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Probability Distribution of Bijvoet Differences when the Group of Normal Scatterers is Partly Centrosymmetric*

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Cumulative functions of the normalized Bijvoet differences x and Δ and their expectation values for a non-centrosymmetric crystal in which the group of normal scatterers is partly centrosymmetric are worked out for the cases when the number (P) of anomalous scatterers in the unit cell is one and many (MN and MC cases) respectively. The results are used to obtain the percentage of reflexions for which $\Delta \geq 0{\cdot}05$. It is found that even when 50% of the normal scatterers form a single centrosymmetric group, the measurability of the Bijvoet difference is not affected significantly by the partial centrosymmetry of the group of normal scatterers.

Introduction

The probability distribution of the normalized Bijvoet difference x has been worked out by Parthasarathy & Srinivasan (1964) (PS, 1964 for brevity) for a non-centrosymmetric crystal containing an ideally non-centrosymmetric group of normal scatterers† of similar scattering power besides a group of anomalous scatterers in the unit cell. Four cases have been considered, namely, those for which $P=1$, 2 and many (MN‡ and MC cases) respectively. The Q group met with in actual crystals quite often contains a centrosymmetric part (called the Qc group in this paper; *e.g.* a benzene ring) attached to a group of other light atoms which form a non-centrosymmetric configuration (called the Qn group). It would therefore be useful to study how the distribution of x (and hence the measurability of the Bijvoet difference) is modified in the presence of such a centrosymmetric group of atoms in the Q group. Since the cumulative function of the normalized Bijvoet difference§ $\Delta(=|\Delta I|/\sigma_N^2)$ is the relevant quantity and since this could be obtained from that of x [see equation (24) below], we shall first obtain the cumulative function of x. We shall consider only three cases, namely, the cases with $P=1$, MN and MC respectively since the theoretical result for the case $P=2$ is not expressible in a simple form. We shall also work out the expectation value of x for the various cases.

The effect of the Q group and its centrosymmetry on the distribution of Δ has been found to be expressible in terms of two parameters, namely, (i) σ_2^2 which is the fractional contribution from all the Q atoms* to the local mean intensity relative to the whole structure and (ii) r which is the fractional contribution to the local mean intensity from the Qc group relative to the whole Q group.

The notation in this paper closely follows that in the earlier paper (PS, 1964). It may also be noted that the distributions derived here are generalizations of those obtained in PS (1964) since the earlier results follow from those derived here under the limiting condition $r \rightarrow 0$.

Derivation of the cumulative function of x

Consider a non-centrosymmetric crystal (space group $P1$) containing, besides a group of P anomalous scatterers of the same type, Q normal scatterers of which a number Qc of atoms form a *single* centrosymmetric group and the rest $Q-Qc$ $(=Qn)$ form a non-centrosymmetric group. We shall assume that the Q atoms are of similar scattering power and that the numbers Qc and Qn are such that the structure factors F_{Qc} and F_{Qn} obey the centric and acentric Wilson (1949) distributions respectively. From equation (4) of PS (1964) we obtain the expression for

$$x\ (=|\Delta I|/4\sigma_Q\sigma_P''=|\Delta I|/4k\sigma_Q\sigma_P)$$

to be

$$x=y_P y_Q u \tag{1}$$

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† Following PS (1964) normal scatterers will be referred to as Q atoms and anomalous scatterers as P atoms. P and Q also denote respectively the number of anomalous and normal scatterers in the unit cell.

‡ This has been referred to as MA in PS (1964). The present symbol has been adopted in view of the comments of Rogers (1965).

§ Though the more relevant quantity for this is the Bijvoet ratio δ, we shall not deal with it in this paper owing to the complications involved in the theory. It may be noted that the results regarding the effect of centrosymmetry in the Q group on the measurability of the Bijvoet difference obtained from a study of the distribution of Δ would however agree closely with that obtained from a study of the distribution of δ.

* The fractional contribution to the local mean intensity from the P atoms is denoted by σ_1^2 which is equal to $1-\sigma_2^2$.

where we have used the results

$$y_P^2=|F_P'|^2/\langle|F_P'|^2\rangle=|F_P''|^2/\langle|F_P''|^2\rangle\,, \qquad (2)$$

$$\sigma_P''^2=k^2\sigma_P^2=k^2\sum_{j=1}^{P}f_{Pj}'^2\,, \quad k=\Delta f_P''/(f_P^0+\Delta f_P') \qquad (3)$$

and the variable u ($=|\sin\psi|$) [for the definition of ψ see Fig. 1 of PS (1964)] has the probability density function (hereafter abbreviated pdf)

$$P(u)=\frac{2}{\pi}\frac{1}{\sqrt{1-u^2}}\,, \quad 0\le u\le 1\,. \qquad (4)$$

To obtain the pdf of x it is found to be convenient first to obtain the pdf of the variable t, namely,

$$t=y_Pu\,. \qquad (5)$$

From (1) and (5) it is seen that

$$x=ty_Q\,. \qquad (6)$$

The structure factor F_Q of the Q group can be written as

$$F_Q=F_{Qn}+F_{Qc} \qquad (7)$$

so that

$$\sigma_Q^2=\langle|F_Q|^2\rangle=\langle|F_{Qn}|^2\rangle+\langle|F_{Qc}|^2\rangle=\sigma_{Qn}^2+\sigma_{Qc}^2\,. \qquad (8)$$

The fractional contribution to the local mean intensity from the Qc and Qn groups of atoms will be denoted by σ_{2c}^2 and σ_{2n}^2 respectively. Thus

$$\sigma_{2n}^2=\sigma_{Qn}^2/\sigma_N^2 \quad \text{and} \quad \sigma_{2c}^2=\sigma_{Qc}^2/\sigma_N^2 \qquad (9)$$

so that

$$\sigma_2^2=\sigma_Q^2/\sigma_N^2=\sigma_{2n}^2+\sigma_{2c}^2\,. \qquad (10)$$

We shall denote the ratio of the contributions to the local mean intensity from Qc and Q groups by r, that is

$$r=\sigma_{Qc}^2/\sigma_Q^2=\sigma_{2c}^2/\sigma_2^2\,. \qquad (11)$$

It may be seen that as $r\to 0$ the Q group tends to become completely non-centrosymmetric and this situation is the one dealt with in PS (1964). For the other limiting case, namely, $r\to 1$, the Q group tends to become completely centrosymmetric. It may also be noted that if the Q group contains atoms of similar scattering power, which is usually the case, we can set $r\simeq Qc/Q$. Thus, for a Q group with similar atoms, r represents the fractional number of atoms in the Q group forming the centrosymmetric part.

From (6) it is seen that in order to obtain the pdf of x we require the pdf of $y_Q(=|F_Q|/\sigma_Q)$ which can be deduced from the results of Parthasarathy (1966*b*). Since the Qc and Qn groups considered here are the analogues of the P and Q groups of Parthasarathy (1966*b*), it follows that $P(y_Q)$ needed here can be obtained from equation (8) of Parthasarathy (1966*b*) by replacing the set of quantities (y, σ_1^2 and σ_2^2) by the corresponding set (y_Q, r and $1-r$). We thus have

$$P(y_Q)=\frac{2y_Q}{\sqrt{1-r^2}}\exp\left[-\frac{y_Q^2}{(1-r^2)}\right]I_0\left[\frac{ry_Q^2}{1-r^2}\right]\,. \qquad (12)$$

We shall use the above results to derive the cumulative function of x for the various cases.

One-atom case (*i.e.* $P=1$)

For this case since the pdf of y_P is given by $\delta(y_P-1)$, the pdf of $t(=uy_P)$ could be obtained by making use of (4) in the first result in equation (7) of PS (1964). Thus we obtain

$$P(t)=\frac{2}{\pi\sqrt{1-t^2}}\,, \quad 0\le t\le 1\,. \qquad (13)$$

Since y_Q, y_P and u are independent random variables (PS, 1964) so are y_Q and t, and we obtain from (12) and (13) the joint pdf of y_Q and t to be

$$\begin{aligned}P(y_Q,t)&=P(y_Q)P(t)\\&=\frac{4y_Q}{\pi\sqrt{1-r^2}\sqrt{1-t^2}}\exp\left[-\frac{y_Q^2}{1-r^2}\right]I_0\left[\frac{ry_Q^2}{1-r^2}\right]\,,\\&0\le y_Q<\infty\,,\quad 0\le t\le 1\,.\end{aligned} \qquad (14)$$

The probability that x takes a value which is less than or equal to x_0, say, will be the value of the cumulative function of x at $x=x_0$. We thus obtain from (14) that

$$N(x_0)=\Pr(x\le x_0)=\Pr(y_Qt\le x_0)=\iint_{y_Qt\le x_0}P(y_Q,t)\mathrm{d}y_Q\mathrm{d}t\,. \qquad (15)$$

Making use of (14) in (15) it can be shown that (see Appendix A)

$$\begin{aligned}N(x_0)=&\frac{2}{\sqrt{1-r^2}}\int_0^{x_0}\beta\exp\left[-\frac{\beta^2}{(1-r^2)}\right]I_0\left(\frac{r\beta^2}{1-r^2}\right)\mathrm{d}\beta\\&+\frac{2}{\pi\sqrt{1-r^2}}\int_0^{\frac{1}{(1+x_0^2)}}\exp\left[-\frac{(1-\beta)}{\beta(1-r^2)}\right]I_0\left[\frac{r(1-\beta)}{(1-r^2)\beta}\right]\\&\sin^{-1}\left(x_0\sqrt{\frac{\beta}{1-\beta}}\right)\frac{\mathrm{d}\beta}{\beta^2}\end{aligned} \qquad (16)$$

where we have replaced the dummy variable y_Q in the term I_1 of equation (A3) by β. For any given value of x_0 the integrals in (16) are to be evaluated numerically.

Many-atom (*i.e.* $P=MN$) *case*

Since y_P follows the acentric Wilson distribution and since the pdf of u is given by (4) it follows that the pdf of $t(=uy_P)$ of this paper will be *formally* the same as that obtained in equation (10) of PS (1964) for the variable $y_Q|\sin\psi|$. Thus we have

$$P(t)=\frac{2}{\sqrt{\pi}}\exp(-t^2)\,,\quad 0\le t<\infty\,. \tag{17}$$

From (12) and (17) we obtain the joint pdf of the independent variables t and y_Q to be

$$P(y_Q,t)=\frac{4y_Q}{\sqrt{\pi}\sqrt{1-r^2}}\exp\left[-t^2-\frac{y_Q^2}{(1-r^2)}\right]I_0\left(\frac{ry_Q^2}{1-r^2}\right),$$
$$0\le y_Q<\infty\,,\quad 0\le t<\infty\,. \tag{18}$$

By following the procedure used for the one-atom case it can be shown that (see Appendix B)

$$N(x_0)=1-\frac{2\sqrt{1-r^2}}{\pi}\times\int_0^{\pi/2}\exp\left[-2x_0\sqrt{\frac{1+r\cos 2\varphi}{1-r^2}}\right]\frac{\mathrm{d}\varphi}{(1+r\cos 2\varphi)}\,. \tag{19}$$

Many-atom (i.e. $P=MC$) case

Since y_P follows the centric Wilson distribution and since the pdf of u is given by (4) we obtain, by making use of the first result in equation (7) of PS (1964), the pdf of $t=y_Pu$ to be

$$P(t)=\int_t^\infty\left\{\sqrt{\frac{2}{\pi}}\exp\left(-\frac{y_P^2}{2}\right)\right\}\left\{\frac{2}{\pi\sqrt{1-(t^2/y_P^2)}}\right\}\frac{\mathrm{d}y_P}{y_P}$$
$$=\left(\frac{2}{\pi}\right)^{3/2}\int_t^\infty\frac{\exp(-y_P^2/2)}{\sqrt{y_P^2-t^2}}\mathrm{d}y_P\,. \tag{20}$$

Making use of the substitution $y_P^2-t^2=\varepsilon$ in (20) and then the formula given in equation (13) on p. 138 of Erdelyi (1954) we obtain the pdf of t to be

$$P(t)=\frac{\sqrt{2}}{\pi^{3/2}}\exp(-t^2/4)\,K_0(t^2/4)\,,\quad 0\le t\le\infty\,. \tag{21}$$

A comparison of (21) with equation (14) of PS (1964) shows that the pdf of t of the present paper is *formally* identical with the pdf of x for the two-atom case of PS (1964). This property will be exploited later for the numerical evaluation of the cumulative function of x for the present case. From (12) and (21) we obtain the joint pdf of t and y_Q to be

$$P(y_Q,t)=\left[\frac{\sqrt{2}}{\pi^{3/2}}\exp\left(-\frac{t^2}{4}\right)K_0\left(\frac{t^2}{4}\right)\right]\times\left[\frac{2y_Q}{\sqrt{1-r^2}}\exp\left[-\frac{y_Q^2}{(1-r^2)}\right]I_0\left[\frac{ry_Q^2}{(1-r^2)}\right]\right],$$
$$0\le y_Q<\infty\,,\quad 0\le t<\infty\,. \tag{22}$$

By following the procedure adopted for the one-atom case it can be shown that (see Appendix C)

$$N(x_0)=\frac{1}{\sqrt{1-r^2}}\int_0^1 N_2\left(x_0\sqrt{\frac{\beta}{1-\beta}}\right)\times\exp\left[-\frac{(1-\beta)}{\beta(1-r^2)}\right]I_0\left[\frac{r(1-\beta)}{(1-r^2)\beta}\right]\frac{\mathrm{d}\beta}{\beta^2} \tag{23}$$

where $N_2\left(x_0\sqrt{\frac{\beta}{1-\beta}}\right)$ is used to denote the value of the cumulative function of x at $x=x_0\sqrt{\frac{\beta}{1-\beta}}$ for the two-atom (*i.e.* $P=2$) case of PS (1964).

Cumulative function of Δ

The normalized Bijvoet difference Δ is defined as [see equation (1) of Parthasarathy, 1967)

$$\Delta=|\Delta I|/\langle I_N\rangle\simeq|\Delta I|/\sigma_N^2=4k\sigma_1\sigma_2x\,. \tag{24}$$

Since k, σ_1 and σ_2 are constants it is clear from (24) that the cumulative function of Δ, say $N_\Delta(\Delta)$, could be obtained from that of x, say, $N_x(x)$ from the following result

$$N_\Delta(\Delta)=N_x(\Delta/4k\sigma_1\sigma_2)\,. \tag{25}$$

Since the cumulative function of x (for a given P) depends on the parameter r, it follows from (25) that the cumulative function of Δ will depend on two parameters characterizing the Q group and its centrosymmetry, namely, $\sigma_2^2(=1-\sigma_1^2)$ and r.

Expectation values of x and Δ

Since y_P, y_Q and u are mutually independent we obtain from (1) the expectation value of x to be

$$\langle x\rangle_P=\langle y_P\rangle\,\langle y_Q\rangle\,\langle u\rangle \tag{26}$$

where the subscript P to the expectation symbol characterizes the P group. It is known that $\langle y_P\rangle=1$, $2\sqrt{2}/\pi$, $\sqrt{\pi}/2$ and $\sqrt{2/\pi}$ according as $P=1$, 2, MN and MC respectively (Parthasarathy, 1967). From (4) it is readily seen that $\langle u\rangle=2/\pi$. The expectation value of y_Q can be derived from equation (37g) of Parthasarathy (1966a), by replacing σ_1^2 by r, as

$$\langle y_Q\rangle=\frac{\sqrt{1+r}}{\sqrt{\pi}}E\left(\sqrt{\frac{2r}{1+r}}\right)=\frac{1}{\sqrt{\pi}}m_r\,,\quad\text{say}\,. \tag{27}$$

Substituting the known values of $\langle y_P\rangle$ and $\langle u\rangle$ and (27) in (26) we obtain

$$\langle x\rangle_P=\frac{2m_r}{\pi^{3/2}}\qquad\text{for}\quad P=1$$
$$=\frac{4\sqrt{2}m_r}{\pi^{5/2}}\qquad\text{for}\quad P=2$$

$$= \frac{m_r}{\pi} \quad \text{for} \quad P = MN$$

$$= \frac{2\sqrt{2m_r}}{\pi^2} \quad \text{for} \quad P = MC\,. \tag{28}$$

From (24) it follows that

$$\langle \Delta \rangle_P = 4k\sigma_1\sigma_2 \langle x \rangle_P\,. \tag{29}$$

The expectation value of Δ can thus be obtained by substituting (28) in (29).

Discussion of the theoretical results

It is seen from (26) that the measurability of the Bijvoet difference is determined by the nature of the distribution of x. Hence, we shall first study the features of the distribution of x for the various cases. The cumulative functions of x for the cases $P=1$, MN and MC have been obtained in (16), (19) and (23) and these are in the form of integrals which are to be evaluated by a numerical procedure. The integral in (23) for the case $P=MC$ involves a factor which is formally identical with the cumulative function of x for the two-atom case of PS (1964). To facilitate the numerical evaluation of this, the cumulative function of x for the two-atom case of PS (1964) was obtained first at regular close intervals; interpolation methods were then used to evaluate it for any required value of the argument. The fractional number of reflexions for which $x \geq x_0$ is called the complementary cumulative function $\bar{N}(x_0)$ and is given by

$$\bar{N}(x_0) = 1 - N(x_0)\,. \tag{30}$$

The function $\bar{N}(x_0)$ for the various cases is given in Table 1 for different values of the parameter r. The values of $\bar{N}(x_0)$ for the limiting situation $r=0$ for the cases $P=1$, MN and MC agree with the corresponding values obtained for the situation in which the Q group is completely non-centrosymmetric (Parthasarathy, 1966*c*) as expected. Table 1 also reveals an interesting result, namely, for any given values of P and σ_2^2, even if half the number of atoms in the Q group form a single centrosymmetric group (*i.e.* $Qc=Qn=Q/2$ leading to $r=0{\cdot}5$), the value $\bar{N}(x_0)$ for any x_0 is practically the same as that for the case $r=0$. Thus it turns out that unless the major part of the Q group is centrosymmetric (*i.e.* unless $Qc \gg Qn$) the centrosymmetry of the Q group does not affect the distribution of x significantly.

Table 1. *Values (%) of the complementary cumulative function of x for the cases P=1, MN and MC as a function of r*

x_0 ↓ \ r →	P=1: 0.0	0.2	0.4	0.6	0.8	P=MN: 0.0	0.2	0.4	0.6	0.8	P=MC: 0.0	0.2	0.4	0.6	0.8
0.05	94.4	94.2	94.0	93.7	93.0	90.5	90.4	90.2	89.7	88.8	83.0	83.0	82.7	82.1	80.8
0.10	88.8	88.6	88.3	87.7	86.4	81.9	81.8	81.4	80.6	79.0	72.3	72.2	71.8	70.9	69.2
0.15	83.2	83.0	82.6	81.8	79.9	74.1	73.9	73.4	72.4	70.5	63.8	63.7	63.2	62.3	60.4
0.20	77.7	77.5	77.0	75.9	73.6	67.0	66.9	66.3	65.1	62.9	56.8	56.7	56.2	55.2	53.2
0.25	72.4	72.1	71.5	70.2	67.6	60.7	60.5	59.8	58.6	56.3	50.9	50.7	50.2	49.2	47.2
0.30	67.1	66.9	66.2	64.7	61.8	54.9	54.7	54.0	52.8	50.5	45.8	45.6	45.1	44.1	42.1
0.35	62.1	61.8	61.0	59.4	56.4	49.7	49.5	48.8	47.6	45.4	41.3	41.1	40.6	39.6	37.8
0.40	57.2	56.9	56.0	54.4	51.3	44.9	44.7	44.1	42.9	40.8	37.3	37.2	36.7	35.7	34.0
0.45	52.5	52.2	51.3	49.6	46.6	40.7	40.5	39.8	38.7	36.8	33.8	33.7	33.2	32.3	30.7
0.50	47.9	47.7	46.8	45.1	42.2	36.8	36.6	36.0	34.9	33.2	30.7	30.6	30.1	29.3	27.8
0.55	43.7	43.4	42.5	40.9	38.2	33.3	33.1	32.6	31.6	30.0	27.9	27.8	27.4	26.6	25.2
0.60	39.6	39.3	38.5	36.9	34.6	30.1	30.0	29.4	28.5	27.1	25.4	25.3	24.9	24.2	22.9
0.65	35.8	35.5	34.7	33.3	31.2	27.3	27.1	26.6	25.8	24.6	23.2	23.1	22.7	22.0	20.8
0.70	32.2	32.0	31.2	29.9	28.2	24.7	24.5	24.1	23.3	22.3	21.2	21.1	20.7	20.1	19.0
0.75	28.9	28.6	28.0	26.8	25.4	22.3	22.2	21.8	21.1	20.2	19.3	19.2	18.9	18.3	17.4
0.80	25.8	25.6	25.0	24.0	22.9	20.2	20.1	19.7	19.1	18.4	17.7	17.6	17.3	16.8	15.9
0.85	22.9	22.7	22.2	21.4	20.6	18.3	18.2	17.9	17.4	16.7	16.2	16.1	15.8	15.3	14.6
0.90	20.3	20.1	19.7	19.0	18.5	16.5	16.4	16.2	15.7	15.2	14.8	14.7	14.5	14.1	13.3
0.95	17.9	17.8	17.4	16.9	16.6	15.0	14.9	14.8	14.3	13.8	13.6	13.5	13.3	12.9	12.3
1.00	15.7	15.6	15.3	15.0	14.9	13.5	13.5	13.3	13.0	12.6	12.5	12.4	12.2	11.8	11.3
1.10	12.0	11.9	11.8	11.7	11.9	11.1	11.0	10.9	10.7	10.5	10.5	10.4	10.3	10.0	9.5
1.20	9.0	9.0	9.0	9.1	9.4	9.1	9.0	8.9	8.8	8.7	8.8	8.8	8.7	8.5	8.1
1.30	6.6	6.6	6.7	7.0	7.5	7.4	7.4	7.4	7.3	7.3	7.5	7.4	7.3	7.2	6.9
1.40	4.8	4.8	5.0	5.3	5.8	6.1	6.1	6.1	6.1	6.1	6.3	6.3	6.2	6.1	5.9
1.50	3.4	3.5	3.7	4.0	4.5	5.0	5.0	5.0	5.0	5.1	5.4	5.3	5.3	5.2	5.0
1.60	2.4	2.4	2.7	3.0	3.5	4.1	4.1	4.1	4.2	4.3	4.6	4.5	4.5	4.4	4.3
1.70	1.6	1.7	1.9	2.3	2.7	3.3	3.3	3.4	3.5	3.6	3.9	3.9	3.8	3.8	3.7
1.80	1.1	1.2	1.4	1.7	2.0	2.7	2.7	2.8	2.9	3.1	3.3	3.3	3.3	3.3	3.2
1.90	0.7	0.8	1.0	1.2	1.5	2.2	2.3	2.3	2.4	2.6	2.8	2.8	2.8	2.8	2.7
2.00	0.5	0.5	0.7	0.9	1.1	1.8	1.9	1.9	2.0	2.2	2.4	2.4	2.4	2.4	2.3

Table 2. *Percentage of reflexions for which $\Delta > 0{\cdot}05$ as a function of k, σ_2^2 and r for the cases P=1, MN and MC*

k ↓	σ_2^2 ↓ \ r →	P=1: 0.0	0.2	0.4	0.6	0.8	P=MN: 0.0	0.2	0.4	0.6	0.8	P=MC: 0.0	0.2	0.4	0.6	0.8
0.05	0.10	23.9	23.7	23.1	22.2	21.3	18.9	18.8	18.5	17.9	17.2	16.7	16.6	16.3	15.8	15.0
	0.20	37.7	37.4	36.6	35.1	32.9	28.7	28.5	28.0	27.1	25.8	24.3	24.2	23.8	23.1	21.8
	0.30	44.0	43.8	42.9	41.2	38.6	33.6	33.4	32.9	31.9	30.3	28.2	28.0	27.6	26.8	25.4
	0.40	47.0	46.8	45.9	44.2	41.4	36.0	35.9	35.3	34.2	32.5	30.1	30.0	29.5	28.7	27.2
	0.50	48.0	47.7	46.8	45.1	42.3	36.8	36.6	36.0	34.9	33.2	30.7	30.6	30.1	29.3	27.8
0.10	0.10	55.6	55.3	54.4	52.8	49.7	43.5	43.3	42.6	41.5	39.4	36.1	36.0	35.5	34.5	32.8
	0.20	65.9	65.6	64.9	63.4	60.4	53.5	53.3	52.7	51.4	49.2	44.6	44.4	43.9	42.9	41.0
	0.30	70.0	69.7	69.1	67.7	64.9	58.0	57.8	57.1	55.9	53.6	48.5	48.3	47.8	46.8	44.8
	0.40	71.8	71.6	71.0	69.7	67.0	60.0	59.8	59.7	58.0	55.7	50.5	50.7	49.6	48.6	46.6
	0.50	72.4	72.2	71.5	70.2	67.6	60.7	60.5	59.8	58.6	56.3	50.9	50.7	50.2	49.2	47.2
0.15	0.10	69.4	69.2	68.5	67.1	64.4	57.4	57.2	56.5	55.3	53.0	48.0	47.8	47.3	46.2	44.3
	0.20	76.8	76.6	76.1	75.0	72.6	65.9	65.7	65.2	64.0	61.8	55.8	55.6	55.1	54.1	52.1
	0.30	79.7	79.5	79.0	78.0	75.9	69.5	69.3	68.8	67.7	65.6	59.7	59.1	58.6	57.6	55.6
	0.40	81.0	80.8	80.4	79.4	77.4	71.2	71.0	70.5	69.4	67.3	60.9	60.7	60.7	59.5	57.3
	0.50	81.4	81.2	80.8	79.8	77.8	71.7	71.5	71.0	69.9	67.8	61.4	61.2	60.7	59.8	57.8
0.20	0.10	76.8	76.6	76.1	75.0	72.6	65.9	65.7	65.2	64.0	61.8	55.8	55.6	55.1	54.1	52.1
	0.20	82.5	82.4	81.9	81.0	79.2	73.2	73.0	72.5	71.5	69.5	62.9	67.7	67.3	61.3	59.4
	0.30	84.7	84.6	84.2	83.4	81.7	76.1	76.0	75.5	74.6	72.7	66.0	65.8	65.4	64.4	62.6
	0.40	85.7	85.5	85.2	84.5	82.9	77.5	77.3	76.9	76.0	74.2	67.4	67.3	66.8	65.9	64.1
	0.50	86.0	85.8	85.5	84.8	83.2	77.9	77.7	77.3	76.4	74.6	67.8	67.7	67.3	66.4	64.5
0.25	0.10	81.4	81.2	80.8	79.8	77.8	71.7	71.5	71.0	69.9	67.8	61.4	61.7	60.7	59.8	57.8
	0.20	86.0	85.8	85.5	84.8	83.2	77.9	77.7	77.3	76.4	74.6	67.8	67.7	67.3	66.4	64.5
	0.30	87.7	87.6	87.3	86.7	85.3	80.4	80.3	79.9	79.0	77.4	70.6	70.5	70.1	69.2	67.5
	0.40	88.5	88.4	88.1	87.5	86.2	81.5	81.4	81.0	80.2	78.6	71.9	71.8	71.4	70.5	68.8
	0.50	88.8	88.6	88.3	87.8	86.5	81.9	81.8	81.4	80.6	79.0	72.3	72.2	71.8	70.9	69.2
0.30	0.10	84.4	84.3	83.9	83.1	81.4	75.7	75.6	75.1	74.2	72.3	65.6	65.4	65.0	64.0	62.2
	0.20	88.3	88.2	87.9	87.3	85.9	81.2	81.1	80.7	79.9	78.3	71.5	71.4	71.0	70.1	68.4
	0.30	89.8	89.6	89.4	88.9	87.7	83.4	83.3	82.9	82.2	80.7	74.0	73.9	73.5	72.7	71.1
	0.40	90.4	90.3	90.1	89.6	88.5	84.4	84.3	83.9	83.7	81.8	75.2	75.1	74.7	73.9	72.3
	0.50	90.6	90.5	90.3	89.8	88.7	84.6	84.5	84.2	83.5	82.1	75.6	75.4	75.1	74.3	72.7

NOTE. THE VALUE OF THE TABULATED FUNCTION IS THE SAME FOR BOTH σ_2^2 AND $1-\sigma_2^2$ AND HENCE THE VALUES FOR $\sigma_2^2 > 0.5$ ARE NOT GIVEN HERE.

Table 3. *Expectation value of the normalized Bijvoet difference x for the cases P=1, 2, MN and MC as a function of r*

r →	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
P = 1	0.564	0.564	0.563	0.561	0.558	0.555	0.550	0.544	0.537	0.576	0.508
2	0.508	0.508	0.507	0.505	0.503	0.499	0.495	0.490	0.483	0.474	0.457
MN	0.500	0.500	0.499	0.497	0.495	0.492	0.488	0.482	0.476	0.466	0.450
MC	0.450	0.450	0.449	0.448	0.445	0.443	0.439	0.434	0.428	0.420	0.405

To facilitate the study of the influence of the Q group and its centrosymmetry on the measurability of the Bijvoet difference the percentage of reflexions for which $\Delta > 0{\cdot}05$ is also given in Table 2 for various values of r and σ_2^2. For a given P, k and σ_2^2 it is seen that only when the major part of the Q group is centrosymmetric (*i.e.* $r > 0{\cdot}6$) does the measurability of the Bijvoet difference decrease significantly.

The expectation value of x for the various cases (including the case $P=2$) as obtained from (28) are given in Table 3. For any given case the expectation value of Δ could be obtained from (29) by making use of the known values of k, σ_2^2 and r and the results in Table 3. A study of this Table also confirms the above predictions.

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APPENDIX A

For a given value, x_0, the double integral of equation (15) is to be evaluated over the domain defined by the dotted area in Fig. 1(*a*). This area can be taken to be the sum of two areas, *viz.* (i) the area a_1 of the rectangle $OABC$ defined by the lines $y_Q=0$, $y_Q=x_0$, $t=0$ and $t=1$ and (ii) the area a_2 bounded by the lines $y_Q=x_0$, $t=0$ and the curve $ty_Q=x_0$. Thus the domain of integration in the (y_Q, t) plane is

$$0\le t\le 1\,,\quad 0\le y_Q\le x_0\,;$$
$$0\le t\le x_0/y_Q\,,\quad x_0\le y_Q<\infty\,. \tag{A1}$$

We can therefore rewrite (15) as

$$N(x_0)=\int_0^{x0}\int_0^1 P(y_Q,t)\mathrm{d}t\mathrm{d}y_Q$$
$$\int_{x0}^{\infty}\int_0^{x0/yQ} P(y_Q,t)\mathrm{d}t\mathrm{d}y_Q\,. \tag{A2}$$

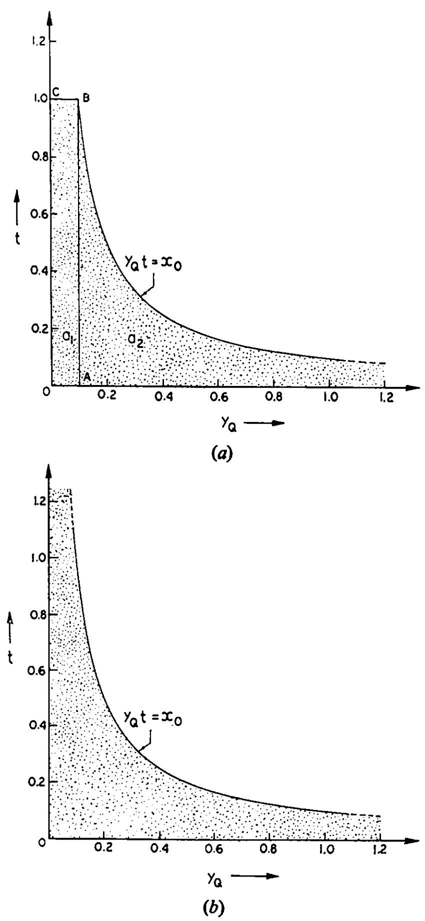

Fig. 1. (*a*) Domain of definition of the joint density function $P(y_Q,t)$ for the one-atom case. (*b*) Domain of definition of the joint density function $P(y_Q,t)$ for the $P=MN$ case.

Substituting (14) in (A2) and carrying out the integration over t first we obtain

$$N(x_0)=\int_0^{x0}\frac{2y_Q}{\sqrt{1-r^2}}\exp\left[-\frac{y_Q^2}{(1-r^2)}\right]I_0\left[\frac{ry_Q^2}{1-r^2}\right]\mathrm{d}y_Q$$
$$+\int_{x0}^{\infty}\frac{4y_Q}{\pi\sqrt{1-r^2}}$$
$$\times\exp\left[-\frac{y_Q^2}{(1-r^2)}\right]I_0\left[\frac{ry_Q^2}{1-r^2}\right]\sin^{-1}(x_0/y_Q)\mathrm{d}y_Q$$
$$=I_1+I_2\,,\quad\text{say}\,. \tag{A3}$$

It is convenient to write I_2 in a form suitable for computation by making use of the substitution $y_Q=\sqrt{(1-\beta)/\beta}$, so that

$$I_2=\frac{2}{\pi\sqrt{1-r^2}}\int_0^{\frac{1}{1+x_0^2}}\exp\left[-\frac{(1-\beta)}{\beta(1-r^2)}\right]I_0\left[\frac{r(1-\beta)}{(1-r^2)\beta}\right]$$
$$\times\sin^{-1}\left(x_0\sqrt{\frac{\beta}{1-\beta}}\right)\frac{\mathrm{d}\beta}{\beta^2}\,. \tag{A4}$$

APPENDIX B

For this case the double integral of equation (15) is to be evaluated over the domain represented by the dotted area in Fig. 1(*b*), namely

$$0\le t\le x_0/y_Q\,,\quad 0\le y_Q<\infty\,. \tag{B1}$$

Substituting (18) in (15) we obtain

$$N(x_0)=\int_0^{\infty}\int_0^{x0/yQ}\frac{4y_Q}{\sqrt{\pi}\sqrt{1-r^2}}$$
$$\times\exp\left[-t^2-\frac{y_Q^2}{(1-r^2)}\right]I_0\left(\frac{ry_Q^2}{1-r^2}\right)\mathrm{d}t\mathrm{d}y_Q\,. \tag{B2}$$

Carrying out the integration over t first we obtain

$$N(x_0)=\int_0^{\infty}\frac{2y_Q}{\sqrt{1-r^2}}$$
$$\times\exp\left[-\frac{y_Q^2}{(1-r^2)}\right]I_0\left(\frac{ry_Q^2}{1-r^2}\right)\mathrm{erf}\left(\frac{x_0}{y_Q}\right)\mathrm{d}y_Q\,. \tag{B3}$$

Making use of the substitution $y_Q^2=\varepsilon$ in (B3), replacing the Bessel function by its integral representation [see equation (9–6.16) on p. 376 of Abramowitz & Stegun (1965)] interchanging the order of the resulting integrations, and finally carrying out the integration with respect to ε first, we obtain

$$N(x_0)=1-\frac{\sqrt{1-r^2}}{\pi}\times\exp\left(-2x_0\sqrt{\frac{1+r\cos\theta}{1-r^2}}\right)\frac{d\theta}{(1+r\cos\theta)} \quad \text{(B4)}$$

where we have made use of the result (7–4.20) on p. 303 of Abramowitz & Stegun (1965). On substitution $\theta=2\varphi$, (B4) yields

$$N(x_0)=1-\frac{2\sqrt{1-r^2}}{\pi}\times\int_0^{\pi/2}\exp\left(-2x_0\sqrt{\frac{1+r\cos 2\varphi}{1-r^2}}\right)\frac{d\varphi}{(1+r\cos 2\varphi)}. \quad \text{(B5)}$$

APPENDIX C

In order to obtain $N(x_0)$ for the present case we have to evaluate the double integral in (15) subject to the limits given by (B1) with equation (22) as the integrand. That is

$$N(x_0)=\int_0^\infty\left\{\frac{2y_Q}{\sqrt{1-r^2}}\exp\left[-\frac{y_Q^2}{(1-r^2)}\right]I_0\left[\frac{ry_Q^2}{1-r^2}\right]\times\int_0^{x_0/y_Q}\frac{\sqrt{2}}{\pi^{3/2}}\exp\left(-\frac{t^2}{4}\right)K_0(t^2/4)dt\right\}dy_Q. \quad \text{(C1)}$$

Remembering that $P(t)$ of (21) is *formally* identical with the function $P(x)$ obtained in PS (1964) for the two-atom case, and that t in (C1) is a dummy variable of integration we can rewrite (C1) as

$$N(x_0)=\int_0^\infty\frac{2y_Q}{\sqrt{1-r^2}}\times\exp\left[-\frac{y_Q^2}{(1-r^2)}\right]I_0\left[\frac{ry_Q^2}{1-r^2}\right]N_2(x_0/y_Q)dy_Q \quad \text{(C2)}$$

where $N_2(x)$ denotes the cumulative function of x for the two-atom case of PS (1964). Making the substitution $y_Q=\sqrt{(1-\beta)/\beta}$ in (C2) we obtain

$$N(x_0)=\frac{1}{\sqrt{1-r^2}}\int_0^1 N_2\left(x_0\sqrt{\frac{\beta}{1-\beta}}\right)\times\exp\left[-\frac{(1-\beta)}{\beta(1-r^2)}\right]I_0\left[\frac{r(1-\beta)}{(1-r^2)\beta}\right]d\beta/\beta^2. \quad \text{(C3)}$$

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