at the carbons are greater. The thione bond is unsymmetrically oriented with respect to the adjacent carbon bonds. This could arise either from repulsion by the methyl group in the same molecule or by a sulfur atom in an adjacent molecule at a distance of 3·29 Å (S_1–S_3, IV, in Table 9).

The spatial arrangement of the molecules is shown in Fig. 4. It consists of rows extending in the b-axis direction with the plane of the molecules in adjacent rows tilted with respect to the a-axis in such a way as to form a herringbone-like pattern when projected onto the x–z plane. This is a common form of packing for small planar organic molecules with weak intermolecular forces.

The non-bonding intramolecular distances are shown in Table 8 and the intermolecular distances shorter than 5 Å are given in Table 9. These distances were computed using an IBM 650 program prepared by Templeton (1957).

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Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 500 words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible; and proofs will not generally be submitted to authors. Publication will be quicker if the contributions are without illustrations.

A polynomial approximation to atomic scattering factor curves.

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1. Introduction

In high speed computers with large memories, the storage of atomic scattering factors presents little difficulty. If 100–160 values of the scattering factor for each atomic species, at 0·006 intervals in sin θ/λ, can be stored, simple table-searching without interpolation yields the desired functions with 1% accuracy (Sparks, Prosen, Kruse & Trueblood, 1956). Greater accuracy is obtained by inter-

polation in tables of f versus $\sin^2 \theta$ (Ahmed & Cruickshank, 1953; Lavine & Rollett, 1956; Rollett, 1957): in this case, 48 to 100 values are stored for each atomic species, adequate accuracy being achieved by linear interpolation even in the 48-values tables if the intervals of tabulation are chosen so as to make successive increments in f approximately equal.

In other computers, a limited memory makes the storage of entire f-tables an impossibility. To this class belongs SILLIAC (the *S*ydney University version of the University of *Ill*inois *A*utomatic *C*omputer), which at

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present handles many crystallographic calculations for Australia and New Zealand (Freeman, 1957, 1958). The present SILLIAC store can hold 1024 40-bit words; even though a magnetic-tape backing-store is available, it is desirable that our codes take a maximum advantage of the immediate-access property of the fast memory, however limited it may be. For this reason the problem of representing atomic scattering factor curves in a condensed form has been investigated.

2. Choice of function

The idea of seeking an analytical representation of atomic scattering functions is not new. Vand, Eiland & Pepinsky have recently (1957) published tables of the constants a, b, A and B for the expression

$$f(\theta) = A \exp(-ax^2) + B \exp(-bx^2) \qquad (x = \sin \theta),$$

which is valid within the Cu $K\alpha$-range. Even before this, Mayer (1953; cf. Sparks, Prosen, Kruse & Trueblood, 1956) explored the use of polynomial series but rejected them as 'not significantly faster than table-searching and ... appreciably less convenient unless the problem of storage room is critical'. We were originally—and independently of these (then unpublished) observations—attracted to the use of the polynomial representation of atomic form-factors by the following considerations:

(a) The required polynomial coefficients can be evaluated directly from the published scattering curves by standard routines available in most computer-liberaries.

(b) The calculation of $f(\theta)$ as a polynomial series is achieved by a particularly simple 'loop' in the program, if it is coded as

$$f(\theta) = a_0 + a_1 x + a_2 x^2 + \ldots + a_n x^n$$
$$= a_0 + x(a_1 + x(a_2 \ldots + x(a_n) \ldots)) .$$

(c) A number of test-cases, using sixth degree polynomials in $x = \sin \theta/2\lambda$, indicated an accuracy better than 1% within the Cu $K\alpha$-range.

3. Method of computation

The fitting of the tabulated $f_t(\theta)$ by the 'best' polynomial of the form $f(\theta) = \sum_n a_n (\sin \theta/2\lambda)^n$ becomes a least-squares problem, if the criterion of excellence is made the minimization of $\Sigma[f(\theta) - f_t(\theta)]^2$ with respect to arbitrary variations of the coefficients a_n. We are able to solve this problem by means of two standard computer-routines (SILLIAC Codes K3 and L7). The first of these reads a list of values of $\sin \theta/2\lambda$ followed by a list of the corresponding $f_t(\theta)$, and produces the $n \times (n+1)$ matrix of the least-squares normal equations. The output-tape from this code becomes the input for the next one, which solves the simultaneous linear equations for the a_n. For the sake of convenience we have coded short auxiliary programs to tabulate and to test the sets of coefficients.

In general we have found that the published $f(\theta)$-values at 0·05 intervals in $\sin \theta/\lambda$ are adequate data for the fitting of the polynomials. For the elements from hydrogen through beryllium the curves were plotted and twice this number of points of observation were used. The f-curves of Viervoll & Ögrim (1949) are published

at intervals of 0·0796 in $\sin \theta/\lambda$, and for these curves we have also found it necessary to read additional points from plotted curves.

The choice of $\sin \theta/2\lambda$ for the variable in these polynomials has been made for reasons of scaling, since the quantity $\sin \theta/2\lambda \leq 1/2\lambda$ is fractional for all likely values of λ.

4. Results

Our coefficients for those of the lighter elements, for which there exist scattering curves calculated from electron-distributions taking account of exchange, are listed in Table 1. Table 2 contains coefficients for curves calculated without exchange. We have not included our coefficients for the form-factors for heavier atoms recently recalculated by Thomas & Umeda (1957) since the restriction to the Cu $K\alpha$-range becomes serious for calculations involving the heavier atoms. (Our own crystal-structure programs use these coefficients scaled down by 10^{-6}. Copies of the complete tables on this scale are available.)

5. Adequacy

The criterion of fit used by Vand, Eiland & Pepinsky (1957) for their two-term Gaussian representation of atomic scattering factors was a standard deviation, $\sigma = (\Sigma(\Delta f)^2)^{\frac{1}{2}}/m^{\frac{1}{2}}$, where m was the number of tabulated values to which the function was fitted. This standard deviation, when expressed as a percentage of N, the number of electrons associated with an atom or ion, was usually smaller than unity.

We have adopted the same criterion for the curves calculated in the present work. The values of σ and σ/N are included in Tables 1 and 2. In only one case (Li, $\sigma/N = 0.97\%$) does the percentage standard deviation exceed 0·5%. An equally close fit is obtained for the Thomas–Umeda f-curves: some representative values illustrate this.

$Z = N$	σ	$\sigma/N(\%)$
29	0·027	0·09
46	0·033	0·07
53	0·034	0·06
77	0·037	0·05

On the other hand, the fact that σ/N is smaller than 1% is no guarantee that deviations greater than 1% of $f(\theta)$ do not occur over parts of the curve: this is shown by the values of f_{carbon} from the paper of Vand et al. (1957), which we have reproduced in Table 3 for comparison with the tabulated values and with the values calculated by the sixth-degree polynomial approximation.

To the adequacy-criterion represented by σ/N we have therefore added the qualification that $|f_{\text{calc}} - f_{\text{tab}}|/f_{\text{tab}}$ shall nowhere along the curve exceed 1%. All the polynomials for which the coefficients are listed in Tables 1 and 2 have been tested at the data-values of θ. For representative curves, intermediate values of $f(\theta)$ were also calculated and were compared with values interpolated graphically in the published functions: the deviations at these intermediate points were nowhere significantly greater than those at the data-points. The following cases are the only ones where deviations of more than 1% of $f(\theta)$ occurred: (The figures in parenthesis show the greatest deviation expressed first in terms of electrons

Table 1. *Polynomial coefficients for atomic scattering factors of light elements (with exchange)*

	a_6	a_5	a_4	a_3	a_2	a_1	a_0	σ	σ/N (%)	Ref.
H	−5699·0	+8133·7	−4551·3	+1225·52	−145·08	+0·878	+1·000	0·003	0·30	M
He	+3135·0	−2909·5	+610·9	+173·40	−72·96	+0·244	+1·999	0·001	0·05	M
Li	−46616·0	+50394·1	−20094·8	+3495·03	−209·14	−11·596	+3·032	0·029	0·97	B
Be	−75408·0	+87981·7	−39064·4	+8014·30	−684·18	−0·119	+3·998	0·020	0·50	B
B	−58217·0	+71813·4	−34444·5	+7862·05	−780·81	+4·473	+4·998	0·005	0·10	I
C	−26924·0	+38145·9	−21321·1	+5756·99	−686·38	+5·072	+5·996	0·006	0·10	B
N	−3433·0	+11253·4	−9881·7	+3647·05	−551·57	+3·562	+6·996	0·007	0·10	B
O	+6115·0	−666·0	−4242·3	+2469·09	−466·40	+2·593	+7·997	0·009	0·11	B
F	+309·0	+5138·7	−6373·2	+2842·01	−505·30	+3·015	+8·997	0·005	0·06	B
F⁻	−37735·0	+48543·1	−25195·5	+6595·76	−807·11	+1·422	+10·001	0·005	0·05	B
Ne	+10776·0	−8096·3	+102·3	+1385·46	−379·39	+1·399	+9·998	0·006	0·06	B
Na	−48450·0	+50327·9	−19824·9	+3814·54	−366·94	−13·214	+11·014	0·003	0·03	B
Mg⁺⁺	−217·0	−925·5	+490·4	+238·18	−156·31	+0·339	+9·999	0·003	0·03	B
Si⁴⁺	+391·0	−975·1	+560·9	+30·53	−89·51	+0·173	+10·000	0·001	0·01	B
Cl⁻	−102448·0	+132204·9	−67109·0	+16445·35	−1791·71	+9·485	+17·995	0·007	0·03	B
A	−16480·0	+35861·1	−26722·1	+8905·00	−1256·56	+9·464	+17·991	0·017	0·10	B
K⁺	+20076·0	−10519·8	−4339·5	+3982·16	−820·86	+5·154	+17·994	0·015	0·08	B
Ca	−99390·0	+108430·9	−46225·0	+9756·96	−950·26	−23·825	+20·031	0·061	0·30	B
Cu⁺	+13224·0	−10385·6	+54·9	+2165·92	−673·75	+25·282	+27·999	0·005	0·02	B

B Berghuis *et al.* (1955).   I Ibers (1957).   M McWeeny (1951).

Table 2. *Polynomial coefficients for atomic scattering factors of light elements (without exchange)*

	a_6	a_5	a_4	a_3	a_2	a_1	a_0	σ	σ/N (%)	Ref.
Mg	−69841·0	+81247·2	−35724·7	+7299·30	−643·18	−15·069	+12·033	0·048	0·40	V
Al³⁺	+84·0	−1023·8	+551·0	+149·60	−129·69	+0·423	+10·000	0·001	0·01	B
Al	−26710·0	+33656·4	−15562·3	+3122·12	−191·73	−39·383	+13·012	0·032	0·25	V
Si	−75917·0	+90560·6	−40383·0	+8014·88	−572·88	−38·033	+14·034	0·043	0·31	V
P	−128692·0	+159337·2	−74656·0	+16072·77	−1436·16	−9·682	+15·042	0·051	0·34	V
S	−94339·0	+121360·0	−60042·4	+13874·37	−1344·56	−10·814	+15·991	0·035	0·22	V
Cl	−75806·0	+103854·3	−55084·1	+13771·70	−1469·53	−3·224	+16·985	0·038	0·22	V
K	+27256·0	−21729·6	+3006·5	+1396·10	−323·88	−39·820	+18·990	0·027	0·14	V
Sc	+54454·0	−62794·5	+27139·2	−5458·07	+618·08	−95·488	+21·017	0·048	0·23	Q
Ti	+43895·0	−48869·3	+20267·1	−3900·60	+465·93	−94·032	+22·013	0·045	0·20	Q
V	+46652·0	−51300·1	+20912·4	−3895·37	+440·59	−93·630	+23·015	0·049	0·21	Q
Cr²⁺	+2741·0	+3547·5	−7230·8	+3876·27	−792·73	+4·125	+21·997	0·007	0·03	B
Cr	−7594·0	+17896·9	−13514·3	+4456·65	−549·66	−49·790	+24·017	0·039	0·16	V
Zn	−105337·0	+121536·7	−55120·5	+12577·83	−1440·98	−0·452	+30·008	0·022	0·07	B
Ga	−110598·0	+125995·5	−55808·0	+12220·31	−1314·12	−12·117	+31·015	0·034	0·11	B
Ge	−138666·0	+156368·9	−67783·8	+14171·60	−1396·41	−18·359	+32·023	0·049	0·15	B
As	−170146·0	+197704·9	−88729·7	+19191·41	−1943·88	+0·576	+33·009	0·030	0·09	B
Rb⁺	−39618·0	+66201·4	−42101·3	+12731·50	−1751·41	+12·446	+35·989	0·021	0·06	B

B Berghuis *et al.* (1955).   Q Qurashi (1954).   V Viervoll & Ögrim (1949).

Table 3. *Tabulated and calculated values of $f(\theta)$ for carbon*

		2-term Gaussian			6th degree polynomial		
sin θ/λ	f (tabulated)	f (calculated)	Δf	$(\Delta f/f)$ %	f (calculated)	Δf	$(\Delta f/f)$ %
0·00	6·000	6·000	0·000	0·0	5·996	0·004	0·1
0·05	5·764	5·781	0·017	0·3	5·776	0·012	0·2
0·10	5·141	5·188	0·047	0·9	5·131	0·010	0·2
0·15	4·362	4·403	0·041	0·9	4·355	0·007	0·2
0·20	3·612	3·618	0·006	0·0	3·619	0·007	0·2
0·25	3·003	2·969	0·034	1·1	3·006	0·003	0·1
0·30	2·538	2·501	0·037	1·5	2·539	0·001	0·0
0·35	2·212	2·196	0·016	0·7	2·208	0·004	0·2
0·40	1·983	2·002	0·019	1·0	1·981	0·002	0·1
0·50	1·707	1·762	0·055	3·2	1·711	0·004	0·2
0·60	1·548	1·574	0·026	1·7	1·548	0·000	0·0
0·70	1·423	1·384	0·039	2·7	1·427	0·004	0·3

and then as a fraction of $f(\theta)$ at the corresponding point of the curve).

Table 1: Li (0·02, 2 %), Be (0·04, 3 %).

Table 2: Mg (0·01, 1·8 %), Al (0·07, 1·2 %), Si (0·08, 1·2 %), P (0·08, 1·2 %), V (0·1, 1·1 %).

Trial calculations have shown that no significant advantage is gained within the Cu $K\alpha$-range from the use of polynomials of degrees higher than the sixth. At values of sin $\theta/\lambda > 0·7$ the polynomials diverge wildly from the tabulated functions.

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On the determination of intermolecular vectors in molecular crystals by a modified Patterson function.

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The localization of the molecules in the unit cell after their orientation has been approximately established is one of the main difficulties involved in the application of the Fourier-transform method in the preliminary stages of a structure determination. If the Fourier transform $T_M(S)$ of each molecule at

$$S = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* \qquad (1)$$

is supposed to be known to a certain degree of accuracy, the problem reduces to determine the $\mathbf{R}_M$ vectors appearing in the structure amplitude expressed as

$$F(S) = \sum_M T_M(S) \exp\{2\pi i S.\mathbf{R}_M\}, \qquad (2)$$

where

$$T_M(S) = \sum_n f_n.\exp\{2\pi i S.\mathbf{r}_n\} \qquad (3)$$

$$\mathbf{R}_M = X_M\mathbf{a} + Y_M\mathbf{b} + Z_M\mathbf{c} \qquad (4)$$

are vectors from the origin of the unit cell to a reference point in the Mth molecule, and

$$\mathbf{r}_n = x_n\mathbf{a} + y_n\mathbf{b} + z_n\mathbf{c} \qquad (5)$$

are vectors from the reference points in the molecule to the nth atom.

In the special case when all the molecules have the same orientation either in space or in projection, (2) may be written as

$$F(S) = T(S).A(S), \qquad (6)$$

where

$$A(S) = \sum_M \exp\{2\pi i S.\mathbf{R}_m\}. \qquad (7)$$

The $\mathbf{R}_M$ vectors may then be obtained (Booth, 1948) as those quantities which satisfy relation (6). On the basis of relation (6), Taylor (1954) has developed a method for determining the $\mathbf{R}$'s which may also be applied to cases where the molecules have not necessarily the same orientation. However, Taylor's method, though interesting, has several limitations in its practical application, the most restrictive one being due to the inaccuracy with which the quantities $A(S)$ may be obtained.

A modification of the Booth–Taylor method, applicable to centrosymmetric molecules, has been suggested by Liquori & Ripamonti (1956) which overcomes the above difficulty. However, the solutions are not always unique, especially when the number of independent molecules is larger than two. A similar method has been more recently proposed by Taylor (1957).

It is obvious that in view of the poor accuracy of the $A(S)$ values, the efficiency of a method of determining the $\mathbf{R}_M$ vectors should increase with increasing the number of $A(S)$ which can be used. The automatic averaging which would result should in part reduce both the number of false solutions and the inaccuracy of the true solutions. The above consideration suggests that a suitable modified Patterson function would lend itself to this purpose. In fact, it is a common observation that the Patterson projection of a structure containing groups of atoms arranged in centro-symmetric regular assemblies in the unit cell does contain maxima corresponding to vectors between centers of such assemblies (Patterson, 1949). However, it is usually difficult to recognize these maxima when the unit cell contains a large number of atoms.

It may be shown that it is possible to enhance the maxima corresponding to intermolecular vectors with respect to those corresponding to interatomic vectors by a suitable modification of the vector functions.

An idealized structure will be considered here consisting of identical atoms and located at the centers of the molecules. If the Fourier transform of the molecule is calculated taking its center as origin, the electron-density distribution of the idealized structure is:

$$\varrho(\mathbf{R}) = \frac{1}{V}\sum_S G(S) \exp\{2\pi i S.\mathbf{R}\}, \qquad (8)$$

where