Neutron- and Synchrotron X-Ray Scattering

(The theoretical principles)

W.E. Fischer
Paul Scherrer Institut
CH-5232 Villigen PSI

Abstract

We give an introduction to the principles of neutron- and X-ray scattering. After a short layout of the kinematical complementarity, we discuss in some detail the elementary interaction of these probes with a sample. Based on the different nature of the coupling of these probes to the various degrees of freedom in the sample we then emphasize the dynamical complementarity.

1 Introduction

1.1 Historical Development

Since the propagation of light has been recognized to be a form of electromagnetic radiation, light-scattering is used as a tool to investigate matter and its structure. A gradual sophistication of the treatment for these scattering processes can be noticed during the last hundred years. Tyndale and Rayleigh studied scattering of light at dust grains and in a turbid medium of molecules respectively. The corresponding scattering law they obtained is

$$\frac{d\sigma}{d\Omega} \sim \frac{1}{\lambda^4}(1+\cos^2\vartheta). \tag{1.1}$$

where λ is the wave length and ϑ the scattering angle of the light. The scattering intensity

is given by some contrast difference of the dielectric constant or the refraction index. It was of course already at that time of great interest to note that (1.1) is valid for visible light for gaseous O_2, H_2, N_2, CO_2 - and hence explains the blue sky - but not for H_2O. Einstein and Smoluchowski with their statistical treatment of the density fluctuations and the corresponding optical inhomogenuities derived the law

$$\frac{d\sigma}{d\Omega} \sim \frac{kT}{\lambda^4}(1+\cos^2\vartheta)\chi_T \tag{1.2}$$

with the isothermal compression

$$\chi_T = \frac{1}{T}(\partial_p V)_T. \tag{1.3}$$

For an ideal gas the result of Rayleigh is reproduced. Note that already at this level the scattering law depends on thermodynamic variables and hence on the equation of state of the scattering medium.

The next step was introduced by Ornstein and Zernike. They emphasized that correlations between the fluctuating cells due to their mutual interactions may be of importance. The volume is subdivided into small cells V_i with the number density of scatteres n_i subject to fluctuations

$$n_i =< n_i > +\Delta n_i \tag{1.4}$$

The phase differences between the various cells leads to an average phase of

$$<\mid \Phi \mid^2>=< n_i >^2 \sum_{i,j}^{m} e^{i(\varphi_i-\varphi_j)} + \sum_{i,j} < \Delta n_i \Delta n_j > e^{i(\varphi_i-\varphi_j)}$$

The first term is $\sim< n_i >^2$ and survives only with $\varphi_i = \varphi_j$ - it describes the transmitted beam. The second depends on self- and pair-correlations between the cells and describes the scattering due to fluctuations. For an ideal gas it vanishes and hence there is in this model no scattering for this case. For a spherical correlation function with correlation length $\xi = 1/\kappa$ one obtains the scattering law

$$\frac{d\sigma}{d\Omega} \sim \frac{1}{\lambda^4}(1+\cos^2\vartheta)\left(1+\frac{A}{\pi}\frac{\lambda^2}{\vartheta^2}\right) \tag{1.5}$$

for a correlation function

$$g(r) = A\frac{e^{-\kappa r}}{r}. \tag{1.6}$$

Note that for $\vartheta \to 0$ the law diverges but what is here more important the "blue dominance" $1/\lambda^4$ becomes a "whitish" $1/\lambda^2$. Moreover, since the whole procedure is time-independent it still describes elastic scattering only.

Todays state of the art is essentially due to L. van Hove [1]. He developed it for neutron scattering, but it may as well be applied to X-ray scattering (at least in the Thomson regime). While the very early work dealt with the scattering of visible light and hence resolutions of the order of a few thousend Angströms, todays work takes advantage from the availability of probes with wavelength in the region of Angströms. Correspondingly the density fluctuations are formulated on the level of individual scattering centers j, like atoms and molecules at their (time-dependent) positions $\vec{X}_j$

$$\rho(\vec{x}, \tau) = \sum_j \delta(\vec{x} - \vec{X}_j(\tau)). \tag{1.7}$$

The correlation function we are aiming for, by means of scattering experiments are then of the form

$$\boxed{C(\vec{x}, \tau) = \frac{1}{N}\int d^3x' < \rho(\vec{x}', \tau) \cdot \rho(\vec{x} - \vec{x}', 0) >,} \tag{1.8}$$

where ρ means the mass-, charge- or magnetization density depending on to the sampling probe. $<\quad>$ stands for the thermal average over a canonical ensemble. In the convolution of (1.8) translational symmetry of the sample has been assumed (no surface effects). The time dependent self- and pair-correlation contains the dynamics of the sample and implies inelastic scattering (spectroscopy).

1.2 Principles of a Scattering Experiment

As an example we show in Fig. 1 the set-up of an inelastic neutron scattering experiment. A corresponding arrangement may also be imagined for X-rays as probe. The experiment starts with a monochromatic beam and analyses the final neutron energy after the scattering process.

If appropriate either of the two crystal selectors may (for neutrons only) be replaced by a time-of-flight configuration at a pulsed neutron beam. The energy- and momentum-transfer variables

$$\hbar\omega = E_0 - E_1 \tag{1.9}$$

$$\vec{\kappa} = \vec{k}_0 - \vec{k}_1 \tag{1.10}$$

are the kinematical variables of the scattering function $S(\omega, \vec{\kappa})$.

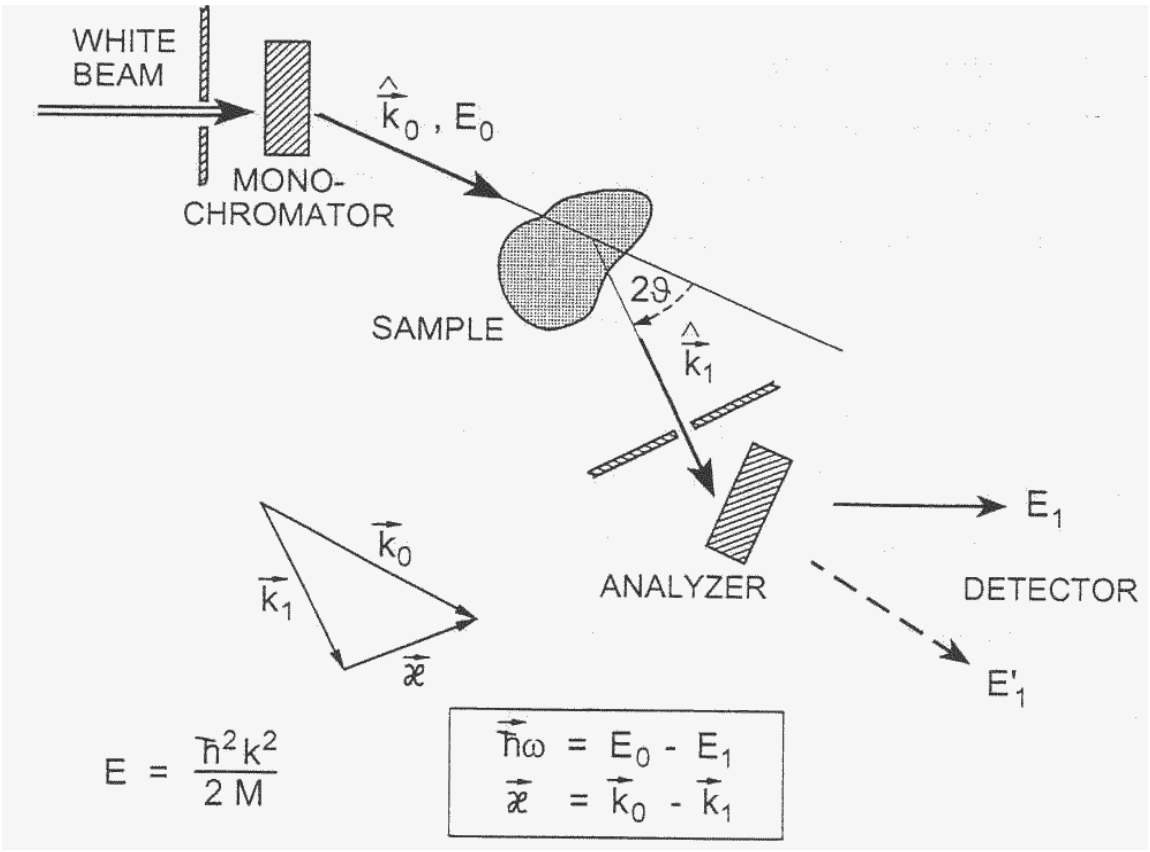


Figure 1: Principle of a set up for an inelastic neutron scattering experiment.

$(E_0, \vec{k}_0)$ and $(E_1, \vec{k}_1)$ are the energy and wave vector of the incident and escaping probe respectively. For neutrons we have

$$\lambda = \frac{2\pi}{|\,\vec{k}\,|} = \frac{h}{mv} \tag{1.11}$$

and

$$E = \frac{\hbar^2 k^2}{2M} = \frac{h^2}{2M}\frac{1}{\lambda^2} \tag{1.12}$$

where λ is the de Broglie wave length and v the velocity of the neutron. M is the neutron mass. For X-rays the corresponding relations are

$$\lambda = \frac{2\pi}{k} = \frac{2\pi\hbar c}{E} \tag{1.13}$$

and

$$E = \hbar\omega = \hbar k c \tag{1.14}$$

Fig. 2 shows the kinematical domain $(\omega, \mid \vec{\kappa} \mid)$ which can be reached with an incident neutron beam of energy E. The lower field - indicated by "Anti-Stokes" - corresponds to an energy transfer from the sample to the incident probe and is therefore only populated for a sample at higher temperature. The ingredients and notions of such a scattering experiment are summarized in Table 1.

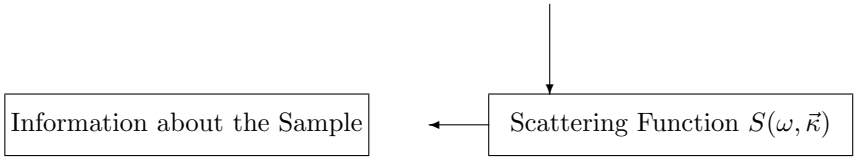
Table 1.1: Notions and ingredients of scattering experiments

Sample - Environment
- pressure
- temperature
- external fields

etc.
Sample normally in thermal equilibrium

Probe - Neutron / Light (x-ray) } beam possibly polarized
- Preparation
  - Energy
  - Momentum
  - Polarization

Observables at probe after **Scattering**
- Energy → Energy transfer
- Momentum → Momentum transfer
- Polarization → Re-/Depolarization due to interaction with the sample



depends on the nature
- nuclear
- electro-magnetic

interaction between probe and sample.

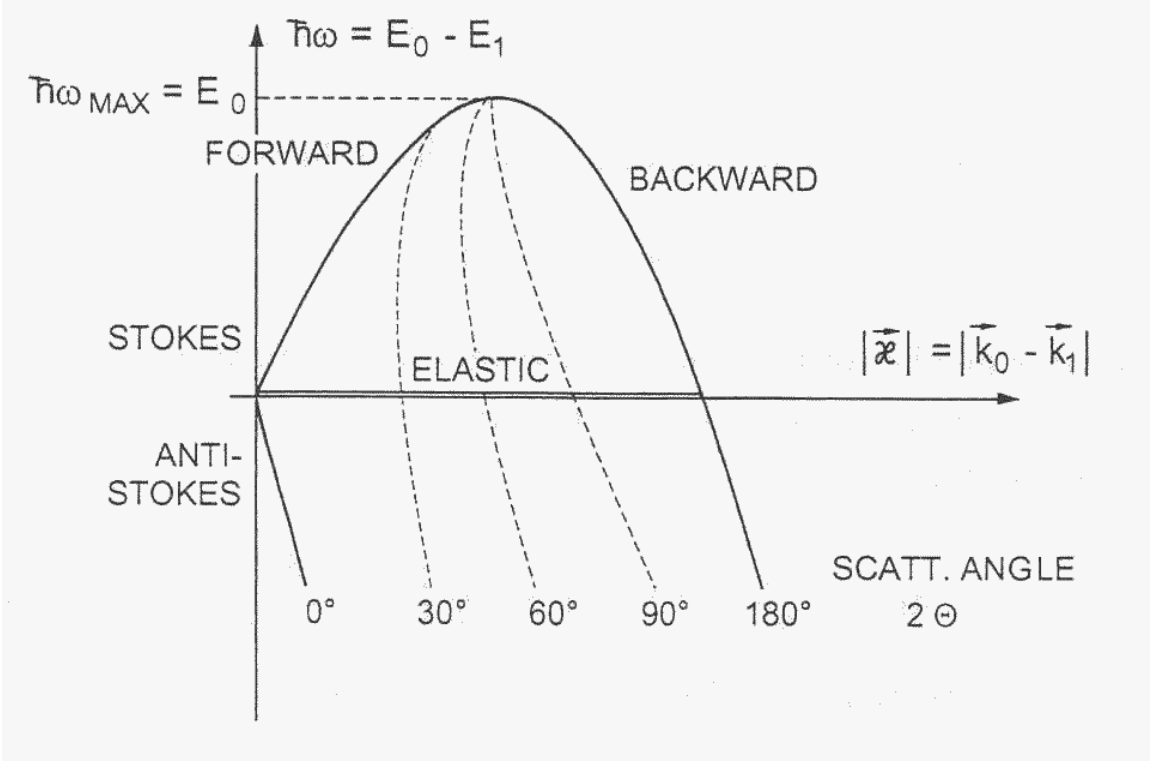


Figure 2: Kinematical domain in energy - and momentum transfer for neutron scattering with incident beam energy E. For the corresponding experiment with X-rays the figure looks similar. The parabola has just to be replaced by a triangle with its upper corner at the level $E_0 = \hbar\omega_{max}$.

2 Complementarity

2.1 Two Energy-(Time) Scales in Condensed Matter (Born-Oppenheimer)

Consider, in view of the atomic structure of matter, the potential $V(\vec{x}, \vec{X})$ between the various particles, where $\vec{x}$ and $\vec{X}$ stand for the set of coordinates of electrons and nuclei respectively. Let T_n and T_e be the kinetic energies of the nuclei and electrons. The system is then described by the Schrödinger equation

$$[T_n + T_e + V(\vec{x}, \vec{X})]\Psi(\vec{x}, \vec{X}) = E_{tot}\Psi(\vec{x}, \vec{X}) \tag{2.1}$$

While it is of course impossible to solve this problem, it is remarkable to note that the existence of a solution has been proved under rather general conditions [2]. In other words it has been shown that for a system with N ions of charge Z

$$\lim_{N\to\infty} E(N)/N \quad \text{exists} \tag{2.2}$$

that is, there exists a finite lower bound of the energy E_{tot} - **hence matter is stable**. Crucial ingredients for this are the **Pauli-principle and the uncertainty relation**. Related to the extremely different masses of the ions and electrons the system tends to split up (under "normal" conditions) into two energy scales and connected with this two different time-scales. Let us write the wave function in the following form:

$$\Psi(\vec{x},\vec{X}) = \sum_n \Phi_n(\vec{X})\phi_n(\vec{x},\vec{X}) \tag{2.3}$$

where $\mid n >$ are the electronic eigenstates for a static nuclear background. Equation (2.1) then splits up into two sets of equations, describing the ionic - and electronic - degrees of freedoms of the system. The hamiltonian for the ions is

$$H_{eff} = -\frac{1}{2M}\sum_k (\delta_{mk}\vec{\nabla}_{\vec{X}} - iA_{mk}(\vec{X}))^2 + \delta_{mn}\epsilon_n(\vec{X}) \tag{2.4}$$

where

$$A_{mk}(\vec{X}) =< \varphi_m \mid \vec{\nabla}_{\vec{X}}\varphi_k >$$

ϵ_n are the energy eigenvalues of the electronic problem for a particular ionic configuration $\vec{X}$. The A_{mk}'s act as electronically screened ionpotentials. If the ionic and electronic degrees of freedom couple only weakly, we may neglect the non-diagonal terms of A_{mk}. This is called the Born-Oppenheimer approximation. In this approximation the electrons can then be described as Bloch-waves, perturbed in first order by electron-phonon interactions. In this spectroscopic picture the electronic and ionic degrees of freedom are to a large extend decoupled. Due to their different energy scale, they also define two different time scales. Already at this point one may expect the neutrons to be well adapted probes to investigate the slow ionic motions, the X-rays, however, to be more suitable for the fast electronic modes.

Of course the Born-Oppenheimer approximation is not always valid. It's break down is indeed of particular interest. For instance, the energy gap of a Cooper-pair being of the same order

of magnitude like phonon modes in the lattice, clearly indicates such a break down at phase transitions.

2.2 Kinematical Complementarity

Due to the different relationship between energy and wave length of various probes, their range of access in reciprocal space of the sample is different. It follows immediately from (1.11) - (1.14) that photons used in optical spectroscopy and energetically well matched to investigate excitations, have too low momentum to cover the whole Brioullin zone.

On the other hand X-rays possessing this momentum ($\lambda \simeq 1.24$ Å) have to high an energy (E_0 = 10 keV) in order to scale properly to the lower lying excitations in a solid. Thermal neutrons ($\lambda = 1.28$ Å) are nearly ideal for this purpose ($E_0 = 50$ meV).

As will be discussed further on, the scattering function is the spatial and temporal Fourier transform of a correlation function (1.8) in space and time [1]. This leads to the following correspondence:

Excitations of internal degrees of freedom	$\longleftrightarrow$	Fluctuations in space and time
Energy, Momentum } -transfer		Life time, relaxation time, spatial resolution, coherence length

This correspondence between **momentum transfer and correlation lengths** on the one hand and **energy transfer and relaxation times** on the other hand, is indicated by the two scales on the axes of Fig. 3. Various experimental methods are indicated in the kinematical field which they can cover. This demonstrates their kinematical complementarity. The methods stated along the left (energy-correl. time) axis are restricted to low momentum and hence probe a small region around the center of the Brillouin zone. These are particularly powerful methods to investigate the temporal correlations and therefore the energetic scale of the excitation spectrum of the sample.

The momentum, carried by neutrons and X-rays as probes allows the exploration of essentially the whole relevant region of $\vec{k}$-space in the sample. This corresponds to spatial correlations within 10^{-5} - 10^{-8} cm. Simultaneously — by means of inelastic scattering experiments — it is possible to investigate the energy scale of the excitations of internal degrees of freedom. This is particularly true for the use of neutrons as probes. As a matter of fact with neutrons the investigation of the whole first Brillouin-zone of almost all practical materials is possible. As a guide to the eye we have drawn schematically into this field the dispersive behaviour of the acoustic and optical branches of phonon excitations in a lattice. We recognize from Fig. 3 that the region for hard phonon branches is within reach of hot neutrons as well as of soft X-rays as probe. A spectrometer with extremely high resolution at a synchrotron light source with high brilliance is however needed for the latter method.

Also from Fig. 3 we reckon how well suited X-rays may be to obtain a clear picture about the electronic dynamics in the sample. As a complement the same is true for the neutrons and the lattice dynamics. Using both methods on the same sample might be appropriate for the interesting cases, where the Born-Oppenheimer approximation ist not valid.

2.3 Dynamical Complementarity

The various probes couple differently to the degrees of freedom in the sample. While the coupling of the neutron to the nuclear scattering density probes the fluctuations of the mass density, X-rays - via their coupling to the electric charge - probe the charge density fluctuations. Although both - X-rays and neutrons - couple to magnetization (albeit much weaker for X-rays) the two probes are again complementary, since their elementary coupling law differ.

We shall present these elementary interactions in more detail in chapter 4. An important remark about the **coupling strength** of probes has to be mentioned here.

> For weakly coupling probes - (like neutrons and X-rays, at least in the Thomson regime) - Born approximation and linear response theory is valid. Perturbation of the sample in the presence of the probe is marginal. Straightforward interpretation of the data in terms of a scattering function, characterizing the unperturbed sample is

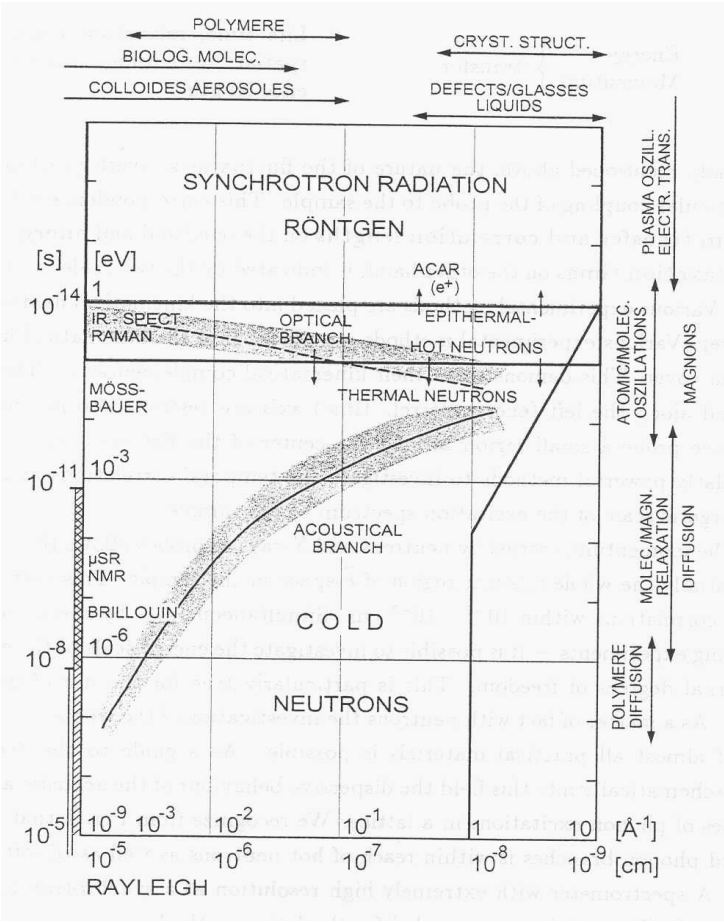


Figure 3: Range of access in energy and momentum by various experimental methods. The correspondance to correlation-time and -length is also indicated.

possible. Kinematical approximation, neglecting all multiscattering effects, is valid.

Probes with strong coupling (usually charged particles) perturb (e.g. polarize) the sample up to the extent that Born approximation and in particular the linear response approach breaks down. A model input to describe the scattering process is generally necessary to interpret the data. Furthermore corrections for multiple scattering effects have often to be applied.

In the following we deal with weakly interacting probes only. In this case the whole information

of the experiment about the sample is contained in the scattering function.

3 Description of the Free Probes

3.1 The Neutron

The neutron has a mass of $M_N = 939.6$ MeV and the quantum numbers

$$T(J^P) = \tfrac{1}{2}\left(\tfrac{1}{2}^+\right)$$

It's mass is 1.3 MeV bigger than that of the proton. Hence it decays into the latter by weak interaction with a mean lifetime of 887 s. However, for our purpose the neutron is stable. The electromagnetic properties of the neutron are characterized by it's vanishing charge but a magnetic moment. This moment has its origin in an electromagnetic form factor which is due to the strong interaction "dressing" by e.g. pion clouds. As a particle with spin 1/2 we describe the neutron by a two component spinor quantized along the z-axis

$$\psi = a_1\chi_1 + a_2\chi_2 = \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} \tag{3.1}$$

in the basis

$$\chi_1 = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \qquad \chi_2 = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{3.2}$$

and with norm

$$\mid a_1 \mid^2 + \mid a_2 \mid^2 = 1 \tag{3.3}$$

For an arbitrary spin direction with polar angles (ϑ, φ)

$$a_1 = \cos\frac{\vartheta}{2}e^{i\varphi/2} \qquad a_2 = \sin\frac{\vartheta}{2}e^{-i\varphi/2} \tag{3.4}$$

The spin density matrix (a vector in the space of 2 x 2 hermitian matrices) is $\psi \otimes \psi^+$:

$$\rho = \begin{pmatrix} a_1a_1^* & a_1a_2^* \\ a_2a_1^* & a_2a_2^* \end{pmatrix} \qquad Sp(\rho) = 1 \tag{3.5}$$

The polarizations are given by the components of this matrix with respect to the basis $\mathbf{1}$, $\vec{\sigma}$ ($\vec{\sigma}$: Pauli matrices) that is

$$\rho = \frac{1}{2}(\mathbf{1} + \vec{P}\vec{\sigma}) \tag{3.6}$$

The components are

$$P_i = Sp(\rho\sigma_i) = \begin{cases} 2\mathcal{R}e(a_1^* a_2) & i = 1 \\ 2\mathcal{I}m(a_1^* a_2) & i = 2 \\ \mid a_1 \mid^2 - \mid a_2 \mid^2 & i = 3 \end{cases} \tag{3.7}$$

With (3.4) we obtain e.g. for P_1:

$$P_1 = \sin\vartheta \cos\varphi \tag{3.8}$$

and for polarization along the 1-axis we have

$$\begin{aligned} &\vartheta = \tfrac{\pi}{2}, \quad \varphi = 0 \qquad P_1 = 1 \qquad \psi = \tfrac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \\ &\vartheta = \tfrac{\pi}{2}, \quad \varphi = \pi \qquad P_1 = -1 \quad \psi = \tfrac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}. \end{aligned} \tag{3.9}$$

The density matrix (3.6) is idempotent that is

$$\rho^2 = \rho \tag{3.10}$$

and describes therefore as a projector pure states. For the description of a partially polarized neutron beam we need the generalization for an ensemble of an incoherent mix of polarization states.

$$\vec{P} = \frac{1}{N} \sum_i \vec{P}_i \tag{3.11}$$

ρ has still the form (3.6)

$$\rho = \frac{1}{2}(\mathbf{1} + \vec{P} \cdot \vec{\sigma}) \qquad \text{but with} \quad 0 \leq \mid \vec{P} \mid \leq 1 \tag{3.12}$$

The expectation value of ρ is

$$\begin{aligned} < \rho >= Sp(\rho\rho) \quad &= \frac{1}{2}(1 + \mid \vec{P} \mid^2) \\ &= \begin{cases} 1/2 \text{ unpolarized} \\ 1 \text{ completely polarized} \end{cases} \end{aligned} \tag{3.13}$$

Due to it's magnetic moment a neutron at rest is a source of a magnetic field. The electrical field for a neutron in flight - induced by Lorentz kinematics is of the order of v/c. In view of the low velocities of thermal neutrons this effect will not be of any concern in our context.

The magnetic moment is given by

$$\vec{\mu}_n = \gamma \mu_N \vec{\sigma} \qquad \left(\vec{s} = \frac{\vec{\sigma}}{2}\right) \tag{3.14}$$

where $\vec{s}$ is the spin operator for spin 1/2,

$$\mu_N = \frac{e\hbar}{2Mc} \tag{3.15}$$

is the nucleon magneton and γ = -1.91 the neutron renormalization factor.

The vector potential for this moment is

$$\vec{A}(\vec{x}) = \frac{\vec{\mu}_N \wedge \vec{x}}{\mid \vec{x} \mid^3} = -\vec{\mu}_N \wedge \vec{\nabla} \frac{1}{\mid \vec{x} \mid}. \tag{3.16}$$

Since the magnetic field for this potential is

$$\vec{B}(\vec{x}) = \vec{\nabla} \wedge A(\vec{x}) \tag{3.17}$$

we obtain with

$$\vec{\nabla} \wedge \vec{\mu}_N \wedge \vec{\nabla} \frac{1}{\mid \vec{x} \mid} = -(\vec{\mu}_N \cdot \vec{\nabla}) \vec{\nabla} \frac{1}{\mid \vec{x} \mid} + \vec{\mu}_N \cdot \Delta \frac{1}{\mid \vec{x} \mid} \tag{3.18}$$

$$\vec{B}(\vec{x}) = \vec{\nabla}(\vec{\mu}_N \cdot \vec{\nabla} \frac{1}{\mid \vec{x} \mid}) + 4\pi \vec{\mu}_N \delta(\vec{x}) \tag{3.19}$$

Hence apart from its strong interaction with the nuclei of the sample, the neutron induces also a magnetic perturbation and therefore may also probe the magnetization density.

The average of a general observable $\hat{O}$ over the spins is given by

$$\boxed{< \hat{O} >= \chi^+ \hat{O} \chi = Sp(\rho \hat{O})}. \tag{3.20}$$

The spatial part of the neutron wave function is described by a usual propagating wave-package.

3.2 Free Photons (Electro-Magn. Field)

The characterization of the photons as vector particles with vanishing mass is somewhat more involved than the simple spinor case of the neutron. In order to make things clear we start with a covariant relativistic formulation. This is a natural procedure - after all photons are relativistic objects. Let us start with the description of the electro-magnetic field as an antisymmetric tensor expressed by a vector field.

$$F^{\mu\nu} = \partial^\mu A^\nu - \partial^\nu A^\mu \tag{3.21}$$

The indices run over the time-space components (0,1,2,3). The diagonal metric used is (+,-,-,-). The inhomogeneous Maxwell equations are then

$$\partial_\mu F^{\mu\nu} = j^\nu \tag{3.22}$$

In vacuum $j^\nu = 0$, and (3.22) becomes equivalent to

$$\boxed{\Box A^\nu - \partial^\nu(\partial_\mu A^\mu) = 0} \tag{3.23}$$

It is well known and obvious from (3.21) that the field $F^{\mu\nu}$ is not unambigously determined by the vector potential A^μ. The ambiguity is

$$A^\mu \longrightarrow A^{\mu'} + \partial_\mu \Lambda(x). \tag{3.24}$$

As a first gauge condition, we chose Λ such that

$$\boxed{\Lambda = -\partial_\mu A^\mu} \tag{3.25}$$

The resulting condition is the Lorentz gauge

$$\partial_\mu A^\mu = 0 \tag{3.26}$$

This condition reduces the number of independent components of A^μ from four to three and the vacuum field equation becomes

$$\boxed{\Box A^\mu = 0} \tag{3.27}$$

However (3.26) does not yet make A^μ unique. If A^μ satisfies the Lorentz conditions, so will $A^{\mu'}$ as long as $\boxed{\Box\Lambda(x) = 0}$. By choosing

$$\partial_t \Lambda = A_0 \tag{3.28}$$

(3.26) becomes

$$\vec{\nabla} \cdot \vec{A} = 0 \tag{3.29}$$

This is called the Coulomb gauge - a name which in view of the subsequent equation

$$\Delta A_0 = 0 \quad \text{(static)} \tag{3.30}$$

is fairly obvious. Herewith $\vec{A}$ becomes a vector field with two independent transversal components. For a propagating field with wave vector $\vec{k}$ we obtain from (3.29)

$$\vec{k}\vec{\epsilon}^{\,(\lambda)}(\vec{k}) = 0 \tag{3.31}$$

where $\vec{\epsilon}^{\,(\lambda)}(\vec{k})(\lambda = 1, 2)$ are two normed base vectors perpendicular to $\vec{k}$.

$$\vec{\epsilon}^{\,(\lambda)}(\vec{k})\vec{\epsilon}^{\,\lambda'}(\vec{k}) = \delta_{\lambda\lambda'}. \tag{3.32}$$

The Coulomb gauge has the advantage that the two-state helicity for a zero mass, spin 1 - particle becomes evident. The disadvantage is that the description of the photon field is not anymore manifestly covariant. However, since we finally are going to use a nonrelativistic description of the sample, this does not matter in our context.

Note that in a polarizable medium (wave guide or a plasma) condition (3.29) can not be fulfilled and the field picks up a longitudinal component.

In quantized form our free field can now be written as

$$\vec{A}(\vec{x}, t) = \left(\frac{1}{2\pi}\right)^3 \int \frac{d^3k}{2k_0} \sum_{\lambda=1,2} \vec{\epsilon}^{\,(\lambda)} \left[a^{(\lambda)}(\vec{k})e^{-ikx} + a^{\lambda+}(\vec{k})e^{ikx}\right] \tag{3.33}$$

with

$$kx = \omega t - \vec{k}\vec{x}, \qquad k^2 = 0, \qquad k_0 = \mid \vec{k} \mid . \tag{3.34}$$

which is equivalent to (1.13) and (1.14). The commutation relations for the field operators are

$$[a^{(\lambda)}(\vec{k})a^{\lambda'+}(\vec{k'})] = 2k_0(2\pi)^3\delta_{\lambda\lambda'}\delta(\vec{k} - \vec{k'}) \tag{3.35}$$

$$[a^{(\lambda)}(\vec{k})a^{\lambda'+}(\vec{k}')] = [a^{\lambda+}(\vec{k})a^{\lambda}(\vec{k}')] = 0 \tag{3.36}$$

The electro-magnetic fields are determined by

$$\vec{E} = -\frac{1}{c}\partial_t \vec{A} \tag{3.37}$$

$$\vec{B} = \vec{\nabla} \wedge \vec{A} \tag{3.38}$$

With (3.37), (3.38) we conclude

$$\vec{E} \sim \vec{\epsilon}^{\,(\lambda)}, \qquad \perp \vec{k} \tag{3.39}$$

$$\vec{B} \sim \vec{k} \wedge \vec{\epsilon}^{\,(\lambda)}, \qquad \perp \vec{k}, \vec{E} \tag{3.40}$$

Let us now choose the transversal unit vectors $\vec{\epsilon}^{\,(1)}$ and $\vec{\epsilon}^{\,(2)}$ as a base to describe the polarization direction

$$\vec{\epsilon} = a_1 \vec{\epsilon}^{\,(1)} + a_2 \vec{\epsilon}^{\,(2)} \tag{3.41}$$

with

$$\mid a_1 \mid^2 + \mid a_2 \mid^2 = 1 \tag{3.42}$$

(3.41) can then be written

$$\vec{\epsilon} = \vec{\epsilon}^{\,(1)} \cos\alpha + \vec{\epsilon}^{\,(2)} \sin\alpha \; e^{i\beta} \tag{3.43}$$

For the choice of $\alpha = \pi/4$ and $\beta = \pm\, \pi/2$ we get

$$\vec{\epsilon}_{\pm} = \vec{\epsilon}^{\,(1)} \pm i\vec{\epsilon}^{\,(2)} \tag{3.44}$$

With (3.33) and (3.37) we recognize that for this case the field vector $\vec{E}$ is rotating around $\vec{k}$ on a circle. This describes right- resp. left handed circular polarization. For an arbitrary α but $\beta = 0$, linear polarization along the α-direction is described. Arbitrary (α, β) describe the elliptical polarizations. The spin density matrix for the photon field has to be something like the direct product of the $\vec{\epsilon}^{\,(\lambda)}$ that is

$$\rho_{ik} \sim \vec{\epsilon}_i^{\,*} \otimes \vec{\epsilon}_k \tag{3.45}$$

As a hermition (2x2)-matrix this can be written as

$$\begin{aligned}\rho &= \tfrac{1}{2}\begin{pmatrix} 1+\xi_3 & \xi_1 - i\xi_2 \\ \xi_1 + i\xi_2 & 1-\xi_3 \end{pmatrix} \\ &= \tfrac{1}{2}(\mathbb{1} + \vec{\xi}\cdot\vec{\tau})\end{aligned} \tag{3.46}$$

with τ being the Pauli-matrices. Note that any three-vector can in this way be represented by a hermitian (2x2)-matrix.

As for the case of spinors in the previous chapter we can project out the components

$$\xi_j = Sp(\rho\tau_j) \tag{3.47}$$

The ξ_j are called Stokes-parameters. For the two field components

$$\begin{aligned}E_1(t) &= a_1 e^{i(\varphi_1(t)-\omega t)} \\ E_2(t) &= a_2 e^{i(\varphi_2(t)-\omega t)}\end{aligned} \tag{3.48}$$

we obtain for the Stokes parameters

$$\xi_1 = 2a_1a_2\cos(\varphi_2-\varphi_1) \tag{3.49}$$

$$\xi_2 = 2a_1a_2\sin(\varphi_2-\varphi_1) \tag{3.50}$$

$$\xi_3 = \mid a_1 \mid^2 - \mid a_2 \mid^2 . \tag{3.51}$$

Recall that ρ in (3.46) is normalized to $Sp\rho = 1$; otherwise we would get here also a

$$\xi_0 = \mid a_1 \mid^2 + \mid a_2 \mid^2 \tag{3.52}$$

as the intensity of the beam. ξ_3 represents the degree of linear polarization, where as the nondiagonal elements measure the degree of circular polarization. What has been said about partial polarization in the last chapter (following equation (3.10)) can be repeated here as well.

3.3 The Polarization Analysis

In both cases, for neutrons and X-rays, the spin density matrix which describes the polarization states has formally the same structure. The deeper reason behind is the homomorphism between

the SU (2) and SO (3) groups. We do not want to discuss this point here, but rather sketch shortly the principles of how to deal with polarization states in connection with cross-sections. We just present the general framework common to both cases here. For every particular experimental set up this has to be done carefully and in an explicite way - a job which may well be rather tedious.

Let be

χ^{in} : a pure spin state of the probe before scattering with momentum $\vec{p}$
χ^{out} : a pure spin state after scattering and with momentum $\vec{p}\,'$

An initial state with partial polarization is then described by the mixture

$$\rho^{in} = \sum_i w_i \mid \chi_i^{(in)} >< \chi_i^{(in)} \mid \tag{3.53}$$

χ^{in} and χ^{out} are connected by the scattering amplitude

$$\chi^{out} = F(\vec{p} \to \vec{p}\,')\chi^{in}. \tag{3.54}$$

For ρ^{out} we then get

$$\rho^{out} = \sum_i w_i \mid \chi_i^{(out)} >< \chi_i^{(out)} \mid = \sum_i w_i F \mid \chi_i^{(in)} >< \chi_i^{(in)} \mid F^+. \tag{3.55}$$

This corresponds to an average over the initial states. Hence we obtain

$$\boxed{\rho^{out} = F(\vec{p} \to \vec{p}\,')\rho\ ^{in}F^+(\vec{p} \to \vec{p}\,')}. \tag{3.56}$$

The trace over ρ^{out} corresponds to the sum over all final states and hence, to the cross section

$$\frac{d\sigma}{d\Omega} = Sp(\rho^{out}). \tag{3.57}$$

We have seen in the previous chapters that ρ has in either case (neutrons or X-rays) the form

$$\frac{\rho}{Sp\rho} = \frac{1}{2}(\mathbf{1} + \vec{\sigma} \cdot \vec{P}). \tag{3.58}$$

The observables like polarizations or Stokes-parameters are then, normalized to the cross-section given by the projections

$$\boxed{P_i = Sp(\sigma_i \rho^{out})} \tag{3.59}$$

4 Interaction with the Scattering Centers

4.1 Nuclear Interaction of Neutrons

If we do not express the isospin dependence of the nuclear interaction of neutrons on nuclei explicitly, we can write for the phenomenological amplitude of neutron-nucleus scattering at very low energies

$$A + B\vec{s}_n \cdot \vec{I} \tag{4.1}$$

where $\vec{s}_n = \frac{1}{2}(\vec{\sigma}_x, \vec{\sigma}_y, \vec{\sigma_z})$ is the neutron spin operator expressed by Pauli spin-matrices and $\vec{I}$ the spin operator for the nucleus. The restriction to the simple form (4.1) is a consequence of the invariance of strong interaction under

i) rotational transformation (conservation of angular momentum)
ii) parity transformation and (conversation of parity)
iii) time reversal

A and B are determined by the strong interaction between the neutron and the nucleus and can - at very low energy - usually be represented by a pseudo-potential (scattering length). Let us consider the partial wave expansion of the spin independent scattering amplitude of (4.1).

$$A(\vartheta) = \frac{1}{2ik}\sum_l (2l+1)(e^{2i\delta_l} - 1)P_l(\cos\vartheta) \tag{4.2}$$

Apart from exceptional resonance conditions the phase shifts δ_l behave as

$$tg\delta_l \longrightarrow const.\ \ k^{2l+1} as \quad k \longrightarrow 0 \tag{4.3}$$

For very low energies we can restrict (4.2) to the contribution from the S-wave only. (There are exceptions like nuclei with high absorption at threshold). δ_0, according to (4.3) is odd in k. We can hence write an even expansion

$$ctg\delta_0 = -\frac{1}{a} + \frac{1}{2}\ r_0^2\ k^2 + O(k^4) \tag{4.4}$$

with a being the scattering length and r_0 the effective range of the interaction. For the scattering amplitude we then get

$$A(\vartheta) = [ctg\delta_0 - ik]^{-1} = -a + ika^2 + O(k^2) \tag{4.5}$$

and therefore a total cross section of

$$\sigma = 4\pi a^2 \tag{4.6}$$

For the application of neutron scattering in the investigation of structure and dynamics of condensed matter, the neutrons are scattered at nuclei bound in molecules or in a lattice. The amplitude of their thermal motion (e.g. vibrations) is very large compared to the range of the strong interaction. Therefore an impulse approximation is by far sufficient to describe the scattering amplitude of the neutron with a bound nucleus and its excitation into the nth-state in the lattice, that is

$$-\frac{M+m}{M} a \int \psi_n^*(\vec{x}) \psi_0(\vec{x}) e^{i\vec{\kappa}\vec{x}} d^3x \tag{4.7}$$

m and M are the masses of the neutron and the nucleus respectively. $\hbar\vec{\kappa}$ is the momentum transfer to the target. We can write the same amplitude formally in Born approximation as:

$$-\frac{2\pi m}{\hbar^2} \int V(\vec{x}\,') e^{i\vec{\kappa}\vec{x}\,'} d^3x' \int \psi_n^*(\vec{x}) \psi_0(\vec{x}) e^{i\vec{\kappa}\vec{x}} d^3x \tag{4.8}$$

(4.7) and (4.8) become identical if we chose for the potential

$$\boxed{V(\vec{x}) = 2\pi\hbar^2 \frac{M+m}{Mm} a\delta(\vec{x}) = \frac{2\pi\hbar^2}{m} b\delta(\vec{x})} \tag{4.9}$$

This is the pseudopotential used as "elementary" interaction in the description of scattering processes of low energy (thermal) neutrons in condensed matter.

A few remarks are in order:

i) While the strong interaction is charge independent, the electromagnetic contribution to the interaction potential violates this internal symmetry. Hence the scattering length b has a specific value for every isotope of the nucleus of the particular element.

ii) The strong interaction being spin dependent (4.1) leads to different scattering lengths for the two amplitudes A and B.

iii) Since amplitudes of different origin according to i) and ii) do not interfere with each other they lead to a contribution of incoherent scattering at a many body system consisting of nuclei with $I_n \neq 0$ and their isotopes with different isospins.

iv) Due to the local nature of the interaction potential ($\sim \delta(\vec{x})$), there appears no form factor for the elementary scattering, that is the differential cross section does not decrease for large momentum transfer (large scattering angles).

4.2 The Electromagnetic Interaction

As stated in the previous chapters the photons and neutrons are electromagnetic probes for the electronic degrees of freedom in a sample. We describe here both probes as external vector potentials coupled to either charge - or magnetization density in the sample. The hamiltonian of the perturbation is then

$$\boxed{H_1 = -\frac{e}{c}\int d^3x \vec{A}(\vec{x})\vec{j}(\vec{x})} \tag{4.10}$$

for the coupling to the charge carriers forming the current $\vec{j}$:

$$\vec{j}(\vec{x}) = \sum_j \frac{1}{2m}\left(\vec{p}_j\delta(\vec{x}-\vec{x}_j) + \delta(\vec{x}-\vec{x}_j)\vec{p}_j\right). \tag{4.11}$$

$\vec{x}_i$ and $\vec{p}_i$ are the positions and the momenta of the electrons.

4.2.1 Photon-Electron Coupling

In order to express this hamiltonian explicitly we start with a relativistically covariant treatment of electrons as Dirac-particles with spin 1/2 in an external electromagnetic field. Notice that electromagnetism is a relativistic business - and indeed the magnetic coupling of photons turns out to be a relativistic effect.

The Dirac equation in momentum representation and usual notation for an electron with mass m is

$$(\gamma^\mu p_\mu - m)\psi(x) = 0. \tag{4.12}$$

We introduce it's coupling to an external field

$$p_\mu \longrightarrow p_\mu - \frac{e}{c}A_\mu \tag{4.13}$$

Using the representation

$$\gamma^0 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \qquad \vec{\gamma} = \begin{pmatrix} 0 & \vec{\sigma} \\ -\vec{\sigma} & 0 \end{pmatrix} \tag{4.14}$$

we obtain with

$$\psi = \begin{pmatrix} \varphi \\ \chi \end{pmatrix} e^{i(mc^2)t} \tag{4.15}$$

the Pauli spinor-equations

$$i\partial_t \varphi = c\vec{\sigma}\left(\vec{p} - \frac{e}{c}\vec{A}\right)\chi + eA_0\varphi \tag{4.16}$$

$$i\partial_t \chi = c\vec{\sigma}\left(\vec{p} - \frac{e}{c}\vec{A}\right)\varphi + eA_0\chi - 2mc^2\chi \tag{4.17}$$

As a first approximation we write χ as

$$\chi = \frac{1}{2mc}\vec{\sigma}(\vec{p} - \frac{e}{c}\vec{A})\varphi \tag{4.18}$$

which leads us to a Schrödinger type of equation for φ

$$i\partial_t \varphi = H_{eff}\varphi \tag{4.19}$$

with an effective hamiltonian

$$H_{eff} = \frac{1}{2m}(\vec{p} - \frac{e}{c}\vec{A})^2 + eA_0 - \frac{e\hbar}{2mc}\vec{\sigma}\vec{B} \tag{4.20}$$

H_{eff} is valid up to $O(v/c)$. It contains (since $s = \frac{1}{2}\sigma$) the correct magnetic moment for the electron with $g = 2$

$$\vec{\mu} = g\mu_B\vec{s} \qquad \mu_B = \frac{e\hbar}{2mc} \tag{4.21}$$

Higher order radiative corrections give a deviation from $g = 2$ of less than 1%. A coupling due to the charge between the field and electrical current from the first term and a Zeeman like term between magnetic field and magnetic moment is evident in (4.20). For a spin-orbit coupling we have to approach the next approximation

$$\chi = \frac{1}{2mc}\left[\vec{\sigma}\vec{p} + \frac{eA_0}{2mc^2}(\vec{\sigma}\vec{p}) + \frac{i}{2mc^2}(\vec{\sigma}\vec{p})\partial_t\right]\varphi. \tag{4.22}$$

In order to still interpret φ as a wave function we have to transform it

$$\varphi \longrightarrow \phi = O\varphi \tag{4.23}$$

such that the norm keeps its significance, that is

$$\int d^3x(\mid \varphi \mid^2 + \mid \chi \mid^2) = \int d^3x \mid \phi \mid^2 . \tag{4.24}$$

Then accordingly H transforms into

$$H \longrightarrow H_{eff} = OH\ O^{-1}. \tag{4.25}$$

This is fulfilled by

$$O = \mathbb{1} + \frac{\vec{p}^{\,2}}{8m^2c^2} \tag{4.26}$$

In this higher approximation we obtain again

$$i\partial_t\phi = H_{eff}\phi \tag{4.27}$$

with

$$\boxed{\begin{aligned} H_{eff} = \ & \frac{1}{2m}(\vec{p} - \frac{e}{c}\vec{A})^2 + \frac{p4}{8m^2c^2} + eA_0 - \frac{e\hbar}{2mc}\vec{\sigma}\vec{B} + \frac{e}{8m^2c^2}\Delta A_0 \\ & -\frac{e\hbar}{4m^2c^2}\vec{\sigma}\cdot\left(\vec{E}\wedge(\vec{p} - \frac{e}{c}\vec{A})\right) \end{aligned}}\ . \tag{4.28}$$

The new additional terms compared to (4.20) are

- a relativistic velocity correction to the kinetic energy. It will be neglected in the following.
- the socalled Darwin term $\sim \Delta A_0$. It has its origin in the positional fluctuation of the charge and will not be considered either
- The last term in (4.28) consists of four different contributions
  1. $\frac{e\hbar}{(2mc)^2}\vec{\sigma}\cdot(\vec{E}\wedge\vec{p})$ spin orbit coupling
  2. $\frac{e\hbar}{(2mc)^2}\vec{\sigma}\left(-\frac{e}{c^2}\right)\partial_t\vec{A}\wedge\vec{A}$ magnetic Thomson scattering
     This is the magnetic "analog" to the $\vec{A}^2$-term of (4.28).
  3. Two terms linear in $\vec{A}$ or $\partial_t\vec{A}$.

4.2.2 Neutron-Electron Coupling

In principle the neutron may be treated the same way as the electrons in the previous chapter. There are however some important modifications:

- Its charge vanishes - hence the corresponding terms prop. to $\vec{A}$ do not appear.
- Its mass is three orders of magnitude larger than the mass of the electron - hence at thermal energy the velocities are so small that terms like $\vec{E} \wedge \vec{p}$ (spin-orbit) can be neglected (first approximation 4.20 is sufficient).
- Due to strong interaction, the magnetic moment is so highly renormalized (note, even the sign has changed) indicating that the g-factor is dominated by completely different physical effects. In this sense the neutron is not a Dirac-particle.

In view of this, we consider a neutron traversing a sample, to plough its magnetic field (3.19) through the lattice interacting with the electronic magnetic moments and currents. Using (4.11) for the currents, (3.16) for the vector potential we get from (4.10)

$$\boxed{H_1 = -\gamma\mu_N \frac{e}{2m_e c} \sum_j \left(\vec{p}_j \frac{\vec{\sigma}_n \wedge \vec{x}_j}{\mid \vec{x}_j \mid^3} + \frac{\vec{\sigma}_n \wedge \vec{x}_j}{\mid \vec{x}_j \mid^3} \vec{p}_j \right)}. \tag{4.29}$$

For the interaction with electronic moments we write

$$H_1 = -\int \vec{\mu}_e \vec{B}_n(\vec{x}) d^3x \tag{4.30}$$

with

$$\vec{\mu}_e(\vec{x}) = -2\mu_B \sum_j \vec{s}_j \delta(\vec{x} - \vec{x}_j) \tag{4.31}$$

and obtain with the help of (3.19)

$$\boxed{H_1 = \gamma\mu_N 2\mu_B \vec{\sigma}_n \cdot \sum_j \vec{\nabla} \frac{\vec{s}_j \wedge \vec{x}_j}{\mid \vec{x}_j \mid^3}} \tag{4.32}$$

Look at the expression (3.19) of the magnetic field, and you recognize that (4.32) contains the dipol-dipol - as well as the hyperfine interaction. In both expressions for H_1 the sum runs over those charge carriers in the sample which are active for the magnetization.

4.3 The Matrix Elements

4.3.1 Neutron-Nuclear Interaction

For a whole set of scattering centers at the positions $\vec{X}_i$ we obtain from (4.9)

$$V(\vec{x}) = \frac{2\pi\hbar}{m} \sum_j b_j \delta(\vec{x} - \vec{X}_j(t)). \tag{4.33}$$

The normalization has been taken such, that the elastic cross section is

$$\frac{d\sigma}{d\Omega} = |< \vec{k}_1 \mid V \mid \vec{k}_0 >|^2 \tag{4.34}$$

with

$$\boxed{\begin{aligned} < \vec{k}_1 \mid V \mid \vec{k}_0 > \quad &= \sum_j b_j \int d^3x e^{-i\vec{k}_1\vec{x}} \delta(\vec{x} - \vec{X}_j(t)) e^{i\vec{k}_0\vec{x}} \\ &= \sum_j b_j e^{i\vec{\kappa}\vec{X}_j(t)} \qquad \vec{\kappa} = \vec{k}_0 - \vec{k}_1 \end{aligned}} \tag{4.35}$$

4.3.2 Neutron-Magnetic Interaction

This matrix element is obtained from (4.28) and (4.32), by using the following Fourier representations

$$\frac{\vec{x}}{\mid \vec{x} \mid^3} = -\vec{\nabla}\frac{1}{\mid \vec{x} \mid} = -\frac{1}{2\pi^2}\vec{\nabla}\int d^3q \frac{1}{q^2} e^{i\vec{q}\vec{x}} \tag{4.36}$$

By means of these expressions and for a momentum transfer $\vec{\kappa} = \vec{k}_0 - \vec{k}_1$ we obtain for the matrix elements between $< \vec{k}_0 \mid$ and $\mid \vec{k}_1 >$

$$4\pi \sum_j e^{i\vec{\kappa}\vec{x}_j} \vec{\sigma}_n [\hat{\vec{\kappa}} \wedge \vec{s}_j \wedge \hat{\vec{\kappa}}] \tag{4.37}$$

for the spin part and

$$4\pi i \sum_j \frac{e^{i\vec{\kappa}\vec{x}_j}}{\hbar \mid \vec{\kappa} \mid} \vec{\sigma}_n [\hat{\vec{\kappa}} \wedge \vec{p}_j] \tag{4.38}$$

where $\hat{\vec{\kappa}} = \frac{\vec{\kappa}}{|\vec{\kappa}|}$.

Note that both terms are proportional to κ^{-2}. Furthermore the sum over j runs over the magnetically active electrons, hence a formfactor for the magnetization has to be expected. Therefore, contrary to the case of nuclear scattering (pseudo-potential), the magnetic scattering will be damped for large momentum transfers. We now define the transvers part of a vector with respect to $\vec{\kappa}$ by

$$\vec{Q}_\perp = \hat{\vec{\kappa}} \wedge \vec{Q} \wedge \hat{\vec{\kappa}} \tag{4.39}$$

Hence, the sum of (4.37) and (4.38) is the transverse part (to $\vec{\kappa}$) of the operator

$$\boxed{Q = 4\pi \sum_j e^{i\vec{\kappa}\vec{x}_j} [\vec{s}_j - \frac{i}{\hbar\kappa^2}(\vec{\kappa} \wedge \vec{p}_j)]}. \tag{4.40}$$

4.3.3 Photon-Charge Interaction

The coupling to the charge is described by the first term of (4.28). Apart from $\vec{p}_j^{\,2}$ which just describes the kinetic enery, we have the terms prop. to $\vec{p}_j \vec{A}(\vec{x}_j)$ and $\vec{A}^{\,2}(\vec{x}_j)$. According to (3.33) the first term is linear in the creation and destruction operators of the photon. Therefore it cannot contribute in first order to scattering states with initial and final photons. In first order they describe photo-emission and -absorption.

The corresponding matrix elements are for

- photoabsorption

$$\mid n_0 \vec{k}_0 > \longrightarrow \mid n_1 >; \qquad < n_1 \mid \sum_j e^{i\vec{k}_0 \vec{x}_j} \vec{\epsilon}^{\,(\lambda)}(\vec{k}_0) \vec{p}_j \mid n_0 \vec{k}_0 > \tag{4.41}$$

- photoemission

$$\mid n_0 > \longrightarrow \mid n_1 \vec{k}_1 >; \qquad < n_1 \vec{k}_1 \mid \sum_j e^{-i\vec{k}_1 \vec{x}_j} \vec{\epsilon}^{\,(\lambda)*}(\vec{k}_1) \vec{p}_j \mid n_0 > \tag{4.42}$$

n_0 and n_1 describe an initial and final state of an atom or molecule. The sum j runs over the electrons of these scattering centers. Since these processes are localized to e.g. an atom the wave length is usually larger than this active object (> 1 Å, say ...). In this case the dipol approximation is valid and the exp-function may be replaced by $\mathbf{1}$.

For photonic frequencies in the vicinity of an internal excitation with energy E_i, that is $\hbar\omega \simeq E_{n_0} - E_i$ the corresponding resonance denominator of the **second order contribution** to scattering may amplify its contribution up to domination of the scattering process. (4.41) and (4.42) are then the vertex functions.

The term quadratic in $\vec{A}$ describes a scattering process in first order perturbation

$$\mid n_0\vec{k}_0 > \longrightarrow \mid n_1\vec{k}_1 >; \qquad < n_1\vec{k}_1 \mid \sum_j e^{i\vec{\kappa}\vec{x}_j} \mid n_0k_0 > \vec{\epsilon}_i^{\lambda} \cdot \vec{\epsilon}_f^{\lambda'} \tag{4.43}$$

This is the "Thomson-scattering", which dominates the whole scattering process in absence of any excitations of the scatterers, that is for $\hbar\omega \gg E_{n_0} - E_i$.

4.3.4 Photon-Magnetic Scattering

In an analogous way the linear "Zeeman"-term contributes to scattering processes only in second order of the perturbation (4.46).

The first order term, prop. to $\dot{\vec{A}}\vec{A}$ - we call it here the magnetic "Thomson scattering" has the matrix element

$$\boxed{-\frac{i\hbar\omega}{mc^2} < n_1\vec{k}_1 \mid \sum_j e^{i\vec{\kappa}\vec{x}_j} \cdot \vec{s}_j \mid n_0k_0 > \vec{\epsilon}_f^{\,(\lambda)} \wedge \vec{\epsilon}_i^{\,\lambda'}}. \tag{4.44}$$

4.3.5 Second Order Contributions

These terms contain a denominator of the form $\left(E_{n_0} - E_i + \hbar\omega_k - i\frac{\Gamma}{2}\right)^{-1}$. If $\hbar\omega_k$ is near to the energy difference between the initial and the intermediate state $(E_{n_0} - E_i)$, these terms clearly dominate the cross section. **Moreover this is the regime of "anomalous" dispersion**. Away from this regime, when the frequency of the incident and emitted radiation (ω_k and ω_k') is not too different and larger than the energy differences between levels in the sample, that is

$$\omega_k \sim \omega_k' \gg \frac{1}{\hbar}(E_{n_0} - E_c) \tag{4.45}$$

The resonance denominators become proportional to $1/\hbar\omega$. After summation over intermediate states using closure we obtain the two terms

$$\boxed{\begin{aligned} &-i\frac{\hbar\omega}{mc^2} < n_1\vec{k}_1 \mid \sum_j e^{i\vec{\kappa}\vec{x}_j}(i\frac{\vec{\kappa}\wedge\vec{p}_j}{\hbar\kappa^2}(\vec{\epsilon}_f\wedge\vec{\epsilon}_i) \mid n_0k_0> \\ &-i\frac{\hbar\omega}{mc^2} < n_1\vec{k}_1 \mid \sum_j e^{i\vec{\kappa}\vec{x}_j}\cdot\vec{s}_j\cdot\vec{\mathcal{B}} \mid n_0k_0> \end{aligned}} \tag{4.46}$$

$\vec{\mathcal{B}}$ is a vector function depending on the initial and final polarization of the radiation field. It is explicitely given in the fourth line of the following table.

4.3.6 Summary

Taking all these terms into consideration leads to the rather complicated cross section formula as given by M. Blume [3]. Instead of writing it down in its full glory (see Altarelli's lecture), we prefer for our qualitative discussion to present a summary of the most relevant terms.

Table 4.2: Relevant terms of the X-ray scattering cross section

$$\frac{e^2}{mc^2} <\mid \sum_j e^{i\vec{\kappa}\vec{x}_j}\hat{O} \mid > f(\vec{\epsilon}_f,\vec{\epsilon}_i)$$

	$\hat{O}$	MAGNITUDE	$f(\vec{\epsilon}_f,\vec{\epsilon}_i)$	PERTURB. ORDER
$\vec{A}^2$	$\mathbb{1}$	1 (THOMSON)	$\vec{\epsilon}_f\cdot\vec{\epsilon}_i$	FIRST
$\vec{p}\vec{A}$	$i\frac{\vec{\kappa}\wedge\vec{p}_j}{\hbar\kappa^2}$	$-i\frac{\hbar\omega}{mc^2}$	$\vec{\epsilon}_f\wedge\vec{\epsilon}_i$	SECOND
$\dot{\vec{A}}\vec{A}$	$\vec{s}_j$	$-i\frac{\hbar\omega}{mc^2}$	$\vec{\epsilon}_f\wedge\vec{\epsilon}_i$	FIRST
$(\vec{\nabla}\wedge\vec{A}$	$\vec{s}_j$	$-i\frac{\hbar\omega}{mc^2}$	$(\hat{\vec{k}}_1\wedge\vec{\epsilon}_f)(\hat{\vec{k}}_1\vec{\epsilon})-$	
			$(\hat{\vec{k}}_0\wedge\vec{\epsilon}_i)(\hat{\vec{k}}_0\vec{\epsilon}_f)-$	SECOND
			$(\hat{\vec{k}}_1\wedge\vec{\epsilon}_f)\wedge(\hat{\vec{k}}_0\wedge\vec{\epsilon}_i)$	

Table 2 shows the relevant terms for X-ray scattering at an energy which is large compared to the energy level of the scattering constituents. In column 4 we also give the explicit dependence on incident- and final-proton polarization. A few remarks are in order here:

1. Neutron Scattering

   From (4.32) and (4.40) we expect the following order of magnitudes for the cross sections

   (a) nuclear: $4\pi \mid b \mid^2$

   (b) magnetic: $\left(\frac{e^2}{mc^2}\right)^2 \gamma^2 \mu_N^2$

   For small momentum transfer these two interactions are of the **same order of magnitude**. The ratio depends on the momentum transfer since nuclear scattering has, in contrast to magnetic scattering, no elementary form factor. That is, the magnetic contribution fades off with increasing momentum transfer.

2. X-ray Scattering

   From Table 2 we recognize cross sections of the following order of magnitude

   - Charge (Thomson) $\left(\frac{e^2}{mc^2}\right)^2 N^2$
   - magnetic $\left(\frac{e^2}{mc^2}\right)^2 \left(\frac{\hbar\omega}{mc^2}\right)^2 N_m^2$

   where N_m is the number of "magnetically active" electrons, $N_m \sim \frac{1}{10}N$. Assuming the magnetic form factor to be roughly the same as for the charge distribution and an X-ray energy of 10 keV, the **ratio between charge - and magnetic scattering is $4 \cdot 10^{-6}$**. The magnetic scattering is hence a small (relativistic) contribution to the scattering at charge fluctuations. Its observation is, however, not hopeless, since there exists the possibility to "switch off" the otherwise dominant Thomson scattering by an adequate choice of the initial and final polarization geometry in the scattering process ($\vec{\epsilon}_i \cdot \vec{\epsilon}_f = 0$).

   Furthermore it is possible to isolate the interference term between charge- and magnetic scattering by using circular polarization. This can be seen in the following way. We use (3.56) for this interference contribution and obtain

$$iSp\{\rho_{in}[M_m^+ M_c]\} = P_c(1-\alpha)2\mathcal{R}e(b) \tag{4.47}$$

   where

$$M_c = F(\vec{\kappa}) \begin{pmatrix} 1 & 0 \\ 0 & \cos^2\vartheta \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & \alpha \end{pmatrix} \tag{4.48}$$

   and

$$M_m = \begin{pmatrix} a & b \\ b* & c \end{pmatrix} \tag{4.49}$$

represent the scattering matrices for charge- and magnetic-scattering. ρ_{in} is the polarization matrix (3.46) of the incident beam.

$$\rho_{in} = \begin{pmatrix} 1 - P_{\parallel} & -iP_c \\ iP_c & 1 + P_{\parallel} \end{pmatrix} \tag{4.50}$$

(4.47) shows that a circularly polarized beam picks out the interference term which is proportonal to $\frac{\hbar\omega}{mc^2}$ only. X-ray cross sections with polarized beam and polarization analysis are further discussed in [4] and [5].

3. Comparison between X-rays and Neutrons

   The relevant interactions for structural investigations are (4.35) and (4.43). The cross sections are **of the same order of magnitude for light elements**. While the Thomson cross section increases with Z^2 for heavier atoms, the nuclear cross sections show a non-systematic variation with the atomic numbers. They may be very different even for different isotopes of the same element. Obviously this property can be used - by special preparation of the sample - for contrast variation. This is an opportunity which is unique for neutron scattering.

   The ratio between the two probes for magnetic scattering is of the order 10^4 in favor of the neutrons. The kinematic properties of the neutrons together with their relatively strong magnetic interaction give them their favorite position as samples to probe the magnetic dynamical properties of the sample. These kind of investigations will hardly ever be possible with X-rays.

   In the investigation of magnetic structures certain informations can however be obtained with X-rays, which are not accessible with neutrons. From (4.39, 4.40) we observe that neutrons "see" only the transversal part of the magnetization density, in contrast to X-rays (see table 2). In order to measure the "other" component of the magnetization with neutrons, a second experiment with the sample crystal rotated correspondingly has to be made. Furthermore it can be shown [4] that the matrix elements for magnetic scattering can be represented by

$$M_m = \frac{1}{2}\vec{L}(\vec{\kappa}) \cdot \vec{\mathcal{A}} + S(\vec{\kappa})\vec{\mathcal{B}} \tag{4.51}$$

   for X-rays; and

$$M_m = \left[\frac{1}{2}\vec{L}(\vec{\kappa}) + \vec{S}(\vec{\kappa})\right] \vec{\kappa} \wedge (\vec{\sigma} \wedge \vec{\kappa}) \tag{4.52}$$

for neutrons.

$\vec{L}(\vec{\kappa})$ and $\vec{S}(\vec{\kappa})$ are the Fourier transforms of magnetization densities from atomic orbitals and electron-moments respectively. $\vec{\mathcal{A}}$ and $\vec{\mathcal{B}}$ are two (different!) vector functions of the photon momenta and polarizations. Hence it is in principle possible to obtain separate information about orbital- and spin-contribution to the magnetization with X-rays. According to (4.52) this is obviously not possible with neutron scattering.

5 Cross Section and Correlation Function

5.1 The Form Factor

The operators (4.35, 4.40) are all the form

$$\sum_j e^{i\vec{\kappa}\vec{Z}_j}\hat{O} \tag{5.1}$$

$\vec{Z}_j$ are the positions of the particles which scatter the probe:
either the positions of the nuclei $\vec{X}_j$
or the positions of electrons $\vec{x}_j$.

Assuming the $\vec{X}_j$ to be the lattice sites, we decompose

$$\vec{x}_j = \vec{X}_j + \vec{\xi}_k^{(j)} \qquad k = 1, ...Z \tag{5.2}$$

and define the electronic form factor

$$\begin{aligned} F_j(\vec{\kappa}) &= \sum_{k=1}^{Z} \int d^3\xi \varphi^*(\vec{\xi})\delta(\vec{\xi} - \xi_k^{(j)})\varphi(\vec{\xi})e^{i\vec{\kappa}\vec{\xi}} \\ &= \int d^3\xi \rho(\vec{\xi})e^{i\vec{\kappa}\vec{\xi}} \end{aligned} \tag{5.3}$$

where $\rho(\vec{\xi})$ is the charge density. For magnetic scattering the sum runs only over those electrons (unpaired) which contribute to the magnetization. For simplicity we consider a Bravais Lattice. Otherwise an additional sum over the sites within the cell has to be introduced. We define now the operator

$$\boxed{A_{\vec{\kappa}}(\vec{X}_j) = F(\vec{\kappa})e^{i\vec{\kappa}\vec{X}_j}\hat{O}}. \tag{5.4}$$

Note that $F(\vec{\kappa}) = 1$ for the neutron nuclear scattering.

5.2 The Differential Cross-Section

The measured cross section of an inelastic process is defined as the ratio of the number of scattered particles with momentum $\vec{k}_1$ within the solid angle $d\Omega$ and an energy resolution ΔE, to the incident flux with momentum $\vec{k}_0$. Note that $\vec{k}_1$ determines the direction Ω and the energy E_1 of the scattered particles.

$$\vec{\kappa} = \vec{k}_0 - \vec{k}_1 \equiv k_i - k_f \quad ; \quad \hbar\omega = E_0 - E_1 \equiv E_i - E_f \tag{5.5}$$

are the momentum and the energy transfer in the scattering process. (We change notation here.) In Born approximation (linear response) we obtain

$$\frac{d^2\sigma}{d\Omega dE} = C \mid F(\vec{\kappa}) \mid^2 \sum_{i,f} p_i \sum_{l,k} < i \mid A^+_{\vec{\kappa}}(\vec{X}_\ell) \mid f >< f \mid A_{\vec{\kappa}}(\vec{X}_k) \mid i > \cdot\delta(\hbar\omega + E_i - E_f) \tag{5.6}$$

We now introduce the integral representation of the δ-function and represent the scattering operators as time dependent Heisenberg operators

$$\begin{aligned} < f \mid e^{i/\hbar E_f t} A_\kappa(\vec{X}_j) e^{-i/\hbar E_i t} \mid i > &=< f \mid e^{i/\hbar H_s t} A_\kappa(\vec{X}_j(0)) e^{-i/\hbar H_s t} \mid i > \\ &=< f \mid A_{\vec{\kappa}}(\vec{X}_j(t)) \mid i > \end{aligned} \tag{5.7}$$

where H_s is the hamiltonian of the sample. Using the property of completeness of the final states (closure) we obtain

$$\begin{aligned} \frac{d^2\sigma}{d\Omega dE} &= C \mid F(\vec{\kappa}) \mid^2 \int_{-\infty}^{+\infty} dt e^{-i\omega t} \sum_i p_i \sum_{l,k} < i \mid A^+_{\vec{\kappa}}(\vec{X}_k(0)) A_{\vec{\kappa}}(\vec{X}_\ell(t)) \mid i > \\ &= C \mid F(\vec{\kappa}) \mid^2 S(\kappa, \vec{\omega}) \end{aligned} \tag{5.8}$$

$$\boxed{S(\vec{\kappa},\omega) = \frac{1}{2\pi\hbar N} \int_{-\infty}^{+\infty} dt e^{-i\omega t} \sum_i p_i \sum_{l,k} < i \mid A^+_{\vec{\kappa}}(\vec{X}_k(0)) A_{\vec{\kappa}}(\vec{X}_\ell(t)) \mid i >} \tag{5.9}$$

S is the general scattering function for unpolarized beams and no polarization analysis at the probe. C is a characteristic constant which describes the coupling strength between probe and sample. According to our previous considerations we have for C:

i) **neutron-nuclear scattering**

$$C = N\frac{k_f}{k_i} \mid b \mid^2 = N\frac{k_f}{k_i}\frac{\sigma}{4\pi} \tag{5.10}$$

σ is the elementary coherent or incoherent total cross section of the neutron on the nuclei of the sample. Since the scattering lengths for neutron scattering are sensitive on various isotopes and nuclear spins (4.1) the coherence phase relations may be lost. This leads to a contribution of incoherent scattering which is typical for neutrons. In the double sum of (5.6) b_k and b_ℓ may be different in a random way for a stochastic distribution of the isotopes in the sample. For the average over the sample we write

$$\overline{b_k^* b_\ell} = \overline{b}_k^* \overline{b}_\ell = \mid \overline{b} \mid^2 \quad \text{for} \quad k \neq \ell \tag{5.11}$$

For $\ell = k$

$$\overline{b_k^* b_\ell} = \overline{\mid b_k \mid^2} = \overline{\mid b \mid^2} \tag{5.12}$$

is obvious. For the double sum we then get

$$\sum_{k \neq \ell} \overline{b_k^* b_\ell} = N(N-1) \mid \overline{b} \mid^2 \tag{5.13}$$

$$\sum_{k=\ell} \overline{b_k^* b_\ell} = N\overline{\mid b \mid^2} \tag{5.14}$$

and hence all together

$$\begin{aligned} \sum_{k,\ell} \overline{b_k^* b_\ell} &= N^2 \mid \overline{b} \mid^2 + N(\overline{\mid b \mid^2} - \mid \overline{b} \mid^2) \\ &= N^2 \mid \overline{b} \mid^2 + N\overline{(\delta b)^2} \end{aligned} \tag{5.15}$$

The first term - proportional to N^2 - describes the coherent scattering, whereas the second term is responsible for the incoherent part. Note that the incoherent part contains in the matrix element of (5.9) only self-correlation terms with $\ell = k$.

Hence we have two scattering function S_c and S_{inc}, one being proportional to

$$C \sim \sigma_c = 4\pi \mid \overline{b} \mid^2 \qquad \text{and} \qquad C \sim \sigma_{in} = 4\pi\overline{(\delta b)^2} \tag{5.16}$$

A similar phenomenon may appear in X-ray scattering at an alloy.

ii) **magnetic neutron scattering**

$$C = \frac{k_f}{k_i}\gamma^2 r_0^2 \left\{\frac{1}{2} g F(\vec{\kappa})\right\}^2 \tag{5.17}$$

$r_0 = \frac{e^2}{mc^2}$ is the classical electron radius and γ the gyro-factor of the neutron. g is a Lande factor taking into consideration the contributions of orbital - and spin-magnetization [6].

iii) **X-ray - Thomson scattering**

$$C = \frac{\omega_f}{\omega_i} r_0^2 (\vec{\epsilon_i} \cdot \vec{\epsilon_f})^2 \mid F(\vec{\kappa}) \mid^2 \tag{5.18}$$

with $F(\vec{\kappa})$ as atomic form factor. The multiplicative split of an atomic form factor is obviously only allowed for the cases where the Born-Oppenheimer approximation is valid.

iv) **X-ray magnetic scattering**
Even for pure magnetic scattering we cannot write the cross section in the simple form (5.8). As indicated by (4.52) we have to introduce two form factors - one for orbital, the other for spin-contributions. We hence refrain from writing down a closed expression at this place (see Ref. [4]).

With reference to (5.9) a few remarks are in order concerning the averaging procedure over the initial states of the sample. This is where the temperature dependence of the scattering process enters. The scattering function has the general form

$$\sum_i p_i < i \mid \hat{Q} \mid i > \tag{5.19}$$

which represents the statistical expectation value of the observable $\hat{Q}$ of the sample. For a many body system the probabilities of the populations depend on its temperature. If we assume **the sample to be in thermal equilibrium** this population is given by the **canonical ensemble**. The density operator of the sample is given by its hamiltonian H_s

$$\rho = \frac{1}{Sp(e^{-\beta H_s})} \cdot e^{-\beta H_s} \tag{5.20}$$

and its temperature $\beta = 1/kT$

The trace (spur) represents the **canonical partition function**

$$Z = Sp(e^{-\beta H_s}) = e^{-\beta F_s} \tag{5.21}$$

where F_s **is the free energy**

$$F_s = -kTlnZ \tag{5.22}$$

We can then write for (5.19)

$$< Q >_T = Sp(\rho\hat{Q}) = \frac{1}{Z} Sp(e^{-\beta H_s}\hat{Q}) \tag{5.23}$$

By this procedure we assume that the scattering is an isentropic (adiabatic) process, that is the perturbation of the sample by the probe is efficiently dissipated over the sample by the corresponding degrees of freedom. This is an important condition, which has to be fulfilled in order to guarantee the applicability of a linear response approach.

5.3 The Correleation Function

The $A_{\vec{\kappa}}(\vec{X}_j)$ are Fourier transforms of spatial operator functions. For example

$$\begin{aligned} \sum_j e^{-i\vec{\kappa}\vec{x}_j}\vec{s}_j &= \int d^3x e^{i\vec{\kappa}\vec{x}} \sum_j \vec{s}_j \delta(\vec{x} - \vec{x}_j) \\ &= \frac{1}{2\mu_B} \int d^3x e^{i\vec{\kappa}\vec{x}} \vec{M}_s(\vec{x}) \end{aligned} \tag{5.24}$$

with

$$\vec{M}_s(\vec{x}) = -2\mu_B \sum_j \vec{s}_j \delta(\vec{x} - \vec{x}_j) \tag{5.25}$$

or for the mass density

$$\sum_j e^{-i\vec{\kappa}\vec{X}_j} = \int d^3x e^{i\vec{\kappa}\vec{x}} \sum_j \delta(\vec{x} - \vec{X}_j) = \int d^3x e^{i\vec{\kappa}\vec{x}} \rho(\vec{x}) \tag{5.26}$$

with

$$\rho(\vec{x}) = \sum_j \delta(\vec{x} - \vec{X}_j) \tag{5.27}$$

The product of Fourier transforms in reciprocal space corresponds to a Fourier transform of a convolution in real space. We can therefore write for the back-transform of the scattering function

$$\boxed{C(\vec{x},t) = \frac{1}{N}\int d^3x' < \tilde{A}(\vec{x}\,',t)\tilde{A}(\vec{x}-x\,',0) >_T} \tag{5.28}$$

which is - for neutron scattering nothing else than (1.8). The product contains a sum over ℓ and k - the scattering centers. According to (5.15) we distinguish

i) sum over all ℓ and k - coherent correlation function
ii) sum over $\ell = k$ only - self correlation for incoherent scattering

The correlation function contains the information about structure and collective excitations in dependence of the temperature of the sample. The incoherent correlation function describes among others diffusion processes in the sample. For very large times we can assume that the time dependent correlations have faded, that is

$$\lim_{t\to\infty} < A^+_{\vec{\kappa}}(0)A_{\vec{\kappa}}(t) >=< A^+_{\vec{\kappa}} >< A_\kappa > \tag{5.29}$$

Accordingly we may split C into

$$C(\vec{x},t) = C(\vec{x},\infty) + C'(\vec{x},t) \tag{5.30}$$

with

$$\lim_{t\to\infty} C'(\vec{x},t) = 0 \tag{5.31}$$

$C(\vec{x},\infty)$ is then related to the persistent structure of the sample (e.g. crystal structure) and is hence determined by elastic scattering. $C'(\vec{x},t)$ - as a consequence of its time dependence introduces other frequency components into the wave of the scattered particles then the incident one. Therefore C' is determined by the inelastic scattering events.

The general properties of the scattering - and the correlation function, as well as their connection to a linear response theory are presented in the literature [6] and have been discussed on an earlier occasion [7] at this sequence of schools.

References

[1] L. Van Hove, *Phys. Rev.* 95, 249, 1374 (1954)

[2] E. Lieb in *The Stability of Matter*, ed. W. Thirring, (Springer, Berlin, 1997), ISBN 3-54061565-2

[3] M. Blume, *J. Appl. Phys.* 57, 1, 3615 (1985)

[4] S.W. Lovesey, *J. Phys. C: Solid State Phys.* 20, 5625 (1987); M. Blume, D. Gibbs, *Phys. Rev. B* 37, 4, 1779 (1988)

[5] W. Zinn, 23. Ferienkurs 23.3. - 3.4.1992, Forschungszentrum Jülich, ISBN 3-89336-180-4

[6] S.W. Lovesey, *Theory of Neutron Scattering from Condensed Matter*, Vol. 1 and 2 (Clarendon Press, Oxford, 1987)

[7] W.E. Fischer, *4th Summer School on Neutron Scattering, Introduction into Theoretical Principles* (Zuoz 1996), PSI-Proceedings 96-02 (PSI-Villigen, 1996), p. 155