

8.7. ANALYSIS OF CHARGE AND SPIN DENSITIES

 Table 8.7.3.4. *Orbital–multipole relations for square-planar complexes (point group D_{4h})*

		P_{00}	P_{20}	P_{40}	P_{44+}
P_{20}	a_{1g}	0.200	1.039	1.396	0.00
P_{21+}	e_g	0.200	0.520	−0.931	0.00
P_{21-}		0.200	0.520	−0.931	0.00
P_{22+}	b_{1g}	0.200	−1.039	0.233	1.570
P_{22-}	b_{2g}	0.200	−1.039	0.233	−1.570

The d -orbital occupancies can be derived from the experimental multipole populations by the inverse expression,

$$\mathbf{P}_{ij} = \mathbf{M}^{-1} \mathbf{P}_{imp} \quad (8.7.3.78)$$

(Holladay, Leung & Coppens, 1983).

The matrix \mathbf{M}^{-1} is given in Table 8.7.3.3. Point-group-specific expressions can be derived by omission of symmetry-forbidden terms. Matrices for point group $4/mmm$ (square planar) and for trigonal point groups (3, $\bar{3}$, 32 , $3m$, $\bar{3}m$) are listed in Tables 8.7.3.4 and 8.7.3.5, respectively. Point groups with and without vertical mirror planes are distinguished by the occurrence of both d_{lm+} and d_{lm-} functions in the latter case, and only d_{lm+} in the former, with m being restricted to n , the order of the rotation axis. The d_{lm-} functions can be eliminated by rotation of the coordinate system around a vertical axis through an angle ψ_0 given by $\psi_0 = (1/n) \arctan(P_{lm-}/P_{lm+})$.

8.7.3.7. Thermal smearing of theoretical densities

8.7.3.7.1. General considerations

In the Born–Oppenheimer approximation, the electrons rearrange instantaneously to the minimum-energy state for each nuclear configuration. This approximation is generally valid, except when very low lying excited electronic states exist. The thermally smeared electron density is then given by

$$\langle \rho(\mathbf{r}) \rangle = \int \rho(\mathbf{r}, \mathbf{R}) P(\mathbf{R}) d(\mathbf{R}), \quad (8.7.3.79)$$

where \mathbf{R} represents the $3N$ nuclear space coordinates and $P(\mathbf{R})$ is the probability of the configuration \mathbf{R} . Evaluation of (8.7.3.79) is possible if the vibrational spectrum is known, but requires a large number of quantum-mechanical calculations at points along the vibrational path. A further approximation is the convolution approximation, which assumes that the charge density near each nucleus can be convoluted with the vibrational motion of that nucleus,

$$\langle \rho(\mathbf{r}) \rangle = \sum_n \int \rho_n(\mathbf{r} - \mathbf{u} - \mathbf{R}_n) P_n(\mathbf{u}) d\mathbf{u}, \quad (8.7.3.80)$$

where ρ_n stands for the density of the n th pseudo-atom. The convolution approximation thus requires decomposition of the density into atomic fragments. It is related to the thermal-motion formalisms commonly used, and requires that two-centre terms in the theoretical electron density be either projected into the atom-centred density functions, or assigned the thermal motion of a point between the two centres. In the LCAO approximation (8.7.3.9), the two-centre terms are represented by

$$\rho_{\mu\nu}(\mathbf{r}) = P_{\mu\nu} \chi_\mu(\mathbf{r} - \mathbf{R}_\mu) \chi_\nu(\mathbf{r} - \mathbf{R}_\nu), \quad (8.7.3.81)$$

where χ_μ and χ_ν are basis functions centred at \mathbf{R}_μ and \mathbf{R}_ν , respectively. As the motion of a point between the two vibrating atoms depends on their relative phase, further assumptions must

 Table 8.7.3.5. *Orbital–multipole relations for trigonal complexes*

	P_{00}	P_{2-}	P_{40}	P_{43+}	P_{43-}
(a) In terms of d orbitals					
P_{20}	0.200	1.039	1.396	0.00	0.00
P_{21+}	0.200	0.520	−0.931	0.00	0.00
P_{21-}	0.200	0.520	−0.931	0.00	0.00
P_{22+}	0.200	−1.039	0.233	0.00	0.00
P_{22-}	0.200	−1.039	0.233	0.00	0.00
$P_{21+/22+}$	0.00	0.00	0.00	2.094	0.00
$P_{21+/22-}$	0.00	0.00	0.00	0.00	2.094
$P_{21-/22+}$	0.00	0.00	0.00	0.00	2.094
$P_{21-/22-}$	0.00	0.00	0.00	−2.094	0.00
(b) In terms of symmetry-adapted orbitals*†					
$P_1(a_{1g})$	0.200	1.039	1.396	0.00	
$P_2(e_g)$	0.400	−1.039	−0.310	−1.975	
$P_3(e'_g)$	0.400	0.00	−1.087	1.975	
$P_4(e_{g^+}e'_g + e_{g^-}e'_g)$	0.00	−2.942	2.193	1.397	

* The electron density in terms of the symmetry-adapted orbitals is given by:

$$\rho_{3d} = P_1 a_{1g}^2 + \frac{1}{2} P_2 (e_{g^+}^2 - e_{g^-}^2) + \frac{1}{2} P_4 (e_{g^+} e'_g + e_{g^-} e'_g),$$

with: $a_{1g} = d_{z^2}$; $e_{g^+} = \sqrt{(2/3)} d_{x^2-y^2} - \sqrt{(1/3)} d_{xz}$; $e_{g^-} = \sqrt{(2/3)} d_{xy} + \sqrt{(1/3)} d_{yz}$; $e'_{g^+} = \sqrt{(1/3)} d_{x^2-y^2} + \sqrt{(2/3)} d_{xz}$; and $e'_{g^-} = \sqrt{(1/3)} d_{xy} - \sqrt{(2/3)} d_{yz}$. † The signs given here imply a positive e'_g lobe in the positive xz quadrant. Care should be exercised in defining the coordinate system if this lobe is to point towards a ligand atom.

be made. The simplest is to assume a gradual variation of the thermal motion along the bond, which gives at a point \mathbf{r}_i on the internuclear vector of length $R_{\mu\nu}$

$$U_{ij}(\mathbf{r}_i) = [U_{ij}(\mathbf{R}_\mu) |\mathbf{R}_\mu - \mathbf{r}_i| + U_{ij}(\mathbf{R}_\nu) |\mathbf{R}_\nu - \mathbf{r}_i|] / R_{\mu\nu}. \quad (8.7.3.82)$$

This expression may be used to assign thermal parameters to a bond-centred function.

8.7.3.7.2. Reciprocal-space averaging over external vibrations

Thermal averaging of the electron density is considerably simplified for modes in which adjacent atoms move in phase. In molecular crystals, such modes correspond to rigid-body vibrations and librations of the molecule as a whole. Their frequencies are low because of the weakness of intermolecular interactions. Rigid-body motions therefore tend to dominate thermal motion, in particular at temperatures for which kT ($k = 0.7 \text{ cm}^{-1}$) is large compared with the spacing of the vibrational energy levels of the external modes (internal modes are typically not excited to any extent at or below room temperature).

For a translational displacement (\mathbf{u}), the dynamic density is given by

$$\rho_{\text{dyn}}(\mathbf{r}) = \int \rho(\mathbf{r} - \mathbf{u}) P(\mathbf{u}) d\mathbf{u}, \quad (8.7.3.83)$$

with $\rho(\mathbf{r})$ defined by (8.7.3.81) (Stevens, Rees & Coppens, 1977). In the harmonic approximation, $P(\mathbf{u})$ is a normalized three-dimensional Gaussian probability function, the exponents