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Exact and explicit expression of the atomic pair distribution function as obtained from X-ray total scattering experiments

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The atomic pair distribution function (PDF) as obtained from X-ray or neutron total scattering experiments has proved to be powerful in obtaining valuable structural information for many complex functional materials, be they amorphous or crystalline. In the case of measurements made with X-rays and for samples containing more than one kind of atom, the usefulness of the PDF is, however, somewhat hampered because of the lack of an exact and simple expression relating it to the structure of the materials. Only an approximate relationship exists, which is still in use today. This is particularly detrimental given the wide availability of X-ray sources and the increasing quality of PDFs obtained with laboratory sources. In this paper, the exact and explicit expression of the PDF as obtained from X-ray scattering is derived with respect to partial functions. This expression allows exact and efficient calculation of the PDF from any structure model without using approximate formulae.

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1. Introduction

The atomic pair distribution function (PDF) as obtained from X-ray or neutron total scattering experiments is playing an increasing role in crystallography and condensed matter physics. Combined with powerful computational methods, it has proved to be of great value in determining the atomic arrangement of many emerging complex functional materials (Billinge & Kanatzidis, 2004; Juhás *et al.*, 2006; Billinge & Levin, 2007; Cliffe *et al.*, 2010), knowledge of which is required for further theoretical understanding of their properties. Its usefulness comes from the fact that it contains information from both Bragg and diffuse scattering, which makes it sensitive to the intrinsic short-range and nanoscale structural fluctuations in materials, be they crystalline or amorphous. A detailed description of the PDF, related crystallographic methods and experimental considerations can be found elsewhere (Egami & Billinge, 2003).

The experimental PDF, $g(r)$, is defined as the truncated sine Fourier transform of the reduced structure factor, $s(Q)$,¹ obtained from the normalized elastic differential scattering cross section of the sample, *i.e.*

$$g(r) = (2/\pi) \int_0^{Q_{\max}} s(Q) \sin(Qr) dQ, \quad (1)$$

where Q is the magnitude of the scattering vector [$Q = (4\pi/\lambda)\sin\theta$, where θ is half the scattering angle and λ is the

wavelength of the incident radiation] and Q_{\max} is its maximum experimentally reachable value.² Extracting structural information from the experimental PDF is a tricky mathematical inverse problem. It generally requires the calculation of PDFs from trial structure models (determined by *ab initio* calculations or molecular dynamics simulations or reverse Monte Carlo methods or least-squares refinements *etc.*), which in turn are compared with the experimental data in order to assess the quality of the models. For samples containing different types of atoms, *i.e.* in multi-component systems, the experimental PDF is related not only to the density of atom pairs in the material but also to the chemical complexity of the material and the type of radiation used for the experiment. In the case of neutron scattering, the PDF is just a weighted linear combination of partial PDFs (Egami & Billinge, 2003). In the case of X-rays, however, no such simple and exact relation can be given. This comes from the fact that the Q dependence of the atomic scattering factors differs from one kind of atom to another. This shortcoming has been known for a long time and was first partly overcome in 1936 by Warren, Krutter and Morningstar (WKM; Warren *et al.*, 1936) by using a mean form factor with an effective number of electrons per atom. This approximation is still in use today, more than 70 years later, and is implemented in most popular PDF analysis software (*e.g.* *PDFFIT*; Proffen & Billinge, 1999). However, it has three major drawbacks: (i) it is not defined in a unique way, (ii) its accuracy is unknown, and (iii) it can introduce significant errors for materials combining both heavy and light elements

¹ Reduced functions are related to conventional quantities as follows: $s(Q) = Q[S(Q) - 1]$ and $g(r) = 4\pi r \rho_0 [G(r) - 1]$, with $S(Q) \rightarrow 1$ and $G(r) \rightarrow 1$ for large Q and r , respectively.

² Small-angle scattering signal is not included in $s(Q)$ with this definition.

(Korsunskiy & Neder, 2005). The use of this approximation can thus be a serious limitation for obtaining subtle structural details that are often responsible for the properties of functional materials. The Q dependence of the atomic scattering factors can be correctly handled by first calculating $s(Q)$ from a structure model and using equation (1) to obtain $g(r)$. This approach has the advantage of avoiding approximation but is cumbersome and time consuming in practice and still does not give an explicit and transparent expression for the experimental PDF. All these reasons have somewhat hampered the usefulness of the PDF as measured from X-ray scattering experiments. This is particularly detrimental as X-ray sources are widely available and experimental PDFs of increasing quality can be obtained with laboratory sources. In this paper, we address this issue by deriving the exact and explicit expression of the experimental total PDF with respect to partial PDFs, which allows exact and efficient calculation of the PDF from any structure model.

2. Formulation of the problem

Let us first formulate precisely the problem for the X-ray scattering case by introducing relevant quantities. In samples containing more than one kind of atom, $s(Q)$ can be related to partial functions, each defined with respect to a given pair of atoms. The most usual form of decomposition is that devised by Faber and Ziman (FZ; Faber & Ziman, 1965):

$$s(Q) = \sum_{\alpha,\beta} \gamma_{\alpha\beta}(Q) s_{\alpha\beta}(Q), \quad (2)$$

with

$$s_{\alpha\beta}(Q) = \int_0^\infty g_{\alpha\beta}(r) \sin(Qr) dr \quad (3)$$

and

$$\gamma_{\alpha\beta}(Q) = c_\alpha c_\beta f_\alpha(Q) f_\beta^*(Q) / |f(Q)|^2, \quad (4)$$

where $s_{\alpha\beta}$, $g_{\alpha\beta}$ and $\gamma_{\alpha\beta}$ are the FZ partial structure function, partial PDF and weighting factor, respectively, for a given pair of atoms of type α and β , and c_α (c_β) and f_α (f_β) are the atomic concentration and scattering factor for atomic species α (β). The sum in equation (2) is over all kinds of pairs in the sample. The partial functions $s_{\alpha\beta}$ and $g_{\alpha\beta}$ are very useful as they depend only on the structure of the material and are independent of the experimental technique. In particular, the partial PDF is of prime importance as it gives the deviation of the local atomic density, $\rho_{\alpha\beta}(r)$, of the atoms of type α at a distance r from the atoms of type β with respect to the average atomic density in the sample, ρ_0 , *i.e.*

$$g_{\alpha\beta}(r) = 4\pi r [\rho_{\alpha\beta}(r) / c_\alpha c_\beta - \rho_0]. \quad (5)$$

It has thus a direct physical meaning and can be calculated from any structure model. In practical applications, partial PDFs are combined together to form the total PDF, which in turn is compared (or refined) against the experimental PDF. From equation (4) it is obvious that $\gamma_{\alpha\beta}(Q)$ depends on Q . For this reason, there is no simple way of combining $g_{\alpha\beta}$ in order to

obtain g . In particular, an exact weighted linear combination of partial functions, analogous to that of equation (2) for $s(Q)$, is strictly impossible. Within the WKM approximation, the scattering factors are approximated by $f_\alpha(Q) = Z_\alpha^{\text{eff}} f_c(Q)$, where Z_α^{eff} is an effective number of electrons for species α and $f_c(Q)$ is an average scattering factor per electron for the sample (Egami & Billinge, 2003). This in turn is equivalent to having constant FZ weights defined as

$$\gamma_{\alpha\beta}^{\text{eff}} = c_\alpha c_\beta Z_\alpha^{\text{eff}} Z_\beta^{\text{eff}} / \langle Z^{\text{eff}} \rangle^2, \quad (6)$$

which allows g to be approximated as a weighted linear combination of partial PDFs, *i.e.*

$$g(r) \cong \sum_{\alpha,\beta} \gamma_{\alpha\beta}^{\text{eff}} g_{\alpha\beta}(r). \quad (7)$$

In most studies, the effective number of electrons is taken to be equal to the atomic number, but other arbitrary choices can be made. As stated in the *Introduction*, approximating $\gamma_{\alpha\beta}(Q)$ by the constant effective value given in equation (6) can be a very poor choice for samples containing both heavy and light elements since the Q dependence of $f(Q)$ is quite different for light and heavy atoms. It is worth noting that, in the case of neutron scattering experiments, the atomic scattering factors in equation (4) are replaced by the coherent bound neutron scattering lengths, which do not depend on Q , so that the FZ weights $\gamma_{\alpha\beta}$ are constant values and the form of equation (7) becomes exact.

3. Derivation of the exact expression

Let us now derive the exact and explicit expression relating g to the structure-related partial PDFs, $g_{\alpha\beta}$. Introducing equation (2) into equation (1) we get

$$g(r) = \sum_{\alpha,\beta} (2/\pi) \int_0^{Q_{\text{max}}} \gamma_{\alpha\beta}(Q) s_{\alpha\beta}(Q) \sin(Qr) dQ. \quad (8)$$

This is the sine Fourier transform of a product. Applying the convolution theorem, and implicitly considering $\gamma_{\alpha\beta}$ and $s_{\alpha\beta}$ as even and odd functions, respectively, we obtain

$$g(r) = \sum_{\alpha,\beta} (1/\pi) \int_0^{Q_{\text{max}}} \gamma_{\alpha\beta}(Q) \cos(Qr) dQ \otimes (2/\pi) \int_0^\infty s_{\alpha\beta}(Q) \sin(Qr) dQ, \quad (9)$$

where \otimes denotes the convolution product. Recognizing the partial PDF, $g_{\alpha\beta}$, on the right side of the convolution product in equation (9) we obtain

$$g(r) = \sum_{\alpha,\beta} \Gamma_{\alpha\beta}(r) \otimes g_{\alpha\beta}(r), \quad (10)$$

with

$$\Gamma_{\alpha\beta}(r) = (1/\pi) \int_0^{Q_{\text{max}}} \gamma_{\alpha\beta}(Q) \cos(Qr) dQ, \quad (11)$$

which is equivalent to expressions proposed in earlier work (Waser & Schomaker, 1953; Warren, 1969).

Now, let us expand the FZ weighting functions, $\gamma_{\alpha\beta}(Q)$, into Fourier series in the range $-Q_{\max} < Q < Q_{\max}$. We obtain

$$\gamma_{\alpha\beta}(Q) = a_{\alpha\beta}(0) + 2 \sum_{k=1}^{+\infty} a_{\alpha\beta}(r_k) \cos(Qr_k), \quad (12)$$

with

$$r_k = \frac{\pi}{Q_{\max}} k \quad \text{and} \quad a_{\alpha\beta}(r_k) = \frac{1}{Q_{\max}} \int_0^{Q_{\max}} \gamma_{\alpha\beta}(Q) \cos(Qr_k) dQ. \quad (13)$$

Here, we implicitly considered $\gamma_{\alpha\beta}$ as a periodic function of period $2Q_{\max}$. Substituting equation (12) into equation (11) and integrating with respect to Q , we obtain

$$\Gamma_{\alpha\beta}(r) = \frac{\sin(Q_{\max}r)}{\pi r} a_{\alpha\beta}(0) + \sum_{k=1}^{+\infty} a_{\alpha\beta}(r_k) \left\{ \frac{\sin[Q_{\max}(r-r_k)]}{\pi(r-r_k)} + \frac{\sin[Q_{\max}(r+r_k)]}{\pi(r+r_k)} \right\}. \quad (14)$$

Now, substituting equation (14) into equation (10) and using the translation invariance property of the convolution product, *i.e.* $f(r \pm r_k) \otimes g(r) = f(r) \otimes g(r \pm r_k)$, we obtain

$$g(r) = \frac{\sin(Q_{\max}r)}{\pi r} \otimes \sum_{\alpha,\beta} \left\{ a_{\alpha\beta}(0) g_{\alpha\beta}(r) + \sum_{k=1}^{+\infty} a_{\alpha\beta}(r_k) [g_{\alpha\beta}(r-r_k) + g_{\alpha\beta}(r+r_k)] \right\}. \quad (15)$$

This is the exact expression of $g(r)$, containing the effect of the variation of $\gamma_{\alpha\beta}(Q)$ with Q . The left member of the convolution product is the cardinal sine function as a result of the truncation of the Fourier transform in equation (1). Such a function produces the well known termination ripples on the PDF, manifested as both peak broadening and oscillating wings. It only depends on the Q_{\max} value whatever the type of radiation used and does not contain any structural information. It is usually omitted for the sake of clarity in the expressions of the PDF, as was done in equation (7). In doing so for equation (15), we obtain

$$g(r) = \sum_{\alpha,\beta} \left\{ a_{\alpha\beta}(0) g_{\alpha\beta}(r) + \sum_{k=1}^{+\infty} a_{\alpha\beta}(r_k) [g_{\alpha\beta}(r-r_k) + g_{\alpha\beta}(r+r_k)] \right\}. \quad (15a)$$

This expression can also be rewritten in a more convenient form for comparison with the usual approximate WKM expression or the exact expression of neutron experiments. Introducing a modified partial function, $g_{\alpha\beta}^X$, defined as

$$g_{\alpha\beta}^X(r) = g_{\alpha\beta}(r) + \sum_{k=1}^{+\infty} w_{\alpha\beta}(r_k) [g_{\alpha\beta}(r-r_k) + g_{\alpha\beta}(r+r_k)], \quad (16)$$

with

$$w_{\alpha\beta}(r_k) = a_{\alpha\beta}(r_k) / a_{\alpha\beta}(0), \quad (17)$$

we obtain

$$g(r) = \sum_{\alpha,\beta} a_{\alpha\beta}(0) g_{\alpha\beta}^X(r). \quad (18)$$

The PDF is now expressed as a simple linear combination of modified partial functions. Equations (16)–(18) are equivalent to equation (15a).

4. Discussion

Several comments can be made from this point. The form of equation (18) resembles the WKM expression in equation (7) but the involved quantities have different meanings. The linear combination in equation (18) involves the modified partial PDF, $g_{\alpha\beta}^X$, which depends on the scattering factors through $w_{\alpha\beta}(r_k)$, instead of the true partial functions, $g_{\alpha\beta}$. In addition, the weights used in this combination are exactly and uniquely defined as the mean values of the FZ factors over the $[0, Q_{\max}]$ interval, *i.e.*

$$a_{\alpha\beta}(0) = \frac{1}{Q_{\max}} \int_0^{Q_{\max}} \gamma_{\alpha\beta}(Q) dQ. \quad (19)$$

Given the definition of $\gamma_{\alpha\beta}(Q)$ in equation (4), it can be readily verified that the weights $a_{\alpha\beta}(r_k)$ satisfy

$$\sum_{\alpha,\beta} a_{\alpha\beta}(0) = 1 \quad \text{and} \quad \sum_{\alpha,\beta} a_{\alpha\beta}(r_{k>0}) = 0. \quad (20)$$

Also, according to the mean value theorem, there exists Q_0 such that $\gamma_{\alpha\beta}(Q_0) = a_{\alpha\beta}(0)$. This allows us to define the numbers $Z_{\alpha/\beta}^{\text{eff}} = f_{\alpha/\beta}(Q_0)$ for the calculation of $a_{\alpha\beta}(0)$, which makes the viewpoint of the effective number of electrons used in the WKM approximation compatible to some extent with our equation (18).

Let us now focus on the expression for $g_{\alpha\beta}^X$ in equation (16). This function is related to the true partial function $g_{\alpha\beta}$ by very simple mathematical operations, in particular involving no integral operators, which has important consequences in practical applications. It can be seen as a simple modification of the true $g_{\alpha\beta}(r)$ by superposing its weighted and symmetrically shifted ‘ghosts’, with weights $w_{\alpha\beta}(r_k)$ and shifts $\pm r_k$. According to equation (17) the weights $w_{\alpha\beta}(r_k)$ are the normalized [*i.e.* $w_{\alpha\beta}(0) = 1$] Fourier coefficients of the FZ weighting factors. Following the general shape of the latter (*cf.* below), it is expected that $w_{\alpha\beta}(r_k)$ decreases rather rapidly with r_k so that, although the sum in equation (16) [or in equation (15)] extends to infinity, only a few terms should be sufficient to calculate $g_{\alpha\beta}^X$ to a very good accuracy. Consequently, the degree of approximation can be easily chosen by truncating the series expansion at an appropriate order k . In addition, the calculation of the PDF from a structure model is performed in practice at discrete values with constant r step, so if the step is chosen to be equal to (or a fraction of) the Nyquist interval (Shannon, 1949; Farrow *et al.*, 2011), π/Q_{\max} , then no interpolation is needed for the computation of shifted ghost functions. All these points make the computation of $g_{\alpha\beta}^X$, and thus g , very simple and fast. We can also note that in the case where $\gamma_{\alpha\beta}(Q)$ is constant over the Q range, one has

Table 1

Calculated values of the $a_{\alpha\beta}(0)$, $w_{\alpha\beta}(r_{k=1\dots 8})$ and $\gamma_{\alpha\beta}^{\text{eff}}$ (with $Z^{\text{eff}} = Z$) LaB₆ coefficients for $Q_{\text{max}} = 17 \text{ \AA}^{-1}$.

$\alpha-\beta$	$a_{\alpha\beta}(0)$	$\gamma_{\alpha\beta}^{\text{eff}}$	$w_{\alpha\beta}(r_1)$	$w_{\alpha\beta}(r_2)$	$w_{\alpha\beta}(r_3)$	$w_{\alpha\beta}(r_4)$	$w_{\alpha\beta}(r_5)$	$w_{\alpha\beta}(r_6)$	$w_{\alpha\beta}(r_7)$	$w_{\alpha\beta}(r_8)$
La-La	0.5824	0.4292	-0.0495	-0.0111	-0.0347	-0.0162	-0.0131	-0.0043	-0.0035	0.0001
La-B	0.3595	0.4518	0.0534	0.0087	0.0364	0.0156	0.0128	0.0034	0.0028	-0.0006
B-B	0.0584	0.1189	0.1649	0.0620	0.1216	0.0703	0.0523	0.0264	0.0184	0.0071

Table 2

Calculated values of the $a_{\alpha\beta}(0)$ and $w_{\alpha\beta}(r_{k=1\dots 9})$ LaB₆ coefficients for $Q_{\text{max}} = 40 \text{ \AA}^{-1}$.

$\alpha-\beta$	$a_{\alpha\beta}(0)$	$w_{\alpha\beta}(r_1)$	$w_{\alpha\beta}(r_2)$	$w_{\alpha\beta}(r_3)$	$w_{\alpha\beta}(r_4)$	$w_{\alpha\beta}(r_5)$	$w_{\alpha\beta}(r_6)$	$w_{\alpha\beta}(r_7)$	$w_{\alpha\beta}(r_8)$	$w_{\alpha\beta}(r_9)$
La-La	0.6907	-0.1240	0.0059	-0.0051	0.0000	-0.0113	-0.0095	-0.0117	-0.0080	-0.0082
La-B	0.2726	0.2498	-0.0238	0.0093	-0.0023	0.0193	0.0153	0.0188	0.0129	0.0130
B-B	0.0372	0.4719	0.0775	0.0272	0.0303	0.0681	0.0783	0.0788	0.0672	0.0578

$w_{\alpha\beta}(r_k) = 0$, so that $g_{\alpha\beta}^x = g_{\alpha\beta}$ and $a_{\alpha\beta}(0) = \gamma_{\alpha\beta}(0)$, i.e. we obtain the well known expression for the neutron case.

We now illustrate the efficiency of our expression in calculating the PDF for the case of the LaB₆ compound. This is a widely used material in diffraction experiments with a well known and simple structure that contains both heavy and light elements. For this purpose, the LaB₆ PDF was synthesized using three different expressions: (i) equation (1), i.e. the exact Fourier sine transform of $s(Q)$, (ii) equation (15), i.e. our expression with various k values, and (iii) equation (7), i.e. the WKM approximation with $Z^{\text{eff}} = Z$. In all cases we started from the same LaB₆ partial functions calculated using *PDFFIT* and the structural parameters given by Eliseev *et al.* (1986). The computation of equation (1) required the prior calculation of the partial structure factors using equation (3), which in turn were combined using equation (2) to obtain the total structure factor. In order to integrate over a limited range in equation (3), a small dampening of the partial PDF

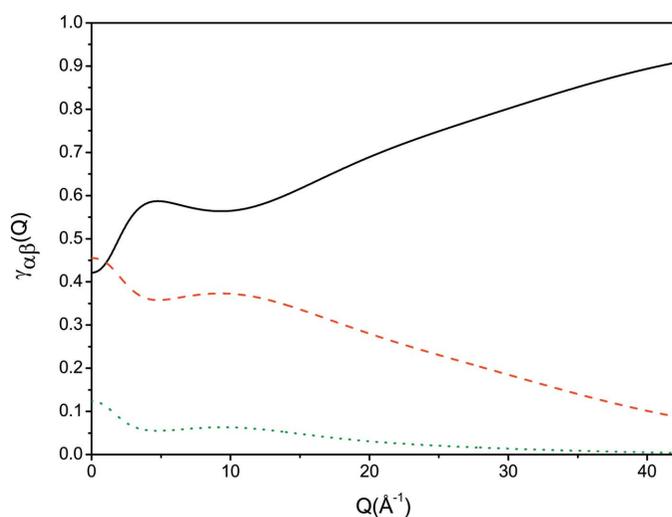


Figure 1

Variation as a function of Q of the LaB₆ Faber–Ziman coefficients: (black solid line) La–La atom pairs, (red dashed line) La–B pairs and (green short-dashed line) B–B atom pairs.

peaks (Q_{damp} parameter set to 0.02 in *PDFFIT*) was added. This corresponds to experimental Q -resolution effects and makes the partial functions reach their asymptotic value of zero at finite R value (500 \AA in the present case). The FZ coefficients were computed using the scattering factors given by Waasmaier & Kirfel (1995) and were Fourier transformed in order to obtain the relevant $a_{\alpha\beta}(0)$ and $w_{\alpha\beta}(r_k)$ coefficients. The Q_{max} effect was assessed by choosing two different values in the calculations: a relatively short one, $Q_{\text{max}} = 17 \text{ \AA}^{-1}$, typical for X-ray laboratory instruments and a larger one, $Q_{\text{max}} = 40 \text{ \AA}^{-1}$, common with synchrotron sources. Finally, for the calculation using equation (7), the convolution by the cardinal

sine function resulting from the truncation of the Fourier transform was also performed.

The FZ coefficients are plotted in Fig. 1. The $a_{\alpha\beta}(0)$, $w_{\alpha\beta}(r_k)$ and $\gamma_{\alpha\beta}^{\text{eff}}$ coefficients calculated for the two values of Q_{max} are gathered in Tables 1 and 2. The synthetic LaB₆ PDFs calculated using equations (1), (15) and (7) for the two values of Q_{max} are plotted in Figs. 2 and 3. We can observe in Fig. 1 the large departure of the FZ coefficients from their values calculated at $Q = 0$, in particular the dramatic decrease of $\gamma_{\text{B-B}}$ and increase of $\gamma_{\text{La-La}}$ with increasing Q . This clearly illustrates the prominent effect of heavy elements at large Q and the fact that taking $Z^{\text{eff}} = Z$ [i.e. $\gamma_{\alpha\beta}^{\text{eff}} = \gamma_{\alpha\beta}(0)$] for both La and B atoms in the WKM approximation is not a pertinent choice. This latter point is confirmed in Figs. 2 and 3, where it appears that the WKM approximation leads to very poor results and significant errors with respect to the exact calculation. With our expression, on the contrary, the accuracy is very good even at relatively small k . In the case where

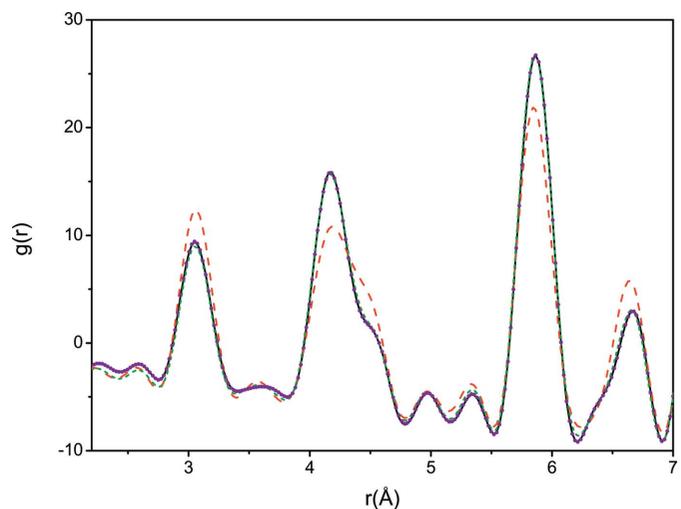


Figure 2

Synthesized LaB₆ PDFs calculated with $Q_{\text{max}} = 17 \text{ \AA}^{-1}$ using equation (1) (black solid line), equation (7) (red dashed line), equation (15) with $k = 0$ (green short-dashed line) and equation (15) with $k = 5$ (purple filled circles).

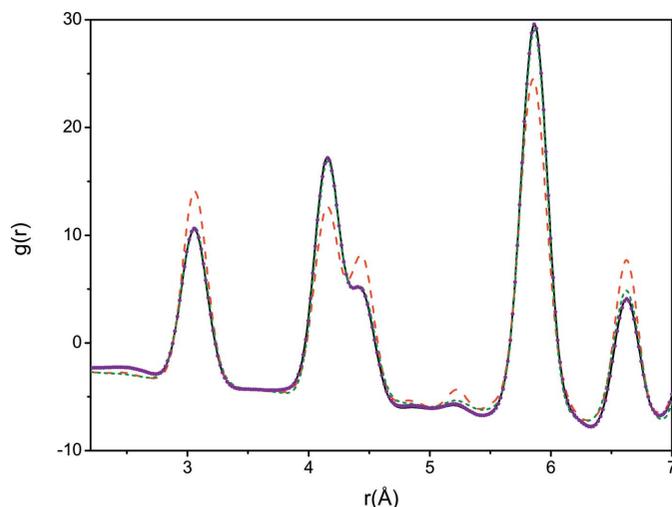


Figure 3
Synthesized LaB_6 PDFs calculated with $Q_{\text{max}} = 40 \text{ \AA}^{-1}$ using equation (1) (black solid line), equation (7) (red dashed line), equation (15) with $k = 1$ (green short-dashed line) and equation (15) with $k = 12$ (purple filled circles).

$Q_{\text{max}} = 17 \text{ \AA}^{-1}$, differences are already hardly noticeable except in the baseline for $k = 0$ (i.e. $g_{\alpha\beta}^X = g_{\alpha\beta}$), and are completely negligible for $k = 5$. In the case where $Q_{\text{max}} = 40 \text{ \AA}^{-1}$, we obtain a reasonable approximation with $k = 1$ and an expansion up to the 12th term is necessary to achieve a perfect match. The optimum values for k thus depend on the experimental conditions (in particular on Q_{max}) and the chemical composition of the sample but remain low and reasonable from a computational point of view. Most of the computation time in equation (16) corresponds to partial function evaluation and only a small overhead is needed to add shifted ‘ghost’ functions. However, although consistent with the decreasing trend of $w_{\alpha\beta}(r_k)$ with k , the optimum value of k does not seem directly related to a threshold value of $w_{\alpha\beta}(r_k)$. This makes its exact prediction not easy in practice. However, as stated above, changing k does not require new function evaluation, which should make the software implementation easily tunable. Consequently, the question of predicting the optimal k is not essential. One can imagine starting with some default k value and increasing it to reach convergence on the total PDF.

5. Conclusion

Extracting fine structural information from the experimental PDF generally requires the precise calculation of a simulated PDF from a structure model. For multi-component systems, this is usually achieved by first computing partial PDFs (which only depend on the structure) from the model and then combining them to construct the total PDF. Thus far, the only

exact formula for constructing the PDF was for neutron scattering experiments, for which the PDF is a weighted (by the Faber–Ziman factors) linear combination of partial functions. In the case of X-ray experiments, only an approximate definition has existed since the pioneering work of Warren and coworkers in 1936. In the present paper, we have derived the exact and explicit form of the experimental PDF with respect to partial PDFs, which allows exact and efficient calculation of the PDF from any structure model. It is shown that the PDF can still be obtained by combining partial functions but in a more complicated way than for the neutron case. It can be expressed as a weighted linear combination of modified partial functions. The weights are exactly and uniquely defined as the mean values of the Faber–Ziman factors over the $[0, Q_{\text{max}}]$ interval. The modified partial functions are obtained by superposing on the true partial PDFs their weighted and symmetrically shifted ‘ghosts’. Although the superposition of the shifted ‘ghosts’ must theoretically be expanded to infinity, it is shown that only a few terms are necessary for achieving a perfect approximation, which makes our expression practical and efficient. Finally, it is worth noting that this explicit definition could also be useful for obtaining explicit and exact expressions of quantities involving integral operation on the PDF over a given r range, such as for example the calculation of coordination numbers. We hope that this work will constitute a solid basis to extract subtle structural features from X-ray total scattering PDF analysis and will contribute to the further development of the PDF method.

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