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Expectation Value of the Bijvoet Ratio*

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The theoretical expressions for the expectation values of the Bijvoet difference and the Bijvoet ratio have been derived for a non-centrosymmetric crystal in which the anomalous scatterers are all of the same type. The dependence of the expectation value of the Bijvoet ratio on the number and the strength of the anomalous scatterers in the unit cell is discussed and this is used to obtain the best conditions for accurate measurement of the Bijvoet differences of a fairly large percentage of reflexions.

1. Introduction

The increasing importance of the anomalous dispersion method in crystal structure analysis necessitates a theoretical study of the measurability of Bijvoet differences. One approach to this would be a study of the statistical distribution of Bijvoet differences, ΔI. The distribution of Bijvoet differences in a normalized form, *viz.* $x=|\Delta I|/4[\langle I_Q\rangle\langle I''_P\rangle]^{\frac{1}{2}}$ (where P and Q refer to the anomalous and normal scatterers respectively) has already been worked out (Parthasarathy & Srinivasan, 1964). However, the distribution of ΔI normalized by the local mean intensity, $\langle I_N\rangle$ (where $N=P+Q$) rather than by the factor $4[\langle I_Q\rangle\langle I''_P\rangle]^{\frac{1}{2}}$ is probably more useful. The distribution of this quantity Δ $(=|\Delta I|/\langle I_N\rangle)$ can easily be obtained from the known distribution of x, since we have in the usual notation

$$\Delta = \frac{|\Delta I|}{\langle I_N\rangle} = \frac{|\Delta I|}{4[\langle I_Q\rangle\langle I''_P\rangle]^{\frac{1}{2}}} \times \frac{4[\langle I_Q\rangle\langle I''_P\rangle]^{\frac{1}{2}}}{\langle I_N\rangle} = 4k\sigma_1\sigma_2 x \quad (1)$$

where $k=f''_P/f'_P$, the ratio of the imaginary to the total real part of the atomic scattering factor of the anomalous scatterer and σ_1^2 and σ_2^2 are the fractional contribution to the mean intensity by the P- and the Q-atoms respectively.

A better normalization factor would be the mean intensity I of the Bijvoet pair of reflexions, *i.e.* $I=\frac{1}{2}[I(\mathbf{H})+I(\bar{\mathbf{H}})]$. The normalized Bijvoet difference $|\Delta I|/I$ (denoted by δ) is called the Bijvoet ratio in this paper. The distribution function of δ is difficult to cal-

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culate, since ΔI and I are dependent variables. The expectation value $\langle\delta\rangle$ of δ can however be worked out and it can provide a useful criterion for the measurability of Bijvoet differences. We shall presently obtain the expressions for $\langle x\rangle$, $\langle\Delta\rangle$ and $\langle\delta\rangle$, restricting ourselves to the commonly occurring case of a crystal containing only one type of anomalous scatterer in the unit cell.

2. Derivation of the expectation values of x, Δ and δ

To obtain the expressions for $\langle x\rangle$, $\langle\Delta\rangle$ and $\langle\delta\rangle$, we use a simple theorem in probability theory: If $f(x,y,z)$ is a simple function of the random variables x, y and z and if $P(x,y;z)$ is the conditional joint density function of x and y for a given z and if $P(z)$ is the density function of z, then

$$\langle f(x,y,z);z\rangle=\int_x\int_y f(x,y,z)\,P(x,y;z)dxdy \quad (2)$$

and

$$\langle f(x,y,z)\rangle=\int_z\langle f(x,y,z);z\rangle\,P(z)dz. \quad (3)$$

2.1 *Expectation values of x and Δ*

The magnitude of the Bijvoet difference is given by (see Ramachandran & Raman, 1956):

$$|\Delta I|=4|F''_P|\,|F'_N|\,|\sin\theta|=4k|F'_N|\,|F'_P|\,|\sin\theta| \quad (4)$$

where F'_P is the contribution to the structure factor of a reflexion $\mathbf{H}$ ($=hkl$) from the real parts of the atomic scattering factors of the anomalous scatterers in the unit cell and F'_N is that from the real parts of the atomic scattering factors of all the atoms in the unit cell. In (4), θ represents the phase angle between F'_N and F'_P. Making use of (2) in (4), we obtain.

$$\langle|\Delta I|;|F'_P|\rangle=4k|F'_P|\langle|F'_N|\,|\sin\theta|;|F'_P|\rangle\,. \quad (5)$$

It is clear from the right hand side of (5) that the required mean value, $\langle|\Delta I|;|F'_P|\rangle$, can be obtained if we know the joint density function of $|F'_N|$ and θ for a given $|F'_P|$, namely the function $P(|F'_N|,\theta;|F'_P|)$. The required expression is already available from another very similar problem considered earlier (Parthasarathy, 1965). The distribution that has been obtained earlier, namely $P(|F_N|,\theta;|F_P|)$ corresponds to the problem when all the atoms in the P- and Q-groups are normal scatterers. In the present problem however, we consider the total real part which when added to F_Q leads to F'_N. A reference to the derivation given earlier (Parthasarathy, 1965) shows immediately that, since there is no change in the vector F_Q, the earlier expression can be completely taken over to the present case. Thus we can write, using equation (5) of Parthasarathy (1965),

$$P(|F'_N|,\theta;|F'_P|)=(|F'_N|/\pi\sigma_Q^2)\exp\left[-(|F'_N|^2+|F'_P|^2-2|F'_N|\,|F'_P|\cos\theta)/\sigma_Q^2\right]. \quad (6)$$

From (5) and (6), we obtain

$$\langle|\Delta I|;|F'_P|\rangle=\frac{4k|F'_P|}{\pi\sigma_Q^2}\int_0^\infty\int_{-\pi}^{\pi}|F'_N|^2\,|\sin\theta|\times\exp\left[-(|F'_N|^2+|F'_P|^2-2|F'_N|\,|F'_P|\times\cos\theta)/\sigma_Q^2\right]d|F'_N|d\theta\,. \quad (7)$$

On integration (see (A-4) of Appendix A) (7) simplifies to

$$\langle|\Delta I|;|F'_P|\rangle=4\pi^{-\frac{1}{2}}k\sigma_Q|F'_P|\,. \quad (8)$$

From (3) and (8) we have

$$\langle|\Delta I|\rangle=4\pi^{-\frac{1}{2}}k\sigma_Q\langle|F'_P|\rangle=4\pi^{-\frac{1}{2}}k\sigma_P\sigma_Q\langle y_P\rangle\,, \quad (9)$$

where $y_P=|F'_P|/\sigma_P$. From (9), we obtain

$$\langle x\rangle=\left\langle\frac{|\Delta I|}{4k\sigma_P\sigma_Q}\right\rangle=\pi^{-\frac{1}{2}}\langle y_P\rangle \quad (10)$$

and

$$\langle\Delta\rangle=\left\langle\frac{|\Delta I|}{\sigma_N^2}\right\rangle=4\pi^{-\frac{1}{2}}k\sigma_1\sigma_2\langle y_P\rangle=4k\sigma_1\sigma_2\langle x\rangle\,. \quad (11)$$

From (10) and (11), it is clear that $\langle x\rangle$ and $\langle\Delta\rangle$ depend on the number of P-atoms and we shall consider four important cases, *viz.*, 1, 2, *M.C.* (*i.e.* P=many, P-group centric) and *M.A.* (*i.e.* P=many, P-group acentric). Since $\langle y_P\rangle$ takes values 1, $2\sqrt{2/\pi}$, $\sqrt{(2/\pi)}$ and $\sqrt{\pi}/2$ for $P=1$, 2, *M.C.* and *M.A.* respectively [these values can easily be obtained from the density function $P(y_P)$ of y_P given in 19(a) to (d)], the respective values of $\langle x\rangle$ are $1/\sqrt{\pi}$, $(2/\pi)^{3/2}$, $\sqrt{2}/\pi$ and $\frac{1}{2}$. In a similar way, we have from (11) that

$$\langle\Delta\rangle=\begin{cases}4\pi^{-\frac{1}{2}}k\sigma_1\sigma_2=2\cdot2568k\sigma_1\sigma_2 & \text{for } P=1\\ 8\sqrt{2}\pi^{-3/2}k\sigma_1\sigma_2=2\cdot0318k\sigma_1\sigma_2 & \text{for } P=2\\ 4\sqrt{2}\pi^{-1}k\sigma_1\sigma_2=1\cdot8008k\sigma_1\sigma_2 & \text{for } P=M.C.\\ 2k\sigma_1\sigma_2 & \text{for } P=M.A.\end{cases} \quad (12)$$

2.2 *Expectation value of δ*

The mean intensity of the Bijvoet pair of reflexions is known to be (see Ramachandran & Raman, 1956)

$$I=\tfrac{1}{2}[I(\mathbf{H})+I(\overline{\mathbf{H}})]=|F'_N|^2+|F''_P|^2\,. \quad (13)$$

In most cases $|F''_P|\ll|F'_N|$, so that we may omit $|F''_P|^2$ in comparison with $|F'_N|^2$. With this approximation we can write the expression for δ as

$$\delta=4|F''_P|\,|\sin\theta|/|F'_N|=4k|F'_P|\,|\sin\theta|/|F'_N|\,. \quad (14)$$

From (2), (6) and (14), we obtain

$$\langle\delta;|F'_P|\rangle=4k|F'_P|\langle|\sin\theta|/|F'_N|;|F'_P|\rangle$$
$$=\frac{4k|F'_P|}{\pi\sigma_Q^2}\int_0^\infty\int_{-\pi}^{\pi}|\sin\theta|\exp\left[-(|F'_N|^2+|F'_P|^2-2|F'_N|\,|F'_P|\cos\theta)/\sigma_Q^2\right]d|F'_N|d\theta\,. \quad (15)$$

Performing the integration over θ (as in (A-2) of Appendix A) we obtain

$$\langle\delta;|F'_P|\rangle=\frac{8k}{\pi}\exp(-|F'_P|^2/\sigma_Q^2)\times\int_0^\infty\sinh(2|F'_N|\,|F'_P|/\sigma_Q^2)\exp(-|F'_N|^2/\sigma_Q^2)$$

$$\times |F'_N|^{-1} d|F'_N| = \frac{4k}{\pi} \exp(-|F'_P|^2/\sigma_Q^2) \times \int_0^\infty \sinh(2|F'_P| x^{\frac{1}{2}}/\sigma_Q) \exp(-x) \frac{dx}{x}, \quad (16)$$

where $x = |F'_N|^2/\sigma_Q^2$.

From (3) and (16) we obtain

$$\langle\delta\rangle = \int_{|F'_P|} \langle\delta; |F'_P|\rangle P(|F'_P|) d|F'_P| = \int_{y_P} \langle\delta; y_P\rangle P(y_P) dy_P = \frac{4k}{\pi} \int_{y_P} \left\{ \int_{x=0}^\infty \sinh(2ay_P x^{\frac{1}{2}}) \exp(-x) \frac{dx}{x} \right\} \times \exp(-\sigma_1^2 y_P^2/\sigma_1^2) P(y_P) dy_P \quad (17)$$

where

$$a = \sigma_P/\sigma_Q = \sigma_1/\sigma_2 = \sqrt{r}, \text{ say.} \quad (18)$$

From (17) it is clear that the value of $\langle\delta\rangle$ depends on the number of atoms in the P-group. Substituting the functions $P(y_P)$ – depending on the number of atoms in the P-group – given below in (19), and carrying out the integrations, we obtain the value of $\langle\delta\rangle$ in each case. The density function of y_P is known to be (Srinivasan, 1960; Ramachandran & Srinivasan, 1959)

$$P(y_P) = \begin{cases} \delta(y_P - 1) \text{ for } P = 1 \\ \sqrt{2}\pi^{-1}(1 - y_P^2/2)^{-\frac{1}{2}},\ 0 \le y_P \le \sqrt{2} \text{ for } P = 2 \\ (2/\pi)^{\frac{1}{2}} \exp(-y_P^2/2) \text{ for } P = M.C. \\ 2y_P \exp(-y_P^2) \text{ for } P = M.A. \end{cases} \quad (19a\text{–}d)$$

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

From (17) and (19*a*) we have

$$\langle\delta\rangle = \frac{4k}{\pi} \exp(-\sigma_1^2/\sigma_2^2) \times \int_0^\infty \sinh(2ax^{\frac{1}{2}}) \exp(-x) \frac{dx}{x}, \quad (20)$$

which is obtained by carrying out the integration over y_P first. Using the power series expansion of sinh (x), it follows that

$$\int_0^\infty \sinh(bx^{\frac{1}{2}}) \exp(-x) \frac{dx}{x} = \sum_{n=1}^\infty \frac{\Gamma(n-\frac{1}{2})}{\Gamma(2n)} b^{2n-1}. \quad (21)$$

From (20) and (21) we obtain

$$\langle\delta\rangle = \frac{4k}{\sqrt{\pi}} \exp(-r) \sum_{n=1}^\infty \frac{r^{n-\frac{1}{2}}}{(n-\frac{1}{2})\Gamma(n)}, \quad (22)$$

where we have used the duplication formula for the gamma function in p. 11 of Sneddon (1961).

Two atom case (*i.e.* $P=2$)

From (17) and (19*b*) we obtain

$$\langle\delta\rangle = \frac{4\sqrt{2}k}{\pi^2} \int_{y_P=0}^{\sqrt{2}} \left\{ (1 - y_P^2/2)^{-\frac{1}{2}} \exp(-\sigma_1^2 y_P^2/\sigma_2^2) \times \int_{x=0}^\infty \sinh(2ay_P x^{\frac{1}{2}}) \exp(-x) \frac{dx}{x} \right\} dy_P. \quad (23)$$

On integration (see (*B*-4) of Appendix B), (23) gives

$$\langle\delta\rangle = \frac{4k}{\pi} \exp(-2r) \times \sum_{n=1}^\infty \frac{(2r)^{n-\frac{1}{2}}}{(n-\frac{1}{2})\Gamma(n+\frac{1}{2})} {}_1F_1(\tfrac{1}{2}; n+\tfrac{1}{2}; 2r). \quad (24)$$

Many atom case (*i.e.* $P = M.C.$)

From (17) and (19*c*) we obtain

$$\langle\delta\rangle = \frac{4\sqrt{2}k}{\pi^{3/2}} \int_0^\infty \exp(-x) \frac{dx}{x} \times \int_0^\infty \sinh(2ay_P x^{\frac{1}{2}}) \exp\left[-\left(\frac{\sigma_1^2}{\sigma_2^2} + \frac{1}{2}\right) y_P^2\right] dy_P \quad (25)$$

which on integration (see (*C*-7) of Appendix C) becomes

$$\langle\delta\rangle = \frac{4k}{\pi} \frac{\sigma_2}{\sqrt{1+\sigma_1^2}} \log_e[(1+\alpha)/(1-\alpha)] \quad (26)$$

where

$$\alpha = [2\sigma_1^2/(1+\sigma_1^2)]^{\frac{1}{2}}. \quad (27)$$

Many atom case (*i.e.* $P = M.A.$)

From (17) and (19*d*) we obtain

$$\langle\delta\rangle = \frac{8k}{\pi} \int_{y_P=0}^\infty \left\{ \int_{x=0}^\infty \sinh(2ay_P x^{\frac{1}{2}}) \times \exp(-x) \frac{dx}{x} \right\} \exp\left[-\left(\frac{\sigma_1^2}{\sigma_2^2} + 1\right) y_P^2\right] y_P dy_P, \quad (28)$$

which on integration (see (*D*-2) of Appendix D) yields

$$\langle\delta\rangle = 4k\sigma_1\sigma_2. \quad (29)$$

3. Discussion of the theoretical results

When σ_1^2 takes the limiting values, *viz.* 0 and 1, the structure will effectively be made up of one type of atom alone and so will not exhibit any Bijvoet difference, even though the structure is non-centrosymmetric (see James, 1954). That is, $P(\delta) = \delta(\delta)$ and $P(\Delta) = \delta(\Delta)$ in these cases. Thus,

$$\langle\Delta\rangle = \langle\delta\rangle = 0 \quad \text{for} \quad \sigma_1^2 = 0 \text{ or } 1. \quad (30)$$

It is easy to show that the functions $\langle\Delta\rangle$ and $\langle\delta\rangle$ obtained in the previous section satisfy (30).

We can write the expression for $\langle\Delta\rangle$ [see (12)] as

$$\langle\Delta\rangle = ck\sqrt{\sigma_1^2(1-\sigma_1^2)} \quad (31)$$

where c takes values 2·2568, 2·0318, 1·8008 and 2 respectively for $P = 1$, 2, $M.C.$ and $M.A.$ Equation (31) shows that $\langle\Delta\rangle$ attains a maximum value for $\sigma_1^2 = 0{\cdot}5$ in all the cases and that it decreases to zero in a symmetrical way about $\sigma_1^2 = 0{\cdot}5$. It is also seen that for a given value of σ_1^2, the value of $\langle\Delta\rangle$ decreases as P increases in the order $P = 1$, 2, $M.A.$ and $M.C.$ This shows that, for any given value of σ_1^2, the most pronounced anomalous dispersion effects are observed when P is just one in number. A similar statement does not hold for $\langle\delta\rangle$ for all values of σ_1^2, but requires modification (see below).

The functional relationship of $\langle\delta\rangle$ and σ_1^2 is not simple (except in the case $P=M.A.$) so that the value of σ_1^2 at which $\langle\delta\rangle$ attains a maximum cannot be analytically worked out. However, from the table of values of $\langle\delta\rangle$ as a function of σ_1^2 in the various cases (see Table 1), it is seen that $\langle\delta\rangle$ attains a maximum very close to (but *not exactly* at) $\sigma_1^2=0{\cdot}5$ – the case $P=M.A.$ being an exception. Further, the fall of $\langle\delta\rangle$ about the maximum is *not* exactly symmetrical about $\sigma_1^2=0{\cdot}5$ (the case $P=M.A.$ being an exception). For a fixed value of σ_1^2, when σ_1^2 is not very high (say $\sigma_1^2<0{\cdot}7$) the value of $\langle\delta\rangle$ decreases as P is in the order $P=1$, 2, $M.A.$ and $M.C.$, just as for the value of $\langle\Delta\rangle$ also. For higher (and fixed) values of σ_1^2 (say $\sigma_1^2>0{\cdot}8$) the value of $\langle\delta\rangle$ decreases with P in the order $P=M.A.$ or $M.C.$, 2 and 1. However, the differences between the various cases are not very prominent for $\sigma_1^2>0{\cdot}8$.

A study of Table 1 shows that $\langle\delta\rangle$ is more sensitive to variation of k than to that of σ_1^2. It is also seen that large values of $\langle\delta\rangle$ can be achieved by choosing a suitable heavy atom for which σ_1^2 is close to 0·5 and for which the value of k is as large as possible and it may often be necessary to make a compromise between the values of k and σ_1^2 in practical cases.

Table 1. *Expectation value of the Bijvoet ratio* ($\times 100$) *as a function of the nature* ($k=f''/f'$), *the number* (P) *and the fractional contribution* (σ_1^2) *of the anomalous scatterers in the unit cell*

σ_1^2	P	k 0·04	0·06	0·08	0·10	0·12	0·14	0·16	0·18	0·20	0·22	0·24	0·26	0·28	0·30
0	1														
	2														
	M.A.	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	M.C.														
0·1	1	6	8	11	14	17	20	22	25	28	31	34	36	39	42
	2	5	7	10	12	15	17	20	22	25	27	30	32	34	37
	M.A.	5	7	10	12	14	17	19	22	24	26	29	31	34	36
	M.C.	4	6	8	10	13	15	17	19	21	23	25	27	29	31
0·2	1	8	11	15	19	23	27	31	34	38	42	46	50	54	57
	2	7	10	13	16	20	23	26	30	33	36	39	43	46	49
	M.A.	6	10	13	16	19	22	26	29	32	35	38	42	45	48
	M.C.	5	8	11	14	16	19	22	25	27	30	33	36	38	41
0·3	1	9	13	18	22	27	31	36	40	45	49	54	58	63	67
	2	8	11	15	19	23	26	30	34	38	41	45	49	53	56
	M.A.	7	11	15	18	22	26	29	33	37	40	44	48	51	55
	M.C.	6	9	12	15	19	22	25	28	31	34	37	40	43	46
0·4	1	10	14	19	24	29	34	39	43	48	53	58	63	68	72
	2	8	12	16	20	24	28	32	36	40	43	47	51	55	59
	M.A.	8	12	16	20	24	27	31	35	39	43	47	51	55	59
	M.C.	7	10	13	16	20	23	26	30	33	36	39	43	46	49
0·5	1	10	15	19	24	29	34	39	44	49	53	58	63	68	73
	2	8	12	16	20	24	27	31	35	39	43	47	51	55	59
	M.A.	8	12	16	20	24	28	32	36	40	44	48	52	56	60
	M.C.	7	10	13	17	20	24	27	30	34	37	40	44	47	51
0·6	1	9	14	18	23	27	32	36	41	45	50	54	59	63	68
	2	7	11	15	19	22	26	30	33	37	41	44	48	52	56
	M.A.	8	12	16	20	24	27	31	35	39	43	47	51	55	59
	M.C.	7	10	13	17	20	24	27	30	34	37	40	44	47	50
0·7	1	8	11	15	19	23	27	30	34	38	42	46	49	53	57
	2	7	10	13	17	20	23	27	30	33	36	40	43	46	50
	M.A.	7	11	15	18	22	26	29	33	37	40	44	48	51	55
	M.C.	6	10	13	16	19	23	26	29	32	36	39	42	45	49
0·8	1	5	8	11	14	16	19	22	24	27	30	33	35	38	41
	2	6	8	11	14	17	20	22	25	28	31	34	36	39	42
	M.A.	6	10	13	16	19	22	26	29	32	35	38	42	45	48
	M.C.	6	9	12	15	18	21	24	27	30	33	36	39	42	45
0·9	1	3	5	6	8	10	11	13	14	16	18	19	21	23	24
	2	4	6	9	11	13	15	17	19	21	23	26	28	30	32
	M.A.	5	7	10	12	14	17	19	22	24	26	29	31	34	36
	M.C.	5	8	10	13	15	18	20	23	25	28	30	33	35	38
1·0	1														
	2														
	M.A.	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	M.C.														

The values of $k[=\Delta f''/(f_0+\Delta f')]$ for commonly used anomalous scatterers were calculated for Cu $K\alpha$ and Mo $K\alpha$ radiations and these are given in Table 2. Since f_0 decreases with $(\sin\theta/\lambda)$, while $\Delta f''$ and $\Delta f'$ are very nearly independent of $(\sin\theta/\lambda)$, the value of k increases as $(\sin\theta/\lambda)$ increases. In practical cases because of the thermal vibrations of the electron cloud, the reflexions for which θ is large (say $\theta>50°$) may be too weak for measurement of Bijvoet differences (Hall & Maslen, 1965). The value of k was therefore averaged over the range $\theta=0$ to 50° and this average value of k (denoted by $\bar{k}$) is given in Table 2 along with the value of k corresponding to the forward direction ($\theta=0$, denoted by k_0).

Table 2. *The value of* k $(=f''/f')$ *for a few typical atoms which scatter* Cu $K\alpha$ *and* Mo $K\alpha$ *radiations anomalously*

Atoms	Atomic number Z	Cu $K\alpha$ k_0*	Cu $K\alpha$ $\bar{k}$†	Mo $K\alpha$ k_0	Mo $K\alpha$ $\bar{k}$
S	16	0·04	0·07	0·01	0·04
Cl	17	0·04	0·08	0·01	0·04
Ca	20	0·07	0·14	0·02	0·05
Cr	24	0·11	0·21	0·03	0·09
Mn	25	0·12	0·23	0·04	0·10
Fe	26	0·14	0·25	0·04	0·11
Co	27	0·16	0·30	0·04	0·12
Zn	30	0·03	0·04	0·05	0·15
Br	35	0·04	0·07	0·07	0·20
I	53	0·14	0·22	0·05	0·10
Pt	78	0·11	0·16	0·13	0·28
Hg	80	0·12	0·17	0·14	0·30

* k_0 is the value of the ratio f''/f' corresponding to the forward direction (*i.e.* $\theta=0$).

† $\bar{k}$ is the mean value of the ratio f''/f' corresponding to the range of θ given by $0\le\theta\le 50°$. In the calculation of $\bar{k}$, the dispersion corrections as listed in *International Tables for X-ray Crystallography* (1962) and the atomic scattering factors as obtained from the analytic constants using self consistent wave functions listed by Moore (1963) were used.

For Cu $K\alpha$ radiation Cr, Fe, Co, I, Pt and Hg seem to be suitable, of which Co is the best. For Mo $K\alpha$ radiation Zn, Br, Pt and Hg are probably most suitable, of which Hg comes first. The choice of the anomalous scatterer in any particular case is also dependent on the number of light atoms, since we have also the condition that the value of σ_1^2 could be closer to 0·5.

Another important point worthy of notice is that the structural features play as important a role as the quantities k and σ_1^2 for the measurability of Bijvoet differences. The above discussion on $\langle\delta\rangle$ and $\langle\Delta\rangle$ strictly holds only for a structure in which the non-anomalous atoms are randomly distributed. If the distribution of the latter atoms in the unit cell of a non-centrosymmetric crystal shows a tendency to be nearly centrosymmetric, it is clear that even through the optimum conditions, *viz.*, $\sigma_1^2 = 0.5$ and k large, are satisfied, the structure may not exhibit any measurable Bijvoet differences.

APPENDIX A

Equation (7) involves only $|\sin\theta|$, so that it can be written

$$\langle|\Delta I|;\,|F_P'|\rangle = -\frac{8k|F_P'|}{\pi\sigma_Q^2}\exp(-|F_P'|^2/\sigma_Q^2) \times\int_0^\infty |F_N'|^2\exp(-|F_N'|^2/\sigma_Q^2)d|F_N'| \times\int_0^\pi \exp(2|F_N'|\,|F_P'|\cos\theta/\sigma_Q^2)d\cos\theta\,. \quad (A\text{-}1)$$

Carrying out the integration over θ, we obtain from (A-1):

$$\langle|\Delta I|;\,|F_P'|\rangle = \frac{8k}{\pi}\exp(-|F_P'|^2/\sigma_Q^2)\times\int_0^\infty \sinh(2|F_N'|\,|F_P'|/\sigma_Q^2)\times\exp(-|F_N'|^2/\sigma_Q^2)\,|F_N'|d|F_N'|\,. \quad (A\text{-}2)$$

Making the substitution $|F_N'|^2/\sigma_Q^2=y$ in (A-2), we obtain

$$\langle|\Delta I|;\,|F_P'|\rangle = \frac{4k}{\pi}\sigma_Q^2\exp(-|F_P'|^2/\sigma_Q^2)\times\int_0^\infty \sinh(2|F_P'|y^{\frac{1}{2}}/\sigma_Q)\exp(-y)dy\,. \quad (A\text{-}3)$$

Using (34) in p. 165, Vol. I of Erdelyi (1954) in (A-3), we have

$$\langle|\Delta I|;\,|F_P'|\rangle = 4\pi^{-\frac{1}{2}}k\sigma_Q|F_P'|\,. \quad (A\text{-}4)$$

APPENDIX B

Making the substitution $y_P^2/2=z$ in (23), we obtain

$$\langle\delta\rangle = \frac{4k}{\pi^2}\int_0^1\Big[z^{-\frac{1}{2}}(1-z)^{-\frac{1}{2}}\exp(-2\sigma_1^2z/\sigma_2^2)\times\int_0^\infty \sinh(2^{3/2}a\sqrt{zx})\exp(-x)\frac{dx}{x}\Big]dz\,. \quad (B\text{-}1)$$

Using (21) in (B-1) we obtain

$$\langle\delta\rangle = \frac{4k}{\pi^2}\sum_{n=1}^\infty \frac{\Gamma(n-\frac{1}{2})}{\Gamma(2n)}(2^{3/2}a)^{2n-1}\times\int_0^1 z^{n-1}(1-z)^{-\frac{1}{2}}\exp(-2\sigma_1^2z/\sigma_2^2)dz\,, \quad (B\text{-}2)$$

where we have interchanged the order of integration and summation. We know from p. 46 of Sneddon (1961) that

$$\exp(-ax) = {}_1F_1(c;\,c;\,-ax)\,, \quad (B\text{-}3)$$

where ${}_1F_1\,(a;\,b;\,x)$ is the Kummer's confluent hypergeometric function. Substituting (B-3) in (B-2) and carrying out the integration with the use of (16) in p. 47 of Sneddon (1961), we obtain

$$\begin{aligned}\langle\delta\rangle &= \frac{4k}{\pi^2}\sum_{n=1}^\infty (2^{3/2}a)^{2n-1}\frac{\Gamma(n-\frac{1}{2})}{\Gamma(2n)}\times\beta(n,\tfrac{1}{2})_2F_2(c,n;\,c,n+\tfrac{1}{2};\,-2\sigma_1^2/\sigma_2^2)\\ &= \frac{4k}{\pi^2}\sum_{n=1}^\infty (2^{3/2}a)^{2n-1}\frac{\Gamma(n-\frac{1}{2})}{\Gamma(2n)}\times\beta(n,\tfrac{1}{2})_1F_1(n;\,n+\tfrac{1}{2};\,-2\sigma_1^2/\sigma_2^2)\\ &= \frac{4k}{\pi}\exp(-2r)\sum_{n=1}^\infty\frac{(2r)^{n-\frac{1}{2}}}{(n-\frac{1}{2})\Gamma(n+\frac{1}{2})}\times{}_1F_1(\tfrac{1}{2};\,n+\tfrac{1}{2};\,2r)\end{aligned} \quad (B\text{-}4)$$

where we have used the duplication formula in p. 11 and equation (11–14) in p. 38 of Sneddon (1961).

APPENDIX C

Making the substitution $(\frac{1}{2}+\sigma_1^2/\sigma_2^2)y_P^2=z$ in (25), we obtain

$$\langle\delta\rangle = \left(\frac{2}{\pi}\right)^{3/2}\frac{k}{l_1}\int_0^\infty \exp(-x)\frac{dx}{x} \times \int_0^\infty z^{-\frac{1}{2}}\sinh\left(\frac{2a}{l_1}\sqrt{xz}\right)\exp(-z)dz\,, \quad (C\text{-}1)$$

where

$$l_1^2=\tfrac{1}{2}+\sigma_1^2/\sigma_2^2=(1+\sigma_1^2)/2\sigma_2^2\,. \quad (C\text{-}2)$$

Using (38) in p.166, Vol.I of Erdelyi (1954) in (C-1), we obtain

$$\langle\delta\rangle = \frac{2^{3/2}}{\pi}\frac{k}{l_1}\int_0^\infty \operatorname{erf}(ax^{\frac{1}{2}}/l_1) \times \exp[(a^2/l_1^2-1)x]\frac{dx}{x}\,. \quad (C\text{-}3)$$

From p.295, Vol.II of Erdelyi (1954), we know that

$$\exp(x^2)\operatorname{erf}(x)=2\pi^{-\frac{1}{2}}x\,{}_1F_1(1;\tfrac{3}{2};x^2)\,. \quad (C\text{-}4)$$

Using (C-4) in (C-3), we obtain

$$\langle\delta\rangle = \frac{4\sqrt{2}}{\pi^{3/2}}\frac{ka}{l_1^2}\int_0^\infty x^{-\frac{1}{2}}\exp(-x)\,{}_1F_1(1;\tfrac{3}{2};a^2x/l_1^2)\,dx = \frac{4\sqrt{2}}{\pi}\frac{ka}{l_1^2}\,{}_2F_1(1,\tfrac{1}{2};\tfrac{3}{2};a^2/l_1^2)\,, \quad (C\text{-}5)$$

where we have used [17(i)] in p.48 of Sneddon (1961). Using 1(v) in p.42 of Sneddon (1961), in (C-5) we obtain

$$\langle\delta\rangle = \frac{2\sqrt{2}}{\pi}\frac{k}{l_1}\log_e[(1+a/l_1)/(1-a/l_1)]\,. \quad (C\text{-}6)$$

Substituting for a from (18) and for l_1 from (C-2) in (C-6) we obtain

$$\langle\delta\rangle = \frac{4k}{\pi}\frac{\sigma_2}{\sqrt{1+\sigma_1^2}}\log_e[(1+\alpha)/(1-\alpha)]\,, \quad (C\text{-}7)$$

where

$$\alpha=[2\sigma_1^2/(1+\sigma_1^2)]^{\frac{1}{2}}\,. \quad (C\text{-}8)$$

APPENDIX D

Making the substitution $y_P^2/\sigma_2^2=z$ in (28) and interchanging the order of integration, we obtain

$$\langle\delta\rangle = \frac{4k}{\pi}\sigma_2^2\int_{x=0}^\infty \exp(-x)\frac{dx}{x} \times \int_{z=0}^\infty \sinh(2a\sigma_2\sqrt{xz})\exp(-z)dz\,, \quad (D\text{-}1)$$

where we have used the simplification $\sigma_1^2/\sigma_2^2+1=1/\sigma_2^2$. Using (34) in p.165, Vol.I of Erdelyi (1954) in (D-1) we obtain

$$\langle\delta\rangle = \frac{4k}{\sqrt{\pi}}a\sigma_2^3\int_0^\infty x^{-\frac{1}{2}}\exp(-\sigma_2^2x)\,dx = 4ka\sigma_2^2=4k\sigma_1\sigma_2\,, \quad (D\text{-}2)$$

where we have used (1) in p.137, Vol.I of Erdelyi (1954) and (18).

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