ECP
LSD
2016 - 2017

Reconstruction of DOSY NMR signals - Part I

1 Introduction

The measurement of diffusion by Nuclear Magnetic Resonance (NMR) is used in various application fields (agro-alimentary, pharmaceutical, ecology) to analyze the properties of complex chemical mixtures in order to determine their molecular structure and dynamics. After the immersion of the matter in a strong magnetic field, all the nuclear spins align to an equilibrium state along the field orientation. The application of a short magnetic pulse, i.e. the pulsed field gradient, in resonance with the spin motion disturbs the spin orientation. NMR aims at analyzing the process which corresponds to the re-establishment of the spin into its equilibrium state. During the DOSY (Diffusion Order SpectroscopY) experiment, proposed by Morris and Johnson in 1992, a series of measurements is acquired for different pulsed field gradient strengths, the data are then analyzed with the aim to separate different species according to their diffusion coefficient.

The DOSY NMR data $y = (y^{(m)})_{1 \leq m \leq M} \in \mathbb{R}^M$ gathers the results of M experiments characterized by $t = (t^{(m)})_{1 \leq m \leq M} \in \mathbb{R}^M$ related to the pulsed field gradient strength and to the acquisition time. The relation between y and t can be expressed as the following Laplace transform :

$$(\forall m \in \{1, \dots, M\}) \quad y^{(m)} = \int \chi(T) \exp(-t^{(m)} T) dT, \tag{1}$$

where $\chi(T)$ is the unknown diffusion distribution. The problem is then to reconstruct $\chi(T)$ on the sampled grid $T = (T^{(n)})_{1 \leq n \leq N}$, from the measurements y. After discretization and appropriate normalization, the observation model reads

$$y = K\overline{x} + w, \tag{2}$$

where $K \in \mathbb{R}^{M \times N}$ is given by

$$(\forall m \in \{1, \dots, M\})(\forall n \in \{1, \dots, N\}) \qquad K^{(m,n)} = \exp(-T^{(n)} t^{(m)}), \tag{3}$$

$\overline{x} \in \mathbb{R}^N$ is the sought signal, related to $\big(\chi(T^{(n)})\big)_{1 \leq n \leq N}$ and $w \in \mathbb{R}^M$ is a perturbation noise. We propose here to find an estimate $\widehat{x} \in \mathbb{R}^N$ of $\overline{x}$ by solving the following minimization problem, requiring the knowledge of K and y :

$$\widehat{x} = \underset{x \in \mathbb{R}^N}{\operatorname{argmin}} \ \frac{1}{2} \|Kx - y\|^2 + \beta g(x) \tag{4}$$

where $g \in \Gamma_0(\mathbb{R}^N)$ denotes a regularization term and $\beta \geq 0$. Note that, in practice, a very large number of DOSY NMR acquisitions (typically 10^4) are conduced for various settings of the pulsed gradient field, so that problem (4) must be solved many times, which motivates the search for a fast reconstruction method.

2 Generation of synthetic data

1. Download on the website the diffusion signal $\overline{x} \in \mathbb{R}^N$, with size $N = 200$.
2. Create T using an exponential sampling strategy :

$$(\forall n \in \{1, \ldots, N\}) \quad T^{(n)} = T_{\min} \exp\left(-(n-1)\frac{\log(T_{\min}/T_{\max})}{N-1}\right), \tag{5}$$

   with $T_{\min} = 1$ and $T_{\max} = 1000$.
3. Display the original signal $\overline{x}$ as a function of T (use log scale on the horizontal axis).
4. Create t using a regular sampling strategy :

$$(\forall m \in \{1, \ldots, M\}) \quad t^{(m)} = t_{\min} + \frac{m-1}{M-1}(t_{\max} - t_{\min}), \tag{6}$$

   with $M = 50$, $t_{\min} = 0$, and $t_{\max} = 1.5$.
5. Construct matrix K using (3).
6. Simulate the noisy data according to model (2), by taking $w \sim \mathcal{N}(0, \sigma^2 I_M)$ with $\sigma = 0.01\, z^{(1)}$, where $z = K\overline{x}$.
7. Display the resulting noisy data y as a function of t.

3 Comparison of regularization strategies

For every penalization functions g listed at the end of the document,

1. Discuss the existence and uniqueness of a solution to Problem (4),
2. Propose an approach to solve problem (4),
3. Implement it, and display the restored signal $\widehat{x}$,
4. Compute the normalized quadratic error between $\widehat{x}$ and $\overline{x}$:

$$E(\widehat{x}, \overline{x}) = \frac{\|\widehat{x} - \overline{x}\|^2}{\|\overline{x}\|^2}. \tag{7}$$

5. When needed, search manually for the best choice for parameter β in terms of reconstruction error.

Smoothness prior :

$$(\forall x \in \mathbb{R}^N) \quad g(x) = \frac{1}{2}\|Dx\|^2 \tag{8}$$

where $D \in \mathbb{R}^{N\times N}$ is the discrete gradient operator such that,

$$(\forall n = \{1,\dots,N\}) \quad [Dx]^{(n)} = x^{(n)} - x^{(n-1)} \tag{9}$$

with the circular convention $x^{(0)} = x^{(N)}$. The role of such regularization term is to promote the reconstruction of smooth signals.

Smoothness prior + constraints :

$$(\forall x \in \mathbb{R}^N) \quad g(x) = \frac{1}{2}\|Dx\|^2 + \iota_{[x_{\min},x_{\max}]^N}(x) \tag{10}$$

with $0 < x_{\min} < x_{\max}$ the minimum and maximum values of the original signal $\overline{x}$.

Sparsity prior :

$$(\forall x \in \mathbb{R}^N) \quad g(x) = \|x\|_1 \tag{11}$$