1. GENERAL RELATIONSHIPS AND TECHNIQUES

$$S^{\#}(\tau_{\mathbf{x}}f) = \tau_{S(\mathbf{x})}R^{\#}f \quad \text{and} \quad [S^{\#}(\tau_{\mathbf{x}}f)]^{\vee} = \tau_{-S(\mathbf{x})}R^{\#}\breve{f};$$

and

$$S_1^{\#}f_1 * S_2^{\#}f_2 = S_1^{\#}[f_1 * (S_1^{-1}S_2)^{\#}f_2] = S_2^{\#}[(S_2^{-1}S_1)^{\#}f_1 * f_2].$$

The cross correlation $\breve{\rho}_1^0 * \rho_2^0$ between motifs is therefore

$$\breve{\rho}_1^0 * \rho_2^0 = \sum_{j_1}\sum_{j_2}\sum_{\gamma_{j_1}}\sum_{\gamma_{j_2}}[S_{\gamma_{j_1}}^{\#}(\tau_{\mathbf{x}_{j_1}^{(1)}}\rho_{j_1}^{(1)})]^{\vee} * [S_{\gamma_{j_2}}^{\#}(\tau_{\mathbf{x}_{j_2}^{(2)}}\rho_{j_2}^{(2)})]$$

$$= \sum_{j_1}\sum_{j_2}\sum_{\gamma_{j_1}}\sum_{\gamma_{j_2}}\tau_{S_{\gamma_{j_2}}(\mathbf{x}_{j_2}^{(2)})-S_{\gamma_{j_1}}(\mathbf{x}_{j_1}^{(1)})}[(R_{\gamma_{j_1}}^{\#}\breve{\rho}_{j_1}^{(1)}) * (R_{\gamma_{j_2}}^{\#}\rho_{j_2}^{(2)})]$$

which contains a peak of shape $(R_{\gamma_{j_1}}^{\#}\breve{\rho}_{j_1}^{(1)}) * (R_{\gamma_{j_2}}^{\#}\rho_{j_2}^{(2)})$ at the interatomic vector $S_{\gamma_{j_2}}(\mathbf{x}_{j_2}^{(2)}) - S_{\gamma_{j_1}}(\mathbf{x}_{j_1}^{(1)})$ for each $j_1 \in J_1$, $j_2 \in J_2$, $\gamma_{j_1} \in G/G_{\mathbf{x}_{j_1}^{(1)}}$, $\gamma_{j_2} \in G/G_{\mathbf{x}^{(2)}}$.

The cross-correlation $r * \breve{\rho}_1^0 * \rho_2^0$ between the original electron densities is then obtained by further periodizing by $\mathbb{Z}^3$.

Note that these expressions are valid for any choice of 'atomic' density functions $\rho_{j_1}^{(1)}$ and $\rho_{j_2}^{(2)}$, which may be taken as molecular fragments if desired (see Section 1.3.4.4.8).

If G contains elements g such that $\mathbf{R}_g$ has an eigenspace E_1 with eigenvalue 1 and an invariant complementary subspace E_2, while $\mathbf{t}_g$ has a nonzero component $\mathbf{t}_g^{(1)}$ in E_1, then the Patterson function $r * \breve{\rho}^0 * \rho^0$ will contain *Harker peaks* (Harker, 1936) of the form

$$S_g(\mathbf{x}) - \mathbf{x} = \mathbf{t}_g^{(1)} \oplus (S_g^{(2)}(\mathbf{x}) - \mathbf{x})$$

[where $S_g^{(s)}$ represent the action of g in E_2] in the translate of E_1 by $\mathbf{t}_g^{(1)}$.

1.3.4.3. Crystallographic discrete Fourier transform algorithms

1.3.4.3.1. Historical introduction

In 1929, W. L. Bragg demonstrated the practical usefulness of the Fourier transform relation between electron density and structure factors by determining the structure of diopside from three principal projections calculated numerically by 2D Fourier summation (Bragg, 1929). It was immediately realized that the systematic use of this powerful method, and of its extension to three dimensions, would entail considerable amounts of numerical computation which had to be organized efficiently. As no other branch of applied science had yet needed this type of computation, crystallographers had to invent their own techniques.

The first step was taken by Beevers & Lipson (1934) who pointed out that a 2D summation could be factored into successive 1D summations. This is essentially the tensor product property of the Fourier transform (Sections 1.3.2.4.2.4, 1.3.3.3.1), although its aspect is rendered somewhat complicated by the use of sines and cosines instead of complex exponentials. Computation is economized to the extent that the cost of an $N \times N$ transform grows with N as $2N^3$ rather than N^4. Generalization to 3D is immediate, reducing computation size from N^6 to $3N^4$ for an $N \times N \times N$ transform. The complication introduced by using expressions in terms of sines and cosines is turned to advantage when symmetry is present, as certain families of terms are systematically absent or are simply related to each other; multiplicity corrections must, however, be introduced. The necessary information was tabulated for each space group by Lonsdale (1936), and was later incorporated into Volume I of *International Tables*.

The second step was taken by Beevers & Lipson (1936) and Lipson & Beevers (1936) in the form of the invention of the 'Beevers–Lipson strips', a practical device which was to assist a whole generation of crystallographers in the numerical computation of crystallographic Fourier sums. The strips comprise a set of 'cosine strips' tabulating the functions

$$A\cos\left(\frac{2\pi hm}{60}\right) \quad (A = 1, 2, \ldots, 99; \; h = 1, 2, \ldots, 99)$$

and a set of 'sine strips' tabulating the functions

$$B\sin\left(\frac{2\pi hm}{60}\right) \quad (B = 1, 2, \ldots, 99; \; h = 1, 2, \ldots, 99)$$

for the 16 arguments $m = 0, 1, \ldots, 15$. Function values are rounded to the nearest integer, and those for other arguments m may be obtained by using the symmetry properties of the sine and cosine functions. A Fourier summation of the form

$$Y(m) = \sum_{j=1}^{n}\left[A_j\cos\left(\frac{2\pi h_j m}{60}\right) + B_j\sin\left(\frac{2\pi h_j m}{60}\right)\right]$$

is then performed by selecting the n cosine strips labelled (A_j, h_j) and the n sine strips labelled (B_j, h_j), placing them in register, and adding the tabulated values columnwise. The number 60 was chosen as the l.c.m. of 12 (itself the l.c.m. of the orders of all possible nonprimitive translations) and of 10 (for decimal convenience). The limited accuracy imposed by the two-digit tabulation was later improved by Robertson's sorting board (Robertson, 1936a,b) or by the use of separate strips for each decimal digit of the amplitude (Booth, 1948b), which allowed three-digit tabulation while keeping the set of strips within manageable size. Cochran (1948a) found that, for most structures under study at the time, the numerical inaccuracies of the method were less than the level of error in the experimental data. The sampling rate was subsequently increased from 60 to 120 (Beevers, 1952) to cope with larger unit cells.

Further gains in speed and accuracy were sought through the construction of special-purpose mechanical, electro-mechanical, electronic or optical devices. Two striking examples are the mechanical computer RUFUS built by Robertson (1954, 1955, 1961) on the principle of previous strip methods (see also Robertson, 1932) and the electronic analogue computer X-RAC built by Pepinsky, capable of real-time calculation and display of 2D and 3D Fourier syntheses (Pepinsky, 1947; Pepinsky & Sayre, 1948; Pepinsky *et al.*, 1961; see also Suryan, 1957). The optical methods of Lipson & Taylor (1951, 1958) also deserve mention. Many other ingenious devices were invented, whose descriptions may be found in Booth (1948b), Niggli (1961) and Lipson & Cochran (1968).

Later, commercial punched-card machines were programmed to carry out Fourier summations or structure-factor calculations (Shaffer *et al.*, 1946a,b; Cox *et al.*, 1947, 1949; Cox & Jeffrey, 1949; Donohue & Schomaker, 1949; Grems & Kasper, 1949; Hodgson *et al.*, 1949; Greenhalgh & Jeffrey, 1950; Kitz & Marchington, 1953).

The modern era of digital electronic computation of Fourier series was initiated by the work of Bennett & Kendrew (1952), Mayer & Trueblood (1953), Ahmed & Cruickshank (1953b), Sparks *et al.* (1956) and Fowweather (1955). Their Fourier-synthesis programs used Beevers–Lipson factorization, the program by Sparks *et al.* being the first 3D Fourier program useable for all space groups (although these were treated as $P1$ or $P\bar{1}$ by data expansion). Ahmed & Barnes (1958) then proposed a

general programming technique to allow full use of symmetry elements (orthorhombic or lower) in the 3D Beevers–Lipson factorization process, including multiplicity corrections. Their method was later adopted by Shoemaker & Sly (1961), and by crystallographic program writers at large.

The discovery of the FFT algorithm by Cooley & Tukey in 1965, which instantly transformed electrical engineering and several other disciplines, paradoxically failed to have an immediate impact on crystallographic computing. A plausible explanation is that the calculation of large 3D Fourier maps was a relatively infrequent task which was not thought to constitute a bottleneck, as crystallographers had learned to settle most structural questions by means of cheaper 2D sections or projections. It is significant in this respect that the first use of the FFT in crystallography by Barrett & Zwick (1971) should have occurred as part of an iterative scheme for improving protein phases by density modification in real space, which required a much greater number of Fourier transformations than any previous method. Independently, Bondot (1971) had attracted attention to the merits of the FFT algorithm.

The FFT program used by Barrett & Zwick had been written for signal-processing applications. It was restricted to sampling rates of the form 2^n, and was not designed to take advantage of crystallographic symmetry at any stage of the calculation; Bantz & Zwick (1974) later improved this situation somewhat.

It was the work of Ten Eyck (1973) and Immirzi (1973, 1976) which led to the general adoption of the FFT in crystallographic computing. Immirzi treated all space groups as $P1$ by data expansion. Ten Eyck based his program on a versatile multi-radix FFT routine (Gentleman & Sande, 1966) coupled with a flexible indexing scheme for dealing efficiently with multidimensional transforms. He also addressed the problems of incorporating symmetry elements of order 2 into the factorization of 1D transforms, and of transposing intermediate results by other symmetry elements. He was thus able to show that in a large number of space groups (including the 74 space groups having orthorhombic or lower symmetry) it is possible to calculate only the unique results from the unique data within the logic of the FFT algorithm. Ten Eyck wrote and circulated a package of programs for computing Fourier maps and re-analysing them into structure factors in some simple space groups ($P1$, $P\bar{1}$, $P2$, $P2/m$, $P2_1$, $P222$, $P2_12_12_1$, $Pmmm$). This package was later augmented by a handful of new space-group-specific programs contributed by other crystallographers ($P2_12_12$, $I222$, $P3_121$, $P4_12_12$). The writing of such programs is an undertaking of substantial complexity, which has deterred all but the bravest: the usual practice is now to expand data for a high-symmetry space group to the largest subgroup for which a specific FFT program exists in the package, rather than attempt to write a new program. Attempts have been made to introduce more modern approaches to the calculation of crystallographic Fourier transforms (Auslander, Feig & Winograd, 1982; Auslander & Shenefelt, 1987; Auslander *et al.*, 1988) but have not gone beyond the stage of preliminary studies.

The task of fully exploiting the FFT algorithm in crystallographic computations is therefore still unfinished, and it is the purpose of this section to provide a systematic treatment such as that (say) of Ahmed & Barnes (1958) for the Beevers–Lipson algorithm.

Ten Eyck's approach, based on the reducibility of certain space groups, is extended by the derivation of a universal transposition formula for intermediate results. It is then shown that space groups which are not completely reducible may nevertheless be treated by three-dimensional Cooley–Tukey factorization in such a way that their symmetry may be fully exploited, whatever the shape of their asymmetric unit. Finally, new factorization methods with built-in symmetries are presented. The unifying concept throughout this presentation is that of 'group action' on indexing sets, and of 'orbit exchange' when this action has a

composite structure; it affords new ways of rationalizing the use of symmetry, or of improving computational speed, or both.

1.3.4.3.2. Defining relations and symmetry considerations

A finite set of reflections $\{F_{\mathbf{h}_l}\}_{l\in L}$ can be periodized without aliasing by the translations of a suitable sublattice $\mathbf{N}^T\Lambda^*$ of the reciprocal lattice Λ^*; the converse operation in real space is the sampling of ρ at points $\mathbf{X}$ of a grid of the form $\mathbf{N}^{-1}\Lambda$ (Section 1.3.2.7.3). In standard coordinates, $\{F_{\mathbf{h}_l}\}_{l\in L}$ is periodized by $\mathbf{N}^T\mathbb{Z}^3$, and ρ is sampled at points $\mathbf{x}\in\mathbf{N}^{-1}\mathbb{Z}^3$.

In the absence of symmetry, the unique data are
– the $F_{\mathbf{h}}$ indexed by $\mathbf{h}\in\mathbb{Z}^3/\mathbf{N}^T\mathbb{Z}^3$ in reciprocal space;
– the $\rho_{\mathbf{x}}$ indexed by $\mathbf{x}\in(\mathbf{N}^{-1}\mathbb{Z}^3)/\mathbb{Z}^3$; or equivalently the $\rho_{\mathbf{m}}$ indexed by $\mathbf{m}\in\mathbb{Z}^3/\mathbf{N}\mathbb{Z}^3$, where $\mathbf{x}=\mathbf{N}^{-1}\mathbf{m}$.

They are connected by the ordinary DFT relations:

$$F_{\mathbf{h}} = \frac{1}{|\det\mathbf{N}|}\sum_{\mathbf{x}\in(\mathbf{N}^{-1}\mathbb{Z}^3)/\mathbb{Z}^3}\rho_{\mathbf{x}}\exp(2\pi i\mathbf{h}\cdot\mathbf{x})$$

or

$$F_{\mathbf{h}} = \frac{1}{|\det\mathbf{N}|}\sum_{\mathbf{m}\in\mathbb{Z}^3/\mathbf{N}\mathbb{Z}^3}\rho_{\mathbf{m}}\exp[2\pi i\mathbf{h}\cdot(\mathbf{N}^{-1}\mathbf{m})]$$

and

$$\rho_{\mathbf{x}} = \sum_{\mathbf{h}=\mathbb{Z}^3/\mathbf{N}^T\mathbb{Z}^3}F_{\mathbf{h}}\exp(-2\pi i\mathbf{h}\cdot\mathbf{x})$$

or

$$\rho_{\mathbf{m}} = \sum_{\mathbf{h}\in\mathbb{Z}^3/\mathbf{N}^T\mathbb{Z}^3}F_{\mathbf{h}}\exp[-2\pi i\mathbf{h}\cdot(\mathbf{N}^{-1}\mathbf{m})].$$

In the presence of symmetry, the unique data are
– $\{\rho_{\mathbf{x}}\}_{\mathbf{x}\in D}$ or $\{\rho_{\mathbf{m}}\}_{\mathbf{m}\in D}$ in real space (by abuse of notation, D will denote an asymmetric unit for $\mathbf{x}$ or for $\mathbf{m}$ indifferently);
– $\{F_{\mathbf{h}}\}_{\mathbf{h}\in D^*}$ in reciprocal space.

The previous summations may then be subjected to orbital decomposition, to yield the following 'crystallographic DFT' (CDFT) defining relations:

$$F_{\mathbf{h}} = \frac{1}{|\det\mathbf{N}|}\sum_{\mathbf{x}\in D}\rho_{\mathbf{x}}\left[\sum_{\gamma\in G/G_{\mathbf{x}}}\exp\{2\pi i\mathbf{h}\cdot[S_\gamma(\mathbf{x})]\}\right]$$

$$= \frac{1}{|\det\mathbf{N}|}\sum_{\mathbf{x}\in D}\rho_{\mathbf{x}}\left[\frac{1}{|G_{\mathbf{x}}|}\sum_{g\in G}\exp\{2\pi i\mathbf{h}\cdot[S_g(\mathbf{x})]\}\right],$$

$$\rho_{\mathbf{x}} = \sum_{\mathbf{h}\in D^*}F_{\mathbf{h}}\left[\sum_{\gamma\in G/G_{\mathbf{h}}}\exp\{-2\pi i\mathbf{h}\cdot[S_\gamma(\mathbf{x})]\}\right]$$

$$= \sum_{\mathbf{h}\in D^*}F_{\mathbf{h}}\left[\frac{1}{|G_{\mathbf{h}}|}\sum_{g\in G}\exp\{-2\pi i\mathbf{h}\cdot[S_g(\mathbf{x})]\}\right],$$

with the obvious alternatives in terms of $\rho_{\mathbf{m}}, \mathbf{m}=\mathbf{Nx}$. Our problem is to evaluate the CDFT for a given space group as efficiently as possible, in spite of the fact that the group action has spoilt the simple tensor-product structure of the ordinary three-dimensional DFT (Section 1.3.3.3.1).

Two procedures are available to carry out the 3D summations involved as a succession of smaller summations:

references