

and  $b_{33}$  of  $-1.54$ ,  $0.62$  and  $0.92 \text{ \AA}^2$  respectively (final values were  $-1.42$ ,  $0.39$  and  $1.03 \text{ \AA}^2$ ). Treatment of anisotropy in this way made difference maps less noisy and this facilitated the further interpretation of the structure.

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## General Density Function Corresponding to X-ray Diffraction with Anomalous Scattering Included

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#### Abstract

The generalized density function that is the Fourier transform of X-ray diffraction as observed when anomalous scattering occurs is described. This is a complex function in contrast to the purely real electron-density function that pertains when only the 'normal' Thomson scattering component is present. The imaginary component of this general density function produces an image of the anomalous scattering centers and is more accurate than the Kraut approximation commonly used in macromolecular crystallography to produce such images.

#### Introduction

The Fourier transform of the electron-density distribution in an atom yields the normal atomic scattering factor for X-rays. Conversely, a Fourier synthesis of the structure factors from a crystal composed of such normal scatterers gives back the true electron-density

function,  $\rho(\mathbf{x})$ . This 'normal' situation pertains if the scattering from each point is directly proportional to that from a free electron. In reality, the scattering process can involve resonance with the natural frequencies of bound electrons and this leads to additional phase-shifted contributions - the anomalous scattering (James, 1948). A Fourier synthesis of the structure factors from a crystal that includes anomalous scatterers does not produce the true electron-density distribution, which is real and non-negative, but by analogy we can define a general density function,  $\rho^*(\mathbf{x})$ , as the Fourier transform of the actual X-ray diffraction rather than just the normal scattering component. This function is complex and the imaginary component depends only on the anomalous scattering centers. The Bijvoet-difference Fourier synthesis proposed by Kraut (1968), a function which has proved useful in macromolecular crystallography, is an approximation of the true imaginary component (Chacko & Srinivasan, 1970). In this paper we examine the properties of the general density function, test approximations with simulated diffracted data, and discuss applications with experimental data.

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**Theoretical analysis**

The atomic scattering factor can be written as

$$f = f^0 + f' + if'', \quad (1)$$

where  $f^0$  is the normal scattering factor and  $f'$  and  $f''$  are respectively the real and imaginary components of the anomalous scattering. If we designate by  $F^0(\mathbf{h}) = |F^0(\mathbf{h})| \exp[i\varphi^0(\mathbf{h})]$  the structure factor for reflection  $\mathbf{h}$  that corresponds to the normal scattering contributions, then the true electron-density function is

$$\begin{aligned} \rho(\mathbf{x}) &= (1/V) \sum_{-\infty}^{\infty} F^0(\mathbf{h}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{x}) \\ &= (2/V) \sum_0^{\infty} |F^0(\mathbf{h})| \cos[\varphi^0(\mathbf{h}) - 2\pi \mathbf{h} \cdot \mathbf{x}], \quad (2) \end{aligned}$$

where  $\mathbf{x}$  is a fractional position in the unit cell of volume  $V$ .† The analogous general density function is then

$$\rho^*(\mathbf{x}) = (1/V) \sum_{-\infty}^{\infty} F(\mathbf{h}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{x}), \quad (3)$$

where  $F(\mathbf{h})$  is the total structure factor.  $F(\mathbf{h})$  comprises contributions of  $F'(\mathbf{h})$  from the real components of scattering ( $f^0 + f'$ ) and of  $F''(\mathbf{h})$  from the imaginary components ( $if''$ ). Thus

$$F(\mathbf{h}) = F'(\mathbf{h}) + F''(\mathbf{h}). \quad (4)$$

Furthermore,  $F'(-\mathbf{h}) = |F'(\mathbf{h})| \exp[-i\varphi'(\mathbf{h})]$  and  $F''(-\mathbf{h}) = |F''(\mathbf{h})| \exp\{-i[\varphi''(\mathbf{h}) + \pi]\}$ . [Note that  $|F''|$  and  $\varphi''$  compare respectively to  $\delta$  and  $\psi + \omega$  in an earlier nomenclature (Hendrickson, 1979).] After replacement of  $F(\mathbf{h})$  by (4), (3) reduces to

$$\begin{aligned} \rho^*(\mathbf{x}) &= (2/V) \sum_0^{\infty} |F'(\mathbf{h})| \cos[\varphi'(\mathbf{h}) - 2\pi \mathbf{h} \cdot \mathbf{x}] \\ &+ (2i/V) \sum_0^{\infty} |F''(\mathbf{h})| \sin[\varphi''(\mathbf{h}) - 2\pi \mathbf{h} \cdot \mathbf{x}]. \quad (5) \end{aligned}$$

This result bears superficial resemblance to a density equation stated by Okaya & Pepinsky (1956), but the coefficients in their formulation are not correct.

It is clear from (5) that  $\text{Im}(\rho^*)$  obtains exclusively from the anomalous scattering centers, and that in the absence of anomalous scattering  $F = F' = F^0$  and (5) reduces to (2). However, this formulation is not particularly useful as  $F'$  and  $F''$  are not readily evaluated separately from experimental measurements.

The general density function can also be expressed in terms of the actual structure factors,  $F(\mathbf{h})$ . Following Kraut (1968), we define

$$\bar{\varphi} \equiv \frac{1}{2}[\varphi(\mathbf{h}) - \varphi(-\mathbf{h})] \quad (6)$$

† The symbol  $\sum_0^{\infty}$  here signifies a summation of  $\mathbf{h}$  over zero and positive values of the indices  $\mathbf{h}$ ,  $\mathbf{k}$  and  $\mathbf{l}$  with half weight assigned to the  $F(000)$  term.

and in addition introduce

$$\Delta\varphi \equiv \frac{1}{2}[\varphi(\mathbf{h}) + \varphi(-\mathbf{h})]. \quad (7)$$

Thus,  $\varphi(\mathbf{h}) = \bar{\varphi} + \Delta\varphi$  and  $\varphi(-\mathbf{h}) = -\bar{\varphi} + \Delta\varphi$ . Upon substitution into (3),

$$\begin{aligned} \rho^*(\mathbf{x}) &= \frac{1}{V} \sum_0^{\infty} [|F(\mathbf{h})| + |F(-\mathbf{h})|] \cos \Delta\varphi \cos(\bar{\varphi} - 2\pi \mathbf{h} \cdot \mathbf{x}) \\ &- \frac{1}{V} \sum_0^{\infty} [|F(\mathbf{h})| - |F(-\mathbf{h})|] \sin \Delta\varphi \sin(\bar{\varphi} - 2\pi \mathbf{h} \cdot \mathbf{x}) \\ &+ \frac{i}{V} \sum_0^{\infty} [|F(\mathbf{h})| - |F(-\mathbf{h})|] \cos \Delta\varphi \sin(\bar{\varphi} - 2\pi \mathbf{h} \cdot \mathbf{x}) \\ &+ \frac{i}{V} \sum_0^{\infty} [|F(\mathbf{h})| + |F(-\mathbf{h})|] \sin \Delta\varphi \cos(\bar{\varphi} - 2\pi \mathbf{h} \cdot \mathbf{x}). \quad (8) \end{aligned}$$

At the level of approximation that  $\Delta\varphi \approx 0$ , (8) yields the Bijvoet-difference Fourier synthesis (Kraut, 1968)

$$\begin{aligned} \text{Im}[\rho^*(\mathbf{x})] &\approx (1/V) \sum_0^{\infty} [|F(\mathbf{h})| - |F(-\mathbf{h})|] \\ &\times \sin(\varphi - 2\pi \mathbf{h} \cdot \mathbf{x}). \quad (9) \end{aligned}$$

This computationally useful formulation of the general density function, equation (8), can also be derived directly from the formulation which is based on atomic origins of the scattering, equation (5). From definitions pertaining to the components of (4) it follows that  $2F'(\mathbf{h}) = F(\mathbf{h}) + F^*(-\mathbf{h})$  and that  $2F''(\mathbf{h}) = F(\mathbf{h}) - F^*(-\mathbf{h})$ . Substitution of these values into the generating function for (5) gives a formulation that corresponds to that of Chacko & Srinivasan (1970). (This function also follows from basic attributes of complex functions.) Expansion with reference to phase definitions (6) and (7) then yields (8).

**Tests with simulated data**

The Bijvoet-difference Fourier synthesis, equation (9), is frequently used to locate anomalous scattering centers in macromolecules and to choose the correct enantiomorph for a structure. Since this function is shown here to be an approximation, it is of interest to check its validity as a representation of the structure of anomalous scatterers. Chacko & Srinivasan (1970) have reported such calculations for a small molecule structure. Here we report quantitative comparisons for a typical macromolecular problem. We have generated simulated data from an atomic model of myohemerythrin to make these tests. Myohemerythrin is a dimeric-iron protein of 118 amino-acid residues that crystallizes with one molecule in the asymmetric unit of space group  $P2_12_12_1$  (Hendrickson, Klippenstein & Ward, 1975). Model XVIII.3,

Table 1. *Density function comparisons from simulated anomalous scattering in diffraction data from myohemerythrin*

Atom	B	Density at atomic positions			Kraut (1968)
		$\Delta F \cos \Delta\varphi$	$\bar{F} \sin \Delta\varphi$	$\text{Im}(\rho^*)$	
Fe 1	8.2	153.4	212.8	366.2	150.7
Fe 2	7.7	167.7	231.6	399.3	165.8
Cys35S $\gamma$	10.6	21.8	32.4	54.2	21.6
Met61S $\delta$	21.7	15.6	27.6	43.2	16.1
Met62S $\delta$	13.4	18.8	38.9	57.7	18.0
Met76S $\delta$	23.4	14.7	27.5	42.3	14.0
Cys99S $\gamma$	13.6	19.8	33.8	53.6	19.0
R.m.s. density value		2.8	2.9	1.7	2.8

which had been refined to  $R=0.166$  against the experimental observations to spacings of 1.3 Å along **b** and 1.7 Å along **a** and **c**, was used in these tests. It has 1164 atoms including 162 waters and two azide ions in the solvent and five residues modeled as disordered. Overall anisotropic thermal factor increments were used in the refinements (Sheriff & Hendrickson, 1987a) and individual isotropic thermal factors were refined. These same parameters were carried over to the simulation. Anomalous scattering factors of  $f''=3.204$ , 0.557 and 0.0 were used for Fe, S and all others, respectively. The calculation was made for the 7175 structure factors at 2 Å resolution for which the observed data have  $|F| > 4\sigma_F$ .

Four different Fourier syntheses were compared: (1)  $\text{Im}(\rho^*)$  from equation (8); (2) the  $\Delta F \cos(\Delta\varphi)$  component of  $\text{Im}(\rho^*)$ ; (3) the  $2\bar{F} \sin(\Delta\varphi)$  component of  $\text{Im}(\rho^*)$ ; and (4) the Kraut function, equation (9). Results are tabulated in Table 1. The Bijvoet-difference synthesis of Kraut is a very good approximation of the  $\Delta F \cos(\Delta\varphi)$  component, as can be expected from the small difference angles of  $\langle\Delta\varphi\rangle=6.4^\circ$  in this case. However, the neglected  $2\bar{F} \sin(\Delta\varphi)$  component actually contributes even more to the true imaginary density function than does the  $\Delta F \cos(\Delta\varphi)$  component. Thus, the Kraut function accounts for less than half of the total peak density in the  $\text{Im}(\rho^*)$  function. Relative to the r.m.s. level, the maxima are down by more than a factor of four. But despite variations in signal-to-noise ratios, the top seven peaks in all four syntheses correspond to atomic positions of anomalous scatterers. The positions of these peaks are within 0.1 Å of the true sites in the  $\text{Im}(\rho^*)$  synthesis and within 0.3 Å in the Kraut function.

It is to be expected that the validity of the approximation will depend on the strength of anomalous scattering. To examine this question, we have simulated hypothetical structures in which the iron atoms are replaced by sulfur or samarium. The results are shown in Table 2. As expected, Bijvoet differences (both magnitude and phase) increase on average as S, Fe and Sm respectively are used at the iron sites

Table 2. *Effects of main-site replacement in myohemerythrin simulations of anomalous diffraction*

	Fe as S	Fe as Fe	Fe as Sm
$f''(\text{Fe site})$ (e)	0.577	3.204	12.320
R.m.s. ( $\Delta\varphi$ ) ( $^\circ$ )	1.9	6.4	23.1
R.m.s. ( $\Delta F$ )/r.m.s. ( $\bar{F}$ )	0.012	0.041	0.131
Average distance from S site to nearest peak (Å)			
True $\text{Im}(\rho^*)$	0.06	0.07	0.14
Kraut approx.	0.08	0.14	1.37
Average density at Fe sites			
True $\text{Im}(\rho^*)$	66.4	382.7	1472.4
Kraut approx.	27.8	158.3	481.2
Average density at S sites			
True $\text{Im}(\rho^*)$	50.9	50.2	47.8
Kraut approx.	21.4	17.7	-5.0
R.m.s. density			
True $\text{Im}(\rho^*)$	0.5	1.7	6.2
Kraut approx.	0.8	2.8	10.2

in these myohemerythrin simulations. Also, as it must, the true imaginary component of the general density function faithfully reproduces the anomalous scatterer structure in all cases. Discrepancies that do exist (e.g. imperfect location and variation in average density at sulfur sites) arise from series termination and computational truncation effects. However, the Kraut approximation becomes less valid as the strength of anomalous scattering increases. When Sm replaces Fe the peaks nearest to true sulfur positions are off by 1.4 Å on average and these peaks rank

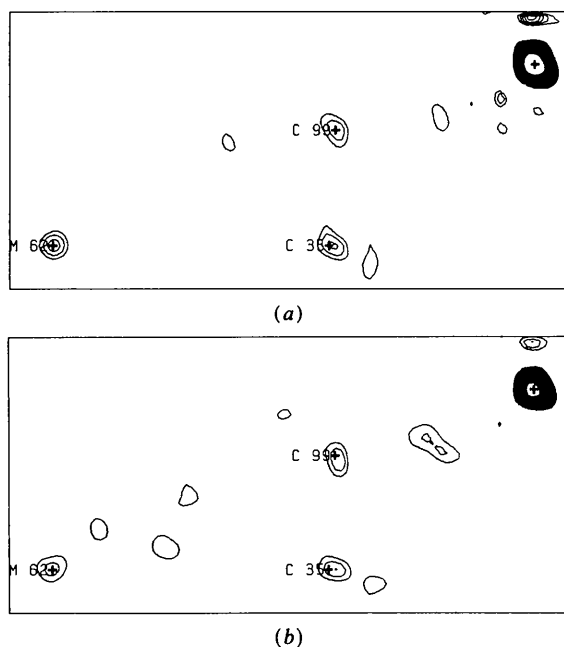


Fig. 1. Section through a plane defined by Met62S $\delta$ , Cys35S $\gamma$  and Fe 1 (unlabeled cross) from maps using phases from S as C model. Also shown is site Cys99S $\gamma$  which lies 0.45 Å above plane. Maps are contoured at intervals of  $1\sigma$  starting at  $2\sigma$ , where  $\sigma$  is the r.m.s. density of the map upon exclusion of the iron sites. (a)  $\text{Im}(\rho^*)$  Fourier map, r.m.s. density is  $0.0352 \text{ e} \text{ \AA}^{-3}$ ; (b) Kraut Bijvoet-difference Fourier map, r.m.s. density is  $0.0354 \text{ e} \text{ \AA}^{-3}$ .

Table 3. *Density functions based on experimental magnitudes and on phases from the refined atomic model of myohemerythrin*

Atom	Density at peak nearest atomic site*			
	Kraut (1968)		Im ( $\rho^*$ )	
	S as S	S as C†	S as S	S as C†
Fe 1	36.1 (2)	35.5 (2)	91.9 (2)	92.2 (2)
Fe 2	37.6 (1)	37.4 (1)	96.4 (1)	97.5 (1)
Cys35S $\gamma$	4.6 (3)	5.0 (3)	12.6 (4)	5.4 (3)
Met61S $\delta$	3.6 (14)	3.4 (23)	9.9 (6)	4.7 (5)
Met62S $\delta$	3.3 (28)	3.7 (12)	12.8 (3)	5.2 (4)
Met76S $\delta$	2.6 (145)	2.9 (86)	8.6 (7)	2.9 (83)
Cys99S $\gamma$	4.1 (6)	4.7 (4)	11.9 (5)	4.6 (6)
Solvent	3.9 (7)		3.2 (25)	
Solvent	2.3 (303)		3.0 (38)	
Average solvent‡	2.0 (514)		2.1 (393)	

\* Peak density values are given in units of standard deviations as defined by the r.m.s. density value of the map, which upon excluding the iron sites was approximately  $0.035 \text{ e } \text{\AA}^{-3}$  for all four maps. The rank ordering of peaks, excluding ripples around the iron atoms, is cited in parentheses.

† In S as C calculations the structure factors were calculated from a model that included sulfur atoms in the cysteine and methionine side chains, but not in any solvent positions. In S as C calculations carbon scattering factors were used for all sulfur atomic sites.

‡ Density values for 'average solvent' sites are averages, over all solvent sites, of the densities at the highest peaks within  $1 \text{ \AA}$  of these sites. Rank is the average rank for these highest peaks.

from 76 to 572 in the asymmetric unit. Moreover, the density at true positions is actually negative in four of the five cases.

### Applications with experimental data

Practical use of the imaginary Fourier synthesis of course requires that phases as well as magnitudes be known for the Friedel mates. These data, particularly the  $\Delta\varphi(\mathbf{h})$  values, may not be readily available in some cases such as in conventional isomorphous replacement phasing. However, if anomalous scattering has been used in the phase determination, then the necessary values can be extracted. Moreover, in the event that a refined structure is already available, then both  $\varphi(\mathbf{h})$  and  $\varphi(-\mathbf{h})$  are readily evaluated and Im ( $\rho^*$ ) can be computed. This function can be useful for identifying the sites of relatively minor anomalous scattering centres.

Results of an application to the refined myohemerythrin structure are reported in Table 3. The observed diffraction magnitudes were used together with phases calculated from refined model XVIII.3 ( $R=0.166$ ) in these syntheses at  $2.0 \text{ \AA}$  resolution (Sheriff & Hendrickson, 1987b). The densities from Im ( $\rho^*$ ), (8), and from the Kraut approximation (9) are compared with both sulfur and carbon scattering factors used at the sulfur sites in the protein model. In all cases the dominant iron sites are strongly represented. However, the weaker sulfur sites are appreciably stronger on average in the Im ( $\rho^*$ ) maps than in the Kraut maps. Inclusion of

the  $2\bar{F} \sin \Delta\varphi$  terms does introduce a bias toward the anomalous scattering centers included in the phase calculations, but even when this bias is removed in the sulfur-as-carbon model the Im ( $\rho^*$ ) function is superior. Comparative sections are shown in Fig. 1. These maps were useful in confirming that the first cysteine is at position 35 rather than at 34 as indicated by the original chemical sequence and that two of the solvent sites were occupied by sulfate ions (Sheriff & Hendrickson, 1987b).

Although normal procedures for phase determination based on anomalous scatterers do not separately evaluate  $\varphi(\mathbf{h})$  and  $\varphi(-\mathbf{h})$  these can readily be extracted if the structure of the dominant anomalous scatterers is known. It follows from (4) that

$$\varphi(\mathbf{h}) = \tan^{-1} \left( \frac{|F'| \sin \varphi' + |F''| \sin \varphi''}{|F'| \cos \varphi' + |F''| \cos \varphi''} \right) \quad (10)$$

$$\varphi(-\mathbf{h}) = \tan^{-1} \left( \frac{-|F'| \sin \varphi' + |F''| \sin \varphi''}{|F'| \cos \varphi' - |F''| \cos \varphi''} \right). \quad (11)$$

In the case of resolved anomalous phasing or isomorphous replacement phasing for structures containing anomalous scatterers, one typically evaluates phases for the average of Friedel mates which give  $\varphi'$  to good approximation (Hendrickson, Smith & Sheriff, 1985) since also from (4)  $F(\mathbf{h}) + F^*(-\mathbf{h}) = 2|F'(\mathbf{h})| \exp[i\varphi'(\mathbf{h})]$ . From structure factor calculations based on refined anomalous scatterer positions,  $|F''|$  and  $\varphi''$  can be calculated. Then, since from (4)

$$|F'| = \frac{1}{2} (|F(\mathbf{h})|^2 + |F(-\mathbf{h})|^2 - 2|F''|)^{1/2}, \quad (12)$$

all parameters needed in (10) and (11) are known. Comparable evaluations can be made in the case of phasing based on multiple wavelength measurements.

In conclusion, the 'imaginary Fourier synthesis' can be a useful function for selectively producing images of anomalous scattering centers. It can be used to special advantage for finding the positions of minor anomalous centers when the sites of the more dominant anomalous scatterers are known and have been used to evaluate approximate phases. The positions of minor anomalous scatterers such as sulfur atoms can be useful landmarks in macromolecular chain tracing and in distinguishing bound solvent ions from water molecules.

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## A Real-Space Computer-Based Symmetry Algebra

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### Abstract

A computer-based symmetry algebra is described which permits the reconstruction of an infinite bond network from the asymmetric connectivity without an *a priori* knowledge of atomic coordinates. The algebra requires not only an algorithmic ordering of the Wyckoff groups but the designation of one site in each Wyckoff group as a special-position representative (SPR) site. The algebra is designed to be used for analysing the bonding network of compounds appearing in the Inorganic Crystal Structure Database.

### Introduction

With the advent of crystal structure databases, computers are now used for the systematic examination of the structures of large numbers of related compounds. The program *SINDBAD* (Altermatt & Brown, 1985) has been used to calculate the bond vectors in the asymmetric unit from the atomic coordinates obtained from the Inorganic Crystal Structure Database (Bergerhoff, Hundt, Sievers & Brown, 1983). A systematic application of *SINDBAD* to entries stored in this database has resulted in the creation of a file (BONDFILE) containing the asymmetric bond sets of several thousand compounds. To expand the asymmetric set of bonds into the full bonding network requires the application of the symmetry operations of the appropriate space group. This can be done by computer, provided that proper care is taken in treating the bonds formed by atoms on special positions. This paper describes an algebra for doing this which, *inter alia*, requires an algorithm for

ordering the special positions and their representative sites.

### Expansion of an asymmetric bond set

The BONDFILE contains the asymmetric set of bond vectors, each bond being identified by its two terminal atoms. Because of space limitations the atomic coordinates are not stored in the file. The asymmetric set of bond vectors is expanded into the full bond network by generating all the bonds around each of the terminal atoms of the network in turn. Each atom is identified by an index indicating which symmetry operator and which lattice vector is used to generate it from the given atom in the asymmetric unit. This index consists of five numbers, the first referring to an ordered list of atoms in the asymmetric unit, the second to an ordered list of symmetry operators, and the last three numbers to the lattice translation vector. The ordered list of symmetry operators could be a list of Seitz matrices which is stored explicitly in the BONDFILE, but we have found it more convenient to regenerate this list as required from the space-group symbol. Several programs are available to do this. The older ones interpret the Hermann–Mauguin symbol but recently new space-group symbols have been proposed (Hall, 1981; Shmueli, 1984) that are specifically designed to avoid the setting ambiguities inherent in the Hermann–Mauguin symbol. We have chosen to use the Hall (1981) symbol and the ordering of symmetry operators produced by the program *SGNAME* in *XTAL* (Stewart & Hall, 1983). This ordering is symbol dependent (it is even different for different symbols describing the same space-group setting), but since the Hall symbol that was used to generate the asymmetric set of bonds is the one stored in the BONDFILE, the program can always reconstruct the ordered list of symmetry operators appropriate to the problem.

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