X-ray absorption spectroscopy

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XI School on Synchrotron Radiation
Duino, 5 - 16 September 2011

Basic attenuation mechanisms for X-rays

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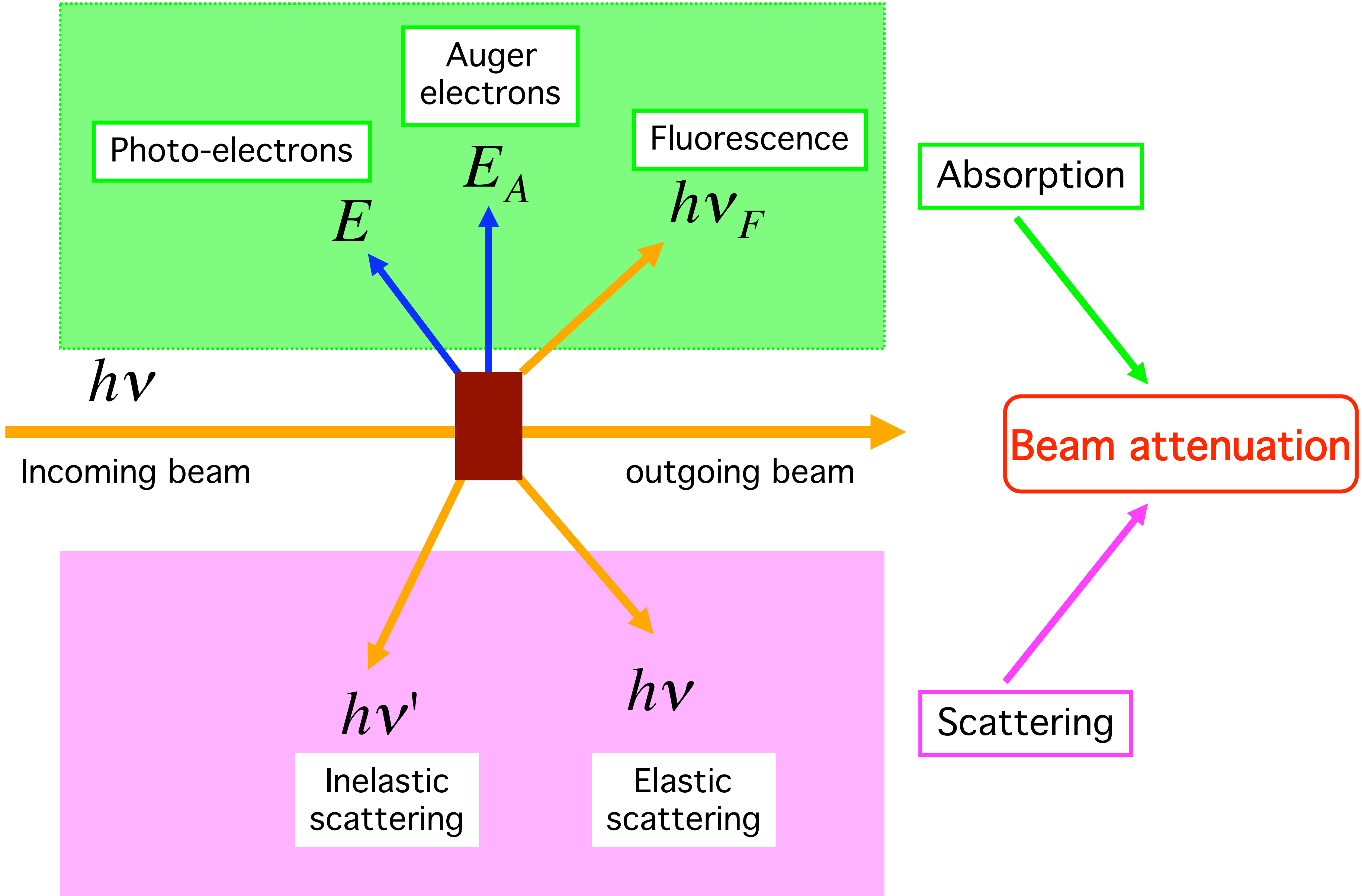

X-RAYS and X-ray techniques

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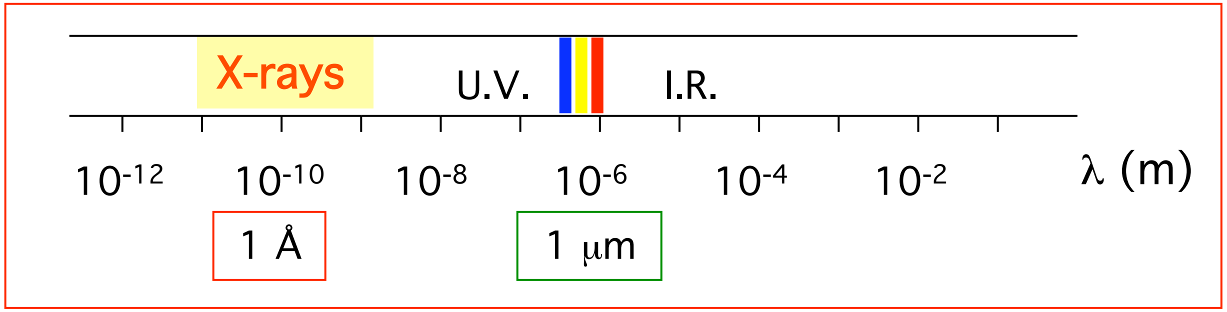
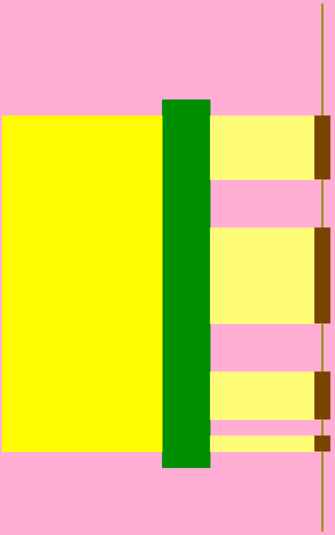
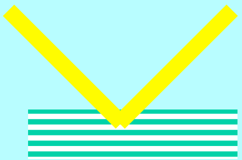


$$E[\text{keV}] = \frac{12.4}{\lambda[\text{Å}]}$$

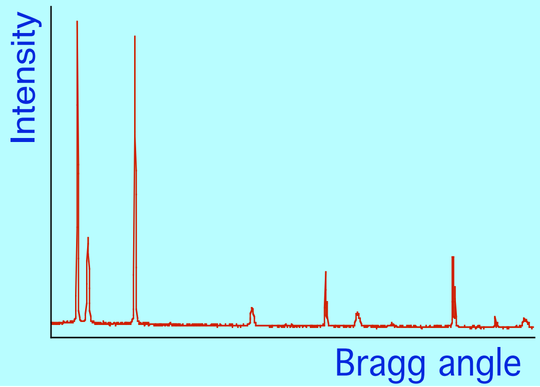
Imaging



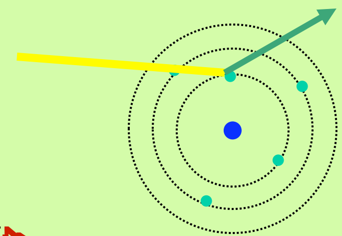
Scattering

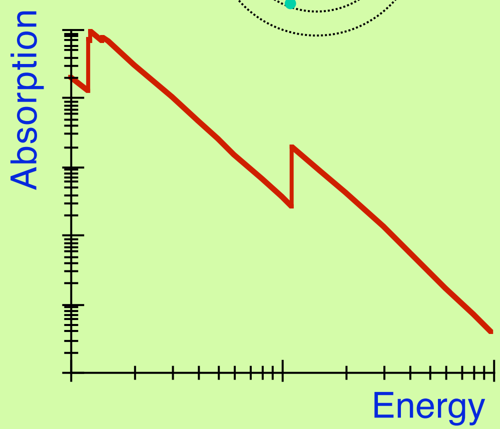


$$\lambda = 2d\sin\theta$$



Spectroscopy





Structural techniques

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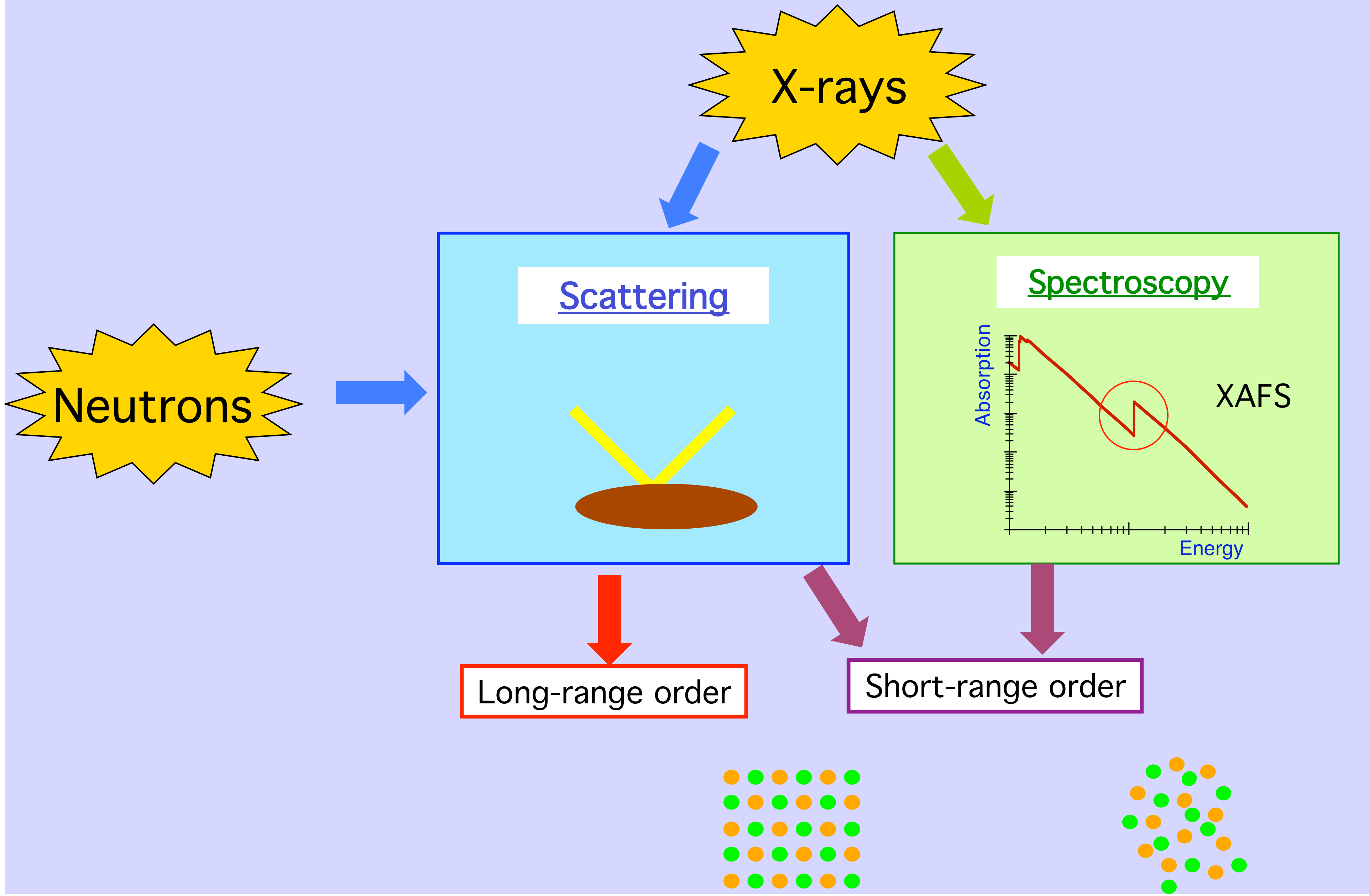

- X-rays absorption – phenomenology
- X-rays absorption - theory
- EXAFS: theoretical background
- EXAFS experiments
- EXAFS: data analysis, examples

X-rays, 1897

X-rays absorption - phenomenology

Attenuation of X-rays

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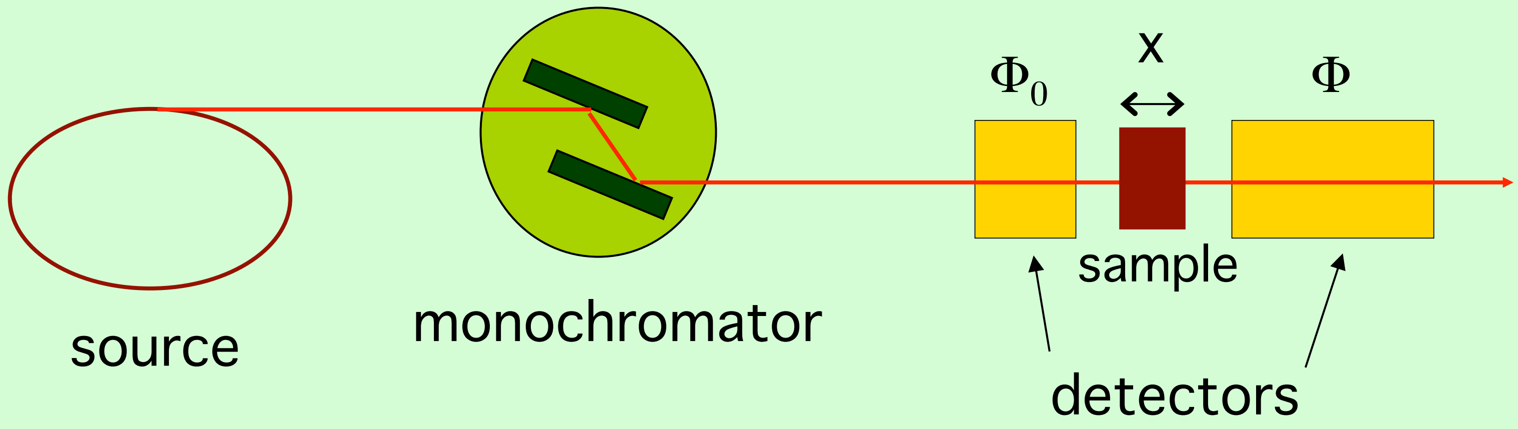

Exponential attenuation $$\Phi = \Phi_0 \exp\left[-\mu(\omega)\, x\right]$$

Attenuation coefficient $$\mu(\omega) = \frac{1}{x} \ln \frac{\Phi_0}{\Phi}$$

Atomic cross sections

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$$\mu(\omega) = \frac{N_a \rho}{A} \mu_a(\omega)$$

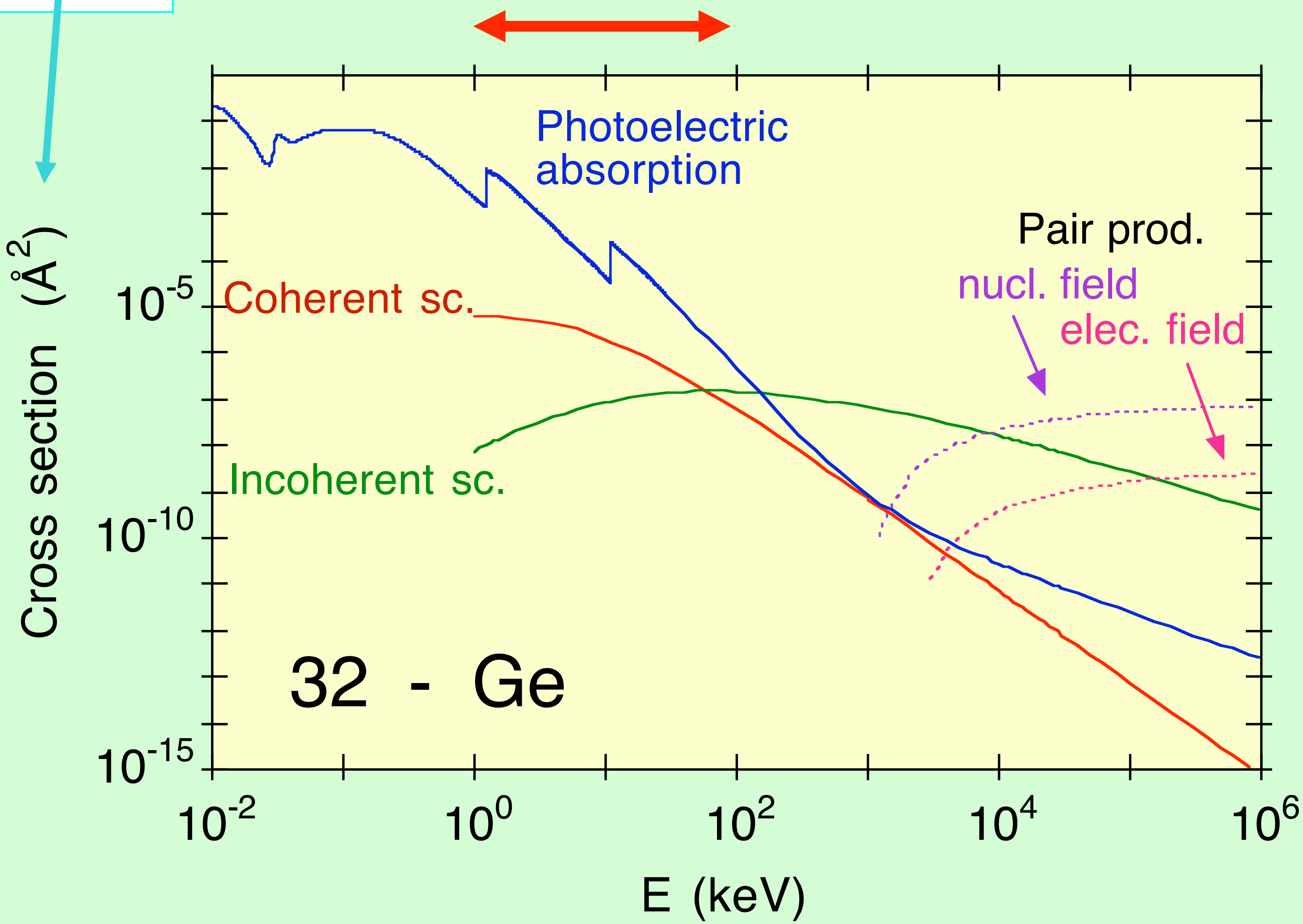

Photo-electric absorption

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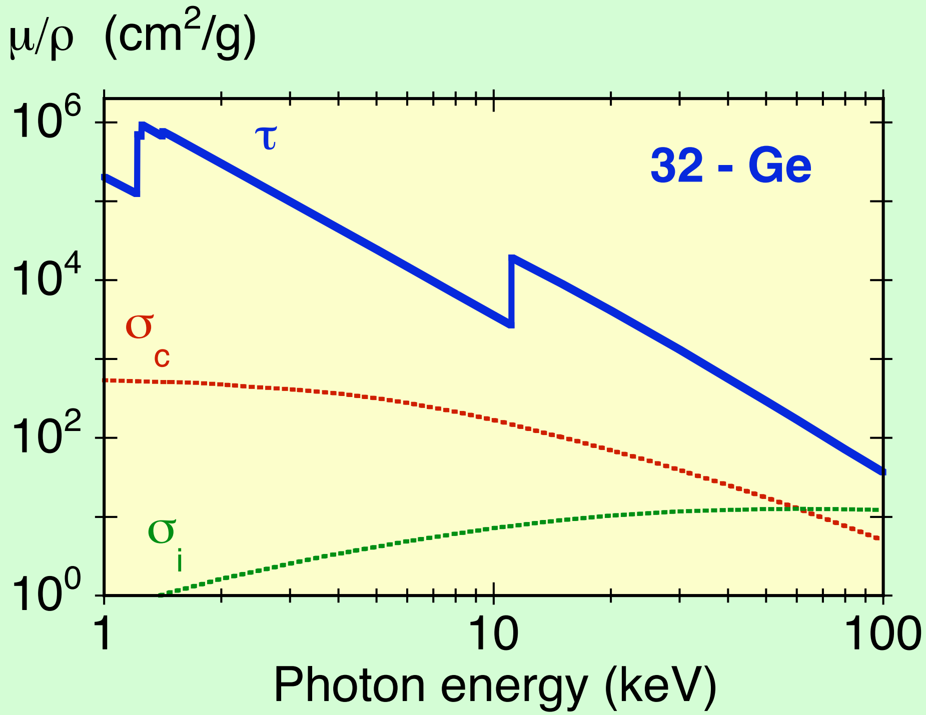
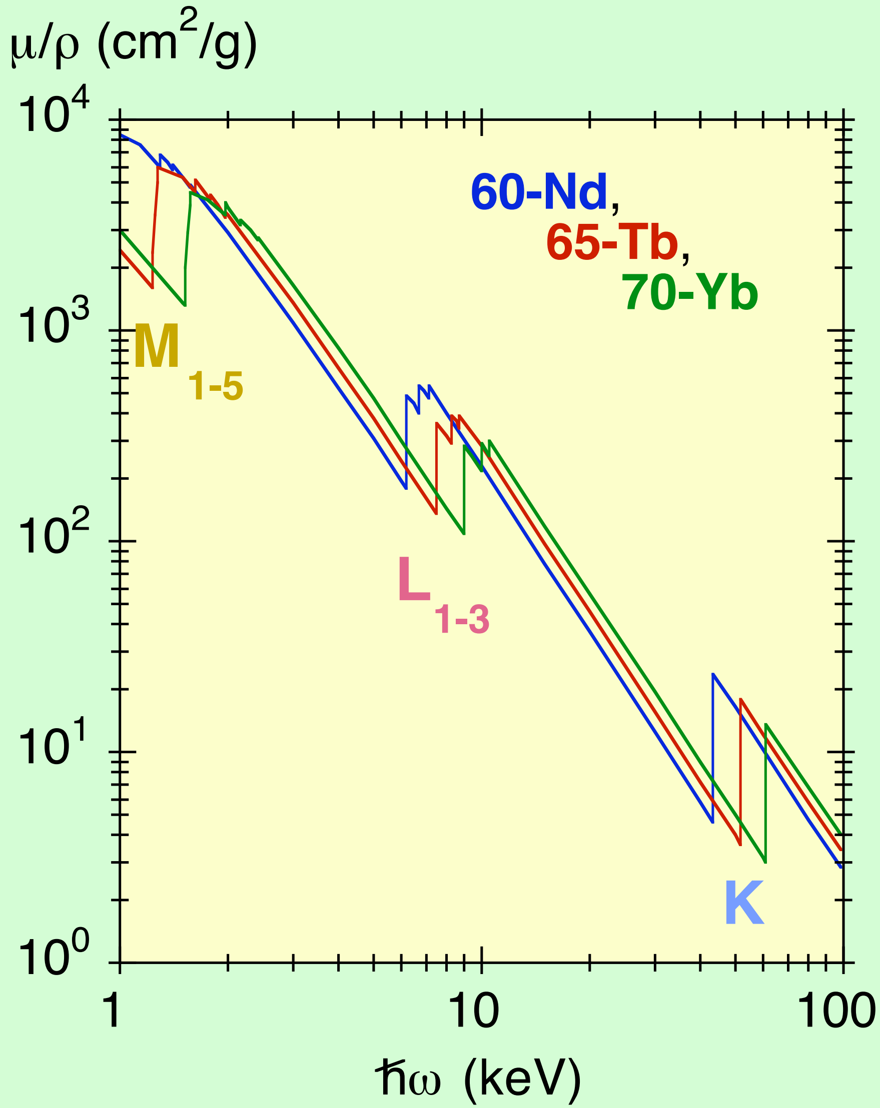


$$\tau(\omega) \propto \frac{Z^4}{(\hbar\omega)^3}$$

+

Edges



Excitation and ionization

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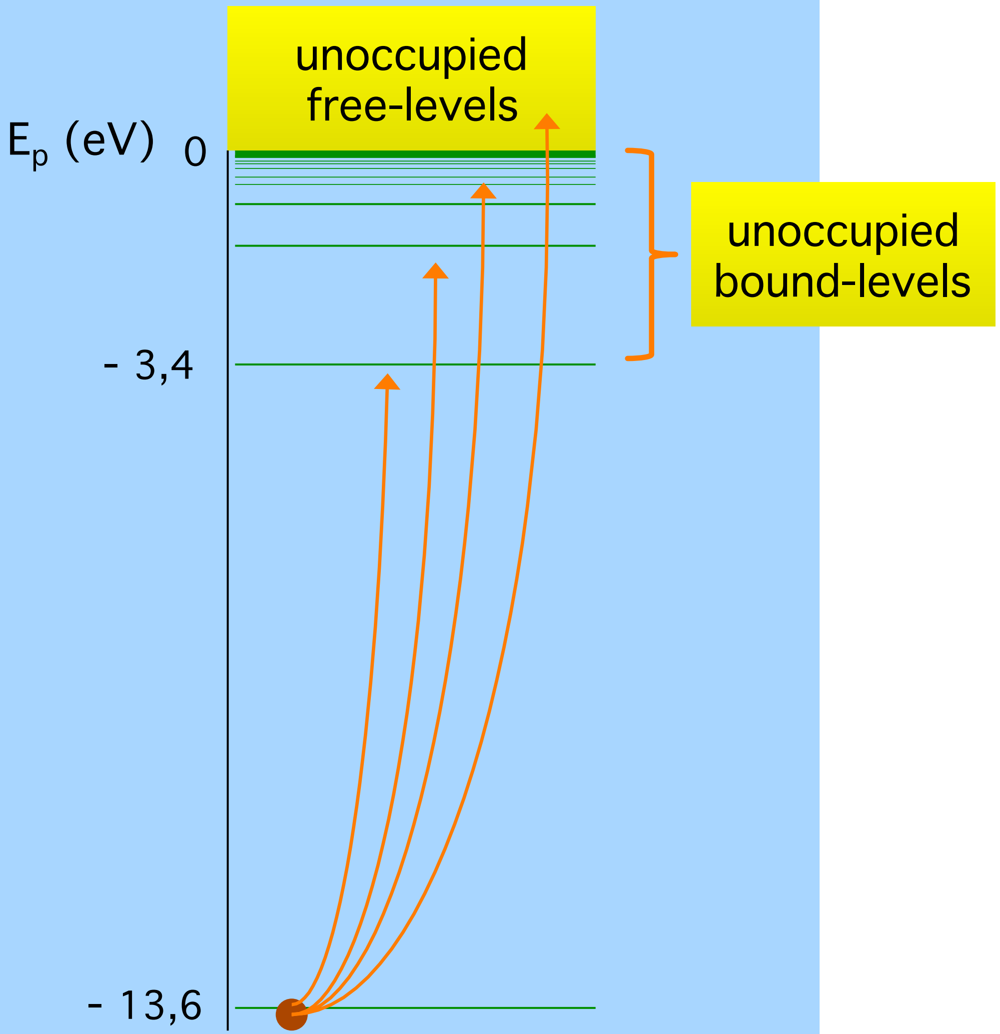
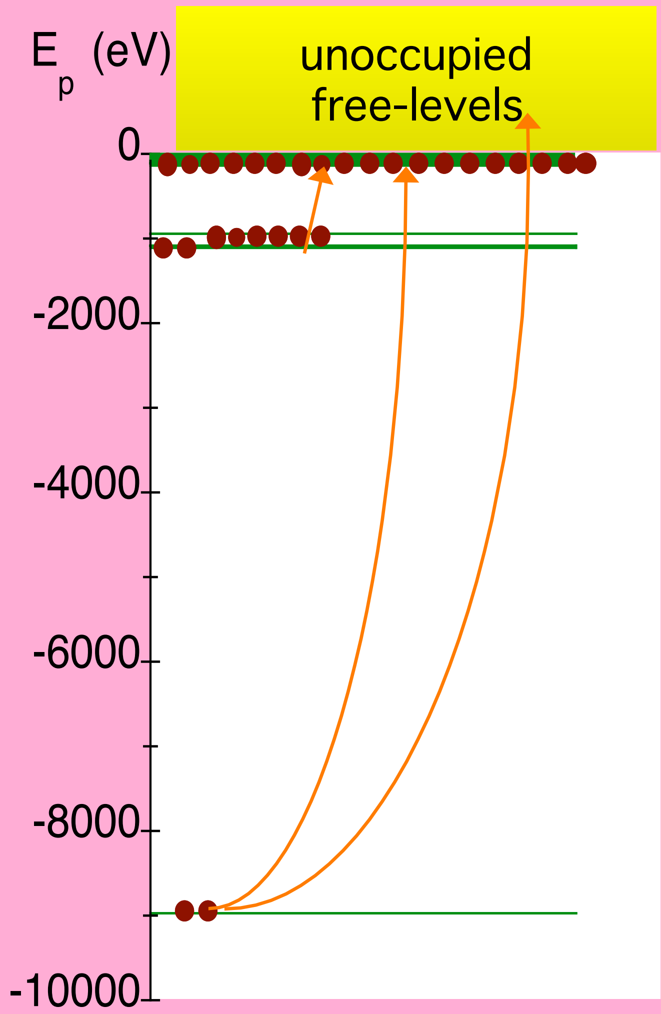
1- Hydrogen



29 - Copper



Absorption edges

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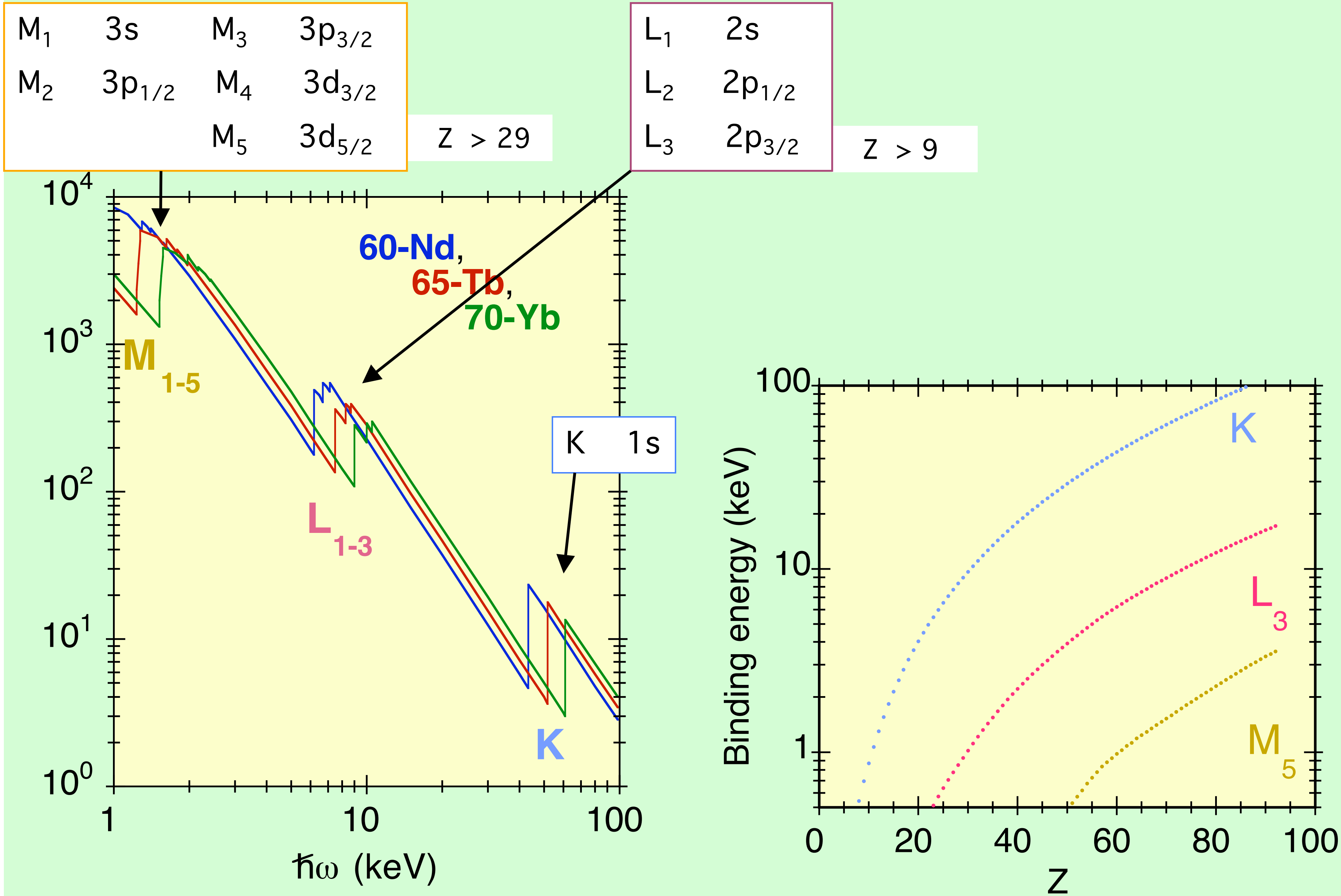

Absorption edge fine structure

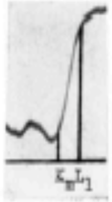

Fig. 1.

Aluminium.

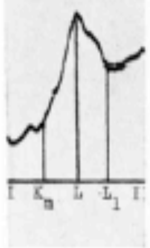

Fig. 2.

Phosphorus.

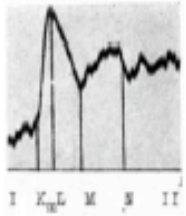

Fig. 3.

Sulphur.

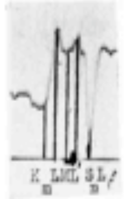

Fig. 4.

Potassium.

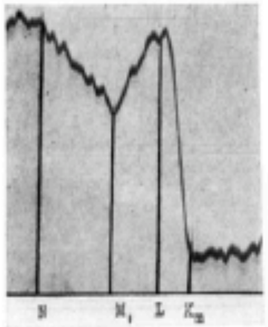

Fig. 5.

Scandium.

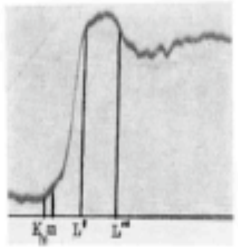

Fig. 6.

Titanium.

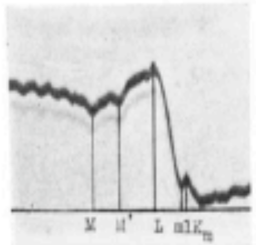

Fig. 7.

Vanadium.

Fig. 8.

Chromium.

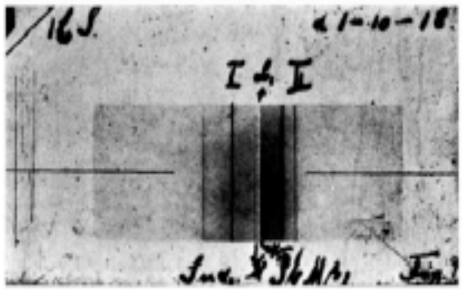

Fig. 9.

Sulphur.

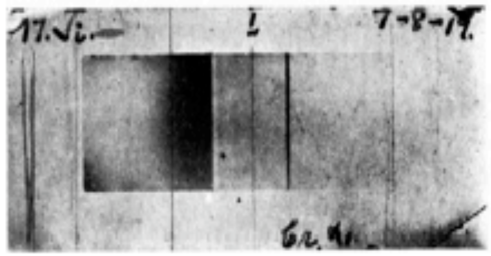

Fig. 10.

Titanium.

Physical Review <u>16</u>, 202 (1920)

Atomic gases: edge fine structure

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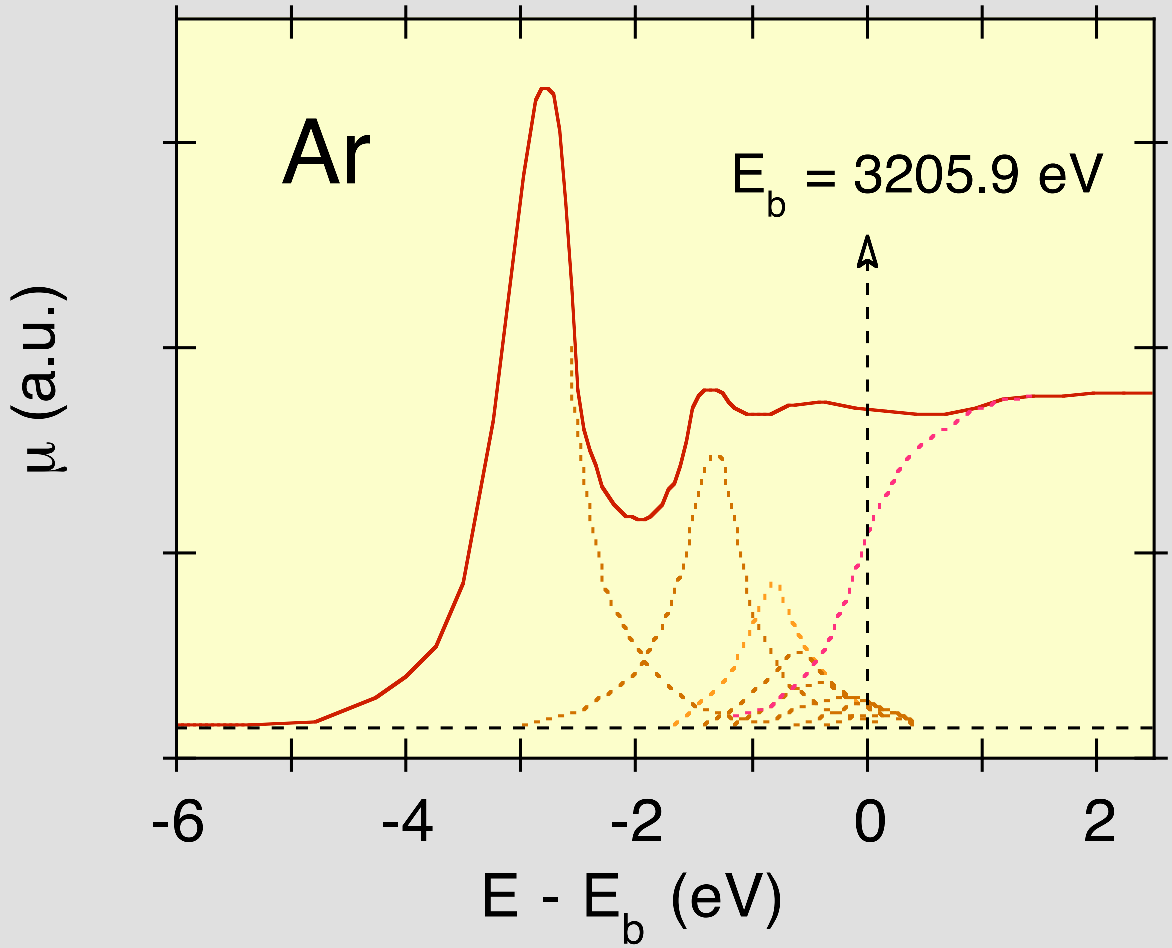
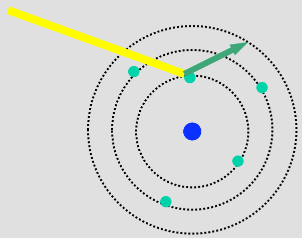


L. G. Parrat,
Phys. Rev. 56, 295 (1939)

Core level → Unoccupied bound levels (Rydberg levels)



Atomic gases: smooth absorption coefficient

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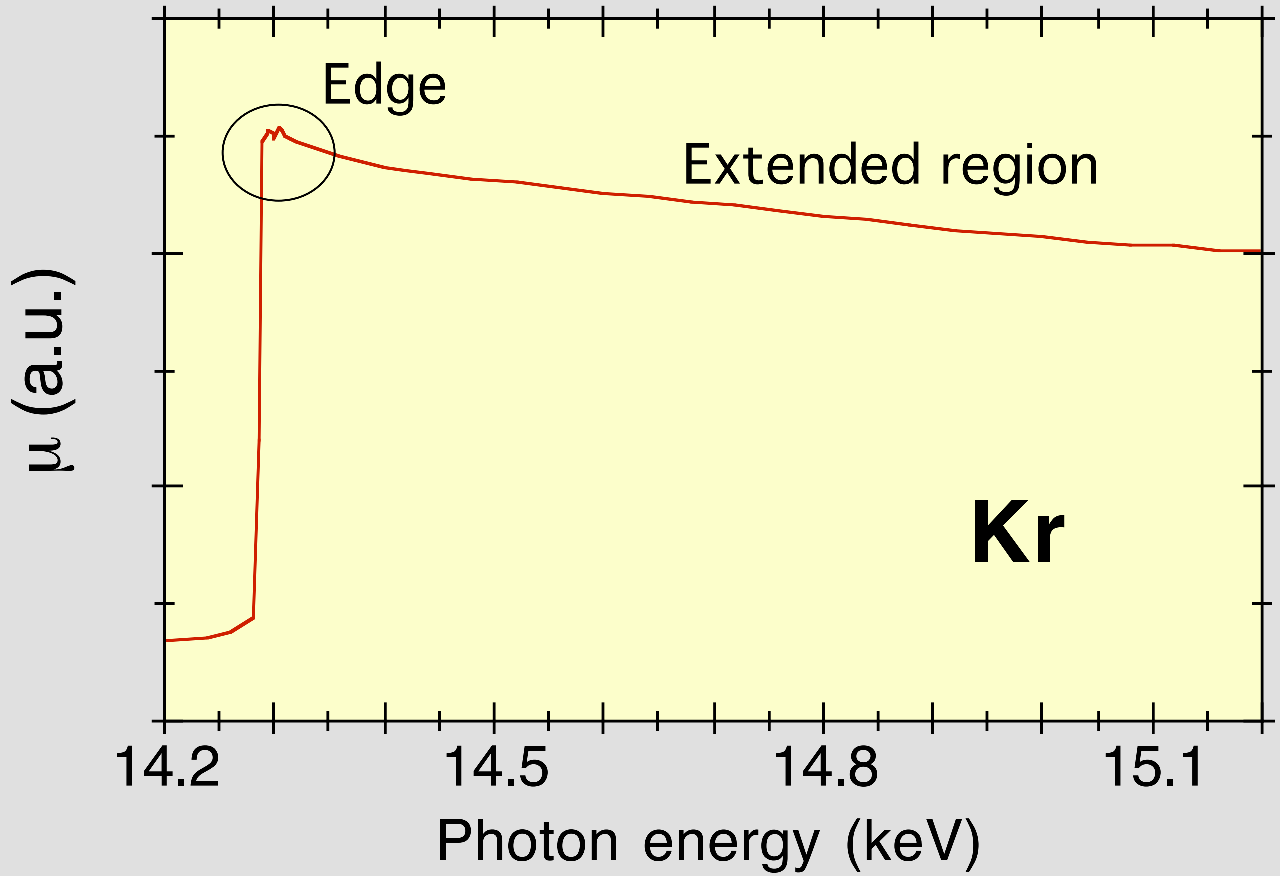
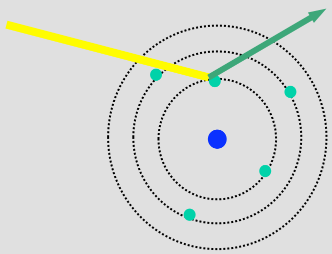


Core level → Unoccupied free levels (continuum)



Molecular gases: Fine structure

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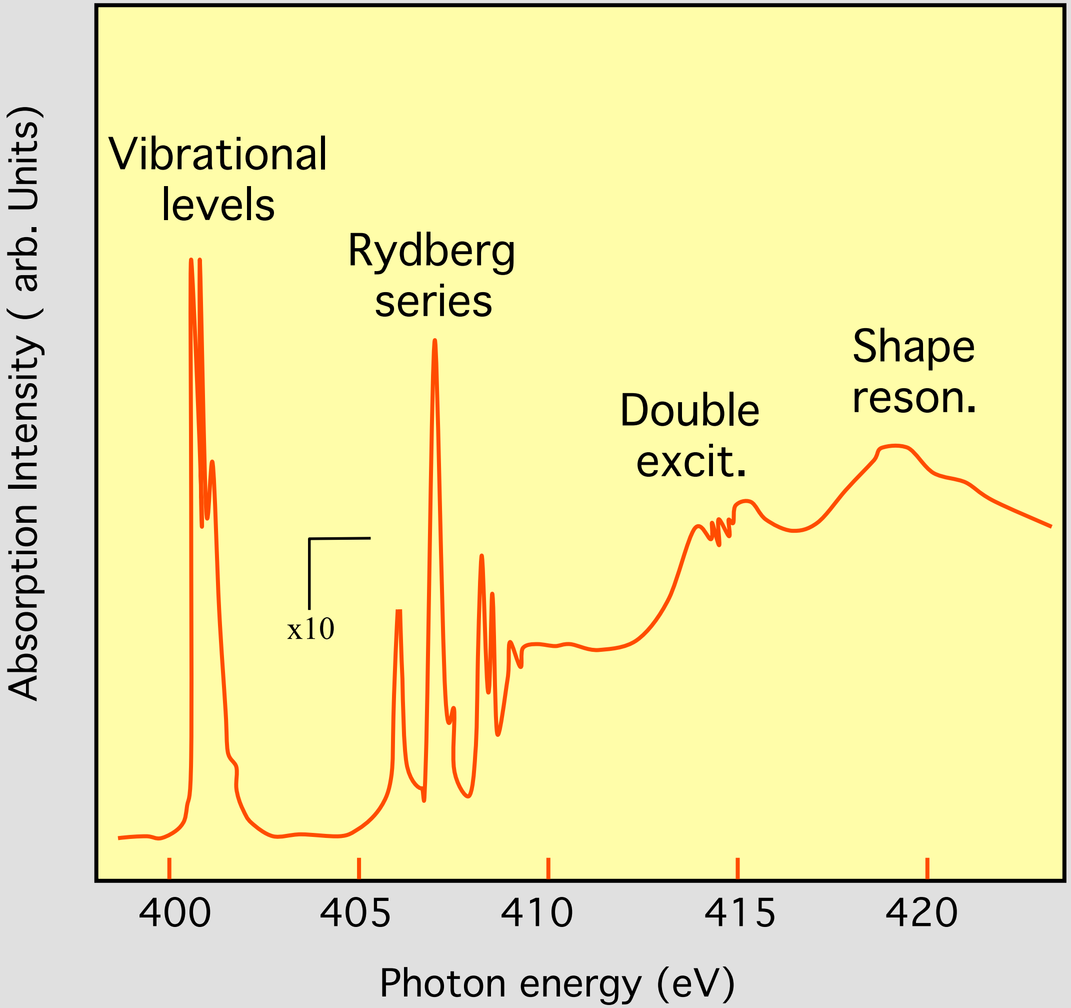
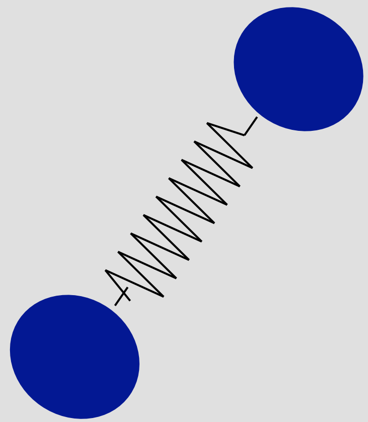


K-shell - gas-phase N_2



C.T. Chen and F. Sette,
Phys. Rev. A 40 (1989)

Core level → Unoccupied bound levels
Unoccupied free levels

Condensed systems: Fine structure

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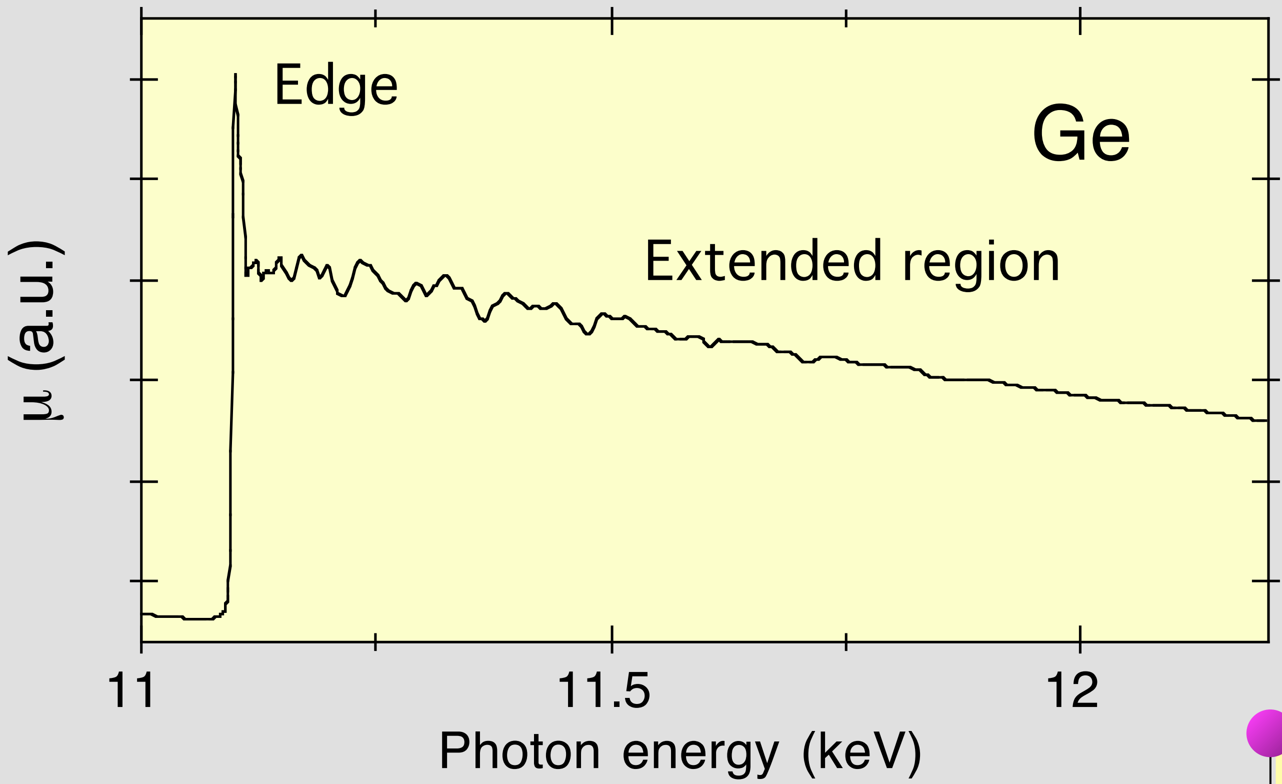

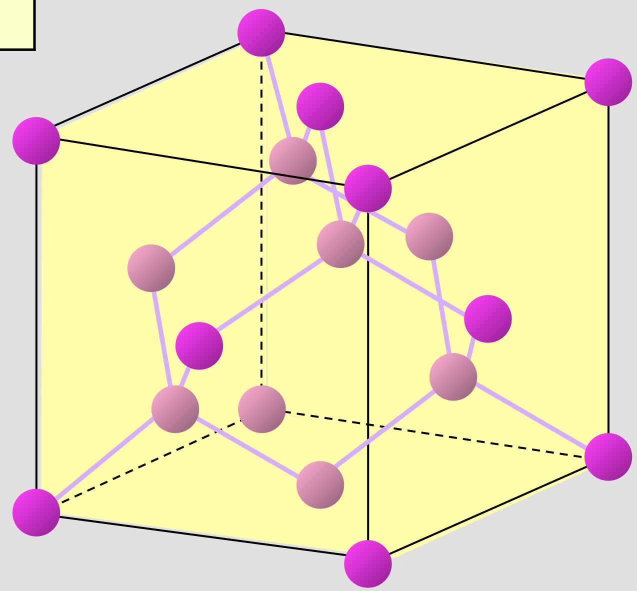

Core level → Unoccupied bound levels
Unoccupied free levels

XAFS: X-ray Absorption Fine Structure

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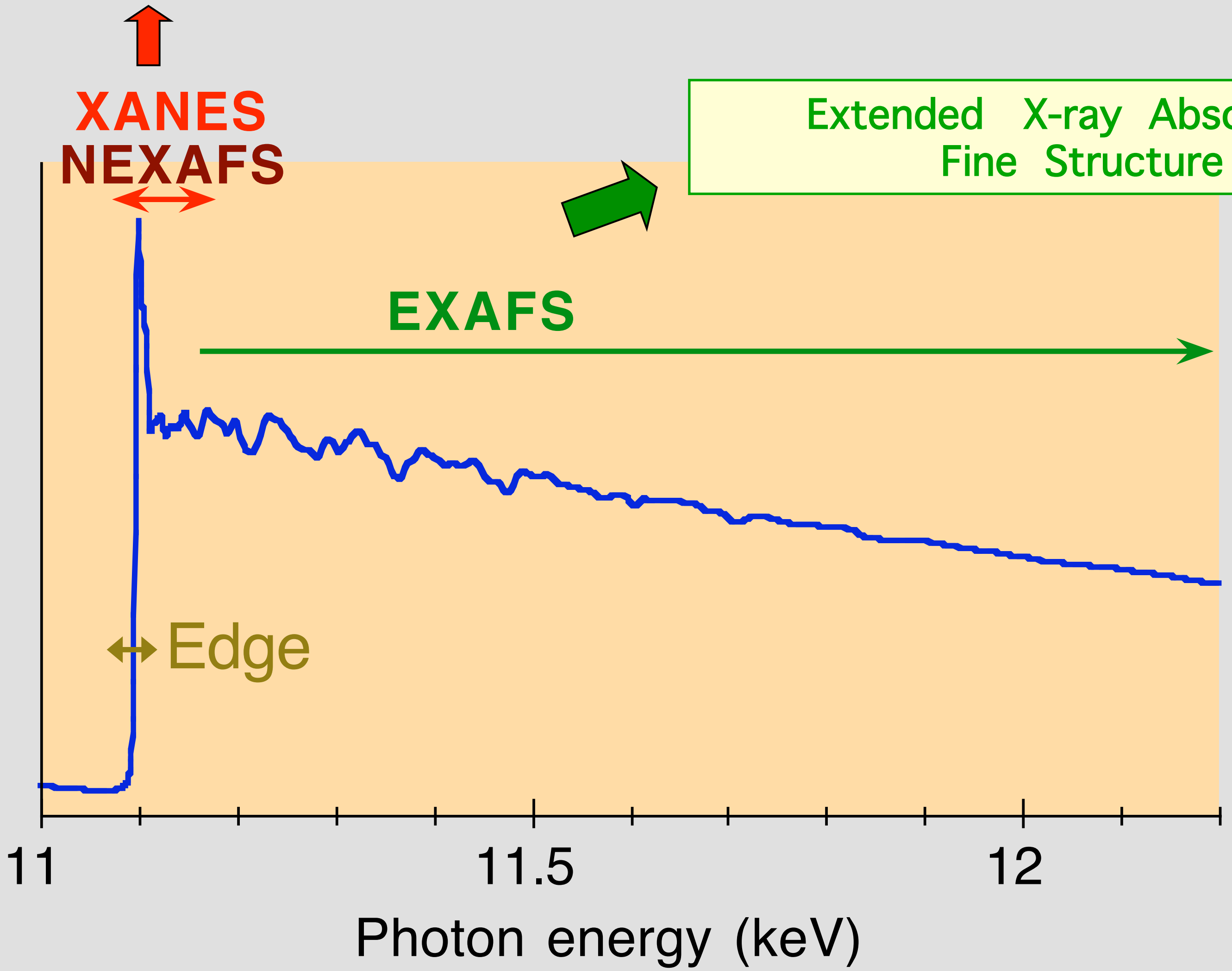
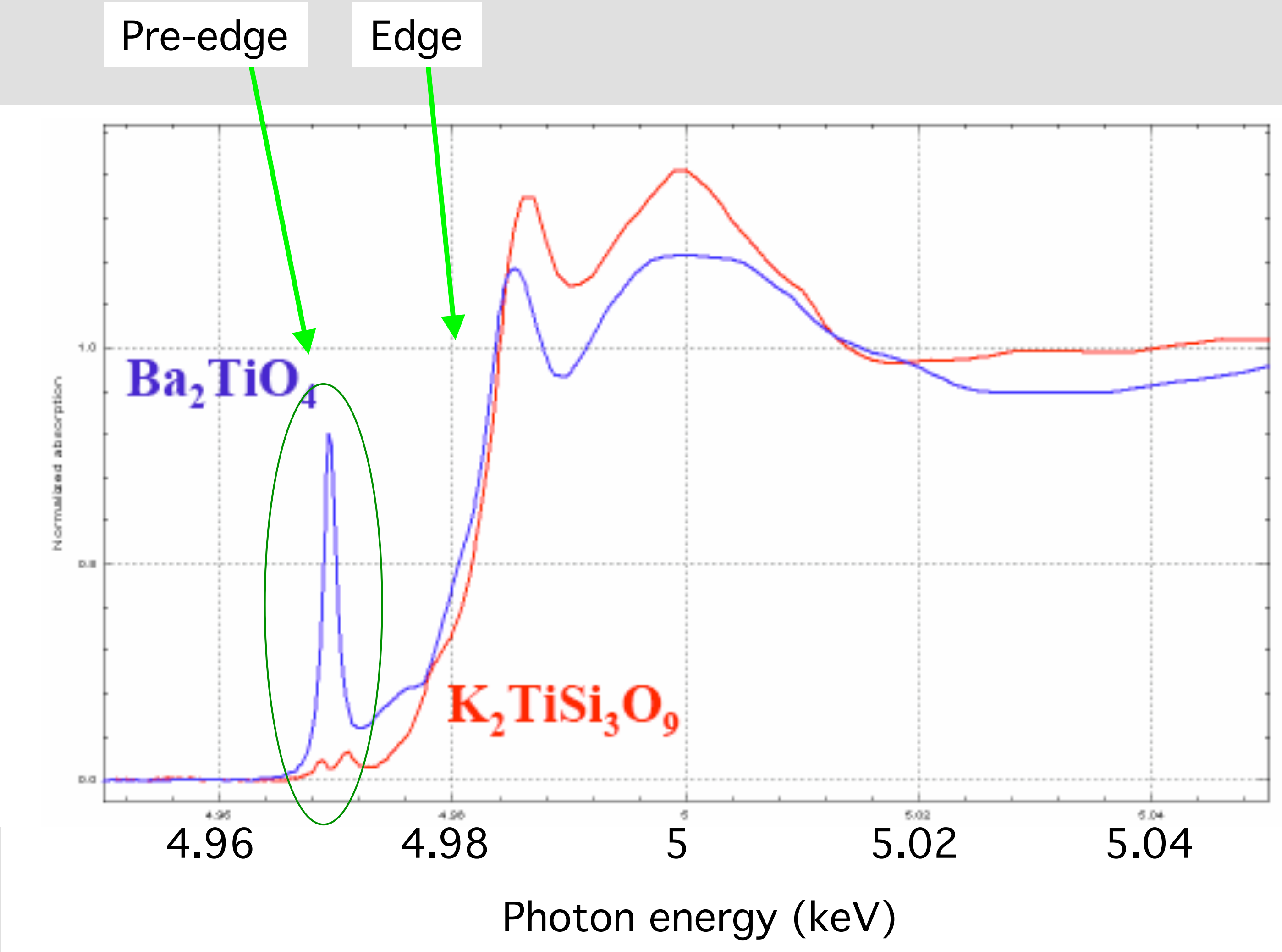
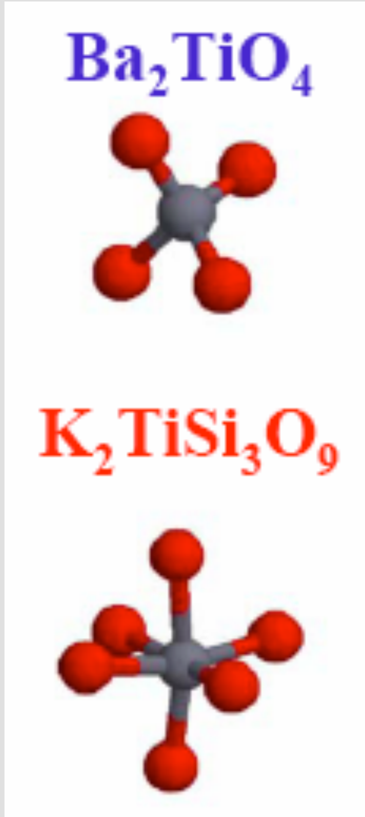
X-ray Absorption Near Edge Structure
Near Edge X-ray Absorption Fine Structure

Extended X-ray Absorption
Fine Structure



XAFS: edge and pre-edge





Lectures on XAFS

EXAFS
- introduction
- basic theory
- experiments
- data analysis

P. Fornasini

XANES
phenomenological
approach

C. Meneghini

XAFS
multiple scattering
approach

M. Benfatto

Applications

XAFS & Materials science
F. Boscherini

SR & Environmental science
P. Lattanzi

SR & Earth science
S. Quartieri

SR & Cultural heritage
S. Quartieri

SR & Chemistry
A. Martorana

X-rays absorption - theory

X-ray attenuation

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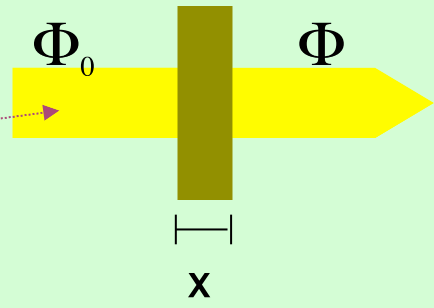
Energy density $u = \frac{\varepsilon_0 E_0^2}{2} = \frac{\varepsilon_0 \omega^2 A_0^2}{2}$



- Linear attenuation coefficient

$$\mu(\omega) = -\frac{1}{u}\frac{du}{dx} = \frac{1}{x}\ln\frac{\Phi_0}{\Phi} = \frac{N_a \rho}{A}\mu_a(\omega)$$

N_a = Avogadro number
A = atomic weight
r = mass density

μ_a = atomic cross section

- Mass attenuation coefficient

Elements:

$$\frac{\mu}{\rho} = \frac{N_a}{A}\mu_a$$

Chemical compounds P_xQ_y...

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

A_i = atomic weights, M = molecular weight

Absorption coefficient

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Absorption coefficient

Atomic density

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

Vector potential amplitude

Transition probability per unit time

i = initial ground state

f = final excited states

$$E_f - E_i = \hbar\omega$$

$P_{if} = ?$

Radiation-matter interaction

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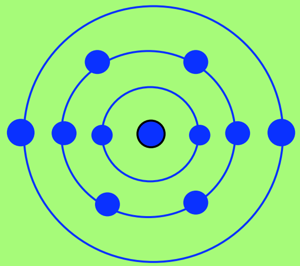
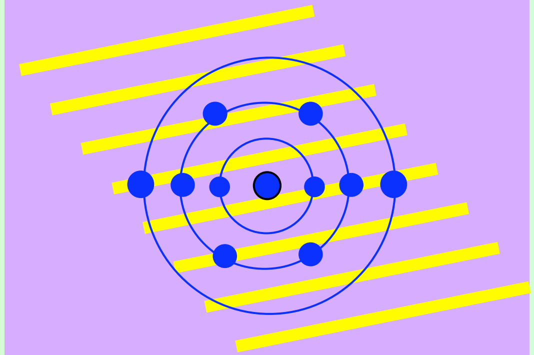
Initial atomic state



$|\Psi_i\rangle$

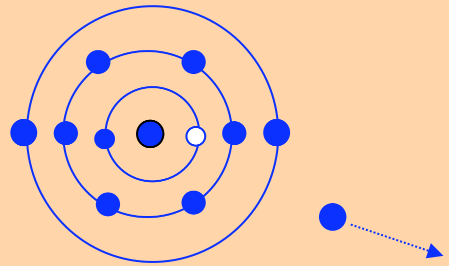
Stationary ground state

Interaction



$|\Psi(t)\rangle$

Final atomic state



$|\Psi_f\rangle$

Stationary excited state

$P_{if} = ?$

Perturbation approach

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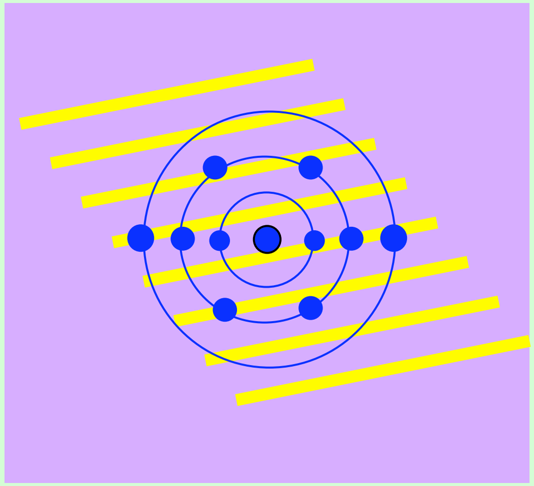
System = atom (quantum treatment)



Weak perturbation = electromagnetic field
(classical treatment)

Hamiltonian for atom in e.m. field

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Radiation gauge

$\vec{\nabla} \cdot \vec{A} = 0$ $\quad \vec{E} = \partial \vec{A} / \partial t$

$\Phi = 0$ $\quad \vec{B} = \vec{\nabla} \times \vec{A}$

$\vec{J} = 0$ $\quad \vec{\nabla} \cdot \vec{A} = \vec{A} \cdot \vec{\nabla}$

Sum over electrons

Vector potential

Electron spin

e-e and e-p interact.

$$H = \sum_j \left\{ \frac{1}{2m} \left[\vec{p}_j - q\vec{A}(\vec{r}_j, t) \right]^2 - \frac{q}{m} \vec{s}_j \cdot \vec{B}(\vec{r}_j, t) \right\} + V(\vec{r}_1 \ldots \vec{r}_N)$$

$$= \sum_j \left[\frac{p_j^2}{2m} + V(\vec{r}_1 \ldots \vec{r}_N) \right] + \sum_j \left[\frac{e}{m} \vec{p}_j \cdot \vec{A}(\vec{r}_j, t) + \frac{e}{m} \vec{s}_j \cdot \vec{B}(\vec{r}_j, t) + \frac{e^2}{2m} A^2(\vec{r}_j, t) \right]$$

H_0 — Unperturbed

H_I — Interaction

$q = -e < 0$

Interaction Hamiltonian

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Sum over electrons

$$H_I = \sum_j \left[\frac{e}{m} \vec{p}_j \cdot \vec{A}(\vec{r}_j, t) + \frac{e}{m} \vec{s}_j \cdot \vec{B}(\vec{r}_j, t) + \frac{e^2}{2m} A^2(\vec{r}_j, t) \right]$$

Relevant terms

Time dependence:

$$\vec{A} = \mathrm{Re}\left[A_0 \, \hat{\eta} \, e^{i(\vec{k}\cdot\vec{r} - \omega t)} \right]$$

sinusoidal perturbation
frequency ω

Time dependent perturbation theory

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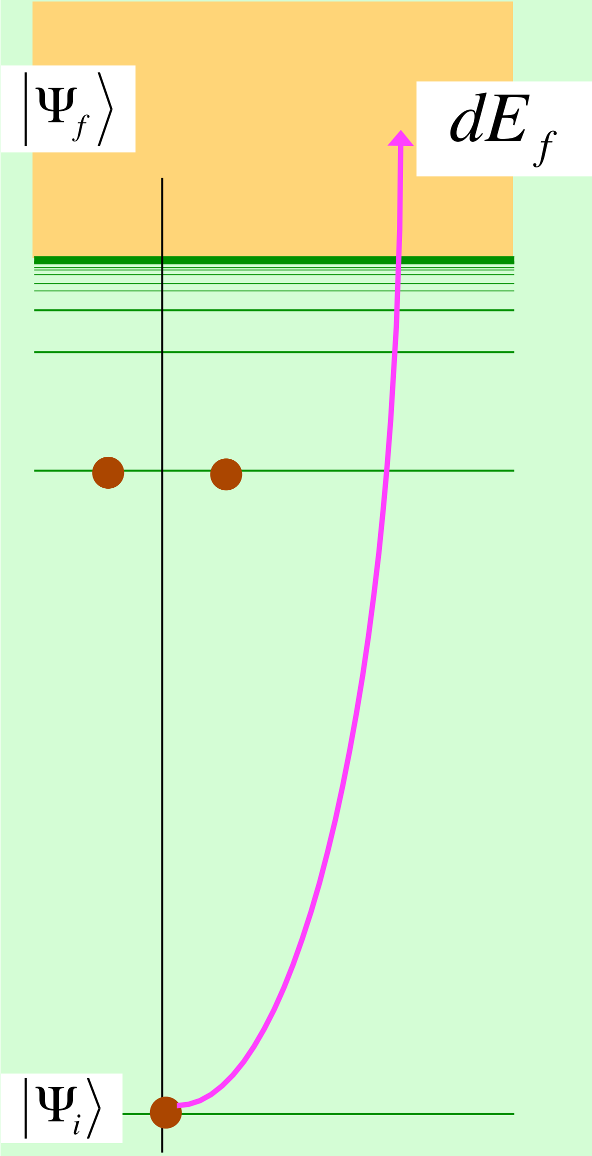

1 st-order perturbation

Transition to continuum states

Probability density

$$\frac{dP_{if}}{dE_f} = \rho(E_f)\ \left|\langle\Psi_f|H_I|\Psi_i\rangle\right|^2\ t\ \ \delta\left(E_f - E_i - \hbar\omega\right)\frac{2\pi}{\hbar}$$

Density of states ↑ — Time ↑ — Energy conservation ↑

"Golden rule"

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Probability density per unit time

$$w_{if} = \frac{dP_{if}}{dE_f\,dt} = \rho(E_f)\ \left|\langle \Psi_f | H_I | \Psi_i \rangle\right|^2\ \delta\left(E_f - E_i - \hbar\omega\right)\frac{2\pi}{\hbar}$$

$$H_I = \sum_j \frac{e}{m}\ \vec{p}_j \cdot \vec{A}\left(r_j, t\right)$$

$$\vec{A} = \mathrm{Re}\left[A_0\,\hat{\eta}\,e^{i\vec{k}\cdot\vec{r}}\right]$$

$$w_{if} = \frac{\pi\hbar e^2}{m^2}\left|A_o\right|^2 \left|\left\langle \Psi_i \left| \sum_j e^{i\vec{k}\cdot\vec{r}_j}\,\hat{\eta}\cdot\vec{\nabla}_j \right| \Psi_f \right\rangle\right|^2 \rho\left(E_f\right)\delta\left(E_f - E_i - \hbar\omega\right)$$

Golden rule

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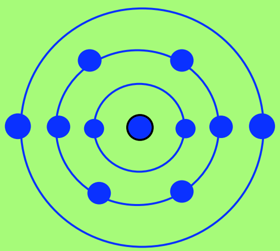
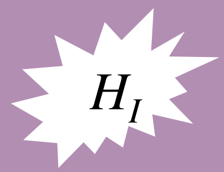
Time-dependent perturbation theory (1st-order)

Initial atomic state



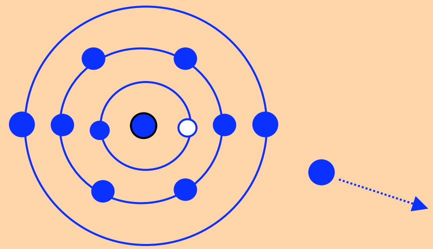
$|\Psi_i\rangle$

Stationary ground state



Interaction with e.m. field

Final atomic state



$|\Psi_f\rangle$

Stationary excited state

$$w_{if} \propto \left|\langle \Psi_i | H_I | \Psi_f \rangle\right|^2 \rho(E_f)$$

matrix element

density of final states

$$E_f - E_i = \hbar\omega$$

One-electron approximation

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

- 1 core electron excited
- N-1 passive electrons relaxed

→ EXAFS coherent signal

- 1 core electron excited
- Other electrons excited

$$\mu_{\text{el}}(\omega) \propto \left| \left\langle \Psi_i^{N-1} \psi_i \right| e^{i\vec{k}\cdot\vec{r}} \hat{\eta}\cdot\vec{p} \left| \psi_f \Psi_f^{N-1} \right\rangle \right|^2 \rho(\varepsilon_f)$$

Electric dipole approximation

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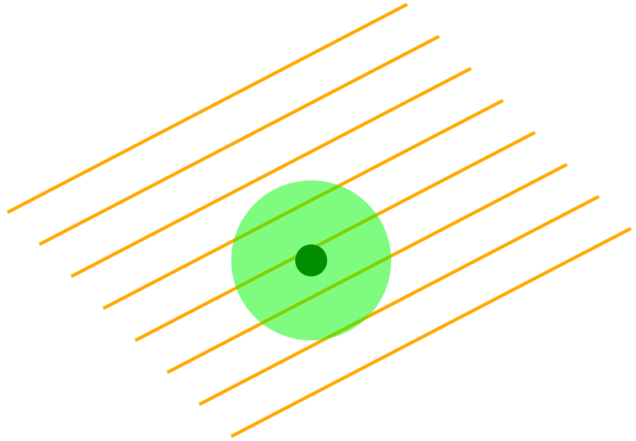

$$e^{i\vec{k}\cdot\vec{r}} = 1 + i\vec{k}\cdot\vec{r} - \ldots \approx 1$$

$$H_I \propto e^{i\vec{k}\cdot\vec{r}}\,\hat{\eta}\cdot\vec{p} \approx \hat{\eta}\cdot\vec{p} = \omega^2\,\hat{\eta}\cdot\vec{r}$$

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

Dipole selection rules:

$\Delta\ell = \pm 1 \qquad \Delta s = 0$

$\Delta j = 0,\pm 1, \qquad \Delta m = 0,\pm 1$

Validity of dipole approximation

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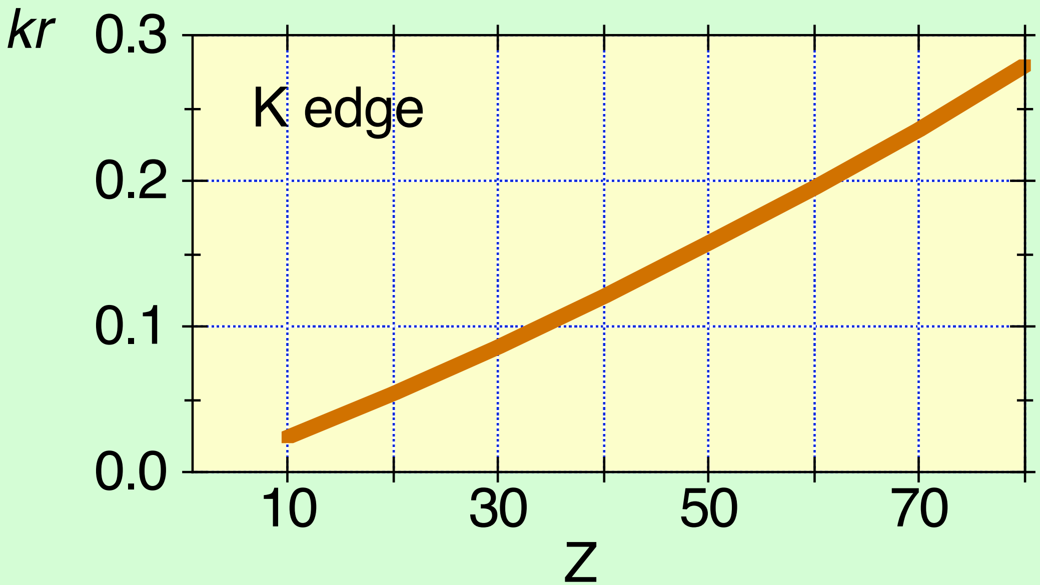
$$e^{i\vec{k}\cdot\vec{r}} = 1 + i\vec{k}\cdot\vec{r} - \ldots \approx 1$$

$$\lambda >> 2\pi r \quad \Leftrightarrow \quad kr << 1$$

1s orbital - K edge

$$r \approx \frac{a_0}{Z} \quad \left(a_0 = 0.53\text{Å}\right)$$

$$\lambda \approx \frac{1}{Z^2}$$



Beyond the electric dipole approximation

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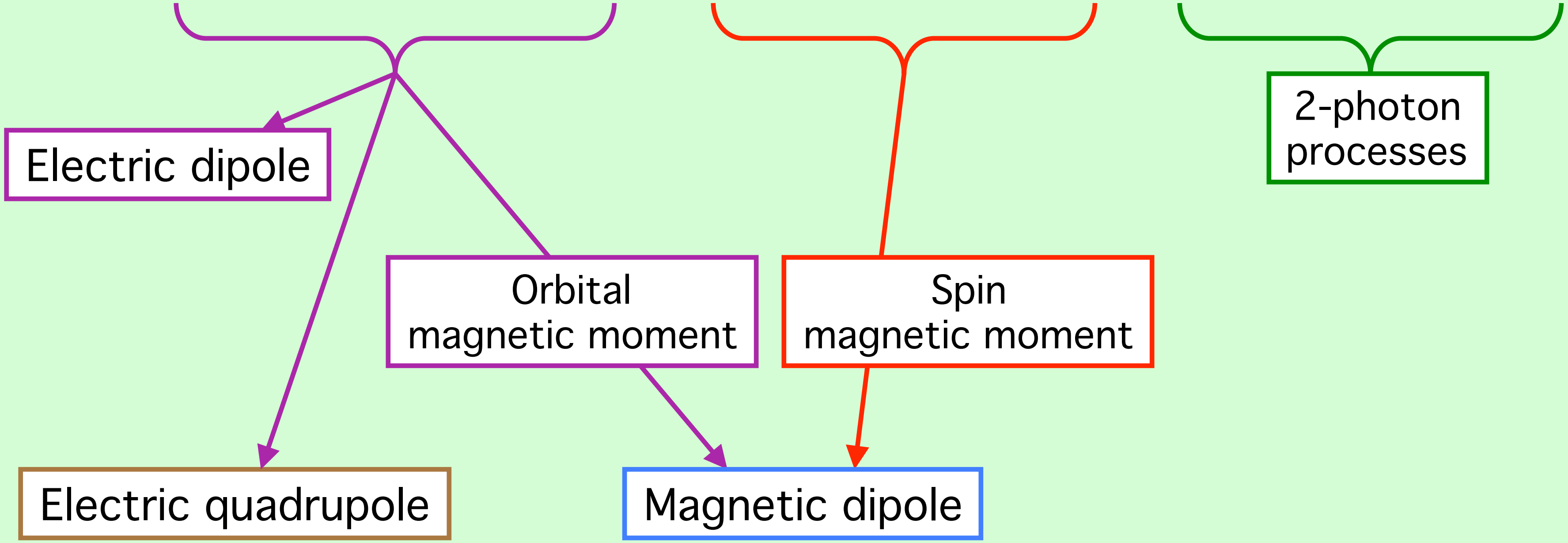
$$e^{i\vec{k}\cdot\vec{r}} = 1 + i\vec{k}\cdot\vec{r} - \dots$$

For one electron:

$$H_I = \frac{e}{m}\,\vec{p}_j \cdot \vec{A}(\vec{r}_j,t) \;+\; \frac{e}{m}\,\vec{s}_j \cdot \vec{B}(\vec{r}_j,t) \;+\; \frac{e^2}{2m} A^2(\vec{r}_j,t)$$



Sudden approximation

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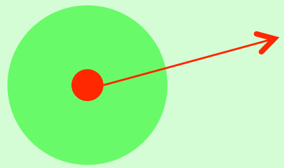
No interaction between photoelectron and passive electrons



$$\left|\Psi^{N-1}\psi\right\rangle = \left|\Psi^{N-1}\right\rangle\left|\psi\right\rangle$$

1 active electron

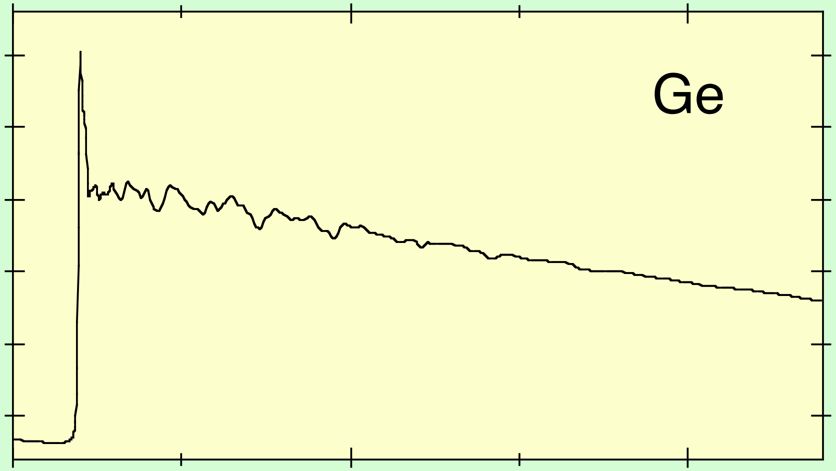
N-1 passive electrons

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

$$S_0^2 \approx 0.6 \div 0.9$$

Structural information

The final state



Fine structure ⟷ $|\psi_f\rangle$ at the core site

$|\psi_f\rangle$

- Molecular orbitals theories
- Band theories
- Multiple scattering approach
- Single scattering approximation ⟷ Basic EXAFS mechanism

EXAFS: the mechanism

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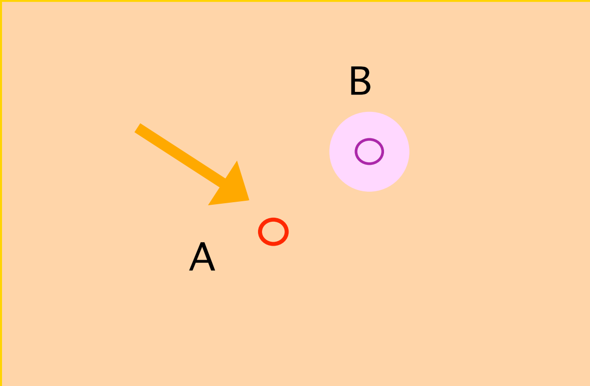


X-ray photon absorption.
Photo-electron emission.

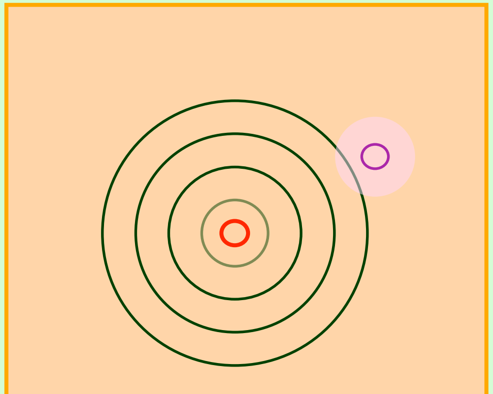


Photo-electron
propagation.

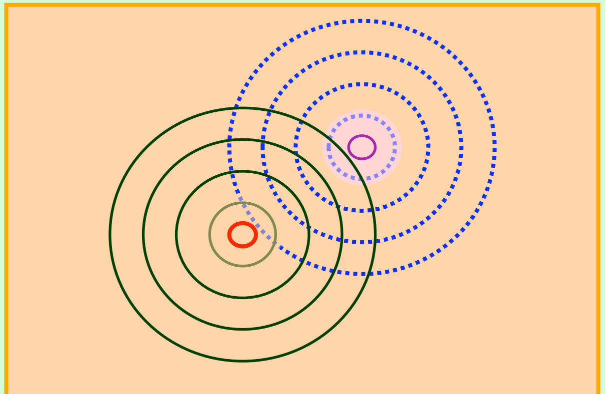
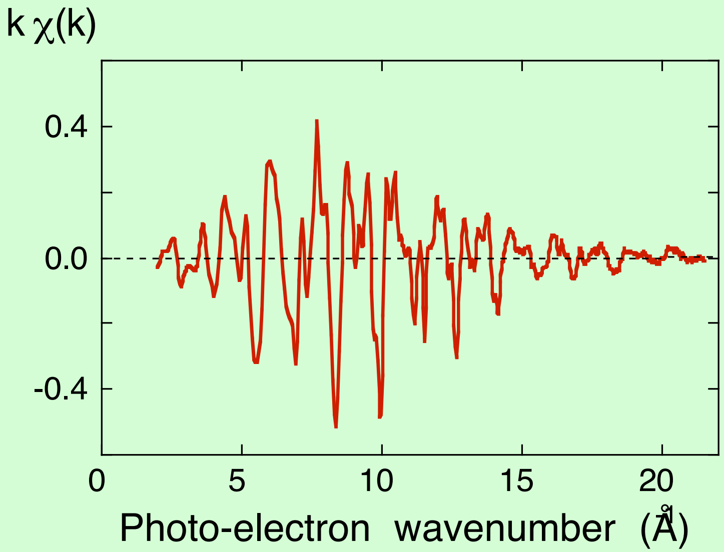


Photo-electron
back-scattering.

Superposition
at the core site.

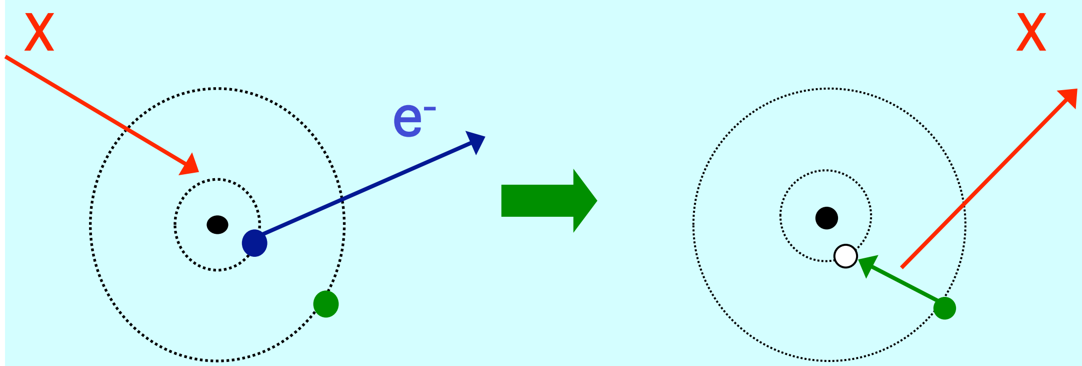
Modulation of
absorption coefficient



De-excitation mechanisms

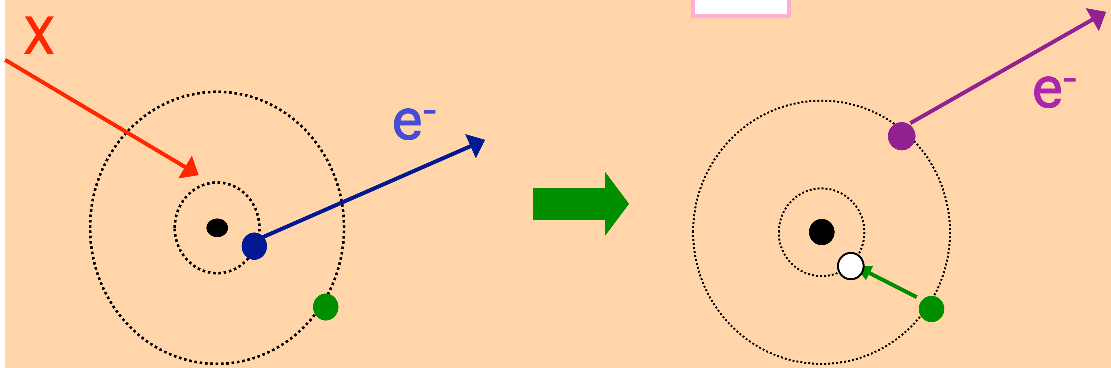
Radiative: fluorescence

X



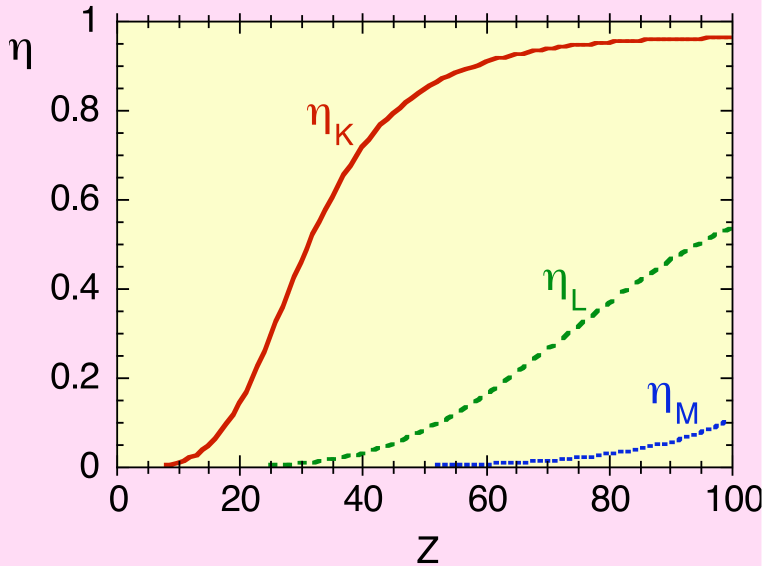
Non-radiative: Auger

A



Fluorescence yield

$$\eta = \frac{X}{X + A}$$



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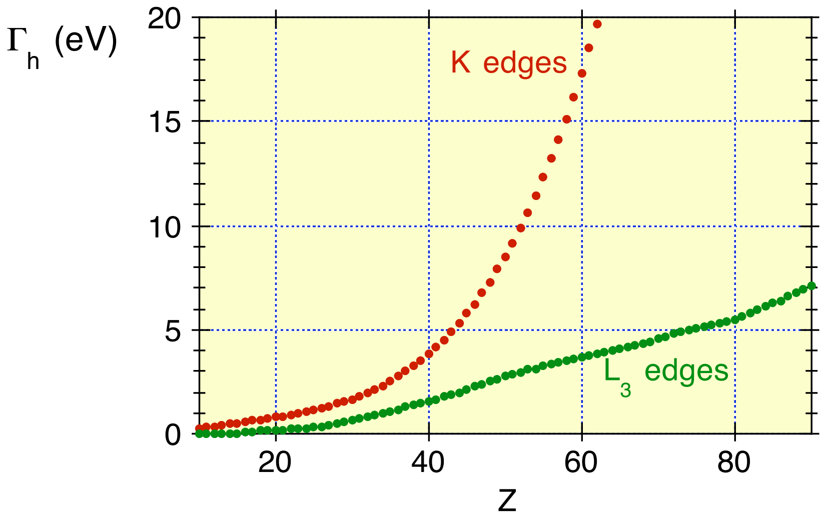
Lifetime of the excited state
$\tau_h \sim 10^{-16} - 10^{-15}$ s

$$\tau_h \approx 1/\Gamma_h$$

Energy width of the excited state
Γ_h



τ_h

Contribution to photo-electron life-time

Γ_h

Energy resolution of XAFS spectra

EXAFS: theoretical background

Photon → photo-electron

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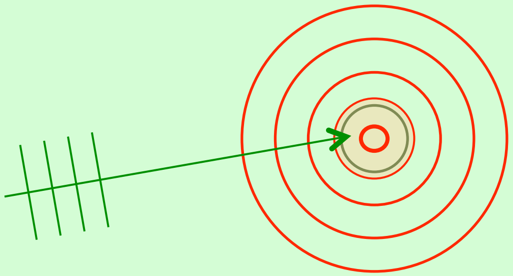

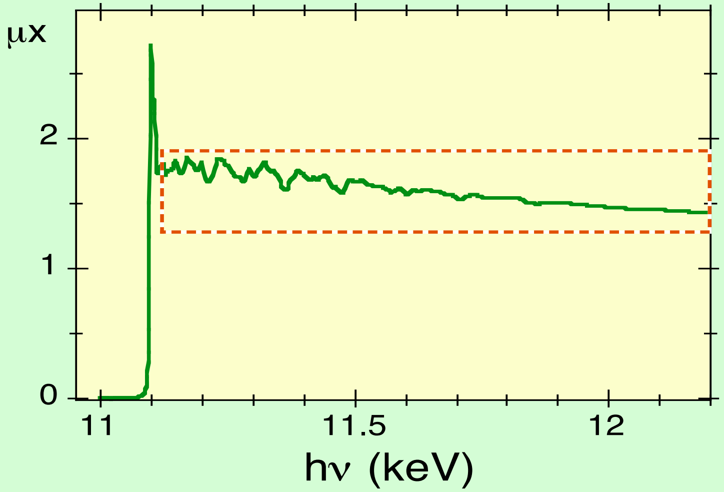

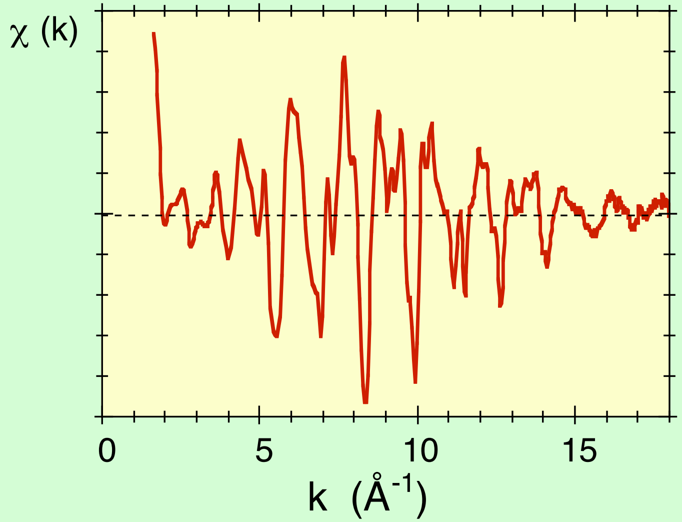

Photon energy

Photo-electron wavenumber

$$\sqrt{\frac{2m}{\hbar^2}\left(h\nu - E_b\right)} = \sqrt{\frac{2m}{\hbar^2}\varepsilon} = k = \frac{2\pi}{\lambda}$$

Angular emission of photo-electron

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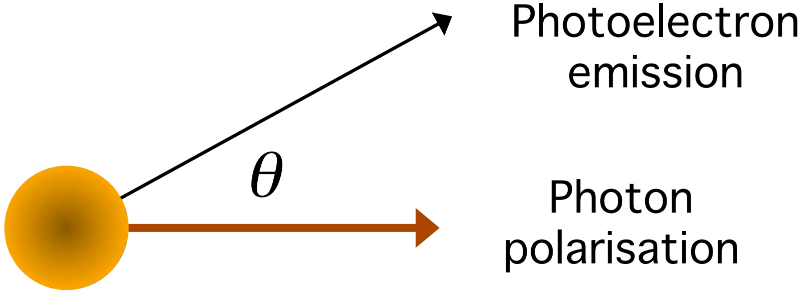
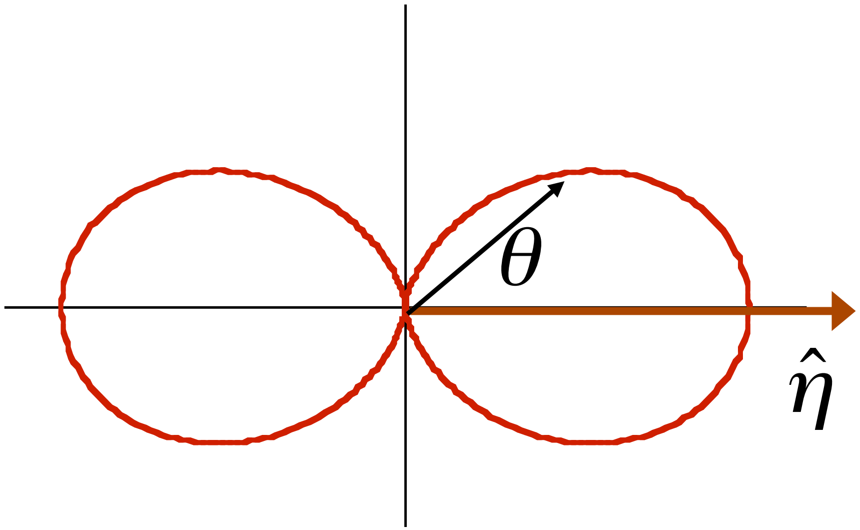


asimmetry parameter

$$N(\theta) \propto 1 + \frac{\beta}{2}\left(3\cos^2\theta - 1\right)$$



$\beta = 2$

Emission from s orbitals

$$N(\theta) \propto 3\cos^2\theta = 3\left|\hat{\eta}\cdot\hat{r}\right|^2$$

Photo-electron parameters

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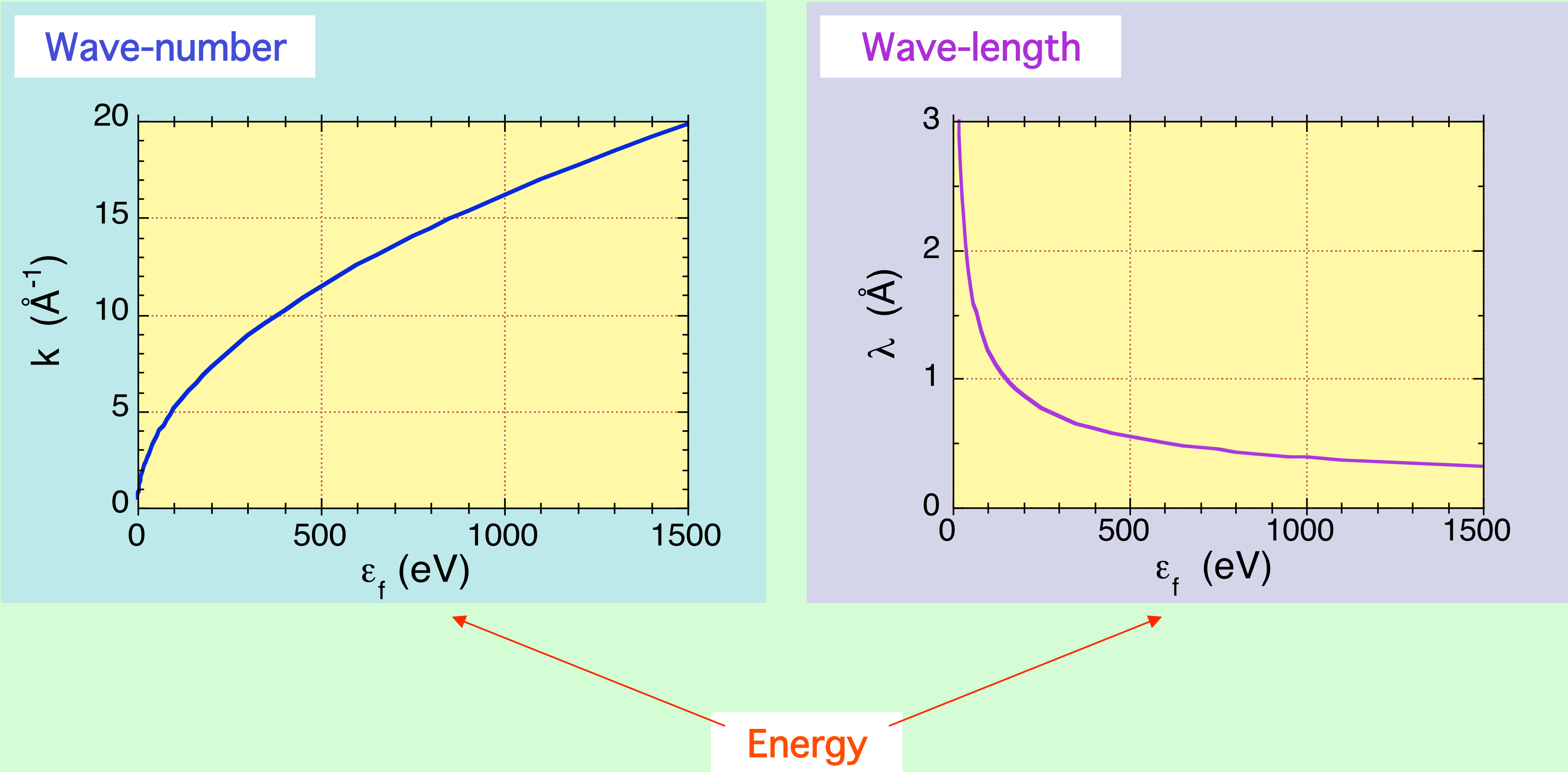

EXAFS normalisation

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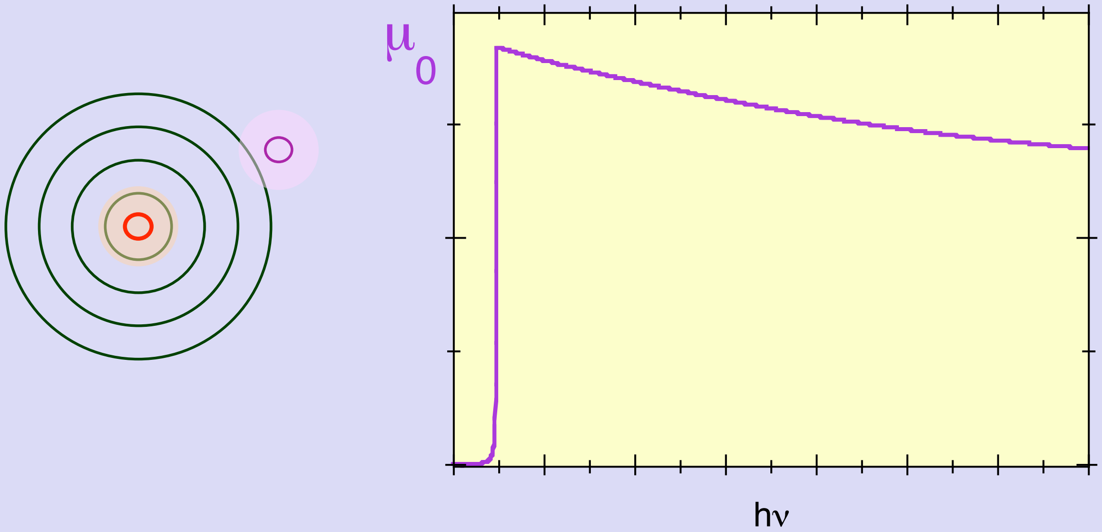
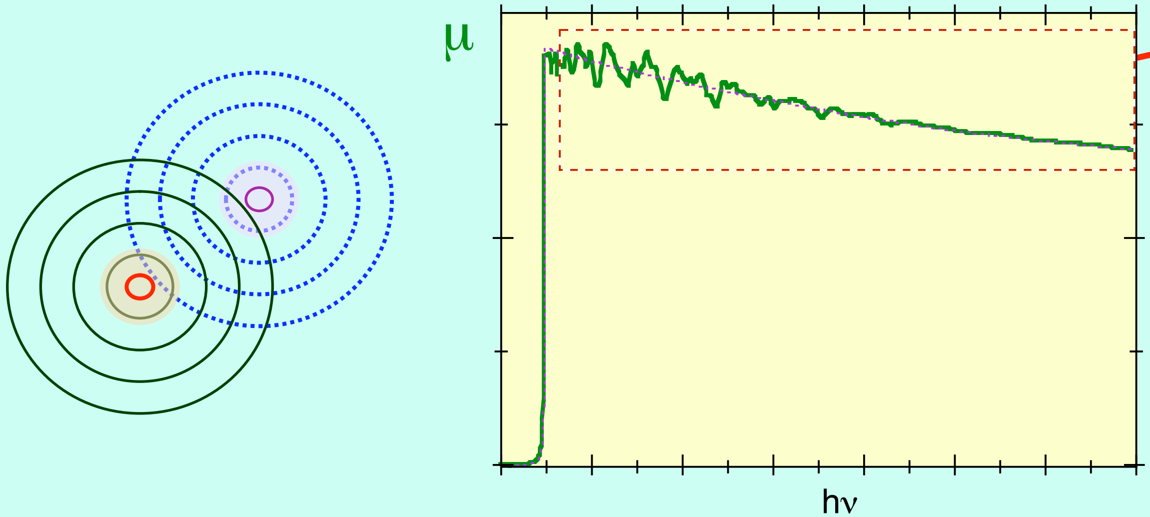


$$\mu_0(\omega) \propto \left| \langle \psi_i | \hat{\eta} \cdot \vec{r} | \psi_f^0 \rangle \right|^2$$

$$\chi(k) = \frac{\mu - \mu_0}{\mu_0}$$



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

The EXAFS function (a)

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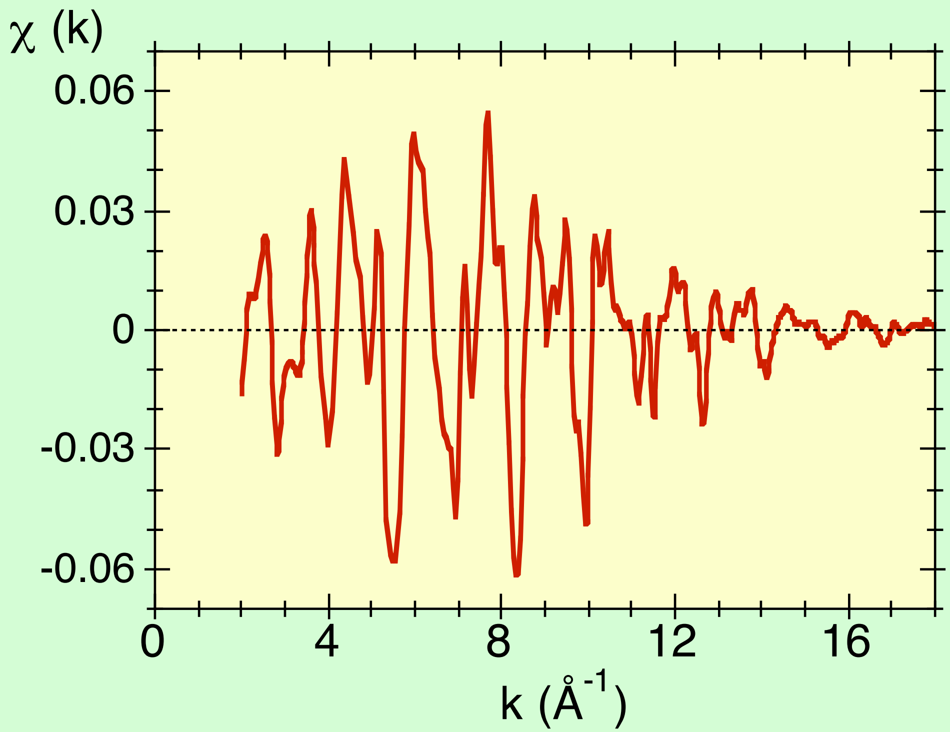

$$\chi(k) = \frac{\mu - \mu_0}{\mu_0}$$

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

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

(weak interaction)

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

?

The EXAFS function (b)

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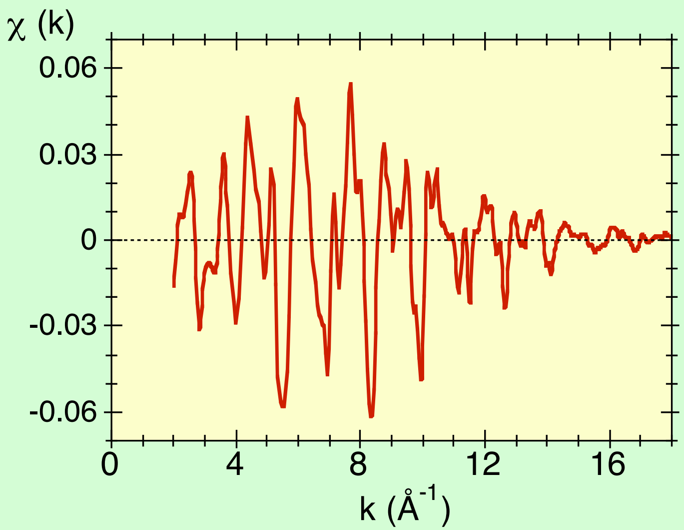
$$\chi(k) = \frac{\mu - \mu_0}{\mu_0}$$



Quantum states → wavefunctions

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

?

Core orbital = source & detector

EXAFS: Two-atomic system (a)

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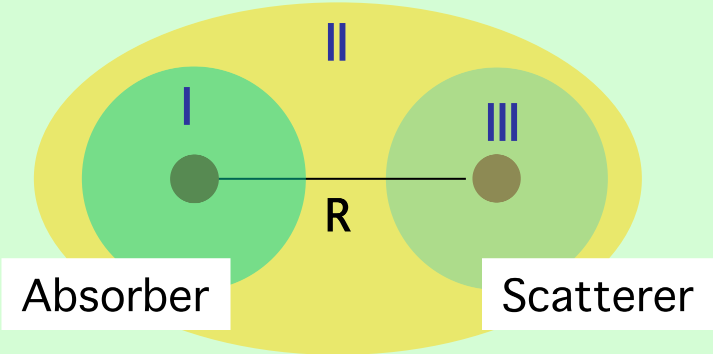

- Scattering theory in plane-wave approximation
- Muffin tin potential

At the absorber core site

Interaction

$$\delta\psi_f \propto \psi_f^0 \, \mathrm{i} \, e^{i\delta} \, \frac{\exp(\mathrm{i}kR)}{2kR} \, f(k,\pi) \, \frac{\exp(\mathrm{i}kR)}{R} \, e^{i\delta}$$

Propagators

EXAFS: Two-atomic system (b)

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$$\delta\psi_f \propto \psi_f^0 \, \mathrm{i}\, e^{i\delta} \frac{\exp(\mathrm{i}kR)}{2kR} \, f(k,\pi) \, \frac{\exp(\mathrm{i}kR)}{R} \, e^{i\delta}$$

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

polarisation

back-scattering amplitude

central atom phase-shift

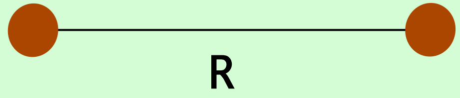
$$\chi(k) = 3 \left|\hat{\eta}\cdot\hat{R}\right|^2 \frac{1}{kR^2} \mathrm{Im}\left[f(k,\pi) \; \exp(2\mathrm{i}\delta_1) \; \exp(2\mathrm{i}kR)\right]$$

spherical wave attenuation

back & forth path

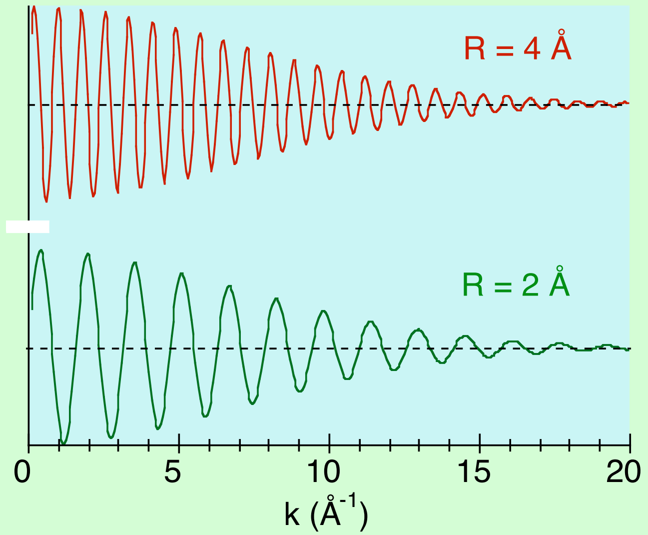
Basic interference effect

$$\chi(k) = 3\,\left|\hat{\eta}\cdot\vec{R}\right|\,\frac{1}{kR^2}\,\mathrm{Im}\left[f(k,\pi)\exp(2i\delta_1)\exp(2ikR)\right]$$



$$f(k,\pi)\,e^{2i\delta} = \left|f(k,\pi)\right|\,e^{i\phi}$$

$$\chi(k) = 3\,\left|\hat{\eta}\cdot\hat{R}\right|^2\,\frac{1}{kR^2}\,\left|f(k,\pi)\right|\,\sin\left[2kR+\phi(k)\right]$$



EXAFS frequency ⟷ Inter-atomic distance

Amplitudes and phase-shifts

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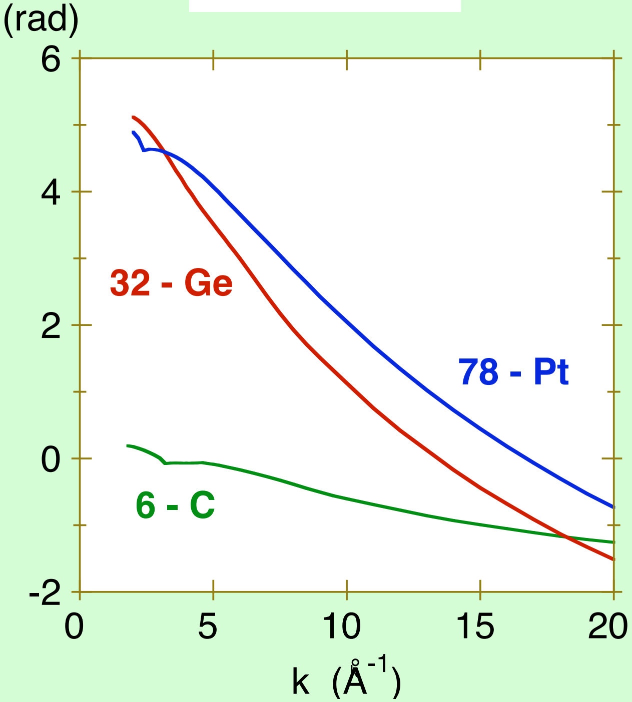
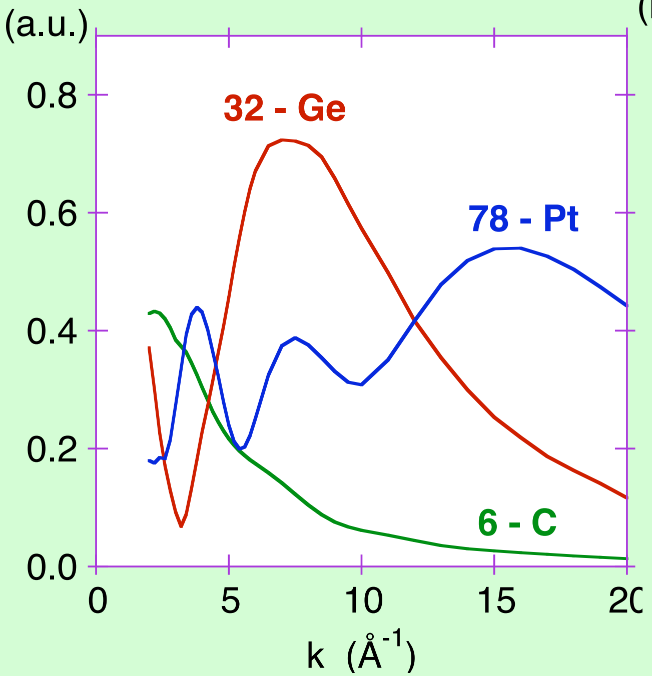
Central-atom

Phase-shift

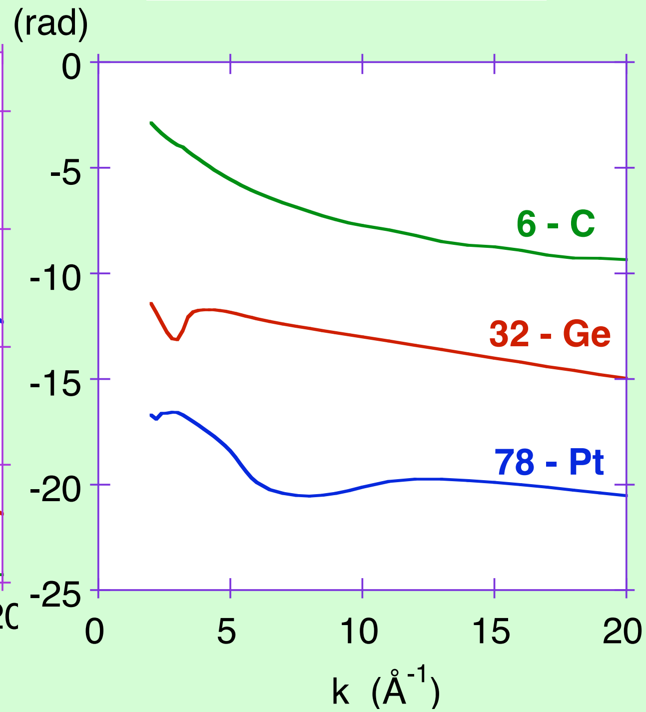


Back-scattering

Amplitude



Phase-shift



Z dependence

[Calculated by FEFF 6.01]

Many-atomic systems

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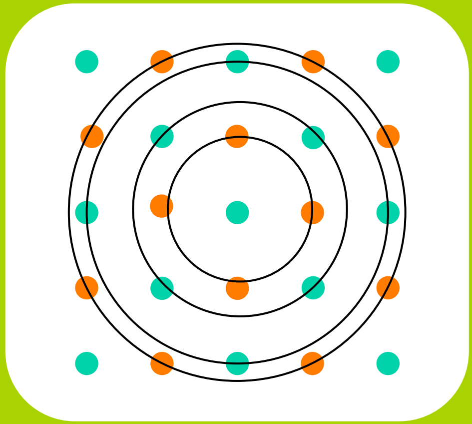
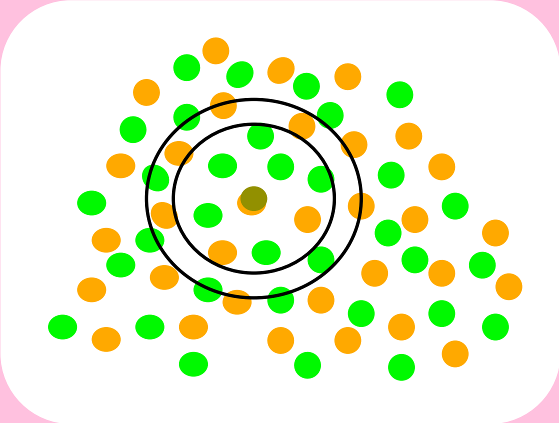
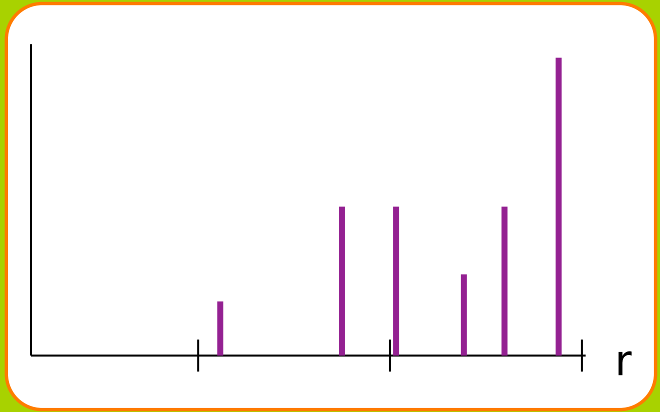
Crystals

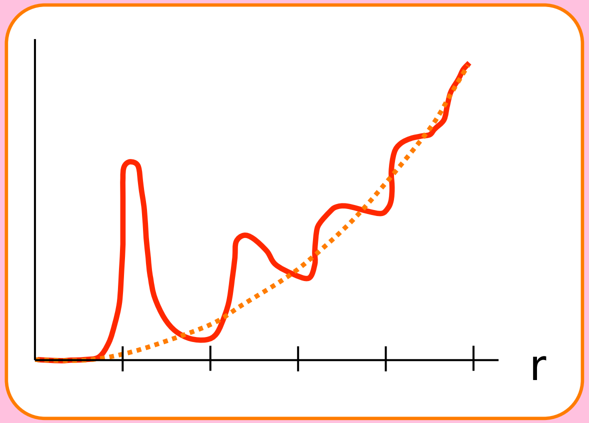
Amorphous systems





Radial Distribution Functions





Coordination shells

Coordination shells

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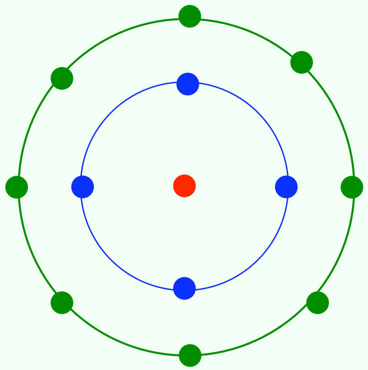
$$\chi(k) = 3\left|\hat{\eta}\cdot\vec{R}\right| \frac{1}{kR^2}\,\mathrm{Im}\left[f(k,\pi)\,e^{2i\delta_1}\,\exp(2ikR)\right]$$

Coordination shells



Isotropic samples: $\left\langle 3\left|\hat{\eta}\cdot\hat{R}\right|^2\right\rangle = 1$

$$\chi(k) = \frac{1}{k}\sum_{shell} N_s\,\mathrm{Im}\left[f_s(k,\pi)\,\mathrm{e}^{2i\delta_1}\,\frac{1}{R_s^2}\exp(2ikR_s)\right]$$

Coordination number

Single and multiple scattering

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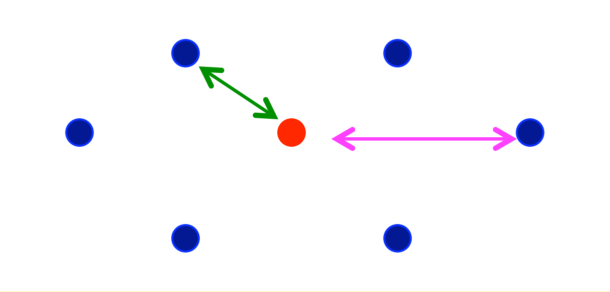
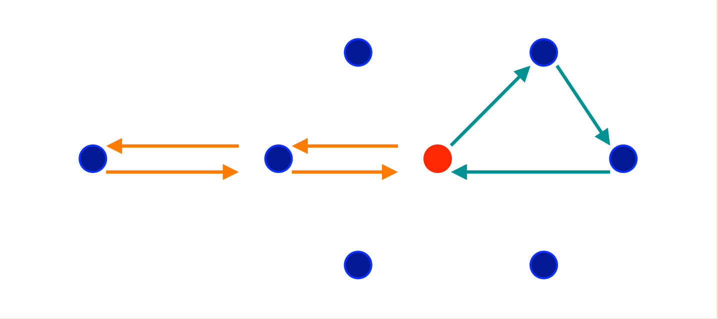
Scattering paths

SS = Single scattering



MS = Multiple scattering



Multiple scattering series

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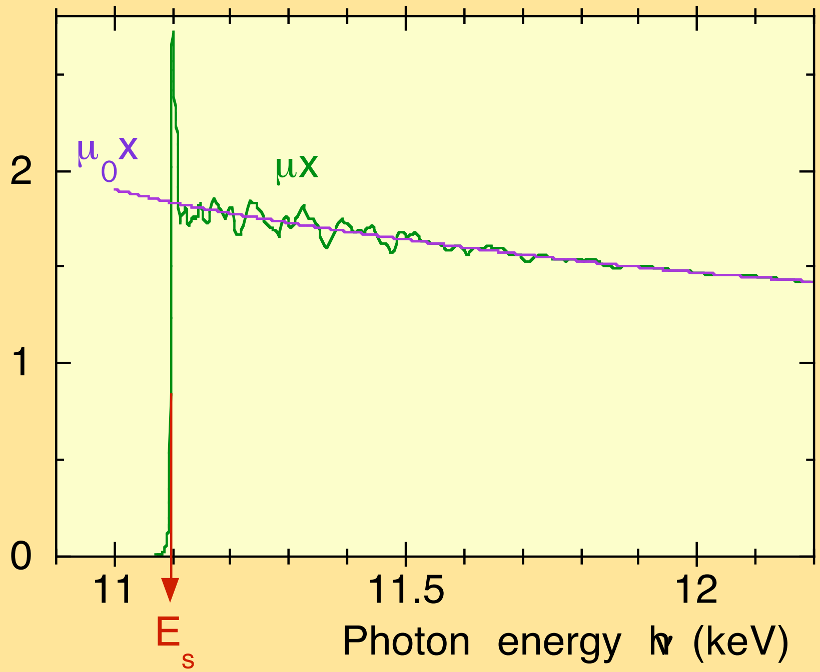
$$\chi(k) = \frac{\mu - \mu_0}{\mu_0}$$

Single Scattering

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

Multiple Scattering

$$\mu(k) = \mu_0(k)\left[1 + \chi_2(k) + \chi_3(k) + \chi_4(k) + \ldots\right]$$



Multiple scattering paths

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$$\chi(k) = \frac{\mu - \mu_0}{\mu_0}$$

Single Scattering

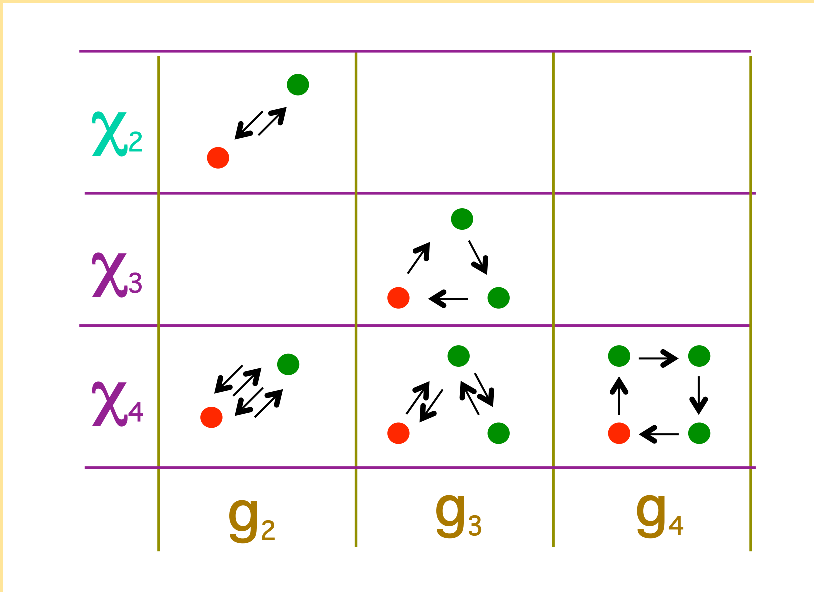
$$\mu(k) = \mu_0(k)\,\left[1 + \chi(k)\right]$$

Multiple Scattering

$$\mu(k) = \mu_0(k)\,\left[1 + \chi_2(k) + \chi_3(k) + \chi_4(k) + \ldots\right]$$

$\chi_n(k)$

Contribution from all n-order paths



g_n = n-body correlation function

Multiple scattering contributions

$$\mu(k) = \mu_0(k)\left[1 + \chi_2(k) + \chi_3(k) + \ldots \chi_n(k) + \ldots\right]$$

Set of coordinates

Photo-electron path

$$\chi_n(k) = A\left(k, \{\vec{r}\}\right) \sin\left[kR_p + \phi\left(k, \{\vec{r}\}\right)\right]$$

Functions of potential

Neglecting thermal disorder !

Intrinsic losses

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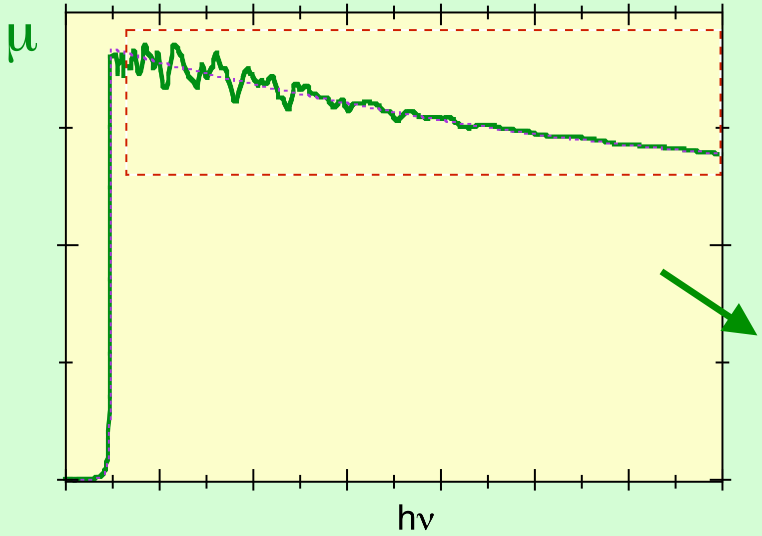

$$\mu_{\text{tot}}(\omega) = \mu_{\text{el}}(\omega) + \mu_{\text{inel}}(\omega)$$

From experiment

One-electron theory

$$\chi_{\text{exp}}(k) = \frac{\mu - \mu_0}{\mu_0} < \chi_{\text{th}}(k)$$

$$\chi_{\text{exp}}(k) = S_0^2 \, \chi_{\text{th}}(k)$$

Attenuation factor

$$S_0^2 = \left| \left\langle \Psi_i^{N-1} \middle| \Psi_f^{N-1} \right\rangle \right|^2 \approx 0.6 \div 0.9$$

Photo-electron mean-free-path

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Core-hole lifetime $\tau_h \rightarrow \lambda_h$

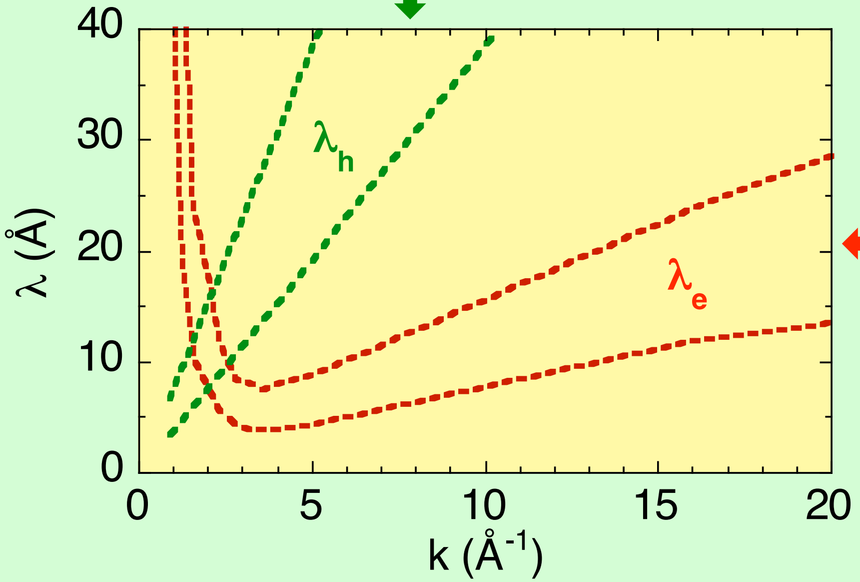

Photo-electron lifetime

$\tau_e \Leftrightarrow \lambda_e$

$$\frac{1}{\lambda} = \frac{1}{\lambda_h} + \frac{1}{\lambda_e}$$

Attenuation factor $\exp\left[-\frac{2R}{\lambda(k)}\right]$

EXAFS and inelastic effects

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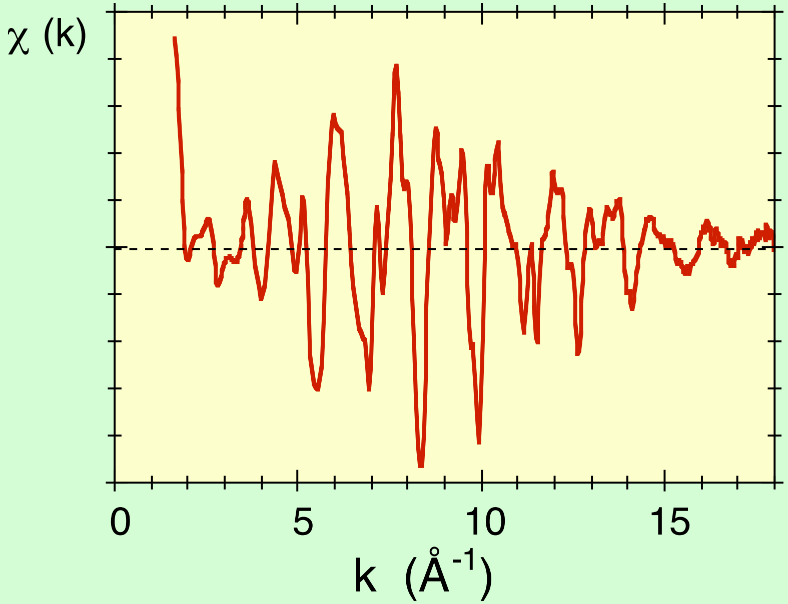
Intrinsic inelastic effects

Photo-electron mean-free-path

$$\chi(k) = \frac{S_0^2}{k} \sum_{shell} N_s \, \mathrm{Im}\left[f_s(k,\pi)\, e^{2i\delta_1} \, \frac{e^{-2R_s/\lambda(k)}}{R_s^2} \exp(2ikR_s) \right]$$

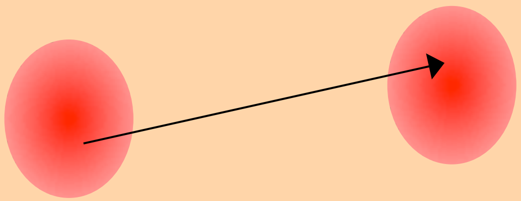
Atoms frozen in equilibrium positions !



Disorder effects ?

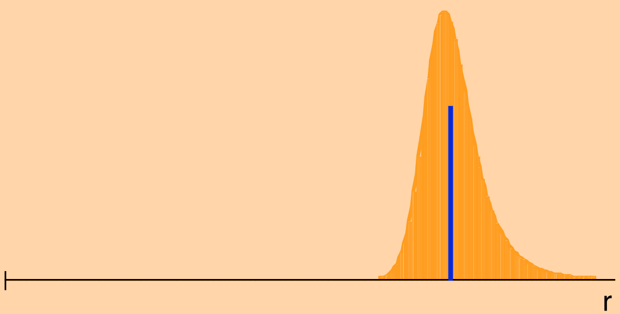
Local disorder

Thermal disorder



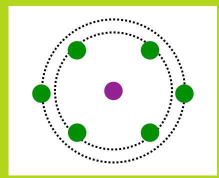
$\tau_{vib} \approx 10^{-12}$ s

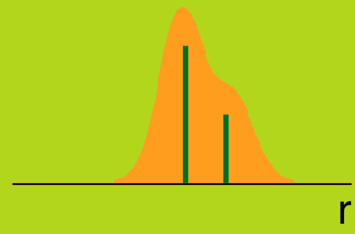
$\tau_{exafs} \approx 10^{-15}$ s



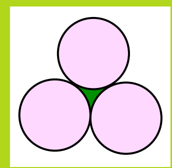
Structural disorder - examples

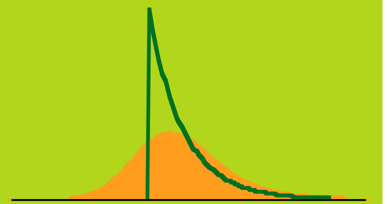
- Distorted coordination shells



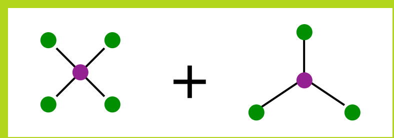


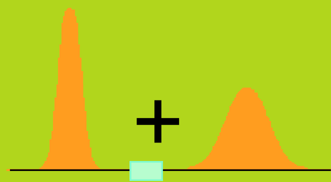
- Free-volume models





- Sites disorder





Distance → Distribution of distances

Thermal disorder in crystals

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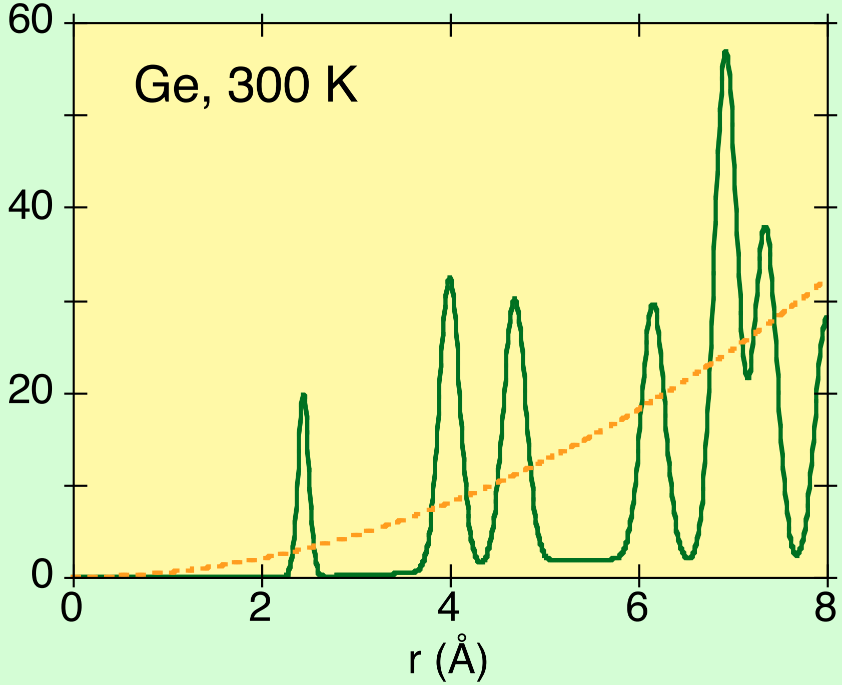
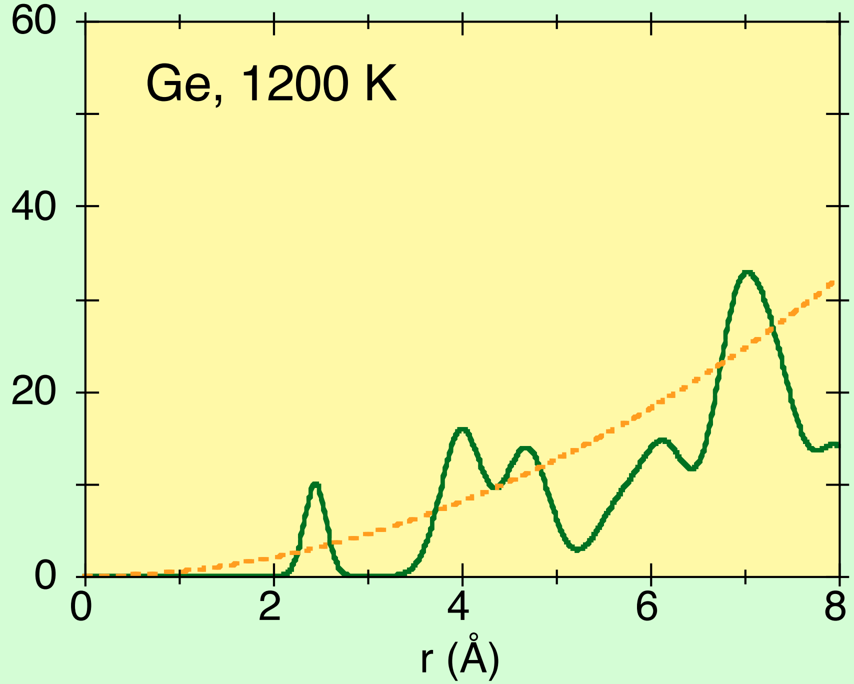
Simulated distributions for c-Ge





Separability of coordination shells ?

Distributions of distances

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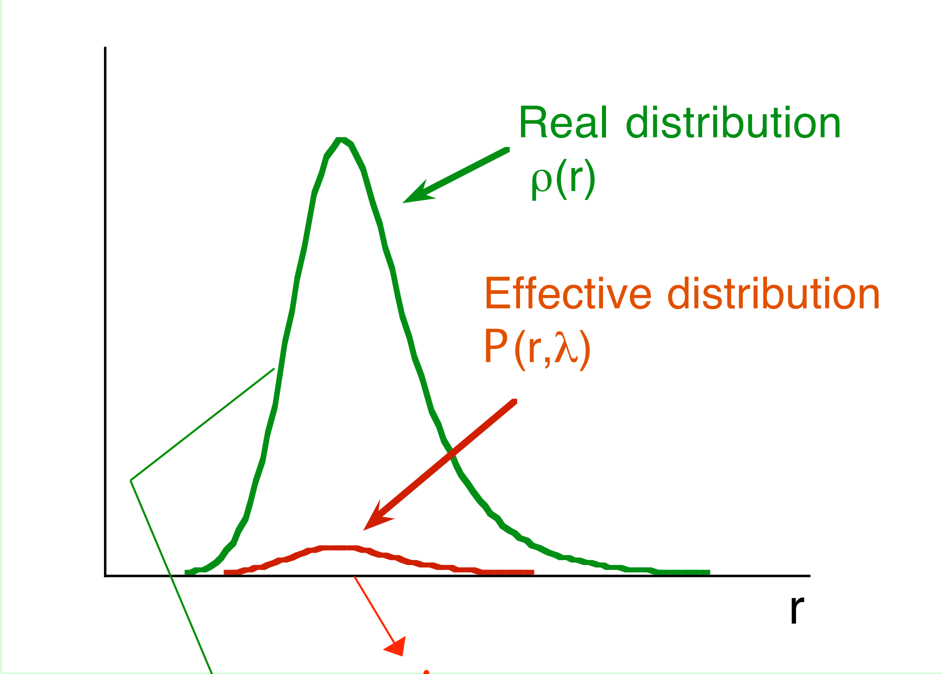
Thermal + structural disorder

⇒ distribution of distances



$$\chi(k) = \frac{S_0^2}{k} \sum_{shell} N_s \, \mathrm{Im}\left[f_s(k,\pi)\, e^{2i\delta_1} \int_0^{\infty} \rho_s(r) \frac{e^{-2r_s/\lambda(k)}}{r_s^2} e^{2ikr_s} dr \right]$$

Real and effective distributions

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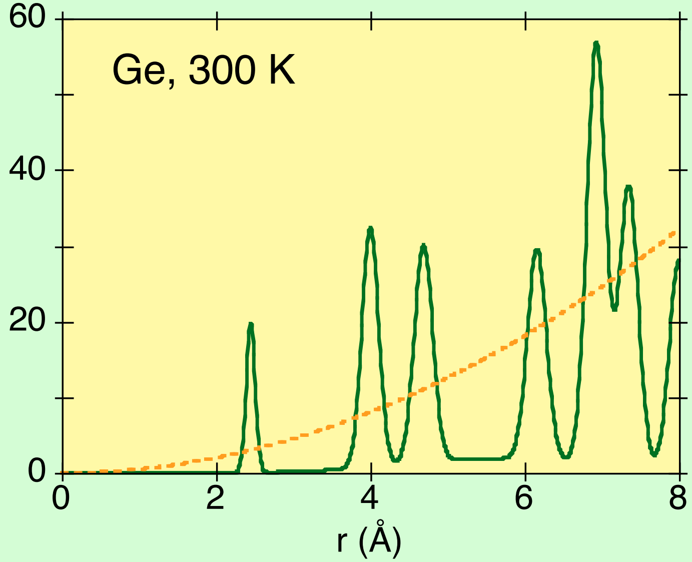
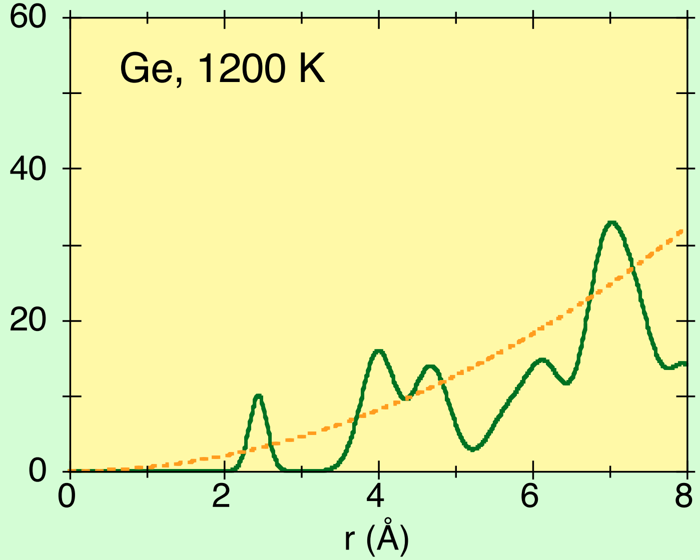
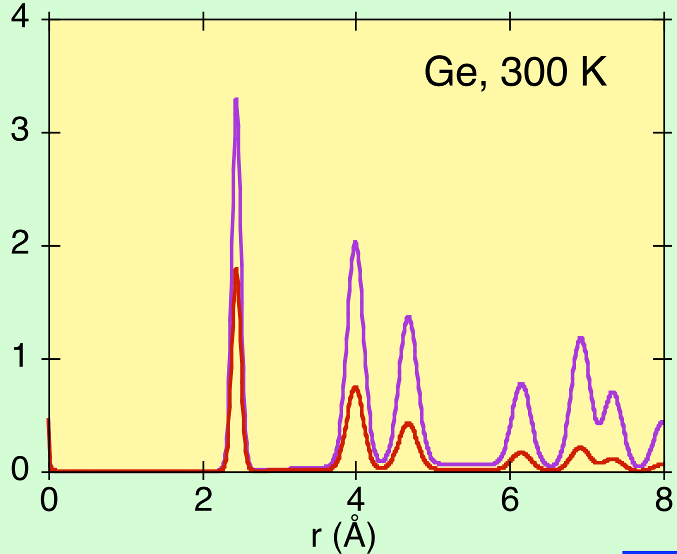




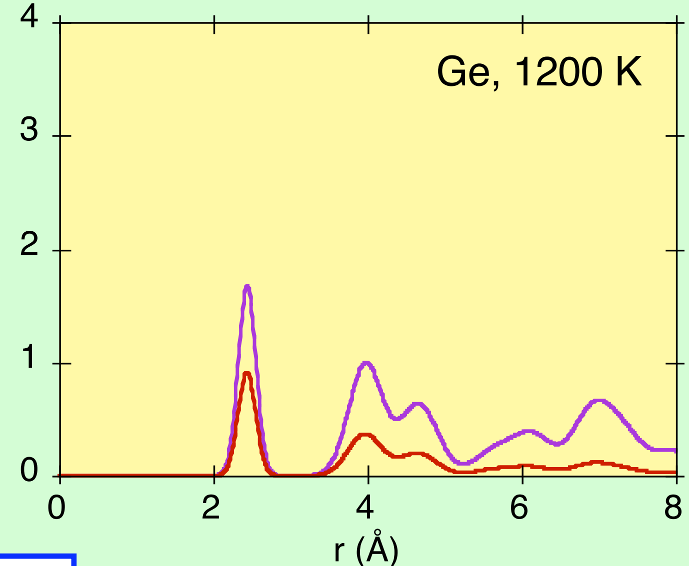
$$\rho(r)$$

$$\frac{\rho(r)}{r^2}$$



$$P(r,\lambda) = \frac{\rho(r)}{r^2}\, e^{-2r/\lambda}$$

$$(\lambda = 8\,Å)$$



EXAFS = short-range probe

The inversion problem

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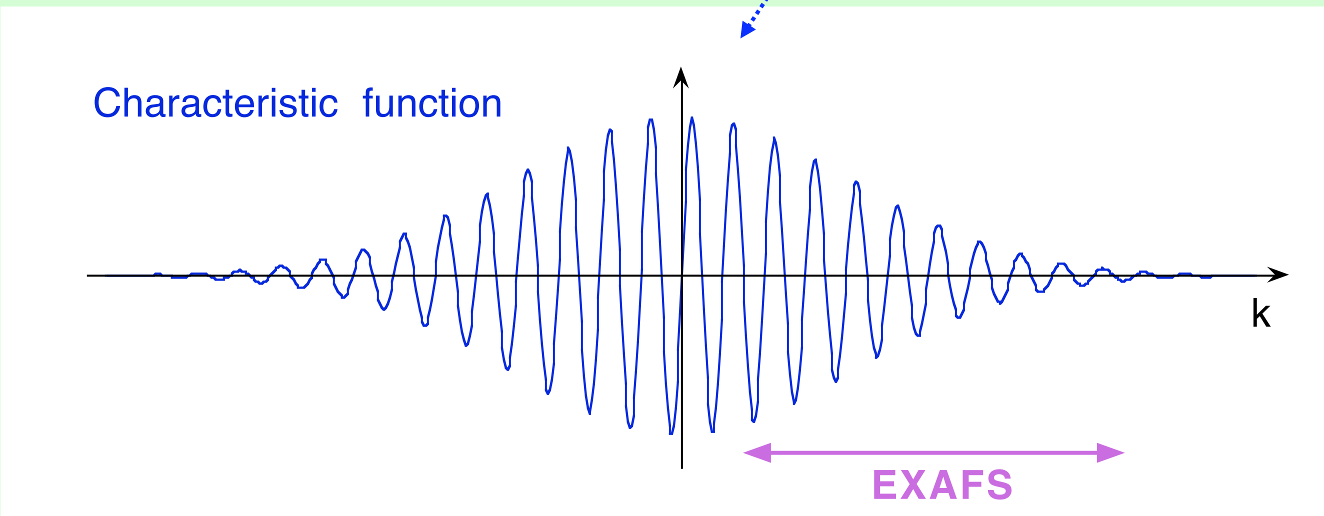
$$\chi(k) = \frac{S_0^2}{k} \sum_{shell} N_s \, \mathrm{Im}\left[f_s(k,\pi)\, e^{2i\delta_1} \int_0^\infty \rho_s(r)\, \frac{e^{-2r_s/\lambda(k)}}{r_s^2}\, e^{2ikr_s}\, dr \right]$$



$$\chi(k) \Rightarrow \rho(r) \quad ?$$

Structural models and fitting procedure

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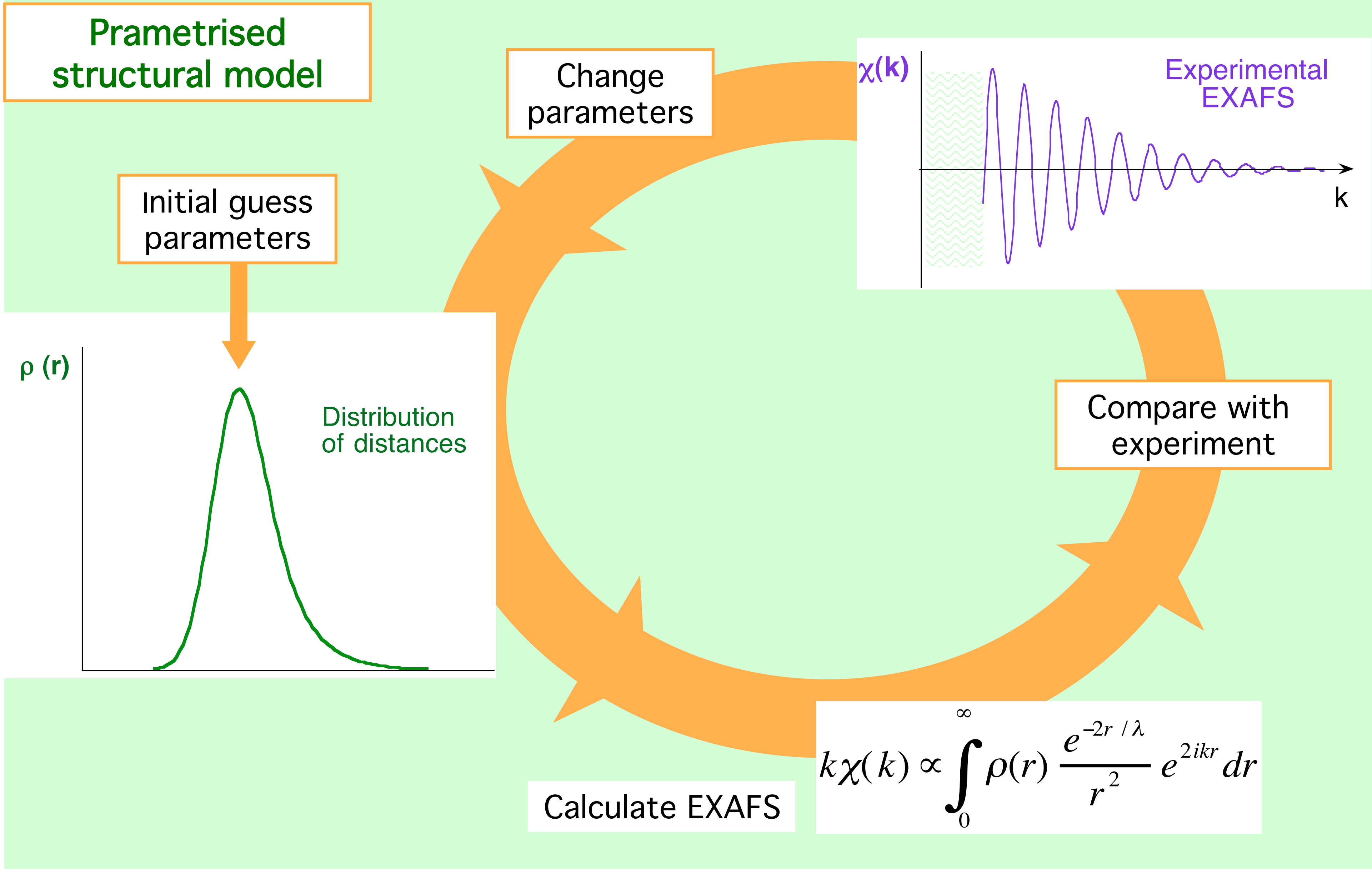

The simplest model: gaussian approximation

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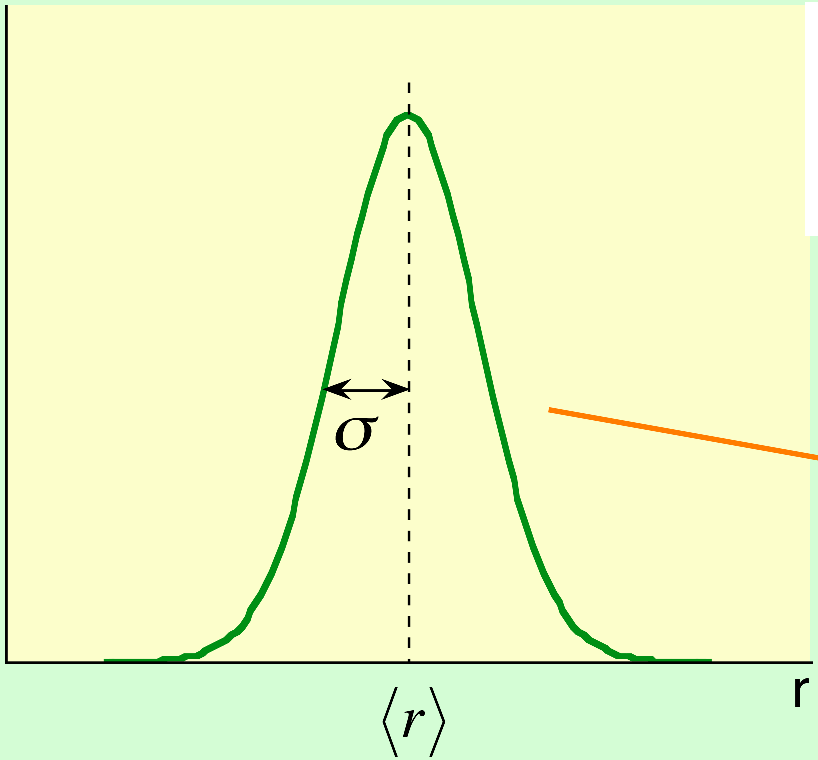

$$P(r,\lambda) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[\frac{\left(r - \langle r \rangle\right)^2}{2\sigma^2} \right]$$

$$C_2 = \sigma^2 = \left\langle \left(r - \langle r \rangle\right)^2 \right\rangle$$

Distribution width
(EXAFS Debye-Waller factor)

$$C_1 = \langle r \rangle_{\mathrm{eff}} = \langle r \rangle_{\mathrm{real}} - \frac{2\sigma^2}{\langle r \rangle}\left(1 - \frac{\langle r \rangle}{\lambda}\right)$$

Average distance

Gaussian parametrization of EXAFS (one shell)

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Approx.: Single Scattering
Plane waves

- Theory (interaction potentials + scattering theory)
- Experiment (reference samples)

Inelastic terms

Back-scattering amplitude

Total phase-shift

$$k\,\chi(k) = \frac{S_0^2\, e^{-2C_1/\lambda}}{C_1^2}\,|f(k,\pi)|\,N \exp\left[-2k^2\sigma^2\right]\sin\left[2kC_1 + \phi(k)\right]$$

Coordination number .... N

Debye-Waller .... σ^2

Average distance .... C_1

Including weak asymmetry

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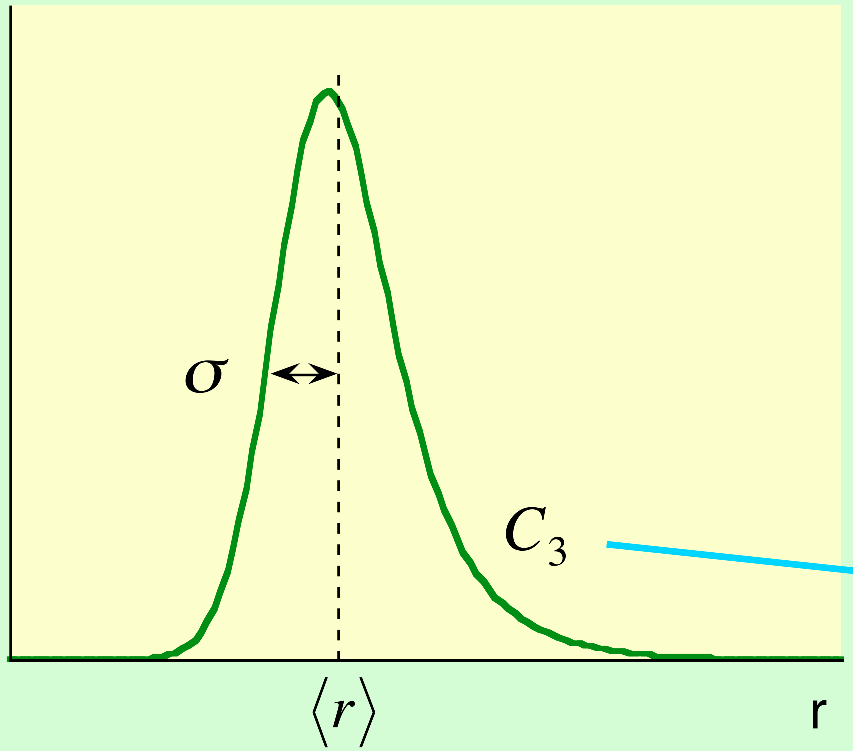
Asymmetric distribution



$$C_2 = \sigma^2 = \left\langle \left(r - \langle r \rangle \right)^2 \right\rangle$$

$$C_3 = \left\langle \left(r - \langle r \rangle \right)^3 \right\rangle$$

Third cumulant
Asymmetry parameter

$$C_1 = \langle r \rangle_{\mathrm{eff}} = \langle r \rangle_{\mathrm{real}} - \frac{2\sigma^2}{\langle r \rangle}\left(1 - \frac{\langle r \rangle}{\lambda}\right)$$

Better for first shell

EXAFS including asymmetry (one shell)

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Approx.: Single Scattering
Plane waves

- **Theory** (interaction potentials + scattering theory)
- **Experiment** (reference samples)

Inelastic terms | Back-scattering amplitude | Total phase-shift

$$k\,\chi(k) = \frac{S_0^2\, e^{-2C_1/\lambda}}{C_1^2}\,|f(k,\pi)|\,N\,\exp\left[-2k^2\sigma^2\right]\sin\left[2kC_1 - \frac{4}{3}k^3C_3 + \phi(k)\right]$$

Coordination number .... N

Debye-Waller .... σ^2

Average distance and asymmetry .... C_1 C_3

XAFS and other techniques

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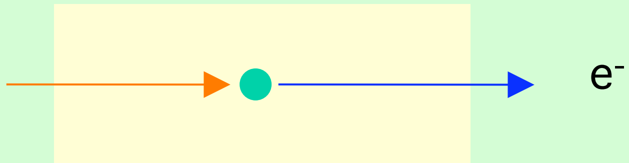
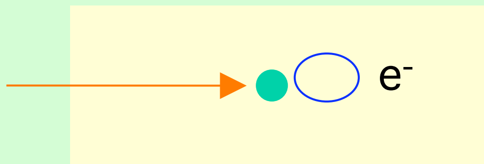
Photo-ionization

XPS - X-ray photo-electron spectroscopy



Info on
bound electronic states

XAFS – X-ray absorption fine structure



Info on
- free electronic states
- local structure

XAFS = structural probe – Comparison with diffraction ?

Bragg diffraction .vs. EXAFS

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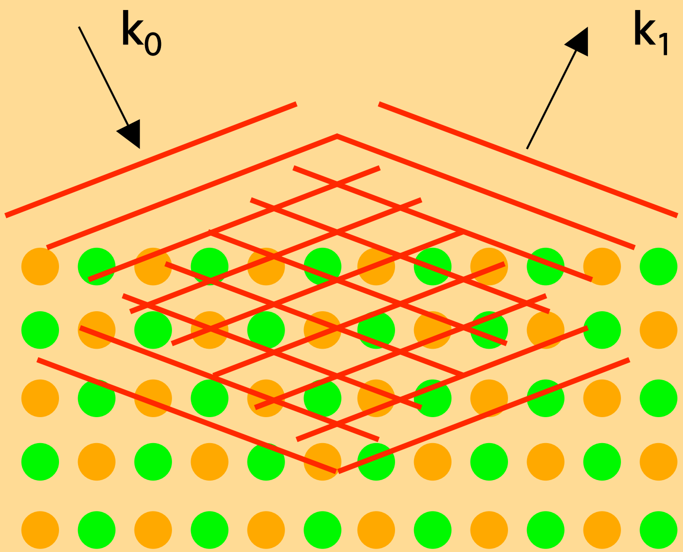
Bragg diffraction



X-ray or neutron plane waves

- long-range sensitivity
- atomic positions
- atomic thermal factors

Structural probe

EXAFS

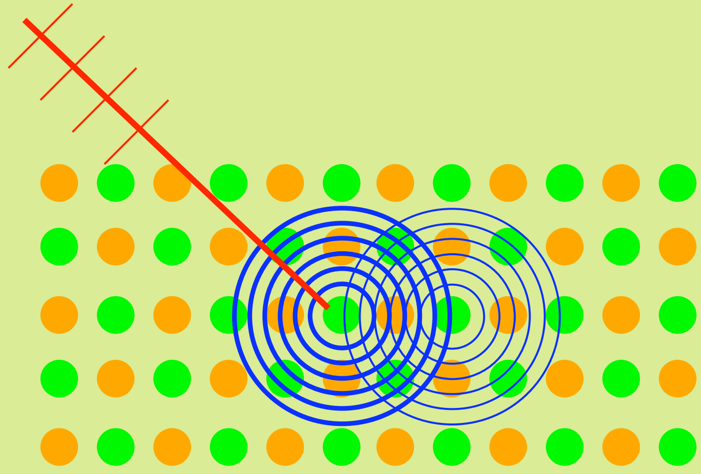


photo-electron spherical wave

- short-range sensitivity
- inter-atomic distances
- relative displacements

EXAFS: a structural probe

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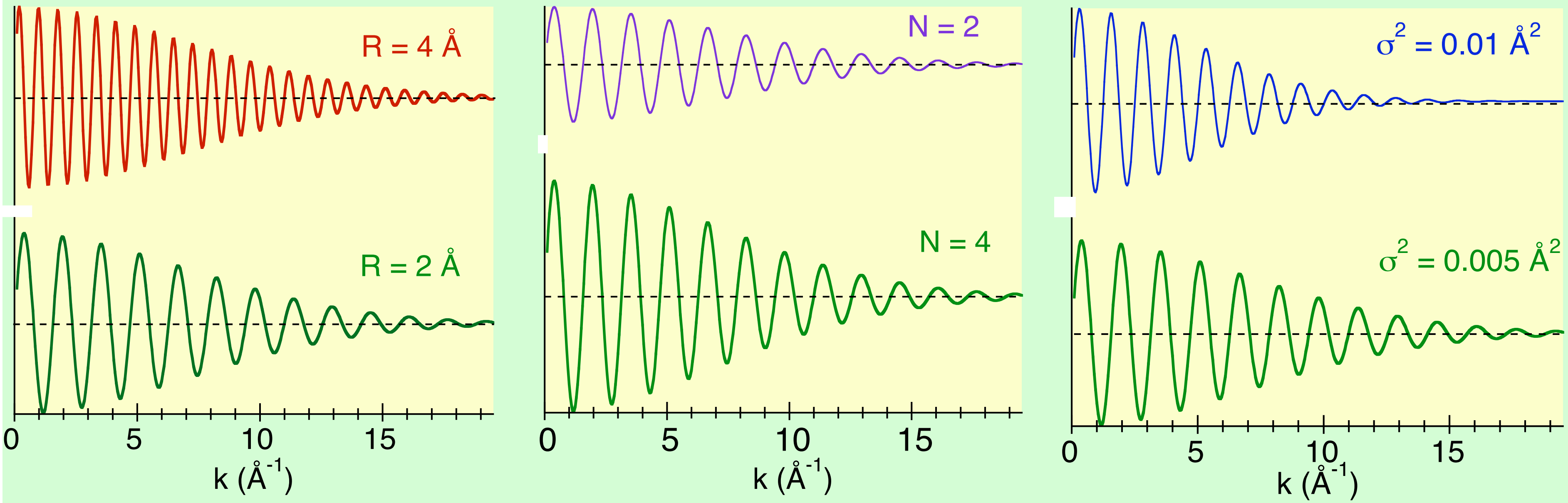

Frequency → Inter-atomic distance

Amplitude → Coordination number

Damping → Disorder

- Selectivity of atomic species
- Insensitivity to long-range order

EXAFS applications

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Non-crystalline materials

- mono-atomic
- many-atomic

Active sites embedded in a matrix

- Inorganic heterogeneos catalysts
- Metallo-proteins
- Impurities in semiconductors
- Luminescent atoms

Local properties different from average properties

- Crystalline ternary random alloys
- Lattice dynamics studies
- Negative thermal expansion

EXAFS experiments

XAFS: experimental layout

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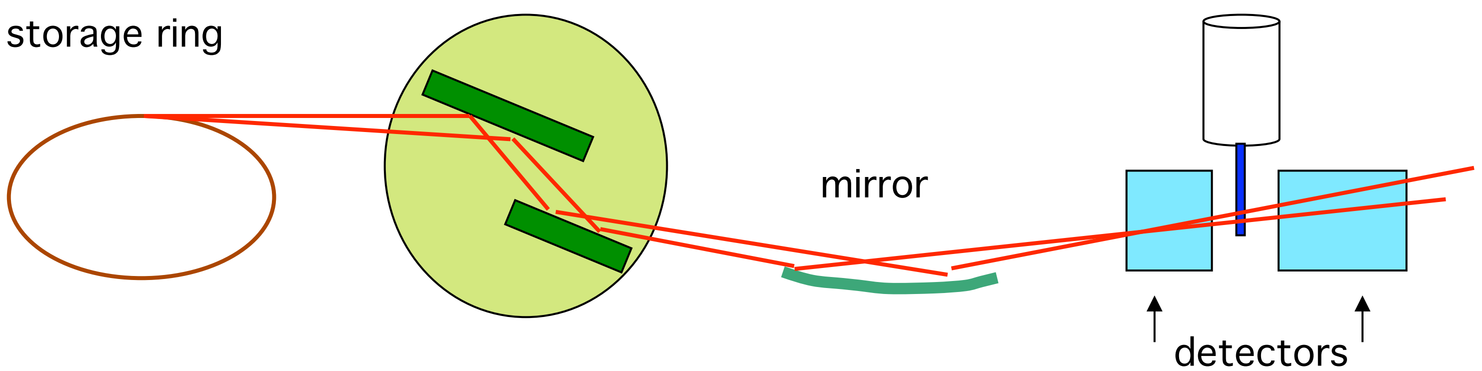

Source	Optical apparatus	Experim. apparatus
• storage ring • beamlines	• monochromators • mirrors	• sample holder • detectors

Alternative layouts

- dispersive EXAFS
- refl-EXAFS

……

Sample conditioning:

cryostat
oven
reactor
manipulators

Detection:

transmission
fluorescence
electron yield
…….

XAFS: experimental

- Monochromators and mirrors

X-ray crystal monochromators

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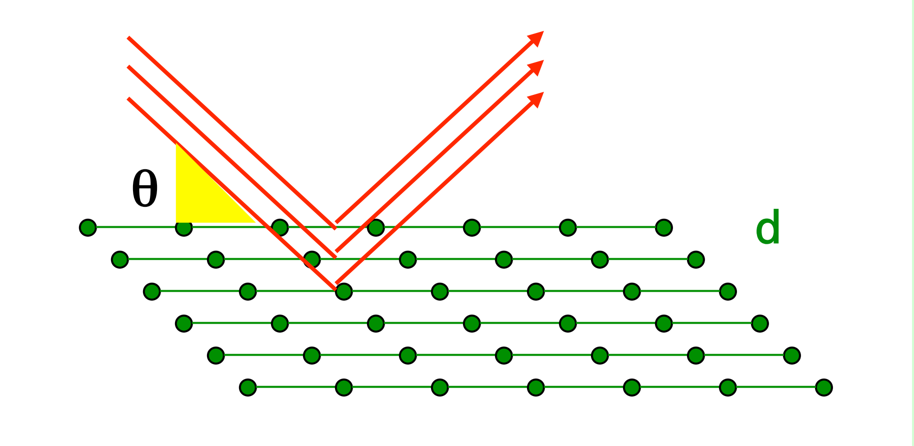
Bragg law

$$2\,d_{hkl}\,\sin\theta = n\,\lambda$$

Incidence angle ⇔ wavelength



	2d
Si (111)	6.2708
Si (220)	3.84
Si (311)	3.28
Si (331)	2.5
Si (511)	2.08
Ge (111)	6.5328
Ge (220)	4.0004

- Forbidden ‘reflections’
- Harmonics
- Spurious reflections

Crystal reflectivity

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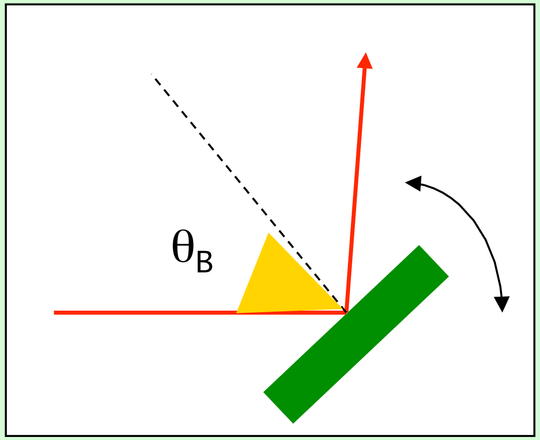

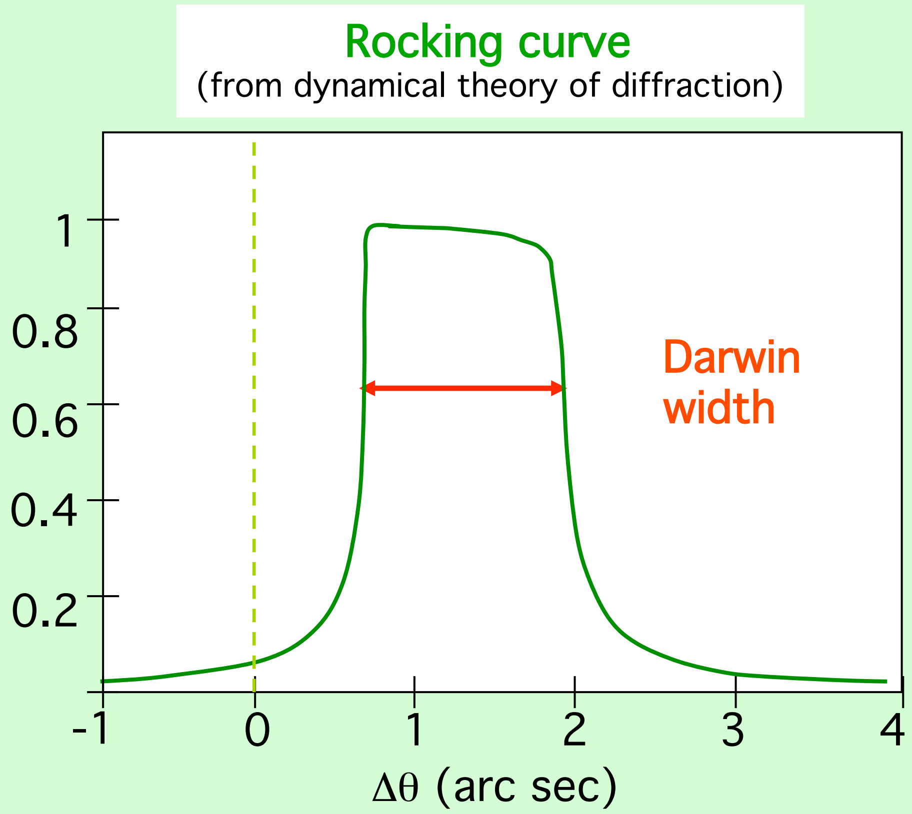

Higher order reflections have narrower rocking curves.

Energy resolution

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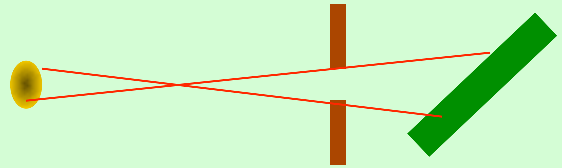
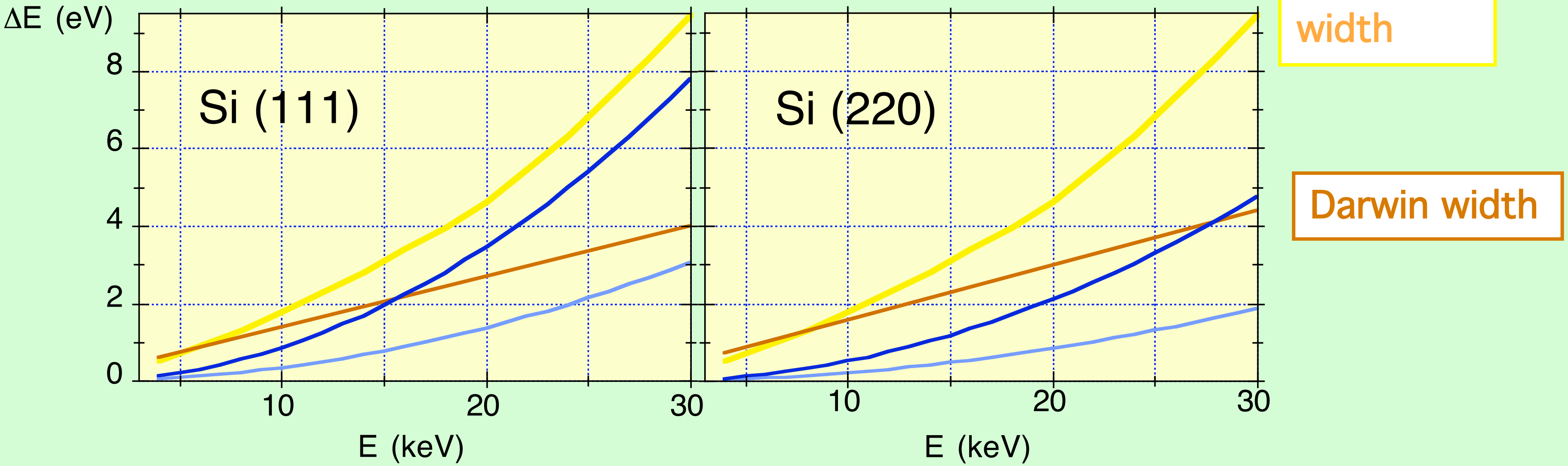
Darwin width (Intrinsic resolution) + Beam divergence = Total angle $\Delta\Theta$



$$\frac{\Delta E}{E} = \frac{\Delta\lambda}{\lambda} = \Delta\Theta \,\mathrm{cotg}\,\theta_B$$



Two-crystal monochromators

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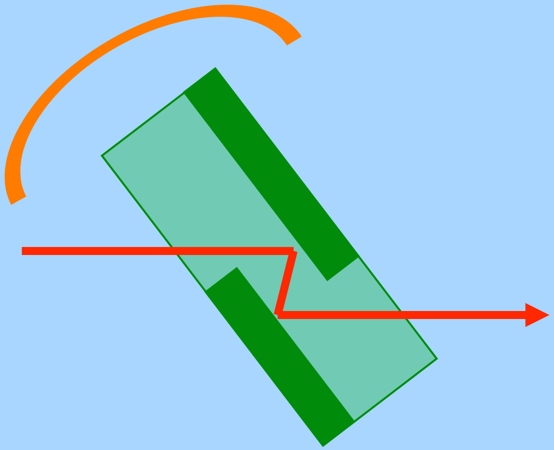
Horizontal output beam

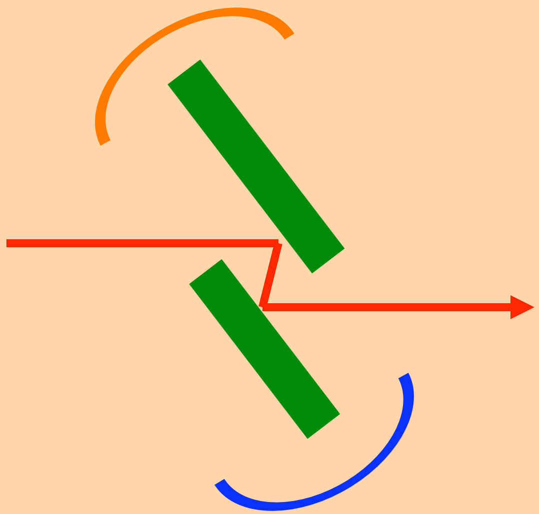
“Channel-cut”



☺ Mechanical simplicity
☺ Stability

☹ Harmonics
☹ Spurious reflections

Independent crystals



☺ Detuning: harmonic reduction
☺ Possibility of focussing

☹ Mechanical complexity
☹ Instability

Crystals detuning

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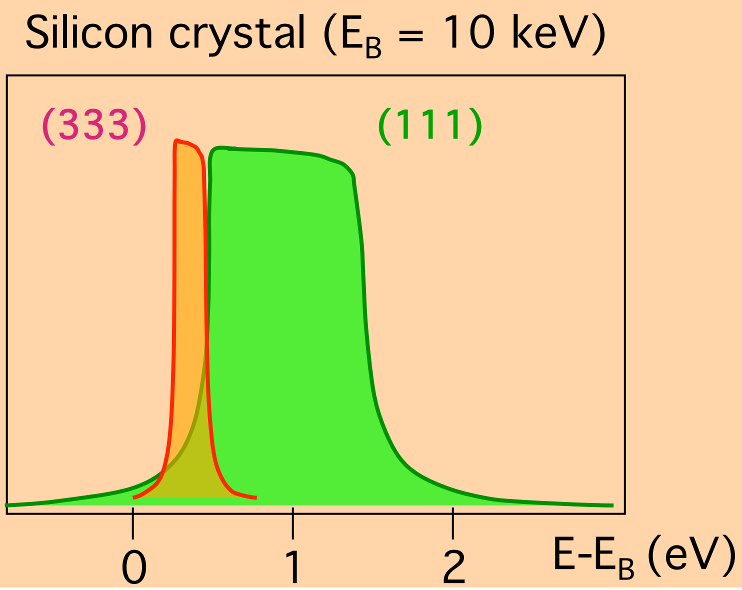

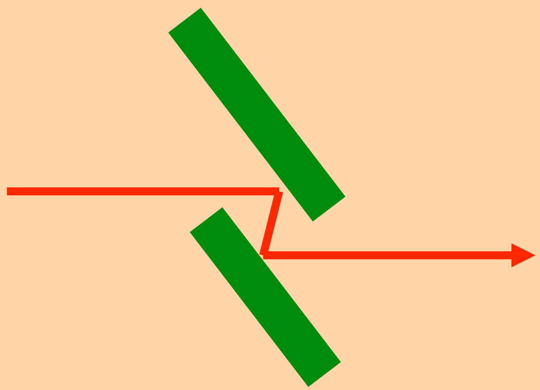

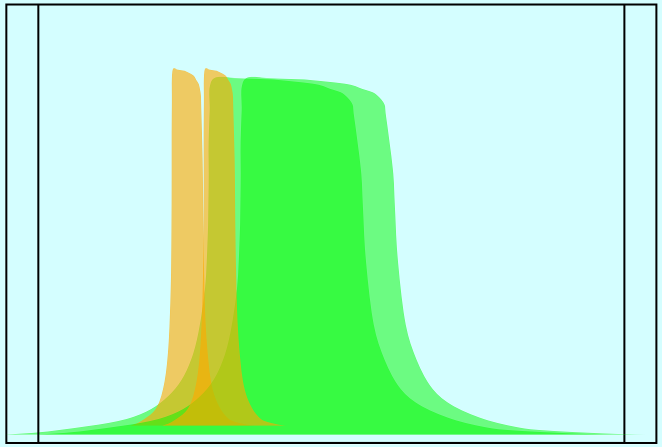

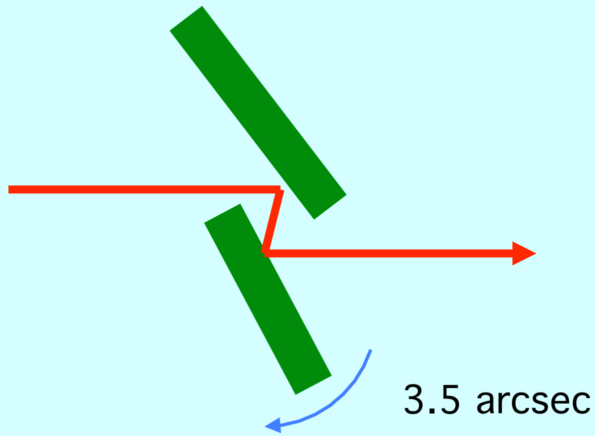

X-ray mirrors

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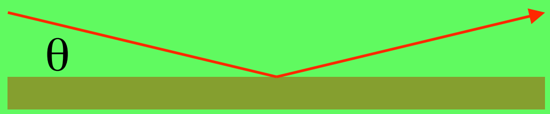
Complex refractive index

$$n = 1 - \delta - i\beta$$

$\delta \approx 10^{-6} \div 10^{-5}$
for x - rays

absorption

Total external reflection : $\theta < \theta_c$

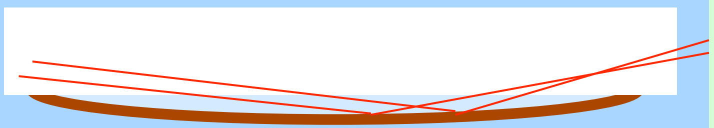


$$\theta_c = \sqrt{2\delta} \propto \lambda \sqrt{\rho}$$

grazing incidence
$\theta \approx 10^{-3}$ rad

harmonics rejection

Surface bending



Beam collimation
and
focalisation

XAFS: experimental

- ♠ Detection schemes

XAFS: direct transmission measurements

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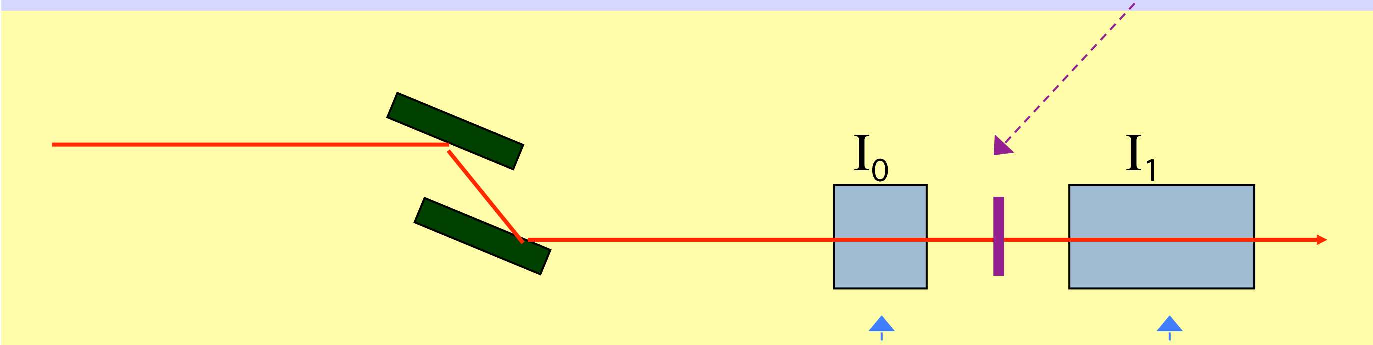
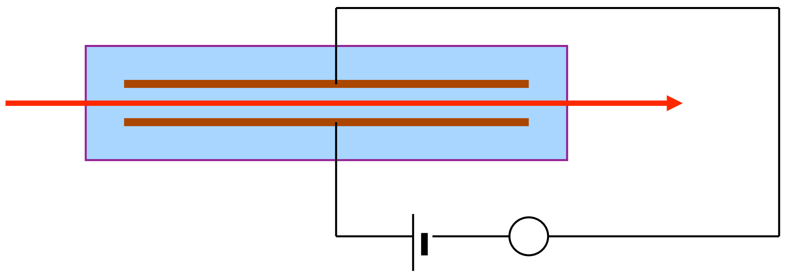
Sample:

- Powders or thin films
- Thickness ≈ 10 μm
- No holes or inhomogeneities



Detectors: ionisation chambers



V ≈ 100 V/cm

I ≈ $10^{-10} \div 10^{-8}$ A

Direct transmission measurements

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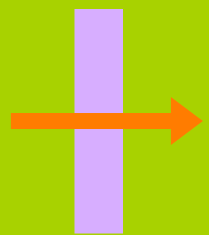
OK

Bulk information
(not fom surface)
from:

Thin samples



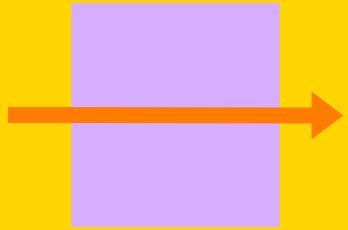
Non-diluted samples

Homogeneous samples

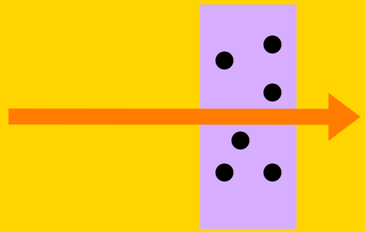
High accuracy attainable

NO

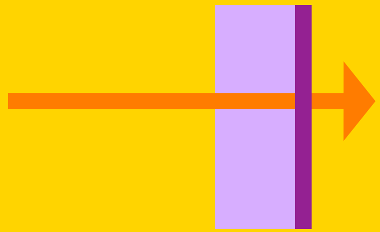
Thick samples



Diluted samples



Surface
information



Indirect detection methods

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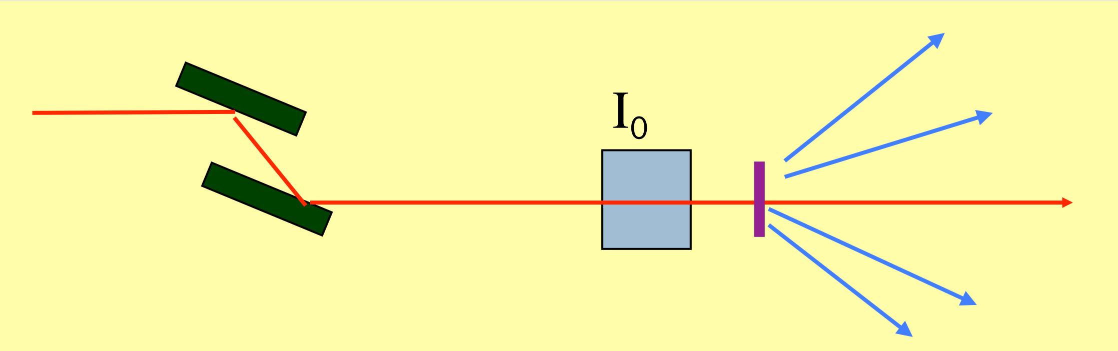

Detection of decay products

- X-ray fluorescence — FLY = FLuorescence Yield
- Electrons
  - AEY = Auger Electron Yield
  - PEY = Partial Eletron Yield
  - TEY = Total Electron Yield
- Optical luminescence — XEOL-PLY = X-ray Ecxited Optical Luminescence Photo Luminescence Yield

XAFS: fluorescence detection (FLY)

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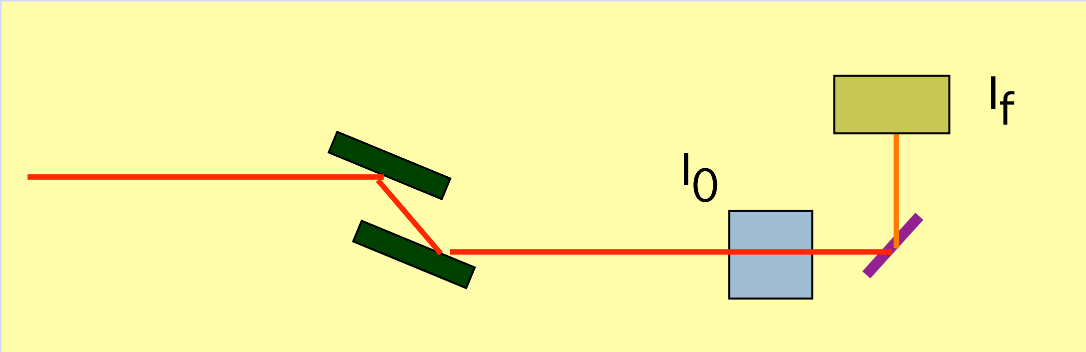

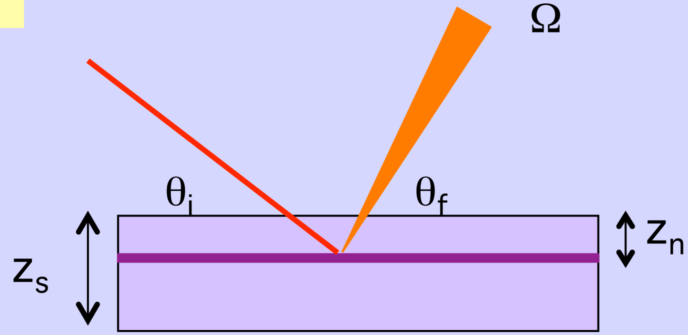

$$I_f(z_n)\,dz = I_0(\omega)\;\exp\left[-\frac{\mu_s(\omega)z_n}{\sin\theta_i}\right]\;\eta_f\mu_a(\omega)\frac{dz}{\sin\theta_i}\;\exp\left[-\frac{\mu_s(\omega_f)z_n}{\sin\theta_f}\right]\;\frac{\Omega}{2\pi}$$

Absorption

Fluorescence

Absorption

Fluorescence: total intensity

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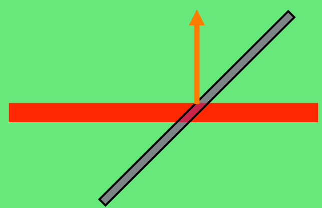
Sample of thickness z_s

$\theta_i = \theta_f = 45°$

$$I_f = I_0(\omega)\,\eta_f\,\frac{\Omega}{4\pi}\,\frac{\mu_a(\omega)}{\mu_s(\omega)+\mu_s(\omega_f)}\left\{1-\exp(A)\right\}$$

$$A = -\sqrt{2}z_s\left[\mu_s(\omega)+\mu_s(\omega_f)\right]$$

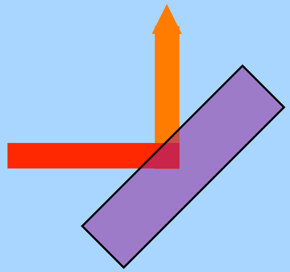
Thin samples



$$1-\exp(A) \approx 1-1-A = -A$$

$$I_f \propto \mu_a(\omega)$$

Thick samples



$$1-\exp(A) \approx 1$$

$$I_f = I_0(\omega)\,\eta_f\,\frac{\Omega}{4\pi}\,\frac{\mu_a(\omega)}{\mu_s(\omega)+\mu_s(\omega_f)}$$

OK for diluted samples (< 1%)

Fluorescence signal

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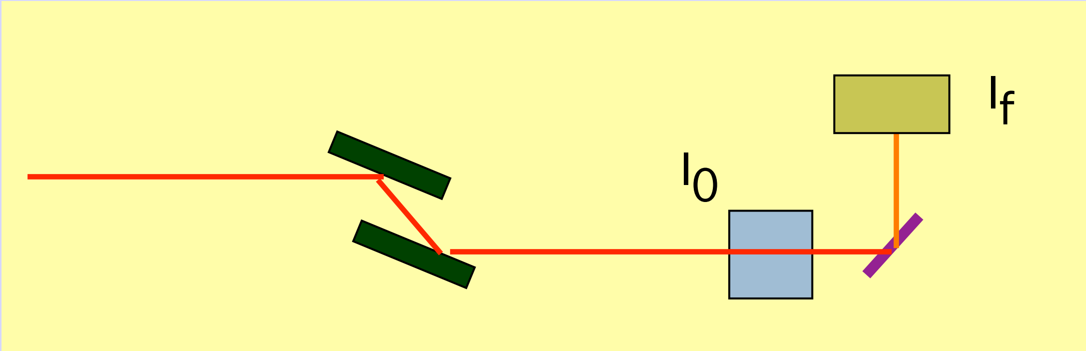

Background signals

Elastic scattering
Compton scattering
Other fluorescences

→ Energy selective detectors
Filters + Soller slits

XAFS: electron detection (a)

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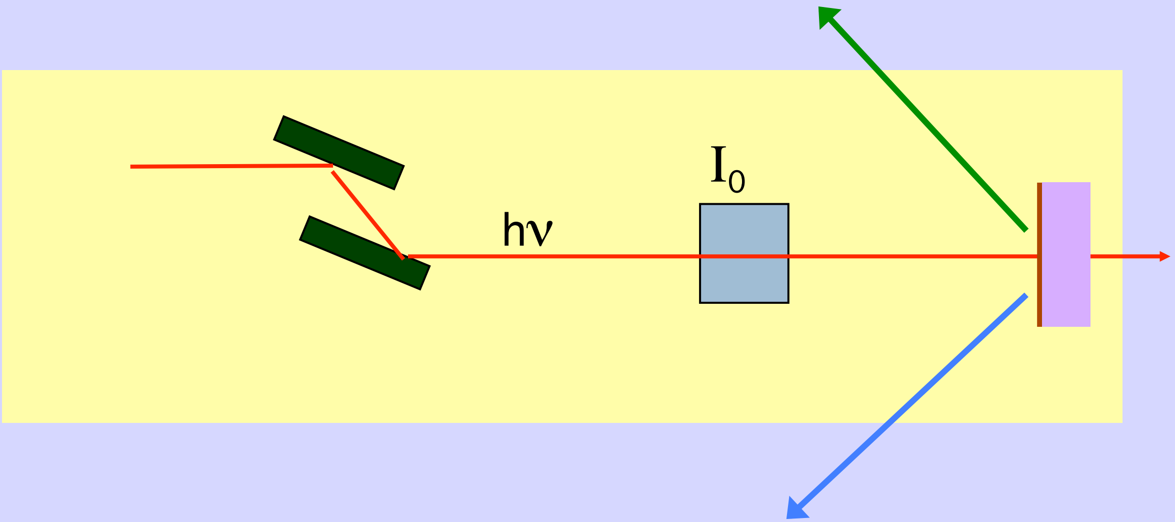
Photo-electrons:
- Energy varies with hν
- Intensity ∝ μx

⇒ **XAFS signal**



Auger electrons:
- Fixed energy ⇒ atomic selectivity
- Intensity ∝ μx

⇒ **XAFS signal**

Electron mean free path:
- adsorbates
- thin layers

Indirect processes and escape depth

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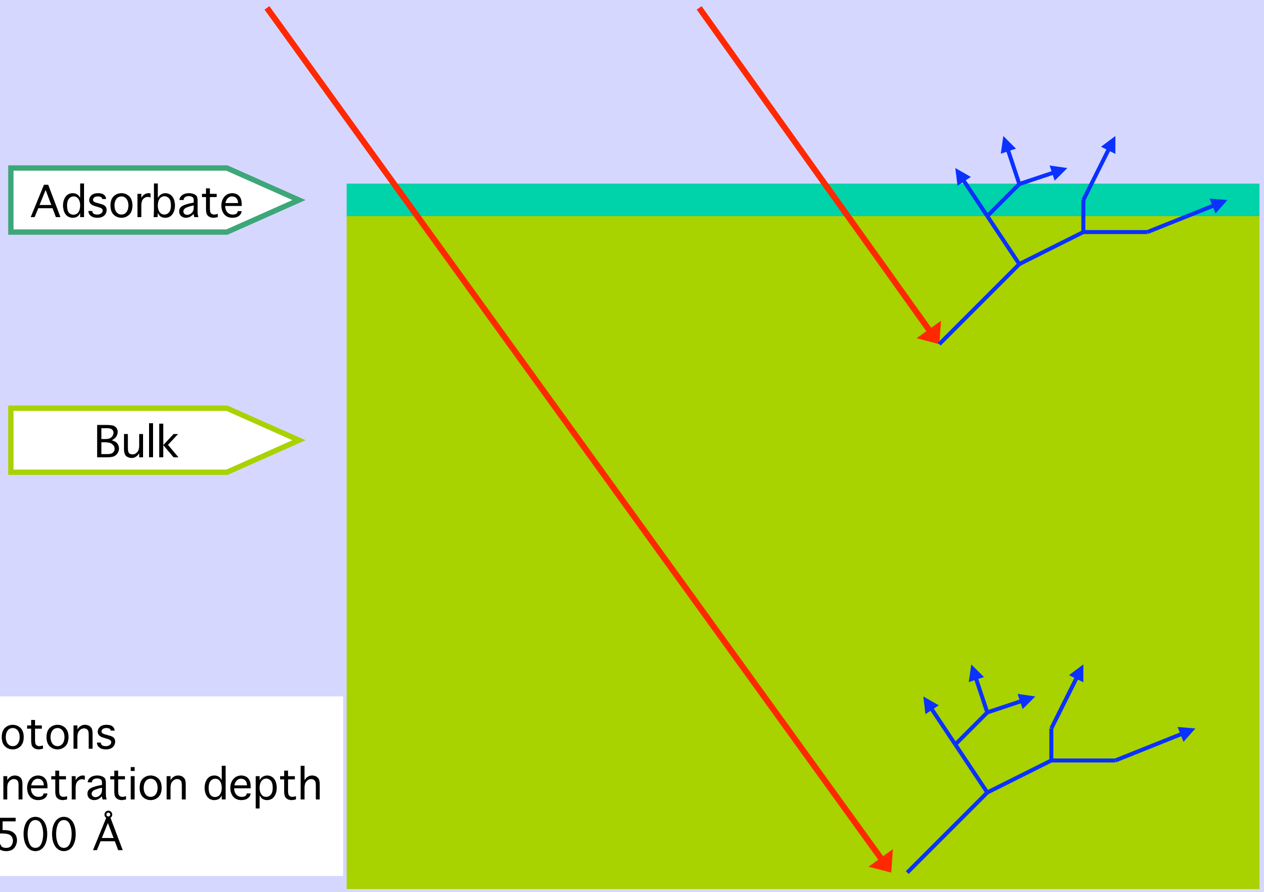
Primary electrons
mean free path
~ 5 - 10 Å



Secondary electrons
escape depth
~ 50 - 100 Å

Photons
penetration depth
~ 500 Å

XAFS: electron detection (b)

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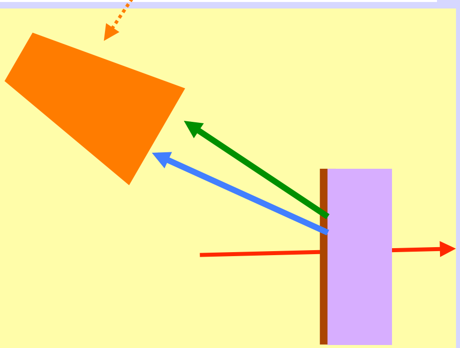
XAFS of adsorbates



AEY - PEY - TEY

AEY = Auger Electron Yield
- narrow energy window
- only direct Auger electrons
- spurious structures from photoelectrons

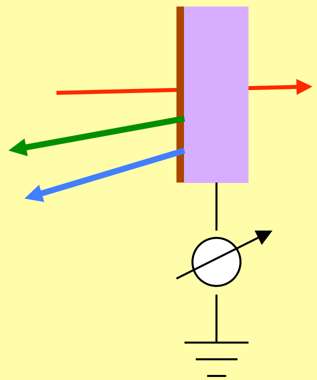
PEY = Partial Eletron Yield
- large energy window
- Auger (direct + secondary) = XAFS signal
- Photoel. (direct + secondary) = background

TEY = Total Electron Yield
- all electrons collected

- Auger (direct + second.) = XAFS signal
- Photoel. (direct + second.) = background

- XAFS from Auger and photoel.

Bulk materials



TEY

XAFS: experimental

♠ Alternative layouts

Dispersive XAFS (a)

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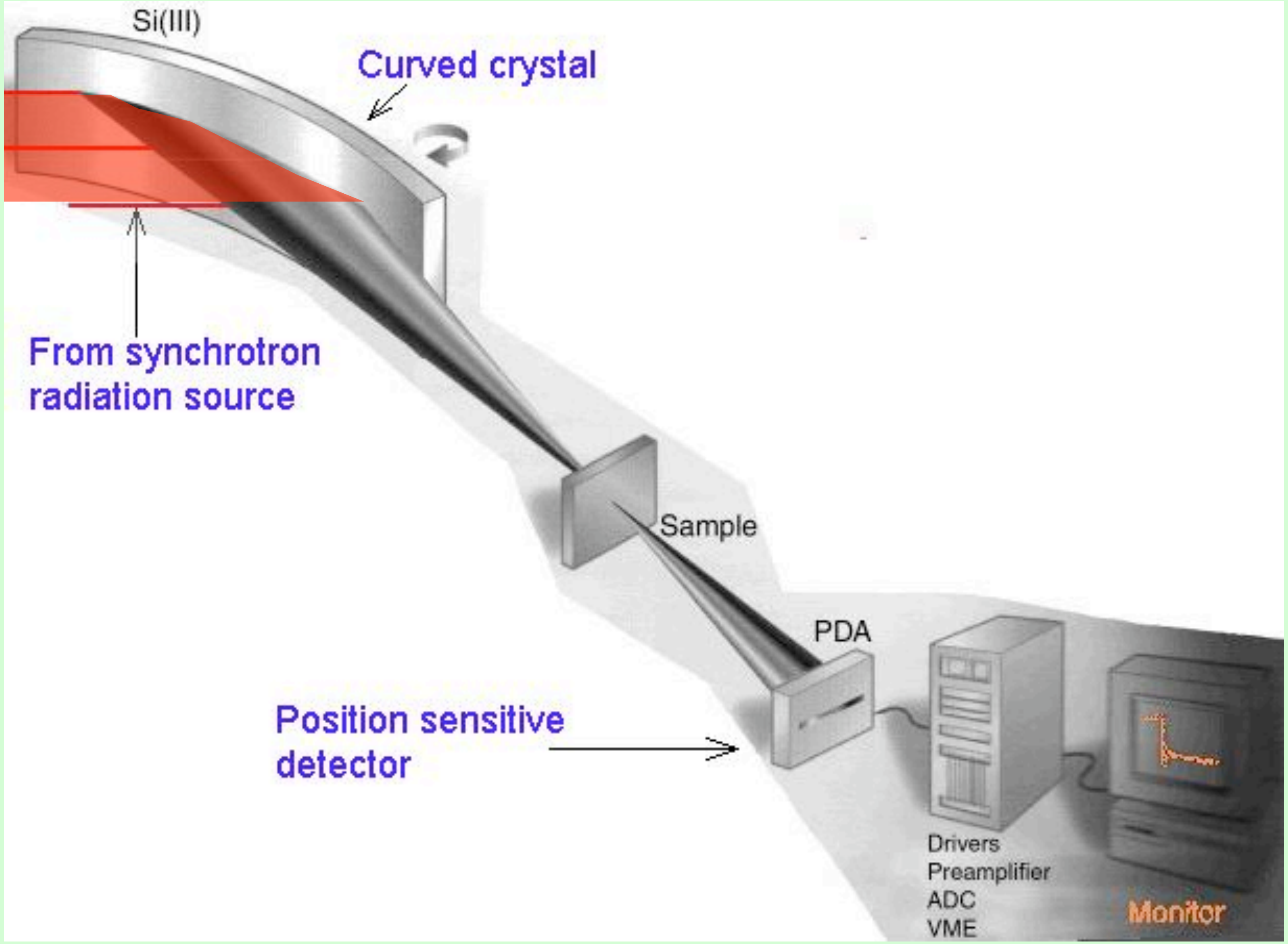

Dispersive XAFS (b)

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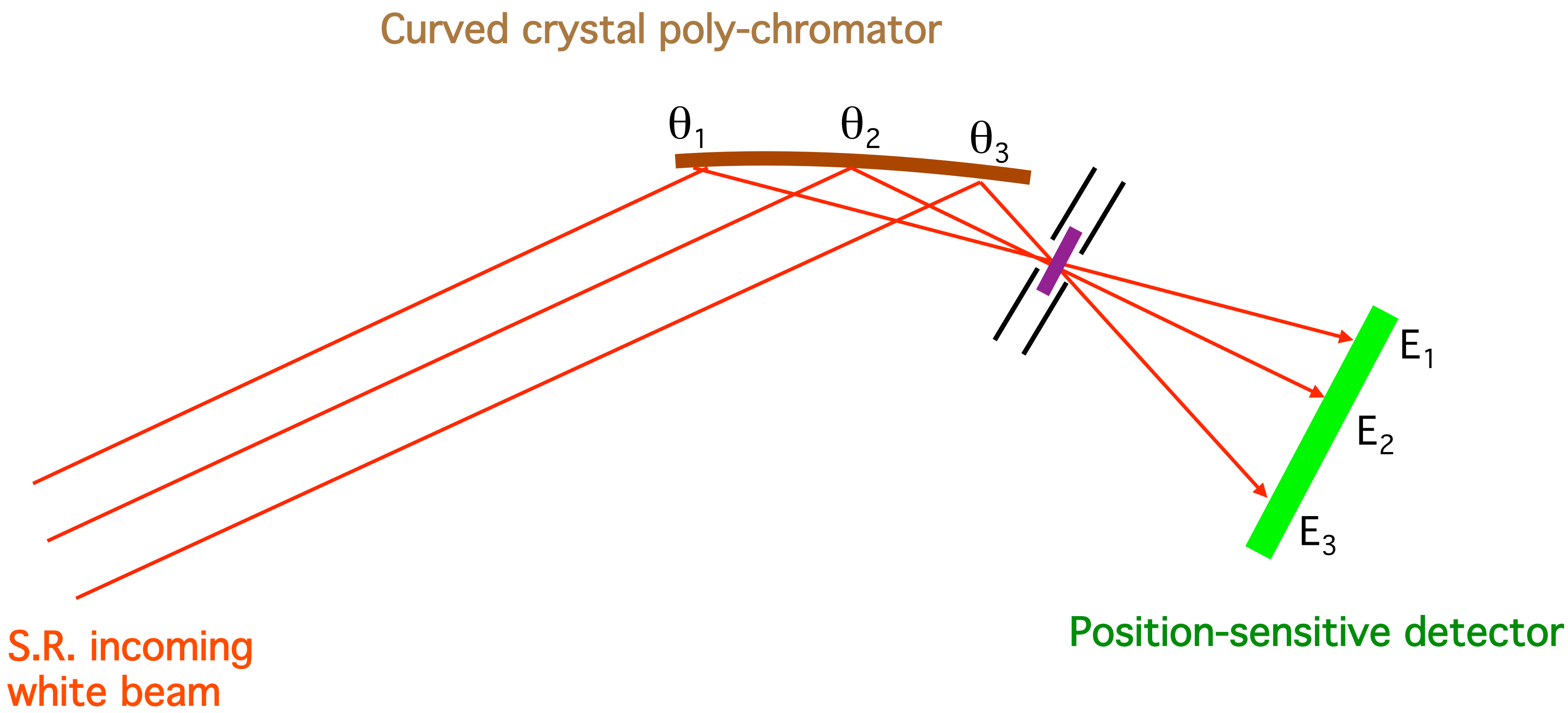
$$2d \sin\theta = \lambda$$



Dispersive XAFS (c)

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☺ No mechanical movements (no dead times)
☺ Simultaneous acquisition of all data points
☺ Acquisition time determined by acceptable statistics

OK for time-resolved measurements

☹ Critical in terms of temporal and spatial beam stability and sample presentation
☹ Only trasmission mode
☹ X-ray beam not perfectly focussed through the sample
☹ No reference measurements during acquisition

NO accurate quantitative results

EXAFS: data analysis, examples

Analysis - Available software

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List of available software:

XAFS Society web-site = `http://xafs.org/Software`

FEFF: ab initio MS calculations of EXAFS and XANES for clusters of atoms.
The code yields scattering amplitudes and phases, as well as various other properties.

IFEFFIT: interactive program for XAFS analysis.

Athena: interactive graphical utility for processing EXAFS data.
Artemis: interactive graphical utility for fitting EXAFS data using theoretical standards from FEFF and sophisticated data modelling.library.

GNXAS: EXAFS data analysis based on MS calculations and advanced fitting of raw experimental data.
Main peculiarities: MS associated with 2, 3, and 4- atom configurations, multi-electron excitation, various model peaks for distribution functions.

EXAFS data analysis

- ♠ Extraction of EXAFS signal

Total absorption coefficient

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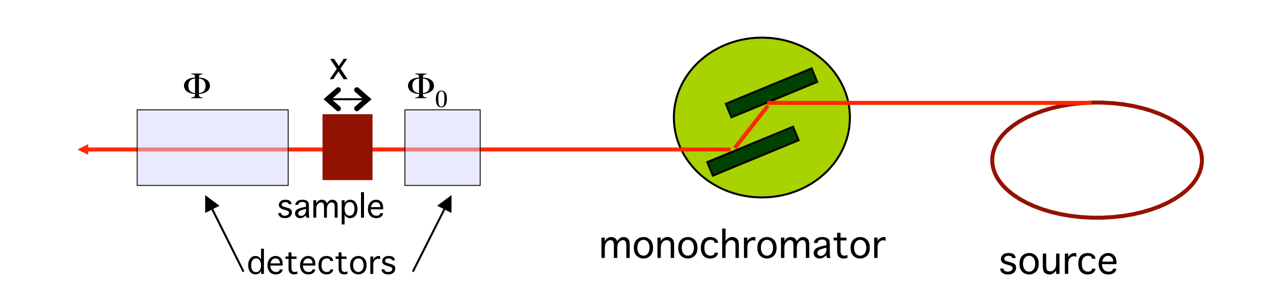
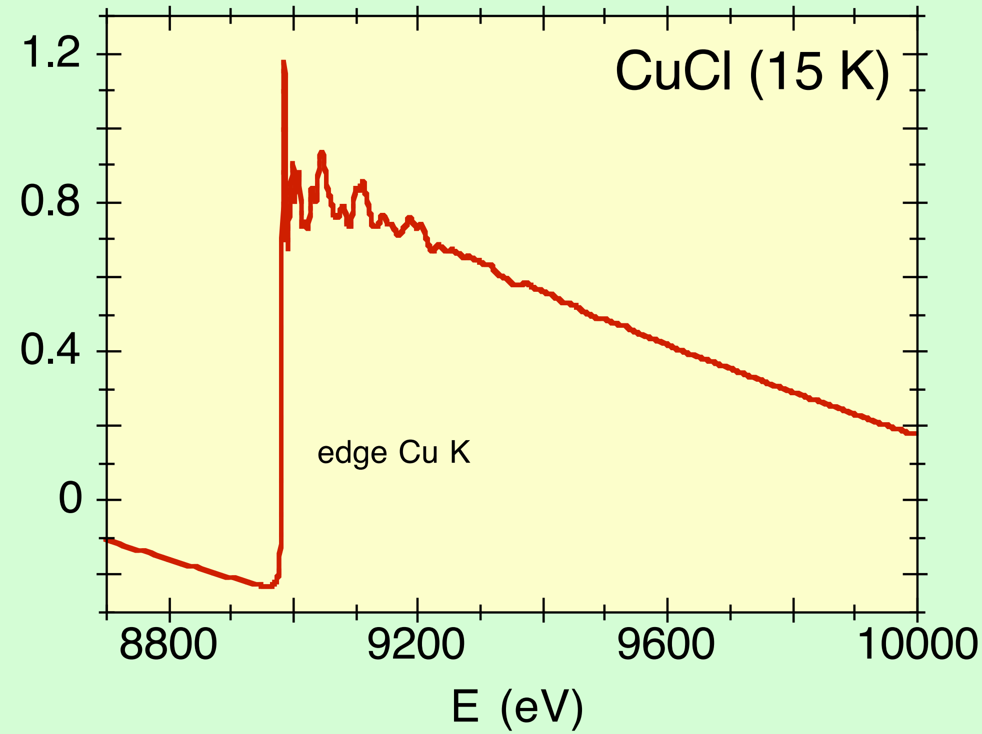


$$\ln\frac{I_0}{I} = \ln\frac{\Phi_0}{\Phi} + C' = \mu_{tot}x + C'$$



Edge absorption coefficient

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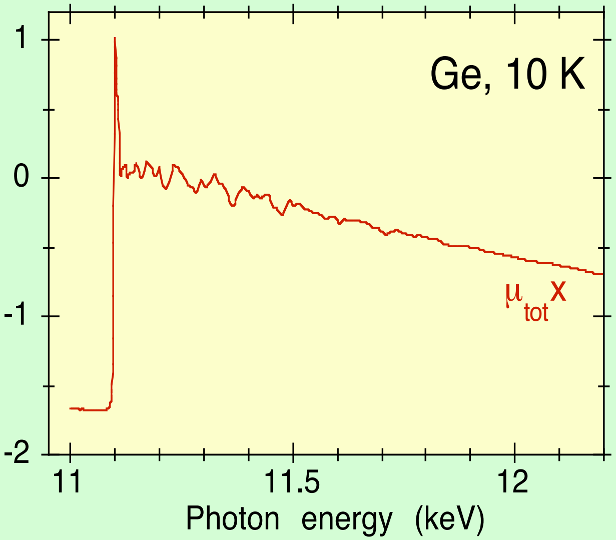
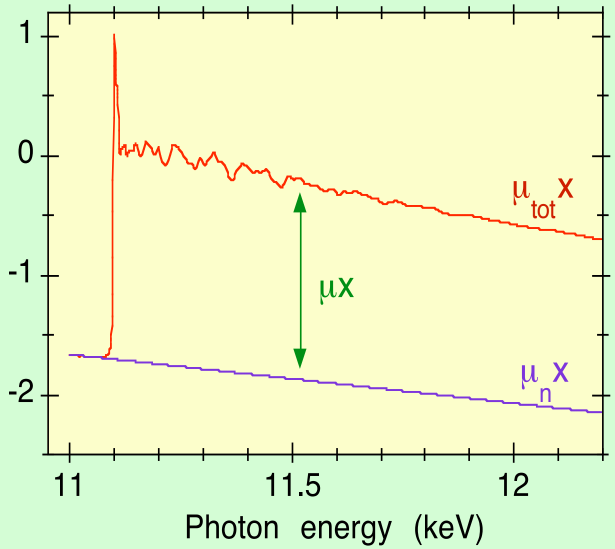
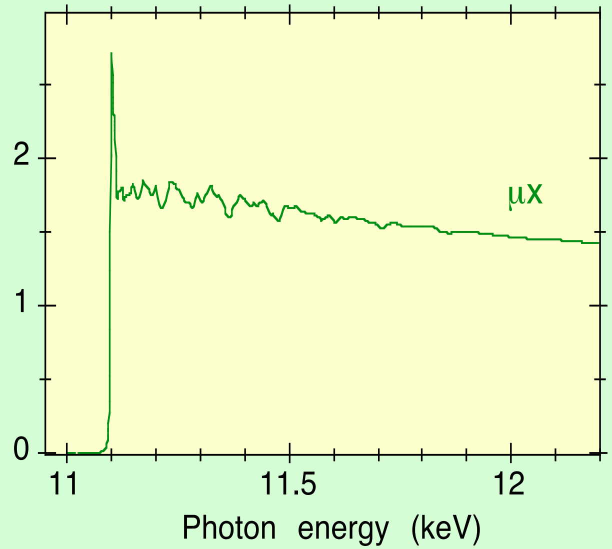
Experimental signal



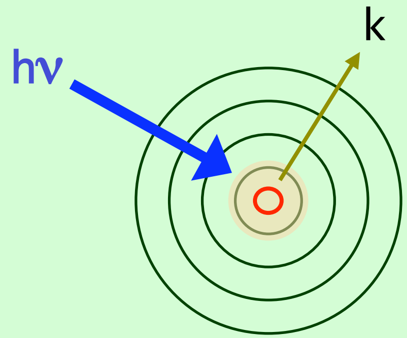
Extrapolation of pre-edge behaviour

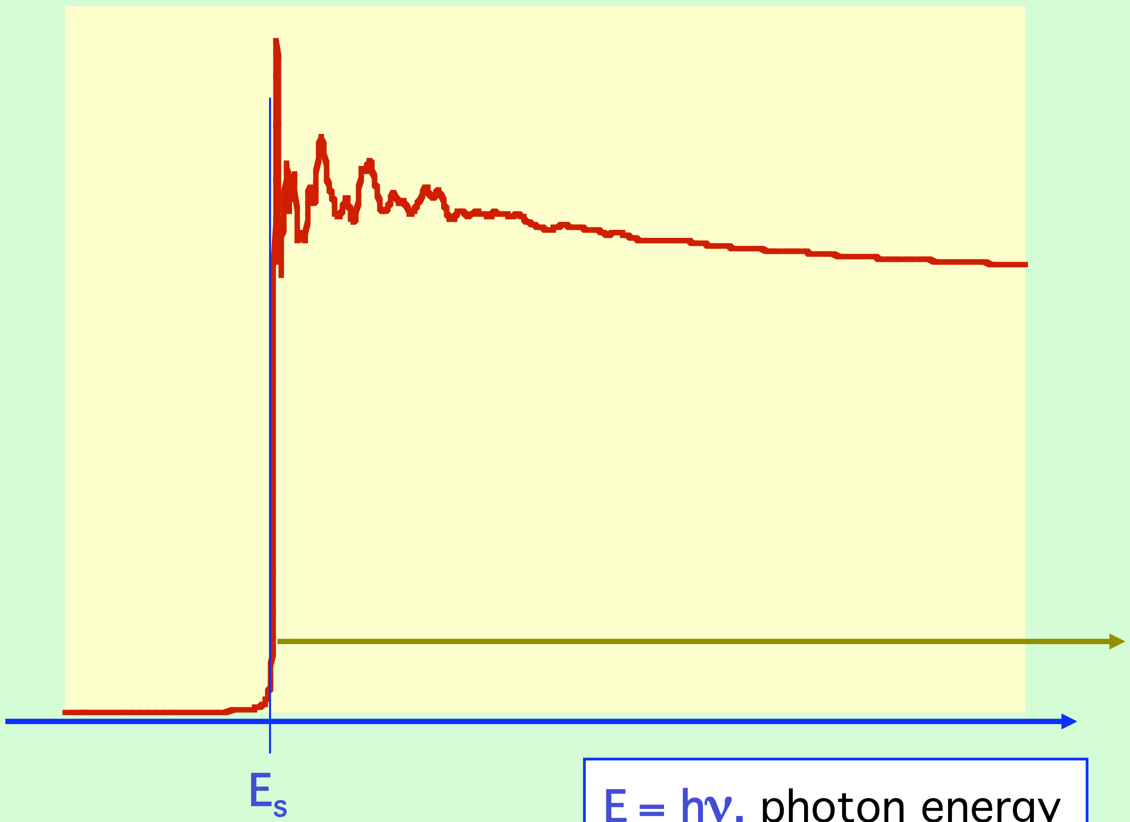


Edge absorption coefficient



Photoelectron wavenumber





Photoelectron wavenumber

$$k = \sqrt{\frac{2m}{\hbar^2}\left(h\nu - E_s\right)}$$

$E = h\nu$, photon energy

Edge energy

?

Experimental convention

E_s = 1st maximum of 1st derivative

Atomic absorption coefficient

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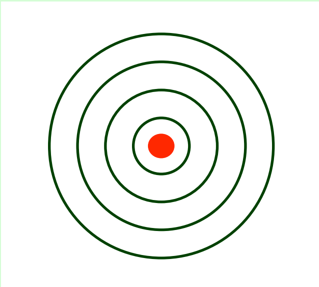
EXAFS function

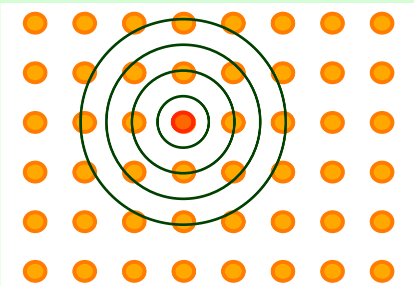
$$\chi(k) = \frac{\mu - \mu_0}{\mu_0}$$

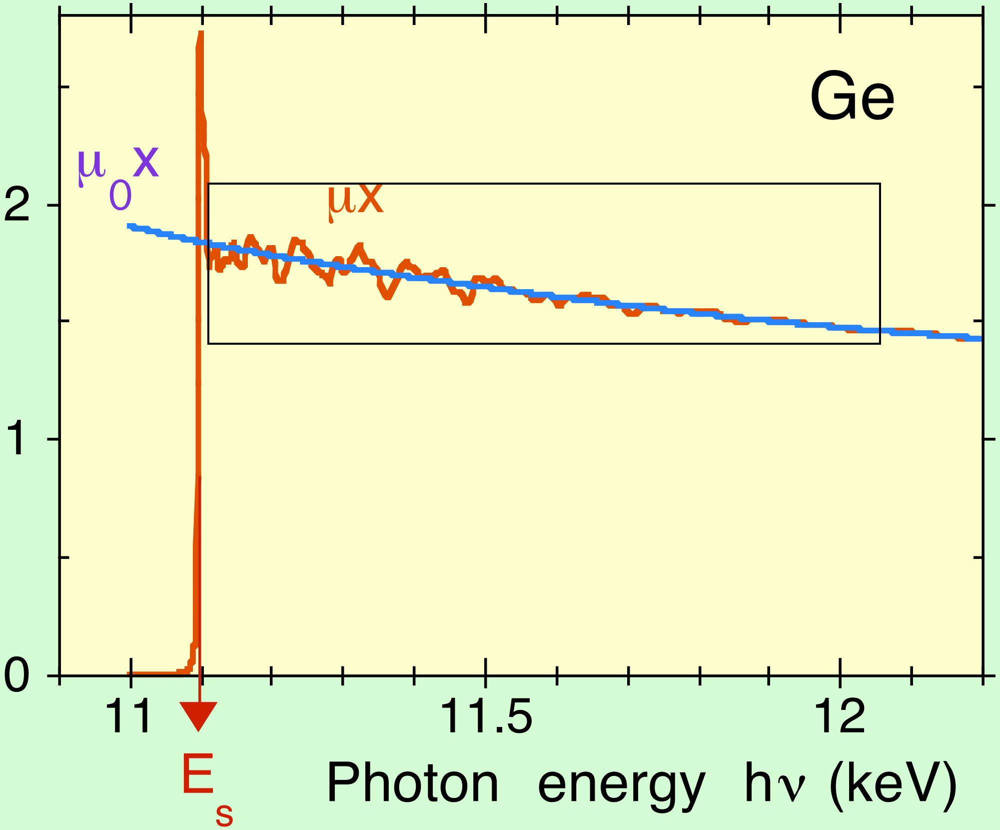
μ_0 ?

Isolated atom



Embedded atom





Best-fitting polynomial spline

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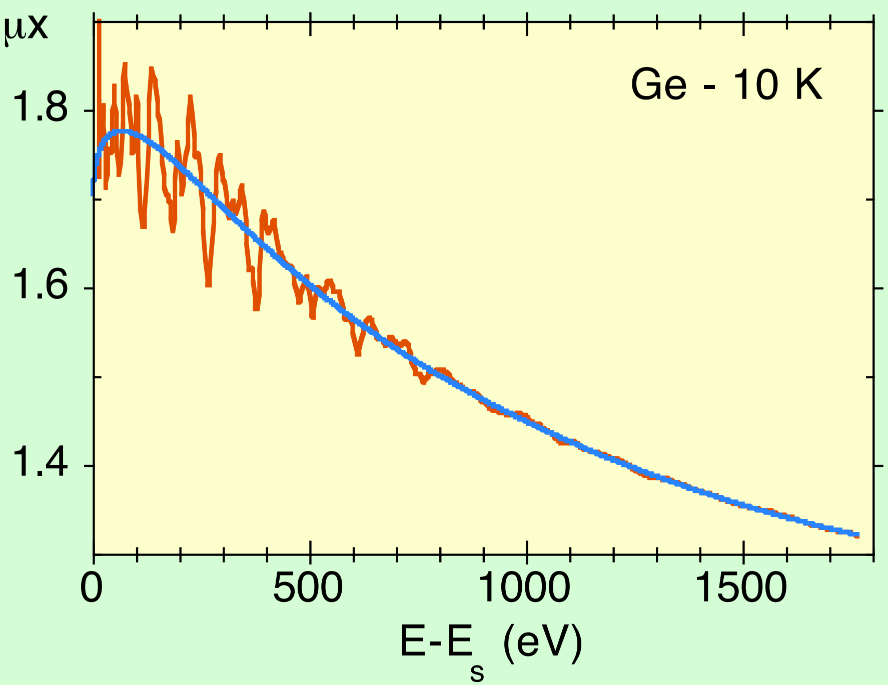
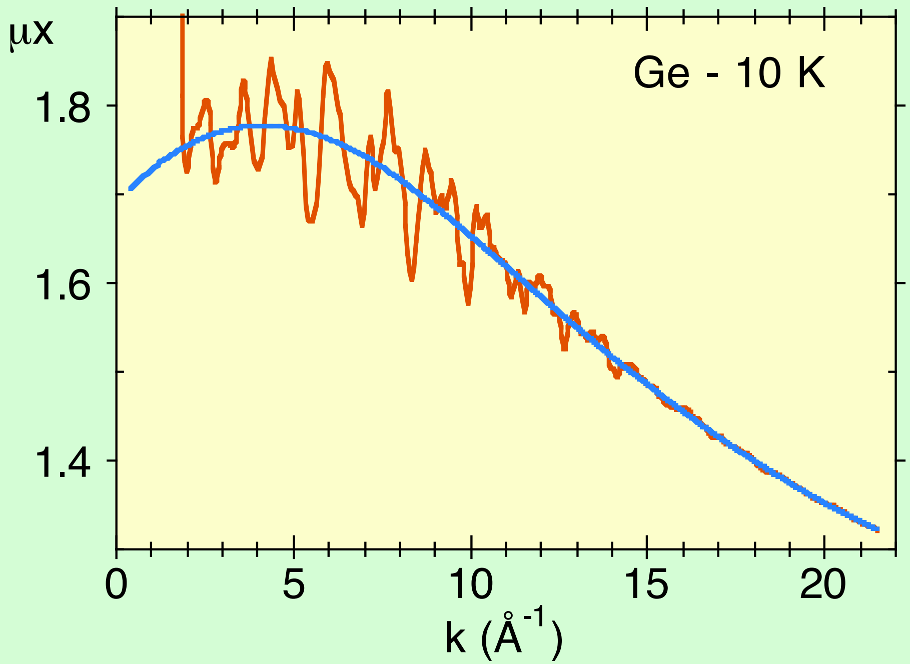
$$\chi(k) = \frac{\mu - \boxed{\mu_0}}{\mu_0}$$

Polynomial spline - best fit

E space



k space



Fit optimization

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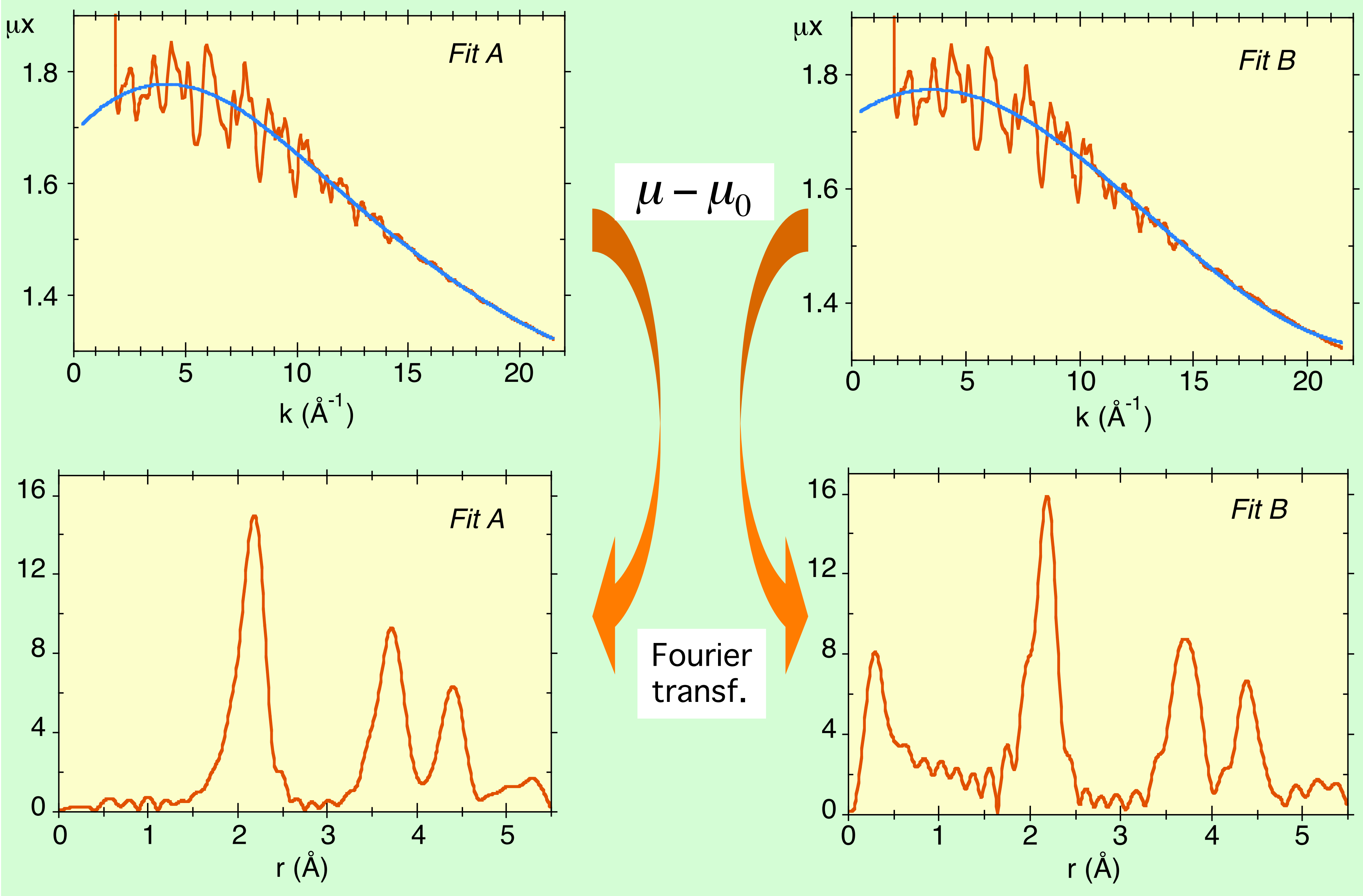

EXAFS signal

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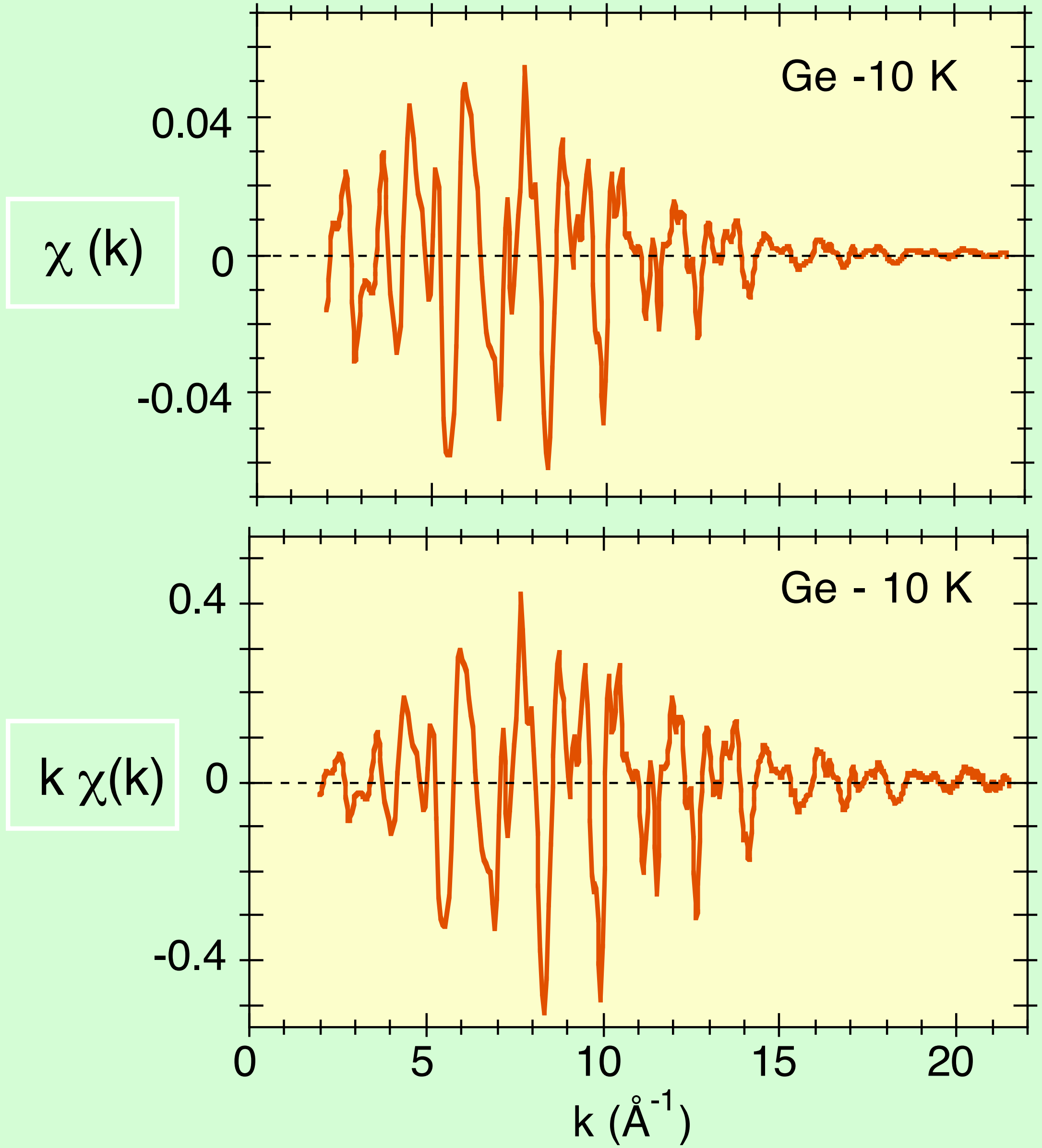
$$\chi(k) = \frac{\mu - \mu_0}{\mu_1}$$



EXAFS signals: examples

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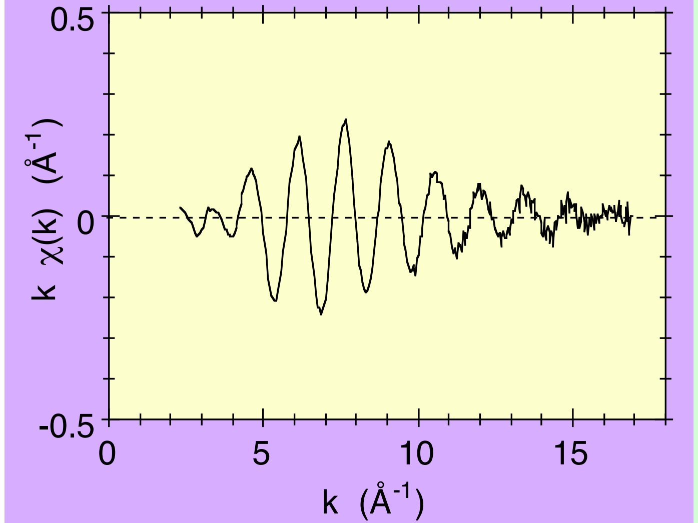
Amorphous Germanium

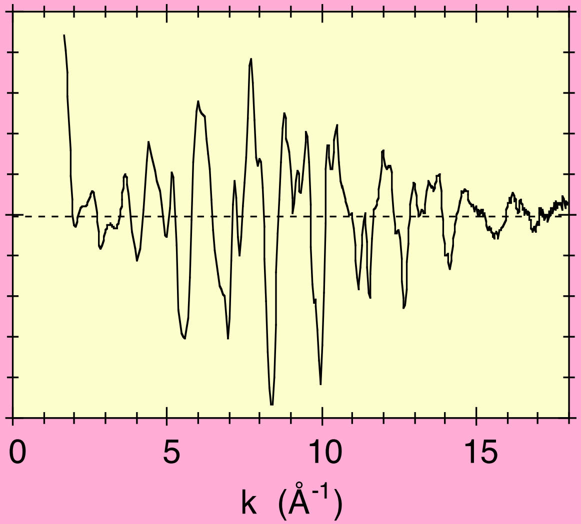
T = 77 K



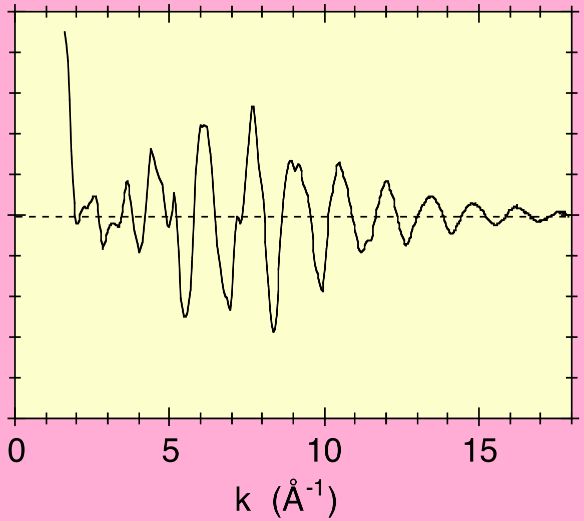
1 coord. shell

Crystalline Germanium

T = 77 K



T = 300 K



Several coord. shells

Temperature effect

Diffraction .vs. EXAFS - (b)

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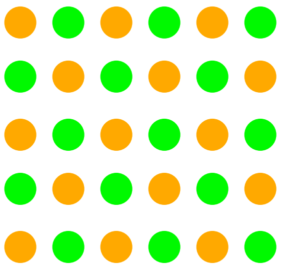
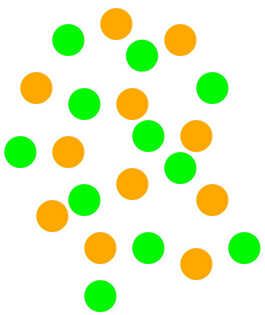
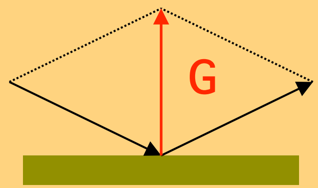
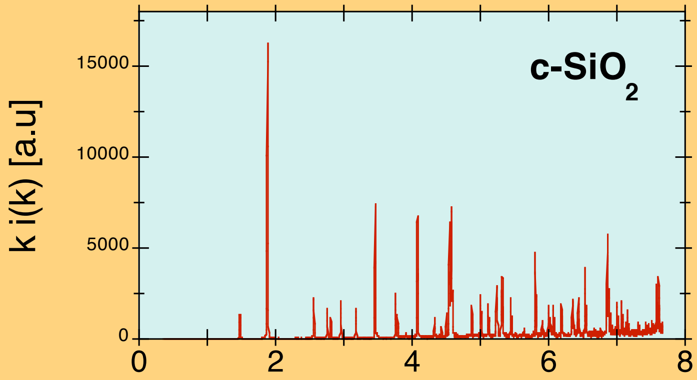
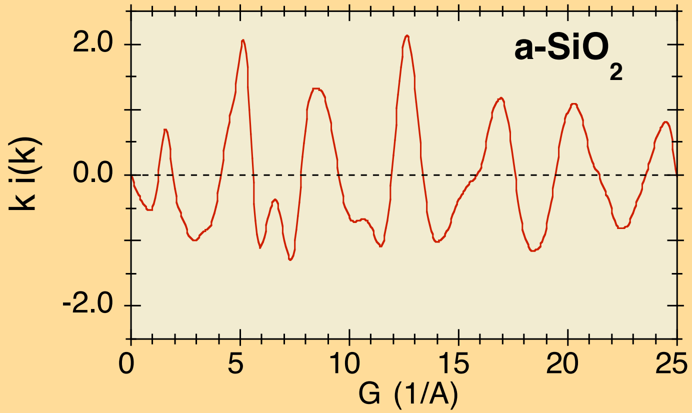




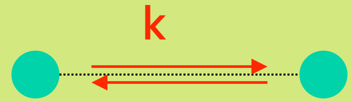
Diffraction

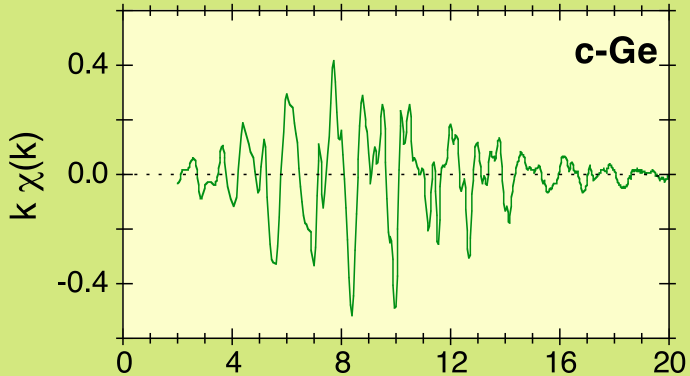


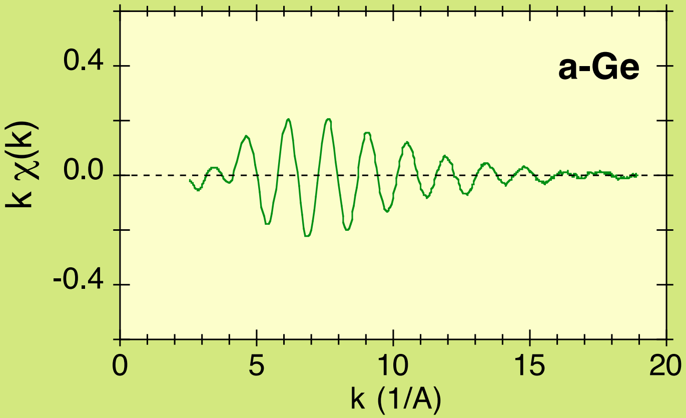




EXAFS







Quantitative analysis of EXAFS

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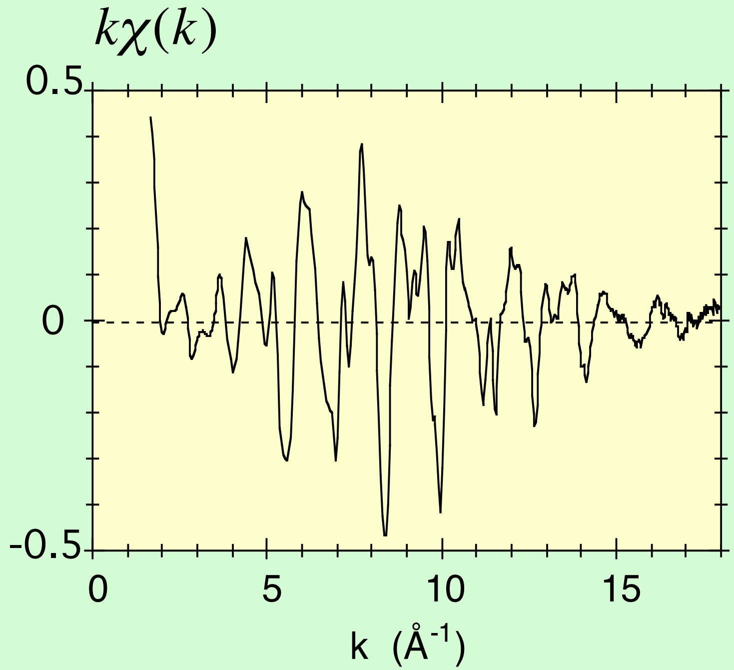
$$\chi(k) = \sum_i A_i(k) \sin \Phi_i(k)$$

Sum over:
- S.S. paths (coord. shells)
- M.S. paths



Input for each path:
- backscattering amplitude
- phaseshifts
- inelastic terms

Different analysis procedures

EXAFS data analysis

- ♠ Fourier transform

Data analysis - Fourier Transform k→r

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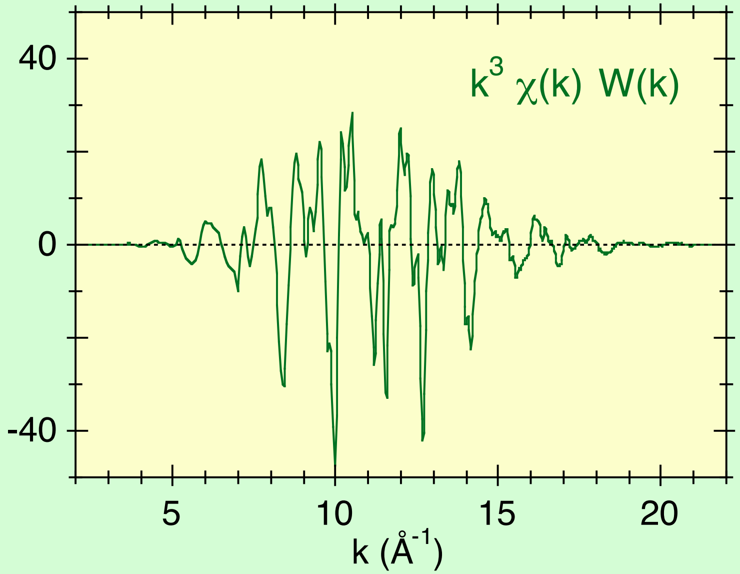
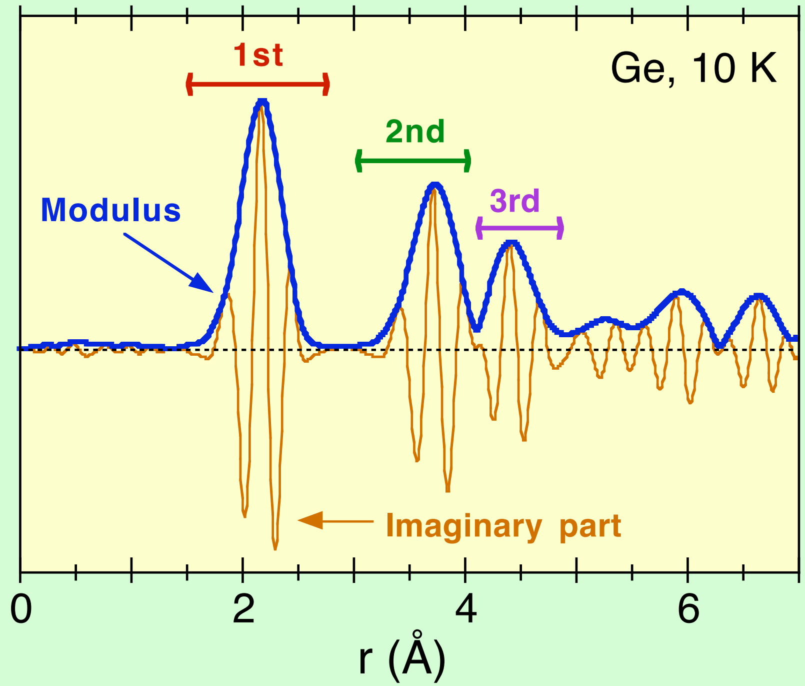


weight   window

$$F(r) = \int_{k_{min}}^{k_{max}} \chi(k)\, k^n\, W(k)\, e^{2ikr}\, dk$$



Peak's position and shape influenced by:

- total phaseshifts
- disorder
- Fourier transform window

Fourier Transform and distribution

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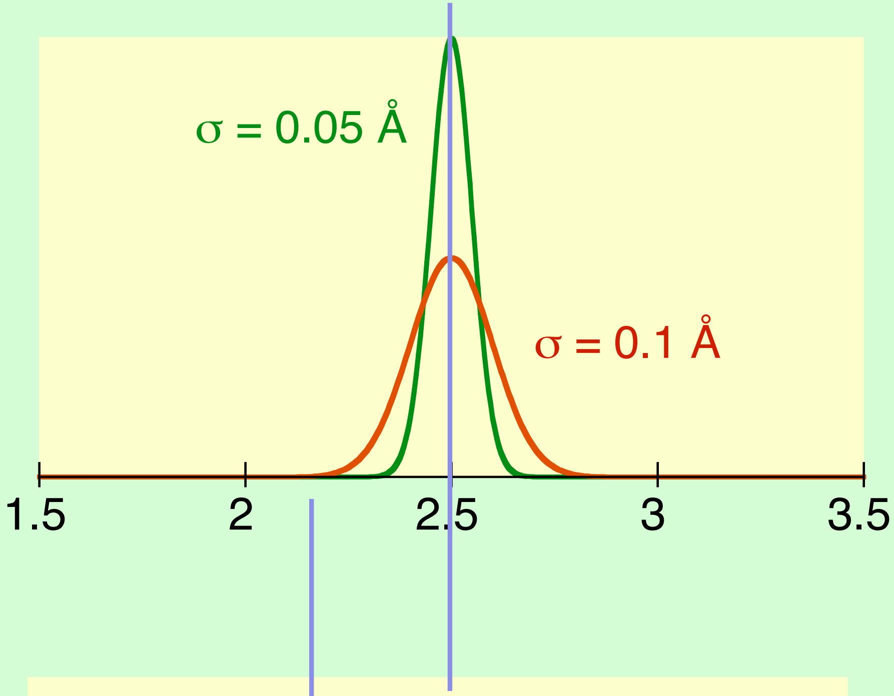
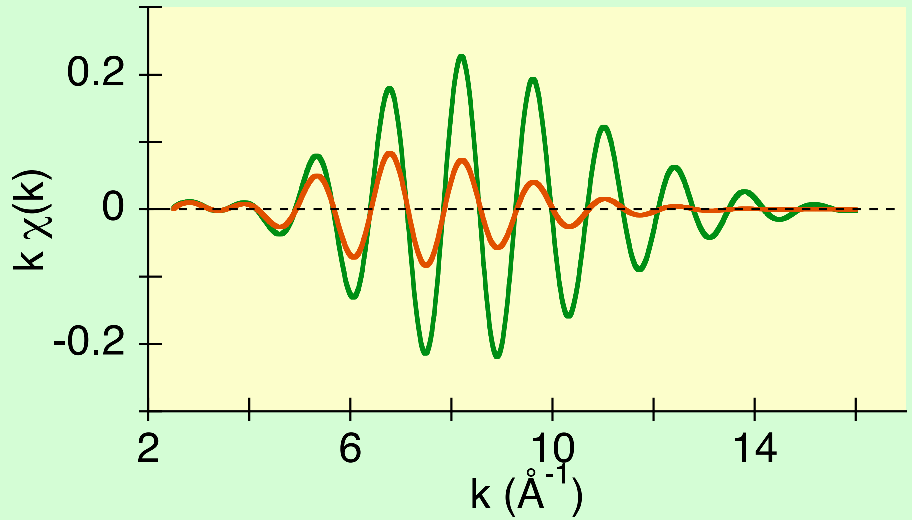
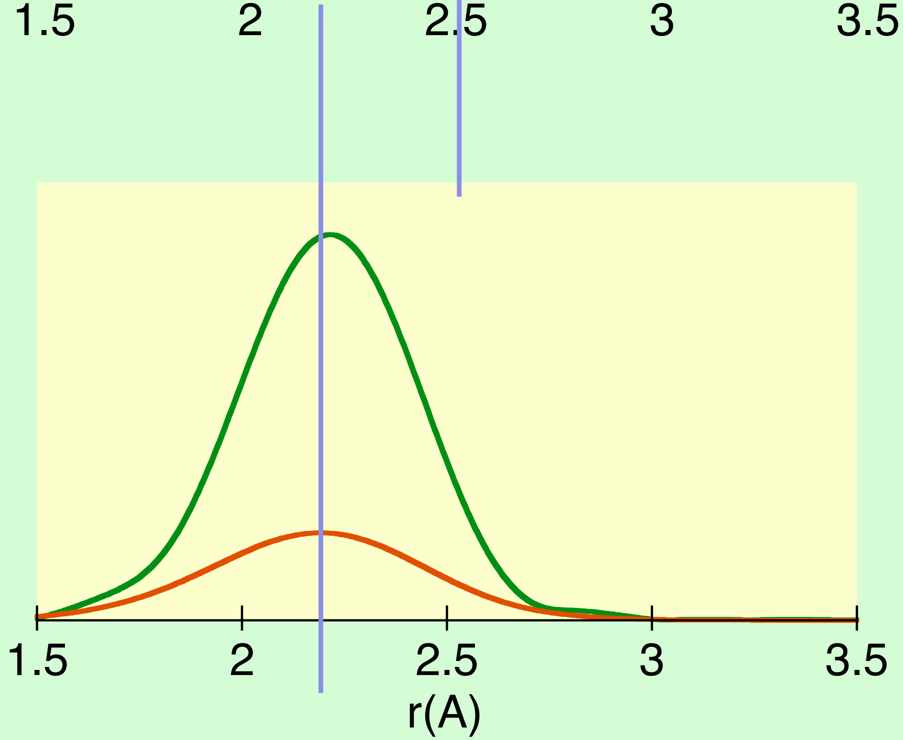


EXAFS simulation
(Ge phases and amplit.)



F.T.: k=2.5-16
K^3, square w.



26 - Iron: bcc structure

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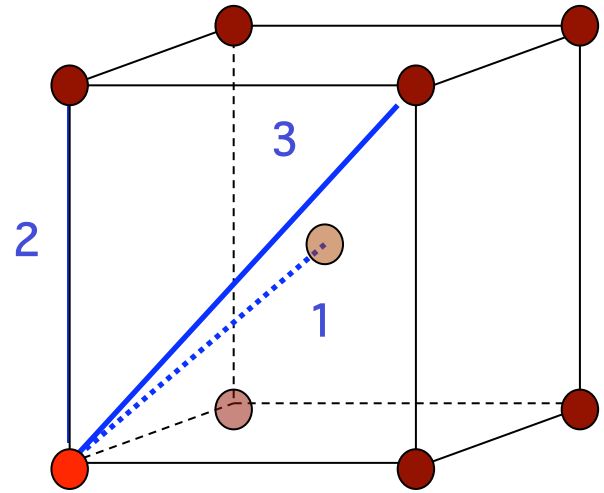
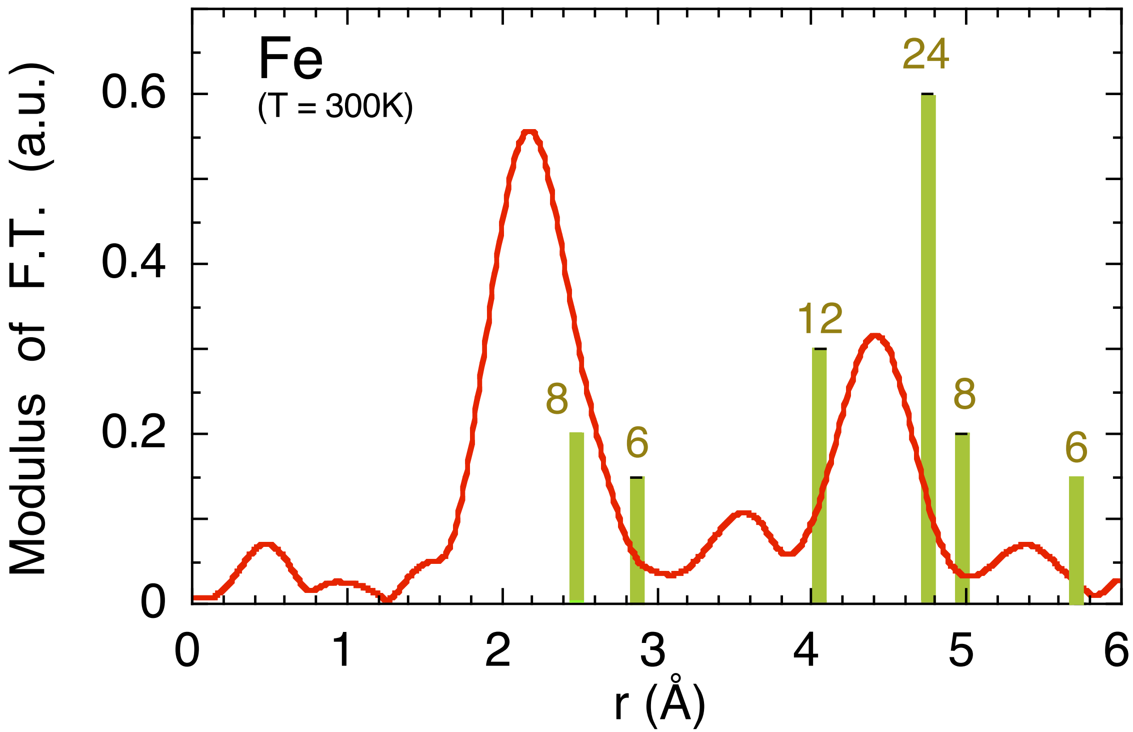
i	N_i	R_i (Å)
1	8	2.48
2	6	2.86
3	12	4.05
4	24	4.75
5	8	4.96
6	6	5.73





- Peak shift
- Superposition of shells

29 - Copper: fcc structure

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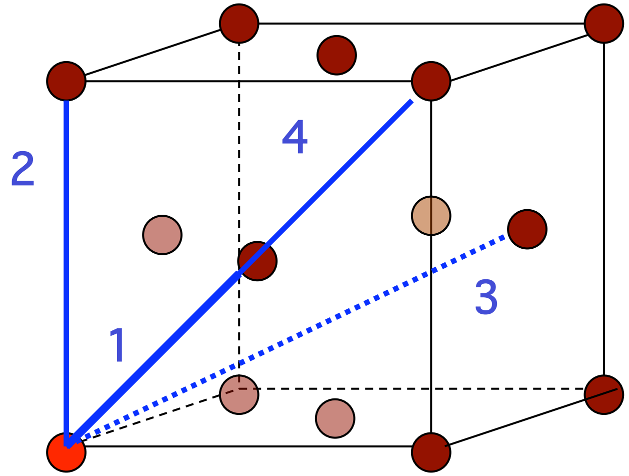
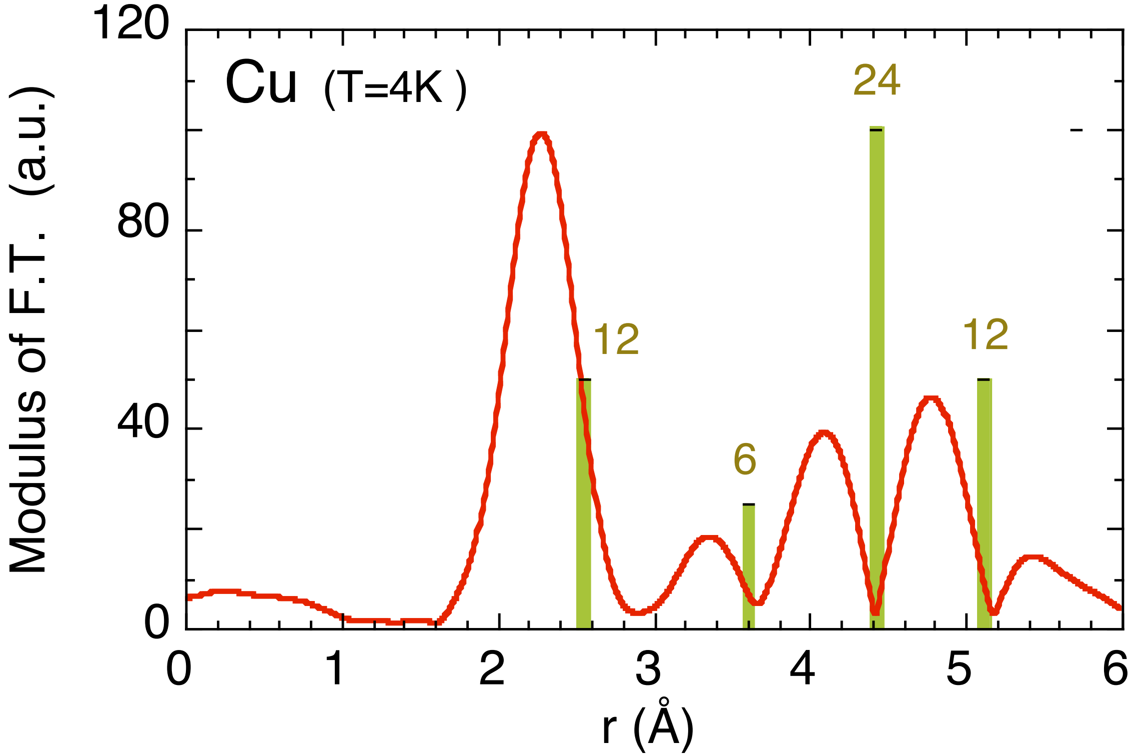
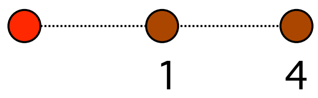
i	N_i	R_i (Å)
1	12	2.55
2	6	3.61
3	24	4.42
4	12	5.10
5	24	5.70
6	8	6.25





- Peak shift
- Focussing effect



29-Cu: temperature effects

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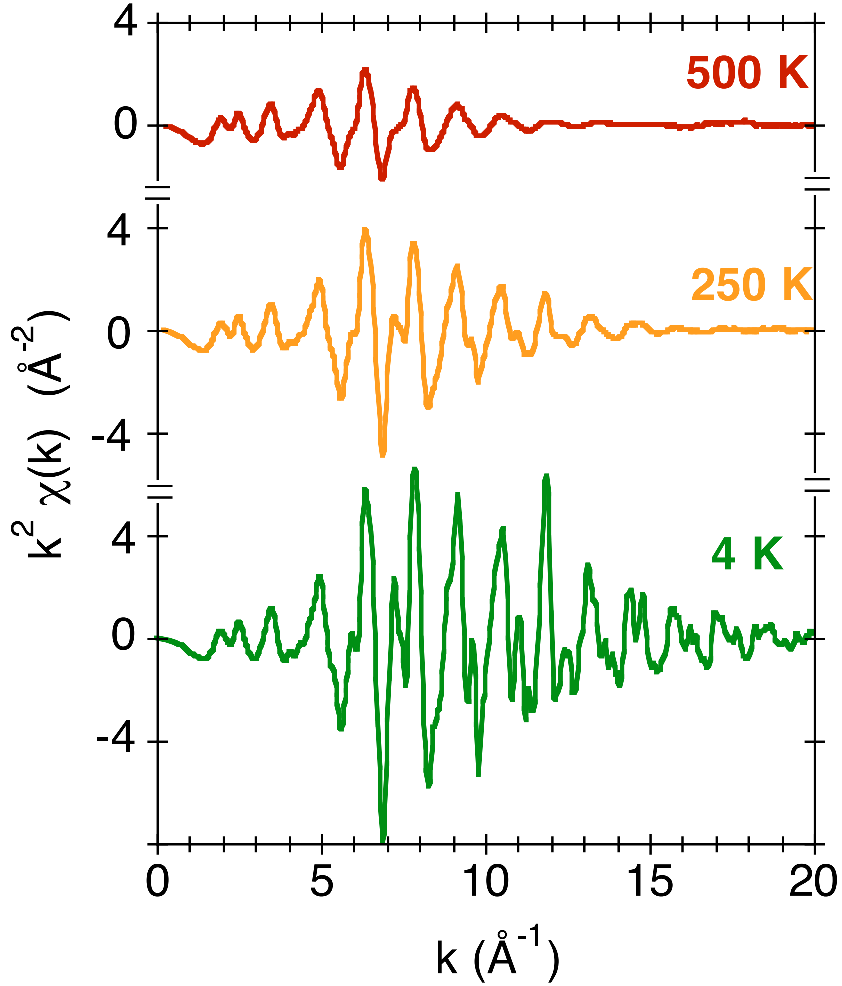
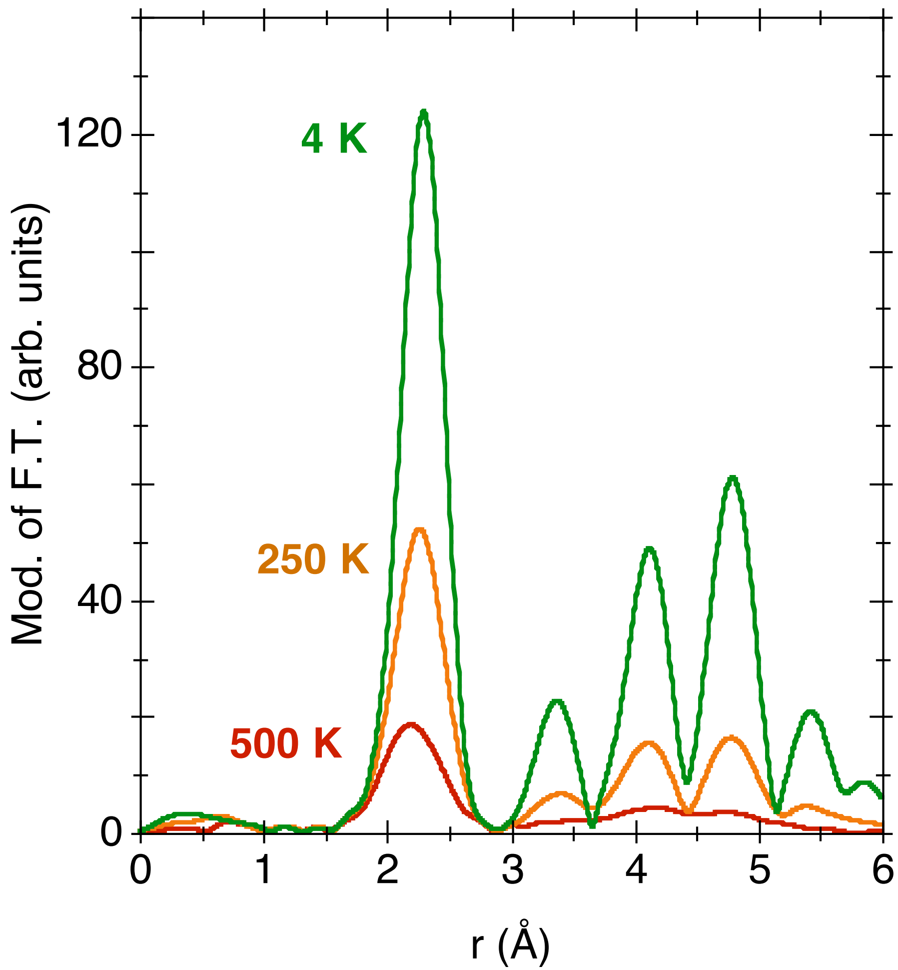
- EXAFS signals



- Fourier transforms



32 - Germanium: diamond structure

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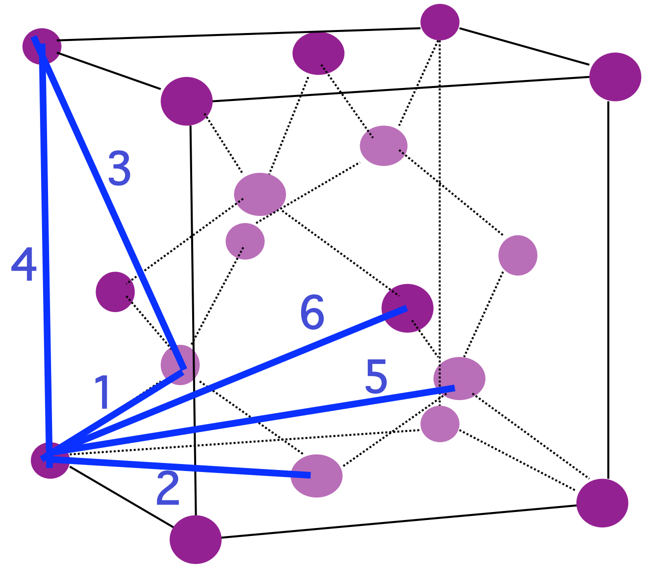
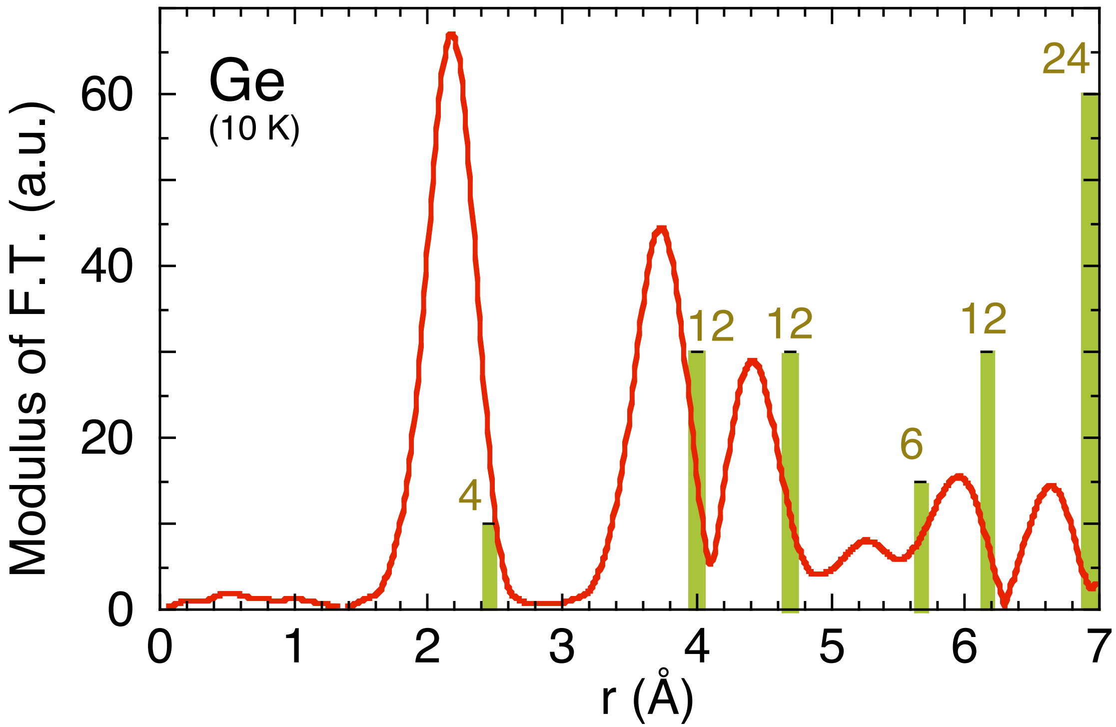
i	N_i		R_i (Å)
1	4	$a(\sqrt{3})/4$	2.45
2	12	$a/\sqrt{2}$	4.00
3	12	$a(\sqrt{11})/4$	4.69
4	6	a	5.66
5	12	$a(\sqrt{19})/4$	6.16
6	24	$a(\sqrt{6})/2$	6.93



a = 5.66 Å



32-Ge: crystalline and amorphous

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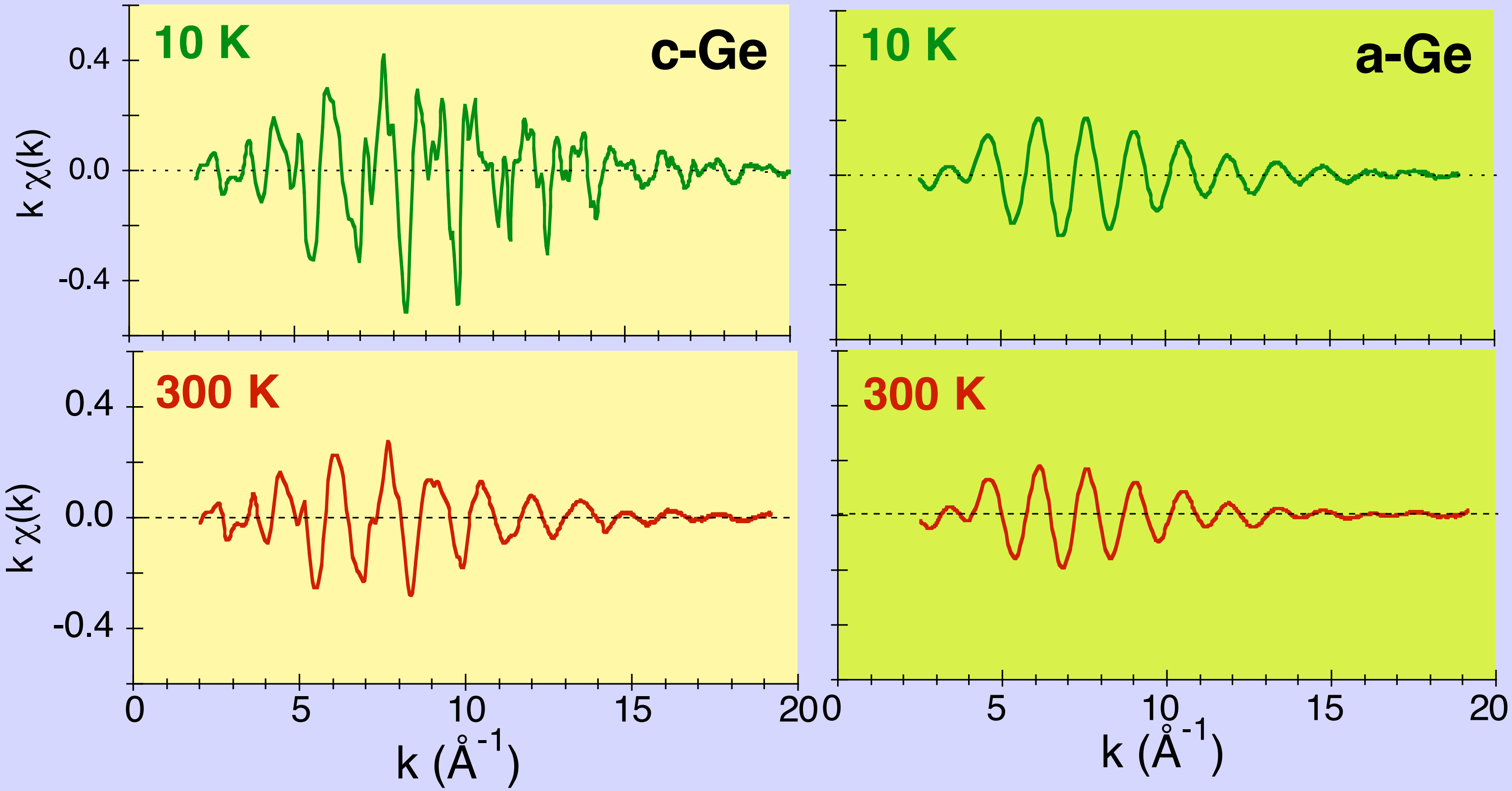
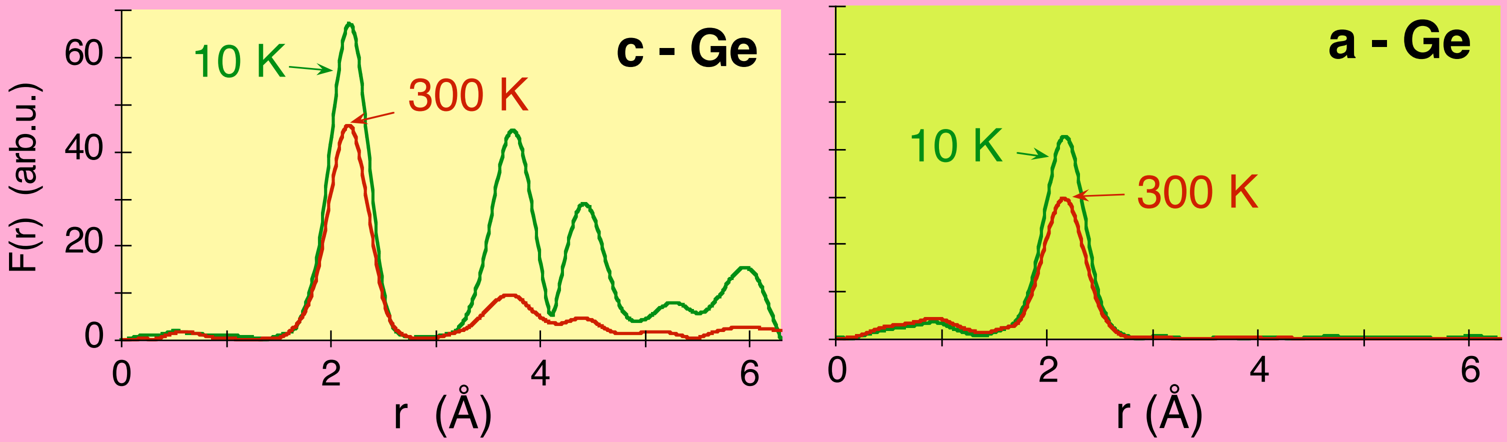
EXAFS signals



Fourier transforms



EXAFS data analysis

- ♠ First shell analysis

1st-shell Fourier back-transform

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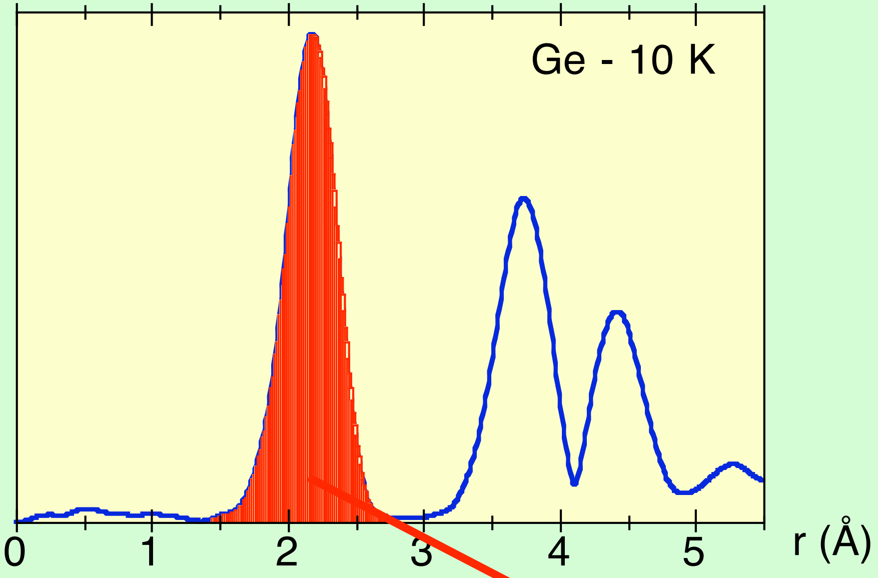
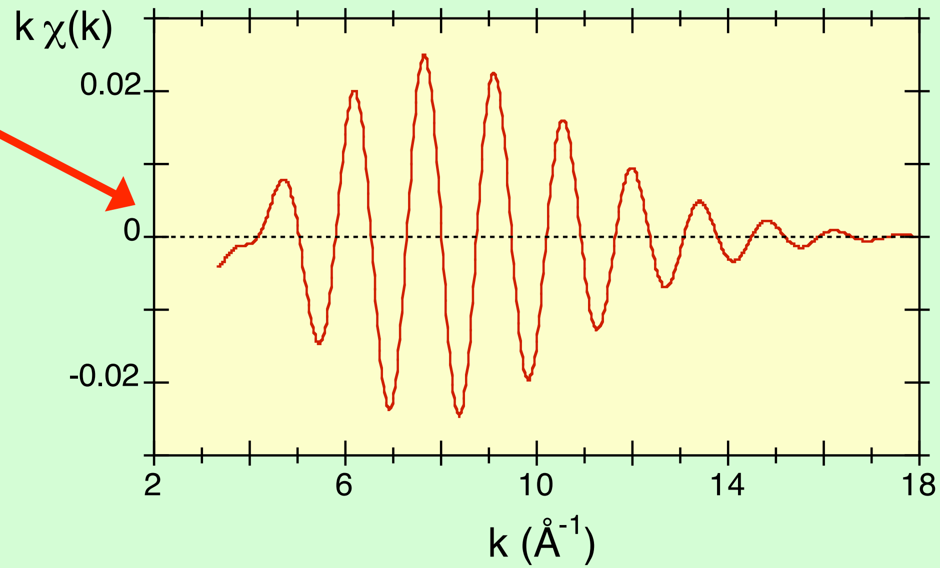


$$\chi'(k) = (2/\pi)\int_{r_{\min}}^{r_{\max}} F(r)\, W'(r)\, e^{-2ikr}\, dr$$

First-shell contribution



- No peak superposition
- No MultipleScattering
- F.T. artifacts

1st-shell distribution of distances

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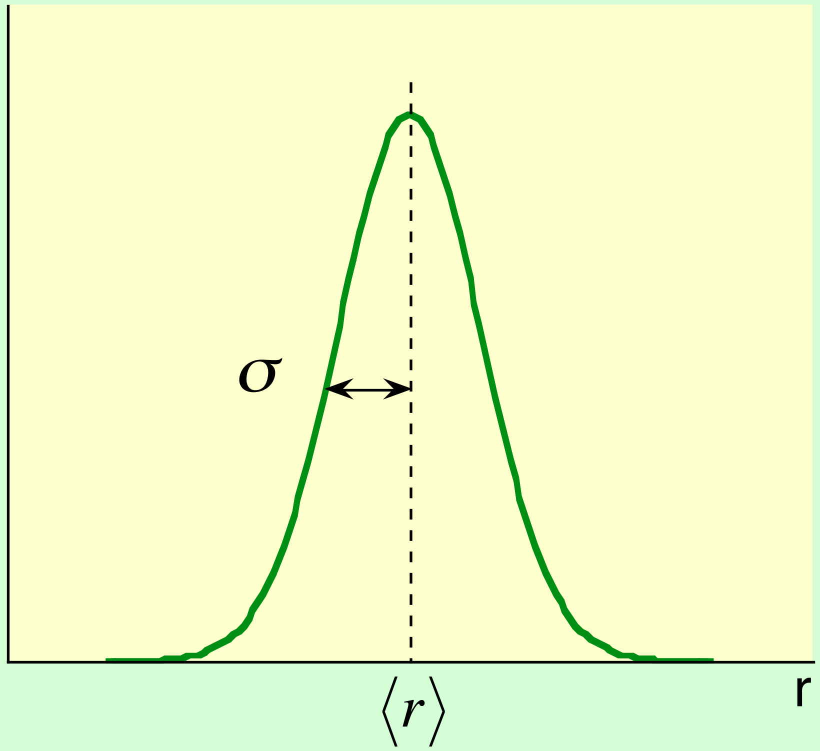
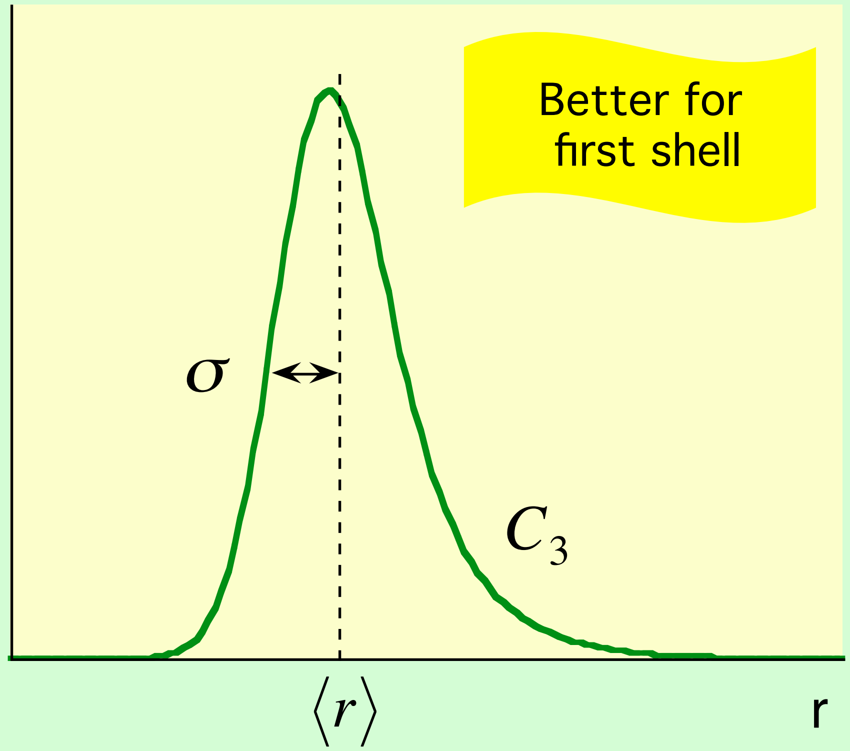
Gaussian approximation



Asymmetric distribution



$$\sigma^2 = \left\langle \left(r - \langle r \rangle\right)^2 \right\rangle$$

$$C_3 = \left\langle \left(r - \langle r \rangle\right)^3 \right\rangle$$

EXAFS distance

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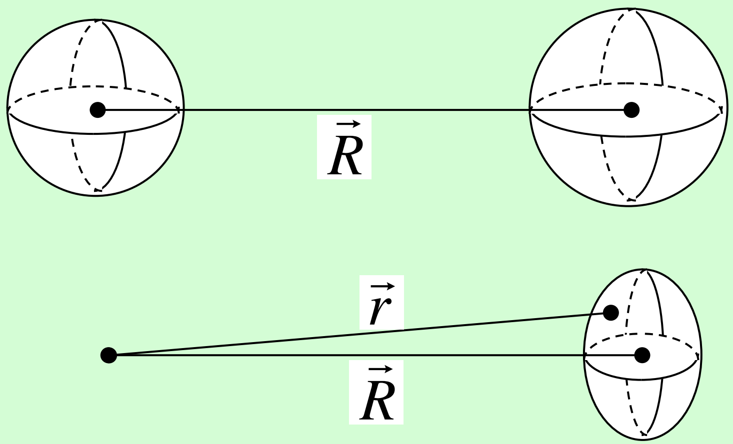

EXAFS, diffuse scattering

$$\langle r \rangle = \langle |\vec{r}_b - \vec{r}_a| \rangle$$

Bragg diffraction, dilatometry

$$R = |\langle \vec{r}_b \rangle - \langle \vec{r}_a \rangle|$$

$$\langle r \rangle > R$$

Real and effective distributions

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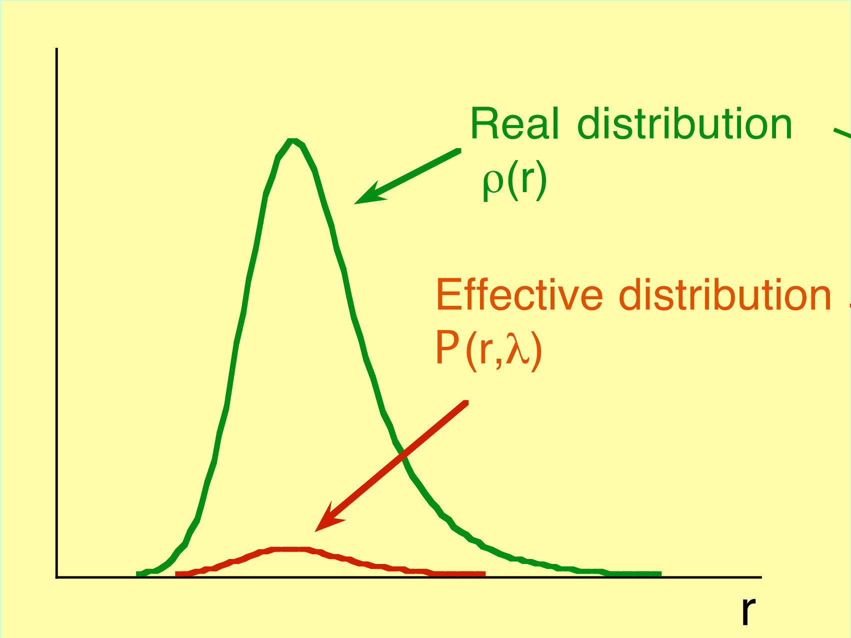

$$\rho_s(r)\,\frac{e^{-2r_s/\lambda(k)}}{r_s^2}$$

$$\langle r\rangle_{\text{eff}} = \langle r\rangle_{\text{real}} - \frac{2\sigma^2}{\langle r\rangle}\left(1-\frac{\langle r\rangle}{\lambda}\right)$$

C_1 $\langle r\rangle$

EXAFS for first shell

Approx.: Single Scattering
Plane waves

- Theory (interaction potentials + scattering theory)
- Experiment (reference samples)

Inelastic terms

Back-scattering amplitude

Total phase-shift

$$k\,\chi(k) = \frac{S_0^2\, e^{-2C_1/\lambda}}{C_1^2}\,|f(k,\pi)|\,N \exp\left[-2k^2\sigma^2\right] \sin\left[2kC_1 - \frac{4}{3}k^3 C_3 + \phi(k)\right]$$

Coordination number .... N

Debye-Waller .... σ^2

Average distance and asymmetry .... C_1 C_3

Analysis - non-linear fitting method

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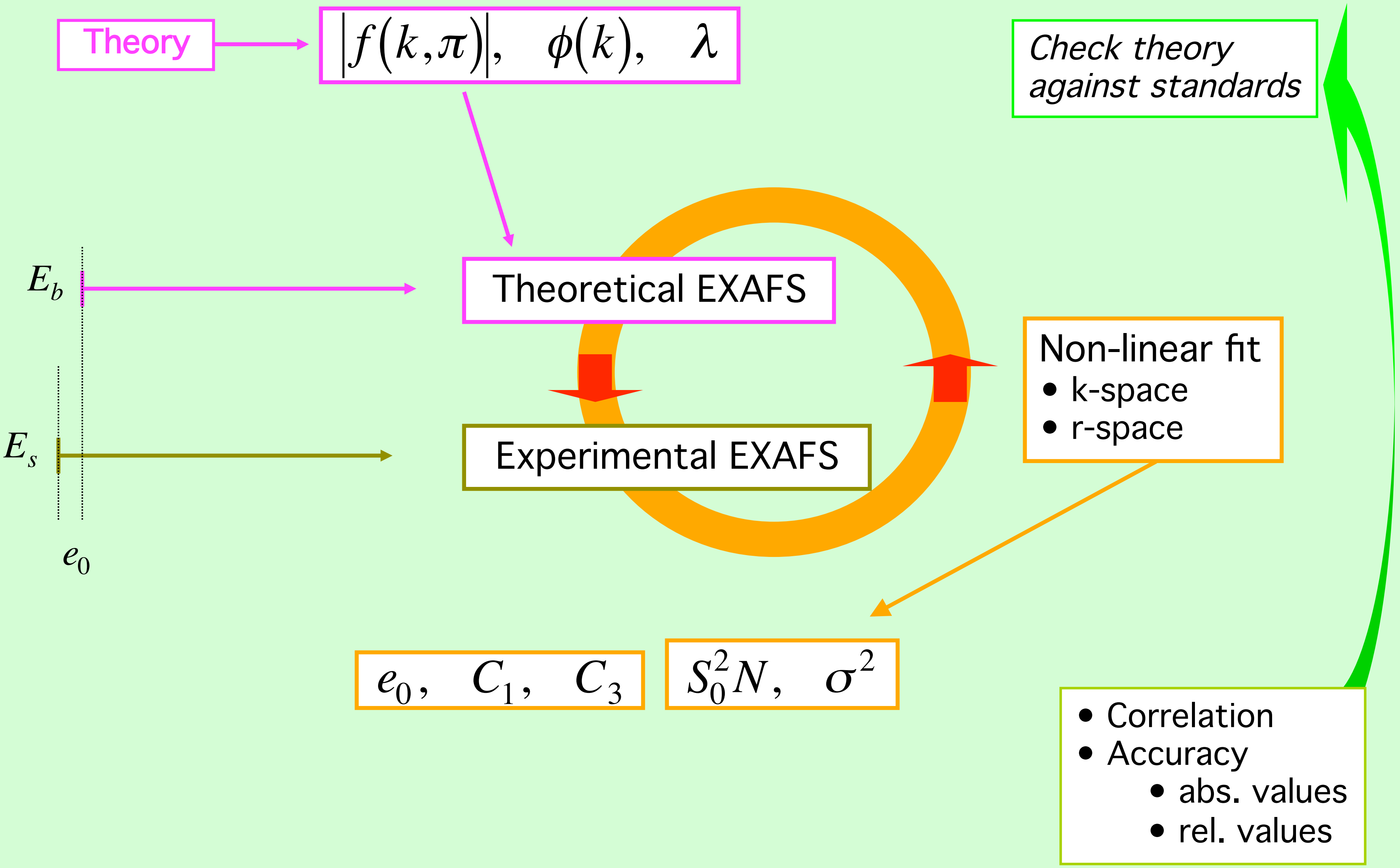

EXAFS data analysis

♠ 1st shell phase and amplitude analysis

Separate evaluation of phase and amplitude

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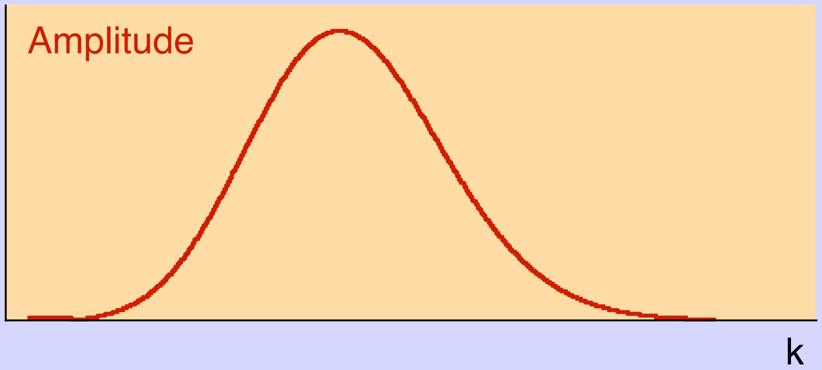
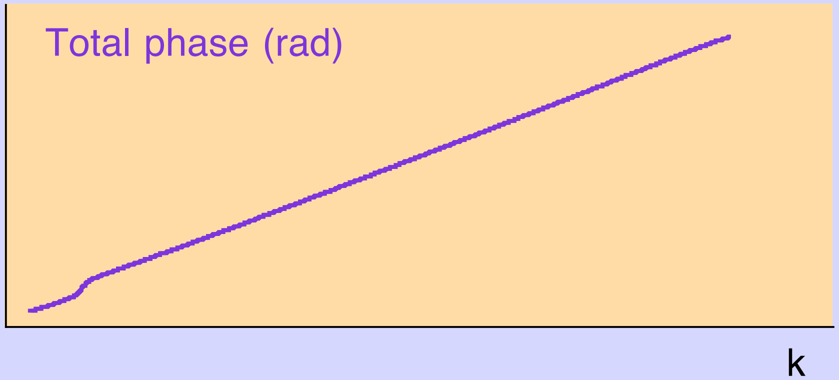
From complex Fourier transform and back-transform





$$A(k) = \frac{S_0^2\, e^{-2C_1/\lambda}}{C_1^2} \left| f(k,\pi) \right| N \exp\left[-2k^2 C_2 + \frac{2}{4} k^4 C_4 + \dots \right]$$

?

$$\Phi(k) = 2kC_1 - \frac{4}{3} k^3 C_3 + \dots + \phi(k)$$

?

“Ratio method” - phases

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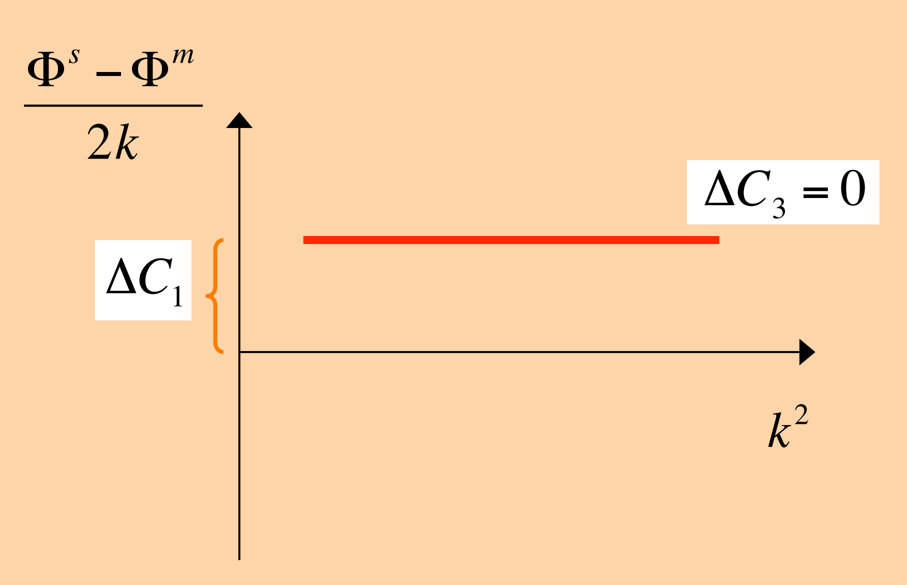
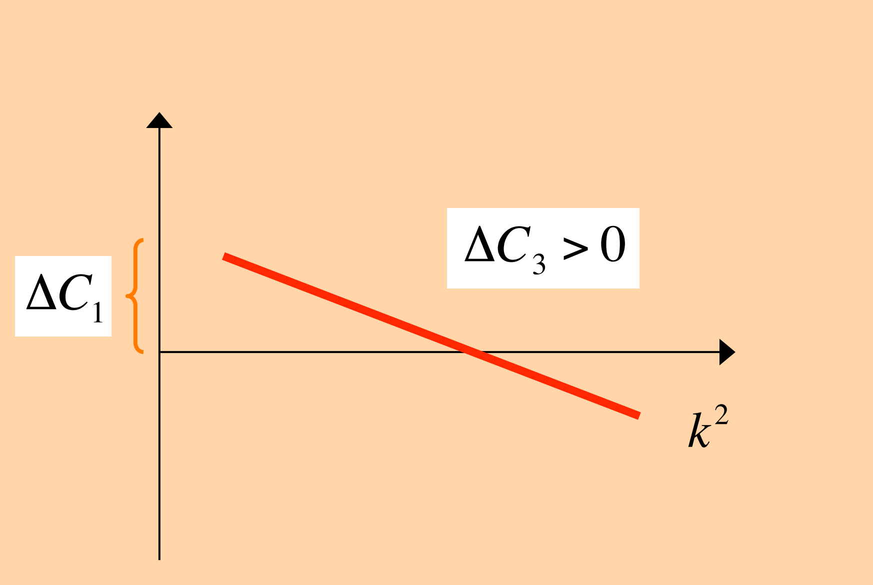
If suitable model compound available ...

s = sample
m = model

$$\Phi^s - \Phi^m = 2k\left(C_1^s - C_1^m\right) - \frac{4}{3}k^3\left(C_3^s - C_3^m\right)$$

$$\frac{\Phi^s - \Phi^m}{2k} = \left(C_1^s - C_1^m\right) - \frac{4}{3}k^2\left(C_3^s - C_3^m\right)$$





"Ratio method" - amplitudes

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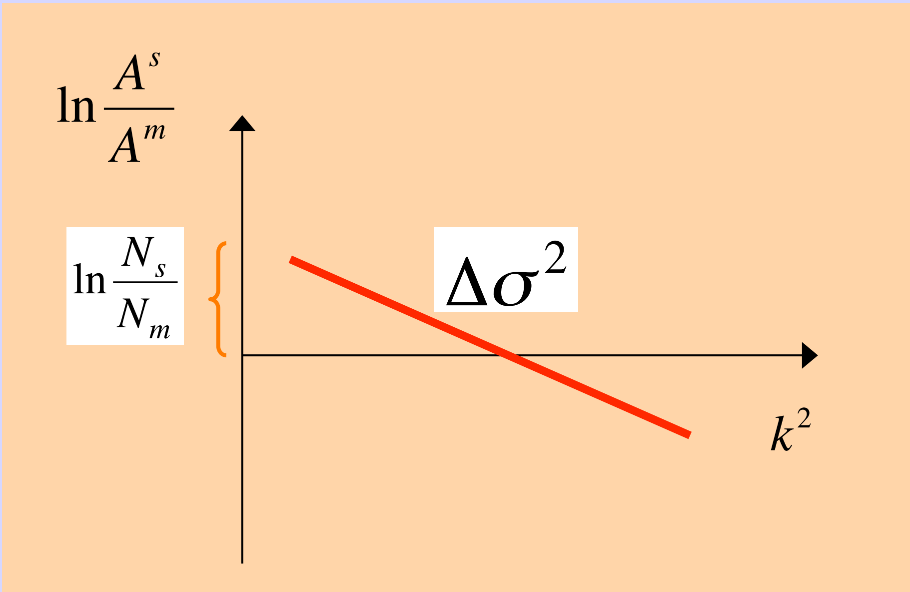
If suitable model compound available ...

s = sample
m = model

$$\ln \frac{A^s}{A^m} \cong \ln \frac{N^s}{N^m} - 2k^2\left(\sigma_s^2 - \sigma_m^2\right)$$

intercept: $\ln \frac{N^s}{N^m}$

Slope: $-2k^2\left(\sigma_s^2 - \sigma_m^2\right)$



"Ratio method" - results

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Ratio of coordination numbers

$$\frac{N^s}{N^m}$$

Relative values :

$$\begin{cases} \Delta C_1 \\ \Delta\sigma^2 \\ \Delta C_3 \end{cases}$$

→ Thermal expansion

Width

Asymmetry

- Absolute values ?
- Physical meaning ?

“Ratio method” - OK when ...

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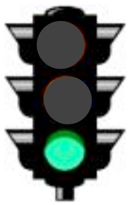
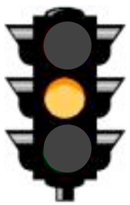
- *Only Single Scattering*
- *Only one distance*
- *Suitable reference model available*

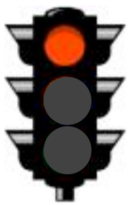
$$\chi(k) \quad = \quad A(k)\sin\Phi(k)$$



- First coordination shell, one distance
- Same sample-model chemical environment
  T or p-dep. Studies
  Amorphous .vs. crystalline samples



- 1st shell, different sample-model
  chemical environment
- Separated outer shells, weak M.S.



- 1st shell in bcc structure (2 distances)
- Superposed outer shells
- M.S. contributions

Depending on sought accuracy

EXAFS data analysis

- ♠ Outer shells analysis

Analysis - Outer shells back-transform r→k

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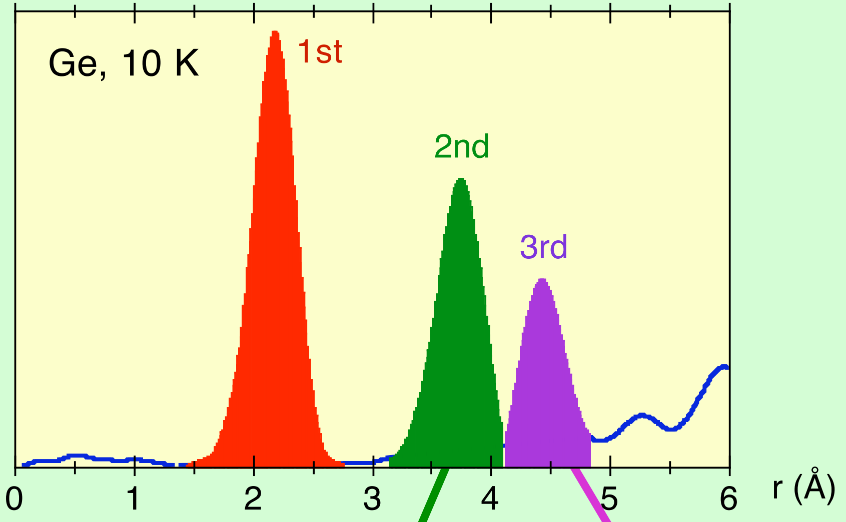
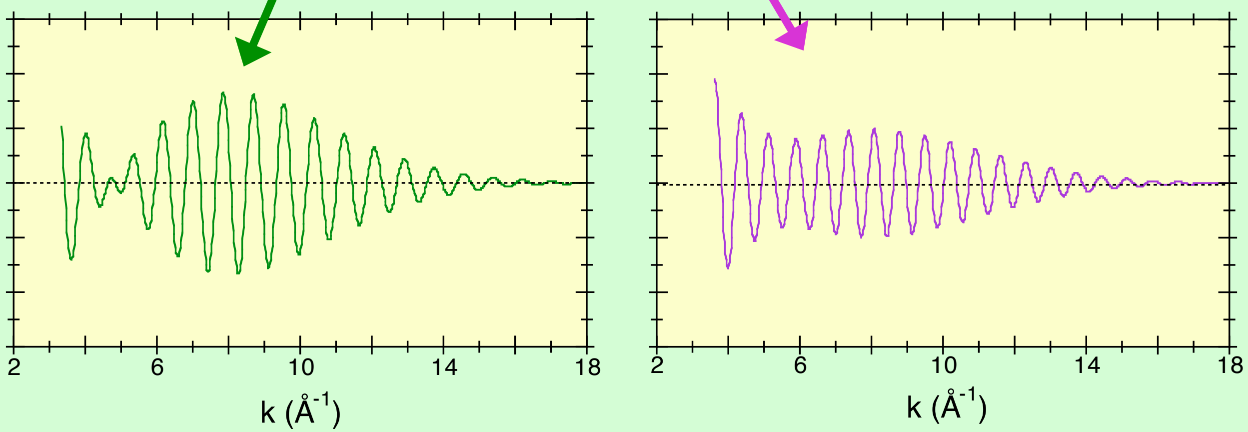


- Peak superposition
- MultipleScattering
- F.T. artifacts

$$\chi'(k) = (2/\pi)\int_{r_{min}}^{r_{max}} F(r)\, W'(r)\, e^{-2ikr}\, dr$$



Sometimes OK
for D.W. factors

Analysis - non-linear fitting of outer shells

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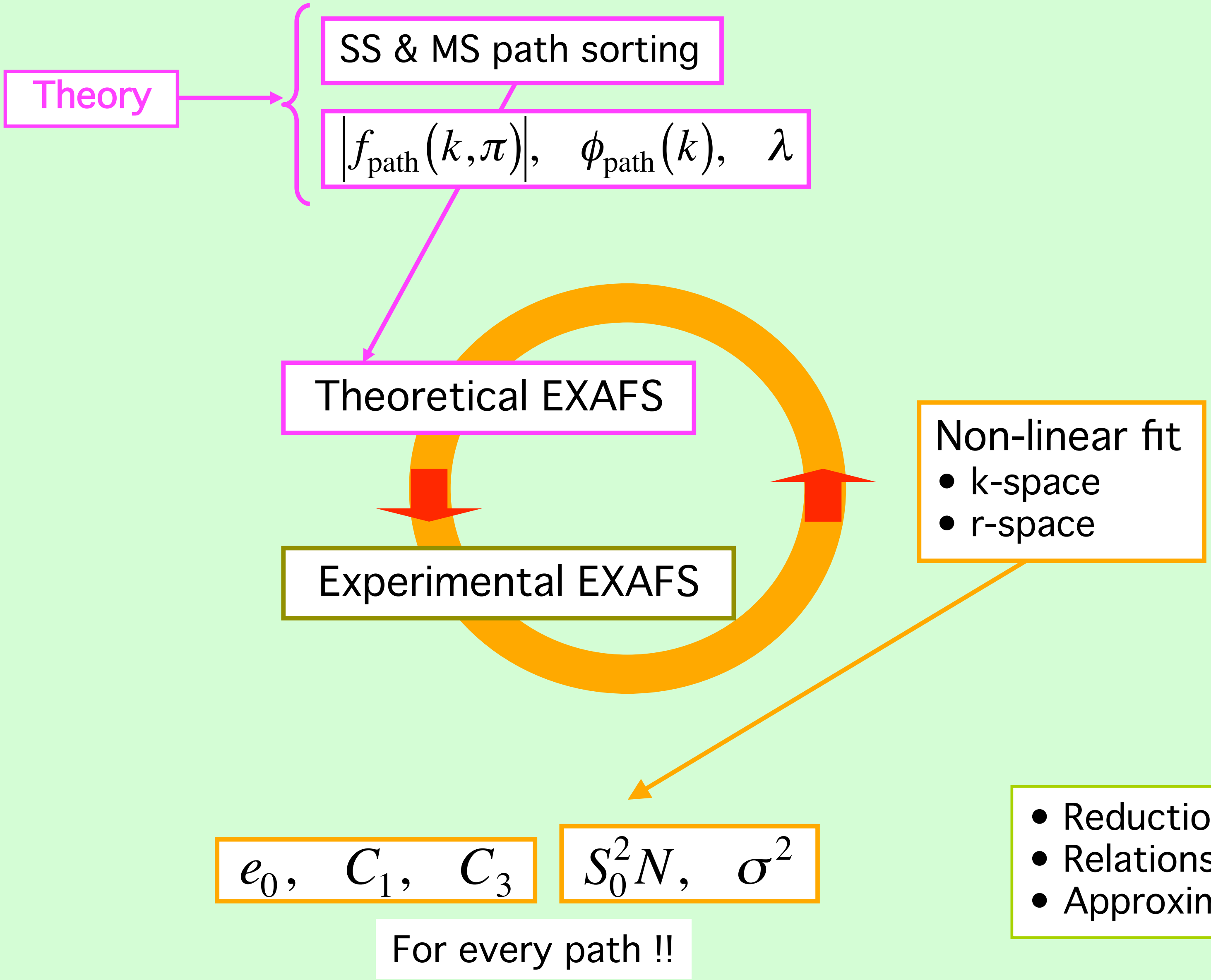

• Reduction of free param.
• Relations between param.
• Approximations

Analysis - Independent parameters

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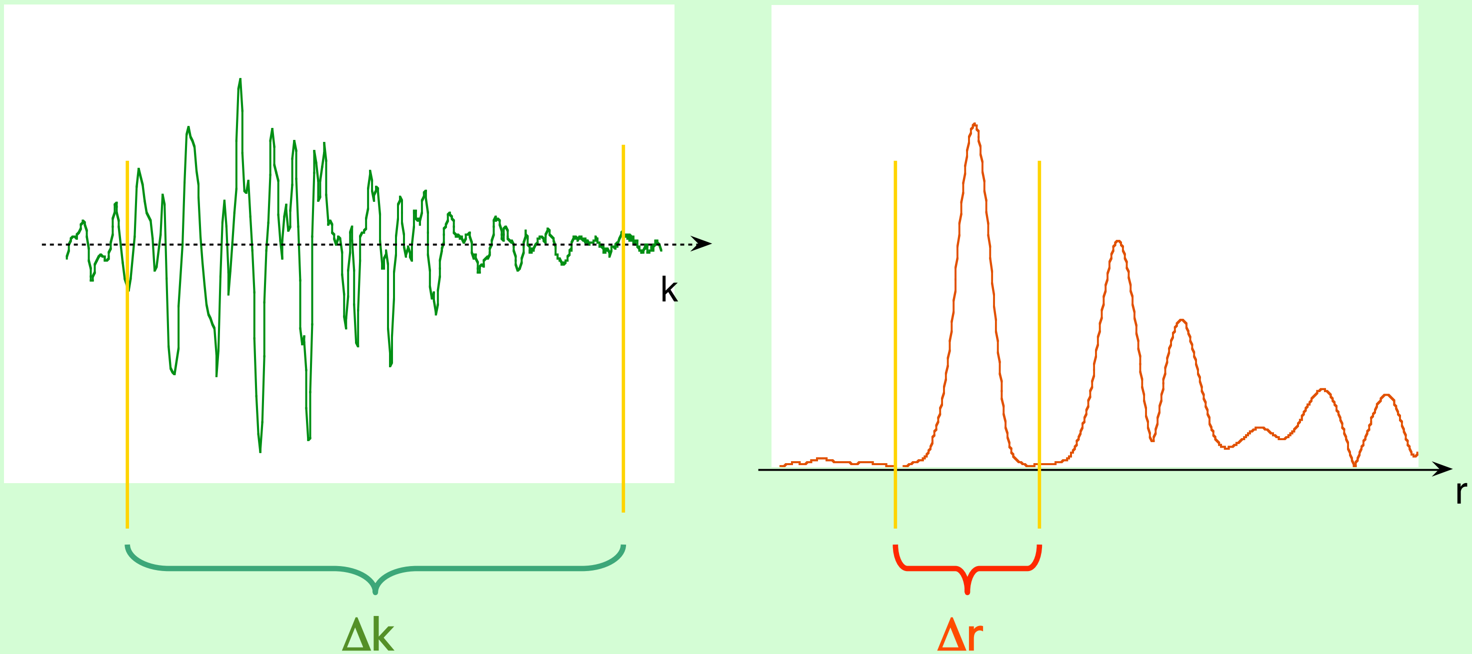

$$N_{ind} = \frac{2\,\Delta k\,\Delta r}{\pi} + 1$$

Maximum number
of independent parameters

Correlation of
parameters

EXAFS data analysis

- ♠ Interpretation of results

Thermal expansion

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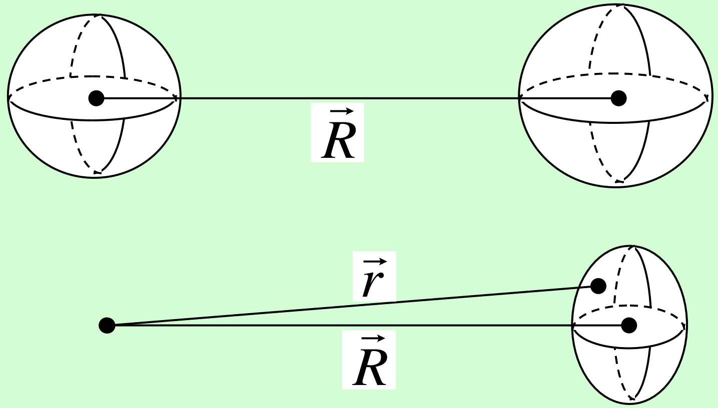
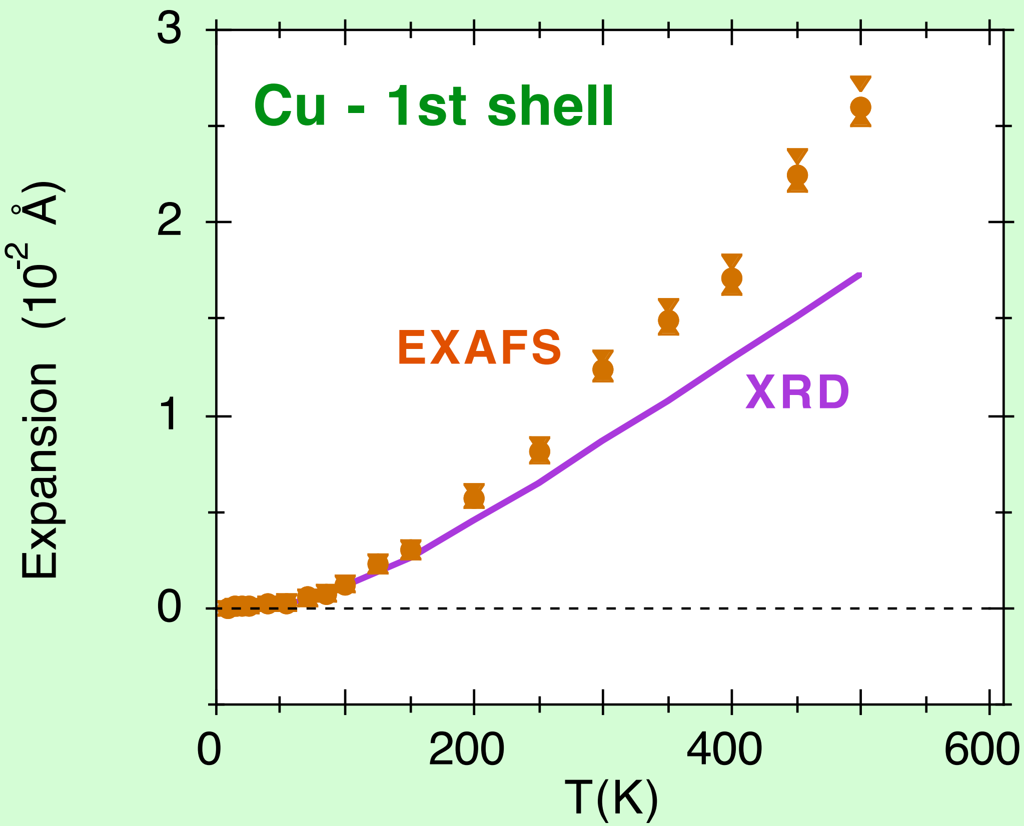
Bragg diffraction ➔ lattice expansion

EXAFS ➔ bond expansion





Complementarity EXAFS - XRD:
Info on perpendicular vibrations

Mean Square Relative Displacements

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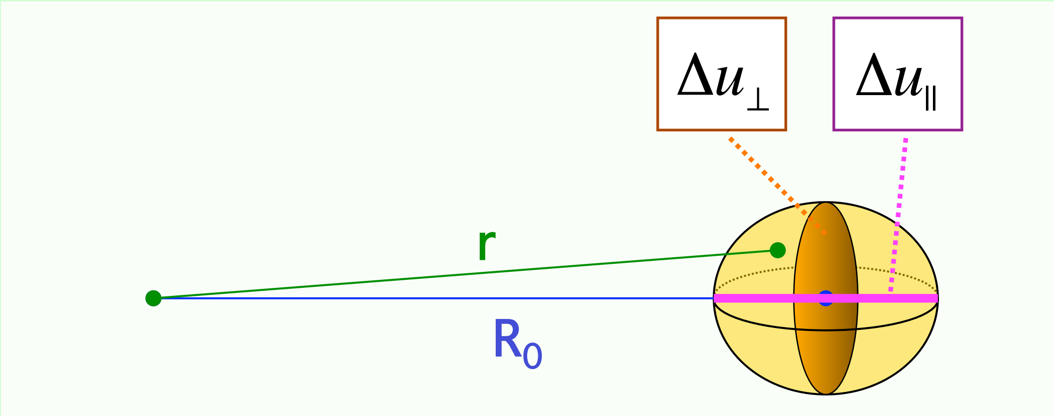

Mean values (harmonic approximation)

$$\langle \Delta u_\parallel \rangle = 0$$

$$\langle r \rangle \approx R_0 + \frac{\langle \Delta u_\perp^2 \rangle}{2R_0}$$

$$\sigma^2 \approx \langle \Delta u_\parallel^2 \rangle$$

$MSRD_\perp$

$MSRD_\parallel$

Bond distances

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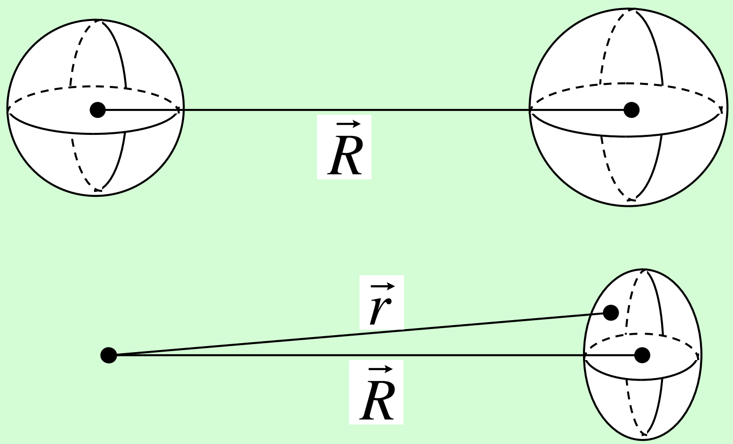

EXAFS, diffuse scattering

$$\langle r \rangle = \langle |\vec{r}_b - \vec{r}_a| \rangle$$

"True" bond length

"True" bond expansion

Bragg diffraction, dilatometry

$$R = |\langle \vec{r}_b \rangle - \langle \vec{r}_a \rangle|$$

"Apparent" bond length

"Apparent" bond expansion

EXAFS Debye-Waller factor

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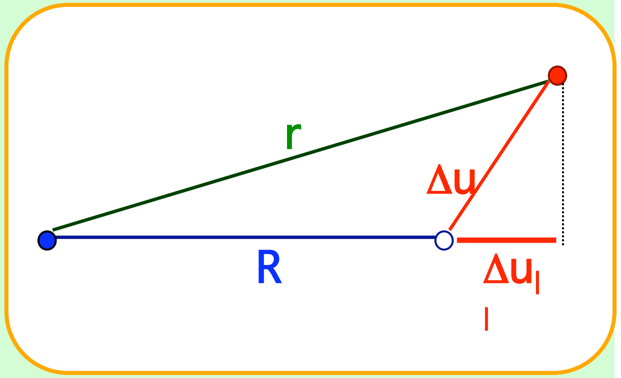
$$\sigma^2 \approx MSRD = \left\langle \Delta u_{\parallel}^2 \right\rangle = \left\langle \left[\hat{R} \cdot (\vec{u}_b - \vec{u}_a) \right]^2 \right\rangle$$

$$= \left\langle \left(\hat{R} \cdot \vec{u}_b \right)^2 \right\rangle + \left\langle \left(\hat{R} \cdot \vec{u}_a \right)^2 \right\rangle - 2 \left\langle \left(\hat{R} \cdot \vec{u}_b \right) \left(\hat{R} \cdot \vec{u}_a \right) \right\rangle$$



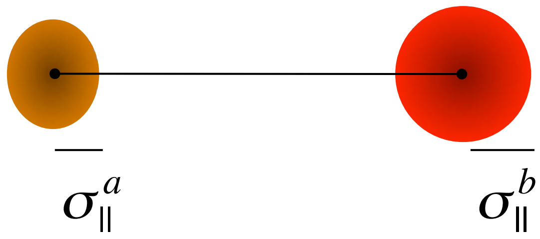
MSD
Mean Square Displacements

DCF
Displacement Correlation Function

Thermal factors from Bragg diffraction:

$$U_{\parallel}^a = \left\langle \left(\hat{R} \cdot \vec{u}_a \right)^2 \right\rangle = \left(\sigma_{\parallel}^a \right)^2$$

$$U_{\parallel}^b = \left\langle \left(\hat{R} \cdot \vec{u}_b \right)^2 \right\rangle = \left(\sigma_{\parallel}^b \right)^2$$



Debye-Waller factor – Debye model

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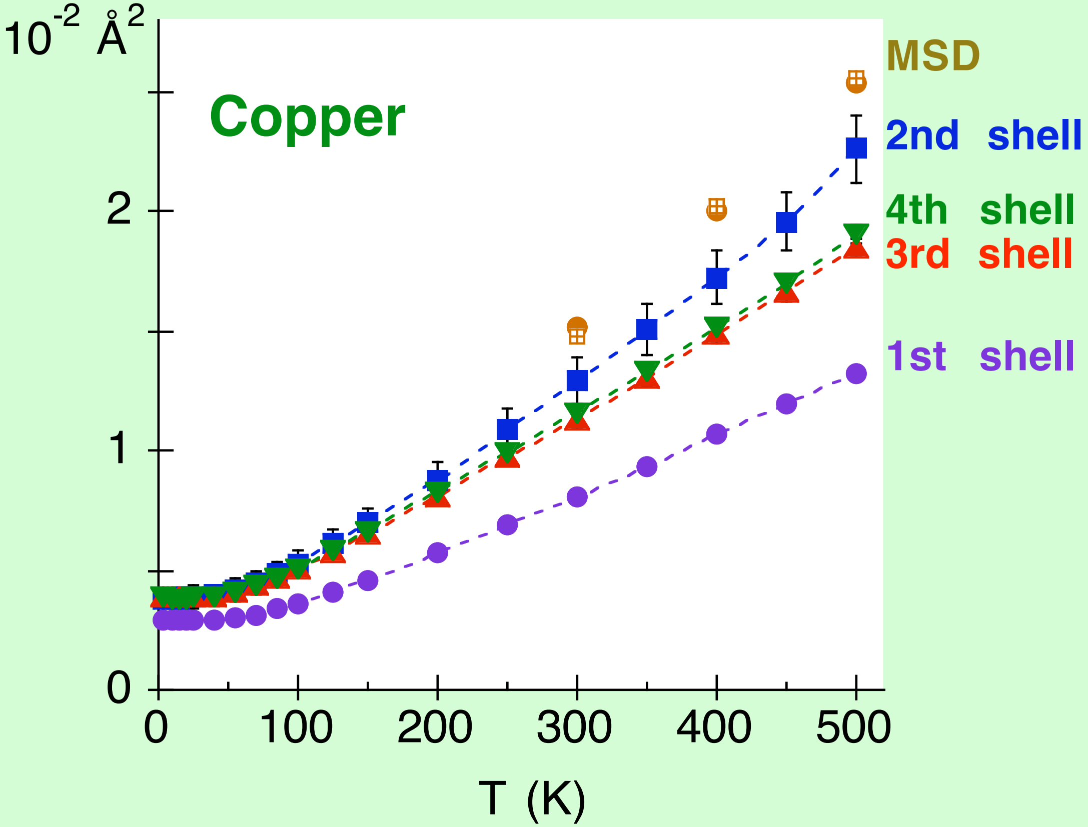
Absolute values
from fit to theoretical models

Debye correlated model
(OK for metals)

$$\sigma^2 = \frac{3\hbar}{2\omega_D^3\mu}\int_0^{\omega_D} \omega \coth\frac{\hbar\omega}{2k_BT}\left[1-\frac{\sin(\omega q_D R)}{\omega q_D R}\right] d\omega$$



θ_D = 315 K
θ_M = 313 K

θ_4 = 321 K
θ_3 = 322 K
θ_2 = 283 K
θ_1 = 328 K

σ^2

- increases with T
- depends on the shell

Correlation

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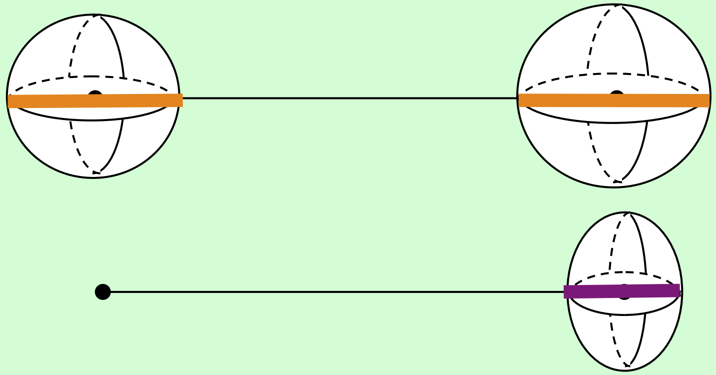
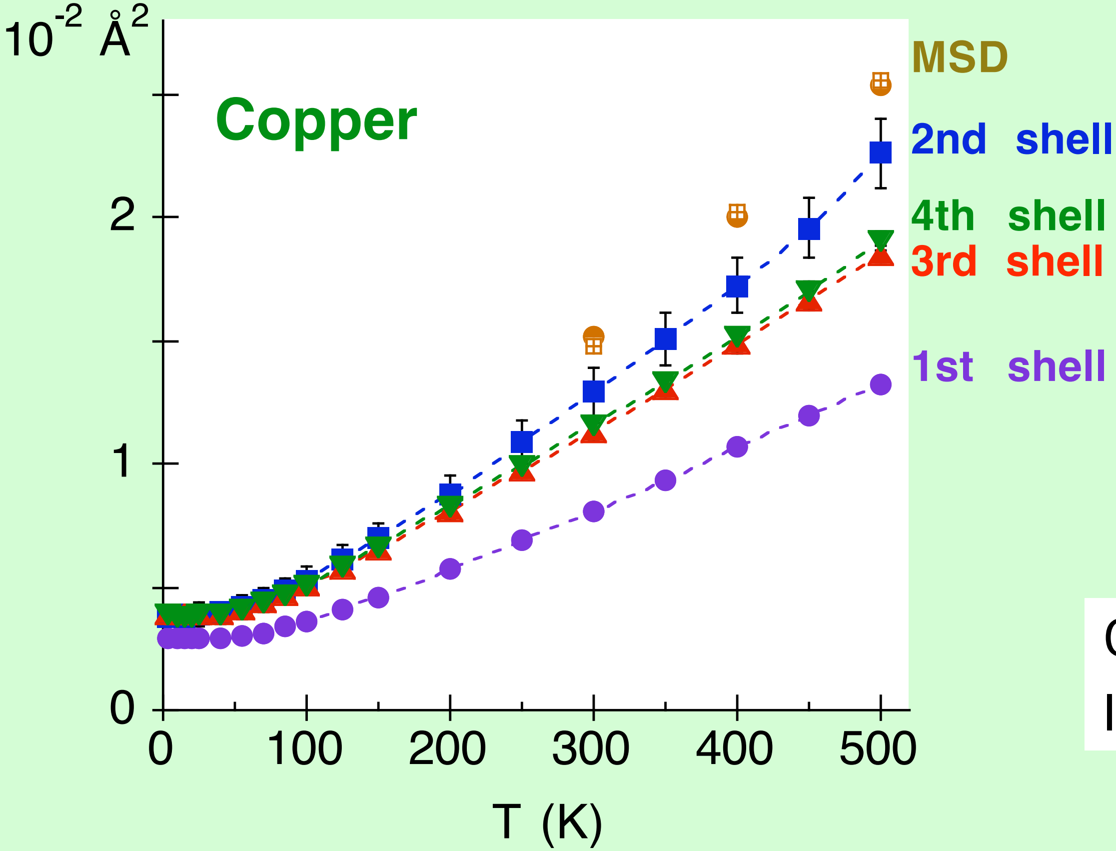
Bragg diffraction ➔ absolute vibrations

EXAFS ➔ relative vibrations



(along the bond)



Complementarity EXAFS - XRD:
Info on vibrations correlation

Debye-Waller factor – Einstein model

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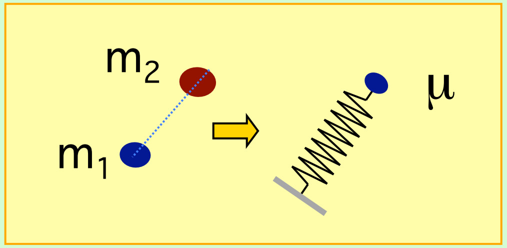
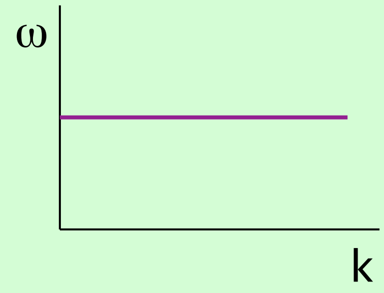
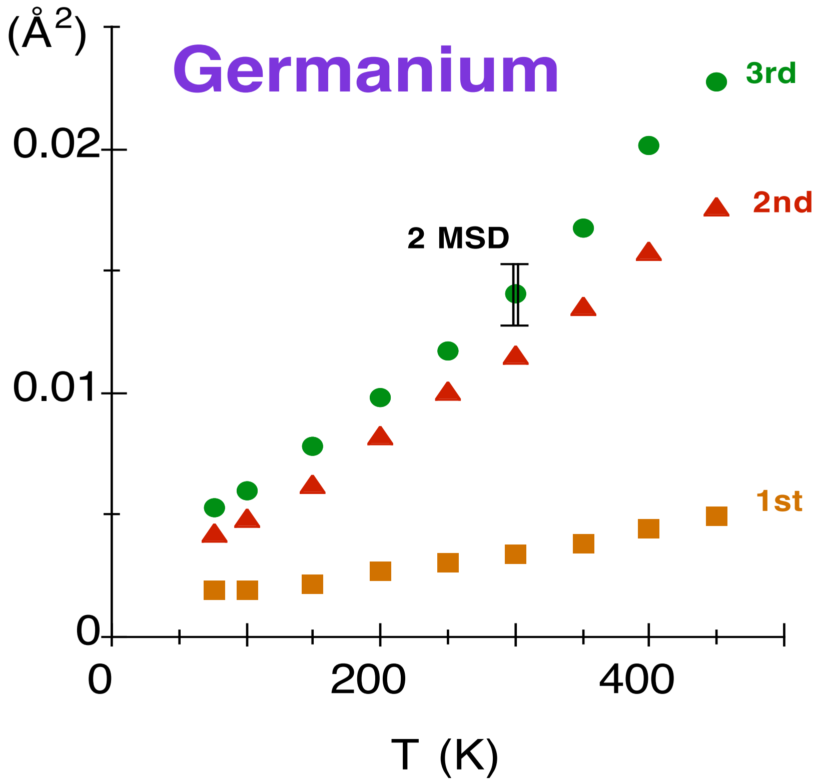


$$\langle \Delta u_{\parallel}^2 \rangle = \frac{\hbar}{2\mu\omega_E} \coth\left(\frac{\hbar\omega_E}{2kT}\right)$$





Non-Bravais crystals

Debye

θ_D = 354 K
θ_M = 290 K

θ_3 = 290 K
θ_2 = 299 K
θ_1 = 460 K

Einstein

$\nu = \omega/2\pi$ (THz)	$k = \mu\omega^2$ (eV/Å²)
ν_3 = 3.95	k_3 = 2.18
ν_2 = 4.21	k_2 = 2.48
ν_1 = 7.55	k_1 = 8.15

Parallel and perpendicular MSRD

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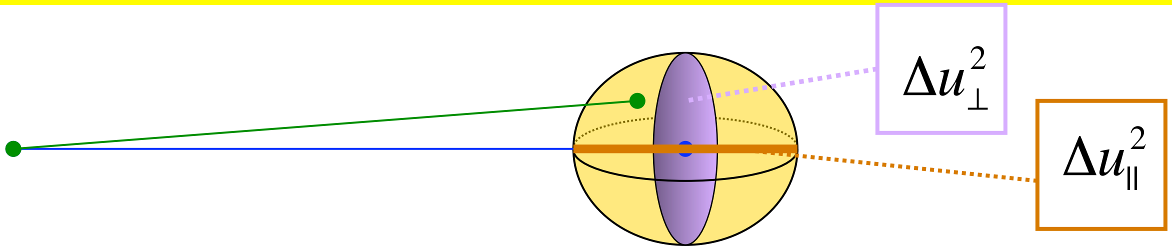

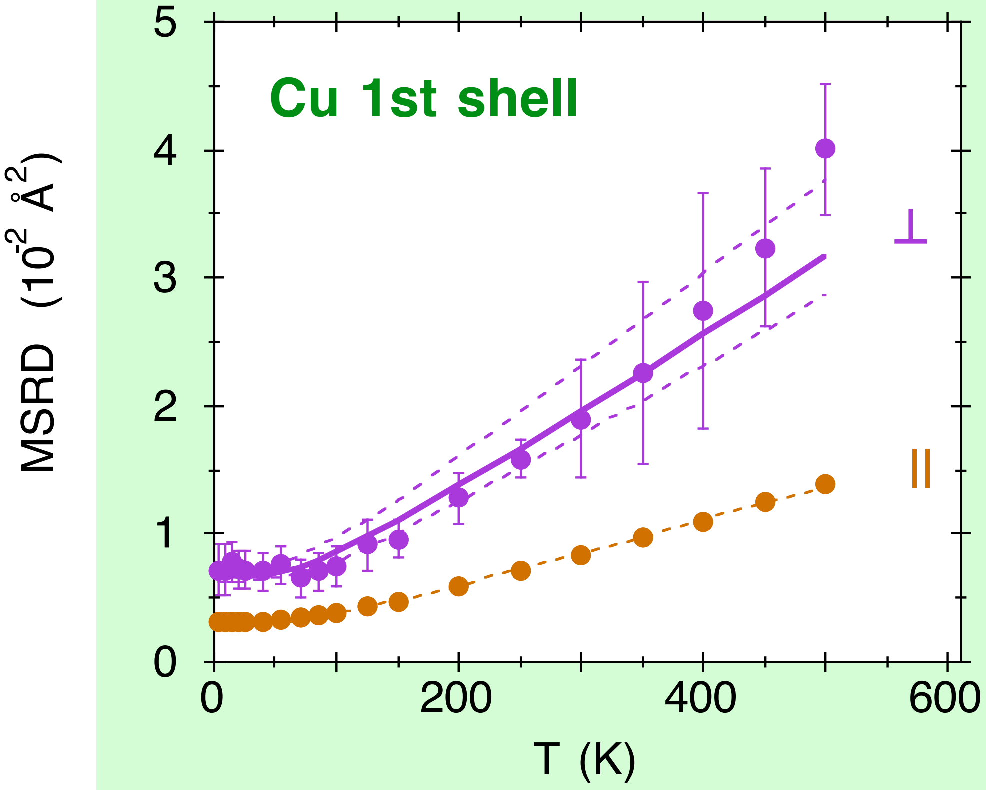

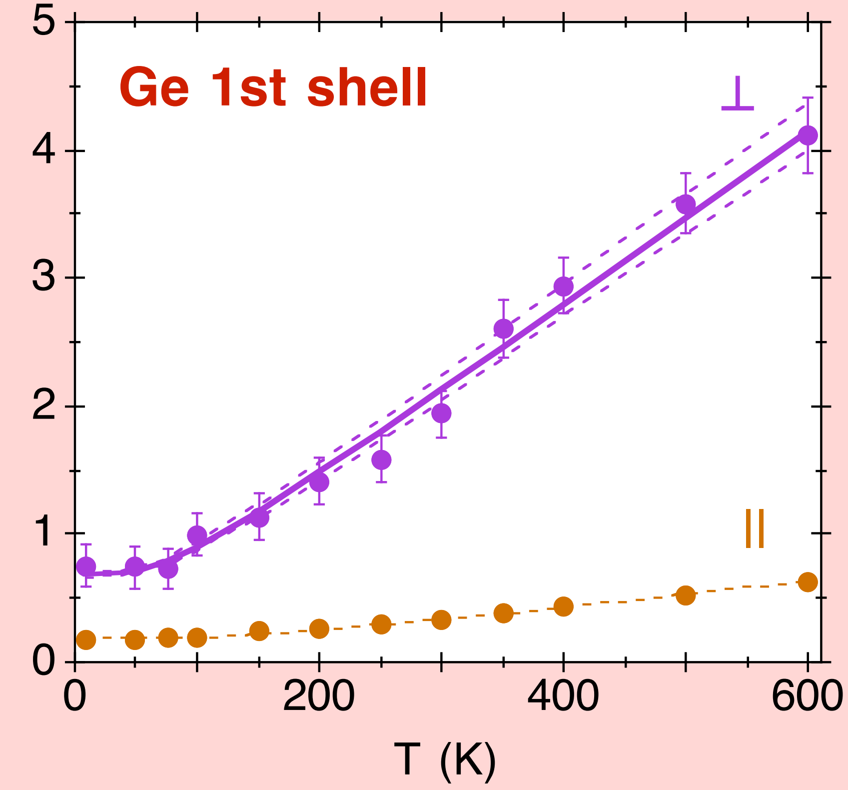

Perpendicular-parallel anisotropy

$$\frac{\langle \Delta u_{\perp}^{2} \rangle}{\langle \Delta u_{\parallel}^{2} \rangle}$$

Cu: 2.7

Ge: 6

First-shell distribution asymmetry

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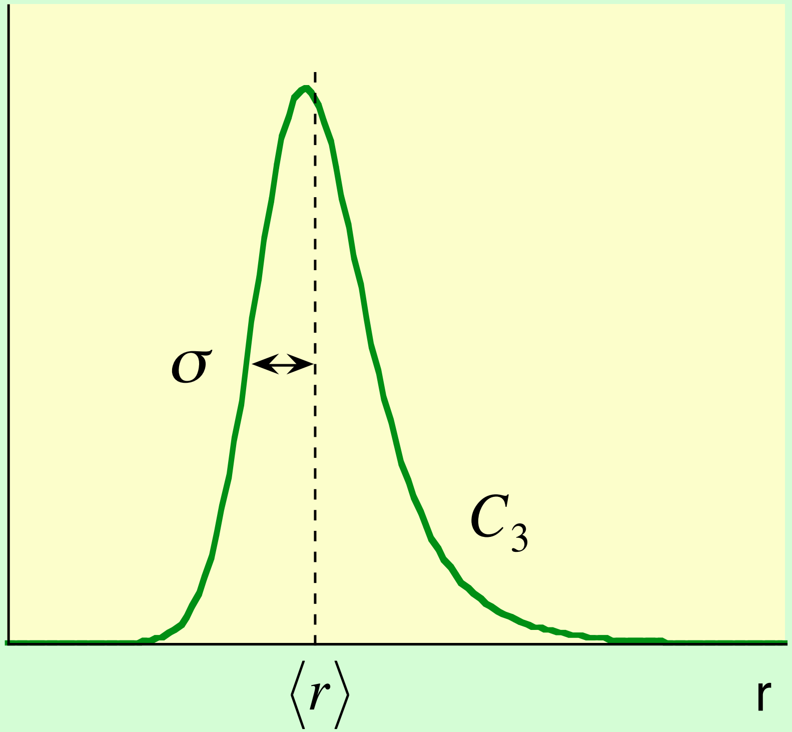
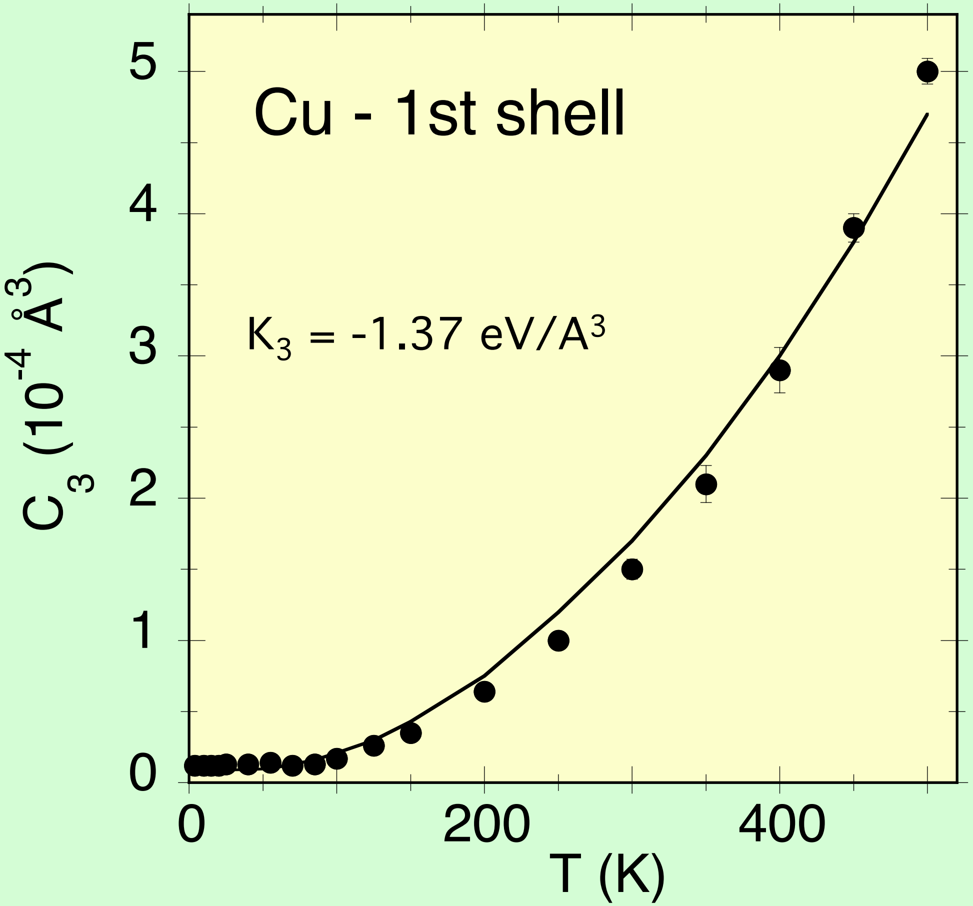


$$C_3^*(T) \approx -\frac{2k_3\sigma_0^4}{k_0}\ \frac{z^2+10z+1}{(1-z)^2}$$



The end

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