Peter Luger

Modern X-Ray Analysis on Single Crystals

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Dr. rer. nat. Peter Luger
Professor of Crystallography
Department of Chemistry
Freie Universität Berlin
Takustraße 6
D 1000-Berlin 33

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Preface

Seventeen years after the discovery of X-rays by Wilhelm Conrad Röntgen in 1895, von Laue and his collaborators Friedrich and Knipping found that this novel type of radiation showed the property of diffraction when passed through a crystal lattice. In their classic experiment of 1912 they proved that X-rays, like all other electromagnetic waves, interact with the electron sheath when exposed to a sample of matter, thus causing a diffraction process.

This experiment can be regarded as the foundation of X-ray analysis, a new method for determining the structure of solid matter. However, in the first half-century after its invention this method could seldom be applied, and then only under restrictive conditions. The execution of one structure determination frequently took several months, in some cases even a few years. Moreover the results were of limited accuracy and not always unambiguous.

This situation has changed totally in the last few years. In a dynamic development modern X-ray analysis has become an instrument of structure determination which yields the most detailed, safe and precise information on molecular and crystal geometry available.

Two major reasons can be given for this decisive progress. First, it is a consequence of the development of the so called "Direct Methods" of phase determination in the last 20 years. From this it is now possible to work on a large number of compounds, especially of organic chemistry, which could never have been treated before. Second, the possibility of executing the extensive numerical calculations with the help of ever faster and larger computers has reduced the time needed for a structure determination or has even made its execution possible in the case of larger structures.

Today it can be stated that an X-ray analysis can be performed on any crystalline compound within a reasonable amount of time if its molecular weight is not too large.

Being now comparable in speed and expense to other methods and superior in results, the application of X-ray analysis is increasing not only in all chemical laboratories but also in biological and biochemical as well as in physical research projects; the number of scientists using this method is becoming larger from year to year.

Today, by means of highly sophisticated computer programs controlling fairly automatically the measuring and structure determination process, an X-ray analysis can be processed with little effort on the part of the user. In general, extensive previous knowledge of theoretical crystallography is unnecessary; instead, much practical experience is more helpful for the experimenter to continue his investigation. However, in spite of automation several sources of error remain for the user, each capable of preventing a succesful solution to a structural problem.

It seemed therefore appropriate to have a guide for practical work in X-ray analysis directed at those who are not highly experienced in crystallography but who need structure determination as a method for solving some of their problems. In this book the fundamentals of crystallography are presented together with those topics that are helpful for the execution of a structure analysis. The contents were selected with respect to practical applicability; most questions arising in the course of practical work are treated. This book is addressed to graduate students intending to use this method in any part of an examination as well as to scientists in any research or industrial laboratory, hence to all people concerned with a structural problem which might be solved by the method of single crystal analysis.

In the first part mainly theoretical aspects are presented. Note that no effort has been made to derive all results of diffraction theory. This is not the aim of this book since we are more interested in practical problems. In the second and subsequent parts we describe the process of an X-ray structure determination in all details, starting with the diffraction experiments, then dealing with the phase determination, the refinement and finally with the representation and documentation of results. The presentation of three structures as examples supports the orientation of this book toward practical work.

I have tried to give as modern a formulation as possible of the mathematical aspects that figure so largely in X-ray analysis because the modern mathematical language seems to be the most appropriate for a clear understanding, despite its somewhat abstract nature.

It is the aim of this book to serve as a guide and to enable the reader to solve his structural problems almost without further preparation. It is desired that this book will be a contribution to the further dissemination of X-ray analysis as a modern method of structure determination to an ever increasing number of scientists.

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Berlin, May 1979 *Peter Luger*

Contents

1 Theoretical Basis

1.1 Matrices, Vectors

1.1.1 *Introduction*

The first part of this chapter is concerned with some mathematics which will be used in the later chapters of this book. We assume that the fundamentals of arithmetic and of integral and differential calculus are well-known to the reader, but students of chemistry often have difficulties with the theory of vector and matrix algebra. Since we will make frequent use of these mathematical formalisms, the most important properties of vectors and matrices are briefly discussed.

1.1.2 *Matrices, Determinants, Linear Equations*

A rectangular array, A, arranged in the form

$$A = \begin{pmatrix} a_{11} & a_{12} & a_{13} & \cdots & a_{1n} \\ a_{21} & a_{22} & a_{23} & \cdots & a_{2n} \\ a_{31} & a_{32} & a_{33} & \cdots & a_{3n} \\ \cdot & & & & \cdot \\ a_{m1} & a_{m2} & a_{m3} & \cdots & a_{mn} \end{pmatrix}$$

is called a matrix. The elements a_{ik} can be arbitrary numbers. If the number of rows is m and the number of columns is n, the matrix is said to be of the order $m \times n$. If $m = n$ the matrix is called a square matrix of order n. The index i of the element a_{ik} indicates its row and the index k the corresponding column. As will be shown in the next chapter, the matrix formalism is a very convenient way to describe vector operations, vector transformations and it provides a very elegant method for solving linear equations.

The introduction of matrices requires a knowledge of matrix algebra. First, we define the basic arithmetic operations of matrices.

The equality of matrices. Two matrices are said to be of equal type if their numbers of rows and columns are equal. Two matrices are equal, if they are of equal type and if all elements in corresponding rows and columns are equal.

Example:

(a) The matrices

$$A = \begin{pmatrix} 4 & 0 \\ 0 & 1 \end{pmatrix} \quad \text{and} \quad B = \begin{pmatrix} 4 & 0 \\ 1 & 0 \end{pmatrix}$$

are of the same type. They are square matrices of order 2. But they are not equal. For instance, the element in the second row and first column a_{21} is equal to zero and is not equal to $b_{21} = 1$.

(b) The matrices

$$\begin{pmatrix} 4 & 0 \\ 0 & 1 \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} 2^2 & 0 \\ 0 & e^0 \end{pmatrix} \quad \text{are equal.}$$

Now we can proceed to the algebraic operations. If $A = (a_{ik})$, $B = (b_{ik})$ are matrices of the same type, the matrix $C = (c_{ik})$ is called the sum (difference) of A and B,

$$C = A \pm B$$

if

$$c_{ik} = a_{ik} \pm b_{ik} \tag{1.1}$$

It can be clearly seen that C must be of the same type as A and B, and that the calculation of a sum or difference is impossible if A and B are of different types.

The product λA of a matrix $A = (a_{ik})$ with a single factor λ is defined by

$$\lambda A = \begin{pmatrix} \lambda a_{11} & \lambda a_{12} & \dots & \lambda a_{1n} \\ \lambda a_{21} & \lambda a_{22} & \dots & \lambda a_{2n} \\ \vdots & & & \\ \lambda a_{m1} & \lambda a_{m2} & \dots & \lambda a_{mn} \end{pmatrix}$$

Example:

(a) Given

$$A = \begin{pmatrix} 2 & 3 \\ -3 & 2 \end{pmatrix} \quad B = \begin{pmatrix} 1 & -1 & 1 \\ -1 & 1 & -1 \end{pmatrix},$$

calculate $A - (1/2)B$.

Answer: This calculation is impossible, because A and B are of different type. If we change

$$B \text{ to } B' = \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix}$$

we obtain

$$A - (1/2)B' = \begin{pmatrix} (2 - 1/2) & (3 + 1/2) \\ -(3 - 1/2) & (2 - 1/2) \end{pmatrix}.$$

(b) Let

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$$A = \begin{pmatrix} a & b \\ c & d \end{pmatrix} \quad E = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

and λ an arbitrary constant. Calculate $B = A - \lambda E$.

Solution:

$$B = \begin{pmatrix} (a-\lambda) & b \\ c & (d-\lambda) \end{pmatrix}.$$

The product of two matrices is not as simple an operation as that of the sum and difference. Let $A = (a_{ik})$ be a matrix of order $m \times n$, $B = (b_{ik})$ a matrix of order $n \times p$. The $m \times p$ matrix, $C = (c_{ik})$ is said to be the product of A and B,

$$C = AB$$

if

$$c_{ik} = \sum_{\varrho=1}^{n} a_{i\varrho} b_{\varrho k}$$

for

$$i = 1, \ldots, m \quad \text{and} \quad k = 1, \ldots, p \tag{1.2}$$

The definition of the matrix product is not self-evident and at this stage no simple reason for this extraordinary operation can be given. It can only be stated that a large number of important operations can be expressed by way of matrix products in a very clear and simple way.

Let us give an explanation of (1.2) which may be somewhat clearer. The element c_{ik} of the product matrix C is obtained by multiplication of the elements of the i-th row of A by the corresponding elements of the k-th column of B followed by summation of the n products. A stringent requirement for this procedure is that the length of rows of the first matrix is equal to the length of columns of the second. That is, if A has n columns, B must have n rows, otherwise the product is not defined.

Problem:

(a) Let $P(x_0, y_0)$ be an arbitrary point in a plane, with (x_0, y_0) its cartesian coordinates. Show that the rotation of P about an angle φ can be expressed by a special matrix.

(b) Show that the rotation about φ followed by a rotation about ω can be expressed by a matrix product.

Answer:

(a) As shown in Fig. 1.1, we solve the problem by rotating the $x - y$ system about the same angle φ. In the new $x_\varphi - y_\varphi$ system the point P′ has the coordinates $x_\varphi = \overline{OC}$ and $y_\varphi = \overline{P'C}$ which are of course equal to x_0 and y_0. Then we have (see Fig. 1.1)

$$x' = \overline{OA} = \overline{OB} - \overline{AB} = \overline{OB} - \overline{DC} = x_0 \cos\varphi - y_0 \sin\varphi$$

$$y' = \overline{AP'} = \overline{AD} + \overline{DP'} = \overline{BC} + \overline{DP'} = x_0 \sin\varphi + y_0 \cos\varphi$$

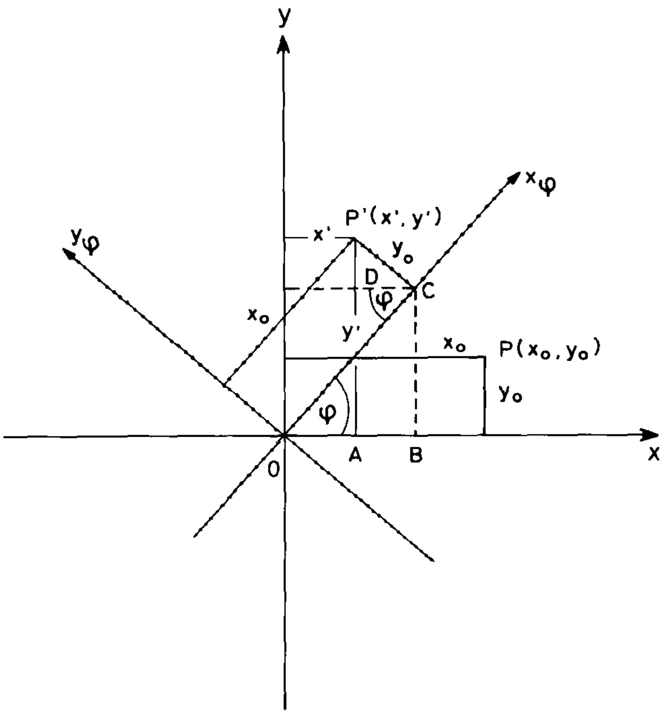

Fig. 1.1. Rotation of a point P about an angle φ.

If we now write (x', y') and (x_0, y_0) as 2×1 matrices, we get

$$\begin{pmatrix} x' \\ y' \end{pmatrix} = \begin{pmatrix} \cos\varphi & -\sin\varphi \\ \sin\varphi & \cos\varphi \end{pmatrix} \begin{pmatrix} x_0 \\ y_0 \end{pmatrix} \tag{1.3}$$

and the matrix

$$A(\varphi) = \begin{pmatrix} \cos\varphi & -\sin\varphi \\ \sin\varphi & \cos\varphi \end{pmatrix}$$

represents the rotation about the angle φ.

(b) From the rotation of P' by the angle ω we get P'' (x'', y'') and (x'', y'') are obtained by

$$x'' = x'\cos\omega - y'\sin\omega$$
$$y'' = x'\sin\omega + y'\cos\omega.$$

With the expressions of (a) for x' and y' we have then

$$x'' = (x_0\cos\varphi - y_0\sin\varphi)\cos\omega - (x_0\sin\varphi + y_0\cos\varphi)\sin\omega$$
$$y'' = (x_0\cos\varphi - y_0\sin\varphi)\sin\omega + (x_0\sin\varphi + y_0\cos\varphi)\cos\omega$$

or

$$x'' = (\cos\omega\cos\varphi - \sin\omega\sin\varphi)\,x_0 + (-\cos\omega\sin\varphi - \sin\omega\cos\varphi)\,y_0$$
$$y'' = (\sin\omega\cos\varphi + \cos\omega\sin\varphi)\,x_0 + (-\sin\omega\sin\varphi + \cos\omega\cos\varphi)\,y_0$$

The last two equations become quite simple when written as matrix product:

$$\begin{pmatrix} x'' \\ y'' \end{pmatrix} = \begin{pmatrix} \cos\omega & -\sin\omega \\ \sin\omega & \cos\omega \end{pmatrix} \begin{pmatrix} \cos\varphi & -\sin\varphi \\ \sin\varphi & \cos\varphi \end{pmatrix} \begin{pmatrix} x_0 \\ y_0 \end{pmatrix}$$

By evaluating the last matrix product you get the expressions developed above.

On the other hand we get from multiple angle formulae

$$\begin{aligned} \cos\omega\cos\varphi - \sin\omega\sin\varphi &= \cos(\omega+\varphi) \\ -(\cos\omega\sin\varphi + \sin\omega\cos\varphi) &= -\sin(\omega+\varphi) \\ \sin\omega\cos\varphi + \cos\omega\sin\varphi &= \sin(\omega+\varphi) \\ -\sin\omega\sin\varphi + \cos\omega\cos\varphi &= \cos(\omega+\varphi) \end{aligned}$$

Hence we get

$$\begin{pmatrix} x'' \\ y'' \end{pmatrix} = A(\omega+\varphi)\begin{pmatrix} x_0 \\ y_0 \end{pmatrix} \quad \text{or } A(\omega+\varphi) = A(\omega)\,A(\varphi).$$

Some properties of the arithmetic operations of matrices are as follows:

(1) $A \pm B = B \pm A$

(2) $(A + B) + C = A + (B + C)$

(3) $\lambda(A + B) = \lambda A + \lambda B$

(4) $\mu(\lambda A) = (\mu\lambda)A$

(5) $(\mu + \lambda)A = \mu A + \lambda A$

(6) $(AB)C = A(BC)$

(7) $A(B + C) = AB + AC$

(8) In general, the matrix product is not cummutative, that is, $AB \neq BA$ (the reader may show this by an example).

Special matrices are as follows:

(a) A matrix O with all elements being equal to zero is called a null matrix. It has the property $A + O = O + A = A$ for all matrices A of the same type.

(b) A square matrix $E = (e_{ik})$ with $e_{ik} = \Delta_{ik}$ (Kronecker symbol) is called a unit matrix. It has the property $EA = AE = A$ for all square matrices of the same order.

(c) For a given matrix $A = (a_{ik})$, its transposition matrix A' is defined by

$$A' = (a_{ki}) = \begin{pmatrix} a_{11} & a_{21} & \dots & a_{m1} \\ a_{12} & a_{22} & \dots & a_{m2} \\ \vdots & & & \vdots \\ a_{1n} & a_{2n} & \dots & a_{mn} \end{pmatrix}$$

A' is obtained by reflection of the elements of A across the principal diagonal, which is defined by the elements $a_{11}, a_{22}, \dots a_{ii} \dots$ etc.

(d) For a given square matrix A the matrix B is called the inverse matrix of A, if $BA = E$. B is then denoted by $B = A^{-1}$.

The problem of how to find the inverse matrix of A is very important, but its solution is not trivial. Let us demonstrate the importance of the inverse matrix by an example:

A system of n linear equations is of the form

$$\begin{aligned} a_{11}x_1 + a_{12}x_2 + \dots a_{1n}x_n &= b_1 \\ a_{21}x_1 + a_{22}x_2 + \dots a_{2n}x_n &= b_2 \\ \vdots \qquad\qquad\quad \vdots \quad &\;\; \vdots \\ a_{n1}x_1 + a_{n2}x_2 + \dots a_{nn}x_n &= b_n \end{aligned} \tag{1.4}$$

In matrix notation, with

$$A = (a_{ik}),\; b = \begin{pmatrix} b_1 \\ \vdots \\ b_n \end{pmatrix},\quad x = \begin{pmatrix} x_1 \\ \vdots \\ x_n \end{pmatrix},$$

we obtain

$$Ax = b.$$

If we were able to calculate the inverse matrix, we could have immediately the solution for x,

$$x = A^{-1}b.$$

The example shows that there is a close connection between the solution of n linear equations and the calculation of the inverse matrix and we shall see that the procedure of solution is the same for both problems. Before starting this, we must define a determinant.

Let $A = (a_{ik})$ be a square matrix of order n. Let us denote by A_{ik} the matrix obtained from A by deleting the i-th row and k-th column:

$$A_{ik} = \left(\begin{array}{ccc|ccc} a_{11} & \cdots & a_{1,k-1} & a_{1,k+1} & \cdots & a_{1n} \\ \vdots & & & & & \\ a_{i-1,1} & \cdots & a_{i-1,k-1} & a_{i-1,k+1} & \cdots & a_{i-1,n} \\ \hline a_{i+1,1} & \cdots & a_{i+1,k-1} & a_{i+1,k+1} & \cdots & a_{i+1,n} \\ \vdots & & & & & \\ a_{n1} & \cdots & a_{n,k-1} & a_{n,k+1} & \cdots & a_{nn} \end{array}\right)$$

A_{ik} is then of order $n-1$.

Let

$$A = \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix},$$

a square matrix of order 2. Its determinant $|A|$ is a number obtained from A by

$$|A| = a_{11}a_{22} - a_{21}a_{12}$$

The determinant of a square matrix of higher order is defined iteratively:

Let $A = (a_{ik})$ be a square matrix of order n. Its determinant $|A|$ is defined by

$$|A| = \sum_{k=1}^{n} (-1)^{1+k} a_{1k} |A_{1k}|$$

This expansion is done with respect to the first row. It can be shown that the expansion is independent of our choice of the row; furthermore it can be done referring to a column. This property is expressed by the *Theorem of Laplace*:

The determinant $|A|$ of a square matrix $A = (a_{ik})$ is given by

$$|A| = \sum_{k=1}^{n} (-1)^{i+k} a_{ik} |A_{ik}| \text{ for arbitrary } i = 1, \ldots, n$$

or (1.5)

$$|A| = \sum_{i=1}^{n} (-1)^{i+k} a_{ik} |A_{ik}| \text{ for arbitrary } k = 1, \ldots, n$$

For convenience, the expression $(-1)^{i+k}|A_{ik}|$ shall have its own name. It is called the minor of the matrix element a_{ik} and designated α_{ik}.

With the notation of minors, Laplace theorem reads

$$|A| = \sum_{k=1}^{n} a_{ik}\alpha_{ik} \text{ for } i = 1, \ldots, n$$

or

$$|A| = \sum_{i=1}^{n} a_{ik}\alpha_{ik} \text{ for } k = 1, \ldots, n.$$

In practice the calculation of a determinant of higher order is a joyless task. There is some help from the rules for the arithmetic of determinants, but we shall not describe them because in the progress of a structure analysis the calculation of the determinants is done by the computer and at most we ourselves calculate determinants of order two or three.

The application of all these rules for determinant arithmetic leads to an important generalization of the Laplace theorem:

Generalized Expansion Theorem: Let A be a square matrix of order n. Then for its determinant the following equations hold:

$$|A|\Delta_{ik} = \sum_{s=1}^{n} a_{is}\alpha_{ks}$$

$$|A|\Delta_{ik} = \sum_{s=1}^{n} a_{si}\alpha_{sk}$$

(Δ_{ik} = Kronecker-Symbol)

For i = k we get the Laplace theorem. Its generalization largely contains the solution of the inverse matrix problem.

Let us regard a matrix, denoted by A^A, containing the minors α_{ki} as elements. Note that, in A^A the usual order of subscripts is exchanged. In $A = (a_{ik})$ the element a_{ik} is positioned in the i-th row and k-th column, while in A^A the corresponding minor α_{ik} is in the k-th row and i-th column. The minor matrix A^A has the important property, that $AA^A = |A|E$ holds.

Proof: From the definition of matrix product we get

$$\begin{pmatrix} a_{11} & \cdots & a_{1n} \\ \vdots & & \vdots \\ a_{n1} & & a_{nn} \end{pmatrix} \cdot \begin{pmatrix} \alpha_{11} & \cdots & \alpha_{n1} \\ \vdots & & \vdots \\ \alpha_{1n} & & \alpha_{nn} \end{pmatrix} = \left(\sum_{s=1}^{n} a_{is}\alpha_{ks}\right)$$

The sum on the right side is equal to $|A|\Delta_{ik}$, from generalized expansion theorem. So we get

$$AA^A = \begin{pmatrix} |A| & & 0 \\ & |A| & \\ 0 & & |A| \end{pmatrix} = |A|E$$

Now it is easy to see how to calculate the inverse matrix A^{-1}. It is simply

$$A^{-1} = (1/|A|)A^A \quad \text{if } |A| \neq 0 \tag{1.6}$$

For a matrix A with $|A| = 0$, A^{-1} does not exist!

Problem:
Given

$$A = \begin{pmatrix} -1 & 0 & 1 \\ 2 & 1 & -1 \\ 3 & -2 & 0 \end{pmatrix},$$

calculate A^{-1}.

Solution: The determinant $|A|$, calculated by expansion with respect to the third column is

$$|A| = 1\begin{vmatrix} 2 & 1 \\ 3 & -2 \end{vmatrix} - (-1)\begin{vmatrix} -1 & 0 \\ 3 & -2 \end{vmatrix} = -5.$$

Since $|A| \neq 0$, A^{-1} exists. The minors α_{ik} are then

$$\alpha_{11} = \begin{vmatrix} 1 & -1 \\ -2 & 0 \end{vmatrix} = -2 \qquad \alpha_{12} = -\begin{vmatrix} 2 & -1 \\ 3 & 0 \end{vmatrix} = -3$$

$$\alpha_{13} = \begin{vmatrix} 2 & 1 \\ 3 & -2 \end{vmatrix} = -7 \cdot \qquad \alpha_{21} = -\begin{vmatrix} 0 & 1 \\ -2 & 0 \end{vmatrix} = -2$$

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