

8. REFINEMENT OF STRUCTURAL PARAMETERS

$$q' = q, \quad (8.7.3.42)$$

and for the transformed first and second moments

$$\begin{aligned} \mu'_x &= \mu_x - q\mathbf{X}; \quad \mu'_y = \mu_y - q\mathbf{Y}; \quad \mu'_z = \mu_z - q\mathbf{Z}; \\ \mu'_{\alpha\alpha} &= \mu_{\alpha\alpha} - 2\mu_{\alpha}R_{\alpha} + qR_{\alpha}^2; \\ \mu'_{\alpha\beta} &= \mu_{\alpha\beta} - \mu_{\alpha}R_{\beta} - \mu_{\beta}R_{\alpha} + qR_{\alpha}R_{\beta}. \end{aligned} \quad (8.7.3.43)$$

For the traceless quadrupole moments, the corresponding equations are obtained by substitution of $\mathbf{r}'_{\alpha} = \mathbf{r}_{\alpha} - \mathbf{R}_{\alpha}$ and $\mathbf{r}' = \mathbf{r} - \mathbf{R}$ into (8.7.3.17), which gives

$$\begin{aligned} \Theta'_{\alpha\beta} &= \Theta_{\alpha\beta} + \frac{1}{2}(3\mathbf{R}_{\alpha}\mathbf{R}_{\beta} - \mathbf{R}^2\delta_{\alpha\beta})q \\ &\quad - \frac{3}{2}(\mathbf{R}_{\beta}\mu_{\alpha} + \mathbf{R}_{\alpha}\mu_{\beta}) + \sum_{\gamma}(\mathbf{R}_{\gamma}\mu_{\gamma})\delta_{\alpha\beta}. \end{aligned} \quad (8.7.3.44)$$

Similar expressions for the higher moments are reported in the literature (Buckingham, 1970).

We note that *the first non-vanishing moment is origin-independent*. Thus, the dipole moment of a neutral molecule, but not that of an ion, is independent of origin; the quadrupole moment of a molecule without charge and dipole moment is not dependent on the choice of origin and so on. The molecular electric moments are commonly reported with respect to the centre of mass.

8.7.3.4.1.4. *Total moments as a sum over the pseudoatom moments*

The moments of a molecule or of a molecular fragment are obtained from the sum over the atomic moments, plus a contribution due to the shift to a common origin for all but the monopoles. If individual atomic coordinate systems are used, as is common if chemical constraints are applied in the least-squares refinement, they must be rotated to have a common orientation. Expressions for coordinate system rotations have been given by Cromer, Larson & Stewart (1976) and by Su & Coppens (1994a).

The transformation to a common coordinate origin requires use of the origin-shift expressions (8.7.3.42)–(8.7.3.44), with, for an atom at \mathbf{r}_i , $\mathbf{R} = -\mathbf{r}_i$. The first three moments summed over the atoms i located at \mathbf{r}_i become

$$q_{\text{total}} = \sum_i q_i, \quad (8.7.3.45)$$

$$\mu_{\text{total}} = \sum_i \mu_i + \sum_i \mathbf{r}_i q_i, \quad (8.7.3.46)$$

and

$$\mu_{\alpha\beta, \text{total}} = \sum_i (\mu_{\alpha\beta i} + r'_{\beta i} \mu_{\alpha} + r'_{\alpha i} \mu_{\beta} + r'_{\alpha i} r'_{\beta i} q_i) \quad (8.7.3.47)$$

with $\alpha, \beta = x, y, z$; and expressions equivalent to (8.7.3.44) for the traceless components $\Theta_{\alpha\beta}$.

8.7.3.4.1.5. *Electrostatic moments of a subvolume of space by Fourier summation*

Expression (8.7.3.16) for the outer moment of a distribution within a volume element V_T may be written as

$$\mu_{\alpha_1\alpha_2\dots\alpha_l} = \int_{V_T} \rho(\mathbf{r}) \hat{\gamma}_{\alpha_1\alpha_2\dots\alpha_l} \mathbf{dr}, \quad (8.7.3.16)$$

with $\hat{\gamma}_{\alpha_1\alpha_2\dots\alpha_l} = r_{\alpha_1} r_{\alpha_2} r_{\alpha_3} \dots r_{\alpha_l}$, and integration over the volume V_T .

Replacement of $\rho(\mathbf{r})$ by the Fourier summation over the structure factors gives

$$\begin{aligned} \mu^l_{(V_T)} &= \frac{1}{V} \int_{V_T} \hat{\gamma}_l \sum F(\mathbf{h}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{r}) \mathbf{dr} \\ &= \frac{1}{V} \sum F(\mathbf{h}) \int_{V_T} \hat{\gamma}_l \exp(-2\pi i \mathbf{h} \cdot \mathbf{r}) \mathbf{dr}, \end{aligned} \quad (8.7.3.48)$$

where $\hat{\gamma}_l$ is the product of l coordinates according to (8.7.3.16), and μ^l represents the moment of the static distribution if the $F(\mathbf{h})$ are the structure factors on an absolute scale after deconvolution of thermal motion. Otherwise, the moment of the thermally averaged density is obtained.

The integral $\int_{V_T} \hat{\gamma}_l \exp(-2\pi i \mathbf{h} \cdot \mathbf{r}) \mathbf{dr}$ is defined as the *shape transform* S of the volume V_T .

$$\mu^l(V_T) = \frac{1}{V} \sum F(\mathbf{h}) S_{V_T}(\hat{\gamma}_l, \mathbf{h}).$$

For regularly shaped volumes, the integral can be evaluated analytically. A volume of complex shape may be subdivided into integrable subvolumes such as parallelepipeds. By choosing the subvolumes sufficiently small, a desired boundary surface can be closely approximated.

If the origin of each subvolume is located at \mathbf{r}_i , relative to a coordinate system origin at P , the total electronic moment relative to this origin is given by

$$\mu^l \left(\sum_i V_{T,i} \right) = \frac{1}{V} \sum_{\mathbf{h}} F(\mathbf{h}) S_{V_T}(\hat{\gamma}_l, \mathbf{h}) \sum_i \exp(-2\pi i \mathbf{h} \cdot \mathbf{r}_i). \quad (8.7.3.49)$$

Expressions for S_{V_T} for $l \leq 2$ and a subvolume parallelepipedal shape are given in Table 8.7.3.2. Since the spherical order Bessel functions $j_n(x)$ that appear in the expressions generally decrease with increasing x , the moments are strongly dependent on the low-order reflections in a data set. An example is the shape transform for the dipole moment. Relative to an origin O ,

$$S(\hat{\gamma}_1, \mathbf{h}) = \int_{V_i} \mathbf{r}_0 \exp(-2\pi i \mathbf{h} \cdot \mathbf{r}_0) \mathbf{dr}.$$

A shift of origin by $-\mathbf{r}_i$ leads to

$$\begin{aligned} \mu^l(V_T) &= \frac{1}{V} \sum F(\mathbf{h}) \left[S_{V_T}(\hat{\gamma}_l, \mathbf{h}) + \mathbf{r}_i \int \exp(-2\pi i \mathbf{h} \cdot \mathbf{r}_0) \mathbf{dr} \right] \\ &\quad \times \exp(-2\pi i \mathbf{h} \cdot \mathbf{r}_i) \\ &= \mu^l(V_T) + \mathbf{r}_i q, \end{aligned}$$

in agreement with (8.7.3.46).

8.7.3.4.2. *The electrostatic potential*

8.7.3.4.2.1. *The electrostatic potential and its derivatives*

The electrostatic potential $\Phi(\mathbf{r}')$ due to the electronic charge distribution is given by the Coulomb equation,

$$\Phi(\mathbf{r}') = -k \int \frac{\rho(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \mathbf{dr}, \quad (8.7.3.50)$$

where the constant k is dependent on the units selected, and will here be taken equal to 1. For an assembly of positive point nuclei and a continuous distribution of negative electronic charge, we obtain

$$\Phi(\mathbf{r}') = \sum_M \frac{Z_M}{|\mathbf{R}_M - \mathbf{r}'|} - \int \frac{\rho(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \mathbf{dr}, \quad (8.7.3.51)$$

in which Z_M is the charge of nucleus M located at \mathbf{R}_M .