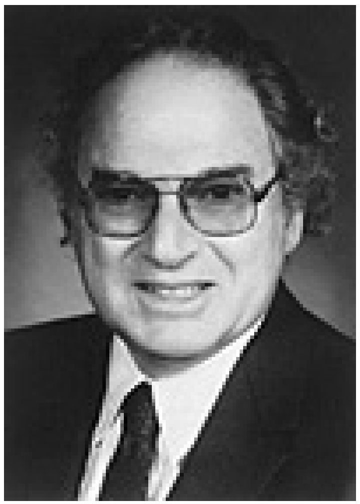
The Nobel Prize in Chemistry 1985

"for their outstanding achievements in the development of direct methods for the determination of crystal structures"



Herbert A. Hauptman

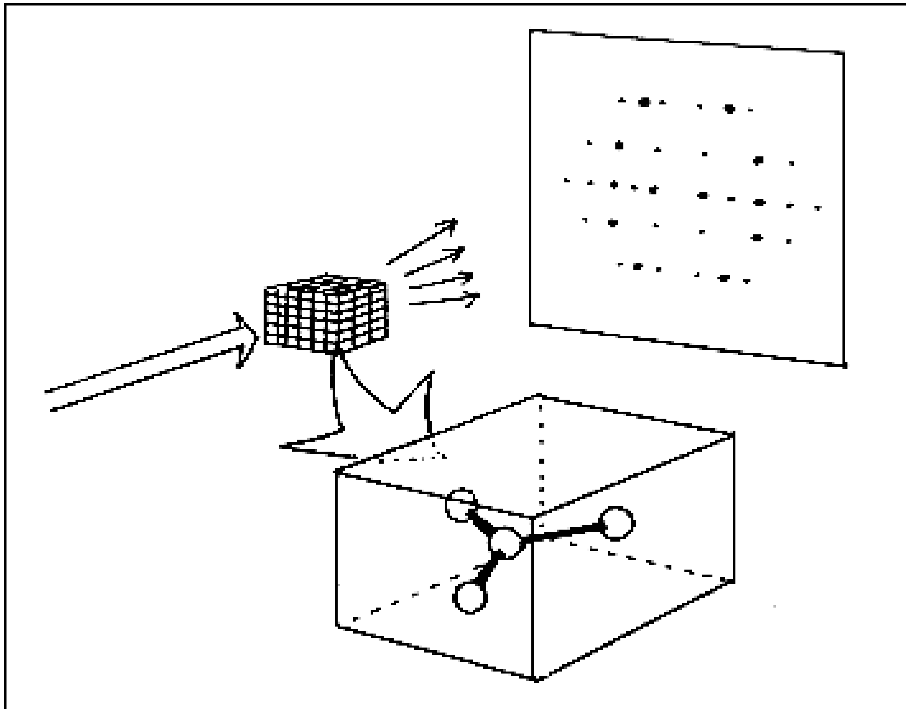
The Medical Foundation of Buffalo
Buffalo, NY, USA
b. 1917

Jerome Karle

US Naval Research Laboratory
Washington, DC, USA
b. 1918

The Nobel Committee Version:

X-rays strike a crystal. The crystal contains a molecule, which is repeated throughout the whole crystal in all directions. The crystal deflects the x-rays in certain definite directions so that the radiation can be seen as spots of different intensity such as in a holographic film. To determine the structure the "phase" of each ray that is deflected must also be known. This determination can be carried out by using the "direct methods".



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

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.

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

$$\begin{vmatrix} F_0 & F_{-\mathbf{h}_1} & F_{-\mathbf{h}_2} \\ F_{\mathbf{h}_1} & F_0 & F_{\mathbf{h}_1-\mathbf{h}_2} \\ F_{\mathbf{h}2} & F_{-\mathbf{h}_1+\mathbf{h}_2} & F_0 \end{vmatrix} = \text{Det} > 0$$

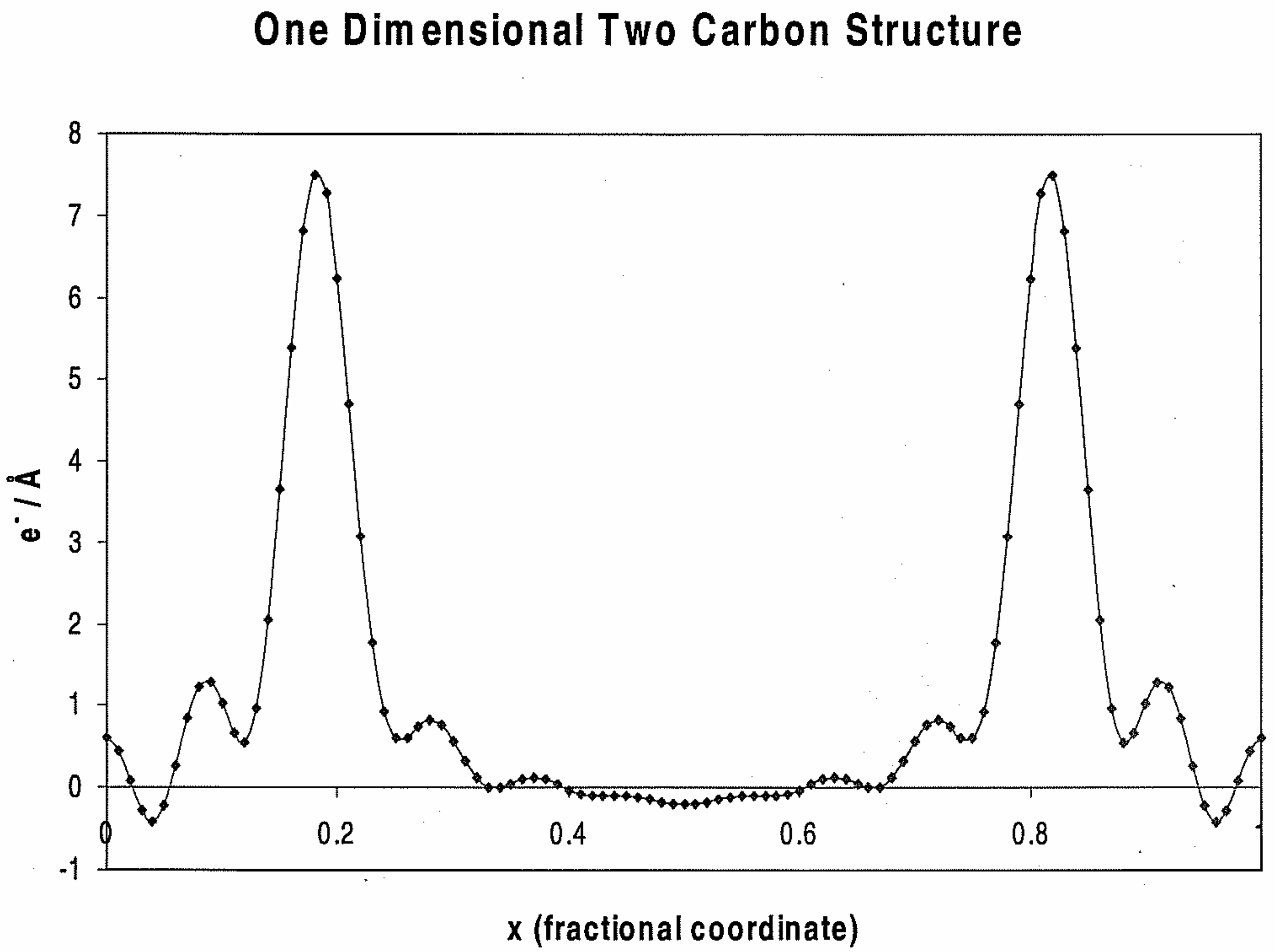
Note φ_{-h} **=-** φ_h and that $e^{i\varphi} + e^{-i\varphi} = 2 \cos \varphi$, so...

$$\mathrm{Det} = F_{\mathbf{0}}(F_{\mathbf{0}}^2 - F_{\mathbf{h}_1}^2 - F_{\mathbf{h}_2}^2 - F_{-\mathbf{h}_1+\mathbf{h}_2}^2) + |F_{\mathbf{h}_1}||F_{\mathbf{h}_2}||F_{-\mathbf{h}_1+\mathbf{h}_2}|\cos(\varphi_{\mathbf{h}_1} - \varphi_{\mathbf{h}_2} + \varphi_{-\mathbf{h}_1+\mathbf{h}_2})$$

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 the above equation the cosine term must be +1, requiring the phase angles to sum to 0, or the signs (S) to be related by $S_{\underline{h}_1} S_{\underline{-h}_2} = S_{\underline{-h}_1 + \underline{h}_2}$ **(but remember here** $S_{\underline{h}} = S_{\underline{-h}}$**).**

What are some combinations of *hkl* that would lead to phase relationships?

.. again



One Dimensional Two Carbon Structure
8
7
6
5
4
3
2
1
0
-1
e⁻ / Å
0
0.2
0.4
0.6
0.8
x (fractional coordinate)

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. 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

the “correct” sign combination is #4, what about the others?

#1 and #6 are incorrect but can only be discarded by looking at other combinations or a higher order determinant

By judicious choice of the first column of structure factors we have a determinant that includes all but F_4, which is relatively weak

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

triplets

maximize $\cos(\varphi_{h_1} - \varphi_{h_2} + \varphi_{-h_1+h_2})$

$-\mathbf{h}_2$ (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

What if these make different predictions?
Tsoucaris says most probable is highest value determinant....average these out by taking the sum

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

The tangent formula...........

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

Origin fixing…

Just as changing all the phases of the odd reflections for the one dimensional carbon atom structure shifted the origin by ½, the shift of origin (now in three dimensions) changes the signs of the structure factors (but of course the intensity is not altered).

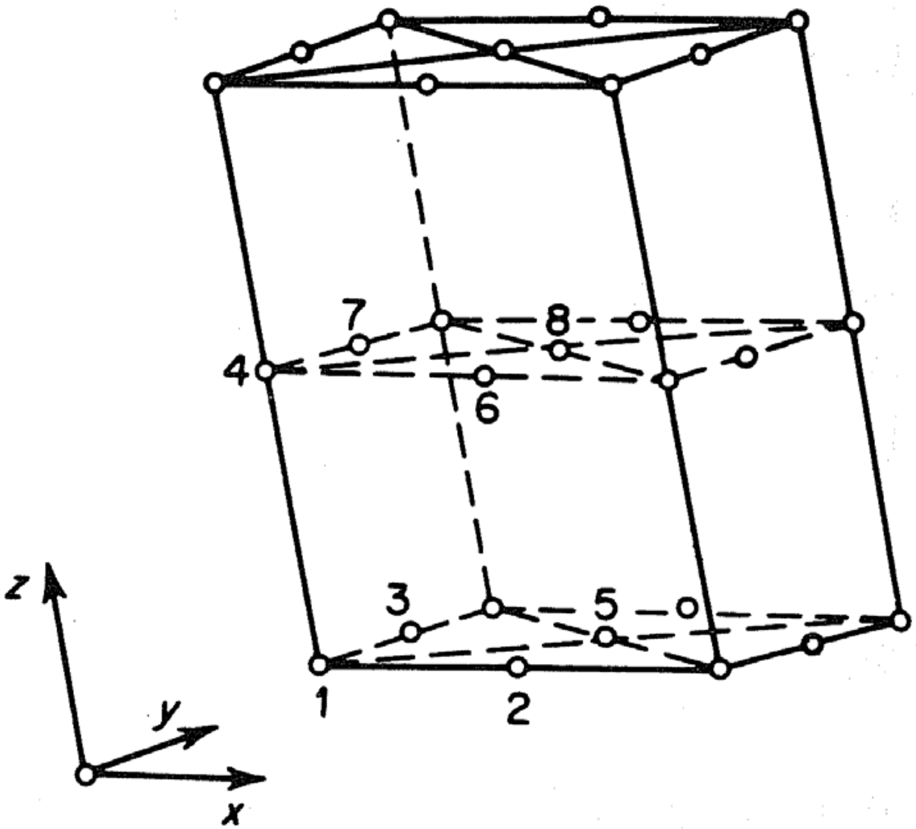


Figure 11.4. Unit cell of a centrosymmetric structure showing centers of symmetry and alternative origins.

TABLE 11.5 Relative Sign Relationships for Possible Origins

		Reflection Kind							
Origin	Shift	eee	oee	eoe	eeo	ooe	oeo	eoo	ooo
1	0	+	+	+	+	+	+	+	+
2	$a/2$	+	−	+	+	−	−	+	−
3	$b/2$	+	+	−	+	−	+	−	−
4	$c/2$	+	+	+	−	+	−	−	−
5	$(a+b)/2$	+	−	−	+	+	−	−	+
6	$(a+c)/2$	+	−	+	−	−	+	−	+
7	$(b+c)/2$	+	+	−	−	−	−	+	+
8	$(a+b+c)/2$	+	−	−	−	+	+	+	−