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Magn. Reson. Discuss., referee comment RC2
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Reply on RC1

Anonymous Referee #1

Referee comment on "Simulation of NMR spectra at zero- and ultra-low field 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-RC2, 2022

In response to the Author and Community comments so far:

I think that this paper could eventually end up being a good source of reference for ZULF NMR as the authors intend, but for now it lacks in both clarity and detail.

I still find the objective unclear. The abstract promises "detail, including the tricks that are usually omitted from research papers and assuming as little prior knowledge from the reader as possible". However, the paper is not written clearly, several details are omitted, neither appear any tricks, and there are several inaccuracies (see the end) that can confuse readers regardless of their level of familiarity with theory of NMR.

Here is what I would expect the paper to contain for those entering the ZULF NMR field, or those with little experience of simulations, in this order:

- An overview of common situations where ZULF NMR simulations may be useful, maybe because analytical expressions are not available in: (a) complex spin systems, (b) free evolution near the edge of the ZULF regime, (c) evolution under pulses, e.g. dc pulses, composite pulses, (d) evolution during field sweeps, level crossings, such as those used in ZULF parahydrogen-induced polarization protocols, (e) evolution during dynamical decoupling sequences or the ZULF-TOCSY type of spin locking experiments done by the Ivanov group, (f) relaxation, (g) errors in pulse sequences or spin Hamiltonian parameters, (h) simulation of geometric effects such as sample shape, detector position, or inhomogeneous fields. The authors do not have to cover all of these in detail, but it would help to specify what they are, and give literature examples for each.
- An overview of the simulation "choices" that can be made by beginners: (a) eigenvector/eigenvalue analysis in either Hilbert of Liouville space, so that for time intervals where the Hamiltonian is constant you simply take an exponential of the eigenfrequency, rather than the whole matrix, (b) use of other symmetry-adapted bases, e.g. Zeeman vs. total angular momentum, and treat smaller subspaces one by one, (c) brute-force propagation of the Liouville von-Neumann or Schrodinger equation, say in the Zeeman basis. In the manuscript, it appears that a combination of (a) and (c) has been used, but it is not completely clear when and how.
- A few illustrative examples from the list (a)-(g) above. Novelty is not required if these examples reproduce the results of previous work with appropriate citation. Such as "In work (author et al., 20xx) this was shown. We will now show the reader how this can be simulated by …" and then proceed to do so, step by step, without leaving any gaps

or diverting the reader to sources elsewhere. I will concede that the examples given by the authors are acceptable for a tutorial paper, but they do lack the complete start-to-finish detail that would allow a graduate student with a basic knowledge of quantum mechanics to sit down at a computer and work through them without getting stuck.

In my opinion, the authors are assuming a lot more of the reader than they realize, so their work can only be followed by someone who already has an expert level of experience in spin dynamics simulations for NMR, and who is probably capable of looking up the PhD theses already mentioned in the previous review comment.

Below are some specific or technical comments that I recommend the authors address:

- Line 21: "Use frequency dispersion" instead of "chemical shift dispersion"
- Line 24: The reference "(Thayer and Pines, 1987)" does not seem an appropriate citation with the 1.2 GHz NMR magnet?
- Line 29: "Mumetal", rather than "μ-metal"
- Line 31: "does no longer influence the outcome of the experiment" is highly ambiguous. Consider replacing with "where the Larmor period is much longer than the coherence time, so that the field can be completely neglected".
- Line 47: "at ZULF, there is no such intuition as the vector model". Is that really true? The AX spin system can often partitioned into an isolated 2LS where cyclically commuting operators can be represented as a vector model picture, see for example https://doi.org/10.1063/PT.3.1948 or https://doi.org/10.1021/acs.jpca.6b04017 supporting information.
- Line 56 and 77: "using a theoretical framework coming from atomic physics". I don't think this is ok. You apply the rules of addition of angular momentum. This is not specific to atomic physics – it is just as widely used in molecular (e.g. rotational) spectroscopy and NMR.
- Line 69: "we assume the reader is familiar with general concepts of NMR but not necessarily with simulation". This is not a clear sentence.
- Line 82: Spinach already has a large set of examples for zero-field NMR, e.g., http://spindynamics.org/wiki/index.php?title=Zerofield.m and http://spindynamics.org/wiki/index.php?title=Zulf_abrupt.m (sudden field drop), and probably SpinDynamica does too. These could be mentioned more directly, even though the above links are not permanent ones.
- Line 269: "is sometimes referred to as the sandwich formula" needs a reference. The only time I have read about "sandwich formulae" in the context of NMR is the rotation sandwich formulae in Levitt's book "Spin Dynamics: basics of nuclear magnetic resonance". These are specific to cyclically commuting triads of operators, i.e. fictitious spin-half representation of a two-level subspace
- Line 272: the "propagation operator" is a propagator
- Starting line 341: For the sake of clarity, let us not call signal or time a vector. Perhaps "list" or "array" of time points or time-amplitude pairs
- Line 505- 507: The phenomenon described is not nutation. Better to refer to the excitation curves as "Rabi curves"
- Style comment: please cite equations as "…, see Equation (x)" rather than "see (x)".