The molecular orbital treatment given by Dunitz & Orgel (1953) for the complex anion $Ru_2OCl_{10}^{-4}$ would seem directly applicable to the $Re_2OCl_{10}^{-4}$ ion since the two have the same molecular geometry. The result of this group-theoretical treatment for $Re_2OCl_{10}^{-4}$ would be a sigma representation involving five chlorine and one oxygen bonds to metal and a representation providing E_u (bonding and antibonding), B_{2g}, B_{2u}, and E_g orbitals, these latter three types being approximately degenerate. Ten electrons, three from each rhenium and the four $p(x, y)$ from oxygen, can be placed in these orbitals, but the relatively high energy antibonding E_u orbital is not needed. The bonding E_u orbital is described by Dunitz & Orgel (1953) as a degenerate bonding pi orbital. With four electrons in the E_u bonding orbital, six remain to be placed in the approximately degenerate group mentioned above. If Hund's Rule is followed, one expects to find two of these six electrons unpaired and to find a paramagnetism of one unpaired electron per rhenium. The experimental magnetic susceptibility (Jezowska-Trzebiatowska & Wajda, 1954) is extremely small and temperature independent and may, according to Jezowska-Trzebiatowska & Wajda, even be due to contamination with related paramagnetic rhenium oxychloro complex compounds. This fact suggests that Hund's Rule is violated and that all the electrons are paired.

References

AMINOFF, B. (1936). *Z. Kristallogr.* **94**, 246.
BERGHUIS, J., HAANAPPEL, IJ. M., POTTERS, M., LOOP-STRA, B. O., MACGILLAVRY, C. H. & VEENENDAAL, A. L. (1955). *Acta Cryst.* **8**, 479.
BUERGER, M. J. (1959). *Vector Space.* New York: Wiley.
CRUICKSHANK, D. W. J. (1949). *Acta Cryst.* **2**, 65.
DUNITZ, J. D. & ORGEL, L. E. (1953). *J. Chem. Soc.* **1953**, 2594.
FREEMAN, A. J. (1959). *Acta Cryst.* **12**, 261.
HOWELLS, E. R., PHILLIPS, D. C. & ROGERS, D. (1950). *Acta Cryst.* **3**, 210.
HOWELLS, R. G. (1950). *Acta Cryst.* **2**, 65.
International Tables for X-ray Crystallography (1952). Vol. II. Birmingham: Kynoch Press.
Internationale Tabellen zur Bestimmung von Kristall-strukturen (1935). Vol. II. Berlin: Borntraeger.
JEZOWSKA-TRZEBIATOWSKA, B. (1953). *Trav. Soc. Sci.. Wroclaw.* Ser. B, No. 39, 24.
JEZOWSKA-TRZEBIATOWSKA, B. & WAJDA, S. (1954). *Bull. Acad. Pol. Sci.* Classe III, **2**, No. 5.
KARTHA, G. & AHMED, F. R. (1960). *Acta Cryst.* **13**, 532.
LIPSON, H. & COCHRAN, W. (1953). *The Crystalline State.* Vol. III. London: Bell.
MATHIESON, A. McL., MELLOR, D. P. & STEPHENSON, N. C. (1952). *Acta Cryst.* **5**, 185.
MORROW, J. C. (1960). *Acta Cryst.* **13**, 443.
NODDACK, W. & NODDACK, I. (1933). *Z. anorg. Chem.* **215**, 129.
VIERVOLL, H. & ØGRIM, O. (1949). *Acta Cryst.* **2**, 279.
WYCKOFF, R. G. W. (1948). *Crystal Structures*, Ch. III, Table p. 15. New York: Interscience.

Effect of Errors of Atomic Co-ordinates on Structure Amplitude and Bijvoet Inequality

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The effect of errors of atomic parameters on the calculated values of the structure amplitude and the Bijvoet inequality is considered. Expressions for the standard deviations of the structure amplitude, Bijvoet inequality and the phase angle are derived and discussed. It is also shown that the fractional error in the structure amplitude can have as large a value as 50% or more for weak reflections at high values of sin θ even for a reasonably accurate structure.

1. Introduction

While the problem of finding out how the errors in intensity $|F|^2$ or structure amplitude $|F|$ affect the atomic positions has been discussed by a number of authors (see for instance Lipson & Cochran, 1957), not much attention seems to have been paid to the converse problem namely how any errors in the atomic co-ordinates affect the calculated values of $|F|$. This problem was met with in connection with the author's work on the evaluation of the anomalous dispersion factor $\Delta f''$ from experimental measurements of the Bijvoet inequality $(\Delta I/I)$ for various reflections hkl (Parthasarathy, 1961). Consequently this general

problem was considered and the results obtained are presented below. The case of a non-centric symmetric crystal (symmetry $P1$) is first considered and the discussion is then extended to a centro-symmetric crystal (symmetry $P\bar{1}$). Luzzati (1952) has also considered the effect of errors of atomic co-ordinates on quantities as the structure amplitude $|F|$ or the residual R, by employing a more elaborate method, using the probability methods and Wilson's intensity statistics. However, he has not given any explicit relation connecting the standard deviations in $|F|$ and the atomic coordinates which would be convenient for numerical work. Using the present method which is basically very simple and direct, though somewhat less rigorous, a simple and explicit relation between the standard deviations of structure amplitude and atomic co-ordinates is derived.

2. Effect of errors on structure amplitude $|F|$ for $P1$

Let us first take the case of a crystal containing N atoms per unit cell. Since we need consider but one unit cell and not the entire lattice, we may as well employ an orthogonal set of axes without loss of generality.* Suppose that the position of the jth atom ($j = 1$ to N) in the unit cell is given by $\mathbf{r}_j$ (x_j, y_j, z_j) where x_j, y_j and z_j have standard deviations $\sigma(x_j)$, $\sigma(y_j)$ and $\sigma(z_j)$ respectively. We shall suppose that the errors in the co-ordinates are isotropic i.e., the position of the jth atom is distributed spherically around its mean position with a root mean square radius $\sigma(|\mathbf{r}_j|)$ ($= \sigma_{rj}$ say in Å) with the centre of the sphere at the tip of the vector $\mathbf{r}_j$. σ_{rj} is then related to the standard deviations $\sigma(x_j)$, $\sigma(y_j)$ and $\sigma(z_j)$ by the relations:

$$\sigma(x_j) = \sigma(y_j) = \sigma(z_j) = \sigma_{rj}/\sqrt{3} . \quad (1)$$

The problem is then to find out the standard deviation of $|F|$ in terms of σ_{rj} for a particular reflection. We have

$$F = \sum_j f_j \exp 2\pi i \mathbf{H} . \mathbf{r}_j$$
$$= \sum_j f_j \exp 2\pi i (hx_j/a + ky_j/b + lz_j/c) , \quad (2)$$

where $\mathbf{H}$ is the reciprocal lattice vector. (For convenience indices hkl are omitted and the structure factor of a general reflection F_{hkl} will be simply denoted by F). For arbitrary displacements $\delta \mathbf{r}_j$ of $\mathbf{r}_j$ the change $\delta|F|$ of $|F|$ is given by

$$\delta|F| = \sum_{j=1}^{N} \mathrm{grad}_j |F| . \delta \mathbf{r}_j , \quad (3)\dagger$$

where N is the number of independent $\mathbf{r}_j$ i.e., in this

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* Thanks are due to the referee for some remarks concerning this point.

† In writing equation (3), we take only the first term of the Taylor expansion and this is equivalent to the assumption that the function D given by equation (9) of Luzzati takes the value unity.

case, the number of atoms in the unit cell. In order to evaluate $\mathrm{grad}_j |F|$, we note that $\mathrm{grad}_j |F|^2 = 2|F| \, \mathrm{grad}_j |F|$ and since $|F|^2 = A^2 + B^2$ we have

$$\mathrm{grad}_j |F| = (1/|F|) \, (A \, \mathrm{grad}_j A + B \, \mathrm{grad}_j B) \quad (4)$$

and equation (3) becomes

$$\delta|F| = (1/|F|) \sum_{j=1}^{N} |(A \, \mathrm{grad}_j A + B \, \mathrm{grad}_j B) . \delta \mathbf{r}_j . \quad (5)$$

Since

$$A = \sum_j f_j \cos \varphi_j \quad \text{and} \quad B = \sum_j f_j \sin \varphi_j ,$$

where

$$\varphi_j = 2\pi (hx_j/a + ky_j/b + lz_j/c) \quad (6)$$

we obtain

$$\mathrm{grad}_j A = -2\pi f_j \sin \varphi_j \, \mathbf{H} . \delta \mathbf{r}_j \quad (7)$$

and

$$\mathrm{grad}_j B = 2\pi f_j \cos \varphi_j \, \mathbf{H} . \delta \mathbf{r}_j . \quad (8)$$

Substitution of equations (7) and (8) in equation (4) leads to the expression for $\delta|F|$ as

$$\delta|F| = (2\pi/|F|) \sum_{j=1}^{N} f_j (B \cos \varphi_j - A \sin \varphi_j) \mathbf{H} . \delta \mathbf{r}_j . \quad (9)$$

On squaring this and averaging over the differentials, we have

$$\langle (\delta|F|)^2 \rangle = (4\pi^2/|F|^2) \sum_i^N \sum_j^N f_i f_j (B \cos \varphi_i - A \sin \varphi_i)$$
$$\times (B \cos \varphi_j - A \sin \varphi_j)$$
$$\times \langle (\mathbf{H} . \delta \mathbf{r}_i)(\mathbf{H} . \delta \mathbf{r}_j) \rangle . \quad (10)$$

Here $|F|^2$, $\mathbf{H}$ and $(B \cos \varphi_j - A \sin \varphi_j)$ are constants for a particular reflection and the averaging need be done only over the displacements $\delta \mathbf{r}_j$ of the various atoms. The averanging may be performed in two steps, first over all orientations of $\delta \mathbf{r}_j$ and next over all magnitudes of these. Now

$$\mathbf{H} . \delta \mathbf{r}_i = |H| \, |\delta r_i| \cos \varepsilon_i$$
$$\mathbf{H} . \delta \mathbf{r}_j = |H| \, |\delta r_j| \cos \varepsilon_j ,$$

where ε_i, ε_j are the angles made by $\delta \mathbf{r}_i$ and $\delta \mathbf{r}_j$ with the reciprocal lattice vector $\mathbf{H}$. Hence

$$\langle (\mathbf{H} . \delta \mathbf{r}_i)(\mathbf{H} . \delta \mathbf{r}_j) \rangle = H^2 \overline{|\delta r_i| \, |\delta r_j|} \{ \cos \varepsilon_i \cos \varepsilon_j \} . \quad (11a)$$

Here the bar indicates the average over all the values of $\delta|r_j|$ and the curly bracket indicates the average over the surface of a unit sphere (i.e., over the angle variables). Since the displacements $\delta \mathbf{r}_i$ and $\delta \mathbf{r}_j$ are independent, the product $\cos \varepsilon_i \cos \varepsilon_j$ would have a mean value zero where $i \neq j$ and a mean value $\frac{1}{3}$ when $i = j$. We have then

$$\langle (\mathbf{H} . \delta \mathbf{r}_i)(\mathbf{H} . \delta \mathbf{r}_j) \rangle = \begin{cases} 0 & \text{for } i \neq j \\ \frac{1}{3} H^2 \sigma_{rj}^2 & \text{for } i = j \end{cases} \quad (11b)$$

where we have denoted $\overline{|\delta r_j|^2}$ by σ_{rj}^2.

Using equation (11b) in equation (10), we have

$$\langle (\delta|F|)^2 \rangle = (4\pi^2 H^2/3|F|^2) \sum_{j=1}^{N} (B \cos \varphi_j - A \sin \varphi_j)^2 f_j^2 \sigma_{rj}^2 . \quad (12)$$

As in general the standard deviation of the position of the atom is inversely proportional to the 'heaviness' of the atom, $f_j^2 \sigma_{rj}^2$ can be taken to be reasonably a constant for all j's equal to $\langle f_j^2 \sigma_{rj}^2 \rangle_{av.}$ say, and hence this factor can be taken out of the summation. We shall indicate its square root for convenience by $(f\sigma_r)$ so that $\langle f_j^2 \sigma_{rj}^2 \rangle_{av.} = (f\sigma_r)^2$. Thus

$$\langle (\delta|F|)^2 \rangle = (4\pi^2 H^2/3|F|^2)(f\sigma_r)^2 \sum_{j=1}^{N} (B \cos \varphi_j - A \sin \varphi_j)^2 . \tag{13}$$

Equation (13) represents the mean square deviation corresponding to a given σ_r. However, it contains the expression $(B \cos \varphi_j - A \sin \varphi_j)$ which has to be calculated for each reflection, knowing A, B and φ_j. In this investigation, we are interested more in the order of magnitude of errors rather than its actual value. Consequently, we make an approximation and use the average value of the above summation in the expression for the variance of $|F|$. If we take that the N atom in the unit cell are distributed at random, then it follows that

$$\sum_j (B \cos \varphi_j - A \sin \varphi_j)^2 \approx N(B \cos \varphi_j - A \sin \varphi_j)^2_{av.} ,$$

which is equal to
$$(N/2)(A^2 + B^2) ,$$
since

$$\langle \cos^2 \varphi_j \rangle_{av.} = \langle \sin^2 \varphi_j \rangle_{av.} = \tfrac{1}{2} \text{ and } \langle \cos \varphi_j \sin \varphi_j \rangle_{av.} = 0.$$

Thus, the average value of the sum is just $(N/2)|F|^2$. Denoting the mean value of $\langle (\delta|F|)^2 \rangle$ by $\sigma^2(|F|)$, the expression for this assumes the simple form (since $H^2 = 1/d^2$)

$$\sigma^2(|F|) = (2\pi^2 N/3d^2)(f\sigma_r)^2. \tag{14}$$

It follows from this that the fractional error in $|F|$ is

$$\sigma(|F|)/|F| = (2\pi^2 N/3)^{\frac{1}{2}} (f\sigma_r)/(|F|d) . \tag{15}$$

(An alternative derivation of equation (14) which is not so rigorous, but which uses direct physical arguments is given in Appendix I.)

Equation (15) shows that in general, the fractional error $\sigma(|F|)/|F|$ increases with increasing Bragg angle i.e., for planes having larger and larger indices hkl and hence the value of $|F|$ is very sensitive to atomic parameters at high angles. This indicates the importance of high angle reflections for refinement. It can be also seen that, for reflections of medium intensity, i.e., with

$$|F|^2 \approx \langle |F|^2 \rangle \approx \sum_j f_j^2 \approx N\langle f^2 \rangle$$

the fractional error is independent of the actual number N; for putting $|F|^2 \approx N f^2$. Equation (15) becomes

$$\sigma(|F|)/|F| \approx (2\pi^2/3)^{\frac{1}{2}} (N/d)(\langle f^2 \sigma_r^2 \rangle)^{\frac{1}{2}}/(N\langle f^2 \rangle)^{\frac{1}{2}}$$
$$\approx (2\pi^2/3)^{\frac{1}{2}} \sigma_r/d$$

where σ_r can be considered to be the mean of the standard deviations of the various atoms. On the other hand $\sigma(|F|)/|F|$ assumes very large values for weak reflections especially at high angles. Taking a typical case of a weak reflection with its structure amplitude having one fifth the mean value i.e., $|F| \sim \tfrac{1}{5}\langle |F|^2 \rangle^{\frac{1}{2}} \sim \sqrt{(N)}f/5$ and the following orders of magnitude, namely $d = 1$ Å, $\sigma(x) = \sigma(y) = \sigma(z) = \sigma_r/\sqrt{3} = 0.02$ Å the value of $\sigma(|F|)/|F|$ is approximately 45%. Thus, even with a reasonably accurate structure, the fractional error in $|F|$ can have as large a value as 50% or more for weak reflections.

3. Effect of errors on structure amplitude $|F|$ for $P\bar{1}$

In this section we shall extend the results of the previous section to the case of the centrosymmetric space group $P\bar{1}$. Let the total number of atoms in the unit cell be $N(=2n)$, n being the number of atoms in the asymmetric unit. The structure factor equation takes the simple form

$$F = \sum_{j=1}^{N} f_j \exp 2\pi i \mathbf{H} . \mathbf{r}_j \tag{16}$$

$$= 2 \sum_{j=1}^{n} f_j \cos 2\pi \mathbf{H} . \mathbf{r}_j . \tag{16a}$$

$$= A \text{ (say)} .$$

The change $\delta|F|$ in $|F|$ for arbitrary displacements δr_j of $\mathbf{r}_j$ is given by

$$\delta|F| = |\delta F| = |\delta A| = \left| 2 \sum_{j=1}^{n} \text{grad}_j A . \delta \mathbf{r}_j \right|$$

$$= 4\pi \left| \sum_{j=1}^{n} f_j \sin \varphi_j (\mathbf{H}.\delta \mathbf{r}_j) \right| . \tag{17}$$

On squaring this and following the procedure of the previous section for averaging over the differentials, we get

$$\langle (\delta|F|)^2 \rangle = (16\pi^2 H^2/3)(f\sigma_r)^2 \sum_{j=1}^{n} \sin^2 \varphi_j . \tag{18}$$

As before, we make an approximation at this stage and put

$$\sum_{j=1}^{n} \sin^2 \varphi_j = n (\sin^2 \varphi)_{av.} \approx (n/2)$$

when equation (18) reduces to the simple form (since $H^2 = 1/d^2$)

$$\sigma^2(|F|) = \langle (\delta|F|)^2 \rangle = (8\pi^2 n/3d^2)(f\sigma_r)^2$$
$$= (4\pi^2 N/3d^2)(f\sigma_r)^2. \tag{19}$$

The expression for the fractional error thus takes the form

$$\sigma(|F|)/|F| = (4\pi^2 N/3)^{\frac{1}{2}} (f\sigma_r)/|F|d . \tag{20}$$

A comparison of equation (20) with equation (15) shows that, other quantities being the same in both, the fractional error for a centro-symmetrical crystal

is greater than that of a non-centro symmetrical crystal by a factor $\sqrt{2}$. This result is the reciprocal of the more commonly known result in connection with the refinement procedures, namely that the standard deviation of the atomic co-ordinate for a non-centrosymmetric crystal is greater than that for a centro-symmetric crystal.

The results for the space groups, $P2$ and $P2_1$ are also stated here without proof. For a general reflection hkl the fractional error in $|F|$ is given by

$$\sigma(|F|)/|F| = (2\pi^2 N/3)^{\frac{1}{2}} (f\sigma_r)/|F|d , \qquad (21)$$

which is the same as for the non-centrosymmetric $P1$. However, for reflections of the type $h0l$ corresponding to the centrosymmetric projection parallel to the b axis, the fractional error is given by

$$\sigma(|F|)/|F| = (4\pi^2 N/3)^{\frac{1}{2}} (f\sigma_r)/|F|d , \qquad (22)$$

which corresponds to $P\bar{1}$.

Equations (21) and (22) can be obtained by writing down the explicit expressions for the structure factor equation in terms of A and B and following the methods of the section 2 and 3.

4. Effect of errors on Bijvoet inequality

In this section, the standard deviation and the fractional error of the Bijvoet inequality are derived in terms of the standard deviations of the atomic co-ordinates. This problem of estimating the fractional error in Bijvoet inequality was met with in connection with the author's work on the evaluation of the anomalous dispersion factor $\Delta f''_{\text{Cl}}$ from the measured values of the Bijvoet inequalities $(\Delta I/I)$ for various reflections for the compound L-tyrosine hydrochloride (Parthasarathy, 1961). L-tyrosine hydrochloride contains two chlorine atoms which are the anomalous scatterers and a number of non-anomalous light atoms. Choosing the origin midway between the two chlorine atoms, it can be shown (Parthasarathy, 1961) that the expression for the Bijvoet inequality takes the simple form

$$(\Delta I/I) = 4A''_{\text{Cl}}B/|F|^2, \qquad (23)$$

where $A''_{\text{Cl}} = 2\Delta f''_{\text{Cl}} \cos \alpha_{\text{Cl}}$, $B = |F| \sin \alpha$. α is the phase angles of the structure factor and $\alpha_{\text{Cl}} = 2\pi \mathbf{H}.\mathbf{r}_{\text{Cl}}$. $|F|^2$ is the mean intensity of two inverse reflections, which may for all practical purposes, be put equal to the value calculated without including $\Delta f''$. It is clear from equation (23) that the atomic co-ordinates vitally enter into the calculation of $(\Delta I/I)$ and the calculated value of the Bijvoet inequality depends on the actual co-ordinates used. Now the problem is to estimate the fractional error in Bijvoet inequality $\sigma(\Delta I/I)/(\Delta I/I)$ knowing the standard deviation of the atomic co-ordinates.

The positions of the anomalous scatterers, which are usually rather heavy, are known to a greater accuracy than the rest and hence the factor A''_{Cl} in

the numerator of equation (23) for $(\Delta I/I)$ can be regarded as a constant having no error. Equation (23) then takes the form

$$(\Delta I/I) = kB/|F|^2, \qquad (24)$$

where

$$k = 4A''_{\text{Cl}} .$$

By applying arguments similar to those employed in Section 2 for deriving equation (15) from equation (2), it can be shown that the fractional error in Bijvoet inequality is given by

$$\sigma(\Delta I/I)/(\Delta I/I) = (2\pi^2 N/3)^{\frac{1}{2}} (f\sigma_r)/Bd . \qquad (25)$$

Equation (25) shows that, in general, $\sigma(\Delta I/I)/(\Delta I/I)$ increases with increasing number of atoms N in the unit cell, increasing angle of scattering θ and decreasing B. Equation (25) has been applied to the calculation of the fractional error in $(\Delta I/I)$ in the actual case of L-tyrosine hydrochloride (Parthasarathy, 1961) and it was found that even for this fairly accurate structure (standard deviation of the light atoms is less than 0·02 Å) the fractional error $\sigma(\Delta I/I)/(\Delta I/I)$ was quite large, especially for weak reflections at high values of $(\sin \theta/\lambda)$.

5. Effect of errors on the phase angle α for $P1$

The phase angle α is given by

$$\alpha = \tan^{-1} (B/A) . \qquad (26)$$

Since A and B are functions of $\mathbf{r}_j$ the method of Section 2 can be adopted here and a similar procedure leads to the standard deviation $\sigma(\alpha)$ of the phase angle to be

$$\sigma(\alpha) = (2\pi^2 N/3)^{\frac{1}{2}} (f\sigma_r)/|F|d . \qquad (27)$$

The following useful results can also be derived by a similar method.

$$\sigma(A) = \sigma(B) = \sigma(|F|) = |F|\sigma(\alpha) . \qquad (28)$$

APPENDIX I

We shall give here another derivation of equation (14) using a direct physical approach. The structure factor equation

$$\mathbf{F} = \sum_j f_j \exp i\varphi_j = \sum_j \mathbf{l}_j , \qquad (I\cdot1)$$

where

$$\varphi_j = 2\pi (\mathbf{H}.\mathbf{r}_j) \qquad (I\cdot2)$$

is represented in an Argand diagram in Fig. 1(a). The F and l (bold face) indicates that they are vectors in the Argand plane. A small error $\delta\mathbf{r}_j(\delta x_j, \delta y_j, \delta z_j)$ in the atomic co-ordinates will produce corresponding small changes $\Delta\mathbf{l}_j$ in the vectors $\mathbf{l}_j$ which are all shown together at the terminus of the sum vector $\mathbf{F}$. Thus this vector changes from its original position OP to a new one OQ, PQ being denoted by $\Delta\mathbf{F}$. It is obvious that if the errors in the co-ordinates $\delta\mathbf{r}_j$ are random,

then the point Q would be distributed all around the mean position P with circular symmetry. The length PQ on the other hand will have a mean square value $\langle |\Delta F|^2 \rangle = \Delta^2$ (say).

Clearly then

$$\langle |\Delta F|^2 \rangle = \sum_i \sum_j \langle \delta l_i \cdot \delta l_j^* \rangle . \qquad (\text{I·3})$$

Substituting for δl_i, δl_j from (I·1) and (I·2) we have

$$\langle |\Delta F|^2 \rangle = \sum_i^N \sum_j^N f_i f_j \exp\left[i(\varphi_i - \varphi_j)\langle(\mathbf{H}.\delta \mathbf{r}_i)(\mathbf{H}.\delta \mathbf{r}_j)\rangle\right] . \qquad (\text{I·4})$$
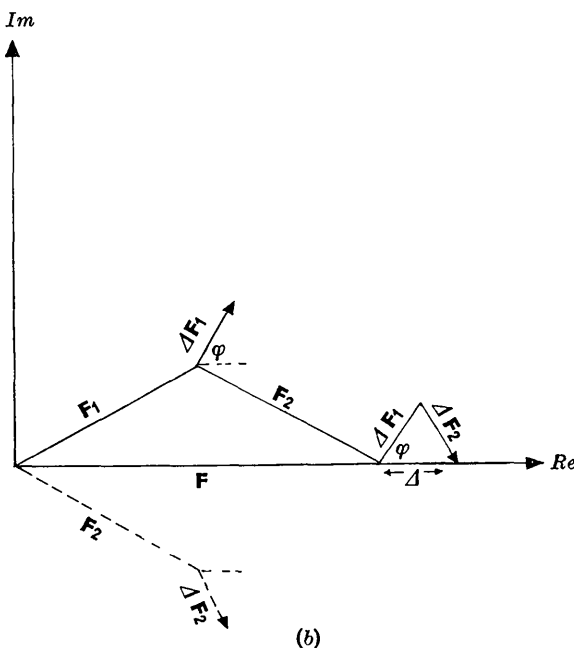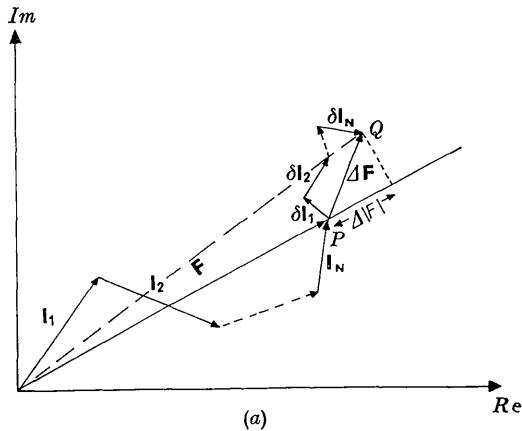

(a)

(b)

Fig. 1. (a) Structure factor equation in the Argand plane for the space group $P1$. (b) Structure factor equation in the Argand plane for the space group $P\bar{1}$.

Using equation (11b)

$$\Delta^2 = (4\pi^2 N/3d^2)(f\sigma_r)^2 . \qquad (\text{I·5})$$

Now in general the vector $\Delta \mathbf{F}$ makes a variable angle φ with $\mathbf{F}$ so that, $\delta|F|$, the component of $\Delta \mathbf{F}$ parallel to $\mathbf{F}$ is given by

$$\delta|F| = \Delta \cos \varphi . \qquad (\text{I·6})$$

On squaring this and averaging over all orientations of $\Delta \mathbf{F}$ (i.e., values of φ from 0 to 2π) we obtain

$$\langle(\delta|F|)^2\rangle = \Delta^2 \langle \cos^2 \varphi \rangle = (\Delta^2/2) . \qquad (\text{I·7})$$

Substituting from equation (I:5) we have finally

$$\sigma^2(|F|) = (2\pi^2 N/3d^2)(f\sigma_r)^2, \qquad (\text{I·8})$$

which is the same as equation (14).

The above discussion can be readily extended to the case of the centro-symmetrical space group $P\bar{1}$. Denoting the two asymmetric units in the unit cell by subscripts 1 and 2, we can write the structure factor as (see Fig. 1(b))

$$\mathbf{F} = \mathbf{F}_1 + \mathbf{F}_2 . \qquad (\text{I·9})$$

Also

$$\Delta \mathbf{F} = \Delta \mathbf{F}_1 + \Delta \mathbf{F}_2 . \qquad (\text{I·10})$$

Even though $|\Delta F_1| = |\Delta F_2| = \delta$ (say), the phase angles of $\Delta \mathbf{F}$ and $\Delta \mathbf{F}_2$ are different. Hence equation (I·10) can be written as

$$\Delta \mathbf{F} = \delta \left[\exp (i\varphi) + \exp (-i\varphi)\right] = 2\delta \cos \varphi , \qquad (\text{I·11})$$

where δ^2 has a value, analogous to (I·5),

$$\delta^2 = (4\pi^2 n/3d^2)(f\sigma_r)^2 \qquad (\text{I·12})$$

and φ is the angle made by ΔF_1, with the real axis. On squaring equation (I·11) and averaging over the values of the variable angle φ i.e., from $\varphi = 0$ to 2π, we get

$$\sigma^2(|F|) = \langle |\Delta F|^2 \rangle = 2\delta^2 = (4\pi^2 N/3d^2)(f\sigma_r)^2, \qquad (\text{I·13})$$

which is the same as equation (19).

References

LIPSON, H. & COCHRAN, W. (1957). *The determination of Crystal Structures.* London: Bell.
LUZZATI, V. (1952). *Acta Cryst.* 5, 802.
PARTHASARATHY, R. (1961). *Acta Cryst.* (In press.)