Proximal Algorithm for L_1 combined with MAxent prior: a new approach for DOSY signal processing

Cherni Afef [1,2], Chouzenoux Émilie[1], Delsuc Marc-André[2]

[1] Université Paris-Est, LIGM (UMR 8049), CNRS, ENPC, ESIEE Paris, UPEM, Marne-la-Vallée, France.
[2] Institut de Génétique et de Biologie Moléculaire et Cellulaire (IGBMC), INSERM U596, CNRS UMR 7104
Université de Strasbourg, 67404 Illkirch-Graffenstaden, France

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DOSY NMR

Diffusion Ordered SpectroscopY is a Nuclear Magnetic Resonance experiment using PFG (Pulsed Field Gradient), used to identify species in a complex chemical mixture by measuring its diffusion distribution.

• **DOSY NMR Signal**

$$I(q) = \int_{D_{min}}^{D_{max}} X(D) exp(-D\Delta q^2) dD$$

whith $X(D)$ is the diffusion distribution of the molecular species, I is the signal intensity, $q = \gamma\delta g$ presents the measure of the phase dispersion created by the PFG. γ is the gyromagnetic ratio of the studied spin, and δ and g are the duration and intensity of the PFG respectively.

• **Goal**

Find the chemical species from its diffusion profile by inverting the Laplace equation $\rightsquigarrow$ Ill posed problem.

Theory

• **Lagrangian formulation**

$$\underset{X \in \mathbb{R}^N}{\text{minimise}} \quad \|\boldsymbol{H}X - Y\|^2 + \mu\Psi(X) \tag{1}$$

• **Proposition : Hybrid regularisation**

$$\Psi(X) = \lambda\, \text{ent}(X, a) + (1-\lambda)\ell_1(X) \tag{2}$$

$$\text{ent}(X,a) = \begin{cases} \sum_{n=1}^{N} \frac{x_n}{a} \log\left(\frac{x_n}{a}\right) & \text{if } x_n > 0 \\ 0 & \text{if } x_n = 0 \\ +\infty & \text{elsewhere.} \end{cases} \qquad \ell_1(X) = \sum_{n=1}^{N} |x_n|$$

Proximal solution

$$\text{prox}_{\Psi}(X) = (p(x_n))_{1 \le n \le N} \tag{3}$$

with

$$p(x_n) = \begin{cases} \frac{\lambda}{a} \mathsf{W}\left[\frac{a}{\lambda} \exp\left(\frac{a x_n - a(1-\lambda)}{\lambda} + \log(a) - 1\right)\right] & \text{if} \quad \lambda \in]0,1] \\ \text{sign}(x_n) \max\left(|x_n| - (1-\lambda), 0\right) & \text{if} \quad \lambda = 0 \end{cases} \tag{4}$$

W states for the Lambert function, defined as the inverse function of $f : z \to ze^z$ for all $z \in \mathbb{C}$ i.e :

$$z = we^w \quad \Leftrightarrow \quad w = \mathsf{W}(z).$$

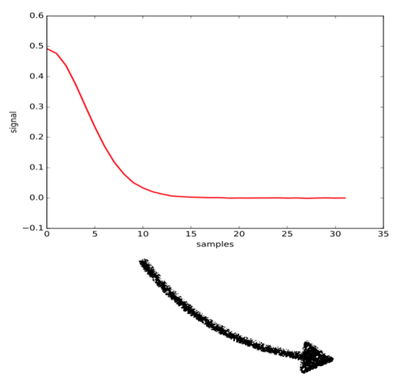
PALMA algorithm

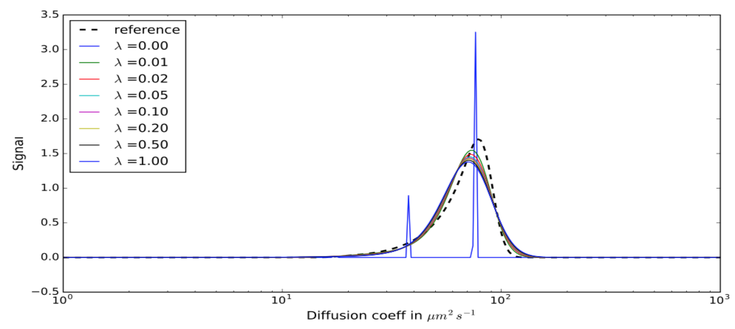
Proximal **A**lgorithm for **L1** combined with **MA**xent prior, available on the web site `http://palma.labo.igbmc.fr`, allows the analyse of your DOSY experiment in simple, efficient and easy way !

Simulated tests

• **Polydisperse species**

PALMA reconstruction for various values of λ of the simulated asymmetric distribution built from 15 log-normal components, ranging from 18 to $85\mu m^2/s$, with intensities ranging from 0.1 to 10. The intensities are chosen as $10/(1.4^{i-1})$, $i = 1, ..., 15$.
$M = 64$, $N = 256$, with noise level 0.1%.

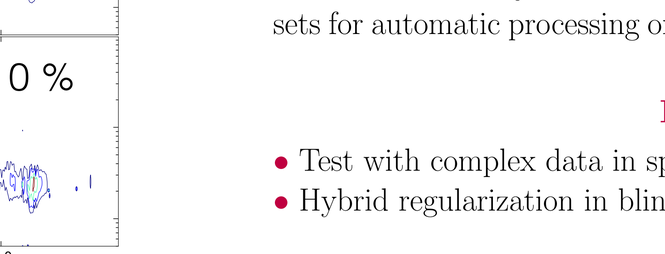




$\rightsquigarrow$ **Best choice of $\lambda = 0.01$**

• **Comparaison with other algorithms**

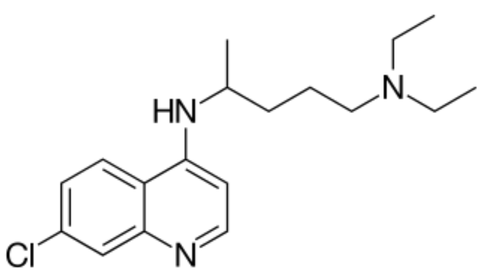
Comparison between our approach and other alogrithms proposed to solve the ill-posed problem in DOSY NMR by recovering the signal defined in the above.



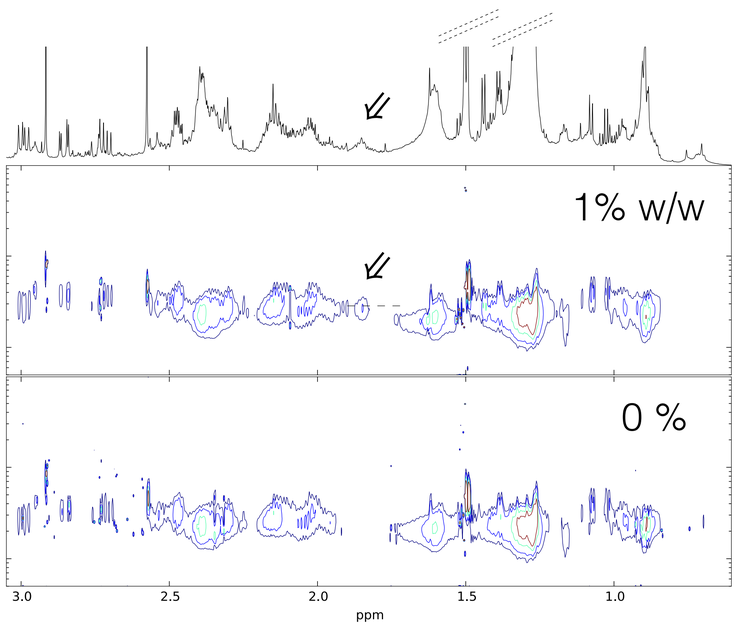
Algorithm	Qlty reconstruction $\left(-10\log_{10}\left(\frac{\|x_{rec}-x_{orig}\|}{\|x_{orig}\|}\right)\right)$ *Higher is better*
ITAMeD	08.89
ITAMeD with ℓ_p	06.18
TRAIn	06.60
PALMA with $\lambda = 0.01$	14.60

$\rightsquigarrow$ **Best reconstruction with PALMA algorithm**

Application polydisperse polymers



DOSY detection
in a plant extract



Comparison of two DOSY experiments on a brown algae extracts, one with 1% w/w $0.16\, mg\, mL^{-1}$ Chloroquine added to the sample. The aliphatic region is shown, with the CH_2 signal of the Chloroquine higlighted with an arrow. The dashed horizontal label is at $285\mu m^2/s$.

Conclusion

• PALMA algorithm is a good tool to recovert the DOSY NMR signal. It can be run in a fully automatic manner, where users may submit their datasets for automatic processing on the web site `http.palma.labo.igbmc.fr`

Perspectives

• Test with complex data in spectrometry field.
• Hybrid regularization in blind signal restoration problems