

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.