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Denoising NMR time-domain signal by singular-value decomposition accelerated by graphics processing units

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ABSTRACT

We present a post-processing method that decreases the NMR spectrum noise without line shape distortion. As a result the signal-to-noise (S/N) ratio of a spectrum increases. This method is called Cadzow enhancement procedure that is based on the singular-value decomposition of time-domain signal. We also provide software whose execution duration is a few seconds for typical data when it is executed in modern graphic-processing unit. We tested this procedure not only on low sensitive nucleus ^{29}Si in hybrid materials but also on low gyromagnetic ratio, quadrupole nucleus ^{87}Sr in reference sample $Sr(NO_3)_2$. Improving the spectrum S/N ratio facilitates the determination of T/Q ratio of hybrid materials. It is also applicable to simulated spectrum, resulting shorter simulation duration for powder averaging. An estimation of the number of singular values needed for denoising is also provided.

1. Introduction

The accuracy and efficiency of data post-processing and quantification are paramount for NMR applications. In medical applications, reliable estimates of NMR spectral parameters must be deduced from low signal-to-noise (S/N) ratio spectrum [1]. In solid state NMR, time-domain signal averaging is common practice for improving S/N ratio of spectrum, but this increases NMR machine time. We apply the Cadzow enhancement procedure [2] for denoising NMR time-domain signal, resulting spectrum with better S/N ratio, which permits us to shorten NMR machine time.

This enhancement procedure is based on the singular-value decomposition (SVD) of an Hankel matrix [3] constructed with the NMR time-domain signal. Theoretical investigations focused on signal enhancement of a sum of sinusoids [2,4]. This procedure is already involved in numerous NMR applications [5–12]. Denoising signal becomes a preliminary step before the application of model-fitting methods to extract spectral parameters.

SVD of a large matrix is a computationally-intense operation, which limited its introduction in NMR processing software. Fortunately, modern graphics processing unit (GPU), whose original purpose is to improve graphics acceleration operations in 3D computer games, becomes programmable for general-purpose computation [13–17]. GPU becomes a co-processor of the main central processing unit for massive parallel computation.

In this article, we first describe the Cadzow enhancement procedure for denoising NMR time-domain signal. Then we test our SVD programs [18,19] not only to insensitive nucleus ^{29}Si in hybrid materials, but also to low gyromagnetic ratio, quadrupole nucleus ^{87}Sr ($I=9/2$, 7.02% natural abundance) [20] in reference sample $Sr(NO_3)_2$ studied by Larsen and co-workers [21] and Bowers and co-workers [22]. Furthermore, ^{29}Si MAS spectrum with large S/N ratio facilitates the determination of T/Q ratio of hybrid materials from spectrum decomposition. The Q species describe the connectivity of the silicate network and the T species are indicative of a silicon atom from a silicate network that is bound to a carbon atom. We also denoise time-domain signals simulated with SIMPSON [23], whose line shapes are asymmetric. Thanks to modern GPU, SVD execution duration has been shorten dramatically, from 80 down to 2 s for typical solid state NMR data.

2. Cadzow enhancement procedure

The enhancement procedure of NMR time-domain signal involves Hankel matrix [3,24], **H**, in which each descending diagonal from right

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to left is constant:

$$H_{i,j} = H_{i-1,j+1} \quad (1)$$

First, we fill the first row and the last column of **H** with the complex numbers of the time-domain signal [2,25]. Fig. 1A shows a simple 4×3 matrix **H** where the time-domain digitised data are the series [*a*, *b*, *c*, *d*, *e*, *f*] coloured in red. The remaining matrix elements are filled according to Eq. (1). Second, **H** is decomposed [1,26] as shown in Fig. 1B where the singular-value matrix **Σ** consists of three positive values Σ_1, Σ_2 and Σ_3. Third, we zero the weakest singular value Σ_3. Fourth, we construct a new 4×3 matrix with this reduced number of singular value (N_{SVD}) matrix as shown in Fig. 1C; however, this new matrix is not of Hankel structure. Finally, we restore this matrix to Hankel one by averaging the elements of each descending diagonal from right to left as shown Fig. 1D. The denoised time-domain signal is provided by the first row and the last column of this matrix, which are coloured in red in Fig. 1D. If the corresponding spectrum is still too noisy, we repeat the procedure to the denoised time-domain signal by keeping the number of singular values smaller than or equal to the previous case. Cadzow [2] used Toeplitz matrix [27] instead of Hankel one in his presentation, in which each descending diagonal from left to right is constant.

From a practical point of view, an $m \times n$ Hankel complex matrix represents a free induction decay (FID) whose size is $N = m + n - 1$. The number of columns n of **H** should be much larger than the optimum number of singular values, because the enhanced signal strongly depends on n and N [1].

As we also want to improve the time-domain signals of quadrupole nuclei [28], which usually have asymmetric line shapes, we proceed in another way as shown the flow chart in Fig. 2. The problem is that the optimum number of singular values cannot be guessed. We first apply the line broadening (LB) processing to decrease the noise [4]. After the decomposition of **H**, it is simpler to start with the first singular value, which has the

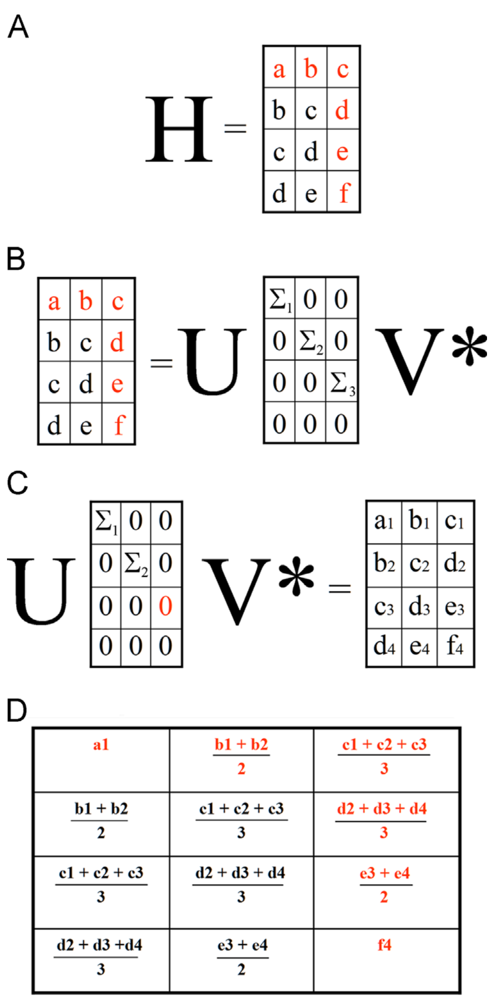

Fig. 1. Cadzow enhancement procedure: (A) 4×3 Hankel matrix **H** containing the digitised noisy time-domain signal series [*a*, *b*, *c*, *d*, *e*, *f*] in its first row and its last column; (B) decomposition of **H** where the three singular values are Σ_1, Σ_2 and Σ_3; (C) the time-domain signal series is denoised by zeroing the smallest singular value Σ_3 ($N_{SVD}=2$) then a new 4×3 Hankel matrix is recomposed; (D) the matrix elements resulting from (c) are averaged so that the matrix is of Hankel structure; the denoised time-domain signal series is located in its first row and its last column. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

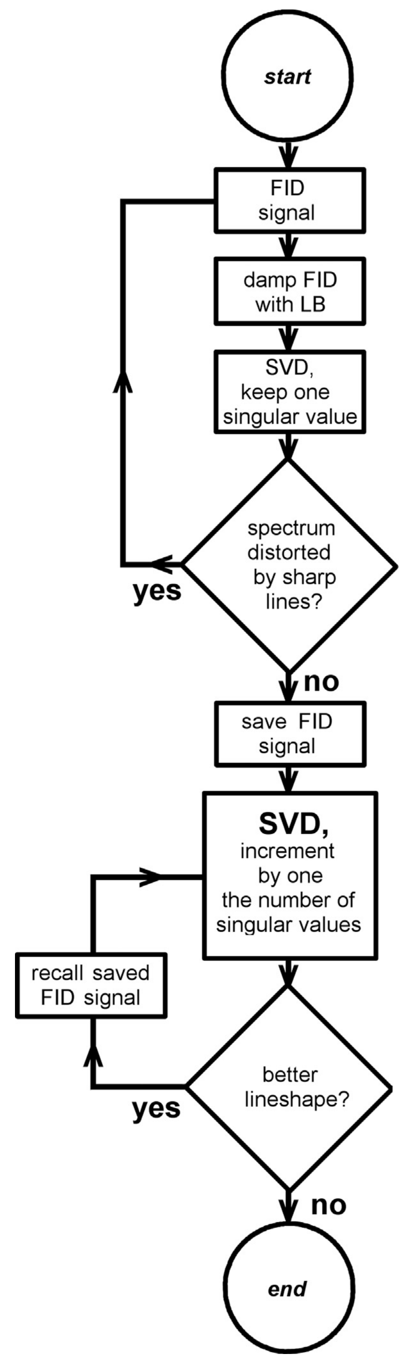

Fig. 2. Flow chart for SVD denoising time-domain signal, free induction decay (FID) for short.

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