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SHORT COMMUNICATIONS

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Determination of the positions of anomalous scatterers: probabilistic coefficients for a Patterson synthesis. By G. CASCARANO and C. GIACOVAZZO, *Istituto di Mineralogia e Petrografia, Università Palazzo Ateneo, 70121 Bari, Italy*

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Abstract

The conditional joint probability distribution of the phase $\varphi = \varphi_{\mathbf{h}} + \varphi_{-\mathbf{h}}$ given $|F^+|$, $|F^-|$ is used in order to suggest coefficients for a Patterson synthesis for the determination of the positions of anomalous scatterers. A theoretical comparison with Rossmann's approach [Rossmann, M. G. (1981). *Acta Cryst.* 14, 383–388] is made.

Definitions

N	number of atoms in the unit cell
$f = f' + if''$	general expression for the atomic scattering factor; f' and f'' are its real and imaginary parts
F^+ , F^-	structure factors of the reflexions \mathbf{h} and $-\mathbf{h}$, respectively
R^+ , φ^+ , R^- , φ^-	normalized structure factor and phase of the reflexion \mathbf{h} and $-\mathbf{h}$, respectively
$\Sigma = \sum_{j=1}^N (f_j'^2 + f_j''^2)$	average value of $ F_{\mathbf{h}} ^2$ at a given $ \mathbf{h} $
$c_1 = \sum_{j=1}^N (f_j'^2 - f_j''^2) / \Sigma$	
$c_2 = 2 \sum_{j=1}^N f_j' f_j'' / \Sigma$	
$c = [1 - (c_1^2 + c_2^2)]^2$	
$\Phi = \varphi^+ + \varphi^-$	
$F'' = \sum_{j=1}^N f_j'' \exp(2\pi i \mathbf{h} \cdot \mathbf{r}_j)$	
F^0	structure factor (imaginary component of anomalous dispersion omitted)

An important application of the observed anomalous scattering for the determination of the positions of the anomalous scatterers has been described by Rossmann (1961). In his approach a Patterson synthesis with $(|F^+| - |F^-|)^2$ coefficients is used which will produce peaks at the ends of vectors that relate anomalous scatterers. The 'best' *ad hoc* Patterson synthesis (having $|F''|^2$ coefficients) is not available from one-wavelength techniques: thus Rossmann's coefficients can be considered a useful approximation of the 'best' coefficients. The approximation is good if the Petsko (1976) approximation holds (see Fig. 1):

$$|F^0| \approx \frac{1}{2}(|F^+| + |F^-|). \quad (1)$$

Indeed, if we replace (1) in

$$|F^0|^2 = \frac{1}{2}(|F^+|^2 + |F^-|^2) - |F''|^2, \quad (2)$$

(3) is obtained:

$$|F''|^2 \approx \frac{1}{4}(|F^+| - |F^-|)^2. \quad (3)$$

Relation (1) holds if Φ is small enough, that is to say, if $|F''|$ is small compared with $|F^+|$ and $|F^-|$. Such conditions are not always fulfilled, especially if: (a) synchrotron radiation is used; indeed the anomalous components of the

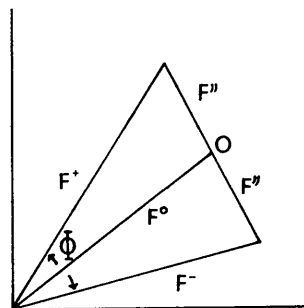


Fig. 1. Argand diagram in the case of anomalous scattering.

scattering factors can become rather large owing to the tunability of the radiation; (b) small molecules are investigated.

A better approximation of the $|F''|^2$ coefficients may be obtained by probabilistic methods. The conditional probability distribution of Φ given R^+ and R^- has been recently secured by Hauptman (1982) and Giacovazzo (1983):

$$P(\Phi|R^+, R^-) \approx [2\pi I_0(Q)]^{-1} \exp\{Q \cos(\Phi - q)\}, \quad (4)$$

where

$$Q = \frac{2R^+R^-}{\sqrt{c}} [c_1^2 + c_2^2]^{1/2},$$

$$\cos q = c_1/(c_1^2 + c_2^2)^{1/2}, \quad \sin q = c_2/(c_1^2 + c_2^2)^{1/2}.$$

By standard techniques, (5) follows from (4):

$$\langle \cos \Phi | R^+, R^- \rangle = \cos q D_1(Q), \quad (5)$$

where $D_1(Q) = I_1(Q)/I_0(Q)$ is the ratio of the modified Bessel functions of order 1 and 0.

Since (see Fig. 1)

$$|F^+|^2 + |F^-|^2 - 2|F^+||F^-| \cos \Phi = 4|F''|^2,$$

the expected value of $|F''|^2$ given $|F^+|$ and $|F^-|$ is

$$\langle |F''|^2 | |F^+|, |F^-| \rangle \approx \frac{1}{4} [|F^+|^2 + |F^-|^2 - 2|F^+||F^-| D_1(Q) \cos q]. \quad (6)$$

If (6) is compared with (3) we see that Rossmann's coefficients always assume $Q \approx \infty$ and $q \approx 2\pi$. The first approximation may be rough if R^+R^- is small enough; the second if c_2 is not negligible with respect to $(c_1^2 + c_2^2)^{1/2}$.

Relation (6) may find useful application even in two-wavelength techniques applied to crystal structures with one type of anomalous scatterers (Singh & Ramaseshan, 1968; Cascarano, Giacovazzo, Peerdeman & Kroon, 1982). There the analysis of experimental data leads to two possible values for $|F''|$, the most probable of which may be chosen in accordance with (6).

It may finally be noted that the distribution $P(|F''| | |F^+|, |F^-|)$ is implicitly defined by our approach and may be found by applying the well known formula

$$P_2(y) = P_1[x(y)] \frac{d[x(y)]}{dy},$$

where x is a function of the random variable y . In our case

$$x = \cos \Phi = (|F^+|^2 + |F^-|^2 - 4|F''|^2)/2|F^+F^-|, \quad y = |F''|,$$

$$P_1(x) \approx [\pi I_0(Q)]^{-1} (1 - x^2)^{-1/2} \exp(Qx).$$

We only note here that the larger Q is, the more reliable is the estimation for $|F''|$ provided by the (6).

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Aufbau algorithms and the structure of small molecular clusters.* By B. W. VAN DE WAAL, *Chemical Physics Laboratory, Twente University of Technology, PO Box 217, 7500 AE Enschede, The Netherlands*

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Abstract

In a comment [van de Waal (1981). *Acta Cryst.* **A37**, 762–764] on a paper by D. E. Williams [*Acta Cryst.* (1980), **A36**, 715–723] on the conformation of small clusters of benzene molecules, it was understood that Williams's results had been obtained from the application of an *aufbau* algorithm. Subsequently, it was made clear by Williams (private communication) that his results were actually derived from the reversed procedure. In the present note a comparison is made between the two approaches.

obtained from the application of an *aufbau* algorithm (van de Waal, 1981). Professor Williams has made clear, however, (Williams, 1981) that the conformation of each N -molecule cluster was actually derived by removing two molecules (related by a centre of symmetry) from an optimized $(N+2)$ cluster, rather than by adding two molecules to an optimized $(N-2)$ cluster. The process was started with a crystal-structure fragment.

Since this latter approach is not equivalent to the former, our comment needs some correction. It is the purpose of the present note to discuss briefly the relative merits of both methods (to which we shall refer as the *aufbau* algorithm and the reversed *aufbau* algorithm, respectively), and to amend our comment accordingly.

In our comment on Williams's (1980) paper, it was understood that the equilibrium conformations of clusters of benzene molecules, as reported by Williams, had been

The *aufbau* algorithm has been used by several authors (McGinty, 1971; Hoare & Pal, 1971; Pan & Eters, 1980) to calculate equilibrium conformations of clusters of atoms, interacting through a pair potential, usually a Lennard-Jones (LJ) potential. Essentially, it consists of adding individual atoms to a selected seed structure of small

* *Editorial note:* This paper suffered undue delay because the co-editor handling it inadvertently mislaid it.