

Evaluation of the Electron Density in a General Plane: Application to 4,4'-Dichlorodiphenylsulfone

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A program has been devised for the execution of a three-dimensional Fourier synthesis on a general plane in a crystal of monoclinic or higher symmetry. The program accepts the crystal cell data, the orthogonal equation of the plane, and the measured structure factors. It computes from a designated array of points in x and y the corresponding values of z to within $c/7200$ Å of the exact general plane and performs the synthesis at each point.

The method has been applied to 4,4'-dichlorodiphenylsulfone, using both $F_{\text{meas.}}$ and difference data. The $F_{\text{meas.}}$ synthesis shows clearly the details of the molecular structure in the plane and confirms the positional coordinates previously derived by a least-squares refinement. The difference synthesis reveals the positions of hydrogen atoms. A small residual at the sulfur atom, together with a calculation of F_{error} 's demonstrates a probable inconsistency in the choice of scattering factor for sulfur in the original least-squares refinement.

Introduction

The problem of evaluating the electron-density distribution in a general plane has increased in frequency as the technique of measuring the full three-dimensional diffraction data has become practicable. An early solution was obtained by graphically interpolating the electron densities computed at a regular and well-spaced array of points (Abrahams, Robertson & White, 1949). In applying this method, the value of the intersection of the general plane with the direction of interpolation was first required, and the interpolation was then made over intervals of 1/60th of the cell edge. This solution did not win wide-spread acceptance, due no doubt to the large number of hand operations involved. However, a knowledge of the variation in any Fourier series function* in the plane formed by three or more linked atoms can reveal important information.

A program has now been written (cf. Cruickshank, 1956) for a modern computing machine (the IBM 704 computer) by means of which this function can be determined for any space group of monoclinic or higher symmetry, in any plane

$$x' + k_2y' + k_3z' + d = 0,$$

where x' , y' and z' are orthogonal coordinates and k_2 , k_3 and d are arbitrary constants. In the following sections, the logic of this program will be presented,

* The term 'electron density' used throughout this paper may readily be generalized into any function of the form

$$\zeta(xyz) = \frac{1}{\kappa} \sum_{x-h}^h \sum_{y-k}^k \sum_{z-l}^l \Phi(hkl) \exp[-2\pi i(hx + ky + lz)],$$

where κ is a constant and $\Phi(hkl)$ is a measure of the structure factor, such as $F_{\text{meas.}}$, $F_{\text{calc.}}$, ΔF etc., whether determined by X-ray, electron or neutron diffraction.

together with an illustration in the case of 4,4'-dichlorodiphenylsulfone, the structure of which has recently been reported by Sime & Abrahams (1960).

Logical procedure

The computational problem is to find the electron density at each point of a regular array lying in the plane of interest. This requires the determination of the crystal coordinates of each such point which, in an oblique plane, are not generally integral fractions of the cell axes. The actual program was developed from earlier two- and three-dimensional Fourier synthesis programs (Treuting, 1958) in which the electron density is obtained at points (x, y, z) such that

$$hx + ky + lz = M/N, \quad (1)$$

where M and N are integers. This permits M to be used as the argument of a table of N cosines and sines that need be computed (or read in) but once. The necessity of calculating independently each of very many cosine terms is thus avoided.

To reconcile the efficiency of the stored-table method with the non-integral nature of the crystal coordinates of points on the general plane, an array of points (X, Y, Z) satisfying the conditions of equation (1) with $N=3600$ is used. No such point deviates from the exact general plane by more than $c/7200$ Å. The set is obtained by first choosing an array of points (X, Y) in the ab plane for which X and Y are integers and

$$X = 3600x, \quad Y = 3600y,$$

where (x, y, z) are crystal coordinates. The corresponding values of z (for a crystal of monoclinic or higher symmetry) are obtained by appropriate transformation

of the plane equation, given below. Each Z is then taken as the nearest integral value of $3600z$. The execution of the synthesis is now straightforward, using the expression

$$\rho(X, Y, Z) = (1/V)[F(000) + 2 \sum_{h=0}^H \sum_{k=-K}^K \sum_{l=-L}^L F(hkl) \cos 2\pi(hX + kY + lZ)] \quad (2)$$

for the centrosymmetric case.

Outline of the program*

Equation (2) requires that all reflections included in one-half the reciprocal lattice be used as input data. A short preliminary program generates the symmetry-related terms for a particular space group from the measured structure factors. A second subsidiary program generates the cosine and sine tables over the range 0 to 2π , and at intervals of 0.1 degree, by recursion formulae. It writes these as well as the structure factor data in binary on a tape for input to the main program. These programs are written in Fortran.† The main program storage requires 1733 words; variable storage requires 19,306 words including provision for 2500 indexed structure factors.

The main program computes a set of Z values corresponding to the specified (X, Y) array and then performs the synthesis at each point. The Z values are obtained by a double transformation of the plane equation reduced to a single expression for expediency. Consider, in a monoclinic (or higher symmetry) crystal, the relations:

$$x' = xa + zc \cos \beta, \quad y' = yb, \quad z' = zc \sin \beta,$$

where (x', y', z') are orthogonal coordinates, a, b, c the crystal axes, and (x, y, z) are crystal coordinates as before.

Now if the equation of a general plane in orthogonal coordinates is

$$x' + k_2 y' + k_3 z' + d = 0,$$

on substituting,

$$z = -\frac{[xa + (k_2 b)y + d]}{c(\cos \beta + k_3 \sin \beta)}, \quad (3)$$

which in terms of the (X, Y, Z) array becomes

$$Z = -\frac{[aX + (k_2 b)Y + 3600d]}{c(\cos \beta + k_3 \sin \beta)} \quad (4)$$

on converting the crystal coordinates to the integer coordinates.

Hence the program requires as further input data

* This has been written for a machine of 32,768 word storage; a modification of the present program for a machine of 4,096 word storage has been written by J. L. Katz.

† Except that a SAP patch is required to evaluate equation (5) as the value of M can exceed the integer capacity of Fortran.

the values of the coefficients k_2, k_3, d and the cell constants a, b, c and β . Also needed are the origin, range, and intervals of the (X, Y) array, as well as the value of $F(000)$ and a scale factor. The latter is adjusted to confine any summation total to an integer less than 10,000. The program provides for the execution of successive arrays. The dimensions of any single array are limited by print-out requirements to 21 columns in Y and, for convenience, to 31 rows in X .

The sequence of execution, after reading in the tape, the constant parameters, and the dimensions of the first array, is first, to scale the structure factors including $F(000)$ and then to calculate the constant terms of equation (4). The values of Z for each point on the given (X, Y) array are then generated, stored in integer form, and printed out. The summation of equation (2) is performed at each successive point on the array by forming the quantity

$$M = hX + kY + lZ \quad (5)$$

for each reflection, setting M in the range $0 \leq M \leq 3600$ when necessary, by additions or subtractions of 3600 (corresponding to 2π), and extracting the $(M+1)$ term from the table of cosines. The sum of the successive terms of equation (2) is accumulated at each point over the number of reflections, added to the scaled $F(000)$, rounded to the nearest integer, stored, and finally, printed out for all points in the array.

After completion of one array the program returns to read in the dimensions of the next, executes it, and so continues until a sense card is read which terminates the calculation. The time entailed is very close to 2 milliseconds per reflection-point.

The crystal structure of 4,4'-dichlorodiphenylsulfone

A full account of the determination of the crystal and molecular structure of 4,4'-dichlorodiphenylsulfone has been given by Sime & Abrahams (1960). The refinement of the structure of this monoclinic crystal* was accomplished by the iterative application of the method of least squares. Busing & Levy's (1957) comprehensive program was used, in which 78 parameters were determined including all the positional and anisotropic temperature parameters for the non-hydrogen atoms, for an input of 1706 non-equivalent reflections. In this refinement the hydrogen atom contributions were included in the calculated structure factors, using Bacon's (1957) isotropic values of B and his x - and z -coordinates as initial values, together with y -coordinates derived from the plane equation of the benzene ring. After three complete refinement cycles, new hydrogen coordinates were deduced, based on $C-H = 1.08 \text{ \AA}$ and located on the extended C_2-C_5 and

* With lattice constants $a = 20.204 \pm 0.010$, $b = 5.009 \pm 0.010$, $c = 12.259 \pm 0.010 \text{ \AA}$, $\beta = 90^\circ 34' \pm 15'$, $Z = 4$ and space group $I2/a$.

C₃-C₆ lines. At no time were hydrogen coordinates subjected to refinement.

The final coordinates led to a molecule in which all the atoms, except sulfur and oxygen, lay within 0.015 Å of the plane

$$x' + 1.4208y' - 0.6237z' - 6.0373 = 0. \quad (6)$$

The sulfur atom is 0.062 ± 0.002 Å and the oxygen atom 0.382 ± 0.004 Å from this plane. The primed parameters in equation (6) are obtained by orthogonalizing the monoclinic crystal axes with the transformation $x' = x + z \cos \beta$, $y' = y$, $z' = z \sin \beta$.

Application to 4,4'-dichlorodiphenylsulfone

The program described above was initially used with the $F_{\text{meas.}}$ data given in Table 1 of Sime & Abrahams' (1960) paper as the coefficients $\Phi(hkl)$. Since the program uses all the reflections in a hemisphere of reciprocal space, a total of 2167 structure factors (there are 1158 observed non-equivalent $F_{\text{meas.}}$) formed the input data. The Z -values defined by equation (4) were evaluated for each X, Y point with X ranging from 0 to 1200/3600 at intervals of 30/3600, and Y from 0 to 3960/3600 at intervals of 90/3600. Each Z -value so obtained lies within $c/7200 = 0.0017$ Å of the plane in equation (6). The electron density at each point was then computed.

The two-dimensional array of electron densities thus obtained is defined by the projection of the crystal a - and b -axes onto the plane of equation (6), which results in the axes a' and b' , where

$$a' = 11.22, \quad b' = 10.31 \text{ Å}, \quad \gamma = 39^\circ 50'.$$

The results of this calculation are shown in Fig. 1. The program was also used with $\Phi(hkl) = F_{\text{meas.}} - F_{\text{calc.}}$. In deriving $F_{\text{calc.}}$, the contributions of all atoms save the hydrogens were calculated with a separate program which made use of the same scattering factors as did Sime & Abrahams, and the positional and anisotropic thermal parameters derived by them. The contour map corresponding to this calculation is shown in Fig. 2.

Discussion

The electron-density contour map of Fig. 1 contains several features of interest. First, the positional parameters of the heavy (non-hydrogen) atoms, except oxygen, are found to be in substantial agreement with the results of the earlier least-squares refinement. The oxygen atom coordinates are displaced as this atom lies 0.382 Å distant from the plane of equation (6). Then the considerable ellipticity of the chlorine atom offers immediate confirmation of the anisotropic vibration found by the method of least squares. From the latter, the thermal displacement of chlorine in the molecular plane was computed to be 0.395 Å normal to the S, Cl vector, compared with 0.239 Å along this

vector. Indications of variation in the C-C bond electron densities are apparent. Finally, the 0.5 e.Å⁻³ line shape (broken in Fig. 1) in the neighborhood of C₂, C₃, C₅ and C₆ suggests the presence of hydrogen atoms.

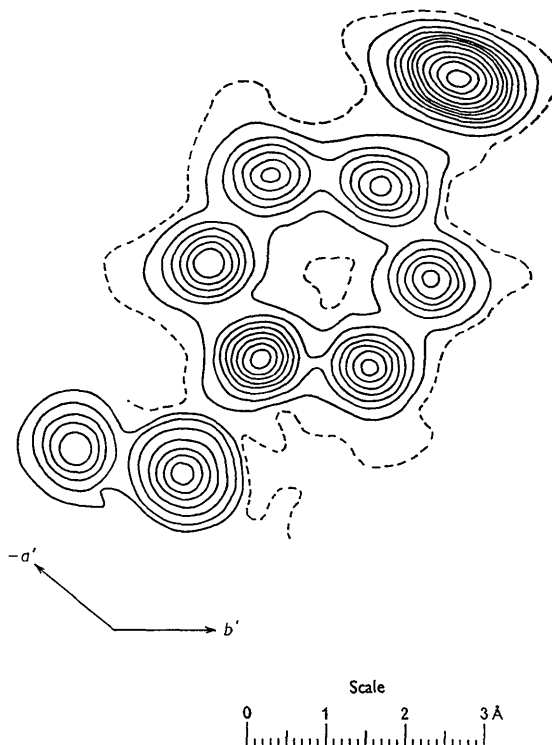


Fig. 1. Electron density of 4,4'-dichlorodiphenylsulfone in the plane of equation (6), ($F_{\text{meas.}}$ Fourier coefficients). The broken line represents 0.5 e.Å⁻³ and the first solid line 1 e.Å⁻³. Contours thereafter are at 1 e.Å⁻³ intervals for the oxygen and carbon atoms; for sulfur the contours above 2 e.Å⁻³ are at 5 e.Å⁻³ and for chlorine above 6 e.Å⁻³ at 2 e.Å⁻³ intervals.

The latter circumstance prompted the performance of the difference synthesis in the plane of the molecule. All the features indicated in Fig. 1 can be examined more clearly in the difference map given in Fig. 2. (In comparing these figures the differences in contour intervals are to be noted.) The maxima in the expected vicinity of the hydrogens are distinctly above the average background and are consistent both as to magnitude (0.45-0.65 e.Å⁻³) and location with the presence of hydrogen atoms. 'Estimated standard deviations' in the electron densities were not computed. The resulting C-H bond distances are in good agreement with the value of 1.08 Å assumed by Sime & Abrahams in their final refinement cycles; there is some deviation from their postulated positions on the extended C₂-C₅ and C₃-C₆ lines (cf. Table 7 of Sime & Abrahams, 1960).

The positional coordinates of the hydrogen atoms were then determined independently by computing the electron density along lines, parallel with the

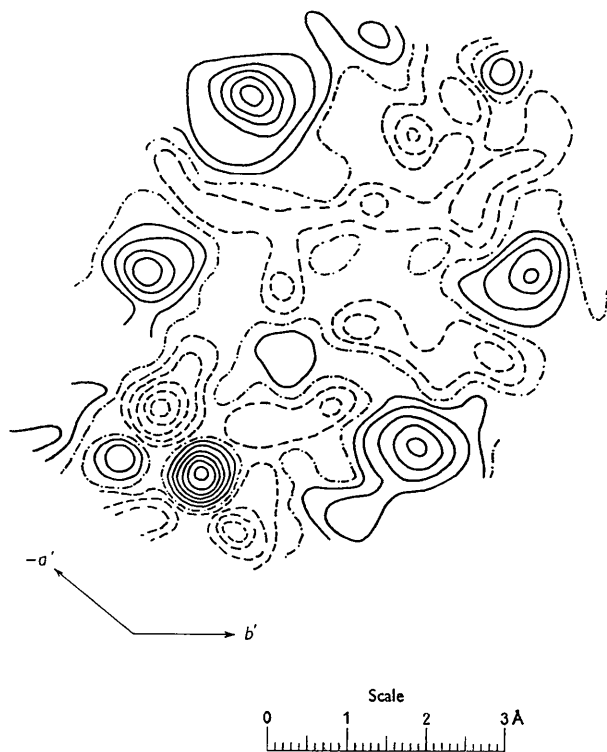


Fig. 2. Difference electron density of 4,4'-dichlorodiphenylsulfone in the plane of equation (6), ($F_{\text{meas.}} - F_{\text{calc.}}$ Fourier coefficients). Contours are at $0.1 \text{ e.}\text{\AA}^{-3}$ intervals. The dot-dash line represents $0 \text{ e.}\text{\AA}^{-3}$, the solid lines are positive and the broken lines negative densities.

crystal axes, through the centers of gravity of the hydrogen atoms in Fig. 2. An iterative procedure was used here, with new lines taken to correspond to any apparent changes in the positions of the centers of gravity. The coordinates thus found are collected in Table 1.

Table 1. Measured values of the hydrogen atom position coordinates

| | x | y | z |
|----------------|-------|-------|-------|
| H ₂ | 0.144 | 0.400 | 0.896 |
| H ₃ | 0.048 | 0.663 | 0.963 |
| H ₅ | 0.134 | 0.721 | 0.273 |
| H ₆ | 0.222 | 0.386 | 0.198 |

The position coordinates of all the non-hydrogen atoms except sulfur, as seen in Fig. 2, lie in regions of very small slope, and of small absolute height. This confirms the position coordinates used in obtaining the $F_{\text{calc.}}$ values. The sulfur atom lies at a density of $0.64 \text{ e.}\text{\AA}^{-3}$, and is surrounded by other features of comparable height. For comparison, the peak density of the sulfur atom in Fig. 1 is $27.5 \text{ e.}\text{\AA}^{-3}$. As a means of investigating this residual density at and close to the sulfur atom site, hydrogen structure factors corresponding to the coordinates in Table 1 using Bacon & Curry's (1960) temperature factors and McWeeny's

(1951) atomic form factor for hydrogen were then computed. The residuals remaining after subtracting the resulting hydrogen atom structure factors from the coefficients used in deriving Fig. 2 then represent the ultimate errors (F_{error}) in the measured and calculated structure factors. These residuals were then used to perform F_{error} syntheses in the regions of the sulfur and hydrogen atoms. All the data were used including those for reflections to which the hydrogen contributions were negligible; these are thus complete error syntheses.

These syntheses provide a test of the possibility that the small peaks in the electron-density distribution corresponding to the positions in Table 1 are produced by the ultimate remaining errors in the structure factors, rather than by scattering from hydrogen atoms. The results of this test are presented in Table 2.

Table 2. Maximum electron density

| With | (a) $\Phi(hkl) = F_{\text{meas.}} - F(\text{S, Cl, O, C})$ | (b) $\Phi(hkl) = F_{\text{meas.}} - F(\text{S, Cl, O, C, H})$ |
|----------------|--|---|
| Atom | Density (a) | Density (b) |
| H ₂ | $0.45 \text{ e.}\text{\AA}^{-3}$ | $0.09 \text{ e.}\text{\AA}^{-3}$ |
| H ₃ | 0.62 | 0.25 |
| H ₅ | 0.41 | 0.04 |
| H ₆ | 0.54 | 0.13 |
| S | 0.64 | 0.64 |

All the 'hydrogen' atom peaks become very significantly reduced in case (b), although H₃ remains about double the background density. The 'sulfur' peak is completely unaffected by inclusion of the hydrogen atom contributions in the calculated structure factors. It may also be added that in the general neighborhood of the sulfur atom, the maximum change from case (a) to case (b) is less than $0.05 \text{ e.}\text{\AA}^{-3}$.

The largest absolute value of any F_{error} is 20.41, for the reflection 202. In all, there are nine F_{error} terms with magnitude greater than 10, and eleven others greater than 7. The maximum change produced in the electron density if all these 20 largest F_{error} terms are reduced to zero is $0.17 \text{ e.}\text{\AA}^{-3}$. That the average value of the density in Fig. 2 not at the sulfur atom, nor at a hydrogen atom site, is small (*ca.* $\pm 0.1 \text{ e.}\text{\AA}^{-3}$) indicates the non-random nature of the F_{error} terms. It is evident that the residual electron density in Fig. 2 around the sulfur atom site is produced by these error terms. The relative absence of large density around the chlorine atom, a scatterer of about equal weight and absorption, suggests that the cause of the non-random F_{error} terms may lie in the particular form factor used for sulfur, in the final stages of the least-squares refinement. Small departures from isotropy in the true form factor could place the anisotropic thermal vibrations associated with the sulfur atom in error, thus causing corresponding false detail in the difference map.

In summary, the method described here for per-

forming a three-dimensional electron-density synthesis on a general plane affords a ready and graphic means of surveying the crystal structure of a planar molecule to the fullest extent permitted by the measured structure factors.

It is a pleasure to thank Dr Ronald Sass, one of whose programs first demonstrated to us the advantages of the stored table method in computing Fourier series, and Mr J. G. Sime for his part in the earlier three-dimensional structure analysis.

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A Direct Graphical Method for the Precise Determination of Lattice Parameters of Tetragonal or Hexagonal Crystals

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A direct graphical method for the precise determination of lattice parameters of tetragonal or hexagonal crystals is described. The method is applied to a binary equiatomic Ti-Al alloy and the results presented.

Introduction

Methods for the precise determination of lattice parameters of tetragonal or hexagonal crystals involve dealing with three unknowns, a , c , and the drift or systematic error. This may be done analytically, as in the Cohen's least-squares method (Klug & Alexander, 1954, p. 485), or graphically by the method of Taylor & Floyd (1950) or the method of successive approximations (Klug & Alexander, 1954, p. 481).

The least-squares solution involving three unknowns is likely to be very tedious and cumbersome, and will yield erroneous results if the diffraction pattern is not perfectly indexed, which is sometimes difficult to do unambiguously in the complex back reflection region. The least-squares method offers no means of checking the validity of input data until after the solution is completed. In addition, this method applies equal emphasis on strong, easily measured reflections and on weak, poorly defined ones.

The graphical method of successive approximations requires a separation of the data into two sets for extrapolation to approximate values of a and c separately. The approximate c/a ratio is used to repeat the extrapolation and obtain more refined values for a , c , and c/a , and the procedure is repeated as many times as necessary for a stable solution. The method of Taylor & Floyd (1950) uses $hk0$ reflections to

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determine a and the slope of the drift line by extrapolation. Then, from a prior estimation of the c/a ratio, an extrapolation for c may be made even if only a single $00l$ reflection is available by using the drift slope from the a determination, multiplied by the c/a ratio.

The direct graphical method

In the course of an investigation on the effects of ternary additions on the lattice parameters of the tetragonal TiAl gamma phase, a direct graphical extrapolation method for tetragonal crystals has been developed. This method can be used as readily for hexagonal crystals, as will be shown later.

The direct graphical method depends upon finding the line of best fit (the drift curve) for a series of straight lines in three dimensional space, each straight line being derived from a particular crystal lattice reflection. Each reflection must, of course, be indexed in order to plot the straight line, which represents the locus of all possible a and c values that can account for the reflection, but an advantage of the method is that it shows immediately, by comparison with the other data, when any errors have been made and aids in the correct indexing. While interpretation of the method is based upon a three dimensional concept, its application requires only two dimensions, in effect, a two dimensional projection of the three dimensional situation.

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