tion which can exist among these parameters for certain values of them; if $\chi_s = 0$, $\omega_s$ and $\varphi_s$ rotations are equivalent, and a matrix singularity results. For small values of $\chi_s$, the high correlation hampers the refinement. The same problem occurs if three other rotations (*e.g.* about mutually orthogonal axes) are chosen as parameters instead of $\omega_s$, $\chi_s$ and $\varphi_s$.

A clue to a reliable automation of the procedure is given in Busing's (1970) remark that the orientation parameters of the BL method 'simply define the orthogonal matrix **U** and need not correspond to any reflections actually observed'. Indeed, we can take this further: they need not correspond even to points of the reciprocal lattice, *i.e.* to reflections with integral indices.

To take advantage of this, we can *define* the initial orienting reflection angles to be $\omega_1 = \chi_1 = \varphi_1 = \omega_2 = \chi_2 = 0$, $\varphi_2 = 90°$. The corresponding non-integral 'indices' are derived from the initial **UB** matrix: from BL equations (19) and (22), the desired indices are given by

$$\mathbf{UBh} = \begin{pmatrix}1\\0\\0\end{pmatrix} \quad \text{and} \quad \begin{pmatrix}0\\1\\0\end{pmatrix}$$

respectively, and are thus six of the elements of $\mathbf{V} = (\mathbf{UB})^{-1}$, *viz* $v_{11}$, $v_{21}$, $v_{31}$ for the first, and $v_{12}$, $v_{22}$, $v_{32}$ for the second dummy reflection ($v_{13}$, $v_{23}$, $v_{33}$ represents a dummy reflection with $\omega = 0$, $\chi = 90°$ and arbitrary $\varphi$). The three parameters $\chi_1$, $\varphi_1$ and $\chi_2$ are refined, together with the cell parameters (1–6, depending on symmetry constraints) by the standard BL method. It should be noted (as is stated in BL) that, after the refinement, the two vectors corresponding to the orienting 'reflections' will no longer lie exactly in the equatorial plane. This is immaterial, as the purpose of refining the three orientation parameters is purely to obtain the best estimate for the matrix **U** subject to the unit-cell symmetry constraints, *i.e.* for the matrix which minimizes the least-squares function $\sum wA^2$, where $A = y_{obs} - y_{calc}$, and $y$ is, in turn, $2\theta$, $\omega$, and $\chi$ for each centred reflection (BL's type 1, 3 and 5 observations). We use a weighting scheme whereby $w = 1$ for $\chi$, 2 for $2\theta$, and 4 for $\omega$, which roughly reflects the relative precisions obtained for these measurements in our reflection centring method.

We have included this 'automated BL' method in the software for our four-circle diffractometer, written in Extended Basic for Data General Eclipse and Nova computers (Clegg, 1981). Reflection-angle data are obtained by an automatic centring routine and held on a computer disc file together with preliminary parameters. The only input required from the user is a command to perform refinement and a code number specifying the crystal symmetry. The method is indeed considerably slower (by a factor of about 5–15, depending on symmetry) than the Tichý method, which is also incorporated in the program, but it is just as simple to use. In any case, the slower refinement is no great drawback, as this refinement is performed normally only once for each crystal under investigation.

### References


BUSING, W. R. (1970). *Crystallographic Computing*, edited by F. R. AHMED, pp. 319–330. Copenhagen: Munksgaard.

BUSING, W. R. & LEVY, H. A. (1967*a*). *Acta Cryst.* **22**, 457–464.

BUSING, W. R. & LEVY, H. A. (1967*b*). Report ORNL-4054. Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA.

CLEGG, W. (1981). *Acta Cryst.* A**37**, C313–C314.

GABE, E. J. (1980). *Computing in Crystallography*, edited by R. DIAMOND, S. RAMASESHAN & K. VENKATESAN, pp. 1.01–1.31. Bangalore: Indian Academy of Sciences.

HAMILTON, W. C. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 273–284. Birmingham: Kynoch Press.

SHOEMAKER, D. P. & BASSI, G. (1970). *Acta Cryst.* A**26**, 97–101.

SPARKS, R. A. (1976). *Crystallographic Computing Techniques*, edited by F. R. AHMED, pp. 452–467. Copenhagen: Munksgaard.

TICHÝ, K. (1970). *Acta Cryst.* A**26**, 295–296.


*Acta Cryst.* (1983). A**39**, 171–173

## Diffraction by a one-dimensionally disordered crystal. III. Relation between the matrix and the probability tree methods.*

By JIRO KAKINOKI, *Higashi* 1-17, *Hagiwaradai, Kawanishi* 666, *Japan*

(*Received* 5 *January* 1982; *accepted* 16 *August* 1982)


### Abstract

The calculation of the diffraction from a one-dimensionally disordered crystal is shown to be easier using the matrix (M) method than with the probability tree (PT) method. If the order of the difference equation is high, an analytical solution cannot be obtained by the PT method unless the model is highly simplified. There is no such limitation in the M method.


From the relations between $m$th and $(m+1)$th layers in the probability trees in Fig. 1 of Howard (1977), the **P** matrix (Kakinoki, 1967) is obtained as

$$\mathbf{P} = \begin{array}{c} \begin{matrix} A^+ & A^* & B^+ & B^* & C^+ & C^* \end{matrix} \\ \left(\begin{array}{cc:cc:cc} & & 1-p & 0 & 0 & p \\ \multicolumn{2}{c:}{0} & q & 0 & 1-q & 0 \\ \hdashline 0 & p & \multicolumn{2}{c:}{} & 1-p & 0 \\ \multicolumn{2}{c:}{1-q\quad 0} & \multicolumn{2}{c:}{0} & q & 0 \\ \hdashline 1-p & 0 & 0 & p & \multicolumn{2}{c}{} \\ q & 0 & 1-q & 0 & \multicolumn{2}{c}{0} \end{array}\right) \end{array} \begin{matrix} A^+ \\ A^* \\ B^+ \\ B^* \\ C^+ \\ C^* \end{matrix} \begin{matrix} w^+/3 \\ w^*/3 \\ w^+/3 \\ w^*/3 \\ w^+/3 \\ w^*/3 \end{matrix},$$

where Howard's second parameter $q$ is used and where $A^+$, $B^+$ and $C^+$ denote the original or 2nd, 4th,... inserted layers and $A^*$, $B^*$ and $C^*$ denote the 1st, 3rd,... inserted layers.

* Part II: Kakinoki (1967).

0567-7394/83/010171-03$01.50

There are five steps for calculating the intensity equation.

Step 1: From $\mathbf{P}$, we have

$$\mathbf{P}_1=\begin{pmatrix}1-p & 0\\ q & 0\end{pmatrix} \quad \text{and} \quad \mathbf{P}_2=\begin{pmatrix}0 & p\\ 1-q & 0\end{pmatrix}.$$

Step 2: From the relations $\mathbf{w}\tilde{\mathbf{1}}=1$ and $\mathbf{w}(\mathbf{P}_1+\mathbf{P}_2)=\mathbf{w}$, where $\mathbf{w}=(w^+\ w^*)$ and $\mathbf{1}=(1\ 1)$, we obtain

$$\mathbf{w}=\frac{1}{1+p}(1\ p).$$

Step 3: From $T_m=\mathbf{w}(\varepsilon\mathbf{P}_1+\varepsilon^*\mathbf{P}_2)^m\tilde{\mathbf{1}}$ with $\varepsilon=\exp\{(2\pi/3)i(h-k)\}$, $T_0=1$ and

$$T_1=\frac{1}{1+p}\{\varepsilon(1-p+pq)+\varepsilon^* p(2-q)\}. \tag{1}$$

Step 4: The secular equation

$$F(x)=\det(x\mathbf{E}-\varepsilon\mathbf{P}_1-\varepsilon^*\mathbf{P}_2)$$

is

$$\begin{aligned}F(x)&=a_0x^2+a_1x+a_2\\&=x^2-\varepsilon(1-p)x-p\{q+\varepsilon(1-q)\}=0.\end{aligned}$$

Therefore, $a_0=1$, $a_1=-\varepsilon(1-p)$ and $a_2=-p\{q+\varepsilon(1-q)\}$.

Step 5: The intensity equation is given by

$$D(\varphi)=\frac{D_0+D_1e^{i\varphi}+\text{complex conjugate}}{C_0+(C_1e^{i\varphi}+C_2e^{i2\varphi})+(\text{complex conjugate})}$$

where

$$\begin{aligned}C_0&=1+a_1a_1^*+a_2a_2^*,\\C_1&=a_1^*+a_1a_2^*,\\C_2&=a_2^*,\\D_0&=1+a_1a_1^*-a_2a_2^*+a_1T_1^*+a_1^*T_1\\D_1&=a_1^*+a_2^*T_1+T_1^*,\end{aligned}$$

therefore

$$D(\varphi)=\frac{3p(1-p+pq)}{1+p}\times\frac{S}{Q}$$

with $S=2-q(1+p)-2(1-q)\cos(\varphi\mp60°)$

$$\begin{aligned}Q&=2(1-p+p^2)-3p^2q(1-q)\\&\quad+(1-p)(1+2p-3pq)\cos\varphi+p(1-3q)\cos2\varphi\\&\quad\mp\sqrt{3}\{(1-p)(1+pq)\sin\varphi+p(1-q)\sin2\varphi\}.\end{aligned}$$

On the other hand, the process of getting $D(\varphi)$ with $q=p$ by the PT method of Howard (1977) is as follows:

(i) By inspection of probability trees with $q=p$, Howard derived

$$\begin{cases}G_1+G_2+G_3+G_4+G_5+G_6=1, \quad P_m^A=G_1+G_4,\\P_{m+1}^A=pG_2+(1-p)G_3+(1-p)G_5+pG_6,\\P_{m+2}^A=pG_1+(1-p)^2G_2+p(1-p)G_3\\\qquad+(1-2p+2p^2)G_4+p(1-p)G_5\\\qquad+p(1-p)G_6,\\P_{m+3}^A=(1-3p+4p^2-2p^3)G_1+p(2-4p+3p^2)G_2\\\qquad+p(1-p^2)G_3+2p(1-2p+p^2)G_4\\\qquad+p(1-p^2)G_5+(1-3p+4p^2-p^3)G_6.\end{cases}$$

(ii) Eliminating the six $G_i$s from these equations, Howard obtained the difference equation and its characteristic equation $F_H(x)$ as

$$\begin{aligned}&P_{m+3}^A+(1-2p)P_{m+2}^A+(1-2p)P_{m+1}^A\\&\quad+p(1-3p+3p^2)P_m^A=1-p-p^2+p^3.\end{aligned}$$

Therefore, $F_H(x)=x^3+(1-2p)x^2+(1-2p)x+p(1-3p+3p^2)=0$.

(iii) The solution of $F_H(x)=0$ is $X_1=-p$ and $X_2=p+\varepsilon(1-p)=X_3^*$.

(iv) Howard determined $K_l$, $L_l$ and $M_l$ in his expressions as

$$P_m^A=\tfrac{1}{3}+\sum_{l=1}^{3}K_lX_l^m, \quad P_m^B=\tfrac{1}{3}+\sum_{l=1}^{3}L_lX_l^m$$

and

$$P_m^C=\tfrac{1}{3}+\sum_{l=1}^{3}M_lX_l^m. \tag{2}$$

(v) Using $X_l$, $K_l$, $L_l$ and $M_l$, Howard derived his intensity equation as

$$D_H(\pi l)=\frac{3p(1-p)}{2(1+p)(1-4p+7p^2)}\left(\frac{U}{V}+\frac{W}{Y}\right)$$

with $U=(1+p)(1-p+4p^2)\pm2p(1-2p)\sqrt{3}\sin\pi l$

$$\begin{aligned}V&=1+p^2+2p\cos\pi l\\W&=2-9p+9p^2+2p^3-3(1-p)(1-2p)\cos\pi l\\&\quad\mp(1-2p)(1-3p)\sqrt{3}\sin\pi l\\Y&=2-3p+3p^2+(1-3p)\cos\pi l\\&\quad\mp(1-p)\sqrt{3}\sin\pi l,\end{aligned}$$

which can be transformed to our $D(\varphi)$ with $q=p$ and $\varphi=\pi l$.

Thus, the PT method is unnecessarily laborious and if the order of the characteristic equation becomes higher, it is impossible to get an analytical solution. This limits the model.

On the contrary, in the matrix method, once we determine $\mathbf{P}_1$ and $\mathbf{P}_2$ by the model, $D(\varphi)$ is derived by routine matrix calculation. Moreover, we need not use $G_l$, $P_m^A$, $P_m^B$, $P_m^C$, $K_l$, $L_l$ and $M_l$. But they are easily derived by matrices as follows:

(i) $P_{m+n}^A=\mathbf{g}\tilde{\boldsymbol{\alpha}}_n$ with

$$\begin{cases}\mathbf{g}=(G_1\ G_4\ G_2\ G_5\ G_3\ G_6)\\\boldsymbol{\alpha}_0=(1\ 1\ 0\ 0\ 0\ 0)\text{ and }\tilde{\boldsymbol{\alpha}}_n=\mathbf{P}\tilde{\boldsymbol{\alpha}}_{n-1}.\end{cases}$$

(ii) Putting $T_m=c_1X_1^m+c_2X_2^m$, we solve $c_l$ by (1) with $q=p$ and $T_0=1$. Therefore

$$\begin{cases}c_1=3p[p(1+p)-\varepsilon(1-p)(1-2p)]/R\\c_2=[1-3p+4p^3+\varepsilon3p(1-p)(1-2p)]/R\end{cases}$$

with $R=(1+p)(1-4p+7p^2)$.

From the physical meaning of $T_m$, *i.e.* $T_m=P_m^A+\varepsilon P_m^B+\varepsilon^*P_m^C$, we get

$$3P_m^A=1+T_m+T_m^*, \quad 3P_m^B=1+\varepsilon^*T_m+\varepsilon T_m^*$$

and

$$3P_m^C=1+\varepsilon T_m+\varepsilon^*T_m^*.$$

Hence, from (2), we have:

$$3K_1 = c_1 + c_1^*, \quad 3K_2 = 3K_3^* = c_2,$$
$$3L_1 = \varepsilon^* c_1 + \varepsilon c_1^*, \quad 3L_2 = 3L_3^* = \varepsilon^* c_2,$$
$$3M_1 = \varepsilon c_1 + \varepsilon^* c_1^*, \quad 3M_2 = 3M_3^* = \varepsilon c_2.$$

Furthermore, $F_H(x)$ and $F(x)$ with $q = p$ are expressed as

$$F_H(x) = (x - X_1)(x - X_2)(x - X_2^*) = 0$$

and

$$F(x) = (x - X_1)(x - X_2) = 0.$$

The order of $F_H(x)$ is higher than that of $F(x)$ with $q = p$.

In the case of $q \neq p$, the characteristic equation $F'_H(x)$ was not shown by Howard but it is given by $F'_H(x) = F(x)F^*(x)$ and then the difference equation is

$$P^A_{m+4} + (1-p)P^A_{m+3} + (1 - p + p^2 - 3pq)P^A_{m+2} + p(1-p)(2-3q)P^A_{m+1} + p^2(1 - 3q + 3q^2)P^A_m = 1 - 2pq + p^2q^2 = (\text{sum of five coefficients})/3.$$

In the PT method, $F'_H(x) = F(x)F^*(x) = 0$ must be solved but in the matrix method, the necessary quantities are not the roots but the coefficients in $F(x) = 0$.

Thus, the matrix method is superior to the PT method.

### References

HOWARD, C. J. (1977). *Acta Cryst.* A**33**, 29–32.
KAKINOKI, J. (1967). *Acta Cryst.* **23**, 875–885.

*Acta Cryst.* (1983). A**39**, 173

## Restrictions on the components of third-order tensors for site symmetry 3*m*: Correction of an error in Volume IV of *International Tables for X-ray Crystallography*.

By C. SCHERINGER, *Institut für Mineralogie der Universität Marburg, D* 3550 *Marburg, Federal Republic of Germany*

(*Received* 18 *August* 1982; *accepted* 6 *September* 1982)

### Abstract

For site symmetry 3*m*, the covariant components 112 and 122 of the third-order tensors are not independent, and in row C38* of Table 5.5C (p. 329) of the *International Tables for X-ray Crystallography* [(1974), Vol. IV. Birmingham: Kynoch Press] the symbol *D* should twice be replaced by $-A/2$. The result was established by applying the 3*m* symmetry operations which hold for the covariant components of the third-order tensor, and was confirmed by calculating the covariant components from the contravariant components. All other information is given in the *Abstract*.

*Acta Cryst.* (1983). A**39**, 173

## Corrections to Table 2.2B of Volume IV of *International Tables for X-ray Crystallography*.

By RICHARD E. MARSH and KIRBY J. SLAGLE, *Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California* 91125, *USA*

(*Recived* 18 *October* 1982; *accepted* 8 *November* 1982)

### Abstract

Corrections are given for two of the coefficients for the analytical approximations to X-ray scattering factors in Table 2.2B of *International Tables for X-ray Crystallography* [(1974), Vol. IV. Birmingham: Kynoch Press]. For $Ru^{+4}$ (p. 100), the coefficient $b_3$ should be 0·036495 rather than 0·36495; for $Bi^{+5}$ (p. 101), the coefficient $b_2$ should be 0·039042 rather than 0·39042.

All information is given in the *Abstract*. We thank Dr Don T. Cromer for confirming that the numbers were indeed misprinted as indicated.

0567-7394/83/010173-01$01.50 