

# Methoden moderner Röntgenphysik II: Streuung und Abbildung

## Lecture 5

Vorlesung zum Haupt/Masterstudiengang Physik

SS 2013

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Location: Hörs AP, Physik, Jungiusstrasse

Tuesdays 12.45 – 14.15

Thursdays 8:30 – 10.00

# ■ Methoden moderner Röntgenphysik II: Streuung und Abbildung

## Introduction

Overview, Introduction to X-ray scattering

## X-ray Scattering Primer

Elements of X-ray scattering

## Sources of X-rays, Synchrotron Radiation

Laboratory sources, accelerator based sources

## Reflection and Refraction

Snell's law, Fresnel equations,

## Kinematical Diffraction (I)

Diffraction from an atom, molecule, liquids, glasses, ..

## Kinematical Diffraction (II)

Diffraction from a crystal, reciprocal lattice, structure factor, ..

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## Small Angle Scattering, and Soft Matter

Introduction, form factor, structure factor, applications, ..

## Anomalous Diffraction

Introduction into anomalous scattering,..

## Introduction into Coherence

Concept, First order coherence, ..

## Coherent Scattering

Spatial coherence, second order coherence,..

## Applications of coherent Scattering

Imaging and Correlation spectroscopy,..

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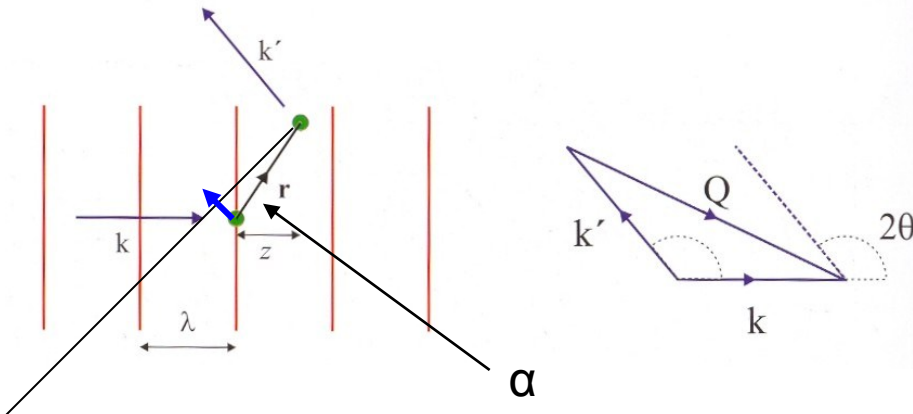
# Kinematical Diffraction

# Kinematical Diffraction

One of the main applications of X-rays is the determination of structure(s) using diffraction.

Assume the scattering to be weak; multiple scattering effects are to be neglected: weak scattering limit  $\equiv$  kinematical approximation.

Consider a 2 electron system:



$$z = r \cos \alpha; k z = k r \cos \alpha = \mathbf{k} \cdot \mathbf{r}$$

$$y = r \cos \beta; k' y = k' r \cos \beta = \mathbf{k}' \cdot \mathbf{r}$$

path- or phase difference:

$$\Delta \Phi = z - y = \mathbf{k} \cdot \mathbf{r} - \mathbf{k}' \cdot \mathbf{r} = \mathbf{Q} \cdot \mathbf{r}$$

with

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

scattering amplitude for 2 electrons:

$$A(\mathbf{Q}) = -r_0 [1 + \exp(i\mathbf{Q}\mathbf{r})]$$

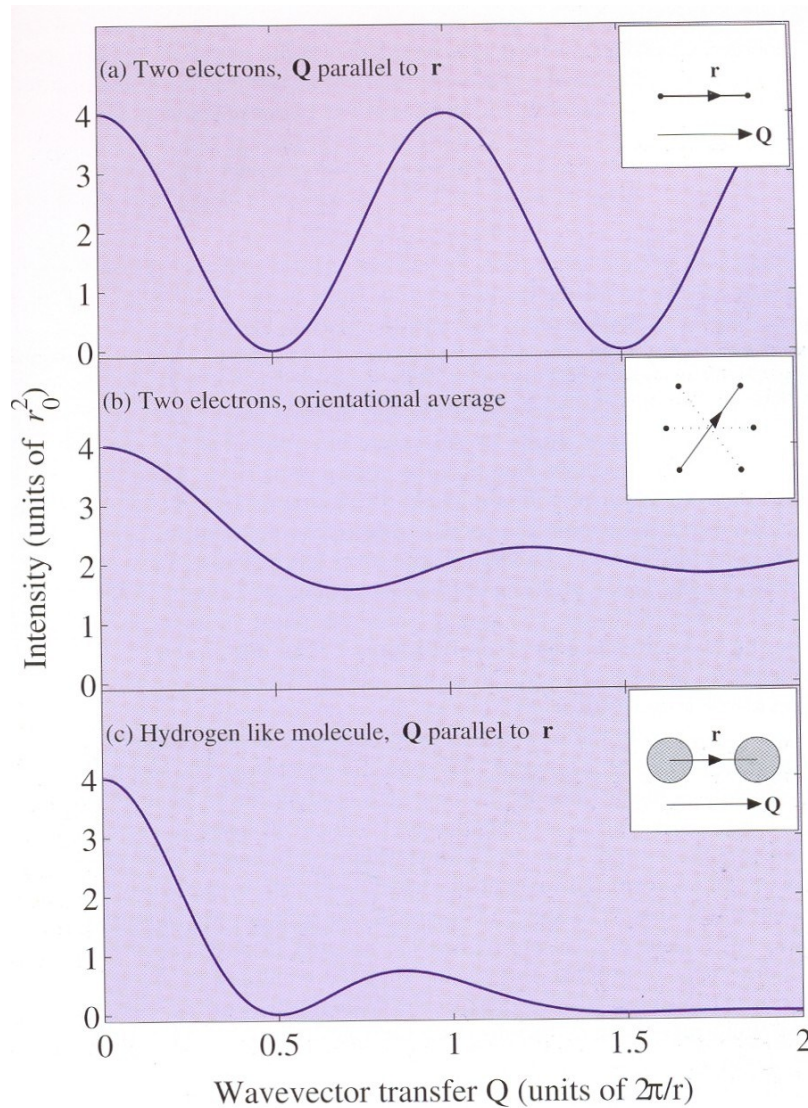
$$\begin{aligned} I(\mathbf{Q}) &= A(\mathbf{Q}) A(\mathbf{Q})^* \\ &= 2r_0^2 [1 + \cos(Qr)] \end{aligned}$$

see Fig. 4.2

for many electrons:

$$A(\mathbf{Q}) = -r_0 \sum_j \exp(i\mathbf{Q}\mathbf{r}_j)$$

# Kinematical Diffraction

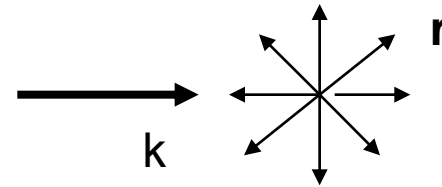


Two electron system:

$$I(Q) = 2r_0^2 [1 + \cos(Qr)]$$

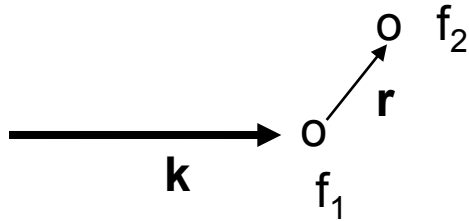
$Q \parallel r$

orientational average



“smeared”, no more “point-like” particles

for many systems, e.g. molecules the orientation of  $\mathbf{r}$  will be random wrt  $\mathbf{k}$



Orientational averaging: assume one electron at  $r=0$ , a second at  $r$

$$A(Q) = f_1 + f_2 \exp(i\mathbf{Q}\mathbf{r})$$

$$I(Q) = f_1^2 + f_2^2 + f_1 f_2 \exp(i\mathbf{Q}\mathbf{r}) + f_1 f_2 \exp(-i\mathbf{Q}\mathbf{r})$$

orientational averaging:  $\langle \exp(i\mathbf{Q}\mathbf{r}) \rangle = \langle \exp(-i\mathbf{Q}\mathbf{r}) \rangle$

$$\langle I(Q) \rangle = f_1^2 + f_2^2 + 2f_1 f_2 \langle \exp(i\mathbf{Q}\mathbf{r}) \rangle$$

$$\langle \exp(i\mathbf{Q}\mathbf{r}) \rangle = \frac{\int \exp(iQr \cos\theta) \sin\theta \, d\theta \, d\Phi}{\int \sin\theta \, d\theta \, d\Phi} \leftarrow 4\pi$$

$$\int \exp(iQr \cos\theta) \sin\theta \, d\theta \, d\Phi$$

$$= 2\pi \int \exp(iQr \cos\theta) \sin\theta \, d\theta$$

$$= 2\pi (-1/iQr) \int_{iQr}^{-iQr} \exp(x) \, dx$$

$$= 4\pi \sin(Qr)/Qr$$

$$\langle I(Q) \rangle = f_1^2 + f_2^2 + 4\pi f_1 f_2 \sin(Qr)/Qr$$

see figure 4.2 b

if the position of the electrons distributed or smeared: see Figure 4.2c

# Scattering from an atom:

scattering amplitude of an atom  $\equiv$  atomic form factor  $f_0(Q)$  [in units of  $r_0$ ]

$\rho(r)$ : electronic number density  $\equiv$  charge density

$$f_0(Q) = \int \rho(r) \exp(iQr) dr$$

$$= \begin{cases} Z & Q \rightarrow 0 \\ 0 & Q \rightarrow \infty \end{cases}$$

note: atomic form factor is FT of electronic charge distribution

$f_0(Q/4\pi)$  tabulated:

$$f_0(Q/4\pi) = \sum_{j=1}^4 a_j \exp -b_j(Q/4\pi)^2 + c$$

	$a_1$	$b_1$	$a_2$	$b_2$	$a_3$	$b_3$	$a_4$	$b_4$	$c$
C	2.3100	20.8439	1.0200	10.2075	1.5886	0.5687	0.8650	51.6512	0.2156
O	3.0485	13.2771	2.2868	5.7011	1.5463	0.3239	0.8670	32.9089	0.2508
F	3.5392	10.2825	2.6412	4.2944	1.5170	0.2615	1.0243	26.1476	0.2776
Si	6.2915	2.4386	3.0353	32.333	1.9891	0.6785	1.5410	81.6937	1.1407
Cu	13.338	3.5828	7.1676	0.2470	5.6158	11.3966	1.6735	64.820	1.5910
Ge	16.0816	2.8509	6.3747	0.2516	3.7068	11.4468	3.683	54.7625	2.1313
Mo	3.7025	0.2772	17.236	1.0958	12.8876	11.004	3.7429	61.6584	4.3875

table 4.1: J. Als-Nielsen & D. McMorrow

note:

$$f = f_0(Q) + f' + f''$$

corrections  $f'$  and  $f''$  arise from the fact that the electrons are bound in the atom

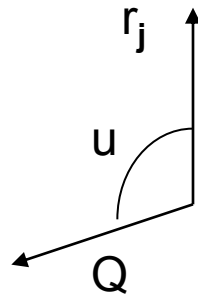
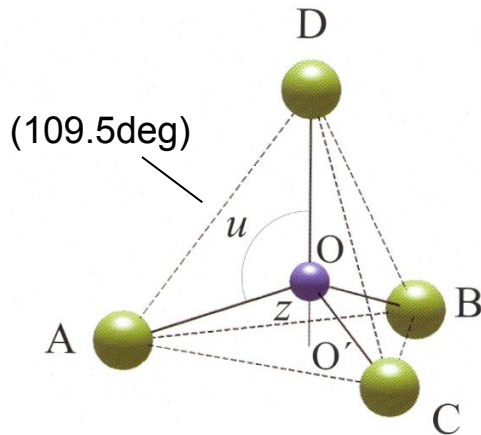


# Scattering from a molecule:

$$F^{\text{mol}}(\mathbf{Q}) = \sum_{r_j} f_j(\mathbf{Q}) \exp(i\mathbf{Q}r_j)$$

example:  $\text{CF}_4$ :

assume  $OA=OB=OC=OD=1$ ;  $z=OO'=\cos(u)=1/3$

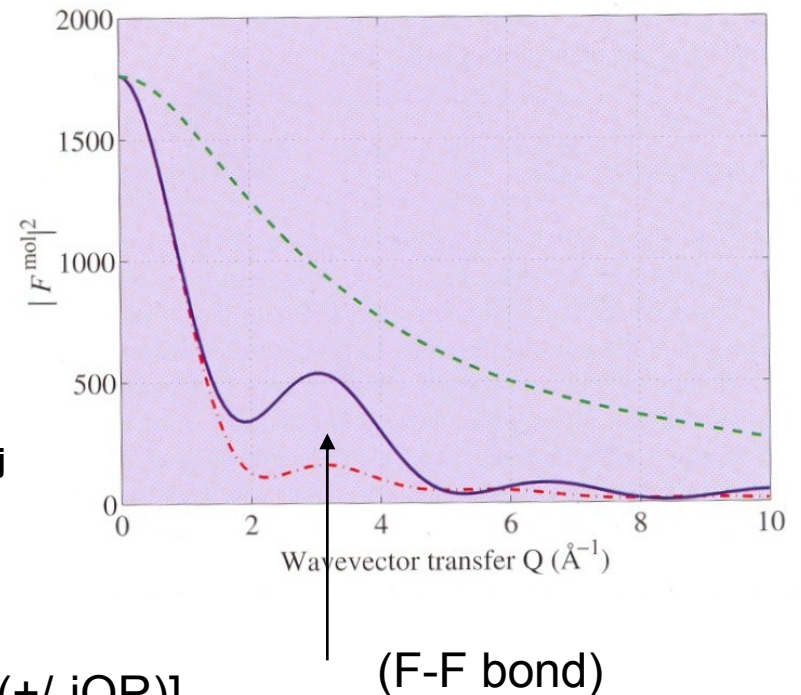


$$Qr_j = r_j \cos(u) = (1/3)Qr_j$$

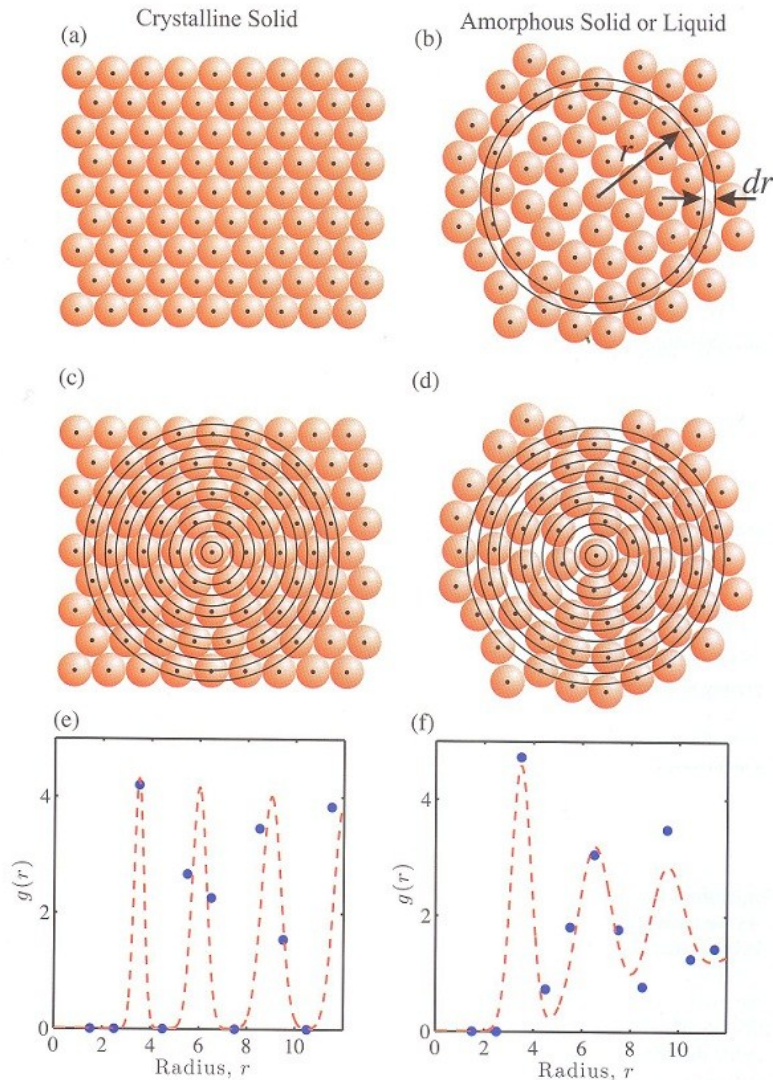
Assume:  $Q \parallel \text{C-F bond}$

$$\begin{aligned} F^{\text{mol}} &= f^{\text{C}}(\mathbf{Q}) + f^{\text{F}}(\mathbf{Q}) [\exp(i\mathbf{Q}R) + 3\exp(i\mathbf{Q}r_j)] \\ &= f^{\text{C}}(\mathbf{Q}) + f^{\text{F}}(\mathbf{Q}) [3\exp(-/+i\mathbf{Q}R/3) + \exp(+/-i\mathbf{Q}R)] \end{aligned}$$

—  $\text{CF}_4$   
 - . . .  $\text{CF}_4$   $Q$  not  $\parallel$  C-F  
 - - - - molybdenum  
 (also 42 electrons)



# Scattering from liquids and glasses



The positions of atoms in non-crystalline materials changes over a wide range of timescales (from nanoseconds in the case of liquids to millennia or more in the case of glasses).

X-rays are a fast probe delivering snapshots of the structure as shown schematically in the figure.

Radial density:  $\rho(r) = N(r) / (2\pi r dr)$

$N(r)$  number of atoms in annulus  $r+dr$   
with  $2\pi r dr$  being the annulus' area

Radial distribution function:  $g(r) = \rho(r)/\rho_a$

$\rho_a$  average areal number density

The radial distribution function of a non-crystalline material damps and broadens as a function of  $r$  with  $g(r)$  tending to unity.

# ▪ The liquid structure factor

Consider mono-atomic or mono-molecular system:

$$I(\mathbf{Q}) = f(\mathbf{Q})^2 \sum_n \exp(i\mathbf{Q}\mathbf{r}_n) \sum_m \exp(i\mathbf{Q}\mathbf{r}_m) = f(\mathbf{Q})^2 \sum_n \sum_m \exp i\mathbf{Q}(\mathbf{r}_n - \mathbf{r}_m)$$

with  $f(\mathbf{Q})$  formfactor

separate summations

$$I(\mathbf{Q}) = Nf(\mathbf{Q})^2 + f(\mathbf{Q})^2 \sum_n \sum_{m \neq n} \exp i\mathbf{Q}(\mathbf{r}_n - \mathbf{r}_m)$$

Replace  $m \neq n$  sum by integral and separate out average density  $\rho_{at}$ :

$$I(\mathbf{Q}) = Nf(\mathbf{Q})^2 + \underbrace{f(\mathbf{Q})^2 \sum_n \int_V [\rho_n(\mathbf{r}_{nm}) - \rho_{at}] \exp i\mathbf{Q}(\mathbf{r}_n - \mathbf{r}_m) dV_m}_{I_{SRO}(\mathbf{Q})} + \underbrace{f(\mathbf{Q})^2 \rho_{at} \sum_n \int_V \exp i\mathbf{Q}(\mathbf{r}_n - \mathbf{r}_m) dV_m}_{I_{SAXS}(\mathbf{Q})}$$

$I_{SRO}(\mathbf{Q})$

measures short-range order since  
 $\rho_n(\mathbf{r}_{nm}) \rightarrow \rho_{at}$  after few atomic spacings  
 and the term oscillates then towards zero

$I_{SAXS}(\mathbf{Q})$

contributes only for  $Q \rightarrow 0$   
 (otherwise oscillates to zero)

where  $\rho_n(\mathbf{r}_{nm})dV_m$  is the number of atoms in volume element  $dV_m$  located at  $\mathbf{r}_m - \mathbf{r}_n$  relative to  $\mathbf{r}_n$ .

# ▪ The liquid structure factor

Average over different choices for the origin  $\langle \rho_n(\mathbf{r}_{nm}) \rangle \rightarrow \rho(r)$

Isotropy:  $\rho(\mathbf{r}) \rightarrow \rho(r)$

$$I(Q) = Nf(Q)^2 + Nf(Q)^2 \int_0^\infty [\rho(r) - \rho_{at}] 4\pi r^2 \frac{\sin(Qr)}{Qr} dr$$

$$\Rightarrow S(Q) = I^{SRO}(Q)/Nf(Q)^2 = 1 + 4\pi/Q \int_0^\infty r [\rho(r) - \rho_{at}] \sin(Qr) dr$$

For  $Q \rightarrow \infty$ :  $S(Q) \rightarrow 1$

For  $Q \rightarrow 0$ :  $\sin(Qr)/Q \rightarrow r \Rightarrow S(Q) = 1 + 4\pi \int_0^\infty r^2 dr [\rho(r) - \rho_{at}]$

$S(Q) \propto [\rho(r) - \rho_{at}]$  proportional to the density fluctuations

Density fluctuations become strong when the compressibility  $\kappa_T$  is large. If, at a critical point, the compressibility diverges  $S(0)$  might become so strong that the sample becomes opaque: critical opalescence.

For an ideal gas:  $P = \rho_{at} k_B T$  and  $\kappa_T = 1/(\rho_{at} k_B T)$  since  $\kappa_T = (\partial \rho / \partial P)_T$

For interacting gas:  $\kappa_T$  diverges at critical point

Actually:  $S(0) = \rho_{at} \kappa_T k_B T = 1$  (for all  $Q$ ) for an ideal gas

- The pair correlation function  $g(r)$ :

$$S(Q) = 1 + 4\pi/Q \int_0^\infty r [\rho(r) - \rho_{at}] \sin(Qr) dr$$

⇒ Radial distribution function for a liquid or glass:

$$g(r) = 1 + (1/2\pi^2 r \rho_{at}) \int_0^\infty Q [S(Q) - 1] \sin(Qr) dQ$$

Note:

It was assumed that the scattering is dominated by elastic scattering events. This holds for a glass but not for a liquid. However e.g. 10 keV photons are far more energetic than any relevant excitation in a liquid (typically 10 meV); thus any inelastic effect is negligibly small.

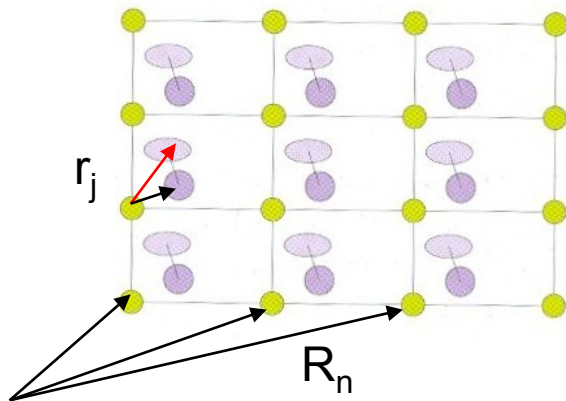
However this does not hold for neutrons.

# Scattering from a crystal

$$A(\mathbf{Q}) = -r_0 \sum_{\mathbf{r}_j} \exp(i \mathbf{Q} \mathbf{r}_j')$$

an extension to crystalline matter is simplified since there is translational symmetry.

crystalline matter:  $\mathbf{r}_j' = \mathbf{R}_n + \mathbf{r}_j$



$$A(\mathbf{Q}) = -r_0 \underbrace{\sum_{\mathbf{R}_n} \exp(i \mathbf{Q} \mathbf{R}_n)}_{\text{lattice sum}} \underbrace{\sum_{\mathbf{r}_j} \exp(i \mathbf{Q} \mathbf{r}_j)}_{\text{unit cell structure factor}}$$

lattice sum

unit cell structure factor

## Crystallography:

determine electron density within unit cell

Note: one does measure  $I(\mathbf{Q}) = A(\mathbf{Q}) A^*(\mathbf{Q})$  and is thus not sensitive to phase shifts