Table 3. *The final parameters of hydrogen atoms*

	x	y	z	B	Bonded to
H(1)	0·133	1·094	0·659	3·3	N
H(2)	0·027	0·964	0·766	1·7	N
H(3)	0·126	1·073	0·936	6·1	N
H(4)	0·208	0·459	1·035	4·4	O(2)
H(5)	0·165	0·735	0·581	0·3	C(4)
H(6)	0·337	0·979	0·530	3·3	C(2)
H(7)	0·365	1·074	1·010	7·6	C(3)
H(8)	0·381	0·865	1·037	3·9	C(3)
H(9)	0·478	1·017	0·887	4·8	C(3)
H(10)	0·434	0·631	0·695	4·9	C(1)
H(11)	0·488	0·780	0·552	4·1	C(1)
H(12)	0·370	0·664	0·458	2·3	C(1)

$\langle\sigma(x)\rangle=0{\cdot}07$ $\langle\sigma(y)\rangle=0{\cdot}08$ $\langle\sigma(z)\rangle=0{\cdot}07$ Å
$\langle\sigma(B)\rangle=1{\cdot}9$ Å^2

There are significant differences between the temperature factors of the two investigations; the differences may be due to the neglect of absorption. Significant differences are also found in the positional parameters. For example, the difference in x of O(1) is 10σ; x of O(2), 9σ; y of O(1), 12σ; z of O(2), 8σ; z of C(5), 7σ, where the σ's are the standard deviations in our result. It is interesting that all these atoms belong to the carboxyl group; the differences resulted in a large deviation of the configuration of the carboxyl group. Most of the differences of the bond lengths and angles are, however, not significant considering the experimental accuracies. The bond lengths and angles in the valine molecule are shown in Fig. 1; the averages of their standard deviations are 0·009 Å and 0·6° (Parthasarathy's values, 0·018 Å and 1·5°).

Parthasarathy suggested the possible existence of a bifurcated hydrogen bond among N, Cl″ and O(1″) (see Fig. 3 of Parthasarathy's paper). In the present study, however, only the N–H(2)···Cl″ contact seems to be a hydrogen bond, while N···O(1″) seems to be a normal ionic contact, because the H(2)···O(1″) distance of 2·60 Å corresponds to a normal van der Waals contact, and H(2) is too far from the line of N···O(1″), though the distance of N···O(1″) corresponds to that of the weakest hydrogen bond. The N···O(1″) distance is 2·99 Å in Parthasarathy's result but 3·06 Å in ours. The atoms, N, H(2), Cl″ and O(1″), are roughly coplanar, and they are shown in Fig. 2. Many examples have been reported in which four negatively charged atoms approach a protonated amino group within hydrogen-bonding distances and only three of them are hydrogen-bonded.

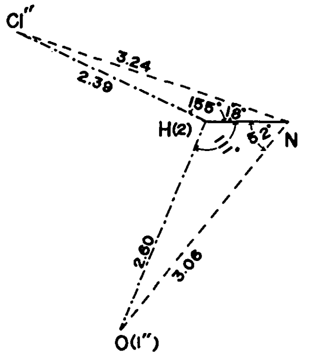

Fig. 2. The environment of the H(2) atom. The contact between H(2) and O(1″) does not seem to be a hydrogen bond.

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Application of the molecular replacement equations to the heavy atom technique.

By Michael G. Rossmann,
Department of Biological Sciences, Purdue University, Lafayette, Indiana, U.S.A.

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A set of non-linear phase equations is derived. The coefficients depend on the knowledge of structure amplitudes and the position of some 'heavy atoms'. An approximate set of phases based on structure factor calculations using the known heavy atoms can then be refined to satisfy the equations exactly. Thus non-heavy-atom structural information can be derived without interpretation of heavy-atom based Fourier maps which may require chemical information and intuition.

Main & Rossmann (1966) and Main (1967) have shown that the use of the molecular replacement equations may lead to a satisfactory solution of the phase problem whenever the asymmetric unit can be divided into different parts with related structures. Let us now divide the unit cell into a known (heavy-atom) and unknown part.

Let the structure factor of reflexion $\mathbf{p}$ of the known part of the cell be $\mathbf{f}_p$. Then by definition,

$$\mathbf{f}_p=\int_U \varrho(\mathbf{x})\exp\{2\pi i\mathbf{p}\,.\,\mathbf{x}\}\,.\,d\mathbf{x}\,, \tag{1}$$

where the integral is taken over the volume U of the known part of the cell, and $\varrho(\mathbf{x})$ is the total electron density distribution within the cell.

But

$$\varrho(\mathbf{x})=\frac{1}{V}\sum_h \mathbf{F}_h\exp\{-2\pi i\mathbf{h}\,.\,\mathbf{x}\}\,.\,d\mathbf{x}\,. \tag{2}$$

Hence by substituting (2) in (1) we have

$$\mathbf{f}_p=\frac{1}{V}\sum_h \mathbf{F}_h\int_U \exp\{2\pi i(\mathbf{p}-\mathbf{h})\,.\,\mathbf{x}\}\,.\,d\mathbf{x}\,.$$

The integral can be easily evaluated if we consider each of the N known atoms to be enclosed in a sphere of radius R and centred at S_n, the total volume enclosed being U. Then

$$\int_U \exp\{2\pi i(\mathbf{p}-\mathbf{h}) . \mathbf{x}\} . d\mathbf{x} = \frac{4\pi R^3}{3} G_{hp} \sum_{n=1}^{N} \exp\{2\pi i(\mathbf{p}-\mathbf{h}) . S_n\} ,$$

where

$$G_{hp} = \frac{3[\sin(2\pi HR) - (2\pi HR)\cos(2\pi HR)]}{(2\pi HR)^3}$$

and

$$H = |(\mathbf{p}-\mathbf{h})| .$$

Hence

$$\mathbf{f}_p = \frac{4\pi R^3}{3V} \sum_h \mathbf{F}_h G_{hp} \left[\sum_{n=1}^{N} \exp\{2\pi i(\mathbf{p}-\mathbf{h}) . \mathbf{S}_n\}\right] . \qquad (3)$$

The equations (3) are of the same form as the molecular replacement equations, although there will be many more significant terms per equation owing to the slower decrease of G as H increases. They express the relationship between the structure factors $\mathbf{F}_h$ when part of the cell is of known structure.

Now $\mathbf{f}_p$ can be calculated and an initial solution of the phases of $\mathbf{F}_h$ can be found from the usual heavy-atom techniques. Improvement of these phases can then be made by the methods described in the paper by Main (1967) in order to achieve better satisfaction of equations (3). Hence the heavy-atom phases may be improved without any chemical knowledge. An application of these equations may therefore be of help when a heavy atom is sufficiently weak not to permit easy recognition of chemical information, when resolution is too poor for recognition of chemical groups, or when approximate phases have been determined by means of poorly isomorphous derivatives.

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Proposed method of separating the particle size and distortion coefficients in line profile analysis.

By T. H. Ungár, *Eötvös University, Budapest* VIII, *Museum körut* 6–8, *Hungary*

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The moments method in X-ray line-profile analysis described by Harrison yields automatically the so-called 'particle-size' coefficients besides the deformation moments. Simple matrix inversion gives the deformation moments multiplied by the particle-size coefficient and, since the zero-order moment has to be equal to one, the particle size coefficient can be obtained directly.

Harrison (1966) has described the possibility of determining the distribution of deformation on the basis of distortion coefficients obtained from X-ray diffraction lines. We should like to contribute to this work by showing that if we do not suppose that the deformation and particle-size coefficients have already been separated by some other method, then the moments method described by Harrison yields automatically the particle-size coefficients besides the deformation moments.

Using the notation of Harrison let us put down the Fourier coefficients of a diffraction line of a cubic crystal expanded by the deformation moments:

$$A_n = A_n^s - \frac{1}{2!}(2\pi h_0 L/a)^2 A_n^s \langle e_L^2 \rangle + \frac{1}{4!}(2\pi h_0 L/a)^4 A_n^s \langle e_L^4 \rangle - \ldots \qquad (1)$$

$$B_n = -(2\pi h_0 L/a) A_n^s \langle e_L \rangle + \frac{1}{3!}(2\pi h_0 L/a)^3 A_n^s \langle e_L^3 \rangle - \ldots \qquad (2)$$

where $\langle e_L^k \rangle$ denotes the kth moment of deformation e_L, index L denotes the averaging distance in the crystal, a is the length of the unit-cell edge in the direction of the diffraction and $h_0^2 = h^2 + k^2 + l^2$.

Harrison (1966) has shown that if the particle-size coefficients A_n^s are known, then by measuring a number of reflexions, say m, the deformation distribution can be determined with the help of equation systems (1) and (2).

Let us construct the vectors $\mathbf{a}_n$ and $\mathbf{b}_n$ from the coefficients A_n and B_n belonging to the same n suffixes but to different reflexions and the vectors $\mathbf{e}_e$ and $\mathbf{e}_o$ from the even and odd moments $\langle e_L^{2k} \rangle$ and $\langle e_L^{2k+1} \rangle$ (where $k = 0,1,2,\ldots m-1$). Here we have supposed that the $2m$th or higher deformation moments can be neglected. Let us further denote the following square matrices of order m by P_n and R_n

$$P_n = \begin{pmatrix} 1 - \frac{1}{2!}(2\pi h_0 L/a)^2 \ldots \\ 1 - \frac{1}{2!}(2\pi h_0' L/a)^2 \ldots \end{pmatrix} \qquad (3)$$

$$R_n = \begin{pmatrix} -(2\pi h_0 L/a) \frac{1}{3!}(2\pi h_0 L/a)^3 \ldots \\ -(2\pi h_0' L/a) \frac{1}{3!}(2\pi h_0' L/a)^3 \ldots \end{pmatrix} , \qquad (4)$$

where each row of the matrix belongs to a certain reflexion, the rows being arranged in increasing order of the reflexions downward.

The equation systems (1) and (2) can be written in the following form:

$$\mathbf{a}_n = A_n^s P_n \mathbf{e}_e \qquad (5)$$

$$\mathbf{b}_n = A_n^s R_n \mathbf{e}_o . \qquad (6)$$