Chemistry 208

Examples of Karle-Hauptmann Determinants and Their Use in Direct Methods of X-Ray Structure Analysis

Introduction

The problem in converting X-ray intensities into an electron density map (equivalent to locating the atom positions in the unit cell of the crystal) is that we measure the magnitude of the structure factor amplitude, $|F_{hk\ell}|$, rather than the structure factor itself, which has a phase represented by the phase angle $\varphi_{hk\ell}$. The structure factor is generally a complex number and can be written as shown in Equation 1

$$F_{hk\ell} = | F_{hk\ell} | e^{i\varphi_{hk\ell}} \tag{1}$$

If we use **h** to represent the vector (h, k, ℓ) and **x** to represent the vector (x, y, z) we can write the electron density function (in electrons per $Å^3$) as shown in Equation 2. Here summing over **h** represents a triple sum over h, k ℓ within the limits of data collected, or a practical limit beyond which there are no significant structure factor amplitudes. In general the intensity of structure factors drops off fairly rapidly with sin θ/λ. The more diffuse the electron density the more rapid this drop off.

$$\rho(\mathbf{x}) = (\mathbf{1}/\mathrm{V})\sum_{\mathbf{h}} F_{\mathbf{h}} e^{-2\pi \mathbf{h}\bullet\mathbf{x}} \tag{2}$$

The phase problem is that, while we know the magnitudes $|F_{hk\ell}|$ we do not know the phase angles $\varphi_{hk\ell}$. Thus if we have a thousand structure factor amplitudes it would seem that we have a thousand unknowns. However the situation is not so hopeless, since any random choice of phases will lead to electron density maps that have large negative peaks, an impossibility since the electron density must be everywhere ≥ 0. If we think of the unit cell being cut into 10 pieces along each of the three edges of the cell, this generates a thousand cubelets within the unit cell where the electron density must be ≥ 0. In effect this is a thousand constraints on the 1000 unknown phase angles. In fact, if the resolution limit d_{min} is the same in all directions of the crystal the limiting values for h, k, and l are such that the grid size specified by the d spacing corresponds to the number of data. The more data collected, the smaller d_{min} and the greater the resolution—and the greater the number of points where we know the electron density must not be negative.

The K-H Determinant. Karle and Hauptmann showed in the 1950's that this kind of constraint requires that all derivatives of the type

$$\begin{vmatrix} F_{\mathbf{0}} & F_{-h_1} & F_{-h_2} \\ F_{h_1} & F_{\mathbf{0}} & F_{h_1-h_2} \\ F_{h2} & F_{-h_1+h_2} & F_{\mathbf{0}} \end{vmatrix} = \mathrm{Det} > 0 \tag{3}$$

must be greater than zero. Here $F_{\mathbf{0}}$ represents the $F_{0,0,0}$ reflection (the unmeasurable origin amplitude, which is equal to the total number of electrons within the unit cell). Placing structure factors for the Miller indices $\mathbf{h}_1$ and $\mathbf{h}_2$ along the first column and the corresponding structure factors for $-\mathbf{h}$ along the first row of the determinant is then followed by placing the structure factor whose Miller indices are the vector sum of the values of **h** for the corresponding row and column. Since $F_{-\mathbf{h}} = F_{\mathbf{h}}^*$ we note that the lower triangular elements are simply the complex conjugate of the transpose of the upper right elements. Hence the matrix is Hermitian.

Expanding this determinant gives equation (4). This expansion uses the fact that $\varphi_{-\mathbf{h}} = -\varphi_{\mathbf{h}}$ and that $e^{i\varphi} + e^{-i\varphi} = 2\cos\varphi$.

$$\text{Det} = F_0(F_0^2 - F_{h_1}^2 - F_{h_2}^2 - F_{-h_1+h_2}^2) + |F_{h_1}||F_{h_2}||F_{-h_1+h_2}|\cos(\varphi_{h_1} - \varphi_{h_2} + \varphi_{-h_1+h_2}) \qquad (4)$$

For a centrosymmetric structure the only possible phase angles are 0 or π, which is equivalent to saying that the structure factor is real and either positive or negative. To maximize equation 4 the cosine term must be +1. This requires that $\varphi_{h_1} - \varphi_{h_2} + \varphi_{-h_1+h_2} = 0$. For a centrosymmetric structure this means $S_{h_1} S_{-h_2} = S_{-h_1+h_2}$, where S is the sign of the structure factor. This is the Sayre equation.

Example—The One Dimensional Two-Carbon Structure

A one-dimensional centric structure of two carbon atoms at ±1.833 Å cell is described in Stout and Jensen. The corresponding structure factors are shown below. Suppose we have measured the magnitude of these structure factors but we do not yet know the phases. We have seen the Fourier series that result when some phases are incorrect. Let's now examine the Karle-Hautpmann determinant.

h	F_h
0	12
±1	5
±2	-7
±3	-8
±4	-1
±5	5
±6	4
±7	-1
±8	-4
±9	-2
±10	2
±11	3
±12	1

Consider the determinant formed by F_1, F_2 and F_3. The various possible values are shown below

$$\begin{vmatrix} F_0 & F_{-1} & F_{-3} \\ F_1 & F_0 & F_{-2} \\ F_3 & F_2 & F_0 \end{vmatrix} = \begin{vmatrix} 12 & \pm 5 & \pm 8 \\ \pm 5 & 12 & \pm 7 \\ \pm 8 & \pm 7 & 12 \end{vmatrix} = \text{Det}$$

#	F_1	F_2	F_3	Det
1	5	7	8	632
2	5	7	-8	-488
3	5	-7	8	-488
4	5	-7	-8	632
5	-5	7	8	-488
6	-5	7	-8	632
7	-5	-7	8	632
8	-5	-7	-8	-488

Note that the "correct" sign combination is #4. However changing all the odd reflections corresponds to just a change in origin of 1/2 (as we saw in the Fourier series) and so solution #7 is an equally correct solution. Solutions #1 and #6 are incorrect but can only be discarded by looking at other combinations or a higher order determinant.

Now consider the fifth order Karle-Hauptmann determinant shown below. By judicious choice of the first column of structure factors we have a determinant that includes all but F_4, which is relatively weak and hence not so important. Remember that $F_{-h} = F_h$ (the negative indices are kept here to show the construction). The spreadsheet program Excel makes solving such determinants very easy. It is given by (for example)

=MDETERM(A12:E16)

where A12 is the cell address of the upper left element and E16 the lower right element of the determinant. Some results (beginning with the "correct" structure) are shown below. The symbol ζ marks sign changes of a structure factor (others are kept the same) from the correct structure. Note that already the determinant has become very powerful in assigning phases.

$$\text{Det} = \begin{vmatrix} F_0 & F_{-8} & F_{-6} & F_1 & F_{-11} \\ F_8 & F_0 & F_2 & F_9 & F_{-3} \\ F_6 & F_{-2} & F_0 & F_7 & F_{-5} \\ F_{-1} & F_{-9} & F_{-7} & F_0 & F_{-12} \\ F_{11} & F_3 & F_5 & F_{12} & F_0 \end{vmatrix}$$

F_1	F_2	F_3	F_4	F_5	F_6	F_7	F_8	F_9	F_{10}	F_{11}	F_{12}	Det
+	–	–	–	+	+	–	–	–	+	+	+	57510
		ζ										-66266
		ζ					ζ					-126138
											ζ	52162
		ζ			ζ							29854

Problem:

Is the first "correct" combination the one that gives the highest value determinant? Try some others to test your conjecture.

Problem:

Which of the following K-H determinants would be useful for determining the phase of F_4 assuming that the other phases were correct? Which would be most reliable?

$$\begin{vmatrix} F_0 & F_{-4} & F_{-8} \\ F_4 & F_0 & F_{-4} \\ F_8 & F_4 & F_0 \end{vmatrix} \quad \text{or} \quad \begin{vmatrix} F_0 & F_{-4} & F_{-1} \\ F_4 & F_0 & F_3 \\ F_1 & F_{-3} & F_0 \end{vmatrix} \quad \text{or} \quad \begin{vmatrix} F_0 & F_{-2} & F_2 \\ F_2 & F_0 & F_4 \\ F_{-2} & F_{-4} & F_0 \end{vmatrix}$$

Inequalities. For three-dimensional structures the smallest possible Karle-Hauptmann determinant is shown in Equation 5, which leads to the case shown.

$$\begin{vmatrix} F_{\mathbf{0}} & F_{\mathbf{h}} \\ F_{-\mathbf{h}} & F_{\mathbf{0}} \end{vmatrix} > 0 \text{ implies } F_{000}^2 - |F_{hkl}|^2 > 0 \qquad (5)$$

For the next larger 3 by 3 determinant we note that there will be two independent reciprocal atom vectors (Miller indices), $\mathbf{h}_1$ and $\mathbf{h}_2$ and the determinant is given by equation (3). Expansion of that determinant gives equation (4).

Tsoucaris has shown that the most probable combination of phases maximizes the value of the determinant in equation (4). That means if the phases for $F_{\mathbf{h}_1}$ and $F_{\mathbf{h}_2}$ are known the most probable value of $\varphi_{\mathbf{h}_2-\mathbf{h}_1}$ will be such that the sum of the 3 angles is 0 or π, thereby maximizing the cosine. As noted earlier, for centrosymmetric structures this is equivalent to the Sayre Equation. Given the phase assignment for two of the reflections in the related triplet the third can be predicted.

For noncentric structures we know that one determinant of triplets predicts the most probable phase for a third phase angle when the first two are known. But different specific pairs may give different predictions. Consider that we may have some known phases and we want to determine a specific unknown remaining phase. In particular, suppose that we want to know the phase of the $F_{5,3,1}$ structure factor. We make a table (see below) whose structure factors have Miller indices of $\mathbf{h}_2$ and $\mathbf{h}_1$-$\mathbf{h}_2$ such that the sum of the Miller indices always equal the Miller indices 5, 3, 1 the structure factor $\mathbf{h}_1$ whose phase we are trying to determine.

$-\mathbf{h}_2$ (known)	**$\mathbf{h}_1-\mathbf{h}_2$ (known)**	**$\mathbf{h}_1$ (unknown)**
1,1,3	**4,2,-2**	**5,3,1**
1,2,1	**4,1,2**	**5,3,1**
6,0,0	**- 1,3,1**	**5,3,1**

For each of these triplets there will be a determinant as shown in Equation (4) and maximizing the value of the determinant involves maximizing the only variable quantity in the determinant, the cosine of the sums of the three angles. Since we will have many different individual predictions which may disagree somewhat with each other, we can average out errors by maximizing the sum of the variable parts of determinant as shown in Equation (5).

$$\sum_{\mathbf{h}_2} Det_{\mathbf{h}_1,\mathbf{h}_2} = \sum_{\mathbf{h}_2} |F_{\mathbf{h}_1}||F_{\mathbf{h}_2}||F_{-\mathbf{h}_1+\mathbf{h}_2}|\cos(\varphi_{\mathbf{h}_1} - \varphi_{\mathbf{h}_2} + \varphi_{-\mathbf{h}_1+\mathbf{h}_2}) \qquad (5)$$

Since the magnitude $|F_{\mathbf{h}_1}|$ is constant with respect to the summation over $\mathbf{h}_2$ we can bring it outside the sum. Remember also the trigonometric identity that says $\cos(\alpha-\beta) = \cos\alpha\cos\beta + \sin\alpha\sin\beta$. This gives us Equation (6).

$$\begin{aligned}\sum_{\mathbf{h}_2} Det_{\mathbf{h}_1,\mathbf{h}_2} &= |F_{\mathbf{h}_1}|\cos(\varphi_{\mathbf{h}_1})\sum_{\mathbf{h}_2}|F_{\mathbf{h}_2}||F_{-\mathbf{h}_1+\mathbf{h}_2}|\cos(\varphi_{\mathbf{h}_2} - \varphi_{-\mathbf{h}_1+\mathbf{h}_2}) \\ &+ |F_{\mathbf{h}_1}|\sin(\varphi_{\mathbf{h}_1})\sum_{\mathbf{h}_2}|F_{\mathbf{h}_2}||F_{-\mathbf{h}_1+\mathbf{h}_2}|\sin(\varphi_{\mathbf{h}_2} - \varphi_{-\mathbf{h}_1+\mathbf{h}_2})\end{aligned} \qquad (6)$$

Now instead of maximizing one determinant we want to maximize the sum of the determinants, which means the derivative of the sum of the determinants with respect to the unknown phase angle $\varphi_{\mathbf{h}_1}$ should be 0. This finally gives us Equation (7) which we can rearrange to Equation (8), the famous tangent formula, which gives phase assignments for reflections based on a few reflections whose phases have already been assigned.

$$\sin\varphi_{\mathbf{h}_1} \sum_{\mathbf{h}_2} F_{\mathbf{h}_2} \| F_{-\mathbf{h}_1+\mathbf{h}_2} | \cos(\varphi_{\mathbf{h}_2} - \varphi_{-\mathbf{h}_1+\mathbf{h}_2}) = \cos\varphi_{\mathbf{h}_1} \sum_{\mathbf{h}_2} | F_{\mathbf{h}_2} \| F_{-\mathbf{h}_1+\mathbf{h}_2} | \sin(\varphi_{\mathbf{h}_2} - \varphi_{-\mathbf{h}_1+\mathbf{h}_2}) \qquad (7)$$

$$\tan\varphi_{\mathbf{h}_1} = \frac{\sum_{\mathbf{h}_2} |F_{\mathbf{h}_2}| |F_{-\mathbf{h}_1+\mathbf{h}_2}| \sin\left(\varphi_{\mathbf{h}_2} - \varphi_{-\mathbf{h}_1+\mathbf{h}_2}\right)}{\sum_{\mathbf{h}_2} |F_{\mathbf{h}_2}| |F_{-\mathbf{h}_1+\mathbf{h}_2}| \cos\left(\varphi_{\mathbf{h}_2} - \varphi_{-\mathbf{h}_1+\mathbf{h}_2}\right)} \qquad (8)$$