## 8.7. ANALYSIS OF CHARGE AND SPIN DENSITIES

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

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

$$M_L(\mathbf{h}) = \tfrac{1}{2} \int \mathbf{r} \times \mathbf{j}(\mathbf{r}) f(\mathbf{h} \cdot \mathbf{r}) \, d\mathbf{r},$$

which leads to

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

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 $f(0) = 1$,

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

as expected.

### 8.7.4.6.1. *The dipolar approximation*

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

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

One obtains

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

$\mathbf{M}_{L,n}(\mathbf{h})$ 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

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

where

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

$j_l$ 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

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

with

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

and

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

$U_n(r)$ 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

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

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

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

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:

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

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

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

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

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

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

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

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.

#### 8.7.4.7.1. *Vector fields*

The vector potential field is defined as

$$\mathbf{A}(\mathbf{r}) = \int \frac{\mathbf{m}_s(\mathbf{r}') \times (\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^3}\, d\mathbf{r}'. \qquad (8.7.4.87)$$

In the case of a crystal, it can be expanded in Fourier series:

$$\mathbf{A}(\mathbf{r}) = \frac{2i}{V} \sum_{\mathbf{h}} \left\{ \frac{\mathbf{M}_S(\mathbf{h}) \times \mathbf{h}}{h^2} \right\} \exp(-2\pi i \mathbf{h} \cdot \mathbf{r}); \qquad (8.7.4.88)$$

the magnetic field is simply

$$\mathbf{B}(\mathbf{r}) = \boldsymbol{\nabla} \times \mathbf{A}(\mathbf{r})$$
$$= -\frac{4\pi}{V} \sum_{\mathbf{h}} \left[ \frac{\mathbf{h} \times \mathbf{M}_S(\mathbf{h}) \times \mathbf{h}}{h^2} \right] \exp(-2\pi i \mathbf{h} \cdot \mathbf{r}). \qquad (8.7.4.89)$$

One notices that there is no convergence problem for the $\mathbf{h} = 0$ term in the $\mathbf{B}(\mathbf{r})$ expansion.

The magnetostatic energy, *i.e.* the amount of energy that is required to obtain the magnetization $\mathbf{m}_s$, is

$$E_{ms} = -\tfrac{1}{2} \int_{\text{cell}} \mathbf{m}_s(\mathbf{r}) \cdot \mathbf{B}(\mathbf{r})\, dr$$
$$= \frac{2\pi}{V} \sum_{\mathbf{h}} \frac{[\mathbf{M}_s(-\mathbf{h}) \times \mathbf{h}] \cdot [\mathbf{M}_S(\mathbf{h}) \times \mathbf{h}]}{h^2}. \qquad (8.7.4.90)$$

It is often interesting to look at the magnetostatics of a given subunit: for instance, in the case of paramagnetic species.

For example, the vector potential outside the magnetized system can be obtained in a similar way to the electrostatic potential (8.7.3.30):

$$\mathbf{A}(\mathbf{r}') = \int \frac{[\boldsymbol{\nabla} \times \mathbf{m}_s(\mathbf{r})]}{|\mathbf{r} - \mathbf{r}'|}\, d\mathbf{r}. \qquad (8.7.4.91)$$

If $r' \gg r$, $1/|\mathbf{r} - \mathbf{r}'|$ can be easily expanded in powers of $1/r'$, and $\mathbf{A}(\mathbf{r}')$ can thus be obtained in powers of $1/r'$. If $\mathbf{m}_s(\mathbf{r}) = \langle \mathbf{S} \rangle s(\mathbf{r})$,

$$\mathbf{A}(\mathbf{r}') = \langle \mathbf{S} \rangle \times \int \frac{\boldsymbol{\nabla} s(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|}\, d\mathbf{r}. \qquad (8.7.4.92)$$

#### 8.7.4.7.2. *Moments of the magnetization density*

Among the various properties that are derivable from the delocalized spin density function, the dipole coupling tensor is of particular importance:

$$D_{nij}(\mathbf{R}_n) = \int s(\mathbf{r}) \frac{[3\, r_{ni} r_{nj} - r_n^2\, \delta_{ij}]}{r_n^5}\, d\mathbf{r}, \qquad (8.7.4.93)$$

where $\mathbf{R}_n$ is a nuclear position and $\mathbf{r}_n = \mathbf{r} - \mathbf{R}_n$. This dipolar tensor is involved directly in the hyperfine interaction between a nucleus with spin $\mathbf{I}_n$ and an electronic system with spin $\mathbf{s}$, through the interaction energy

$$\sum_{i,j} I_{ni} D_{nij} S_j. \qquad (8.7.4.94)$$

This tensor is measurable by electron spin resonance for either crystals or paramagnetic species trapped in matrices. The complementarity with scattering is thus of strong importance (Gillon, Becker & Ellinger, 1983).

Computational aspects are the same as in the electric field gradient calculation, $\rho(\mathbf{r})$ being simply replaced by $s(\mathbf{r})$ (see Subsection 8.7.3.4).

#### 8.7.4.8. *Comparison between theory and experiment*

Since it is a measure of the imbalance between the densities associated with the two spin states of the electron, the spin-density function is a probe that is very sensitive to the exchange forces in the system. In an independent-particle model (Hartree–Fock approximation), the exchange mean field potential involves exchange between orbitals with the same spin. Therefore, if the numbers of ↑ and ↓ spins are different, one expects $V_{\text{exch}}\!\uparrow$ to be different from $V_{\text{exch}}\!\downarrow$. The main consequence of this is the necessity to solve two different Fock equations, one for each spin state. This is known as the spin-polarization effect: starting from a paired orbital, a slight spatial decoupling arises from this effect, and closed shells do have a participation in the spin density.

It can be shown that this effect is hardly visible in the charge density, but is enhanced in the spin density.

Spin densities are a very good probe for calculations involving this spin-polarization effect: The unrestricted Hartree–Fock approximation (Gillon, Becker & Ellinger, 1983).

From a common spin-restricted approach, spin polarization can be accounted for by a mixture of Slater determinants (configuration interaction), where the configuration interaction is only among electrons with the same spin. There is also a correlation among electrons with different spins, which is more difficult to describe theoretically. There seems to be evidence for such effects from comparison of experimental and theoretical spin densities in radicals (Delley, Becker & Gillon, 1984), where the unrestricted Hartree–Fock approximation is not sufficient to reproduce experimental facts. In such cases, local-spin-density functional theory has revealed itself very satisfactorily. It seems to offer the most efficient way to include correlation effects in spin-density functions.

As noted earlier, analysis of the spin-density function depends more on modelling than that of the charge density. Therefore, in general, 'experimental' spin densities at static densities and the problem of theoretical averaging is minor here. Since spin density involves essentially outer-electron states, resolution in reciprocal space is less important, except for analysis of the polarization of the core electrons.

#### 8.7.4.9. *Combined charge- and spin-density analysis*

Combined charge- and spin-density analysis requires performing X-ray and neutron diffraction experiments at the same temperature. Magnetic neutron experiments are often only feasible around 4 K, and such conditions are more difficult to achieve by X-ray diffraction. Even if the two experiments are to be performed at different temperatures, it is often difficult to identify compounds suitable for both experiments.

Owing to the common parametrization of $\rho(\mathbf{r})$ and $s(\mathbf{r})$, a combined least-squares-refinement procedure can be implemented, leading to a description of $\rho_\uparrow(\mathbf{r})$ and $\rho_\downarrow(\mathbf{r})$, the spin-dependent electron densities. Covalency parameters are obtainable together with spin polarization effects in the closed shells, by allowing $\rho_\uparrow$ and $\rho_\downarrow$ to have different radial behaviour.

Spin-polarization effects would be difficult to model from the spin density alone. But the arbitrariness of the modelling is strongly reduced if both $\rho$ and $s$ are analysed at the same time (Becker & Coppens, 1985; Coppens, Koritszansky & Becker, 1986).

references