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SHORT COMMUNICATIONS

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Karle–Hauptman determinants and entropy. By STIG STEENSTRUP,* *CSIRO, Division of Chemical Physics, PO Box 160, Clayton, Victoria 3168, Australia*

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Abstract

That positivity of all the Karle–Hauptman determinants and the positivity of the electron density in the unit cell are equivalent conditions is well known. A simple way of deriving this result is presented providing at the same time a relation between these determinants and the logarithm of the electron density. The relationship of this logarithm of the electron density to the entropy is also discussed.

The Karle–Hauptman determinants are determinants of matrices involving the structure factors $F_{\mathbf{H}}$ (Karle & Hauptman 1950),

$$F_{\mathbf{H}} = (1/V) \int \rho(\mathbf{r}) \exp(2\pi i \mathbf{Hr}) d\mathbf{r}.$$

The structure factors are arranged into a matrix by writing $\mathbf{H} = h_1 \mathbf{b}_1 + h_2 \mathbf{b}_2 + h_3 \mathbf{b}_3$, where \mathbf{b}_i are the reciprocal-lattice vectors, and by grouping the three indices h_1, h_2, h_3 into one, 'm', by writing

$$m = h_1 + N(h_2 - 1) + N^2(h_3 - 1), \quad (1)$$

where $(N-1)$ is the maximum value of h_i to be included in the matrix. A matrix D^N of order N^3 with elements

$$D_{mn}^N = F_{m-n} \quad m, n = 1, \dots, N^3$$

can now be formed. The Karle–Hauptman determinants up to order N^3 are all the principal minors of D^N , including $\det(D^N)$ and are positive if and only if $\rho(\mathbf{r}) > 0$.

Narayan & Nityananda (1982) showed that:

$$\lim_{N \rightarrow \infty} (1/N^3) \log [\det(D^N)] \rightarrow (1/V) \int \log \rho(\mathbf{r}) d\mathbf{r}. \quad (2)$$

Both of these results will be recovered together with some other results.

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For the derivation, the unit cell is considered to be divided into N^3 pixels, N divisions along each space direction, with integers j_1, j_2, j_3 specifying a pixel. As shown in the Appendix there exist values $\bar{\rho}_{\mathbf{j}}$ such that

$$F_{\mathbf{h}} = (1/N^3) \sum_{\mathbf{j}} \bar{\rho}_{\mathbf{j}} \exp(2\pi i \mathbf{jh}/N),$$

with $\bar{\rho}_{\mathbf{j}}$ a sampled value of the electron density $\rho(\mathbf{r})$ in pixel \mathbf{j} . In the same way as for the structure factors, the indices \mathbf{j} are arranged into one, κ , by the same type of formula as (1).

The numbers $\bar{\rho}_{\kappa}$ are now considered to be the diagonal elements of a diagonal matrix B , i.e. B has elements $B_{\mu\kappa} = \rho_{\kappa} \delta_{\mu\kappa}$, with $\delta_{\mu\kappa}$ the Kronecker delta. By a unitary transformation R the matrix B is transformed into D^N as follows: Let the matrix R have elements $R_{\kappa n} = (1/N^{3/2}) \exp(2\pi i \mathbf{jnh}/N)$, with κ related to \mathbf{j} and n to \mathbf{h} via (1), and let R^* denote the Hermitian conjugate of R , then it is easy to show that R is unitary, i.e. $R^*R = I$, I the identity matrix, and that

$$D^N = R^*BR.$$

It is here understood that in the matrix multiplication the summation over, say, κ , related to \mathbf{h} via (1), from 1 to N^3 is really a sum over h_1, h_2 and h_3 , each from 1 to N . It is obvious that ρ_1, \dots, ρ_N are the eigenvalues of the matrix D^N . The results now follow by the following theorems (Wilkinson, 1965).

(a) A necessary and sufficient condition for a Hermitian matrix to be positive definite is that all its eigenvalues are positive.

(b) A necessary and sufficient condition for a Hermitian matrix to be positive definite is that all its principal minors are positive.

In essence then, if $\rho(\mathbf{r}) > 0$ then by (a) D^N is positive definite and by (b) all the principal minors (Karle–

Hauptman determinants) are positive. Conversely, if all the Karle–Hauptman determinants (all principal minors) are positive then by (b) D^N is positive definite and by (a) the positivity of $\bar{\rho}_\kappa$ follows. The result applies to any order N^3 in the sense that if for a finite N D^N is positive definite, then the numbers $\bar{\rho}_1, \dots, \bar{\rho}_N$ are all positive, $\bar{\rho}_\kappa$ being the electron density somewhere in pixel κ .

Furthermore, since the determinant is invariant under a unitary transformation it follows that

$$\det(D^N) = \prod_{\kappa=1}^{N^3} \bar{\rho}_\kappa, \quad (3)$$

or taking logarithms:

$$\log[\det(D^N)] = \sum_{\kappa=1}^{N^3} \log \bar{\rho}_\kappa. \quad (4)$$

Dividing now by N^3 and letting N go to infinity the less-general result (2) follows.

In all the above ‘positive definite’ can be substituted by ‘positive semi-definite’, substituting at the same time all ‘greater than zero’ with ‘greater than or equal to zero’, so that if in any of the pixels the electron density becomes strictly zero, then it follows from (3) that $\det(D^N) = 0$.

The result (3) also offers a simple way of obtaining Goedkoop’s (1950) result concerning unitary structure factors. His result is that if the matrices D^N are constructed with the unitary structure factors U_H then the only nonzero determinants are those $\det(D^N)$ for which $N^3 < M$, where M is the number of atoms in the unit cell. The unitary structure factors are constructed from a model in which it is assumed that all the electrons of an atom are concentrated at the center of the atom. In such a model a maximum of M pixels can have electron densities different from zero.

It has been claimed (Britten & Collins, 1982; Narayan & Nityananda, 1982; Piro, 1983) that the maximum determinant method (MDM) and the maximum entropy principle (MEP) are equivalent. From the identity (4) it is obvious that the MDM is equivalent to maximization of $\sum \log \rho_\kappa$ for arbitrary N . As pointed out by Steenstrup & Wilkins (1984), however, there is in general no relation between entropy and $\sum \log \rho_\kappa$. Only under fairly restrictive conditions as given by Steenstrup & Wilkins (1984) is the MEP equivalent to maximizing $\sum \log \rho_\kappa$. This means that unless these conditions are fulfilled the MDM and the MEP are not equivalent.

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APPENDIX

For the proof of the relation

$$F_h = (1/N^3) \sum_j \bar{\rho}_j \exp(2\pi i j h / N),$$

the sampling theorem is used. This theorem is explained in most textbooks on Fourier transforms; a useful reference is Brillouin (1962). For ease of notation the proof is given in one dimension, the extension to three being obvious.

Let $\rho(x)$ be a periodic function with period 1, and let F_h be its Fourier coefficients:

$$F_h = \int_{-1/2}^{1/2} \rho(x) \exp(2\pi i x h) dx, \quad h = -\infty, \dots, \infty.$$

Let

$$f_j = \sum_{h=-H+1}^H F_h \exp(-2\pi i h j / 2H),$$

then the function $f(x)$, defined by

$$f(x) = \sum_{j=-H+1}^H f_j \frac{\sin[\pi(2H+1)(x-j/2H)]}{\sin[\pi(x-j/2H)]},$$

coincides with $\rho(x)$ for $x = j/2H$, $j = -H+1, \dots, H$. A straightforward calculation establishes the result. In words: if only the H first Fourier coefficients of a periodic function are different from zero, then the function is completely determined by its value sampled at $2H+1$ points.

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