

## 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  $\psi_0$  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  $\rho_n$  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  $\chi_\mu$  and  $\chi_\nu$  are basis functions centred at  $\mathbf{R}_\mu$  and  $\mathbf{R}_\nu$ , 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

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of which may be obtained by rigid-body analysis of the experimental data. In general, for a translational displacement ( $\mathbf{u}$ ) and a librational oscillation ( $\omega$ ),

$$\rho_{\text{dyn}}(\mathbf{r}) = \left( \sum P_{\mu\nu} \chi_{\mu} \chi_{\nu} \right) * P(\mathbf{u}, \omega). \quad (8.7.3.84)$$

If correlation between  $\mathbf{u}$  and  $\omega$  can be ignored (neglect of the screw tensor  $\mathbf{S}$ ),  $P(\mathbf{u}, \omega) = P(\mathbf{u})P(\omega)$ , and both types of modes can be treated independently. For the translations

$$\begin{aligned} \langle \rho \rangle_{\text{trans}} &= \sum P_{\mu\nu} \{ \chi_{\mu}(\mathbf{r}) \chi_{\nu}(\mathbf{r}) * P(\mathbf{u}) \} \\ &= \sum P_{\mu\nu} F^{-1} \{ f_{\mu\nu}(\mathbf{h}) \cdot T_{\text{tr}}(\mathbf{h}) \}, \end{aligned} \quad (8.7.3.85)$$

where  $F^{-1}$  is the inverse Fourier transform operator, and  $T_{\text{tr}}(\mathbf{h})$  is the translational temperature factor.

If  $\mathbf{R}$  is an orthogonal rotation matrix corresponding to a rotation  $\omega$ , we obtain for the librations

$$\begin{aligned} \langle \rho \rangle_{\text{libr}} &= \sum P_{\mu\nu} \{ \chi_{\mu}(\mathbf{R}\mathbf{r}) \chi_{\nu}(\mathbf{R}\mathbf{r}) * P(\omega) \} \\ &= \sum P_{\mu\nu} F^{-1} \{ \langle f_{\mu\nu}(\mathbf{R}\mathbf{h}) \rangle \}, \end{aligned} \quad (8.7.3.86)$$

in which  $f(\mathbf{h})$  has been averaged over the distribution of orientations of  $\mathbf{h}$  with respect to the molecule;

$$\langle f_{\mu\nu}(\mathbf{h}) \rangle = \int f_{\mu\nu}(\mathbf{R}\mathbf{h}) P(\omega) d\omega. \quad (8.7.3.87)$$

Evaluation of (8.7.3.85) and (8.7.3.86) is most readily performed if the basis functions  $\psi$  have a Gaussian-type radial dependence, or are expressed as a linear combination of Gaussian radial functions.

For Gaussian products of  $s$  orbitals, the molecular scattering factor of the product  $\psi_{\mu} \psi_{\nu} = N_{\mu} \exp[-\alpha_{\mu}(\mathbf{r} - \mathbf{r}_A)^2] \times N_{\nu} \exp[-\alpha_{\nu}(\mathbf{r} - \mathbf{r}_B)^2]$ , where  $N_{\mu}$  and  $N_{\nu}$  are the normalization factors of the orbitals  $\mu$  and  $\nu$  centred on atoms  $A$  and  $B$ , is given by

$$\begin{aligned} f_{\text{stat}}^{s,s}(\mathbf{h}) &= N_{\mu} N_{\nu} \exp\left(-\frac{\alpha_{\mu} \alpha_{\nu}}{\alpha_{\mu} + \alpha_{\nu}} |\mathbf{r}_A - \mathbf{r}_B|^2\right) \left(\frac{\pi}{\alpha_{\mu} + \alpha_{\nu}}\right)^{3/2} \\ &\times \exp\left(\frac{-\pi^2 |\mathbf{h}|^2}{\alpha_{\mu} + \alpha_{\nu}}\right) \exp(2\pi i \mathbf{h} \cdot \mathbf{r}_c), \end{aligned} \quad (8.7.3.88)$$

where the centre of density  $\mathbf{r}_c$  is defined by  $\mathbf{r}_c = (\alpha_{\mu} \mathbf{r}_A + \alpha_{\nu} \mathbf{r}_B) / (\alpha_{\mu} + \alpha_{\nu})$ .

For the translational modes, the temperature-factor exponent  $-2\pi^2 \sum_i \sum_j U_{ij} h_i h_j$  is simply added to the Gaussian exponent in (8.7.3.88) to give

$$\exp\left(-\frac{\pi^2 |\mathbf{h}|^2}{\alpha_{\mu} + \alpha_{\nu}}\right) - 2\pi^2 \sum_i \sum_j U_{ij} h_i h_j.$$

For librations, we may write

$$\mathbf{R}\mathbf{r} = \mathbf{r} + \mathbf{u}_{\text{lib}}$$

As  $(\mathbf{R}\mathbf{h}) \cdot \mathbf{r} = \mathbf{h} \cdot \mathbf{R}^T \mathbf{r} = \mathbf{h} \cdot \mathbf{r} - (\mathbf{R}\mathbf{h}) \cdot \mathbf{u}_{\text{lib}}$ , for a function centred at  $\mathbf{r}$ ,

$$\begin{aligned} \langle \exp(2\pi \mathbf{h} \cdot \mathbf{r}_c) \rangle &= \sum \exp[2\pi i (\mathbf{R}\mathbf{h}) \cdot \mathbf{r}_c] P(\delta) d\omega \\ &= \exp(2\pi \mathbf{h} \cdot \mathbf{r}_c) \int \exp[-2\pi i (\mathbf{R}\mathbf{h}) \cdot \mathbf{u}_{\text{lib}}^c] P(\omega) d\omega, \end{aligned} \quad (8.7.3.89)$$

which shows that for  $ss$  orbital products the librational temperature factor can be factored out, or

$$f_{\text{dyn}}^{s,s} = f_{\text{stat}}^{s,s} \int \exp[-2\pi i (\mathbf{R}\mathbf{h}) \cdot \mathbf{u}_{\text{lib}}^c] P(\omega) d\omega. \quad (8.7.3.90)$$

Expressions for  $P(\omega)$  are described elsewhere (Pawley & Willis, 1970).

For general Cartesian Gaussian basis functions of the type

$$\psi(\mathbf{r}) = (x - x_A)^m (y - y_A)^n (z - z_A)^p \exp(-\alpha |\mathbf{r} - \mathbf{r}_A|^2), \quad (8.7.3.91)$$

the scattering factors are more complicated (Miller & Krauss, 1967; Stevens, Rees & Coppens, 1977), and the librational temperature factor can no longer be factored out. However, it may be shown that, to a first approximation, (8.7.3.90) can again be used. This 'pseudotranslation' approximation corresponds to a neglect of the change in orientation (but not of position) of the two-centre density function and is adequate for moderate vibrational amplitudes.

Thermally smeared density functions are obtained from the averaged reciprocal-space function by performing the inverse Fourier transform with phase factors depending on the position coordinates of each orbital product

$$\langle \rho \rangle = \frac{1}{V} \sum P_{\mu\nu} \sum_{\mathbf{h}} f_{\mu\nu}(\mathbf{h}) \exp[-2\pi i \mathbf{h} \cdot (\mathbf{r} - \mathbf{r}_c)], \quad (8.7.3.92)$$

where the orbital product  $\chi_{\mu} \chi_{\nu}$  is centred at  $\mathbf{r}_c$ . If the summation is truncated at the experimental limit of  $(\sin \theta)/\lambda$ , both thermal vibrations and truncation effects are properly introduced in the theoretical densities.

### 8.7.3.8. Uncertainties in experimental electron densities

It is often important to obtain an estimate of the uncertainty in the deformation densities in Table 8.7.3.1. If it is assumed that the density of the static atoms or fragments that are subtracted out are precisely known, three sources of uncertainty affect the deformation densities: (1) the uncertainties in the experimental structure factors; (2) the uncertainties in the positional and thermal parameters of the density functions that influence  $\rho_{\text{calc}}$ ; and (3) the uncertainty in the scale factor  $k$ .

If we assume that the uncertainties in the observed structure factors are not correlated with the uncertainties in the refined parameters, the variance of the electron density is given by

$$\begin{aligned} \sigma^2(\Delta\rho) &= \sigma^2(\rho'_{\text{obs}}) + \sigma^2(\rho_{\text{calc}}) + (\rho'_{\text{obs}})^2 \frac{\sigma^2(k)}{k^2} \\ &+ \sum_p \frac{\delta\rho_{\text{calc}}}{\delta u_p} \sigma(u_p) \rho'_{\text{obs}} \frac{\sigma(k)}{k} \gamma(u_p, k), \end{aligned} \quad (8.7.3.93)$$

where  $\rho'_{\text{obs}} = \rho_{\text{obs}}/k$ ,  $u_p$  is a positional or thermal parameter, and the  $\gamma(u_p, k)$  are correlation coefficients between the scale factor and the other parameters (Rees, 1976, 1978; Stevens & Coppens, 1976).

Similarly, for the covariance between the deformation densities at points  $A$  and  $B$ ,

$$\begin{aligned} \text{cov}(\Delta\rho_A, \Delta\rho_B) &= \text{cov}(\rho_{\text{obs},A}, \rho_{\text{obs},B}) / k^2 \\ &+ \text{cov}(\rho_{\text{calc},A}, \rho_{\text{calc},B}) \\ &+ \rho_{\text{obs},A} \rho_{\text{obs},B} [\sigma(k)/k]^2, \end{aligned} \quad (8.7.3.94)$$

where it is implied that the second term includes the effect of the scale factor/parameter correlation.

Following Rees (1976), we may derive a simplified expression for the covariance valid for the space group  $P\bar{1}$ . Since the structure factors are not correlated with each other,