

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 ψ in (8.7.2.4) is an antisymmetrized product of molecular orbitals ψ_i , expressed in terms of a linear combination of atomic orbitals χ_μ , $\psi_i = \sum_\mu c_{i\mu} \chi_\mu$ (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}_μ and \mathbf{R}_ν defining the centres of χ_μ and χ_ν , 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 ΔP_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 ζ 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 ∇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 ζ . 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.