8.7. ANALYSIS OF CHARGE AND SPIN DENSITIES

$$\text{cov}\left(\rho_{\text{obs},A}, \rho_{\text{obs},B}\right) \simeq \sum \frac{\partial \rho_{\text{obs},A}}{\partial F_{\text{obs}}(\mathbf{h})} \frac{\partial \rho_{\text{obs},B}}{\partial F_{\text{obs}}(\mathbf{h})} \sigma^2 \left[F_{\text{obs}}(\mathbf{h})\right]$$

$$\simeq \frac{2}{V^2} \sum_{1/2} \sigma^2(F_{\text{obs}}) \left[\cos 2\pi(\mathbf{r}_A + \mathbf{r}_B) \cdot \mathbf{h}\right.$$

$$\left. + \cos 2\pi(\mathbf{r}_A - \mathbf{r}_B) \cdot \mathbf{h}\right], \qquad (8.7.3.95)$$

where the latter equality is specific for $P\bar{1}$, and $\sum_{1/2}$ indicates summation over a hemisphere in reciprocal space. In general, the second term rapidly averages to zero as $h_{\max}$ increases, while the first term may be replaced by its average

$$\left\langle \cos 2\pi(\mathbf{r}_A - \mathbf{r}_B) \cdot \mathbf{h}\right\rangle = 3(\sin u - u \cos u)/u^3 \equiv C(u),$$
$$(8.7.3.96)$$

with $u = 2\pi|\mathbf{r}_A - \mathbf{r}_B|h_{\max}$, or $\text{cov}(\rho_{\text{obs},A}\rho_{\text{obs},B}) \simeq (2/V^2)C(u) \times \sum_{1/2} \sigma^2(F_0)$ and $\sigma^2(\rho_{\text{obs}}) \simeq (2/V^2) \sum_{1/2} \sigma^2(F_0)$, a relation derived earlier by Cruickshank (1949). A discussion of the applicability of this expression in other centrosymmetric space groups is given by Rees (1976).

8.7.3.9. *Uncertainties in derived functions*

The electrostatic moments are functions of the scale factor, the positional parameters x, y and z of the atoms, and their charge-density parameters κ and P_{lmp}. The standard uncertainties in the derived moments are therefore dependent on the variances and covariances of these parameters.

If M_p represents the $m \times m$ variance–covariance matrix of the parameters p_j, and T is an $n \times m$ matrix defined by $\partial \mu^l / \partial p_j$ for the lth moment with n independent elements, the variances and covariances of the elements of m^l are obtained from

$$M_\mu = T M_p T^T. \qquad (8.7.3.96a)$$

If a moment of an assembly of pseudo-atoms is evaluated, the elements of T include the effects of coordinate rotations required to transfer atomic moments into a common coordinate system.

A frequently occurring case of interest is the evaluation of the magnitude of a molecular dipole moment and its standard deviation. Defining

$$y = \mu^2 = \mu G \mu^T, \qquad (8.7.3.96b)$$

where μ is the dipole-moment vector and G is the direct-space metric tensor of the appropriate coordinate system. If Y is the 1×3 matrix of the derivatives $\partial y / \partial \mu_i$,

$$\sigma^2(y) = Y M_\mu Y^T, \qquad (8.7.3.96c)$$

where M_μ is defined by (8.7.3.96a). The standard uncertainty in μ may be obtained from $\sigma(\mu) = \sigma(y)/2\mu$. Significant contributions often result from uncertainties in the positional and charge-density parameters of the H atoms.

8.7.4. Spin densities

8.7.4.1. *Introduction*

Magnetism and magnetic ordering are among the central problems in condensed-matter research. One of the main issues in macroscopic studies of magnetism is a description of the magnetization density μ as a function of temperature and applied field: phase diagrams can be explained from such studies.

Diffraction techniques allow determination of the same information, but at a microscopic level. Let $\mathbf{m}(\mathbf{r})$ be the microscopic magnetization density, a function of the position $\mathbf{r}$ in the unit cell (for crystalline materials). Macroscopic and microscopic magnetization densities are related by the simple expression

$$\mu = \frac{1}{V} \int_{\text{cell}} \mathbf{m}(\mathbf{r}) \, d\mathbf{r}, \qquad (8.7.4.1)$$

where V is the volume of the unit cell, $\mathbf{m}(\mathbf{r})$ is the sum of two contributions: $\mathbf{m}_s(\mathbf{r})$ originating from the spins of the electrons, and $\mathbf{m}_L(\mathbf{r})$ originating from their orbital motion.

$$\mathbf{m}(\mathbf{r}) = \mathbf{m}_s(\mathbf{r}) + \mathbf{m}_L(\mathbf{r}). \qquad (8.7.4.2)$$

8.7.4.2. *Magnetization densities from neutron magnetic elastic scattering*

The scattering process is discussed in Section 6.1.3 and only the features that are essential to the present chapter will be summarized here.

For neutrons, the nuclear structure factor $F_N(\mathbf{h})$ is given by

$$F_N(\mathbf{h}) = \sum_j b_j T_j \exp(2\pi i \mathbf{h} \cdot \mathbf{R}_j). \qquad (8.7.4.3)$$

b_j, T_j, $\mathbf{R}_j$ are the coherent scattering length, the temperature factor, and the equilibrium position of the jth atom in the unit cell.

Let σ be the spin of the neutron (in units of $\hbar/2$). There is a dipolar interaction of the neutron spin with the electron spins and the currents associated with their motion. The magnetic structure factor can be written as the scalar product of the neutron spin and an 'interaction vector' $\mathbf{Q}(\mathbf{h})$:

$$F_M(\mathbf{h}) = \sigma \cdot \mathbf{Q}(\mathbf{h}). \qquad (8.7.4.4)$$

$\mathbf{Q}(\mathbf{h})$ is the sum of a spin and an orbital term: $\mathbf{Q}_s$ and $\mathbf{Q}_L$, respectively. If $r_0 = \gamma r_e \sim 0.54 \times 10^{-12}$ cm, where γ is the gyromagnetic factor ($=1.913$) of the neutron and r_e the classical Thomson radius of the electron, the spin term is given by

$$\mathbf{Q}_s(\mathbf{h}) = r_0 \hat{\mathbf{h}} \times \mathbf{M}_s(\mathbf{h}) \times \hat{\mathbf{h}}, \qquad (8.7.4.5)$$

$\hat{\mathbf{h}}$ being the unit vector along $\mathbf{h}$, while $\mathbf{M}_s(\mathbf{h})$ is defined as

$$\mathbf{M}_s(\mathbf{h}) = \left\langle \sum_j \sigma_j \exp\left(2\pi i \mathbf{h} \cdot \mathbf{r}_j\right) \right\rangle, \qquad (8.7.4.6)$$

where σ_j is the spin of the electron at position $\mathbf{r}_j$, and angle brackets denote the ensemble average over the scattering sample. $\mathbf{M}_s(\mathbf{h})$ is the Fourier transform of the spin-magnetization density $\mathbf{m}_s(\mathbf{r})$, given by

$$\mathbf{m}_s(\mathbf{r}) = \left\langle \sum_j \sigma_j \delta(\mathbf{r} - \mathbf{r}_j) \right\rangle. \qquad (8.7.4.7)$$

This is the spin-density vector field in units of $2\mu_B$.

The orbital part of $\mathbf{Q}(\mathbf{h})$ is given by

$$\mathbf{Q}_L(\mathbf{h}) = -\frac{ir_0}{2\pi h} \hat{\mathbf{h}} \times \left\langle \sum_j \mathbf{p}_j \exp\left(2\pi i \mathbf{h} \cdot \mathbf{r}_j\right) \right\rangle, \qquad (8.7.4.8)$$

where $\mathbf{p}_j$ is the momentum of the electrons. If the current density vector field is defined by

$$\mathbf{j}(\mathbf{r}) = -\frac{e}{2m} \left\langle \sum_j \left\{ \mathbf{p}_j \delta(\mathbf{r} - \mathbf{r}_j) + \delta(\mathbf{r} - \mathbf{r}_j) \mathbf{p}_j \right\} \right\rangle, \qquad (8.7.4.9)$$

$\mathbf{Q}_L(\mathbf{h})$ can be expressed as

$$\mathbf{Q}_L(\mathbf{h}) = -\frac{ir_0}{2\pi h} \hat{\mathbf{h}} \times \mathbf{J}(\mathbf{h}), \qquad (8.7.4.10)$$

where $\mathbf{J}(\mathbf{h})$ is the Fourier transform of the current density $\mathbf{j}(\mathbf{r})$.

725

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