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Solving Crystal Structures without Fourier Mapping. I. Centrosymmetric Case

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Abstract

A recursive algebraic procedure for solving one-dimensional monoatomic crystal structures is presented. (If applied to projections, also a three-dimensional atom arrangement may be reconstructed.) Moduli of the geometrical parts of the corresponding structure factors serve as experimental input. The atom coordinates are found from the roots of a polynomial. For space group $P\bar{1}$ with m atoms in the asymmetric unit, the first $m + 1$ reflections are needed for finding their signs by means of a determinant technique. Using Monte Carlo calculations, the influence of the standard uncertainties of the data on the uncertainties of the derived coordinates is simulated. In a similar way, hints for discriminating between sign variations are obtained. The resolution in direct space is better than that of a one-dimensional Fourier summation over the same number of reflections. Error-free data provide a unique solution (if homometries are excluded). For data affected by experimental uncertainties, all possible solutions (compatible with the data) are found. Their number is always finite, and it may be further reduced by employing reflection orders higher than $m + 1$. Some applications of the method are discussed.

1. Introduction

Notation and symbols for this paper are given in Table 1.

It is almost trivial to state that the mathematical procedure of Fourier summation (or transform) appears to be indispensable in most structure-solution methods that are used today. Determination of structure-factor phases permits the calculation of E maps and (at least) heavy atoms are found from a Patterson function. In both cases, peaks of a density distribution (though approximated owing to the inevitably incomplete set of Fourier coefficients) are located and used for establishing a first structure model to be completed and refined in subsequent steps.

Despite their overwhelming success, Fourier techniques have a few weak points. Firstly, signs or phases of the coefficients are determined with high probability, however not with certainty. [This does not apply to directly measured signs of structure invariants, *e.g. via* '*Umweganregung*' effects (Hümmer & Billy, 1982)]. Secondly, in direct methods, not all phases are found for computing the first E map – only the 'important' ones associated with high moduli. And, finally, accidentally extinct (or nearly extinct) reflections do not (or not essentially) contribute to the density distribution and thus to the initial structure model. On the other hand, from the 'good old times of trial-and-error' solution techniques, it is well known that those reflections with $F = 0$ (or $|F| \simeq 0$) contain important structure information without the need to determine their phases.

Table 1. *List of symbols and definitions*

Starting from equation (4), i is used as a running index throughout this paper [except for equation (3), taken from Ott (1928), where $i = (-1)^{1/2}$ is obvious].

h, i, j, k, l, n	Running indices
N	No. of atoms in the unit cell
m	No. of (symmetrically) independent atoms in the unit cell, also for a partial structure
a	Anomalous scattering atoms
$f(\lambda, \sin\theta/\lambda)$	Atomic scattering factor $= f^\circ(\sin\theta/\lambda) + f'(\lambda) + if''(\lambda)$
B	Thermal displacement factor
F	Structure factor
F_a	Partial structure factor of a atoms. $\|F_a\|$ is obtained by measuring $\|F\|^2$ at various wavelengths close to an absorption edge λ_a of a according to Karle (1980).
F_a°	As above, but based on dispersive-free f_a°
$g_\mathbf{h}$	Modulus of the geometrical part of the structure factor (of one atomic species, *i.e.* of a partial structure) for m atoms in the asymmetric unit. In space group $P\bar{1}$, $g_h = g(hkl) = \left\|\sum_{j=1}^m \cos(2\pi\mathbf{h}\cdot\mathbf{r}_j)\right\|$ For a central reciprocal-lattice row, *e.g.* $h00$ reflections, $g_h = g(h00) = \left\|\sum_{j=1}^m \cos(2\pi h x_j)\right\|$
$S_\mathbf{h} \equiv S(hkl)$	Geometrical part of the structure factor $F_h = F(hkl)$ for a monoatomic noncentrosymmetric partial structure
s	Sign of the structure factor, partial structure factor or of its geometrical part
P_h	Sum of powers of $\cos(2\pi x_j)$ with power h
$\mathbf{P}$	Matrix with elements P_h
D_n	Determinant of the matrix $\mathbf{P}$ (for n, see text)
$R(c)$	Polynomial in $c = \cos(2\pi x)$
$R(\alpha)$	Polynomial in $\alpha = \exp(2\pi i x)$
Q_i	Coefficients of the polynomial $R(c)$
q_i	Coefficients of the polynomial $R(\alpha)$
$\mathbf{Q}$	Vector $(-Q_0, Q_1, -Q_2, \ldots, (-1)^m Q_{m-1}, (-1)^{m+1} Q_m)$
$\Sigma_1 = 0$	Criterion for correct sign variation (Knof, 1989)
$d_n = 0$	Criterion for correct sign variation (determinant method)

Structure factors for different $\mathbf{h}_i$ are intimately related by the set of atomic positions $\mathbf{r}_j$ ($j = 1, \ldots, N$). From these relationships, *e.g.* Karle–Hauptmann determinants or probability expressions for phase combinations, well known tools for determining phases of selected $F(\mathbf{h}_i)$ have been developed. Exact algebraic equations (without need for statistics or approximations) may be derived when both the structure and the set of $\mathbf{h}_i$ are properly reduced:

(i) Consider a centrosymmetric structure (or partial structure) of chemically identical 'point' atoms at rest. Thus, all physical factors determining $|F|$ [such as $f^\circ(\sin\theta/\lambda)$ or $f'(\lambda)$ and $f''(\lambda)$ and anisotropic displacement coefficients] are disposed off, and an averaged f_j is avoided. For simplicity, one may further assume space group $P\bar{1}$ and no special positions being occupied. As a consequence, $F(\mathbf{h})$ is reduced to its geometrical part

$$2s_{\mathbf{h}}g_{\mathbf{h}} = 2\sum_{j=1}^{m}\cos(2\pi\mathbf{h}\cdot\mathbf{r}_j) \qquad (1)$$

with $m = N/2$.

(ii) In reciprocal space, we restrict the sets of $\mathbf{h}_i$ to series of central lattice rows, *i.e.* to 'harmonic' reflections $\mathbf{h}_i, 2\mathbf{h}_i, \ldots$ starting with the first order. This confines the problem to solving one-dimensional projections of the structure, *e.g.* deriving x_j coordinates from $g(h00)$.

[In another paper (Fischer & Pilz, 1997, Section 5), we have described a method that may lead from one-dimensional projections of a monoatomic structure to an unambiguous geometrical ('point') model *via* a three-dimensional reconstruction: The $y_{j'}$ coordinates, for example, independently found from the $g(0k0)$, are allocated to the x_j or $-x_j$ by using 'diagonal' coordinates obtained from $g(hh0)$. Similarly, the $z_{j''}$ can be allocated to the two-dimensional projection. Thus, five reciprocal-lattice rows are sufficient. This holds if all projections can be obtained with appropriate resolution and if unique solutions exist for all projections. The above-mentioned restrictions associated with harmonic reflections may thus be compensated for.]

The argument for any cosine term j becomes a multiple of that of the first-order reflection. Consequently, any $\cos(2\pi hx_j)$ can be expressed by powers up to h of $\cos 2\pi x_j$, leading to algebraic equations.

To our knowledge, Ott (1928) presented the first ideas for algebraic solutions of structures starting from accidental extinctions as mentioned above. His method, as well as a similar one of Avrami (1939), did not become popular for two reasons: In the late twenties, the atomic scattering factors were insufficiently known. Consequently, approximations to the pure geometrical part of the structure factor were unreliable, in particular for different kinds of atoms. In addition, the lack of computing power caused severe restrictions on practical applications. Nowadays, we can separate, *e.g.* by anomalous (resonant) scattering contrast, the partial structure amplitudes of one atomic species from those for the rest of the structure (Karle, 1980; Hendrickson, 1985; Prandl, 1990) and high-speed computing is available at our desks.

The object of this paper is to present an algebraic tool for the direct solution of a partial structure projected onto one direction, along with a method for phase determination, the determinant technique. The first is derived from parts of Ott's (and Avrami's) work, which seems to have been forgotten. We feel it deserves new attention and ought to be reconsidered for practical use with modern possibilities. Determinants for obtaining signs (Banerjee, 1933) were independently developed by one of us (Pilz, 1996) and generalized for inclusion of high-order reflections.

Our paper is divided into two main parts: After some preliminaries, we describe theoretical aspects and general features of the one-dimensional algebraic technique. Within this section, we first (§§2.1, 2.2, 2.3) deal with mapping the atomic positions as roots of a polynomial under the assumption that the phases of the structure factors are known. The technique of sign determination is treated later, since it is partly based on the coefficients of the polynomial described before. In §3, we discuss the resolution in direct space and the influence of uncertainties. Finally, some conclusions are offered for further discussion.

While this paper was with the referees, we learnt about a rather different algebraic approach to the phase problem (more general but more demanding) by Cervellino & Ciccariello (1996). It is based on a finite set of intensities (or unitary structure amplitudes) from appropriately selected reflections. We wish to thank Professor Ciccariello for providing a reprint.

2. Theoretical aspects

2.1. *Preliminaries, requirements*

Again, suppose space group $P\bar{1}$ with no special positions occupied. [Symmetries higher than $P\bar{1}$ may be easily accounted for in most cases: we experienced no essential problem in examining a structure with space group *Pnma* (Pilz, 1996). For special positions, see §2.6.]

In addition, we omit any physical approximation for the case of atoms with different scattering powers. Hence, we assume a monoatomic crystal structure (or a partial structure of atoms designated '*a*'). Partial structure amplitudes $|F_a|$ or $|F_a^\circ|$ can be separated (Karle, 1980; Hendrickson, 1985; Prandl, 1990) if the *a* atoms are anomalous scatterers (as widely used in MAD techniques). The representation of atoms by points with unit weight is achieved by reducing $|F_a^\circ|$ (or $|F_a|$) according to

$$|F_a^\circ(h)|/2f_a^\circ T_h = g_h \quad \text{with} \quad T_h = \exp[-B_a\sin^2\theta(h)/\lambda^2], \qquad (2)$$

which, of course, implies knowledge of the ('absolute') scale factor and the (overall) displacement factor.

Consider a one-dimensional projection of the unit cell, *e.g.* parallel to **b** and **c** onto **a**, and assume sufficient (in principle 'infinite') resolution. (For accidental coincidence of point atoms, see end of §2.3.) The corresponding structure factors are

$$2s_h g_h = 2\sum_{j=1}^{m} \cos(2\pi h x_j) \tag{1a}$$

with $m = N/2$.

Solving a sufficient set of g_h for the x_j was first suggested by Ott (1928).

2.2. *Early work*

Ott (1928) and Avrami (1939) have published an algebraic method for determining mono- and multiatomic structures. Avrami's more general approach proposed an 'overall' $f(hkl)$ for approximating $S(hkl)$ in order to deal with structures consisting of different atomic species. Ott presented (for the general noncentrosymmetric case) a 'characteristic equation', which for x coordinates and $h00$ reflections reads in our notation

$$\begin{aligned} R(\alpha) &= \prod_{j=1}^{N}(\alpha - \alpha_j) \\ &= \alpha^N + q_1\alpha^{N-1} + q_2\alpha^{N-2} + \ldots + q_N \\ &= 0 \end{aligned}$$

with

$$S_h = \sum_{j=1}^{N} \exp(2\pi i h x_j) = \sum_{j=1}^{N} \alpha_j^h \tag{3}$$

and

$$\ln \alpha_j = 2\pi i (x_j h).$$

Using Newton's formulas (Korn & Korn, 1967), the S_h and q_i are related by [taken from Ott's equation (5)]:

$$\begin{aligned} S_1 + q_1 &= 0 \\ S_2 + q_1 S_1 + q_2 2 &= 0 \\ &\vdots \\ S_N + q_1 S_{N-1} + \ldots + q_N N &= 0 \\ S_{N+1} + q_1 S_N + \ldots + q_N S_1 &= 0 \\ &\vdots \end{aligned} \tag{4}$$

The N roots of the polynomial $R(\alpha)$ provide the coordinates x_j. Owing to the required but unknown phases, at that time only rather simple (and special) structures could be treated. Ott started with central reciprocal-lattice rows. In order to reduce the task of sign determination, he selected rows possessing as many accidental extinctions as possible. (In a later paper, he generalized his algebra to reciprocal-lattice planes.) In the following section, we present an algorithm independent of accidental extinctions. How these facilitate the solution and also reduce computational efforts will be discussed in §2.5.

2.3. *Recursive technique*

Starting from the early ideas, Knof (1989) developed a doubly recursive algorithm for centrosymmetric one-dimensional projections, *i.e.* reducing N to $m = N/2$. Cosines of order $h > 1$ were transformed in a first recursion into P_h by applying the 'addition formulae' for $\cos(nx)$. He found a general sum of powers (Knof, 1989, p. 28):

$$\begin{aligned} P_h &:= \sum_{j=1}^{m} \cos^h(2\pi x_j) \\ &= \left[s_h g_h - \sum_{j=1}^{[h/2]} (-1)^j 2^{h-1-2j} \frac{h}{h-j} \binom{h-j}{j} P_{h-2j} \right] 2^{1-h} \end{aligned} \tag{5}$$

with $[h/2]$ the integer part of $h/2$ and $P_0 = g_0 = m$. Note: This is one type of relation between different $s_h g_h$ (as mentioned in §1), without explicit reference to the coordinates x_j.

The number of variations of signs s_h is limited. Consequently, all possible sets of P_h ($h = 1, \ldots, m$) are accessible. In a second recursive step, the quantities Q_i are calculated by using the same arguments as for deriving equations (4), *i.e.* the P_h and Q_i are related by

$$\begin{aligned} -P_1 + Q_1 &= 0 \\ -P_2 + Q_1 P_1 - Q_2 2 &= 0 \\ &\vdots \\ -P_m + Q_1 P_{m-1} - \ldots + (-1)^{m+1} Q_m m &= 0 \\ -P_{m+1} + Q_1 P_m - \ldots + (-1)^{m+1} Q_m P_1 &= 0 \\ &\vdots \end{aligned} \tag{6}$$

From (6) follows

$$Q_i = \left[\sum_{j=0}^{i=1} (-1)^{i-j-1} P_{i-j} Q_j \right] \Big/ i \tag{6a}$$

with $i = 1, \ldots, m$ and $Q_0 = 1$.

In analogy to (3), the Q_i are coefficients of a polynomial $R(c)$ in $c = \cos(2\pi x)$:

$$\begin{aligned} R(c) &= \prod_{j=1}^{m} (c - c_j) \\ &= c^m - Q_1 c^{m-1} + Q_2 c^{m-2} - \ldots + (-1)^m Q_m. \end{aligned} \tag{7}$$

Its roots, $c_j = \cos(2\pi x_j)$, provide the x coordinates ($j = 1, \ldots, m$) because the cosine function obeys the symmetry of the object. $R(c)$ can easily be mapped as a function of x: $R(x)$. Figs. 1 and 2 give two examples for $m = 5$ (solid lines computed from $s_h g_h$ with $h = 1, \ldots, 5$, Table 2). In space group $P\bar{1}$, $R(x)$ is periodic in $0 \le x \le 1$ with $0 \le x \le \frac{1}{2}$ being the asymmetric part. [For higher symmetries, the period for $R(x)$ may be smaller, *e.g.* $0 \le x \le \frac{1}{2}$ for a screw axis 2_1 parallel to **a**. Then, the investigator has to find out whether a given x_j, say 0.1, represents an atom with $x = 0.1$ or 0.4. Resolving these and other ambiguities will be dealt with separately.] If two (or more) coordinates coincide owing to the projection from three dimensions into one, a corresponding degenerate solution is found for this coordinate. (Coordinates nos. 4 and 5 in example I approximate this possibility. See also Fig. 1.)

The degree m of the polynomial $R(c)$, which equals the number of atoms in the asymmetric unit, must be known. Consequently, signs of the first m 'harmonic' reflection orders are required for obtaining P_h according to (5) [or later to (12)] in order to solve the one-dimensional projection by using equations (6) and (7).

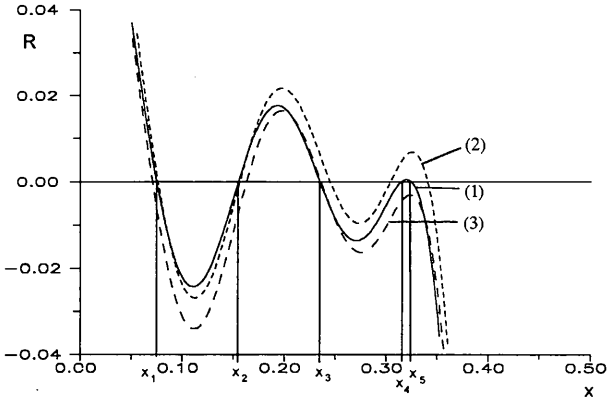

Fig. 1. Polynomial R for a one-dimensional structure (example I) with atom coordinates $x_1 = 0.075$, $x_2 = 0.155$, $x_3 = 0.235$, $x_4 = 0.315$, $x_5 = 0.325$. (1) Exact g_h; (2), (3) g_h with assumed uncertainties: (2) $\langle\Delta(g_h)\rangle = 0.05 g_h$; (3) $\langle\Delta(g_h)\rangle = 0.12 g_h$, see §3.1.

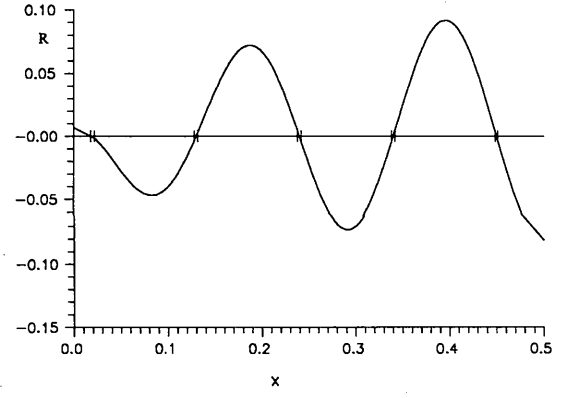

Fig. 2. Polynomial R plotted *versus* x for a one-dimensional structure (example II) with atom coordinates $x_1 = 0.02$, $x_2 = 0.13$, $x_3 = 0.24$, $x_4 = 0.34$, $x_5 = 0.45$ [error bars indicate standard uncertainties of coordinates for assumed standard uncertainties of the geometrical parts $\sigma(g_h) = 0.1 g_h$, see §3.1].

2.4. *Sign determination, determinant technique*

After fixing s_1, 2^{m-1} sign variations exist for calculating 'possible' sets of P_h, $h = 1, \ldots, m$. As each of them may offer 'solutions', a criterion is needed for discarding the wrong ones. Knof (1989) calculated $g_{h,\mathrm{cal}}$ from the coordinates of each of these possible solutions, compared them with the experimental $g_{h,\mathrm{obs}}$, and used the minimum

$$\Sigma_1 = \left[\sum_{h=1}^{m+1} (g_{h,\mathrm{obs}} - g_{h,\mathrm{cal}})^2\right]^{1/2} \tag{8}$$

as a figure of merit, since Σ_1 vanishes for the correct sign variation, provided the experimental g's are free of error.

An improved strategy emerges from a closer inspection of equations (6) and (6*a*). It saves the effort of finding all 'possible' sets of x_j ($j = 1, \ldots, m$) from the above sign variations. From (6*a*), it follows that

$$\begin{aligned} Q_0 &:= 1 \\ Q_1 &= P_1 Q_0 = P_1 \\ Q_2 &= (P_1 Q_1 - P_2 Q_0)/2 = (P_1^2 - P_2)/2 \\ &\vdots \\ Q_m &= [P_1 Q_{m-1} - P_2 Q_{m-2} + \ldots + (-1)^m P_{m-1} Q_1 \\ &\quad + (-1)^{m+1} P_m Q_0]/m. \end{aligned}$$

Reformulating this system of equations by including P_h ($h > m$) yields

$$\begin{pmatrix} P_1 & 1 & 0 & \ldots & 0 & 0 \\ P_2 & P_1 & 2 & \ldots & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ P_m & P_{m-1} & P_{m-2} & \ldots & P_1 & m \\ P_{m+1} & P_m & P_{m-1} & \ldots & P_2 & P_1 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \end{pmatrix} \begin{pmatrix} -Q_0 \\ Q_1 \\ -Q_2 \\ \vdots \\ (-1)^m Q_{m-1} \\ (-1)^{m+1} Q_m \end{pmatrix}$$

$$= \begin{pmatrix} 0 \\ 0 \\ 0 \\ \vdots \\ 0 \\ 0 \end{pmatrix} \quad \text{or} \quad \mathbf{P} \cdot \mathbf{Q} = \mathbf{0}. \tag{9}$$

Selecting from (9) any $m + 1$ equations produces a square matrix with the consequence that the chosen

Table 2. *Theoretical g_h for examples I and II*

h	Example I s_h	Example I g_h	Example II s_h	Example II g_h
1	+	0.696	+	0.253
2	−	2.035	+	0.297
3	+	0.831	+	0.376
4	−	0.480	+	0.524
5	−	1.696	+	0.221
6	+	0.831	+	0.646
7	−	0.616	−	0.915
8	−	1.818	+	1.384
9			+	3.324

system of equations has nontrivial solutions for Q_i only if

$$D = \det(\mathbf{P}) = 0. \tag{10}$$

This holds for g_h without error. In order to find all signs (*e.g.* of the first $m+1$ harmonic reflections in the reciprocal-lattice row under investigation), the variations of all signs $s_2, \ldots, s_{m+1}$ are again checked in terms of equation (9). This accounts for 2^m possibilities. (s_1 being arbitrarily selected as long as the origin of the projection has not been fixed otherwise.) We denote this determinant using the lowest possible number of reflection orders by

$$D_1 = \begin{vmatrix} P_1 & 1 & 0 & \ldots & 0 & 0 \\ P_2 & P_1 & 2 & \ldots & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ P_m & P_{m-1} & P_{m-2} & \ldots & P_1 & m \\ P_{m+1} & P_m & P_{m-1} & \ldots & P_2 & P_1 \end{vmatrix}. \tag{10a}$$

For a special centrosymmetric case with $m = 7$, Banerjee (1933) has derived a similar determinant, starting from Ott's (1928) equation. Banerjee's determinant [his equation (8)] has the same pattern but contains (mainly) S_h instead of P_h. Mathematically, it is identical with D_1. It is, however, built up by using a polynomial of double rank. Banerjee demonstrated how to determine signs of five $00l$ reflections from eight structure-factor moduli, three of which were zero. (See also §2.5.)

D_1 can be evaluated (Pilz, 1996, p. 27) using

$$D_1 = \sum_{j_1=0}^{\left[m+1-\sum_{l=2}^{m+1} j_l\right]} \sum_{j_2=0}^{\left[\left(m+1-\sum_{l=3}^{m+1} j_l\right)/2\right]} \cdots \sum_{j_m=0}^{[(m+1-j_m)/m]} \sum_{j_{m+1}=0}^{1} (-1)^{m+1-\sum_{i=1}^{m+1} j_i} \times \left[\binom{m+1}{m+1-j_1}(m+1-j_1)! \Big/ \prod_{i=1}^{m+1} i^{j_i} \prod_{i=2}^{m+1} j_i!\right] \times \prod_{i=1}^{m+1} P_i^{j_i}$$

with

$$\sum_{i=1}^{m+1} i j_i = m+1 \tag{11}$$

and replacing the P_h by

$$P_h = \begin{cases} \dfrac{1}{2^{h-1}} \displaystyle\sum_{j=0}^{[h/2]} \binom{h}{j} s_{h-2j} g_{h-2j}, & h \text{ odd} \\ \dfrac{1}{2^{h-1}} \left[\dfrac{m}{2}\binom{h}{h/2} + \displaystyle\sum_{j=0}^{h/2-1} \binom{h}{j} s_{h-2j} g_{h-2j}\right], & h \text{ even.} \end{cases} \tag{12}$$

Equation (12) is derived from Knof's (1989) equation (5) and saves one recursion.

Using D_1 [from (11)] as criterion for correct signs requires twice as many test runs compared to using Σ_1 [(8)]. Fortunately, however, this is more than compensated for, since D_1 can be calculated prior to solving for the coordinates. (On a small desk PC, our preliminary program gives a result within 5 min for 10 coordinates from 11 g_h and employing D_1 as the criterion for finding all the signs.)

Higher reflection orders can easily be introduced by exchanging two rows in $\mathbf{P}$. Using P_h and thus $s_h g_h$ with h up to $m+n$ (instead of $m+1$) leads to

$$D_n = \begin{vmatrix} P_1 & 1 & 0 & \ldots & 0 & 0 \\ P_2 & P_1 & 2 & \ldots & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ P_m & P_{m-1} & P_{m-2} & \ldots & P_1 & m \\ P_{m+n} & P_{m+n-1} & P_{m+n-2} & \ldots & P_{n+1} & P_n \end{vmatrix} = 0. \tag{13}$$

Of course, working with $m+n$ reflection orders produces even more sign variations, namely $2m+n-1$. This can, however, be avoided by introducing (12) into (13), which furnishes expressions of the type

$$D_n(g_1, s_2 g_2, \ldots, s_{m+n} g_{m+n}) = 0.$$

For example, from

$$\begin{aligned} D_1 = 0 \quad &\text{follows} \quad s_{m+1} g_{m+1} = f_1(g_1, s_2 g_2, \ldots, s_m g_m) \\ D_2 = 0 \quad &\text{follows} \quad s_{m+2} g_{m+2} \\ &\qquad = f_2(g_1, s_2 g_2, \ldots, s_{m+1} g_{m+1}) \\ D_n = 0 \quad &\text{follows} \quad s_{m+n} g_{m+n} \\ &\qquad = f_n(g_1, s_2 g_2, \ldots, s_{m+n-1} g_{m+n-1}). \end{aligned} \tag{14}$$

(Note that this type of equation between different g_h depends on m.) By suitable combination of these equations, all $s_h g_h$ with $h > m$ can be expressed by those of the first m reflection orders as illustrated below for

$m = 3$. Here one obtains

$$\begin{aligned}
s_4 g_{4,\mathrm{cal}} &= (-12g_1^2 + 4g_1^4 + 6s_2g_2 - 12g_1^2 s_2 g_2 + 3g_2^2 \\
&\quad + 8g_1 s_3 g_3)/3 \\
s_5 g_{5,\mathrm{cal}} &= (15g_1 - 30g_1^3 + 8g_1^5 + 15g_1 s_2 g_2 - 20g_1^3 s_2 g_2 \\
&\quad + 10g_1^2 s_3 g_3 + 5s_2 g_2 s_3 g_3)/3 \\
s_6 g_{6,\mathrm{cal}} &= (-9 + 36g_1^2 - 36g_1^4 + 8g_1^6 - 12g_1^4 s_2 g_2 \\
&\quad + 9g_2^2 - 18g_1^2 g_2^2 + 3s_2 g_2^3 + 8g_1^3 s_3 g_3 \\
&\quad + 12g_1 s_2 g_2 s_3 g_3 + 2g_3^2)/3 \qquad (15)
\end{aligned}$$

etc.

The $g_{h,\mathrm{cal}}$, resulting from experimental g_h of lower order, can be compared with the corresponding experimental values $g_{h,\mathrm{obs}}$:

$$d_n := \left[\sum_{i=1}^{n} (g_{m+i,\mathrm{cal}} - g_{m+i,\mathrm{obs}})^2\right]^{1/2}. \qquad (16)$$

For any $g_{m+n,\mathrm{cal}}$ derived from 'exact' g_h (*i.e.* without errors) and for error-free $g_{m+n,\mathrm{obs}}$, d_n must again vanish. Fig. 3 shows Σ_1, d_1 and d_3 for an example with $m = 5$. (For reasons not discussed here, Σ_1 and d_1 are equal not only for the 'true' but also for all 16 sign variations in this special case.)

Using (12) through (16) implies that only 2^{m-1} sign variations need to be tested, independent of how many g_h with $h > m$ are considered. Thus, higher spatial resolution can be expected without exponential increase in computer time.

Finally, we wish to stress that one and only one sign variation is found to be the correct one if two conditions are fulfilled: all g_h must be free from error and (extremely rare) homometry is absent. (Note, however, that homometries that do not exist in the three-dimensional structure may appear in one- or two-dimensional projections.) Should two or more 'homometric sets' (Buerger, 1959) exist, one finds two or more sign variations with $d_1 = 0$. For correct g_h, a uniquely determined set of signs s_h thus produces an unambiguous solution for all x_j. (Difficulties introduced by experimental uncertainties are discussed in §3.)

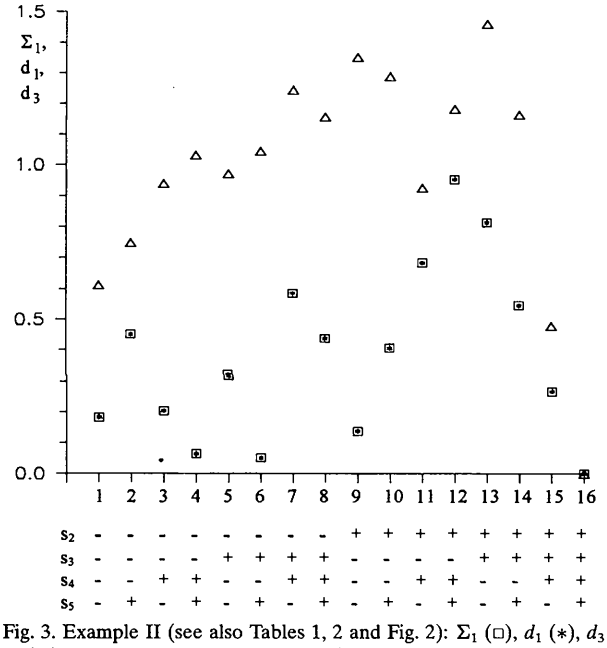

Fig. 3. Example II (see also Tables 1, 2 and Fig. 2): Σ_1 (□), d_1 (*), d_3 (Δ) for all variations of s_2, ..., s_5 (g_h without errors).

2.5. *Accidentally extinct partial structure amplitudes*

Unobserved $|F_a(\mathbf{h})|$ and the corresponding $g_{\mathbf{h}}$ bear important information and facilitate the algebraic solution. This was one of the key arguments in Ott's (1928) paper. On the other hand, they play no role in Fourier summation, structure-factor inequalities and most direct methods. Let us assume a g_h exactly zero. Then its sign need not be determined and equations (14) are evaluated more easily. Take for example equations (15) (case $m = 3$) and assume $g_1 = 0$. Then, setting $s_3 = +1$, one finds

$$\begin{aligned}
s_4 g_{4,\mathrm{cal}} &= g_2^2 + 2s_2 g_2 = g_2(g_2 + 2s_2) \\
s_5 g_{5,\mathrm{cal}} &= \tfrac{5}{3} s_2 g_2 g_3 \qquad (15a) \\
s_6 g_{6,\mathrm{cal}} &= -3 + 3g_2^2 + s_2 g_2^3 + \tfrac{2}{3} g_3^2,
\end{aligned}$$

from which follows: $s_5 = s_2$; $s_h g_h = f(s_2 g_2, g_3)$ for all $h > 5$; g_5 can be calculated from g_2 and g_3 without knowing their signs; $g_4 = g_2^2 \pm g_2$.

For $m = 3$ and the special case $g_1 = g_2 = 0$, one can again define $s_3 = +1$ and deduce

$$g_h = \begin{cases} 0 & \text{for } h \neq 3n \\ f(g_3) & \text{for } h = 3n \\ & (e.g.\ s_6 g_6 = -3 + \tfrac{2}{3} g_3^2), \end{cases}$$

which reduces the problem to the much simpler case of $m = 1$ by introducing $h' = 3h$ and determining $3x$ instead of x.

Thus, we conclude that each accidental $g_h = 0$ imposes constraints on the solution and reduces the number of phase variations by at least a factor of two. (This does not apply to systematic space-group extinctions.)

2.6. *Special positions*

Assume an inversion centre in $P\bar{1}$ to be occupied. Suppose its coordinate is $x_m = \frac{1}{2}$ (thus labelling this atom as the last one.) Then, equation (1*a*) reads

$$(s_h g_h)_{sp1} = \begin{cases} \sum_{j=1}^{m-1} \cos(2\pi h x_j) - \frac{1}{2} & \text{for } h \text{ odd} \\ \sum_{j=1}^{m-1} \cos(2\pi h x_j) + \frac{1}{2} & \text{for } h \text{ even.} \end{cases} \qquad (17)$$

The number of unknowns is reduced by 1. (If desired, a change of x_m to 0 includes a change of s_1.)

In the case when both special positions are occupied, *i.e.* $x_m = 0$ and $x_{m-1} = \frac{1}{2}$, this must be detected first and can then be handled with

$$(s_h g_h)_{sp2} = \begin{cases} \sum_{j=1}^{m-2} \cos(2\pi h x_j) & \text{for } h \text{ odd} \\ \sum_{j=1}^{m-2} \cos(2\pi h x_j) + 1 & \text{for } h \text{ even.} \end{cases} \quad (18)$$

For some additional aspects, see §3.3. Other possibilities, such as occupation of 3 to 8 symmetry centres in the three-dimensional structure, fail to pose new or severe problems and need not be discussed further.

2.7. *Conclusions*

In general, we may state that the recursive algebraic technique offers a straightforward unique solution for the structure-factor signs and the coordinates of a one-dimensional centrosymmetric crystal structure (or of any centrosymmetric projection of a three-dimensional structure onto one lattice direction) if the geometrical parts of monoatomic (*i.e.* partial) structure factors are exactly known, and if their number, starting from $h = 1$, exceeds the number of independent atoms. In the next section, we shall discuss how this statement becomes less rigorous for g_h affected by experimental uncertainties.

3. Data with experimental uncertainties

3.1. *General aspects, resolution in direct space*

So far, the method has been applied to 'exact' g_h quantities. The results are mathematically exact and they provide infinite resolution, in contrast to a Fourier summation over a limited set of reflections. In the following, we set out to demonstrate that data with experimental uncertainties may still lead to a solution superior to that from a Fourier series.

The technique described requires partial structure amplitudes $|F_a|$ or $|F_a^\circ|$ on an absolute scale and a known displacement factor B_a. Both are obtained, at least approximately, from Wilson's statistics, if a more or less complete data set is available. For a one-dimensional data set (or five of them), this is not feasible. B_a may, however, be fairly well estimated from experience. Small deviations of B_a (or B_{overall}) are not severe for reasons best seen in expressions for Q_i, derived from (6) and (9) (here for $m = 3$), which also demonstrates the influence of errors in g_h:

$$Q_1 = g_1$$
$$Q_2 = \tfrac{1}{2}g_1^2 - \tfrac{1}{4}s_2 g_2 - \tfrac{3}{4}$$
$$Q_3 = \tfrac{1}{6}g_1^3 - \tfrac{1}{2}g_1 - \tfrac{1}{4}g_1 s_2 g_2 + \tfrac{1}{12}s_3 g_3.$$

Table 3. *Results of Monte Carlo calculations for examples I and II*

	Theoretical	'Experimental' $\langle x_j \rangle \pm \sigma(x_j)$ with $\sigma(g_h) = 0.05 g_h$		$\sigma(g_h) = 0.1 g_h$	
j	x_j	$\langle x_j \rangle$	$\sigma(x_j)$	$\langle x_j \rangle$	$\sigma(x_j)$
Example I					
1	0.075	0.075	0.003	0.075	0.005
2	0.155	0.156	0.007	0.157	0.014
3	0.235	0.234	0.008	0.233	0.018
4	0.315	0.311	0.011	0.307	0.016
5	0.325	0.329	0.011	0.333	0.015
Example II					
1	0.020	0.0200	0.0011	0.0199	0.0022
2	0.130	0.1300	0.0009	0.1300	0.0018
3	0.240	0.2400	0.0009	0.2400	0.0019
4	0.340	0.3400	0.0009	0.3400	0.0018
5	0.450	0.4500	0.0007	0.4500	0.0014

g_1 enters the coefficients Q_i of the polynomial $R(c)$ [equation (7)] with powers between 1 and m, whereas higher harmonics are associated with lower powers. It is thus obvious that relative errors of the displacement factor (with exponent proportional to $-B_h^2$) do not 'pile up' as severely as corresponding uncertainties in g_h (for small h). Consequently, low-order g_h should be obtained with special care (*via* the $|F_a|$ separation from measured $|F|^2$ at three or more wavelengths).

The work of Knof (1989) had already resulted in the conjecture that his doubly recursive solution technique offers a good spatial resolution. However, owing to the recursion, an explicit expression for error propagation, *i.e.* from $\sigma(g_h)$ to $\sigma(x_j)$, cannot be derived in a straightforward way. Therefore, Monte Carlo calculations on theoretical examples I and II were carried out assigning different degrees of uncertainty to the simulated g_h. We assumed Gaussian distribution of individual relative errors with, *e.g.*, $\sigma(g_h) = 0.05 g_h$ (or $0.1 g_h$), respectively, for one-dimensional structures with five independent atoms. Table 3 gives results for these examples.

The $\sigma(x_j)$ obtained for example II are also indicated in Fig. 2. We may conclude that $\sigma(x_j)$ is at least partly determined by $\partial R/\partial x$ at $x = x_j$. Fig. 1 presents results for example I from theoretically 'exact' g_h (solid line) and two selected 'bad' individual data sets. While x_1, x_2 and x_3 are not severely affected, x_4 and x_5, being rather close, may even appear to be degenerate or as complex roots. (Then, our program finds the real part of the two complex roots, which can be split using personal discretion, because the number m of coordinates is known.) Degenerate (or nearly degenerate) solutions usually produce larger coordinate uncertainties. See, *e.g.*, example I (Tables 1 and 2) and Fig. 1 in Fischer & Pilz (1997).

Another aspect is offered for a simple case $m = 2$, which may also be considered in connection with the experimental example described in Fischer & Pilz

(1997): $R(x)$ permits direct calculation of the coordinates (without 'root-finding') from

$$R(x) = \cos^2(2\pi x) - Q_1\cos(2\pi x) + Q_2$$
$$= \cos^2(2\pi x) - g_1\cos(2\pi x) + \tfrac{1}{2}g_1^2 - \tfrac{1}{4}s_2g_2 - \tfrac{1}{2}, \quad (19)$$

yielding

$$x_{1,2} = (1/2\pi)\arccos[\tfrac{1}{2}g_1 \pm \tfrac{1}{2}(2 - g_1^2 + s_2g_2)^{1/2}].$$

Including two necessary conditions, namely

$$g_1^2 \le s_2g_2 + 2 \quad \text{and} \quad |\cos(2\pi x)| \le 1,$$

the four derivatives $\partial x_j/\partial g_h$ are small within the main parts of the regions permitted for g_h and x, respectively:

$$-0.1 \le \partial x_1/\partial g_1 \le 0.1, \quad -0.1 \le \partial x_1/\partial g_2 \le 0.05,$$
$$-0.15 \le \partial x_2/\partial g_1 \le -0.1, \quad 0.01 \le \partial x_2/\partial g_2 \le 0.06.$$

An assumed $\partial x/\partial g = 0.1$ causes a coordinate change of 0.02 owing to an error of 0.2 in g, *i.e.* 10% of the maximal possible $g_{max} = m = 2$. The region where $|\partial x/\partial g| > 1$ is only ~0.005 wide in g and ~0.008 in x. Consequently, even small errors in g cause either a 'forbidden' (and thus impossible) region or lead to a small $|\partial x/\partial g|$, which results in a high spatial resolution. Fig. 4 shows $|\partial x_1/\partial g_1|$ as an example. See also Pilz & Fischer (1996*b*).

In Fig. 5, standard uncertainties of d_1 and d_3, respectively, are also shown as obtained from Monte Carlo calculations similar to those mentioned above. They are quite instructive and helpful in deciding whether a given sign variation is the only possible one or not (see also §3.2).

Let us try to compare the coordinates obtained from the recursive algebra with those from a Fourier summation (based on the same number of harmonics): in the latter, each coefficient enters only once and independently of the others. The maxima are built up by linear combinations of those harmonics and all 'zero' moduli are omitted. In contrast, imaging the locations of the structure by the roots of $R(c)$ or $R(x)$, respectively, is achieved by sums of powers of all the coefficients including those with zero value (or nearly so). They also enter R repeatedly and with varying exponents (*i.e.* with different weights).

How robust the algebraic method will behave with respect to experimental uncertainties can best be investigated by actual experiments. So far, we have performed only one study on the partial structures of Sb and Se in Cu_3SbSe_3 (Fischer & Pilz, 1997). For determining the partial structures of Se and Sb, we used 22 and 26 $g_{h,obs}$, respectively, from six central reciprocal-lattice rows each. Compared to $g_{h,cal}$ calculated from the known structure (refined on 1540 reflections, $R = 0.042$), the agreements in terms of a conventional R factor were 0.38 and 0.37 for the respective g_h sets (Pilz *et al.*, 1994, 1995; Pilz & Fischer, 1996*a*). From the $g_{h,obs}$, we obtained coordinates that differed by 0.07 Å (averaged over all seven independent positional Sb and Se parameters and relative to the parameters from the refinement mentioned above). This structure was certainly a rather small one, however with quite a few elements of pseudosymmetry. *E.g.* one of the systematically produced non-Harker Se–Se vectors in a Harker plane. We consider this example encouraging.

3.2. *Higher reflection orders*

Experimental uncertainties of the g_h (and consequently of d_1 for all sign variations) may preclude a unique solution from the first $m + 1$ reflection orders.

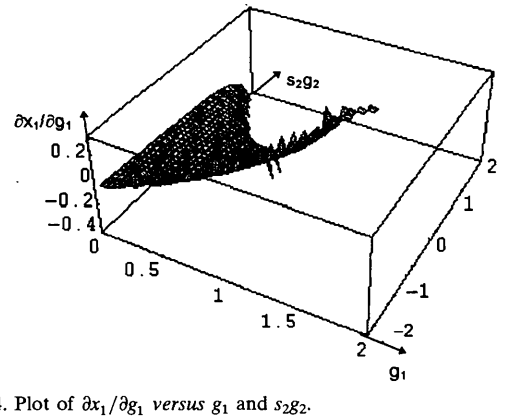

Fig. 4. Plot of $\partial x_1/\partial g_1$ *versus* g_1 and s_2g_2.

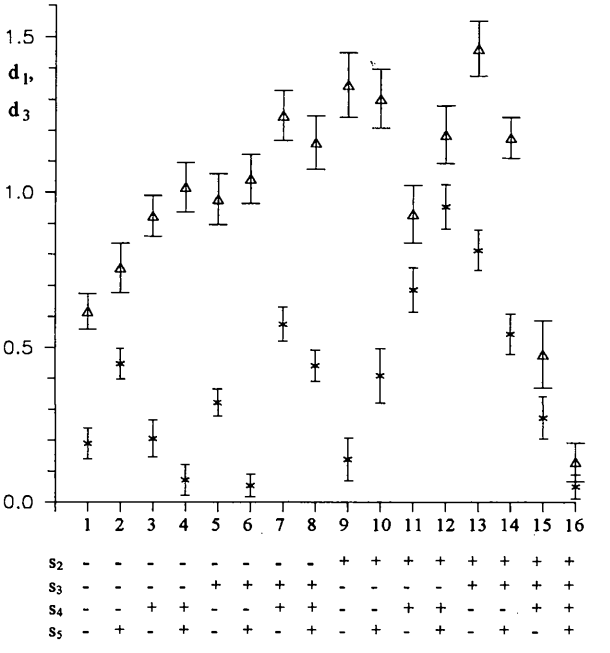

Fig. 5. Example II: mean values and standard uncertainties of d_1 (*) and d_3 (Δ) [g_h with assumed $\sigma(g_h) = 0.05g_h$, see §3.1].

This is demonstrated in Fig. 5: three or perhaps four possible solutions (sign variations nos. 4, 6, 16 and perhaps 9) cannot be distinguished by d_1. (Compare with Fig. 3, drawn to the same scale.) If, however, three higher harmonics are added to the sign-determination process, the resulting d_3 permit identification of variation No. 16 as the only possible one. Thus, a unique result could be obtained by using d_3 instead of d_1. (Higher standard uncertainties for d_3, compared with d_1, are natural because adding more reflections along with their errors increases the noise, while the dimension of the problem remains unaltered. Nevertheless, owing to increased resolution power, the use of higher harmonics is always helpful.)

3.3. *Special positions, pseudosymmetry*

If, in the beginning, a special position is not known to be occupied, the polynomial will tell it. Suppose, as a simple example, a structure with two atoms: $x_2 = \frac{1}{2}$ and x_1. Then, the 'standard' program finds one atom with 'double' weight (double root) at x_1 and the other with 'single' weight at or close to $x = \frac{1}{2}$, though both with rather high uncertainties. Fig. 6(*a*) presents the first polynomial calculated from g_h's with relative σ of 10%. Having noticed the occupation of a special position, one can use the program modified according to (17) and obtains Fig. 6(*b*) [which also shows substantially reduced $\sigma(x)$].

Let us finally consider a few cases of pseudosymmetry and how the algebraic algorithm can handle it. Fig. 2 (example II in Tables 2 and 3) shows a pseudo-subcell of 1/9. Its Patterson function $P(u)$ would exhibit multiple peaks at $u \simeq 1/9, 2/9, \ldots$ caused by a strong $g_9 = 3.3_2$ as 'fundamental' reflection (g with smaller h tend to be weak 'superstructure' reflections: $\langle g_h \rangle = 0.58$ for $h = 1, \ldots, 8$). These g_h may cause problems in determining their signs by direct methods. In our example, this difficulty was circumvented by the present technique after having fixed the signs using reflection orders up to $h = 8$. The standard deviations $\sigma(x)$ of the coordinates x_j resulting from $\sigma(g_h)$ are usually small (see Table 3).

Another example is a structure similar to that of Fig. 6 but with x_2 very close to though not exactly at $\frac{1}{2}$. Owing to the asymmetry of the error distribution (showing a one-sided limit), the deviation $\frac{1}{2} - x_2$ appears exaggerated. This may assist in finding a qualitatively correct model structure.

Suppose a structure possesses almost inversion symmetry, which means that the phases, at least of the low-order reflections, do not differ much from zero or π. This case (with g_h having small imaginary parts) can still be handled by the program. Owing to the asymmetry of the coordinate shifts from special positions (plus their uncertainties, see above), a qualitatively correct model for the structure can be obtained, thus presenting the shift(s) of atom(s) away from the inversion centre(s). (Of course, even with 'theoretical' g_h, $D = 0$ cannot be obtained in this case. However, atoms being located at *e.g.* $x = 0.20$ and 0.81, *i.e.* not close to a 'special' position, cannot be separated by the present program because they almost coincide in the asymmetric unit.)

Quite a few more pseudosymmetric cases could be discussed here. If a successful solution is obtained by the recursive algebra, it can be ascribed to its good resolution power.

4. Conclusions

A one-dimensional centrosymmetric projection of a monoatomic structure can be solved using a rather limited number of reflections from the corresponding

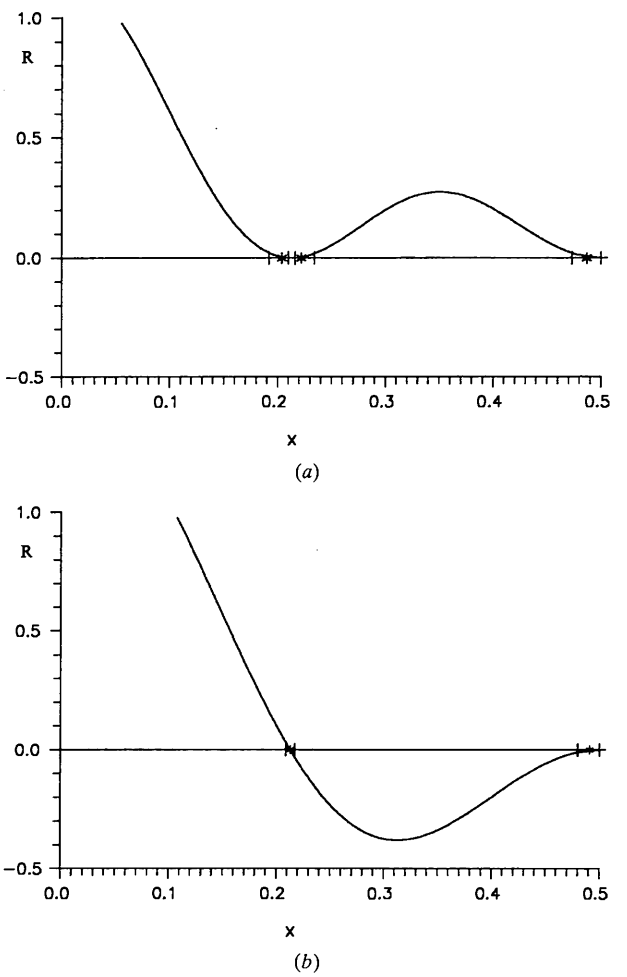

Fig. 6. (*a*) Polynomial for test structure with $x_{1a,b} = 0.213$, $x_2 = \frac{1}{2}$ [* indicate mean values and the error bars indicate standard uncertainties of the coordinates caused by assuming $\sigma(g_h) = 0.1 g_h$]. (*b*) Polynomial for test structure with $x_1 = 0.213$, $x_2 = \frac{1}{2}$, calculated with the modified program according to equation (17) [* indicate the mean values and the error bars indicate the standard uncertainties caused by assuming $\sigma(g_h) = 0.1 g_h$].

reciprocal-lattice row. The recursive algebraic method does not require statistics or approximations (besides Monte Carlo calculations for obtaining individual standard uncertainties for the coordinates and for D_n or d_n). Its prerequisites are: a known number of point atoms with unit weight at rest. (Consequently, disordered distributions with different site occupations infer additional complications or must be excluded, at least from a principle point of view.) The physical approximations are: known scale factor, approximately known anisotropic displacement factor (common to all atoms under consideration).

The technique of determinants provides a mathematically exact criterion for finding the correct reflection signs, independent of accidental extinctions (which, however, permit a faster and safer solution). If homometries are excluded, the sign determination gives a unique answer (quality and number of data are assumed sufficient). Consequently, an unambiguous coordinate determination is possible. If insufficient quality of data precludes the determination of a single set of signs, a unique solution can be achieved by introducing higher reflection orders and thus providing higher resolution in direct space (Pilz, 1996, p. 117). If no unambiguous solution can be obtained at all, at least all possible solutions are found. Their number may be reduced by employing other arguments.

For a structure having m independent atoms, the first $m+1$ reflection orders are needed for obtaining m signs of structure factors. Generally, m grows with cell volume v, the number of accessible reflection orders, however, with $v^{1/3}$ only. Therefore, the algebraic method will reach a limit for larger m. Also, deviations of the determinants from their theoretical value increase with m, in particular due to higher powers for the lower harmonic data.

The recursive algebraic method finds the point coordinates x_j as roots of a polynomial. Compared with the number of data needed, the resolution (and standard uncertainties of coordinates) appears superior to that of Fourier summations. Without repeating the arguments mentioned in §3.1, this may have two reasons: The algebra searches for point-atom locations x_j represented as roots of R. Their standard uncertainties $\sigma(x_j)$ may be estimated (zero-order approximation only) from $|\partial R/\partial x|$ at x_j. In a Fourier map, one looks for maxima of a density distribution $\rho(\mathbf{r})$ (or its approximation). Their positional uncertainties depend on the method of evaluation. One possibility is to derive them from $|\partial^2\rho/\partial r^2|$ at the position of the maximum. In this case, the additional second derivative may cause larger errors (contrary to smoothing by integration). The recursive algorithm does not 'know' series-termination effects [but transforms them into $\sigma(x)$]. Double roots are easily identified (perhaps best by inspecting a plot of the polynomial) and all atoms are found at once.

The weakest point of the method arises from an experimental problem, *i.e.* the determination of the scale factor. If not obtained otherwise, we have, at present, no solution to this problem. (The obvious constraint that no g_h may exceed m plus perhaps some estimated error appears to be insufficient because it is a one-sided limit.)

After having successfully applied the recursive algebra to a centrosymmetric three-dimensional structure and being able to show that the solution was unique [at least for the main part (Fischer & Pilz, 1997)], we are now trying to develop the theory towards also solving noncentrosymmetric structures.

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