



| The European Synchrotron

# Fundamentals of X-ray Absorption Fine Structure

**Sakura Pascarelli**

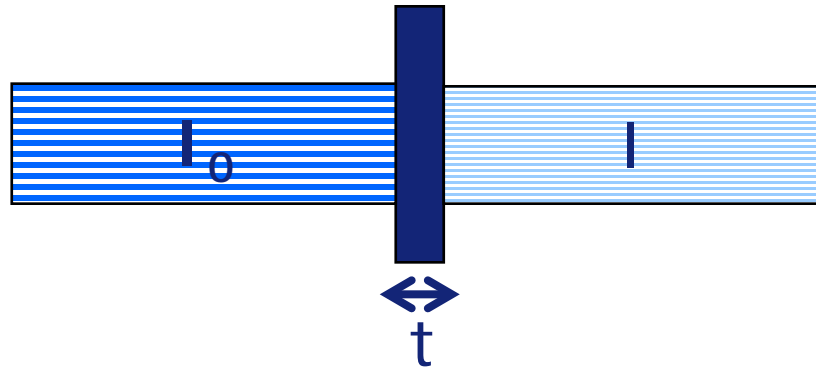
European Synchrotron Radiation Facility, Grenoble, France

# X-ray Absorption

## Main X-ray based techniques

- o **Two fundamental X-ray-matter interactions:**
  - | photoelectric absorption
  - | scattering (elastic, inelastic)
  
- o **Two families of experimental techniques:**
  - q spectroscopy à exchange of energy (electronic structure, local structure of matter)
    - | absorption (XAS, EXAFS, XANES, ..)
    - | emission (XES, HERFD, ..)
    - | inelastic scattering (IXS, RIXS, X-ray Raman, etc..)
  
  - q elastic diffusion à no exchange of energy (microscopic geometric structure)
    - | “diffraction” for crystalline solids (XRD, GIXRD, ..)
    - | “scattering” for amorphous solids, liquids (XRS, WAXS, SAXS, ...)

## The Absorption Coefficient $m$



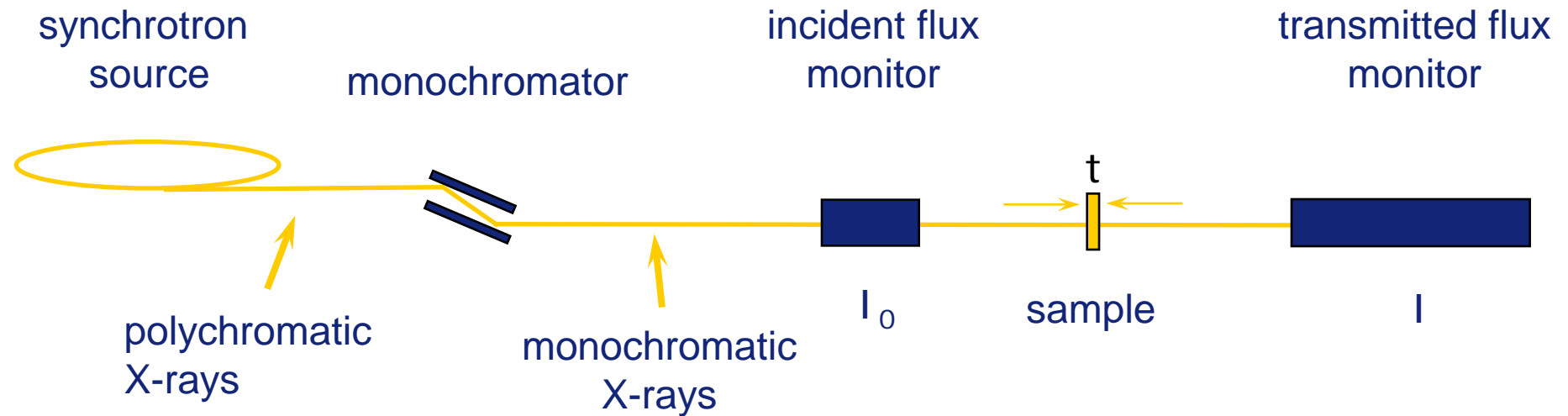
$$I = I_0 \exp[-mt]$$



linear absorption coefficient

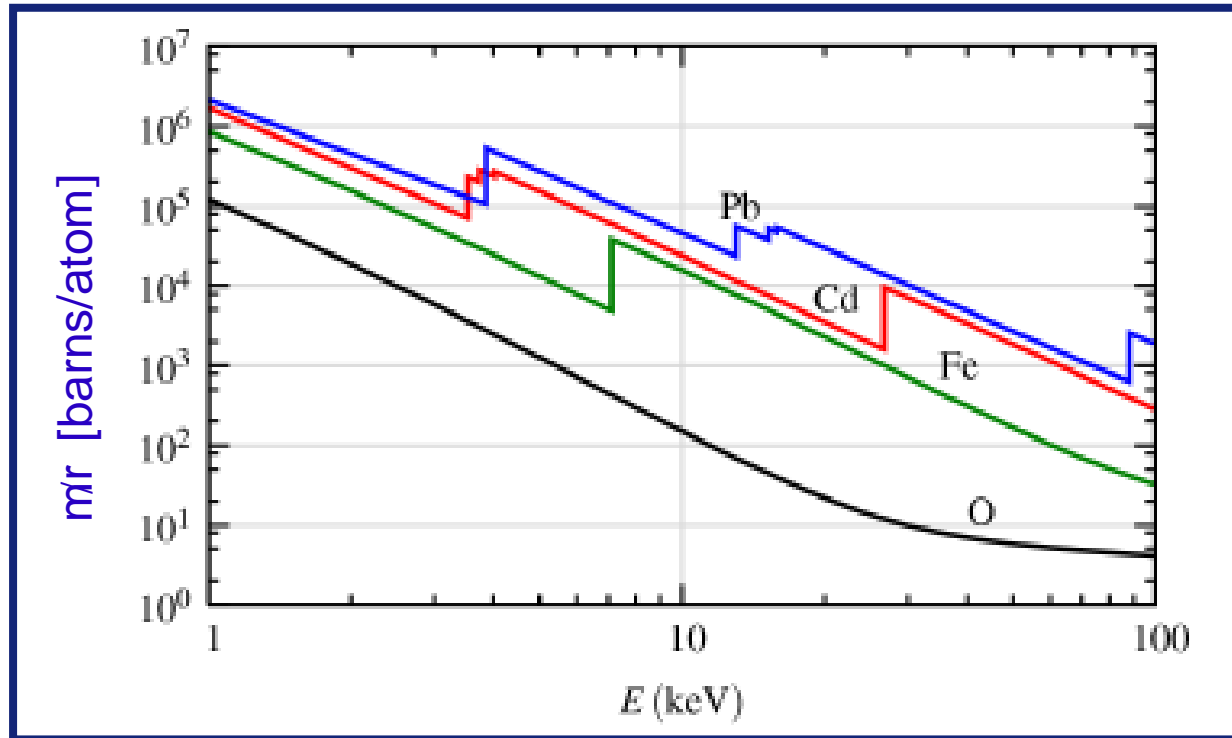
$$mt = \ln [ I_0 / I ]$$

## The Absorption Coefficient $m$



1. Measure  $I_0$  and  $I$  as a function of  $E_x$
2. Calculate:  $mt = \ln [I_0/I]$

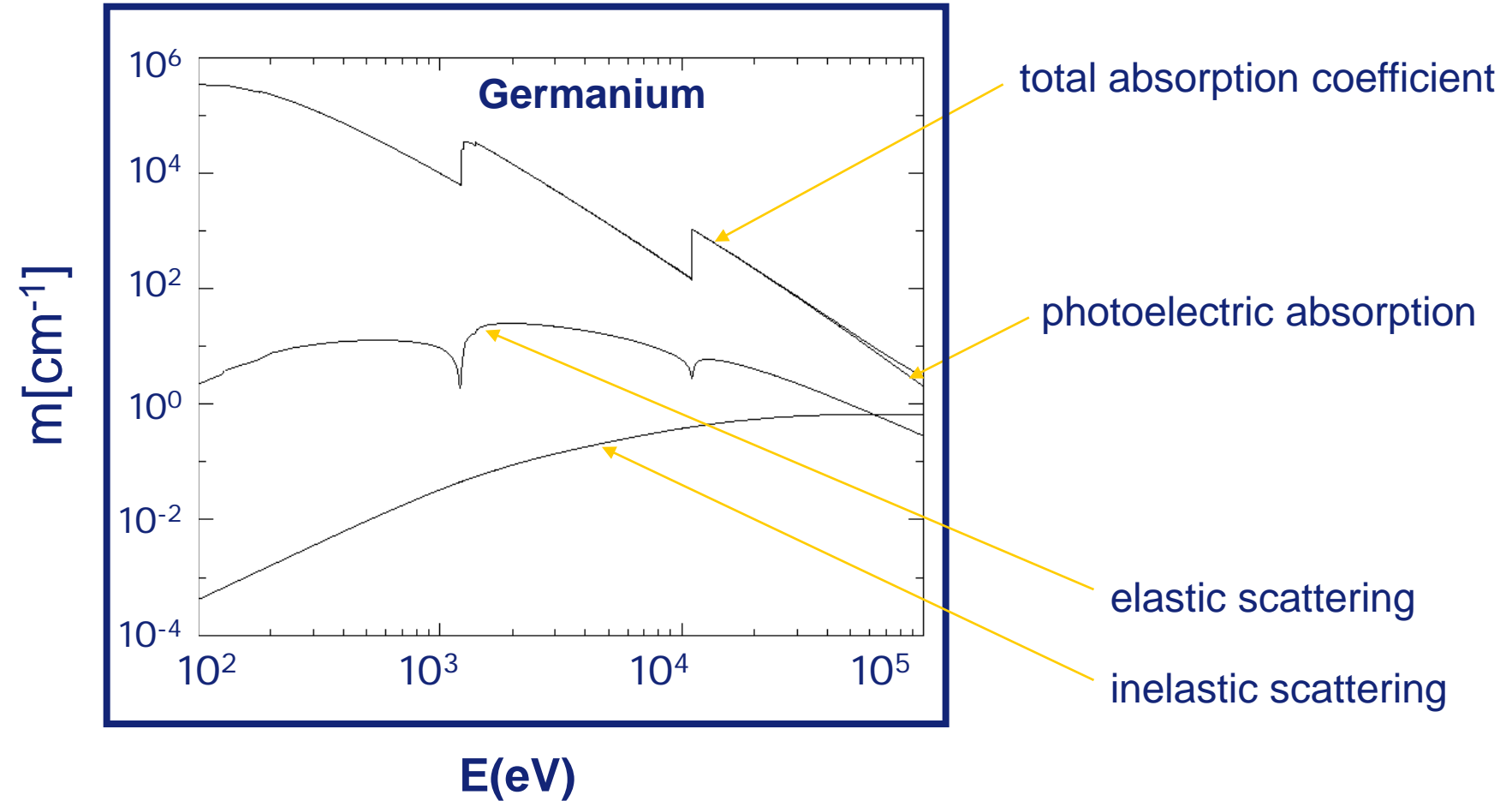
# The Absorption Coefficient $m$



$m$  depends strongly on X-ray energy  $E$  and atomic number  $Z$ , the density  $r$  and atomic mass  $A$

$$m \gg \frac{r Z^4}{A E^3}$$

$m$  has sudden jumps (**absorption edges**) which occur at energies characteristic of the element.



**Photoelectric absorption** dominates the absorption coefficient in this energy range



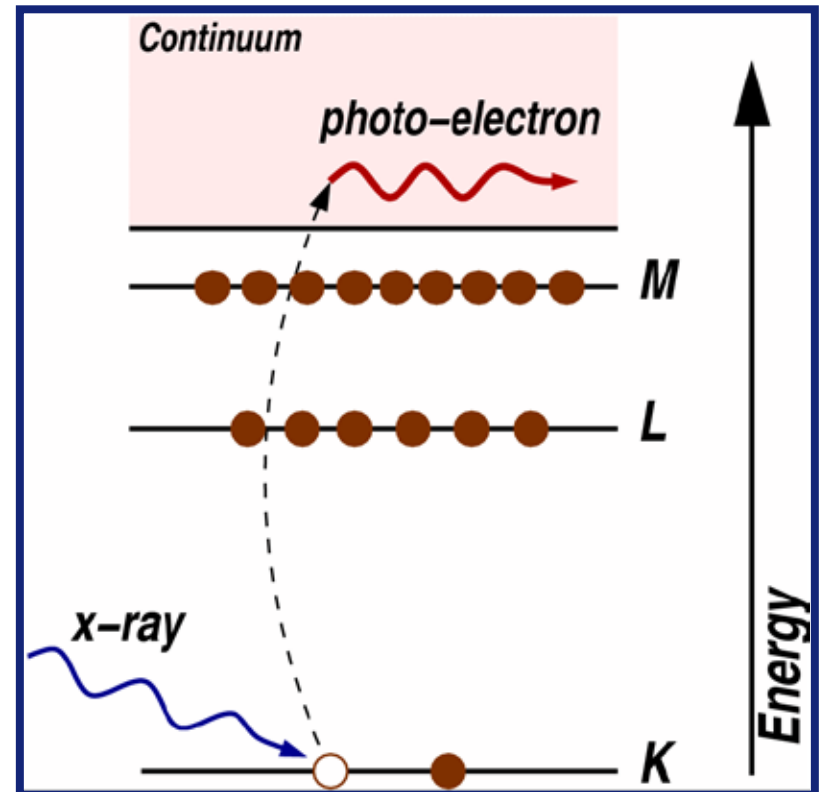
# Photoelectric Absorption

X-rays (light with wavelength  $0.06 \leq \lambda \leq 12 \text{ \AA}$  or energy  $1 \leq E \leq 200 \text{ keV}$ ) 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**.

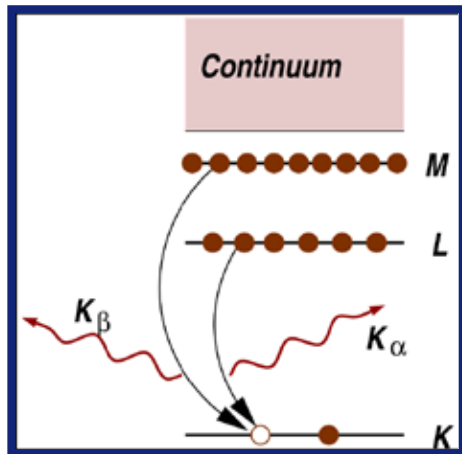


# De-excitation: Fluorescence and Auger Effect

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.

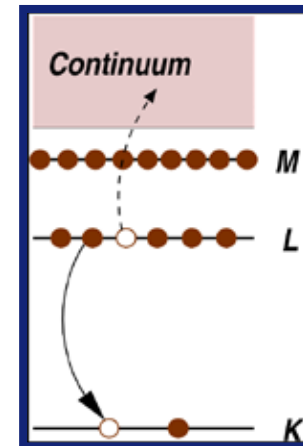
## X-ray Fluorescence:

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



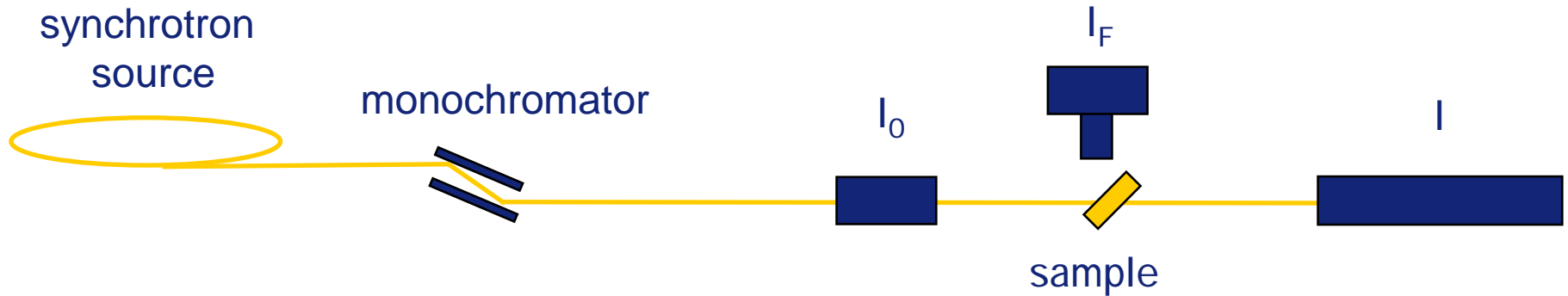
## Auger Effect:

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



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

# 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:

## Transmission:

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

$$I = I_0 e^{-\mu(E)t}$$

$$\mu(E)t = -\ln(I/I_0)$$

## Fluorescence:

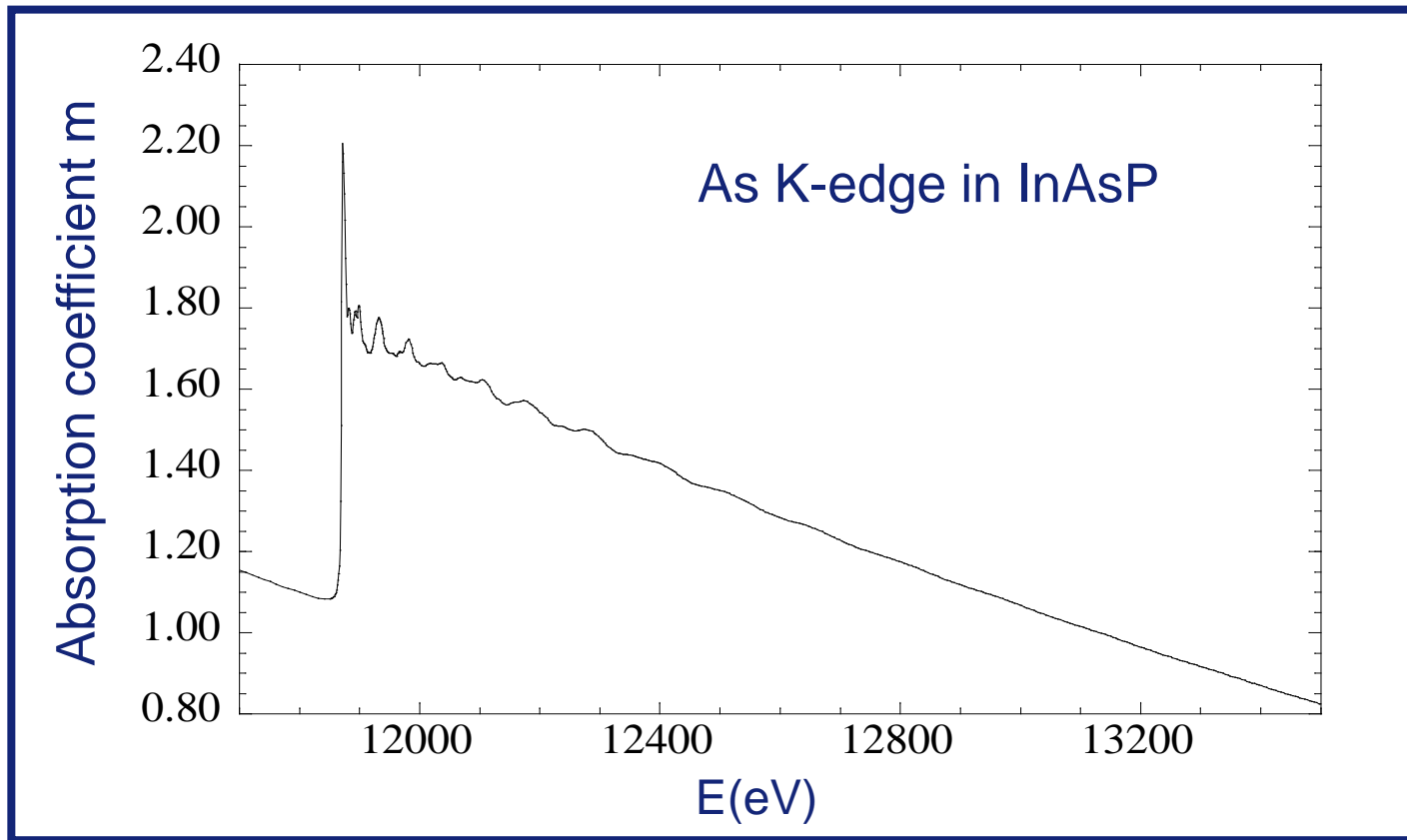
The re-filling the deep core hole is detected. Typically the fluorescent X-ray is measured:

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

# X-ray Absorption Fine Structure

# What is XAFS?

X-ray **A**bsorption **F**ine **S**tructure: oscillatory variation of the X-ray absorption as a function of photon energy beyond an absorption edge.



Proximity of neighboring atoms strongly modulates the absorption coefficient

## EXAFS and XANES

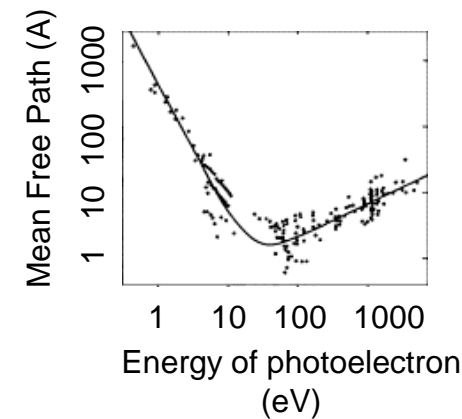
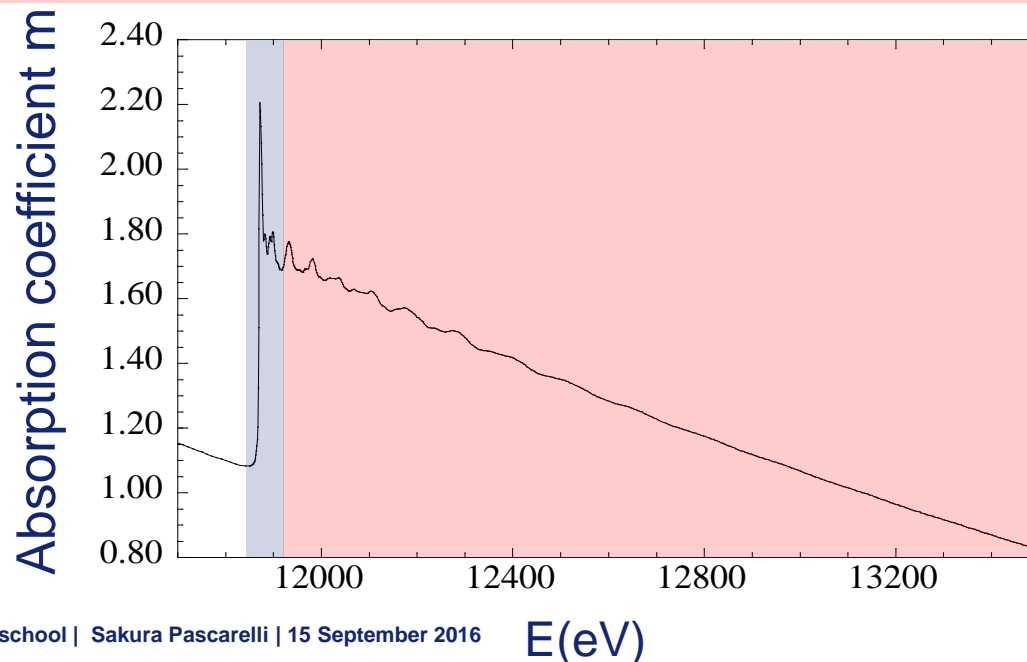
XAFS is also referred to as X-ray Absorption Spectroscopy (**XAS**) and is broken into 2 regimes:

**XANES**    X-ray Absorption Near-Edge Spectroscopy  
**EXAFS**    Extended X-ray Absorption Fine-Structure

which contain related, but slightly different information about an element's local coordination and chemical state.

**XANES** : transitions to unfilled bound states, nearly bound states, continuum - **low energy photoelectrons**

**EXAFS**: ~ 50 – 1000 eV from edge, transitions to continuum – **high energy photoelectrons**

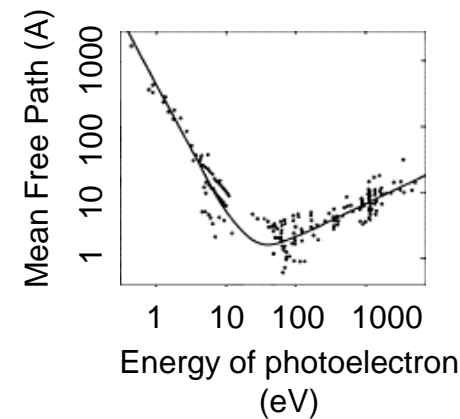
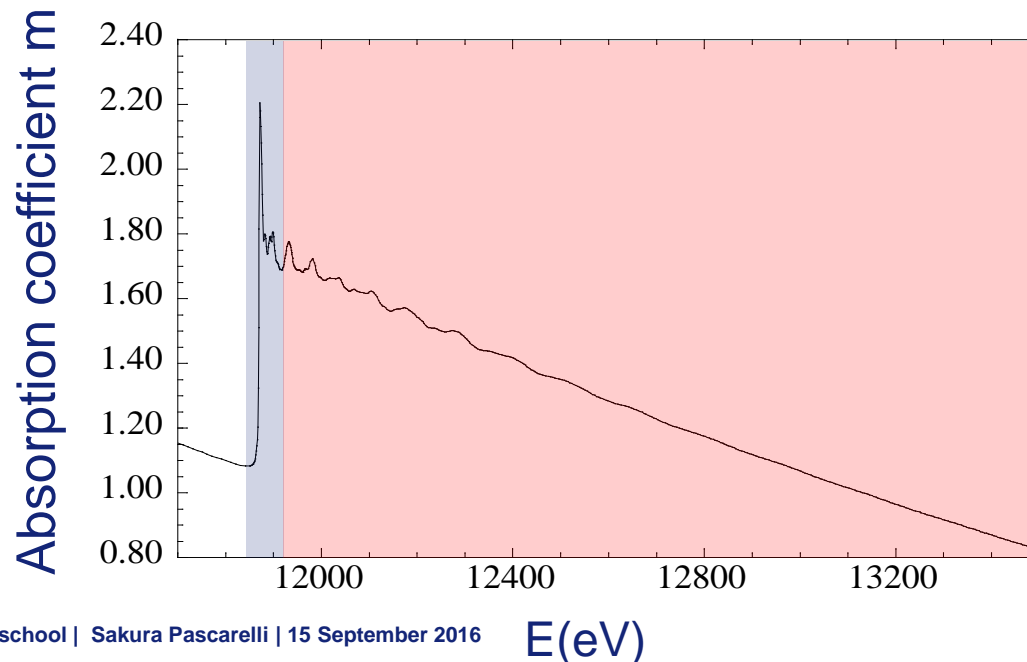


# EXAFS and XANES

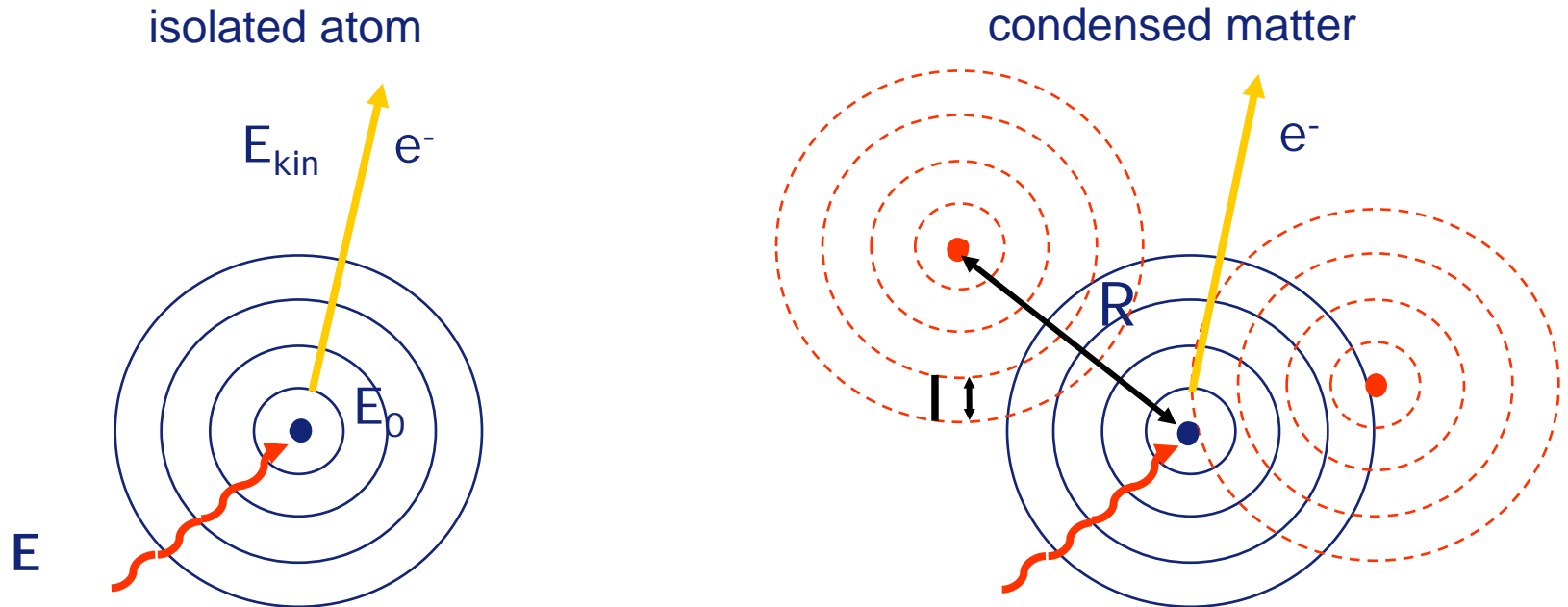
1. Approximations can be used to interpret EXAFS, that are not valid for XANES
2. Cannot be analyzed in the same way
3. Different information content.

**XANES:** local site symmetry, charge state, orbital occupancy

**EXAFS:** local structure (bond distance, number, type of neighbors....)



# EXAFS qualitatively



The kinetic energy of the ejected photoelectron  $E_{kin}$  is:

$$E_{kin} = E - E_0 = \frac{p^2}{2m} = \frac{h^2 k^2}{2m}$$

$$l = 2 p/k$$

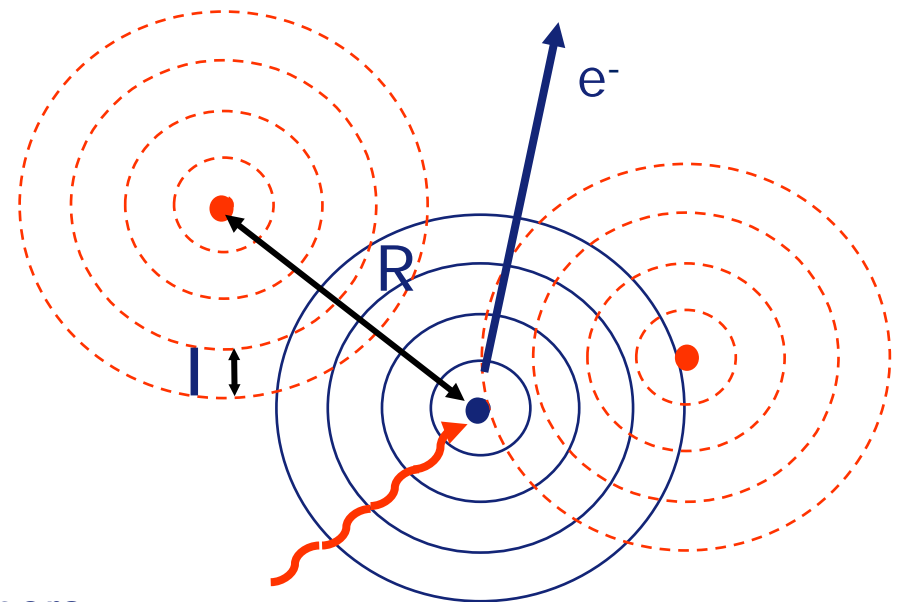


# Where do the oscillations come from?

Due to a **quantum effect**, the autointerference of photoelectron wave modifies the absorption coefficient value:

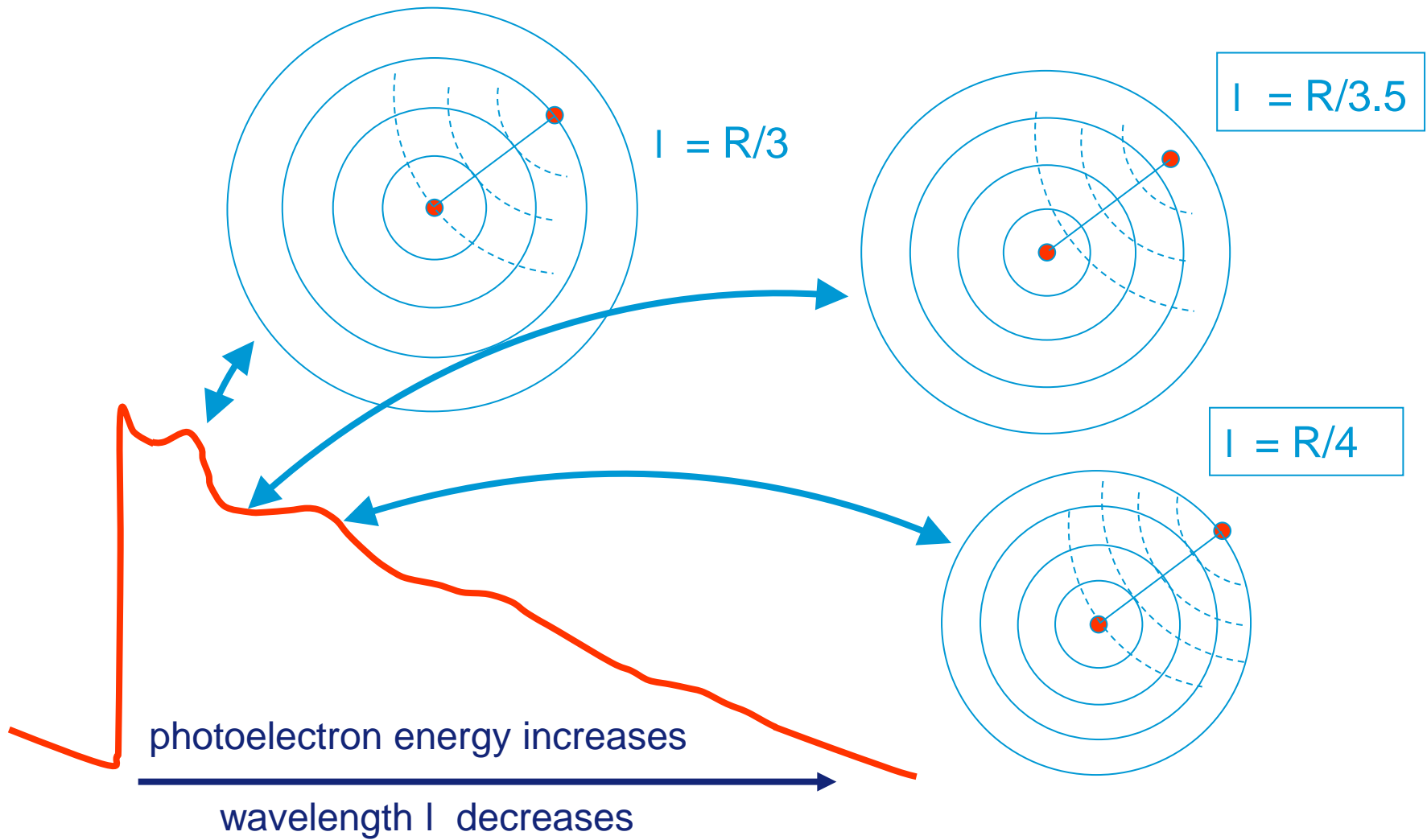
1. As  $E$  is scanned above  $E_0$ ,  $E_{kin}$  is varied, and consequently  $k$  and  $I$ .
2. The outgoing and backscattered parts of the wave interfere either constructively or destructively, depending on the ratio between  $I$  and  $R$ .
3. It is the **interference** between outgoing and incoming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

$$E_{kin} = E - E_0 = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}$$



- $p$  frequency  $\sim$  distance from neighbors
- $p$  amplitude  $\sim$  number and type of neighbors

# FUNDAMENTALS OF X-RAY ABSORPTION FINE STRUCTURE: EXAFS



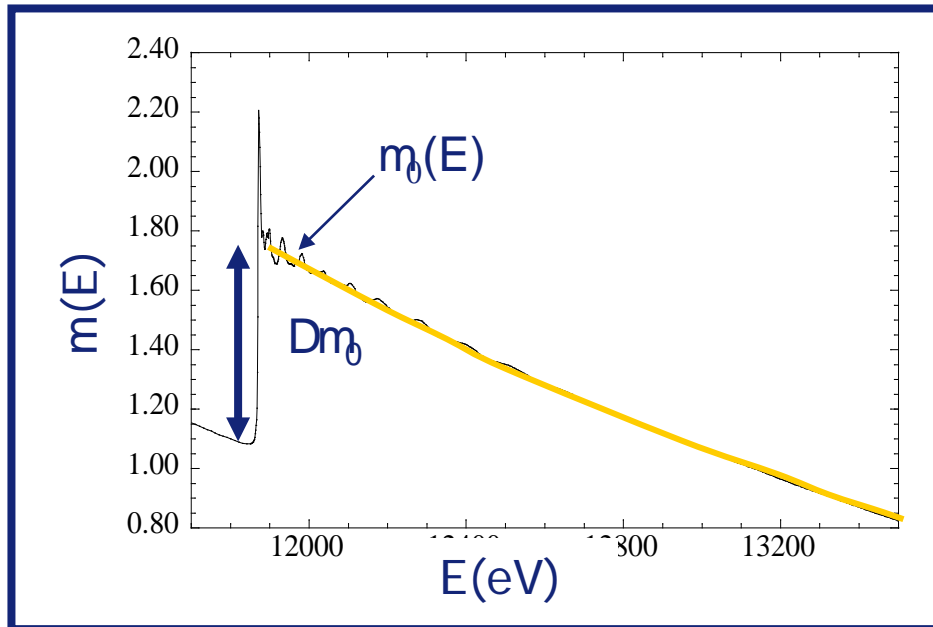
The probability of absorption oscillates due to constructive and destructive interference

# The EXAFS signal $c$

We're interested in the energy dependent oscillations in  $\mu(E)$ , as these will tell us something about the neighboring atoms, so we define the EXAFS as:

$$c(E) = \frac{\mu(E) - \mu_0(E)}{D\mu_0(E_0)}$$

We subtract off the smooth "bare atom" background  $\mu_0(E)$ , and divide by the edge step  $D\mu_0(E_0)$ , to give the oscillations normalized to 1 absorption event.

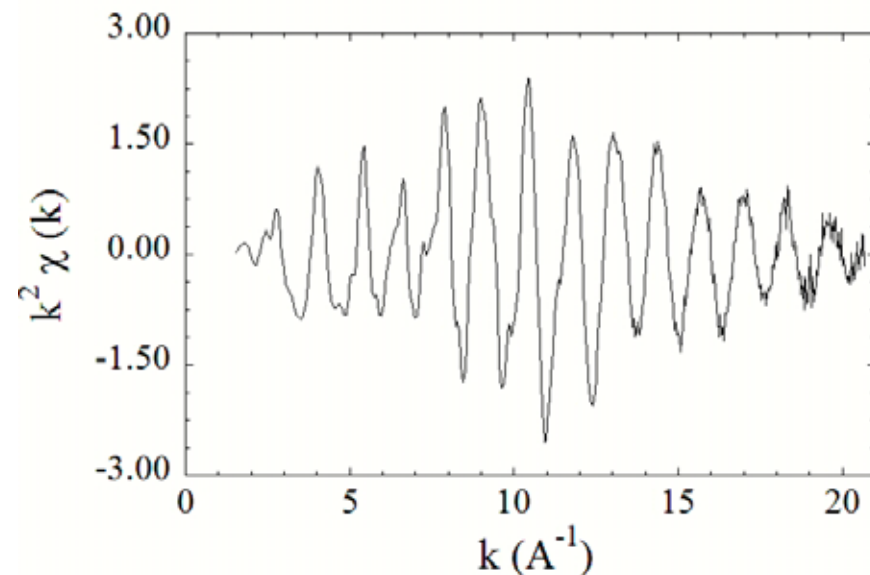
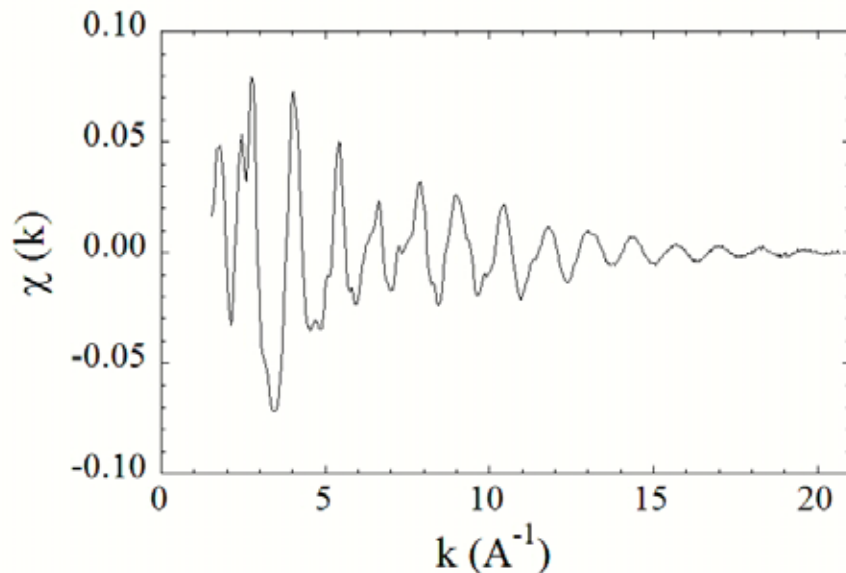


# EXAFS: $\chi(k)$

XAFS is an **interference effect**, and depends on the wave-nature of the photoelectron. It's convenient to think of XAFS in terms of **photoelectron wavenumber**,  $k$ , rather than X-ray energy

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

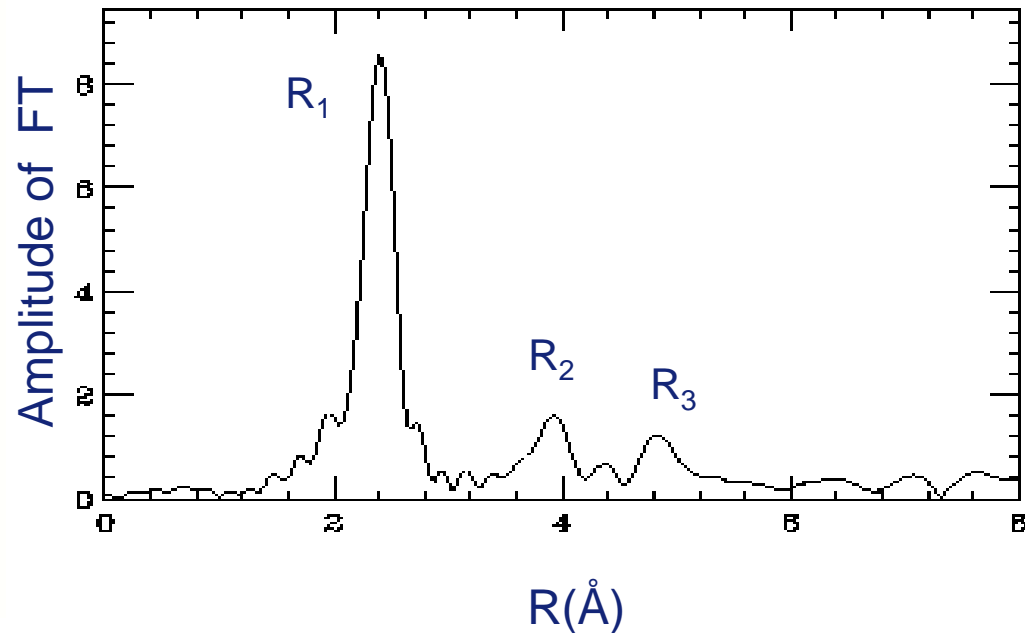
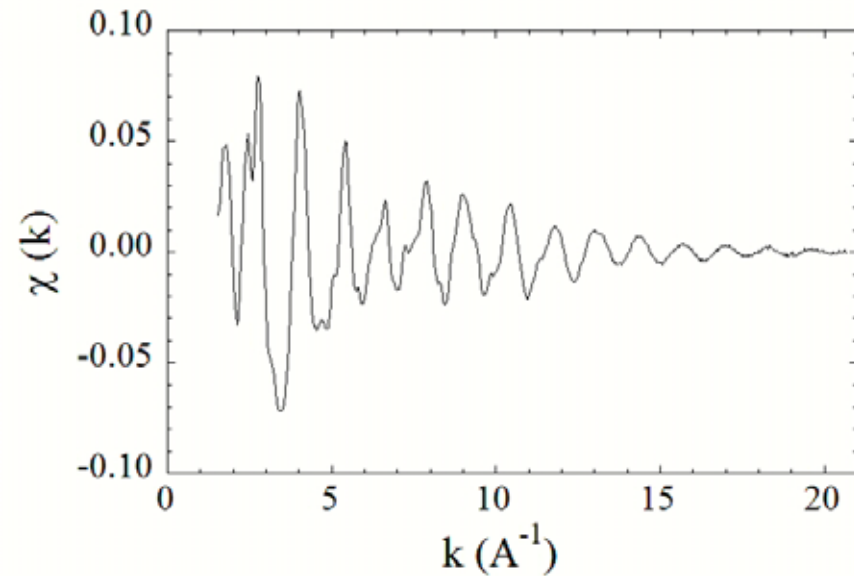
$\chi(k)$  is often shown weighted by  $k^2$  or  $k^3$  to amplify the oscillations at high- $k$ :



# Qualitative picture of local coordination in R space

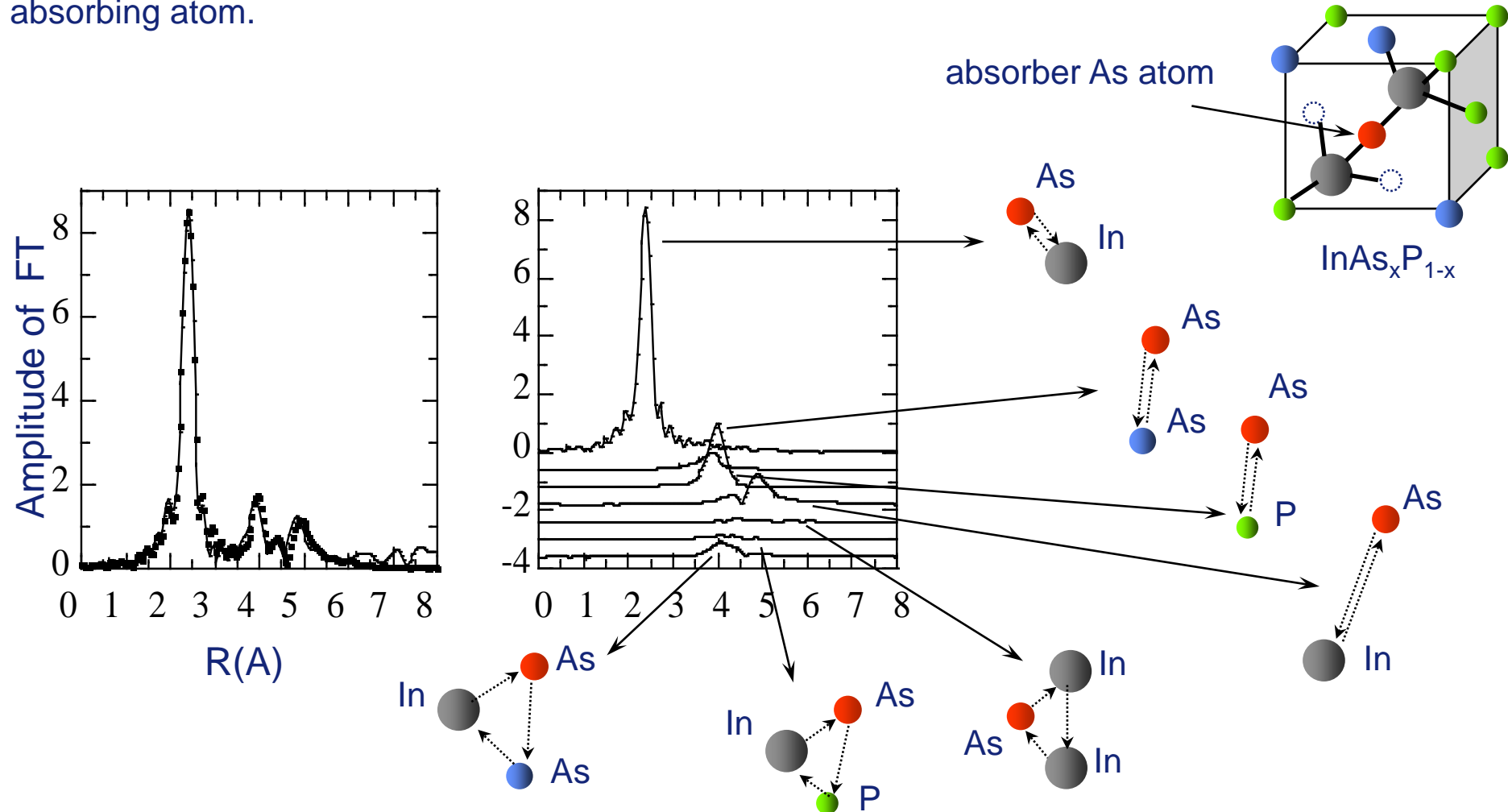
The **frequencies** contained in the EXAFS signal depend on the **distance** between the absorbing atom and the neighboring atoms (i.e. the length of the scattering path).

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.



## c: sum of damped waves

$c(k)$  is the sum of contributions  $c_j(k)$  from backscattered wavelets:

$$c(k) = \sum_j c_j(k)$$

- Path expansion
- implies photoel w/short mean free path
  - true only for EXAFS

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

$$c_j(k) = A_j(k) \sin [j_j(k)]$$

The larger the number of neighbors, the larger the signal

$$N_j f_j(k) e^{-2k^2 s^2}$$

The stronger the scattering amplitude, the larger the signal

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

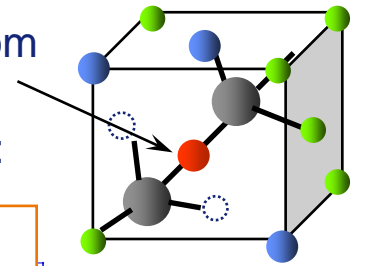
$$2k R_j + d_j(k)$$

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

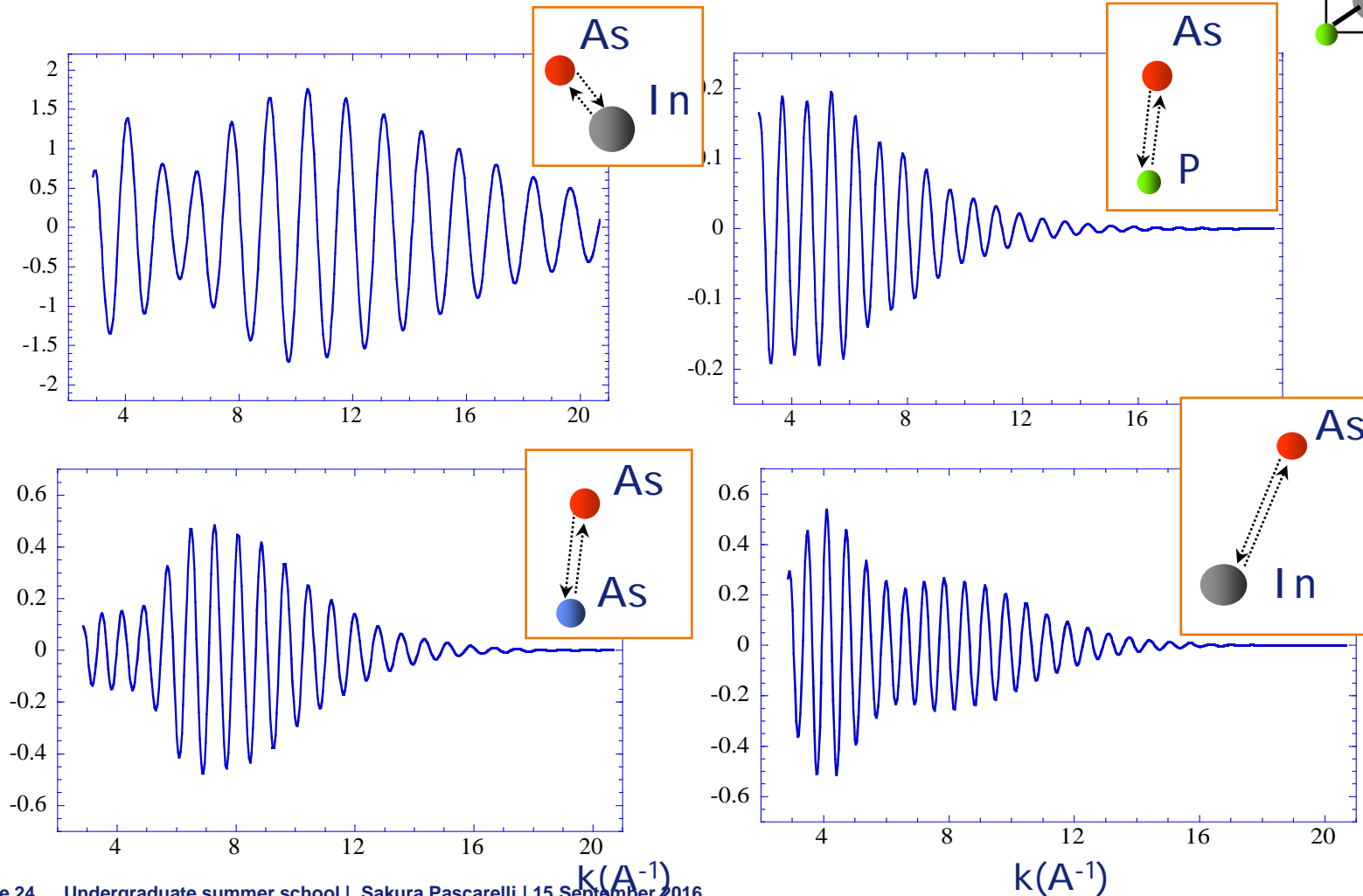
## Amplitudes

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

absorber As atom



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

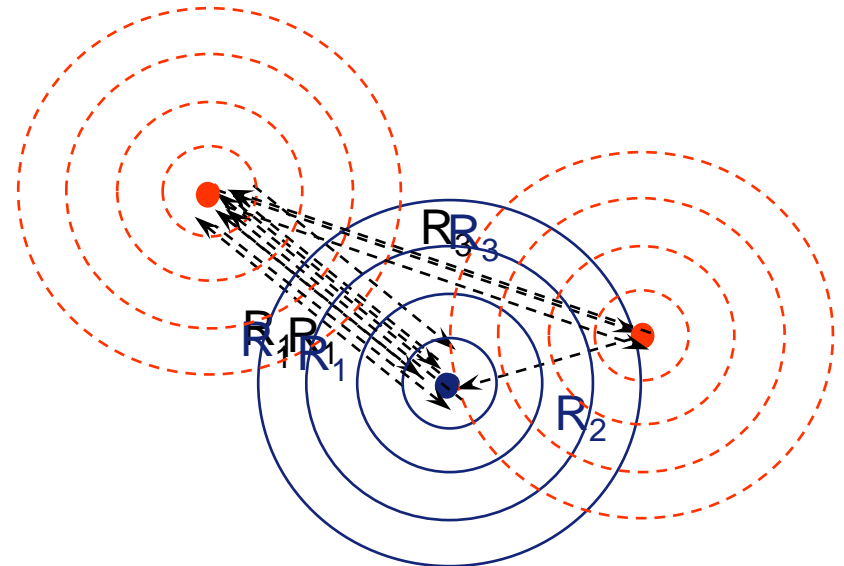




# Frequencies: Single and Multiple Scattering paths

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

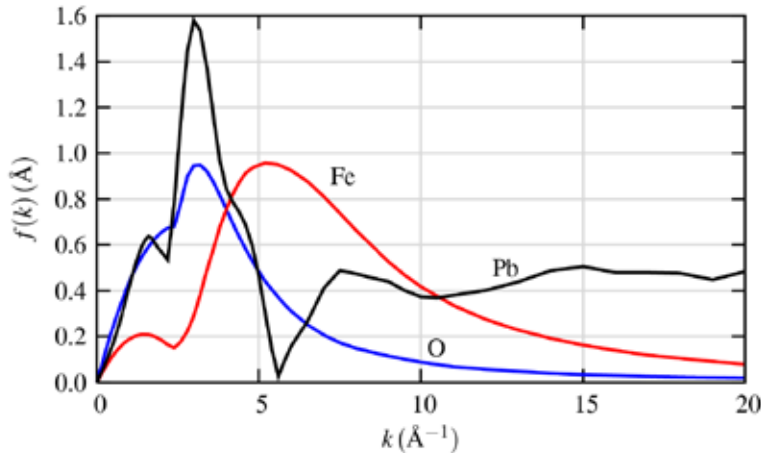
- SS  $\Rightarrow$   $g_2(r)$   $f = 2 R_1$
- MS  $\Rightarrow$   $g_2(r)$   $f = 4 R_1$
- MS  $\Rightarrow$   $g_3(r)$   $f = R_1 + R_2 + R_3$
- MS  $\Rightarrow$   $g_3(r)$   $f = 2R_1 + 2R_3$



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

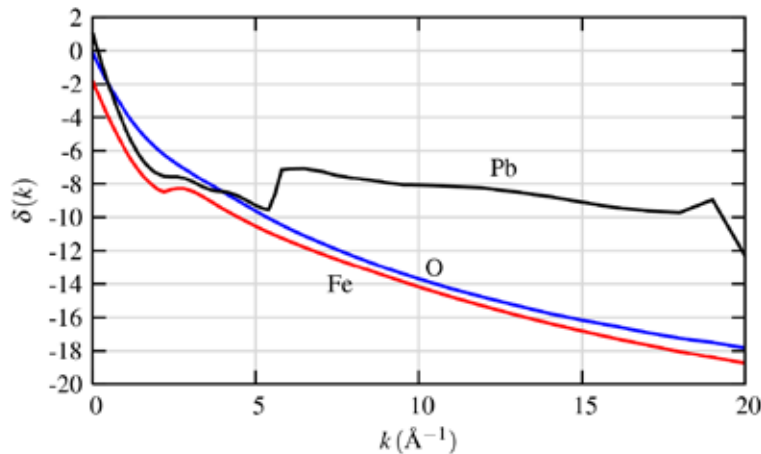
# Scattering Amplitude and Phase-Shift: $f(k)$ and $d(k)$

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



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

The phase shift  $d(k)$  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.

## Calculating $f(k)$ and $d(k)$

These days, we can calculate  $f(k)$  and  $d(k)$  easily using different software codes.

These programs take as input:

1. a list of atomic  $x, y, z$  coordinates for a physical structure
2. a selected central atom

The result is a set of files containing the  $f(k)$ , and  $d(k)$  for a particular scattering “shell” or “scattering path” for that cluster of atoms.

Many analysis programs use these files directly to model EXAFS data.

A structure that is close to the expected structure can be used to generate a model, and used in the analysis programs to refine distances and coordination numbers.

# XAFS vs Diffraction Methods

## q Diffraction Methods (X-rays, Neutrons)

§ Crystalline materials with long-range ordering -> 3D picture of atomic coordinates

§ Materials with only short-range order (amorphous solid, liquid, or solution) -> 1D radial distribution function containing interatomic distances due to all atomic pairs in the sample.

## q XAFS

§ 1D radial distribution function (centered at the absorber)

§ Element selectivity

§ Higher sensitivity to local distortions (i.e. within the unit cell)

§ Charge state sensitivity (XANES)

§ Structural information on the environment of each type of atom:

§ distance, number, kind, static and thermal disorder

§ 3-body correlations

§ Investigation of matter in the solid (crystalline or amorphous), liquid, solution or gaseous state with same degree of accuracy

## EXAFS: typical applications

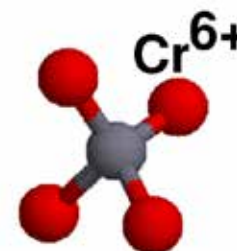
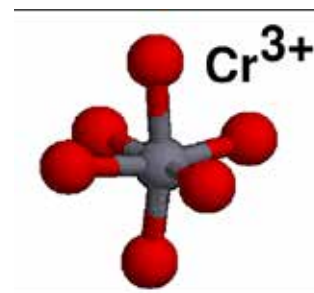
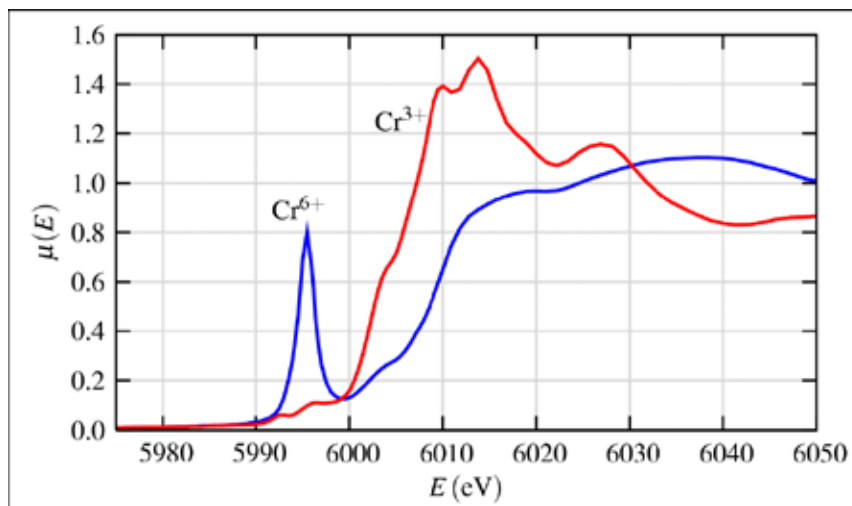
Element selectivity  
Local structure sensitivity



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

# XANES

# XANES Analysis: Oxidation State and Coordination Chemistry

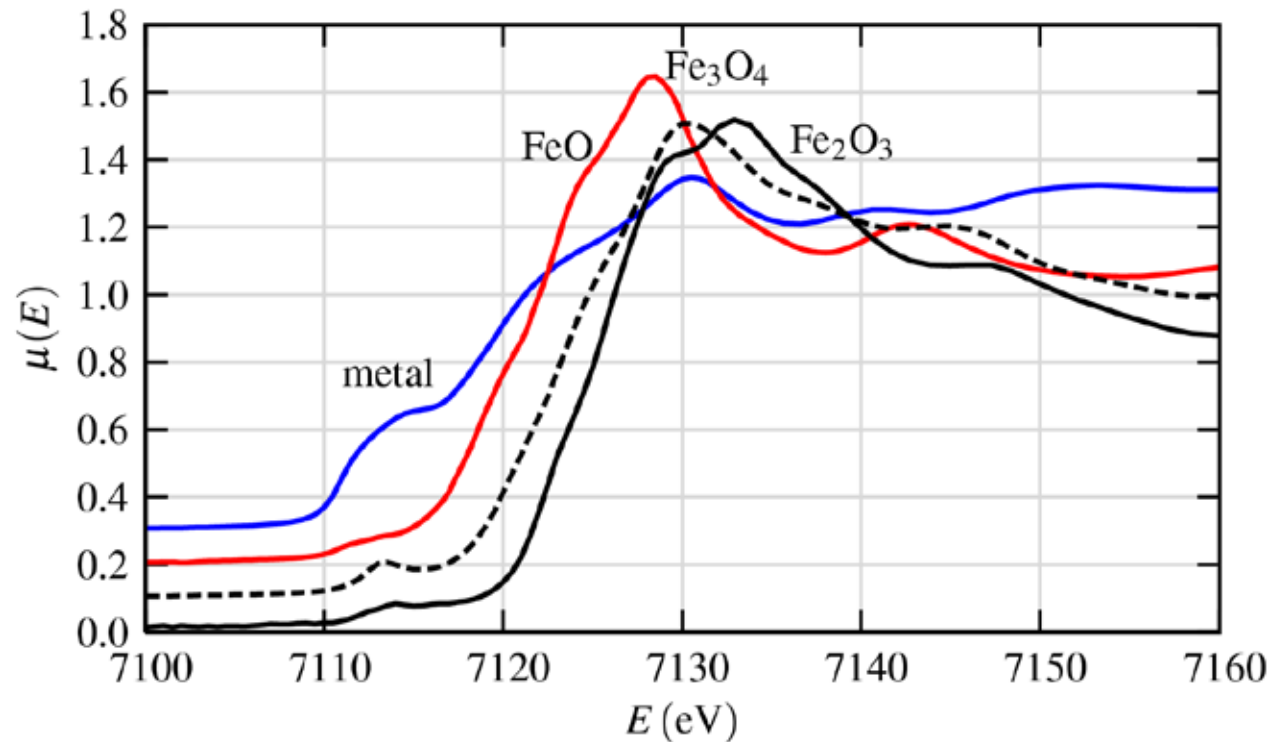


The XANES of Cr<sup>3+</sup> and Cr<sup>6+</sup> shows a dramatic dependence on oxidation state and coordination chemistry.

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 in Fe oxides



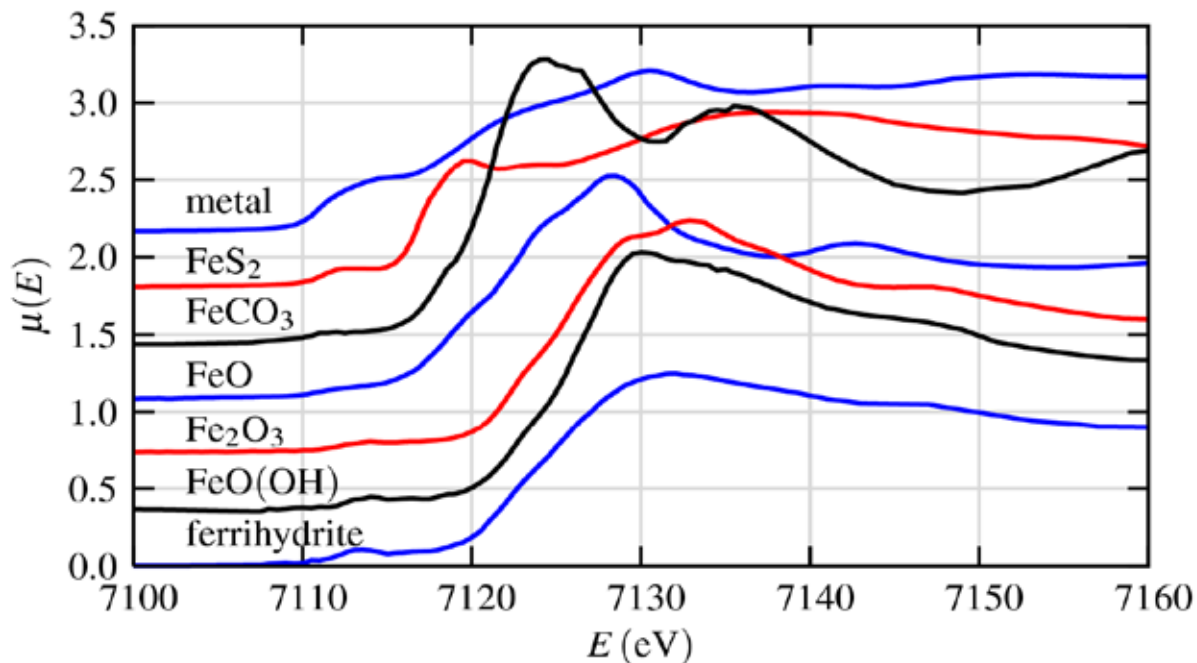
The shift of the edge position can be used to determine the valence state

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



## XANES Analysis: Oxidation State

The Normalized XANES from several Fe compounds:



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

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

## XANES Interpretation

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

We do not have a 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, of course:

What electronic states can the photoelectron fill?

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.

This situation is improving, so stay tuned to the progress in XANES calculations . . . .

# Examples of Applications

**Sakura Pascarelli**

European Synchrotron Radiation Facility, Grenoble, France

# LATTICE DISTORTIONS AROUND IMPURITIES IN DILUTE ALLOYS

PHYSICAL REVIEW B

VOLUME 44, NUMBER 18

1 NOVEMBER 1991-II

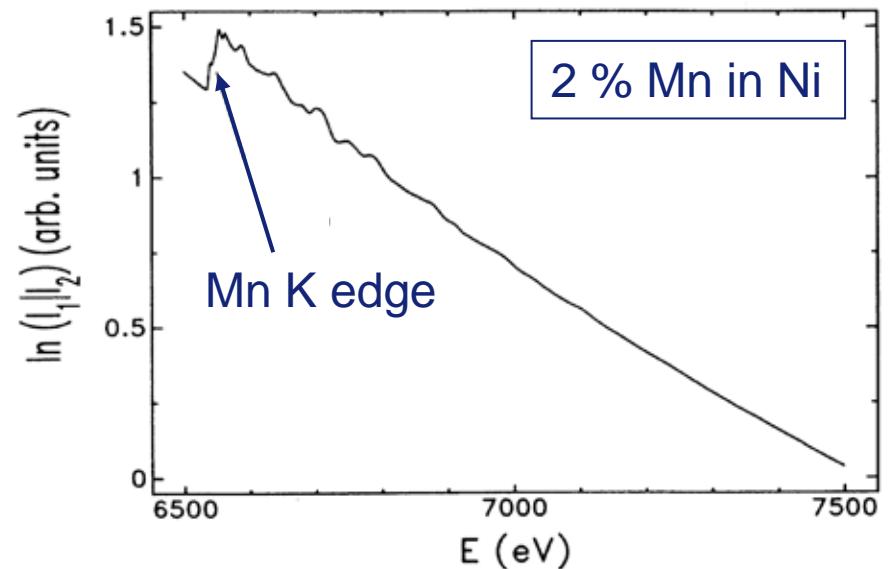
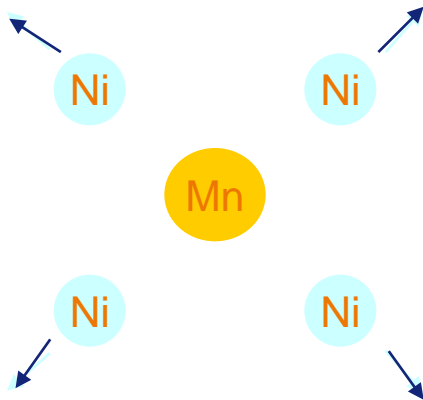
## Lattice distortion of solute atoms in metals studied by x-ray-absorption fine structure

U. Scheuer and B. Lengeler

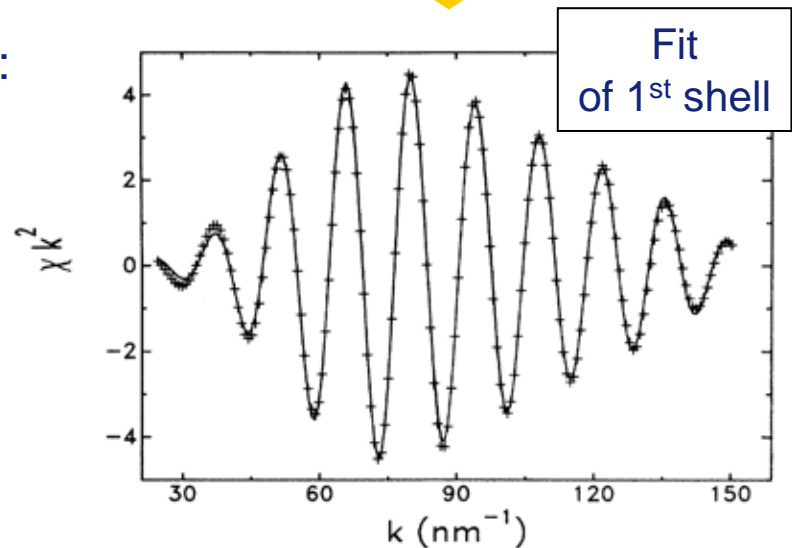
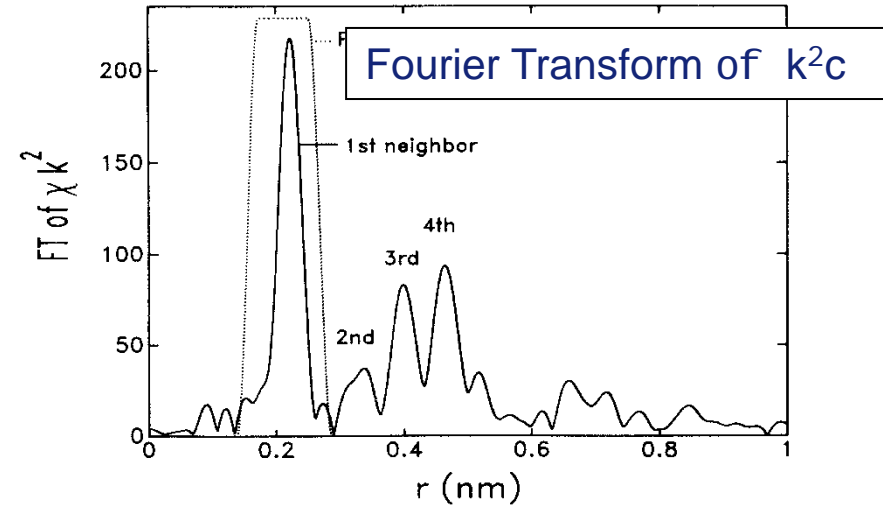
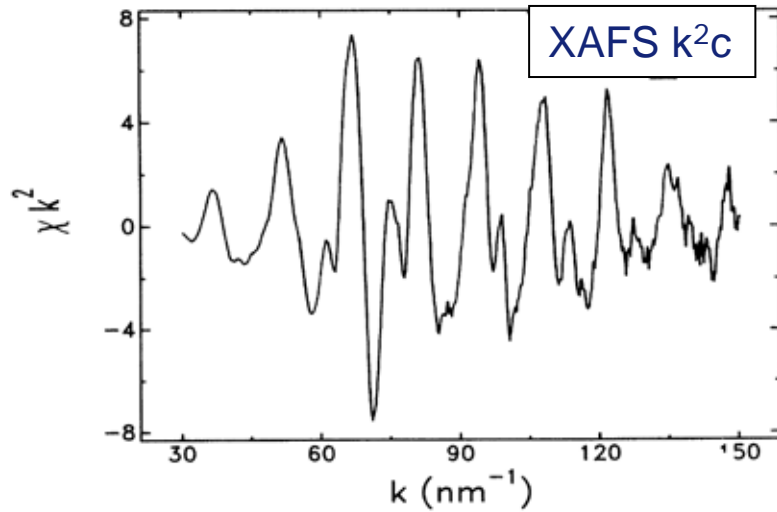
*Institut für Festkörperforschung, Forschungszentrum Jülich, D-5170 Jülich, Germany*

(Received 14 February 1991)

- systematic study of substitutional impurities in fcc and bcc metals
- important shifts in first shell bond length detected



# LATTICE DISTORTIONS AROUND IMPURITIES IN DILUTE ALLOYS

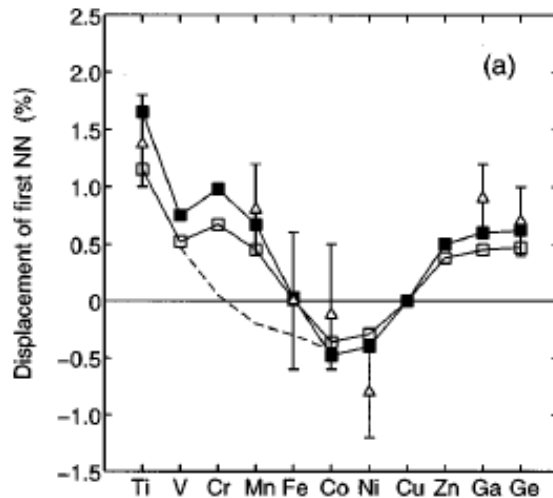


Mn shifts 12 Ni nearest neighbors outwards by:

$$0.023 \pm 0.004 \text{ \AA}$$

(1 % of distance)

## Comparison to band structure calculations



□ ■ Band structure calculations  
 △ XAS

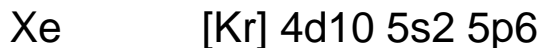
N. Papanikolaou et al., Phys. Rev. B 55, 4157 (1997)

Displacements  $d$  has two contributions:

- Valence difference** between impurity and host
  - change of charge density in impurity cell
  - parabolic dependence  $d(Z)$
- Magnetoelastic contribution** Cr, Mn, Fe in Cu → majority and minority bands are split
  - large magnetic moment
  - low DOS at Fermi level
  - low binding energy
  - increased interatomic distance

# CHEMISTRY OF XENON AT EXTREME CONDITIONS

Understand abundance of Xe in atmospheres of giant planets  
 Deficiency in Earth and Mars atmospheres



§ "Rare gases reluctant to form bonds"

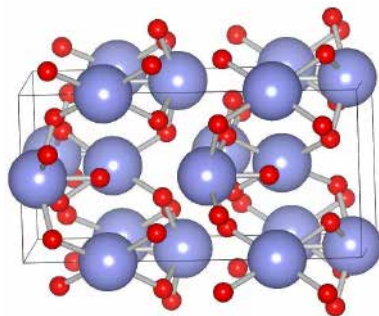
§ Xe oxides not stable at ambient P, T

§ Xe-O interactions at HP



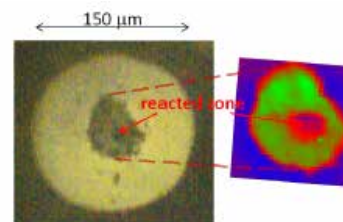
Stability of xenon oxides at high pressures

None of the predicted phases observed  
 XRD alone unable to determine oxide structure

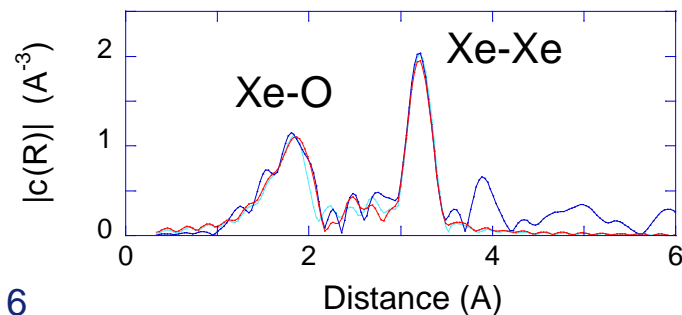
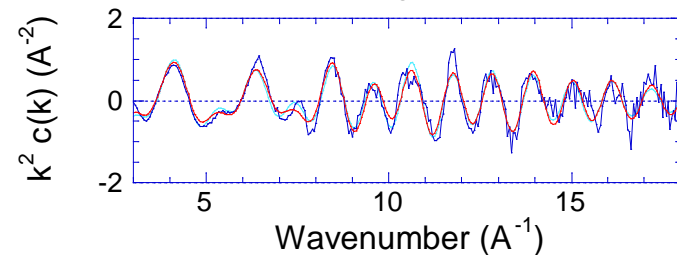
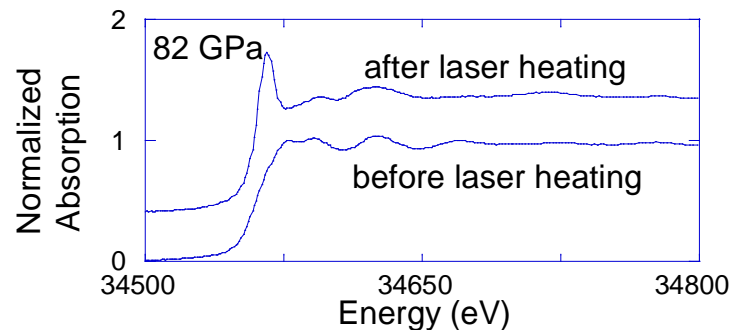


Xe2O5  
 P4/ncc space group

Dewaele Nature Chemistry 2016



BM23





## Web links

**International XAFS Society:** <http://ixs.iit.edu/>

**Tutorials and other Training Material:** <http://xafs.org/Tutorials>

à <http://gbxafs.iit.edu/training/tutorials.html>

### Software Resources EXAFS:

<http://xafs.org/Software>

<http://leonardo.phys.washington.edu/feff>

<http://gnxas.unicam.it/>

## Books and Review Articles

### Fundamentals of XAFS

Introduction to XAFS: A Practical Guide to X-ray Absorption Fine Structure Spectroscopy,  
G. Bunker, Cambridge University Press, 2012

X-ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS, and XANES, in Chemical Analysis, D. C. Koningsberger and R. Prins, ed., John Wiley & Sons, 1988

### Recent Review XAS XES:

X-Ray Absorption and X-Ray Emission Spectroscopy: Theory and Applications  
Copyright © 2016 John Wiley & Sons, Ltd  
Editor(s): Jeroen A. Van Bokhoven, Carlo Lamberti  
Published Online: 22 JAN 2016 09:48PM EST  
DOI: 10.1002/9781118844243

### ***FEFF***

*Theoretical approaches to x-ray absorption fine structure*

J. Rehr et al., Rev. Mod. Phys. 72, 621 - 654 (2000)

### **GNXAS**

*X-ray absorption spectroscopy and n-body distribution functions in condensed matter (I): theory of the GNXAS data-analysis method*

A. Filipponi, A. Di Cicco and C. R. Natoli, Phys. Rev. B 52, 15122 (1995)

### **MXAN**

*Geometrical fitting of experimental XANES spectra by a full multiple-scattering procedure*

M. Benfatto and S. Della Longa J. Synchr. Rad. 8, 1087 (2001)



## How to calculate $m$

energy density  $u$  carried by X-ray beam is:

$$u = \frac{e_0 E_0^2}{2} = \frac{e_0 \omega^2 A_0^2}{2}$$

linear absorption coefficient  $m$  measures the **energy density reduction** due to the interaction with the system of atoms:

$$m(\omega) = - \frac{1}{u} \frac{du}{dx}$$

$$m(\omega) = - \frac{2}{e_0 \omega^2 A_0^2} \frac{du}{dx}$$

$$m(\omega) = - \frac{2}{e_0 \omega^2 A_0^2} \frac{d}{dx} [h \omega n_{ph}]$$

$$m(\omega) = - \frac{2h}{e_0 \omega A_0^2} \frac{d}{dx} [n_{ph}]$$

$$m(\omega) = \frac{2h}{e_0 \omega A_0^2} n \dot{a}_f W_{if}$$

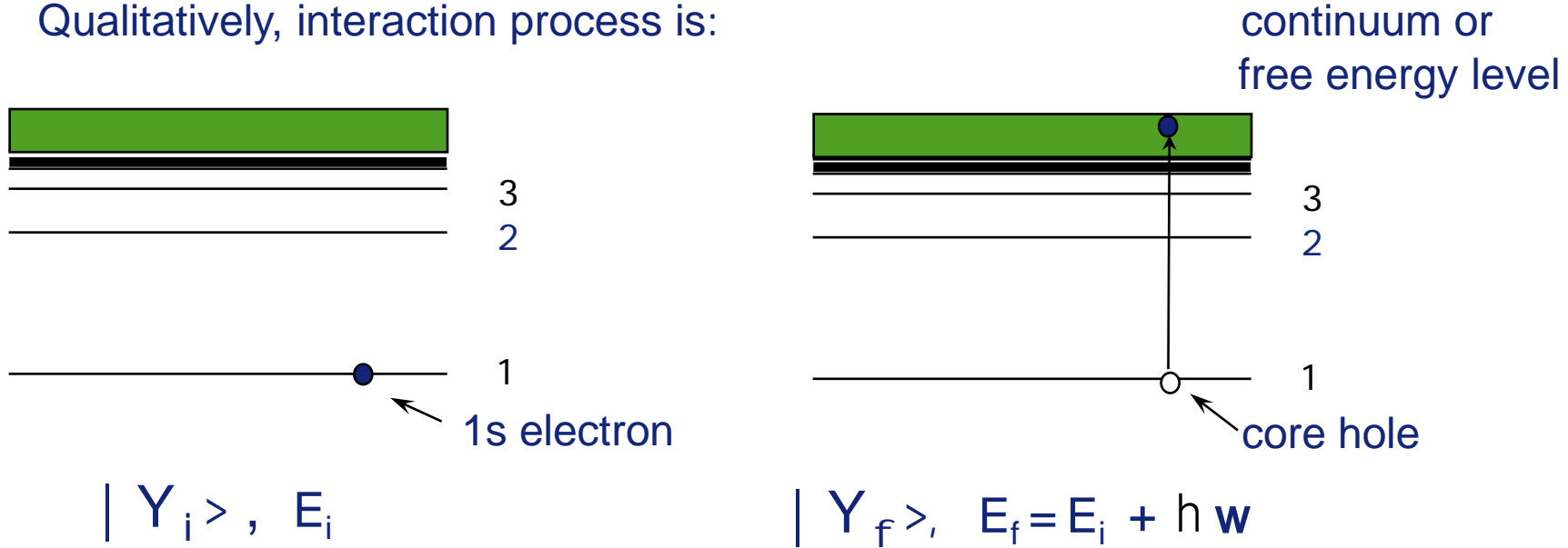
$n$  = atomic density  
 $W_{if}$  = transition probability

# X-ray Absorption

I. Lets consider the interaction between:  
**Monochromatic X-ray beam** ( $w = 2\pi\nu$ ) + **monoatomic sample**  
 EM field (classic) + atom (quantistic)  
 (semi-classical description)

II.  $m \sim m_{\text{photoelectric absorption}}$  for  $1 < E < 50 \text{ keV}$

III. Qualitatively, interaction process is:



# Transition probability: Golden Rule

$m(\omega)$  depends on:

- atomic density  $n$
- transition probability  $W_{if}$  of atom from  $|Y_i\rangle$  to  $|Y_f\rangle$

$$m(\omega) = \frac{2\hbar}{e_0 \omega A_0^2} n \mathbf{a}_f W_{if} \quad (1)$$

**time-dependent perturbation theory** (power series of EM field - atom interaction potential)

The interaction is in general **WEAK**: can limit series to 1st order: **Golden Rule**

$$W_{if} = \frac{2\rho}{\hbar} \left| \langle Y_f | \hat{H}_I | Y_i \rangle \right|^2 r(E_f) \quad (2)$$

$\hat{H}_I$

EM field - atom interaction hamiltonian operator

$\langle Y_f | \hat{H}_I | Y_i \rangle$

Matrix element of  $H_I$  between initial and final state

$r(E_f)$

Density of final states, compatible with energy conservation:  $E_f = E_i + \hbar\omega$

I the interaction hamiltonian for photoelectric absorption (see Appendix 1) is (to 1<sup>st</sup> order):

$$\hat{H}_I = ih \frac{e}{m} \dot{\mathbf{a}}_j^r A(r_j^r) \times \mathbf{N}_j^l \quad (3)$$

where  $\dot{A}(r_j^r) = A_0 \hat{\mathbf{e}} e^{ik \cdot r_j^r}$

I the transition probability for photoelectric absorption of a monochromatic, polarized and collimated photon beam is [(3) into (2)]:

$$W_{if} = \frac{\rho h e^2}{m^2} |A_0|^2 \left| \left\langle Y_f \left| \dot{\mathbf{a}}_j^r e^{ik \cdot r_j^r} \hat{\mathbf{e}} \times \mathbf{N}_j^l \right| Y_i \right\rangle \right|^2 r(E_f) \quad (4)$$

## Dipole approximation

further simplification:

$$e^{i\mathbf{k} \cdot \mathbf{r}_j} = 1 + i\mathbf{k} \cdot \mathbf{r}_j - \frac{(\mathbf{k} \cdot \mathbf{r}_j)^2}{2!} \ll 1 \quad \text{if} \quad |\mathbf{k} \cdot \mathbf{r}_j|^2 \ll 1$$

transition probability in dipole approximation:

$$W_{if} = \frac{\rho h e^2}{m^2} |A_0|^2 \left| \langle Y_f | \hat{\mathbf{a}} \cdot \hat{\mathbf{e}} \cdot \mathbf{r}_j | Y_i \rangle \right|^2 r(E_f)$$

alternative and equivalent expression (see Appendix 2):

$$W_{if} = \frac{\rho e^2 \omega^2}{h} |A_0|^2 \left| \langle Y_f | \hat{\mathbf{a}} \cdot \hat{\mathbf{e}} \cdot \mathbf{r}_j | Y_i \rangle \right|^2 r(E_f) \quad (5)$$

finally one gets [(5) into (1)]:

$$m(\omega) = \frac{2 \rho e^2 \omega}{e_0} n \left| \langle Y_f | \hat{\mathbf{a}} \cdot \hat{\mathbf{e}} \cdot \mathbf{r}_j | Y_i \rangle \right|^2 r(E_f) \quad (6)$$



$$m(\omega) = \frac{2 p e^2 \omega}{e_0} n_f \dot{\mathbf{a}}_f \left| \left\langle Y_f \left| \dot{\mathbf{a}}_j \hat{\mathbf{e}} \times \mathbf{r}_j \right| Y_i \right\rangle \right|^2 r(E_f)$$

I if  $|Y_i\rangle$  and  $|Y_f\rangle$  are known (if wavefunctions and energies can be calculated):

- 1) calculate  $W_{if}$
- 2) calculate  $m(\omega)$

I in practice, one is interested in inverse process:

- 1) measure  $m(\omega)$
- 2) extract EXAFS
- 3) obtain information on local structure through  $|Y_f\rangle$

I but, to obtain structural info, one still needs to calculate  $|Y_i\rangle$  and  $|Y_f\rangle$  or at least be able to express their structural properties in parametric form

$|Y_i\rangle$  relatively easy  $\hat{=}$  ground state of atom

$|Y_f\rangle$  in general very complicated  $\hat{=}$  in principle, all electrons are involved (multi body process, final state strongly influenced by environment)

# Single electron approximation

large part of  $m$  due to **elastic** transitions:

- only 1 electron out of  $N$  modifies its state: leaves its deep core level
- all other  $N-1$  “passive” electrons relax their orbitals to adapt to the new potential created by presence of core hole

remaining part of  $m$  due to **inelastic** transitions:

- **primary excitation** of core electron **provokes successive excitations** of other (external) electrons (shake up, shake off processes)
- excess energy distributed among all excited electrons

$$m(w) = m_{el}(w) + m_{inel}(w)$$

where 
$$m_{el}(w) \propto \left| \left\langle \left\langle Y_f^{N-1} y_f \right| \hat{e} \times \frac{\mathbf{r}}{r} \left| Y_i^{N-1} y_i \right\rangle \right\rangle^2 r(e_f)$$

$Y_i^{N-1}$  Slater determinant of “passive” electrons’ wavefunctions

$y, r, e_f$  Wavefunction, position vector, final energy of “active” electron

## “Sudden” approximation and overlap factor

If photoelectron energy is sufficiently high ( $E > \text{few } 10 \text{ eV}$  above edge)

§ time to exit atom  $\ll$  relaxation time of passive electrons

§ its state not influenced by passive electrons relaxation

$$m_{el}(w) \approx \mu S_0^2 \left| \langle \mathbf{y}_f | \hat{\mathbf{e}} \times \mathbf{r} | \mathbf{y}_i \rangle \right|^2 r(e_f) \quad (7)$$

where

$$S_0^2 = \left| \langle \mathbf{Y}_f^{N-1} | | \mathbf{Y}_i^{N-1} \rangle \right|^2 \quad (S_0^2 \sim 0.7 - 1.0)$$

à Allows to reduce interpretation of EXAFS to the calculation of the final state of **ONLY** the photoelectron

$$m(\omega) \gg \frac{a}{f} \left| \langle y_i | \hat{\epsilon} \cdot \mathbf{r} | y_f \rangle \right|^2$$



dipole operator

$$P_{\alpha}^q = \boldsymbol{\epsilon} \cdot \mathbf{r} = \boldsymbol{\epsilon}_{\alpha}^q \cdot \mathbf{r}$$

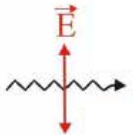
$a = x, y, z$       X-ray prop direction  
 $q = +1, 0, -1$       polarization states  
 (qh photon angular momentum)

electron position vector       $\mathbf{r} = x\mathbf{e}_x + y\mathbf{e}_y + z\mathbf{e}_z$

photon  
polarization  
vectors

$$\boldsymbol{\epsilon}_x^0 = \boldsymbol{\epsilon}_x = \mathbf{e}_x \quad \boldsymbol{\epsilon}_y^0 = \boldsymbol{\epsilon}_y = \mathbf{e}_y \quad \boldsymbol{\epsilon}_z^0 = \boldsymbol{\epsilon}_z = \mathbf{e}_z \quad \text{linear polarization}$$

$$\boldsymbol{\epsilon}_z^{\pm} = \mp \frac{1}{\sqrt{2}} (\boldsymbol{\epsilon}_x \pm i\boldsymbol{\epsilon}_y) \quad \text{circular polarization with } \mathbf{k} // z$$



dipole operator in terms of  
spherical harmonics

$$P_z^{\pm} = \boldsymbol{\epsilon}_z^{\pm} \cdot \mathbf{r} = \mp \frac{1}{\sqrt{2}} (x \pm iy) = r \sqrt{\frac{4\pi}{3}} Y_{1,\pm 1}$$

$$P_z^0 = \boldsymbol{\epsilon}_z \cdot \mathbf{r} = z = r \sqrt{\frac{4\pi}{3}} Y_{1,0}$$

$$m(\omega) \gg \frac{\hbar}{f} \left| \langle \psi_f | \hat{e} \cdot \mathbf{r} | \psi_i \rangle \right|^2$$



$$\underbrace{\delta(m'_s, m_s)}_{\text{spin}} \underbrace{\langle R_{n',l}(r) | r | R_{n,c}(r) \rangle}_{\text{radial}} \underbrace{\sum_{m_c, m_l, p} e_{\alpha,p}^q \langle l, m_l | C_p^{(1)} | c, m_c \rangle}_{\text{angular}}$$

matrix elements factor into spin, radial and angular parts

By looking at the non-zero matrix elements we get the **dipole selection rules**

$$\begin{aligned} \Delta l &= l' - l = \pm 1, \\ \Delta m_l &= m'_l - m_l = q = 0, \pm 1, \\ \Delta s &= s' - s = 0, \\ \Delta m_s &= m'_s - m_s = 0. \end{aligned}$$

where  $q\hbar$  is the X-ray angular momentum

## Appendix 1: Interaction Hamiltonian

- EM field (E, B) described by Coulomb Gauge:

$$\nabla \cdot A = 0$$

$$A(r,t) : \quad \begin{array}{l} A_{\perp}(r,t) \neq 0 \\ A_{//}(r,t) = 0 \end{array}$$

- Atom described by charged particles  $\alpha$ :

$$\begin{array}{l} m_{\alpha}, q_{\alpha} \\ r_{\alpha}, p_{\alpha} \end{array} \rightarrow \frac{\hbar}{i} \nabla_{\alpha}$$

- Total Hamiltonian:

$$H = \sum_{\alpha} \frac{1}{2m_{\alpha}} [p_{\alpha} - q_{\alpha} A(r_{\alpha})]^2 - \sum_{\alpha} \frac{g_{\alpha} q_{\alpha}}{m_{\alpha}} S_{\alpha} \cdot B(r_{\alpha}) + V_{Coul} + H_{rad}$$

(1)
(2)
(3)
(4)

A<sub>1</sub>: Total hamiltonian terms

(1) Kinetic energy  $\sum_{\alpha} \frac{1}{2m_{\alpha}} [p_{\alpha} - q_{\alpha} A(r_{\alpha})]^2 = \sum_{\alpha} \frac{1}{2} m_{\alpha} \dot{r}_{\alpha}^2$

$$\dot{r}_{\alpha} = \frac{1}{i\hbar} [r_{\alpha}, H] = \frac{\partial H}{\partial p_{\alpha}} = \frac{1}{m_{\alpha}} [p_{\alpha} - q_{\alpha} A(r_{\alpha})]$$

(2) Magnetic term  $\sum_{\alpha} \frac{g_{\alpha} q_{\alpha}}{m_{\alpha}} S_{\alpha} \cdot B(r_{\alpha})$

(3) Coulomb energy between pairs of charged particles  $V_{Coul}$

(4) Transverse field energy density  $H_{rad}$

A<sub>1</sub>: Interaction terms

$$H = H_0 + H_I = H_{particles} + H_{Rad} + H_I$$

$$H_0 = H_{particles} + H_{rad} = \sum_{\alpha} \frac{p_{\alpha}^2}{2m_{\alpha}} + V_{Coul} + H_{rad}$$

well defined eigenstates  
valid for atoms, molecules,  
solids

$$H_I = - \sum_{\alpha} \left[ \frac{q_{\alpha}}{m_{\alpha}} p_{\alpha} A(r_{\alpha}) \right] - \sum_{\alpha} \left[ \frac{g_{\alpha} q_{\alpha}}{m_{\alpha}} S_{\alpha} B(r_{\alpha}) \right] + \sum_{\alpha} \left[ \frac{q_{\alpha}^2}{2m_{\alpha}} A^2(r_{\alpha}) \right]$$

 $H_{I1}$ 
 $H_{I2}^{spin}$ 
 $H_{I2}$ 

linear in A: photon creation  
or absorption

quadratic in A: scattering  
(one photon in, one photon out)



A<sub>1</sub>: Orders of magnitude

$$\frac{H_{I2}}{H_{I1}} = \frac{\frac{q^2 A^2}{m}}{\frac{q A p}{m}} = \frac{q A p}{p^2} \approx \frac{H_{I1}}{H_{particles}} \ll 1$$

intensity of X-ray source weak

spin order of magnitude

$$B = \nabla \times A, \quad |B| = ik A$$

$$\frac{H_{I2}^{spin}}{H_{I1}} = \frac{\frac{q}{m} h k A}{\frac{q}{m} p A} \approx \frac{a_0(1s)}{\lambda} \ll 1$$

X-ray photon ( $\lambda \sim 1\text{\AA}$ ) interacts  
with core electron, with  
wavefunction highly concentrated  
close to nuclei

Appendix 2

$$\begin{cases} -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \Psi_2^* = E_2 \Psi_2^* \\ -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \Psi_1 = E_1 \Psi_1 \end{cases}$$

$$\begin{cases} x \Psi_1 \times \left[ -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \Psi_2^* = E_2 \Psi_2^* \right] \\ x \Psi_2^* \times \left[ -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \Psi_1 = E_1 \Psi_1 \right] \end{cases}$$

$$-\frac{\hbar^2}{2m} \int_{-\infty}^{+\infty} \left[ x \Psi_1 \frac{d^2}{dx^2} \Psi_2^* - x \Psi_2^* \frac{d^2}{dx^2} \Psi_1 \right] dx = (E_2 - E_1) \int_{-\infty}^{+\infty} [\Psi_2^* x \Psi_1] dx$$

## Appendix 2 cont

$$\int_{-\infty}^{+\infty} \left[ x \Psi_1 \frac{d^2}{dx^2} \Psi_2^* - x \Psi_2^* \frac{d^2}{dx^2} \Psi_1 \right] dx = -\frac{2m}{\hbar^2} (E_2 - E_1) \int_{-\infty}^{+\infty} [\Psi_2^* x \Psi_1] dx$$

(1)                      (2)

$$(1) \quad \int_{-\infty}^{+\infty} \left[ x \Psi_1 \frac{d^2}{dx^2} \Psi_2^* \right] dx = \left[ x \cancel{\Psi_1} \frac{d}{dx} \cancel{\Psi_2^*} \right]_{-\infty}^{+\infty} - \int_{-\infty}^{+\infty} \left[ \Psi_1 \frac{d}{dx} \Psi_2^* \right] dx$$

$$(2) \quad \int_{-\infty}^{+\infty} \left[ x \Psi_2^* \frac{d^2}{dx^2} \Psi_1 \right] dx = \left[ x \cancel{\Psi_2^*} \frac{d}{dx} \cancel{\Psi_1} \right]_{-\infty}^{+\infty} - \int_{-\infty}^{+\infty} \left[ \Psi_2^* \frac{d}{dx} \Psi_1 \right] dx$$

$$\left( - \int_{-\infty}^{+\infty} \left[ \Psi_1 \frac{d}{dx} \Psi_2^* \right] dx \right) - \left( \int_{-\infty}^{+\infty} \left[ \Psi_2^* \frac{d}{dx} \Psi_1 \right] dx \right) = -\frac{2m}{\hbar^2} (E_2 - E_1) \int_{-\infty}^{+\infty} [\Psi_2^* x \Psi_1] dx$$

$$\begin{aligned} & \swarrow \\ & = \left[ \cancel{\Psi_1} \cancel{\Psi_2^*} \right]_{-\infty}^{+\infty} - \left( \int_{-\infty}^{+\infty} \left[ \Psi_2^* \frac{d}{dx} \Psi_1 \right] dx \right) \end{aligned}$$

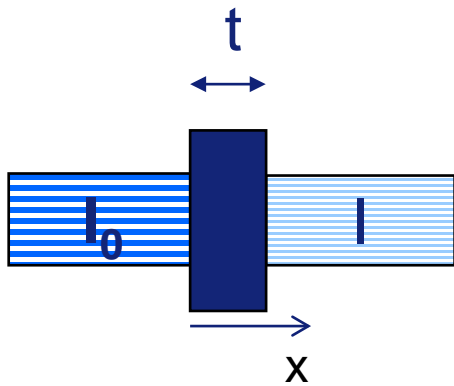
Appendix 2 cont

$$2 \left( \int_{-\infty}^{+\infty} \Psi_2^* \frac{d}{dx} \Psi_1 dx \right) = -\frac{2m}{\hbar^2} (E_2 - E_1) \int_{-\infty}^{+\infty} [\Psi_2^* x \Psi_1] dx$$

$$\int_{-\infty}^{+\infty} \left[ \Psi_2^* \frac{d}{dx} \Psi_1 \right] dx = -\frac{m}{\hbar^2} (E_2 - E_1) \int_{-\infty}^{+\infty} [\Psi_2^* x \Psi_1] dx$$

$$\int_{-\infty}^{+\infty} \left[ \Psi_2^* \frac{d}{dx} \Psi_1 \right] dx = -\frac{m\omega}{\hbar} \int_{-\infty}^{+\infty} [\Psi_2^* x \Psi_1] dx$$

# The absorption coefficient $m$



$$- dl = I(x) N \frac{dx}{t} s_a$$

$\swarrow$   $\searrow$   
 $at/cm^2$        $cm^2/at$

$$- \int_0^t \frac{dl}{I(x)} = N \frac{s_a}{t} \int_0^t dx$$

$$\ln I(t) - \ln I(0) = -Ns_a$$

$$\frac{I(t)}{I(0)} = e^{-Ns_a} = e^{-mt}$$

$$\frac{I(t)}{I(0)} = e^{-Ns_a} = e^{-mt}$$

§ mis related to the atomic cross section:

$$m(w) = s_a(w) \frac{N}{t} = s_a(w) \frac{N_a}{A} r \quad \frac{\text{cm}^2}{\text{g}} \frac{\text{mole}}{\text{cm}^3} = [\text{cm}^{-1}]$$

- in general you find tabulated the mass absorption coefficient  $m/r$  :

$$\frac{m}{r} = s_a \frac{N_a}{A} \quad \frac{\text{cm}^2}{\text{g}} \frac{\text{mole}}{\text{cm}^3} = \frac{\text{cm}^2}{\text{g}}$$

- for a generic sample  $P_x Q_y \dots$ :

$$\frac{\mu_{\text{tot}}}{\rho} = x \frac{\mu_p}{\rho_p} \frac{A_p}{M} + y \frac{\mu_q}{\rho_q} \frac{A_q}{M} + K$$

# Recipe for calculating t for transmission XAS

$$\frac{I(t)}{I(0)} = e^{-Ns_a} = e^{-mt}$$

1. Total absorption above the edge must not be too high:

$$m_{\text{above edge}} t = 2 \text{ à } 5$$

$$I / I_0 \sim 0.14 \text{ à } 0.007$$

ideally

$$m_{\text{above edge}} t = 2-3$$

2. Contrast at edge must be as large as possible:

$$[ m_{\text{above edge}} - m_{\text{below edge}} ] t > 0.1$$

ideally

$$[ m_{\text{above edge}} - m_{\text{below edge}} ] t = 1$$

If absorber is very dilute, and matrix absorbs a lot, then this is not possible à  
fluorescence detection