



# A new approach to the determination of the uncertainty in neutron diffraction experiments with isotopic substitution method



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## ABSTRACT

Neutron diffraction experiment with isotopically substituted substances is a powerful approach claiming to yield unambiguous information about the local atomic structure in disordered materials. This information is expressed in the partial structure factors, and extracting them from a series of measurements requires solution of a set of linear equations that is affected by experimental errors. In this article, we suggest a method for the determination of the optimal set of H/D compositions with or without taking into account the experimental error. For the case of water, our investigations show that the selection of the isotope concentrations and the distribution of measurement time among the various samples have a critical role if one wants to utilize the limited neutron beam time efficiently.

It is very well known that measurements of pure H<sub>2</sub>O introduce fairly large errors in the partial structure factors due to its very strong incoherent scattering. In water and methanol as examples, we investigated the propagation of random errors to the partial structure factors using partial pair-correlation functions from molecular dynamics simulation. It is shown in the example of water that it is not worthwhile to measure pure H<sub>2</sub>O.

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## 1. Introduction

In a disordered material containing  $n$  distinguishable elements, the  $n \times (n + 1)/2$  independent structure factors can be determined in principle from the same number of scattering experiments through the inversion of a set of linear equations. Sets of independent scattering intensities can be obtained by isotopic substitution in the case of neutron scattering. The general principles of the isotopic substitution technique are rather simple. Samples with different isotopic compositions (isotopes with markedly different coherent scattering lengths) yield different diffraction patterns while the underlying structural features remain unchanged. The neutron diffraction isotopic substitution (NDIS) method has been described in several articles [1]; it has been applied successfully for many years to a wide range of liquids, e.g., water [2], ethanol [3], aqueous glycine solution [4], formic acid [5], ethanediol [6], aqueous liquid mixtures [7], aqueous solutions [8], and polymer electrolytes [9], as well as to glassy materials. However, some important unresolved issues remain. In particular, the sensitivity of the final results (partial structure or correlation functions) [10] to the details of the sample preparation and handling as well as to the data treatment (normalization, correction term) remains an open question.

The technique has been applied successfully for many years as a method of obtaining the partial structure factors of systems of type  $RX_n$ , where  $R$  denotes a central part of this system without substitution and  $X_n$  denotes the isotope to be substituted. For example, in the case of water or methanol, the oxygen atom or the CD<sub>3</sub>O group can be denoted as  $R$  and  $X$  means hydrogen or deuterium.

Matrix formalism can be used to describe the relation between experimental total and partial structure factors or radial distribution functions

$$\mathbf{F} = \mathbf{W} \times \mathbf{Y} \quad (1)$$

where a column vector  $\mathbf{y}_j = (RR, RX_n, X_n X_n)^T$  of matrix  $\mathbf{Y}$  contains the partial structure factors (psf) or partial pair-correlation functions (ppcf)  $RR$ ,  $RX_n$ , and  $X_n X_n$  to be obtained at the  $j$ -th  $s$  or  $r$  value (inverse or direct space variables),  $\mathbf{W}$  is the neutron scattering weighting matrix. The column vectors of matrix  $\mathbf{F}$  are  $\mathbf{f}_j = (f_1, f_2, f_3)^T$  for the independent experimental total structure functions at the  $j$ -th  $s$  or  $r$  variable. For the sake of simplicity we use the notation  $\mathbf{f}_j$  for the  $j$ -th column vector of  $\mathbf{F}$  and we use  $f_i$ , if the  $i$ -th element of one of the vectors is concerned.  $f_1, f_2$ , and  $f_3$  mean for example results on samples with different isotopic compositions, e.g., for water D<sub>2</sub>O, H<sub>2</sub>O, and 0.64H<sub>2</sub>O + 0.36H<sub>2</sub>O, where the latter is called “null mixture”.

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The rows of the matrix  $\mathbf{W}$ ,  $W_{RR,i}$ ,  $W_{HH,i}$ ,  $W_{RH,i}$  are the corresponding elements of the neutron scattering weight matrix, and they can be given in the following form

$$\begin{aligned} W_{RR,i} &= b_{RR}^2 \\ W_{HH,i} &= (x_{H,i} \cdot b_H + (1-x_{H,i}) \cdot b_D)^2 \\ W_{RH,i} &= 2 \cdot b_{RR} \cdot (x_{H,i} \cdot b_H + (1-x_{H,i}) \cdot b_D) \end{aligned} \quad (2)$$

where  $x_{H,i}$  is the mole fraction of H, and  $b_{RR}$ ,  $b_H$  and  $b_D$  are the scattering lengths of the R group, hydrogen ( $-0.376$  fm) and deuterium ( $0.664$  fm), respectively. Obviously, the elements of the  $\mathbf{W}$  matrix only depend on the mole fraction of hydrogen.

There are several methods to solve Eq. (1). Throughout this work, we used the singular value decomposition (SVD) method to solve the sets of linear equations. This is a standard method to characterize how the experimental and systematic errors propagate into the results. According to this method, the inverse of  $\mathbf{W}$  is

$$\mathbf{W}^{-1} = \mathbf{V} \text{diag}(1/\sigma_i) \mathbf{U}^T \quad (3)$$

where  $\mathbf{V}$  and  $\mathbf{U}$  are orthogonal matrices and  $\text{diag}(1/\sigma_i)$  is a diagonal matrix formed from the  $\sigma_i$  singular values of the  $\mathbf{W}$  matrix. In this case, if the right side of the Eq. (1) has a certain error, then

$$\delta \mathbf{y}_j = \sum_i \frac{\delta \mathbf{f}_j \mathbf{u}_i}{\sigma_i} \quad (4)$$

where the  $\mathbf{u}_i$  and  $\mathbf{v}_i$  are the orthonormal column vectors of  $\mathbf{U}$  and  $\mathbf{V}$ . This equation shows that  $\mathbf{y}_j$  will be most sensitive to the error associated with the smallest singular value. The components of  $\mathbf{v}_j$  are the projections to the  $RR$ ,  $RX_n$  and  $X_n X_n$  directions, respectively.

In a previous paper [11], we studied how an inequality known from linear algebra can be used for the determination of the inherent uncertainties of the  $psf$ -s or  $ppcf$ -s determined from neutron diffraction isotopic substitution experiments. This inequality establishes a relationship between the relative uncertainties of the partial pair-correlation functions or partial structure factors, the norm of the neutron scattering weighting matrix and the relative error of the experiments, as given by Eq. (4) of [11]:

$$\frac{\|\delta \mathbf{y}_j\|}{\|\mathbf{y}_j\|} \leq \|\mathbf{W}\| \times \|\mathbf{W}^{-1}\| \frac{\|\delta \mathbf{f}_j\|}{\|\mathbf{f}_j\|} \quad (5)$$

The quantity  $\|\mathbf{W}\| \times \|\mathbf{W}^{-1}\|$ , denoted as  $\kappa$  hereafter, is known as the condition number, and it is a measure of the error amplification due to the employed inversion. A set of linear equations is termed “well conditioned” when the conditional number is small [10c,12]. The theoretical smallest value is  $\kappa = 1$ . If the solution is very sensitive to the values of the coefficients, the problem is “ill conditioned.” It is expected in the cases, if the matrix is nearly singular, i.e., some of its rows are almost linearly dependent. The second term of the right hand side of Eq. (5),  $\|\delta \mathbf{f}_j\|/\|\mathbf{f}_j\|$ , is related to the relative uncertainties in the experiment. During our work, there is an underlying assumption that all the errors are confined to the experimental vector  $\mathbf{f}_j$ . Unfortunately, this assumption may be unrealistic; errors in scattering lengths and mole fractions may incorporate into the inequality an additional term, which would be proportional to  $\|\delta \mathbf{W}\|/\|\mathbf{W}\|$ , where  $\delta \mathbf{W}$  is the uncertainty of the  $\mathbf{W}$  matrix.

We used in our test cases the Euclidean vector and matrix norms [12]

$$\|\mathbf{f}\|_2 = \left( \sum_i f_i^2 \right)^{0.5} \quad (6)$$

$$\|\mathbf{W}\|_2 = \left( \sum_{i,j} w_{ij}^2 \right)^{0.5} \quad (7)$$

In the case of the Euclidean matrix norm,  $\|\cdot\|_2$ , the condition number can be expressed as

$$\kappa = \frac{\sigma_{\max}}{\sigma_{\min}} \quad (8)$$

where  $\sigma_{\max}$  and  $\sigma_{\min}$  are the largest and smallest singular values of the weighting matrix. We chose the SVD algorithm to solve the sets of linear equations, because it provides the singular values to calculate condition number, as well.

The relative experimental error (sampling errors, absolutisation error, modelling errors, and instrumental errors, coming mainly from the H atom due to its large inelastic scattering power) is defined as

$$\begin{aligned} I_{\text{tot}}^j &= I_{\text{coh,selfscat}}^j + I_{\text{incoh,selfscat}}^j + I_{\text{scat}}^j \\ I_{\text{scat}}^j &= \left( \sum_i \langle b_i \rangle^2 \right) \\ \mathbf{f}_j &\cong I_{\text{scat}}^j \\ d\mathbf{f}_j &\cong \frac{I_{\text{tot}}^j}{I_{\text{scat}}^j} \end{aligned} \quad (9)$$

where  $b_i$  is the neutron scattering length of atom  $i$ ;  $I_{\text{scat}}$  denotes the scattering power and  $I_{\text{tot},j}$  is the total scattering (coherent, incoherent) intensity of the  $j$ -th experiment. This error mainly depends on the inelasticity of the scattering centre. The scattering lengths for the investigated systems are given in Table 1.

With the above mentioned equation, it should be possible to minimize the upper limit of the solution error, i.e., the resulting  $psf$ -s or  $ppcf$ -s, by determining the set of  $x_{H,i}$  mole fractions for which the conditional number of the neutron scattering weighting matrix has a minimal value.

In our previous study [11] we applied our numerical estimations of the optimum set of  $x_{H,i}$  for several systems investigated earlier by isotope substitution experiments. An additional constraint was used there, namely, that the condition number should be minimal when one of the measurements is made on a completely deuterated solution. We showed also that if the presented method is applied to an over-determined set of equations (i.e., containing more equations than unknowns), the condition number is significantly reduced in all cases.

## 2. Uncertainty analyses in NDIS experiments using optimization

In the first part of the present work, we applied a full optimization process (using the simplex algorithm) without any constraint for any concentration. We investigated the extreme values of the condition number (first part of the right side in Eq. (5)) as a function of compositions and we obtained the optimum set of hydrogen concentrations for which the condition numbers are minima for both the uniquely determined and the over-determined equations.

The variation of the condition number with respect to the increasing number of experiments is shown in Fig. 1 in the case of water. The corresponding compositions are collected in Table 2. We apply a notation

**Table 1**  
The neutron scattering lengths of the investigated systems [13].

	Water	Methanol	Ethanol	Ethane-diol
$b_R$ ( $10^{-14}$ m)	0.583	3.248	5.246	3.828
$b_H$ ( $10^{-14}$ m)	-0.748	-0.374	-0.374	-0.748
$b_D$ ( $10^{-14}$ m)	1.334	0.667	0.667	1.334

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