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### References

- ALTONA, C., DE GRAAF, R. A. G., LEEUWSTEIN, C. H. & ROMERS, C. (1971). *Chem. Commun.* p. 1305-1307.
- BAK, B., LED, J. J., NYGAARD, L., RASTRUP-ANDERSEN, J. & SØRENSEN, G. O. (1969). *J. Mol. Struct.* **3**, 369-378.
- BASTIANSSEN, O. & DERISSEN, J. L. (1966). *Acta Chem. Scand.* **20**, 1089-1092.
- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- CAHN, R. W. (1954). *Advanc. Phys.* **3**, 363-445.
- CHANG, C. H., PORTER, R. F. & BAUER, S. H. (1970). *J. Mol. Struct.* **7**, 89-99.
- CHIANG, J. F. (1970). *J. Chin. Chem. Soc. (Taiwan)*, **17**, 65-71.
- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321-324.
- DONOHUE, J., HUMPHREY, G. L. T. & SCHOMAKER, V. (1945). *J. Amer. Chem. Soc.* **67**, 332-335.
- GERMAIN, G. & WOOLFSON, M. M. (1968). *Acta Cryst.* **B24**, 91-96.
- JOHNSON, C. K. (1970). *Crystallographic Computing*. Edited by F. R. AHMED, pp. 220-226. Copenhagen: Munksgaard.
- SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 63-76.
- SEMMEHACK, M. F. & DEFranco, R. J. (1971). *Tetrahedron Lett.* p. 1061-1064.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175-3187.
- WOERNER, L. M. & HARMONY, M. D. (1966). *J. Chem. Phys.* **45**, 2339-2343.
- ZALKIN, A. (1965). *FORDAP*. A Fortran Program for Fourier Calculations, University of California, Berkeley.

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## Use of Constraints on Thermal Motion in Structure Refinement of Molecules with Librating Side Groups

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Explicit formulae are derived which express, for molecules consisting of a rigid core to which side groups that are free to librate around a single bond are attached, the second and third cumulants of the scattering density function as functions of molecular translation and libration parameters. These formulae and their derivatives with respect to the molecular motion parameters have been incorporated into a least-squares refinement program which determines directly the values of the position and thermal-motion parameters which give the best fit to the observed data.

### Introduction

It was originally pointed out by Cruickshank (1956), that molecular librations cause a systematic displacement of the maxima of scattering density away from the actual equilibrium positions of atoms in the molecule. Cruickshank (1961) also pointed out that in the case of anisotropic librations the nature of these displacements can be very complex. More recently, Schomaker & Trueblood (1968) analyzed the motions of rigid molecules in terms of translations, librations, and screw motions. These are represented by three tensors, designated **T**, **L**, and **S**, whose values may be determined by a least-squares fit to the anisotropic thermal parameters resulting from a conventional crystal structure refinement. Johnson (1970a) extended this analysis to segmented rigid bodies, in which portions of molecules are relatively rigid but are connected together by single bonds, allowing two or more segments to rotate

with respect to one another about the direction of the bond.

Willis & Pawley (1970), Pawley & Willis (1970), and Pawley (1970) have discussed various aspects of the problem of relating the structure factor formula directly to molecular motion parameters, and thereby constraining the thermal parameters in a refinement to fit a physical model. Johnson (1969, 1970b) has described a procedure, applicable to centrosymmetric rigid molecules, for relating the second and third cumulant coefficients in the structure-factor formula to the molecular motion parameters.

This paper extends Johnson's treatment to molecules consisting of a rigid core and one or more attached side groups which are free to librate around a single bond. The resulting formulae have been incorporated into a least-squares program using thermal constraints. No *a priori* assumptions are made about the configuration of the molecule, but thermal parameters are con-

strained to conform to the segmented rigid-body model. The following paper (Prince, Schroeder & Rush, 1973) describes the application of this program to a neutron-diffraction refinement of the crystal structure of durene.

### Mathematical analysis

Consider a molecule occupying a position in a crystal such that the molecule is fixed by a center of symmetry. The molecule has a rigid core which includes an atom with an equilibrium position defined by the vector  $\mathbf{r}_a$ . An atom with equilibrium position  $\mathbf{r}_b$  is attached by a single bond to the atom at  $\mathbf{r}_a$ . A third atom, with equilibrium position  $\mathbf{r}$  and bonded to the atom at  $\mathbf{r}_b$ , is part of a rigid side group which can librate around the vector  $\mathbf{r}_b - \mathbf{r}_a$  (see Fig. 1). We shall assume that most of the motion of the atom at  $\mathbf{r}_b$  can be accounted for by motion of the core of the molecule, and that the part of its motion due to bending of the single bond can be neglected. The displacement,  $\mathbf{w}$ , of the atom at  $\mathbf{r}$  is the resultant of a displacement  $\mathbf{u}$  due to the rotational displacement of the molecule as a whole and a displacement  $\mathbf{v}$  due to rotation about the vector  $\mathbf{r}_b - \mathbf{r}_a$ .

In evaluating these vectors we shall follow the treatment given by Johnson (1970*b*) which is essentially equivalent to that of Schomaker & Trueblood (1968). According to Euler's theorem any motion of a rigid body possessing a fixed point can be represented by a finite rotation about some axis passing through the fixed point. We can therefore describe the instantaneous displacement of the molecule from its equilibrium position by means of an axial vector  $\lambda$ , with components  $\lambda_1$ ,  $\lambda_2$ , and  $\lambda_3$  (referred to an orthonormal coordinate system) and magnitude  $\lambda$ , equal to  $(\lambda_1^2 + \lambda_2^2 + \lambda_3^2)^{1/2}$ , the angular rotation, in radians, around the direction  $\lambda$ . For any finite rotation the displacement,  $\mathbf{u}$ , of a point whose equilibrium position is  $\mathbf{r}$  is given by

$$\mathbf{u} = (\sin \lambda / \lambda) (\lambda \wedge \mathbf{r}) + [(1 - \cos \lambda) / \lambda^2] [\lambda \wedge (\lambda \wedge \mathbf{r})], \quad (1)$$

where  $\wedge$  indicates vector product. Let us define a vector  $\mathbf{r}' \equiv \mathbf{r}_b - \mathbf{r}_a$ . The change,  $\mathbf{u}'$ , in  $\mathbf{r}'$  due to rigid-body rotation can be expressed simply by substituting  $\mathbf{r}'$  for  $\mathbf{r}$  in equation 1. Let us define another vector  $\mathbf{r}'' \equiv \mathbf{r} - \mathbf{r}_b$ . The displacement  $\mathbf{v}$  can then be expressed by a rotation of  $\mathbf{r}''$  through an angle  $\theta$  about the vector  $\mathbf{r}' + \mathbf{u}'$ . Noting that, in a rigid body,  $|\mathbf{r}' + \mathbf{u}'| = |\mathbf{r}'|$ , we define a vector  $\theta$  by  $\theta \equiv \theta(\mathbf{r}' + \mathbf{u}') / \mathbf{r}'$ , and then, by analogy with equation 1 we can express  $\mathbf{v}$  by

$$\mathbf{v} = (\sin \theta / \theta) [\theta \wedge (\mathbf{r}'' + \mathbf{u}')] + [(1 - \cos \theta) / \theta^2] \{ \theta \wedge [\theta \wedge (\mathbf{r}'' + \mathbf{u}')] \}. \quad (2)$$

If we make the approximations

$$\sin \lambda / \lambda \simeq 1 - \lambda^2 / 6, \quad (3a)$$

and

$$(1 - \cos \lambda) / \lambda^2 \simeq \frac{1}{2} - \lambda^2 / 24, \quad (3b)$$

equation (1) becomes

$$\mathbf{u} \simeq (1 - \lambda^2 / 6) (\lambda \wedge \mathbf{r}) + (\frac{1}{2} - \lambda^2 / 24) [\lambda \wedge (\lambda \wedge \mathbf{r})], \quad (4)$$

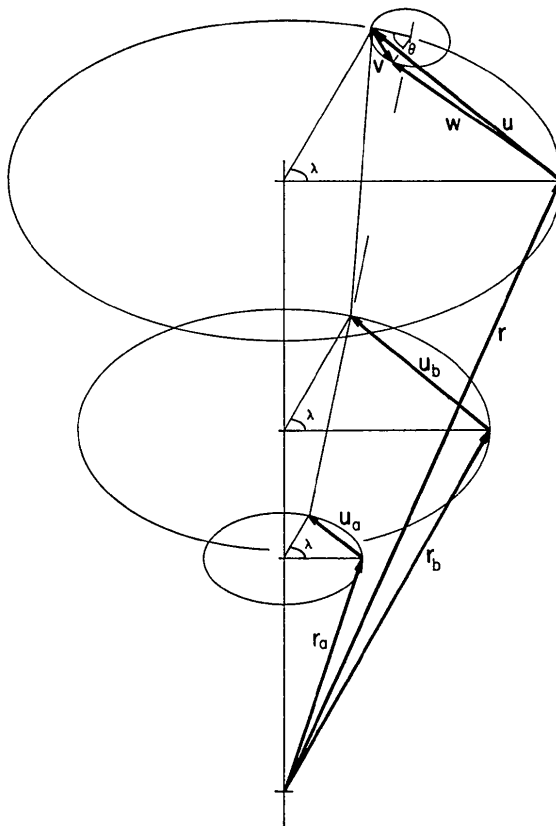


Fig. 1. Diagram showing the displacement,  $\mathbf{w}$ , of a side-group atom whose equilibrium position is  $\mathbf{r}$  due to a rigid-body rotation combined with a rotation about the bond joining two other atoms whose equilibrium positions are  $\mathbf{r}_a$  and  $\mathbf{r}_b$ .

and we can express the  $i$ th component of  $\mathbf{u}$  as

$$u_i \simeq \sum_{j=1}^3 \{ A(\mathbf{r})_{ij} \lambda_j + \sum_{k=1}^3 [ B(\mathbf{r})_{ijk} \lambda_j \lambda_k + \sum_{l=1}^3 ( C(\mathbf{r})_{ijkl} \lambda_j \lambda_k \lambda_l + \sum_{m=1}^3 D(\mathbf{r})_{ijklm} \lambda_j \lambda_k \lambda_l \lambda_m ) ] \}, \quad (5)$$

where  $A$ ,  $B$ ,  $C$ , and  $D$  represent the coefficients of the corresponding terms in equation 4. These coefficients are linear functions of the components of  $\mathbf{r}$ , and are listed in Table 1.

Table 1. The values of the coefficients  $A(\mathbf{r})_{ij}$ ,  $B(\mathbf{r})_{ijk}$ ,  $C(\mathbf{r})_{ijkl}$ , and  $D(\mathbf{r})_{ijklm}$

In each case if  $k < j$ ,  $l < k$  or  $m < l$  the value of the corresponding coefficient is zero.

| $A(\mathbf{r})$<br>$i \setminus j$  | 1                 | 2                | 3                |                   |                  |                   |
|-------------------------------------|-------------------|------------------|------------------|-------------------|------------------|-------------------|
| 1                                   | 0                 | $r_3$            | $-r_2$           |                   |                  |                   |
| 2                                   | $-r_3$            | 0                | $r_1$            |                   |                  |                   |
| 3                                   | $r_2$             | $-r_1$           | 0                |                   |                  |                   |
| $B(\mathbf{r})$<br>$i \setminus jk$ | 11                | 12               | 13               | 22                | 23               | 33                |
| 1                                   | 0                 | $\frac{1}{2}r_2$ | $\frac{1}{2}r_3$ | $-\frac{1}{2}r_1$ | 0                | $-\frac{1}{2}r_1$ |
| 2                                   | $-\frac{1}{2}r_2$ | $\frac{1}{2}r_1$ | 0                | 0                 | $\frac{1}{2}r_3$ | $-\frac{1}{2}r_2$ |
| 3                                   | $-\frac{1}{2}r_3$ | 0                | $\frac{1}{2}r_1$ | $-\frac{1}{2}r_3$ | $\frac{1}{2}r_2$ | 0                 |

Table 1 (cont.)

| $C(\mathbf{r})$   |                   | 111               | 112               | 113               | 122 | 123               | 133               | 222              | 223               | 233              | 333               |
|-------------------|-------------------|-------------------|-------------------|-------------------|-----|-------------------|-------------------|------------------|-------------------|------------------|-------------------|
| $i \setminus jkl$ |                   | 111               | 112               | 113               | 122 | 123               | 133               | 222              | 223               | 233              | 333               |
| 1                 | 0                 | $\frac{-1}{6}r_3$ | $\frac{1}{6}r_2$  | 0                 | 0   | 0                 | $\frac{-1}{6}r_3$ | $\frac{1}{6}r_2$ | $\frac{-1}{6}r_3$ | $\frac{1}{6}r_2$ | $\frac{-1}{6}r_3$ |
| 2                 | $\frac{1}{6}r_3$  | 0                 | $\frac{-1}{6}r_1$ | $\frac{1}{6}r_3$  | 0   | 0                 | $\frac{1}{6}r_3$  | 0                | $\frac{-1}{6}r_1$ | 0                | $\frac{-1}{6}r_1$ |
| 3                 | $\frac{-1}{6}r_2$ | $\frac{1}{6}r_1$  | 0                 | $\frac{-1}{6}r_2$ | 0   | $\frac{-1}{6}r_2$ | $\frac{1}{6}r_1$  | 0                | $\frac{1}{6}r_1$  | 0                | 0                 |

| $D(\mathbf{r})$    |                   | 1111               | 1112               | 1113              | 1122              | 1123              | 1133               | 1222               | 1223               | 1233               | 1333               | 2222              | 2223               | 2233              | 2333               | 3333              |
|--------------------|-------------------|--------------------|--------------------|-------------------|-------------------|-------------------|--------------------|--------------------|--------------------|--------------------|--------------------|-------------------|--------------------|-------------------|--------------------|-------------------|
| $i \setminus jklm$ |                   | 1111               | 1112               | 1113              | 1122              | 1123              | 1133               | 1222               | 1223               | 1233               | 1333               | 2222              | 2223               | 2233              | 2333               | 3333              |
| 1                  | 0                 | $\frac{-1}{24}r_2$ | $\frac{-1}{24}r_3$ | $\frac{1}{24}r_1$ | 0                 | $\frac{1}{24}r_1$ | $\frac{-1}{24}r_2$ | $\frac{-1}{24}r_3$ | $\frac{-1}{24}r_3$ | $\frac{-1}{24}r_2$ | $\frac{-1}{24}r_3$ | $\frac{1}{24}r_1$ | 0                  | $\frac{1}{12}r_1$ | 0                  | $\frac{1}{24}r_1$ |
| 2                  | $\frac{1}{24}r_2$ | $\frac{-1}{24}r_1$ | 0                  | $\frac{1}{24}r_2$ | $\frac{1}{24}r_3$ | $\frac{1}{24}r_3$ | $\frac{1}{24}r_2$  | 0                  | 0                  | $\frac{1}{24}r_1$  | 0                  | 0                 | $\frac{-1}{24}r_3$ | $\frac{1}{24}r_2$ | $\frac{-1}{24}r_3$ | $\frac{1}{24}r_2$ |
| 3                  | $\frac{1}{24}r_3$ | 0                  | $\frac{-1}{24}r_1$ | $\frac{1}{24}r_2$ | $\frac{1}{24}r_3$ | $\frac{1}{24}r_3$ | 0                  | $\frac{-1}{24}r_1$ | $\frac{-1}{24}r_1$ | 0                  | $\frac{-1}{24}r_1$ | $\frac{1}{24}r_3$ | $\frac{1}{24}r_2$  | $\frac{1}{24}r_3$ | $\frac{1}{24}r_2$  | 0                 |

Let us define two more vectors  $\mathbf{R} \equiv \mathbf{r}' \wedge \mathbf{r}''$  and  $\mathbf{R}' \equiv \mathbf{r}' \wedge \mathbf{R}$ . These vectors transform under rigid-body rotations to  $\mathbf{R} + \mathbf{U}$  and  $\mathbf{R}' + \mathbf{U}'$  respectively. Because rigid-body rotations preserve all distances and angles, the vector  $\mathbf{R} + \mathbf{U}$  is perpendicular to  $\mathbf{r}' + \mathbf{u}'$  and  $\mathbf{r}'' + \mathbf{u}''$ , and, using the definition of  $\theta$ , is in fact equal to  $(r'/\theta)[\theta \wedge (\mathbf{r}'' + \mathbf{u}'')]$ . Similarly  $\mathbf{R}' + \mathbf{U}' = (r'/\theta)^2 \{ \theta \wedge \lambda [\theta \wedge (\mathbf{r}'' + \mathbf{u}'')]$ . Therefore, using equation 5 and retaining terms up to the fourth degree in angular displacements,

$$[\theta \wedge (\mathbf{r}'' + \mathbf{u}'')]_i = (\theta/r') \left\{ R_i + \sum_{j=1}^3 [A(\mathbf{R})_{ij} \lambda_j + \sum_{k=1}^3 (B(\mathbf{R})_{ijk} \lambda_j \lambda_k + \sum_{l=1}^3 C(\mathbf{R})_{ijkl} \lambda_j \lambda_k \lambda_l)] \right\}, \quad (6a)$$

and

$$\{ \theta \wedge [\theta \wedge (\mathbf{r}'' + \mathbf{u}'')] \}_i = (\theta/r')^2 \left[ R'_i + \sum_{j=1}^3 (A(\mathbf{R}')_{ij} \lambda_j + \sum_{k=1}^3 B(\mathbf{R}')_{ijk} \lambda_j \lambda_k) \right]. \quad (6b)$$

Making the approximations of equation (3) we obtain

$$v_i = \theta R_i / r' + \theta^2 R'_i / 2r'^2 - \theta^3 R_i / 6r' - \theta^4 R'_i / 24r'^2 + \sum_{j=1}^3 \{ A(\mathbf{R})_{ij} \lambda_j \theta / r' - A(\mathbf{R})_{ij} \lambda_j \theta^3 / 6r' + A(\mathbf{R}')_{ij} \lambda_j \theta^2 / 2r'^2 + \sum_{k=1}^3 [B(\mathbf{R})_{ijk} \lambda_j \lambda_k \theta / r' + B(\mathbf{R}')_{ijk} \lambda_j \lambda_k \theta^2 / 2r'^2 + \sum_{l=1}^3 C(\mathbf{R})_{ijkl} \lambda_j \lambda_k \lambda_l \theta / r'] \}. \quad (7)$$

The total displacement of the atom from its equilibrium position is  $\mathbf{w} = \mathbf{u} + \mathbf{v}$ . The first, second, and third moments of the distribution of  $\mathbf{w}$  with respect to the equilibrium position are defined by

$${}^1\mu_i = \langle w_i \rangle \quad (8a)$$

$${}^2\mu_{ij} = \langle w_i w_j \rangle \quad (8b)$$

and

$${}^3\mu_{ijk} = \langle w_i w_j w_k \rangle \quad (8c)$$

where the angle brackets indicate a time average.

In order to evaluate these quantities we make the following definitions:

$$L_{ij} \equiv \langle \lambda_i \lambda_j \rangle \quad (9a)$$

$$\Theta \equiv \langle \theta^2 \rangle. \quad (9b)$$

If we assume that the variables  $\lambda_i$  and  $\theta$  have a Gaussian distribution with zero mean, we can employ the following relations (Johnson, 1970b):

$$\begin{aligned} \langle \lambda_i \lambda_j \lambda_k \lambda_l \rangle &= \langle \lambda_i \lambda_j \rangle \langle \lambda_k \lambda_l \rangle + \langle \lambda_i \lambda_k \rangle \langle \lambda_j \lambda_l \rangle \\ &\quad + \langle \lambda_i \lambda_l \rangle \langle \lambda_j \lambda_k \rangle \\ &= L_{ij} L_{kl} + L_{ik} L_{jl} + L_{il} L_{jk}, \end{aligned} \quad (10a)$$

$$\langle \theta^2 \lambda_i \lambda_j \rangle = \Theta L_{ij}, \quad (10b)$$

$$\langle \theta^4 \rangle = 3\Theta^2, \quad (10c)$$

$$\langle \theta \lambda_i \rangle = 0. \quad (10d)$$

We are implicitly assuming here that the libration of the side group is uncorrelated with the libration of the core molecule. We shall also assume

$$\langle \theta \rangle = \langle \theta^3 \rangle = \langle \lambda_i \rangle = \langle \lambda_i \lambda_j \lambda_k \rangle = \langle \theta^2 \lambda_i \rangle = \langle \theta \lambda_i \lambda_j \rangle = 0. \quad (10e)$$

If the center of mass of the molecule is displaced from its equilibrium position by the vector  $\mathbf{t}$ , and we define the translation tensor,  $T_{ij}$ , by  $T_{ij} \equiv \langle t_i t_j \rangle$ , the first three cumulants are given by the relations (Johnson, 1969; Kubo, 1962)

$${}^1\kappa_i = r_i + {}^1\mu_i, \quad (11a)$$

$${}^2\kappa_{ij} = T_{ij} + {}^2\mu_{ij} - {}^1\mu_i {}^1\mu_j, \quad (11b)$$

$${}^3\kappa_{ijk} = {}^3\mu_{ijk} - {}^1\mu_i {}^2\mu_{jk} - {}^1\mu_j {}^2\mu_{ik} - {}^1\mu_k {}^2\mu_{ij}, \quad (11c)$$

and the structure factor,  $F(\mathbf{h})$  is given by (Johnson, 1970b),

$$\begin{aligned} F(\mathbf{h}) &= \sum_{\substack{\text{atoms} \\ \text{in cell}}} f(\mathbf{h}) \{ \exp 2\pi i \sum_{j=1}^3 {}^1\kappa_j h_j \\ &\quad + [(2\pi i)^2 / 2!] \sum_{j,k=1}^3 {}^2\kappa_{jk} h_j h_k \\ &\quad + [(2\pi i)^3 / 3!] \sum_{j,k,l=1}^3 {}^3\kappa_{jkl} h_j h_k h_l \} \end{aligned} \quad (12)$$

where  $\mathbf{h}$  is the vector of Miller indices and  $f(\mathbf{h})$  is the atomic scattering factor.

The vector  ${}^1\mu$  is explicitly the 'libration correction', and is given by

$$\begin{aligned}
{}^1\mu_i &= \sum_{j,k=1}^3 [B(\mathbf{r})_{ijk}L_{jk} \\
&+ \sum_{l,m=1}^3 D(\mathbf{r})_{ijklm}(L_{jk}L_{lm} + L_{jl}L_{km} + L_{jm}L_{kl})] \\
&+ (\Theta/2r'^2)[R'_i + \sum_{j,k=1}^3 B(\mathbf{R}')_{ijk}L_{jk}] - (R'_i\Theta^2/8r'^2). \quad (13)
\end{aligned}$$

In the case of a rigid body undergoing isotropic libration  $L_{11}=L_{22}=L_{33}=L$  and  $L_{12}=L_{13}=L_{23}=0$ , so that equation (13) reduces to

$${}^1\mu_i = r_i[-L + (\frac{\Theta}{12})L^2], \quad (14)$$

in agreement with the result of Willis & Pawley (1970).

Making use of relations (8), (9), (10), and (11) we can write expressions for the second and third cumulants and their derivatives with respect to  $L_{ij}$  and  $\Theta$ . They are

$$\begin{aligned}
{}^2\kappa_{ij} &= \sum_{k=1}^3 \sum_{l=1}^3 [A(\mathbf{r})_{ik}A(\mathbf{r})_{jl} + (\Theta/r'^2)(A(\mathbf{R}))_{ik}A(\mathbf{R})_{jl} \\
&+ B(\mathbf{R})_{ikl}R_j + B(\mathbf{R})_{jkl}R_i] \\
&+ (\Theta/2r'^2)(A(\mathbf{r})_{ik}A(\mathbf{R}')_{jl} + A(\mathbf{R}')_{ik}A(\mathbf{r})_{jl})L_{kl} \\
&+ \sum_{k=1}^3 \sum_{l=1}^3 \sum_{m=1}^3 \sum_{n=1}^3 [A(\mathbf{r})_{ik}(C(\mathbf{r})_{jlmn} + C(\mathbf{r})_{jmln} \\
&+ C(\mathbf{r})_{jnml}) + A(\mathbf{r})_{jk}(C(\mathbf{r})_{ilmn} + C(\mathbf{r})_{imln} + C(\mathbf{r})_{inlm}) \\
&+ B(\mathbf{r})_{ikm}B(\mathbf{r})_{jln} + B(\mathbf{r})_{ikn}B(\mathbf{r})_{jlm}]L_{kl}L_{mn} \\
&+ (\Theta R_i R_j / r'^2)(1 - \Theta) - \Theta^2 R'_i R'_j / 4r'^4 + T_{ij}. \quad (15)
\end{aligned}$$

$$\begin{aligned}
\frac{\partial({}^2\kappa_{ij})}{\partial L_{kl}} &= \sum A(\mathbf{r})_{ik}A(\mathbf{r})_{jl} + A(\mathbf{r})_{jk}A(\mathbf{r})_{il} \\
&+ (\Theta/r'^2)[(\frac{1}{2}A(\mathbf{r})_{ik}A(\mathbf{R}')_{jl} + A(\mathbf{R}')_{ik}A(\mathbf{r})_{jl} \\
&+ A(\mathbf{r})_{il}A(\mathbf{R}')_{jk} + A(\mathbf{R}')_{il}A(\mathbf{r})_{jk}] \\
&+ A(\mathbf{R})_{ik}A(\mathbf{R})_{jl} + A(\mathbf{R})_{il}A(\mathbf{R})_{jk} + R_i(B(\mathbf{R})_{jkl} \\
&+ B(\mathbf{R})_{jlk}) + R_j(B(\mathbf{R})_{ikl} + B(\mathbf{R})_{ilk}) \\
&+ 2 \sum_{m=1}^3 \sum_{n=1}^3 L_{mn}[A(\mathbf{r})_{ik}(C(\mathbf{r})_{jlmn} + C(\mathbf{r})_{jmln} \\
&+ C(\mathbf{r})_{jnml}) + A(\mathbf{r})_{jk}(C(\mathbf{r})_{ilmn} + C(\mathbf{r})_{imln} \\
&+ C(\mathbf{r})_{inlm}) + A(\mathbf{r})_{il}(C(\mathbf{r})_{jkmn} + C(\mathbf{r})_{jmnk} \\
&+ C(\mathbf{r})_{jnkm}) + A(\mathbf{r})_{jk}(C(\mathbf{r})_{ikmn} + C(\mathbf{r})_{imkn} \\
&+ C(\mathbf{r})_{inkn}) + B(\mathbf{r})_{ikm}B(\mathbf{r})_{jln} + B(\mathbf{r})_{ikn}B(\mathbf{r})_{jlm} \\
&+ B(\mathbf{r})_{ilm}B(\mathbf{r})_{jkn} + B(\mathbf{r})_{iln}B(\mathbf{r})_{jkm}]/(1 + \delta_{kl}), \quad (16)
\end{aligned}$$

where  $\delta_{kl} = 1$  if  $k = l$  and 0 otherwise.

$$\begin{aligned}
\frac{\partial({}^2\kappa_{ij})}{\partial \Theta} &= (1/r'^2)\{-2\Theta(R_i R_j + R'_i R'_j / 4r'^2) + R_i R_j \\
&+ \sum_{k=1}^3 \sum_{l=1}^3 L_{kl}[A(\mathbf{R})_{ik}A(\mathbf{R})_{jl} \\
&+ \frac{1}{2}(A(\mathbf{r})_{ik}A(\mathbf{R}')_{jl} + A(\mathbf{R}')_{ik}A(\mathbf{r})_{jl}) \\
&+ B(\mathbf{R})_{ikl}R_j + B(\mathbf{R})_{jkl}R_i]\}. \quad (17)
\end{aligned}$$

$$\begin{aligned}
{}^3\kappa_{ijk} &= 2 \sum_{l=1}^3 \sum_{m=1}^3 \sum_{n=1}^3 \sum_{p=1}^3 L_{lm}L_{np}(A(\mathbf{r})_{il}A(\mathbf{r})_{jn}B(\mathbf{r})_{kmp} \\
&+ A(\mathbf{r})_{jl}A(\mathbf{r})_{kn}B(\mathbf{r})_{imp} \\
&+ A(\mathbf{r})_{kl}A(\mathbf{r})_{in}B(\mathbf{r})_{jmp}) \\
&+ \Theta/r'^2 \sum_{l=1}^3 \sum_{m=1}^3 L_{lm}[R_i(A(\mathbf{R}))_{jl}A(\mathbf{r})_{km} \\
&+ A(\mathbf{r})_{jl}A(\mathbf{R})_{km}) + R_j(A(\mathbf{R}))_{il}A(\mathbf{r})_{km} \\
&+ A(\mathbf{r})_{il}A(\mathbf{R})_{km} \\
&+ R_k(A(\mathbf{R}))_{il}A(\mathbf{r})_{jm} + A(\mathbf{r})_{il}A(\mathbf{R})_{jm}]. \quad (18)
\end{aligned}$$

$$\begin{aligned}
\frac{\partial({}^3\kappa_{ijk})}{\partial L_{lm}} &= \{(\Theta/r'^2)[R_i(A(\mathbf{R}))_{jl}A(\mathbf{r})_{km} + A(\mathbf{r})_{jl}A(\mathbf{R})_{km} \\
&+ A(\mathbf{R})_{jm}A(\mathbf{r})_{kl} + A(\mathbf{r})_{jm}A(\mathbf{R})_{kl}) \\
&+ R_j(A(\mathbf{R}))_{il}A(\mathbf{r})_{km} + A(\mathbf{r})_{il}A(\mathbf{R})_{km} \\
&+ A(\mathbf{R})_{im}A(\mathbf{r})_{kl} + A(\mathbf{r})_{im}A(\mathbf{R})_{kl}) \\
&+ R_k(A(\mathbf{R}))_{il}A(\mathbf{r})_{jm} + A(\mathbf{r})_{il}A(\mathbf{R})_{jm} \\
&+ A(\mathbf{R})_{im}A(\mathbf{r})_{jl} + A(\mathbf{r})_{im}A(\mathbf{R})_{jl}] \\
&+ 4 \sum_{n=1}^3 \sum_{p=1}^3 L_{np}(A(\mathbf{r})_{il}A(\mathbf{r})_{jn}B(\mathbf{r})_{kmp} \\
&+ A(\mathbf{r})_{jl}A(\mathbf{r})_{kn}B(\mathbf{r})_{imp} + A(\mathbf{r})_{kl}A(\mathbf{r})_{in}B(\mathbf{r})_{jmp} \\
&+ A(\mathbf{r})_{im}A(\mathbf{r})_{jn}B(\mathbf{r})_{klp} + A(\mathbf{r})_{jm}A(\mathbf{r})_{kn}B(\mathbf{r})_{ilp} \\
&+ A(\mathbf{r})_{km}A(\mathbf{r})_{in}B(\mathbf{r})_{jlp}]/(1 + \delta_{lm}). \quad (19)
\end{aligned}$$

$$\begin{aligned}
\frac{\partial({}^3\kappa_{ijk})}{\partial \Theta} &= (1/r'^2) \sum_{l=1}^3 \sum_{m=1}^3 L_{lm}[R_i(A(\mathbf{R}))_{jl}A(\mathbf{r})_{km} \\
&+ A(\mathbf{r})_{jl}A(\mathbf{R})_{km}) + R_j(A(\mathbf{R}))_{il}A(\mathbf{r})_{km} \\
&+ A(\mathbf{r})_{il}A(\mathbf{R})_{km}) + R_k(A(\mathbf{R}))_{il}A(\mathbf{r})_{jm} \\
&+ A(\mathbf{r})_{il}A(\mathbf{R})_{jm}] \\
&+ (2\Theta/r'^4)(R'_i R_j R_k + R_i R'_j R_k + R_i R_j R'_k) \quad (20)
\end{aligned}$$

### Application to least-squares refinement

The expressions derived above can be used in a least-squares refinement procedure in order to enable the rigid body motion parameters,  $L_{ij}$ ,  $T_{ij}$ , and  $\Theta$  to be used in place of the independent thermal parameters. Following this procedure greatly reduces the number of refined parameters, and it also allows the use of third cumulants in the refinement without any increase in the number of parameters. In addition, for structures where the constraints represent a reasonable physical model, a comparison of constrained and unconstrained refinements, employing statistical methods such as the  $R$ -index ratio test (Hamilton, 1965), can be used to judge the adequacy of the model. For this purpose we have modified the program *RFINE* (Finger, 1968, available on request) to follow this procedure.

Because the previous formulae are derived assuming an orthonormal coordinate system, it is necessary to

make the appropriate transformations between that system and the one defined by the crystal axes. For this purpose a subroutine is called once at the beginning of a computer run to derive the transformations to convert a vector from the crystal system to the orthonormal system and to convert the second and third cumulant tensors from the orthonormal system back to the crystal system. The derivatives of the anisotropic temperature factors,  $\beta_{ij}$ , with respect to the elements of the translation tensor,  $T_{ij}$ , are dependent only on crystal geometry, and these are therefore also computed at this time. Another subroutine is called at the beginning of the run and again at the end of each cycle of refinement. Its function is to convert all atom parameters to the orthonormal system, apply the libration correction appropriate to the current values of  $L_{ij}$  and  $\Theta$ , compute the second and third cumulant coefficients and their derivatives, and transform them back to the crystal system. The derivative information is used by the subroutine which sets up the least-squares normal matrix equation to determine for each reflection the derivatives of the structure factor,  $F$ , with respect to each of the thermal motion parameters.

In practice we have found (Prince, Schroeder & Rush, 1973) that using zero as the starting value for the rigid-body thermal parameters is such a bad approximation that the structure will not refine if all parameters are allowed to vary simultaneously. However, if the position parameters, the scale factor, and the extinction parameter are first determined by means of a conventional refinement with anisotropic temperature factors, and these are then held fixed while the rigid-body motion parameters are refined, the motion parameters quickly converge to reasonable values. After this has happened the position, scale, and extinction parameters can also be allowed to vary, and the refinement will proceed smoothly to a stable minimum.

The expressions used in this procedure neglect atomic motions due to internal modes of oscillation other than the librational motion of the side group. The effect of the neglect of internal modes will be to distort the molecular motion parameters somewhat, as the least-squares process attempts to fit the overall motion with the available parameters. In particular we

have neglected those internal modes that correspond to 'wagging' of the side group with respect to the core of the molecule. For this reason the applicability of this method is restricted to cases in which the amplitudes of these motions are much smaller than the amplitude of the libration around the bond. Neglect of these internal modes will tend to exaggerate somewhat the motions of the core atoms, and underestimate the motions of side group atoms that are treated as part of the rigid core. The model should be most appropriate for light side groups, such as methyl groups or amino groups, attached to a much heavier core.

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### References

- CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 754-756.  
 CRUICKSHANK, D. W. J. (1961). *Acta Cryst.* **14**, 896-897.  
 FINGER, L. W. (1968). *RFINE. A Fortran IV Computer Program for Structure Factor Calculation and Least-Squares Refinement of Crystal Structures*. Geophysical Laboratory, Carnegie Institution of Washington (unpublished).  
 HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502-510.  
 JOHNSON, C. K. (1969). Abstracts of American Crystallographic Association Winter Meeting, Seattle, Washington, p. 55.  
 JOHNSON, C. K. (1970a). In *Thermal Neutron Diffraction*. Edited by B. T. M. WILLIS, pp. 132-160. London: Oxford Univ. Press.  
 JOHNSON, C. K. (1970b). In *Crystallographic Computing*. Edited by F. R. AHMED, pp. 207-219. Copenhagen: Munksgaard.  
 KUBO, R. (1962). *J. Phys. Soc. Japan*, **17**, 1100-1120.  
 PAWLEY, G. S. (1970). In *Thermal Neutron Diffraction*. Edited by B. T. M. WILLIS, pp. 161-170. London: Oxford Univ. Press.  
 PAWLEY, G. S. & WILLIS, B. T. M. (1970). *Acta Cryst.* **A26**, 260-262.  
 PRINCE, E., SCHROEDER, L. W. & RUSH, J. J. (1973). *Acta Cryst.* **B29**, 000.  
 SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 63-76.  
 WILLIS, B. T. M. & PAWLEY, G. S. (1970). *Acta Cryst.* **A26**, 254-259.