Evaluation of a Fourier Synthesis in a General Plane of a Crystal

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A program has been devised to compute a three-dimensional Fourier synthesis on a general plane in a crystal of any symmetry. The region in which the electron density will be evaluated is defined by giving two directions **p**, **q**, the elementary translations Δp, Δq and the total number of translations M and N in the **p** and **q** directions respectively. The extension to computation of a slab of given thickness, in which a general plane is the mean plane, is also given. Applications to the 1:1 molecular complex between 1,3,7,9-tetramethyluric acid and pyrene are presented.

The evaluation of electron-density distribution in a general plane is particularly useful in the structure analysis of crystals containing planar groups of atoms. Abrahams, Robertson & White (1949) evaluated the electron density in the mean molecular plane of naphthalene by graphically interpolating the three-dimensional Fourier synthesis. More recently, programs for computing Fourier series in a general plane were made available. The method followed, together with an outline of the program for the IBM 704 computer, was discussed by Treuting & Abrahams (1961). The method, limited to crystals of monoclinic or higher symmetry, required the generation of an array of points satisfying the equation of the plane, and the evaluation of the Fourier synthesis point by point.

In the three-dimensional structure analysis of the molecular complexes between 1,3,7,9-tetramethyluric acid (TMU) and aromatic hydrocarbons, undertaken in this laboratory, a general program for computation of Fourier sections and Fourier syntheses in a general plane and for any space group was desirable.* In this paper the logic of this program, written in machine language for an IBM 1620/20K computer, and some applications to the case of the molecular complexes between TMU and aromatic hydrocarbons are reported.

Method of computation

A Fourier synthesis

$$\varrho(\mathbf{x}) = \frac{1}{V} \sum_{\mathbf{h}} |F(\mathbf{h})| \cos [2\pi \mathbf{h} . \mathbf{x} - \alpha(\mathbf{h})] \qquad (1)$$

can be performed in any plane of equation

$$1 = m_1 x^1 + m_2 x^2 + m_3 x^3 = m_i x^i \qquad (2)$$

by calculating the Fourier series in an array of points with crystal coordinates x^i, satisfying the conditions of

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* Space groups different from the triclinic are handled as space group $P1$ through formula (1).

equation (2), or transforming the Miller indices h_i of all the terms of the series from the crystal system a_i to a system with an axis normal to the given plane and then calculating the related section. We have found it more convenient to use the first approach, following a method different from that discussed by Treuting & Abrahams in order to reduce computer time and storage requirements.

Let us define the ordered array of points $P_{m,n}$ in a general plane, at which the Fourier series must be evaluated, by the vectors

$$_{m,n}\mathbf{X} = {}_{0,0}\mathbf{x} + m\Delta_{\mathbf{p}} + n\Delta_{\mathbf{q}}$$

where $_{0,0}\mathbf{x}$ is the vector connecting the origin to the point $P_{0,0}$ and $\Delta_{\mathbf{p}}$ and $\Delta_{\mathbf{q}}$ are the primitive translations along two given directions **p** and **q** lying on the plane. The Fourier synthesis can be written:

$$\varrho(_{m,n}\mathbf{x}) = \frac{1}{V} \sum_{\mathbf{h}} |F(\mathbf{h})|$$

$$\cos [2\pi(\mathbf{h} . {}_{0,0}\mathbf{x} + m\mathbf{h} . \Delta_{\mathbf{p}} + n\mathbf{h} . \Delta_{\mathbf{q}}) - \alpha(\mathbf{h})] , \qquad (4)$$

where the quantities $\mathbf{h} . {}_{0,0}\mathbf{x}$, $\mathbf{h} . \Delta_{\mathbf{p}}$ and $\mathbf{h} . \Delta_{\mathbf{q}}$ are constants for each value of **h**.

It follows that it is not necessary to generate the coordinates of all the $P_{m,n}$ points of the grid and that the summation can be performed with high efficiency going point by point along rows, *i.e.* from $P_{0,0}$ to $P_{M,0}$, from $P_{0,1}$ to $P_{M,1}$ ... from $P_{0,N}$ to $P_{M,N}$, where M and N are the maximum numbers of the intervals along **p** and **q** respectively. The possibility of choosing general boundary directions **p** and **q** allows one to perform the Fourier synthesis only at points of a specified region of the given plane. It has been found convenient to define the region with reference to an orthogonal system u_i with two axes in the molecular plane (Fig. 1). Obviously this implies a transformation from the orthogonal system u_i to the crystal system a_i to obtain the components of the vectors $_{0,0}\mathbf{x}$, $\Delta_{\mathbf{p}}$ and $\Delta_{\mathbf{q}}$ used in (4).

The orthogonal right-handed system has been defined with u_1 normal to the plane, u_2 parallel through

the origin of the crystal system to the line joining the intersections of a normal through the same origin and of the axis a_2 with the plane and $u_3 = u_1 \times u_2$.

The coordinates in Å of the point $P_{0,0}$ choosen at the corner of the network in the system u_t are d, $_0X^2$, $_0X^3$, where d is the origin-to-plane distance and the boundary directions p and q are defined by the angle δ_1 between u_2 and p and the angle δ_2 between u_2 and q. (δ_1 and δ_2 measured counter-clockwise.)

In order to compute the Fourier synthesis, it is necessary to calculate the matrix α_i^j which transforms the components of the vectors from the system u_t to the crystal system a_t, according to

$$x^j = X^i \alpha_i^j. \tag{5}$$

Obviously the inverse transformation

$$X^j = x^i \beta_i^j \tag{6}$$

allows one to express crystal coordinates in terms of the system u_t and then to compute projections along a

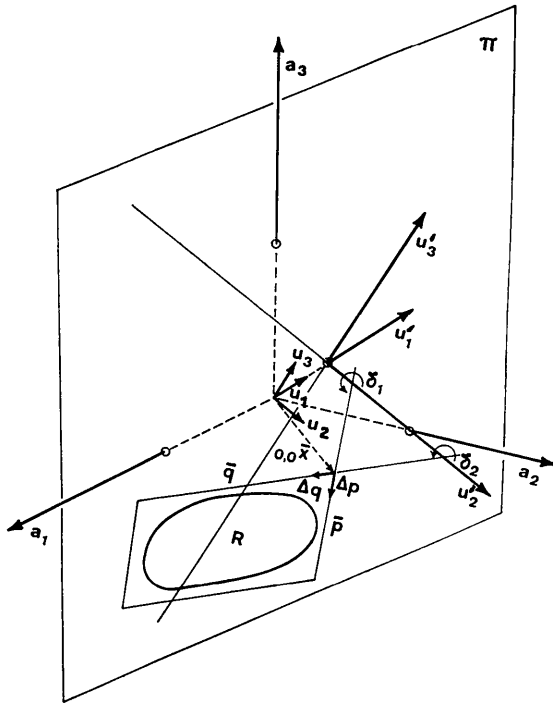Fig. 1. Relations between the crystal system a and the orthogonal system u. u_2' and u_3' are parallel to u_2 and u_3 and pass through the intersection of the plane π with its normal from the origin of the crystal system. R is the region limited by p and q.

general direction u_1. This problem can be easily solved, using the relations between crystal vectors a_t and reciprocal vectors a^i, setting

$$u_1 = d(m_i a^i)$$

$$u_2 = \left(\frac{a_2}{m_2} - d u_1\right)\left[\left(\frac{a_2}{m_2}\right)^2 - d^2\right]^{-\frac{1}{2}} = \left(\frac{a_2}{m_2} - d u_1\right) \cdot D^{-1} \tag{7}$$

$$u_3 = u_1 \times u_2$$

where D is the distance between the foot of the normal to the plane from the origin of a_t and the intersection of a_2 with the plane. The elements of the matrices α_i^j and β_i^j are given in Table 1 in terms of d, D and m_t and of the components of the metric tensor. The notation is that of Patterson (1959).

The expression for the Fourier synthesis of a slab with (2) as equation for the mean plane can be easily derived by integration in the direction of the normal to the plane. The result in terms of the crystal system a_t can be written:

$$\varrho(x, \Delta x) \propto \sum_h j_0(\pi h \cdot \Delta x)|F(h)|$$
$$\cos[2\pi h \cdot x_m - \alpha(h)] \tag{8}$$

where j_0 is the spherical Bessel function of zero order, x_m a vector from the origin to a point of the mean plane defined by (2) and Δx the normal to the plane (2) with modulus $|\Delta x|$ equal to the thickness of the slab. For a given vector h the scalar product $h \cdot \Delta x$ is a constant and we can write, substituting $F'(h)$ for $F(h)$ $j_0(\pi h \cdot \Delta x)$,

$$\varrho(x, \Delta x) \propto \sum_h F'(h) \cos[2\pi h \cdot x_m - \alpha(h)] ; \tag{9}$$

thus all that is needed for application of formula (4) is the transformation of the Fourier coefficient $F(h)$.

As examples relevant to the crystal structure of the 2:1 molecular complexes TMU–3,4-benzpyrene and TMU–coronene, two applications derived for the case of the 1:1 molecular complex TMU–pyrene are reported here. The crystal geometry of the 1:1 molecular complex of TMU and pyrene has been reported previously (De Santis, Giglio, Liquori & Ripamonti, 1961), and more recently the refined structure has been published (Damiani, De Santis, Giglio, Liquori, Puliti & Ripamonti, 1965).

The mean square planes of pyrene and TMU are

$$1.025\,x + 2.667\,y - 2.979\,z = 1$$

and

$$-2.613\,x - 7.835\,y + 7.547\,z = 1$$

Table 1. *Matrix elements for transformation between crystal system a_t and orthogonal system u_t*

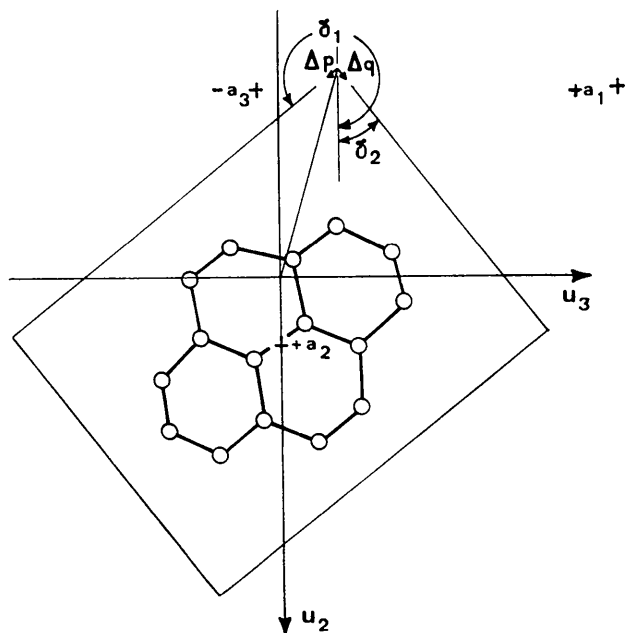|	1	2	3
$\alpha_1{}^j$	$d(m_i g^{i1})$	$d(m_i g^{i2})$	$d(m_i g^{i3})$
$\alpha_2{}^j$	$-d^2 D^{-1}(m_i g^{i1})$	$(m_2 D)^{-1} - d^2 D^{-1}(m_i g^{i2})$	$-d^2 D^{-1}(m_i g^{i3})$
$\alpha_3{}^j$	$d(g)^{-\frac{1}{2}} m_2^{-1} D^{-1}(m_2 g_{23} - m_3 g_{22})$	$d(g)^{-\frac{1}{2}} m_2^{-1} D^{-1}(m_3 g_{21} - m_1 g_{23})$	$d(g)^{-\frac{1}{2}} m_2^{-1} D^{-1}(m_1 g_{22} - m_2 g_{21})$
$\beta_1{}^j$	$d m_1$	$(\alpha_2{}^i g_{i1})$	$(\alpha_3{}^i g_{i1})$
$\beta_2{}^j$	$d m_2$	$(\alpha_2{}^i g_{i2})$	$(\alpha_3{}^i g_{i2})$
$\beta_3{}^j$	$d m_3$	$(\alpha_2{}^i g_{i3})$	$(\alpha_3{}^i g_{i3})$

Fig. 2. Schematic drawing of the pyrene molecule on the mean plane. p, q are directions defined by the angles δ_1 and δ_2 to obtain a regular boundary of the molecule. The values of the increments Δ_p and Δ_q are 0·3 Å. The intersections of the crystal axes a_1, a_2, a_3 with the mean plane are indicated.

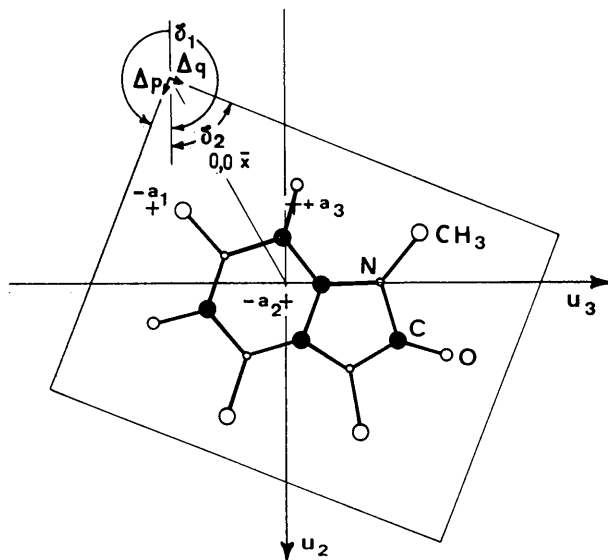Fig. 3. Schematic drawing of the TMU molecule on the mean plane. Values of the increments Δ_p, Δ_q are 0·3 Å.

with distances from the origin of the crystal cell 2.576 and 0.908 Å respectively. Using these equations for the planes the projections of the molecules are as reported in Figs. 2 and 3, where the intersections of the axes with the mean plane and the boundaries selected for the computation are indicated. In Fig. 4 is shown the Fourier section computed in this region for the pyrene molecule, and in Fig. 5 the Fourier slab for TMU. A value of 0.3 Å has been used for the thickness of the
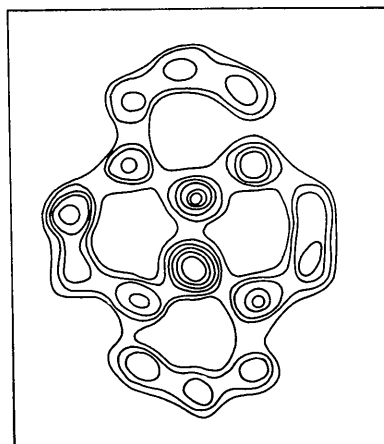

Fig. 4. Fourier synthesis in the molecular plane of the pyrene molecule. The region is as defined in Fig. 2. Contours are at intervals of 0·5 e.Å^{-3} starting at 2 e.Å^{-3}.
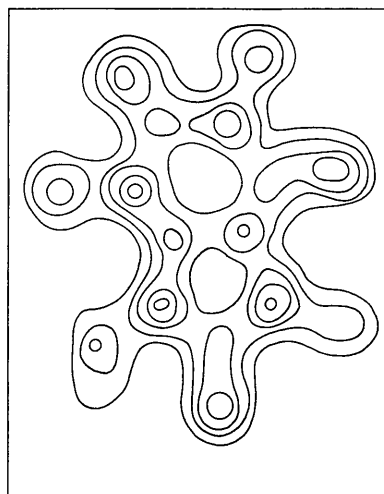

Fig. 5. Fourier slab synthesis, with a thickness of 0·3 Å, of the TMU molecule. The region is as defined in Fig. 3. Contours at arbitrary intervals.

slab to take into account the more pronounced deviations from the least-squares plane of some of the TMU atoms.

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