



| The European Synchrotron

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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

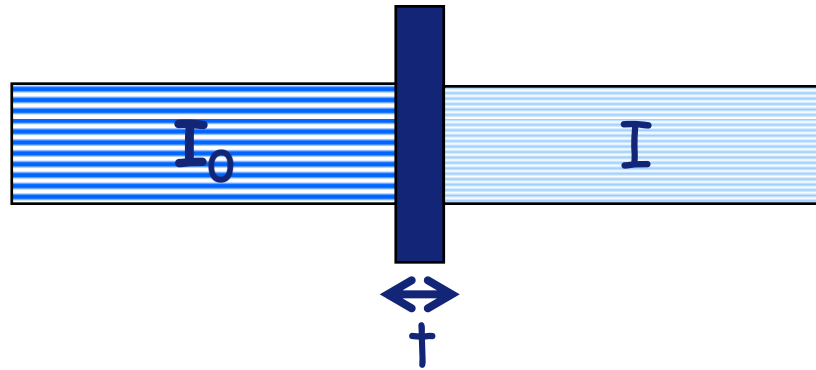
- **Two fundamental X-ray-matter interactions:**
 - photoelectric absorption
 - scattering (elastic, inelastic)

- **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 μ



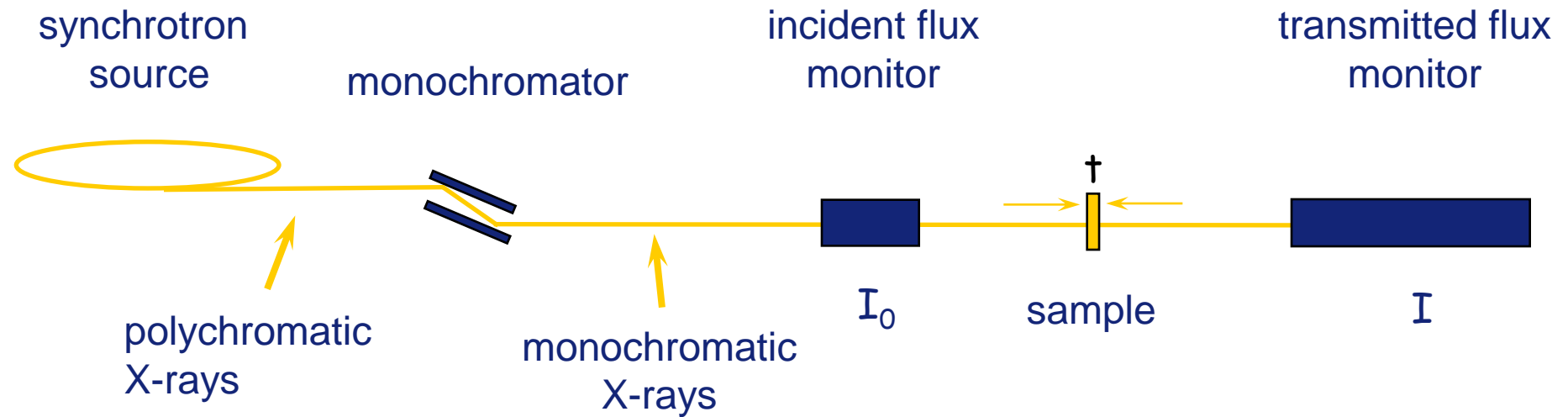
$$I = I_0 \exp[-\mu t]$$



linear absorption coefficient

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

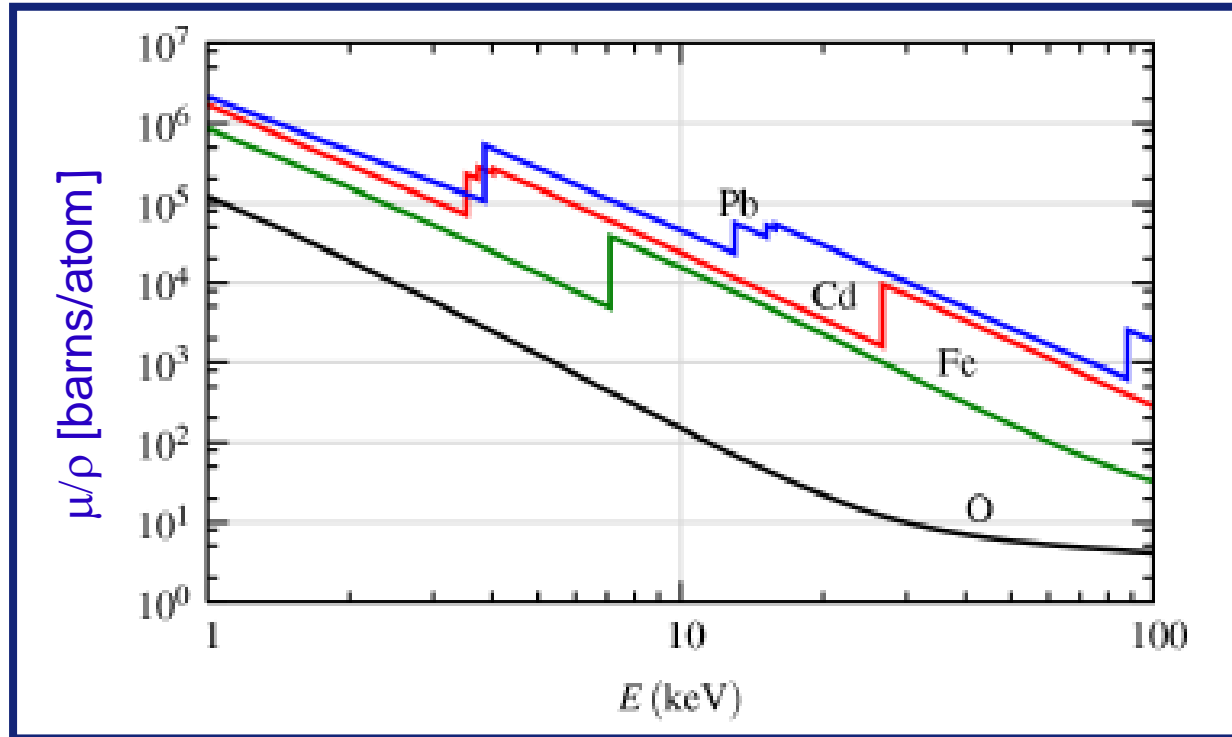
The Absorption Coefficient μ



1. Measure I_0 and I as a function of E_x

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

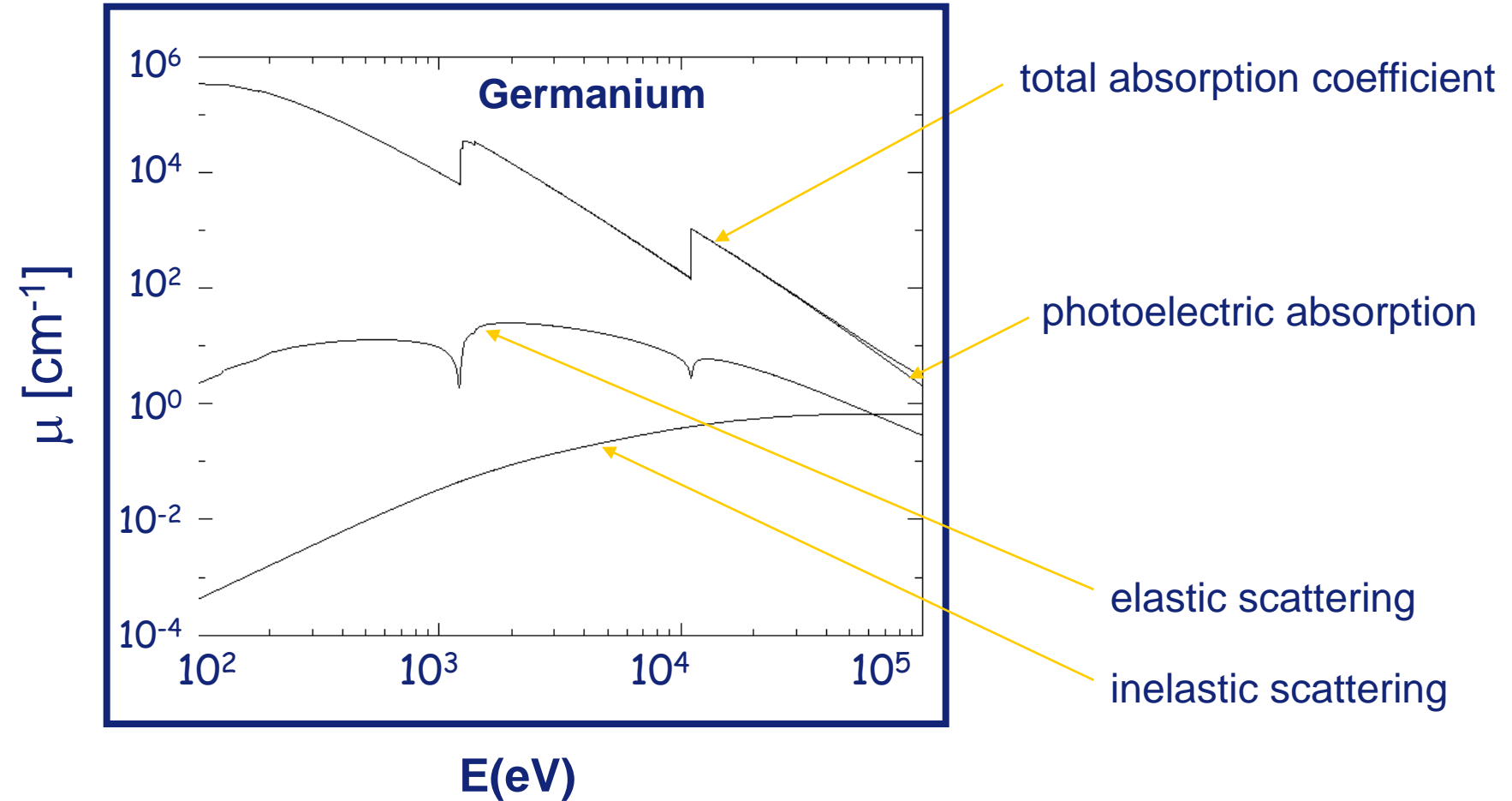
The Absorption Coefficient μ



μ depends strongly on X-ray energy **E** and atomic number **Z**, 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

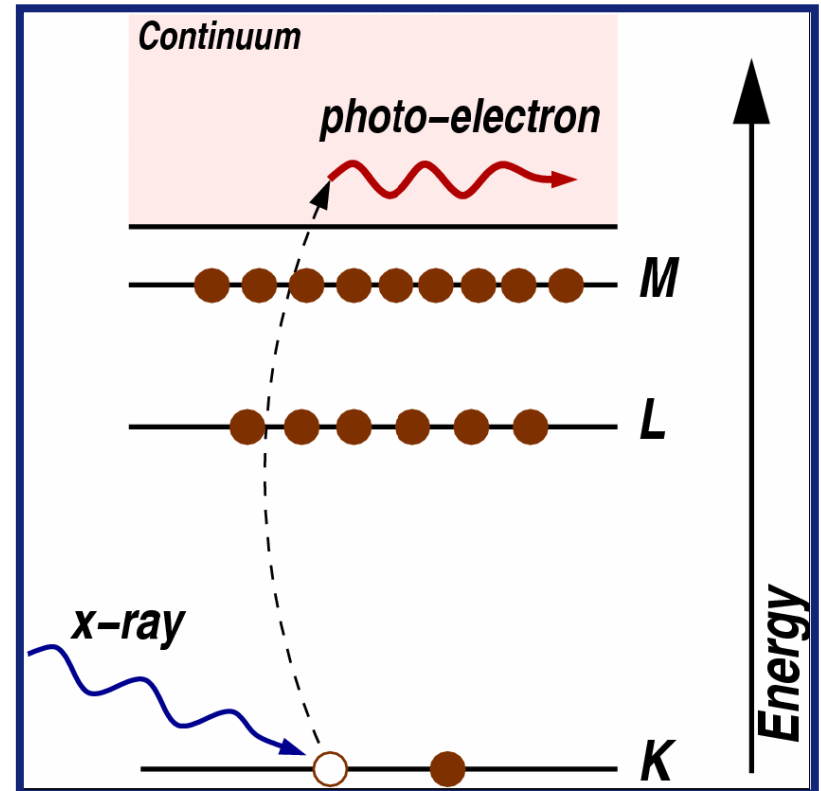
Photoelectric Absorption

X-rays (light with wavelength $0.06 \leq \lambda \leq 12 \text{ \AA}$ 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**.

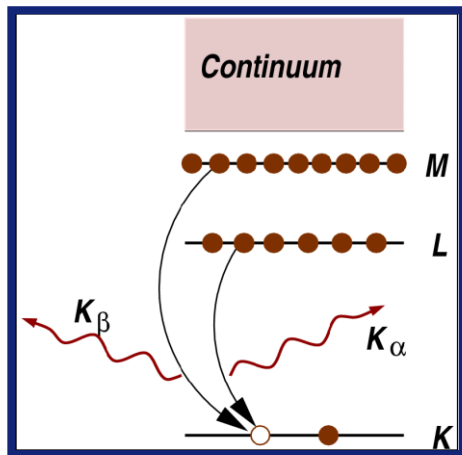


De-excitation: Fluorescence and Auger Effect

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.

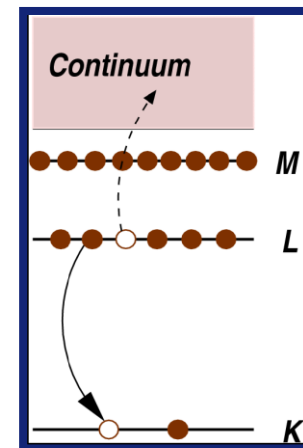
X-ray Fluorescence:

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



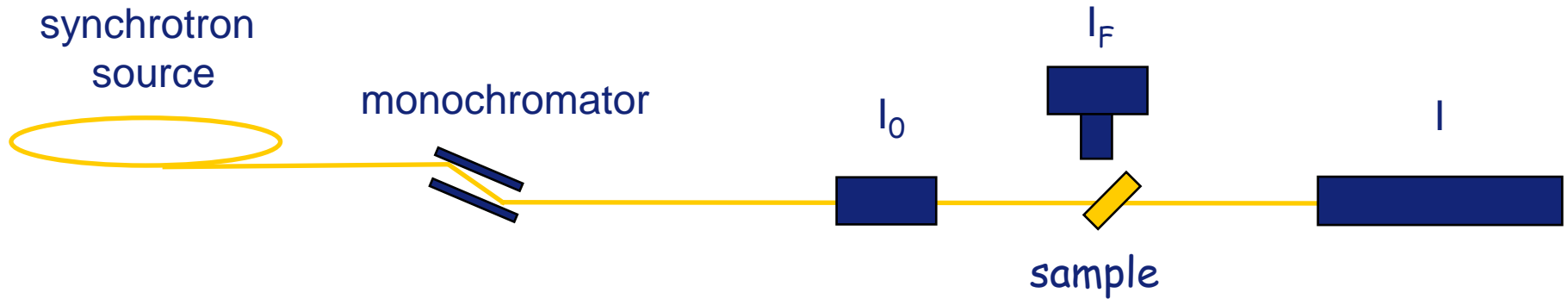
Auger Effect:

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:

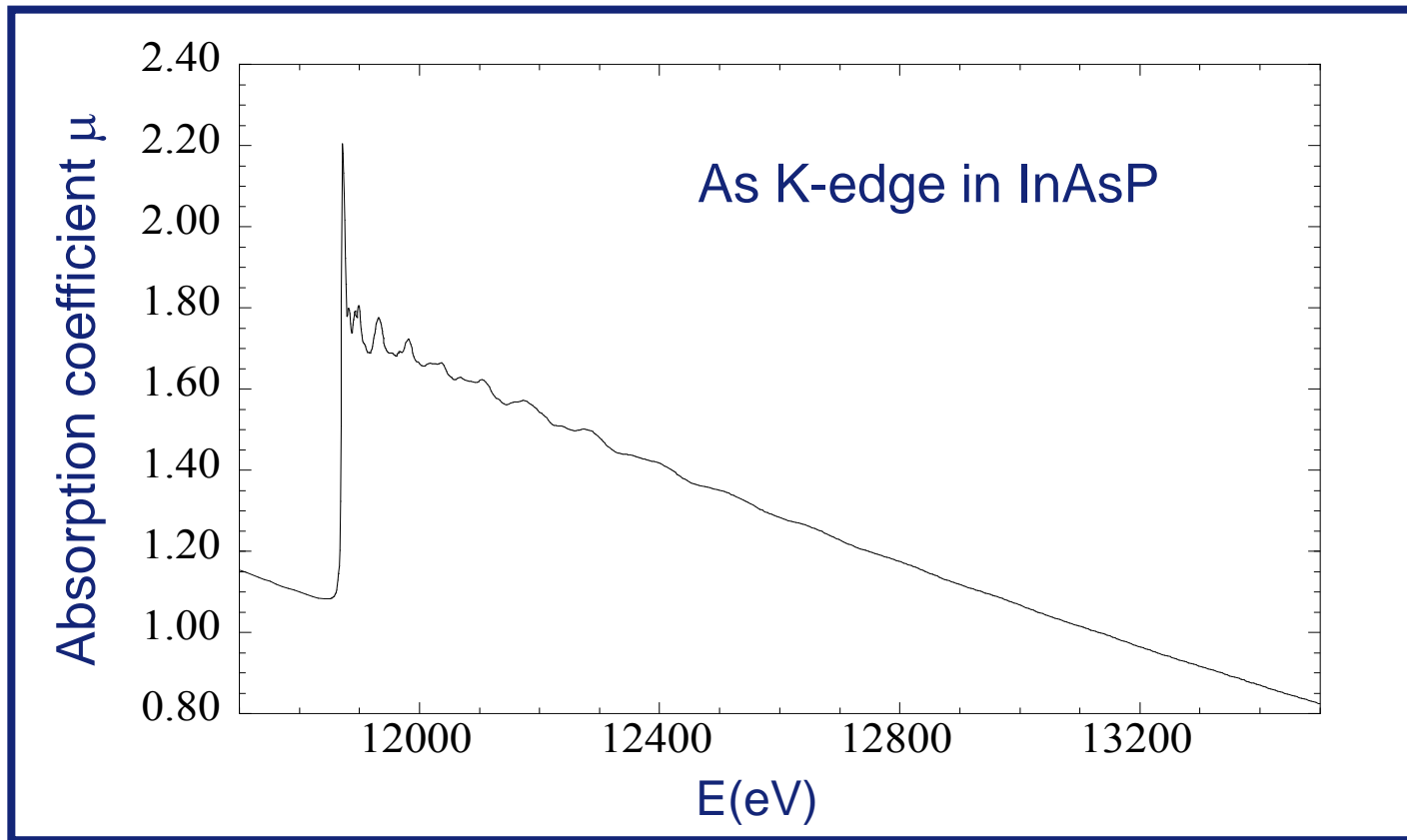
The re-filling the deep core hole is detected. Typically the fluorescent X-ray is measured:

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

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

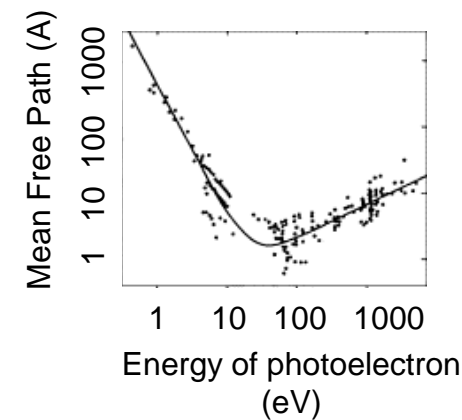
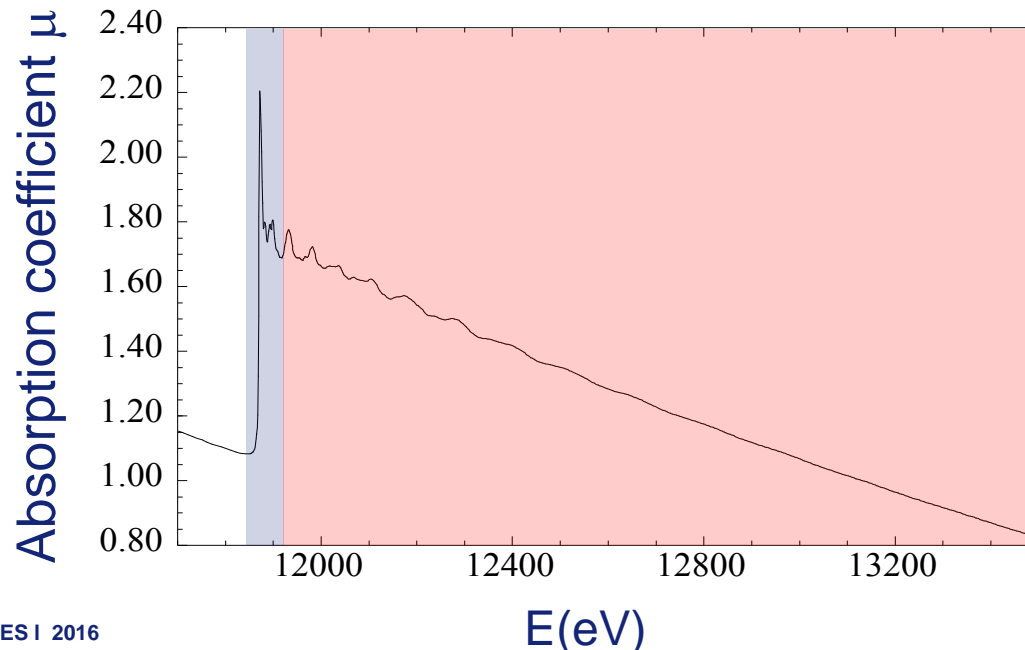
XAFS is also referred to as X-ray Absorption Spectroscopy (**XAS**) and is broken into 2 regimes:

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**

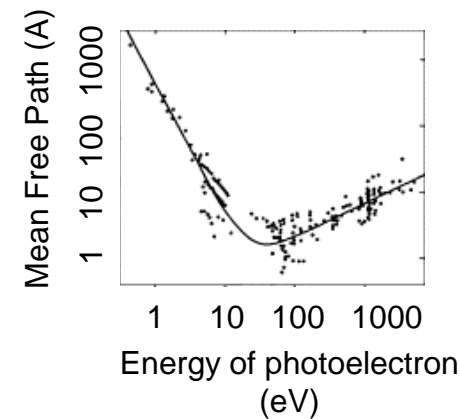
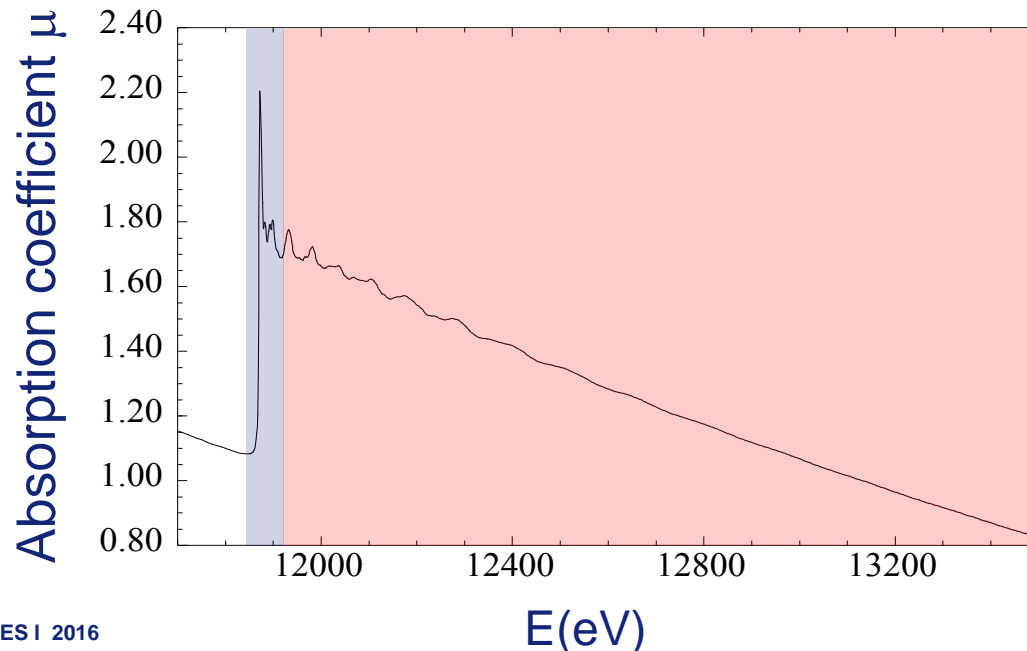


EXAFS and XANES

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.

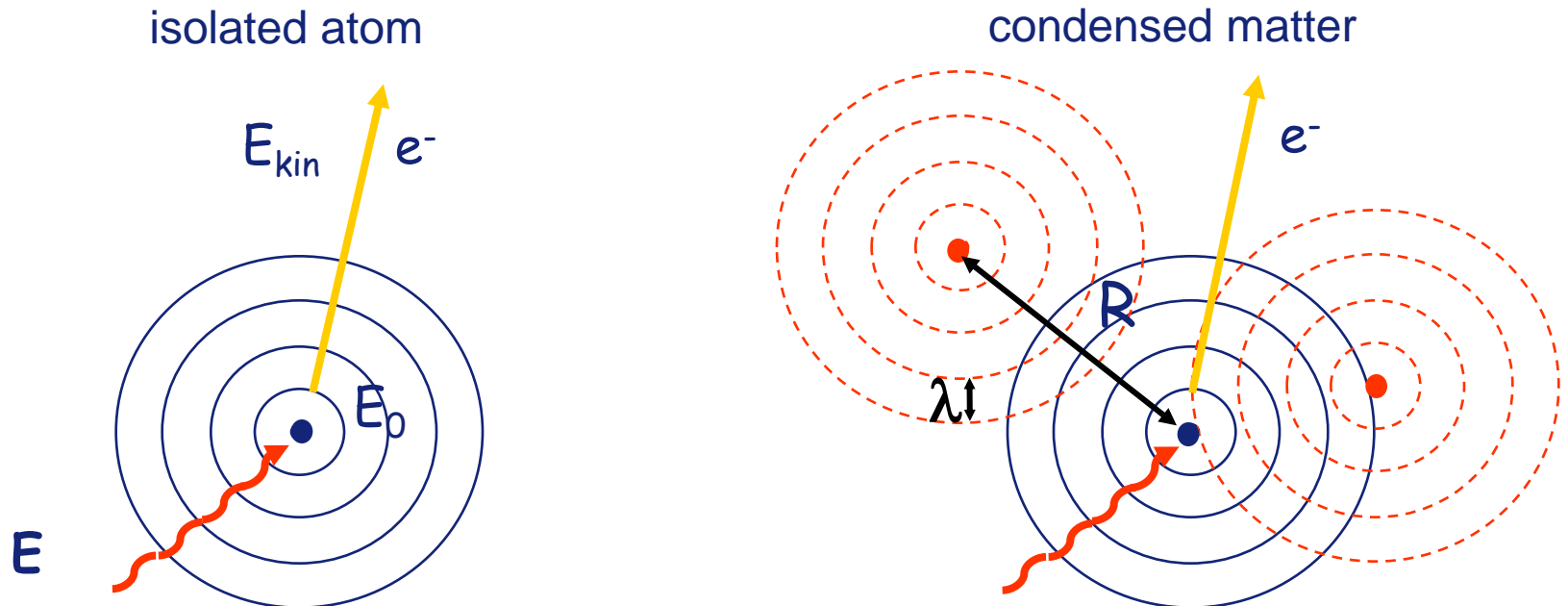
XANES: local site symmetry, charge state, orbital occupancy

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:

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

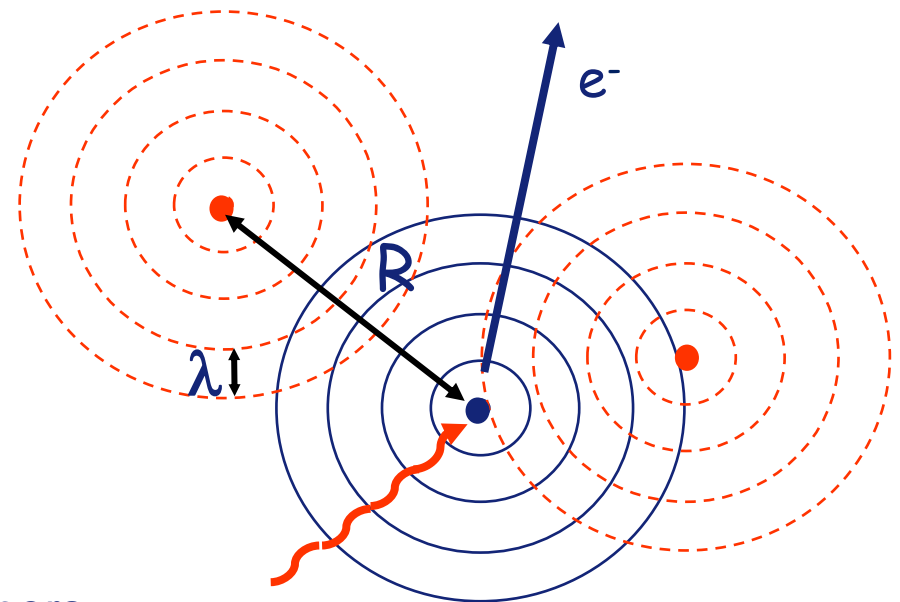
$$\lambda = 2\pi/k$$

Where do the oscillations come from?

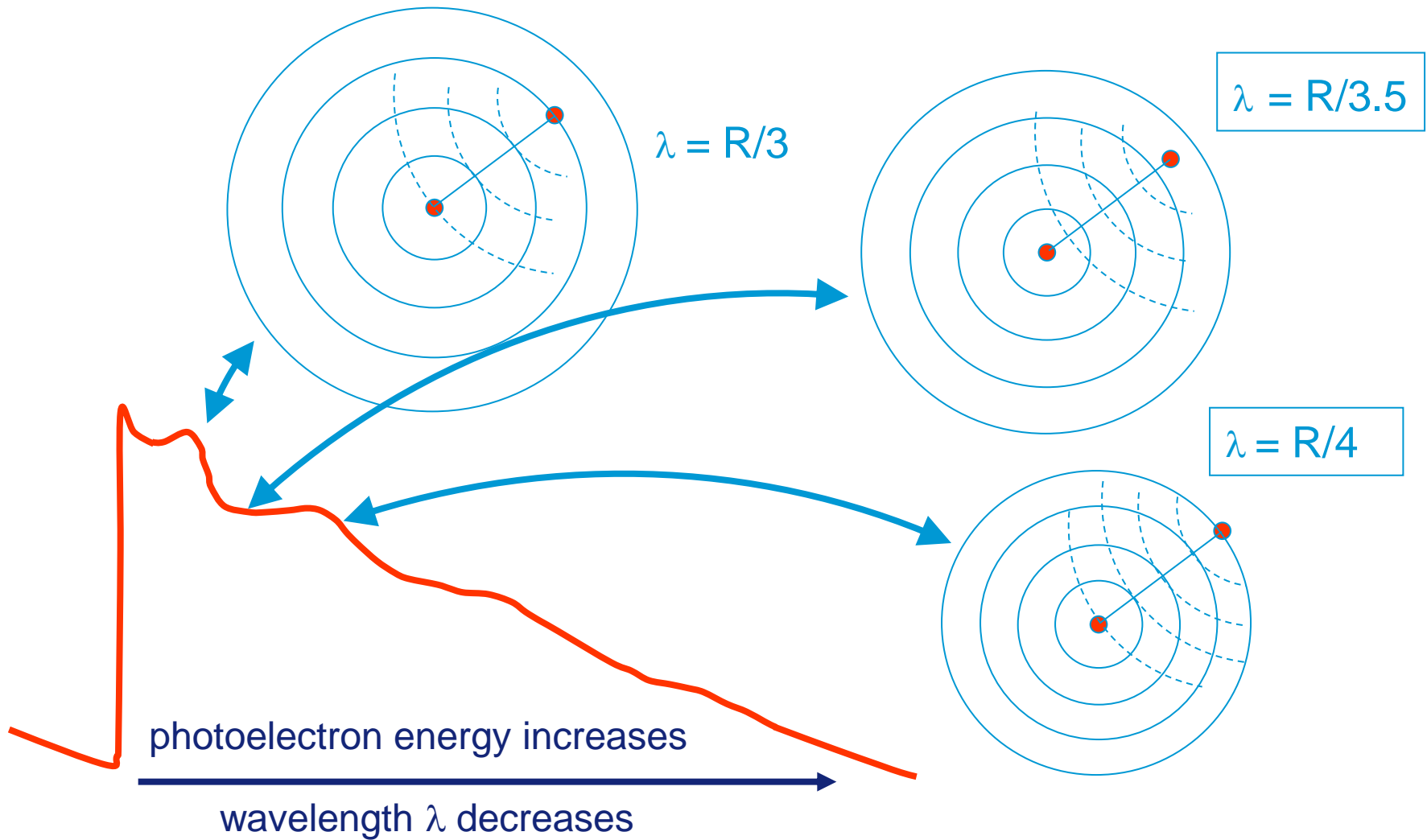
Due to a **quantum effect**, the autointerference of photoelectron wave modifies the absorption coefficient value:

1. As E is scanned above E_0 , E_{kin} is varied, and consequently k and 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 $\mu(E)$
- 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



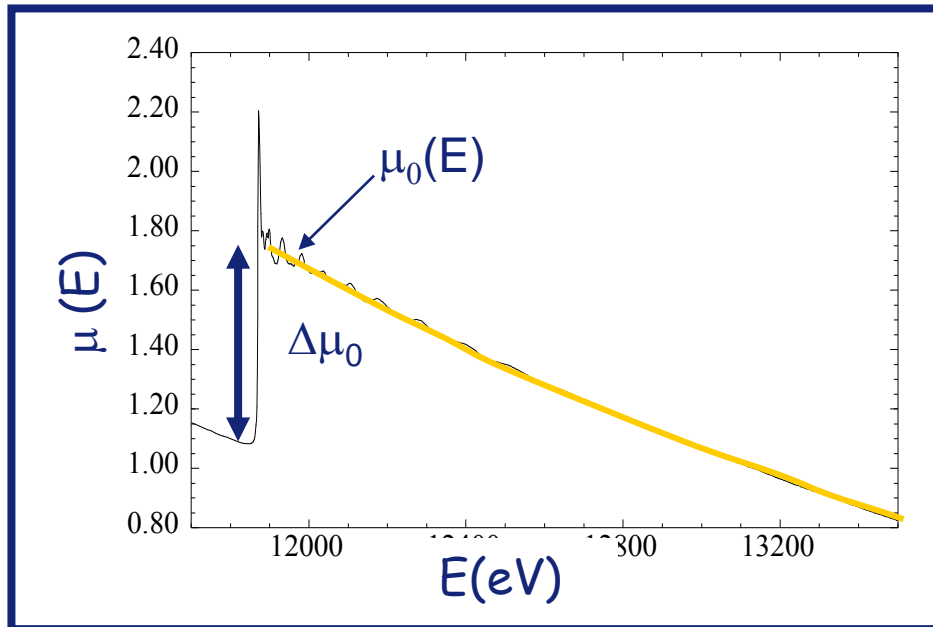
The probability of absorption oscillates due to constructive and destructive interference

The EXAFS signal χ

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.



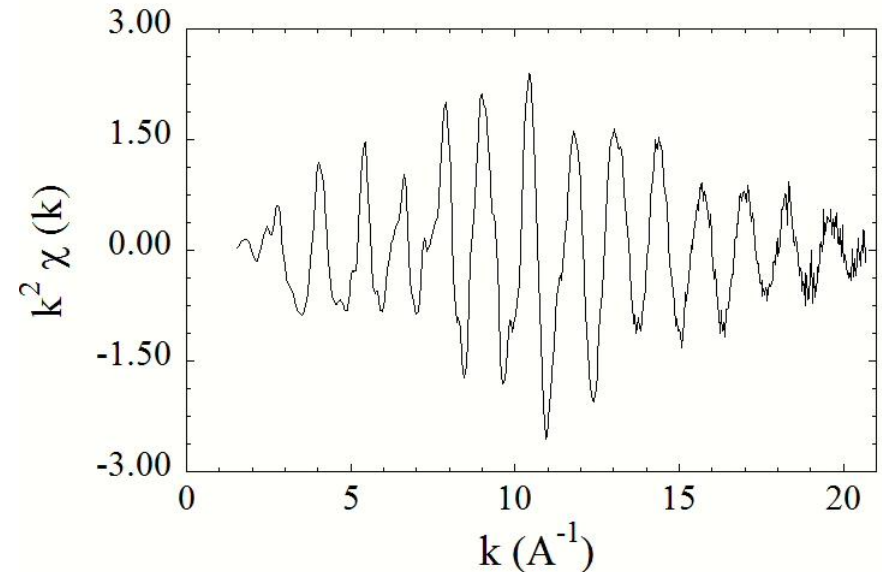
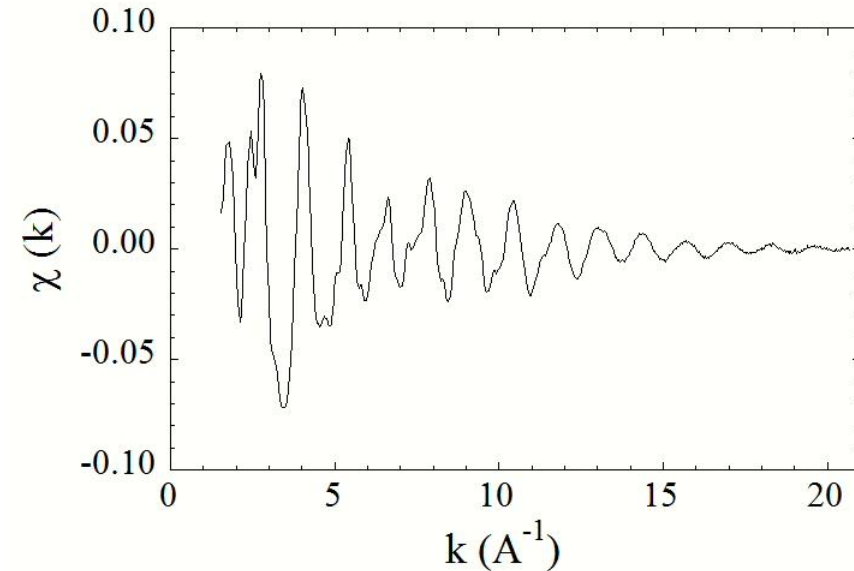
EXAFS: $\chi(k)$

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

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

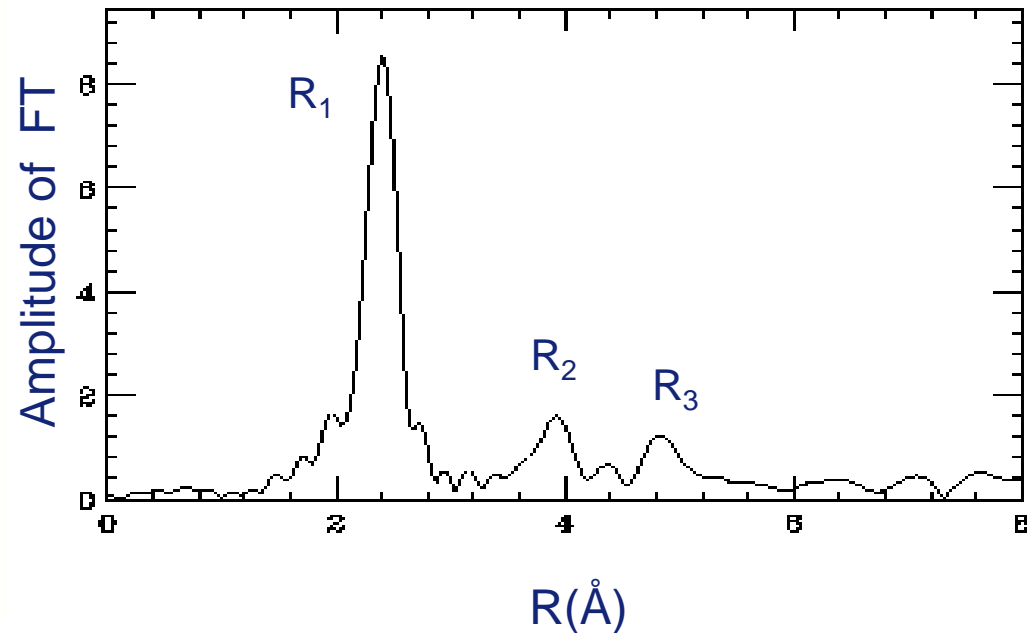
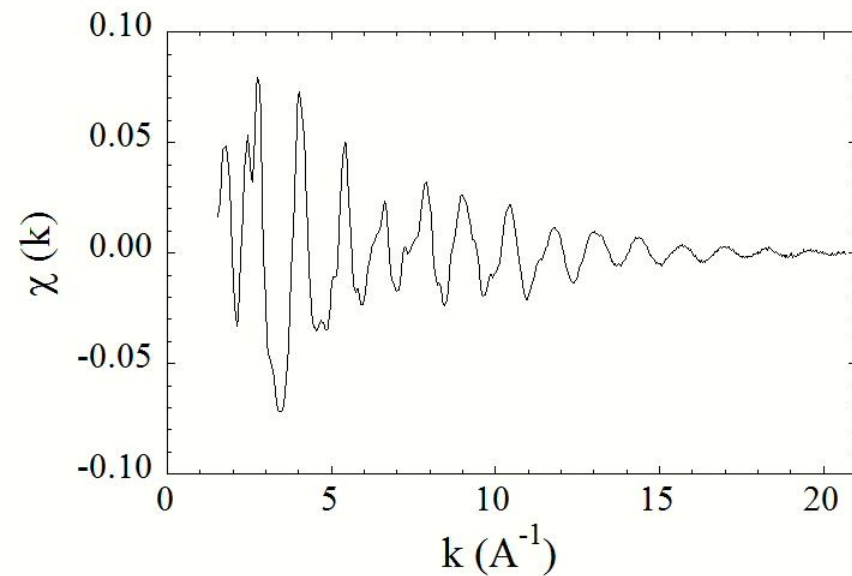
$\chi(k)$ is often shown weighted by k^2 or k^3 to amplify the oscillations at high- k :



Qualitative picture of local coordination in R space

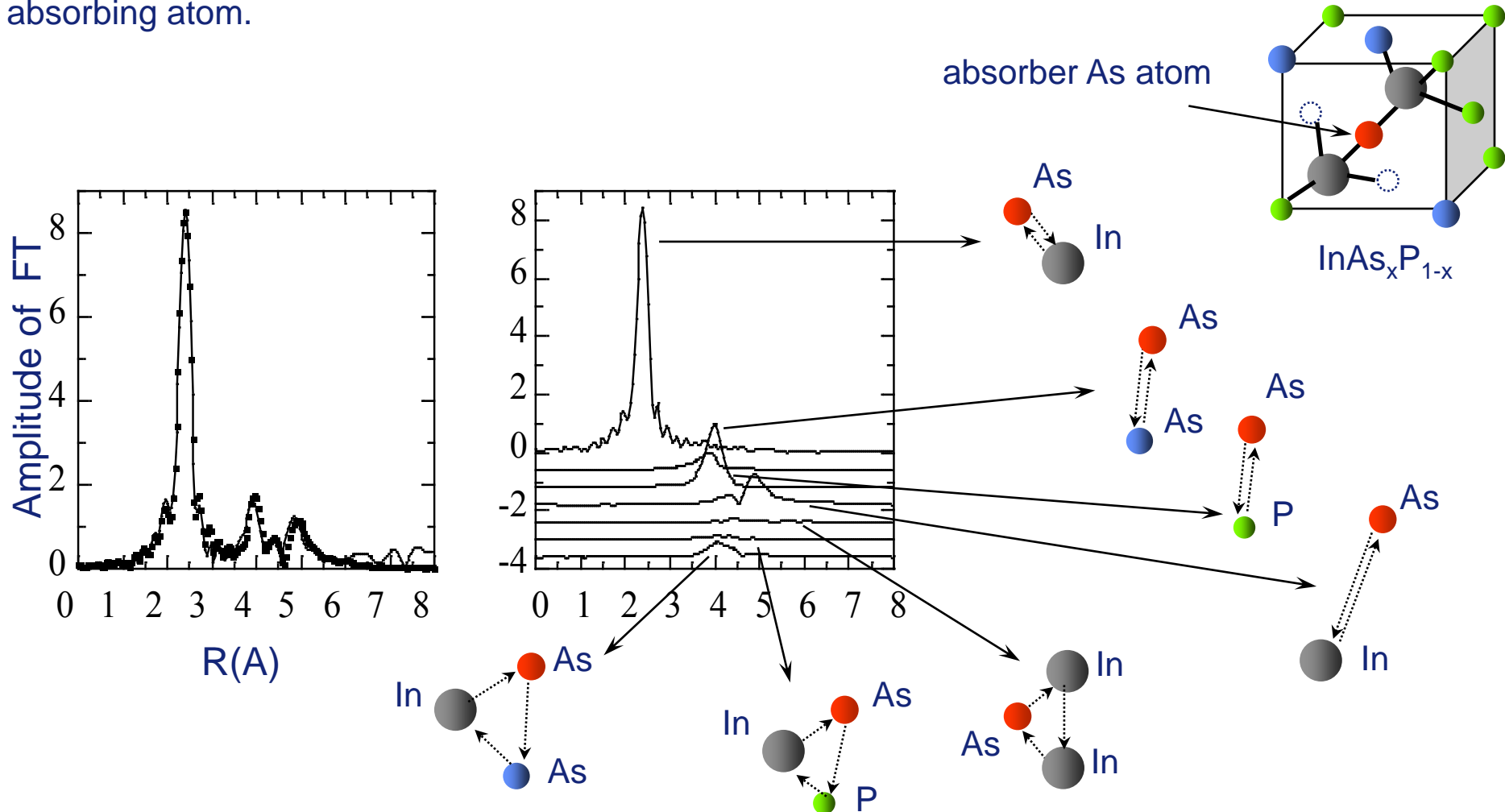
The **frequencies** contained in the EXAFS signal depend on the **distance** between the absorbing atom and the neighboring atoms (i.e. the length of the scattering path).

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.



χ : 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

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

The stronger the scattering amplitude, the larger the signal

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

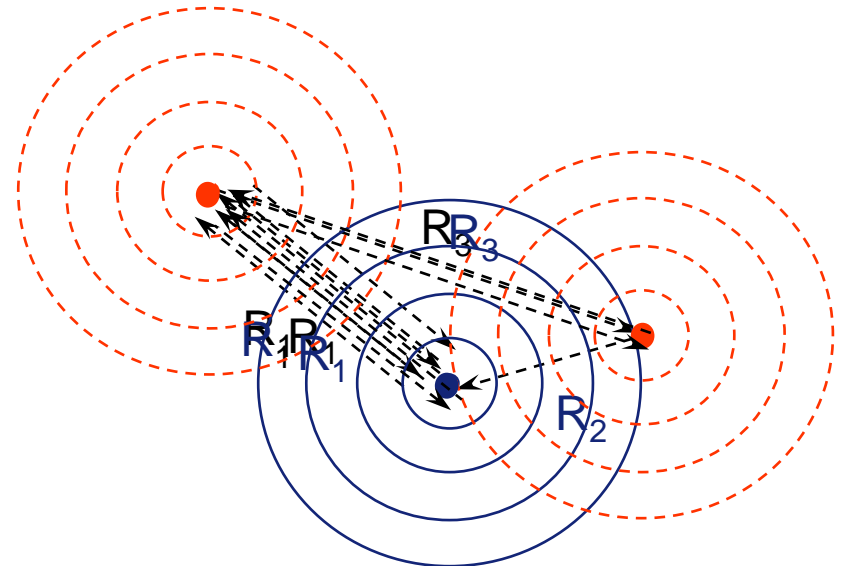
$$2kR_j + \delta_j(k)$$

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 (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 \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 $g_3(r)$ $f = 2R_1 + 2R_3$

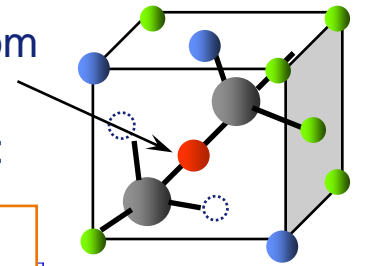


EXAFS can give information on the n-body distribution functions $g_n(r)$.

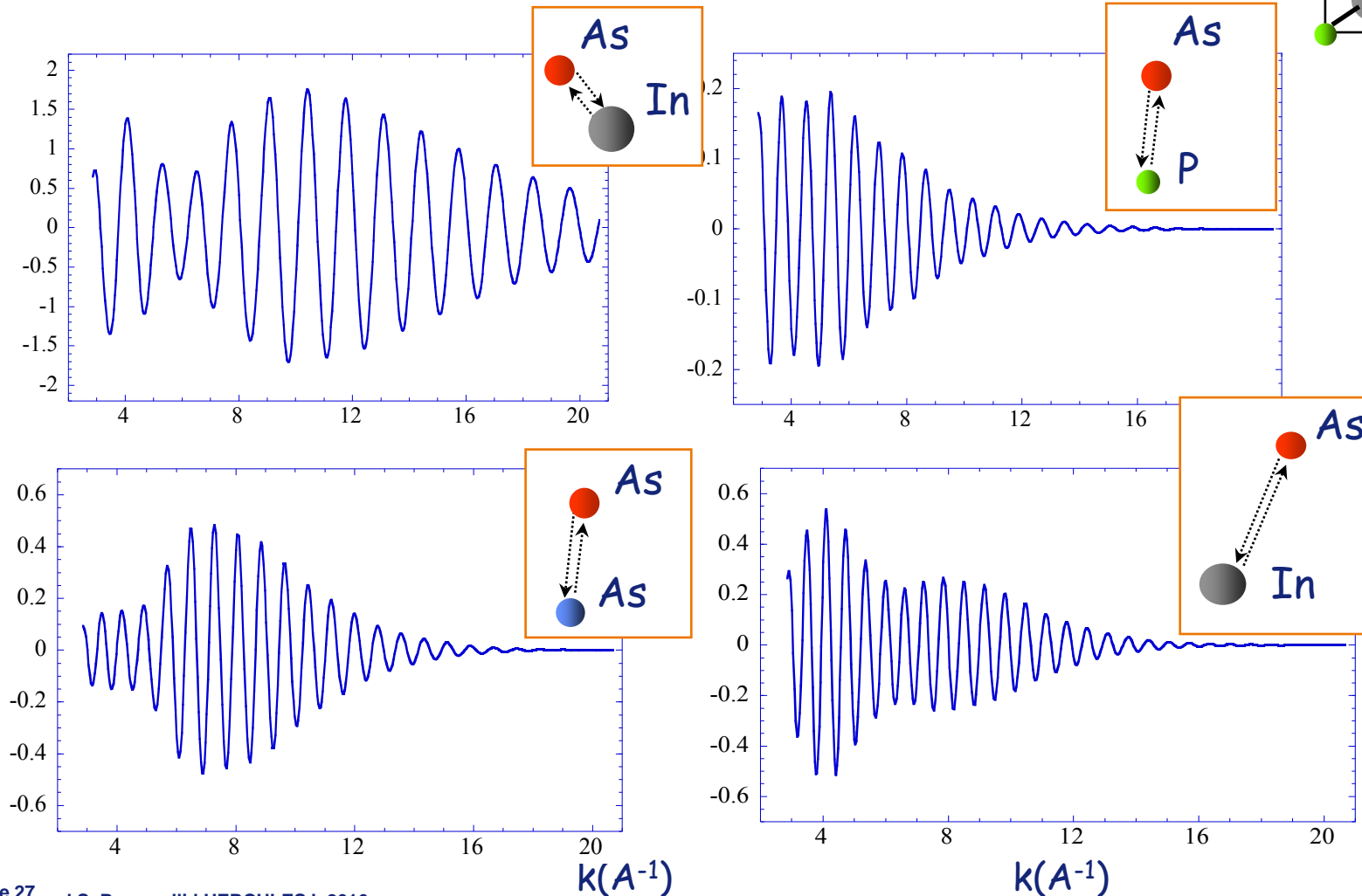
Amplitudes

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

absorber As atom

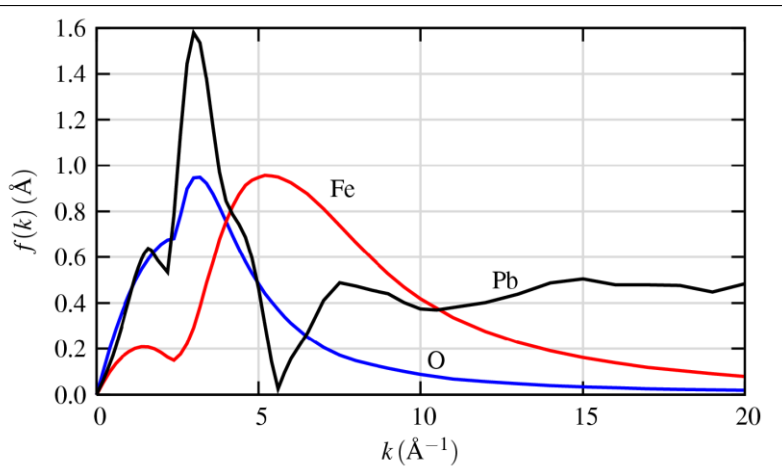


shape of the envelope of each wave indicative of nature of backscatterer atom:



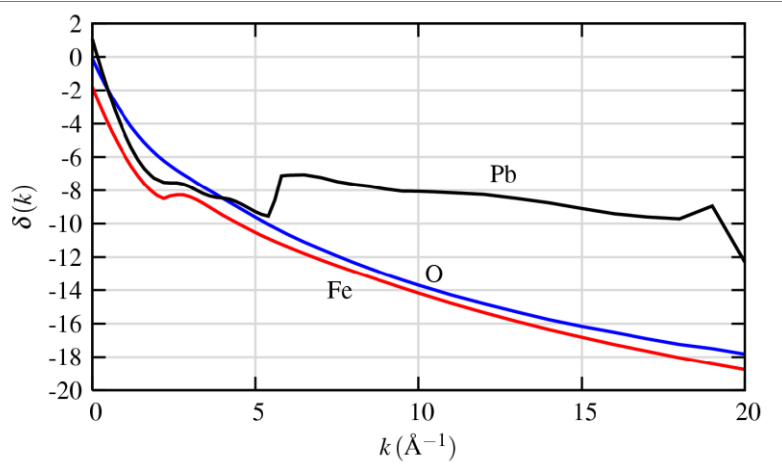
Scattering Amplitude and Phase-Shift: $f(k)$ and $\delta(k)$

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)

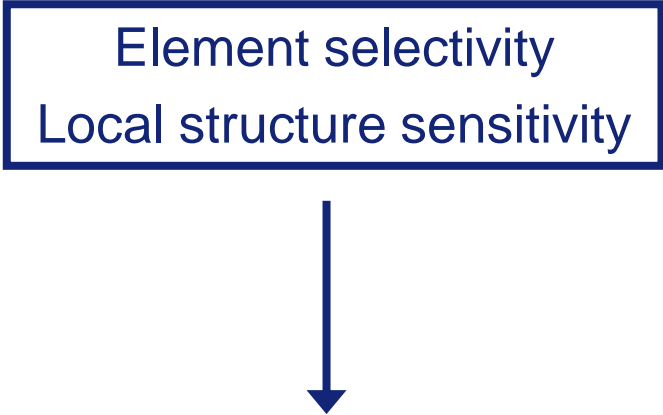
- Crystalline materials with long-range ordering -> 3D picture of atomic coordinates
- Materials with only short-range order (amorphous solid, liquid, or solution) -> 1D radial distribution function containing interatomic distances due to all atomic pairs in the sample.

□ 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

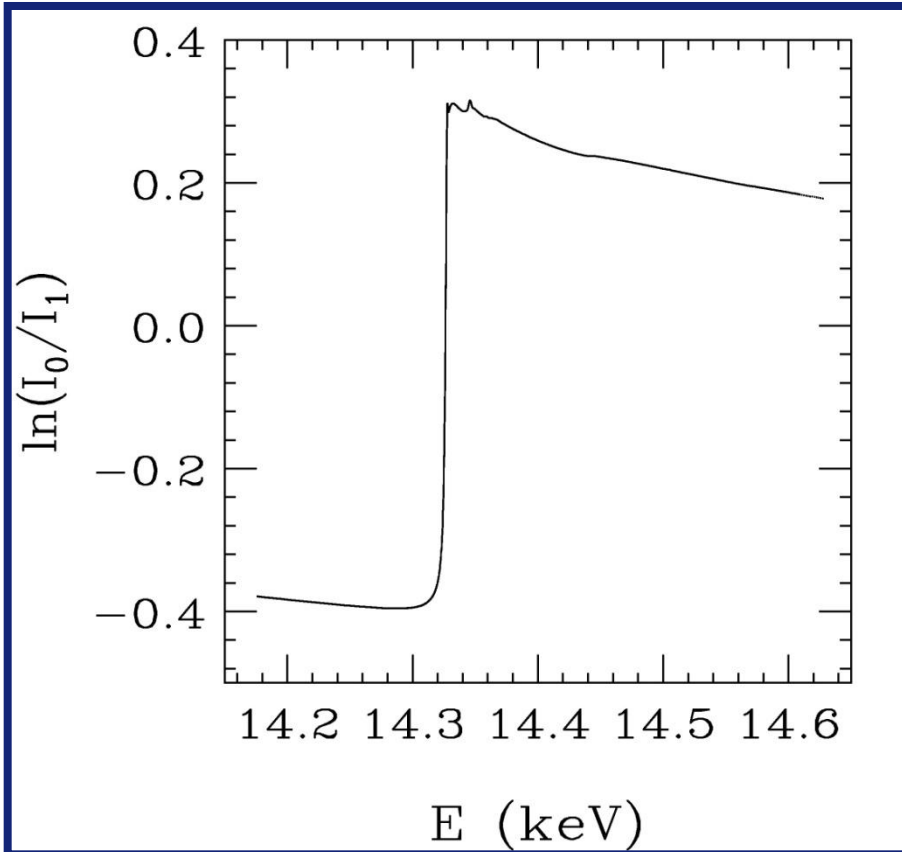
Element selectivity
Local structure sensitivity



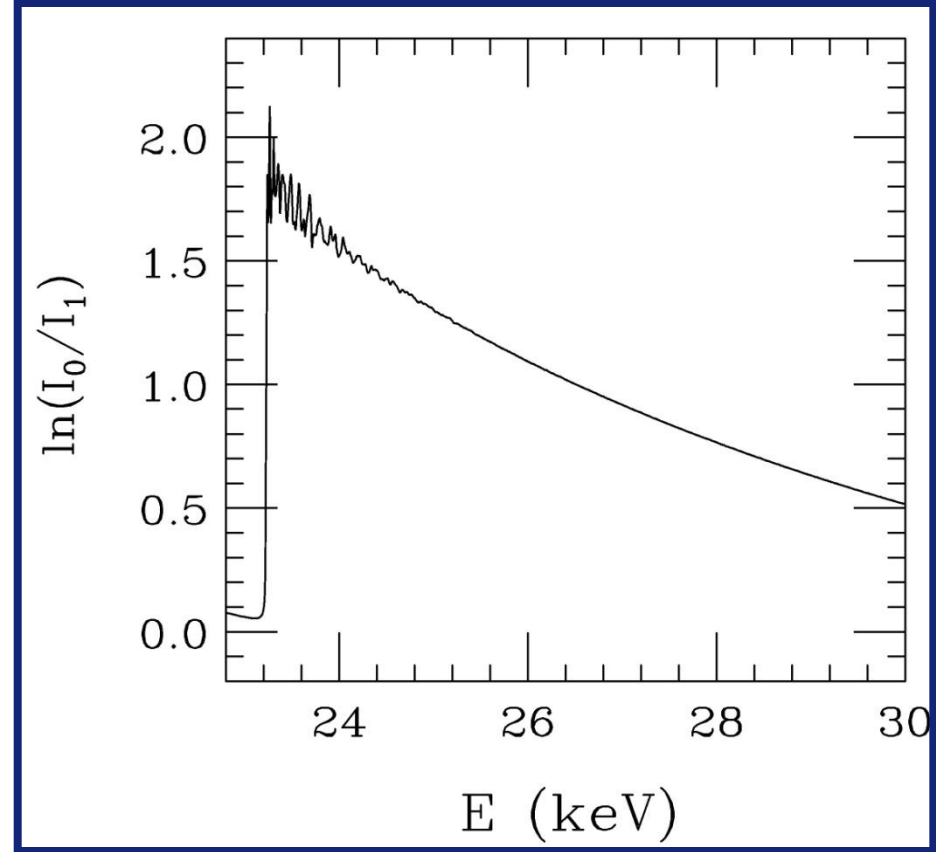
- Local structure in non-crystalline matter
- Local environment of an atomic impurity in a matrix of different atomic species
- Study of systems whose local properties differ from the average properties
- Detection of very small distortions of local structure

Simple Theoretical Description

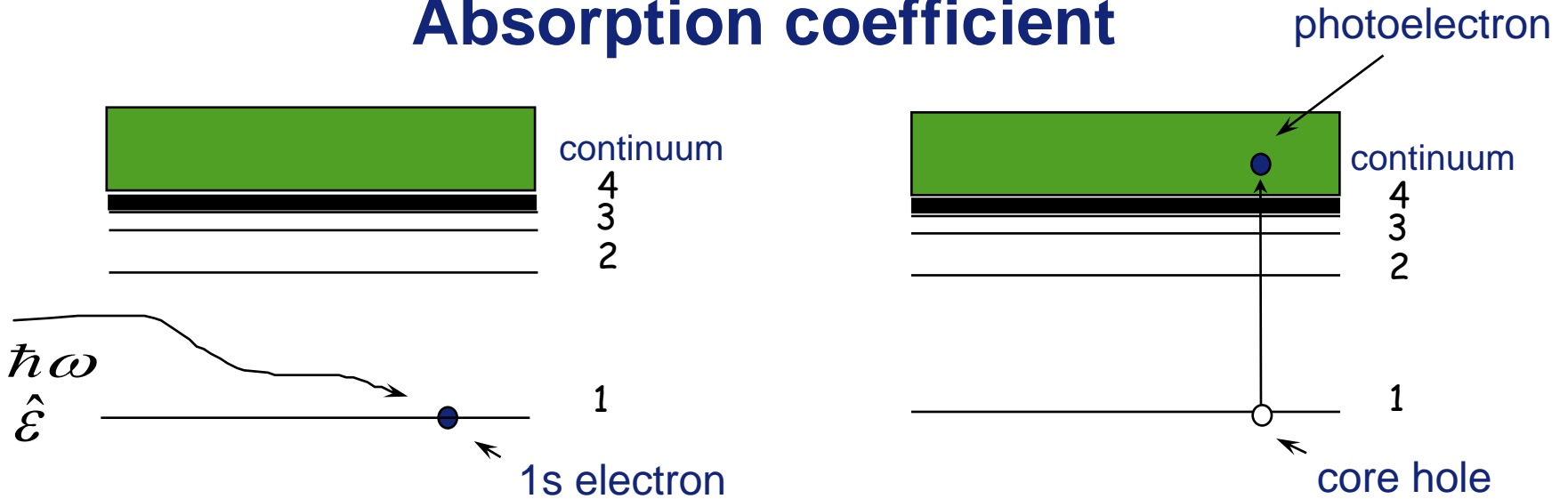
Kr gas



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

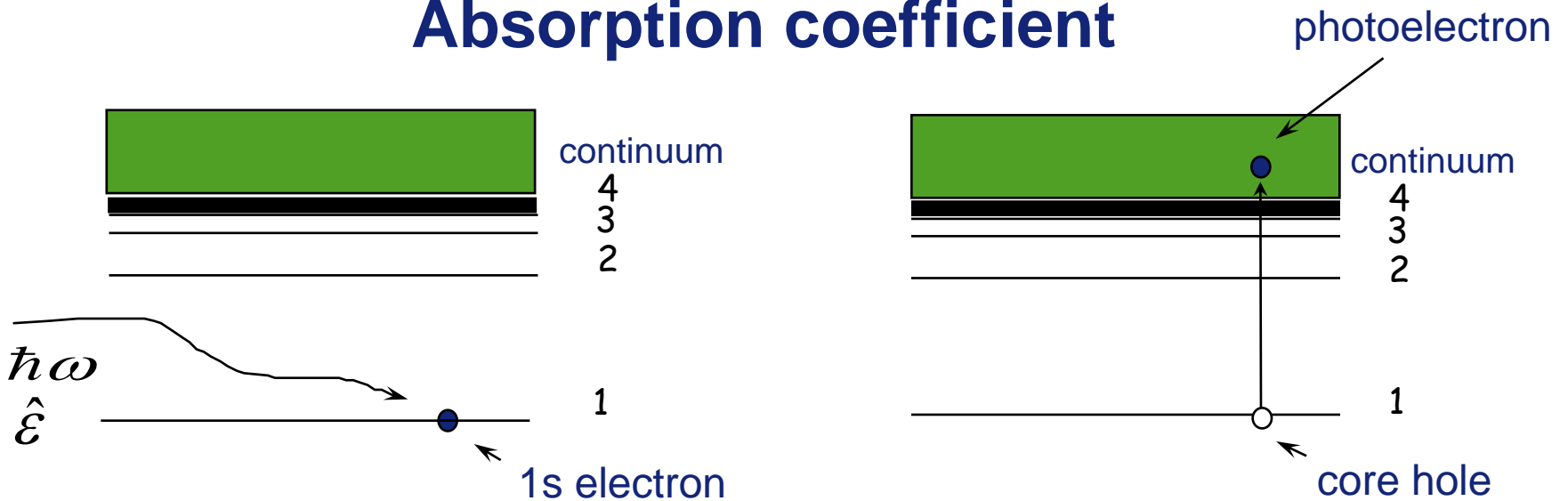
$$\approx \sum_f \left| \langle \Psi_f^{N-1} \psi_f | \hat{\epsilon} \cdot \vec{r} | \Psi_i^{N-1} \psi_i \rangle \right|^2 \approx S_0^2 \sum_f \left| \langle \psi_f | \hat{\epsilon} \cdot \vec{r} | \psi_i \rangle \right|^2$$

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⁻ 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**

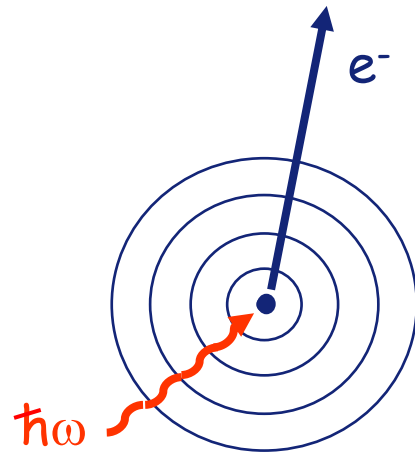
$$\begin{aligned} \Delta l &= l' - l = \pm 1, \\ \Delta m_l &= m'_l - m_l = q = 0, \pm 1, \\ \Delta s &= s' - s = 0, \\ \Delta m_s &= m'_s - m_s = 0. \end{aligned}$$

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

For 1-electron transitions:

| <u>edge</u> | <u>initial state ψ_i</u> | <u>final state ψ_f</u> |
|---------------------------------|--|--|
| K, L ₁ | s (l=0) | p (l=1) |
| L ₂ , L ₃ | p (l=1) | s (l=0), d (l=2) |

Isolated atom: atomic absorption coefficient



e^- photoelectron free to travel away undisturbed

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

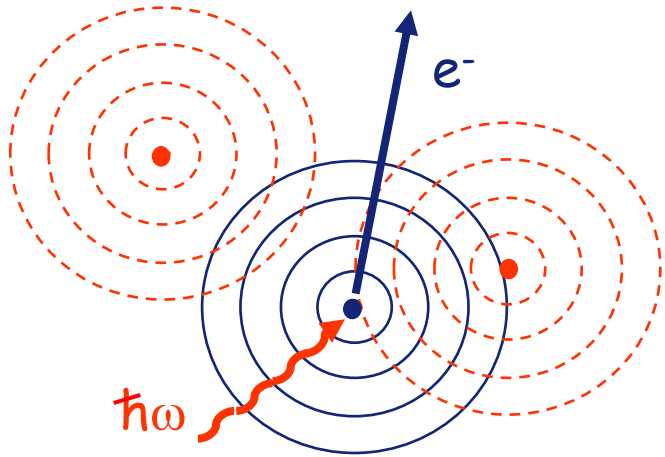
outgoing spherical wave originating from the absorbing atom

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

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

→ 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.

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

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

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

$\mu_0(\omega)$

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

↑
EXAFS

Origin of EXAFS

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

χ : fractional change in μ 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.

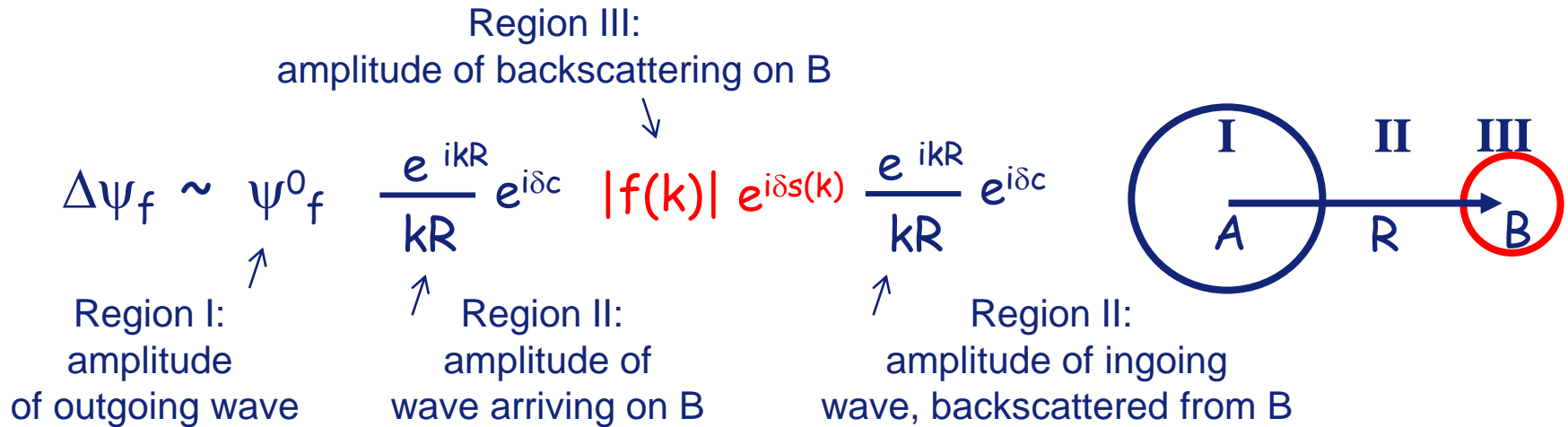
σ^2 mean-square disorder of neighbor distance.

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:



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 σ^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:

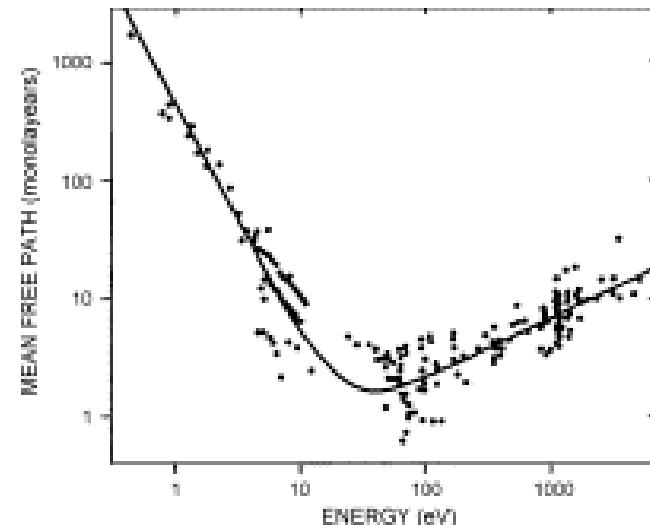
$$\chi(k) \sim S_0^2 \sum_j N_j \frac{f_j(k)}{kR_j^2} e^{-2R/\lambda(k)} e^{-2k^2\sigma_j^2} \sin [2kR_j + \delta_j(k)]$$

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

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

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):

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

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.

How to calculate μ

energy density u carried by X-ray beam is:

$$u = \frac{\varepsilon_0 E_0^2}{2} = \frac{\varepsilon_0 \omega^2 A_0^2}{2}$$

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

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

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

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

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

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

n = atomic density

W_{if} = transition probability

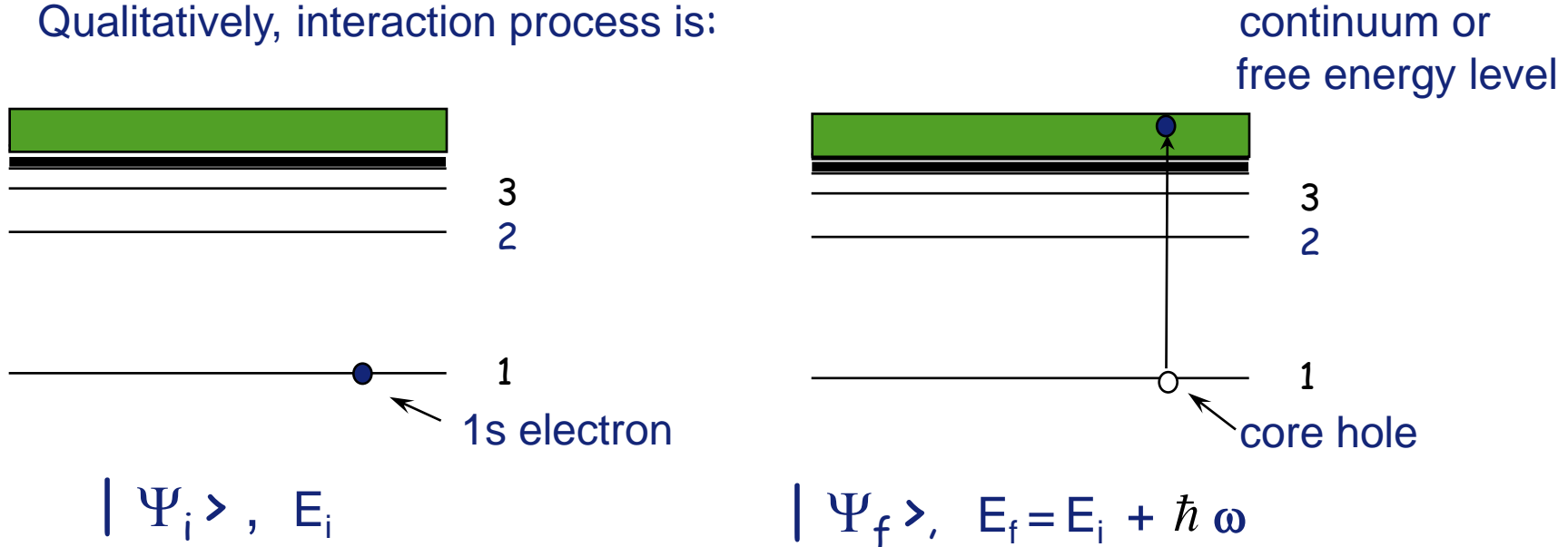
X-ray Absorption

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 $|\Psi_f\rangle$

$$\mu(\omega) = \frac{2\hbar}{\epsilon_0 \omega A_0^2} n \sum_f W_{if} \quad (1)$$

- **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 1st 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 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

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

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 ($E > \text{few } 10 \text{ eV}$ above edge)

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

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

where

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

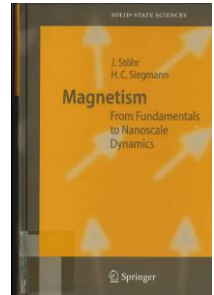
→ Allows to reduce interpretation of EXAFS to the calculation of the final state of **ONLY** the photoelectron

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

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)

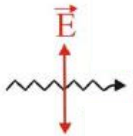


electron position vector $\mathbf{r} = x\mathbf{e}_x + y\mathbf{e}_y + z\mathbf{e}_z$

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 α :

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

- 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)

A₁: 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}

A₁: 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)

A₁: 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)

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

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

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

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

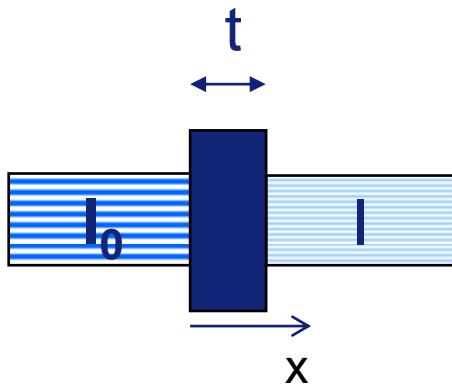
Appendix 2 cont

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

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

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

The absorption coefficient μ



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

\uparrow at/cm^2 \uparrow cm^2/at

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

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

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

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

- μ 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 μ/ρ :

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

- 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