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False minima in the least-squares refinement of non-centrosymmetric crystal structures.

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The rigorous evaluation of least-squares equations to evaluate a set of parameters $\hat{u}_j$ which are the best estimates of true parameters $\bar{u}_j$, requires that the equations be evaluated with the parameters $\bar{u}_j$. When an initial set of parameters $(u_j)_0$ is used instead, the set of parameters obtained for a fixed weighting scheme is dependent on the choice of $(u_j)_0$ and variances are consequently incorrectly estimated. To avoid false minima and to continue refinement it is necessary to use a weighting scheme that incorporates phase reliability and is evaluated each refinement cycle.

Introduction

Notation used in this paper is that developed in a previous paper (Rae, 1974) in which it was shown that it has been customary to refine non-centrosymmetric crystal structures with an incorrect set of least-squares equations. The subscript h implies the hth observable and the subscript 0 implies evaluation with parameters $(u_j)_0$.

In the least-squares equations

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

where

$$A_{ij}=\tfrac{1}{2}\sum_h\left[\left(\frac{\partial\Delta}{\partial u_i}\right)^*_{0h} w_h\left(\frac{\partial\Delta}{\partial u_j}\right)_{0h}+\left(\frac{\partial\Delta}{\partial u_i}\right)_{0h} w_h\left(\frac{\partial\Delta}{\partial u_j}\right)^*_{0h}\right]$$

$$B_i=-\tfrac{1}{2}\sum_h\left[\Delta^*_{0h}\, w_h\left(\frac{\partial\Delta}{\partial u_i}\right)_{0h}+\Delta_{0h} w_h\left(\frac{\partial\Delta}{\partial u_i}\right)^*_{0h}\right],(i,j=1\text{ to }m)$$

it has been customary to consider Δ_h to be a real quantity $(A_o-A_c)_h\cos\alpha_{0h}+(B_o-B_c)_h\sin\alpha_{0h}$ rather than the complex quantity $(A_o-A_c)_h+i(B_o-B_c)_h$ where $\tan\alpha_{0h}=(B_c/A_c)_{0h}$.

As a consequence, different parameter shifts are estimated with the incorrect equations. This causes discrepancies in pseudosymmetric crystal structures that are so drastic that the mismatch between bond lengths and temperature parameters involving pseudo-equivalent atoms cannot be regarded as significant. These discrepancies are so large that they must be considered to be a consequence of errors in the refinement process. It is of interest to note that if we use a weighting scheme that is determined solely from counting statistics, namely $w_h^{-1}=\mathrm{var}(|F_o|_h)$, then continuation of the refinement with the correct form of the least-squares equations does not remedy the initial fault.

$$B_i=\sum_h\left[\cos\alpha_{0h}\left(\frac{\partial A_c}{\partial u_i}\right)_{0h}+\sin\alpha_{0h}\left(\frac{\partial B_c}{\partial u_i}\right)_{0h}\right]w_h(|F_o|_h-|F_c|_{0h})$$

for both the correct and incorrect least-squares equations and refinement is complete when $B_i=0$ for all i, not when $\sum_h \Delta^*_h w_h\Delta_h$ is an absolute minimum. Further refinement is only possible if the weighting scheme is altered.

Theory

Consider equations $\sum_j A_{ij}[\hat{u}_j-(u_j)_0]=B_i$ and $\sum_j C_{ij}[\hat{u}_j-(u_j)_0]=0$, $(i,j=1$ to $m)$ which may be simultaneously satisfied for some values of $\Delta u_j=\hat{u}_j-(u_j)_0$. We may express these equations in matrix notation $A\Delta u=B$ and $C\Delta u=0$. The equations $A\Delta u=B$ are satisfied by values of Δu_j given by $\Delta u=(A+\lambda C)^{-1}B$ where λ is any $m\times m$ matrix chosen such that the determinant of $A+\lambda C$ is non-zero. Substituting for Δu we see that $A\Delta u=A(A+\lambda C)^{-1}B=[(A+\lambda C)A^{-1}]^{-1}B=(I+\lambda CA^{-1})^{-1}B$ where I is the $m\times m$ unit matrix. Thus

$$A\Delta u=B+\sum_{n=1}^{\infty}(-\lambda CA^{-1})^nB=B$$

since

$$CA^{-1}B=C\Delta u=0\,.$$

Conditions $A\Delta u=B$ and $C\Delta u=0$ are always simultaneously generated for non-centrosymmetric structure refinements. The equations $A\Delta u=B$ are the least-squares equations to minimize $S_1=\sum_h w_h[(A_o-A_c)\cos\alpha_0+(B_o-B_c)\sin\alpha_0]_h^2$ and the equations $C\Delta u=0$ are the least-squares equations to minimize

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

$[(A_o-A_c)\cos\alpha_0+(B_o-B_c)\sin\alpha_0]_h$ and $[-(A_o-A_c)\sin\alpha_0+(B_o-B_c)\cos\alpha_0]_h$ are the components of $[(F_o)_0-F_c]_h$ at 0 and $\pi/2$ to α_{0h}, the phase direction of the calculated value $(F_c)_{0h}$ assumed to be the phase of the observed amplitude $(F_o)_{0h}$.

Discussion

The rigorous derivation (Rae, 1974) of the correct least-squares equations puts $\lambda=I$ but only under the condition that $w_h^{-1}=\langle|(F_o)_{0h}-F_h|^2\rangle=\langle|E_1|^2+|E_2|^2+|E_3|^2\rangle$ is the expectation value of the square of the modulus of $(F_o)_{0h}-F_h$. $(F_o)_{0h}$ is $|F_o|_{0h}\exp i\alpha_{0h}$ and F_h is the value of

$$(F_c)_h=(F_c)_{0h}+\sum_j\alpha_{hj}[u_j-(u_j)_0]$$

when $u_j=\bar{u}_j$ and $a_{hj}=(\partial F_c/\partial u_j)_{0h}$. $\langle|E_1|^2\rangle$ is var $(|F_o|_h)$, $\langle|E_2|^2\rangle$ involves the variance associated with the choice of phase of $(F_o)_{0h}$, and $\langle|E_3|^2\rangle$ involves any systematic error in the calculation of F_h as an estimate of the true value $\bar{F}_h$. With the correct weighting scheme $\sum_h w_h|\Delta_h|^2/(n-m)$ reduces to one in a single cycle and the amount $\langle|E_2|^2\rangle$ makes a significant contribution to w_h^{-1}.

Re-estimation of $\langle|E_2|^2\rangle$ each cycle is essential for meaningful refinement to continue, as this allows a meaningful selection of λ and allows non-zero values of the B_i elements of the equations. If an incorrect weighting scheme is used λ is an unknown quantity and variances will be underestimated since the evaluation of variances assumes that values $\hat{u}_j-\bar{u}_j$ are randomly distributed and do not have systematic error.

Reference

RAE, A. D. (1974). *Acta Cryst.* A30, 761–768.