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Addition of Higher Cumulants to the Crystallographic Structure-Factor Equation: A Generalized Treatment for Thermal-Motion Effects*

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The usual crystallographic structure-factor equation, with three positional and six anisotropic-temperature-factor coefficients, assumes that the thermal-motion probability density function is centrosymmetric. However, phenomena such as libration and anharmonic vibration can cause skewness. In this study, ten more coefficients per atom representing the third cumulant of the probability density function for thermal-motion are added to the structure-factor equation to permit a determination of the nature of the skewness. The Edgeworth series expansion based on the normal probability density function is used to analyze the results. The equations are generalized to include also the fourth cumulant, which describes kurtosis. The 'cumulant-expansion model' for thermal motion is a statistical model without kinematic constraints and provides an unbiased estimate for the skewness of the density function for thermal motion. Application of the model to neutron diffraction data from crystals containing methyl groups (which are undergoing torsional oscillation) confirms the assumption that the density functions for the hydrogen atoms of a methyl group are skewed as an arc about the axis of torsional oscillation. The model has not been applied with X-ray diffraction data; if it were, the resulting parameters would describe the skewness of the combined electron and thermal-motion probability density functions.

1. Normal density function

A variety of mathematical models can be used to describe the time-averaged vibrational displacement of an atom in a crystal. The most popular model in current use is based on the frequency function or probability density function (p.d.f.) of the trivariate normal distribution, which is written as

$$\Phi(u^1,u^2,u^3) = \frac{|p|^{\frac{1}{2}}}{(2\pi)^{3/2}} \times \exp\left[-\tfrac{1}{2}\sum_{i,j=1}^{3} p_{ij}(u^i-x^i)\,(u^j-x^j)\right], \quad (1)$$

where u^1,u^2,u^3 are the contravariant components of a 3-dimensional random variable (displacement vector), x^1,x^2,x^3 are the parameters of the mean of the p.d.f., and the matrix $||p_{ij}||$ with covariant components is the inverse of the dispersion (variance–covariance) matrix $||\sigma^{ij}||$ defined in equation (2) below. The determinant of $||p_{ij}||$ is denoted as $|p|$.

The characteristic function or Fourier transform of the p.d.f. defined in equation (1) is

$$\varphi(t_1,t_2,t_3) = \exp\left(i\sum_{i=1}^{3} x^i t_i - \tfrac{1}{2}\sum_{i,j=1}^{3}\sigma^{ij}t_i t_j\right), \quad (2)$$

where i, if not used as an index, is $\sqrt{-1}$. If we make the change of variables $t_i=2\pi h_i$ and $||\sigma^{ij}||=||b^{ij}||/2\pi^2$ $(i,j=1,2,3)$, then multiply $\varphi(h_1,h_2,h_3)$ by the atomic scattering factor $f(h_1,h_2,h_3)$ and sum over the n atoms of the unit cell, we obtain

$$F(h_1,h_2,h_3) = \sum_{k=1}^{n} f_k(h_1,h_2,h_3) \times \exp\left(2\pi i\sum_{i=1}^{3} x_k^i h_i - \sum_{i,j=1}^{3} b_k^{ij} h_i h_j\right), \quad (3)$$

which is the usual formulation for the structure-factor equation with Miller indices h_1,h_2,h_3, anisotropic-temperature-factor coefficients b^{ij} $(i,j=1,2,3)$ and fractional positional parameters x^1,x^2,x^3. In other words, a characteristic function transformed by the change of variables $t_i=2\pi h_i$ $(i=1,2,3)$, is a structure-factor equation for a unit point scatterer. The use of the trivariate normal p.d.f. model is called the quadratic approximation because of the quadratic form which appears in equation (1). Although equation (3) is an adequate model for most investigations in structural crystallography, there are instances when a more elaborate model is justified, for example, in systems involving librations or anharmonic vibrations.

2. Edgeworth series expansion

Let us expand the characteristic function ψ of an arbitrary trivariate p.d.f. Ψ in terms of cumulants as

$$\psi(t_1,t_2,t_3) = \exp\left(i\sum_{i=1}^{3} {}^1\kappa^i t_i + \frac{i^2}{2!}\sum_{i,j=1}^{3} {}^2\kappa^{ij} t_i t_j + \frac{i^3}{3!}\sum_{i,j,k=1}^{3} {}^3\kappa^{ijk} t_i t_j t_k + \frac{i^4}{4!}\sum_{i,j,k,l=1}^{3} {}^4\kappa^{ijkl} t_i t_j t_k t_l + \ldots\right). \quad (4)$$

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The terms ${}^1\boldsymbol{\kappa}$, ${}^2\boldsymbol{\kappa}$, ${}^3\boldsymbol{\kappa}$, and ${}^4\boldsymbol{\kappa}$ are by definition the first four cumulants or semi-invariants (Kendall & Stuart, 1958) of the p.d.f. Ψ; they are tensors of rank 1 through 4 consecutively. Each of the tensors is invariant to pairwise interchanges of its indices, so that there are 3, 6, 10, and 15 unique elements in the 4 successive tensors in the general case of site symmetry 1. The numbers of unique elements for the 32 possible site symmetries are given in Table 1. The four tensors describe the mean, the dispersion, the skewness, and the kurtosis (peakedness-flatness) of the corresponding p.d.f.

The p.d.f. Ψ whose characteristic function is equation (4) can be approximated by an Edgeworth series expansion*

$$\Psi(u^1,u^2,u^3)=\{1-\tfrac{1}{6}\sum_{i,j,k=1}^{3}{}^3\kappa^{ijk}D_iD_jD_k+[\tfrac{1}{24}\sum_{i,j,k,l=1}^{3}{}^4\kappa^{ijkl}D_iD_jD_kD_l+\tfrac{1}{72}\sum_{i,j,k,q,r,s=1}^{3}{}^3\kappa^{ijk}\,{}^3\kappa^{qrs}D_iD_jD_kD_qD_rD_s]\}\times\Phi(u^1,u^2,u^3)\,, \qquad (5)$$

in which Φ, defined in equation (1), is called the developing normal p.d.f. with $\mathbf{x}\equiv{}^1\boldsymbol{\kappa}$ and $\boldsymbol{\sigma}\equiv{}^2\boldsymbol{\kappa}$. The symbol D_i represents the covariant differential operator $\partial/\partial u^i$. The individual D operators are commutative since the space is Euclidean. For example, $D_jD_lD_iD_k=D_iD_jD_kD_l=\partial^4/\partial u^i\partial u^j\partial u^k\partial u^l$. The correction term in square brackets in equation (5) is omitted if ${}^4\boldsymbol{\kappa}$ is not determined. For purposes of numerical evaluation, equation (5) can be reformulated in terms of the cumulants and multivariate Hermite polynomials (Chambers, 1967; Johnson, 1969).

When a least-squares fitting procedure based on observed intensities is used to evaluate the coefficients in the cumulant expansion (4) truncated after the third

Table 1. *Number of unique coefficients in cumulant tensors of ranks* 1–4 [*from Higman* (1955)]

	Site symmetry		${}^1K$	${}^2K$	${}^3K$	${}^4K$
Triclinic	1	C_1	3	6	10	15
	$\bar{1}$	C_i	0	6	0	15
Monoclinic	m	C_s	2	4	6	9
	2	C_2	1	4	4	9
	$2/m$	C_{2h}	0	4	0	9
Orthorhombic	$mm2$	C_{2v}	1	3	3	6
	222	D_2	0	3	1	6
	mmm	D_{2h}	0	3	0	6
Tetragonal	4	C_4	1	2	2	5
	$\bar{4}$	S_4	0	2	2	5
	$4/m$	C_{4h}	0	2	0	5
	$4mm$	C_{4v}	1	2	2	4
	$\bar{4}2m$	S_{4v}	0	2	1	4
	422	D_4	0	2	0	4
	$4/mmm$	D_{4h}	0	2	0	4
Trigonal	3	C_3	1	2	4	5
	$\bar{3}$	S_6	0	2	0	5
	$3m$	C_{3v}	1	2	3	4
	32	D_3	0	2	1	4
	$\bar{3}m$	D_{3d}	0	2	0	4
Hexagonal	$\bar{6}$	C_{3h}	0	2	2	3
	6	C_6	1	2	2	3
	$6/m$	C_{6h}	0	2	0	3
	$\bar{6}m2$	D_{3h}	0	2	1	3
	$6mm$	C_{6v}	1	2	2	3
	622	D_6	0	2	0	3
	$6/mmm$	D_{6h}	0	2	0	3
Cubic	23	T	0	1	1	2
	$m3$	T_h	0	1	0	2
	$\bar{4}3m$	T_d	0	1	1	2
	432	O	0	1	0	2
	$m3m$	O_h	0	1	0	2

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* This expansion was introduced by Edgeworth (1905). The literature on the expansion is summarized by Wallace (1958). The justification for its use with multivariate probability density functions is a quite recent development discussed by Chambers (1967). Helpful texts for the univariate case are chapter 17 of Cramer (1946), chapter 8 of Gnedenko & Kolmogorov (1954) and chapter 6 of Kendall & Stuart (1958). Modes and cumulants are discussed in chapters 2 and 3 of Kendall & Stuart.

or fourth cumulants, the values obtained are biased by the missing cumulants, which are implicitly set to zero. In this paper, a true cumulant is designated by $\boldsymbol{\kappa}$ and the least-squares estimate by **K**. If all odd-order cumulants past $^1\mathbf{K}$ are omitted, as in the normal model, we obtain an unbiased estimate of the mean.† If all even-order cumulants past $^2\mathbf{K}$ are omitted, we obtain an unbiased estimate of the dispersion. For these reasons, it is better to use the mean and dispersion obtained with the use of the normal structure-factor equation (3) in the developing normal p.d.f. Φ. To combine the results from the normal refinement with the results from the use of the cumulant-expansion model, we must use the extended Edgeworth expansion (Wallace, 1958). We define

$$^1\mathbf{L}={}^1\mathbf{K}-\mathbf{x} \quad \text{and} \quad {}^2\mathbf{L}={}^2\mathbf{K}-\boldsymbol{\sigma}$$

and using the summation convention, write the Edgeworth expansion as

$$\begin{aligned}\Psi(u^1,u^2,u^3)=\{1-{}^1L^iD_i-\tfrac{1}{6}\,{}^3K^{ijk}D_iD_jD_k\\ +[\tfrac{1}{2}\,{}^2L^{ij}D_iD_j+\tfrac{1}{2}\,{}^1L^i\,{}^1L^jD_iD_j\\ +\tfrac{1}{6}\,{}^1L^i\,{}^3K^{jkl}D_iD_jD_kD_l+\tfrac{1}{24}\,{}^4K^{ijkl}D_iD_jD_kD_l\\ +\tfrac{1}{72}\,{}^3K^{ijk}\,{}^3K^{qrs}D_iD_jD_kD_qD_rD_s]\}\\ \times\Phi(u^1,u^2,u^3)\,. \qquad (6)\end{aligned}$$

The quantity in square brackets is omitted if $^4\mathbf{K}$ is not determined.

3. Structure factor equation

If the procedure used to derive equation (3) from equation (2) is applied to equation (4), the resulting structure-factor equation presented below, can be considered the 'cumulant-expansion model'. The form of the equation is related to but not identical with the 'generalized structure-factor formalism' of Dawson (1967). The cumulant-expansion model is basically a statistical model, free of kinematic assumptions, as is the trivariate normal p.d.f. model (3). In order to simplify the testing of this model, it seems advisable to truncate the expansion after the third cumulant.

For a crystal with n atoms in the unit cell, the structure factor for $\mathbf{h}=(h_1,h_2,h_3)$ is

$$F(\mathbf{h})=A(\mathbf{h})+iB(\mathbf{h})\,, \qquad (7)$$

where

$$A(\mathbf{h})=\sum_{r=1}^{n}\beta_r(\mathbf{h})\,\{f'_r(\mathbf{h})\cos[\alpha_r(\mathbf{h})]-f''_r(\mathbf{h})\sin[\alpha_r(\mathbf{h})]\}$$

$$B(\mathbf{h})=\sum_{r=1}^{n}\beta_r(\mathbf{h})\,\{f'_r(\mathbf{h})\sin[\alpha_r(\mathbf{h})]+f''_r(\mathbf{h})\cos[\alpha_r(\mathbf{h})]\}\,, \qquad (8)$$

and

$$\alpha_r(\mathbf{h})=2\pi\sum_{i=1}^{3}x^i_rh_i-\sum_{i,j,k=1}^{3}c^{ijk}_rh_ih_jh_k$$

$$\beta_r(\mathbf{h})=\exp\,(-\sum_{i,j=1}^{3}b^{ij}_rh_ih_j)\,. \qquad (9)$$

The variable coefficients x^i, b^{ij} and c^{ijk} are $^1K^i$, $(2\pi^2)\,{}^2K^{ij}$, and $(4\pi^3/3)\,{}^3K^{ijk}$ $(i,j,k=1,2,3)$. The atomic scattering factor $f(\mathbf{h})$ is complex with real part $f'(\mathbf{h})$ and imaginary part $f''(\mathbf{h})$ to account for the effects of anomalous dispersion.

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† The $^1\mathbf{K}$ values by themselves should not be considered as usable estimates for the atomic positional parameters when the series is truncated after the third or fourth cumulants; instead it appears best to continue to use the unbiased estimates of the mean obtained with the normal model. Some combination of the least-squares estimates to the odd-order cumulants may prove to be a usable alternate estimate.

Table 2. *Least-squares refinement of normal model and three-cumulant model from neutron diffraction data*

Compound Asymmetric unit	Photodimer of isophorone[(a)] $C_6H_5O(CH_3)_3$	Copper acetate monohydrate[(b)] $Cu(C_2H_3O_2)^2.H_2O$	Xenon tetrafluoride[(c)] $\frac{1}{2}(XeF_4)$	UO_2[(d)] (1·038 Å)	 (0·866 Å)
Neutron data used	2488	2490	622	14	17
Parameters in normal model	218	167	27	4	2
Parameters in 3-cumulant model	458	347	47	5	3
R based on F^2 or F for normal model	0·0523	0·0818	0·0479	0·0029 (F)	0·0068 (F)
R based on F^2 or F for 3-cumulant model	0·0426	0·0672	0·0441	0·0021 (F)	0·0032 (F)
Ratio of weighted R factors	$\frac{0·0710}{0·0535}=1·33$	$\frac{0·0981}{0·0825}=1·19$	$\frac{0·0749}{0·0693}=1·08$	$\frac{0·0024}{0·0018}=1·33$	$\frac{0·0085}{0·0030}=2·83$
R factor ratio for 0·005 level of significance[(e)]	1·06	1·05	1·04	1·59	1·34

(*a*) Vos & Johnson (1969).
(*b*) Chidambaram & Brown (1969).
(*c*) Burns, Agron & Levy (1963).
(*d*) Rouse, Willis & Pryor (1968).
(*e*) Hamilton (1965).

4. Example refinements

The Oak Ridge structure-factor least-squares program was modified to incorporate equations (7)–(9) and used to refine several crystal structures. Results on the refinement of crystal structures with the new model are summarized below. With a full set of three-dimensional data, the variables are usually sufficiently independent to produce a well-conditioned linearized problem which can be readily solved with the usual least-squares normal-equations method.

Neutron diffraction data from four different structures were used to compare the three-cumulant model with the normal model defined by (3). Statistical data pertaining to the refinements are summarized in Table 2 and with one exception, represent highly significant improvements.

The models were each refined to convergence under as nearly identical conditions as possible. The extinction correction of Zachariasen (1967) with one adjustable parameter was included in the least-squares program. A photodimer of isophorone (Vos & Johnson, 1969) and copper acetate monohydrate (Chidambaram & Brown, 1969) were chosen because in these structures there are important torsional motions of the methyl groups and relatively large overall librations of the molecules. The hydrogen atoms on the two methyl groups in copper acetate monohydrate have root-mean-square displacement of nearly 0·5 Å and should provide a rather severe test for the applicability of the cumulant-expansion model for libration effects. Xenon tetrafluoride (Burns, Agron & Levy, 1963) was chosen because of the very favorable ratio of number of observations to variable parameters. The parameters and

Table 3. *Structure parameters for* XeF_4 *from neutron data of Burns, Agron & Levy* (1963)

Equations 3 and 9 define the coefficients for the normal model and the three-cumulant model. The b^{ij} and c^{ijk} terms listed are scaled by 10^4 and 10^5 respectively.

Standard errors are in parentheses

	Xe		F(1)		F(2)	
	Normal	3-Cumulant	Normal	3-Cumulant	Normal	3-Cumulant
x	0	0	0·2644 (2)	0·2644 (4)	0·2356 (2)	0·2353 (4)
y	0	0	0·1481 (2)	0·1481 (4)	0·0297 (2)	0·0294 (3)
z	0	0	−0·1536 (2)	−0·1531 (3)	0·3002 (1)	0·2994 (3)
b_{11}	267 (4)	264 (4)	440 (4)	441 (4)	439 (4)	438 (4)
b_{22}	130 (3)	130 (3)	285 (3)	283 (3)	249 (3)	249 (2)
b_{33}	161 (3)	161 (3)	330 (3)	331 (3)	216 (3)	217 (2)
b_{12}	14 (3)	14 (2)	−59 (3)	−58 (3)	−8 (3)	−7 (2)
b_{13}	50 (3)	50 (2)	167 (3)	167 (2)	−30 (2)	−31 (2)
b_{23}	−2 (2)	−2 (2)	26 (3)	26 (2)	−13 (2)	−13 (2)
c_{111}	—	0	—	−6 (12)	—	−36 (12)
c_{222}	—	0	—	−16 (7)	—	−4 (5)
c_{333}	—	0	—	16 (8)	—	−20 (5)
c_{112}	—	0	—	25 (6)	—	−16 (6)
c_{122}	—	0	—	3 (5)	—	−3 (5)
c_{113}	—	0	—	−8 (6)	—	−1 (5)
c_{133}	—	0	—	−5 (6)	—	13 (3)
c_{223}	—	0	—	5 (4)	—	−1 (4)
c_{233}	—	0	—	2 (5)	—	4 (3)
c_{123}	—	0	—	4 (4)	—	−1 (3)

Table 4. *Element in Cartesian cumulant tensors*

After Birss (1964)

Site symmetry \ *ijk* Mult.	111 (1)	222 (1)	333 (1)	112 (3)	122 (3)	113 (3)	133 (3)	223 (3)	233 (3)	123 (6)	Elements total
1	111	222	333	112	122	113	133	223	233	123	10
m	111	222	0	112	122	0	133	0	233	0	6
2	0	0	333	0	0	113	0	223	0	123	4
*mm*2	0	0	333	0	0	113	0	223	0	0	3
222, $\bar{4}$2*m*, 23, $\bar{4}$3*m*	0	0	0	0	0	0	0	0	0	123	1
4, 4*mm*, 6, 6*mm*	0	0	333	0	0	113	0	113	0	0	2
$\bar{4}$	0	0	0	0	0	113	0	−113	0	123	2
3	111	222	333	−222	−111	113	0	113	0	0	4
3*m*	111	0	333	0	−111	113	0	113	0	0	3
32, $\bar{6}$*m*2	0	222	0	−222	0	0	0	0	0	0	1
$\bar{6}$	111	222	0	−222	−111	0	0	0	0	0	2

standard errors from the XeF_4 refinements based on equations (7), (8), (9) and (3) are given in Table 3 in order to record the numerical results for one of the example calculations. Finally, UO_2 was included to permit a comparison with the generalized structure-factor formalism of Dawson (1967) which has been used to demonstrate anharmonic vibration in UO_2.

Anharmonic vibration has been demonstrated in several different crystals with the site symmetry $\bar{4}3m$ (Rouse, Willis & Pryor, 1968; Dawson, Hurley & Maslen, 1967). The Dawson structure-factor equation is derived by multiplying equation (1) by an expansion in powers of the displacement of the atom from its equilibrium position, and then performing a term by term Fourier transform to obtain a complex-valued expression for the temperature factor. By rearranging equation (10) of Dawson, Hurley & Maslen it is seen that Dawson's equation is related to the cumulant expansion (4) by a power series expansion of an exponential factor containing the third-cumulant tensor. Consequently, the two methods are expected to produce similar results. The present calculated structure factors for UO_2 are in near perfect agreement with those of Rouse, Willis & Pryor. The ${}^3K^{123}$ term is the only element allowed in $\bar{4}3m$ site symmetry (see Table 4); its derived value in contravariant components based on the crystal system is $(19 \pm 7) \times 10^{-8}$ for the 1·038 Å data and $(23 \pm 2) \times 10^{-8}$ for the 0·866 Å data (see Rouse, Willis & Pryor).*

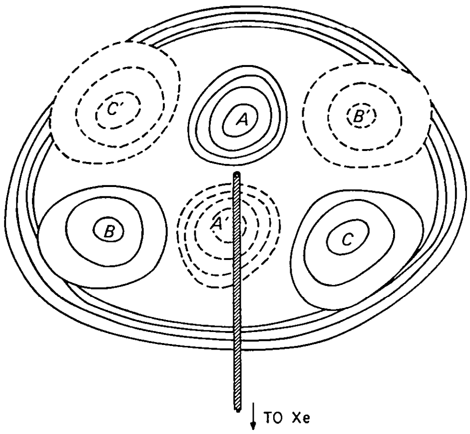

Fig. 1. Skew density map for atom F(2) of XeF_4 superimposed on the Edgeworth density map with the same contour levels drawn and higher contour levels omitted. The contour interval is 0·02 in units of 10^{-12} cm.Å^{-3}. Negative contours are dashed and the zero contour is omitted. The heavy line designating the direction of the Xe–F bond originates at the normal mean. This map is in the plane of the XeF_4 molecule.

5. Skew maps

The p.d.f. Ψ for the three cumulant form of equation (6) is computed from the normal mean $\mathbf{x}$, the displacement from the mean ${}^1\mathbf{L} = {}^1\mathbf{K} - \mathbf{x}$, the dispersion matrix $||\sigma||$ from the normal refinement (which is found to be statistically identical to ${}^2\mathbf{K}$), and the third-rank tensor ${}^3\mathbf{K}$ as

$$\Psi(u^1,u^2,u^3) = \Big(1 - \sum_{i=1}^{3} {}^1L^i D_i - \tfrac{1}{6} \sum_{i,j,k=1}^{3} {}^3K^{ijk} D_i D_j D_k\Big) \Phi(u^1,u^2,u^3) \qquad (10)$$

where Φ is defined by equation (1). Departures from the trivariate normal model (1) can be computed as the antisymmetric function

$$\chi(u^1,u^2,u^3) = \Big(- \sum_{i=1}^{3} {}^1L^i D_i - \tfrac{1}{6} \sum_{i,j,k=1}^{3} {}^3K^{ijk} D_i D_j D_k\Big) \Phi(u^1,u^2,u^3) . \qquad (11)$$

The computer program ORTEP (Johnson, 1965) was modified to calculate 'Edgeworth density maps' defined by (10) and 'skew density maps' defined by (11). Fig. 1 shows the skew map for fluorine atom F(2) of XeF_4 superimposed on the corresponding Edgeworth map with the same contour levels drawn. This figure illustrates how the cumulant expansion model tends to correct the normal density function for the effects of libration. The ${}^1\mathbf{L}$ term of (11) moves the entire ellipsoid of the normal model toward the effective axis of libration at Xe. The ${}^3K$ term then adds a concentrated peak at position A on the side of the ellipsoid away from Xe and subtracts a corresponding peak at A' on the opposite side. The net effect is a six-point checkerboard arrangement of positive and negative peaks antisymmetric about the normal mean. The perfection of the result shown in Fig. 1 is considered fortuitous; and the corresponding skew map for atom F(1) (not shown) is not so easily interpreted.

Fig. 2 shows similar maps for the methyl hydrogen atoms of copper acetate monohydrate. There are some small non-positive regions in the Edgeworth maps but in the worst case, H(3), the minimum is only 3% of the maximum peak height. Considering the fact that only the first three cumulants are used, this result is considered quite satisfactory. It should be emphasized that the results are unbiased in that no kinematic constraints are imposed in the model.

6. Mode calculation

The modes and antimodes of a p.d.f. are the local maxima and minima of probability density. In a centrosymmetric p.d.f. the center of gravity (mean) and a mode (or antimode) coincide. For a non-centrosym-

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* In the notation of Rouse, Willis & Pryor (1968) ${}^3K^{123} = \left(\frac{B}{8\pi^2 a}\right)^3 \frac{\beta}{kT}$ where B is the isotropic temperature factor, a is the cubic unit-cell parameter, k is Boltzman's constant, T is temperature and β is the coefficient of the third-order term in their expansion of the single-particle potential distribution. This transformation produces values of β in complete agreement with those of Rouse *et al.*

metric p.d.f. they may differ. The mode nearest the mean for an atom is closely related to the corresponding maximum in a crystallographic Fourier map and can be used as an alternate estimate of the equilibrium position of the atom. Modes cannot usually be obtained with sufficient accuracy from a Fourier map because of diffraction ripple and other perturbing effects. The Edgeworth expansion (10) allows an alternate method for locating modes by calculating the roots $\mathbf{z}=(z^1,z^2,z^3)$ of the simultaneous non-linear equations

$$D_s\Psi(\mathbf{z})=0 \quad s=1,2,3\,.$$

If we have an initial estimate $\mathbf{z}_0$ for a mode we can use the Newton method (Forsythe & Moler, 1967) to obtain a better estimate $\mathbf{z}_1=\mathbf{z}_0+\Delta\mathbf{z}$ by solving the matrix equation

$$\mathbf{G}\Delta\mathbf{z}=\mathbf{Y}$$

where

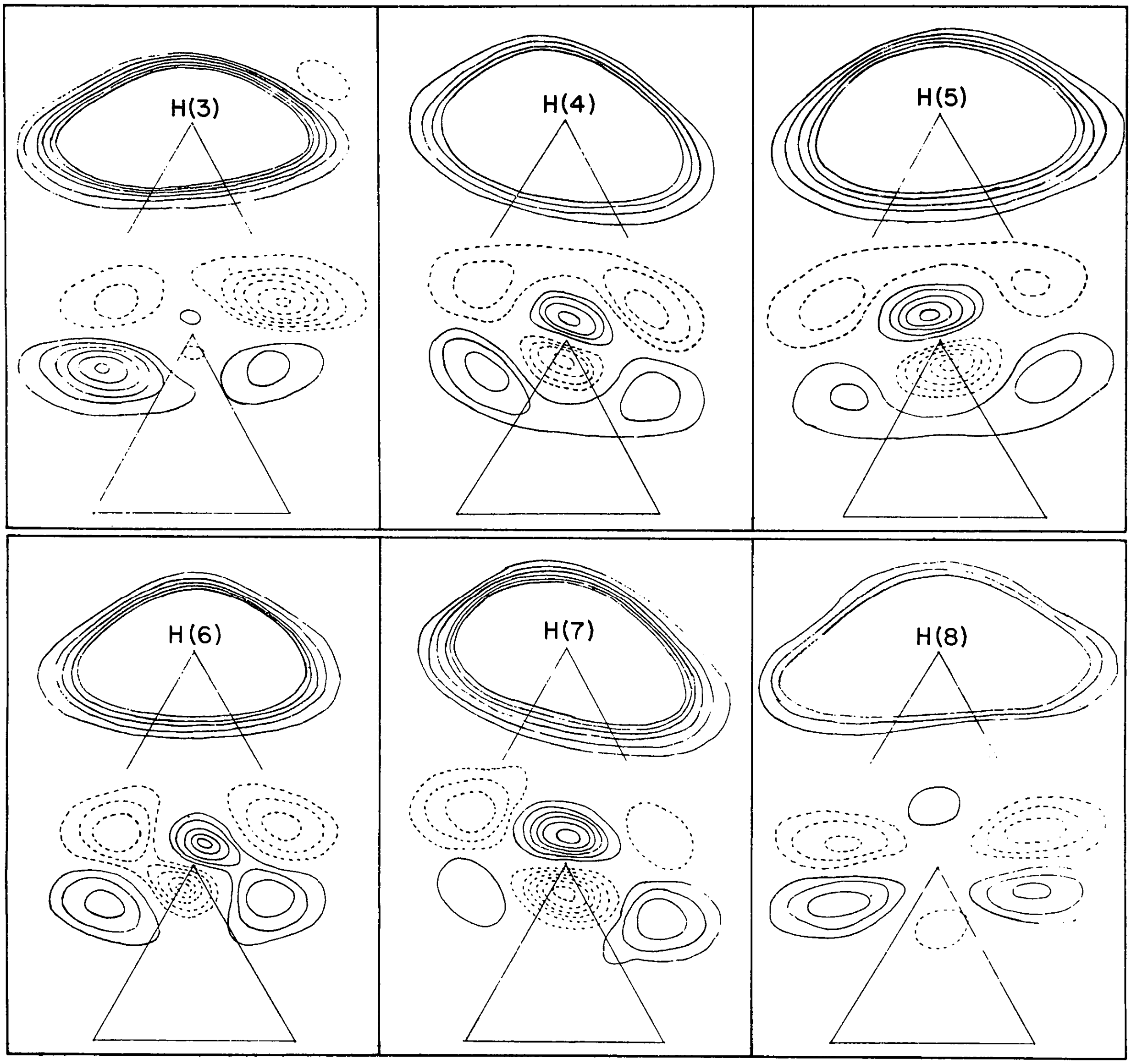

Fig. 2. Edgeworth density maps and skew density maps for the six hydrogen atoms on the methyl groups in copper acetate monohydrate. The maps are in the plane of the hydrogen atoms of a methyl group. The contour interval is 0·02 in units of 10^{-12} cm.Å^{-3}. The zero contours and higher level contours are omitted. The dashed contours signify the subtraction regions of the skew maps. The solid contours represent constant values of negative scattering density for the negative-scattering hydrogen atoms. The vertices of the triangles designate the normal mean positions of the three hydrogen atoms in a methyl group, as obtained by the normal least-squares refinement.

$$G_{rs}=D_rD_s\Psi(\mathbf{z}_0)\ ,\ (r,s=1,2,3)$$

$$Y_s=-D_s\Psi(\mathbf{z}_0)\ ,\ (s=1,2,3)\ .$$

If there is a single major mode sufficiently near the mean, it can be found by setting $\mathbf{z}_0$ equal to the mean. Additional options were added to the computer program ORTEP to calculate modes by Newton's method. In practice, convergence was obtained in 2 to 4 cycles. The intermean and intermode distances for the photodimer of isophorone are shown in Fig. 3. It is apparent that a mode is located with less precision than is a mean, but it is also apparent that the intermode distances tend to correct for foreshortened bond distances caused by thermal libration of the hydrogen atoms.

7. Third-rank tensors

A major conceptual difficulty encountered with third-rank tensors is the problem of developing some insight into what the individual coefficients mean. A first-rank tensor can be considered as a point in 3-space and a second-rank tensor as an ellipsoid; but higher-rank tensors are more difficult. Table 4 (adapted from Birss, 1964) lists the unique coefficients in a Cartesian system for symmetric third-rank tensors on the allowed site symmetries of Table 1. An examination of Table 4 gives some indications for the significance of certain of the coefficients. A more comprehensive approach is to decompose the tensors in Table 4 by group theory into sums of tensors of decreasing symmetry. For any site symmetry it is possible to find a set of orthonormal tensor bases which span the space (one to ten dimensions) of the tensor coefficients. The general procedure for a tensor of any rank is given by Sirotin (1960*a*,*b*; 1961, 1964). A detailed decomposition of the fourth-rank tensors of elastic constants is given by Tu (1968).

8. Conclusions

The addition of the third cumulant to the structure factor equation leads to an unbiased estimate for the skewness of the probability density function of thermal motion. This approach is advantageous when the detailed kinematics of thermal motion are not known or are poorly understood. Models based on mechanistic considerations usually require fewer parameters than the present statistical model and if applicable may be expected to produce specific results with higher precision. For example, the model for torsional oscillation derived by Brown & Chidambaram (1967) produces C–H bond lengths for the methyl groups of copper acetate monohydrate with much better internal consistency than the intermodal distances calculated with the present model. Those results are presented elsewhere (Chidambaram & Brown, 1969). A number of models have been proposed which treat the libration aspects of thermal motion from a mechanistic viewpoint. The published equations and several new ones are analyzed in great detail in a treatise on thermal motion by E. N. Maslen to be published in a book on accurate structure analysis being prepared by H. H. Cady, P. Coppens, R. F. Stewart & E. N. Maslen. This definitive work is highly recommended for those concerned with thermal-motion analysis.

In the present paper, the cumulant expansion model is applied only to neutron diffraction data because of the simplifying effect of the constant neutron scattering amplitude. The model may also be applied with X-ray diffraction data but the results will describe the convolution of electron density with thermal displacement. The cumulant expansion model goes over to the generalized structure-factor formalism of Dawson (1967) if exponentionals containing the higher cumulants are expanded in series.

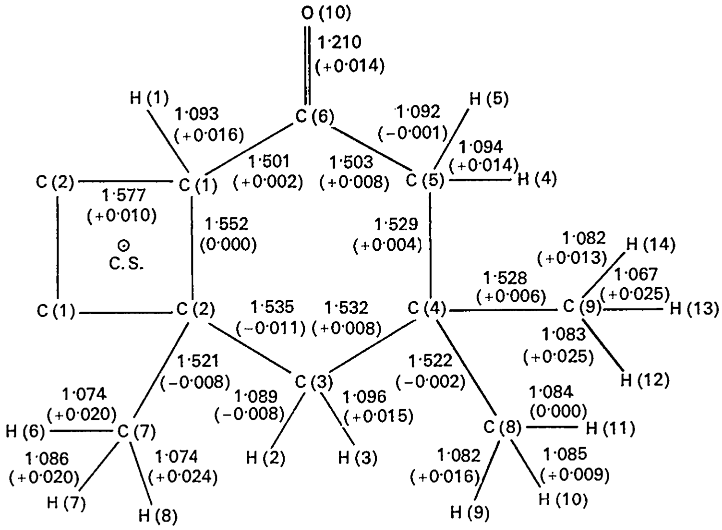

Fig. 3. A comparison of intermean distances and intermode distances in the *cis-anti-cis*-head-to-tail photodimer of isophorone. Values for intermode-minus-intermean distances are in parentheses below the intermean distances.

The coefficients of the third-cumulant tensor should provide additional data for interpreting the thermal motion of molecules in terms of the rigid-body model. Further work along this line is planned.

A more detailed analysis of the cumulant expansion model will be published elsewhere (Johnson, 1969).

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DISCUSSION

See page 204.

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Comparison of X-Ray and Neutron Diffraction Structural Results: A Study in Methods of Error Analysis*

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A number of crystal structures have been precisely analyzed by both X-ray and neutron diffraction. Comparison between the results can lead to some understanding of the type and magnitude of error present in one or both methods. We discuss here the nature of systematic error in crystallographic experiments and in crystal structure refinement models. Statistical methods are presented for testing the significance of the difference between the parameters derived in two crystallographic experiments. These methods are applied to existing neutron and X-ray diffraction data on oxalic acid dihydrate, hydroxyapatite, *s*-triazine, potassium hydrogen diaspirinate and methylglyoxal bisguanylhydrazone. These tests show that there are strong systematic differences in thermal parameters for heavy atoms and in all parameters for hydrogen atoms. Differences in positional parameters for heavy atoms are marginal. The pattern of results strongly suggests that the differences between neutron and X-ray experiments have some physical basis rather than being due entirely to systematic error in one or both experiments. The results may also be interpreted as indicating that both position parameters and root-mean-square amplitudes of vibration may with care be determined to a precision of 0·001 Å and an accuracy of 0·005 Å in structures with a moderate number of atoms in the asymmetric unit.

Introduction

In the experimental part of the classical crystallographic diffraction experiment, an attempt is made to measure the magnitude of the structure factor $|F|$, where F is the Fourier transform of the contents of one unit cell of the crystal:

$$F(\mathbf{h}) = \int_{\text{cell}} \varrho(\mathbf{r}) \exp(2\pi i \mathbf{h} \cdot \mathbf{r}) d\mathbf{r} . \qquad (1)$$

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