

8.7. ANALYSIS OF CHARGE AND SPIN DENSITIES

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

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

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

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

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

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

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

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.