8. REFINEMENT OF STRUCTURAL PARAMETERS

of which may be obtained by rigid-body analysis of the experimental data. In general, for a translational displacement (**u**) and a librational oscillation (ω),

$$\rho_{\text{dyn}}(\mathbf{r}) = \left(\sum P_{\mu\nu}\chi_\mu\chi_\nu\right) * P(\mathbf{u}, \omega). \quad (8.7.3.84)$$

If correlation between **u** and ω can be ignored (neglect of the screw tensor **S**), $P(\mathbf{u}, \omega) = P(\mathbf{u})P(\omega)$, and both types of modes can be treated independently. For the translations

$$\langle\rho\rangle_{\text{trans}} = \sum P_{\mu\nu}\{\chi_\mu(\mathbf{r})\chi_\nu(\mathbf{r}) * P(\mathbf{u})\}$$
$$= \sum P_{\mu\nu}F^{-1}\{f_{\mu\nu}(\mathbf{h}) \cdot T_{\text{tr}}(\mathbf{h})\}, \quad (8.7.3.85)$$

where F^{-1} is the inverse Fourier transform operator, and $T_{\text{tr}}(\mathbf{h})$ is the translational temperature factor.

If **R** is an orthogonal rotation matrix corresponding to a rotation ω, we obtain for the librations

$$\langle\rho\rangle_{\text{libr}} = \sum P_{\mu\nu}\{\chi_\mu(\mathbf{Rr})\chi_\nu(\mathbf{Rr}) * P(\omega)\}$$
$$= \sum P_{\mu\nu}F^{-1}\{\langle f_{\mu\nu}(\mathbf{Rh})\rangle\}, \quad (8.7.3.86)$$

in which $f(\mathbf{h})$ has been averaged over the distribution of orientations of **h** with respect to the molecule;

$$\langle f_{\mu\nu}(\mathbf{h})\rangle = \int f_{\mu\nu}(\mathbf{Rh})P(\omega)\,d\omega. \quad (8.7.3.87)$$

Evaluation of (8.7.3.85) and (8.7.3.86) is most readily performed if the basis functions ψ have a Gaussian-type radial dependence, or are expressed as a linear combination of Gaussian radial functions.

For Gaussian products of *s* orbitals, the molecular scattering factor of the product $\psi_\mu\psi_\nu = N_\mu \exp[-\alpha_\mu(\mathbf{r} - \mathbf{r}_A)^2] \times N_\nu \exp[-\alpha_\nu(\mathbf{r} - \mathbf{r}_B)^2]$, where N_μ and N_ν are the normalization factors of the orbitals μ and ν centred on atoms A and B, is given by

$$f_{\text{stat}}^{s,s}(\mathbf{h}) = N_\mu N_\nu \exp\left(-\frac{\alpha_\mu\alpha_\nu}{\alpha_\mu + \alpha_\nu}|\mathbf{r}_A - \mathbf{r}_B|^2\right)\left(\frac{\pi}{\alpha_\mu + \alpha_\nu}\right)^{3/2}$$
$$\times \exp\left(\frac{-\pi^2|h|^2}{\alpha_\mu + \alpha_\nu}\right)\exp(2\pi i\mathbf{h} \cdot \mathbf{r}_c), \quad (8.7.3.88)$$

where the centre of density $\mathbf{r}_c$ is defined by $\mathbf{r}_c = (\alpha_\mu\mathbf{r}_A + \alpha_\nu\mathbf{r}_B)/(\alpha_\mu + \alpha_\nu)$.

For the translational modes, the temperature-factor exponent $-2\pi^2\sum_i\sum_j U_{ij}h_ih_j$ is simply added to the Gaussian exponent in (8.7.3.88) to give

$$\exp\left(-\frac{\pi^2|h|^2}{\alpha_\mu + \alpha_\nu}\right) - 2\pi^2\sum_i\sum_j U_{ij}h_ih_j.$$

For librations, we may write

$$\mathbf{Rr} = \mathbf{r} + \mathbf{u}_{\text{lib}}$$

As $(\mathbf{Rh}) \cdot \mathbf{r} = \mathbf{h} \cdot \mathbf{R}^T\mathbf{r} = \mathbf{h} \cdot \mathbf{r} - (\mathbf{Rh}) \cdot \mathbf{u}_{\text{lib}}$, for a function centred at **r**,

$$\langle\exp(2\pi\mathbf{h} \cdot \mathbf{r}_c)\rangle = \sum \exp[2\pi i(\mathbf{Rh}) \cdot \mathbf{r}_c]P(\delta)\,d\omega$$
$$= \exp(2\pi\mathbf{h} \cdot \mathbf{r}_c)\int\exp[-2\pi i(\mathbf{Rh}) \cdot \mathbf{u}_{\text{lib}}^c]P(\omega)\,d\omega, \quad (8.7.3.89)$$

which shows that for *ss* orbital products the librational temperature factor can be factored out, or

$$f_{\text{dyn}}^{s,s} = f_{\text{stat}}^{s,s}\int\exp[-2\pi i(\mathbf{Rh}) \cdot \mathbf{u}_{\text{lib}}^c]P(\omega)\,d\omega. \quad (8.7.3.90)$$

Expressions for $P(\omega)$ are described elsewhere (Pawley & Willis, 1970).

For general Cartesian Gaussian basis functions of the type

$$\psi(\mathbf{r}) = (x - x_A)^m(y - y_A)^n(z - z_A)^p\exp(-\alpha|\mathbf{r} - \mathbf{r}_A|^2),$$
$$(8.7.3.91)$$

the scattering factors are more complicated (Miller & Krauss, 1967; Stevens, Rees & Coppens, 1977), and the librational temperature factor can no longer be factored out. However, it may be shown that, to a first approximation, (8.7.3.90) can again be used. This 'pseudotranslation' approximation corresponds to a neglect of the change in orientation (but not of position) of the two-centre density function and is adequate for moderate vibrational amplitudes.

Thermally smeared density functions are obtained from the averaged reciprocal-space function by performing the inverse Fourier transform with phase factors depending on the position coordinates of each orbital product

$$\langle\rho\rangle = \frac{1}{V}\sum P_{\mu\nu}\sum_{\mathbf{h}}f_{\mu\nu}(\mathbf{h})\exp[-2\pi i\mathbf{h} \cdot (\mathbf{r} - \mathbf{r}_c)], \quad (8.7.3.92)$$

where the orbital product $\chi_\mu\chi_\nu$ is centred at $\mathbf{r}_c$. If the summation is truncated at the experimental limit of $(\sin\theta)/\lambda$, both thermal vibrations and truncation effects are properly introduced in the theoretical densities.

8.7.3.8. *Uncertainties in experimental electron densities*

It is often important to obtain an estimate of the uncertainty in the deformation densities in Table 8.7.3.1. If it is assumed that the density of the static atoms or fragments that are subtracted out are precisely known, three sources of uncertainty affect the deformation densities: (1) the uncertainties in the experimental structure factors; (2) the uncertainties in the positional and thermal parameters of the density functions that influence ρ_{calc}; and (3) the uncertainty in the scale factor k.

If we assume that the uncertainties in the observed structure factors are not correlated with the uncertainties in the refined parameters, the variance of the electron density is given by

$$\sigma^2(\Delta\rho) = \sigma^2(\rho'_{\text{obs}}) + \sigma^2(\rho_{\text{calc}}) + (\rho'_{\text{obs}})^2\frac{\sigma^2(k)}{k^2}$$
$$+ \sum_p\frac{\delta\rho_{\text{calc}}}{\delta u_p}\sigma(u_p)\rho'_{\text{obs}}\frac{\sigma(k)}{k}\gamma(u_p, k), \quad (8.7.3.93)$$

where $\rho'_{\text{obs}} = \rho_{\text{obs}}/k$, u_p is a positional or thermal parameter, and the $\gamma(u_p, k)$ are correlation coefficients between the scale factor and the other parameters (Rees, 1976, 1978; Stevens & Coppens, 1976).

Similarly, for the covariance between the deformation densities at points A and B,

$$\text{cov}(\Delta\rho_A, \Delta\rho_B) = \text{cov}(\rho_{\text{obs},A}, \rho_{\text{obs},B})/k^2$$
$$+ \text{cov}(\rho_{\text{calc},A}, \rho_{\text{calc},B})$$
$$+ \rho_{\text{obs},A}\rho_{\text{obs},B}[\sigma(k)/k]^2, \quad (8.7.3.94)$$

where it is implied that the second term includes the effect of the scale factor/parameter correlation.

Following Rees (1976), we may derive a simplified expression for the covariance valid for the space group $P\bar{1}$. Since the structure factors are not correlated with each other,

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

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

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

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 $u = 2\pi|\mathbf{r}_A - \mathbf{r}_B|h_{\text{max}}$, 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

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

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 $\partial y/\partial \mu_i$,

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

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

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

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

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

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 $\mathbf{j}(\mathbf{r})$.

references