X-RAY SMALL ANGLE SCATTERING

A New Deconvolution Method for Evaluating Electron Density Distributions from Small Angle Scattering Diagrams

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ABSTRACT The direct determination of the electron density distributions of multilayered specimens with a small number of unit cells from X-ray small angle scattering experiments via the Q-function method of Hosemann and Bagchi includes the deconvolution of the so-called Q_o-function, the generalized Patterson function of one unit cell. In this paper a new and direct deconvolution method on the basis of Fourier series is presented which is suitable for one-dimensional centrosymmetrical (or antisymmetrical) density distributions. A FORTRAN-program has been written which has an execution time of ca. 20 s on an UNIVAC 1106-computer. The procedure has been successfully tested on some convolution functions generated by membrane-type electron density distributions.

INTRODUCTION

The fundamental problem in structure determination from X-ray investigations is the proper choice of the phases of the scattered waves. Multilayered specimens of biological interest such as nerve myelin, bimolecular lipid leaflets, and layered systems of membrane-bounded vesicles can be considered as one-dimensional structures with a center of symmetry. In this case the phase factors can have only the two values $+1$ and -1. Thus, for n reflections one has to select one from the 2^n possible sets of phases.

Hosemann and Bagchi (1962) have shown that for scattering systems with a small enough number of coherently diffracting unit cells the intensity function can contain more information than in the conventional case of crystals with a practically infinite number of unit cells. In this special case the corresponding generalized Patterson function is not ideally periodic, but has a so-called "tile-structure," from which the Q_o-function, the distance distribution function of a single unit cell can be isolated. This Q_o-function is the "folding square" of the one-dimensional electron density distribution in one unit cell $\rho_o(x)$, and a deconvolution of $Q_o(x)$ in principle then offers a straightforward analysis of the experimental data.

Kreutz (1968, 1970) has first applied the Q_o-method to biological objects in his X-ray investigations of the photosynthetic membrane of chloroplasts. More recently Lesslauer et al. (1971) and Lesslauer and Blasie (1972) have used this method in their determinations of the electron density distributions in bimolecular lipid leaflets and have emphasized its advantages over conventional Fourier methods.

The authors cited above have applied the deconvolution method of Hosemann and Bagchi (1962); this will first be outlined briefly. Let us denote the projected electron density distribution onto a line normal to the plane of the layer by $\rho(x)$

$$\rho(x) = \rho_o(x) * (z(x) \cdot s(x)), \tag{1}$$

where $\rho_o(x)$ = the electron distribution in one repeating unit; $z(x)$ = a one-dimensional lattice function; $s(x)$ = a shape function, defined as $s(x) = 1$ for $0 \leq |x| \leq ([N \cdot L]/2)$, and $s(x) = 0$ otherwise; L = length of the unit cell; N = number of coherently scattering unit cells in a multilayer; and $*$ = convolution symbol. The convolution square of Eq. 1, defined by $\rho(x) * \rho(-x)$ is then given by

$$Q(x) = Q_o(x) * [z(x) \cdot (s(x) * s(-x))] \cdot 1/L, \tag{2}$$

where $Q_o(x) = \rho_o(x) * \rho_o(-x)$.

This $Q(x)$, the generalized Patterson function, is related to the scattered intensity function by

$$Q(x) = \kappa \mathfrak{F}^{-1}(I_{\text{corr}}(b)), \tag{3}$$

where b is the vector in reciprocal space, $\mathfrak{F}$ is the symbol for Fourier transformation, and I_{corr} means that the integral intensity function must be corrected by the Lorentz and polarization factors, and by factors due to the lateral extension of the layers and to the orientation of the specimen (Blaurock and Worthington, 1966). κ means a proportionality factor.

Usually $z(x)$ and $s(x)$ are known, or recognizable from $Q(x)$, so that $Q_o(x)$ can be separated. Details of examples are given by Kreutz (1968, 1970) and by Lesslauer et al. (1971, 1972). The deconvolution itself consists in the solution of the integral equation

$$Q_o(x) = \int_{-\infty}^{+\infty} \rho_o(t)\rho_o(t - x)\, \mathrm{d}t \tag{4}$$

for $\rho_o(x)$.

The method of Hosemann and Bagchi (1962, pp. 122–131), applied by Kreutz and Lesslauer et al. is a recursion formula, based on an inversion of Eq. 4 when represented by an approximate formula for integrating.

Following Hosemann and Bagchi $Q_o(x)$ and $\rho_o(x)$ are divided into N small intervals Δx and two new functions $p(x)$ and $\mu(x)$ are defined.

$$p(x) = \int_{x-(\Delta x/2)}^{x+(\Delta x/2)} Q_o(t)\, dt;\ \mu(x) = \int_{x-(\Delta x/2)}^{x+(\Delta x/2)} \rho_o(t)\, dt;\ x = L/N, \qquad (5)$$

where Δx is small enough that $Q_o(x)$ and $\rho_o(x)$ are constant in Δx. So we have in the one-dimensional case

$$p(n \cdot \Delta x) = \sum_{i=0}^{N-1-i} \mu(i\Delta x)\mu((i - n)\Delta x);\ n = 0, 1, 2, \cdots N - 1. \qquad (6)$$

For a centrosymmetrical structure with $\mu_i = \mu_{N-1-i}$ we begin at the outer values of $p(x)$ and have

$$\begin{aligned} p(N - 1) &= \mu^2(N - 1) \\ p(N - 2) &= 2\mu(N - 1)\mu(N - 2) \\ &\cdot \\ &\cdot \\ &\cdot \\ &\cdot \end{aligned} \qquad (7)$$

Eq. 7 can be solved for $\mu(x)$ and successively the values of $\rho_o(x)$ can be calculated.

The main disadvantage of this method, and also of a second method of Hosemann and Bagchi which operates with convolution polynomials, is its great sensitivity to errors, both experimental errors and rounding errors of the computer.

On the one hand Δx has to be chosen as small as possible but the smaller Δx the smaller is the part of $p(x)$ from which the next value of $\rho_o(x)$ must be calculated. Lesslauer et al. recently mentioned the difficulties which arise from the error propagation of this recursion process.

These errors could lead to artificial oscillations of $\rho_o(x)$—even for model functions—and therefore a motive arose for the development of another method of deconvolution based on Fourier series.

THE FOURIER-ANALYTICAL DECONVOLUTION METHOD

Let the centrosymmetrical one-dimensional electron density $\rho_o(\hat{x})$ in the interval $(-L/2, +L/2)$ be given by a pure and limited cosine-series (it is always possible to transform the unit cell of length L into the interval $(-\pi, +\pi)$ by $x = 2\pi\hat{x}/L$)

$$\rho_o(x) = a_o + \sum_{k=1}^{N} a_k \cos kx;\ -\pi \leqq x \leqq +\pi. \qquad (8)$$

The corresponding $Q_o(x)$, or, more exactly, the right half of the always centrosym-

metrical convolution square $Q_o(x)$, may be represented by

$$Q_o(x) = c_o + \sum_{k=1}^{N} (c_k \cos kx + d_k \sin kx); 0 \leqq x \leqq 2\pi. \tag{9}$$

Note that the limited domain in which this $Q_o(x)$ differs from zero eliminates the left half of the usual $Q_o(x)$ and thus destroys its centrosymmetric character.

All the information about $\rho_o(x)$ is contained in this right half of $Q_o(x)$, and it is necessary to take only the right half, because the sine-Fourier coefficients of $Q_o(x)$ will vanish for the whole of $Q_o(x)$.

The new Fourier-analytical deconvolution method (briefly FAD method) now is characterized by two steps of execution: (*1*) From the Fourier-cosine-coefficients c_k of the half of $Q_o(x)$ in the interval $(0, 2\pi)$ we get in a first step immediately the absolute values of the Fourier-cosine-coefficients a_k of the centrosymmetrical function $\rho_o(x)$. (*2*) The second step consists in the determination of the signs of the coefficients a_k of $\rho_o(x)$ from a system of linear equations generated through the Fourier-sine-coefficients d_k of the half of $Q_o(x)$ in the interval $(0, 2\pi)$.

The Q_o-function given in terms of the Fourier-cosine-coefficients a_k of $\rho_o(x)$ is (details in the Appendix)

$$Q_o(x) = a_0^2(2\pi - x) + \sum_{k=1}^{N} \frac{1}{2} a_k^2 \left[(2\pi - x) \cos kx - \frac{\sin kx}{k} \right]$$
$$+ \sum_{k=1}^{N} 2ka_k \sin kx \sum_{\substack{l=0 \\ l \neq k}}^{N} \frac{(-1)^{k+l} a_l}{l^2 - k^2} \qquad (0 \leqq x \leqq 2\pi). \tag{10}$$

Their Fourier-cosine-coefficients c_k, defined by

$$c_k = \frac{1}{\pi} \int_0^{2\pi} Q_o(x) \cos kx \, dx \tag{11}$$

are related to the coefficients a_k of $\rho_o(x)$ by

$$c_0 = 2\pi a_0^2$$
$$c_k = \frac{1}{2} \pi a_k^2; k = 1, 2, \cdots N. \tag{12}$$

This is easily seen by putting $Q_o(x)$ into Eq. 11 and integrating. From Eq. 12 the absolute values of the $(N + 1)$ coefficients a_k of $\rho_o(x)$ are determined.

The Fourier-sine-coefficients d_k of the half of $Q_o(x)$ in the interval $(0, 2\pi)$ given by

$$d_k = \frac{1}{\pi} \int_0^{2\pi} Q_o(x) \sin kx \, dx. \tag{13}$$

Inserting of Eq. 10 into Eq. 13, we get

$$d_k = (2a_0^2/k) - (a_k^2/4k) - \sum_{\substack{l=1 \\ l\neq k}}^{N} (ka_l^2/(l^2 - k^2)) + \sum_{\substack{l=0 \\ l\neq k}}^{N} (2ka_ka_l(-1)^{k+l}/[l^2 - k^2]). \quad (14)$$

Introducing the signs of the coefficients a_k of $\rho_o(x)$ by

$$a_k = s_k \mid a_k \mid, \quad (15)$$

we can transform Eq. 14 into a system of linear equations for the determination of N signs. The sign of the $(N + 1)$-th coefficient, for example that of a_o, can always be chosen independently because a complete change of all signs does not alter the Q_o-function. The reason for this is that $\rho_o(x)$ and $-\rho_o(x)$ have the same Q_o-function.

The linear system is given by

$$\frac{a_o}{k^2} = \sum_{\substack{l=1 \\ l\neq k}}^{N} \frac{(-1)^l \mid a_l \mid s_l}{(l^2 - k^2)} - \hat{d}_k \mid a_k \mid s_k ; k = 1, 2, \cdots N. \quad (16)$$

where $\hat{d}_k$ is known and related to d_k by

$$\hat{d}_k = \left[(d_k/2k) - (a_0^2/k^2) + (a_k^2/8k^2) - \sum_{\substack{l=1 \\ l\neq k}}^{N} (a_l^2/2[k^2 - l^2]) \right] ((-1)^k/a_k^2). \quad (17)$$

Details again are seen in the Appendix.

A FORTRAN-program has been written for this FAD procedure which makes use of an IBM-SSP (Science Subroutine Package) subroutine for solving the system of linear equations by a Gauss-algorithm. The complete program has an execution time of only about 20 s on an UNIVAC 1106-computer.

Two special advantages of the FAD-method may be pointed out:

(*1*) For the calculation of every value of $\rho_o(x)$ all the values of the right half of $Q_o(x)$ are used simultaneously.

(*2*) The sampling interval Δx of $Q_o(x)$ can be reduced to any small value without disadvantageous influence on the accuracy of the method. On the contrary the accuracy increases with decreasing Δx of $Q_o(x)$.

Three examples follow. They demonstrate the accuracy and usefulness of the new method.

DISCUSSION

It is seen from Figs. 1–3 that the application of the FAD method to the deconvolution of model functions is successful. The deviations are of the order of 1%, and

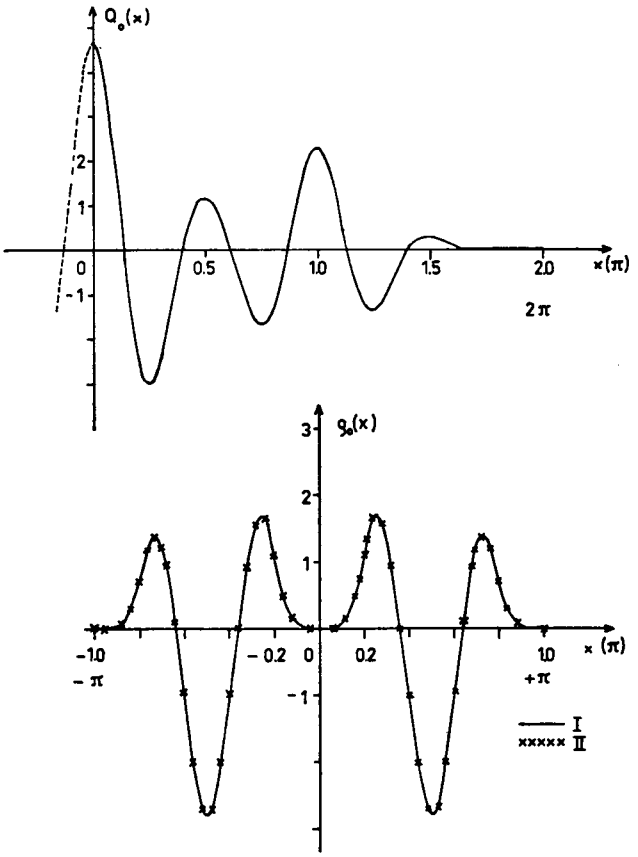

FIGURE 1 Deconvolution of $Q_o(x)$ by a Fourier analysis of the half of $Q_o(x)$. Distance distribution function $Q_o(x)$ (above) for a centrosymmetrical model function $\rho_o(x)$ (below, curve I). The result of the deconvolution of $Q_o(x)$ with the FAD method is compared with $\rho_o(x)$ (below, curve II). (2π corresponds to the length L of one repeating layer).

are therefore not visible in the graphical representation. With a finer sampling of $Q_o(x)$ and the use of "double precision" numbers one can get in principle a perfect agreement.

As is known, $\rho_o(x)$ and $-\rho_o(x)$ have the same convolution square $Q_o(x)$ and we must remember that in every example $-\rho_o(x)$, the mirror image of the $\rho_o(x)$, is an equivalent solution.

Furthermore, it must be mentioned that the deconvolution of the Q_o-function of antisymmetrical functions is also possible in a very similar way.

The limit of summation N can be determined in principle either from Eq. 9 for $Q_o(0)$ or from Parseval's equation. In practice it has been proved that the best way to limit the higher frequency cosine waves in $\rho_o(x)$ is given by the solution of the

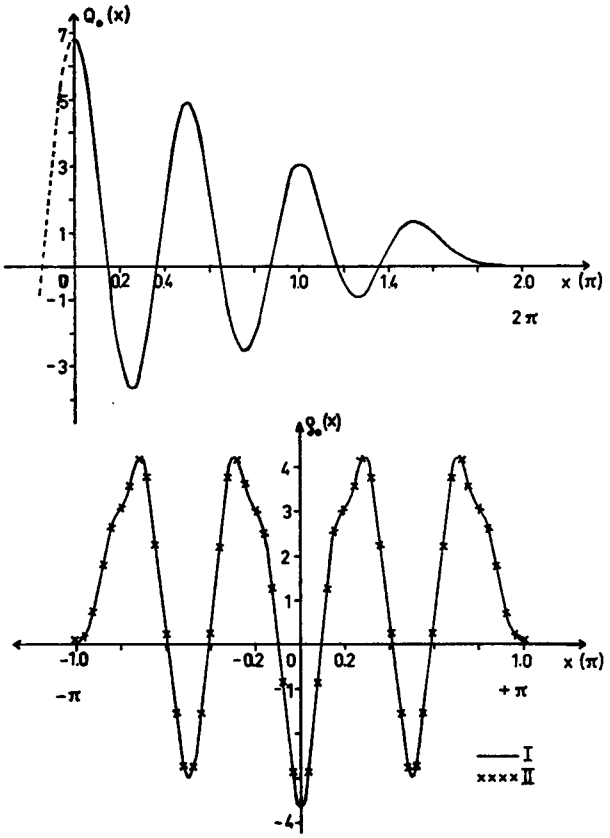

FIGURE 2 See legend to Fig. 1.

system of linear equations. Starting always at $N = 20$, the distinction between real and artificial waves (this means the reduction of N), is possible in the following way. Successively all a with $k \leqq 20$ are eliminated when $| s_k | < 0.1$. The first a_k with $| s_k | \geqq 0.1$ then defines the new limit N as is demonstrated in Table I for example 1. The barrier 0.1 is established arbitrarily.

The question arising now is: What is the physical meaning of the a_k's of $\rho_o(x)$? In the representation of $\rho_o(x)$ as the inverse Fourier transform of the square root of the intensity in the reciprocal lattice points

$$\hat{\rho}(x) = \frac{2}{L} \sum_{k=0}^{k_{max}} [I(b_k)]^{1/2} \cos\left(\frac{2\pi kx}{L}\right), \tag{18}$$

one can immediately see that a_k's are strictly related to the intensity at the Bragg angles.

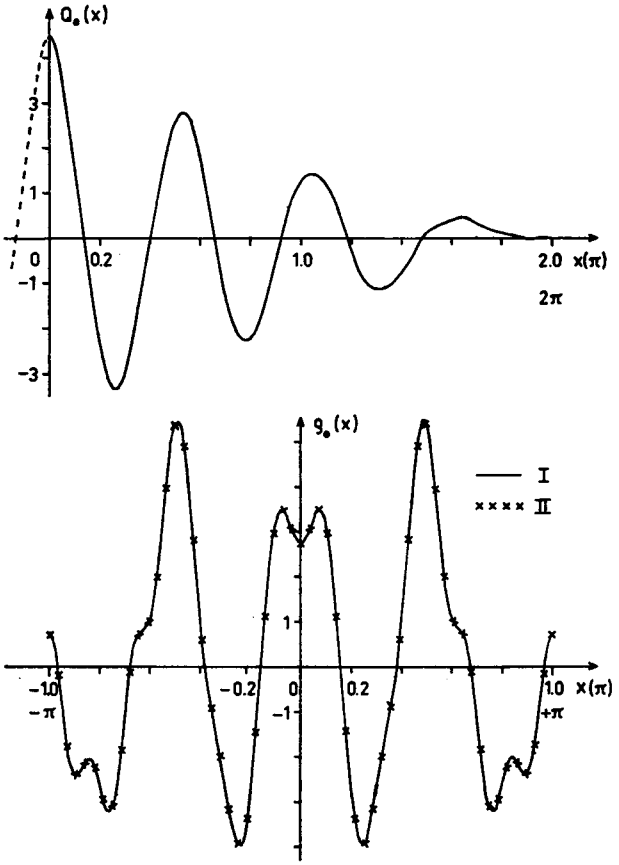

FIGURE 3 See legend to Fig. 1.

An interesting aspect furthermore is the following: Why is it impossible to determine the phases directly for an unlimited crystal and why is this possible in the case of a crystal or layered system with a small number of unit cells? The answer lies in the possibility of the separation of $Q_o(x)$ from $Q(x)$. This can be seen in detail in Eq. 10. The third term of Eq. 10, the double sum, which offers the possibility of direct phasing, is a completely antisymmetric function relative to the lattice points $x = n \cdot L$. For an unlimited crystal the parts of this function have equal weight on every point $x = n \cdot L$ and therefore all these alternating parts compensate to zero. In the other case on the contrary these parts have a weight of $(N_o - n)/N_o$ with $n = 0, 1, \cdots N_o - 1$ where N_o is the number of unit cells and therefore the third term of Eq. 10 is obtainable when N_o is sufficiently small. The remaining difficulty is then to find the proper experimental conditions that justify the assumptions, especially the assumption of regular packing of a few centrosymmetric unit cells.

TABLE I

REDUCTION OF THE LIMIT OF SUMMATION $N = 20$ (INITIAL) TO $N = 14$ THROUGH THE SOLUTION OF THE SYSTEM OF LINEAR EQUATIONS (EXAMPLE 1)

k	s_k	Sign	a_k	$a_o = 0.250$
1	−1.000	(−)	−0.769	
2	−1.001	(−)	−0.847	
3	1.001	(+)	0.273	
4	0.989	(+)	13.833	
5	1.000	(+)	0.881	
6	−1.001	(−)	−5.407	
7	−0.904	(−)	−0.068	
8	−1.071	(−)	−0.590	
9	−1.031	(−)	−0.431	
10	0.513	(+)	0.050	
11	−0.496	(−)	−0.034	
12	0.561	(+)	0.606	
13	0.192	(+)	0.095	
14	−0.126	(−)	−0.163	
15	0.003			
16	−0.004			
17	0.001			
18	−0.001			
19	0.001			
20	−0.001			

Program descriptions are available from the author.

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APPENDIX

All the calculations are elementary, but for completeness a short review of the derivation will be given. The following formulas of addition of trigonometric functions are used:

$$\begin{aligned} 2\cos kx \cos lx &= \cos (k + l)x + \cos (k - l)x \\ 2\cos lx \sin kx &= \sin (k + l)x + \sin (k - l)x \\ 2\sin lx \sin kx &= \cos (k - l)x - \cos (k + l)x. \end{aligned} \tag{19}$$

Derivation of $Q_o(x)$ in Terms of the Fourier-Cosine Coefficients a_k of $\rho_o(x)$

We have to integrate the equation

$$Q_o(x) = \int_{-\pi+x}^{+\pi} \left(a_o + \sum_{k=1}^{N} a_k \cos kt\right)\left(a_o + \sum_{l=1}^{N} a_l \cos l(t - x)\right) \mathrm{d}t$$

$$(0 \leqq x \leqq 2\pi) \quad (20)$$

Though $\rho(x)$ is represented as an ideal periodic and infinitely extended function, we get through this special choice of limits of integration the distance distribution function $Q_o(x)$ of a single unit cell, i.e. of $\rho_o(x)$.

The complete integral (Eq. 20) is divided into five parts I_1 to I_5; every part is then easily calculated.

$$Q_o(x) = I_1 + I_2 + I_3 + I_4 + I_5$$

$$I_1 = \sum_{k=1}^{N} a_o a_k \int_{-\pi+x}^{+\pi} \cos kt \, \mathrm{d}t = \sum_{k=1}^{N} (-1)^{k+1} a_o a_k \frac{\sin kx}{k}$$

$$I_2 = \sum_{k=1}^{N} a_o a_k \int_{-\pi+x}^{+\pi} \cos k(t - x) \, \mathrm{d}t = \sum_{k=1}^{N} (-1)^{k+1} a_o a_k \frac{\sin kx}{k}$$

$$I_3 = \int_{-\pi+x}^{+\pi} a_o^2 \, \mathrm{d}t = (2\pi - x) a_o^2.$$

From the double sum we first take the terms with $k = l$:

$$I_4 = \sum_{k=1}^{N} \int_{-\pi+x}^{+\pi} a_k^2 \cos kt \cos k(t - x) \, \mathrm{d}t$$

$$= \frac{1}{2} \sum_{k=1}^{N} a_k^2 \left[(2\pi - x) \cos kx - \frac{\sin kx}{k}\right]$$

Then follow the terms with $k \neq l$:

$$I_5 = \sum_{k=1}^{N} a_k \sum_{l=1}^{N} a_l \int_{-\pi+x}^{+\pi} \cos kt \cos l(t - x) \, \mathrm{d}t$$

$$= \sum_{k=1}^{N} a_k \sum_{l=1}^{N} a_l (-1)^{k+l} \frac{(k \sin kx - l \sin lx)}{l^2 - k^2}.$$

The interchange of k and l does not alter the sign of this expression. So we have

$$I_5 = \sum_{k=1}^{N} 2a_k k \sin kx \sum_{\substack{l=1 \\ l \neq k}}^{N} \frac{(-1)^{k+l} a_l}{l^2 - k^2}.$$

I_1 and I_2 can be included in the sum I_5 and the result is then finally

$$Q_o(x) = a_o^2(2\pi - x) + \sum_{k=1}^{N} \frac{1}{2} a_k^2 \left[(2\pi - x) \cos kx - \frac{\sin kx}{k} \right] + \sum_{k=1}^{N} 2ka_k \sin kx \sum_{\substack{l=0 \\ l \neq k}}^{N} \frac{(-1)^{k+l} a_l}{l^2 - k^2} \qquad (0 \leqq x \leqq 2\pi). \quad (21)$$

Derivation of the System of Linear Equations for the Determination of the Signs s_k of the Coefficients a_k of $\rho_o(x)$

The integration of Eq. 13 yields the Fourier-sine-coefficients d_k of the right half of $Q_o(x)$ by Eq. 14:

$$d_k = (2a_o^2/k) - (a_k^2/4k) - \sum_{\substack{l=1 \\ l \neq k}}^{N} (ka_l^2/[l^2 - k^2]) + \sum_{\substack{l=0 \\ l \neq k}}^{N} (2ka_k a_l(-1)^{k+l}/[l^2 - k^2]).$$

$$k = 1, 2, \cdots N \quad (22)$$

The first two terms and the first sum of the right side of Eq. 22 are known and therefore it is more convenient to introduce Eq. 24 instead of Eq. 22 with the $\hat{d}_k$ defined by Eq. 23.

$$\hat{d}_k = \left[(d_k/2k) - (a_o^2/k^2) + (a_k^2/8k^2) - \sum_{\substack{l=1 \\ l \neq k}}^{N} (a_l^2/2[k^2 - l^2]) \right] ((-1)^k/a_k^2) \quad (23)$$

$$d_k a_k = \sum_{\substack{l=0 \\ l \neq k}}^{N} \frac{(-1)^l a_l}{(l^2 - k^2)}; \qquad k = 1, 2, \cdots N. \quad (24)$$

If we now define N signs s_k by $a_k = s_k \cdot |a_k|$ and in every row move a_o for example to the left side, we get the linear system

$$\frac{a_o}{k^2} = \sum_{\substack{l=1 \\ l \neq k}}^{N} \frac{(-1)^l |a_l| s_l}{(l^2 - k^2)} - \hat{d}_k |a_k| s_k; \qquad k = 1, 2, \cdots N. \quad (25)$$

We remember that one sign can be chosen independently (here the sign of a_o), because a complete change of all signs of the a_k does not alter the Q_o-function. This follows from the fact that $\rho_o(x)$ and $-\rho_o(x)$ have the same convolution square $Q_o(x)$.

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