

Derivation of the Joint Probability Distribution of Structure-Factor Components Without Assuming Independent Atoms: Relation to the Sparse-Density Principle

P. VERWER,*‡ H. KRABBENDAM† AND J. KROON

Laboratory of Crystal and Structural Chemistry, Bijvoet Centre for Biomolecular Research, University of Utrecht, Padualaan 8, 3584 CH Utrecht, The Netherlands. E-mail: p.verwer@organon.akzonobel.nl

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Abstract

In this paper, a number of equations based on the sparse-density principle [Verwer, Krabbendam & Kroon (1991). *Acta Cryst.* A47, 143–144] are given. The corresponding joint probability distributions (j.p.d.'s) are derived, both with the assumption of independent atoms and without. It is concluded that the sparse-density principle is equivalent to the assumption of independent atoms, which leads to the neglect of n -atom interactions for which $\mathbf{r}_1 \pm \mathbf{r}_2 \pm \dots \pm \mathbf{r}_n \equiv \mathbf{0} \pmod{\mathbf{1}}$, which would influence the n th-order moments that appear in the j.p.d.

1. Introduction

The sparse-density principle states that, as the atomic electron-density function is concentrated around a limited number of discrete points (the atomic positions), a relatively large volume of the unit cell has small or zero density. This property of the electron-density function can be recast into a mathematical form by noting that, as a consequence of this property, the chance is small that the electron-density function and the electron-density function inverted through an arbitrarily chosen origin will exhibit a large degree of overlap. This means that $\rho(\mathbf{r})\rho(-\mathbf{r}) \simeq 0$, *i.e.* is likely to be zero. An obvious exception is the case that the chosen origin coincides with an inversion centre in a centrosymmetric structure. This assumption about the shape of the electron-density function, together with the assumption of non-overlap of atoms, leads to the sparse-density equations, which are convolution equations between the structure-factor components. These sparse-density equations are closely related to the less-restrictive Sayre equation (Sayre, 1952). The algebraic derivation of the sparse-density equations was given by Fan (1965). Further investigations were instigated by Verwer, Krabbendam & Kroon (1991), who employed one of the equations to find a solution for the phase ambiguity in the method of single-wavelength anomalous diffraction. The algebraic derivation of one of the sparse-density equations is given

in equation (5) of their paper:

$$A_{\mathbf{h}} = -2[f(\mathbf{h})/{}_2f(\mathbf{h})V] \sum_{\mathbf{k}} B_{\mathbf{k}} B_{\mathbf{h}-\mathbf{k}}, \quad (1)$$

which is based on the relation

$$\begin{aligned} \sum_{\mathbf{k}} B_{\mathbf{k}} B_{\mathbf{h}-\mathbf{k}} &= -V^2 \mathcal{F}_{\mathbf{h}} \{ ([\rho(\mathbf{r}) - \rho(-\mathbf{r})]/2)^2 \} \\ &= -\frac{1}{2} [{}_2f(\mathbf{h})V/f(\mathbf{h})] A_{\mathbf{h}} \\ &\quad + V^2 \mathcal{F}_{\mathbf{h}} \{ \rho(\mathbf{r})\rho(-\mathbf{r})/2 \}. \end{aligned} \quad (2)$$

In (1) and (2), A and B are the components of the structure factors, ρ is the electron density, V is the cell volume and \mathcal{F} denotes the Fourier transformation. The symbols f and ${}_2f$ refer to the scattering factors of the normal and squared atomic electron densities, respectively. The validity of (1) was shown by Verwer, Krabbendam & Kroon (1991) by application to data of four small-molecule crystal structures. A paper demonstrating the strength of the sparse-density equations at different resolution levels and the application to single-wavelength anomalous scattering is in preparation.

The last term in (2) depends on the overlap between the structure and its inverse and may be considered negligible according to the sparse-density principle, reducing (2) to (1). If part of the structure, however, exhibits exact centrosymmetry and the sparse-density principle applies to the rest of the structure, this last term can be written

$$\begin{aligned} V^2 \mathcal{F}_{\mathbf{h}} \{ \rho(\mathbf{r})\rho(-\mathbf{r})/2 \} &= (V^2/2) \mathcal{F}_{\mathbf{h}} \{ [\rho'(\mathbf{r})]^2 \} \\ &= \frac{1}{2} \sum_{\mathbf{k}} A'_{\mathbf{k}} A'_{\mathbf{h}-\mathbf{k}} \\ &= \frac{1}{2} [{}_2f(\mathbf{h})V/f(\mathbf{h})] A'_{\mathbf{h}}, \end{aligned} \quad (3)$$

where the quantities that only depend on the centric part of the structure have been written ρ' and A' . Thus, (1) can be written

$$A_{\mathbf{h}} - A'_{\mathbf{h}} = -2[f(\mathbf{h})/{}_2f(\mathbf{h})V] \sum_{\mathbf{k}} B_{\mathbf{k}} B_{\mathbf{h}-\mathbf{k}}. \quad (4)$$

Along the same lines, it can be derived that

$$A_{\mathbf{h}} + A'_{\mathbf{h}} = 2[f(\mathbf{h})/{}_2f(\mathbf{h})V] \sum_{\mathbf{k}} A_{\mathbf{k}} A_{\mathbf{h}-\mathbf{k}}. \quad (5)$$

‡ Present address: NV Organon, PO Box 20, 5340 BH Oss, The Netherlands.

† Deceased 4 November 1995.

It can also be shown that, for point atoms, *i.e.* using quasi-normalized structure factors, the sparse-density principle is exactly valid (the electron-density function does not occupy any space at all), apart from the possible presence of partial exact centrosymmetry. If then the contribution of the centrosymmetric substructure to the structure factor is taken into account, the following equations result:

$$\langle B_{\mathbf{k}} B_{\mathbf{h}-\mathbf{k}} \rangle_{\mathbf{k}} = -\frac{1}{2} N^{-1/2} (A_{\mathbf{h}} - A'_{\mathbf{h}}) \quad (6)$$

$$\langle A_{\mathbf{k}} A_{\mathbf{h}-\mathbf{k}} \rangle_{\mathbf{k}} = \frac{1}{2} N^{-1/2} (A_{\mathbf{h}} + A'_{\mathbf{h}}). \quad (7)$$

In (6) and (7), A and B are the components of the normalized structure factors and $A'_{\mathbf{h}}$ refers to the normalized structure factor of the centrosymmetric part of the structure (*i.e.* centrosymmetric relative to the chosen origin). As a consequence of the algebraic nature of the derivation, the average is to be taken over an infinite range of \mathbf{k} values.

A statistical derivation of (6) and (7) has been given by Karle (1966) for the case that $A'_{\mathbf{h}} = 0$, assuming that no pseudo-centrosymmetric substructure (relative to the chosen origin) is present. His derivation was based on the expressions for the joint probability distributions (j.p.d.'s) $P(X, Y)$ of $B_{\mathbf{k}}, B_{\mathbf{h}-\mathbf{k}}$ and $A_{\mathbf{k}}, A_{\mathbf{h}-\mathbf{k}}$, respectively. Because of the statistical nature of this derivation, restrictions on the range of \mathbf{k} can be applied; however, restrictions on the range of \mathbf{k} will affect the standard deviation in the result. It follows from this that the sparse-density principle, or the expectation that exact pseudo-centrosymmetry is absent for the case of point atoms, is not new information that could be applied to improve the existing expressions for the j.p.d.'s of structure factors: the principle must already have been introduced in the derivations. The point of introduction of the sparse-density principle into the derivation is obvious: it is where the characteristic function, containing information on all atomic coordinates, is written as a product of atomic characteristic functions. This is only justified if the atomic contributions to the structure factors are mutually independent.

The purpose of this paper is to study the relation between the sparse-density principle and the concept of independent atoms, as used in the derivation of the j.p.d.'s of structure factors. We will do this by rederiving the j.p.d.'s of structure-factor components (A 's and B 's), without writing the characteristic function as a product of atomic characteristic functions, *i.e.* without introducing the notion of independent atoms.

2. Theory

As an example of the way expressions for the j.p.d.'s of structure-factor components are derived, we take the derivation of $P(X_1, X_2)$ of $A_{\mathbf{h}}, B_{\mathbf{h}}$.

The Fourier transform of $P(X_1, X_2)$ is the characteristic function

$$Q(t_1, t_2) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} P(X_1, X_2) \times \exp\{i(t_1 X_1 + t_2 X_2)\} dX_1 dX_2 = \langle \exp\{i(t_1 X_1 + t_2 X_2)\} \rangle, \quad (8)$$

in which t_1, t_2 are carrying variables. The quantities $A_{\mathbf{h}}$ and $B_{\mathbf{h}}$ can both be expressed as a sum over a large number of random variables x_{1j}, x_{2j} :

$$A_{\mathbf{h}} = N^{-1/2} \sum_{j=1}^N x_{1j} \quad (9)$$

$$B_{\mathbf{h}} = N^{-1/2} \sum_{j=1}^N x_{2j},$$

in which

$$x_{1j} = \cos(2\pi\mathbf{h} \cdot \mathbf{r}_j) \quad (10)$$

$$x_{2j} = \sin(2\pi\mathbf{h} \cdot \mathbf{r}_j).$$

Introduction of $X_1 = N^{-1/2} \sum_{j=1}^N x_{1j}$ and $X_2 = N^{-1/2} \sum_{j=1}^N x_{2j}$ into (8) gives

$$Q(t_1, t_2) = \left\langle \exp\left\{i\left[t_1 N^{-1/2} \sum_{j=1}^N x_{1j} + t_2 N^{-1/2} \sum_{j=1}^N x_{2j}\right]\right\} \right\rangle = \left\langle \prod_{j=1}^N \exp\{iN^{-1/2}[t_1 x_{1j} + t_2 x_{2j}]\} \right\rangle. \quad (11)$$

At this point, we do not assume that the random variables x_{1j} and x_{2j} ($j = 1, \dots, N$) are independent [this would mean interchanging the product and averaging operators in (11)] but instead we proceed with expanding (11) into a Taylor series right away:

$$Q(t_1, t_2) = \left\langle \prod_{j=1}^N \left[1 + \sum_{\substack{\nu_1=0 \\ \text{not } \nu_1=\nu_2=0}}^{\infty} \sum_{\nu_2=0}^{\infty} \left(\frac{i^{\nu_1+\nu_2} N^{-(\nu_1+\nu_2)/2}}{\nu_1! \nu_2!} \right) \times t_1^{\nu_1} x_{1j}^{\nu_1} t_2^{\nu_2} x_{2j}^{\nu_2} \right] \right\rangle. \quad (12)$$

Multiplication of the series, neglecting terms with powers ν_1, ν_2 for which $\nu_1 + \nu_2 > 2$, leads to

$$Q(t_1, t_2) = 1 + iN^{-1/2} t_1 \left\langle \sum_{j=1}^N x_{1j} \right\rangle$$

$$\begin{aligned}
& + it_2 N^{-1/2} \left\langle \sum_{j=1}^N x_{2j} \right\rangle \\
& - (1/2N) t_1^2 \left\langle \left\{ \sum_{j=1}^N x_{1j} \right\}^2 \right\rangle \\
& - (1/2N) t_2^2 \left\langle \left\{ \sum_{j=1}^N x_{2j} \right\}^2 \right\rangle \\
& - (t_1 t_2 / N) \left\langle \sum_{j_1=1}^N x_{1j_1} \sum_{j_2=1}^N x_{2j_2} \right\rangle \\
& = 1 + it_1 m_{10} + it_2 m_{01} - \frac{1}{2} t_1^2 m_{20} \\
& \quad - \frac{1}{2} t_2^2 m_{02} - t_1 t_2 m_{11} \quad (13)
\end{aligned}$$

with the moments $m_{\nu_1 \nu_2}$ defined as

$$\begin{aligned}
m_{\nu_1 \nu_2} & \equiv \left\langle \left\{ N^{-1/2} \sum_{j_1=1}^N x_{1j_1} \right\}^{\nu_1} \left\{ N^{-1/2} \sum_{j_2=1}^N x_{2j_2} \right\}^{\nu_2} \right\rangle \\
& = \langle X_1^{\nu_1} X_2^{\nu_2} \rangle. \quad (14)
\end{aligned}$$

Assuming $m_{10} = m_{01} = 0$ and introducing the approximation $1 + z \simeq \exp z$, we may write (13) as

$$Q(t_1, t_2) \simeq \exp\left\{-\frac{1}{2}(t_1^2 m_{20} + t_2^2 m_{02} + 2t_1 t_2 m_{11})\right\}. \quad (15)$$

The inverse Fourier transform of (15) then results in the desired j.p.d:

$$\begin{aligned}
P(X_1, X_2) & = (2\pi)^{-1} m_{20}^{-1/2} m_{02}^{-1/2} \exp\left\{-\frac{1}{2}(X_1^2/m_{20} \right. \\
& \quad \left. - (X_2^2/2m_{02}) + (m_{11}/m_{20} m_{02}) X_1 X_2\right\}. \quad (16)
\end{aligned}$$

Equation (16) is valid for any pair of quantities, with actual values X_1, X_2 , which can be written as a sum of random variables, as in (9). For every specific case of X_1, X_2 , it suffices to specify the moments m_{20}, m_{02}, m_{11} .

To evaluate $P(X_1, X_2)$ of $A_{\mathbf{h}}, B_{\mathbf{h}}$, we calculate the moments *via* (14) using the expressions for x_{1j} and x_{2j} given by (10). Then,

$$\begin{aligned}
m_{20} & = \langle A_{\mathbf{h}}^2 \rangle \\
& = N^{-1} \left\langle \left[\sum_{j=1}^N \cos(2\pi \mathbf{h} \cdot \mathbf{r}_j) \right]^2 \right\rangle \\
& = N^{-1} \sum_{j_1=1}^N \sum_{j_2=1}^N \langle \cos(2\pi \mathbf{h} \cdot \mathbf{r}_{j_1}) \cos(2\pi \mathbf{h} \cdot \mathbf{r}_{j_2}) \rangle \\
& = \frac{1}{2} N^{-1} \sum_{j_1=1}^N \sum_{j_2=1}^N \langle \cos[2\pi \mathbf{h} \cdot (\mathbf{r}_{j_1} - \mathbf{r}_{j_2})] \rangle \\
& \quad + \frac{1}{2} N^{-1} \sum_{j_1=1}^N \sum_{j_2=1}^N \langle \cos[2\pi \mathbf{h} \cdot (\mathbf{r}_{j_1} + \mathbf{r}_{j_2})] \rangle. \quad (17)
\end{aligned}$$

To evaluate the averages, first the nature of the statistical experiment must be established. In the classical treatment, which is followed here, it is assumed

that the random variables $2\pi \mathbf{h} \cdot \mathbf{r}_j$ ($j = 1, \dots, N$), which constitute the random quantities x_{1j}, x_{2j} , are uniformly distributed on the unit circle in the complex plane. This can be achieved by (i) fixing the atomic coordinates (unknown but fixed) and letting the reciprocal vector \mathbf{h} range uniformly through the reciprocal lattice (Karle & Hauptman, 1953) or (ii) fixing the reciprocal vector \mathbf{h} and letting the atomic coordinates range uniformly through the unit cell (Heinerman, 1977). The latter statistical experiment cannot be the basis of our treatment as a uniform distribution of atomic coordinates is not compatible with our assumption of dependency between the atomic coordinates. So, resorting to (i), the average in (17) is calculated by letting \mathbf{h} vary uniformly through the reciprocal lattice. In the first term of (17), there is a contribution $(2N)^{-1}$ to the double summation each time $j_1 = j_2$ (N times), otherwise the contribution is zero, amounting to a total contribution of $N(2N)^{-1} = \frac{1}{2}$. In the second term, there is a contribution of $(2N)^{-2}$ to the double summation each time a j_1, j_2 combination occurs for which $\mathbf{r}_{j_1} = -\mathbf{r}_{j_2}$, *i.e.* for each pair of atoms that is centrosymmetrically arranged with respect to the chosen origin; if such a combination occurs then it occurs twice, and the contribution of such an occurrence is $2(2N)^{-1} = 1/N$. If the centrosymmetric substructure consists of p atoms, then the contribution of the second term to m_{20} is $p/2N \equiv \Delta/2$, in which $\Delta \equiv p/N$, so $m_{20} = \frac{1}{2}(1 + \Delta)$. In the same way, it is found that $m_{02} \equiv \langle B_{\mathbf{h}}^2 \rangle_{\mathbf{h}} = \frac{1}{2}(1 - \Delta)$ and $m_{11} = 0$. It can be easily seen that the assumption $m_{10} = m_{01} = 0$, applied to derive the formal expression (16), is still valid in the present case. Introduction of the values for the moments just established in (16) gives the expression for $P(X_1, X_2)$ of $A_{\mathbf{h}}, B_{\mathbf{h}}$:

$$\begin{aligned}
P(X_1, X_2) & = \pi^{-1} (1 + \Delta)^{-1/2} (1 - \Delta)^{-1/2} \\
& \quad \times \exp\left\{-[X_1^2/(1 + \Delta)] \right. \\
& \quad \left. - [X_2^2/(1 - \Delta)]\right\}. \quad (18)
\end{aligned}$$

Equation (18) is accurate up to order $N^{-1/2}$; at this level of approximation, the information on atomic interdependence that is needed to evaluate the expression for the j.p.d. is the fraction Δ of atoms in the centrosymmetric substructure; no information on the coordinates of the atoms in the substructure is needed. Note that

$$\begin{aligned}
\langle |E_{\mathbf{h}}|^2 \rangle & = \langle A_{\mathbf{h}}^2 \rangle + \langle B_{\mathbf{h}}^2 \rangle \\
& = m_{20} + m_{02} \\
& = \frac{1}{2}(1 + \Delta) + \frac{1}{2}(1 - \Delta) \\
& = 1 \quad (19)
\end{aligned}$$

so $\langle |E_{\mathbf{h}}|^2 \rangle$ is independent of the degree of centricity around the chosen origin, as is to be expected for an origin-invariant quantity.

Table 1. Expressions for the moments of $P(X_1, X_2)$

X_1	X_2	m_{20}	m_{02}	m_{11}
A_h	B_h	$\frac{1}{2}(1 + \Delta)$	$\frac{1}{2}(1 - \Delta)$	0
B_k	B_{h-k}	$\frac{1}{2}(1 - \Delta)$	$\frac{1}{2}(1 - \Delta)$	$-\frac{1}{2}N^{-1/2}(A_h - A'_h)$
A_k	A_{h-k}	$\frac{1}{2}(1 + \Delta)$	$\frac{1}{2}(1 + \Delta)$	$\frac{1}{2}N^{-1/2}(A_h + A'_h)$
A_k	B_{h-k}	$\frac{1}{2}(1 + \Delta)$	$\frac{1}{2}(1 - \Delta)$	$\frac{1}{2}N^{-1/2}B_h$

To calculate expressions for $P(X_1, X_2)$ of (B_k, B_{h-k}) , (A_k, A_{h-k}) , (A_k, B_{h-k}) , respectively, we resort to a modified statistical experiment: again, the structure is fixed but h is also fixed and the reciprocal vector k ranges uniformly through the reciprocal lattice. The calculation of the moments goes along the same lines as for the example given above. The moments are collected in Table 1; the corresponding j.p.d.'s can be found by introducing the expressions for the moments into (16).

It is seen from Table 1 that to establish the expressions for $P(X_1, X_2)$ of B_k, B_{h-k} and of A_k, A_{h-k} , if A_h is given (e.g. calculated from anomalous diffraction data), not only knowledge about the degree of centricity around the chosen origin is needed but also detailed knowledge about the coordinates of the atoms in the centrosymmetric substructure (to calculate A'_h).

From the given expressions for m_{11} , (6) and (7) follow immediately.

3. Higher-order moments

The probability expressions derived in the preceding section are restricted to the main term of each distribution. This corresponds to a moment expansion of the characteristic function with moments up to order 2. The information on atomic dependence that is needed to calculate these moments appears to be purely information on the existence of pseudo-centrosymmetry. In this section, we will investigate the nature of the information that is needed to calculate the higher-order moments and thus the higher-order terms of the series expansion of the distributions.

We take, as an example, the j.p.d. $P(X_1, X_2)$ of A_k, B_{h-k} . One of the third-order moments is

$$\begin{aligned}
 m_{30} &= \langle A_k^3 \rangle_k \\
 &= N^{-3/2} \sum_{j_1=1}^N \sum_{j_2=1}^N \sum_{j_3=1}^N \langle \cos(2\pi k \cdot r_{j_1}) \\
 &\quad \times \cos(2\pi k \cdot r_{j_2}) \cos(2\pi k \cdot r_{j_3}) \rangle_k \\
 &= (N^{-3/2}/4) \sum_{\epsilon_1=\pm 1} \sum_{\epsilon_2=\pm 1} \sum_{j_1=1}^N \sum_{j_2=1}^N \sum_{j_3=1}^N \\
 &\quad \times \langle \cos[2\pi k \cdot (r_{j_1} + \epsilon_1 r_{j_2} + \epsilon_2 r_{j_3})] \rangle_k. \quad (20)
 \end{aligned}$$

Contributions to m_{30} occur for those combinations of $j_1, j_2, j_3, \epsilon_1, \epsilon_2$ for which

$$r_{j_1} + \epsilon_1 r_{j_2} + \epsilon_2 r_{j_3} \equiv 0 \pmod{1}. \quad (21)$$

These contributions arise if three atoms are in a special position relative to the chosen origin; four cases can be distinguished, i.e. for the four possible combinations of ϵ_1 and ϵ_2 (Fig. 1). All combinations involve the interaction between the atomic coordinates of three atoms, as is imposed by (21). An example of a configuration that gives a number of contributions to m_{30} is a phenyl ring with the origin chosen at the centre of the ring; all four cases shown in Fig. 1 will contribute to m_{30} . Counting all contributions, this adds up to 24, thus m_{30} would be equal to $6N^{-3/2}$ in this case. Note that $m_{30} = 0$ if no such special three-atom interactions exist. If the expressions for the other third-order moments are worked out, it appears that m_{03} and m_{21} both depend on $\langle \sin[2\pi k \cdot (r_{j_1} + \epsilon_1 r_{j_2} + \epsilon_2 r_{j_3})] \rangle_k$ and are, consequently, systematically equal to zero (independent of the presence of three-atom interactions); also, it appears that $m_{12} = -N^{-1}A''_h$, where A''_h is the contribution to the real part of the structure factor originating from atoms j_1 for which $r_{j_1} - \epsilon_1 r_{j_2} - \epsilon_2 r_{j_3} \equiv 0 \pmod{1}$ (for any j_2, j_3).

In the same way, it can be surmised that fourth-order moments will be influenced by four-atom interactions and, in general, n th-order moments by n -atom interactions.

4. Discussion

In the preceding sections, the j.p.d.'s of pairs of structure-factor components were derived without the usual assumption that the atomic contributions to the structure-factor components are independent. To compare this with the treatment in which the atomic contributions are assumed to be independent, we accept this assumption for the time being, and start with (11) for the characteristic function. As a consequence of the independent-atom assumption, the product of averages

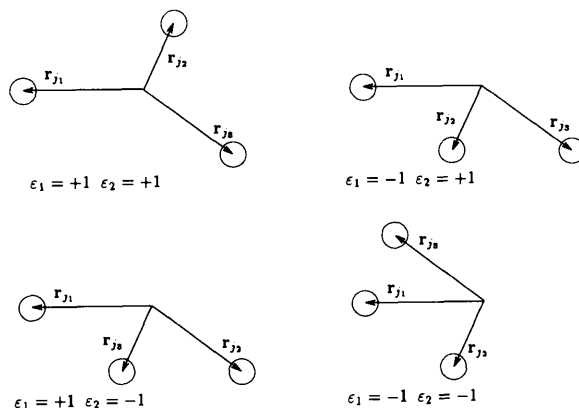


Fig. 1. Three-atom interactions with $r_{j_1} + \epsilon_1 r_{j_2} + \epsilon_2 r_{j_3} \equiv 0$ for the four combinations of $\epsilon_1 = \pm 1, \epsilon_2 = \pm 1$.

can be replaced by an average over products, giving

$$Q(t_1, t_2) = \prod_{j=1}^N q_j(t_1, t_2), \quad (22)$$

where

$$q_j(t_1, t_2) \equiv \langle \exp\{i[t_1 x_{1j} + t_2 x_{2j}]\} \rangle \quad (23)$$

is the characteristic function that pertains only to the contribution of one atom j . The next step is to expand $q_j(t_1, t_2)$ into a power series:

$$q_j(t_1, t_2) = 1 + \sum_{\nu_1=0}^{\infty} \sum_{\nu_2=0}^{\infty} (i^{\nu_1+\nu_2} t_1^{\nu_1} t_2^{\nu_2} / \nu_1! \nu_2!) \times m_{\nu_1 \nu_2}(j). \quad (24)$$

In (24), $\sum \sum'$ is a double summation over ν_1 and ν_2 such that 'not $\nu_1 = \nu_2 = 0$ '; the moments $m_{\nu_1 \nu_2}(j)$ (pertaining to one atom j) are defined as

$$m_{\nu_1 \nu_2}(j) \equiv \langle x_{1j}^{\nu_1} x_{2j}^{\nu_2} \rangle. \quad (25)$$

As the introduction of the series expansion (24) into (22) results in a rather unattractive product of many series expansions, the way one proceeds is to expand $\log q_j(t_1, t_2)$ in a Taylor series (the 'cumulant expansion'); then,

$$Q(t_1, t_2) = \exp \left\{ \sum_{j=1}^N \log q_j(t_1, t_2) \right\}. \quad (26)$$

The result of this operation is that a product of series is replaced by a sum over one series (the cumulant expansion), which is easier to evaluate. Without going into the technical details, the result is again that the reverse Fourier transform of the cumulant expansion results in an expression for $P(X_1, X_2)$. This expansion can then be transformed into one that contains moments, and appears to be formally identical to our expression (16) but now with a different definition of the moments, *i.e.*

$$m_{\nu_1, \nu_2} \equiv \sum_{j=1}^N m_{\nu_1, \nu_2}(j) = \sum_{j=1}^N \langle x_{1j}^{\nu_1} x_{2j}^{\nu_2} \rangle. \quad (27)$$

If this definition of moments is compared with the definition (14), *i.e.* the definition for the case that the atomic contributions are not considered to be independent, then it is apparent that in (14) a moment is essentially defined as a *product of sums* and in (27) as a *sum of products*. In the latter, the average pertains to the contribution of one atom at a time; this results in the loss of interactions between atoms. The difference will be apparent if we recalculate m_{20} for $P(X_1, X_2)$ of A_h, B_h using (27):

$$m_{20} = N^{-1} \sum_{j=1}^N \langle \cos^2(2\pi \mathbf{k} \cdot \mathbf{r}_j) \rangle_{\mathbf{k}} = \frac{1}{2}$$

compared with

$$m_{20} = N^{-1} \left\langle \left[\sum_j \cos(2\pi \mathbf{h} \cdot \mathbf{r}_j) \right]_{\mathbf{k}}^2 \right\rangle = \frac{1}{2}(1 + \Delta)$$

as was the result of (17).

In our treatment, where the characteristic function Q is not written as a product of atomic characteristic functions, there is no way to circumvent the computational burden to have to multiply a great number of series expansions, *e.g.* by applying a cumulant expansion of $\log Q$. If one wants to attempt to include higher-order terms in the expression for the j.p.d., this might require a considerable effort, though the effort will be mainly of a book-keeping nature. Without actually establishing the expressions for the higher-order terms, one can, nevertheless, foresee that they will depend on the higher-order moments. It was argued in §3 that moments $m_{\nu_1 \nu_2}$ will be influenced by interactions between $(\nu_1 + \nu_2)$ atoms. For $\nu_1 + \nu_2 = 2$, these interactions are given by the condition $\mathbf{r}_{j_1} + \mathbf{r}_{j_2} \equiv \mathbf{0} \pmod{\mathbf{1}}$ (the condition of pseudo-centrosymmetry); they influence only the main term of the distribution. For $\nu_1 + \nu_2 = 3$, the third-order moments will be influenced by three-atom interactions, given by the condition $\mathbf{r}_{j_1} + \varepsilon_1 \mathbf{r}_{j_2} + \varepsilon_2 \mathbf{r}_{j_3} \equiv \mathbf{0} \pmod{\mathbf{1}}$ ($\varepsilon_1 = \pm 1, \varepsilon_2 = \pm 1$); these third-order moments will affect higher-order terms of the distribution. Clearly, if one has no quantitative knowledge of the 2-, 3-, 4-, ... atom interactions, one has to resort to the assumption that the atoms are independent (and use the corresponding probability distribution). In this sense, the sparseness principle, which states that the electron density in the crystal is so sparse that two-atom interactions are unlikely to occur, can be sharpened to exclude all interactions (meaning that interactions of any kind are unlikely to occur) and is thus the basis of all probability distributions in direct methods that are in practical use.

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