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An introduction to X-ray Absorption Spectroscopy

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An introduction to X-ray Absorption Spectroscopy

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Outline

- ☐ X-ray Absorption Spectroscopy
- ☐ X-ray Absorption Fine Structure (EXAFS and XANES)

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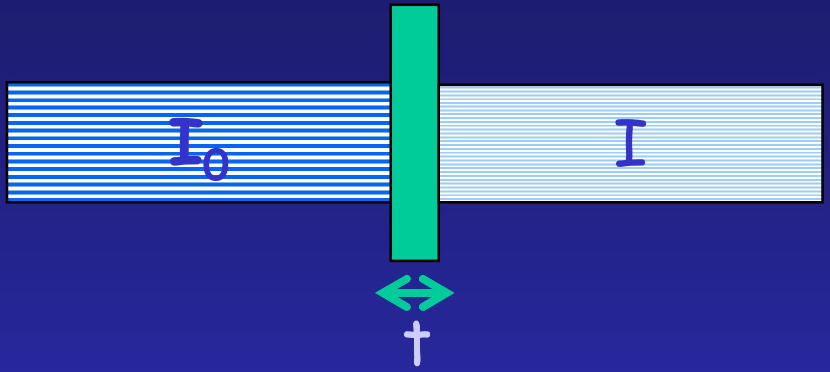
- ☐ X-ray Absorption Fine Structure (EXAFS and XANES)

Main X-ray based techniques

- ❑ Two fundamental X-ray-matter interactions:
  - ● photoelectric absorption
  - ● scattering (elastic, inelastic)

- ❑ Two families of experimental techniques:
  - ❑ spectroscopy → electronic structure, local structure of matter
    - ● absorption
    - ● emission
    - ● inelastic scattering
  - ❑ elastic diffusion → microscopic geometric structure
    - ● diffraction (crystalline solids)
    - ● scattering (amorphous solids, liquids)

The Absorption Coefficient μ



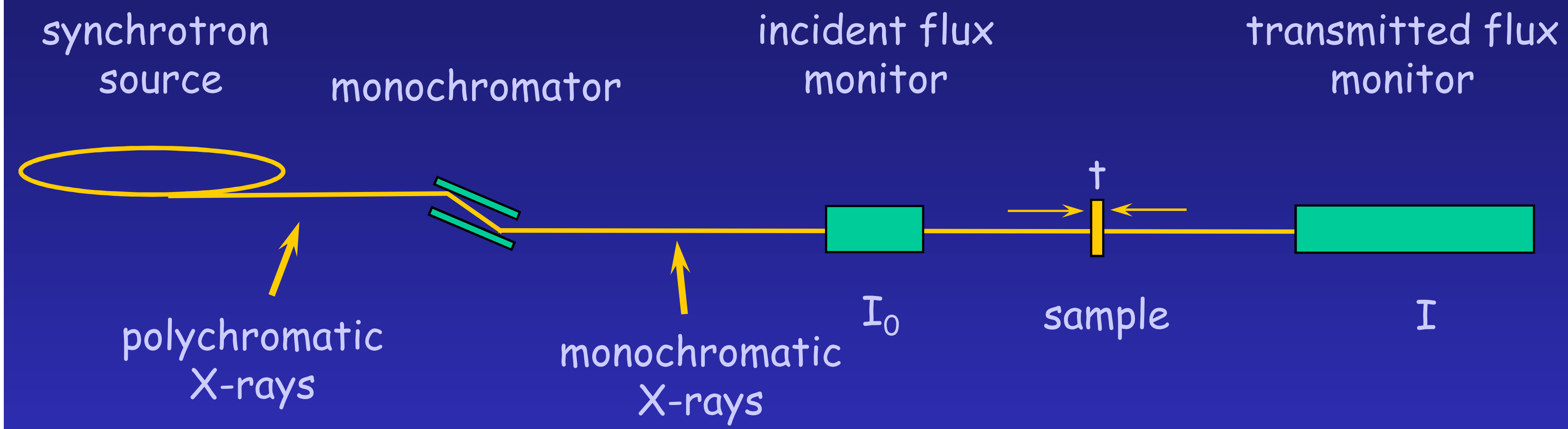
$$I = I_0 \exp[-\mu t]$$

↓

linear absorption coefficient

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

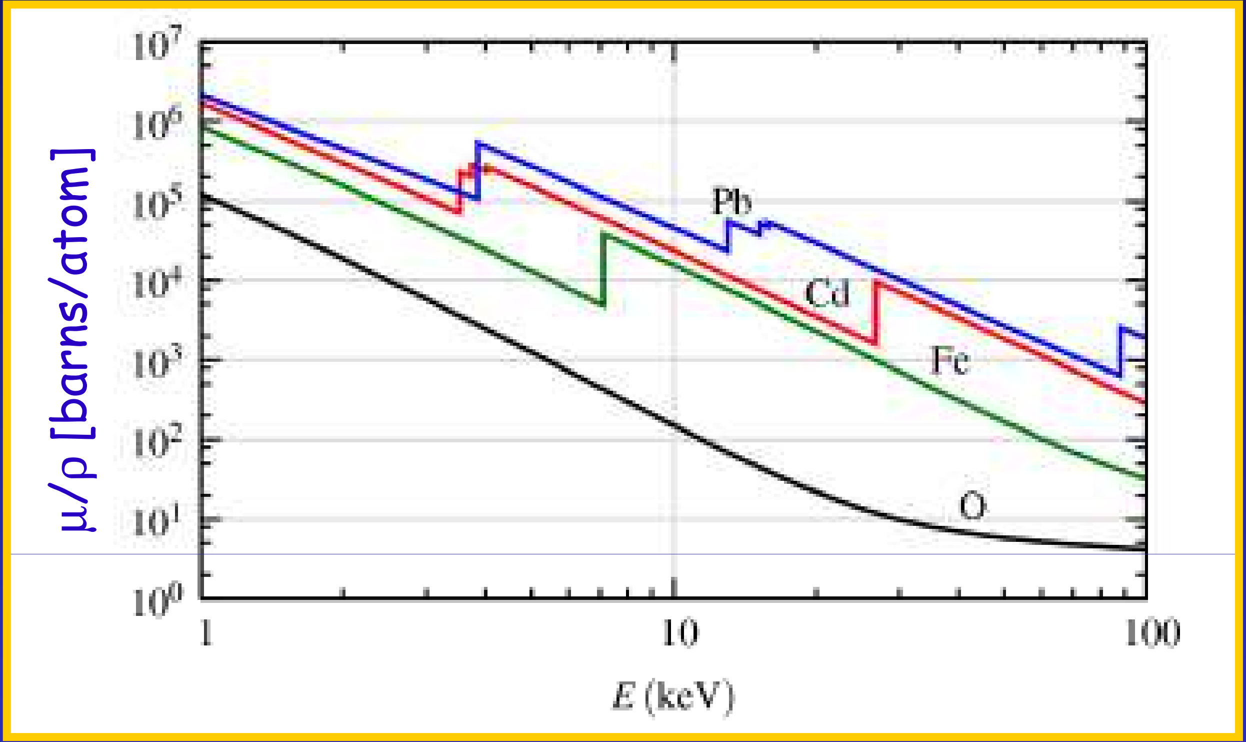
The Absorption Coefficient μ



1. Measure I_0 and I as a function of E_X

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

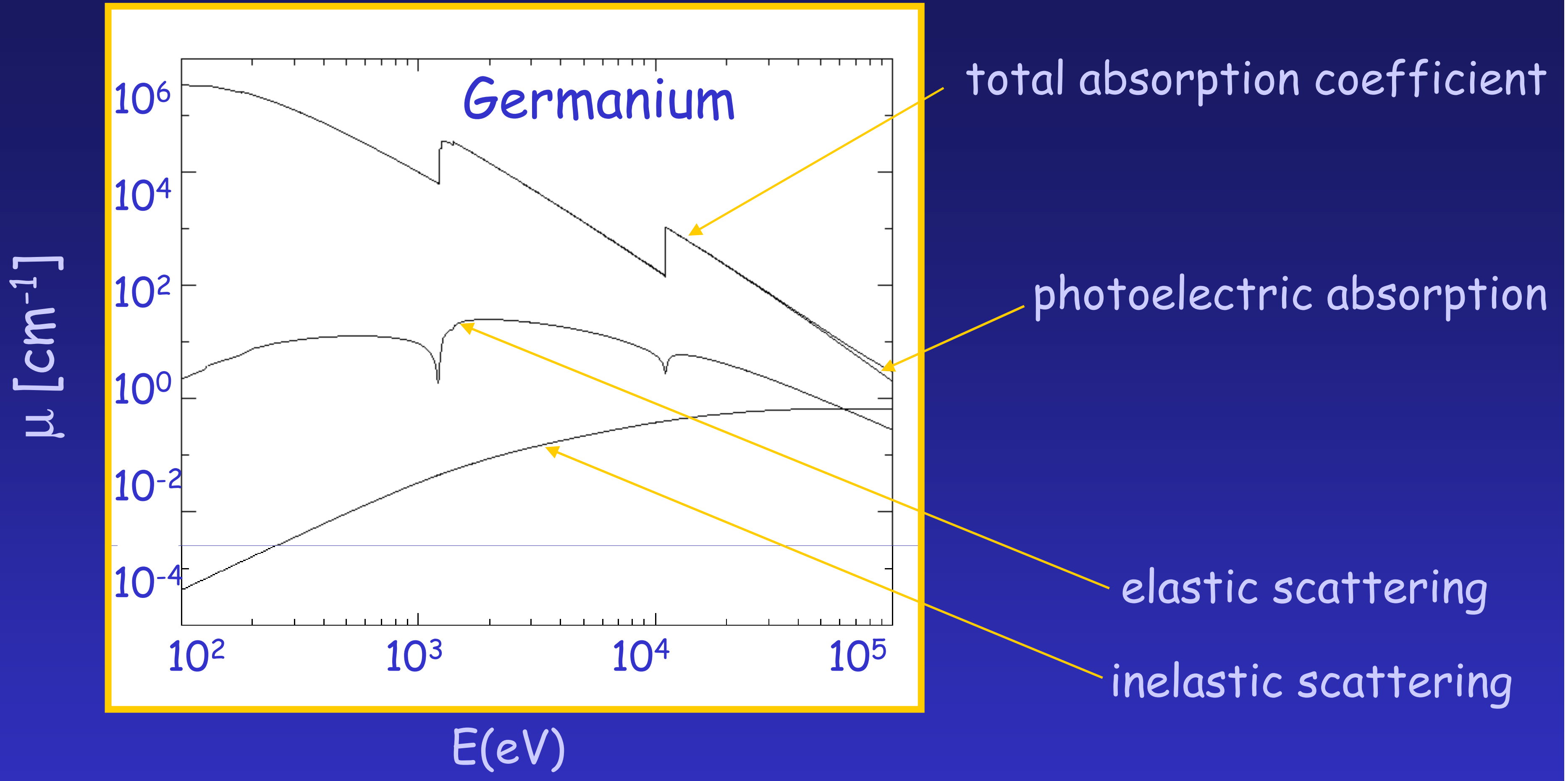
The Absorption Coefficient μ



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

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

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



Photoelectric absorption dominates the absorption coefficient in this energy range

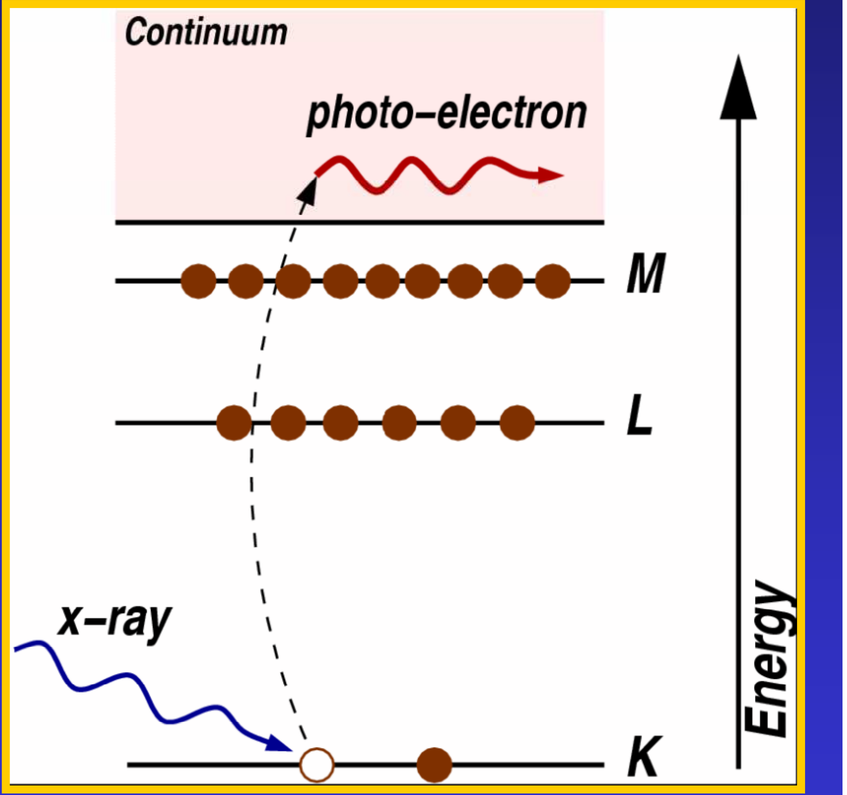
Photoelectric Absorption

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

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

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

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

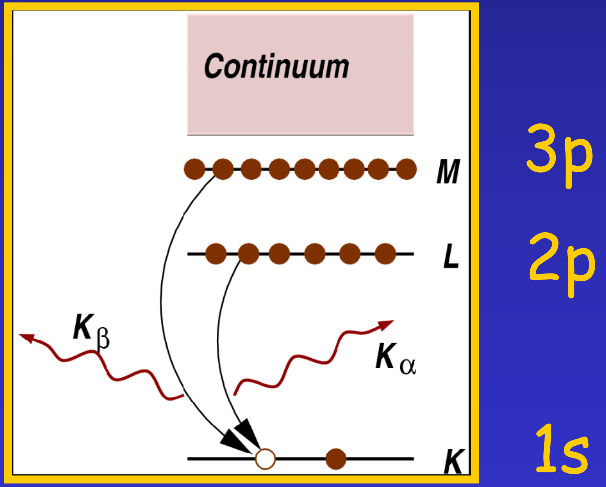


De-excitation: Fluorescence and Auger Effect

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:

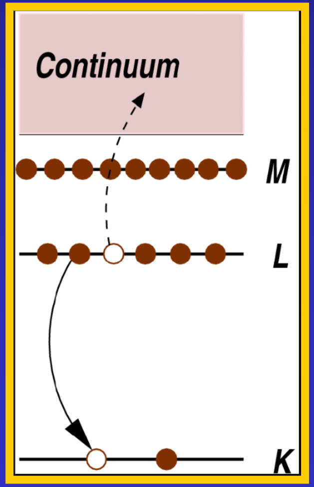
An x-ray with energy = the difference of the core-levels is emitted.



$K_\alpha : L \rightarrow K, \quad K_\beta : M \rightarrow K$

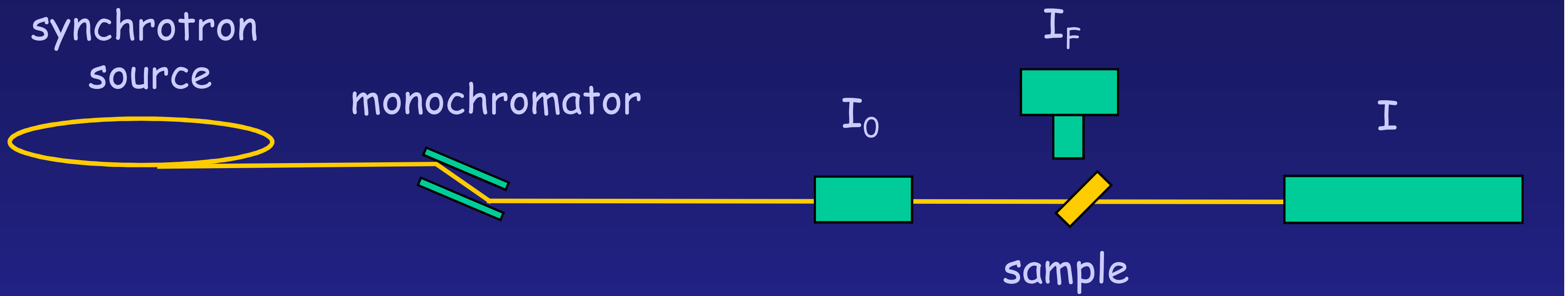
Auger Effect:

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 μ(E) at and above the absorption edge of a selected element.
μ(E) can be measured in several 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.

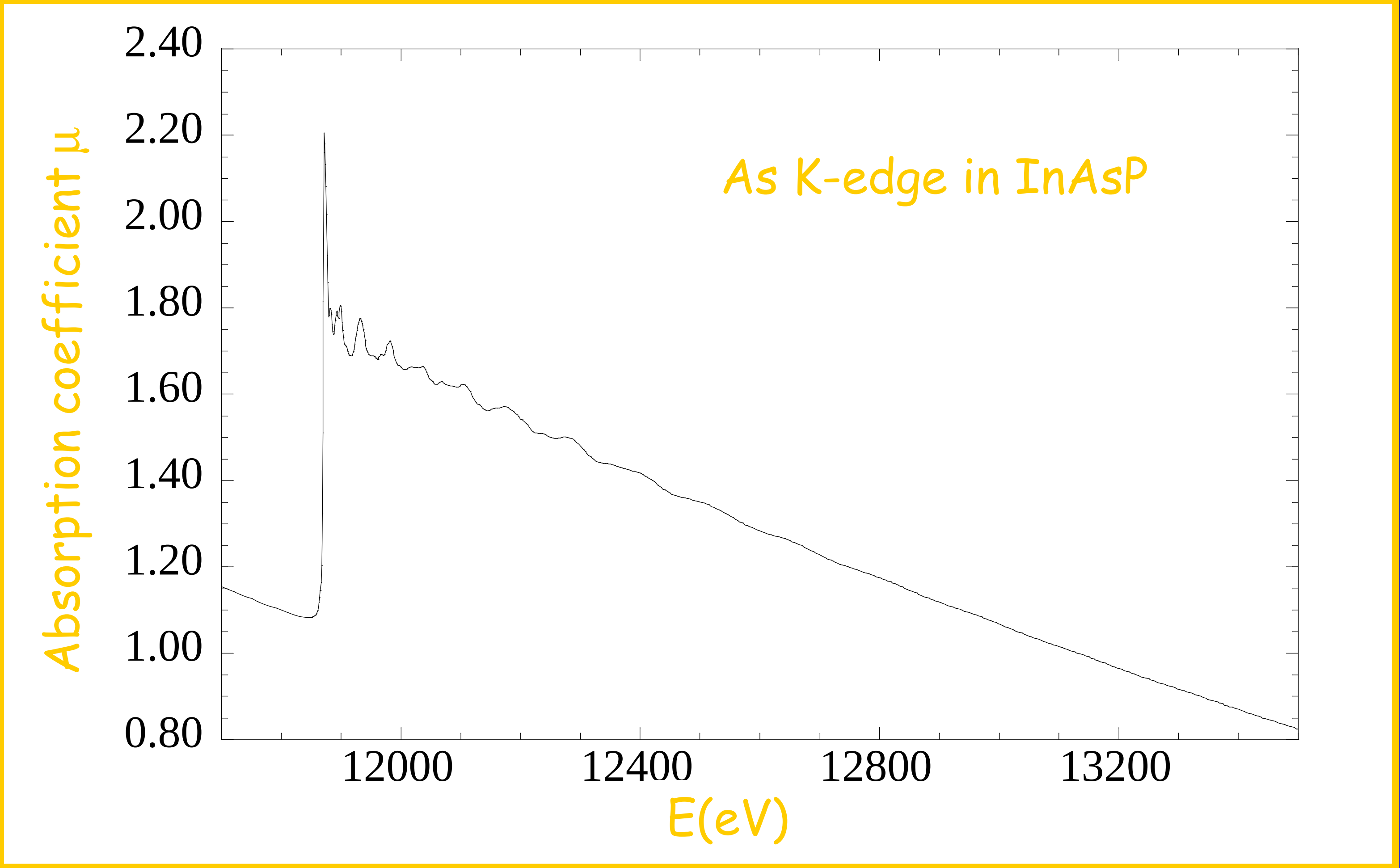
$$\mu(E) \sim I_F / I_0$$

Outline

- ☐ X-ray Absorption Spectroscopy
- ☐ X-ray Absorption Fine Structure (EXAFS and XANES)

What is XAFS ?

X-ray Absorption Fine Structure: 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

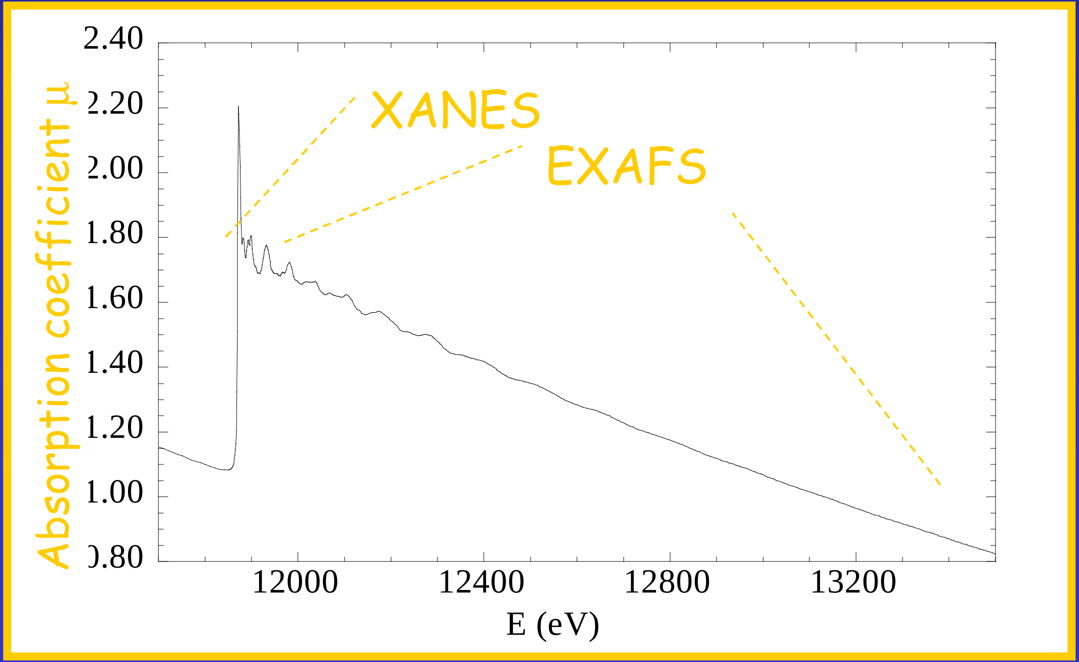
EXAFS and XANES

XAFS is often 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.

As K-edge in InAsP



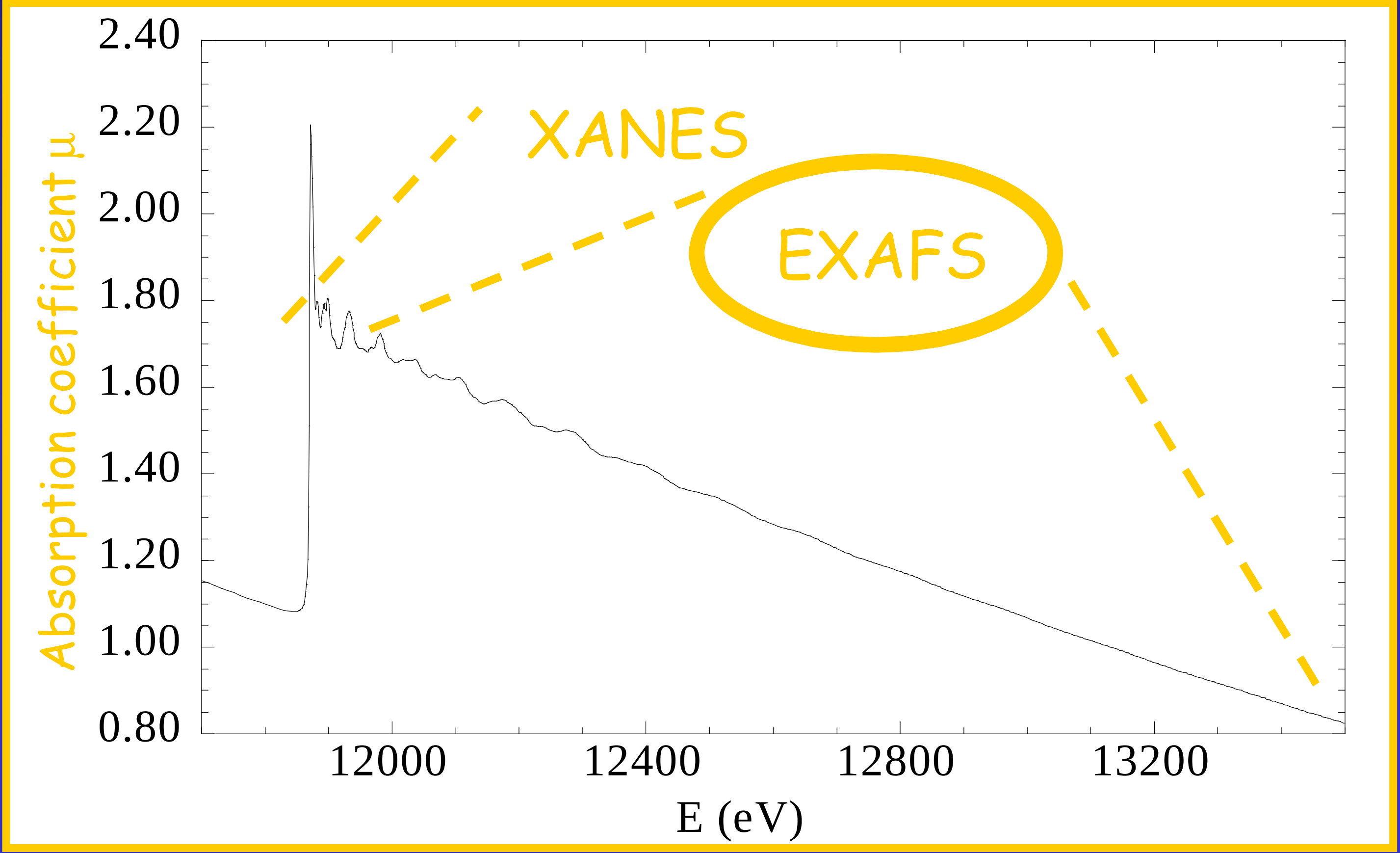
EXAFS and XANES

XANES: transitions to unfilled bound states, nearly bound states, continuum

→ local site symmetry, charge state, orbital occupancy

EXAFS: 50 - 1000 eV after edge due to transitions to continuum

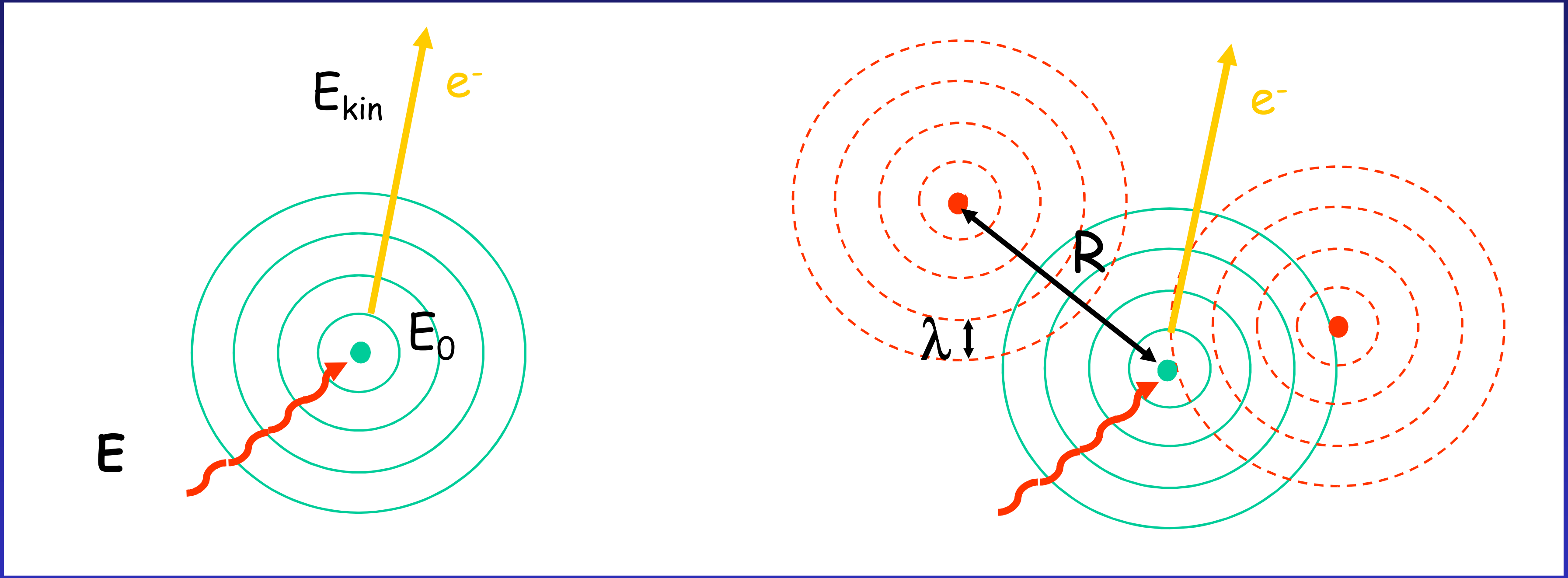
→ local structure (bond distance, number, type of neighbors….)



EXAFS qualitatively

isolated atom

condensed matter



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

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

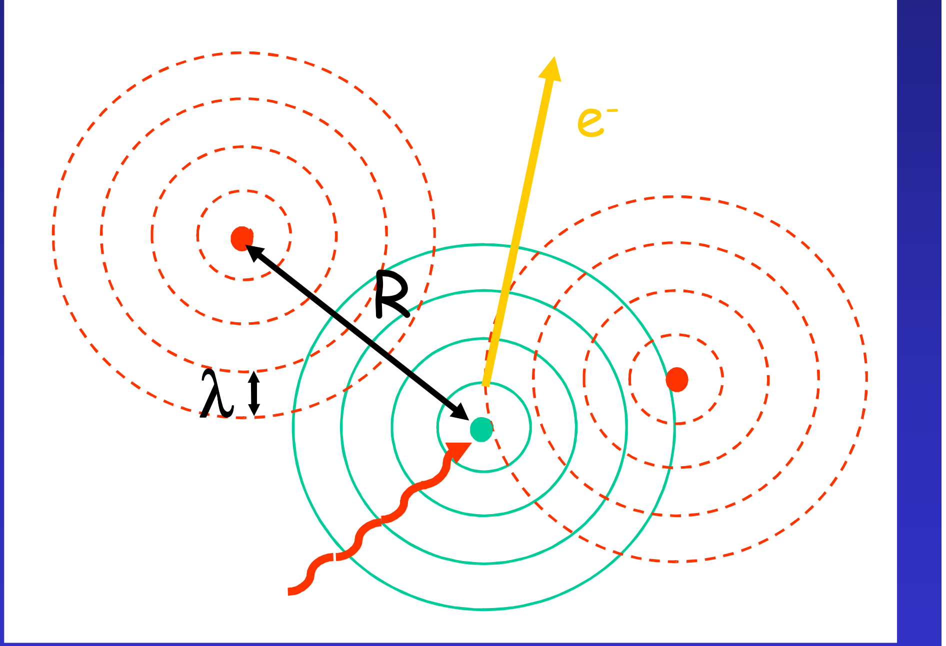
$$\boxed{\lambda = 2\pi/k}$$

Where do the oscillations come from ?

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

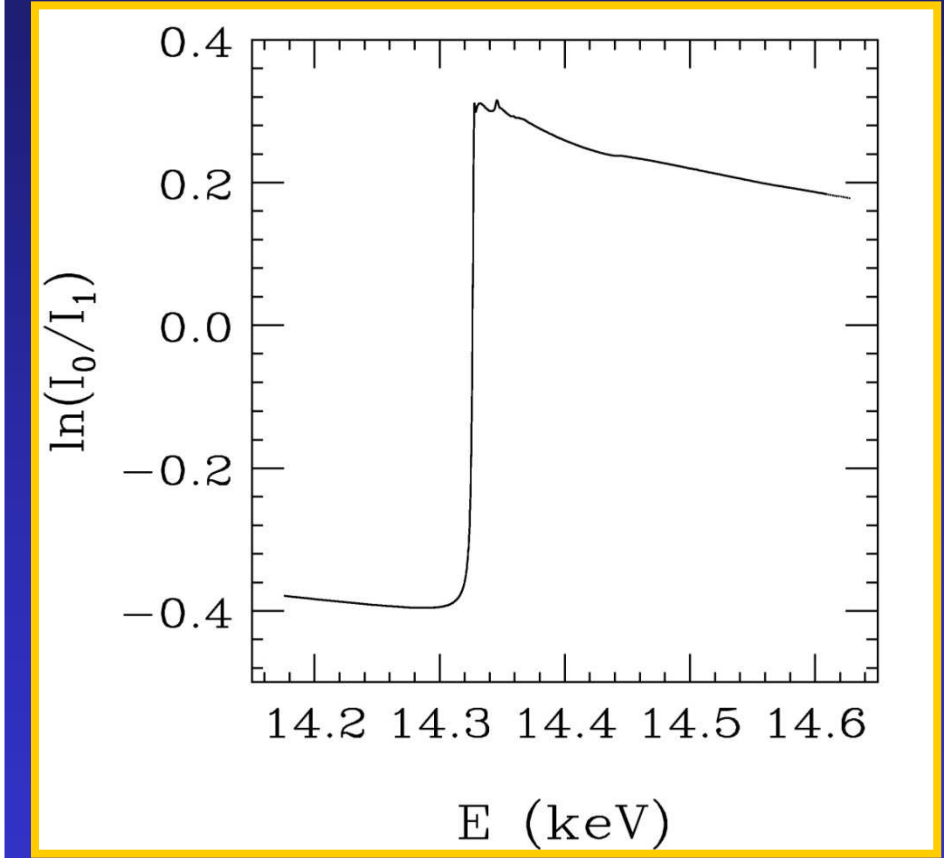
$$E_{kin} = E - E_0 = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}$$

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

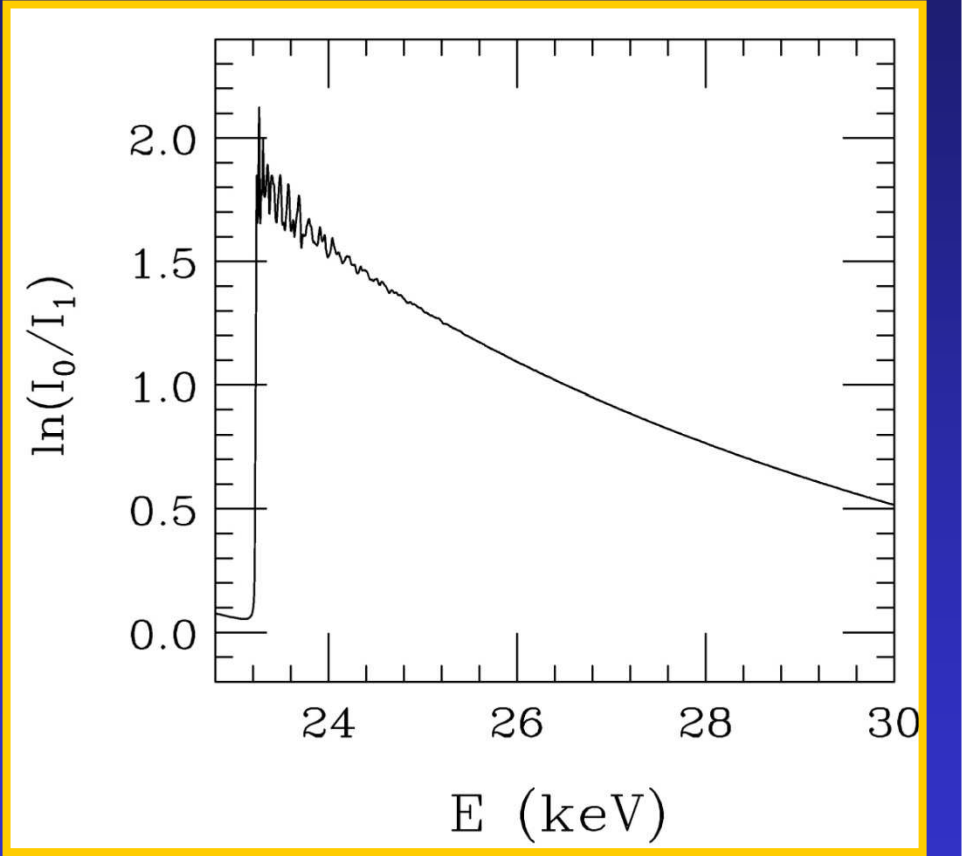


- frequency ~ distance from neighbors
- amplitude ~ number and type of neighbors

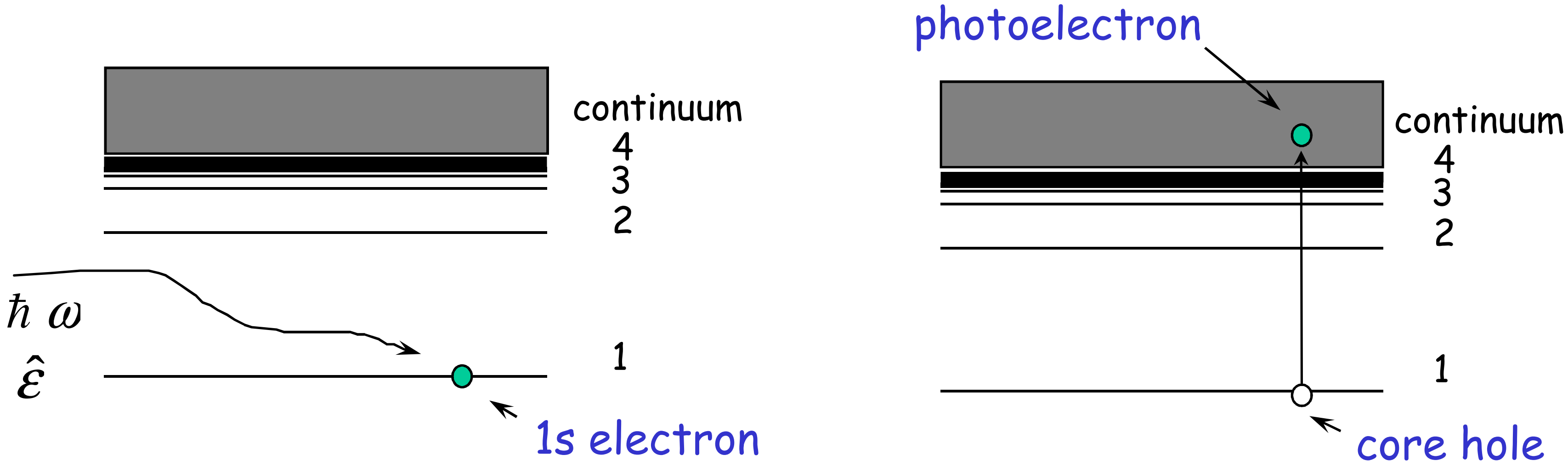
Kr gas



Rh metal



Absorption coefficient



in principle, all electrons are involved → multi body process

$$\mu(E) \approx \sum_f \left|\left\langle \Psi_i \right| \hat{H}_I \left| \Psi_f \right\rangle\right|^2 \approx \sum_f \left|\left\langle \Psi_i \right| \hat{\varepsilon}\cdot\hat{r} \left| \Psi_f \right\rangle\right|^2$$

dipole

$$H_I \approx \sum_j \vec{A}(\vec{r}_j)\cdot\vec{\nabla}_j$$

$$\approx A_0 \sum_j \hat{\varepsilon}\cdot\vec{\nabla}_j \approx A_0 \sum_j \hat{\varepsilon}\cdot\vec{r}_j$$

$$\approx \sum_f \left|\left\langle \Psi_i^{N-1}\psi_i \right| \hat{\varepsilon}\cdot\vec{r} \left| \Psi_f^{N-1}\psi_f \right\rangle\right|^2 \approx S_0^2 \sum_f \left|\left\langle \psi_i \right| \hat{\varepsilon}\cdot\vec{r} \left| \psi_f \right\rangle\right|^2$$

single electron

sudden

$$S_0^2 \approx \sum_f \left|\left\langle \Psi_i^{N-1} \middle| \middle| \Psi_f^{N-1} \right\rangle\right|^2$$

Consequences of dipole approximation: Selection rules

$\Delta l = \pm 1$

$\Delta s = 0$

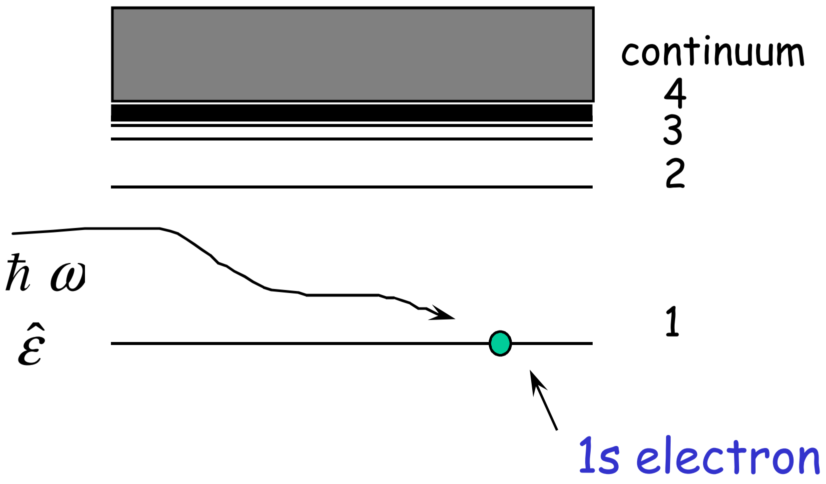
$\Delta j = \pm 1$

$\Delta m = 0$

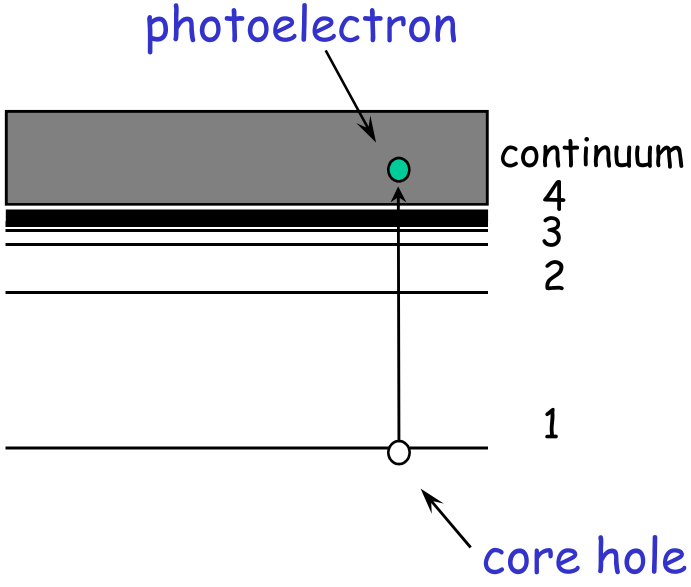
- For 1-electron transitions:

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)

Absorption coefficient



$\langle\psi_i| = \langle 1s|$ $\qquad E_i$



$|\psi_f\rangle = |\varepsilon p\rangle$ $\qquad E_f = \hbar\omega + E_i$

$$\boxed{\mu(E) \approx \sum_f \left|\langle\psi_i|\hat{\varepsilon}\cdot\vec{r}|\psi_f\rangle\right|^2}$$

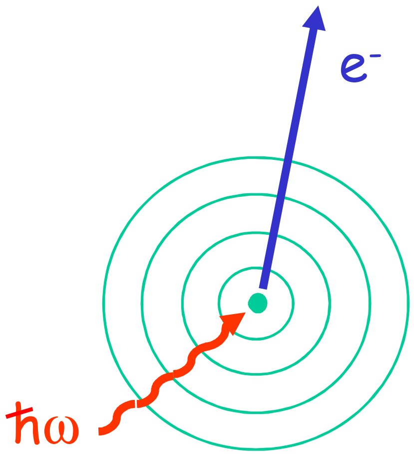
Approx:
dipole + single electron + sudden

ε : photon polarization **r**: electron position

$|\psi_i>$ relatively easy → ground state of atom; i.e. 1s e^- wavefunction

$|\psi_f>$ very complicated → final state strongly influenced by environment

Isolated atom: atomic absorption coefficient



photoelectron free to travel away undisturbed

$$|\psi_f\rangle = |\psi_f^0\rangle$$

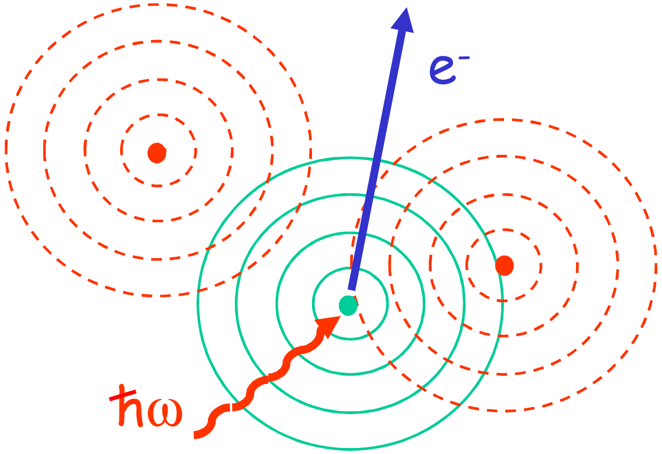
outgoing spherical wave originating
from the absorbing atom

$$\mu_0(\omega) \propto \left| \langle \psi_i | \; \hat{\varepsilon}\cdot\vec{r} \; | \psi_f^0 \rangle \right|^2$$

$$\mu_0(\omega) \propto \int d\vec{r} \left| \psi_i^*(\vec{r}) \; \hat{\varepsilon}\cdot\vec{r} \;\; \psi_f^0(\vec{r}) \right|^2$$

➡ overlap integral of initial and final state wavefunctions:
monotonically decreases as function of E

Non-isolated atom



$$|\psi_f\rangle = |\psi_f^0 + \delta\psi_f\rangle$$

sum of the outgoing and all the incoming waves, one per each neighboring atom.

$$\mu(\omega) \propto \left| \langle \psi_i | \ \hat{\varepsilon}\cdot\vec{r} \ | \ \psi_f^0 + \delta\psi_f \ \rangle \right|^2$$

$$\mu(\omega) \propto \int d\vec{r} \left| \psi_i^*(\vec{r}) \ \hat{\varepsilon}\cdot\vec{r} \left[\ \psi_f^0(\vec{r}) + \delta\psi_f(\vec{r}) \ \right] \right|^2$$

$$\mu(\omega) \propto \int d\vec{r} \left| \psi_i^*(\vec{r}) \ \hat{\varepsilon}\cdot\vec{r} \ \psi_f^0(\vec{r}) \ \right|^2 + 2\,\mathrm{Re}\int d\vec{r} \ \left[\psi_i(\vec{r}) \ \hat{\varepsilon}\cdot\vec{r} \ \psi_f^{0*}(\vec{r})\right]\left[\psi_i^*(\vec{r}) \ \hat{\varepsilon}\cdot\vec{r} \ \delta\psi_f(\vec{r})\right]$$

$$\cancel{+ \int d\vec{r} \ \left| \psi_i^*(\vec{r}) \ \hat{\varepsilon}\cdot\vec{r} \ \delta\psi_f(\vec{r}) \ \right|^2}$$

EXAFS

Origin of EXAFS

$$\mu = \mu_0 \left[1 + \chi\right]$$

χ : fractional change in μ introduced by the neighbors

$$\chi(k) = \frac{2\,\mathrm{Re} \int d\vec{r}\, \left[\psi_i(\vec{r})\, \hat{\varepsilon}\cdot\vec{r}\, \psi_f^{0^*}(\vec{r})\right] \left[\psi_i^*(\vec{r})\, \hat{\varepsilon}\cdot\vec{r}\, \delta\psi_f(\vec{r})\right]}{\int d\vec{r} \left|\psi_i^*(\vec{r})\, \hat{\varepsilon}\cdot\vec{r}\, \psi_f^0(\vec{r})\right|^2} \qquad (1)$$

Interference between outgoing wavefunction and backscattered wavelets

Dominant contribution to integral comes from spatial region close to absorber atom nucleus, where the core orbital wavefunction $\psi_i \neq 0$.

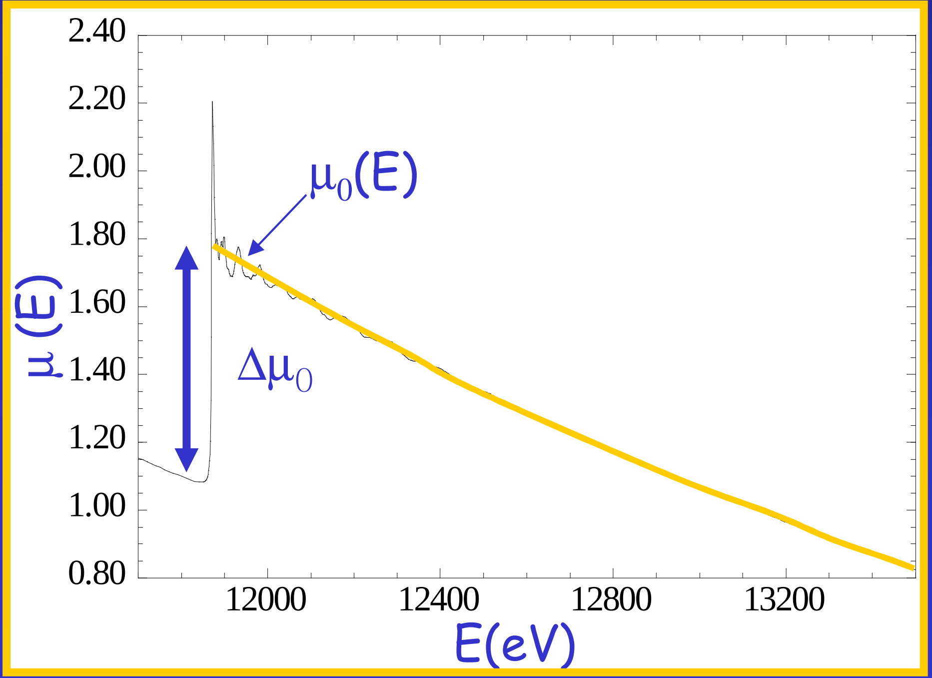
The region where $\psi_i \neq 0$ represents simultaneously
the source and the detector for the photoelectron
that probes the local structure around the absorber atom

The EXAFS signal χ

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

$$\boxed{\chi(E) = \frac{\mu(E) - \mu_0(E)}{\Delta\mu_0(E_0)}}$$

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



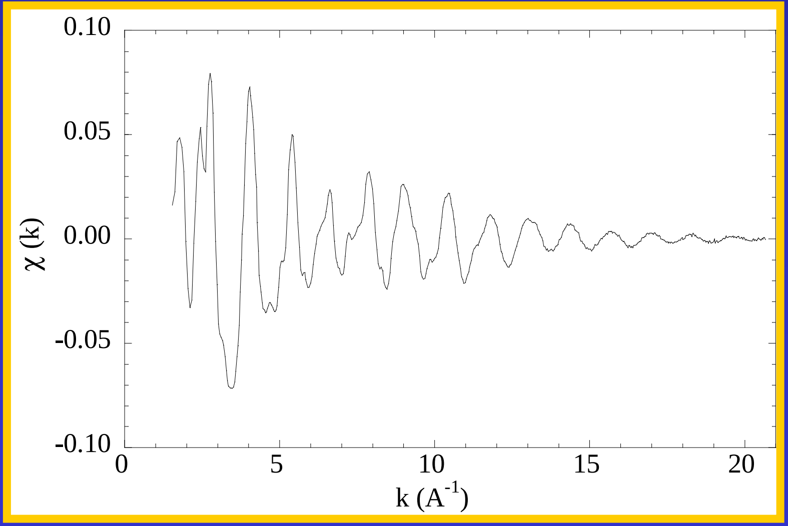
EXAFS : χ (k)

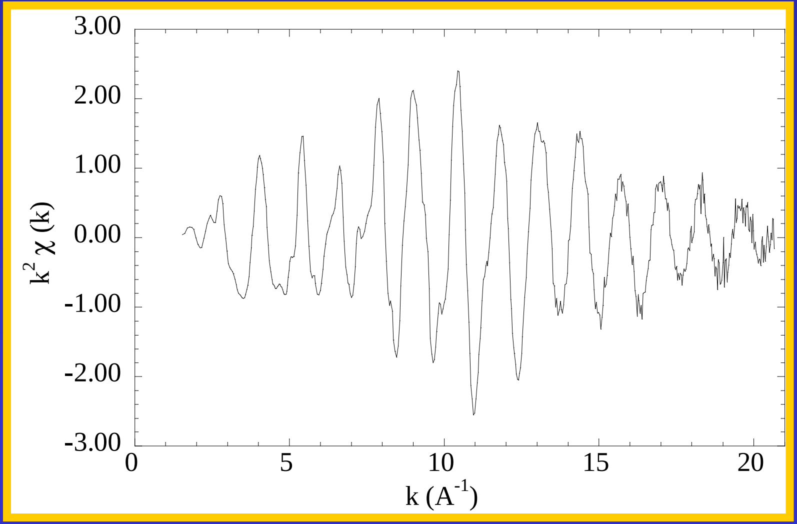
XAFS is an *interference effect*, and depends on the wave-nature of the photoelectron.

It's convenient to think of XAFS in terms of *photoelectron wavenumber*, k, rather than x-ray energy

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

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

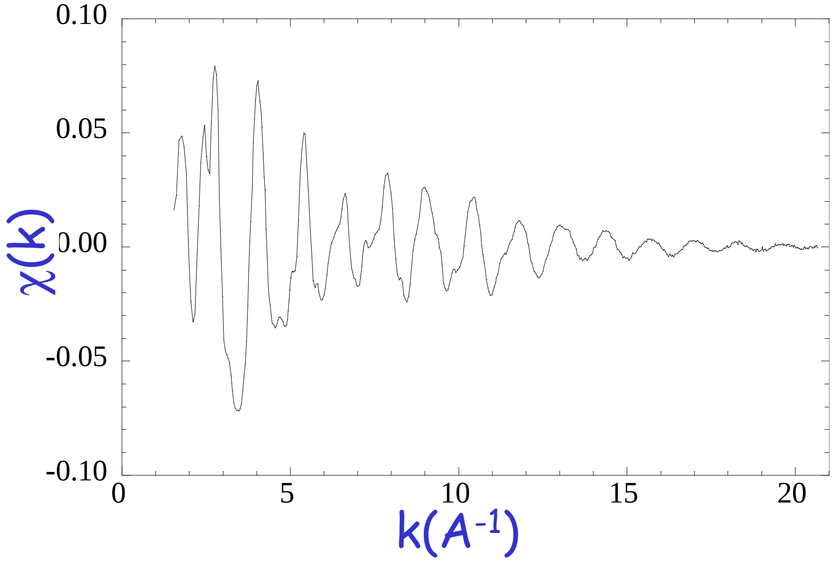


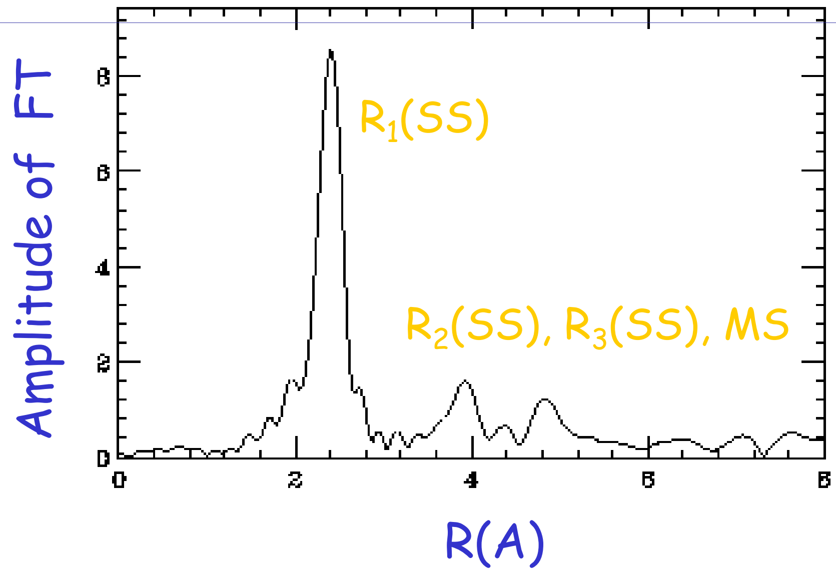


Qualitative picture of local coordination in R space

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).

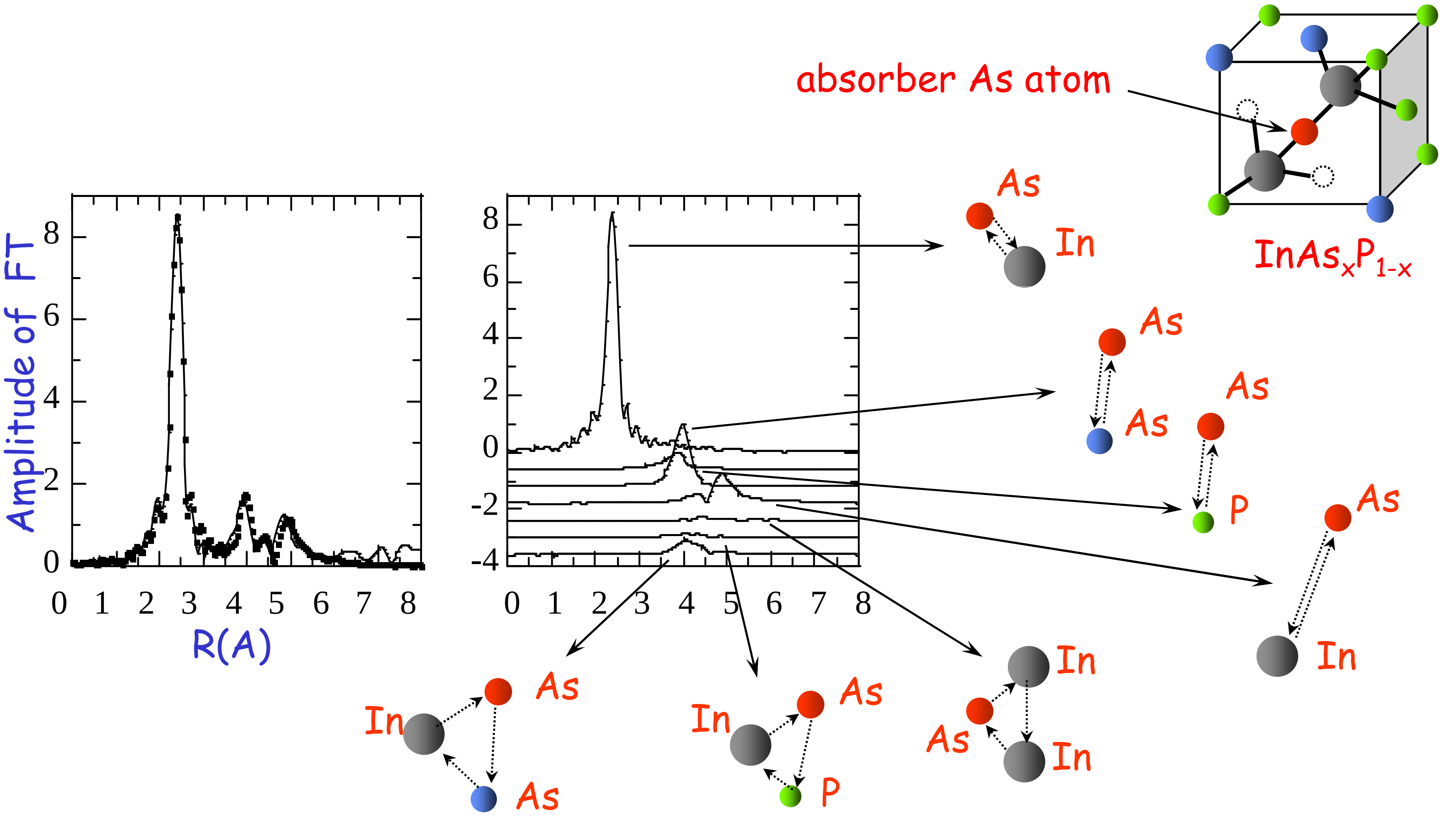
A Fourier Transform of the EXAFS signal provides a photoelectron scattering profile as a function of the radial distance from the absorber.





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.



χ : 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:

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

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

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

The larger the number of neighbors, the larger the signal

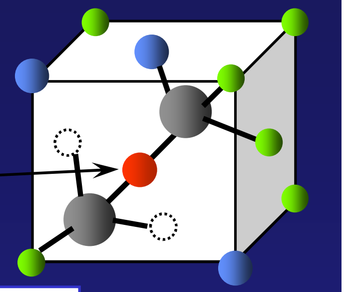
The stronger the scattering amplitude, the larger the signal

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

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

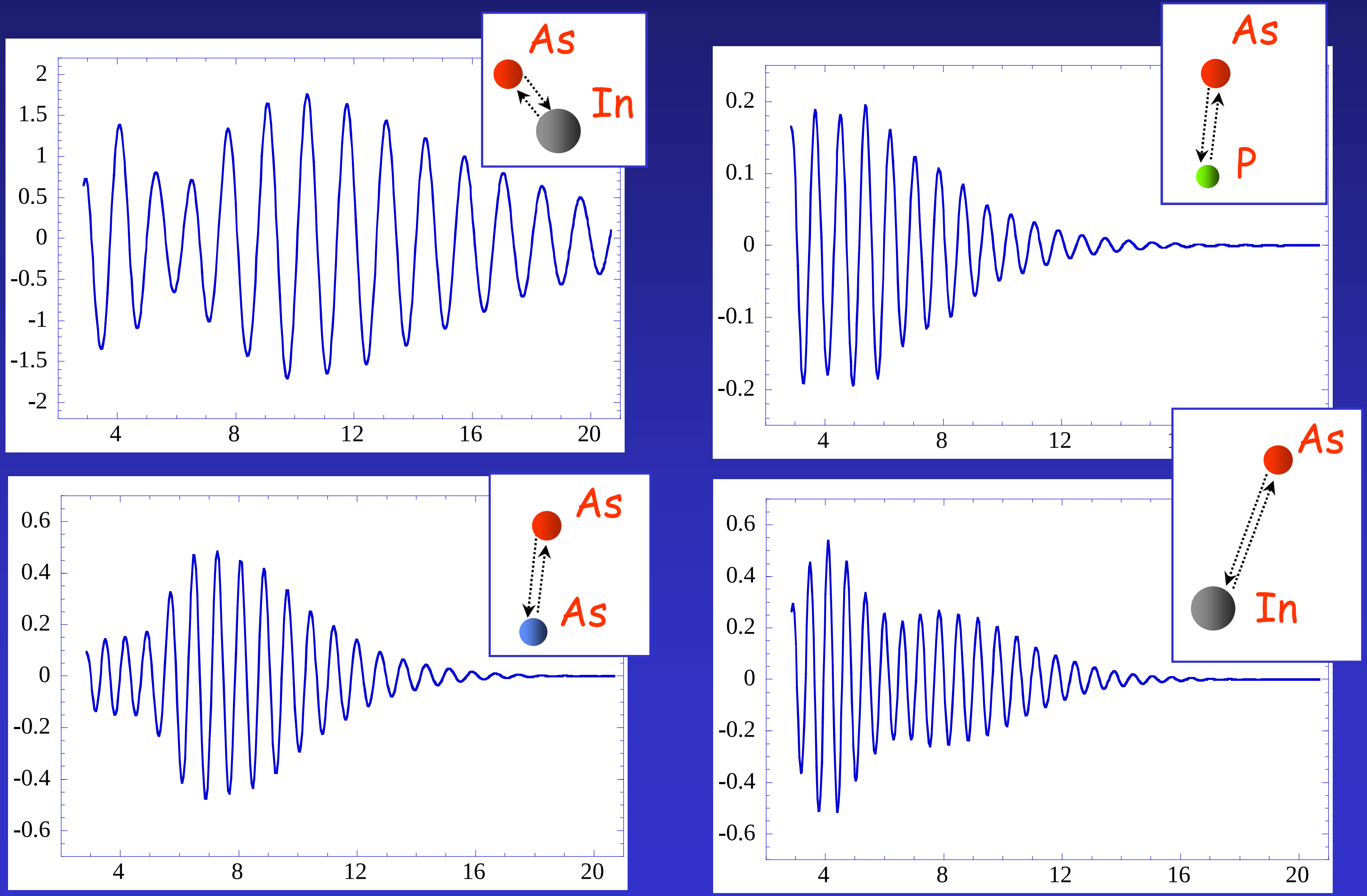
Amplitudes

$InAs_xP_{1-x}$



absorber As atom

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



$k(A^{-1})$ $k(A^{-1})$

Frequencies:
Single and Multiple Scattering paths

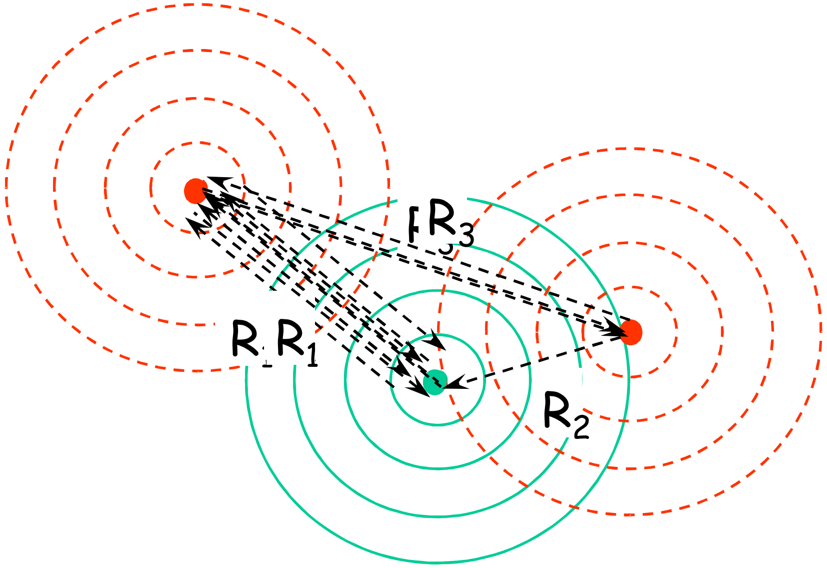
The sum over paths in the EXAFS equation includes many shells of atoms (1st neighbor, 2nd neighbor, 3rd neighbor, . . .), but can also include multiple scattering paths, in which the photoelectron scatters from more than one atom before returning to the central atom.

SS ⇨ $g_2(r)$
$f = 2\,R_1$

MS ⇨ $g_2(r)$
$f = 4\,R_1$

MS ⇨ $g_3(r)$
$f = R_1 + R_2 + R_3$

MS ⇨ $g_3(r)$
$f = 2R_1 + 2R_3$



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

The EXAFS equation

To model the EXAFS, we use the *EXAFS Equation*

$$\chi(k) = -\ S_0^2\ \Sigma_j\ N_j\ \frac{\boxed{f_j(k)}}{kR_j^{\,2}}\ e^{-2k^2\sigma_j^{\,2}}\ \sin\left[2kR_j + \boxed{\delta_j(k)}\right]$$

where f(k) and δ(k) are *photoelectron scattering properties* of the neighboring atom. (The sum is over “shells” of similar neighboring atoms). If we know these properties, we can determine:

R distance to neighboring atom.

N coordination number of neighboring atom.

σ^2 mean-square disorder of neighbor distance.

The scattering amplitude f(k) and phase-shift δ(k) depend on atomic number *Z* of the scattering atom, so we can also determine the species of the neighboring atom.

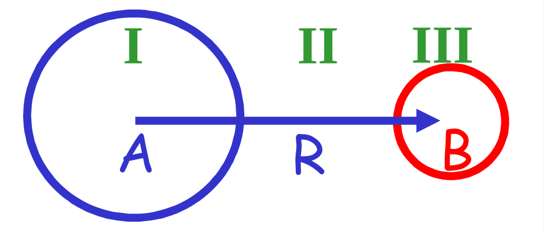
The EXAFS equation: simple description

With spherical wave for the propagating photoelectron:
and a scattering atom at a distance r = R, we get:

$$\frac{e^{ikr}}{kr}$$

Region III:
amplitude of backscattering on B

$$\Delta\psi_f \sim \psi^0{}_f\ [i\,\frac{e^{\,ikR}}{2kR}\,e^{i\delta c}\,]\ |f(k)|\ e^{i\delta s(k)}\ \frac{e^{\,ikR}}{kR}\,e^{i\delta c}\ ]$$



Region I:
amplitude
of outgoing wave

Region II:
amplitude of
wave arriving on B

Region II:
amplitude of ingoing
wave, backscattered from B

where the neighboring atom gives the amplitude $|f(k)|$ and phase-shift $\delta_s(k)$ to the scattered photoelectron.
Substituting into equation (1) and after some math we get:

$$\chi(k) = -\frac{f(k)}{kR^2}\sin[2kR + \delta(k)]$$

$$\delta(k) = \delta_s(k) + 2\,\delta_c(k)$$

for 1 scattering atom.

Development of the EXAFS equation

For N scattering atoms, and with a thermal and static Gaussian disorder of σ^2, giving the mean square disorder in R*, we have

$$\chi(k) = -\ S_0^2\ N \frac{f(k)}{kR^2}\ e^{-2k^2\sigma^2} \sin[2kR + \delta(k)]$$

A real system will have neighboring atoms at different distances and of different types. We add all these contributions to get a version of the EXAFS equation:

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

To obtain this formula we used a spherical wave for the photoelectron: $\dfrac{e^{ikr}}{kr}$

* EXAFS takes place on a time scale much shorter than that of atomic motion, so the measurement serves as an instantaneous snapshot of the atomic configuration

The photoelectron mean free path

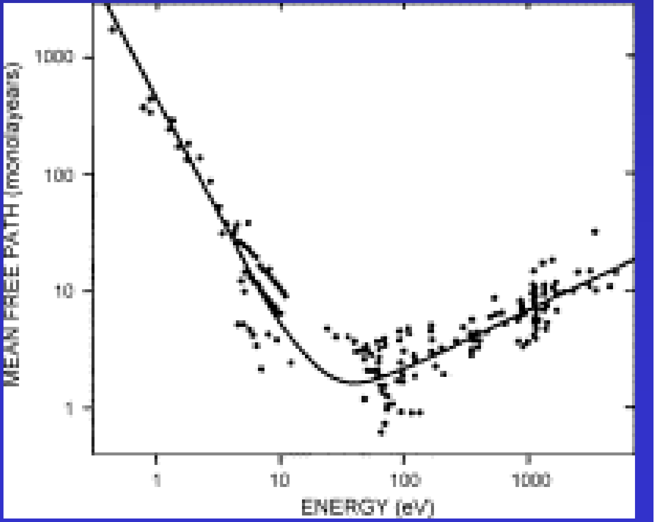
But the photoelectron can also *scatter inelastically**, and may not be able to get back the absorbing atom. Also: The *core-hole has a finite lifetime***, limiting how far the photoelectron can go.

Using a damped wave-function: $\frac{e^{ikr}}{kr} e^{-r/\lambda(k)}$ where λ(k) is the photo electron's *mean free path* (including core hole lifetime), the EXAFS equation becomes:

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

The mean free path λ depends on k.
For the EXAFS k range, λ < 25 Å.

The λ and R^{-2} terms make EXAFS *a local atomic probe.*



* Electrons that have suffered inelastic losses will not have the proper wave vector to contribute to the interference process.

** the photoelectron and core hole exist simultaneously

S_0^2 : Amplitude Reduction Term

Another important Amplitude Reduction Term is due to the relaxation of all the other electrons in the absorbing atom to the hole in the core level:

$$S_0^2 \approx \sum_f \left| \left\langle \Psi_i^{N-1} \middle| \middle| \Psi_f^{N-1} \right\rangle \right|^2$$

where Ψ_f^{N-1} accounts for the relaxation of the other N-1 electrons relative to these electrons in the unexcited atom: Ψ_0^{N-1}. Typically S_0^2 is taken as a constant:

$$0.7 < S_0^2 < 1.0$$

which is found for a given central atom, and simply multiplies the XAFS χ.

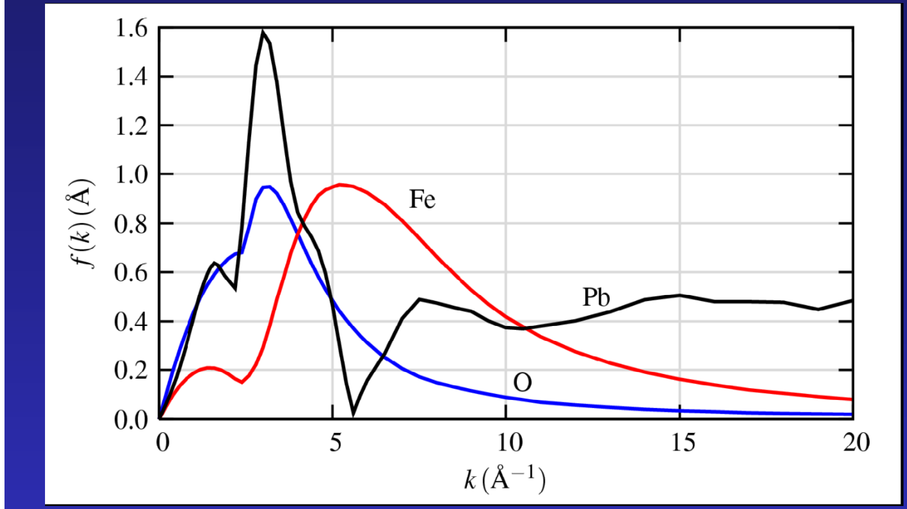
Note that S_0^2 is completely correlated with N.

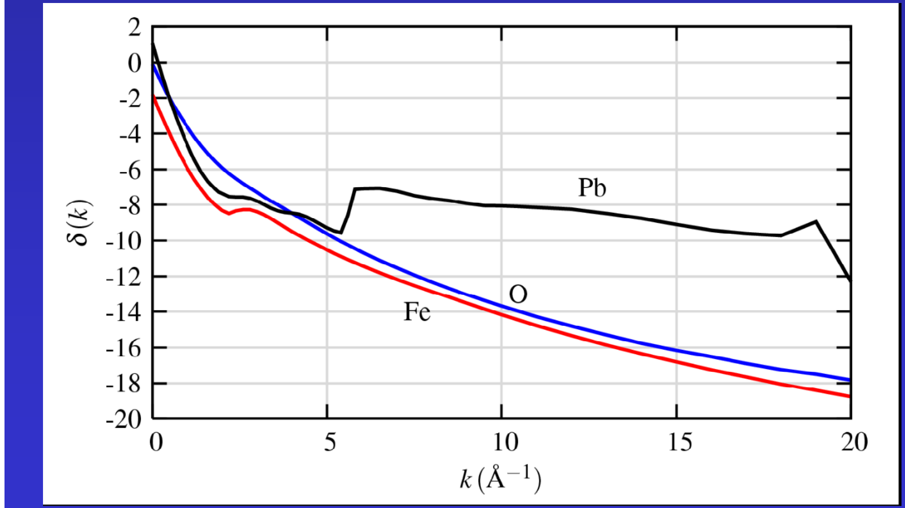
This, and other experimental and theoretical issues, make EXAFS amplitudes (and therefore N) less precise than EXAFS phases (and therefore R).

Usually S_0^2 is found from a “standard” (data from a sample with well-known structure) and applied to a set of unknowns as a scale factor.

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

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





The scattering amplitude f (k) peaks at different k values 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 (say 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 δ (k)

These days, we can calculate f (k) and δ (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 δ (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

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

EXAFS: typical applications

Element selectivity
Local structure sensitivity

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

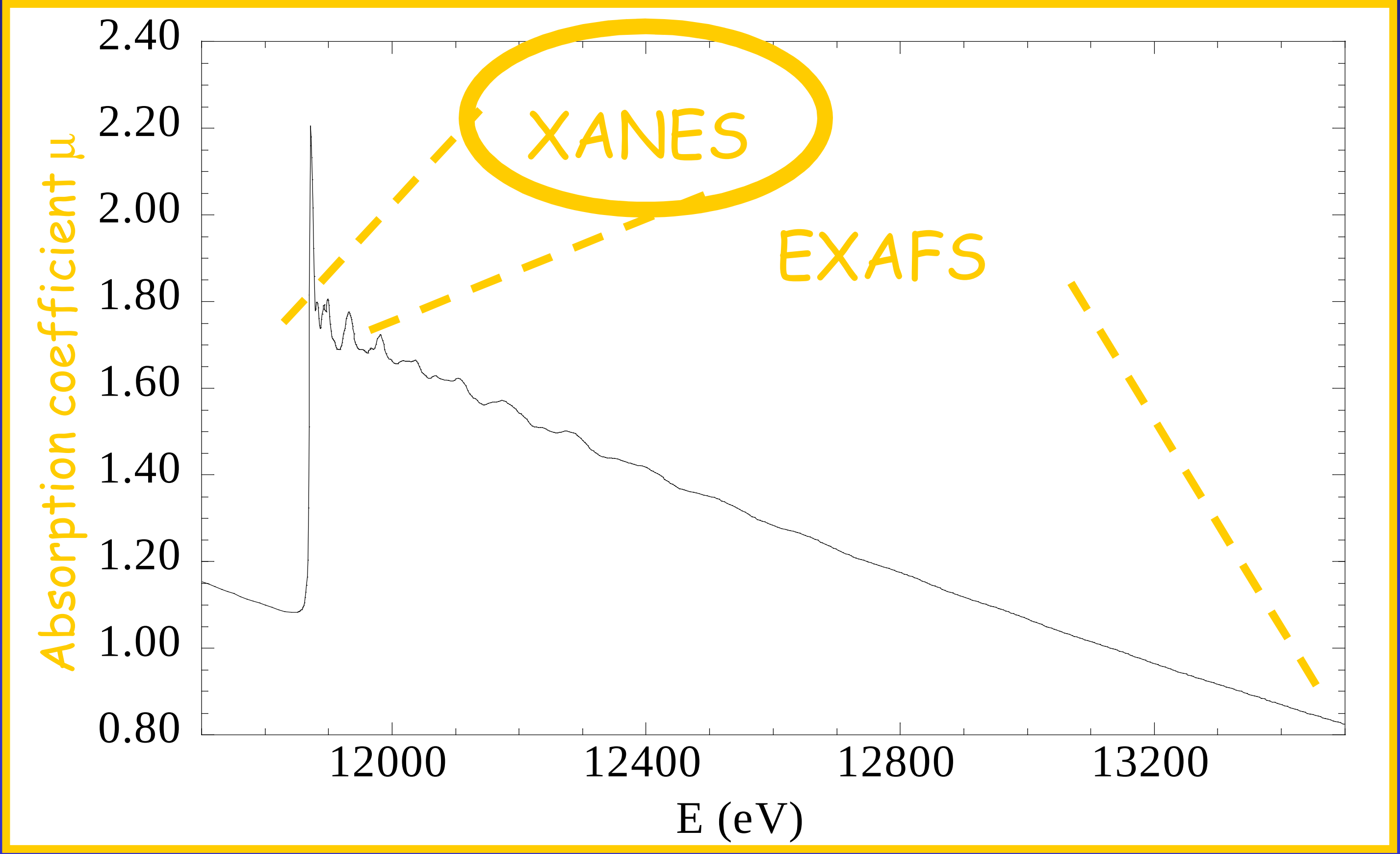
EXAFS and XANES

XANES: transitions to unfilled bound states, nearly bound states, continuum

→ local site symmetry, charge state, orbital occupancy

EXAFS: 50 - 1000 eV after edge due to transitions to continuum

→ local structure (bond distance, number, type of neighbors….)



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:

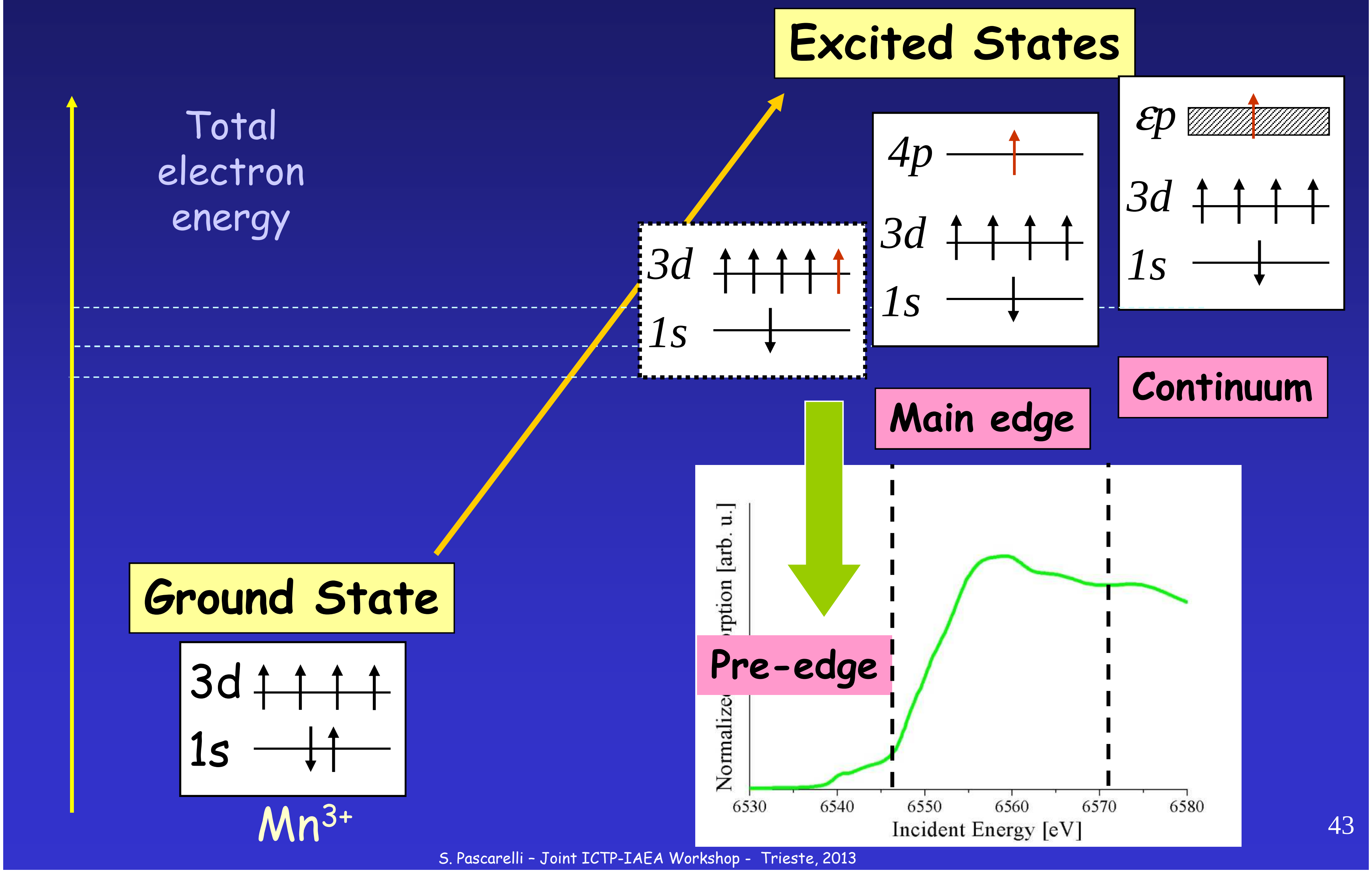
What electronic states can the photoelectron fill?

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...

K-Edge XANES

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



Excited States

Ground State

Mn^{3+}

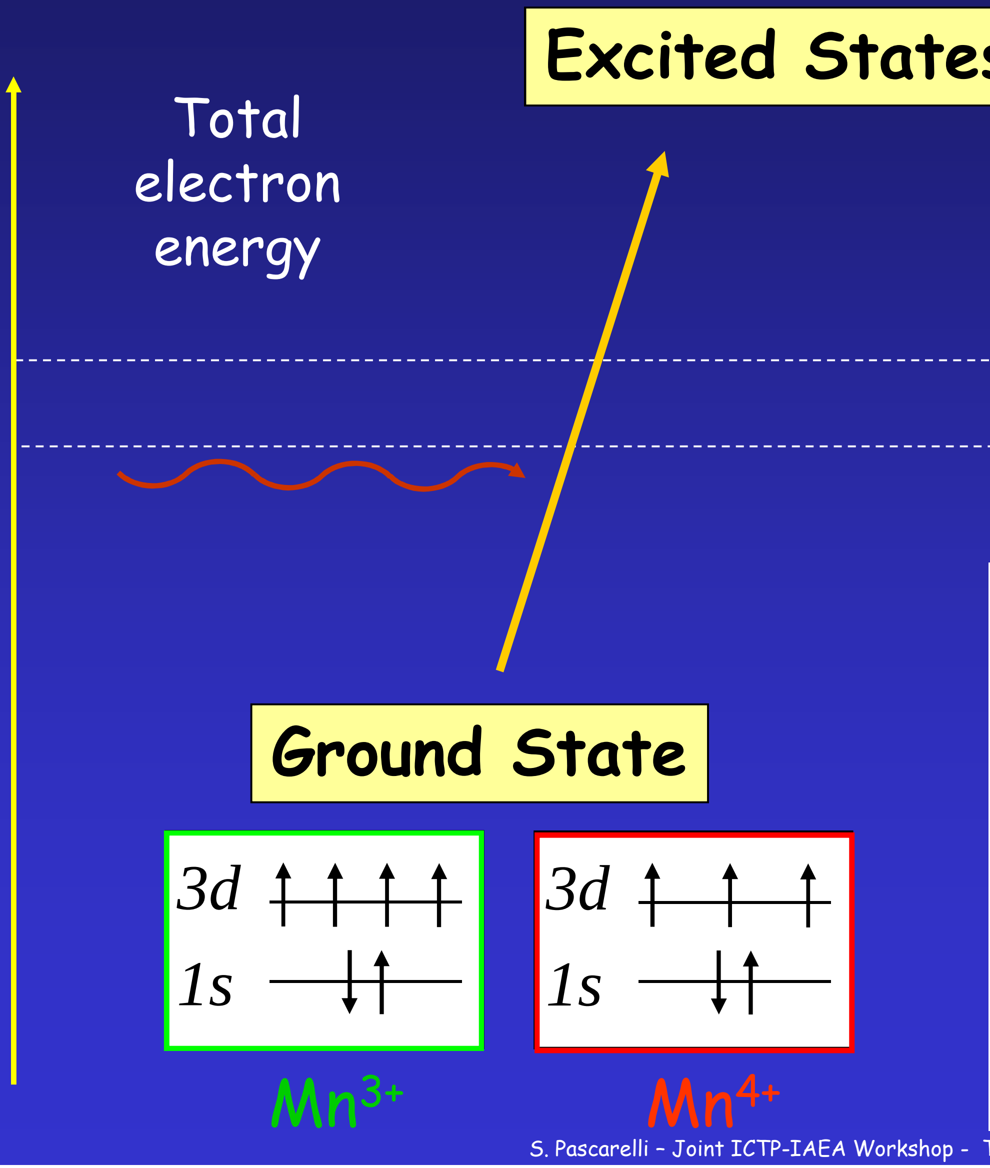
Main edge

Continuum

Pre-edge

Chemical Shift

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



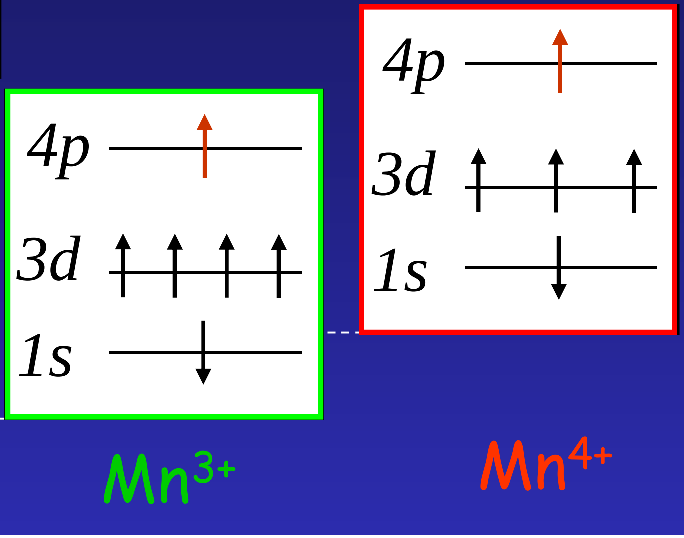
Total electron energy

Excited States

Ground State

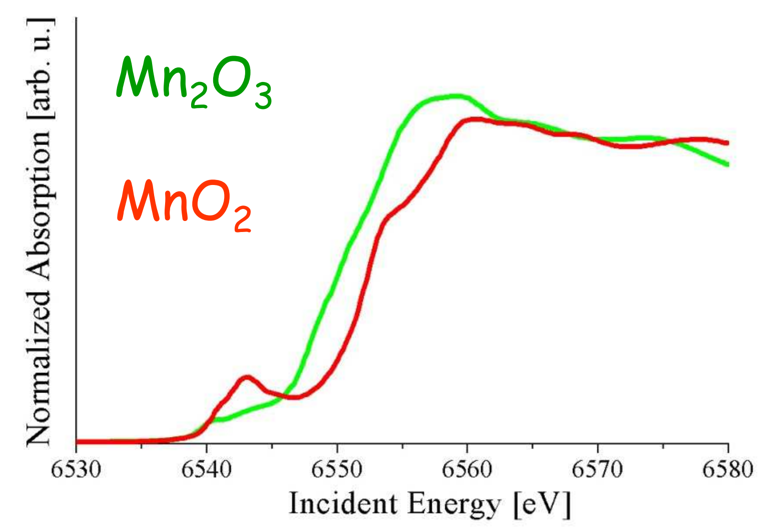
Mn^{3+}

Mn^{4+}

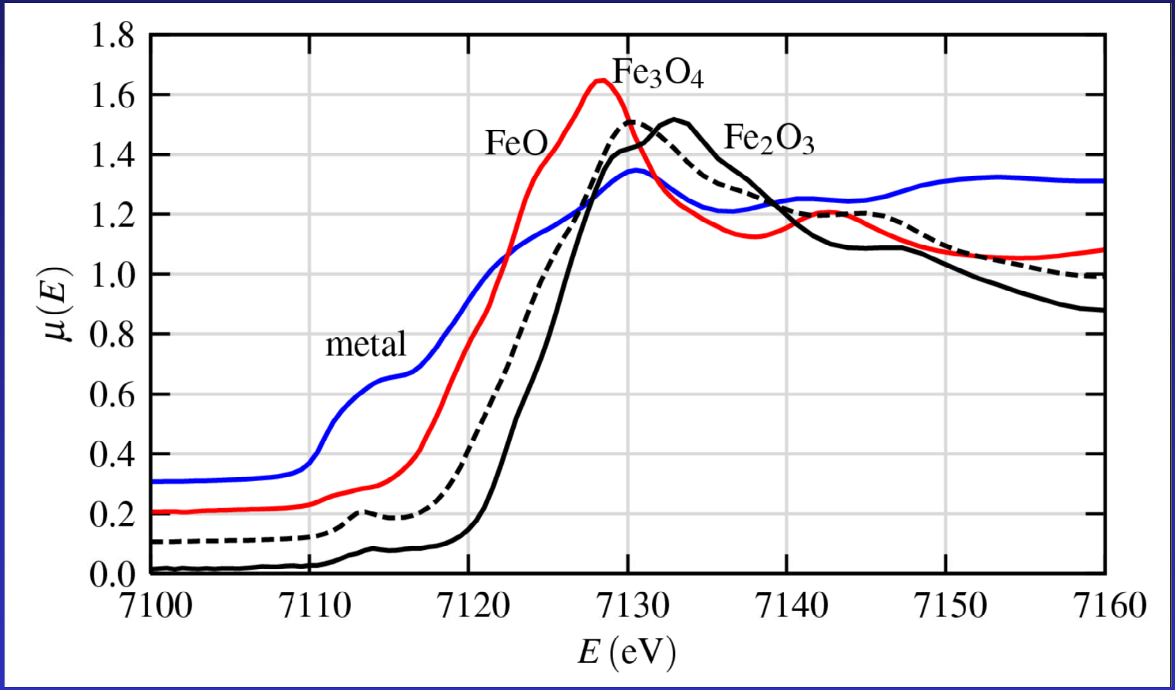


Mn^{3+}

Mn^{4+}



Edge Shifts and Pre-edge Peaks in Fe oxides

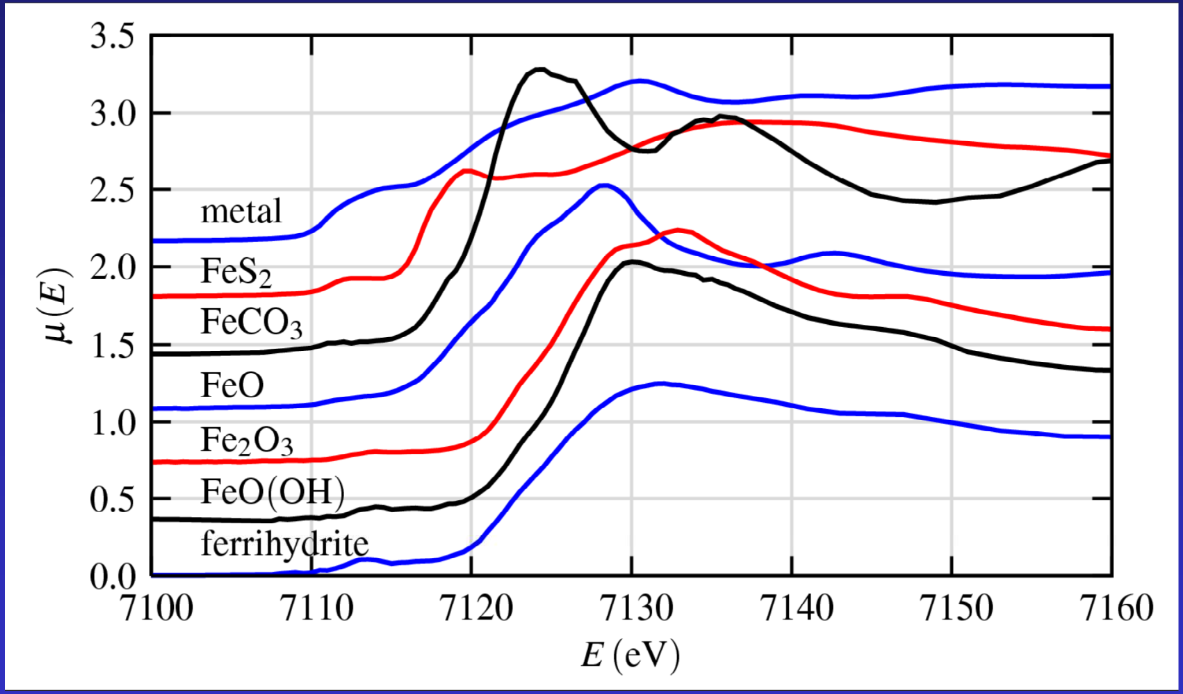


XANES for Fe oxides and metal

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 sometimes used to determine Fe^{3+}/Fe^{2+} ratios.

XANES Analysis: Oxidation State

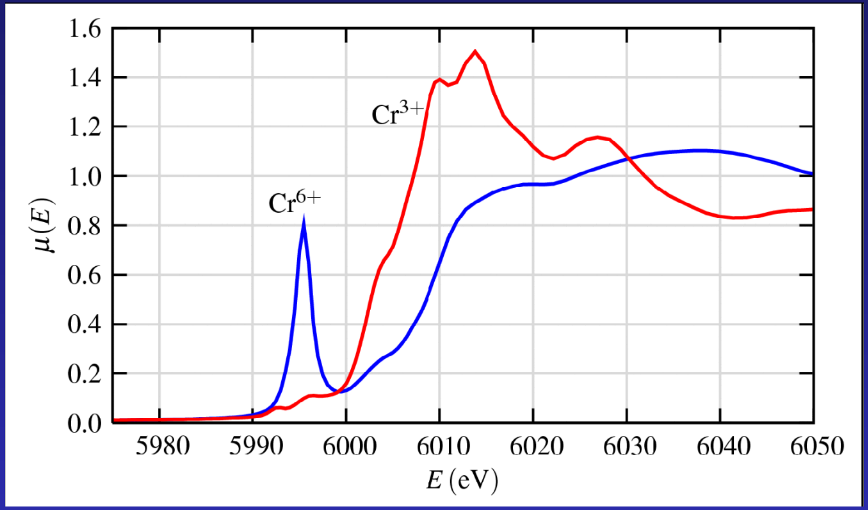
The Normalized XANES from several Fe compounds:

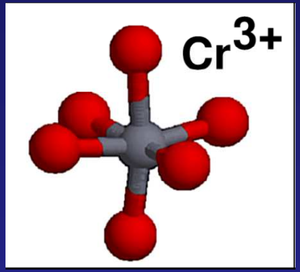


XANES can be used simply as a fingerprint of phases and oxidation state.

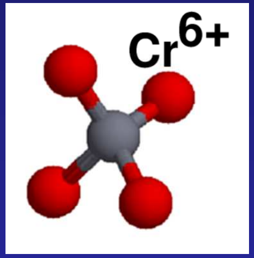
XANES analysis can be as simple as making linear combinations of “known” spectra to get compositional fraction of these components.

XANES Analysis: Coordination Chemistry





O_h centrosymm
only weak quadrupole channel



T_d non-centrosymm
p-d mixing
dipole channel

The XANES of Cr^{3+} and Cr^{6+} 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.

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 . . . .

More information: web links

International XAFS Society: http://ixs.iit.edu/

Tutorials and other Training Material: http://xafs.org/Tutorials

Software Resources EXAFS:

http://xafs.org/Software
- http://leonardo.phys.washington.edu/feff
- http://gnxas.unicam.it/

More information: 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* 92
D. C. Koningsberger and R. Prins, ed., John Wiley & Sons, 1988.

Basic Principles and Applications of EXAFS, Chapter 10 in *Handbook of Synchrotron Radiation*, pp 995–1014.
E. A. Stern and S. M. Heald, E. E. Koch, ed., North-Holland, 1983

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 measure the absorption coefficient μ

$$-dI = I(x)\,\underset{\substack{\uparrow\\ \text{at/cm}^2}}{N}\,\frac{dx}{t}\,\underset{\substack{\uparrow\\ \text{cm}^2\text{/at}}}{\sigma_a}$$

$$-\int_0^t \frac{dI}{I(x)} = N\,\frac{\sigma_a}{t}\int_0^t dx$$

$$\ln I(t) - \ln I(0) = -N\sigma_a$$

$$\frac{I(t)}{I(0)} = e^{-N\sigma_a} = e^{-\mu t}$$

$$\boxed{\frac{I(t)}{I(0)} = e^{-N\sigma_a} = e^{-\mu t}}$$

- μ is related to the atomic cross section:

$$\mu(\omega) = \sigma_a(\omega)\frac{N}{t} = \sigma_a(\omega)\frac{N_a}{A}\rho \qquad \left[\frac{cm^2}{at}\right]\frac{\left[\frac{at}{mole}\right]}{\left[\frac{gr}{mole}\right]}\left[\frac{gr}{cm^3}\right] = \left[cm^{-1}\right]$$

- in general you find tabulated the mass absorption coefficient μ/ρ:

$$\frac{\mu}{\rho} = \sigma_a\frac{N_a}{A} \qquad \left[\frac{cm^2}{at}\right]\frac{\left[\frac{at}{mole}\right]}{\left[\frac{gr}{mole}\right]} = \left[\frac{cm^2}{gr}\right]$$

- for a generic sample P_xQ_y.....:

$$\left(\frac{\mu}{\rho}\right)_{tot} = x\left(\frac{\mu}{\rho}\right)_P \frac{A_P}{M} + y\left(\frac{\mu}{\rho}\right)_Q \frac{A_Q}{M} + \ldots$$

Recipe for calculating t for transmission XAS

$$\frac{I(t)}{I(0)} = e^{-N\sigma_a} = e^{-\mu t}$$

1. Total absorption above the edge must not be too high:
   $\mu_{\text{above edge}}\, t = 2 \rightarrow 5$ $I / I_0 \sim 0.14 \rightarrow 0.007$

   ideally $\boxed{\mu_{\text{above edge}}\, t = 2\text{-}3}$

2. Contrast at edge must be as large as possible:
   $[\mu_{\text{above edge}} - \mu_{\text{below edge}}]\, t > 0.1$

   ideally $\boxed{[\mu_{\text{above edge}} - \mu_{\text{below edge}}]\, t = 1}$

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

How to calculate μ

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

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

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

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

$$\mu(\omega) = -\frac{2}{\varepsilon_0 \omega^2 A_0^2}\frac{du}{dx}$$

$$\mu(\omega) = -\frac{2}{\varepsilon_0 \omega^2 A_0^2}\frac{d}{dx}\left[\hbar\omega\, n_{ph}\right]$$

$$\mu(\omega) = -\frac{2\hbar}{\varepsilon_0 \omega A_0^2}\frac{d}{dx}\left[n_{ph}\right]$$

$$\mu(\omega) = \frac{2\hbar}{\varepsilon_0 \omega A_0^2}\; n \sum_f W_{if}$$

X-ray Absorption

I. Lets consider the interaction between:

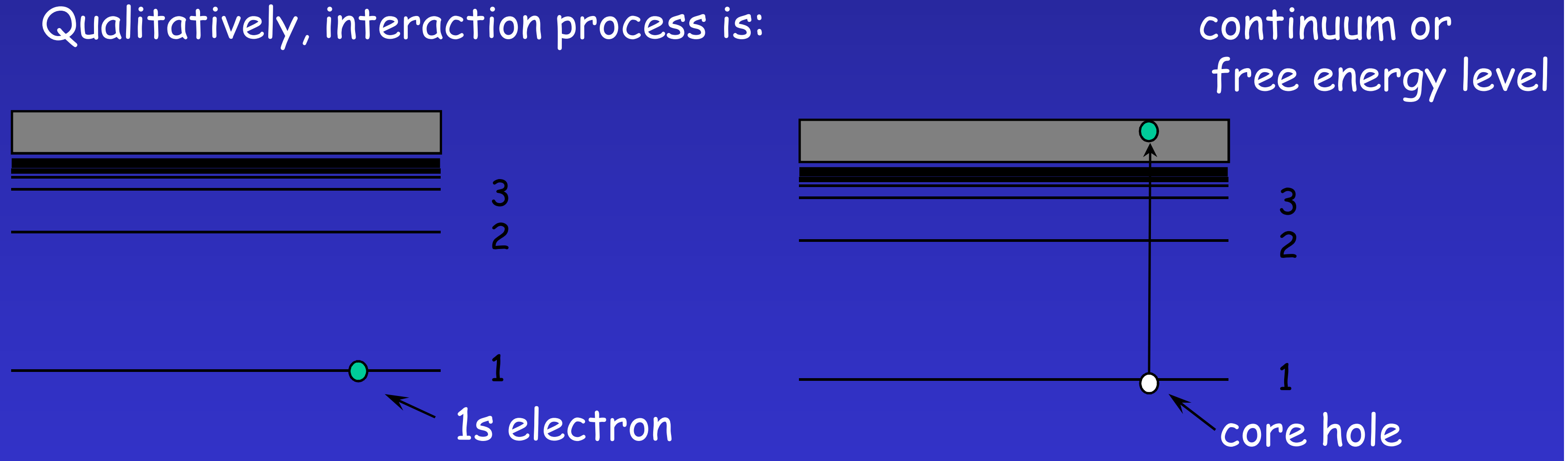
Monochromatic X-ray beam ($\omega = 2\pi\nu$) + monoatomic sample

EM field (classic) + atom (quantistic)

(semi-classical description)

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

III. Qualitatively, interaction process is:



$| \Psi_i >,\ E_i$

$| \Psi_f >,\ E_f = E_i + \hbar\omega$

Transition probability: Golden Rule

- $\mu(\omega)$ depends on:
  - atomic density n
  - transition probability W_{if} of atom from $|\Psi_i>$ to $|\Psi_f>$

$$\mu(\omega) = \frac{2\hbar}{\varepsilon_0\,\omega\,A_0^2}\,n\sum_f W_{if} \qquad (1)$$

- to calculate W_{if} : time-dependent perturbation theory based on power series of EM field - atom interaction potential.
- The interaction is in general WEAK
- Can limit series to 1st order: Golden Rule

$$W_{if} = \frac{2\pi}{\hbar}\left|\left\langle \Psi_i \middle| \hat{H}_I \middle| \Psi_f \right\rangle\right|^2 \rho(E_f) \qquad (2)$$

$\hat{H}_I$ EM field - atom interaction hamiltonian operator

$\left|\left\langle \Psi_i \middle| \hat{H}_I \middle| \Psi_f \right\rangle\right|$ Matrix element of H_I between initial and final state

$\rho(E_f)$ Density of final states, compatible with energy conservation:

$$E_f = E_i + \hbar\omega$$

- the interaction hamiltonian for photoelectric absorption (see Appendix 1) is (to 1st order):

$$H_I = i\hbar \frac{e}{m} \sum_j \vec{A}\left(\vec{r}_j\right) \cdot \vec{\nabla}_j \qquad (3)$$

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

$$W_{if} = \frac{\pi \hbar e^2}{m^2} \left|A_0\right|^2 \left| \left\langle \Psi_i \right| \sum_j e^{i\vec{k}\cdot\vec{r}_j} \hat{\varepsilon} \cdot \vec{\nabla}_j \left| \Psi_f \right\rangle \right|^2 \rho\left(E_f\right) \qquad (4)$$

Dipole approximation

- further simplification:

$$e^{i\vec{k}\cdot\vec{r}_j} = 1 + i\,\vec{k}\cdot\vec{r}_j - \frac{\left(\vec{k}\cdot\vec{r}_j\right)^2}{2!} \ldots \cong 1$$

$$\text{if} \quad \left|\vec{k}\cdot\vec{r}_j\right|^2 << 1$$

- transition probability in dipole approximation:

$$W_{if} = \frac{\pi\,\hbar\,e^2}{m^2}\,|A_0|^2\,\left|\left\langle\Psi_i\right|\sum_j \hat{\varepsilon}\cdot\vec{\nabla}_j\left|\Psi_f\right\rangle\right|^2\,\rho(E_f)$$

- alternative and equivalent expression :

$$W_{if} = \frac{\pi e^2\omega^2}{\hbar}\,|A_0|^2\,\left|\left\langle\Psi_i\right|\sum_j \hat{\varepsilon}\cdot\vec{r}_j\left|\Psi_f\right\rangle\right|^2\,\rho(E_f) \qquad (5)$$

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

$$\mu(\omega) = \frac{2\,\pi\,e^2\,\omega}{\varepsilon_0}\,n\sum_f\left|\left\langle\Psi_i\right|\sum_j \hat{\varepsilon}\cdot\vec{r}_j\left|\Psi_f\right\rangle\right|^2\,\rho(E_f) \qquad (6)$$

$$\mu(\omega) = \frac{2\pi e^2 \omega}{\varepsilon_0} n \sum_f \left| \left\langle \Psi_i \right| \sum_j \hat{\varepsilon} \cdot \vec{r}_j \left| \Psi_f \right\rangle \right|^2 \rho(E_f)$$

- if $|\Psi_i>$ and $|\Psi_f>$ are known (if wavefunctions and energies can be calculated):
  1) calculate W_{if}
  2) calculate $\mu(\omega)$
- in practice, one is interested in inverse process:
  1) measure $\mu(\omega)$
  2) extract EXAFS
  3) obtain information on local structure through $|\Psi_f>$
- but, to obtain structural info, one still needs to calculate $|\Psi_i>$ and $|\Psi_f>$ or at least be able to express their structural properties in parametric form
  - $|\Psi_i>$ relatively easy
    - ground state of atom
  - $|\Psi_f>$ in general very complicated
    - in principle, all electrons are involved -> multi body process
    - final state strongly influenced by environment

Single electron approximation

- large part of μ 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 μ 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

$$\mu(\omega) = \mu_{el}(\omega) + \mu_{inel}(\omega)$$

where $$\mu_{el}(\omega) \propto \left| \left\langle \Psi_i^{N-1} \psi_i \right| \hat{\varepsilon} \cdot \vec{r} \left| \Psi_f^{N-1} \psi_f \right\rangle \right|^2 \rho(\varepsilon_f)$$

Ψ_i^{N-1} Slater determinant of "passive" electrons' wavefunctions

ψ, r, ε_f Wavefunction, position vector, final energy of "active" electron

"Sudden" approximation and overlap factor

- if photoelectron energy is sufficiently high (E > few 10 eV above edge)

  - ☐ time to exit atom << relaxation time of passive electrons
  - ☐ its state not influenced by passive electrons relaxation

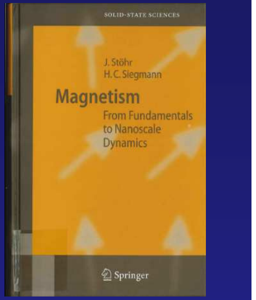
$$\mu_{el}(\omega) \propto \left| \langle \psi_i | \; \hat{\varepsilon} \cdot \vec{r} \; | \psi_f \rangle \right|^2 \; S_0^2 \; \rho(\varepsilon_f) \qquad (7)$$

where $S_0^2 = \left| \langle \Psi_i^{N-1} | | \Psi_f^{N-1} \rangle \right|^2$ ($S_0^2 \sim 0.7 - 0.9$)

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

The polarization dependent dipole operator

$$\mu(E) \approx \sum_f \left|\langle \psi_i | \hat{\varepsilon}\cdot\vec{r} | \psi_f \rangle\right|^2$$



SOLID-STATE SCIENCES

J. Stöhr
H.C. Siegmann

Magnetism

From Fundamentals to Nanoscale Dynamics

Springer

dipole operator

$$P^q_\alpha = \boldsymbol{\epsilon}\cdot\mathbf{r} = \boldsymbol{\epsilon}^q_\alpha\cdot\mathbf{r}$$

α = x, y , z X-ray prop direction

q = +1, 0, -1 polarization states

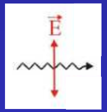
(qħ photon angular momentum)

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

photon polarization vectors

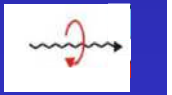
$$\epsilon^0_x = \epsilon_x = e_x \qquad \epsilon^0_y = \epsilon_y = e_y \qquad \epsilon^0_z = \epsilon_z = e_z$$

linear polarization



$$\epsilon^\pm_z = \mp\frac{1}{\sqrt{2}}(\epsilon_x \pm \mathrm{i}\,\epsilon_y)$$

circular polarization with **k** // z



dipole operator in terms of spherical harmonics

$$P^\pm_z = \boldsymbol{\epsilon}^\pm_z\cdot\mathbf{r} = \mp\frac{1}{\sqrt{2}}(x \pm \mathrm{i}y) = r\sqrt{\frac{4\pi}{3}}\,Y_{1,\pm1}$$

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

The dipole selection rules

$$\mu(E) \approx \sum_f \left| \langle \psi_i | \hat{\varepsilon} \cdot \vec{r} | \psi_f \rangle \right|^2$$

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

matrix elements factor into spin, radial and angular parts

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

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

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