

Short Communications

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Some new relations following from the Herglotz theorem.* By MASAO ATOJI, *Institute for Atomic Research and Department of Chemistry, Iowa State College, Ames, Iowa, U.S.A.*

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The use of positive-definite determinants of Fourier coefficients (Herglotz, 1911) for the phase determination has been extensively discussed by Karle & Hauptman (1950). Under a modified form of the Herglotz theorem, Pepinsky & MacGillavry (1951) have shown that the effectiveness of inequalities following from a known maximum value of the electron density is of little value. However, if we know the electron-density distribution in parts of the unit cell, useful relations may be obtained from the Herglotz theorem. For example, if the space group has a mirror plane at $z = \frac{1}{4}$ and $\frac{3}{4}$, and if no atom is on the mirror plane, then the maximum possible value Q of the electron density $\rho(x, y, \frac{1}{4}$ or $\frac{3}{4}$) may be small enough such that

$$|QV - F(000)| < F(000), \quad (1)$$

where V is volume of the unit cell. From the positive-definite determinant of order two, we have

$$|QV - F(000)| \geq \sum_{l=2n} (-1)^n F(hkl), \quad (2)$$

for any h and k combination, n taking all positive and negative integral values. From the determinant of order three, we have

$$\left\{ \frac{\sum_{l=2n} (-1)^n F(hkl)}{QV - F(000)} \right\}^2 \leq \frac{1}{2} + \frac{\frac{1}{2} \sum_l F(2h, 2k, 2l)}{QV - F(000)}, \quad (3)$$

for a centrosymmetric structure. For example, $\sum_{l=2n} (-1)^n F(2, 4, l)$ and $\sum_l F(4, 8, 2l)$ may be compared using (3). As seen from (3), other inequalities can be easily obtained from determinants of higher order by the method described by Karle & Hauptman (1950); namely, in their inequalities, replace $F(000)$ by $|QV - F(000)|$ and $F(000)$ and $F(hkl)$ by the summation form. These modified inequalities are effective for the phase determination in cases where some of the phases of $F(hkl)$ are known by other methods or only a few relatively strong reflections are observed in a reciprocal zone. If no chemical bonding occurs across the mirror plane, $QV - F(000)$ may be small enough to make the inequalities more effective. This method may be combined with the one discussed by Tesche (1953).

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It is also possible to derive a set of inequalities from a known minimum or maximum value of the curvature of the Fourier peaks in the unit cell. But it is found that these inequalities would not be of great help in phase determination except in very special cases. However, the following may be worth while to note here.

The curvature with respect to the x axis in an orthogonal system is

$$a^2 \frac{\partial^2 \rho(x, y, z)}{\partial x^2} = -\frac{1}{V} \sum_3 4\pi^2 h^2 F(hkl) \times \exp \left\{ -2\pi i \left(\frac{hx}{a} + \frac{ky}{b} + \frac{lz}{c} \right) \right\}. \quad (4)$$

If the temperature factor is known, the minimum possible value of the curvature may be estimated (Atoji, 1957), namely, it is possible to find a positive value R so that

$$|a^2 \partial^2 \rho(x, y, z) / \partial x^2| \leq R. \quad (5)$$

The positive-definite determinant of order two for (4) gives

$$VR / 4\pi^2 h^2 \geq |F(hkl)|. \quad (6)$$

Then, we may correlate the minimum possible value of R and the maximum possible value of $F(hkl)$. The other inequalities based on (5) are, in almost any case, very insensitive to the phase of the structure factor. However, if many like atoms are overlapped in projection so as to reduce R considerably, then these inequalities may be of value in phase determination. A similar discussion of equations (1)–(3) can also be extended to the curvature, provided that R in a plane or region of the electron-density map is known to be very small.

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References

- ATOJI, M. (1957). *Acta Cryst.* **10**, 291.
 HERGLOTZ, G. (1911). *Ber. sächs. Ges. (Akad.) Wiss.* **63**, 501.
 KARLE, J. & HAUPTMAN, H. (1950). *Acta Cryst.* **3**, 181.
 PEPINSKY, R. & MACGILLAVRY, C. H. (1951). *Acta Cryst.* **4**, 284.
 TESCHE, O. A. (1953). *Acta Cryst.* **6**, 564.