

## 8.7. ANALYSIS OF CHARGE AND SPIN DENSITIES

represents the component of the charge distribution  $\rho(\mathbf{r})$  that gives a non-zero contribution to the integral for the electrostatic multipole moment  $q_{lmp}$ ,

$$q_{lmp} = - \int \rho_{\text{atom}}(\mathbf{r}) r^l c_{lmp} \, d\mathbf{r}, \quad (8.7.3.8)$$

where the functions  $c_{lmp}$  are the Cartesian representations of the real spherical harmonics (Coppens, 1992).

More general models include non-atom centred functions. If the wavefunction  $\psi$  in (8.7.2.4) is an antisymmetrized product of molecular orbitals  $\psi_i$ , expressed in terms of a linear combination of atomic orbitals  $\chi_\mu$ ,  $\psi_i = \sum_\mu c_{i\mu} \chi_\mu$  (LCAO formalism), the integration (8.7.2.4) leads to

$$\rho(\mathbf{r}) = \sum_\mu \sum_\nu P_{\mu\nu} \chi_\mu(\mathbf{r} - \mathbf{R}_\mu) \chi_\nu(\mathbf{r} - \mathbf{R}_\nu), \quad (8.7.3.9)$$

with  $\mathbf{R}_\mu$  and  $\mathbf{R}_\nu$  defining the centres of  $\chi_\mu$  and  $\chi_\nu$ , respectively,  $P_{\mu\nu} = \sum_i n_i c_{i\mu} c_{i\nu}$ , and the sum is over all molecular orbitals with occupancy  $n_i$ . Expression (8.7.3.9) contains products of atomic orbitals, which may have significant values for orbitals centred on adjacent atoms. In the 'charge-cloud' model (Hellner, 1977), these products are approximated by bond-centred, Gaussian-shaped density functions. Such functions can often be projected efficiently into the one-centre terms of the spherical harmonic multipole model, so that large correlations occur if both spherical harmonics and bond-centred functions are adjusted independently in a least-squares refinement.

According to (8.7.2.4) and (8.7.3.9), the population of the two-centre terms is related to the one-centre occupancies. A molecular-orbital based model, which implicitly incorporates such relations, has been used to describe local bonding between transition-metal and ligand atoms (Becker & Coppens, 1985).

## 8.7.3.3. Physical constraints

There are several physical constraints that an electron-density model must satisfy. With the exception of the electroneutrality constraint, they depend strongly on the electron density close to the nucleus, which is poorly determined by the diffraction experiment.

## 8.7.3.3.1. Electroneutrality constraint

Since a crystal is neutral, the total electron population must equal the sum of the nuclear charges of the constituent atoms. A constraint procedure for linear least squares that does not increase the size of the least-squares matrix has been described by Hamilton (1964). If the starting point is a neutral crystal, the constraint equation becomes

$$\sum \Delta P_i S_i = 0, \quad (8.7.3.10)$$

where  $S_i = \int g(\mathbf{r}) \, d\mathbf{r}$ ,  $g$  being a general density function, and the  $\Delta P_i$  are the shifts in the population parameters. For the multipole model, only the monopolar functions integrate to a non-zero value. For normalized monopole functions, this gives

$$\sum_{\text{monopoles}} \Delta P_i = 0. \quad (8.7.3.11)$$

If the shifts without constraints are given by the vector  $\mathbf{y}$  and the constrained shifts by  $\mathbf{y}_c$ , the Hamilton constraint is expressed as

$$\mathbf{y}_c^T = \mathbf{y}^T - \mathbf{y}^T \mathbf{Q}^T (\mathbf{Q} \mathbf{A}^{-1} \mathbf{Q}^T)^{-1} \mathbf{Q} \mathbf{A}^{-1}, \quad (8.7.3.12)$$

where the superscript  $T$  indicates transposition,  $\mathbf{A}$  is the least-squares matrix of the products of derivatives, and  $\mathbf{Q}$  is a row vector of the values of  $S_i$  for elements representing density functions and zeros otherwise.

Expression (8.7.3.12) cannot be applied if the unconstrained refinement corresponds to a singular matrix. This would be the case if all population parameters, including those of the core functions, were to be refined together with the scale factor. In this case, a new set of independent parameters must be defined, as described in Chapter 8.1 on least-squares refinements. Alternatively, one may set the scale factor to one and rescale the population parameters to neutrality after completion of the refinement. This will in general give a non-integral electron population for the core functions. The proper interpretation of such a result is that a core-like function is an appropriate component of the density basis set representing the valence electrons.

## 8.7.3.3.2. Cusp constraint

The electron density at a nucleus  $i$  with nuclear charge  $Z_i$  must satisfy the electron-nuclear cusp condition given by

$$\lim_{r_i \rightarrow 0} \left( \frac{\partial}{\partial r_i} + 2Z_i \right) \rho_{0i}(\mathbf{r}_i) = 0, \quad (8.7.3.13)$$

where  $\rho_{0i}(\mathbf{r}_i) = (1/4\pi) \int \rho(\mathbf{r}) \, d\Omega_i$  is the spherical component of the expansion of the density around nucleus  $i$ .

Only  $1s$ -type functions have non-zero electron density at the nucleus and contribute to (8.7.3.13). For the hydrogen-like atom or ion described by a single exponent radial function  $R(r) = N \exp(-\zeta r)$ , (8.7.3.13) gives  $\zeta = 2Z/a_0$ , where  $Z$  is the nuclear charge, and  $a_0$  is the Bohr unit. Thus, a modification of  $\zeta$  for  $1s$  functions, as implied by (8.7.3.6) and (8.7.3.7) if applied to H atoms, leads to a violation of the cusp constraint. In practice, the electron density at the nucleus is not determined by a limited resolution diffraction experiment; the single exponent function  $R(r)$  is fitted to the electron density away from, rather than at the nucleus.

## 8.7.3.3.3. Radial constraint

Poisson's electrostatic equation gives a relation between the gradient of the electric field  $\nabla^2 \Phi(\mathbf{r})$  and the electron density at  $\mathbf{r}$ .

$$\nabla^2 \Phi(\mathbf{r}) = -4\pi \rho(\mathbf{r}). \quad (8.7.3.14)$$

As noted by Stewart (1977), this equation imposes a constraint on the radial functions  $R(r)$ . For  $R_l(r) = N_l r^{l(0)} \exp(-\zeta_l r)$ , the condition  $n(l) \geq l$  must be obeyed for  $R_l r^{-l}$  to be finite at  $r = 0$ , which satisfies the requirement of the non-divergence of the electric field  $\nabla V$ , its gradient  $\nabla^2 V$ , the gradient of the field gradient  $\nabla^3 V$ , etc.

## 8.7.3.3.4. Hellmann-Feynman constraint

According to the electrostatic Hellmann-Feynman theorem, which follows from the Born-Oppenheimer approximation and the condition that the forces on the nuclei must vanish when the nuclear configuration is in equilibrium, the nuclear repulsions are balanced by the electron-nucleus attractions (Levine, 1983). The balance of forces is often achieved by a very sharp polarization of the electron density very close to the nuclei (Hirshfeld & Rzotkiewicz, 1974), which may be represented in the X-ray model by the introduction of dipolar functions with large values of  $\zeta$ . The Hellmann-Feynman constraint offers the possibility for obtaining information on such functions even though they may contribute only marginally to the observed X-ray scattering (Hirshfeld, 1984).

As the Hellmann-Feynman constraint applies to the static density, its application presumes a proper deconvolution of the thermal motion and the electron density in the scattering model.