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where the integral has been replaced by a summation.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

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

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.

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

where the angle brackets refer to the thermally averaged functions.

The experimental information may be reduced in the opposite sequence:

Table 8.7.3.3. *The matrix M^{-1} relating d-orbital occupancies P_{ij} to multipole populations P_{lm} (from Holladay, Leung & Coppens, 1983)*

d-orbital populations	Multipole populations					
	P_{00}	P_{20}	P_{22+}	P_{40}	P_{42+}	P_{44+}
P_z^2	0.200	1.039	0.00	1.396	0.00	0.00
P_{xz}	0.200	0.520	0.942	-0.931	1.108	0.00
P_{yz}	0.200	0.520	-0.942	-0.931	-1.108	0.00
$P_{x^2-y^2}$	0.200	-0.039	0.00	0.233	0.00	1.571
P_{xy}	0.200	-1.039	0.00	0.233	0.00	-1.571

Mixing terms

	P_{21}	P_{21-}	P_{22+}	P_{22-}	P_{41+}	P_{41-}	P_{42+}	P_{42-}	P_{43+}	P_{43-}	P_{44-}
$P_{z^2/xz}$	1.088	0.00	0.00	0.00	2.751	0.00	0.00	0.00	0.00	0.00	0.00
$P_{z^2/yz}$	0.00	1.088	0.00	0.00	0.00	2.751	0.00	0.00	0.00	0.0	0.00
P_{z^2/x^2-y^2}	0.00	0.00	-2.177	0.00	0.00	0.00	1.919	0.00	0.00	0.0	0.00
$P_{z^2/xy}$	0.00	0.00	0.00	-2.177	0.00	0.00	0.00	1.919	0.00	0.0	0.00
$P_{xz/yz}$	0.00	0.00	0.00	1.885	0.00	0.00	0.00	2.216	0.00	0.0	0.00
P_{xz/x^2-y^2}	1.885	0.00	0.00	0.00	-0.794	0.00	0.00	0.00	2.094	0.0	0.00
$P_{xz/xy}$	0.00	1.885	0.00	0.00	0.00	-0.794	0.00	0.00	0.00	2.094	0.00
P_{yz/x^2-y^2}	0.00	-1.885	0.00	0.00	0.00	0.794	0.00	0.00	0.00	2.094	0.00
$P_{yz/xy}$	1.885	0.00	0.00	0.00	-0.794	0.00	0.00	0.00	-2.094	0.00	0.00
$P_{x^2-y^2/xy}$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3.142

$$
\begin{array}{ccccc}
\text{electrostatic} \\
\text{properties} \\
\uparrow \\
\rho(\mathbf{r}) & \leftarrow & \langle\rho(\mathbf{r})\rangle & \leftarrow & F(\mathbf{h}) & \leftarrow & I(\mathbf{h}) \\
\downarrow & & \downarrow \\
\Delta\rho(\mathbf{r}) & \leftarrow & \langle\Delta\rho(\mathbf{r})\rangle.
\end{array}
$$

$$(8.7.3.75)$$

The crucial step in each sequence is the thermal averaging (top sequence) or the deconvolution of thermal motion (bottom sequence), which in principle requires detailed knowledge of both the internal (molecular) and the external (lattice) modes of the crystal. Even within the generally accepted Born–Oppenheimer approximation, this is a formidable task, which can be simplified for molecular crystals by the assumption that the thermal smearing is dominated by the larger-amplitude external modes. The procedure (8.7.3.65) requires an adequate thermal-motion model in the structure-factor formalism applied to the experimental structure amplitudes. The commonly used models may include anharmonicity, as described in Volume B, Chapter 1.2 (*IT*B, 1992), but assume that a density function centred on an atom can be assigned the thermal motion of that atom, which may be a poor approximation for the more diffuse functions.

The missing link in scheme (8.7.3.75) is the sequence $\psi \leftarrow \Gamma^1(1,1) \leftarrow \rho(\mathbf{r})$. In order to describe the wavefunction analytically, a basis set is required. The number of coefficients in the wavefunction is minimized by the use of a minimal basis for the molecular orbitals, but calculations in general lead to poor-quality electron densities.

If the additional approximation is made that the wavefunction is a single Slater determinant, the idempotency condition can be used in the derivation of the wavefunction from the electron density. A simplified two-valence-electron two-orbital system has been treated in this manner (Massa, Goldberg,

Frishberg, Boehme & La Placa, 1985), and further developments may be expected.

A special case occurs if the overlap between the orbitals on an atom and its neighbours is very small. In this case, a direct relation can be derived between the populations of a minimal basis set of valence orbitals and the multipole coefficients, as described in the following sections.

8.7.3.6. *Occupancies of transition-metal valence orbitals from multipole coefficients*

In general, the atom-centred density model functions describe both the valence and the two-centre overlap density. In the case of transition metals, the latter is often small, so that to a good approximation the atomic density can be expressed in terms of an atomic orbital basis set d_i, as well as in terms of the multipolar expansion. Thus,

$$
\rho_d = \sum_{i=1}^{5}\sum_{j\geq i}^{5} P_{ij} d_i d_j,
$$
$$
= \sum_{l=0}^{4} \kappa'^3 \left\{ R_l(\kappa'r) \sum_{m=0}^{l}\sum_p P_{lmp} d_{lmp} \right\},
\qquad (8.7.3.76)
$$

in which d_{lmp} are the density functions.

The orbital products $d_i d_j$ can be expressed as linear combinations of spherical harmonic functions, with coefficients listed in Volume B, Chapter 1.2 (*IT*B, 1992), which leads to relations between the P_{ij} and P_{lmp}. In matrix notation,

$$
\mathbf{P}_{lmp} = \mathbf{M}\mathbf{P}_{ij},
\qquad (8.7.3.77)
$$

where $\mathbf{P}_{lmp}$ is a vector containing the coefficients of the 15 spherical harmonic functions with $l = 0$, 2, or 4 that are generated by the products of d orbitals. The matrix $\mathbf{M}$ is also a function of the ratio of orbital and density-function normalization coefficients, given in Volume B, Chapter 1.2 (*IT*B, 1992).