Short Communications

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On an application of inequality methods to centrosymmetric crystals with partly known structures.

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The use of inequality methods for structure determination has been recently emphasised by many authors. We wish to show in our present paper a modified application of inequality methods to crystals with partly known structures. This happens when some of the atoms lie in special positions by space-group requirements or when some atoms have already been fixed by Patterson function or by other methods.

The unitary structure factor U_{hkl} for crystals with centres of symmetry can be written as follows:

$$U_{hkl} = \sum_{i'} n'_i \cos 2\pi(hx'_i+ky'_i+lz'_i) + \sum_{i''} n''_i \cos 2\pi(hx''_i+ky''_i+lz''_i) = U'_{hkl}+U''_{hkl}\,, \quad (1)$$

where, the notation being the same as in our previous paper (1952*b*), $n_i = Z_i/F_{000}$, Z_i being the number of electrons in the ith atom, and single primes refer to the atoms in known and double primes to those in unknown positions. If the part U''_{hkl} is modified as follows:

$$\hat{U}''_{hkl} = \frac{U''_{hkl}}{\sum_{i''} n''_i} \equiv \frac{U_{hkl} - \sum_{i'} n_i \cos 2\pi(hx'_i+ky'_i+lz'_i)}{1-\sum_{i'} n'_i}\,, \quad (2)$$

this should of course satisfy the inequalities of Harker & Kasper or ours, and, being intensified by $1/\sum_{i''} n''_i$ as compared with original U''_{hkl}, will be more adequate for the application of the inequality methods. Although we cannot obtain directly the value of $\hat{U}''_{hkl}$ if the sign of U_{hkl} is unknown, still $\hat{U}''_{hkl}$ should possess either

$$\frac{|U_{hkl}| - \sum_{i'} n'_i \cos 2\pi(hx'_i+ky'_i+lz'_i)}{1-\sum_{i'} n'_i}$$

$$\text{or} \quad \frac{-|U_{hkl}| - \sum_{i'} n'_i \cos 2\pi(hx'_i+ky'_i+lz'_i)}{1-\sum_{i'} n'_i}\,,$$

the inadequate alternative being possibly precluded by the use of the inequality methods and leading thus to the knowledge of the correct sign of U_{hkl}. Obviously, if one of the alternatives comes out to be of absolute value greater than unity, this should be excluded and the sign of U_{hkl} will thus be determined directly. It may be added that, in subtracting the effect of the known part U'_{hkl} from U_{hkl}, one should be careful to adjust the arbitrary parameters (Okaya & Nitta, 1952*a*, *b*), due to choice of the origin, between the expressions U_{hkl} and $\sum_{i'} n'_i \cos 2\pi(hx'_i+ky'_i+lz'_i)$.

Actual examples of the application of this method will be given later.

In conclusion, the authors wish to thank Mr Y. Tomiie for his valuable suggestions on the present problem.

References

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Application of our linear inequalities and some remarks on B. S. Magdoff's paper on 'Forbidden reflections in the Harker–Kasper inequalities'.

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Magdoff (1951) had made some useful and interesting applications of the Harker–Kasper inequalities for space-group extinctions and for half odd indices, using the 'sum and difference' inequality of Harker & Kasper (1947, 1948). By the linear inequalities for crystals with centres of symmetry which we have found recently (Okaya & Nitta, 1952*b*), we can obtain analogous but more convenient inequality relations. The inequality (18) in our paper (Okaya & Nitta, 1952*b*),

$$\begin{aligned} &p^2+q^2+2r^2+p^2U_{2h,\,2k,\,2l}+q^2U_{2h',\,2k',\,2l'} \\ &+2pq(U_{h+h',\,k+k',\,l+l'}+U_{h-h',\,k-k',\,l-l'}) \\ &\geqq 4r|pU_{hkl}+qU_{h'k'l'}|, \quad r \geqq 0\,, \end{aligned} \quad (1)$$

can be modified to the following form by putting $r=0$:

$$\begin{aligned} &p^2+q^2+p^2U_{2h,\,2k,\,2l}+q^2U_{2h',\,2k',\,2l'} \\ &\pm 2pq(U_{h+h',\,k+k',\,l+l'}+U_{h-h',\,k-k',\,l-l'}) \\ &\geqq 0\times|pU_{hkl}\pm qU_{h'k'l'}|\,. \end{aligned} \quad (2)$$

Putting further $p = 1$ and $q = 1$ in (2), we obtain

$$1+\tfrac{1}{2}U_{2h,2k,2l}+\tfrac{1}{2}U_{2h',2k',2l'}\pm(U_{h+h',k+k',l+l'}+U_{h-h',k-k',l-l'}) \geqq 0\times|U_{hkl}\pm U_{h'k'l'}|\,, \quad (3)$$

which is an analogue to the Harker–Kasper 'sum and difference' inequality. Our linear inequality (2) also implies other practical formulae by selecting appropriate p and q values.

Magdoff has shown some examples using the U_{hkl}'s (in her paper these have the notation $U(hkl)$) of *p*-di-tertiary-butylbenzene, with centrosymmetric space group C_{2h}^5–$P2_1/n$, the data being reproduced in Table 1.

Table 1. *Observed U_{hkl} values from* p-*di-tertiary-butylbenzene* (Magdoff, 1951)

hkl	U_{hkl}	
103	0·695	
$20\bar{8}$	0·195	
$30\bar{5}$	0·877	
$40\bar{2}$	0·661	
430	0·717	
440	0·577	
$70\bar{7}$	0·190	
$h0l$	0	when $h+l$ is odd
$0k0$	0	when k is odd

By putting appropriate U_{hkl} values in (3), we can obtain the following inequalities analogous to those described there:

$$1+\tfrac{1}{2}U_{40\bar{2}}+\tfrac{1}{2}U_{20\bar{8}}\pm(U_{103}+U_{30\bar{5}}) \geqq 0\times|U_{20\bar{1}}\pm U_{10\bar{4}}|\,, \quad (4)$$

$$1+\tfrac{1}{2}U_{70\bar{7}}+\tfrac{1}{2}U_{103}\pm(U_{30\bar{5}}+U_{40\bar{2}}) \geqq 0\times|U_{3\frac{1}{2},0,\bar{3}\frac{1}{2}}\pm U_{\frac{1}{2},0,1\frac{1}{2}}|\,, \quad (5)$$

$$1+\tfrac{1}{2}U_{870}+\tfrac{1}{2}U_{010}\pm(U_{430}+U_{440}) \geqq 0\times|U_{4,3\frac{1}{2},0}\pm U_{0,\frac{1}{2},0}|\,. \quad (6)$$

Magdoff has obtained the following relations:

$$S_{103} = -S_{30\bar{5}},\; S_{30\bar{5}} = -S_{40\bar{2}} \quad\text{and}\quad S_{430} = -S_{440}\,,$$

where S_{hkl} signifies the sign of U_{hkl} (written as $S(hkl)$ in her paper). However, as we have already pointed out in our previous papers (Okaya & Nitta, 1952*a*, *b*), preliminary considerations on the arbitrariness in the choice of the signs of the structure factors arising from some symmetry relations should be made at the beginning of the inequality procedures.

For the crystals with space group C_{2h}^5–$P2_1/n$, there are the following arbitrary parameters:

First, concerning U_{h0l}'s appearing only for $h+l=2n$, one has two arbitrary parameters: one, ξ, connected to the U_{h0l}'s with $h+l = 2\times$ even and h and l bot hodd, and the other, η, to those with $h+l = 2\times$ odd and h and l both even. (U_{h0l}'s with $h+l = 2\times$ odd and h and l both odd must then have the parameter $\xi\eta$.) These two parameters are indeterminable by any inequality and are arbitrarily assigned before calculating the Fourier series. Thus, S_{103} and $S_{70\bar{7}}$ must have the arbitrary parameter ξ, $S_{30\bar{5}}$ $\xi\eta$, $S_{40\bar{2}}$ and $S_{20\bar{8}}$ η. If we consider (4), it becomes

$$1+0\cdot331S_{40\bar{2}}+0\cdot098S_{20\bar{8}}\pm[0\cdot695S_{103}+0\cdot877S_{30\bar{5}}] \geqq 0\,, \quad (7)$$

from which we obtain

$$1+0\cdot331a\eta+0\cdot098b\eta\pm[0\cdot695c\xi+0\cdot877d\xi\eta] \geqq 0\,, \quad (8)$$

where a, b, c and d are to be determined uniquely to be $+1$ or -1. Here, if we choose $c\xi = d\xi\eta$, that is $d\eta = c$, equation (8) requires that $a\eta = b\eta = +1$, the numerical contradiction being due to the errors in U_{hkl}'s concerned, and we can get $a = b = d/c = cd$. This is also the case for (5), which becomes, using the above notation,

$$1+0\cdot095S_{70\bar{7}}+0\cdot348S_{103}\pm[0\cdot877S_{30\bar{5}}+0\cdot661S_{40\bar{2}}] \geqq 0\,, \quad (9)$$

from which we obtain

$$1+0\cdot095e\xi+0\cdot348c\xi\pm[0\cdot877d\xi\eta+0\cdot662a\eta] \geqq 0\,. \quad (10)$$

Here, if we choose $d\xi\eta = a\eta$, (10) can be satisfied by $e\xi = c\xi = +1$, the numerical contradiction being also due to the errors in U_{hkl}'s concerned. Thus we have $e = c = d/a = ad$.

Secondly, for U_{hk0}'s, the situation is similar to the case of U_{h0l}'s. We have another arbitrary parameter ζ, which is connected to the U_{hk0}'s with k odd. The inequality (6) becomes

$$1+0\cdot00S_{870}+0\cdot00S_{010}\pm[0\cdot717S_{430}+0\cdot577S_{440}] \geqq 0\,, \quad (11)$$

and, using the notation as above, we have

$$1+0\cdot00f\zeta+0\cdot00\pm[0\cdot717g\zeta+0\cdot577h] \geqq 0\,, \quad (12)$$

S_{440} being uniquely determinable. Here, if we assign $g\zeta = h$, which is also possible, we confront ourselves with some numerical contradictions; these are due either to some errors in U_{430} and U_{440}, which may be greater than the true values, or to those in U_{870}, which may not be really equal to zero. U_{010} is really equal to zero by the extinction rule. If U_{870} be not equal to zero, it must have the sign $f\zeta$, with $f = g/h = gh$.

The soundness of all these considerations can be acertained by combining them with another linear inequality which we have obtained (to be reported soon), namely

$$p^2+q^2-p^2U_{2h,2k,2l}-q^2U_{2h',2k',2l'} \pm 2pq(U_{h+h',k+k',l+l'}-U_{h-h',k-k',l-l'}) \geqq 0\,, \quad (13)$$

or with the main linear inequalities of Table 1 or the like in our previous paper (Okaya & Nitta, 1952*b*), (3) or (13) in the present paper being merely a modification of one of them.

Thus it may be concluded that Magdoff was unfortunate in being led to ambiguous conclusions by not having paid *a priori* consideration to the characteristic circumstances arising from the arbitrariness in the choice of signs of the structure factors. This is the reason why, in our previous papers (Okaya & Nitta, 1952*a*, *b*), we have emphasized the importance of the conception of arbitrariness.

References

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