8. REFINEMENT OF STRUCTURAL PARAMETERS

8.7.3.4.2.2. *Electrostatic potential outside a charge distribution*

Hirshfelder, Curtiss & Bird (1954) and Buckingham (1959) have given an expression for the potential at a point $\mathbf{r}_i$ outside a charge distribution:

$$\Phi(\mathbf{r}_i) = \frac{q}{r_i} + \frac{\mu_\alpha r_\alpha}{r_i^3} + \tfrac{1}{2}\left[3r_\alpha r_\beta - r^2\delta_{\alpha\beta}\right]\frac{\Theta_{\alpha\beta}}{r_i^5}$$
$$+ \left[5r_\alpha r_\beta r\gamma - r^2\left(r_\alpha\delta_{\beta\gamma} + r_\beta\delta_{\gamma\alpha} + r_\gamma\delta_{\alpha\beta}\right)\right]\frac{\Omega_{\alpha\beta\gamma}}{5r_i^7} + \ldots,$$

(8.7.3.61)

where summation over repeated indices is implied. The outer moments q, μ_α, $\Phi_{\alpha\beta}$ and $\Omega_{\alpha\beta\gamma}$ in (8.7.3.61) must include the nuclear contributions, but, for a point outside the distribution, the spherical neutral-atom densities and the nuclear contributions cancel, so that the potential outside the charge distribution can be calculated from the deformation density.

The summation in (8.7.3.61) is slowly converging if the charge distribution is represented by a single set of moments. When dealing with experimental charge densities, a multicentre expansion is available from the analysis, and (8.7.3.61) can be replaced by a summation over the distributed moments centred at the nuclear positions, in which case r_i measures the distance from a centre of the expansion to the field point. The result is equivalent to more general expressions given by Su & Coppens (1992), which, for very large values of r_i, reduce to the sum over atomic terms, each expressed as (8.7.3.61). The interaction between two charge distributions, A and B, is given by

$$E_{AB} = \int \Phi_A(\mathbf{r})\rho_B(\mathbf{r})\,d\mathbf{r},$$

where ρ_B includes the nuclear charge distribution.

8.7.3.4.2.3. *Evaluation of the electrostatic functions in direct space*

The electrostatic properties of a well defined group of atoms can be derived directly from the multipole population coefficients. This method allows the 'lifting' of a molecule out of the crystal, and therefore the examination of the electrostatic quantities at the periphery of the molecule, the region of interest for intermolecular interactions. The difficulty related to the origin term, encountered in the reciprocal-space methods, is absent in the direct-space analysis.

In order to express the functions as a sum over atomic contributions, we rewrite (8.7.3.51), (8.7.3.54) and (8.7.3.57) for the electrostatic properties at point P as a sum over atomic contributions.

$$\Phi(\mathbf{R}_p) = \sum_{M\neq P}\frac{Z_M}{|\mathbf{R}_{MP}|} - \sum_M \int\frac{\rho_{e,M}(\mathbf{r}_M)}{|\mathbf{r}_p|}\,d\mathbf{r}_M, \quad (8.7.3.62)$$

$$\mathbf{E}(\mathbf{R}_p) = -\sum_{M\neq P}\frac{Z_{MP}\mathbf{R}_{MP}}{|\mathbf{R}_{MP}|^3} + \sum_M \int\frac{\mathbf{r}_p\rho_{e,M}(\mathbf{r}_M)}{|\mathbf{r}_p|^3}\,d\mathbf{r}_M, \quad (8.7.3.63)$$

$$\nabla\mathbf{E}_{\alpha\beta}(\mathbf{R}_p) = -\sum_{M\neq P}\frac{Z_M(3R_\alpha R_\beta - \delta_{\alpha\beta}|R_{MP}|^2)}{|R_{MP}|^5}$$
$$+ \sum_M \int\frac{\rho_{e,M}(\mathbf{r}_M)(3r_\alpha r_\beta - \delta_{\alpha\beta}|\mathbf{r}_p|^2)}{|\mathbf{r}_p|^5}\,d\mathbf{r}_M, \quad (8.7.3.64)$$

in which the exclusion of $M = P$ only applies when the point P coincides with a nucleus, and therefore only occurs for the central contributions. Z_M and $\mathbf{R}_M$ are the nuclear charge and the position vector of atom M, respectively,

while $\mathbf{r}_P$ and $\mathbf{r}_M$ are, respectively, the vectors from P and from the nucleus M to a point $\mathbf{r}$, such that $\mathbf{r}_P = \mathbf{r} - \mathbf{R}_P$, and $\mathbf{r}_M = \mathbf{r} - \mathbf{R}_M = \mathbf{r}_P + \mathbf{R}_P - \mathbf{R}_M = \mathbf{r}_P - \mathbf{R}_{MP}$. The subscript M in the second, electronic part of the expressions refers to density functions centred on atom M.

Expressions for the evaluation of (8.7.3.62)–(8.7.3.64) from the charge-density parameters of the multipole expansion have been given by Su & Coppens (1992). They employ the Fourier convolution theorem, used by Epstein & Swanton (1982) to evaluate the electric field gradient at the atomic nuclei. A direct-space method based on the Laplace expansion of $1/|\mathbf{R}_p - \mathbf{r}|$ was reported by Bentley (1981).

8.7.3.4.3. *Electrostatic functions of crystals by modified Fourier summation*

Expression (8.7.3.49) is an example of derivation of electrostatic properties by direct Fourier summations of the structure factors. The electrostatic potential and its derivatives may be obtained in an analogous manner.

In order to obtain the electrostatic properties of the total charge distribution, it is convenient to define the 'total' structure factor $F_{\text{total}}(\mathbf{h})$ including the nuclear contribution,

$$F_{\text{total}}(\mathbf{h}) = F_N(\mathbf{h}) - F(\mathbf{h}),$$

where $F_N(\mathbf{h}) = \sum_j Z_j \exp(2\pi i\mathbf{h}\cdot\mathbf{R}_j)$, the summation being over all atoms j with nuclear charge Z_j, located at R_j. If $\Phi(\mathbf{h})$ is defined as the Fourier transform of the direct-space potential, we have

$$\Phi(\mathbf{r}) = \int \Phi(\mathbf{h})\exp(-2\pi i\mathbf{h}\cdot\mathbf{r})\,d\mathbf{h}$$

and

$$\nabla^2\Phi(\mathbf{r}) = -4\pi^2\int h^2\Phi(\mathbf{h})\exp(-2\pi i\mathbf{h}\cdot\mathbf{r})\,d\mathbf{h},$$

which equals $-4\pi\rho_{\text{total}}$ according to the Poisson equation (8.7.3.59). One obtains with

$$\rho_{\text{total}}(\mathbf{r}) = \int F_{\text{total}}(\mathbf{h})\exp(-2\pi i\mathbf{h}\cdot\mathbf{r})\,d\mathbf{h},$$
$$\Phi(\mathbf{h}) = +F_{\text{total}}(\mathbf{h})/\pi h^2, \quad (8.7.3.65)$$

and, by inverse Fourier transformation of (8.7.3.65),

$$\Phi(\mathbf{r}) = \frac{1}{\pi V}\sum F_{\text{total}}(\mathbf{h})/h^2 \exp(-2\pi i\mathbf{h}\cdot\mathbf{r}) \quad (8.7.3.66)$$

(Bertaut, 1978; Stewart, 1979). Furthermore, the electric field due to the electrons is given by

$$\mathbf{E}(\mathbf{r}) = -\nabla_r\Phi(\mathbf{r}) = -\nabla\int\Phi(\mathbf{h})\exp(-2\pi i\mathbf{h}\cdot\mathbf{r})\,d\mathbf{h}$$
$$= 2\pi i\int\mathbf{h}\Phi(\mathbf{h})\exp(-2\pi i\mathbf{h}\cdot\mathbf{r})\,d\mathbf{h}.$$

Thus, with (8.7.3.65),

$$\mathbf{E}(\mathbf{r}) = \frac{2i}{V}\sum\left[F_{\text{total}}(\mathbf{h})/h^2\right]\mathbf{h}\exp(-2\pi i\mathbf{h}\cdot\mathbf{r}), \quad (8.7.3.67a)$$

which implies

$$\mathbf{E}(\mathbf{h}) = \frac{2i}{h^2}\mathbf{h}F_{\text{total}}(\mathbf{h}).$$

Similarly, the $\mathbf{h}$ Fourier component of the electric field gradient tensor with trace $4\pi\rho(\mathbf{r})$ is

$$[\nabla:\mathbf{E}](\mathbf{h}) = +4\pi^2\mathbf{h}:\mathbf{h}\Phi(\mathbf{h}) = +4\pi\mathbf{h}:\mathbf{h}F_{\text{total}}(\mathbf{h})/h^2,$$

(8.7.3.67b)

720