Methoden moderner Röntgenphysik I: Struktur und Dynamik kondensierter Materie

Vorlesung zum Haupt/Masterstudiengang Physik

WS 2008/9

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Location: SemRm 4, Physik, Jungiusstrasse

Thursdays 10.15 – 11.45

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Hard X-Rays - Small Angle and Anomalous Scattering

Lecture 4

23.10.	Introduction	(GG)
30.10.	Sources of X-rays, Refraction and Reflexion	(GG)
6.11.	Kinematical Scattering Theory	(GG)
13.11.	Small Angle and Anomalous Scattering	(GG)
20.11. - 11.12.	Modern Crystallography	(AM)
18.12. - 15. 1.	Coherence base techniques	(CG)
22. 1. - 5. 2.	Soft Matter Applications	(SR)

Coherence of light and matter I: from basic concepts to modern applications

Introduction into X-ray physics: 23.10.-13.11.

Introduction

Overview, Introduction to X-ray Scattering (Scattering from atoms, crystals,.., absorption, reflection,coherence,..)

Sources, Reflection and Refraction

Sources of X-rays, Refraction, reflection, Snell's law, Fresnel equations

Kinematical Diffraction

Diffraction from an atom, molecule, crystal, reciprocal lattice, structure factor,..

SAXS, Anomalous Diffraction

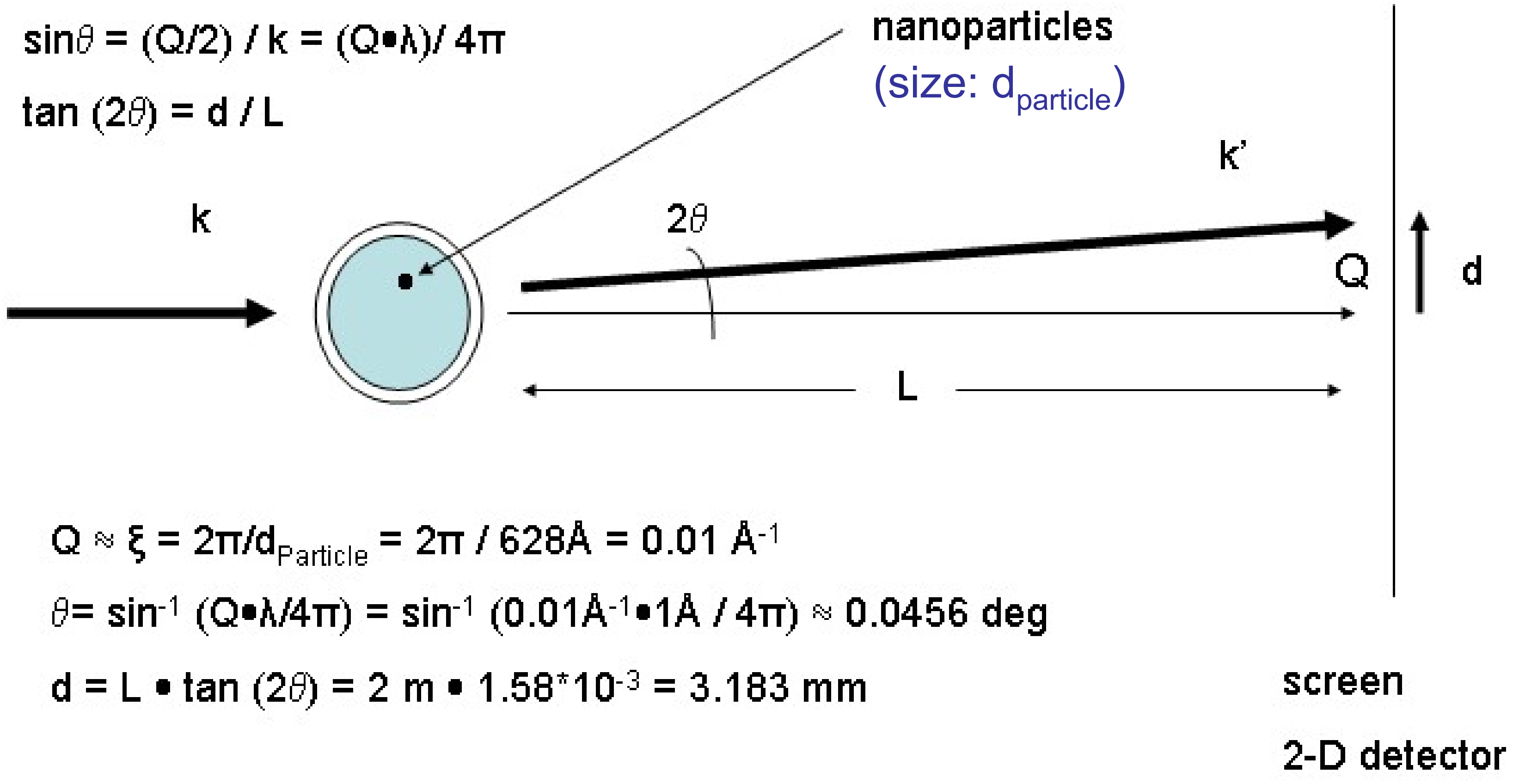
Introduction into small angle scattering and anomalous scattering

Small Angle X-ray Sacttering (SAXS)

Consider objects (nano-structures) of sub-µm size

$\sin\theta = (Q/2) / k = (Q \bullet \lambda)/ 4\pi$

$\tan(2\theta) = d / L$



$Q \approx \xi = 2\pi/d_{Particle} = 2\pi / 628Å = 0.01\ Å^{-1}$

$\theta = \sin^{-1}(Q \bullet \lambda/4\pi) = \sin^{-1}(0.01Å^{-1} \bullet 1Å / 4\pi) \approx 0.0456\ \mathrm{deg}$

$d = L \bullet \tan(2\theta) = 2\ \mathrm{m} \bullet 1.58{*}10^{-3} = 3.183\ \mathrm{mm}$

Small Angle X-ray Scattering

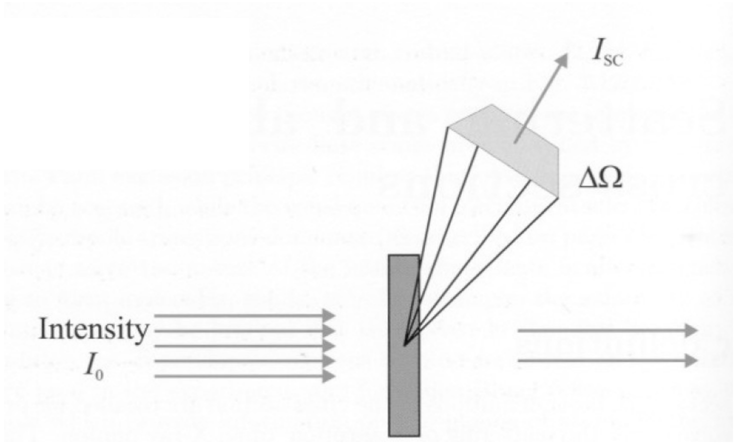
$I_{scattered} = Io\, N\, \Delta\Omega\, (d\sigma/d\Omega)$

Io: incident intensity

N: number objects

$\Delta\Omega$: solid angle

$(d\sigma/d\Omega)$: differential cross section



$(d\sigma/d\Omega)/V = r_o^2\, n\, (\rho_p-\rho_s)^2\, v^2\, F(Q)\, S(Q)$

n: volume fraction
ρ: electron density
v: particle volume

F(Q) formfactor

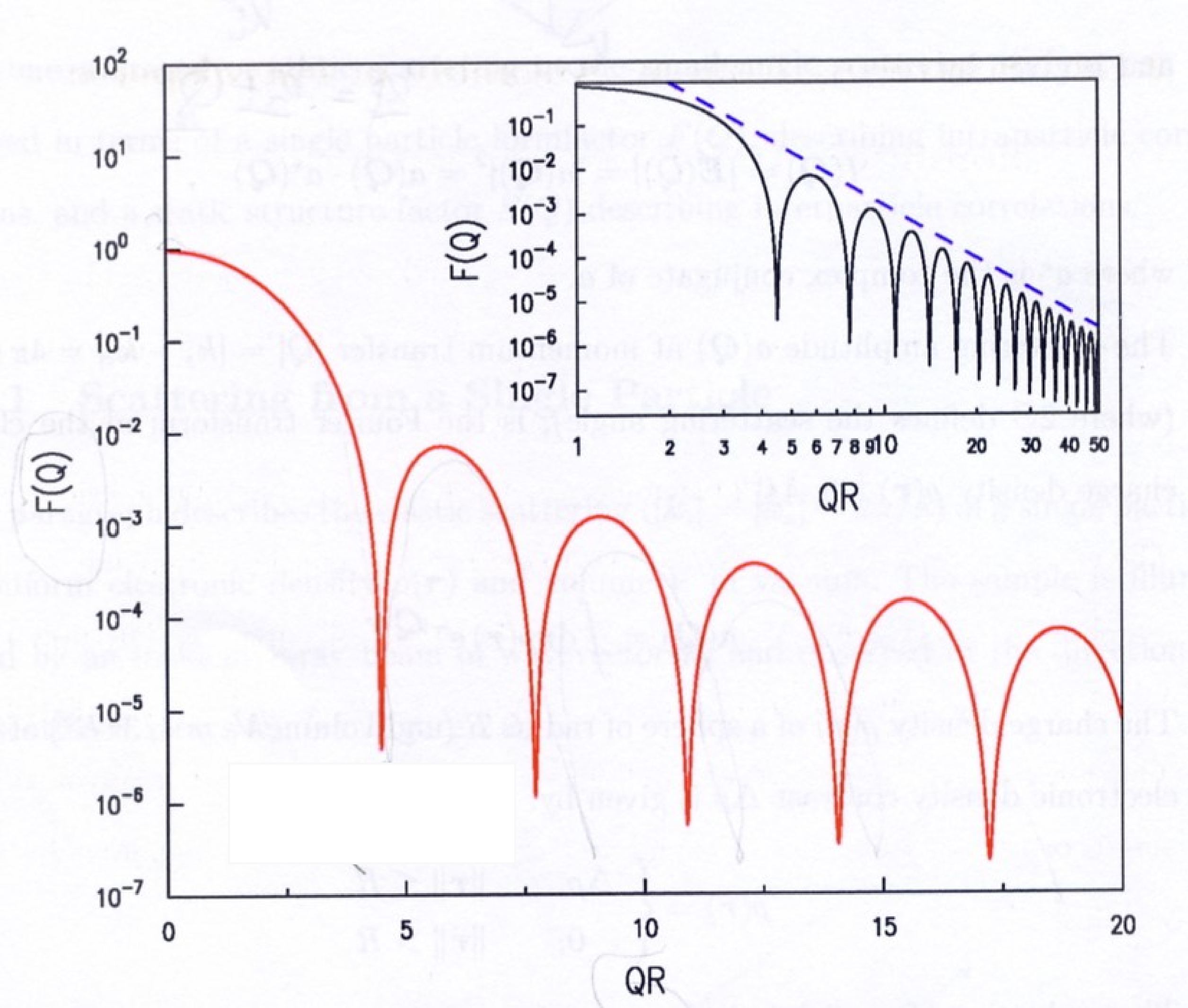
$F(Q) = \int d^3r \exp(i\mathbf{qr})\, \rho(\mathbf{r})$

for homogeneous spheres of radius R:

$F(Q) = [3/(QR)^3]^2\, [\sin(QR) - (Qr)\cos(QR)]^2$

sphere form factor

Formfactor (spheres)



Structure Factor

S(Q): structure factor

$$S(Q) = 1/nN \left\langle \sum_{i,j}^{N} \exp(i\mathbf{Q}(R_i-R_j)) \right\rangle$$

$$= \int d^3r \exp(iQr) \cdot g(r)$$

$$g(r) = 1/n \left\langle 1/N \sum_{i,j}^{N} \delta(\mathbf{r} - [\mathbf{R}_i-\mathbf{R}_j]) \right\rangle$$

pair distribution function

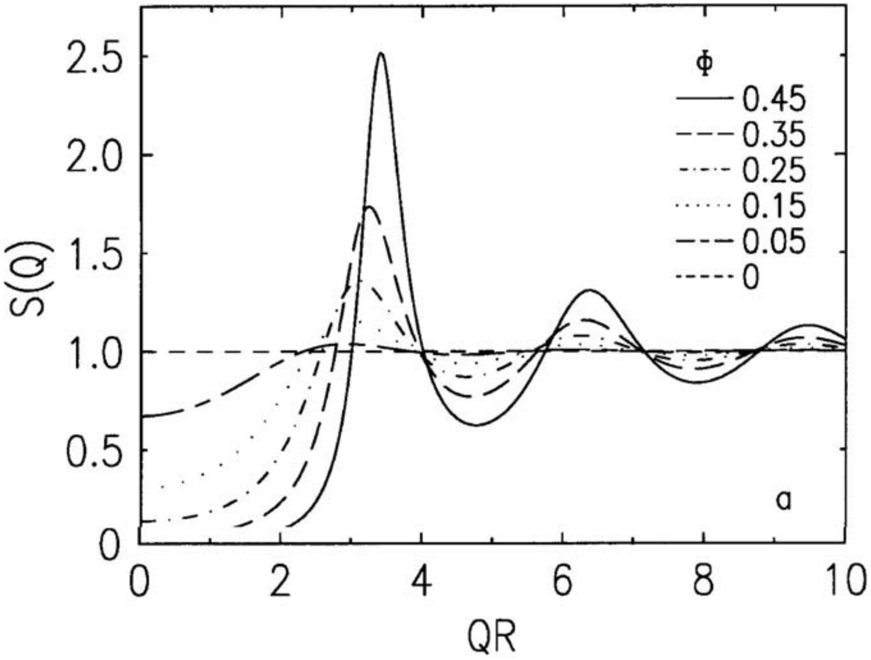
$$= 1+4\pi n \int [g(r)-1] \sin(QR)/QR \, r^2 dr$$

$$g(r) = [V(r)/kT]$$

Hard sphere structure factor:

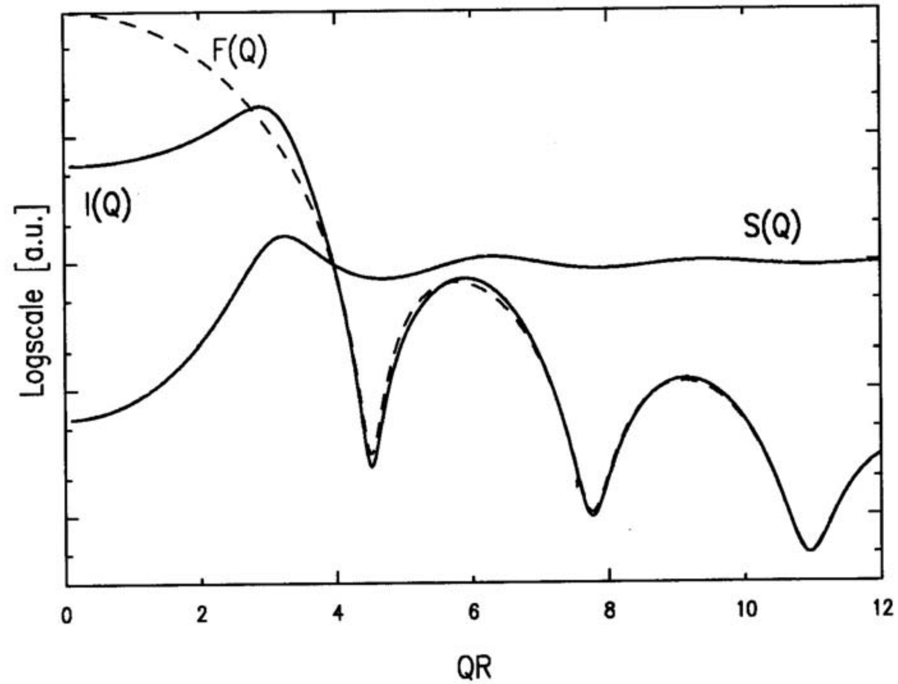
$V(r) = 0$ for $r \geq d$

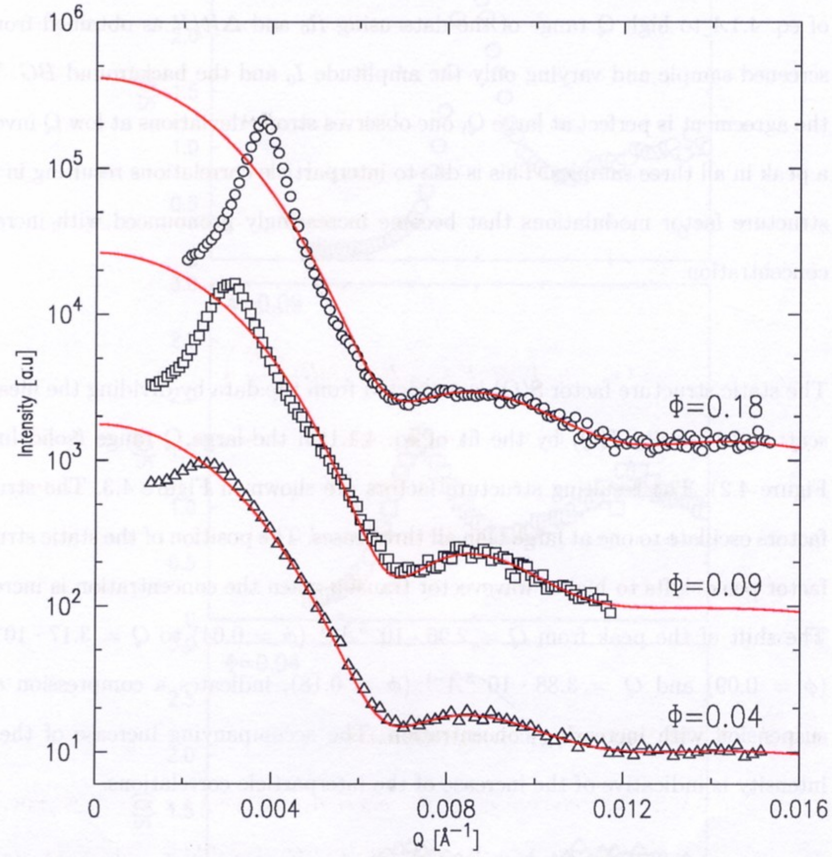
$V(r) = \infty$ for $r<d$



SAXS experiment

- measure I(Q)
- modell F(Q)
- for spherical particles I(Q)=F(Q)•S(Q)
- get and modell S(Q)





Small Angle X-ray Scattering

Anomalous Small Angle Scattering (ASAXS)

Grazing Incidence Small Angle Scattering (GISAXS)

Resonant Scattering (phasing, magnetism,..)

Scattering length of an atom: $- r_0 f^0(\mathbf{Q})$

$f^0(\mathbf{Q})$ atomic form factor (fourier transform of charge distribution)

r_0 thomson scattering length of single electron

in order to include absorption effects (f '') atoms a more elaborate model than the free electron gas is needed.

→ Electrons are bound to atoms

→ Forced oscillator modell with resonant frequency ω_s and damping constant Γ

<u>include dispersion corrections (f', f''):</u>

[note: $f'' = (k/4\pi r_0)\, \sigma_a$]

$$f(\mathbf{Q}, \omega) = f^0(\mathbf{Q}) + f'(\omega) + i\, f''(\omega)$$

[in units of r_0]

Resonant Scattering

classical model of
an electron bound
in an atom in E field

$$\mathbf{E}(\mathbf{r},t) = \hat{x}\, E_o \exp\{-i\omega t\} \longrightarrow$$

equation of motion
of the electron

$$\boxed{\ddot{x} + \Gamma \dot{x} + \omega_S^2 x = -\left(\frac{e E_0}{m}\right) \exp\{-i\omega t\}}$$

Γ = damping

ω_S resonant frequency

<u>Solution:</u> $x(t) = x_0 \exp\{-i\omega t\} \longrightarrow$

$$x_0 = -\left(\frac{e E_0}{m}\right) \frac{1}{(\omega_S^2 - \omega^2 - i\omega\Gamma)} \qquad \text{(A)}$$

radiated field strength at
distance R and time t

$$E_{rad}(R,t) = \left(\frac{e}{4\,\varepsilon_0 R c^2}\right) \ddot{x}\,(t - R/c) \qquad \text{(B)}$$

↑

acceleration at “earlier” time (t-R/c)

Resonant scattering

inserting $\ddot{x}(t - R/c) = \omega^2 x_0 \exp\{-i\omega t\} \exp\{i(\omega/c)R\}$ using (A) into (B):

$$E_{rad}(R,t) = \frac{\omega^2}{(\omega_S^2 - \omega^2 - i\omega\Gamma)} \left(\frac{e^2}{4\,\varepsilon_0\, m\, c^2}\right) E_0 \exp\{-i\omega t\} \left(\frac{\exp\{ikR\}}{R}\right)$$

or

$$\boxed{\frac{E_{rad}(R,t)}{E_{in}} = -\, r_0 \underbrace{\frac{\omega^2}{(\omega_S^2 - \omega^2 + i\omega\Gamma)}} \left(\frac{\exp\{ikR\}}{R}\right)}$$

atomic scattering length f_s (in units of $-r_0$) for bound electron (C)

note: $f_s \rightarrow 1$ ($\omega \gg \omega_s$)

<u>total cross-section:</u> $\sigma_T = (8\pi/3)\, r_o^2$ (free electron)

$$\boxed{\sigma_T = \left(\frac{8\pi}{3}\right) \frac{\omega^4}{(\omega^2 - \omega_S^2)^2 + (\omega\Gamma)^2}\, r_0^2}$$

<u>for $\Gamma = 0$ and $\omega \ll \omega_s$:</u> $\sigma_T = (8\pi/3) r_o^2 (\omega / \omega_S)^4$: "Rayleigh Scattering"

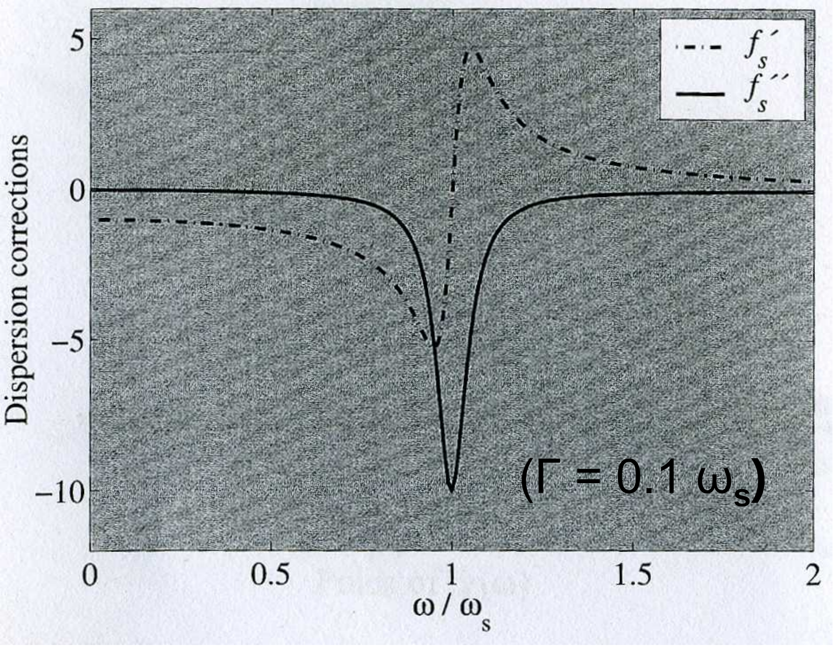
Resonant scattering

$$f_s = \frac{\omega^2 - \omega_s^2 + i\omega\Gamma + \omega_s^2 - i\omega\Gamma}{(\omega^2 - \omega_s^2 + i\omega\Gamma)}$$

$$= 1 + \frac{\omega_s^2 - i\omega\Gamma}{(\omega^2 - \omega_s^2 + i\omega\Gamma)}$$

$$\approx 1 + \underbrace{\frac{\omega_s^2}{(\omega^2 - \omega_s^2 + i\omega\Gamma)}}_{\text{dispersion correction } \chi(\omega)}$$

$$\chi(\omega) = f'_s + i f''_s = \frac{\omega_s^2}{(\omega^2 - \omega_s^2 + i\omega\Gamma)}$$



$(\Gamma = 0.1\ \omega_s)$

with:

$$f'_s = \frac{\omega_s^2(\omega^2 - \omega_s^2)}{(\omega^2 - \omega_s^2)^2 + (\omega\Gamma)^2}$$

$$f''_s = \frac{\omega_s^2\,\omega\,\Gamma}{(\omega^2 - \omega_s^2)^2 + (\omega\Gamma)^2}$$

Resonant scattering

Note: since f ’’ = -(k/4π) σ_a (E) (see J. A-N. & D. McM. p. 70) it follows that the absorption cross-section for a single oscillator model is:

$$\sigma_{a,s}(\omega) = 4\pi r_0 c \frac{\omega_s^2 \Gamma}{(\omega^2 - \omega_s^2)^2 + (\omega\Gamma)^2}$$

this function has:

- sharp peak at $\omega = \omega_s$
- $\Delta\omega_{FWHM} \approx \Gamma$

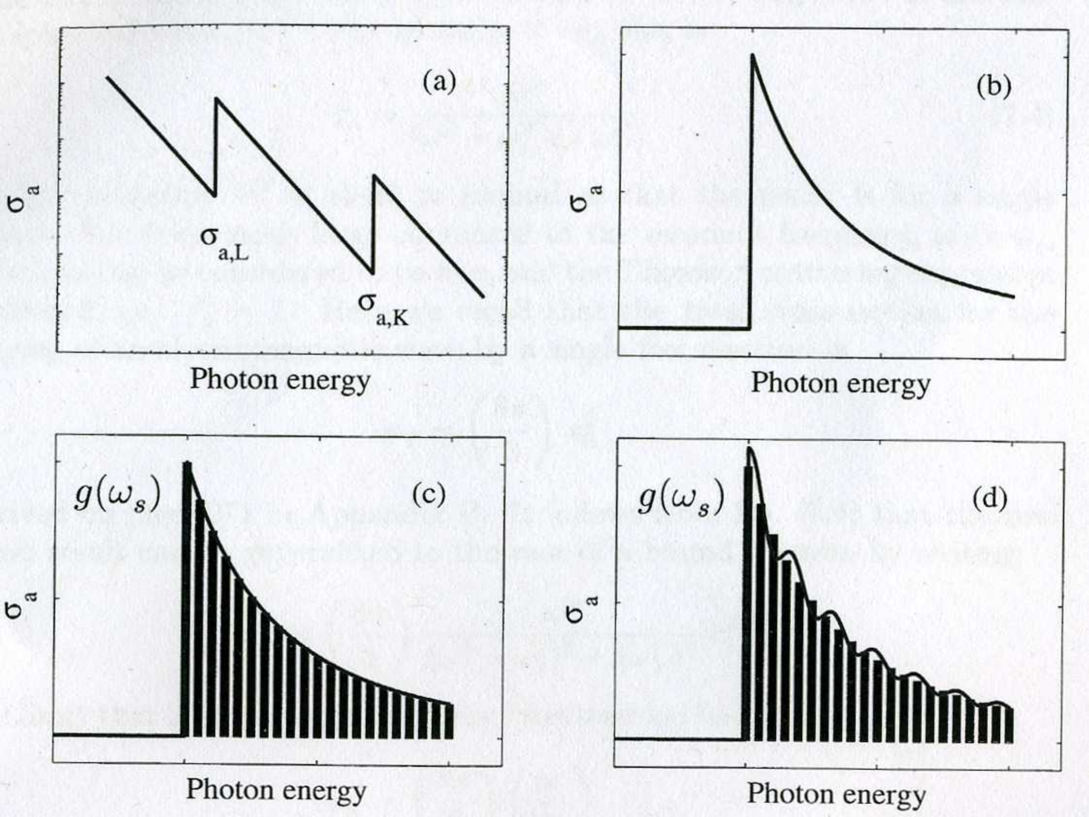
thus σ_a (E) may be written with help of a delta function:

$$\sigma_{a,s}(\omega) = 4\pi r_0 c \frac{\pi}{2} \delta(\omega - \omega_s) \qquad \text{(D)}$$

Resonant scattering

The experimentally observed absorption cross-section is NOT a single line spectrum as suggested by (D).

There is a continuum of free states above an absorption edge that the electron can be excited into. This implies a series of different ω_s:



Resonant scattering

Absorption cross section for multiple harmonic oscillators:

$$\sigma_a(\omega) = 2\pi^2 r_0 c \sum_s g(\omega_s)\, \delta(\omega - \omega_s)$$

where $g(\omega_s)$ is the relative weight of each transition

The real part of the dispersion becomes:

$$f'(\omega) = \sum_s g(\omega_s)\, f'_s(\omega,\omega_s) \qquad \text{(F)}$$

(F) does not describe e.g. “white lines” or “EXAFS” oscillations (see figure) in the absorption cross section arising from the particular environement of the resonantly scattering atom.

Resonant scattering

measure absorption cross-section and use (E) to obtain f ”:

$$f''(\omega) = -\left(\frac{\omega}{4\pi r_0 c}\right)\sigma_a(\omega)$$

use Kramers-Kronig relations to obtain f ’:

$$f'(\omega) = \frac{1}{\pi} P \int_{-\infty}^{+\infty} \frac{f''(\omega')}{(\omega' - \omega)}\, d\omega' = \frac{2}{\pi} P \int_{0}^{+\infty} \frac{\omega' f''(\omega')}{(\omega'^2 - \omega^2)}\, d\omega'$$

$$f''(\omega) = -\frac{1}{\pi} P \int_{-\infty}^{+\infty} \frac{f'(\omega')}{(\omega' - \omega)}\, d\omega' = -\frac{2\omega}{\pi} P \int_{0}^{+\infty} \frac{f'(\omega')}{(\omega'^2 - \omega^2)}\, d\omega'$$

P stands for “principal value” (see also comments J. A-N & D. McM p. 242)

Resonant scattering

Friedel’s law and Bijvoet pairs

The phase problem in crystallography

The MAD method

(Resonant) Magnetic Scattering

The End