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

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

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

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

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

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

with

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

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

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

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 $2\mu_B$):

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

$\mathbf{r}_j$ and $\hat{\boldsymbol{\sigma}}_j$ are, respectively, the position and the spin operator (in $\hbar$ units) of the jth 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:

$$\hat{\mathbf{S}} = \sum_j \hat{\boldsymbol{\sigma}}_j. \tag{8.7.4.17}$$

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: $M_S = S$.)

$$2M_S = [n_\uparrow - n_\downarrow], \tag{8.7.4.18}$$

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

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

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

$$m_{Sz}(\mathbf{r}) = M_S s(\mathbf{r}). \tag{8.7.4.20}$$

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

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

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

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

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,

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

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

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

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

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

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

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

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 $(M_S = -S, \ldots, S)$ are now populated according to Boltzmann statistics. We are interested in the thermal equilibrium spin-magnetization density:

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

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

references