8.7. ANALYSIS OF CHARGE AND SPIN DENSITIES

where $\mathbf{i} : \mathbf{k}$ represents the tensor product of two vectors. This leads to the expression for the electric field gradient in direct space,

$$[\nabla : \mathbf{E}](\mathbf{r}) = \frac{4\pi}{V} \sum \mathbf{h} : \mathbf{h} F_{\text{total}}(\mathbf{h})/h^2 \exp(-2\pi i \mathbf{h} \cdot \mathbf{r}). \quad (8.7.3.68)$$

(The elements of $\mathbf{h} : \mathbf{h}$ are the products $h_i h_j$.)

The components of $\mathbf{E}$ and the elements of the electric field gradient defined by (8.7.3.67a) and (8.7.3.68) are with respect to the reciprocal-lattice coordinate system. Proper transforms are required to get the values in other coordinate systems. Furthermore, to get the traceless $\nabla \mathbf{E}$ tensor, the quantity $-(4\pi/3)\rho_e(\mathbf{r}) = -(4\pi/3V) \sum F(\mathbf{h}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{r})$ must be subtracted from each of the diagonal elements $\nabla \mathbf{E}_{ii}$.

The Coulombic self-electronic energy of the crystal can be obtained from

$$E_{\text{Coulombic, electronic}} = \frac{1}{2} \int \int \frac{\rho_e(\mathbf{r})\rho_e(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r} \, d\mathbf{r}',$$
$$= \frac{1}{2} \int \Phi_e(\mathbf{r})\rho(\mathbf{r}) \, d\mathbf{r}.$$

Since $\int \Phi(\mathbf{r})\rho(\mathbf{r}) \, d\mathbf{r} = \int \Phi(\mathbf{h})F(\mathbf{h}) \, d\mathbf{h}$ (Parseval's rule), the summation can be performed in reciprocal space,

$$E_{\text{Coulombic, electronic}} = \frac{1}{2\pi V} \sum F^2(\mathbf{h})/h^2, \quad (8.7.3.69a)$$

and, for the total Coulombic energy,

$$E_{\text{Coulombic, total}} = \frac{1}{2\pi V} \sum F_{\text{total}}^2(\mathbf{h})/h^2, \quad (8.7.3.69b)$$

where the integral has been replaced by a summation.

The summations are rapidly convergent, but suffer from having a singularity at $\mathbf{h} = 0$ (Dahl & Avery, 1984; Becker & Coppens, 1990). The contribution from this term to the potential cannot be ignored if different structures are compared. The term at $\mathbf{h} = 0$ gives a constant contribution to the potential, which, however, has no effect on the energy of a neutral system. For polar crystals, an additional term occurs in (8.7.3.69a, b), which is a function of the dipole moment D of the unit cell (Becker, 1990),

$$E_{\text{Coulombic, total}} = \frac{1}{2\pi V} \sum F_{\text{total}}^2(\mathbf{h})/h^2 + \frac{2\pi}{3V} D^2. \quad (8.7.3.69c)$$

To obtain the total energy of the static crystal, electron exchange and correlation as well as electron kinetic energy contributions must be added.

8.7.3.4.4. *The total energy of a crystal as a function of the electron density*

One can write the total energy of a system as

$$E = e_c[\rho] + T + E_{xc}, \quad (8.7.3.70)$$

where T is the kinetic energy, E_{xc} represents the exchange and electron correlation contributions, and $E_c[\rho]$, the Coulomb energy, discussed in the previous section, is given by

$$E_c = \frac{1}{2} \sum_{i \neq j} \frac{Z_i Z_j}{R_{ij}} - \sum_i Z_i \Phi(\mathbf{R}_i) + \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r} \, d\mathbf{r}', \quad (8.7.3.71)$$

where Z_i is the nuclear charge for an atom at position $\mathbf{R}_i$, and $\mathbf{R}_{ij} = \mathbf{R}_j - \mathbf{R}_i$.

Because of the theorem of Hohenberg & Kohn (1964), E is a unique functional of the electron density ρ, so that $T + E_{xc}$ must be a functional of ρ. Approximate density functionals are discussed extensively in the literature (Dahl & Avery, 1984) and are at the centre of active research in the study of electronic structure of various materials. Given an approximate functional, one can estimate non-Coulombic contributions to the energy from the charge density $\rho(\mathbf{r})$.

In the simplest example, the functionals are those applicable to an electronic gas with slow spatial variations (the 'nearly free electron gas'). In this approximation, the kinetic energy T is given by

$$T = c_k \int \rho t[\rho] \, d^3\mathbf{r}, \quad (8.7.3.72)$$

with $c_k = (3/10)(2\pi^2)^{2/3}$; and the function $t[\rho] = \rho^{2/3}$. The exchange-correlation energy is also a functional of ρ,

$$E_{xc} = -c_x \int \rho e_{xc}[\rho] \, d^3\mathbf{r},$$

with $c_x = (3/4)(3/\pi)^{1/3}$ and $e_{xc}[\rho] = \rho^{1/3}$.

Any attempt to minimize the energy with respect to ρ in this framework leads to very poor results. However, cohesive energies can be described quite well, assuming that the change in electron density due to cohesive forces is slowly varying in space.

An example is the system AB, with closed-shell subsystems A and B. Let ρ_A and ρ_B be the densities for individual A and B subsystems. The interaction energy is written as

$$\Delta E = E_c[\rho] - E_c[\rho_A] - E_c[\rho_B]$$
$$+ c_k \int d\mathbf{r} \{ \rho t[\rho] - \rho_A t[\rho_A] - \rho_B t[\rho_B] \}$$
$$- c_x \int d\mathbf{r} \{ \rho e_{xc}[\rho] - \rho_A e_{xc}[\rho_A] - \rho_B e_{xc}[\rho_B] \}. \quad (8.7.3.73)$$

This model is known as the Gordon–Kim (1972) model and leads to a qualitatively valid description of potential energy surfaces between closed-shell subsystems. Unlike pure Coulombic models, this density functional model can lead to an equilibrium geometry. It has the advantage of depending only on the charge density ρ.

8.7.3.5. *Quantitative comparison with theory*

Frequently, the purpose of a charge density analysis is comparison with theory at various levels of sophistication. Though the charge density is a detailed function, the features of which can be compared at several points of interest in space, it is by no means the only level at which comparison can be made. The following sequence represents a progression of functions that are increasingly related to the experimental measurement.

$$\psi(1, 2, \ldots, n) \to \Gamma^1(1, 1) \quad \begin{array}{c} \text{electrostatic} \\ \text{properties} \\ \uparrow \\ \to \rho(\mathbf{r}) \to \langle \rho(\mathbf{r}) \rangle \to F(\mathbf{h}) \to I(\mathbf{h}) \\ \downarrow \\ \Delta\rho(\mathbf{r}) \to \langle \Delta\rho(\mathbf{r}) \rangle, \end{array}$$
$$(8.7.3.74)$$

where the angle brackets refer to the thermally averaged functions.

The experimental information may be reduced in the opposite sequence: