

5. DYNAMICAL THEORY AND ITS APPLICATIONS

multiplied by R , the classical electron radius, they become entirely equivalent to the corresponding quantities in neutron usage, which are lengths. It should be noted that the presence of different isotopes and the effect of nuclear spin (disordered except under very special conditions) give rise to incoherent elastic neutron scattering, which has no equivalent in the X-ray case. The scattering length corresponding to R times the atomic scattering factor for X-rays is therefore the coherent scattering length, b_{coh} , obtained by averaging the scattering length over the nuclear spin state and isotope distribution.

5.3.2.3. Absorption

Neutron absorption is related to a nuclear reaction in which the neutron combines with the absorbing nucleus to form a compound nucleus, usually in a metastable state which then decays. The scattering length describing this resonance scattering process depends on the neutron energy and contains an imaginary part associated with absorption in complete analogy with the imaginary part of the dispersion correction for the X-ray atomic scattering factors. The energies of the resonances are usually far above those of interest for crystallography, and the linear absorption coefficient varies approximately as $1/\nu$ or λ . It is important to note that, except for a very few cases (notably ^3He , ^6Li , ^{10}B , In, Cd, Gd), the absorption of neutrons is very small compared with that of X-rays, and even more so compared with that of electrons, and can be neglected to a first approximation.

5.3.2.4. Differences between neutron and X-ray scattering

There are major differences in the experimental aspects of neutron and X-ray scattering. Neutrons are only available in large facilities, where allocation of beam time to users is made on the basis of applications, and where admittance is restricted because of the hazards which nuclear technology can present in the hands of ill-intentioned users. Because of the radiation shielding necessary, as well as the large size of neutron detectors, neutron-scattering instrumentation is much bulkier than that for X-rays. Neutron beams are in some aspects similar to synchrotron radiation, in particular because in both cases the beams are initially ‘white’ and for most applications have to be monochromated. There is, however, a huge difference in the order of magnitudes of the intensities. Neutron beams are weak in comparison with laboratory X-ray sources, and weaker by many orders of magnitude than synchrotron radiation. Also, the beam sources are large in the case of neutrons, since they are essentially the moderators, whereas the source is very small in the case of synchrotron radiation, and this difference again increases the ratio of the brilliances in favour of X-rays. This encourages the use of large specimens in all neutron-scattering work, and makes the extinction problem more important than for X-rays. Furthermore, many experiments that are quick using X-rays become very slow, and give rise to impaired resolution, in the neutron case.

There are also at least two additional aspects of neutron scattering in comparison with X-ray scattering, apart from the effect of the magnetic moment associated with the intrinsic (spin) angular momentum of the neutron. On the one hand, the small velocity of neutrons, compared with the velocity of light, makes time-of-flight measurements possible, both in standard neutron diffraction and in investigations of perfect crystals. Because this velocity is of the same order of magnitude as that of ultrasound, the effect of ultrasonic excitation on neutron diffraction is slightly different from that in the X-ray case. On the other hand, the fact that neutrons have mass and a magnetic moment implies that they can be affected by external fields, such as gravity and magnetic fields, both during their propagation in air or in a vacuum and while being diffracted within crystals (Werner, 1980) (see Section 5.3.5).

Experiments completely different from the X-ray case can thus be performed with perfect crystals and with neutron interferometers (see Sections 5.3.6 and 5.3.7.3).

5.3.2.5. Translating X-ray dynamical theory into the neutron case

As shown in Chapter 5.1, the basic equations of dynamical theory, *viz* Maxwell’s equations for the X-ray case and the time-independent Schrödinger equation in the neutron case, have exactly the same form when the effect of the neutron spin can be neglected, *i.e.* in situations that do not involve magnetism and when no externally applied potential is taken into account. The translation scheme for the scattering factors and structure factors is described above. The one formal difference is that the wavefunction is scalar in the neutron case, hence there is no equivalent to the parallel and perpendicular polarizations of the X-ray situation: C in equation (5.1.2.20) of Chapter 5.1 should therefore be set to 1.

The physics of neutron diffraction by perfect crystals is therefore expected to be very similar to that of X-ray diffraction, with the existence of wavefields, *Pendellösung* effects, anomalous transmission, intrinsic rocking-curve shapes and reflectivity *versus* thickness behaviour in direct correspondence. All experimental tests of these predictions confirm this view (Section 5.3.6).

Basic discussions of dynamical neutron scattering are given by Stassis & Oberteuffer (1974), Sears (1978), Rauch & Petrascheck (1978), and Squires (1978).

5.3.3. Neutron spin, and diffraction by perfect magnetic crystals

5.3.3.1. Polarization of a neutron beam and the Larmor precession in a uniform magnetic field

A polarized neutron beam is represented by a two-component spinor,

$$|\varphi\rangle = \begin{pmatrix} c \\ d \end{pmatrix} = c \begin{pmatrix} 1 \\ 0 \end{pmatrix} + d \begin{pmatrix} 0 \\ 1 \end{pmatrix},$$

which is the coherent superposition of two states, of different amplitudes c and d , polarized in opposite directions along the spin-quantization axis. The spinor components c and d are generally space- and time-dependent. We suppose that $\langle\varphi|\varphi\rangle = cc^* + dd^* = 1$. The polarization vector \mathbf{P} is defined as

$$\mathbf{P} = \langle\varphi|\boldsymbol{\sigma}|\varphi\rangle,$$

where the vector $\boldsymbol{\sigma}$ represents the set of Pauli matrices σ_x , σ_y and σ_z . The components of \mathbf{P} are

$$\begin{aligned} P_x &= (c^* \ d^*)\sigma_x \begin{pmatrix} c \\ d \end{pmatrix} = (c^* \ d^*) \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} c \\ d \end{pmatrix} \\ &= c^*d + cd^* \\ P_y &= (c^* \ d^*)\sigma_y \begin{pmatrix} c \\ d \end{pmatrix} = (c^* \ d^*) \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} c \\ d \end{pmatrix} \quad (5.3.3.1) \\ &= i(cd^* - c^*d) \\ P_z &= (c^* \ d^*)\sigma_z \begin{pmatrix} c \\ d \end{pmatrix} = (c^* \ d^*) \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} c \\ d \end{pmatrix} \\ &= cc^* - dd^*, \end{aligned}$$

from which it is clearly seen that, unlike P_z , the polarization components P_x and P_y depend on the phase difference between the spinor components c and d .

5.3. DYNAMICAL THEORY OF NEUTRON DIFFRACTION

In a region of a vacuum in which a uniform magnetic field \mathbf{B} is present, a neutron beam experiences a magnetic potential energy represented by the matrix

$$-\mu_n \boldsymbol{\sigma} \cdot \mathbf{B} = \begin{pmatrix} -\mu_n B & 0 \\ 0 & \mu_n B \end{pmatrix},$$

μ_n being the neutron magnetic moment, if the directions of \mathbf{B} and of the spin-quantization axis coincide. Consequently, different indices of refraction $n = 1 \pm (\mu_n B / 2E)$, where E is the neutron energy, should be associated with the spinor components c and d ; this induces between these spinor components a phase difference which is a linear function of the time (or, equivalently, of the distance travelled by the neutrons), hence, according to (5.3.3.1), a rotation around the magnetic field of the component of the neutron polarization perpendicular to this magnetic field. The time frequency of this so-called Larmor precession is $2\mu_n B / h$, where h is Planck's constant.

A neutron beam may be partially polarized; such a beam is conveniently represented by a spin-density matrix ρ , which is the statistical average of the spin-density matrices associated to the polarized beams which are mixed incoherently, the density matrix associated to the spinor

$$|\varphi\rangle = \begin{pmatrix} c \\ d \end{pmatrix}$$

being

$$|\varphi\rangle\langle\varphi| = \begin{pmatrix} c \\ d \end{pmatrix} \begin{pmatrix} c^* & d^* \end{pmatrix} = \begin{pmatrix} cc^* & cd^* \\ c^*d & dd^* \end{pmatrix}.$$

The polarization vector \mathbf{P} is then obtained as

$$\mathbf{P} = \text{Tr}(\boldsymbol{\sigma}\rho). \quad (5.3.3.2)$$

In the common case of a non-polarized beam, the spin-density matrix is

$$\rho = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}.$$

It is easily seen that all components of \mathbf{P} are then equal to 0.

Equation (5.3.3.2) is therefore applicable to the general case (polarized, partially polarized or non-polarized beam). The inverse relation giving the density matrix ρ as function of \mathbf{P} is

$$\rho = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \frac{1}{2} \mathbf{P} \cdot \boldsymbol{\sigma}. \quad (5.3.3.3)$$

5.3.3.2. Magnetic scattering by a single ion having unpaired electrons

The spin and orbital motion of unpaired electrons in an atom or ion give rise to a surrounding magnetic field $\mathbf{B}(\mathbf{r})$ which acts on the neutron *via* the magnetic potential energy $-\boldsymbol{\mu}_n \cdot \mathbf{B}(\mathbf{r})$, where $\boldsymbol{\mu}_n$ is the neutron magnetic moment. Since this is a long-range interaction, in contrast to the nuclear interaction, the magnetic scattering length p , which is proportional to the Fourier transform of the magnetic potential energy distribution $-\boldsymbol{\mu}_n \cdot \mathbf{B}(\mathbf{r})$, depends on the angle of scattering.

The classical relation $\text{div } \mathbf{B}(\mathbf{r}) = 0$ shows clearly that the vector $\mathbf{B}(\mathbf{s})$, which is the Fourier transform of $\mathbf{B}(\mathbf{r})$, is perpendicular to the reciprocal-space vector \mathbf{s} . If we consider the magnetic field $\mathbf{B}(\mathbf{r})$ as resulting from a point-like magnetic moment $\boldsymbol{\mu}$ at position $\mathbf{r} = 0$, we get

$$\mathbf{B}(\mathbf{r}) = \frac{\mu_0}{4\pi} \text{curl} \frac{\boldsymbol{\mu} \times \mathbf{r}}{r^3},$$

where $\mu_0 = 4\pi \times 10^{-7} \text{ H m}^{-1}$ is the permittivity of a vacuum and

\times denotes the cross product. $\mathbf{B}(\mathbf{r})$ can be Fourier-transformed into

$$\mathbf{B}(\mathbf{s}) = \mu_0 \mathbf{s} \times \frac{\boldsymbol{\mu} \times \mathbf{s}}{s^2} = \mu_0 \boldsymbol{\mu}_\perp(\mathbf{s}), \quad (5.3.3.4)$$

where $\boldsymbol{\mu}_\perp(\mathbf{s})$ is the projection of $\boldsymbol{\mu}$ on the plane perpendicular to \mathbf{s} (reflecting plane).

This result can be applied by volume integration to the more general case of a spatially extended magnetization distribution, which for a single magnetic ion corresponds to the atomic shell of the unpaired electrons. It is thus shown that the magnetic scattering length is proportional to $\boldsymbol{\mu}_n \cdot \boldsymbol{\mu}_{i\perp}$, where $\boldsymbol{\mu}_{i\perp}$ is the projection of the magnetic moment of the ion on the reflecting plane.

For a complete description of magnetic scattering, which involves the spin-polarization properties of the scattered beam, it is necessary to represent the neutron wavefunction in the form of a two-component spinor and the ion's magnetic moment as a spin operator which is a matrix expressed in terms of the Pauli matrices $\boldsymbol{\sigma} (\sigma_x, \sigma_y, \sigma_z)$. The magnetic scattering length is therefore itself a (2×2) matrix:

$$(p) = -(2\pi m / h^2) \mu_n \boldsymbol{\sigma} \cdot \mathbf{B}(\mathbf{s}) = -\mu_0 (2\pi m / h^2) \mu_n \boldsymbol{\sigma} \cdot \boldsymbol{\mu}_{i\perp}(\mathbf{s}) f_i(\sin \theta / \lambda), \quad (5.3.3.5)$$

where $f_i(\sin \theta / \lambda)$ is the dimensionless magnetic form factor of the ion considered and tends towards a maximum value of 1 when the scattering angle θ tends towards 0 (forward scattering). The value of $\mu_0 (2\pi m / h^2) \mu_n \mu_i$ is $p_1 = 2.70 \times 10^{-15} \text{ m}$ for $\mu_i = 1$ Bohr magneton.

According to (5.3.3.4) or (5.3.3.5), there is no magnetic scattering in directions such that the scattering vector \mathbf{s} is in the same direction as the ion magnetic moment $\boldsymbol{\mu}_i$. Magnetic scattering effects are maximum when \mathbf{s} and $\boldsymbol{\mu}_i$ are perpendicular.

The matrix (p) is diagonal if the direction of $\boldsymbol{\mu}_{i\perp}(\mathbf{s})$ is chosen as the spin-quantization axis. Therefore, there is no spin-flip scattering if the incident beam is polarized parallel or antiparallel to the direction of $\boldsymbol{\mu}_{i\perp}(\mathbf{s})$.

It is more usual to choose the spin-quantization axis (Oz) along $\boldsymbol{\mu}_i$. Let β be the angle between the vectors $\boldsymbol{\mu}_i$ and \mathbf{s} ; the (x, y, z) components of $\boldsymbol{\mu}_{i\perp}(\mathbf{s})$ are then $(-\mu_i \sin \beta \cos \beta, 0, \mu_i \sin^2 \beta)$ if the y axis is chosen along $\boldsymbol{\mu}_i \times \mathbf{s}$. The total scattering length, which is the sum of the nuclear and the magnetic scattering lengths, is then represented by the matrix

$$(q) = \begin{pmatrix} b + p \sin^2 \beta & -p \sin \beta \cos \beta \\ -p \sin \beta \cos \beta & b - p \sin^2 \beta \end{pmatrix}, \quad (5.3.3.6)$$

where b is the nuclear scattering length and

$$p = -\mu_0 \frac{2\pi m}{h^2} \mu_n \mu_i f_i \left(\frac{\sin \theta}{\lambda} \right) = -p_1 \mu_i f_i \left(\frac{\sin \theta}{\lambda} \right),$$

with μ_i expressed in Bohr magnetons. The relations

$$(q) \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} b + p \sin^2 \beta \\ -p \sin \beta \cos \beta \end{pmatrix} \quad \text{and} \\ (q) \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} -p \sin \beta \cos \beta \\ b - p \sin^2 \beta \end{pmatrix}$$

show clearly that the diagonal and the non-diagonal elements of the matrix (q) are, respectively, the spin-flip and the non-spin-flip scattering lengths. It is usual to consider the scattering cross sections, which are the measurable quantities. The cross sections for neutrons polarized parallel or antiparallel to the ion magnetic moment are

$$(d\sigma / d\Omega)_\pm = b^2 \pm 2bp \sin^2 \beta + (p \sin \beta)^2. \quad (5.3.3.7)$$