

Magn. Reson. Discuss., author comment AC3
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Reply on RC2

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Author 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-AC3>, 2021

Thank you for the comments and for agreeing that perspective is sometimes important. We did not comment on other implications, indeed. This article was written to provide additional insight into several papers on the singlet-development route (notably Sarkar et al., JACS 2007, Sarkar et al., Chemphyschem 2007, Ahuja et al., JACS 2009) and to comment on the difference between long-lived coherences and zero-quantum coherences. By no means did we intend it to be a comprehensive review of the available literature, as there are already such papers describing extensively, notably from Malcolm Levitt's group (M.H. Levitt JMR 2019, G. Pileio, PNMRS, 2017). However, we did expand the scope, as described above, to comment on recent sequences designed for weakly-coupled spin systems (M2S) and discuss them in parallel with the ZZ+ZQx sequence mentioned above.

Other comments:

- *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.*
- We performed all conversion from Cartesian product operators to Singlet-Triplet Operator using SpinDynamica. We will upload the notebook as SI. The conversion can be easily reproduced.
- *The figures generated in SpinDynamica are confusing. For example in Figure 1, the LLS would be a vector located in the ZQx/2IzSz 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 $2I_z S_z$ 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 $2I_z S_z$? Similarly, in Figure 2. Maybe something else is being portrayed in these figures? In which case it could be better explained.

- We saw the issue of how figures may have been misleading and corrected accordingly, thank you for pointing this out. We meant to show the evolution of the density operator projected on its three different components (ZQ_x , ZQ_y and $I_z S_z$), thus rendering a visual 3D dynamics during the pulse sequence. We never intended to state that the zero-quantum coherences evolve due to the scalar coupling.

- *In Eq. (8) should the Hamiltonian just be $\Omega_1 I_z + \Omega_2 S_z$ since ZQ_x commutes with $2I_z S_z$ the latter term is not needed?*

- We agree, this was corrected accordingly

- *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?*

- In Eq (10) we showed the expression for long-lived coherences (the counterparts of long-lived states) in terms of product operators. Even though they are a combination of singlet-quantum coherences, they do display a long lifetime under CW irradiation much greater than the one corresponding to transverse magnetization (see Sarkar, Ahuja, Vasos, Bodenhausen, PRL, 2010), though not as big as the one corresponding to long-lived states.

- *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 $2I_z S_z$?*

- We modified Figure 5 to avoid any misunderstanding. The evolution of ZQ and LLC is displayed under the Zeeman Hamiltonian for a pair of magnetically nonequivalent and scalar coupled spins.

- *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 $I_x S_z$ or $I_z S_x$ type terms which are also destroyed by the gradient g_1 ?*

- After the spin-echo (point B) only the anti-phase terms are present which will be completely converted by a 45° pulse with phase γ into a sum of zero- and double-quantum coherences as well as zz -order magnetization.

- *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?*

- We modified Figure 1 accordingly and add a full description of the pulse sequence and comment on the above. The phase of the lock is of no consequence, as the locked operator has spherical symmetry. We made this clear in the revised Ms.

- *In figure 2, should Q_{LLS} be in the opposite quadrant if it is given by $-4/3(ZQ_x + I_z S_z)$?*

- We have deleted the minus sign (thus reversing the population difference we refer to).

- *Is there a typo on the RHS of Eq (8), second term should be ZQ_y ?*

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- *Figure 1, timepoint A should be after the 90° pulse?*

- Corrected, thank you.