8.7. ANALYSIS OF CHARGE AND SPIN DENSITIES

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

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

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

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:

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

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

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

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

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

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

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

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

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

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

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

with the Lande factor

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

and, equivalently,

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

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:

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

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