

8. REFINEMENT OF STRUCTURAL PARAMETERS

$$\rho_{d\sigma} = \sum P_{ij}^\sigma d_i d_j \quad (8.7.4.61)$$

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 κ 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