EXAFS

Extended X-Ray Absorption Fine Structure

EXAFS

5th School on X-Ray Spectroscopy Methods

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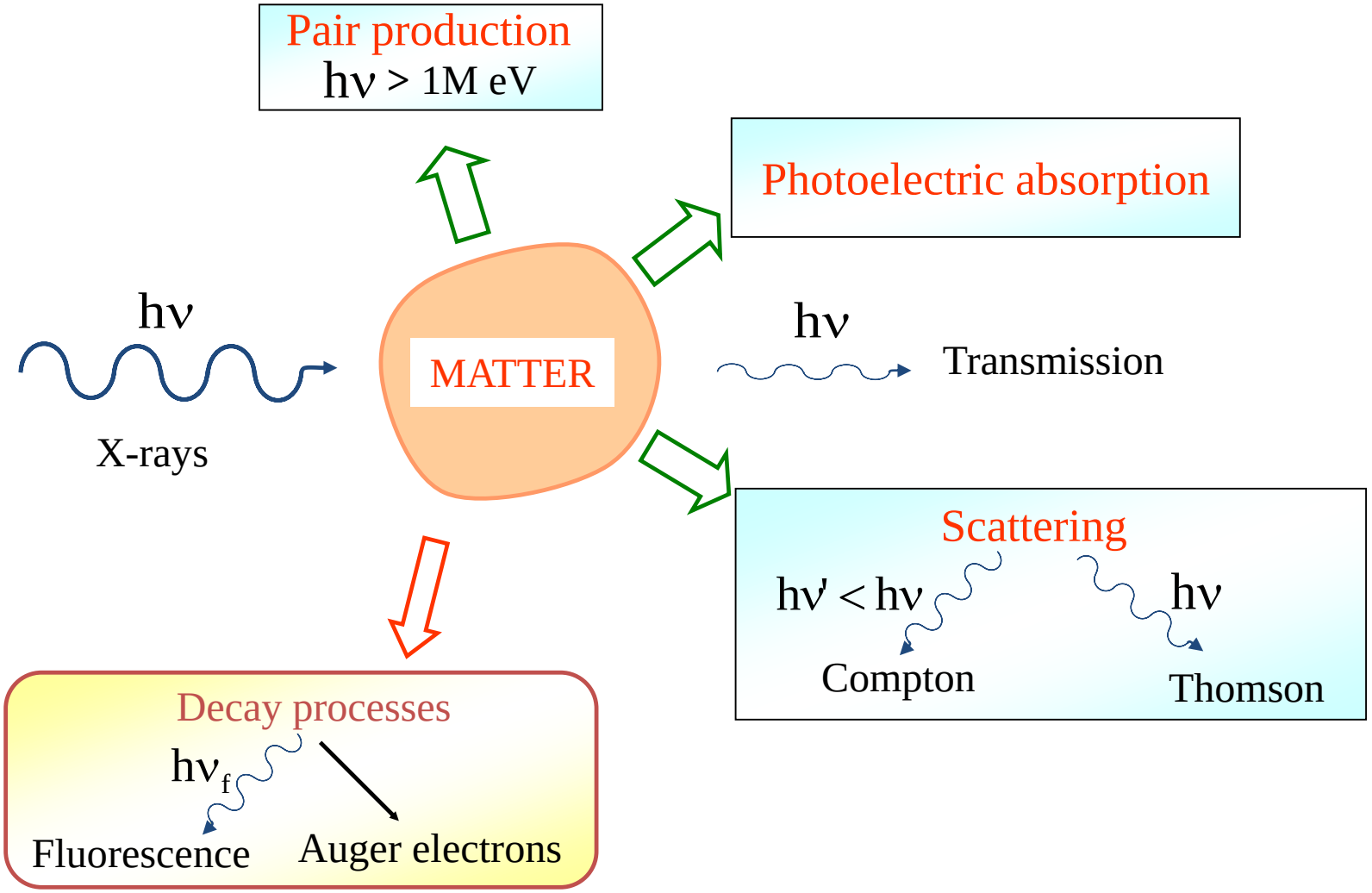
Overview

1. Interaction of X-rays with matter
2. Basics aspects about XAFS
3. Understanding the EXAFS equation

Interaction of X-rays with matter

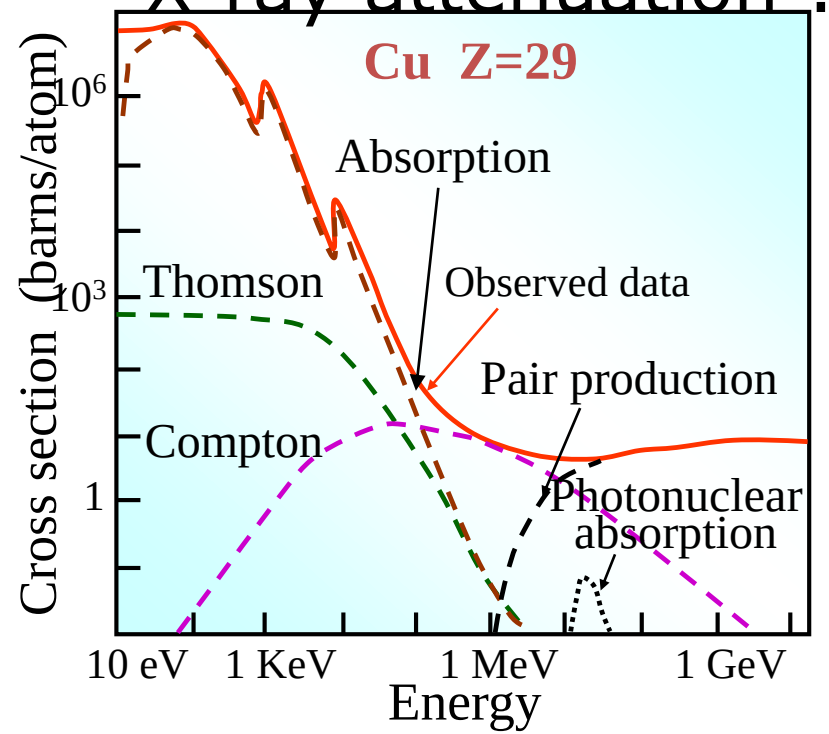


Primary competing processes and some radiative and non-radiative decay processes

Interaction of X-rays with matter

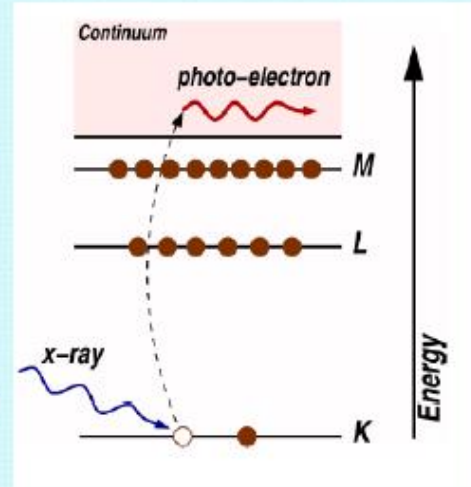
X-ray attenuation :

Photoelectric effect is the dominating process at the x-ray energy range (200-100 keV)



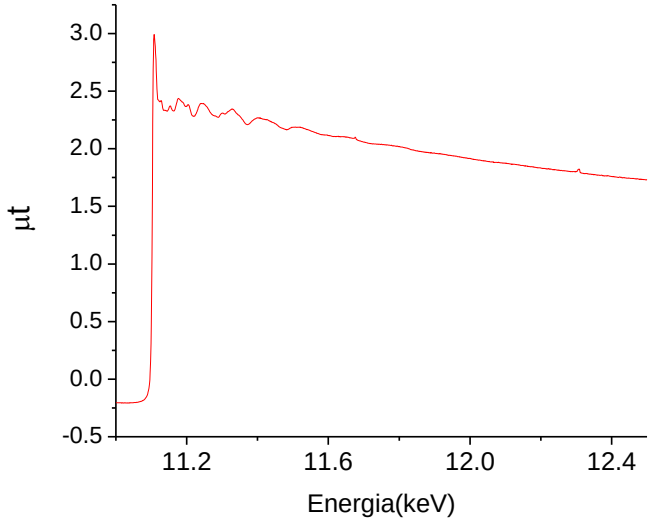
X-rays are absorbed predominantly from the photo-electric effect in the range of energies ranging from 200 eV to 100 keV;

- ✓ **X-ray absorption by an atom by photoelectric effect: absorption edge;**
- ✓ **An excited state with a hole ("core hole") is created;**
- ✓ **The excess energy of X-rays is transferred to the ejected photoelectron.**



Basics aspects about XAFS

- What is XAFS?
  - XAFS studies the details of the x-ray absorption coefficient around an absorption edge.
  - It reveals a wealth of information regarding the geometric and electronic structure of materials.

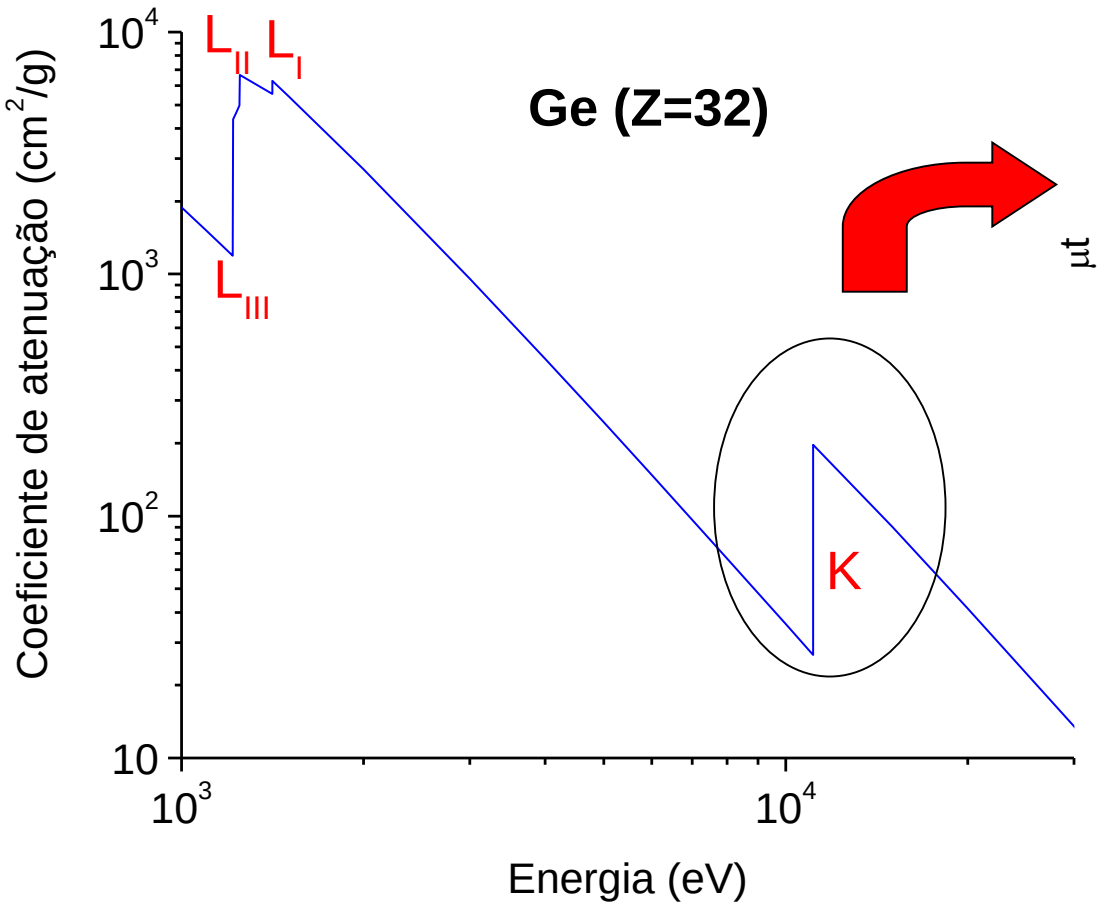


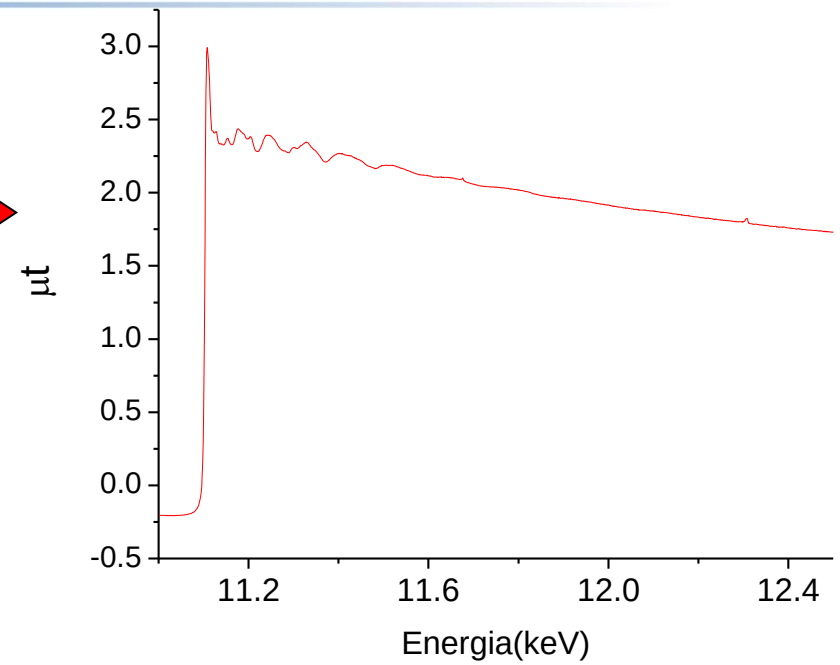
Basics aspects about XAFS

Main characteristics of XAS technique

- Most atoms of the periodic table can be studied;
- Selectivity at the atomic level;
- Sensitive to oxidation state, coordination number and interatomic distance kind of atom;
- Structure of amorphous and crystalline materials and highly diluted systems;
- Solids, liquids and gases can have their specific local structure.
- Different environments (pressure, temperature, magnetic field, gas ...)
- Limitations ....
- We can not distinguish neighboring atoms in the periodic table;
- Only the local order can be precisely determined;
- A source of X-ray wavelength variable is required.

Basics aspects about XAFS





Absorption edges

K	$1s \rightarrow p$
L_1	$2s \rightarrow p$
L_2	$2p_{1/2} \rightarrow s, d$
L_3	$2p_{3/2} \rightarrow s, d$

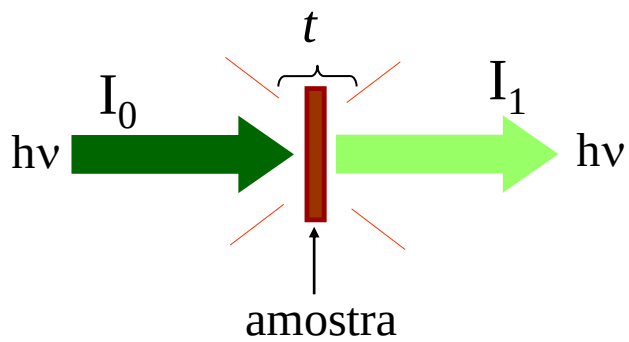
XAFS: Study the details of the variation on the absorption coefficient (fine structure) after the edge.

Basics aspects about XAFS

X-ray attenuation

Absorption coefficient:

$$\mathrm{d}I = -\mu I \mathrm{d}t$$



$$I_1 = I_0 \exp(-\mu t)$$

μ : linear absorption coefficient

t : thickness

μt: absorbance

Includes contributions from all scattering and absorption precesses

Mass absorpion coefficient:

$$\frac{\mu}{\rho} = \sum_j g_j \left(\frac{\mu}{\rho}\right)_j$$

units (cm^2/g)

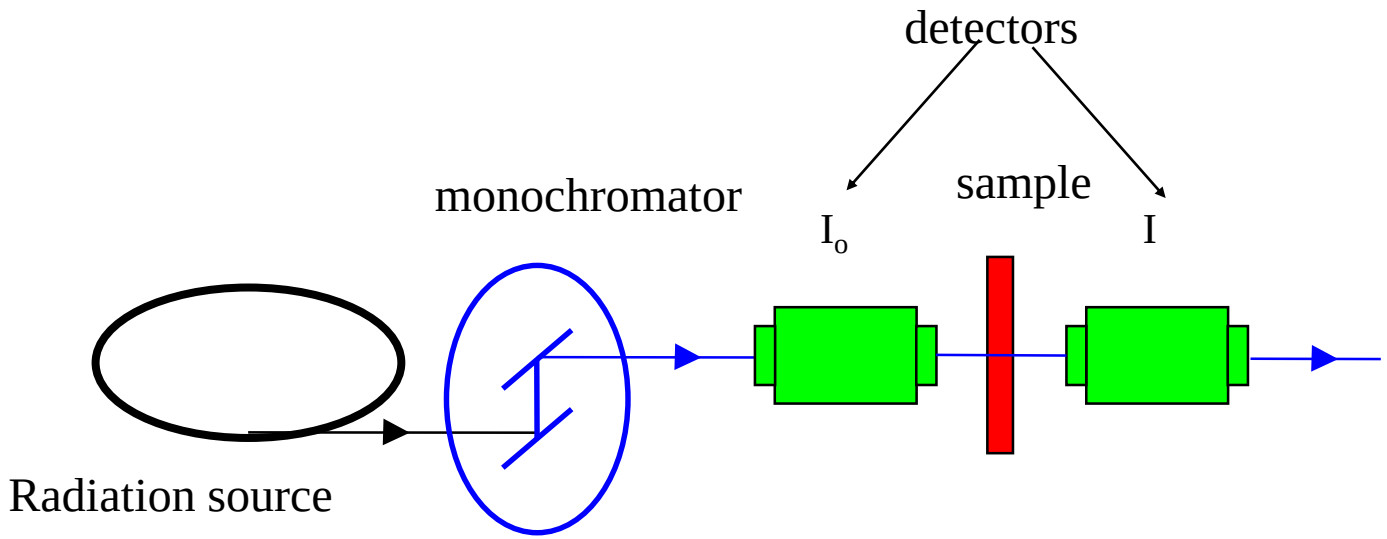
Mass fraction of el. *j*

Atomic absorption coefficient:

$$\mu_j^a = \left(\frac{\mu}{\rho}\right)_j \left[A_j / N \right]$$

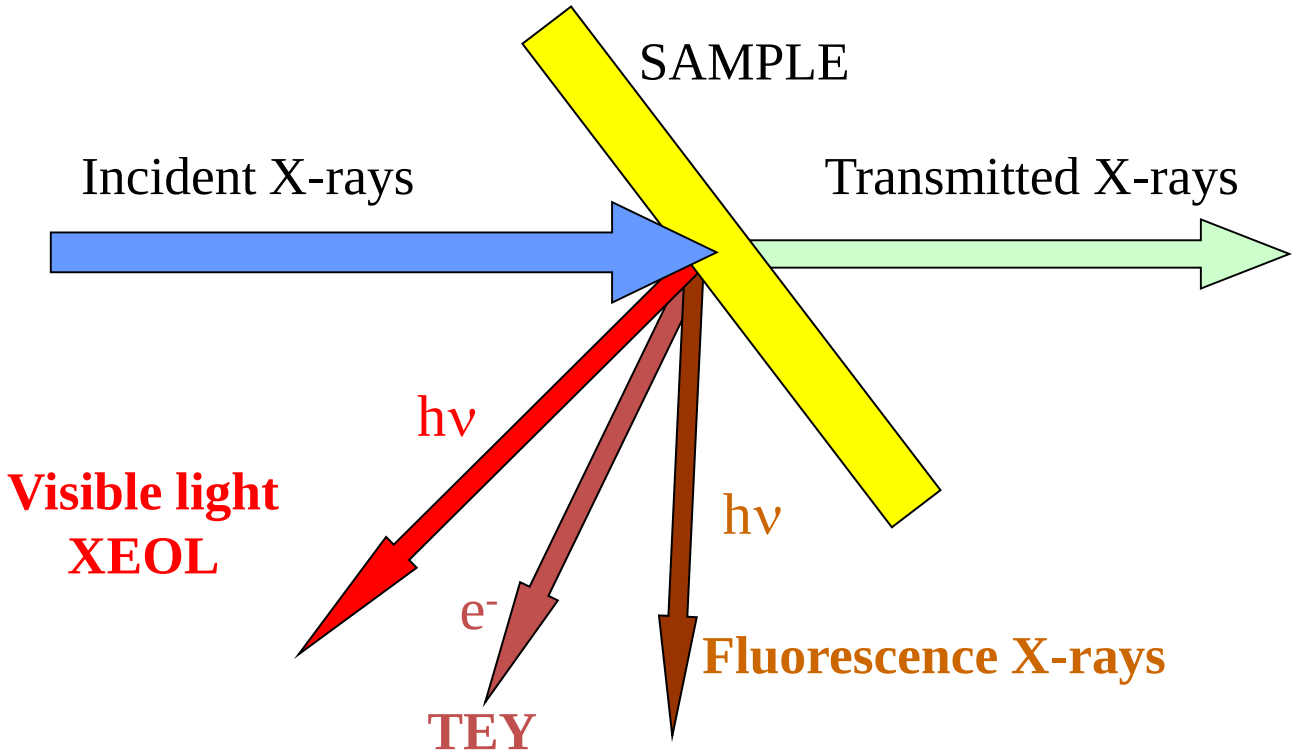
Units: $10^{-24} cm^2$ (1 barn)

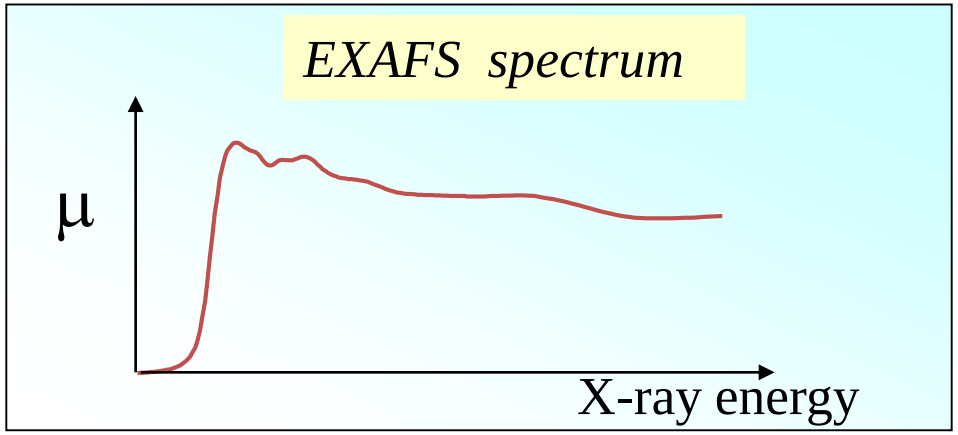
Basic XAFS experiment – sequential mode



$$\mu t = \log\left(\frac{I_0}{I_1}\right)$$

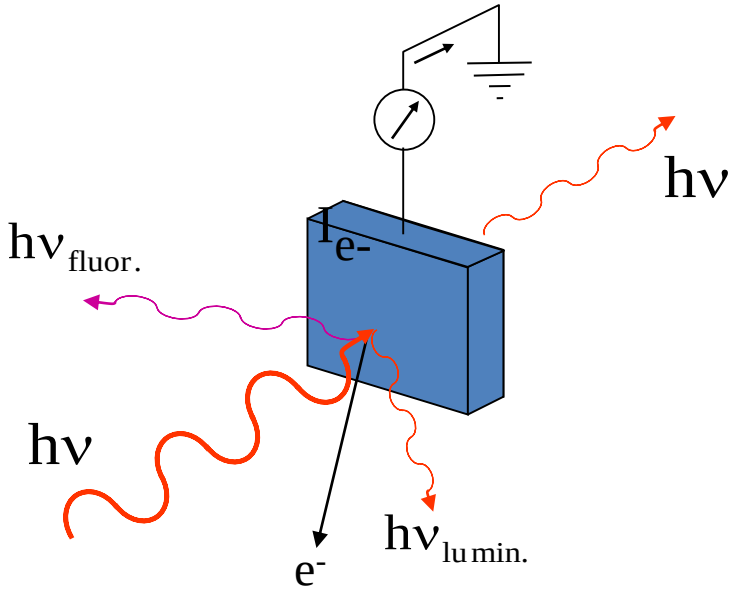
Basics aspects about EXAFS





Basics aspects about XAFS

Which method for which application?



The most important criterion:
The best signal to noise ratio for the element of interest

Always transmission, if possible
Most accurate method, best overall S/N counting statistics of about 10^{-4} from beamlines with more than 10^{8} photons/s)

Fluorescence for very diluted samples
A specific signal reduces the large background (but maximum tolerable detector count-rate can result in very long measuring times).

Total electron yield (TEY)
for surface sensitivity and surface XAFS (adsorbates on surfaces)
TEY for thick samples that cannot be made uniform.

XEOL X-ray excited optical luminescence
VIS/UV detection from luminescent samples

Basics aspects about XAFS

X-ray Absorption Near Edge Strucuture

XAFS = XANES + EXAFS

Extended X-ray Absorption Fine Strucuture

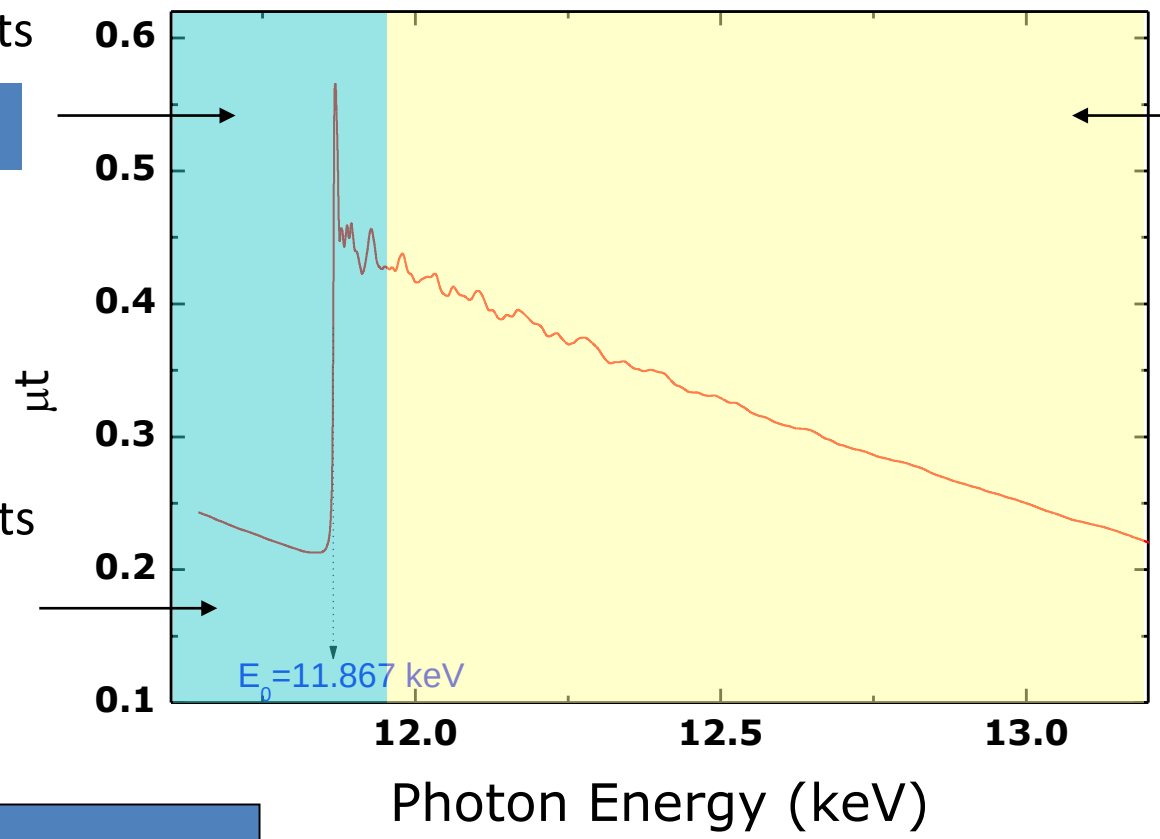
InAs - As *K*-Edge

high Z elements

XANES

low Z elements

NEXAFS



EXAFS

Near Edge X-ray Absorption Fine Strucuture

XANES is the region ~50 eV around the edge

Basics aspects about XAFS

XANES : *transitions to unoccupied states (localized and continuum)*

low energy photoelectron → multiple scattering (MS)

Information content

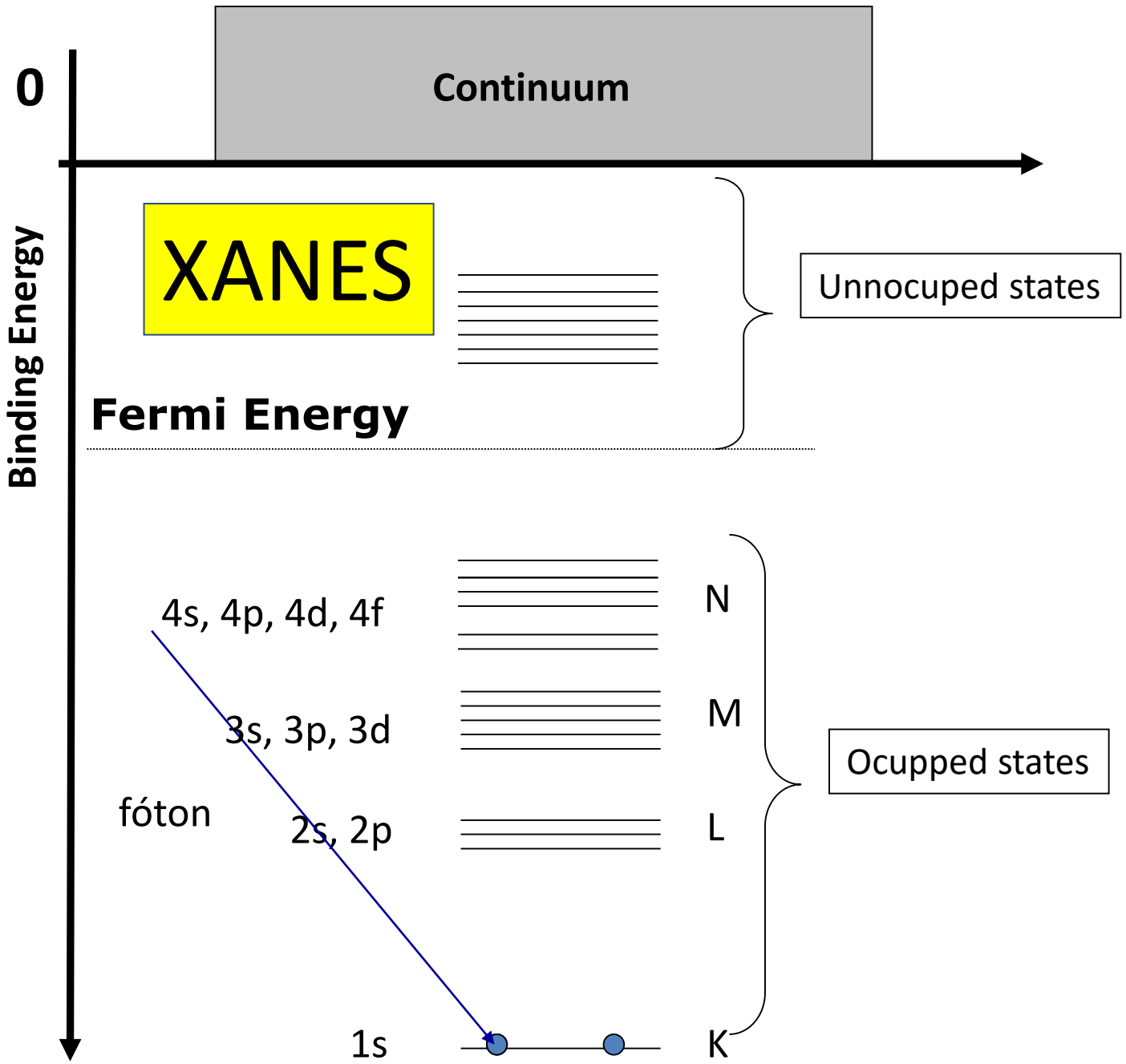
- Fermi energy
- Projected density of unoccupied states
- Oxidation states
- Coordination symmetry

EXAFS: *high energy photoelectron → single scattering + some important MS*

Information content

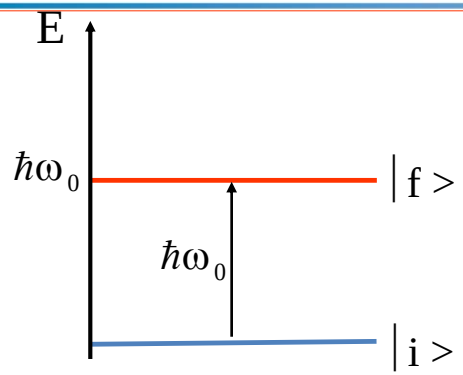
- interatomic distances
- disorder
- coordination numbes
- Bond-angle distributions
- Partial pair distribution
- Vibrational properties.

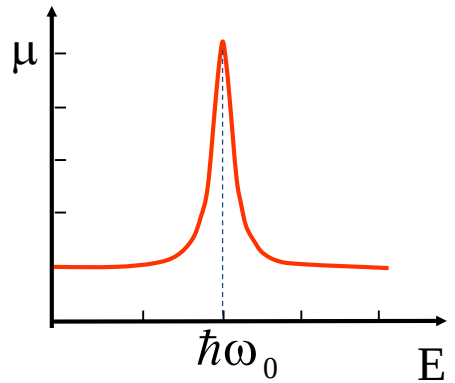
Basics aspects about XAFS

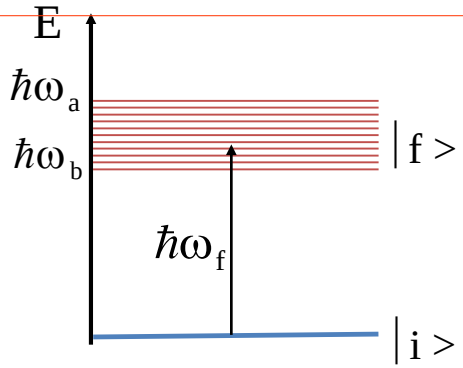


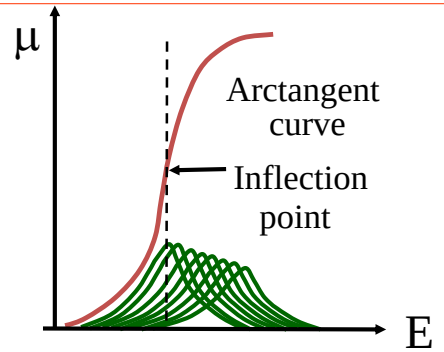
XANES: pre edge structure

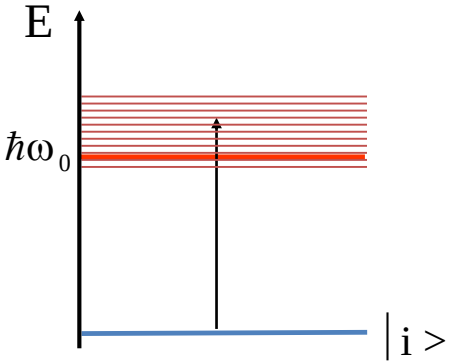
Fermi Golden rule

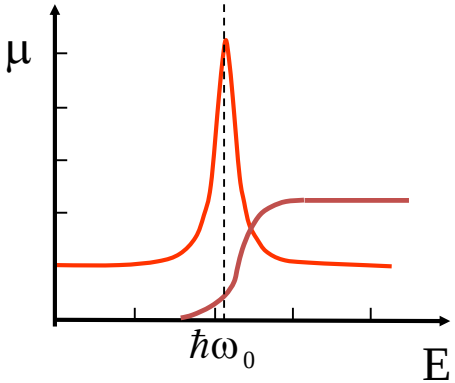




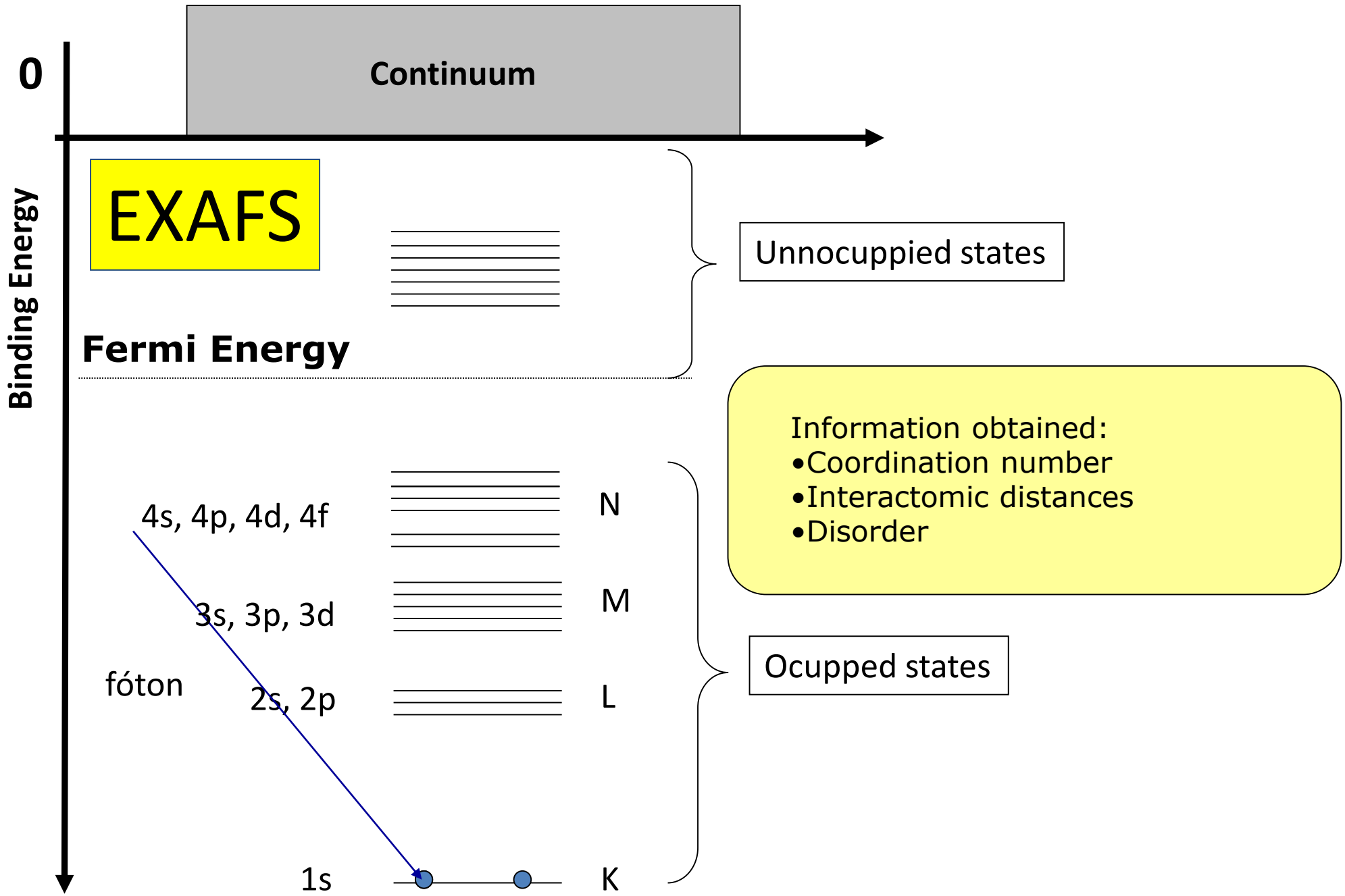






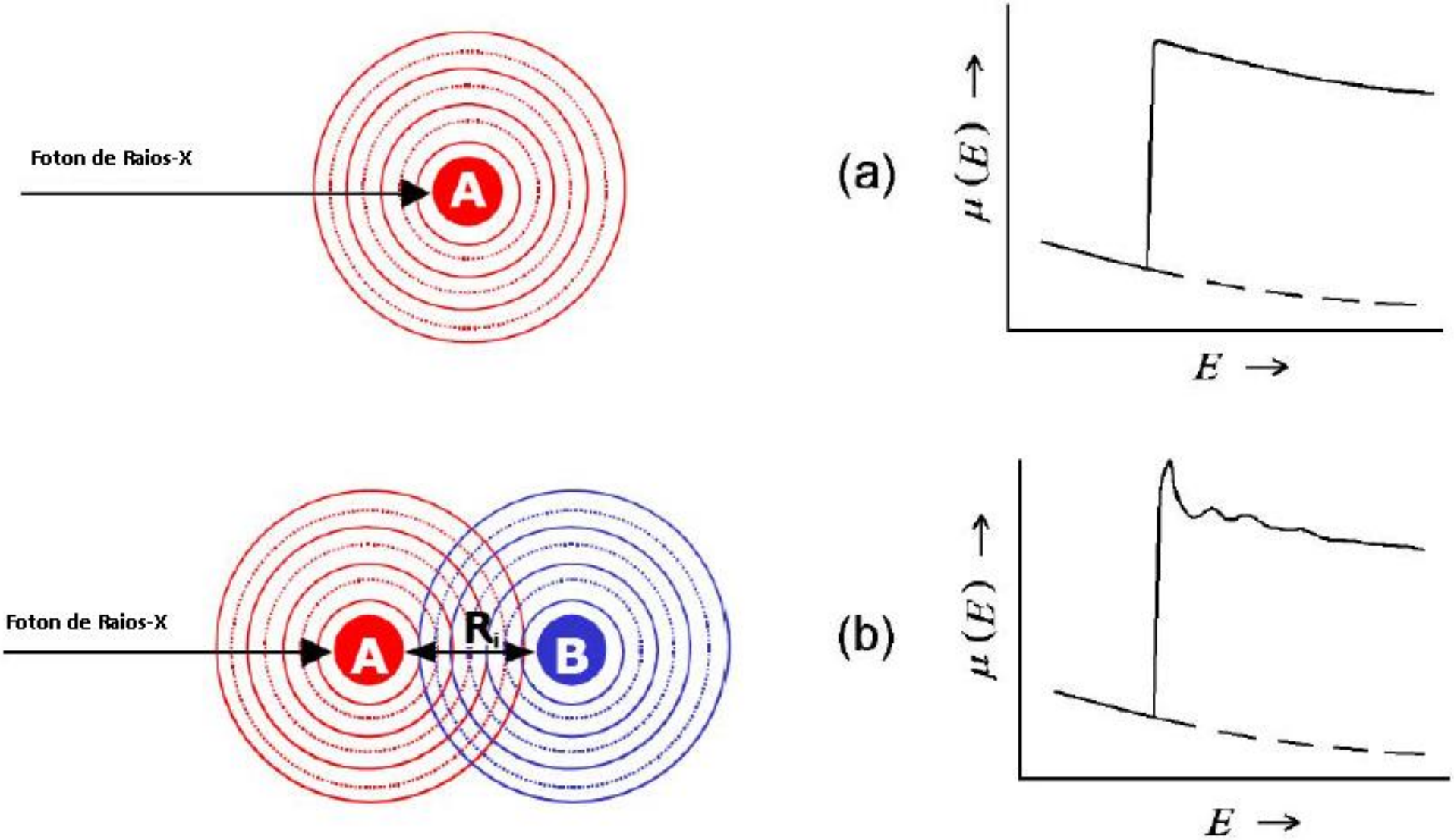


Basics aspects about XAFS



Information obtained:
- Coordination number
- Interactomic distances
- Disorder

Basics aspects about XAFS

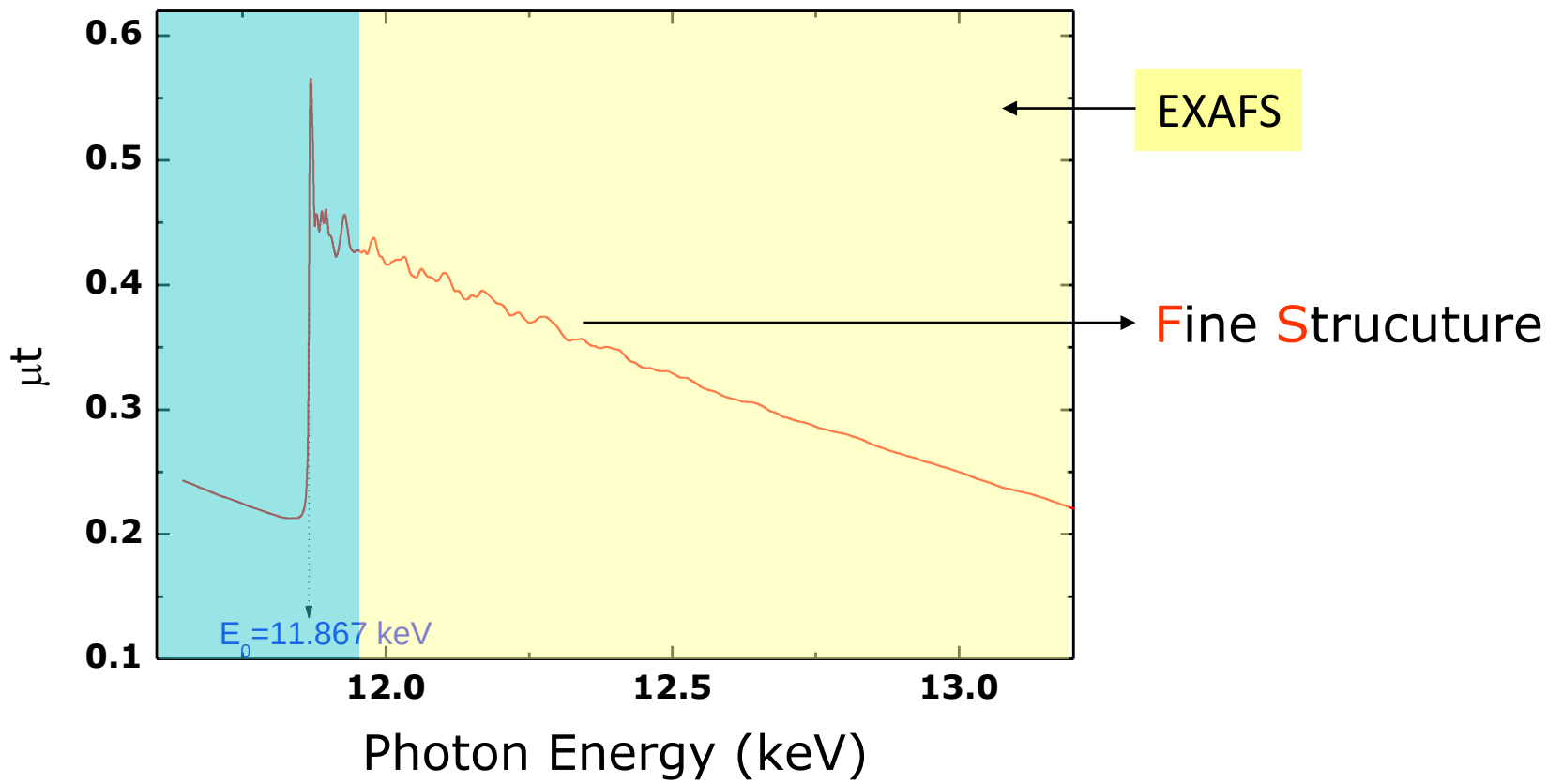


Basics aspects about XAFS

XAFS = XANES + EXAFS

Extended X-ray Absorption
Fine Strucuture

InAs - As *K*-Edge



EXAFS is the region from 50 – 1200 eV after the edge

Understanding the XAFS equation

- Photon energy ($E\gamma$) > Binding Energy (E_l): Photoelectric effect.

- Kinetic energy of the photoelectron (E_c)= E_γ - E_L

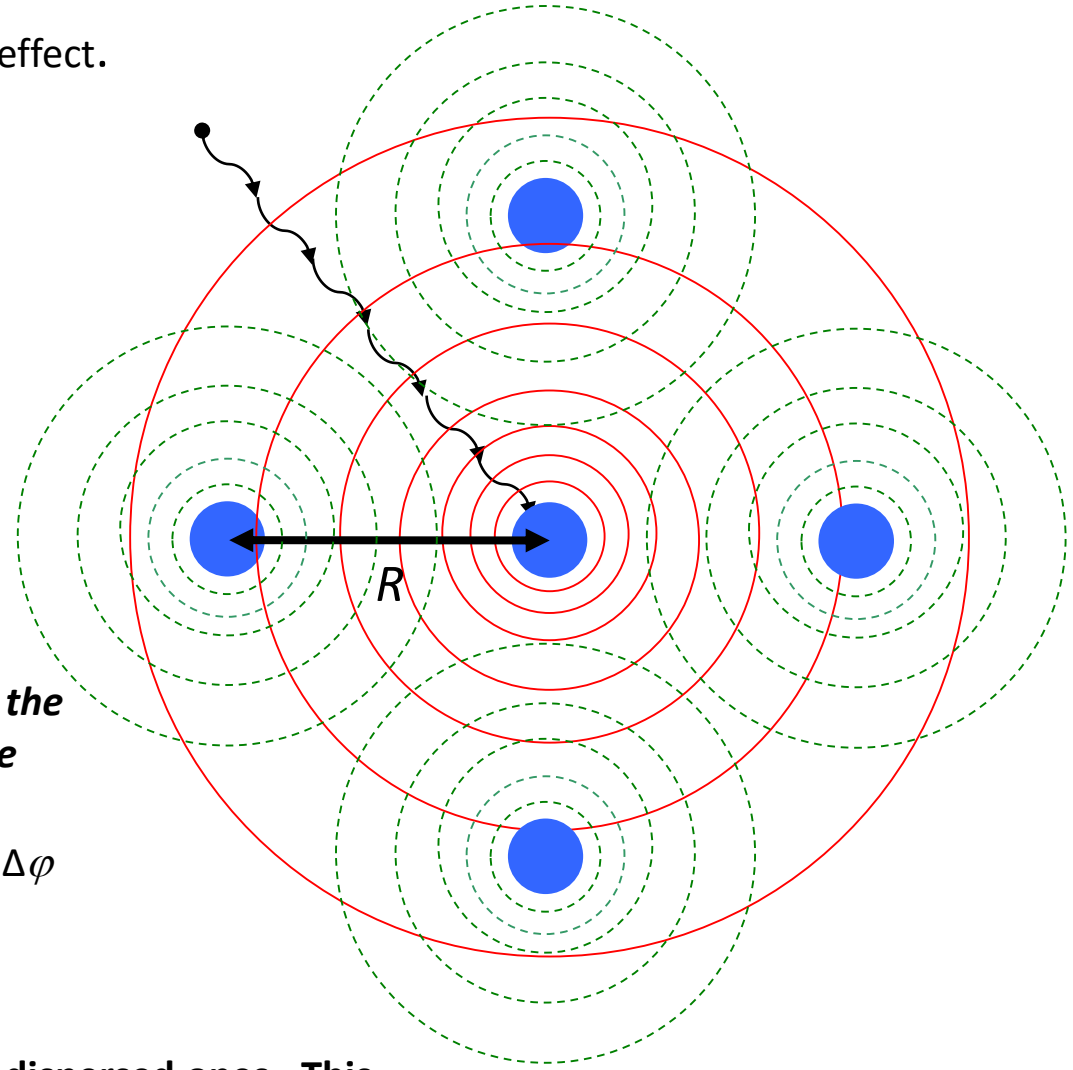
- Wave-Particle duality: The photoelectron travel as a esferic wave: $E_c = h\nu$

- Wavevector of the photoelectron: *K*

$$k = \sqrt{\frac{2m_e(E_\gamma - E_L)}{\hbar^2}}$$

- ***Quantical state of the photoelectron: superposition of the propagating wave with the retrodispersed waves on the neightbourgs***
- Phase difference of the incoming and outgoing waves: $\Delta\varphi$

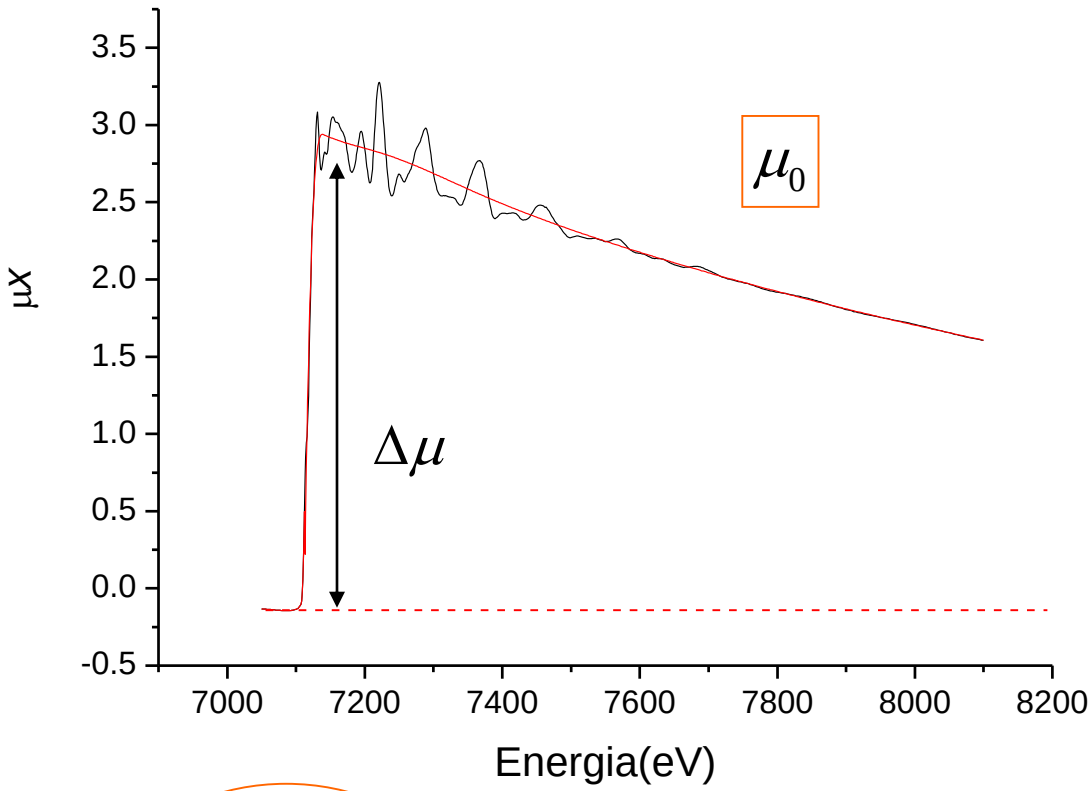
$$\Delta\varphi \approx 2kR$$

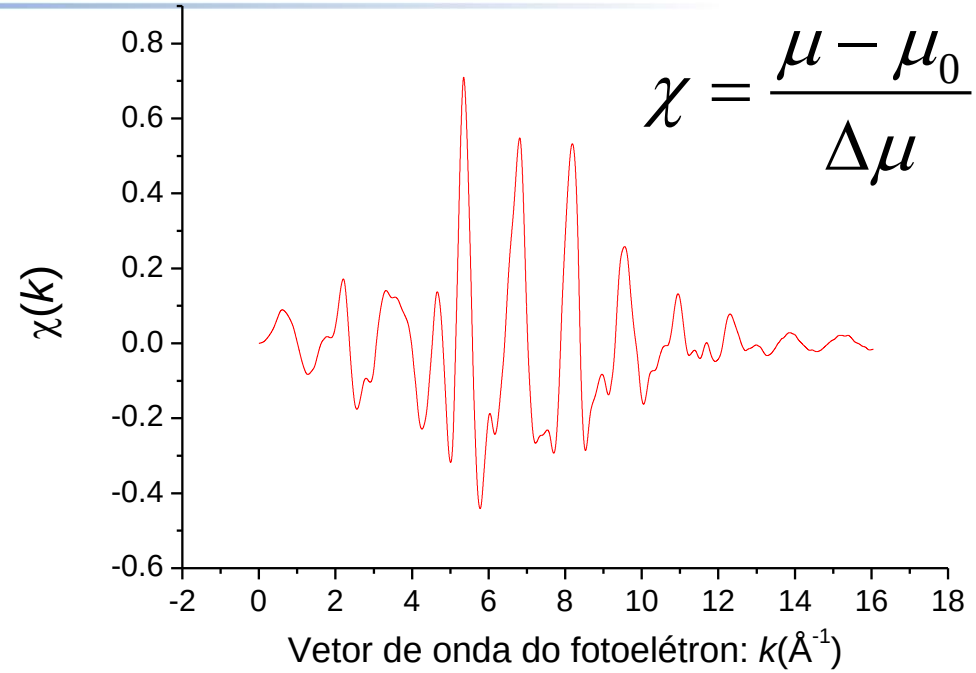


- **Interference in between propagating waves and retrodispersed ones. This moduls the absorption coefficient.**

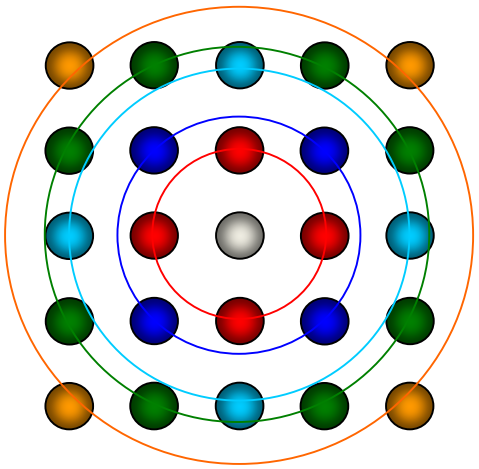
- Oscilation frequence: 2R
- Oscilation amplitudes: number of neightbourgs and disorder

Understanding the XAFS equation





Here we add (superpose) oscilations of different frequencies (radial distances), one for each coordination shell



- **Coordination shell**: Refers to the aggrupation's of atoms at the same distance to the absorber atom.
- **Coordination Number**: amount of atoms in a coordination shell

Understanding the XAFS equation

Principal hypothesis:

- Final states are plane waves
- Gaussian disorder
- Dipolares transitions
- One active electron
- Photoelectron dispersion is single

Sayers *et al.*,PRL 27, 1204 (1971)

$$\mu(E) \propto \sum_{f}^{E_f > E_F} \left| \langle f | \hat{e} \bullet \vec{r} | i \rangle \right|^2 \delta(E_f)$$

$$\chi(k) = \sum_i \frac{N_i}{kR_i^{\,2}} S_0^2 F_i(k) e^{-2k^2\sigma_i^2} e^{\left[\frac{-2R_i}{\lambda}\right]} \sin[2kR_i - \phi_i(k)]$$

Estructural parameters

R_i

N_i

$\sigma^2{}_i$

Atomic parameters:
Absoption and dispersion of the Photoelectron

λ

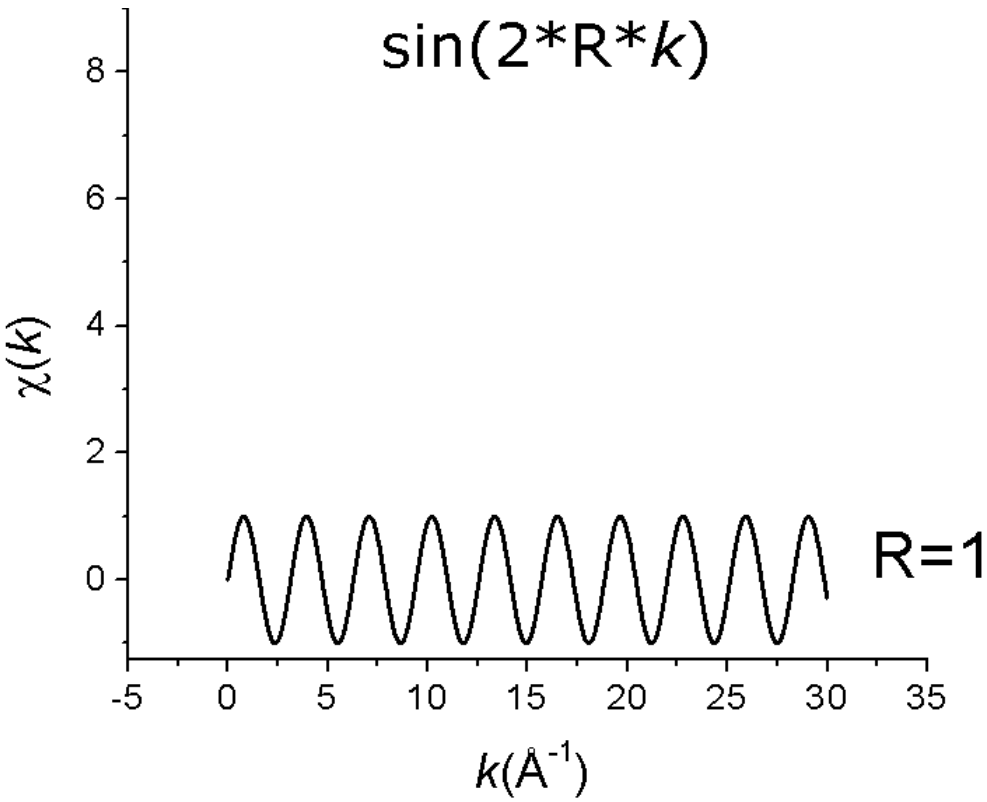
$F(k)$ S_0^2

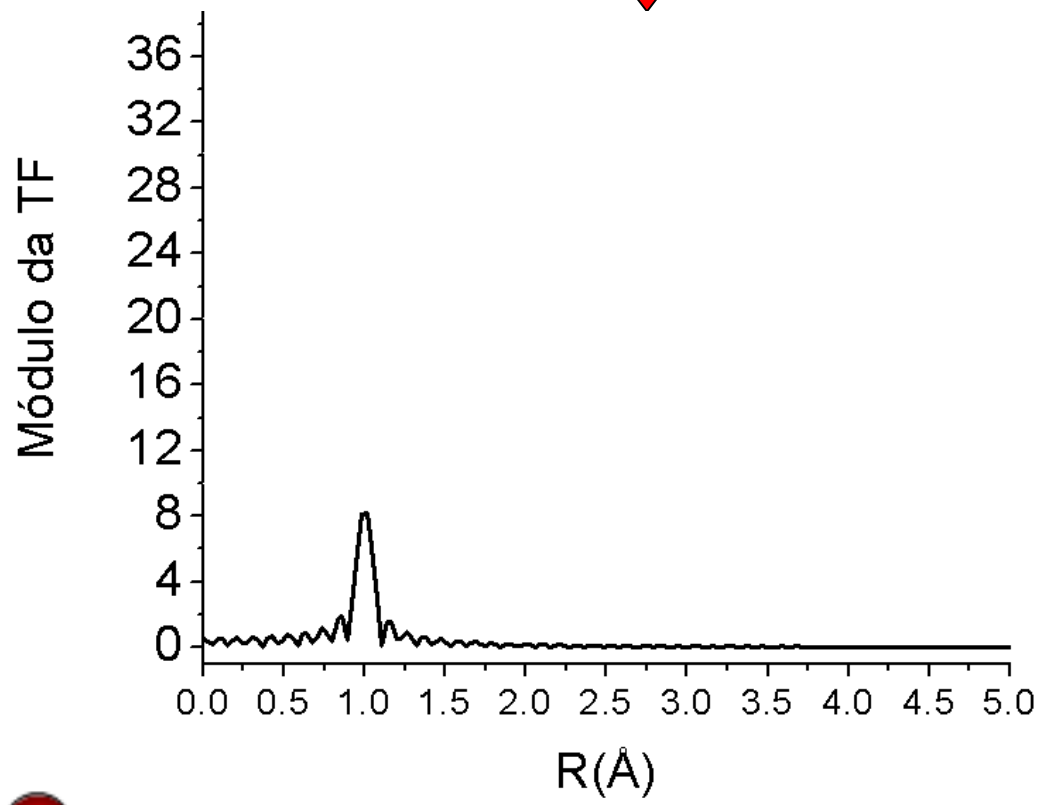
$\phi(k)$

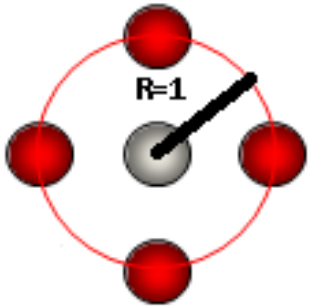
$\longleftrightarrow$ *ab initio*

Understanding the XAFS equation

$$TF(R) = \frac{1}{\sqrt{2\pi}} \int_{k_{min}}^{k_{max}} \chi(k) e^{i2Rk} dk$$

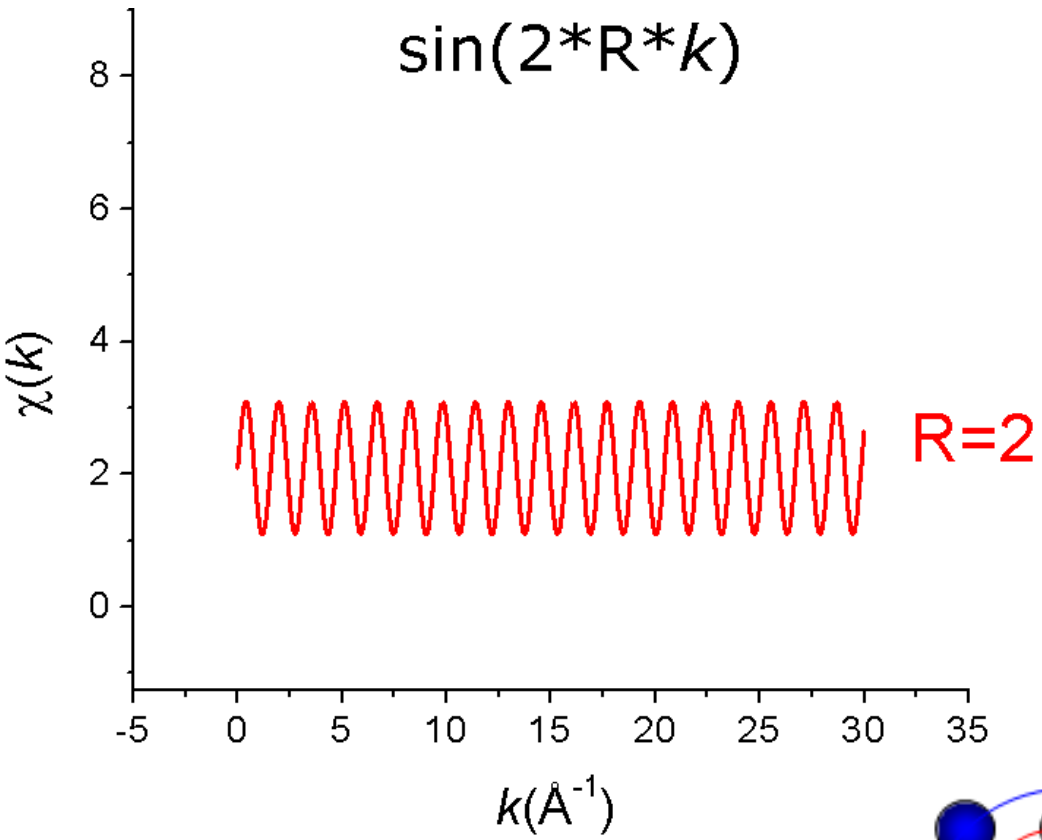


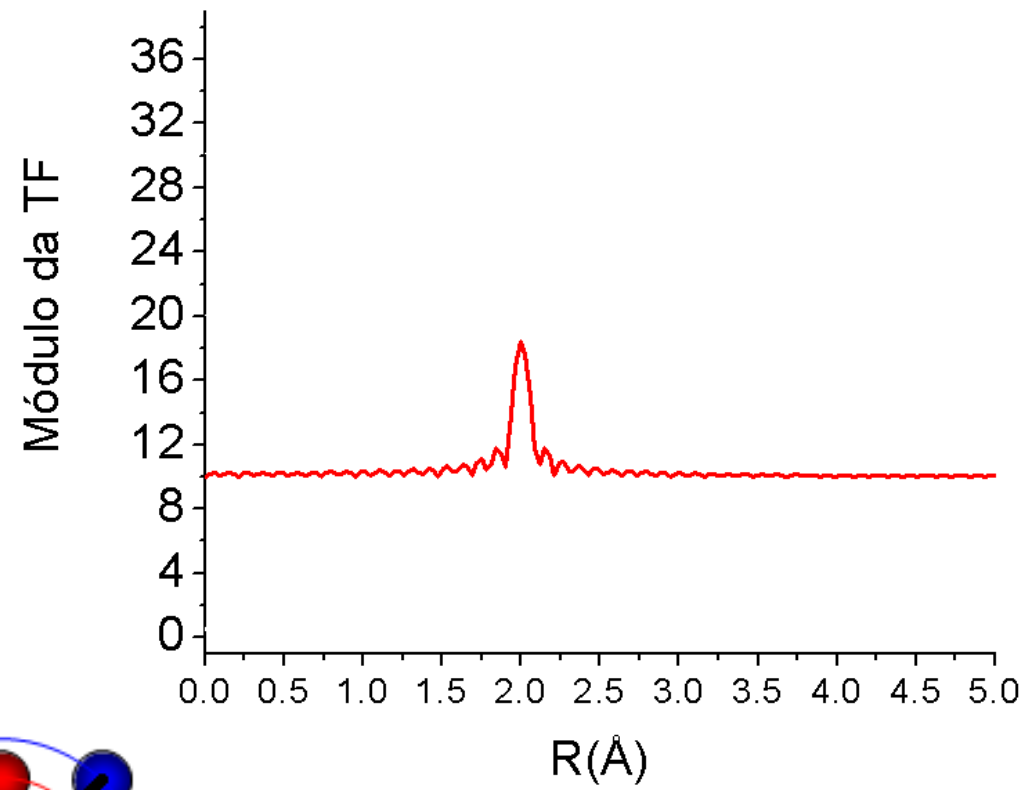


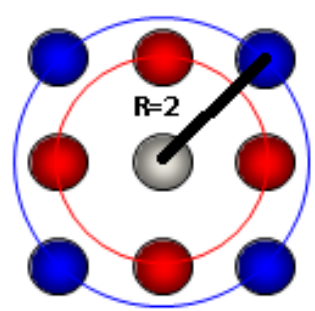


Understanding the XAFS equation

$$TF(R) = \frac{1}{\sqrt{2\pi}} \int_{k_{min}}^{k_{max}} \chi(k) e^{i2Rk} dk$$







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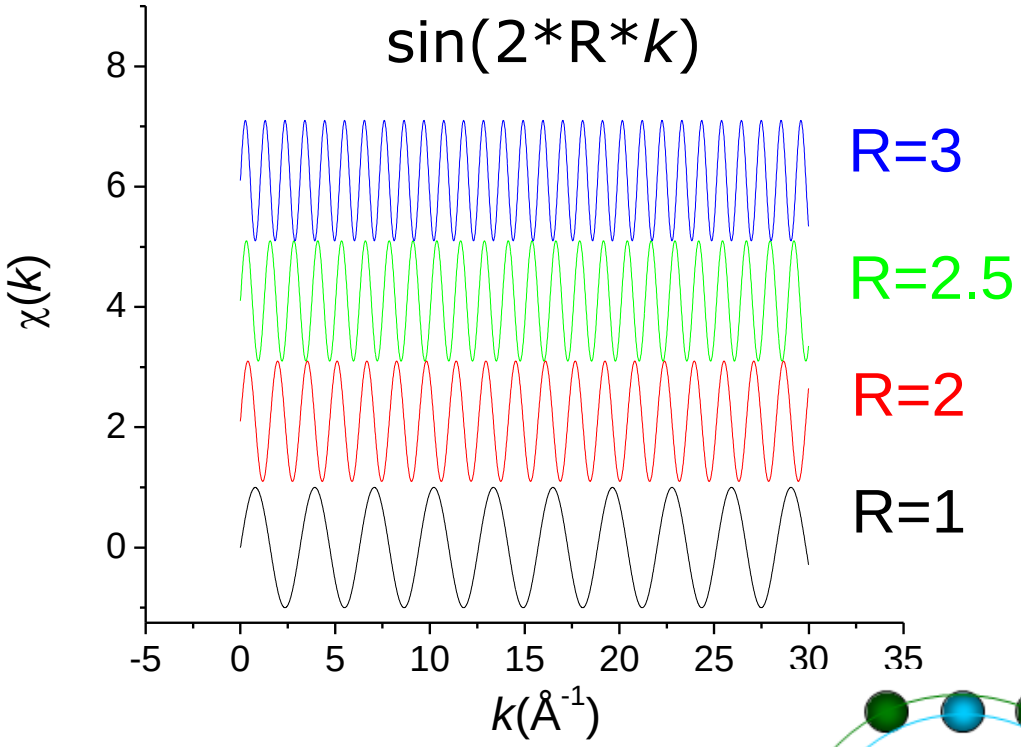
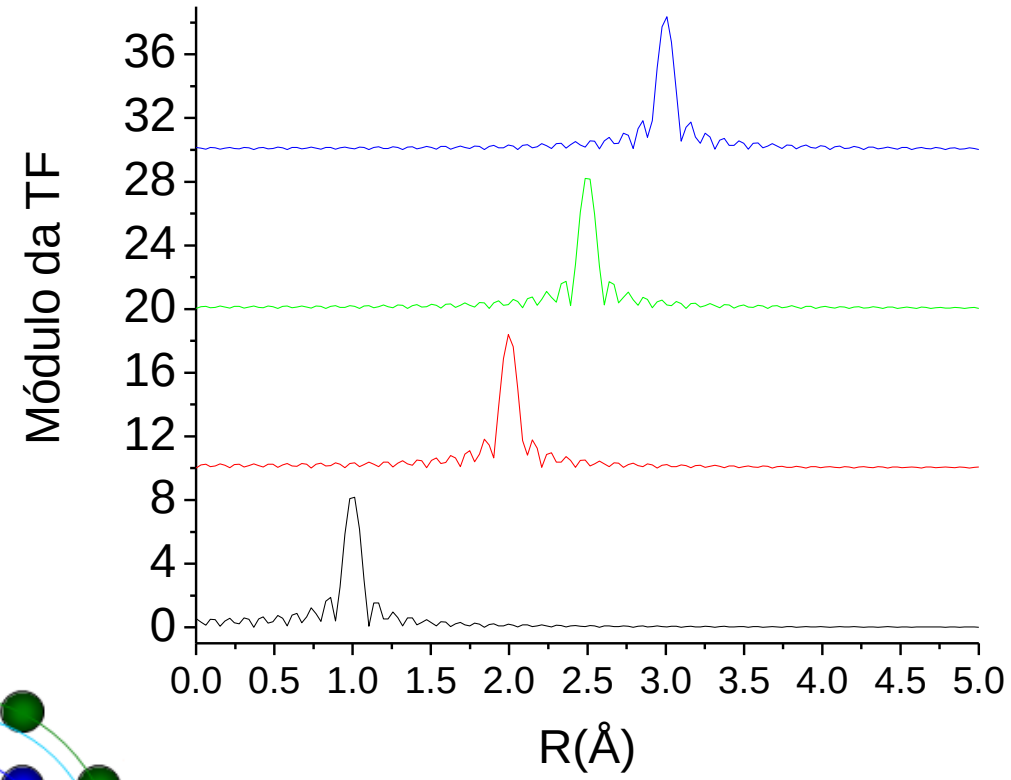
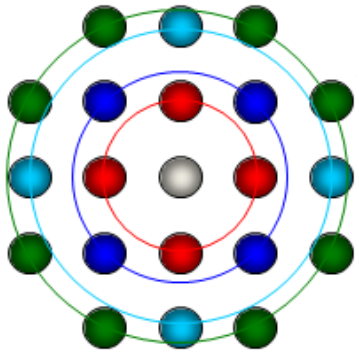


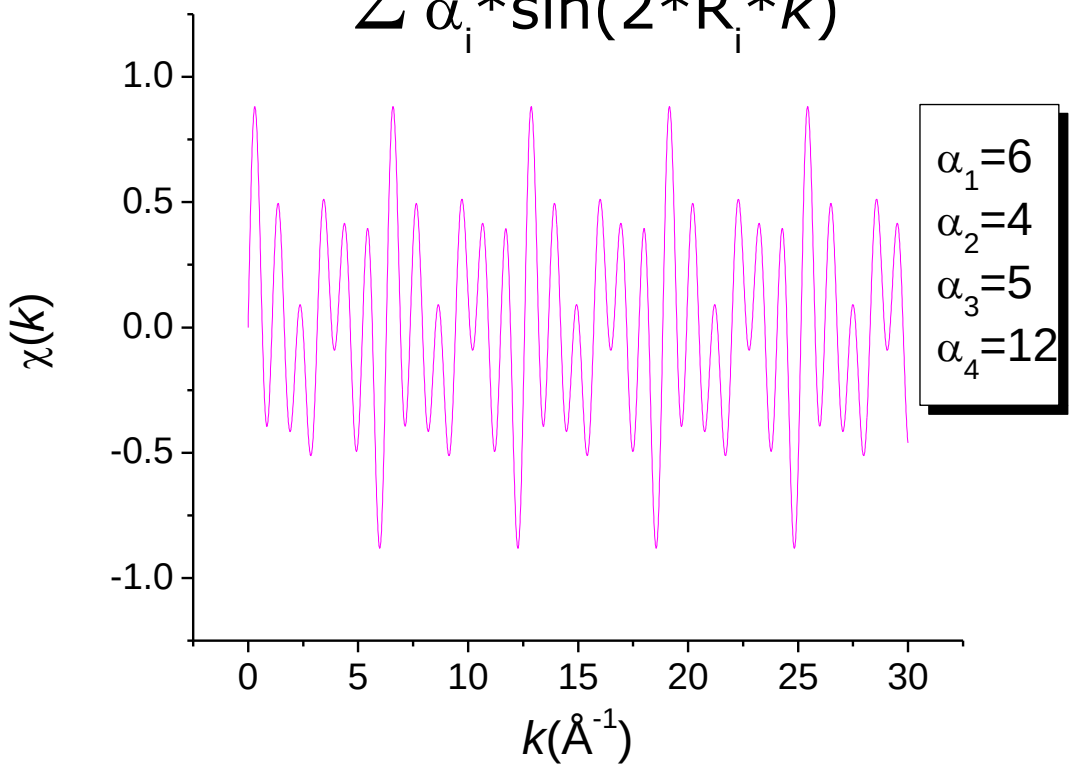


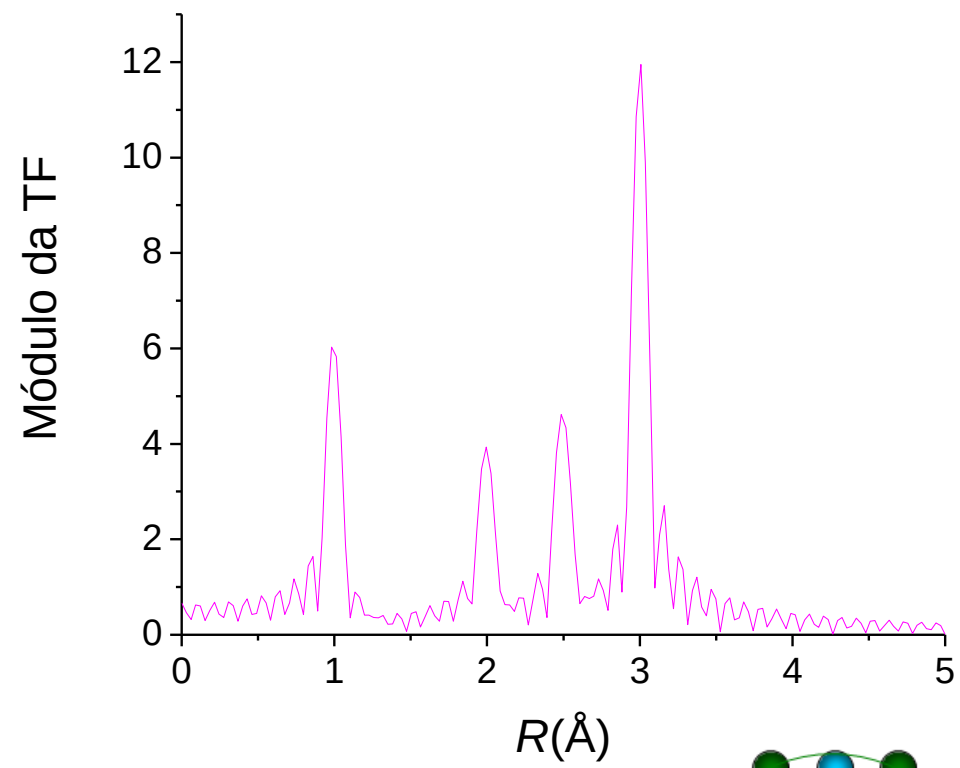


Understanding the XAFS equation

$$TF(R) = \frac{1}{\sqrt{2\pi}} \int_{k_{min}}^{k_{max}} \chi(k) e^{i2Rk} dk$$

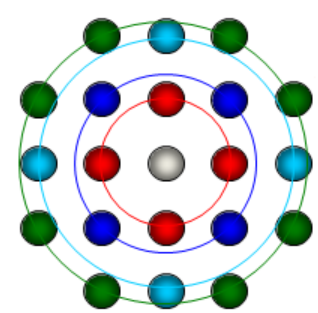
$\sum \alpha_i * \sin(2 * R_i * k)$





α_i

$$\chi(k) = \sum_i \frac{N_i}{kR_i^2} S_0^2 F_i(k) e^{-2k^2\sigma_i^2} e^{\left[\frac{-2R_i}{\lambda}\right]} \sin[2kR_i - \phi_i(k)]$$



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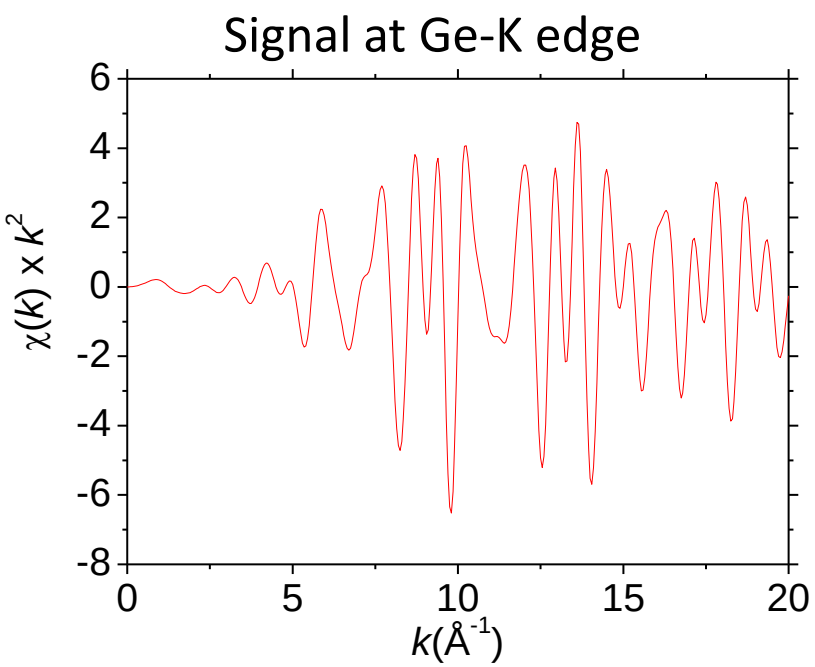
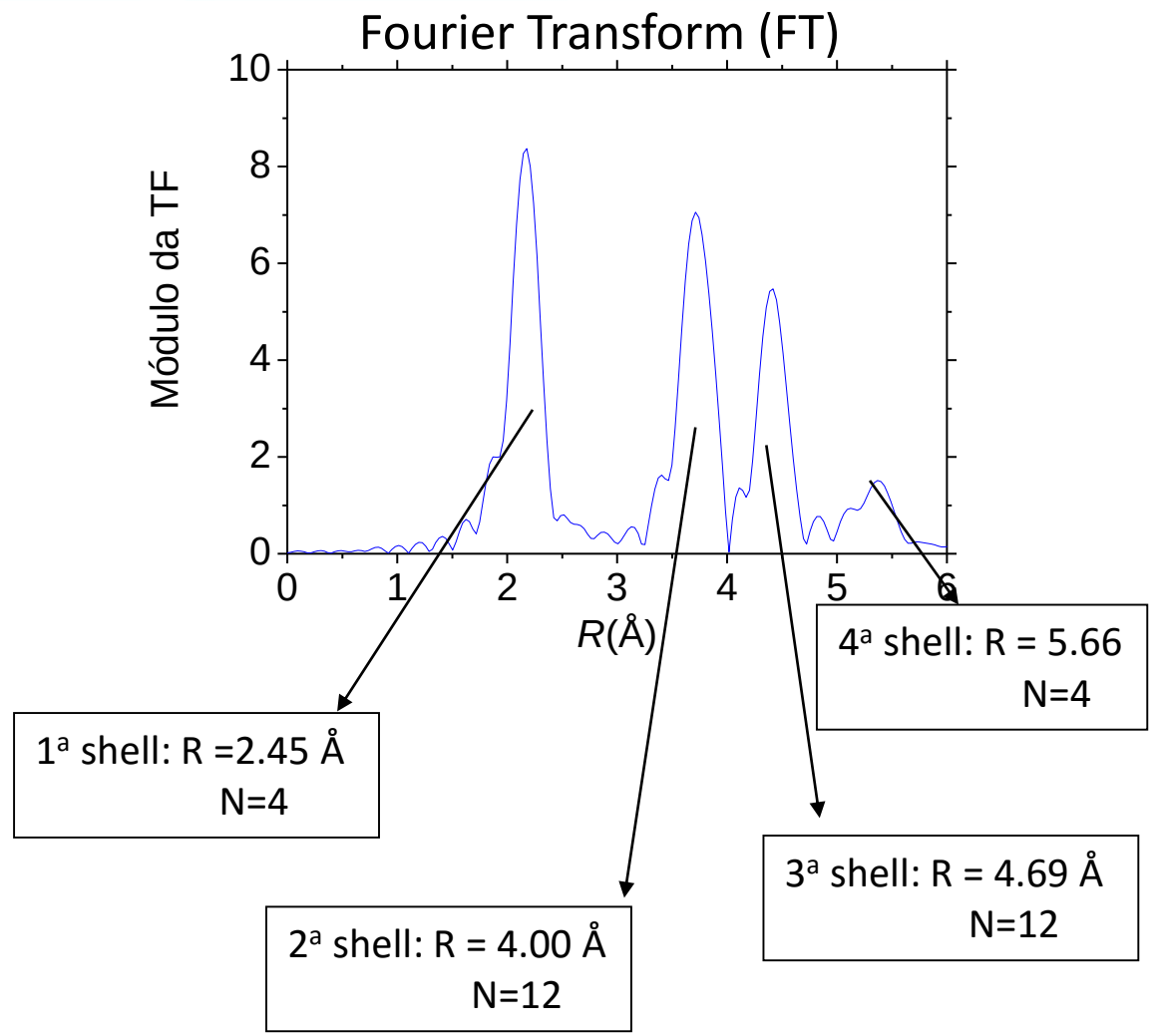




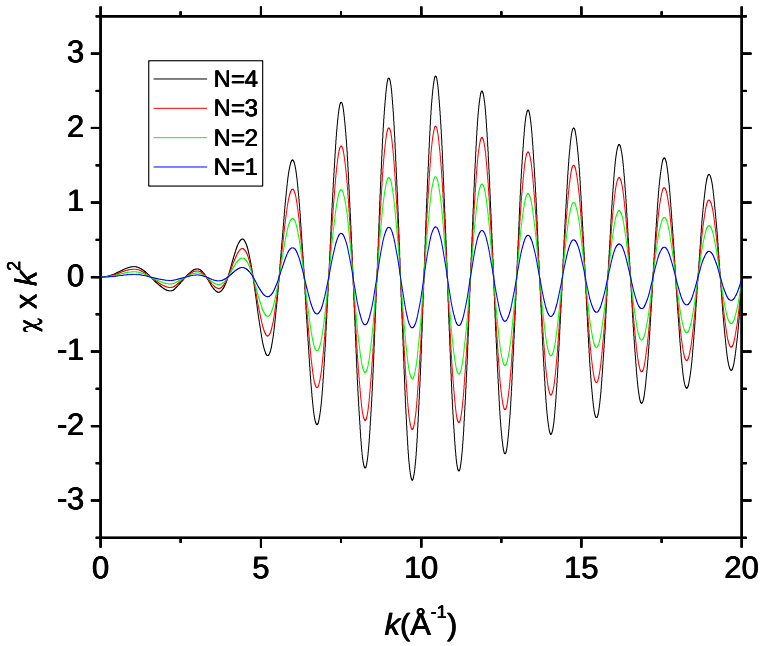
FT: is not a Radial Distribution function but have some resemblance

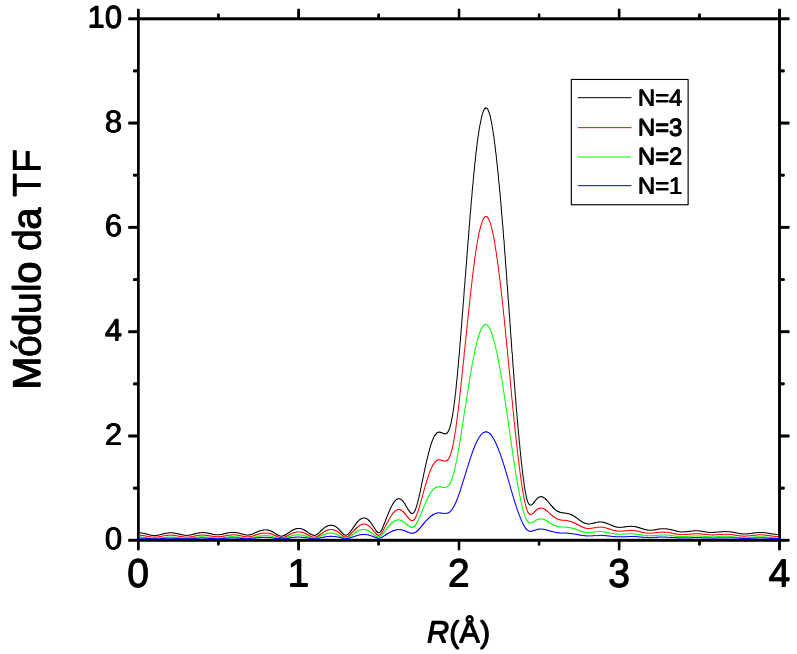
oK

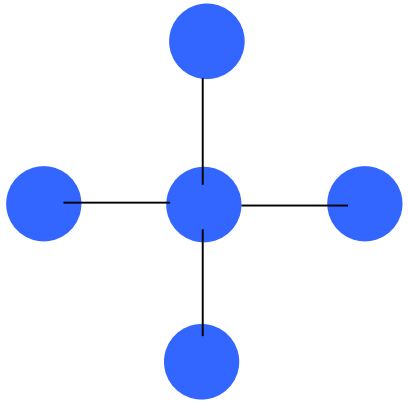
$$\chi(k) = \sum_i \frac{N_i}{kR_i^2} S_0^2 F_i(k) e^{-2k^2\sigma_i^2} e^{\left[\frac{-2R_i}{\lambda}\right]} \sin[2kR_i - \phi_i(k)]$$

Understanding the XAFS equation

Changes on the EXAFS signal with variations on the Coordination number







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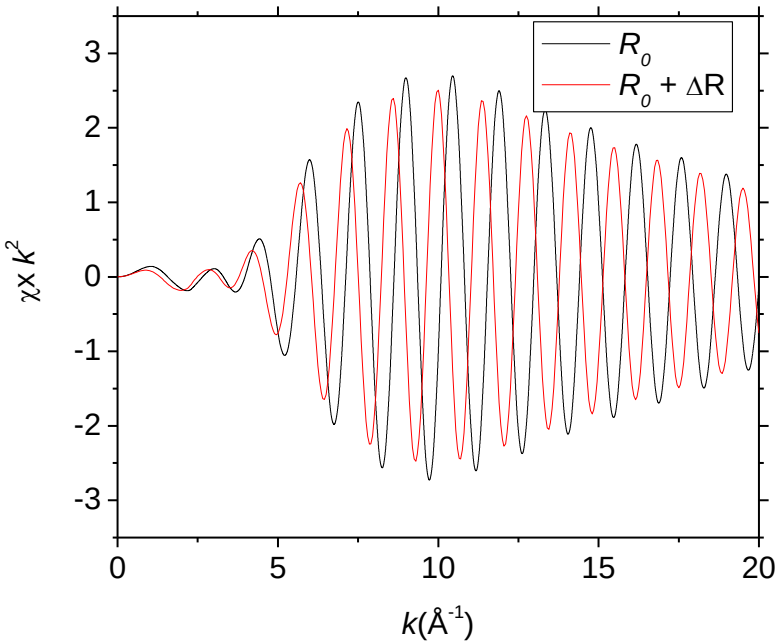
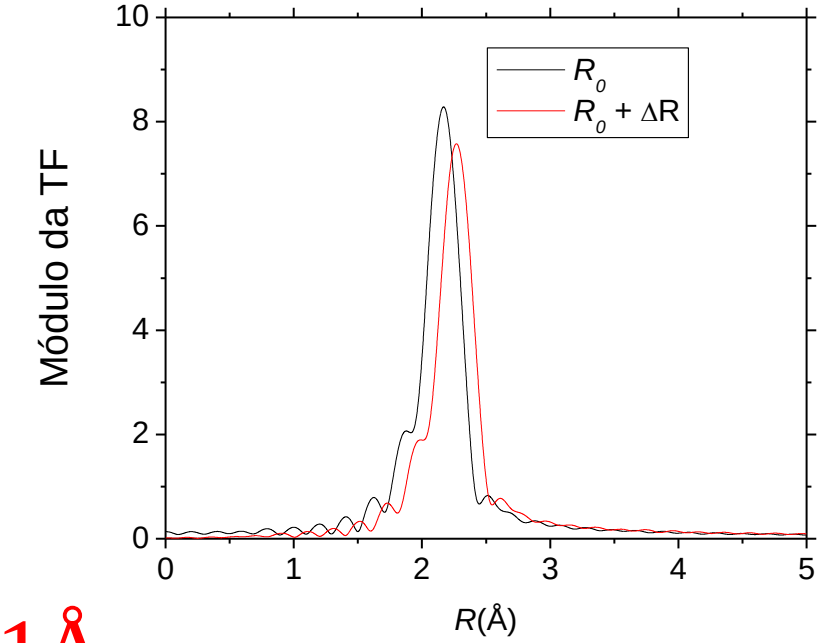
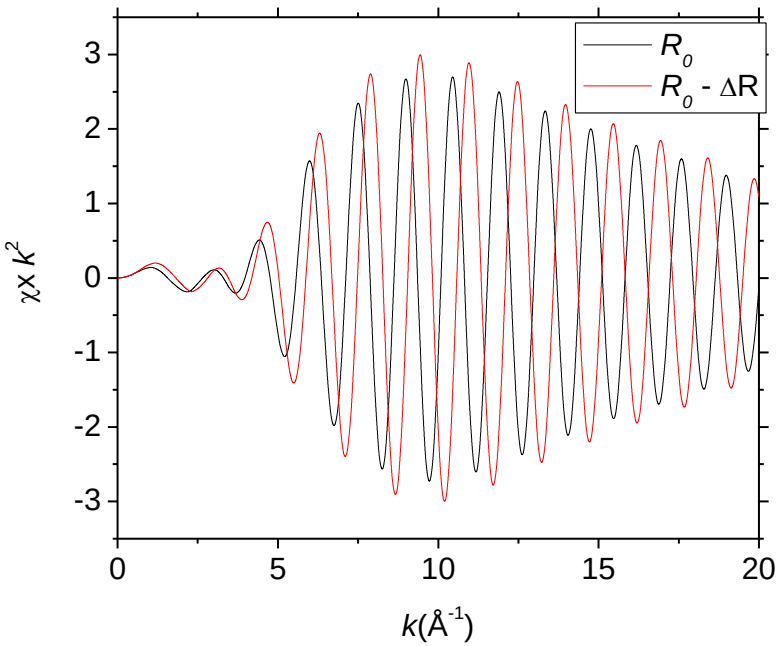
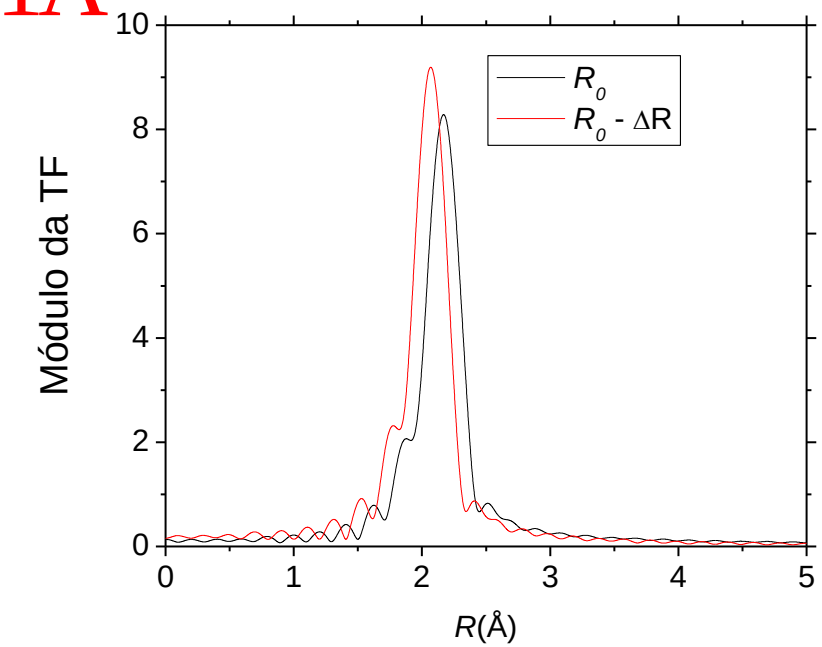


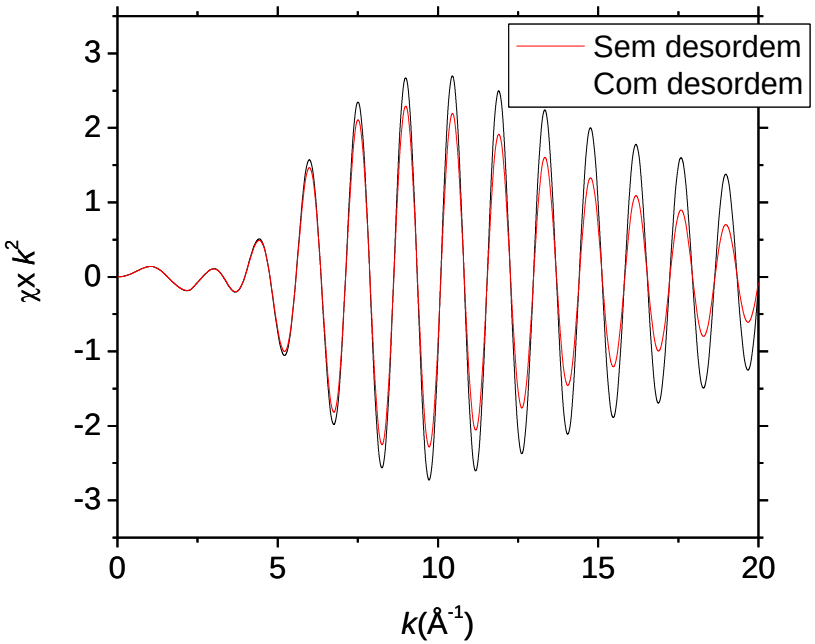


Changes on the EXAFS signal with a variation on the

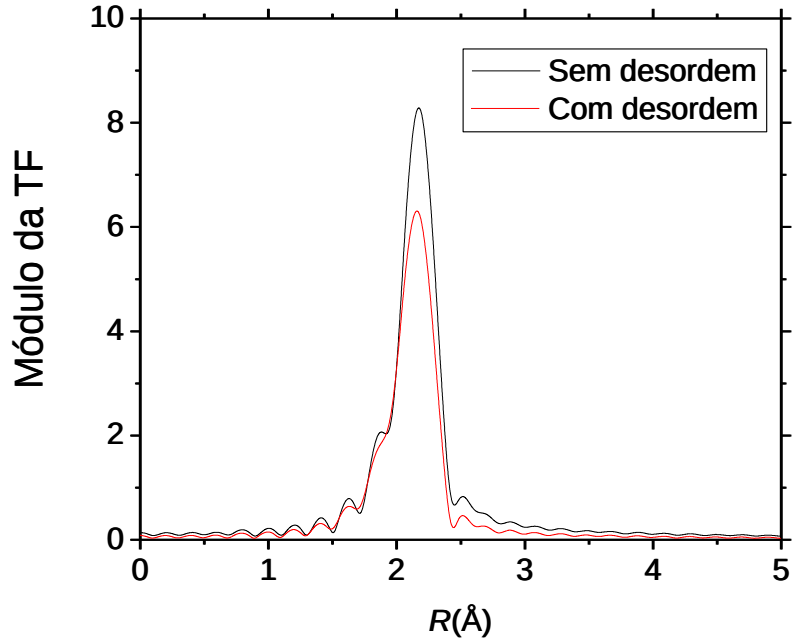
$$\Delta R = 0.1\text{Å}$$



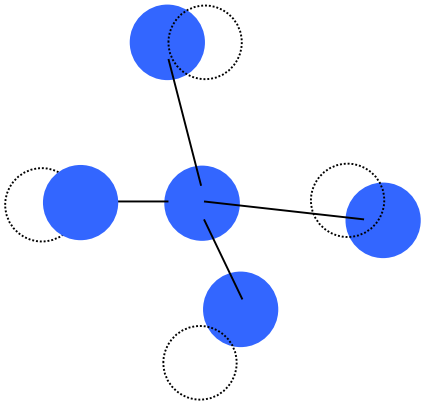




Changes on the EXAFS with a variation on the structural disorder



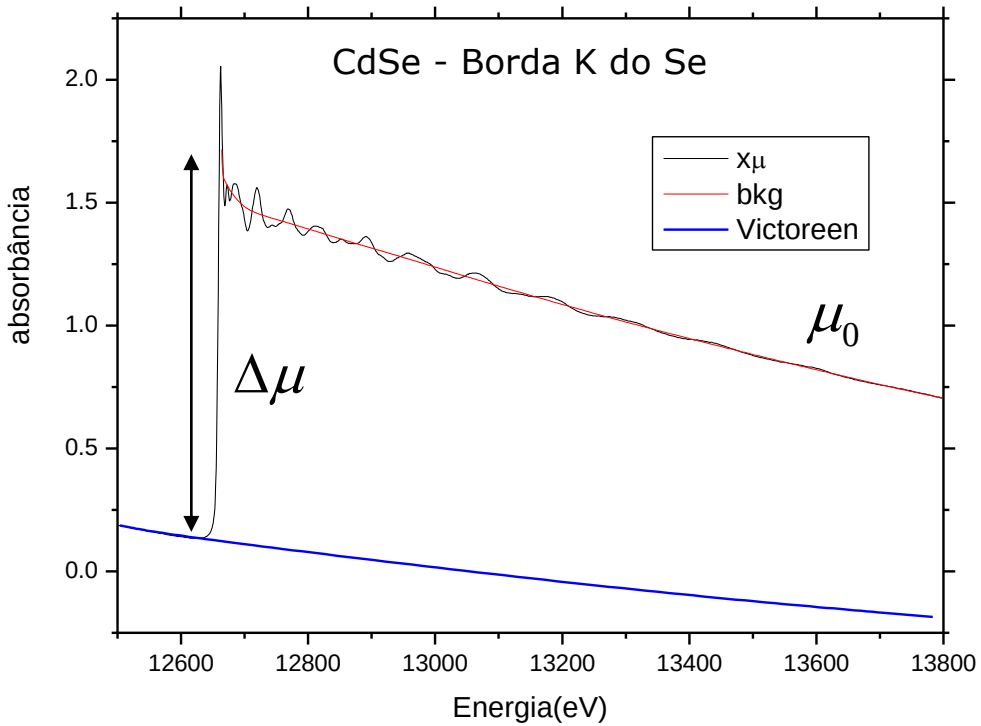
Gaussian Disorder: σ = 0.03 Å

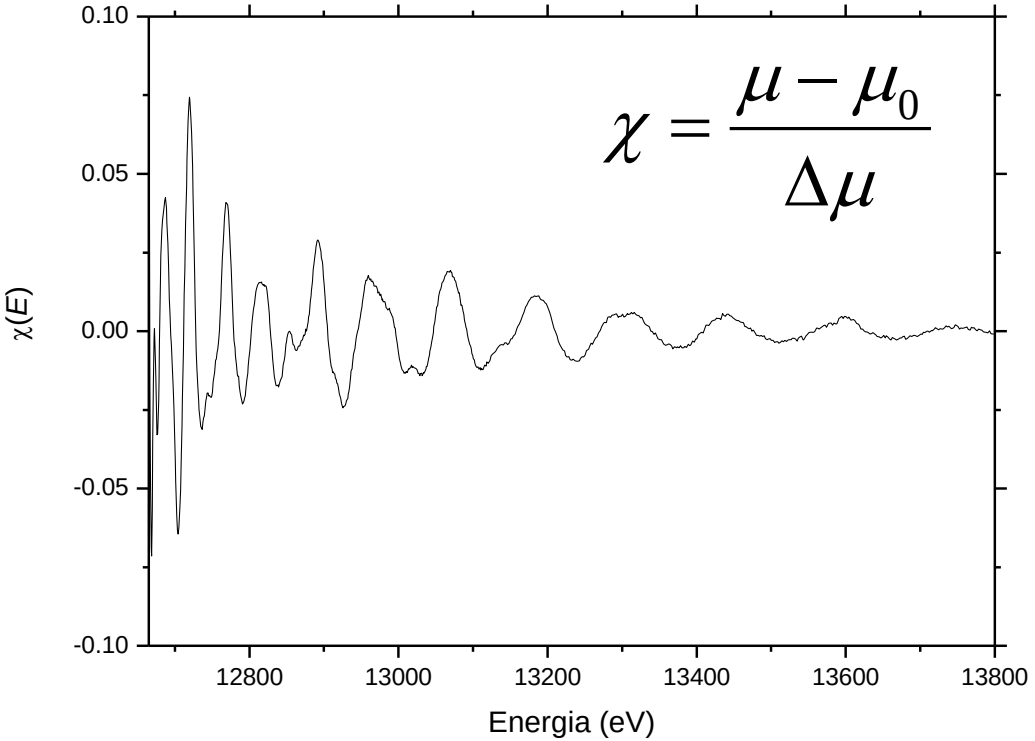


Understanding the XAFS equation

1 – background extraction

Data treatment

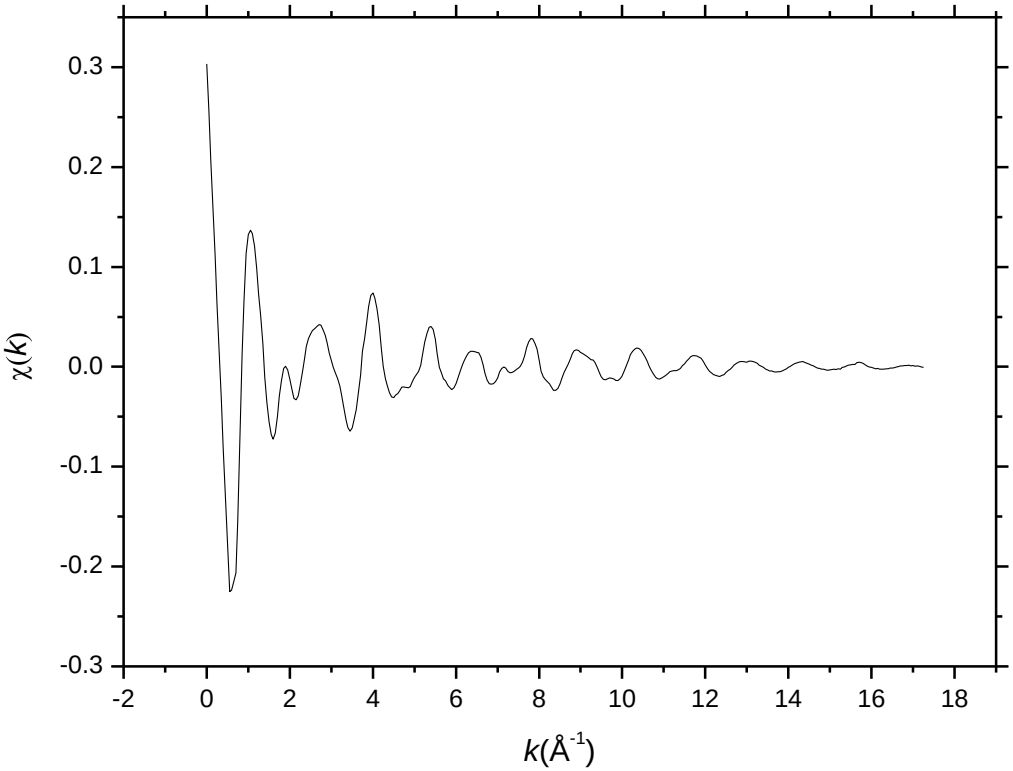




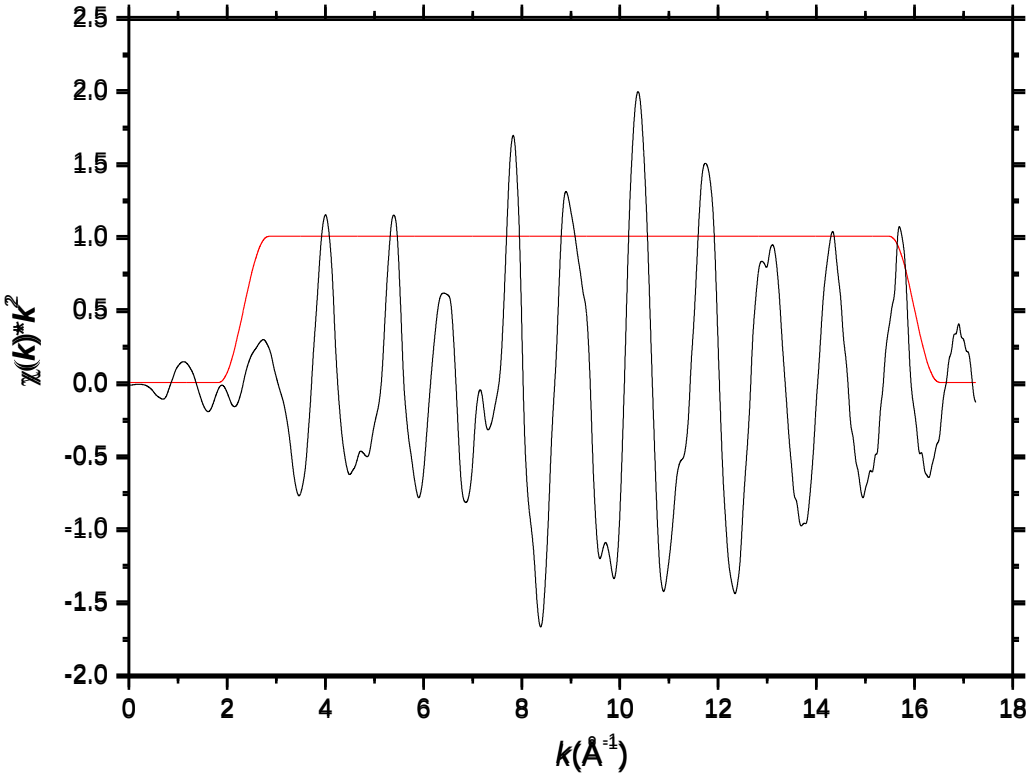
Understanding the XAFS equation

Conversion E→*k*

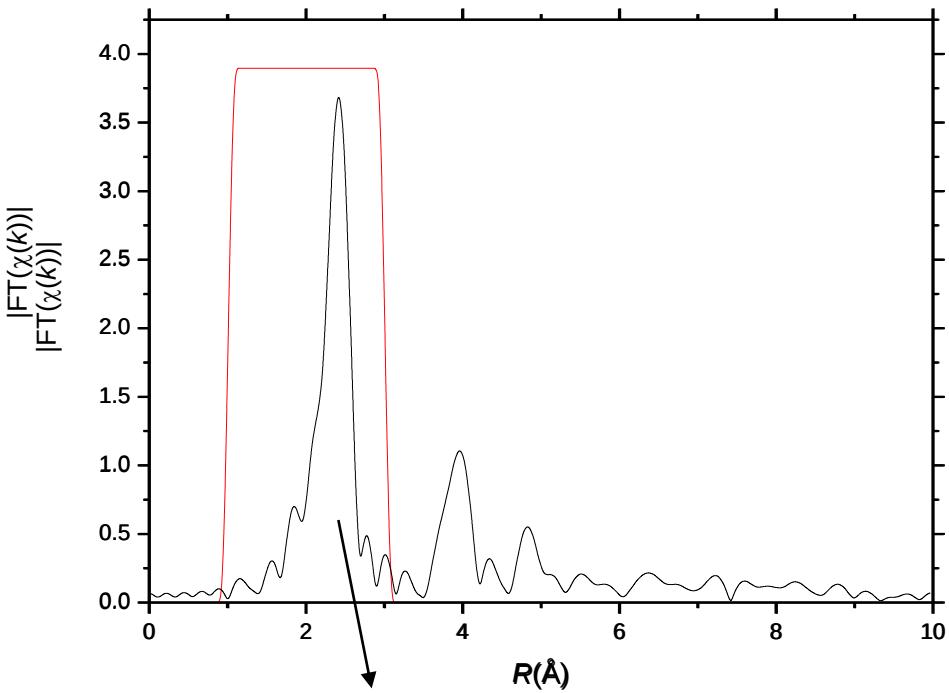
$$k = \sqrt{\frac{2m_e(E_\gamma - E_L)}{\hbar^2}}$$



K-weigthing

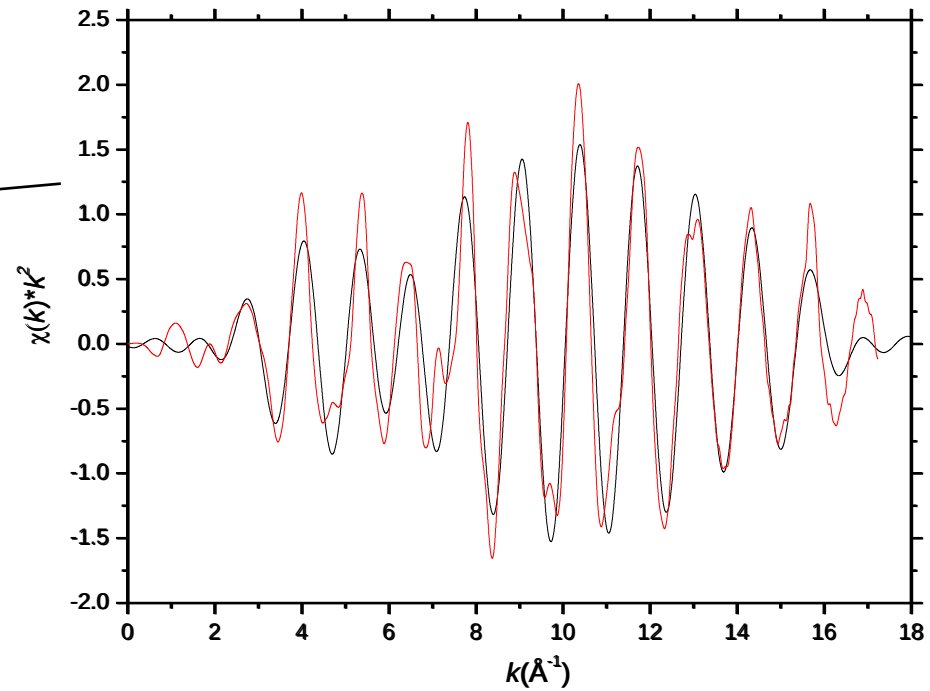


Understanding the XAFS equation



Structural parameters:
Minimal Square fitting

Phases and amplitudes of the retrodispersion



Understanding the XAFS equation

Principal hypothesis:

- Final states are plane waves
- Gaussian disorder
- Dipolares transitions
- One active electron
- Photoelectron dispersion is single

Sayers *et al.*,PRL 27, 1204 (1971)

$$\mu(E) \propto \sum_{f}^{E_f > E_F} \left| \langle f | \hat{e} \bullet \vec{r} | i \rangle \right|^2 \delta(E_f)$$

$$\chi(k) = \sum_i \frac{N_i}{kR_i^{\,2}} S_0^2 F_i(k) e^{-2k^2\sigma_i^2} e^{\left[\frac{-2R_i}{\lambda}\right]} \sin[2kR_i - \phi_i(k)]$$

Estructural parameters

R_i

N_i

$\sigma^2{}_i$

Atomic parameters:
Absoption and dispersion of the Photoelectron

λ

$F(k)$ S_0^2

$\phi(k)$

$\longleftrightarrow$ *ab initio*

But remeber....

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Studying a system with one technique is equivalent to studying it with zero techniques

- Bruce Ravel citing anonymous source

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Obrigado pela sua atenção!

Questions, please email me:

santiago.figueroa@lnls.br

More info about XAFS:

https://speakerdeck.com/bruceravel?page=2

http://cars.uchicago.edu/ifeffit/Mailing_List

http://xafs.org/Tutorials

http://www.ixasportal.net/ixas/

http://cars.uchicago.edu/ifeffit/Documentation

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