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Abstract

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ON THE NORMALIZATION OF THE INTENSITY CURVE IN THE RADIAL DISTRIBUTION METHOD

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As is known, inversion of the intensity curve $I(s)$ for the scattering of X-rays or electrons by gases, amorphous and liquid bodies by means of the Fourier integral gives the radial distribution function in the object under study (see, for example, (^{1})). Normalization of $I(s)$ makes it possible to consider not only the positions, but also the weights of the peaks of the radial distribution function, i.e., ultimately to find the number of nearest neighbors of a given atom.

Owing to the great difficulties of measuring the absolute intensity, the normalization of $I(s)$ to the scattering by some group of n atoms is performed by using the damping of the oscillations of $I(s)$ at large s, when

$$I_n(s) \approx \sum_{i=1}^{n} f_i^2(s). \tag{1}$$

Here $f_i(s)$ is the atomic scattering factor. The use of (1) is based on the fact that, for large s, interference effects in scattering by an aggregation of atoms are small, and, in a certain approximation, it may be assumed that the object scatters as a collection of the same atoms, but isolated and situated at a large distance from one another (“gas scattering”).

Normalization according to condition (1) has the following drawbacks: (a) neglect of the nevertheless present effects of oscillations of $I(s)$ at large s, which may give some absolute error, and (b) the smallness of the values of $I(s)$ at large s, which increases the relative error of the normalization.

For normalization, a possible way is to use the curve $I(s)$ as a whole. If the distribution of scattering matter in the object is $\rho(\mathbf{r})^*$, then the intensity is determined by means of the Fourier integral as the square of the modulus of the amplitude:

$$I(s) = |f(s)|^2 = \left| \int \rho(\mathbf{r})\, e^{-i(\mathbf{sr})}\, dv_r \right|^2 . \tag{2}$$

Fig. 1. Oscillations of the curve $I_n(s)s^2$ (2) about the curve $\sum_{i=1}^{n} f_i^2(s)s^2$ (1)

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The functions $f(s)$ and $\rho(r)$ are related by the completeness condition for the Fourier integral:

$$\int |\rho(\mathbf{r})|^2 \, dv_r = \frac{1}{8\pi^3} \int |f(s)|^2 \, dv_s, \tag{3}$$

where the integral on the left is taken over the entire volume of the object, and that on the right over the entire volume of reciprocal space.

* The consideration carried out is general for all three diffraction methods: X-ray diffraction, electron diffraction, and neutron diffraction. Accordingly, by $\rho(\mathbf{r})$ in these three cases one should understand the electron density, the electrostatic potential, and the nuclear scattering power of the object as a whole; by $\rho_i(\mathbf{r})$, that of an individual atom; and by $f_i(s)$, the corresponding atomic scattering factor.

Condition (3) is valid for the object as a whole, and also for each of the atoms comprising it:

$$4\pi \int_0^\infty \rho_i(r)\, r^2 \, dr = \frac{1}{2\pi^2} \int_0^\infty f_i^2(s)\, s^2 \, ds = G_i. \tag{4}$$

This expression is written no longer in Cartesian, but in spherical coordinates. Since the object is a collection of atoms, and taking into account also that $\rho(r)$ is everywhere real and positive and assumes large values only in atoms, instead of the left-hand side of (3) one may write

$$\int |\rho(r)|^2 \, dv_r = \sum_i \int \rho_i^2(r) \, dv_r. \tag{5}$$

Fig. 1. Oscillations of the curve $I_n(s)s^2$ (2) about the curve $\sum\limits_{i=1}^{n} f_i^2(s)s^2$ (1)

Using now (4) and expressing (2) likewise in spherical coordinates (for the class under consideration, the object $I(s)$ is spherically symmetric owing to statistical averaging), we obtain

$$\int_0^\infty I_n(s)\, s^2 \, ds = \sum_{i=1}^{n} \int_0^\infty f_i^2(s)\, s^2 \, ds = 2\pi^2 \sum_{i=1}^{n} G_i. \tag{6}$$

This is the normalization condition, since the sum on the right can be calculated. The physical meaning of expression (6) is that the interference that occurs for a certain mutual arrangement of atoms cannot change the total scattering intensity by these atoms, but only redistributes the intensity (the discussion is, of course, of coherent scattering; incoherent scattering will also be taken into account below). Thus, the curve $I_n(s)s^2$ oscillates about the curve $\sum_{i=1}^{n} f_i^2(s)s^2$; the areas under both curves are equal, and the areas bounded by them above and below the curve $\sum_{i=1}^{n} f_i^2(s)s^2$ are also equal (Fig. 1).* It also follows from (6) that, on the average over a sufficiently wide interval (s_1, s_2),

$$\overline{I_n(s)s^2} = \overline{\sum_{n} f_i^2(s)s^2} \tag{7}$$

or, less rigorously, that

$$\overline{I(s)} \approx \sum_{i=1}^{n} f_i^2(s). \tag{8}$$

At large s, when the oscillation of $I(s)$ is small, this gives (1). Statistical relations of type (8) are known in structural analysis of crystals ([2]); the analogous expression (6) in the case of crystals contains on the left a sum of the squares of the structure factors ([3]). We, however, consider the case of a continuous distribution of intensity. If the object consists of crystalline and amorphous phases, its total intensity is likewise determined by the general expression (6).

In practice, (6) can be applied not in the ideal limits $s = 0$ and $s = \infty$, but for some small $s' \approx 0$ and limiting s'' (Fig. 1). For this it is necessary, within the same limits, to find (by numerical or graphical integration) from the theoretical curves the right-hand side of (6), to find in the same way from the experimental (unnormalized) values $I(s)$ the magnitude of the left-hand side of (6), and to equate it to the computed value of the right-hand side, thus obtaining $I_n(s)$.

The natural procedure is normalization to n atoms (of one or several kinds) entering into the molecule or chemical formula of the given substance. Then the radial distribution function constructed from $I_n(s)$ will be a superposition of the distributions of all atoms of the object around each of the selected n atoms.

In the investigation of amorphous and liquid bodies, as well as gases, the thermal motion of atoms is seldom taken into account. If this is done, the atomic factor $f_i(s)$ in (6) must be replaced by the atom-temperature factor $f_{iT} = f_i f_T$, where

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* The characteristic factor s^2 is present everywhere because, when intensity values are summed over all reciprocal space, the volume element with a constant value of $I(s)$ inside it is a spherical shell of volume $4\pi s^2 ds$.

the value of the temperature multiplier $f_T = \exp[-B(\sin\theta/\lambda)^2]$ is determined by the choice of the thermal-motion parameter B.

The quantities G_i (4) entering into (6) are constant for each kind of atom. It was shown earlier that in X-ray diffraction (^{3}) and electron diffraction (^{4}) there is a dependence of the form

$$G_i = kZ_i^{\alpha}q, \tag{9}$$

where k and α are numerical parameters depending on the value of B; Z is the atomic number, and the factor q accounts for truncation.

Thus, if thermal motion is taken into account and the data on k, α, and q (^{3,4}) are used, the normalization (6) can be carried out without calculating the integrals (4). If thermal motion is not taken into account, the integrals (4) converge poorly, and the rigorous expressions (4), (6) are replaced by integration over finite limits s' and s'' (see Fig. 1).

Equation (6) was written without taking incoherent scattering I_{H} into account. Taking it into account,

$$\int_0^\infty (I_{\text{K}} + I_{\text{H}})_n s^2\,ds = 2\pi^2 \sum_{i=1}^n G_i + \sum_{i=1}^n \int_0^\infty I_{\text{H}i}(s) s^2\,ds, \tag{10}$$

where $I_{\text{H}i}$ is the incoherent scattering by atom i, calculated in a known way (see, for example, (^{1,5})). Thus, in this case as well, the intensity can be normalized and then the fraction of coherent scattering (6) can be separated from it. We note that in electron-diffraction investigations I_{H} is small, and it can often be neglected.

When constructing the radial distribution function $u(r)$, what is substituted into the Fourier integral is not $I_n(s)$ directly, but the function

$$i(s) = \left[I_n(s) - \sum_{i=1}^n f_i^2(s) \right] / f_{\text{ed}}^2(s), \tag{11}$$

so that

$$4\pi r^2 u(r) = 4\pi r^2 u_0 + \frac{2r^2}{\pi} \int_0^\infty i(s) s^2 \frac{\sin sr}{sr}\,ds. \tag{12}$$

Subtracting $\sum f_i^2(s)$ in (11) removes the trivial zero peak of the function $u(r)$ at $r = 0$. It is easy to see that the normalization (6) automatically ensures the equality $u(r) = 0$. Division by the unit curve $f_{\text{ed}}^2(s)$, chosen in a definite way, leads, as is known, to a "sharpening" of the peaks of $u(r)$. In the case of sufficiently sharp oscillation, $I(s)$ makes it possible to determine, not without hope, the form of the curve $f_{\text{ed}}^2(s) \sim \sum_{i=1}^n f_i^2(s)$ from experiment on the basis of conditions (6) and (7) (see Fig. 1), without invoking theoretical data.

The proposed normalization method was used and gave positive results in an electron-diffraction study of amorphous antimony trisulfide.

In conclusion, let us dwell on one more property of the normalized quantities $I_n(s)s^2$, which may prove useful in analyzing the structure of molecules in vapors and gases, when calculated and experimental intensity values are compared. For any correct or erroneous model A, B, ⋯etc., the calculated intensity values obey condition (6):

$$\int I_{n_A}(s)s^2\,ds = \int I_{n_B}(s)s^2\,ds = \ldots = \int I_{n_{\text{exp}}}(s)s^2\,ds = 2\pi^2 \sum_{i=1}^{n} G_i, \tag{13}$$

i.e., the total intensity does not depend on the arrangement of the atoms. But the expression

$$\int (I_{n_{\text{exp}}} - I_{n_{\text{calc}}})s^2\,ds, \tag{14}$$

whose minimum will correspond to the best model, may serve as a criterion of the correctness of the solution. The ideal case in which (14) is equal to zero is practically unattainable because of experimental errors (in determining I_{exp}) and the imperfection of the theory (in calculating I_{calc}). Division of (14) by (13) will give a coefficient that can characterize the quality of the investigation; to some extent this coefficient resembles the so-called reliability factor in the structural analysis of crystals.

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References Cited

[1] R. James, *The Optical Principles of the Diffraction of X-rays*, IL, 1950, Chap. IX.
[2] A. J. G. Wilson, *Acta Crystallogr.*, **2**, 318 (1949).
[3] B. K. Vainshtein, *DAN*, **93**, 821 (1953); *ZhETF*, **27**, 44 (1954).
[4] B. K. Vainshtein, *Crystallography*, **1**, 495 (1956).
[5] Z. G. Pinsker, *Electron Diffraction*, Publishing House of the USSR Academy of Sciences, 1949, Chap. XI.

Note: Figure translations are in progress. See original paper for figures.

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