

## 8. REFINEMENT OF STRUCTURAL PARAMETERS

## 8.7.3. Charge densities

## 8.7.3.1. Introduction

The charge density is related to the elastic X-ray scattering amplitude  $F(\mathbf{S})$  by the expression

$$\langle \rho(\mathbf{r}) \rangle = \int F(\mathbf{S}) \exp(-2\pi i \mathbf{S} \cdot \mathbf{r}) d\mathbf{S}, \quad (8.7.3.1)$$

or, for scattering by a periodic lattice,

$$\langle \rho(\mathbf{r}) \rangle = \frac{1}{V} \sum_{\mathbf{h}} F(\mathbf{h}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{r}).$$

As  $F(\mathbf{h})$  is in general complex, the Fourier transform (8.7.3.1) requires calculation of the phases from a model for the charge distribution. In the centrosymmetric case, the free-atom model is in general adequate for calculation of the signs of  $F(\mathbf{h})$ . However, for non-centrosymmetric structures in which phases are continuously variable, it is necessary to incorporate deviations from the free-atom density in the model to obtain estimates of the experimental phases.

Since the total density is dominated by the core distribution, differences between the total density  $\rho(\mathbf{r})$  and reference densities are important. The reference densities represent hypothetical states without chemical bonding or with only partial chemical bonding. Deviations from spherical, free-atom symmetry are obtained when the reference state is the *promolecule*, the superposition of free-space spherical atoms centred at the nuclear positions. This difference function is referred to as the *deformation density* (or standard deformation density)

$$\Delta\rho(\mathbf{r}) = \rho(\mathbf{r}) - \rho_p(\mathbf{r}), \quad (8.7.3.2)$$

where  $\rho_p(\mathbf{r})$  is the promolecule density. In analogy to (8.7.3.1), the deformation density may be obtained from

$$\langle \Delta\rho(\mathbf{r}) \rangle = \frac{1}{V} \sum_{\mathbf{h}} [F_{\text{obs}}(\mathbf{h}) - F_{\text{calc, free atom}}(\mathbf{h})] \exp(-2\pi i \mathbf{h} \cdot \mathbf{r}), \quad (8.7.3.3)$$

where  $F_{\text{obs}}$  and  $F_{\text{calc}}$  are in general complex.

Several other different density functions analogous to (8.7.3.3), summarized in Table 8.7.3.1, may be defined. Particularly useful for the analysis of effects of chemical bonding is the fragment deformation density, in which a chemical fragment is subtracted from the total density of a molecule. The fragment density is calculated theoretically and thermally smeared before subtraction from an experimental density. 'Prepared' atoms rather than spherical atoms may be used as a reference state to emphasize the electron-density shift due to covalent bond formation.

## 8.7.3.2. Modelling of the charge density

The electron density  $\rho(\mathbf{r})$  in the structure-factor expression

$$F_{\text{calc}}(\mathbf{h}) = \int_{\text{unit cell}} \rho(\mathbf{r}) \exp(2\pi i \mathbf{h} \cdot \mathbf{r}) d\mathbf{r} \quad (8.7.3.4a)$$

can be approximated by a sum of non-normalized density functions  $g_i(\mathbf{r})$  with scattering factor  $f_i(\mathbf{h})$  centred at  $\mathbf{r}_i$ ,

$$\rho(\mathbf{r}) = \sum_i g_i(\mathbf{r}) * \delta(\mathbf{r} - \mathbf{r}_i). \quad (8.7.3.5)$$

Substitution in (8.7.3.4a) gives

$$F(\mathbf{h}) = \sum_i f_i(\mathbf{h}) \exp(2\pi i \mathbf{h} \cdot \mathbf{r}_i). \quad (8.7.3.4b)$$

When  $g_i(\mathbf{r})$  is the spherically averaged, free-atom density, (8.7.3.4b) represents the free-atom model. A distinction is often made between *atom-centred* models, in which all functions  $g(\mathbf{r})$

Table 8.7.3.1. Definition of difference density functions

$$\Delta\rho = \frac{2}{V} \left\{ \sum_0^{1/2} (A_1 - A_2) \cos 2\pi \mathbf{h} \cdot \mathbf{r} + \sum_0^{1/2} (B_1 - B_2) \sin 2\pi \mathbf{h} \cdot \mathbf{r} \right\}$$

with  $F = A + iB$ .

(a) Residual map	$A_1, B_1$ from observations calculated with model phases. $A_2, B_2$ from refinement model.
(b) X - X deformation map	$A_1, B_1$ from observation, with model phases. $A_2, B_2$ from high-order refinement, free-atom model, or other reference state.
(c) X - N deformation map [as (b) but]	$A_2, B_2$ calculated with neutron parameters.
(d) X - (X + N) deformation map [as (b) but]	$A_2, B_2$ calculated with parameters from joint refinement of X-ray neutron data.
(e) X - X, X - N, X - (X + N) valence map	As (b), (c), (d) with $A_1, B_1$ calculated with core-electron contribution only.
(f) Dynamic model map	$A_1, B_1$ from model. $A_2, B_2$ with parameters from model refinement and free-atom functions.
(g) Static model map	$\rho_{\text{model}} - \rho_{\text{free atom}}$ , where $\rho_{\text{model}}$ is sum of static model density functions.

are centred at the nuclear positions, and models in which additional functions are centred at other locations, such as in bonds or lone-pair regions.

A simple, atom-centred model with spherical functions  $g(\mathbf{r})$  is defined by

$$\rho_{\text{atom}}(\mathbf{r}) = P_{\text{core}} \rho_{\text{core}}(\mathbf{r}) + \kappa^3 P_{\text{valence}} \rho_{\text{valence}}(\kappa \mathbf{r}). \quad (8.7.3.6)$$

This 'kappa model' allows for charge transfer between atomic valence shells through the population parameter  $P_{\text{valence}}$ , and for a change in nuclear screening with electron population, through the parameter  $\kappa$ , which represents an expansion ( $\kappa < 1$ ), or a contraction ( $\kappa > 1$ ) of the radial density distribution.

The atom-centred, spherical harmonic expansion of the electronic part of the charge distribution is defined by

$$\rho_{\text{atom}}(\mathbf{r}) = P_{\text{c}} \rho_{\text{core}}(\mathbf{r}) + P_{\text{v}} \kappa^3 \rho_{\text{valence}}(\kappa \mathbf{r}) + \sum_{l=0}^{l(\text{max})} \kappa'^3 R_l(\kappa' \zeta r) \sum_{m=0}^l \sum_p P_{lmp} d_{lmp}(\theta, \varphi), \quad (8.7.3.7)$$

where  $p = \pm$  when  $m$  is larger than 0, and  $R_l(\kappa' \zeta r)$  is a radial function.

The real spherical harmonic functions  $d_{lmp}$  and their Fourier transforms have been described in *International Tables for Crystallography*, Volume B, Chapter 1.2 (Coppens, 1992). They differ from the functions  $y_{lmp}$  by the normalization condition, defined as  $\int |d_{lmp}| d\Omega = 2 - \delta_{l0}$ . The real spherical harmonic functions are often referred to as *multipoles*, since each