

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

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$$f(x) = -\frac{1}{x^2} \int_0^{ix} t^l dt, \quad (8.7.4.73)$$

the expression for $\mathbf{M}_L(\mathbf{h})$ is obtained by Fourier transformation of (8.7.4.72):

$$\mathbf{M}_L(\mathbf{h}) = \frac{1}{2} \int \mathbf{r} \times \mathbf{j}(\mathbf{r}) f(\mathbf{h} \cdot \mathbf{r}) d\mathbf{r},$$

which leads to

$$\mathbf{M}_L(\mathbf{h}) = \frac{1}{4} \left\langle \sum_j \{ \mathbf{l}_j f(2\pi\mathbf{h} \cdot \mathbf{r}_j) + f(2\pi\mathbf{h} \cdot \mathbf{r}_j) \mathbf{l}_j \} \right\rangle \quad (8.7.4.74)$$

by using the definition (8.7.4.9) of \mathbf{j} .

This expression clearly shows the connection between orbital magnetism and the orbital angular momentum of the electrons. It is of general validity, whatever the origin of orbital magnetism.

Since $f(0) = 1$,

$$\mathbf{M}_L(0) = \frac{1}{2} \langle \mathbf{L} \rangle, \quad (8.7.4.75)$$

as expected.

8.7.4.6.1. The dipolar approximation

The simplest approximation involves decomposing $\mathbf{j}(\mathbf{r})$ into atomic contributions:

$$\mathbf{j}(\mathbf{r}) = \sum_n \mathbf{j}_n(\mathbf{r} - \mathbf{R}_n). \quad (8.7.4.76)$$

One obtains

$$\mathbf{M}_L = \sum_n \mathbf{M}_{L,n}(\mathbf{h}) \exp(2\pi i \mathbf{h} \cdot \mathbf{R}_n). \quad (8.7.4.77)$$

$\mathbf{M}_{L,n}(\mathbf{h})$ is the atomic magnetic orbital structure factor.

We notice that $f(2\pi\mathbf{h} \cdot \mathbf{r})$ as defined in (8.7.4.73) can be expanded as

$$f(2\pi\mathbf{h} \cdot \mathbf{r}) = 4\pi \sum_l \sum_m (i)^l \gamma_l(2\pi h r) Y_{lm}(\hat{r}) Y_{lm}^*(\hat{h}), \quad (8.7.4.78)$$

where

$$\gamma_l(x) = \frac{2}{x^2} \int_0^x t j_l(t) dt. \quad (8.7.4.79)$$

j_l is a spherical Bessel function of order l , and Y_{lm} are the complex spherical harmonic functions.

If one considers only the spherically symmetric term in (8.7.4.78), one obtains the 'dipolar approximation', which gives

$$\mathbf{M}_{L,n}^D = \frac{1}{2} \langle \mathbf{L}_n \rangle \langle \gamma_{0n} \rangle, \quad (8.7.4.80)$$

with

$$\langle \gamma_{0n} \rangle = \int_0^\infty 4\pi r^2 U_n^2(r) \gamma_0(2\pi h r) dr,$$

and

$$\gamma_0(x) = \frac{2}{x^2} (1 - \cos x). \quad (8.7.4.81)$$

$U_n(r)$ is the radial function of the atomic electrons whose orbital momentum is unquenched. Thus, in the dipolar approximation, the atomic orbital scattering is proportional to the effective orbital angular momentum and therefore to the orbital part of the magnetic dipole moment of the atom.

Within the same level of approximation, the spin structure factor is

$$\mathbf{M}_S = \sum_n \mathbf{M}_{S,n}(\mathbf{h}) \exp(2\pi i \mathbf{h} \cdot \mathbf{R}_n), \quad (8.7.4.82)$$

with

$$\mathbf{M}_{S,n}(\mathbf{h}) = \langle \mathbf{S}_n \rangle \langle j_{0n} \rangle,$$

and

$$\langle j_{0n} \rangle = \int_0^\infty 4\pi r^2 U_n^2(r) j_0(2\pi h r) dr.$$

Finally, the atomic contribution to the total magnetic structure factor is

$$\mathbf{M}_n^D = \langle \mathbf{S}_n \rangle \langle j_{0n} \rangle + \frac{1}{2} \langle \mathbf{L}_n \rangle \langle \gamma_{0n} \rangle. \quad (8.7.4.83)$$

If $\langle \mathbf{J}_n \rangle$ is the total angular momentum of atom n and g_n its gyromagnetic ratio, (8.7.4.35)–(8.7.4.37) lead to:

$$\mathbf{M}_n^D = \langle \mathbf{J}_n \rangle \left\{ [g_n - 1] \langle j_{0n} \rangle + \frac{2 - g_n}{2} \langle \gamma_{0n} \rangle \right\}. \quad (8.7.4.84a)$$

Another approach, which is applicable only to the atomic case, is often used, which is based on Racah's algebra (Marshall & Lovesey, 1971). At the dipolar approximation level, it leads to a slightly different result, according to which $\langle \gamma_{0n} \rangle$ is replaced by

$$\langle \gamma_{0n} \rangle \sim \langle j_{0n} \rangle + \langle j_{2n} \rangle. \quad (8.7.4.85)$$

The two results are very close for small \mathbf{h} where the dipolar approximation is correct. With (8.7.4.35)–(8.7.4.37), (8.7.4.84a) can also be written as

$$\mathbf{M}_n^D = \mathbf{M}_{S,n}^D + \langle \mathbf{S}_n \rangle \frac{2 - g_n}{2(g_n - 1)} \langle \gamma_{0n} \rangle, \quad (8.7.4.84b)$$

where the second term is the 'orbital correction'. Its magnitude clearly depends on the difference between g_n and 2, which is small in 3d elements but can become important for rare earths.

8.7.4.6.2. Beyond the dipolar approximation

Expressions (8.7.4.74) and (8.7.4.78) are valid in any situation where orbital scattering occurs. They can in principle be used to estimate from the diffraction experiment the contribution of a few configurations that interact due to the $\mathbf{L} \cdot \mathbf{S}$ operator. In delocalized situations, (8.7.4.74) is the most suitable approach, while Racah's algebra can only be applied to one-centre cases.

8.7.4.6.3. Electronic structure of rare-earth elements

When covalency is small, the major aims are the determination of the ground state of the rare-earth ion, and the amount of delocalized magnetization density via the conduction electrons.

The ground state $|\psi\rangle$ of the ion is written as

$$|\psi\rangle = \sum_M a_M |JM\rangle, \quad (8.7.4.86)$$

which is well suited for the Johnston (1966) and Marshall-Lovesey (1971) formulation in terms of general angular-momentum algebra. A multipolar expansion of spin and orbital components of the structure factor enables a determination of the expansion coefficient a_M (Schweizer, 1980).

8.7.4.7. Properties derivable from spin densities

The derivation of electrostatic properties from the charge density was treated in Subsection 8.7.3.4. Magnetostatic properties can be derived from the spin-magnetization density $\mathbf{m}_s(\mathbf{r})$ using parallel expressions.