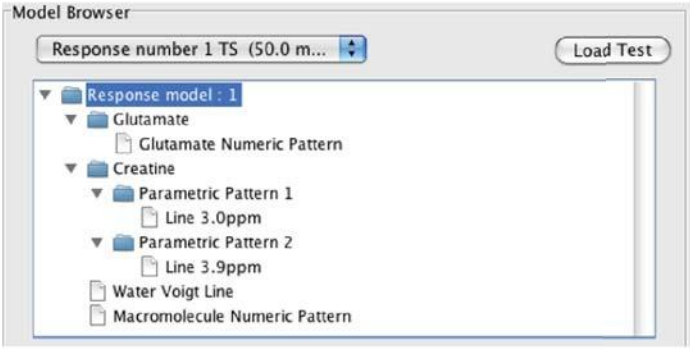


Figure 1. This shows an example of model tree structure. The top combo box shows the selected spectrum (with saturation time 50ms) in a set of responses. The glutamate was combined from multiple voigt lines into a numeric pattern to reduce the complexity of the model. Creatine consists of two parametric patterns. Water is a voigt line, and macromolecules are from imported spectra.

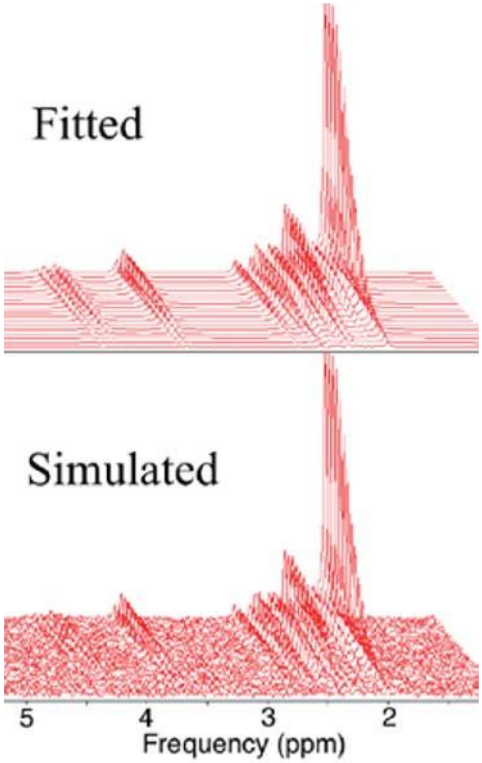


Figure 2. Simulated and fitted saturation recovery experiment for NAA plus glutamate. The 2 ppm peak (T1=2500ms) of NAA was set up to have a longer T1 than the other peaks of NAA (T1=750ms) and glutamate (T1=1000ms). Saturation recovery times from 50ms to 12000ms in logarithmic spacing. SNR would not be sufficient to fit all spectra separately, while the 2D fit enforces appropriate parameter values based on the high SNR spectra.

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Iterative improvement of lineshape estimation

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Purpose/Introduction: Magnetic Resonance Spectroscopy is a technique for noninvasive monitoring of metabolites anywhere in a patient. Static and dynamic inhomogeneity of the magnetic field applied to the patient distorts the function that governs the natural damping of the signals. Ideally, the damping function of metabolites in liquids is exponential, but under in vivo conditions it is unknown due to heterogeneity of the tissue of a patient. We investigate by way of simulations whether the iterative improvement of lineshape estimation can improve the overall result.
Subjects and Methods: Our method consists of an extension of that in [1] by means of iterations, estimating a common damping function for a me-

tabolite database [2]. An asymmetric triangular function is multiplied by a simulation signal [3], then Hankel Singular Value decomposition (HSVD) is used as initial modeling method to calculate the first parameter estimates that will be used in Eq.(1). We used iterations in order to improve the parameter estimations as follows:
Step i. Estimation of the damping function using Eq.(1).
Step ii. Denoising of the obtained damping function.
Step iii. Final fitting of the signal using the damping function estimated at Step iv. Steps i to Step iii applied iteratively until parameters' convergence is reached.

$$g(t) = \frac{y_{ML}(t)}{\sum_{k=1}^{K} \alpha_k e^{j2\pi f_k t}} \qquad (1)$$

where $y_{ML}(t)$ is the distorted metabolites signal and the parameters in the denominator are estimated with HSVD and Nonlinear Squares (NLLS) fit.
Results: We could prove that the reconstructed lineshape obtained by iterations improves significantly. Results of estimations and the corresponding residuals are shown in fig.1-2. In fig.2 one can see how the residuals diminish comparing the first and the last iteration. We consider the bias-variance trade-off because increasing the number of sinusoids decreases the bias but increases the variance and vice versa, so we look for an optimal order that leads us to the best possible results.
Discussion/Conclusion: Although perfect estimation of the lineshape distortion is difficult, simulations are important to find a good approximation. Since parameters estimated in an iteration are used for the next one, a bad initial estimate will affect the final result. Iterations provided the expected successive improvements.
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3. Vanhamme L, et al, 1997, J. Magn. Reson, 129, 35-43.
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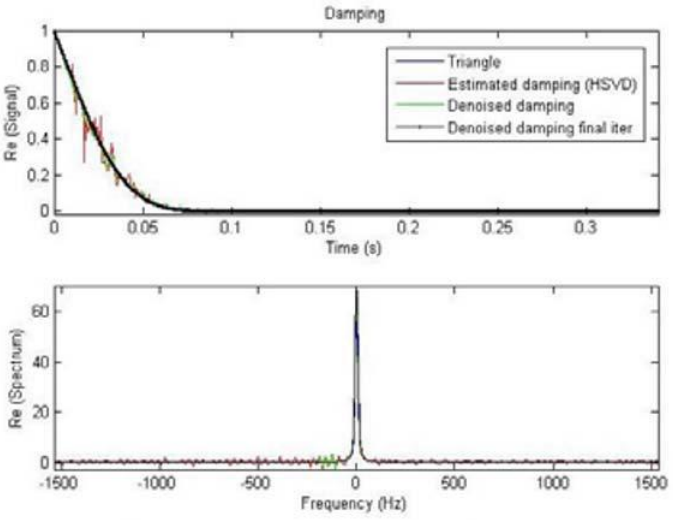


Fig.1 Time and frequency domain representation of the asymmetric triangular function. Initial estimated damping function and denoised damping function after several iterations (top) and corresponding spectrum (bottom).

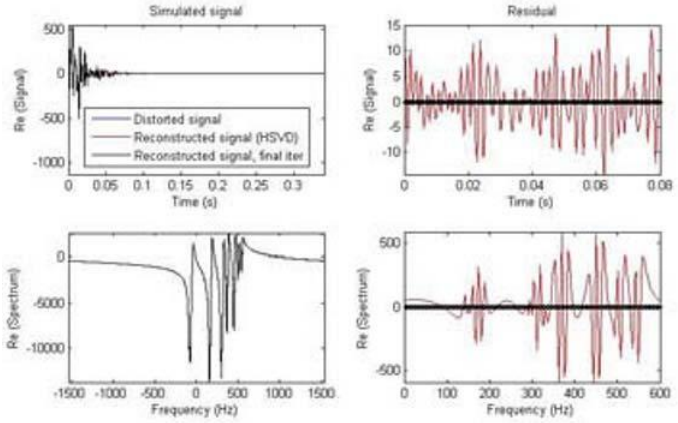


Fig.2 Simulation signal in time and frequency domain with the fitting results and the corresponding residuals after applying the damping function estimated in Step iii. Left: Real part of the signal in the time domain (top) and the corresponding Real part of the spectrum (bottom). Right: the corresponding residuals. As can be observed in the residual plots, there is a large improvement.

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NMR spin Hamiltonian parameters for the polyamines of prostate tissue from ab initio calculations

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Introduction: Knowledge of chemical shifts δ and coupling constants J for metabolites is of paramount importance for simulation of metabolite signals to be used as basis-set in spectral analysis algorithms. These NMR spin Hamiltonian parameters can be estimated from NMR spectra of solutions or calculated from ab initio methods. Spin-coupling constants are very difficult to determine from spectra of solutions especially when they display complicated multiplet structures as those of the polyamines: putrescine, spermidine and spermine, present in prostate tissue. Thanks to *ab initio* calculations, they can be derived once the geometrical structure of the molecule is known. To the best of our knowledge no J values are yet at disposal in literature for spermine, spermidine and putrescine. In this study, we have 1) calculated δ and J values for isolated and solvated polyamines, 2) simulated the corresponding NMR spectra that we compared to the experimental spectra obtained in D_2O at 400MHz.
Methods: Present quantum chemical *ab initio* calculations are based on Density Functional Theory (DFT) with the hybrid B3LYP functional and using Gaussian basis sets 6-311++G(d,p). Chemical shifts are calculated using the Gauge Invariant Atomic Orbital (GIAO) method with TMS chosen as reference. Solvatation effects are taken into account through the Polarisable Continuum Model (PCM). All calculations have been carried out using the computational package Gaussian03 [1] and the graphical interface Gabedit [2].