$$\Theta_{lmp} = -P_{lmp} \int \widehat{O}_{lmp}\left[d_{lmp} R_l\right] \mathrm{d}\mathbf{r}. \tag{8.7.3.26}$$

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

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

where the definitions

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

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

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

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

$$\mu_x = -\int P_{11+} d_{11+} R_1 x \, \mathrm{d}\mathbf{r} = -\frac{20}{3\kappa'\zeta} P_{11+}. \tag{8.7.3.30}$$

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

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

and, for the other elements,

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

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

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

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

$$\begin{aligned}
\mu_{xx}(\rho_{\text{total}}) &= \int \rho x^2 \, \mathrm{d}\mathbf{r} \\
&= \int \rho_{\text{promolecule}} x^2 \, \mathrm{d}\mathbf{r} + \int \Delta\rho x^2 \, \mathrm{d}\mathbf{r}.
\end{aligned} \tag{8.7.3.34}$$

The promolecule is the sum over spherical atom densities, or

$$\begin{aligned}
\int \rho_{\text{promolecule}} x^2 \, \mathrm{d}\mathbf{r} &= \int \sum_i \rho_{\text{spherical atom},i} x^2 \, \mathrm{d}\mathbf{r} \\
&= \sum_i \int \rho_{\text{spherical atom},i} x^2 \, \mathrm{d}\mathbf{r}.
\end{aligned} \tag{8.7.3.35}$$

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

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

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 $\langle r_i^2 \rangle = \int \rho_i(r) r^2 \, \mathrm{d}\mathbf{r}$,

$$\int \rho_{\text{promolecule}} x^2 \, \mathrm{d}\mathbf{r} = \tfrac{1}{3} \sum_{\text{atoms}} \langle r^2 \rangle_{\text{spherical atom}}, \tag{8.7.3.37}$$

and, by substitution in (8.7.3.34),

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

with

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

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

The last term in (8.7.3.38*a*) 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 (8.7.3.38*a*) 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

$$\Theta_{\alpha\beta}(\Delta\rho) = \tfrac{3}{2} \mu_{\alpha\beta}(\Delta\rho) - \tfrac{1}{2} \delta_{\alpha\beta} \int \Delta\rho \, r^2 \, \mathrm{d}\mathbf{r}. \tag{8.7.3.39}$$

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

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

and

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

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 $\mathbf{R}_\alpha$, or $\mathbf{X}$, $\mathbf{Y}$, $\mathbf{Z}$ in the original coordinate system. In three dimensions, we get, for the first moment, the charge q,

references