Supporting information: Numerical recipes for faster MAS-DNP simulations

Frederic Mentink-Vigier*
National High Magnetic Field Laboratory, Florida State University, 1800 E. Paul Dirac Dr, FL, 32310, USA
fmentink@magnet.fsu.edu

Table of Contents

Full Liouville versus Hilbert / Liouville formalism

Figure S1 reports the time dependence of the polarization of a 3 spins system {2 electrons – 1 proton} after 100 ms of evolution. The simulations were carried out via two methods, the full Liouville and the Hilbert/Liouville formalism, corresponding respectively to the full lines or the dashed lines. The two methods are nearly identical.

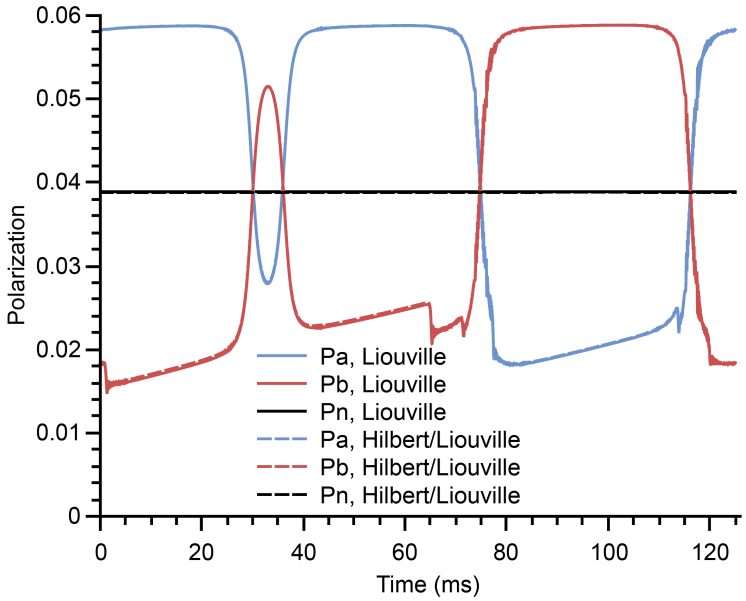

Fig. SI 1: Single crystal MAS-DNP simulations with a 3 spins system {2 electrons – 1 proton} computed with two methods: the full Liouville (full line) or the Hilbert/Liouville (dashed line). Blue, polarization of electron spin a, red polarization of electron spin b, black proton polarization.

Hilbert Liouville simulations, S>1/2

Figure Fig. SI 2 corresponds to the broader MAS-DNP spectra reported in figure 9 in the main text. For the CE case (right), one can observe enhancement outside of the central transition region which seems to correspond to satellite transition (3/2<->1/2, -3/2<->-1/2, 5/2<->3/2, -5/2<->-3/2) that generate cross effect.

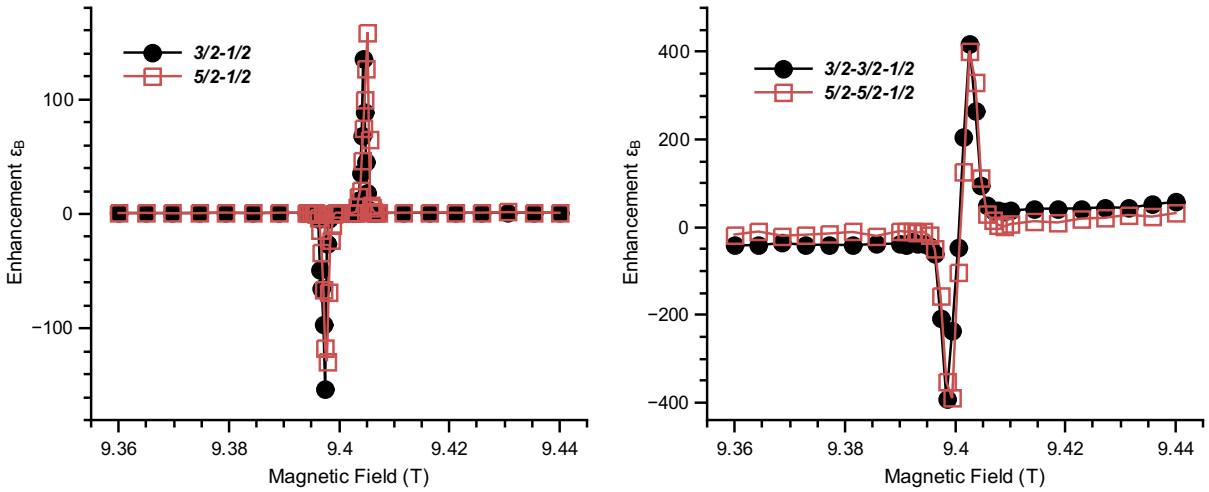

Fig. SI 2: MAS-DNP field profile computed with the hybrid Hilbert/Liouville method after 25 ms evolution. Left, Solid Effect case with one electron spin 3/2 (black circles) or 5/2 (red open squares) and one carbon atom; Right, Cross-Effect case with two electrons spin 3/2 (black circles) or 5/2 (red open squares) and one carbon. All spectra were computed with the equidistant integration and 2048 points.

Figure Fig. SI 3 corresponds to the calculated MAS-DNP field profile of {electron spin 3/2 - electron spin 3/2 and carbon} computed for two different evolution durations: 12.5 ms and 100 ms. Both MAS-DNP spectra are identical.

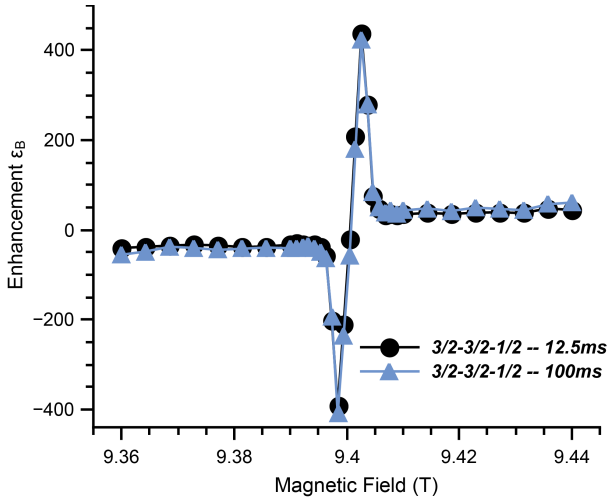

Fig. SI 3: MAS-DNP field profile computed with the hybrid Hilbert/Liouville method evolution. Cross-Effect case with two electrons spin 3/2 and one carbon computed after 12.5 ms (black circles) and 100 ms (blue triangles) of free evolution. All spectra were computed with the equidistant integration and 2048 points.

Impact of the ^{15}N relaxation times on the proton polarization

Fig. SI 4 reports the impact of the ^{15}N longitudinal relaxation time on the proton enhancement. Even for short ^{15}N longitudinal relaxation times, the proton polarization is unaffected. This confirms that the nitrogen spin dynamics on the biradicals can safely be neglected in the regime tested.

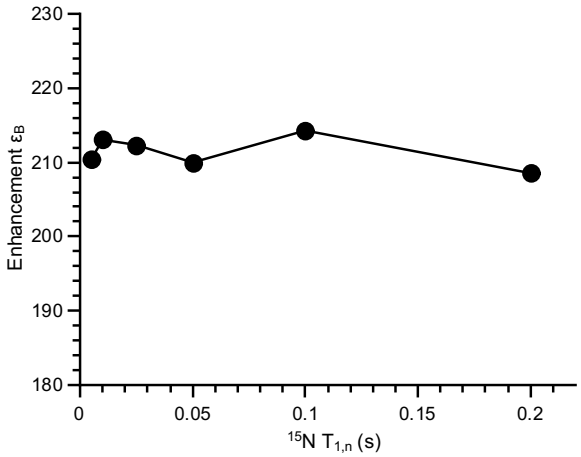

Fig. SI 4: MAS-DNP proton enhancement ϵ_B computed with the hybrid Hilbert/Liouville method after 100 ms of free evolution of a spin mimicking a AMUPol labelled with ^{15}N. Black circles represent a 5 spins system {2 electrons spin ½, 2 ^{15}N, 1 proton}. Both secular and pseudo-secular ^{15}N hyperfine coupling terms are considered, and the ^{15}N relaxation time is varied. $T_{2,n}^{15\mathrm{N}}$ was set to 3 ms.