School on
Synchrotron Light Sources
and their Applications

ICTP

6 - 17 December 2021
An ICTP Virtual Meeting
Trieste, Italy

Further information:
http://indico.ictp.it/event/9645/
smr3611@ictp.it

SESAME

Synchrotron-light for
Experimental Science and
Applications in the Middle East

School on Synchrotron Light Sources and their Applications, 6 - 17 Dec. 2021

Fundamentals of X-ray Absorption Fine Structure

Messaoud Harfouche

Synchrotron-light for Experimental Science and Applications in the Middle East, Jordan

Acknowledgment

Some slides are derived from other presentations by:

Sakura Pascarelli ➔ scientific director at European XFEL, Hamburg, Germany

Matthew Newville ➔ Beamline Scientist GSECARS, APS, Argonne National Laboratory, USA

Bruce Ravel ➔ Lead Beamline Scientist for beamline 6-BM, NSLSII, USA

François Farges ➔ Professeur des universités 1ère classe au Muséum national d'Histoire naturelle, Paris, France

Daniel Grolimund➔ Group Leader of the Chemical Imaging Group and Project Head of the microXAS Beamline Project, PSI, SLS, Switzerland

X-ray Absorption

Main X-ray based techniques

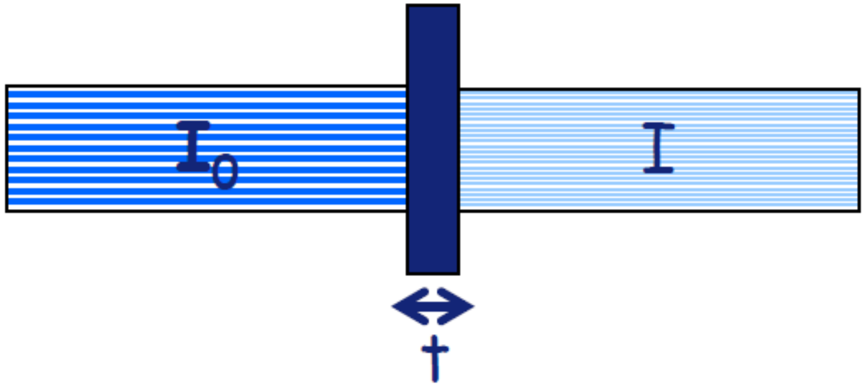
- ☐ **Two fundamental X-ray-matter interactions**:
  - ✓ photoelectric absorption
  - ✓ scattering (elastic, inelastic)

- ☐ **Two families of experimental techniques:**

  - ➢ **spectroscopy → exchange of energy (**electronic structure, local structure of matter**)**
    - absorption (XAS, EXAFS, XANES, ..)
    - emission (XES, HERFD, ..)
    - inelastic scattering (IXS, RIXS, X-ray Raman, etc..)

  - ➢ **elastic diffusion → no exchange of energy (microscopic geometric structure)**
    - “diffraction” for crystalline solids (XRD, GIXRD, ….)
    - “scattering” for amorphous solids, liquids (XRS, WAXS, SAXS, …)

The Absorption Coefficient μ

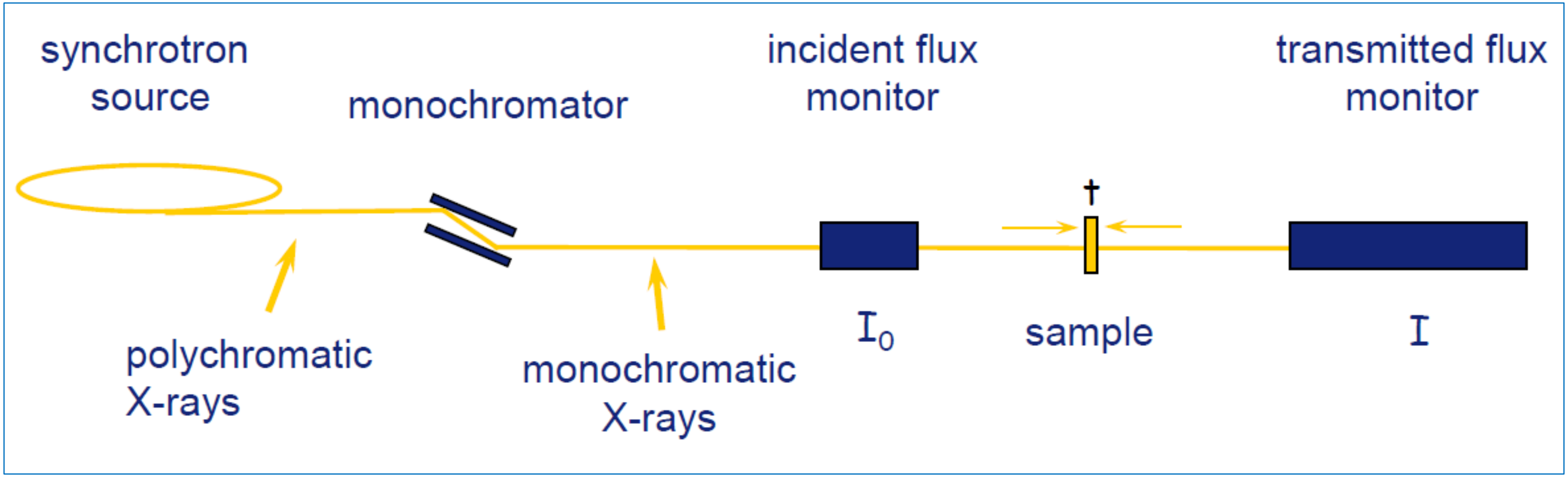


$$I = I_0 \exp[-\mu t]$$

linear absorption coefficient

$$\mu t = \ln [I_0/I]$$

The Absorption Coefficient μ



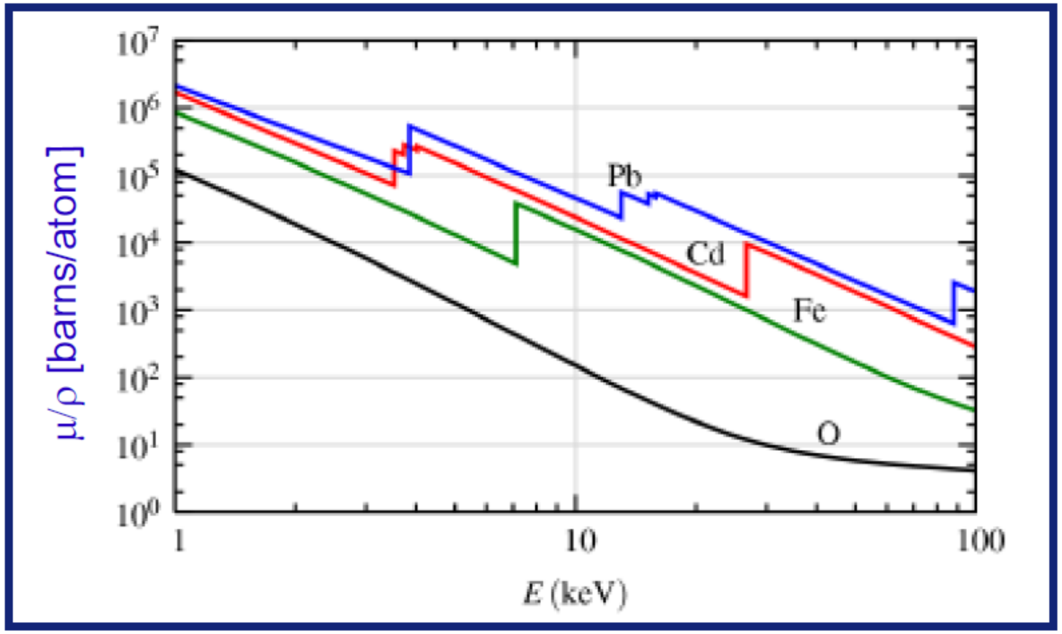
Measure I_0 and I as a function of E_X

Calculate: $\mu t = \ln[I_0/I]$

The Absorption Coefficient μ

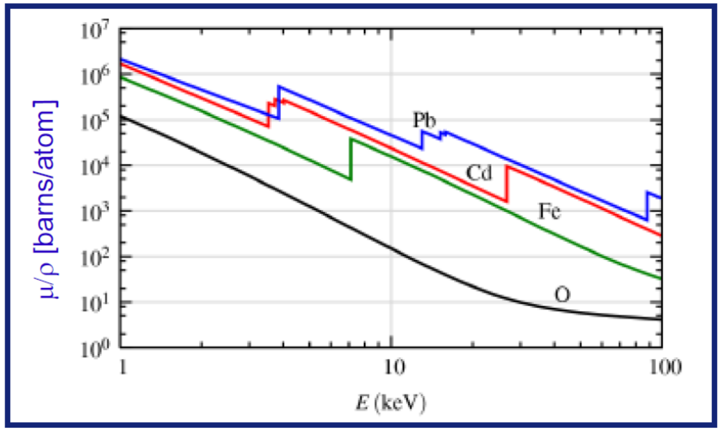
μ depends strongly on
- x-ray energy **E,**
- atomic number **Z,**
- the density **ρ,**
- atomic mass **A**

$$\boxed{\mu = \frac{\rho Z^4}{A E^3}}$$

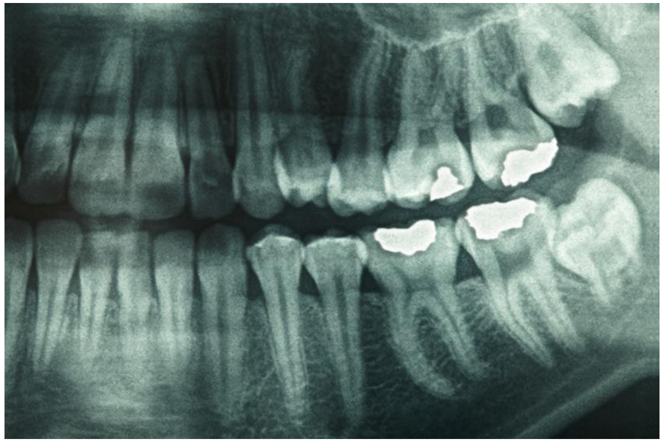


Discontinuities in $\mu = f(E)$ are observed, called absorption edges and related to the excitation of core electrons

The Absorption Coefficient μ

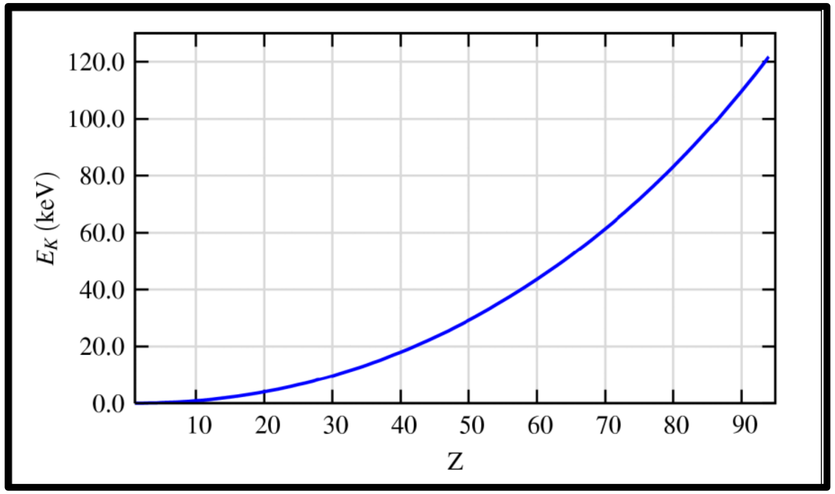


$$\mu = \frac{\rho z^4}{AE^3}$$

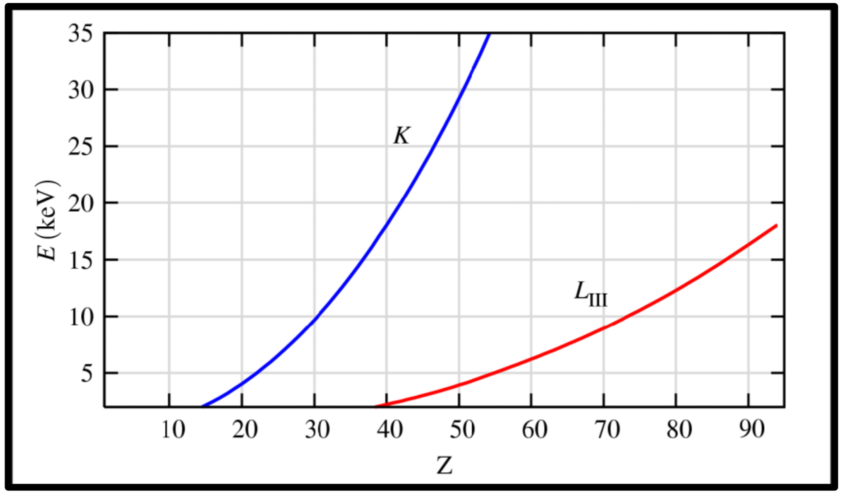


Absorption Edges Energies

Edge: . . .	M_5	M_4	M_3	M_2	M_1	L_3	L_2	L_1	K
Core level: . . .	$3d_{5/2}$	$3d_{3/2}$	$3p_{3/2}$	$3p_{1/2}$	3s	$2p_{3/2}$	$2p_{1/2}$	2s	1s



The energies of the K absorption edges go roughly as $E_K \sim Z^2$



All elements with Z > 16 have either a **K-**, or **L-** edge between **2** and **35** keV, which can be accessed at many synchrotron sources

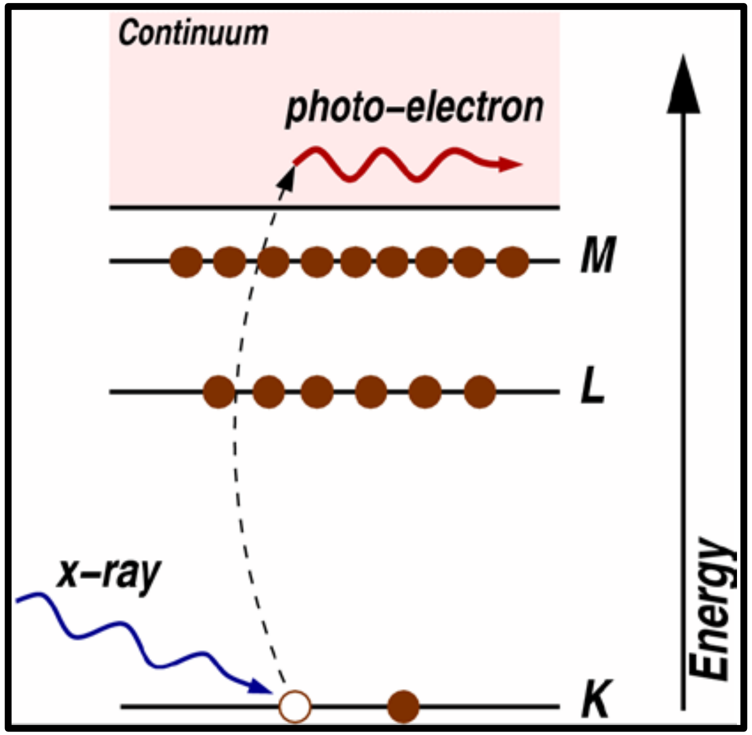
Photoelectric Absorption

X-rays (*light with wavelength 0.06 ≤ λ ≤ 12 Å or energy 1 ≤ E ≤ 200 keV*) are absorbed by all matter through the **photoelectric effect**

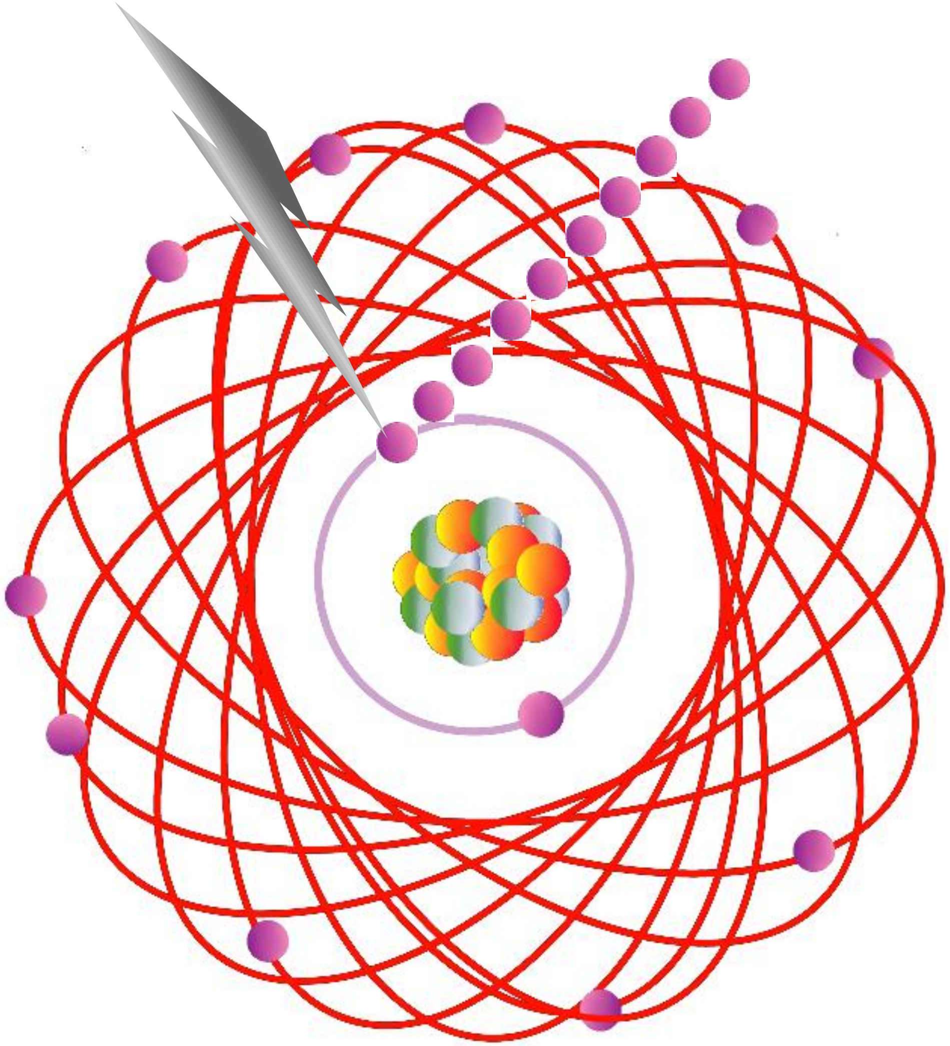
An X-ray is **absorbed** by an atom when the energy of the X-ray is transferred to a core-level electron (*K*, *L*, or *M* shell) which is ejected from the atom.

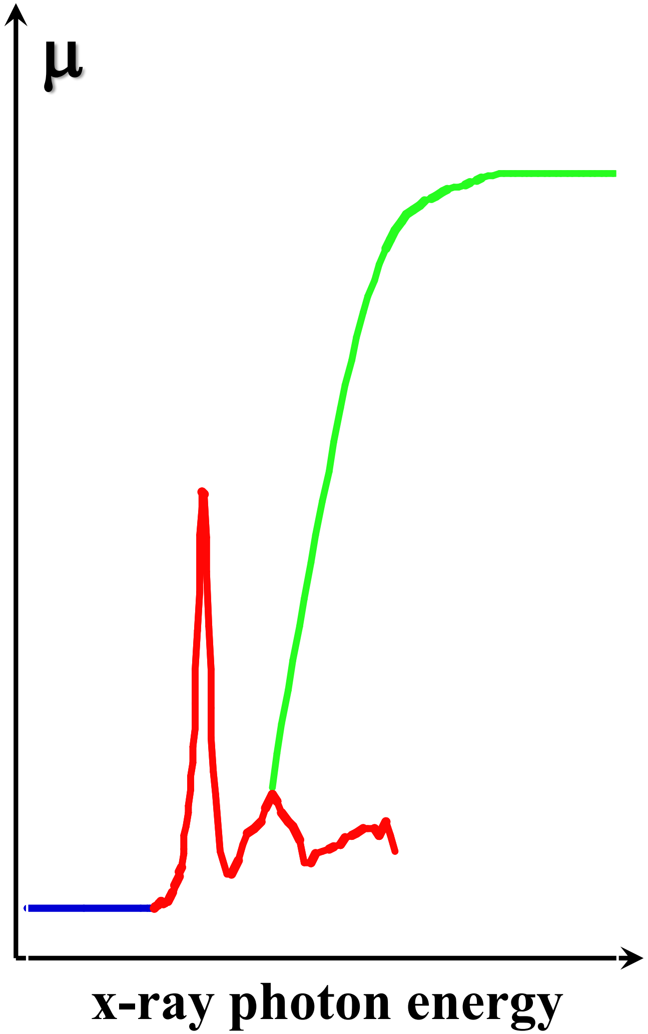
The atom is left in an **excited state** with an empty electronic level (a core hole).

Any excess energy from the X-ray is given to the ejected **photoelectron**.



FUNDAMENTALS OF X-RAY ABSORPTION FINE STRUCTURE: BASIC PRINCIPLES





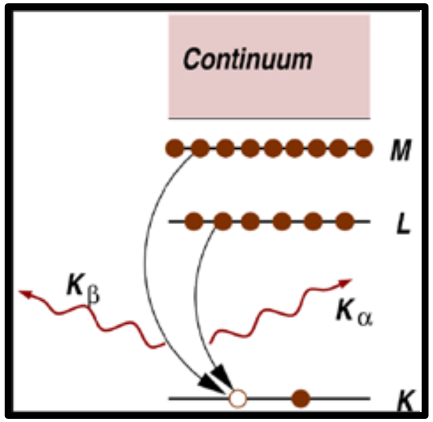
De-excitation: *Fluorescence and Auger Effect*

Absorption → Excited state → Decay to the ground state

When X-rays are absorbed by the photoelectric effect, the excited core-hole will relax back to a "ground state" of the atom. A higher level core electron drops into the core hole, and a fluorescent X-ray or Auger electron is emitted.

X-ray Fluorescence:

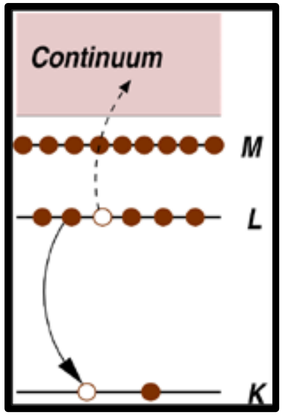
An X-ray with energy = the difference of the core-levels is emitted.



X-ray fluorescence and Auger emission occur at discrete energies characteristic of the absorbing atom, and can be used to identify the absorbing atom.

Auger Effect:

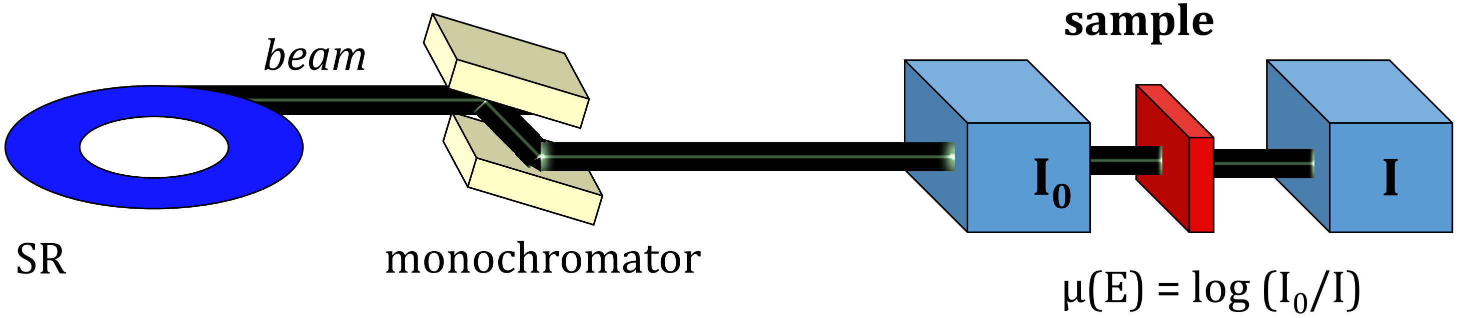
An electron is promoted to the continuum from another core-level.



XAS measurements

XAS measures the energy dependence of the X-ray absorption coefficient $\mu(E)$ at and above the absorption edge of a selected element. $\mu(E)$ can be measured two ways:

I) Transmission mode



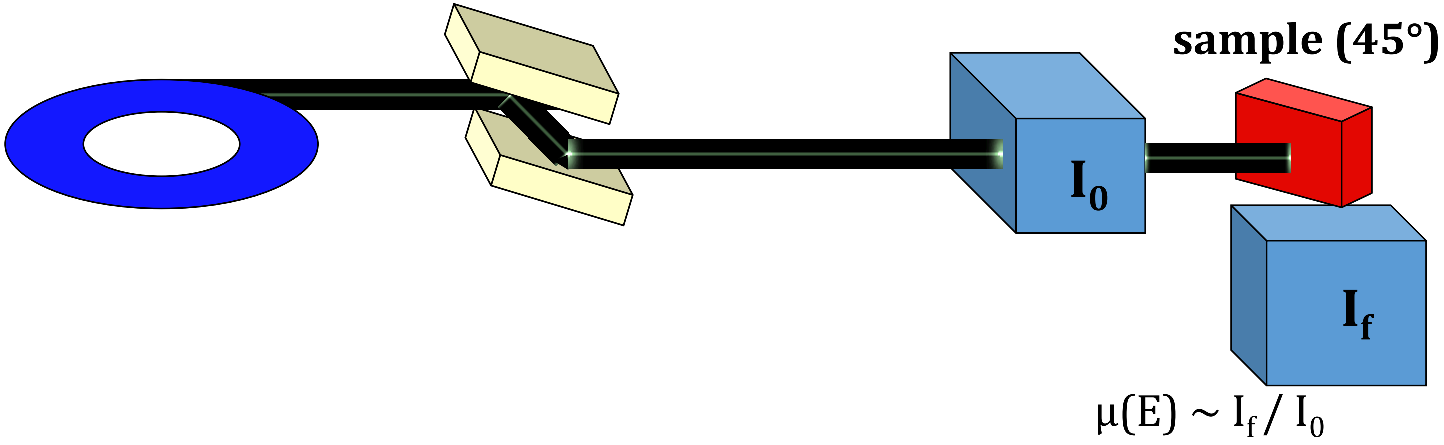
The absorption is measured directly by measuring what is transmitted through the sample:

$$I = I_0 e^{-\mu(E)t} \quad \Longrightarrow \quad \mu(E)t = \log(I_0/I)$$

XAS measurements

XAS measures the energy dependence of the X-ray absorption coefficient μ(E) at and above the absorption edge of a selected element. μ(E) can be measured two ways:

II) Fluorescence mode



$\mu(E) \sim I_f / I_0$

The re-filling of the deep core hole is detected. Typically the fluorescent X-ray is measured:

$$\mu(E) \sim I_f / I_0$$

XAFS

(X-ray Absorption Fine Structure)

X-ray Absorption Fine Structure (XAFS)

What ?

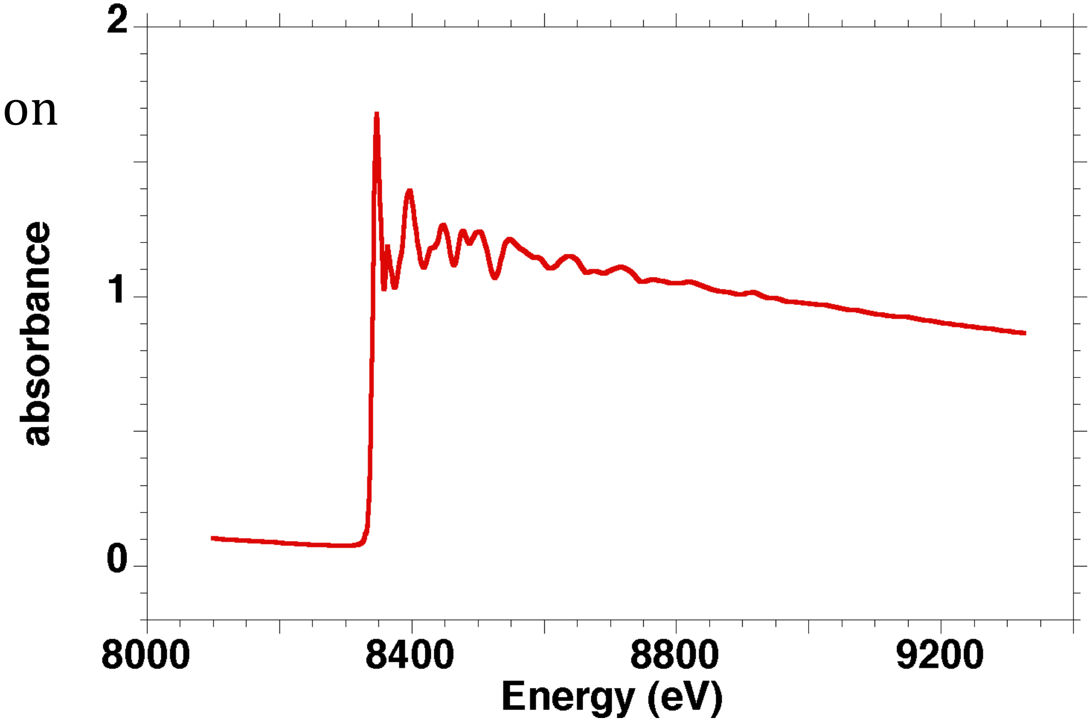
Oscillatory variation of the X-ray absorption as a function of photon energy beyond an absorption edge.

When ?

Non isolated atoms

Why ?

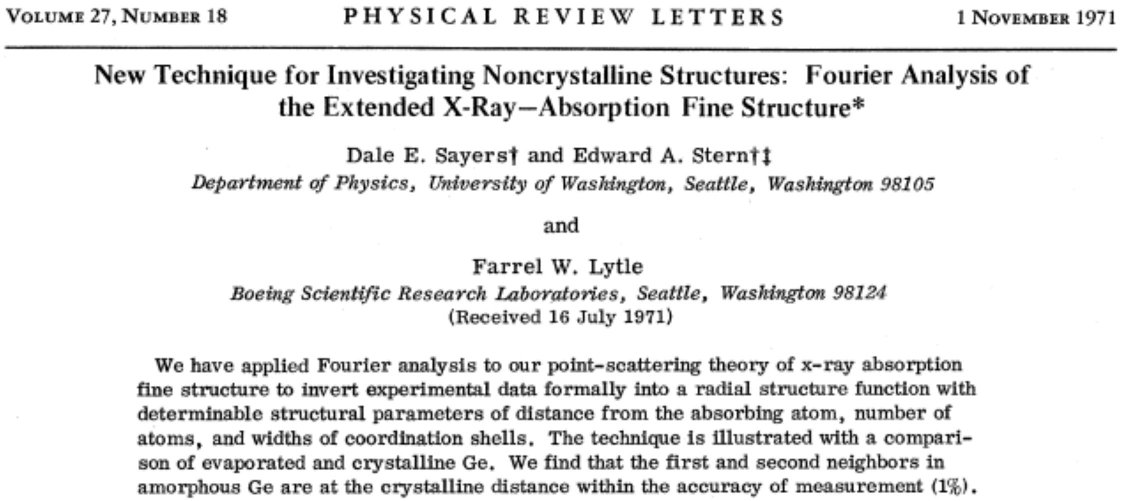
Proximity of neighboring atoms strongly modulates the absorption coefficient



FUNDAMENTALS OF X-RAY ABSORPTION FINE STRUCTURE: XAFS

A little history...

1895	Discovery of X-rays (Röngten) (high penetration depth)
1912	First X-ray diffraction experiments (Laue, Bragg)
1913	Bohr's atom electron energy levels
1920	First experimental observation of fine structure
1931	First attempt to explain XAFS in condensed matter (Krönig)
. .	
1970	Availability of synchrotron radiation sources for XAFS
1971	XAFS becomes a quantitative tool for structure determination



Volume 27, Number 18 PHYSICAL REVIEW LETTERS 1 November 1971

New Technique for Investigating Noncrystalline Structures: Fourier Analysis of the Extended X-Ray—Absorption Fine Structure*

Dale E. Sayers† and Edward A. Stern†‡
Department of Physics, University of Washington, Seattle, Washington 98105

and

Farrel W. Lytle
Boeing Scientific Research Laboratories, Seattle, Washington 98124

(Received 16 July 1971)

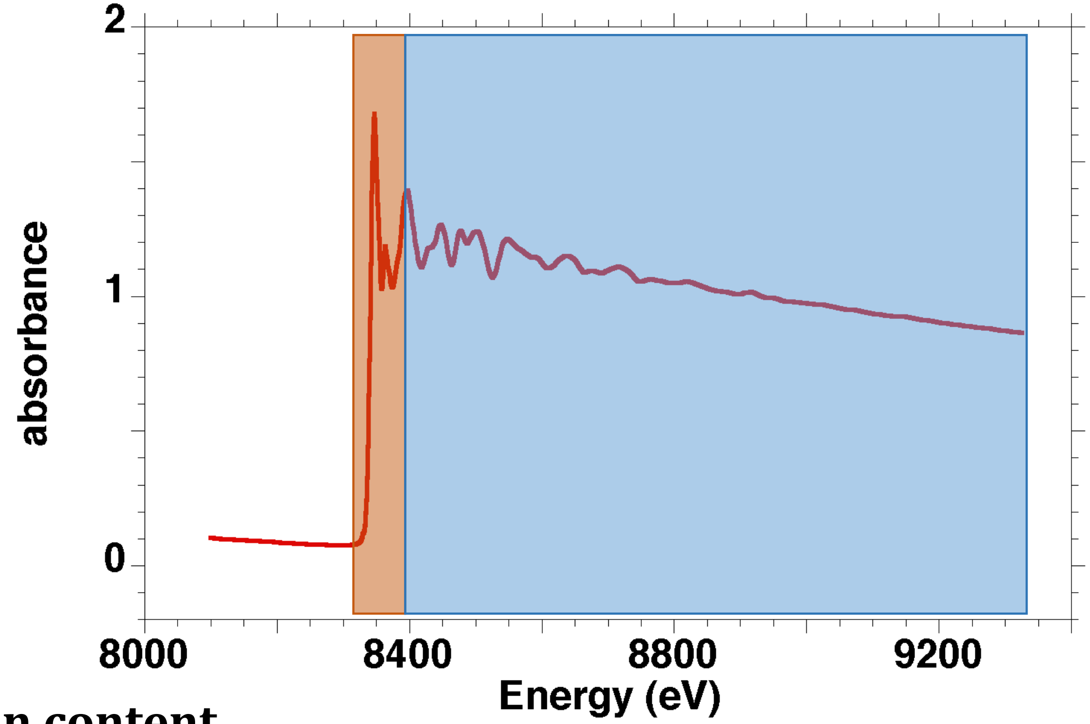
We have applied Fourier analysis to our point-scattering theory of x-ray absorption fine structure to invert experimental data formally into a radial structure function with determinable structural parameters of distance from the absorbing atom, number of atoms, and widths of coordination shells. The technique is illustrated with a comparison of evaporated and crystalline Ge. We find that the first and second neighbors in amorphous Ge are at the crystalline distance within the accuracy of measurement (1%).

XANES and EXAFS

XAFS is also referred to as X-ray Absorption Spectroscopy **(XAS)** and is broken into 2 regimes:

XANES
X-ray
Absorption
Near-
Edge
Structure

up to ~ 60 eV above the edge



EXAFS
Extended
X-ray
Absorption
Fine
Structure

~ 60 eV to 1200 eV above the edge

- **Different information content.**
- **Cannot be analized in the same way**
- **Approximations can be used to interpret EXAFS, that are not valid for XANES**

XAFS = XANES + EXAFS

X-ray Absorption
Near Edge Structure

XANES ⇐ **same physical origin** ⇒ **EXAFS**

Extend X-ray Absorption
Fine Structure

transitions to
unfilled bound states, nearly bound states, continuum

- Oxidation state
- Coordination chemistry of the absorbing atom
- Orbital occupancy

transitions to
the continuum

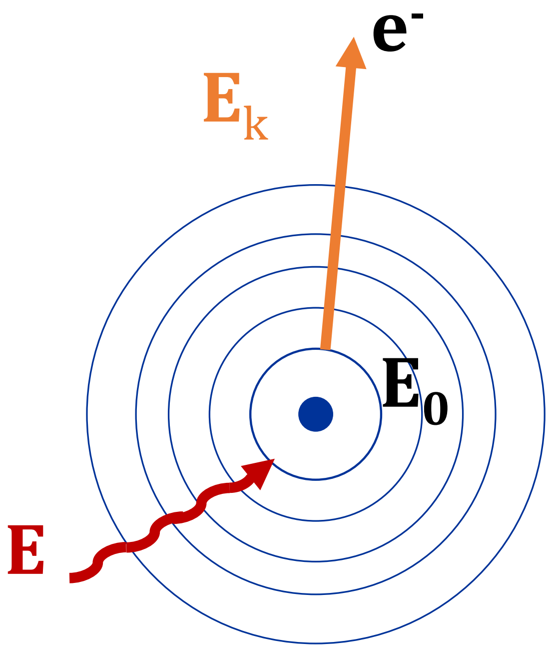
- Radial distribution of atoms around the photo-absorber (bond distance, number and type of neighbors)

EXAFS

(Extend X-ray Absorption Fine Structure)

EXAFS qualitatively

Isolated atom



The photoelectron can be described by a wave function approximated by a spherical wave

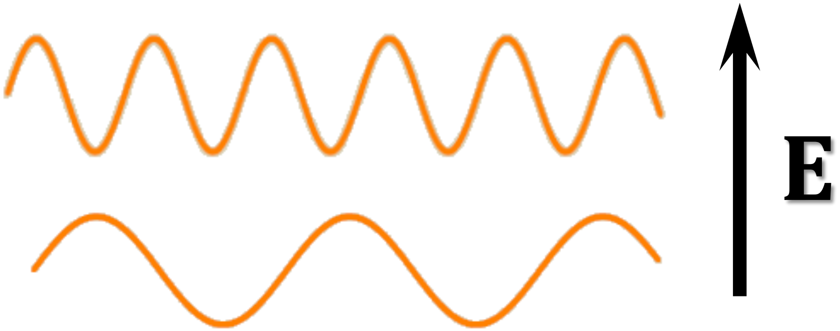
X-ray photon with enough energy ejects one core (photo)electron (photoelectric effect)

$$E_k = E_{h\nu} - E_0 = \frac{p^2}{2m} = \frac{(\hbar k)^2}{2m}$$ Kinetic energy of the p.e.

$$k = \sqrt{[2m(E_{h\nu} - E_0)/\hbar^2]}$$ Wave-vector of the p.e.

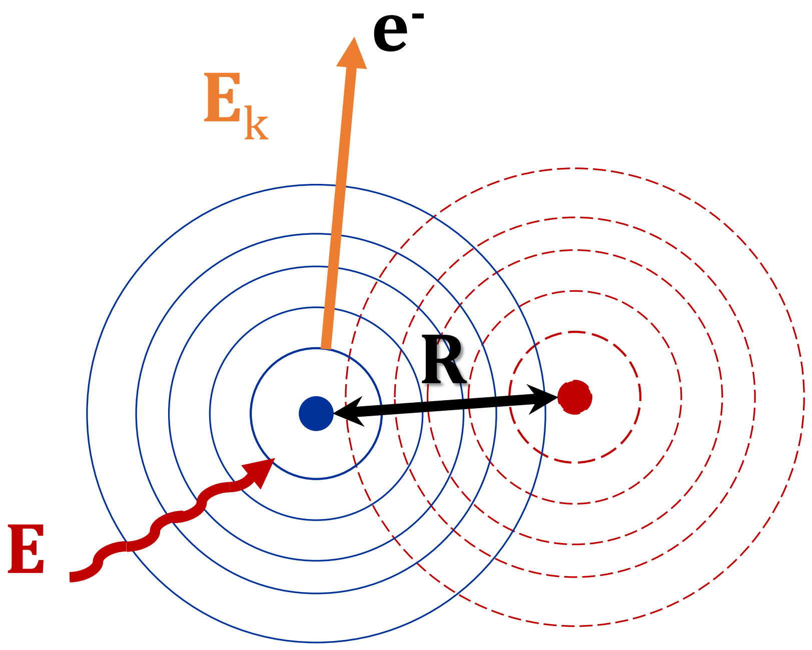
$$\lambda = 2\pi/k$$ wavelength of the p.e.

$$\lambda = \frac{1}{\sqrt{E - E_0}}$$



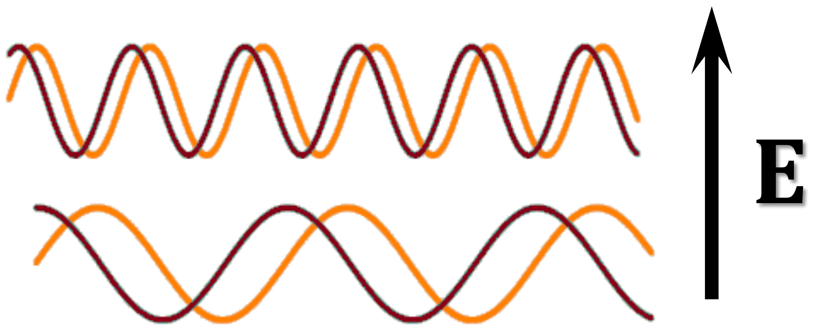
EXAFS qualitatively

Condensed Matter



- ☐ The photoelectron can be described by a wave function approximated by a spherical wave coming back to the absorbing atom
- ☐ The outgoing and ingoing waves may interfere.

$$\lambda = \frac{1}{\sqrt{E - E_0}}$$

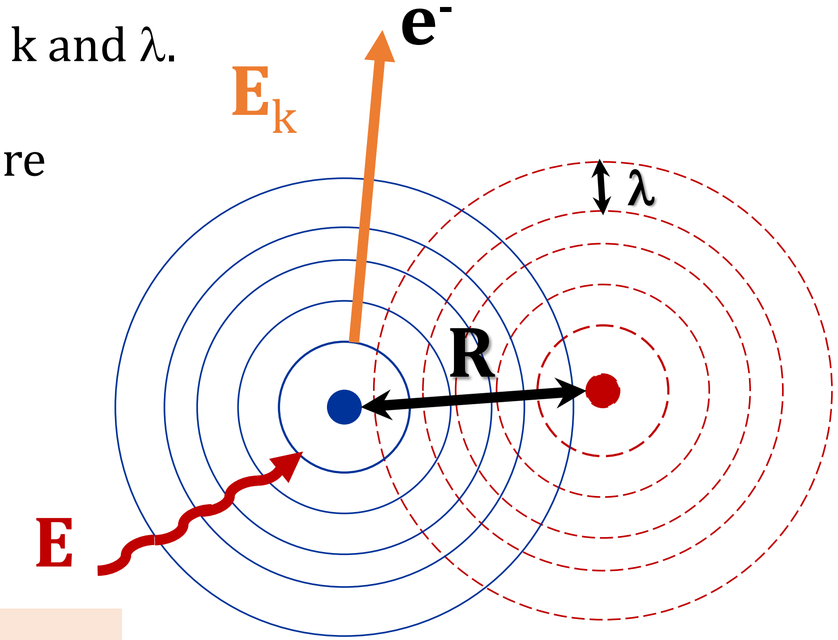


Where do the oscillations come from?

Due to a quantum effect**,** the auto-interference of photoelectron wave modifies the absorption coefficient μ(E)value:

$$E_k = E_{h\nu} - E_0 = \frac{p^2}{2m} = \frac{(\hbar k)^2}{2m}$$

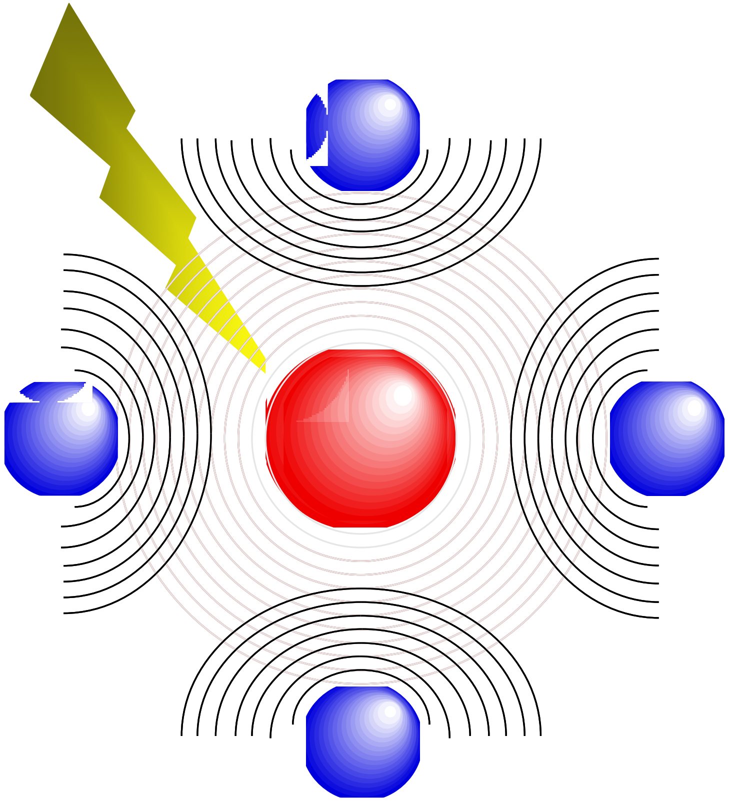
- As E is scanned above E_0, E_{kin} is varied, and consequently k and λ.
- The outgoing and backscattered parts of the wave interfere either constructively or destructively, depending on the ratio between λ and R.
- It is the interference between outgoing and incoming waves that gives rise to the sinusoidal variation of μ(E)

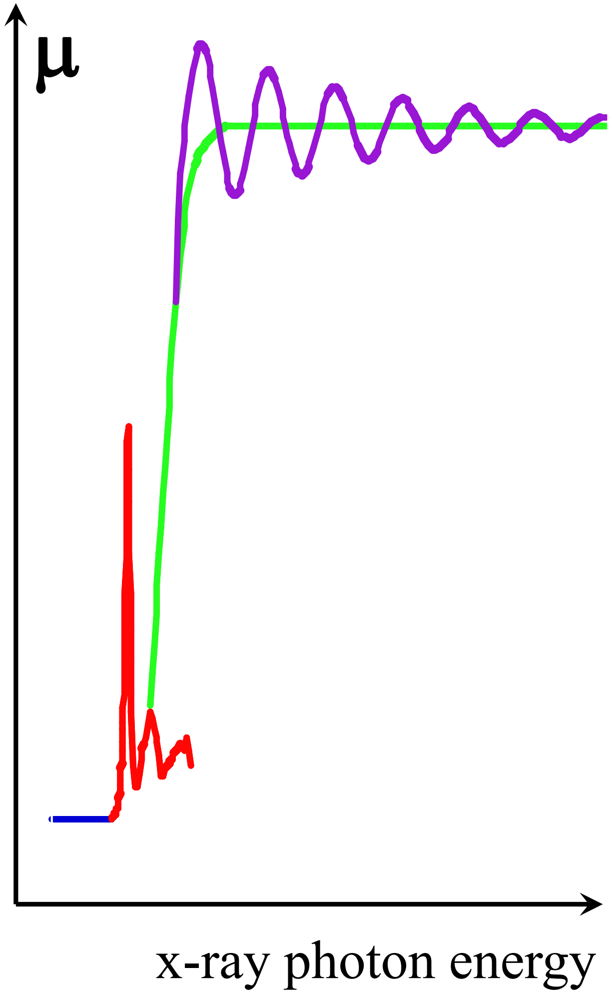


Frequency of oscillation ➔ distance from neighbors

amplitude of oscillation ➔ number and type of neighbors

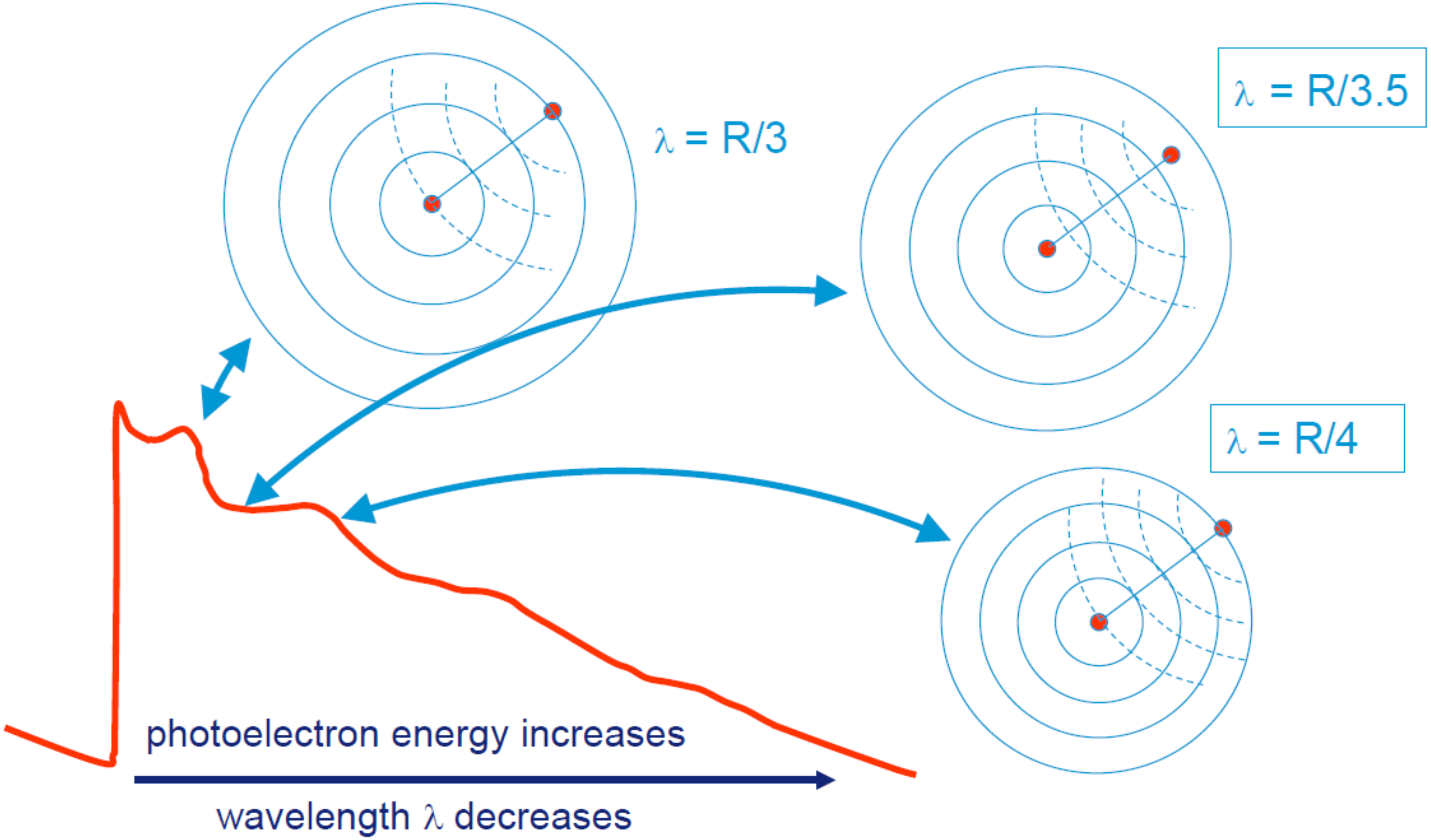
FUNDAMENTALS OF X-RAY ABSORPTION FINE STRUCTURE: EXAFS





FUNDAMENTALS OF X-RAY ABSORPTION FINE STRUCTURE: EXAFS

The probability of absorption oscillates due to constructive and destructive interference



λ = R/3

λ = R/3.5

λ = R/4

photoelectron energy increases

wavelength λ decreases

The EXAFS signal $\chi(E)$

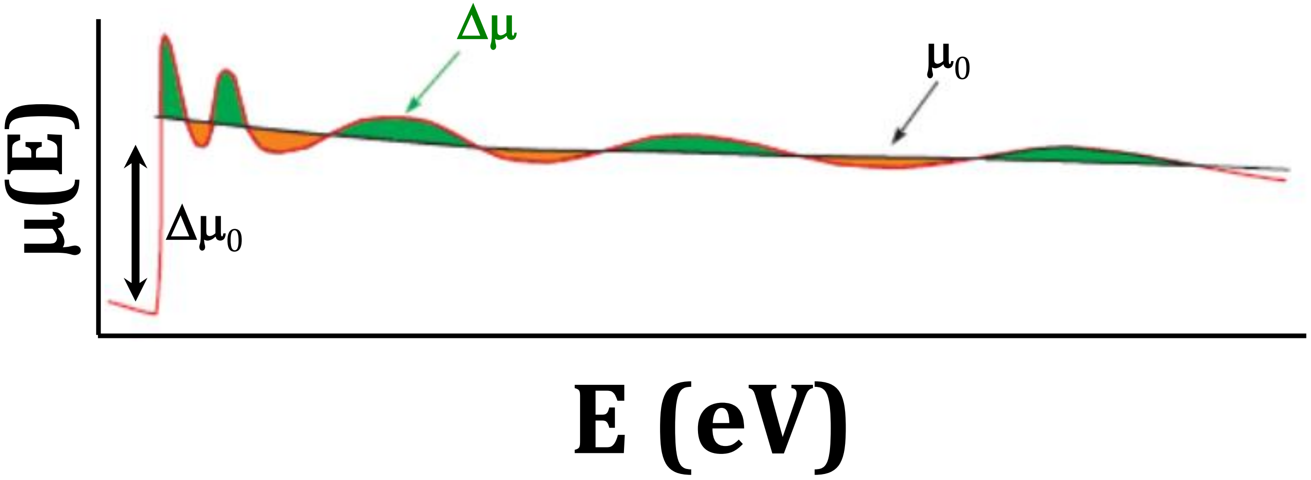
The EXAFS signal is generally expressed as a function of the wave-vector of the photoelectron

$$k = \sqrt{\frac{2m(E-E_0)}{\hbar^2}}$$

We're interested in the energy dependent oscillations in μ(E), as these will tell us something about the neighboring atoms,

so we define the EXAFS as:

$$\boxed{\chi(E) = \frac{\mu(E)-\mu_0(E)}{\Delta\mu_0(E)}}$$



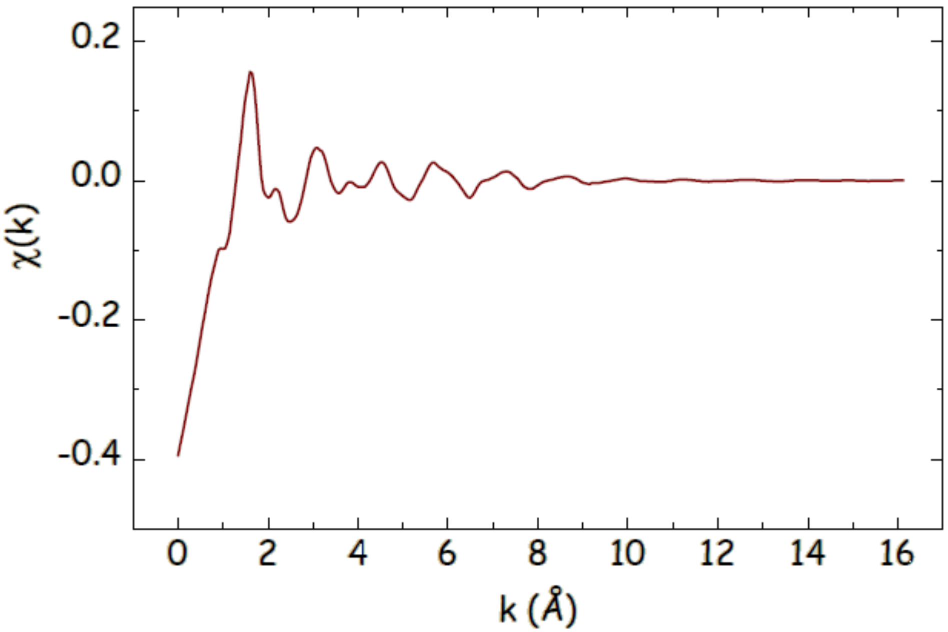
$\mu_0(E)$ Smooth function representing the bare atomic background

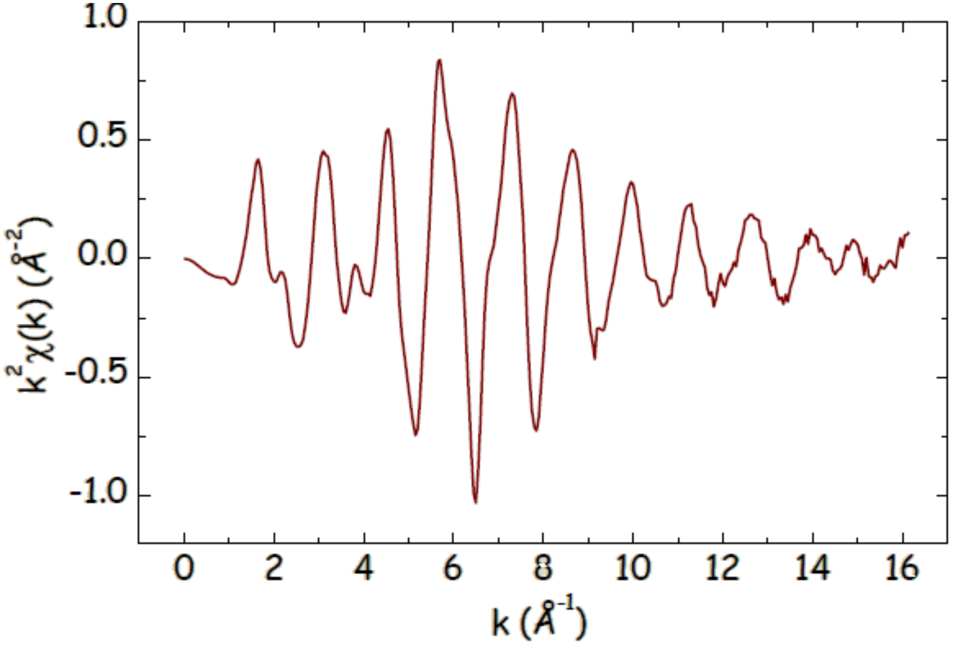
$\Delta\mu_0$ Edge step at the absorption edge normalized to one absorption event

The EXAFS signal $\chi(k)$

XAFS is an interference effect, and depends on the wave-nature of the photoelectron.

χ (k) is often shown weighted by k^2 or k^3 to amplify the oscillations at high-k:





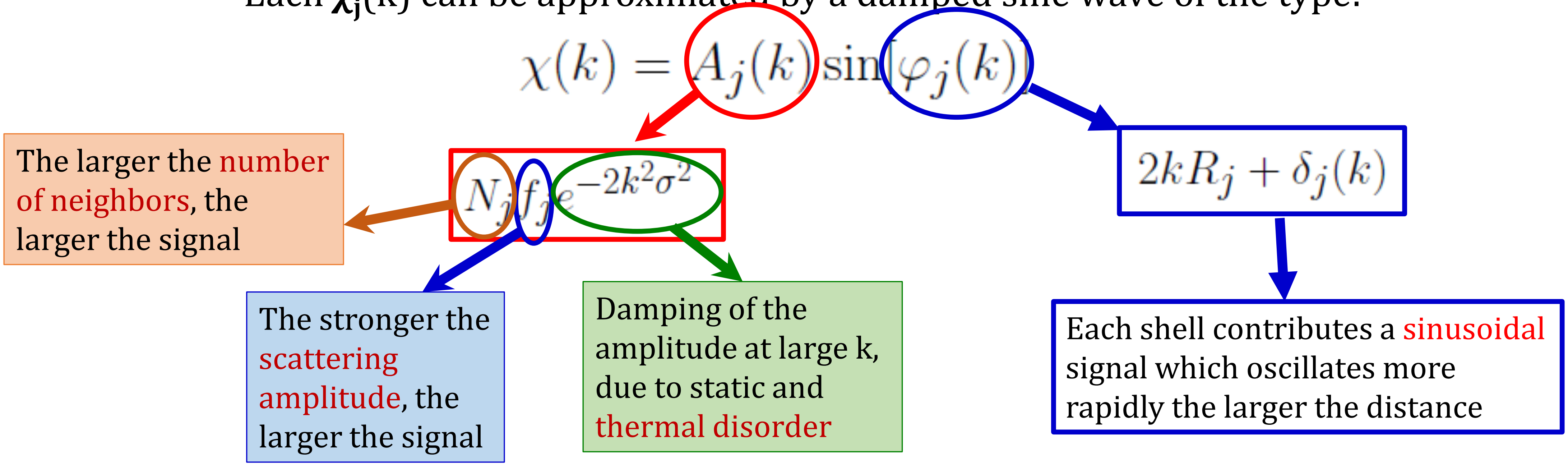
Quantitative EXAFS

χ(k): sum of damped waves

χ(k) is the sum of contributions $\chi_j(k)$ from backscattered wavelets:

$$\chi(k) = \sum_j = \chi_j(k)$$

Each $\chi_j(k)$ can be approximated by a damped sine wave of the type:



$$\chi(k) = \boxed{A_j(k)} \sin[\varphi_j(k)]$$

$$A_j(k) = N_j f_j e^{-2k^2\sigma^2}$$

$$\varphi_j(k) = 2kR_j + \delta_j(k)$$

The larger the number of neighbors, the larger the signal

The stronger the scattering amplitude, the larger the signal

Damping of the amplitude at large k, due to static and thermal disorder

Each shell contributes a sinusoidal signal which oscillates more rapidly the larger the distance

Quantitative EXAFS

EXAFS formula:

$$\chi(\mathrm{k}) = \sum_{\mathrm{j}} \frac{\mathrm{N_j S_0^2 f_j(k) e^{-2R_j/\lambda(k)}\, e^{-2k^2\sigma_j^2}}}{\mathrm{kR_j}^2} \sin[2\mathrm{kR_j} + \delta_{\mathrm{j}}(\mathrm{k})]$$

$f(k)$ scattering amplitude

$\delta_j(k)$ phase-shift

} scattering properties of the atoms neighboring the photo-absorber (depend on the atomic number)

$\lambda(k)$ Mean free path

R Distance to the neighboring atom

N Coordination number of the neighboring atom

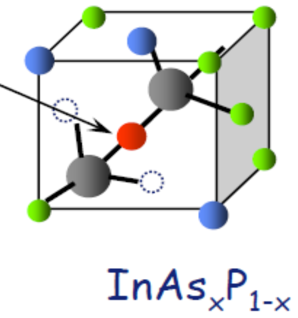
σ^2 Disorder in the neighbor distance

S_0^2 many-body amplitude reduction

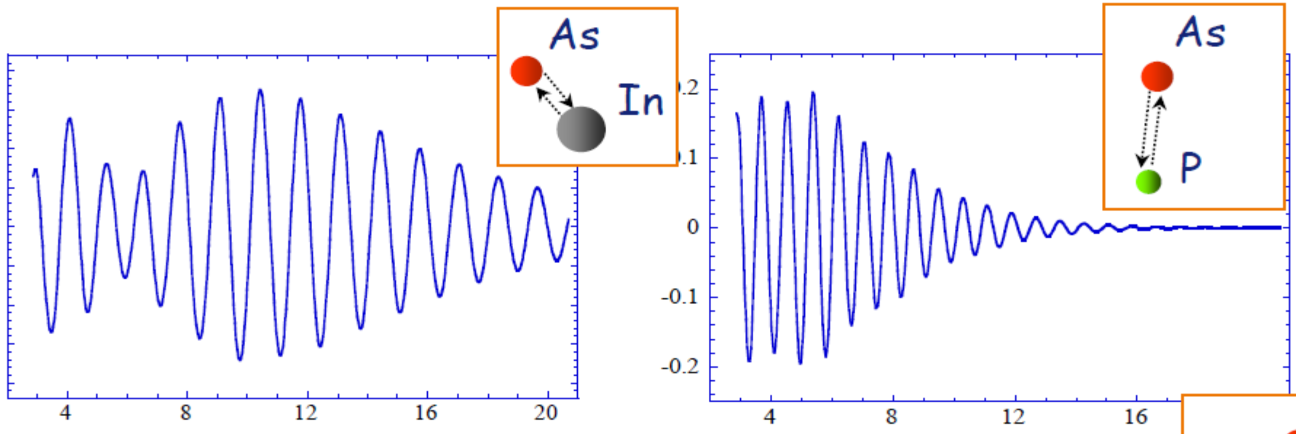
Amplitudes:

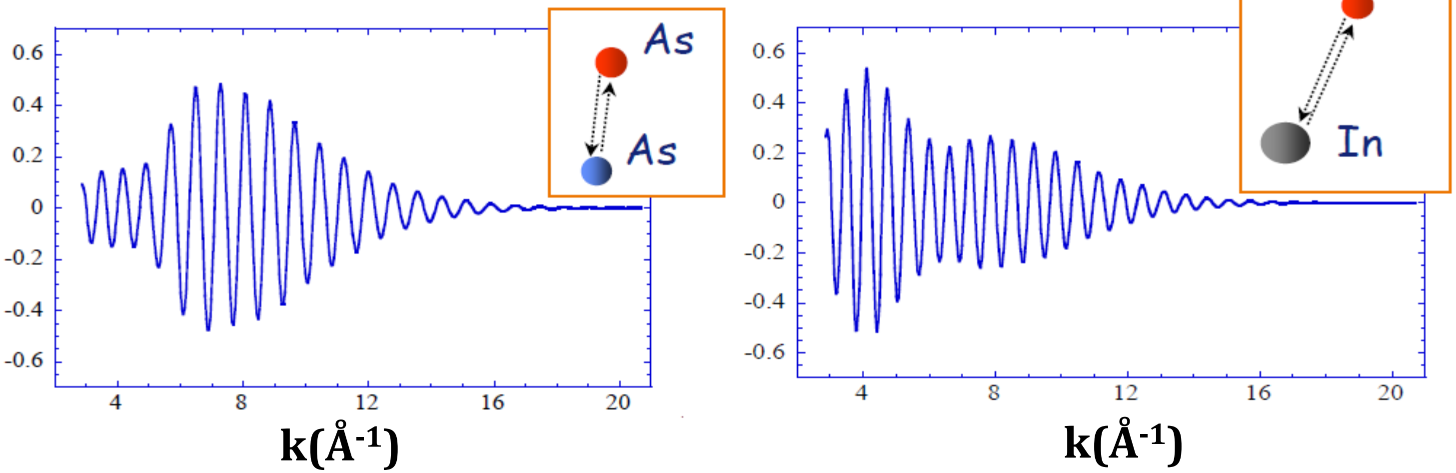
$$A_j(k) \sim N_j\, f_j(k)\, e^{-2k^2\sigma^2}$$

absorber As atom



shape of the envelope of each wave indicative of nature of backscatterer atom:





Frequencies: Single and Multiple Scattering paths

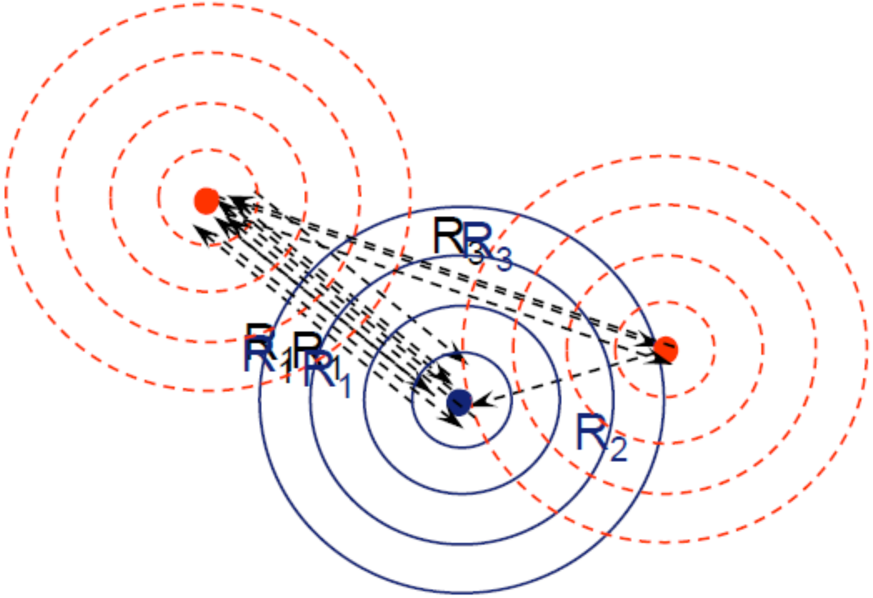
The sum over paths in the EXAFS equation includes many shells of atoms (1st, 2nd, 3rd neighbor, . . .), but can also include multiple scattering paths, in which the photoelectron scatters from more than one atom before returning to the central atom.

SS ➔ g2(r)
f = 2 R1

MS ➔ g2(r)
f = 4 R_1

MS ➔ g3(r)
f = $R_1 + R_2 + R_3$

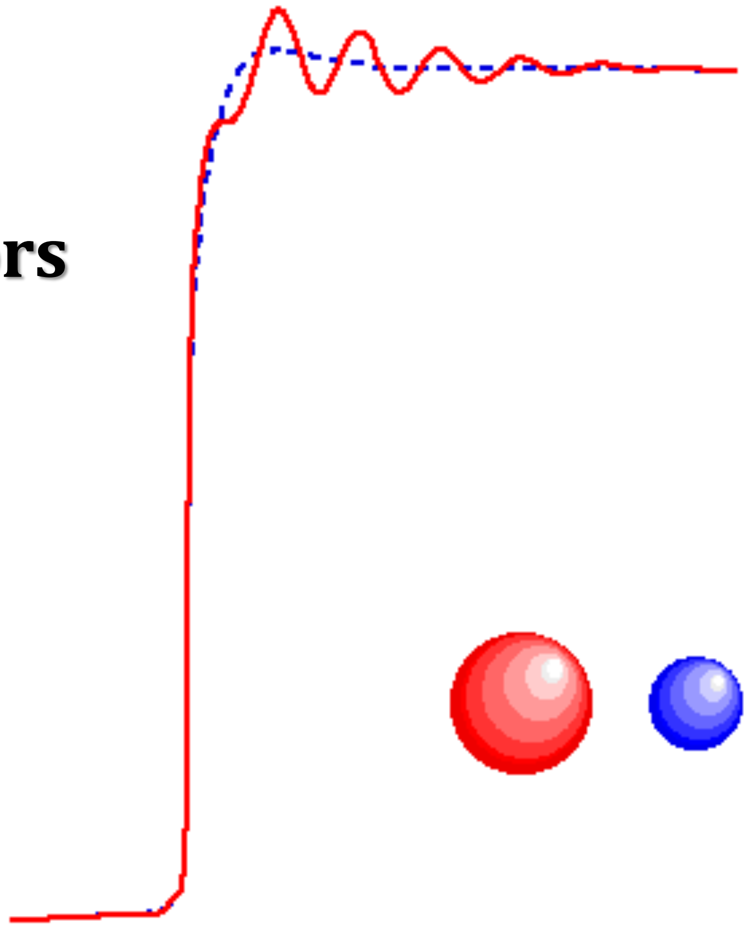
MS ➔ g3(r)
f = $2R_1 + 2R_3$



Through multiple scattering EXAFS can give information on the n-body distribution functions $g_n(r)$

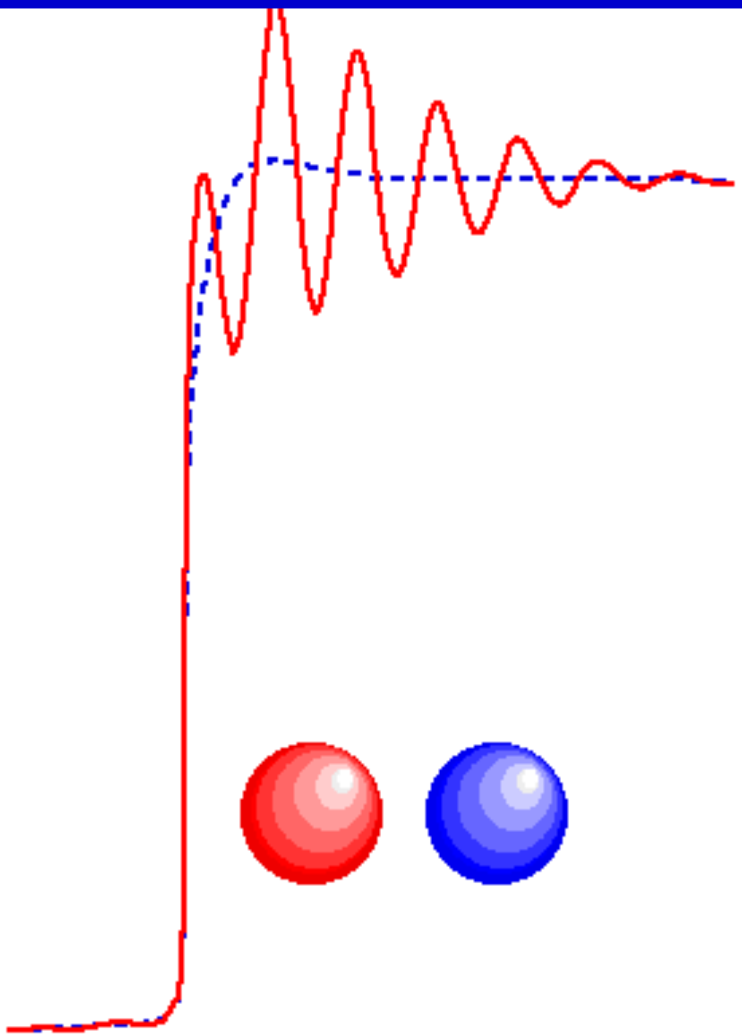
FUNDAMENTALS OF X-RAY ABSORPTION FINE STRUCTURE: EXAFS

effect of the number of neighbors



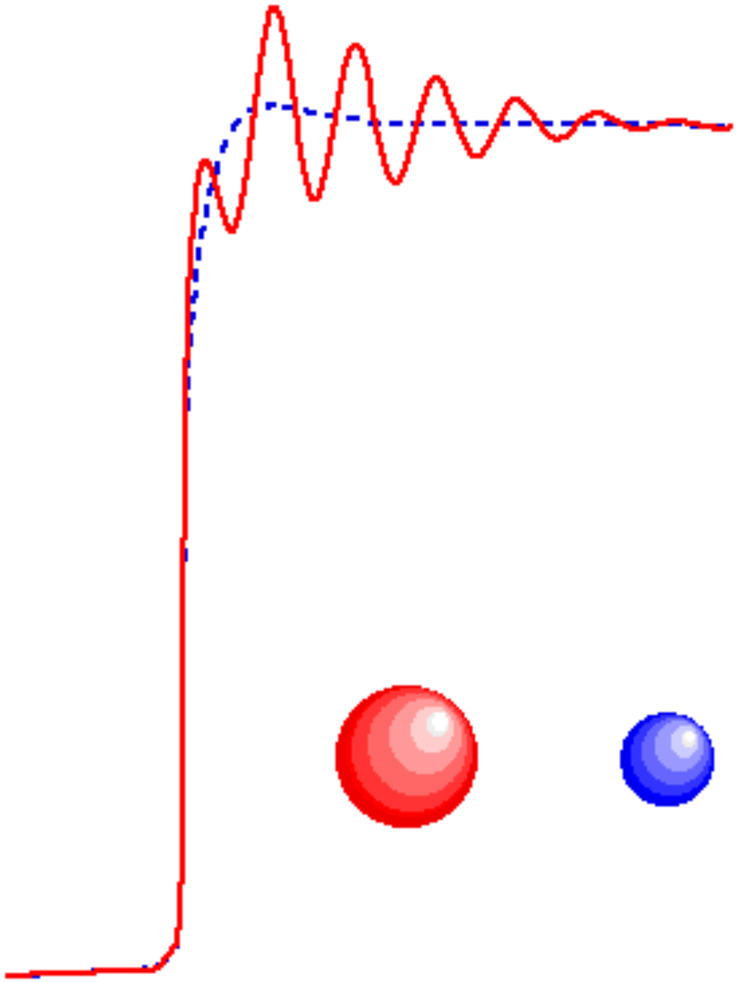
FUNDAMENTALS OF X-RAY ABSORPTION FINE STRUCTURE: EXAFS

effect of inter-atomic distance



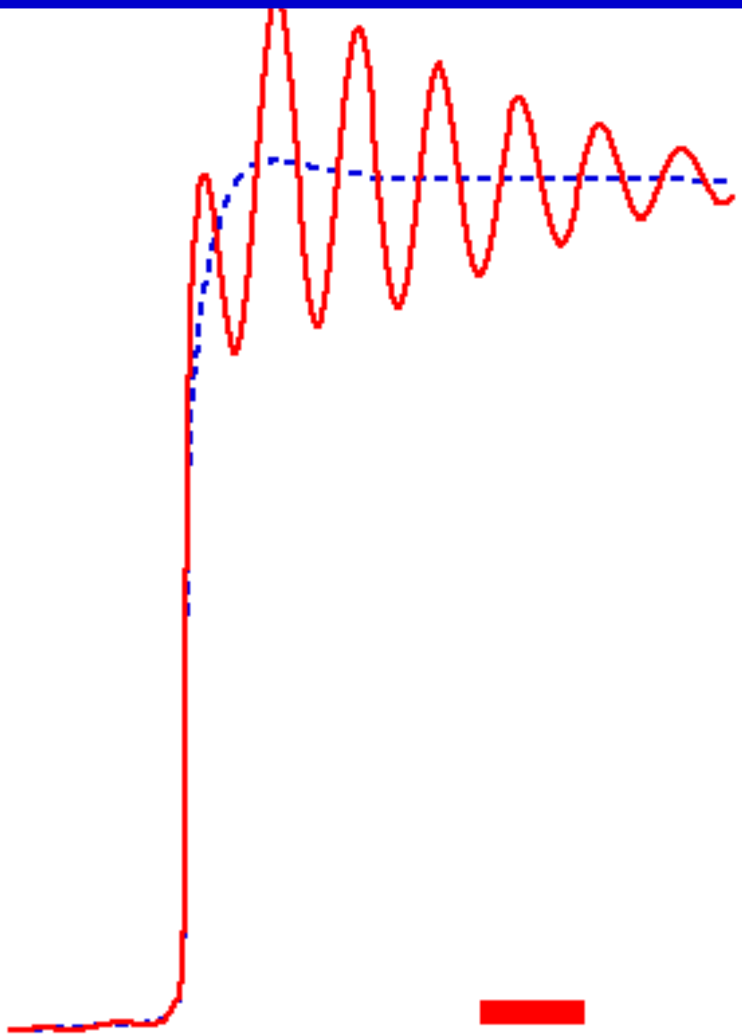
FUNDAMENTALS OF X-RAY ABSORPTION FINE STRUCTURE: EXAFS

effect of the neighbor’s Z



FUNDAMENTALS OF X-RAY ABSORPTION FINE STRUCTURE: EXAFS

effect of disorder



FUNDAMENTALS OF X-RAY ABSORPTION FINE STRUCTURE: EXAFS

Tough : disorder….

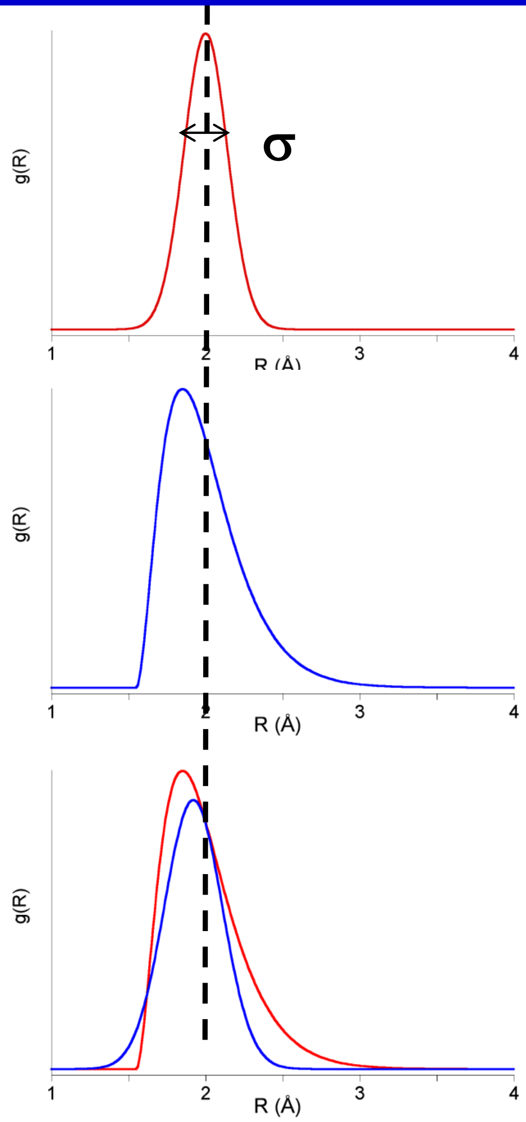
low temperature

or/and covalent bond

high temperature

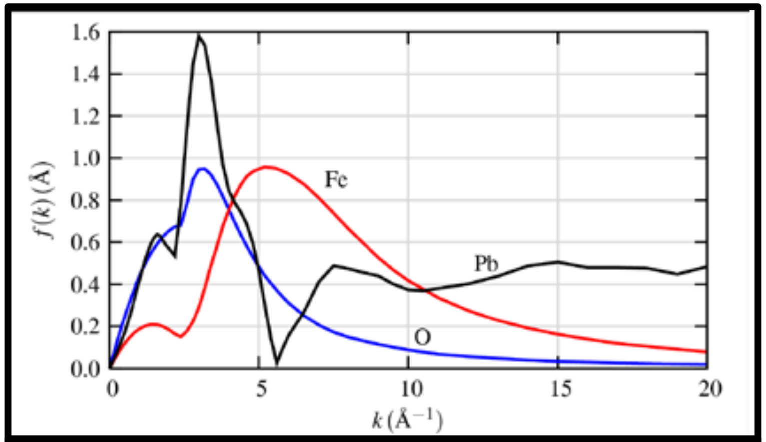
or/and ionic bond

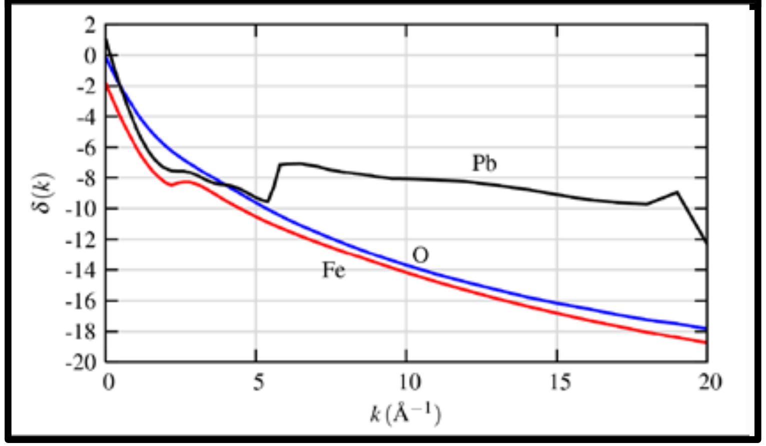
in case of a mis-estimate…



Scattering Amplitude and Phase-Shift: f(k) and δ(k)

The scattering amplitude **f(k)** and phase-shift **δ(k)** depend on atomic number.





The scattering amplitude **f(k)** peaks at different k values extends to higher-k for heavier elements. For very heavy elements, there is structure in **f(k)**.

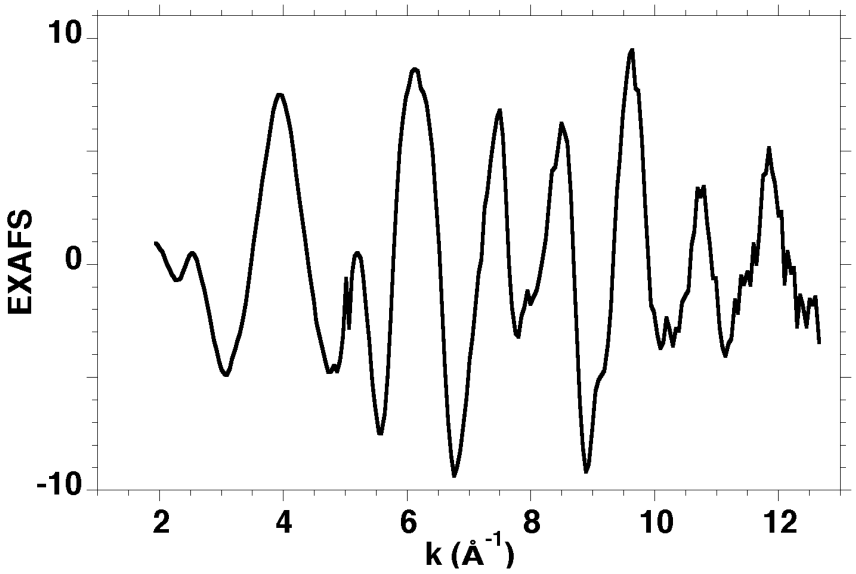
The phase shift **δ(k)** shows sharp changes for very heavy elements.

These scattering functions can be accurately calculated (i.e. with the programs FEFF, GNXAS, etc.), and used in the EXAFS modeling.

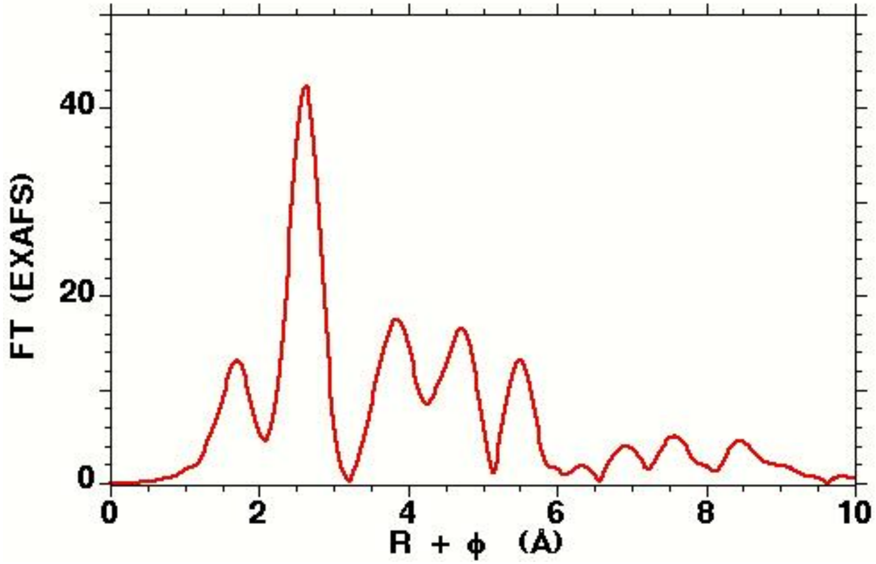
Z can usually be determined to within 5 or so. Fe and O can be distinguished, but Fe and Mn cannot be.

Qualitative picture of local coordination in R space

The frequencies contained in the EXAFS signal depend on the distance between the absorbing atom and the neighboring atoms (i.e. the length of the scattering path).

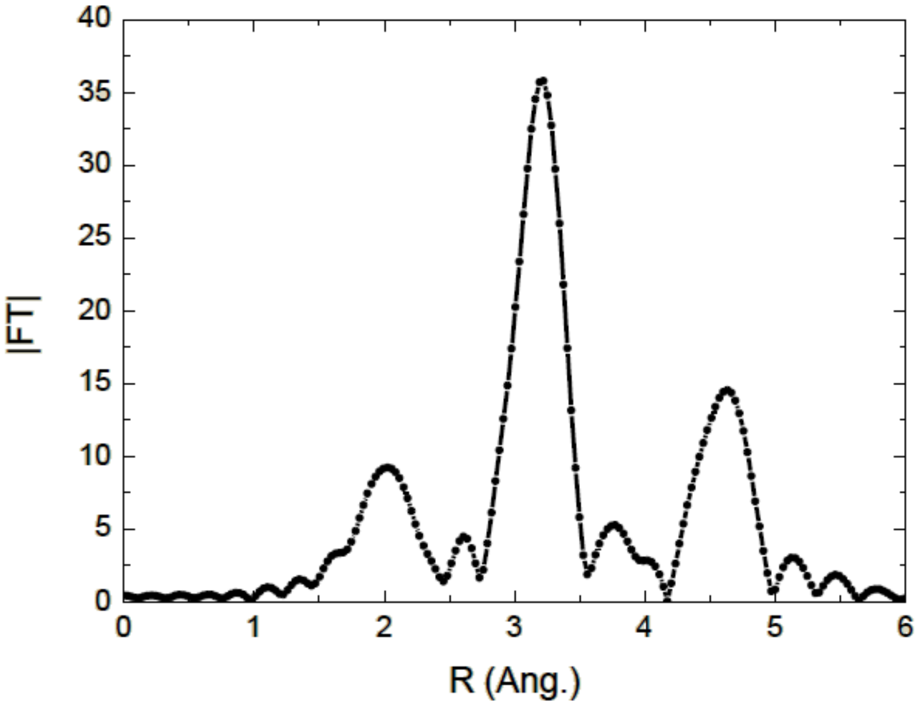


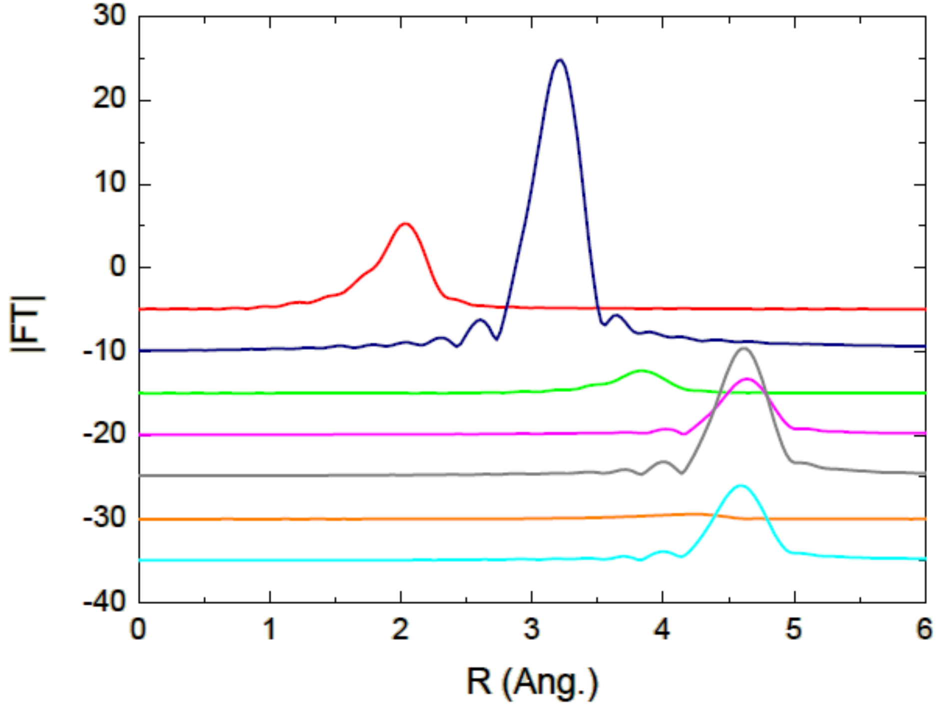
A Fourier Transform of the EXAFS signal provides a photoelectron scattering profile as a function of the radial distance from the absorber.



Quantitative structural determination

Structural determinations depend on the feasibility of resolving the data into individual waves corresponding to the different types of neighbors (SS) and bonding configurations (MS) around the absorbing atom





XAFS vs. Diffraction Methods

Diffraction Methods (X-rays, Neutrons)

- Crystalline materials with long-range ordering -> 3D picture of atomic coordinates **BUT**
- Materials with only short-range order (amorphous solid, liquid, or solution) ➔ 1D RDF containing interatomic distances due to all atomic pairs in the sample

XAFS :

- ❑ 1D radial distribution function (centered at the absorber)
- ❑ Higher sensitivity to local distortions (i.e. within the unit cell)
- ❑ Charge state sensitivity (XANES)
- ❑ Element selectivity
- ❑ Structural information on the environment of each type of atom:
  - Distance, number, type, static and thermal disorder
- ❑ Investigation of matter in the solid (crystalline or amorphous), liquid, solution or gaseous state with same degree of accuracy.

EXAFS: typical applications

- ☐ **Element selectivity**
- ☐ **Local structure sensitivity**

- ➢ Local structure in non-crystalline matter
- ➢ Local environment of an atomic impurity in a matrix of different atomic species
- ➢ Study of systems whose local properties differ from the average properties
- ➢ Detection of very small distortions of local structure

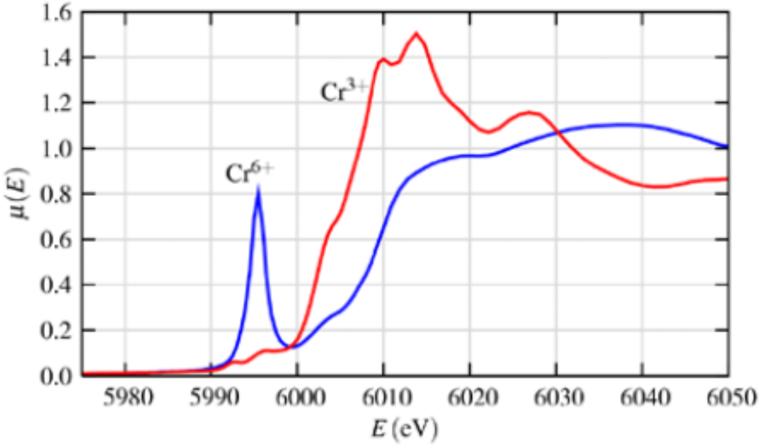
XANES

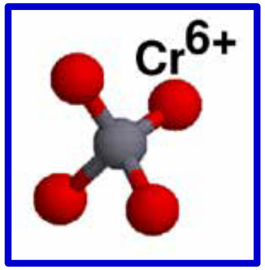
(X-ray Absorption Near-Edge Structure)

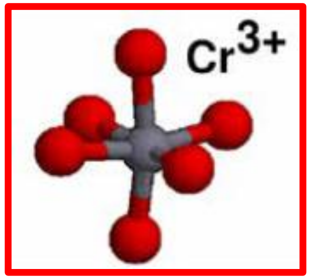
FUNDAMENTALS OF X-RAY ABSORPTION FINE STRUCTURE: XANES

XANES Analysis:

Oxidation State and Coordination Chemistry







The XANES of Cr(III) and Cr(VI) shows a dramatic dependence on oxidation state and coordination chemistry.

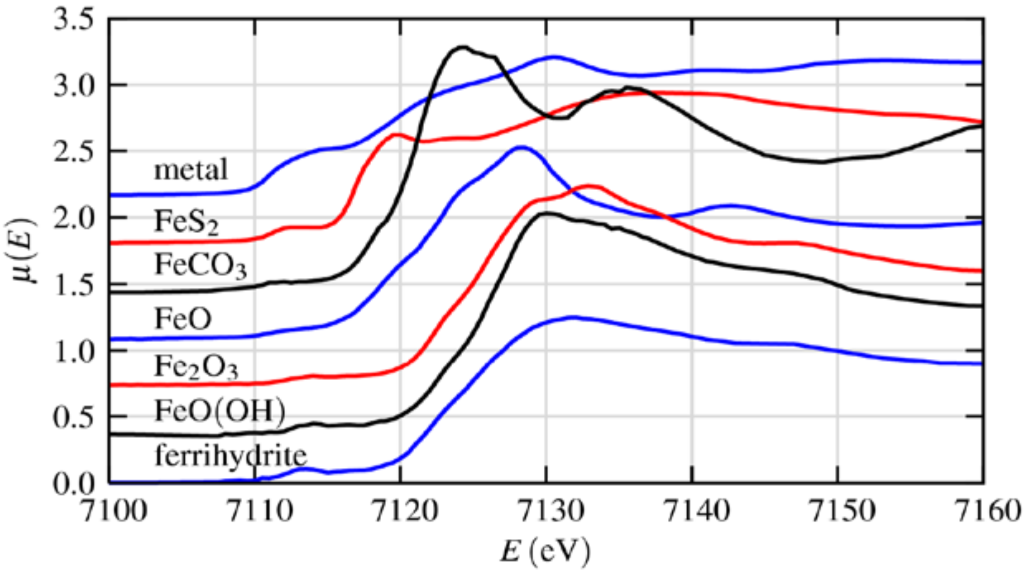
For ions with partially filled **d** shells, the **p-d** hybridization changes dramatically as regular octahedra distort, and is very large for tetrahedral coordination.

This gives a dramatic pre-edge peak – absorption to a localized electronic state.

Edge Shifts and Pre-edge Peaks

The **shift** of the edge position can be used to determine the **valence state**

XANES can be used simply as a **fingerprint** of phases and oxidation state.



The heights and positions of **pre-edge peaks** can also be reliably used to determine Fe^{3+}/Fe^{2+} ratios (and similar ratios for many cations).

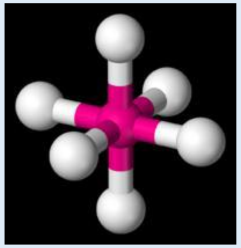
XANES Analysis can be as simple as making **linear combinations** of “known” spectra to get compositional fraction of these components.

Transition metals K pre-edge peaks

Transition with a quadrupolar character

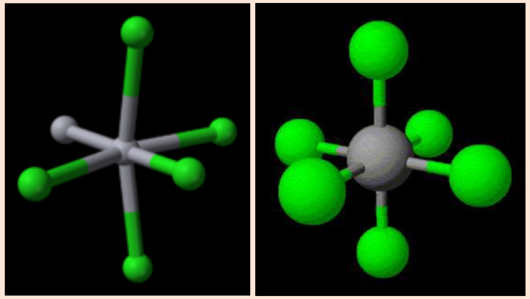
Pure octahedron

Centro-symmetry: no p-d mixing allowed
only (weak) quadrupolar transitions
No, or very low intensity prepeak



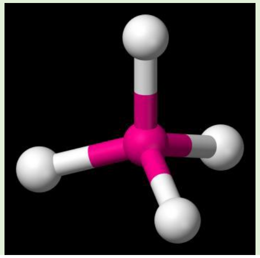
Distorted octahedron

Centro-symmetry broken: p-d mixing allowed
dipole transition in the edge
moderate intensity prepeak



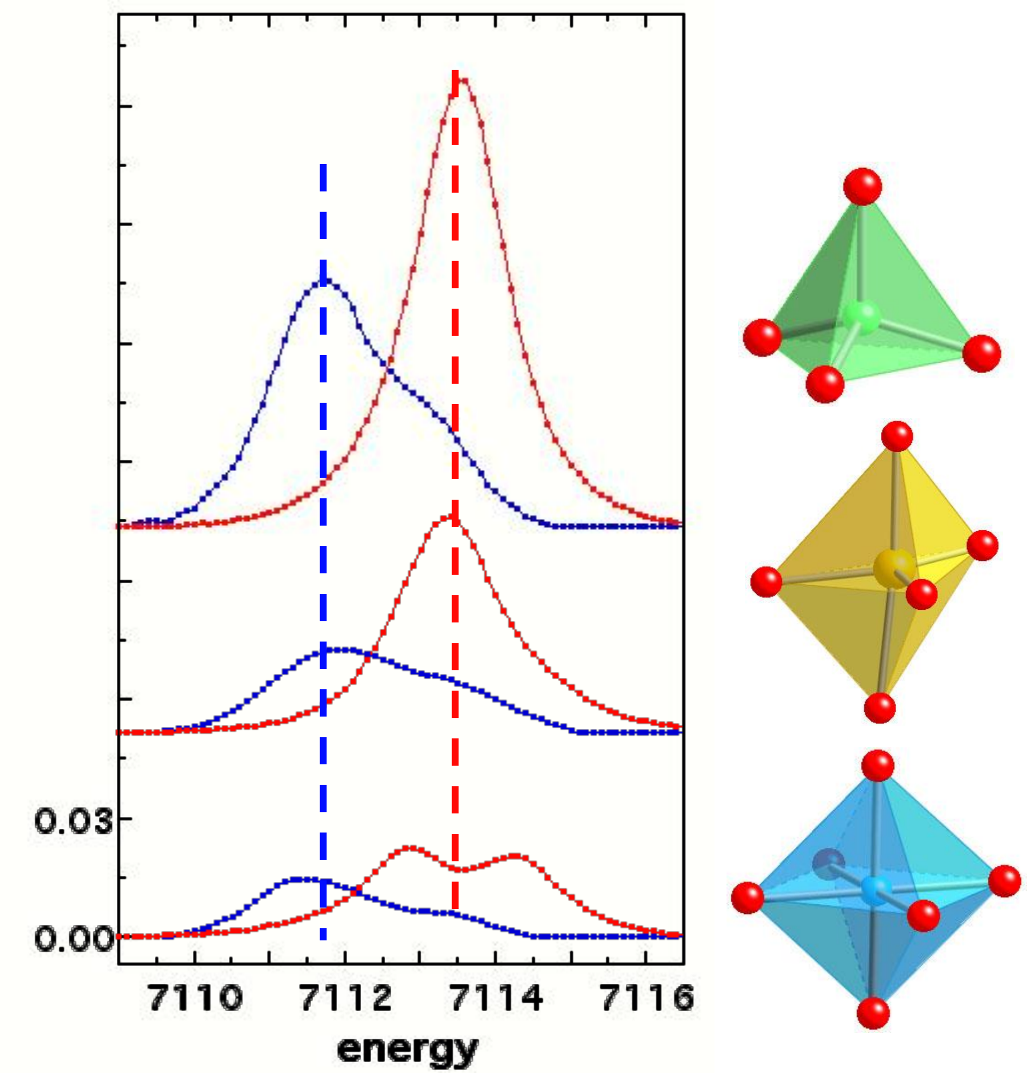
Tetrahedron

No Centro-symmetry : p-d mixing allowed dipole
transition in the edge high intensity prepeak



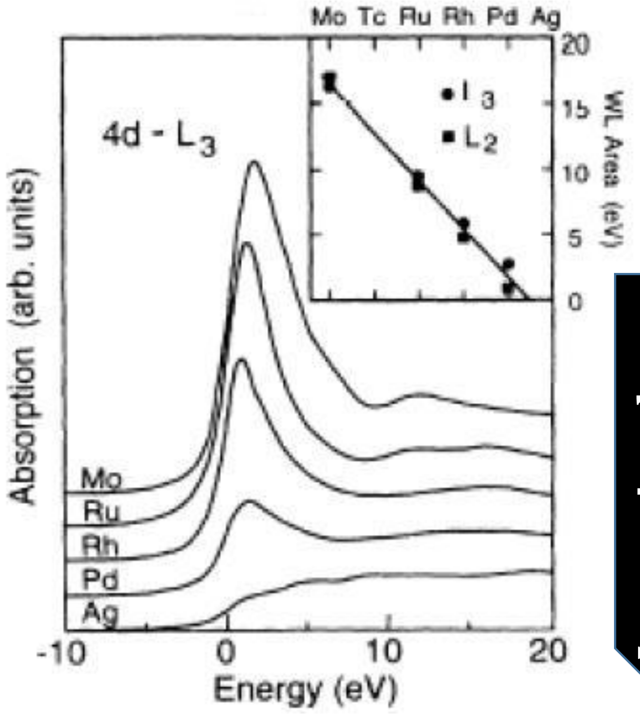
XANES Pre-edge Analysis

- redox
- symmetry



White line intensity of L3-edge XANES

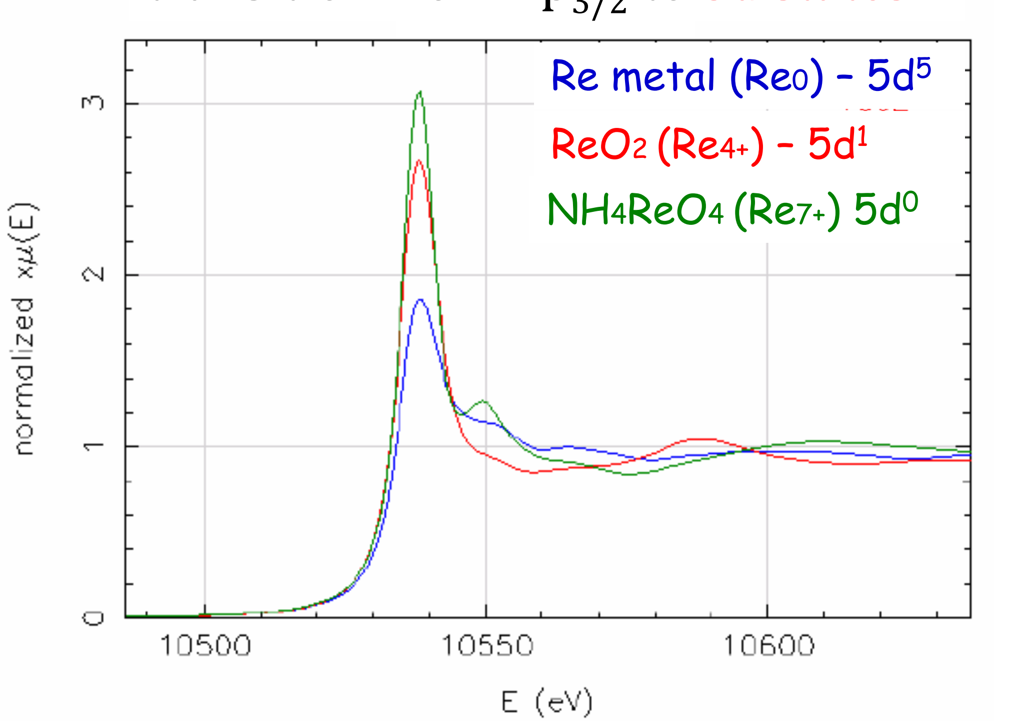
transition from $2p_{3/2}$ to 4d states



Increasing d states occupancy

Linear correlation between white line area and number of 4d-holes for Mo to Ag

transition from $2p_{3/2}$ to 5d states



XANES Interpretation

The EXAFS Equation breaks down at low-k, and the mean-free-path goes up.
This complicates XANES interpretation:

There is no simple equation for XANES

XANES can be described qualitatively (and nearly quantitatively) in terms of

coordination chemistry	regular, distorted octahedral, tetrahedral, . . .
molecular orbitals	p-d orbital hybridization, crystal-field theory, . . .
band-structure	the density of available electronic states
multiple-scattering	multiple bounces of the photoelectron

These chemical and physical interpretations are all related

XANES calculations are becoming reasonably accurate and simple. These can help explain what bonding orbitals and/or structural characteristics give rise to certain spectral features.

Quantitative XANES analysis using first-principles calculations are still rare, but becoming possible...

XANES: Conclusions

XANES is a much larger signal than EXAFS

XANES can be done at lower concentrations, and less-than-perfect sample conditions.

XANES is easier to crudely interpret than EXAFS

For many systems, the XANES analysis based on linear combinations of known spectra from "model compounds" is sufficient.

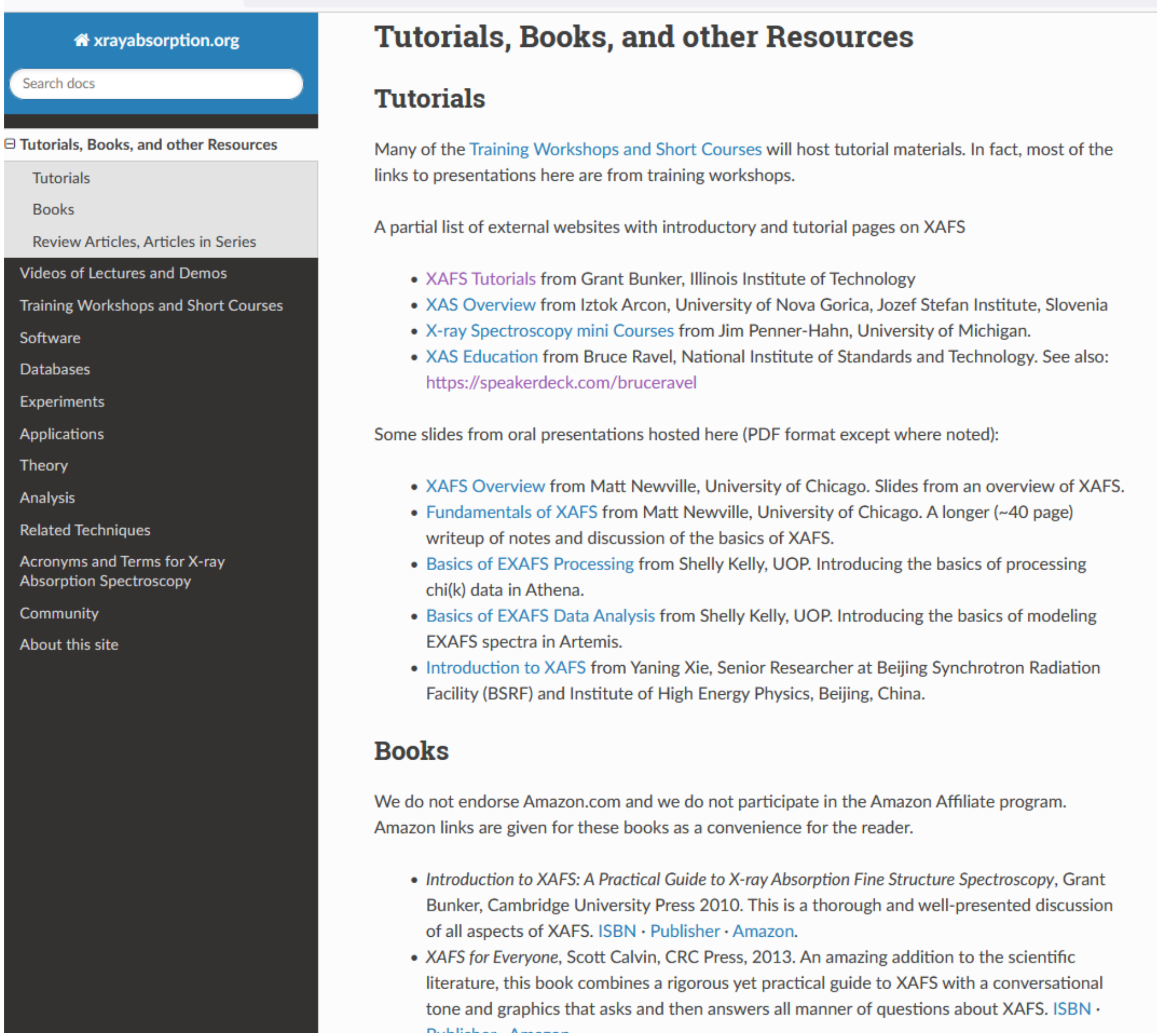
XANES is harder to fully interpret than EXAFS

The exact physical and chemical interpretation of all spectral features is still difficult to do accurately, precisely, and reliably.

Work is ongoing to improve the interpretation of XANES…

MORE INFORMATION

https://xafs.xrayabsorption.org/



Tutorials, Books, and other Resources

Tutorials

Many of the Training Workshops and Short Courses will host tutorial materials. In fact, most of the links to presentations here are from training workshops.

A partial list of external websites with introductory and tutorial pages on XAFS

- XAFS Tutorials from Grant Bunker, Illinois Institute of Technology
- XAS Overview from Iztok Arcon, University of Nova Gorica, Jozef Stefan Institute, Slovenia
- X-ray Spectroscopy mini Courses from Jim Penner-Hahn, University of Michigan.
- XAS Education from Bruce Ravel, National Institute of Standards and Technology. See also: https://speakerdeck.com/bruceravel

Some slides from oral presentations hosted here (PDF format except where noted):

- XAFS Overview from Matt Newville, University of Chicago. Slides from an overview of XAFS.
- Fundamentals of XAFS from Matt Newville, University of Chicago. A longer (~40 page) writeup of notes and discussion of the basics of XAFS.
- Basics of EXAFS Processing from Shelly Kelly, UOP. Introducing the basics of processing chi(k) data in Athena.
- Basics of EXAFS Data Analysis from Shelly Kelly, UOP. Introducing the basics of modeling EXAFS spectra in Artemis.
- Introduction to XAFS from Yaning Xie, Senior Researcher at Beijing Synchrotron Radiation Facility (BSRF) and Institute of High Energy Physics, Beijing, China.

Books

We do not endorse Amazon.com and we do not participate in the Amazon Affiliate program. Amazon links are given for these books as a convenience for the reader.

- *Introduction to XAFS: A Practical Guide to X-ray Absorption Fine Structure Spectroscopy*, Grant Bunker, Cambridge University Press 2010. This is a thorough and well-presented discussion of all aspects of XAFS. ISBN · Publisher · Amazon.
- *XAFS for Everyone*, Scott Calvin, CRC Press, 2013. An amazing addition to the scientific literature, this book combines a rigorous yet practical guide to XAFS with a conversational tone and graphics that asks and then answers all manner of questions about XAFS. ISBN ·

MORE INFORMATION

Web links

International XAFS Society:

http://ixs.iit.edu/

Tutorials and other Training Material:

http://gbxafs.iit.edu/training/tutorials.html
https://bruceravel.github.io/home/

Software Resources EXAFS:

https://xafs.xrayabsorption.org/software.html

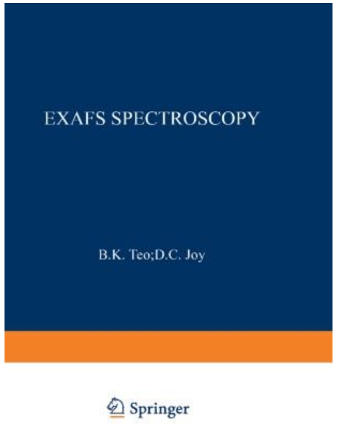
Demeter, WinXAS, DL, Excurv, EXAFSPAK, XAID, GNXAS,

SixPACK, Larch, LASE Viper, ~~XAFS~~, Xanda, ……

FDMNES, FEFF, TT-Multiplets ……

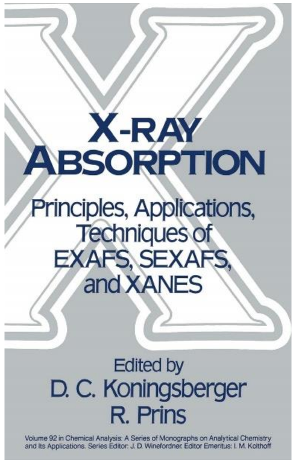
MORE INFORMATION

Books


EXAFS SPECTROSCOPY

B.K. Teo;D.C. Joy

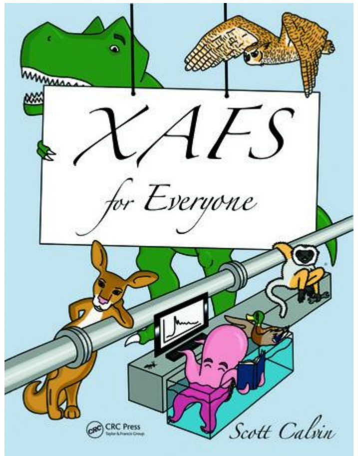
Springer


X-RAY ABSORPTION

Principles, Applications, Techniques of EXAFS, SEXAFS, and XANES

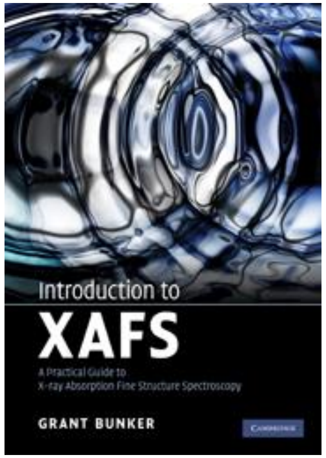
Edited by
D. C. Koningsberger
R. Prins

Volume 92 in Chemical Analysis: A Series of Monographs on Analytical Chemistry and Its Applications. Series Editor: J. D. Winefordner Editor Emeritus: I. M. Kolthoff


XAFS for Everyone

Scott Calvin

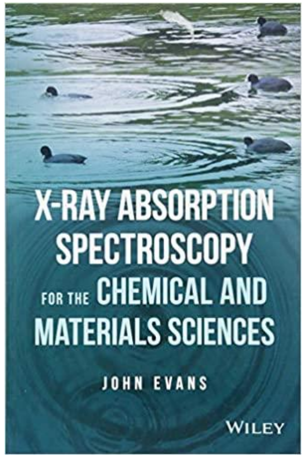
CRC Press


Introduction to XAFS

A Practical Guide to X-ray Absorption Fine Structure Spectroscopy

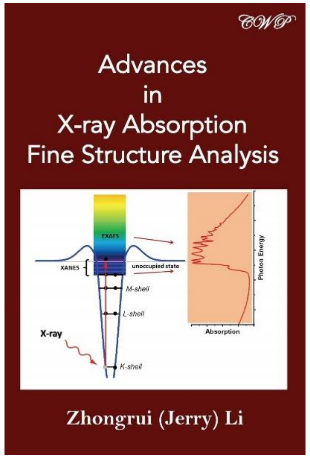
GRANT BUNKER

CAMBRIDGE


X-RAY ABSORPTION SPECTROSCOPY FOR THE CHEMICAL AND MATERIALS SCIENCES

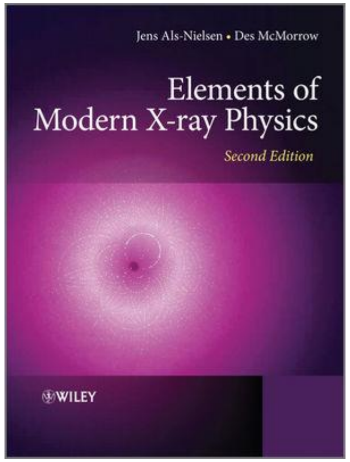
JOHN EVANS

WILEY


CWP

Advances in X-ray Absorption Fine Structure Analysis

Zhongrui (Jerry) Li


Jens Als-Nielsen • Des McMorrow

Elements of Modern X-ray Physics

Second Edition

WILEY