

8.7. ANALYSIS OF CHARGE AND SPIN DENSITIES

$$\begin{aligned} \text{cov}(\rho_{\text{obs},A}, \rho_{\text{obs},B}) &\simeq \sum \frac{\partial \rho_{\text{obs},A}}{\partial F_{\text{obs}}(\mathbf{h})} \frac{\partial \rho_{\text{obs},B}}{\partial F_{\text{obs}}(\mathbf{h})} \sigma^2 [F_{\text{obs}}(\mathbf{h})] \\ &\simeq \frac{2}{V^2} \sum_{1/2} \sigma^2(F_{\text{obs}}) [\cos 2\pi(\mathbf{r}_A + \mathbf{r}_B) \cdot \mathbf{h} \\ &\quad + \cos 2\pi(\mathbf{r}_A - \mathbf{r}_B) \cdot \mathbf{h}], \end{aligned} \quad (8.7.3.95)$$

where the latter equality is specific for $P\bar{1}$, and $\sum_{1/2}$ indicates summation over a hemisphere in reciprocal space. In general, the second term rapidly averages to zero as h_{max} increases, while the first term may be replaced by its average

$$\langle \cos 2\pi(\mathbf{r}_A - \mathbf{r}_B) \cdot \mathbf{h} \rangle = 3(\sin u - u \cos u)/u^3 \equiv C(u), \quad (8.7.3.96)$$

with $u = 2\pi|\mathbf{r}_A - \mathbf{r}_B|/h_{\text{max}}$, or $\text{cov}(\rho_{\text{obs},A}, \rho_{\text{obs},B}) \simeq (2/V^2)C(u) \times \sum_{1/2} \sigma^2(F_0)$ and $\sigma^2(\rho_{\text{obs}}) \simeq (2/V^2) \sum_{1/2} \sigma^2(F_0)$, a relation derived earlier by Cruickshank (1949). A discussion of the applicability of this expression in other centrosymmetric space groups is given by Rees (1976).

8.7.3.9. Uncertainties in derived functions

The electrostatic moments are functions of the scale factor, the positional parameters x , y and z of the atoms, and their charge-density parameters κ and P_{imp} . The standard uncertainties in the derived moments are therefore dependent on the variances and covariances of these parameters.

If M_p represents the $m \times m$ variance–covariance matrix of the parameters p_j , and T is an $n \times m$ matrix defined by $\partial \mu^l / \partial p_j$ for the l th moment with n independent elements, the variances and covariances of the elements of m^l are obtained from

$$M_\mu = TM_p T^T. \quad (8.7.3.96a)$$

If a moment of an assembly of pseudo-atoms is evaluated, the elements of T include the effects of coordinate rotations required to transfer atomic moments into a common coordinate system.

A frequently occurring case of interest is the evaluation of the magnitude of a molecular dipole moment and its standard deviation. Defining

$$y = \mu^2 = \boldsymbol{\mu} \mathbf{G} \boldsymbol{\mu}^T, \quad (8.7.3.96b)$$

where $\boldsymbol{\mu}$ is the dipole-moment vector and \mathbf{G} is the direct-space metric tensor of the appropriate coordinate system. If \mathbf{Y} is the 1×3 matrix of the derivatives $\partial y / \partial \mu_i$,

$$\sigma^2(y) = \mathbf{Y} M_\mu \mathbf{Y}^T, \quad (8.7.3.96c)$$

where M_μ is defined by (8.7.3.96a). The standard uncertainty in μ may be obtained from $\sigma(\mu) = \sigma(y)/2\mu$. Significant contributions often result from uncertainties in the positional and charge-density parameters of the H atoms.

8.7.4. Spin densities

8.7.4.1. Introduction

Magnetism and magnetic ordering are among the central problems in condensed-matter research. One of the main issues in macroscopic studies of magnetism is a description of the magnetization density $\boldsymbol{\mu}$ as a function of temperature and applied field: phase diagrams can be explained from such studies.

Diffraction techniques allow determination of the same information, but at a microscopic level. Let $\mathbf{m}(\mathbf{r})$ be the microscopic magnetization density, a function of the position \mathbf{r} in the unit cell (for crystalline materials). Macroscopic and

microscopic magnetization densities are related by the simple expression

$$\boldsymbol{\mu} = \frac{1}{V} \int_{\text{cell}} \mathbf{m}(\mathbf{r}) \, d\mathbf{r}, \quad (8.7.4.1)$$

where V is the volume of the unit cell, $\mathbf{m}(\mathbf{r})$ is the sum of two contributions: $\mathbf{m}_s(\mathbf{r})$ originating from the spins of the electrons, and $\mathbf{m}_L(\mathbf{r})$ originating from their orbital motion.

$$\mathbf{m}(\mathbf{r}) = \mathbf{m}_s(\mathbf{r}) + \mathbf{m}_L(\mathbf{r}). \quad (8.7.4.2)$$

8.7.4.2. Magnetization densities from neutron magnetic elastic scattering

The scattering process is discussed in Section 6.1.3 and only the features that are essential to the present chapter will be summarized here.

For neutrons, the nuclear structure factor $F_N(\mathbf{h})$ is given by

$$F_N(\mathbf{h}) = \sum_j b_j T_j \exp(2\pi i \mathbf{h} \cdot \mathbf{R}_j). \quad (8.7.4.3)$$

b_j , T_j , \mathbf{R}_j are the coherent scattering length, the temperature factor, and the equilibrium position of the j th atom in the unit cell.

Let $\boldsymbol{\sigma}$ be the spin of the neutron (in units of $\hbar/2$). There is a dipolar interaction of the neutron spin with the electron spins and the currents associated with their motion. The magnetic structure factor can be written as the scalar product of the neutron spin and an ‘interaction vector’ $\mathbf{Q}(\mathbf{h})$:

$$F_M(\mathbf{h}) = \boldsymbol{\sigma} \cdot \mathbf{Q}(\mathbf{h}). \quad (8.7.4.4)$$

$\mathbf{Q}(\mathbf{h})$ is the sum of a spin and an orbital term: \mathbf{Q}_s and \mathbf{Q}_L , respectively. If $r_0 = \gamma r_e \sim 0.54 \times 10^{-12}$ cm, where γ is the gyromagnetic factor (= 1.913) of the neutron and r_e the classical Thomson radius of the electron, the spin term is given by

$$\mathbf{Q}_s(\mathbf{h}) = r_0 \hat{\mathbf{h}} \times \mathbf{M}_s(\mathbf{h}) \times \hat{\mathbf{h}}, \quad (8.7.4.5)$$

$\hat{\mathbf{h}}$ being the unit vector along \mathbf{h} , while $\mathbf{M}_s(\mathbf{h})$ is defined as

$$\mathbf{M}_s(\mathbf{h}) = \left\langle \sum_j \boldsymbol{\sigma}_j \exp(2\pi i \mathbf{h} \cdot \mathbf{r}_j) \right\rangle, \quad (8.7.4.6)$$

where $\boldsymbol{\sigma}_j$ is the spin of the electron at position \mathbf{r}_j , and angle brackets denote the ensemble average over the scattering sample. $\mathbf{M}_s(\mathbf{h})$ is the Fourier transform of the spin-magnetization density $\mathbf{m}_s(\mathbf{r})$, given by

$$\mathbf{m}_s(\mathbf{r}) = \left\langle \sum_j \boldsymbol{\sigma}_j \delta(\mathbf{r} - \mathbf{r}_j) \right\rangle. \quad (8.7.4.7)$$

This is the spin-density vector field in units of $2\mu_B$.

The orbital part of $\mathbf{Q}(\mathbf{h})$ is given by

$$\mathbf{Q}_L(\mathbf{h}) = -\frac{ir_0}{2\pi\hbar} \hat{\mathbf{h}} \times \left\langle \sum_j \mathbf{p}_j \exp(2\pi i \mathbf{h} \cdot \mathbf{r}_j) \right\rangle, \quad (8.7.4.8)$$

where \mathbf{p}_j is the momentum of the electrons. If the current density vector field is defined by

$$\mathbf{j}(\mathbf{r}) = -\frac{e}{2m} \left\langle \sum_j \{ \mathbf{p}_j \delta(\mathbf{r} - \mathbf{r}_j) + \delta(\mathbf{r} - \mathbf{r}_j) \mathbf{p}_j \} \right\rangle, \quad (8.7.4.9)$$

$\mathbf{Q}_L(\mathbf{h})$ can be expressed as

$$\mathbf{Q}_L(\mathbf{h}) = -\frac{ir_0}{2\pi\hbar} \hat{\mathbf{h}} \times \mathbf{J}(\mathbf{h}), \quad (8.7.4.10)$$

where $\mathbf{J}(\mathbf{h})$ is the Fourier transform of the current density $\mathbf{j}(\mathbf{r})$.

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The electrodynamic properties of $\mathbf{j}(\mathbf{r})$ allow it to be written as the sum of a rotational and a nonrotational part:

$$\mathbf{j}(\mathbf{r}) = \nabla\psi + \nabla \times [\mathbf{m}_L(\mathbf{r})], \quad (8.7.4.11)$$

where $\nabla\psi$ is a 'conduction' component and $\mathbf{m}_L(\mathbf{r})$ is an 'orbital-magnetization' density vector field.

Substitution of the Fourier transform of (8.7.4.11) into (8.7.4.10) leads in analogy to (8.7.4.5) to

$$\mathbf{Q}_L(\mathbf{h}) = r_0 \hat{\mathbf{h}} \times \mathbf{M}_L(\mathbf{h}) \times \hat{\mathbf{h}}, \quad (8.7.4.12)$$

where $\mathbf{M}_L(\mathbf{h})$ is the Fourier transform of $\mathbf{m}_L(\mathbf{r})$. The rotational component $\nabla\psi$ of $\mathbf{j}(\mathbf{r})$ does not contribute to the neutron scattering process. It is therefore possible to write $\mathbf{Q}(\mathbf{h})$ as

$$\mathbf{Q}(\mathbf{h}) = r_0 \hat{\mathbf{h}} \times \mathbf{M}(\mathbf{h}) \times \hat{\mathbf{h}}, \quad (8.7.4.13)$$

with

$$\mathbf{M}(\mathbf{h}) = \mathbf{M}_s(\mathbf{h}) + \mathbf{M}_L(\mathbf{h}) \quad (8.7.4.14)$$

being the Fourier transform of the 'total' magnetization density vector field, and

$$\mathbf{m}(\mathbf{r}) = \mathbf{m}_s(\mathbf{r}) + \mathbf{m}_L(\mathbf{r}). \quad (8.7.4.15)$$

As $\mathbf{Q}(\mathbf{h})$ is the projection of $\mathbf{M}(\mathbf{h})$ onto the plane perpendicular to \mathbf{h} , there is no magnetic scattering when \mathbf{M} is parallel to \mathbf{h} . It is clear from (8.7.4.13) that $\mathbf{M}(\mathbf{h})$ can be defined to any vector field $\mathbf{V}(\mathbf{h})$ parallel to \mathbf{h} , *i.e.* such that $\mathbf{h} \times \mathbf{V}(\mathbf{h}) = 0$.

This means that in real space $\mathbf{m}(\mathbf{r})$ is defined to any vector field $\mathbf{v}(\mathbf{r})$ such that $\nabla \times \mathbf{v}(\mathbf{r}) = 0$. Therefore, $\mathbf{m}(\mathbf{r})$ is defined to an arbitrary gradient.

As a result, magnetic neutron scattering cannot lead to a uniquely defined orbital magnetization density. However, the definition (8.7.4.7) for the spin component is unambiguous.

However, the integrated magnetic moment $\boldsymbol{\mu}$ is determined unambiguously and must thus be identical to the magnetic moment defined from the principles of quantum mechanics, as discussed in §8.7.4.5.1.3.

Before discussing the analysis of magnetic neutron scattering in terms of spin-density distributions, it is necessary to give a brief description of the quantum-mechanical aspects of magnetization densities.

8.7.4.3. Magnetization densities and spin densities

8.7.4.3.1. Spin-only density at zero temperature

Let us consider first an isolated open-shell system, whose orbital momentum is quenched: it is a spin-only magnetism case. Let $\hat{\mathbf{m}}_s$ be the spin-magnetization-density operator (in units of $2\mu_B$):

$$\hat{\mathbf{m}}_s = \sum_j \hat{\boldsymbol{\sigma}}_j \delta(\mathbf{r} - \mathbf{r}_j). \quad (8.7.4.16)$$

\mathbf{r}_j and $\hat{\boldsymbol{\sigma}}_j$ are, respectively, the position and the spin operator (in \hbar units) of the j th electron. This definition is consistent with (8.7.4.7).

The system is assumed to be at zero temperature, under an applied field, the quantization axis being Oz . The ground state is an eigenstate of $\hat{\mathbf{S}}^2$ and \hat{S}_z , where $\hat{\mathbf{S}}$ is the total spin:

$$\hat{\mathbf{S}} = \sum_j \hat{\boldsymbol{\sigma}}_j. \quad (8.7.4.17)$$

Let S and M_s be the eigenvalues of $\hat{\mathbf{S}}^2$ and \hat{S}_z . (M_s will in general be fixed by Hund's rule: $M_s = S$.)

$$2M_s = [n_\uparrow - n_\downarrow], \quad (8.7.4.18)$$

where n_\uparrow and n_\downarrow are the numbers of electrons with (\uparrow : $+\frac{1}{2}$) and (\downarrow : $-\frac{1}{2}$) spin, respectively.

The spin-magnetization density is along \mathbf{z} , and is given by

$$m_{Sz}(\mathbf{r}) = \left\langle \psi_{SM_s} \left| \sum_j \hat{\boldsymbol{\sigma}}_{jz} \delta(\mathbf{r} - \mathbf{r}_j) \right| \psi_{SM_s} \right\rangle. \quad (8.7.4.19)$$

$m_{Sz}(\mathbf{r})$ is proportional to the normalized spin density that was defined for a pure state in (8.7.2.10).

$$m_{Sz}(\mathbf{r}) = M_s s(\mathbf{r}). \quad (8.7.4.20)$$

If $\rho_\uparrow(\mathbf{r})$ and $\rho_\downarrow(\mathbf{r})$ are the charge densities of electrons of a given spin, the normalized spin density is defined as

$$s(\mathbf{r}) = [\rho_\uparrow(\mathbf{r}) - \rho_\downarrow(\mathbf{r})] \frac{1}{[n_\uparrow - n_\downarrow]}, \quad (8.7.4.21)$$

compared with the total charge density $\rho(\mathbf{r})$ given by

$$\rho(\mathbf{r}) = \rho_\uparrow(\mathbf{r}) + \rho_\downarrow(\mathbf{r}). \quad (8.7.4.22)$$

A strong complementarity is thus expected from joint studies of $\rho(\mathbf{r})$ and $s(\mathbf{r})$.

In the particular case of an independent electron model,

$$\rho_\alpha(\mathbf{r}) = \sum_{i=1}^{N_\alpha} |\varphi_{i\alpha}(\mathbf{r})|^2 \quad (\alpha = \uparrow, \downarrow), \quad (8.7.4.23)$$

where $\varphi_{i\alpha}(\mathbf{r})$ is an occupied orbital for a given spin state of the electron.

If the ground state is described by a correlated electron model (mixture of different configurations), the one-particle reduced density matrix can still be analysed in terms of its eigenvectors $\psi_{i\alpha}$ and eigenvalues $n_{i\alpha}$ (natural spin orbitals and natural occupancies), as described by the expression

$$\rho_\alpha(\mathbf{r}) = \sum_{i=1}^{\infty} n_{i\alpha} |\psi_{i\alpha}(\mathbf{r})|^2, \quad (8.7.4.24)$$

where $\langle \psi_{i\alpha} | \psi_{j\beta} \rangle = \delta_{ij} \delta_{\alpha\beta}$, since the natural spin orbitals form an orthonormal set, and

$$n_{i\alpha} \leq 1 \quad \sum_{i=1}^{\infty} n_{i\alpha} = n_\alpha. \quad (8.7.4.25)$$

As the quantization axis is arbitrary, (8.7.4.20) can be generalized to

$$\mathbf{m}_s(\mathbf{r}) = \hat{\mathbf{S}} s(\mathbf{r}). \quad (8.7.4.26)$$

Equation (8.7.4.26) expresses the proportionality of the spin-magnetization density to the normalized spin density function.

8.7.4.3.2. Thermally averaged spin-only magnetization density

The system is now assumed to be at a given temperature T . S remains a good quantum number, but all (SM_s) states ($M_s = -S, \dots, S$) are now populated according to Boltzmann statistics. We are interested in the thermal equilibrium spin-magnetization density:

$$\mathbf{m}_s(\mathbf{r}) = \sum_{M_s=-S}^{+S} p(M_s) \langle \psi_{SM_s} | \hat{\mathbf{m}}_s | \psi_{SM_s} \rangle, \quad (8.7.4.27)$$

where $p(M_s)$ is the population of the M_s state. The operator $\hat{\mathbf{m}}_s$ fulfils the requirements to satisfy the Wigner-Eckart theorem (Condon & Shortley, 1935), which states that, within the S manifold, all matrix elements of $\hat{\mathbf{m}}_s$ are proportional to $\hat{\mathbf{S}}$. The consequence of this remarkable property is that

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$$\langle \psi_{SM_S} | \hat{\mathbf{m}}_s | \psi_{SM_S} \rangle = \langle \psi_{SM_S} | \hat{\mathbf{S}} | \psi_{SM_S} \rangle f_S(\mathbf{r}), \quad (8.7.4.28)$$

where $f_S(\mathbf{r})$ is a function that depends on S , but not on M_S . Comparison with (8.7.4.26) shows that $f_S(\mathbf{r})$ is the normalized spin-density function $s(\mathbf{r})$, which therefore is an invariant for the S manifold [$s(\mathbf{r})$ is calculated as the normalized spin density for any M_S]. Expression (8.7.4.27) can thus be written as

$$\mathbf{m}_s(\mathbf{r}) = \langle \mathbf{S} \rangle s(\mathbf{r}), \quad (8.7.4.29)$$

where $\langle \mathbf{S} \rangle$ is the expected value for the total spin, at a given temperature and under a given external field. As $s(\mathbf{r})$ is normalized, the total moment of the system is

$$\boldsymbol{\mu}_S = \langle \mathbf{S} \rangle.$$

The behaviour of $\langle \mathbf{S} \rangle$ is governed by the usual laws of magnetism: it can be measured by macroscopic techniques. In paramagnetic species, it will vary as T^{-1} to a first approximation; unless the system is studied at very low temperatures, the value of $\langle \mathbf{S} \rangle$ will be very small. The dependence of $\langle \mathbf{S} \rangle$ on temperature and orienting field is crucial.

Finally, (8.7.4.29) has to be averaged over vibrational modes. Except for the case where there is strong magneto-vibrational interaction, only $s(\mathbf{r})$ is affected by thermal atomic motion. This effect can be described in terms similar to those used for the charge density (Subsection 8.7.3.7).

The expression (8.7.4.29) is very important and shows that the microscopic spin-magnetization density carries two types of information: the nature of spin ordering in the system, described by $\langle \mathbf{S} \rangle$, and the delocalized nature of the electronic ground state, represented by $s(\mathbf{r})$.

8.7.4.3.3. Spin density for an assembly of localized systems

A complex magnetic system can generally be described as an ensemble of well defined interacting open-shell subsystems (ions or radicals), where each subsystem has a spin $\hat{\mathbf{S}}_n$, and S_n^2 is assumed to be a good quantum number. The magnetic interaction occurs essentially through exchange mechanisms that can be described by the Heisenberg Hamiltonian:

$$\mathcal{H} = - \sum_{n < m} J_{nm} \hat{\mathbf{S}}_n \cdot \hat{\mathbf{S}}_m - \sum_n \mathbf{B}_0 \cdot \mathbf{S}_n, \quad (8.7.4.30)$$

where J_{nm} is the exchange coupling between two subsystems, and \mathbf{B}_0 an applied external field (magneto-crystalline anisotropic effects may have to be added). Expression (8.7.4.30) is the basis for the understanding of magnetic ordering and phase diagrams. The interactions lead to a local field \mathbf{B}_n , which is the effective orienting field for the spin \mathbf{S}_n .

The expression for the spin-magnetization density is

$$\mathbf{m}_s(\mathbf{r}) = \sum_n \langle \mathbf{S}_n \rangle s_n(\mathbf{r}). \quad (8.7.4.31)$$

The relative arrangement of $\langle \mathbf{S}_n \rangle$ describes the magnetic structure; $s_n(\mathbf{r})$ is the normalized spin density of the n th subsystem.

In some metallic systems, at least part of the unpaired electron system cannot be described within a localized model: a band-structure description has to be used (Lovesey, 1984). This is the case for transition metals like Ni, where the spin-magnetization density is written as the sum of a localized part [described by (8.7.4.31)] and a delocalized part [described by (8.7.4.29)].

8.7.4.3.4. Orbital magnetization density

We must now address the case where the orbital moment is not quenched. In that case, there is some spin-orbit coupling, and the

description of the magnetization density becomes less straightforward.

The magnetic moment due to the angular momentum \mathbf{l}_j of the electron is $\frac{1}{2}\mathbf{l}_j$ (in units of $2\mu_B$). As \mathbf{l}_j does not commute with the position \mathbf{r}_j , orbital magnetization density is defined as

$$\mathbf{m}_L(\mathbf{r}) = \frac{1}{4} \left\langle \sum_j \{ \mathbf{l}_j \delta(\mathbf{r} - \mathbf{r}_j) + \delta(\mathbf{r} - \mathbf{r}_j) \mathbf{l}_j \} \right\rangle. \quad (8.7.4.32)$$

If \mathbf{L} is the total orbital moment,

$$\mathbf{L} = \sum_j \mathbf{l}_j. \quad (8.7.4.33)$$

Only open shells contribute to the orbital moment. But, in general, neither \mathbf{L}^2 nor \mathbf{L}_z are constants of motion. There is, however, an important exception, when open-shell electrons can be described as localized around atomic centres. This is the case for most rare-earth compounds, for which the $4f$ electrons are too close to the nuclei to lead to a significant interatomic overlap. It can also be a first approximation for the d electrons in transition-metal ions. Spin-orbit coupling will be present, and thus only \mathbf{L}^2 will be a constant of motion. One may define the total angular momentum

$$\mathbf{J} = \mathbf{L} + \mathbf{S} \quad (8.7.4.34)$$

and $\{J^2, L^2, S^2, J_z\}$ become the four constants of motion.

Within the J manifold of the ground state, $\mathbf{m}_s(\mathbf{r})$ and $\mathbf{m}_L(\mathbf{r})$ do not, in general, fulfil the conditions for the Wigner-Eckart theorem (Condon & Shortley, 1935), which leads to a very complex description of $\mathbf{m}(\mathbf{r})$ in practical cases.

However, the Wigner-Eckart theorem can be applied to the magnetic moments themselves, leading to

$$\mathbf{L} + 2\mathbf{S} = g\mathbf{J}, \quad (8.7.4.35)$$

with the Lande factor

$$g = 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)} \quad (8.7.4.36)$$

and, equivalently,

$$\begin{aligned} \mathbf{S} &= (g-1)\mathbf{J} \\ \mathbf{L} &= (2-g)\mathbf{J}. \end{aligned} \quad (8.7.4.37)$$

The influence of spin-orbit coupling on the scattering will be discussed in Subsection 8.7.4.5.

8.7.4.4. Probing spin densities by neutron elastic scattering

8.7.4.4.1. Introduction

The magnetic structure factor $F_M(\mathbf{h})$ [equation (8.7.4.4)] depends on the spin state of the neutron. Let $\boldsymbol{\lambda}$ be the unit vector defining a quantization axis for the neutron, which can be either parallel (\uparrow) or antiparallel (\downarrow) to $\boldsymbol{\sigma}$. If $I_{\sigma\sigma'}$ stands for the cross section where the incident neutron has the polarization σ and the scattered neutron the polarization σ' , one obtains the following basic expressions:

$$\begin{aligned} I_{\uparrow\uparrow} &= |F_n + \boldsymbol{\lambda} \cdot \mathbf{Q}|^2 \\ I_{\downarrow\downarrow} &= |F_n - \boldsymbol{\lambda} \cdot \mathbf{Q}|^2 \\ I_{\uparrow\downarrow} &= I_{\downarrow\uparrow} = |\boldsymbol{\lambda} \times \mathbf{Q}|^2. \end{aligned} \quad (8.7.4.38)$$

If no analysis of the spin state of the scattered beam is made, the two measurable cross sections are

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$$\begin{aligned} I_{\uparrow} &= I_{\uparrow\uparrow} + I_{\uparrow\downarrow} \\ I_{\downarrow} &= I_{\downarrow\downarrow} + I_{\downarrow\uparrow}, \end{aligned} \quad (8.7.4.39)$$

which depend only on the polarization of the incident neutron.

8.7.4.4.2. Unpolarized neutron scattering

If the incident neutron beam is not polarized, the scattering cross section is given by

$$I = \frac{1}{2}[I_{\uparrow} + I_{\downarrow}] = |F_N|^2 + |\mathbf{Q}|^2. \quad (8.7.4.40)$$

Magnetic and nuclear contributions are simply additive. With $x = Q/F_N$, one obtains

$$I = |F_N|^2[1 + |x|^2]. \quad (8.7.4.41)$$

Owing to its definition, $|x|$ can be of the order of 1 if and only if the atomic moments are ordered close to saturation (as in the ferro- or antiferromagnets). In many situations of structural and chemical interest, $|x|$ is small.

If, for example, $|x| \sim 0.05$, the magnetic contribution in (8.7.4.41) is only 0.002 of the total intensity. Weak magnetic effects, such as occur for instance in paramagnets, are thus hardly detectable with unpolarized neutron scattering.

However, if the magnetic structure does not have the same periodicity as the crystalline structure, magnetic components in (8.7.4.40) occur at scattering vectors for which the nuclear contribution is zero. In this case, the unpolarized technique is of unique interest. Most phase diagrams involving antiferromagnetic or helimagnetic order and modulations of such ordering are obtained by this method.

8.7.4.4.3. Polarized neutron scattering

It is generally possible to polarize the incident beam by using as a monochromator a ferromagnetic alloy, for which at a given Bragg angle $I_{\downarrow}(\text{monochromator}) = 0$, because of a cancellation of nuclear and magnetic scattering components. The scattered-beam intensity is thus I_{\uparrow} . By using a radio-frequency (r.f.) coil tuned to the Larmor frequency of the neutron, the neutron spin can be flipped into the (\downarrow) state for which the scattered beam intensity is I_{\downarrow} . This allows measurement of the 'flipping ratio' $R(\mathbf{h})$:

$$R(\mathbf{h}) = \frac{I_{\uparrow}(\mathbf{h})}{I_{\downarrow}(\mathbf{h})}. \quad (8.7.4.42)$$

As the two measurements are made under similar conditions, most systematic effects are eliminated by this technique, which is only applicable to cases where both F_N and F_M occur at the same scattering vectors. This excludes any antiferromagnetic type of ordering.

The experimental set-up is discussed by Forsyth (1980).

8.7.4.4.4. Polarized neutron scattering of centrosymmetric crystals

If λ is assumed to be in the vertical Oz direction, $\mathbf{M}(\mathbf{h})$ will in most situations be aligned along Oz by an external orienting field. If α is the angle between \mathbf{M} and \mathbf{h} , and

$$x = \frac{r_0 M(\mathbf{h})}{F_N(\mathbf{h})}, \quad (8.7.4.43)$$

with F_N expressed in the same units as r_0 , one obtains, for centrosymmetric crystals,

$$R = \frac{1 + 2x \sin^2 \alpha + x^2 \sin^2 \alpha}{1 - 2x \sin^2 \alpha + x^2 \sin^2 \alpha}. \quad (8.7.4.44)$$

If $x \ll 1$,

$$R \sim 1 + 4x \sin^2 \alpha. \quad (8.7.4.45)$$

For $x \sim 0.05$ and $\alpha = \pi/2$, R now departs from 1 by as much as 20%, which proves the enormous advantage of polarized neutron scattering in the case of low magnetism.

Equation (8.7.4.44) can be inverted, and x and its sign can be obtained directly from the observation. However, in order to obtain $M(\mathbf{h})$, the nuclear structure factor $F_N(\mathbf{h})$ must be known, either from nuclear scattering or from a calculation. All systematic errors that affect $F_N(\mathbf{h})$ are transferred to $M(\mathbf{h})$.

For two reasons, it is not in general feasible to access all reciprocal-lattice vectors. First, in order to have reasonable statistical accuracy, only reflections for which both I_{\uparrow} and I_{\downarrow} are large enough are measured; *i.e.* reflections having a strong nuclear structure factor. Secondly, $\sin \alpha$ should be as close to 1 as possible, which may prevent one from accessing all directions in reciprocal space. If \mathbf{M} is oriented along the vertical axis, the simplest experiment consists of recording reflections with \mathbf{h} in the horizontal plane, which leads to a projection of $\mathbf{m}(\mathbf{r})$ in real space. When possible, the sample is rotated so that other planes in the reciprocal space can be recorded.

Finally, if $\alpha = \pi/2$, $I_{\uparrow\downarrow}$ vanishes, and neutron spin is conserved in the experiment.

8.7.4.4.5. Polarized neutron scattering in the noncentrosymmetric case

If the space group is noncentrosymmetric, both F_N and M have a phase, φ_N and φ_M , respectively.

If for simplicity one assumes $\alpha = \pi/2$, and, defining $\delta = \varphi_M - \varphi_N$,

$$R = \frac{1 + |x|^2 + 2|x| \cos \delta}{1 + |x|^2 - 2|x| \cos \delta}, \quad (8.7.4.46)$$

which shows that $|x|$ and δ cannot both be obtained from the experiment.

The noncentrosymmetric case can only be solved by a careful modelling of the magnetic structure factor as described in Subsection 8.7.4.5.

In practice, neither the polarization of the incident beam nor the efficiency of the r.f. flipping coil is perfect. This leads to a modification in the expression for the flipping ratios [see Section 6.1.3 or Forsyth (1980)].

8.7.4.4.6. Effect of extinction

Since most measurements correspond to strong nuclear structure factors, extinction severely affects the observed data. To a first approximation, one may assume that both $I_{\uparrow\uparrow}$ and $I_{\downarrow\downarrow}$ will be affected by this process, though the spin-flip processes $I_{\uparrow\downarrow}$ and $I_{\downarrow\uparrow}$ are not. If $y_{\uparrow\uparrow}$ and $y_{\downarrow\downarrow}$ are the associated extinction factors, the observed flipping ratio is

$$R_{\text{obs}} \sim \frac{I_{\uparrow\uparrow} y_{\uparrow\uparrow} + I_{\uparrow\downarrow}}{I_{\downarrow\downarrow} y_{\downarrow\downarrow} + I_{\downarrow\uparrow}}, \quad (8.7.4.47)$$

where the expressions for $y_{\uparrow\uparrow, \downarrow\downarrow}$ are given elsewhere (Bonnet, Delapalme, Becker & Fuess, 1976).

It should be emphasized that, even in the case of small magnetic structure factors, extinction remains a serious problem since, even though $y_{\uparrow\uparrow}$ and $y_{\downarrow\downarrow}$ may be very close to each other,

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so are $I_{\uparrow\uparrow}$ and $I_{\downarrow\downarrow}$. An incorrect treatment of extinction may entirely bias the estimate of x .

8.7.4.4.7. Error analysis

In the most general case, it is not possible to obtain x , and thus $M(\mathbf{h})$ directly from R . Moreover, it is unlikely that all Bragg spots within the reflection sphere could be measured. Modelling of $M(\mathbf{h})$ is thus of crucial importance. The analysis of data must proceed through a least-squares routine fitting R_{calc} to R_{obs} , minimizing the error function

$$\varepsilon = \sum_{\mathbf{h}} \frac{1}{\sigma^2(R)} [R_{\text{obs}}(\mathbf{h}) - R_{\text{calc}}(\mathbf{h})]^2, \quad (8.7.4.48)$$

observed

where R_{calc} corresponds to a model and $\sigma^2(R)$ is the standard uncertainty for R .

If the same counting time for I_{\uparrow} and for I_{\downarrow} is assumed, only the counting statistical error may be considered important in the estimate of R , as most systematic effects cancel. In the simple case where $\alpha = \pi/2$, and the structure is centrosymmetric, a straightforward calculation leads to

$$\frac{\sigma^2(x)}{x^2} = \frac{\sigma^2(R)}{R^2} \frac{R}{(R-1)^2}; \quad (8.7.4.49)$$

with

$$\frac{\sigma^2(R)}{R^2} \sim \frac{1}{I_{\uparrow}} + \frac{1}{I_{\downarrow}}, \quad (8.7.4.50)$$

one obtains the result

$$\frac{\sigma^2(x)}{x^2} = \frac{1}{8} \frac{(F_N^2 + M^2)}{(F_N M)^2}. \quad (8.7.4.51)$$

In the common case where $x \ll 1$, this reduces to

$$\frac{\sigma^2(x)}{x^2} \sim \frac{1}{8} \frac{1}{M^2} = \frac{1}{8F_N^2} \frac{1}{x^2}. \quad (8.7.4.52)$$

In addition to this estimate, care should be taken of extinction effects.

The real interest is in $M(\mathbf{h})$, rather than x :

$$\frac{\sigma^2(M)}{M^2} = \frac{\sigma^2(x)}{x^2} + \frac{\sigma^2(F_N)}{F_N^2}. \quad (8.7.4.53)$$

If F_N is obtained by a nuclear neutron scattering experiment,

$$\sigma^2(F_N) \sim a + bF_N^2,$$

where a accounts for counting statistics and b for systematic effects.

The first term in (8.7.4.53) is the leading one in many situations. Any systematic error in F_N can have a dramatic effect on the estimate of $M(\mathbf{h})$.

8.7.4.5. Modelling the spin density

In this subsection, the case of spin-only magnetization is considered. The modelling of $\mathbf{m}_s(\mathbf{r})$ is very similar to that of the charge density.

8.7.4.5.1. Atom-centred expansion

We first consider the case where spins are localized on atoms or ions, as it is to a first approximation for compounds involving transition-metal atoms. The magnetization density is expanded as

$$\mathbf{m}_s(\mathbf{r}) = \sum_j \langle \mathbf{S}_j \rangle \langle s_j(\mathbf{r} - \mathbf{R}_j) \rangle, \quad (8.7.4.54)$$

where $\langle \mathbf{S}_j \rangle$ is the spin at site j , and $\langle s_j \rangle$ the thermally averaged normalized spin density $f_j(\mathbf{h})$, the Fourier transform of $s_j(\mathbf{r})$, is known as the 'magnetic form factor'. Thus,

$$\mathbf{M}(\mathbf{h}) = \sum_j \langle \mathbf{S}_j \rangle f_j(\mathbf{h}) T_j \exp(2\pi\mathbf{h} \cdot \mathbf{R}_j), \quad (8.7.4.55)$$

where T_j and \mathbf{R}_j are the Debye–Waller factor and the equilibrium position of the j th site, respectively.

Most measurements are performed at temperatures low enough to ensure a fair description of T_j at the harmonic level (Coppens, 1992). T_j represents the vibrational relaxation of the open-shell electrons and may, in some situations, be different from the Debye–Waller factor of the total charge density, though at present no experimental evidence to this effect is available.

8.7.4.5.1.1. Spherical-atom model

In the crudest model, $s_j(\mathbf{r})$ is approximated by its spherical average. If the magnetic electrons have a wavefunction radial dependence represented by the radial function $U(r)$, the magnetic form factor is given by

$$f(h) = \int_0^{\infty} U^2(r) 4\pi r^2 dr j_0(2\pi hr) = \langle j_0 \rangle, \quad (8.7.4.56)$$

where j_0 is the zero-order spherical Bessel function. For free atoms and ions, these form factors can be found in *IT IV* (1974).

One of the important features of magnetic neutron scattering is the fact that, to a first approximation, closed shells do not contribute to the form factor. Thus, it is a unique probe of the electronic structure of heavy elements, for which theoretical calculations even at the atomic level are questionable. Relativistic effects are important. Theoretical relativistic form factors can be used (Freeman & Desclaux, 1972; Desclaux & Freeman, 1978). It is also possible to parametrize the radial behaviour of U . A single contraction-expansion model [κ refinement, expression (8.7.3.6)] is easy to incorporate.

8.7.4.5.1.2. Crystal-field approximation

Crystal-field effects are generally of major importance in spin magnetism and are responsible for the spin state of the ions, and thus for the ground-state configuration of the system. Thus, they have to be incorporated in the model.

Taking the case of a transition-metal compound, and neglecting small contributions that may arise from spin polarization in the closed shells (see Subsections 8.7.4.9 and 8.7.4.10), the normalized spin density can be written by analogy with (8.7.3.76) as

$$s(\mathbf{r}) = \sum_{i=1}^5 \sum_{j \geq i}^5 D_{ij} d_i(\mathbf{r}) d_j(\mathbf{r}), \quad (8.7.4.57)$$

where D_{ij} is the normalized spin population matrix. If $\rho_{d\uparrow}$ and $\rho_{d\downarrow}$ are the densities of a given spin,

$$s(\mathbf{r}) = \frac{\rho_{d\uparrow} - \rho_{d\downarrow}}{n_{\uparrow} - n_{\downarrow}}, \quad (8.7.4.58)$$

the d -type charge density is

$$\rho_d(\mathbf{r}) = \rho_{d\uparrow} + \rho_{d\downarrow} \quad (8.7.4.59)$$

and is expanded in a similar way to $s(\mathbf{r})$ [see (8.7.3.76)],

$$\rho_d(\mathbf{r}) = \sum_i \sum_{j \geq i} P_{ij} d_i d_j; \quad (8.7.4.60)$$

writing

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$$\rho_{d\sigma} = \sum P_{ij}^\sigma d_i d_j \quad (8.7.4.61)$$

with $\sigma = \uparrow$ and \downarrow , one obtains

$$P_{ij} = P_{ij}^\uparrow + P_{ij}^\downarrow$$

$$D_{ij} = (P_{ij}^\uparrow - P_{ij}^\downarrow)/(n_\uparrow - n_\downarrow). \quad (8.7.4.62)$$

Similarly to $\rho_d(\mathbf{r})$, $s(\mathbf{r})$ can be expanded as

$$s(\mathbf{r}) = U^2(r) \sum_{l=0}^4 \sum_{m=0}^l \sum_p D_{lmp} y_{lmp}(\theta, \varphi), \quad (8.7.4.63)$$

where $U(r)$ describes the radial dependence. Spin polarization leads to a further modification of this expression. Since the numbers of electrons of a given spin are different, the exchange interaction is different for the two spin states, and a spin-dependent effective screening occurs. This leads to

$$\rho_{d\sigma}(\mathbf{r}) = \kappa_\sigma^3 U^2(\kappa_\sigma r) \sum_{lmp} P_{lmp}^\sigma y_{lmp}, \quad (8.7.4.64)$$

with $\sigma = \uparrow$ or \downarrow , where two κ parameters are needed.

The complementarity between charge and spin density in the crystal field approximation is obvious. At this particular level of approximation, expansions are exact and it is possible to estimate d -orbital populations for each spin state.

8.7.4.5.1.3. Scaling of the spin density

The magnetic structure factor is scaled to $F_N(\mathbf{h})$. Whether the nuclear structure factors are calculated from refined structural parameters or obtained directly from a measurement, their scale factor is not rigorously fixed.

As a result, it is not possible to obtain absolute values of the effective spins (\mathbf{S}_n) from a magnetic neutron scattering experiment. It is necessary to scale them through the sum rule

$$\sum_n \langle \mathbf{S}_n \rangle = \boldsymbol{\mu}, \quad (8.7.4.65)$$

where $\boldsymbol{\mu}$ is the macroscopic magnetization of the sample.

The practical consequences of this constraint for a refinement are similar to the electroneutrality constraint in charge-density analysis (§8.7.3.3.1).

8.7.4.5.2. General multipolar expansion

In this subsection, the localized magnetism picture is assumed to be valid. However, each subunit can now be a complex ion or a radical. Covalent interactions must be incorporated.

If $\chi_\mu(\mathbf{r})$ are atomic basis functions, the spin density $s(\mathbf{r})$ can always be written as

$$s(\mathbf{r}) = \sum_\mu \sum_\nu D_{\mu\nu} \chi_\mu(\mathbf{r} - \mathbf{R}_\mu) \chi_\nu(\mathbf{r} - \mathbf{R}_\nu), \quad (8.7.4.66)$$

an expansion that is similar to (8.7.3.9) for the charge density.

To a first approximation, only the basis functions that are required to describe the open shell have to be incorporated, which makes the expansion simple and more flexible than for the charge density.

As for the charge density, it is possible to project (8.7.4.66) onto the various sites of the ion or molecule by a multipolar expansion:

$$s(\mathbf{r}) \sim \sum_j s_j(\mathbf{r} - \mathbf{R}_j) * P_j(\mathbf{R}_j),$$

$$s_j(\mathbf{r}) = \sum_j \kappa_j^3 R_{lj}(\kappa_j r) \sum_m \sum_p D_{jlm} y_{jlm}. \quad (8.7.4.67)$$

$P(\mathbf{R}_j)$ is the vibrational p.d.f. of the j th atom, which implies use of the convolution approximation.

The monopolar terms D_{j00} give an estimate of the amount of spin transferred from a central metal ion to the ligands, or of the way spins are shared among the atoms in a radical.

The constraint (8.7.4.65) becomes

$$\sum_n \langle \mathbf{S}_n \rangle \sum_j D_{j00}^{(n)} = \boldsymbol{\mu}, \quad (8.7.4.68)$$

where (n) refers to the various subunits in the unit cell. Expansion (8.7.4.67) is the key for solving noncentrosymmetric magnetic structure (Boucherle, Gillon, Maruani & Schweizer, 1982).

8.7.4.5.3. Other types of model

One may wish to take advantage of the fact that, to a good approximation, only a few molecular orbitals are involved in $s(\mathbf{r})$. In an independent particle model, one expands the relevant orbitals in terms of atomic basis functions (LCAO):

$$\varphi_{i\sigma} = \sum_\mu c_{i\mu}^\sigma \chi_\mu^\sigma(\mathbf{r} - \mathbf{R}_\mu) \quad (8.7.4.69)$$

with $\sigma = \uparrow$ or \downarrow , and the spin density is expanded according to (8.7.4.21) and (8.7.4.23). Fourier transform of two centre-term products is required. Details can be found in Forsyth (1980) and Tofield (1975).

In the case of extended solids, expansion (8.7.4.69) must refer to the total crystal, and therefore incorporate translational symmetry (Brown, 1986).

Finally, in the simple systems such as transition metals, like Ni, there is a d - s type of interaction, leading to some contribution to the spin density from delocalized electrons (Mook, 1966). If s_l and s_d are the localized and delocalized parts of the density, respectively,

$$s(\mathbf{r}) = a s_l(\mathbf{r}) + [1 - a] s_d(\mathbf{r}), \quad (8.7.4.70)$$

where a is the fraction of localized spins. $s_d(\mathbf{r})$ can be modelled as being either constant or a function with a very small number of Fourier adjustable coefficients.

8.7.4.6. Orbital contribution to the magnetic scattering

$Q_L(\mathbf{h})$ is given by (8.7.4.10) and (8.7.4.12). Since $\nabla\psi$ in (8.7.4.11) does not play any role in the scattering cross section, we can use the restriction

$$\mathbf{j}(\mathbf{r}) = \nabla \times \mathbf{m}_L(\mathbf{r}), \quad (8.7.4.71)$$

where $\mathbf{m}_L(\mathbf{r})$ is defined to an arbitrary gradient. It is possible to constrain $\mathbf{m}_L(\mathbf{r})$ to have the form

$$\mathbf{m}_L(\mathbf{r}) = \hat{\mathbf{r}} \times \mathbf{v}(\mathbf{r}),$$

since any radial component could be considered as the radial component of a gradient. With spherical coordinates, (8.7.4.71) becomes

$$\mathbf{j} = -\frac{1}{r} \frac{\partial}{\partial r} [r\mathbf{v}],$$

which can be integrated as

$$\mathbf{r} \times \mathbf{v} = - \int_r^\infty \mathbf{y} \hat{\mathbf{r}} \times \mathbf{j}(\mathbf{y} \hat{\mathbf{r}}) dy;$$

one finally obtains

$$\mathbf{m}_L(\mathbf{r}) = \frac{1}{r} \int_{y=r}^{y=\infty} \hat{\mathbf{r}} \times \mathbf{j}(\mathbf{y} \hat{\mathbf{r}}) dy. \quad (8.7.4.72)$$

With $f(x)$ defined by

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$$f(x) = -\frac{1}{x^2} \int_0^{ix} t^l dt, \quad (8.7.4.73)$$

the expression for $\mathbf{M}_L(\mathbf{h})$ is obtained by Fourier transformation of (8.7.4.72):

$$\mathbf{M}_L(\mathbf{h}) = \frac{1}{2} \int \mathbf{r} \times \mathbf{j}(\mathbf{r}) f(\mathbf{h} \cdot \mathbf{r}) d\mathbf{r},$$

which leads to

$$\mathbf{M}_L(\mathbf{h}) = \frac{1}{4} \left\langle \sum_j \{ \mathbf{l}_j f(2\pi\mathbf{h} \cdot \mathbf{r}_j) + f(2\pi\mathbf{h} \cdot \mathbf{r}_j) \mathbf{l}_j \} \right\rangle \quad (8.7.4.74)$$

by using the definition (8.7.4.9) of \mathbf{j} .

This expression clearly shows the connection between orbital magnetism and the orbital angular momentum of the electrons. It is of general validity, whatever the origin of orbital magnetism.

Since $f(0) = 1$,

$$\mathbf{M}_L(0) = \frac{1}{2} \langle \mathbf{L} \rangle, \quad (8.7.4.75)$$

as expected.

8.7.4.6.1. The dipolar approximation

The simplest approximation involves decomposing $\mathbf{j}(\mathbf{r})$ into atomic contributions:

$$\mathbf{j}(\mathbf{r}) = \sum_n \mathbf{j}_n(\mathbf{r} - \mathbf{R}_n). \quad (8.7.4.76)$$

One obtains

$$\mathbf{M}_L = \sum_n \mathbf{M}_{L,n}(\mathbf{h}) \exp(2\pi i \mathbf{h} \cdot \mathbf{R}_n). \quad (8.7.4.77)$$

$\mathbf{M}_{L,n}(\mathbf{h})$ is the atomic magnetic orbital structure factor.

We notice that $f(2\pi\mathbf{h} \cdot \mathbf{r})$ as defined in (8.7.4.73) can be expanded as

$$f(2\pi\mathbf{h} \cdot \mathbf{r}) = 4\pi \sum_l \sum_m (i)^l \gamma_l(2\pi hr) Y_{lm}(\hat{r}) Y_{lm}^*(\hat{h}), \quad (8.7.4.78)$$

where

$$\gamma_l(x) = \frac{2}{x^2} \int_0^x t j_l(t) dt. \quad (8.7.4.79)$$

j_l is a spherical Bessel function of order l , and Y_{lm} are the complex spherical harmonic functions.

If one considers only the spherically symmetric term in (8.7.4.78), one obtains the 'dipolar approximation', which gives

$$\mathbf{M}_{L,n}^D = \frac{1}{2} \langle \mathbf{L}_n \rangle \langle \gamma_{0n} \rangle, \quad (8.7.4.80)$$

with

$$\langle \gamma_{0n} \rangle = \int_0^\infty 4\pi r^2 U_n^2(r) \gamma_0(2\pi hr) dr,$$

and

$$\gamma_0(x) = \frac{2}{x^2} (1 - \cos x). \quad (8.7.4.81)$$

$U_n(r)$ is the radial function of the atomic electrons whose orbital momentum is unquenched. Thus, in the dipolar approximation, the atomic orbital scattering is proportional to the effective orbital angular momentum and therefore to the orbital part of the magnetic dipole moment of the atom.

Within the same level of approximation, the spin structure factor is

$$\mathbf{M}_S = \sum_n \mathbf{M}_{S,n}(\mathbf{h}) \exp(2\pi i \mathbf{h} \cdot \mathbf{R}_n), \quad (8.7.4.82)$$

with

$$\mathbf{M}_{S,n}(\mathbf{h}) = \langle \mathbf{S}_n \rangle \langle j_{0n} \rangle,$$

and

$$\langle j_{0n} \rangle = \int_0^\infty 4\pi r^2 U_n^2(r) j_0(2\pi hr) dr.$$

Finally, the atomic contribution to the total magnetic structure factor is

$$\mathbf{M}_n^D = \langle \mathbf{S}_n \rangle \langle j_{0n} \rangle + \frac{1}{2} \langle \mathbf{L}_n \rangle \langle \gamma_{0n} \rangle. \quad (8.7.4.83)$$

If $\langle \mathbf{J}_n \rangle$ is the total angular momentum of atom n and g_n its gyromagnetic ratio, (8.7.4.35)–(8.7.4.37) lead to:

$$\mathbf{M}_n^D = \langle \mathbf{J}_n \rangle \left\{ [g_n - 1] \langle j_{0n} \rangle + \frac{2 - g_n}{2} \langle \gamma_{0n} \rangle \right\}. \quad (8.7.4.84a)$$

Another approach, which is applicable only to the atomic case, is often used, which is based on Racah's algebra (Marshall & Lovesey, 1971). At the dipolar approximation level, it leads to a slightly different result, according to which $\langle \gamma_{0n} \rangle$ is replaced by

$$\langle \gamma_{0n} \rangle \sim \langle j_{0n} \rangle + \langle j_{2n} \rangle. \quad (8.7.4.85)$$

The two results are very close for small \mathbf{h} where the dipolar approximation is correct. With (8.7.4.35)–(8.7.4.37), (8.7.4.84a) can also be written as

$$\mathbf{M}_n^D = \mathbf{M}_{S,n}^D + \langle \mathbf{S}_n \rangle \frac{2 - g_n}{2(g_n - 1)} \langle \gamma_{0n} \rangle, \quad (8.7.4.84b)$$

where the second term is the 'orbital correction'. Its magnitude clearly depends on the difference between g_n and 2, which is small in 3d elements but can become important for rare earths.

8.7.4.6.2. Beyond the dipolar approximation

Expressions (8.7.4.74) and (8.7.4.78) are valid in any situation where orbital scattering occurs. They can in principle be used to estimate from the diffraction experiment the contribution of a few configurations that interact due to the $\mathbf{L} \cdot \mathbf{S}$ operator. In delocalized situations, (8.7.4.74) is the most suitable approach, while Racah's algebra can only be applied to one-centre cases.

8.7.4.6.3. Electronic structure of rare-earth elements

When covalency is small, the major aims are the determination of the ground state of the rare-earth ion, and the amount of delocalized magnetization density via the conduction electrons.

The ground state $|\psi\rangle$ of the ion is written as

$$|\psi\rangle = \sum_M a_M |JM\rangle, \quad (8.7.4.86)$$

which is well suited for the Johnston (1966) and Marshall-Lovesey (1971) formulation in terms of general angular-momentum algebra. A multipolar expansion of spin and orbital components of the structure factor enables a determination of the expansion coefficient a_M (Schweizer, 1980).

8.7.4.7. Properties derivable from spin densities

The derivation of electrostatic properties from the charge density was treated in Subsection 8.7.3.4. Magnetostatic properties can be derived from the spin-magnetization density $\mathbf{m}_s(\mathbf{r})$ using parallel expressions.

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8.7.4.7.1. Vector fields

The vector potential field is defined as

$$\mathbf{A}(\mathbf{r}) = \int \frac{\mathbf{m}_s(\mathbf{r}') \times (\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^3} d\mathbf{r}'. \quad (8.7.4.87)$$

In the case of a crystal, it can be expanded in Fourier series:

$$\mathbf{A}(\mathbf{r}) = \frac{2i}{V} \sum_{\mathbf{h}} \left\{ \frac{\mathbf{M}_s(\mathbf{h}) \times \mathbf{h}}{h^2} \right\} \exp(-2\pi i \mathbf{h} \cdot \mathbf{r}); \quad (8.7.4.88)$$

the magnetic field is simply

$$\begin{aligned} \mathbf{B}(\mathbf{r}) &= \nabla \times \mathbf{A}(\mathbf{r}) \\ &= -\frac{4\pi}{V} \sum_{\mathbf{h}} \left[\frac{\mathbf{h} \times \mathbf{M}_s(\mathbf{h}) \times \mathbf{h}}{h^2} \right] \exp(-2\pi i \mathbf{h} \cdot \mathbf{r}). \end{aligned} \quad (8.7.4.89)$$

One notices that there is no convergence problem for the $\mathbf{h} = 0$ term in the $\mathbf{B}(\mathbf{r})$ expansion.

The magnetostatic energy, *i.e.* the amount of energy that is required to obtain the magnetization \mathbf{m}_s , is

$$\begin{aligned} E_{ms} &= -\frac{1}{2} \int_{\text{cell}} \mathbf{m}_s(\mathbf{r}) \cdot \mathbf{B}(\mathbf{r}) d\mathbf{r} \\ &= \frac{2\pi}{V} \sum_{\mathbf{h}} \frac{[\mathbf{M}_s(-\mathbf{h}) \times \mathbf{h}] \cdot [\mathbf{M}_s(\mathbf{h}) \times \mathbf{h}]}{h^2}. \end{aligned} \quad (8.7.4.90)$$

It is often interesting to look at the magnetostatics of a given subunit: for instance, in the case of paramagnetic species.

For example, the vector potential outside the magnetized system can be obtained in a similar way to the electrostatic potential (8.7.3.30):

$$\mathbf{A}(\mathbf{r}') = \int \frac{[\nabla \times \mathbf{m}_s(\mathbf{r})]}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}. \quad (8.7.4.91)$$

If $r' \gg r$, $1/|\mathbf{r} - \mathbf{r}'|$ can be easily expanded in powers of $1/r'$, and $\mathbf{A}(\mathbf{r}')$ can thus be obtained in powers of $1/r'$. If $\mathbf{m}_s(\mathbf{r}) = \langle \mathbf{S} \rangle s(\mathbf{r})$,

$$\mathbf{A}(\mathbf{r}') = \langle \mathbf{S} \rangle \times \int \frac{\nabla s(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}. \quad (8.7.4.92)$$

8.7.4.7.2. Moments of the magnetization density

Among the various properties that are derivable from the delocalized spin density function, the dipole coupling tensor is of particular importance:

$$D_{nij}(\mathbf{R}_n) = \int s(\mathbf{r}) \frac{[3r_{ni}r_{nj} - r_n^2 \delta_{ij}]}{r_n^5} d\mathbf{r}, \quad (8.7.4.93)$$

where \mathbf{R}_n is a nuclear position and $\mathbf{r}_n = \mathbf{r} - \mathbf{R}_n$. This dipolar tensor is involved directly in the hyperfine interaction between a nucleus with spin I_n and an electronic system with spin s , through the interaction energy

$$\sum_{i,j} I_{ni} D_{nij} S_j. \quad (8.7.4.94)$$

This tensor is measurable by electron spin resonance for either crystals or paramagnetic species trapped in matrices. The complementarity with scattering is thus of strong importance (Gillon, Becker & Ellinger, 1983).

Computational aspects are the same as in the electric field gradient calculation, $\rho(\mathbf{r})$ being simply replaced by $s(\mathbf{r})$ (see Subsection 8.7.3.4).

8.7.4.8. Comparison between theory and experiment

Since it is a measure of the imbalance between the densities associated with the two spin states of the electron, the spin-density function is a probe that is very sensitive to the exchange forces in the system. In an independent-particle model (Hartree-Fock approximation), the exchange mean field potential involves exchange between orbitals with the same spin. Therefore, if the numbers of \uparrow and \downarrow spins are different, one expects $V_{\text{exch}\uparrow}$ to be different from $V_{\text{exch}\downarrow}$. The main consequence of this is the necessity to solve two different Fock equations, one for each spin state. This is known as the spin-polarization effect: starting from a paired orbital, a slight spatial decoupling arises from this effect, and closed shells do have a participation in the spin density.

It can be shown that this effect is hardly visible in the charge density, but is enhanced in the spin density.

Spin densities are a very good probe for calculations involving this spin-polarization effect: The unrestricted Hartree-Fock approximation (Gillon, Becker & Ellinger, 1983).

From a common spin-restricted approach, spin polarization can be accounted for by a mixture of Slater determinants (configuration interaction), where the configuration interaction is only among electrons with the same spin. There is also a correlation among electrons with different spins, which is more difficult to describe theoretically. There seems to be evidence for such effects from comparison of experimental and theoretical spin densities in radicals (Delley, Becker & Gillon, 1984), where the unrestricted Hartree-Fock approximation is not sufficient to reproduce experimental facts. In such cases, local-spin-density functional theory has revealed itself very satisfactorily. It seems to offer the most efficient way to include correlation effects in spin-density functions.

As noted earlier, analysis of the spin-density function depends more on modelling than that of the charge density. Therefore, in general, 'experimental' spin densities at static densities and the problem of theoretical averaging is minor here. Since spin density involves essentially outer-electron states, resolution in reciprocal space is less important, except for analysis of the polarization of the core electrons.

8.7.4.9. Combined charge- and spin-density analysis

Combined charge- and spin-density analysis requires performing X-ray and neutron diffraction experiments at the same temperature. Magnetic neutron experiments are often only feasible around 4K, and such conditions are more difficult to achieve by X-ray diffraction. Even if the two experiments are to be performed at different temperatures, it is often difficult to identify compounds suitable for both experiments.

Owing to the common parametrization of $\rho(\mathbf{r})$ and $s(\mathbf{r})$, a combined least-squares-refinement procedure can be implemented, leading to a description of $\rho_{\uparrow}(\mathbf{r})$ and $\rho_{\downarrow}(\mathbf{r})$, the spin-dependent electron densities. Covalency parameters are obtainable together with spin polarization effects in the closed shells, by allowing ρ_{\uparrow} and ρ_{\downarrow} to have different radial behaviour.

Spin-polarization effects would be difficult to model from the spin density alone. But the arbitrariness of the modelling is strongly reduced if both ρ and s are analysed at the same time (Becker & Coppens, 1985; Coppens, Koritszansky & Becker, 1986).

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8.7.4.10. Magnetic X-ray scattering separation between spin and orbital magnetism

8.7.4.10.1. Introduction

In addition to the usual Thomson scattering (charge scattering), there is a magnetic contribution to the X-ray amplitude (de Bergevin & Brunel, 1981; Blume, 1985; Brunel & de Bergvin, 1981; Blume & Gibbs, 1988). In units of the chemical radius r_e of the electron, the total scattering amplitude is

$$A_x = F_C + F_M, \quad (8.7.4.95)$$

where F_C is the charge contribution, and F_M the magnetic part.

Let $\hat{\epsilon}$ and $\hat{\epsilon}'$ be the unit vectors along the electric field in the incident and diffracted direction, respectively. \mathbf{k} and \mathbf{k}' denote the wavevectors for the incident and diffracted beams. With these notations,

$$F_C = F(\mathbf{h}) \hat{\epsilon} \cdot \hat{\epsilon}', \quad (8.7.4.96)$$

where $F(\mathbf{h})$ is the usual structure factor, which was discussed in Section 8.7.3 [see also Coppens (1992)].

$$F_M = -i \frac{\hbar\omega}{mc^2} \{ \mathbf{M}_L(\mathbf{h}) \cdot \mathbf{A} + \mathbf{M}_S(\mathbf{h}) \cdot \mathbf{B} \}. \quad (8.7.4.97)$$

\mathbf{M}_L and \mathbf{M}_S are the orbital and spin-magnetization vectors in reciprocal space, and \mathbf{A} and \mathbf{B} are vectors that depend in a rather complicated way on the polarization and the scattering geometry:

$$\begin{aligned} \mathbf{A} &= 4 \sin^2 \theta \hat{\epsilon} \times \hat{\epsilon}' - (\hat{\mathbf{k}} + \hat{\epsilon})(\hat{\mathbf{k}} \cdot \hat{\epsilon}') + (\hat{\mathbf{k}}' \times \hat{\epsilon}')(\hat{\mathbf{k}}' \cdot \hat{\epsilon}) \\ \mathbf{B} &= \hat{\epsilon}' \times \hat{\epsilon} + (\mathbf{k}' + \epsilon')(\mathbf{k} \cdot \epsilon) - (\hat{\mathbf{k}} \times \hat{\epsilon})(\hat{\mathbf{k}} \cdot \hat{\epsilon}') \\ &\quad - (\hat{\mathbf{k}}' \times \hat{\epsilon}') \times (\hat{\mathbf{k}} \times \hat{\epsilon}). \end{aligned} \quad (8.7.4.98)$$

For comparison, the magnetic neutron scattering amplitude can be written in the form

$$F_M^{\text{neutron}} = [\mathbf{M}_L(\mathbf{h}) + \mathbf{M}_S(\mathbf{h})] \cdot \mathbf{C}, \quad (8.7.4.99)$$

with $\mathbf{C} = \hat{\mathbf{h}} \times \boldsymbol{\sigma} \times \hat{\mathbf{h}}$.

From (8.7.4.99), it is clear that spin and orbital contributions cannot be separated by neutron scattering. In contrast, the polarization dependencies of \mathbf{M}_L and \mathbf{M}_S are different in the X-ray case. Therefore, owing to the well defined polarization of synchrotron radiation, it is in principle possible to separate experimentally spin and orbital magnetization.

However, the prefactor $(\hbar\omega/mc^2) \sim 10^{-2}$ makes the magnetic contributions weak relative to charge scattering. Moreover, F_C is roughly proportional to the total number of electrons, and F_M to the number of unpaired electrons. As a result, one expects $|F_M/F_C|$ to be about 10^{-3} .

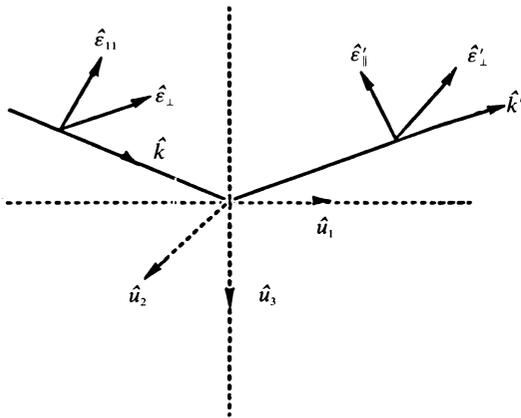


Fig. 8.7.4.1. Some geometrical definitions.

It should also be pointed out that F_M is in quadrature with F_C . In many situations, the total X-ray intensity is therefore

$$I_x = |F_C|^2 + |F_M|^2.$$

Thus, under these conditions, the magnetic effect is typically 10^{-6} times the X-ray intensity.

Magnetic contributions can be detected if magnetic and charge scattering occur at different positions (antiferromagnetic type of ordering). Furthermore, Blume (1985) has pointed out that the photon counting rate for $|F_M|^2$ at synchrotron sources is of the same order as the neutron rate at high-flux reactors.

Finally, situations where the 'interference' $F_C F_M$ term is present in the intensity are very interesting, since the magnetic contribution becomes 10^{-3} times the charge scattering.

The polarization dependence will now be discussed in more detail.

8.7.4.10.2. Magnetic X-ray structure factor as a function of photon polarization

Some geometrical definitions are summarized in Fig. 8.7.4.1, where parallel (\parallel) and perpendicular (\perp) polarizations will be chosen in order to describe the electric field of the incident and diffracted beams. In this two-dimensional basis, vectors \mathbf{A} and \mathbf{B} of (8.7.4.98) can be written as (2×2) matrices:

$$\mathbf{A} = \sin^2 \theta \begin{pmatrix} 0 & -(\hat{\mathbf{k}} + \hat{\mathbf{k}}') \\ (\hat{\mathbf{k}} + \hat{\mathbf{k}}') & 2(\hat{\mathbf{k}} \times \hat{\mathbf{k}}') \end{pmatrix} \begin{matrix} \perp \\ \parallel \end{matrix}$$

$i \rightarrow \perp \qquad \qquad \parallel \qquad \uparrow f$

(i and f refer to the incident and diffracted beams, respectively);

$$\mathbf{B} = \begin{pmatrix} \hat{\mathbf{k}} \times \hat{\mathbf{k}}' & -2\hat{\mathbf{k}}' \sin^2 \theta \\ 2\hat{\mathbf{k}} \sin^2 \theta & \hat{\mathbf{k}} \times \hat{\mathbf{k}}' \end{pmatrix}. \quad (8.7.4.100)$$

By comparison, for the Thomson scattering,

$$\hat{\epsilon} \cdot \hat{\epsilon}' = \begin{pmatrix} 1 & 0 \\ 0 & \cos 2\theta \end{pmatrix}. \quad (8.7.4.101)$$

The major difference with Thomson scattering is the occurrence of off-diagonal terms, which correspond to scattering processes with a change of polarization. We obtain for the structure factors A_{if} :

$$\begin{aligned} A_{\perp\perp} &= F - i \frac{\hbar\omega}{mc^2} (\hat{\mathbf{k}} \times \hat{\mathbf{k}}') \cdot \mathbf{M}_S \\ A_{\perp\parallel} &= -2i \frac{\hbar\omega}{mc^2} \sin^2 \theta \{ (\hat{\mathbf{k}} + \hat{\mathbf{k}}') \cdot \mathbf{M}_L + \hat{\mathbf{k}}' \cdot \mathbf{M}_S \} \\ A_{\parallel\perp} &= 2i \frac{\hbar\omega}{mc^2} \sin 2\theta \{ (\hat{\mathbf{k}} + \hat{\mathbf{k}}') \cdot \mathbf{M}_L + \hat{\mathbf{k}}' \cdot \mathbf{M}_S \} \\ A_{\parallel\parallel} &= F \cos^2 \theta - i \frac{\hbar\omega}{mc^2} (\hat{\mathbf{k}} \times \hat{\mathbf{k}}') \cdot \{ 4 \sin^2 \theta \mathbf{M}_L \mathbf{M}_S \}. \end{aligned} \quad (8.7.4.102)$$

For a linear polarization, the measured intensity in the absence of diffracted-beam polarization analysis is

$$I_\alpha = |A_{\perp\perp} \cos \alpha + A_{\perp\parallel} \sin \alpha|^2 + |A_{\parallel\perp} \cos \alpha + A_{\parallel\parallel} \sin \alpha|^2, \quad (8.7.4.103)$$

where α is the angle between \mathbf{E} and $\hat{\epsilon}$. In the centrosymmetric system, without anomalous scattering, no interference term occurs in (8.7.4.103). However, if anomalous scattering is present, $F = F' + iF''$, and terms involving $F''M_S$ or $F''M_L$ appear in the intensity expression.

The radiation emitted in the plane of the electron or positron orbit is linearly polarized. The experimental geometry is

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generally such that $(\hat{\mathbf{k}}, \hat{\mathbf{k}}')$ is a vertical plane. Therefore, the polarization of the incident beam is along $\hat{\mathbf{e}}$ ($\alpha = 0$). If a diffracted-beam analyser passes only \parallel components of the diffracted beam, one can measure $|A_{\perp\parallel}|^2$, and thus eliminate the charge scattering.

For non-polarized radiation (with a rotating anode, for example), the intensity is

$$I = \frac{1}{2}[|A_{\parallel\parallel}|^2 + |A_{\parallel\perp}|^2 + |A_{\perp\parallel}|^2 + |A_{\perp\perp}|^2]. \quad (8.7.4.104)$$

The radiation emitted out of the plane of the orbit contains an increasing amount of circularly polarized radiation. There also exist experimental devices that can produce circularly polarized radiation. For such incident radiation,

$$E_{\parallel} = \pm iE_{\perp} \quad (8.7.4.105)$$

for left- or right-polarized photons. If \mathbf{E}' is the field for the diffracted photons,

$$\begin{aligned} E'_{\perp} &= A_{\perp\perp} + iA_{\parallel\perp} \\ E'_{\parallel} &= A_{\parallel\perp} + iA_{\parallel\parallel}. \end{aligned} \quad (8.7.4.106)$$

In this case, 'mixed-polarization' contributions are in phase with F , leading to a strong interference between charge and magnetic scattering.

The case of radiation with a general type of polarization is more difficult to analyse. The most elegant formulation involves Stokes vectors to represent the state of polarization of the incident and scattered radiation (see Blume & Gibbs, 1988).

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