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Phase Reliability and the Refinement of Pseudosymmetric Crystal Structures

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The assumption that the phases calculated from a trial structure are indeed correct results in incorrect estimates of the variances of parameters. Modifications to least-squares equations and the evaluation of appropriate weighting schemes are discussed. It is shown that for a non-centrosymmetric structure a unique minimum is not to be expected, establishing a strong case for initial refinement of crystal structures with constrained refinement procedures. A method of obtaining an unbiased estimate of the variance - covariance matrix is given.

Introduction

Notation used in this paper is that developed in previous papers (Rae, 1973, 1974*a*) concerning the refinement of pseudosymmetric crystal structures. The subsequent implementation of the generally stated considerations in these papers (Rae, Robinson & Rodley, 1975) prompted further investigation of refinement procedure and data collection requirements. It is necessary to classify pseudosymmetric structures, as the nature of the problems encountered depends on this classification.

Pseudosymmetry

If we transform all points $\mathbf{r}$ in the unit cell to $(\theta,\mathbf{t})\mathbf{r}=\theta\mathbf{r}+\mathbf{t}$ where θ is a point-group operation and $\mathbf{t}$ is a translation, the electron density becomes $\varrho\{(\theta,\mathbf{t})^{-1}\mathbf{r}\}$ with corresponding X-ray structure factor $F_{(\theta,\mathbf{t})}(\mathbf{S})=\exp(2\pi i\mathbf{t}\,.\,\mathbf{S})F(\theta^{-1}\mathbf{S})$ where $\mathbf{S}$ is the reciprocal-lattice vector of magnitude $2\sin\theta/\lambda$. If $(\theta,\mathbf{t})$ is an operator of order n then $(\theta,\mathbf{t})^n=(1,\hat{\mathbf{t}})$ where $\hat{\mathbf{t}}\,.\,\mathbf{S}$ is integral for any allowed value of $\mathbf{S}$. For closure of the space group we regard operators $(\theta_1,\mathbf{t}_1)$ and $(\theta_2,\mathbf{t}_2)$ as identical if $\theta_1=\theta_2$ and $\exp(2\pi i\mathbf{t}_1\,.\,\mathbf{S})=\exp(2\pi i\mathbf{t}_2\,.\,\mathbf{S})$ for any allowed value of $\mathbf{S}$. Since

$$(\theta,\mathbf{t})^{m'}=(\theta^{m'},\sum_{m=0}^{m'-1}\theta^m\mathbf{t})$$

we obtain

$$F_{(\theta,\mathbf{t})^{m'}}(\mathbf{S})=\exp(2\pi i\sum_{m=0}^{m'-1}\theta^m\mathbf{t}\,.\,\mathbf{S})F(\theta^{-m'}\mathbf{S})\,.$$

If we define a quantity

$$F_m(\mathbf{S})=\frac{1}{n}\sum_{m'=1}^{n}\exp(2\pi imm'/n)F_{(\theta,\mathbf{t})^{m'}}(\mathbf{S}) \tag{1}$$

then we may describe the true electron density as

$$\varrho(\mathbf{r})=\sum_{m=0}^{n-1}\varrho_m(\mathbf{r})$$

and the true structure factor as

$$F(\mathbf{S})=\sum_{m=0}^{n-1}F_m(\mathbf{S})$$

where

$$\varrho_m(\mathbf{r})=\frac{1}{n}\sum_{m'=1}^{n}\exp(-2\pi imm'/n)\varrho\{(\theta,\mathbf{t})^{-m'}\mathbf{r}\} \tag{2}$$

is an apparent electron density giving rise to the structure factor $F_m(\mathbf{S})$.

If $\theta\mathbf{S}=\mathbf{S}$ then $F_{(\theta,\mathbf{t})^{m'}}(\mathbf{S})=\exp(2\pi im'\mathbf{t}\,.\,\mathbf{S})F(\mathbf{S})$ and $F_m(\mathbf{S})=0$ unless $\exp(2\pi i\mathbf{t}\,.\,\mathbf{S})=\exp(2\pi im/n)$ under which condition $F(\mathbf{S})=F_m(\mathbf{S})$ and is the structure factor for the apparent electron density $\varrho_m(\mathbf{r})$.

Now if $(\theta,\mathbf{t})$ is a symmetry element, $\varrho_m(\mathbf{r})\equiv 0$ unless $m=0$, whereas, if $(\theta,\mathbf{t})$ is a pseudosymmetry element, $\varrho_0(\mathbf{r})$ is the electron density assuming the pseudosymmetry is real. The components $F_m(\mathbf{S})$ of the structure factor may be associated with the components $\varrho_m(\mathbf{r})$ of the electron density which describe the asymmetry.

If the pseudosymmetry element is the inversion operator $(\bar{1},0)$ then $F_0(\mathbf{S})=\frac{1}{2}\{F(\mathbf{S})+F(-\mathbf{S})\}$ and $F_1(\mathbf{S})=\frac{1}{2}\{F(\mathbf{S})-F(-\mathbf{S})\}$ corresponding to $\frac{1}{2}\{\varrho(\mathbf{r})+\varrho(-\mathbf{r})\}$ and $\frac{1}{2}\{\varrho(\mathbf{r})-\varrho(-\mathbf{r})\}$ respectively. To allow for anomalous scattering it is convenient to use an operator $K(\bar{1},0)$ where the operator K changes the scattering density to its complex conjugate.

Thus $F_0(\mathbf{S})=A(\mathbf{S})$ corresponding to $\frac{1}{2}\{\varrho(\mathbf{r})+\varrho(-\mathbf{r})^*\}$ and $F_1(\mathbf{S})=iB(\mathbf{S})$ corresponding to $\frac{1}{2}\{\varrho(\mathbf{r})-\varrho(-\mathbf{r})^*\}$.

The number of pseudosymmetry elements is always an integral multiple of the number of true symmetry elements and any pseudosymmetry element is describable with appropriate choice of origin as a product of symmetry and pseudosymmetry elements $(\theta_3,\mathbf{t}_3)$ $(\theta_2,\mathbf{t}_2)$ $(\theta_1,\mathbf{t}_1)$ $(\theta_0,\mathbf{t}_0)$ where $(\theta_0,\mathbf{t}_0)$ is a real symmetry element and the other operators are either the identity element $(1,0)$ or else a pseudosymmetry element of definite type. $(\theta_1,\mathbf{t}_1)$ may be a pseudosymmetry element which if real would increase the Laue symmetry of the space group and $(\theta_1,\mathbf{t}_1)^n=(1,0)$ under the conditions of closure for every value of n for which $\theta_1^n=1$. $(\theta_2,\mathbf{t}_2)$ may be the operator $(\bar{1},0)$ and $(\theta_3,\mathbf{t}_3)$ may be $(1,\mathbf{t}_3)$ where

$\mathbf{t}_3 . \mathbf{S}$ may be nonintegral for allowed values of $\mathbf{S}$. Since $(\bar{1},\mathbf{t}_1)(\bar{1},\mathbf{t}_2)=(1,\mathbf{t}_1-\mathbf{t}_2)$ only one pseudo or real inversion operator need be included and this may be placed at the origin.

If the pseudosymmetry operator $K(\bar{1},0)$ is used instead of $(\bar{1},0)$ when applicable, then the pseudosymmetry operators just described each have a mutually independent way of obtaining $F_m(\mathbf{S})$ values. We may always form an invariant subgroup from generators of the type $(\theta_0,\mathbf{t}_0)$ and $(\theta_1,\mathbf{t}_1)$ with an Abelian factor group obtained from generators of the type $(\theta_2,\mathbf{t}_2)$ and $(\theta_3,\mathbf{t}_3)$. This implies that the limited factor groups permitted by our restricted choice of $(\theta_2,\mathbf{t}_2)$ and $(\theta_3,\mathbf{t}_3)$ are of no consequence in understanding the problem. Initial operation by generators of the type $(\theta_0,\mathbf{t}_0)$ and $(\theta_1,\mathbf{t}_1)$ only change the value of $\mathbf{S}$ being considered.

(i) *The pseudosymmetry operator* $(1,\mathbf{t})$

$\theta\mathbf{S}=\mathbf{S}$ for all data when $(\theta,\mathbf{t})$ is the pseudotranslational operator $(1,\mathbf{t})$ so that $F_m(\mathbf{S})=0$ unless $\exp(2\pi i\mathbf{t}.\mathbf{S})=\exp(2\pi im/n)$ when $F_m(\mathbf{S})=F(\mathbf{S})$. n is the order of the symmetry operation $(1,\mathbf{t})$. If disordering over atom sites is used to describe $\varrho_0(r)$ which is the Fourier transform of $F_0(\mathbf{S})$ then this model is incapable of phasing data for which $\mathbf{t}.\mathbf{S}$ is non-integral.

(ii) *The pseudosymmetry operator* $(\bar{1},0)$

The pseudosymmetry may cause extra reflexions when $\theta\mathbf{S}=\mathbf{S}$ for some θ (*e.g.* space group $P2$ instead of $P2/c$). In this instance a pseudosymmetry operator $(\theta,\mathbf{t})$ exists which is a product of a real symmetry element and $(\bar{1},0)$ and $\mathbf{t}.\mathbf{S}$ may be non-integral. $(\theta,\mathbf{t})$ is necessarily of order 2. When $\theta\mathbf{S}=\mathbf{S}$ and $\mathbf{t}.\mathbf{S}$ is integral then $F(\mathbf{S})=F(-\mathbf{S})$ so that $F_1(\mathbf{S})$ is zero and when $\theta\mathbf{S}=\mathbf{S}$ and $\mathbf{t}.\mathbf{S}$ is half integral $F(\mathbf{S})=F(-\mathbf{S})$ so that $F_0(\mathbf{S})$ is zero.

If no extra reflexions are possible (*e.g.* space group $Pna2_1$ instead of $Pnma$) then there is always a choice between a disordered structure of electron density $\varrho_0(\mathbf{r})$ and an ordered structure of electron density $\varrho(\mathbf{r})=\varrho_0(\mathbf{r})+\varrho_1(\mathbf{r})$. $F_1(\mathbf{S})$ cannot be phased from $F_0(\mathbf{S})$ and, when no extra reflexions occur as a result of pseudosymmetry not being real, the reality of $\varrho_1(\mathbf{r})$ can only be established by tests for physical effects associated with the non-centrosymmetric space group or by significant improvement in the matching of observed and calculated values of $F(\mathbf{S})$. This makes low-intensity data and extra reflexions very important since only then can $F_1(\mathbf{S})$ greatly affect the magnitude of $F(\mathbf{S})$. Likewise if $(\theta,\mathbf{t})$ is a real or pseudosymmetry element, data for reflexions with $\theta\mathbf{S}=\mathbf{S}$ and $\mathbf{t}.\mathbf{S}$ integral are very important as these data are free of any error associated with $F_1(\mathbf{S})$.

(iii) *The simultaneous existence of pseudosymmetry operators* $(1,\mathbf{t})$ *and* $(\bar{1},0)$

Alternative factor groups of pseudosymmetry operators which do not alter the Laue symmetry are describable as a product of various powers of the generators $(1,\mathbf{t})$, $(\bar{1},0)$ and a real symmetry element $(\theta_0,\mathbf{t}_0)$ where $(\theta_0,\mathbf{t}_0)$ is of order 2. These alternative factor groups are Abelian. Consequently if n is the order of the Abelian factor group then by using the operator K in conjunction with $(\bar{1},0)$ we can identify components $F_m(\mathbf{S})$, $m=1$ to n where $F_m(\mathbf{S})$ is either zero, the real or the imaginary component of $F(\mathbf{S})$. If $F(\mathbf{S})$ is the Fourier transform of $\varrho(r)$ then $F^*(S)$ is the Fourier transform of $K(\bar{1},0)\,\varrho(\mathbf{r})=\varrho^*(-\mathbf{r})$. K_2ZnCl_4 (Klug & Sears, 1945; Dix, 1972) has pseudosymmetry generators $(1,\mathbf{a}/3)$ and $(\bar{1},0)$ and space group $Pna2_1$. The factor group may alternatively be described by the generator $K(m_c,\mathbf{a}/3+\mathbf{c}/2)$ where the mirror operation m_c changes z to $-z$. From (1) we obtain

$$\begin{aligned}F_m(hkl)&=\tfrac{1}{6}[1+2\cos\{2\pi(m+h)/3\}]\,[F(hkl)\\&\quad+(-1)^{l+m}F^*(\bar{h}\bar{k}l)]\\&=\tfrac{1}{6}[1+2\cos\{2\pi(m+h)/3\}]\,[F(hkl)\\&\quad+(-1)^{m}F^*(hkl)]\,,\end{aligned}$$

which is the same result as would be obtained with generators $(1,\mathbf{a}/3)$ and $K(\bar{1},0)$ separately.

(iv) *Pseudosymmetry elements which if real would increase the Laue symmetry*

Pseudo-equivalent reflexions are of different intensity and the symmetry may be resolved by initial phasing from the model $\varrho_0(\mathbf{r})$ and simply removing constraints on certain positional, occupancy and temperature parameters. It is the difference in amplitudes of pseudo-equivalent reflexions which resolves the asymmetry. If the cyclic subgroup of the pseudosymmetry generator is of an order n, where n is not a prime number, then there may be a subgroup of n' true symmetry elements (*e.g.* space group $P2_1$ rather than $P4_1$). In this case $F_m(\mathbf{S})$ is zero if $m\neq0$ unless mn'/n is non-integral and only those values of $F_{(\theta,\mathbf{t})m'}(\mathbf{S})$ with $m'n'/n$ non-integral need be included in the evaluation of $F_m(\mathbf{S})$ from (1).

Least-squares refinement

In the application of any iterative procedure the time per refinement cycle is an important factor which is weighed against the benefits to be obtained by optimizing the refinement per cycle. Consequently in deriving least-squares equations certain terms are assumed to be zero. The nature of these assumptions determines the form of the least-squares equations. Equations derived in a previous paper (Rae, 1974*a*) are subject to such limitations. Least-squares estimates $\hat{u}_j$ of true parameters $\bar{u}_j$ were obtained by minimizing $\sum_h \Delta_h^* w_h \Delta_h$, where Δ_h is the complex quantity $(F_o)_{0h}-(F_c)_h$ and w_h^{-1} is the expectation value of $|\Delta_h|^2$ when $u_j=\bar{u}_j$ in the approximation $\Delta_h=\Delta_{0h}-\sum_j a_{hj}[u_j-(u_j)_0]$ where $a_{hj}=(\partial F_c/\partial u_j)_{0h}=(\partial A_c/\partial u_j)_{0h}+i(\partial B_c/\partial u_j)_{0h}$. The subscript 0 implies evaluation involving parameters $(u_j)_0$ and the subscript h implies the hth of n observables (the hth value of **S** in a crystallographic context). In matrix notation the equations are $A\Delta u = B$ where

$$A_{ij} = \tfrac{1}{2} \sum_h (a^*_{hi} w_h a_{hj} + a_{hi} w_h a_{hj}{}^*) ,$$

$$B_i = \tfrac{1}{2} \sum_h (a^*_{hi} w_h \Delta_{0h} + a_{hi} w_h \Delta^*_{0h}) ,$$

and $\Delta u_j = u_j - (u_j)_0$.

If $\bar{\alpha}_h$ is the phase of $(F_o)_h$ and α_{0h} is the phase of $(F_c)_{0h}$ then we may describe Δ_h as $\Delta'_h + i\Delta''_h$ where Δ'_h is the component of Δ_h in the direction of the phase of α_{0h} and Δ''_h is the component at $\pi/2$ to this phase direction. The least-squares equations may be regarded as the equal combination of least-squares equations $A'\Delta u = B'$ and $A''\Delta u = B''$ where

$$A_{ij} = A'_{ij} + A''_{ij}$$

$$B_i = B'_i + B''_i ,$$

$$A'_{ij} = \sum_h a'_{hi} w_h a'_{hj}, A''_{ij} = \sum_h a''_{hi} w_h a''_{hj} ,$$

$$B'_i = \sum_h a'_{hi} w_h \Delta'_{0h} ,$$

$$B''_i = \sum_h a''_{hi} w_h \Delta''_{0h} ,$$

$$\Delta_{0h} = \exp(i\alpha_{0h}) (\Delta'_{0h} + i\Delta''_{0h}) ,$$

$$\Delta'_{0h} = |F_o|_h \cos(\bar{\alpha}_h - \alpha_{0h}) - |F_c|_{0h} ,$$

$$\Delta''_{0h} = |F_o|_h \sin(\bar{\alpha}_h - \alpha_{0h}) ,$$

$$a'_{hi} = \cos \alpha_{0h} (\partial A_c/\partial u_i)_{0h} + \sin \alpha_{0h} (\partial B_c/\partial u_i)_{0h}$$

and

$$a''_{hi} = -\sin \alpha_{0h} (\partial A_c/\partial u_i)_{0h} + \cos \alpha_{0h} (\partial B_c/\partial u_i)_{0h} .$$

The equations $A'\Delta u = B'$ minimize $\sum_h w_h |\Delta'_h|^2$ and the equations $A''\Delta u = \mathrm{B}''$ minimize $\sum_h w_h |\Delta''_h|^2$.

However, $\bar{\alpha}_h$ is unknown and so expectation values of B'_i and B''_i must be estimated enabling estimation of expectation values of Δu_j from equations $A\langle\Delta u\rangle = \langle B'\rangle + \langle B''\rangle$. It is possible to estimate the result of parameter changes by estimating $|F_o|_h \sin(\bar{\alpha}_h - \alpha_{0h})$ as $\sum_j a''_{hj} \langle\Delta u_j\rangle$ making $\langle B''_i\rangle = \sum_j A''_{ij} \langle\Delta u_j\rangle$ so that the equations to solve become $A'\langle\Delta u\rangle = \langle B'\rangle$ where $\langle B'_i\rangle = \sum_h a'_{hi} w_h (|F_o|_h \langle\cos(\bar{\alpha}_h - \alpha_{0h})\rangle - |F_c|_{0h})$. This assumes that the equations $A'\langle\Delta u\rangle = \langle B'\rangle$ and $A''\langle\Delta u\rangle = \langle B''\rangle$ have a unique simultaneous solution. However as pointed out previously (Rae, 1974*b*) and verified experimentally (Rae, Robinson & Rodley, 1975), if $\langle B''\rangle = 0$ and $\langle B'\rangle \neq 0$ then values of $\langle\Delta u\rangle$ given by $\langle\Delta u\rangle = (A' + \lambda A'')^{-1} \langle B'\rangle$ will satisfy the equations $A'\langle\Delta u\rangle = \langle B'\rangle$ since $A''\langle\Delta u\rangle = 0$ is a redundancy relationship. These values also satisfy $A\langle\Delta u\rangle = \langle B'\rangle$. If we assume $\langle\cos(\bar{\alpha}_h - \alpha_{0h})\rangle = 1$ for all data then $\langle B''\rangle \equiv 0$ and we only obtain one of many equivalent solutions of $A'\langle\Delta u\rangle = \langle B'\rangle$, customarily choosing the solution corresponding to $\lambda = 0$. If the solution corresponding to $\lambda = 1$ is used instead, parameter shifts are damped, minimizing the change in phase and allowing the refinement of centrosymmetric structures in non-centrosymmetric space groups. In the light of these observations a reappraisal of the estimation of the covariance matrix is obviously required and is considered later.

Modifications to the least-squares equations

A feature of the equations derived by Rae (1974*a*) is the apparent assumption that either $\langle |D'_h|^2\rangle = \langle |D''_h|^2\rangle$ or $D''_h \equiv \Delta''_h \equiv 0$ since equal weights are given the hth observable for inclusion in the component equations $A'\langle\Delta u\rangle = \langle B'\rangle$ and $A''\langle\Delta u\rangle = \langle B''\rangle$. D'_h and D''_h are the values of Δ'_h and Δ''_h respectively when $u_j = \bar{u}_j$ for all j. This is obviously untrue as errors in phase contribute mainly to D''_h while errors in amplitude contribute mainly to D'_h. By choosing new residuals which are linear combinations of old residuals we can alter the form of the least-squares equations since different combinations of terms are assumed to be zero. For example, components $F_m(\mathbf{S})$ rather than $F(\mathbf{S})$ values themselves could be used where the $F_m(\mathbf{S})$ values are constructed as in (1) from pseudo-equivalent reflexions.

We wish to minimize the variance in a function $f - f_0 = \sum_j d_j [u_j - (u_j)_0]$ where $\bar{f}$ is the true value of f corresponding to parameters $u_j = \bar{u}_j$ and $\hat{f}$ is the value of f corresponding to $u_j = \hat{u}_j$. The $\hat{u}_j$ values are obtained from least-squares equations involving residual $\Delta_h = (F_o)_{0h} - (F_c)_h$ where $(F_c)_h = (F_c)_{0h} + \sum_j a_{hj} [u_j - (u_j)_0]$ and $a_{hj} = (\partial F_c/\partial u_j)_{0h}$. We assume that $\hat{f} - \bar{f}$ may be written as

$$\hat{f} - \bar{f} = \sum_j d_j (\hat{u}_j - \bar{u}_j) = \sum_h C_h D_h = \sum_h C_h a_{hj} (\hat{u}_j - \bar{u}_j)$$

where D_h is the value of Δ_h corresponding to $u_j = \bar{u}_j$ and $d_j = \sum_h C_h a_{hj}$. Both D_h and D^*_h should be included on the list of residuals since if the C_h parameters are chosen so that the best least-squares estimate of $\hat{f} - \bar{f}$ is $\sum_h C_h D_h$ then the best least-squares estimate of $\hat{f}^* - \bar{f}^*$ is $\sum_h C^*_h D^*_h$.

The variance of $\hat{f}$ is defined as $\mathrm{var}(\hat{f}) = \langle (\hat{f} - \bar{f})^* (\hat{f} - \bar{f}) \rangle$. Simplification of the problem at this initial stage is made by assuming

$$\langle \sum_{h_1 \neq h_2} D^*_{h_2} D_{h_1} C^*_{h_2} C_{h_1} \rangle = 0 ,$$

making $\mathrm{var}(\hat{f}) = \langle \sum_h |C_h|^2 |D_h|^2 \rangle$. The weights in the subsequently derived least-squares equations are given by $w_h^{-1} = \langle |D_h|^2 \rangle$ so that the form of the resulting equations depends on what we regard as a residual, new residuals being describable as linear combinations of old residuals. In particular D_h may be described as $\exp(i\beta_h) (D'_h + iD''_h)$ where

$$2D'_h = \exp(-i\beta_h) D_h + \exp(i\beta_h) D^*_h$$

and

$$2iD''_h = \exp(-i\beta_h) D_h - \exp(i\beta_h) D^*_h$$

so that residuals D_h and D_h^* may be replaced by residuals D_h' and D_h'' where both D_h' and D_h'' are real. β_h may be chosen to have any value. Thus an alternative approximation to var (f) is $\langle\sum\limits_h|C_h'|^2|D_h'|^2+\sum\limits_h|C_h''|^2|D_h''|^2\rangle$ assuming the sum of the remaining terms to be zero. If D_h'' is necessarily zero we assume $C_h''=0$.

We minimize

$$\text{var}\,(\hat{f})-\sum_j\{\lambda_j(\sum_h C_ha_{hj}-d_j)+\lambda_j^*(\sum_h C_h^*a_{hj}^*-d_j^*)\}$$

where Lagrange multipliers λ_j enable the evaluation of C_h values under the constraint $d_j=\sum\limits_h C_ha_{hj}$. For var $(\hat{f})$ to be a minimum ∂ var $(\hat{f})/\partial C_h=0$ implying

$$\langle|D_h|^2\rangle C_h^*=\sum_j\lambda_ja_{hj}$$

and

$$\text{var}\,(\hat{f})=\sum_j\lambda_jd_j=\sum_j\lambda_j^*d_j^*\,.$$

Thus

$$d_j=\sum_i\lambda_i^*A_{ij}\text{ where }A_{ij}=\sum_h a_{hi}^*a_{hj}/\langle|D_h|^2\rangle$$

making

$$\lambda_i^*=\sum_j d_j(A^{-1})_{ji}$$

and

$$C_h=\sum_{ij}d_j(A^{-1})_{ji}a_{hi}^*/\langle|D_h|^2\rangle\,.$$

It follows that

$$\sum_j d_j(\hat{u}_j-\bar{u}_j)=\sum_h C_hD_h=\sum_{ij}d_j(A^{-1})_{ji}\bar{B}_i$$

where

$$\bar{B}_i=\sum_h a_{hi}^*D_h/\langle|D_h|^2\rangle\,.$$

This equation is satisfied irrespective of the values of d_j if

$$\sum_j A_{ij}(\hat{u}_j-\bar{u}_j)=\bar{B}_i\,.$$

The minimum value of var $(\hat{f})$ is

$$\sum_i\lambda_i^*d_i^*=\sum_{ij}d_i^*(A^{-1})_{ji}d_j$$

and since

$$\hat{f}-\bar{f}=\sum_j d_j(\hat{u}_j-\bar{u}_j)$$

then

$$M_{ij}=\langle(\hat{u}_i-\bar{u}_i)^*\,(\hat{u}_j-\bar{u}_j)\rangle=(A^{-1})_{ji}=(A^{-1})_{ij}^*\,.$$

Also

$$\langle\bar{B}_i^*\bar{B}_j\rangle=A_{ij}^*$$

since

$$\hat{u}_j-\bar{u}_j=\sum_i(A^{-1})_{ji}\bar{B}_i\,.$$

The inclusion of both D_h and D_h^* in the residual list implies that both A_{ij} and $\bar{B}_i$ are real for real parameters u_j, making

$$A_{ij}=\tfrac{1}{2}\sum_h(a_{hi}^*w_ha_{hj}+a_{hi}w_ha_{hj}^*)$$

and

$$\bar{B}_i=\tfrac{1}{2}\sum_h(a_{hi}^*w_hD_h+a_{hi}w_hD_h^*)\,,$$

where

$$w_h^{-1}=\langle|D_h|^2\rangle\,.$$

Since the parameters $\bar{u}_j$ are unknown, the parameters $\hat{u}_j$ are obtained by extrapolation from parameters $(u_j)_0$ for which there exist residuals Δ_{0h}. The equations become

$$\sum_j A_{ij}\Delta u_j=B_i$$

where

$$\Delta u_j=\hat{u}_j-(u_j)_0$$

and

$$B_i=\sum_h w_ha_{hi}^*\Delta_{0h}\,.$$

We have already seen that the inclusion of residuals D_h and D_h^* enables the choice of alternative residuals D_h' and D_h'' from the transformation $D_h=\exp\,(i\beta_h)\,(D_h'+iD_h'')$ where D_h' and D_h'' are real and β_h is chosen so that D_h' and D_h'' do not covary. Thus if we assume that $\langle\sum\limits_h(|C_h'|^2|D_h'|^2+|C_h''|^2|D_h''|^2)\rangle$ is a better approximation to var $(\hat{f})$ than is $\langle\sum\limits_h|C_h|^2|D_h|^2\rangle$, then

$$A_{ij}=A_{ij}'+A_{ij}''\,,\ \ B_i=B_i'+B_i''\,,$$

where

$$A_i'=\sum_h a_{hi}'w_h'a_{hj}'\,,\ \ A_{ij}''=\sum_h a_{hi}''w_h''a_{hj}''\,,$$

$$B_i'=\sum_h a_{hi}'w_h'\Delta_{0h}'\,,\ \ B_i''=\sum_h a_{hi}''w_h''\Delta_{0h}''$$

and

$$w_h'=1/\langle|D_h'|^2\rangle$$

need not equal

$$w_h''=1/\langle|D_h''|^2\rangle\,. \qquad (3)$$

If we assume β_h is α_{0h} the phase of $(F_c)_h$ for initial parameters $(u_j)_0$, then the assumption that $A'\langle\Delta u\rangle=\langle B'\rangle$ and $A''\langle\Delta u\rangle=\langle B''\rangle$ have a unique simultaneous solution is satisfied by solving the equations $A'\langle\Delta u\rangle=\langle B'\rangle$ and redefining the phase of $(F_o)_h$ to satisfy $A''\langle\Delta u\rangle=\langle B''\rangle$. However the concept of a unique simultaneous solution cannot be justified, as has been shown experimentally (Rae, Robinson & Rodley, 1975), the solution obtained being dependent on the initial parameters, and hence on the initial choice of phase. This is accentuated in the case where a crystal is almost centrosymmetric and the equations $A'\langle\Delta u\rangle=\langle B'\rangle$ are almost ill-conditioned.

Estimation of variances and covariances

The equations

$$(A'+A'')\,(\hat{u}-\bar{u})=\bar{B}'+\bar{B}''$$

were derived as the correct form of the least-squares equations with variance–covariance matrix

$$M=(A'+A'')^{-1}\,.$$

Implicit in this statement is the understanding that

$$A'(\hat{u}-\bar{u})=\bar{B}' \text{ and } A''(\hat{u}-\bar{u})=\bar{B}''$$

should not be expected to have simultaneous solutions. However since phases are not experimentally observable they must be determined in a biased way from the refinement itself. Since we have more phases than variables it is possible to constrain the choice of phase so that the equations

$$A'\langle\Delta u\rangle=\langle B'\rangle \text{ and } A''\langle\Delta u\rangle=\langle B''\rangle$$

have simultaneous solutions with $\langle B''\rangle=0$. This will not give a unique solution since $A''\langle\Delta u\rangle=0$ is now a redundancy condition so that the solution obtained depends on the value of the matrix λ in the equations

$$(A'+\lambda A'')\langle\Delta u\rangle=\langle B'\rangle$$

and the initial values of $(u_j)_0$.

Despite this source of systematic error we must still endeavour to estimate

$$M_{ij}=\langle(\hat{u}_i-\bar{u}_i)^*(\hat{u}_j-\bar{u}_j)\rangle\,.$$

Since phases cannot be measured, an unbiased estimate of M_{ij} values should be from equations that do not constrain phase changes. Therefore

$$A''(\hat{u}-\bar{u})=\langle\bar{B}''\rangle=0$$

is subtracted from the least-squares equations to give

$$A'(\hat{u}-\bar{u})=\bar{B}'+\bar{B}''=\bar{B}$$

and thus

$$M_{ij}=\sum_{kl}(A'^{-1})_{ik}\langle\bar{B}_k\bar{B}_l\rangle(A'^{-1})_{lj}\,,$$

where

$$\langle\bar{B}_k\bar{B}_l\rangle=A_{kl}=A'_{kl}+A''_{kl}\,,$$

provided a correct weighting scheme is used.

This concept may be generalized to the case where weights w'_h and w''_h in (3) may not be correct and where certain linearly independent parameters $u_j, j=m+1$ to m' are excluded from the least-squares equations. The first m least-squares equations using the correct weighting scheme and all refinable parameters may be written as

$$\sum_{j=1}^{m}A_{ij}(\hat{u}_j-\bar{u}_j)=\bar{B}_i-\sum_{j=m+1}^{m'}A_{ij}(\hat{u}_j-\bar{u}_j)=\bar{C}_i$$

where $\hat{u}_j=(u_j)_0$ for $j>m$. If the only known contribution to $\bar{C}_i$ is

$$\sum_{j=1}^{m}(A_0)_{ij}(\hat{u}_j-\bar{u}_j)\,,$$

then the unknown contribution is estimated as

$$\sum_{j=1}^{m'}(A-A_0)_{ij}(\hat{u}_j-\bar{u}_j)=0$$

and, to exclude this unbiased estimate as a constraint on the solution, the equations are subtracted to give

$$\sum_{j=1}^{m}(A_0)_{ij}(\hat{u}_j-\bar{u}_j)=\bar{C}_i$$

and hence $M=A_0^{-1}(1+\lambda)$ if we say

$$\begin{aligned}\langle\bar{C}_k\bar{C}_l\rangle&=A_{kl}+\sum_{i,j=m+1}^{m'}A_{ki}\langle(\hat{u}_i-\bar{u}_i)\,(\hat{u}_j-\bar{u}_j)\rangle A_{jl}\\&=[(1+\lambda)A_o]_{kl};\ k,l=1 \text{ to } m\,. \qquad (4)\end{aligned}$$

Because of these considerations there is an extremely good argument for using constrained refinement, holding certain structural features to agree with what is expected, and only when such refinement is complete to allow those parameters which permit deviation from expectation to be refined. The use of equations $(A'+A'')\langle\Delta u\rangle=\langle B'\rangle$ will reduce the shifts then obtained compared with the use of equations $\Delta'\langle\Delta u\rangle=\langle B'\rangle$. The equations $A'\langle\Delta u\rangle=\langle B'\rangle$ are of course almost twice as fast to use and allow faster convergence as they imply that $A'\langle\Delta u\rangle=\langle B'\rangle$ and $A''\langle\Delta u\rangle=\langle B''\rangle$ have simultaneous solutions, which, although not exactly true, is a good approximation in the early stages of refinement. It is difficult to see how minor deviations from equivalence in bond lengths and angles can be considered significant if initial constrained refinement making this equivalence exact has not been used. Constrained refinement actually reduces computing time per cycle and there seems no reason why sophisticated constraint refinements should not come into more general use.

Weighting schemes

As has been pointed out (Rae, 1974*a*) the estimation of $w_h=\langle|D_h|^2\rangle^{-1}$ values involves the estimation of three components, E_1 the error in the amplitude of $(F_o)_{0h}$, E_2 the error in the phase of $(F_o)_{0h}$ and E_3 the systematic error involved in the model

$$F_h=(F_o)_{0h}+\sum_j a_{hj}[\bar{u}_j-(u_j)_0]$$

to estimate the true value $\bar{F}_h$ of the hth observable quantity since

$$D_h=(F_o)_{0h}-F_h=E_1+E_2+E_3$$

where

$$E_1=(|F_o|_h-|\bar{F}_h|)\bar{F}_h/|\bar{F}_h|\ ,\ E_2=(F_o)_{0h}-\bar{F}_h|F_o|_h/|\bar{F}_h|$$

and

$$E_3=\bar{F}_h-F_h\ .$$

The inverse of the variance in the phase direction α_h may be described as $1/\sigma^2=\cos^2(\alpha_h-\beta_h)/\sigma^2_{1h}+\sin^2(\alpha_h-\beta_h)/\sigma^2_{2h}$ where β_h is the phase direction of the principal axis σ^2_{1h} of the variance–covariance matrix of D_h. Since the error in the amplitude of $(F_o)_{0h}$ is a maximum in the phase direction of $(F_o)_{0h}$, it may be presumed that $\beta_h=\alpha_{0h}$ so that in (3) $w'_h=1/\sigma^2_{1h}$ and $w''_h=1/\sigma^2_{2h}$. We must estimate $\langle B'_i\rangle$ with estimates $\langle\Delta'_{0h}\rangle=|F_o|_h\langle\cos\alpha_{0h}-\bar{\alpha}_h)\rangle-|F_c|_{0h}$ while we estimate $\langle B''_i\rangle$ as zero. The values of σ^2_{1h} and σ^2_{2h} are estimated as

$$\sigma^2_{ih}=\langle|E_1|^2+|E_2|^2+|E_3|^2\rangle_i\ ,\ i=1,2$$

where

$$\langle|E_1|^2\rangle_1=\langle\cos^2(\alpha_{0h}-\bar{\alpha}_h)\rangle\sigma^2(|F_o|_h)\ ,$$
$$\langle|E_1|^2\rangle_2=\langle\sin^2(\alpha_{0h}-\bar{\alpha}_h)\rangle\sigma^2(|F_o|_h)\ ,$$
$$\langle|E_2\rangle_1|^2=|F_o|^2_h\langle\{\cos(\alpha_{0h}-\bar{\alpha}_h)-\langle\cos(\alpha_{0h}-\bar{\alpha}_h)\rangle\}^2\rangle$$
$$=|F_o|^2_h(\langle\cos^2(\alpha_{0h}-\bar{\alpha}_h)\rangle-\langle\cos(\alpha_{0h}-\bar{\alpha}_h)\rangle^2)\ ,$$

and

$$\langle|E_2|^2\rangle_2=|F_o|^2_h\langle\sin^2(\alpha_{0h}-\bar{\alpha}_h)\rangle\ . \qquad (5)$$

To evaluate the expectation values of geometric functions of $\alpha_{0h}-\bar{\alpha}_h$ it is helpful to attribute a variance–covariance matrix to $(F_c)_{0h}$ since the parameters $(u_j)_0$ are only estimates of the true parameters u_j. If we assume the quantities $X=[(F_o)_h-(F_c)_{0h}]/\sigma_h$ all belong to the same normal distribution, where σ^2_h is var $(F_c)_{0h}$ in the phase direction of $(F_o)_h-(F_c)_{0h}$, where $(F_o)_h=|F_o|_h\exp i\bar{\alpha}_h$, then we can allow $\alpha=\alpha_{0h}-\bar{\alpha}_h$ to vary over the range 0–2π and so evaluate the expectation values of functions of α as

$$\langle f(\alpha)\rangle=\int_0^{2\pi}P(\alpha)f(\alpha)\mathrm{d}\alpha\Big/\int_0^{2\pi}P(\alpha)\mathrm{d}\alpha\ .$$

$P(\alpha)$ varies as $\exp(-|X|^2/2)$ and so varies as $\exp\{Y\times(\cos\alpha-1)\}$ where $Y=|F_o|_h|F_c|_h/\sigma^2_h$.

If we assume that our initial structural model is unbiased, then any atom has equal probability of being displaced in any direction from its true position for the evaluation of $(F_c)_{0h}$, there being no correlation between the displacements of non-symmetry-related atoms. There are then just two simple cases to consider:

(1) $P(\alpha)=0$ unless $\alpha=0,\pi$, and

(2) σ^2_h and hence Y is constant with changing α.

In case (1)

$$\langle\cos\alpha\rangle=1-2/(1+\exp 2Y)\ ,\ \langle\cos^2\alpha\rangle=1$$

and

$$\langle(\cos\alpha-\langle\cos\alpha\rangle)^2\rangle=1-\langle\cos\alpha\rangle^2\ .$$

In case (2) $\langle\cos\alpha\rangle=Y\langle\sin^2\alpha\rangle$ but $\langle\cos\alpha\rangle$ must be evaluated numerically. For small values of $Y(Y<0{\cdot}1)$ $\langle\cos^2\alpha\rangle=\langle\sin^2\alpha\rangle=0{\cdot}5$, while for large values of $Y(Y>100)\langle\cos\alpha\rangle=1{\cdot}0$. Tabulated values of $\langle\cos\alpha\rangle$ are given in Table 1. Values of $\langle|E_2|^2\rangle_1$ and $\langle|E_2|^2\rangle_2$ [see (5)] are $\sigma^2_h g_1|F_o|_h/|F_c|_{0h}$ and $\sigma^2_h g_2|F_o|_h/|F_c|_{0h}$ respectively where $g_1=Y\langle(\cos\alpha-\langle\cos\alpha\rangle)^2\rangle$ and for case (2) $g_2=Y\langle\sin^2\alpha\rangle=\langle\cos\alpha\rangle$. We note the discrimination in favour of data with $|F_c|_{0h}>|F_o|_h$.

Table 1. *Values of* $\langle\cos\alpha\rangle$ *and* $g_1=Y\langle(\cos\alpha-\langle\cos\alpha\rangle)^2\rangle$ *where* $Y=|F_o|_h|F_c|_{0h}/\sigma^2_h$

	Centrosymmetric		Non-centrosymmetric	
$\log_{10} Y$	$\langle\cos\alpha\rangle$	g_1	$\langle\cos\alpha\rangle$	g_1
−1·0	0·100	0·099	0·050	0·050
−0·8	0·157	0·155	0·079	0·079
−0·6	0·246	0·236	0·124	0·123
−0·4	0·378	0·341	0·195	0·188
−0·2	0·559	0·434	0·300	0·274
0·0	0·762	0·420	0·446	0·355
0·2	0·919	0·117	0·616	0·367
0·4	0·987	0·065	0·766	0·271
0·6	0·999	0·003	0·864	0·147
0·8	1·0	0·0	0·917	0·083
1·0	1·0	0·0	0·949	0·050
1·2	1·0	0·0	0·968	0·030
1·4	1·0	0·0	0·980	0·017
1·6	1·0	0·0	0·987	0·010
1·8	1·0	0·0	0·992	0·005
2·0	1·0	0·0	0·995	0·002

The values of $\langle|E_2|^2\rangle_i$, $i=1,2$ for a particular value of $|\mathrm{S}|$ depend upon index conditions. Symmetry related atoms at $\mathbf{r}$ and $\theta\mathbf{r}+\mathbf{t}$ make contributions to $F(\mathrm{S})$ of

$$f(\mathrm{S})T(\mathrm{S})\exp(2\pi i\mathbf{r}\,.\,\mathrm{S})$$

and

$$f(\mathrm{S})T(\theta^{-1}\mathrm{S})\exp\{2\pi i(\mathbf{r}\,.\,\theta^{-1}\mathrm{S}+\mathbf{t}\,.\,\mathrm{S})\}\ ,$$

where $f(S)$ is the scattering factor and $T(\mathrm{S})$ the temperature factor for the atom at $\mathbf{r}$. If $\theta\mathrm{S}\neq\pm\mathrm{S}$ then random variation in $\mathbf{r}$ of individual atoms in the asymmetric unit will show no correlation with equivalent atoms related by the symmetry operation $(\theta,\mathbf{t})$ when this random variation is averaged over all possibilities.

However if $\theta\mathrm{S}=\mathrm{S}$ then $\mathbf{t}\,.\,\mathrm{S}$ must be integral for the reflexion to be observed and two symmetry-related atoms make a contribution of $2f(\mathrm{S})T(\mathrm{S})\exp(2\pi i\mathbf{r}\,.\,\mathrm{S})$ to $F(\mathrm{S})$. If $\theta\mathrm{S}=-\mathrm{S}$ then two symmetry-related atoms make a contribution of

$$f(\mathrm{S})T(\mathrm{S})\exp(2\pi i\mathbf{r}\,.\,\mathrm{S})$$
$$+f(\mathrm{S})T(-\mathrm{S})\exp(-2\pi i\mathbf{r}\,.\,\mathrm{S})\exp(2\pi i\mathbf{t}\,.\,\mathrm{S})$$

to $F(\mathrm{S})$.

If we assume $f(\mathrm{S})T(\mathrm{S})=f(\mathrm{S})T(-\mathrm{S})$ is real, then this contribution may be expressed as $2f(\mathrm{S})T(\mathrm{S})\exp(\pi i\mathbf{t}\,.\,\mathrm{S})\cos(2\pi\mathbf{r}\,.\,\mathrm{S}-\pi\mathbf{t}\,.\,\mathrm{S})$. In both these cases the symmetry-related atoms show perfect correlation in their contribution to $F(\mathbf{S})$. When $\theta\mathbf{S}=\mathbf{S}$ atoms at $\mathbf{r}$ and $\theta\mathbf{r}+\mathbf{t}$ act as double-weight atoms while when $\theta\mathbf{S}=-\mathbf{S}$ atoms at $\mathbf{r}$ and $\theta\mathbf{r}+\mathbf{t}$ act as double-weight atoms for changes in the phase direction $\pi\mathbf{t}.\mathbf{S}$ and as zero-weight atoms for changes in the phase direction $\pi\mathbf{t}.\mathbf{S}+\pi/2$.

Let us consider for example the space group $Pna2_1$: $\theta\mathbf{S}=\mathbf{S}$ for $0kl$ data and the equivalent position $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z$; $\theta\mathbf{S}=\mathbf{S}$ for $h0l$ data and the equivalent position $\frac{1}{2}+x, \frac{1}{2}-y, z$; and $\theta\mathbf{S}=-\mathbf{S}$ for $hk0$ data and the equivalent positions $\bar{x}, \bar{y}, \frac{1}{2}+z$. Thus we have case (1) for $hk0$, $h00$ and $0k0$ with σ_h^2 for a particular value of $|\mathbf{S}|$ having values of $2Z$, $4Z$ and $4Z$ respectively while we have case (2) for hkl, $0kl$, $h0l$ and $00l$ data with σ_h^2 having values of Z, $2Z$, $2Z$ and $4Z$ respectively. If atoms are arranged pseudo-centrosymmetrically in the space group $Pna2_1$ then the assumption that the pseudosymmetry is real would result in all data belonging to case (1) with σ_h^2 for a particular value of $|\mathbf{S}|$ having values of $2Z'$ for hkl data, $4Z'$ for $0kl$, $h0l$ and $hk0$ data, and $8Z'$ for $h00$, $0k0$ and $00l$ data. σ_h^2 may be estimated by assuming $(F_o)_{0h}$ values are correct while the $(F_c)_{0h}$ values are in error since the correct parameters $\bar{u}_j$ have not been used and by assuming that the statistical distribution of $(\varDelta'_{0h})^2$ values is the same as the statistical distribution of σ_h^2 values taking into account the effects of index conditions just discussed. σ_h^2 may be assumed to vary as $\sum\limits_i (f_i(\mathbf{S})T_i(\mathbf{S})|\mathbf{S}|)^2$ where $f_i(\mathbf{S})$ is the scattering factor and $T_i(\mathbf{S})$ the temperature factor of the ith atom.

It remains to consider the systematic error connected with the extrapolation $\bar{F}_h=(F_c)_{0h}+\sum\limits_j a_{hj}[\bar{u}_j-(u_j)_0]$ as an estimate of the true value of the hth observable. The contribution to $\langle|E_3|^2\rangle$ from omitted atoms may be estimated as $\sum\limits_i [f_i(\mathbf{S})T_i(\mathbf{S})]^2$, where i is summed over the omitted atoms. If there are no omitted atoms and it is assumed that all weights are simply out by a multiplying constant, then it may be readily shown that average values of $w'_h|\hat{\varDelta}'_h|^2$ are larger for larger intensities [$\hat{\varDelta}'_h$ is the best least-squares value of the in-phase component of $(F_o)_{0h}-(F_c)_h$]. An example of this characteristic is given by Rae (1974*a*) for K_2ZnCl_4 where a pseudo-translational symmetry element $(1, \mathbf{a}/3)$ causes data with $h\neq 3n$ to be much weaker than data with $h=3n$. For a final R of 0·064

$$\langle w'_h|\hat{\varDelta}'_h|^2\rangle_{h=3n}/\langle w'_h|\hat{\varDelta}'_h|^2\rangle_{h\neq 3n}=6{\cdot}5 \text{ not } 1{\cdot}0$$

when w'_h was determined from counting statistics only. The consequent increased values of variances obtained by an incorrect weighting scheme were also discussed. It is fairly realistic to regard a component of systematic error to be a constant percentage error in the intensity of observed data, the actual percentage being determined to give a correct scale for $\sum\limits_h w'_h|\hat{\varDelta}'_h|^2/(n-m)$.

Discussion

An attempt has been made to use the different weighting schemes and different values of $\langle\cos\alpha\rangle$ implied above to determine whether a structure was ordered, and thus had space group $Pna2_1$, or disordered, and thus had space group $Pnma$ (Rae, Robinson & Rodley, 1975). Definite improvements in R obtained using $\langle\cos\alpha\rangle$ values rather than assuming $\langle\cos\alpha\rangle=1$ are readily understood since data with $|F_c|_{0h}\ll|F_o|_h$ has $|F_o|_h\langle\cos\alpha\rangle\ll|F_o|_h$ while data with $|F_c|_{0h}\gg|F_o|_h$ has $\langle\cos\alpha\rangle=1$.

The structure factor $F(\mathbf{S})=A(\mathbf{S})+iB(\mathbf{S})$ has $A(\mathbf{S})$ corresponding to an apparent electron density $\varrho_0(\mathbf{r})=\frac{1}{2}\{\varrho(\mathbf{r})+\varrho(-\mathbf{r})^*\}$ and $iB(\mathbf{S})$ corresponding to an apparent electron density $\varrho_1(\mathbf{r})=\frac{1}{2}\{\varrho(\mathbf{r})-\varrho^*(-\mathbf{r})\}$.

Only two atoms in the structure need necessarily be disordered to achieve the space group $Pnam$, it being possible to relate one half of the molecule to the other by a mirror plane at $z=\frac{1}{4}$. An apparent substantiation of the space group $Pna2_1$ was initially made, giving a value of $R=0{\cdot}063$ for data with $|F_o|_h>3\sigma(|F_o|_h)$ compared with a value of $R=0{\cdot}074$ for the centrosymmetric space group (Rodley & Robinson, 1972). However a greater degree of freedom was given to the description of $\varrho_0(\mathbf{r})$ for the space group $Pna2_1$, allowing atom sites of symmetry-related atoms to be described by two approximately coincident half-weight atoms. This description of $\varrho_0(\mathbf{r})$ in space group $Pnam$ is not really feasible because constraining phases to be 0 and π makes the least-squares equations ill-conditioned with $\det(A)\equiv 0$ should any half-weight atoms coincide. It is the variation in phase from 0 and π that allows refinement in the space group $Pna2_1$. The contribution of $\varrho_1(\mathbf{r})$ is most significant for weak intensities and so a better data set was collected and all data used to compare the two space groups. It was consequently shown that there is no justification for the space group $Pna2_1$, this interpretation being understood as a counterbalancing of the improvement in the description of $\varrho_0(\mathbf{r})$ with the extra parameters available in space group $Pna2_1$, with the disadvantage of assuming $\varrho_1(\mathbf{r})$ to be non-zero. More detailed discussion is given elsewhere (Rae, Robinson & Rodley, 1975).

Two important details should be considered with relation to problems such as the above. Approximately coincident half-weight atoms as described by $\varrho_0(\mathbf{r})$ show bad covariance between positional and thermal parameters. These problems may be largely overcome in the non-centrosymmetric case by assuming equal isotropic temperature parameters for pseudo-equivalent atoms. However the mismatch in bond lengths and angles may still be bad as may be understood from the earlier discussion of the estimation of variances when certain refinable parameters are omitted from the least-squares equations. Systematic errors in the equal-isotropic-atom assumption cause systematic error in atom positions, this contribution to the error being ignored if we assume

$$\sum_{i,j=m+1}^{m'} A_{ki}\langle(\hat{u}_i-\bar{u}_i)\,(\hat{u}_j-\bar{u}_j)\rangle A_{jl}=0$$

in (4).

In the centrosymmetric case it is impossible to describe $\varrho_0(\mathbf{r})$ by a two-centred description of the probability density of two approximately coincident half-weight atoms. However such a probability density can be most conveniently described as a single-centred description using higher-order cumulants.

Rae (1975) has indicated how three third-order cumulant parameters and six fourth-order cumulant parameters may be used as an alternative to the three extra positional parameters and six extra temperature parameters to describe the electron density distribution as a deviation from the electron density for a single anisotropic atom. The mean of the electron density of two half-weight atoms is the mean of the means of the individual half-weight atoms, and the use of the three third-order cumulant parameters more accurately describes the mean, as it allows the mean and position of maximum probability to be non-coincident, the three parameters describing this displacement. The six fourth-order cumulants allow the electron density at the maximum to be different from that imposed by the single anisotropic atom that best describes the electron density. The seven third-order cumulant parameters omitted are incapable of displacing the mean from the position of maximum probability and the nine fourth-order cumulant parameters omitted are incapable of changing the value of the electron density at the maximum. This approach however does not eliminate covariance problems, the third-order cumulant parameters and the positional parameters being highly covariant, as are the fourth-order cumulant parameters and the anisotropic thermal parameters. It is possible to fit two almost coincident anisotropic atoms to the probability density function described by the cumulant model, but this procedure is very dependent on the accuracy of the higher-order cumulants. Constraints on parameters and their consequent non-inclusion in the least-squares equations can be used to reduce the apparent variances of the remaining parameters, but this advantage can be illusory if the excluded parameters covary with the included parameters and suffer from systematic error.

References

Dix, M. F. (1972). Ph. D. Thesis, University of New South Wales.

Klug, H. P. & Sears, G. W. (1945). *J. Amer. Chem. Soc.* **67**, 878.

Rae, A. D. (1973). *Acta Cryst.* A**29**, 74–77.

Rae, A. D. (1974*a*). *Acta Cryst.* A**30**, 761–768.

Rae, A. D. (1974*b*). *Acta Cryst.* A**30**, 853.

Rae, A. D. (1975). *Acta Cryst.* A**31**, 334–337.

Rae, A. D., Robinson, W. T. & Rodley, G. A. (1975). *Acta Cryst.* B. To be submitted.

Rodley, G. A. & Robinson, W. T. (1972). *Nature, Lond.* **235**, 438–439.

Acta Cryst. (1975). A**31**, 582

The Crystal Symmetry and Powder Pattern of Hexamethylbenzene Below 116 K

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Laue patterns of very thin single-crystal platelets of hexamethylbenzene at a temperature (80 K) below the cold-phase transition (116 K) have been recorded. In this colder phase (Ph. III), whose flat plate pattern is interpretable as a precession photograph because of the probable ordered fragmentation of the sample, the crystal symmetry appears to be hexagonal (or trigonal), as confirmed also by previous optical and spectroscopic observations. The X-ray diffraction spectrum of the powder taken at the same temperature gives 3·59 Å as the distance between the planes containing the molecular rings, and was indexed on the basis of a hexagonal cell with $a=31{\cdot}5$, $c=3{\cdot}59$ Å, containing 12 molecules (probable space group $P6mm$, with all molecules lying in special positions); the length of the basal axis is exactly four times that of the elementary mesh obtained from the hexagonal grid on which the single-crystal pattern lies.

Triclinic crystals of hexamethylbenzene (HMB) (Brockway & Robertson, 1939) undergo a λ-type phase transition at 116 K (Frankosky & Aston, 1965) and until now conclusive structural data on the colder phase (Ph. III) have not been obtained either by X-ray or by neutron diffraction techniques because of the