NON-APPROXIMATE ANALYSIS OF EXPERIMENTAL STRUCTURE AMPLITUDES

I. Method

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1. Introduction

During the last few years, X-ray intensity measurements have been made with greater accuracy than before for the determination of the structure amplitudes of crystals, and this has created an obvious need for mathematical methods of analysis elaborated in such a manner that the improved accuracy benefits the interpretation of the measurements. However, it is unavoidable even in the very best experiments that the sequence of measured structure amplitudes breaks off at a rather early point because the wave length of the radiation employed in the experiments sets a limit in this respect. In consequence, the residual-term problem has become critically significant in highly accurate analyses.

In connection with our previous work [8] we observed that the method for calculating atomic scattering factors discussed there presents opportunities for a critical consideration of the residual-term question. A method of analysis utilizing these opportunities would therefore imply an improvement in the analysis refinement technique, particularly as regards the reliability of the results. At the same time its application would throw further light on the general question what kind of information one may expect to derive from X-ray scattering measurements on crystals.

In some simple cases, calculations of atomic scattering factors of the said kind have already been made [5, 6, 7], but no attention has been paid to these general possibilities. The purpose of the present work is to carry out an analysis of the said kind as completely as possible, starting with the situation that the phase problem has already been solved for all measured reflections. For our object we have chosen the trigonal $NaNO_3$ crystal, for which the high-grade measurement values of INKINEN [3] are available, which have not so far been analysed in greater detail.

It goes without saying that the task is an extensive one and that a great number of questions of different character must be considered. It should be understood that our purpose is, on the one hand, to present and elaborate the method, on the other to find tangible physical results for the $NaNO_3$ crystal. The highest achievable accuracy of analysis, which is our goal, further requires that special attention be paid to the effects of the different kinds of potential error occurring in the experimental values.

It is obvious that such a presentation renders the material quite bulky and unwieldy, and we are therefore compelled to divide its treatment into several parts. In this first part we mainly concern ourselves with matters of principle and outline the programme for the analysis. It is only natural that this presentation has points of contact with the preceding paper [8], where the calculation of the atomic scattering factor, which constitutes the essential substance of the method, has been dealt with in greater detail, and where several references relating to these points can be found.

2. The Non-approximate Methods of Treatment

The first requirement to be imposed on the performance of an accurate analysis on the basis of given experimental values is that the operations applied delete none of the information that may be contained in the experimental material, and add nothing extraneous. Of this we can be positive only if we avoid all kinds of approximation and employ exclusively methods of calculation in which the measured values as such are used.

This fundamental condition is not satisfied, for instance, if one employs graphical or analytical means to find simple atomic scattering factor functions that show the best possible fit with the experimental values, and substitute them for the actual measured values in the analysis. An accurate analysis by such means absolutely requires complementation by an analysis of the differences between the measured values and their approximations, and at this stage at least recourse must be had to non-approximate methods (cf. e.g. [2]).

As we have at our disposal the measured structure amplitudes F_{h_ν} of the crystal, we may, in our pursuit of this principle, make use of the Fourier series

$$(1) \qquad \varrho\,(\mathbf{r}) = \frac{1}{V_0} \sum_\nu F_{h_\nu}\, e^{-2\pi i\, \mathbf{h}_\nu \cdot \mathbf{r}}\,,$$

which represents the electron distribution density in the crystal, and of the series derived from it,

$$(2) \qquad f_T\,(\mathbf{h}) = \frac{1}{V_0} \sum_\nu F_{h_\nu}\, \sigma_T\,(\mathbf{h} - \mathbf{h}_\nu)\,,$$

which represents the structure amplitude of the region T separated from the distribution (1), [8], and in which σ_T is the so-called shape transform of the region T:

$$\sigma_T\,(\mathbf{h}) = \int_T e^{2\pi i\, \mathbf{h} \cdot \mathbf{r}}\, d\tau_\mathbf{r}\,.$$

Obviously, we may also use some theoretical model and calculate the corresponding difference series,

(1a)
$$\Delta\varrho(\mathbf{r}) = \frac{1}{V_0} \sum_{\nu}' (F - F_{theor}) \, e^{-2\pi i \, \mathbf{h}_\nu \cdot \mathbf{r}}$$

(2a)
$$\Delta f_T(\mathbf{h}) = \frac{1}{V_0} \sum_{\nu} (F - F_{theor}) \, \sigma_T(\mathbf{h} - \mathbf{h}_\nu) \, ,$$

which represent the deviation of the said quantities from the respective quantities consistent with the model.

Of course, the Fourier series and its uses require no detailed presentation. The series (2) is rendered useful in the present instance by the fact that, by an appropriate choice of region, we can make it represent the atomic scattering factor of a given atom in the crystal (or the structure amplitude of a group of atoms). The only condition for this is that the region T separates the atom in question from its surroundings [8 : § 13]. It is true that there are cases in which regional separation of an atom is not possible, but as a rule this problem presents no unsurmountable difficulties. If we take for each atom the respective, clearly distinguished distribution peak, (2a) reveals the manner in which the atom differs from the theoretical atom in respect of this, its principal contribution. This contribution also contains practically everything that can be said of the atom as an independent particle on the strength of the measured values.

3. On the Treatment of the Residual Term

When the series (1) and (2) are used, the reliability of the results is only dependent on how completely the coefficients $F_{\mathbf{h}_\nu}$ have been obtained from the measurements. The sequence of coefficients mostly breaks off at such an early point that the residual terms of the series are of considerable magnitude. As always, the estimation of them therefore constitutes a central problem in the structure analysis. As a matter of fact, if the residual term were entirely neglected, the analysis in its entirety would only amount to an interpretation of the calculated values of these series. The ultimate significance of the formulation of our method is indeed only that we try to find the most advantageous mode of treatment for this problem.

We may specify the principle to be used in our estimation of the residual term as follows:

1) to find a reasonable continuation for the sequence of measured structure amplitudes,

2) to determine the limits within which this continuation can be varied without loss of its reasonability.

The successful accomplishment of both parts of this programme would obviously be equivalent to a solution of the entire residual-term problem.

However, the concept of »reasonability» leaves fairly much room for interpretation. In principle it should include all that is known *a priori* about the crystal. From our point of view, its most essential content is expressed by the following statement: The crystal contains certain atoms, the general trend of whose scattering factors is known in advance with greater or smaller accuracy, as the case may be. We can construct residual terms satisfying this condition by the aid of model crystals, that is, by calculating the structure amplitudes of a crystal consisting of atoms with theoretical scattering factors varying in the known manner.

Our chances to find a reasonable continuation by this procedure are chiefly based on two important characteristics of the Fourier series and Fourier integrals, namely:

1) their convergence is local, that is, convergence in a given point or region is only dependent on the characteristics in this point or region of the function they are required to represent;

2) the rate of convergence is higher the greater the regularity of the function at the point in question. In other words, the sequence of Fourier coefficients, or the Fourier transform, of a regular and gently changing function shows rapid decrease with increasing $|\mathbf{h}|$.

According to these observations, the convergence is slowest at the distribution peaks corresponding to the different atoms, and it is fast in the region between such peaks (cf. [8 : § *14*]). This implies that the residual term is mainly composed of the contributions from the different atoms, and, unless the sequence is broken off too early, the distribution that may exist in the intervening space furnishes a negligible contribution.

Inversely, the contribution of each atom to the residual term carries significance only with respect to that atom itself, particularly so when difference series are used, in which case the greatest concern over the interior parts of the atoms with their slow convergence is eliminated. This renders the contributions of the different atoms to the coefficients independent in the sense that we may treat each of them separately, and we are fully justified in speaking of the reasonability of the continuation for each atom separately. Within practical limits of accuracy it is therefore correct to say that the continuation provided by a given model is reasonable if it is reasonable for each atom separately. If we manage to find a reasonable continuation for the contribution of each atom to the structure amplitudes, and if we are able to control the possible variations of each contribution within the scope of reasonability, we shall have accomplished the programme outlined above.

4. The Correct Model

The contribution of a single atom to the structure amplitude is constituted by the scattering factor of that atom, taken at the respective points h, and multiplied by the exponential factor corresponding to the location of its centre. The requirement of reasonability of the continuation desired for the sequence of measured structure amplitudes, with respect to a given atom, therefore implies that the location of the centre of the atom is known and that the atomic scattering factor of the model provides a reasonable continuation of the true atomic scattering factor beyond the point at which the series break off.

Once more we can refer to the general convergence properties stated in the preceding section. According to these, the contribution due to the interior parts of the atom is decisive in the atomic scattering factor with high values of $|h|$ (cf. [8 : § 15]). We have reason to believe that the available theoretical atomic scattering factors have their best validity as regards these very parts. At least it is a generally accepted opinion that quantal calculation of the electron distribution gives a reliable picture of the complete inner electron shells (cf. e.g. [1 : 1.9]), and at the same time deformations caused by the crystal environment may be expected in the interior parts least of all. If the model atom has the same state of motion as the interior part of the real atom, its scattering factor can be considered correct at high values of $|h|$ and may be written $f = f_{theor} + \Delta f$, where Δf rapidly decreases to a negligible magnitude in comparison with f_{theor}.

There is then, obviously, a »correct crystal model», in which each atom has its correct location and state of motion. The actual structure amplitudes deviate from those consistent with the correct model, in respect of each atom, only by the contribution Δf of this atom, and this contribution is therefore solely responsible for the fact that the residual term of the correct model with respect to the atom in question is different from the true residual term. If the deformations of the atom are slight, so that its Δf is negligible from the break-off point onwards, we may consider the residual term consistent with the correct model to be correct as regards this atom. If, on the other hand, Δf is still appreciable in magnitude at the break-off point, the residual term of the correct model must be improved by the contribution of it in order to be correct. As the quantities Δf are rapidly decreasing functions at all events, they make only a small contribution to the residual term, and the correct model always supplies the main part of the residual term. Its determination will therefore be the first important step in the analysis.

It is clearly of importance to specify what is understood by a rapid decrease of Δf, as the position of the break-off point in relation to the

decrease of Δf enters our considerations as a most essential point. As yet little experience is at hand in this question. According to an analysis [7] carried out on the basis of VIHINEN's [9] measurements, $\frac{\sin \Theta}{\lambda} = \frac{1}{2} |\mathbf{h}| =$ 0.6 Å^{-1} seems, in the case of the NaCl crystal, to be the limit where the effects of the deformations cease and from which onwards the theoretical atomic scattering factors coincide with the experimental values. However, as this is obviously a case of slight deformations, caution is indicated in applying the principles presented to series of measurements extending that far, or to shorter series. (INKINEN's series of measurements on NaNO$_3$, which constitutes the object of our study, breaks off at $\frac{\sin \Theta}{\lambda} = 0.62$ Å^{-1}, which is also the practical upper limit for work done with Cu radiation ($1/\lambda \approx$ 0.648 Å^{-1}).)

5. Determination of the Correct Model

So far we have only established the existence in principle of the correct model. This model must be found if the analysis is to be carried out. We start with the assumption that some kind of approximate model is already available for the crystal in question. In actual practice this implies no additional assumption beyond that made at the outset, namely that the phase problem has been solved for the measured reflections. (In the case of the NaNO$_3$ crystal in hand, the theoretical model used by INKINEN [3] serves excellently as such a starting point.) We may then appropriately use in our calculations the difference series with the coefficients $F_{\mathrm{exp}} - F_{\mathrm{theor}}$; the break-off error in the results will then be the same as the difference between the true residual term and that consistent with the model, and according to section 3 it is in principle divisible into contributions from the different atoms. It is also assumed that the theoretical atoms employed are well consistent with the facts as regards the inner electron shells; the considerations in section 4 are then valid.

In compliance with our presentation, the factors responsible for the deviation of the experimental values from the model can now be broadly classified as follows: errors in atom location, errors in state of motion, atom deformations, and interatomic distributions (and, of course, experimental errors, to which no attention is paid in this connection). Determination of the correct model is conditional on our being able to isolate the two first-mentioned factors from the others and to compensate for them.

The Fourier series offers the most straightforward means of adjustment of the atom loci, and the procedures by which it is applied are generally

known. We wish to select and use a criterion on which the other factors exert the least possible influence. It seems natural to direct our attention to the distribution maximum point itself, which corresponds to the centre of the atom. In actual fact this is our sole choice if we want to avoid as completely as possible also the effects of the asymmetric deformations of the atom itself on the result. We may then specify the condition that the maximum points in the experimental and theoretical truncated Fourier series coincide or, what is equivalent, that the difference series is symmetric in the immediate vicinity of this point.

Separation of the effects of the state of motion and deformations can be based on the foregoing considerations. The method applied there, according to which each atom (or, more accurately, each atomic scattering factor) is treated separately, can only be realized by using the series (2) and studying the different atomic scattering factors by means of it. It should be noted that the treatment of the atomic scattering factors is rendered rather well practicable by the fact that they are regular and nearly spherically symmetric functions, and it is sufficient to calculate their values in rather few points to obtain a good idea of their character. The effects of deformations and of the state of motion on the atomic scattering factor are different in principle, and it can be said as a general observation that the two factors can be separated on this basis with such accuracy as can be achieved at all with a given experimental material. In principle, a separation of the two factors has already been made by the division $f = f_{\text{theor}} + \Delta f$. Unless the deformation is a very heavy one, Δf decreases to a negligible magnitude before the break-off point. This gives us a criterion for the determination of the thermal motion: the state of motion of the atom has been correctly assessed when the calculated Δf_T of that atom decreases to zero in a regular manner before the break-off point is reached (cf. [4]); Δf_T itself will then represent the deformation of the atom in question (i.e., $\Delta f_T = \Delta f$).

In our attempt to determine the state of motion by means of the series (2) it is obviously most important of all that the considered region T specifically includes the interior part of the atom; it cannot be very significant whether one has succeeded in enclosing in this region the entire distribution belonging to the atom.

Furthermore, a study of the distribution by the aid of the Fourier series provides a useful check of the state of motion. As we do not expect any heavy deformations in the interior parts of the atom, the model should there give a picture of the distribution consistent with that obtained experimentally if the state of motion is correct.

The accuracy with which we require the criteria for the determination of the state of motion to be valid for each atom is to some degree a matter of choice. If, in the atom, deformation of considerable magnitude seems

possible, we shall have to permit larger deviations of its Δf_T from the criterion. However, the calculated Δf_T itself always provides at least a qualitative basis for an estimation of the order of magnitude of the deformations because it approximately represents them, and on this basis we may set up the limits within which the true Δf function of the atom is to be found. The choice of the state of motion must be such that the Δf_T calculated on this assumption remains within the said limits. In this manner we find a corresponding set of limits bracketing the state of motion, and this is the closest we can get to a determination of the states of motion from the experimental material at hand.

The error of the residual term in the Δf_T values calculated on the basis of different states of motion does not actually produce any error in such an estimate of the state of motion. We know that when the correct model is used for the atom, the break-off error in its Δf_T is due only to the Δf of the atom, and it is small so that $\Delta f_T \approx \Delta f$. When now, on variation of the state of motion, Δf_T runs through the permissible range, it must also necessarily coincide with the correct function $\Delta f_T = \Delta f$ for a particular state of motion, which is the correct one. But after all, the choice of model is affected by the break-off errors in a certain manner. If the Δf_T curves calculated with different motion parameters are compared with each other, it is found that the change of the state of motion affects them close to the break-off point considerably less than it affects the f_{theor} values. This is specifically due to the effect of the break-off errors; it is seen that they reduce in this manner the sensitivity of the determination of the state of motion and compel us to set wider limits for the correct state of motion.

The completed determination of the correct model implies that we have at our disposal residual terms for the series (1) and (2). Now we can obviously continue the analysis since we may calculate values of these series as required and interpret them. When the model is varied within the limits found for it, the residual terms of the series vary within corresponding limits, which essentially determine the possible accuracy of all results. The correct residual term has little chance to fall outside the limits within which the residual term consistent with the model may vary, but the highest attainable accuracy of the analysis requires that attention be paid to the possibility however little reason there may seem to be for it. Heavy deformations, and distributions in the interatomic space, may possibly give rise to an extra break-off error in their own region and its immediate neighbourhood (for instance, in the $NaNO_3$ crystal under consideration we may expect in connection with the NO_3 group the possible existence of distributions whose effect must not be neglected in the residual term). For the assessment of their effect there is nothing to fall back upon but the data obtained through the analysis, concerning the magnitude and shape of the deforma-

tions and of the interatomic distributions. They can hardly have any influence on the choice of model beyond that already taken into account in the scrutiny of the validity of the state-of-motion criterion. If we adhere scrupulously to the general programme for the estimation of the residual term outlined in section 3, we are bound to admit that because of these factors the continuation of the correct model may join the measured values with a discontinuity; if the discontinuity is great enough not to be masked by the experimental errors, it is an indisputable defect in respect of the »reasonability» of the continuation provided by the correct model, and requires to be rectified. We shall have occasion later to return to this question.

Summary

For the detailed non-approximate analysis of the electron distribution in crystals a method is suggested which is based partially on the Fourier series (1) representing the density of distribution, and partially on the series (2) representing the structure amplitude of a region T separated from it, or on the corresponding difference series (1a), (2a).

It is concluded on the strength of the properties of Fourier series and Fourier integrals that

— treatment of the residual term can be carried out for each atom separately;

— there is a »correct model», the residual term consistent with it constituting the main part of the correct residual term.

In determining the correct model, adjustment of the centres, when necessary, will be made by the aid of the Fourier series; otherwise mainly the series (2) will be used. By means of it the differences Δf_T between the experimental atomic scattering factors and those consistent with the model will be calculated and the states of motion determined so as to make these quantities decrease smoothly to zero before the break-off point is reached. However, deviations from this rule have to be permitted, depending on the degree of deformation of the atom, the calculated Δf_T itself furnishing a certain possibility of assessing this deformation. The Fourier series may be employed as a check.

The model found in this manner will be employed in the analysis, and the possibilities of variation of the model within the limits found for it will essentially determine the accuracy of all results. Some additional, local inaccuracy in the residual term may arise from heavy deformations and interatomic distributions.

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