

1. GENERAL RELATIONSHIPS AND TECHNIQUES

Table 1.2.8.3. Products of two real spherical harmonic functions y_{lmp} in terms of the density functions d_{lmp} defined by equation (1.2.7.3b)

$y_{00} y_{00} = 1.0000d_{00}$
$y_{10} y_{00} = 0.43301d_{10}$
$y_{10} y_{10} = 0.38490d_{20} + 1.0d_{00}$
$y_{11\pm} y_{00} = 0.43302d_{11\pm}$
$y_{11\pm} y_{10} = 0.31831d_{21\pm}$
$y_{11\pm} y_{11\pm} = 0.31831d_{22\pm} - 0.19425d_{20} + 1.0d_{00}$
$y_{11+} y_{11-} = 0.31831d_{22-}$
$y_{20} y_{00} = 0.43033d_{20}$
$y_{20} y_{10} = 0.37762d_{30} + 0.38730d_{10}$
$y_{20} y_{11\pm} = 0.28864d_{31\pm} - 0.19365d_{11\pm}$
$y_{20} y_{20} = 0.36848d_{40} + 0.27493d_{20} + 1.0d_{00}$
$y_{21\pm} y_{00} = 0.41094d_{21\pm}$
$y_{21\pm} y_{10} = 0.33329d_{31\pm} + 0.33541d_{11\pm}$
$y_{21\pm} y_{11\pm} = \pm 0.26691d_{32\pm} - 0.21802d_{30} + 0.33541d_{10}$
$y_{21\pm} y_{11\mp} = -0.26691d_{32-}$
$y_{21\pm} y_{20} = 0.31155d_{41\pm} + 0.13127d_{21\pm}$
$y_{21\pm} y_{21\pm} = \pm 0.25791d_{42\pm} \pm 0.22736d_{22\pm} - 0.24565d_{40} + 0.13747d_{20} + 1.0d_{00}$
$y_{21+} y_{21-} = 0.25790d_{42-} + 0.22736d_{22-}$
$y_{22\pm} y_{00} = 0.41094d_{22\pm}$
$y_{22\pm} y_{10} = 0.26691d_{32\pm}$
$y_{22\pm} y_{11\pm} = \pm 0.31445d_{33\pm} - 0.083323d_{31\pm} + 0.33541d_{11\pm}$
$y_{22\pm} y_{11\mp} = 0.31445d_{33-} \pm 0.083323d_{31-} \mp 0.33541d_{11-}$
$y_{22\pm} y_{20} = 0.22335d_{42\pm} - 0.26254d_{22\pm}$
$y_{22\pm} y_{21\pm} = \pm 0.23873d_{43\pm} - 0.089938d_{41\pm} + 0.22736d_{21\pm}$
$y_{22\pm} y_{21\mp} = 0.23873d_{43-} \pm 0.089938d_{41-} \mp 0.22736d_{21-}$
$y_{22\pm} y_{22\pm} = \pm 0.31831d_{44\pm} + 0.061413d_{40} - 0.27493d_{20} + 1.0d_{00}$
$y_{22+} y_{22-} = 0.31831d_{44-}$

Table 1.2.11.1. The arrays G_{ijkl} and H_{ijkl} to be used in the observational equations $U_{ij} = G_{ijkl}L_{kl} + H_{ijkl}S_{kl} + T_{ij}$ [equation (1.2.11.9)]

G_{ijkl}

ij	kl					
	11	22	33	23	31	12
11	0	z^2	y^2	$-2yz$	0	0
22	z^2	0	x^2	0	$-2xz$	0
33	y^2	x^2	0	0	0	$-2xy$
23	$-yz$	0	0	$-x^2$	xy	xz
31	0	$-xz$	0	xy	$-y^2$	yz
12	0	0	$-xy$	xz	yz	$-z^2$

H_{ijkl}

ij	kl								
	11	22	33	23	31	12	32	13	21
11	0	0	0	0	$-2y$	0	0	0	$2z$
22	0	0	0	0	0	$-2z$	$2x$	0	0
33	0	0	0	$-2x$	0	0	0	$2y$	0
23	0	$-x$	x	0	0	y	0	$-z$	0
31	y	0	$-y$	z	0	0	0	0	$-x$
12	$-z$	z	0	0	x	0	$-y$	0	0

displacements of the L_2 and L_3 axes are obtained by permutation of the indices. If all three axes are appropriately displaced, only the diagonal terms of S remain. Referred to the principal axes of L , they represent screw correlations along these axes and are independent of origin shifts.

The elements of the reduced T are

$${}^rT_{II} = \widehat{T}_{II} - \sum_{K \neq I} (\widehat{S}_{KI})^2 / \widehat{L}_{KK}$$

$${}^rT_{IJ} = \widehat{T}_{IJ} - \sum_K \widehat{S}_{KI} \widehat{S}_{KJ} / \widehat{L}_{KK}, \quad J \neq I. \quad (1.2.11.12)$$

The resulting description of the average rigid-body motion is in terms of six independently distributed instantaneous motions – three screw librations about nonintersecting axes (with screw pitches given by $\widehat{S}_{11}/\widehat{L}_{11}$ etc.) and three translations. The parameter set consists of three libration and three translation amplitudes, six angles of orientation for the principal axes of L and T , six coordinates of axis displacement, and three screw pitches, one of which has to be chosen arbitrarily, again for a total of 20 variables.

Since diagonal elements of S enter into the expression for ${}^rT_{IJ}$, the indeterminacy of $\text{Tr}(S)$ introduces a corresponding indeterminacy in rT . The constraint $\text{Tr}(S) = 0$ is unaffected by the various rotations and translations of the coordinate systems used in the course of the analysis.

1.2.12. Treatment of anharmonicity

The probability distribution (1.2.10.2) is valid in the case of rectilinear harmonic motion. If the deviations from Gaussian shape are not too large, distributions may be used which are expansions with the Gaussian distribution as the leading term. Three such distributions are discussed in the following sections.

1.2.12.1. The Gram–Charlier expansion

The three-dimensional Gram–Charlier expansion, introduced into thermal-motion treatment by Johnson & Levy (1974), is an expansion of a function in terms of the zero and higher derivatives of a normal distribution (Kendall & Stuart, 1958). If D_j is the operator d/du^j ,

about the axis l and translation parallel to this axis. This quantity, like $T_{ij}l_j$, depends on the choice of origin, although the sum of the two quantities is independent of the origin.

The nonsymmetrical tensor S can be written as the sum of a symmetric tensor with elements $S_{ij}^S = (S_{ij} + S_{ji})/2$ and a skew-symmetric tensor with elements $S_{ij}^A = (S_{ij} - S_{ji})/2$. Expressed in terms of principal axes, S^S consists of three principal screw correlations $\langle \lambda_{IT} \rangle$. Positive and negative screw correlations correspond to opposite senses of helicity. Since an arbitrary constant may be added to all three correlation terms, only the differences between them can be determined from the data.

The skew-symmetric part S^A is equivalent to a vector $(\lambda \times t)/2$ with components $(\lambda \times t)_i/2 = (\lambda_j t_k - \lambda_k t_j)/2$, involving correlations between a libration and a perpendicular translation. The components of S^A can be reduced to zero, and S made symmetric, by a change of origin. It can be shown that the origin shift that symmetrizes S also minimizes the trace of T . In terms of the coordinate system based on the principal axes of L , the required origin shifts $\widehat{\rho}_i$ are

$$\widehat{\rho}_1 = \frac{\widehat{S}_{23} - \widehat{S}_{32}}{\widehat{L}_{22} + \widehat{L}_{33}}, \quad \widehat{\rho}_2 = \frac{\widehat{S}_{31} - \widehat{S}_{13}}{\widehat{L}_{11} + \widehat{L}_{33}}, \quad \widehat{\rho}_3 = \frac{\widehat{S}_{12} - \widehat{S}_{21}}{\widehat{L}_{11} + \widehat{L}_{22}}, \quad (1.2.11.10)$$

in which the carets indicate quantities referred to the principal axis system.

The description of the averaged motion can be simplified further by shifting to three generally nonintersecting libration axes, one each for each principal axis of L . Shifts of the L_1 axis in the L_2 and L_3 directions by

$${}^1\widehat{\rho}_2 = -\widehat{S}_{13}/\widehat{L}_{11} \quad \text{and} \quad {}^1\widehat{\rho}_3 = \widehat{S}_{12}/\widehat{L}_{11}, \quad (1.2.11.11)$$

respectively, annihilate the S_{12} and S_{13} terms of the symmetrized S tensor and simultaneously effect a further reduction in $\text{Tr}(T)$ (the presubscript denotes the axis that is shifted, the subscript the direction of the shift component). Analogous equations for

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Table 1.2.12.1. *Some Hermite polynomials (Johnson & Levy, 1974; Zucker & Schulz, 1982)*

$H(\mathbf{u}) = 1$ $H_j(\mathbf{u}) = w_j$ $H_{jk}(\mathbf{u}) = w_j w_k - p_{jk}$ $H_{jkl}(\mathbf{u}) = w_j w_k w_l - (w_j p_{kl} + w_k p_{lj} + w_l p_{jk}) = w_j w_k w_l - 3w_j(p_{kl})$ $H_{jklm}(\mathbf{u}) = w_j w_k w_l w_m - 6w_j(w_k p_{lm}) + 3p_{j(k} p_{l)m}$ $H_{jklmn}(\mathbf{u}) = w_j w_k w_l w_m w_n - 10w_j(w_m w_n p_{jk}) + 15w_j(p_{jk} p_{lm})$ $H_{jklmnp}(\mathbf{u}) = w_j w_k w_l w_m w_n w_p - 15w_j(w_k w_l w_m p_{jk}) + 45w_j(w_k p_{lm} p_{np}) - 15p_{j(k} p_{l} p_{m} p_{n)p}$ <p style="font-size: small; margin-top: 5px;">where $w_j \equiv p_{jk} u^k$ and p_{jk} are the elements of σ^{-1}, defined in expression (1.2.10.2). Indices between brackets indicate that the term is to be averaged over all permutations which produce distinct terms, keeping in mind that $p_{jk} = p_{kj}$ and $w_j w_k = w_k w_j$ as illustrated for H_{jkl}.</p>
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$$P(\mathbf{u}) = [1 - c^j D_j + \frac{1}{2!} c^{jk} D_j D_k - \frac{1}{3!} c^{jkl} D_j D_k D_l + \dots + (-1)^r \frac{c^{\alpha_1} \dots c^{\alpha_r}}{r!} D_{\alpha_1} D_{\alpha_2} \dots D_{\alpha_r}] P_0(\mathbf{u}), \quad (1.2.12.1)$$

where $P_0(\mathbf{u})$ is the harmonic distribution, $\alpha_i = 1, 2$ or 3 , and the operator $D_{\alpha_1} \dots D_{\alpha_r}$ is the r th partial derivative $\partial^r / (\partial u^{\alpha_1} \dots \partial u^{\alpha_r})$. Summation is again implied over repeated indices.

The differential operators D may be eliminated by the use of three-dimensional Hermite polynomials $H_{\alpha_1 \dots \alpha_r}$ defined, by analogy with the one-dimensional Hermite polynomials, by the expression

$$D_{\alpha_1} \dots D_{\alpha_r} \exp(-\frac{1}{2} \sigma_{jk}^{-1} u^j u^k) = (-1)^r H_{\alpha_1 \dots \alpha_r}(\mathbf{u}) \exp(-\frac{1}{2} \sigma_{jk}^{-1} u^j u^k), \quad (1.2.12.2)$$

which gives

$$P(\mathbf{u}) = \left[1 + \frac{1}{3!} c^{jkl} H_{jkl}(\mathbf{u}) + \frac{1}{4!} c^{jklm} H_{jklm}(\mathbf{u}) + \frac{1}{5!} c^{jklmn} H_{jklmn}(\mathbf{u}) + \frac{1}{6!} c^{jklmnp} H_{jklmnp}(\mathbf{u}) + \dots \right] P_0(\mathbf{u}), \quad (1.2.12.3)$$

where the first and second terms have been omitted since they are equivalent to a shift of the mean and a modification of the harmonic term only. The permutations of j, k, l, \dots here, and in the following sections, include all combinations which produce different terms.

The coefficients c , defined by (1.2.12.1) and (1.2.12.2), are known as the *quasimoments* of the frequency function $P(\mathbf{u})$ (Kutznetsov *et al.*, 1960). They are related in a simple manner to the moments of the function (Kendall & Stuart, 1958) and are invariant to permutation of indices. There are 10, 15, 21 and 28 components of c for orders 3, 4, 5 and 6, respectively. The multivariate Hermite polynomials are functions of the elements of σ_{jk}^{-1} and of u^k , and are given in Table 1.2.12.1 for orders ≤ 6 (IT IV, 1974; Zucker & Schulz, 1982).

The Fourier transform of (1.2.12.3) is given by

$$T(\mathbf{H}) = \left[1 - \frac{4}{3} \pi^3 i c^{jkl} h_j h_k h_l + \frac{2}{3} \pi^4 c^{jklm} h_j h_k h_l h_m + \frac{4}{15} \pi^5 i c^{jklmn} h_j h_k h_l h_m h_n - \frac{4}{45} \pi^6 c^{jklmnp} h_j h_k h_l h_m h_n h_p + \dots \right] T_0(\mathbf{H}), \quad (1.2.12.4)$$

where $T_0(\mathbf{H})$ is the harmonic temperature factor. $T(\mathbf{H})$ is a power-series expansion about the harmonic temperature factor, with even and odd terms, respectively, real and imaginary.

1.2.12.2. The cumulant expansion

A second statistical expansion which has been used to describe the atomic probability distribution is that of Edgeworth (Kendall & Stuart, 1958; Johnson, 1969). It expresses the function $P(\mathbf{u})$ as

$$P(\mathbf{u}) = \exp \left(\kappa^j D_j + \frac{1}{2!} \kappa^{jk} D_j D_k - \frac{1}{3!} \kappa^{jkl} D_j D_k D_l + \frac{1}{4!} \kappa^{jklm} D_j D_k D_l D_m - \dots \right) P_0(\mathbf{u}). \quad (1.2.12.5a)$$

Like the moments μ of a distribution, the cumulants κ are descriptive constants. They are related to each other (in the one-dimensional case) by the identity

$$\exp \left\{ \kappa_1 t + \frac{\kappa_2 t^2}{2!} + \dots + \frac{\kappa_r t^r}{r!} + \dots \right\} = 1 + \mu_1 t + \frac{\mu_2 t^2}{2!} + \dots + \frac{\mu_r t^r}{r!}. \quad (1.2.12.5b)$$

When it is substituted for t , (1.2.12.5b) is the characteristic function, or Fourier transform of $P(t)$ (Kendall & Stuart, 1958).

The first two terms in the exponent of (1.2.12.5a) can be omitted if the expansion is around the equilibrium position and the harmonic term is properly described by $P_0(\mathbf{u})$.

The Fourier transform of (1.2.12.5a) is, by analogy with the left-hand part of (1.2.12.5b) (with t replaced by $2\pi i h$),

$$T(\mathbf{H}) = \exp \left[\frac{(2\pi i)^3}{3!} \kappa^{jkl} h_j h_k h_l + \frac{(2\pi i)^4}{4!} \kappa^{jklm} h_j h_k h_l h_m + \dots \right] T_0(\mathbf{H}) = \exp \left[-\frac{4}{3} \pi^3 i \kappa^{jkl} h_j h_k h_l + \frac{2}{3} \pi^4 \kappa^{jklm} h_j h_k h_l h_m + \dots \right] T_0(\mathbf{H}), \quad (1.2.12.6)$$

where the first two terms have been omitted. Expression (1.2.12.6) is similar to (1.2.12.4) except that the entire series is in the exponent. Following Schwarzenbach (1986), (1.2.12.6) can be developed in a Taylor series, which gives

$$T(\mathbf{H}) = \left\{ 1 + \frac{(2\pi i)^3}{3!} \kappa^{jkl} h_j h_k h_l + \frac{(2\pi i)^4}{4!} \kappa^{jklm} h_j h_k h_l h_m + \dots + \frac{(2\pi i)^6}{6!} \left[\kappa^{jklmp} + \frac{6!}{2!(3!)^2} \kappa^{jkl} \kappa^{mnp} \right] h_j h_k h_l h_m h_n h_p + \text{higher-order terms} \right\} T_0(\mathbf{H}). \quad (1.2.12.7)$$

This formulation, which is sometimes called the Edgeworth approximation (Zucker & Schulz, 1982), clearly shows the relation to the Gram-Charlier expansion (1.2.12.4), and corresponds to the probability distribution [analogous to (1.2.12.3)]

$$P(\mathbf{u}) = P_0(\mathbf{u}) \left\{ 1 + \frac{1}{3!} \kappa^{jkl} H_{jkl}(\mathbf{u}) + \frac{1}{4!} \kappa^{jklm} H_{jklm}(\mathbf{u}) + \dots + \frac{1}{6!} \left[\kappa^{jklmnp} + 10 \kappa^{jkl} \kappa^{mnp} \right] H_{jklmnp} + \text{higher-order terms} \right\}. \quad (1.2.12.8)$$

The relation between the cumulants κ^{jkl} and the quasimoments c^{jkl} are apparent from comparison of (1.2.12.8) and (1.2.12.4):

$$\begin{aligned} c^{jkl} &= \kappa^{jkl} \\ c^{jklm} &= \kappa^{jklm} \\ c^{jklmn} &= \kappa^{jklmn} \\ c^{jklmnp} &= \kappa^{jklmnp} + 10 \kappa^{jkl} \kappa^{mnp}. \end{aligned} \quad (1.2.12.9)$$

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The sixth- and higher-order cumulants and quasimoments differ. Thus the third-order cumulant κ^{jkl} contributes not only to the coefficient of H_{jkl} , but also to higher-order terms of the probability distribution function. This is also the case for cumulants of higher orders. It implies that for a finite truncation of (1.2.12.6), the probability distribution cannot be represented by a finite number of terms. This is a serious difficulty when a probability distribution is to be derived from an experimental temperature factor of the cumulant type.

1.2.12.3. The one-particle potential (OPP) model

When an atom is considered as an independent oscillator vibrating in a potential well $V(\mathbf{u})$, its distribution may be described by Boltzmann statistics.

$$P(\mathbf{u}) = N \exp\{-V(\mathbf{u})/kT\}, \quad (1.2.12.10)$$

with N , the normalization constant, defined by $\int P(\mathbf{u}) \, d\mathbf{u} = 1$. The classical expression (1.2.12.10) is valid in the high-temperature limit for which $kT \gg V(\mathbf{u})$.

Following Dawson (1967) and Willis (1969), the potential function may be expanded in terms of increasing order of products of the contravariant displacement coordinates:

$$V = V_0 + \alpha_j u^j + \beta_{jk} u^j u^k + \gamma_{jkl} u^j u^k u^l + \delta_{jklm} u^j u^k u^l u^m + \dots \quad (1.2.12.11)$$

The equilibrium condition gives $\alpha_j = 0$. Substitution into (1.2.12.10) leads to an expression which may be simplified by the assumption that the leading term is the harmonic component represented by β_{jk} :

$$P(\mathbf{u}) = N \exp\{-\beta'_{jk} u^j u^k\} \times \{1 - \gamma'_{jkl} u^j u^k u^l - \delta'_{jklm} u^j u^k u^l u^m - \dots\}, \quad (1.2.12.12)$$

in which $\beta' = \beta/kT$ etc. and the normalization factor N depends on the level of truncation.

The probability distribution is related to the spherical harmonic expansion. The ten products of the displacement parameters $u^j u^k u^l$, for example, are linear combinations of the seven octapoles ($l=3$) and three dipoles ($l=1$) (Coppens, 1980). The thermal probability distribution and the aspherical atom description can be separated only because the latter is essentially confined to the valence shell, while the former applies to all electrons which follow the nuclear motion in the atomic scattering model.

The Fourier transform of the OPP distribution, in a general coordinate system, is (Johnson, 1970a; Scheringer, 1985a)

$$T(\mathbf{H}) = T_0(\mathbf{H}) \left[1 - \frac{4}{3} \pi^3 i \gamma'_{jkl} G^{jkl}(\mathbf{H}) + \frac{2}{3} \pi^4 \delta'_{jklm} G^{jklm}(\mathbf{H}) + \frac{4}{15} \pi^5 i \varepsilon'_{jklmn} G^{jklmn}(\mathbf{H}) - \frac{4}{45} \pi^6 i \varphi'_{jklmnp} G^{jklmnp}(\mathbf{H}) \dots \right], \quad (1.2.12.13)$$

where T_0 is the harmonic temperature factor and G represents the Hermite polynomials in reciprocal space.

If the OPP temperature factor is expanded in the coordinate system which diagonalizes β_{jk} , simpler expressions are obtained in which the Hermite polynomials are replaced by products of the displacement coordinates u^j (Dawson *et al.*, 1967; Coppens, 1980; Tanaka & Marumo, 1983).

1.2.12.4. Relative merits of the three expansions

The relative merits of the Gram–Charlier and Edgeworth expansions have been discussed by Zucker & Schulz (1982), Kuhs (1983), and by Scheringer (1985b). In general, the Gram–Charlier expression is found to be preferable because it gives a better fit in

the cases tested, and because its truncation is equivalent in real and reciprocal space. The latter is also true for the one-particle potential model, which is mathematically related to the Gram–Charlier expansion by the interchange of the real- and reciprocal-space expressions. The terms of the OPP model have a specific physical meaning. The model allows prediction of the temperature dependence of the temperature factor (Willis, 1969; Coppens, 1980), provided the potential function itself can be assumed to be temperature independent.

It has recently been shown that the Edgeworth expansion (1.2.12.5a) always has negative regions (Scheringer, 1985b). This implies that it is not a realistic description of a vibrating atom.

1.2.13. The generalized structure factor

In the generalized structure-factor formalism developed by Dawson (1975), the complex nature of both the atomic scattering factor and the generalized temperature factor are taken into account. We write for the atomic scattering factor:

$$f_j(\mathbf{H}) = f_{j,c}(\mathbf{H}) + i f_{j,a}(\mathbf{H}) + f'_j + i f''_j \quad (1.2.13.1a)$$

$$T_j(\mathbf{H}) = T_{j,c}(\mathbf{H}) + i T_{j,a}(\mathbf{H}) \quad (1.2.13.1b)$$

and

$$F(\mathbf{H}) = A(\mathbf{H}) + iB(\mathbf{H}), \quad (1.2.13.2)$$

where the subscripts c and a refer to the centrosymmetric and noncentrosymmetric components of the underlying electron distribution, respectively. Substitution in (1.2.4.2) gives for the real and imaginary components A and B of $F(\mathbf{H})$

$$A(\mathbf{H}) = \sum_j (f_{j,c} + f'_j) [\cos(2\pi\mathbf{H} \cdot \mathbf{r}_j) T_c - \sin(2\pi\mathbf{H} \cdot \mathbf{r}_j) T_a] - (f_{j,a} + f''_j) [\cos(2\pi\mathbf{H} \cdot \mathbf{r}_j) T_a + \sin(2\pi\mathbf{H} \cdot \mathbf{r}_j) T_c] \quad (1.2.13.3a)$$

and

$$B(\mathbf{H}) = \sum_j (f_{j,c} + f'_j) [\cos(2\pi\mathbf{H} \cdot \mathbf{r}_j) T_a + \sin(2\pi\mathbf{H} \cdot \mathbf{r}_j) T_c] + (f_{j,a} + f''_j) [\cos(2\pi\mathbf{H} \cdot \mathbf{r}_j) T_c - \sin(2\pi\mathbf{H} \cdot \mathbf{r}_j) T_a] \quad (1.2.13.3b)$$

(McIntyre *et al.*, 1980; Dawson, 1967).

Expressions (1.2.13.3) illustrate the relation between valence-density anisotropy and anisotropy of thermal motion.

1.2.14. Conclusion

This chapter summarizes mathematical developments of the structure-factor formalism. The introduction of atomic asphericity into the formalism and the treatment of thermal motion are interlinked. It is important that the complexities of the thermal probability distribution function can often be reduced by very low temperature experimentation. Results obtained with the multipole formalism for atomic asphericity can be used to derive physical properties and d -orbital populations of transition-metal atoms (ITC, 2004). In such applications, the deconvolution of the charge density and the thermal vibrations is essential. This deconvolution is dependent on the adequacy of the models summarized here.

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