No theoretical justification has been made, on the other hand, for the use of the pseudo-nolrmaized structure factors E' proposed by Karle & Karle (1966).

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The Phase Problem and its Implications in the Least-squares Refinement of Crystal Structures

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It is found that covariance problems encountered in pseudosymmetric crystal structures are caused by an incorrect use of the least-squares refinement procedure. Rederivation of the least-squares equations for the situation in which the residual need not have the phase angle α or $\alpha+\pi$, where α is the phase angle associated with a trial structure, reveals that the minimization of the component at $\pi/2$ to α has been omitted from the least-squares equations. Inclusion of the extra terms associated with this minimization reveals that it should now be possible to refine a centrosymmetric crystal in an non-centrosymmetric space group. It is also shown that the use of weights derived from counting statistics alone is incorrect and, with a correct weighting scheme, $\sum w\Delta^2/(n-m)$ should reduce to one in a single cycle. The weighting scheme is re-evaluated for further refinement cycles.

Introduction

For the least-squares refinement of single-crystal structures from X-ray diffraction data it has been customary (*International Tables for X-ray Crystallography*, 1959) to minimize the sum of the n weighted squared residuals $S_1=\sum_h w_h(|F_o|_h-|F_c|_h)^2$, where $w_h^{-1}=\text{var}\,(|F_o|_h)$, by solving the equations

$$\sum_j \sum_h w_h \left(\frac{\partial \Delta}{\partial u_i}\right)_{0h} \left(\frac{\partial \Delta}{\partial u_j}\right)_{0h} [u_j-(u_j)_0] = -\sum_h w_h \Delta_{0h} \left(\frac{\partial \Delta}{\partial u_i}\right)_{0h}; \quad i=1 \text{ to } m,$$

where $\Delta=|F_o|-|F_c|$, the difference between the measured and calculated amplitudes. Throughout this paper the subscript h implies the hth observable and the subscript 0 implies evaluation with parameters $(u_j)_0$ of a trial structure. Now for $\Delta=|F_o|-|F_c|$ and $\tan\alpha_0=(B_c/A_c)_0$ we use $(\partial\Delta/\partial u_i)_{0h}=-(\partial|F_c|/\partial u_i)_{0h}=-[\cos\alpha_0(\partial A_c/\partial u_i)_0+\sin\alpha_0(\partial B_c/\partial u_i)_0]_h$.

The application of this procedure reveals two apparent faults. Firstly the assumption that $w_h^{-1}=\text{var}\,(|F_o|_h)$ because $(F_c)_h$ is without error does not produce the expected result that $\sum_h w_h\Delta_h^2=n-m$ in a single cycle. Secondly, in pseudosymmetric structures the apparent variances of parameters u_j are usually in excess of calculated variances (Rae, 1973). This suggests that both the weighting scheme and the actual least-squares equations are at fault. Investigation shows that this hypothesis is indeed true and that the situation may be remedied.

Theory

The least-squares equations

Account should be taken of the fact that we are dealing with quantities $F=A+iB$ that do not have a fixed phase. If $(F_o)_0$ is an initial estimate of the phased quantity F_o for which only the magnitude $|F_o|$ has been experimentally determined, then it is found that a different set of least-squares equations are generated by

considering the minimization of $\sum_h w_h \Delta_h^* \Delta_h$ where Δ_h is the phased quantity $(F_o)_{0h}-(F_c)_h$ rather than the unphased quantity $||F_o|_h-|F_c|_h|$. These equations are seen to minimize S_1+S_2 rather than S_1 where

$$S_1=\sum_h w_h[(A_o-A_c)\cos\alpha_0+(B_o-B_c)\sin\alpha_0]_h^2,$$

$$S_2=\sum_h w_h[-(A_o-Ac)\sin\alpha_0+(B_o-B_c)\cos\alpha_0]_h^2$$

and

$$\tan\alpha_{0h}=(B_c/A_c)_{0h}.$$

$[-(A_o-A_c)\sin\alpha_0+(B_o-B_c)\cos\alpha_0]_h$ is the component of $[(F_o)_0-F_c]_h$ at $\pi/2$ to α_{0h}, the phase of the calculated value $(F_c)_{0h}$ obtained from an initial set of parameters $(u_i)_0$. $S_1+S_2=\sum_h w_h[(A_o-A_c)^2+(B_o-B_c)^2]_h$.

Let us initially ignore the implications of the weighting scheme and minimize S_1+S_2 for a particular weighting scheme, where w_h is real. An estimate of Δ_h is $\hat{\Delta}_h=(F_o)_{0h}-\hat{F}_h$, where $\hat{F}_h$ is an estimate of the quantity $(\hat{F}_c)_h$ associated with the parameters $\hat{u}_i$ in the approximation

$$\hat{F}_h=(F_c)_{0h}+\sum_i a_{hi}[\hat{u}_i-(u_i)_0],$$

where

$$a_{hi}=\left(\frac{\partial F_c}{\partial u_i}\right)_{0h}=\left(\frac{\partial A_c}{\partial u_i}\right)_{0h}+i\left(\frac{\partial B_c}{\partial u_i}\right)_{0h},$$

i.e. $\hat{\Delta}_h=\Delta_{0h}-\sum_i a_{hi}[\hat{u}_i-(u_i)_0]$, where $\Delta_{0h}=(F_o)_{0h}-(F_c)_{0h}$. We select u_i values to minimize $\hat{S}=\sum_h \hat{\Delta}_h^* w_h \hat{\Delta}_h$. An increment in $\hat{S}$ is given by $\sum_{ih}(\delta u_i)^* a_{hi}^* w_h \hat{\Delta}_h+$complex conjugate. If we evaluate the a_{hi} values for real parameters u_i then $\hat{S}$ is a minimum for any real δu_i if

$$\sum_h a_{hi}^* w_h \hat{\Delta}_h+\text{complex conjugate}=0;\ i=1\text{ to }m.$$

These m equations can be expressed as

$$\sum_j A_{ij}[u_j-(u_j)_0]=B_i,$$

where

$$A_{ij}=A_{ji}=\tfrac{1}{2}\sum_h a_{hi}^* w_h a_{hj}+\text{complex conjugate};$$

$$B_i=\tfrac{1}{2}\sum_h a_{hi}^* w_h \Delta_{0h}+\text{complex conjugate}.$$

More explicitly

$$A_{ij}=\sum_h\left(\left(\frac{\partial A_c}{\partial u_i}\right)_{0h} w_h\left(\frac{\partial A_c}{\partial u_j}\right)_{0h}+\left(\frac{\partial B_c}{\partial u_i}\right)_{0h} w_h\left(\frac{\partial B_c}{\partial u_j}\right)_{0h}\right)$$

and

$$B_i=\sum_h\left(\left(\frac{\partial A_c}{\partial u_i}\right)_{0h} w_h(A_o-A_c)_{0h}+\left(\frac{\partial B_c}{\partial u_i}\right)_{0h} w_h(B_o-B_c)_{0h}\right).$$

If $(F_o)_{0h}$ and $(F_c)_{0h}$ are assumed to have the same phase α_{0h} then

$$B_i=\sum(\cos\alpha_{0h}(\partial Ac/\partial u_i)_{0h}+\sin\alpha_{0h}(\partial B_c/\partial u_i)_{0h})w_h(|F_o|_h-|Fc|_{0h}).$$

The weighting scheme

To evaluate the variance–covariance matrix of real parameters $\hat{u}_j$ we need to evaluate $M_{ij}=M_{ji}=\langle(\hat{u}_i-\bar{u}_i)(\hat{u}_j-\bar{u}_j)\rangle$ where $\bar{u}_j$ is the true value of the parameter u_j and the symbol $\langle\ \rangle$ is used to denote expectation values. Now if $\bar{u}_j$ is known then $\hat{u}_j-\bar{u}_j$ can be evaluated without error by putting $(u_j)_0=\bar{u}_j$ in the least-squares equations

$$\sum_j A_{ij}[\hat{u}_j-(u_j)_0]=B_i.$$

Then

$$\hat{u}_j-\bar{u}_j=\sum_k (A^{-1})_{jk}\bar{B}_k$$

without error only if the estimate of the true value $\bar{F}_h$ given by

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

is used to evaluate $\bar{B}_k$, for then we may say

$$(F_o)_{0h}-F_h=\hat{\Delta}_h+\sum_j a_{hj}(\hat{u}_j-\bar{u}_j)$$

where

$$\hat{\Delta}_h=(F_o-F_c)_{0h}-\sum_j a_{hj}[\hat{u}_j-(u_j)_0]$$

so that

$$\bar{B}_k=\tfrac{1}{2}\sum_h(a_{hk}^* w_h\hat{\Delta}_h+a_{hk}w_h\hat{\Delta}_h^*)+\tfrac{1}{2}\sum_{hj}(a_{hk}^* w_h a_{hj}+a_{hk}w_h a_{hj}^*)(\hat{u}_j-\bar{u}_j)=\sum_j A_{kj}(\hat{u}_j-\bar{u}_j)$$

and

$$M_{ij}=\sum_{kl}(A^{-1})_{il}\langle\bar{B}_l\bar{B}_k\rangle(A^{-1})_{kj}.$$

However we do not know $\bar{u}_j$ and the estimation of M_{ij} as $(A^{-1})_{ij}\sigma^2$ implies that $\langle\bar{B}_l\bar{B}_k\rangle=A_{lk}\sigma^2$. If σ^2 is chosen to be $\sum_h w_h\hat{\Delta}_h^*\hat{\Delta}_h/(n-m)$ then we imply that the quantities $w_h^{1/2}[(F_o)_{0h}-F_h]$ all belong to the same distribution with variance σ^2, but imply nothing about the form of this distribution and so significance levels can only be obtained by experimental determination of the distribution from actual $w_h^{1/2}[(F_o)_{0h}-F_h]$ values. However if weights of $\langle|(F_o)_{0h}-F_h|^2\rangle^{-1}$ are estimated and used and $\sum_h w_h\hat{\Delta}_h^*\hat{\Delta}_h=\sum_h w_h\Delta_{0h}^*\Delta_{0h}+2\sum_i B_i[\hat{u}_i-(u_i)_0]$ does not equal $n-m$ then we can say that the estimates of $\langle|(F_o)_{0h}-F_h|^2\rangle$ are wrong.

The rigorous derivation of the correct least-squares equations

A derivation of the correct least-squares equations to solve can be obtained by minimizing the variance

in a function $f-f_0=\sum_j d_j[u_j-(u_j)_0]$ where $d_j=(\partial f/\partial u_j)_0$. If $\bar{f}$ is the true value of f using the true values $\bar{u}_j$, and $\hat{f}$ is the value of f using parameters $\hat{u}_j$ obtained from least-squares equations involving residuals, $D_h=(F_o)_{0h}-F_h$, then

$$\hat{f}-\bar{f}=\sum_j d_j(\hat{u}_j-\bar{u}_j)=\sum_h C_hD_h=\sum_{hj} C_ha_{hj}(\hat{u}_j-\bar{u}_j)$$

where

$$a_{hj}=\left(\frac{\partial F_c}{\partial u_j}\right)_{0h}.$$

$(F_o)_{0h}$ is the observed estimate of the true quantity $\bar{F}_h$ for which calculated estimates are made using $\hat{F}_h=(F_c)_{0h}+\sum_j a_{hj}[\hat{u}_j-(u_j)_0]$. F_h is the estimate of $\bar{F}_h$ using $F_h=(F_c)_{0h}+\sum_j a_{hj}[\bar{u}_j-(u_j)_0]$ since only then can we say $\sum_j C_ha_{hj}(\hat{u}_j-\bar{u}_j)=C_h(\hat{F}_h-F_h)$ and that $\sum_h C_h[(F_o)_{0h}-F_h]=\sum_h C_h(\hat{F}_h-F_h)$ exactly. The C_h coefficients are not unique if n, the number of $(F_o)_{0h}$ values, exceeds m, the number of u_j parameters.

The variance of $\hat{f}$ is $\mathrm{var}\,(\hat{f})=\langle(\hat{f}-\bar{f})^*(\hat{f}-\bar{f})\rangle=\langle\sum_{h_1h_2}(D^*_{h_2}D_{h_1}C^*_{h_2}C_{h_1})\rangle$. It is customary (Hamilton, 1964) at this stage to continue assuming that the problem is a real-number problem, but this assumes that D_h can only have a phase of α or $\alpha+\pi$, so that only the value of D_h in the phase direction of $(F_c)_{0h}$ need be considered. However it is beneficial to assume D_h can have any phase and we shall continue using components parallel (subscript 1) and at $\pi/2$ (subscript 2) to an arbitrary direction.

To find the values of C_h we minimize

$$\mathrm{var}\,(\hat{f})-\sum_j(\lambda_j\sum_h C_ha_{hj}+\lambda^*_j\sum_h C^*_ha^*_{hj})+\sum_j(\lambda_jd_j+\lambda^*_jd^*_j).$$

Since $d_j=\sum_h C_ha_{hj}$ we are still only minimizing var $(\hat{f})$, but the Lagrange multipliers λ_j enable the determination of the C_h values under the constraint $d_j=\sum_h C_ha_{hj}$.

Great simplification is achieved if we choose a scale for our calculations of $(F_c)_h$ either by adding a constant to all $(F_c)_h$ or by multiplying all $(F_c)_h$ by a constant depending on the type of problem, so that $\langle\sum_{h_1\neq h_2} D^*_{h_2}D_{h_1}C^*_{h_2}C_{h_1}\rangle=0$ making var $(\hat{f})=\langle\sum_h|D_h|^2|C_h|^2\rangle$. This will eliminate any correlation between observations and avoid the possibility of having to minimize sums of the form $\sum_{h_1h_2}\Delta^*_{h_2}w_{h_2h_1}\Delta_{h_1}$. For example the n real numbers x_i can be put on such a scale to minimize the variance of $\sum_i(\hat{x}_i-\bar{x}_i)$ by adding $k-\hat{x}$ where $\hat{x}=\sum_i x_i/n$.

Then $\sum_{i\neq j}(x_i+k-\hat{x})\,(x_j+k-\hat{x})=n(n-1)k^2-\sum_i(x_i-\hat{x})^2=0$ if $k=\pm[\sum_i(x_i-\hat{x})^2/n(n-1)]^{1/2}$, *i.e.* the real numbers x_i are put on scale by making $\sum_i x_i=\sum_i\bar{x}_i$. Any dependence of a value for an observation upon any other observation should be included in the model for calculating $(F_c)_h$ by including parameters u_j whose coefficients a_{hj} depend on $(F_o)_{0h}$ values.

A method of notation will be adopted henceforth in which the appropriate subscripts are included in order in brackets after the terms to which the subscripts apply. For example the real part of $\lambda_jC_ha_{hj}=(\lambda_j)_1(C_h)_1(a_{hj})_1-(\lambda_j)_1\,(C_h)_2\,(a_{hj})_2-(\lambda_j)_2\,(C_h)_1\,(a_{hj})_2-(\lambda_j)_2(C_h)_2(a_{hj})_1$ will be written as $\lambda_jC_ha_{hj}$ (111 − 122 − 212 − 221).

From $\dfrac{\partial\ \mathrm{var}\,(\hat{f})}{\partial(C_h)_1}=0$ we obtain

$$\langle|D_h|^2\rangle\,(C_h)_1=\sum_j\lambda_ja_{hj}\ (11-22).$$

From $\dfrac{\partial\ \mathrm{var}\,(\hat{f})}{\partial(C_h)_2}=0$ we obtain

$$\langle|D_h|^2\rangle\,(C_h)_2=-\sum_j\lambda_ja_{hj}\ (12+21).$$

If it is assumed that

$$\sum_h a_{hi}a_{hj}/\langle|D_h|^2\rangle\ (12-21)=0$$

for any i, j it follows that

$$\sum_h C_ha_{hi}\ (11-22)=\sum_j A_{ij}(\lambda_j)_1$$

and that

$$-\sum_h C_ha_{hi}\ (12+21)=\sum_j A_{ij}(\lambda_j)_2$$

where

$$A_{ij}=A_{ji}=\sum_h\langle|D_h|^2\rangle^{-1}a_{hi}a_{hj}\ (11+22)$$
$$=\tfrac{1}{2}\sum_h\langle|D_h|^2\rangle^{-1}\,(a^*_{hi}a_{hj}+a_{hi}a^*_{hj})$$

is independent of the phase chosen for evaluating components. A_{ij} and $(A^{-1})_{ij}$ are real and consequently we do not associate component subscripts 1 and 2 with these quantities.

We now obtain

$$(\lambda_i)_1=\sum_{jh}C_ha_{hj}(A^{-1})_{ji}\ (11-22)$$
$$(\lambda_i)_2=-\sum_{jh}C_ha_{hj}(A^{-1})_{ji}\ (12+21)$$

$$\langle|D_h|^2\rangle\,(C_h)_1=\sum_{ijh'}C_{h'}a_{h'j}(A^{-1})_{ji}a_{hi}\ (111-221+122+212)$$

and

$$\langle|D_h|^2\rangle\,(C_h)_2=\sum_{ijh'}C_{h'}a_{h'j}(A^{-1})_{ji}a_{hi}\ (121+211-112+222).$$

It follows that

$$\sum_j(d_j)_1(\hat{u}_j-\bar{u}_j)=\sum_h(C_hD_h)_1=\sum_h C_hD_h\ (11-22)=\sum_{ij}(d_j)_1(A^{-1})_{ji}\bar{B}_i$$

and

$$\sum_j(d_j)_2(\hat{u}_j-\bar{u}_j)=\sum_h(C_hD_h)_2=-\sum_h C_hD_h\ (12+21)=\sum_{ij}(d_j)_2(A^{-1})_{ji}\bar{B}_i$$

where

$$(d_j)_1=\sum_h (C_h a_{hj})_1=\sum_h C_h a_{hj}\ (11-22),$$

$$(d_j)_2=-\sum_h C_h a_{hj}\ (12+21)$$

and

$$\bar{B}_i=\sum_h \langle|D_h|^2\rangle^{-1} a_{hi} D_h\ (11+22)$$

$$=\tfrac{1}{2}\sum_h \langle|D_h|^2\rangle^{-1}(a^*_{hi}D_h+a_{hi}D^*_h)\ .$$

The equations $\sum_j d_j(\hat{u}_j-\bar{u}_j)=\sum_{ij} d_j(A^{-1})_{ji}\bar{B}_i$ are satisfied if $\sum_j A_{ij}(\hat{u}_j-\bar{u}_j)=\bar{B}_i$ $i=1$ to m irrespective of the values of d_j.

It can also be seen at this stage that the minimum value var $(\hat{f})$ takes up is

$$\sum_{ijhh'}[C_{h'}a_{h'j}\ (11-22)\ (A^{-1})_{ji}a_{hi}C_h\ (11-22)$$
$$+C_{h'}a_{h'j}\ (12+21)\ (A^{-1})_{ji}a_{hi}C_h\ (12+21)]$$
$$=\sum_{ij} d_j(A^{-1})_{ji}d_i\ (11+22)=\sum_{ij} d^*_j(A^{-1})_{ji}d_i\ .$$

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

$$\text{var}\ (\hat{f})=\sum_{ij} d^*_j\langle(\hat{u}_j-\bar{u}_j)\ (\hat{u}_i-\bar{u}_i)\rangle d_i$$

it is seen that cov $(\hat{u}_j, \hat{u}_i)=(A^{-1})_{ji}$ provided the parameters $\hat{u}_j$ are obtained from the least-squares equations $\sum_j A_{ij}[\hat{u}_j-(u_j)_0]=B_i$ where

$$B_i=\tfrac{1}{2}\sum_h\{a^*_i w_h[(F_o)_{0h}-(F_c)_{0h}]+a_{hi}w_h[(F_o)_{0h}-(F_c)_{0h}]^*\},$$

$$A_{ij}=\tfrac{1}{2}\sum_h(a^*_{hi}w_h a_{hj}+a_{hi}w_h a^*_{hj})\ \text{and}\ w_h^{-1}=\langle|D_h|^2\rangle.$$

To do this it is important to preserve the linearity of the residuals and this implies that $D_h=(F_o)_{0h}-F_h$ where $F_h=(F_c)_{0h}+\sum_j a_{hj}\ [u_j-(u_j)_0]$ and is not necessarily the true value $\bar{F}_h$ for two reasons. Firstly the coefficients a_{hj} are evaluated for the parameters $(u_j)_0$, not the parameters $\bar{u}_j$ and any non-linearity of the residuals causes a variation of the coefficient a_{hj} with choice of $(u_j)_0$. Secondly it has been assumed that the model for calculation is correct with all relevant parameters u_j included. It is therefore wrong to say $\langle|D_h|^2\rangle=$ var $(|F_o|_h)$ as this assumes that there is no error in the phase of $(F_o)_{0h}$ and that there is no error in the model $F_h=(F_c)_{0h}+\sum_j a_{hj}\ [\bar{u}_j-(u_j)_0]$ for calculating $\bar{F}_h$ from the true parameters $\bar{u}_j$. It is equally wrong to say that any error not accounted for can be included by saying $\langle|D_h|^2\rangle=\sigma^2$ var $(|F_o|_h)$ where σ^2 is a constant.

Now $D_h=[(F_o)_{0h}-\hat{F}_h]+[\hat{F}_h-F_h]$ where $(F_o)_{0h}-\hat{F}_h=\hat{\Delta}_h=(F_o)_{0h}-(F_c)_{0h}-\sum_j a_{hj}[\hat{u}_j-(u_j)_0]$ and $\hat{F}_h-F_h=\sum_j a_{hj}(\hat{u}_j-\bar{u}_j)$. We readily see that if $\langle\hat{F}_h-F_h\rangle=0$ and $w_h^{-1}=\langle|D_h|^2\rangle$, then

$$\sum_h w_h|D_h|^2=n=\sum_h w_h|\hat{\Delta}_h|^2+\sum_{hij} w_h a^*_{hi}a_{hj}M_{ij}\ .$$

Now the variance–covariance matrix $M_{ij}=(A^{-1})_{ij}$ so that

$$n=\sum_h w_h|\hat{\Delta}_h|^2+\sum_{ij} A_{ij}(A^{-1})_{ij}$$

giving $\sum_h w_h|\hat{\Delta}_h|^2=n-m$ for an ideal weighting system.

Applied to the problem of obtaining the estimate $\hat{x}$ of the true value $\bar{x}$ from a number of observations x_h we see that if we have n equally weighted observations a consistent result is obtained for $\hat{x}=\sum_h x_h/n$, and

$$w_h^{-1}=\sum_h(x_h-\hat{x})^2/n+\sum_h(x_h-\hat{x})^2/n\ (n-1)$$

where

$$\sum_h (x_h-\hat{x})^2/n \text{ is the estimate of } (x_h-\hat{x})^2$$

and

$$\sum_h (x_h-\hat{x})^2/n(n-1)=\text{var}\ (\hat{x})\ .$$

We see that $w_h^{-1}=\sum_h(x_h-\hat{x})^2/(n-1)$ is the estimate of $(x_h-\bar{x})^2$ and since $a_{h1}=1$ we also see that $A_{11}=\sum_h w_h a^2_{h1}$ gives

$$(A^{-1})_{11}=\sum_h (x_h-\hat{x})^2/n(n-1)=\text{var}\ (\hat{x})=\langle(\hat{x}-\bar{x})^2\rangle$$

and that

$$\sum_h w_h(x_h-\hat{x})^2=n-1\ .$$

The estimation of $w_h^{-1}=\langle|D_h|^2\rangle$

We have seen that $D_h=\hat{\Delta}_h+\sum_j a_{hj}(\hat{u}_j-\bar{u}_j)=(F_o)_{0h}-F_h$ where $\hat{\Delta}_h=(F_o)_{0h}-(F_c)_{0h}-\sum_j a_{hj}[\hat{u}_j-(u_j)_0]$. We assume $\langle\hat{u}_j-\bar{u}_j\rangle=0$ which gives $\langle|D_h|^2\rangle=\langle|\hat{\Delta}_h|^2\rangle+\sum_{ij} a^*_{hi}a_{hj}\hat{M}_{ij}$ where $\hat{M}_{ij}$ is an estimate of the variance–covariance matrix. Now the approximate value of $\langle|\hat{\Delta}_h|^2\rangle/\langle|D_h|^2\rangle=(n-m)/n$, so the accuracy of the estimate of $\hat{M}_{ij}$ will not matter too much if $(n-m)/m\gg 1$. An actual value of $\hat{\Delta}_h$ can be obtained by iteration from the initial values $(u_j)_0$. However if the actual value of $|\hat{\Delta}_h|^2$ is used to evaluate $\langle|D_h|^2\rangle$ the refinement will iterate to the point where m values $\hat{F}_h$ have perfect agreement and only those other values of $\hat{F}_h$ which also perfectly agree with $(F_o)_{0h}$ will have a non-zero weight.

It is best to evaluate $\langle|D_h|^2\rangle$ by saying $D_h=(F_o)_{0h}-F_h=E_1+E_2+E_3$ 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 $E_3=\bar{F}_h-F_h$ so that $\langle|D_h|^2\rangle=\langle|E_1|^2+|E_2|^2+|E_3|^2\rangle$, since each of the terms E_1, E_2 and E_3 may be reasonably assumed to show no covariance. $\langle|E_1|^2\rangle$ is simply var $(|F_o|_h)$, $\langle|E_2|^2\rangle$ is the variance associated with the choice of phase of $(F_o)_{0h}$ and E_3 is the systematic error associated with the model $F_h=(F_c)_{0h}+\sum_j a_{hj}[\bar{u}_j-(u_j)_0]$ to estimate $\bar{F}_h$. E_3 will have a contribution due to the variation of the coefficients a_{hj} with choice of $(u_j)_0$ but it is also possible to have a contribution to E_3 due to the inaccuracy of the algebraic form for calculating $(F_c)_h$. In X-ray crystal

structure analyses the omission of atoms, absorption and extinction corrections and the use of isotropic temperature factors and rigid groups of atoms all fall into this category.

The estimation of error in the phase of the observation

We can attribute a variance–covariance matrix to the components of $(F_c)_{0h}=(A_c)_{0h}+i(B_c)_{0h}$ associated with parameters $(u_j)_0$ since $(F_c)_h$ changes to F_h when $(u_j)_0$ changes to $\bar{u}_j$ in the model

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

Since $a_{hj}=(a_{hj})_1+i(a_{hj})_2$ we can say

$$\text{var } (A_c)_{0h}=\sum_{ij}(a_{hi})_1(a_{hj})_1(M_{ij})_0,$$

$$\text{var } (B_c)_{0h}=\sum_{ij}(a_{hi})_2(a_{hj})_2(M_{ij})_0$$

$$\text{and cov } (A_c)_{0h}(B_c)_{0h}=\sum_{ij}(a_{hi})_1(a_{hj})_2(M_{ij})_0$$

$$\text{where } (M_{ij})_0=\langle[(u_i)_0-\bar{u}_i]\,[(u_j)_0-\bar{u}_j]\rangle.$$

$(M_{ij})_0$ can be determined from an initial setting up of the least-squares equations $\sum_j A_{ij}[\hat{u}_j-(u_j)_0]=B_i$ with weights w_{0h}. Then

$$(M_{ij})_0=[\hat{u}_i-(u_i)_0]\,[\hat{u}_j-(u_j)_0]+\text{cov }(\hat{u}_i\hat{u}_j)$$

where cov $(\hat{u}_i\hat{u}_j)$ is

$$(A^{-1})_{ij}\{\sum_h w_{0h}\hat{\Delta}^*_{0h}\hat{\Delta}_{0h}+2\sum_k B_k[\hat{u}_k-(u_k)_0]\}/(n-m).$$

The inverse of the variance in the phase direction α is given by $1/\sigma^2=\cos^2(\alpha-\beta)/\sigma_1^2+\sin^2(\alpha-\beta)/\sigma_2^2$ where β is the phase direction of the principle axis σ_1^2 of the variance–covariance matrix of $(F_c)_{0h}$ given by

$$\tan 2\beta=2\text{ cov }(A_c)_{0h}(B_c)_{0h}/(\text{var }(A_c)_{0h}-\text{var }(B_c)_{0h});$$

$$\sigma_1^2=\cos^2\beta\text{ var }(A_c)_{0h}+\sin^2\beta\text{ var }(B_c)_{0h}+\sin 2\beta\text{ cov }(A_c)_{0h}(B_c)_{0h}$$

$$\text{and }\sigma_2^2=\sin^2\beta\text{ var }(A_c)_{0h}+\cos^2\beta\text{ var }(B_c)_{0h}-\sin 2\beta\text{ cov }(A_c)_{0h}(B_c)_{0h}.$$

This gives

$$\sigma^2=\frac{\text{var }(A_c)_{0h}\text{ var }(B_c)_{0h}-[\text{cov }(A_c)_{0h}(B_c)_{0h}]^2}{\cos^2\alpha\text{ var }(B_c)_{0h}+\sin^2\alpha\text{ var }(A_c)_{0h}-\sin 2\alpha\text{ cov}(A_c)_{0h}(B_c)_{0h}}.$$

If var $(A_c)_{0h}$ var $(B_c)_{0h}=(\text{cov }(A_c)_{0h}(B_c)_{0h})^2$ then $\sigma_2^2=0$ and $\sigma^2=\sigma_1^2$ when $\alpha=\beta$ or $\beta+\pi$ and zero elsewhere. This situation is well known in X-ray crystallography, being the case for all reflexions in crystals having a centre of symmetry and for special reflexions for many other space groups, *e.g.* *h*0*l* data of space group *P*2.

Now

$$E_2=(F_o)_{0h}-\bar{F}_h|F_o|_h/|\bar{F}_h|=|F_o|_h(\exp i\alpha_{0h}-\exp i\bar{\alpha}_h)$$

where the assumed value of the phase angle of $(F_o)_{0h}$ is α_{0h} while the true value of α_h is $\bar{\alpha}_h$, and this makes $\langle|E_2|^2\rangle=|F_o|_h^2[2-2\langle\cos(\alpha_{0h}-\bar{\alpha}_h)\rangle]$. Obviously if $(F_c)_{0h}=0$, $\langle\cos(\alpha_{0h}-\bar{\alpha}_h)\rangle=0$ and $\langle|E_2|^2\rangle=2|F_o|_h^2$ while if $|F_o|_h^2=0$ $|E_2|^2=0$ and we see that this term discriminates in favour of observations for which $|F_o|_h<|(F_c)_{0h}|$.

To evaluate $\langle\cos(\alpha_{0h}-\bar{\alpha}_h)\rangle$, $\bar{\alpha}_h$ is unknown and some probability function is necessary. If we assume that quantities $[(F_o)_h-(F_c)_{0h}]/\sigma$ all belong to the same normal distribution, σ^2 being var $(F_c)_{0h}$ in the direction of $(F_o)_h-(F_c)_{0h}$, then we can allow $\bar{\alpha}_h$ to range over 0–2π and say

$$\langle\cos(\alpha_{0h}-\bar{\alpha}_h)\rangle=\int_0^{2\pi}\cos(\alpha_{0h}-\bar{\alpha}_h)\exp-\frac{X^2}{2}\,d\bar{\alpha}_h\Big/\int_0^{2\pi}\exp-\frac{X^2}{2}\,d\bar{\alpha}_h$$

where

$$X^2=\frac{A^2\text{ var }(B_c)_{0h}+B^2\text{ var }(A_c)_{0h}-2AB\text{ cov }(A_c)_{0h}(B_c)_{0h}}{\text{var }(A_c)_{0h}\text{ var }(B_c)_{0h}-[\text{cov }(A_c)_{0h}(B_c)_{0h}]^2},$$

$A=|F_o|_h\cos\bar{\alpha}_h-(A_c)_{0h}$ and $B=|F_o|_h\sin\bar{\alpha}_h-(B_c)_{0h}$. In the case when $\sigma_2^2=0$, $\cos(\alpha_{0h}-\bar{\alpha}_h)$ can only take values of ±1 and $\langle|E_2|^2\rangle=4|F_o|_h^2/[1+\exp(2|F_c|_{0h}|F_o|_h/\sigma_1^2)]$.

The estimation of systematic error

An amount $\langle|E_3|^2\rangle=\langle|\bar{F}_h-F_h|^2\rangle$ has to be estimated and included in the weight so that $\sum_h w_h\hat{\Delta}^*_h\hat{\Delta}_h=n-m$ after refinement. It is advantageous to distribute this error in a more meaningful way than simply to say that it is a constant. One obvious contribution in an X-ray crystallographic application is $\langle f^2\rangle$ the mean-squared scattering power of any omitted atoms. The most meaningful distribution of error will minimize

$$\sum_h\left(\frac{\hat{\Delta}^*_h\hat{\Delta}_h}{\langle|E_1|^2+|E_2|^2+|E_3|^2\rangle_h}-\frac{n-m}{n}\right)^2$$

and expressing E_3 as a function of three or four variables is a justifiable attempt to locate the cause of systematic error.

Application to X-ray crystallography

The refinement of non-centrosymmetric crystal structures

We see that it has been customary to refine a wrong set of least-squares equations since the component of $(F_o)_{0h}-F_h$ at $\pi/2$ to the phase angle α_{0h} of $(F_c)_{0h}$ has been ignored. It is important that we try to explain the difficulties that are encountered in the refinement of pseudo-centrosymmetric crystal structures. We can

most simply do this in a two-dimensional example in which $(\partial A_c/\partial u_1)_{0h}=(\partial A_c/\partial u_2)_{0h}$ and $(\partial B_c/\partial u_1)_{0h}=-(\partial B_c/\partial u_2)_{0h}$.

The least-squares equations thus obtained have cov $(u_1+u_2)\,(u_1-u_2)=0$ and are

$$\begin{vmatrix} A_1+A_2 & A_1-A_2 \\ A_1-A_2 & A_1+A_2 \end{vmatrix} \begin{vmatrix} u_1-(u_1)_0 \\ u_2-(u_2)_0 \end{vmatrix} = \begin{vmatrix} B_1+B_2 \\ B_1-B_2 \end{vmatrix}$$

where $B_1=\sum_h w_h(\partial A_c/\partial u_1)_{0h}(F_o-F_c)_{0h}\cos\alpha_{0h}$ and $B_2=\sum_h w_h(\partial B_c/\partial u_1)_{0h}(F_o-F_c)_{0h}\sin\alpha_{0h}$ but the values of A_1 and A_2 depend on whether or not the correct equations are used. Using the correct equations $A_1=\sum_h w_h(\partial A_c/\partial u_1)^2_{0h}$ and $A_2=\sum_h w_h(\partial B_c/\partial u_1)^2_{0h}$, while using the incorrect equations $A_1'=\sum_h w_h\cos^2\alpha_{0h}(\partial A_c/\partial u_1)^2_{0h}$ and $A_2'=\sum_h w_h\sin^2\alpha_{0h}(\partial B_c/\partial u_1)_{0h}$ assuming $\sum_h w_h\cos\alpha_{0h}\sin\alpha_{0h}\times(\partial A_c/\partial u_1)_{0h}(\partial B_c/\partial u_1)_{0h}=0$. We can thus say $A_1'=\langle\cos^2\alpha\rangle A_1$ and $A_2'=\langle\sin^2\alpha\rangle\ A_2$ though $\langle\cos^2\alpha\rangle+\langle\sin^2\alpha\rangle=1$ only if $A_1'/A_1+A_2'/A_2=1$. If certain data can only have phase α_h or $\alpha_h+\pi$ then $\langle\cos^2\alpha\rangle+\langle\sin^2\alpha\rangle$ can be greater than one. The solutions of the least-squares equations are

$$\Delta u_1+\Delta u_2=B_1/A_1\,,\quad \Delta u_1-\Delta u_2=B_2/A_2$$

where

$$\Delta u_i=\hat{u}_i-(u_i)_0$$

if the correct equations are used. If the incorrect equations are used these shifts are B_1/A_1' and B_2/A_2' respectively. Thus when the incorrect equations are used the shifts are overemphasized by $1/\langle\cos^2\alpha\rangle$ and $1/\langle\sin^2\alpha\rangle$. The corresponding variances are estimated as being $1/\langle\cos^2\alpha\rangle$ and $1/\langle\sin^2\alpha\rangle$ greater than before also. However these variances are underestimated as we can see using the true parameters $\bar{u}_1$, $\bar{u}_2$ as our starting values of $(u_1)_0$, $(u_2)_0$.

The variances are defined as $\langle(\hat{u}_1+\hat{u}_2-\bar{u}_1-\bar{u}_2)^2\rangle$ and $\langle(\hat{u}_1-\hat{u}_2-\bar{u}_1+\bar{u}_2)^2\rangle$ and are thus $1/\langle\cos^2\alpha\rangle^2$ and $1/\langle\sin^2\alpha\rangle^2$ greater for the incorrect equations than for the correct equations. The correct least-squares equations to use were derived for an expansion about the true values $\bar{u}_1$, $\bar{u}_2$ using coefficient a_{hj} evaluated for $(u_j)_0$. The uncertainty of the phase of $(F_c)_{0h}-F_h$ is not the same as the uncertainty of the phase of $\hat{F}_h-F_h$ and this allows refinement of the incorrect least-squares equations despite the fact that no restraint is imposed on the component of $(F_o)_{0h}-\hat{F}_h$ at $\pi/2$ to α_{0h}. It should be noted that in the example we have used A_1 approximates A_2 and the covariance of parameters u_1 and u_2, which has bedevilled least-squares refinement with the incorrect equations, is largely removed. As a consequence it should now be possible with the correct equations to refine a centrosymmetric structure in a non-centrosymmetric space group since atoms at x, y, z and $\bar{x}$, $\bar{y}$, $\bar{z}$ will no longer have a correlation coefficient of 1. Thus in a space group such as $C2/m$ it will be possible to say more certainly that this is indeed the space group and not $C2$ or Cm.

The refinement of a structure showing pseudo translational symmetry

In a crystal showing pseudo translational symmetry only a simple fraction of the data (*e.g.* $\frac{1}{2}$, $\frac{1}{3}$ *etc.*) will have high average intensity and the ordered nature of the variation from translational symmetry is best determined by the weak data. For example only data with $h=2n+1$ can distinguish between fractional coordinates x and $x+\frac{1}{2}$. When data are weighted according to counting statistics only, it is commonly found that

$\langle 1\rangle$, the value of $\langle w_h|D_h|^2\rangle$ for the $h=2n$ data is greater than

$\langle 2\rangle$, the value of $\langle w_h|D_h|^2\rangle$ for the $h\neq 2n$ data

because of an overestimate of the ability of high-intensity data to refine the structure.

It is of interest to investigate the consequence of this situation. Let us consider a two-parameter problem for fractional coordinates x_1 and x_2 separated by about $\frac{1}{2}$ and cov $[(x_1+x_2)\,(x_1-x_2)]=0$. For $h=2n$ we obtain contributions to the least-squares equations of

$$\begin{vmatrix} A_1 & A_1(1-\delta_1) \\ A_1(1-\delta_1) & A_1 \end{vmatrix} \begin{vmatrix} \Delta x_1 \\ \Delta x_2 \end{vmatrix} = \begin{vmatrix} B_1+b_1 \\ B_1-b_1 \end{vmatrix}$$

where $\Delta x_i=\hat{x}_i-(x_i)_0$. On their own these data give $\Delta x_1+\Delta x_2=2B_1/A_1(2-\delta_1)$ and $\Delta x_1-\Delta x_2=2b_1/A_1\delta_1$ where var $(\Delta x_1+\Delta x_2)=2\langle 1\rangle/A_1(2-\delta_1)$ and var $(\Delta x_1-\Delta x_2)=2\langle 1\rangle/A_1\delta_1$.

For $h\neq 2n$ data we obtain contributions

$$\begin{vmatrix} A_2 & -A_2(1-\delta_2) \\ -A_2(1-\delta_2) & A_2 \end{vmatrix} \begin{vmatrix} \Delta x_1 \\ \Delta x_2 \end{vmatrix} = \begin{vmatrix} B_2+b_2 \\ -B_2+b_2 \end{vmatrix}.$$

On their own these data give $\Delta x_1+\Delta x_2=2b_2/A_2\delta_2$ and $\Delta x_1-\Delta x_2=2B_2/A_2(2-\delta_2)$ where

$$\text{var}\,(\Delta x_1+\Delta x_2)=2\langle 2\rangle/A_2\delta_2$$

$$\text{and var}\,(\Delta x_1-\Delta x_2)=2\langle 2\rangle/A_2(2-\delta_2).$$

If we combine the results of the $h=2n$ and the $h\neq 2n$ data to obtain the minimum variances for the non-covarying parameters x_1+x_2 and x_1-x_2 then we should weight the data as the inverse of the variances. Then

$$\Delta x_1+\Delta x_2=(2B_1\langle 2\rangle+2b_2\langle 1\rangle)/(A_1(2-\delta_1)\langle 2\rangle+A_2\delta_2\langle 1\rangle)$$

$$\text{and } \Delta x_1-\Delta x_2=(2B_2\langle 1\rangle+2b_1\langle 2\rangle)/(A_2(2-\delta_2)\langle 1\rangle+A_1\delta_1\langle 2\rangle)$$

$$\text{where var}\,(x_1+x_2)=2\langle 1\rangle\,\langle 2\rangle/(A_1(2-\delta_1)\langle 2\rangle+A_2\delta_2\langle 1\rangle)$$

$$\text{and var}\,(x_1-x_2)=2\langle 1\rangle\,\langle 2\rangle/(A_1\delta_1\langle 2\rangle+A_2(2-\delta_2)\langle 1\rangle).$$

Combining the two sets of data, ignoring the fact that $\langle 1\rangle\neq\langle 2\rangle$, we obtain

$$\begin{vmatrix} A_1+A_2 & A_1(1-\delta_1)-A_2(1-\delta_2) \\ A_1(1-\delta_1)-A_2(1-\delta_2) & A_1+A_2 \end{vmatrix} \begin{vmatrix} \Delta x_1 \\ \Delta x_2 \end{vmatrix} = \begin{vmatrix} B_1+B_2+b_1+b_2 \\ B_1-B_2-b_1+b_2 \end{vmatrix}$$

giving

$$\Delta x_1+\Delta x_2=\frac{2B_1+2b_2}{A_1(2-\delta_1)+A_2\delta_2},$$

$$\Delta x_1-\Delta x_2=\frac{2B_2+2b_1}{A_1\delta_1+A_2(2-\delta_2)},$$

$$\text{var}\,(\Delta x_1+\Delta x_2)=\frac{\langle 1\rangle+\langle 2\rangle}{A_1(2-\delta_1)+A_2\delta_2}$$

and

$$\text{var}\,(\Delta x_1-\Delta x_2)=\frac{\langle 1\rangle+\langle 2\rangle}{A_1\delta_1+A_2(2-\delta_2)}.$$

These answers are only the same as before if $\langle 1\rangle=\langle 2\rangle$.

The differences in the two answers are given as

$$(\langle 1\rangle-\langle 2\rangle)\frac{[2B_1/A_1(2-\delta_1)-2b_2/A_2\delta_2]A_1(2-\delta_1)A_2\delta_2}{[A_1(2-\delta_1)+A_2\delta_2]\,[A_1(2-\delta_1)\langle 2\rangle+A_2\delta_2\langle 1\rangle]}$$

for $\Delta x_1+\Delta x_2$

and

$$(\langle 1\rangle-\langle 2\rangle)\frac{[2b_1/A_1\delta_1-2B_2/A_2(2-\delta_2)]A_1\delta_1A_2(2-\delta_2)}{[A_1\delta_1+A_2(2-\delta_2)]\,[A_1\delta_1\langle 2\rangle+A_2(2-\delta_2)\langle 1\rangle]}$$

for $\Delta x_1-\Delta x_2$.

Now the true variance from the combined data set is the variance from the minimum-variance combination of the data sets plus the expectation value of the square of the difference in the answers using var $[2B_1/A_1(2-\delta_1)]=2\langle 1\rangle/A_1(2-\delta_1)$ *etc.* and assuming that the covariance of the various contributions B_1, B_2, b_1, b_2 are zero. Thus

$$\text{var}\,(x_1+x_2)=\frac{2\langle 1\rangle\,\langle 2\rangle}{A_1(2-\delta_1)\,\langle 2\rangle+A_2\delta_2\langle 1\rangle}\times\left[1+\frac{A_1(2-\delta_1)A_2\delta_2}{[A_1(2-\delta_1)+A_2\delta_2]^2}\,\frac{(\langle 1\rangle-\langle 2\rangle)^2}{\langle 1\rangle\,\langle 2\rangle}\right]$$

and

$$\text{var}\,(x_1-x_2)=\frac{2\langle 1\rangle\,\langle 2\rangle}{A_1\delta_1\langle 2\rangle+A_2(2-\delta_2)\,\langle 1\rangle}\times\left[1+\frac{A_1\delta_1A_2(2-\delta_2)}{[A_1\delta_1+A_2(2-\delta_2)]^2}\,\frac{(\langle 1\rangle-\langle 2\rangle)^2}{\langle 1\rangle\,\langle 2\rangle}\right].$$

When $\langle 1\rangle>\langle 2\rangle$ the incorrectly estimated variances are too high for $\Delta x_1-\Delta x_2$ and too low for $\Delta x_1+\Delta x_2$. It should be noted that the removal of the $x+\frac{1}{2}$ translational symmetry element halves the number of symmetry elements in the supercell and the implications of non-centrosymmetric refinements discussed earlier are commonly an additional feature of these refinements.

The crystal structure of K_2ZnCl_4 has been investigated (Dix, 1972) and has pseudo translational symmetry elements of $x+\frac{1}{3}$, $x+\frac{2}{3}$ and also a pseudo mirror plane, crystallizing in the space group $Pna2_1$. Using unit weights with discrimination to exclude 10% of the data with low $|F_c|_h<|F_o|_h$ and fractional coordinate shifts proved to be the best initial method of refinement with the conventional but incorrect least-squares equations. Final refinement using weights from counting statistics gave a final value for R of 0·064. At this stage weighting by counting statistics gave

$$\langle w_h|D_h|^2\rangle_{h=3n}/\langle w_h|D_h|^2\rangle_{h\neq 3n}=6\cdot 5 \text{ not } 1\cdot 0.$$

There are twelve different Zn–Cl bonds in this structure and a standard deviation evaluated from the set of twelve bond lengths gave a value of 0·025 Å compared with the average estimate of 0·0072 Å. We consider the value of 0·025 Å to be more representative of the true variance using this incorrect approach. As a result of these considerations further refinement of this structure is in progress.

Polar space groups

In the past when a full-matrix refinement procedure has been used it has been found necessary to impose some restraint on atom shifts for polar space groups. This need is directly attributable to the fact that the component of $(F_o)_{0h}-(F_c)_h$ at $\pi/2$ to the phase direction of $(F_c)_{0h}$ has been completely ignored. Translation of atoms in the crystal implies multiplication by a phase factor, or in other words a change in phase angle. If the component of $(F_o)_{0h}-(F_c)_h$ at $\pi/2$ to α_{0h} is minimized then so is the amount of translation of atoms in the polar direction.

Approximations to the error in the phase of $(F_o)_{0h}$ using X-ray data

We saw earlier that

$$\langle|E_2|^2\rangle=|F_o|_h^2[2-2\langle\cos(\alpha_{0h}-\bar{\alpha}_h)\rangle].$$

For an acentric crystal we assume that at a particular value of $\sin\theta/\lambda$, $\sigma_1^2=\sigma_2^2$ is a constant σ^2 for general reflexions and $\sigma_1^2=2\sigma^2$ when $\sigma_2^2=0$. For general reflexions $\langle\cos(\alpha_{0h}-\bar{\alpha}_h)\rangle$ is evaluated as

$$\int_0^{2\pi}\cos(\alpha_{0h}-\bar{\alpha}_h)\exp\left(\frac{-X^2}{2}\right)\mathrm{d}\bar{\alpha}_h\Big/\int_0^{2\pi}\exp\left(\frac{-X^2}{2}\right)\mathrm{d}\bar{\alpha}_h$$

where X^2 is now

$$[|F_o|_h^2+|(F_c)_0|_h^2-2|F_o|_h|(F_c)_0|_h\cos(\alpha_{0h}-\bar{\alpha}_h)]/\sigma^2$$

so that

$$\langle\cos(\alpha_{0h}-\bar{\alpha}_h)\rangle=\int_0^{2\pi}\cos\alpha\exp(|F_o|_h|(F_c)_0|_h\cos\alpha/\sigma^2)\mathrm{d}\alpha\Big/\int_0^{2\pi}\exp(|F_o|_h|(F_c)_0|_h\cos\alpha/\sigma^2)\mathrm{d}\alpha.$$

σ^2 may be estimated as $\langle|(F_o)_{0h}-(F_c)_{0h}|^2\rangle$ at angle θ and to a good approximation will vary as $\sum_i(f_i 2\sin\theta/\lambda)^2$ where f_i is the scattering factor of the ith atom corresponding to the value of $2\sin\theta/\lambda$. Values of $\langle\cos(\alpha_{0h}-\bar{\alpha}_h)\rangle$ for various values of $|F_o|_h|(F_c)_0|_h/\sigma^2$ can

be incorporated in a table for use in the least-squares refinement procedure and only a single parameter need be used for the estimation of σ^2.

Conclusion

It has been demonstrated that the major cause of covariance problems in the least-squares refinement of crystal structures has been caused by the use of incorrect least-squares equations and the insistence on weighting according to counting statistics. With the approach outlined in this paper it is possible to refine a centrosymmetric structure in a non-centrosymmetric space group. In such an application, if one starts from exactly centrosymmetric coordinates, refinement proceeds to a false minimum since the structure will stay centrosymmetric. However, if one is trying to test the validity of a structural parameter defining a rigid group of atoms, for example the angle which a plane of atoms makes with a symmetry axis, then an initial perturbation involving this parameter may be tested.

The problem of false minima is a necessary part of refining a crystal structure with a fixed weighting scheme (Rae, 1974). It is unrealistic to rely on the redefinition of the phase of $(F_o)_h$ to enable refinement to proceed. The contribution to the weighting scheme of $\langle|E_2|^2\rangle$ and $\langle|E_3|^2\rangle$ far outweighs the counting statistic contribution $\langle|E_1|^2\rangle$ in all but the final refinement cycle since $\sum_h w_h|\Delta_i|^2 \gg 1$ with $w_h^{-1}=\langle|E_1|^2\rangle$.

The point is made that the refinement is only as good as the weighting scheme. Because data with $|(F_c)_h| > |(F_o)_h|$ are weighted preferentially, scale constants should be refined on their own in a separate least-squares cycle in the initial refinement stages with $\langle|F_h|^2\rangle=\sum_i f_h^2$ where f_i is the scattering factor for the ith atom in the crystal. The better the weighting scheme the more rapid and correct the convergence. The only extra computing time involved is in the actual multiplication of derivatives to form the matrix.

When refinement is complete $w_h^{1/2}\Delta_h$ values will enable a probability distribution to be evaluated. By multiplying w_h by the probability associated with the value of $w_h^{1/2}\Delta_h$ it should be possible to improve the refinement since the variance associated with the square of a normal distribution is half the variance associated with the normal distribution function itself.

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On the Libration of 9, 10-Anthraquinone at Five Temperatures

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Potential energy profiles corresponding to libration of 9,10-anthraquinone about its molecular axes were constructed for the five structures derived from data which were collected at −170, −112, −72, −12·5 and 20·5 °C [Lonsdale, Milledge & El Sayed (1966). *Acta Cryst.* **20**, 1–13]. These profiles were represented by fourth-degree least-squares polynomials, whereafter r.m.s. libration amplitudes and rigid rotator frequencies of 9,10-anthraquinone were evaluated in the quadratic approximation. The temperature dependence of the calculated quantities is in most cases close to that of the observed ones thus reproducing, by comparison with observed Raman frequencies, the pseudoharmonic behaviour of 9,10-anthraquinone. Calculated r.m.s. libration amplitudes are only qualitatively comparable to the experimental ones and appear to be somewhat too low. The present representation of energy profiles makes it possible to estimate conveniently the contribution of anharmonicity to the profile shape.

Introduction

The availability of semiempirical potential functions enables one to construct approximate potential energy profiles corresponding to a specified type of molecular motion in the crystal. Such profiles were first shown by Shmueli & Goldberg (1973) to be a valuable tool for a critical examination of the librational motion indicated by an analysis of anisotropic thermal parameters. Thus, in cases of well behaved librational motion nearly parabolic potential wells were obtained while most

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