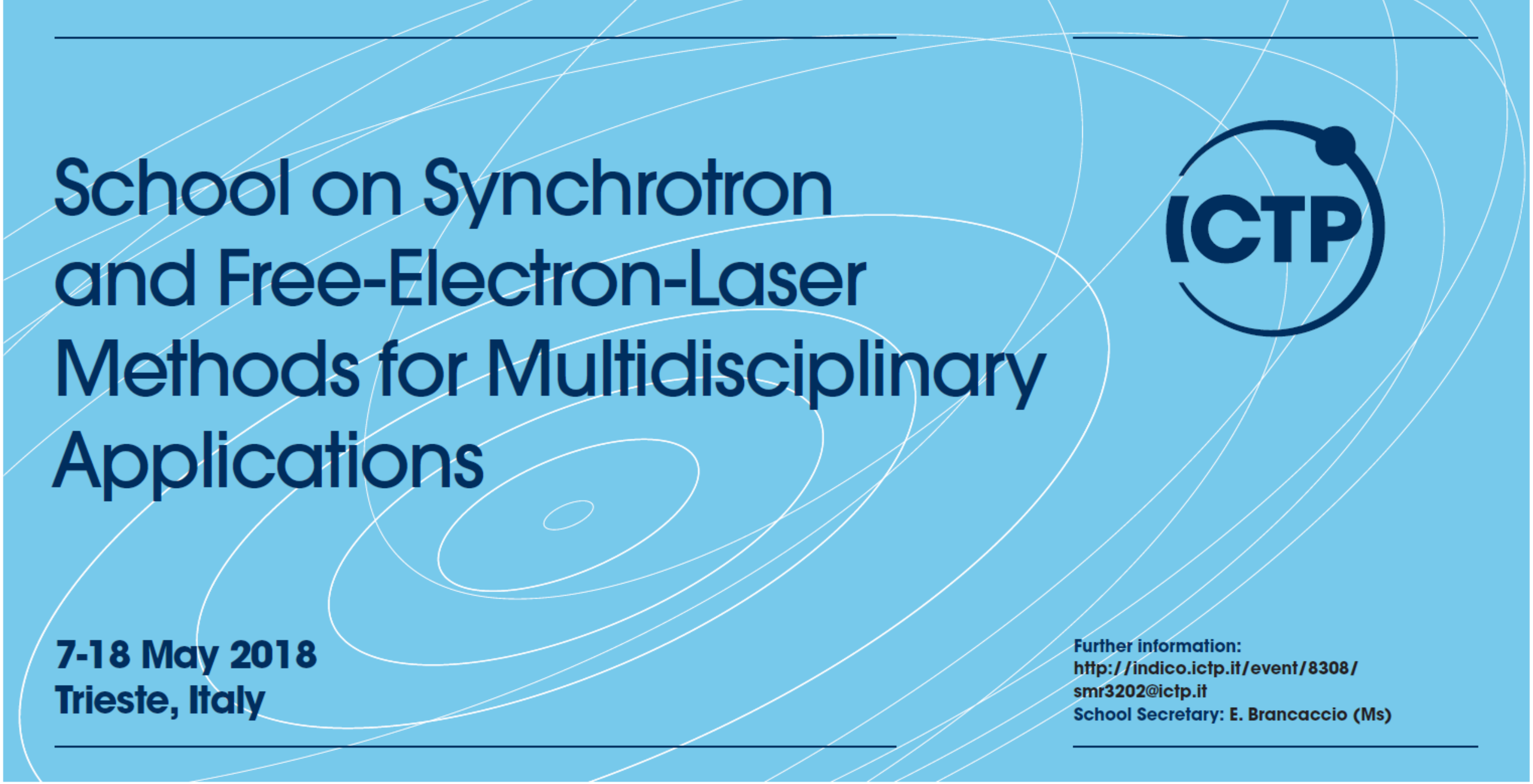

School on Synchrotron and Free-Electron-Laser Methods for Multidisciplinary Applications

7-18 May 2018
Trieste, Italy

Further information:
http://indico.ictp.it/event/8308/
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School Secretary: E. Brancaccio (Ms)

X-ray absorption spectroscopy: principles, methods and data analysis

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Outline

- X-ray absorption
- X-ray absorption fine structure
- XANES
- EXAFS data analysis

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X-ray absorption

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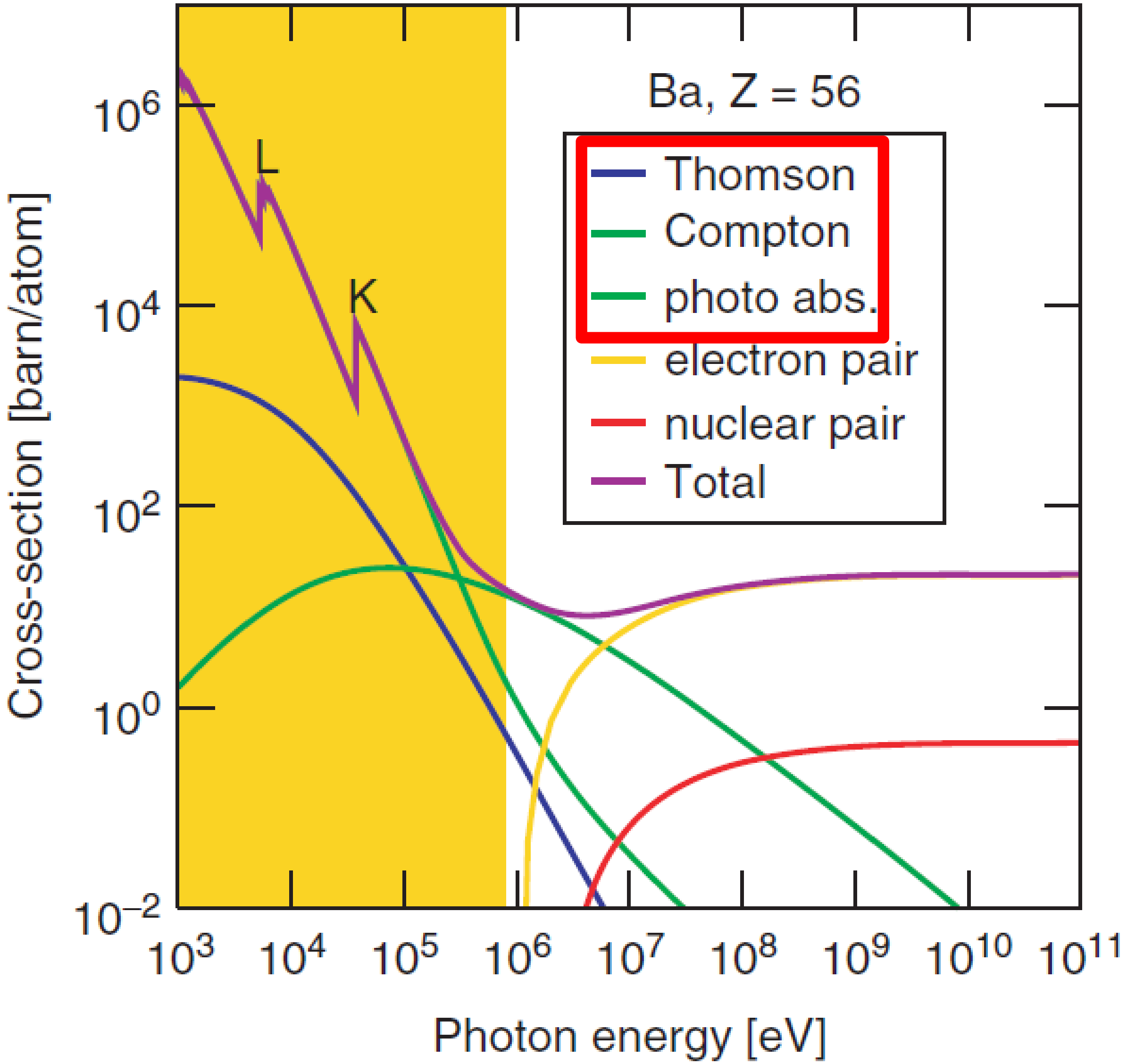
Introduction: x-rays-matter interaction



X-rays – matter interaction

- Photoelectric absorption

  one photon is absorbed and the atom is ionized or excited

- Scattering

  photons are deflected form the original trajectory by collision with an electron

  - *Elastic* (Thomson scattering): the photon wavelength is unmodified by the scattering process
  - *Inelastic* (Compton scattering): the photon wavelength is modified

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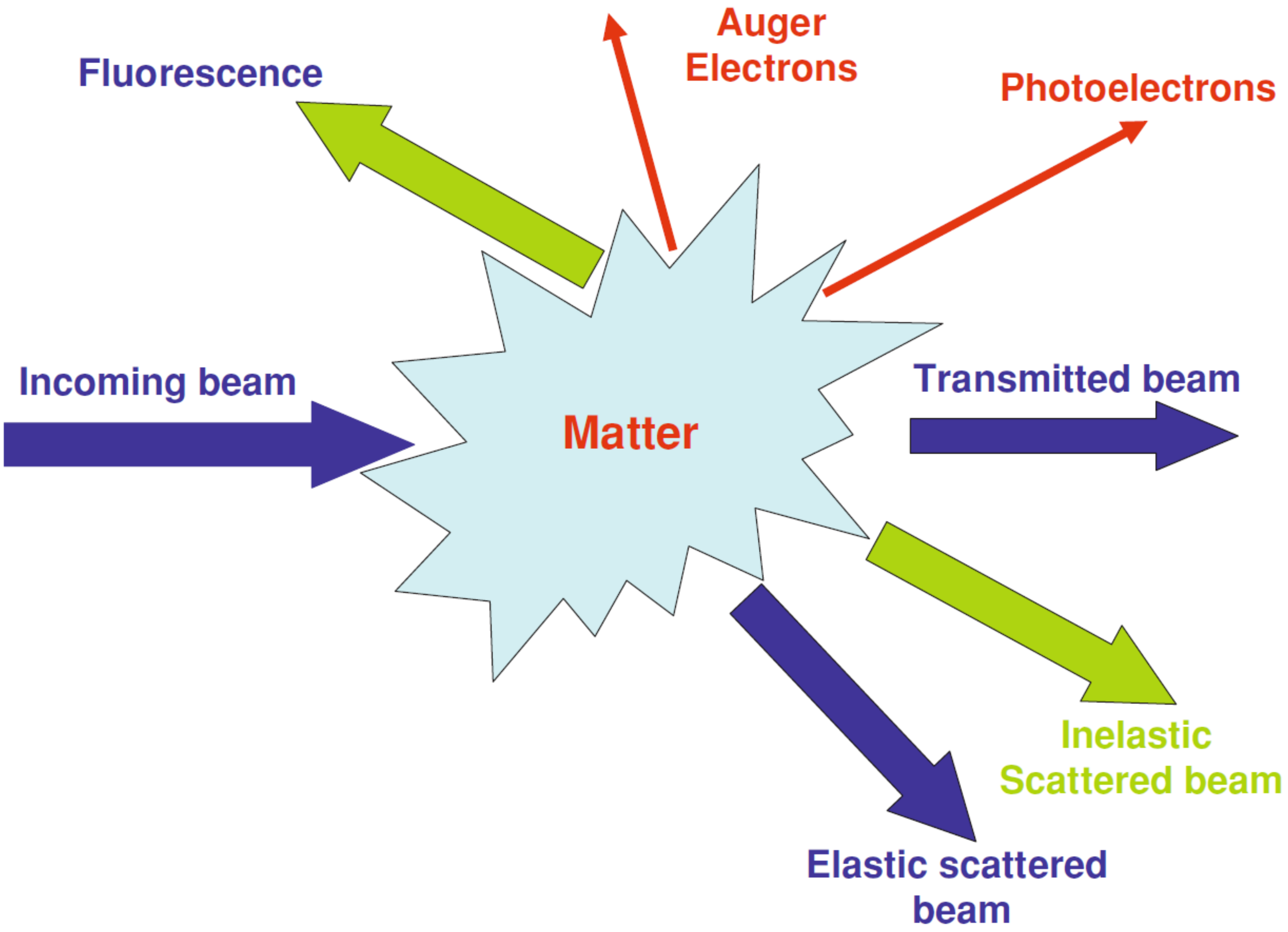
X-ray – matter interaction



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Main x-ray experimental techniques

- Spectroscopy

  atomic and electronic structure of matter

  - *Absorption*
  - *Emission*
  - *Photoelectron spectroscopy*

- Imaging

  macroscopic pictures of a sample, based on the different absorption of x-rays by different parts of the sample (medical radiography and x-ray microscopy)

- Scattering
  - *Elastic:* Microscopic geometrical structure of condensed systems
  - *Inelastic:* Collective excitations

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Spectroscopic methods

- They measure the response of a system as a function of energy

- The energy that is scanned can be that of the incident beam or the energy of the outgoing particles (photons in x-ray fluorescence, electrons in photoelectron spectroscopy)

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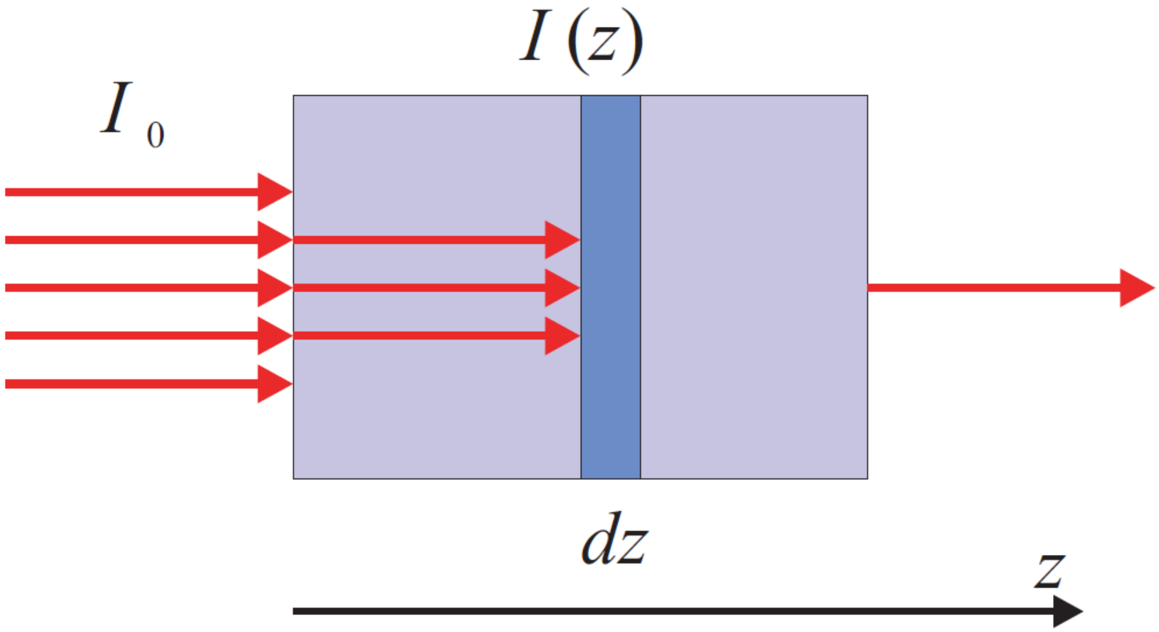
The absorption coefficient - 1

- Quantitatively, the absorption is given by the linear absorption coefficient μ
- μdz : attenuation of the beam through an infinitesimal thickness dz at a depth z from the surface



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The absorption coefficient - 2

The intensity $I(z)$ through the sample fulfills the condition

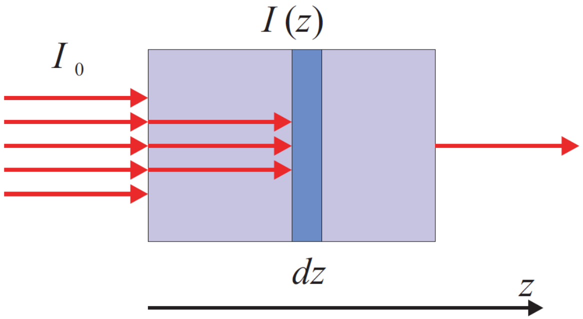
$$-dI = I(z)\mu dz$$

which leads to the differential equation

$$\frac{dI}{I(z)} = -\mu dz$$

If $I(z=0) = I_0$, (I_0: incident beam intensity at $z = 0$) then

$$\boxed{I(z) = \ I_0 e^{-\mu z}}$$



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The absorption coefficient - 3

$$I(z) = I_0 e^{-\mu z} \Rightarrow ln\frac{I_0}{I} = \mu z$$

Experimentally, μ can be determined as the log of the ratio of the beam intensities with and without the samples (or beam intensity before and after the sample)

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Atomic cross section

mass density

Avogadro's number

$$\mu = \boxed{\rho_{at}}\boldsymbol{\sigma_a} = \left(\frac{\boxed{\rho_m}\boxed{N_A}}{\boxed{A}}\right)\boldsymbol{\sigma_a}$$

Atomic number density

Atomic mass

$$\sigma_a[\mathrm{cm}^2]$$

$$\sigma_a[barn] \qquad 1\ barn = 10^{-28}\ \mathrm{m}^2$$

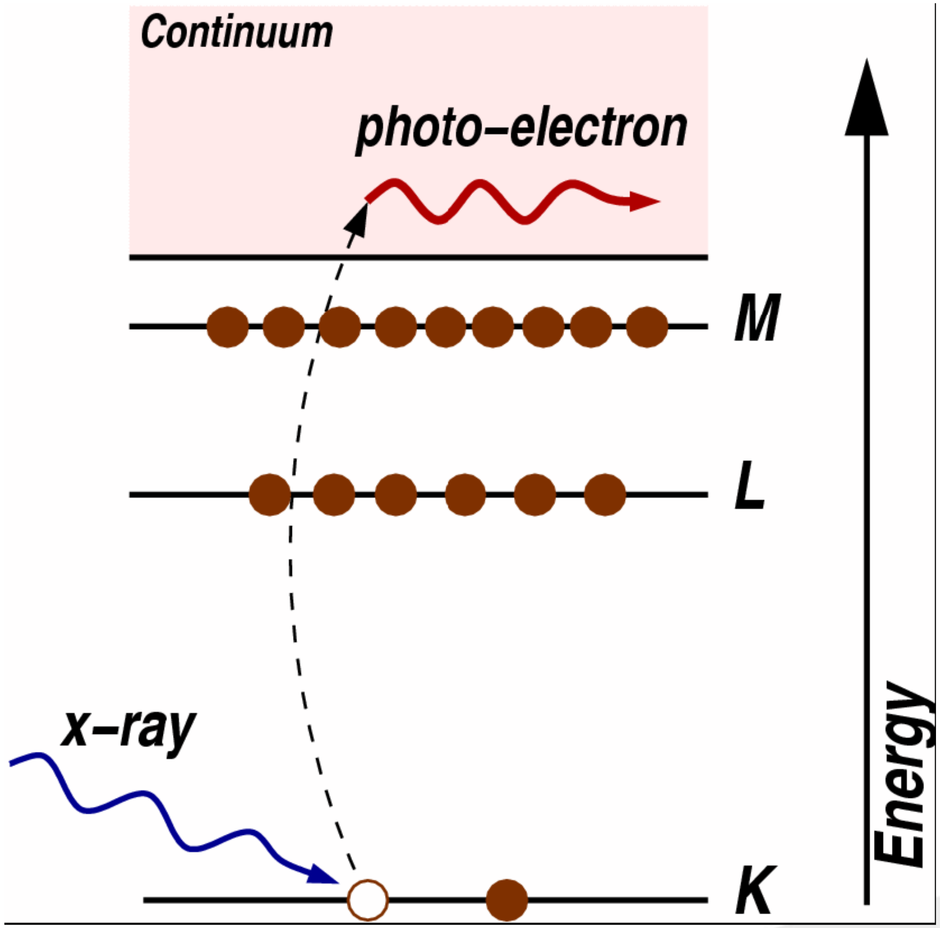
$$\sigma_a\left[\frac{\mathrm{cm}^2}{\mathrm{g}}\right] = \frac{N_A}{A}\,\sigma_a\,[\mathrm{cm}^2] = \frac{\mu}{\rho_m}$$

Photoelectric absorption

- 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*.



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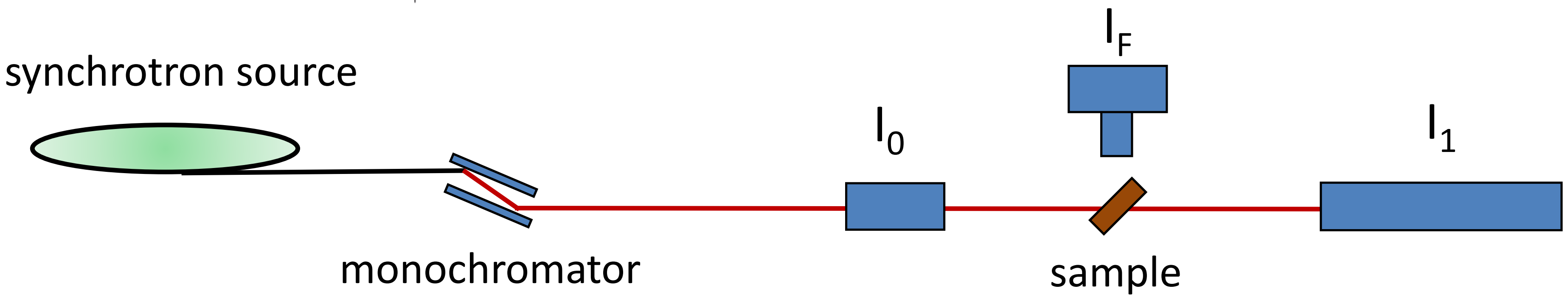
Absorption measurements in real life



Transmission

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

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

$$\mu(E)t = \alpha = \ln I_0/I_1$$

Fluorescence

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

$$\alpha \propto I_F/I_0$$

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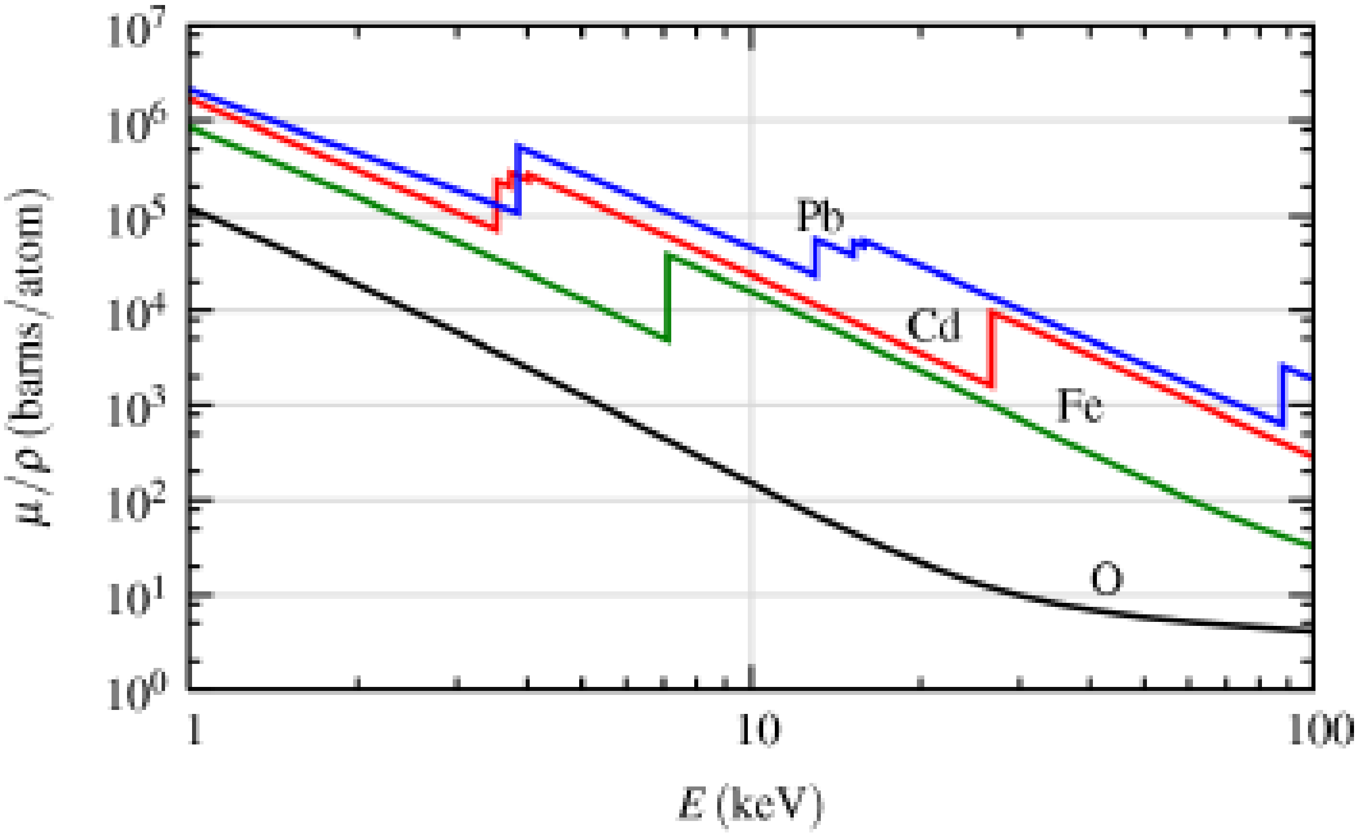
μ vs E and μ vs Z

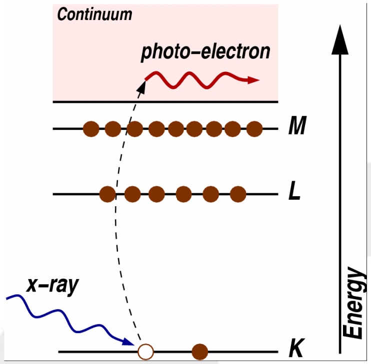
μ depends strongly on:

- x-ray energy E
- atomic number Z
- density ρ
- atomic mass A

$$\mu \approx \frac{\rho Z^4}{AE^3}$$



In addition, μ has sharp *absorption edges* corresponding to the characteristic core-level energy of the atom which originate when the photon energy becomes high enough to extract an electron from a deeper level



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$$\mu \approx \frac{\rho Z^4}{AE^3}$$

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The absorption coefficient

- It is element-specific and a function of the x-ray energy
- It increases with the atomic number of the element ($\propto Z^4$)
- It decreases with increasing photon energy ($\propto E^{-3}$)
- The absorption coefficient is essentially an indication of the electron density in the material and the electron binding energy.
- For instance, if a particular chemical substance can assume different geometric (‘allotropic’) forms and thereby have different densities, will be different accordingly
- Conversely, compounds that are chemically distinct but contain the same number of electrons per formula unit and have similar mass densities will have similar absorption properties (except close to absorption edges).

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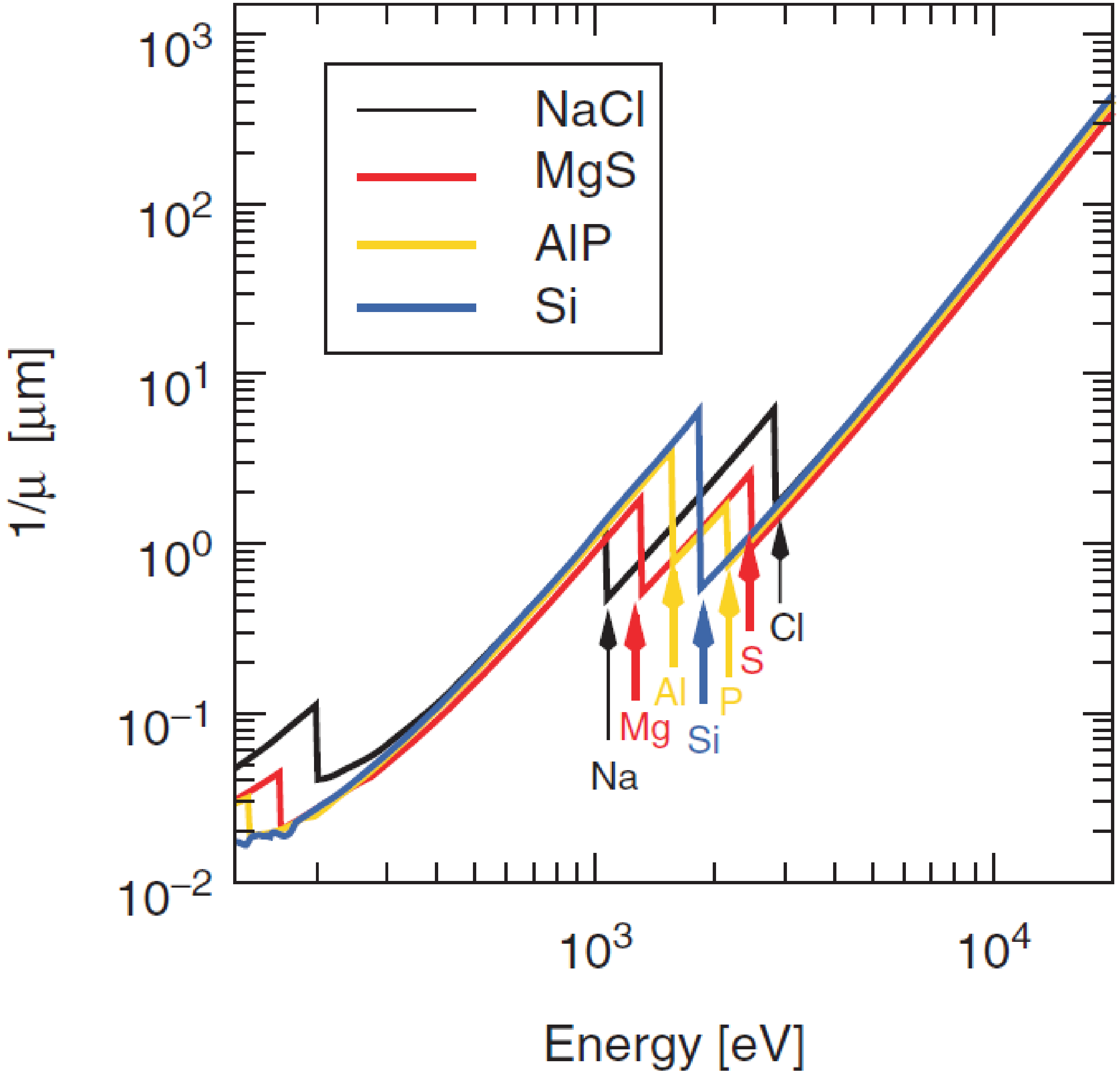
The absorption coefficient



Attenuation length: $1/\mu$

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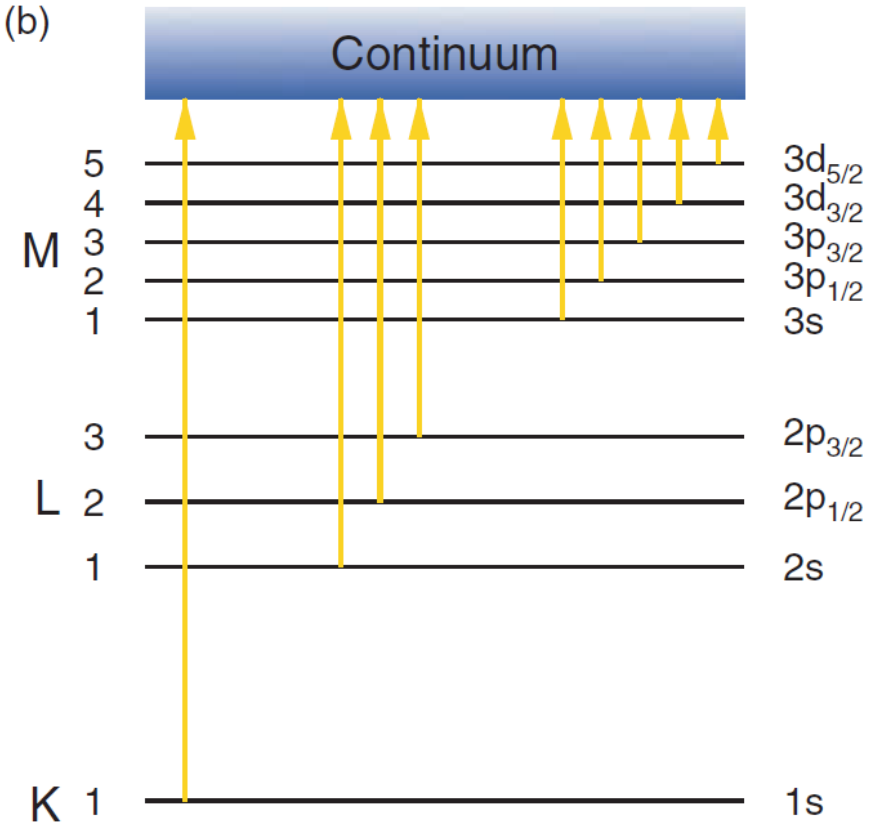
Absorption edges and nomenclature

Table 2.1 *Correspondence between x-ray absorption edges and their electronic configurations.*

Edge	Configuration	Edge	Configuration
K	$1s$	N_1	$4s$
L_1	$2s$	N_2	$4p_{1/2}$
L_2	$2p_{1/2}$	N_3	$4p_{3/2}$
L_3	$2p_{3/2}$	N_4	$4d_{3/2}$
M_1	$3s$	N_5	$4d_{5/2}$
M_2	$3p_{1/2}$	N_6	$4f_{5/2}$
M_3	$3p_{3/2}$	N_7	$4f_{7/2}$
M_4	$3d_{3/2}$	O_1	$5s$
M_5	$3d_{5/2}$	O_2	$5p_{1/2}$



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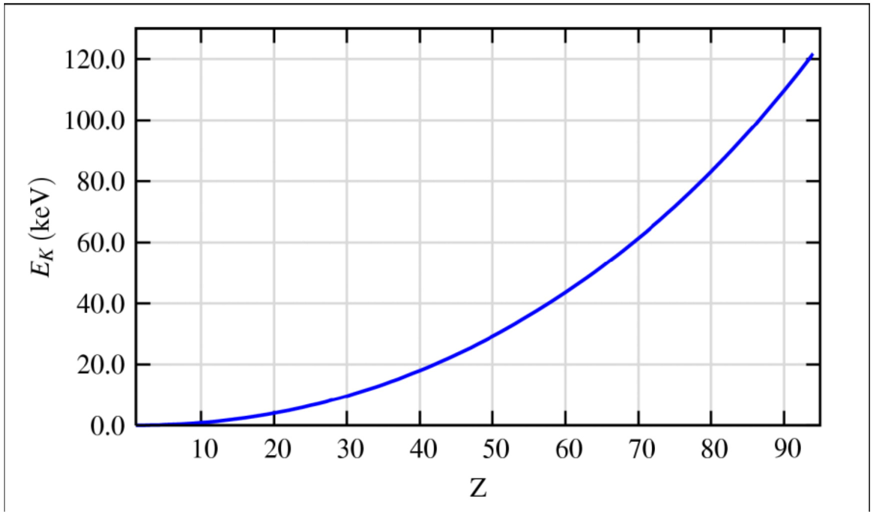
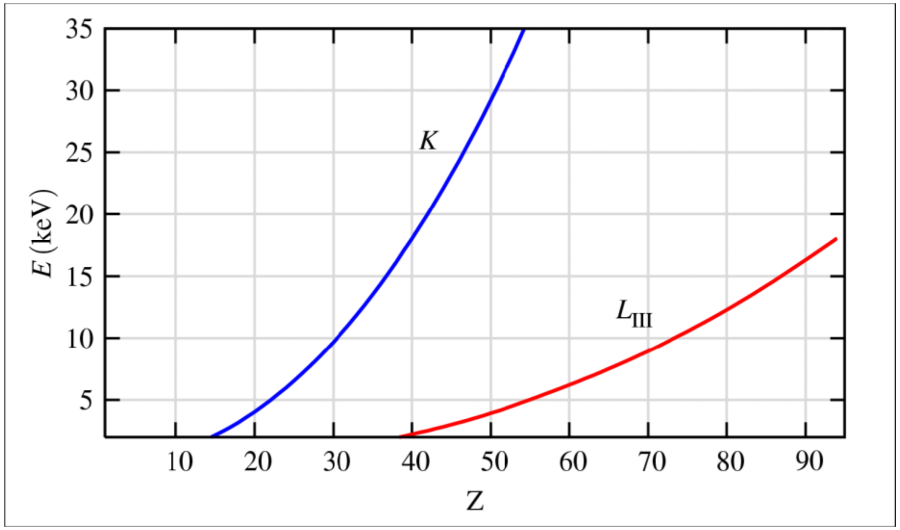
Absorption edge energies

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

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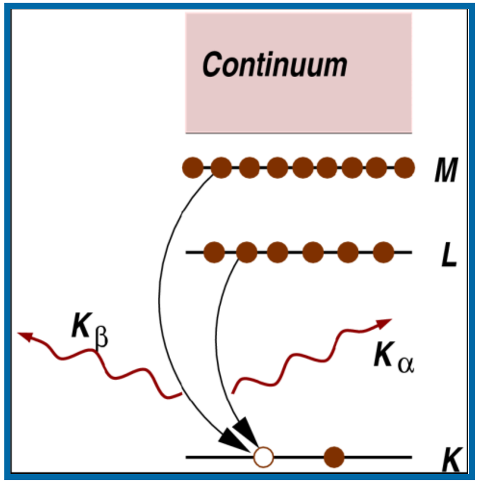
De-excitation process

Absorption → Excited state → Decay to the ground state

Core hole +
photoelectron

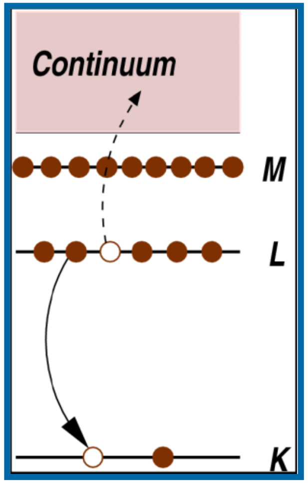
X-ray Fluorescence

An x-ray with energy equal to the difference of the core-levels is emitted



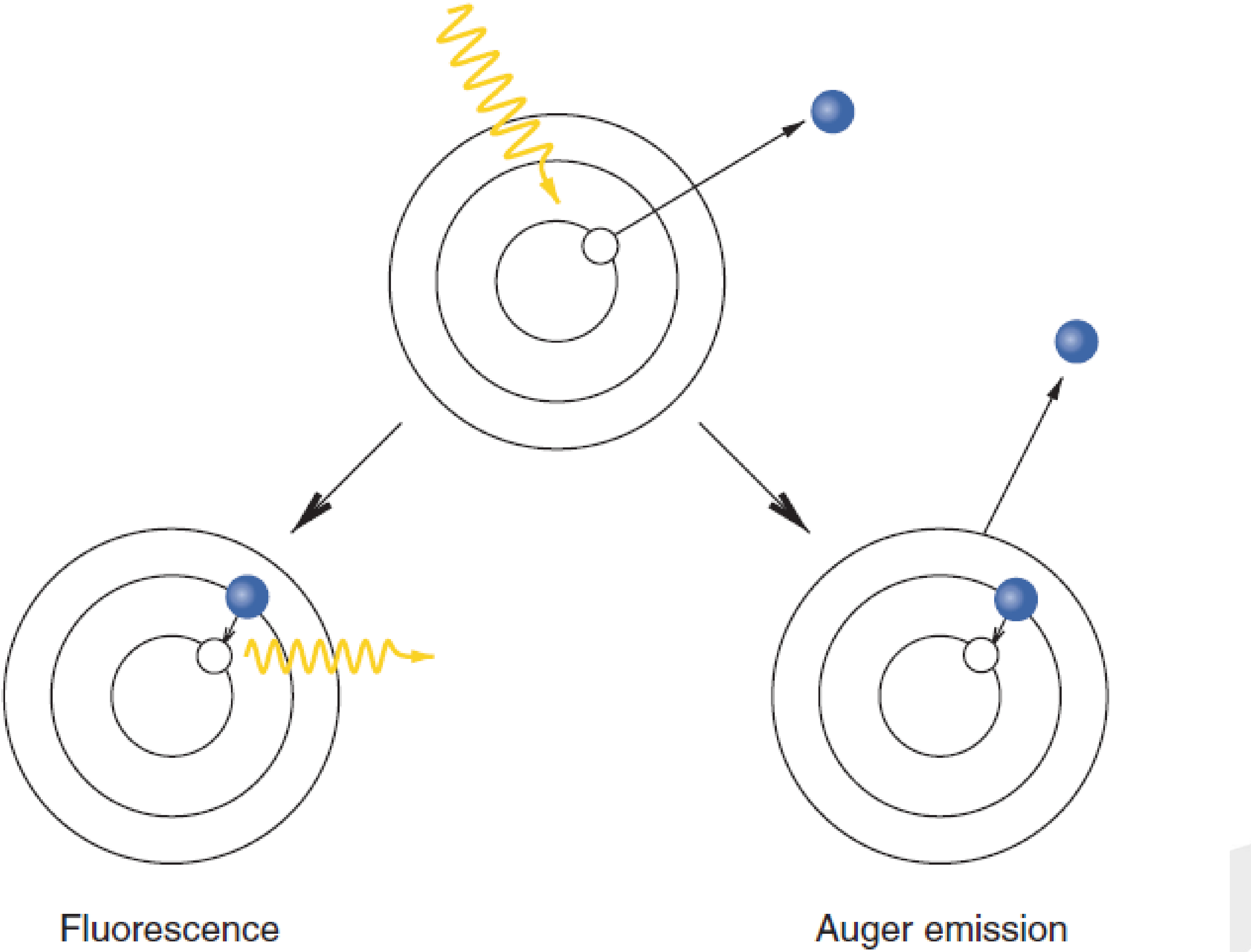
Auger Effect

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

Secondary effects



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X-ray fluorescence

- These characteristic x-ray lines result from the transition of an outer-shell electron relaxing to the hole left behind by the ejection of the photoelectron from the atom.
- This occurs on a timescale of the order of 10 to 100 fs.
- As the energy difference between the two involved levels is well defined, these lines are exceedingly sharp.
- From Heisenberg's uncertainty principle $\Delta E \Delta t \sim \hbar$, the natural linewidth is therefore of the order of 0.01 eV, although this depends on the element and the transition

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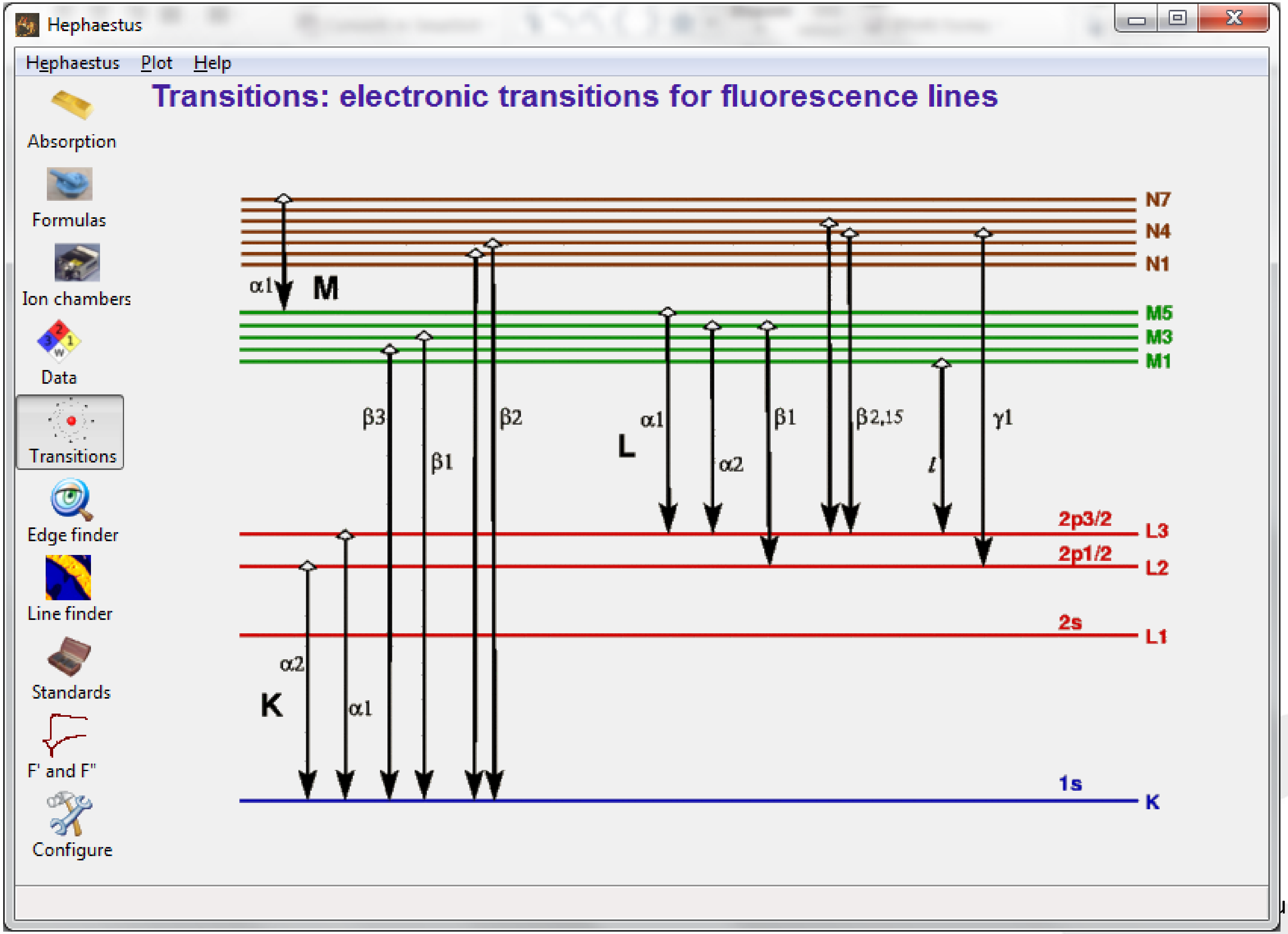
Emission lines nomenclature

$K = 2.47 \times 10^{15}\ \text{Hz}$

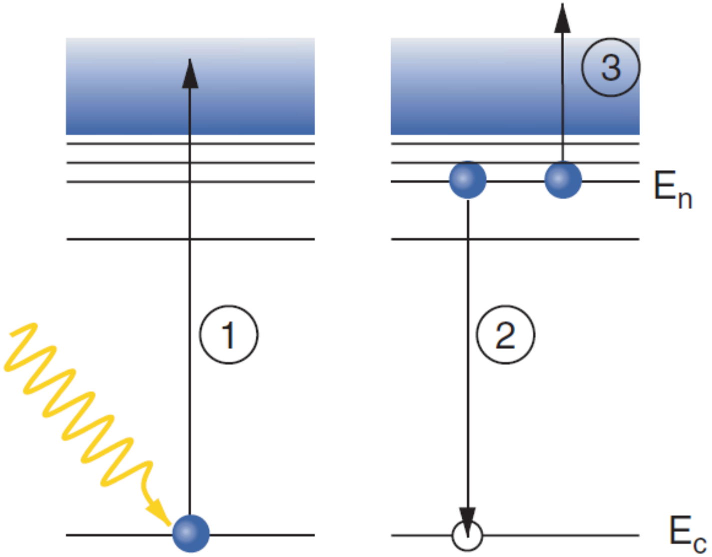
$\nu = \boxed{K}(Z-1)^2$ Characteristic energy of the Kα line (Moseley law)



Transitions: electronic transitions for fluorescence lines

Auger Emission - 1

- It is a three-electron process
- Auger electrons are produced when an outer shell electron relaxes to the core-hole produced by the ejection of a photoelectron.
- The excess energy produced in this process is $|E_c - E_n|$, whereby E_c and E_n are the core- and outer-shell binding energies, respectively
- Instead of being manifested as a fluorescence x-ray photon, the energy can also be channelled into the ejection of another electron if its binding energy is less than the excess energy.



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Auger Emission - 2

- In case the Auger electron comes from the same shell as that of the electron which relaxed to the core-level hole, then the electron energy is $|E_c - 2E_n|$
- More generally, the kinetic energy is $|E_c - E_n - E_m{}'|$, where $E_m{}'$ is the binding energy of the Auger electron. The prime shows that the binding energy of this level has been changed (normally increased) because the electron ejected from this level originates from an already ionized atom.
- Typical Auger electron energies are in the range of 100 to 500 eV which have escape depths of only a few nanometres, hence Auger spectroscopy is very surface sensitive.
- In contrast to photoelectrons, the energies of Auger electrons ($|E_c - E_n - E_m{}'|$) are independent of the incident photon energy, although the amount of Auger electrons emitted is directly proportional to the absorption cross-section in the surface region.

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Fluorescence or Auger?

- Auger-electron emission and x-ray fluorescence are competitive processes
- The rate of spontaneous fluorescence, is proportional to the third power of the energy difference between the upper and lower state. Hence, for a given atom, *K*-emission lines are more probable than *L*-emission
- Fluorescence is stronger for heavier atoms, which have a more attractive positive nuclear charge and therefore a larger energy difference separating adjacent shells

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Fluorescence or Auger?

- The probability of an Auger electron being emitted increases with decreasing energy difference between the excited atom and the atom after Auger emission.
- LMM events are more likely than KLL events.
- Low atomic-number atoms have higher Auger yields than do heavier atoms.
- High atomic-number elements have a large positive charge at the nucleus, which binds electrons more tightly, reducing the probability of Auger emission

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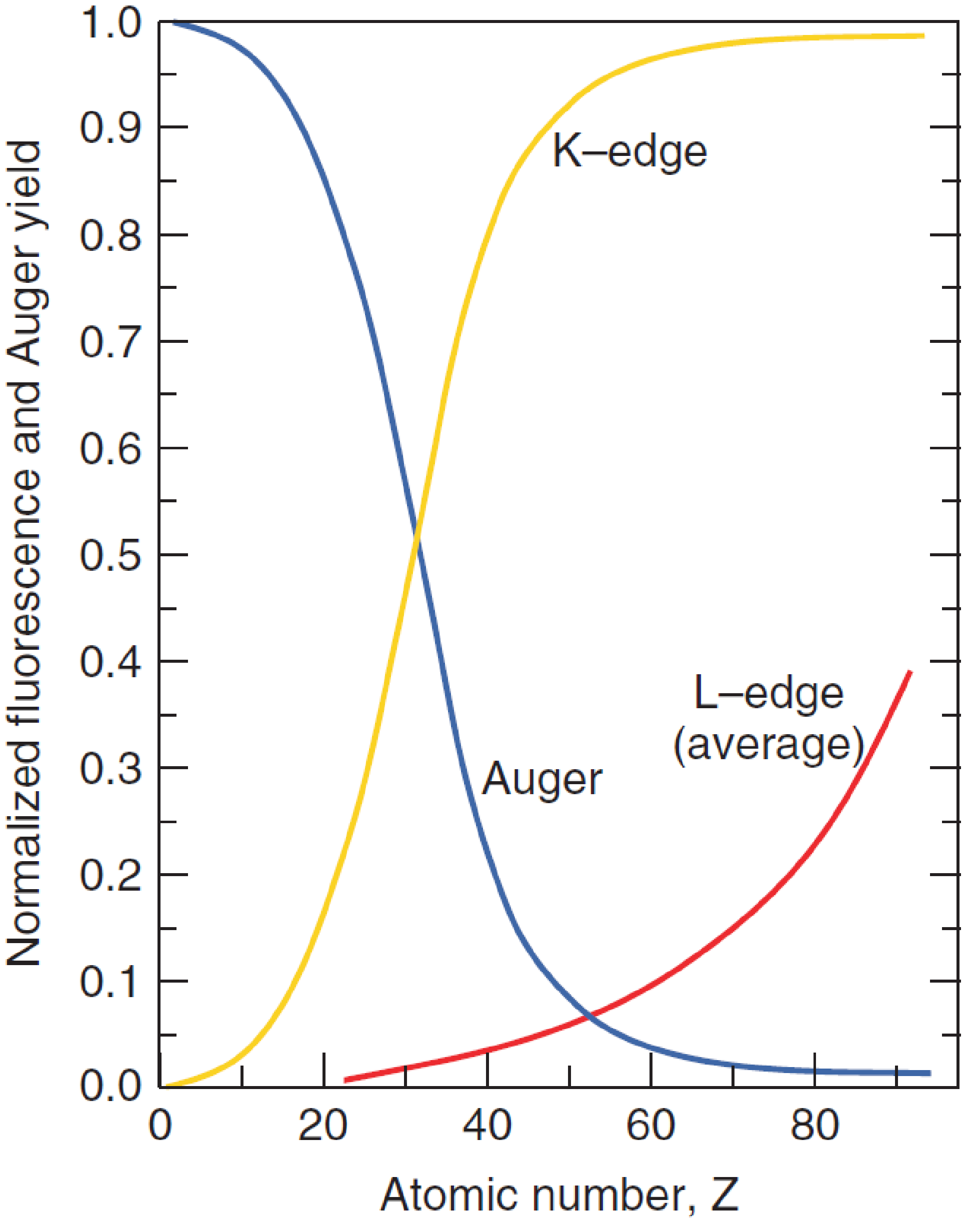
Fluorescence or Auger?



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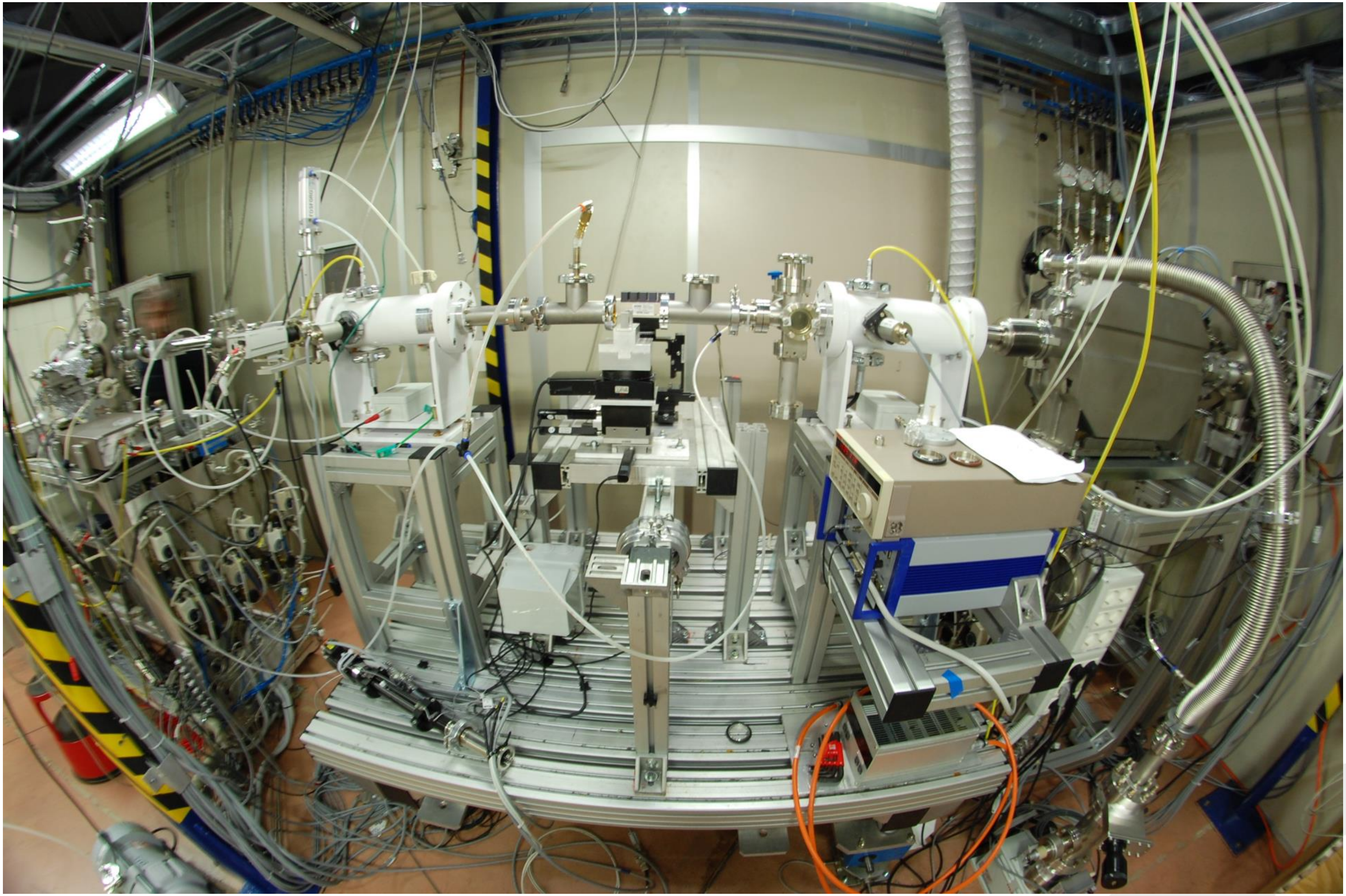
XAFS at Elettra



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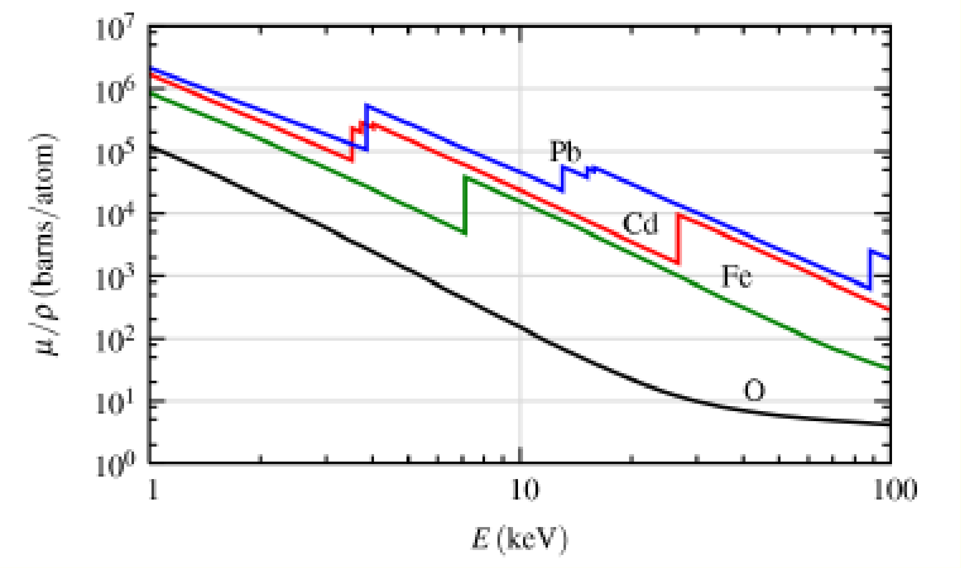
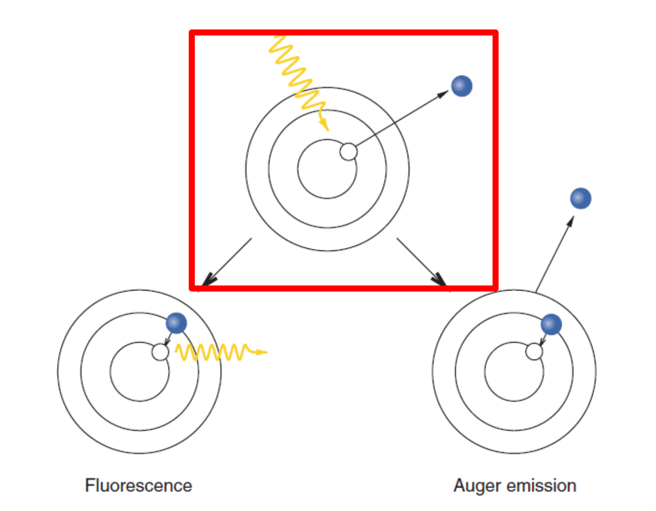
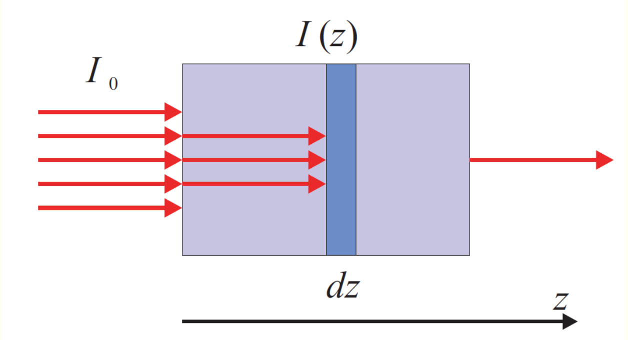
Summary Absorption



$$\mu \approx \frac{\rho Z^4}{AE^3}$$





$$ln\frac{I_0}{I} = \mu z$$

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X-ray absorption fine structure

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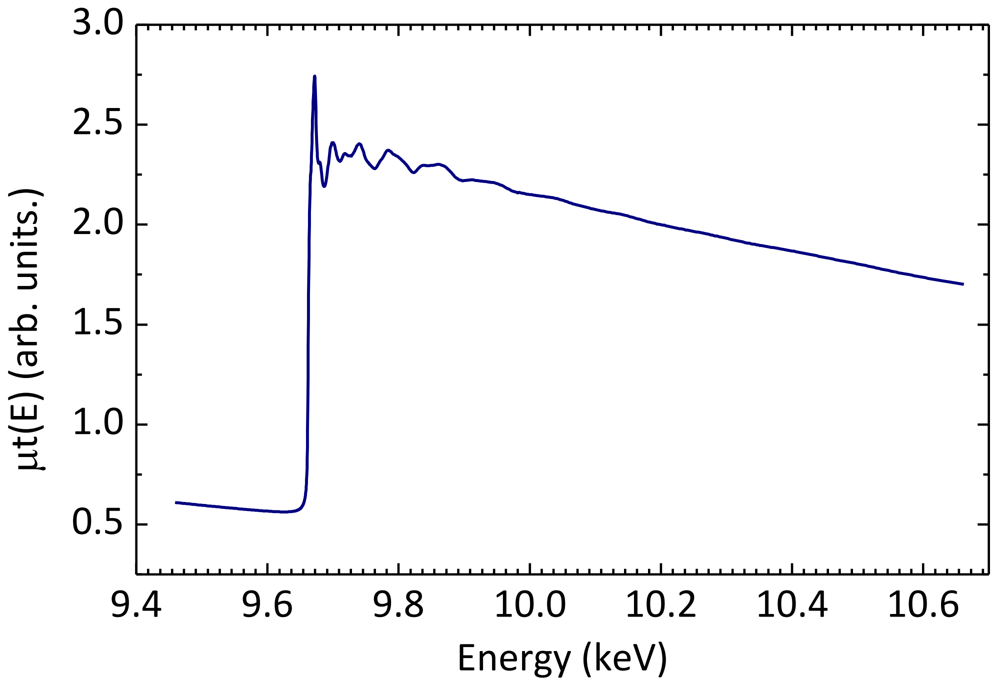
X-ray Absorption Fine Structure



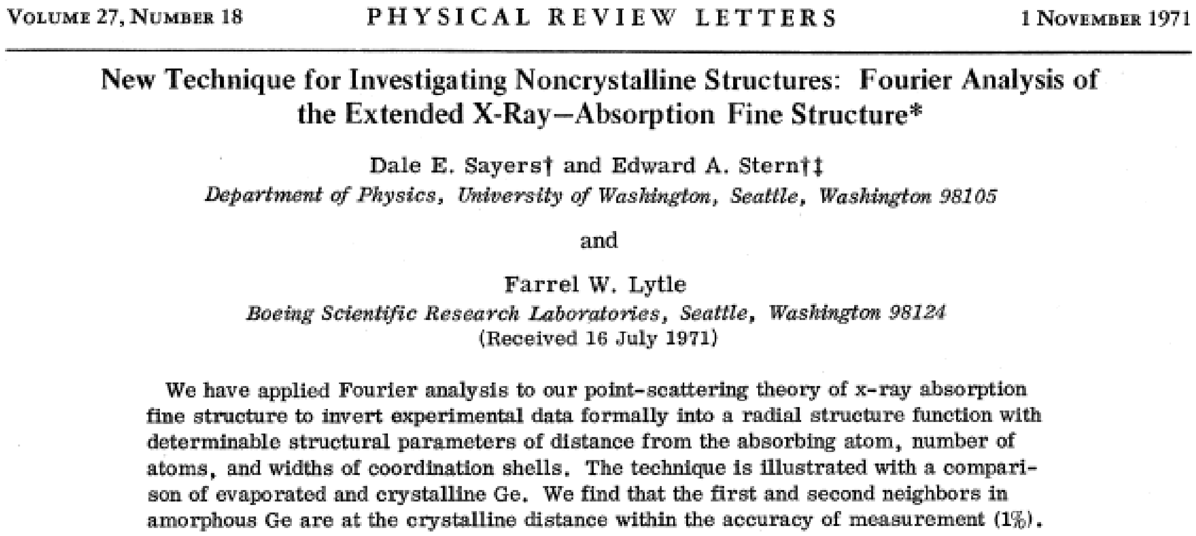
What? Oscillatory behaviour of the of the x-ray absorption as a function of photon energy beyond an absorption edge

When? Non isolated atoms

Why? Proximity of neighboring atoms strongly modulates the absorption coefficient

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



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

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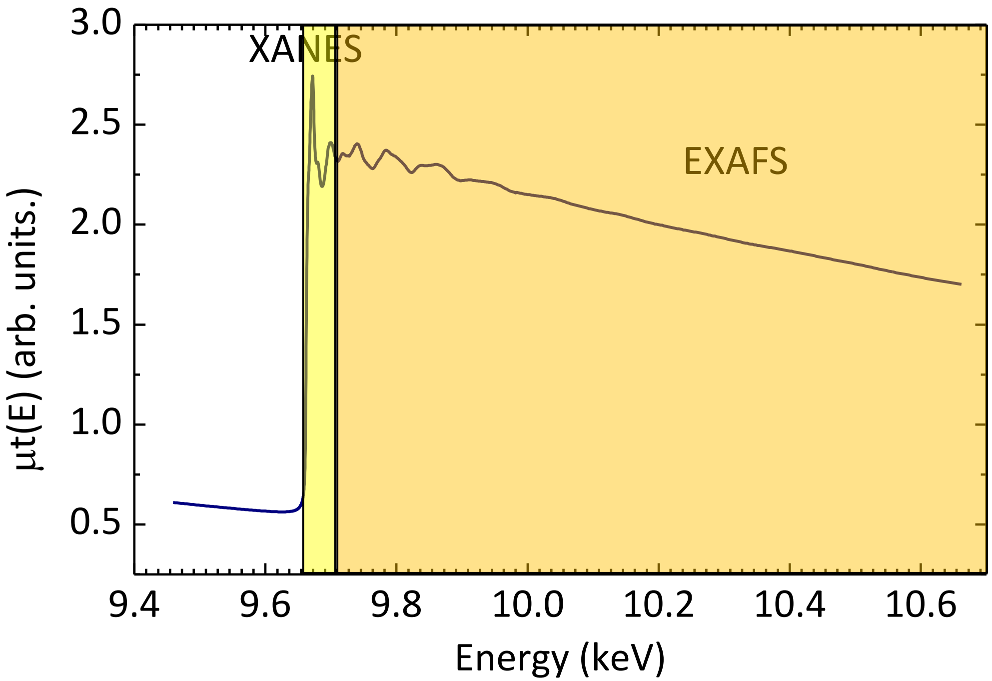
(Received 16 July 1971)

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 - 1



X-ray
Absorption
Near
Edge
Structure

up to ~ 60 eV
above the edge

Extended
X-ray
Absorption
Fine
Structure

from ~ 60 eV
to 1200 eV
above the edge

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XANES and EXAFS - 2

XANES ⇦ same physical origin ⇨ EXAFS

transitions to
unfilled bound states,
nearly bound states,
continuum

⇩

- Oxidation state
- Coordination chemistry (tetrahedral, octahedral) of the absorbing atom
- Orbital occupancy

transitions to
the continuum

⇩

- Radial distribution of atoms around the photoabsorber (bond distance, number and type of neighbours)

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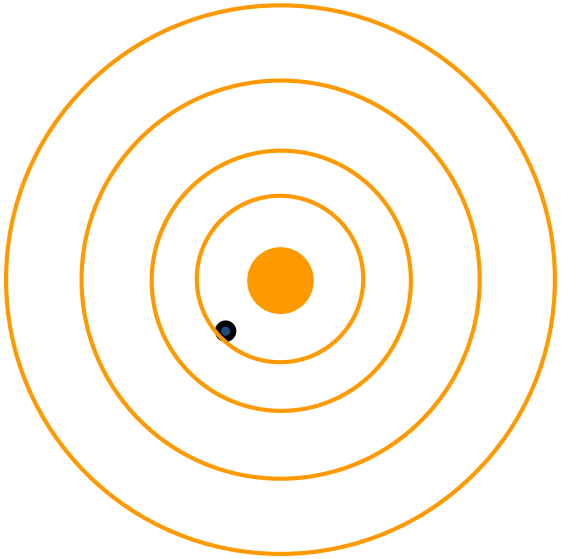
EXAFS qualitatively – isolated atom



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

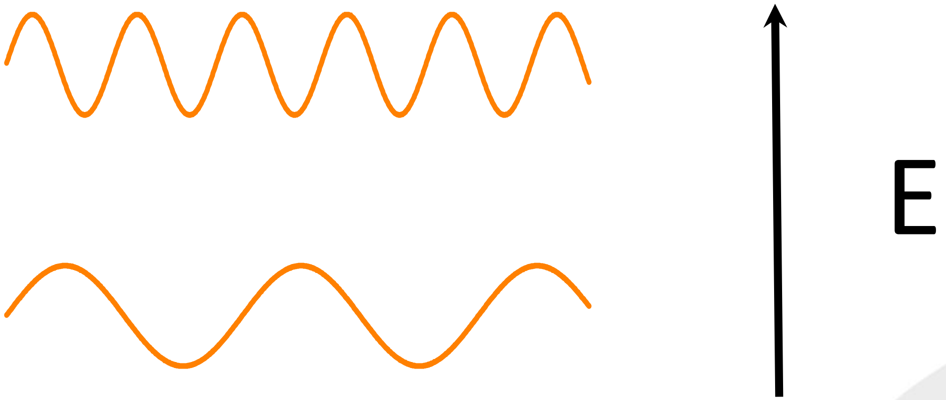
$$E_k = E_{h\nu} - E_0 = \frac{p^2}{2m} = \frac{(\hbar k)^2}{2m}$$ Kinetic energy of the p.e.

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

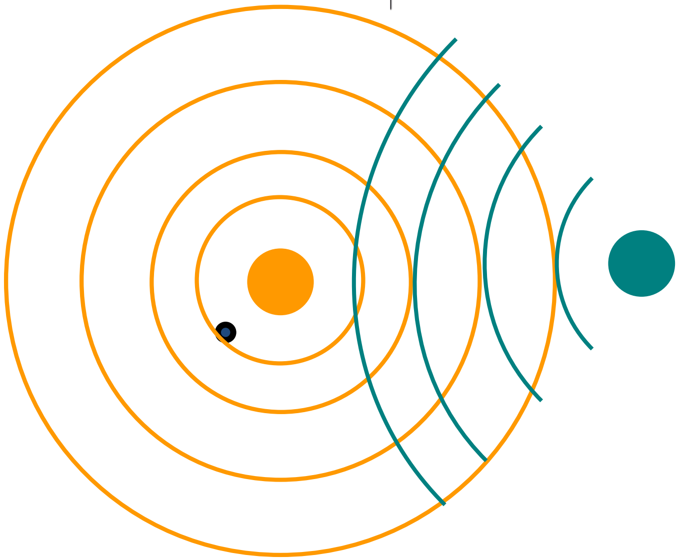
$$\lambda = 2\pi/k$$ wavelength of the p.e.

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

$$\lambda \propto 1/E - E_0$$

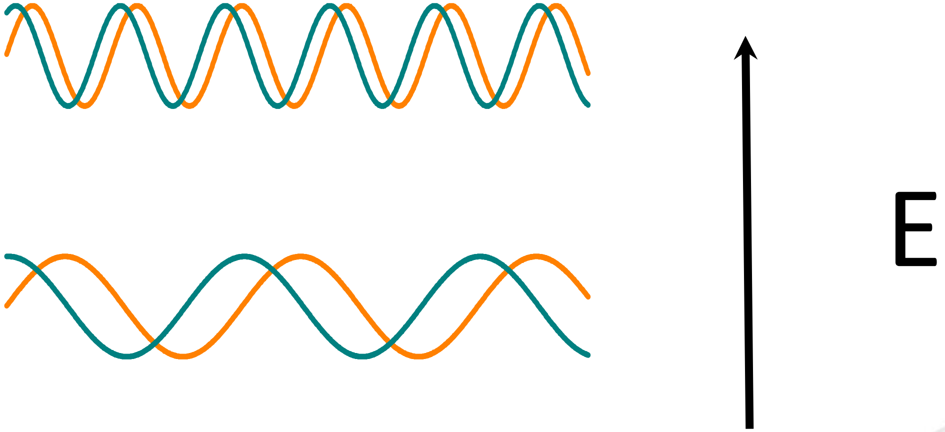


EXAFS qualitatively – condensed matter



- The photoelectron can scatter from a neighbouring atom giving rise to an incoming spherical wave coming back to the absorbing atom
- The outgoing and ingoing waves may interfere

$$\lambda \propto 1/E - E_0$$



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Origin of the fine structure (oscillations)

- The interference between the outgoing and the scattering part of the photoelectron at the absorbing atom changes the probability for an absorption of x-rays i.e. alters the absorption coefficient μ(E) that is no longer smooth as in isolated atoms, but oscillates.
- In the extreme of destructive interference, when the outgoing and the backscattered waves are completely out of phase, they will cancel each other, which means that no free unoccupied state exists in which the core-electron could be excited to.
- Thus absorption is unlikely to occur and the EXAFS oscillations will have a minimum.
- The phase relationship between outgoing and incoming waves depends on photoelectron wavelength (and so on the energy of x-rays) and interatomic distance R.
- The amplitude is determined by the number and type of neighbours since they determine how strongly the photoelectron will be scattered

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Which information

Frequency of the oscillations

⇩

Distance from neighbours

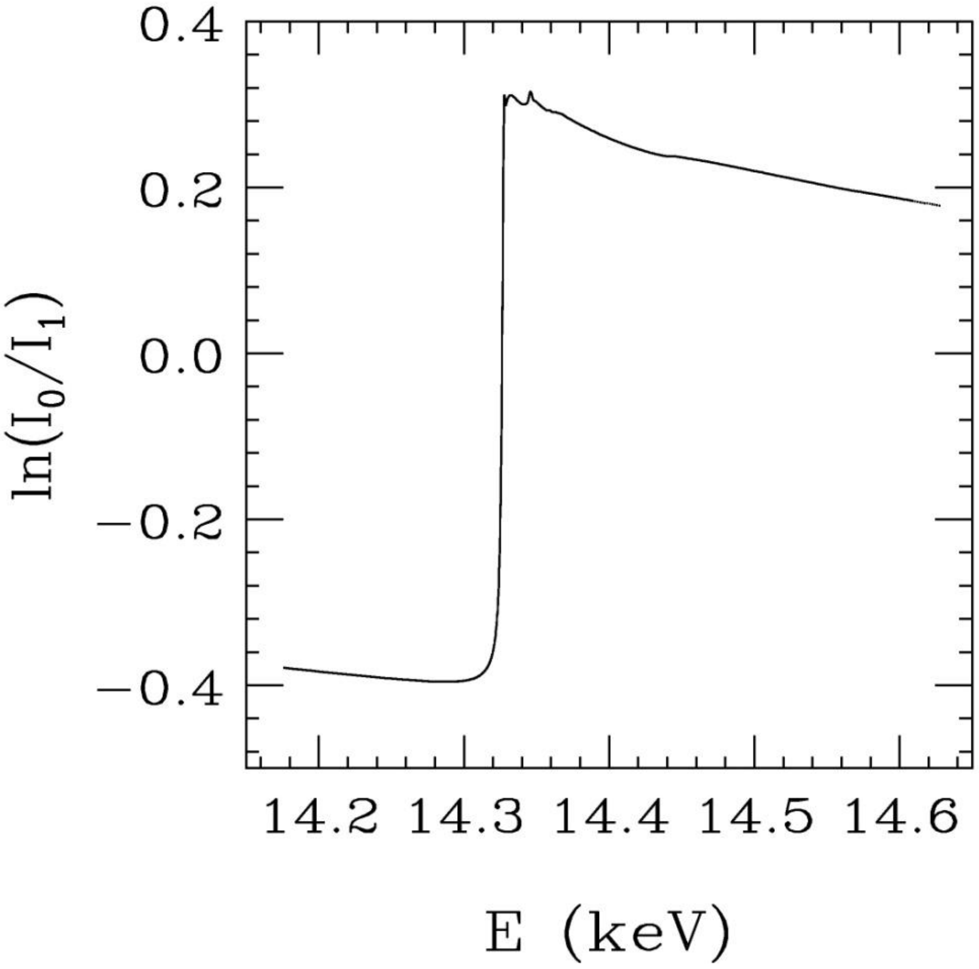
Amplitude of the oscillations

⇩

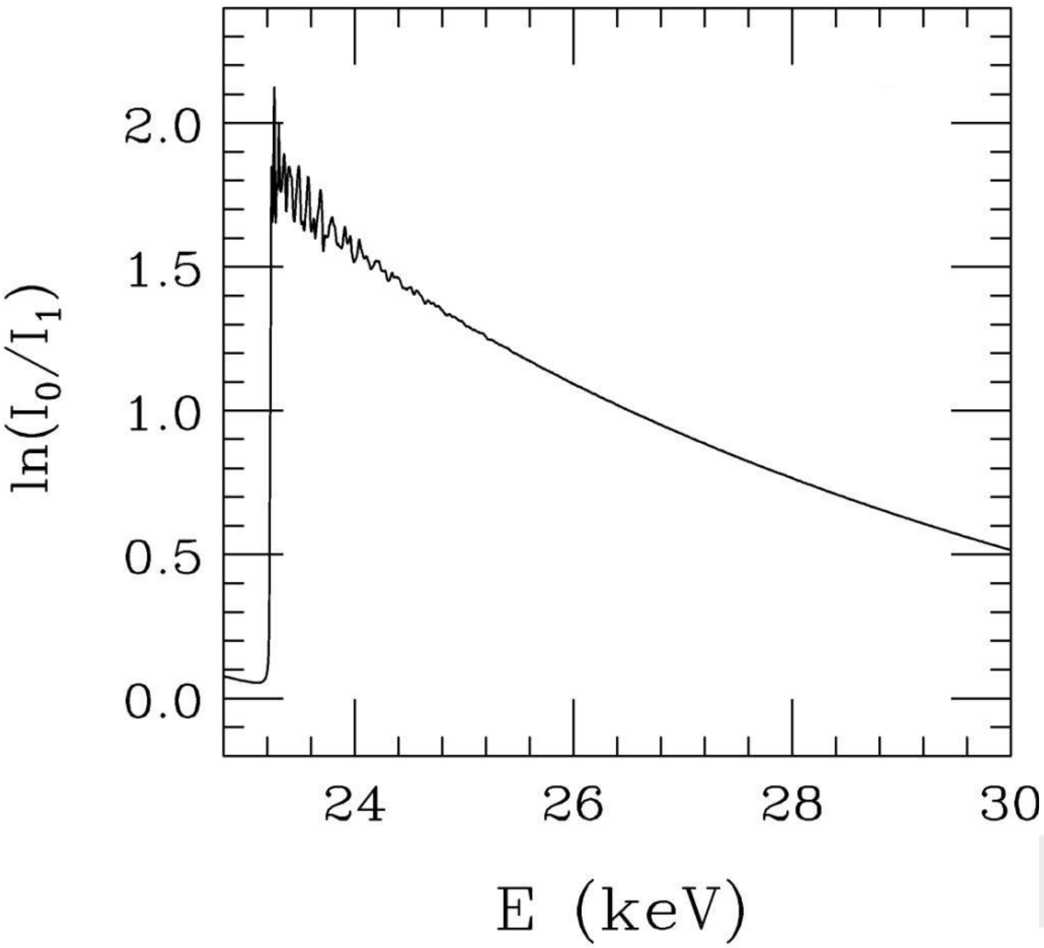
Number and type of neighbours

Some spectra

Kr gas



Rh metal



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Fermi’s Golden rule

According to the time dependent perturbation theory, the Fermi’s Golden rule gives the transition rate (probability of transition per unit time) per unit volume between an initial and a final eigenstate due to a perturbation

$$w_{fi} = \frac{2\pi}{\hbar} \left|\langle \Psi_f | \mathcal{H}_{int} | \Psi_i \rangle\right|^2 \rho(E_f)$$

$$\mu = -\frac{1}{I}\frac{dI}{dz} = \sum_f \frac{2\pi c}{\omega^2 {A_0}^2} N\hbar\omega w_{fi}$$

Density of final states compatible with the energy conservation Ef=Ei+$\hbar\omega$

Sum over all final states

Number of microscopic absorbing element per unit volume

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Absorption process

$$\mu \propto \sum_f \left|\langle \psi_f | \hat{\boldsymbol{\varepsilon}} \cdot \boldsymbol{r} | \psi_i \rangle\right|^2 \rho(E_f)$$

photon polarization

Electron position

|i› : initial state of energy E_i

- core electron (*e.g.* 1s electron wave function)
- very localized
- NOT altered by the presence of the neighboring atoms

<f| : final state of energy $E_f = E_i + \hbar\omega$

- core hole + photoelectron
- multibody process
- altered by neighbouring atoms

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Initial and final states

Wavefunction of the initial state:

$|i>= Y_{l_0,m_0}(\hat{\mathbf{r}})R^0_{l_0}(r)$ Where l_0 angular momentum of the electron

$Y_{l0,m0}$ spherical harmonic functions

(solution of the angular part of the Schrödinger equation)

For the final state a potential must take into account that the electron moves in the condensed matter

Muffin Tin Potential

Spherical regions centered on each atom in which the potential has a spherical symmetry. Wavefunctions described by a radial + angular part

Interstitial region with a constant potential. Wavefunctions described by plane waves

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Dipole selection rules

The dipolar selection rules determine the transition from the initial to the final state

$$\boxed{\begin{aligned} \Delta\ell &= \pm 1 \\ \Delta s &= 0 \\ \Delta j &= \pm 1, 0 \\ \Delta m &= 0 \end{aligned}}$$

EDGE	INITIAL STATE	FINAL STATE
K, L_1	s (ℓ=0)	p (ℓ=1)
L_2, L_3	p (ℓ=1)	s (ℓ=0), d (ℓ=2)

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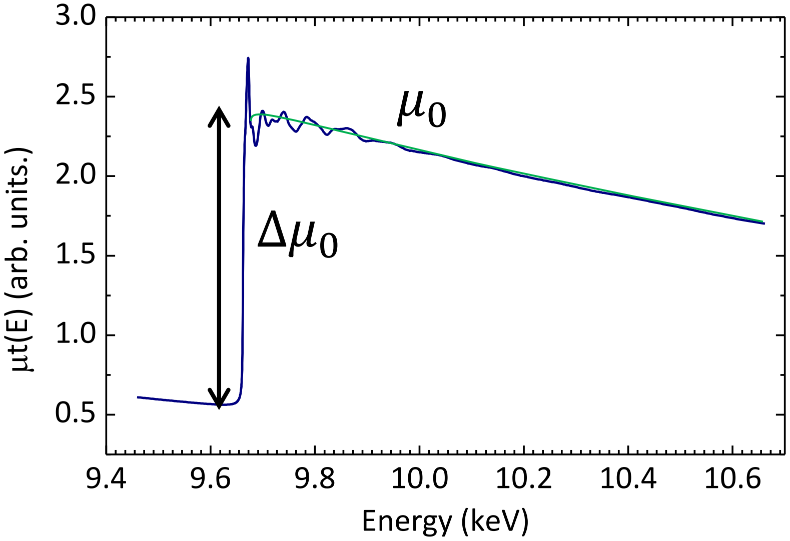
The EXAFS signal $\chi(k)$ - 1

- The EXAFS signal is generally espressed as a function of the wavevector of the photoelectron $k = \sqrt{[2m(E_{h\nu} - E_0)/\hbar^2]}$
- The oscillatory part of the spectrum contains the structural information
- We define the EXAFS function as $\chi(k) = \frac{\mu - \mu_0}{\Delta\mu_0}$



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

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

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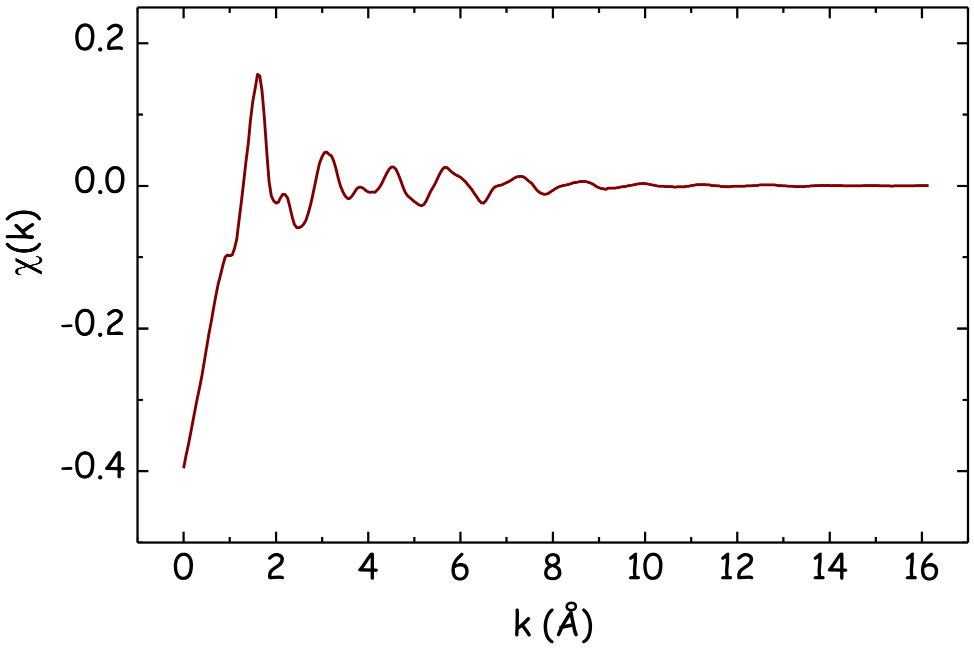
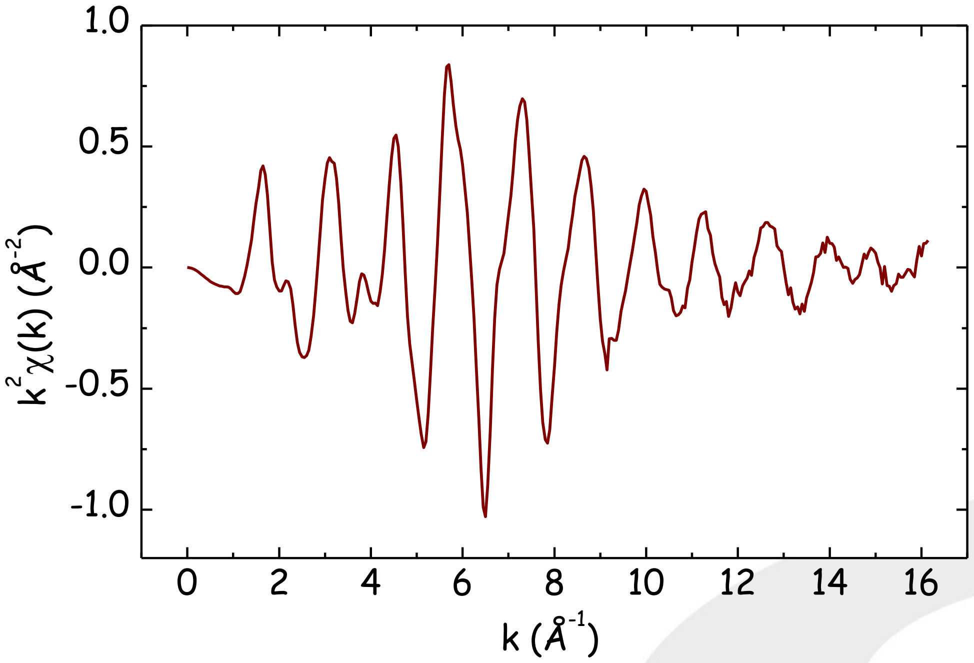
The EXAFS signal $\chi(k)$ - 2

XAFS originates from an *interference effect*,
and depends on the wave-nature of the photoelectron.

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





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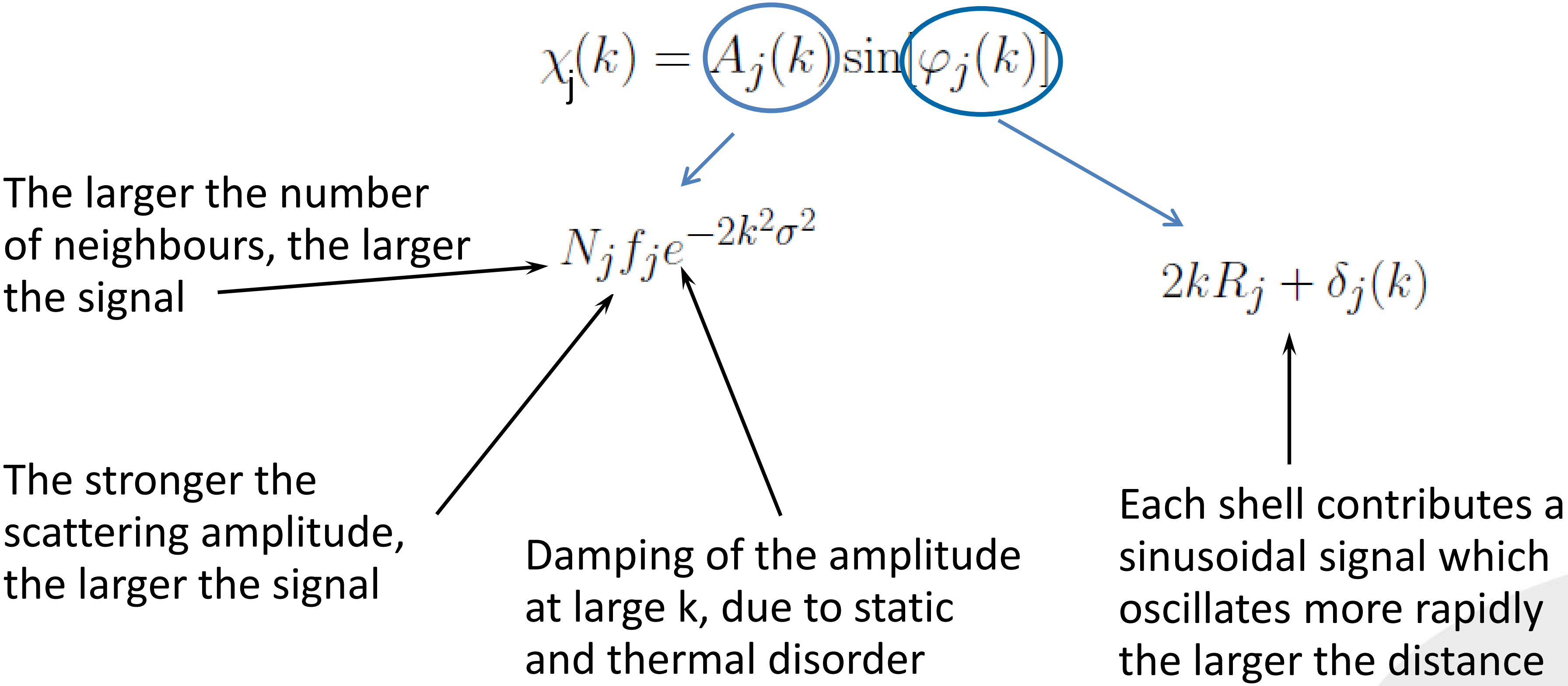
$\chi(k)$: sum of damped waves

χ(k) is the sum of contributions **χ**$_j$(k) from backscattered wavelets:

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

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



$$\chi_j(k) = \boxed{A_j(k)} \sin\left[\boxed{\varphi_j(k)}\right]$$

$$N_j f_j e^{-2k^2\sigma^2}$$

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

The larger the number of neighbours, 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

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EXAFS formula

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

$f(k)$ scattering amplitude

$\delta_j(k)$ phase-shift

} scattering properties of the atoms neighbouring the photoabsorber (depend on the atomic number)

R Distance to the neighbouring atom

N Coordination number of the neighbouring atom

σ^2 Disorder in the neighbouring distance

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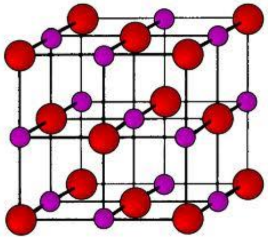
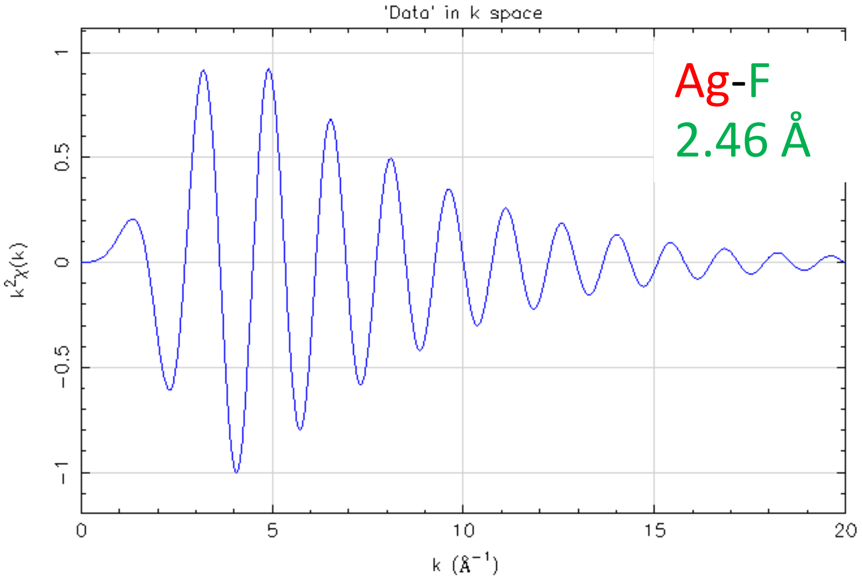
Amplitudes

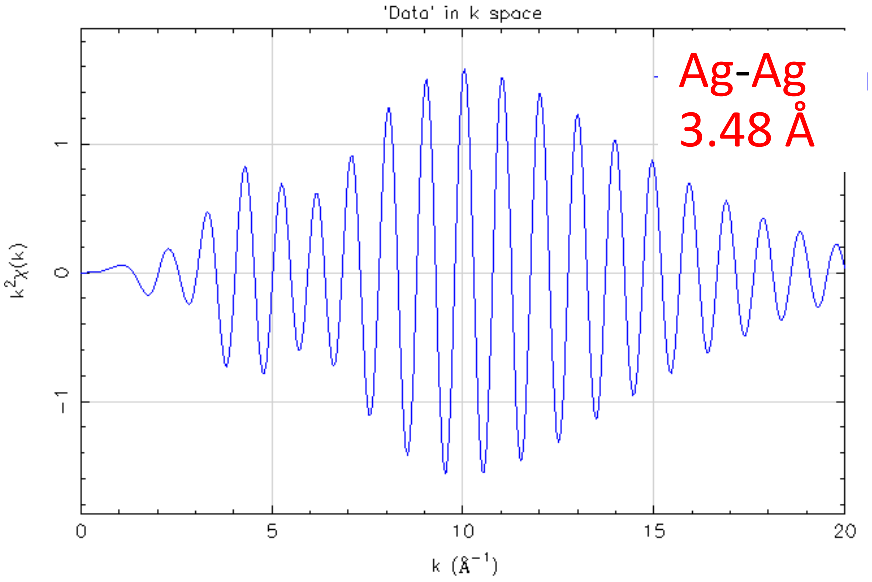
The shape of the envelope of each wave is indicative of the nature of backscatterer atom

AgF (rocksalt structure)





Ag-F
2.46 Å

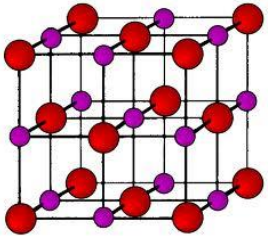


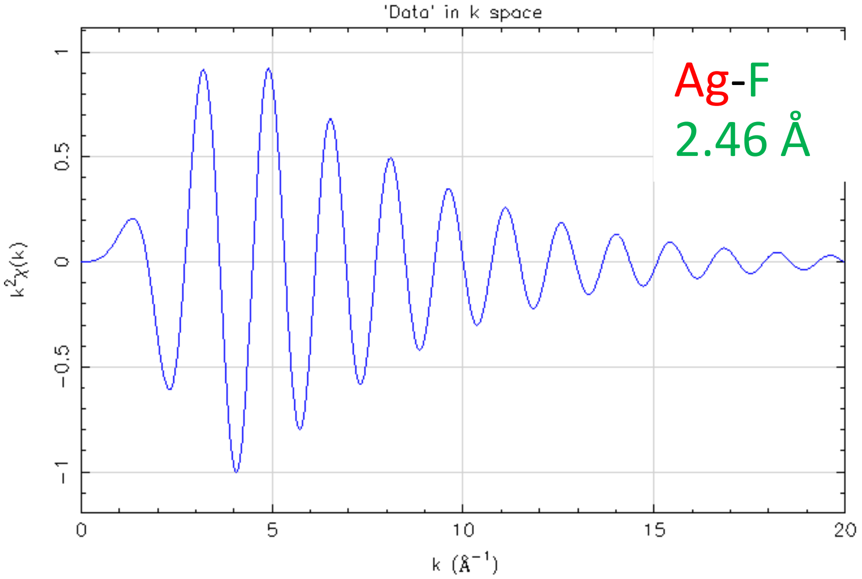
Ag-Ag
3.48 Å

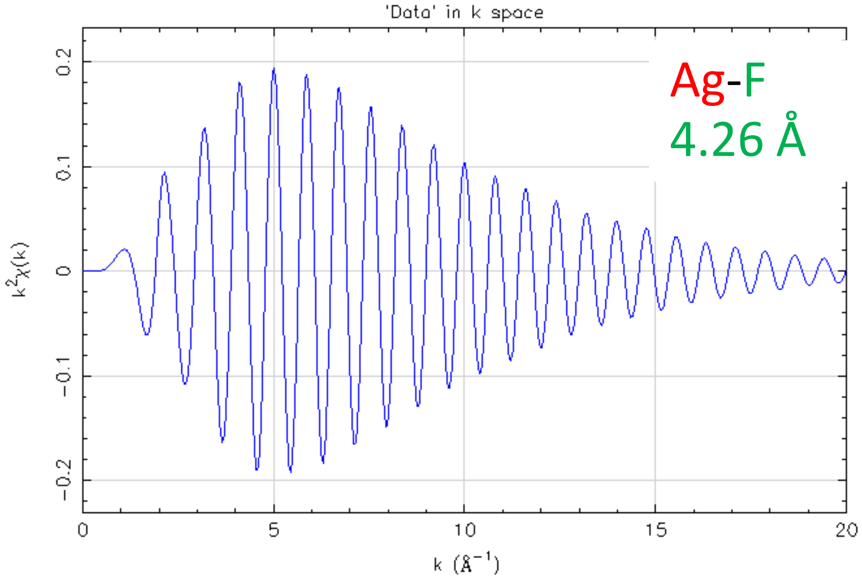
Frequencies

The frequency of the single wave, for the same atomic pair, is indicative of the distance of the backscatterer atom (the lower the frequency the closer the neighbour)

AgF (rocksalt structure)

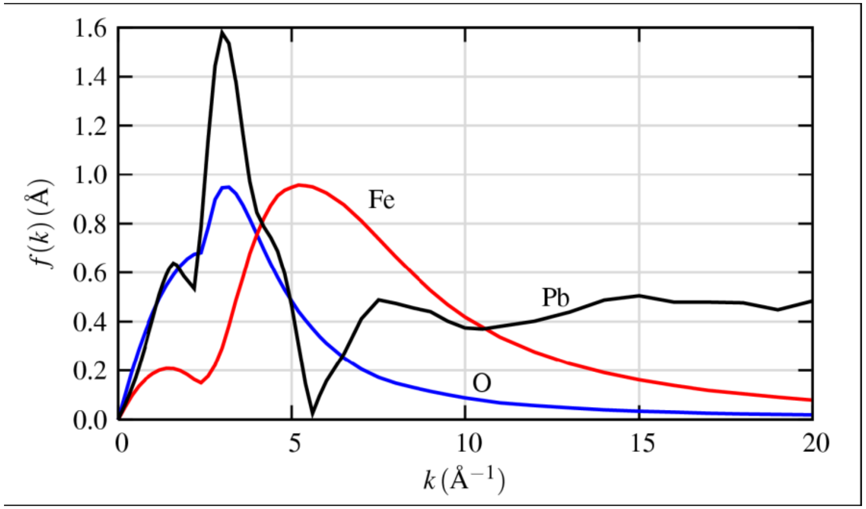


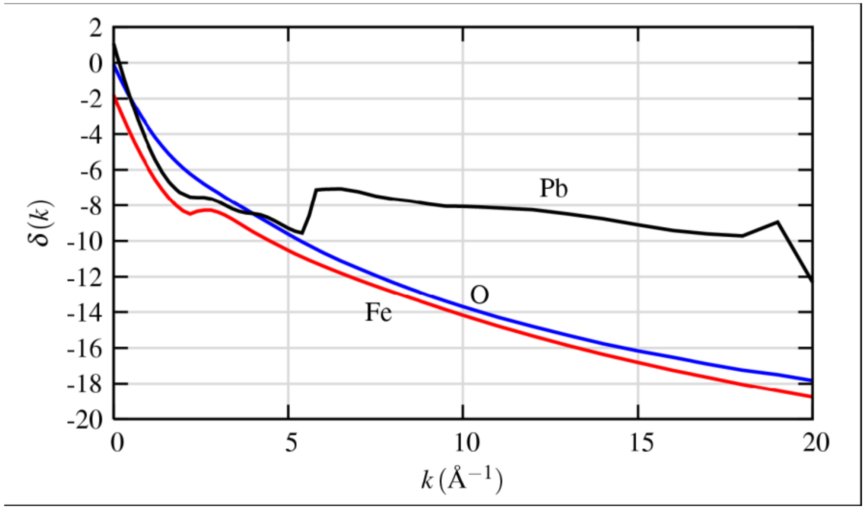




Scattering amplitude and phase shift: F(k) and δ(k)

The scattering amplitude F(k) and phase shift δ(k) depend on the 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 δ(k) shows sharp changes for very heavy elements.

These scattering functions can be accurately calculated 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

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Multiple scattering

Multiple scattering events may occur

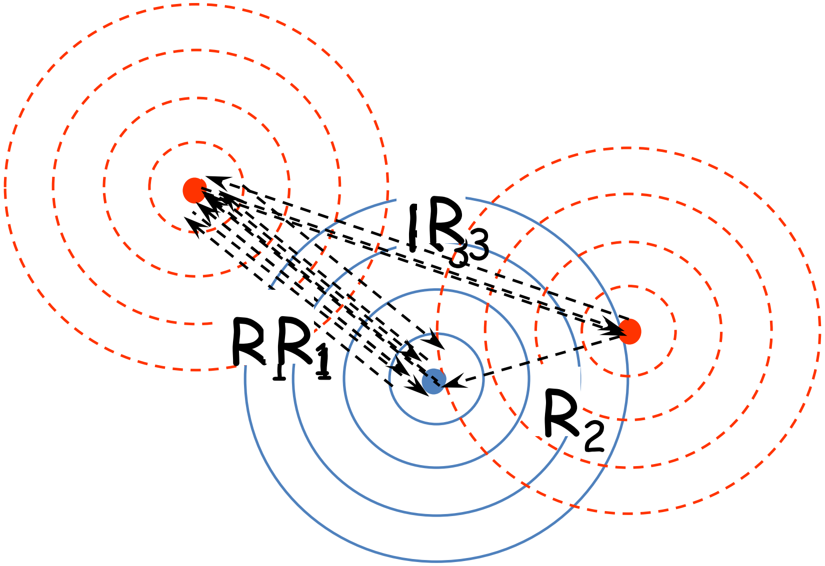
The photoelectron scatter from more than one atom before returning to the central atom

SS ⇨ $g_2(r)$
$f = 2\ R_1$

MS ⇨ $g_2(r)$
$f = 4\ R_1$

MS ⇨ $g_3(r)$
$f = R_1 + R_2 + R_3$

MS ⇨ $g_3(r)$
$f = 2R_1 + 2R_3$



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

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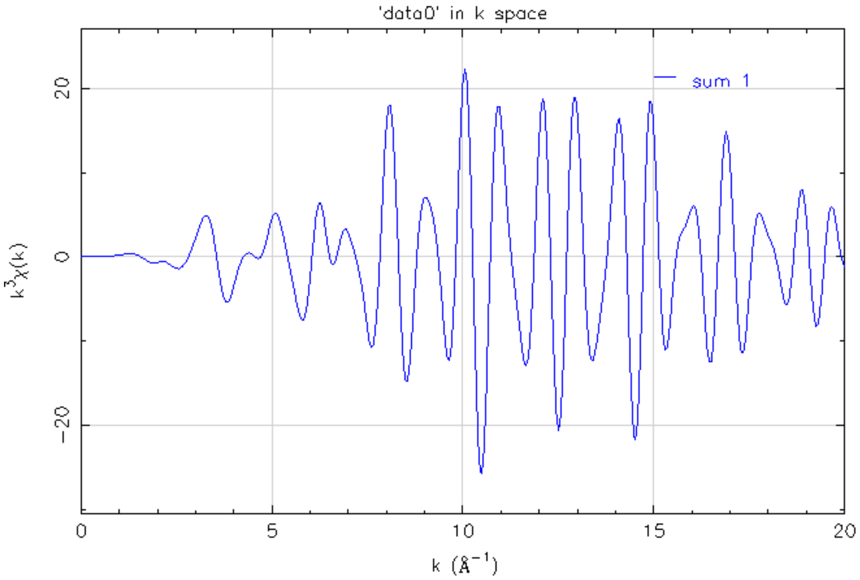
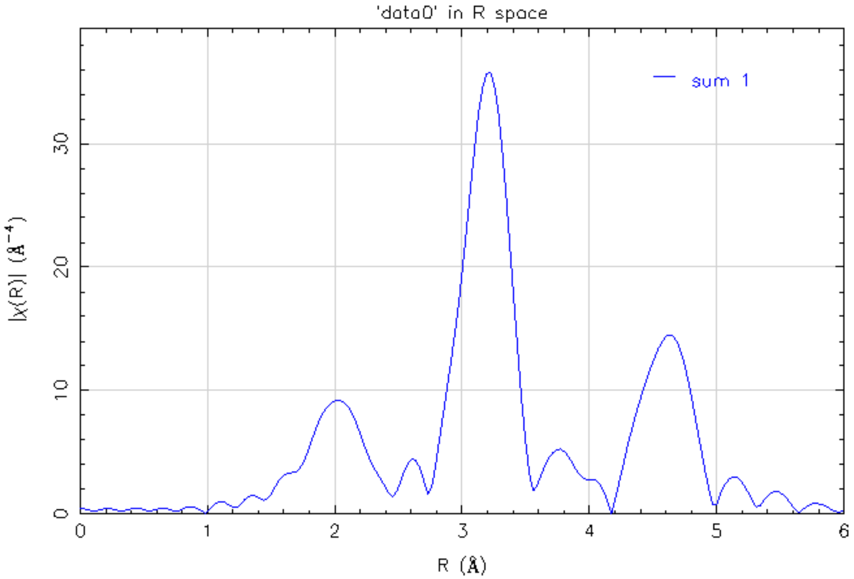
Qualitative picture of local coordination in R space

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

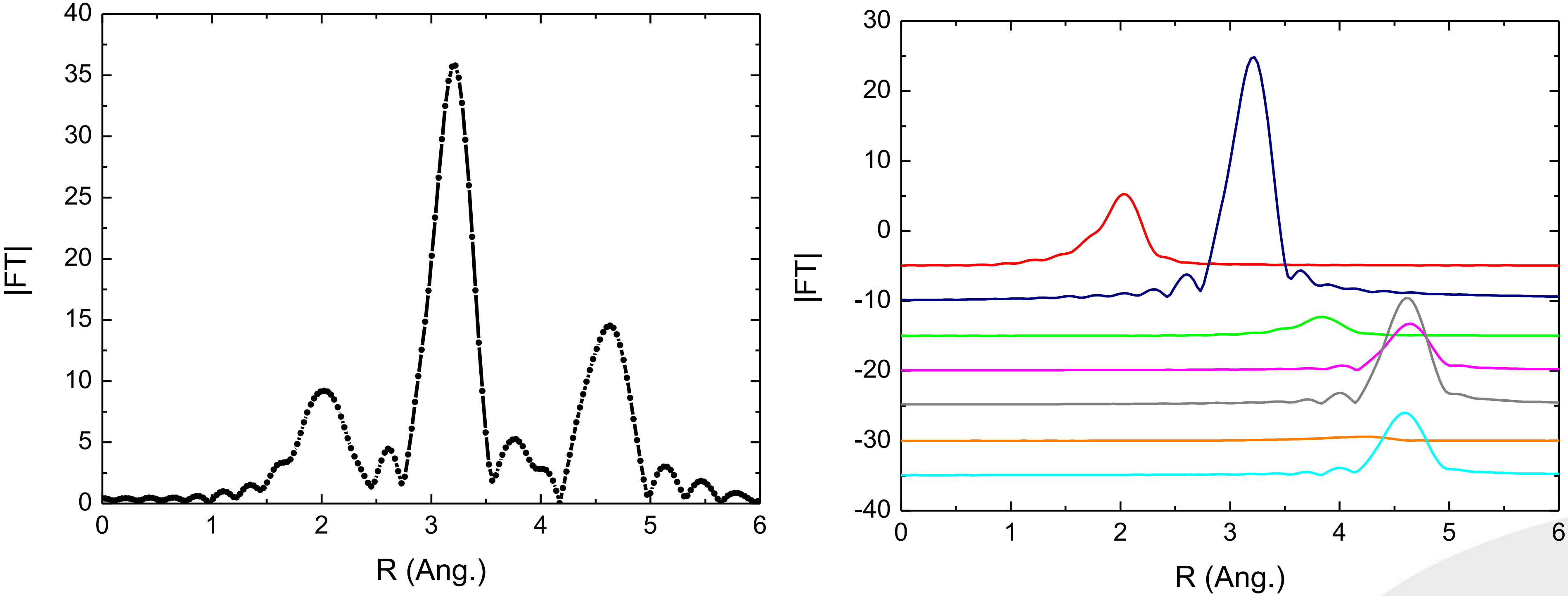
A Fourier Transform of the EXAFS signal provides a photoelectron scattering profile as a function of the radial distance from the absorber.





Quantitative structural determination

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



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XAS vs diffraction methods

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 RDF containing interatomic distances due to all atomic pairs in the sample

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

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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

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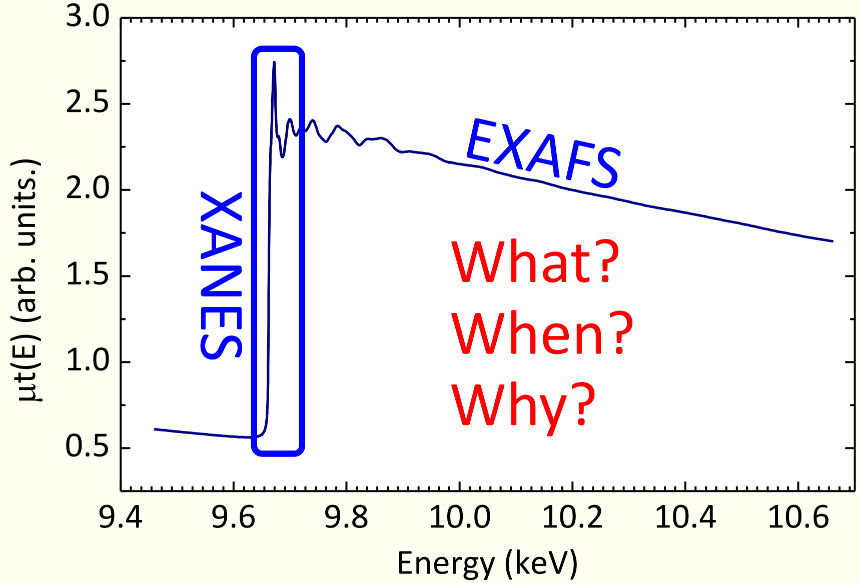
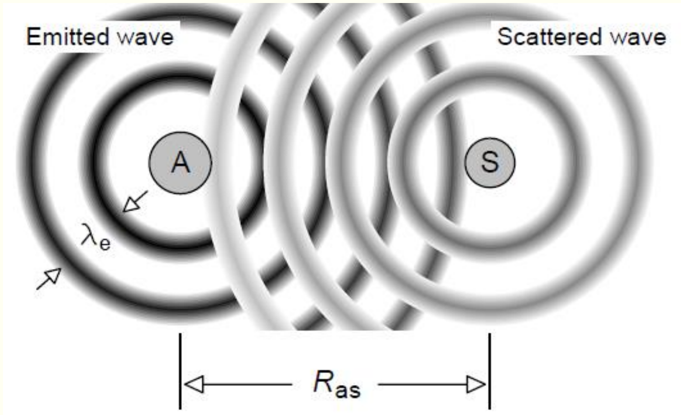
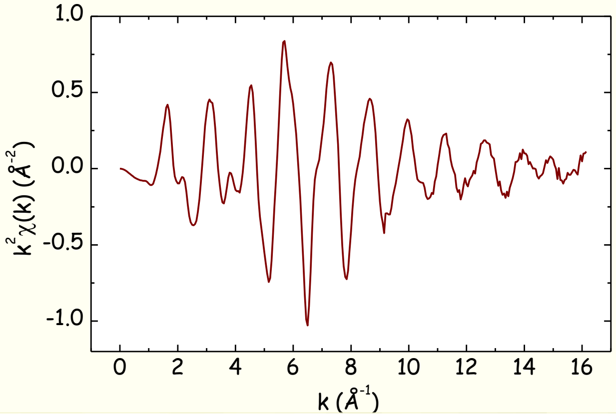
Summary X-ray absorption fine structure







$$\chi(k) = \sum_j \frac{N_j S_0^2 f_j(k) e^{-2R_j/\lambda(k)} e^{-2k^2\sigma_j^2}}{kR_j{}^2} \sin[2kR_j + \delta_j(k)]$$

- Chemical selectivity
- Local structure
- Electronic structure
- Same degree of accuracy independently of the aggregation state

XANES

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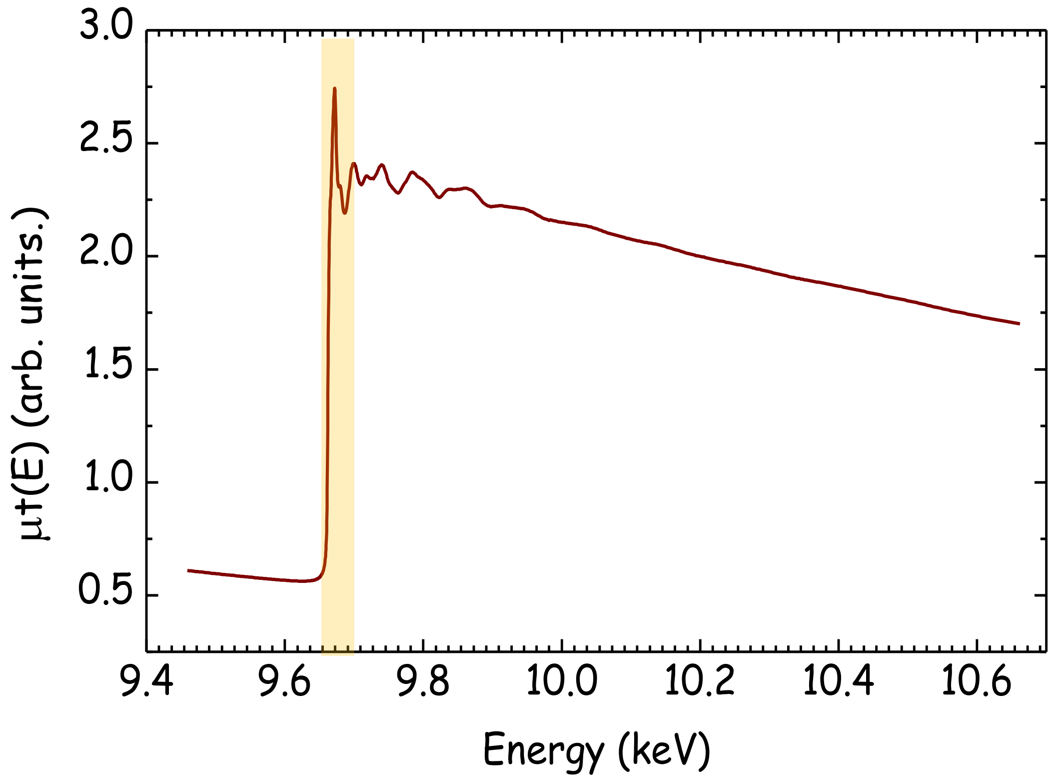
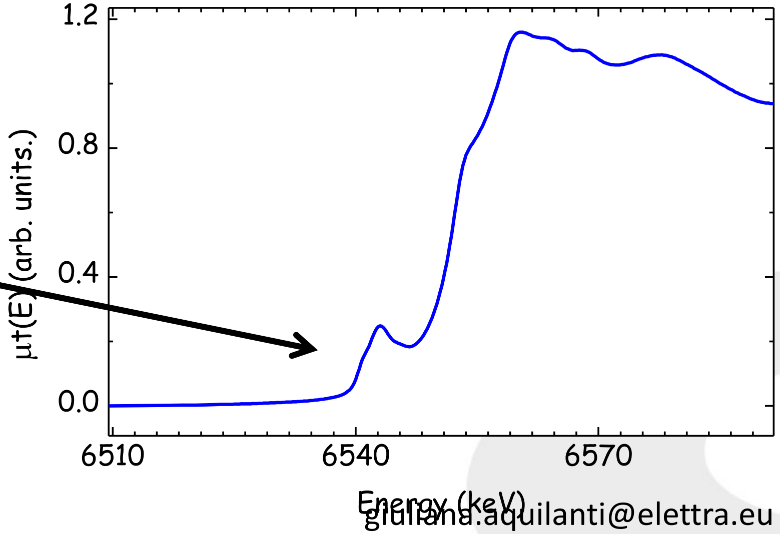
XANES



XANES is the region of the absorption spectrum within ~ 60 eV of the absorption edge

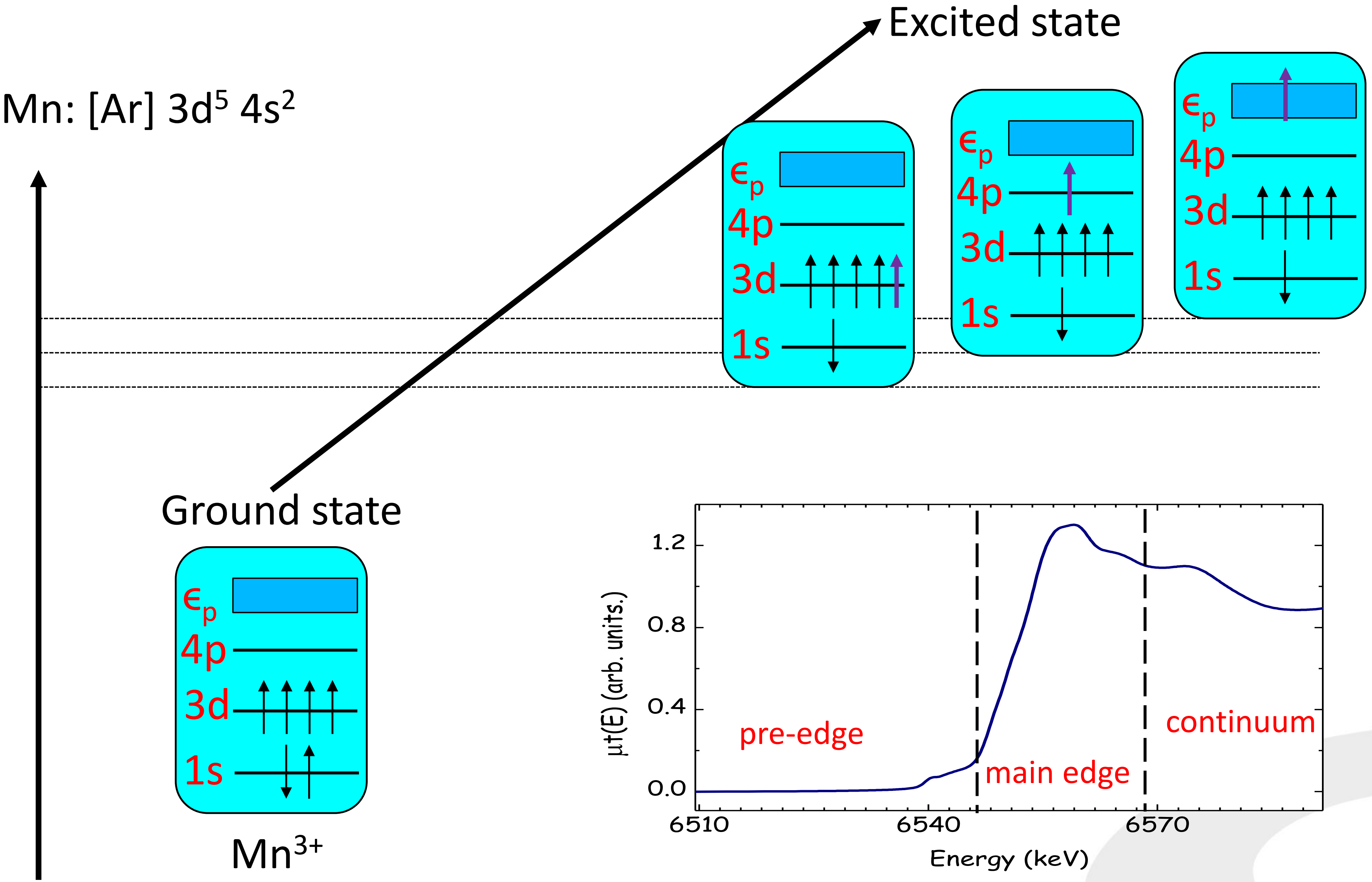
X-ray
Absorption
Near
Edge
Structure

XANES includes also the “pre-edge features” if any



K-edge XANES

Mn: [Ar] $3d^5\ 4s^2$



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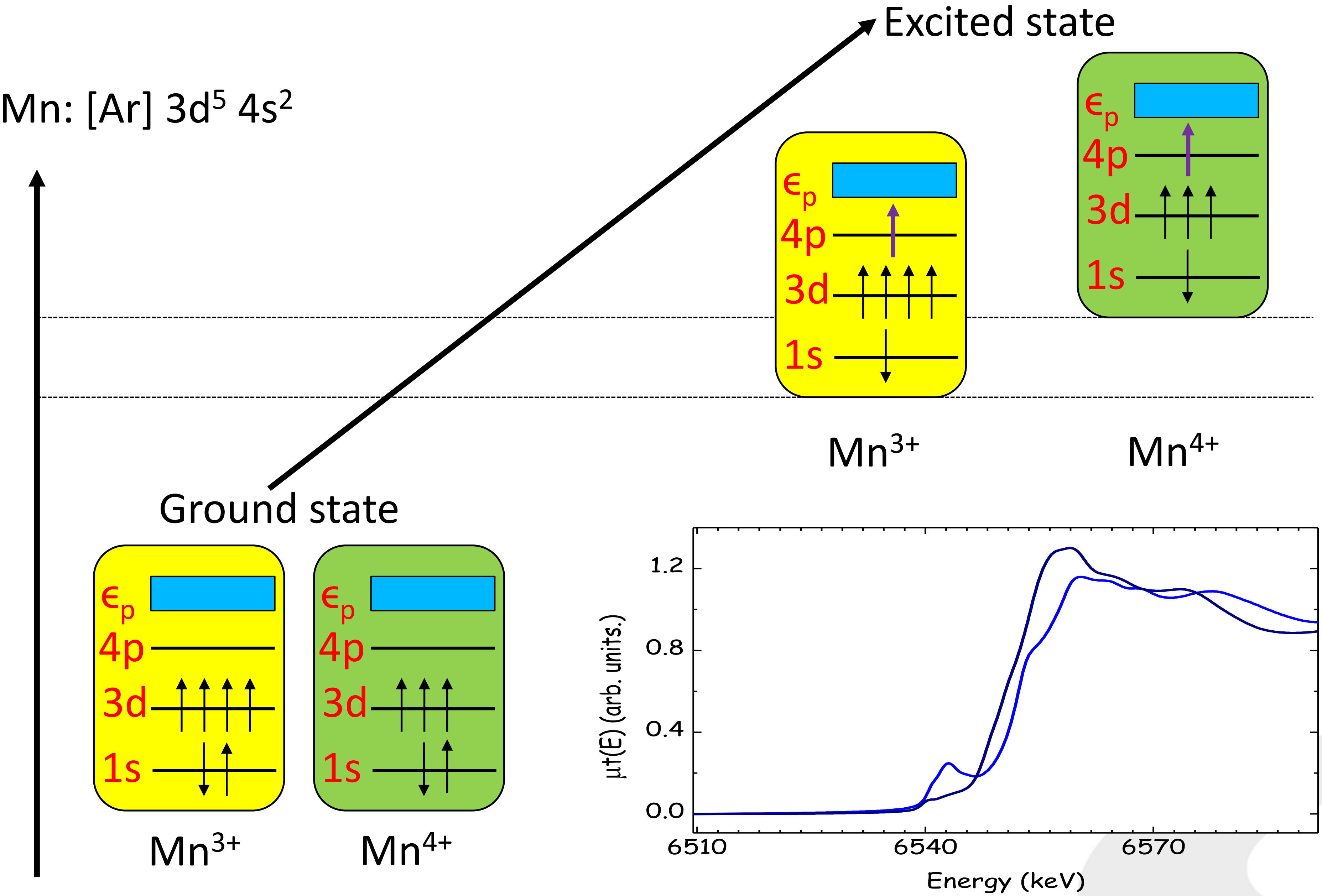
Chemical shift

Mn: [Ar] $3d^5\ 4s^2$



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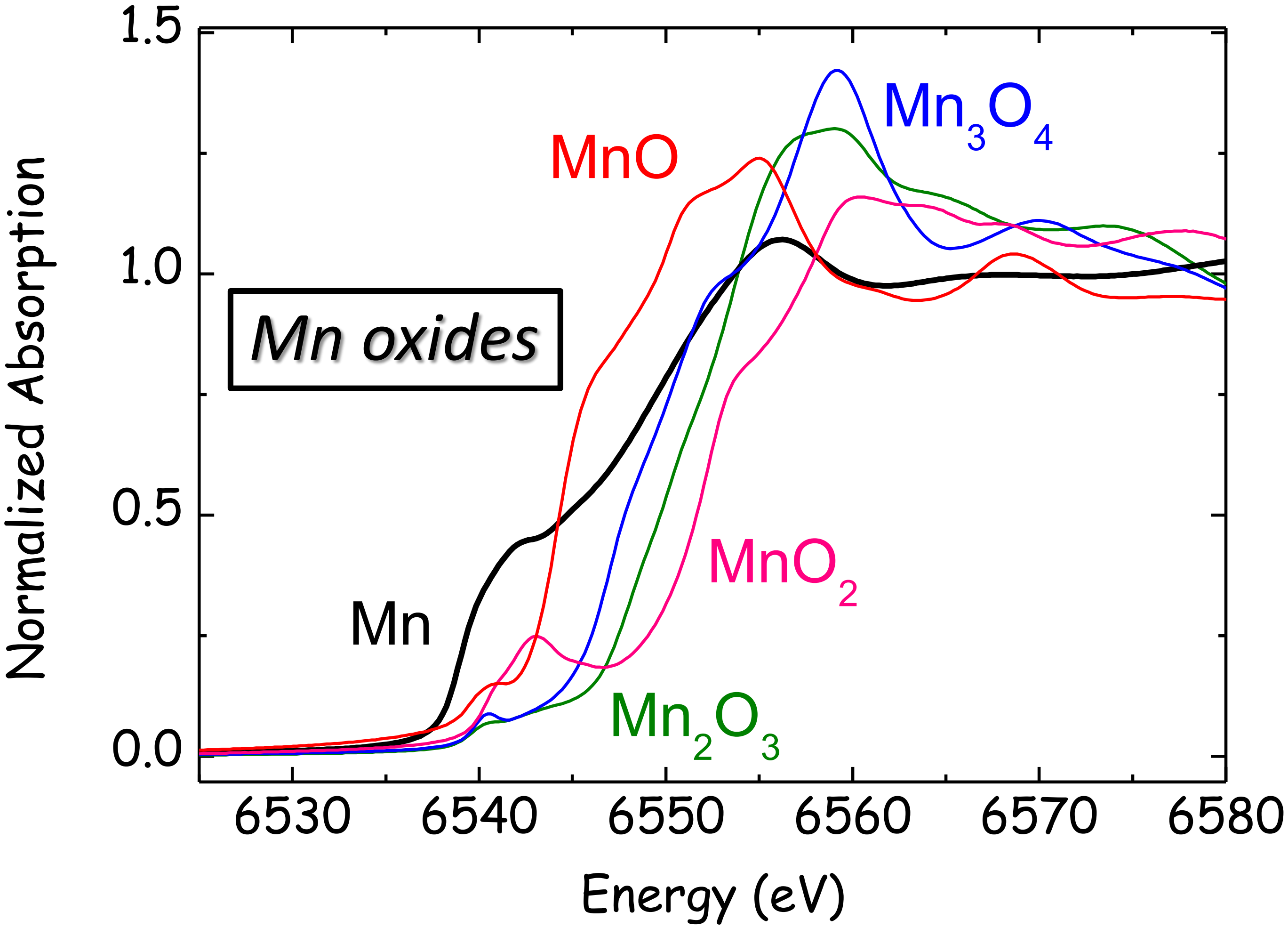
Edge position: oxidation state - 1



The edges of many elements show significant edge shifts (binding energy shifts) with oxidation state.

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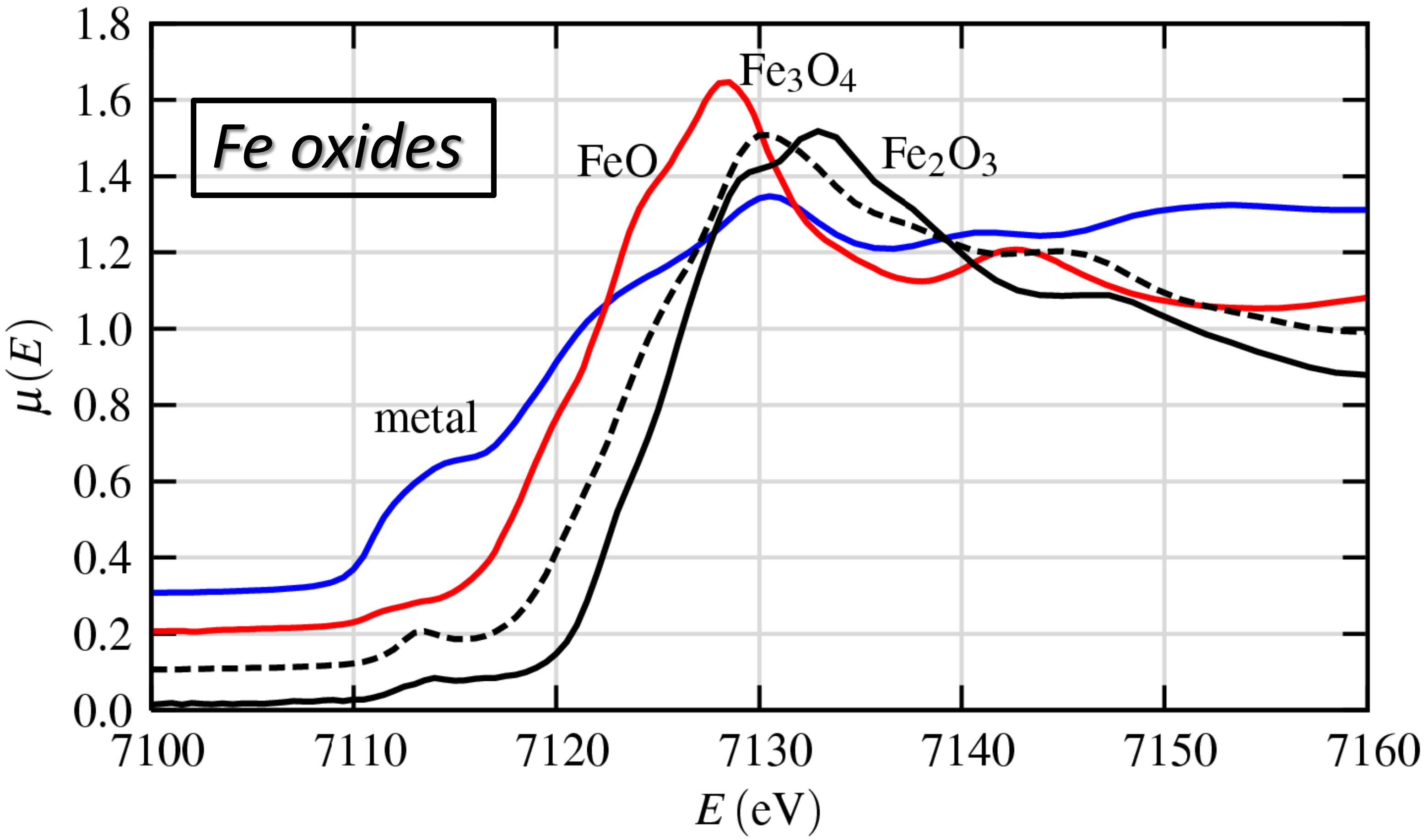
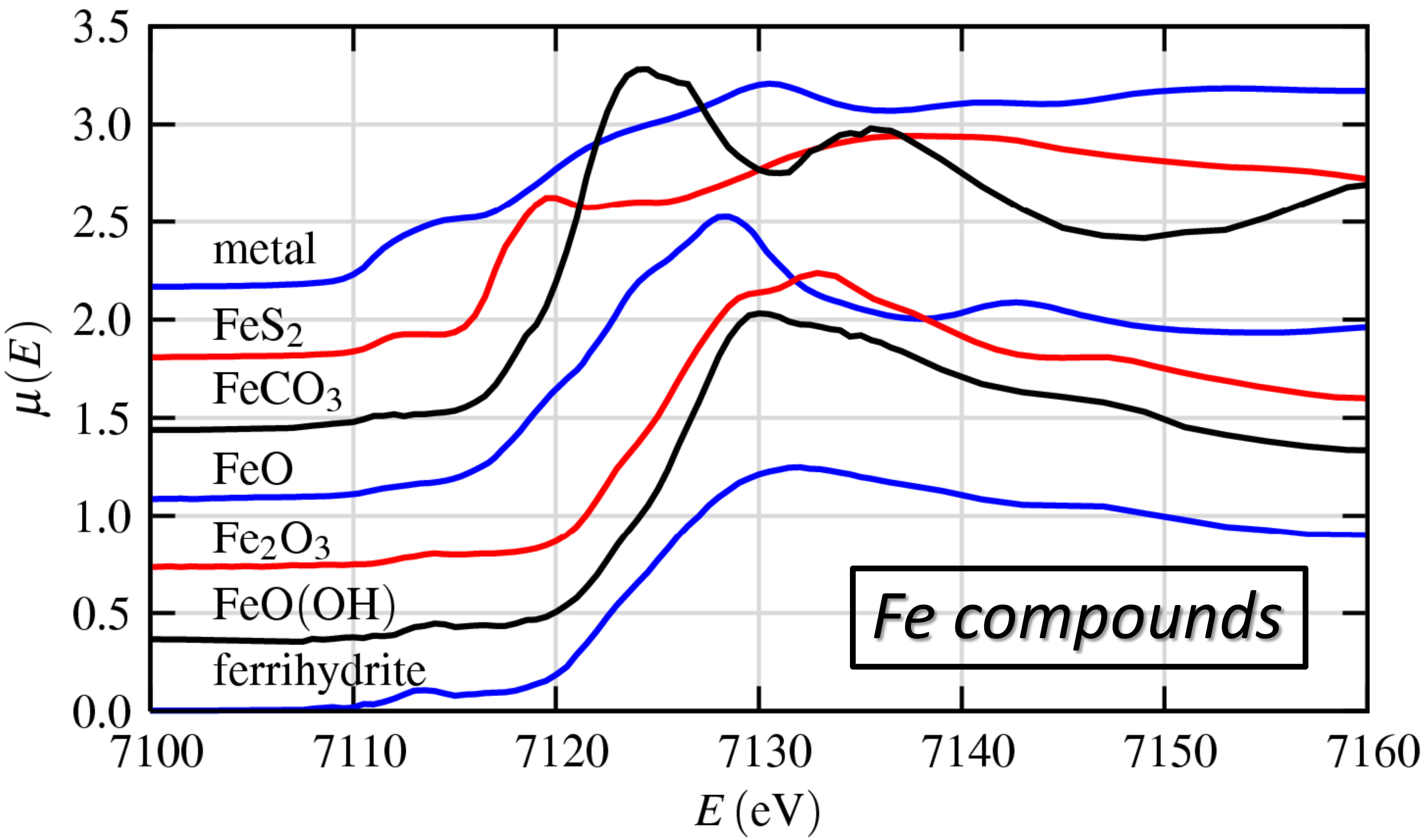
Edge position: oxidation state - 2



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)

Edge position: oxidation state - 3



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

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XANES transition

Dipole selection rules apply:

$$\boxed{\begin{aligned}\Delta\ell &= \pm 1\\ \Delta s &= 0\\ \Delta j &= \pm 1, 0\\ \Delta m &= 0\end{aligned}}$$

EDGE	INITIAL STATE	FINAL STATE
K, L_1	s (ℓ=0)	p (ℓ=1)
L_2, L_3	p (ℓ=1)	s (ℓ=0), d (ℓ=2)

The final state is usually not atomic-like and may have mixing (hybridization) with other orbitals.

This is often the interesting part of the XANES

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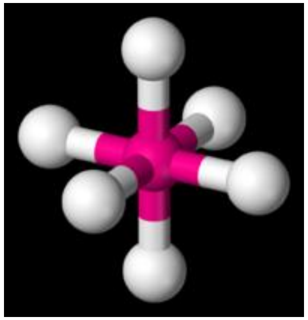
Transition metals pre-edge peaks

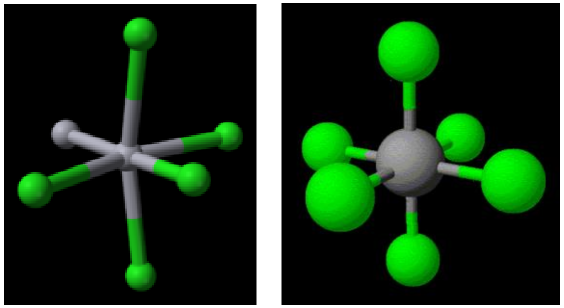
Transition from 1s to 4p states

Pure octahedron



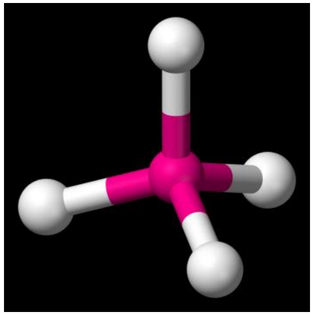
- Centro-symmetry: no p-d mixing allowed
- Only (weak) quadrupolar transitions
- No, or very low intensity prepeak

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

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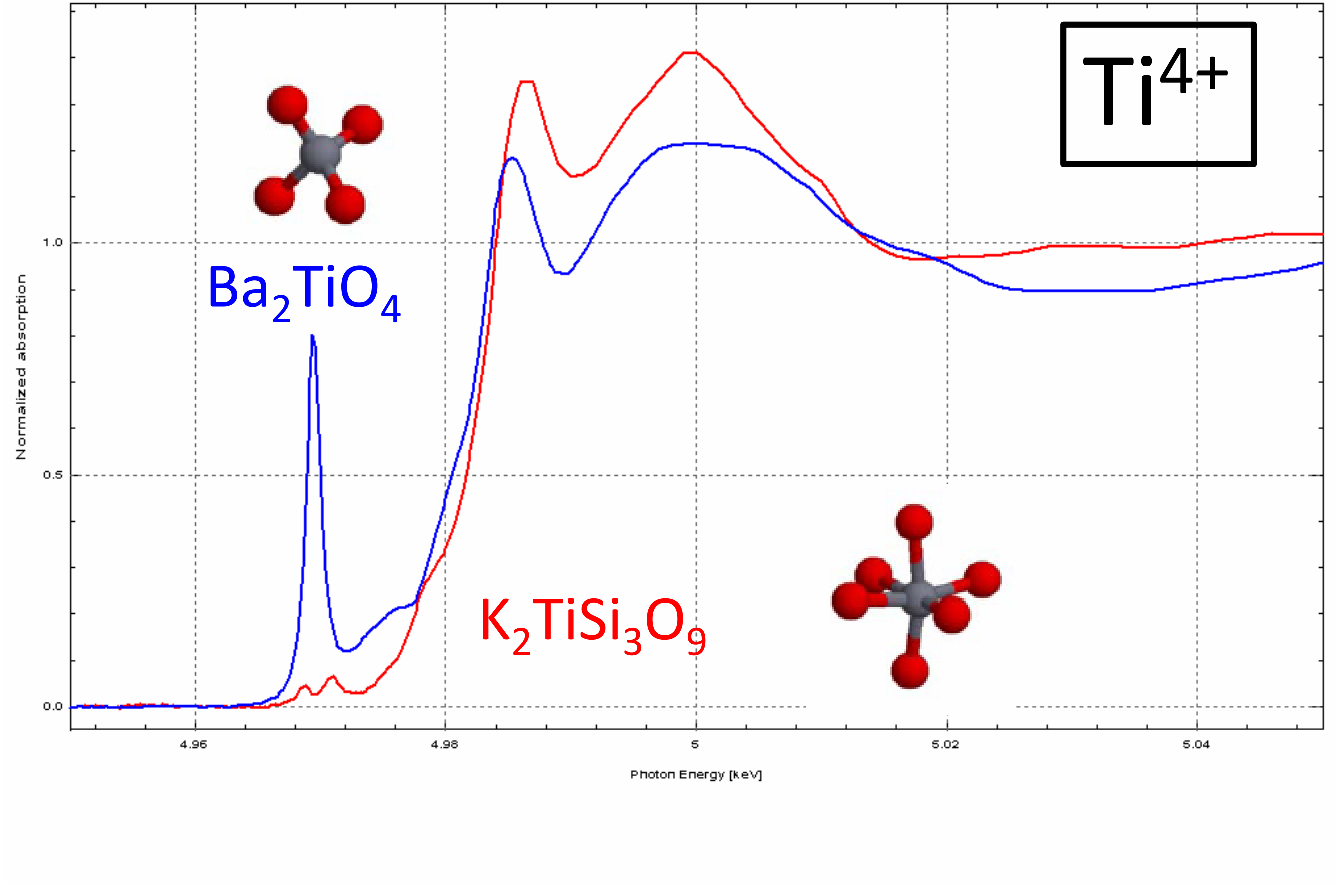
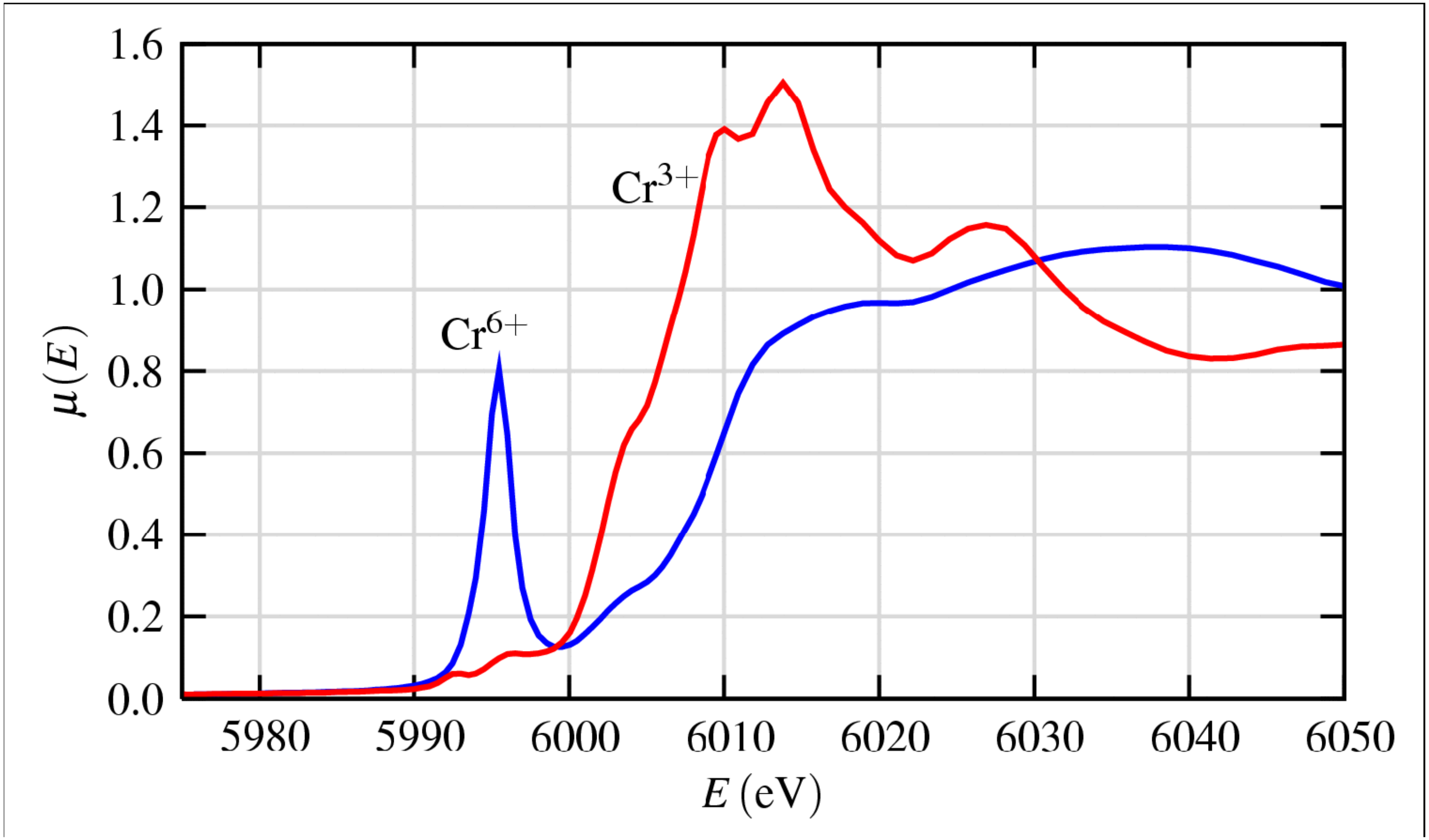
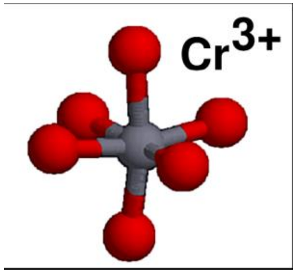
Prepeak: local coordination environment

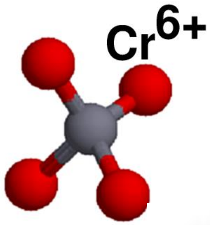


Ti K-edge XANES shows dramatic dependence on the local coordination chemistry

Pre-peak : oxidation state



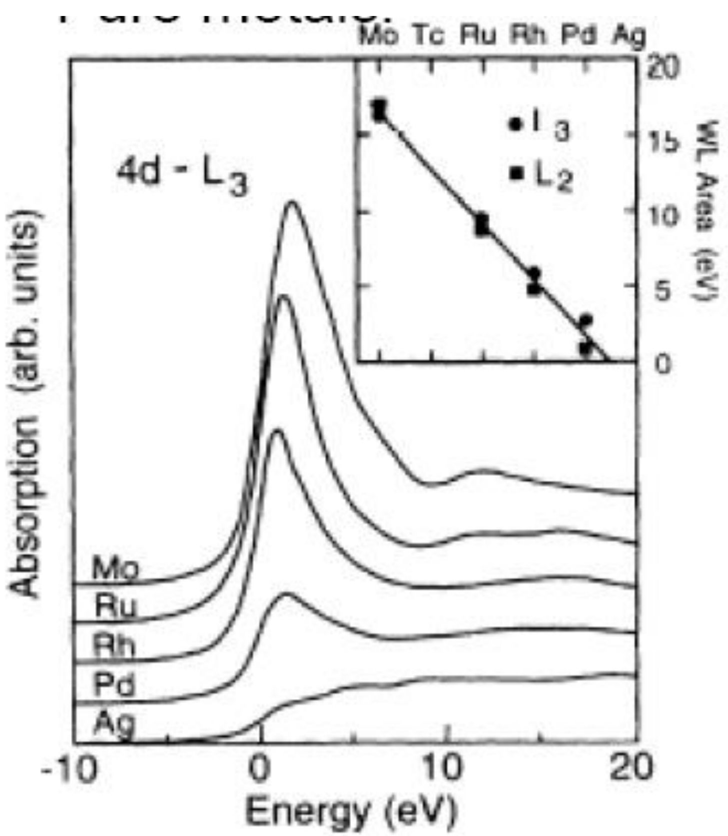




The XANES of Cr^{3+} and Cr^{6+} shows a dramatic dependence on oxidation state and coordination chemistry.

White line intensity of L_3-edge of XANES of 4d metals

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



Linear correlation between

white line area and number of

4d-holes for Mo to Ag

Increasing d states occupancy

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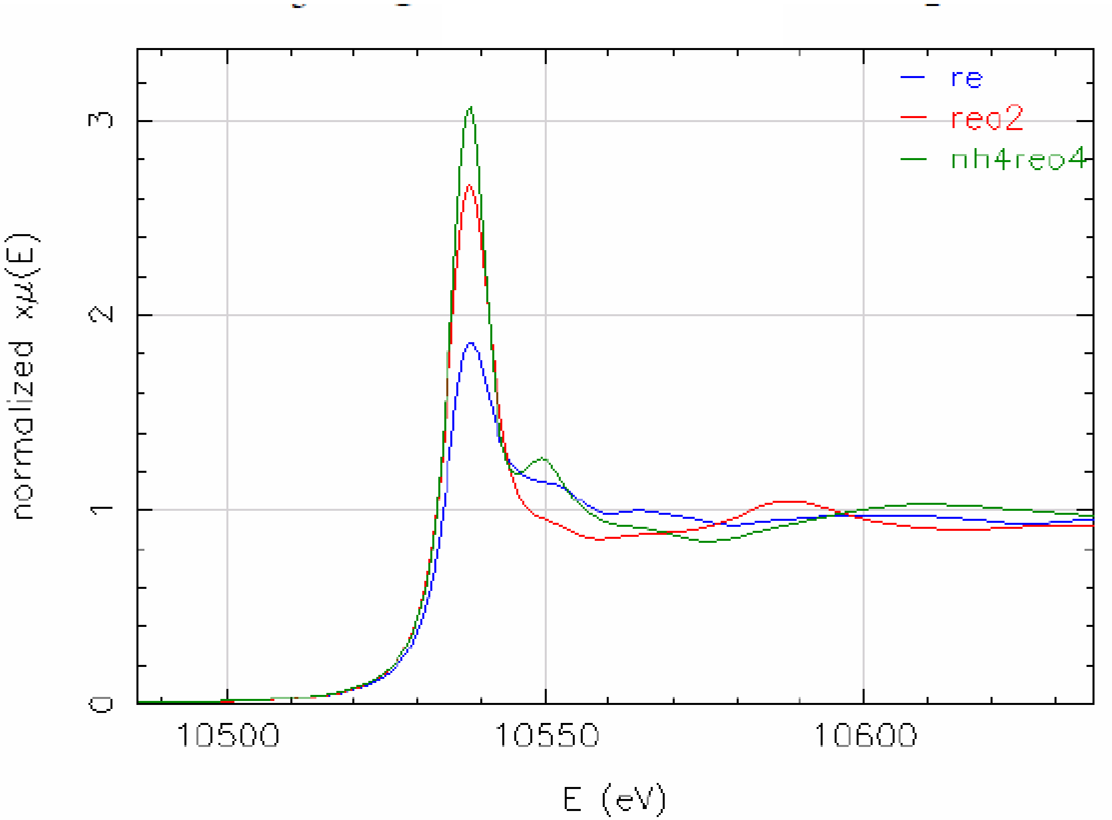
White line intensity: oxidation state

Re L_3-edge: transition from $2p_{3/2}$ to 5d states



Re metal (Re^0) – $5d^5$

ReO_2 (Re^{4+}) – $5d^1$

NH_4ReO_4 (Re^{7+}) $5d^0$

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XANES: interpretation

The EXAFS equation breaks down at low-k, and the mean-free-path goes up.

This complicates XANES interpretation:

A simple equation for XANES does not exist

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

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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 combination of known spectra form "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.

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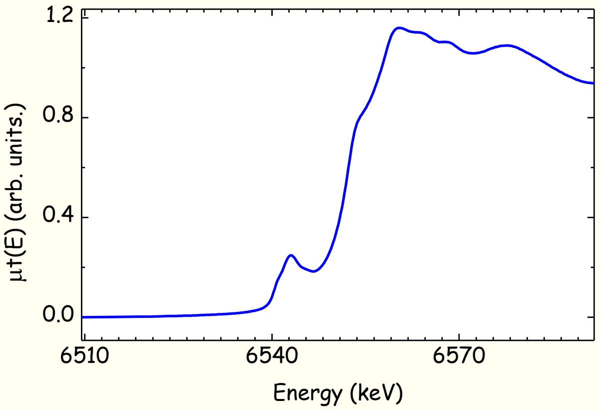
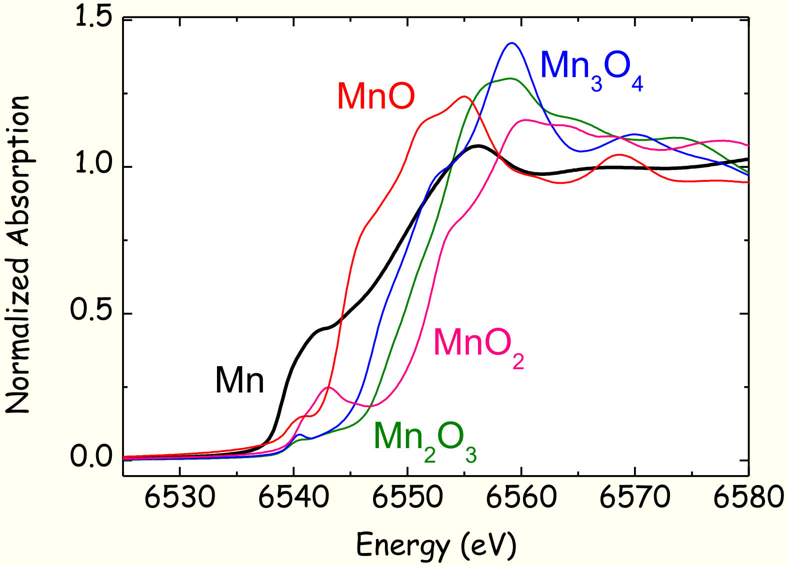
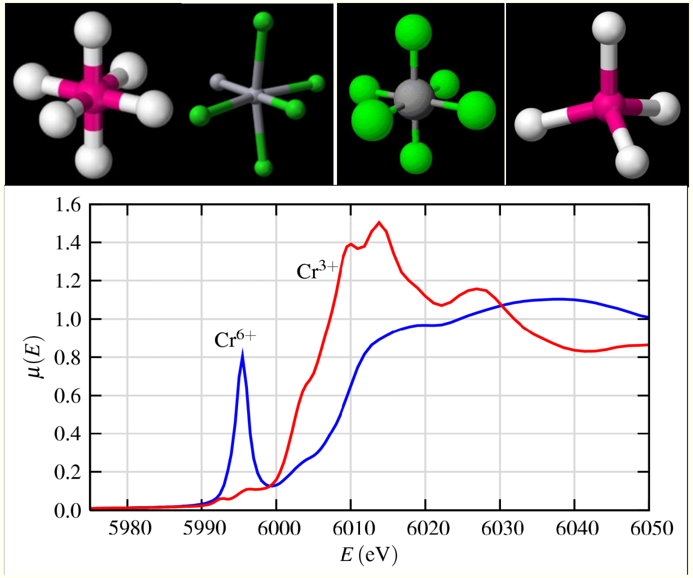
Summary XANES



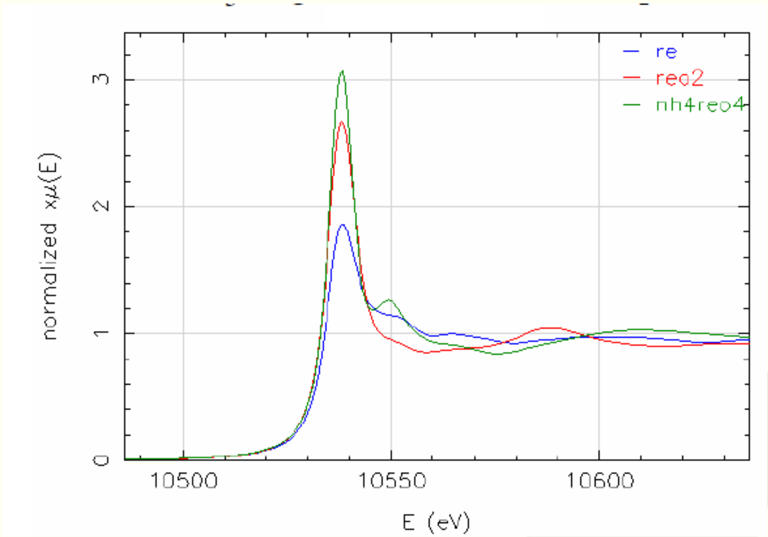
redox



Local geometry



Orbital occupancy



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EXAFS data analysis

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Data treatment: strategy

Step for reducing measured data to $\mu(E)$ and then to $\chi(k)$:

1. convert measured intensities to $\mu(E)$
2. subtract a smooth pre-edge function, to get rid of any instrumental background, and absorption from other edges.
3. normalize $\mu(E)$ to go from 0 to 1, so that it represents 1 absorption event
4. remove a smooth post-edge background function to approximate $\mu_0(E)$ to isolate the XAFS χ.
5. identify the threshold energy E_0, and convert from E to k space: $k=\frac{\sqrt{2m(E-E_0)}}{\eta^2}$
6. weight the XAFS $\chi(k)$ and Fourier transform from k to R space.
7. isolate the $\chi(k)$ for an individual “shell” by Fourier filtering.

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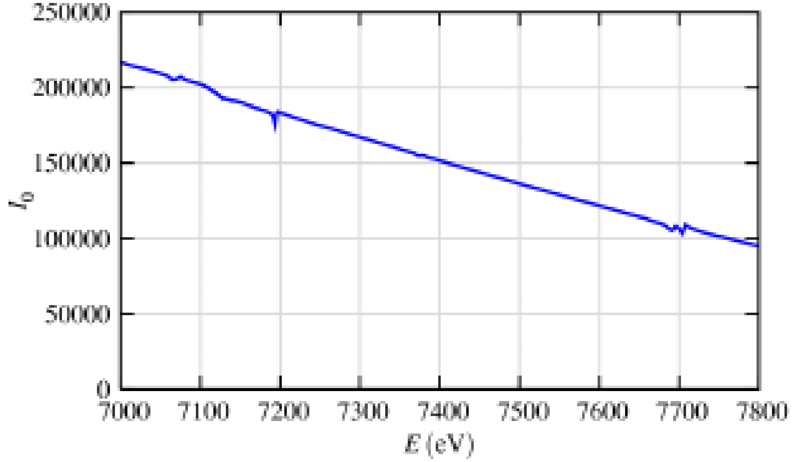
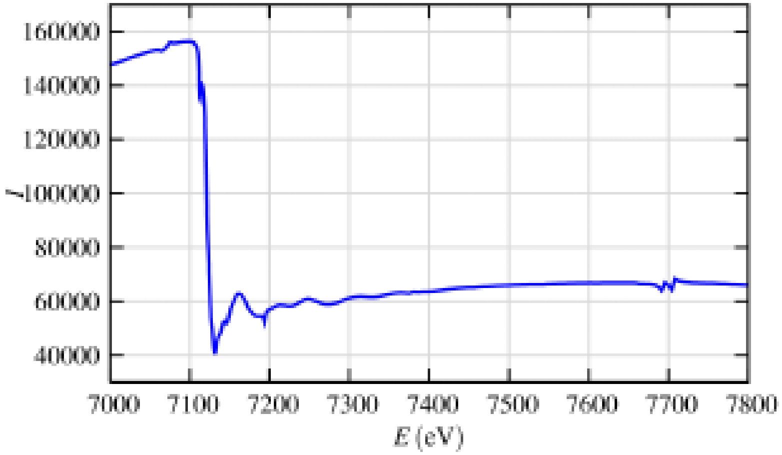
Converting raw data to μ(E)

I_0



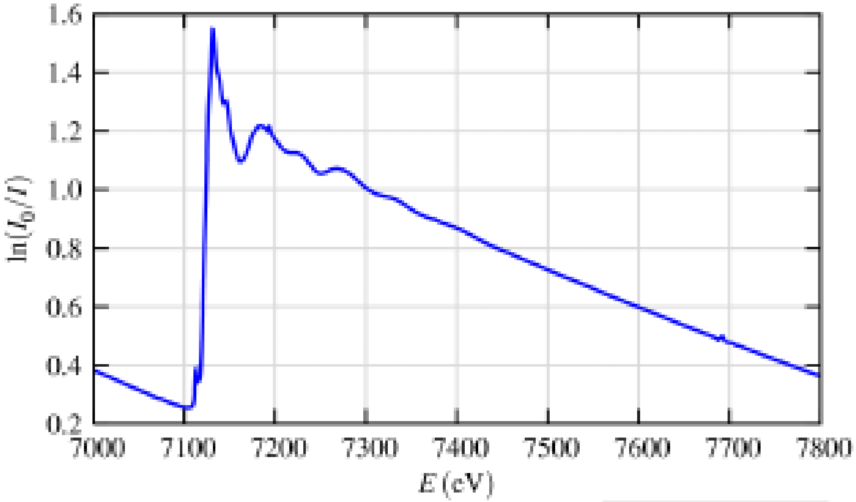
I



For transmission XAFS:

$$I = I_0 \exp[-\mu(E)\, t]$$

$$\mu(E)\, t = \ln [I_0/I]$$



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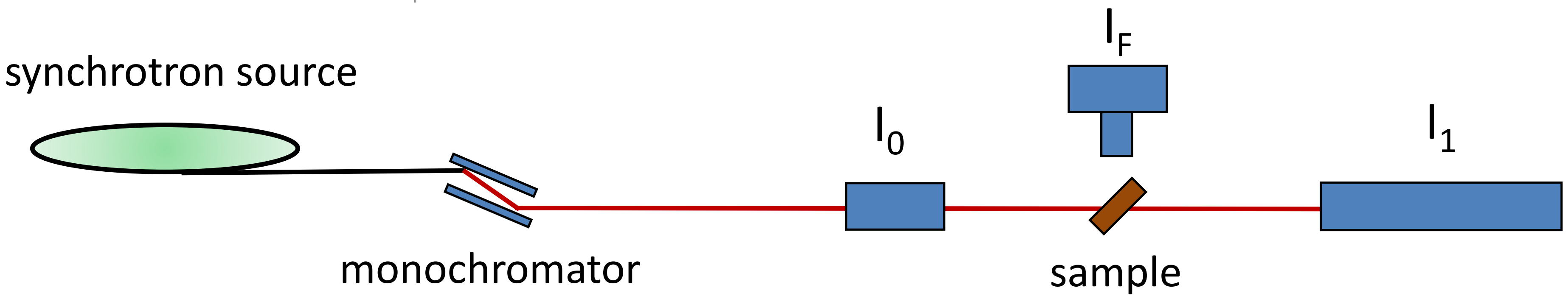
Absorption measurements in real life



Transmission

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

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

$$\mu(E)t = \alpha = \ln I_0/I_1$$

Fluorescence

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

$$\alpha \propto I_F/I_0$$

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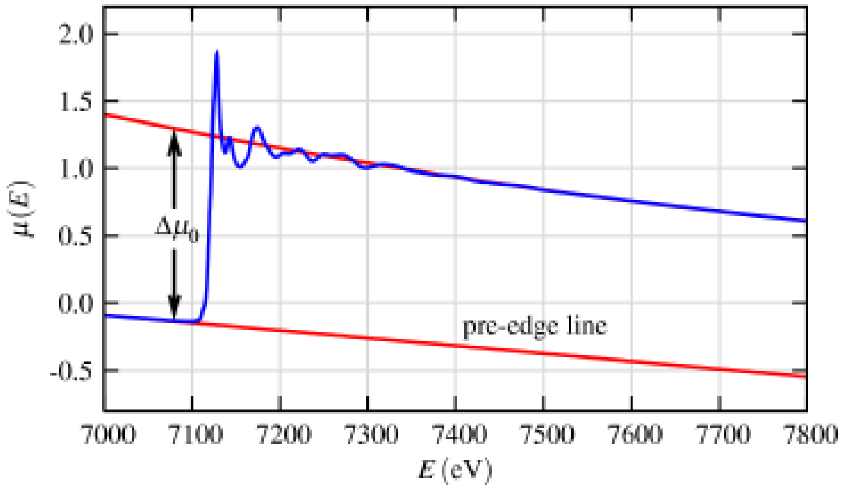
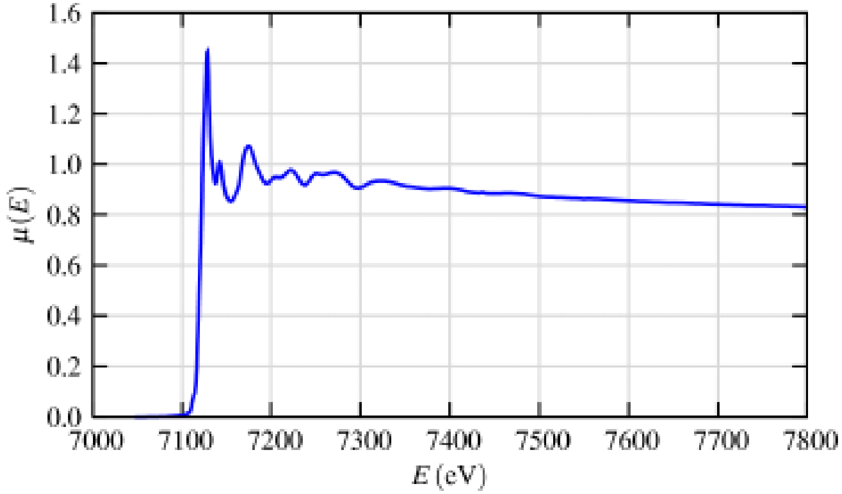
Pre-edge subtraction and normalization





Pre-edge subtraction

We subtract away the background that fits the *pre edge* region. This gets rid of the absorption due to other edges (say, the Fe L_I edge).

Normalization

We estimate the *edge step*, $\mu_0(E_0)$ by extrapolating a simple fit to the above $\mu(E)$ to the edge.

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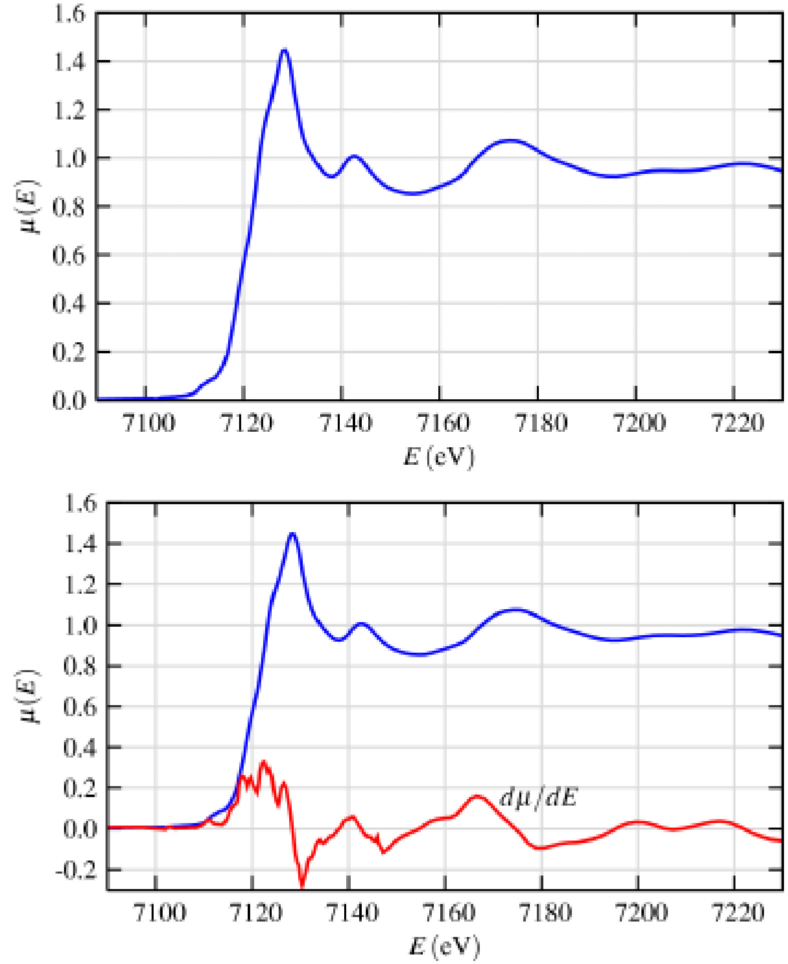
Determination of E_0



Derivative and E_0

We can select E_0 roughly as the energy with the maximum derivative. This is somewhat arbitrary, so we will keep in mind that we may need to refine this value later on.

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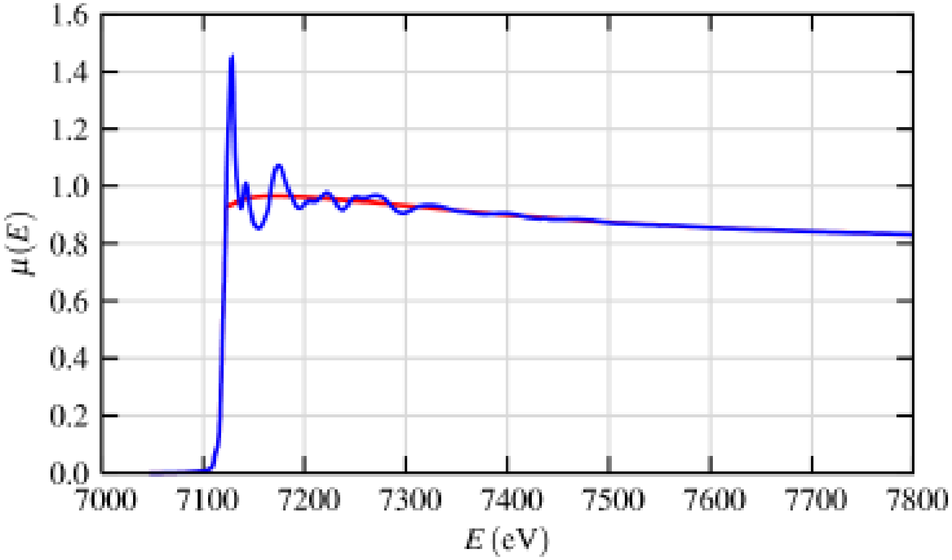
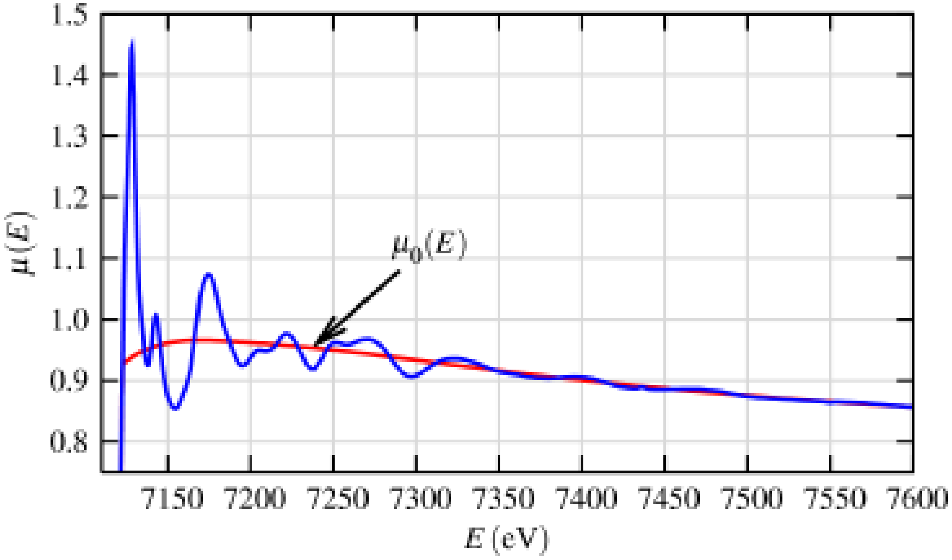
Post-edge background subtraction





Post-edge background

- We do not have a measurement of $\mu_0(E)$ (the absorption coefficient without neighboring atoms).
- We approximate $\mu_0(E)$ by an adjustable, smooth function: a *spline*.
- A flexible enough spline should not match the $\mu(E)$ and remove all the EXAFS. We want a spline that will match the *low frequency* components of $\mu_0(E)$.

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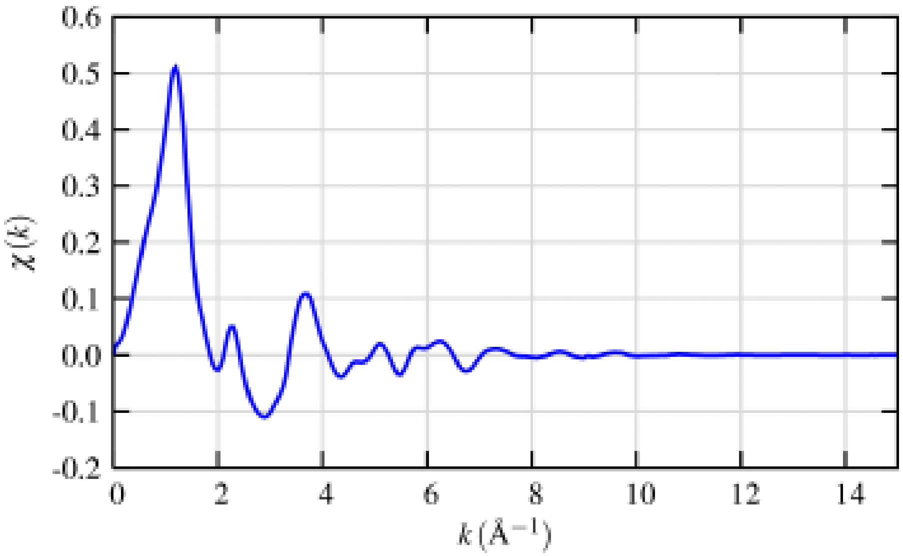
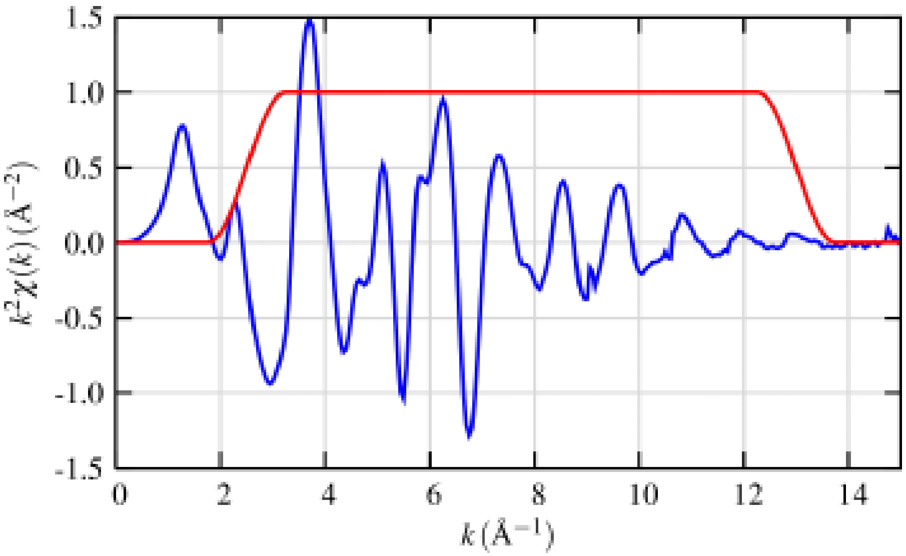
X(k), k-weighting



$\chi(k)$

The raw EXAFS $\chi(k)$ usually decays quickly with k, and difficult to assess or interpret by itself.

It is customary to weight the higher k portion of the spectra by multiplying by k^2 or k^3.

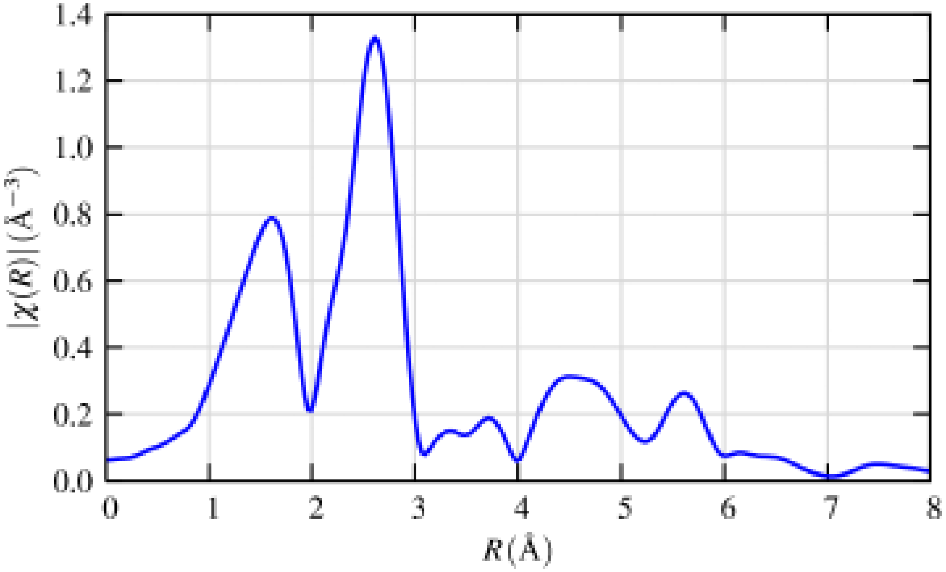


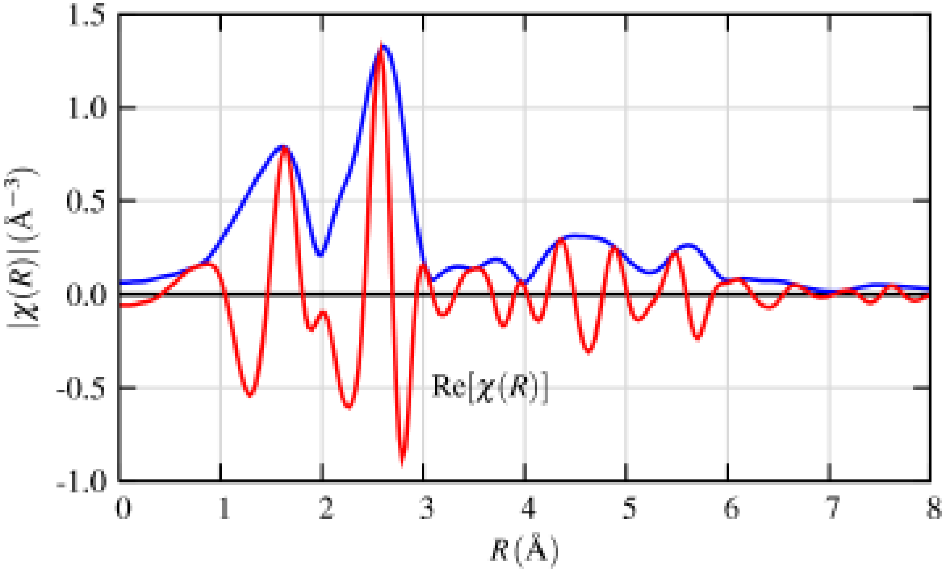
k-weighted $\chi(k)$: $k^2\chi(k)$

$\chi(k)$ is composed of sine waves, so we'll Fourier Transform from k to R-space.

To avoid "ringing", we'll multiply by a *window function*.

Fourier Transform: χ(R)





χ(R)

The Fourier Transform of k^2(k) has 2 main peaks, for the first 2 coordination shells: Fe-O and Fe- Fe.
The Fe-O distance in FeO is 2.14Å , but the first peak is at 1.66Å .
This shift in the first peak is due to the *phase-shift*, δ(k): sin[2kR + δ(k)] .

A shift of -0.5 Å is typical.

χ(R) is complex:

The FT makes χ(R) complex.
Usually only the amplitude is shown, but there are really oscillations in χ(R).
Both real and imaginary components are used in modeling.

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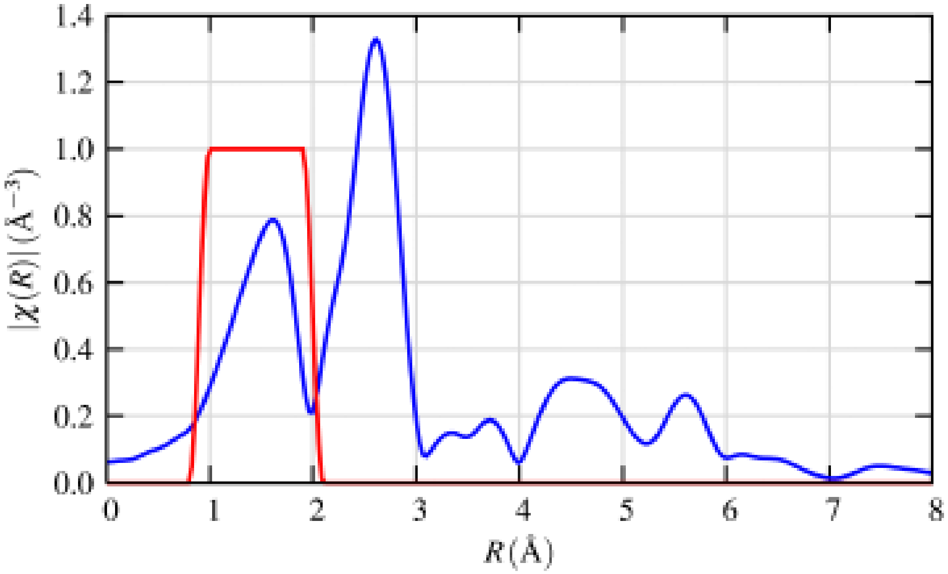
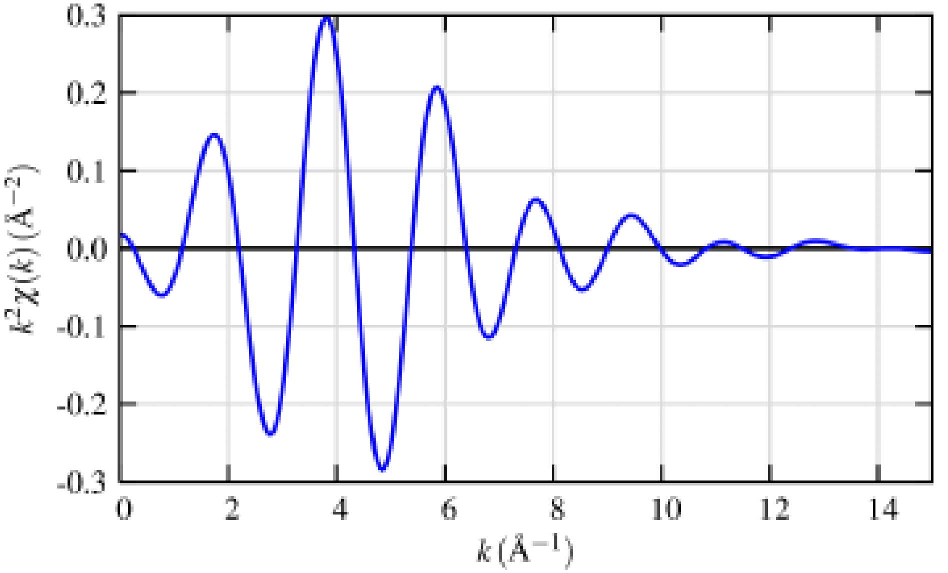
Fourier filtering





$\chi(R)$ often has well separated peaks for different “shells”.

This shell can be isolated by a Filtered Back-Fourier Transform, using the window shown for the first shell of FeO.

This results in the filtered $\chi(k)$ for the selected shell. Many analysis programs use such filtering to remove shells at higher R.

Beyond the first shell, isolating a shell in this way can be difficult.

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The information content of EXAFS

- The number of parameters we can reliably measure from our data is limited:

$$N \approx \frac{2 \Delta k \Delta R}{\pi}$$

  where Δk and ΔR are the k- and R-ranges of the usable data.
- For the typical ranges like k = [3.0, 12.0] $Å^{-1}$ and R = [1.0, 3.0] Å, there are ~ 11 parameters that can be determined from EXAFS.
- The "Goodness of Fit" statistics, and confidence in the measured parameters need to reflect this limited amount of data.
- It is often important to constrain parameters R, N, σ^2 for different paths or even different data sets (different edge elements, temperatures, etc)
- Chemical Plausibility can also be incorporated, either to weed out obviously bad results or to use other knowledge of local coordination, such as the Bond Valence Model (relating valence, distance, and coordination number).
- Use as much other information about the system as possible!

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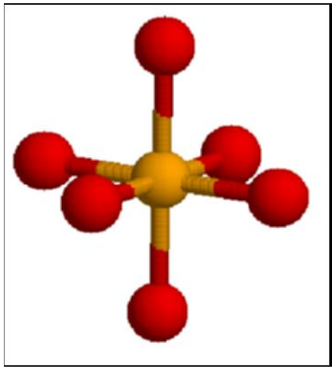
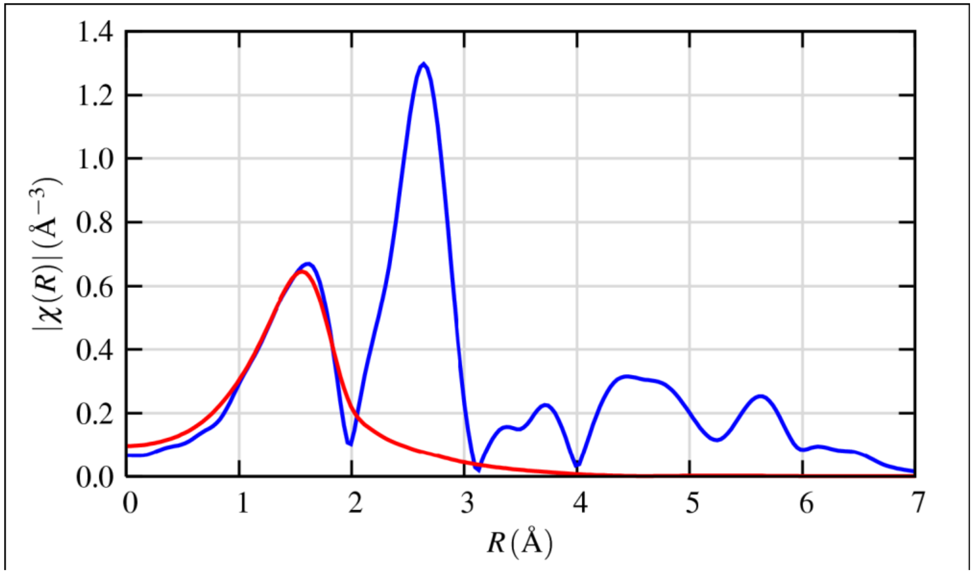
Modeling the first shell of FeO - 1

FeO has a rock-salt structure.

To model the FeO EXAFS, we calculate the scattering amplitude f(k) and phase-shift δ(k), based on a guess of the structure, with Fe-O distance R = 2.14 Å (a regular octahedral coordination).

We will use these functions to *refine* the values R, N, σ^2, and E_0 so our model EXAFS function matches our data.





|χ(R)| for FeO (blue), and a 1st shell fit (red).

Fit results

N = 5.8 ± 1.8

R = 2.10 ± 0.02 Å

E_0 = -3.1 ± 2.5 eV

σ^2 = 0.015 ± 0.005 Å ^{2}.

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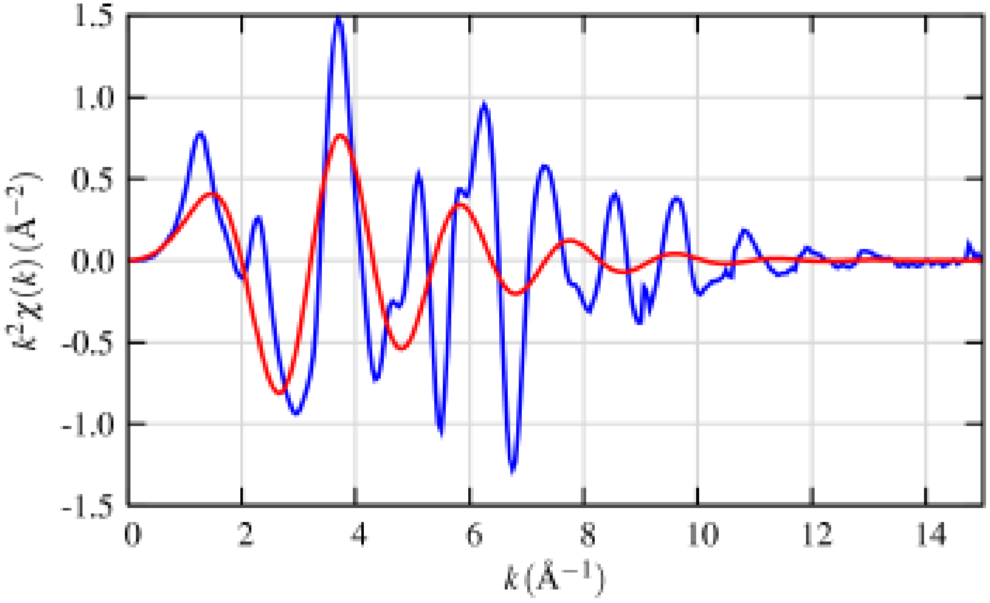
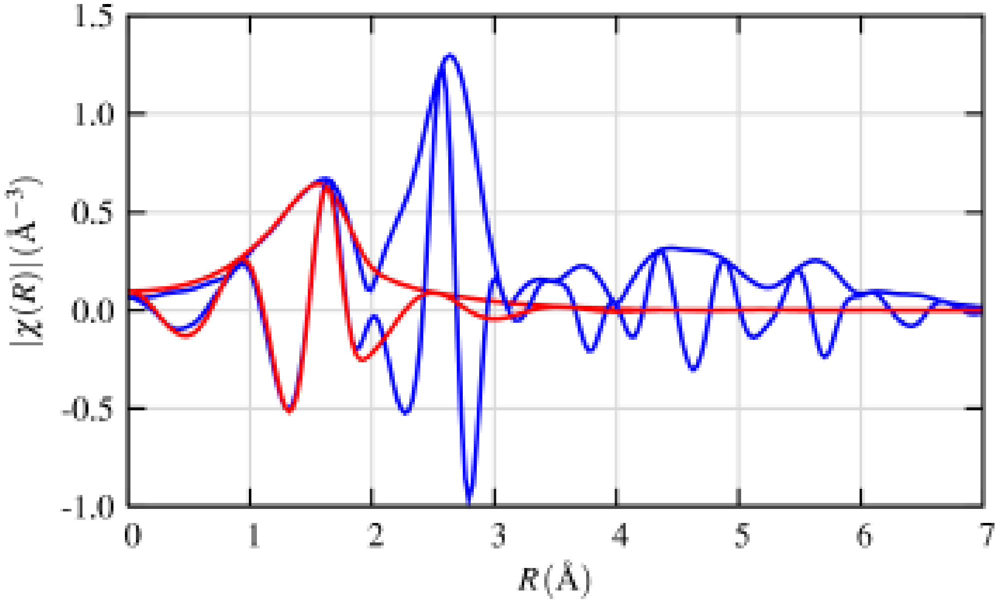
Modeling the first shell of FeO - 2



1^{st} shell fit in k space

The 1^{st} shell fit to FeO in k space.

There is clearly another component in the XAFS



1^{st} shell fit in R space

|χ(R)| and Re[χ(R)] for FeO (blue), and a 1^{st} shell fit (red).

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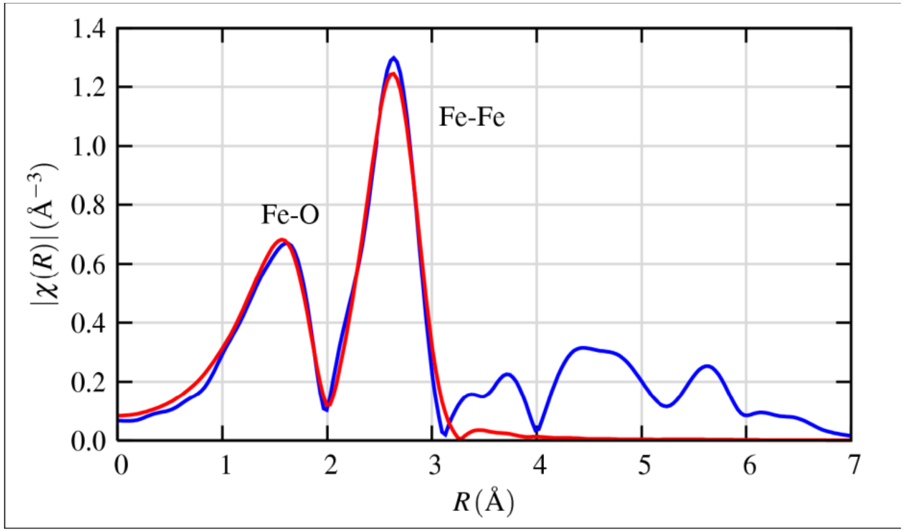
Modeling the second shell of FeO - 1

To add the second shell Fe to the model, we use calculation for f(k) and δ(k) based on a guess of the Fe-Fe distance, and refine the values R,N, σ^2.

Such a fit gives a result like this:



$|\chi(R)|$ data for FeO (blue), and fit of 1st and 2nd shells (red).

The results are fairly consistent with the known values for crystalline FeO:

6 O at 2.13Å, 12 Fe at 3.02Å .

Fit results (uncertainties in parentheses):

Shell	N	R (Å)	σ^2 (Å^2)	ΔE_0 (eV)
Fe-O	6.0(1.0)	2.10(.02)	0.015(.003)	-2.1(0.8)
Fe-Fe	11.7(1.3)	3.05(.02)	0.014(.002)	-2.1(0.8)

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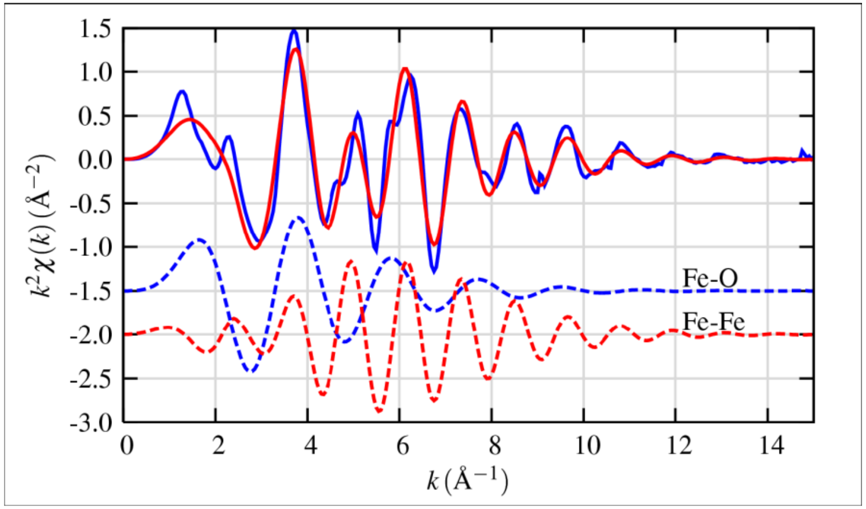
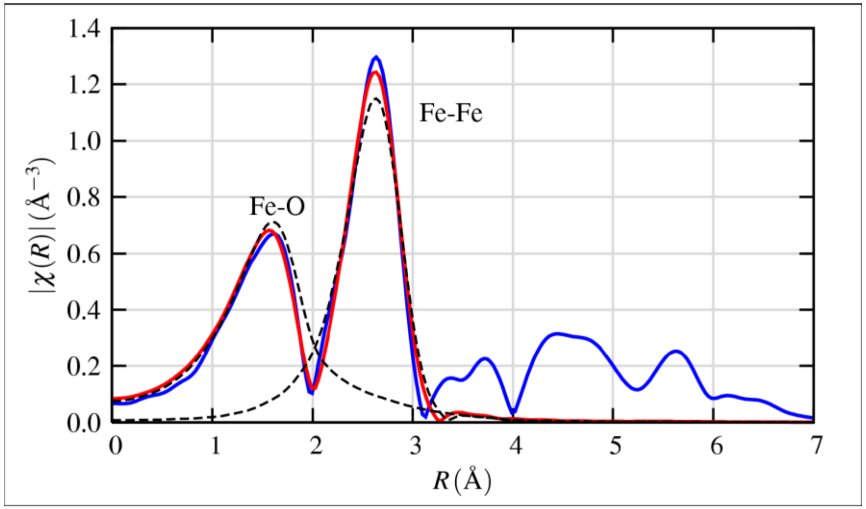
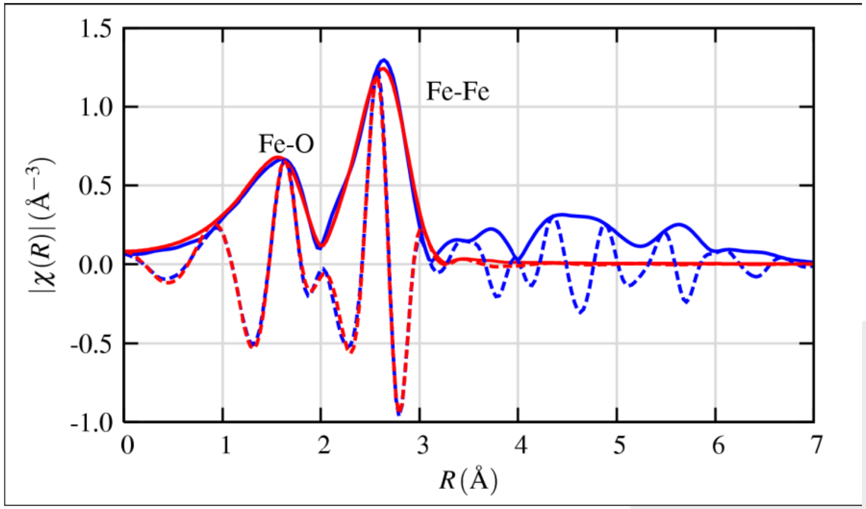
Modeling the second shell of FeO - 2

Other views of the data and two-shell fit:



The Fe-Fe EXAFS extends to higher-k than the Fe-O EXAFS.
Even in this simple system, there is some *overlap* of shells in R-space.
The agreement in Re[χ(R)] look especially good – this is how the fits are done.
The modeling can get more complicated than this





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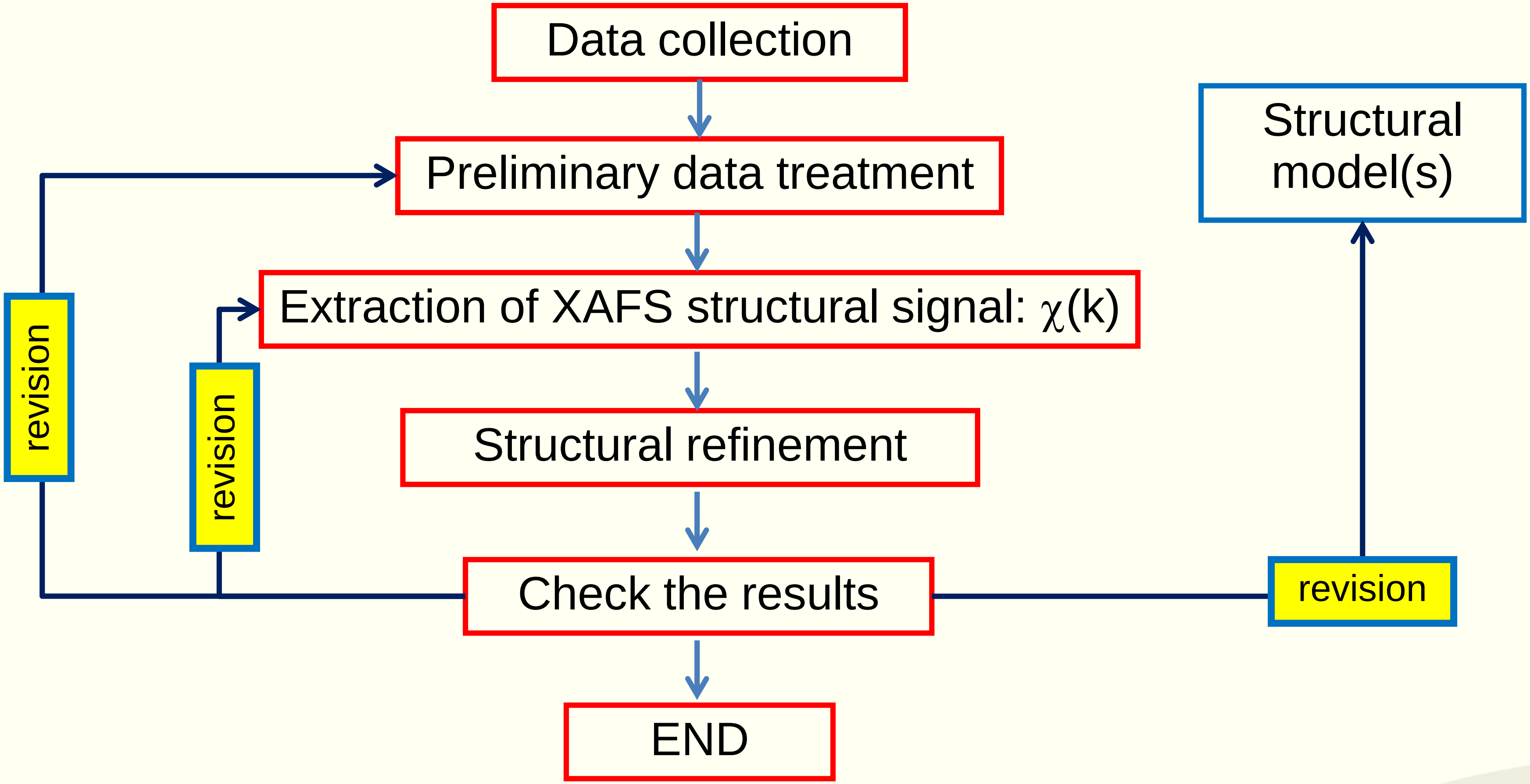
Summary data analysis



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