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Discussions

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Comment on mr-2021-36

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Referee comment on "Mechanisms of coherent re-arrangement for long-lived spin order" by Florin Teleanu and Paul R. Vasos, Magn. Reson. Discuss., https://doi.org/10.5194/mr-2021-36-RC2, 2021

The work by Florin Teleanu and Paul Vasos gives an overview of the pulse sequences developed for the excitation and manipulation of long-lived spin order in solution state NMR. Particular reference is made to previous work describing broad band excitation sequences developed for excitation of singlet state magnetization and previously reported in J Am Chem Soc 129, 328-334 (2007). I agree that aspects of basic science and methodological development can sometimes be obscured by ‘utilitarian perspective’ and that the latter should never be an impediment to the former. Unfortunately, no funding would follow, my feeling is the two need to go hand in hand. The current work gives an interesting overview of some of the thinking that underscored this work. However, it does not appear to give much additional analysis or insight that is not already contained either within the original JACS paper or in the Supplemental Info to that paper. In this context the current work reads partway between a review article and a personal reflection, rather than a novel research work per se. If the purpose is a review article then the scope should be expanded to include other works, and maybe include some areas of application. If it is intended as a novel work in its own right, then this needs to be spelled out much more clearly.

Some specific aspects that might be considered:

- I personally find it very difficult to see the equivalence between operators in the singlet-triplet basis and Cartesian operators. The latter are much more intuitive for understanding the response to pulse sequences. I had to refer to the SI to the JACS paper to follow the interconversions here. In the absence of this SI and the transformations required, it is very difficult to follow the current manuscript, switching from one basis set to another.
- The figures generated in SpinDynamica are confusing. For example in Figure 1, the LLS would be a vector located in the $ZQ_x/2I_zS_z$ plane given by Eq (3) and that interconversion between ZQ_x and ZQ_y takes place at the difference in chemical shifts

under the Hamiltonian $H = \Omega_1 I_z + \Omega_2 S_z$. However, as it is drawn it looks like the evolution of zero quantum coherence is under the influence of the scalar coupling $2I_zS_z$ which interconverts ZQ_x and ZQ_y at a frequency $\Delta\Omega$. This can't be what is intended as ZQ is invariant under the active coupling which means it shouldn't rotate about $2I_zS_z$? Similarly, in Figure 2. Maybe something else is being portrayed in these figures? In which case it could be better explained.

- In Eq. (8) should the Hamiltonian just be $\Omega_1 I_z + \Omega_2 S_z$ since ZQ_x commutes with $2I_zS_z$ the latter term is not needed?
- Please clarify what is meant by Eq (10)? The expression on the RHS is not a LLS? Isn't it SQ evolution of the in phase and antiphase components of the doublet under the scalar coupling? Which means it's not long lived?
- Figure 5 needs better explaining for the same reason as point 2) above. Should the left-hand evolution of ZQ_x and ZQ_y at a frequency $\Delta\Omega$ be under the Zeeman Hamiltonian $\Omega_1 I_z + \Omega_2 S_z$. While the evolution in the right-hand diagram at a frequency J should be under the active coupling Hamiltonian $2I_zS_z$?
- In the pulse sequence in Figure 1, it looks like the density operator at time point C should contain more terms than described? Should there not be some I_xS_z or I_zS_x type terms which are also destroyed by the gradient g1?
- Please define all parameters in the pulse sequences in the figure captions. There is a great deal of detail missing. How are all the delays defined? Label all pulse phases? Does the phase of the spin lock matter? There is no mention of any phase cycling. The pulse sequence in Figure 1 looks like it needs a phase cycle? Otherwise would Zeeman terms be excited by the final pulse and contribute to the spectrum?

Minor points:

- In figure 2, should Q_{LLS} be in the opposite quadrant if it is given by $-4/3(ZQ_x + I_zS_z)$?
- Is there a typo on the RHS of Eq (8), second term should be ZQ_y?
- Figure 1, timepoint A should be after the 90° pulse?