X-ray absorption spectroscopy

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Attenuation mechanisms for X-rays

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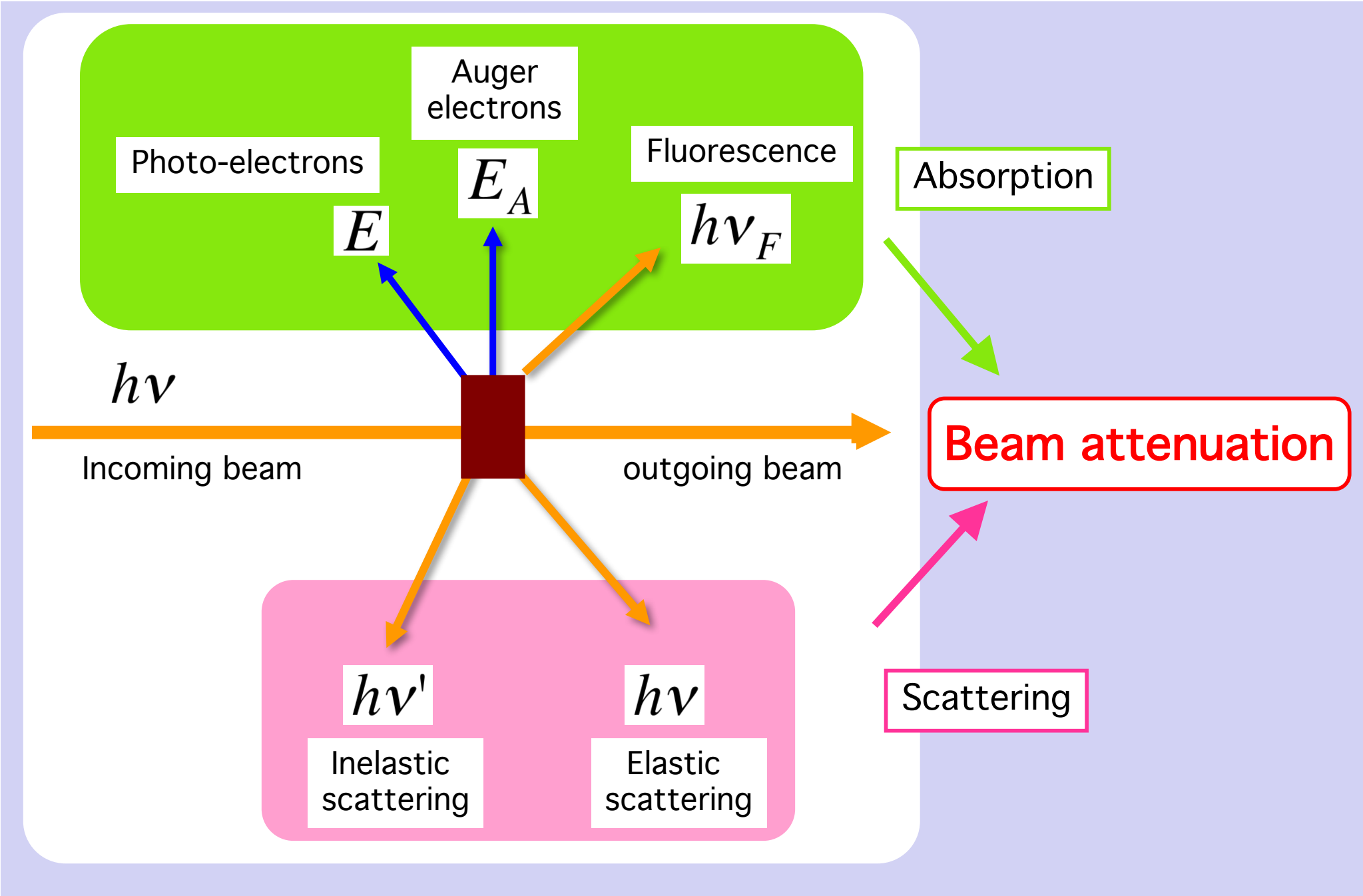

Basic X-ray techniques

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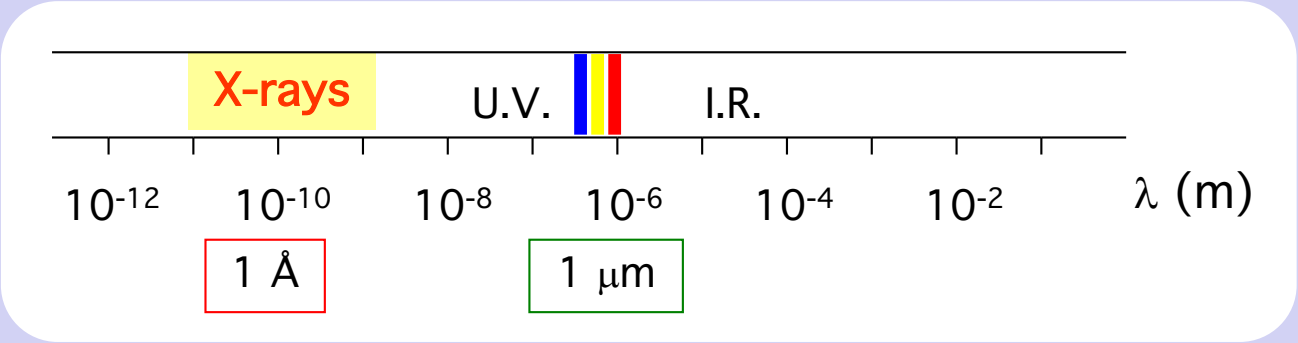
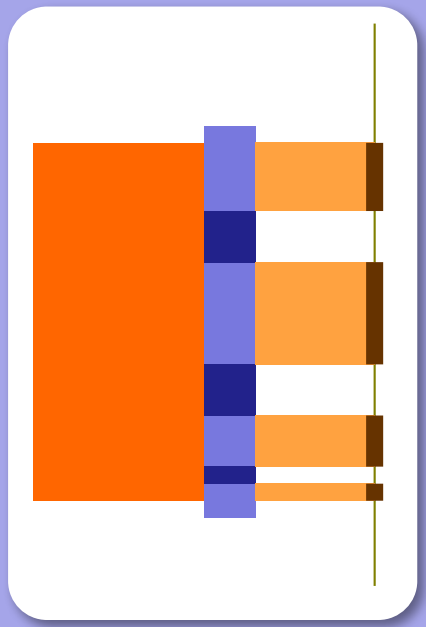
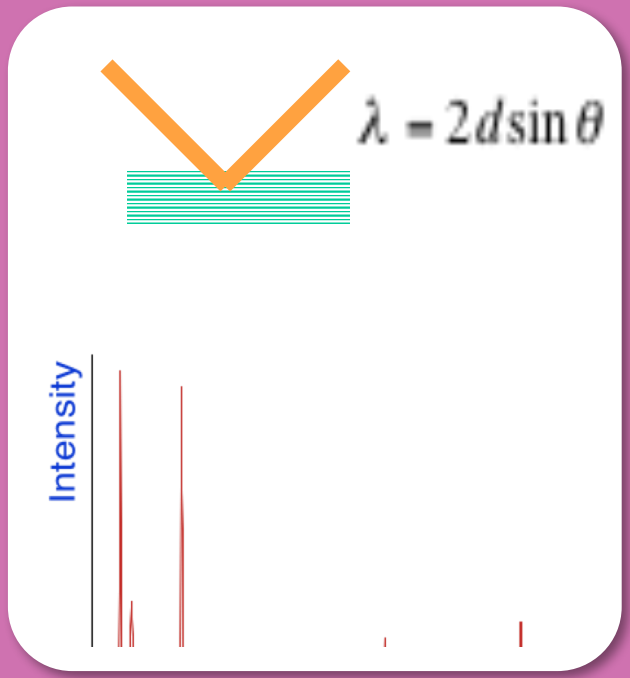


$$E[\mathrm{keV}] = \frac{12.4}{\lambda[\text{Å}]}$$

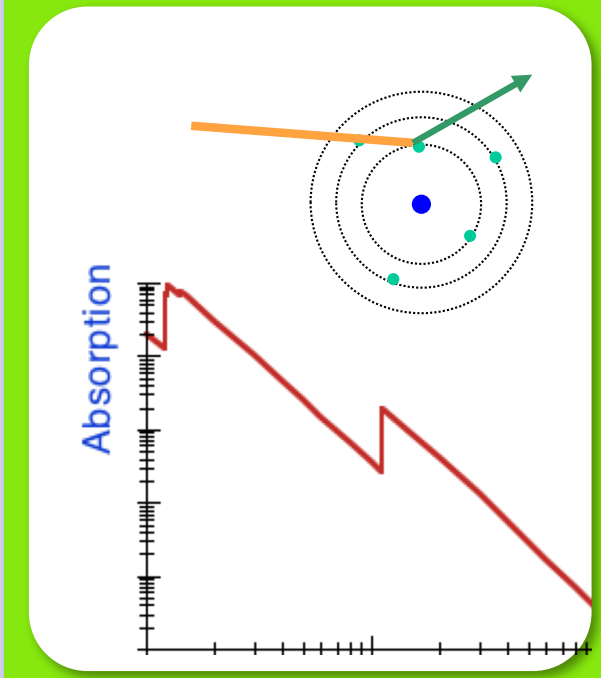
Imaging



Scattering



Spectroscopy



Structural techniques

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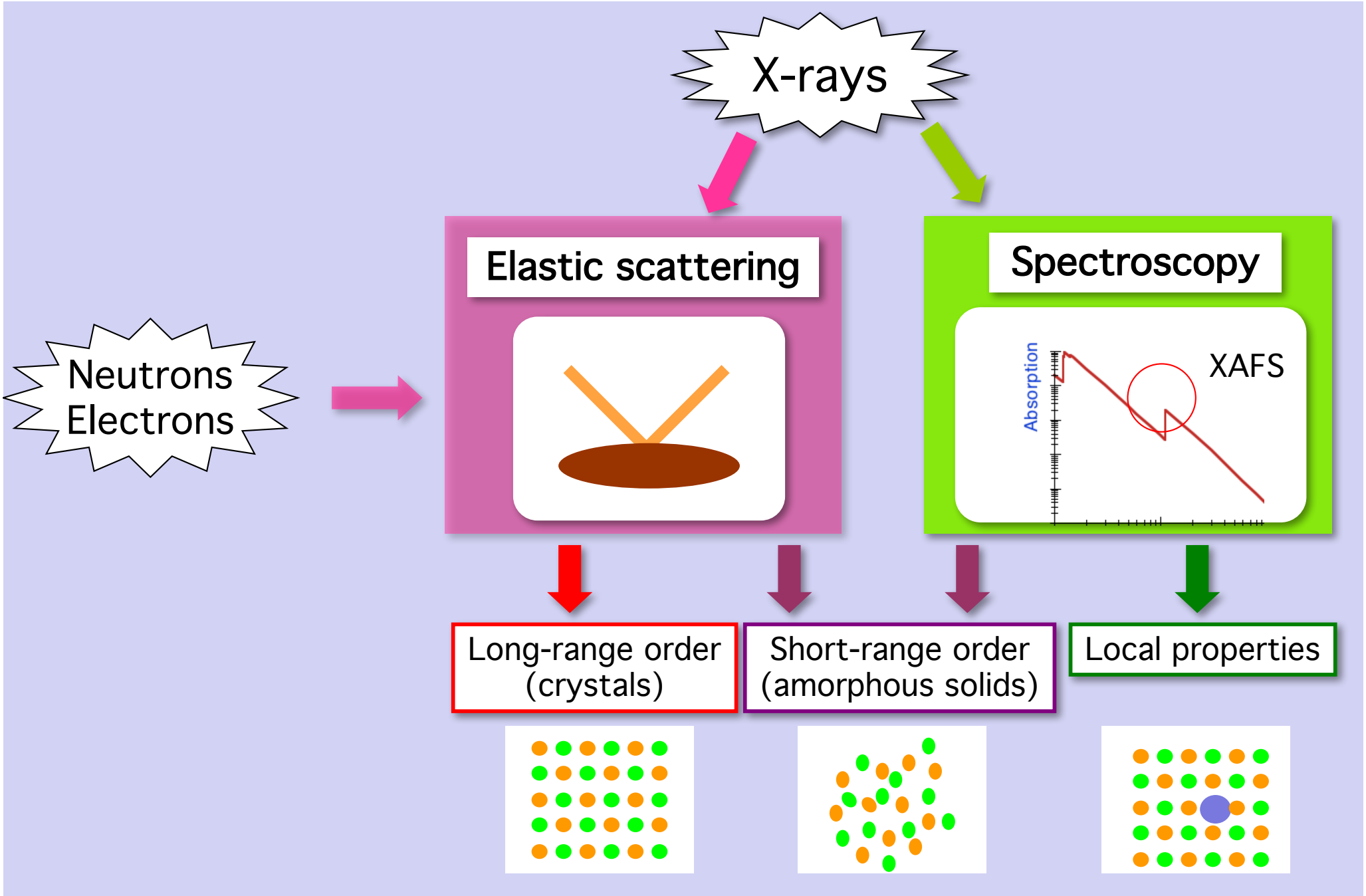

Summary

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

X-rays absorption - phenomenology

The attenuation coefficient

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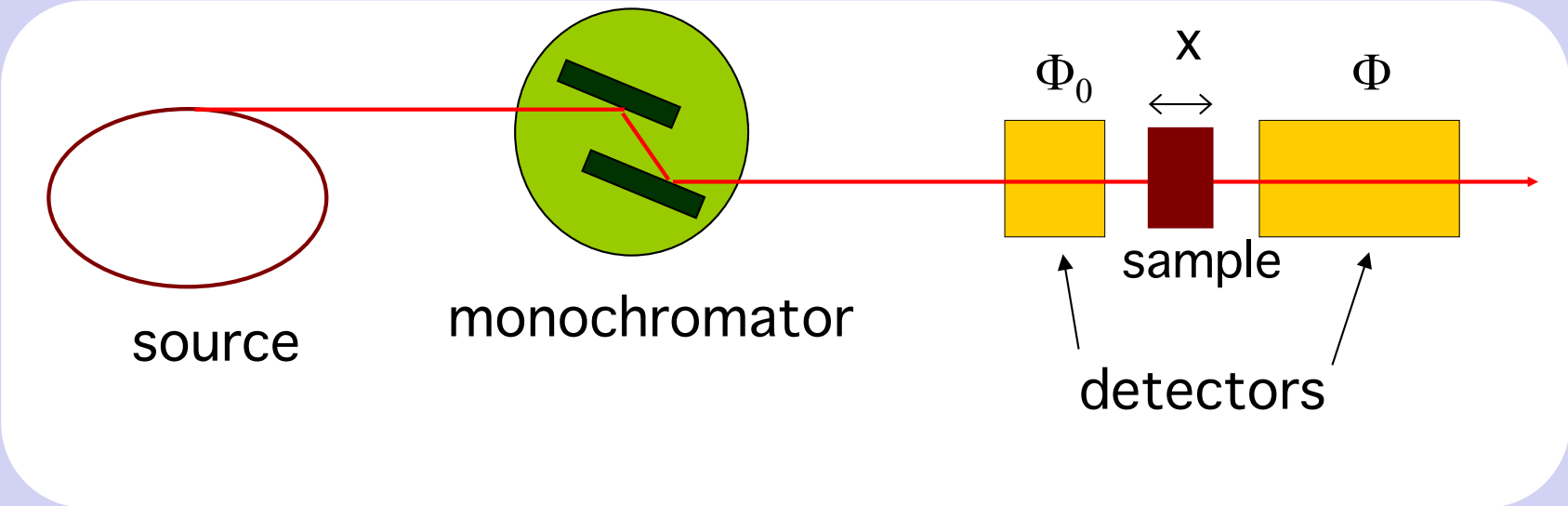
The attenuation depends on X-ray energy and on sample composition



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 – different contributions

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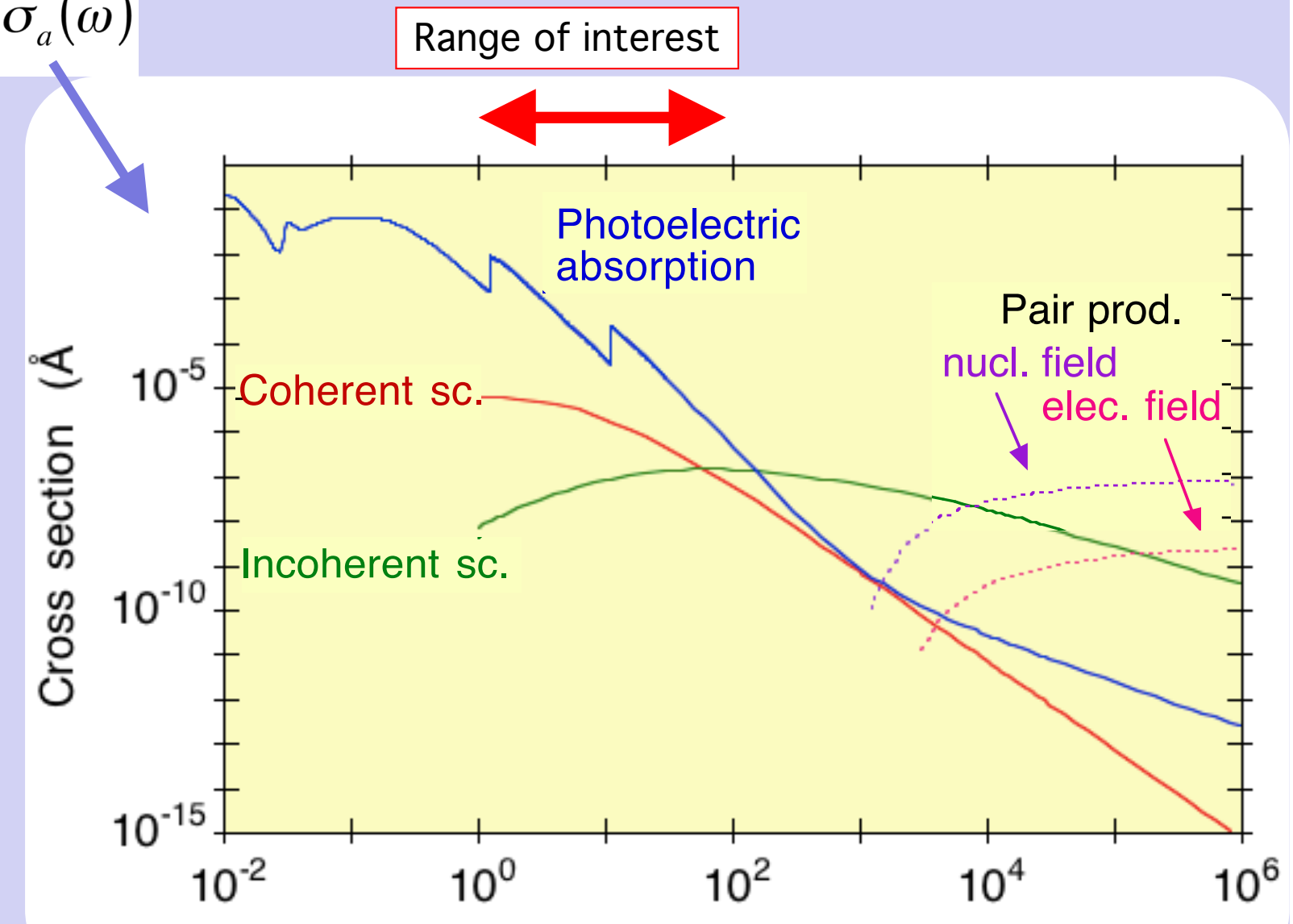
$$\mu(\omega) = \frac{N_A \rho}{A} \sigma_a(\omega)$$

ρ = density
N_A = Avogardo nr
A = atomic mass



Excitation and ionization

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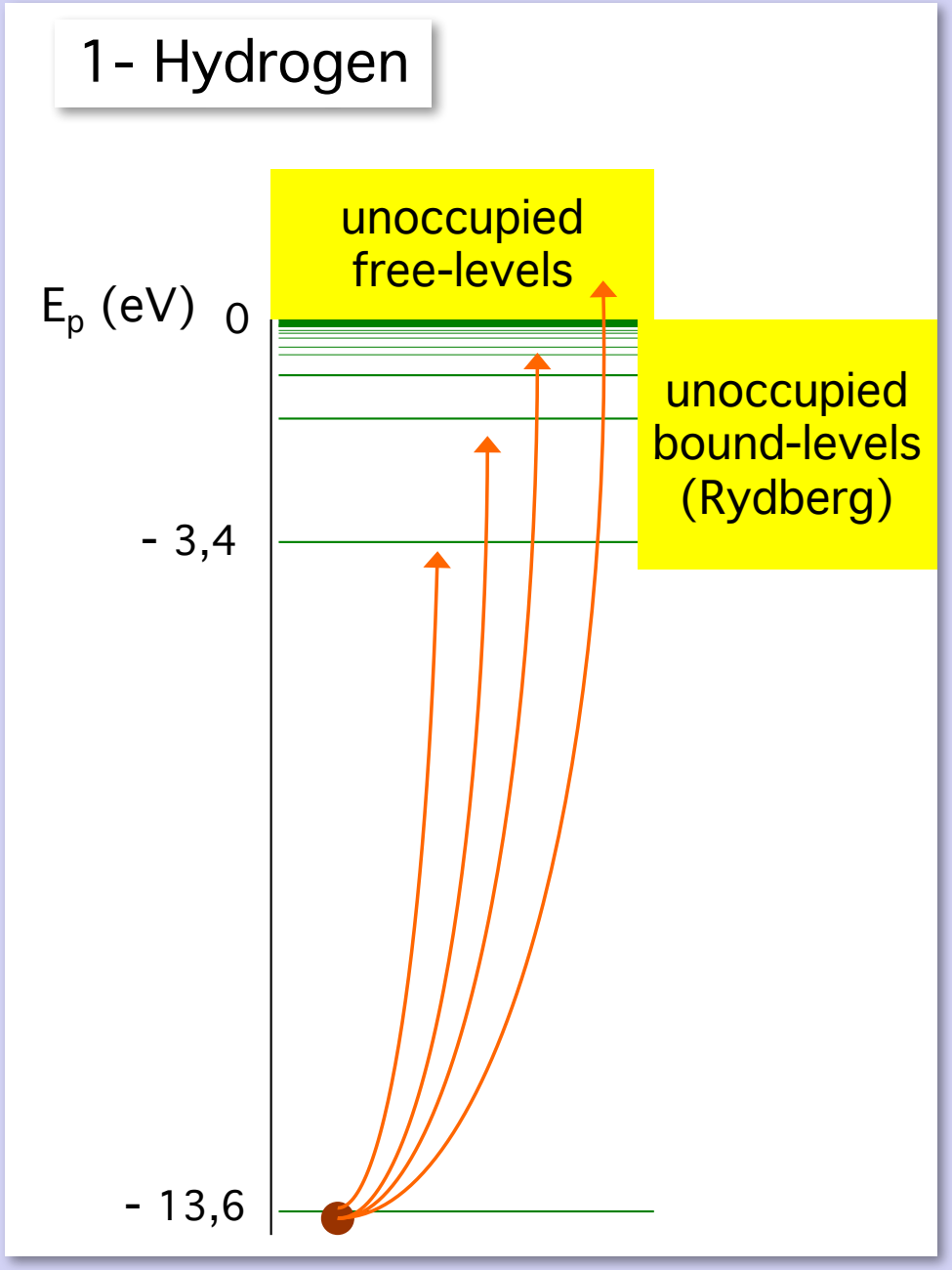

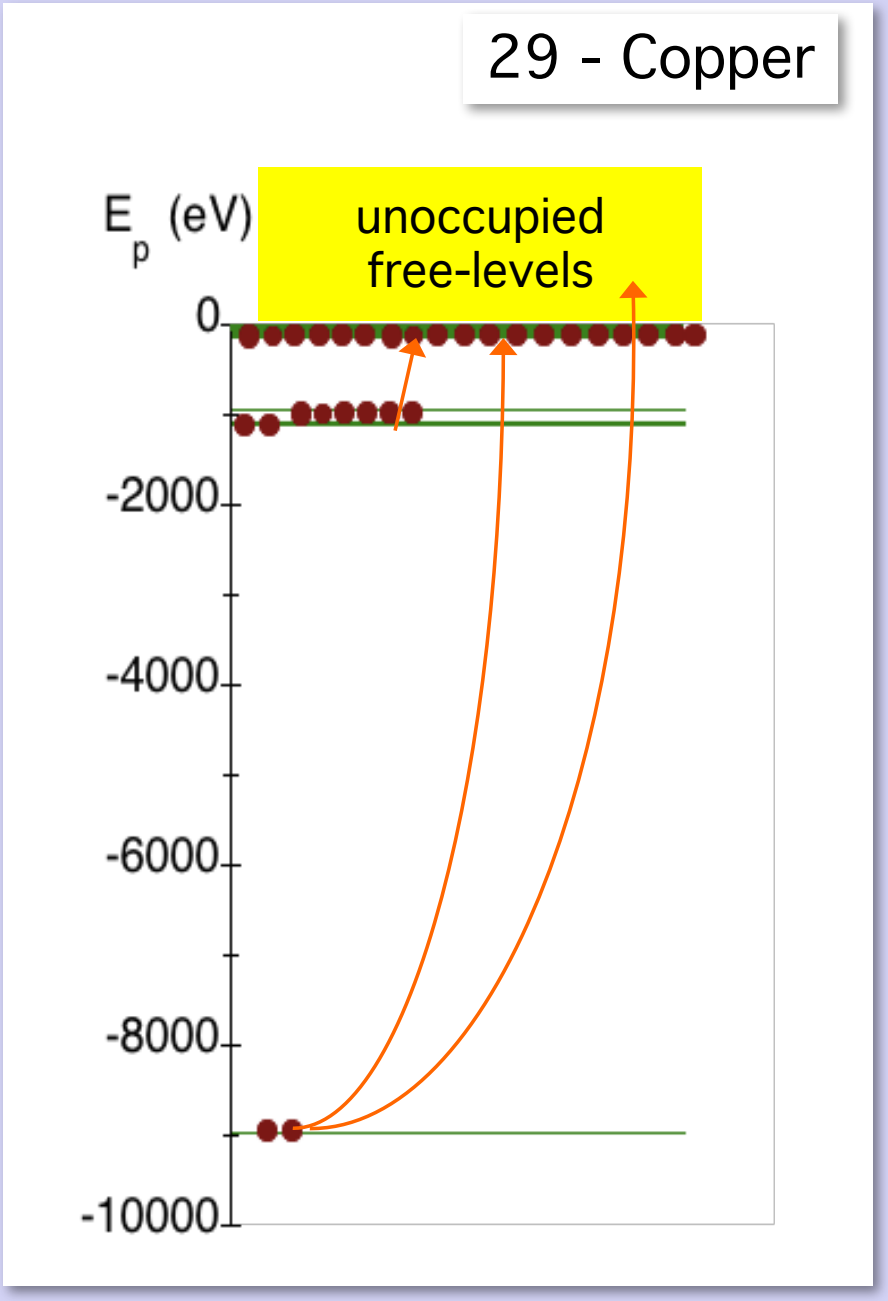

X-ray absorption

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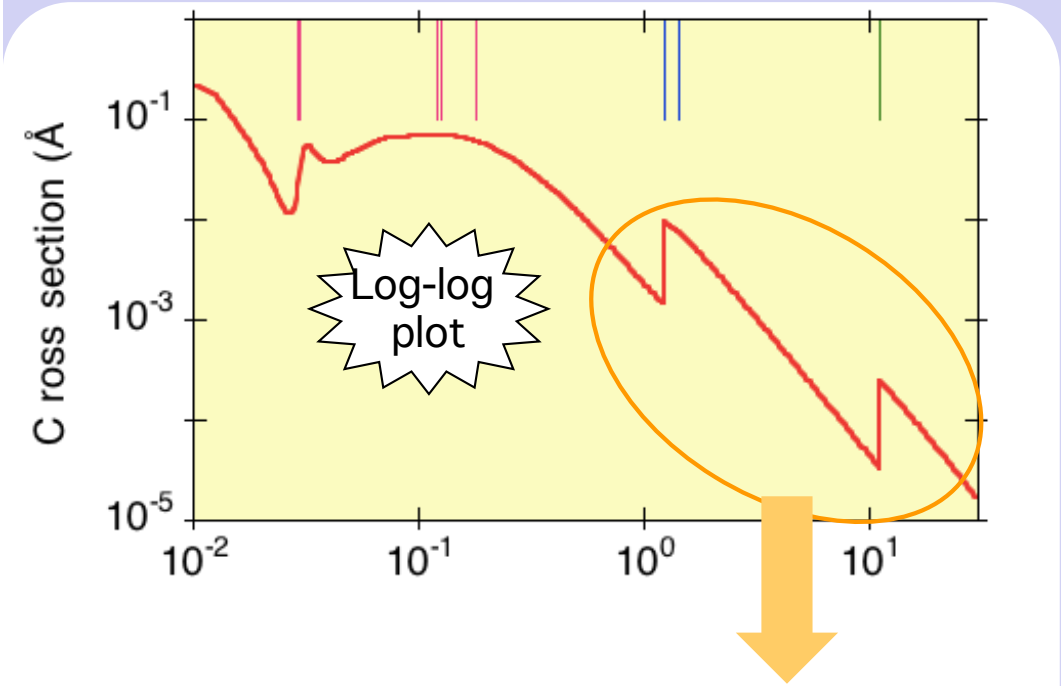

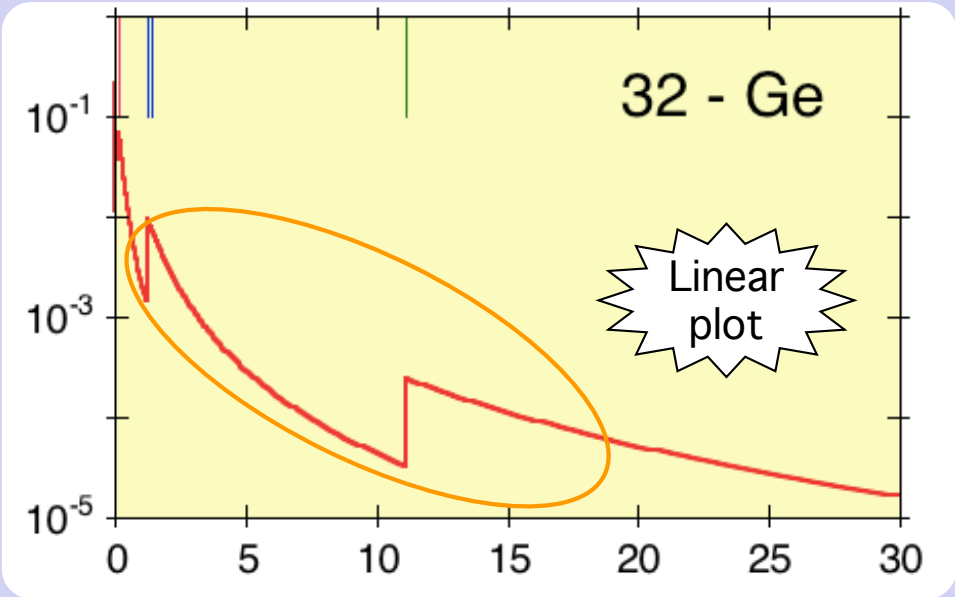

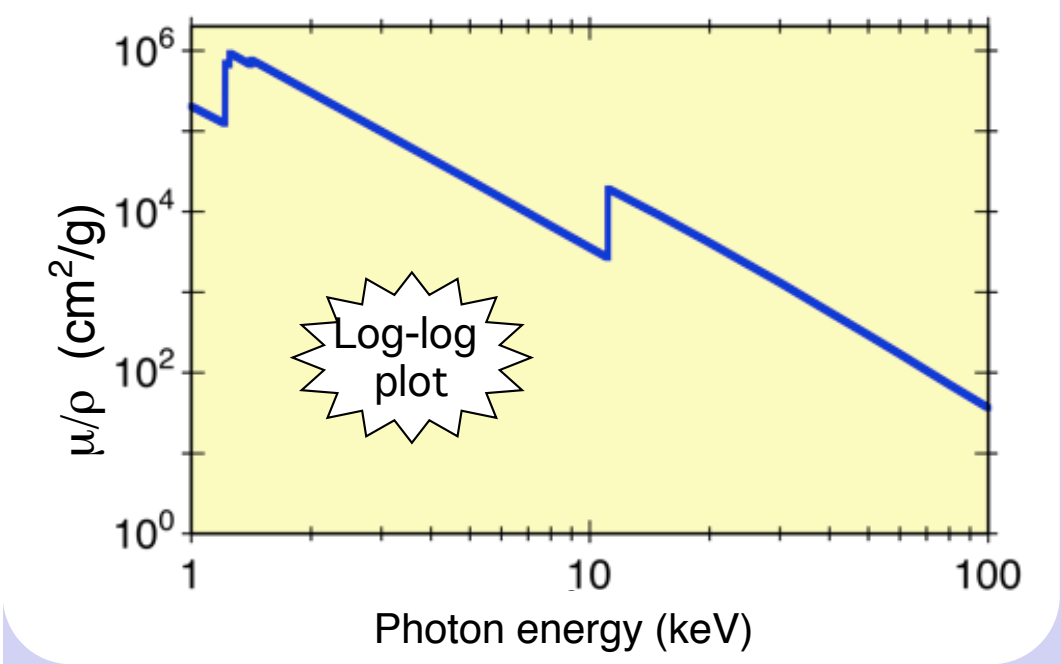

$$\mu(\hbar\omega) \simeq \frac{Z^4}{(\hbar\omega)^3} + \text{edges}$$

X-rays absorption edges

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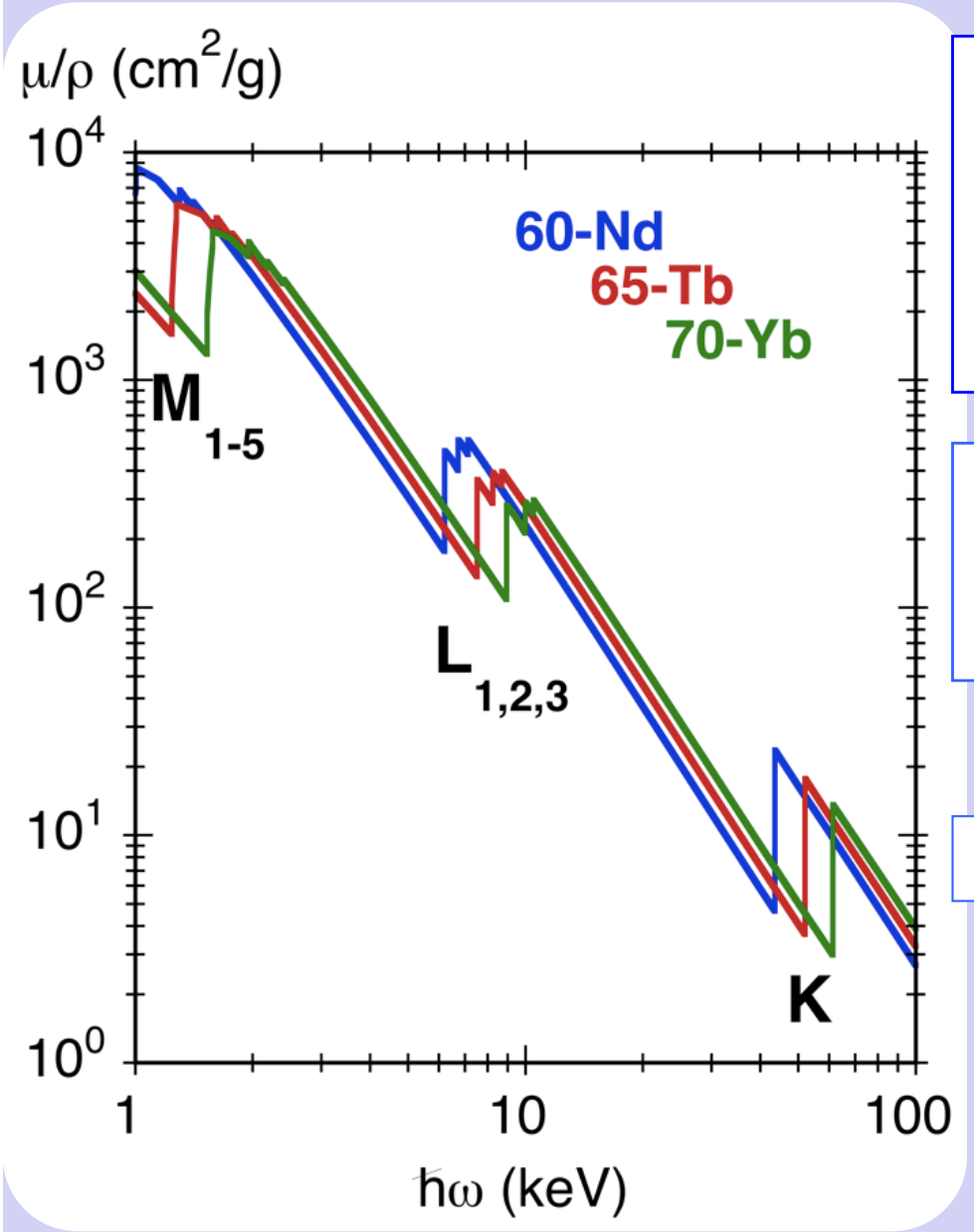


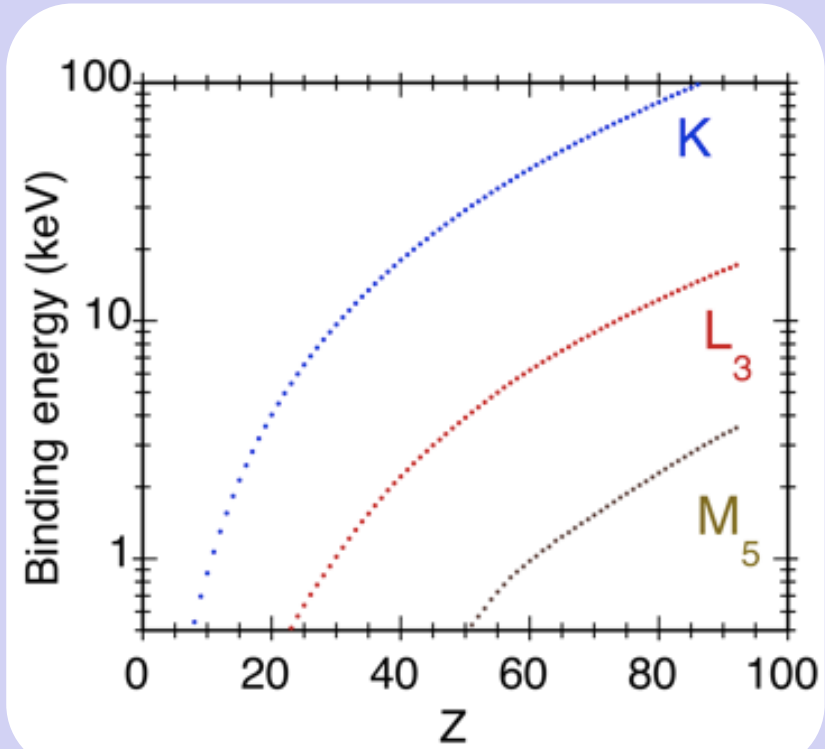
M_5 $3d_{5/2}$
M_4 $3d_{3/2}$
M_3 $3p_{3/2}$
M_2 $3p_{1/2}$
M_1 $3s$

L_3 $2p_{3/2}$
L_2 $2p_{1/2}$
L_1 $2s$

K 1s

Nomenclature

Z - dependence



Atomic gases: edge fine structure

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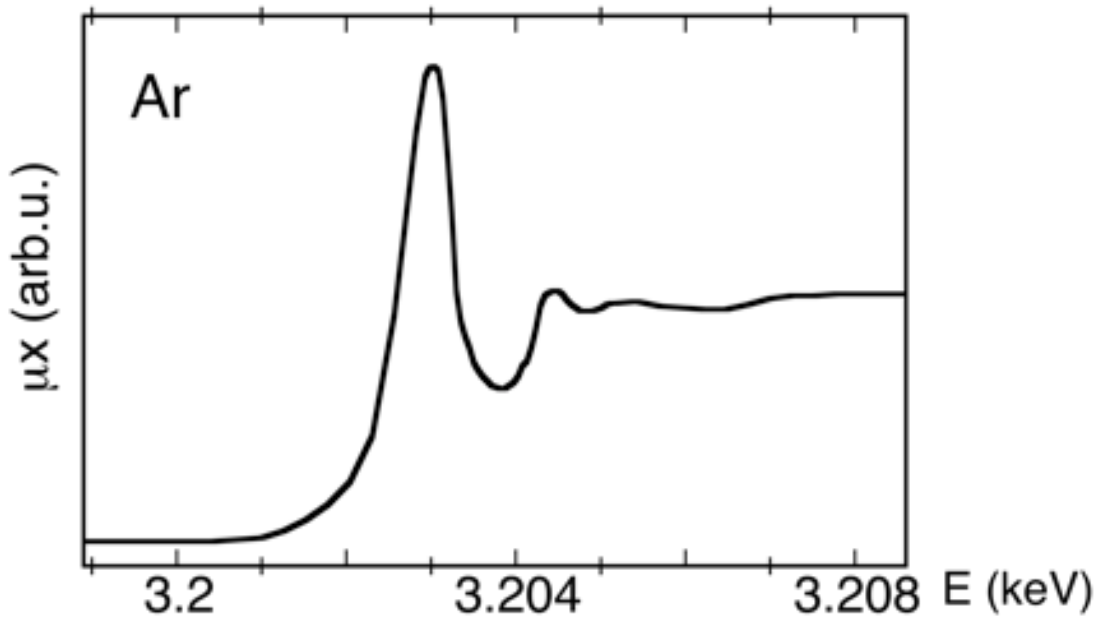
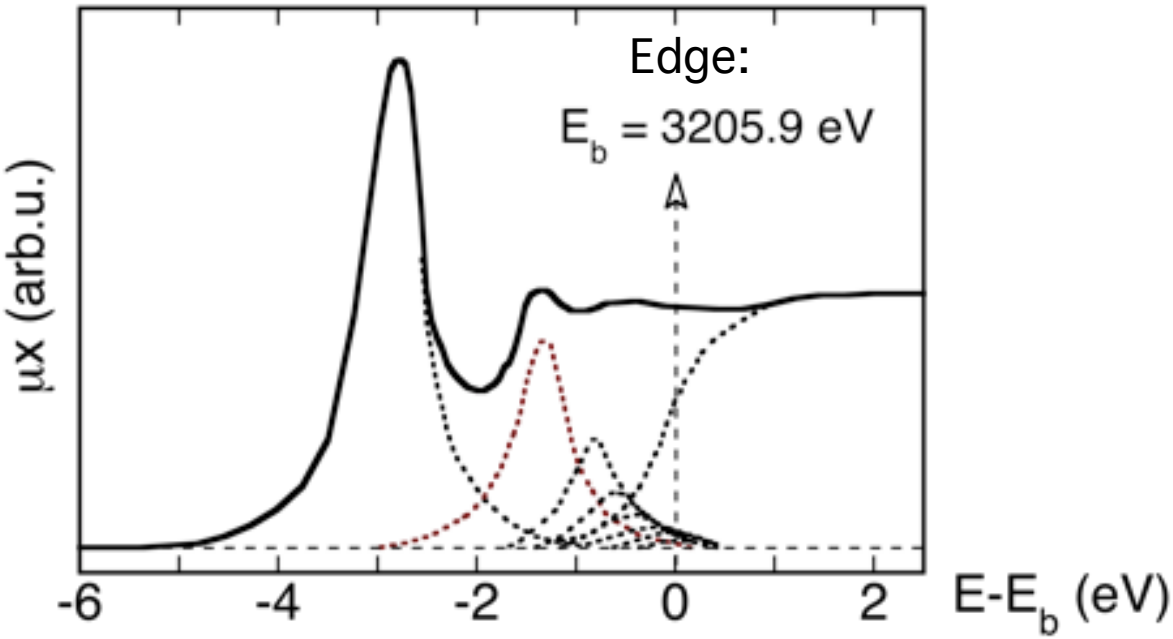


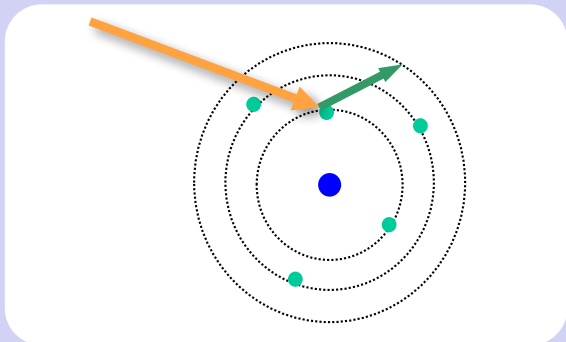
Experiment

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

Energy resolution ~ 0.6 eV



Interpretation:
- Rydberg levels
- edge to continuum



Atomic gases: smooth absorption coefficient

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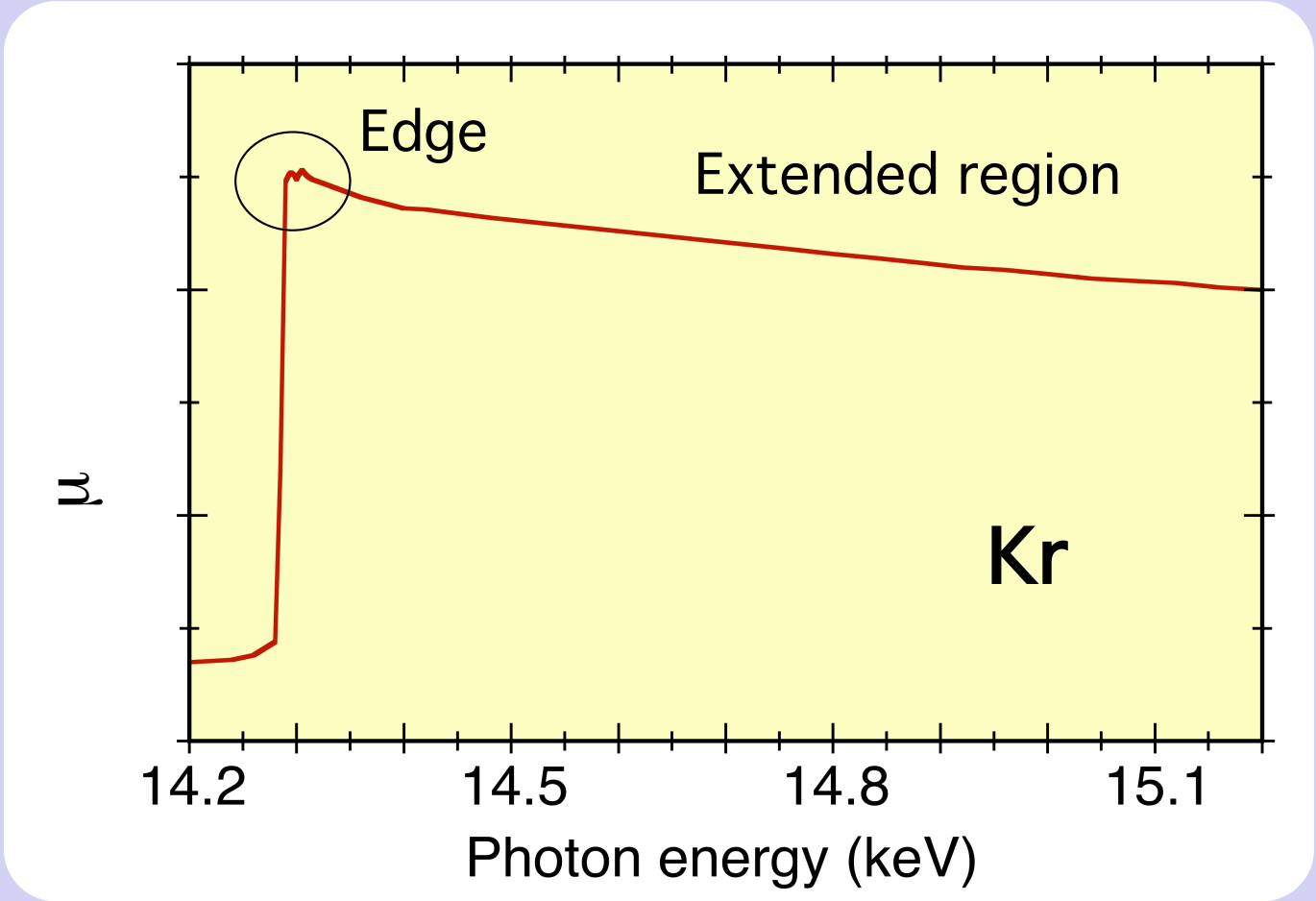
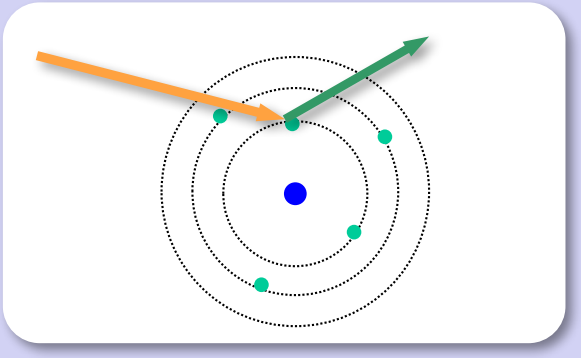


Core level → - Unoccupied bound levels (poor resolution)
- Continuum (smooth)



Atomic gases and condensed states

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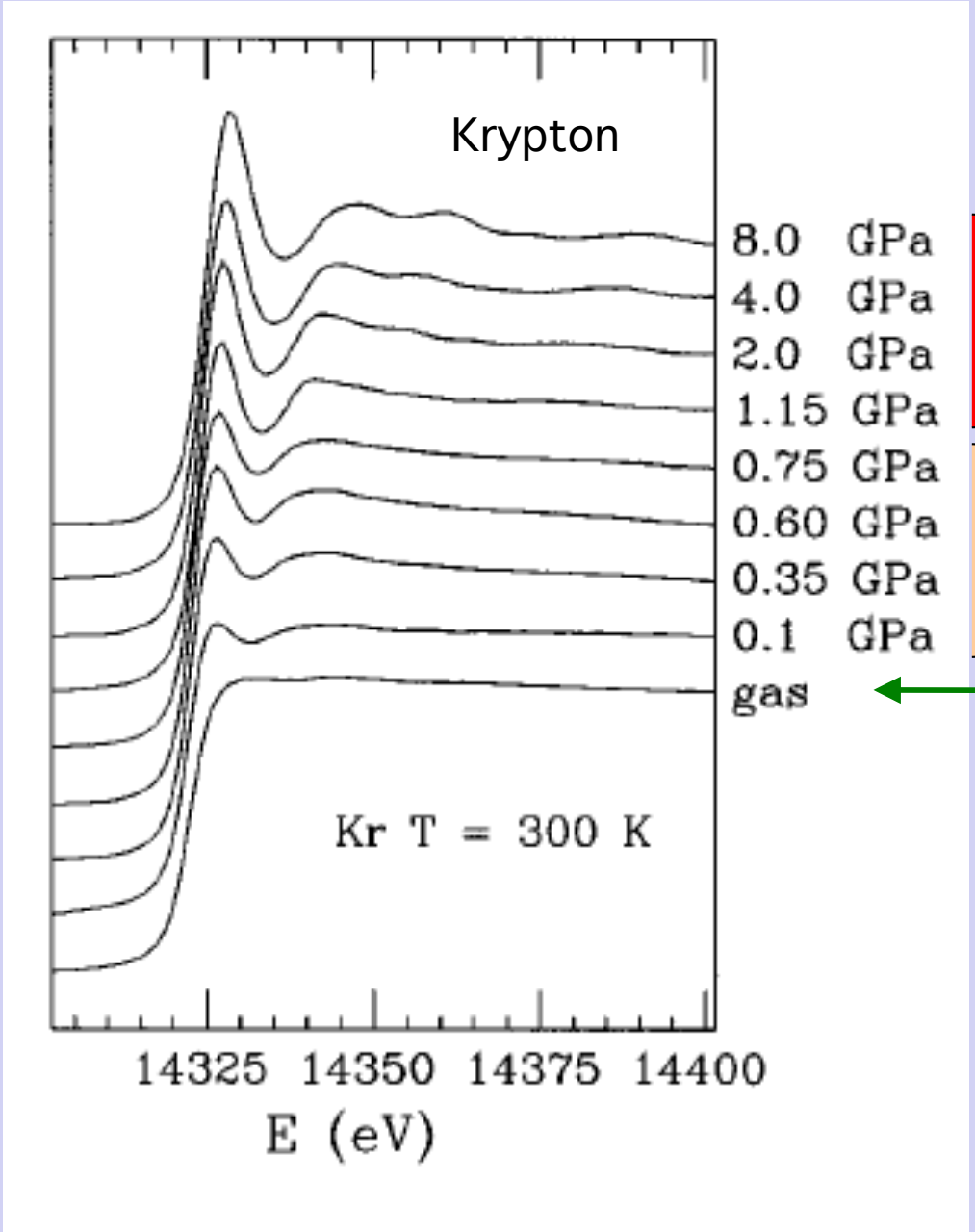

Solid

Liquid

Gas

Energy resolution ~ 2.5 eV

Pressure

A. Di Cicco et al.,
Phys. Rev. B 54, 9086 (1996)

Molecular gases: Fine structure

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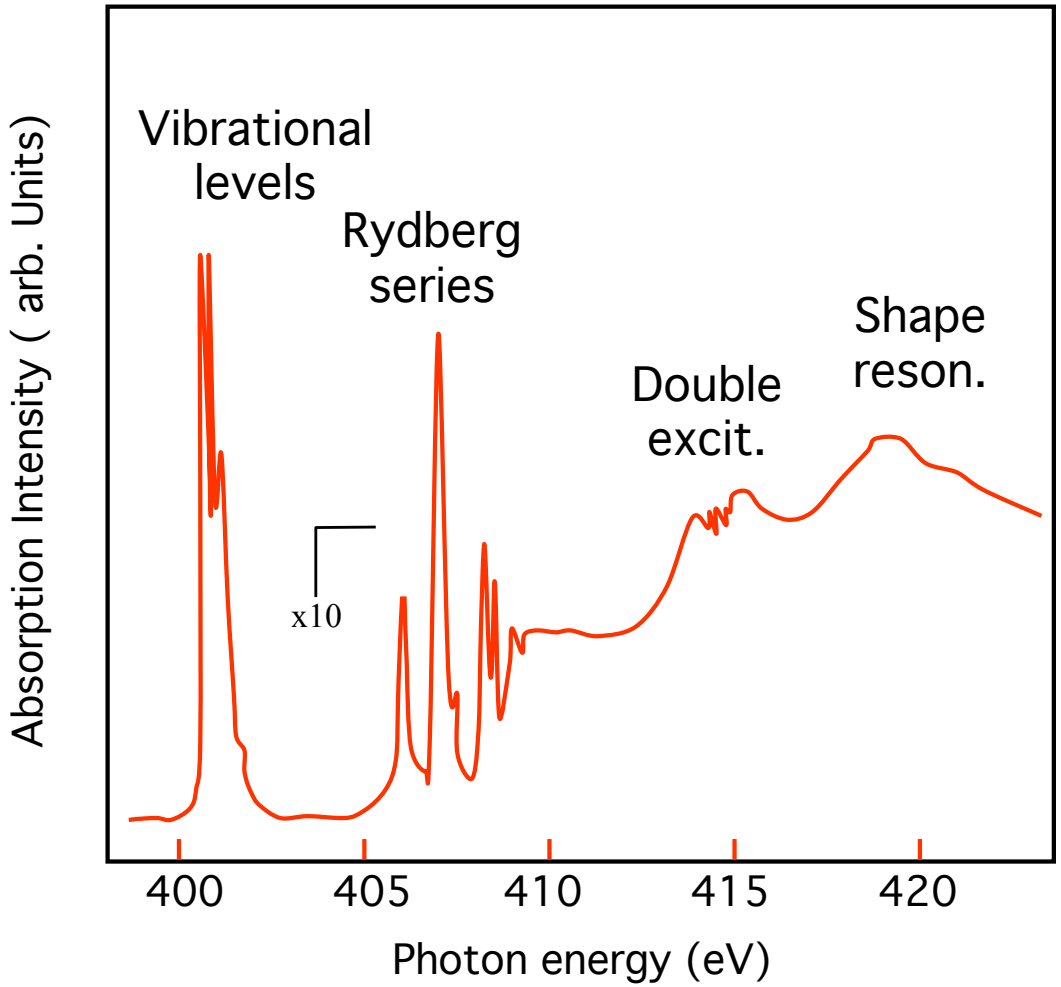
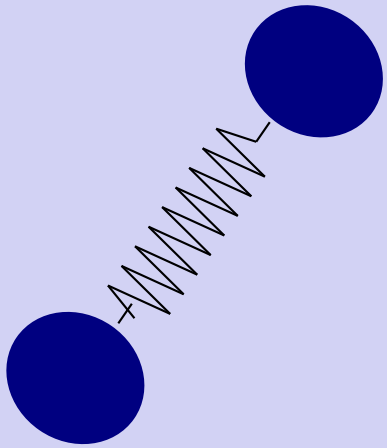


Gas-phase N_2
K-edge



Core level → Unoccupied bound levels
Unoccupied free levels

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

Condensed systems: Fine structure

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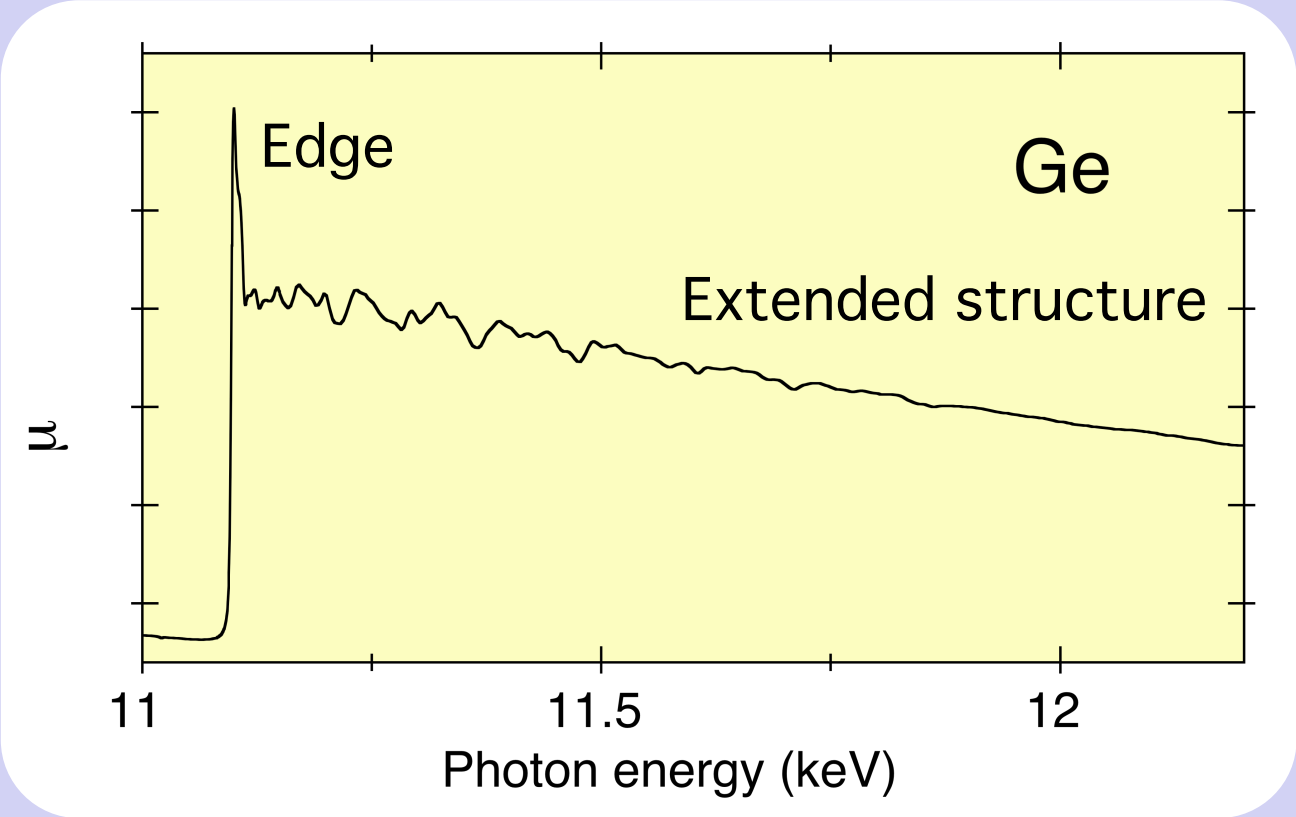

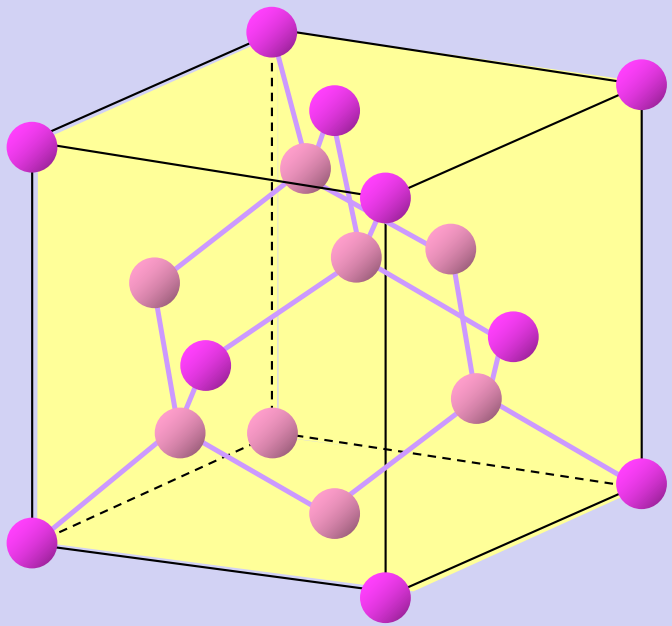

Core level → Unoccupied bound levels
Unoccupied free levels

XAFS: Nomenclature

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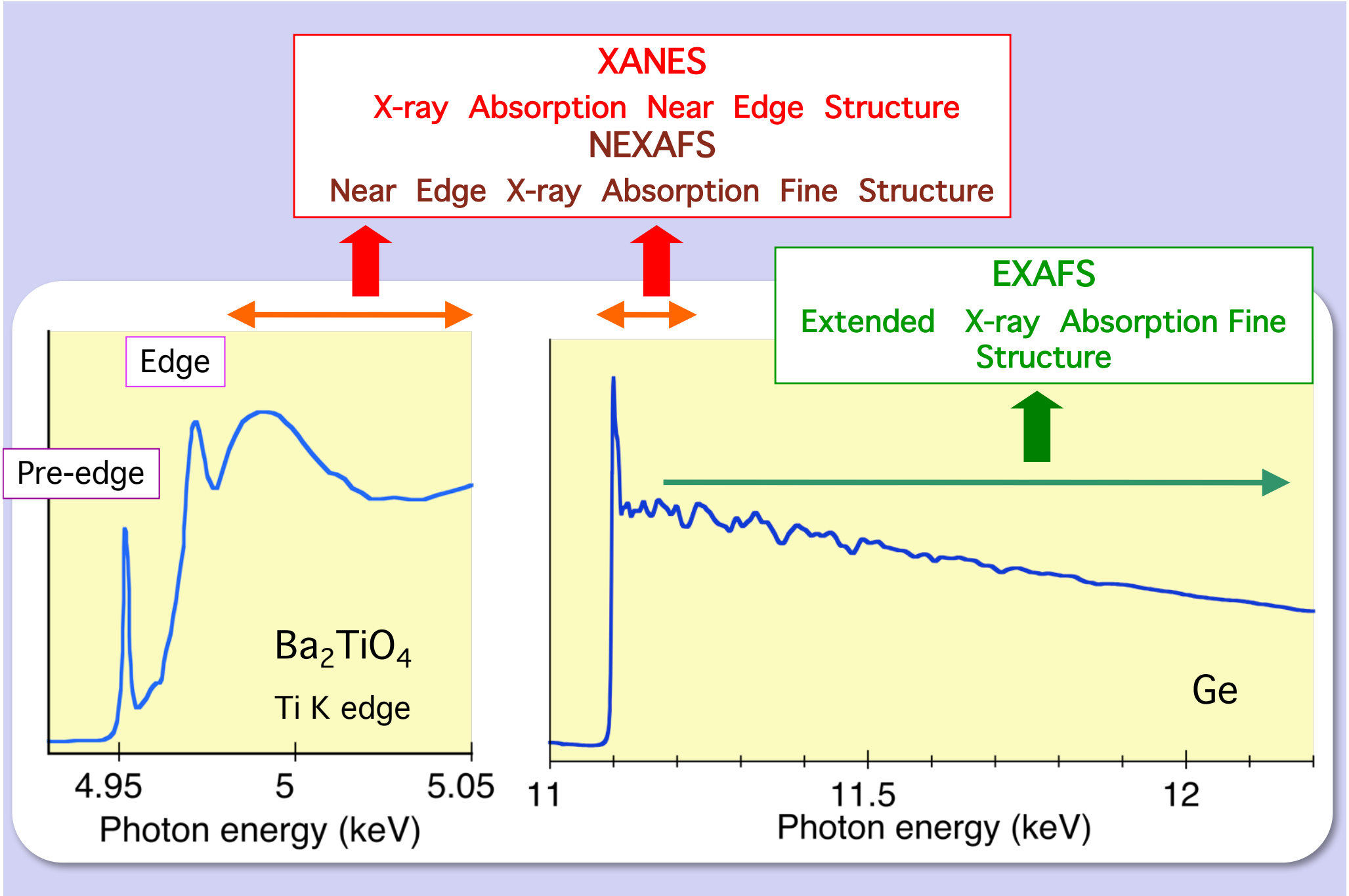

L edges .vs. K edge

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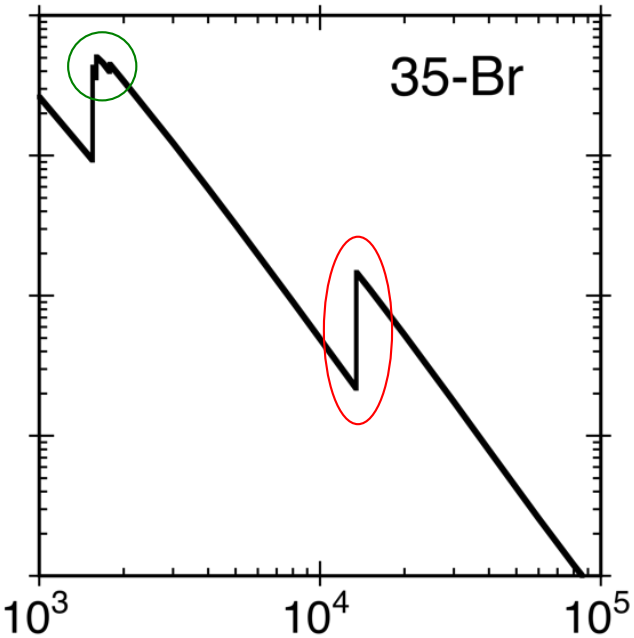
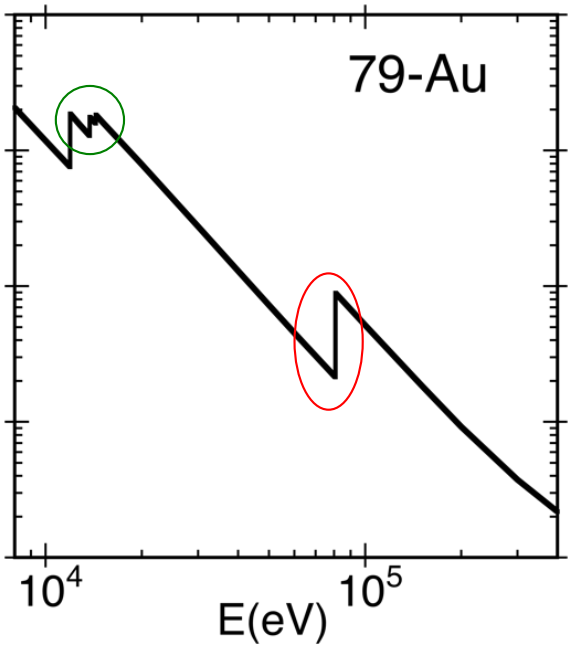
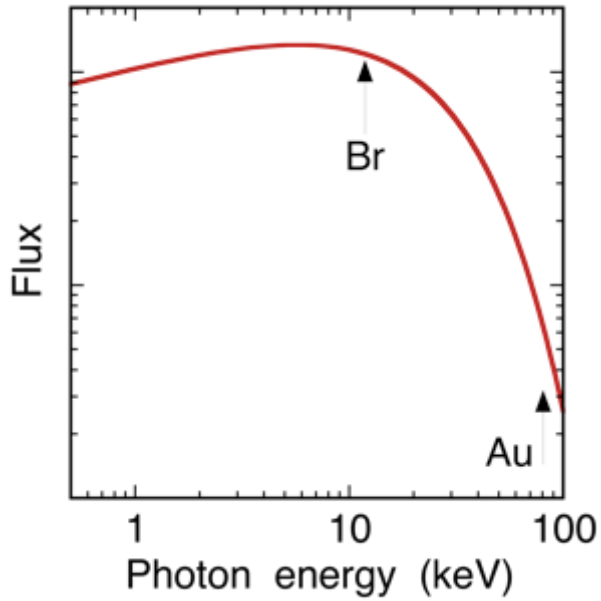




S.R. flux at the K edge



Energy resolution at the K edge

35-Br $\Delta E \sim 2.5$ eV

79-Au $\Delta E \sim 52$ eV

K edges unsuited for heavy elements
L edges ?

L_2 and L_3 edges: Spin-orbit splitting

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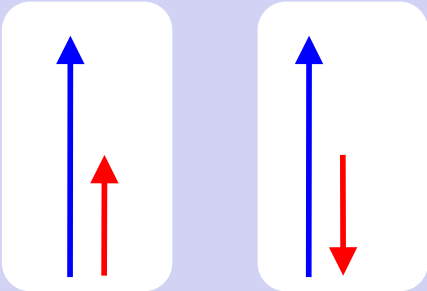
L_3 L_2



ℓ_z=1 ℓ_z=1

s_z=1/2 s_z=−1/2

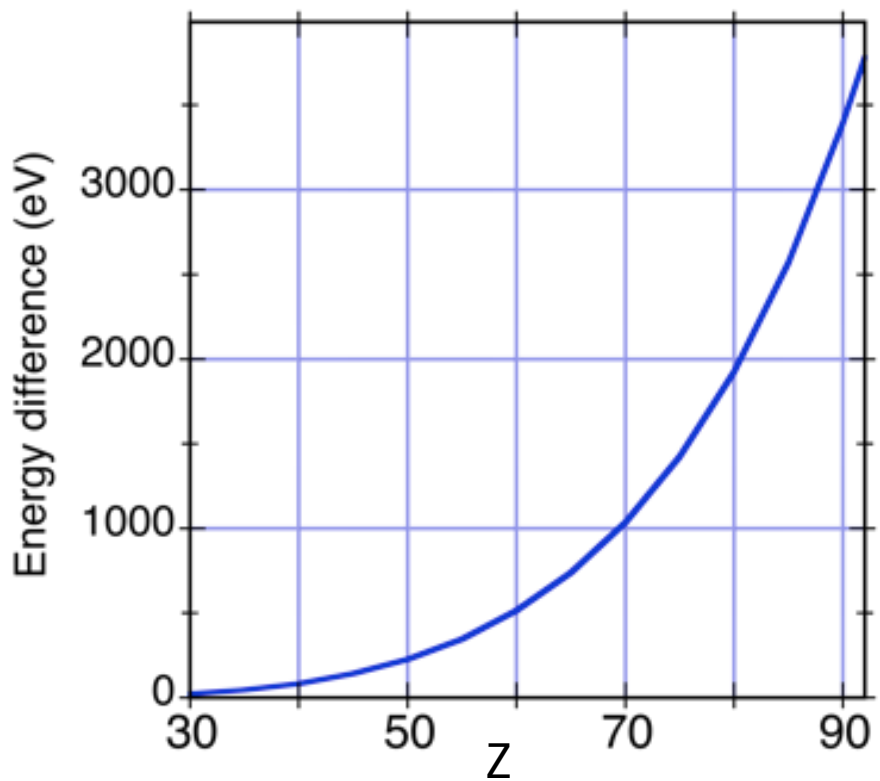
$2p_{3/2}$ $2p_{1/2}$

Spin-orbit splitting:

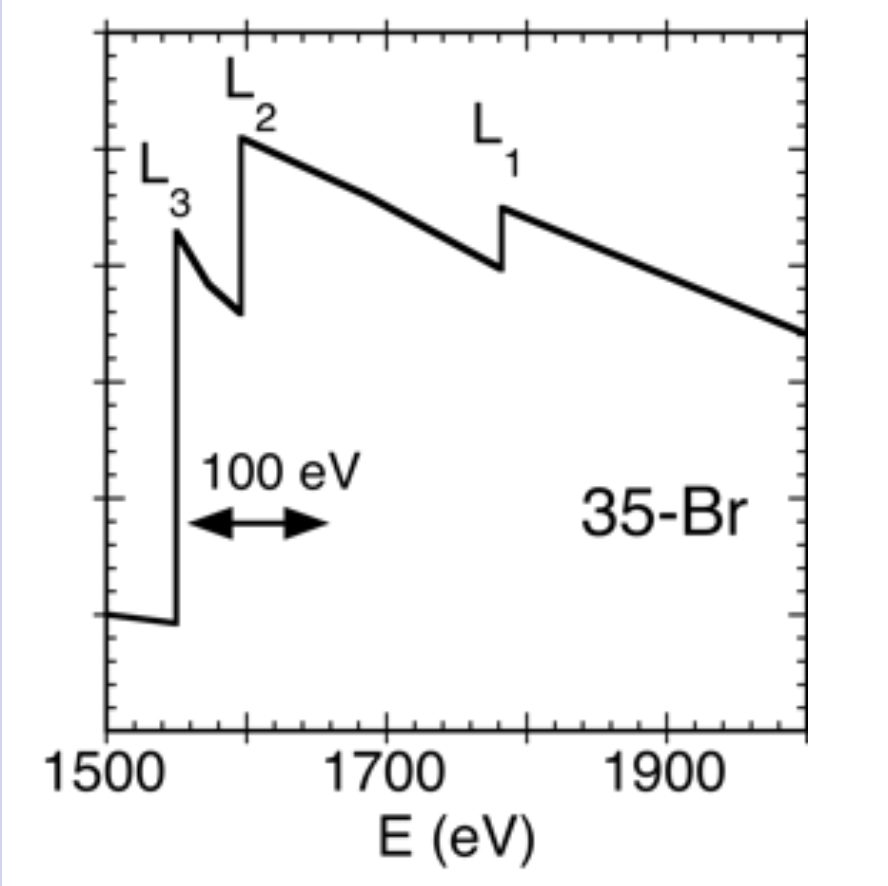
$$\Delta E_{SL} = \frac{|E_{n\ell}| Z^2 \alpha^2}{n\ell(\ell+1)} \simeq 5.32 \times 10^{-5} \frac{|E_{n\ell}| Z^2}{n\ell(\ell+1)}$$

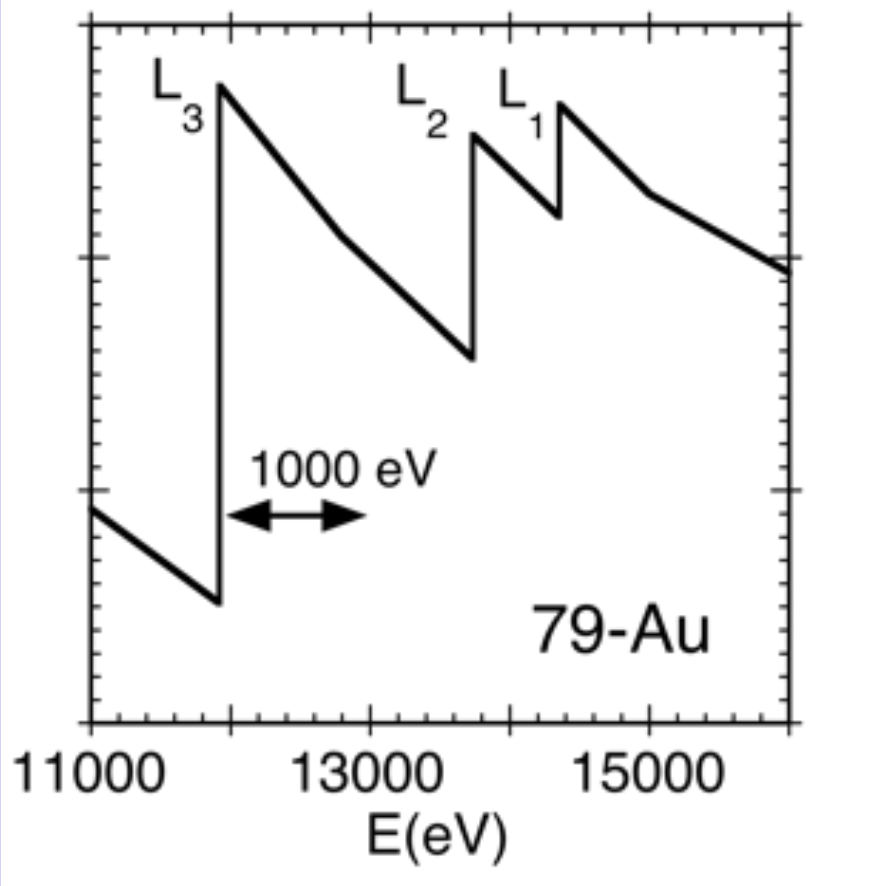
$$\alpha = \frac{1}{4\pi\epsilon_0} \frac{e^2}{\hbar c} = \frac{1}{137}$$

$$\Delta E_{L_2-L_3} \simeq 1.33 \times 10^{-5} \left|E_{n\ell}\right| Z^2$$



L edges XAFS





Edge & XANES: all L edges

EXAFS: L_2 and L_1 edges EXAFS polluted by L_3 EXAFS
L_3 EXAFS sufficiently extended only for heavy elements

Fine Structure: Molecules and Condensed systems

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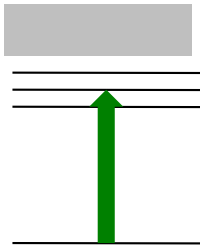
$h\nu \leq$ binding energy

Unoccupied free levels

Core level



→ Pre-edge structures

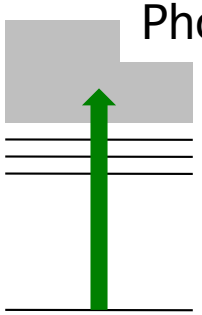
Edge structures

$h\nu >$ binding energy

Continuum levels

Photo-electron

Core level



Back-scattering from neighbouring atoms

Single scattering
Multiple scattering

→ EXAFS

XANES

EXAFS: phenomenological mechanism

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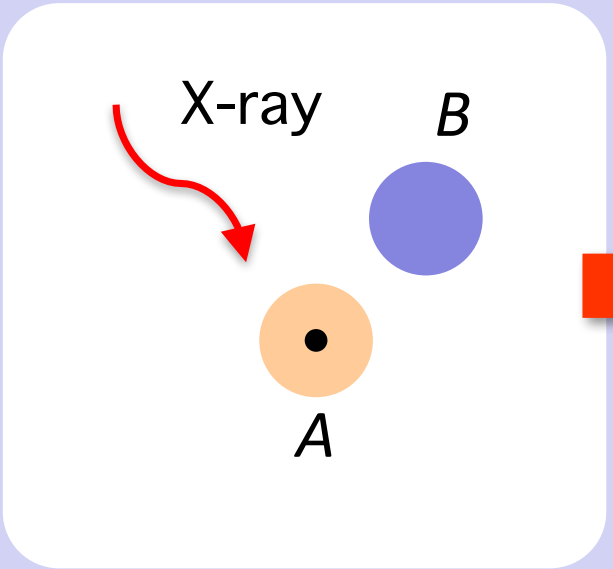

X-ray photon absorption.
Photo-electron emission.

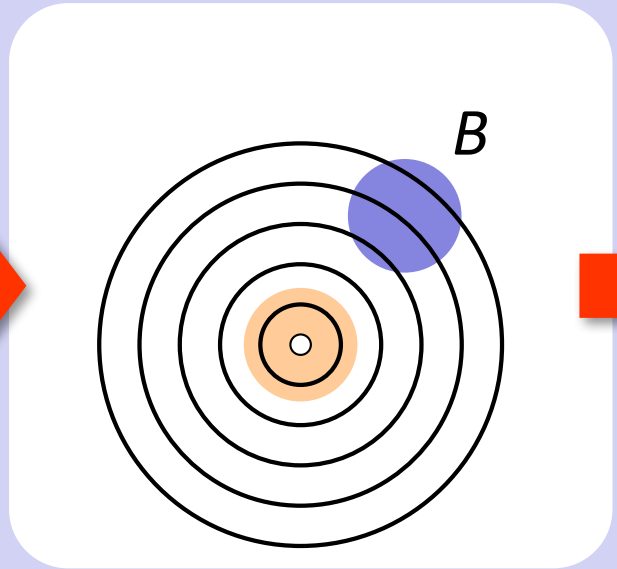

Photo-electron
propagation.

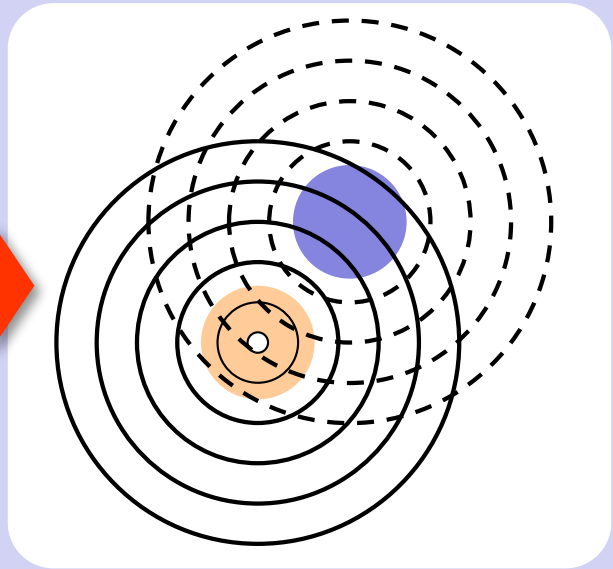

Photo-electron
back-scattering.

Superposition at
the core site.

Modulation of
absorption coefficient

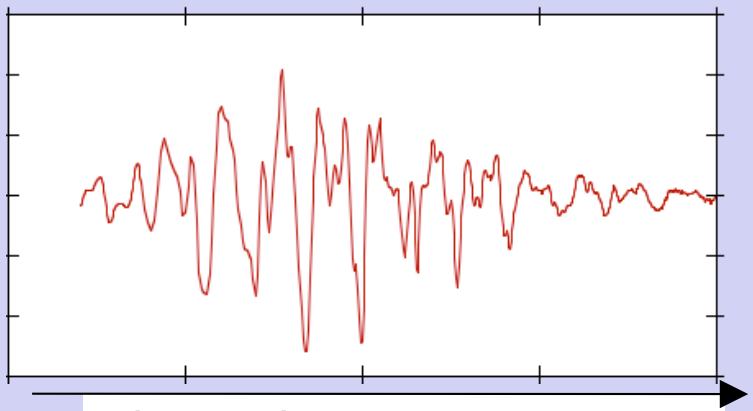

Photo-electron wavevector

Lectures on XAFS

EXAFS
- introduction
- basic theory
- experiments
- data analysis

P. Fornasini

XANES

M. Benfatto
C. Meneghini

Data analysis

C. Meneghini
M. Merlini

Applications

XAFS in nanostructures & materials science
F. Boscherini

SR & Matter in extreme conditions
G. Aquilanti

SR & Environmental science
P. Lattanzi

SR & Earth sciences
G. Artioli

SR & Chemistry
A. Martorana

SR & catalysts
C.Lamberti

X-rays absorption - theory

Photon flux

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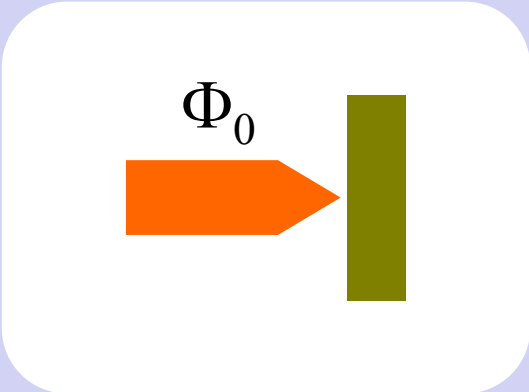
Vector potential

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



Energy flux

$$\Phi = \langle u \rangle\, c = \frac{\epsilon_0 \omega^2 A_0^2 c}{2}$$

J m^{-2} s^{-1}

Photon flux

$$\Phi = \frac{\text{energy flux}}{\text{photon energy}} = \frac{(\epsilon_0 \omega^2 A_0^2/2)c}{\hbar\omega} = \frac{\epsilon_0 \omega A_0^2 c}{2\hbar}$$

m^{-2} s^{-1}

Absorption coefficient

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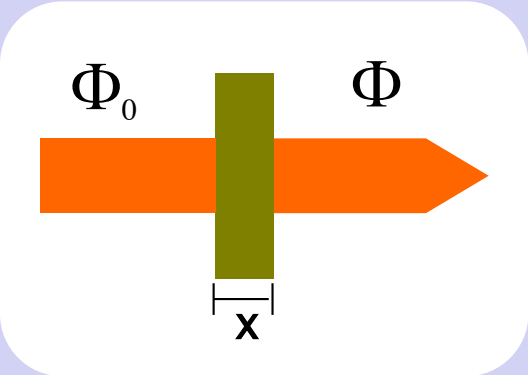

total attenuation

photo-electric absorption

atomic cross-section

$$\mu(\omega) \cong \tau(\omega) = \frac{1}{x}\ln\frac{\Phi_0}{\Phi} = n\,\sigma_a(\omega)$$

$$n = \frac{N_a \rho}{A}$$

number density depends on mass density

Mass attenuation coefficient (indep. of mass density)

Elements $\frac{\mu}{\rho} = \frac{N_a}{m_{at}}\sigma_a$

Compounds P_xQ_y... $\left(\frac{\mu}{\rho}\right)_{tot} = x\left(\frac{\mu}{\rho}\right)_P \frac{m_P}{M} + y\left(\frac{\mu}{\rho}\right)_Q \frac{m_Q}{M} + K$

N_a = Avogadro number; m_{at} = atomic mass; M = molecular mass

http://physics.nist.gov/PhysRefData/XrayMassCoef/tab3.html

Half-thickness

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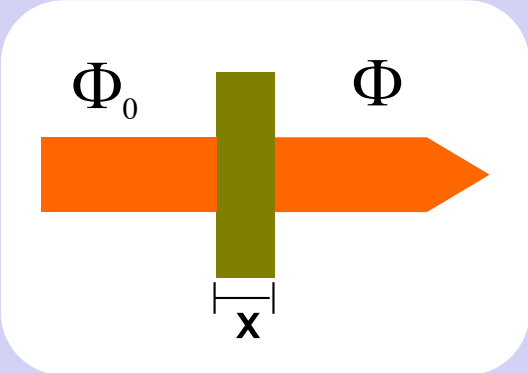

Thickness for which the flux is halved

$$\Phi = \frac{\Phi_0}{2} \quad \Rightarrow \quad x_{1/2} = \frac{\ln 2}{\mu} = \frac{0.693}{\left(\frac{\mu}{\rho}\right)\rho}$$

Table 2.1: Half-thickness (cm) for selected substances at selected X-ray wavelengths.

$\hbar\omega$ (keV)	Air	Mylar	Be	Al	Cu	Pb	
	0.0012	1.39	1.85	2.7	8.96	11.34	density (g/cm^3)
5	14.05	0.018	0.0085	0.001	0.0005	8.3e-5	
20	727.33	0.860	1.6641	0.075	0.0023	0.0007	
50	2719.8	2.468	2.4105	0.697	0.0296	0.0076	

Cross section and transition rates

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Photon flux

$$\Phi = \frac{\epsilon_0 \omega^2 A_0^2 c}{2\hbar}$$

Number density

$$\mu(\hbar\omega) = n\,\sigma_a(\hbar\omega) = \frac{1}{\Phi_0}\, n \sum\nolimits_f w_{fi} = \frac{2\hbar}{\epsilon_0 \omega\, A_0^2 c}\, n \sum\nolimits_f w_{fi}$$

Transition probability per unit time = w_{fi} = Transition rate

Semi-classical approximation

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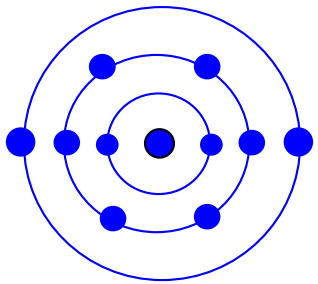
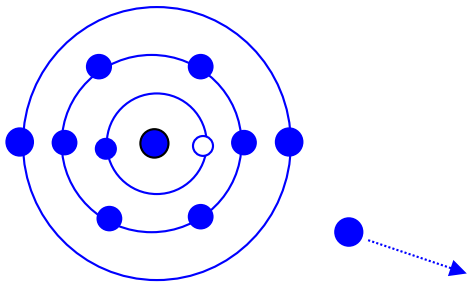
- Quantum treatment of atoms
- Classical treatment of field

w_{fi} = Transition probability per unit time = Transition rate

Initial state: $|\Psi_i\rangle$
atom in ground state



Final state: $|\Psi_f\rangle$
excited atom
+ photoelectron



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

Radiation-matter interaction

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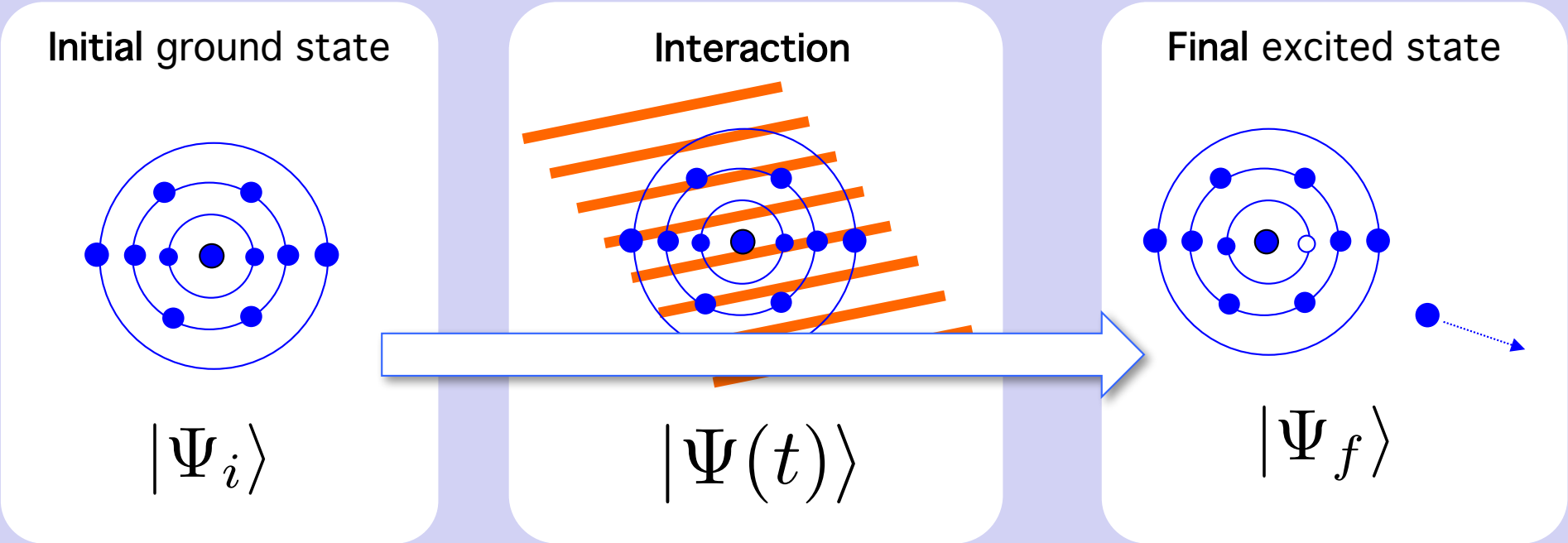

$$w_{fi} = \quad ??$$

Fermi's Golden Rule

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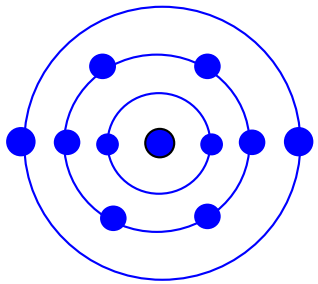
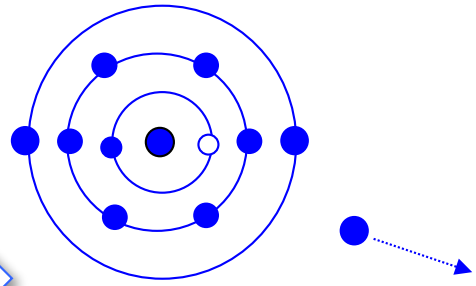
Initial ground state



$|\Psi_i\rangle$

Time-dependent perturbation theory. 1st order

Final excited state



$|\Psi_f\rangle$

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

Interaction Hamiltonian

$$H_I(\vec{r}) = \frac{e}{m} \sum_f \vec{p}_j \cdot \vec{A}(\vec{r})$$

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

Coordinates representation

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

$$w_{fi} = \frac{\pi}{2\hbar} \left| \int \Psi_f(\vec{r})\, H_I(\vec{r})\, \Psi_i(\vec{r})\, d\vec{r} \right|^2 \rho(E_f)$$

$$H_I(\vec{r}) = \frac{e}{m} \sum_f \vec{p}_j \cdot \vec{A}(\vec{r})$$

Transition rates and absorption coefficient

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$$
\begin{aligned}
w_{fi} &= \frac{\pi}{2\hbar} \left|\langle \Psi_f | H_I | \Psi_i \rangle\right|^2 \rho(E_f) \\
&= \frac{\pi e^2 A_0^2}{2\hbar m^2} \left| \left\langle \Psi_f \left| \sum_j e^{i\vec{k}\cdot\vec{r}_j} \hat{\eta}\cdot\vec{p}_j \right| \Psi_i \right\rangle \right|^2 \rho(E_f)
\end{aligned}
$$

Sum over electrons

$$
\begin{aligned}
\mu(\hbar\omega) &= \frac{2\hbar}{\epsilon_0 \omega A_0^2 c} n \sum_f w_{fi} \\
&= \frac{\pi e^2}{\epsilon_0 \omega m^2 c} n \sum_f \left| \left\langle \Psi_f \left| \sum_j e^{i\vec{k}\cdot\vec{r}_j} \hat{\eta}\cdot\vec{p}_j \right| \Psi_i \right\rangle \right|^2 \rho(E_f)
\end{aligned}
$$

Sum over final states

Sum over electrons

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

A first summary

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Sum over final states

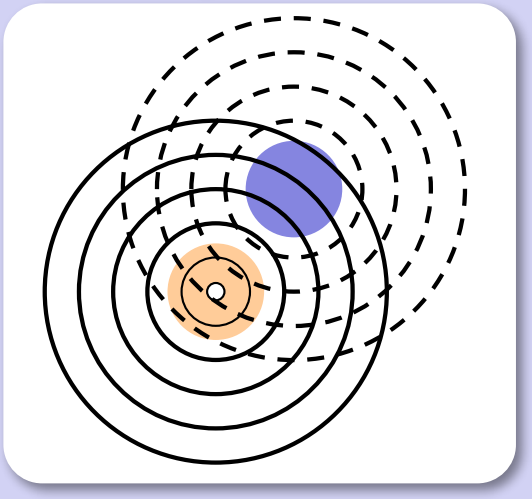
Sum over electrons

$$\mu(\hbar\omega) \propto \sum_f \left| \left\langle \Psi_f \left| \sum_j e^{i\vec{k}\cdot\vec{r}_j} \hat{\eta}\cdot\vec{p}_j \right| \Psi_i \right\rangle \right|^2 \rho(E_f)$$

Oscillating e.m. field

Final atomic state

?



Further approximations

Final states

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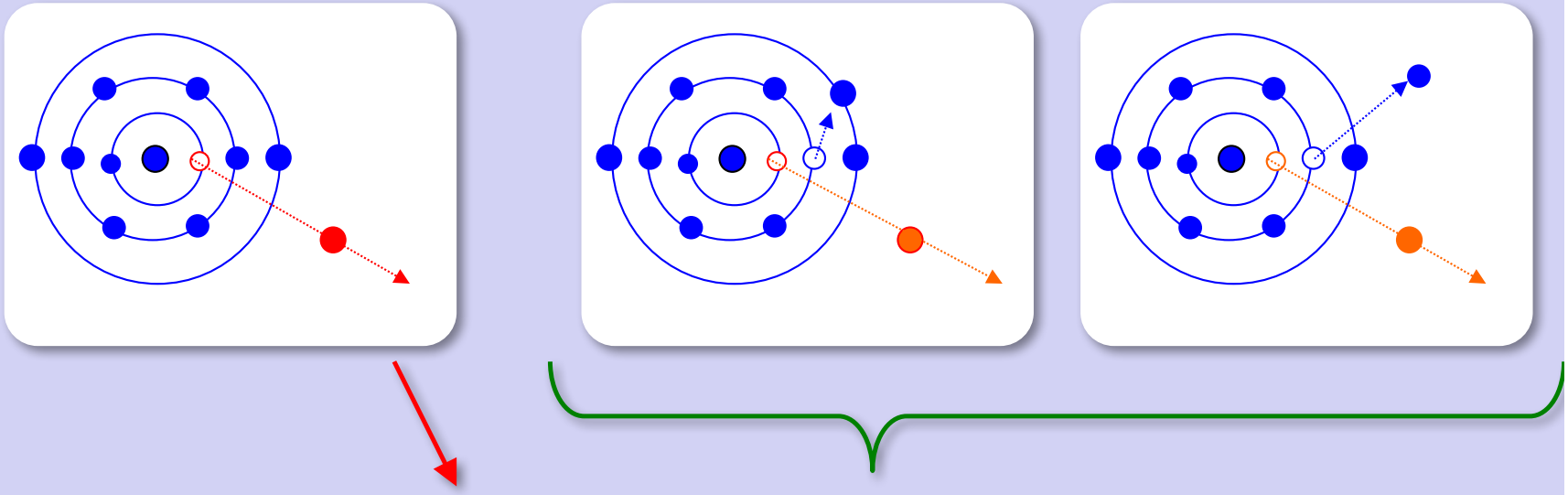
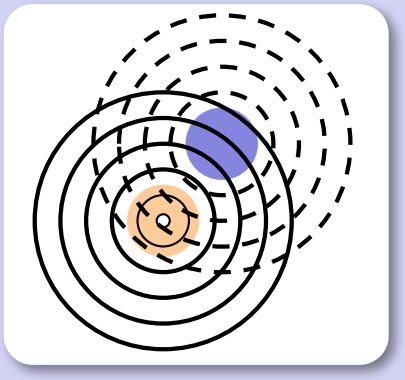


$$\mu_{\mathrm{tot}}(\hbar\omega) = \mu_{\mathrm{el}}(\hbar\omega) + \mu_{\mathrm{inel}}(\hbar\omega)$$



EXAFS coherent signal

One-electron approximation

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

$$\propto w_{\rm el} + \sum w_{\rm inel}$$

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

- 1 core electron excited
- Other electrons excited

see below

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

one-electron position

Electric dipole approximation

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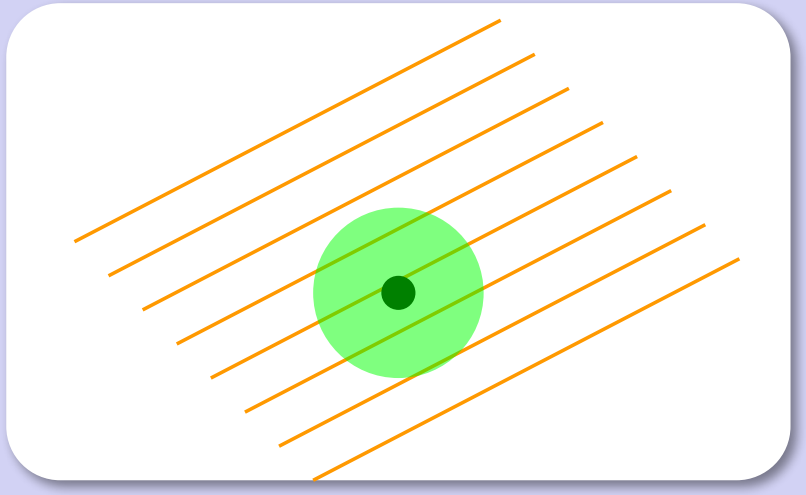
$$e^{i\vec{k}\cdot\vec{r}} = 1 + i\vec{k}\cdot\vec{r} - \ldots \simeq 1$$



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

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

Dipole selection rules:

$\Delta l = \pm 1$ $\quad\quad$ $\Delta s = 0$

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

Sudden approximation

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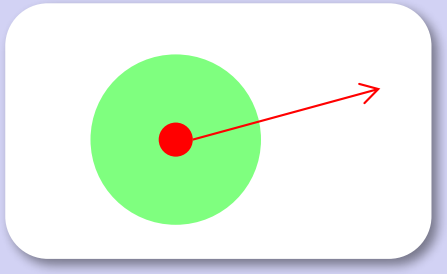
No interaction between photoelectron and passive electrons

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



1 active electron

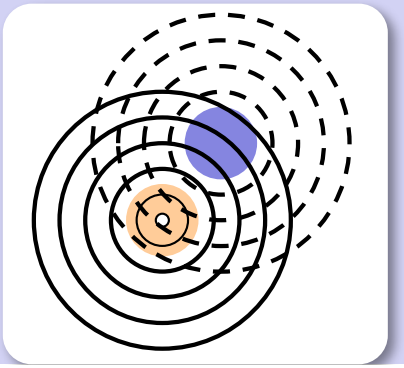
N-1 passive electrons

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

$$S_0^2 \simeq 0.6 - 0.9$$

One-electron final state

Structural info



The final state

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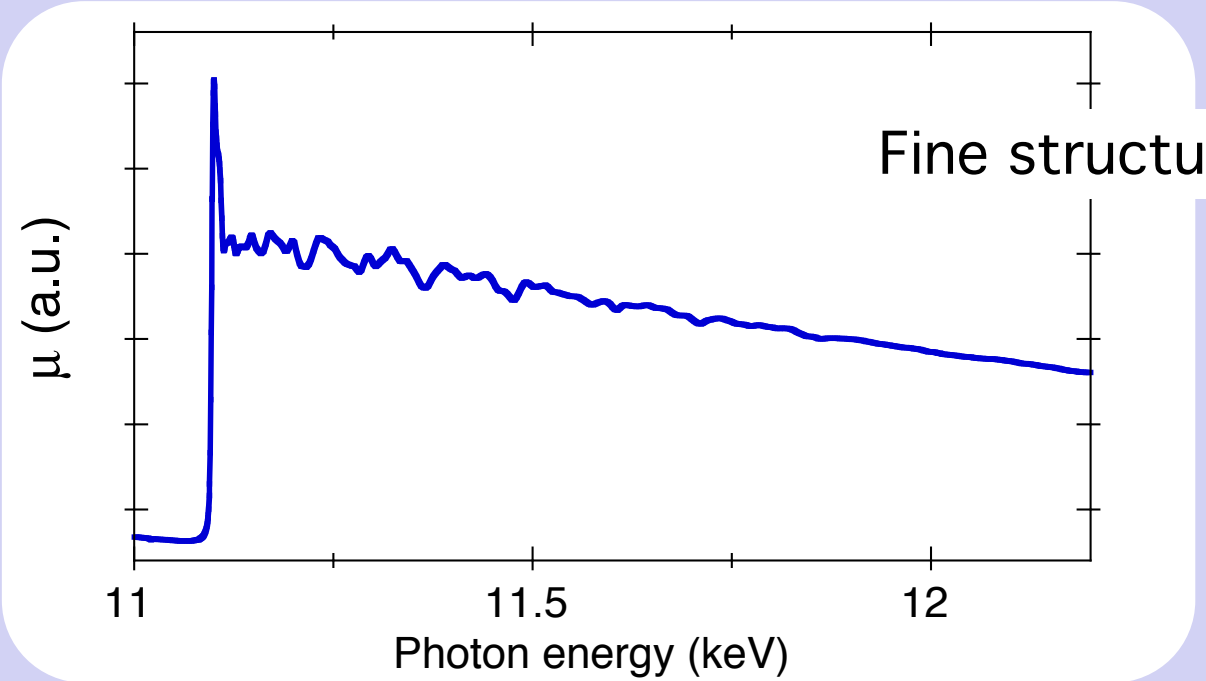

Fine structure ⟷ $|\psi_f\rangle$ at the core site

$|\psi_f\rangle$ ⟨

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

Atomic de-excitation

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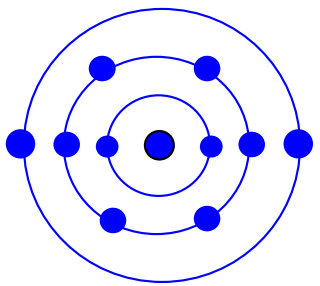
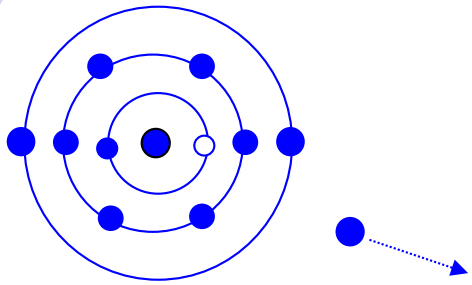
Ground state



$|\Psi_i\rangle$

X-ray absorption

Core-excited state + photoelectron



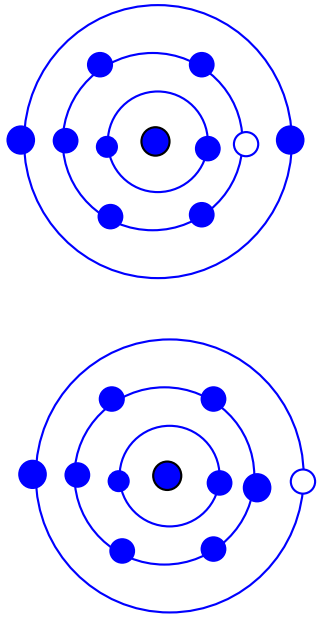
$|\Psi_f\rangle$

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

XAFS

τ_h

Core de-excitation



Excitation transferred to outer levels

τ_h = lifetime of core excited

τ_h is shorter for higher atomic number Z

Core-hole lifetime and energy width

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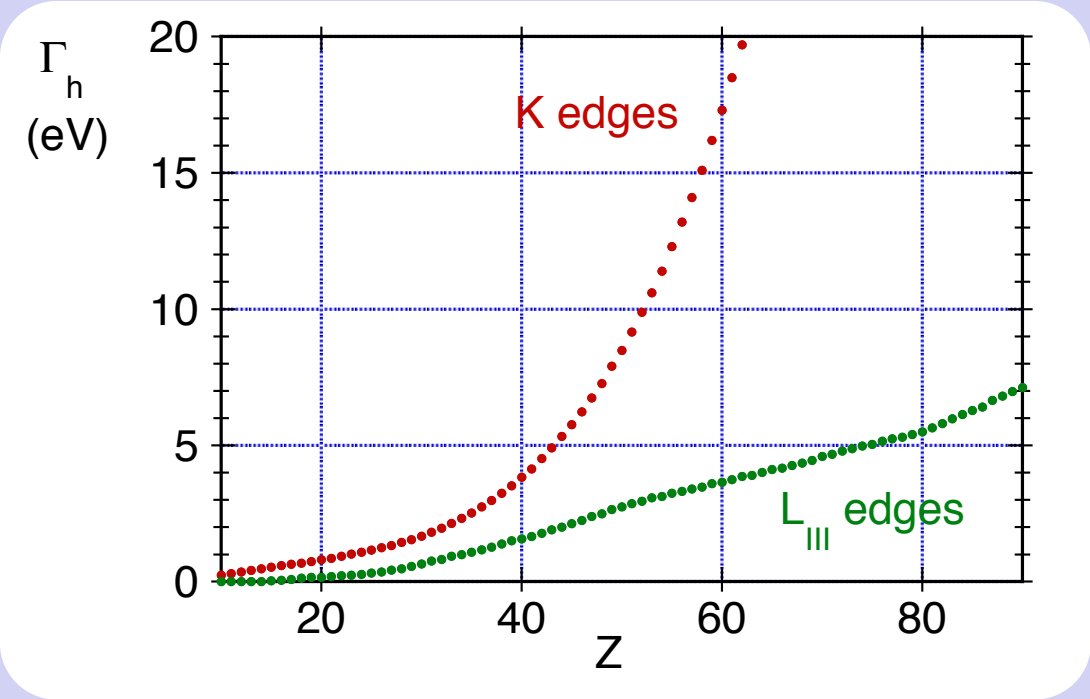
Lifetime
of the excited state
$\tau_h \sim 10^{-16} - 10^{-15}$ s

$$\tau_h \propto \frac{1}{\Gamma_h}$$

Energy width
of the excited state
Γ_h



Dependence on Z

τ_h

Contribution to
photo-electron life-time

Γ_h

Energy resolution
of XAFS spectra

De-excitation mechanisms

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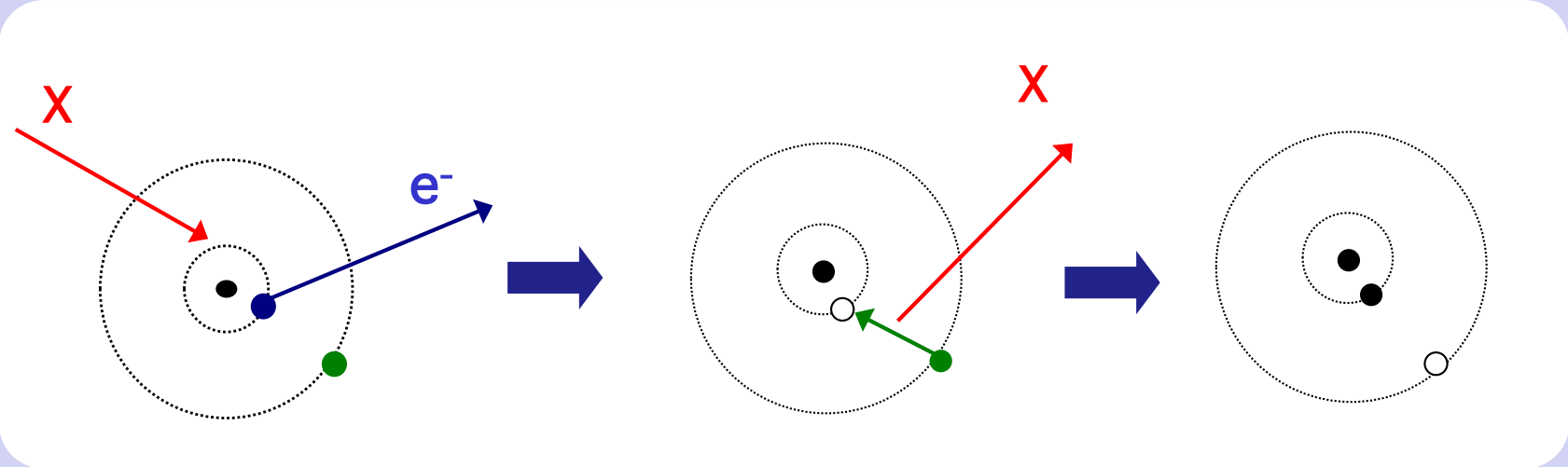
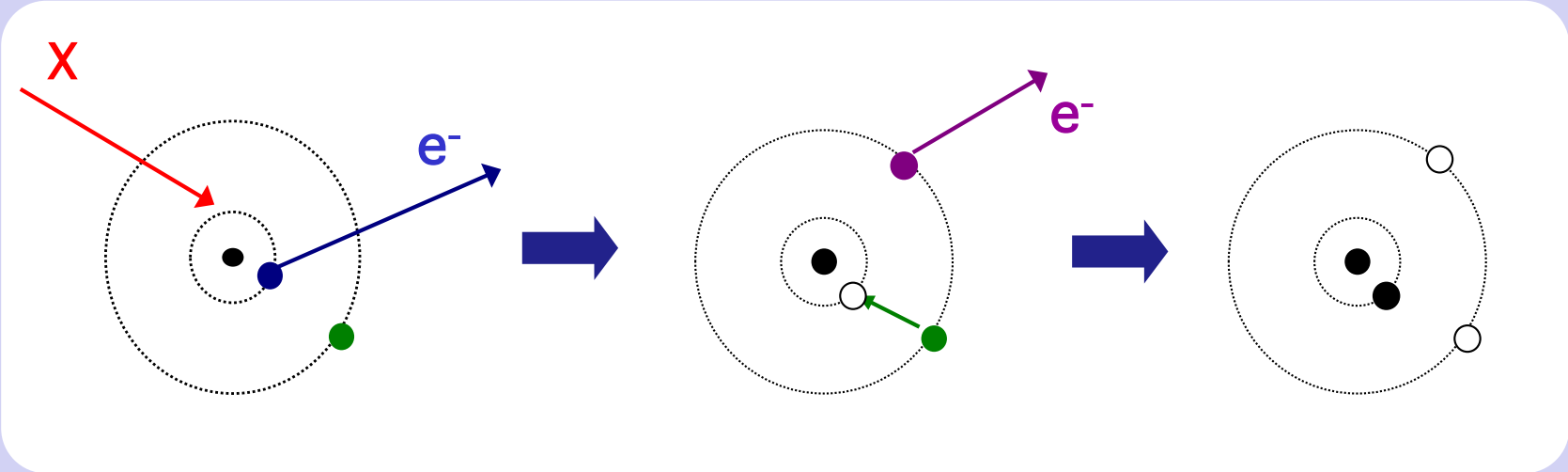
Radiative: fluorescence X



Non-radiative: Auger A



Fluorescence yield

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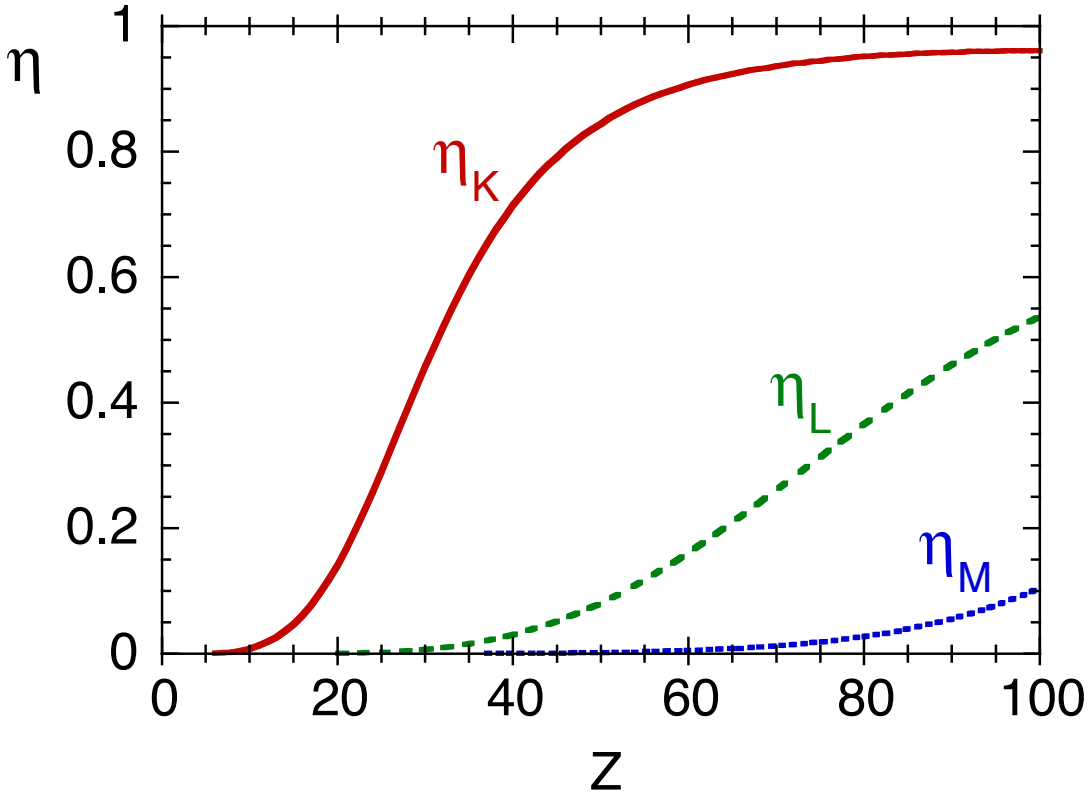
Fluorescence versus Auger

Fluorescence yield

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



Both fluorescence and Auger yields intensities are proportional to the absorption coefficient

→ Alternative measurements of XAFS

EXAFS: theoretical background

Absorption coefficient

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$$\mu(\hbar\omega) = \frac{2\hbar}{\epsilon_0 \omega A_0^2 c} n \sum_f w_{fi}$$

Time-dep. perturbation theory

$$W_{if} \propto \left|\left\langle \Psi_f \middle| \hat{H}_I \middle| \Psi_i \right\rangle\right|^2 \rho(E_f)$$

- one-electron approx.
- sudden approx.
- electric dipole approx.

1 active electron

N-1 passive electrons

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

Structural information

$$S_0^2 \simeq 0.6 - 0.9$$

A: isolated atom

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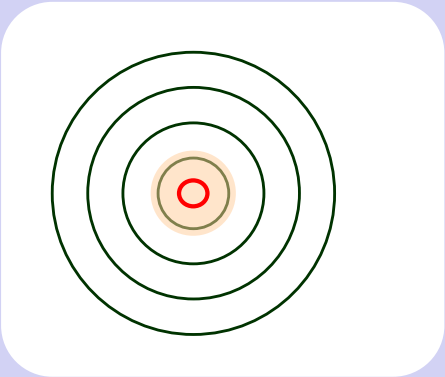

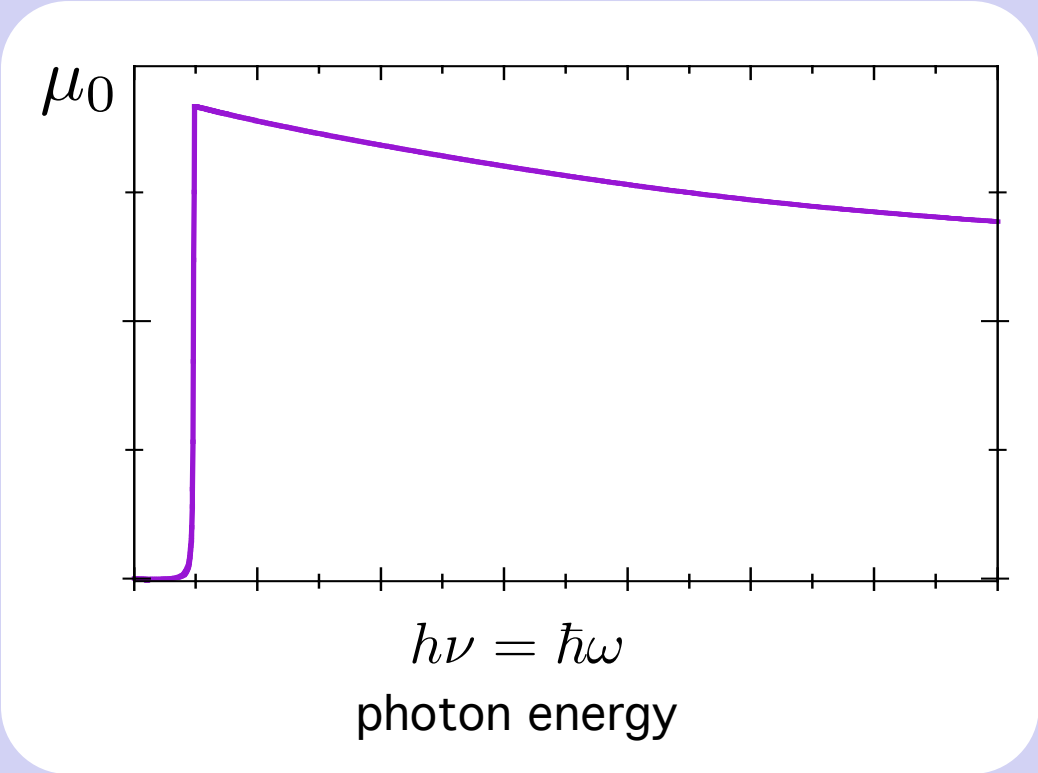

$$\mu_0(\omega) \propto \left| \left\langle \psi_f^0 \left| \hat{\eta} \cdot \vec{r} \right| \psi_i \right\rangle \right|^2$$

outgoing electron

core state

Photon → photo-electron

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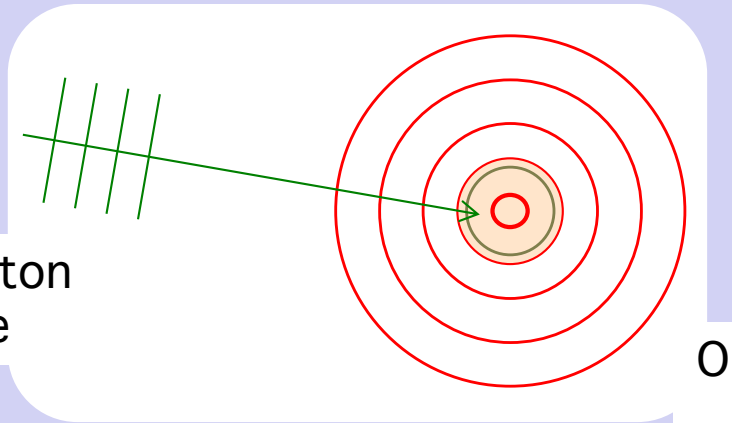

Incoming photon plane wave

Outgoing photo-electron spherical wave

Photon energy

Photo-electron wavenumber

$$\sqrt{\frac{2m}{\hbar^2}\left(\hbar\omega - E_b\right)} = \sqrt{\frac{2m}{\hbar^2}\,\epsilon} = k = \frac{2\pi}{\lambda}$$

Core-electron binding energy

Photo-electron parameters

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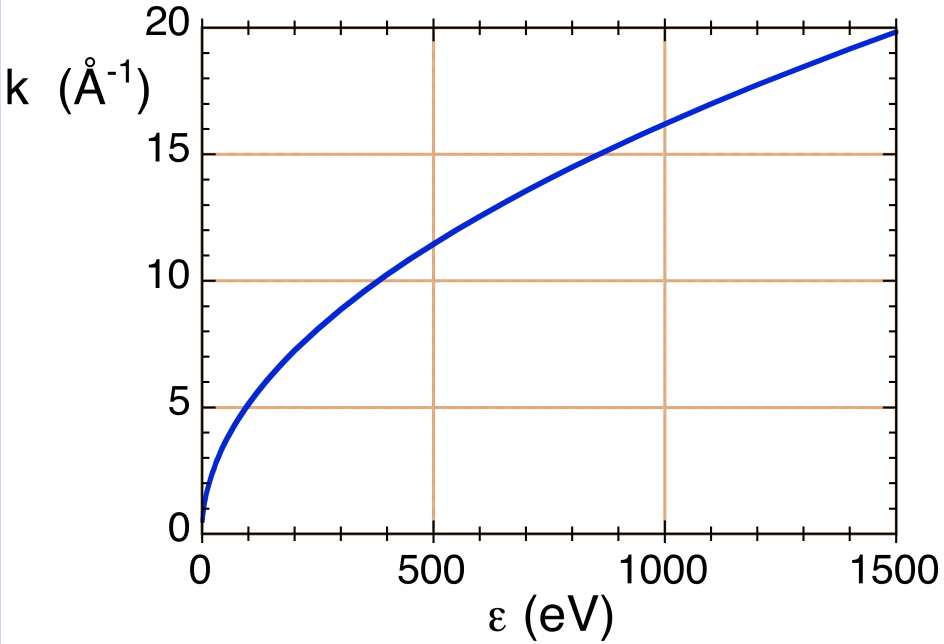
Wave-number



Wave-length

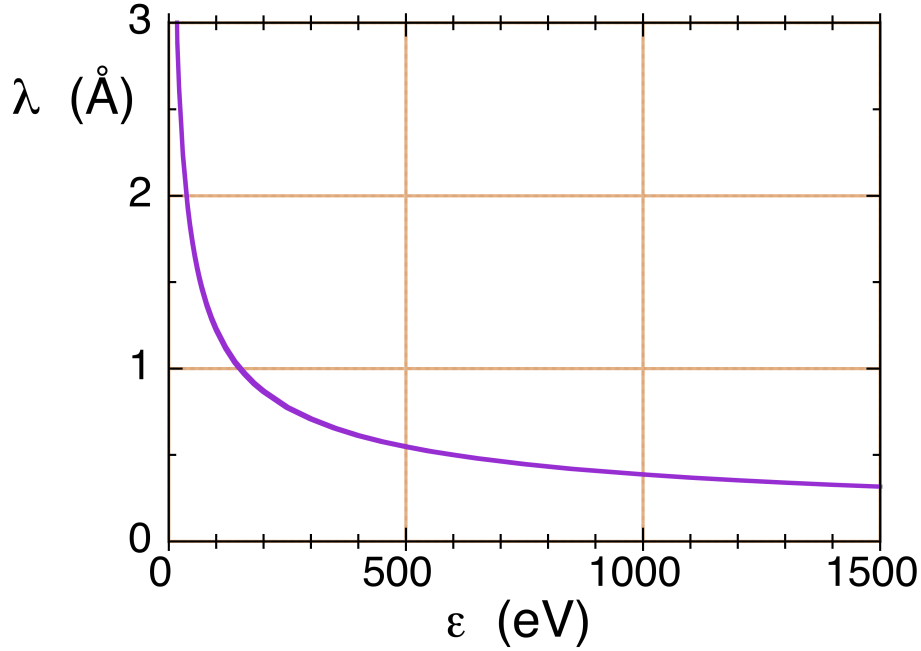


Photo-electron Energy

Angular emission of photo-electron

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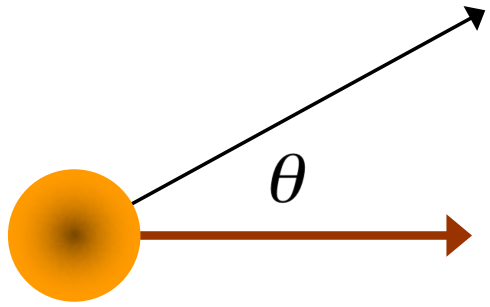
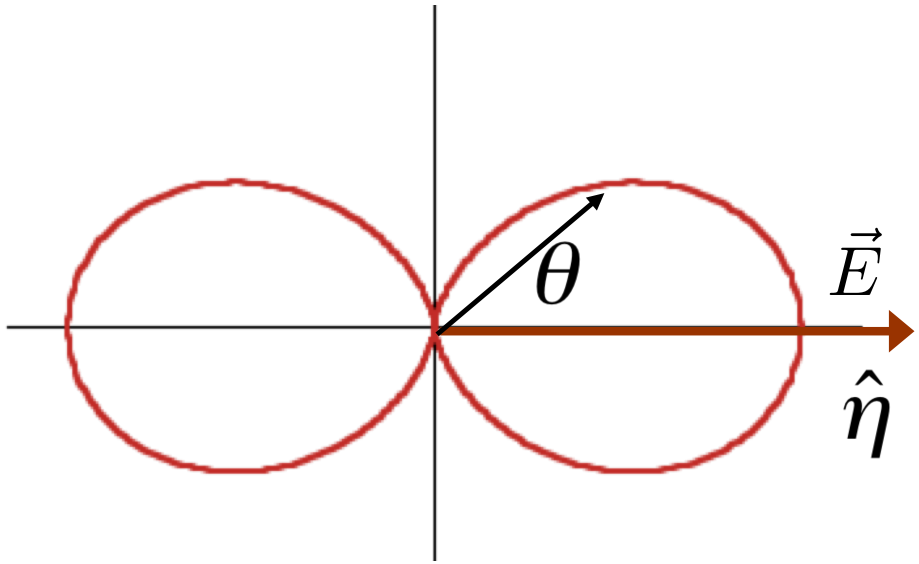


Photoelectron emission

Photon polarisation

asimmetry parameter

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



$$\beta = 2$$

Emission from s orbitals

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

B: non-isolated atom

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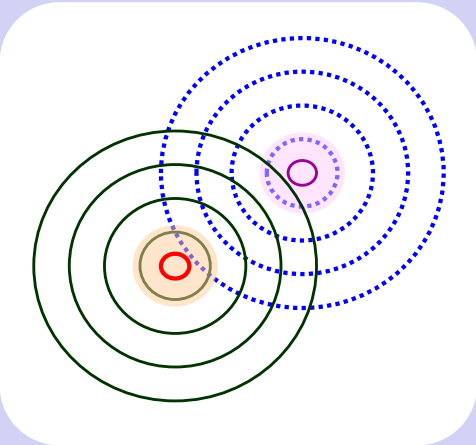

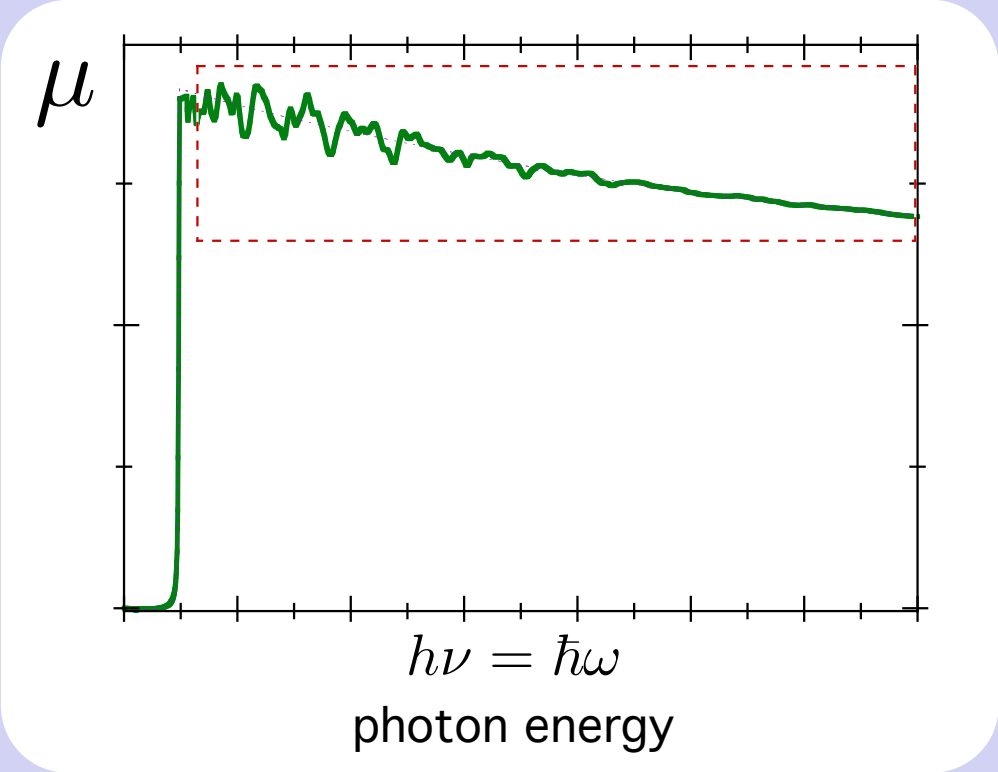

$$\mu(\omega) \propto \left|\langle \psi_f \left| \hat{\eta} \cdot \vec{r} \right| \psi_i \rangle\right|^2$$

Outgoing + scattered electron

core state

The EXAFS normalized signal $\chi(k)$

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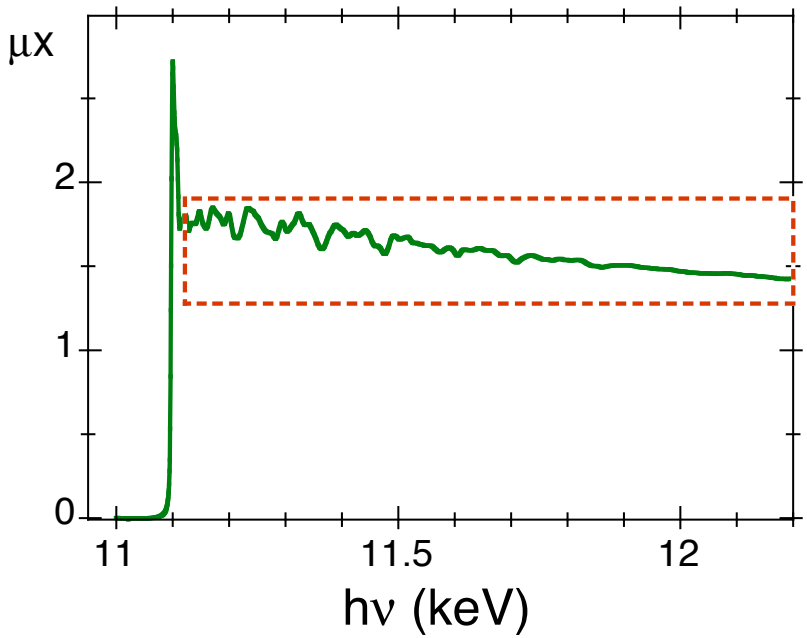


photon energy

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

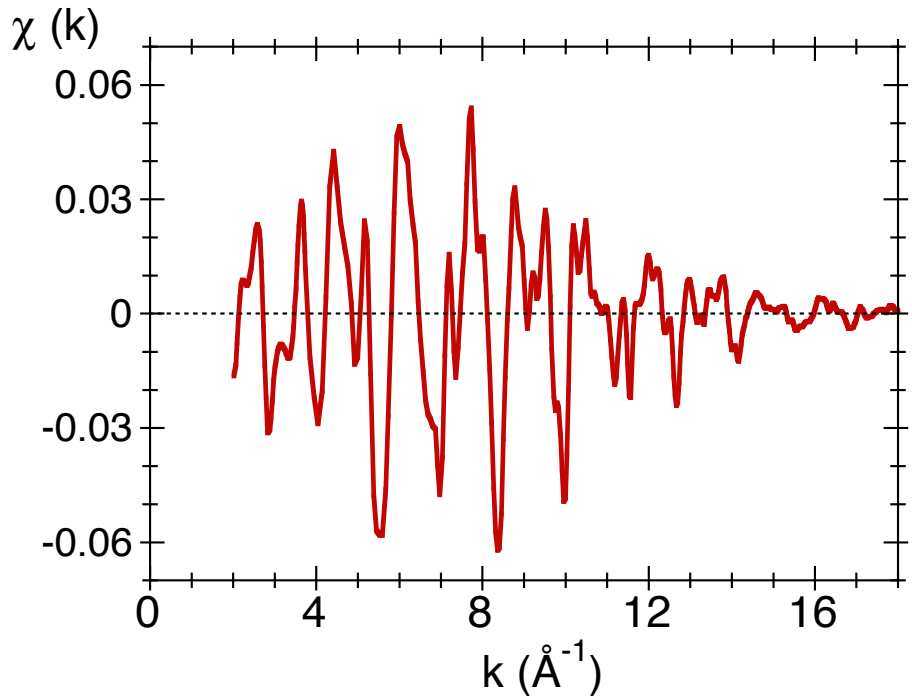
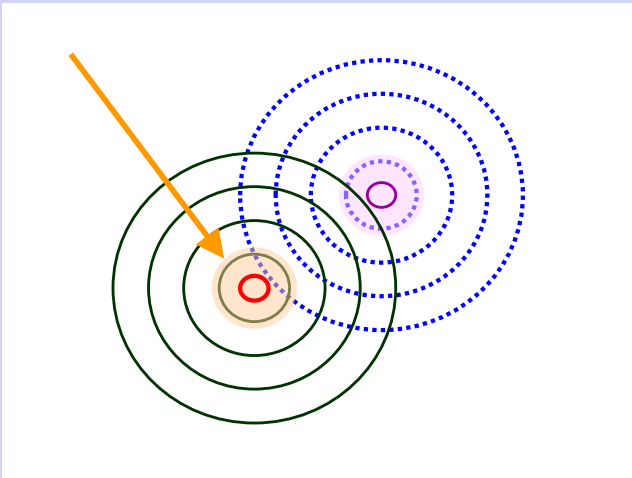


photo-electron wave-number



The absorption coefficient

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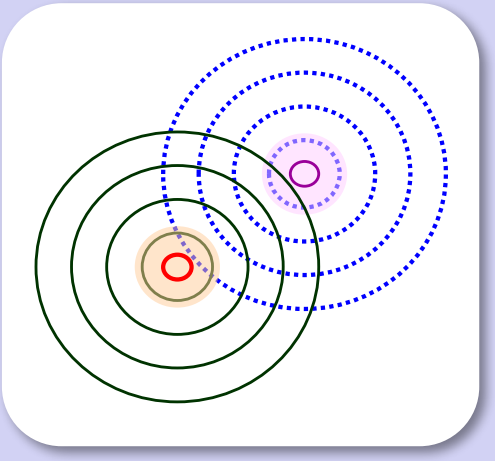

Final state

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

Perturbation
due to photoelectron scattering

Structural
info

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

$$\begin{aligned} \mu(\omega) \quad \propto \quad & \left|\left\langle \psi_f^0 \left|\hat{\eta}\cdot\vec{r}\right| \psi_i \right\rangle\right|^2 \\ + \quad & 2\mathrm{Re}\left\{\left\langle \psi_f^0 \middle|\hat{\eta}\cdot\vec{r}\middle| \psi_i \right\rangle \left\langle \delta\psi_f \middle|\hat{\eta}\cdot\vec{r}\middle| \psi_i \right\rangle\right\} \\ + \quad & \left|\left\langle \delta\psi_f \left|\hat{\eta}\cdot\vec{r}\right| \psi_i \right\rangle\right|^2 \end{aligned}$$

μ_0

EXAFS oscill.

?

$$\boxed{\delta\psi_f = ?}$$

Two-atomic system: $\delta\psi_f$

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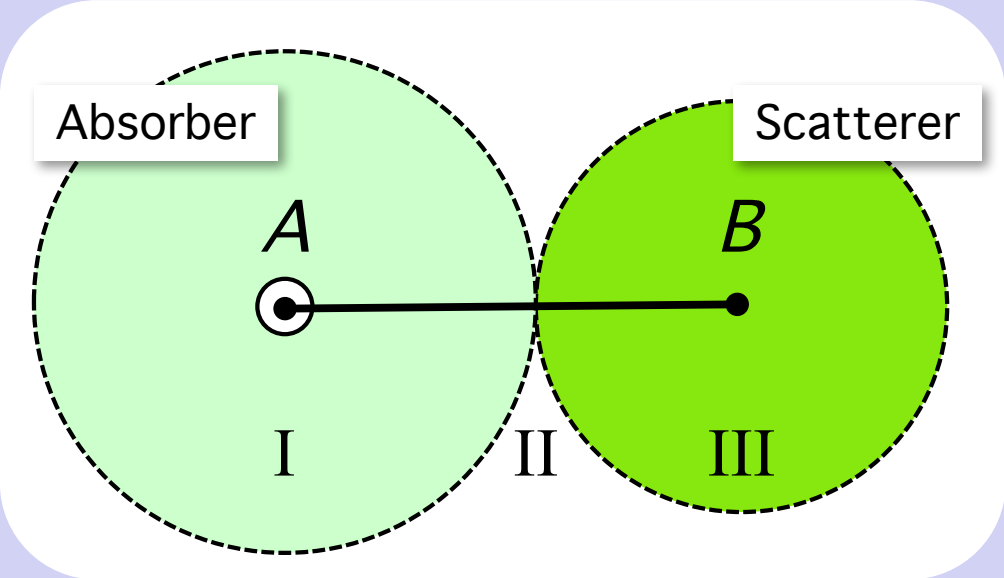

$$\delta\psi_f = ?$$

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

At the absorber core site

Interactions

A B A

$$\delta\psi_f \propto \psi_f^0 \frac{1}{2k} e^{i\delta} \frac{\exp(ikR)}{R} f(k,\pi) \frac{\exp(ikR)}{R} e^{i\delta}$$

A➔B B➔A

Propagators

Two-atomic system: absorption coefficient

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Central-atom phaseshift

Total propagator

Back-scattering amplitude

$$\delta\psi_f \propto \psi_f^0 \frac{1}{2k} e^{i2\delta} \frac{\exp(\mathrm{i}2kR)}{R^2} f(k,\pi)$$

$$\mu \propto \underbrace{\left|\left\langle \psi_f^0 \left| \hat{\eta}\cdot\vec{r} \right| \psi_i \right\rangle\right|^2}_{\mu_0(\omega)} + \underbrace{2\mathrm{Re}\left\{\left\langle \psi_f^0 \left| \hat{\eta}\cdot\vec{r} \right| \psi_i \right\rangle \left\langle \delta\psi_f \left| \hat{\eta}\cdot\vec{r} \right| \psi_i \right\rangle\right\}}_{\text{Superposition } \psi_f^0 \leftrightarrow \delta\psi_f} + \underbrace{\left|\left\langle \delta\psi_f \left| \hat{\eta}\cdot\vec{r} \right| \psi_i \right\rangle\right|^2}_{\text{Non-oscillating weak smooth contribution – added to } \mu_0}$$

EXAFS

Normalized EXAFS function

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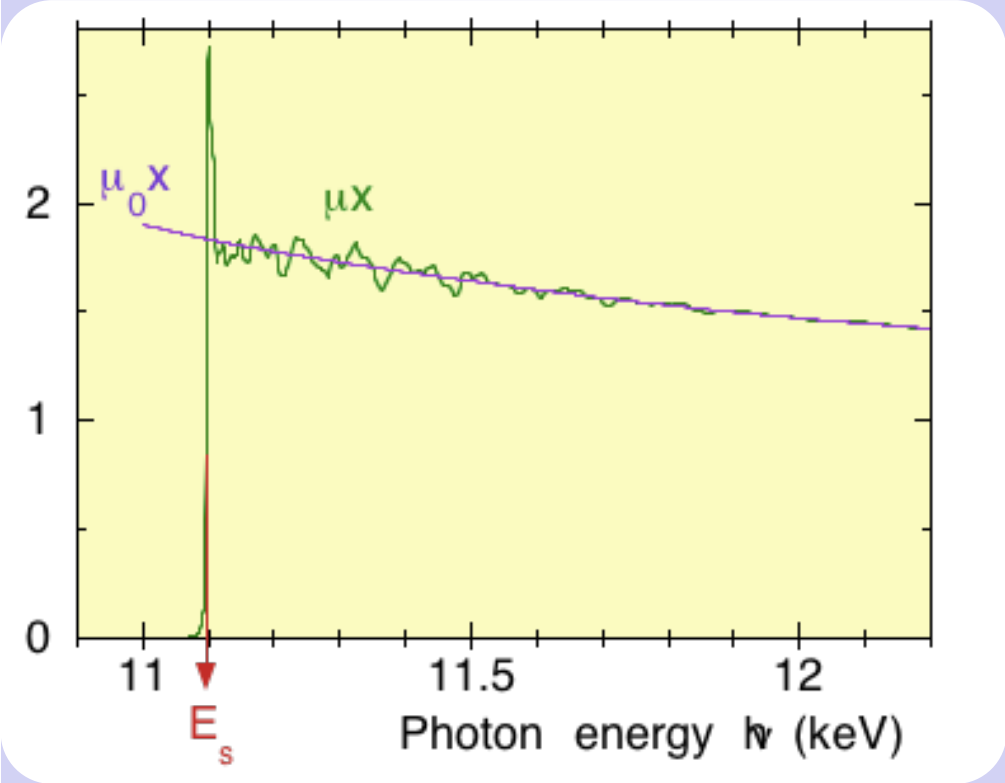

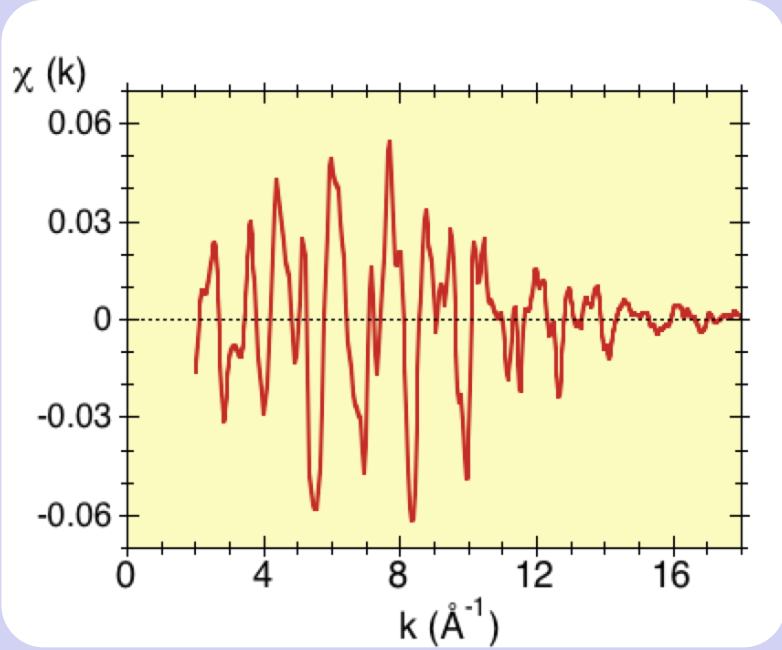

$$\chi(k) = \frac{\mu - \mu_0}{\mu_0}$$

$$\mu - \mu_0 = 2\mathrm{Re}\left\{\left\langle \psi_f^0 | \hat{\eta}\cdot\vec{r} | \psi_i \right\rangle \left\langle \delta\psi_f | \hat{\eta}\cdot\vec{r} | \psi_i \right\rangle\right\}$$

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

EXAFS function in coordinate representation

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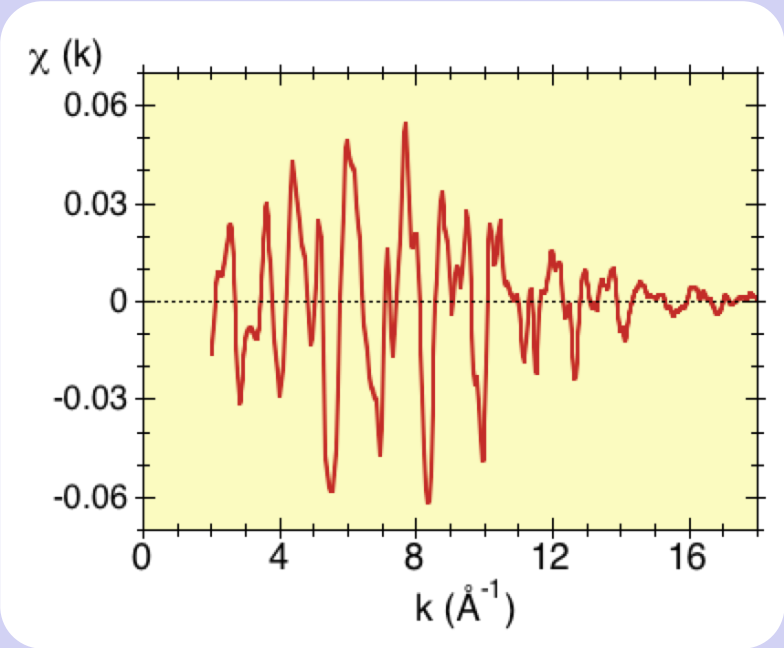
$$\chi(k) = \frac{\mu - \mu_0}{\mu_0}$$

Quantum states → wavefunctions



$$\delta\psi_f$$

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

Core orbital = **source** & **detector**

EXAFS for a two-atomic system

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

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

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

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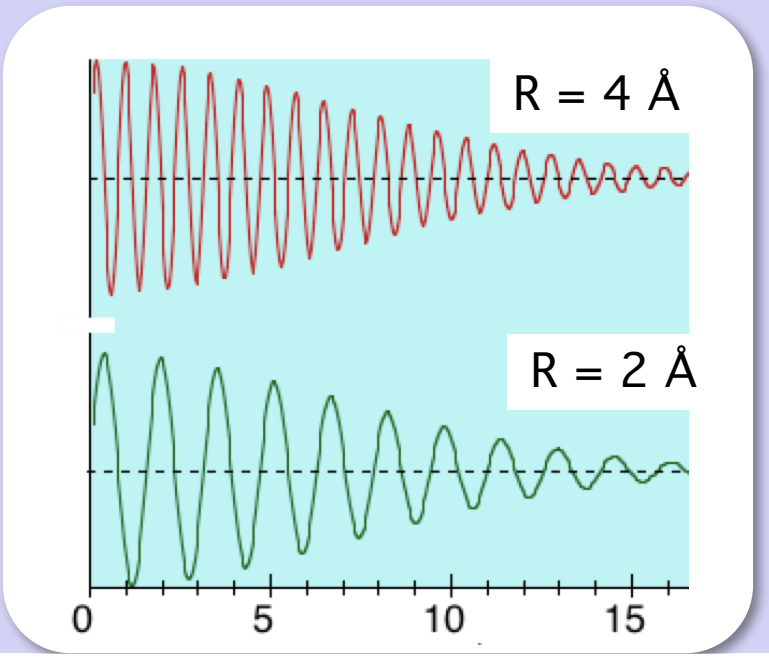
Complex form

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

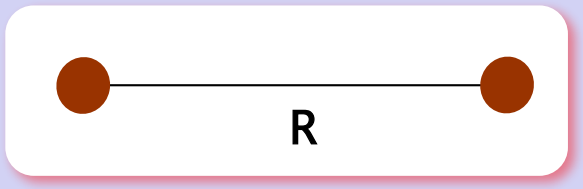
$$f(k,\pi)\,e^{2i\delta} = |f(k,\pi)|\,e^{i\phi}$$

Real form

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



EXAFS frequency ⟷ Inter-atomic distance



Amplitudes and phase-shifts

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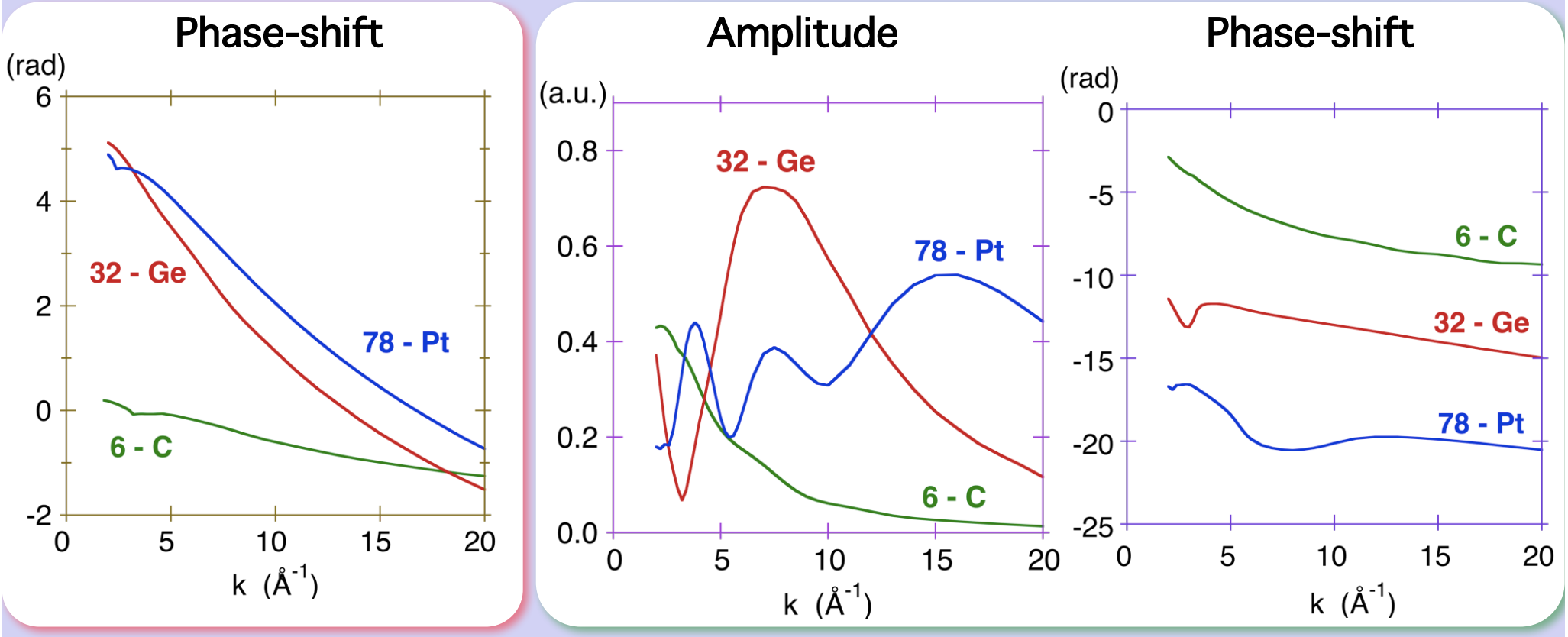
Central-atom

Back-scattering atom



[Calculated by FEFF 6.01]

Z dependence → sensitivity to atomic species

Many-atomic systems

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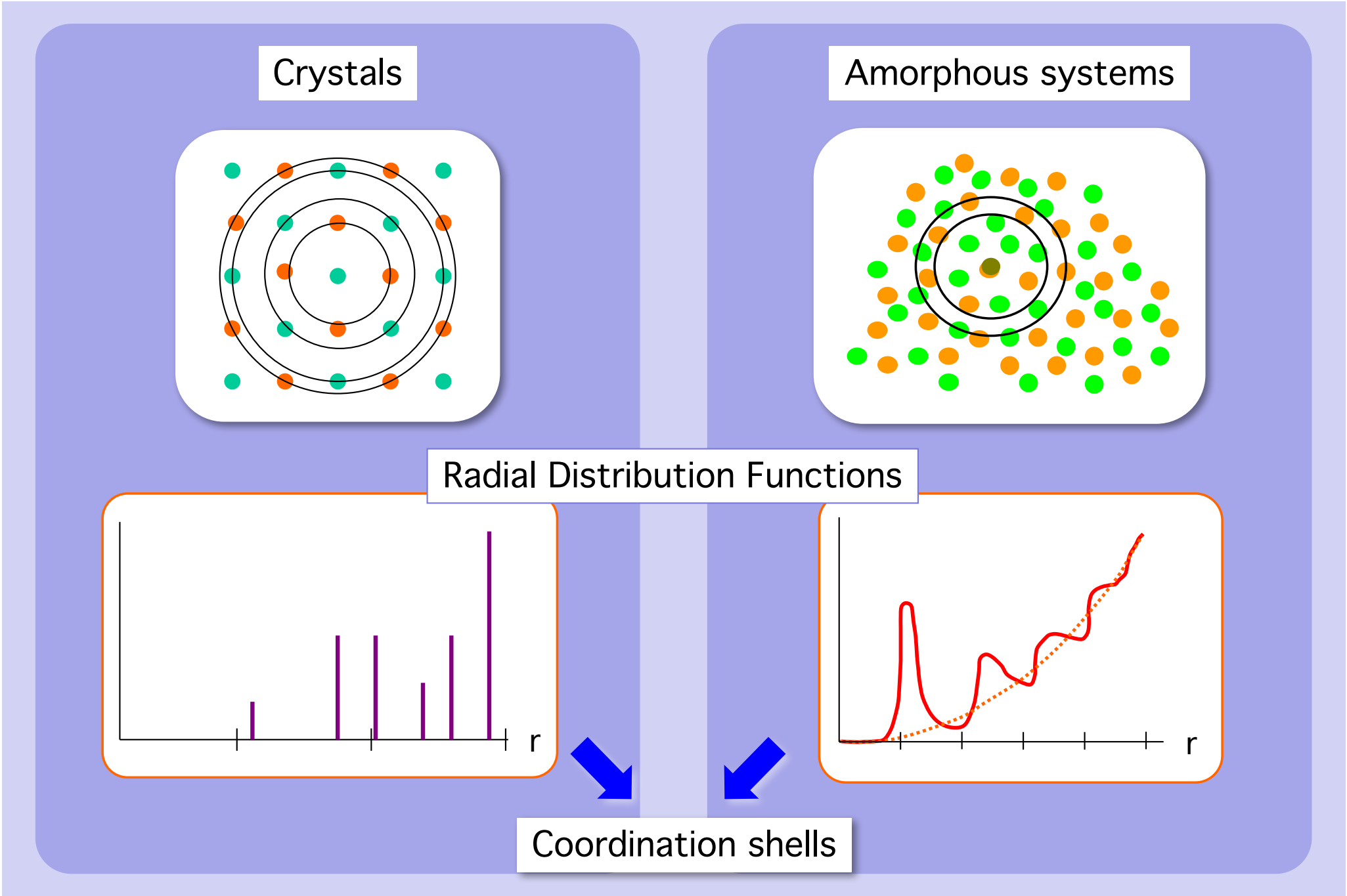

N atoms at the same distance

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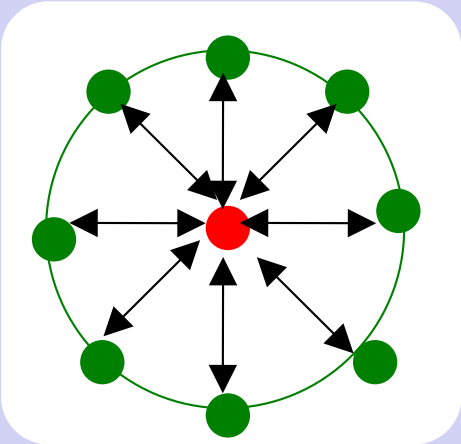

Final state

$$\left|\psi_f\right\rangle = \left|\psi_f^0 + N\,\delta\psi\right\rangle$$

Scattering from N neighbours

Absorption coefficient

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

$$\mu(\omega) \propto \underbrace{\left|\left\langle \psi_f^0 \left|\hat{\eta}\cdot\vec{r}\right| \psi_i \right\rangle\right|^2}_{\mu_0(\omega)} + \underbrace{2N\mathrm{Re}\left\{\left\langle \psi_f^0 \middle|\hat{\eta}\cdot\vec{r}\middle| \psi_i \right\rangle \left\langle \delta\psi_f \middle|\hat{\eta}\cdot\vec{r}\middle| \psi_i \right\rangle\right\}}_{\text{N EXAFS terms}} + \underbrace{N^2 \left|\left\langle \delta\psi_f \left|\hat{\eta}\cdot\vec{r}\right| \psi_i \right\rangle\right|^2}_{\text{Non-oscillating weak smooth contribution – added to } \mu_0}$$

Coordination number

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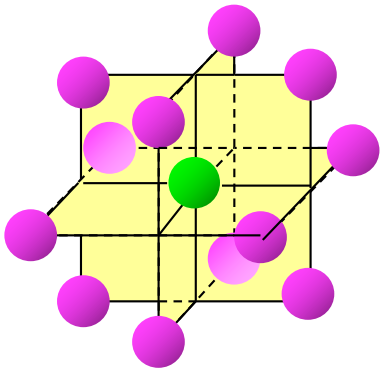
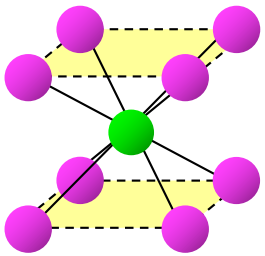
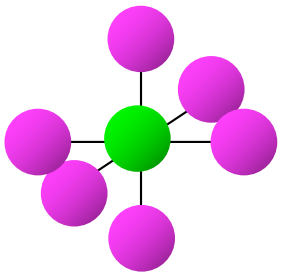
Number of of atoms in the first coordination shell (nearest-neighbours)



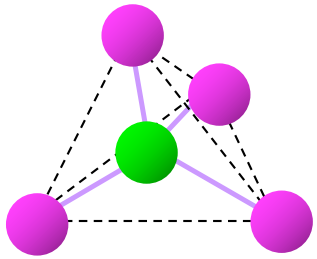
N=12 (e.g. fcc)



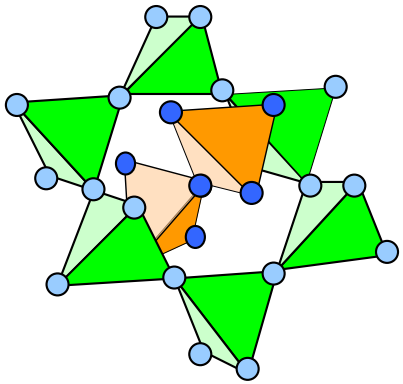
N=8 (e.g. bcc)

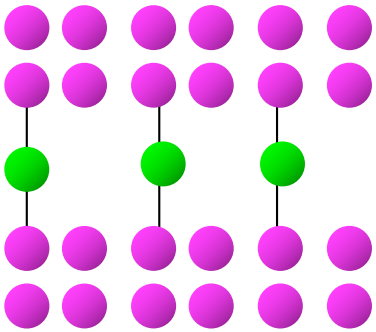


N=6 (e.g. NaCl)

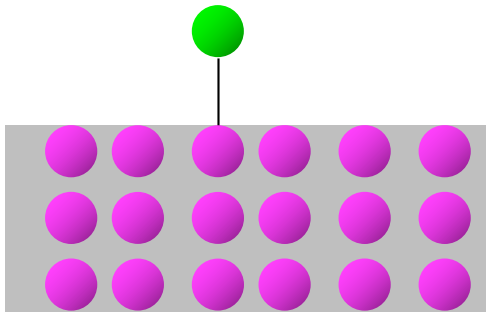


N=4 (e.g. diamond)





N=2



N=1 (e.g. adsorbates)

Polarisation effect

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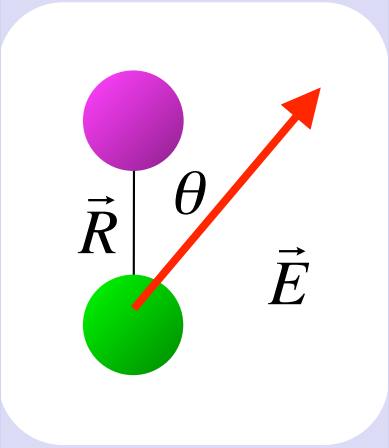
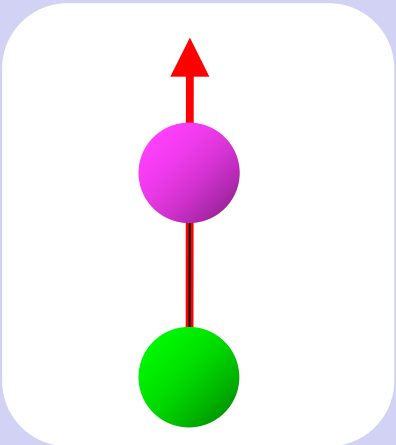
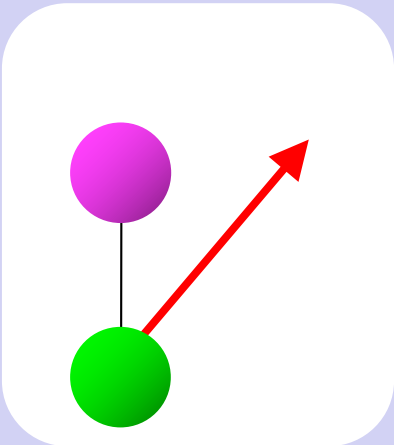


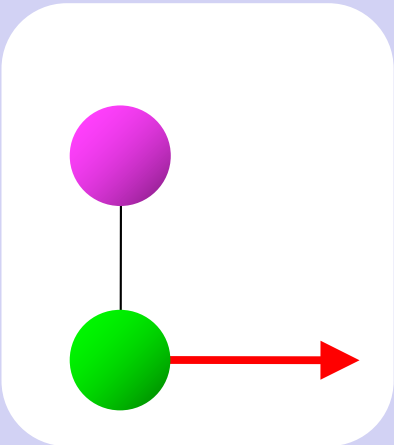
Sum over atoms

$$\chi(k) = \frac{1}{k} \sum_j \underbrace{3\,|\hat{\eta}\cdot\hat{R}|^2}_{3\cos^2\theta_j} \,\mathrm{Im}\left\{ f_j(k,\pi)\, e^{2i\delta_1}\, \frac{1}{R_j^2}\, e^{2ikR_j} \right\}$$

Effective coordination number $N^* = 3\sum_j \cos^2\theta_j$







Coordination shells

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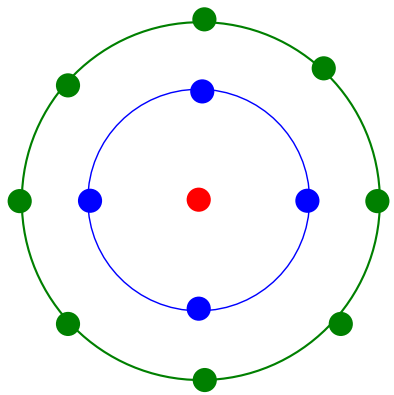
Sum over atoms

$$\chi(k) = \frac{1}{k} \sum_j 3\,|\hat{\eta}\cdot\hat{R}|^2\,\mathrm{Im}\left\{ f_j(k,\pi)\, e^{2i\delta_1}\, \frac{1}{R_j^2}\, e^{2ikR_j} \right\}$$

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

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

Coordination shells



Sum over shells

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

Nr of atoms in the shell

Single and multiple scattering

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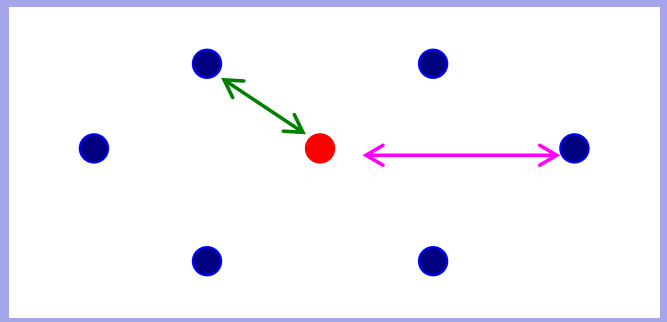
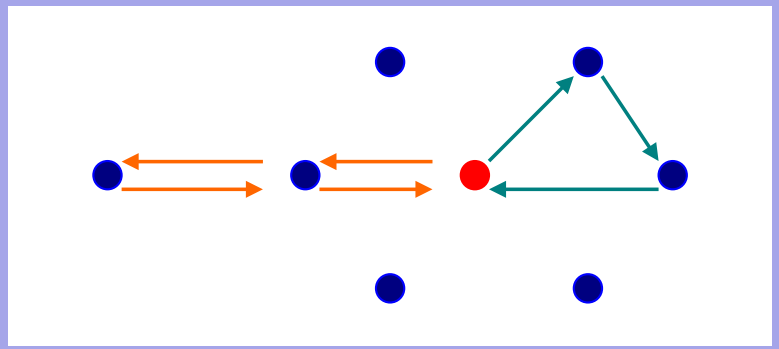
Scattering paths

SS = Single scattering



MS = Multiple scattering



Multiple scattering series

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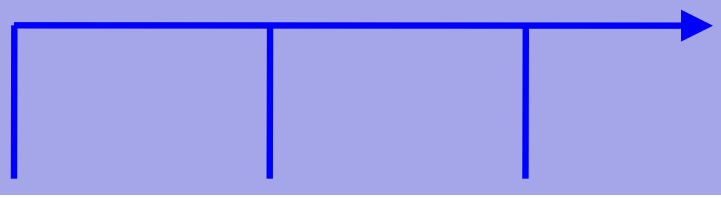
Multiple Scattering



$\chi_n(k) = n - \text{legs paths}$

$$\frac{\mu - \mu_0}{\mu_0} = \sum \chi_2(k) + \sum \chi_3(k) + \sum \chi_4(k) + \ldots$$

$$\mu(k) = \mu_0(k)\left\{1 + \sum \chi_2(k) + \sum \chi_3(k) + \sum \chi_4(k) + \ldots\right\}$$

Single Scattering

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

only 2-legs paths
➔ coordination shells

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

Sum over paths and over correlations

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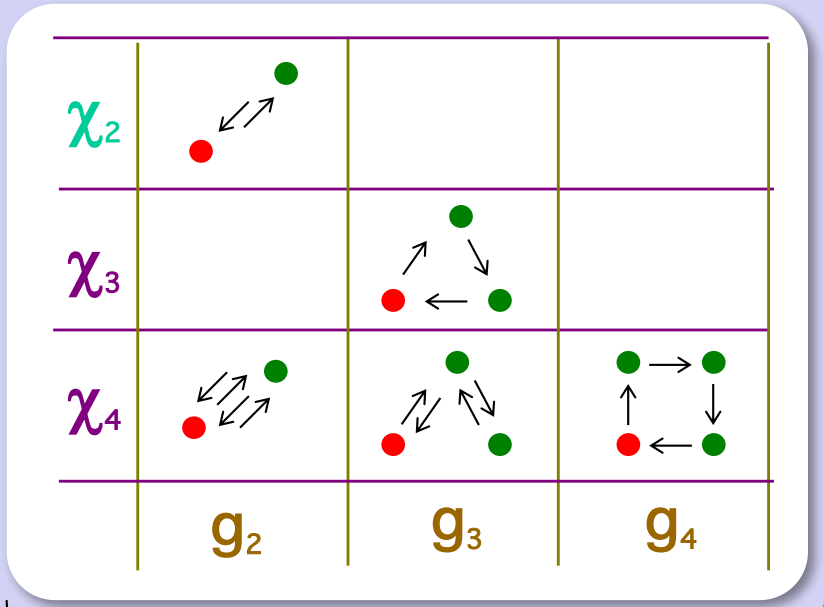
$$\mu(k) = \mu_0(k)\left\{1 + \sum \chi_2(k) + \sum \chi_3(k) + \sum \chi_4(k) + \ldots\right\}$$

Contribution from all n-order paths



g_n = n-body correlation function

$$\mu(k) = \mu_0(k)\left\{1 + \sum \mu^{(2)}(k) + \sum \mu^{(3)}(k) + \sum \mu^{(4)}(k) + \ldots\right\}$$

Multiple scattering series

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$$\mu(k) = \mu_0(k)\left\{1 + \sum \chi_2(k) + \sum \chi_3(k) + \sum \chi_4(k) + \ldots\right\}$$

Full Multiple Scattering	Intermediate Multiple Scattering	Single Scattering

Photo-electron wave-number k

Multiple scattering contributions

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$$\begin{aligned}\mu(k) &= \mu_0(k)\left\{1+\sum\chi_2(k)+\sum\chi_3(k)+\sum\chi_4(k)+\ldots\right\}\\ &= \mu_0(k)\left\{1+\sum\chi_n(k)\right\}\end{aligned}$$

Set of coordinates

Photo-electron path

$$\chi_n(k) = A(k,\{\vec{r}\})\,\sin\left\{kR_{\text{path}}+\phi(k,\{\vec{r}\})\right\}$$

Functions of potential

Neglecting thermal disorder !

Intrinsic losses

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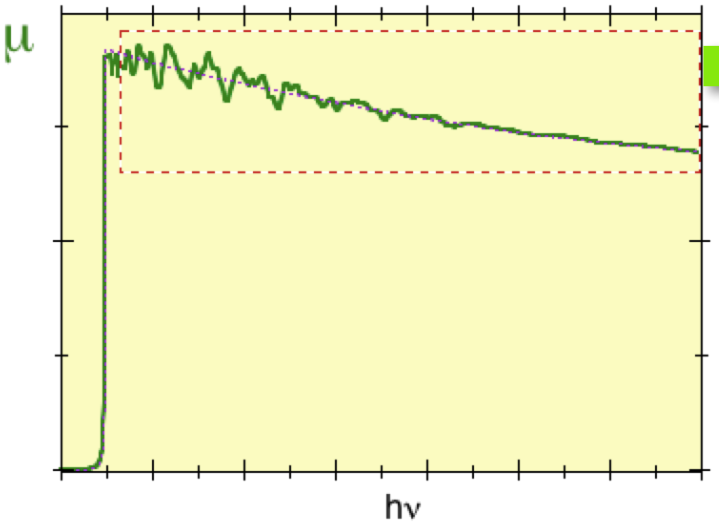

$$\mu_{\mathrm{tot}}(\hbar\omega) = \mu_{\mathrm{el}}(\hbar\omega) + \mu_{\mathrm{inel}}(\hbar\omega)$$

From experiment

One-electron theory

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

$$\chi_{\mathrm{exp}}(k) = \chi_{\mathrm{th}}(k) \times S_0^2$$

Reduction 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 $\tau_h \rightarrow \lambda_h$

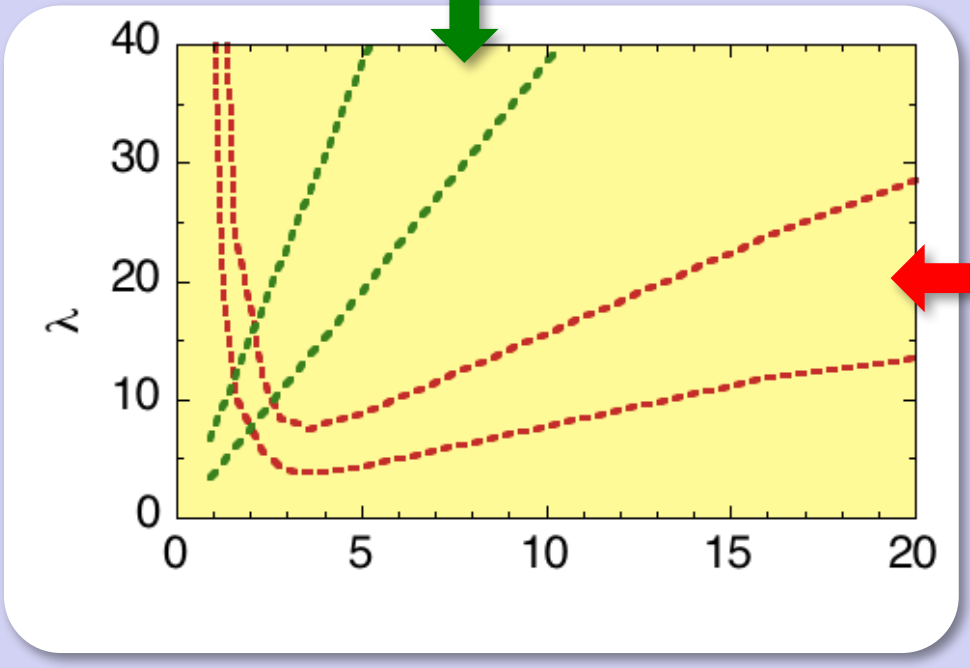

Photo-electron lifetime
$\tau_e \Leftrightarrow \lambda_e$

TOTAL

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

Reduction factor

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

EXAFS and inelastic effects

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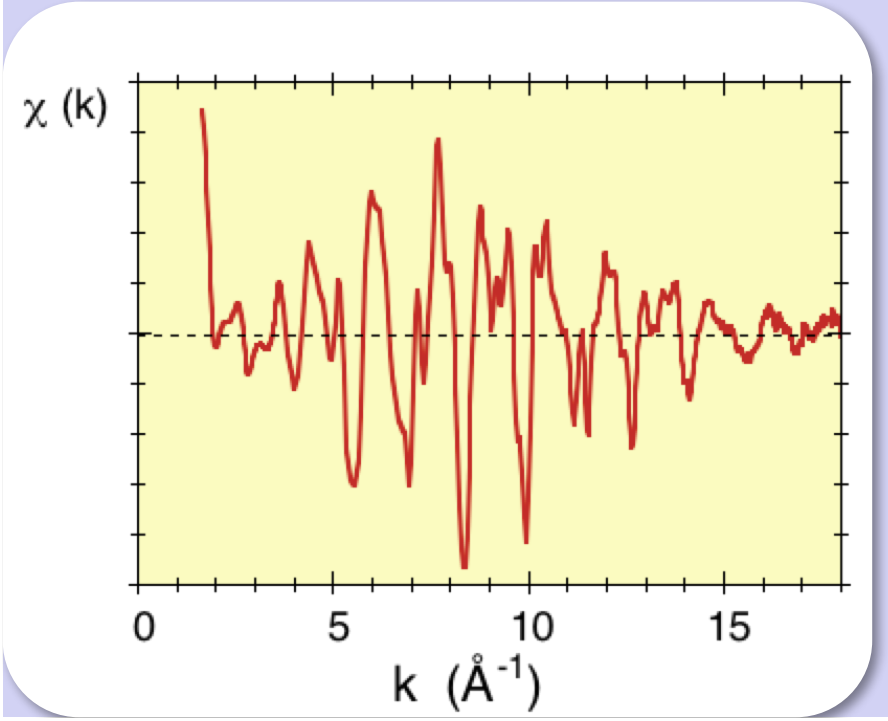
Intrinsic inelastic effects

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
at equilibrium positions !



Thermal disorder effects ?

Vibrational disorder

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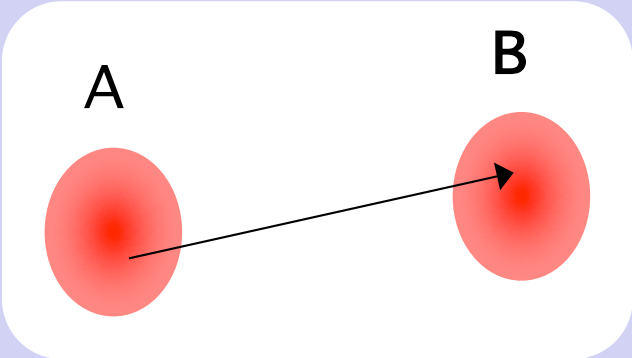
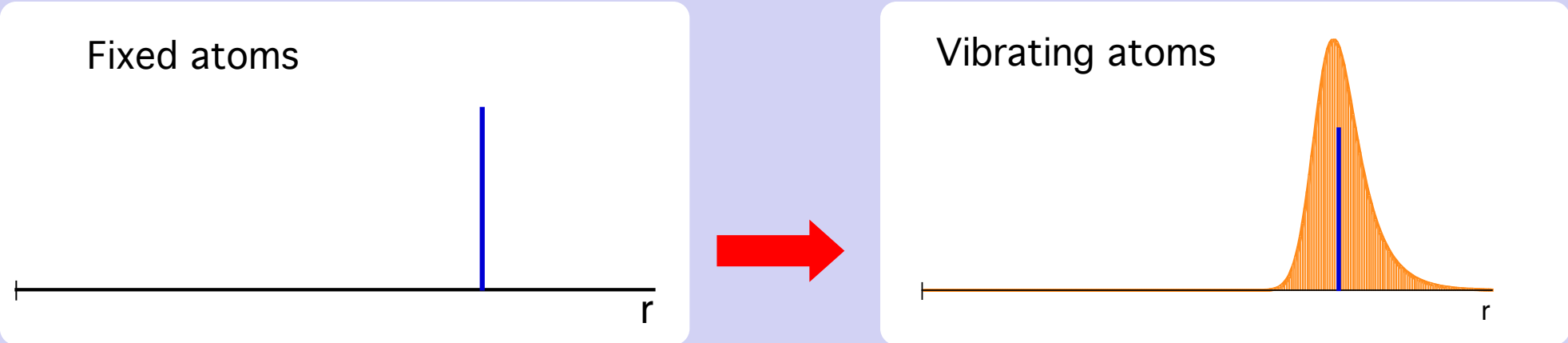


Period of atomic vibrations $\tau_{vib} \approx 10^{-12}$ s

Photoelectron time of flight $\tau_{EXAFS} \approx 10^{-15}$ s

One photoelectron → Instantaneous distance

EXAFS spectrum → Distribution of distances



Distance → Distribution of distances

Vibrational disorder in crystals

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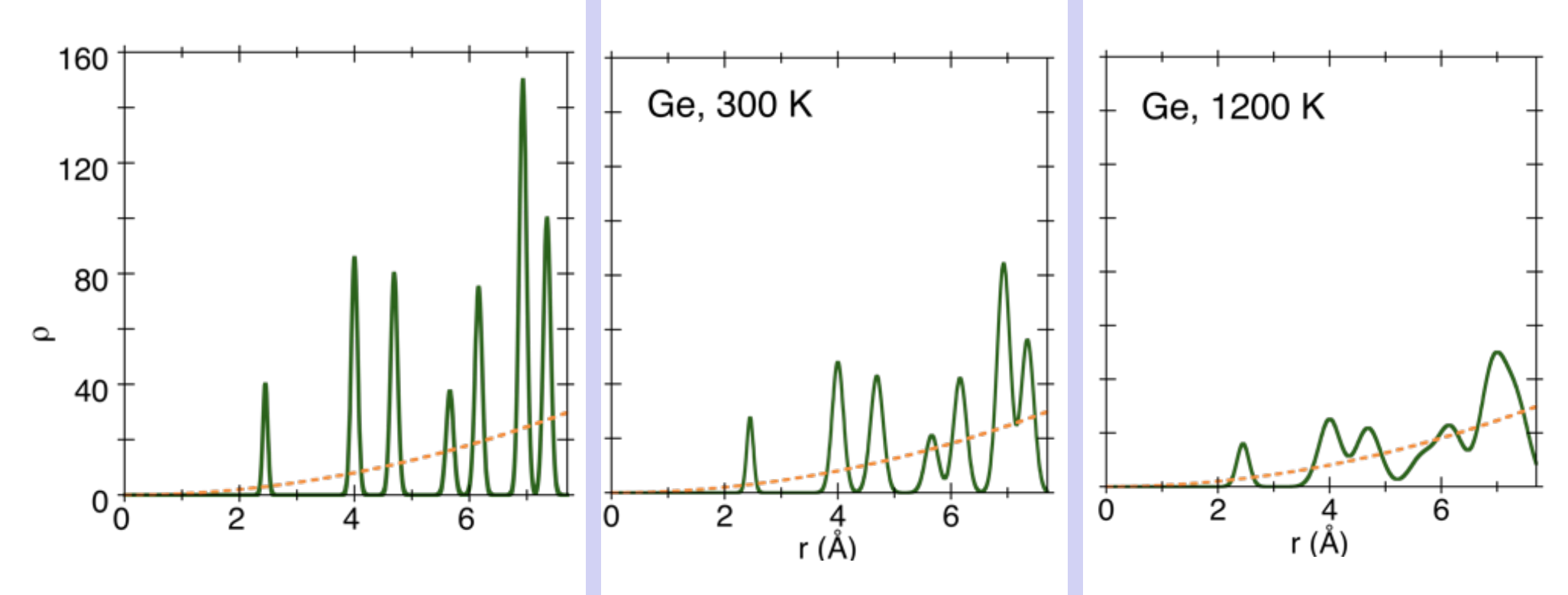
Simulated radial distributions for c-Ge



Separability of coordination shells ?

Structural disorder

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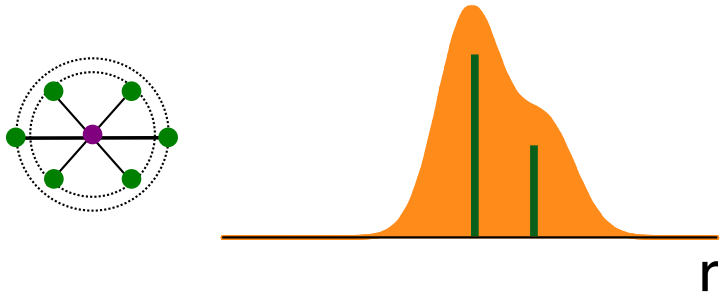
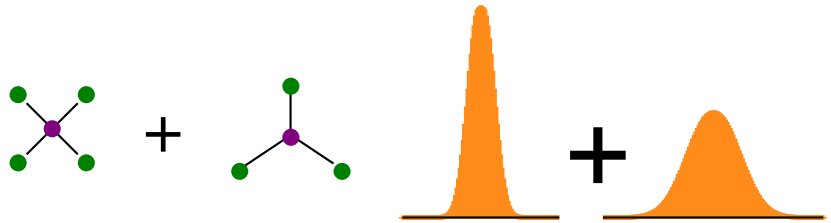
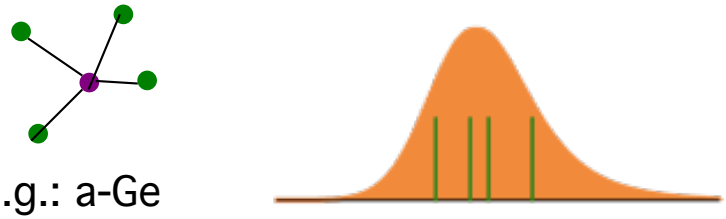
Distorted shells in crystals



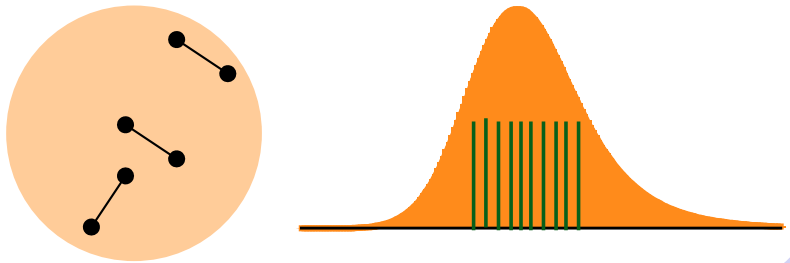
Sites disorder in crystals



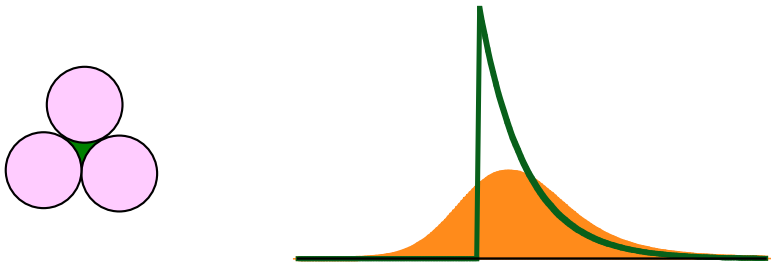
Non-crystalline systems



Nano-structures



Free-volume models



Enlarged distributions of distances

Distributions of distances

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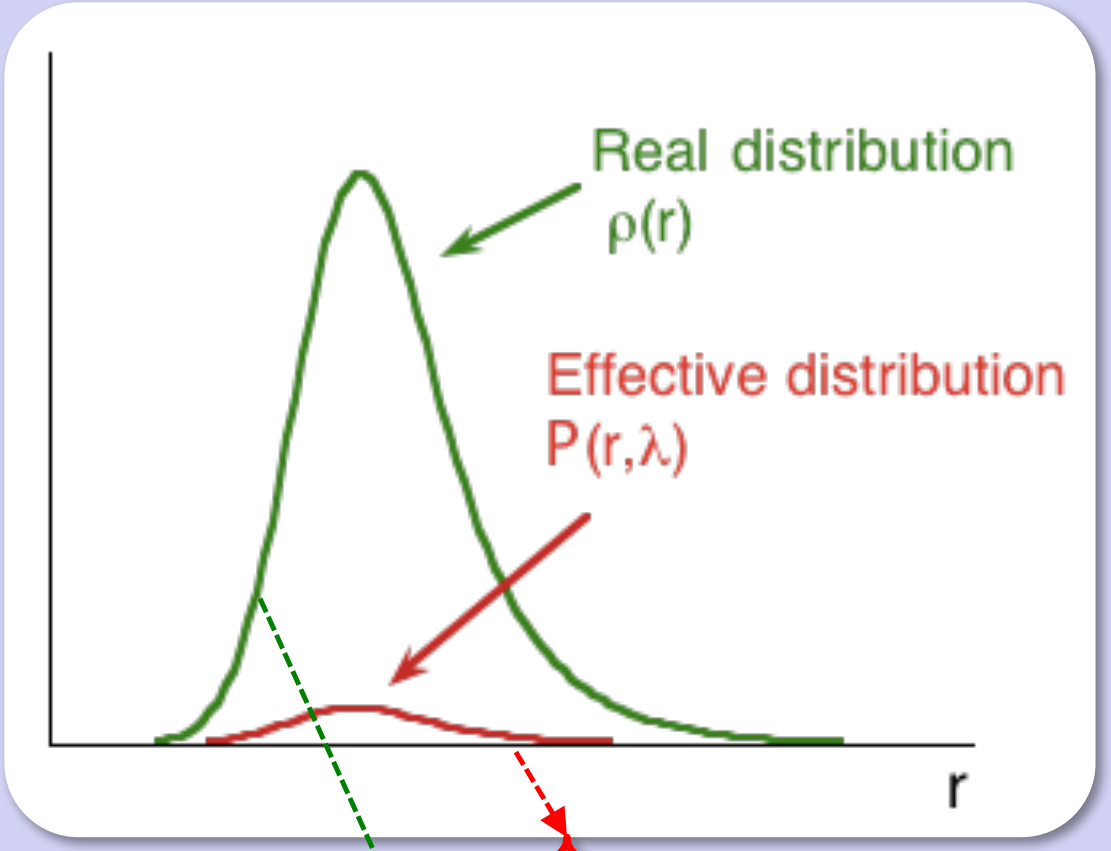
Thermal + structural disorder

$\Rightarrow$ distribution of distances



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

Real and effective distributions

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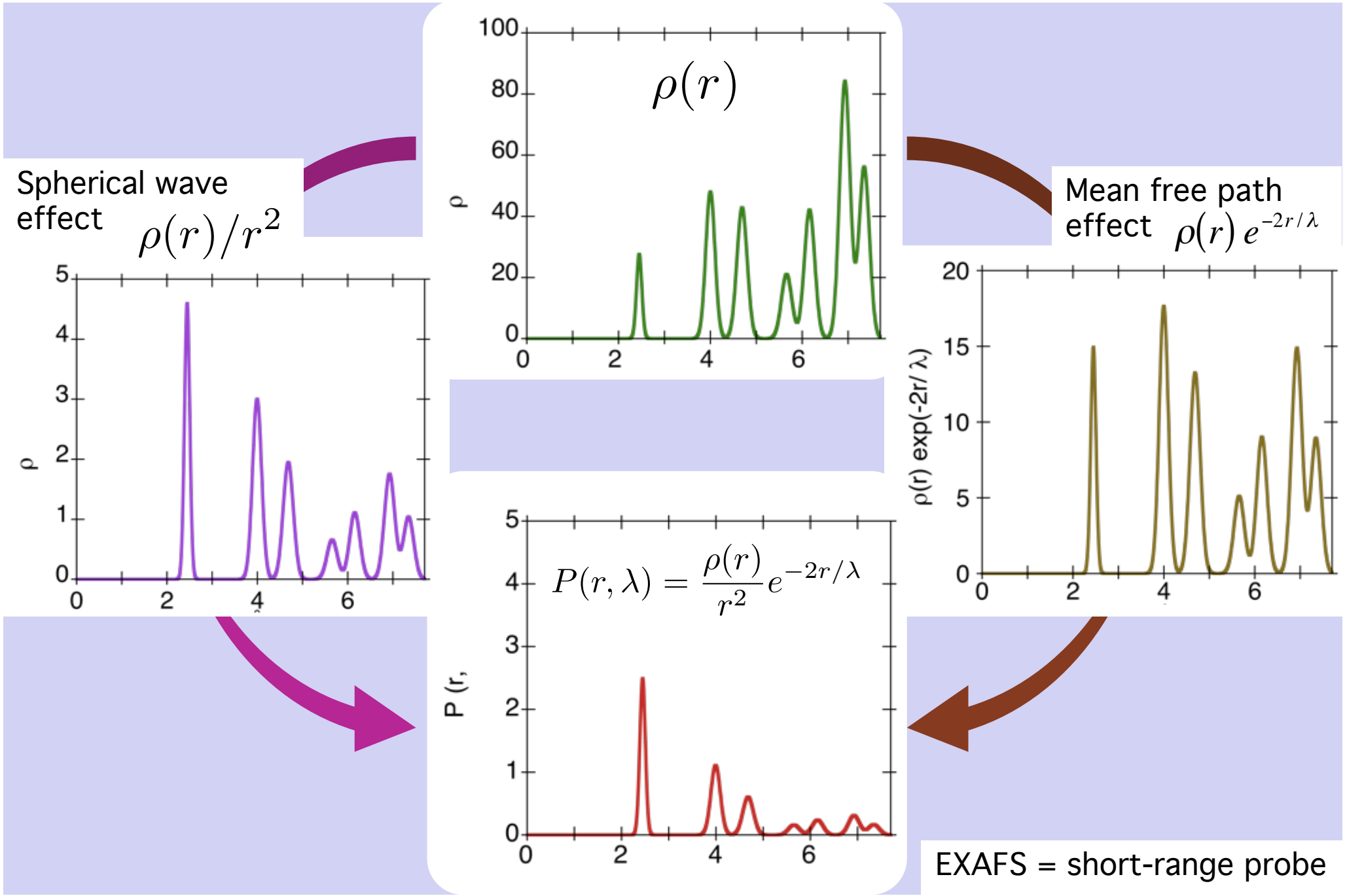

The inversion problem

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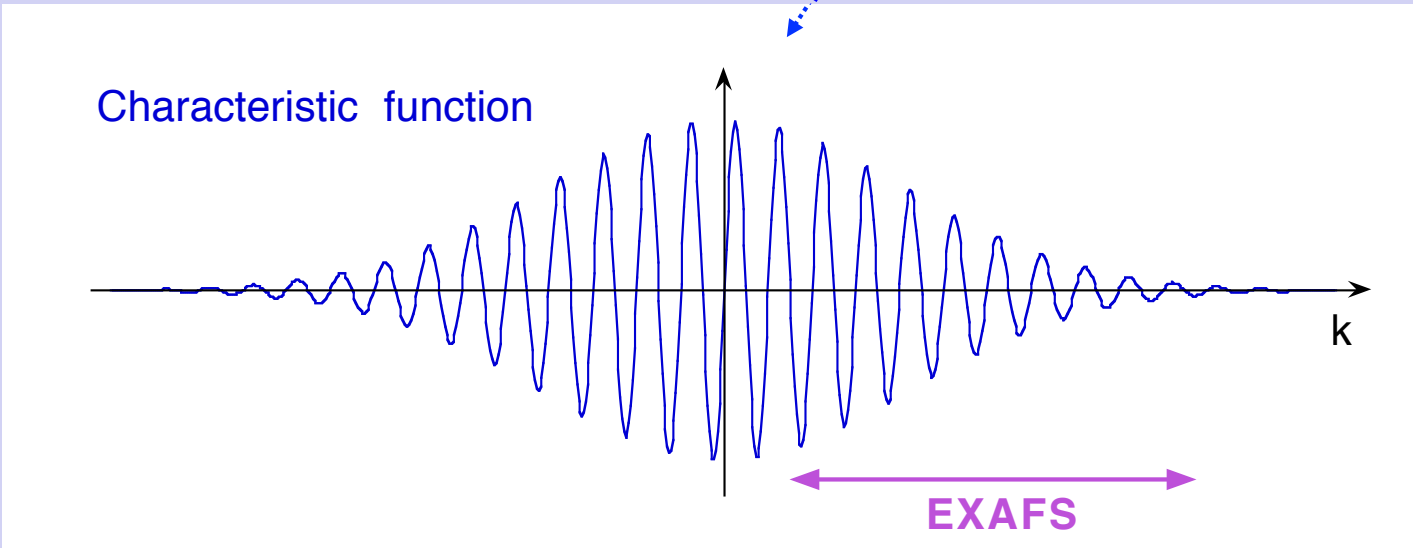
$$\chi(k) = \frac{S_0^2}{k} \sum_{shell} N_s \, \mathrm{Im}\left[f_s(k,\pi)\, e^{2i\delta_1} \int_0^\infty \rho_s(r) \frac{e^{-2r_s/\lambda(k)}}{r_s^2} e^{2ikr_s} dr \right]$$



$$\chi(k) \Rightarrow \rho(r) \quad \boxed{?}$$

Structural models and fitting procedure

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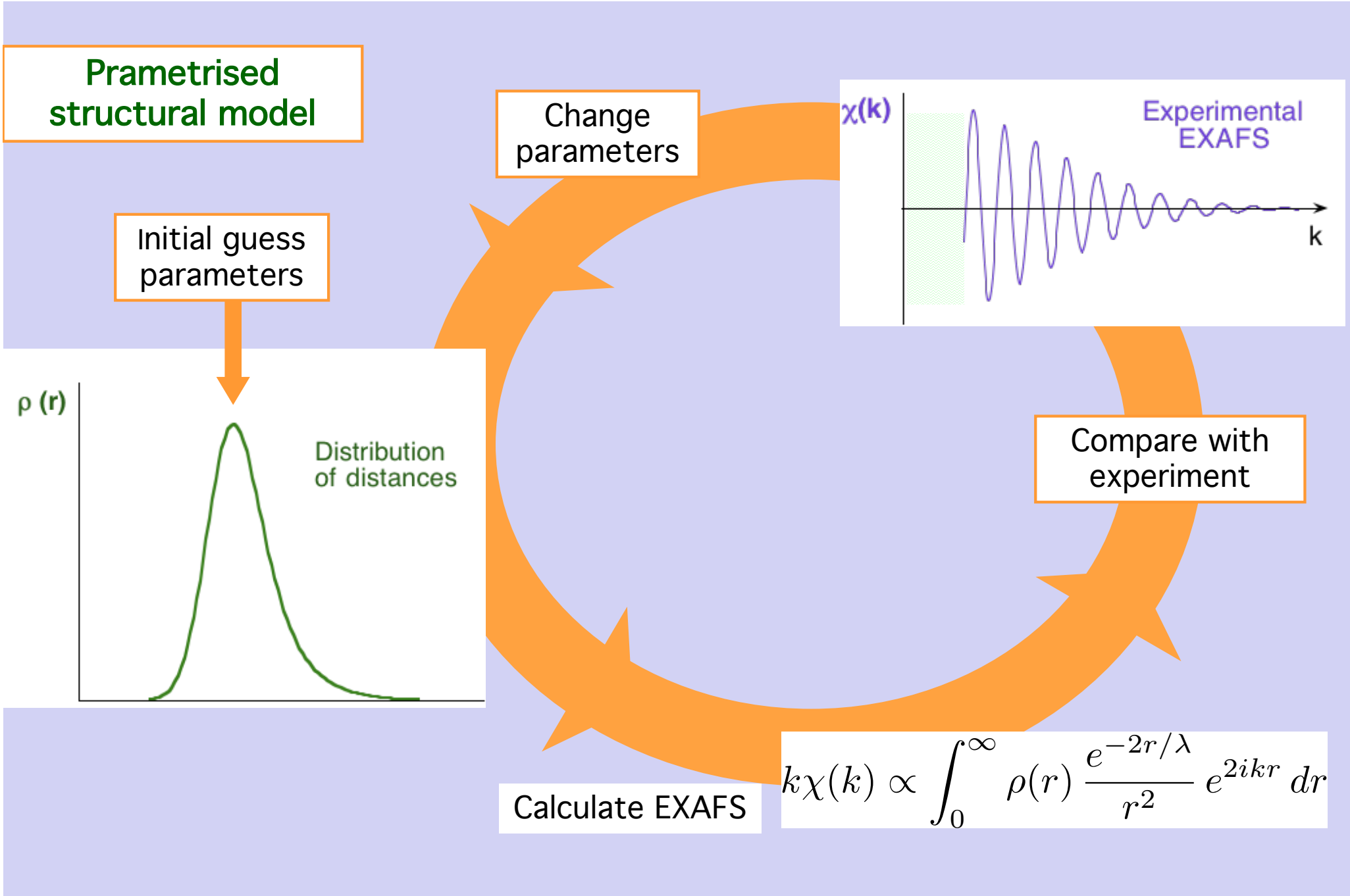

$$k\chi(k) \propto \int_0^\infty \rho(r)\,\frac{e^{-2r/\lambda}}{r^2}\,e^{2ikr}\,dr$$

The simplest model: gaussian approximation

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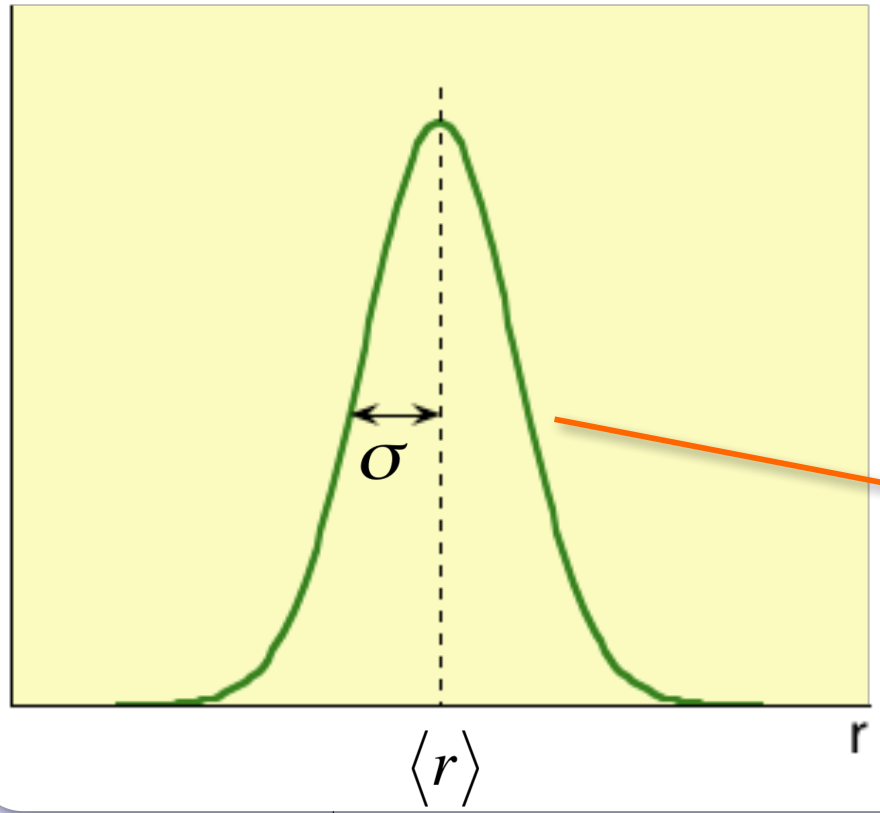

$$P(r,\lambda) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[\frac{\left(r - \langle r \rangle\right)^2}{2\sigma^2}\right]$$

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

Distribution width
(EXAFS Debye-Waller factor)

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

Average distance

Including weak asymmetry

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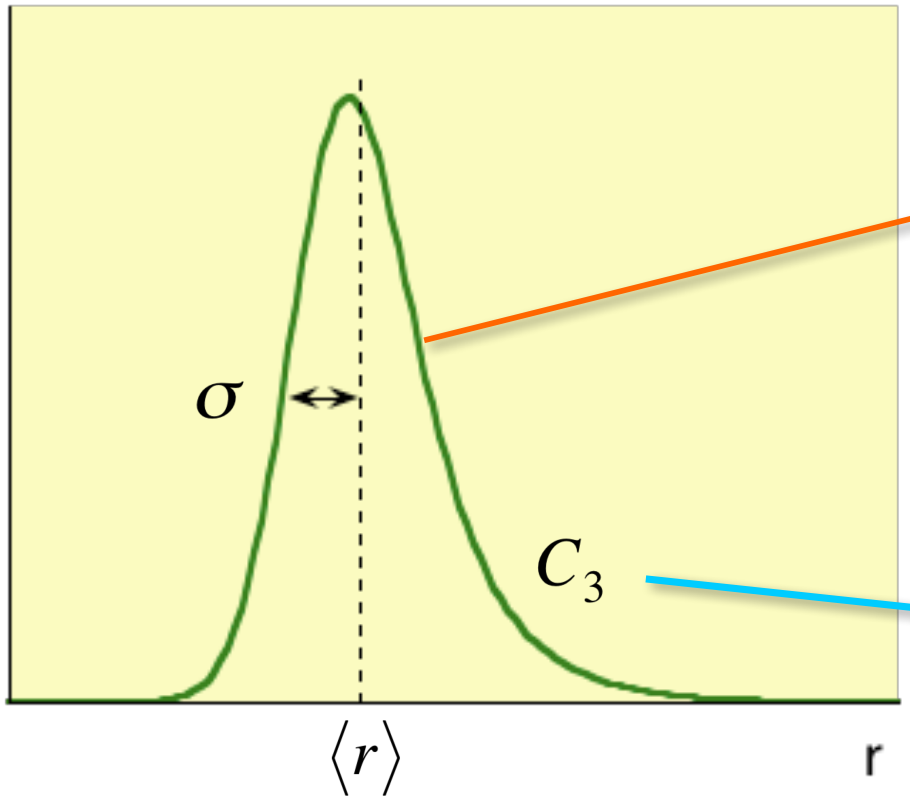
Asymmetric distribution



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

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

Third cumulant
Asymmetry parameter

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

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

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

Coordination number — N

Debye-Waller — σ^2

Average distance and asymmetry — C_1, C_3

XAFS and other techniques

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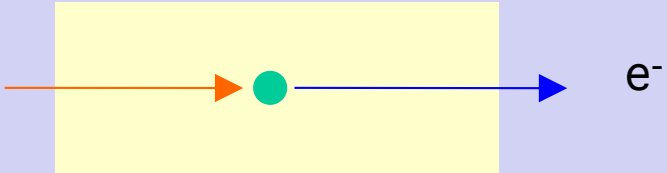
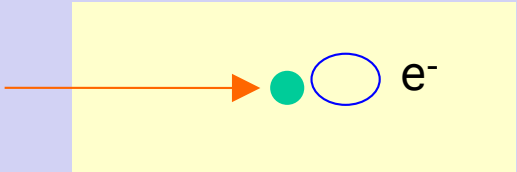
Photo-ionization

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 scattering .vs. EXAFS

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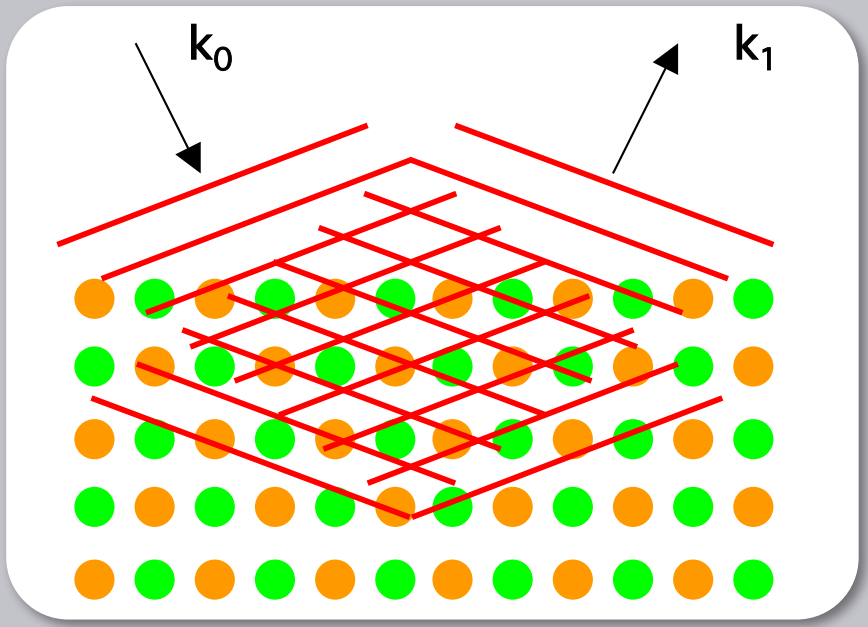
Bragg scattering



X-ray or neutron plane waves

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

Structural probe

EXAFS

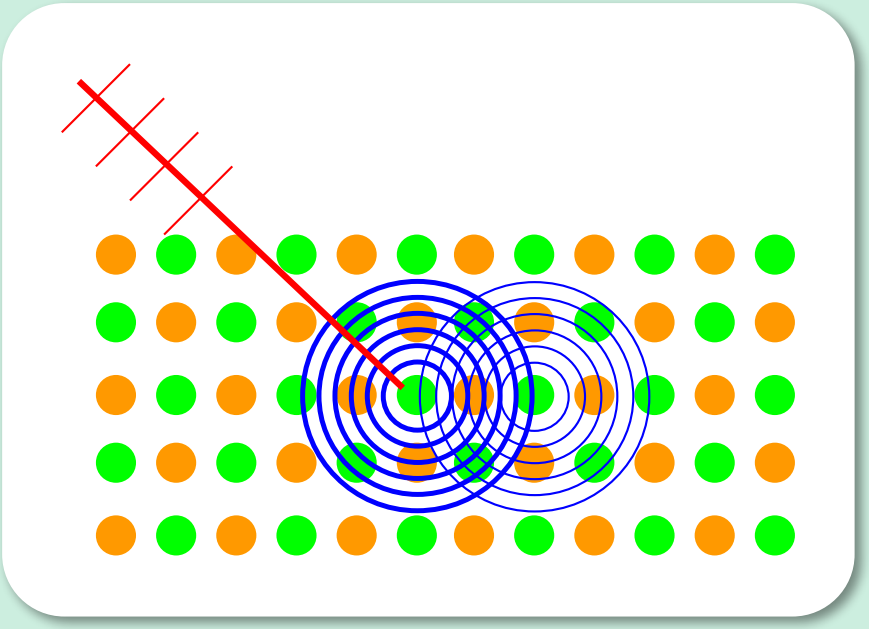


photo-electron spherical wave

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

EXAFS: a structural probe

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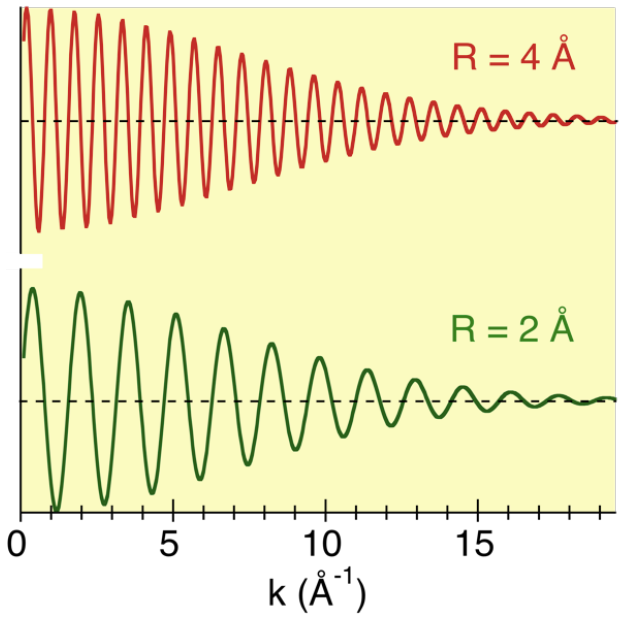
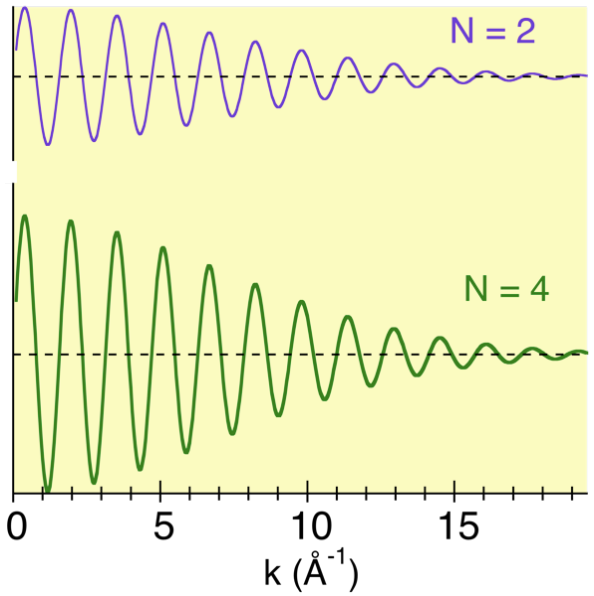
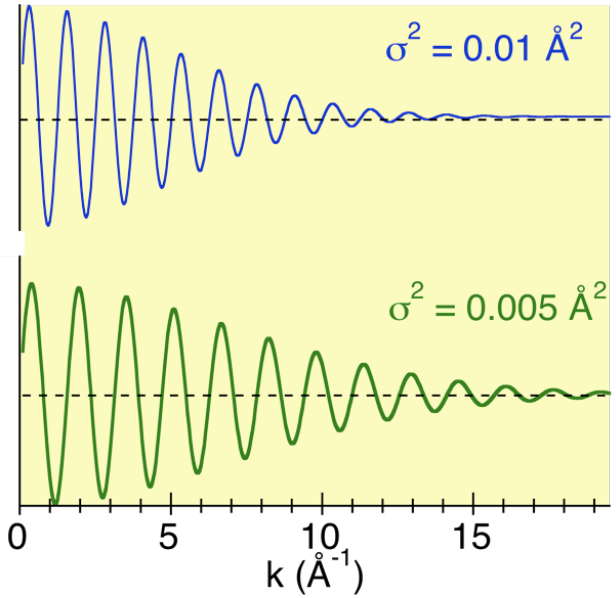


Frequency



Amplitude



Damping

Inter-atomic distance

Coordination number

Disorder

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

Main 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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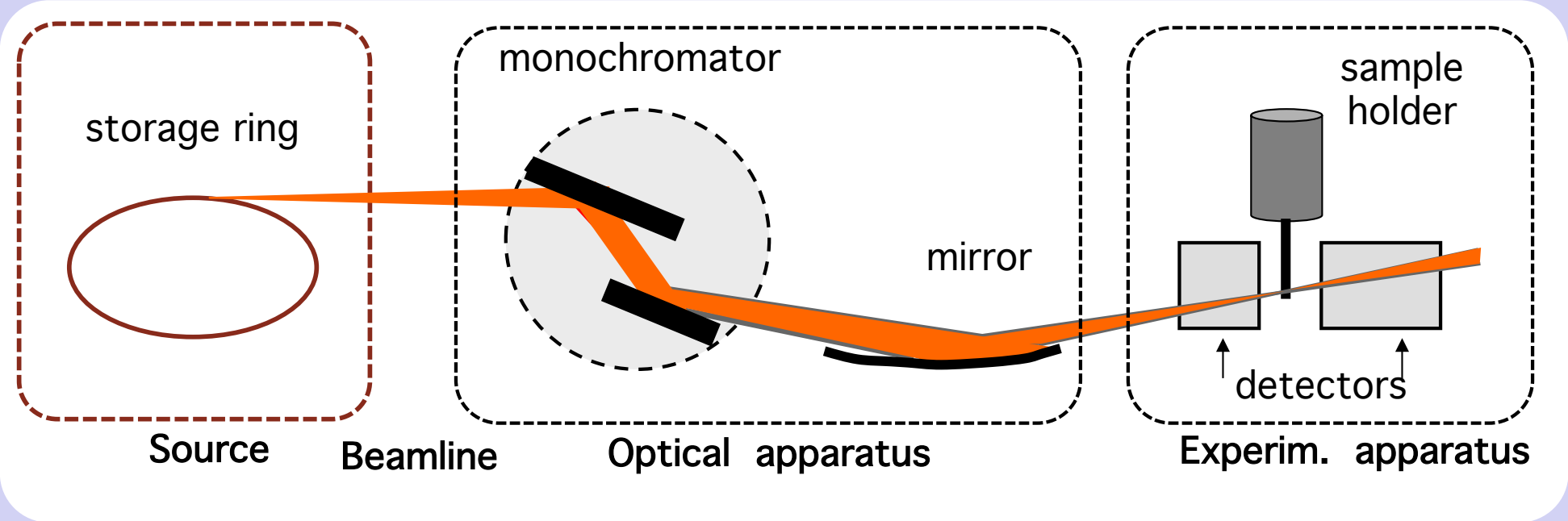

Sample conditioning:

cryostat
oven
reactor
manipulators

Detection:

transmission
fluorescence
electron yield
.....

Alternative layouts:

- dispersive EXAFS
- refl-EXAFS

.....

XAFS: experimental

- ♠ Sources

Wigglers and bending magnets

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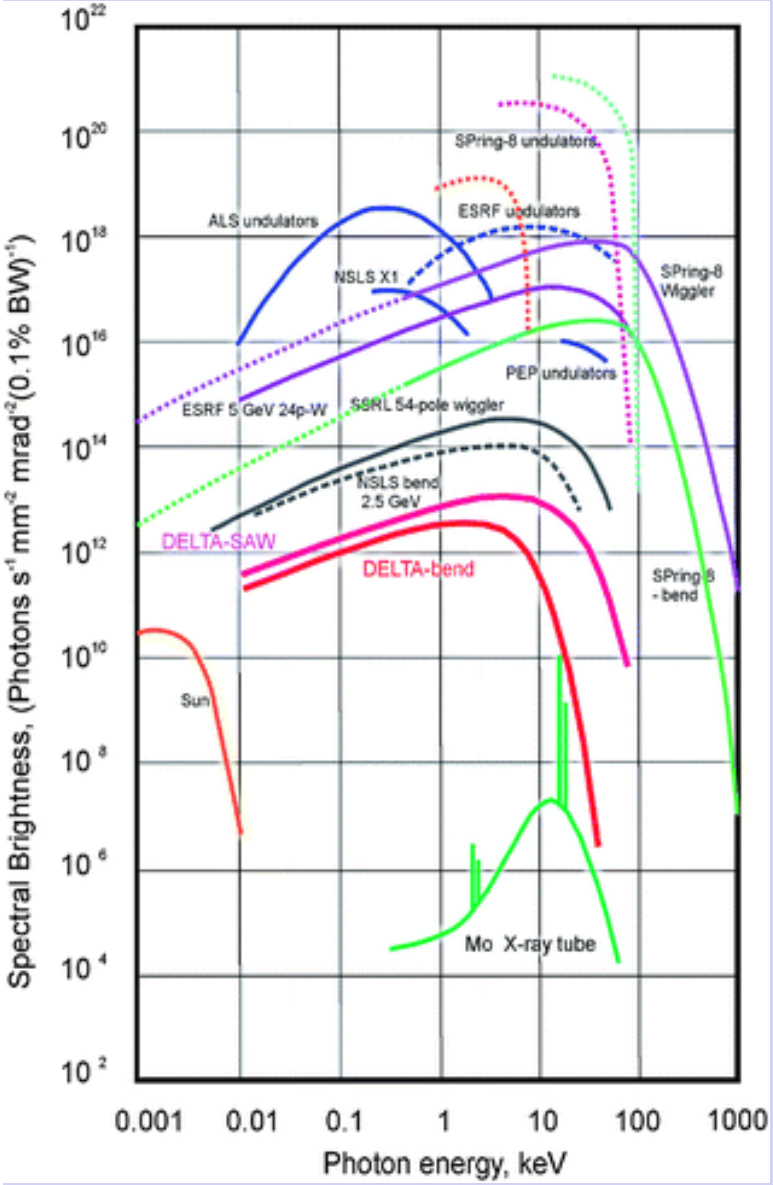
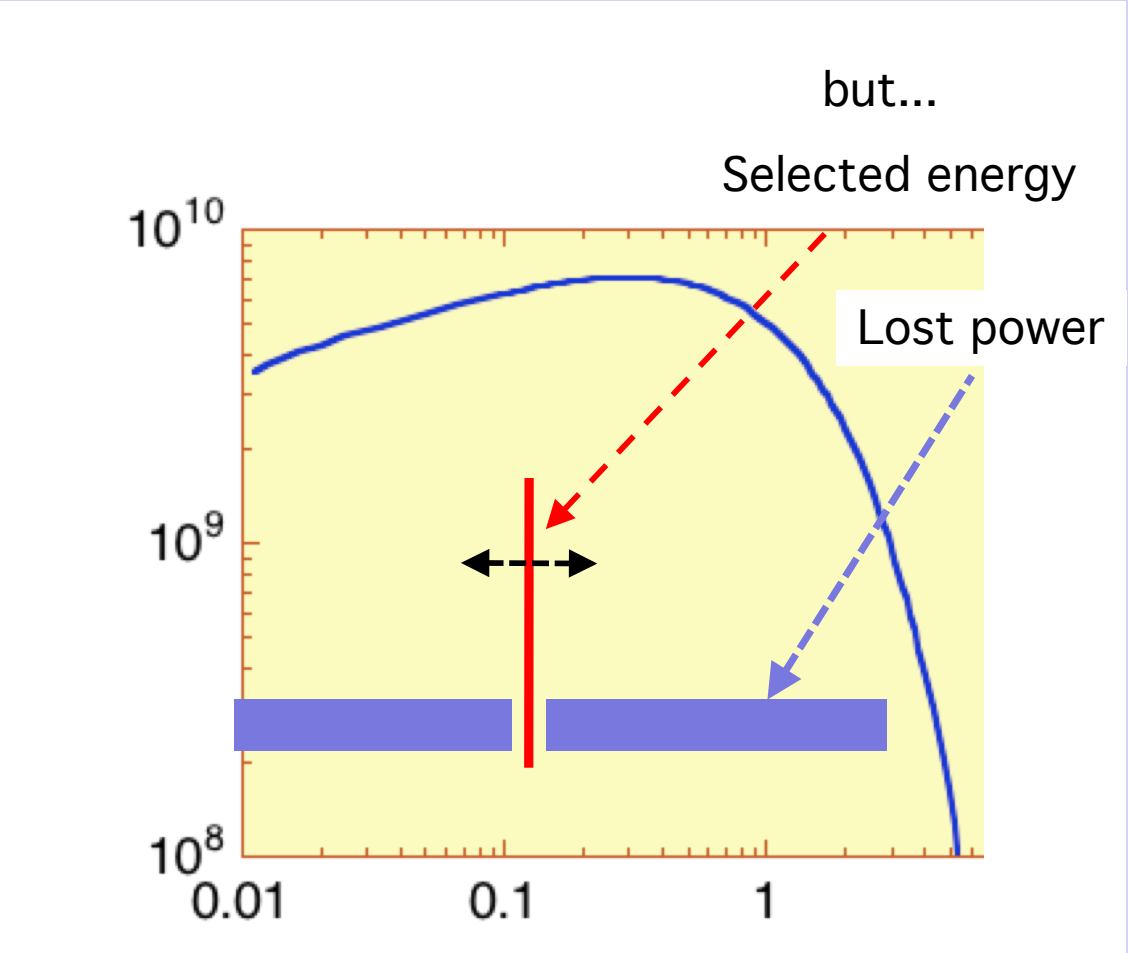


Intense and continuum spectrum – OK for EXAFS



Undulators

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Energy of n-th harmonic (one electron)

$$E_n(\theta) = \frac{2hc\gamma^2 n/\lambda_u}{1 + K^2/2 + \gamma^2\theta^2}.$$

To obtain a continuous spectrum:

1. Angle-integrated flux
2. Large horizontal e-beam size
   (high-beta sections)
3. Modify K by modifying the gap
   3a – Vertical shift of magnet arrays
   3b - Tapered undulators

Collimated intense beams, useful for:

- small samples (e.g. pressure measurements)
- fast measurements

XAFS: experimental

- <u>Monochromators and mirrors</u>

X-ray crystal monochromators

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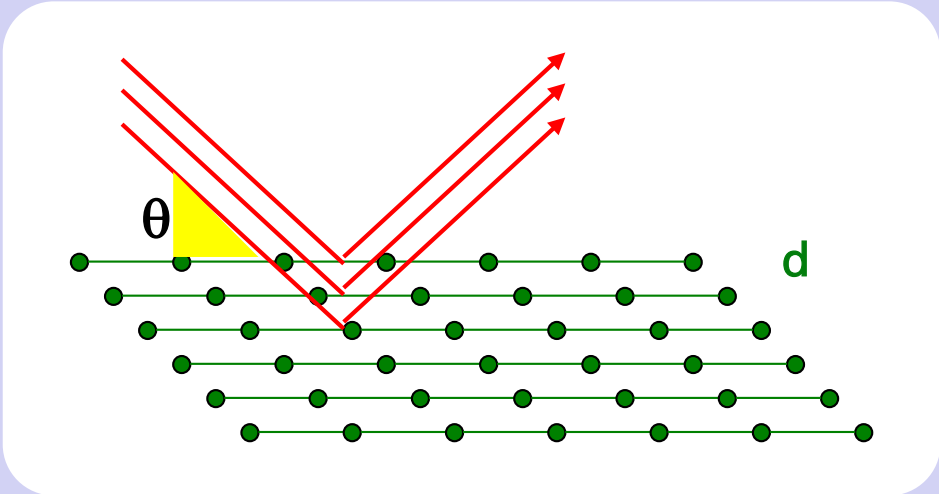
Bragg law

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

Angle ⇔ wavelength

$$2\,d_{hkl}[\text{Å}]\,\sin\theta = \frac{n\;12.4}{E[keV]}$$



	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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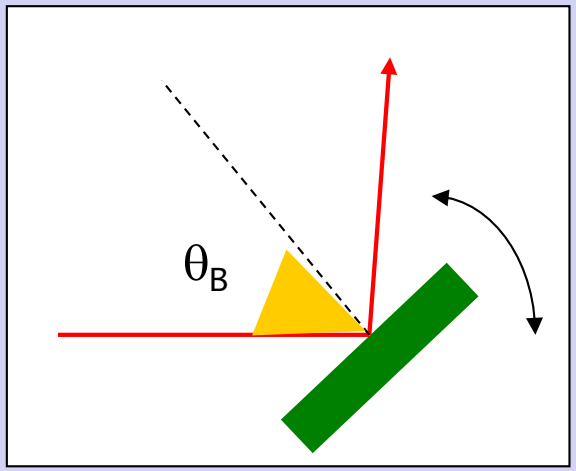

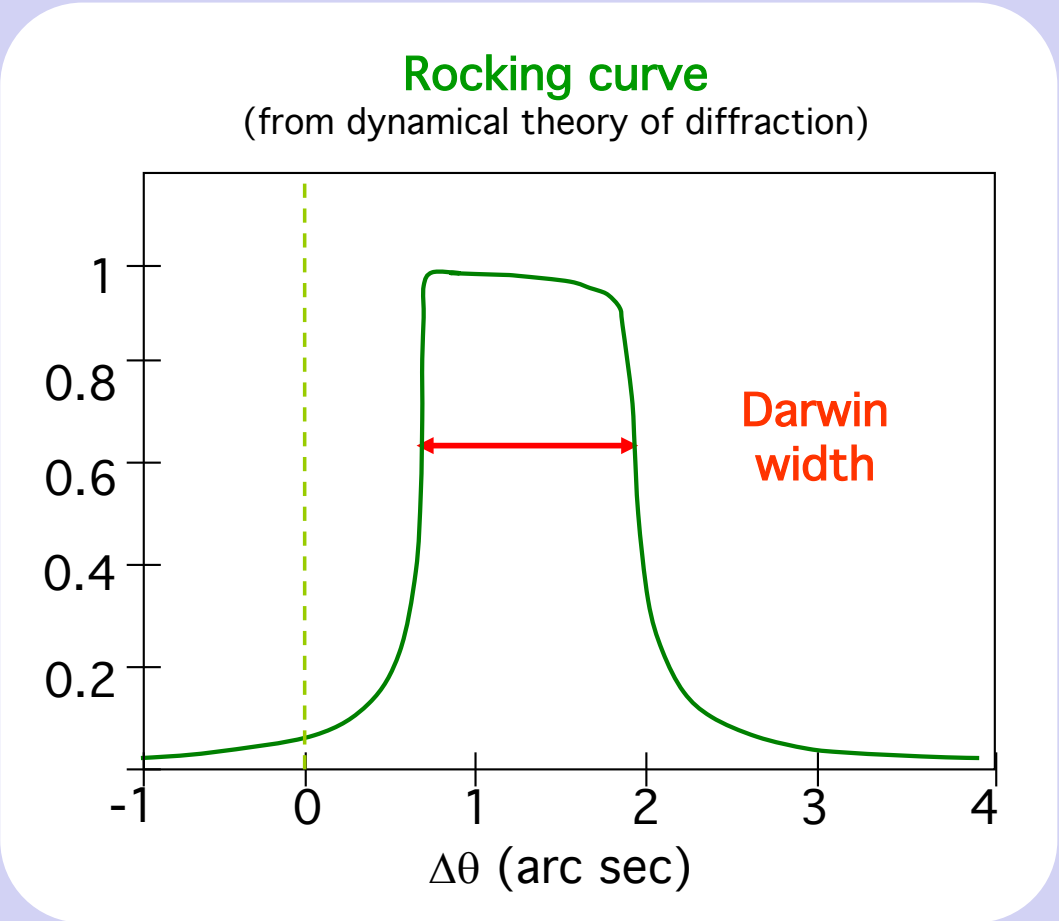

Higher order reflections have narrower rocking curves.

Energy resolution

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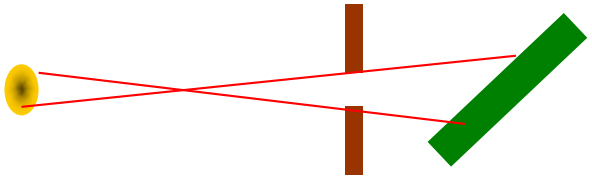
Darwin width
(Intrinsic resolution)

+

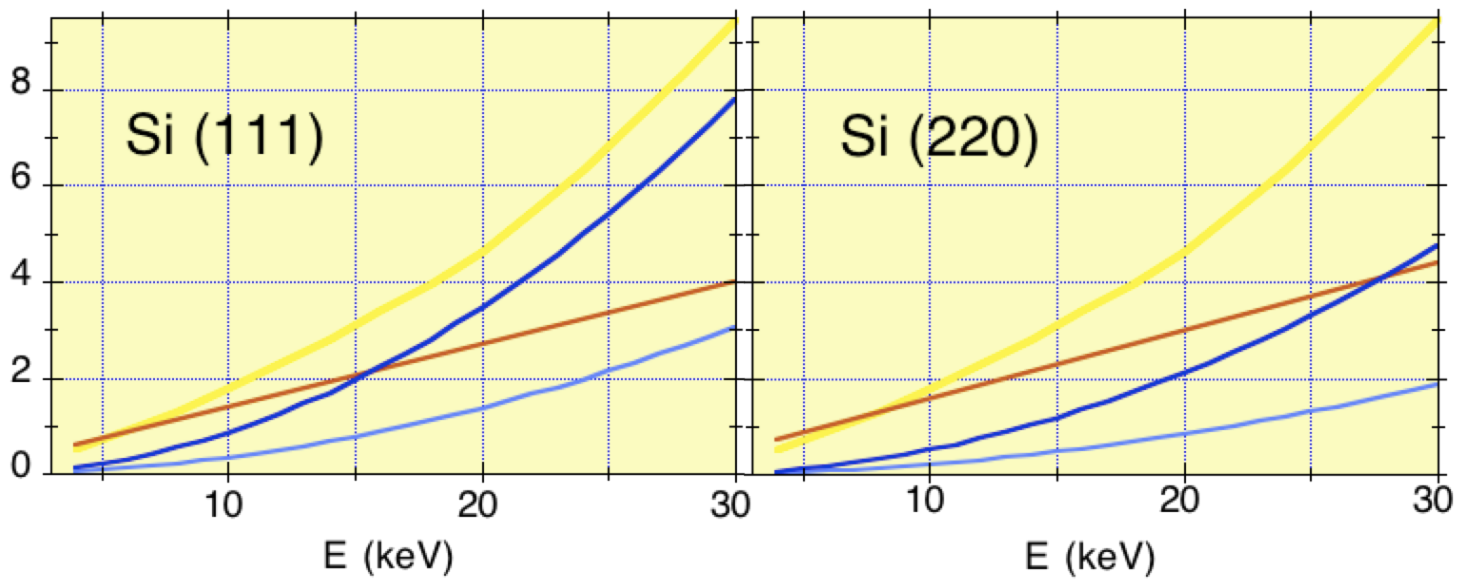
Beam divergence



=

Total angle $\Delta\Theta$

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



Core-level width

Darwin width

Two-independent-crystals monochromators

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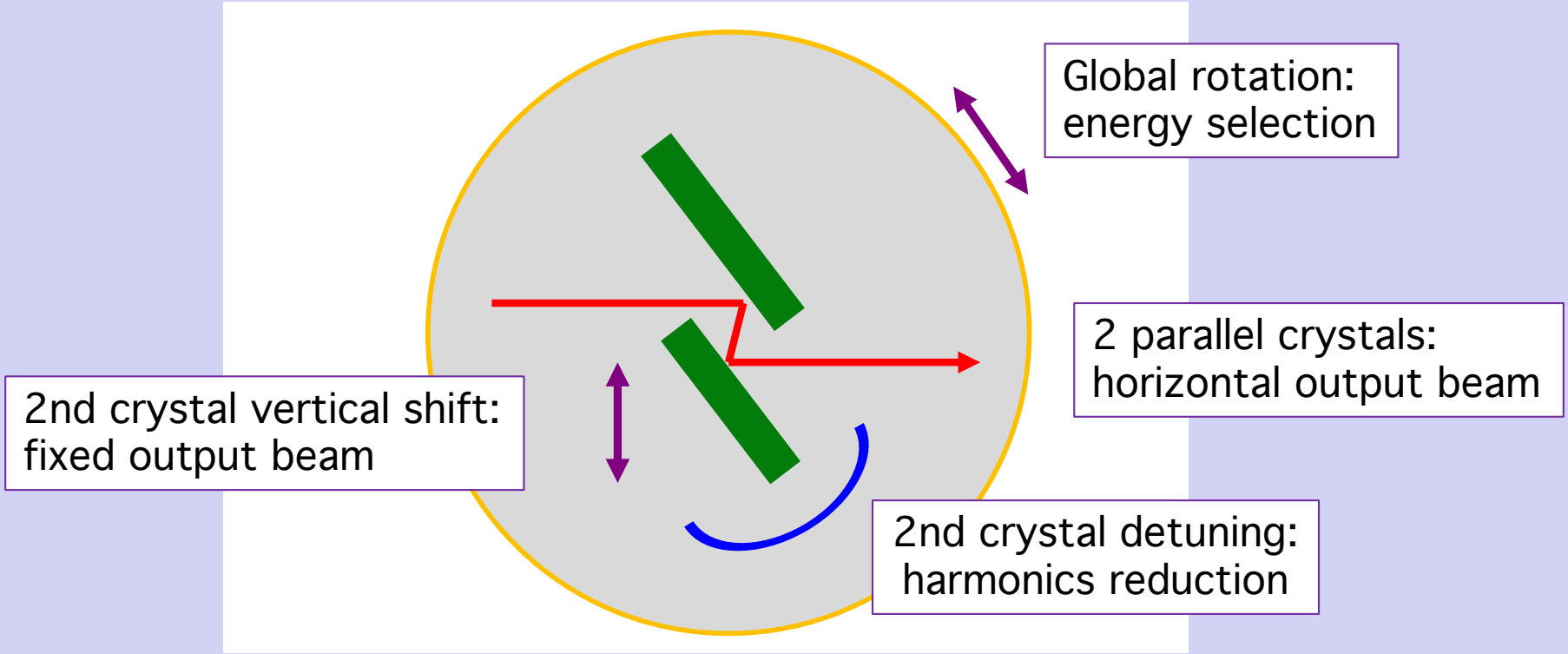

But: ☺ Mechanical complexity
☹ possible instabilities

Independent crystals detuning

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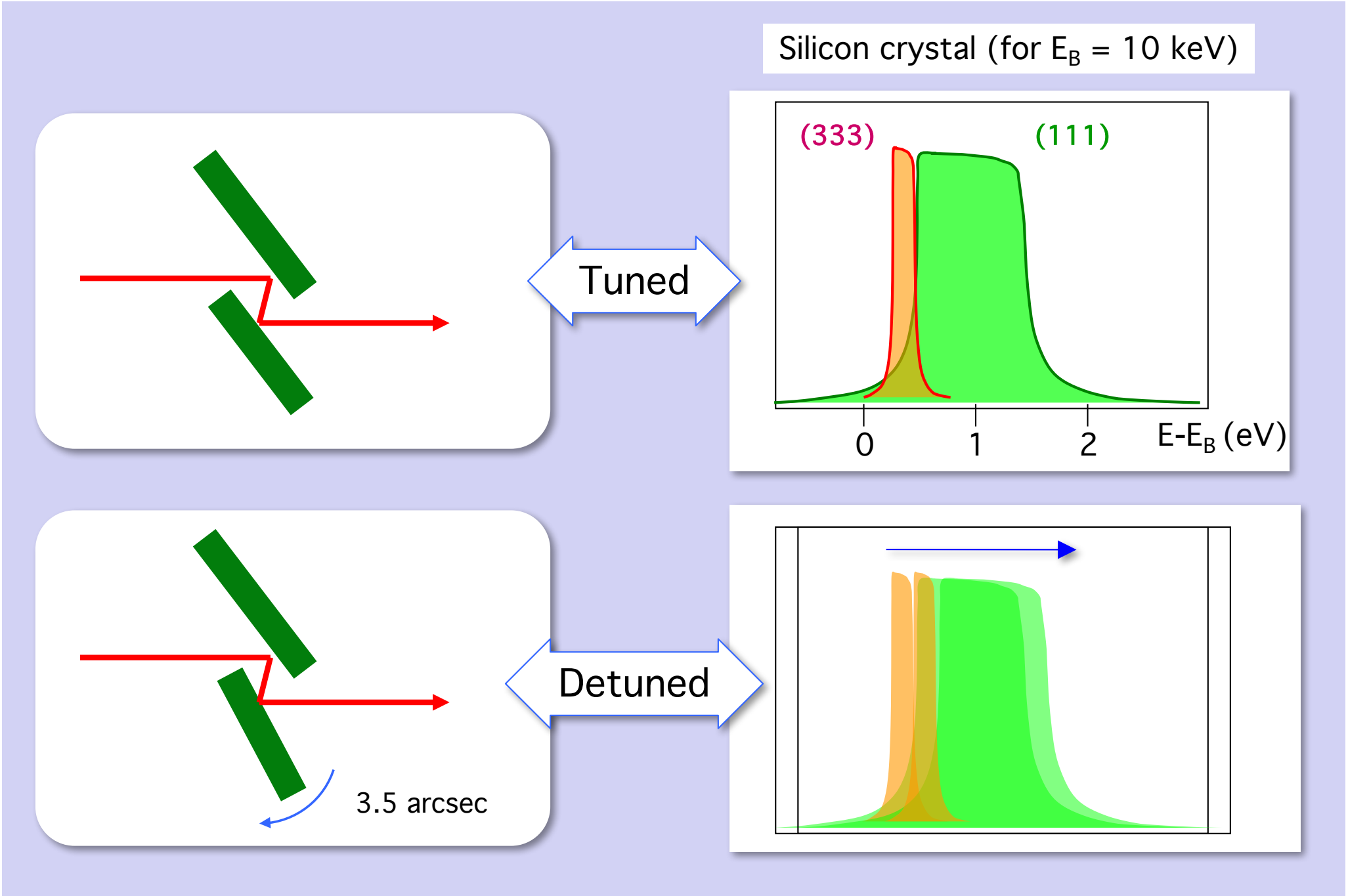

X-ray mirrors – harmonics rejection

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Negligible reflectivity from metal surfaces → no traditional mirrors

Complex refractive index $n = 1 - \delta - i\beta$

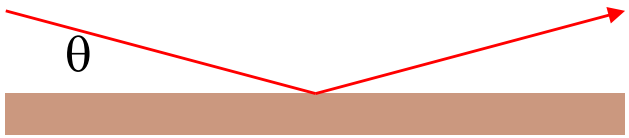
$$\delta \simeq 10^{-6} - 10^{-5}$$

$$n_{\mathrm{real}} < 1$$

Total external reflection for $\theta < \theta_c$

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

$$\theta_c \simeq 10^{-3}\,\mathrm{rad}$$



$$\theta_c \propto \lambda$$

$$\theta_c(\lambda/n) < \theta < \theta_c(\lambda)$$

harmonics rejection

X-ray mirrors – beam focalisation

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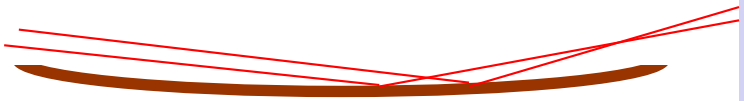
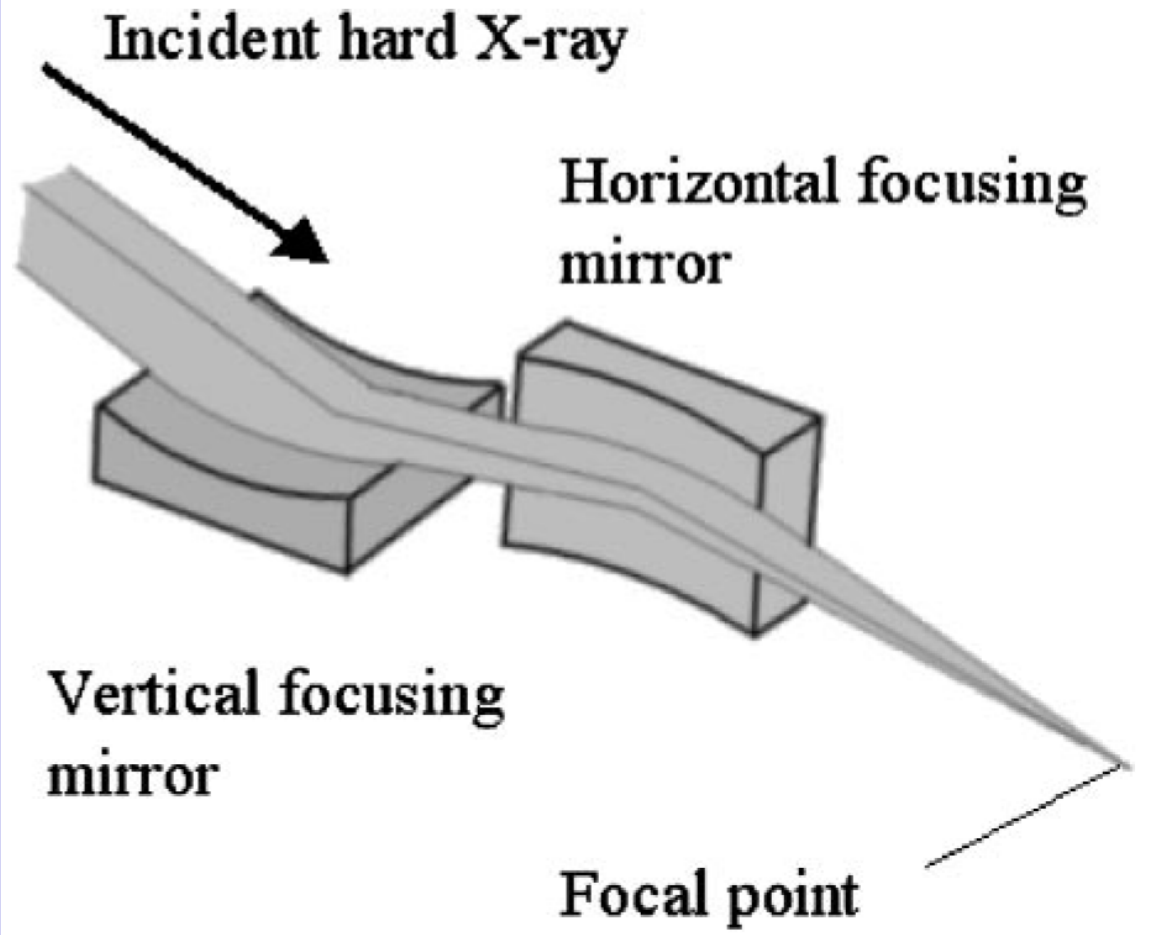
Surface bending



Beam collimation
and
focalisation



XAFS: experimental

- ♠ Detection schemes

XAFS: direct transmission measurements

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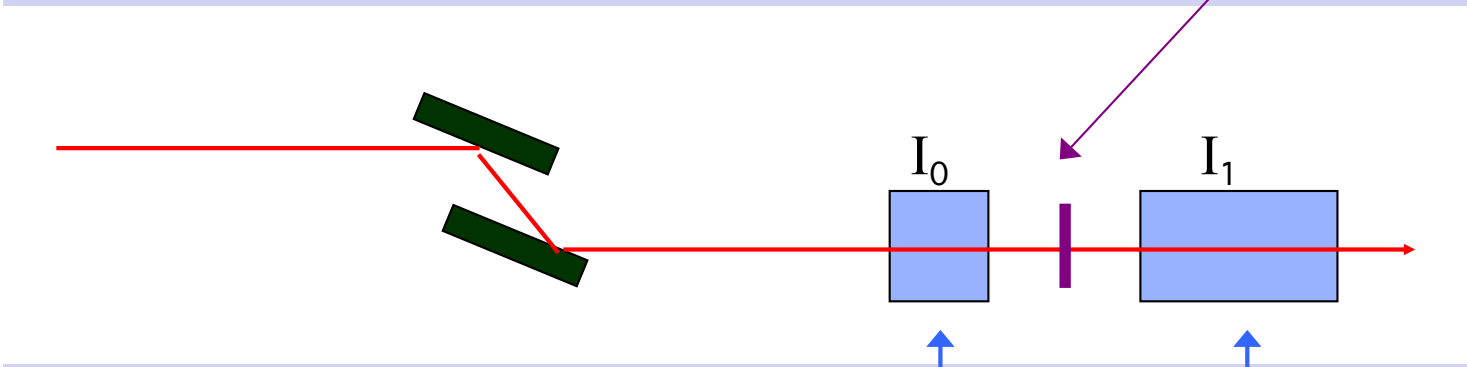
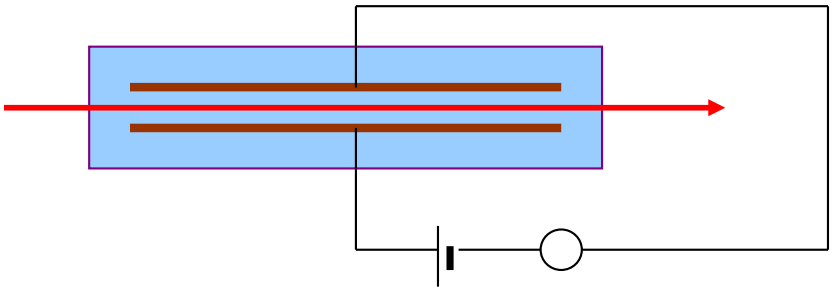
Sample:

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



Detectors: ionisation chambers



E ≈ 100 V/cm

I ≈ $10^{-10} \div 10^{-8}$ A

Direct transmission measurements

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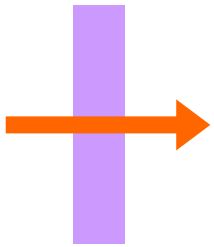
OK

Bulk information (not fom surface) from:

Thin samples



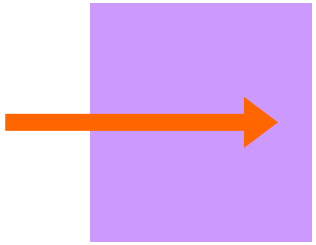
Non-diluted samples

Homogeneous samples

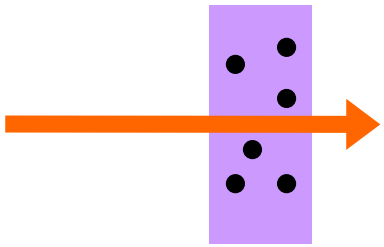
High accuracy attainable

NO

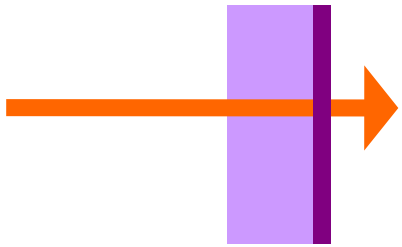
Thick samples



Diluted samples



Surface information



Indirect detection methods

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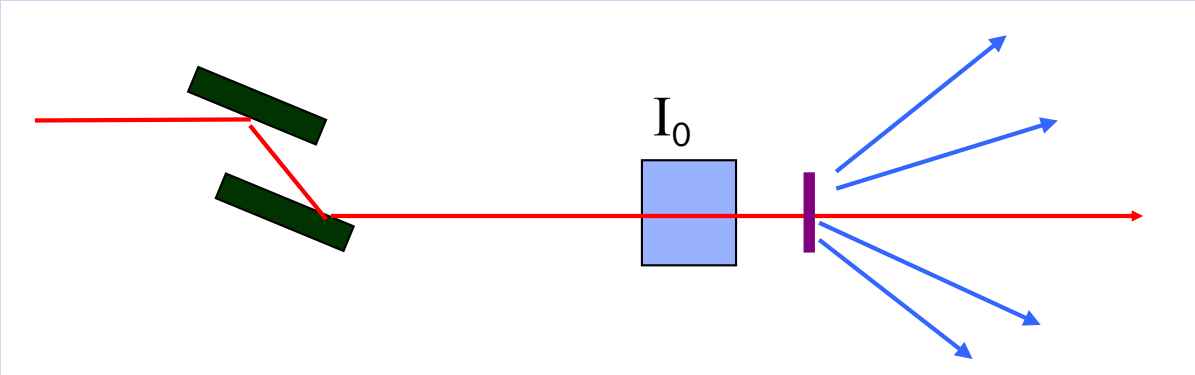

Detection
of decay products

- 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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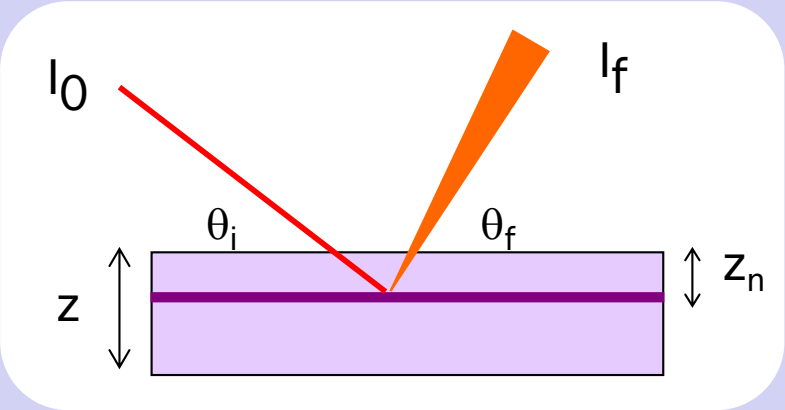
a = absorbing species



Fluorescence from a thin layer

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

Absorption | Fluorescence | Absorption

Total fluorescence: Sample of thickness z and $\theta_i = \theta_f = 45°$

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

$$A = -\sqrt{2}\,z\left[\mu_{tot}(\omega)+\mu_{tot}(\omega_f)\right]$$

Fluorescence: thin samples

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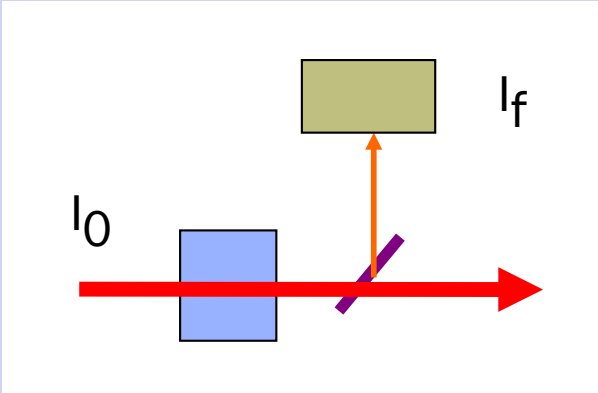
$$I_f = I_0(\omega)\,\eta_f\,\frac{\Omega}{4\pi}\,\frac{\mu_a(\omega)}{\mu_{\text{tot}}(\omega)+\mu_{\text{tot}}(\omega_f)}\{1-\exp(A)\}$$

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



Small fraction of I_0 absorbed

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

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

Fluorescence: thick samples

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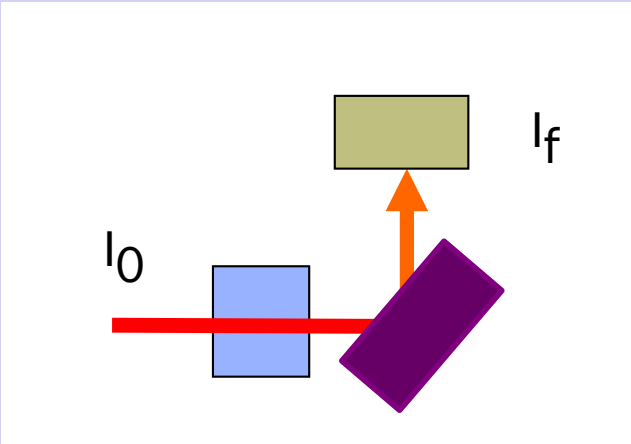
$$I_f = I_0(\omega)\,\eta_f\,\frac{\Omega}{4\pi}\,\frac{\mu_a(\omega)}{\mu_{tot}(\omega)+\mu_{tot}(\omega_f)}\{1-\exp(A)\}$$

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



All I_0 is absorbed

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

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

"a" concentrated

$$\mu_a(\omega)\cong\mu_{tot}(\omega)$$

$$\mu_{tot}(\omega)>>\mu_{tot}(\omega_f)$$

no XAFS

NO

"a" diluted (<1%)

$$\mu_a(\omega)<<\mu_{tot}(\omega)$$

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

OK

Fluorescence detection

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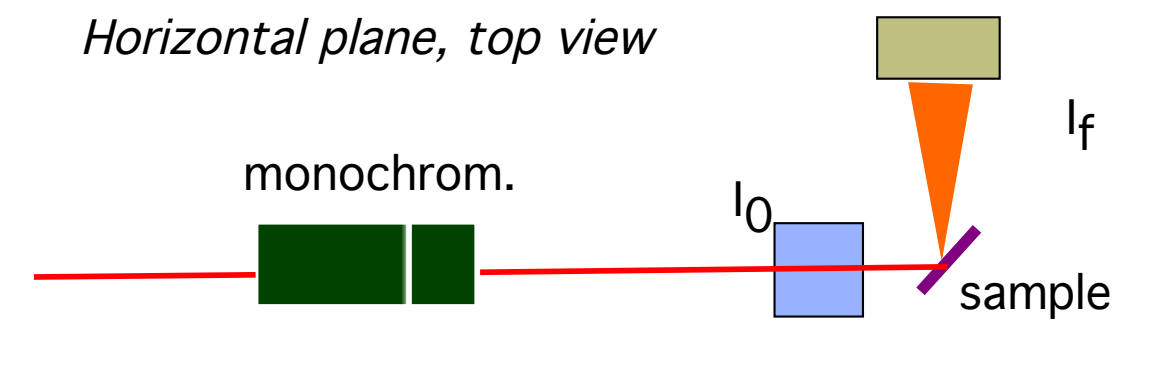

Fluorescence signal

+

Background:
- elastic scattering
- inelastic scattering
- unwanted fluorescence

To reduce background :

A) Detection at 90° minimises scattering (less effective for large solid angles)

B) Detection schemes

1. Filter + slits systems
2. Multi-element solid state detectors (energy dispersive)
3. Crystal analysers

XAFS: electron detection (a)

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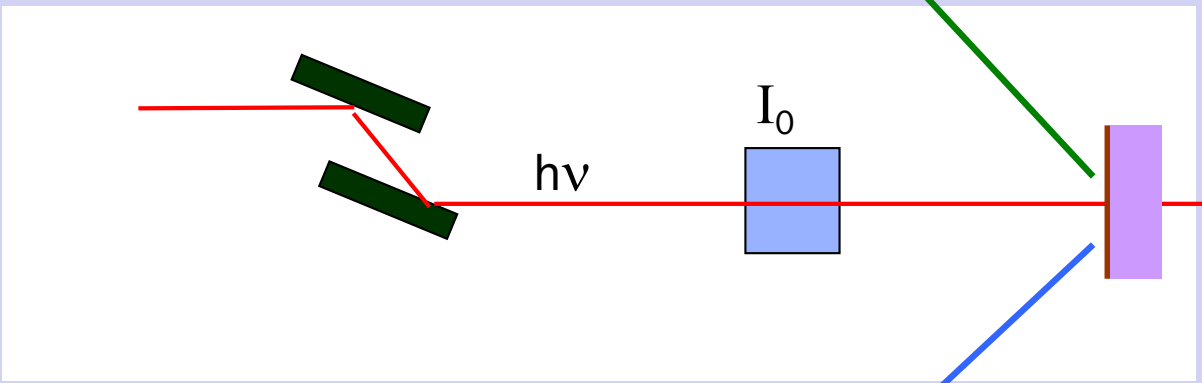
Photo-electrons:

- Energy varies with $h\nu$
- Intensity $\propto \mu x$

$\Rightarrow$ XAFS signal



Auger electrons:

- Fixed energy $\Rightarrow$ atomic selectivity
- Intensity $\propto \mu x$

$\Rightarrow$ XAFS signal

Electron mean free path:

- adsorbates
- thin layers

Indirect processes and escape depth

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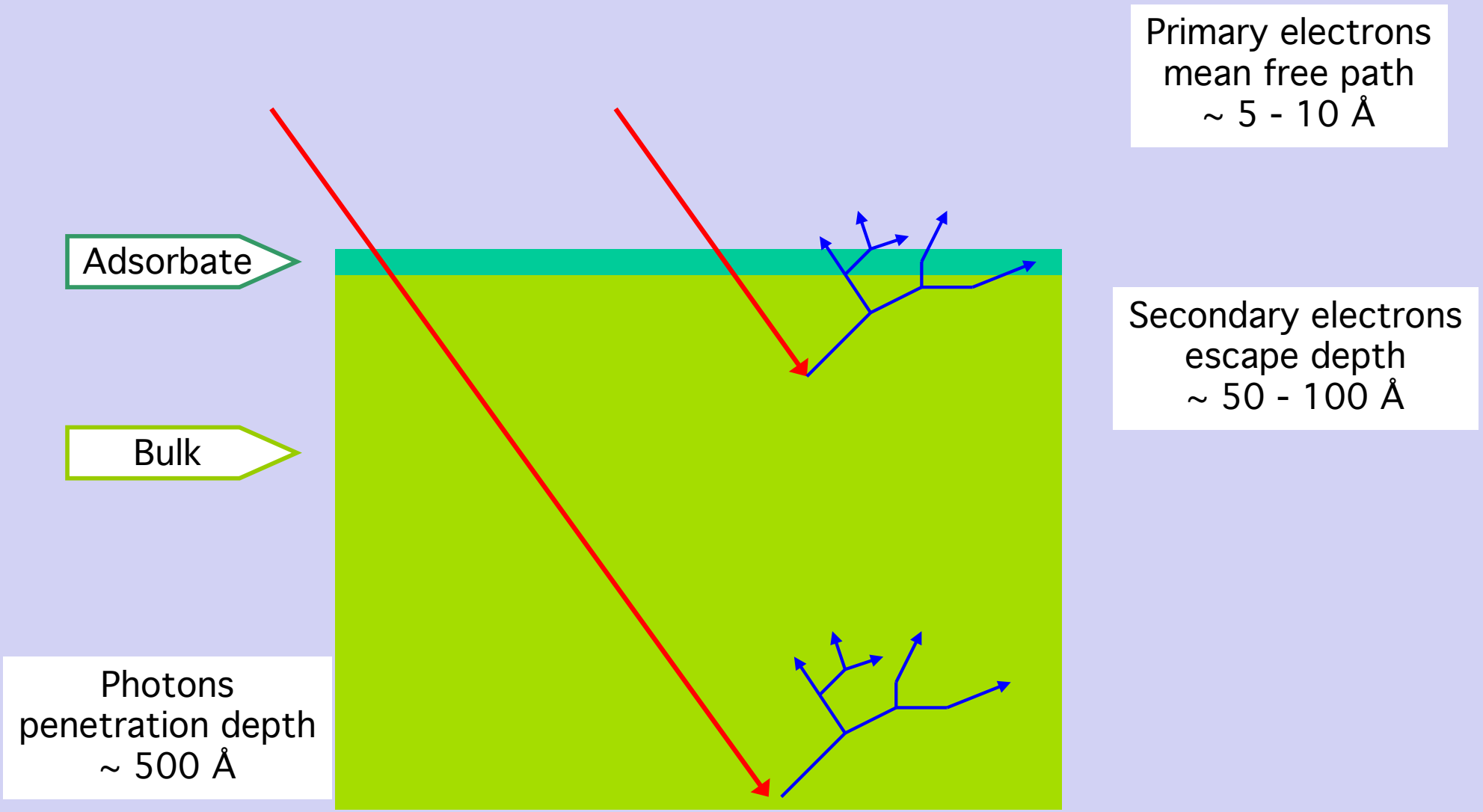

XAFS: electron detection (b)

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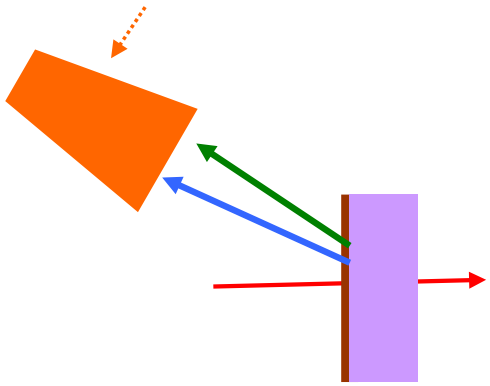
XAFS of adsorbates



AEY - PEY - TEY

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

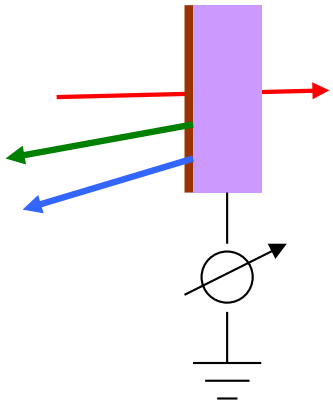
PEY = Partial Eletron Yield
- large energy window
- Auger (direct + secondary) = XAFS signal
- Photoel. (direct + secondary) = background

TEY = Total Electron Yield
- all electrons collected

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

- XAFS from Auger and photoel.

Bulk XAFS



TEY

Dispersive XAFS (a)

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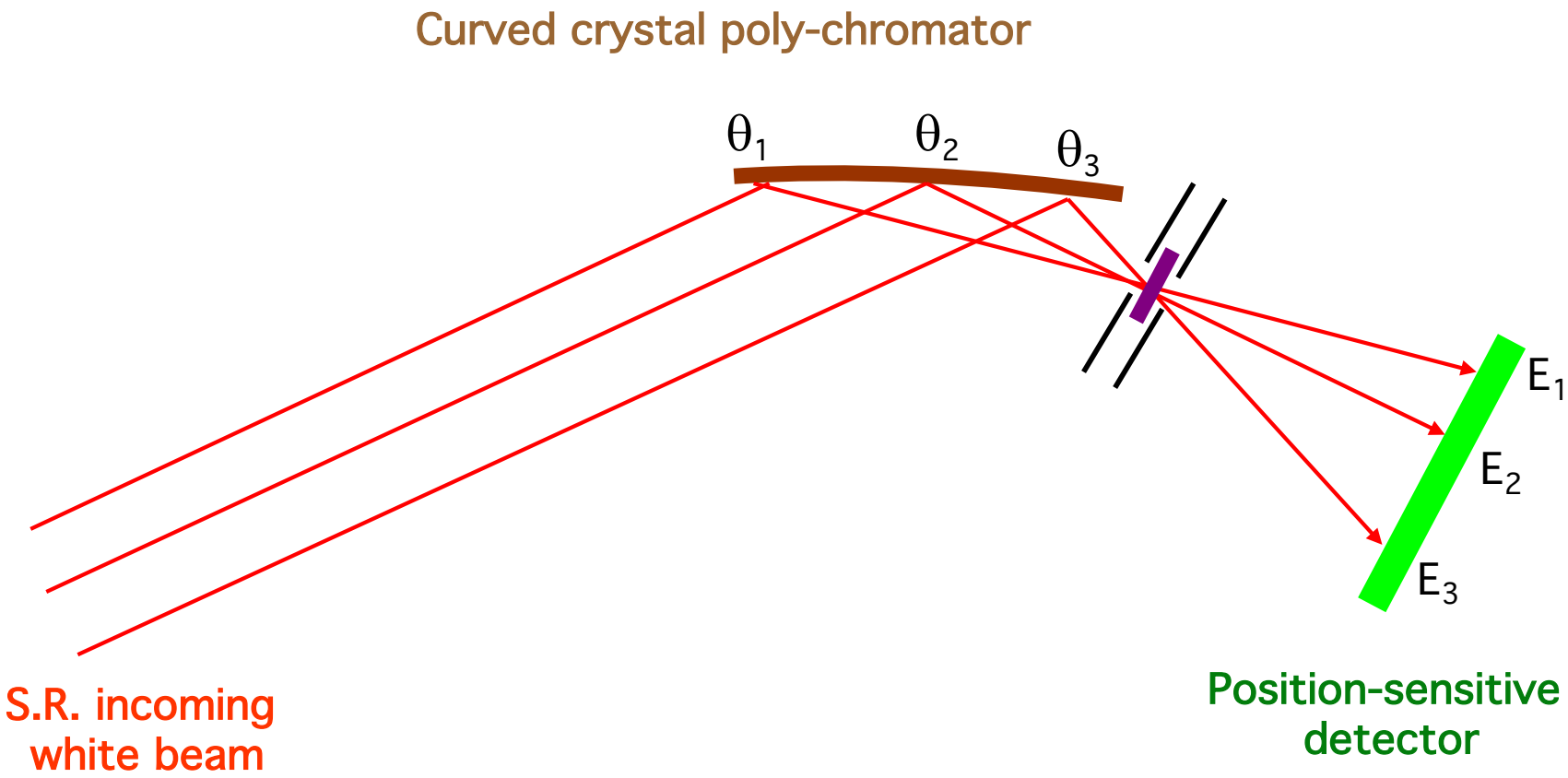
$$2d \sin\theta = \lambda$$



Dispersive XAFS (b)

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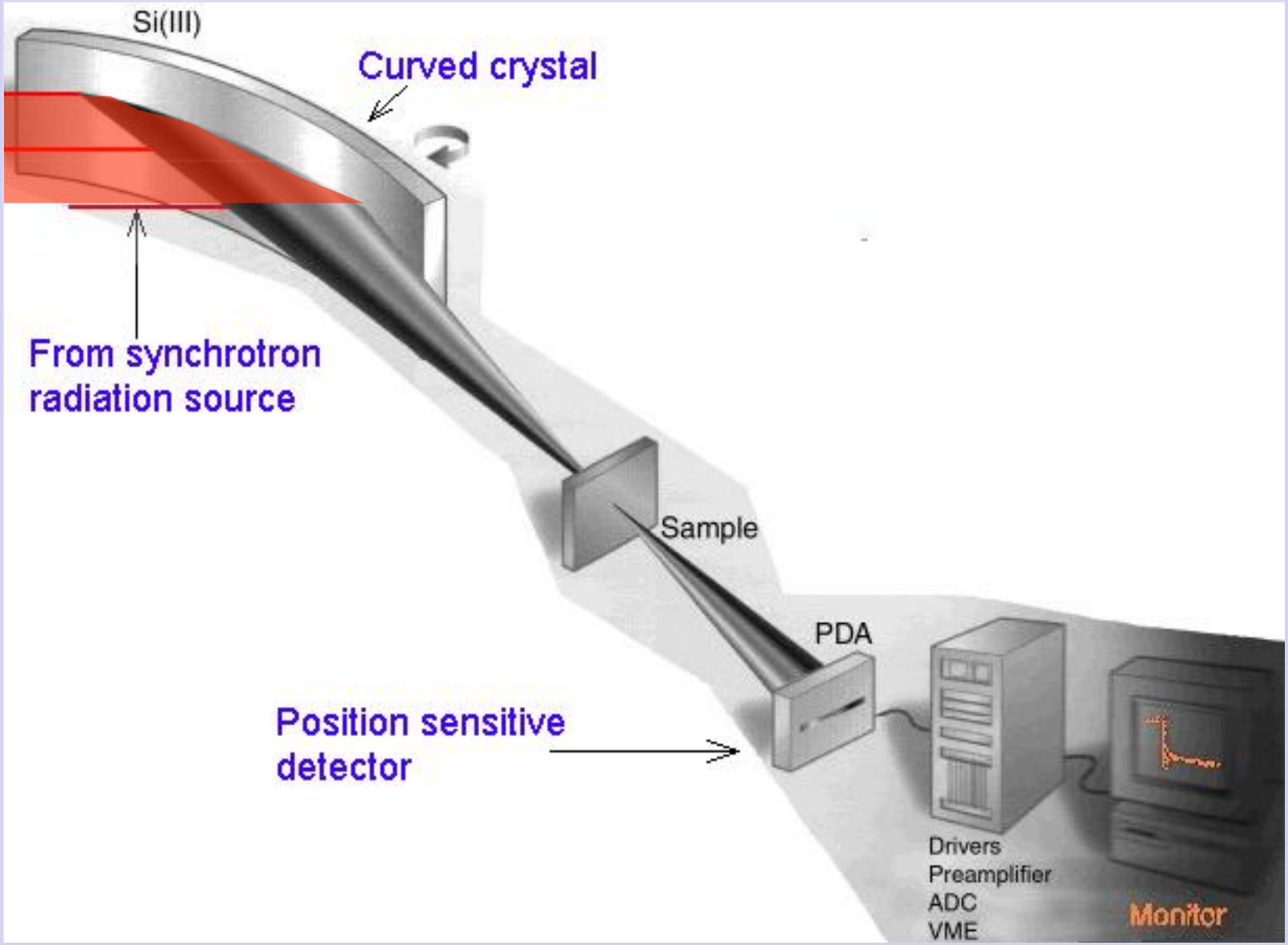

Dispersive XAFS (b)

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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:
`http://www.esrf.eu/Instrumentation/software/data-analysis/Links/xafs`

FEFF project (University of Washington, USA):
http://leonardo.phys.washington.edu/feff/

IFEFFIT (University of Chicago, USA) + Athena, Artemis, Demeter
http://cars9.uchicago.edu/ifeffit/.

GNXAS project (University of Camerino, Italy):
http://gnxas.unicam.it/XASLABwww/pag_gnxas.html

EXAFS data analysis

- Extraction of EXAFS signal

Total absorption coefficient

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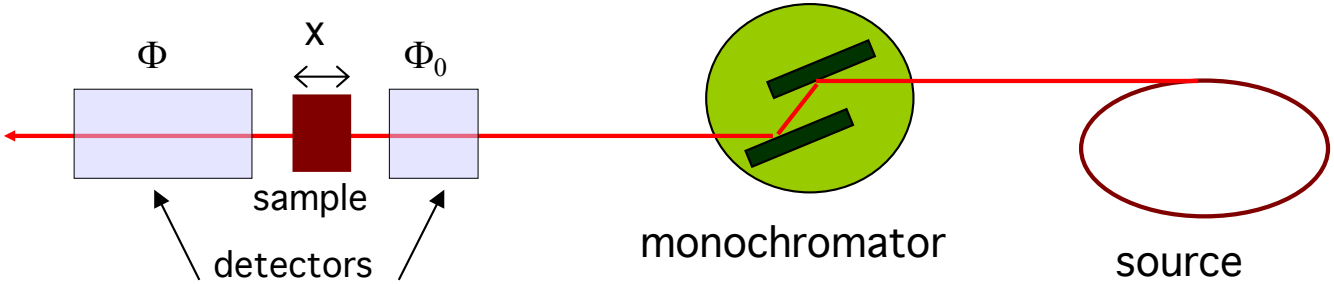
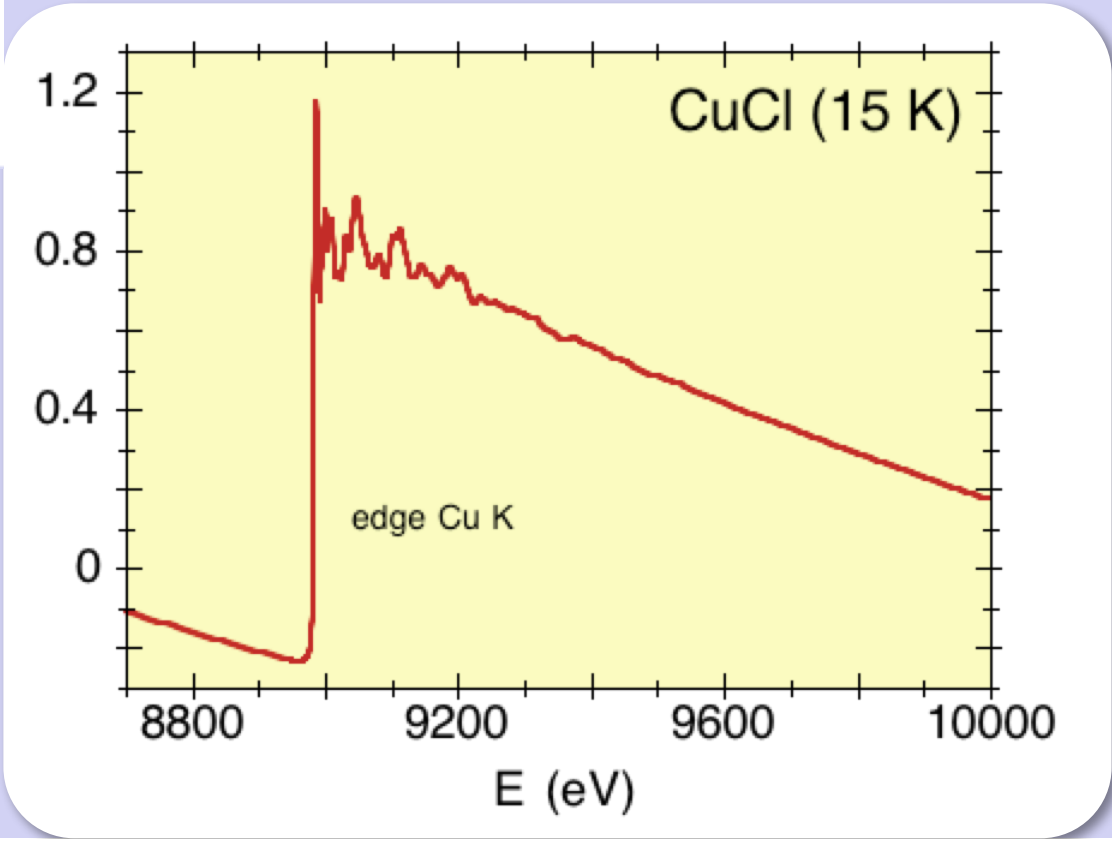


$$\ln\frac{I_0}{I} = \ln\frac{\Phi_0}{\Phi} + C' = \mu_{tot}x + C'$$



Edge absorption coefficient

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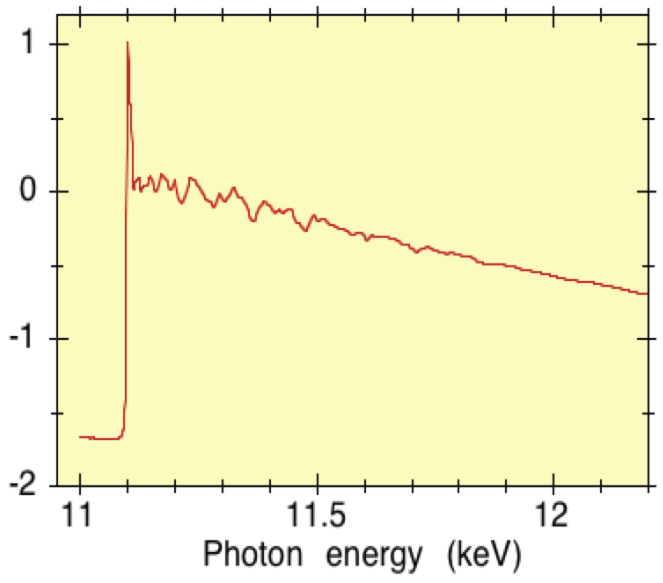
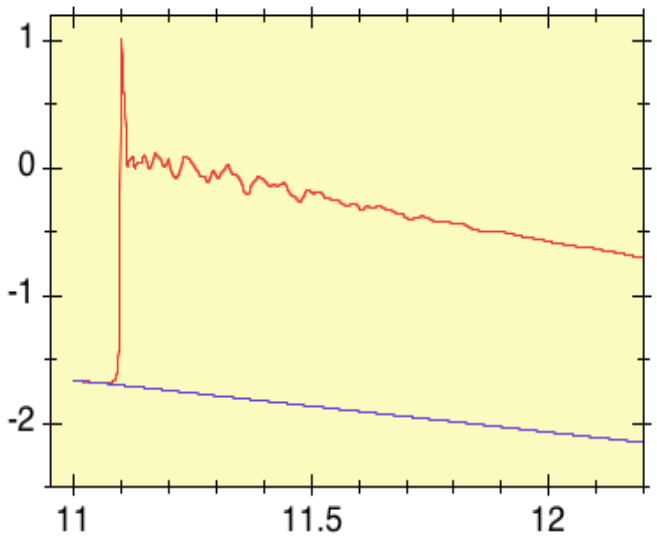
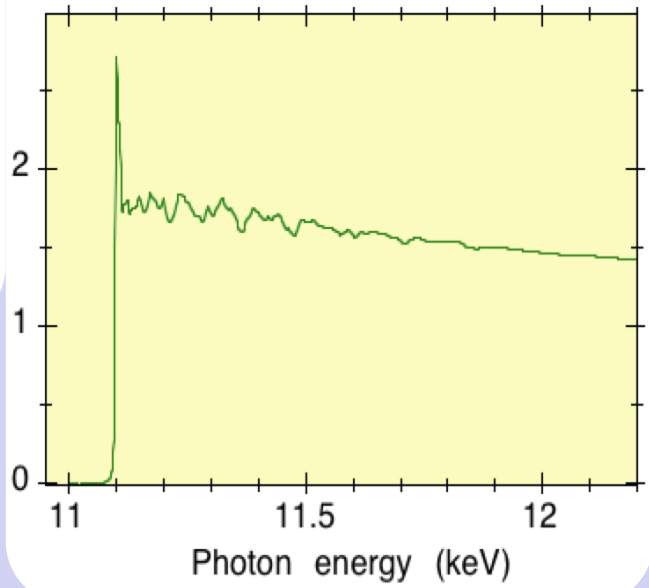
Experimental signal



Extrapolation of pre-edge behaviour



Edge absorption coefficient



Photoelectron wavenumber

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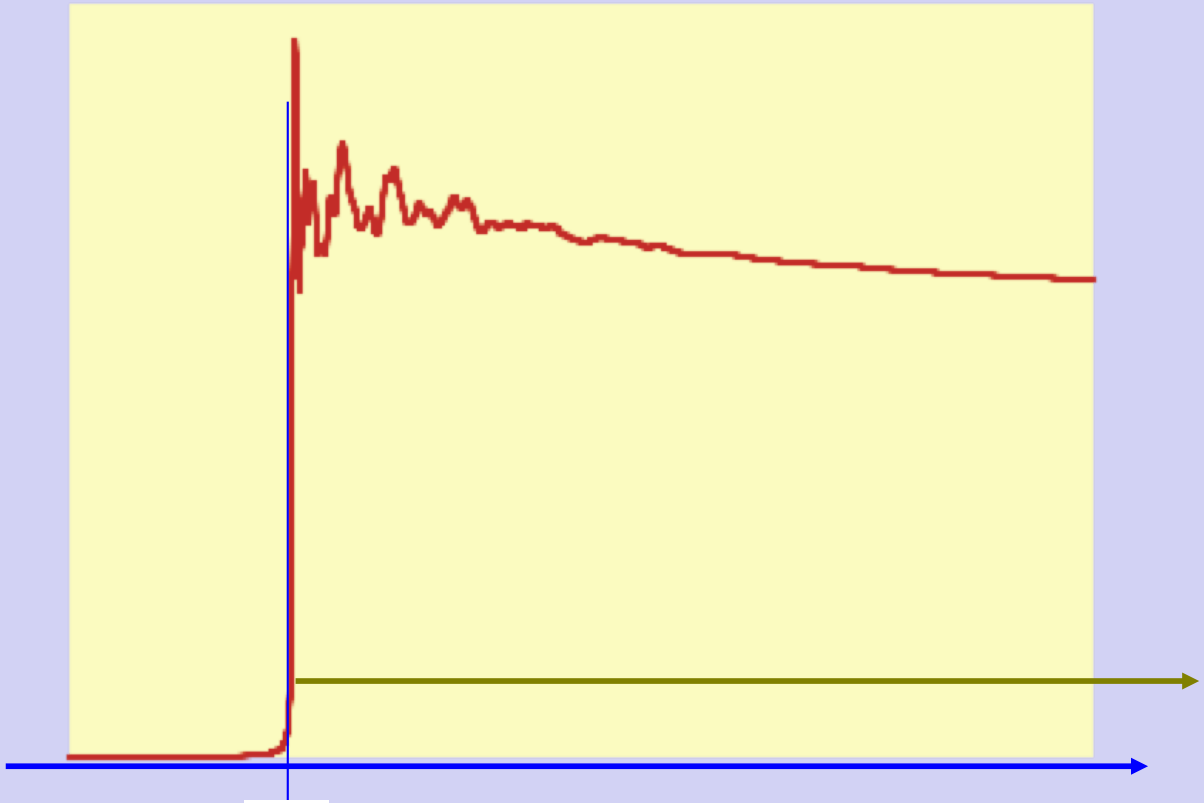
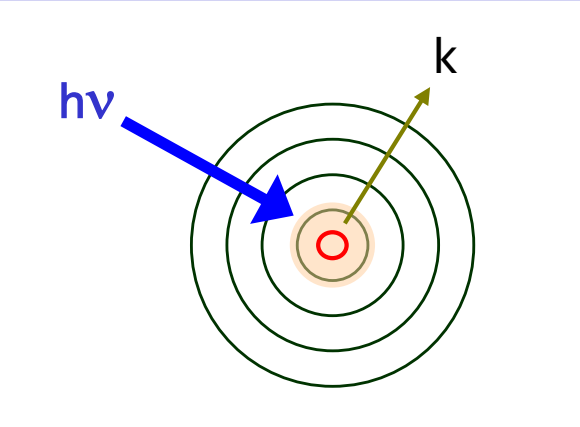


E_s

Edge energy

?

$E = h\nu$, photon energy



Photoelectron wavenumber

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

Experimental convention

E_s = 1st maximum of 1st derivative

Atomic absorption coefficient

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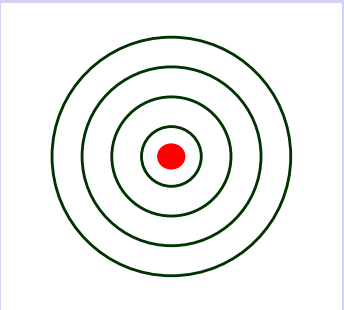
EXAFS function

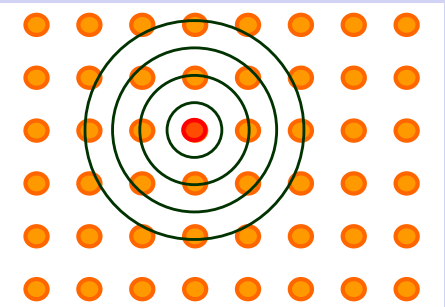
$$\chi(k) = \frac{\mu - \mu_0}{\mu_0}$$

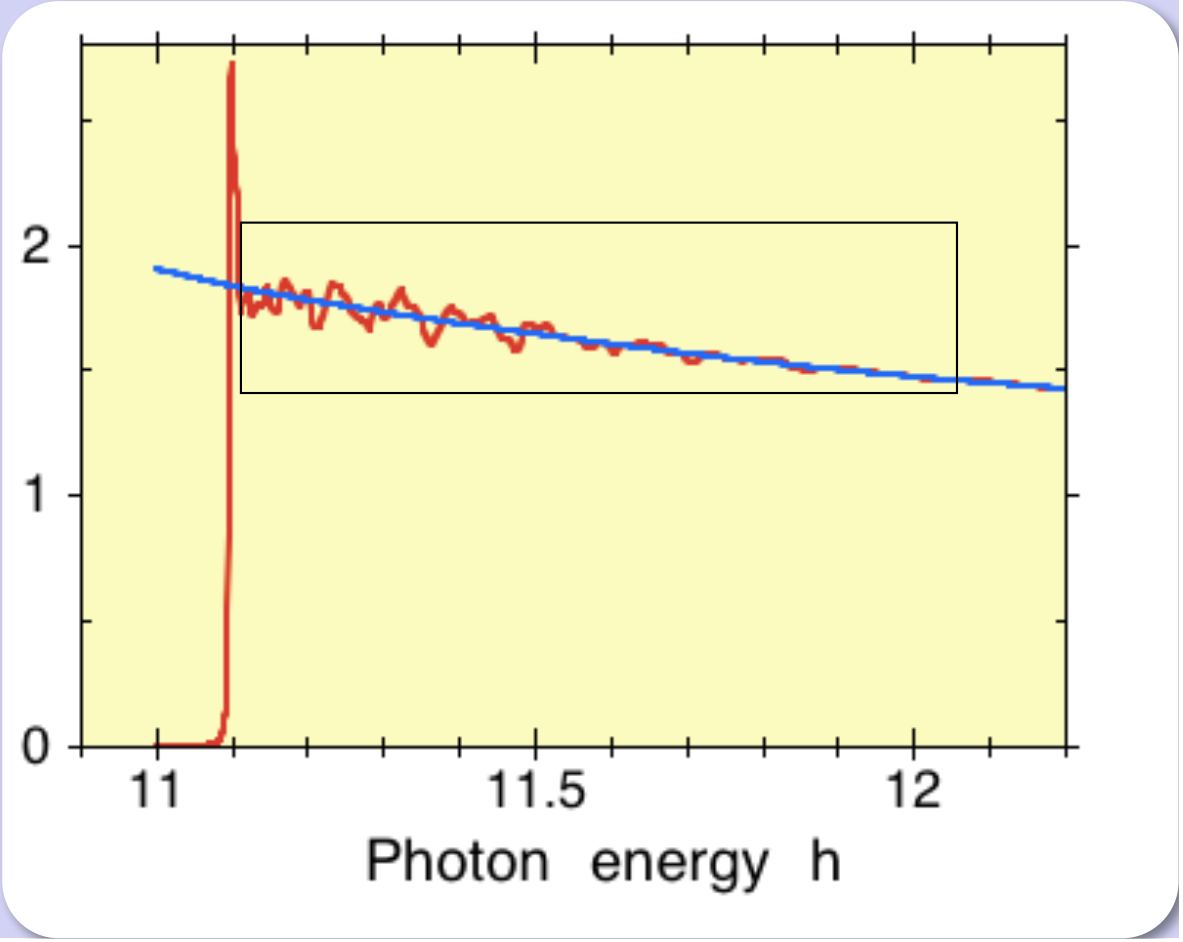
μ_0 ?

Isolated atom



Embedded atom





Best-fitting polynomial spline

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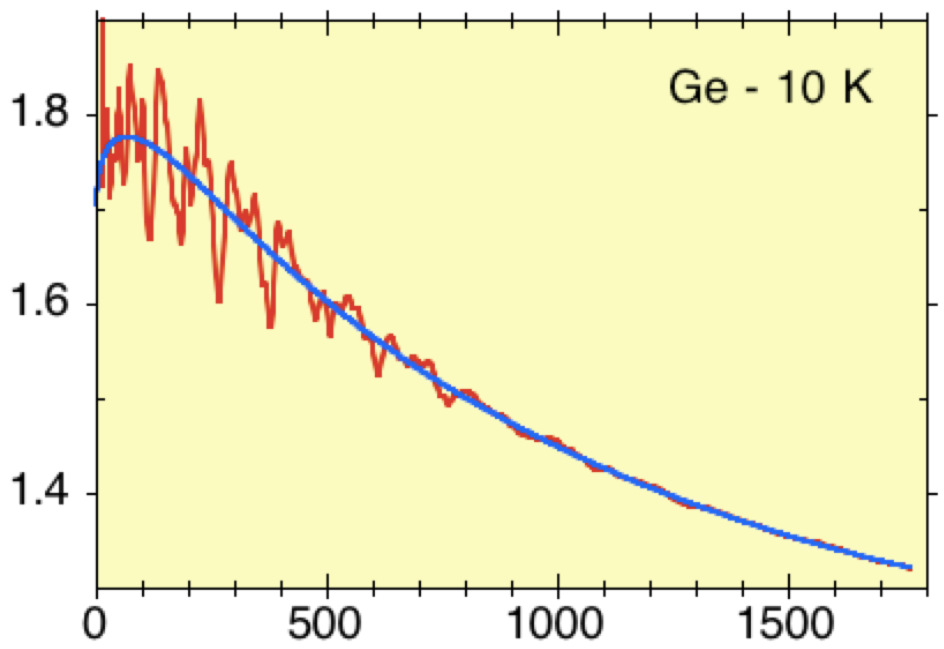
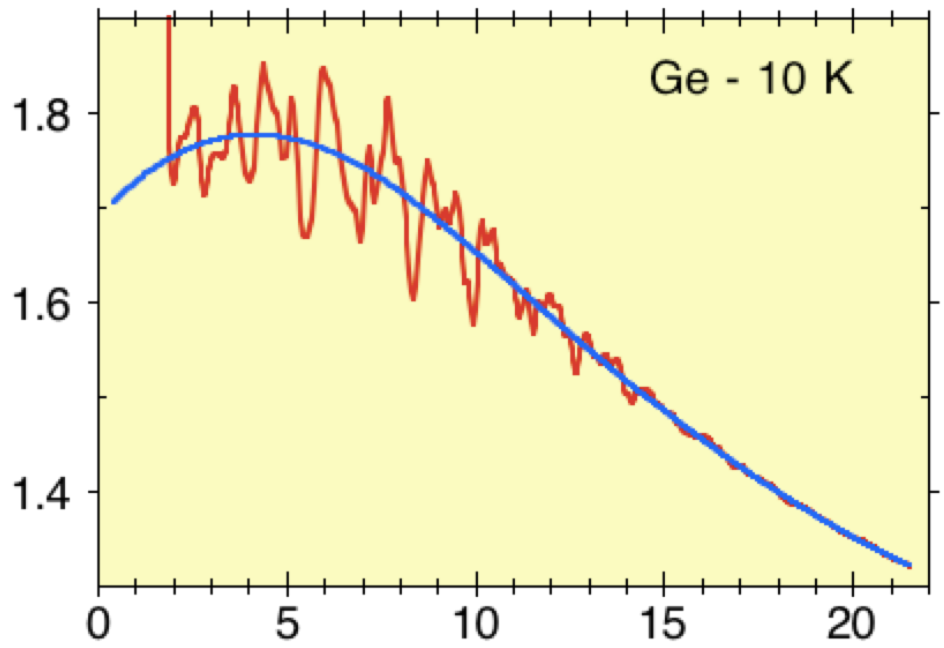
$$\chi(k) = \frac{\mu - \mu_0}{\mu_0}$$

Polynomial spline - best fit

E space



k space



Fit optimization

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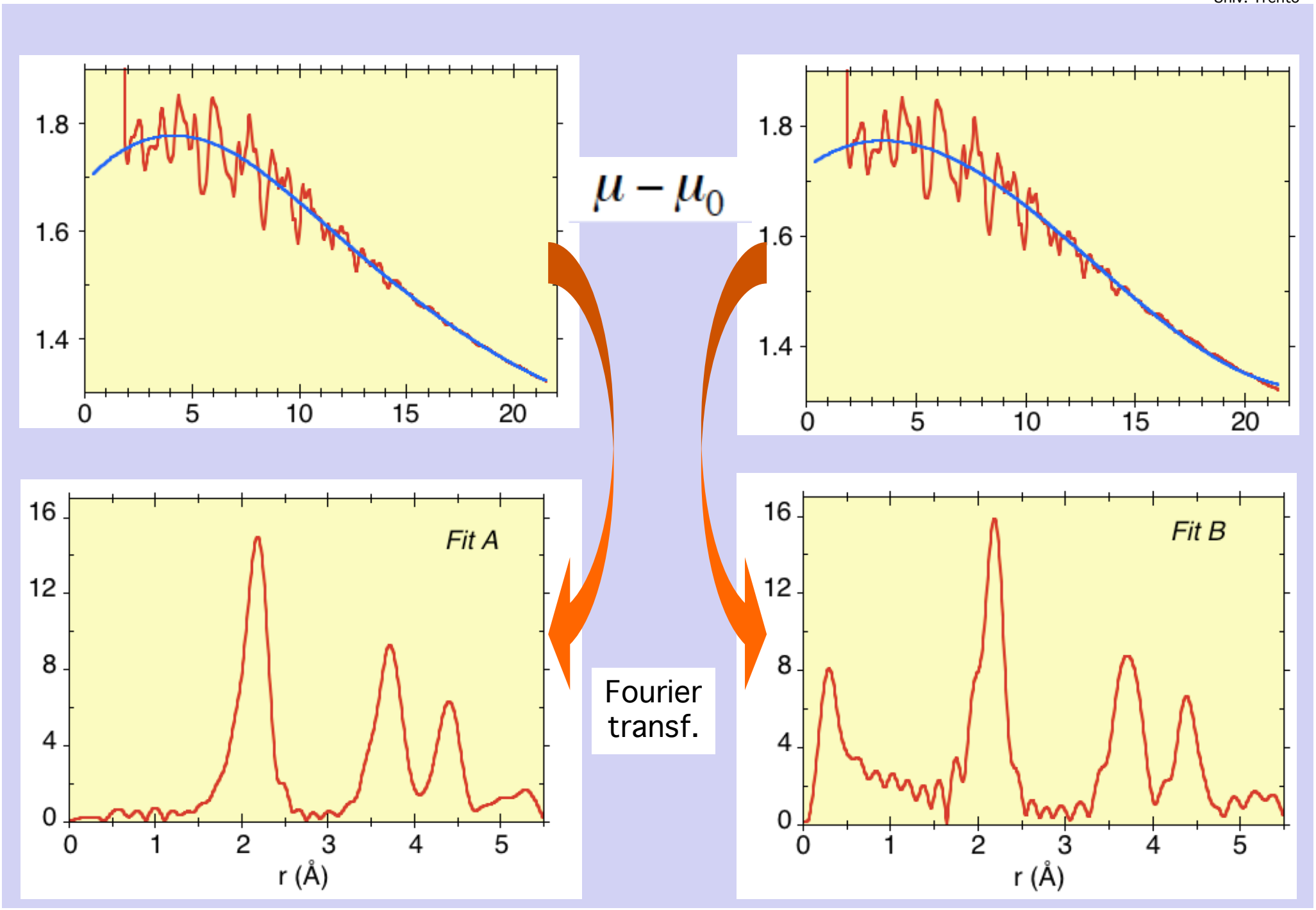

Quantitative analysis of EXAFS

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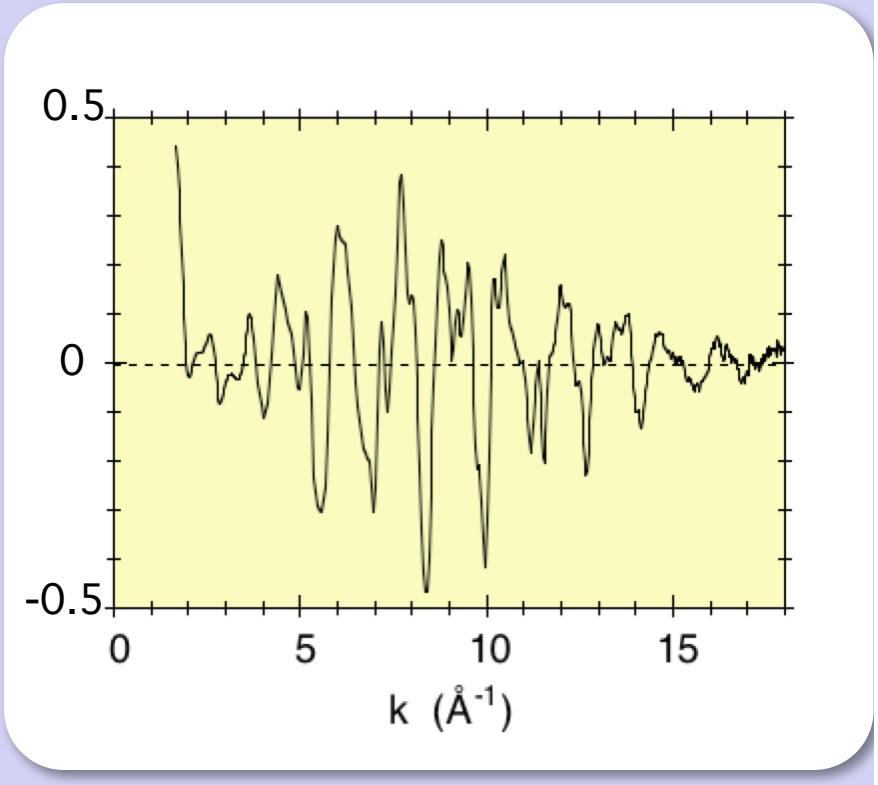
$$\chi(k) = \sum_i A_i(k) \sin \Phi_i(k)$$

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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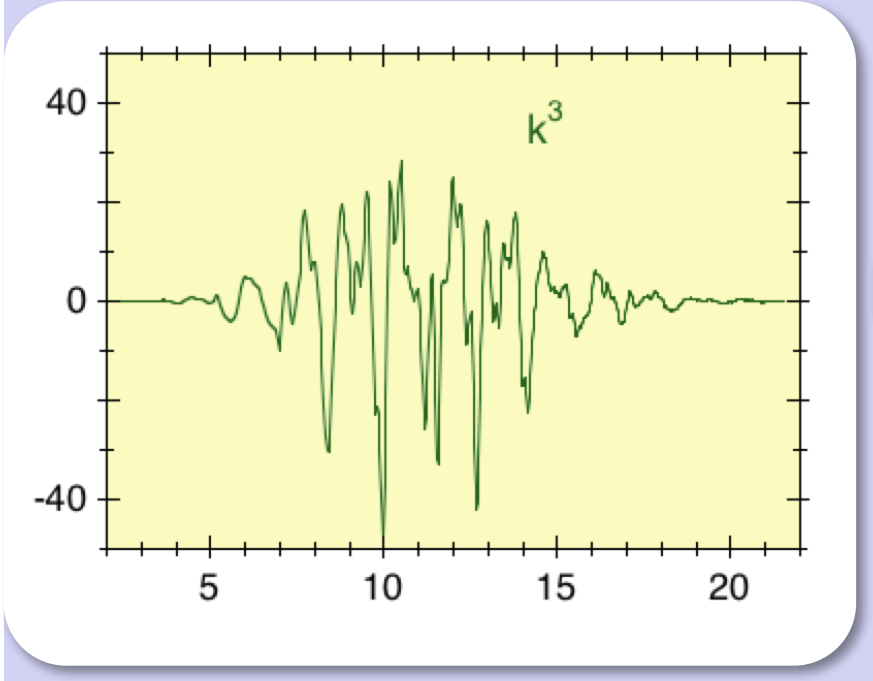
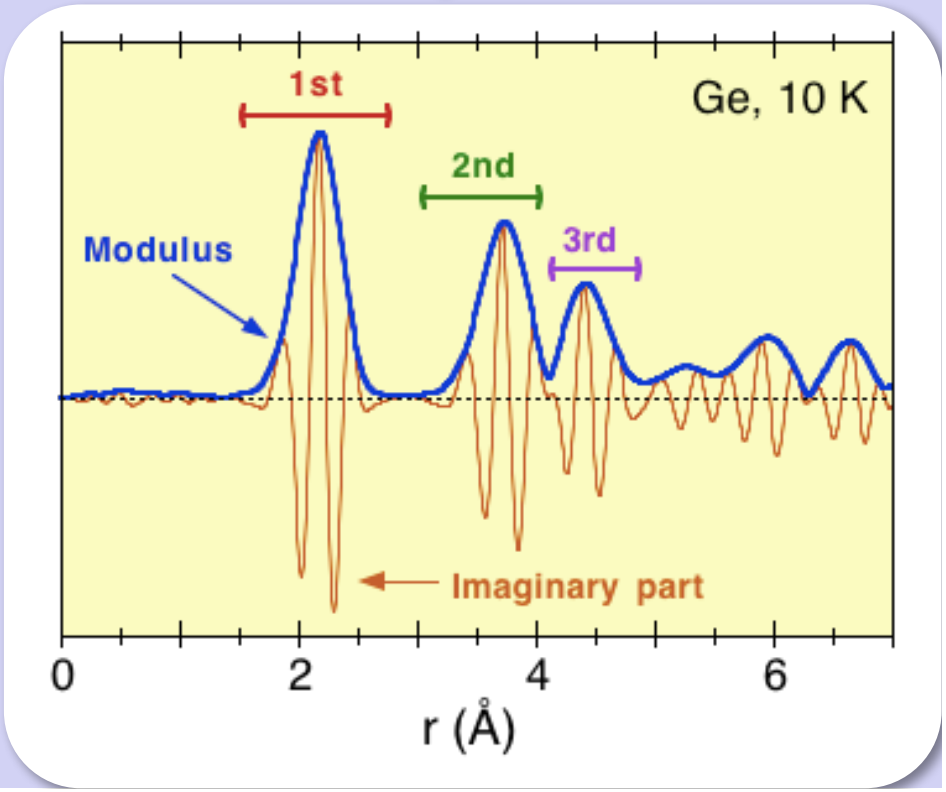


weight window

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



Peak's position and shape influenced by:

- total phaseshifts
- disorder
- Fourier transform window

Fourier Transform and distribution

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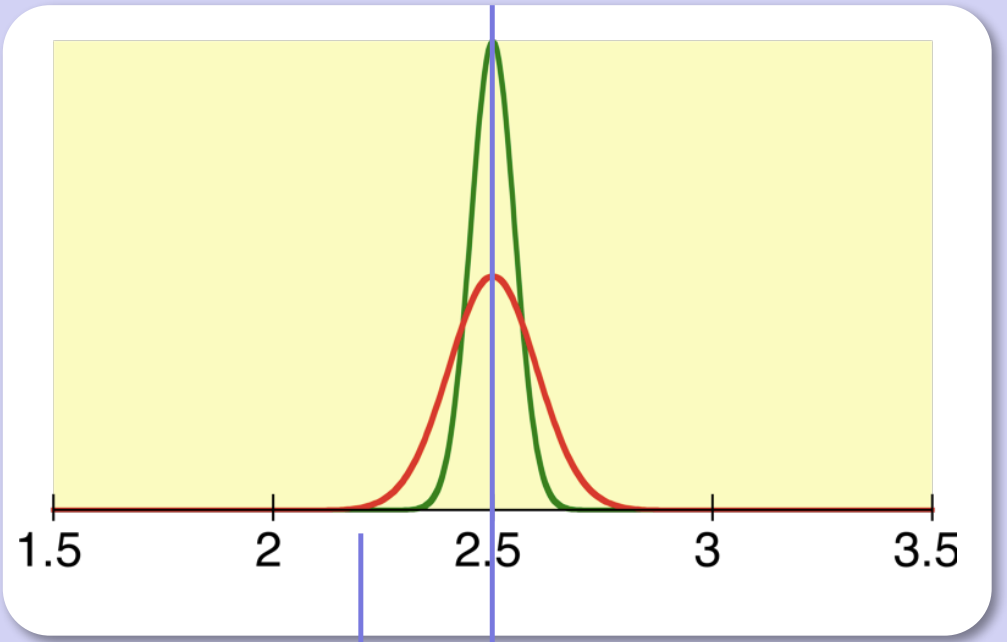
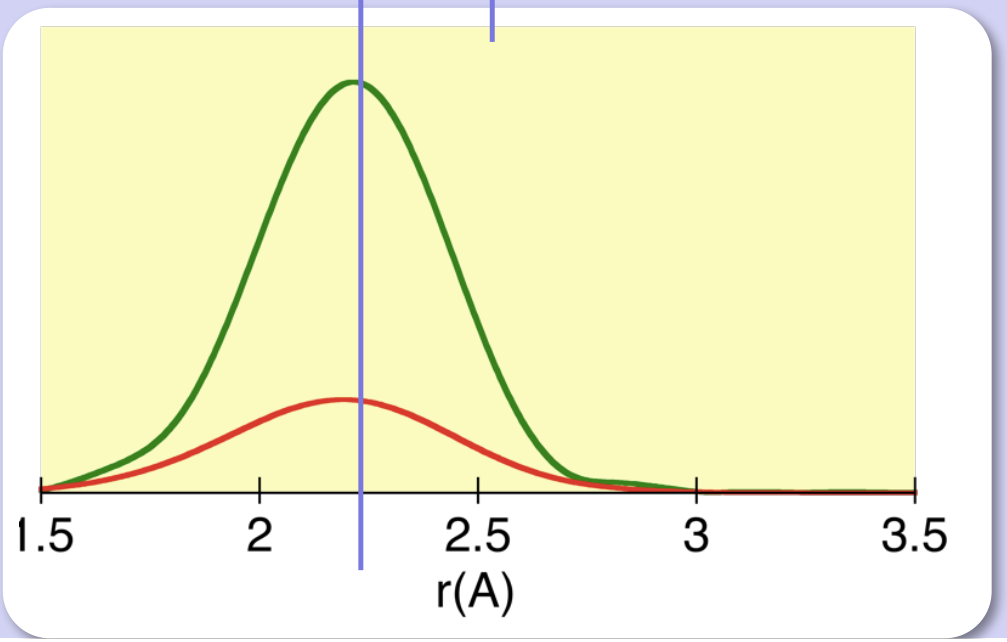
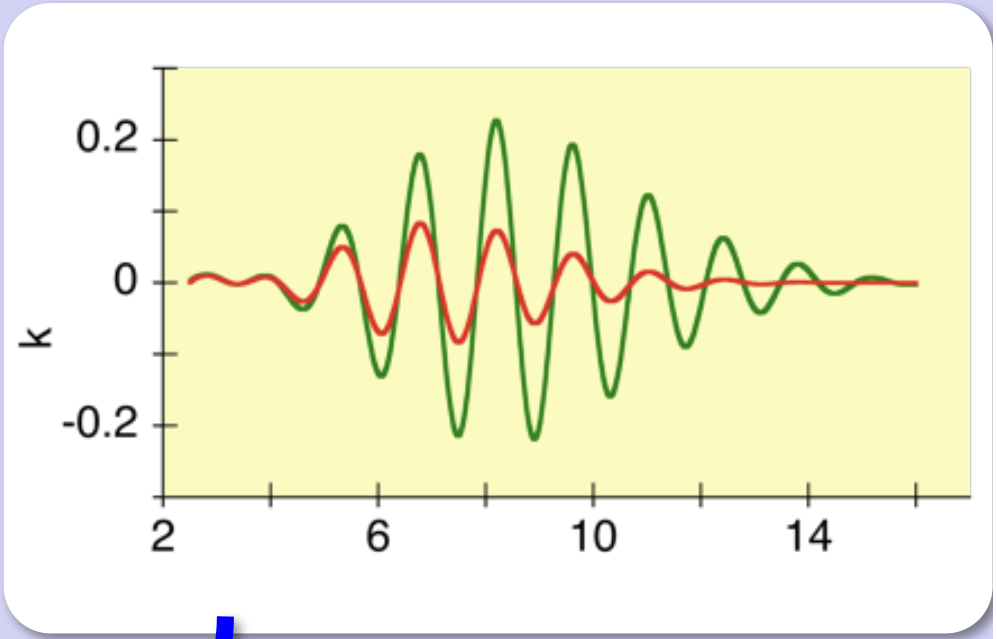




EXAFS simulation
(Ge phases and amplit.)



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

bcc structure (26-Fe)

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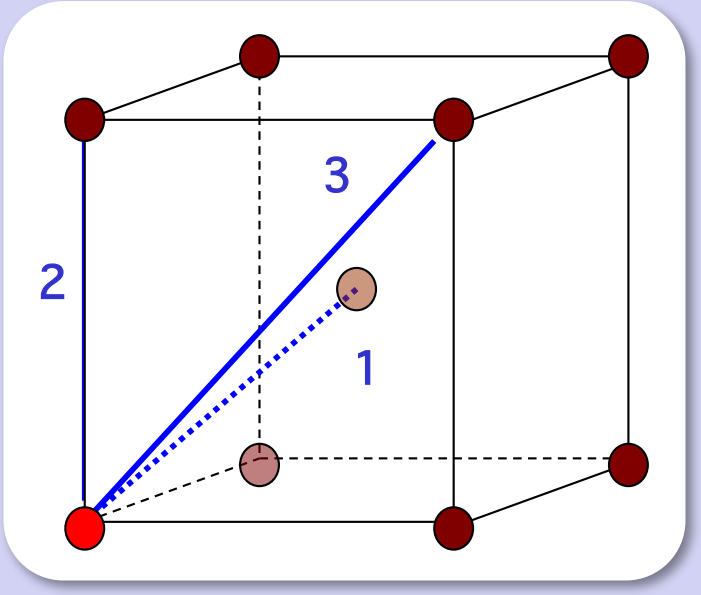
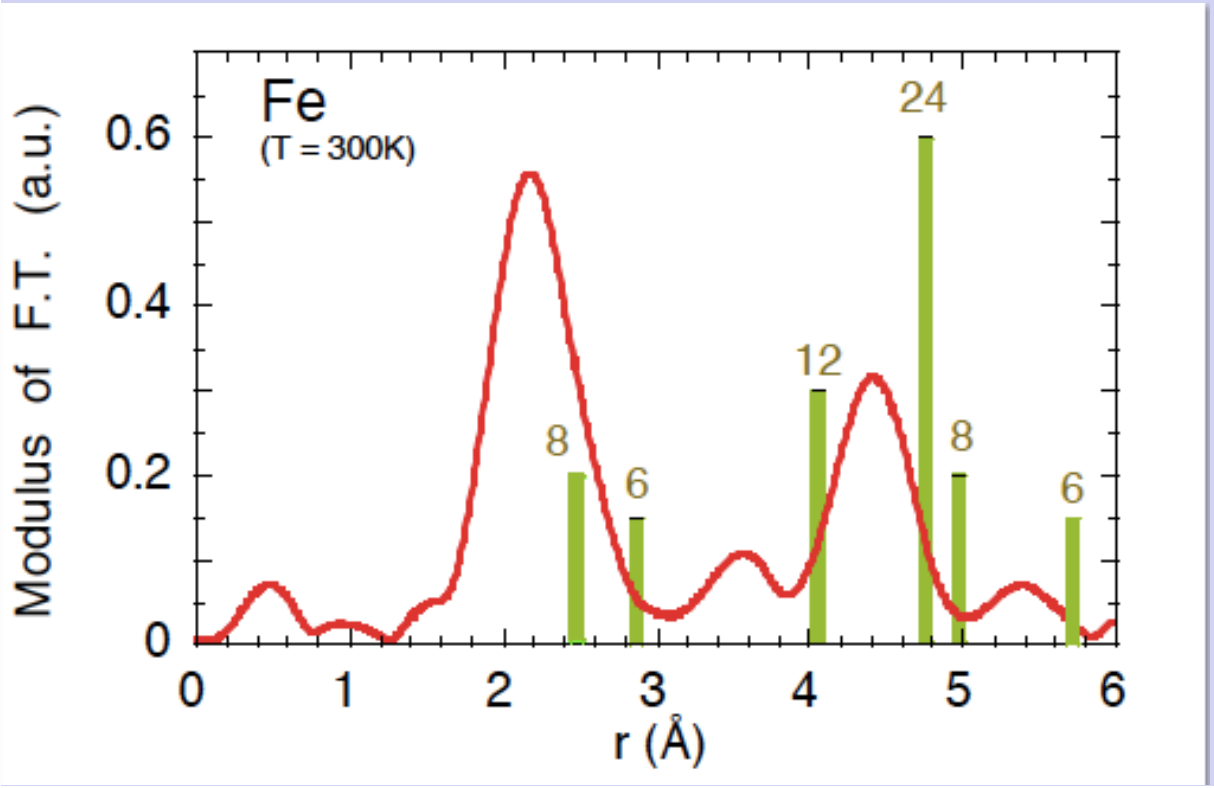
i	N_i	R_i (Å)
1	8	2.48
2	6	2.86
3	12	4.05
4	24	4.75
5	8	4.96
6	6	5.73





- Peak shift
- Superposition of shells

fcc structure (29-Cu)

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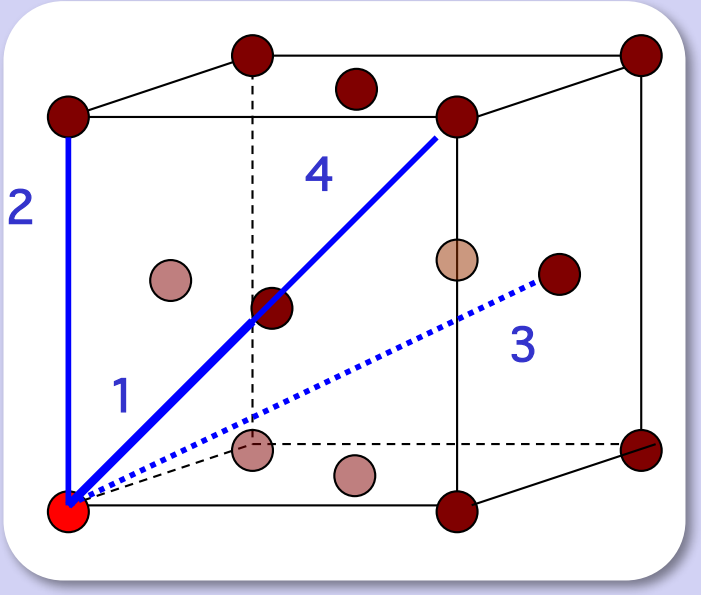
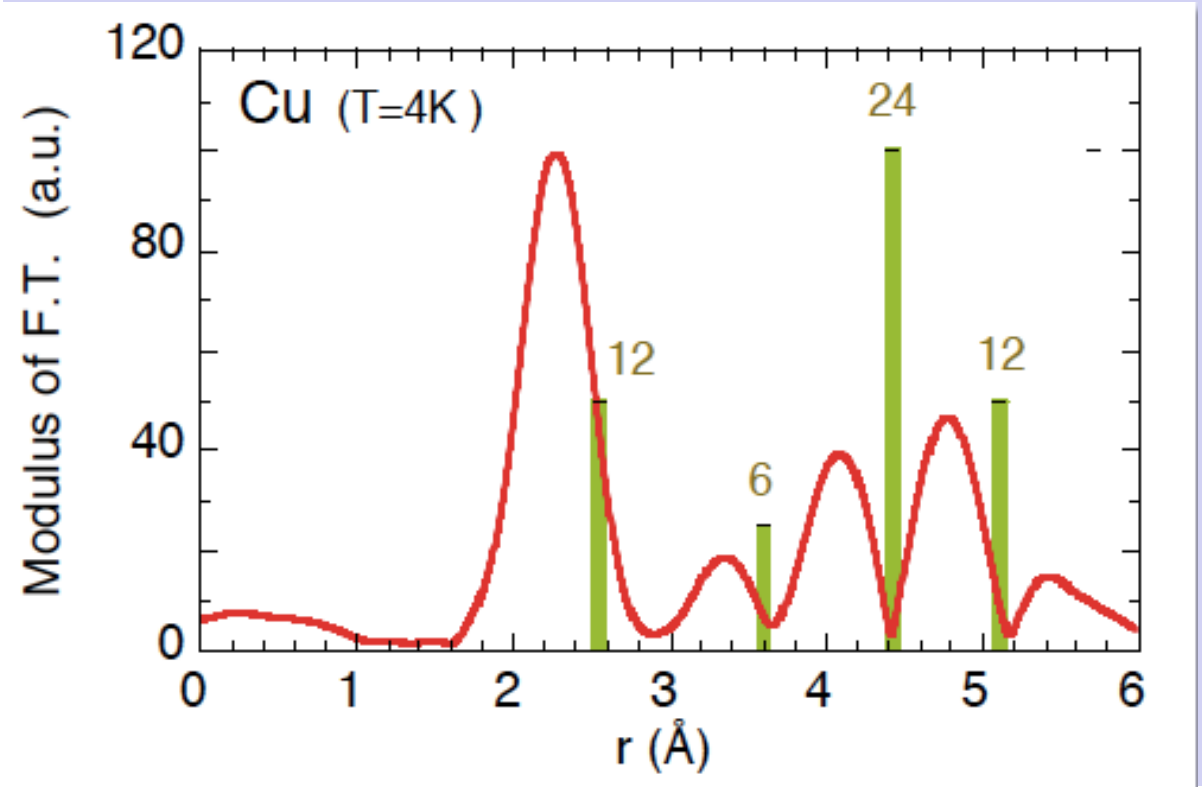
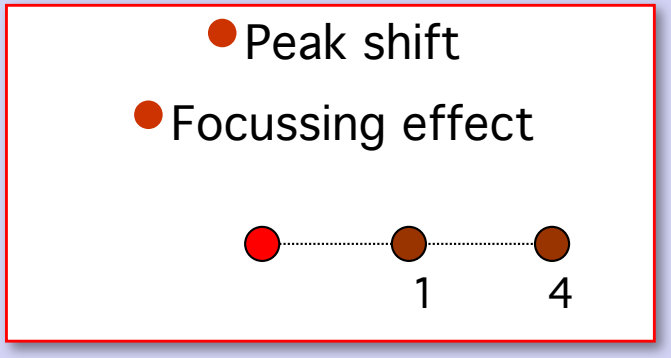
i	N_i	R_i (Å)
1	12	2.55
2	6	3.61
3	24	4.42
4	12	5.10
5	24	5.70
6	8	6.25







29 - Copper: fcc structure – Multiple Scattering

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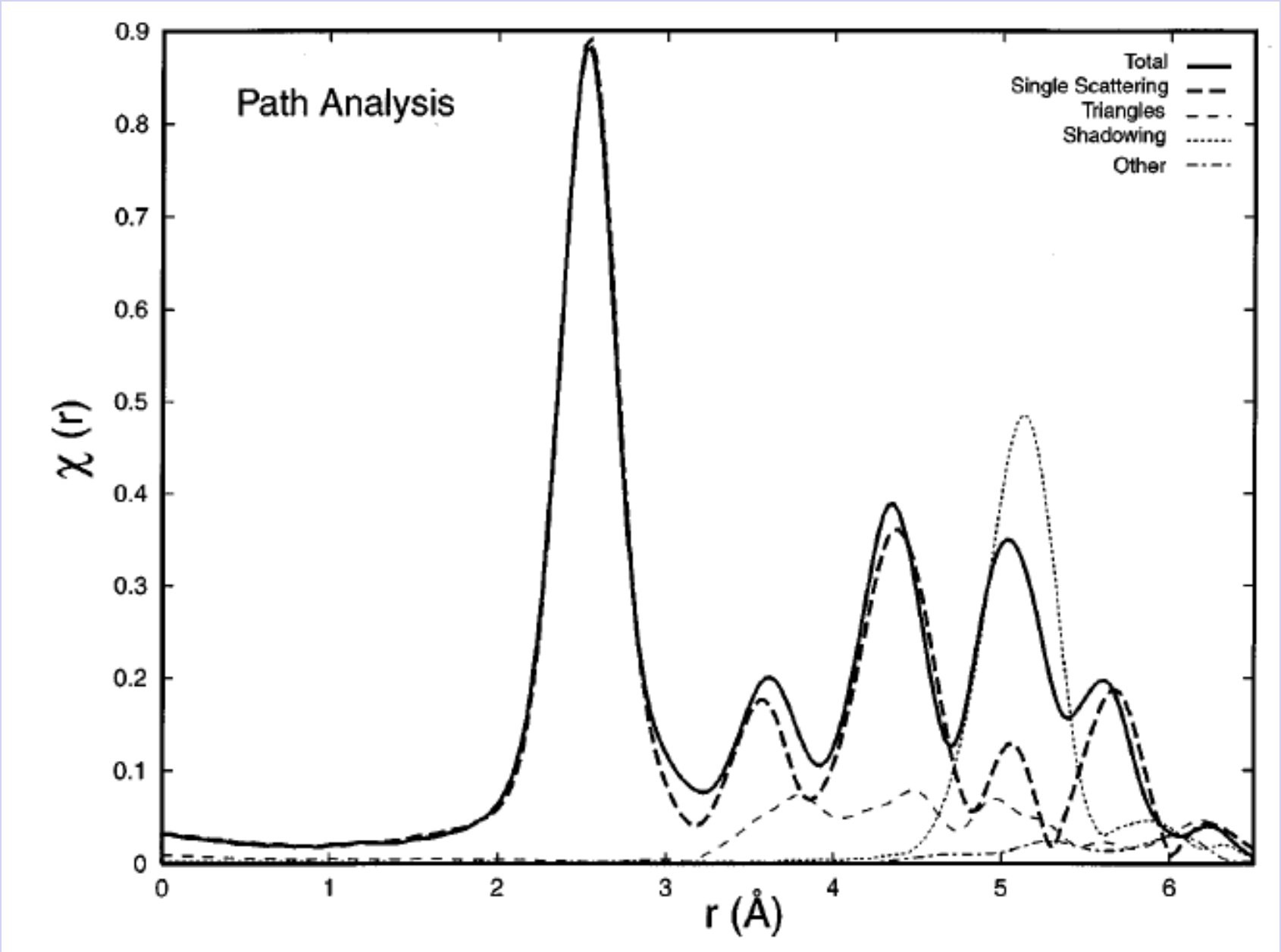

Rehr &Albers, Rev. Mod. Phys. 72, 621(2000)

Diamond structure (32-Ge)

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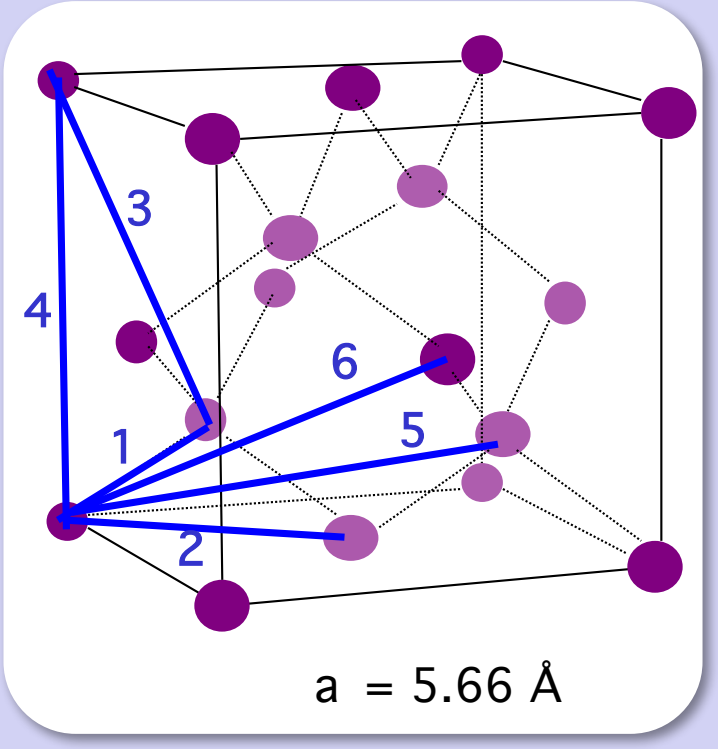
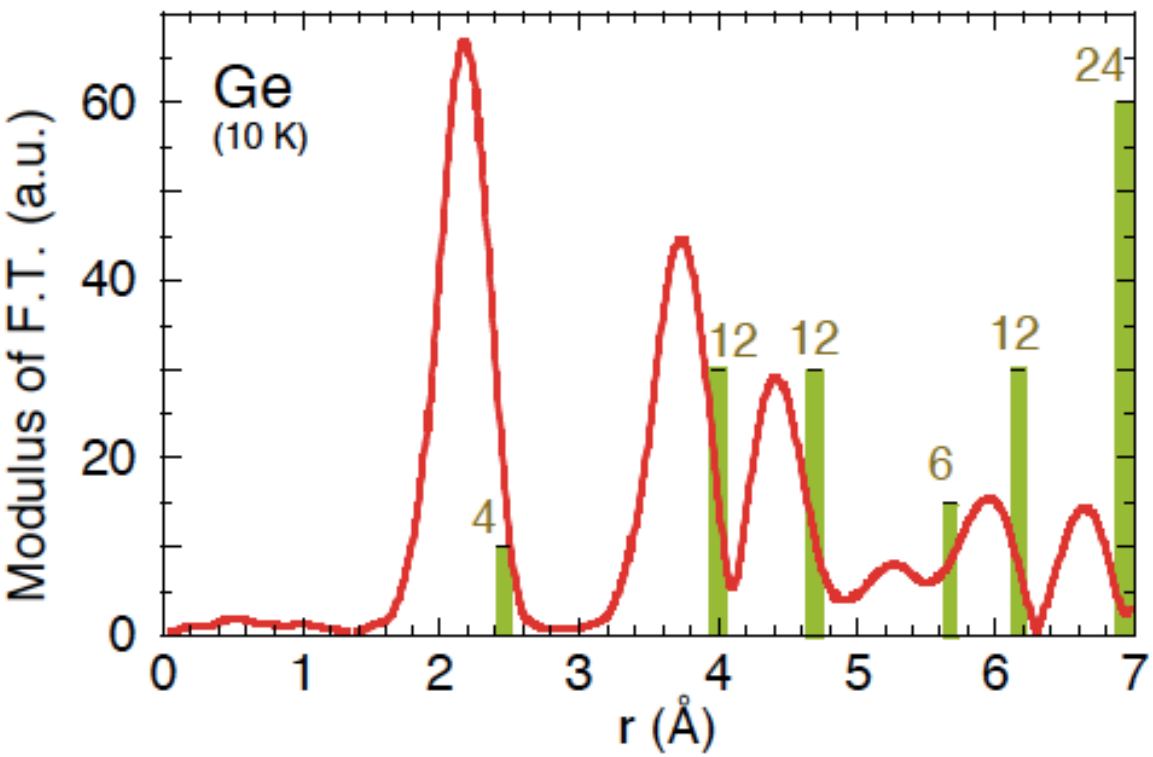
i	N_i		R_i (Å)
1	4	$a(\sqrt{3})/4$	2.45
2	12	$a/\sqrt{2}$	4.00
3	12	$a(\sqrt{11})/4$	4.69
4	6	a	5.66
5	12	$a(\sqrt{19})/4$	6.16
6	24	$a(\sqrt{6})/2$	6.93





Crystalline and amorphous Ge – EXAFS signals

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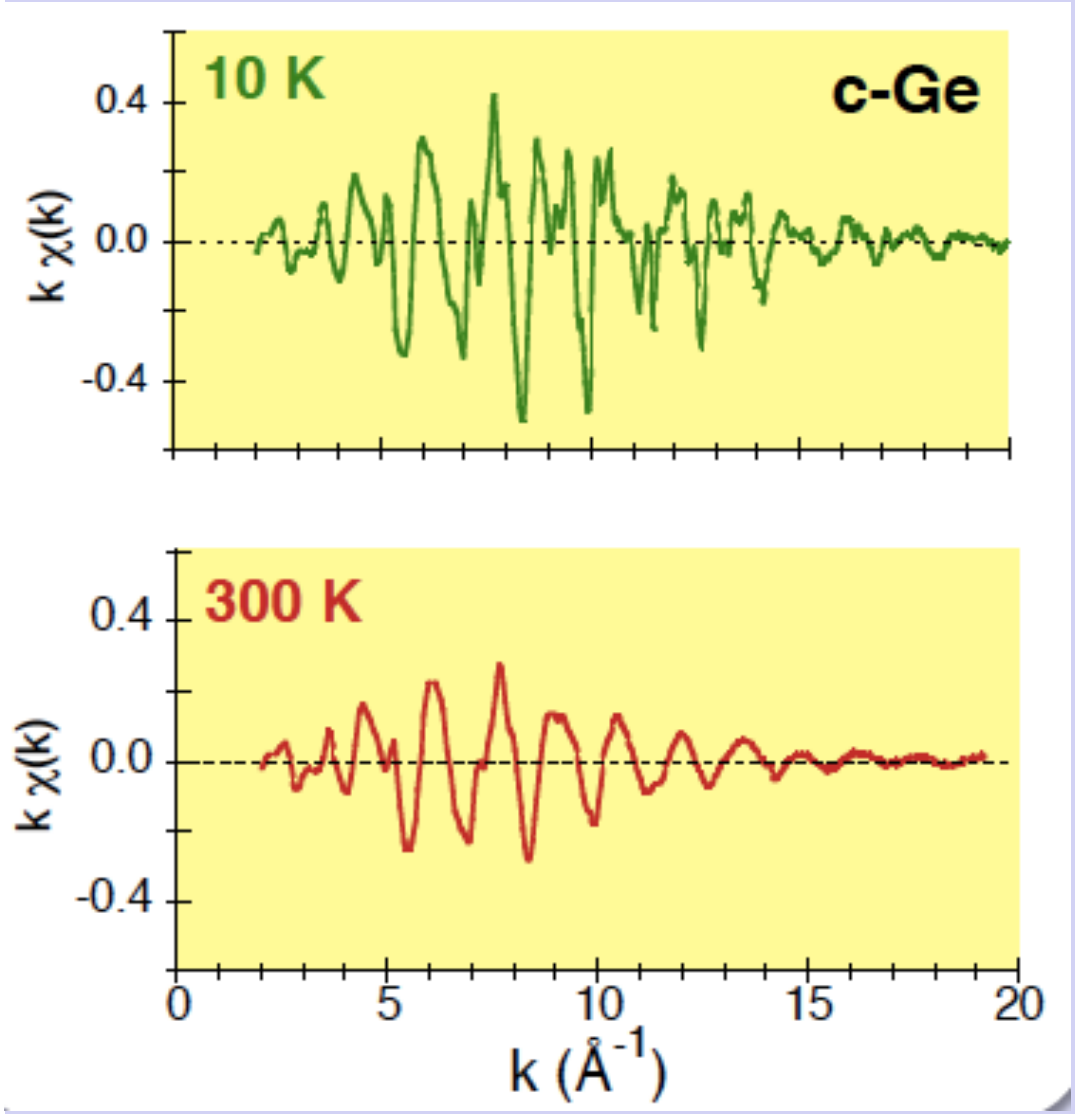

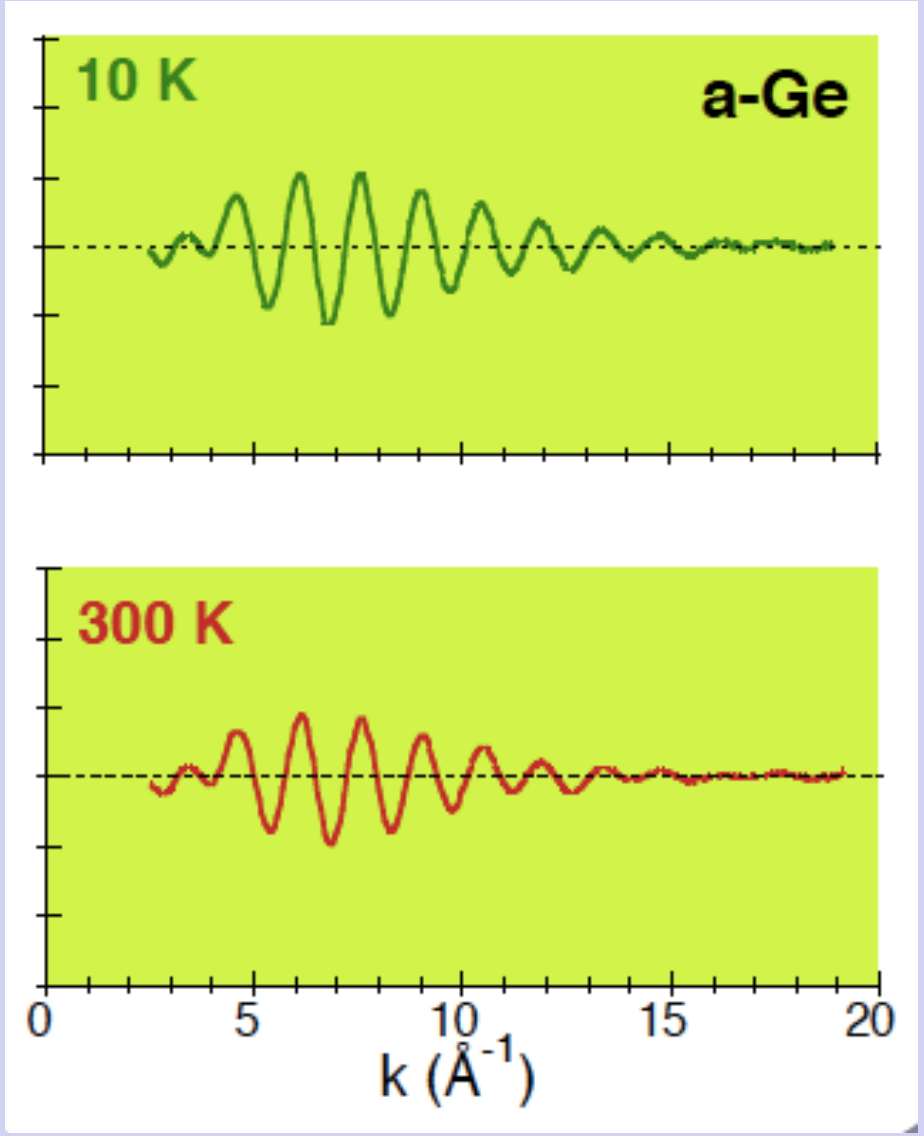

Crystalline and amorphous Ge: F.T.

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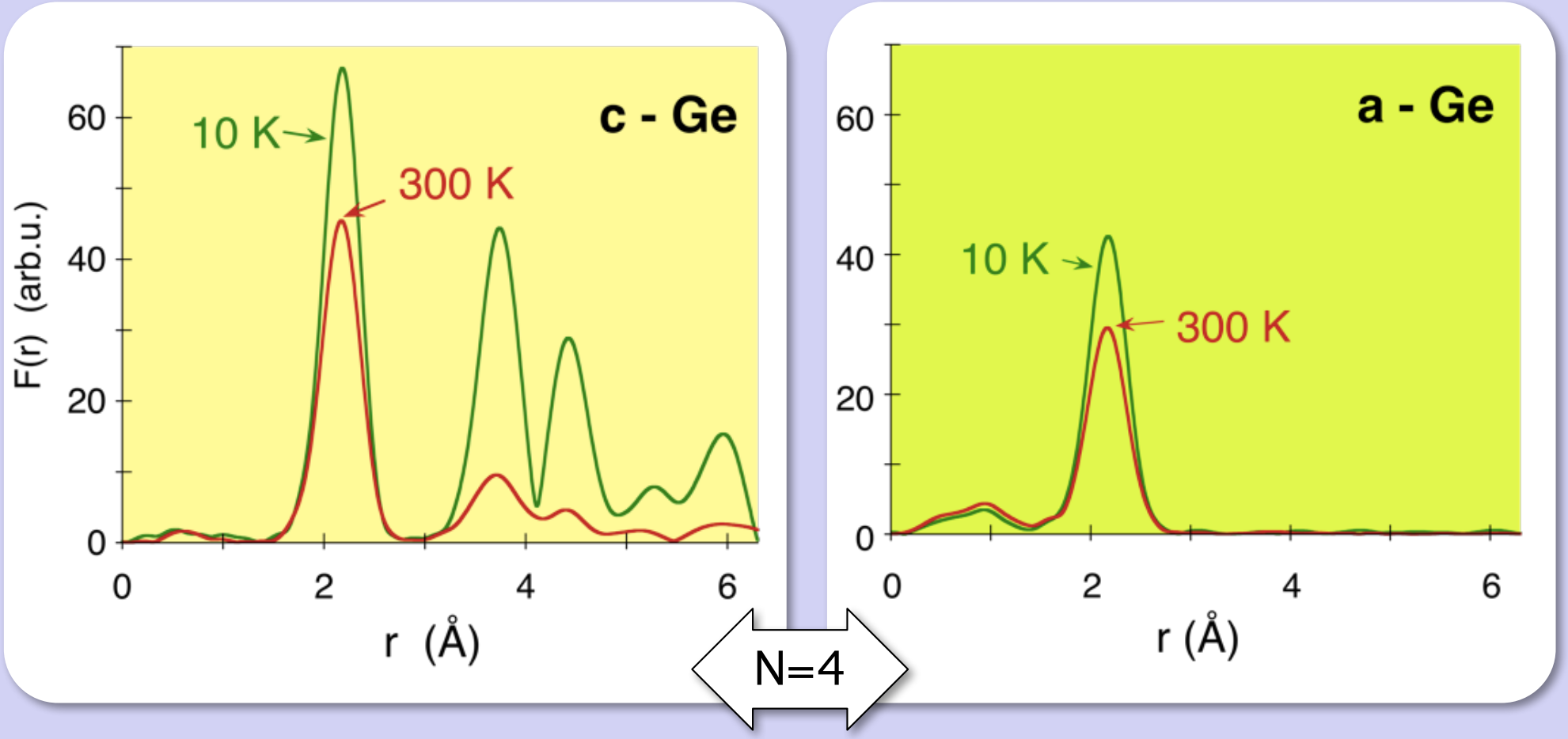

- Structural disorder
- stronger for outer shells

- Only 1st shell
- Thermal disorder
- Structural disorder

EXAFS data analysis

- First shell analysis

1st-shell Fourier back-transform

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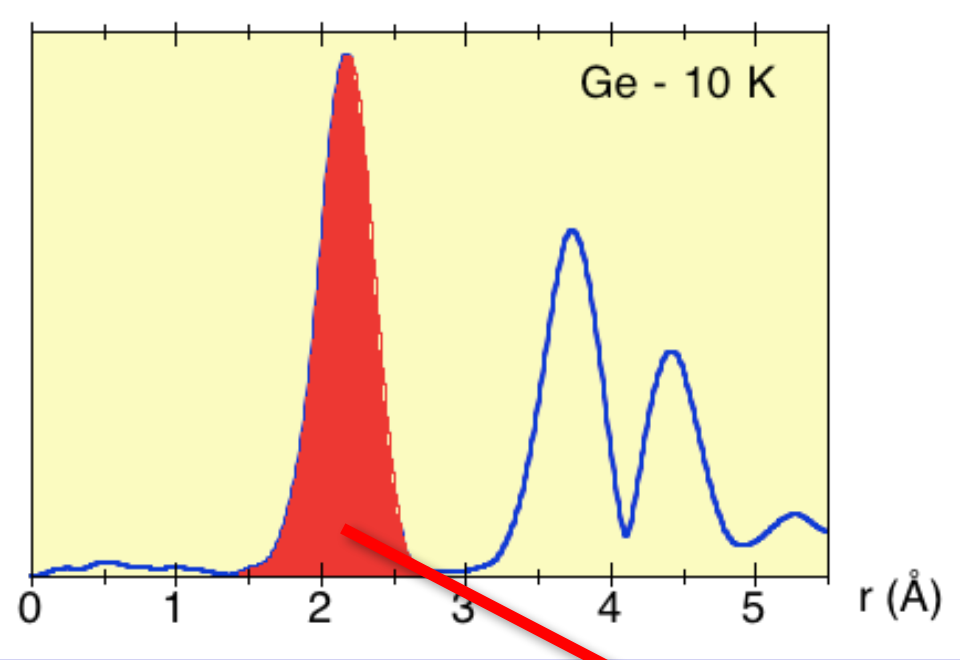
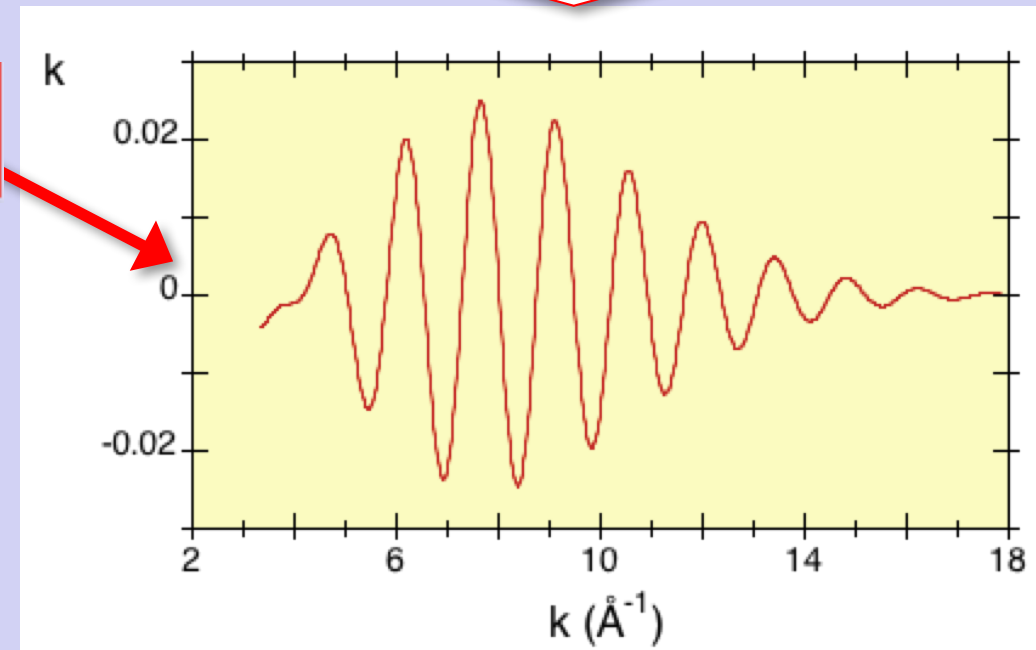


$$\chi'(k) = (2/\pi)\int_{r_{min}}^{r_{max}} F(r)\, W'(r)\, e^{-2ikr}\, dr$$

First-shell contribution



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

1st-shell distribution of distances

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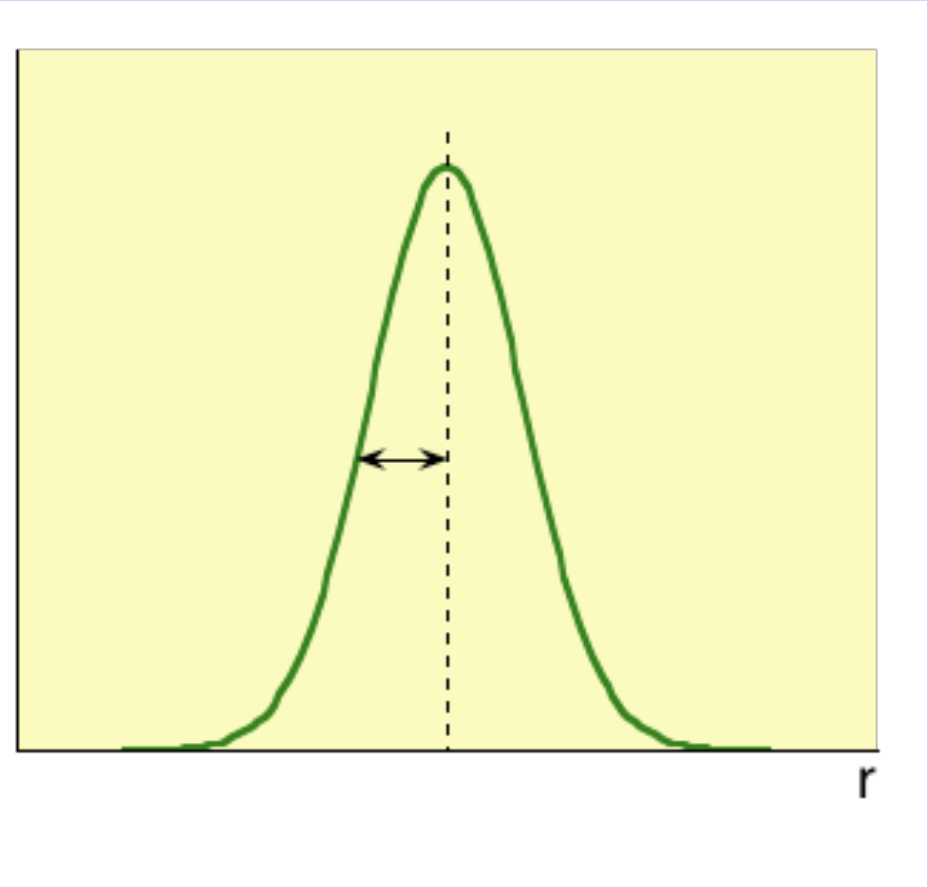
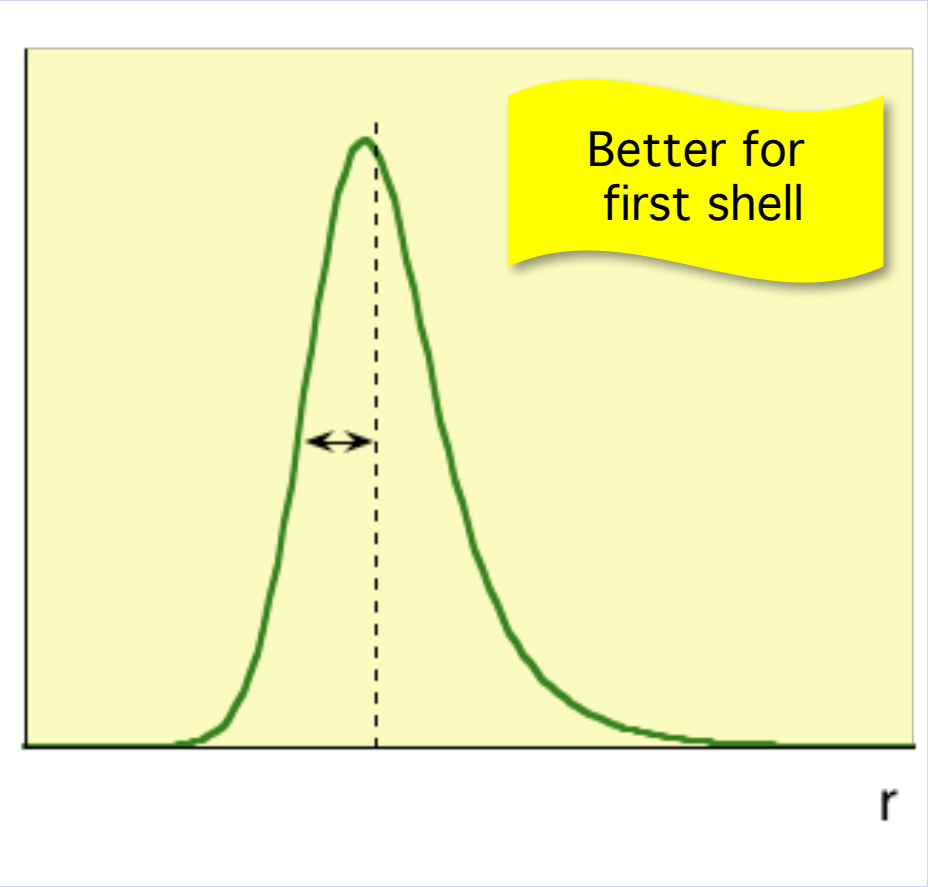
Gaussian approximation



Asymmetric distribution



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

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

Real and effective distributions

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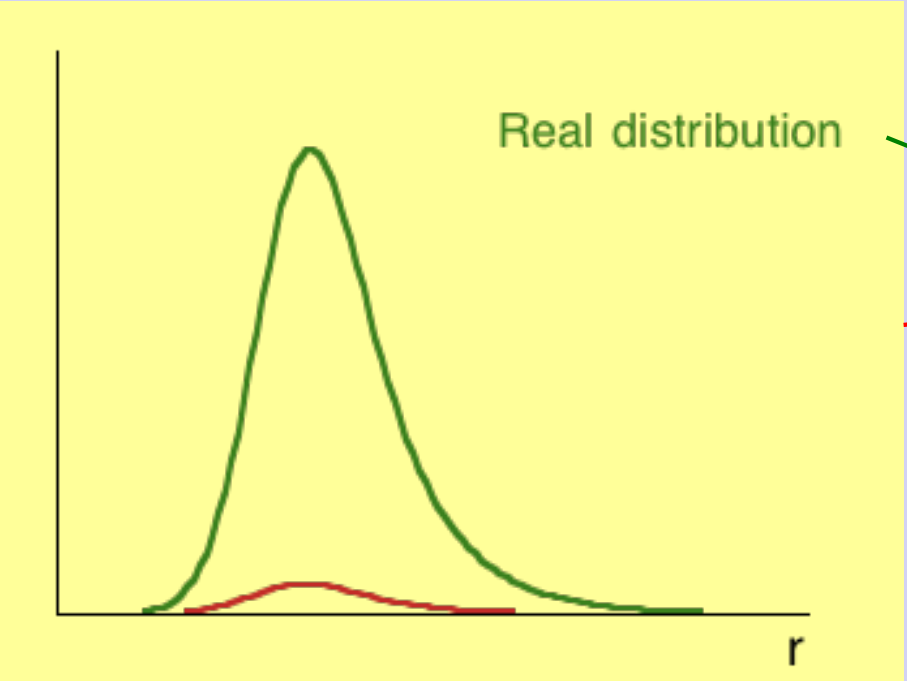

$$\rho_s(r)\,\frac{e^{-2r_s/\lambda(k)}}{r_s^2}$$

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

C_1 $\langle r\rangle$

EXAFS for first shell, including asymmetry

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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

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

Coordination number — N

Debye-Waller — σ^2

Average distance and asymmetry — C_1, C_3

Non-linear fitting method

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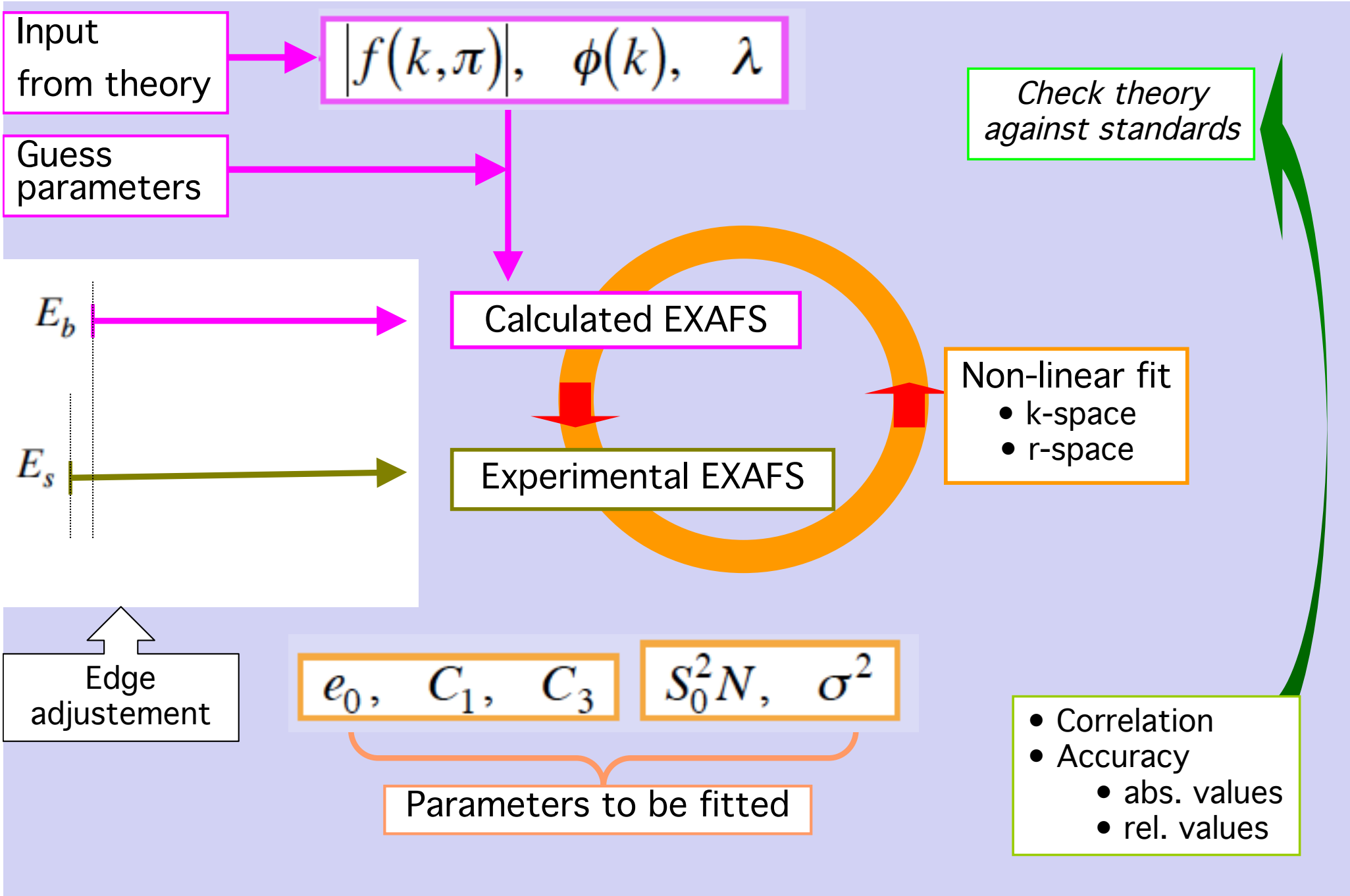

EXAFS data analysis

- 1st shell phase and amplitude analysis

Separate evaluation of phase and amplitude

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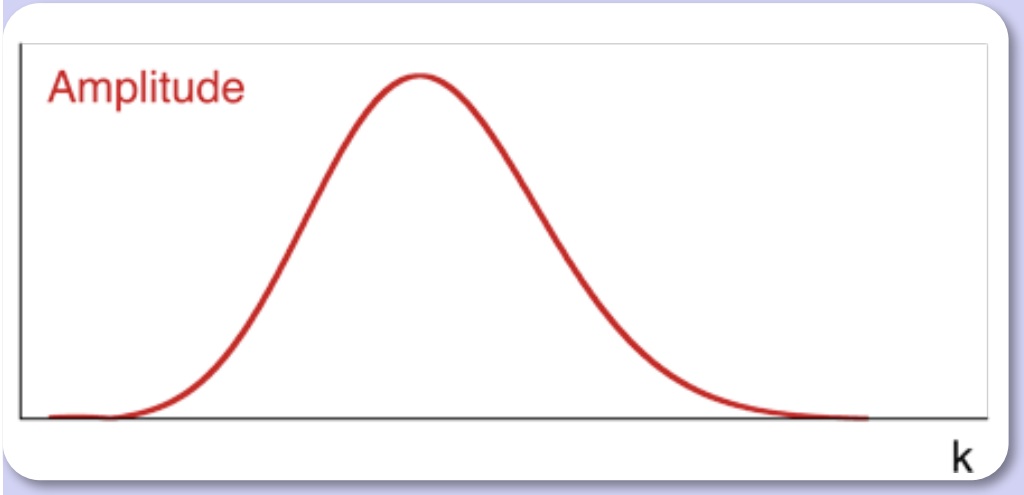
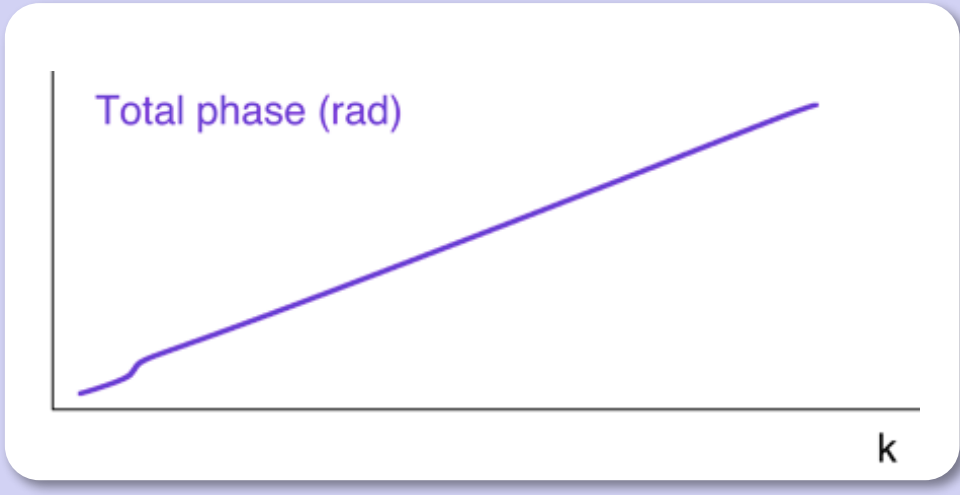
From complex Fourier transform and back-transform





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

?

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

?

“Ratio method” - phases

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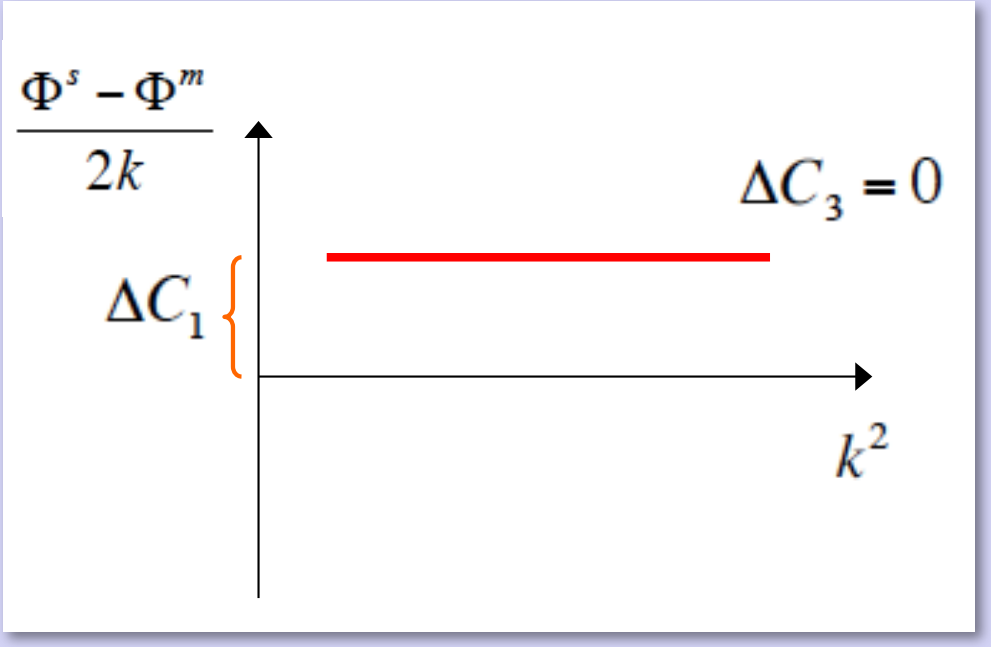
Univ. Trento

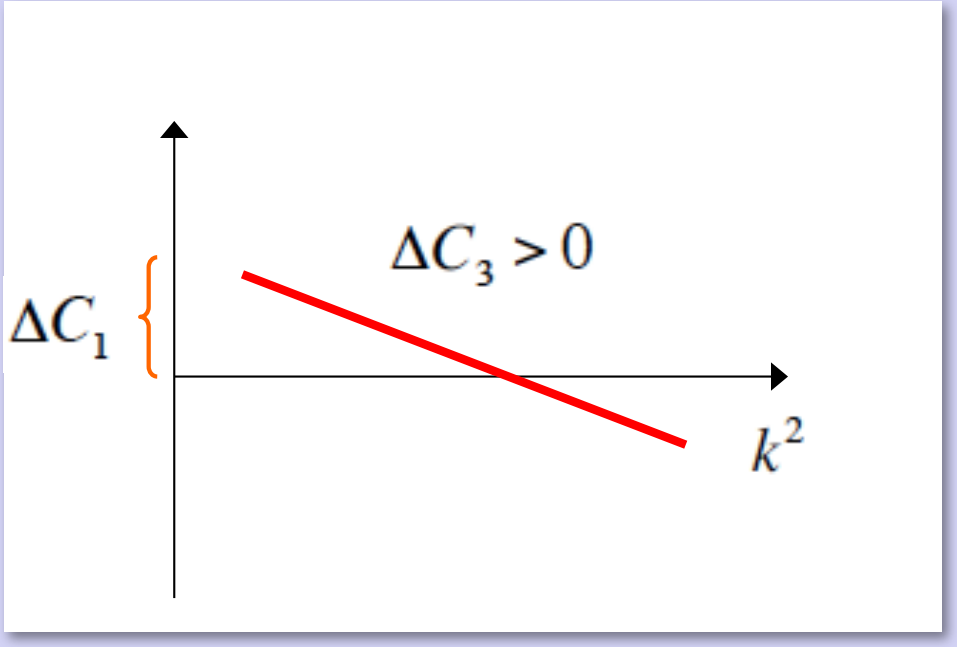
If suitable model compound available ...

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 – 2 cumulant

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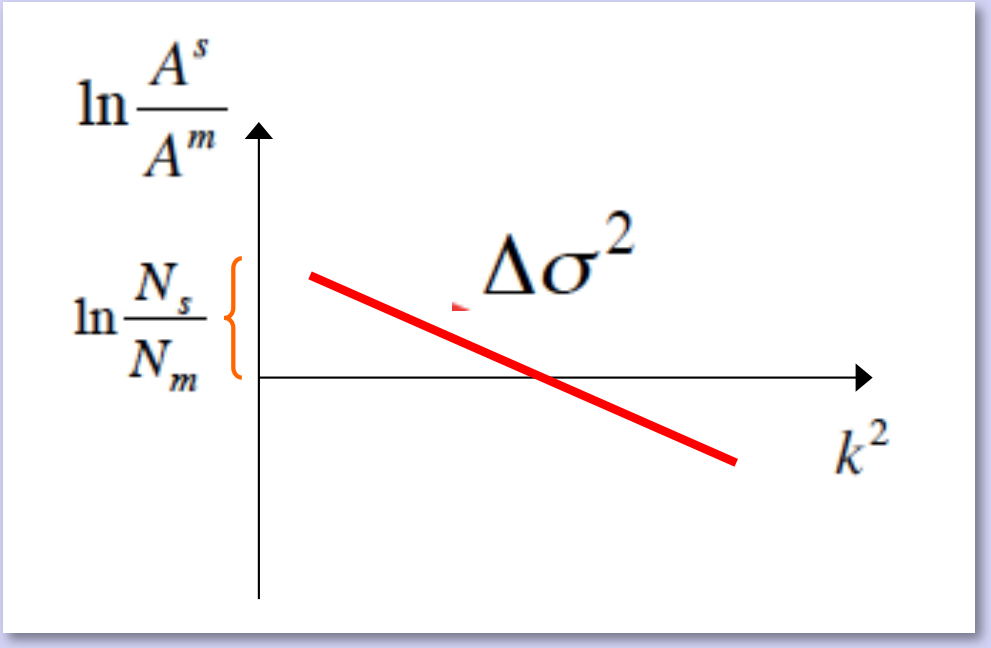
If suitable model compound available ...

s = sample
m = model

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



“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 difference

Asymmetry difference

“Ratio method” - OK when ...

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

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

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

- 1st shell, different sample-model 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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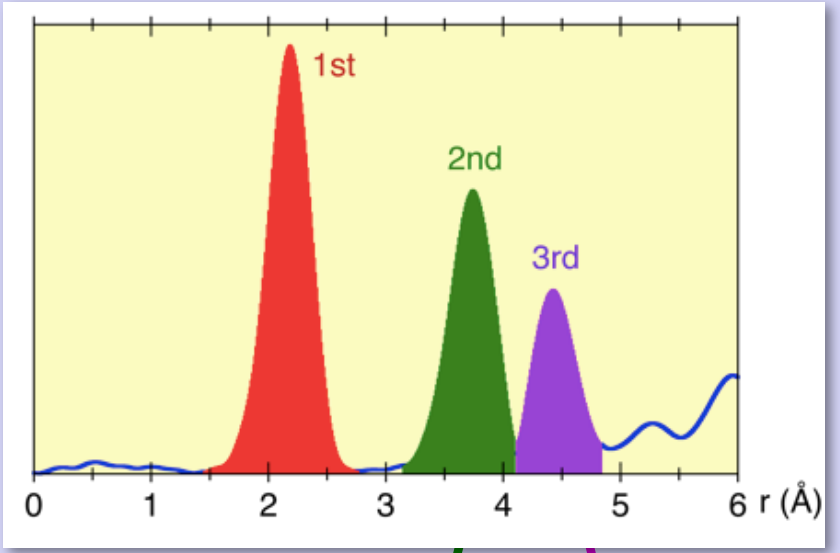

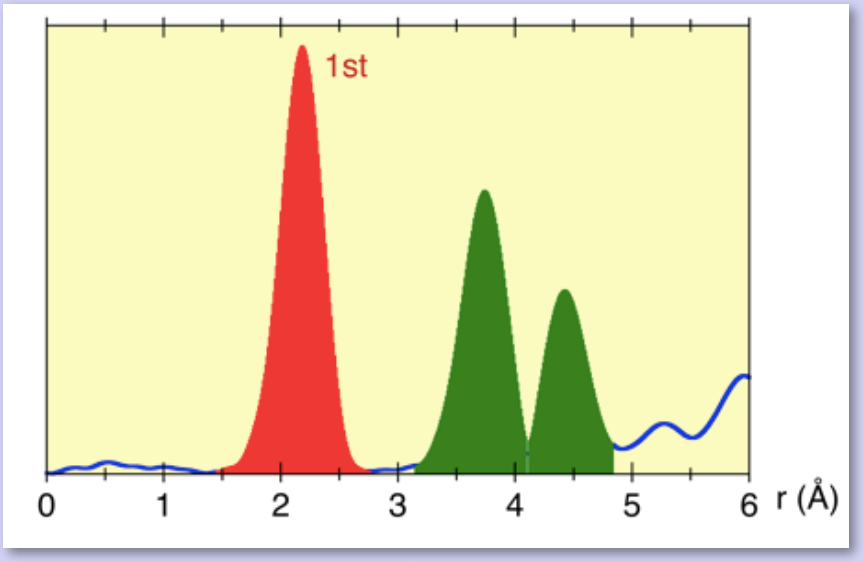

$$\chi'(k) = (2/\pi)\int_{r_{min}}^{r_{max}} F(r)\, W'(r)\, e^{-2ikr}\, dr$$

2nd shell

3rd shell

Joint analysis

- Peak superposition
- Multiple Scattering
- (F.T. artefacts)

- No superposition problems
- Including M.S.
- (F.T. artefacts)

Analysis - non-linear fitting of outer shells

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Input from theory

SS & MS path sorting

$$\left|f_{\text{path}}(k,\pi)\right|, \quad \phi_{\text{path}}(k), \quad \lambda$$

Calculated EXAFS

Experimental EXAFS

Non-linear fit
- k-space
- r-space

$$e_0, \quad C_1, \quad C_3 \qquad S_0^2 N, \quad \sigma^2$$

Parameters to be fitted

For every path !!

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

Analysis – Maximum available information

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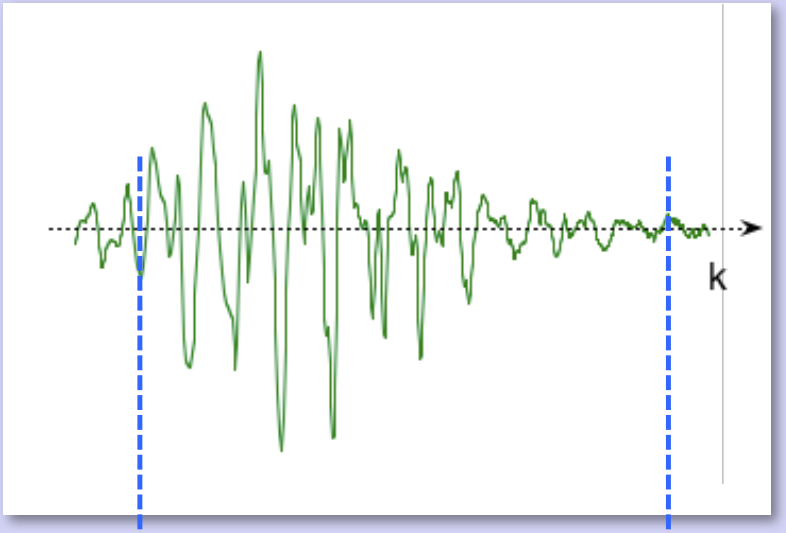

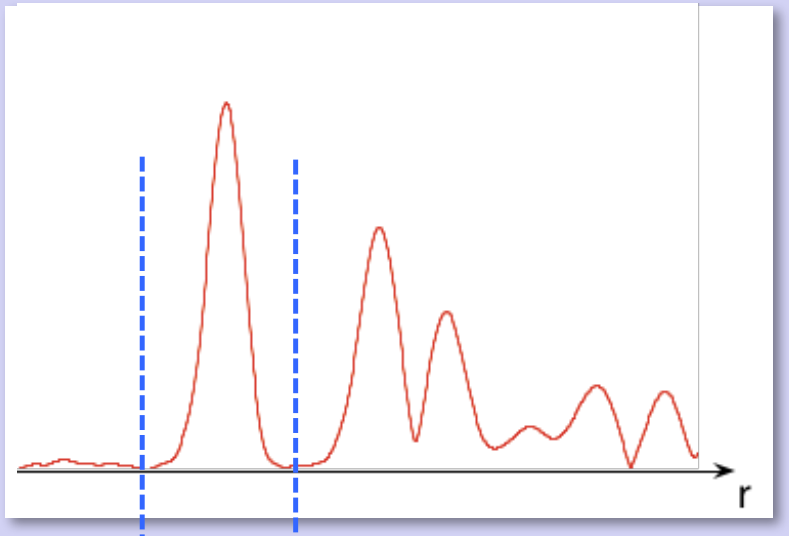

Δk

Δr

Maximum number
of independent
quantities
from an EXAFS spectrum

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

- Signal quality
- Correlation effects

Analysis – Accuracy evaluation

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$$\langle r \rangle = 2.85\,\text{Å}$$
$$N = 12$$
$$\sigma^2 = 5.34 \times 10^{-3}\,\text{Å}^2$$

$$\langle r \rangle = (2.85 \pm 0.02)\,\text{Å}$$
$$N = 12 \pm 3$$
$$\sigma^2 = (5.34 \pm 0.2) \times 10^{-3}\,\text{Å}^2$$

$$X = X_0 \pm \delta X$$

Uncertainty

- Random experimental fluctuations
- Estimate of systematic errors
- Statistical uncertainties of data analysis

Repeat measurements !!

Quantitative uncertainty from experiment

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Repeated measurements	• Same run, different data files • Different beamlines, different times • ... • Different edges (signal contamination ?)	Indep. data Gaussian distr.?
Quality of data	Ratio method, highly sensitive	
Data analysis	• Background subtraction • FT windows • Fitting intervals •	Non-indep. data Uniform distr.?
Definition of phys. quantities	• Average .vs. crystallographic distance • Debye temperature •	
Systematic errors	??	

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EXAFS data analysis

- Examples and interpretation of results

(comparison EXAFS-XRD)

Diffraction .vs. EXAFS

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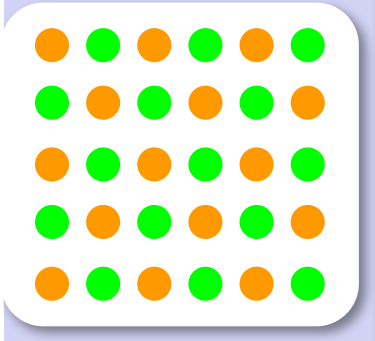
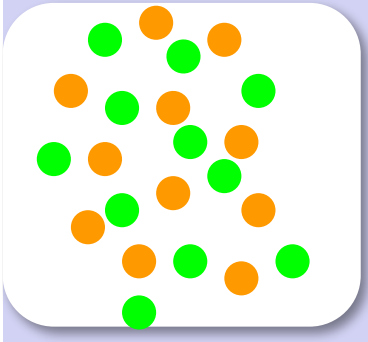
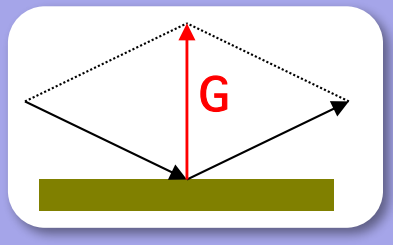
Crystals

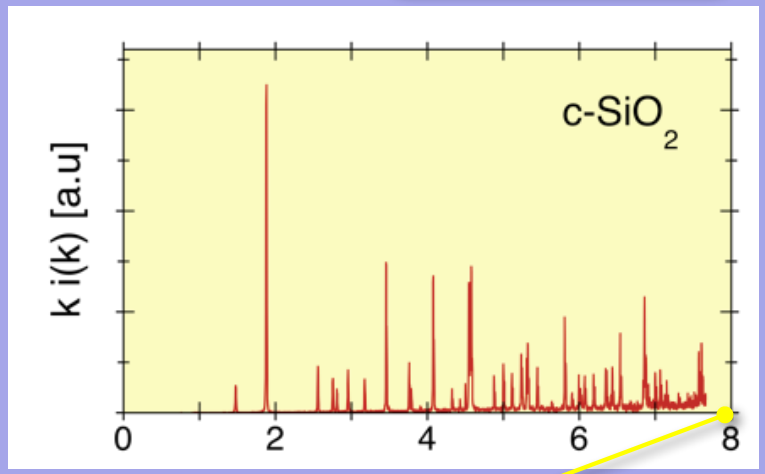


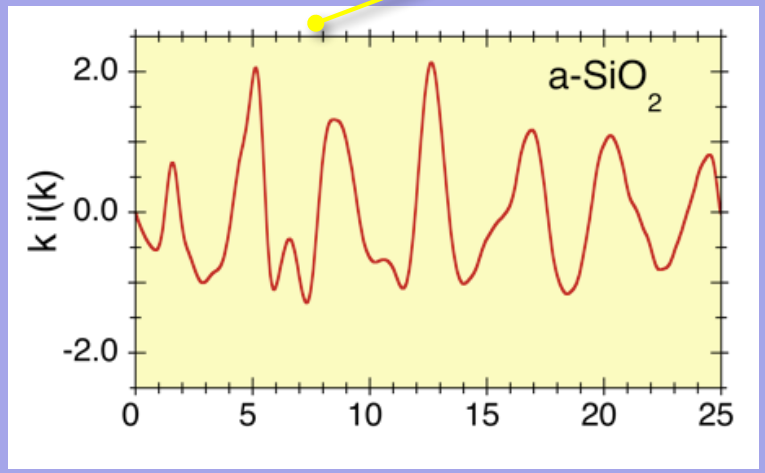
Non-cryst.



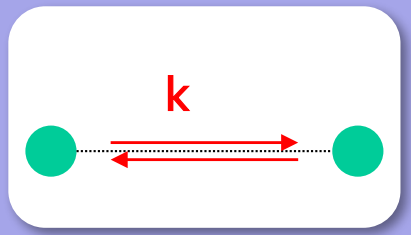
Diffraction

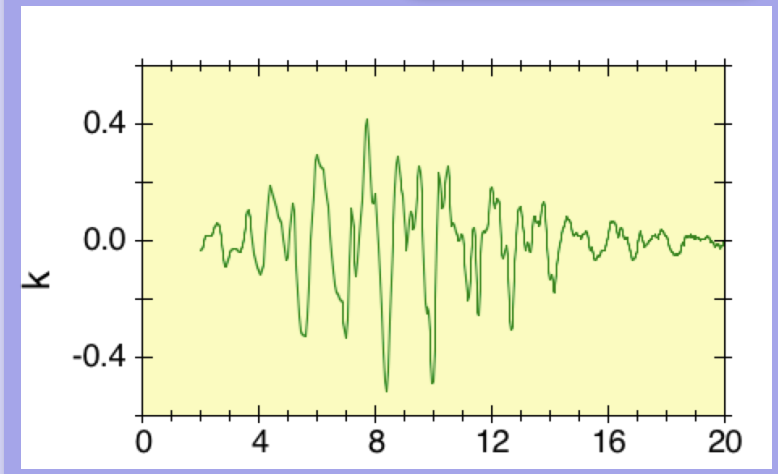


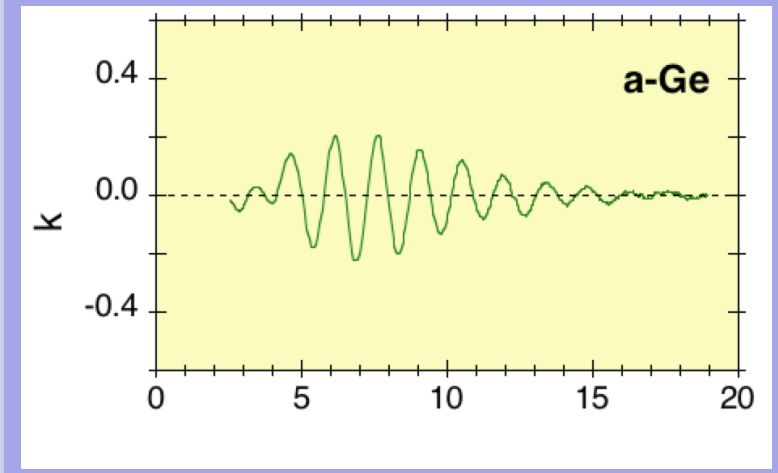




EXAFS







Random solid solutions (a)

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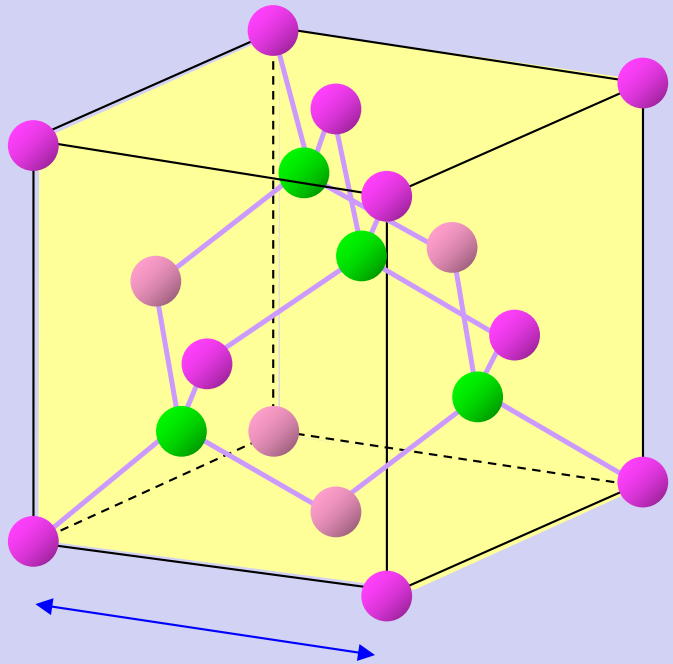

III	IV	V
B	C	N
Al	Si	P
Ga	Ge	As
In	Sn	Sb

Direct-gap ternary alloys

GaN
InN → $Ga_{1-x}In_xN$

GaAs
InAs → $Ga_{1-x}In_xAs$

		GaAs	$In_xGa_{1-x}As$	InAs
Lattice parameter (XRD)	a (Å)	5.653	→	6.055
N-N distance (EXAFS)	r (Å)	2.448	→	2.622
Energy gap	E_g (eV)	1.43	→	0.36

Random solid solutions (b)

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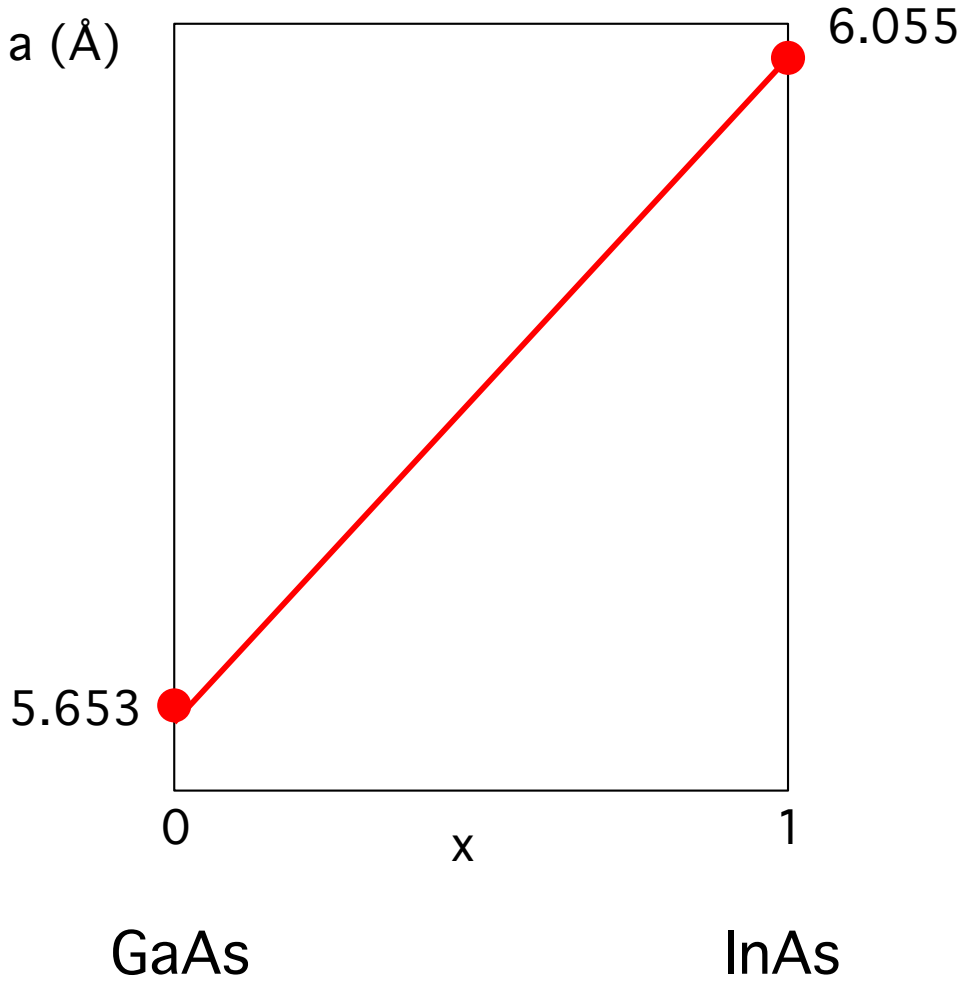
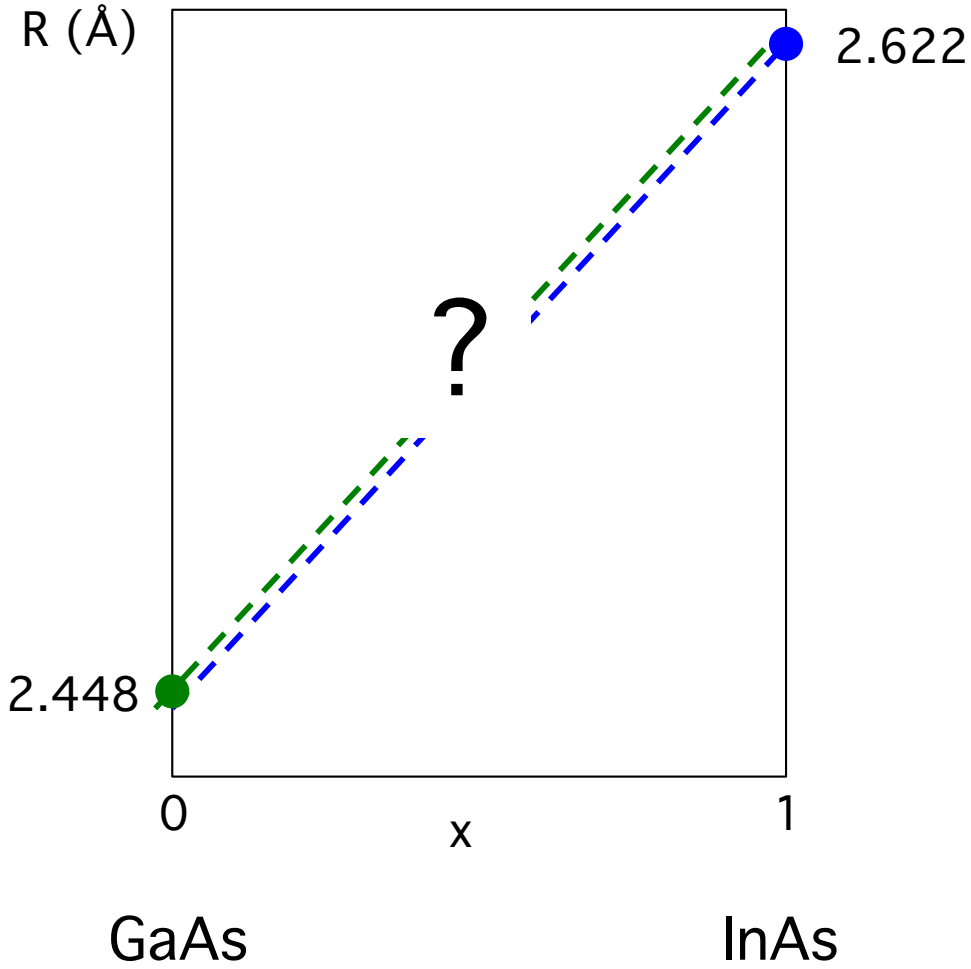
Lattice parameter (from XRD)
Vegard's law



N-N distance
Virtual crystal approximation



Random solid solutions (c)

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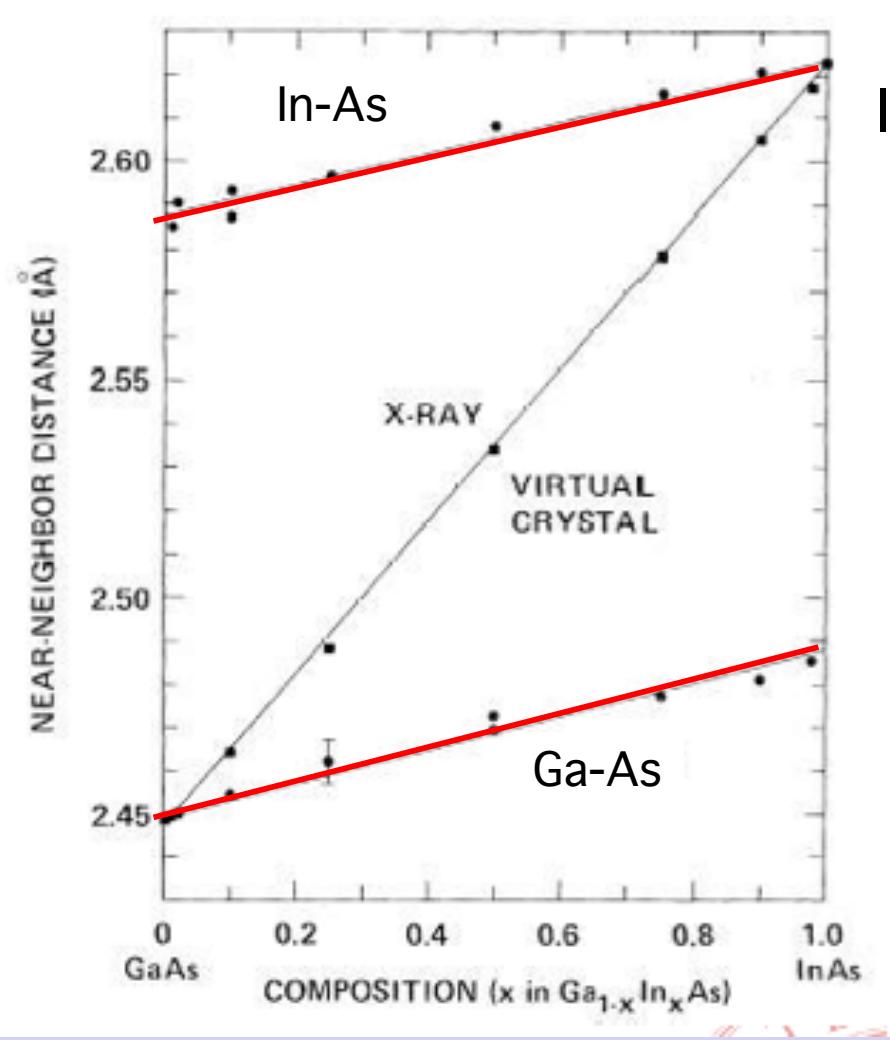
EXAFS: selectivity of atomic species



In K edge, 4 As NN

EXAFS results
for Nearest-Neighbours

Ga K edge, 4 As NN

Distortion
of the virtual crystal

Mikkelsen & Boyce, 1983

Effects of thermal vibrations in crystals

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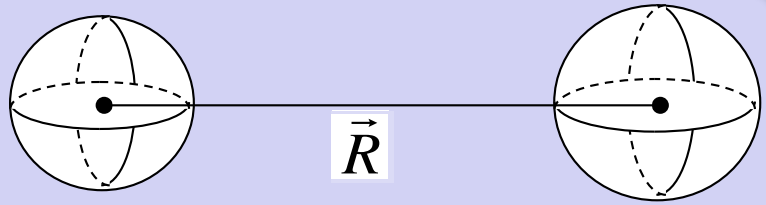
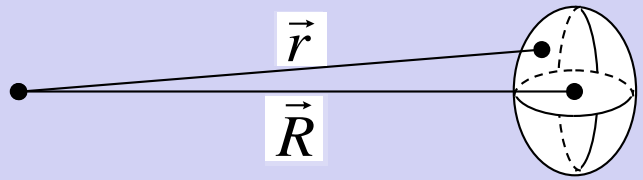
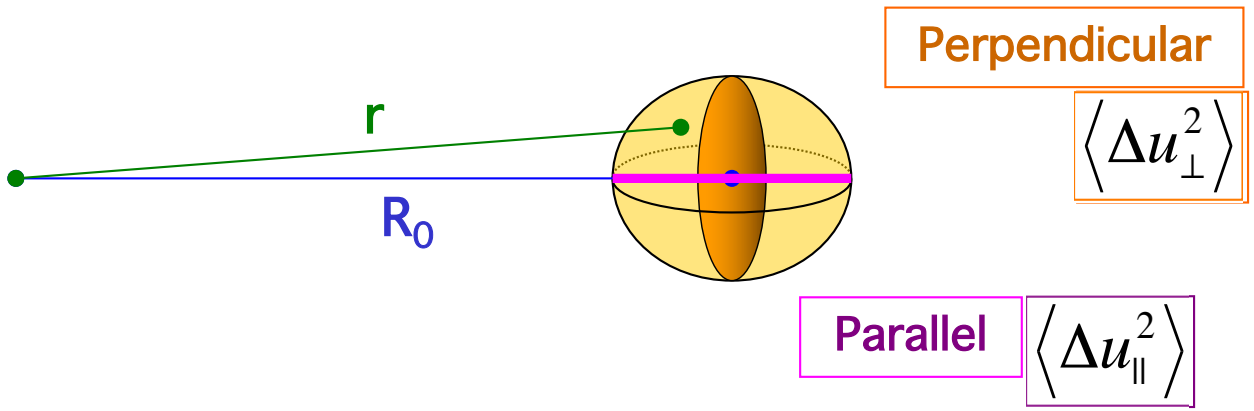
XRD ➔ atomic thermal ellipsoids



EXAFS ➔ relative thermal ellipsoids



Relative vibrations: MSRDs



EXAFS $\sigma^2 = \langle \Delta u_\parallel^2 \rangle$

EXAFS (& diffraction) $\langle \Delta u_\perp^2 \rangle$

Bond distances in crystals

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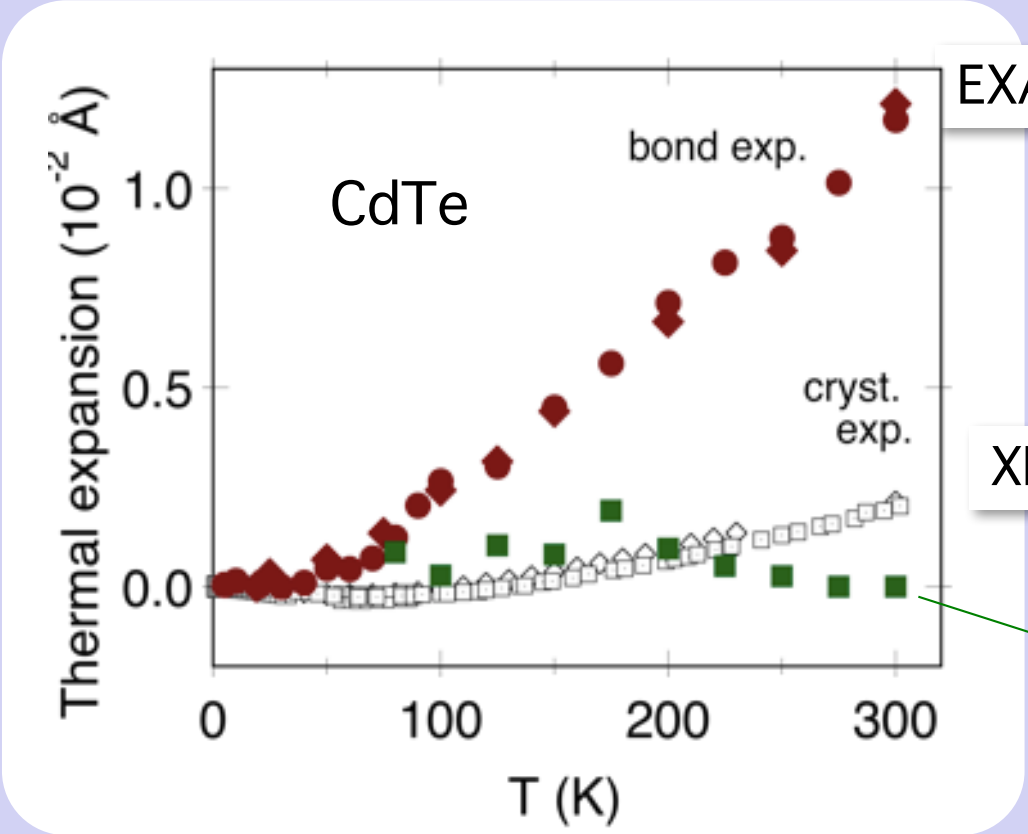

EXAFS

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

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

XRD

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

EXAFS
neglecting 3rd cumulant

Difference (Å)

T(K)	Cu	Ge	CdTe
5	1.3×10^{-3}	1.5×10^{-3}	1×10^{-3}
300	4×10^{-3}	8×10^{-3}	11×10^{-3}

EXAFS Debye-Waller factor

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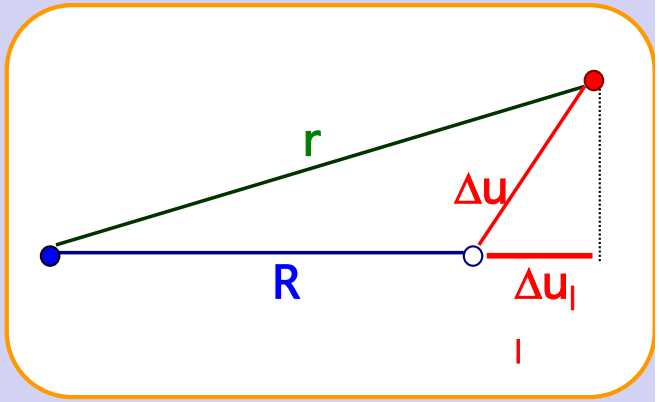
$$\sigma^2 \approx MSRD = \left\langle \Delta u_{\parallel}^2 \right\rangle = \left\langle \left[\hat{R} \cdot \left(\vec{u}_b - \vec{u}_a \right) \right]^2 \right\rangle$$

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



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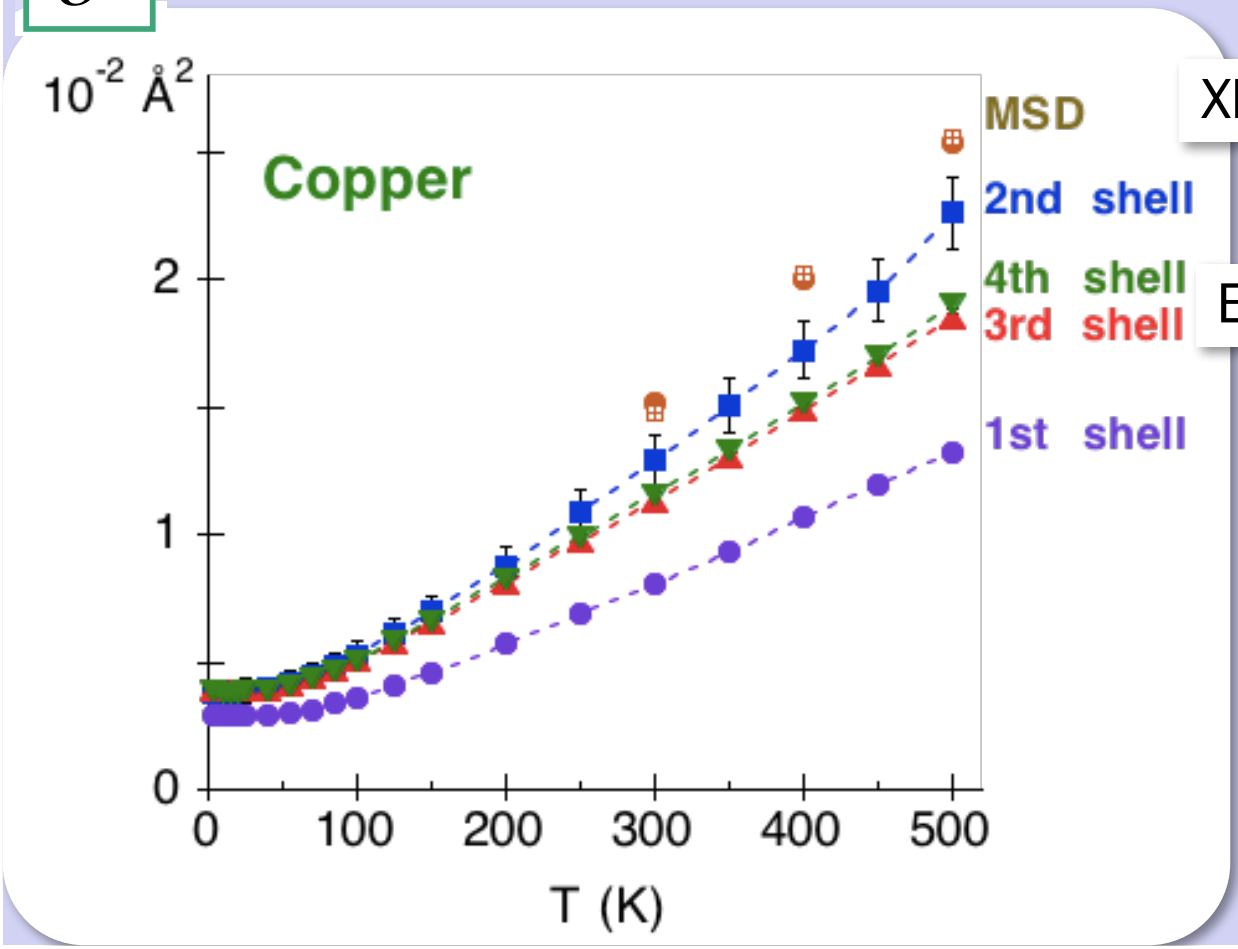
$$\sigma^2 = \frac{3\hbar}{2\omega_D^3\mu}\int_0^{\omega_D}\omega\coth\frac{\hbar\omega}{2k_BT}\left[1-\frac{\sin(\omega q_D R)}{\omega q_D R}\right]d\omega$$

σ^2



XRD

EXAFS

Debye temperature

$$\theta_D = \frac{\hbar\omega}{k_B}$$

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

Debye-Waller factor – Einstein model

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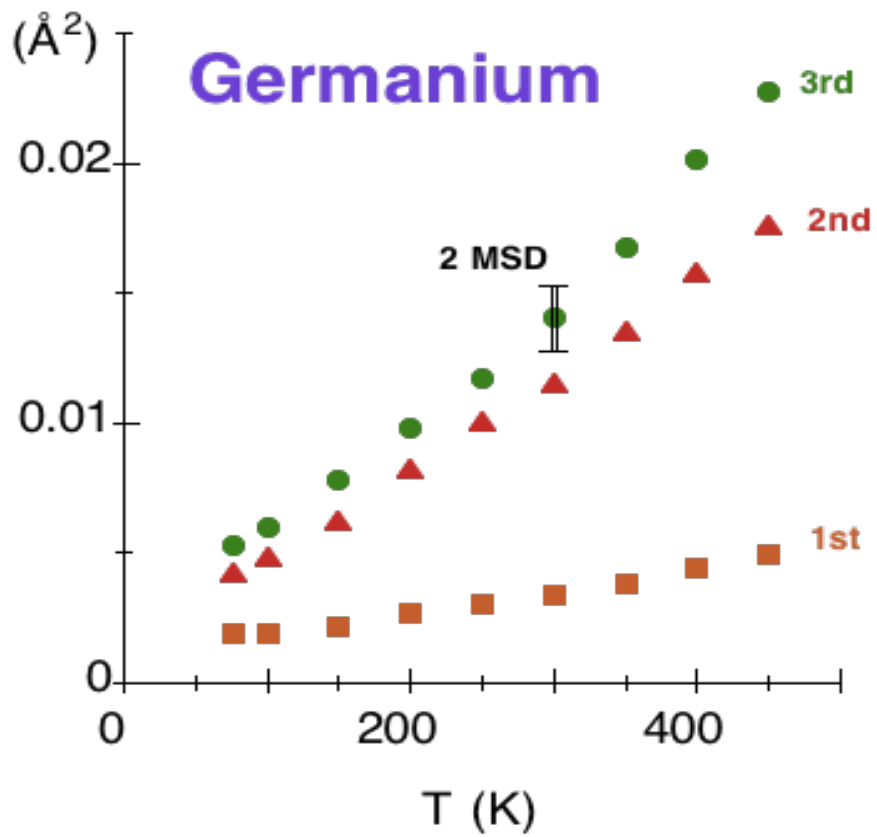
$$\sigma^2 = \frac{\hbar}{2\mu\omega_E}\coth\left(\frac{\hbar\omega_E}{2kT}\right)$$

σ^2



Non-Bravais crystal

Debye temperatures	Einstein frequency	Einstein force const.
θ_D = 354 K	$\nu = \omega/2\pi$ (THz)	$k = \mu\omega^2$ (eV/Å²)
θ_M = 290 K		
θ_3 = 290 K	ν_3 = 3.95	k_3 = 2.18
θ_2 = 299 K	ν_2 = 4.21	k_2 = 2.48
θ_1 = 460 K	ν_1 = 7.55	k_1 = 8.15

The end

Basic bibliography

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