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A Modified Asymptotic Development of the Density Distribution of a Structure Factor in $P\bar{1}$

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Abstract

A concise and very precise formula has been obtained for the density of a structure factor in space group $P\bar{1}$ under the assumption that the atomic position vectors are distributed uniformly and independently over the unit cell.

1. Introduction

Let $E_{\mathbf{h}} = (2/N^{1/2}) \sum_{j=1}^{N/2} \cos(2\pi\mathbf{r}_j.\mathbf{h})$ denote the normalized structure factor for reciprocal-lattice vector $\mathbf{h}$ in space group $P\bar{1}$ for a unit cell containing N equal atoms. Now let $\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_n$ $(n = N/2)$ be n random vectors that are distributed independently and uniformly over the unit cell and consider the random variable

$$\hat{E}_{\mathbf{h}} = (2/N^{1/2}) \sum_{j=1}^{n} \cos(2\pi\mathbf{x}_j.\mathbf{h}) \qquad (n = N/2). \quad (1)$$

Let us denote by $E \to \hat{p}(E)$ the probability density of the random variable $\hat{E}_{\mathbf{h}}$.

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2. Formula

$$p(E)=[1/\sigma(2\pi)^{1/2}]\delta_N \exp(-E\mathbb{E})I_0(2\mathbb{E}/N^{1/2})^{N/2} \quad \text{for } N\geq 5, \quad (2)$$

where

$|E|<N^{1/2}$;

$x\to I_n(x)$ denotes the modified Bessel function of order n;

$\alpha_n(x)=I_n(x)/I_0(x)$ for every real x;

$\mathbb{E}$ is the unique real number such that

$$\alpha_1(2\mathbb{E}/N^{1/2})=EN^{-1/2};$$

$$\sigma^2=1+\alpha_2(2\mathbb{E}/N^{1/2})-2[\alpha_1(2\mathbb{E}/N^{1/2})]^2;$$

$$\delta_N=[\sigma/(2\pi)^{1/2}]\int_{-\infty}^{+\infty}\exp(-iv E)\varphi(v;\mathbb{E})^{N/2}\,dv;$$

$$\varphi(v;\mathbb{E})=J_0(2v/N^{1/2}) + 2\sum_{k=1}^{\infty} i^k\alpha_k(2\mathbb{E}/N^{1/2})J_k(2v/N^{1/2}).$$

A formal asymptotic expansion of δ_N up to order N^{-1} yields

$$\delta_N=1-(3/8\sigma^4N)\gamma_4-(15/8\sigma^6N)\gamma_3^2+O(N^{-2}),$$

where

$$\gamma_3=\alpha_1(2\mathbb{E}/N^{1/2})+\tfrac{1}{3}\alpha_3(2\mathbb{E}/N^{1/2})-2\alpha_1(2\mathbb{E}/N^{1/2}) \times[1+\alpha_2(2\mathbb{E}/N^{1/2})]+\tfrac{8}{3}[\alpha_1(2\mathbb{E}/N^{1/2})]^3,$$

$$\gamma_4=16[\alpha_1(2\mathbb{E}/N^{1/2})]^4+8\alpha_1(2\mathbb{E}/N^{1/2}) \times[\alpha_1(2\mathbb{E}/N^{1/2})+\tfrac{1}{3}\alpha_3(2\mathbb{E}/N^{1/2})] +2[1+\alpha_2(2\mathbb{E}/N^{1/2})]^2 -1-\tfrac{4}{3}\alpha_2(2\mathbb{E}/N^{1/2})-\tfrac{1}{3}\alpha_4(2\mathbb{E}/N^{1/2}) -16[\alpha_1(2\mathbb{E}/N^{1/2})]^2[1+\alpha_2(2\mathbb{E}/N^{1/2})].$$

3. Discussion

Let $(E_1, E_2, \ldots, E_m)\to p(E_1, E_2, \ldots, E_m)$ denote the joint density distribution of m structure factors in, for example, space group $P\bar{1}$, under the assumption that the atomic position vectors are uniformly and independently distributed over the unit cell. For phase determination, one is interested in a simple formula that approximates

$$\exp\left(\tfrac{1}{2}\sum_{j=1}^{m}E_j^2\right)p(E_1, E_2, \ldots, E_m)$$

as well as possible. To this end, let us consider the simple case of one structure factor and let us try to obtain a good approximation for $(2\pi)^{1/2}\exp(\tfrac{1}{2}E^2)p(E)$.

The usual Edgeworth or Charlier expansion gives, to order N^{-1},

$$(2\pi)^{1/2}\exp(\tfrac{1}{2}E^2)p(E) =1-(1/8N)(E^4-6E^2+3)+O(1/N^2). \quad (3)$$

For large E and N values (3) becomes strongly negative, contradicting the fact that (3) must remain positive. So we must conclude that (3) can only represent $(2\pi)^{1/2}\exp(\tfrac{1}{2}E^2)p(E)$ for a very restricted range of E values; the range of these E values is roughly given by $|E|\leq\alpha N^{1/2}$ where $1-\alpha^4N/8=0$, that is for $|E|\leq(8/N)^{1/4}N^{1/2}=8^{1/4}N^{1/4}$.

Even for the range $|E|\leq 8^{1/4}N^{1/4}$, terms of order $1/N^2$ and possibly higher will have to be calculated in the Edgeworth-Charlier expansion of $p(E)$ in order to obtain an acceptable accuracy for $(2\pi)^{1/2}\exp(\tfrac{1}{2}E^2)p(E)$.

Another possibility is that indicated by Karle & Hauptman (1953) where one puts

$$(2\pi)^{1/2}\exp(\tfrac{1}{2}E^2)p(E) =\exp[-(1/8N)(E^4-6E^2+3)]+O(1/N^2). \quad (4)$$

For high E values, *e.g.* for $|E|\simeq N^{1/2}$, (4) gives

$$(2\pi)^{1/2}\exp(\tfrac{1}{2}E^2)p(E)\simeq\exp(-N/8)\simeq 0.$$

So (4) seems to be better than (3). However, (4) has the disadvantage that it will be rather difficult to investigate its asymptotic behaviour; on the other hand, the asymptotic behaviour of δ_N in (2) may be proved in the same way as in Brosius (1987). Formula (2) possesses other interesting features. Indeed, one can prove that

$$\lim_{E\to N^{1/2}}\{(1/\sigma)\exp(\tfrac{1}{2}E^2-E\mathbb{E})[I_0(2\mathbb{E}/N^{1/2})]^{N/2}\}=0 \quad \text{if } N\geq 5. \quad (5)$$

Furthermore, the asymptotic development of δ_N up to order N^{-1} seems to give a good accuracy even for values of σ^2 as low as 0·0466 (*i.e.* for $|E|N^{-1/2}\simeq 0{\cdot}9$); one then obtains

$$\delta_N\simeq 1-0{\cdot}3/N. \quad (6)$$

Hence δ_N remains positive whenever $N\geq 1$.

So (2) seems to be very good for relatively high N values and for E values in the range $|E|\leq 0{\cdot}9N^{1/2}$.

4. Derivation of (2)

One has

$$p(E)=(1/2\pi)\int_{-\infty}^{+\infty}\exp(-iuE)[J_0(2u/N^{1/2})]^{N/2}\,du. \quad (7)$$

After the change of variables $u=-i\mathbb{E}+v$ one obtains [where $\alpha_1(2\mathbb{E}/N^{1/2}) = EN^{-1/2}$ and $|E| < N^{1/2}$]

$$p(E) = \exp(-E\mathbb{E})(1/2\pi) \int_{+i\mathbb{E}-\infty}^{i\mathbb{E}+\infty} \exp(-ivE) \times \{J_0[(-2i\mathbb{E}+2v)/N^{1/2}]\}^{N/2} \, dv. \quad (8)$$

Put $f(v) = \exp(-ivE)\{J_0[(-2i\mathbb{E}+2v)/N^{1/2}]\}^{N/2}$ and let $R > 0$. In accordance with Cauchy's theorem one has

$$\int_{i\mathbb{E}-R}^{i\mathbb{E}+R} f(v)\, dv = \int_{-R}^{R} f(v)\, dv + i \int_{\mathbb{E}}^{0} f(iy-R)\, dy + i \int_{0}^{\mathbb{E}} f(iy+R)\, dy. \quad (9)$$

From $(A1)$, $f(iy-R)$ and $f(iy+R)$ tend to 0 when R tends to infinity as $R^{-N/4}$, uniformly in y if $0 \le |y| \le |\mathbb{E}|$. So one gets, for $N \ge 5$,

$$\int_{+i\mathbb{E}-\infty}^{i\mathbb{E}+\infty} f(v)\, dv = \int_{-\infty}^{+\infty} f(v)\, dv. \quad (10)$$

Since

$$J_0[(-2i\mathbb{E}+2v)/N^{1/2}] = I_0(2\mathbb{E}/N^{1/2}) \left[J_0(2v/N^{1/2}) + 2 \sum_{k=1}^{\infty} i^k \alpha_k(2\mathbb{E}/N^{1/2}) J_k(2v/N^{1/2}) \right], \quad (11)$$

one obtains

$$p(E) = \exp(-E\mathbb{E})[I_0(2\mathbb{E}/N^{1/2})]^{N/2}(1/2\pi) \times \int_{-\infty}^{+\infty} \exp(-ivE)[\varphi(v;\mathbb{E})]^{N/2}\, dv. \quad (12)$$

Notice that $|\varphi(v;\mathbb{E})| \le 1$. Moreover let $P_{\mathbb{E}}$ be the probability measure on $[0, 2\pi]$ defined by

$$dP_{\mathbb{E}}(\theta) = [2\pi I_0(2\mathbb{E}/N^{1/2})]^{-1} \times \exp[+(2\mathbb{E}/N^{1/2}) \cos\theta]\, d\theta \quad (13)$$

and let X denote the random variable defined on the probability space $([0, 2\pi], P_{\mathbb{E}})$ by

$$X(\theta) = (2/N^{1/2}) \cos\theta \quad \text{for } 0 \le \theta \le 2\pi. \quad (14)$$

Then one readily verifies that

$$\int_{0}^{2\pi} \exp[ivX(\theta)]\, dP_{\mathbb{E}}(\theta) = \varphi(v;\mathbb{E}). \quad (15)$$

Hence $v \to \varphi(v;\mathbb{E})$ is a characteristic function. So we obtain, with the usual Edgeworth-Charlier expansion, from (12)

$$p(E) = \exp(-E\mathbb{E})[I_0(2\mathbb{E}/N^{1/2})]^{N/2}(1/2\pi) \times \int_{-\infty}^{+\infty} \exp(-\tfrac{1}{2}\sigma^2 v^2)[1 - (v^4/8N)\gamma_4 - (v^6/8N)\gamma_3^2 + O(1/N^2)] \quad (16)$$

where all terms of the form v^{2k+1} in the asymptotic expansion in (16) have been omitted. With the help of $(A2)$ one obtains (2).

Finally, let us remark that δ_N can also be obtained from a Fourier series (Shmueli, Weiss, Kiefer & Wilson, 1984). Indeed, let $X_1, X_2, \ldots, X_n$ be n independent random variables distributed as X [see (14) and (13)] and put

$$Y = \sum_{i=1}^{n} X_i. \quad (17)$$

Let $y \to p_0(y)$ be the density of Y. Then one obtains

$$p_0(E) = [1/\sigma(2\pi)^{1/2}]\delta_N. \quad (18)$$

But also

$$p_0(E) = (1/2N^{1/2}) \sum_{k=-\infty}^{+\infty} \exp(-ik\pi E/N^{1/2}) \times [\varphi(k\pi/N^{1/2};\mathbb{E})]^{N/2}. \quad (19)$$

APPENDIX

$$J_0(z) = (2/\pi z)^{1/2}[\cos(z - \pi/4) + \exp(|\text{Im } z|) O(|z|^{-1})] \quad |\arg z| < \pi. \quad (A1)$$

$$\int_{-\infty}^{+\infty} \exp(-\tfrac{1}{2}\sigma^2 v^2) v^{2n}\, dv = [(2n-1)!!/\sigma^{2n}](2\pi/\sigma^2)^{1/2} \quad (\sigma > 0) \quad (A2)$$

where $(2n-1)!! = 1 \times 3 \times 5 \times \ldots \times (2n-1)$.

These results are obtained from Abramowitz & Stegun (1970).

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