

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_{obs} and F_{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 ρ_{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_{valence} , and for a change in nuclear screening with electron population, through the parameter κ , 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

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represents the component of the charge distribution $\rho(\mathbf{r})$ that gives a non-zero contribution to the integral for the electrostatic multipole moment q_{lmp} ,

$$q_{lmp} = - \int \rho_{\text{atom}}(\mathbf{r}) r^l c_{lmp} \, d\mathbf{r}, \quad (8.7.3.8)$$

where the functions c_{lmp} are the Cartesian representations of the real spherical harmonics (Coppens, 1992).

More general models include non-atom centred functions. If the wavefunction ψ in (8.7.2.4) is an antisymmetrized product of molecular orbitals ψ_i , expressed in terms of a linear combination of atomic orbitals χ_μ , $\psi_i = \sum_\mu c_{i\mu} \chi_\mu$ (LCAO formalism), the integration (8.7.2.4) leads to

$$\rho(\mathbf{r}) = \sum_\mu \sum_\nu P_{\mu\nu} \chi_\mu(\mathbf{r} - \mathbf{R}_\mu) \chi_\nu(\mathbf{r} - \mathbf{R}_\nu), \quad (8.7.3.9)$$

with \mathbf{R}_μ and \mathbf{R}_ν defining the centres of χ_μ and χ_ν , respectively, $P_{\mu\nu} = \sum_i n_i c_{i\mu} c_{i\nu}$, and the sum is over all molecular orbitals with occupancy n_i . Expression (8.7.3.9) contains products of atomic orbitals, which may have significant values for orbitals centred on adjacent atoms. In the ‘charge-cloud’ model (Hellner, 1977), these products are approximated by bond-centred, Gaussian-shaped density functions. Such functions can often be projected efficiently into the one-centre terms of the spherical harmonic multipole model, so that large correlations occur if both spherical harmonics and bond-centred functions are adjusted independently in a least-squares refinement.

According to (8.7.2.4) and (8.7.3.9), the population of the two-centre terms is related to the one-centre occupancies. A molecular-orbital based model, which implicitly incorporates such relations, has been used to describe local bonding between transition-metal and ligand atoms (Becker & Coppens, 1985).

8.7.3.3. Physical constraints

There are several physical constraints that an electron-density model must satisfy. With the exception of the electroneutrality constraint, they depend strongly on the electron density close to the nucleus, which is poorly determined by the diffraction experiment.

8.7.3.3.1. Electroneutrality constraint

Since a crystal is neutral, the total electron population must equal the sum of the nuclear charges of the constituent atoms. A constraint procedure for linear least squares that does not increase the size of the least-squares matrix has been described by Hamilton (1964). If the starting point is a neutral crystal, the constraint equation becomes

$$\sum \Delta P_i S_i = 0, \quad (8.7.3.10)$$

where $S_i = \int g(\mathbf{r}) \, d\mathbf{r}$, g being a general density function, and the ΔP_i are the shifts in the population parameters. For the multipole model, only the monopolar functions integrate to a non-zero value. For normalized monopole functions, this gives

$$\sum_{\text{monopoles}} \Delta P_i = 0. \quad (8.7.3.11)$$

If the shifts without constraints are given by the vector \mathbf{y} and the constrained shifts by \mathbf{y}_c , the Hamilton constraint is expressed as

$$\mathbf{y}_c^T = \mathbf{y}^T - \mathbf{y}^T \mathbf{Q}^T (\mathbf{Q} \mathbf{A}^{-1} \mathbf{Q}^T)^{-1} \mathbf{Q} \mathbf{A}^{-1}, \quad (8.7.3.12)$$

where the superscript T indicates transposition, \mathbf{A} is the least-squares matrix of the products of derivatives, and \mathbf{Q} is a row vector of the values of S_i for elements representing density functions and zeros otherwise.

Expression (8.7.3.12) cannot be applied if the unconstrained refinement corresponds to a singular matrix. This would be the case if all population parameters, including those of the core functions, were to be refined together with the scale factor. In this case, a new set of independent parameters must be defined, as described in Chapter 8.1 on least-squares refinements. Alternatively, one may set the scale factor to one and rescale the population parameters to neutrality after completion of the refinement. This will in general give a non-integral electron population for the core functions. The proper interpretation of such a result is that a core-like function is an appropriate component of the density basis set representing the valence electrons.

8.7.3.3.2. Cusp constraint

The electron density at a nucleus i with nuclear charge Z_i must satisfy the electron–nuclear cusp condition given by

$$\lim_{r_i \rightarrow 0} \left(\frac{\partial}{\partial r_i} + 2Z_i \right) \rho_{0i}(\mathbf{r}_i) = 0, \quad (8.7.3.13)$$

where $\rho_{0i}(\mathbf{r}_i) = (1/4\pi) \int \rho(\mathbf{r}) \, d\Omega_i$ is the spherical component of the expansion of the density around nucleus i .

Only $1s$ -type functions have non-zero electron density at the nucleus and contribute to (8.7.3.13). For the hydrogen-like atom or ion described by a single exponent radial function $R(r) = N \exp(-\zeta r)$, (8.7.3.13) gives $\zeta = 2Z/a_0$, where Z is the nuclear charge, and a_0 is the Bohr unit. Thus, a modification of ζ for $1s$ functions, as implied by (8.7.3.6) and (8.7.3.7) if applied to H atoms, leads to a violation of the cusp constraint. In practice, the electron density at the nucleus is not determined by a limited resolution diffraction experiment; the single exponent function $R(r)$ is fitted to the electron density away from, rather than at the nucleus.

8.7.3.3.3. Radial constraint

Poisson’s electrostatic equation gives a relation between the gradient of the electric field $\nabla^2 \Phi(\mathbf{r})$ and the electron density at \mathbf{r} .

$$\nabla^2 \Phi(\mathbf{r}) = -4\pi \rho(\mathbf{r}). \quad (8.7.3.14)$$

As noted by Stewart (1977), this equation imposes a constraint on the radial functions $R(r)$. For $R_l(r) = N_l r^{l(0)} \exp(-\zeta_l r)$, the condition $n(l) \geq l$ must be obeyed for $R_l r^{-l}$ to be finite at $r = 0$, which satisfies the requirement of the non-divergence of the electric field ∇V , its gradient $\nabla^2 V$, the gradient of the field gradient $\nabla^3 V$, etc.

8.7.3.3.4. Hellmann–Feynman constraint

According to the electrostatic Hellmann–Feynman theorem, which follows from the Born–Oppenheimer approximation and the condition that the forces on the nuclei must vanish when the nuclear configuration is in equilibrium, the nuclear repulsions are balanced by the electron–nucleus attractions (Levine, 1983). The balance of forces is often achieved by a very sharp polarization of the electron density very close to the nuclei (Hirshfeld & Rzotkiewicz, 1974), which may be represented in the X-ray model by the introduction of dipolar functions with large values of ζ . The Hellmann–Feynman constraint offers the possibility for obtaining information on such functions even though they may contribute only marginally to the observed X-ray scattering (Hirshfeld, 1984).

As the Hellmann–Feynman constraint applies to the static density, its application presumes a proper deconvolution of the thermal motion and the electron density in the scattering model.