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### **Part I: Fundamentals of X-ray Absorption Fine Structure: basic principles**

- X-ray Absorption
- X-ray Absorption Fine Structure
- Simple Theoretical Description
- Derivation of EXAFS Equation

### **Part II: Fundamentals of X-ray Absorption Fine Structure: data analysis**

- EXAFS Analysis: near neighbor  $R$ ,  $N$ , and atomic species
- XANES Analysis: formal valence and coordination chemistry

### **Part III: Examples of Applications**

- Major historical EXAFS breakthroughs
- Selection of recent results at the ESRF

## Part I

# Fundamentals of X-ray Absorption Fine Structure: basic principles

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# Basic Principles:

X-ray Absorption

X-ray Absorption Fine Structure

Simple Theoretical Description

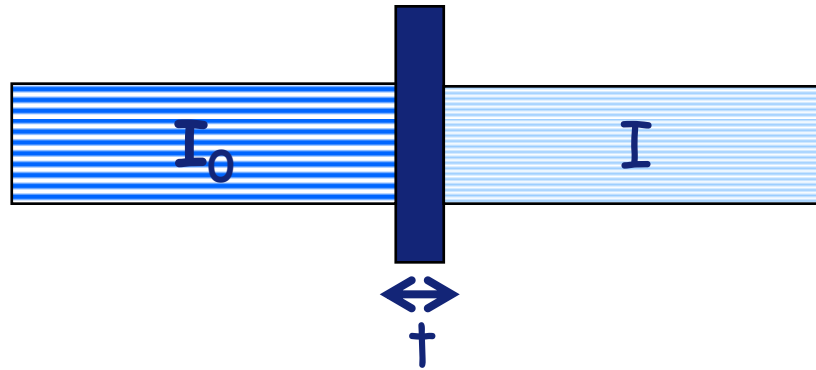
Derivation of EXAFS Equation

# X-ray Absorption

## Main X-ray based techniques

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

## The Absorption Coefficient $\mu$



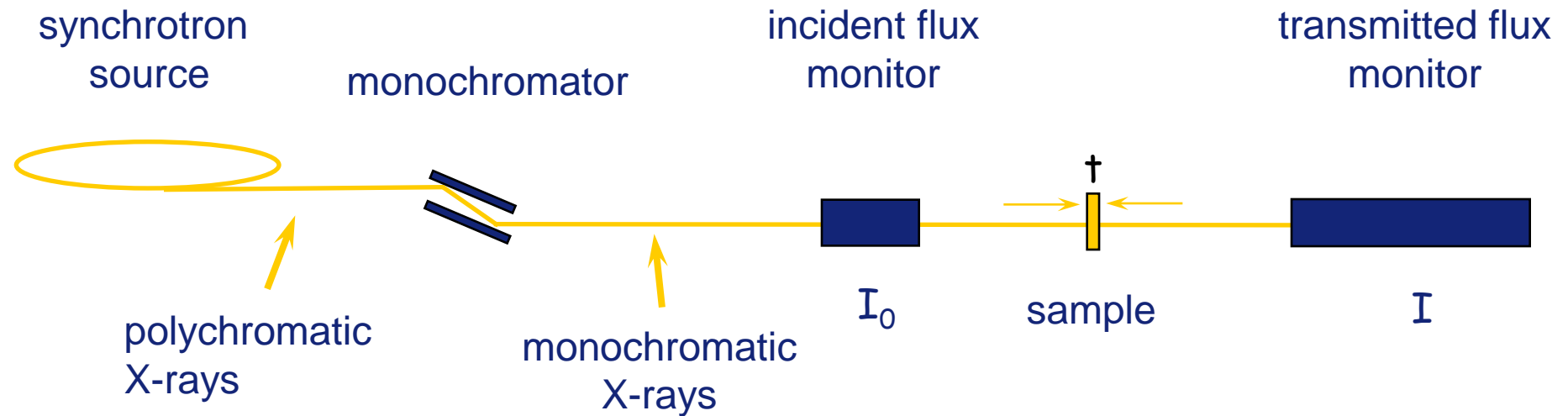
$$I = I_0 \exp[-\mu t]$$



linear absorption coefficient

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

## The Absorption Coefficient $\mu$

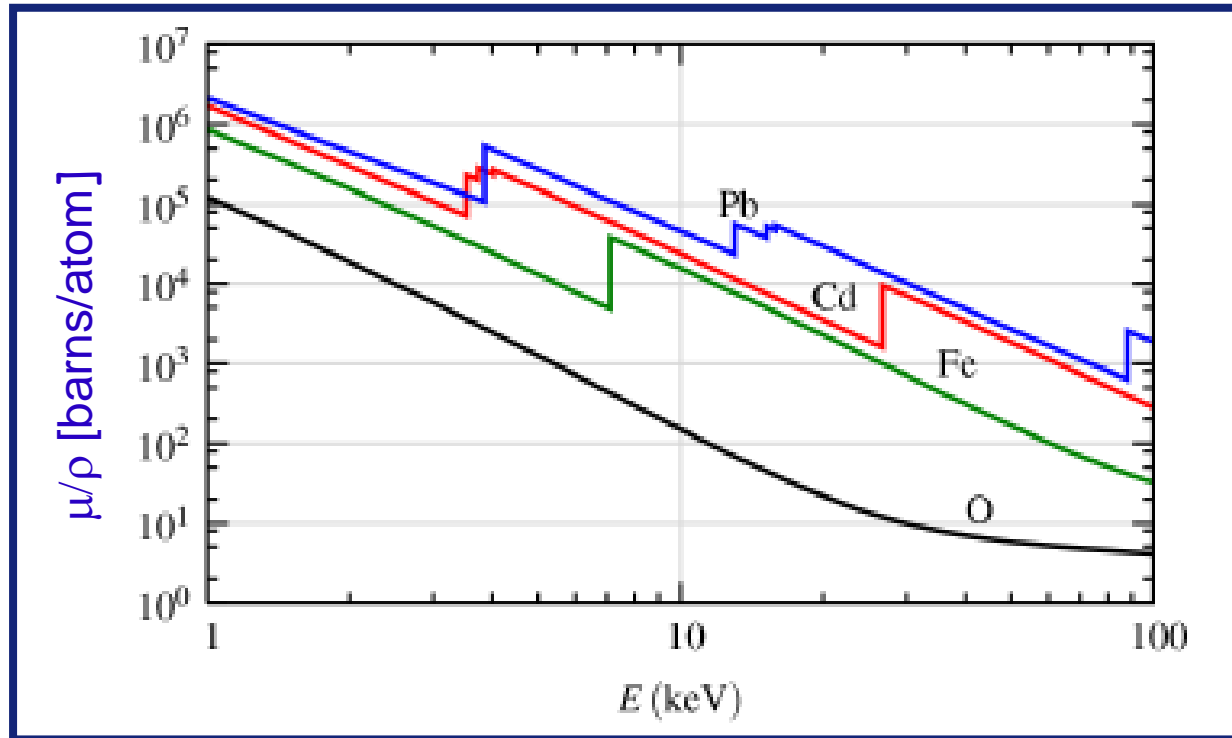


1. Measure  $I_0$  and  $I$  as a function of  $E_x$

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



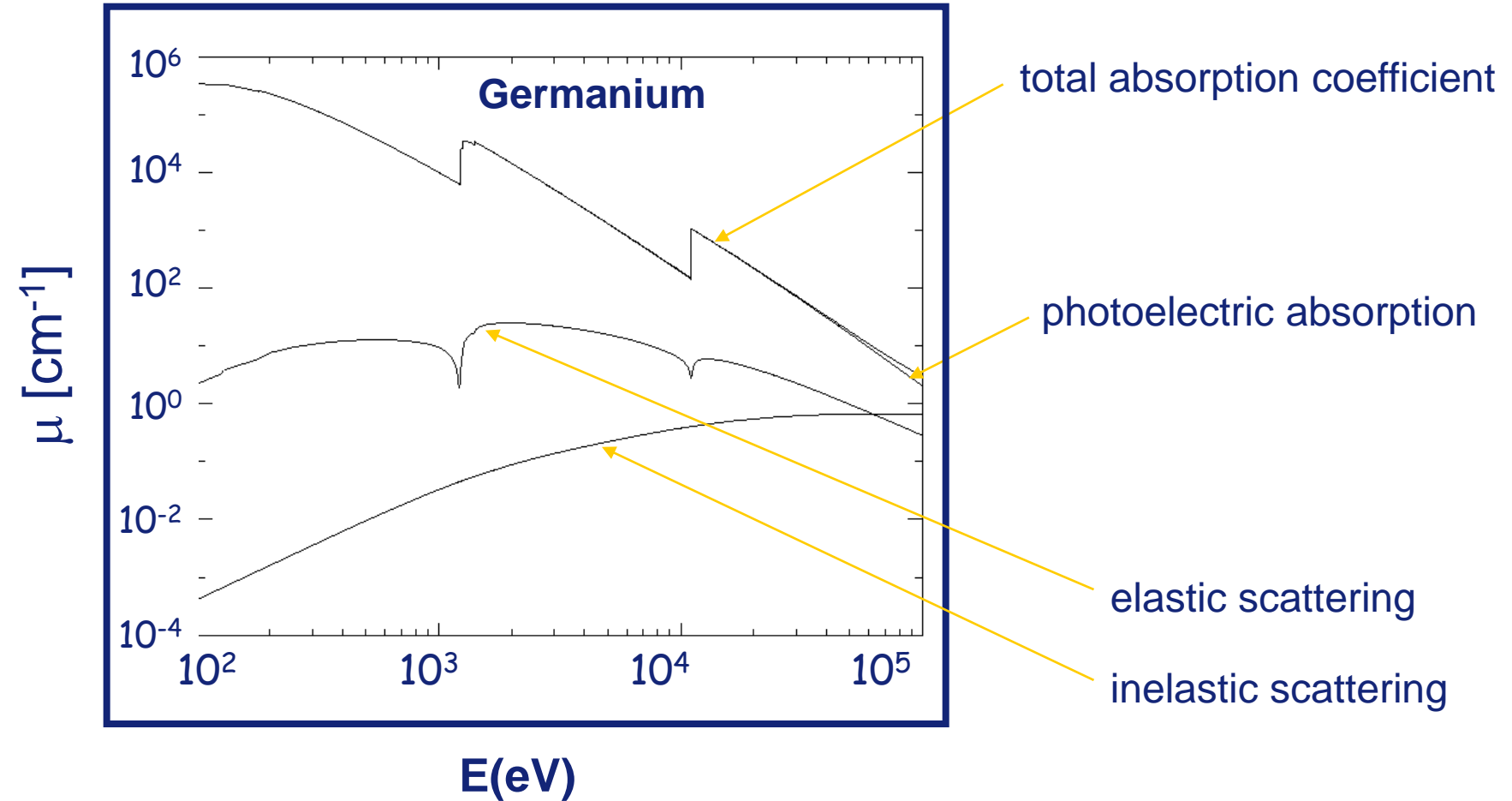
# The Absorption Coefficient $\mu$



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

$\mu$  depends strongly on X-ray energy **E** and atomic number **Z**, the density  $\rho$  and atomic mass **A**

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



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

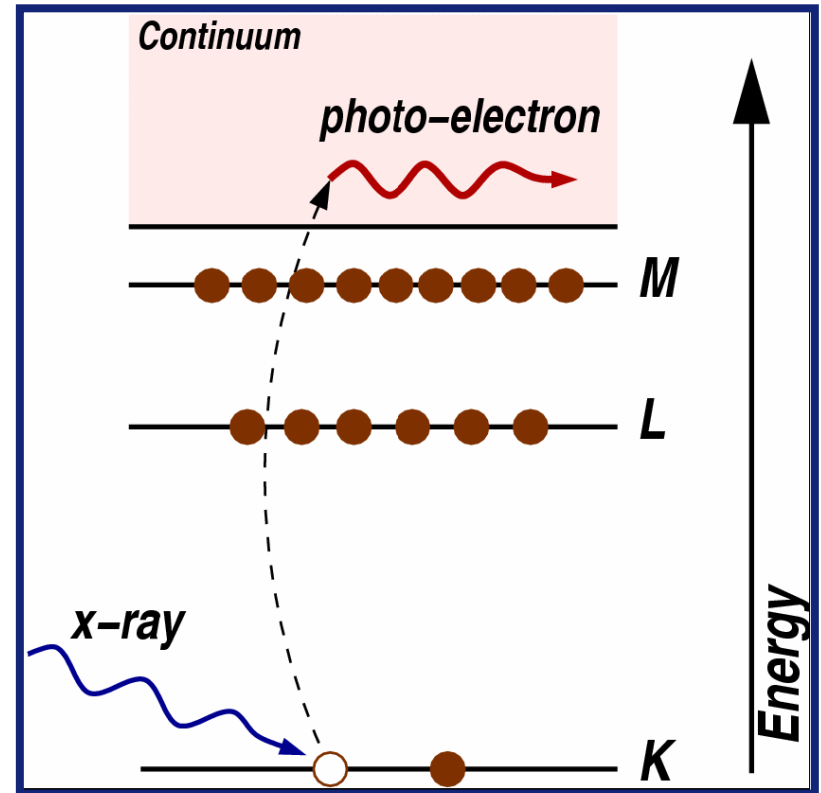
# Photoelectric Absorption

X-rays (light with wavelength  $0.06 \leq \lambda \leq 12 \text{ \AA}$  or energy  $1 \leq E \leq 200 \text{ keV}$ ) are absorbed by all matter through the **photoelectric effect**

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

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

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

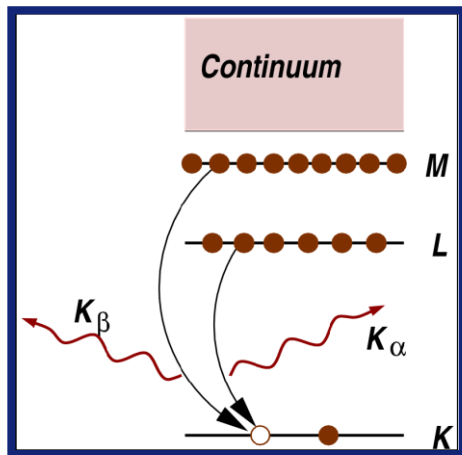


# De-excitation: Fluorescence and Auger Effect

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

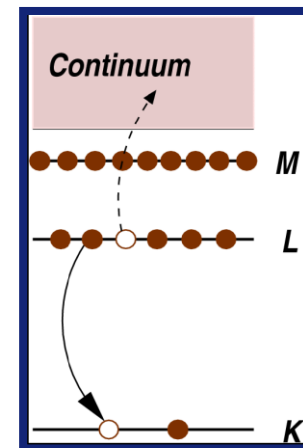
## X-ray Fluorescence:

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



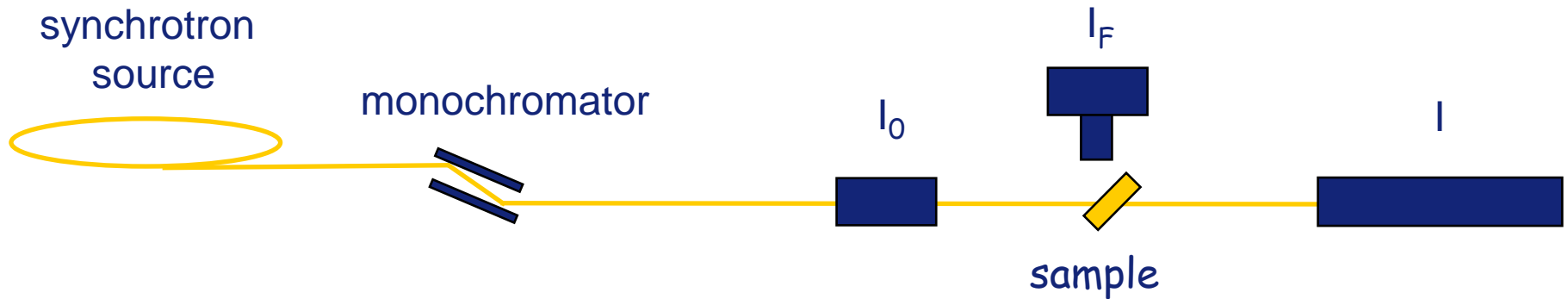
## Auger Effect:

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



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

# XAS measurements



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

## Transmission:

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

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

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

## Fluorescence:

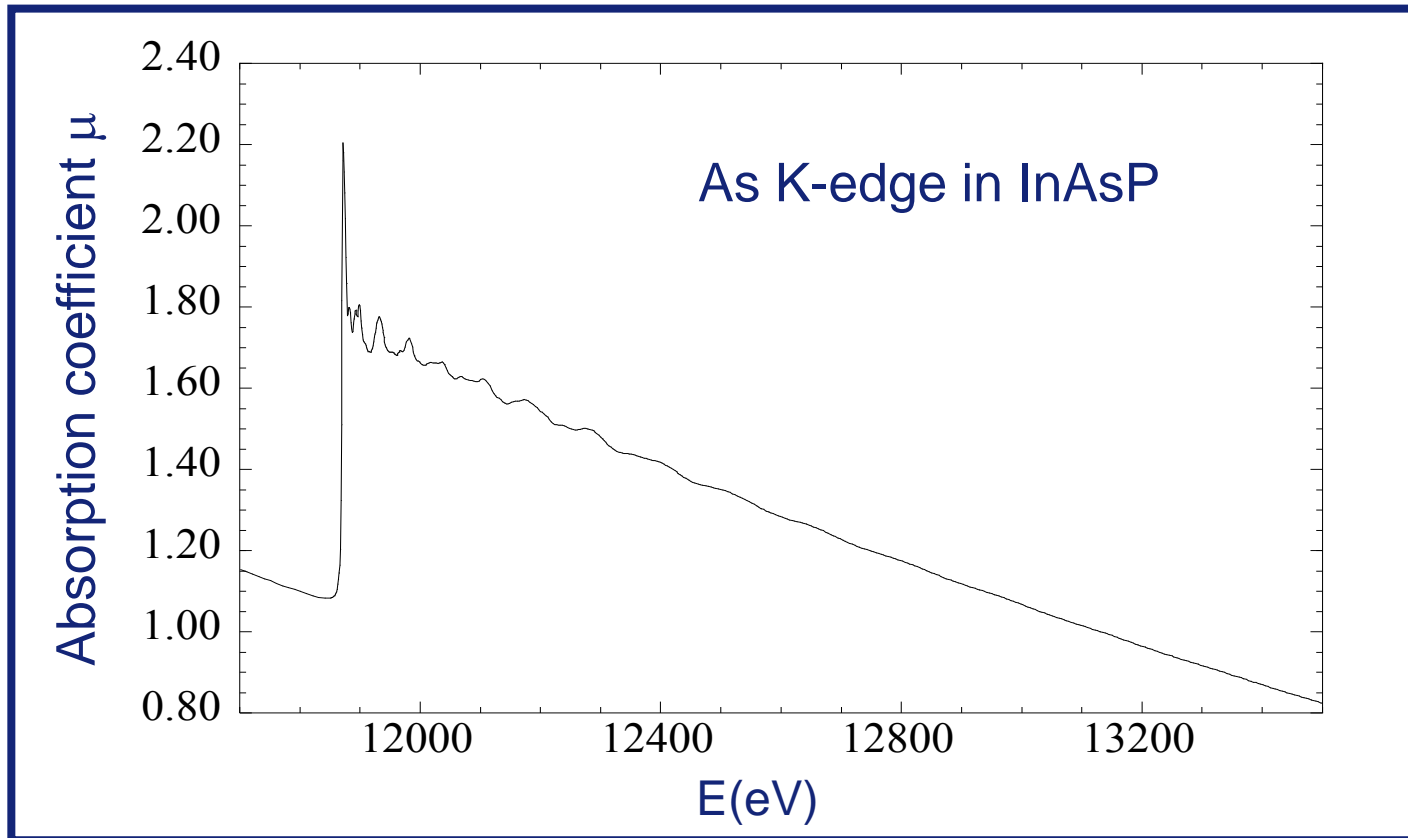
The re-filling the deep core hole is detected. Typically the fluorescent X-ray is measured:

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

# X-ray Absorption Fine Structure

## What is XAFS?

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



Proximity of neighboring atoms strongly modulates the absorption coefficient

## EXAFS and XANES

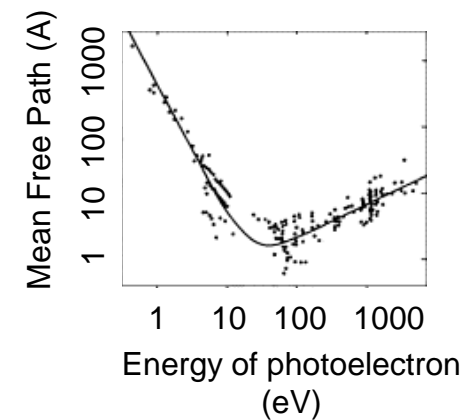
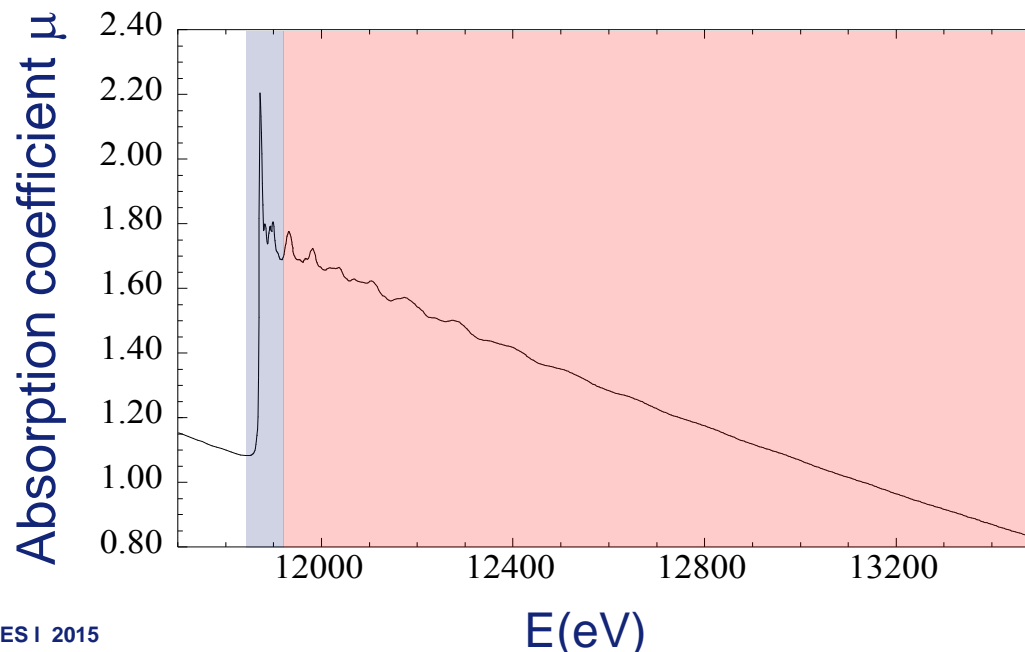
XAFS is also referred to as X-ray Absorption Spectroscopy (**XAS**) and is broken into 2 regimes:

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

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

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

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



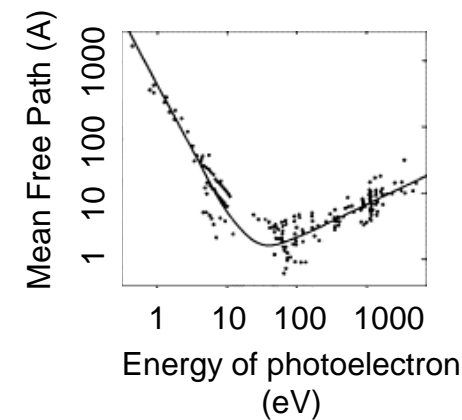
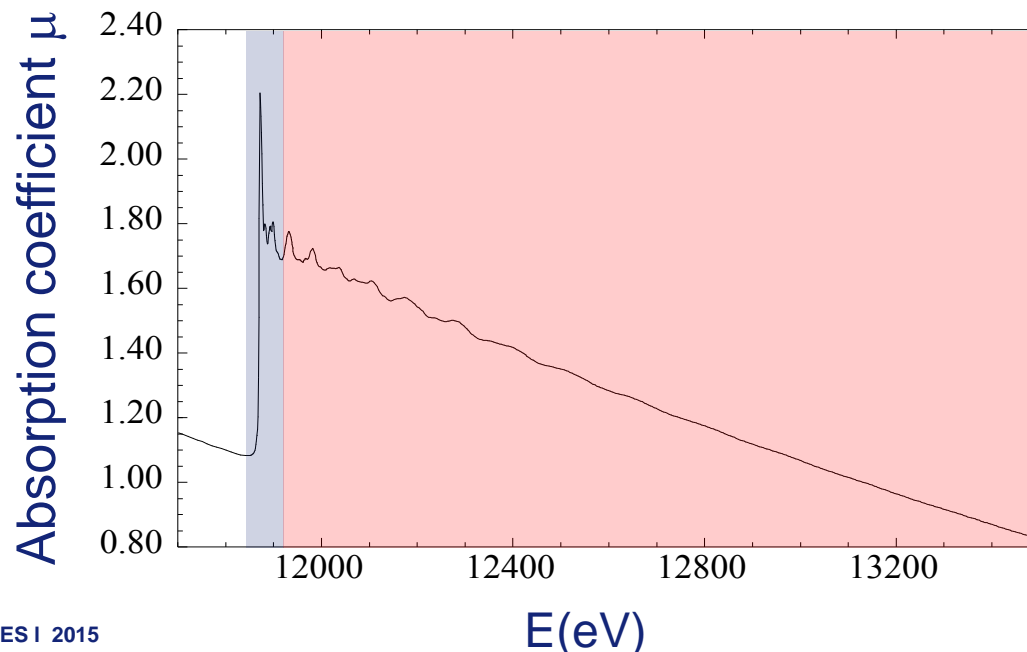


# EXAFS and XANES

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

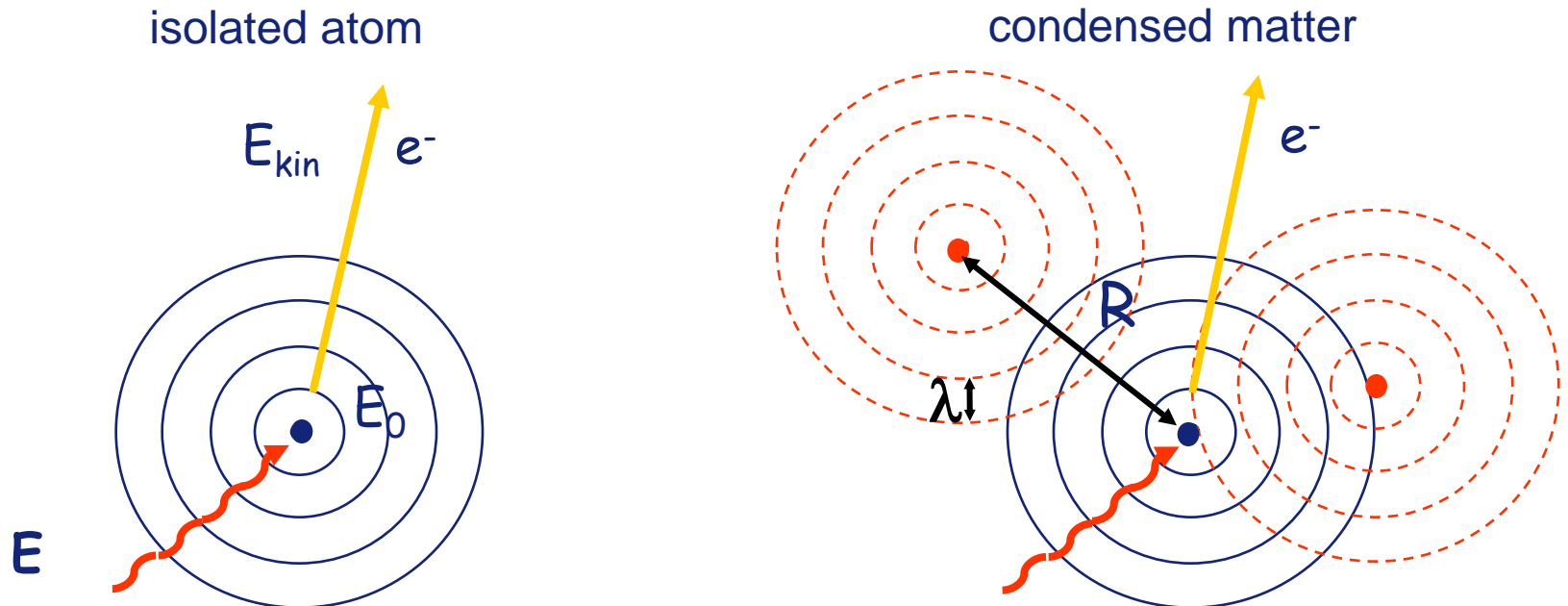
**XANES:** local site symmetry, charge state, orbital occupancy

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



# EXAFS qualitatively

Absorption coefficient = probability of photon absorption  
 ~ probability of electron presence at origin = “amount of wave” at origin



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

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

$$\lambda = 2\pi/k$$

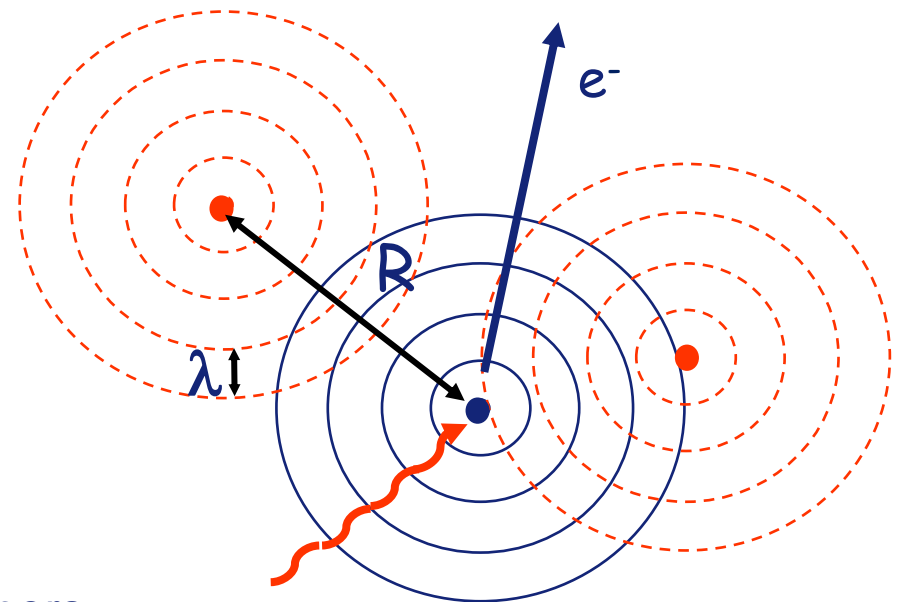
## Where do the oscillations come from?

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

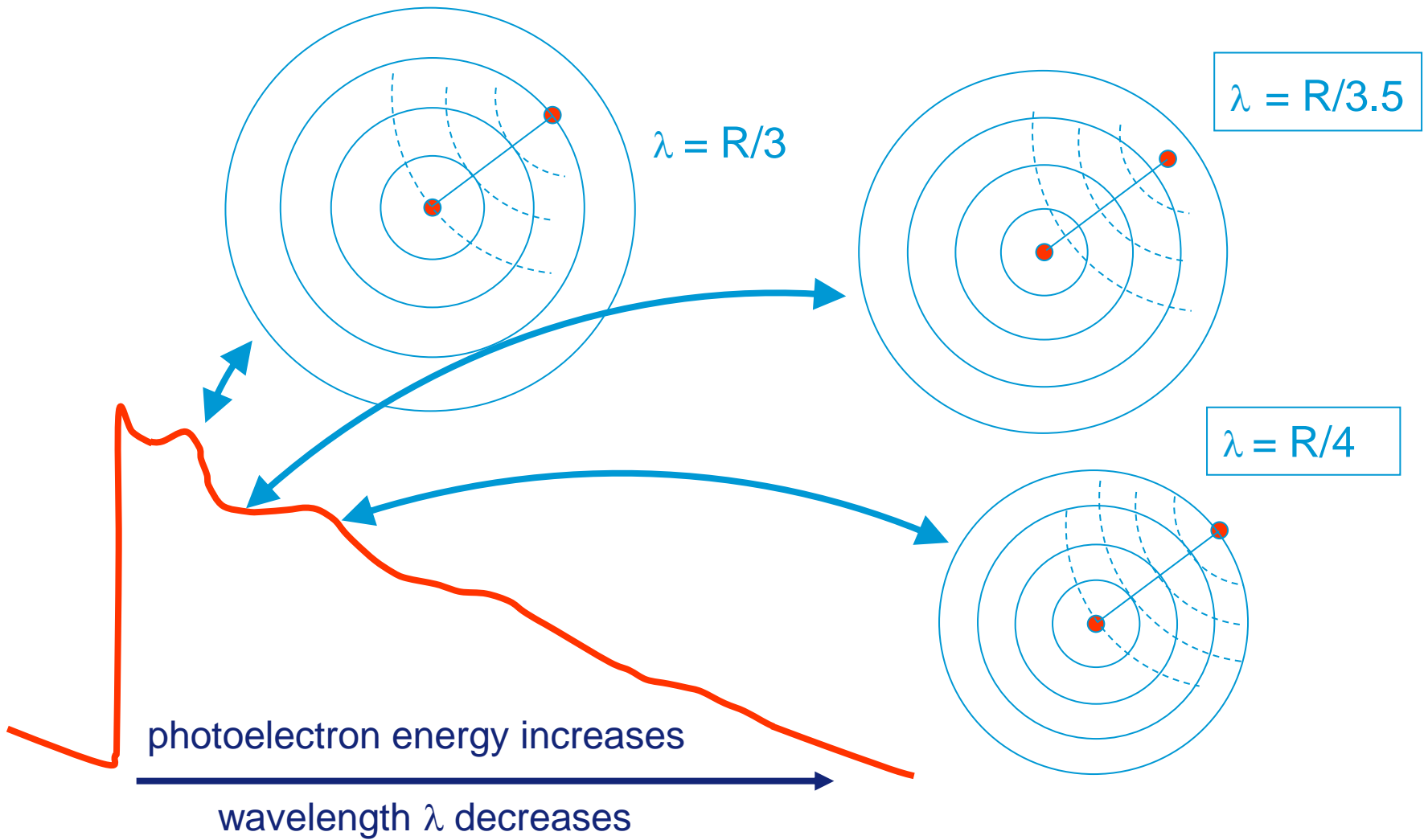
1. As  $E$  is scanned above  $E_0$ ,  $E_{kin}$  is varied, and consequently  $k$  and  $\lambda$ .
2. The outgoing and backscattered parts of the wave interfere either constructively or destructively, depending on the ratio between  $\lambda$  and  $R$ .
3. It is the **interference** between outgoing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

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

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



# FUNDAMENTALS OF X-RAY ABSORPTION FINE STRUCTURE: BASIC PRINCIPLES



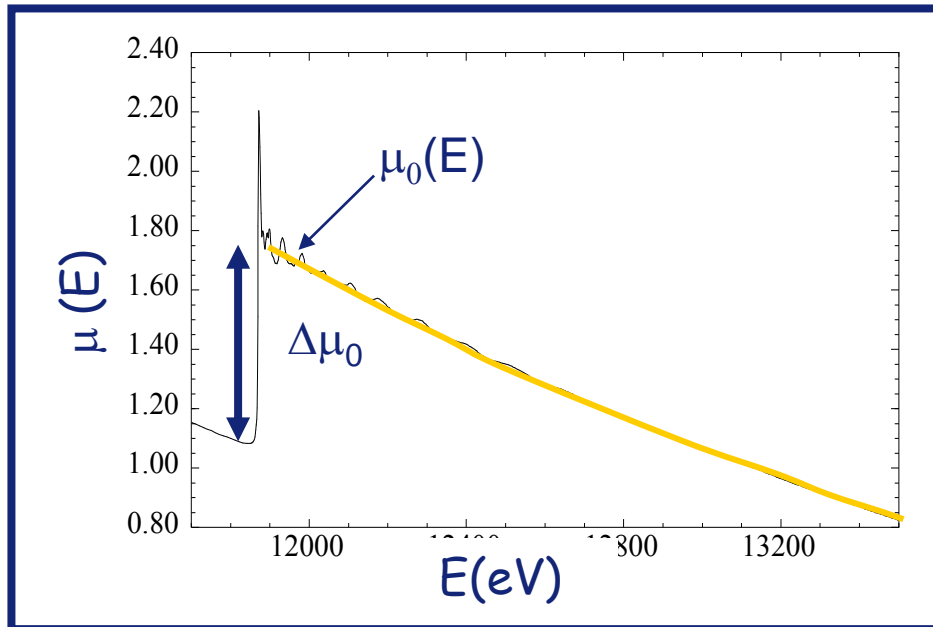
The probability of absorption oscillates due to constructive and destructive interference

# The EXAFS signal $\chi$

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

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

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.

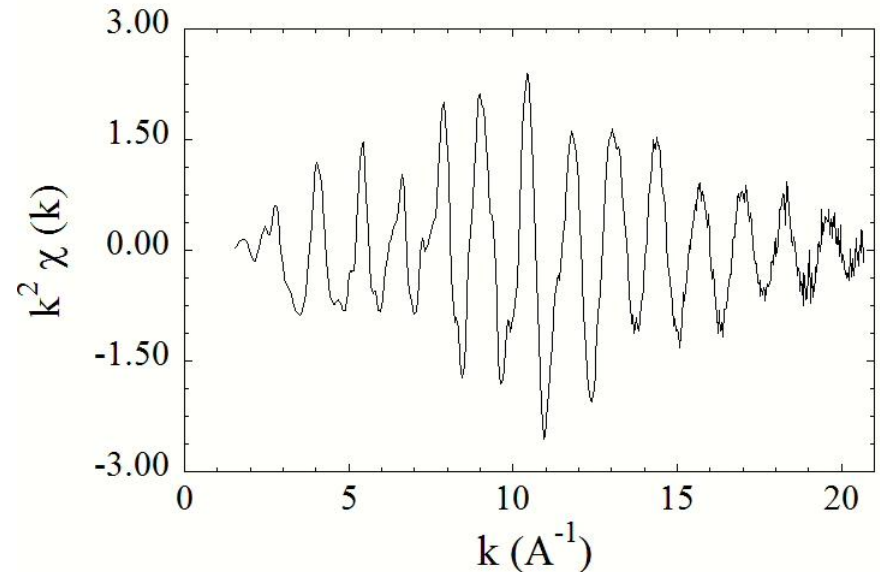
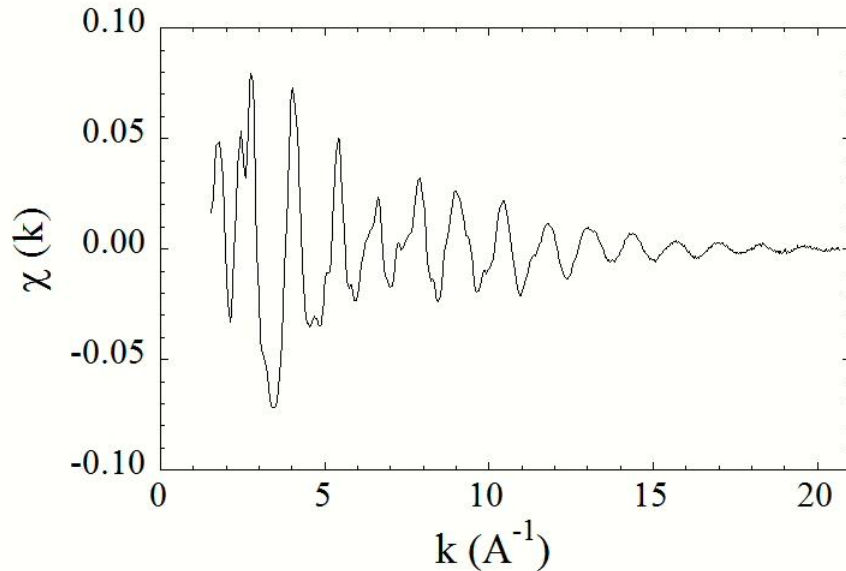


# EXAFS: $\chi(k)$

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

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

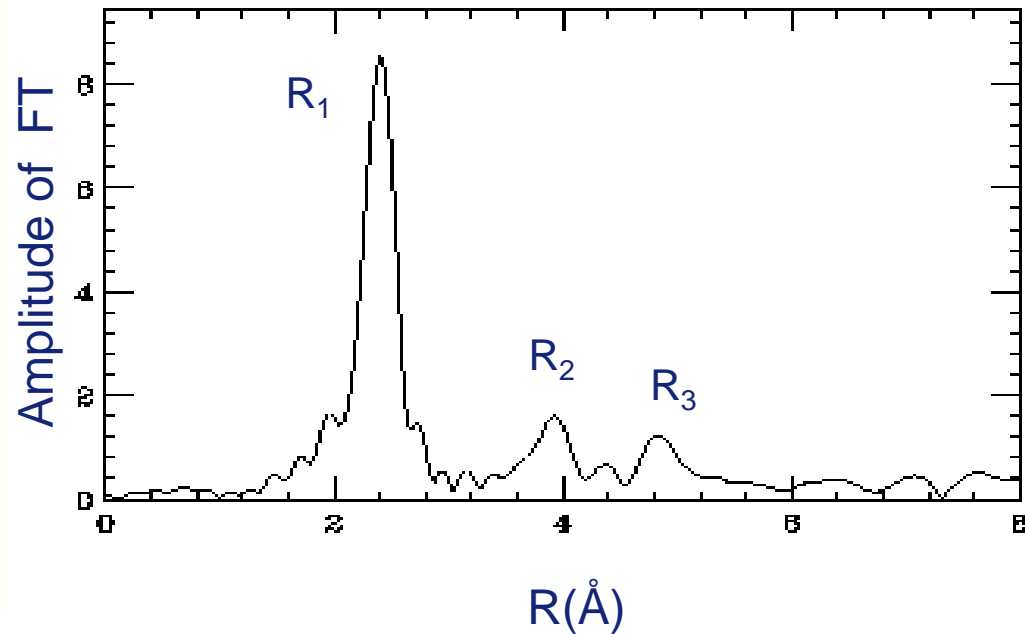
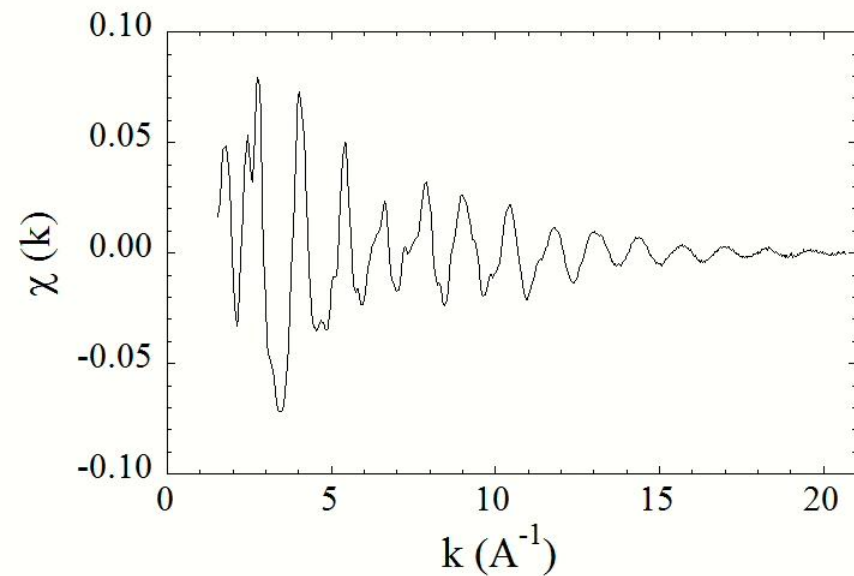
$\chi(k)$  is often shown weighted by  $k^2$  or  $k^3$  to amplify the oscillations at high- $k$ :



# Qualitative picture of local coordination in R space

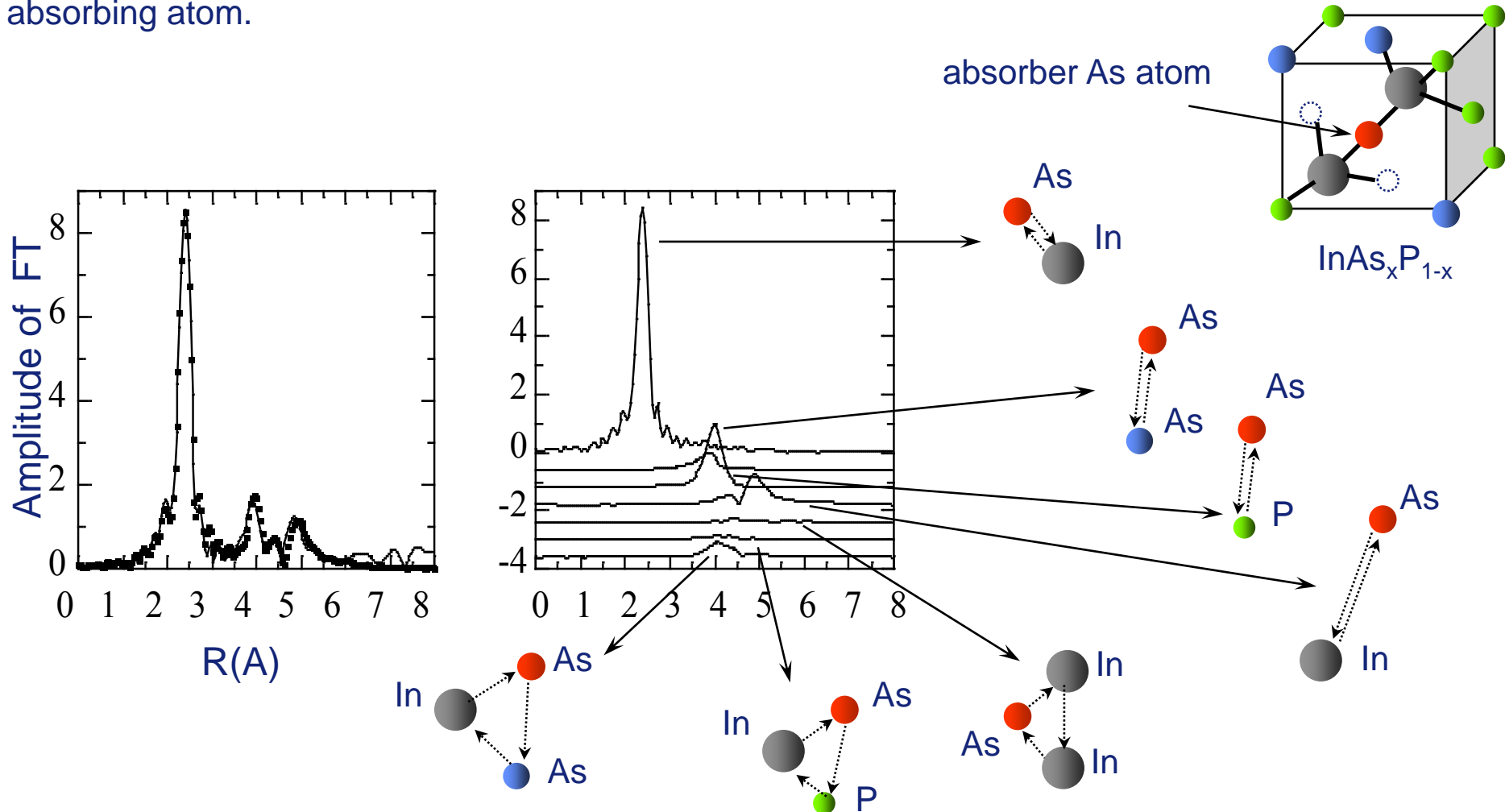
The **frequencies** contained in the EXAFS signal depend on the **distance** between the absorbing atom and the neighboring atoms (i.e. the length of the scattering path).

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



# Quantitative structural determination

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





# $\chi$ : sum of damped waves

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

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

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

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

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

The larger the number of neighbors, the larger the signal

The stronger the scattering amplitude, the larger the signal

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

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

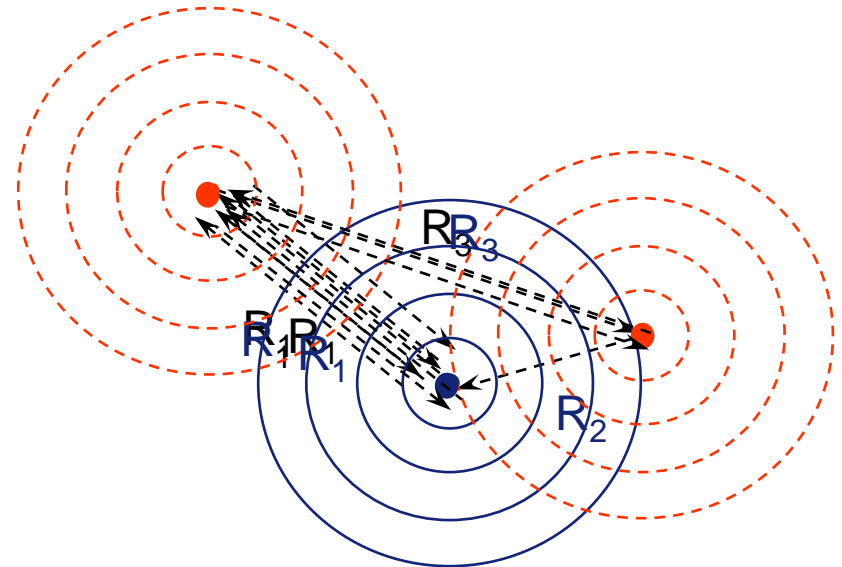
$$2kR_j + \delta_j(k)$$

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

# Frequencies: Single and Multiple Scattering paths

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

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

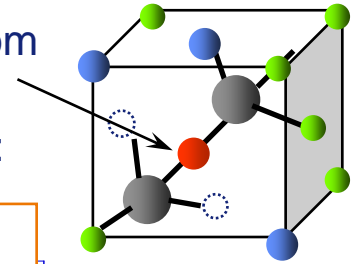


EXAFS can give information on the n-body distribution functions  $g_n(r)$ .

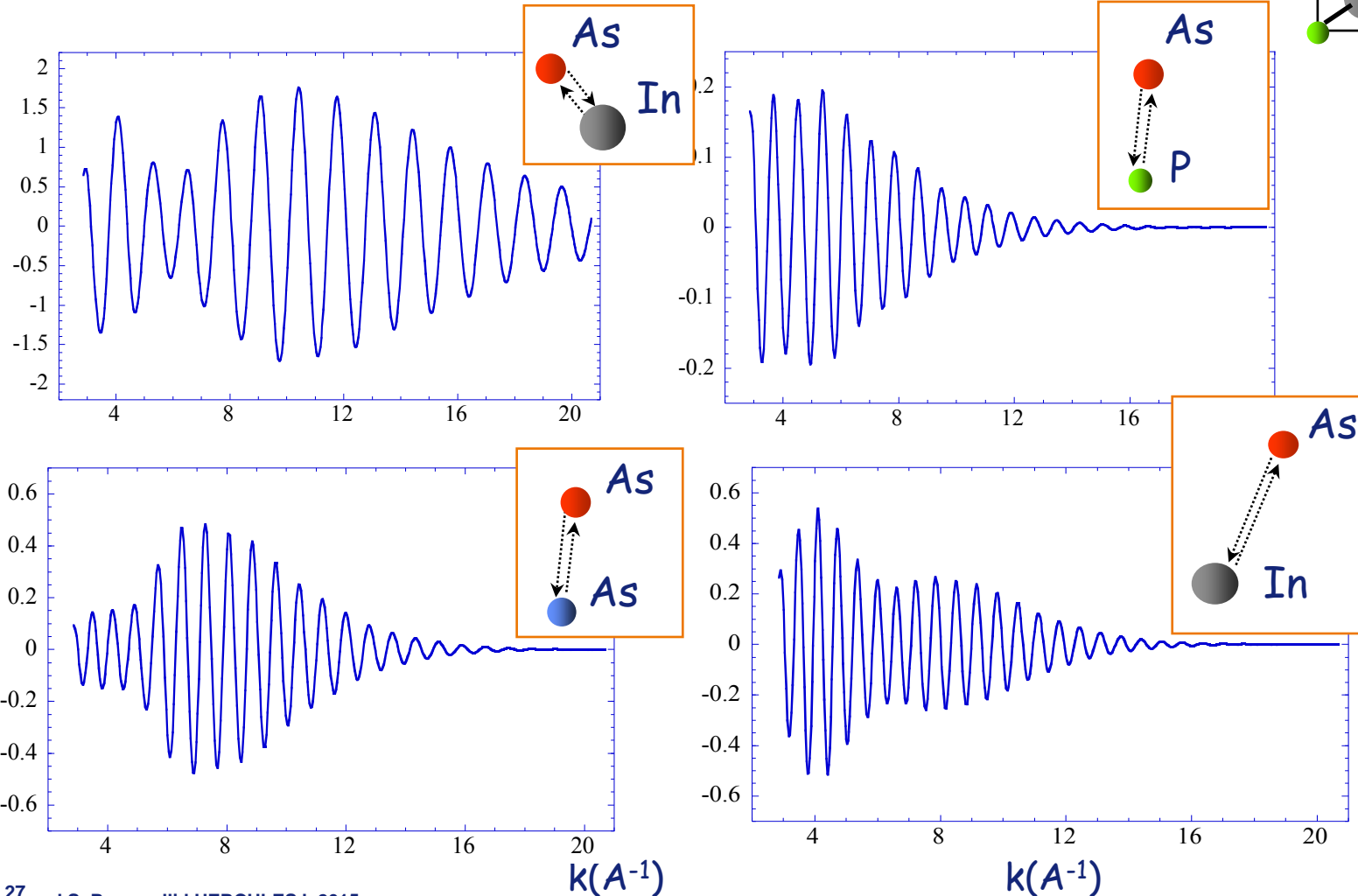
## Amplitudes

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

absorber As atom

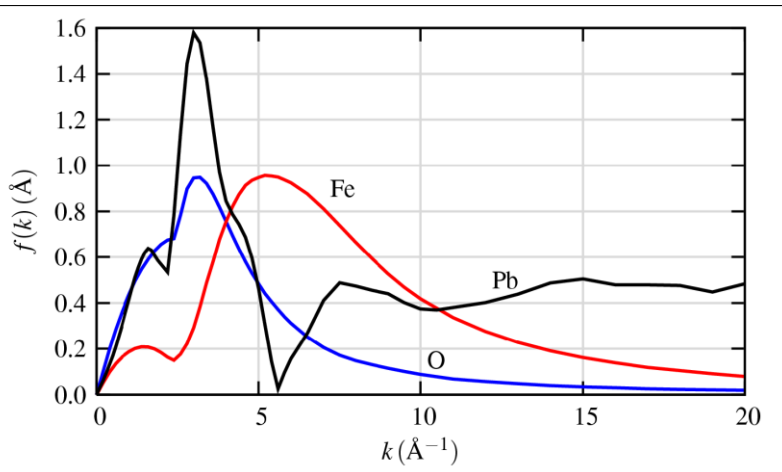


shape of the envelope of each wave indicative of nature of backscatterer atom:



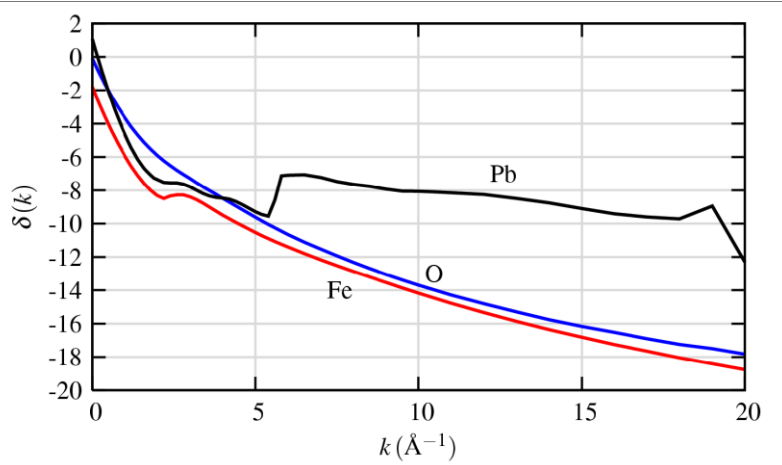
# Scattering Amplitude and Phase-Shift: $f(k)$ and $\delta(k)$

The scattering amplitude  $f(k)$  and phase-shift  $\delta(k)$  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  $\delta(k)$  shows sharp changes for very heavy elements.



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

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

## Calculating $f(k)$ and $\delta(k)$

These days, we can calculate  $f(k)$  and  $\delta(k)$  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  $\delta(k)$  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)

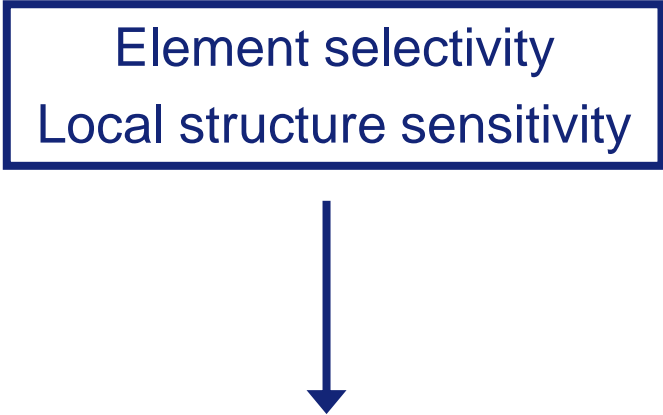
- Crystalline materials with long-range ordering -> 3D picture of atomic coordinates
- Materials with only short-range order (amorphous solid, liquid, or solution) -> 1D radial distribution function containing interatomic distances due to all atomic pairs in the sample.

### □ 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

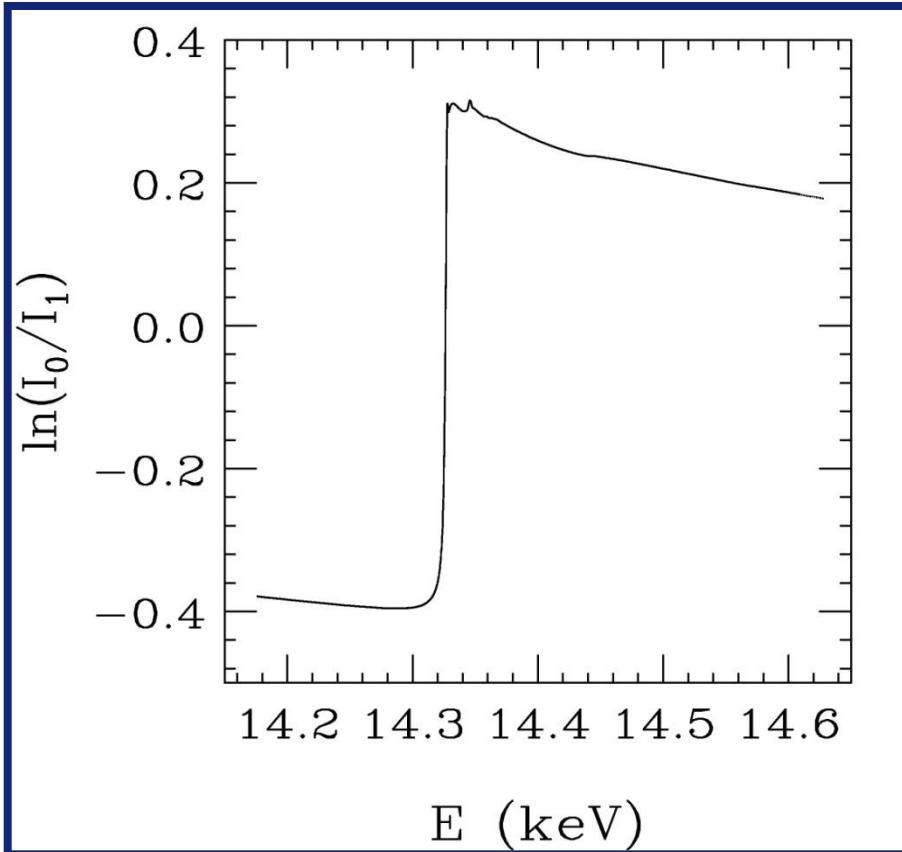


- Local structure in non-crystalline matter
- Local environment of an atomic impurity in a matrix of different atomic species
- Study of systems whose local properties differ from the average properties
- Detection of very small distortions of local structure

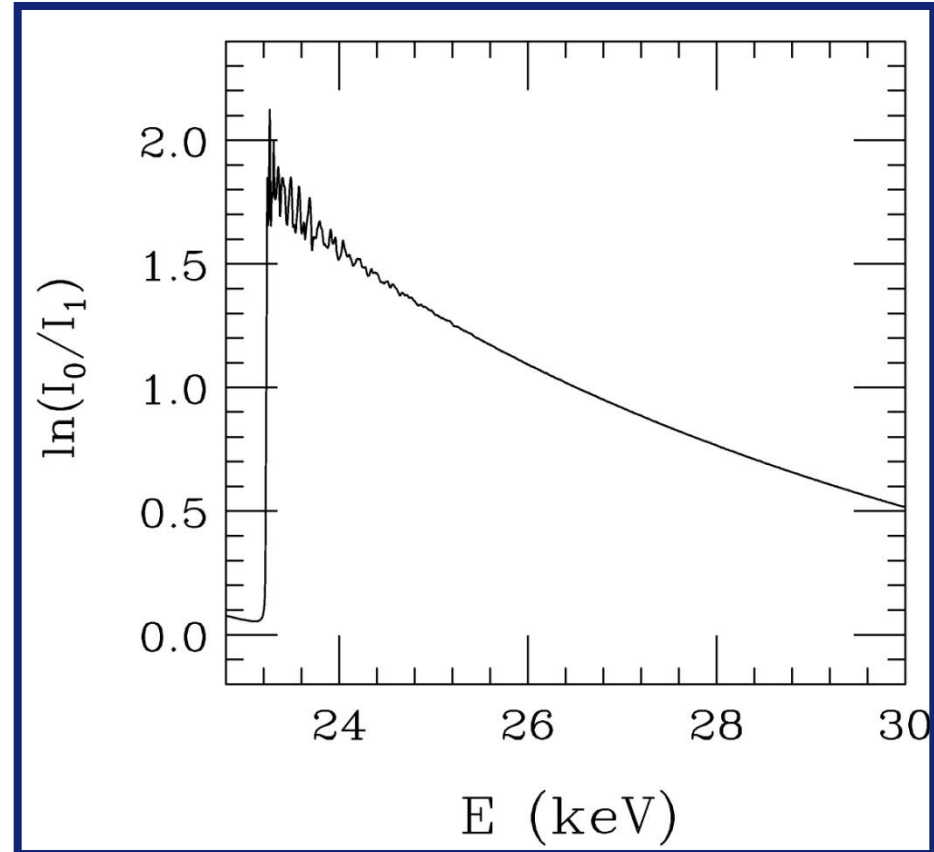
# Simple Theoretical Description



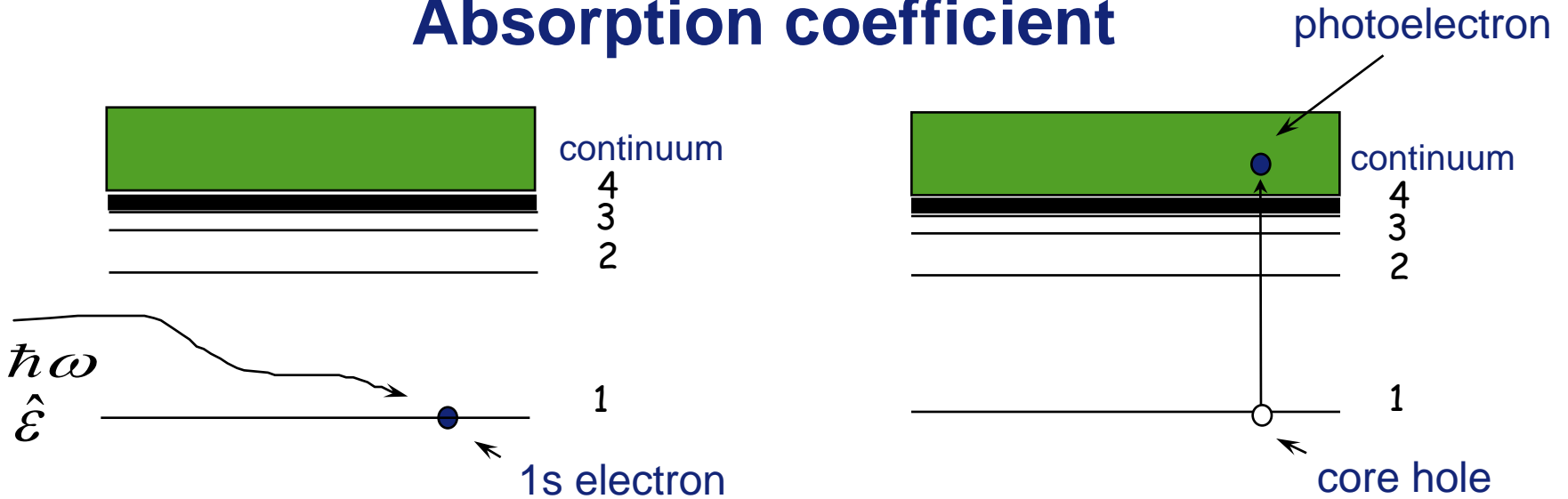
## Kr gas



## Rh metal



# Absorption coefficient



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

slides 48-50 dipole slide 51

$$\hat{H}_I \approx \sum_j \vec{A}(\vec{r}_j) \cdot \vec{\nabla}_j$$

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

in principle, all electrons are involved → multi body process

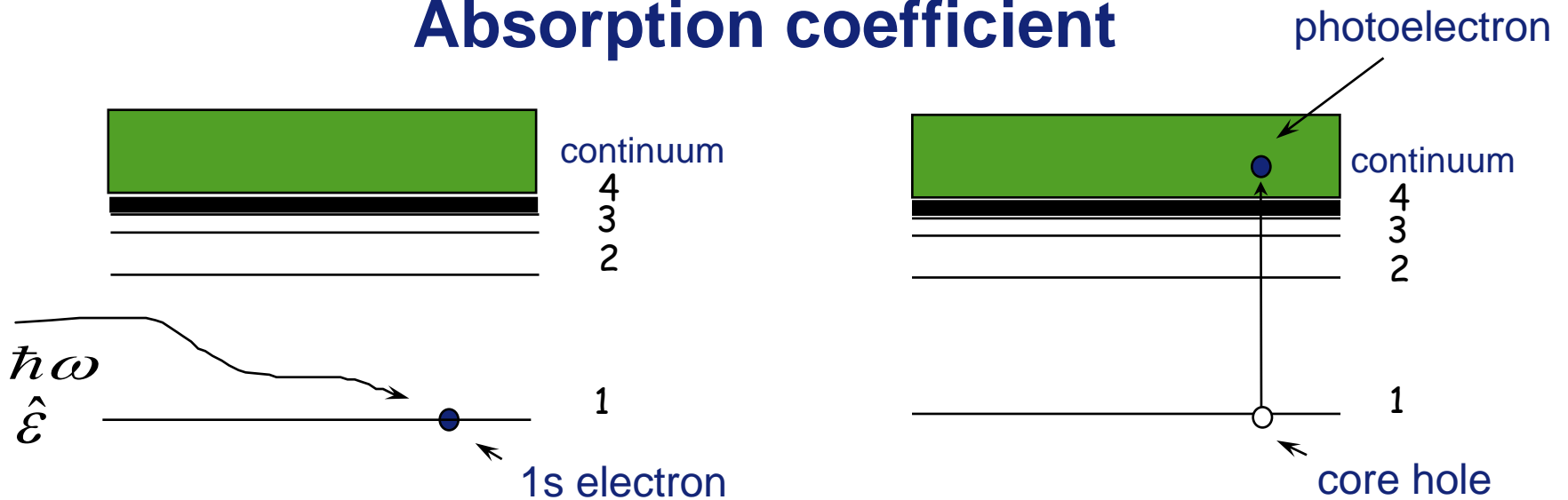
$$\approx \sum_f \left| \langle \Psi_f^{N-1} \psi_f | \hat{\epsilon} \cdot \vec{r} | \Psi_i^{N-1} \psi_i \rangle \right|^2 \approx S_0^2 \sum_f \left| \langle \psi_f | \hat{\epsilon} \cdot \vec{r} | \psi_i \rangle \right|^2$$

single electron sudden

slide 53 slide 54

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

# Absorption coefficient



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

$$| \psi_f \rangle = | \epsilon p \rangle \quad E_f = \hbar\omega + E_i$$

$$\mu(\omega) \approx S_0^2 \sum_f \left| \langle \psi_f | \hat{\epsilon} \cdot \vec{r} | \psi_i \rangle \right|^2$$

Approximations

dipole + single electron + sudden

$\hat{\epsilon}$  : photon polarization

$\vec{r}$  : electron position

$|\psi_i\rangle$  relatively easy  $\rightarrow$  ground state of atom; i.e. 1s e<sup>-</sup> wavefunction

$|\psi_f\rangle$  very complicated  $\rightarrow$  final state strongly influenced by environment

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



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

matrix elements factor into spin, radial and angular parts

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

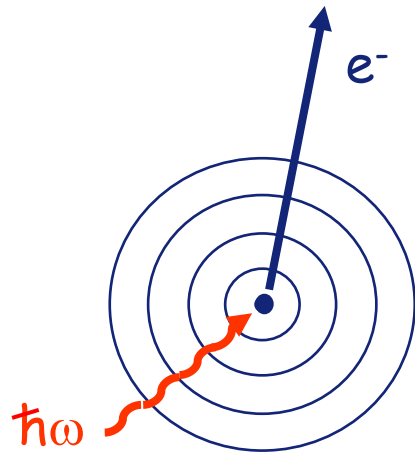
$$\begin{aligned} \Delta l &= l' - l = \pm 1, \\ \Delta m_l &= m'_l - m_l = q = 0, \pm 1, \\ \Delta s &= s' - s = 0, \\ \Delta m_s &= m'_s - m_s = 0. \end{aligned}$$

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

For 1-electron transitions:

<u>edge</u>	<u>initial state <math>\psi_i</math></u>	<u>final state <math>\psi_f</math></u>
K, L <sub>1</sub>	s (l=0)	p (l=1)
L <sub>2</sub> , L <sub>3</sub>	p (l=1)	s (l=0), d (l=2)

# Isolated atom: atomic absorption coefficient



$e^-$  photoelectron free to travel away undisturbed

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

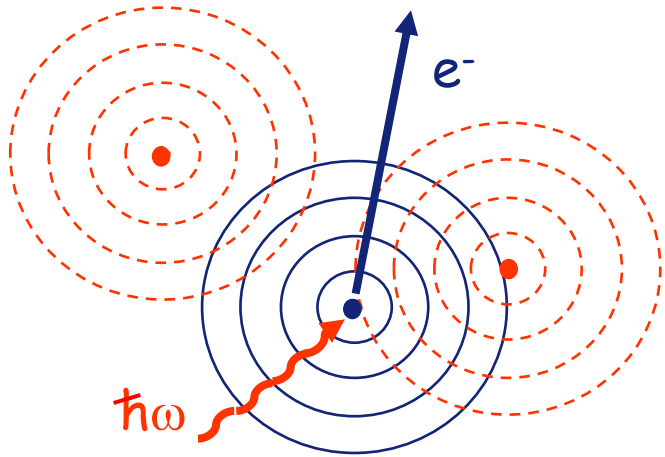
outgoing spherical wave originating from the absorbing atom

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

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

→ 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.

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

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

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

$\mu_0(\omega)$

↑  
**EXAFS**

## Origin of EXAFS

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

$\chi$ : fractional change in  $\mu$  introduced by the neighbors

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

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 equation

To model the EXAFS, we use the EXAFS Equation

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

where  $f(k)$  and  $\delta(k)$  are photoelectron scattering properties of the neighboring atom.

(the sum is over “shells” of similar neighboring atoms)

If we know  $f(k)$  and  $\delta(k)$ , we can determine:

R distance to neighboring atom.

N coordination number of neighboring atom.

$\sigma^2$  mean-square disorder of neighbor distance.

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



# Derivation of the EXAFS equation

# The EXAFS equation: simple description

With spherical wave  $e^{ikr}/kr$  for the propagating photoelectron, and a scattering atom at a distance  $r = R$ , we get:

$$\Delta\Psi_f \sim \underbrace{\Psi_f^0}_{\substack{\text{Region I:} \\ \text{amplitude} \\ \text{of outgoing wave}}} \underbrace{\frac{e^{ikR}}{kR} e^{i\delta_c}}_{\substack{\text{Region II:} \\ \text{amplitude of} \\ \text{wave arriving on B}}} \underbrace{|f(k)| e^{i\delta_s(k)}}_{\substack{\text{Region III:} \\ \text{amplitude of backscattering on B}}} \underbrace{\frac{e^{ikR}}{kR} e^{i\delta_c}}_{\substack{\text{Region II:} \\ \text{amplitude of ingoing} \\ \text{wave, backscattered from B}}}$$

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 (for 1 scattering atom):

$$\chi(k) \sim S_0^2 \frac{f(k)}{kR^2} \sin [2kR + \delta(k)] \quad \delta(k) = \delta_s(k) + 2\delta_c(k)$$

## Development of the EXAFS equation

For  $N$  scattering atoms, distributed around average distance  $R$  with a thermal and static disorder of  $\sigma^2$  (mean square disorder in  $R^*$ ), we have:

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

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:

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

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

\* 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 to 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  $\lambda(k)$  is the photoelectron's **mean free path**

(including core hole lifetime), the EXAFS equation becomes:

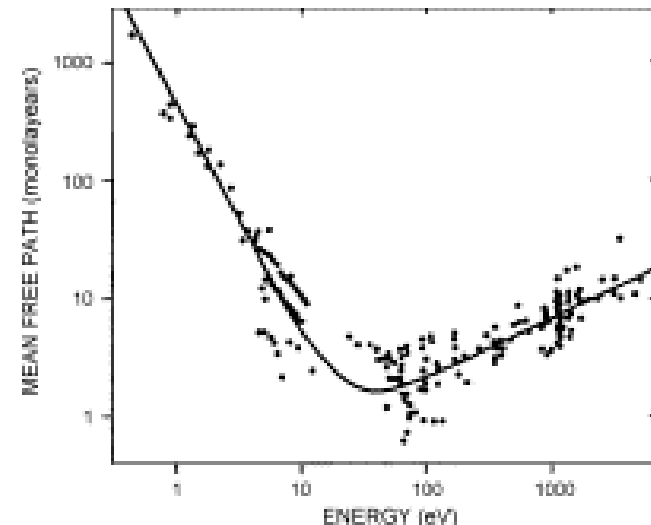
$$\chi(k) \sim S_0^2 \sum_j N_j \frac{f_j(k)}{kR_j^2} e^{-2R/\lambda(k)} e^{-2k^2\sigma_j^2} \sin [2kR_j + \delta_j(k)]$$

The mean free path  $\lambda$  depends on  $k$ .  
(for the EXAFS  $k$  range,  $\lambda \sim 10\text{-}20 \text{ \AA}$ )

The  $\lambda$  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

The **amplitude reduction** term is due to the relaxation of all the other electrons in the absorbing atom to the hole in the core level (slides 53-54):

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

where  $\Psi_f^{N-1}$  accounts for the relaxation of the other N-1 electrons relative to these electrons in the unexcited atom:  $\Psi_0^{N-1}$ . 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  $\chi$ .

**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.



## How to calculate $\mu$

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

$$u = \frac{\epsilon_0 E_0^2}{2} = \frac{\epsilon_0 \omega^2 A_0^2}{2}$$

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

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

$$\mu(\omega) = -\frac{2}{\epsilon_0 \omega^2 A_0^2} \frac{du}{dx}$$

$$\mu(\omega) = -\frac{2}{\epsilon_0 \omega^2 A_0^2} \frac{d}{dx} [\hbar \omega n_{ph}]$$

$$\mu(\omega) = -\frac{2\hbar}{\epsilon_0 \omega A_0^2} \frac{d}{dx} [n_{ph}]$$

$$\mu(\omega) = \frac{2\hbar}{\epsilon_0 \omega A_0^2} n \sum_f W_{if}$$

$n$  = atomic density

$W_{if}$  = transition probability

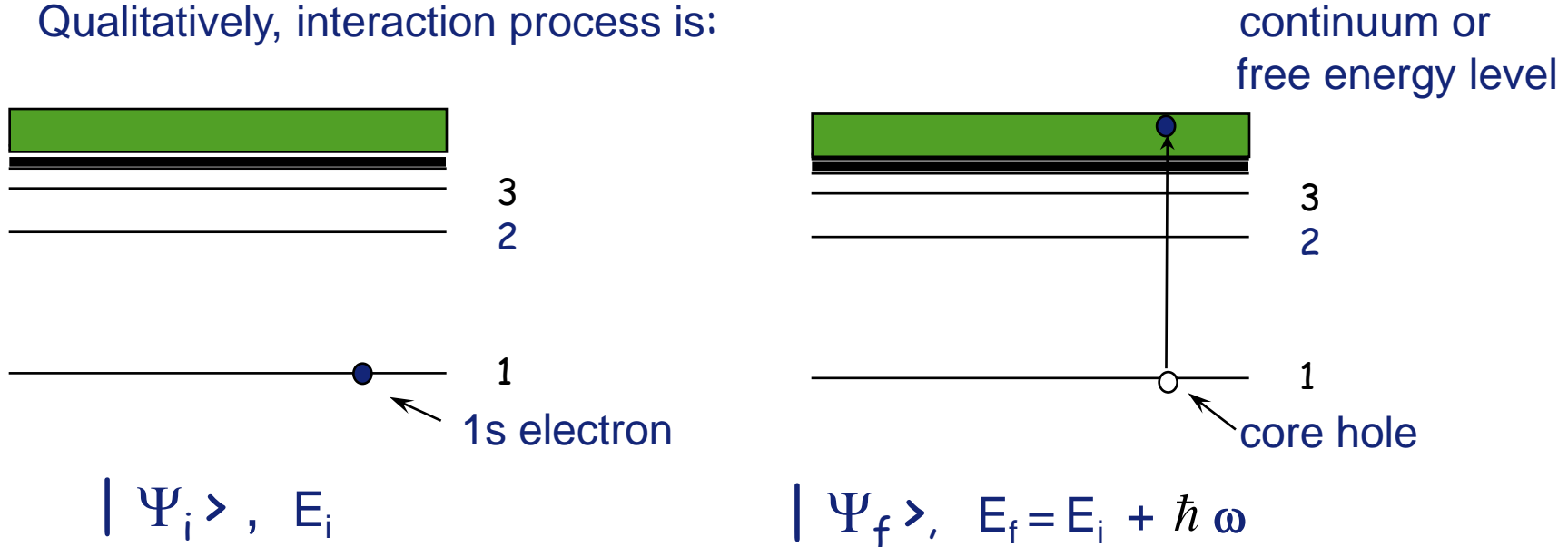
# X-ray Absorption

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.  $\mu \sim \mu$  photoelectric absorption for  $1 < E < 50$  keV

III. Qualitatively, interaction process is:





## Transition probability: Golden Rule

- $\mu(\omega)$  depends on:

- atomic density  $n$

- transition probability  $W_{if}$  of atom from  $|\Psi_i\rangle$  to  $|\Psi_f\rangle$

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

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

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

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

 $\hat{H}_I$ 

EM field - atom interaction hamiltonian operator

 $\langle \Psi_f | \hat{H}_I | \Psi_i \rangle$ 

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 1<sup>st</sup> order):

$$\hat{H}_I = i\hbar \frac{e}{m} \sum_j \vec{A}(\vec{r}_j) \cdot \vec{\nabla}_j \quad (3)$$

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

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

## Dipole approximation

- further simplification:

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

- transition probability in dipole approximation:

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

- alternative and equivalent expression (see Appendix 2):

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

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

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

$$\mu(\omega) = \frac{2 \pi e^2 \omega}{\epsilon_0} n \sum_f \left| \langle \Psi_f | \sum_j \hat{\epsilon} \cdot \vec{r}_j | \Psi_i \rangle \right|^2 \rho(E_f)$$

- if  $|\Psi_i\rangle$  and  $|\Psi_f\rangle$  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  $|\Psi_f\rangle$
- but, to obtain structural info, one still needs to calculate  $|\Psi_i\rangle$  and  $|\Psi_f\rangle$  or at least be able to express their structural properties in parametric form

$|\Psi_i\rangle$  relatively easy  $\rightarrow$  ground state of atom

$|\Psi_f\rangle$  in general very complicated  $\rightarrow$  in principle, all electrons are involved (multi body process, final state strongly influenced by environment)

# Single electron approximation

- large part of  $\mu$  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  $\mu$  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

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

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

$\psi, r, \epsilon_f$  Wavefunction, position vector, final energy of “active” electron

## “Sudden” approximation and overlap factor

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

- time to exit atom  $\ll$  relaxation time of passive electrons
- its state not influenced by passive electrons relaxation

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

where

$$S_0^2 = \left| \langle \Psi_f^{N-1} | | \Psi_i^{N-1} \rangle \right|^2 \quad (S_0^2 \sim 0.7 - 1.0)$$

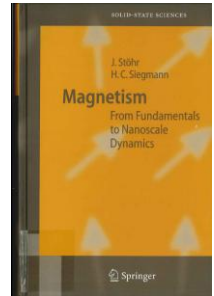
→ Allows to reduce interpretation of EXAFS to the calculation of the final state of **ONLY** the photoelectron

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

dipole operator

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

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

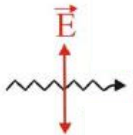


electron position vector       $\mathbf{r} = x\mathbf{e}_x + y\mathbf{e}_y + z\mathbf{e}_z$

photon  
polarization  
vectors

$$\epsilon_x^0 = \epsilon_x = e_x \quad \epsilon_y^0 = \epsilon_y = e_y \quad \epsilon_z^0 = \epsilon_z = e_z \quad \text{linear polarization}$$

$$\epsilon_z^{\pm} = \mp \frac{1}{\sqrt{2}} (\epsilon_x \pm i\epsilon_y) \quad \text{circular polarization with } \mathbf{k} // z$$



dipole operator in terms of  
spherical harmonics

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

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

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



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

matrix elements factor into spin, radial and angular parts

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

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

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



## Appendix 1: Interaction Hamiltonian

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

$$\nabla \cdot A = 0$$

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

- Atom described by charged particles  $\alpha$ :

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

- Total Hamiltonian:

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

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

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

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

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

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

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

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

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

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

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

well defined eigenstates  
valid for atoms, molecules,  
solids

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

$H_{I1}$

$H_{I2}^{spin}$

$H_{I2}$

linear in A: photon creation  
or absorption

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

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

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

intensity of X-ray source weak

spin order of magnitude

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

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

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

Appendix 2

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

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

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

## Appendix 2 cont

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

(1)                      (2)

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

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

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

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

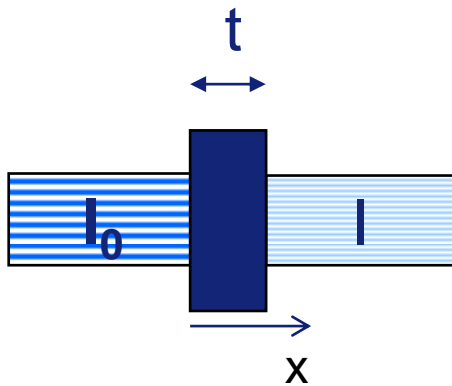
Appendix 2 cont

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

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

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

# The absorption coefficient $\mu$



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

$\uparrow$   $\text{at/cm}^2$                        $\uparrow$   $\text{cm}^2/\text{at}$

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

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

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



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

- $\mu$  is related to the atomic cross section:

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

- in general you find tabulated the mass absorption coefficient  $\mu/\rho$ :

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

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

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

# 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

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

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

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

ideally

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

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