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Noise Suppression of NMR Signal by Piecewise Polynomial Truncated Singular Value Decomposition

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***Abstract*:** Singular value decomposition (SVD) has been used during past few decades in the advanced NMR data processing and in many applicable areas. A new modified SVD, piecewise polynomial truncated SVD (PPTSVD) was developed for the large solvent peak suppression and noise elimination in NMR signal processing. PPTSVD consists of two algorithms of truncated SVD (TSVD) and L_1 problems. In TSVD, some unwanted large solvent peaks and noises are suppressed with a certain soft threshold value while signal and noise in raw data are resolved and eliminated out in L_1 problem routine. The advantage of the current PPTSVD method compared to many SVD methods is to give the better S/N ratio in spectrum, and less time consuming job that can be applicable to multidimensional NMR data processing.

INTRODUCTION

Most NMR spectroscopists are primarily interested in the resonance peaks giving molecular information and in even very tiny peaks directly originated from sample. However, efforts for obtaining the exact information of NMR signals are disturbed by typical noises arising from many reasons such as imperfections of instrumentation and conditions of sample during the NMR data collections. Many useful techniques enhancing the signal to noise ratio by eliminating typical noise or unwanted huge solvent peaks have been developed in past few decades to overcome this problem. Many window functions were developed at the beginning of the time domain signal, and they have given a powerful ability of noise reduction or resolution enhancement. Even though many window functions have been useful in signal processing, the serious limitation of the noise reduction is given by the decrease of spectral resolution during the noise elimination process. Many efforts have been tried to overcome this limitation, and some successful methods including linear prediction (LP)[1,2], maximum entropy reconstruction (MaxEnt)[3,4], maximum likelihood meth-

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od (MLM)[5], etc, have been developed as an advanced tool of NMR signal processing.

Singular value decomposition (SVD) has been used to obtain linear prediction (LP) coefficients[1] in an area of NMR signal processing for a long time. Because this method gives a stable and promising result, most people have use SVD to acquire LP coefficients. SVD is an important mathematical method to identify the pure signal from the noise-contaminated signals. The resulting eigenvalues directly give a information of signal intensities. In recent, noise elimination method[6] and large solvent peak suppression method[7,8] have been developed by using basic properties of SVD.

Hansen has developed piecewise polynomial truncated singular value decomposition (PPTSVD) method to identify discontinuity of the earth's radial density function[9]. In his work, PPTSVD gives a more acceptable result as compare to other SVD based methods. The discontinuity obviously identified from unclear original earth radial density signal. These methods were applied to the advanced NMR data processing in obtaining a clear signal from noise-contaminated signal and in suppression large solvent peaks in this work. Basic theories of SVD and PPTSVD are described to simplify the mathematical method, and to develop algorithms. All mathematical algorithms were systematically coded with C++/C language and were incorporated into HyNMR™(Hanyang NMR data processor) for the advanced NMR data processing.

THEORETICAL BACKGROUND

Singular Value Decomposition (SVD)

The SVD matrix A for a given NMR signal can be represented by $m \times n$ dimension elements as in Eq. (1)

$$A = U\Sigma V^T = \sum_{i=1}^{n} u_i \sigma_i v_i^T \quad , \tag{1}$$

where these matrices U and V are the square matrices carrying $m \times m$ and $n \times n$ dimensional size, respectively. These matrices basically have an orthonormal property, i.e., $U^T U = V^T V = I_n$, and are related to the phase of the matrix A. The upper capital letter T refers to the transverse matrix. Where $\Sigma = diag(\sigma_1, \sigma_2, \sigma_3, \cdots, \sigma_n)$ is a diagonal matrix whose diagonal elements σ_i. The singular values satisfy $\sigma_1 \geq \sigma_2 \geq \cdots \geq \sigma_n \geq 0$ and its mean is the magnitude of the elements of matrix A. A certain NMR signal represented with matrices can be explained with a simple matrix manipulation as shown in Figure 1. An arbitrary phase of NMR signal can be changed with V^T matrix, and subsequently spectral magnitude can be adjusted with Σ matrix, and finally an reorientation to the original phase can be achieved by the matrix U operation. In other words, the operational components of A

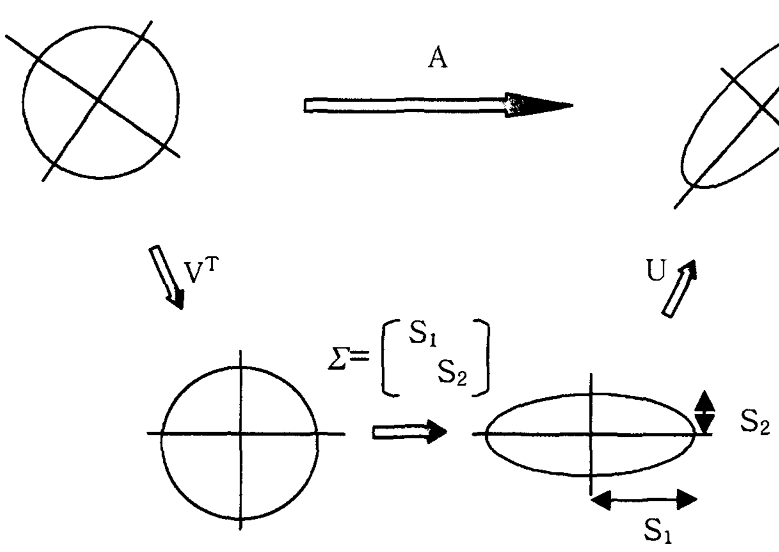

Fig. 1. A graphical presentations showing a general SVD procedure. A resulting matrix of the operation of matrix A can be divided into three matrix operations, a phase correction (V^T), an adjustment of spectral magnitude (Σ), and finally an reorientation to the original phase (U).

can be manipulated by three decomposed matrix operations. The phase of original NMR signal can be changed by the operation of matrixes U and V. In order to suppress large unwanted signal or to remove small components (noises), the matrix Σ has only to be properly managed.

Truncated Singular Value Decomposition (TSVD)

In this method, one simply ignores all the small singular values originated from noise, and approximates a rank-n full matrix A_n by a rank k matrix A_k in which only the largest k singular values are retained:

$$A_k = \sum u_i \delta_i v_i^T \qquad \text{with} \quad k < n \tag{2}$$

In this way, matrix A_n is replaced by A_k that has a well defined null space of dimension n-k spanned by the right singular value vectors $v_{k+1},\cdots\cdots,v_n$. Then the original linear system of Eq. (2) is replaced by the following problem set of Eq. (3), and the solution of Eq. (3) called the TSVD solution x_k is given by Eq. (4).

$$\min\|x\|_2 \text{ subjected to } \|A_k x - b\|_2 = \min \tag{3}$$

$$x_k = \sum_{i=1}^{k} \frac{u_i^T b}{\delta_i} v_i \tag{4}$$

Piecewise Polynomial Truncated Singular Value Decomposition (PPTSVD)

The PPTSVD method solves the problem[9,10] of Eq. (5) where L is a discrete approximation to a derivative operator, and is represented as a matrix notation (6).

$$\min\|Lx\|_1 \text{ subjected to } \|A_k x - b\|_2 = \min \tag{5}$$

$$L_1 = \begin{pmatrix} 1 & -1 & & \\ & \ddots & \ddots & \\ & & 1 & -1 \end{pmatrix} \tag{6}$$

The solution of Eq. (5) is obtained by solving the Eq. (7) giving values of w

$$\min\|(LV_k)w - Lx_k\|_1 \tag{7}$$

The resulting PPTSVD solution, $\bar{x}_k$ consists of the TSVD solution, x_k and a modification factor, $-V_k w_k$ term as illustrated in Eq. (8).

$$\bar{x}_{L,k} = x_k - V_k w_k \tag{8}$$

A self-consistent value for the solution of Eq. (8) is accomplished in that point an extra norm, $\|\bar{x}_{L,k}\|_2$ equals to the square root of the value of TSVD term and value of w.

$$\|\bar{x}_{L,k}\|_2 = (\|x_k\|_2^2 + \|w_k\|_2^2)^{1/2} \tag{9}$$

The important mathematical expressions necessary for the coding and application of PPTSVD method to NMR data processing are summarized in Figure 2 as a flow chart diagram.

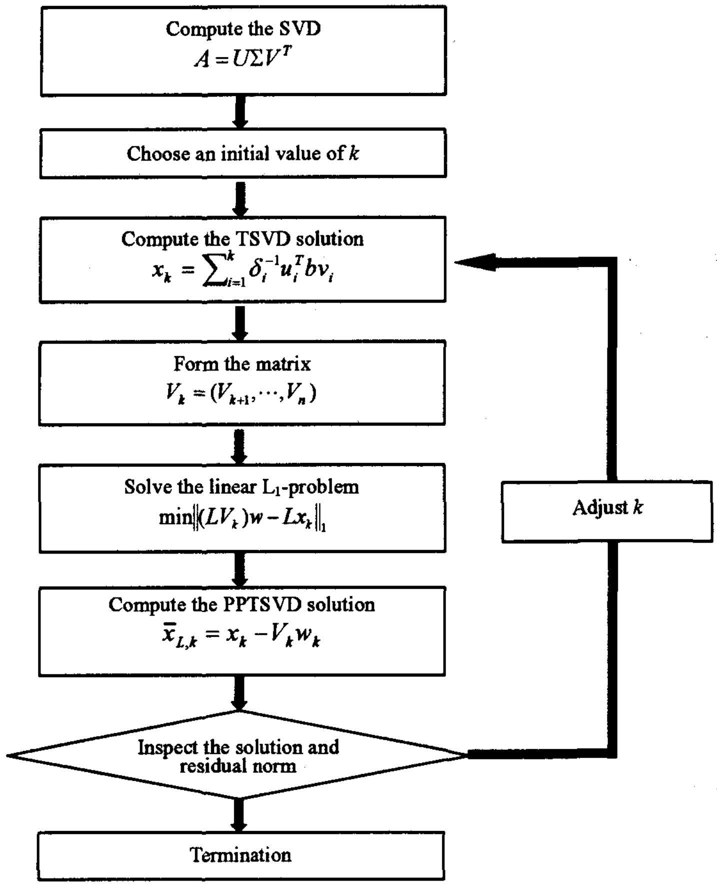

Fig. 2. A flow diagram of PPTSVD calculations applying to the advanced NMR signal processing

EXPERIMENTS

NMR experiment

10*m*M Zinc binding Leutenizing hormone releasing hormone (Zn-LHRH) dissolved in DMSO-d6/H_2O mixed solvent. The large HOD peak at off resonance region was used to test current NMR data processing. NMR data were recorded on a Varian UNITY plus 500 MHz NMR spectrometer with 2048 data points. This data converted to HyNMR data format and processed on HyNMR multidimensional NMR data processor.

Program Coding

C++/C code routines to suppress the noise and large unwanted solvent peak using

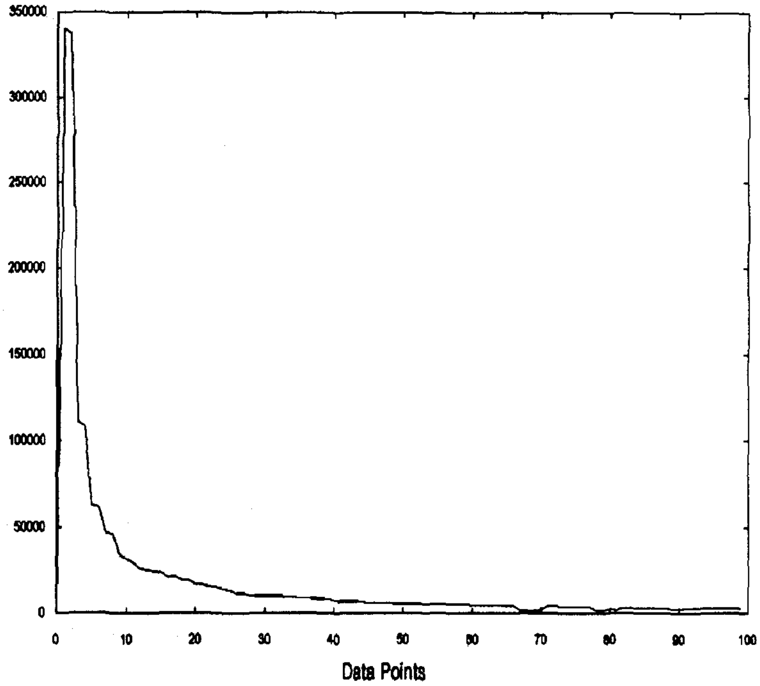

Fig. 3. Diagonal elements of Σ matrix having magnitude information showing first 4 points larger than others and last 20 points with noise intensity information.

basic SVD properties were programmed on SGI Octane workstation. These routines were completely cooperated into HyNMR NMR data processing software.

In conventional SVD methods, the first step of this program is to make Toeplitz matrix from the NMR raw signal, and then the diagonal elements of Σ matrix are manipulated after the execution of SVD calculation. First few points are necessary to be replaced with zero or given small value in order to suppress the large solvent peak, and then the peaks suppressed Toeplitz matrix are reconstructed by matrix product operation. The noise suppression procedure are accomplished by assuming that last few points close to zero are from the noises, and by calaulating the average value and standard deviation of signals. The other parts of eigenvalues are modified by the calculated standard deviation value to obtain a noise free signal. The extract NMR signal can be obtained by filling zero to the tail region and noise region, and subsequently by reconstructing the matrix.

In PPTSVD methods, the programs solve TSVD and L_l-problem to determine the optimal solution of equation. First step of whole procedures is TSVD calculation. Second step is to find the solution of Eq. (7) which gives the modification factor with the results of first step. Third step is to calculate the exact solution with the modification factor obtained from previous step. Figure 2 illustrates the detail procedure of stepwise calculation methods.

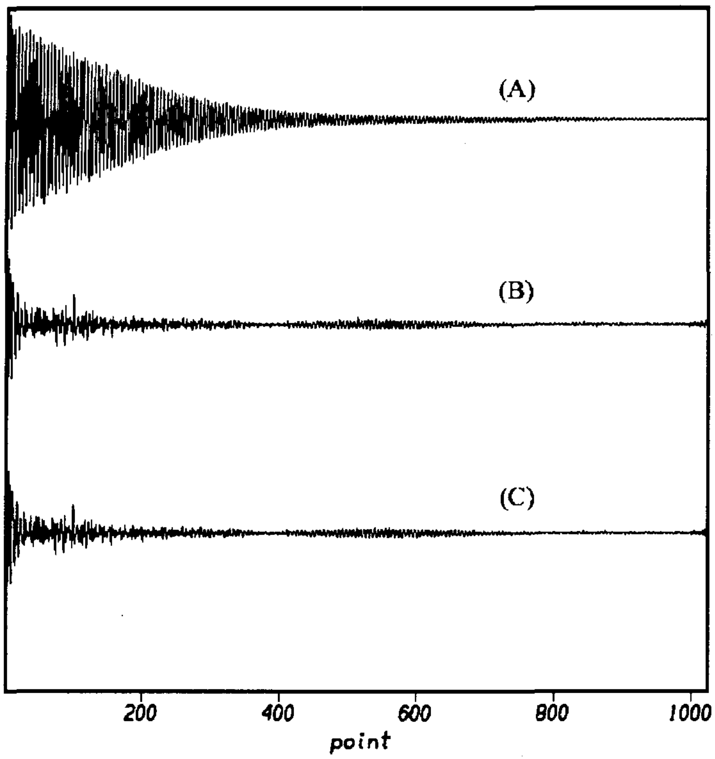

Fig. 4. Free induction decay carrying a large water peak (A), and after treatment of large peak suppression routine (B), and an enhanced NMR signal after the additional noise elimination procedure (C).

RESULTS and DISCUSSION

Toeplitz matrix was constructed with a rank of 100 in this work. As exhibiting in Figure 3, the Σ matrix consists of four large values in front of graph, and small or almost flat tail region through the diagonal components after SVD calculation. The diagonal elements of Σ matrix correspond to the magnitude of each peak of the spectrum.

The large four points in front represent huge solvent peak, so zero filling to four points and product of matrices of U and V^T gave a water eliminated spectrum. The last 20 points close to zero can be interpreted as magnitude of noise. Noise was suppressed by applying some selected noise points to entire matrix elements in previous studies, however, ranks are adjusted to 80 points excepting the noise components to resolve the magnitude in the current PPTSVD method giving better spectrum. Computations were made after front 4 data points were chosen as magnitude of water peak and last 20 points were chosen as magnitude of noise. Resulting spectrum shows effective suppression of water signal, and

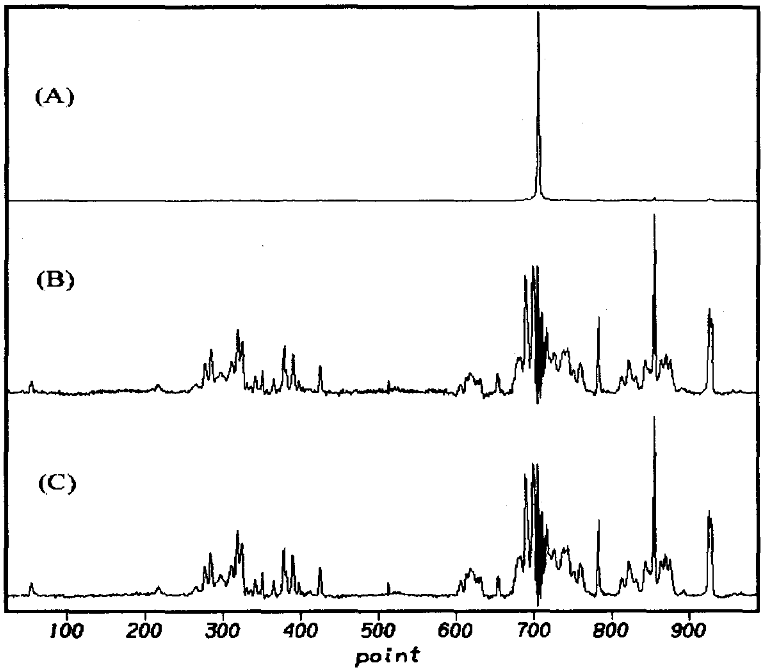

Fig. 5. ^{1}H-NMR spectrum of Zn-LHRH carrying a large water peak (A), and after treatment of large peak suppression routine (B). An noise reduced spectrum after additional noise elimination procedure (C).

some improvement of spectrum are shown in Figure 4 and 5. SVD and L_1-problem solver are in general both time consuming procedure compared to other processing methods, but this routine is not time consuming computation that sufficiently valuable to apply this procedure for spectrum having large solvent peak and poor S/N ratio. These routines are now completely merged in HyNMR that can be extended to multidimensional NMR data processing. In summary, the advantage of the current PPTSVD method compared to many SVD methods is to give the better signal enhanced spectrum, and less time consuming job that can be applicable to multidimensional NMR data processing.

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