

Magn. Reson. Discuss., referee comment RC4
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Comment on mr-2022-18

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Referee comment on "Simulation of NMR spectra at zero and ultralow fields from A to Z – a tribute to Prof. Konstantin L'vovich Ivanov" by Quentin Stern and Kirill Sheberstov, Magn. Reson. Discuss., <https://doi.org/10.5194/mr-2022-18-RC4>, 2022

This is a well written and clearly presented tutorial paper. I think that a pedagogical paper supported by a well-documented and accessible simulation code to bridge the gap between a basic NMR understanding using the vector picture and advanced product operator simulation packages like SPINACH and Spin Dynamica will be of benefit to the NMR community. This paper goes a long way to providing this link; however, I think that focus on ZULF NMR simulations, particularly in the earlier sections of the paper, may be confusing for many non-experts and may therefore limit the audience for this very nice contribution. The final section of the paper is quite theoretically challenging for the non-expert and will likely only be of interest to those in the ZULF community. Overall I think that this paper is publishable with minor revisions; however, the addition of some clearer links to high-field NMR simulations (see specific suggestions below) along with a slightly modified version of the MATLAB code to allow the user to perform a more familiar HF NMR simulation to compare with the ZULF simulations would make this a much more broadly useful contribution.

Specific Comments:

- There are a few concepts that are mentioned by not defined clearly and so may confuse a less knowledgeable reader
 - Hilbert space (p6 line 154) is mentioned but not explicitly defined
 - Bra-ket notion is used in eq. 17 and 18 without being explained/introduced
 - On a related note it would be helpful to define the alpha and beta kets with the matrix notation when they are first introduced. I don't think it is made quite clear the relationship between these states and the columns/rows of the matrices.
 - P8 line 201 is the first explicit mention of eigenstates. I think it would be useful when introducing the Zeeman Hamiltonian (eq 5) to explicitly define the alpha and beta kets as the eigenstates and to show the relationship between these states and the matrix representation. This would also be an opportunity to introduced the time-independent Schrodinger equation for 1 spin before the introduction of the Liouville

von-Neuman equation for the density matrix (see point 3 below).

- Eq. 11 – the use of I_x , I_y and I_z to denote the sum of the angular momentum operators over a number of spins is confusing as this same notation is used in eqs. 3 and 13 to denote just the 2x2 angular momentum matrices. I suggest using a different letter such as L to denote a sum over multiple spins. I had a similar issue with the definitions in eqs 48-51, where I was unsure of the definitions of various terms and found the use of bold and italics unclear/inconsistent.
- Eq. 23 for the equilibrium matrix includes implicitly within it a two-spin-order term that emerges from the product. It is common in NMR textbooks, when analysing pulse sequences using product operators to express the equilibrium starting state as just the sum of the I_z operators for the various spins of interest and to omit any higher spin order terms. I think it would be useful to explicitly show the expansion and explain why, and under what circumstances, the single spin operators are a reasonable approximation of the equilibrium density matrix at thermal equilibrium.
- I think it would be useful prior to Eq. 26 to explicitly give the Liouville-von Neumann equation to which it is a solution.
- On p14 line 350 T_2 is defined as the “coherence time constant”, which is a true definition but will be unfamiliar to most readers who will better know this as the spin-spin relaxation or transverse relaxation time constant.
- In section 2.7, the focus is put on the acquisition parameters for ZULF spectra without any discussion of how these relate to the acquisition parameters for standard HF spectra, where the spectrum is acquired in the rotating frame and Larmor frequencies are defined as chemical shift offsets relative to a reference frequency. As the ppm scale and HF NMR is the most natural reference point for most readers, I think it is important to describe the two regimes and the relationship between them. Indeed, that is what I was expecting in the “comparison with high-field NMR” section.
- Due to the focus on ZULF NMR the non-standard case of static field pulses is introduced but the standard representation of ideal RF pulses in the high field regime using rotation operators is not described. The first mention of a rotation operator is on line 599 (p26). This is potentially confusing as the role of rotation operators in NMR simulations has not been described previously. I think it would be helpful in the pedagogical spirit of this paper to include a brief description of this in the theory section.
- In the introduction to ZULF NMR the authors choose to define ULF NMR as where there is a Zeeman contribution but this is not dominant. This definition excludes NMR in the tens of μT regime, notably Earth’s field NMR. By excluding EFNMR a key step in the development of ZULF NMR is omitted, from the initial EFNMR experiments by Packard and Varian in 1954 (Phys Rev), where pre-polarisation and non-adiabatic field switching was first used to the first pulsed EFNMR work of Callaghan and LeGros (American Journal of Physics, 1982) and up to the work by Appelt et al (Nature Physics 2006), who was the first to introduce the idea of using a Halbach for prepolarisation at a few Tesla before detection in μT fields.

Technical corrections

I noted a couple equation references that appear to be incorrect:

- I think on p17 line 411 it should be eq 36 while line 412 should be eq 37.
- I think on p18 line 456 it should be eq 35.

