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Direct Phase Determination of Triple Products from Bijvoet Inequalities. II. A Probabilistic Approach

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Probability calculations confirm a recently proposed formula for the calculation of $\sin \bar{\varphi}_{\mathbf{hk}}$ from Bijvoet inequalities, where $\bar{\varphi}_{\mathbf{hk}}$ is the average phase of the triple products $F_{\mathbf{h}}F_{\mathbf{k}}F_{\overline{\mathbf{h}+\mathbf{k}}}$ and $F_{\bar{\mathbf{h}}}F_{\bar{\mathbf{k}}}F_{\mathbf{h}+\mathbf{k}}$ [paper I: Kroon, Spek & Krabbendam (1977), *Acta Cryst.* A**33**, 382–385]. In paper I it was shown that $\bar{\varphi}_{\mathbf{hk}}$ could be calculated quite accurately without knowledge of the positions of the anomalous scatterers, provided an appropriate scaling procedure was applied. If the magnitudes of the individual structure factors are considered in addition to the magnitudes of the triple products, an improved formula is obtained which leads to even better results without any scaling procedure. The efficacy of the improved formula is demonstrated by test calculations for the same structure as in paper I (space group $P1$, two Br ions): (i) the phases of 5139 triple products formed from 322 reflexions (observed) with $|E| > 1{\cdot}2$ are calculated with a mean error in $\bar{\varphi}_{\mathbf{hk}}$ of 16° (paper I: 21°), (ii) the phases of 3832 triple products formed from 258 reflexions (calculated) with $|E| > 1{\cdot}2$ are calculated with a mean error in $\bar{\varphi}_{\mathbf{hk}}$ of 8° (paper I: 14°).

Introduction

In a recent paper (Kroon, Spek & Krabbendam, 1977, referred to as paper I) a method was given for determining the phases of triple products from Bijvoet inequalities. The formula used in paper I is

$$\sin \bar{\varphi}_{\mathbf{hk}} = \frac{|\tau_{\mathbf{hk}}|^2 - |\tau_{\bar{\mathbf{h}}\bar{\mathbf{k}}}|^2}{4\tau''_{\mathbf{hk}}[\frac{1}{2}(|\tau_{\mathbf{hk}}|^2 + |\tau_{\bar{\mathbf{h}}\bar{\mathbf{k}}}|^2) - |\tau'_{\mathbf{hk}}|^2]^{1/2}},\ddagger \quad (1)$$

where $\bar{\varphi}_{\mathbf{hk}} = \frac{1}{2}(\varphi_{\mathbf{hk}} - \varphi_{\bar{\mathbf{h}}\bar{\mathbf{k}}})$, $\varphi_{\mathbf{hk}}$ is the phase of $\tau_{\mathbf{hk}} = F_{\mathbf{h}}F_{\mathbf{k}}F_{\overline{\mathbf{h}+\mathbf{k}}}$ and $\tau''_{\mathbf{hk}}$ is a contribution to the imaginary part of $\tau_{\mathbf{hk}}$. If the structure contains only two identical anomalous heavy scatterers with form factors $f(\mathbf{h}) + if''$§ and interatomic distance vector $\mathbf{U}$, then $\tau'_{\mathbf{hk}}$ can be approximated by

$$\tau'_{\mathbf{hk}} \simeq 2f''[f(\mathbf{h})f(\mathbf{k}) + f(\mathbf{h})f(\overline{\mathbf{h}+\mathbf{k}}) + f(\mathbf{k})f(\overline{\mathbf{h}+\mathbf{k}})] \times [1 + \cos 2\pi\mathbf{h}.\mathbf{U} + \cos 2\pi\mathbf{k}.\mathbf{U} + \cos 2\pi(\mathbf{h}+\mathbf{k}).\mathbf{U}]. \quad (2)$$

It was shown that if $\mathbf{U}$ is not known, the omission of the cosine terms in (2) giving

$$\tau'_{\mathbf{hk}} \simeq 2f''[f(\mathbf{h})f(\mathbf{k}) + f(\mathbf{h})f(\overline{\mathbf{h}+\mathbf{k}}) + f(\mathbf{k})f(\overline{\mathbf{h}+\mathbf{k}})] \quad (3)$$

leads to good results provided a scaling procedure is applied; the problem of choosing between φ and $\pi - \varphi$ as possible values for the phase of a triple product was solved by taking the one nearer to zero (paper I).

(1) was derived on the basis that the complex double Patterson function, of which the $\tau_{\mathbf{hk}}$ are the Fourier coefficients, can be regarded as a 'structure' containing a number of 'anomalous scatterers'. For the case when there are two identical anomalous scatterers we shall derive by probability calculations (Heinerman, Krabbendam & Kroon, 1977) the formulae for the sines of the most probable values of $\varphi_{\mathbf{hk}}$ and $\varphi_{\bar{\mathbf{h}}\bar{\mathbf{k}}}$. These formulae appear to be in agreement with (1). We shall also show that the cosines in (2) can be estimated from the magnitudes of the individual structure factors. If these estimates are employed, there will be no need for a scaling procedure.

Probabilities

For a structure containing anomalous scatterers

$$F_{\mathbf{h}} = \sum_{j=1}^{N} [f_j(\mathbf{h}) + if_j''] \exp(2\pi i\mathbf{h}.\mathbf{r}_j). \quad (4)$$

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‡ For both centrosymmetric and non-centrosymmetric configurations of the anomalous scatterers in the structure, (1) can be applied so far as only the centrosymmetric part of the configuration of the 'anomalous scatterers' in the double Patterson function is taken into account.

§ Assuming that the form factors include temperature factors, the f'' should be labelled with a reciprocal-lattice vector. However, to keep to the formulae in paper I, we abandon this kind of notation. This is permissible if the structure factors are assumed to be divided by the temperature factor $\exp(-B \sin^2 \theta/\lambda^2)$.

For two identical anomalous scatterers, $f_1(\mathbf{h}) = f_2(\mathbf{h}) = f(\mathbf{h}), f_1'' = f_2'' = f''$, the triple products $\tau_{\mathbf{hk}}$ and $\tau_{\bar{\mathbf{h}}\bar{\mathbf{k}}}$ can be written as

$$\tau_{\mathbf{hk}} = O_R + iO_I + S_R + iS_I \tag{5}$$

and

$$\tau_{\bar{\mathbf{h}}\bar{\mathbf{k}}} = O_R + iO_I + S_R^* + iS_I^*, \tag{6}$$

where

$$O_R = \sum_{j=1}^{N} f_j(\mathbf{h}) f_j(\mathbf{k}) f_j(\overline{\mathbf{h}+\mathbf{k}}) - 2f''^2[f(\mathbf{h}) + f(\mathbf{k}) + f(\overline{\mathbf{h}+\mathbf{k}})], \tag{7}$$

$$O_I = 2f''[f(\mathbf{h})f(\mathbf{k}) + f(\mathbf{h})f(\overline{\mathbf{h}+\mathbf{k}}) + f(\mathbf{k})f(\overline{\mathbf{h}+\mathbf{k}}) - f''^2], \tag{8}$$

$$S_R = \sum_{\substack{j_1=1 \\ \text{not} j_1=j_2=j_3}}^{N} \sum_{j_2=1}^{N} \sum_{j_3=1}^{N} [f_{j_1}(\mathbf{h}) f_{j_2}(\mathbf{k}) f_{j_3}(\overline{\mathbf{h}+\mathbf{k}}) - f_{j_1}(\mathbf{h}) f_{j_2}'' f_{j_3}'' - f_{j_1}'' f_{j_2}(\mathbf{k}) f_{j_3}'' - f_{j_1}'' f_{j_2}'' f_{j_3}(\overline{\mathbf{h}+\mathbf{k}})] \times \exp\{2\pi i[\mathbf{h}.(\mathbf{r}_{j_1} - \mathbf{r}_{j_3}) + \mathbf{k}.(\mathbf{r}_{j_2} - \mathbf{r}_{j_3})]\}, \tag{9}$$

$$S_I = \sum_{\substack{j_1=1 \\ \text{not} j_1=j_2=j_3}}^{N} \sum_{j_2=1}^{N} \sum_{j_3=1}^{N} [f_{j_1}(\mathbf{h}) f_{j_2}(\mathbf{k}) f_{j_3}'' + f_{j_1}(\mathbf{h}) f_{j_2}'' f_{j_3}(\overline{\mathbf{h}+\mathbf{k}}) + f_{j_1}'' f_{j_2}(\mathbf{k}) f_{j_3}(\overline{\mathbf{h}+\mathbf{k}}) - f_{j_1}'' f_{j_2}'' f_{j_3}''] \times \exp\{2\pi i[\mathbf{h}.(\mathbf{r}_{j_1} - \mathbf{r}_{j_3}) + \mathbf{k}.(\mathbf{r}_{j_2} - \mathbf{r}_{j_3})]\} \tag{10}$$

and S_R^* and S_I^* are the complex conjugates of S_R and S_I respectively.

The joint probability distribution $P(R_1,R_2,\Phi_1,\Phi_2)$ of the magnitudes and phases of $\tau_{\mathbf{hk}}$ and $\tau_{\bar{\mathbf{h}}\bar{\mathbf{k}}}$ is equal to the product of the conditional joint probability distribution $P(R_1,\Phi_1|R_2,\Phi_2)$ of the magnitude and phase of $\tau_{\mathbf{hk}}$ given the magnitude and phase of $\tau_{\bar{\mathbf{h}}\bar{\mathbf{k}}}$ and the joint probability distribution $P(R_2,\Phi_2)$ of the magnitude and phase of $\tau_{\bar{\mathbf{h}}\bar{\mathbf{k}}}$. If we assume that $P(R_2,\Phi_2)$ is a von Mises distribution we obtain (Heinerman, Krabbendam & Kroon, 1977)

$$P(R_2,\Phi_2) = \frac{R_2}{\pi V_2} \exp\left\{-\frac{1}{V_2}[R_2^2 - 2Q_2R_2\cos(\Phi_2 - q_2) + Q_2^2]\right\}, \tag{11}$$

in which

$$Q_2 \exp(iq_2) = \langle \tau_{\bar{\mathbf{h}}\bar{\mathbf{k}}} \rangle = O_R + iO_I \tag{12}$$

and

$$V_2 = \langle |\tau_{\bar{\mathbf{h}}\bar{\mathbf{k}}}|^2 \rangle - |\langle \tau_{\bar{\mathbf{h}}\bar{\mathbf{k}}} \rangle|^2, \tag{13}$$

where the averages are performed with respect to the atomic position vectors. In the same way we obtain

$$P(R_1,\Phi_1|R_2,\Phi_2) = \frac{R_1}{\pi V_{12}} \exp\left\{-\frac{1}{V_{12}}[R_1^2 - 2Q_{12}R_1\cos(\Phi_1 - q_{12}) + Q_{12}^2]\right\}, \tag{14}$$

in which

$$Q_{12}\exp(iq_{12}) = \langle \tau_{\mathbf{hk}}|\tau_{\bar{\mathbf{h}}\bar{\mathbf{k}}}\rangle = \langle \tau_{\bar{\mathbf{h}}\bar{\mathbf{k}}}^* + 2iO_I + 2iS_I|\tau_{\bar{\mathbf{h}}\bar{\mathbf{k}}}\rangle = \tau_{\bar{\mathbf{h}}\bar{\mathbf{k}}}^* + 2iO_I = R_2\cos\Phi_2 + i(2O_I - R_2\sin\Phi_2) \tag{15}$$

if $\langle S_I|\tau_{\bar{\mathbf{h}}\bar{\mathbf{k}}}\rangle = 0$, and

$$V_{12} = \langle |\tau_{\mathbf{hk}}|^2|\tau_{\bar{\mathbf{h}}\bar{\mathbf{k}}}\rangle - |\langle \tau_{\mathbf{hk}}|\tau_{\bar{\mathbf{h}}\bar{\mathbf{k}}}\rangle|^2. \tag{16}$$

By multiplying (11) by (14) we obtain $P(R_1,R_2,\Phi_1,\Phi_2)$. From this distribution the conditional joint probability distribution $P(\Phi_1,\Phi_2|R_1,R_2)$ is found by fixing the magnitudes of $\tau_{\mathbf{hk}}$ and $\tau_{\bar{\mathbf{h}}\bar{\mathbf{k}}}$. The result is

$$P(\Phi_1,\Phi_2|R_1,R_2) = C\exp\left\{\frac{2R_2}{V_2}(O_R\cos\Phi_2 + O_I\sin\Phi_2) + \frac{2}{V_{12}}[R_1R_2\cos(\Phi_1+\Phi_2) + 2O_IR_1\sin\Phi_1 + 2O_IR_2\sin\Phi_2]\right\}, \tag{17}$$

where C is a normalizing constant. $P(\Phi_1,\Phi_2|R_1,R_2)$ is only symmetric in 1 and 2, as it should be, if in (17) the part containing V_2 is neglected with respect to the part containing V_{12}. For the test structure in paper I numerical calculations justify the omission of the V_2 part:

$$P(\Phi_1,\Phi_2|R_1,R_2) \simeq C'\exp\left\{\frac{2}{V_{12}}[R_1R_2\cos(\Phi_1+\Phi_2) + 2O_IR_1\sin\Phi_1 + 2O_IR_2\sin\Phi_2]\right\}. \tag{18}$$

The sines of the most probable values for $\varphi_{\mathbf{hk}}$ and $\varphi_{\bar{\mathbf{h}}\bar{\mathbf{k}}}$ are found from the position of the maximum of (18) and can be shown to be

$$\sin\Phi_{1\,\text{m.p.}} = \frac{R_1^2 - R_2^2 + 4O_I^2}{4O_IR_1} \tag{19a}$$

and

$$\sin\Phi_{2\,\text{m.p.}} = \frac{R_2^2 - R_1^2 + 4O_I^2}{4O_IR_2}. \tag{19b}$$

When $O_I \ll R_1,R_2$ and $R_1 \simeq R_2$, (19) is in agreement with (1) and (3) ($|\tau_{\mathbf{hk}}| = R_1$, $|\tau_{\bar{\mathbf{h}}\bar{\mathbf{k}}}| = R_2$, $\tau'_{\mathbf{hk}} = O_I$, the term f''^3 in O_I is negligible). In the same way we obtained the formulae for $\sin\Phi_{1\,\text{m.p.}}$ and $\sin\Phi_{2\,\text{m.p.}}$ in which use is made of the positions of the anomalous scatterers; then $O_I + \langle S_I|\tau_{\bar{\mathbf{h}}\bar{\mathbf{k}}}\rangle = O_I[1 + \cos 2\pi\mathbf{h}.\mathbf{U} + \cos 2\pi\mathbf{k}.\mathbf{U} + \cos 2\pi(\mathbf{h}+\mathbf{k}).\mathbf{U}]$ replaces O_I in (19). If the same assumptions are made as in the preceding case these formulae are in agreement with (1) and (2).

An improved formula

To obtain good results with (1) and (3) a scaling procedure involving all participating triple products appeared to be necessary (paper I). This was ascribed to the fact that the sum of three cosines in (2) is

Table 1. *Results of the phase determination of triple products obtained by using the Bijvoet inequalities with the data of dexetimide*

						With scaling procedure*			Without scaling procedure		
Set No.	F used†	Minimum $\|F\|$	Minimum $\|E\|$	Number of reflexions	Number of triple products	Heavy-atom positions included	$\langle\|\Delta\varphi\|\rangle$‡	$\langle\Delta^2\varphi\rangle^{1/2}$§	Heavy-atom positions included¶	$\langle\|\Delta\varphi\|\rangle$‡	$\langle\Delta^2\varphi\rangle^{1/2}$§
1	F^o	40	1·3	103	506	no	15°	20°	est.	13°	16°
2	F^o	40	1·3	103	506	yes	14	19	yes	13	17
3	F^c	40	1·3	86	342	no	10	15	est.	7	10
4	F^c	40	1·3	86	342	yes	10	15	yes	10	14
5	F^o	50	0·0	87	441	no	22	34	est.	17	30
6	F^o	50	0·0	87	441	yes	21	37	yes	21	37
7	F^c	50	0·0	64	223‖	no	16	30	est.	13	28
8	F^c	50	0.0	64	223‖	yes	16	31	yes	16	32
9	F^o	25	1·2	322	5139	no	21	37	est.	16	20
10	F^c	25	1·2	258	3832	no	14	19	est.	8	11

* Results of paper I.
† $F^o = F$ observed, $F^c = F$ calculated from the refined structure.
‡ $\Delta\varphi = \bar{\varphi}^{\text{calc}}_{\mathbf{hk}} - \bar{\varphi}^{\text{true}}_{\mathbf{hk}}$ where $\bar{\varphi}^{\text{true}}_{\mathbf{hk}}$ is the average value of the phases $\varphi_{\mathbf{hk}}$ and $-\varphi_{\overline{\mathbf{hk}}}$ obtained from the refined structure.
§ $\Delta^2\varphi \equiv |\Delta\varphi|^2$.
¶ est. = estimation of cosines.
‖ In paper I this number was erroneously given as 342.

systematically positive and large. It appears that the formula containing the cosine terms gives satisfactory results *without* the scaling procedure (Table 1). This indicates that for unknown heavy-atom positions an estimation of the cosines, if this proves possible, might provide us with individual scaling factors.

Let us consider $\cos 2\pi\mathbf{h}.\mathbf{U}$. This cosine multiplied by $2Z^2/\sigma_2$ is one term of

$$|E_{\mathbf{h}}|^2 - 1 = \sum_{\substack{j_1=1 \\ j_1<j_2}}^{N} \sum_{j_2=1}^{N} \frac{2Z_{j_1}Z_{j_2}}{\sigma_2} \cos 2\pi\mathbf{h}.(\mathbf{r}_{j_1} - \mathbf{r}_{j_2}), \quad (20)$$

where Z_j is the atomic number of atom j, $Z_1 = Z_2 = Z$ and

$$\sigma_n = \sum_{j=1}^{N} Z_j^n. \quad (21)$$

Therefore, the following estimation seems reasonable, especially if Z is large,

$$\cos 2\pi\mathbf{h}.\mathbf{U} \simeq K(|E_{\mathbf{h}}|^2 - 1), \quad (22)$$

where K is obtained by minimizing

$$\langle[\cos 2\pi\mathbf{h}.\mathbf{U} - K(|E_{\mathbf{h}}|^2 - 1)]^2\rangle,$$

which leads to

$$K = Z^2 \frac{\sigma_2}{\sigma_2^2 - \sigma_4}. \quad (23)$$

Then for two anomalous scatterers $\tau'_{\mathbf{hk}}$ can be estimated thus:

$$\tau'_{\mathbf{hk}} \simeq 2f''[f(\mathbf{h})f(\mathbf{k}) + f(\mathbf{h})f(\overline{\mathbf{h}+\mathbf{k}}) + f(\mathbf{k})f(\overline{\mathbf{h}+\mathbf{k}})] \times [1 + K(|E_{\mathbf{h}}|^2 + |E_{\mathbf{k}}|^2 + |E_{\mathbf{h}\ \mathbf{k}}|^2 - 3)]. \quad (24)$$

With (1) and (24) we obtained results which are extremely good (last two columns of Table 1). Sines calculated larger than 1 and smaller than -1 were put equal to 1 and -1 respectively, and the problem of choosing between φ and $\pi-\varphi$ was solved by selecting the one nearer to zero. The structure used for this test is the same as in paper I: dexetimide, $C_{23}H_{27}N_2O_2Br.\frac{1}{2}H_2O$, space group $P1$, $z = 2$. Especially interesting for practical applications is entry No. 9 in Table 1, where the phases of 5139 triple products were calculated. In paper I the mean error in $\bar{\varphi}_{\mathbf{hk}}$ was 21°; whereas a mean error of 16° is obtained when we use the estimates for the cosines.

Test calculations with calculated structure factors for artificial structures obtained from dexetimide (i) by replacing H_2O by a Br ion (the structure then contains three Br ions), and (ii) by replacing one H by a Br ion and adding another Br ion in such a way that the configuration of the four Br ions is centrosymmetric, yield results which are comparable with or even better than those in Table 1: for (i) the phases of 537 triple products formed from 107 reflexions with $|F| > 40$ and $|E| > 1{\cdot}3$ were calculated with a mean error in $\bar{\varphi}_{\mathbf{hk}}$ of 11° (nine cosine terms were estimated, see Appendix; neglecting these terms and applying the scaling procedure of paper I results in 14°); for (ii) the phases of 3293 triple products formed from 207 reflexions with $|F| > 40$ and $|E| > 1{\cdot}3$ were calculated with a mean error in $\bar{\varphi}_{\mathbf{hk}}$ of 4° (12 cosine terms were estimated, see Appendix; neglecting these terms and applying the scaling procedure of paper I results in 15°).

Discussion

Our probability calculations show that (1) and (2) and (1) and (3) correspond to most probable values for

phases of triple products. Before performing these calculations we had expected that when the heavy-atom positions were unknown we would find an improved formula related to (1) and (3), with a scaling factor depending on the magnitudes of $\tau_{\mathbf{hk}}$ and $\tau_{\bar{\mathbf{h}}\bar{\mathbf{k}}}$. However, no improved formula was obtained; this, we think, is probably due to our use of the assumption $\langle S_I | \tau_{\bar{\mathbf{h}}\bar{\mathbf{k}}} \rangle = 0$.

In the improvement described in the preceding section we employ the magnitudes of the individual structure factors. In view of the excellent results it is expected that more intricate calculations *via* the joint probability distribution of the magnitudes and phases of $F_{\mathbf{h}}$, $F_{\mathbf{k}}$, $F_{\overline{\mathbf{h}+\mathbf{k}}}$, $F_{\bar{\mathbf{h}}}$, $F_{\bar{\mathbf{k}}}$ and $F_{\mathbf{h}+\mathbf{k}}$ will lead to a formula for $\sin \bar{\varphi}_{\mathbf{hk}}$ which is closely related to our improved formulae (1) and (24).

Surprisingly, for dexetimide the results with the improved formula are better than the results with the formula in which the exact values of the cosines are used (Table 1). Therefore it follows that here the estimates compensate for the approximations made to obtain (1) and (2).

APPENDIX

(i) If there are three identical anomalous scatterers one may approximate

$$\begin{aligned}\tau''_{\mathbf{hk}} &\simeq 3f''[f(\mathbf{h})f(\mathbf{k}) + f(\mathbf{h})f(\overline{\mathbf{h}+\mathbf{k}}) + f(\mathbf{k})f(\overline{\mathbf{h}+\mathbf{k}})] \\ &\times \left\{1 + \tfrac{2}{3}\sum_{i=1}^{3} [\cos 2\pi\mathbf{h}.\mathbf{U}_i + \cos 2\pi\mathbf{k}.\mathbf{U}_i \right. \\ &\left. + \cos 2\pi(\mathbf{h}+\mathbf{k}).\mathbf{U}_i]\right\} \\ &\simeq 3f''[f(\mathbf{h})f(\mathbf{k}) + f(\mathbf{h})f(\overline{\mathbf{h}+\mathbf{k}}) + f(\mathbf{k})f(\overline{\mathbf{h}+\mathbf{k}})] \\ &\times [1 + 2K(|E_{\mathbf{h}}|^2 + |E_{\mathbf{k}}|^2 + |E_{\mathbf{h}+\mathbf{k}}|^2 - 3)],\end{aligned}$$

where the $\mathbf{U}_i$ are the vectors between the anomalous scatterers and K is given by (23).

(ii) If there are four identical anomalous scatterers with a centrosymmetric configuration one may approximate

$$\begin{aligned}\tau''_{\mathbf{hk}} &\simeq 4f''[f(\mathbf{h})f(\mathbf{k}) + f(\mathbf{h})f(\overline{\mathbf{h}+\mathbf{k}}) + f(\mathbf{k})f(\overline{\mathbf{h}+\mathbf{k}})] \\ &\times \left\{1 + \tfrac{1}{2}\sum_{i=1}^{2} [\cos 2\pi\mathbf{h}.\mathbf{U}_i + \cos 2\pi\mathbf{k}.\mathbf{U}_i \right. \\ &+ \cos 2\pi(\mathbf{h}+\mathbf{k}).\mathbf{U}_i] \\ &+ \sum_{i=1}^{2} [\cos 2\pi\mathbf{h}.\mathbf{V}_i + \cos 2\pi\mathbf{k}.\mathbf{V}_i \\ &\left. + \cos 2\pi(\mathbf{h}+\mathbf{k}).\mathbf{V}_i]\right\} \\ &\simeq 4f''[f(\mathbf{h})f(\mathbf{k}) + f(\mathbf{h})f(\overline{\mathbf{h}+\mathbf{k}}) + f(\mathbf{k})f(\overline{\mathbf{h}+\mathbf{k}})] \\ &\times [1 + 3K(|E_{\mathbf{h}}|^2 + |E_{\mathbf{k}}|^2 + |E_{\mathbf{h}+\mathbf{k}}|^2 - 3)],\end{aligned}$$

where the $\mathbf{U}_i$ are the single vectors between the anomalous scatterers and the $\mathbf{V}_i$ are the double vectors. Again K is given by (23).

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Overlapping Patterson Peaks and Direct Methods: The Structure of Prostratin

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A generalized discussion of direct methods of solving the phase problem leads to the suggestion that overlapping vectors in the Patterson function may be the cause of failures in these methods. A simple removal of these overlapping vectors is proposed, which produces modified $|E|$ values. These were used with the program *MULTAN* to solve the structure of a prostratin derivative, $C_{22}H_{28}O_6$, which had otherwise resisted solution.

1. Direct methods

For the discussion of direct methods which follows, an analogy with the heavy-atom method may be useful. After the first stage (finding the heavy atoms) one has quite accurate knowledge of small parts of the electron density, complete ignorance concerning the remaining electron density, and approximations to the phases throughout reciprocal space. With a direct method of phase determination, after assigning values for a few

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