

8. REFINEMENT OF STRUCTURAL PARAMETERS

8.7.3.4. *Electrostatic moments and the potential due to a charge distribution*

8.7.3.4.1. *Moments of a charge distribution**

Use of the expectation value expression

$$\langle O \rangle = \int \widehat{O} \rho(\mathbf{r}) \, d\mathbf{r}, \quad (8.7.3.15)$$

with the operator $\widehat{O} = \widehat{\gamma} r_{\alpha_1} r_{\alpha_2} r_{\alpha_3} \cdots r_{\alpha_l} = r_{\alpha_1} r_{\alpha_2} r_{\alpha_3} \cdots r_{\alpha_l}$ gives for the electrostatic moments of a charge distribution $\rho(\mathbf{r})$

$$\mu_{\alpha_1 \alpha_2 \alpha_3 \dots \alpha_l} = \int \rho(\mathbf{r}) r_{\alpha_1} r_{\alpha_2} r_{\alpha_3} \cdots r_{\alpha_l} \, d\mathbf{r}, \quad (8.7.3.16)$$

in which the r_{α} are the three components of the vector \mathbf{r} ($\alpha_i = 1, 2, 3$), and the integral is over the complete volume of the distribution.

For $l = 0$, (8.7.3.16) represents the integral over the charge distribution, which is the total charge, a scalar function described as the *monopole*. The higher moments are, in ascending order of l , the *dipole*, a vector, the *quadrupole*, a second-rank tensor, and the *octupole*, a third-rank tensor. Successively higher moments are named the *hexadecapole* ($l = 4$), the *tricontadipole* ($l = 5$), and the *hexacontatetrapole* ($l = 6$). An alternative, traceless, definition is often used for moments with $l \geq 2$. In the traceless definition, the quadrupole moment, $\Theta_{\alpha\beta}$, is given by

$$\Theta_{\alpha\beta} = \frac{1}{2} \int \rho(\mathbf{r}) [3r_{\alpha} r_{\beta} - r^2 \delta_{\alpha\beta}] \, d\mathbf{r}, \quad (8.7.3.17)$$

where $\delta_{\alpha\beta}$ is the Kronecker delta function. The term $\int \rho(\mathbf{r}) r^2 \, d\mathbf{r}$, which is subtracted from the diagonal elements of the tensor, corresponds to the spherically averaged second moment of the distribution.

Expression (8.7.3.17) is a special case of the following general expression for the l th-rank traceless tensor elements.

$$M_{\alpha_1 \alpha_2 \dots \alpha_l}^{(l)} = \frac{(-1)^l}{l!} \int \rho(\mathbf{r}) r^{2l+1} \frac{\partial^l}{\partial r_{\alpha_1} \partial r_{\alpha_2} \dots \partial r_{\alpha_l}} \left(\frac{1}{r} \right) \, d\mathbf{r}. \quad (8.7.3.18)$$

Though the traceless moments can be derived from the unabridged moments, the converse is not the case because the information on the spherically averaged moments is no longer present in the traceless moments. The general relations between the traceless moments and the unabridged moments follow from (8.7.3.18). For the quadrupole moments, we obtain with (8.7.3.17)

$$\begin{aligned} \Theta_{xx} &= \frac{3}{2} \mu_{xx} - \frac{1}{2} (\mu_{xx} + \mu_{yy} + \mu_{zz}) \\ &= \mu_{xx} - \frac{1}{2} (\mu_{yy} + \mu_{zz}), \end{aligned}$$

and

$$\Theta_{xy} = \frac{3}{2} \mu_{xy}. \quad (8.7.3.19)$$

Expressions for the other elements are obtained by simple permutation of the indices.

For a site of point symmetry 1, the electrostatic moment $\mu_{\alpha_1 \alpha_2 \alpha_3 \dots \alpha_l}$ of order l has $(l+1)(l+2)/2$ unique elements. In the traceless definition, not all elements are independent. Because the trace of the tensor has been set to zero, only $2l+1$ independent components remain. For the quadrupole there are 5 independent components of the form (8.7.3.19).

In a different form, the traceless moment operators can be written as the Cartesian spherical harmonics c_{lmp} (ITB, 1992) multiplied by r^l , which defines the *spherical* electrostatic moments

* An excellent review of experimental results has appeared in the literature (Spackman, 1992).

$$\Theta_{lmp} = \int \rho(\mathbf{r}) c_{lmp} r^l \, d\mathbf{r}. \quad (8.7.3.20)$$

The expressions for c_{lmp} are listed in Volume B of *International Tables for Crystallography* (ITB, 1992); for the $l = 2$ moment, the c_{lmp} have the well known form $3z^2 - 1$, xz , yz , $(x^2 - y^2)/2$, and xy , where x , y and z are the components of a unit vector from the origin to the point being described. The spherical electrostatic moments have $(2l+1)$ components, which equals the number of independent components in the traceless definition (8.7.3.18), as it should. The linear relationships are

$$\begin{aligned} \Theta_{zz} &= (1/2)\Theta_{20}, \\ \Theta_{xx} &= (1/2)[3\Theta_{22+} - (1/2)\Theta_{20}], \\ \Theta_{yy} &= (1/2)[-3\Theta_{22+} - (1/2)\Theta_{20}], \\ \Theta_{xz} &= (3/2)\Theta_{21+}, \\ \Theta_{yz} &= (3/2)\Theta_{21-}, \\ \Theta_{xy} &= (3/2)\Theta_{22-}. \end{aligned} \quad (8.7.3.21)$$

8.7.3.4.1.1. *Moments as a function of the atomic multipole expansion*

In the multipole model [expression (8.7.3.7)], the charge density is a sum of atom-centred density functions, and the moments of a whole distribution can be written as a sum over the atomic moments plus a contribution due to the shift to a common origin. An atomic moment is obtained by integration over the charge distributions $\rho_{\text{total},i}(\mathbf{r}) = \rho_{\text{nuclear},i} - \rho_{e,i}$ of atom i ,

$$\mu_{\alpha_1 \alpha_2 \alpha_3 \dots \alpha_l} = \int \rho_{\text{total},i}(\mathbf{r}) r_{\alpha_1} r_{\alpha_2} r_{\alpha_3} \cdots r_{\alpha_l} \, d\mathbf{r}, \quad (8.7.3.22)$$

where the electronic part of the atomic charge distribution is defined by the multipole expansion

$$\begin{aligned} \rho_{e,i}(\mathbf{r}) &= P_{i,c} \rho_{\text{core}}(r) + P_{i,v} \kappa_i^3 \rho_{i,\text{valence}}(\kappa_i r) \\ &+ \sum_{l=0}^{\text{max}} \kappa_i^3 R_{i,l}(\kappa_i r) \sum_{m=0}^l \sum_p P_{i,lmp} d_{lmp}(\theta, \varphi), \end{aligned} \quad (8.7.3.23)$$

where $p = \pm$ when $m > 0$, and $R_l(\kappa_i r)$ is a radial function.

We get for the j th moment of the valence density

$$\begin{aligned} \mu^j &= \mu_{\alpha_1 \alpha_2 \alpha_3 \dots \alpha_l} \\ &= - \int \left[P_{i,v} \kappa_i^3 \rho_{i,\text{valence}}(\kappa_i r) + \sum_{l=0}^{\text{max}} \kappa_i^3 R_{i,l}(\kappa_i r) \right. \\ &\quad \left. \times \sum_{m=0}^l \sum_p P_{i,lmp} d_{lmp}(\theta, \varphi) \right] r_{\alpha_1} r_{\alpha_2} \cdots r_{\alpha_l} \, d\mathbf{r}, \end{aligned} \quad (8.7.3.24)$$

in which the minus sign arises because of the negative charge of the electrons.

We will use the symbol \widehat{O} for the moment operators. We get

$$\mu^j = -\kappa_i^3 \int \widehat{O}_j \sum_{l=1}^{\text{max}} \left[\sum_{m=0}^l \sum_p P_{lmp} d_{lmp} R_l \right] \, d\mathbf{r}, \quad (8.7.3.25)$$

where, as before, $p = \pm$. The requirement that the integrand be totally symmetric means that only the dipolar terms in the multipole expansion contribute to the dipole moment. If we use the traceless definition of the higher moments, or the equivalent definition of the moments in terms of the spherical harmonic functions, only the quadrupolar terms of the multipole expansion will contribute to the quadrupole moment; more generally, in the traceless definition *the l th-order multipoles are the sole contributors to the l th moments*. In terms of the spherical moments, we get

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$$\Theta_{lmp} = -P_{lmp} \int \widehat{O}_{lmp} [d_{lmp} R_l] \mathbf{dr}. \quad (8.7.3.26)$$

Substitution with $R_l = \{(\kappa'\zeta)^{n(l)+3}/[n(l)+2]!\} r^{n(l)} \exp(-\zeta r)$ and $\widehat{O}_{lmp} = c_{lmp} r^l$ and subsequent integration over r gives

$$\Theta_{lmp} = -P_{lmp} \frac{1}{(\kappa'\zeta)^l} \frac{[n(l)+l+2]!}{[n(l)+2]!} \frac{1}{D_{lm} M_{lm}} \int y_{lmp}^2 \sin \theta \, d\theta \, d\varphi, \quad (8.7.3.27)$$

where the definitions

$$d_{lmp} = L_{lm} c_{lmp} = \left(\frac{L_{lm}}{M_{lm}}\right) y_{lmp} \quad \text{and} \quad c_{lmp} = \left(\frac{1}{M_{lm}}\right) y_{lmp} \quad (8.7.3.28)$$

have been used (ITB, 1992). Since the y_{lmp} functions are wavefunction normalized, we obtain

$$\Theta_{lmp} = -P_{lmp} \frac{1}{(\kappa'\zeta)^l} \frac{[n(l)+l+2]!}{[n(l)+2]!} \frac{L_{lm}}{(M_{lm})^2}. \quad (8.7.3.29)$$

Application to dipolar terms with $n(l)=2$, $L_{lm}=1/\pi$ and $M_{lm}=(3/4\pi)^{1/2}$ gives the x component of the atomic dipole moment as

$$\mu_x = - \int P_{11+} d_{11+} R_{1x} \mathbf{dr} = - \frac{20}{3\kappa'\zeta} P_{11+}. \quad (8.7.3.30)$$

For the atomic quadrupole moments in the spherical definition, we obtain directly, using $n(l)=2$, $l=2$ in (8.7.3.29),

$$\Theta_{20} = - \frac{30}{(\kappa'\zeta)^2} \frac{L_{20}}{(M_{20})^2} P_{20} = - \frac{36\sqrt{3}}{(\kappa'\zeta)^2} P_{20}, \quad (8.7.3.31)$$

and, for the other elements,

$$\Theta_{2mp} = - \frac{30}{(\kappa'\zeta)^2} \frac{L_{2m}}{(M_{2m})^2} P_{2mp} = - \frac{6\pi}{(\kappa'\zeta)^2} P_{2mp}. \quad (8.7.3.32)$$

As the traceless quadrupole moments are linear combinations of the spherical quadrupole moments, the corresponding expressions follow directly from (8.7.3.31), (8.7.3.32) and (8.7.3.21). We obtain with $n(2)=2$

$$\begin{aligned} \Theta_{zz} &= - \frac{18\sqrt{3}}{(\kappa'\zeta)^2} P_{20}, \\ \Theta_{yy} &= + \frac{9}{(\kappa'\zeta)^2} \left(\sqrt{3} P_{20} + \pi P_{22+} \right), \\ \Theta_{xx} &= \frac{9}{(\kappa'\zeta)^2} \left(\sqrt{3} P_{20} - \pi P_{22+} \right), \end{aligned}$$

and

$$\Theta_{xz} = - \frac{9\pi}{(\kappa'\zeta)^2} P_{21+}, \quad (8.7.3.33)$$

and analogously for the other off-diagonal elements.

8.7.3.4.1.2. Molecular moments based on the deformation density

The moments derived from the total density $\rho(\mathbf{r})$ and from the deformation density $\Delta\rho(\mathbf{r})$ are not identical. To illustrate the relation for the diagonal elements of the second-moment tensor, we rewrite the xx element as

$$\begin{aligned} \mu_{xx}(\rho_{\text{total}}) &= \int \rho x^2 \mathbf{dr} \\ &= \int \rho_{\text{promolecule}} x^2 \mathbf{dr} + \int \Delta\rho x^2 \mathbf{dr}. \end{aligned} \quad (8.7.3.34)$$

The promolecule is the sum over spherical atom densities, or

$$\begin{aligned} \int \rho_{\text{promolecule}} x^2 \mathbf{dr} &= \int \sum_i \rho_{\text{spherical atom},i} x^2 \mathbf{dr} \\ &= \sum_i \int \rho_{\text{spherical atom},i} x^2 \mathbf{dr}. \end{aligned} \quad (8.7.3.35)$$

If $\mathbf{R}_i = (X_i, Y_i, Z_i)$ is the position vector for atom i , each single-atom contribution can be rewritten as

$$\begin{aligned} \mu_{i,xx,\text{spherical atom}} &= \int \rho_{i,\text{spherical atom}} x^2 \mathbf{dr} \\ &= \int \rho_{i,\text{spherical atom}} (x - X_i)^2 \mathbf{dr} \\ &\quad + X_i \int \rho_{i,\text{spherical atom}} 2(x - X_i) \mathbf{dr} \\ &\quad + X_i^2 \int \rho_{i,\text{spherical atom}} \mathbf{dr}. \end{aligned} \quad (8.7.3.36)$$

Since the last two integrals are proportional to the atomic dipole moment and its net charge, respectively, they will be zero for neutral spherical atoms. Substitution in (8.7.3.35) gives, with $\langle (x - X_i)^2 \rangle = \frac{1}{3} \langle r_i^2 \rangle$, and $\langle r_i^2 \rangle = \int \rho_i(r) r^2 \mathbf{dr}$,

$$\int \rho_{\text{promolecule}} x^2 \mathbf{dr} = \frac{1}{3} \sum_{\text{atoms}} \langle r^2 \rangle_{\text{spherical atom}}, \quad (8.7.3.37)$$

and, by substitution in (8.7.3.34),

$$\mu_{xx}(\rho_{\text{tot}}) = \mu_{xx}(\Delta\rho) + \frac{1}{3} \sum_{\text{atoms}} \langle r^2 \rangle_{\text{spherical atom}}, \quad (8.7.3.38a)$$

with

$$\mu_{xx}(\Delta\rho) = \sum_i \left(\int \Delta\rho_i x^2 \mathbf{dr} + 2X_i \mu_i + X_i^2 q_i \right), \quad (8.7.3.38b)$$

in which μ_i and q_i are the atomic dipole moment and the charge on atom i , respectively.

The last term in (8.7.3.38a) can be derived rapidly from analytical expressions for the atomic wavefunctions. Results for Hartree-Fock wavefunctions have been tabulated by Boyd (1977). Since the off-diagonal elements of the second-moment tensor vanish for the spherical atom, the second term in (8.7.3.38a) disappears, and the off-diagonal elements are identical for the total and deformation densities.

The relation between the second moments $\mu_{\alpha\beta}$ and the traceless moments $\Theta_{\alpha\beta}$ of the deformation density can be illustrated as follows. From (8.7.3.17), we may write

$$\Theta_{\alpha\beta}(\Delta\rho) = \frac{3}{2} \mu_{\alpha\beta}(\Delta\rho) - \frac{1}{2} \delta_{\alpha\beta} \int \Delta\rho r^2 \mathbf{dr}. \quad (8.7.3.39)$$

Only the spherical density terms contribute to the integral on the right. Assuming for the moment that the spherical deformation is represented by the valence-shell distortion (*i.e.* neglect of the second monopole in the aspherical atom expansion), we have, with density functions ρ normalized to 1, for each atom

$$(\Delta\rho)_{\text{spherical}} = \kappa^3 P_{\text{valence}} \rho_{\text{valence}}(\kappa r) - P_{\text{valence}}^0 \rho_{\text{valence}}(r) \quad (8.7.3.40)$$

and

$$\begin{aligned} \int \Delta\rho r^2 \mathbf{dr} &= \int \sum_i \left[\kappa_i^3 P_{\text{valence},i} \rho_{\text{valence},i}(\kappa_i r) \right. \\ &\quad \left. - P_{\text{valence},i}^0 \rho_{\text{valence},i}(r) \right] r^2 \mathbf{dr} \\ &= \sum_i \left(P_{\text{valence},i} / \kappa_i^2 - P_{\text{valence}}^0 \right) \langle r_i^2 \rangle_{\text{spherical valence shell}} \\ &\quad + R_i^2 \left(P_{\text{valence},i} - P_{\text{valence},i}^0 \right), \end{aligned} \quad (8.7.3.41)$$

which, on substitution in (8.7.3.39), gives the required relation.

8.7.3.4.1.3. The effect of an origin shift on the outer moments

In general, the multipole moments depend on the choice of origin. This can be seen as follows. Substitution of $\mathbf{r}'_{\alpha} = \mathbf{r}_{\alpha} - \mathbf{R}_{\alpha}$ in (8.7.3.16) corresponds to a shift of origin by \mathbf{R}_{α} , or \mathbf{X} , \mathbf{Y} , \mathbf{Z} in the original coordinate system. In three dimensions, we get, for the first moment, the charge q ,