Acta Crystallographica Section A
Foundations of Crystallography
ISSN 0108-7673

Received 6 June 2007
Accepted 4 June 2008

The quartet revisited

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Using an unbiased and very general joint density of the atomic position vectors we are able to calculate different probabilities for the sign of the quartet given its second neighborhood. One already knows that additional chemical information alters the joint probability distribution (j.p.d.) of structure factors. That is, they can and will give different j.p.d.'s for the quartet invariant given its second neighborhood. In this paper we show that even without additional chemical information the j.p.d.'s of structure factors can be strongly different from the classical ones if we impose a general j.p.d. for the atomic vectors based on the fact that the real distribution of the atomic position vectors is a sum of δ functions.

1. Introduction

The use of nonuniform joint probability distributions (j.p.d's) for the atomic position vectors based on a modified Patterson function has been advocated by Brosius (1979) (see also Brosius, 1985, 1989). There are two main approaches in this research. A first one is to use a j.p.d. $f(\mathbf{x}_1, \ldots, \mathbf{x}_N)$ defined by

$$f(\mathbf{x}_1, \ldots, \mathbf{x}_N) = \mathrm{Cte} \prod_{i<j} Q(\mathbf{x}_i - \mathbf{x}_j),$$

where Cte is a normalization constant. $Q(\mathbf{u})$ is the modified Patterson function,

$$Q(\mathbf{u}) \equiv \sum_{\mathbf{q}} \left(\frac{R_{\mathbf{q}}^2 - 1}{N - 1} \right) \cos(2\pi \mathbf{q} \cdot \mathbf{u}).$$

The $\mathbf{x}_i$ are then no longer independent random variables (r.v.'s). In this approach we must solve the problem of calculating j.p.d.'s of structure factors $E_{\mathbf{h}}$ for non-independent $\mathbf{x}_i$. We claim that this issue is solved to first order by Brosius (2008). A second approach is to use the additional information still present in the Patterson function given one or more interatomic vectors, *e.g.* the interatomic vector $\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2$. Such information has also been used with success by Giacovazzo (1991) (the theoretical background) and by Altomare *et al.* (1992*a*,*b*, 1994). However, our approach is different and is again based on a modified version of $f(\mathbf{x}_1, \ldots, \mathbf{x}_N)$ above. Since $\mathbf{r}_1$ and $\mathbf{r}_2$ are given, we can consider the much simpler j.p.d.

$$f_1(\mathbf{x}_1, \ldots, \mathbf{x}_N) = \mathrm{Cte} \prod_{i=1}^{N} Q(\mathbf{x}_i - \mathbf{r}_1) Q(\mathbf{x}_i - \mathbf{r}_2).$$

A first remark: for this j.p.d. the r.v.'s $\mathbf{x}_i$ are independent. Since the origin is not fixed yet, we can apply the transformation $\mathbf{x}_i \rightarrow \mathbf{x}_i + \mathbf{r}_1$ in $f_1(\mathbf{x}_1, \ldots, \mathbf{x}_N)$ above. We then get

$$f_2(\mathbf{x}_1, \ldots, \mathbf{x}_N) = \mathrm{Cte} \prod_{i=1}^{N} Q(\mathbf{x}_i) Q(\mathbf{x}_i + \mathbf{r}_{12}).$$

The function $Q(\mathbf{x}_i)Q(\mathbf{x}_i + \mathbf{r}_{12})$ is nothing other than a modified Patterson superposition function.

Another question one can ask is: Is there any additional information besides the modified Patterson function $Q(\mathbf{x}_i - \mathbf{x}_j)$ that we can still impose on the $\mathbf{x}_i$? The answer is yes; additional chemical information was applied by Heinerman *et al.* (1977). There was still some difficulty to be solved in that the $\mathbf{x}_i$ are not independent: to calculate j.p.d.'s of invariants the authors introduce a Von Mises distribution [a similar form was also obtained by Brosius (2008)]. It is also interesting to note that in this paper a general expression was needed for the orientational average of $\exp[2\pi i(\mathbf{h} \cdot \mathbf{x} + \mathbf{k} \cdot \mathbf{y} + \mathbf{l} \cdot \mathbf{z})]$. This problem was solved by Brosius (1978) with the $B(z, t, s)$ formula, which is a generalization of Hauptman's $B(z, t)$ formula (Hauptman, 1965) and also a generalization of the well known formula of Debye [the orientational average of $\exp(2\pi i \mathbf{h} \cdot \mathbf{x})$].

However, there still remains the question whether it is possible to use additional information *without* using Patterson functions or additional chemical information. The answer is yes, as we will show in this paper. Let us recall the two main statistical methods used. The first one considers the reciprocal vectors as the primitive r.v.'s [see *e.g.* Karle & Hauptman (1958), who introduced this method]. The structure factors $E_{\mathbf{h}}$ are then r.v.'s depending on $\mathbf{h}$. This is an interesting approach and has also led to various very interesting algebraic formulas. The second approach considers the atomic vectors $\mathbf{x}_i$ as the primitive r.v.'s [see *e.g.* Klug (1958), Giacovazzo (1977) or van der Putten & Schenk (1977), to name a few]. In this approach, the primitive r.v.'s are independent and range *with uniform weight* over the entire unit cell. The aim of this paper is to show that there is still some general and important additional information present and not used. Using this information we are able to obtain different statistical j.p.d.'s of structure factors. We especially treat the case of the quartet invariant in $P\bar{1}$ given its second neighborhood.

2. The joint distribution $f(\mathbf{x}_1, \ldots, \mathbf{x}_t)$

We consider the space group $P\bar{1}$ and an equal-atom structure. The (normalized) structure factor for $t = N/2$ atoms in the asymmetric unit is then given by

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

where the $\mathbf{r}_i$ are the atomic position vectors in the asymmetric unit. Let $\mathbf{x}_1, \ldots, \mathbf{x}_t$ be t random vector variables ranging over the unit cell. Instead of considering a uniform density $f(\mathbf{x}_1, \ldots, \mathbf{x}_t) = 1$ where the random vector variables range *uniformly* over the unit cell, we imagine the set of all piecewise linear paths in the unit cell with t vertices. Every path then represents a possible configuration of the crystal. We now want the $\mathbf{x}_i$ to range *only* over these t vertices and afterwards we want to integrate over all these paths. To put it differently, we *know* that the actual distribution of the atomic vectors is a sum of Dirac δ functions. This is *important* and *general* information. However, it remains to be shown that using this information we can also get drastically different j.p.d.'s. This paper will show that this is indeed the case. We know that a *better a priori* guess for the j.p.d. $f(\mathbf{x}_1, \ldots, \mathbf{x}_t)$ of the $\mathbf{x}_i$ is given by the density

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

where the $\mathbf{y}_s$ are points in the unit cell. We can still go further and impose possible additional information on the $\mathbf{y}_s$. That is, we can consider the more general setting

$$f(\mathbf{x}_1, \ldots, \mathbf{x}_t) \propto \prod_{i=1}^{t} h(\mathbf{y}_1, \ldots, \mathbf{y}_t) \sum_{s=1}^{t} \delta(\mathbf{x}_i - \mathbf{y}_s).$$

Now $\sum_{s=1}^{t} \delta(\mathbf{x}_j - \mathbf{y}_s)$ is proportional to $\sum_{\mathbf{q}} [\hat{E}_{\mathbf{q}}(\mathbf{y})/N^{1/2}] \times \exp(-2\pi i \mathbf{q} \cdot \mathbf{x}_j)$, where $\hat{E}_{\mathbf{q}}(\mathbf{y}) = (2/N^{1/2}) \sum_{s=1}^{t} \cos(2\pi \mathbf{q} \cdot \mathbf{y}_s)$ and $\mathbf{y} = (\mathbf{y}_1, \ldots, \mathbf{y}_t)$. So we have the following setup:

$$f(\mathbf{x}_1, \ldots, \mathbf{x}_t) = f(\mathbf{x}_1, \ldots, \mathbf{x}_t | \mathbf{y}_1, \ldots, \mathbf{y}_t) h(\mathbf{y}_1, \ldots, \mathbf{y}_t), \qquad (1)$$

where

$$f(\mathbf{x}_1, \ldots, \mathbf{x}_t | \mathbf{y}_1, \ldots, \mathbf{y}_t) = \prod_{j=1}^{t} \left[\sum_{\mathbf{q}} \frac{\hat{E}_{\mathbf{q}}(\mathbf{y})}{N^{1/2}} \exp(-2\pi i \mathbf{q} \cdot \mathbf{x}_j) \right], \qquad (2)$$

where $\mathbf{y}_1, \ldots, \mathbf{y}_t$ are t random vector variables ranging over the unit cell with some j.p.d. $h(\mathbf{y}_1, \ldots, \mathbf{y}_t)$ to be discussed shortly and where

$$\hat{E}_{\mathbf{q}}(\mathbf{y}) \equiv (2/N^{1/2}) \sum_{i=1}^{t} \cos(2\pi \mathbf{q} \cdot \mathbf{y}_i). \qquad (3)$$

We also denote by $\hat{E}_{\mathbf{q}}(\mathbf{x})$ the r.v.

$$\hat{E}_{\mathbf{q}}(\mathbf{x}) \equiv \hat{E}_{\mathbf{q}}(\mathbf{x}_1, \ldots, \mathbf{x}_t) \equiv (2/N^{1/2}) \sum_{i=1}^{t} \cos(2\pi \mathbf{q} \cdot \mathbf{x}_i). \qquad (4)$$

Some remark is perhaps needed. Contrary to a widely used custom we shall not replace $\hat{E}_{\mathbf{q}}(\mathbf{x})$ by $[\hat{E}_{\mathbf{q}}(\mathbf{x}) - \langle \hat{E}_{\mathbf{q}}(\mathbf{x}) \rangle]/\sigma[\hat{E}_{\mathbf{q}}(\mathbf{x})]$ where $\sigma^2[\hat{E}_{\mathbf{q}}(\mathbf{x})]$ is the variance of $\hat{E}_{\mathbf{q}}(\mathbf{x})$. This is not necessary and puts an additional burden on the already laborious calculations. So we shall not include these coefficients $\sigma[\hat{E}_{\mathbf{x}}(\mathbf{q})]$. We shall also see below that $\langle \hat{E}_{\mathbf{q}}^2 \rangle = O(1)$ with respect to N, which is what we want.

3. The quartet and its second neighborhood in $P\bar{1}$

We consider the structure factors $E_1 \equiv E_{\mathbf{h}}$, $E_2 \equiv E_{\mathbf{k}}$, $E_3 \equiv E_{\mathbf{l}}$, $E_4 \equiv E_{\mathbf{h}+\mathbf{k}+\mathbf{l}}$, $E_5 \equiv E_{\mathbf{h}+\mathbf{k}}$, $E_6 \equiv E_{\mathbf{h}+\mathbf{l}}$, $E_7 \equiv E_{\mathbf{k}+\mathbf{l}}$. Thus let $\mathbf{x}_1, \ldots, \mathbf{x}_t$ be t random vector variables representing the t atomic position vectors $\mathbf{r}_1, \ldots, \mathbf{r}_t$.

$\hat{E}_1(\mathbf{x})$ stands for $\hat{E}_{\mathbf{h}}(\mathbf{x})$ *etc.* and $\hat{E}_1(\mathbf{y})$ stands for $\hat{E}_{\mathbf{h}}(\mathbf{y})$. Let $\hat{Z}(\mathbf{x}_1, \ldots, \mathbf{x}_t)$ be an r.v. depending on the r.v.'s $\mathbf{x}_1, \ldots, \mathbf{x}_t$. Then we shall denote by

$$\langle \hat{Z}(\mathbf{x}) \rangle_{\mathbf{x}} \equiv \textstyle\int \mathrm{d}\mathbf{x}_1 \ldots \mathrm{d}\mathbf{x}_t \, f(\mathbf{x}_1, \ldots, \mathbf{x}_t) \hat{Z}(\mathbf{x}_1, \ldots, \mathbf{x}_t) \qquad (5)$$

the average of $\hat{Z}(\mathbf{x}_1, \ldots, \mathbf{x}_t)$ with respect to $\mathbf{x}_1, \ldots \mathbf{x}_t$. In the same way we denote by

$$\langle \hat{Z}(\mathbf{y}) \rangle_{\mathbf{y}} \equiv \textstyle\int \mathrm{d}\mathbf{y}_1 \ldots \mathrm{d}\mathbf{y}_t \, h(\mathbf{y}_1, \ldots, \mathbf{y}_t) \hat{Z}(\mathbf{y}_1, \ldots, \mathbf{y}_t) \qquad (6)$$

the average of the r.v. $\hat{Z}(\mathbf{y}_1, \ldots, \mathbf{y}_t)$ with respect to $\mathbf{y}_1, \ldots, \mathbf{y}_t$. Sometimes we shall simply denote an r.v. $\hat{Z}$ without an argument when it is clear from the context whether $\hat{Z}$ means either $\hat{Z}(\mathbf{x})$ or $\hat{Z}(\mathbf{y})$ (but we shall always denote an r.v. with a circumflex, ˆ).

We want to calculate the j.p.d.

$$\begin{aligned} P(E_1, E_2, E_3, E_4, E_5, E_6, E_7) \\ \equiv (1/2\pi)^7 \int_{-\infty}^{\infty} \mathrm{d}u_1 \ldots \mathrm{d}u_7 \exp(-u_1 E_1 - \ldots - u_7 E_7) \\ \times \phi(u_1, \ldots, u_7), \end{aligned} \qquad (7)$$

where

$$\phi(u_1, \ldots, u_7) = \langle \exp[i u_1 \hat{E}_1(\mathbf{x}) + \ldots + i u_7 \hat{E}_7(\mathbf{x})] \rangle_{\mathbf{x}} \qquad (8)$$

is the characteristic function. It then follows from the definition of $f(\mathbf{x}_1, \ldots, \mathbf{x}_t | \mathbf{y}_1, \ldots, \mathbf{y}_t)$ that

$$\varphi(u_1, \ldots, u_7) = \textstyle\int \mathrm{d}\mathbf{y}_1 \ldots \mathrm{d}\mathbf{y}_t \, h(\mathbf{y}_1, \ldots, \mathbf{y}_t) \phi(u_1, \ldots, u_7, \mathbf{y})^t, \qquad (9)$$

where

$$\begin{aligned} \phi(u_1, \ldots, u_7, \mathbf{y}) \equiv \int \mathrm{d}\mathbf{x}_1 \left[\sum_{\mathbf{q}} \frac{\hat{E}_{\mathbf{q}}(\mathbf{y})}{N^{1/2}} \exp(-2\pi i \mathbf{q} \cdot \mathbf{x}_1) \right] \\ \times \exp\left\{ \frac{2iu_1}{N^{1/2}} \cos(2\pi \mathbf{h} \cdot \mathbf{x}_1) + \ldots \right. \\ \left. + \frac{2iu_7}{N^{1/2}} \cos[2\pi(\mathbf{k}+\mathbf{l}) \cdot \mathbf{x}_1] \right\}. \end{aligned} \qquad (10)$$

Then

$$\begin{aligned} \phi(u_1, \ldots, u_7, \mathbf{y}) = 1 + \frac{2}{N} \varphi_1(\mathbf{y}) + \frac{2}{N} \varphi_2 + \frac{2}{N(N)^{1/2}} \varphi_3(\mathbf{y}) \\ + \frac{2}{N(N)^{1/2}} \varphi_4(\mathbf{y}) + \frac{2}{N(N)^{1/2}} \varphi_5 + \frac{2u_1 u_2 u_3 u_4}{N^2} \\ + \mathcal{O}'\left(\frac{1}{N^2}\right), \end{aligned} \qquad (11)$$

where

$$\varphi_1(\mathbf{y}) = iu_1\hat{E}_1(\mathbf{y}) + \ldots + iu_7\hat{E}_7(\mathbf{y}), \quad (12)$$

$$\varphi_2 = -\tfrac{1}{2}u_1^2 - \ldots - \tfrac{1}{2}u_7^2, \quad (13)$$

$$\begin{aligned}\varphi_3(\mathbf{y}) = {} & (iu_1)(iu_2)\hat{E}_5(\mathbf{y}) + (iu_1)(iu_3)\hat{E}_6(\mathbf{y}) + (iu_1)(iu_4)\hat{E}_7(\mathbf{y}) \\ & + (iu_1)(iu_5)\hat{E}_2(\mathbf{y}) + (iu_1)(iu_6)\hat{E}_3(\mathbf{y}) + (iu_1)(iu_7)\hat{E}_4(\mathbf{y}) \\ & + (iu_2)(iu_3)\hat{E}_7(\mathbf{y}) + (iu_2)(iu_4)\hat{E}_6(\mathbf{y}) + (iu_2)(iu_5)\hat{E}_1(\mathbf{y}) \\ & + (iu_2)(iu_6)\hat{E}_4(\mathbf{y}) + (iu_2)(iu_7)\hat{E}_3(\mathbf{y}) + (iu_3)(iu_4)\hat{E}_5(\mathbf{y}) \\ & + (iu_3)(iu_5)\hat{E}_4(\mathbf{y}) + (iu_3)(iu_6)\hat{E}_1(\mathbf{y}) + (iu_3)(iu_7)\hat{E}_2(\mathbf{y}) \\ & + (iu_4)(iu_5)\hat{E}_3(\mathbf{y}) + (iu_4)(iu_6)\hat{E}_2(\mathbf{y}) + (iu_4)(iu_7)\hat{E}_1(\mathbf{y}),\end{aligned} \quad (14)$$

$$\begin{aligned}\varphi_4(\mathbf{y}) = {} & \tfrac{1}{2}(iu_1)^2\hat{E}_{2\mathbf{h}}(\mathbf{y}) + \ldots + \tfrac{1}{2}(iu_7)^2\hat{E}_{2\mathbf{k}+2\mathbf{l}}(\mathbf{y}) \\ & + (iu_1)(iu_2)\hat{E}_{\mathbf{h}-\mathbf{k}}(\mathbf{y}) + (iu_1)(iu_3)\hat{E}_{\mathbf{h}-\mathbf{l}}(\mathbf{y}) \\ & + (iu_1)(iu_4)\hat{E}_{2\mathbf{h}+\mathbf{k}+\mathbf{l}}(\mathbf{y}) + (iu_1)(iu_5)\hat{E}_{2\mathbf{h}+\mathbf{k}}(\mathbf{y}) \\ & + (iu_1)(iu_6)\hat{E}_{2\mathbf{h}+\mathbf{l}}(\mathbf{y}) + (iu_1)(iu_7)\hat{E}_{\mathbf{h}-\mathbf{k}-\mathbf{l}}(\mathbf{y}) \\ & + (iu_2)(iu_3)\hat{E}_{\mathbf{k}-\mathbf{l}}(\mathbf{y}) + (iu_2)(iu_4)\hat{E}_{\mathbf{h}+2\mathbf{k}+\mathbf{l}}(\mathbf{y}) \\ & + (iu_2)(iu_5)\hat{E}_{\mathbf{h}+2\mathbf{k}}(\mathbf{y}) + (iu_2)(iu_6)\hat{E}_{\mathbf{h}-\mathbf{k}+\mathbf{l}}(\mathbf{y}) \\ & + (iu_2)(iu_7)\hat{E}_{2\mathbf{k}+\mathbf{l}}(\mathbf{y}) + (iu_3)(iu_4)\hat{E}_{\mathbf{h}+\mathbf{k}+2\mathbf{l}}(\mathbf{y}) \\ & + (iu_3)(iu_5)\hat{E}_{\mathbf{h}+\mathbf{k}-\mathbf{l}}(\mathbf{y}) + (iu_3)(iu_6)\hat{E}_{\mathbf{h}+2\mathbf{l}}(\mathbf{y}) \\ & + (iu_3)(iu_7)\hat{E}_{\mathbf{k}+2\mathbf{l}}(\mathbf{y}) + (iu_4)(iu_5)\hat{E}_{2\mathbf{h}+2\mathbf{k}+\mathbf{l}}(\mathbf{y}) \\ & + (iu_4)(iu_6)\hat{E}_{2\mathbf{h}+\mathbf{k}+2\mathbf{l}}(\mathbf{y}) + (iu_4)(iu_7)\hat{E}_{\mathbf{h}+2\mathbf{k}+2\mathbf{l}}(\mathbf{y}) \\ & + (iu_5)(iu_6)[\hat{E}_{\mathbf{k}-\mathbf{l}}(\mathbf{y}) + \hat{E}_{2\mathbf{h}+\mathbf{k}+\mathbf{l}}(\mathbf{y})] \\ & + (iu_5)(iu_7)[\hat{E}_{\mathbf{h}-\mathbf{l}}(\mathbf{y}) + \hat{E}_{\mathbf{h}+2\mathbf{k}+\mathbf{l}}(\mathbf{y})] \\ & + (iu_6)(iu_7)[\hat{E}_{\mathbf{h}-\mathbf{k}}(\mathbf{y}) + \hat{E}_{\mathbf{h}+\mathbf{k}+2\mathbf{l}}(\mathbf{y})]\end{aligned} \quad (15)$$

and

$$\begin{aligned}\varphi_5 = {} & (iu_1)(iu_2)(iu_5) + (iu_3)(iu_4)(iu_5) + (iu_1)(iu_3)(iu_6) \\ & + (iu_2)(iu_4)(iu_6) + (iu_1)(iu_4)(iu_7) + (iu_2)(iu_3)(iu_7).\end{aligned} \quad (16)$$

$\mathcal{O}'(1/N^2)$ denotes terms of order $1/[N^2(N)^{1/2}]$ or terms of order $1/N^2$ that will not contribute to the calculation of the phase invariant. From now on, all r.v.'s $\hat{E}_\mathbf{q}$ will denote r.v.'s $\hat{E}_\mathbf{q}(\mathbf{y})$ unless the contrary is explicitly stated. Let us now first take a look at equation (9). Suppose the joint density $h(\mathbf{y}_1, \ldots, \mathbf{y}_t)$ depends on the $\mathbf{y}_i$ as a function of the $\hat{E}_{\mathbf{q}_k}$, *i.e.* suppose $h(\mathbf{y}_1, \ldots, \mathbf{y}_t) = \mathcal{F}[\hat{E}_{\mathbf{q}_1}(\mathbf{y}), \hat{E}_{\mathbf{q}_2}(\mathbf{y}), \ldots, \hat{E}_{\mathbf{q}_m}(\mathbf{y})]$. Let then $P_0[(E_\mathbf{q})_\mathbf{q}]$ be the classical j.p.d. of all structure factors, *i.e.*

$$P_0[(E_\mathbf{q})_\mathbf{q}] \equiv \int \mathrm{d}\mathbf{x}_1 \ldots \mathrm{d}\mathbf{x}_t \prod_\mathbf{q} \delta[\hat{E}_\mathbf{q}(\mathbf{x}) - E_\mathbf{q}]. \quad (17)$$

Since $\phi(u_1, \ldots, u_7, \mathbf{y})$ manifestly depends on the $\mathbf{y}_i$ as a function of some $\hat{E}_\mathbf{q}(\mathbf{y})$ we can state (proved in the Appendix)

$$\begin{aligned}\phi(u_1, \ldots, u_7) & = \int \mathrm{d}\mathbf{y}_1 \ldots \mathrm{d}\mathbf{y}_t\, h(\mathbf{y}_1, \ldots, \mathbf{y}_t)\phi(u_1, \ldots, u_7, \mathbf{y})^t \\ & = \int_{-\infty}^{\infty} \prod_\mathbf{q} \mathrm{d}E_\mathbf{q}\, P_0[(E_\mathbf{q})_\mathbf{q}]\mathcal{F}(E_{\mathbf{q}_1}, E_{\mathbf{q}_2}, \ldots, E_{\mathbf{q}_m}) \\ & \quad \times \bar{\phi}(u_1, \ldots, u_7, \mathbf{y})^t,\end{aligned} \quad (18)$$

where in equation (18) $\bar{\phi}(u_1, \ldots, u_7, \mathbf{y})^t$ denotes $\phi(u_1, \ldots, u_7, \mathbf{y})^t$ but where all occurrences of $\hat{E}_\mathbf{q}(\mathbf{y})$ are replaced by $E_\mathbf{q}$. We might take *e.g.* $h(\mathbf{y}_1, \ldots, \mathbf{y}_t) = P_0[\hat{E}_\mathbf{h}(\mathbf{y}), \ldots, \hat{E}_{\mathbf{k}+\mathbf{l}}(\mathbf{y})]$. We will not pursue this idea here further and take instead the much simpler density

$$h(\mathbf{y}_1, \ldots, \mathbf{y}_t) = 1. \quad (19)$$

We shall now use the notation $\phi(u_1, \ldots, u_7, \mathbf{y})^t$ instead of the correct notation $\bar{\phi}(u_1, \ldots, u_7, \mathbf{y})^t$. Then $\phi(u_1, \ldots, u_7)$ becomes

$$\phi(u_1, \ldots, u_7) = \int_{-\infty}^{\infty} \prod_\mathbf{q} \mathrm{d}E_\mathbf{q}\, P_0[(E_\mathbf{q})_\mathbf{q}]\phi(u_1, \ldots, u_7, \mathbf{y})^t. \quad (20)$$

Next we use $\phi(u_1, \ldots, u_7, \mathbf{y})^t = \exp[(N/2)\ln \phi(u_1, \ldots, u_7, \mathbf{y})]$ to develop $\phi(u_1, \ldots, u_7, \mathbf{y})^t$ asymptotically. We get

$$\begin{aligned}\frac{N}{2} & \ln \phi(u_1, \ldots, u_7, \mathbf{y}) \\ & = \varphi_1(\mathbf{y}) + \varphi_2 + \frac{1}{N^{1/2}}[\varphi_3(\mathbf{y}) + \varphi_4(\mathbf{y}) + \varphi_5] \\ & \quad + \frac{u_1u_2u_3u_4}{N} - \frac{1}{N}[\varphi_1(\mathbf{y}) + \varphi_2]^2 + \mathcal{O}'\left(\frac{1}{N}\right).\end{aligned} \quad (21)$$

Then

$$\begin{aligned}\phi(& u_1, \ldots, u_7, \mathbf{y})^t \\ & = \exp[(N/2)\ln \phi(u_1, \ldots, u_7, \mathbf{y})] \\ & = \exp[\varphi_1(\mathbf{y}) + \varphi_2]\Big\{1 + \frac{1}{N^{1/2}}[\varphi_3(\mathbf{y}) + \varphi_4(\mathbf{y}) + \varphi_5] \\ & \quad + \frac{u_1u_2u_3u_4}{N} + \frac{1}{2N}[\varphi_3(\mathbf{y}) + \varphi_4(\mathbf{y}) + \varphi_5]^2 \\ & \quad - \frac{1}{N}[\varphi_1(\mathbf{y}) + \varphi_2]^2 + \mathcal{O}'\left(\frac{1}{N}\right)\Big\} \quad (22) \\ & = \exp(\varphi_2)\Big\{\left(1 + \frac{1}{N^{1/2}}\varphi_5 + \frac{1}{2N}\varphi_5^2 - \frac{1}{N}\varphi_2^2 + \frac{u_1u_2u_3u_4}{N}\right) \\ & \quad \times \exp[\varphi_1(\mathbf{y})] + \frac{1}{N^{1/2}}\varphi_3(\mathbf{y})\exp[\varphi_1(\mathbf{y})] \\ & \quad + \frac{1}{N^{1/2}}\varphi_4(\mathbf{y})\exp[\varphi_1(\mathbf{y})] + \frac{1}{2N}\exp[\varphi_1(\mathbf{y})][\varphi_3(\mathbf{y})^2 \\ & \qquad + \varphi_4(\mathbf{y})^2 + 2\varphi_3(\mathbf{y})\varphi_4(\mathbf{y}) + 2\varphi_3(\mathbf{y})\varphi_5 + 2\varphi_4(\mathbf{y})\varphi_5] \\ & \quad - \frac{1}{N}\exp[\varphi_1(\mathbf{y})][\varphi_1(\mathbf{y})^2 + 2\varphi_1(\mathbf{y})\varphi_2] + \mathcal{O}'\left(\frac{1}{N}\right)\Big\}\end{aligned}$$

$$= \exp(\varphi_2)\left\{\left(1+\frac{1}{N^{1/2}}\varphi_5+\frac{1}{2N}\varphi_5^2-\frac{1}{N}\varphi_2^2+\frac{u_1u_2u_3u_4}{N}\right)\right.$$

$$\times \exp[\varphi_1(\mathbf{y})]+\frac{1}{N^{1/2}}\left(1+\frac{1}{N^{1/2}}\varphi_5\right)\varphi_3(\mathbf{y})\exp[\varphi_1(\mathbf{y})]$$

$$+\frac{1}{2N}\exp[\varphi_1(\mathbf{y})]\varphi_3(\mathbf{y})^2$$

$$+\frac{1}{N^{1/2}}\left(1+\frac{1}{N^{1/2}}\varphi_5\right)\varphi_4(\mathbf{y})\exp[\varphi_1(\mathbf{y})]$$

$$+\frac{1}{2N}\exp[\varphi_1(\mathbf{y})]\varphi_4(\mathbf{y})^2 \tag{23}$$

$$+\frac{1}{N}\exp[\varphi_1(\mathbf{y})]\varphi_3(\mathbf{y})\varphi_4(\mathbf{y})-\frac{1}{N}\exp[\varphi_1(\mathbf{y})]\varphi_1(\mathbf{y})^2$$

$$-\frac{2}{N}\exp[\varphi_1(\mathbf{y})]\varphi_1(\mathbf{y})\varphi_2 \tag{24}$$

$$\left.+\mathcal{O}'\left(\frac{1}{N}\right)\right\}. \tag{25}$$

Next we define $\bar{\varphi}_i$ as $\varphi_i(\mathbf{y})$ with every occurrence of $\hat{E}_{\mathbf{q}}(\mathbf{y})$ replaced by $E_{\mathbf{q}}$.

In the following, we examine different terms in the previous equations in turn.

(1) The term

$$\int \mathrm{d}\mathbf{y}_1\ldots\mathrm{d}\mathbf{y}_t\left(1+\frac{1}{N^{1/2}}\varphi_5+\frac{1}{2N}\varphi_5^2-\frac{1}{N}\varphi_2^2+\frac{u_1u_2u_3u_4}{N}\right)\times\exp[\varphi_1(\mathbf{y})].$$

We have

$$\begin{aligned}\textstyle\int \mathrm{d}\mathbf{y}_1\ldots\mathrm{d}\mathbf{y}_t\exp[\varphi_1(\mathbf{y})] &= \textstyle\int \mathrm{d}E_1\ldots\mathrm{d}E_7\,P_0(E_1,\ldots,E_7)\\ &\quad\times\exp(iu_1E_1+\ldots+iu_7E_7)\\ &=\phi_0(u_1,\ldots u_7),\end{aligned} \tag{26}$$

where

$$\phi_0(u_1,\ldots u_7) = \exp(\varphi_2)\left[1+\frac{1}{N^{1/2}}\varphi_5+\frac{u_1u_2u_3u_4}{N}+\frac{1}{2N}\varphi_5^2+\mathcal{O}'\left(\frac{1}{N}\right)\right]. \tag{27}$$

(2) The term

$$\int \mathrm{d}\mathbf{y}_1\ldots\mathrm{d}\mathbf{y}_t\,\frac{1}{N^{1/2}}\left(1+\frac{1}{N^{1/2}}\varphi_5\right)\varphi_3(\mathbf{y})\exp[\varphi_1(\mathbf{y})].$$

Consider a term from $\varphi_3(\mathbf{y})$, say $(iu_1)(iu_2)\hat{E}_5(\mathbf{y})$. Then

$$\begin{aligned}&\int \mathrm{d}\mathbf{y}_1\ldots\mathrm{d}\mathbf{y}_t\,\frac{1}{N^{1/2}}(iu_1)(iu_2)\hat{E}_5(\mathbf{y})\exp[\varphi_1(\mathbf{y})]\\
&=\int \mathrm{d}E_1\ldots\mathrm{d}E_7\,P_0(E_1,\ldots,E_7)\frac{1}{N^{1/2}}(iu_1)(iu_2)E_5\\
&\quad\times\exp(iu_1E_1+\ldots+iu_7E_7)\\
&=\int \mathrm{d}E_1\ldots\mathrm{d}E_7\left(\frac{1}{2\pi}\right)^{7/2}\exp(-\tfrac{1}{2}E_1^2-\ldots-\tfrac{1}{2}E_7^2)\\
&\quad\times\exp(iu_1E_1+\ldots iu_7E_7)\left[1+\frac{E_1E_2E_5}{N^{1/2}}+\frac{E_3E_4E_5}{N^{1/2}}\right.\\
&\quad\left.+\frac{E_1E_3E_6}{N^{1/2}}+\frac{E_2E_4E_6}{N^{1/2}}+\frac{E_1E_4E_7}{N^{1/2}}+\frac{E_2E_3E_7}{N^{1/2}}+O\left(\frac{1}{N}\right)\right]\\
&\quad\times\frac{1}{N^{1/2}}(iu_1)(iu_2)E_5\\
&=\exp(-\tfrac{1}{2}u_1^2-\ldots-\tfrac{1}{2}u_7^2)\left\{\frac{(iu_1)(iu_2)(iu_5)}{N^{1/2}}\right.\\
&\quad\left.+\frac{(iu_1)(iu_2)(iu_3)(iu_4)}{N}[(iu_5)^2+1]+\mathcal{O}'\left(\frac{1}{N}\right)\right\},\end{aligned} \tag{28}$$

where $\mathcal{O}'(1/N)$ means terms of order $1/[N(N)^{1/2}]$ or terms of order $1/N$ that do not contribute to the phase of the quartet. On the other hand, the term $(iu_1)(iu_5)\hat{E}_2(\mathbf{y})$ contributes

$$\begin{aligned}&\int \mathrm{d}\mathbf{y}_1\ldots\mathrm{d}\mathbf{y}_t\frac{1}{N^{1/2}}(iu_1)(iu_5)\hat{E}_2(\mathbf{y})\exp[\varphi_1(\mathbf{y})]\\
&=\int \mathrm{d}E_1\ldots\mathrm{d}E_7\,P_0(E_1,\ldots,E_7)\frac{1}{N^{1/2}}(iu_1)(iu_5)E_2\\
&\quad\times\exp(iu_1E_1+\ldots+iu_7E_7)\\
&=\int \mathrm{d}E_1\ldots\mathrm{d}E_7\left(\frac{1}{2\pi}\right)^{7/2}\exp(-\tfrac{1}{2}E_1^2-\ldots-\tfrac{1}{2}E_7^2)\\
&\quad\times\exp(iu_1E_1+\ldots+iu_7E_7)\left[1+\frac{E_1E_2E_5}{N^{1/2}}+\frac{E_3E_4E_5}{N^{1/2}}\right.\\
&\quad\left.+\frac{E_1E_3E_6}{N^{1/2}}+\frac{E_2E_4E_6}{N^{1/2}}+\frac{E_1E_4E_7}{N^{1/2}}+\frac{E_2E_3E_7}{N^{1/2}}+O\left(\frac{1}{N}\right)\right]\\
&\quad\times\frac{1}{N^{1/2}}(iu_1)(iu_5)E_2\\
&=\exp(-\tfrac{1}{2}u_1^2-\ldots-\tfrac{1}{2}u_7^2)\left[\frac{(iu_1)(iu_2)(iu_5)}{N^{1/2}}\right.\\
&\quad\left.+\frac{(iu_1)(iu_2)(iu_3)(iu_4)}{N}(iu_5)^2+\mathcal{O}'\left(\frac{1}{N}\right)\right].\end{aligned} \tag{29}$$

Also

$$\begin{aligned}&\int \mathrm{d}\mathbf{y}_1\ldots\mathrm{d}\mathbf{y}_t\,\frac{1}{N^{1/2}}(iu_2)(iu_5)\hat{E}_1(\mathbf{y})\exp[\varphi_1(\mathbf{y})]\\
&=\exp(-\tfrac{1}{2}u_1^2-\ldots-\tfrac{1}{2}u_7^2)\\
&\quad\times\left[\frac{(iu_1)(iu_2)(iu_5)}{N^{1/2}}+\frac{(iu_1)(iu_2)(iu_3)(iu_4)}{N}(iu_5)^2+\mathcal{O}'\left(\frac{1}{N}\right)\right].\end{aligned} \tag{30}$$

Hence

$$\int \mathrm{d}\mathbf{y}_1 \ldots \frac{1}{N^{1/2}}\varphi_3(\mathbf{y}) \exp[\varphi_1(\mathbf{y})]$$
$$\longrightarrow \exp(-\tfrac{1}{2}u_1^2 - \ldots - \tfrac{1}{2}u_7^2)\frac{1}{N^{1/2}}\Big\{3(iu_1)(iu_2)(iu_5) + 3(iu_1)(iu_3)(iu_6) + 3(iu_1)(iu_4)(iu_7) + 3(iu_2)(iu_3)(iu_7) + 3(iu_2)(iu_4)(iu_6) + 3(iu_3)(iu_4)(iu_5) + 6\frac{(iu_1)(iu_2)(iu_3)(iu_4)}{N^{1/2}}[(iu_5)^2 + (iu_6)^2 + (iu_7)^2] + 6\frac{(iu_1)(iu_2)(iu_3)(iu_4)}{N^{1/2}}\Big\} + \mathcal{O}'\left(\frac{1}{N}\right)$$
$$\longrightarrow \exp(-\tfrac{1}{2}u_1^2 - \ldots - \tfrac{1}{2}u_7^2) \times \frac{1}{N^{1/2}}\Big\{3\varphi_5 + 6\frac{(iu_1)(iu_2)(iu_3)(iu_4)}{N^{1/2}} \times [(iu_5)^2 + (iu_6)^2 + (iu_7)^2] + 6\frac{(iu_1)(iu_2)(iu_3)(iu_4)}{N^{1/2}}\Big\} + \mathcal{O}'\left(\frac{1}{N}\right). \quad (31)$$

(3) The term

$$\textstyle\int \mathrm{d}\mathbf{y}_1 \ldots \mathrm{d}\mathbf{y}_t\, (1/2N)\varphi_3(\mathbf{y})^2 \exp[\varphi_1(\mathbf{y})].$$

We have

$$\int \mathrm{d}\mathbf{y}_1 \ldots \mathrm{d}\mathbf{y}_t\, \frac{1}{2N}\varphi_3(\mathbf{y})^2 \exp[\varphi_1(\mathbf{y})] = \frac{1}{2N}\int \mathrm{d}E_1 \ldots \mathrm{d}E_7\, P_0(E_1, \ldots, E_7)\bar{\varphi}_3^2 \times \exp(iu_1E_1 + \ldots + iu_7E_7)$$
$$= \frac{1}{2N}\int \mathrm{d}E_1 \ldots \mathrm{d}E_7\left[\frac{1}{(2\pi)^{1/2}}\right]^7 \exp(-\tfrac{1}{2}E_1^2 - \ldots - \tfrac{1}{2}E_7^2) \times \exp(iu_1E_1 + \ldots + iu_7E_7)\bar{\varphi}_3^2 + \mathcal{O}'\left(\frac{1}{N}\right). \quad (32)$$

We must see how we can get terms proportional to $u_1u_2u_3u_4$. For instance, consider the term $(iu_1)(iu_2)E_5$, which we represent by (125), from $\bar{\varphi}_3$. We can pair this term with the terms $(iu_3)(iu_4)E_5$ which we represent by (345). Then

$$\left[\frac{1}{(2\pi)^{1/2}}\right]^7 \frac{1}{2N}\int \mathrm{d}E_1 \ldots \mathrm{d}E_7\, \exp(-\tfrac{1}{2}E_1^2 - \ldots - \tfrac{1}{2}E_7^2) \times \exp(iu_1E_1 + \ldots + iu_7E_7)(iu_1)(iu_2)E_5(iu_3)(iu_4)E_5$$
$$= \frac{1}{2N}\exp(-\tfrac{1}{2}u_1^2 - \ldots - \tfrac{1}{2}u_7^2)(iu_1)(iu_2)(iu_3)(iu_4) \times [(iu_5)^2 + 1]. \quad (33)$$

On the other hand, the pairing of $(iu_1)(iu_2)E_5$ with $(iu_4)(iu_5)E_3$ gives

$$\left[\frac{1}{(2\pi)^{1/2}}\right]^7 \frac{1}{2N}\int \mathrm{d}E_1 \ldots \mathrm{d}E_7\, \exp(-\tfrac{1}{2}E_1^2 - \ldots - \tfrac{1}{2}E_7^2) \times \exp(iu_1E_1 + \ldots + iu_7E_7)(iu_1)(iu_2)E_5(iu_4)(iu_5)E_3$$
$$= \frac{1}{2N}\exp(-\tfrac{1}{2}u_1^2 - \ldots - \tfrac{1}{2}u_7^2)(iu_1)(iu_2)(iu_3)(iu_4)(iu_5)^2. \quad (34)$$

We also get the above contribution [equation (34)] for the pairings of (125) with (534), (251) with (345) or (453) or (534), and (512) with (345) or (453) or (534).

The sum of these nine pairings gives (a multiplication factor of 2 must be taken into account)

$$(1/2N)\exp(-\tfrac{1}{2}u_1^2 - \ldots - \tfrac{1}{2}u_7^2)2(iu_1)(iu_2)(iu_3)(iu_4)[9(iu_5)^2 + 1]. \quad (35)$$

We can repeat the same process for the terms (136) and (137). We then get

$$\frac{1}{2N}\int \mathrm{d}E_1 \ldots \mathrm{d}E_7\, P_0(E_1, \ldots, E_7)\bar{\varphi}_3^2 \exp(iu_1E_1 + \ldots + iu_7E_7) = \frac{1}{N}\exp(-\tfrac{1}{2}u_1^2 - \ldots - \tfrac{1}{2}u_7^2)(iu_1)(iu_2)(iu_3)(iu_4) \times \{9[(iu_5)^2 + (iu_6)^2 + (iu_7)^2] + 3\} + \mathcal{O}'\left(\frac{1}{N}\right). \quad (36)$$

(4) The term

$$\int \mathrm{d}\mathbf{y}_1 \ldots \mathrm{d}\mathbf{y}_t \frac{1}{N^{1/2}}\left(1 + \frac{1}{N^{1/2}}\varphi_5\right)\varphi_4(\mathbf{y}) \exp[\varphi_1(\mathbf{y})].$$

Consider a term from $\varphi_4(\mathbf{y})$, say $(iu_1)(iu_2)\hat{E}_{\mathbf{h}-\mathbf{k}}(\mathbf{y})$. Then

$$\int \mathrm{d}\mathbf{y}_1 \ldots \mathrm{d}\mathbf{y}_t\, \frac{1}{N^{1/2}}(iu_1)(iu_2)\hat{E}_{\mathbf{h}-\mathbf{k}}(\mathbf{y}) \exp[\varphi_1(\mathbf{y})] = \int \mathrm{d}E_1 \ldots \mathrm{d}E_7\, \mathrm{d}E_{\mathbf{h}-\mathbf{k}}\, P_0(E_1, \ldots, E_7, E_{\mathbf{h}-\mathbf{k}}) \times \frac{1}{N^{1/2}}(iu_1)(iu_2)E_{\mathbf{h}-\mathbf{k}} \exp(iu_1E_1 + \ldots + iu_7E_7)$$
$$= \int \mathrm{d}E_1 \ldots \mathrm{d}E_7\left(\frac{1}{2\pi}\right)^{7/2} \exp(-\tfrac{1}{2}E_1^2 - \ldots - \tfrac{1}{2}E_7^2) \times \exp(iu_1E_1 + \ldots + iu_7E_7)\left(1 + \frac{E_1E_2E_{\mathbf{h}-\mathbf{k}}}{N^{1/2}} + \ldots\right) \times \frac{1}{N^{1/2}}(iu_1)(iu_2)E_{\mathbf{h}-\mathbf{k}}$$
$$= \exp(-\tfrac{1}{2}u_1^2 - \ldots - \tfrac{1}{2}u_7^2)\frac{1}{N}(iu_1)^2(iu_2)^2 + \mathcal{O}'\left(\frac{1}{N}\right). \quad (37)$$

So this term does not contribute to the the quartet term $(iu_1)(iu_2)(iu_3)(iu_4)$. The same holds true for the terms $\frac{1}{2}(iu_1)^2\hat{E}_{2\mathbf{h}}(\mathbf{y})$ and $(iu_5)(iu_6)\hat{E}_{\mathbf{k}-\mathbf{l}}(\mathbf{y})$ from $\varphi_4(\mathbf{y})$. Hence $\int \mathrm{d}\mathbf{y}_1 \ldots \mathrm{d}\mathbf{y}_t\, (1/N^{1/2})\varphi_4(\mathbf{y}) \exp[\varphi_1(\mathbf{y})]$ does not contribute to the phase of the quartet.

(5) Other terms of equations (23) and (24). Upon inspection, these terms are either of order $1/[N(N)^{1/2}]$ or of order

$1/N$ containing no contribution to the quartet term $(iu_1)(iu_2)(iu_3)(iu_4)$.

(6) $\phi(u_1, \ldots, u_7)$. Collecting the terms from the preceding section we obtain

$$\begin{aligned}\phi(u_1, \ldots, u_7) &= \exp(-u_1^2 - \ldots - u_7^2) \\ &\times \Bigg(\left(1 + \frac{1}{N^{1/2}}\varphi_5 + \frac{1}{2N}\varphi_5^2 - \frac{1}{N}\varphi_2^2 + \frac{u_1u_2u_3u_4}{N}\right) \\ &\times \left[1 + \frac{1}{N^{1/2}}\varphi_5 + \frac{u_1u_2u_3u_4}{N} + \frac{1}{2N}\varphi_5^2 + \mathcal{O}'\left(\frac{1}{N}\right)\right] \\ &+ \left(1 + \frac{1}{N^{1/2}}\varphi_5\right)\frac{1}{N^{1/2}}\left\{3\varphi_5 + 6\frac{(iu_1)(iu_2)(iu_3)(iu_4)}{N^{1/2}}\right. \\ &\times \left.[(iu_5)^2 + (iu_6)^2 + (iu_7)^2] + 6\frac{(iu_1)(iu_2)(iu_3)(iu_4)}{N^{1/2}}\right\} \\ &+ \frac{1}{N}(iu_1)(iu_2)(iu_3)(iu_4)\{9[(iu_5)^2 + (iu_6)^2 + (iu_7)^2] + 3\} \\ &+ \mathcal{O}'\left(\frac{1}{N}\right)\Bigg) \qquad (38)\end{aligned}$$

$$\begin{aligned}&= \exp(-u_1^2 - \ldots - u_7^2)\Bigg(1 + \frac{1}{N^{1/2}}(1+3+1)\varphi_5 \\ &+ \frac{3+1+1}{N}\varphi_5^2 + \frac{1}{N}(iu_1)(iu_2)(iu_3)(iu_4) \\ &\times \Big\{\underbrace{(9+6)}_{15}[(iu_5)^2 + (iu_6)^2 + (iu_7)^2] + \underbrace{3+1+1+6}_{11}\Big\} \\ &+ \mathcal{O}'\left(\frac{1}{N}\right)\Bigg) \qquad (39)\end{aligned}$$

$$\begin{aligned}&= \exp(-u_1^2 - \ldots - u_7^2)\Bigg(1 + \frac{5}{N^{1/2}}\varphi_5 + \frac{5}{N}\varphi_5^2 \\ &+ \frac{1}{N}(iu_1)(iu_2)(iu_3)(iu_4)\{15[(iu_5)^2 + (iu_6)^2 + (iu_7)^2] + 11\} \\ &+ \mathcal{O}'\left(\frac{1}{N}\right)\Bigg) \qquad (40)\end{aligned}$$

$$\begin{aligned}&= \exp(-u_1^2 - \ldots - u_7^2)\Bigg(1 + \frac{5}{N^{1/2}}[(iu_1)(iu_2)(iu_5) \\ &+ (iu_3)(iu_4)(iu_5) + (iu_1)(iu_3)(iu_6) + (iu_2)(iu_4)(iu_6) \\ &+ (iu_1)(iu_4)(iu_7) + (iu_2)(iu_3)(iu_7)] \\ &+ \frac{1}{N}(iu_1)(iu_2)(iu_3)(iu_4)\Big\{\underbrace{(15+10)}_{25}[(iu_5)^2 + (iu_6)^2 \\ &+ (iu_7)^2] + 11\Big\} + \mathcal{O}'\left(\frac{1}{N}\right)\Bigg). \qquad (41)\end{aligned}$$

(7) The term $P(E_1, \ldots, E_7)$. We recall that

$$\begin{aligned}P(E_1, \ldots, E_7) &= (1/2\pi)^7 \int_{-\infty}^{\infty} \mathrm{d}u_1 \ldots \mathrm{d}u_7 \exp(-iu_1E_1 - \ldots - iu_7E_7) \\ &\times \phi(u_1, \ldots, u_7). \qquad (42)\end{aligned}$$

We now apply the transformation $u_i \longrightarrow u_i/2^{1/2}$. Then

$$\begin{aligned}P(E_1, \ldots, E_7) &= \left(\frac{1}{2\pi}\right)^7\left(\frac{1}{2^{1/2}}\right)^7 \int_{-\infty}^{\infty} \mathrm{d}u_1 \ldots \mathrm{d}u_7 \exp[-iu_1(E_1/2^{1/2}) - \ldots \\ &- iu_7(E_7/2^{1/2})]\phi\left(\frac{u_1}{2^{1/2}}, \ldots, \frac{u_7}{2^{1/2}}\right). \qquad (43)\end{aligned}$$

Using the formulas from the Appendix we can write

$$\begin{aligned}P(E_1, \ldots, E_7) &\propto \exp(-\tfrac{1}{4}E_1^2 - \ldots - \tfrac{1}{4}E_7^2)\Big\{1 + \frac{5}{8N^{1/2}}(E_1E_2E_5 + E_3E_4E_5 \\ &+ E_1E_3E_6 + E_2E_4E_6 + E_1E_4E_7 + E_2E_3E_7) \\ &+ \frac{1}{16N}E_1E_2E_3E_4\left[\frac{25}{2}\left(\frac{E_5^2}{4} + \frac{E_6^2}{4} + \frac{E_7^2}{4} - 3\right) + 11\right] \\ &+ \mathcal{O}'\left(\frac{1}{N}\right)\Big\}. \qquad (44)\end{aligned}$$

This gives to order $1/[N(N)^{1/2}]$ the following formula for the probability P_+ of the quartet being positive given the absolute values $|E_1|, \ldots, |E_7|$:

$$P_+ = \tfrac{1}{2} + \tfrac{1}{2}\tanh\left\{\frac{1}{16N}|E_1E_2E_3E_4| \times \left[\frac{25}{2}\left(\frac{E_5^2}{4} + \frac{E_6^2}{4} + \frac{E_7^2}{4} - 3\right) + 11\right]\right\}. \qquad (45)$$

We then get for $|E_5| = |E_6| = |E_7| = 1$

$$\begin{aligned}P_+ &= \tfrac{1}{2} + \tfrac{1}{2}\tanh\left\{\frac{1}{16N}|E_1E_2E_3E_4|\left[\frac{25}{2} \times \left(-\frac{9}{4}\right) + 11\right]\right\} \\ &\approx \tfrac{1}{2} - \tfrac{1}{2}\tanh\left(\frac{|E_1E_2E_3E_4|}{N}\right). \qquad (46)\end{aligned}$$

The classical formula would give instead

$$P_{+,\mathrm{classical}} = \tfrac{1}{2} + \tfrac{1}{2}\tanh\left(\frac{|E_1E_2E_3E_4|}{N}\right). \qquad (47)$$

4. Conclusion

Based on an acceptable nonuniform density $f(\mathbf{x}_1, \ldots, \mathbf{x}_t) \neq 1$ of the atomic random vector variables, we are able to derive a modified probability formula for the quartet invariant given its second neighborhood. Our formula is

$$P_+ = \tfrac{1}{2} + \tfrac{1}{2}\tanh\left\{\frac{1}{16N}|E_1E_2E_3E_4| \times \left[\frac{25}{2}\left(\frac{E_5^2}{4} + \frac{E_6^2}{4} + \frac{E_7^2}{4} - 3\right) + 11\right]\right\}. \qquad (48)$$

The overall tendency is the same as for the classical formula,

$$P_{+,\mathrm{classical}} = \tfrac{1}{2} + \tfrac{1}{2}\tanh\left[\frac{1}{N}|E_1E_2E_3E_4|(E_5^2 + E_6^2 + E_7^2 - 2)\right]. \qquad (49)$$

The difference is noticeable. For instance, equation (49) cannot predict negative signs for the quartet if $|E_5| = |E_6| = |E_7| = 1$!

The calculation for higher neighborhoods quickly becomes very laborious. An interesting idea would be to calculate such formulas with a computer; see Peschar & Schenk (1987).

APPENDIX *A*

$$\int_{-\infty}^{\infty} (iu)^n \exp(-iuE)\exp(-\tfrac{1}{2}u^2)\,\mathrm{d}u = (2\pi)^{1/2}\exp(-\tfrac{1}{2}E^2)H_n(E). \tag{50}$$

$$H_0(E) = 1. \tag{51}$$

$$H_1(E) = E. \tag{52}$$

$$H_2(E) = E^2 - 1. \tag{53}$$

$$H_3(E) = E^3 - 3E. \tag{54}$$

$$H_4(E) = E^4 - 6E^2 + 3. \tag{55}$$

$$H_5(E) = E^5 - 10E^3 + 15E. \tag{56}$$

$$\int_{-\infty}^{\infty} E\exp(iuE)\exp(-\tfrac{1}{2}E^2)\,\mathrm{d}E = (2\pi)^{1/2}(iu)\exp(-\tfrac{1}{2}u^2). \tag{57}$$

$$\int_{-\infty}^{\infty} E^2\exp(iuE)\exp(-\tfrac{1}{2}E^2)\,\mathrm{d}E = (2\pi)^{1/2}[(iu)^2 + 1]\exp(-\tfrac{1}{2}u^2). \tag{58}$$

$$\int_{-\infty}^{\infty} E^3\exp(iuE)\exp(-\tfrac{1}{2}E^2)\,\mathrm{d}E = (2\pi)^{1/2}[(iu)^3 + 3(iu)]\exp(-\tfrac{1}{2}u^2). \tag{59}$$

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

$$\begin{aligned}\int\varphi[u;\hat{E}_{\mathbf{h}}(\mathbf{y})]\,\mathrm{d}\mathbf{y} &= \int\mathrm{d}\mathbf{y}\int\varphi(u;E_{\mathbf{h}})\delta[E_{\mathbf{h}} - \hat{E}_{\mathbf{h}}(\mathbf{y})]\,\mathrm{d}E_{\mathbf{h}}\\ &= \int\varphi(u;E_{\mathbf{h}})\,\mathrm{d}E_{\mathbf{h}}\underbrace{\int\mathrm{d}\mathbf{y}\,\delta[E_{\mathbf{h}} - \hat{E}_{\mathbf{h}}(\mathbf{y})]}_{P_0(E_{\mathbf{h}})}\\ &= \int\varphi(u;E_{\mathbf{h}})P_0(E_{\mathbf{h}})\,\mathrm{d}E_{\mathbf{h}}.\end{aligned} \tag{60}$$

References

Altomare, A., Cascarano, G. & Giacovazzo, C. (1992*a*). *Acta Cryst.* A**48**, 30–36.
Altomare, A., Cascarano, G. & Giacovazzo, C. (1992*b*). *Acta Cryst.* A**48**, 495–500.
Altomare, A., Giacovazzo, C. & Moliterni, A. G. G. (1994). *Acta Cryst.* A**50**, 585–588.
Brosius, J. (1978). *Acta Cryst.* A**34**, 955–959.
Brosius, J. (1979). PhD thesis, Katholieke Universiteit van Leuven, Belgium.
Brosius, J. (1985). *Acta Cryst.* A**41**, 613–617.
Brosius, J. (1989). *Acta Cryst.* A**45**, 463–468.
Brosius, J. (2008). *Acta Cryst.* A**64**, 571–586.
Giacovazzo, C. (1977). *Acta Cryst.* A**33**, 50–54.
Giacovazzo, C. (1991). *Acta Cryst.* A**47**, 256–263.
Hauptman, H. (1965). *Z. Kristallogr.* **121**, 1–8.
Heinerman, J. J. L., Krabbendam, H. & Kroon, J. (1977). *Acta Cryst.* A**33**, 873–878.
Karle, J. & Hauptman, H. (1958). *Acta Cryst.* **11**, 264–269.
Klug, A. (1958). *Acta Cryst.* **11**, 515–543.
Peschar, R. & Schenk, H. (1987). *Acta Cryst.* A**43**, 513–522.
Putten, N. van der & Schenk, H. (1977). *Acta Cryst.* A**33**, 856–858.