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Interactive comment on "Heteronuclear and Homonuclear Finite Pulse Radio Frequency Driven Recoupling" *by* Evgeny Nimerovsky et al.

Anonymous Referee #1

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I would like to thank the authors for the extensive explanations and response to my original review. While it clarifies some points, there are still points where I disagree with the paper and explanation. I will respond to some of the comments that I consider still unclear and not solved.

(1) The authors talk about offsets and chemical-shift differences. While I understand that in the homonuclear case the chemical-shift difference plays an important role in the classical description of RFDR, I do not see that the chemical-shift difference is important in the heteronuclear case. I can see that offset effects are important because they change the nutation frequency and the nutation axes and introduce small errors in the 180 degree pulses that could play an important role in the polarization transfer. This might sound like semantics but I think this is an important point that needs to be

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clarified whether offsets or chemical-shift differences are relevant in which case.

(2) In the Theory section, the authors talk about analytical integration of the Hamiltonian as written in Eq. (1.4) that is used in the numerical simulations. I still think that in the context discussed here, Eq. (1.4) is wrong and needs a Dyson time ordering operator in front of the exp{ } term. The Hamiltonian used here cannot be integrated analytically because it does not commute with itself at different times even over a small time periode. The only exception is the heteronuclear case without rf pulses where the Hamiltonian is diagonal in the product basis and can be integrated analytically. In all other cases, either rf on both channels or homonuclear dipolar couplings, there are no analytical solutions. Of course, one can do the integration in a first-order average Hamiltonian sense but then this is not an analytical solution. This can also be seen from Fig. 1 where the simulation changes with increasing N which would not be the case if the integration could indeed be solved analytically. Again, this could be semantics, but I think it is important semantics because an analytical solution is clearly defined.

(3) Model Hamiltonians: Of course, one can use any model Hamiltonian that one wishes to use and see whether it can explain the polarization transfer pathways observed in the experiments. However, it would be good if these model Hamiltonian make also physical sense. I can understand that one argues that the transverse terms in the Hamiltonian are truncated leaving only the zz terms but I cannot understand why on e would use a truncated Hamiltonian scaled by 3/2 for the homonuclear case. I also do not see why one would use an isotropic Hamiltonian because if the zz term is not relevant, the zq Hamiltonian would remain. I think it is important to motivate why certain model Hamiltonians are considered.

I had a quick look at the experimental section and was wondering why the conditions are different from most of the simulations. Especially in Table 3 and 4 it says 100 kHz MAS and rf fields of 50.2/47/49.31 kHz. How can one get a 180 degree pulse in a rotor period if the rf field is smaller than half the spinning frequency? Is the description

presented in the theory and simulations still correct for these conditions? This is basically a windowless pulse sequence (with some of the pulses obviously truncated short) and is very close to the CPPI method of Reif (without the amplitude jump). In addition, this is basically the n=0 Hartmann-Hahn condition where second-order transfer could happen. Have the authors evaluated whether such contributions are a source of the experimental polarization transfer? These conditions don't seem to be part of the simulations that are done mostly at much slower MAS rates with a much lower ratio of pulse and rotor period. I start wondering whether the experiments are not better described by two synchronized R sequences on both channels. As far as I can remember there are some papers about such sequences.

All in all, I think there are too many (sometimes minor) problems that add up and make a judgement of the paper as a whole very difficult.

I think this paper needs a major rewrite to make it more consistent and have a better connection between the parts. I would eliminate the theory/simulation part and start around Fig. (5) to illustrate the different pathways and then make sure that simulations and experimental conditions match.

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