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A Rigorous Treatment of the Asymptotic Development of the Probability Density of a Structure Factor in $P\bar{1}$

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Abstract

It is shown that an asymptotic development up to order N^{-2} exists for the density of the structure factor in $P\bar{1}$. An upper bound for the error is calculated.

1. Definitions

We shall consider the centrosymmetric case $P\bar{1}$. For N equal atoms and reciprocal-lattice vector $\mathbf{h}$,

$$E_{\mathbf{h}}=(2/N^{1/2})\sum_{j=1}^{n}\cos(2\pi\mathbf{r}_j.\mathbf{h})\quad(n=N/2)$$

is the normalized structure factor. Now let $\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_n$ $(n=N/2)$ be n vectors that are distributed independently and uniformly over the unit cell and consider the random variable

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

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

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2. Theorem

$$\begin{aligned}|P(E)-&(2\pi)^{-1/2}[\exp(-E^2/2)]\{1-(1/8N)H_4(E)\\&+(1/N^2)[+(1/18)H_6(E)+(1/128)H_8(E)]\}|\\&\le[8/N^3(2\pi)^{1/2}](15{\cdot}2+22{\cdot}7/N+195{\cdot}52/N^2\\&\quad+11\,217{\cdot}28/N^3)\\&\quad+(N^{1/2}/2\pi)[J_0(1)]^{(N/2)-4}\int_1^\infty|J_0(x)|^4\,dx\\&\quad+(N^{1/2}/2\pi)\int_1^\infty\exp(-Nu^2/8)\,du\end{aligned}\qquad(2)$$

where

$$\begin{aligned}H_4(E)&=E^4-6E^2+3\\H_6(E)&=E^6-15E^4+45E^2-15\\H_8(E)&=E^8-28E^6+210E^4-420E^2+105.\end{aligned}\qquad(3)$$

3. Proof

One readily verifies that the characteristic function φ of $\hat{E}_h$ is given by

$$\varphi(t) = J_0[(2/n)^{1/2}t]^n \quad (n = N/2) \qquad (4)$$

where t is real and J_0 is the Bessel function of order 0. Using equation $(A1)$ of the Appendix, we obtain

$$\varphi(t) = \left(1 - \frac{1}{2n}t^2 + \frac{1}{16n^2}t^4 - \frac{1}{8\times 6^2 n^4}t^6 + \dots\right)^n. \qquad (5)$$

Next define the function ψ by

$$\psi(t) = -\tfrac{1}{2}t^2 - \frac{1}{16n}t^4 - \frac{1}{72n^2}t^6. \qquad (6)$$

Define the function g by

$$g(t) = \exp(-\tfrac{1}{2}t^2) \times \left[1 - \frac{1}{16n}t^4 + \frac{1}{n^2}\left(-\frac{1}{72}t^6 + \frac{1}{2\times 16^2}t^8\right)\right]. \qquad (7)$$

Define the functions $(u, t) \to \varphi(u, t)$ and $(u, t) \to \delta(u, t)$ by

$$\varphi(u, t) = -\tfrac{1}{16}ut^4 - \tfrac{1}{72}u^2t^6$$

$$\delta(u, t) = \exp[\varphi(u, t)] - \left[1 - \frac{1}{16}ut^4 + u^2\left(-\frac{1}{72}t^6 + \frac{1}{2\times 16^2}t^8\right)\right]. \qquad (8)$$

Since $\mathrm{d}^m\delta(u, t)/\mathrm{d}u^m|_{u=0} = 0$ for $m = 0, 1, 2$, one has, using $(A2)$ for positive u,

$$|\delta(u, t)| \le (u^3/3!) \sup_{0\le a\le u} |\partial^3\delta(a, t)/\partial a^3| \le (u^3/3!) \sup_{0\le a\le u} |D_a^3 \exp[\varphi(a, t)]| \qquad (9)$$

(where $D_a \equiv \partial/\partial a$). Hence one has

$$|\delta(u, t)| \le \frac{u^3}{3!}\left[\frac{1}{12\times 16}t^{10} + \frac{1}{16^3}t^{12} + u\left(\frac{1}{16^2\times 12}t^{14} + \frac{1}{12\times 36}t^{12}\right) + u^2\left(\frac{1}{16\times 12\times 36}t^{16}\right) + u^3\left(\frac{1}{16^3}t^{18}\right)\right] \quad (u \ge 0). \qquad (10)$$

Insertion of $u = 1/n$ in (10) gives

$$|\exp[\psi(t)] - g(t)| \le [\exp(-\tfrac{1}{2}t^2)] \times \frac{1}{3!n^3}\left[\frac{t^{10}}{12\times 16} + \frac{t^{12}}{16^3} + \frac{1}{n}\left(\frac{t^{14}}{16^2\times 12} + \frac{t^{12}}{12\times 36}\right) + \frac{1}{n^2}\frac{t^{16}}{16\times 12\times 36} + \frac{1}{n^3}\frac{t^{18}}{16^3}\right]. \qquad (11)$$

For $|t| \le 2(n/2)^{1/2}$ one defines

$$h(t) = n \log J_0[(2/n)^{1/2}t] - \psi(t). \qquad (12)$$

Clearly $D^m h(0) = 0$ for $m = 0, 1, \dots, 7$; and so

$$D^8 h(t) = \frac{16}{n^3} D^8 \log J_0[(2/n)^{1/2}t] \quad \text{for } |t| \le (2n)^{1/2}.$$

Now one verifies that $D^8 h(t) \le 0$ for $|t| \le (n/2)^{1/2}$. Thus we can state, for $|t| \le (n/2)^{1/2}$,

$$\begin{aligned} |\varphi(t) - \exp[\psi(t)]| &= |\{\exp[h(t)] - 1\}\exp[\psi(t)]| \\ &\le |h(t)|\exp[\psi(t)] \\ &\le \frac{16t^8}{8!n^3} \sup_{0\le u\le t} |D^8 \log J_0[(2/n)^{1/2}u]| \exp(-\tfrac{1}{2}t^2). \end{aligned} \qquad (13)$$

An inspection of $D^8 \log J_0(x)$ reveals that

$$\sup_{0\le u\le t} |D^8 \log J_0[(2/n)^{1/2}u]| \le 333 \quad \text{for } |t| \le (n/2)^{1/2}.$$

Hence (13) becomes

$$|\varphi(t) - \exp[\psi(t)]| \le (16\times 333/8!n^3)t^8 \exp(-\tfrac{1}{2}t^2) \quad \text{if } |t| \le (n/2)^{1/2}. \qquad (14)$$

So, finally,

$$\begin{aligned} &\left|P(E) - (2\pi)^{-1/2}\exp(-E^2/2) \times \left\{1 - \frac{1}{8N}H_4(E) + \frac{1}{N^2}[+\tfrac{1}{18}H_6(E) + \tfrac{1}{128}H_8(E)]\right\}\right| \\ &\le (1/2\pi)\int_{-\infty}^{+\infty} |\varphi(t) - \exp[\psi(t)]|\,\mathrm{d}t + (1/2\pi)\int_{-\infty}^{+\infty} |\exp[\psi(t)] - g(t)|\,\mathrm{d}t \\ &\le (1/2\pi)\int_{|t|\le(n/2)^{1/2}} |\varphi(t) - \exp[\psi(t)]|\,\mathrm{d}t + (1/2\pi)\int_{|t|\ge(n/2)^{1/2}} |\varphi(t)|\,\mathrm{d}t \\ &\quad + (1/2\pi)\int_{|t|\ge(n/2)^{1/2}} \exp[\psi(t)]\,\mathrm{d}t + (1/2\pi)\int_{-\infty}^{+\infty} |\exp[\psi(t)] - g(t)|\,\mathrm{d}t. \end{aligned} \qquad (15)$$

If we substitute (11), (14) and $(A3)$ in (15), we obtain (2), after observing that $J_0(x) \le J_0(1)$ for $x \ge 1$.

4. Discussion

Let us recall that the zeroth-order approximation was first discovered by Wilson (1949, 1950) and the asymptotic expansion was first derived by Karle & Hauptman (1953). The present theorem, however, shows in a mathematically rigorous way that an asymptotic development up to order N^{-2} exists for the density P of a structure factor in $P\bar{1}$.

Let us consider the result in more detail. To this end let us put

$$P_{\text{calc}}(E)=(2\pi)^{-1/2}\exp(-\tfrac{1}{2}E^2)\{1-(1/8N)H_4(E)+(1/N^2)[\tfrac{1}{18}H_6(E)+\tfrac{1}{128}H_8(E)]\}, \quad (16)$$

$$\varepsilon_N=[8/N^3(2\pi)^{1/2}](15{\cdot}2+22{\cdot}7/N+195{\cdot}52/N^2+11\,217{\cdot}28/N^3)+(N^{1/2}/2\pi)[J_0(1)]^{(N/2)-4}\int_1^\infty |J_0(x)|^4\,dx+(N^{1/2}/2\pi)\int_1^\infty \exp(-Nu^2/8)\,du. \quad (17)$$

Then the theorem asserts that [since $P(E)\geq 0$]

$$\max[P_{\text{calc}}(E)-\varepsilon_N, 0]\leq P(E)\leq P_{\text{calc}}(E)+\varepsilon_N \quad (18)$$

for every value of E, where $\max(x,y)$ denotes the greater value of the two numbers x and y. That is, the calculated function P_{calc} approximates the true density function P *uniformly* within an error ε_N. Moreover $\varepsilon_N\to 0$ as $N\to\infty$. For $N=10$, 20, 30, 50 and 100, one obtains $\varepsilon_{10}\leq 0{\cdot}17$, $\varepsilon_{20}\leq 0{\cdot}028$, $\varepsilon_{30}\leq 0{\cdot}014$, $\varepsilon_{50}\leq 9\times10^{-4}$ and $\varepsilon_{100}\leq 5\times10^{-5}$, respectively. Relation (18) is shown graphically in Fig. 1 for $N=10$, 20 and 30. The graph of the true density $E\to P(E)$ lies in the shaded region containing the curve $E\to P_{\text{calc}}(E)$. It may be noted that this region becomes narrower with increasing N.

APPENDIX

$$J_0(x)=\sum_{k=0}^{\infty}(-\tfrac{1}{4}x^2)^k/(k!)^2. \quad (A1)$$

Let f be a complex-valued function defined on an open set U of the real line, having continuous derivatives D^kf for $k=1,2,\ldots,n$.

Let x, $x+h\in U$. Then

$$f(x+h)=f(x)+\sum_{k=1}^{n-1}(h^k/k!)D^kf(x)+[h^n/(n-1)!]\int_0^1(1-\theta)^{n-1}D^nf(x+\theta h)\,d\theta \quad (A2)$$

$$\int_{-\infty}^{+\infty}x^{2n}\exp(-\tfrac{1}{2}x^2)\,dx=(2n-1)!!(2\pi)^{1/2} \quad (A3)$$

$$(2\pi)^{-1/2}\int_{-\infty}^{+\infty}(iu)^n\exp(-\tfrac{1}{2}u^2-iux)\,du=H_n(x)\exp(-\tfrac{1}{2}x^2) \quad (A4)$$

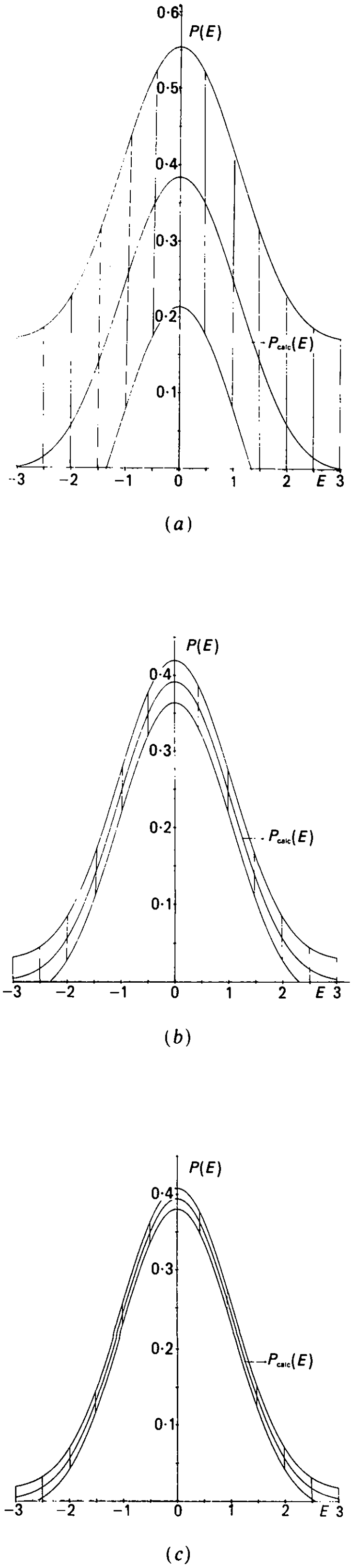

Fig. 1. Graphical representation of equation (17) for (*a*) $N=10$, (*b*) $N=20$, and (*c*) $N=30$.

$$H_{n+1}(x)=xH_n(x)-nH_{n-1}(x)\quad (n\geq 1)\quad (A5)$$

$$H_0(x)=1\quad \text{and}\quad H_1(x)=x\quad (A6)$$

$$\begin{aligned}D^kJ_0(x)=2^{-k}\bigg[J_{-k}(x)-\binom{k}{1}J_{-k+2}(x)\\ +\binom{k}{2}J_{-k+4}(x)+\ldots+(-1)^kJ_k(x)\bigg].\quad (A7)\end{aligned}$$

Calculation of $D^8[\log J_0(x)]$

Substituting $\alpha_n(x)=J_n(x)/J_0(x)$ for $|x|\leq 2$ one obtains

$$\begin{aligned}
D^8[\log J_0(x)] = &-5040[\alpha_1(x)]^8-5040[\alpha_1(x)]^6\\
&\times\{2[1-\alpha_2(x)]-[1-\tfrac{1}{3}\alpha_3(x)/\alpha_1(x)]\}\\
&-[\alpha_1(x)]^4\{6300[1-\alpha_2(x)]^2\\
&-5040[1-\alpha_2(x)]\\
&\times[1-\tfrac{1}{3}\alpha_3(x)/\alpha_1(x)]\\
&-630[1-\tfrac{4}{3}\alpha_2(x)+\tfrac{1}{3}\alpha_4(x)]\\
&+945[1-\tfrac{1}{3}\alpha_3(x)/\alpha_1(x)]^2\\
&+210[1-\tfrac{1}{2}\alpha_3(x)/\alpha_1(x)\\
&+\tfrac{1}{10}\alpha_5(x)/\alpha_1(x)]\}\\
&-[\alpha_1(x)]^2\{1260[1-\alpha_2(x)]^3\\
&-945[1-\alpha_2(x)]^2\\
&\times[1-\tfrac{1}{3}\alpha_3(x)/\alpha_1(x)]\\
&-472{\cdot}5[1-\alpha_2(x)]\\
&\times[1-\tfrac{4}{3}\alpha_2(x)+\tfrac{1}{3}\alpha_4(x)]\\
&+157{\cdot}5[1-\alpha_2(x)]\\
&\times[1-\tfrac{1}{3}\alpha_3(x)/\alpha_1(x)]^2\\
&+105[1-\alpha_2(x)]\\
&\times[1-\tfrac{1}{2}\alpha_3(x)/\alpha_1(x)\\
&+\tfrac{1}{10}\alpha_5(x)/\alpha_1(x)]\\
&+157{\cdot}5[1-\tfrac{1}{3}\alpha_3(x)/\alpha_1(x)]\\
&\times[1-\tfrac{4}{3}\alpha_2(x)+\tfrac{1}{3}\alpha_4(x)]\\
&+17{\cdot}5[1-\tfrac{3}{2}\alpha_2(x)+\tfrac{3}{5}\alpha_4(x)\\
&-\tfrac{1}{10}\alpha_6(x)]\\
&-26{\cdot}25[1-\tfrac{1}{3}\alpha_3(x)/\alpha_1(x)]\\
&\times[1-\tfrac{1}{2}\alpha_3(x)/\alpha_1(x)\\
&+\tfrac{1}{10}\alpha_5(x)/\alpha_1(x)]\\
&-4{\cdot}375[1-\tfrac{3}{5}\alpha_3(x)/\alpha_1(x)\\
&+\tfrac{1}{5}\alpha_5(x)/\alpha_1(x)-\tfrac{1}{35}\alpha_7(x)/\alpha_1(x)]\}\\
&-\{39{\cdot}375[1-\alpha_2(x)]^4\\
&-39{\cdot}375[1-\alpha_2(x)]^2[1-\tfrac{4}{3}\alpha_2(x)\\
&+\tfrac{1}{3}\alpha_4(x)]\\
&+4{\cdot}921\,875[1-\tfrac{4}{3}\alpha_2(x)+\tfrac{1}{3}\alpha_4(x)]^2\\
&+4{\cdot}375[1-\alpha_2(x)]\\
&\times[1-\tfrac{3}{2}\alpha_2(x)+\tfrac{3}{5}\alpha_4(x)-\tfrac{1}{10}\alpha_6(x)]\\
&-0{\cdot}273\,437\,5[1-\tfrac{8}{5}\alpha_2(x)+\tfrac{4}{5}\alpha_4(x)\\
&-\tfrac{8}{35}\alpha_6(x)+\tfrac{1}{35}\alpha_8(x)]\}.
\end{aligned}$$

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Phase Observation in an Organic Crystal (Benzil: $C_{14}H_{10}O_2$) Using Long-Wavelength X-rays

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Abstract

The phase-related asymmetry effect near a multi-beam excitation point has been observed for a noncentrosymmetric organic crystal, benzil ($C_{14}H_{10}O_2$), by using 3·5 keV X-ray synchrotron radiation. A multi-beam theoretical calculation shows good agreement with the experimental data when mosaic spread of the crystal is taken into account. A practical method to extract the cosine of the phase triplet for noncentrosymmetric crystals is also discussed.

Introduction

It has been recognized that multi-beam X-ray diffraction, especially the concept of virtual Bragg scattering

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