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Crystal Structure Refinement by Least-Squares with the ElectroData Computer.*

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Two programs have been coded and used for least-squares refinement by the ElectroData digital computer with three-dimensional data for crystal structures of classes $2/m$ and 222. Relevant details of the computer are given. The method of calculation and the forms of input and output are described. The rate of operation of each program is stated. An expression for predicting the value of the minimisation function has been tested.

Introduction

The ElectroData Corporation of Pasadena, California, have kindly made time on their Datatron digital-computer system available to this laboratory for typical crystallographic calculations. The computer has been programmed to use the least-squares method to carry out the final refinement stages of structure determinations since these are more readily handled by high-speed digital computers than the less routine and less laborious earlier stages of such analyses. Two programs have been tested and used to date, one is capable of handling structures having space groups derived from the $2/m$–C_{2h} crystal class. It has been checked by refining the structure of ferrocene and used for refinements of the structures of dibenzylphosphoric acid and arsenomethane. The other program is capable of handling structures having space groups derived from the 222–D_2 crystal class. It has been used to refine the structure of histidine hydrochloride monohydrate.

Computer

The computer uses a single address, serial command system. Commands and data are in the form of words consisting of 10 binary coded decimals with an additional position reserved for indicating the sign. Storage space for 4000 words in main memory and 80 words in four 20-word quick-access loops is provided by a magnetic drum. During our work on the machine, a paper tape input by means of a photoelectric reader was available at the rate of 2400 words/min.; tape output was possible at the rate of 55 words/min. and electric typewriter output at the rate of 48 words/min.

With the use of quick-access loops only, with the operand in the counter, all operations except multiplication and division are performed in 2 msec. Multiplication requires 8·5 msec.; division, 10·5 msec. Thus, an isolated addition would require 2 msec. for obtaining the operand from memory, 2 msec. for the actual addition and 2 msec. for storing the sum in memory. The usual procedure is to transfer blocks of 20 words—commands or data—from main memory to the quick-access loops and then use only these words until another block transfer is required. Such a block transfer of 20 words requires 10·5 msec., which is the same time required for referring to a single word in main memory. All operation times quoted in this paragraph are mean times; computers described previously have been significantly faster than this (Bennett & Kendrew, 1952; Ahmed & Cruickshank, 1953; Thompson, Caminer, Fantl, Wright & King, 1954).

The effective speed of this computer is increased by a device for repetition of identical operations on data stored in adjacent memory positions. Special commands, indicated by a negative sign, have the contents of an auxiliary counter, the B register, temporarily added to their address portion during execution. Commands are available for setting the B register and for increasing or decreasing its value by one. Thus the same sequence of operations may be applied to properly located new data with one command changing the B register.

Method

The method of least-squares (Whittaker & Robinson, 1937; Hughes, 1941) was selected because (1) it can be applied as soon as the errors in the positional parameters are small compared with the interatomic distances, (2) parameters of all kinds can be refined simultaneously and a systematic allowance made for their interaction, and (3) a weighting system appropriate to the errors in the observations gives final parameters at least as accurate as those obtained by

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any other method. This method is also well suited to automatic machines for which output should be reduced to a minimum and with which it is desirable to carry out completely automatic iterations.

The program for the $2/m$ crystal class will be discussed in this and later sections of this paper, except for the last section which deals specifically with the program for the 222 class.

For centrosymmetric space groups the most convenient choice for $\Delta(hkl)$ is $\Delta = pK|F_o|-F_c$ where F_c is the calculated structure factor, F_o is the observed structure factor on any scale, K is the scale factor for converting F_o to the absolute scale, and p is the sign of F_c. The criterion that $\sum\limits_{hkl} w\Delta^2$ be a minimum, where w is the weighting factor (properly the reciprocal of the variance of Δ), leads to the normal equations for each of the parameters, ξ_i:

$$-\sum_{hkl} w\Delta \frac{\partial\Delta}{\partial\xi_i} = \left[\sum_{hkl} w\left(\frac{\partial\Delta}{\partial\xi_i}\right)^2\right]\Delta\xi_i + \sum_{hkl}\left(w\frac{\partial\Delta}{\partial\xi_i}\right)\left\{\sum_{j\neq i}\frac{\partial\Delta}{\partial\xi_j}\Delta\xi_j\right\},$$

where $\Delta\xi_i$ is the correction to be applied to ξ_i. If all the parameters are atomic positional coordinates referred to orthogonal axes, and if there is a large number of observations corresponding to a complete three-dimensional survey of reciprocal space, then in every normal equation the second term on the right is negligible. In other circumstances this is not necessarily so, and, in particular, there is a systematically large interaction term between positional coordinates of the same atom referred to the non-orthogonal **a** and **c** axes of a monoclinic structure when β is appreciably greater than 90°. Similarly, there is an interaction between the scale factor and some of the thermal vibration parameters.

Program input

The labor required for preparing data for the computer was reduced to a minimum by (1) having the computer prepare automatically any new tape required for the next stage of refinement as part of the preceding stage, (2) placing constants on tapes separate from those carrying information changing from stage to stage, and (3) conveying as much information as possible per word of input tape while, at the same time, maintaining the potential accuracy of the data at a high level. (In some cases the precision available was greater than might conceivably be required because the available space could not have been utilized if the precision were reduced. The scattering-factor tapes provided for scattering factors and first differences from 00·000 to 99·999. Miller indices on the planes tapes could be as high as 99 with the exception of h, for which the values from 96 to 99 were used as signals; structure factors could take relative values from 0000 to 9999. Positional parameters could be expressed to five decimal places and were restricted to positive values; the individual temperature factors, Q_i, could range from 0·00 to 99·99.)

Apart from the program tape, four different kinds of tape were used to prepare the computer. These were:

(*a*) The structure tape. This carried the number of atoms in the asymmetric unit, the constants $\alpha, \ldots, \delta$ of the expression $\sin^2\theta = \alpha h^2+\beta k^2+\gamma l^2+\delta hl$, where θ is the Bragg angle, the value of the smallest non-zero $K|F_o|$, a code for the quantities to be printed for each reflection, and a code for indicating whether l increased by 1 or 2 between successive reflections.

(*b*) The atomic-scattering-factor tapes. These carried $f(\sin^2\theta)$ and first differences of this function, for $\sin^2\theta = 0{\cdot}00[0{\cdot}01]0{\cdot}99$ for each of the chemical types of atom present.

(*c*) The parameter tape. This carried x_i, y_i, z_i, Q_i and C_i for each of the atoms of the structure where x_i, y_i and z_i are positional parameters, Q_i is the parameter in an individual isotropic temperature factor for each atom, $\exp(-Q_i\sin^2\theta)$, and C_i is a code indicating the chemical type.

(*d*) The planes tapes. These carried hkl and $K|F_o|$ for each plane, and signals indicating either the expression to be used for F_c for the planes following or the end of the planes tape.

The structure tapes were quite short, and only one had to be prepared for each analysis unless the output format was to be altered. The parameter tape was also short, and again only one was made by hand for each analysis because the computer prepared a new parameter tape in passing from stage to stage. The principal preparative labor was the hand punching of the planes tapes. Usable tape could be made and checked at the overall rate of 2·5 words/min., so that the time spent on this was comparable with the machine time for a single iteration.

No planes tape carried more than 400 words. Planes having

$$F_c = 4\Sigma_1^{N/4} f_i' \cos 2\pi(hx_i+lz_i)\cos 2\pi ky_i\,,$$

where f_i' is the scattering factor for the ith atom modified by some suitable temperature factor, were preceded by 0·96; planes having

$$F_c = 4\Sigma_1^{N/4} -f_i' \sin 2\pi(hx_i+lz_i)\sin 2\pi ky_i$$

were preceded by 0·97. The end of a planes tape was indicated by 0·98, and the last planes tape carried 0·99 at the end to indicate the end of the refinement stage. The planes were grouped in blocks all having the same structure-factor expression; they were then arranged in groups of constant k and subgroups of constant h, with l advancing by 1 or 2 within each subgroup. Reflections of the type (hkl) and $(\bar{h}kl)$ were considered as separate subgroups.

Program output

Because of the relatively low maximum output speed the program was designed so that any or all of the output could be suppressed, if it was not needed, without affecting the normal progress of the iterative refinements. The program produced four basic kinds of output:

(*a*) The functions *hkl*, $K|F_o|$, F_c, Δ, which could be printed as each structure factor was computed.

(*b*) Safety (partial totals) tapes. These carried the least-squares totals. They could be punched at the end of the calculations for any planes tape, including the last.

(*c*) The accuracy totals $\Sigma w\Delta^2$, $\Sigma K|F_o|$, $\Sigma|F_c|$, $\Sigma|\Delta|$.

(*d*) Parameter shifts and new parameters. These could be printed at the end of each refinement stage.

(*e*) New parameter tape. This could be punched after (*d*) at the end of each refinement stage.

In case of an interruption the last safety tape punched could be read back into memory so that work carried out before it was made would not have to be repeated. The standard deviations of the parameters could be found from the number of degrees of freedom and the final values of $\Sigma w\Delta^2$ and the least-squares totals. The last three accuracy totals were used for computing R factors and for testing the scale factor. The parameter shifts were used as a check on the progress of the refinement. The new parameter tape was of use only if the following refinement stage was interrupted, since the new parameters were also stored in memory for use in that stage.

Program speed, efficiency and capacity

The final results of the structure analyses of ferrocene and dibenzyl phosphoric acid will be published at another time. Ferrocene contains an iron atom on a center of symmetry and five carbon atoms in general positions (hydrogen atoms are ignored). The total number of observed reflections was 1174. The total time for a complete refinement stage in which *hkl*, $K|F_o|$, and Δ were not printed was 115 min., of which 5 min. were used for the initial input operations. Dibenzyl phosphoric acid contains one phosphorus, four oxygen, fourteen carbon and fifteen hydrogen atoms in the asymmetric unit and 2875 reflections were observed. Initial input occupied 10 min. and a complete refinement stage, in which the hydrogen atoms were omitted and *hkl*, $K|F_o|$ and Δ were not printed, required 660 min.

The times given above indicate operating speeds of 60 and 85 atom-planes/min. The exact rate depends on (1) the total number of atoms, (2) the number of tables of scattering factors required, (3) the number of different temperature factors assigned, and (4) the number of quantities to be printed for each reflection.

A quantitative check on the efficiency of convergence of the refinement process was made during the analysis of the **b** projection of dibenzyl phosphoric acid. The decrease of the minimisation function $\Sigma w\Delta^2$ produced by a given set of parameter changes can be predicted by:

$$\delta(\Sigma w\Delta^2) = -\Sigma_i \delta\xi_i \left[\sum_{hkl} w\Delta \frac{\partial\Delta}{\partial\xi_i} \right],$$

where

$$\delta(\Sigma w\Delta^2) = \text{decrease of } \sum_{hkl} w\Delta^2 .$$

Strictly, this equation is valid only for a system of linear equations. The results presented here, however, indicate that it is accurate when least-squares adjustment of atomic positions is based on X-ray data from Cu $K\alpha$ radiation and the r.m.s. shift of position is not more than 0·07 Å. Table 1 gives the observed and calculated changes in $\Sigma w\Delta^2$ for the five sets of shifts in this projection analysis. No two atoms of the structure are separated by less than 0·7 Å in this projection so that neglect of off-diagonal terms in the least-squares is a reasonably good approximation. It can be seen that the program was very efficient at first but that there was some lack of convergence in the last two stages, probably because some of the neglected off-diagonal terms were significant.

Table 1. *Efficiency of refinement*

			Predicted decrease		
Stage	R.m.s. positional shift (Å)	Actual decrease in $\Sigma w\Delta^2$	Total	Positional parameters	Vibrational parameters
1	0·075	45·21	43·92	43·92	—
2	0·035	8·92	9·92	9·92	—
3	0·031	8·90	7·85	7·85	—
4	0·024	17·76	21·18	4·12	17·06
5	0·031	1·96	5·00	2·43	2·57

The program accommodates up to 50 atoms in the asymmetric unit and the least-squares totals for an ordinary organic structure with 50 atoms and 3000 reflections could probably be accumulated without overflow in the counter. In any case, overflow could be avoided with little labor by rescaling the F_o and f_i values. This ability to handle a large number of atoms allows the inclusion of hydrogen atoms in the final stage of refinement for almost all structures. Contributions of all atoms can be included in the structure factors while least-squares calculations may be made, if desired, only for parameters of atoms other than hydrogen.

Calculation procedure

The computer executed a preliminary program which calculated and permanently stored the cos and sin of either $2\pi(z_i)$ or $2\pi(2z_i)$, depending upon the code on the structure tape; the use for these quantities will be explained below.

The planes tape was then read into storage and the computer worked through the reflections one at a time calculating all quantities for all atoms before going to the next reflection. The signal on the planes tape indicating the beginning of a set of reflections of a given type set the program for combining the trigonometric functions in the proper fashion for the structure factors and the least-squares derivatives. The computer tested each *hkl* for change of *k* or *h* and:

(*a*) on change of *k*, computed cos and sin of $2\pi k y_i$ and $2\pi(hx_i+lz_i)$ for all atoms from the arguments, and

(*b*) on change of *h*, computed cos and sin of $2\pi(hx_i+lz_i)$ for all atoms from the arguments, or

(*c*) on no change of *k* or *h* used cos and sin of $2\pi(hx_i+lz_i)$ and of $2\pi(z_i)$ or $2\pi(2z_i)$ in the addition formulae for cos and sin of $2\pi \times (hx_i+(l+1)z_i)$ or $2\pi(hx_i+(l+2)z_i)$.

The efficiency of calculation was greatest when the axes were chosen so that the maximum possible value of c/L was obtained, where c is the cell dimension and $L = 1$ or 2 is the increment in l between successive reflections.

All cos and sin values obtained from the arguments were computed using an economized four-term series for the sine (Hastings, 1951). The resulting high relative accuracy of $\pm 1 \times 10^{-6}$ was required because of the cumulative error introduced by the use of the addition formulae. (When cos (nx) and sin (nx) are computed from cos (x) and sin (x) the absolute values of the errors in cos $(x)+i$ sin (x) and cos $(nx)+i$ sin (nx) are as $1:n$ if all errors are small.)

Once preliminary trigonometric computations were completed for a given reflection, $\sin^2\theta$ was calculated and used for finding the atomic scattering factors, f_i, by interpolation in the stored tables. To save computing time no allowance was made for anisotropic thermal vibrations. However, an isotropic temperature factor for each atom of the form $\exp(-Q_i \sin^2\theta)$ permitted a better fit to the observed data than a single isotropic temperature factor. The higher-order digits of $-Q_i \sin^2\theta$ were used to find sub-factors of the temperature factors in short exponential tables and the lower-order digits were used to construct an additional sub-factor from a two-term series. The sub-factors were combined and then used to obtain f_i' from f_i.

F_c and Δ were evaluated from the prepared trigonometric and atomic-scattering functions and an appropriate decision was made concerning the weight of the plane in the least-squares refinement. Four different classes of plane were distinguished, where $F_{\text{min.}}$ is the smallest structure factor observed:

(*a*) $K|F_o| > 4K|F_{\text{min.}}|$, $\sqrt{w} = 1/(K|F_o|)$;

(*b*) $0 < K|F_o| \le 4K|F_{\text{min.}}|$, $\sqrt{w} = 1/(4K|F_{\text{min.}}|)$;

(*c*) $F_o = 0$, $|F_c| \ge K|F_{\text{min.}}|$, $\sqrt{w} = 1/(4K|F_{\text{min.}}|)$ and for this class $\Delta = pK|F_{\text{min.}}|-F_c$ was used;

(*d*) $F_o = 0$, $|F_c| < K|F_{\text{min.}}|$, $\sqrt{w} = 0$.

For planes of classes (*a*), (*b*) and (*c*) the machine next executed the least-squares section of the program. For planes of class (*d*) this section was omitted. The totals accumulated by the least-squares section were:

$$\begin{array}{cccc}
\sum\limits_{hkl}\left(\frac{\sqrt{w}}{2\pi}\frac{\partial\Delta}{\partial x_i}\right)^2 & & \sum\limits_{hkl}\left(\frac{\sqrt{w}}{2\pi}\frac{\partial\Delta}{\partial x_i}\right)\left(\frac{\sqrt{w}}{2\pi}\frac{\partial\Delta}{\partial z_i}\right) & \sum\limits_{hkl}(\sqrt{w}\Delta)\left(\frac{\sqrt{w}}{2\pi}\frac{\partial\Delta}{\partial x_i}\right) \\
 & \sum\limits_{hkl}\left(\frac{\sqrt{w}}{2\pi}\frac{\partial\Delta}{\partial y_i}\right)^2 & & \sum\limits_{hkl}(\sqrt{w}\Delta)\left(\frac{\sqrt{w}}{2\pi}\frac{\partial\Delta}{\partial y_i}\right) \\
 & & \sum\limits_{hkl}\left(\frac{\sqrt{w}}{2\pi}\frac{\partial\Delta}{\partial z_i}\right)^2 & \sum\limits_{hkl}(\sqrt{w}\Delta)\left(\frac{\sqrt{w}}{2\pi}\frac{\partial\Delta}{\partial z_i}\right) \\
 & & \sum\limits_{hkl}\left(\sqrt{w}\frac{\partial\Delta}{\partial Q_i}\right)^2 & \sum\limits_{hkl}(\sqrt{w}\Delta)\left(\sqrt{w}\frac{\partial\Delta}{\partial Q_i}\right)
\end{array}$$

In the calculation of parameter changes by the final program, correction was made for the factor of 2π omitted from each derivative with respect to a positional parameter.

The quantities associated with each reflection which had previously been selected by the structure tape code were then printed, and the computer proceeded to the next reflection.

The remainder of the computation, the final program, has been briefly indicated in describing the output of the program. It remains to be said that the individual isotropic temperature factors were always evaluated directly from the simple linear equations, without reference to any error in the scale factor, in order to reduce the length of the computations. The operator could choose: (*a*) to refine the isotropic temperature factors by means of the corrections produced by the machine; (*b*) to leave the temperature factors unchanged; (c) to compromise by making alterations by hand on the new parameter tape, so that the number of temperature factors evaluated was small but the main vibrational features of the structure were included.

If the totals $\Sigma K|F_o|$ and $\Sigma|F_c|$ indicated an error in the scale factor it was possible to rescale the $K|F_o|$'s by a short extra program as they were inserted in memory. If necessary, a tape carrying the new $K|F_o|$'s in place of the old could be punched at the same time.

The 222 program

The program designed for the 222 crystal class was similar in all respects to the program just described. Some details concerning changes and slight improvements used for the second program are of interest.

For non-centrosymmetric space groups Δ may be taken as $K|F_o|-|F_c|$ or $K^2|F_o|^2-|F_c|^2$; the difference in the final parameters obtained with either choice can be shown to be negligible if the proper weighting factors are used (V. Schomaker, private communication). The former was selected since it offered a slight advantage in allowing more convenient magnitudes for some intermediate quantities.

The output associated with each reflection was extended by making $K|F_o|\cos\alpha$ and $K|F_o|\sin\alpha$ or $\Delta\cos\alpha$ and $\Delta\sin\alpha$, where α is the phase angle, available for printing in case data for an F_o or (F_o-F_c) synthesis should be desired at some stage in the analysis.

If the original scale factor needed correction when using the $2/m$ program, it was necessary to use an independent program to obtain new values of $K|F_o|$. The 222 program used planes tapes with $|F_o|$ on any scale and a value of K taken from the parameter tape; the values of $K|F_o|$ were generated by the computer. Thus a change in the scale factor merely required a change in K on the parameter tape or in memory.

Instead of calculating the last three accuracy totals,

$$\sum_{hkl} K|F_o|,\ \sum_{hkl}|F_c| \quad\text{and}\quad \sum_{hkl}|\Delta|\,,$$

the 222 program calculated the following terms of the least-squares equations involving the scale factor and an overall isotropic temperature factor:

$$\sum_{hkl} w\left(\frac{\partial\Delta}{\partial K}\right)^2 \qquad \sum_{hkl} w\left(\frac{\partial\Delta}{\partial K}\right)\cdot\left(\frac{\partial\Delta}{\partial\bar{Q}}\right) \qquad \sum_{hkl} w\Delta\frac{\partial\Delta}{\partial K}$$

$$\sum_{hkl} w\left(\frac{\partial\Delta}{\partial\bar{Q}}\right)^2 \qquad \sum_{hkl} w\Delta\frac{\partial\Delta}{\partial\bar{Q}}$$

where $\partial\Delta/\partial\bar{Q} = \sin^2\theta . F_c$.

At the end of a refinement stage ΔK and $\Delta\bar{Q}$ were evaluated from these totals and printed along with the ΔQ_i's calculated as described for the $2/m$ program. Usually K and each Q_i would then be corrected by ΔK and $\Delta\bar{Q}$ respectively and the next refinement stage would be begun. However, if it was desired to assign individual isotropic temperature factors for each atom the operator could choose to apply the ΔQ_i's as corrections to the Q_i's.

This program was used to refine the structure of histidine hydrochloride monohydrate. Each refinement stage, for 13 atoms and 1200 planes, required 6 hr. of machine time.

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