

Structure Assisted NMF Methods for Separation of Degenerate Mixture Data with Application to NMR Spectroscopy

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ABSTRACT

In this paper, we develop structure assisted nonnegative matrix factorization (NMF) methods for blind source separation of degenerate data. The motivation originates from nuclear magnetic resonance (NMR) spectroscopy, where a multiple mixture NMR spectra are recorded to identify chemical compounds with similar structures. Consider the linear mixing model (LMM), we aim to identify the chemical compounds involved when the mixing process is known to be nearly singular. We first consider a class of data with dominant interval(s) (DI) where each of source signals has dominant peaks over others. Besides, a nearly singular mixing process produces degenerate mixtures. The DI condition implies clustering structures in the data points. Hence, the estimation of the mixing matrix could be achieved by data clustering. Due to the presence of the noise and the degeneracy of the data, a small deviation in the estimation may introduce errors in the output. To resolve this problem and improve robustness of the separation, methods are developed in two aspects. One is to find better estimation of the mixing matrix by allowing a constrained perturbation to the clustering output, and it can be achieved by a quadratic programming. The other is to seek sparse source signals by exploiting the DI condition, and it solves an ℓ_1 optimization. If no source information is available, we propose to adopt the nonnegative matrix factorization approach by incorporating the matrix structure (parallel columns of the mixing matrix) into the cost function and develop multiplicative iteration rules for the numerical solutions. We present experimental results of NMR data to show the performance and reliability of the method in the applications arising in NMR spectroscopy.

Key Words: NMF, convex geometry, sparsity, clustering, NMR.

Mathematics Subject Classification (MSC): 65H10, 65K10, 90C05, 94A12.

1 Introduction

Blind source separation (BSS) is a vibrant area of research in signal and image processing. It attempts to separate source signals from their mixtures without the knowledge of the mixing process. BSS has been playing a central role in a wide range

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of signal and image processing problems such as speech recognition, sound unmixing, image separations, and text mining, to name a few (Choi, Cichocki, Park and Lee, 2005), (Cichocki and Amari, 2005), (Comon and Jutten, 2010). The goal of this paper is to study BSS methods for nearly degenerate mixtures arising from nuclear magnetic resonance spectroscopy (NMR). Being one of the preeminent imaging techniques in chemistry, NMR spectroscopy is frequently used by scientists to determine the molecular structures of organic compounds. We shall consider multiple NMR spectra acquired from a mixture of chemical compounds. Each compound has a unique spectral fingerprint defined by the number, intensity and locations of its NMR peaks. However, when the compounds (component molecules) have similar functional groups, the peaks overlap in the composite NMR spectra making it difficult to identify the compounds involved. This makes the data analysis hopeless unless we can unmix or separate the mixed data into a list of source components (source spectra). The simplest model is the linear mixing model (LMM)

$$X = AS, \text{ with } A_{ij} \geq 0, S_{ij} \geq 0, \quad (1.1)$$

where $X \in \mathbb{R}^{m \times p}$, $A \in \mathbb{R}^{m \times n}$, $S \in \mathbb{R}^{n \times p}$. Rows of X represents the measured mixed signals, rows of S are the source signals. The matrices X, S are functions of an acquisition variable such as time, frequency, position, etc. depending on the underlying physical process. The objective of BSS is to solve for A and S given X . If P is a permutation matrix and D an invertible diagonal matrix, one can immediately notice that $AS = (APD)(D^{-1}P^{-1}S)$, hence (A, S) and $(APD, D^{-1}P^{-1}S)$ are considered equivalent solutions in BSS.

There have been mainly two classes of BSS methods for solving (1.1). The first class of methods belong to statistical regime. Among others, independent component analysis (ICA (Cichocki and Amari, 2005)) is the most well studied statistical BSS approach, it decomposes a mixed signal into additive source components based on the mutual independence of the non-Gaussian source signals. The working condition of ICA requires independent source signals, and it however is not always satisfied by realistic data. For instance, the statistical independence does not hold in the NMR spectra of chemical compounds where molecules responsible for each source share common structural features. The second class of methods are deterministic approaches which include nonnegative matrix factorization (NMF) and geometrical methods. Firstly introduced by Paatero and Tapper (Paatero and Tapper, 1994), later popularized by Lee and Seung (Lee and Seung, 1999), NMF has become the prevalent method for solving nonnegative BSS problems. NMF seeks a factorization of X into product of two non-negative matrices by minimizing the cost function of a certain distance or divergence metric (Choi et al., 2005). NMF does not impose source independence, however, some additional constraints such as sparsity and/or smoothness of the sources and/or the mixing matrix, are often incorporated into NMF to control the non-uniqueness and improve the physical meaning of the solutions.

Geometrical BSS methods are based on convex geometry of the data matrix X . The columns of X are non-negative linear combinations of those of A . In the hyperspectral unmixing (HSI) setting, a condition called pure pixel assumption (PPA) was proposed in (Chang, 2007) which requires that at least one pure pixel of each endmember (source signal) needs to be present in the data. Under this assumption, several approaches such as vertex component analysis (VCA) (Nascimento and Bioucas-Dias, 2005), pixel purity index (PPI) (Boardman, 1993), and N-findr (Winter, 1999) exploited certain

geometric features of hyperspectral images to determine the smallest convex cone enclosing the data. In NMR spectroscopy, PPA was reformulated by Naanaa and Nuzillard (Naanaa and Nuzillard, 2005). The source signals are only required to be non-overlapping at some locations of acquisition variable (NNA). This condition was applied to NMR data unmixing and led to a major success of a convex cone method. Such a local sparseness condition has greatly reduce this problem to a convex one which is solvable by linear programming. Another geometric method is to find a simplex (convex cone) of minimum volume enclosing the data set (Craig, 1994; Li and Bioucas-Dias, 2008). This method amounts to solving a non-convex minimization problem by finding a matrix with minimum volume under a constraint.

The different spectra come from Fourier transform of NMR measurement of absorbance of radio frequency radiation by receptive nuclear spins of the same mixture sample at different time segments when exposed to high magnetic fields. The NMR spectra are nonnegative. Besides, NMR spectra of different chemical compounds are usually not independent, especially as compounds (component molecules) have similar functional groups, the peaks overlap in the composite NMR spectra making it difficult to identify the compounds involved. The geometric BSS method proposed in (Naanaa and Nuzillard, 2005) requires that NMR spectral signals to be non-overlapping at certain acquisition locations while allowed to overlap with each other elsewhere. The NN assumption (NNA) requires the source signals to be strictly non-overlapping at some locations of acquisition variable (e.g., frequency). In other words, each source signal must have a stand-alone peak where other sources are strictly zero there. Such a strict sparseness condition leads to a dramatic mathematical simplification of a general non-negative matrix factorization problem (1.1) which is non-convex. Geometrically speaking, the problem of finding the mixing matrix A reduces to the identification of a minimal cone containing the columns of mixture matrix X . The latter can be achieved by linear programming. In this paper, we consider how to separate the data if NN condition is not satisfied, and the mixing process is known to be degenerate. We are concerned with the regime where source signals do not have stand-alone peaks yet one source signal dominates others over certain intervals of acquisition variable. In other words, a dominant interval(s) condition (DI) is required for source signals. This is a reasonable condition for many NMR spectra. For example, the DI condition holds well in the NMR data which motivated us. The data is produced by the so-called DOSY (diffusion ordered spectroscopy) experiment where a physical sample of mixed chemical compounds in solvent (water) is prepared. DOSY tries to distinguish the chemicals based on variation in their diffusion rates. However, DOSY fails to separate them if the compounds have similar chemical functional groups (i.e., they have similar diffusion rates). In this application, the diffusion rates of the chemicals serve as the mixing coefficients. This presents an additional mathematical challenge due to the near singularity of the mixing matrix. Separating these degenerate data is intractable to NN method. New methods need to be invented. Examination the DI condition reveals a great deal about the geometry of the mixtures. Actually, the scattered plot of columns of X must contain several clusters of points, and these clusters are centered at columns of A . Hence, the problem of finding A boils down to the identification of the clusters and their centroids, and it can be accomplished by data clustering methods such as K-means. K-means clustering is computationally fast and easy to implement. Although the data clustering in general produces a fairly good estimate of the mixing matrix, its output deviates from the true solution due to the presence of the noise, initial guess of the clustering

algorithm, and so on. In the case of nearly singular mixing matrix, a small perturbation can lead to considerable errors in the source recovery (e.g., negative spurious peaks). To overcome this difficulty and improve robustness of the separation, we propose two remedies. One is to find better estimation of mixing matrix by allowing a constrained perturbation to the clustering outputs, and it is achieved by a quadratic programming. The intention is to drive the estimates closer to the true solution. The other is to seek sparse source signals by exploiting the DI condition. An ℓ_1 optimization problem is formulated for recovering the source signals.

As a non-convex optimization method, NMF suffers mainly from being sensitive to the initial guess and non-unique solutions. These drawbacks however do not prevent NMF from gaining its popularity in application such as spectroscopy, chemometrics, remote sensing, image processing, and environmental science due to its capability of reduced representation of the original data and its easy implementation. With the limited information (other than the nonnegativity) of the data, NMF remains as the first choice among the separation methods. The past several decades have seen considerable efforts in the development of variants of NMF, for example, sparse NMF, orthogonal NMF, local NMF, etc., (Choi et al., 2005) to steer the NMF towards the desired solutions. One major disadvantage with NMF is the loss of the data geometric structure in the recovery. For instance, the closeness of the columns of X should be preserved or revealed in the factorization which a general NMF usually fails to achieve. Some remedy has been proposed for the preservation of such geometric relationship. In (Cai, He, Han and Huang, 2011) an affinity graph is introduced to steer the NMF towards the implicit geometrical information and seek a matrix factorization which respects the graph structure. In many NMR data cases, it is very likely that only the degeneracy of the mixing matrix is known, but no knowledge of the source signals is available. Then the NMF type methods should be used to seek a solution. In the case of degenerate mixing matrices, we will introduce additional constraints to NMF cost function to steer the solution towards the ground truth. This case scenario that the mixing matrix A is known to be nearly degenerate (similar columns) can also be found in computer vision where the two adjacent frames of a moving scene should not vary much (hence similar).

The paper is outlined as follows; In section 2, we shall review the essentials of NN approach, then we state the new dominant interval condition on the source signals motivated by NMR data, we also discuss two cases of degenerate mixing matrix. In section 3, we present the methods, the first method is based on the convex geometry and cluster structure the data; while the second approach belongs to NMF method where additional constraints are incorporated into the cost function to control the degeneracy of the mixing matrix. In section 4, we illustrate our method with numerical examples including the processing of an experimental DOSY NMR data set. Concluding remarks are in section 5. We shall use the following notations throughout the paper. The notation A^j stands for the j -th column of matrix A , S^j for the j -th column of matrix S , X^j the j -th column of matrix X . While S_j and X_j are the j -th rows of matrix S and X , or the j -th source and mixture, respectively.

2 The Convex Cone Method

2.1 NN Approach

In (Naanaa and Nuzillard, 2005), Naanaa and Nuzillard (NN) presented an efficient sparse BSS method and its mathematical analysis for nonnegative and partially orthogonal signals such as NMR spectra. Consider the determined regime where there are same number of mixtures is no less than that of sources ($m \geq n$), and the mixing matrix A is full rank. In simple terms, NN's key sparseness assumption (referred to as NNA below) on source signals is that each source has a stand-alone peak at some location of the acquisition variable where the other sources are identically zero. More precisely, the source matrix $S \geq 0$ is assumed to satisfy the following condition

Assumption (NNA). : For each $i \in \{1, 2, \dots, n\}$ there exists an $j_i \in \{1, 2, \dots, p\}$ such that $s_{i,j_i} > 0$ and $s_{k,j_i} = 0$ ($k = 1, \dots, i-1, i+1, \dots, n$).

Eq. (1.1) can be rewritten in terms of columns as

$$X^j = \sum_{k=1}^n s_{k,j} A^k, \quad j = 1, \dots, p, \quad (2.1)$$

where X^j denote the j th column of X , and A^k the k th column of A . Assumption NNA implies that $X^{j_i} = s_{i,j_i} A^i$ $i = 1, \dots, n$ or $A^i = \frac{1}{s_{i,j_i}} X^{j_i}$. Hence Eq. (2.1) is rewritten as

$$X^j = \sum_{i=1}^n \frac{s_{i,j}}{s_{i,j_i}} X^{j_i}, \quad (2.2)$$

which says that every column of X is a nonnegative linear combination of the columns of \hat{A} . Here $\hat{A} = [X^{j_1}, \dots, X^{j_n}]$ is the submatrix of X consisting of n columns each of which is collinear to a particular column of A . It should be noted that j_i ($i = 1, \dots, n$) are not known a priori and need to be identified. Once all the j_i s are found, an estimation of the mixing matrix is obtained. The identification of \hat{A} 's columns is equivalent to identifying a convex cone of a finite collection of vectors. The cone encloses the data columns in matrix X , and is the smallest of such cones. Such a minimal enclosing convex cone can be found by linear programming methods. Mathematically, the following constrained equations are formulated for the identification of \hat{A} ,

$$\sum_{j=1, j \neq k}^p X^j \lambda_j = X^k, \lambda_j \geq 0 \quad k = 1, \dots, p. \quad (2.3)$$

Then any column X^k will be a column of \hat{A} if and only if the constrained equation (2.3) is inconsistent. However, if noises are present, the following optimization problems are suggested to estimate the mixing matrix

$$\begin{aligned} \text{minimize score} &= \left\| \sum_{j=1, j \neq k}^p X^j \lambda_j - X^k \right\|_2, \quad k = 1, \dots, p \\ \text{subject to} & \lambda_j \geq 0. \end{aligned}$$

A score is associated with each column. A column with a low score is unlikely to be a column of \hat{A} because this column is roughly a nonnegative linear combination of the

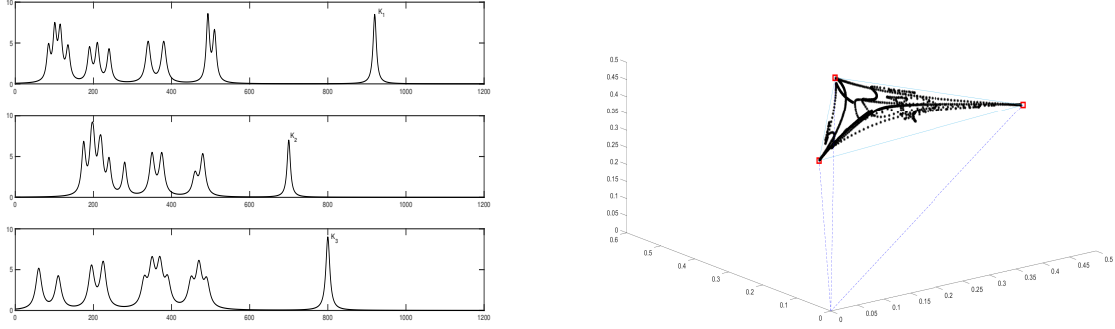


Figure 1: Left : simulated NMR spectra of three SAP sources. Each signal has a stand alone peak indicated by K_1 , K_2 , and K_3 . Right: the scattered plot of X (columns of X) scaling to be on plane $x + y + z = 1$.

other columns of X . On the other hand, a high score means that the corresponding column is far from being a nonnegative linear combination of other columns. Practically, the n columns from X with highest scores are selected to form \hat{A} , the mixing matrix. The Moore-Penrose inverse \hat{A}^+ of \hat{A} is then computed and an estimate to S is obtained: $\hat{S} = \hat{A}^+ X$. NN method proves to be both accurate and efficient if NNA condition holds. However, if the condition is not satisfied, errors and artifacts may be introduced because the true mixing matrix is no longer the smallest enclosing convex cone of columns of the data matrix. As it applies to signals with peak structures such NMR spectra, NNA can be restated as the stand alone peak (SAP) condition: each source signal possesses a stand alone peak over certain acquisition interval, where other sources are identically zero. SAP condition is illustrated by NMR spectra of three sources in the left plot of Fig. 1, it can be seen that each source signal has a stand alone peak denoted by P_1 , P_2 , and P_3 , respectively.

Recently, the authors have developed postprocessing techniques on how to improve NN results with abundance of mixture data, and how to improve mixing matrix estimation with major peak based corrections (Sun, Ridge, del Rio, Shaka and Xin, 2011). The work actually considered a relaxed NNA (rNNA) condition

Assumption (rNNA). : For each $i \in \{1, 2, \dots, n\}$ there exists an $j_i \in \{1, 2, \dots, p\}$ such that $s_{i,j_i} > 0$ and $s_{k,j_i} \approx \epsilon_k$ ($k = 1, \dots, i-1, i+1, \dots, n$), where $s_{i,j_i} \gg \epsilon_k$.

Simply said, each source signal has a dominant peak at acquisition position where the other sources are allowed to be nonzero. NNA condition recovers if all $\epsilon_k = 0$. The rNNA is more realistic and robust than the ideal NNA for real-world NMR data (Naanaa and Nuzillard, 2005).

2.2 Dominant Intervals and Degenerate Matrix

Motivated by the DOSY NMR spectra, we propose here a different relaxed NN condition on the source signals. Note that the rows S_1, S_2, \dots, S_n of S are the source signals, and they are required to satisfy the following condition: For $i = 1, 2, 3, \dots, n$, source signal S_i is required to have dominant interval(s) over $S_n, \dots, S_{i+1}, S_{i-1}, \dots, S_2, S_1$, while S_i is allowed to overlap with other signals at the rest of the acquisition region. More formally, this condition implies that source matrix S satisfies the following condition

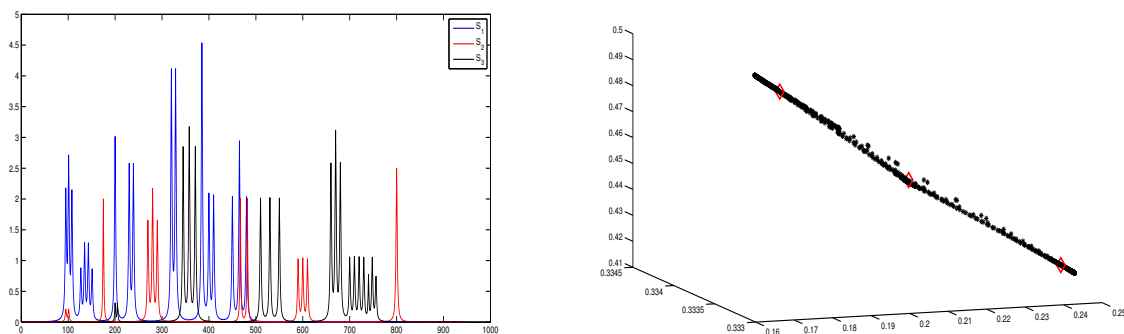


Figure 2: three source signals with dominant intervals (left panel); the geometry of the mixture matrix (right panel). The centers (red diamond) of three clusters are detected by k-means.

Assumption. For each $k \in \{1, 2, 3, \dots, n\}$, there is a set $\mathcal{I}_k \subset \{1, 2, \dots, p\}$ such that for each $l \in \mathcal{I}_k$ $s_{kl} \gg s_{jl}, j = 1, 2, \dots, k-1, k+1, \dots, n$.

We shall call this dominant interval condition, or DI condition. Fig. 2 is an idealized example of three DI source signals. The motivation lies in the similar diffusion rates of the chemicals with similar structure. This poses a mathematical challenge to invert a nearly singular matrix, since a small error in the recovered mixing matrix might lead to a considerable deviation in the source recovery. Among the singularly mixed signals (or degenerate data), in this paper we shall consider the following two types: 1) columns of the mixing matrix are parallel; 2) one column of the mixing matrix is a nonnegative linear combination of others. Case 1 is motivated by NMR of the chemicals with similar diffusion rates. We shall call this condition parallel column condition, or PCC. Case 2 can also be encountered in NMR spectroscopy of chemicals, and we shall call it one column degenerate condition, or OCDC. Throughout the paper, we shall refer to a mixing matrix of PCC or OCDC as degenerate mixing matrix. Please note that both PCC and OCDC should be considered to hold approximately in real-world data.

3 Our Methods

3.1 Data Clustering

Now suppose we have a set of nearly degenerate signals from DI sources. We require that compared to the size of dominant interval(s) in the acquisition region, the source signals overlapping region is much smaller. In fact, this is a reasonable assumption for the NMR data which motivates us. More importantly, this requirement facilitates the successful implementation of the clustering method. Next, we shall estimate the columns of mixing matrix A by clustering. The dominant interval(s) from each of the source signals implies that there is a region where the source S_i dominates others. More precisely, there are columns of X such that

$$X^k = s_{i,k}A^i + \sum_{j=1}^{n-1} o_{j,k}A^j, \quad (3.1)$$

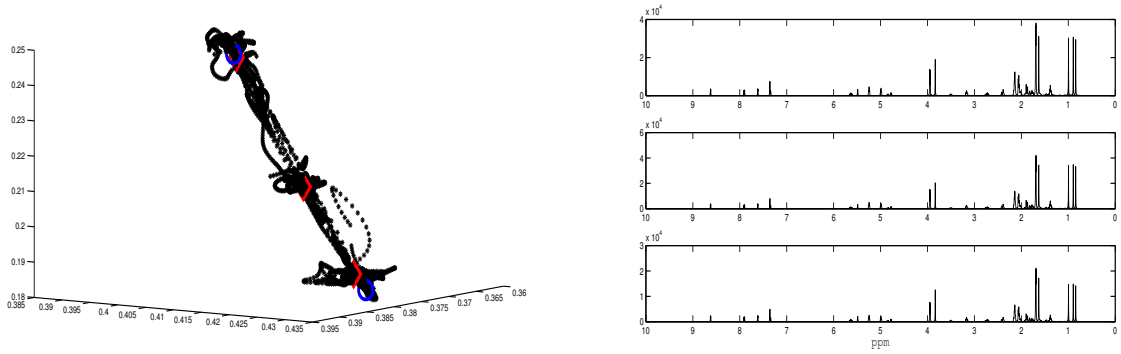


Figure 3: Real data example: three columns of A are identified as the three center points (in red diamond) attracting most points in scatter plots of the columns of X (left), and the three rows of X (right). NN method identifies two columns of A as the points in the blue circle.

where $s_{i,k}$ dominate $o_{i,k}$ ($i = 1, \dots, n - 1$), i.e., $s_{i,k} \gg o_{i,k}$. The identification of A^i ($i = 1, \dots, n$) is equivalent to finding a cluster formed by these X^k 's in \mathbb{R}^m . As illustrated in the geometry plot of X in Fig. 2, three clusters are formed. Many clustering techniques are available for locating these clusters, for example, k-means is one of the simplest clustering analysis methods. We shall use k-means for the data in this paper to locate centers (centroids) of the clusters. Those centers are the estimates of columns of A . Consider an example of three DI source signals with ODCD mixing matrix condition, the three centers shown in Fig. 2. For real-world data, we show an example of NMR spectra of quinine, geraniol, and camphor mixture in Fig. 3. The clusters in the middle implies that ODCD condition hold well for this data. Apparently, NN method (and other convex cone methods) would fail to separate the source signals due to the degeneracy of the mixing matrix. It might be able to identify two columns of A as the two edges, it by no means can locate A 's degenerate column. For the PCC degenerate case, clustering is also able to deliver a good estimation, even when the data is contaminated by noise. We show the results in Fig. 4 where the three clusters are very close due to the PCC degeneracy. NN solution would deviate considerably from the true solution. For the data we tested, clustering techniques like k-means works well when the condition number of the mixing matrix is up to 10^8 . Though the solutions of mixing matrix by clustering methods are rather good estimation to the true solution, small deviations from the true ones will introduce large errors in the source recovery ($S = \text{inverse}(A) X$). Next we propose two approaches to overcome this difficulty. Both approaches need to solve optimization problems. The first one intends to improve the source recovery by seeking a better mixing matrix, while the second approach reduces the spurious peaks by imposing sparsity constraint on the sources.

3.2 Better Inverse of the Mixing Matrix

Suppose the estimation of the mixing matrix by clustering is \hat{A} . As discussed above, errors in \hat{S} could be introduced even by a small deviation in \hat{A} from the ground truth. Negative spurious peaks are produced in most cases, see the Fig. 6 where the negative peaks on the left plot actually can be viewed as bleed through from another source. Clearly, a better estimation of mixing matrix is required to reduce these spu-

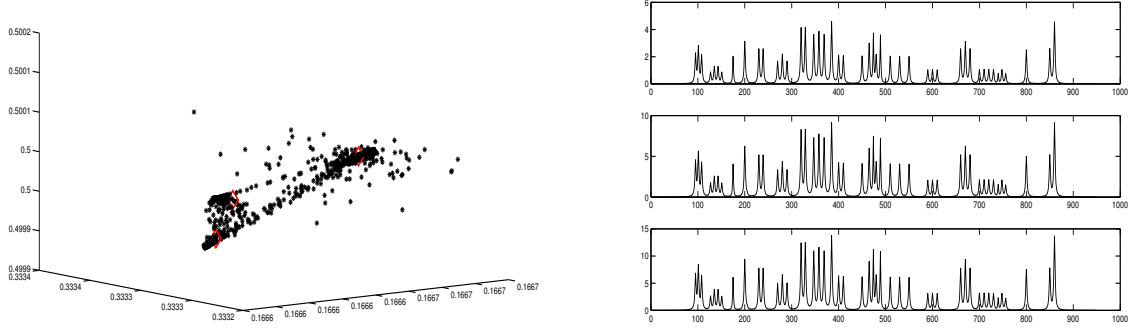


Figure 4: Example of PCC case: left: three columns of A are identified as the centroids (red diamond) of three clusters in the scatter plot of the columns of X (left); Right: three spectral mixtures (rows of X).

rious peaks. Instead of looking for a better mixing matrix, we propose to solve the following optimization problem for a better inverse of the matrix in the determined case ($m = n$, same number of mixtures of sources),

$$\min_B \frac{1}{2} \|I - B\hat{A}\|_2^2 \quad \text{subject to } BX \geq 0, \quad (3.2)$$

where $I \in \mathbb{R}^{n \times n}$ is the identity matrix. The constraint $BX \geq 0$ is used to reduce the negative values introduced in the source recovery. (3.2) is a linearly constrained quadratic program and it can be solved by a variety of methods including interior point, gradient projection, active sets, etc. In this paper, interior point algorithm is used. Once the minimizer B^* is obtained, we solve for the sources by $S = B^* X$. For over-determined mixture ($m > n$, A being a tall matrix), the source recovery is usually obtained by $\hat{S} = (\hat{A}^T \hat{A})^{-1} \hat{A}^T X$, to achieve a better inverse of \hat{A} in the sense of least squares, the following optimization problem is proposed,

$$\min_B \frac{1}{2} \|I - B\hat{A}^T \hat{A}\|_2^2 \quad \text{subject to } B\hat{A}^T X \geq 0, \quad (3.3)$$

which can be solved via an interior point algorithm as well.

3.3 Sparser Source Signals

The method proposed above works well for mixing matrix whose condition number is up to 10^8 . If the mixing matrix is much more ill-conditioned, the problem (1.1) becomes under-determined. Obtaining an exact solution is impossible even an accurate A is provided. However, a meaningful solution is possible if the actual source signals are sparse. It appears that the columns of S possess sparseness due to the dominant intervals condition. Hence, we seek the sparsest solution for each column S^i of S as

$$\min \|S^i\|_0 \quad \text{subject to } \hat{A}S^i = X^i, \quad S^i \geq 0. \quad (3.4)$$

Here $\|\cdot\|_0$ (0-norm) represents the number of nonzeros. Because of the non-convexity of the 0-norm, we minimize the relaxed ℓ_1 -norm:

$$\min \|S^i\|_1 \quad \text{subject to } AS^i = X^i, \quad S^i \geq 0, \quad (3.5)$$

which is a linear program (Donoho and Tanner, 2005) because S^i is non-negative. The fact that data may contain noise suggests solving the following unconstrained optimization problem,

$$\min_{S^i \geq 0} \mu \|S^i\|_1 + \frac{1}{2} \|X^i - AS^i\|_2^2, \quad (3.6)$$

for which Bregman iterative method (Guo and Osher, 2009) combined with a nonnegative projection on convex subset (data nonnegativity) can be applied to retrieve a solution.

3.4 Structure Assisted Nonnegative Matrix Factorization

In the case where the source signals are known to possess dominant intervals and clusters in the data points, convex BSS methods proposed above are suitable choices. While if no knowledge of the source signals is available other than the nonnegativity, we shall opt to use nonnegative matrix factorization approach. Nonnegative matrix factorization (NMF) (Paatero and Tapper, 1994; Lee and Seung, 1999) is the prevalent method for solving nonnegative BSS problems with limited information on the nonnegative source signals and mixing matrices. As a parts-based data compression method, NMF attempts to find two nonnegative matrices whose product approximates the data matrix. Given the mixture matrix $X \in \mathbb{R}^{m \times p}$, NMF seeks the approximate factorization $X \approx AS$, $A \in \mathbb{R}^{m \times n}$, $S \in \mathbb{R}^{n \times p}$ by minimizing the following objective function,

$$J(A, S) = \|X - AS\|_F^2,$$

Where $\|\cdot\|_F$ is the Frobenius matrix norm. $J(A, S)$ is also called Euclidean distance function which is non-convex in A, S . Lee and Seung (Lee and Seung, 1999) proposed a multiplicative iteration rule:

$$a_{ij} \leftarrow a_{ij} \frac{[XS^T]_{ij}}{[ASST]_{ij}}, \quad (3.7)$$

$$s_{jk} \leftarrow s_{jk} \frac{[A^T X]_{jk}}{[A^T AS]_{jk}}, \quad (3.8)$$

and they proved that these iterates converge to a local minimum of $J(A, S)$.

Given the fact that the columns of the mixing are similar (PCC columns). i.e., the sources signals are accounts for approximately same amounts. We should incorporate this constraint into the $J(A, S)$ to steer the solution towards the desired one. The linear mixture model $X = AS$ can be rewritten as follows:

$$[X^1, X^2, \dots, X^p] = [A^1, A^2, \dots, A^n] \begin{pmatrix} S_{11} & S_{12} & \dots & S_{1p} \\ S_{21} & S_{22} & \dots & S_{2p} \\ \vdots & \vdots & \vdots & \vdots \\ S_{n-1,1} & S_{n-1,2} & \dots & S_{n-1,p} \\ S_{n1} & S_{n2} & \dots & S_{n,p} \end{pmatrix}, \quad (3.9)$$

We assume that matrix A is nearly singular as we assume that its columns A^1, A^2, \dots, A^n are similar. This situation holds approximately well in mixtures where the source signals have nearly the same amounts of concentration; or in image processing such as

computer vision, the adjacent frames should vary very little, or look similar. With limited knowledge on the source signals, we shall opt for nonnegative matrix factorization approach (Lee and Seung, 1999), we need to build the mixing matrix structure into the model. The similarity between the columns of A implies that the differences of them (given that the columns are all normalized to unit vectors) are approximately zeros, or

$$A^2 - A^1 \approx \mathbf{0}, A^3 - A^2 \approx \mathbf{0}, \dots, A^i - A^{i-1} \approx \mathbf{0}, \dots, A^n - A^{n-1} \approx \mathbf{0}, A^1 - A^n \approx \mathbf{0}.$$

To account for these similar (parallel) columns, we shall put these conditions into matrix form

$$[A^1 \ A^2 \ A^3 \ \dots \ A^{n-1} \ A^n] \begin{bmatrix} -1 & 0 & 0 & \dots & 0 & 1 \\ 1 & -1 & 0 & \dots & 0 & 0 \\ 0 & 1 & -1 & \dots & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & \dots & -1 & 0 \\ 0 & 0 & 0 & \dots & 1 & -1 \end{bmatrix} \approx \mathbf{0}$$

Where denote $W \in \mathbb{R}^{n \times n}$ as the sparse matrix containing ± 1 's. $\mathbf{0} \in \mathbb{R}^{m \times n}$ is the zero matrix. Now let us consider the following cost function

$$J_\alpha(A, S) = \|X - AS\|_F^2 + \alpha \|AW\|_F^2, \text{ s.t. } A \succeq 0, S \succeq 0. \quad (3.10)$$

Following (Choi et al., 2005) by the gradient descent, we are able to get the update rules for entries of A and S

$$\begin{aligned} a_{ij}^{l+1} - a_{ij}^l &= -\delta_{ij} \frac{\partial J}{\partial a_{ij}} \\ &= \delta_{ij} ([XS^T]_{ij} - [ASS^T]_{ij} - \alpha [AWW^T]_{ij}) \\ s_{jk}^{l+1} - s_{jk}^l &= -\eta_{jk} \frac{\partial J}{\partial s_{jk}} \\ &= \eta_{jk} ([AX^T]_{jk} - [A^T AS]_{ij}) \end{aligned}$$

To ensure the nonnegativity, we shall choose the specific learning rates proposed in (Lee and Seung, 1999)

$$\delta_{ij} = \frac{a_{ij}}{[ASS^T]_{ij}}, \eta_{jk} = \frac{s_{jk}}{[A^T AS]_{jk}}$$

and the resulting multiplicative update formulas are

$$a_{ij} \leftarrow \frac{a_{ij}}{\sum_i a_{ij}}, \quad (3.11)$$

$$a_{ij} \leftarrow a_{ij} \frac{[(XS^T - \alpha AWW^T)_{ij}, 0]_+}{[ASS^T]_{ij}}, \quad (3.12)$$

$$s_{jk} \leftarrow s_{jk} \frac{[A^T X]_{jk}}{[A^T AS]_{jk}}, \quad (3.13)$$

where the operator $[x]_+ = \max(0, x)$ is to ensure nonnegativity in the updates. The proposed NMF cost function addresses the degeneracy of the mixing matrix by imposing

a penalty on the differences of its columns, and shall be termed by column difference NMF, or **CD-NMF**.

Below we propose an alternative cost function for NMF. Noticing that to measure the similarity between vectors, we can use the inner product as a simple yet accurate measure for similarity. For two parallel unit vectors a, b , their inner product $a \cdot b = 1$. Based on this idea, we propose to adopt the following criterion to impose the similarity between the columns of the mixing matrix A . Then we shall have $A^T A = J_n$, here J_n is a square matrix of size n of ones, that is,

$$A^T A = \begin{bmatrix} A^1 \cdot A^1 & A^1 \cdot A^2 & A^1 \cdot A^3 & \dots & A^1 \cdot A^n \\ A^2 \cdot A^1 & A^2 \cdot A^2 & A^2 \cdot A^3 & \dots & A^2 \cdot A^n \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ A^n \cdot A^1 & A^n \cdot A^2 & A^n \cdot A^3 & \dots & A^n \cdot A^n \end{bmatrix} = \begin{bmatrix} 1 & 1 & 1 & \dots & 1 \\ 1 & 1 & 1 & \dots & 1 \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ 1 & 1 & 1 & \dots & 1 \end{bmatrix} = J_n$$

where we can see that the normalization of columns of A , or A^1, A^2, \dots, A^n are all enforced as the diagonals show. We consider the following cost function

$$J_\beta(A, S) = \|X - AS\|_F^2 + \beta \|A^T A - J_n\|_F^2, \text{ s.t. } A \succeq 0, S \succeq 0. \quad (3.14)$$

By a likewise derivation presented in the previous section, we have

$$\begin{aligned} a_{ij}^{l+1} - a_{ij}^l &= -\delta_{ij} \frac{\partial J}{\partial a_{ij}} \\ &= \delta_{ij} ([XS^T]_{ij} - [ASS^T]_{ij} - 2\beta[AA^T A - AJ_n^T]_{ij}) \\ s_{jk}^{l+1} - s_{jk}^l &= -\eta_{jk} \frac{\partial J}{\partial s_{jk}} \\ &= \eta_{jk} ([AX^T]_{jk} - [A^T AS]_{jk}). \end{aligned}$$

We again take the previous learning rates

$$\delta_{ij} = \frac{a_{ij}}{[ASS^T]_{ij}}, \eta_{jk} = \frac{s_{jk}}{[A^T AS]_{jk}}$$

which lead us to the following update rules:

$$a_{ij} \leftarrow a_{ij} \frac{[[XS^T]_{ij} - 2\beta[AA^T A - AJ_n^T]_{ij}, 0]_+}{[ASS^T]_{ij}}, \quad (3.15)$$

$$s_{jk} \leftarrow s_{jk} \frac{[A^T X]_{jk}}{[A^T AS]_{jk}}; \quad (3.16)$$

$$(3.17)$$

This proposed NMF cost function addresses the degeneracy of the mixing matrix by adding a penalty on the inner products of all its columns, and shall be termed by column product NMF, or **CP-NMF**.

4 Numerical experiments

4.1 Singular Mixing Matrix and Dominant Peak Sources

In this section, we present the numerical results solved by the methods. In the first example, two sources signals are to be recovered from two mixtures. The mixtures are constructed from two real NMR source signal by simulating the linear model (1.1). The two columns of mixing matrix are nearly parallel, and its condition number is about 1.25×10^8 . The true mixing matrix A_{TR} , its estimation A_{C} via clustering, and the improved estimate A_{P} by solving (3.2) are (for ease of comparison, the first rows of \hat{A} , A_p are scaled to be same as that of A)

$$\begin{aligned} A_{\text{TR}} &= \begin{pmatrix} 0.894427190999916 & 0.894427182055644 \\ 0.447213595499958 & 0.447213613388501 \end{pmatrix}, \\ A_{\text{C}} &= \begin{pmatrix} 0.894427190999916 & 0.894427182055644 \\ \mathbf{0.447213596792237} & \mathbf{0.447213596447341} \end{pmatrix}, \\ A_{\text{P}} &= \begin{pmatrix} 0.894427190999916 & 0.894427182055644 \\ \mathbf{0.447213595582167} & \mathbf{0.447213613388502} \end{pmatrix}. \end{aligned}$$

It can be seen that A_{P} is a better estimate as it recovered more digits of the ground truth. The mixtures are plotted in Fig. 5, and the results are presented in Fig. 6.

In the second example, three sources are to be separated from three mixtures. The mixing matrix satisfies the OCDC condition, i.e., one of its columns is a nonnegative linear combination of the other two. To test the robustness of the method, we added Gaussian noise (SNR = 60 dB) to the data. The mixtures and their geometric structure are plotted in Fig. 7. First the data clustering was used to obtain an estimation of the mixing matrix, then an ℓ_1 optimization problem is solved to retrieve the sources. The results are shown in Fig. 8. It can be seen that the recovered sources agree well with the ground truth.

For the third example, we provide a set of real data to test our method. The data is produced by diffusion ordered spectroscopy (DOSY) which is an NMR spectroscopy technique used by chemists for mixture separation (Morris, 2001). However, the three compounds used in the experiment (quinine, geraniol, and camphor) have similar chemical functional groups (i.e. there is overlapping in their NMR spectra) (Nilsson, Connel, Davies and Morris, 2006), for which DOSY fails to separate them. The fact that each of the three sources has dominant interval(s) over others in its NMR spectrum can be verified from the three isolated clusters formed in their mixed NMR spectra (point clouds of their mixtures shown in Fig. 9). Here we unmix three sources from three spectral mixtures. Fig. 9 plots the mixtures (rows of X) and their geometry (columns of X) where three clusters of points can be spotted. Then the columns of A are identified as the centriods of the three clusters. The solutions depicted in Fig. 10 are satisfactory comparing with the real source signals side by side. The source signals recovery by NN (Naanaa and Nuzillard, 2005) are also computed and shown in Fig. 11 (some negative (erroneous) peaks in S can be spotted).

4.2 Structure Assisted NMF examples

We proposed nonnegative matrix factorization with two different cost functions to address the nearly degeneracy in the mixing matrix. The first one imposed a penalty

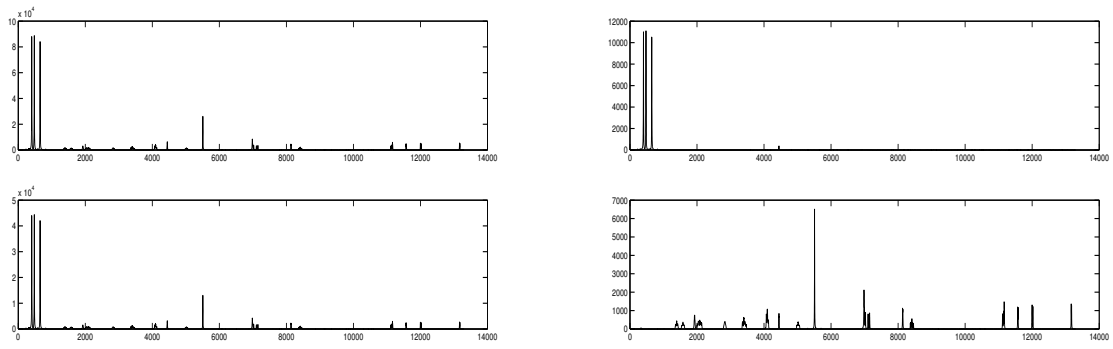


Figure 5: recovered sources by clustering (left panel) and the ground truth (right panel).

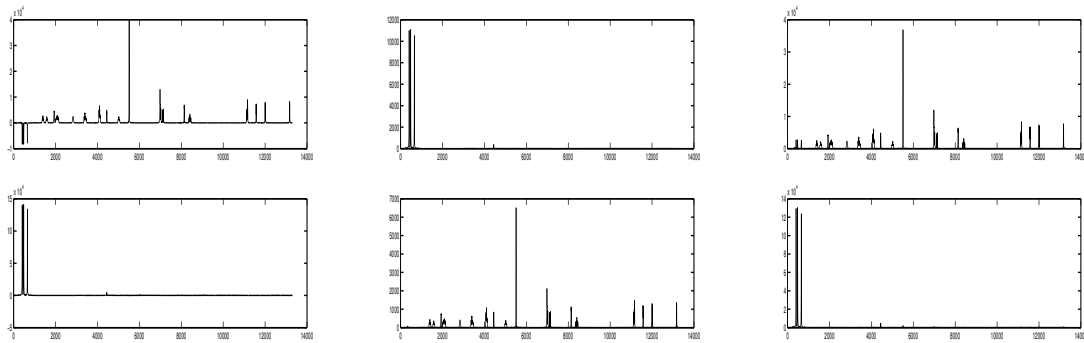


Figure 6: recovered sources by clustering (left column), the ground truth (middle column), and the improved results by a better estimate of mixing matrix (right column).

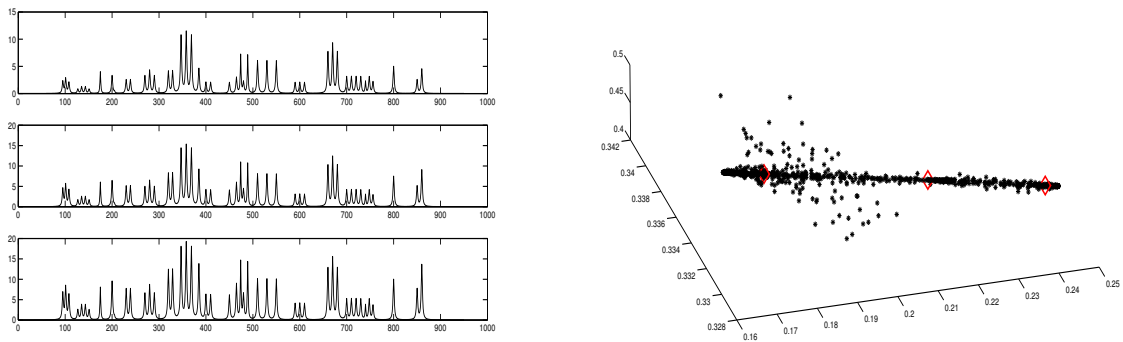


Figure 7: three mixtures (left column) and their scattered plot (right column).

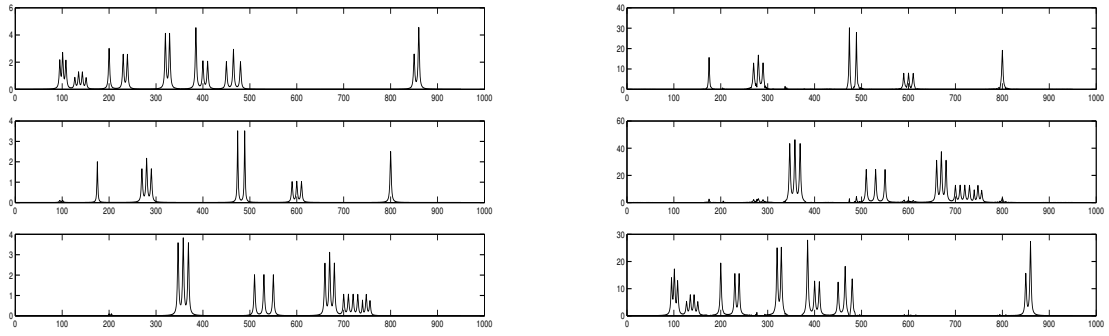


Figure 8: three sources (left column) and their recovery by clustering and ℓ_1 minimization (right column).

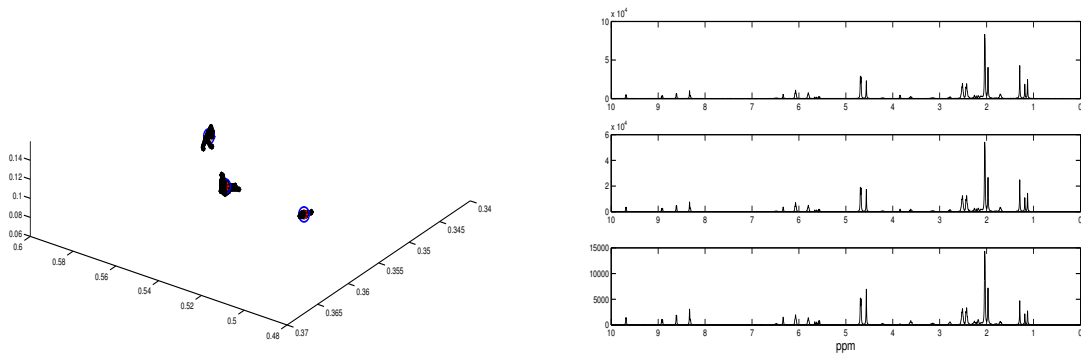


Figure 9: three columns of A are recovered as three centroids (blue circles) of three clusters in scatter plots of the columns of X (left panel), and the three rows of X (right panel).

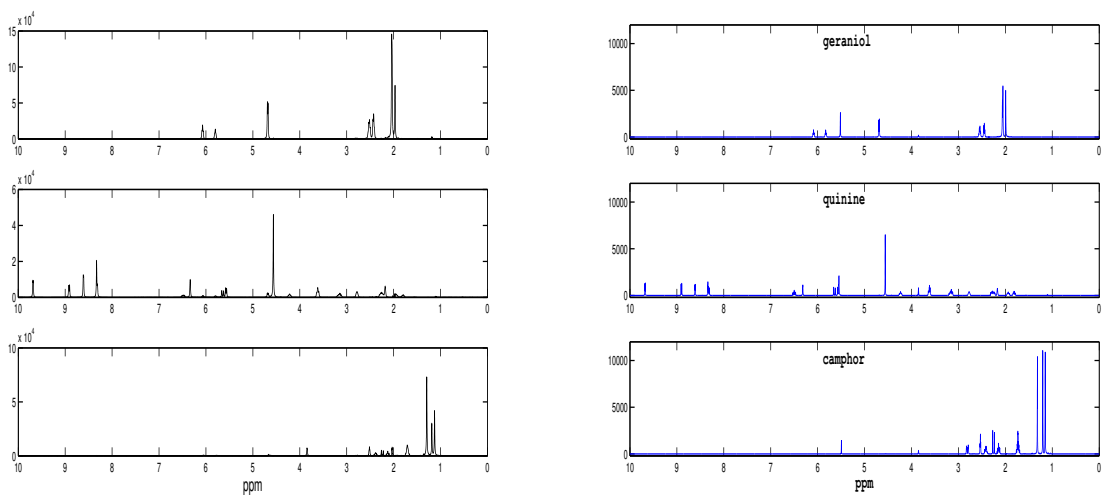


Figure 10: the computed source signals by nonnegative ℓ_1 (left) and the ground truth (right).

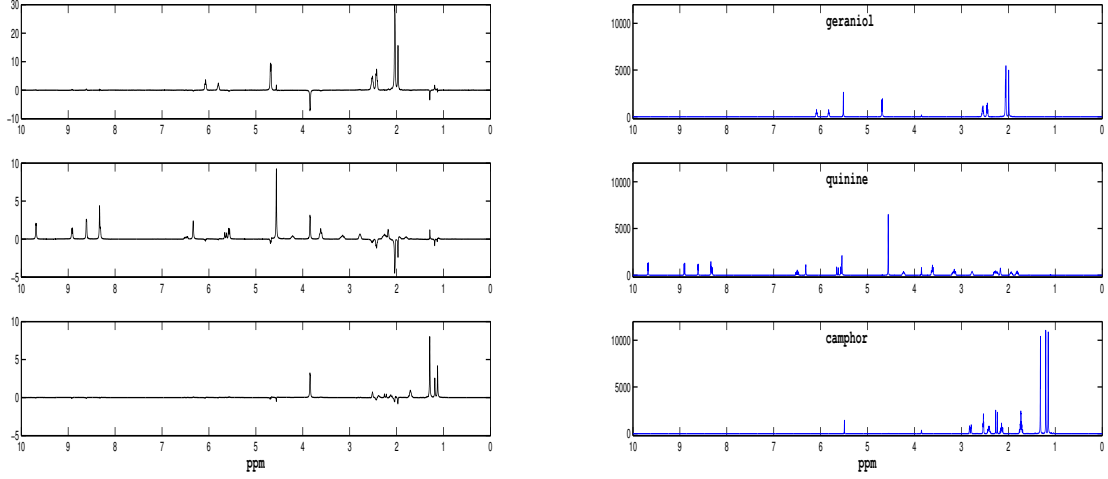


Figure 11: the retrieved source signals via NN method (left) comparing with the ground truth (right).

term on the differences of its columns (termed CD-NMF); while the second cost function addresses the degeneracy of the mixing matrix by adding a penalty on the inner products of all its columns (termed CP-NMF). The comparison of the recovered mixing matrix by CD-NMF method, CP-NMF method, and the ground truth are shown here

$$A_{\text{CD-NMF}} = \begin{pmatrix} 0.230364553564128 & 0.222325645752675 & 0.197973272413603 \\ 0.428178141700514 & 0.426117653427851 & 0.447928422731077 \\ 0.709793002863661 & 0.677723684276001 & 0.563864889947392 \end{pmatrix},$$

$$A_{\text{CP-NMF}} = \begin{pmatrix} 0.242865565572616 & 0.180098969354018 & 0.285524082512094 \\ 0.516635045464442 & 0.309883686246381 & 0.582543757260167 \\ 0.729813101379756 & 0.538325711121780 & 0.857017001731787 \end{pmatrix},$$

$$A_{\text{TR}} = \begin{pmatrix} 1.000013203688969 & 1.099999061455011 & 3.999999720965063 \\ 2.000007131698644 & 2.200024874750488 & 8.000009370903321 \\ 3.000004644386780 & 3.299985225130326 & 12.000000027664264 \end{pmatrix}$$

The condition number of the ground truth matrix A_{TR} is about 5.56×10^6 , we actually started with a singular matrix $\begin{pmatrix} 1 & 1.1 & 4 \\ 2 & 2.2 & 8 \\ 3 & 3.3 & 12 \end{pmatrix}$, then added Gaussian noise of SNR =

100. It is possible to compare the NMF results with the ground truth by scaling the rows of the matrices as in the first example. Here we shall propose a metric to measure the distance of the matrices. The following distance between column degenerate matrices is proposed ¹

Definition 1. Consider two nearly degenerate matrices (parallel columns) A and \bar{A} of size (m, n) with normalized columns. The distance between A and \bar{A} denoted by $\Delta(A, \bar{A})$ is

$$\Delta(A, \bar{A}) = \|A^T \bar{A} - J_n\|_{\mathbf{F}},$$

where J_n is a square matrix of size n of ones.

¹The Comon's index(Comon, 1994) used for measure the distance of nonsingular matrices in BSS problems is not suitable metric for nearly degenerate matrices.

Apparently the smaller distance is, the more similar of the matrices. We computed the following matrix distances.

$$\Delta(A_{\text{TR}}, A_{\text{CD-NMF}}) = 0.005850257335153, \Delta(A_{\text{TR}}, A_{\text{CP-NMF}}) = 0.003635218995144.$$

and the regularization parameters $\alpha = \beta = 0.001$.

5 Conclusion

This paper presented novel methods to retrieve source signals from the nearly degenerate mixtures. The motivation comes from NMR spectroscopy of chemical compounds with similar diffusion rates. Inspired by the NMR spectral structure of these chemicals, we propose a viable source condition which requires dominant interval(s) from each source signal over the others. This condition is well suited for many real-life signals. Besides, the nearly degenerate mixtures are assumed to be generated from the following mixing process: either all the columns of the mixing matrix are parallel or one column is a nonnegative linear combinations of others. We first use data clustering to identify the mixing matrix, then we develop two approaches to improve source signals' recovery. The first approach minimizes a constrained quadratic program for a better mixing matrix, while the second method seeks the sparsest solution for each column of the source matrix by solving an ℓ_1 optimization. If no(or very limited) information on the source signals are available, two NMF variants are proposed by adding regularization terms to enforce the degeneracy of the columns, hence a desired solution can be obtained. Numerical results on NMR spectra data show good performance of our methods. Though the methods are motivated by the NMR spectroscopy, the methods developed may be extended to different data sets in other applications. For future work, we plan to investigate a mixture data separation problem where the mixing matrix has the following form

$$\begin{bmatrix} \exp(-\lambda D_1 g_1^2) & \exp(-\lambda D_2 g_1^2) & \dots & \exp(-\lambda D_n g_1^2) \\ \exp(-\lambda D_1 g_2^2) & \exp(-\lambda D_2 g_2^2) & \dots & \exp(-\lambda D_n g_2^2) \\ \vdots & \vdots & \vdots & \vdots \\ \exp(-\lambda D_1 g_m^2) & \exp(-\lambda D_2 g_m^2) & \dots & \exp(-\lambda D_n g_m^2) \end{bmatrix}$$

Here g is a controllable parameter, and g'_i s are linearly dependent. Hence the entries of each column have nonlinear relations. We plan to study how to impose constraints to guide the NMF solution revealing the nonlinearity among the entries.

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