

- FIGGIS, B. N., GERLOCH, M. & MASON, R. (1964). *Acta Cryst.* **17**, 506.
 HAMILTON, W. C., ROLLETT, J. S. & SPARKS, R. A. (1965). *Acta Cryst.* **18**, 129.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
 JEFFERY, J. W. (1947). *Nature, Lond.* **159**, 610.
 JEFFERY, J. W. (1963). *J. Sci. Instrum.* **40**, 494.
 JEFFERY, J. W. & ROSE, K. M. (1964). *Acta Cryst.* **17**, 343.
 JEFFERY, J. W. & WHITAKER, A. (1965). *Acta Cryst.* **19**, 963.
 KENNARD, O., SPEAKMAN, J. C. & DONNAY, J. D. H. (1967). *Acta Cryst.* **22**, 445.
 MILLS, O. S. (1961). In *Computing Methods and the Phase Problem in X-ray Crystal Analysis*, Ed. PEPINSKY, R., ROBERTSON, J. M. & SPEAKMAN, J. C., p.121. London: Pergamon Press.
 ROLLETT, J. S. & SPARKS, R. A. (1960). *Acta Cryst.* **13**, 273.
 ROSE, K. M. (1965). Ph.D. Thesis, London Univ.
 ROSE, K. M. & JEFFERY, J. W. (1964). *Acta Cryst.* **17**, 21.
 SCOULOUDI, H. (1953). *Acta Cryst.* **6**, 651.
 ZACHARIASEN, W. H. (1963). *Acta Cryst.* **16**, 1139.

Acta Cryst. (1968). **B24**, 662

On a Simple Approximate Matrix in the Least-Squares Determination of Positional Parameters

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The use of a simple approximate matrix in the least-squares determination of positional parameters with X-ray data is discussed. In the approximate matrix the summation over the structure-factor derivatives is no longer carried out, but rather, expected values of the matrix elements are used. The approximate matrix consists of a 3×3 block-diagonal matrix. Each block contains the metric tensor of the crystal, a factor being the square of the number of the electrons of the particular atom, and a universal scale factor. The approximation becomes more legitimate as more structure factors are used. It is shown theoretically that the quality of the approximation can be improved when fewer parameters are refined. Hence the approximation is improved when the number of parameters is reduced by introducing stereochemical restraints. The approximation is tested numerically by means of criteria which have been introduced by Sparks. It is concluded that the approximation is sufficient in the initial stages of a refinement for 1000, 2000, and 5000 data with about 27, 47, and 80 parameters respectively.

Introduction

In least-squares refinement of crystal structures one often does not use the full matrix in the normal equations, but rather approximations (diagonal matrix, block-diagonal matrix *etc.*) in order to save storage space and computing time. As is well known, the use of approximations is permissible because the least-squares postulate only requires that the sequence of the right-hand sides of the normal equations shall converge towards zero (at the correct structure minimum). The form of the matrix is unimportant as long as it ensures that convergence occurs at the correct structure minimum.

Recently a further, very rough approximation for the normal matrix of positional parameters of the single atoms was described by Scheringer (1965*a*). This approximation, however, was intended to be used for re-adjusting positional parameters of the single atoms by means of a set of stereochemical restraints. In the present paper we shall investigate how far this approximation may also be used for the direct refinement of positional parameters. As the calculation of the approximate matrix is very rapid, one could save much computing time. The approximation will normally be too poor for the refinement of the parameters of the

single atoms, but it can be improved by introducing stereochemical restraints. In the following we shall establish this theoretically; further we shall give some criteria to judge the quality of a given approximation [similar to those given by Sparks (1961)], and we shall give some numerical values of the criteria with two structures. With the numerical results thus obtained we shall estimate the range (number of data, number of parameters) in which the approximation may be used.

The approximate matrix

For positional parameters of the single atoms the normal matrix \mathbf{A} can be approximated by

$$\mathbf{Q} = k\mathbf{ZH} \quad (1)$$

(*cf.* Scheringer, 1965*a*). k is a scale factor which can be roughly determined by setting trace (\mathbf{A}) equal to trace (\mathbf{Q}). (How the scale can be improved will be discussed below.) \mathbf{ZH} is a 3×3 block-diagonal matrix with elements $Z_i^2 h_{st}$ for the i th block. Z_i is the number of electrons of the i th atom; h_{st} is a component of the metric tensor of the unit cell. \mathbf{Q} is positive-definite and symmetric. The assumptions made in the approximation are:

- (i) The scattering curves f of all atoms have the same shape: $f_i = f$. Z_i (unitary form factors).
- (ii) The structure-factor data, expressed as points in reciprocal space, are of equal accuracy in each infinitesimal spherical shell of reciprocal space (and hence have to be given a uniform weight in each shell).
- (iii) The density of the structure-factor points in reciprocal space is infinitely high.

If there are chemically different atoms and anisotropic vibrations present, the first assumption means a small systematic deviation from the true structure. The second assumption contains an experimental condition which can often be fulfilled. The third assumption becomes better as more data become available, *i.e.* the larger the unit cell.

Let the normal equations for the single-atom parameters (without constraints) be

$$\mathbf{A}\boldsymbol{\varepsilon}^{\text{free}} = \mathbf{B} \quad (2)$$

(\mathbf{B} can never be expressed by an approximation, because the summation terms in \mathbf{B} contain the measured data, hence no averaging is possible. Thus \mathbf{B} has always to be fully computed.) Using \mathbf{Q} instead of \mathbf{A} we obtain different shifts $\boldsymbol{\varepsilon}^{\text{free}}$, which we denote by $\boldsymbol{\varepsilon}_Q^{\text{free}}$. Similarly to (2) we now have

$$\mathbf{Q}\boldsymbol{\varepsilon}_Q^{\text{free}} = \mathbf{B} \quad (3)$$

From (2) and (3) it follows that

$$\boldsymbol{\varepsilon}_Q^{\text{free}} = \mathbf{Q}^{-1}\mathbf{A}\boldsymbol{\varepsilon}^{\text{free}} \quad (4)$$

If we introduce stereochemical restraints, the equations of constraint have to be put into the form

$$\boldsymbol{\varepsilon}^{\text{con}} = \mathbf{R}\boldsymbol{\varepsilon}^{\text{red}} + \mathbf{R}^0 \quad (5)$$

(Scheringer, 1965*a*). $\boldsymbol{\varepsilon}^{\text{con}}$ are the shifts of the single atoms under the restraints. $\boldsymbol{\varepsilon}^{\text{red}}$ are the shifts which are determined in the reduced system of the normal equations. With the reduced approximate matrix $\mathbf{Q}^{\text{red}} = \mathbf{R}^T\mathbf{Q}\mathbf{R}$ we obtain for the reduced shifts

$$\boldsymbol{\varepsilon}_Q^{\text{red}} = \mathbf{Q}^{\text{red}-1}\mathbf{A}^{\text{red}}\boldsymbol{\varepsilon}^{\text{red}} \quad (6)$$

similar to (4). $\mathbf{A}^{\text{red}} = \mathbf{R}^T\mathbf{A}\mathbf{R}$ (the superscript T denotes the transposed matrix).

It is intended to use the approximation mainly in the initial stage of refinement. Here it is meaningful to introduce as many constraints as possible in order to improve convergence. At the same time many constraints improve the quality of the approximation, as we shall show below.

In an actual computation with the approximate matrix, the scale factor k has first to be determined by a single computation of the trace (or some diagonal elements) of the true normal matrix. After the scale is adjusted by setting $\text{trace}(\mathbf{Q}) = \text{trace}(\mathbf{A})$, a partial shift factor has normally to be applied. According to Sparks (1961) the optimum shift factor is

$$\eta_{\text{op}} = \frac{2}{\lambda_{\text{max}} + \lambda_{\text{min}}} \quad (7)$$

λ_{max} and λ_{min} are the maximum and minimum eigenvalues of $\mathbf{Q}^{-1}\mathbf{A}$ respectively. Values of η_{op} will be given below. In addition, the scale could be controlled by allowing the shifts not to exceed a certain preset value, *e.g.* 0.1 Å.

Estimated standard deviations for the constrained parameters of the single atoms may be calculated according to

$$\sigma_i(\boldsymbol{\varepsilon}^{\text{con}}) = \{[\mathbf{R}(\mathbf{R}^T\mathbf{A}\mathbf{R})^{-1}\mathbf{R}^T]_{ii} \sum w(\Delta F)^2 / (n-p)\}^{1/2} \quad (8)$$

(*cf.* Linnik, 1961). $\sum w(\Delta F)^2$ refers to structure factors; n is the number of independent data, and p the number of the reduced parameters. In (8) it is assumed that the constraints are absolutely valid, whereas in practice they are based on experimental data. Furthermore, we have only \mathbf{Q} instead of \mathbf{A} . Nevertheless (8) may be used with these limitations as a rough estimate of $\sigma_i(\boldsymbol{\varepsilon}^{\text{con}})$ in the initial stage of the refinement.

Criteria for the quality of an approximation

Sparks (1961) developed criteria (and applied them to the example of anthracene) which describe the quality of an approximate matrix compared to the full matrix. These criteria are based on the eigenvalues λ_i of $\mathbf{Q}^{-1}\mathbf{A}$ (which are all positive). In order to be able to compare our results with Sparks's anthracene values, we shall use his μ criterion:

$$\mu = \frac{2\lambda_{\text{min}}}{\lambda_{\text{max}} - \lambda_{\text{min}}}$$

μ is a measure of the speed of convergence of an approximate matrix towards the true matrix.

As a further criterion we use the condition number γ of $\mathbf{Q}^{-1}\mathbf{A}$

$$\gamma = \frac{\lambda_{\text{min}}}{\lambda_{\text{max}}}, \quad \gamma \leq 1$$

The better the approximate matrix, the closer γ is to 1. The values of μ and γ do not depend on the shift factor η_{op} , but it is assumed that η_{op} is applied. μ and γ are invariant with respect to any non-singular linear transformation of the parameter shifts $\boldsymbol{\varepsilon}$. This means that the values of μ and γ do not depend on the particular description that has been chosen for the structure.

In order to recognize immediately how the shifts $\boldsymbol{\varepsilon}$ are influenced by the approximation we also use an R criterion for the elements of $\boldsymbol{\varepsilon} - \eta_{\text{op}}\boldsymbol{\varepsilon}_Q$

$$\mathbf{R}(\boldsymbol{\varepsilon}) = \{ \sum (\boldsymbol{\varepsilon} - \eta_{\text{op}}\boldsymbol{\varepsilon}_Q)^2 / \sum \boldsymbol{\varepsilon}^2 \}^{1/2},$$

$\boldsymbol{\varepsilon}$ being $\boldsymbol{\varepsilon}^{\text{free}}$ or $\boldsymbol{\varepsilon}^{\text{red}}$ respectively. A disadvantage of the $\mathbf{R}(\boldsymbol{\varepsilon})$ criterion is that by even a few different signs of $\boldsymbol{\varepsilon}$ and $\boldsymbol{\varepsilon}_Q$ the $\mathbf{R}(\boldsymbol{\varepsilon})$ value is rather more increased than the quality of the approximate matrix is diminished. A further disadvantage is that the $\mathbf{R}(\boldsymbol{\varepsilon})$ value is not invariant with respect to non-orthogonal linear transformations. Thus the $\mathbf{R}(\boldsymbol{\varepsilon})$ value depends on the particular description chosen for the structure. Therefore we attach more significance to the μ and γ criteria than to the $\mathbf{R}(\boldsymbol{\varepsilon})$ values.

The reduction of the set of parameters

In the following we want to compare the qualities of the approximations \mathbf{Q} and $\mathbf{Q}^{\text{red}} (= \mathbf{R}^T \mathbf{Q} \mathbf{R})$. Both the μ and γ criteria show that an approximation becomes better the less the spectrum of the eigenvalues of $\mathbf{Q}^{-1} \mathbf{A}$ spreads. With the introduction of equations of constraint the spectrum will in general be narrowed, *i.e.* the following inequalities hold

$$\begin{aligned} \lambda_{\min}\{\mathbf{Q}^{\text{red}-1} \mathbf{A}^{\text{red}}\} &\geq \lambda_{\min}\{\mathbf{Q}^{-1} \mathbf{A}\} \\ \lambda_{\max}\{\mathbf{Q}^{\text{red}-1} \mathbf{A}^{\text{red}}\} &\leq \lambda_{\max}\{\mathbf{Q}^{-1} \mathbf{A}\}. \end{aligned} \quad (7)$$

The formal proof of the inequalities (7) is given in the Appendix. We note that (7) does not only hold for the approximation \mathbf{Q} , but for any positive-definite and symmetric approximate matrix. Although the number and the type of the constraints do not enter in the proof of (7), it is obvious that the quality of the approximation becomes better as more constraints are introduced. The relations (7) can also be interpreted in a different manner: By \mathbf{Q}^{red} and \mathbf{A}^{red} we may understand principal submatrices of \mathbf{Q} and \mathbf{A} respectively, where \mathbf{Q}^{red} must be a closed block on the diagonal of \mathbf{Q} (not correlated to the residual matrix). The relations (7) hold for any positive-definite and symmetric matrix in this second interpretation. This is shown in the Appendix. The relations (7), interpreted in this way, are important for a filter technique for positional parameters (Scheringer, 1968): By filtering, some of the eigenshifts are excluded from the refinement. This means that the (diagonal) matrix used is a submatrix of the full diagonal matrix, and (7) can be applied. Therefore the quality of the approximation \mathbf{Q} is generally improved when the filter technique is applied.

Numerical results

We have tested the approximation \mathbf{Q} by using the above criteria with the structures of phenol (PH) (Scheringer, 1963), and of 1,3,5-triphenylbenzene (TR) (Farag, 1954). For comparison we have also computed values of the criteria for the diagonal approximation with structure-factor derivatives. (With the two structures, the diagonal matrix is a reasonable approximation, since all angular lattice constants are equal to 90° .) For both structures a poor, but still refinable trial structure has been chosen. Both sets of X-ray data are three-dimensional, but not very accurate. In order to examine the influence of the number of data, we have computed values of the criteria for the full sets of data (PH, 679 data; TR, 480 data), and for reduced sets of low-angle data (PH, 250 data; TR, 200 data). All data were given unit weight. In order to examine the influence of the number of parameters, we have computed the matrix with the following numbers of parameters of the PH and TR trial structure respectively: PH, 2 molecules (12 rigid-body parameters, 42 single-atom parameters; Table 1), and 1 molecule (6 and 21 parameters respectively; Table 2); TR, 3 phenyl groups

(18 rigid-body parameters, 54 single-atom parameters; Table 3), and 1 group (6 and 18 parameters respectively; Table 4). We determined the scale factor k by setting trace (\mathbf{Q}) equal to trace (\mathbf{A}). In Tables 1–4 values of μ , γ , η_{op} , and $R(\epsilon)$ are listed.

Table 1. Values of μ , γ , η_{op} and R for phenol

Full set of data: 679 reflexions; reduced set: 250 reflexions. Number of single-atom parameters 42 (14 atoms); number of rigid-body parameters 12 (2 molecules).

There are two rows of values listed for each set of parameters: the upper row refers to the approximation \mathbf{Q} , the lower row to the structure-factor diagonal matrix. The same holds for Tables 2, 3, and 4.

Phenol, 679 data	μ	γ	η_{op}	$R(\epsilon)$
Single-atom parameters	0.32	0.14	0.83	0.41
	0.45	0.18	0.94	0.39
Reduced parameters	0.53	0.21	0.82	0.74
	0.81	0.29	0.96	0.76
Phenol, 250 data				
Single-atom parameters	0.11	0.05	0.77	0.58
	0.12	0.06	0.83	0.55
Reduced parameters	0.44	0.18	0.73	0.89
	0.61	0.23	0.83	0.85

Table 2. Values of μ , γ , η_{op} and R for phenol

The same as Table 1, except: number of single-atom parameters 21 (7 atoms); number of rigid-body parameters 6 (1 molecule).

Phenol, 679 data	μ	γ	η_{op}	$R(\epsilon)$
Single-atom parameters	0.56	0.22	0.76	0.39
	0.89	0.31	0.95	0.35
Reduced parameters	1.94	0.49	0.80	0.85
	3.04	0.60	0.87	0.70
Phenol, 250 data				
Single-atom parameters	0.14	0.06	0.76	0.67
	0.18	0.08	0.92	0.65
Reduced parameters	1.12	0.36	0.77	1.13
	1.42	0.42	0.85	0.98

Table 3. Values of μ , γ , η_{op} and R for 1,3,5-triphenylbenzene

Full set of data: 480 reflexions; reduced set: 200 reflexions. Number of single-atom parameters 54 (18 atoms); number of rigid-body parameters 18 (3 phenyl groups).

1,3,5-Triphenylbenzene, 480 data	μ	γ	η_{op}	$R(\epsilon)$
Single-atom parameters	0.18	0.08	1.04	0.46
	0.20	0.09	0.93	0.47
Reduced parameters	0.22	0.10	1.00	0.35
	0.26	0.11	0.94	0.40
1,3,5-Triphenylbenzene, 200 data				
Single-atom parameters	0.06	0.03	0.71	0.68
	0.06	0.03	0.69	0.67
Reduced parameters	0.12	0.06	0.62	0.96
	0.16	0.07	0.69	1.03

Table 4. Values of μ , γ , η_{op} and R for 1,3,5-triphenylbenzene

The same as Table 3, except: number of single-atom parameters 18 (6 atoms); number of rigid-body parameters 6 (1 phenyl group).

1,3,5-Triphenylbenzene, 480 data				
	μ	γ	η_{op}	$R(\epsilon)$
Single-atom parameters	0.82 0.84	0.29 0.30	0.97 0.91	0.44 0.45
Reduced parameters	1.30 1.37	0.39 0.41	0.93 0.87	0.25 0.27
1,3,5-Triphenylbenzene, 200 data				
Single-atom parameters	0.14 0.17	0.07 0.08	0.83 0.87	0.60 0.54
Reduced parameters	0.18 0.22	0.08 0.10	0.66 0.72	0.80 0.76

The values of μ and γ are in all cases better for the smaller sets of parameters (Tables 2 and 4) than for the larger sets (Tables 1 and 3), as predicted by the theory; *cf.* relations (7). (The approximate matrix \mathbf{Q}^{red} used in the case of Table 2 is a closed submatrix of the approximate matrix \mathbf{Q} used in the case of Table 1. The same holds for Tables 4 and 3.) γ is roughly inversely proportional to the number of equivalent parameters (*i.e.* to the number of groups or atoms respectively). Similarly the values of μ and γ are in all cases better for the rigid-body parameters than for the single-atom parameters, as predicted by the theory; *cf.* relations (7). With the rigid-body parameters, μ is larger by a factor of about 1.3–5.0, γ by a factor of about 1.5–8.0. The $R(\epsilon)$ -values are often worse with the rigid-body parameters than with the single-atom parameters. Probably the description of the structure with rigid-body parameters causes those shifts to become numerically large which are likely to have an incorrect sign. In all cases the full sets of data give better values of the criteria than the reduced sets. It is worthy of note that the results obtained with the diagonal matrix, computed with SF derivatives, are insignificantly better than those obtained with the approximation \mathbf{Q} . The values of μ and γ for the SF diagonal matrix are in all cases larger by a factor of no more than 1.54.

In Table 5 we give a survey of the incorrect signs of the shifts which result from the use of the approx-

imate matrices. The percentage of incorrect signs is least with the rigid-body parameters and with the full sets of data (PH+TR, \mathbf{Q} , 12.9%; PH+TR, SF diagonal matrix, 9.2%). Out of 522 signs with the SF diagonal matrix only 3 signs more were correctly computed than with the approximate matrix \mathbf{Q} .

We further conclude from the tables that the optimum shift factor η_{op} has an average value of 0.90 for the full sets of data, and an average value of 0.75 for the reduced sets of data.

It is interesting to compare our values of μ and γ (Tables 1 and 3) with those computed by Sparks (1961, Table 1) for the SF diagonal approximation in the case of anthracene. The tables show that our values are considerably better. The reasons are as follows: The unit cell of anthracene is strongly monoclinic ($\beta = 124^\circ$) and with the pure diagonal approximation those off-diagonal terms which arise from the metric of the cell were neglected. Moreover, the anisotropic thermal parameters always give rise to non-vanishing off-diagonal terms (*cf.* Scheringer, 1966), which were neglected. Finally, in the anthracene case there were 63 parameters, which is more than we used in our Tables 1 and 3. This also may reduce the quality of the approximation with anthracene.

The values of μ , γ , and η_{op} in Tables 1 and 3 for the full sets of data are about as good as those of the 9×9 block-diagonal approximations, which are often used in structure refinement (such as the approximations by Cruickshank and Rollett; *cf.* Sparks, 1961, Table 1, entries 3 and 4). Thus we conclude that \mathbf{Q} is a sufficient approximation if there is a sufficient number of data and a sufficient number of stereochemical restraints. Here we are thinking of organic structures with many atoms and more than 1000 data.

A rough estimate of the number of parameters to be admitted for a given number of data may be gained as follows: We consider $\gamma = 0.2$ as sufficient for the quality of the approximation. We describe the influence of the number of the parameters p by $\gamma = C_1/p$, and the influence of the number of data n by $\gamma = 1 - \exp(-C_2 \cdot n)$. From Tables 1 and 3 we extract $\gamma = 0.2$ for about 20 parameters and 700 data. These values determine the constants C_1 and C_2 , and we obtain for 1000, 2000, 5000 and 10000 data 27, 47, 80 and 96 parameters respectively. This estimate of the number of admissible parameters is rather too low.

Table 5. Incorrect signs of the parameter shifts computed with the approximate matrices

The numbers in brackets are percentage values.

	Single-atom parameters	Reduced parameters	Single-atom and reduced parameters
Full sets of data (679 and 480 respectively)			
Number of shifts	207	54	261
Incorrect signs, \mathbf{Q}	34 (16.4)	7 (12.9)	41 (15.7)
Incorrect signs, SF diagonal matrix	34 (16.4)	5 (9.2)	39 (14.9)
Reduced sets of data (250 and 200 respectively)			
Incorrect signs, \mathbf{Q}	54 (26.1)	13 (24.1)	67 (25.7)
Incorrect signs, SF diagonal matrix	54 (26.1)	12 (22.2)	66 (25.3)

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Appendix

Proof of the relations (7) for the case of constraints being applied

Let F be any non-singular linear transformation, and let $Q_F = F^T Q F$, and $A_F = F^T A F$; then we obtain

$$Q_F^{-1} A_F = F^{-1} Q^{-1} A F; \lambda_i \{Q_F^{-1} A_F\} = \lambda_i \{Q^{-1} A\}. \quad (A1)$$

With Q positive-definite and symmetric we can always find a matrix F such that $Q_F = I$ (where I is the unit matrix). (One possible way to determine F according to $Q_F = I$ is outlined by Sparks, 1961.) With $Q_F = I$ we have

$$\begin{aligned} Q^{\text{red-1}} A^{\text{red}} &= (R^T Q R)^{-1} R^T A R \\ &= (R^T F^T F^{-1} Q_F F^{-1} R)^{-1} R^T F^T F^{-1} A_F F^{-1} R \\ &= (S^T S)^{-1} S^T A_F S \end{aligned}$$

by using $S = F^{-1} R$. Hence the following relation holds for the eigenvalues:

$$\lambda_i \{Q^{\text{red-1}} A^{\text{red}}\} = \lambda_i \{(S^T S)^{-1} S^T A_F S\}. \quad (A2)$$

Moreover, with $Q_F = I$ and with (A1) we have

$$\lambda_i \{Q^{-1} A\} = \lambda_i \{A_F\}. \quad (A3)$$

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Hydrogen Bond Studies. XXIII.* The Crystal Structure of Potassium Hydrogen Diformate

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The crystal structure of potassium hydrogen diformate has been determined at room temperature from three-dimensional single-crystal X-ray data. The crystals are orthorhombic, space group $Pbca$, with eight $KH(HCOO)_2$ units in a unit cell with the dimensions $a = 17.708$, $b = 7.510$, $c = 7.377$ Å. Least-squares refinements with allowance for anisotropic thermal motion gave a final discrepancy index of 0.073. Two crystallographically non-equivalent formate groups are linked into a dimer by a short hydrogen bond (2.45 Å). The potassium ions occur in puckered layers perpendicular to the a axis. The charged dimers and the metal ions are joined by ionic interaction, and the structure is built up of alternating layers of potassium ions and formate dimers. Each potassium ion is surrounded by eight oxygen atoms at the vertices of a distorted square antiprism (K–O distances: 2.77–3.06 Å). The C–O bond lengths in one of the non-equivalent formate groups are 1.24 and 1.25 Å, and in the other 1.22 and 1.26 Å. The corresponding O–C–O angles are 124 and 125°.

Introduction

Several acid salts of monocarboxylic acids with alkali metals have been studied by Speakman and co-workers

If we now make use of a proof given in another paper (Scheringer, 1965a, Appendix), the relations (7) follow from (A2) and (A3).

Proof of the relations (7) for the case of the parameters forming a subset

As Q^{-1} is positive-definite and symmetric, $Q^{-1}A$ is also positive-definite. Let $Q^{\text{red-1}}$ be a non-correlated principal submatrix of Q^{-1} , and A^{red} the corresponding principal submatrix of A (A^{red} generally is correlated), then $Q^{\text{red-1}}A^{\text{red}}$ is a principal submatrix of $Q^{-1}A$. According to the Sturm–Hurwitz theorem (cf. Scheringer, 1965b) the maximum (minimum) eigenvalue of a positive-definite matrix is always larger (smaller) than or equal to the maximum (minimum) eigenvalue of any principal submatrix. Hence the relations (7) hold.

References

- FARAG, M. S. (1954). *Acta Cryst.* 7, 117.
LINNIK, J. W. (1961). *Die Methode der kleinsten Quadrate in moderner Darstellung*, p.184. Berlin: VEB Deutscher Verlag der Wissenschaften.
SCHERINGER, C. (1963). *Z. Kristallogr.* 119, 273.
SCHERINGER, C. (1965a). *Acta Cryst.* 19, 513.
SCHERINGER, C. (1965b). *Acta Cryst.* 19, 504.
SCHERINGER, C. (1966). *Acta Cryst.* 20, 319.
SCHERINGER, C. (1968). *Acta Cryst.* In the press.
SPARKS, R. A. (1961). *Computing Methods and the Phase Problem in X-ray Crystal Analysis*, p.170. Oxford, London, New York, Paris: Pergamon Press.

(e.g. Golič & Speakman, 1965). The negative ions in these compounds are linked as dimers by short hydrogen bonds which in some cases have been regarded as symmetrical. As potassium hydrogen diformate, $KH(HCOO)_2$, is one of the simplest acid salts a determination of its structure is of interest. Moreover, this

* Part XXII: Liminga & Mehlsen Sørensen (1967).