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Comment on mr-2022-18

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-RC1, 2022

The discussion by Stern and Sheberstov introduces to readers some basic principles by which to simulate NMR spectra of simplistic molecules during free evolution of their nuclear magnetization in a zero or ultralow magnetic field (ZULF). Specifically, the compounds must contain two sets of magnetically equivalent spins-1/2, each with a different gyromagnetic ratio, for example a carbon-13 and hydrogen-1.

Technically speaking, the work is correct, but readers should note that the content is not so original, and in my opinion a narrow viewpoint on the topic of near-zero-field NMR. Butler et al. wrote a key paper back in 2013 describing the theory of zero-field NMR in not only AX_n systems as presented in this work, but more complex spin systems A_mX_n and AX_mB_n as well. Many of the results were derived analytically without simulations, for example, using perturbation theory.

Simulations of zero-and-ultralow-field NMR spectra in AX_n, A_mX_n and AX_mB_n are also presented in detail in several PhD theses from the early 2010s: see for example Dr Thomas Theis (2012, UC Berkeley, https://escholarship.org/uc/item/01d528kh), Dr John Blanchard (2014, UC Berkeley, https://escholarship.org/uc/item/2mp738zn) and Dr Tobias Sjolander (2017, UC Berkeley, https://escholarship.org/uc/item/2kj4v04n). Readers are encouraged to consult these original sources.

I encourage the authors to revise the paper by including more original content. For example, simulating the zero-field NMR spectra of compound that has not yet been studied experimentally, or magnetic fields bordering the zero-field condition where the perturbation theory starts to break down. Alternatively, by going beyond summarizing the main results of Butler-2013 and reviewing other works where zero-field NMR spectra are calculated. I believe this would be very useful to readers interested in simulation, not only to do justice to the works listed above. Perhaps a quick way is to use a table: compound or spin system, simulation approach (e.g. exact, perturbation theory), software, literature reference .

Additional comments:

- Authors and Readers should be aware of review article on zero-and-ultralow-field NMR, plus applications, published by Jiang M, Peng X et al. in 2021. This deserves to be mentioned: https://doi.org/10.1016/j.fmre.2020.12.007

- Some of the equations can provide valuable physical insight into how a ZULF NMR experiment works, but it is not explained. Let us take Equation 57 as an example. The total magnetization operator $M_z = g_I I_z + g_S S_z$ is applied to an eigenstate of the zero field, that is $|F, m_F\rangle$ in the case of AX_n. The result is immediately quoted in terms of Clebsch-Gordan coefficients. There is a slightly different way to write the result where the operator is given as $Mz = g_I (I_z + S_z) + (g_S - g_I) S_z$. Here the first term on the right-hand side of the (=) sign leads to the eigenvalue $m_F g_I$, while the second term leads to a sum over other operators, and overall proportional to $(g_S - g_I)$ times the C-G coefficient. The authors may want to mention that this second term leads to ZULF signals where the amplitude of peaks scale with $(g_S - g_I)$.