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Probability Distribution of Anomalous Phase Angles in a Centrosymmetric Crystal

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Theoretical expressions for the complementary cumulative function of the anomalous phase angle α_A are worked out for three cases: a centrosymmetric crystal containing 1, 2 and 4 anomalous scatterers in the unit cell besides a large number of similar normal scatterers. The results are used to study the influence of the number of anomalous scatterers on the distribution of α_A. It is found that neglect of α_A in the computation of the final difference map will lead to the largest spurious effects when the number of anomalous scatterers in the unit cell is least, namely, the $P=1$ case (the other conditions such as k and σ_1^2 being similar).

1. Introduction

The effect of the neglect of the anomalous phase angles α_A (arising from the imaginary part of the atomic scattering factor) on the final difference map computed for the elucidation of finer details in the electron density distribution has been studied earlier (Parthasarathy, Sabesan & Venkatesan, 1970 – hereafter PSV, 1970). This study was substantiated by making use of the theoretical distribution of α_A derived for the specific case of a centrosymmetric crystal containing a *large number* of anomalous scatterers in the unit cell besides a large number of normal scatterers of similar scattering power. Since in many actual cases the unit cell contains a *small* number of heavy atoms and since the distribution of α_A is expected to be dependent on the number of anomalous scatterers in the unit cell, it is interesting to study how the number of anomalous scatterers influences the distribution of α_A. In this paper we shall therefore work out such a distribution for three typical cases: a centrosymmetric crystal containing 1, 2 and 4 anomalous scatterers in the unit cell; we shall refer to these as the one, two and four-atom cases respectively. We follow the notation of the earlier paper (PSV, 1970).

2. Derivation of the probability distribution of α_A

Consider a centrosymmetric crystal containing P anomalous scatterers of the same type and a large number (Q) of normal scatterers of similar scattering power in the unit cell. From PSV (1970) we obtain α_A to be

$$\tan\alpha_A=|F''_P|/|F'_N|=k\sigma_1 y_P/y_N,\quad 0\le\alpha_A\le\pi/2 \qquad (1)$$

where

$$y_N=|F'_N|/\langle|F'_N|^2\rangle^{1/2},\quad y_P=|F'_P|/\langle|F'_P|^2\rangle^{1/2}$$
$$\sigma_1^2=\langle|F'_P|^2\rangle/\langle|F'_N|^2\rangle,\quad k=\Delta f''_P/(f_P^0+\Delta f'_P). \qquad (2)$$

By definition, the cumulative function of α_A representing the probability that the value of the anomalous phase angle, α_A, is less than or equal to a given value α_A^0, say, is given by

$$N(\alpha_A^0)=P_r(\alpha_A\le\alpha_A^0). \qquad (3)$$

Since $\tan\alpha_A$ is a monotonic function of α_A in $0\le\alpha_A\le\pi/2$, we can rewrite (3) by making use of (1) as

$$N(\alpha_A^0)=P_r(\tan\alpha_A\le\tan\alpha_A^0)=P_r(k\sigma_1 y_P/y_N\le\tan\alpha_A^0)$$
$$=P_r(y_N\ge c y_P) \qquad (4)$$

where we have used the abbreviation

$$c=k\sigma_1\cot\alpha_A^0. \qquad (5)$$

For practical applications, it is more useful to obtain the fraction of reflexions for which $\alpha_A\ge\alpha_A^0$ and this, referred to as the complementary cumulative function [and denoted by $N_c(\alpha_A^0)$], is related to the cumulative function through the relation:

$$N_c(\alpha_A^0)=1-N(\alpha_A^0). \qquad (6)$$

From (4) and (6) we obtain:

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$$N_c(\alpha_A^0) = 1 - P_r(y_N \geq cy_P) = P_r(y_N \leq cy_P) = \iint\limits_{y_N \leq cy_P} P(y_N, y_P)\mathrm{d}y_N\mathrm{d}y_P \quad (7)$$

where $P(y_N, y_P)$ is the joint *probability density function* (hereafter called the PDF) of y_N and y_P. Making use of the conditional PDF of y_N for a given y_P available in equation (7) of Srikrishnan & Parthasarathy (1970) we obtain:

$$P(y_N, y_P) = \left(\frac{2}{\pi\sigma_2^2}\right)^{1/2} \exp\left[-(y_N^2 + \sigma_1^2 y_P^2)/2\sigma_2^2\right] \times \cos h\left(\frac{\sigma_1 y_N y_P}{\sigma_2^2}\right) P(y_P) \quad (8)$$

where $P(y_P)$ is the PDF of y_P. Making use of (8) in (7) we obtain:

$$N_c(\alpha_A^0) = \left[\frac{2}{\pi\sigma_2^2}\right]^{1/2} \int_{y_P} \exp\left[-\sigma_1^2 y_P^2/2\sigma_2^2\right] P(y_P)\mathrm{d}y_P \times \int_0^{cy_P} \exp\left(-y_N^2/2\sigma_2^2\right) \cos h(\sigma_1 y_N y_P/\sigma_2^2)\mathrm{d}y_N . \quad (9)$$

The integration over y_N can be carried out by use of the result in equation (5) of Srikrishnan & Parthasarathy (1970). We obtain

$$N_c(\alpha_A^0) = \tfrac{1}{2}\int \left[\operatorname{erf}(\beta_+ y_P) + \operatorname{erf}(\beta_- y_P)\right] P(y_P)\mathrm{d}y_P \quad (10)$$

where we have used the abbreviation

$$\beta_\pm = \frac{\sigma_1}{\sqrt{2}\sigma_2}\left[k \cot \alpha_A^0 \pm 1\right]. \quad (11)$$

Substituting for the PDF of y_P in (10) and carrying out the resulting integration the theoretical expression for the complementary cumulative function of α_A can be obtained for each case.

One-atom case

The single anomalous scatterer in the unit cell will be at the centre of symmetry and $y_P \equiv 1$ for each reflexion. Hence

$$P(y_P) = \delta(y_P - 1). \quad (12)$$

Substituting (12) in (10) and carrying out the integration by use of the property of the delta function, we obtain:

$$N_c(\alpha_A^0) = \tfrac{1}{2}\left[\operatorname{erf}(\beta_+) + \operatorname{erf}(\beta_-)\right]. \quad (13)$$

Table 1. *Percentage of reflexions for which* $\alpha_A \geq 5$, 10 *and* 15° *as a function of k and* σ_1^2 *for the cases* $P = 1, 2, 4$ *and M*

σ_1^2 →	0.10				0.20				0.30				0.40				0.50				0.60				0.70				0.80				0.90			
k ↓ P →	1	2	4	M	1	2	4	M	1	2	4	M	1	2	4	M	1	2	4	M	1	2	4	M	1	2	4	M	1	2	4	M	1	2	4	M
	N_c (α_A=5°)																																			
0.04	11	10	9	9	16	14	12	12	19	16	14	13	21	18	15	14	22	18	15	15	22	17	14	15	19	16	14	15	14	13	12	13	5	8	9	10
0.06	17	15	13	13	24	21	18	17	28	24	20	20	31	26	22	22	33	27	23	23	33	27	23	24	31	26	23	24	26	24	22	23	17	18	18	20
0.08	23	20	18	17	31	27	23	23	37	32	27	27	43	35	30	30	44	37	32	32	45	38	33	34	45	39	34	35	43	39	35	36	40	38	35	37
0.10	28	25	22	21	39	33	29	28	46	39	33	33	51	43	37	37	54	46	40	41	57	49	43	44	59	52	47	47	61	56	51	52	67	62	57	58
0.12	33	29	26	25	46	39	34	34	54	46	40	39	59	51	44	44	64	55	48	49	67	59	52	53	71	64	57	58	77	70	63	64	87	79	71	72
0.14	39	34	30	29	52	45	39	38	61	52	45	45	67	58	50	50	72	63	55	56	77	68	60	60	82	73	65	66	89	79	71	72	96	87	78	80
0.16	44	38	33	33	58	50	43	43	67	58	50	50	74	64	56	56	79	69	61	61	84	75	66	66	90	80	71	71	95	85	76	77	99	90	82	84
0.18	48	42	37	36	64	55	47	47	73	63	55	55	80	69	60	61	85	75	65	66	90	79	70	71	95	84	74	76	98	88	79	81	100	92	85	87
0.20	53	46	40	39	69	59	51	51	78	67	58	58	85	74	64	64	90	79	69	70	94	83	73	74	98	87	77	79	99	90	81	83	100	93	86	89
0.22	57	50	43	42	74	63	54	54	83	71	62	62	89	77	67	68	93	82	72	73	97	85	76	77	99	89	79	81	100	91	83	85	100	94	88	90
0.24	61	53	46	45	78	67	57	57	87	74	64	65	92	80	70	70	96	84	74	75	98	87	78	79	100	90	81	83	100	92	85	87	100	95	89	91
0.26	65	56	49	48	81	70	60	60	90	77	67	67	95	82	72	73	98	86	76	77	99	89	79	81	100	91	82	85	100	93	86	88	100	95	90	92
0.28	69	59	51	50	85	72	62	62	92	79	69	70	96	84	74	75	99	87	77	79	100	90	81	83	100	92	84	86	100	94	87	89	100	96	90	93
0.30	72	62	53	53	87	75	64	65	94	81	71	72	98	85	75	77	99	88	79	81	100	91	82	84	100	92	85	87	100	94	88	90	100	96	91	93
	N_c (α_A=10°)																																			
0.04	6	5	4	4	8	7	6	6	10	8	7	7	11	9	7	7	11	9	7	7	11	8	7	7	9	7	6	7	5	5	5	6	1	3	4	5
0.06	9	8	7	6	12	10	9	9	14	12	10	10	16	13	11	11	16	13	11	11	16	13	10	11	14	11	10	10	9	8	8	9	2	5	6	7
0.08	11	10	9	9	16	14	12	12	19	16	14	13	21	17	14	14	22	18	15	15	21	17	14	15	19	16	13	14	14	12	12	13	3	8	9	10
0.10	14	13	11	11	20	17	15	14	24	20	17	17	26	22	18	18	27	22	19	19	27	22	19	19	25	21	18	19	19	17	16	17	10	12	13	14
0.12	17	15	13	13	24	20	18	17	28	24	20	20	31	26	22	22	33	27	23	23	33	27	23	24	31	26	23	24	26	24	21	23	17	18	18	19
0.14	20	17	15	15	27	24	20	20	33	28	24	23	36	30	26	26	38	32	27	27	39	33	28	29	37	32	28	29	34	31	28	29	27	26	25	27
0.16	23	20	17	17	31	27	23	23	37	32	27	27	41	35	29	29	43	37	31	32	45	38	33	34	44	39	34	35	43	39	35	36	39	37	34	36
0.18	25	22	19	19	35	30	26	25	41	35	30	30	46	39	33	33	49	41	36	36	50	43	38	39	51	45	40	41	52	47	42	44	52	49	46	47
0.20	28	25	22	21	38	33	29	28	45	39	33	33	50	43	37	37	54	46	40	40	56	49	43	44	58	52	46	47	61	55	50	51	66	61	56	57
0.22	31	27	24	23	42	36	31	31	49	42	36	36	55	47	40	40	59	50	44	44	62	54	48	48	65	58	52	52	69	63	57	58	77	71	65	66
0.24	33	29	26	25	45	39	34	33	53	46	39	39	59	50	44	44	63	55	48	48	67	59	52	53	71	64	57	57	76	69	62	63	86	79	71	72
0.26	36	31	27	27	49	42	36	36	57	49	42	42	63	54	47	47	68	59	51	52	72	63	56	57	77	69	61	62	83	75	67	68	92	83	75	76
0.28	38	34	29	29	52	45	39	38	60	52	43	45	67	57	50	50	72	62	55	55	76	67	60	60	82	73	65	65	88	79	71	71	96	87	78	80
0.30	41	36	31	31	55	47	41	40	64	55	47	47	70	61	53	53	76	66	58	58	80	71	63	63	86	76	68	69	92	82	73	74	98	89	80	82
	N_c (α_A=15°)																																			
0.04	4	3	3	3	5	5	4	4	6	5	4	4	7	6	5	5	7	6	5	5	7	5	4	5	6	3	4	4	3	3	3	4	1	2	3	3
0.06	6	5	4	4	8	7	6	6	9	8	7	7	10	9	7	7	11	9	7	7	10	8	7	7	9	7	6	7	5	5	5	6	1	3	4	4
0.08	8	7	6	6	10	9	8	8	13	11	9	9	14	11	9	9	14	12	9	10	14	11	9	10	12	10	8	9	8	7	7	8	2	4	5	6
0.10	9	8	7	7	13	11	10	9	16	13	11	11	17	14	12	12	18	15	12	12	18	14	12	12	15	12	11	12	10	10	9	10	3	6	7	8
0.12	11	10	9	9	16	14	12	11	19	16	13	13	21	17	14	14	22	18	14	15	21	17	14	15	19	15	13	14	13	12	12	13	5	8	9	10
0.14	13	12	10	10	18	16	14	13	22	18	16	15	24	20	17	17	25	21	17	17	25	20	17	17	22	19	16	17	17	15	14	16	8	10	11	13
0.16	15	13	12	11	21	18	15	15	25	21	18	18	27	23	19	19	29	24	20	20	29	23	20	20	26	22	19	20	21	19	17	19	11	13	14	15
0.18	17	15	13	13	23	20	17	17	28	24	20	20	31	26	22	22	32	27	22	23	32	27	23	23	30	26	22	23	26	23	21	22	16	17	17	19
0.20	19	16	14	14	26	22	19	19	31	26	22	22	34	29	24	24	36	30	25	26	36	30	26	26	35	30	26	27	31	28	25	26	22	22	22	23
0.22	20	18	16	15	28	24	21	21	34	29	24	24	37	31	27	27	39	33	28	28	40	34	29	30	39	34	30	31	36	33	29	31	30	29	27	29
0.24	22	20	17	17	31	27	23	22	37	31	27	26	41	34	29	29	43	36	31	31	44	37	32	33	43	38	33	34	42	38	34	35	38	36	33	35
0.26	24	21	19	18	33	29	25	24	39	34	29	28	44	37	31	32	46	39	34	34	48	41	36	36	48	42	37	38	48	43	39	40	46	44	41	42
0.28	26	23	20	20	36	31	27	26	42	36	31	31	47	40	34	34	50	42	37	37	52	45	39	40	53	47	41	42	54	49	44	45	55	52	48	49
0.30	28	24	21	21	38	33	28	28	45	38	33	33	50	42	36	36	53	45	39	40	55	48	42	43	57	51	45	46	59	54	49	50	64	60	55	58

Two-atom case

Since the PDF of y_P is known to be

$$P(y_P)=\frac{\sqrt{2}}{\pi}\,\frac{1}{(1-y_P^2/2)^{1/2}},\quad 0\le y_P\le\sqrt{2}$$

we obtain from (10):

$$N_c(\alpha_A^0)=\frac{1}{\sqrt{2\pi}}\int_0^{\sqrt{2}}[\operatorname{erf}(\beta_+y_P)+\operatorname{erf}(\beta_-y_P)]\frac{\mathrm{d}y_P}{(1-y_P^2/2)^{1/2}}. \quad (14)$$

Making the substitution $y_P^2/2=x$ in (14) and then expressing the error function in terms of the hypergeometric function by use of equation [11(iii)] on p. 46 of Sneddon (1961), we obtain

$$N_c(\alpha_A^0)=\frac{\sqrt{2}}{\pi^{3/2}}\int_0^1(1-x)^{-1/2}[\beta_{+\,1}F_1(\tfrac{1}{2};\tfrac{3}{2};-2\beta_+^2x)+\beta_{-\,1}F_1(\tfrac{1}{2};\tfrac{3}{2};-2\beta_-^2x)]\mathrm{d}x \quad (15)$$

which on integration by use of equation [16(i)] on p. 47 of Sneddon (1961) yields

$$N_c(\alpha_A^0)=\left(\frac{2}{\pi}\right)^{3/2}[\beta_{+\,2}F_2(\tfrac{1}{2},1;\tfrac{3}{2},\tfrac{3}{2};-2\beta_+^2)+\beta_{-\,2}F_2(\tfrac{1}{2},1;\tfrac{3}{2},\tfrac{3}{2};-2\beta_-^2)]. \quad (16)$$

(16) is convenient only when $2\beta_\pm^2$ are small. Otherwise, a more convenient method to evaluate $N_c(\alpha_A^0)$ is by numerical integration of

$$N_c(\alpha_A^0)=\frac{1}{\pi}\int_0^{\pi/2}[\operatorname{erf}(\sqrt{2}\beta_+\sin\theta)+\operatorname{erf}(\sqrt{2}\beta_-\sin\theta)]\mathrm{d}\theta \quad (17)$$

which is obtained from (14) after the substitution of $y_P/\sqrt{2}=\sin\theta$.

Four-atom case

Since the PDF of y_P is known to be (Parthasarathy, 1965)

$$P(y_P)=\frac{2}{\pi^2}K(\sqrt{1-y_P^2/4}),\quad 0\le y_P\le 2 \quad (18)$$

we obtain from (10) that

$$N_c(\alpha_A^0)=\frac{1}{\pi^2}\int_0^2[\operatorname{erf}(\beta_+y_P)+\operatorname{erf}(\beta_-y_P)]\times K(\sqrt{1-y_P^2/4})\mathrm{d}y_P. \quad (19)$$

Using the substitution $y_P/2=\sin\theta$ in (19) we obtain

$$N_c(\alpha_A^0)=\frac{2}{\pi^2}\int_0^1[\operatorname{erf}(2\beta_+\sin\theta)+\operatorname{erf}(2\beta_-\sin\theta)]\times K(\cos\theta)\cos\theta\mathrm{d}\theta \quad (20)$$

which can be evaluated numerically.

3. Discussion of theoretical results

The complementary cumulative functions of α_A for the one, two and four-atom cases are obtained in (13), (17) and (20) respectively. These equations show that $N_c(\alpha_A)$ depends on the number of anomalous scatterers in the unit cell as well as on k and σ_1^2 (which depend on the type of the anomalous scatterer and its fractional contribution to the local mean intensity respectively). The values* of $N_c(\alpha_A)$ as a function of k and σ_1^2 corresponding to $\alpha_A=5$, 10 and 15° are given in Table 1 for the various cases. The results for the many-atom case (*i.e.* $P=M$ case) of PSV (1970) are also given to facilitate the comparison. Table 1 shows that the percentage of reflexions for which $\alpha_A\ge5°$, say, is largest when the number of anomalous scatterers in the unit cell is least (*i.e.* $P=1$ case). It is also seen that this percentage for the two-atom case is about midway between that for the one and many-atom cases. It is interesting to note that the result for the four-atom case is close to that of the many-atom case. We may therefore conclude that, when the values of k and σ_1^2 are similar, the spurious details in the final difference map due to neglect of the anomalous phase angle increase as the number of anomalous scatterers in the unit cell decreases and that the spurious details would be the greatest in the one-atom case.

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* For the $P=2$ and 4 cases these values were obtained by numerical integration [see (11), (17) and (20)].

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