

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 .

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.

8. REFINEMENT OF STRUCTURAL PARAMETERS

8.7.3.4.2.2. Electrostatic potential outside a charge distribution

Hirshfelder, Curtiss & Bird (1954) and Buckingham (1959) have given an expression for the potential at a point \mathbf{r}_i outside a charge distribution:

$$\Phi(\mathbf{r}_i) = \frac{q}{r_i} + \frac{\mu_\alpha r_\alpha}{r_i^3} + \frac{1}{2} [3r_\alpha r_\beta - r^2 \delta_{\alpha\beta}] \frac{\Theta_{\alpha\beta}}{r_i^5} + [5r_\alpha r_\beta r_\gamma - r^2 (r_\alpha \delta_{\beta\gamma} + r_\beta \delta_{\gamma\alpha} + r_\gamma \delta_{\alpha\beta})] \frac{\Omega_{\alpha\beta\gamma}}{5r_i^7} + \dots, \quad (8.7.3.61)$$

where summation over repeated indices is implied. The outer moments q , μ_α , $\Phi_{\alpha\beta}$ and $\Omega_{\alpha\beta\gamma}$ in (8.7.3.61) must include the nuclear contributions, but, for a point outside the distribution, the spherical neutral-atom densities and the nuclear contributions cancel, so that the potential outside the charge distribution can be calculated from the deformation density.

The summation in (8.7.3.61) is slowly converging if the charge distribution is represented by a single set of moments. When dealing with experimental charge densities, a multicentre expansion is available from the analysis, and (8.7.3.61) can be replaced by a summation over the distributed moments centred at the nuclear positions, in which case r_i measures the distance from a centre of the expansion to the field point. The result is equivalent to more general expressions given by Su & Coppens (1992), which, for very large values of r_i , reduce to the sum over atomic terms, each expressed as (8.7.3.61). The interaction between two charge distributions, A and B , is given by

$$E_{AB} = \int \Phi_A(\mathbf{r}) \rho_B(\mathbf{r}) d\mathbf{r},$$

where ρ_B includes the nuclear charge distribution.

8.7.3.4.2.3. Evaluation of the electrostatic functions in direct space

The electrostatic properties of a well defined group of atoms can be derived directly from the multipole population coefficients. This method allows the ‘lifting’ of a molecule out of the crystal, and therefore the examination of the electrostatic quantities at the periphery of the molecule, the region of interest for intermolecular interactions. The difficulty related to the origin term, encountered in the reciprocal-space methods, is absent in the direct-space analysis.

In order to express the functions as a sum over atomic contributions, we rewrite (8.7.3.51), (8.7.3.54) and (8.7.3.57) for the electrostatic properties at point P as a sum over atomic contributions.

$$\Phi(\mathbf{R}_p) = \sum_{M \neq P} \frac{Z_M}{|\mathbf{R}_{MP}|} - \sum_M \int \frac{\rho_{e,M}(\mathbf{r}_M)}{|\mathbf{r}_p|} d\mathbf{r}_M, \quad (8.7.3.62)$$

$$\mathbf{E}(\mathbf{R}_p) = - \sum_{M \neq P} \frac{Z_M \mathbf{R}_{MP}}{|\mathbf{R}_{MP}|^3} + \sum_M \int \frac{\mathbf{r}_p \rho_{e,M}(\mathbf{r}_M)}{|\mathbf{r}_p|^3} d\mathbf{r}_M, \quad (8.7.3.63)$$

$$\nabla \mathbf{E}_{\alpha\beta}(\mathbf{R}_p) = - \sum_{M \neq P} \frac{Z_M (3R_\alpha R_\beta - \delta_{\alpha\beta} |\mathbf{R}_{MP}|^2)}{|\mathbf{R}_{MP}|^5} + \sum_M \int \frac{\rho_{e,M}(\mathbf{r}_M) (3r_\alpha r_\beta - \delta_{\alpha\beta} |\mathbf{r}_p|^2)}{|\mathbf{r}_p|^5} d\mathbf{r}_M, \quad (8.7.3.64)$$

in which the exclusion of $M = P$ only applies when the point P coincides with a nucleus, and therefore only occurs for the central contributions. Z_M and \mathbf{R}_M are the nuclear charge and the position vector of atom M , respectively,

while \mathbf{r}_p and \mathbf{r}_M are, respectively, the vectors from P and from the nucleus M to a point \mathbf{r} , such that $\mathbf{r}_p = \mathbf{r} - \mathbf{R}_p$, and $\mathbf{r}_M = \mathbf{r} - \mathbf{R}_M = \mathbf{r}_p + \mathbf{R}_p - \mathbf{R}_M = \mathbf{r}_p - \mathbf{R}_{MP}$. The subscript M in the second, electronic part of the expressions refers to density functions centred on atom M .

Expressions for the evaluation of (8.7.3.62)–(8.7.3.64) from the charge-density parameters of the multipole expansion have been given by Su & Coppens (1992). They employ the Fourier convolution theorem, used by Epstein & Swanton (1982) to evaluate the electric field gradient at the atomic nuclei. A direct-space method based on the Laplace expansion of $1/|\mathbf{R}_p - \mathbf{r}|$ was reported by Bentley (1981).

8.7.3.4.3. Electrostatic functions of crystals by modified Fourier summation

Expression (8.7.3.49) is an example of derivation of electrostatic properties by direct Fourier summations of the structure factors. The electrostatic potential and its derivatives may be obtained in an analogous manner.

In order to obtain the electrostatic properties of the total charge distribution, it is convenient to define the ‘total’ structure factor $F_{\text{total}}(\mathbf{h})$ including the nuclear contribution,

$$F_{\text{total}}(\mathbf{h}) = F_N(\mathbf{h}) - F(\mathbf{h}),$$

where $F_N(\mathbf{h}) = \sum_j Z_j \exp(2\pi i \mathbf{h} \cdot \mathbf{R}_j)$, the summation being over all atoms j with nuclear charge Z_j , located at \mathbf{R}_j . If $\Phi(\mathbf{h})$ is defined as the Fourier transform of the direct-space potential, we have

$$\Phi(\mathbf{r}) = \int \Phi(\mathbf{h}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{r}) d\mathbf{h}$$

and

$$\nabla^2 \Phi(\mathbf{r}) = -4\pi^2 \int h^2 \Phi(\mathbf{h}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{r}) d\mathbf{h},$$

which equals $-4\pi \rho_{\text{total}}$ according to the Poisson equation (8.7.3.59). One obtains with

$$\rho_{\text{total}}(\mathbf{r}) = \int F_{\text{total}}(\mathbf{h}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{r}) d\mathbf{h}, \quad (8.7.3.65)$$

$$\Phi(\mathbf{h}) = +F_{\text{total}}(\mathbf{h})/\pi h^2,$$

and, by inverse Fourier transformation of (8.7.3.65),

$$\Phi(\mathbf{r}) = \frac{1}{\pi V} \sum F_{\text{total}}(\mathbf{h})/h^2 \exp(-2\pi i \mathbf{h} \cdot \mathbf{r}) \quad (8.7.3.66)$$

(Bertaut, 1978; Stewart, 1979). Furthermore, the electric field due to the electrons is given by

$$\mathbf{E}(\mathbf{r}) = -\nabla \Phi(\mathbf{r}) = -\nabla \int \Phi(\mathbf{h}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{r}) d\mathbf{h} = 2\pi i \int \mathbf{h} \Phi(\mathbf{h}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{r}) d\mathbf{h}.$$

Thus, with (8.7.3.65),

$$\mathbf{E}(\mathbf{r}) = \frac{2i}{V} \sum [F_{\text{total}}(\mathbf{h})/h^2] \mathbf{h} \exp(-2\pi i \mathbf{h} \cdot \mathbf{r}), \quad (8.7.3.67a)$$

which implies

$$\mathbf{E}(\mathbf{h}) = \frac{2i}{h^2} \mathbf{h} F_{\text{total}}(\mathbf{h}).$$

Similarly, the \mathbf{h} Fourier component of the electric field gradient tensor with trace $4\pi \rho(\mathbf{r})$ is

$$[\nabla : \mathbf{E}](\mathbf{h}) = +4\pi^2 \mathbf{h} : \mathbf{h} \Phi(\mathbf{h}) = +4\pi \mathbf{h} : \mathbf{h} F_{\text{total}}(\mathbf{h})/h^2, \quad (8.7.3.67b)$$