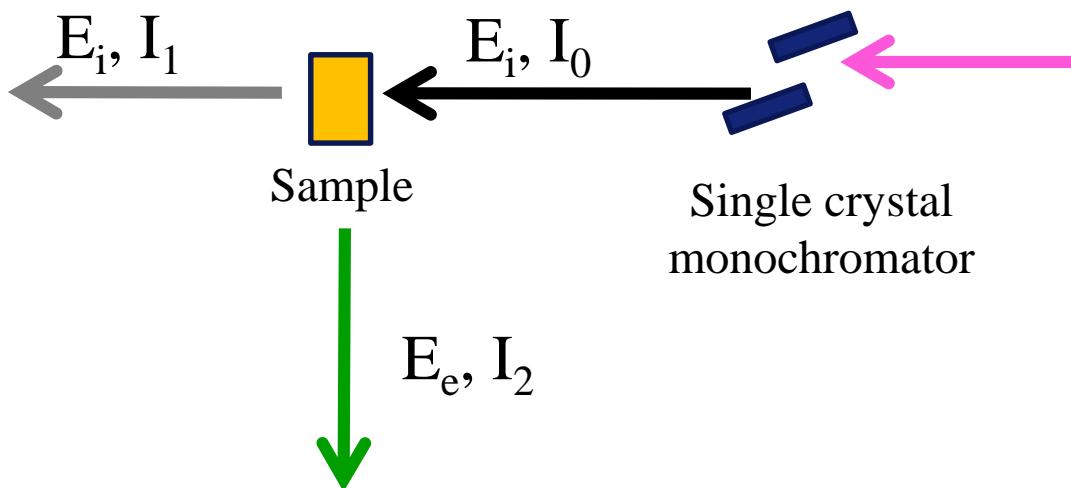
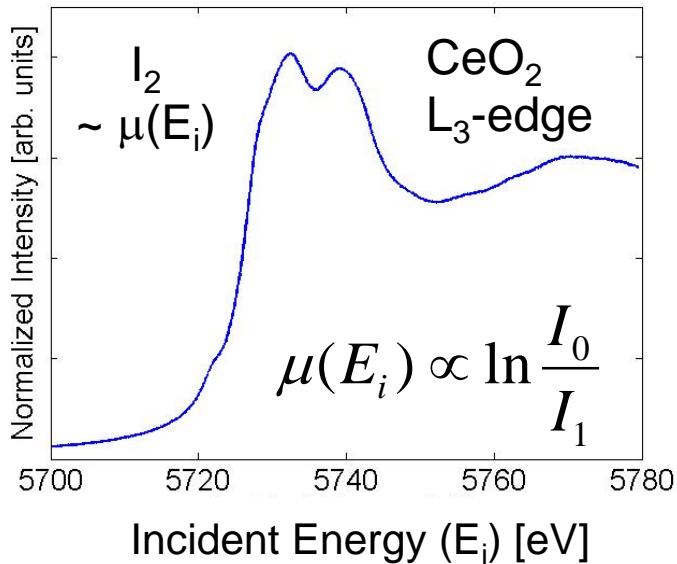
The strictly correct way of measuring μ or σ_{PE} is in transmission because this is how it is defined.

Often this is experimentally difficult or impossible (thick sample, dilute absorber).

The alternative is secondary detection of a process that follows the photoelectric effect:

- 1) Radiative decay (total/partial fluorescence yield)
- 2) Non-radiative decay (total/partial electron yield, ion yield)

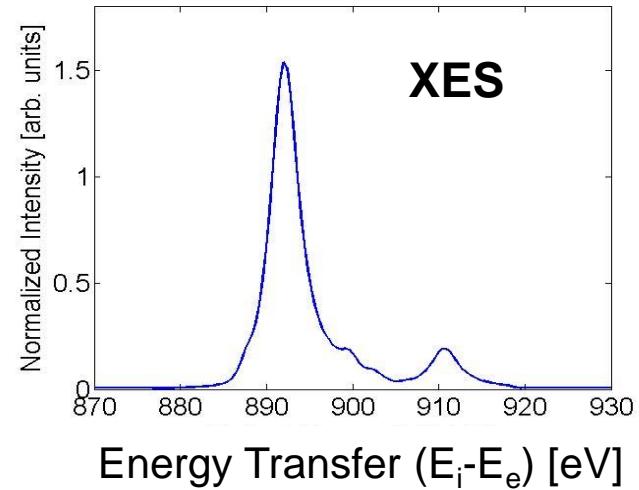
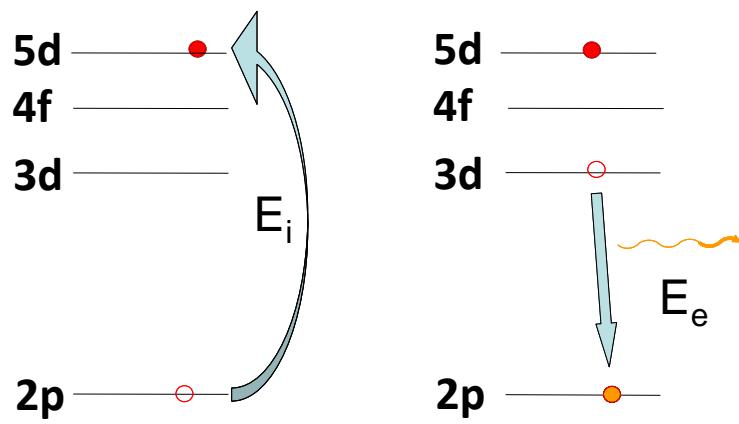
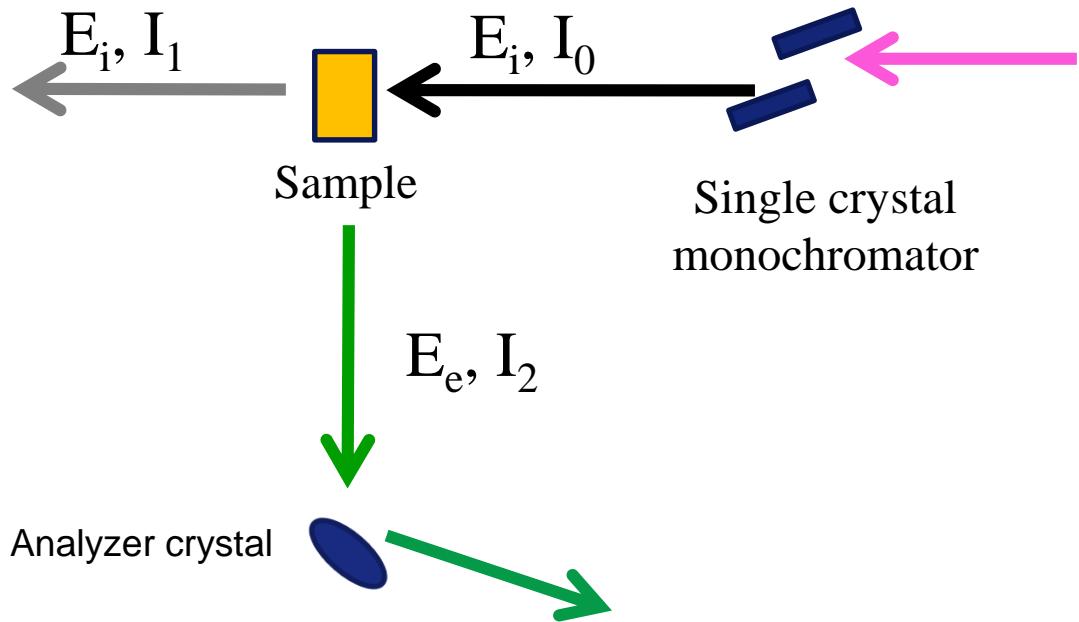
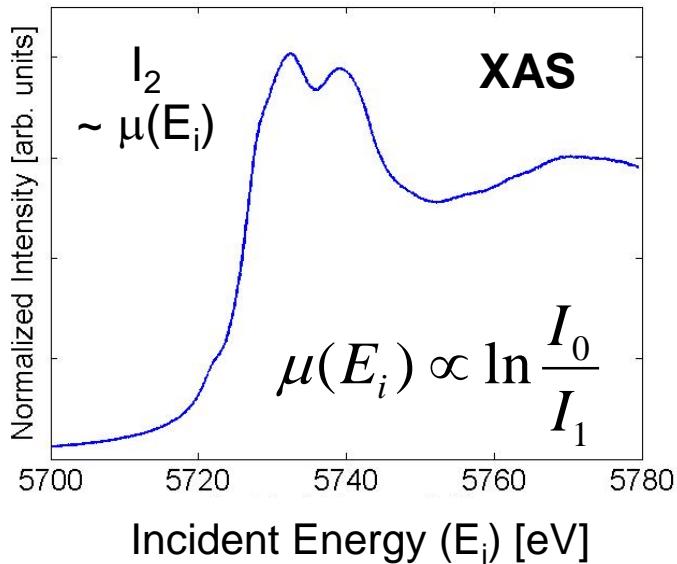
Hard X-ray Photon-in/Photon-out spectroscopy



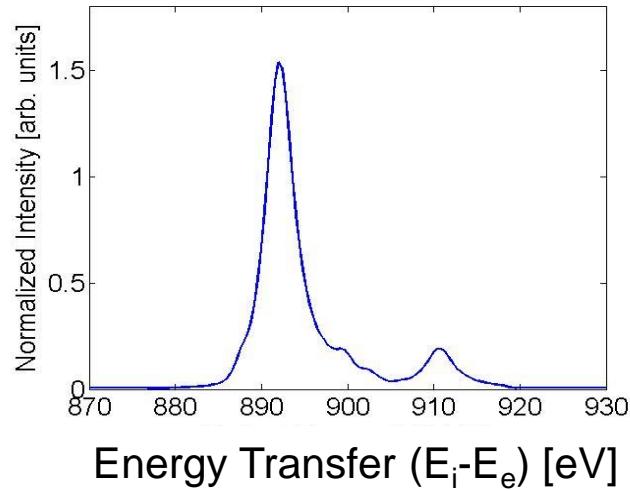
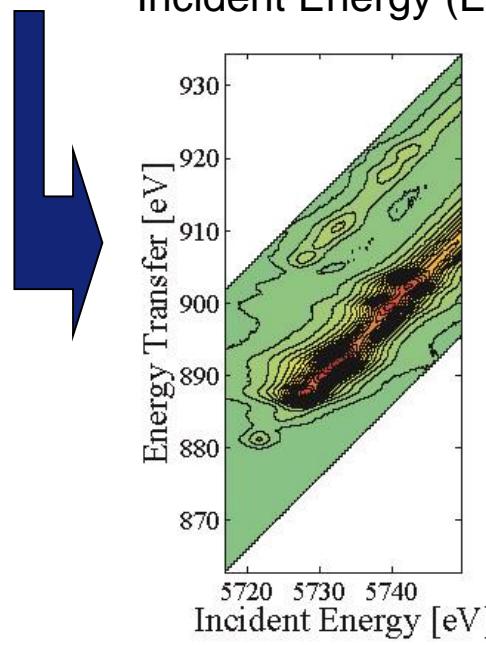
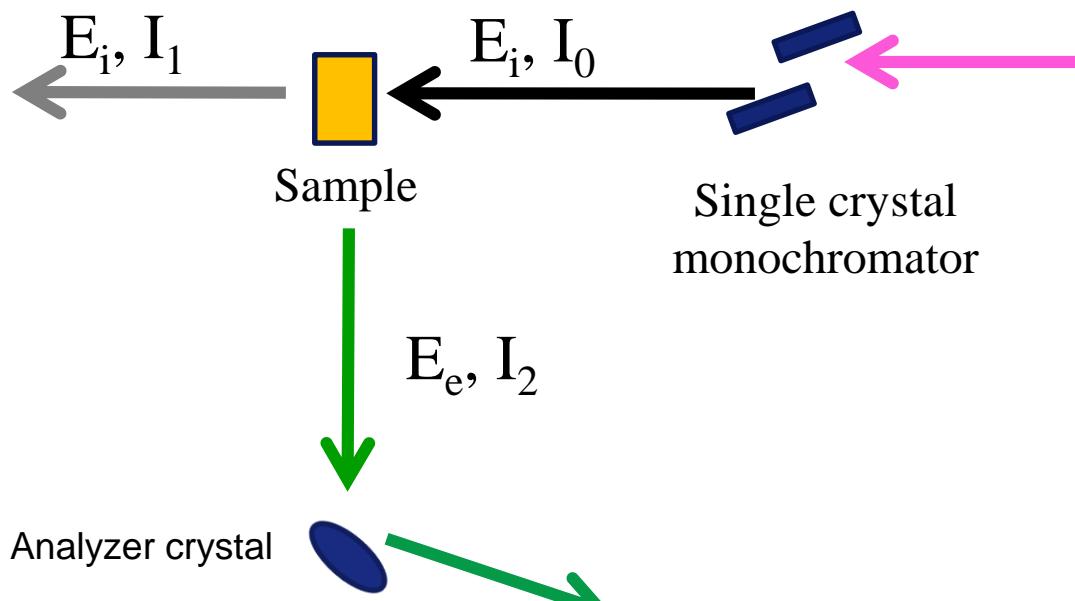
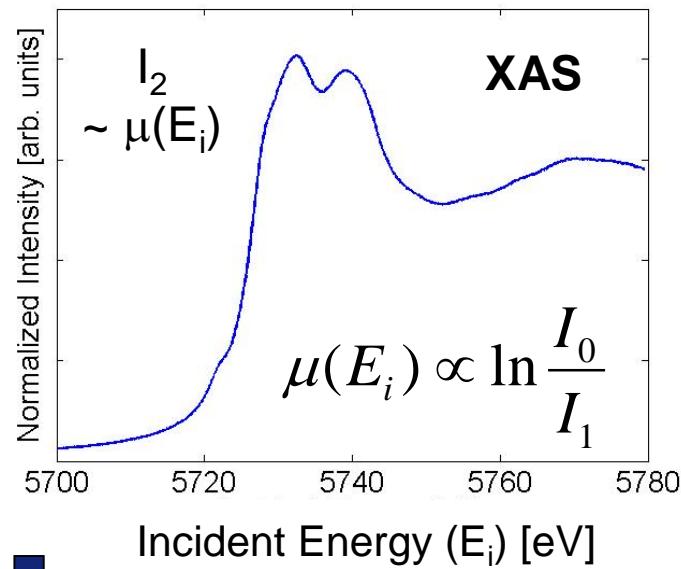
Second order process

Correctly treated with
Kramers-Heisenberg equation

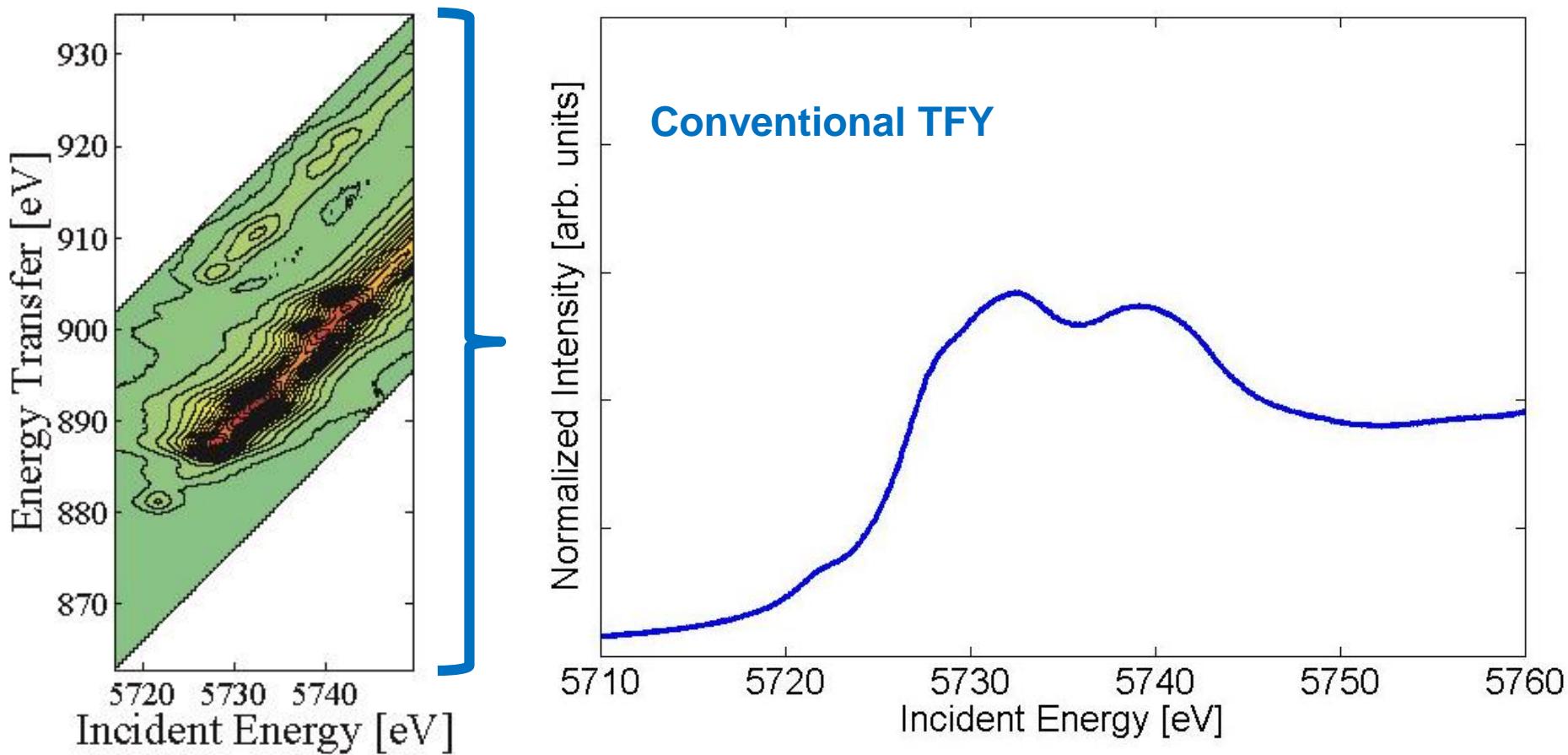
Hard X-ray Photon-in/Photon-out spectroscopy



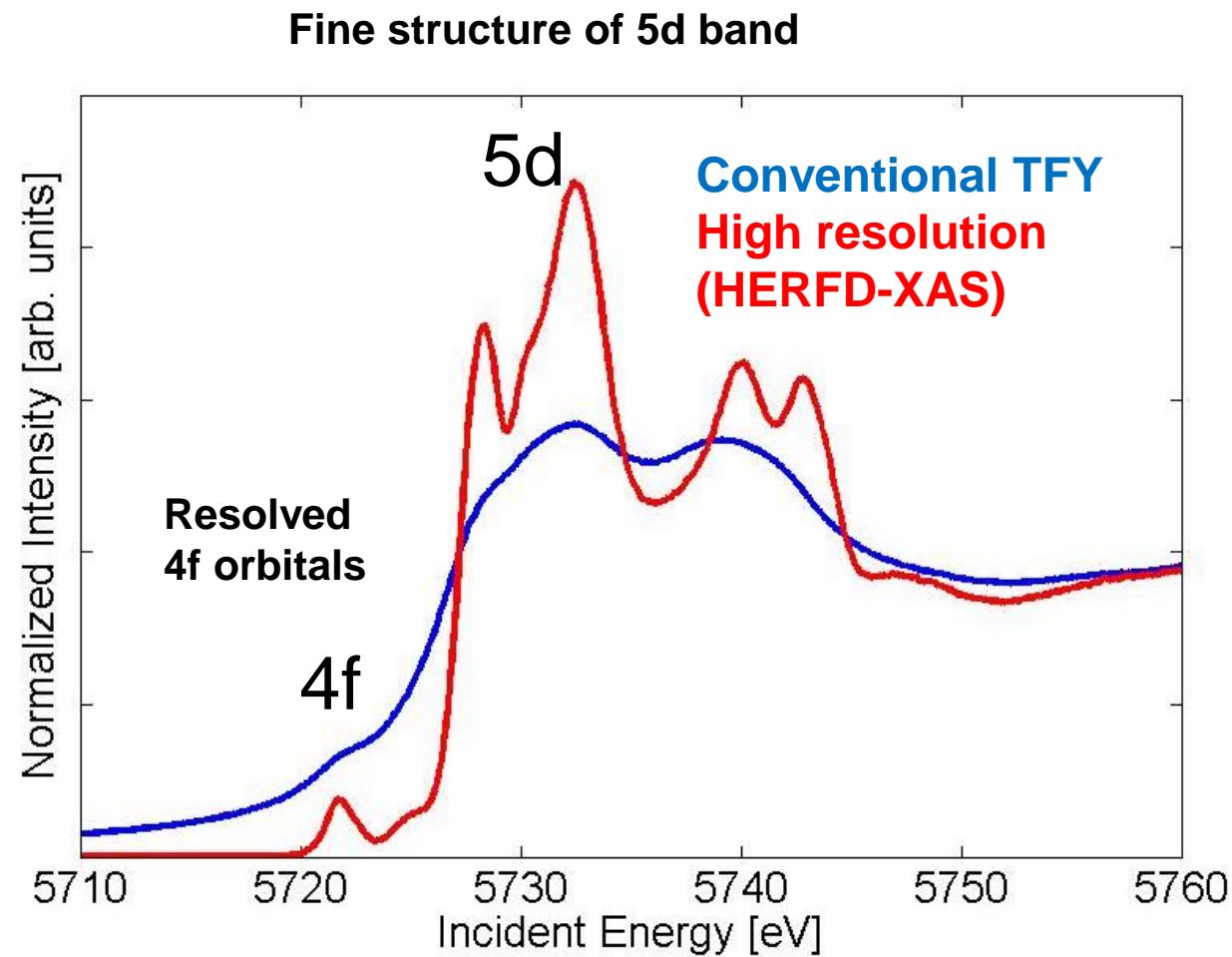
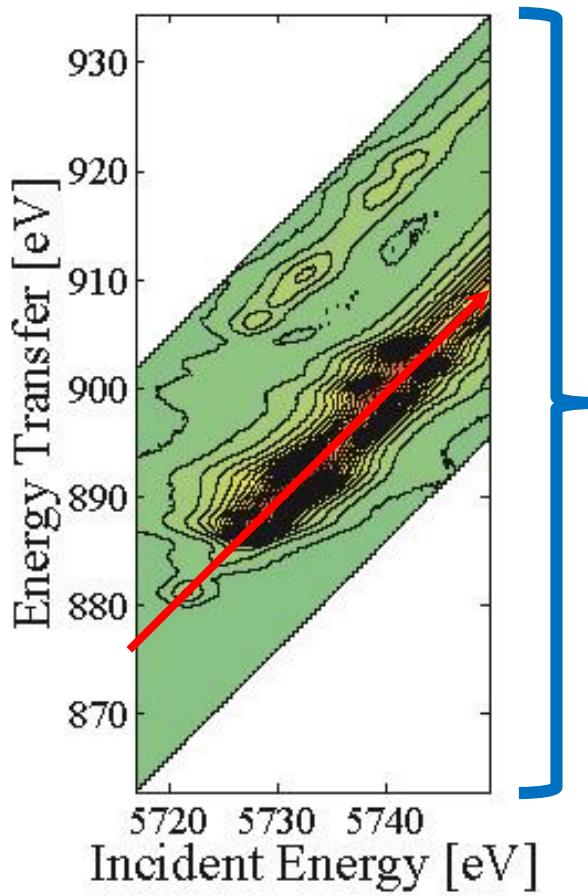
Hard X-ray Photon-in/Photon-out spectroscopy



The Ce L₃-edge of CeO₂



The Ce L₃-edge of CeO₂



High Resolution Fluorescence Detection

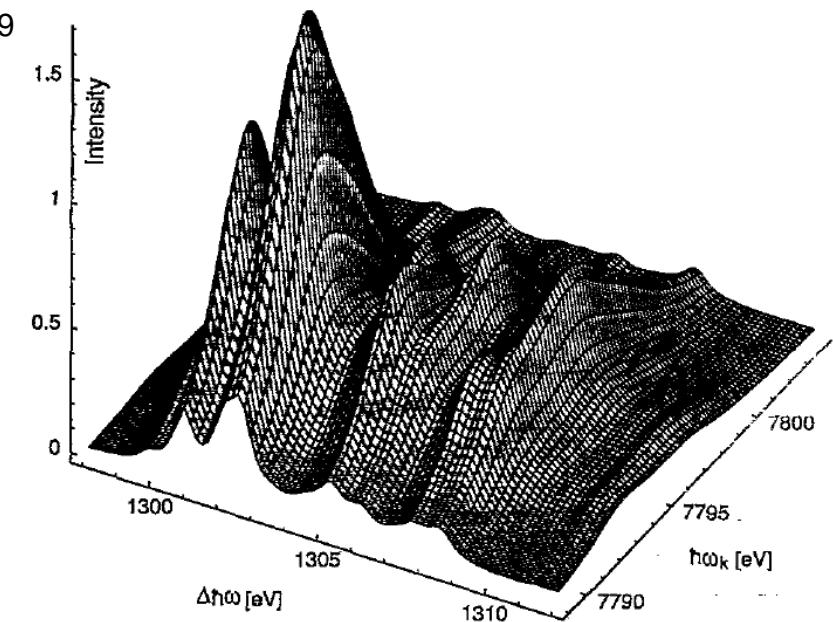
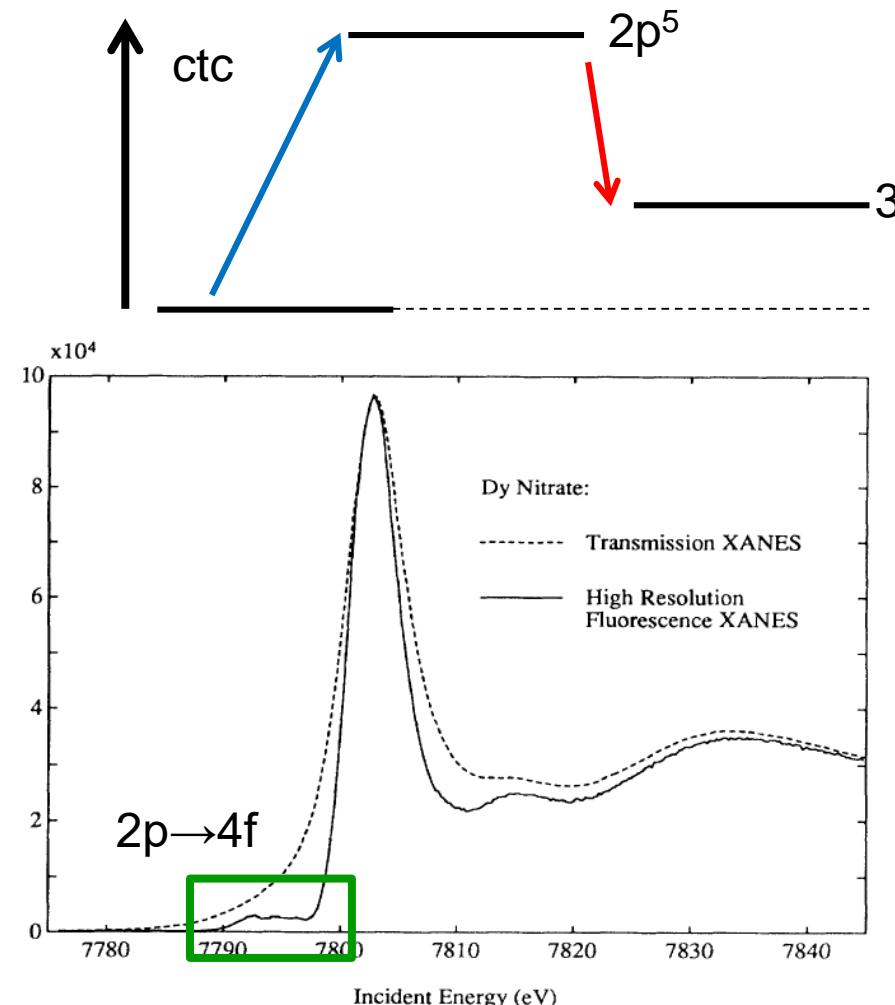
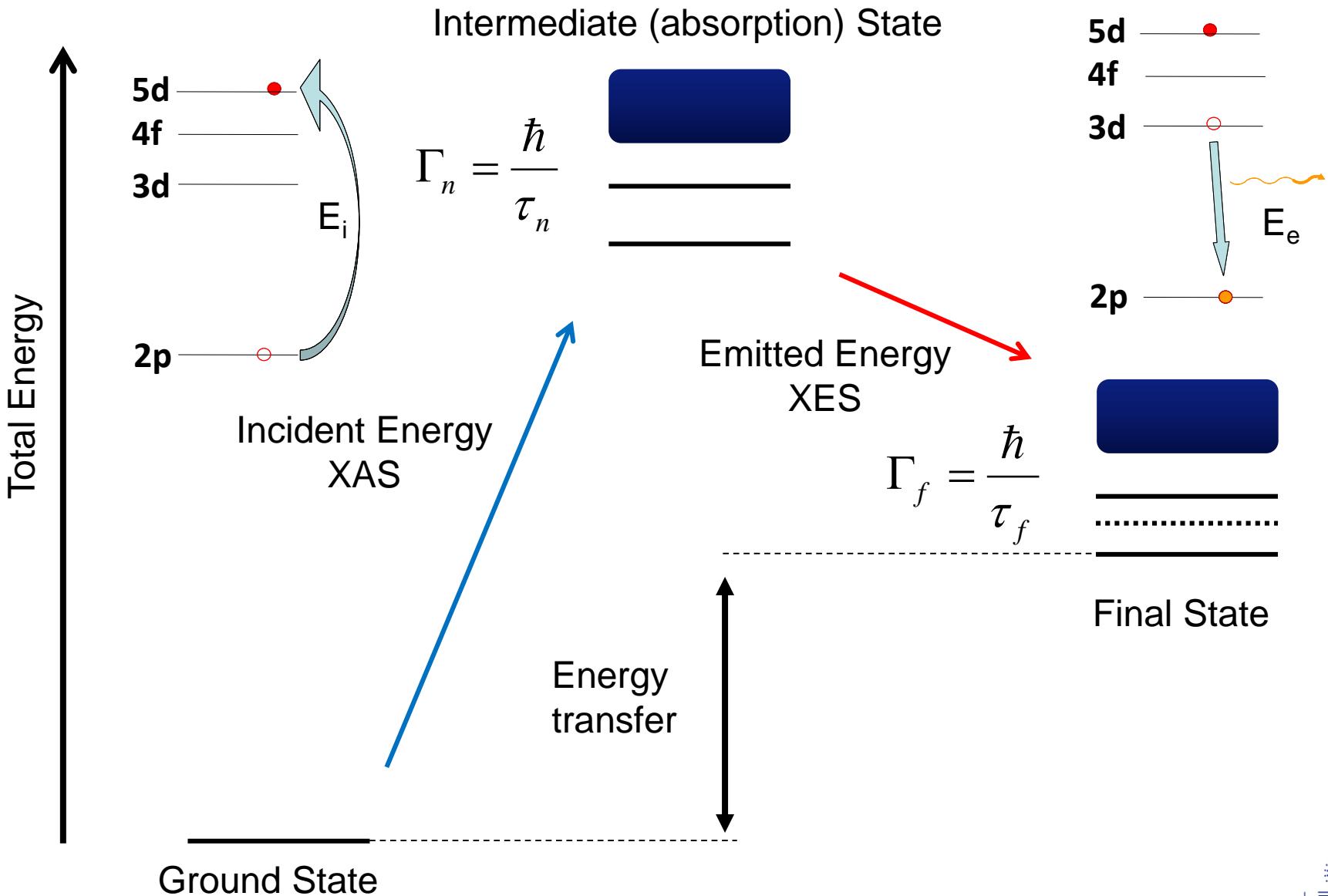


FIG. 2. Numerical calculation of the electric quadrupole \rightarrow dipole part ($2p_{3/2} \rightarrow 4f$, $3d_{5/2} \rightarrow 2p_{3/2}$) of the RRS cross section at the L_3 edge of Dy^{3+} , as a function of ingoing and transferred photon energies.

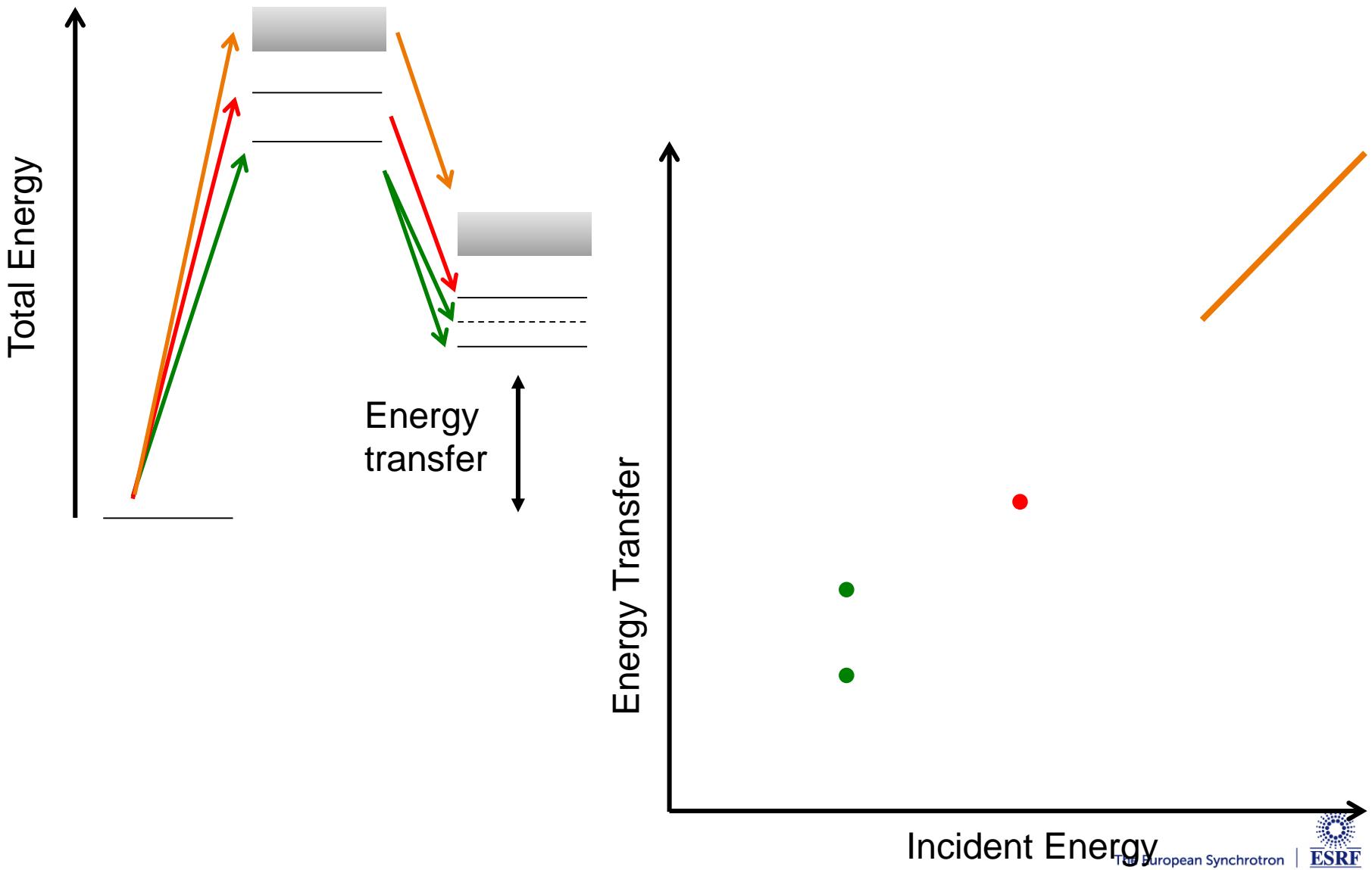
Hämäläinen et al., PRL 67 2850
(1991)

Carra et al. PRL 74 3700 (1995)

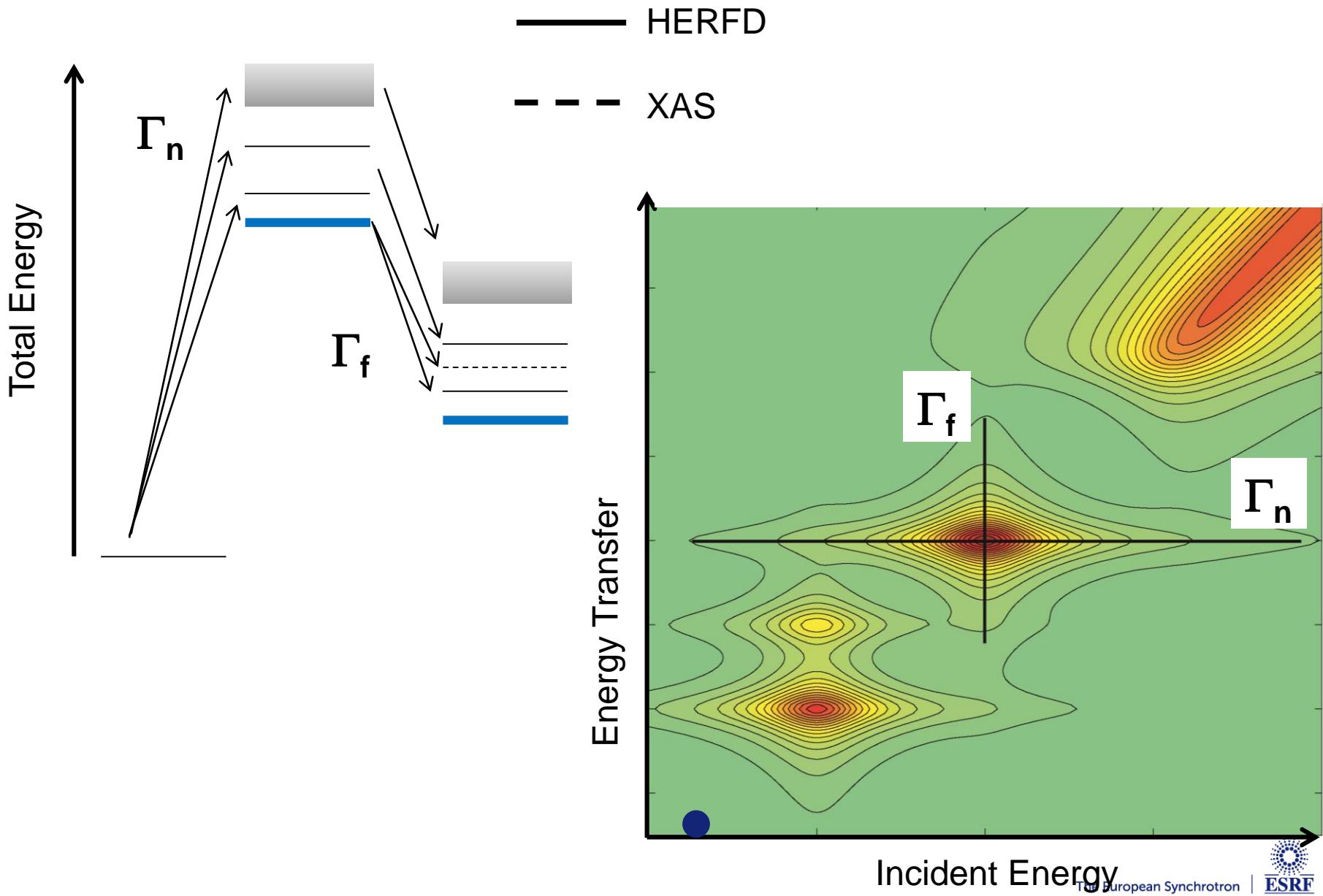
Energy diagram in photon-in/photon-out spectroscopy



The RIXS plane



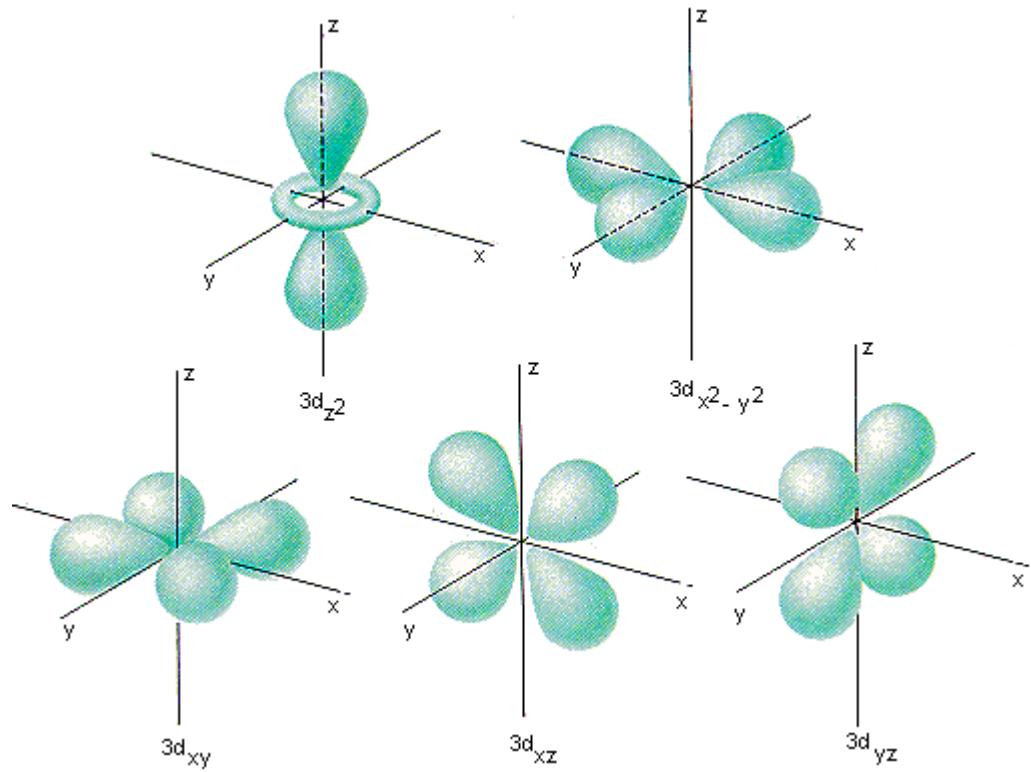
The RIXS/RXES plane



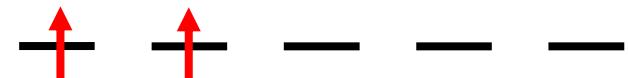
Multiplet Theory

An open shell

3d orbitals



$$E_t = E_{\text{rest}} + E_{3d}$$



$$E_t = E_{\text{rest}} + ?$$

How can we treat open shells? → MULTIPLET THEORY



 two electron operator: $\sum_{i=2}^N \sum_{j=1}^{i-1} g_{ij} \equiv \sum_{i>j} g(\vec{r}_i, \vec{r}_j)$

Matrix element for **two** electron operator:

$$\begin{aligned}
 & \langle \Psi | \sum_{i>j} \sum g_{ij} | \Psi \rangle \\
 &= \sum_{i>j} \sum [\langle ij | g | ij \rangle - \langle ij | g | ji \rangle]
 \end{aligned}$$



 "direct term" > 0 "exchange term" > 0

“Slater integrals or Racah parameters”

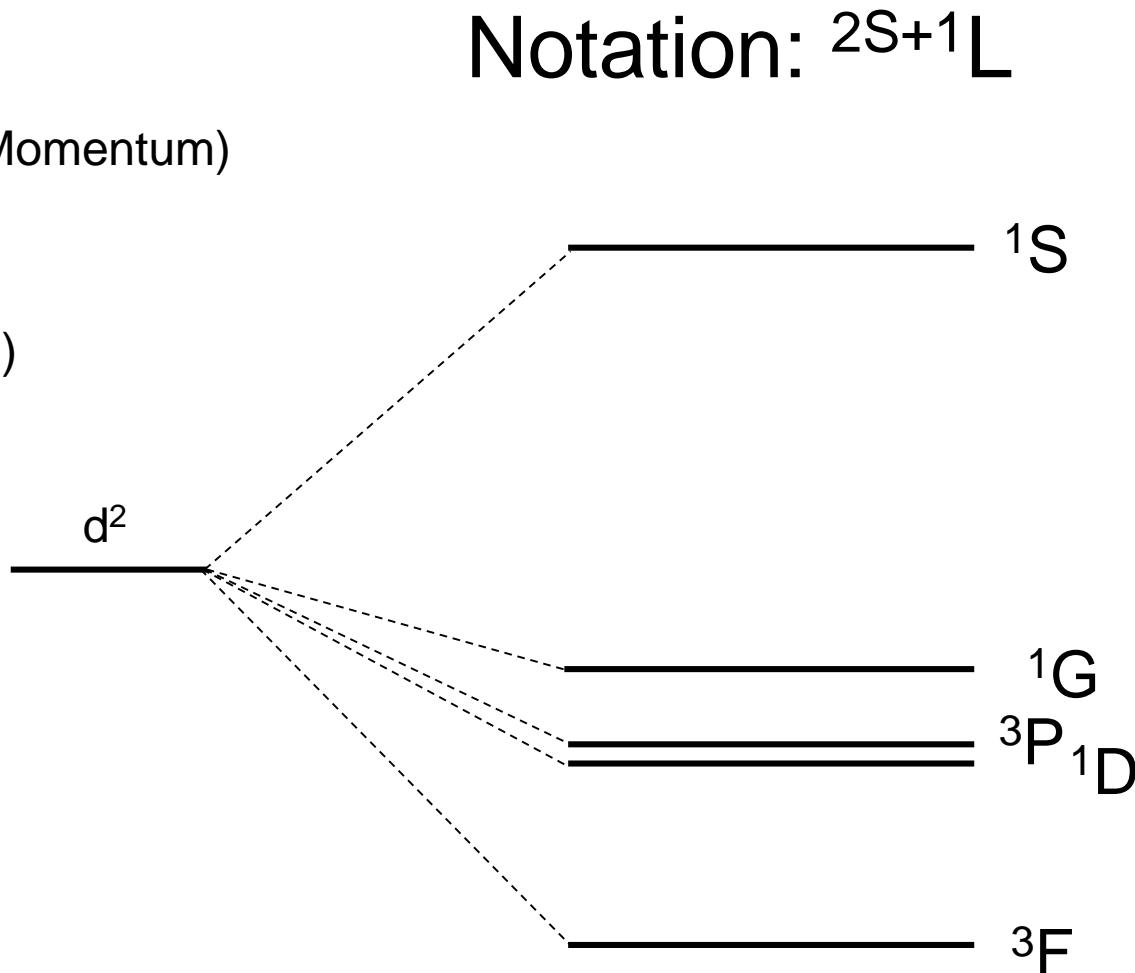
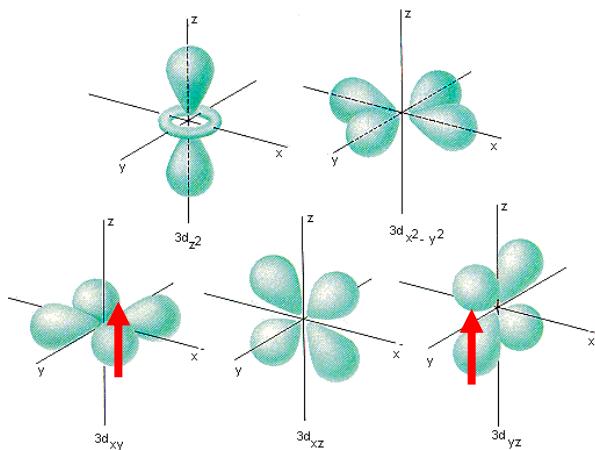
Angular momentum coupling

$$\vec{L} = \vec{l}_1 \otimes \vec{l}_2 \quad (\text{Total Angular Momentum})$$

$$L = |l_1 - l_2| \dots l_1 + l_2$$

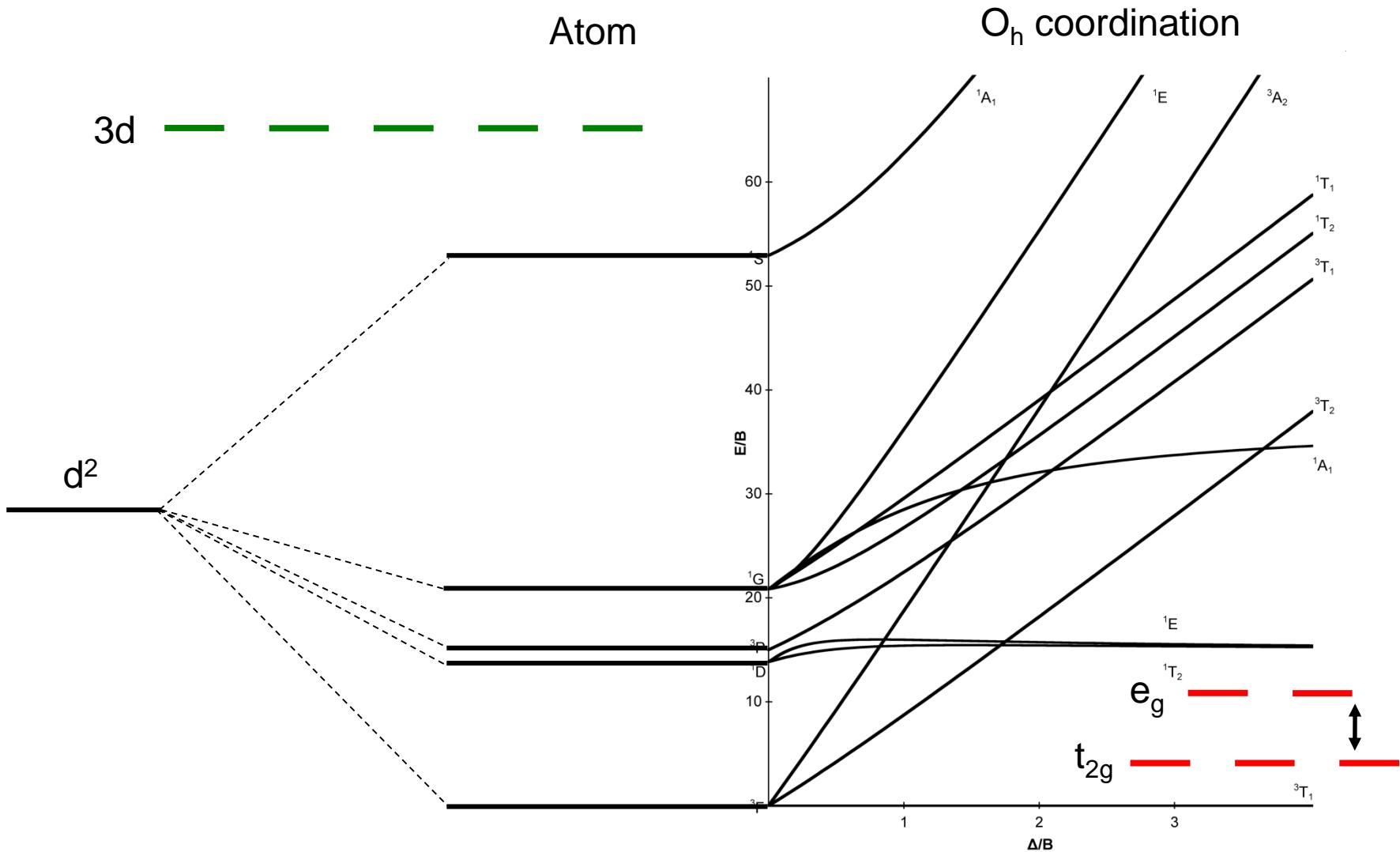
$$l_1 = l_2 = 2 \quad (\text{for d-electrons})$$

$$L = 0 \dots 4 \quad (\text{S,P,D,F,G})$$



The Racah parameters determine the magnitude of the splitting.

Crystal Field Splitting: Tanabe-Sugano diagram



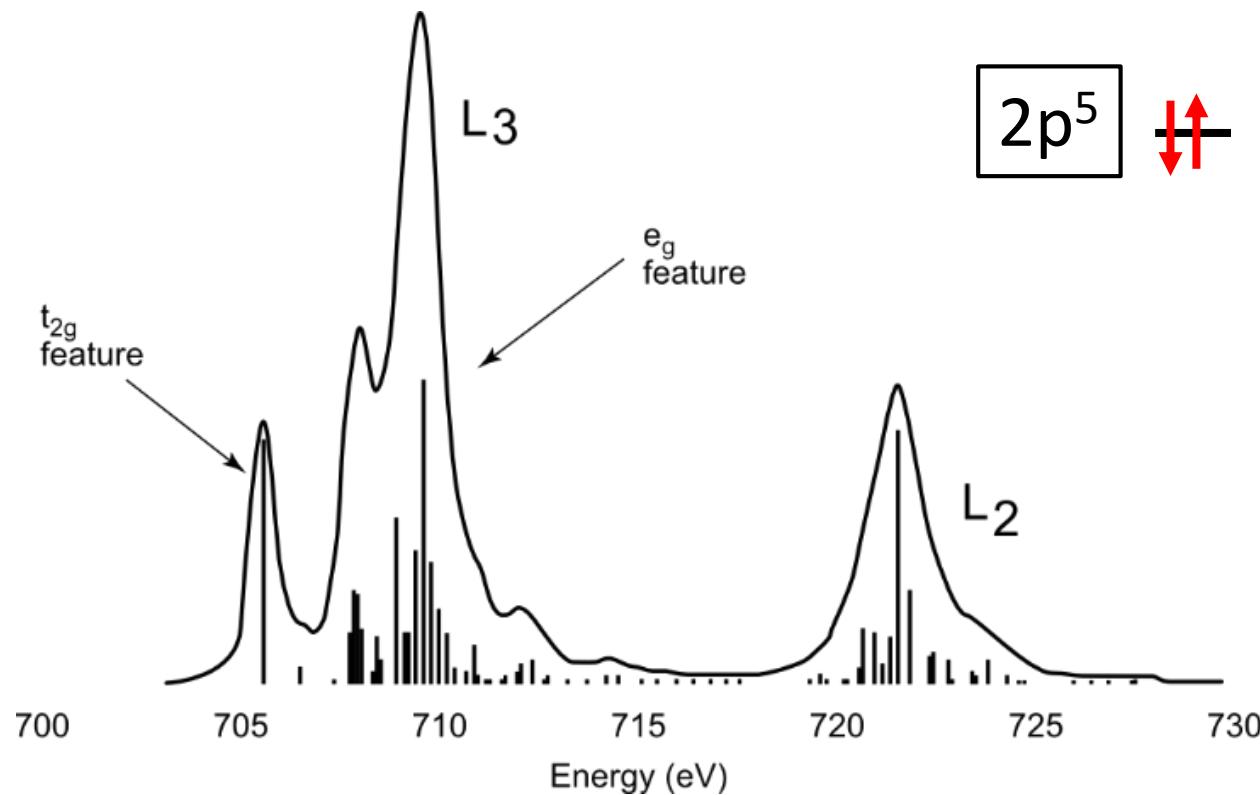
Additional splitting due to orbital hybridization (ligand field theory)
→ The spectra become very very complex already for d^2

Inner-shell spectra are often very complex

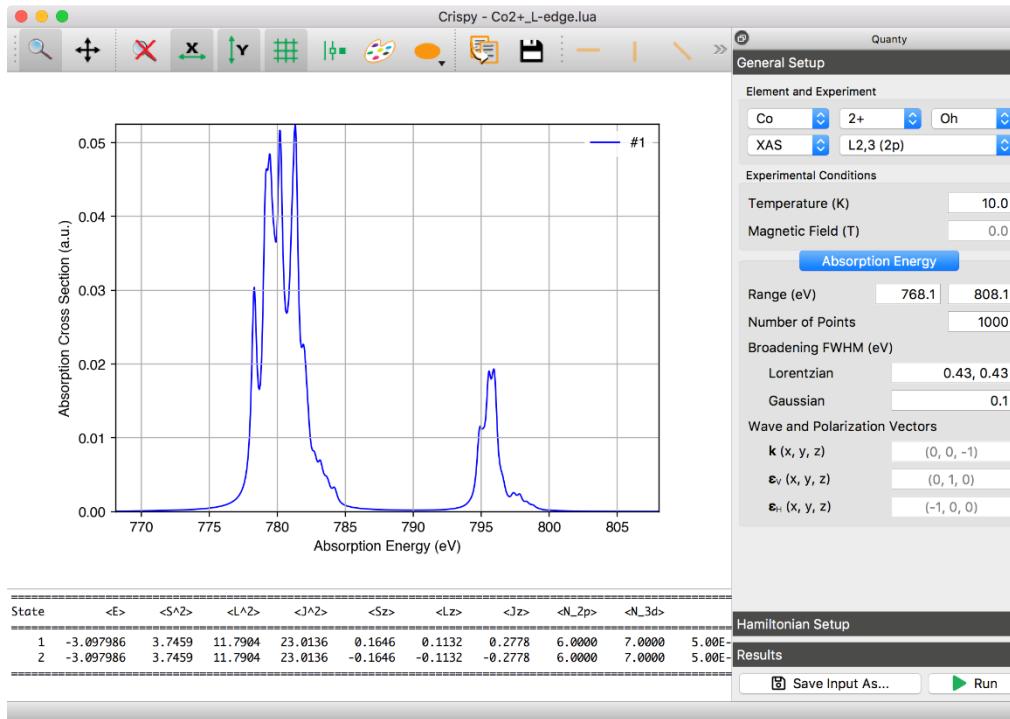
Intra-valence shell electron-electron interactions

Core hole – valence electron interactions

Multi-electron excitations



Crispy: GUI for Core-level Spectroscopy Simulations



**Marius Retegan
Maurits Haverkort**

3d, 4d, 5d
XAS, XPS, XMCD, X(M)LD, RIXS

4f, 5f (first-half)
XAS, XPS, XMCD, X(M)LD

- Crispy is free and open-source software.
- It is easy to install on all operating systems. Try it today!



<http://esrf.eu/computing/scientific/crispy>



crispy + esrf

References

Internet

<http://www.tcd.ie/Physics/People/Cormac.McGuinness/Cowan/>

<http://www.anorg.chem.uu.nl/CTM4XAS/>

Atomic Multiplets

Slater, J. C. Quantum *Theory of Atomic Structure*; McGraw-Hill: New York, 1960; Vols. I, 11.

B. H. Bransden and C. J. Joachain. *Physics of atoms and molecules*. Longman, 1983

R. D. Cowan. *The Theory of Atomic Structure and Spectra*. University of California Press, 1981.

Ligand Field Multiplets

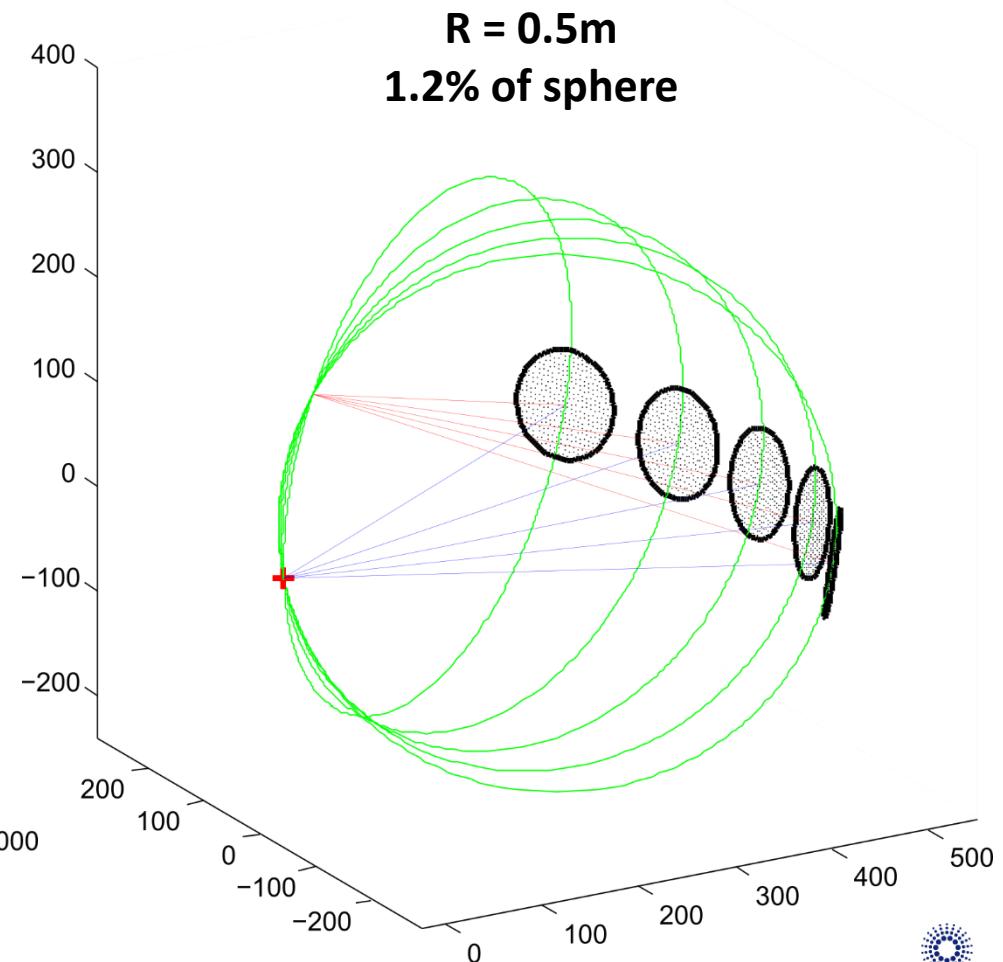
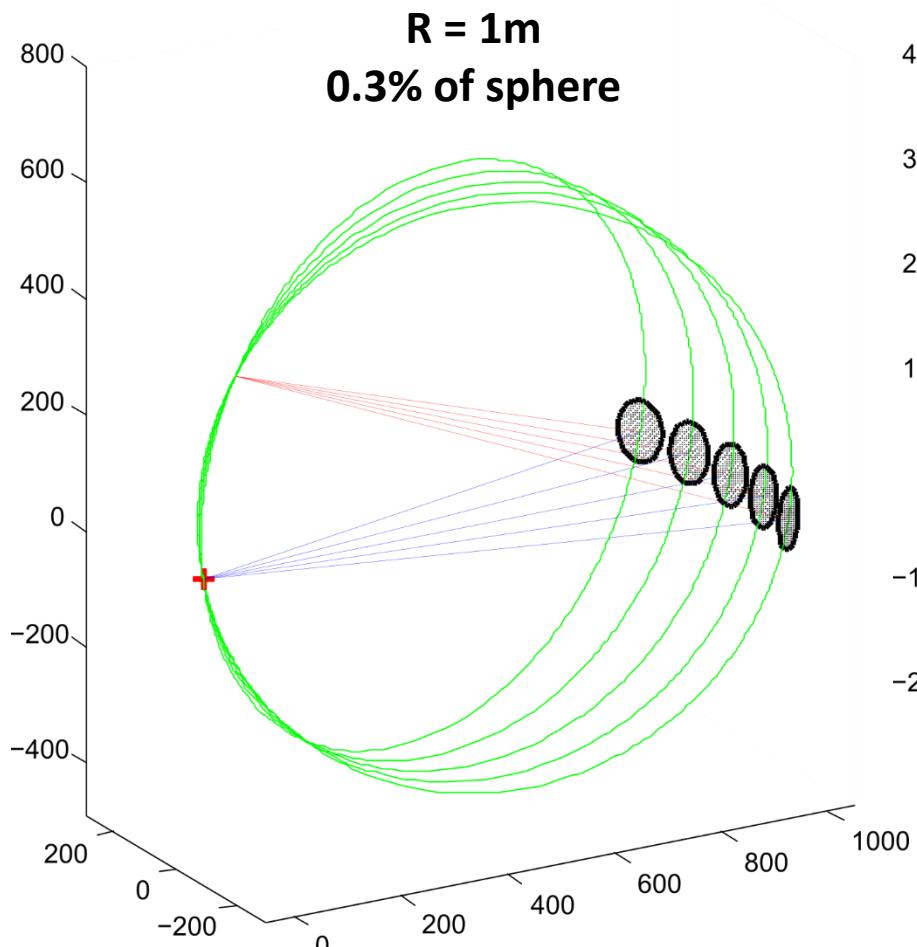
J. S. Griffith. *The theory of transition-metal ions*. University Press, 1964.

Ballhausen, C. J. *Introduction to Ligand Field Theory*; McGraw-Hill: New York, 1962.

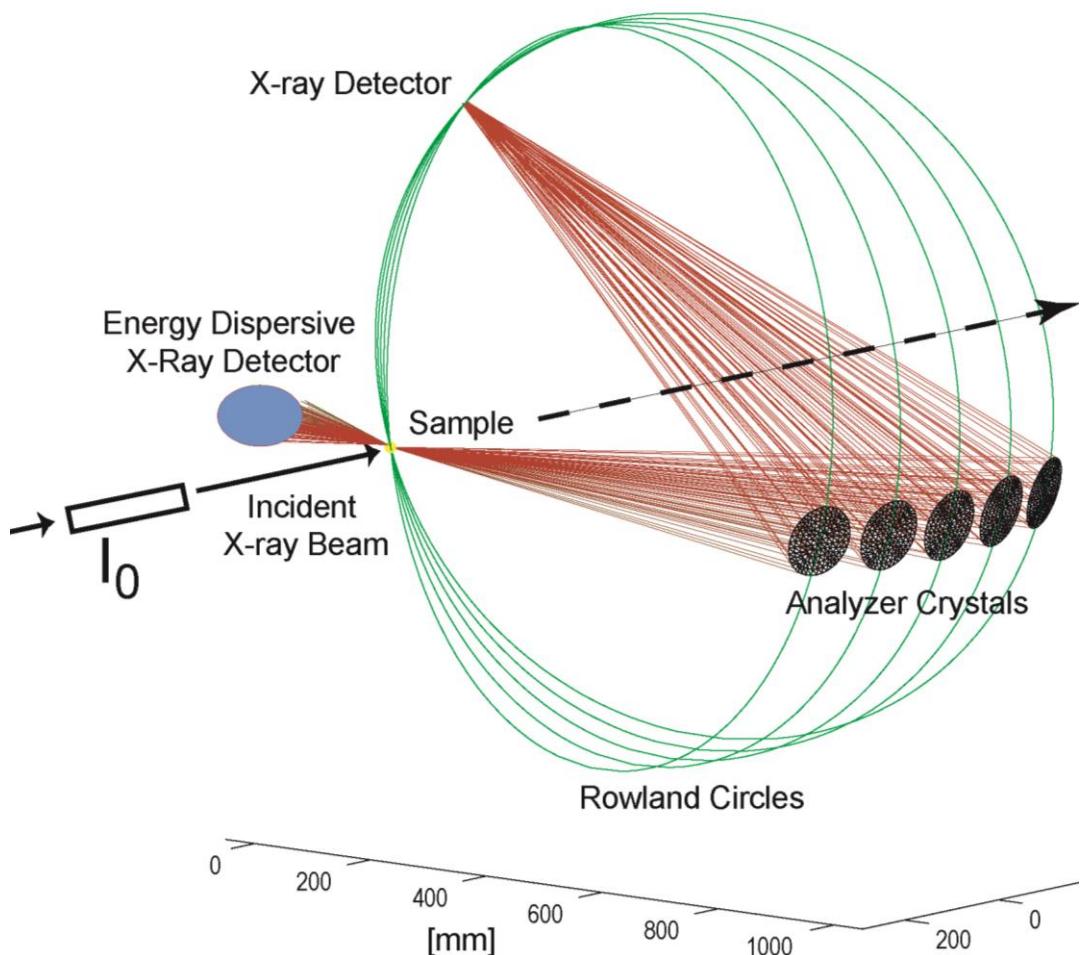
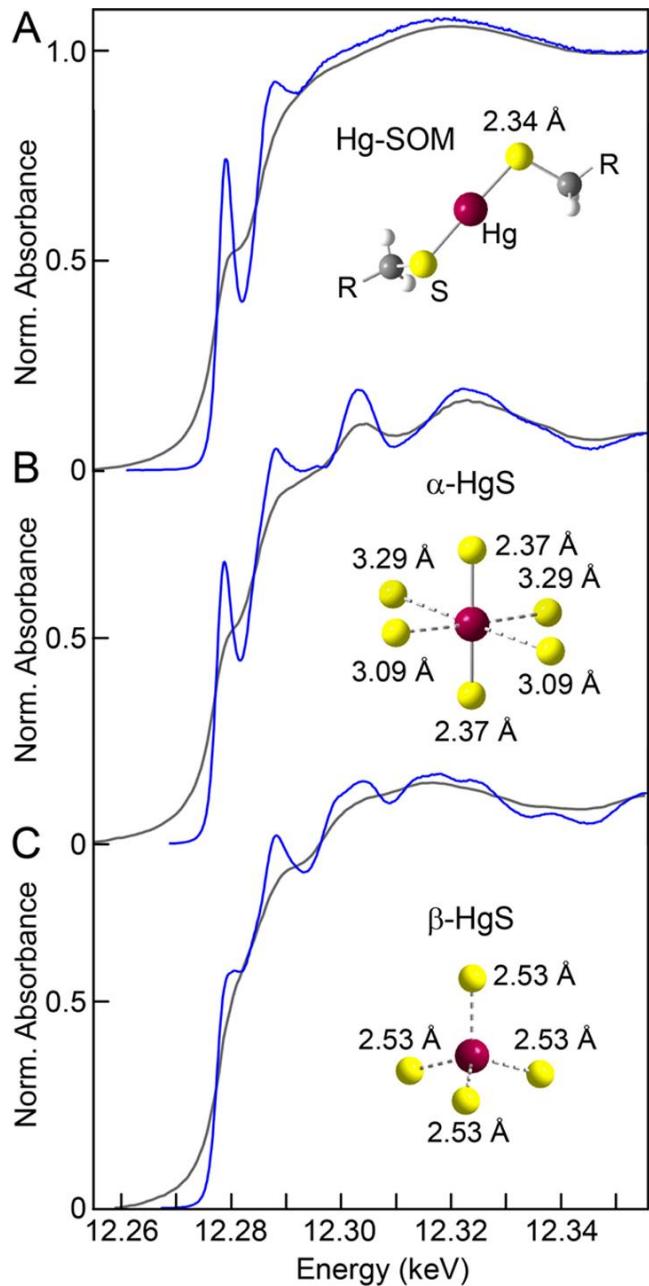
B. N. Figgis. *Introduction to ligand fields*. Interscience Publishers, 1967.

Increasing the efficiency

Increase solid angle by reducing the analyzer crystal bending radius.

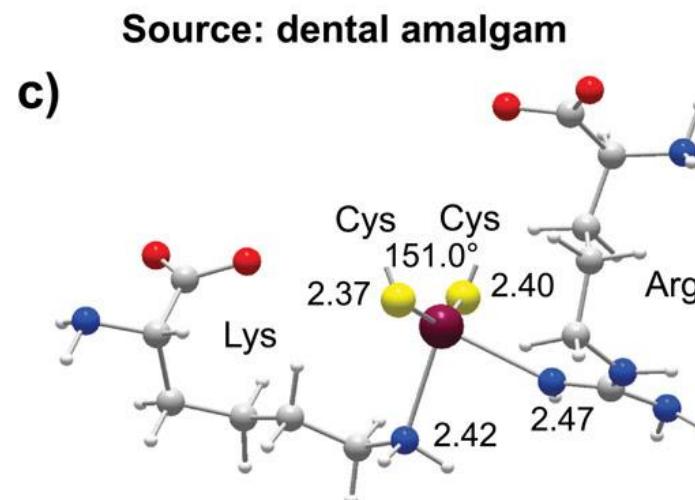
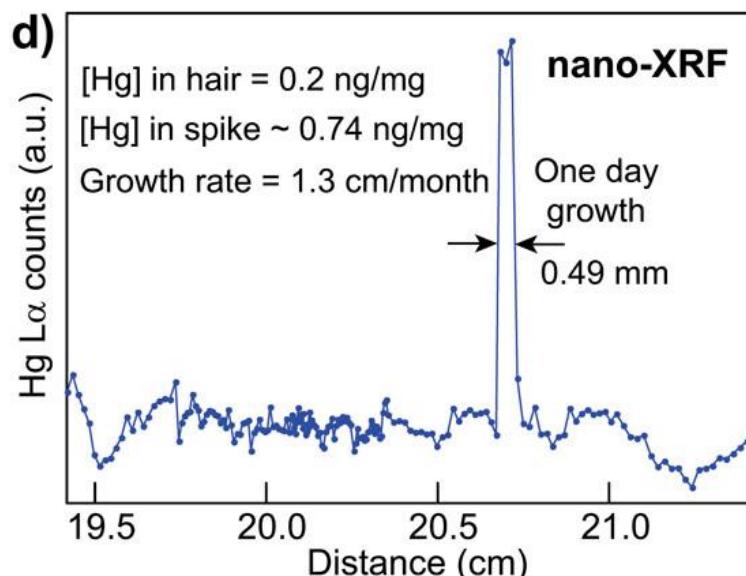
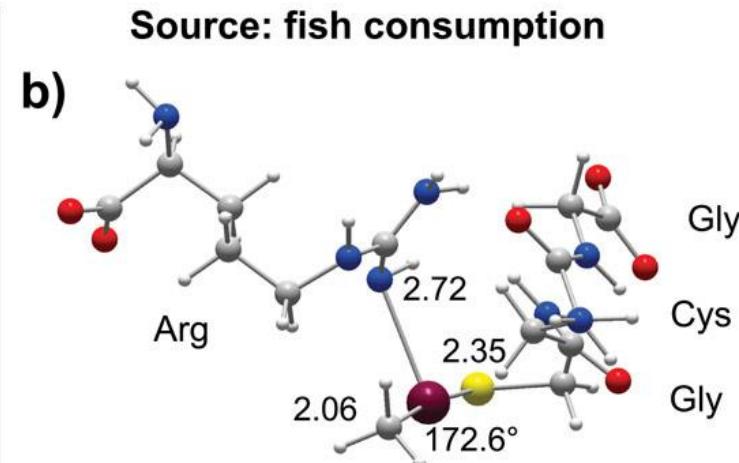
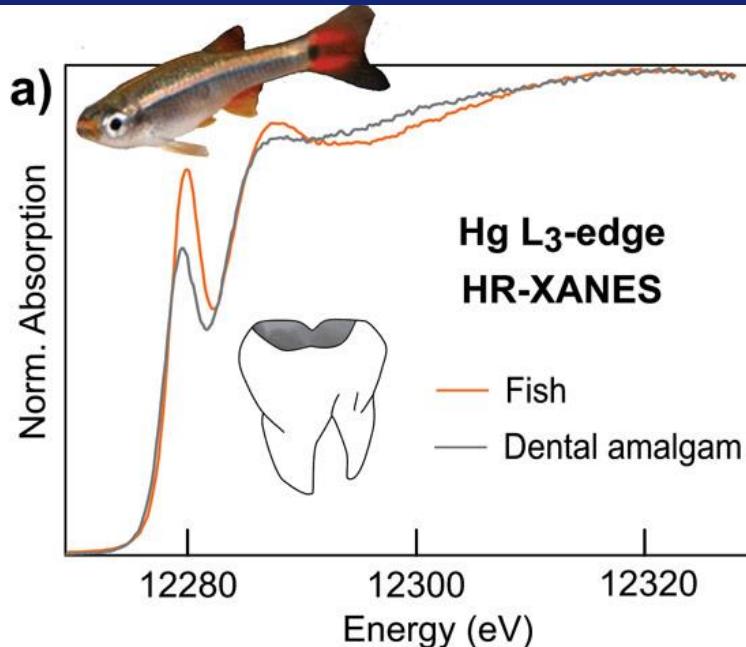


HERFD-XANES in Hg



A. Manceau et al., Env. Sci. & Techn (2015)
A. Manceau et al., Inorg. Chem. (2015)

HERFD-XANES in low concentration: Hg speciation in human hair



Thank you for your attention!

