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The triplet invariant revisited

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It is shown that the formula for the positivity of the triplet invariant in $P\bar{1}$ changes drastically if one uses a different statistical method by imposing acceptable and unbiased additional structural information. We obtain a much lower probability for the strength (almost $\frac{1}{2}$) of the triplet formula than the classical one.

1. Introduction

It is widely believed that the statistical formula for the triplet invariant (see *e.g.* Cochran, 1955; Hauptman, 1976) cannot be enhanced if no additional chemical structural information is used. There are two different approaches for calculating the joint probability distribution (j.p.d.) of a set of structure factors. The first approach was introduced by Karle and Hauptman (see *e.g.* Karle & Hauptman, 1958; Hauptman, 1976). This method also leads to interesting algebraic formulae. It considers the reciprocal vectors as random variables (r.v.'s) and uses a uniform weight on reciprocal space; the atomic vectors are kept fixed. In the second approach, the reciprocal vectors are fixed and the structure factors are considered as r.v.'s of the atomic position vectors, which are themselves considered as r.v.'s ranging over the unit cell. One normally takes a uniform j.p.d. for these atomic vectors (see *e.g.* Klug, 1958; Giacovazzo, 1976). However, one can also take additional (chemical) information into account. In this case we also get new formulas for the j.p.d.'s of structure factors (see *e.g.* Heinerman *et al.*, 1977).

It happens that the two statistical methods mentioned above give the same j.p.d.'s if we consider only a uniform j.p.d. of the atomic position vectors. Maybe this is the reason why it is believed that the j.p.d. of a triplet set of structure factors cannot be enhanced. In this paper we show that using the second statistical method and using general additional information one obtains a new j.p.d. of the structure factors of a triplet.

2. The joint density of the atomic vectors

We consider the space group $P\bar{1}$ and a crystal with N atoms. For the sake of simplicity we consider an equal-atom structure. Let $\mathbf{r}_i$ $[1 \le i \le t = (N/2)]$ be the atomic position vectors in the asymmetric unit. Let

$$E_{\mathbf{h}} = (2/N^{1/2}) \sum_{i=1}^{t} \cos(2\pi \mathbf{h} \cdot \mathbf{r}_i) \tag{1}$$

be the structure factor corresponding to the reciprocal vector $\mathbf{h}$. Denote by $\mathbf{x}_i$ $(1 \le i \le t)$ t random vector variables that range over the unit cell with respect to a joint probability density $f(\mathbf{x}_1, \ldots, \mathbf{x}_t)$ to be determined shortly. The usual approach is to take $f(\mathbf{x}_1, \ldots, \mathbf{x}_t) = 1$ (see *e.g.* Klug, 1958; Peschar & Schenk, 1987; Giacovazzo, 1976).

Suppose we consider the set of all piecewise linear paths with t vertices that lie in the unit cell. We want the $\mathbf{x}_i$ to range (perhaps uniformly) over these t vertices (that represent random atomic position vectors) and then we want to integrate over all paths. We can do this in the following way. Denote these t vertices by $\mathbf{y}_1, \ldots, \mathbf{y}_t$. We consider the *conditional* density

$$f(\mathbf{x}_1, \ldots, \mathbf{x}_t | \mathbf{y}_1, \ldots, \mathbf{y}_t) = \prod_{i=1}^{t} \left[\frac{2}{N} \sum_{s=1}^{t} \delta(\mathbf{x}_i - \mathbf{y}_s) \right] h(\mathbf{x}_1, \ldots, \mathbf{x}_t), \tag{2}$$

where $h(\mathbf{x}_1, \ldots, \mathbf{x}_t)$ is a density that can be imposed; *e.g.* if we let the $\mathbf{x}_i$ range *uniformly* over the t vertices $\mathbf{y}_1, \ldots, \mathbf{y}_t$, then we can take $h(\mathbf{x}_1, \ldots, \mathbf{x}_t) = 1$. We can also imagine that not all paths are equally probable. So we can also consider a joint density $g(\mathbf{y}_1, \ldots, \mathbf{y}_t)$ for the $\mathbf{y}_j$. Then the total joint density $f(\mathbf{x}_1, \ldots, \mathbf{x}_t)$ can be written as

$$f(\mathbf{x}_1, \ldots, \mathbf{x}_t) = \int f(\mathbf{x}_1, \ldots, \mathbf{x}_t | \mathbf{y}_1, \ldots, \mathbf{y}_t) g(\mathbf{y}_1, \ldots, \mathbf{y}_t) \, \mathrm{d}\mathbf{y}_1 \ldots \mathrm{d}\mathbf{y}_t. \tag{3}$$

We recover the usual Bayesian approach. Furthermore, let us denote every random variable $\hat{Z}(\mathbf{x}_1, \ldots, \mathbf{x}_t)$ of the $\mathbf{x}_i$ with a circumflex (ˆ).

3. The triplet invariant

We shall consider the case

$$h(\mathbf{x}_1, \ldots, \mathbf{x}_t) = g(\mathbf{y}_1, \ldots, \mathbf{y}_t) = 1. \tag{4}$$

That is, the $\mathbf{x}_i$ range uniformly over the different $\mathbf{y}_j$ and all paths are equally probable. So what we are doing is to use the additional information that the probability distribution of the r.v. $\mathbf{x}_i$ *must* be a sum of δ functions, *i.e.* $f(\mathbf{x}_1, \ldots, \mathbf{x}_t)$ *must* be proportional to $\prod_{i=1}^{t}\left[\sum_{s=1}^{t}\delta(\mathbf{x}_i-\mathbf{y}_s)\right]$ where the $\mathbf{y}_j$ are parameters.

Next let us define for every reciprocal vector $\mathbf{h}$ the random variable

$$\hat{E}_{\mathbf{h}}=\hat{E}_{\mathbf{h}}(\mathbf{x}_1,\ldots,\mathbf{x}_t)=(2/N^{1/2})\sum_{i=1}^{t}\cos(2\pi\mathbf{h}\cdot\mathbf{x}_i). \qquad (5)$$

This choice of r.v. instead of $\hat{F}_{\mathbf{h}}=N^{1/2}\hat{E}_{\mathbf{h}}$ has nothing to do with any hidden *a priori* uniform distribution but simply with the fact that, as we will see below, $\langle\hat{F}_{\mathbf{h}}^2\rangle=O(N)$ whereas $\langle\hat{E}_h^2\rangle=O(1)$.

For every r.v. $\hat{Z}(\mathbf{x}_1,\ldots,\mathbf{x}_t)$ let us define

$$\langle Z(\mathbf{x}_1,\ldots,\mathbf{x}_t)\rangle\equiv\int\hat{Z}(\mathbf{x}_1,\ldots,\mathbf{x}_t)f(\mathbf{x}_1,\ldots,\mathbf{x}_t)\,\mathrm{d}\mathbf{x}_1\ldots\mathrm{d}\mathbf{x}_t. \quad (6)$$

We want to calculate the j.p.d.

$$P(E_{\mathbf{h}},E_{\mathbf{k}},E_{\mathbf{h}+\mathbf{k}})=\langle\delta(\hat{E}_{\mathbf{h}}-E_{\mathbf{h}})\delta(\hat{E}_{\mathbf{k}}-E_{\mathbf{k}})\delta(\hat{E}_{\mathbf{h}+\mathbf{k}}-E_{\mathbf{h}+\mathbf{k}})\rangle, \qquad (7)$$

where δ is Dirac's delta function $\delta(x-y)=(1/2\pi)\int_{-\infty}^{\infty}\mathrm{d}u\,\exp[iu(x-y)]$. Define

$$E_1=E_{\mathbf{h}},\quad E_2=E_{\mathbf{k}},\quad E_3=E_{\mathbf{h}+\mathbf{k}}. \qquad (8)$$

Then

$$\begin{aligned}P(E_1,E_2,E_3)&=(1/2\pi)^3\int_{-\infty}^{\infty}\mathrm{d}u_1\ldots\int_{-\infty}^{\infty}\mathrm{d}u_3\,\exp(-iu_1E_1\ldots-iu_3E_3)\\&\quad\times\varphi(u_1,u_2,u_3),\end{aligned} \qquad (9)$$

where

$$\varphi(u_1,u_2,u_3)=\langle\exp(iu_1\hat{E}_1+iu_2\hat{E}_2+iu_3\hat{E}_3)\rangle. \qquad (10)$$

Define $\mathbf{h}_1=\mathbf{h},\mathbf{h}_2=\mathbf{k},\mathbf{h}_3=\mathbf{h}+\mathbf{k}$. Then the right-hand side of equation (9) equals

$$\int\mathrm{d}\mathbf{y}_1\ldots\mathrm{d}\mathbf{y}_t\left\{\int\mathrm{d}\mathbf{x}_1\left[(2/N)\sum_{s=1}^{t}\delta(\mathbf{x}_1-\mathbf{y}_s)\right]\times\exp\left[(2i/N^{1/2})\sum_j u_j\cos(2\pi\mathbf{h}_j\cdot\mathbf{x}_1)\right]\right\}^t. \qquad (11)$$

Let us define

$$\varphi(u_1,u_2,u_3,\mathbf{y})\equiv\left\{\int\mathrm{d}\mathbf{x}_1\left[(2/N)\sum_{s=1}^{t}\delta(\mathbf{x}_1-\mathbf{y}_s)\right]\times\exp\left[(2i/N^{1/2})\sum_j u_j\cos(2\pi\mathbf{h}_j\cdot\mathbf{x}_1)\right]\right\}. \qquad (12)$$

Then equation (11) is equal to $\int\mathrm{d}\mathbf{y}_1\ldots\mathrm{d}\mathbf{y}_t\,\varphi(u_1,u_2,u_3,\mathbf{y})^t$. Next, for an equal-atom structure we can replace $(2/N)\sum_{s=1}^{t}\delta(\mathbf{x}_1-\mathbf{y}_s)$ by

$$\sum_{\mathbf{q}}\hat{U}_{\mathbf{q}}(\mathbf{y})\exp(-2\pi i\mathbf{q}\cdot\mathbf{x}_1), \qquad (13)$$

where

$$\hat{U}_{\mathbf{q}}(\mathbf{y})=(1/N^{1/2})\hat{E}_{\mathbf{h}}(\mathbf{y}_1,\ldots,\mathbf{y}_t)\quad\text{and}\quad\mathbf{y}=(\mathbf{y}_1,\ldots,\mathbf{y}_t). \quad (14)$$

Then $\varphi(u_1,u_2,u_3,\mathbf{y})$ is given by

$$\begin{aligned}\varphi(u_1,u_2,u_3,\mathbf{y})&=\int\mathrm{d}\mathbf{x}_1\Big[\sum_{\mathbf{q}}\hat{U}_{\mathbf{q}}(\mathbf{y})\exp(-2\pi i\mathbf{q}\cdot\mathbf{x}_1)\Big]\\&\quad\times\exp\big[(2i/N^{1/2})u_j\cos(2\pi\mathbf{h}_j\cdot\mathbf{x}_1)\big],\end{aligned} \qquad (15)$$

where we have summed over repeated indices. Developing $\varphi(u_1,u_2,u_3,\mathbf{y})$ asymptotically,

$$\begin{aligned}\varphi(u_1,u_2,u_3,\mathbf{y})&=1+\sum_j\frac{2iu_j}{N^{1/2}}\hat{U}_{\mathbf{h}_j}(\mathbf{y})-\sum_j\frac{u_j^2}{N}\\&\quad-\frac{u_1^2}{N}\hat{U}_{2\mathbf{h}}(\mathbf{y})-\frac{u_2^2}{N}\hat{U}_{2\mathbf{k}}(\mathbf{y})-\frac{u_3^2}{N}\hat{U}_{2\mathbf{h}+2\mathbf{k}}(\mathbf{y})\\&\quad-\frac{2u_1u_2}{N}[\hat{U}_{\mathbf{h}+\mathbf{k}}(\mathbf{y})+\hat{U}_{\mathbf{h}-\mathbf{k}}(\mathbf{y})]\\&\quad-\frac{2u_1u_3}{N}[\hat{U}_{\mathbf{k}}(\mathbf{y})+\hat{U}_{2\mathbf{h}+\mathbf{k}}(\mathbf{y})]\\&\quad-\frac{2u_2u_3}{N}[\hat{U}_{\mathbf{h}}(\mathbf{y})+\hat{U}_{\mathbf{h}+2\mathbf{k}}(\mathbf{y})]\\&\quad-\frac{2iu_1u_2u_3}{N(N)^{1/2}}+O\Big(\frac{1}{N^2}\Big).\end{aligned} \qquad (16)$$

In equation (16) $\hat{U}_{\mathbf{q}}(\mathbf{y})$ is considered to be of order $1/N^{1/2}$. Developing asymptotically $\varphi(u_1,u_2,u_3,\mathbf{y})^t$ (where $t=N/2$) we get

$$\begin{aligned}\varphi(u_1,u_2,u_3,\mathbf{y})^t&=\exp[iu_1\hat{E}_{\mathbf{h}}(\mathbf{y})+iu_2\hat{E}_{\mathbf{k}}(\mathbf{y})+iu_3\hat{E}_{\mathbf{h}+\mathbf{k}}(\mathbf{y})]\\&\quad\times\exp(-\tfrac{1}{2}u_1^2-\tfrac{1}{2}u_2^2-\tfrac{1}{2}u_3^2)\\&\quad\times\bigg\{1-\frac{u_1^2}{2N^{1/2}}\hat{E}_{2\mathbf{h}}(\mathbf{y})-\frac{u_2^2}{2N^{1/2}}\hat{E}_{2\mathbf{k}}(\mathbf{y})\\&\quad-\frac{u_3^2}{2N^{1/2}}\hat{E}_{2\mathbf{h}+2\mathbf{k}}(\mathbf{y})-\frac{u_1u_2}{N^{1/2}}[\hat{E}_{\mathbf{h}+\mathbf{k}}(\mathbf{y})+\hat{E}_{\mathbf{h}-\mathbf{k}}(\mathbf{y})]\\&\quad-\frac{u_1u_3}{N^{1/2}}[\hat{E}_{\mathbf{h}}(\mathbf{y})+\hat{E}_{2\mathbf{h}+\mathbf{k}}(\mathbf{y})]\\&\quad-\frac{u_2u_3}{N^{1/2}}[\hat{E}_{\mathbf{k}}(\mathbf{y})+\hat{E}_{\mathbf{h}+2\mathbf{k}}(\mathbf{y})]\\&\quad-\frac{iu_1u_2u_3}{N^{1/2}}+O\Big(\frac{1}{N}\Big)\bigg\}.\end{aligned} \qquad (17)$$

Next we remark that (a proof is given in the Appendix)

$$\begin{aligned}&\int\mathrm{d}\mathbf{y}_1\ldots\mathrm{d}\mathbf{y}_t\,\varphi(u_1,u_2,u_3,\mathbf{y})^t=\\&\exp(-\tfrac{1}{2}u_1^2-\tfrac{1}{2}u_2^2-\tfrac{1}{2}u_3^2)\int_{-\infty}^{\infty}\exp(iu_1E_{\mathbf{h}}+iu_2E_{\mathbf{k}}+iu_3E_{\mathbf{h}+\mathbf{k}})\\&\times\bigg[1-\frac{u_1^2}{2N^{1/2}}E_{2\mathbf{h}}-\frac{u_2^2}{2N^{1/2}}E_{2\mathbf{k}}-\frac{u_3^2}{2N^{1/2}}E_{2\mathbf{h}+2\mathbf{k}}\\&-\frac{u_1u_2}{N^{1/2}}(E_{\mathbf{h}+\mathbf{k}}+E_{\mathbf{h}-\mathbf{k}})-\frac{u_1u_3}{N^{1/2}}(E_{\mathbf{k}}+E_{2\mathbf{h}+\mathbf{k}})\\&-\frac{u_2u_3}{N^{1/2}}(E_{\mathbf{h}}+E_{\mathbf{h}+2\mathbf{k}})-\frac{iu_1u_2u_3}{N^{1/2}}+O\Big(\frac{1}{N}\Big)\bigg]\\&\times P_0(E_{\mathbf{h}},E_{\mathbf{k}},E_{\mathbf{h}+\mathbf{k}},E_{2\mathbf{h}},\ldots,E_{\mathbf{h}+2\mathbf{k}})\mathrm{d}E_{\mathbf{h}}\mathrm{d}E_{\mathbf{k}}\mathrm{d}E_{\mathbf{h}+\mathbf{k}}\mathrm{d}E_{2\mathbf{h}}\ldots\mathrm{d}E_{\mathbf{h}+2\mathbf{k}},\end{aligned} \qquad (18)$$

where $P_0(E_{\mathbf{h}},E_{\mathbf{k}},E_{\mathbf{h}+\mathbf{k}},E_{2\mathbf{h}},\ldots,E_{\mathbf{h}+2\mathbf{k}})$ is the j.p.d. of $E_{\mathbf{h}},\ldots,E_{\mathbf{h}+2\mathbf{k}}$ with respect to the uniform distribution of the $\mathbf{y}_i$, *i.e.*

$$P_0(E_{\mathbf{h}}, E_{\mathbf{k}}, E_{\mathbf{h+k}}, E_{2\mathbf{h}}, \ldots, E_{\mathbf{h+2k}}) = \int \mathrm{d}\mathbf{y}_1 \ldots \mathrm{d}\mathbf{y}_t\, \delta(\hat{E}_{\mathbf{h}} - E_{\mathbf{h}}) \times \ldots \times \delta(\hat{E}_{\mathbf{h+2k}} - E_{\mathbf{h+2k}}), \quad (19)$$

where in equation (19) $\hat{E}_{\mathbf{h}}$ means $\hat{E}_{\mathbf{h}}(\mathbf{y}_1, \ldots, \mathbf{y}_t)$ *etc.* Since *e.g.*

$$\int_{-\infty}^{\infty} P_0(E_{\mathbf{h}}, E_{\mathbf{k}}, E_{\mathbf{h+k}}, E_{\mathbf{h+2k}}) E_{\mathbf{h+2k}}\, \mathrm{d}E_{\mathbf{h+2k}} = O\big(1/N^{1/2}\big), \quad (20)$$

$$\int_{-\infty}^{\infty} P_0(E_{\mathbf{h}}, E_{\mathbf{k}}, E_{\mathbf{h+k}}, E_{2\mathbf{h}}, \ldots, E_{\mathbf{h+2k}}) \times f(E_{\mathbf{h}}, E_{\mathbf{k}}, E_{\mathbf{h+k}})\, \mathrm{d}E_{\mathbf{h}}\, \mathrm{d}E_{\mathbf{k}}\, \mathrm{d}E_{\mathbf{h+k}}\, \mathrm{d}E_{2\mathbf{h}} \ldots \mathrm{d}E_{\mathbf{h+2k}} = \int_{-\infty}^{\infty} P_0(E_{\mathbf{h}}, E_{\mathbf{k}}, E_{\mathbf{h+k}}) f(E_{\mathbf{h}}, E_{\mathbf{k}}, E_{\mathbf{h+k}})\, \mathrm{d}E_{\mathbf{h}}\, \mathrm{d}E_{\mathbf{k}}\, \mathrm{d}E_{\mathbf{h+k}}, \quad (21)$$

and

$$P_0(E_{\mathbf{h}}, E_{\mathbf{k}}, E_{\mathbf{h+k}}) = \left[\frac{1}{(2\pi)^{1/2}}\right]^3 \exp(-\tfrac{1}{2}E_{\mathbf{h}}^2 \ldots - \tfrac{1}{2}E_{\mathbf{h+k}}^2) \times \left[1 + \frac{1}{N^{1/2}} E_{\mathbf{h}} E_{\mathbf{k}} E_{\mathbf{h+k}} + O\left(\frac{1}{N}\right)\right], \quad (22)$$

we obtain (using formulas from the Appendix)

$$\begin{aligned}\varphi(u_1, u_2, u_3) &= \int \mathrm{d}\mathbf{y}_1 \ldots \mathrm{d}\mathbf{y}_t\, \varphi(u_1, u_2, u_3, \mathbf{y})^t \\ &= \left[\frac{1}{(2\pi)^{1/2}}\right]^3 \exp(-\tfrac{1}{2}u_1^2 - \tfrac{1}{2}u_2^2 - \tfrac{1}{2}u_3^2) \\ &\quad \times \int_{-\infty}^{\infty} \mathrm{d}E_{\mathbf{h}}\, \mathrm{d}E_{\mathbf{k}}\, \mathrm{d}E_{\mathbf{h+k}}\, \exp(iu_1E_{\mathbf{h}} + iu_2E_{\mathbf{k}} + iu_3E_{\mathbf{h+k}}) \\ &\quad \times \exp(-\tfrac{1}{2}E_{\mathbf{h}}^2 - \tfrac{1}{2}E_{\mathbf{k}}^2 - \tfrac{1}{2}E_{\mathbf{h+k}^2})\bigg[1 - \frac{iu_1u_2u_3}{N^{1/2}} - \frac{u_1u_2}{N^{1/2}}E_{\mathbf{h+k}} \\ &\quad - \frac{u_1u_3}{N^{1/2}}E_{\mathbf{k}} - \frac{u_2u_3}{N^{1/2}}E_{\mathbf{h}} + \frac{1}{N^{1/2}}E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{h+k}} + O\left(\frac{1}{N}\right)\bigg] \\ &= \exp(-u_1^2 - u_2^2 - u_3^2)\bigg[1 + \frac{(iu_1)(iu_2)(iu_3)}{N^{1/2}}\underbrace{(1+3+1)}_{=5} \\ &\quad + O\left(\frac{1}{N}\right)\bigg]. \end{aligned} \quad (23)$$

Thus [see equation (9)]

$$\begin{aligned} P(E_1, E_2, E_3) &\equiv \left(\frac{1}{2\pi}\right)^3 \int_{-\infty}^{\infty} \mathrm{d}u_1\, \mathrm{d}u_2\, \mathrm{d}u_3\, \varphi(u_1, u_2, u_3) \\ &\quad \times \exp(-iu_1E_1 - iu_2E_2 - iu_3E_3) \\ &= \left(\frac{1}{2\pi}\right)^3 \int_{-\infty}^{\infty} \mathrm{d}u_1\, \mathrm{d}u_2\, \mathrm{d}u_3 \\ &\quad \times \exp(-iu_1E_1 - iu_2E_2 - iu_3E_3) \\ &\quad \times \exp(-u_1^2 - u_2^2 - u_3^2) \\ &\quad \times \left[1 + \frac{5}{N^{1/2}}(iu_1)(iu_2)(iu_3) + O\left(\frac{1}{N}\right)\right] \\ &= \left(\frac{1}{2\pi}\right)^3 \int_{-\infty}^{\infty} \frac{\mathrm{d}u_1}{2^{1/2}}\frac{\mathrm{d}u_2}{2^{1/2}}\frac{\mathrm{d}u_3}{2^{1/2}} \\ &\quad \times \exp\left(-iu_1\frac{E_1}{2^{1/2}} - iu_2\frac{E_2}{2^{1/2}} - iu_3\frac{E_3}{2^{1/2}}\right) \\ &\quad \times \exp(-\tfrac{1}{2}u_1^2 - \tfrac{1}{2}u_2^2 - \tfrac{1}{2}u_3^2) \\ &\quad \times \left[1 + \frac{5}{N^{1/2}}\left(i\frac{u_1}{2^{1/2}}\right)\left(i\frac{u_2}{2^{1/2}}\right)\left(i\frac{u_3}{2^{1/2}}\right) + O\left(\frac{1}{N}\right)\right] \\ &= \left(\frac{1}{2^{1/2}}\right)^3 \left(\frac{1}{2\pi}\right)^{3/2} \exp(-\tfrac{1}{4}E_1^2 - \tfrac{1}{4}E_2^2 - \tfrac{1}{4}E_3^2) \\ &\quad \times \left[1 + \frac{5}{N^{1/2}}\left(\frac{1}{2^{1/2}}\right)^3 \frac{E_1}{2^{1/2}}\frac{E_2}{2^{1/2}}\frac{E_3}{2^{1/2}} + O\left(\frac{1}{N}\right)\right] \\ &= \left(\frac{1}{4\pi}\right)^{3/2} \exp(-\tfrac{1}{4}E_1^2 - \tfrac{1}{4}E_2^2 - \tfrac{1}{4}E_3^2) \\ &\quad \times \left[1 + \frac{5E_1E_2E_3}{8N^{1/2}} + O\left(\frac{1}{N}\right)\right] \\ &= \left(\frac{1}{4\pi}\right)^{3/2} \exp\bigg[-\tfrac{1}{4}E_1^2 - \tfrac{1}{4}E_2^2 - \tfrac{1}{4}E_3^2 \\ &\quad + \frac{5E_1E_2E_3}{8N^{1/2}} + O\left(\frac{1}{N}\right)\bigg]. \end{aligned} \quad (24)$$

From which it follows that the probability P_+ that the sign of the triplet $E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{h+k}}$ is positive given the absolute values $|E_{\mathbf{h}}|, |E_{\mathbf{k}}|, |E_{\mathbf{h+k}}|$ is given by

$$P_+(E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{h+k}}) = \tfrac{1}{2} + \tfrac{1}{2}\tanh\left(\frac{5}{8}\frac{|E_1E_2E_3|}{N^{1/2}}\right), \quad (25)$$

whereas the classical formula (Cochran, 1955) is

$$P_{+,\,\mathrm{classical}}(E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{h+k}}) = \tfrac{1}{2} + \tfrac{1}{2}\tanh\left(\frac{|E_1E_2E_3|}{N^{1/2}}\right). \quad (26)$$

4. Conclusion

The introduction of joint densities $f(\mathbf{x}_1, \ldots, \mathbf{x}_t)$ of atomic variables that differ noticeably from the classical approach can give us new statistical formulas that are very different to the classical formulas. A lot of research has still to be done.

APPENDIX *A*

$$\int_{-\infty}^{\infty} \exp(ibx)\exp(-\tfrac{1}{2}ax^2)\,\mathrm{d}x = (2\pi/a)^{1/2}\exp\big[-\tfrac{1}{2}(b^2/a)\big]. \quad (27)$$

$$\int_{-\infty}^{\infty} \exp(ibx)\exp(-\tfrac{1}{2}x^2)\,\mathrm{d}x = (2\pi)^{1/2}\exp(-\tfrac{1}{2}b^2). \tag{28}$$

$$\int_{-\infty}^{\infty} (iu)^n \exp(-iuE)\exp(-\tfrac{1}{2}u^2)\,\mathrm{d}u = (2\pi)^{1/2}\exp(-\tfrac{1}{2}E^2)H_n(E). \tag{29}$$

$$H_0(x) = 1. \tag{30}$$

$$H_1(x) = x. \tag{31}$$

$$H_2(x) = x^2 - 1. \tag{32}$$

$$H_3(x) = x^3 - 3x. \tag{33}$$

$$H_4(x) = x^4 - 6x^2 + 3. \tag{34}$$

$$H_5(x) = x^5 - 10x^3 + 15x. \tag{35}$$

$$\int_{-\infty}^{\infty} x\exp(ibx)\exp(-\tfrac{1}{2}x^2)\,\mathrm{d}x = (2\pi)^{1/2}ib\exp(-\tfrac{1}{2}b^2). \tag{36}$$

$$\int_{-\infty}^{\infty} x^2\exp(ibx)\exp(-\tfrac{1}{2}x^2)\,\mathrm{d}x = (2\pi)^{1/2}(1-b^2)\exp(-\tfrac{1}{2}b^2). \tag{37}$$

Proof of equation (18): For notational simplicity we consider the case $\varphi[u;\ \hat{E}_{\mathbf{h}}(\mathbf{y})]$ where $\mathbf{y} = (\mathbf{y}_1, \ldots, \mathbf{y}_t)$. Then

$$\begin{aligned}\int \varphi[u;\ \hat{E}_{\mathbf{h}}(\mathbf{y})]\,\mathrm{d}\mathbf{y} &= \int \mathrm{d}\mathbf{y} \int \varphi(u;\ E_{\mathbf{h}})\delta[E_{\mathbf{h}} - \hat{E}_{\mathbf{h}}(\mathbf{y})]\,\mathrm{d}E_{\mathbf{h}} \\ &= \int \varphi(u;\ E_{\mathbf{h}})\,\mathrm{d}E_{\mathbf{h}} \underbrace{\int \mathrm{d}\mathbf{y}\,\delta[E_{\mathbf{h}} - \hat{E}_{\mathbf{h}}(\mathbf{y})]}_{P_0(E_{\mathbf{h}})} \\ &= \int \varphi(u;\ E_{\mathbf{h}})P_0(E_{\mathbf{h}})\,\mathrm{d}E_{\mathbf{h}}.\end{aligned} \tag{38}$$

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