

## 8. REFINEMENT OF STRUCTURAL PARAMETERS

 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	0.00	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	0.00	0.00
$P_{z^2/xy}$	0.00	0.00	0.00	-2.177	0.00	0.00	0.00	1.919	0.00	0.00	0.00
$P_{xz/yz}$	0.00	0.00	0.00	1.885	0.00	0.00	0.00	2.216	0.00	0.00	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	0.00	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

electrostatic properties

$$\begin{array}{c}
 \uparrow \\
 \rho(\mathbf{r}) \quad \leftarrow \quad \langle \rho(\mathbf{r}) \rangle \quad \leftarrow \quad F(\mathbf{h}) \quad \leftarrow \quad I(\mathbf{h}) \\
 \downarrow \\
 \Delta\rho(\mathbf{r}) \quad \leftarrow \quad \langle \Delta\rho(\mathbf{r}) \rangle.
 \end{array}$$

(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 (ITB, 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,

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

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 (ITB, 1992), which leads to relations between the  $P_{ij}$  and  $P_{lmp}$ . In matrix notation,

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

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 (ITB, 1992).