FOURIER TREATMENT OF THE ANOMALOUS DISPERSION CORRECTIONS IN X-RAY DIFFRACTION DATA *

R. SRINIVASAN AND K. K. CHACKO

Centre of Advanced Study in Physics, University of Madras, Madras-25, India

1. Introduction

THE use of anomalous dispersion effect in X-ray scattering for the solution of crystal structure and absolute configuration of molecules is now well known (Peederman and Bijvoet, 1956; Ramachandran and Raman, 1956; Pepinsky and Okaya, 1956). It is essentially based on the fact that for a non-centrosymmetric crystal containing anomalous scatterers the intensities of inverse reflections become unequal. A formal treatment of the effect results in complex quantities in the transform space and is a consequence of the fact that the atomic scattering factor itself is no longer real but a complex quantity. Thus the Patterson function, in the presence of anomalous dispersion effect, can be represented as a complex one (Pepinsky and Okaya, 1956) whose imaginary component termed the $P_s(u)$ function has interesting properties and holds the solution to the structure and absolute configuration. It is obvious that the electron density function can also be similarly represented, in a formal way, as a complex function. No explicit treatment of this seems to be available in the literature particularly from the point of view of practical calculations. The purpose of this paper is to derive the related formulæ and to show how such a Fourier synthesis can be computed in practice from the available data. This method of approach is likely to prove useful in the study of the real and imaginary components of the dispersion corrections to the atomic scattering factors.

2. Fourier Representation of Complex Electron Density

Let $\underline{N}$ denote the total number of atoms in the structure, $\underline{P}$ the number of anomalous scatterers all of the same kind and $\underline{Q}$ the number of non-anomalous scatterers. Denoting the atomic scattering factors by

$$f_P = f_P^0 + \Delta f_P' + i\Delta f_P'' \quad f_P' + i\Delta f_P''$$

and $f_Q = f_Q^0$, the structure factors for the reflections H and $\bar{H}$ can be written as

$$F(H) = F'(H) + iF_P''(H) \tag{1a}$$

$$F(\bar{H}) = F'(\bar{H}) + iF_P''(\bar{H}) \tag{1b}$$

and in particular,

$$F^*(\bar{H}) = F'(H) - iF_P''(H) \tag{1c}$$

where $\underline{F}'$ is the contribution to the structure factor from the total real parts of the scattering of the atoms (*i.e.*, from f'_P and f_Q) and F_P'' is the contribution from the imaginary part $\Delta f_P''$ of the anomalous scatterers. Written in terms of the real and imaginary components of the structure factors (1) becomes

$$F(H) = [A'(H) - B_P''(H)] + i[B'(H) + A_P''(H)]. \tag{2a}$$

$$F(\bar{H}) = [A'(H) + B_P''(H)] + i[A_P''(H) - B'(H)] \tag{2b}$$

and

$$F^*(\bar{H}) = [A'(H) + B_P''(H)] + i[B'(H) - A_P''(H)] \tag{2c}$$

where

$$A'(H) \sum_{i=1}^{Q} f_{Qi} \cos 2\pi \underset{\sim}{H} \cdot \underset{\sim}{r}_{Qi} + \sum_{j=1}^{P} f_{Pj}' \cos 2\pi \underset{\sim}{H} \cdot \underset{\sim}{r}_{Pj}$$

$$A_P''(H) \sum_{j=1}^{P} \Delta f_{Pj}'' \cos 2\pi \underset{\sim}{H} \cdot \underset{\sim}{r}_{Pj} \tag{3}$$

and similarly the $\underline{B}$ components are given in terms of sine functions. (It is understood that quantities with no subscript correspond to the entire structure of $\underset{\sim}{N}$ atoms.)

The electron density distribution $\rho(\underset{\sim}{r})$ can be formally defined as

$$\rho(\underset{\sim}{r}) = \frac{1}{V}\left\{F(O) + \sum_H \left[\frac{F(H) + F^*(\bar{H})}{2}\right] \times \exp. 2\pi i \underset{\sim}{H} . \underset{\sim}{r} + \sum_H \left[\frac{F(H) - F^*(\bar{H})}{2}\right] \exp. 2\pi i \underset{\sim}{H} . \underset{\sim}{r}\right\} \tag{4}$$

where $\underline{F}^*$ is the complex conjugate of $\underline{F}$. It may be readily verified that (4) is the generalization of the electron density representation,

* Contribution No. 215 from the Centre of Advanced Study in Physics, University of Madras.

for when anomalous dispersion effect is absent $\underline{F}(\underline{H}) = \underline{F}^*(\bar{\underline{H}})$ and hence the second summation in (4) will vanish while the remaining terms reduce to the conventional form. In order to interpret the resultant Fourier (4) let us substitute the formulæ from (2) in (4). We get, after some simplification,

$$\rho(\underset{\sim}{r}) = \frac{1}{V}\{F(O) + 2\Sigma'[A'(H) + iB'(H)] \times \exp. 2\pi i \underset{\sim}{H}.\underset{\sim}{r} + 2i\Sigma'[A_P''(H) + iB_P''(H)] \times \exp. 2\pi i \underset{\sim}{H}.\underset{\sim}{r}\} \quad (5)$$

where the primed summation symbol denotes that the summation is over half the reciprocal cell only. Thus from (5) it is seen that the electron density can be formally written as

$$\rho(\underset{\sim}{r}) = \rho_R(\underset{\sim}{r}) + i\rho_I(\underset{\sim}{r}) \quad (6)$$

where ρ_R and ρ_I are the 'real' and 'imaginary' components of the electron density given by

$$\rho_R(\underset{\sim}{r}) = \frac{1}{V}\{F(O) + 2\Sigma'[A'(H)\, iB'(H)] \times \exp. 2\pi i \underset{\sim}{H}.\underset{\sim}{r}\}$$

$$\rho_I(\underset{\sim}{r}) = \frac{2}{V}\Sigma'[A_P''(H) + iB_P''(H)] \times \exp. 2\pi i \underset{\sim}{H}.\underset{\sim}{r} \quad (7)$$

3. Discussion

The functions ρ_R and ρ_I correspond to the total contribution to the structure factor respectively from the entire real and imaginary components of the atomic scattering factors. This is readily visualized by reference to the argand diagram (Fig. 1) where the relations between the structure factors are shown. Half the

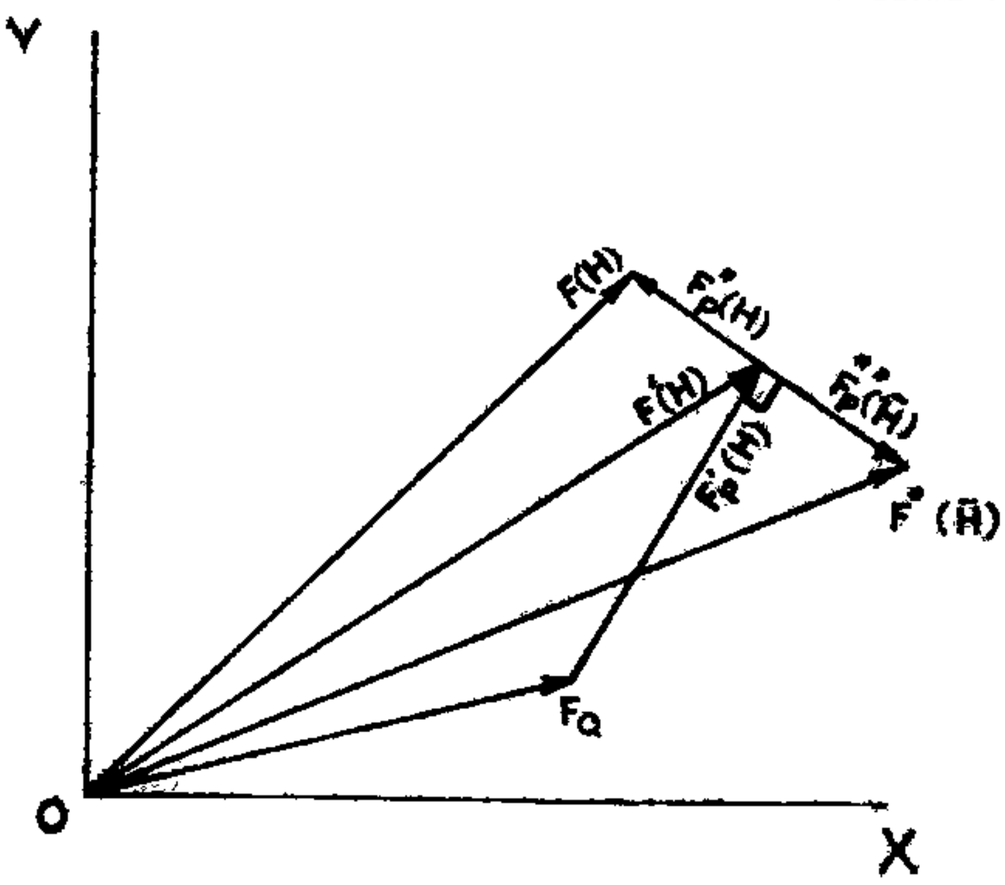

FIG. 1. Relations between the structure factors.

sum and difference of the vectors $\underline{F}(\underline{H})$ and $\underline{F}^*(\bar{\underline{H}})$ may be seen to be respectively the vectors $\underline{F}'(\underline{H})$ and $\underline{F}_P''(\underline{H})$. It may be noticed that the i in (5) is only a consequence of the fact that the imaginary component is $\pi/_2$ ahead of the real component F_P' of the anomalous scatterers.

Our main interest here is in the fact that both ρ_R and ρ_I can be computed. For instance ρ_R is the one normally calculated. In the method of phase determination (Ramachandran and Raman, 1956) it is the phase angle α' corresponding to $\underline{F}'(\underline{H})$ that is calculated (but for an ambiguity). In the initial stages of analysis the magnitude of $|F'(H)|$ may be taken to be approximately $\langle I\rangle^{\frac{1}{2}}$ where $(I) = [I(H) + I(\bar{H})]/2$, while for greater accuracy the exact expression $|F'(H)| = [\langle I\rangle - |F_P''|^2]^{\frac{1}{2}}$ may be used (Ramachandran and Raman, 1956).

Once the structure has been established fully and well refined co-ordinates of all atoms are available one could compute the function ρ_I. The coefficients to be used here are $-i\,[F(H) - F^*(\bar{H})]/2$ where it is understood that one uses the observed amplitudes $|F_0(H)|$ and $|F_0(\bar{H})|$ with the calculated phases $\alpha(H)$ and $\alpha^*(\bar{H})$ which are given by

$$\tan\alpha(H) = \frac{[B'(H) + A_P''(H)]}{[A'(H) - B_P''(H)]} \quad (8\,a)$$

$$\tan\alpha^*(\bar{H}) = \frac{[B'(H) - A_P''(H)]}{[A'(H) + B_P''(H)]} \quad (8\,b)$$

It is clear that the map ρ_I is the Fourier transform of imaginary components of the anomalous scatterers and will contain peaks at $\underset{\sim}{r}_{Pj}$ of strength proportional to $\Delta f_P''$. It may be readily verified that the formula (4) is quite general and is applicable even when there are more than one type of anomalous scatterers in the unit cell. To start with, one could calculate the phases by including only the strongest of the anomalous scatterers but the Fourier map ρ^1 can be expected to reveal the other "lighter" anomalous scatterers. The entire structure could then be developed further with successive approximations. The following are the possible lines that are open at this stage:

(*i*) The map ρ_I can now be treated independently of ρ_R and the structure refined. The positions as given by such a map may be compared with those obtained from ρ_R. Any possible differences which are significant may give us useful information of the electron

density maxima for the entire atom and the inner shells respectively.

(*ii*) The refinement of the ρ_I structure may include also $\Delta f_P''$ and its temperature factor B_J'' as unknown parameters.

The difference Fourier technique and least squares method can be useful for this purpose.

The possibility of a systematic application of these procedures depends to a large extent on the accuracy of the intensity data. In particular since it is the difference in magnitude that enters the Fourier synthesis, the map will be highly sensitive to errors in the measurements. The absolute values of $\Delta f''$ to be obtained will particularly depend on the absolute values of $|\underline{F}(\underline{H})|$ and $|\underline{F}(\bar{\underline{H}})|$.

Coming to the function ρ_R, it is seen that it could be used to study the real part correction $\Delta f'$ and the corresponding electron density distribution. However, this requires measurement of intensities for another wavelength λ_0 for which dispersion effect is absent or negligible. The difference map $\rho_R(\lambda) - \rho_R(\lambda_0)$ can be performed to study $\Delta f'$.

It may be pointed out in this connection that the above method of approach in terms of real and imaginary components is only a formal, and convenient way of studying the dispersion effects. Actually as pointed out by Patterson (1963 ; see also Ibers and Hamilton, 1964) the electron density in atoms should, from a physical point of view, be independent of the wavelength used. Such a representation could still be obtained although it could be achieved only as a limiting approximation. For instance even atoms as light as oxygen have finite detectable dispersion effects (Zachariasen, 1965 ; Marezio, 1965) for normally used wavelengths.

Figure 2 shows the ρ_I map computed for L-tyrosine hydrochloride for the $\underline{C}$ projection. The measured counter data of Parthasarathy (1962) were used and the co-ordinates used were those given by Srinivasan (1959). A strong peak (strength $\simeq 1{\cdot}8\, e/A^2$) at the position of chlorine may be noticed, which is to be expected. The $\Delta f''$ correction for chlorine for CuK α is $\simeq 0{\cdot}66$). There is no other significant feature in the map excepting low peaks which appear to be spurious. It may be mentioned that this is taken only as an example to illustrate the method and is probably not the best one to see, if any, the effects at lighter atoms. The structure had been refined only two-dimensional data, and hence the accuracy in co-ordinates is not high. No attempt was therefore made to refine the ρ_I map.

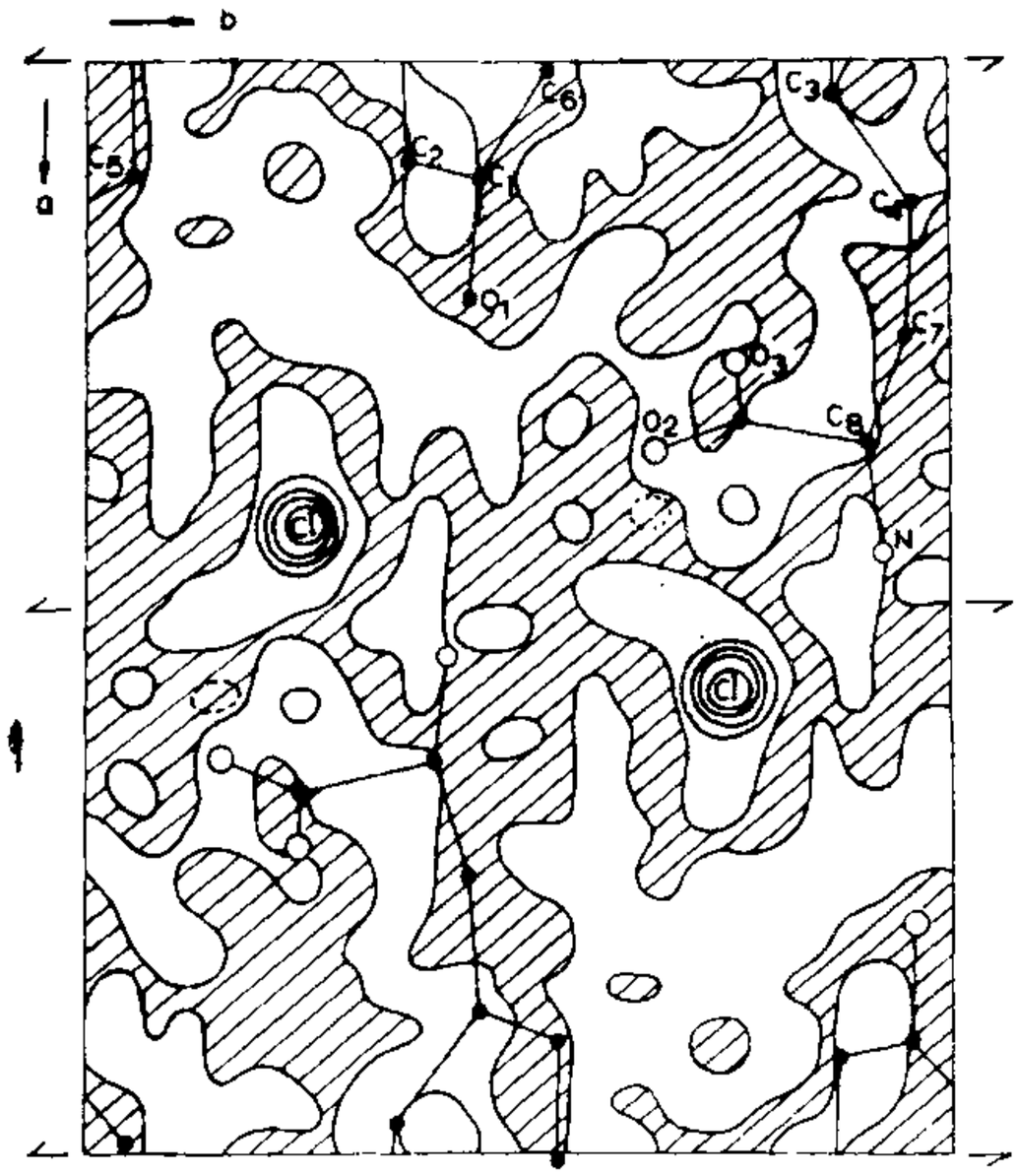

FIG. 2. ρ_I-map for L-tyrosine hydrochloride projected down the c-axis.

Detailed test of these ideas on more accurate structures are in progress and will be reported in due course.

1. Peederman, A. F. and Bijvoet, J. M., *Acta Cryst.*, 1956, **9**, 1012.
2. Ramachandran, G. N. and Ramnn, S., *Curr. Sci.* (India), 1957, **25**, 348.
3. Pepinsky, R. and Okaya, Y., *Proc. Nat Acad. Sci., U.S.*, 1956 **42**, 286.
4. Patterson, A. L., *Acta Cryst.*, 1963, **16**, 1255
5. Ibers, J. A. and Hamilton, W. C., *Ibid.*, 1964, **17**, 781.
6. Zachariasen, W. H., *Ibid.*, 1965, **18**, 714.
7. Marezio, M., *Ibid.*, 1965, **19**, 396.
8. Parthasarathy, R., *Ph.D. Thesis*, University of Madras, 1962
9. Srinivasan, R., *Proc. Ind. Acad. Sci.*, 1959, **50 A**, 19.