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The Fourier Inversion of Diffraction Data

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THERE are two methods, generally speaking, which are used to analyze experimental diffraction data in terms of structure. The one consists in the theoretical calculation of the scattering pattern for various models and comparison with the observed pattern. The other, taking advantage of the trigonometric form of the equations, consists in Fourier inversion, to obtain structural information directly. We may remark that the two methods are equivalent in principle, but that actually they do not entirely replace each other. For example, in the study of gas-molecule structure by electron diffraction, where the two methods are called the correlation method and the radial distribution method, certain aspects of the experimentally determined intensity function are usually better known than others: The correlation method is much better suited to this situation than the less laborious radial distribution method, which requires essentially indiscriminate use of the intensity data. In practice, the radial distribution method is often used to narrow the choice of possible models and parameter values, while the visual method serves to analyze the remaining possibilities.

In this paper many of the problems connected with the use of the Fourier methods will be discussed. Some of these problems have been handled satisfactorily in one way or another before, but we intend to deal with them from a unified point of view, at the core of which are two simple facts of Fourier theory. They are that the Fourier transform of a sum of products is again a sum, the sum of the transforms of these products. The nature of these transforms is discussed most simply with the aid of the convolution or folding theorem, which states that multiplication of two functions corresponds to the folding of their transforms, as discussed in Sec. 3.

A main problem in the inversion of diffraction data arises from the absence of experimental data for scattering angles greater than a limiting angle; it and related problems are treated by considering the effect of modifying the observed intensity function, by multiplication with suitable factors before inversion. A number of such factors—we call them *modification functions*—are discussed and a general treatment of a special class of them is attempted. Next, the difficulties are considered which arise from the presence in the intensity function of the atomic scattering factors and temperature factors, leading to a generalization to include such effects in a *complete* modification function. These matters are all first illustrated by the special one-dimensional case of the electron-diffraction pattern, and later applied to x-ray diffraction of liquids and amorphous solids. Final sections deal with the application of modification functions to the analysis of crystal structures.

1. THE RADIAL DISTRIBUTION FUNCTION IN ELECTRON DIFFRACTION

The structure sensitive part of the expression which describes the scattering of fast electrons by gas molecules not involving internal rotations is of the form[1]

$$sI'(s)=\mathrm{const}\sum_{ij}{}'\frac{[Z_i-f_i(s)][Z_j-f_j(s)]\times\exp(-a_{ij}s^2)\sin sr_{ij}}{s^4r_{ij}},\tag{1-1}$$

where the sum extends over all pairs of atoms of a molecule, atom i having atomic number Z_i and x-ray form factor $f_i(s)$. The effect on the scattering of zero-point and temperature variation of the interatomic distance r_{ij} is described by the so-called temperature factor $\exp(-a_{ij}s^2)$, in which a_{ij} is given by one-half the mean-square variation $\langle\delta r_{ij}^2\rangle_{\mathrm{Av}}$ of r_{ij}. The variable s is $(4\pi/\lambda)\sin(\varphi/2)$, where φ is the angle between incident and scattered beam and λ the electron wavelength.

The factor $(Z_i-f_i(s))$ is often nearly proportional to the average $\langle(Z-f(s))/Z\rangle_{\mathrm{Av}}$ taken over all atoms, so that (1-1) may be approximated by

$$sI'(s)\approx\mathrm{const}\left\langle\frac{Z-f(s)}{Z}\right\rangle_{\mathrm{Av}}^2\times\frac{\exp(-as^2)}{s^4}\sum_{ij}{}'\frac{Z_iZ_j}{r_{ij}}\sin sr_{ij}\exp(-\delta a_{ij}s^2),\tag{1-2}$$

where a is a convenient reference value of the a_{ij} and $\delta a_{ij}=a_{ij}-a$.

The film exposure due to the electrons scattered according to (1-1) or (1-2) is superposed on a smooth, structure-insensitive background caused by the "atomic" elastic scattering (described by the terms with $i=j$, which in (1-1) were omitted from the complete expression), by inelastic scattering, and by processes occasioned by imperfections of the experimental arrangement. It will become evident, however, that the expression

$$sI''(s)=\sum_{ij}{}'\frac{Z_iZ_j}{r_{ij}}\exp(-\delta a_{ij}s^2)\sin sr_{ij}\tag{1-3}$$

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[1] L. O. Brockway, Revs. Modern Phys. 8, 231 (1936).

obtained by suppressing the monotonic factor in front of the summation symbol in (1-2) or an expression of the form of

$$sI'''(s)=\frac{1}{\sum_i(Z_i-f_i(s))^2}\times\sum_{ij}{}'\frac{[Z_i-f_i(s)][Z_j-f_j(s)]}{r_{ij}}\times\exp(-\delta a_{ij}s^2)\sin sr_{ij} \quad (1\text{-}4)$$

obtained by dividing (1-1) by $\sum_i[Z_i-f_i(s)]^2$, or some similar factor, are more convenient for the radial distribution method. Furthermore, (1-3) and (1-4) are the more natural functions to use if diffraction photographs are to be interpreted visually, because what is apparent to the eye is approximately the ratio of the fluctuating part of the intensity distribution to some smooth background.[1] In the correlation method, functions of one of these forms calculated for molecular models of interest are directly compared with the observed intensity distribution.

For the discussion of the radial distribution method the further simplified function

$$sI(s)=\left(\frac{2}{\pi}\right)^{\frac{1}{2}}\sum_{ij}{}'\frac{Z_iZ_j}{r_{ij}}\sin sr_{ij}, \quad (1\text{-}5)$$

which describes the structure sensitive part of the scattering by a rigid molecule made up of point atoms, is a convenient starting point. The factor $(2/\pi)^{\frac{1}{2}}$ provides a suitable normalization. Such a molecule is characterized by a distance spectrum which may formally be expressed by the radial distribution function

$$r^2D_o(r)=\sum{}'_{ij}Z_iZ_j\delta(r-r_{ij}), \quad (1\text{-}6)$$

where $\delta(r)$ is the Dirac delta function, defined by the two conditions[2]

$$\delta(r)=0 \quad \text{unless } r=0 \quad (1\text{-}7)$$

and

$$\int_{-\infty}^{\infty}\delta(r)dr=1.$$

The function $r^2D_o(r)$ has infinitely high and infinitely narrow peaks for values of r which represent interatomic distances. With it Eq. (1-5) may be expressed by

$$sI(s)=(2/\pi)^{\frac{1}{2}}\int_0^{\infty}rD_o(r)\sin srdr. \quad (1\text{-}8)$$

Sine inversion[3] of (1-8) yields

$$rD(r)=(2/\pi)^{\frac{1}{2}}\int_0^{\infty}sI(s)\sin srds, \quad (1\text{-}9)$$

where $rD(r)$ is essentially $rD_o(r)$ except that it is antisymmetrical because $\sin sr$ is odd, whereas $rD_o(r)$ was defined as vanishing for negative r; $rD(r)$ may also be expressed as

$$rD(r)=\sum_{ij}{}'\frac{Z_iZ_j}{r_{ij}}[\delta(r-r_{ij})-\delta(r+r_{ij})]. \quad (1\text{-}10)$$

The problem now is to obtain from the actually observed intensity curve, which is known for a finite range of s only, a radial distribution function which is a faithful representation of the distance spectrum of the molecules.

2. THE LIMITATION OF OBSERVED DATA

If the integration in (1-9) is not extended over the whole range in which the integrand is different from zero, the resulting function shows certain spurious maxima and minima which may make its interpretation very laborious if not impossible. Bragg and West[4] discussed such effects in the case of the two-dimensional Fourier series of crystal structure analysis and pointed out a close analogy to diffraction effects which occur in an optical image in consequence of the finite aperture of the optical system.

These spurious features may be greatly diminished or entirely eliminated by multiplying the integrand of (1-9) by a suitable factor. The function $\exp(-as^2)$ is often used for this purpose, with a chosen so that the resulting integrand has a negligible value beyond the upper limit of s for which experimental data are available. This function has been called the artificial temperature factor, a name suggested by its identity in form to the temperature factors in the intensity formula (1-1). Sommerfeld used this convergence factor in his doctorate thesis,[5] where he succeeded in obtaining with its aid the first precise result concerning the validity of the Fourier integral theorem. Bragg and West,[4] who referred to it as an "arbitrary temperature factor," introduced its use in crystal structure analysis, and Dégard[6] introduced it in electron diffraction investigations, at the suggestion of Professor L. Pauling. A convergence factor of this type was perhaps first introduced by Weierstrass[7] who used the factor $r^{-n^2}(r<1)$ in his discussion of Fourier series.

Quite a different mode of procedure was early used by

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[2] P. A. M. Dirac, *Quantum Mechanics* (Oxford University Press, London, 1947), third edition, p. 58. An example of a δ-function pertinent to Fourier theory is $\delta(x)=\int_{-\infty}^{\infty}\exp(-2\pi ihx)dh$.

[3] The background of Fourier theory needed for our discussion is expounded in various textbooks. See, for example, H. S. Carslaw, *Fourier Series and Integrals* (Macmillan and Company, Ltd., London, 1930) and W. Rogosinski, *Fourier Series* (Chelsea Publishing Company, New York, 1950). Special points will be referred to standard treatises.

[4] W. L. Bragg and J. West, Phil. Mag. **10**, 823 (1930).

[5] H. S. Carslaw, reference 3, p. 321.

[6] C. Dégard, Ph.D. thesis, University of Liège, 1937.

[7] M. Bôcher, Annals of Math. **7**, 81 (1906), footnote, p. 103.

Havighurst, Compton, and James and Firth[8] and has been applied recently by van Reijen[9] in an x-ray analysis of the electron distribution in diamond. It consists in using extrapolated values at large values of s, where $sI(s)$ (or the structure factor in the crystal case) is not experimentally accessible. Although an exact knowledge of $sI(s)$ for even an arbitrarily small range of s would define $sI(s)$ for all values of s, such knowledge (as would define $sI(s)$ and all its derivatives at a given point) can never be obtained experimentally, however small the experimental error, and the extrapolation must be carried out judiciously. Even so, it is difficult to judge the uniqueness of the results, and deceptively false distributions can be produced.[10] For the case of atomic scattering, Hauptman and Karle[11] have recently discussed the use of the criterion that the distribution function should be everywhere positive as an aid towards a unique extrapolation of $sI(s)$. Nevertheless, it would seem that more than the criterion of non-negativeness is required—perhaps also the more complex condition of smoothness of the distribution function and conditions about its asymptotic behavior, e.g., that for finite molecules $rD(r)$ must vanish when r exceeds a certain value.

In electron diffraction the absence of data for s less than some minimum value presents a similar problem which also has often been handled by extrapolation, usually either by use of the theoretical intensities for an approximate model of the molecule or even by some gross appeal to experience.[12] Since the desire is here to locate interatomic distances with precision rather than to study the distribution of the outer electrons, and since the low frequency components contributed by the inner part of the intensity pattern have very little effect on the locations of the peaks of the radial distribution function, this is a valid procedure of convenience, just as the extrapolation beyond the upper limit of s in the crystal case is above reproach if it is only the broad, diffuse aspects of the distribution function about which information is desired. If the extrapolation to $s=0$ is not used,[13] the problem of convergence is similar to the ones discussed earlier in this paragraph; heretofore, however, it does not seem to have been handled by the explicit use of a convergence factor.

3. THE FOLDING THEOREM AND MODIFICATION FUNCTIONS

We shall now consider[14] the problem of the convergence factor and, more generally, of the change in $rD(r)$ to

$$rD'(r)=(2/\pi)^{\frac{1}{2}}\int_0^\infty sI(s)M(s)\sin srds, \tag{3-1}$$

which occurs if $sI(s)$ is multiplied by a modification function $M(s)$. In this discussion the folding theorem of Fourier integrals[3,15,16] is very useful. If $f(x)$, $F(t)$ and $g(x)$, $G(t)$ are two sets of Fourier transforms such that

$$\begin{aligned}f(x)&=(2\pi)^{-\frac{1}{2}}\int_{-\infty}^{\infty}F(t)\exp(itx)dt,\\F(t)&=(2\pi)^{-\frac{1}{2}}\int_{-\infty}^{\infty}f(x)\exp(-itx)dx,\\g(x)&=(2\pi)^{-\frac{1}{2}}\int_{-\infty}^{\infty}G(t)\exp(itx)dt,\\G(t)&=(2\pi)^{-\frac{1}{2}}\int_{-\infty}^{\infty}g(x)\exp(-itx)dx,\end{aligned} \tag{3-2}$$

then the Fourier transform of the product $f(x)\cdot g(x)$ is given by

$$\begin{aligned}R(t)&=(2\pi)^{-\frac{1}{2}}\int_{-\infty}^{\infty}f(x)\cdot g(x)\exp(-itx)dx\\&=(1/2\pi)\int_{-\infty}^{\infty}f(x)\int_{-\infty}^{\infty}G(u)\exp(iux)du\exp(-itx)dx\\&=(1/2\pi)\int_{-\infty}^{\infty}G(u)\int_{-\infty}^{\infty}f(x)\exp[-ix(t-u)]dxdu\\&=(2\pi)^{-\frac{1}{2}}\int_{-\infty}^{\infty}G(u)F(t-u)du.\end{aligned} \tag{3-3}$$

The function $R(t)$ is known as the folding ("Faltung"), resultant, or convolution of G and F. Inversely, the Fourier transform of $R(t)$ is

$$(2\pi)^{-\frac{1}{2}}\int_{-\infty}^{\infty}R(t)\exp(itx)dt=f(x)\cdot g(x), \tag{3-4}$$

so that the multiplication of two functions corresponds to the folding of their transforms in Fourier transform space and inversely. The indicated derivation is only a

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[8] R. J. Havighurst, Phys. Rev. **29**, 1 (1927); A. H. Compton and S. K. Allison, *X-Rays in Theory and Experiment* (D. Van Nostrand Company, Inc., New York, 1935), second edition; R. W. James and E. M. Firth, Proc. Roy. Soc. (London) **A117**, 62 (1927).

[9] L. L. van Reijen, Physica **9**, 461 (1942); J. O. Bouman, *X-Ray Crystallography* (North Holland Publishing Company, Amsterdam, 1951), Chap. 3.

[10] D. W. J. Cruickshank, Acta Cryst. **2**, 65 (1949), see (10.1), (10.2), and appendix; H. Viervoll, Skrifter Norske Videnskaps Akad., Oslo, Mat. Naturv. Kl. No. 2, 1950.

[11] H. Hauptman and J. Karle, Phys. Rev. **77**, 491 (1950).

[12] See, for example, Shaffer, Schomaker, and Pauling, J. Chem. Phys. **14**, 659 (1946).

[13] H. Viervoll, Acta Chem. Scand. **1**, 120 (1947).

[14] J. Waser, Ph.D. thesis, California Institute of Technology, 1944.

[15] E. L. Titchmarsh, *Introduction to the Theory of Fourier Integrals* (Oxford University Press, London, 1937).

[16] S. Bochner, *Vorlesungen über Fouriersche Integrale* (Akademische Verlagsgesellschaft, Leipzig, 1932).

formal one, but the result can be shown to be valid for the functions considered here.[15,16]

An important example is provided by the Gaussian distribution function:

$$\begin{aligned} f(x) &= \exp(-ax^2),\\ F(t) &= (2a)^{-\frac{1}{2}} \exp(-t^2/4a),\\ g(x) &= \exp(-bx^2),\\ G(t) &= (2b)^{-\frac{1}{2}} \exp(-t^2/4b),\\ f(x)g(x) &= \exp[-(a+b)x^2],\\ R(t) &= [2(a+b)]^{-\frac{1}{2}} \exp[-t^2/4(a+b)]. \end{aligned} \tag{3-5}$$

The transform of a Gaussian is again a Gaussian, and the half-widths at half-height, $0.83(a)^{-\frac{1}{2}}$ and $0.83(4a)^{\frac{1}{2}}$ (one finds $\exp(-0.83)^2=0.5$), are in a reciprocal relation. Since the resultant $R(t)$ is the transform of the product $f(x)g(x)$, it must be Gaussian, as shown, with half-width equal to the square root of the sum of the squares of the half-widths of $F(t)$ and $G(t)$.

For the special case that $f(x)$ is odd and $g(x)$ even [the latter so that $f(x)g(x)$ is odd], the above formulas become after absorbing factors $\pm i$

$$\begin{aligned} f(x) &= (2/\pi)^{\frac{1}{2}} \int_0^\infty F(t) \sin txdt = -f(-x),\\ F(t) &= (2/\pi)^{\frac{1}{2}} \int_0^\infty f(x) \sin txdx = -F(-t);\\ g(x) &= (2/\pi)^{\frac{1}{2}} \int_0^\infty G(t) \cos txdt = g(-x),\\ G(t) &= (2/\pi)^{\frac{1}{2}} \int_0^\infty g(x) \cos txdx = G(-t);\\ R(t) &= (2/\pi)^{\frac{1}{2}} \int_0^\infty f(x)\cdot g(x) \sin txdx\\ &= (2\pi)^{-\frac{1}{2}} \int_{-\infty}^\infty F(u)G(t-u)du = -R(-t). \end{aligned} \tag{3-6}$$

For our problem we identify the odd function $sI(s)$ with $f(x)$, the even function $M(s)$ with $g(x)$, the distribution function $rD(r)$ with $F(t)$, and the cosine transform of $M(s)$,

$$T(r) = (2/\pi)^{\frac{1}{2}} \int_0^\infty M(s) \cos srds = T(-r), \tag{3-7}$$

with $G(t)$. The result is

$$rD'(r) = (2\pi)^{-\frac{1}{2}} \int_{-\infty}^\infty uD(u)T(r-u)du, \tag{3-8}$$

which of course pertains to any $uD(u)$ of mathematically allowable form, and is in particular not tied to the very special $rD(r)$ defined by (1-9) and (1-10), which merely serves to provide a simple example. The integrand of (3-8) may be written in several equivalent ways by changing the variable of integration or taking advantage of the symmetries of $T(u)$ and $uD(u)$. Correspondingly, the folding process may be viewed in several ways. The one indicated in (3-8) may be described by the following three steps: (1) Superposition of $uD(u)$ with a (reflected) $T(u)$ whose origin has been shifted by r. (2) Multiplication of corresponding values. (3) Integration over u. This has to be repeated for all (positive) values of r, and is in general a complicated procedure. For the idealized $rD(r)$ (1-10) the result is, however, simply

$$rD'(r) = (2\pi)^{-\frac{1}{2}} \sum_{ij}{}' \frac{Z_iZ_j}{r_{ij}}[T(r-r_{ij}) - T(r+r_{ij})], \tag{3-9}$$

which entails the replacement of the infinitely sharp peaks of $rD(r)$ (1-10) by the features of the function $T(r)$. This suggests that the folding for a continuous distribution may also be viewed in terms of a decomposition of $rD(r)$ into a suitably weighted array of δ-functions, which are then to be replaced by T's and summed. It should be noted that the features of $T(r+r_{ij})$, though centered at $r=-r_{ij}$, may extend across the origin to positive values of r, so that the second term in (3-10) may in some cases be of practical importance.

There are of course other combinations of odd and even functions $f(x)$ and $g(x)$ besides the one discussed here in detail. They lead to equations analogous to (3-6), which are at times very useful.

4. EXAMPLES OF MODIFICATION FUNCTIONS

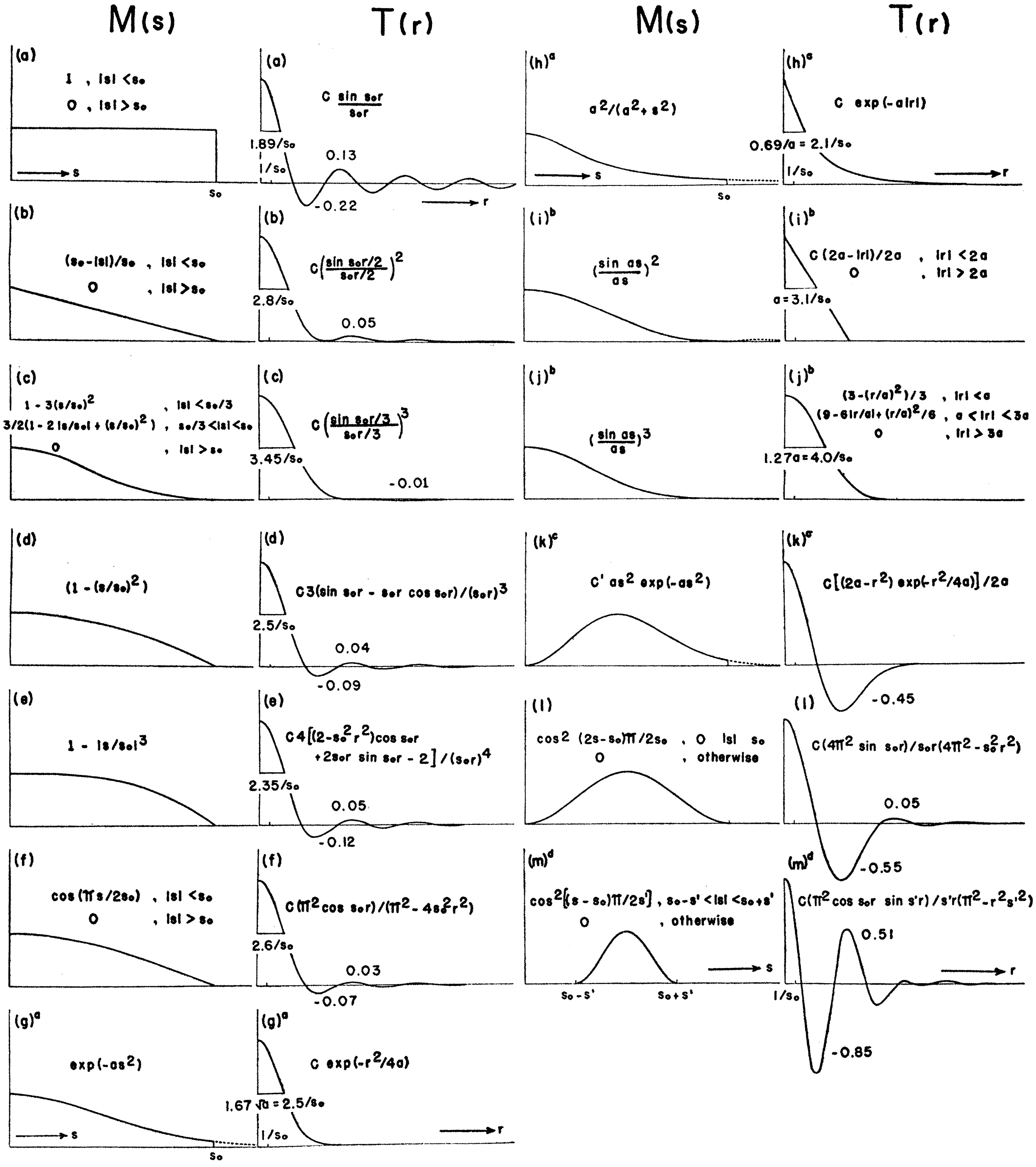
A useful modification function must substantially equal zero outside the s range for which $sI(s)$ is known (or assumed); moreover, the transform $T(r)$ should be such as to make analysis of the resulting $rD'(r)$ in terms of the desired distribution function $rD(r)$ straightforward and economical. In general, the useful transforms will have a main peak flanked by subsidiary features; it will be desired to have the main peak sharp, for resolving closely spaced peaks, and the subsidiary features weak, to minimize the influence of a given peak on all the others. Unfortunately, these requirements are not entirely compatible, and compromise has to be made in the interest of convenience.

Convenience, it must be realized, is all that is ever achieved in practical Fourier analysis: An integral equation

$$sI(s) = (2/\pi)^{\frac{1}{2}} \int_0^\infty rD(r) \sin rsdr \tag{4-1}$$

is merely transformed into another integral equation

$$rD'(r) = (2\pi)^{-\frac{1}{2}} \int_{-\infty}^\infty uD(u)T(r-u)du, \tag{4-2}$$



[a] For a chosen such as to make $M(s_o) = 0.1$.
[b] For a chosen such that the first zero of $M(s_o)$ falls on s_o.
[c] The graphs correspond to C' and a chosen such as to make $M_{\max} = 1.0$ and $M(s_o) = 0.10$.
[d] The graphs correspond to $s' = s_o/2$.

FIG. 1. Examples of modification functions $M(s)$ and their transforms $T(r)$.

which still has to be solved in one way or another. For the applications considered here the convenience achieved is indeed often very great. Even more important is the circumstance that in practice no unique solution is possible without the use of assumptions based on external knowledge—and these assumptions can usually be introduced by far the more easily and naturally into the consideration of the transformed Eq. (4-2). Prime examples are the many successful interpretations which have been made of incomplete electron density functions in the course of the analysis of complex crystal structures.

Figure 1 presents a number of functions for which both function and transform may be expressed in simple form and which might have possible interest as modification functions. The ordinate scales are such that all the functions have the same maximum height; likewise all the transforms. The abscissa scales are all in terms of the same parameter s_o which frequently but not always is identified with the upper limit of s for which experimental information is available. The half-width is included in most cases also. It is a measure of the sharpness of the peak.

The first function (a) corresponds simply to the effect of breaking off of the integral in (1-9) at s_o. The next five examples (the first corresponds to Fejér's summation of a Fourier series by taking first Cesàro means) cut off more gradually at s_o. They lead to less pronounced secondary maxima, but also to a broader main peak.

Some of the remaining functions are defined with reference to s_o even though they do not cut off there. But in practice all the functions have to be assigned the value zero for $s > s_o$, as corresponds [repeated application of (3-3)] to folding the illustrated complete transforms with $(\sin s_o r)/s_o r$. The resulting effective transforms

$$T'(r) = (2\pi)^{-\frac{1}{2}} \int_{-\infty}^{\infty} T(u) \frac{\sin s_o(r-u)}{s_o(r-u)} du \qquad (4\text{-}3)$$

are of somewhat changed shape, usually with added secondary maxima, in a way that one can learn to judge, at least roughly, directly from the $M(s)$ values, indicated in Fig. 1 by broken lines, which have to be neglected. Function (g) is the artificial temperature factor; the graph corresponds to a value of a for which $M(s_o) = 0.10$. Neglecting the values of $M(s)$ for $s > s_o$ leads to a transform which has practically the same half-width at half-height ($\sim 2.7/s_o$) as the one shown but shows weak secondary maxima;[17] actually, it resembles transform b quite closely. The transforms h and k will suffer similar changes, and i and j considerably smaller and somewhat different ones. Examples i and j (and b and c) involve the form $[(\sin as)/as]^n$, which has cosine transforms that differ from zero in a finite region $|r| \leqq na$ only.[16] Functions having this property are of special interest because they correspond exactly—not merely approximately—to the finite upper limit of integration; a general treatment of them is given below.

Functions k and l are of interest if it is desired to give the inner part of $sI(s)$ especially small weight, perhaps either because the small angle data were unreliable or in order to discriminate between terms of $rD(r)$ which had different real temperature factors (i.e., values of $\langle \delta r_{ij}^2 \rangle_{\text{Av}}$). Modification functions such as these of course also tend to emphasize large values of s, and so lead to transforms with relatively sharp main maxima and correspondingly high resolving power. The transforms shown both have large minima adjacent to the main peak which can be confusing. The similar function m is appropriate if $sI(s)$ is known in a certain range of s only, of width $2s'$ and centered about s_o. The transform is more complex than the preceding two, just as might be expected from the more severely restricted s range from which it is obtained.

New modification functions and their transforms can always be formed by linear combination of known modification functions and transforms, because all the relations are linear. Of special interest is the difference of two functions $M_a(s)$ which corresponds to replacing both the lower and upper limits of integration in (1-9) by finite values ($s_1 < s_2$), as may often be desirable and in some laboratories is the usual practice.[13] The transform of this modification function is the weighted difference of the two transforms $T_1(r)$ and $T_2(r)$, the wider one $T_1(r)$ being multiplied with a coefficient proportional to s_1 and subtracted from the other one multiplied with a coefficient proportional to s_2. The result is a transform of increased complexity, compared to $T_a(r)$, although for $s_1 \ll s_2$ this additional complexity is not very troublesome. Of course, multiplication of known modification functions and convolution of their transforms (and perhaps even convolution of modification functions and multiplication of the transforms) can also be used to obtain new results. And in practical work, in any case, it is likely to prove convenient simply to decide upon some modification function that seems to be especially suited to the problem at hand and to evaluate its transform numerically.

5. GENERAL TREATMENT OF THE FINITE UPPER LIMIT

It is desirable to analyze the question of modification functions, we now designate them by $M_F(s)$, which have values different from zero in the range $0 \leqslant |s| \leqslant s_o$ only. For this purpose we introduce[18] the so-called spherical Bessel functions[19]

$$j_n(x) = (\pi/2x)^{\frac{1}{2}} J_{n+\frac{1}{2}}(x), \qquad (5\text{-}1)$$

where $J_{n+\frac{1}{2}}(x)$ is an ordinary Bessel function. These functions can be simply expressed in terms of trigonometric functions as

$$j_n(x) = (-1)^n (2x)^n \frac{d^n}{d(x^2)^n} \left(\frac{\sin x}{x} \right), \qquad (5\text{-}2)$$

the first few members of the set being

$$j_0(x) = (\sin x)/x, \; j_1(x) = (\sin x)/x^2 - (\cos x)/x$$

and

$$j_2(x) = (3/x^3 - 1/x) \sin x - (3 \cos x)/x^2.$$

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[17] V. Schomaker, Ph.D. thesis, California Institute of Technology, 1938.

[18] J. Waser, Phys. Rev. **85**, 745 (1952).

[19] For example, L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1949).

The $j_{2k}(x)$ (of even order) have the desired property[16,20] of possessing a cosine transform which is different from zero in a finite range only, since

$$\int_0^\infty j_{2k}(x)\cos xt\,dx=\begin{cases}(\pi/2)(-1)^kP_{2k}(t), & |t|<1\\ 0, & |t|>1\end{cases}, \quad (5\text{-}3)$$

$$\int_0^1 P_{2k}(t)\cos xt\,dt=(-1)^kj_{2k}(x). \quad (5\text{-}4)$$

Here $P_{2k}(t)$ is the Legendre polynomial of (even) order $2k$. Since the Legendre polynomials form a complete set of orthogonal functions it is an easy matter to expand any reasonably well behaved $M_F(s)$ as

$$M_F(s)=\begin{cases}\sum_k(\pi/2)^{\frac{1}{2}}a_k(-1)^kP_{2k}(s/s_o), & |s|<s_o\\ 0, & |s|>s_o\end{cases}, \quad (5\text{-}5)$$

where $M_F(s)$ is regarded as even so that only even polynomials occur in the expansion. The cosine transform of $M_F(s)$ is then

$$T_F(r)=\sum_k a_kj_{2k}(rs_o). \quad (5\text{-}6)$$

The question as to what transforms $T_F(r)$ exist is accordingly the question of what class of functions can be represented as expansions of the type (5-6), which, if they exist, can be found with the help of the orthogonality and normalization relations

$$\int_0^\infty j_n(x)j_m(x)dx=\begin{cases}0, & m\neq n\\ \frac{1}{2}\pi/(2n+1), & m=n\end{cases}. \quad (5\text{-}7)$$

It is obvious, of course, that this class is limited (the $j_n(x)$ do not form a complete set), but there seems to be no simple criterion for characterizing functions of this type.[21]

Figure 2 shows the first few $T_F(r)$ and $M_F(s)$ components. The first,

$$j_0(s_or)=\frac{\sin s_or}{s_or}\quad\text{and}\quad M_F(s)=\begin{cases}1, & |s|\leqslant s_o\\ 0, & |s|>s_o\end{cases},$$

are of course already familiar.[22]

The examples shown in Figs. 1 and 2 show interesting generalities about which the following remarks appear pertinent. Perhaps the most notable are the indications, confirmed by all our experience, that suppression of subsidiary features of $T(r)$ gives rise to a broadening of the main peak. The properties of $T(r)$ at small values of r are exhibited by the expansion in ascending powers of r:

$$(\pi/2)^{\frac{1}{2}}T(r)=\int_0^{s_o}M(s)ds-\tfrac{1}{2}r^2\int_0^{s_o}s^2M(s)ds+r^4/4!\int_0^{s_o}s^4M(s)ds+\cdots, \quad (5\text{-}8)$$

having as coefficients the even moments of $M(s)$. For large values of r an expansion in inverse powers of r, obtained by repeated partial integration is more appropriate:

$$(\pi/2)^{\frac{1}{2}}T(r)=M(s_o)\frac{\sin s_or}{r}+\frac{M'(s_o)}{r^2}\cos s_or-\frac{M''(s_o)}{r^3}\sin s_or+\cdots. \quad (5\text{-}9)$$

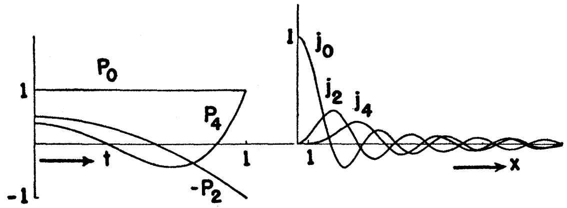

FIG. 2. The first three Legendre and circular Bessel functions of even order.

The first of these expansions confirms the further observation from Fig. 1 that sharp peaks—in the sense of initial curvature—correspond to modification functions which give greatest weight to large s values, whereas the second expansion gives substance to the impression that the dying out of subsidiary features depends on the smoothness with which $M(s)$ reaches zero at s_o.

These expansions show in a broad way the connection between the sharpness of the main peak and the extent of the subsidiary features, but the details are not clear. The sharpest transform shown in Figs. 1 and 2 is $T_a(r)=j_0(r)$, but (5-8) shows that still sharper peaks can be obtained simply by increasing the second moment of $M(s)$ while holding the area of $M(s)$ constant: The limiting case is the useless one of $M(s)=\delta(s-s_o)$.

A rather attractive criterion, on the other hand, might be that for a given peak height

$$T(0)=(2/\pi)^{\frac{1}{2}}\int_0^{s_o}M(s)ds, \quad (5\text{-}10)$$

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[20] G. H. Watson, *Theory of Bessel Functions* (Cambridge University Press, Cambridge, 1944).

[21] See the analysis of the similar case of the Neumann expansion in Bessel functions in references 15 and 20.

[22] The integral (see references 16 and 20)

$$\text{const}\int_{-\infty}^{\infty}\frac{\sin s_o'(r-u)}{s_o'(r-u)}j_{2k}(s_ou)du=j_{2k}(s_or),\quad s_o'\geqslant s_o,$$

expresses in perhaps surprising form a property obvious from the Fourier transform, possessed by any $M_F(s)$, namely, that the transform is unchanged if the integration is broken off at a point $s_o'\geq s_o$. The analogous expression for the special case that $M_F(s)$ itself represents a cutoff (at s_o) is

$$\text{const}\int_{-\infty}^{\infty}\frac{\sin s_ou}{s_ou}\,\frac{\sin s_o'(r-u)}{s_o'(r-u)}du=\begin{cases}\dfrac{\sin s_or}{s_or}, & s_o\leqslant s_o'\\[2mm] \dfrac{\sin s_o'r}{s_o'r}, & s_o\geqslant s_o'.\end{cases}$$

the square fluctuation of $T(r)$

$$\int_0^\infty T^2(r)dr=(1/2\pi)\int_0^\infty M^2(s)ds \qquad (5\text{-}11)$$

(Parseval's relation)[15,16] should be minimized. This leads by a simple variation treatment to just the step function

$$M(s)=\begin{cases}1 & |s|\leq s_o \\ 0 & |s|>s_o\end{cases}, \qquad (5\text{-}12)$$

a result that is unchanged in higher dimensions. Since this result does not seem to be especially well suited to practice, it is evident that more subtle criteria play a decisive role in determining the usefulness of a modification function and its transform. These criteria will depend very much on the information desired and indeed a given problem may warrant making several inversions with different modification functions in order to facilitate different stages and aspects of the interpretation, such as separation of overlapping peaks, location and verification of the presence of small peaks, determination of peak areas, etc.

6. THE ATOMIC SCATTERING FACTOR

In the expression for $sI(s)$ used so far the assumption is contained that the variation of $[Z_i-f_i(s)]/Z_i$ for different atoms may be neglected. In the following this assumption is no longer made.

The molecular scattering intensity of a rigid molecule is proportional to [see Eq. (1-1)]

$$sI_m(s)=\left(\frac{2}{\pi}\right)^{\frac{1}{2}}\sum_{ij}{}'\frac{(Z_i-f_i(s))(Z_j-f_j(s))}{r_{ij}s^4}\sin sr_{ij}$$

$$=\left(\frac{2}{\pi}\right)^{\frac{1}{2}}\sum_{ij}{}'\frac{\psi_i(s)\psi_j(s)}{r_{ij}}\sin sr_{ij}, \qquad (6\text{-}1)$$

where

$$\frac{Z_i-f_i(s)}{s^2}=\psi_i(s) \qquad (6\text{-}2)$$

is the atomic form factor for electrons. When the function $s^5I_m(s)$ is inverted[14] the contributions of each $\sin sr_{ij}/sr_{ij}$ term to the resulting radial distribution function is centered at r_{ij} and has a (symmetrical) shape characteristic of atoms i and j:

$$T_{ij}(r)=\left(\frac{2}{\pi}\right)^{\frac{1}{2}}\int_0^\infty s^4\psi_i(s)\psi_j(s)\cos srds, \qquad (6\text{-}3)$$

so that

$$rD(r)=\left(\frac{2}{\pi}\right)^{\frac{1}{2}}\int_0^\infty s^5I_m(s)\sin srds \qquad (6\text{-}4)$$

is given by

$$(2\pi)^{-\frac{1}{2}}\sum_{ij}{}' r_{ij}^{-1}\int_{-\infty}^{\infty}[\delta(u-r_{ij})-\delta(u+r_{ij})]T_{ij}(r-u)du$$

$$=(2\pi)^{-\frac{1}{2}}\sum_{ij}{}' r_{ij}^{-1}[T_{ij}(r-r_{ij})-T_{ij}(r+r_{ij})]. \qquad (6\text{-}5)$$

The second term in the bracket makes $rD(r)$ antisymmetrical, as it did in (1-10) and (3-9).

The (ideal) peak shape may also be expressed as the result of a folding process

$$T_{ij}(r)=(2\pi)^{-\frac{1}{2}}\int_{-\infty}^{\infty}t_i(u)t_j(r-u)du, \qquad (6\text{-}6)$$

where we made use of the cosine transform $t_i(r)$ of $s^2\psi_i(s)$:

$$t_i(r)=(2/\pi)^{\frac{1}{2}}\int_0^\infty s^2\psi_i(s)\cos srdr. \qquad (6\text{-}7)$$

The atomic form factor $\psi_i(s)$ is related to the density of scattering matter $\rho_i(r)$ of atom i by the equation[1]

$$s^2\psi_i(s)=\text{const}\int_0^\infty \rho_i(r)\frac{\sin sr}{sr}r^2dr \qquad (6\text{-}8)$$

and inversely

$$r\rho_i(r)=\text{const}\int_0^\infty s^2\psi_i(s)(s\sin sr)ds, \qquad (6\text{-}9)$$

which upon comparison with (6-7) yields

$$r\rho_i(r)=-\text{const}\frac{dt_i(r)}{dr} \qquad (6\text{-}10)$$

so that

$$t_i(r)=\text{const}\int_r^\infty u\rho_i(u)du. \qquad (6\text{-}11)$$

Similar relationships are valid for radial distribution functions obtained from the scattering of x-rays and neutrons as well. The ideal peak shapes for such distribution curves may be obtained by inversion of a product as in (6-3) or by operations (6-6) and (6-11). For figures showing the peak shape expected for light atoms like oxygen reference should be made to a paper by Viervoll[23] who chose the latter method for his calculations. If instead of inverting $s^5I_m(s)$, other functions such as (1-4) are inverted, other peak shapes $T_{ij}(r)$ result, but each peak shape is again dependent on the partners i and j and can be calculated by a formula analogous to (6-3).

For a nonrigid molecule with no internal rotation each term in $sI_m(s)$ would be multiplied by a different temperature factor $\exp(-a_{ij}s^2)$ [see Eq. (1-1)], the trans-

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[23] H. Viervoll, Skrifter Norske Videnskaps Akad., Oslo, Mat. Naturv. Kl. No. 2 (1950).

form of which is the Gaussian $(4a_{ij}\pi)^{-\frac{1}{2}}\exp(-r^2/4a_{ij})$. The contribution $rD_{ij}(r)$ by a pair of atoms will then be the resultant of this Gaussian and the transform $T_{ij}(r)$ (6-3):

$$rD_{ij}(r)=(8a_{ij}\pi^2)^{-\frac{1}{2}}\times\int_{-\infty}^{\infty}\exp(-u^2/4a_{ij})T_{ij}(r-u)du. \qquad (6\text{-}12)$$

Each peak in $rD(r)$ may thus contain the transform of a different temperature factor as well as of different form factors.

The fundamental meaning of the temperature factor is of course just this—that the real radial distribution peak is not infinitely sharp but has a finite width due to molecular vibrations. It is interesting that for molecules of the class under discussion the function $(4a_{ij}\pi)^{-\frac{1}{2}}\exp(-r^2/4a_{ij})$ is an appropriate approximation for $r^2D(r)/r_{ij}$ [rather than for $rD(r)$, as given by (6-4)] and that accordingly the conventional temperature factor corresponds to an $r^2D(r)$ equal to the assumed distribution multiplied by the factor r/r_{ij}. This remark[17] suggests simple corrections to the usual temperature factor; the first, for the example of intensity formula (1-1) alters the terms $\exp(-a_{ij}r^2)\sin r_{ij}s$ to the form

$$\left(1+\frac{2a_{ij}}{r_{ij}^2}\right)\exp\left[-\left(1+\frac{2a_{ij}}{r_{ij}^2}\right)a_{ij}s^2\right]\sin\left(1-\frac{2a_{ij}}{r_{ij}^2}\right)r_{ij}s,$$

in which the correction to r_{ij}, at least, will sometimes be important. In the derivation of the temperature factor by James,[24] based on the assumption of normal vibrations, a series expansion is used, the range of validity of which was not established. Karle and Karle,[25] on the other hand, modified the distribution characteristic for normal vibrations [it is not strictly Gaussian in $r^2D(r)$] by multiplication with r/r_{ij} and solved the remaining problem in closed form. Corrections of the sort mentioned above are evidently required, however, for all but the lowest order term, which is nothing more than the usual temperature factor.

The radial distribution functions of molecules involving large temperature librations[26] or internal rotations[27] contain peaks characteristically distorted by being folded with wide probability distributions, analogous to (6-12).

The application of the analysis of modification functions given in the previous section to the functions $rD(r)$ of this section is straightforward. For a given applied modification function, with transform $T(r)$, each contribution to the resulting distribution function will correspond to the folding operation

$$\int_{-\infty}^{\infty}uD_{ij}(u)T(r-u)du, \qquad (6\text{-}13)$$

where $rD_{ij}(r)$, of course, describes the peak which would have been obtained by inverting the unmodified scattering function $s^5I_m(s)$ in the range $0\leq s<\infty$.

All these results [like (6-5), (6-12), (6-13)] involve symmetrical transforms T. This makes it clear why it is preferable to construct $rD'(r)$ rather than $D'(r)$ or $r^2D'(r)$ which might at first glance appear to be the more natural functions to evaluate, because of their more obvious physical interpretation, as evidenced in one instance by the above discussion of the real temperature factor [folding the scattering density $\rho(r)$ with itself and integrating over all orientations leads to $4\pi r^2D(r)$]. The great advantage of $rD'(r)$, as has also been stressed by Viervoll,[23] is that of being composed additively of *symmetrical* peaks whose position, as our discussion shows, is not influenced by any of the multiplicative factors affecting the molecular scattering intensity—either term by term or as a whole. Neither $r^2D'(r)$ nor $D'(r)$ has this important property.

Interpretation of a radial distribution curve should obviously be made in terms of the various expected peak shapes. This may be a simple problem, provided suitable modification functions have been applied. In special cases, however, as instanced by serious overlap of peaks, it becomes necessary to take the expected peak shape into explicit account. This is, of course, the main problem and has to be handled by trial and error—by subtracting peaks from $rD'(r)$, by constructing a synthetic distribution curve, or by other methods. Brief expositions are given by Viervoll.[23] The use of several distribution functions made with different modification functions may be helpful. The expected peak shapes are best calculated by allowing for all the effects on the intensity side [$M(s)$, $\psi_i(s)$, $\psi_j(s)$, temperature factor], and then inverting the complete modification function as in (6-3) rather than by using the several folding processes (6-6), (6-12), and (6-13) in turn, at least if numerical facilities for cosine as well as sine inversion are available.

With regard to the widths of the various peaks the rule may be used that the square of the half-width of a peak is approximately equal to the sum of the squares of the half-widths expected from the various items discussed above, a rule which is rigidly true only if all the modifying effects are Gaussian (3-5). In particular, the half-widths due to the step function $M_a(s)$ and the usual artificial temperature factor $M_g(s)$ (Fig. 1) are $1.9/s_o$ and $2.7/s_o$, respectively, and approximate corrections to obtain the natural peak widths can be made accordingly. For more exact information detailed analysis (or synthesis) of the peak shape is necessary.

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[24] R. W. James, Physik. Z. **33**, 737 (1932).

[25] J. Karle and I. M. Karle, J. Chem. Phys. **18**, 957 (1950).

[26] P. Debye, J. Chem. Phys. **9**, 55 (1941); J. Karle, J. Chem. Phys. **15**, 202 (1947).

[27] J. Karle and H. Hauptman, J. Chem. Phys. **18**, 875 (1950).

7. LIQUIDS AND AMORPHOUS SOLIDS

The foregoing discussion illuminates the following confusing notions to be found in the literature on distribution functions for amorphous substances and liquids:[28]

(1) When several kinds of atoms are involved, "simple Fourier inversion [of the part of the scattering intensity due to interatomic interactions] is no longer possible . . . and . . . approximations have to be used."

(2) The number of interatomic interactions at a given distance is found by inversion of the suitably modified interatomic part of the intensity function and multiplication by r, to obtain an *atomic* distribution function whose peaks have areas proportional to the *numbers* of atom pairs involved in the interactions (as well as to the products of effective atomic numbers).

The Fourier *transform* of the interatomic part of the scattering function can of course always be calculated and (in the ideal case of perfect data for an infinite range) may be regarded as a radial distribution function of scattering density—of electron density in the x-ray case. However, if it is realized that the intensity function can be written as a sum of terms characteristic of different kinds of *pairs* of atoms (rather than of different kinds of atoms), it is clear that all these terms can be *inverted*. And the sum of these terms is identical with the above transform, in consequence of the linearity of the inversion process.

A concrete formulation for the case of x-rays will perhaps be helpful. As stated, the interatomic part $sI(s)$ of the scattering function is the sum

$$sI(s)=\sum_{n\leqslant m} si_{nm}(s) \tag{7-1}$$

of terms $si_{nm}(s)$

$$si_{nm}(s)=(2/\pi)^{\frac{1}{2}}\int_0^\infty rd_{nm}(r)\,\sin srdr, \tag{7-2}$$

each of which concerns atoms of kinds n and m only. Here $rd_{nm}(r)=rd_{mn}(r)$ is a radial distribution function of electron density for atom pairs of kind (n, m): $4\pi r^2 d_{nm}(r)$ is the result of folding the electron density due to atoms of kind n with that due to atoms of kind m and integrating over all orientations. Inversion of (7-2) and (7-1) yields (7-3) and (7-4):

$$rd_{nm}(r)=(2/\pi)^{\frac{1}{2}}\int_0^\infty si_{nm}(s)\,\sin srds; \tag{7-3}$$

$$rD(r)=(2/\pi)^{\frac{1}{2}}\int_0^\infty sI(s)\,\sin srds=\sum_{n\leqslant m} rd_{nm}(r). \tag{7-4}$$

Each of the electronic distribution functions $rd_{nm}(r)$ may be analyzed in terms of an "atomic" distribution function $r\Delta_{nm}(r)$ defined by

$$si_{nm}(s)=f_n(s)f_m(s)\,(2/\pi)^{\frac{1}{2}}\int_0^\infty r\Delta_{nm}(r)\,\sin srdr, \tag{7-5}$$

with $f_n(s)$ the atom form factor for atoms of kind n, so that $r\Delta_{nm}(r)$ is given by

$$r\Delta_{nm}(r)=(2/\pi)^{\frac{1}{2}}\int_0^\infty \frac{si_{nm}(s)}{f_n(s)f_m(s)}\,\sin srds. \tag{7-6}$$

The relation between $r\Delta_{nm}(r)$ and $rd_{nm}(r)$ is again one of folding:

$$rd_{nm}(r)=(2\pi)^{-\frac{1}{2}}\int_{-\infty}^\infty u\Delta_{nm}(u)t_{nm}(u-r)du; \tag{7-7}$$

$$t_{nm}(r)=(2/\pi)^{\frac{1}{2}}\int_0^\infty f_n(s)f_m(s)\,\cos srds. \tag{7-8}$$

Relations analogous to (6-6)–(6-11) connect $t_{nm}(r)$ with the electron densities of atoms n and m.

While this clarifies the meaning of $rD(r)$ in terms of the atomic distribution functions $r\Delta_{nm}(r)$, it is also evident that the problem of separating $rD(r)$ into its components will be difficult if not hopeless, since each $r\Delta_{nm}(r)$ may itself be a complicated function with many features. Frequently, especially for light atoms, the functions $f_n(s)$ are approximately proportional to each other:

$$f_n(s)\approx K_n\frac{\sum_m f_m(s)}{\sum_m Z_m}=K_nf_e(s), \tag{7-9}$$

where K_n is a constant approximately equal to the atomic number Z_n and $f_e(s)$ is the average scattering power per electron. The functions $t_{nm}(r)$ reduce in this case to

$$t_{nm}(r)\approx K_nK_m(2/\pi)^{\frac{1}{2}} \times\int_0^\infty f_e^2(s)\,\cos srds=K_nK_mt_e(r), \tag{7-10}$$

so that all distribution functions $rd_{nm}(r)$ assume similar character. It then becomes possible either to analyze $rD(r)$ in terms of the general peak shape $t_e(r)$, or to form by inversion of $si(s)/f_e^2(s)$ a distribution function

$$r\Delta(r)=\left(\frac{2}{\pi}\right)^{\frac{1}{2}}\int_0^\infty \frac{sI(s)}{f_e^2(s)}\,\sin srds \approx \sum_{n\leqslant m} K_nK_mr\Delta_{nm}(r) \tag{7-11}$$

which is the weighted sum of the various atomic distribution functions. (The actual peak shapes may, of course, be further modified as discussed previously.)

This result, although essentially similar to the usual

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[28] For example, R. W. James, *The Optical Principles of the Diffraction of X-Rays* (Macmillan and Company, Ltd., London, 1950), p. 504.

one,[28] differs from it in being stated explicitly in terms of the different kinds of atom pairs and in being closely related to the precise formulas (7-4) to (7-8) so as to suggest the correct interpretation of $rD(r)$ in terms of atomic distribution functions even when the approximation (7-9) is no longer valid. It is now evident that the difficulties in the conventional exposition are caused by the introduction of functions $\rho_m(r)$ which are characteristic of atoms rather than of atom pairs.

For homoatomic liquids the situation as discussed so far becomes trivial, in agreement with the usual discussion, since all terms in (7-1) and (7-11) reduce to one. However, the analysis of $rD(r)$ into characteristic subdistributions (e.g., temperature-factor Gaussians), as will often be desirable, is in principle just as complex for homoatomic as for heteroatomic liquids, since each subdistribution will have its own characteristic shape (e.g., width). For molecular liquids, indeed, this added bit of complexity can be turned to advantage, since it will usually permit a separation of the intramolecular components of $rD(r)$, which are generally the sharper ones by a large margin from the intermolecular components. The total effect is especially favorable if the desired intramolecular terms are not only the sharper ones but also have the greater weight, pair for pair, as when strongly scattering complex, rigid molecules are dispersed in a weakly scattering, molecularly simple solvent.[29]

Although the general discussion of modification functions given previously applies to this section also, some special remarks seem to be called for.

The modification of $sI(s)$ by multiplication with $f_e^{-2}(s)$ in the construction of $r\Delta(r)$ (7-11) has besides the desirable effect of sharpening peaks the undesirable one of introducing subsidiary features of a nature which may significantly encumber the analysis of the distribution function. This is all the more troublesome, if the distribution function is no longer interpretable in terms of characteristic distances but rather has to be regarded just as a distribution function or a sum of distribution functions in their own rights. This point has been stressed by Finbak.[30]

The conventional multiplication of $rD'(r)$ (the direct result of the inversion) by r is unfortunate because it is in $rD'(r)$ rather than $r^2D'(r)$ that the various multiplicative factors, like form factors and modification factors, leave symmetrical peaks symmetrical and unshifted. It seems appropriate, therefore, even in the case of the atomic distribution function $r\Delta'(r)$ (7-11) not to multiply it with r, but rather to compare it directly with the theoretical function $r^2\Delta_{th}(r)$ of interest divided by r. (The usual additive parabolic term[28] $r^2\Delta_0(\Delta_0=\text{const})$ is of course to be replaced by a linear term $r\Delta_0$. This term arises from the fact that in practice the integral in the inversion (7-4) is assumed to have a negligible value as s approaches zero. However, if the intensity due to a particle of constant scattering density is calculated, it is found to be concentrated at very small values of s, of the order D^{-1} where D is the linear dimension of the particle. This small angle scattering is essentially the same for particles of nonuniform scattering density. Its omission from an inversion like (7-4) has the consequence that the resulting function represents the difference between the actual distribution function and that corresponding to a uniform, average scattering density.)

8. EXTENSION TO SEVERAL DIMENSIONS

In order to extend the previous results to Fourier series such as are used in crystal structure analysis, it seems essential to introduce alternative representations by means of Fourier integrals. In order to illustrate this procedure and to give incidentally yet another example of the power of the folding theorem, the connection between the Fourier transform of the electron density and the structure factors for a crystal will first be established along the lines of Ewald's classic paper.[31]

The electron density of an ideal crystal of infinite size is a triply periodic function,

$$\rho(\mathbf{r})=\rho(\mathbf{r}+n_1\mathbf{a}_1+n_2\mathbf{a}_2+n_3\mathbf{a}_3),\quad n_i=\cdots-2,-1,0,1,2\cdots,\quad i=1,2,3,\tag{8-1}$$

of the position vector with the vector periods $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$, which define the unit cell of the translation lattice of the crystal. In terms of the reciprocal lattice vectors, $\mathbf{h}=h_1\mathbf{b}_1+h_2\mathbf{b}_2+h_3\mathbf{b}_3$,

$$h_i=\cdots,-2,-1,0,1,2\cdots,\tag{8-2}$$

$$\mathbf{a}_i\cdot\mathbf{b}_j=\delta_{ij},\tag{8-3}$$

the Fourier expansion of $\rho(\mathbf{r})$ takes the form[32]

$$\rho(\mathbf{r})=v_{\mathbf{r}}^{-1}\sum\nolimits_{\mathbf{h}}F_{\mathbf{h}}\exp(-2\pi i\mathbf{h}\cdot\mathbf{r}),\tag{8-4}$$

where $v_{\mathbf{r}}$ is the volume of the unit cell and the sum includes all reciprocal lattice points.

The coefficients $F_{\mathbf{h}}$ in this expansion are the structure factors

$$F_{\mathbf{h}}=\int_{\text{unit cell}}\rho(\mathbf{r})\exp(2\pi i\mathbf{h}\cdot\mathbf{r})dv_{\mathbf{r}}.\tag{8-5}$$

If the crystal is not of infinite extent or if $\rho(\mathbf{r})$ is not otherwise really periodic, the above formulation is no longer strictly valid; in any case it is convenient to consider the Fourier transform of $\rho(\mathbf{r})$—we shall call it $F(\mathbf{q})$—for the entire crystal. The two functions are

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[29] Vaughan, Sturdivant, and Pauling, J. Am. Chem. Soc. **72**, 5477 (1950); O. Kratky and W. Worthmann, Monatsh. Chem. **76**, 263 (1947); E. Rumpf, Ann. Physik **9**, 704 (1931).

[30] C. Finbak, Acta Chem. Scand. **3**, 1279, 1293 (1949).

[31] P. P. Ewald, Proc. Phys. Soc. (London) **52**, 167 (1940).

[32] M. von Laue, *Röntgenstrahlinterferenzen* (2nd ed., Akademische Verlagsgesellschaft, Leipzig, 1948); W. H. Zachariasen, *Theory of X-Ray Diffraction in Crystals* (John Wiley and Sons, Inc., New York, 1945); R. W. James, *The Optical Principles of the Diffraction of X-Rays* (Macmillan and Company, Ltd., London, 1950).

symmetrically related,[31] with $F(\mathbf{q})$ a function of the continuously variable vector $\mathbf{q}=q_1\mathbf{b}_1+q_2\mathbf{b}_2+q_3\mathbf{b}_3$ in reciprocal space:

$$F(\mathbf{q})=\int_{\text{crystal}}\rho(\mathbf{r})\exp(2\pi i\mathbf{q}\cdot\mathbf{r})dv_{\mathbf{r}};\tag{8-6}$$

$$\rho(\mathbf{r})=\int F(\mathbf{q})\exp(-2\pi i\mathbf{q}\cdot\mathbf{r})dv_{\mathbf{q}}.\tag{8-7}$$

(The normalization factor corresponding to $(2/\pi)^{\frac{1}{2}}$ of earlier sections becomes unity here due to the inclusion of the factor 2π in the exponent; the variable $\mathbf{q}$ is related to s by $s=2\pi|\mathbf{q}|$.) The integral in (8-7) extends over the whole of reciprocal space.

To establish the connection of the pair (8-4) and (8-5) with the pair (8-6) and (8-7), we note that an infinite periodic crystal may be represented by the folding of the contents of one unit cell into the *lattice function*, which is a sum of δ functions, each situated at a lattice point. The Fourier transform of this lattice function is the so-called *Laue function for infinite crystals*,[32] $L(\mathbf{q})$, which again consists of a collection of δ functions, each multiplied with $1/v_{\mathrm{r}}$ and situated at a reciprocal lattice point.

The Fourier transform

$$F_c(\mathbf{q})=\int_{\text{unit cell}}\rho(\mathbf{r})\exp(2\pi i\mathbf{q}\cdot\mathbf{r})dv_{\mathbf{r}}\tag{8-8}$$

of the electron density of one specified unit cell is related to $F(\mathbf{q})$ by

$$F(\mathbf{q})=F_c(\mathbf{q})L(\mathbf{q})=v_{\mathrm{r}}^{-1}\textstyle\sum_{\mathbf{h}}F_{\mathbf{h}}\delta(\mathbf{q}-\mathbf{h}),\tag{8-9}$$

since the folding of the contents of the specified unit cell with the lattice function to obtain $\rho(\mathbf{r})$ corresponds to multiplication of the transform $F_c(\mathbf{q})$ by the transform $L(\mathbf{q})$. Accordingly, $F(\mathbf{q})$, which refers to a strictly periodic, infinite crystal, is an essentially discontinuous function, proportional to the appropriate structure factor at each reciprocal lattice point and zero elsewhere, as is also evident from the representation of $\rho(\mathbf{r})$ by the Fourier series (8-4). The $F_{\mathbf{h}}$ are a sampling, at reciprocal lattice points, of the continuous transform $F_c(\mathbf{q})$ for a unit cell. It will be noted that although $F_c(\mathbf{q})$ in general depends upon which unit cell is specified, the samples $F_{\mathbf{h}}$ do not.

As Ewald[31] has discussed, the folding theorem is very useful in understanding the effect of crystal size on the shape of reflections. If a shape function be introduced which has the value unity inside the crystal and zero outside, then the electron density of an actual crystal is simply the product of the electron density of the infinite crystal with this shape function. This corresponds to the folding in Fourier space of the discrete transform (8-9) with the transform of the shape function. The resulting transform of the finite crystal consists therefore in a set of broadened features of finite extension in reciprocal space, identical in shape, but scaled proportionally to the structure factors. The crystal reflections are correspondingly broadened, as is the range of small angle-scattering which would be expected in the absence of interdomain and interparticle interference. (For small-angle scattering, of course, these latter effects usually dominate. Their consideration, like the consideration of crystal imperfections, rests fundamentally on the entire density function and its transform, but the manipulation of an ideal density function by multiplication and/or folding will often be profitable,[32a] as it is in our example of the finite crystal.)

The special shape function which covers exactly a specified unit cell leads to an interesting result. For definiteness, let this unit cell be situated with its center at $\mathbf{r}_o$ from the origin and have edges parallel to the crystal axes. The shape transform is then

$$v_{\mathrm{r}}\exp(2\pi i\mathbf{q}\cdot\mathbf{r}_o)\prod_{j=1}^{3}\frac{\sin\pi q_j}{\pi q_j},\tag{8-10}$$

and the corresponding expression for the transform of the contents of one unit cell is

$$F_c(\mathbf{q})=\exp(2\pi i\mathbf{q}\cdot\mathbf{r}_o)\sum_{\mathbf{h}}F_{\mathbf{h}}\prod_{j=1}^{3}\frac{\sin\pi(q_j-h_j)}{\pi(q_j-h_j)}.\tag{8-11}$$

This is the inverse of the sampling picture exposed above: From the samples $F_{\mathbf{h}}$ the transform of a unit cell can be reconstructed by what is known as (three-dimensional) trigonometric interpolation.[33]

Expression (8-11) may suggest a direct determination at least of $|F_c(\mathbf{q})|$, the zeros of which (at any rate in the centrosymmetrical case) might provide important clues to changes in sign between adjacent structure factors. But this is not possible, for the phases of the $F_{\mathbf{h}}$ are as pertinent in (8-11) as are the amplitudes, and knowledge of the phase is essential in the construction of $|F_c(\mathbf{q})|$ also. Even more important, $F_c(\mathbf{q})$ has meaning only in regard to a unit cell of arbitrary shape and position: the phase of $F_c(\mathbf{q})$, in (8-11), would change if the origin were shifted and even more drastic changes would occur if a unit cell of different shape were to be singled out. The only invariant property of all possible interpolations (8-11) is that they have identical values for reciprocal lattice vectors $\mathbf{q}=\mathbf{h}$. All this is to be expected since unit cells, although useful in describing crystals, have no physical reality. Even more generally, it is arbitrary to generate the whole crystal by folding the complete contents of one unit cell with the lattice function, inasmuch as other functions extending over possibly many unit cells may be folded with the lattice function

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[32a] For example, R. Hosemann, Z. Physik **128**, 1, 465 (1950); R. Hosemann and S. N. Bagchi, Acta Cryst. **5**, 612 (1952).

[33] E. T. Whittaker, Proc. Roy. Soc. (Edinburgh) **35**, 181 (1915); *Interpolatory Function Theory* (Cambridge University Press, Cambridge, 1935).

to obtain the same $\rho(\mathbf{r})$. This is especially pertinent in the case of the Patterson function: interpolation of $|F_{\mathbf{h}}|^2$ according to (8-11) yields the transform of one specified unit cell of the Patterson function, but except for $\mathbf{q}=\mathbf{h}$ this transform is not equal to $|F_c(\mathbf{q})|^2$ even when corresponding unit cells have been chosen. Nevertheless, a case for which (8-11) has practical significance is considered at the end of Sec. 10.

It is quite another matter when the unit cell of a molecular crystal is chosen to contain one or a small number of relatively rigid molecules. It may then be possible by external influences continuously to change the size and shape of the unit cell without changing the configurations of the molecules. In this way various samplings of $F_c(\mathbf{q})$, now characteristic of the molecules, may be made from which information about the signs of the structure factors may be deduced in centrosymmetrical cases. This idea was used by Perutz[34] and coworkers in determining the signs of some x-ray reflections of methemoglobin, for which the unit cell size and shape depend on the extent of hydration of the protein.

Projections of three-dimensional density are often useful. Consider first the projection ρ_2 along a crystallographic axis, upon a plane. If the projection axis is inclined it is convenient to project onto a perpendicular plane rather than the plane of the other two crystallographic axes in order that the projections of spherically symmetrical functions shall show circular symmetry. In practice the distinction involves merely the choice of scales and axes for plotting the projected function. We call the axis of projection $\mathbf{a}_3$, the projections of the other two axes $\mathbf{a}_1'$ and $\mathbf{a}_2'$, and the coordinates of $\mathbf{r}$ in this "monoclinic" system of axes x_1', x_2', and x_3'. Further, $\mathbf{R}_2$ is the projection of $\mathbf{r}$, A the area of the projection of the unit cell, $\mathbf{Q}$ the projection of $\mathbf{q}$ on the plane of $\mathbf{b}_1$ and $\mathbf{b}_2$ (which is parallel to the projection plane), and $dA_{\mathbf{Q}}$ the surface element of that plane; finally, $\mathbf{b}_3$ may be replaced by $\mathbf{b}_3'$ so as to obtain a triple $\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3'$, reciprocal to $\mathbf{a}_1', \mathbf{a}_2', \mathbf{a}_3$.

The projection of $\rho(\mathbf{r})$ is given by

$$\begin{aligned}\rho_2(\mathbf{R}_2) &= \int_{-\infty}^{\infty} \rho(\mathbf{r}) a_3 dx_3' \\ &= \int_{-\infty}^{\infty} a_3 dx_3' \int_{-\infty}^{\infty} b_3' dq_3' \exp(-2\pi i q_3' x_3') \\ &\quad \times \int_{-\infty}^{\infty} dA_{\mathbf{Q}} F(q_1, q_2, q_3) \exp(-2\pi i \mathbf{Q}\cdot\mathbf{R}_2) \\ &= \int_{-\infty}^{\infty} F(\mathbf{Q}) \exp(-2\pi i \mathbf{Q}\cdot\mathbf{R}_2) dA_{\mathbf{Q}}, \qquad (8\text{-}12)\end{aligned}$$

where use of the δ-function of footnote 3 has been made. It should be noted that the projection $\rho_2(\mathbf{R}_2)$ is determined by the values of $F(\mathbf{Q})$ in the plane $(\mathbf{b}_1, \mathbf{b}_2)$ parallel to our plane of projection rather than by a projection of $F(\mathbf{q})$ onto it. The expression (8-12) is furthermore not dependent on periodicity of $\rho(\mathbf{r})$ and differs from the more conventional one

$$\int_0^1 \rho(\mathbf{r}) a_3 dx_3' = A^{-1} \sum_{h_1, h_2} F_{h_1h_20} \times \exp(-2\pi i(h_1x_1' + h_2x_2')) \qquad (8\text{-}13)$$

by a factor N_3, the number of layers of (the now periodic) $\rho(\mathbf{r})$ projected in (8-12). (The factor N_3, while obvious in the relationship between the sides of (8-12) and (8-13) pertaining to real space, enters on the transform side of (8-12) through the fact that the Laue function for a one-dimensional crystal of N_3 unit cells has the value N_3 at $q_3=0$).

For the line projection of the electron density, the line on which the projected values are recorded is preferably chosen perpendicular to the directions of projection, which are parallel to a crystallographic plane, for definiteness called (100). We introduce the symbols $\mathbf{a}_1'$ and $\mathbf{R}_1$ for the projections of $\mathbf{a}_1$ and $\mathbf{r}$ and $\mathbf{B}$ for the projection of $\mathbf{q}$ on $\mathbf{b}_1$. The line projection is given by

$$\rho_1(\mathbf{R}_1) = \int_{-\infty}^{\infty} F(\mathbf{B}) \exp(-2\pi i \mathbf{R}_1\cdot\mathbf{B}) dB, \qquad (8\text{-}14)$$

the derivation being analogous to that of ρ_2 and $\rho_1(\mathbf{R}_1)$ being related to

$$\int_0^1 \int_0^1 \rho(\mathbf{r}) (\mathbf{a}_2 \times \mathbf{a}_3) dx_2 dx_3 = (a_1')^{-1} \sum_{h_1=-\infty}^{\infty} F_{h_100} \exp(-2\pi i h_1 x_1') \qquad (8\text{-}15)$$

in a similar way. The expression (8-14) again does not depend on any periodicity of $\rho(\mathbf{r})$, and the line projection is determined by the values of $F(\mathbf{q})$ along a parallel line in reciprocal space.

These relationships are symmetrical in the sense that the line or plane *section* of a function and the line or plane *projection* of its transform are also mutual transforms.

We are of course here mainly interested in the consequences of breaking off the Fourier series after a finite number of terms and, more generally, in the effects of any modification of the coefficients by multiplication with a function of $\mathbf{q}$. As has become evident in earlier sections the complete modification function may be regarded as the product of all factors in the expression to be transformed which are functions just of the variable of integration. Such factors are the imposed convergence and sharpening factors as well as the natural form and temperature factors. We shall some-

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[34] Boyes-Watson, Davidson, and Perutz, Proc. Roy. Soc. (London) **A191**, 83 (1947); for the latest report, see W. L. Bragg and M. F. Perutz, Proc. Roy. Soc. (London) **A213**, 425 (1952).

times single out one or the other of them or, again, treat the complete product, but the nature of the modification function under discussion will always be obvious from the context. A general treatment of these effects appears unfeasible for multidimensional Fourier series without the use of the integral representation.

If

$$\rho'(\mathbf{r}) = \int_{-\infty}^{\infty} M(\mathbf{q})F(\mathbf{q}) \exp(-2\pi i\mathbf{q}\cdot\mathbf{r})dv_{\mathbf{q}}$$

$$= (v_{\mathrm{r}})^{-1} \sum_{\mathbf{h}} M_{\mathbf{h}}F_{\mathbf{h}} \exp(-2\pi i\mathbf{h}\cdot\mathbf{r}) \qquad (8\text{-}16)$$

is the electron density function resulting from the series with modified coefficients and if the transform of $M(\mathbf{q})$ is

$$T(\mathbf{r}) = \int_{-\infty}^{\infty} M(\mathbf{q}) \exp(-2\pi i\mathbf{q}\cdot\mathbf{r})dv_{\mathbf{q}}, \qquad (8\text{-}17)$$

then the (three-dimensional) folding theorem implies

$$\rho'(\mathbf{r}) = \int_{-\infty}^{\infty} T(\mathbf{u})\rho(\mathbf{r}-\mathbf{u})dv_{\mathbf{u}} \qquad (8\text{-}18)$$

in complete analogy to (3-3). The corresponding two- and one-dimensional formulas are

$$\rho_2'(\mathbf{R}_2) = \int_{-\infty}^{\infty} T_2(\mathbf{U})\rho_2(\mathbf{R}_2-\mathbf{U})dA_{\mathbf{U}} \qquad (8\text{-}19)$$

and

$$\rho_1'(\mathbf{R}_1) = \int_{-\infty}^{\infty} T_1(\mathbf{U})\rho_1(\mathbf{R}_1-\mathbf{U})dU, \qquad (8\text{-}20)$$

where T_2 and T_1 are the respective projections of T.

9. RADIAL FUNCTIONS

In this section modification functions $M(\mathbf{q})$ will be discussed which depend on the length only of $\mathbf{q}$. Such functions have been called *radial functions*[16] and their transforms can be reduced to one dimension by introducing appropriate polar coordinates into (8-17):

$$T(r) = \int_0^{\infty}\int_0^{\pi}\int_0^{2\pi} M(q)$$

$$\times\exp(-2\pi iqr\cos\vartheta)d\varphi \sin\vartheta d\vartheta q^2dq, \qquad (9\text{-}1)$$

$$T(r) = 2/r\int_0^{\infty} M(q)\sin(2\pi qr)qdq.$$

The projection $T_2(R_2)$ of $T(r)$ onto a plane is given by the two-dimensional transform

$$T_2(R_2) = \int_{-\infty}^{\infty} M(Q)\exp(-2\pi i\mathbf{Q}\cdot\mathbf{R}_2)dA_{\mathrm{Q}}$$

$$= \int_0^{\infty}\int_0^{2\pi} M(Q)\exp(2\pi iQR_2\cos\varphi)d\varphi QdQ$$

$$= 2\pi\int_0^{\infty} QM(Q)J_o(2\pi QR_2)dQ. \qquad (9\text{-}2)$$

The line projection $T_1(R_1)$, finally, is given by the one-dimensional transform

$$T_1(R_1) = \int_{-\infty}^{\infty} M(B)\exp(-2\pi iR_1B)dB$$

$$= 2\int_0^{\infty} M(B)\cos(2\pi R_1B)dB. \qquad (9\text{-}3)$$

which is of the form already encountered in previous sections. Writing $T_3(r)$ for $T(r)$ and abandoning the formal distinction between r, R_2 and R_1 makes possible a combination of the three formulas (9-1) to (9-3) into one[16]

$$T_i(r) = 2\pi r_i^{1-(i/2)}\int_0^{\infty} M(q)q^{i/2}J_{(i/2)-1}(2\pi qr)dq, \qquad (9\text{-}4)$$

where $J_{(i/2)-1}$ is the Bessel function of order $(i/2)-1$. Between T_1 and T_3 there exist the direct relations

$$T_3(r) = -\frac{1}{2\pi r}\frac{d}{dr}T_1(r)$$

and $\qquad (9\text{-}5)$

$$T_1(r) = 2\pi r\int_r^{\infty} T_3(u)du,$$

so that functions T_3 can be obtained from all functions $T_1(r)$ listed in Fig. 1 simply by differentiation and division by $-2\pi r$; T_2 is connected directly with T_3 and T_1 by the equations

$$T_i(r) = 2\int_r^{\infty} uT_{i+1}(u)(u^2-r^2)^{-\frac{1}{2}}du$$

and $\qquad (9\text{-}6)$

$$T_{i+1}(r) = -\frac{1}{\pi}\int_r^{\infty}\frac{dT_i(u)}{du}(u^2-r^2)^{-\frac{1}{2}}du; \quad i=1, 2.$$

The effect of breaking off a three-, two-, or one-dimensional series by not using terms with $|\mathbf{q}|>q_o$ can be judged by considering the respective transforms of

$$M(q) = \begin{cases} 1, & |q|\leqslant q_o \\ 0, & |q|>q_o \end{cases}; \qquad (9\text{-}7)$$

namely,

$$T_i(r) = 2\pi r^{1-(i/2)}\int_0^{q_o} q^{i/2}J_{(i/2)-1}(2\pi qr)dq$$

$$= (q_o/r)^{i/2}J_{i/2}(2\pi q_or), \qquad (9\text{-}8)$$

where the relation[35]

$$\int x^n J_{n-1}(x)dx = x^n J_n(x) \tag{9-9}$$

has been used. Written out in terms of $s_o = 2\pi q_o$, the three transforms are

$$T_1(r) = \frac{s_o}{\pi} j_0(s_o r) = \frac{1}{\pi r} \sin s_o r,$$

$$T_2(r) = \frac{s_o}{2\pi r} J_1(s_o r),$$

and (9-10)

$$T_3(r) = T(r) = \frac{s_o^2}{2\pi^2 r} j_1(s_o r)$$
$$= \frac{1}{2\pi^2 r^3}[\sin s_o r - s_o r \cos s_o r].$$

The first is familiar from the earlier discussion, and all have been derived by van Reijen,[10] and from a different point of view, by James,[36] who also discusses their shape. The effects of breaking off are evidently less serious the higher the dimensionality, which is not surprising if it is remembered that the section $T_i(r)$ is determined by the projection of $M(q)$ so that the *effective* break-off is more gradual the higher the dimensionality.

An example of a convergence factor which is zero outside the limiting sphere and whose transform can be expressed analytically is example *d* of Fig. 1,

$$M(q) = \begin{cases} 1 - (q/q_o)^2, & |q| \leq q_o \\ 0 \quad , & |q| > q_o \end{cases}; \tag{9-11}$$

the corresponding transforms, obtained by partial integration and the aid of (9-9), are

$$T_i(r) = \frac{q_o^{(i/2)-1}}{\pi r^{(i/2)+1}} J_{(i/2)+1}(2\pi q_o r), \tag{9-12}$$

$$T_1(r) = \frac{2}{\pi r} j_1(s_o r) = \frac{2}{\pi s_o^2 r^3}[\sin s_o r - s_o r \cos s_o r],$$

$$T_2(r) = \frac{1}{\pi r^2} J_2(s_o r),$$

and (9-13)

$$T_3(r) = T(r) = \frac{s_o}{\pi^2 r^2} j_2(s_o r)$$

$$= \frac{1}{\pi^2 s_o^2 r^5}[(3 - (s_o r)^2) \sin s_o r - 3 s_o r \cos s_o r].$$

Again $s_o = 2\pi q_o$ has been introduced for easier comparison with Fig. 1. In keeping with the foregoing remark the present $T_1(r)$ (9-13) is essentially identical with the previous $T_3(r)$ (9-10). The transforms (9-10) and (9-13) are shown in Fig. 3.

The foregoing emphasis on the reduction which is afforded by the use of polar coordinates must not be taken to mean that this is always the best procedure. There are no doubt many counter examples. One is the familiar transform $T_3(\mathbf{r}) = (2a)^{-\frac{3}{2}} \exp(-\pi r^2/2a)$ of the modification function $\exp(-2\pi a q^2)$, for which the projections are easily found by direct integration, either projection or transformation, in Cartesian coordinates (not the coordinates relative to the lattice vectors except for orthogonal crystals), whereas the use of polar coordinates proves unfruitful. The projections are

$$T_i(r) = (2a)^{(-i/2)} \exp(-\pi r^2/2a); \quad i = 1, 2.$$

The anisotropic Gaussian modification function, an important nonradial function, can be handled just as readily in this way. From our example, again, a whole series of mutual transforms and their sections and projections may be derived very simply by differentiation with respect to *a*. Two, (*g*) and (*k*), are shown in Fig. 1; another is the pair

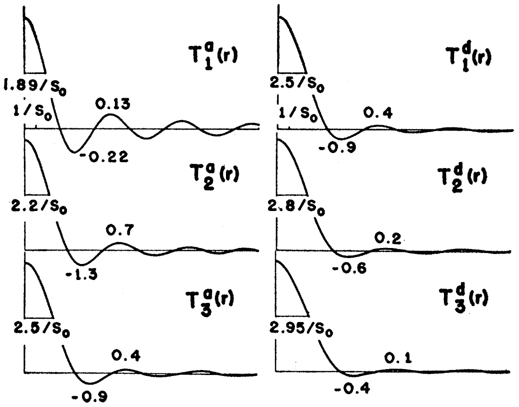

FIG. 3. One-, two-, and three-dimensional transforms corresponding to modification functions (a) and (d) of Fig. 1.

$$M(q) = 4\pi^2 q^4 \exp(-2\pi a q^2),$$
$$T_3(r) = (2a)^{-7/2}[15 - 10\pi r^2/a + \pi^2 r^4/a^2] \exp(-\pi r^2/2a),$$

which has proved most useful in affording a Patterson function with near maximal resolving power. (The alterations corresponding to the necessary finite cutoff are in this case almost entirely negligible.)

10. SERIES TRANSFORMS

It may be useful sometimes, especially in numerical work, to calculate the series transform of a modification function, rather than the integral transform. This transform must again be folded with the original func-

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[35] H. B. Dwight, *Tables of Integrals* (Macmillan and Company, Ltd., New York, 1934), 835.1.

[36] R. W. James, Acta Cryst. 1, 132 (1948).

tion, but the folding integral, in keeping with the periodic property of the series transform, now extends over one unit cell only. The simple development follows.

Consider the series representation (8-4) of $\rho(\mathbf{r})$:

$$\begin{aligned}\rho(\mathbf{r}) &= v_{\mathbf{r}}^{-1}\sum_{\mathbf{h}} F_{\mathbf{h}} \exp(-2\pi i\mathbf{h}\cdot\mathbf{r});\\ F_{\mathbf{h}} &= \int_{\text{unit cell}} \rho(\mathbf{r}) \exp(2\pi i\mathbf{h}\cdot\mathbf{r})dv_{\mathbf{r}}.\end{aligned} \tag{10-1}$$

When the coefficients are modified by multiplication with $M_{\mathbf{h}}$, the series becomes

$$\begin{aligned}\rho''(\mathbf{r}) &= v_{\mathbf{r}}^{-1}\sum_{\mathbf{h}} M_{\mathbf{h}}F_{\mathbf{h}} \exp(-2\pi i\mathbf{h}\cdot\mathbf{r})\\ &= v_{\mathbf{r}}^{-1}\int_{\text{unit cell}} \rho(\mathbf{t})\sum_{\mathbf{h}} M_{\mathbf{h}} \exp[2\pi i\mathbf{h}\cdot(\mathbf{t}-\mathbf{r})]dv_{\mathbf{t}},\end{aligned}$$

which on writing $K(\mathbf{r})$ for the series transforms of $M_{\mathbf{h}}$,

$$K(\mathbf{r}) = v_{\mathbf{r}}^{-1}\sum\nolimits_{\mathbf{h}} M_{\mathbf{h}} \exp(-2\pi i\mathbf{h}\cdot\mathbf{r}), \tag{10-2}$$

simplifies to

$$\rho''(\mathbf{r}) = \int_{\text{unit cell}} \rho(\mathbf{t})K(\mathbf{r}-\mathbf{t})dv_{\mathbf{t}}. \tag{10-3}$$

Pepinsky and his associates[37] have discussed a number of one-dimensional modification functions and the corresponding series transforms, which they call kernel functions, $K(\mathbf{r})$ being the kernel in the integral Eq. (10-3).

Of course $\rho''(\mathbf{r})$ is identical with the previous

$$\rho'(\mathbf{r}) = \int_{-\infty}^{\infty} \rho(\mathbf{t})T(\mathbf{r}-\mathbf{t})dv_{\mathbf{t}}, \tag{10-4}$$

where $T(\mathbf{r})$ is the integral transform of any $M(\mathbf{q})$ interpolated from the values $M(\mathbf{h})$, if only it $[M(\mathbf{q})]$ satisfies the general requirements for the Fourier theorems. Correspondingly, any one of the $T(\mathbf{r})$ on folding with the lattice function results in the same transform $K(\mathbf{r})$, which contains the contributions to a given unit cell of $T(\mathbf{r})$ as displaced successively by all the lattice vectors $\mathbf{l}$:

$$\sum\nolimits_{\mathbf{l}} T(\mathbf{r}+\mathbf{l}) = K(\mathbf{r}) = v_{\mathbf{r}}^{-1}\sum\nolimits_{\mathbf{h}} M_{\mathbf{h}} \exp(-2\pi i\mathbf{h}\cdot\mathbf{r}). \tag{10-5}$$

This equation is essentially Poisson's summation formula.[15,16]

The development so far tends to emphasize $M_{\mathbf{h}}$ and $K(\mathbf{r})$ and to make $M(\mathbf{q})$ and $T(\mathbf{r})$ appear arbitrary and comparatively unimportant. Nevertheless, it is profitable to adopt the point of view that $M(\mathbf{q})$ and $T(\mathbf{r})$ are the important fundamental functions, with $M(\mathbf{q})$ chosen as smooth as possible relative to the reciprocal lattice spacing and $T(\mathbf{r})$ accordingly restricted to relatively small values of $|\mathbf{r}|$, and that $M_{\mathbf{h}}$ and $K(\mathbf{r})$ depend upon them *and* the particular lattice under consideration. For although direct use of $K(\mathbf{r})$, the series transform, has the apparent advantage of at once taking into account the influence on a given peak of $\rho(\mathbf{r})$ by all the peaks of a set equivalent by the lattice translations, so that only the peaks within a unit cell have to be considered explicitly, the extra complexity of $K(\mathbf{r})$, as compared to a suitable $T(\mathbf{r})$, is likely to prove troublesome in practical work as well as general analysis. In effect, the use of the integral transform decomposes a complex total process into two simpler steps.

Some evident features of the situation are the following. In the first place $K(\mathbf{r})$ will lack radial symmetry. In practical work with actual density functions, it will therefore be much more difficult to handle, interaction for interaction, than radially symmetrical functions, which are readily obtained as integral transforms; and the advantage that follows from the smaller number of interactions that have to be considered may be lost. Even numerical evaluation of $K(\mathbf{r})$ is comparatively difficult, since a multidimensional sum has to be evaluated for a very large number of values of $\mathbf{r}$, whereas for $T(\mathbf{r})$ the radially symmetrical cases need to be evaluated in only one direction and by use of polar coordinates may always be reduced (see Sec. 9) to one-dimensional integrals. (Depending on the case and the computational facilities, however, it may be more convenient to deal with the original integral, with other coordinates.) A particular $M(\mathbf{q})$ and $T(\mathbf{r})$, once found satisfactory for a particular investigation, are apt to be suitable for other crystals of roughly similar elastic properties studied with the same equipment, regardless of the unit cell, whereas $K(\mathbf{r})$ evidently has to be calculated anew except in cases of precise isomorphism. On the analytical side, $T(\mathbf{r})$ can often be found in closed form, whereas the analytical evaluation of $K(\mathbf{r})$ would appear to be limited to a few one-dimensional cases and to products of these one-dimensional sums. It is important that even when $T(\mathbf{r})$ is not evaluated exactly, the general point of view affords an insight into the overlap problem which may in fact be adequate; if $K(\mathbf{r})$ has not been evaluated and the integral point of view is rejected, this insight is lacking. Finally, we remark that a radially symmetrical modification function can always be chosen which will restrict the significant overlap to closely neighboring peaks and that in this approximation (except for the smallest unit cells) the practical distinction between the series and integral transforms disappears. In this case it may be the more convenient to evaluate the series, for one especially simple direction of $\mathbf{r}$.

These relations between series and integral transforms afford an elegant and precise understanding of the approximation of the general (one or multidimensional) Fourier integral by a sum spaced at the points of an

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[37] R. Pepinsky, Abstracts of Washington Meeting of the American Crystallographic Association, February, 1951.

arbitrary (one or multidimensional) lattice.[38] This sum will be the folding of the desired transform with the Laue function of the lattice, or stated differently, the sum multiplied by the "volume" of the unit cell of the lattice is the result of superposing the desired transform with its repetitions at all points of a lattice reciprocal to the original one. The approximation will be good only if the unit cell of the original lattice is small enough so there is no important overlap between the repeated transforms. With decreasing lattice spacing, accordingly, the approximation (sum) for compact transforms will converge very rapidly once the lattice spacing is small enough; most remarkably, the sum for any transform which is restricted to a finite range of $\mathbf{r}$ becomes exact in that finite range, for a certain spacing of terms and for smaller spacings is quite independent of the spacing.

The interplay of the series and integral points of view also suggests the discussion of a number of minor questions not always correctly stated, which concern the convergence of the ordinary electron density series and the amount of information it contains regarding the shape $\rho_i(\mathbf{r})$ of the contribution of a particular atom i.

Thus, it is sometimes said[39] that the resolving power of the series will be low unless the number of terms is large. That there should be an effect which is characteristic just of the number of terms seems obvious. However, the fundamental peak shape given by the integral transform is determined solely by the complete modification function, of which the cutoff incidentally limits the number (but not the spacing) of terms, and if the number of terms is varied by varying the spacing, the resolving power is affected only in so far as the overlap of lattice-equivalent peaks is involved.

Again, it is obvious that the series will be affected much or little by a certain increase of the radius of cutoff according to the magnitude of terms so admitted, and concern is consequently sometimes expressed over the question of whether, even when the typical $F_{\mathbf{h}}$ has fallen to a low value, a number of especially strong reflections may happen to be just outside the sphere of reflection, so as to invalidate the conclusion that the only effects of increasing the cut-off radius slightly would correspond to the resulting slight changes in peak shape. The resolution of this situation depends upon the observation that only if the Fourier series is well converged, in the sense that $T(\mathbf{r})$ does not have relatively large oscillations extending to relatively large values of $\mathbf{r}$, will it be true that small changes in $T(\mathbf{r})$, caused perhaps by small changes in the cutoff, will have only small effects on $\rho'(\mathbf{r})$. For otherwise the background, on the average small, resulting from the essentially random superposition of large numbers of these oscillating contributions will typically show large relative variations when these oscillations are but little changed. Accordingly, a well-resolved Fourier series, perhaps by virtue of an imposed convergence factor, will not exhibit large changes when the complete modification function is changed slightly; correspondingly, a density series, for example, which is naturally well resolved will not change sharply as the cutoff is changed. In other words the type of sudden resurgence of strong F's presumed at the beginning of this paragraph cannot actually occur.

Lastly, it has been remarked[40] that if a good experimental determination of the atom form factor is to be desired from crystal reflections, a crystal of large unit cell, affording by its many reflections many samples of $f(\sin\vartheta/\lambda)$, must be used. But the essential problem is again peak overlap, a problem which would indeed be ameliorated if the unit cell could be expanded without adding more atoms, which of course it cannot in actual crystals. The obvious solution lies rather in reducing the temperature far enough to minimize the effects of thermal vibrations and in suitably decreasing the wavelength. Further still, the present considerations lead to an understanding of the problem of how to choose among the infinite number of possible interpolations between the samples of $f(\sin\vartheta/\lambda)$ afforded by a given crystal and wavelength. One must compute $\rho(\mathbf{r})$, partition it into atoms—perhaps quite arbitrarily if there is overlap—and transform one of them to obtain $f(\sin\vartheta/\lambda)$. If the atoms are well resolved in $\rho(\mathbf{r})$, the reasonable partitioning is accomplished—assuming for the present one atom at $\mathbf{r}_o$ per unit cell—by taking the contents of a unit cell centered at $\mathbf{r}_o$ whose boundaries do not slice atoms. But this is equivalent to modifying $\rho(\mathbf{r})$ by multiplication with the unit cell shape function discussed in Sec. 8, and the result for $f(\sin\vartheta/\lambda)$, given by Eq. (8-11), is obtained by folding the transform of this shape function with the reciprocal lattice, as weighted with the observed $F_{\mathbf{h}}$. With more than one atom in the unit cell, or with a lattice so skewed that all possible choices of the unit would slice atoms, the $f_i(\sin\vartheta/\lambda)$ may still be obtained, in an approximation of validity corresponding to the magnitude of any overlap, by the same procedure, now to be carried out with appropriate shape functions—not necessarily parallelepipeds—centered at the respective atoms. Although it is really $\rho'(\mathbf{r})$ and complete atomic modification functions $M_i(\mathbf{h})$ which have to be manipulated, it will be noted that approximations to the true $M_i(\mathbf{q})$ are nevertheless obtained by this procedure and that the $f_i(\sin\vartheta/\lambda)$ inside the cutoff then follow by dividing out the real temperature factors—if they are known—and the imposed modification function. Overlap will be affected by the imposed modification function in a way so complicated, however, as to preclude the use of any formula like (8-11), so that if overlap is important, it becomes necessary somehow to analyze $\rho'(\mathbf{r})$ in terms of the transform of the products of the respective temperature factors by the imposed

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[38] An example is provided by the calculation of structure factors by Fourier summation described by D. Sayre, Acta Cryst. 4, 362 (1951), who also discusses the nature of the approximation involved.

[39] For example, reference 28, bottom of p. 370.

[40] Reference 4, p. 825.

modification function, to suitably decompose the peaks of the resulting $\rho(\mathbf{r})$, if they still overlap, and to calculate their transforms.

11. CONCLUDING REMARKS

It is obvious that the general discussions given in earlier sections pertain to several dimensions as well. A number of specific additional remarks follow.

Modification functions may again be useful to improve convergence of Fourier series, but it is evident that the resulting peak shape will in general depend on the number of dimensions (see Fig. 3; comparison is of course possible only for radial functions), the Gaussian being an exception and the effects of cutoff being less severe the greater the number of dimensions. [The last point may also be seen from general arguments, as in the remark following (9-10) or from a development analogous to (5-9).] Nevertheless, the feasibility of introducing convergence factors does not seem to be generally recognized. For example, the atom form factors describing the scattering of thermal neutrons are constants, so that the only cause for a general decrease of intensities at high scattering angles is the motion of the atoms, and Lonsdale[41] has commented that "only trial and error methods of structure analysis are possible." However, a suitable convergence factor will always lead to sound Fourier maps, as has also been remarked by Thewlis,[42] and the only serious question is the universal one of how to make the compromise between desirable simplicity of interpretation and the concomitant undesirable loss of essential resolving power. But for some crystals the natural temperature effect will already provide adequate convergence with the current experimental conditions, and there is always the possibility, for harder crystals, of shortening the wavelength and so increasing the power of resolution.

Booth[43] has raised objections to the use of a convergence factor on the grounds that they "introduce errors greater than for the elimination of which [they are] applied." In support of this contention he shows a table containing the maximum errors of peak positions which may be caused by terminating a one-, two-, or three-dimensional series, as well as a table of the maximum errors caused by using different artificial temperature factors in a three-dimensional sum. However, these tables would appear to pertain only to the very specific example underlying them, that of two neighbors at a distance of 1.4A (or larger) having radial, Gaussian density distributions of a width characteristic for organic crystals. Unfortunately, no lower distance limit of 1.4A exists for Patterson functions or for projections of the electron density; different results would further be expected for heavier atoms, harder crystals, low temperature data, or neutron diffraction data; finally a number of distant peaks may cause significant shifts in a terminated series, whereas the peak broadening due to a convergence factor will affect close neighbors only. Again, the advantage of using a convergence factor lies in the simplicity of its transform, which facilitates detailed analysis of peak shapes should any be required.

A recently proposed way[44] of handling the breaking-off error is the now often used back-shift method which involves comparison of the Fourier map based on observational data with a similar map obtained from calculated structure factors, all terms which were lacking in the first sum being omitted in the second one also. Alternately,[45] an $F_o - F_c$ synthesis may be carried out using as coefficients the difference between calculated and observed structure factors. Accurate knowledge of the form and temperature factors is a very important requirement, to which, it seems, too little attention is ordinarily given. Weighting with a suitable modification function will be helpful in this connection if the accuracy of the assumed form and temperature factors can be estimated as a function of $\mathbf{h}$.

These methods are equivalent to the peak by peak analysis discussed above. They have the advantage of dealing with the crystal as a whole and thus, if the peaks have not been made reasonably compact, may actually entail less calculation. In a peak by peak analysis, on the other hand, in which important interactions only need to be dealt with in detail, the assumed peak shapes (which is to say the form, temperature, and imposed modification factors) are necessarily checked, or else the correct peak shapes can be taken directly from the map under analysis, at least if it is not hopelessly complicated. If the thermal motions are anisotropic with principal axes oriented unsymmetrically to the principal symmetry elements of the crystal, as often happens, it is inconvenient to make appropriate precise structure factor calculations and the present direct analysis should be especially advantageous.

Van Reijen[9] seems inclined to favor inclusion of extrapolated coefficients in order to avoid termination errors while still making full use of far-out reflections. If not really correct, however, such an extrapolation will lead to error. Indeed, van Reijen's (110) projection of diamond, which he gives as an example, shows questionable high frequency details near the centers of the carbon six-rings which presumably must be attributed either to extrapolation errors or possibly to experimental errors in high order terms.

Imposed modification functions need not be limited to convergence factors and a number of other functions have been found useful so far. Sharpening of peaks by multiplying structure factors with $f_e^{-1}(s)$ or similar

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[41] K. Lonsdale, Nature **164**, 205 (1949).

[42] J. Thewlis, Ann. Repts. Progress Chem. (Chem. Soc., London) **47**, 420 (1950).

[43] A. D. Booth, Proc. Roy. Soc. (London) **A188**, 77 (1946) **190**, 482 (1947); Nature **157**, 517 (1946).

[44] A. D. Booth, Proc. Roy. Soc. (London) **A188**, 77 (1946); *Fourier Technique in X-Ray Organic Structure Analysis* (Cambridge University Press, Cambridge, 1948).

[45] W. Cochran, Acta Cryst. **4**, 408 (1951).

functions is an example. Sharpening is especially important for Patterson functions, where resolution is the crucial consideration, and the limited experience so far seems to show that even in addition to sharpening with $f_e^{-2}\exp(as^2)$ a further emphasis of the far-out data (to be sure with suitable smoothing at the cutoff), as in the examples derived from the Gaussian, mentioned in Sec. 9, is most helpful. Such functions are likely to vanish at the origin, so that the integral of their transform is zero. This requires that the desirable sharp, high peak at the center of the transform at least be balanced by negative values elsewhere, but this is less serious in the three-dimensional case, to which one is forced for even moderately large unit cells, than it is for lower dimensionality, inasmuch as the negative region is of greater extent relative to the central peak. Even so, although it apparently has not yet so turned out in practice,[46] a transform with integral zero could well be most confusing in failing to reveal unresolved concentrations of peaks such as would seem to be possible over regions of atomic or possibly even molecular size. It seems that here is a prime example where the concurrent use of more than one suitably chosen modification function should prove profitable.

As in the one-dimensional cases, the peak shapes for $\rho'(\mathbf{r})$ and $P'(\mathbf{r})$ may be evaluated either by inverting the complete modification function or by folding the transforms of its several factors, the single inversion, usually, being the easier to perform while the successive foldings provide the clearer picture of the situation. Viervoll[23] discusses peak shapes for $\rho(\mathbf{r})$ and $P(\mathbf{r})$ and gives some actual examples. For the shape of ideal Patterson peaks,

$$P_{ij}(r)=\int_{-\infty}^{\infty}\rho_i(t)\rho_j(|\mathbf{t}+\mathbf{r}|)dv_{\mathbf{t}},$$

involving spherically symmetrical atoms, Viervoll[23] uses the expression

$$\frac{2\pi}{r}\int_0^{\infty}t\rho_i(t)\int_{|t-r|}^{t+r}u\rho_j(u)du\,dt,$$

which follows immediately (Viervoll gives a lengthy derivation) from the substitution

$$|\mathbf{t}+\mathbf{r}|=(r^2+t^2+2rt\cos\vartheta)^{\frac{1}{2}}.$$

In a procedure for subtracting the peaks corresponding to certain atoms in a Fourier map, Finbak and Norman[47] use what amounts to an arbitrary, unsymmetrical modification function. The peak shape is obtained by setting up a Fourier series corresponding to one specific atom at its most probable position. This series—our series transform $K(\mathbf{r})$ except for a shifted origin—is terminated in the same way as the original series. In addition Finbak and Norman propose that coefficients be omitted where no terms are available in the original series due to unobservably low intensity of the corresponding x-ray reflection. This corresponds to the omission of terms in back-shift and F_o-F_c syntheses mentioned above. Nevertheless, Finbak and Norman's proposal may lead to grave complications, because the corresponding $M_{\mathbf{h}}$ has scattered zeros and an excessively complicated transform; and we believe it should be adopted only in those cases of duress, important to be sure, where relatively high background or low sensitivity of the instruments of detection lead to a significantly high value for the maximum unobservable $F_{\mathbf{h}}$. Analysis of Fourier maps in terms of such transforms, although possible and more accurate, would in general be very difficult, and the general advisability of the procedure is not demonstrated by Finbak and Norman's example, for which the number of missing large terms is very small. It will be appreciated that if certain reflections were unobservably weak, compared to the strongest reflections, the contribution of the corresponding terms, left out of the original Fourier map, is small and can be neglected in good approximation. In this approximation the original Fourier map still corresponds to a superposition of simple peaks and may be so interpreted, the negligible size of the unobservable terms being a consequence of structure rather than of complexity of atom shapes. Correspondingly, the subtraction of a complex peak shape would only change into complex features the basically simple peaks (possibly complicated by overlap) present in the original map and could not be stopped after dealing with a few peaks, as otherwise would usually be the case. Furthermore a new Fourier would usually have to be evaluated should a change of parameters be desirable, since a simple translation of the transform can only be executed if it is a cover operation of the grid for which the values have been calculated. Again simple peak shapes prove much less cumbersome.

Two related examples can be found in a recent paper by Magnéli.[48] He first considers a one-dimensional structure whose period contains a sequence of eight equidistant lines, the last line of one period and the first line of the next one being at half that distance. The Fourier coefficients of this structure are either large or comparatively small[49] due to the existence of a pseudo-sublattice. Magnéli shows diagrams of the following sums evaluated using a convergence factor such that only terms with $n\leq 40$ are of any significance: (1) corresponding to the above structure, (a) the complete sum and (b) an incomplete sum, including only the four largest terms with $n=0$, 7, 8, 15, which function shows false detail; (2) the series transform $K(\mathbf{r})$ corresponding

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[46] Shoemaker, Donohue, Schomaker, and Corey, J. Am. Chem. Soc. **72**, 2328 (1950); J. Donohue and K. N. Trueblood, Acta Cryst. **5**, 414 (1952).

[47] C. Finbak and N. Norman, Acta Chem. Scand. **2**, 813 (1948).

[48] A. Magnéli, Acta Cryst. **4**, 447 (1951).

[49] The effect of such pseudo-sublattices on the distribution of Fourier coefficients has been discussed by V. Vand, Acta Cryst. **4**, 104 (1951), and by J. W. Jeffery, Proc. Phys. Soc. (London) **A64**, 1003 (1951), in terms of concepts expounded in the foregoing.

to a line at the origin, with (a) all terms and (b) only the four terms corresponding to (1b), the last result being of considerable complexity. Magnéli points out how the incomplete sum for the structure (1b) can be understood as resulting from a superposition of the incomplete series transforms (2b). However, while this is undoubtedly true, the omitted coefficients are by no means small and if the coefficients with $n=6$, 9, 22, 23, 30, whose magnitudes average about 20 percent of that of the largest term, are included a graph results whose main peaks stand out clearly and correspond in position to the original structure. The subsidiary features of this graph are clearly recognizable as such, the largest one being about one-third of the size of the smallest main peak and comparable in size to the subsidiary features of a sum which includes *all* terms with $n\leq 30$. The original structure can thus clearly be reconstructed from this graph despite the fact that the magnitude of many of the terms omitted is still above 5 percent of the size of the largest term. These terms are not really negligible and a detailed complete analysis of the graph would of course require the corresponding incomplete $K(\mathbf{r})$.

An alternative to using this complex transform in cases where the magnitude of the terms which cannot be determined experimentally is relatively large, is to substitute theoretical values for the missing coefficients. This will result in simple peaks provided the parameters used in the calculation of the substituted terms are close to their correct values. This procedure is a special case of one proposed by Cochran[50] which permits giving different weights to different observed values. The use of theoretical values in this way of course increases the provisional character of the electron density function, which usually is considerable anyhow because of the necessity of using theoretical values for the phase angle values of the coefficients.

Magnéli's second example is two-dimensional and concerns his (010) projection of β tungsten oxide. The structure is analogous to the one-dimensional example just discussed, being characteristic of the transform of the tungsten form factor, modified by the omission of a large number of terms and thus comprising a complex system of peaks. Again the original Fourier map may be interpreted in terms of simple transforms, and it is interesting that Magnéli's solution of the structure actually does rest on this point of view.

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[50] W. Cochran, Nature **161**, 765 (1948); Acta Cryst. **1**, 138 (1948).