

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_{lmp} . 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 $\mathbf{j}(\mathbf{r})$.

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