because of the short wavelength. This fact at present limits the amount of detail available in the TDS profiles, and direct extraction of the elastic constants is not possible. The vertical resolution can be improved by the incorporation of horizontal Soller slits, such that the observed TDS profiles would fall off more quickly with **q** in both the transverse and longitudinal directions. If the counting-rate reduction were not too severe, this improvement would provide greater detail within the limits of the one-phonon model.

In summary, the analysis of the resolution function for Mössbauer γ-ray scattering presented here has led to a good understanding of the strengths and limitations of this experimental probe. This better understanding is crucial to the interpretation of TDS measurements and of direct measurements of inelastic and quasi-elastic scattering which are planned for the QUEGS instrument.

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References

ALBANESE, G., GHEZZI, C., MERLINI, A. & PACE, S. (1972). *Phys. Rev. B*, **5**, 1746-1757.

COCHRAN, W. (1966). *Phonons in Perfect Lattices and Lattices with Point Imperfections*, edited by R. W. H. STEVENSON, pp. 153-160. Edinburgh: Oliver & Boyd.

COOPER, M. J. & NATHANS, R. (1967). *Acta Cryst.* **23**, 357-367.

COOPER, M. J. & ROUSE, K. D. (1968). *Acta Cryst.* A**24**, 405-410.

DOLLING, G. & COWLEY, R. A. (1966). *Proc. Phys. Soc. London*, **88**, 463-494.

GHEZZI, G., MERLINI, A. & PACE, S. (1969). *Nuovo Cimento B*, **64**, 103-115.

GRAF, H. A., SCHNEIDER, J. R., FREUND, A. K. & LEHMANN, M. S. (1981). *Acta Cryst.* A**37**, 863-871.

HUNTINGTON, H. B. (1958). *Solid State Phys.* **7**, 213-351.

KASHIWASE, Y. & MINOURA, M. (1983). *Jpn J. Appl. Phys.* **22**, L49-L51.

KREC, K. & STEINER, W. (1984). *Acta Cryst.* A**40**, 459-465.

LEDERER, C. M. & SHIRLEY, V. S. (1978). *Table of Isotopes*, 7th ed. New York: Wiley.

MULLEN, J. G., DJEDID, A., COWAN, D. L., SCHUPP, G., XIE, Q., CROW, M. L., CAO, Y. & YELON, W. B. (1987). In preparation.

MULLEN, J. G., DJEDID, A., HOLMES, C., SCHUPP, G., CROW, M. L. & YELON, W. B. (1986). *Nucl. Instrum. Methods*, B**14**, 323-340.

MULLEN, J. G. & STEVENSON, J. R. (1978). *AIP Conf. Proc.* **38**, 55-57.

NILSSON, G. & NELIN, G. (1972). *Phys. Rev. B*, **6**, 3777-3786.

NILSSON, N. (1957). *Ark. Fys.* **12**, 247-257.

O'CONNOR, D. A. & BUTT, N. M. (1963). *Phys. Lett.* **7**, 233-235.

SCHNEIDER, J. R. (1974). *J. Appl. Cryst.* **7**, 541-546.

SCHNEIDER, J. R. (1983). *J. Cryst. Growth*, **65**, 660-671.

WERNER, S. A. & PYNN, R. (1971). *J. Appl. Phys.* **42**, 4736-4749.

WILLIS, B. T. M. (1969). *Acta Cryst.* A**25**, 277-300.

YELON, W. B. & ROSS, F. K. (1982). *Nucl. Instrum. Methods*, **193**, 285-295.

YELON, W. B., SCHUPP, G., CROW, M. L., HOLMES, C. & MULLEN, J. G. (1986). *Nucl. Instrum. Methods*, B**14**, 341-347.

Acta Cryst. (1987). A**43**, 645-653

On the Fast Rotation Function

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Abstract

An analysis of the mathematical structure of the rotation function is presented. The effect of truncation of the expansions used in the fast rotation function is discussed and an alternative procedure of calculation which drastically reduces the errors is proposed. A method of sampling on spherical surfaces is developed. The rotation function can thus be obtained from the values it takes at the sampling points. The method can also be used to compute expansions in spherical harmonics of Patterson functions restricted to arbitrary domains. Topological properties of the rotation group are used to obtain distortion-free plots of the different sections of the rotation function.

Introduction

In Crowther's formulation of the fast rotation function, emphasis is placed on the expansion of the Patterson functions in terms of the spherical harmonics and the spherical Bessel functions (Crowther, 1972). These expansions lead to slowly convergent series and the relative errors of some contributions can exceed 100% for reflections corresponding to

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certain resolutions, under the conditions of application of the current version of the program. It will be shown that these errors can be drastically reduced if the expansion in radial functions is replaced by a numerical integration rule.

Patterson functions restricted to non-spherical domains will be discussed. In order to take full advantage of the properties of the rotation group these Patterson functions have to be expanded in spherical harmonics, but the coefficients of the expansions have now to be evaluated by numerical integration over the spherical surface. A method of sampling for functions defined on the spherical surface will thus be proposed.

An extension of this method will allow us to recover the rotation function from the values it takes on a set of sampling points.

Finally it will be shown that some topological properties of the rotation group lead, in a unique way, to the metric introduced by Burdina (1971) and Lattman (1972) in order to produce distortion-free plots of the rotation function.

The rotation function

The rotation function is defined as the integral over a spherical region Ω of the product of a given Patterson function $P^{(1)}$ with the rotated version of either itself or another Patterson function $P^{(2)}$ (Rossmann & Blow, 1962).

For any rotation $\boldsymbol{\phi}$, the rotated version of $P^{(2)}$ is the function $T(\boldsymbol{\phi})P^{(2)}$, defined as

$$[T(\boldsymbol{\phi})P^{(2)}](\mathbf{r}) = P^{(2)}[R^{-1}(\boldsymbol{\phi})\mathbf{r}], \tag{1}$$

$R(\boldsymbol{\phi})$ being the operator associated with $\boldsymbol{\phi}$ in a three-dimensional representation of the rotation group.

With this definition the rotation function $\mathcal{R}$ is a functional of $P^{(1)}$ and $P^{(2)}$,

$$\mathcal{R}(\boldsymbol{\phi};\, P^{(1)}, P^{(2)}) = 1/v \int_{\Omega} P^{(1)}(\mathbf{r})[T(\boldsymbol{\phi})P^{(2)}](\mathbf{r})\, \mathrm{d}^3\mathbf{r}, \tag{2}$$

which depends on $\boldsymbol{\phi}$ as a parameter (v is the volume of the spherical region Ω). It can also be considered as a particular matrix element of the operator $T(\boldsymbol{\phi})$,

$$\mathcal{R}(\boldsymbol{\phi};\, P^{(1)}, P^{(2)}) = \langle P^{(1)}|T(\boldsymbol{\phi})|P^{(2)}\rangle. \tag{3}$$

It is then natural to expand the functions $P^{(t)}$ ($t = 1, 2$) in terms of the spherical harmonics Y_{lm}, since they are the standard basis of the irreducible representations of the rotation group (Crowther, 1972). In this basis the matrix representing the operator $T(\boldsymbol{\phi})$ is block diagonal, the blocks being irreducible ones. Besides, as $T(\boldsymbol{\phi})$ is already diagonal in the radial components of $P^{(t)}$, it is not in principle necessary to expand them in any particular set of radial functions.

The Patterson functions are represented by truncated Fourier series

$$P^{(t)}(\mathbf{r}) = \sum_{\mathbf{H}\in\mathcal{H}(t)} |F_{\mathbf{H}}^{(t)}|^2 \exp(2\pi i \mathbf{H}\mathbf{r}), \tag{4}$$

$\mathcal{H}^{(t)}$ being the set of the experimentally available reciprocal vectors of crystal t. Their expansions in spherical harmonics are of the form

$$\sum_{l=0}^{\infty} \sum_{m=-l}^{l} c_{lm}^{(t)}(r)\, Y_{lm}(\hat{\mathbf{r}}), \tag{5}$$

where $r = |\mathbf{r}|$ and $\hat{\mathbf{r}} = \mathbf{r}/r$.

The radial functions $c_{lm}^{(t)}$ are determined by the formula

$$c_{lm}^{(t)}(r) = \int_{\sigma_r} P^{(t)}(\mathbf{r})\, Y_{lm}^*(\hat{\mathbf{r}})\, \mathrm{d}\hat{\mathbf{r}}, \tag{6}$$

where σ_r is the spherical surface of radius r.

Even if the $P^{(t)}$ are defined for all points in a three-dimensional space, we may be interested in the comparison of the Patterson functions restricted to particular regions $\Omega^{(t)}$. These regions are only used to obtain the radial functions $c_{lm}^{(t)}$, and need not be spherical ones.

For an arbitrary domain $\Omega^{(t)}$, the integral (6) extends over the intersection of the spherical surface σ_r with $\Omega^{(t)}$, and has to be evaluated by numerical methods to be discussed later. In this case the expansion (5) represents in fact a new function, say $\tilde{P}^{(t)}$, which coincides with $P^{(t)}$ in $\Omega^{(t)}$ and is zero outside it.

In order to take full advantage of the properties of the rotation group, it is however necessary that Ω, which enters the definition of the rotation function, is a spherical domain.

If one recalls the transformation properties of the spherical harmonics (Landau & Lifschitz, 1972)

$$T(\boldsymbol{\phi})\, Y_{lm'} = \sum_{m=-l}^{l} Y_{lm} D_{mm'}^{l}(\boldsymbol{\phi}), \tag{7}$$

the rotated Patterson function is easily obtained:

$$[T(\boldsymbol{\phi})P^{(2)}](\mathbf{r}) = \sum_{l=0}^{\infty} \sum_{m,m'=-l}^{l} c_{lm'}^{(2)}(r)\, Y_{lm}(\hat{\mathbf{r}})\, D_{mm'}^{l}(\boldsymbol{\phi}). \tag{8}$$

$D^l(\boldsymbol{\phi})$ is the matrix associated with the rotation $\boldsymbol{\phi}$ in the lth canonical irreducible representation of the rotation group.

The rotation function is then (Crowther, 1972)

$$\langle P^{(1)}|T(\boldsymbol{\phi})|P^{(2)}\rangle = \sum_{l=0}^{\infty} \sum_{m,m'=-l}^{l} D_{mm'}^{l}(\boldsymbol{\phi})\, C_{mm'}^{l}(P^{(1)}, P^{(2)}), \tag{9}$$

with

$$C_{mm'}^{l}(P^{(1)}, P^{(2)}) = (1/v) \int_0^a c_{lm}^{(1)*}(r)\, c_{lm'}^{(2)}(r)\, r^2\, \mathrm{d}r \tag{10}$$

Table 1. *Maximum values of the arrays* T^l [*equation* (14)]

l	h	$T^l(h,h)\times10^{-4}$
2	4·034	248·64
4	6·606	92·07
6	9·008	47·57
8	11·329	28·86
10	13·601	19·28
12	15·839	13·73
14	18·053	10·24
16	20·248	7·91
18	22·427	6·28
20	24·594	5·10
22	26·751	4·21
24	28·898	3·53
26	31·038	3·00

(a is the radius of the region Ω). We see that it can be interpreted as an expansion in terms of the complete orthogonal set of functions $D^l_{mm'}$ (Wigner, 1959).

If the $\Omega^{(t)}$ are spherical regions, the radial functions are readily obtained when the expansion (Landau & Lifschitz, 1972)

$$\exp(i\mathbf{pr}) = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^{l} i^l j_l(pr)\, Y^*_{lm}(\hat{\mathbf{p}})\, Y_{lm}(\hat{\mathbf{r}}) \quad (11)$$

(j_l is the spherical Bessel function of order l) is substituted into (4), to give

$$c^{(t)}_{lm}(r) = 4\pi i^l \sum_{\mathbf{H}\in\mathscr{H}(t)} |F^{(t)}_{\mathbf{H}}|^2 j_l(2\pi Hr)\, Y^*_{lm}(\hat{\mathbf{H}}). \quad (12)$$

A closed expression for the coefficients $C^l_{mm'}$ can now be obtained. With the dimensionless quantities $h = 2\pi Ha$ and $k = 2\pi Ka$, the result is

$$C^l_{mm'}(P^{(1)}, P^{(2)}) = 12\pi \sum_{\mathbf{H}\in\mathscr{H}(1)} \sum_{\mathbf{K}\in\mathscr{H}(2)} |F^{(1)}_{\mathbf{H}}|^2 Y_{lm}(\hat{\mathbf{H}}) \times T^l(h,k) |F^{(2)}_{\mathbf{K}}|^2 Y^*_{lm'}(\hat{\mathbf{K}}), \quad (13)$$

where (Watson, 1958)

$$T^l(h,k) = \int_0^1 j_l(hx) j_l(kx) x^2\, dx = \begin{cases} [hj_{l-1}(h)j_l(k) - kj_{l-1}(k)j_l(h)]/(k^2-h^2), & \text{if } h \neq k \\ \frac{1}{2}[j_l^2(h) - j_{l-1}(h)j_{l+1}(h)], & \text{if } h = k. \end{cases} \quad (14)$$

The two-dimensional array T^l takes its maximum value on the diagonal $h = k$. This value is listed as a function of l in Table 1. The contour levels of the arrays T^l, normalized to their maximum values, are shown in Fig. 1.

On practical grounds it is, however, important that the summations on **H** and **K** be performed independently of each other, as was the case in the original equations [(10)–(12)]. This property can be restored in several ways.

One possibility is to expand the $c^{(t)}_{lm}$ in terms of functions f_n ($n = 1, \ldots, N$) which are orthogonal in the interval $(0, a)$, with measure $r^2\, dr$. Furthermore, we have the possibility of choosing different expansion functions for different l's because they refer to distinct irreducible representations of the rotation group. For example, Crowther (1972) chooses Fourier–Bessel expansions based on the j_l's. The $C^l_{mm'}$ will be given by an expression of the form

$$C^l_{mm'}(P^{(1)}, P^{(2)}) \doteq \sum_{n=1}^{N} a^{(1)*}_{lmn} a^{(2)}_{lm'n}. \quad (15)$$

Another possibility is the evaluation of the integral in (10) by means of an approximation of the form

$$C^l_{mm'}(P^{(1)}, P^{(2)}) \doteq \sum_{n=1}^{M} c^{(1)*}_{lm}(r_n) c^{(2)}_{lm'}(r_n) r_n^2 w_n, \quad (16)$$

where w_n is the weight associated with the sampling point r_n.

In both cases we are ultimately calculating T^l in an approximate way. The confrontation with the exact result [(14)] will show the errors implied in any one of the approximations.

Despite the errors in the $C^l_{mm'}$, which can sometimes be very important, and the subsequent errors in the rotation function [(9)], the results still have a full physical sense. The reason is that the effect of the approximation [(15) or (16)] on the rotation function is strictly equivalent to that of some particular projection operator which projects the Patterson functions on a subspace spanned by functions labeled

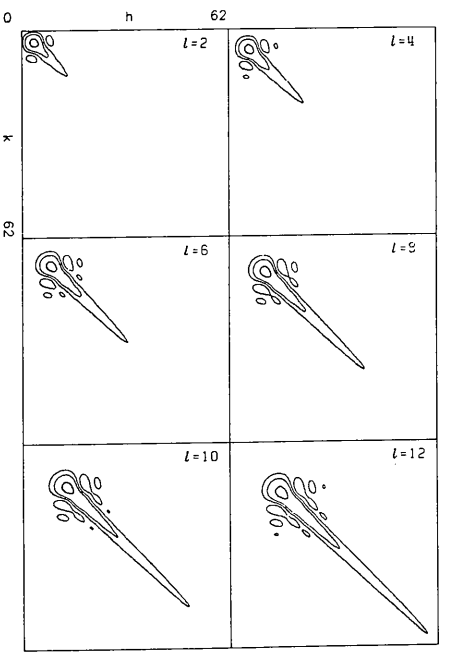

Fig. 1. $T^l(h,k)$ [equation (14)] as a function of h and k. The contour levels are 10, 30 and 80% of the maximum value for each l (see Table 1).

by the numbers (l, m, n). The important point is that the projection is correctly calculated.

Qualitatively the situation is the same as if we computed an R factor using less reflections than available.

This suggests that a selection of the l's entering into (9) can be made on physical grounds. For example, the term $l=0$ may be omitted not only because it simply adds a constant contribution to the rotation function, but also because it represents the contribution of the origin peaks of $P^{(1)}$ and $P^{(2)}$. In fact, according to (6), $c_{00}^{(t)}(r)$ is the spherical average of $P^{(t)}$ at distance r, so that the origin peak, which is normally spherical in shape, will be correctly described by this radial function.

Assume now that a certain Patterson function is roughly ellipsoidal in shape. Then, if one recalls that the Y_{lm} are intimately related to the homogeneous polynomials of degree l in x, y and z (Smirnov, 1972), the terms with $l=2$ will dominate the expansion of that Patterson function in spherical harmonics. If we are looking for a finer structure, such terms should be omitted from (9).

Inspection of Fig. 1 shows that the omission of small l's is somewhat equivalent to omitting low-resolution data in the computation of the Patterson functions, except that now high angular resolution is obtained without omitting any data.

Approximate evaluation of T^l

(a) *Fourier–Bessel expansion*

We shall discuss exclusively the case (essentially the formulation of Crowther) in which $j_l(hx)$ is approximated by the truncated expansion

$$j_l(hx) \doteq \sum_{n=1}^{N} b_{ln}(h) j_l(\lambda_{ln} x). \tag{17}$$

The λ_{ln} are such that $j_l(\lambda_{ln})=0$, *i.e.* they are the zeros of j_l. The coefficients b_{ln} are (Watson, 1958)

$$\begin{aligned} b_{ln}(h) &= 2\int_0^1 j_l(hx) j_l(kx) x^2 \, dx / j_{l-1}(\lambda_{ln})^2 \\ &= 2j_l(h)\lambda_{ln}/[j_{l-1}(\lambda_{ln})(h^2-\lambda_{ln}^2)], \quad h \neq \lambda_{ln}, \end{aligned} \tag{18}$$

and, of course, $b_{ln}(\lambda_{ln})=1$. The array T^l is now approximated by

$$\begin{aligned} T^l(h,k) &\doteq T_N^l(h,k) \\ &= \sum_{n=1}^{N} b_{ln}(h) b_{ln}(k) j_{l-1}^2(\lambda_{ln})/2 \\ &= 2j_l(h) j_l(k) \sum_{n=1}^{N} \lambda_{ln}^2/[(h^2-\lambda_{ln}^2)(k^2-\lambda_{ln}^2)]. \end{aligned} \tag{19}$$

This expansion has the advantage of giving the exact result whenever h or k coincides with one of the zeros of j_l, provided it was included in the summation.

When N tends to infinity this series converges because the large zeros of the Bessel functions behave as $\lambda_{ln} \doteq (n+l/2)\pi$. For h and $k \ll \lambda_{lN}$ the error is of the order of

$$T^l(h,k) - T_N^l(h,k) \doteq 2j_l(h) j_l(k)(\pi\lambda_{lN})^{-1}. \tag{20}$$

For particular values of h and k we have exact summation rules which can be used to assess the error introduced by the truncation. In particular, if h and k are equal to two different zeros of j_{l-1}, say $h=\lambda_{l-1,p}$ and $k=\lambda_{l-1,q}$, then T^l vanishes because of (14) and

$$\sum_{n=1}^{\infty} \lambda_{ln}^2/[(\lambda_{l-1,p}^2-\lambda_{ln}^2)(\lambda_{l-1,q}^2-\lambda_{ln}^2)] = 0. \tag{21}$$

Similarly, if h and k are both equal to a root of j_{l-1} or j_{l+1}, say $h=k=\lambda_{l\pm1,p}$, then

$$4\sum_{n=1}^{\infty} \lambda_{ln}^2/(\lambda_{l\pm1,p}^2-\lambda_{ln}^2)^2 = 1. \tag{22}$$

In practical applications the value N at which the summations are truncated depends on l and on the maximum value $h_{\max}$ taken by h or k. For example, the terms included in the fast rotation function are such that $\lambda_{ln} < h_{\max}$ (Crowther, 1972; Dodson, 1985). The relative errors $|1 - T_N^l/T^l|$ introduced in this case are shown in Fig. 2. Similar calculations, but including

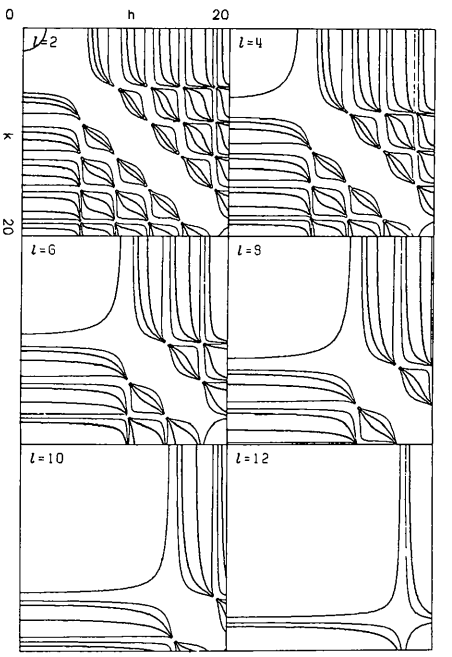

Fig. 2. Percentage errors of $T^l(h,k)$ when evaluated under the conditions of the fast rotation function (Crowther, 1972), for $h_{\max}=20$ and $l=2,\ldots,12$. The contour levels are 20 and 100%.

4 and 20 supplementary roots for each l, are shown in Figs. 3 and 4 respectively.

(b) *Numerical integration*

Here again we have the possibility of choosing a special integration formula for each l and h_{max}. Since the purpose of this presentation is not to find the best quadrature rule but rather to show its usefulness, we chose a unique M-point Legendre-Gauss integration formula

$$T^l(h, k) \doteq T^l_M(h, k) = \sum_{n=1}^{M} j_l(hx_n) j_l(kx_n) x_n^2 w_n. \quad (23)$$

The sampling points x_n are the M positive roots of the Legendre polynomial of degree $2M$. These values as well as their associated weights w_n have been tabulated by several authors (*e.g.* Abramowitz & Stegun, 1964). For a given accuracy, the number M of sampling points is certainly related to the number of oscillations of the integrand, which in turn depends on the order l of the Bessel function and h_{max}. The relative errors of T^l for a 12-point integration formula are shown in Fig. 5. They clearly show the improvement in accuracy that can be expected when using numerical integration techniques.

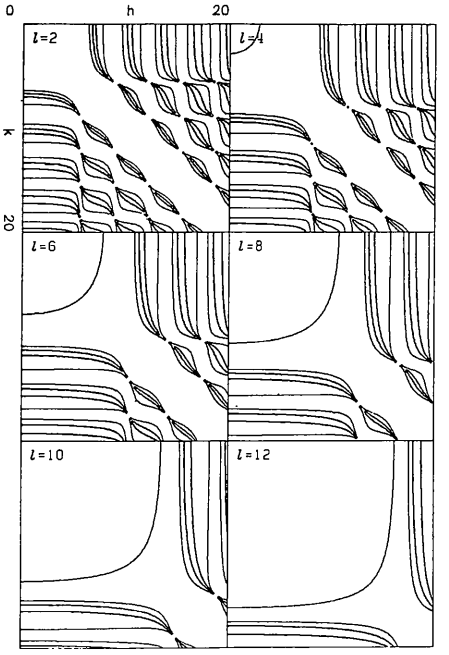

Fig. 3. Same as Fig. 2 but including four supplementary roots for each l. The contour levels are the same as in Fig. 2.

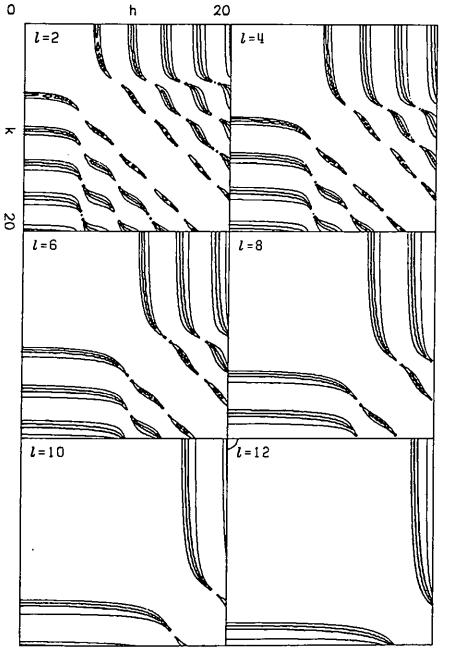

Fig. 4. Same as Fig. 2 but including 20 supplementary roots for each l. The contour levels are the same as in Fig. 2.

Sampling and numerical integration on spherical surfaces

We have seen that the coefficients $C^l_{mm'}$ can be calculated from the values of the radial functions $c^{(t)}_{lm}$ taken at selected radial points. When the domain

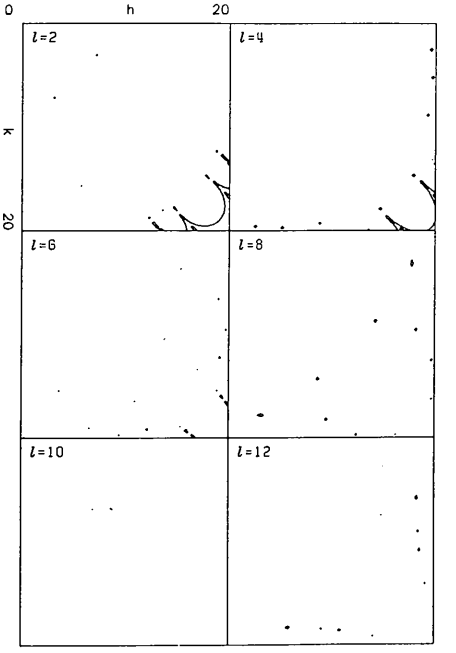

Fig. 5. Percentage errors of $T^l(h, k)$ when evaluated by means of a 12-point Legendre-Gauss integration formula, with h_{max} the same as in Fig. 2. The contour levels are now 0·1 and 1%.

of integration is the whole sphere, these values are given by analytical expressions [(12)], but for arbitrary regions $\Omega^{(t)}$ and selected radial points r_n the quantities $c_{lm}^{(t)}(r_n)$ have in general to be evaluated by numerical methods of integration.

In general terms, our problem is to find points $\hat{\mathbf{r}}_s$ on the surface of the unit sphere σ, and corresponding weights W_s, such that

$$\int_\sigma f(\hat{\mathbf{r}})\, Y_{lm}^*(\hat{\mathbf{r}})\, d\hat{\mathbf{r}} = \sum_{s=1}^{S} f(\hat{\mathbf{r}}_s)\, Y_{lm}^*(\hat{\mathbf{r}}_s)\, W_s \qquad (24)$$

is exact for a sufficiently large class of functions.

The answer to this problem will depend on the prior knowledge we may have about the function f. We shall assume that f can be faithfully represented by a limited expansion in spherical harmonics,

$$f(\hat{\mathbf{r}}) = \sum_{l=0}^{L} \sum_{m=-l}^{l} A_{lm} Y_{lm}(\hat{\mathbf{r}}). \qquad (25)$$

Functions of this type (*i.e.* with $A_{lm} = 0$ for $l > L$) will be called belonging to class $\mathscr{C}_L$.

Since the Y_{lm} are orthogonal on the spherical surface and the product of two functions of classes $\mathscr{C}_L$ and $\mathscr{C}_{L'}$ is a function of class $\mathscr{C}_{L+L'}$, the coefficients $A_{lm} (l \leq L)$ will be given by (24) if the approximate integration formula gives the correct result whenever the integrand is a Y_{lm} of order at most $2L$, that is

$$\int_\sigma Y_{lm}(\hat{\mathbf{r}})\, d\hat{\mathbf{r}} = \sum_{s=1}^{S} Y_{lm}(\hat{\mathbf{r}}_s)\, W_s = (4\pi)^{1/2} \delta_{l0}, \quad l \leq 2L. \qquad (26)$$

One solution to this problem can be obtained by slightly modifying a result of Peirce (1957), concerning the integration of polynomials over the spherical shell.

The result is the following: (26) is satisfied if the points $\hat{\mathbf{r}}_s = (\theta_i, \varphi_k)$ are taken at all the intersections of the cones θ_i $(i = 1, \ldots, L+1)$, with the half planes φ_k $(k = 1, \ldots, 2L+1)$. $\cos(\theta_i)$ are the $L+1$ zeros of the Legendre polynomial of degree $L+1$ and $\varphi_k = 2\pi k/(2L+1)$. The corresponding weights W_s are of the product form $W_s = A_i B_k$, where A_i are the weights of the $(L+1)$-point Legendre-Gauss quadrature formula and the B_k are equal to $2\pi/(2L+1)$.

In fact, Y_{lm} depends on φ through the exponential term $\exp(im\varphi)$, so that its integral is exactly calculated if the function is sampled according to Shannon's theorem of sampling. What survives this first integration is a polynomial of degree l in $\cos\theta$, whose integral is correctly given by a Gaussian quadrature formula.

Substituting for A_{lm} from (24) into (25) and using the addition theorem for spherical harmonics and the recurrence relationship of the Legendre polynomials P_l, we obtain

$$\begin{aligned} f(\hat{\mathbf{r}}) &= \sum_{s=1}^{S} f(\hat{\mathbf{r}}_s) \sum_{l=0}^{L} \sum_{m=-l}^{l} Y_{lm}^*(\hat{\mathbf{r}}_s)\, Y_{lm}(\hat{\mathbf{r}})\, W_s \\ &= \sum_{s=1}^{S} f(\hat{\mathbf{r}}_s) \sum_{l=0}^{L} [(2l+1)/4\pi] P_l(\hat{\mathbf{r}}_s \cdot \hat{\mathbf{r}})\, W_s \\ &= \sum_{s=1}^{S} f(\hat{\mathbf{r}}_s) \{[P_{L+1}(\hat{\mathbf{r}}_s \cdot \hat{\mathbf{r}}) - P_L(\hat{\mathbf{r}}_s \cdot \hat{\mathbf{r}})/(\hat{\mathbf{r}}_s \cdot \hat{\mathbf{r}} - 1)\} \\ &\quad \times W_s (L+1)/4\pi. \end{aligned} \qquad (27)$$

We see that f can be recovered from its values taken on the set $\langle \hat{\mathbf{r}}_s,\ s = 1, \ldots, S \rangle$. Other values of f taken on another set of points may also determine the function f, but it may not be possible or practical to reconstruct f starting from these values. As in Dodson & Silva (1985), a set of points which determines f and allows a reconstruction of f in terms of its values on the set will be called a sampling set of f. Then the abscissas of an approximate integration formula which gives the exact values for all spherical harmonics of order at most $2L$ are a sampling set of functions of class $\mathscr{C}_L$.

It must be noted that the number of independent complex coefficients for a function of class $\mathscr{C}_L$ is $(L+1)^2$, whereas the number of integration points is $(2L+1)(L+1)$. A sampling set for which the number of independent coefficients and that of samples of the function are equal will be called an optimal sampling set.

If the set $\langle \hat{\mathbf{r}}_q,\ q = 1, \ldots, Q \rangle$ is an optimal one, the $f(\hat{\mathbf{r}}_q)$ are all independent values and (27) gives

$$\sum_{l=0}^{Q} (2l+1) P_l(\hat{\mathbf{r}}_{q'} \cdot \hat{\mathbf{r}}_q) = 4\pi / W_{q'}\, \delta_{q'q}. \qquad (28)$$

The first result is that the weights for this sampling, if it exists, are all equal to $4\pi/(Q+1)^2$. A second result is that the angle $\theta_{q'q}$ between any two different sampling points should satisfy the equation

$$\sum_{l=0}^{Q} (2l+1) P_l[\cos(\theta_{q'q})] = 0, \quad q' \neq q. \qquad (29)$$

For a given Q, the roots of (29) give the cosines of all the possible angles. For $Q = 0$ there is no root so that the optimal sampling set is constituted by a single point. For $Q = 1$ there is a single root, $\cos(\theta_{q'q}) = -\frac{1}{3}$, which gives rise to a tetrahedron. For $Q = 2$, we have two possible angles, 73·15 and 133·62°, which do not give any closed figure inscribed on the sphere.

Hence, any rule of approximate integration [(26)] must in general involve more than the theoretical minimum number of points. This assertion does not mean that there is no optimal sampling set for functions of class $\mathscr{C}_L$, but rather that a sampling set obtained from an integration rule is not in general an optimal one.

The results of this paragraph can be applied to the rotation function [(9)] which, in all practical applications, is also a limited expansion in terms of the orthogonal functions $D^l_{mm'}$,

$$\mathcal{R}(\phi) \doteq \mathcal{R}_L(\phi) = \sum_{l=0}^{L} \sum_{m,m'=-l}^{l} D^l_{mm'}(\phi) C^l_{mm'}. \quad (30)$$

Since $D^l_{mm'}$, when written in terms of the Euler angles (α, β, γ), depends on α and γ through the expression $\exp[i(m\alpha + m'\gamma)]$, and since for $m' = 0$ it is proportional to the spherical harmonic Y_{lm}, a quadrature rule can be obtained:

$$\begin{aligned} &\int_{\alpha=0}^{2\pi} d\alpha \int_{\beta=0}^{\pi} d\cos\beta \int_{\gamma=0}^{2\pi} d\gamma \mathcal{R}_L(\alpha, \beta, \gamma) D^{*l}_{mm'}(\alpha, \beta, \gamma) \\ &= \sum_{u=1}^{U} \mathcal{R}_L(\phi_u) D^{*l}_{mm'}(\phi_u) W_u \\ &= C^l_{mm'} 8\pi^2/(2L+1). \end{aligned} \quad (31)$$

It follows that the set $\langle \phi_u = (\alpha_i, \beta_j, \gamma_k);\ i, k = 1, \ldots, 2L+1;\ j = 1, \ldots, L+1 \rangle$, where α_i and γ_k are regularly spaced in the interval $(0, 2\pi)$ and $\cos\beta_j$ are the roots of P_{L+1}, is a sampling set of $\mathcal{R}_L$. The weights W_u are again of the product form, derived from the Legendre–Gauss and Fourier quadrature rules.

Plotting the rotation function

Several authors have discussed different ways of plotting the rotation function in order to obtain undistorted maps (Burdina, 1971; Lattman, 1972).

Distortion appears for example when $\mathcal{R}$ is evaluated and plotted on a grid with equal steps in the Euler angles; if $\beta = 0$ all rotations with a constant value of $\alpha + \gamma$ are the same. This situation is somewhat analogous to that encountered when a function of the Cartesian variables (x, y, z) is computed on a regularly spaced grid in the spherical coordinates (r, θ, φ): the value of the function is independent of φ when $\theta = 0$ or π.

This source of distortion can be avoided, to some extent, if we are able to define a metric, in order to give a sense to the notion of nearness of two elements of the group. This can be done because the rotation group is compact, so that a unique positive-definite invariant metric exists (up to a multiplicative constant) (Normand, 1971)

$$ds^2 = \tfrac{1}{2} \mathrm{Tr}(dR\, dR^+), \quad (32)$$

dR being the variation of the matrix R associated with a rotation in a three-dimensional representation of the rotation group.

This metric confers to the space of the parameters of the group the structure of a Riemannian variety, and cannot be reduced to a Cartesian metric.

Expression (32) is an intrinsic one, *i.e.* independent of the parametrization of the group. When parametrized in terms of the Euler angles, it gives

$$ds^2 = d\alpha^2 + 2\cos(\beta)\, d\alpha\, d\gamma + d\gamma^2 + d\beta^2, \quad (33)$$

which, when written in the new variables $\theta_\pm = \alpha \pm \gamma$, coincides with the expression given by Lattman [1972, equation (7)],

$$ds^2 = \cos^2(\beta/2)\, d\theta_+^2 + \sin^2(\beta/2)\, d\theta_-^2 + d\beta^2. \quad (34)$$

This metric shows that the topology of the surfaces of constant β is that of a plane. In fact, the change of variables

$$\begin{aligned} u &= \cos(\beta/2)\theta_+ \\ v &= \sin(\beta/2)\theta_- \end{aligned} \quad (35)$$

gives the Euclidean metric $ds^2 = du^2 + dv^2$ all over any section. Distortion-free β sections of the rotation function can thus be obtained.

Surfaces of constant $\theta_\pm$ have instead the topology of a spherical surface. Therefore, to obtain distortion-free $\theta_\pm$ sections the rotation function should be represented on the surface of a sphere, with $\beta/2$ and $2\theta_\pm$ playing the role of the colatitude and longitude respectively.

If the group is parametrized by $(\chi, \hat{\mathbf{n}})$, $\hat{\mathbf{n}}$ being the unit vector along the axis of rotation and χ the spin about it, the metric is

$$ds^2 = d\chi^2 + 2(1 - \cos\chi)\, d\hat{\mathbf{n}}^2 \quad (36)$$

[Lattman, 1972, equation (9)].

The distance between any two rotations, defined as the integral of ds along a path joining them, is path dependent. In particular, since the parameters $(\pi, \hat{\mathbf{n}})$ and $(-\pi, \hat{\mathbf{n}})$ represent the same rotation, any path joining them is closed but it cannot be reduced, by means of a continuous deformation, to one of vanishingly small length. This implies that the rotation group is not simply connected.

The important point is that these topological properties are intrinsic ones, and cannot be removed by any particular choice of parametrization of the group.

Some numerical results

A program was written which samples the function $c_{lm}(r)$ [(12)] at different points r_n. The quantities $w_n^{1/2} r_n c_{lm}(r_n)$ can thus be used as an input to the Crowther program, instead of the a_{lmn}, and the rotation function can be calculated. For a given l, the function $j_l(hx) j_l(kx)$ vanishes at most twice in the interval between any two consecutive zeros of j_l. A good estimate of its integral can thus be obtained by sampling it at three points within such an interval. Crowther's method should then be faster than any simple integration method by at most a factor of three.

Actually, this ratio was two for the example here reported.

Even if Figs. 1-5 give a clear idea of the errors involved in either method, we present here a test calculation using a model gramicidine A structure (space group $P2_12_12_1$, $a = 24{\cdot}7$, $b = 32{\cdot}3$, $c = 32{\cdot}5$ Å). Two identical model monomers consisting of a polypeptide helix with three tryptophans and tilted by arbitrary angles with respect to the c axis constituted the asymmetric unit content. The resulting structure showed a slight overlap of some of the tryptophans belonging to different molecules.

The squared norms of each l component of the expansion of the Patterson function in spherical harmonics,

$$\sum_{m=-l}^{l} \sum_{n=1}^{N} |a_{lmn}|^2$$

in Crowther's method and

$$\sum_{m=-l}^{l} \sum_{n=1}^{M} |c_{lm}(r_n)|^2 r_n^2 w_n$$

in the method here presented, should be essentially the same when a great number of n terms are included, so that the differences between them effectively show the relative errors involved in the procedures. With 2 Å data, an overall temperature B factor of 6 Å^2 and an outer radius of 6·5 Å, the relative difference in the squared norms was 18, 7, 11, 28, 34, 62 and 36% for l ranging from 2 to 14.

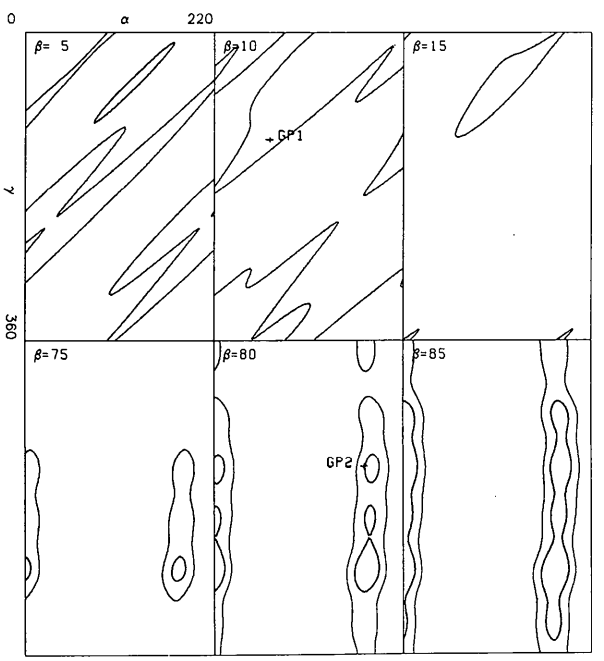

Fig. 6. Contour maps of a cross rotation function as produced by the program written by Crowther (1972) and modified by Dodson (1985). GP1 and GP2 denote the true positions. The contour levels are 60 and 80% of the maximum value of the function.

We then computed a cross rotation function using a single monomer to obtain the second Patterson function to be rotated. Both procedures of calculation showed essentially the same features (Figs. 6 and 7) even if the values differed by 6-15% at the local

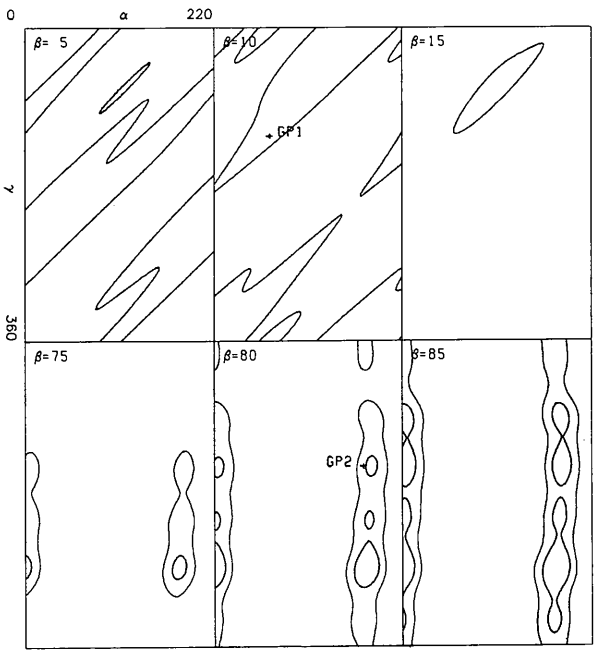

Fig. 7. Same as Fig. 6, but now the cross rotation function was computed using a 12-point Legendre-Gauss integration formula.

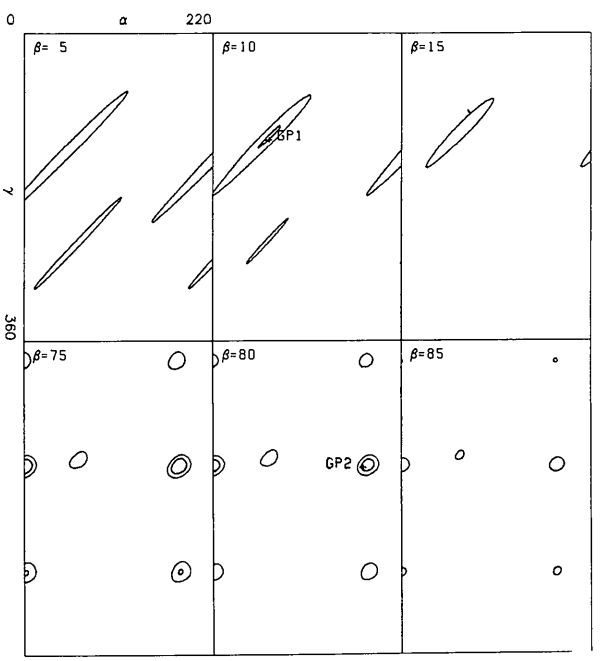

Fig. 8. Same as Fig. 7, but with the contributions of the terms with $l = 2, 4$ omitted from the calculation.

maxima. This result is not surprising because low l terms contribute a substantial portion of the whole Patterson function (after omitting the $l=0$ term) under the conditions of the test. However, as discussed in the article, these very low-l terms can hinder the true solution from showing up. This is clearly shown in Fig. 8, where the terms $l=2, 4$ were omitted from the calculations. It is worth noticing that the two omitted terms contributed 86% of the Patterson squared norm.

References

ABRAMOWITZ, M. & STEGUN, I. A. (1964). *Handbook of Mathematical Functions.* p. 916. Washington, DC: US Government Printing Office.

BURDINA, V. I. (1971). *Sov. Phys. Crystallogr.* **15**, 545.

CROWTHER, R. A. (1972). *The Molecular Replacement Method,* edited by M. G. ROSSMANN, pp. 173-178. New York: Gordon & Breach.

DODSON, E. J. (1985). *Molecular Replacement,* compiled by P. A. MACHIN. Proc. Daresbury Study Weekend, 15-16 February 1985, pp. 33-44.

DODSON, M. M. & SILVA, A. M. (1985). *Proc. R. Ir. Acad. Sect. A,* **85**, 81-108.

LANDAU, L. D. & LIFSCHITZ, E. M. (1972). *Théorie Quantique Relativiste.* Moscow: Mir.

LATTMAN, J. M. (1972). *Acta Cryst.* B**28**, 1065-1068.

NORMAND, J. M. (1971). *Répresentations du Groupe de Rotations.* Saclay: CEA.

PEIRCE, W. H. (1957). *Math. Tables Aid Comput.* **11**, 244-249.

ROSSMANN, M. G. & BLOW, D. M. (1962). *Acta Cryst.* **15**, 24-31.

SMIRNOV, V. (1972). *Cours de Mathématiques Supérieures,* Tome 3. Moscow: Mir.

WATSON, G. N. (1958). *A Treatise on the Theory of Bessel Functions,* 2nd ed. Cambridge Univ. Press.

WIGNER, E. P. (1959). *Group Theory and its Application to the Quantum Mechanics of Atomic Spectra.* New York: Academic Press.

Acta Cryst. (1987). A**43**, 653-655

Measurability of Bijvoet Differences in Triclinic, Monoclinic and Orthorhombic Crystals. II

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Abstract

The probability that the Bijvoet ratio X for the observed reflections of a given crystal is greater than any particular value X_0 depends on space-group symmetry, the number of anomalous scatterers per asymmetric unit and the parameters k and σ_1^2. Numerical values for this probability are obtained as a function of X_0 for different values of k and σ_1^2 for the triclinic, monoclinic and orthorhombic crystals containing p ($=1, 2, 3$ or 4) anomalous scatterers per asymmetric unit. These results are provided in the form of compact tables; Fortran programs that are useful in computing this probability for any given situation are also provided.

1. Introduction

The success of the anomalous-scattering method of structure determination strongly depends on the measurability of Bijvoet differences. The measurability is defined as the probability of the event $\{(X \geq 0{\cdot}1) \cap (y_{\min} \geq 0{\cdot}3)\}$ (Velmurugan & Parthasarathy, 1984; VP, hereafter) where X is the Bijvoet ratio and $y_{\min}$ is the minimum value of the normalized structure-factor magnitudes for the reflection $\mathbf{H}$ and the inverse reflection $\bar{\mathbf{H}}$. Owing to the importance of the anomalous-scattering method, particularly due to the advent of synchrotron radiation as a source for diffraction studies, it would be useful to know *a priori*, in the case of a given crystal, the percentage of *observed* reflections for which the Bijvoet ratio X would be greater than any specific value X_0, say. This information can be obtained from the probability value for the event $\{(X \geq X_0) \cap (y_{\min} \geq 0{\cdot}3)\}$ ($= D$, say) and we shall denote this probability by $M(X_0, 0{\cdot}3)$. The values of $M(X_0, 0{\cdot}3)$ for the particular case of $X_0 = 0{\cdot}1$ were obtained in VP for the triclinic, monoclinic and orthorhombic crystals containing one or two heavy atoms per asymmetric unit for values of k (*i.e.* the ratio of the imaginary to the total real part of the atomic scattering factor of the anomalous scatterer) up to 0·6. Under a pronounced anomalous-scattering effect, k can have larger values for some of the heavy atoms. For example, the values

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