

8.7. ANALYSIS OF CHARGE AND SPIN DENSITIES

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

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 ,

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

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 .