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GENERAL LATTICE HARMONIC EXPANSIONS FOR CRYSTAL ATOMIC FACTORS

BY

K. KURKI-SUONIO

Department of Physics
University of Helsinki
Helsinki, Finland

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Abstract

General expressions are derived for series, which make possible the direct calculation of different terms in harmonic expansions of the electron density and scattering factor of a crystal atom from experimental structure amplitudes in any symmetry. The formulas are of the same general form as those derived earlier for tetrahedral symmetry.

Introduction

Recently the author has pointed out that harmonic expansions of electron densities and scattering factors form, for both physical and mathematical reasons, the most natural means for treating single atoms in crystallographic problems [5]. This is also demonstrated by DAWSON in a set of papers [4]. Special attention has been paid to cubic and tetrahedral symmetries, where the cubic harmonics of VON DER LAGE and BETHE [8] are the basic harmonics of the expansion. In ref. [5] formulas were derived for calculation of such expansions for a spherical region of a crystal using experimental structure amplitudes. Also the corresponding series for the electron density, of the type first presented by ATOJI [3], were given for this special case. In a subsequent study [6] it was shown that the former series makes possible a reliable extraction of the information concerning atomic deformations from experimental data.

The derivation of the formulas in ref. [5] was based on the spherical wave expansion of the exponential in the Fourier series of the electron density. Cubic symmetrization was applied to change the basic spherical harmonics into cubic harmonics. This process was carried through explicitly for the ten lowest orders, each containing at most one linearly independent harmonic. A similar procedure is possible in any symmetry, though it may be rather tedious. Further, it is not immediately clear from such a derivation whether the result will be of the same general form also in orders where several independent harmonics exist. Also the relation of the harmonics K_n to the constants C_n occurring in the formulas of reference [5] is not obvious.

In this paper we give a general derivation, which is applicable to any set of harmonics in any order. The result shows that the form of the expressions given in ref. [5] is, in fact, quite general. Also the meaning of the constants C_n will turn out to be quite simple, and it will allow a straightforward calculation of their numerical values for any harmonics.

The derivation of the formulas

We start by treating a single atom, with the electron density

$$\varrho(\mathbf{r}) = \int f(\mathbf{b}) e^{-2\pi i \mathbf{b}\cdot\mathbf{r}} d^3b \tag{1}$$

and with the scattering factor

$$f(\mathbf{b}) = \int \varrho(\mathbf{r}) e^{2\pi i \mathbf{b}\cdot\mathbf{r}} d^3r \,. \tag{2}$$

Suppose the atom is in a field with a certain symmetry. Both the electron density and the scattering factor can then be expressed as harmonic expansions

$$\varrho(\mathbf{r}) = \sum_{n\alpha} \varrho_{n\alpha}(r) K_{n\alpha}(\theta\,,\varphi)\,, \tag{3}$$

$$f(\mathbf{b}) = \sum_{n\alpha} f_{n\alpha}(b) K_{n\alpha}(u\,,v)\,, \tag{4}$$

where the functions $K_{n\alpha}$ form a complete orthogonal set of harmonics adapted to this symmetry, e.g. the cubic harmonics of VON DER LAGE and BETHE [8] or, more generally, the lattice harmonics treated by ALTMANN and BRADLEY [1] and ALTMANN and CRACKNELL [2]. The index n is the order of the harmonic (or the angular momentum quantum number) and α runs through all independent harmonics of the same order. Further, $r\,,\theta\,,\ \varphi$ and $b\,,\ u\,,\ v$ are the spherical coordinates of the vectors $\mathbf{r}$ and $\mathbf{b}$ respectively.

As stated in ref. [5], all harmonics are Fourier invariant,

$$\int_{(4\pi)} K_{n\alpha}(\theta\,,\varphi) e^{2\pi i \mathbf{b}\cdot\mathbf{r}} d\Omega = 4\pi i^n j_n(2\pi br) K_{n\alpha}(u\,,v)\,, \tag{5}$$

where j_n is the spherical Bessel function of order n and $d\Omega = \sin\theta d\theta d\varphi$. Hence, if we apply the transformations (1) and (2) to the series (3) and (4), we find that each term of one is transformed into the corresponding term of the other, and the radial functions $\varrho_{n\alpha}\,, f_{n\alpha}$ are related by the Fourier-Bessel transformation

$$\varrho_{n\alpha}(r) = 4\pi(-\,i)^n \int_0^\infty f_{n\alpha}(b) j_n(2\pi rb) b^2 db\,, \tag{6}$$

$$f_{n\alpha}(b) = 4\pi i^n \int_0^\infty \varrho_{n\alpha}(r) j_n(2\pi br) r^2 dr \,. \tag{7}$$

We can also write for them the familiar expression of the coefficients of an orthogonal series:

$$\varrho_{n\alpha}(r) = \frac{1}{A_{n\alpha}} \int_{(4\pi)} K^*_{n\alpha}(\theta\,,\varphi) \varrho(\mathbf{r}) d\Omega_{\mathbf{r}}\,, \tag{8}$$

$$f_{n\alpha}(b) = \frac{1}{A_{n\alpha}} \int_{(4\pi)} K^*_{n\alpha}(\theta\,,\varphi) f(\mathbf{b}) d\Omega_{\mathbf{b}}\,, \tag{9}$$

where K^* is the complex conjugate of K, also a harmonic function, and

$$A_{n\alpha} = \int_{(4\pi)} K^*_{n\alpha} K_{n\alpha} d\Omega \,. \tag{10}$$

Now the first problem is to find an integral representation of $\varrho_{n\alpha}$ in terms of $f(\mathbf{b})$. The second problem is to separate from $\varrho(\mathbf{r})$ a spherical region centered at the origin and to express its scattering factor component $f_{n\alpha}(b\,;R)$ also as an integral in terms of the original scattering factor $f(\mathbf{b})$ of the total electron density. The answer to the first question is obtained if we insert the Fourier integral (1) for $\varrho(\mathbf{r})$ in eq. (8) and apply the Fourier invariance theorem (5) of harmonic functions to K^*. This yields

$$\varrho_{n\alpha}(r) = \frac{4\pi(-i)^n}{A_{n\alpha}} \int f(\mathbf{b}) j_n(2\pi br) K^*_{n\alpha}(u\,,v)\, d^3b \,. \tag{11}$$

Similarly, from eq. (9) we get for $f_{n\alpha}$ the real space representation

$$f_{n\alpha}(b) = \frac{4\pi i^n}{A_{n\alpha}} \int \varrho(\mathbf{r}) j_n(2\pi br) K^*_{n\alpha}(\theta\,,\varphi) d^3r \,. \tag{12}$$

The second problem is solved simply by the transformation rule (7). We just have to substitute for $\varrho_{n\alpha}$ the function (11) inside the sphere, and zero outside. Thus we get

$$f_{n\alpha}(b\,;R) = \frac{(4\pi)^2}{A_{n\alpha}} \int_0^R r^2 dr \int d^3b' f(\mathbf{b}') K^*_{n\alpha}(u'\,,v') j_n(2\pi b'r) j_n(2\pi br)\,,$$

or performing the r-integration [7],

$$f_{n\alpha}(b\,;R) = \frac{(4\pi)^2 R^3}{A_{n\alpha}} \int f(\mathbf{b}') K^*_{n\alpha}(u'\,,v') \frac{x j_{n+1}(x) j_n(y) - y j_{n+1}(y) j_n(x)}{x^2 - y^2}\, d^3b' \tag{13}$$

where $x = 2\pi Rb$ and $y = 2\pi Rb'$. The equations (11) and (13) are general results, corresponding to the series found in ref. [5] for one special case.

Finally, to make these formulas applicable to crystal analysis, we must take for $\varrho(\mathbf{r})$ the electron density of a crystal, i.e. a triply periodic function extending to infinity. As is well known, the scattering factor for such an electron density is an infinite pattern of Dirac deltas. If we use the natural dimensionless δ-function defined by

$$\int \varphi(\mathbf{b})\delta(\mathbf{b} - \mathbf{b}_0)d^3b = V^*\varphi(\mathbf{b}_0) \quad \text{for any} \quad \varphi(\mathbf{b}) \, ,$$

where $V^* = \frac{1}{V}$ is the unit volume of $\mathbf{b}$-space, we can write

$$f(\mathbf{b}) = \sum_j F_j \delta(\mathbf{b} - \mathbf{b}_j) \, ,$$

where the summation runs over all reciprocal lattice points $\mathbf{b}_j$ and F_j is the structure amplitude of the crystal.

Any integral including f will now be changed into a sum over reciprocal lattice points. Thus, the Fourier integral (1) becomes the Fourier series

$$\varrho(\mathbf{r}) = \frac{1}{V} \sum_j F_j e^{-2\pi i \mathbf{b}_j \cdot \mathbf{r}} \, .$$

Integral (11) is now changed into the series

$$\varrho_{n\alpha}(r) = \frac{4\pi(-i)^n}{VA_{n\alpha}} \sum_j F_j j_n(2\pi b_j r) K^*_{n\alpha}(u_j \, , v_j) \, , \tag{14}$$

and (13) into

$$f_{n\alpha}(b \, ; R) = \frac{(4\pi)^2 R^3}{VA_{n\alpha}} \sum_j F_j K^*_{n\alpha}(u_j \, , v_j) \frac{x j_{n+1}(x) j_n(x_j) - x_j j_{n+1}(x_j) j_n(x)}{x^2 - x_j^2} \tag{15}$$

with $x = 2\pi Rb$, $x_j = 2\pi Rb_j$. Series (14) represents the radial dependence of the electron density component with the angular behaviour of $K_{n\alpha}(\theta \, , \varphi)$. For small enough values of r this also represents the corresponding term in the expansion (3) for the atom considered, provided the origin is at the center of this atom. Similarly, if R is chosen in a suitable way, the series (15) gives the corresponding term in the expansion (4) of its scattering factor, cf. ref. [6]. These series are valid for any harmonic functions $K_{n\alpha}(\theta \, , \varphi)$, whatsoever. Yet they are of the same general form as those given in [5] except that the summation now runs over all reciprocal lattice points and therefore the multiplicities of reflections do not occur. In practice the harmonics $K_{n\alpha}$ used to represent the electron density can always be taken real, so we can write $K_{n\alpha}$ instead of $K^*_{n\alpha}$. The constant C_n occuring in ref. [5] is seen to be $4\pi/A_{n\alpha}$, where $A_{n\alpha}$ is the normalization integral (10) of $K_{n\alpha}$.

References

[1] ALTMANN, S. L. and BRADLEY, C. J., Rev. Mod. Phys. *37*, 33 (1965).
[2] —»— and CRACKNELL, A. P., Rev. Mod. Phys. *37*, 19 (1965).
[3] ATOJI, M., Acta Cryst. *11*, 827 (1958).
[4] DAWSON, B., Proc. Roy. Soc. A, *298*, 264, 379 and 395 (1967).
[5] KURKI-SUONIO, K. and MEISALO, V., Ann. Acad. Sci. Fenn. A VI *241* (1967).
[6] —»— will be published in Acta Cryst.
[7] LUKE, Y. L., *Integrals of Bessel Functions*, 11.2., McGraw-Hill, New York (1962).
[8] VON DER LAGE, F. C. and BETHE, H. A., Phys. Rev. *71*, 612 (1947).

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