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Fourier syntheses of electron-diffraction data.

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In recent years the methods of Fourier syntheses have been successfully applied to electron-diffraction investigations of crystals (Vainshtein, 1949; Cowley, 1953). In these cases the function which is synthesized refers to the *potential* distribution of the crystal. This is somewhat different from the procedure followed in gas-phase molecular structure investigations, where the Fourier syntheses (radial distribution functions) usually refer to the total charge or to the nuclear charge distribution of the molecule in question.

In the corresponding cases of X-ray diffraction the various types of Fourier syntheses have a direct bearing on the *electron* distribution. In fact, the different syntheses may be developed from the basic equation of coherent scattering†

$$A(\mathbf{q}) = \int \varrho_e(\mathbf{p}) \exp\left[-2\pi i \mathbf{q}\mathbf{p}\right] d\tau\,, \qquad (1)$$

where $\mathbf{q}$ and $\mathbf{p}$ are vectors in the specimen space and the reciprocal space, respectively, and $\varrho_e(\mathbf{p})$ is the electron density. The corresponding equation for electron diffraction is (cf. for example, Pinsker, 1953)

$$A(\mathbf{q}) = \int V(\mathbf{p}) \exp\left[-2\pi i \mathbf{q}\mathbf{p}\right] d\tau\,, \qquad (2)$$

where $V(\mathbf{p})$ is the potential. This equation forms the basis for the Fourier syntheses of the potential distribution. It is seen that in syntheses of this type the amplitude of electron diffraction will appear in the series in exactly the same way as the corresponding X-ray amplitude does in syntheses of electron density functions. By Poisson's equation

$$\nabla^2 V(\mathbf{p}) = -4\pi\varrho_t(\mathbf{p})\,,$$

equation (2) may be transformed to the equations usually used in electron-diffraction investigations of gases, namely:

$$s^2 A(\mathbf{q}) = \int \varrho_t(\mathbf{p}) \exp\left[-2\pi i \mathbf{q}\mathbf{p}\right] d\tau$$

or

$$\frac{z}{(z-f)}\, s^2 A(\mathbf{q}) = \int \varrho_n(\mathbf{p}) \exp\left[-2\pi i \mathbf{q}\mathbf{p}\right] d\tau\,, \qquad (3)$$

where $s = (4\pi/\lambda)\sin\theta$; $(1/s^2)\,(z-f)/z$ is the (average) atomic scattering factor for electrons; and $\varrho_t(\mathbf{p})$ and $\varrho_n(\mathbf{p})$ are the total charge distribution and the nuclear charge distribution, respectively. It is seen that in this case $s^2A(\mathbf{q})$ or $\{z/(z-f)\}s^2A(\mathbf{q})$ has a significance parallel to the amplitude of X-ray diffraction. This means that in the case of electron diffraction we have two 'natural' bases for the Fourier syntheses. One of these, equation (3), has been used for a long time in molecular structure investigations; the other, equation (2), has now been used in crystallographic investigations.

For systems of random orientation the Fourier syntheses are based on radial distribution functions, $D(r)$ or $\sigma(r)$. These may be defined by the equations

$$4\pi r D(r) = \frac{\sigma(r)}{r} = \frac{1}{r}\int \varrho(\mathbf{p})\varrho(\mathbf{p}+\mathbf{r})\, d\tau\, df$$
$$= r\int \varrho(\mathbf{p})\varrho(\mathbf{p}+\mathbf{r})\, d\tau\, d\Omega\,. \qquad (4)$$

Here the vector $\mathbf{p}$ defines a point in the specimen and $d\tau$ is a volume element at that point. The vector $(\mathbf{p}+\mathbf{r})$ defines a point on a sphere of radius r around $\mathbf{p}$; df is a surface element of that sphere, while $d\Omega = df/r^2$ is the corresponding element of solid angle. The radial distribution functions which are usually used in structure determinations refer either to electron charge ϱ_e, total charge ϱ_t or nuclear charge ϱ_n. We may, however, introduce a similar function for the potential, $D_v(r)$ or $\sigma_v(r)$, defined by

$$4\pi r D_v(r) = \frac{\sigma_v(r)}{r} = \frac{1}{r}\int V(\mathbf{p})V(\mathbf{p}+\mathbf{r})\, d\tau\, df$$
$$= r\int V(\mathbf{p})V(\mathbf{p}+\mathbf{r})\, d\tau\, d\Omega\,. \qquad (5)$$

In molecular structure investigations the radial distribution functions are usually evaluated from the observed intensity by means of the following integrals:

$$4\pi r D_t(r) = \frac{\sigma_t(r)}{r} = \frac{2}{\pi}\int I(s)s^5 \sin sr\, ds\,,$$
$$4\pi r D_n(r) = \frac{\sigma_n(r)}{r} = \frac{2}{\pi}\int \frac{I(s)s^5z^2}{(z-f)^2} \sin sr\, ds\,. \qquad (6)$$

Here D_t and σ_t refer to the total charge distribution while D_n and σ_n refer to the nuclear charge distribution. (Frequently the arguments of (6) are multiplied by a damping factor, as mentioned below.) The corresponding function for the potential may be evaluated from

$$4\pi r D_v(r) = \frac{\sigma_v(r)}{r} = \frac{2}{\pi}\int I(s)s \sin sr\, ds\,. \qquad (7)$$

Between the radial distribution functions of the potential and those of the total charge distribution there is the following relation:

$$\frac{d^4}{dr^4}(4\pi r D_v(r)) = \frac{d^4}{dr^4}\left(\frac{\sigma_v(r)}{r}\right) = 4\pi r D_t(r) = \frac{\sigma_t(r)}{r}\,. \qquad (8)$$

Each atom pair in a molecule will give a contribution to the radial distribution function. The form of the individual (ideal) contribution can be calculated when the $\varrho(\mathbf{p})$ or $V(\mathbf{p})$ functions of the two atoms are known (Debye & Pirenne, 1938; Viervoll, 1950). It is interesting to note that, whereas the D_t and σ_t functions give a peak flanked by minima, the D_v and σ_v are positive everywhere, as also are the D_n and σ_n functions. It is well known that radial distribution functions computed from experimental data only are approximate, since the integrations cannot be carried out to the upper limit. The

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† The notations used here and in the following equations are those used in an earlier paper (Viervoll, 1950), where the connexions between the different functions were discussed.

various types of functions differ, however, in rapidity of convergence and in resolution of interatomic distances. The more the argument of the Fourier integral is damped, the more rapidly does the radial distribution function converge (to the ideal one), but the poorer resolution it shows. It has been customary to introduce an 'artificial temperature factor' in order to increase the convergence of the D_t, σ_t, D_n, and σ_n functions. The series of the corresponding D_v and σ_v functions converge so rapidly that the experimental function must be expected to represent a good approximation to the corresponding 'ideal' function of the system. The actual form of these functions will be calculated and discussed elsewhere.

A suggestion by Konobeevskii (1948) to use a similar procedure in the case of crystallographic X-ray investigations seems somewhat far fetched. Usually the actual thermal vibrations are large enough to give sufficient convergence of the series. If this 'natural' convergence is increased by the use of $F/\sin^2\theta$ instead of F in the Fourier syntheses, the peaks on the Fourier map will obviously be too broad to be useful for usual structure determinations.

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References

Cowley, J. M. (1953). *Acta Cryst.* **6**, 522.

Debye, P. & Pirenne, M. M. (1938). *Ann. Phys., Lpz.* **33**, 617.

Konobeevskii, S. T. (1948). *Dokl. Akad. Nauk, SSSR,* **64**, 49.

Pinsker, Z. G. (1953). *Electron Diffraction,* chapter 7. London: Butterworth.

Vainshtein, B. K. (1949). *Dokl. Akad. Nauk SSSR,* **59**, 33.

Viervoll, H. (1950). *Skr. Norske Vidensk. Akad. Oslo, Mat.-Naturv.* Klasse No. 2.

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A correction and a supplement to a note on the crystal structure of Zeise's salt.

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The authors wish to draw attention to errors in a table of atomic co-ordinates which appeared in a note on the crystal structure of Zeise's salt (Wunderlich & Mellor, 1954). We publish below the corrected values and some additional information, namely, approximate values of the co-ordinates of the carbon and oxygen atoms.

	x	*y*	*z*
Pt	0·213	0·000	0·333
Cl(2)	0·213	0·277	0·333
Cl(3)	0·213	0·723	0·333
Cl(1)	0·428	0·000	0·529
K	0·438	0·313	0·933
C(1)	0·01	*	0·26
C(2)	0·07	*	0·99
O	0·05	?	0·58

* One relatively high but diffuse peak near $x = 0.04$ and $y = 0$ in a 'difference synthesis' projection on (001) indicated that both carbon atoms lay close to $y = 0$.

This correction in no way alters the deductions made in our previous communication. The discrepancy factor $R(\Sigma||F_o|-|F_c||\div\Sigma|F_o|)$ at this stage of the refinement is 0·141 for the (*h*0*l*) zone of 134 reflexions and 0·193 for the (*hk*0) zone of 91 reflexions. The contributions of platinum, potassium and the three chlorine atoms were included in the calculation of F_c.

It is therefore evident that the length of the ethylene molecules is perpendicular (or nearly so) to the plane of the $PtCl_3$ group, the average distance between the platinum and carbon atoms being 2·2 Å and the C–C separation being roughly 1·5 Å.

Recently, Chatt (1953) has presented evidence from infra-red measurements in favour of the 'side on' arrangement and has proposed an electronic system in terms of molecular orbitals. Our crystal-structure determination also indicates a 'side on' linkage of ethylene to platinum, and is in agreement with the geometry of the molecule as imposed by Chatt's electronic model.

References

Chatt, J. (1953). *J. Chem. Soc.* p. 2939.

Wunderlich, J. A. & Mellor, D. P. (1954). *Acta Cryst.* **7**, 130.

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