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Full use of symmetry in the maximum-determinant rule. By Y. MAUGUEN, C. DE RANGO & G. TSOUCARIS, *CNRS, Laboratoires de Bellevue, 1 Place A. Briand, 92-Bellevue, France*

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The properties of Hilbert space and group theory are used to point out the fact that the m-dimensional Laplace–Gauss law for m unknown structure factors, involving two Karle–Hauptman determinants, Δ_{m+1} and D_m, can take into account full symmetry information for any space group. It is shown that the ratio (Δ_{m+1}/D_m) is equal to a sum of ratios of Goedkoop determinants.

The aim of this note is to make clear that the m-dimensional Laplace–Gauss law, for m unknown structure factors (Tsoucaris, 1970), can take into account full symmetry information, for any space group. We recall that this law [equation (2)] is expressed in terms of Karle–Hauptman determinants. On the other hand, it is well known that the use of space-group symmetry amounts to expressing a Karle & Hauptman (1950) determinant, as a product of several Goedkoop (1950) determinants $G^{(i)}_{m/s}$:

$$D_m = \prod_i G^{(i)}_{m/s} . \qquad (1)$$

The Goedkoop determinant $G^{(i)}_{m/s}$ is an order m/s Gram determinant which corresponds to the ith irreducible representation of the point group (s is the order of the group). Combining these results, we can state that:

$$p(E_1,\ldots,E_m) = K \exp\left[N\frac{\Delta_{m+1}}{D_m}\right] = K \exp\left[N\sum_i \frac{\Gamma^{(i)}}{G^{(i)}}\right] . \qquad (2)$$

The determinant obtained from $G^{(i)}_{m/s}$ by adding a new column and row containing the random variables is also a Goedkoop determinant of order $(m/s+1)$; for brevity we suppress the indices:

$$\Gamma^{(i)} = \Gamma^{(i)}_{m/s+1}$$

$$G^{(i)} = G^{(i)}_{m/s} .$$

Example

For clearness, we give first an elementary proof in the special case $m=4$, space group $P\bar{1}$. Let us consider the Δ_5 of Table 1, built up by taking the special set of fixed reciprocal-lattice vectors: $\{\mathbf{H},\mathbf{K},-\mathbf{H},-\mathbf{K}\}$. By elementary manipulations (combining rows and columns) this Δ_{m+1} can be rewritten as in Table 2. This Table shows clearly that $D_4 = G^{(1)}_2 G^{(2)}_2$ and provides immediately a statistical interpretation: each Goedkoop determinant forms the covari-

Table 1. *Δ_{m+1} determinant corresponding to a D_m determinant built up from a complete sets of symmetry-related reflexions for $P\bar{1}$* ($\mathbf{H}_p = \mathbf{H},\mathbf{K},-\mathbf{H},-\mathbf{K}$)

$$\Delta_5 = \frac{1}{N}\begin{vmatrix} 1 & U_{\mathbf{H}-\mathbf{K}} & U_{2\mathbf{H}} & U_{\mathbf{H}+\mathbf{K}} & E_{\mathbf{H}-\mathbf{L}} \\ U_{\mathbf{K}-\mathbf{H}} & 1 & U_{\mathbf{K}+\mathbf{H}} & U_{2\mathbf{K}} & E_{\mathbf{K}-\mathbf{L}} \\ U_{-2\mathbf{H}} & U_{-\mathbf{H}-\mathbf{K}} & 1 & U_{-\mathbf{H}+\mathbf{K}} & E_{-\mathbf{H}-\mathbf{L}} \\ U_{-\mathbf{K}-\mathbf{H}} & U_{-2\mathbf{K}} & U_{-\mathbf{K}+\mathbf{H}} & 1 & E_{-\mathbf{K}-\mathbf{L}} \\ E_{-\mathbf{H}+\mathbf{L}} & E_{-\mathbf{K}+\mathbf{L}} & E_{\mathbf{H}+\mathbf{L}} & E_{\mathbf{K}+\mathbf{L}} & N \end{vmatrix}$$

Table 2. *Rearrangement of the Karle–Hauptman determinant given in Table* 1

$$\Delta_5 = \frac{1}{N}\left|\begin{array}{cc:cc:c} 1+U_{2\mathbf{H}} & U_{\mathbf{H}+\mathbf{K}}+U_{\mathbf{H}-\mathbf{K}} & 0 & 0 & \frac{(E_{\mathbf{H}-\mathbf{L}}+E_{-\mathbf{H}-\mathbf{L}})}{\sqrt{2}} \\ U_{\mathbf{H}+\mathbf{K}}+U_{\mathbf{H}-\mathbf{K}} & 1+U_{2\mathbf{K}} & 0 & 0 & \frac{(E_{\mathbf{K}-\mathbf{L}}+E_{-\mathbf{K}-\mathbf{L}})}{\sqrt{2}} \\ \hdashline 0 & 0 & 1-U_{2\mathbf{H}} & U_{\mathbf{H}-\mathbf{K}}-U_{\mathbf{H}+\mathbf{K}} & \frac{(E_{\mathbf{H}-\mathbf{L}}-E_{-\mathbf{H}-\mathbf{L}})}{\sqrt{2}} \\ 0 & 0 & U_{\mathbf{H}-\mathbf{K}}-U_{\mathbf{H}+\mathbf{K}} & 1-U_{2\mathbf{K}} & \frac{(E_{\mathbf{K}-\mathbf{L}}-E_{-\mathbf{K}-\mathbf{L}})}{\sqrt{2}} \\ \hdashline \frac{(E_{-\mathbf{H}+\mathbf{L}}+E_{\mathbf{H}+\mathbf{L}})}{\sqrt{2}} & \frac{(E_{-\mathbf{K}+\mathbf{L}}+E_{\mathbf{K}+\mathbf{L}})}{\sqrt{2}} & \frac{(E_{-\mathbf{H}+\mathbf{L}}-E_{\mathbf{H}+\mathbf{L}})}{\sqrt{2}} & \frac{(E_{-\mathbf{K}+\mathbf{L}}-E_{\mathbf{K}+\mathbf{L}})}{\sqrt{2}} & N \end{array}\right|$$

ance matrix for two independent two-dimensional random column vectors, the elements of which are symmetry adapted linear combinations of structure factors:

$$\boldsymbol{\varepsilon}^{(1)}=\begin{pmatrix}(E_{\mathbf{H-L}}+E_{\mathbf{-H-L}})/\sqrt{2}\\(E_{\mathbf{K-L}}+E_{\mathbf{-K-L}})/\sqrt{2}\end{pmatrix}$$

$$\boldsymbol{\varepsilon}^{(2)}=\begin{pmatrix}(E_{\mathbf{H-L}}-E_{\mathbf{-H-L}})/\sqrt{2}\\(E_{\mathbf{K-L}}-E_{\mathbf{-K-L}})/\sqrt{2}\end{pmatrix}.$$

In the special case $\mathbf{L}=0$, the expression of Δ_5 written in the form (*a*), turns into the form (*b*) or (*c*) (Fig. 1). The probability law of $\boldsymbol{\varepsilon}^{(1)}$ can be derived from the Goedkoop determinants $\Gamma_3^{(1)}$ and $G_2^{(1)}$ corresponding to the totally symmetric representation, since the ratio of the Karle–Hauptman determinants is equal to that of the Goedkoop determinants:*

$$\Delta_5/D_4=\Gamma_3^{(1)}/G_2^{(1)}.$$

General proof

The above results could be generalized for any order, in any space group, following the same factorization process, but the use of the Hilbert space provides a quicker proof.

The vectors $\mathbf{V}_p$ ($p=1\ldots m$) (Tsoucaris, 1970, Appendix *B*), including complete sets of symmetry-related reflexions, are combined to form S.A.L.C. (symmetry adapted linear combination) $\mathscr{V}_r^{(i)}$ by using the projection operators, for each irreducible representation, as defined in group theory ($r=1,\ldots,m/s$; $i=1,\ldots,N_c$; N_c = number of classes).

Vectors $\mathscr{V}_r^{(i)}$ belonging to different irreducible representations are orthogonal. Therefore, the square of the volume of the parallelotope ($V_1, V_2, \ldots, V_m$) (equal to the Karle–Hauptman determinant D_m) is equal to the product of the squares of the volumes of the projections on each subspace (each of which is equal to the corresponding Goedkoop determinant $G^{(i)}$). That is nothing but the limit case of the generalized Hadamard inequality.

Next, for Δ_{m+1}, we decompose the random vector $\mathbf{W}$ into components lying in each irreducible subspace:

$$\mathbf{W}=\sum_i \mathbf{W}^{(i)}. \tag{3}$$

By writing the volume of the parallelotope:

$$(V_1,\ldots,V_m,W)=\sum_i (V_1,\ldots,V_m,W_i) \tag{4}$$

we immediately obtain the equality:

$$\frac{\Delta_{m+1}}{D_m}=\frac{\sum_i \Gamma^{(i)}\prod_{j\neq i} G^{(j)}}{\prod_j G^{(j)}}=\sum_i\frac{\Gamma^{(i)}}{G^{(i)}}. \tag{5}$$

For the special case $\mathbf{L}=0$, we obtain for any space group:

$$\frac{\Delta_{m+1}}{D_m}=\frac{\Gamma^{(1)}}{G^{(1)}} \tag{6}$$

because then $\mathbf{W}_1$ belongs to the subspace corresponding to the totally symmetric representation.

Statistical interpretation

Let us call $\mathscr{U}_{pq}^{(i)}$ the elements of $G^{(i)}$ corresponding to the *i*th irreducible representation of the point group. For Abelian groups:*

$$\mathscr{U}_{pq}^{(i)}=\sum_{v=1}^{s}\chi_v^{(i)}\exp\,[2\pi i\mathbf{H}_p\mathbf{t}_v]U_{(\hat{\varphi}_v\mathbf{H}_p-\mathbf{H}_q)}. \tag{7}$$

$\hat{S}_v$ are the operations of the space group, defined by $\mathbf{r}\hat{S}_v=\mathbf{r}\hat{\varphi}_v+\mathbf{t}_v$ and $\chi_v^{(i)}$ is the character corresponding to $\hat{\varphi}_v$. Defining $\varepsilon_{pq}^{(i)}=\sqrt{N}\mathscr{U}_{pq}^{(i)}$, and using Goedkoop's (1954) formalism it is easy to prove that for equal-atom structures:

$$\langle\varepsilon_{p,m+1}^{(i)}\varepsilon_{q,m+1}^{(j)}\rangle_L=s\delta_{ij}\mathscr{U}_{pq}^{(i)}. \tag{8}$$

The equation (2) is derived from this last result which is equivalent to the following statement: *the covariances of S.A.L.C. of the E's (unknown and variable) are S.A.L.C. of U's (known and fixed).* In other words, the validity of the Laplace–Gauss law when we take into account the symmetry is connected to the fact that Sayre's (1952) equation is symmetry-independent.

The special case where only one ε_q is unknown has already been treated by de Rango (1969) and the results have been quoted by Tsoucaris (1970), equation (11). It is in fact the expression of the well known regression-plane equation with an obvious change of notation (ε_q for E_q and G_{pq} for D_{pq}):†

$$\varepsilon_q=-\frac{1}{G_{qq}}\sum_{\substack{p=1\\p\neq q}}^{m/s}G_{pq}\varepsilon_p\quad\text{(complex-number notation)} \tag{9}$$

$$\tan\varphi(\varepsilon_q)=\frac{\sum_{p=1}^{m/s}|G_{pq}\varepsilon_p|\sin\,[\varphi(\varepsilon_p)+\varphi(G_{pq})]}{\sum_{p=1}^{m/s}|G_{pq}\varepsilon_p|\cos\,[\varphi(\varepsilon_p)+\varphi(G_{pq})]}\quad p\neq q$$

$$\text{(tangent-formula notation)}. \tag{10}$$

A last remark should be made about the statistical origin of the probability laws. Since the random vector $\mathbf{W}$ involves $\mathbf{L}$ and $\mathbf{r}_i$ in a symmetrical way, the results are the same, whether one considers $\mathbf{L}$ fixed and $\mathbf{r}_i$ variable, or inversely, $\mathbf{L}$ variable and $\mathbf{r}_i$ fixed.

* This special case has been treated by Castellano, Podjorny & Navaza, (1973).

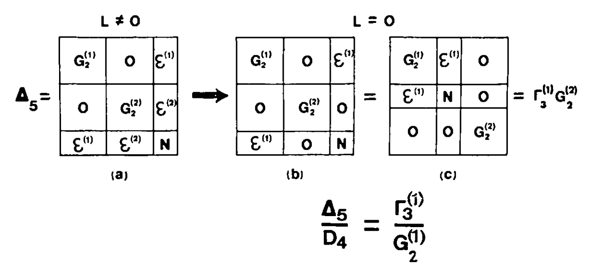

Fig. 1. Diagram showing the degeneracy of the determinant given in Table 2, in the special case $\mathbf{L}=0$.

* In the general case, we have to replace the character $\chi_v^{(i)}$ by a $l_i\times l_i$ matrix if l_i is the dimension of the *i*th representation.

† For clearness the index is deleted.

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