

## 8.7. ANALYSIS OF CHARGE AND SPIN DENSITIES

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  $R_{\text{calc}}$  to  $R_{\text{obs}}$ , 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  $R_{\text{calc}}$  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 [ $\kappa$  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  $\kappa$  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:

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

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

$P(\mathbf{R}_j)$  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