

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

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

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

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

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 $\int_{V_T} \hat{\gamma}_l \exp(-2\pi i \mathbf{h} \cdot \mathbf{r}) \, d\mathbf{r}$ 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 ,

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

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

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

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,

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

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

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

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

8.7. ANALYSIS OF CHARGE AND SPIN DENSITIES

The *electric field* \mathbf{E} at a point in space is the gradient of the electrostatic potential at that point.

$$\mathbf{E}(\mathbf{r}) = -\nabla\Phi(\mathbf{r}) = -\mathbf{i}\frac{\partial\Phi(\mathbf{r})}{\partial x} - \mathbf{j}\frac{\partial\Phi(\mathbf{r})}{\partial y} - \mathbf{k}\frac{\partial\Phi(\mathbf{r})}{\partial z}. \quad (8.7.3.52)$$

As \mathbf{E} is the negative gradient vector of the potential, the electric force is directed 'downhill' and proportional to the slope of the potential function. The explicit expression for \mathbf{E} is obtained by differentiation of the operator $|\mathbf{r} - \mathbf{r}'|^{-1}$ in (8.7.3.50) towards x, y, z and subsequent addition of the vector components. For the negative slope of the potential in the x direction, one obtains

$$\mathbf{E}_x(\mathbf{r}') = \int \frac{\rho_{\text{total}}(\mathbf{r})}{|\mathbf{r}' - \mathbf{r}|^2} \frac{(\mathbf{r}' - \mathbf{r})_x}{|\mathbf{r}' - \mathbf{r}|} \mathbf{d}\mathbf{r} = \int \frac{\rho_{\text{total}}(\mathbf{r})}{|\mathbf{r}' - \mathbf{r}|^3} (\mathbf{r}' - \mathbf{r})_x \mathbf{d}\mathbf{r}, \quad (8.7.3.53)$$

which gives, after addition of the components,

$$\mathbf{E}(\mathbf{r}') = -\nabla\Phi(\mathbf{r}') = \int \frac{\rho_t(\mathbf{r})(\mathbf{r}' - \mathbf{r})}{|\mathbf{r}' - \mathbf{r}|^3} \mathbf{d}\mathbf{r}. \quad (8.7.3.54)$$

The electric field gradient (EFG) is the tensor product of the gradient operator $\nabla = \mathbf{i}\frac{\partial}{\partial x} + \mathbf{j}\frac{\partial}{\partial y} + \mathbf{k}\frac{\partial}{\partial z}$ and the electric field vector \mathbf{E} :

$$\nabla\mathbf{E} = \nabla : \mathbf{E} = -\nabla : \nabla\Phi. \quad (8.7.3.55)$$

It follows that in a Cartesian system the EFG tensor is a symmetric tensor with elements

$$\nabla\mathbf{E}_{\alpha\beta} = -\frac{\partial^2\Phi}{\partial r_\alpha\partial r_\beta}. \quad (8.7.3.56)$$

The EFG tensor elements can be obtained by differentiation of the operator in (8.7.3.53) for \mathbf{E}_α to each of the three directions β . In this way, the traceless result

$$\begin{aligned} \nabla\mathbf{E}_{\alpha\beta}(\mathbf{r}') &= \frac{\partial\mathbf{E}_\alpha}{\partial(r_\beta - r'_\beta)} \\ &= -\int \frac{1}{|\mathbf{r} - \mathbf{r}'|^5} \left\{ 3(r_\alpha - r'_\alpha)(r_\beta - r'_\beta) \right. \\ &\quad \left. - |\mathbf{r} - \mathbf{r}'|^2 \delta_{\alpha\beta} \right\} \rho_{\text{total}}(\mathbf{r}) \mathbf{d}\mathbf{r} \end{aligned} \quad (8.7.3.57)$$

is obtained. We note that according to (8.7.3.57) the electric field gradient can equally well be interpreted as the tensor of the traceless quadrupole moments of the distribution $-2\rho_{\text{total}}(\mathbf{r})/|\mathbf{r} - \mathbf{r}'|^5$ [see equation (8.7.3.17)].

Definition (8.7.3.56) and result (8.7.3.57) differ in that (8.7.3.56) does not correspond to a zero-trace tensor. The situation is analogous to the two definitions of the second moments, discussed above, and is illustrated as follows. The trace of the tensor defined by (8.7.3.56) is given by

$$-\nabla^2\Phi = -\nabla \cdot \nabla\Phi = -\left(\frac{\partial^2\Phi}{\partial x^2} + \frac{\partial^2\Phi}{\partial y^2} + \frac{\partial^2\Phi}{\partial z^2} \right). \quad (8.7.3.58)$$

Poisson's equation relates the divergence of the gradient of the potential $\Phi(\mathbf{r})$ to the electron density at that point:

$$\nabla^2\Phi(\mathbf{r}) = -4\pi[-\rho_e(\mathbf{r})] = 4\pi\rho_e(\mathbf{r}). \quad (8.7.3.59)$$

Thus, the EFG as defined by (8.7.3.56) is not traceless, unless the electron density at \mathbf{r} is zero.

The potential and its derivatives are sometimes referred to as *inner moments* of the charge distribution, since the operators in (8.7.3.50), (8.7.3.52) and (8.7.3.54) contain the negative power of the position vector. In the same terminology, the electrostatic moments discussed in §8.7.3.4.1 are described as the *outer moments*.

Table 8.7.3.2. Expressions for the shape factors S for a parallelepiped with edges $\delta_x, \delta_y,$ and δ_z (from Moss & Coppens, 1981)

j_0 and j_1 are the zero- and first-order spherical Bessel functions: $j_0(x) = \sin x/x, j_1(x) = \sin x/x^2 - \cos x/x; V_T$ is volume of integration.

\hat{y}	Property	$S[\hat{y}(\mathbf{r}), \mathbf{h}]$
1	Charge	$V_T j_0(2\pi h_x \delta_x) j_0(2\pi h_y \delta_y) j_0(2\pi h_z \delta_z)$
r_α	Dipole μ_α	$-iV_T \delta_\alpha j_1(2\pi h_\alpha \delta_\alpha) \times j_0(2\pi h_\beta \delta_\beta) j_0(2\pi h_\gamma \delta_\gamma)$
$r_\alpha r_\beta$	Second moment $\mu_{\alpha\beta}$ off-diagonal	$-V_T \delta_\alpha \delta_\beta j_1(2\pi h_\alpha \delta_\alpha) \times j_1(2\pi h_\beta \delta_\beta) j_0(2\pi h_\gamma \delta_\gamma)$
$r_\alpha r_\alpha$	Second moment $\mu_{\alpha\alpha}$ diagonal	$-V_T \delta_\alpha^2 \left\{ \frac{j_1(2\pi h_\alpha \delta_\alpha)}{\pi h_\alpha \delta_\alpha} - j_0(2\pi h_\alpha \delta_\alpha) \right\} \times j_0(2\pi h_\beta \delta_\beta) j_0(2\pi h_\gamma \delta_\gamma)$

It is of interest to evaluate the electric field gradient at the atomic nuclei, which for several types of nuclei can be measured accurately by nuclear quadrupole resonance and Mössbauer spectroscopy. The contribution of the atomic valence shell centred on the nucleus can be obtained by substitution of the multipolar expansion (8.7.3.7) in (8.7.3.57). The quadrupolar ($l=2$) terms in the expansion contribute to the integral. For the radial function $R_l = \{\zeta^{n(l)+3}/[n(l)+2]!\} r^{n(l)} \exp(-\zeta r)$ with $n(l)=2$, the following expressions are obtained:

$$\begin{aligned} \nabla\mathbf{E}_{11} &= +(3/5) \left(\pi P_{22+} - \sqrt{3} P_{20} \right) Q_r, \\ \nabla\mathbf{E}_{22} &= -(3/5) \left(\pi P_{22+} + \sqrt{3} P_{20} \right) Q_r, \\ \nabla\mathbf{E}_{33} &= +(6/5) \left(\sqrt{3} P_{20} \right) Q_r, \\ \nabla\mathbf{E}_{12} &= +(3/5) \left(\pi P_{22-} \right) Q_r, \\ \nabla\mathbf{E}_{13} &= +(3/5) \left(\pi P_{21+} \right) Q_r, \\ \nabla\mathbf{E}_{23} &= +(3/5) \left(\pi P_{21-} \right) Q_r, \end{aligned} \quad (8.7.3.60)$$

with

$$\begin{aligned} Q_r &= \langle r^3 \rangle_{3d} \\ &= \int_0^\infty [R(r)/r] \mathbf{d}\mathbf{r} \\ &= (\kappa' \zeta)^3 / [n_2(n_2+1)(n_2+2)] \\ &= (\kappa' \zeta)^3 / 120, \end{aligned}$$

in the case that $n_2 = 4$ (Stevens, DeLucia & Coppens, 1980).

The contributions of neighbouring atoms can be subdivided into point-charge, point-multipole, and penetration terms, as discussed by Epstein & Swanton (1982) and Su & Coppens (1992, 1994b), where appropriate expressions are given. Such contributions are in particular important when short interatomic distances are involved. For transition-metal atoms in coordination complexes, the contribution of neighbouring atoms is typically much smaller than the valence contribution.