

## 8. REFINEMENT OF STRUCTURAL PARAMETERS

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

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

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

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

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  $\sigma$  and the scattered neutron the polarization  $\sigma'$ , 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