Reply to Reviewer Report 1

Thank you for your helpful advices! It allows me to improve the manuscript and change passages that might be misunderstood by the audience.

I am writing this reply in the form that the reviewer's comments are in italics and marked "RC1"; my replies are marked "GH".

RC1: My major criticism of the paper is that, in its current form, I cannot think of the intended target audience for this paper. If the work is intended as an extension to the typical product operator formalism, which is popular among those who are new to the field, I believe it lacks sufficient background information and explanation of the various cases that are examined to be helpful to that community - I believe it would be more worthwhile to examine fewer cases in the main text for each dimensionality but discuss them more thoroughly. At this level, analytical expressions can be useful to talk about pulse sequence elements, but they quickly lose their applicability as soon as the experimental complexity becomes more than a few pulses. Furthermore, the use of analytical expressions is difficult to motivate in the time when running these simulations (which in this paper correspond to, at largest, 4-dimensional matrices in the Hilbert space) is trivial. Hence, I believe that it could be expanded into an excellent continuation of what is introduced in the conventional product operator formalism.

GH: The latter is indeed the intention of the original manuscript. I will emphasize this fact more strongly in the revised manuscript. I also agree that some of the examples should be discussed in more detail. The target audience is researchers who need some insight into the different processes within the experiments. Of course, if someone is only interested in the resulting state of the spin system after a pulse sequence, a numerical calculation will suffice. Sometimes, however, you want to take a look inside this black box. The desire or need to do so could be a motivation to deal with analytical contexts.

RC1: I also think that the method is interesting to those who do numerical simulations of spin systems, as this lays out a dimensionality reduction technique that requires no approximation of the system. I acknowledge that this is no longer a topic in the direction of analytical expressions, but I believe it is a paper that is well laid-out for a theoretician in magnetic resonance that would guide them through a dimensionality reduction approach. A section that discusses this possibility might be of interest, although I don't think it is required for publication.

GH: For the revised version, I will add this topic to the conclusion section.

RC1: Broadly, I would like to also ask the author to comment in the article about when this technique can be applied in general, as practical applications are limited to A) Hamiltonians that are time-independent or B) Hamiltonians that can be cast in a frame where they become time-independent, either by use of Average Hamiltonian Theory or other analytical methods like toggling/rotating/interaction frames.

GH: This technique is not restricted to time-independent Hamiltonians! The commutator equations are the same if the Hamiltonian is time-dependent. The problem is "simply" to solve the Liouville-vonNeumann equation, which is now a system of linear differential equations, but with non-constant coefficients. No general solution exists. The matrix exponential only corresponds to a first-order Magnus expansion, a more or less adequate approximation. Nevertheless, some of such equations can be immediately integrated. I also obtained analytical solutions for some cases (for example for dipolar decoupling under MAS), but I did not include them in this manuscript because they seemed to me to be beyond the scope of this article. However, it may be mentioned as an outlook or for further applications.

It should be noted that numerical methods are also sometimes associated with problems. For example, convergence problems may arise in Floquet calculations when the rf strength approaches the spin rate. On the other hand, an analytical solution of the problem could make use of the mathematical properties

of the associated function when the parameters approach critical regions, i.e. make use of previous results of mathematics instead of investigating the power in own numerical research.

So in a revised version, I will add a paragraph on time-dependent Hamiltonians.

RC1: During the process of writing this report, I do have a following major concern with the formulation as it is written. In equation 19, the author presents the formulation of the product $\boldsymbol{L}\cdot\boldsymbol{\rho}$ *as the left-handed multiplication of the Liouvillian with the basis vector of operators. This led to my comment that equation 22 has index typos in it, as the dot product* $\boldsymbol{U}\cdot\boldsymbol{\rho}$ *(also left handed by integration of eq. 19) would generate terms such as* $\hat{A}_2 U_{12}$ *in the evolution of* $\hat{A}_1$*. In equation 35, the author says that the propagation rules are obtained from the columns of the propagator, however that is not the case if the author has formulated the theory with left-handed multiplication. The propagation rules are obtained from the rows of the propagator. At the end of the day, this is only rectified by the fact that the timesymmetry of quantum mechanics allows for this (up to a definition of a phase). As such, either I have misinterpreted how the evolution is calculated (*$\boldsymbol{U}\cdot\boldsymbol{\rho}$*), which is unclear given the ambiguous notation in the appropriate sections, or the author has accidentally taken the wrong set of elements from the propagator.*

GH: At this point, I do not agree with the reviewer comment. I have to admit that this problem also gave me a headache for some time. Now, for my opinion, the notation in Eq. (22) is correct. Please look at the example at the end of this reply.

The reason for this at first sight counterintuitive behaviour is that we are dealing with two spaces, one of which is the dual space of the other, both describing the same phenomenon. One space contains the "normal" density matrix operations and the propagator matrix action, the other contains the commutator equations and the propagation formulae. A matrix from one space is the transpose of the corresponding matrix in the dual space. This explains why the columns and not the rows of the propagator matrix give the propagation formulae.

RC1: Specifically, I note the following points:

Page 2 line 31: "dipol-dipol" is a typo.

GH: This will be corrected.

RC1: Page 4 line 79: Minor, but the author should use proper typesetting for dot products ($\boldsymbol{A}^{\dagger}\cdot\boldsymbol{B}$ *instead of* $\boldsymbol{A}^{\dagger}.\boldsymbol{B}$*). This is a problem throughout page 4, but should be consistent in the entire article.*

GH: This will be corrected.

GH1: Page 5 line 122: "on each operator A" missing the hat on the $\hat{A}$.

GH: This will be corrected.

RC1: Page 6 line 152: I find the notation that is introduced overly confusing for this section, particularly, terms such as the $\lambda_{11}\hat{A}_1$ *term in equation 16 are by definition zero, a point that is made in the very line in question. Thus it leaves the reader somewhat confused as to why equation 16 would contain this term.*

The same can be said of the $\lambda_{22}\hat{A}_2$ term in equation 17. The author should either specifically state that the coefficients λ_{nn} by definition or drop them from the equations.

GH: λ_{11} does not vanish in every case, only for a Hermitian basis. Even though this is true for most but not all examples, I have chosen a formulation that really covers all cases. In the literature (Slichter, Abragam), the density matrix is characterized also by non-hermitian operators, mostly by $\hat{I}_{\pm}$. At the moment I do not see a simpler way to present the procedure in the most general form, but I will think about it.

RC1: Page 7 line 77: "The action of the Liouvillian on any $\hat{A}_2$ ($i \in 1..N$) leads to a linear combination of the $\hat{A}_i$". Firstly, I believe there is a parentheses that is missing in after the *N*.

GH: To be corrected (together with an insertion of curly brackets for denoting a set).

RC1 (continued): However, this is a general result of the operators for spin systems being part of a Lie algebra and is well known. For a detailed explanation, I recommend Spin by Ilya Kuprov.

GH: What was meant was "leads to a linear combination of this limited set of A_i (not the whole basis)". This is used to justify the following sentence. I will make this paragraph more explicit.

RC1: Page 8 line 196: The author has typos in the indices in equation 22. For instance, one should find the term $\hat{A}_2 \cdot U_{12}$ in the evolution of $\hat{A}_1$ (line 196), if I have interpreted correctly that the dot product being calculated is $\mathbf{U} \cdot \left(\hat{A}_1 \ \hat{A}_2 \ \ldots \ \hat{A}_N\right)^{\mathrm{T}}$, which is also unclear as it is not stated and only indicated through the ambiguous arrow with a $\hat{H} \cdot t$ decorated over it. Furthermore, please only use dot products when they are actually between two objects of rank-1 or higher, otherwise it is ambiguous what is intended.

GH: All dots which do not belong to matrix products will be removed.

RC1: Page 8 line 198: "recompose the matrix exponential for each new situation". It is unclear what the author means by "each new situation". Please elaborate or be specific.

GH: I will replace this expression by "… for each new experimental situation. The mathematical structure of the commutator equations is the same for all 3D cases, and the same for all 4D cases. Therefore, the propagators also have an equivalent structure. This means that we can use the generic propagation formulae as a template."

RC1: Page 9 line 227: The author introduces in the case of a 2D subspace the operator basis

$$\left\{\hat{A}_i\right\} = \left\{\left(\hat{I}_{1x} + \hat{I}_{2x}\right), 2\left(\hat{I}_{1z}\hat{I}_{2y} + \hat{I}_{1y}\hat{I}_{2z}\right)\right\}$$

which is a linear combination of the operators that one would typically encounter when exploring a 2spin system for the first time (formed by the permutations of $\{\hat{E}, \hat{I}_x, \hat{I}_y, \hat{I}_z\}$). As such, those unfamiliar with why those operators may be linearly combined would likely be confused by this, as it is a nonintuitive basis to build. The author should discuss how, when this procedure is carried out in the native operator basis where the elements are instead

$$\left\{\hat{A}_i\right\} = \left\{\hat{I}_{1x}, \hat{I}_{2x}, 2\hat{I}_{1z}\hat{I}_{2y}, 2\hat{I}_{1y}\hat{I}_{2z}\right\}$$

how the appropriate matrices appear and how one can further reduce this 4D case to a 2D case. This is a critical part of the procedure that is missing from the article, and is not unique to this instance.

GH: I will add a note to the revised version that this low-dimensional subspace will result from the process. The non-intuitivity is something like the price for the low dimensionality. I will also check the other examples for the need for similar additional explanations.

RC1: Page 10 line 235: If the author wishes to discuss the case of cross polarization, it should be noted that the author has rearranged the initial spin state into $\hat{S}_z - \hat{I}_z$ and $\hat{S}_z + \hat{I}_z$*, the latter of which does not evolve and the former which dictates the polarization transfer. This goes along the lines of explaining the operator basis that is used, as without this, the problem would be at least 3D (if one already has collected the zero-quantum terms into one basis state).*

GH: Yes, it should be shown that the polarization difference is an appropriate variable to have a situation that is POF-like, hence 2D. I will add a note that using single polarizations would lead to a 3D case.

RC1: Page 10 lines 241: "The procedure described above reaches the cancellation condition after three commutators of the kind". This language is ambiguous and makes it sound like equation 33 is a generic result to the method and not specific for the types of systems that belong to the 3D case.

GH: The sentence should begin with "Here we are dealing with those cases where the procedure described above reaches… "

RC1: Page 10 line 246: It would be helpful if the author showed how this was calculated.

GH: I will add a note that the propagator matrix has been calculated from the Liouvillian matrix as matrix exponential corresponding to Eq. (20). This can be done for example by using MATHEMATICA, see also SI. More technical details concerning matrix exponentialization are out of the scope of this manuscript.

RC1: Page 12 line 292: "In resonance" should be "on resonance".

GH: This will be corrected.

RC1: Page 13 line 296: "In resonance" should be "on resonance".

GH: This will be corrected.

RC1: Page 14 line 321: It would be helpful to explain what the LG condition is to the reader.

GH: This sentence will be replaced by:

The interaction between S_1 and S_2 is assumed to be zero. This can be realized experimentally by irradiating the S spins with a resonance offset which is $1/\sqrt{2}$ times the rf strength which is denoted by "Lee-Goldburg condition", see [citation].

GH1: Page 15 line 341: "the more the smaller the rf power" clumsy phrasing.

GH: This sentence will be reworded in the revised manuscript.

Example which demonstrates for a 2D space that the coefficient matrix of the propagation formulae is the transpose of the propagator matrix

Given a propagator matrix **U** which performs the time evolution in a 2D Liouville space of the initial density column $\boldsymbol{\rho}_0 = (\rho_{01} \;\; \rho_{02})^{\mathrm{T}}$ to that of a later time $\boldsymbol{\rho} = (\rho_1 \;\; \rho_2)^{\mathrm{T}} = \mathbf{U}\boldsymbol{\rho}_0$:

$$\begin{pmatrix} \rho_1 \\ \rho_2 \end{pmatrix} = \begin{pmatrix} U_{11} & U_{12} \\ U_{21} & U_{22} \end{pmatrix} \begin{pmatrix} \rho_{01} \\ \rho_{02} \end{pmatrix} \tag{1}$$

Let $\hat{A}$ and $\hat{B}$ be basis operators of this 2D space with the corresponding matrices

$$\mathbf{A} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}; \qquad \mathbf{B} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}.$$

Now let us consider the two cases where (i) $\boldsymbol{\rho}_0$ = **A**, (ii) $\boldsymbol{\rho}_0$ = **B** characterize the initial state. The time evolution will be described by

$$\text{(i)} \qquad \mathbf{UA} = \begin{pmatrix} U_{11} & U_{12} \\ U_{21} & U_{22} \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} U_{11} \\ U_{21} \end{pmatrix} = U_{11} \underbrace{\begin{pmatrix} 1 \\ 0 \end{pmatrix}}_{\mathbf{A}} + U_{21} \underbrace{\begin{pmatrix} 0 \\ 1 \end{pmatrix}}_{\mathbf{B}}$$

$$\text{(ii)} \qquad \mathbf{UB} = \begin{pmatrix} U_{11} & U_{12} \\ U_{21} & U_{22} \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} U_{12} \\ U_{22} \end{pmatrix} = U_{12} \underbrace{\begin{pmatrix} 1 \\ 0 \end{pmatrix}}_{\mathbf{A}} + U_{22} \underbrace{\begin{pmatrix} 0 \\ 1 \end{pmatrix}}_{\mathbf{B}}.$$

Translated to propagation formulae this becomes

$$\begin{aligned} &\text{(i)} \quad \mathbf{A} \;\rightarrow\; U_{11}\,\mathbf{A} + U_{21}\,\mathbf{B} \\ &\text{(ii)} \quad \mathbf{B} \;\rightarrow\; U_{12}\,\mathbf{A} + U_{22}\,\mathbf{B} \end{aligned}$$

or

$$\begin{pmatrix} \mathbf{A} \\ \mathbf{B} \end{pmatrix} \;\rightarrow\; \begin{pmatrix} U_{11} & U_{21} \\ U_{12} & U_{22} \end{pmatrix} \begin{pmatrix} \mathbf{A} \\ \mathbf{B} \end{pmatrix}. \tag{2}$$

Comparing equations (1) and (2), we conclude for this example that the coefficient matrix of the propagation formulae is the transpose of the matrix of the propagator. In other words, the columns of the propagator **U**, not the rows, form the propagation formulae.

■

U and $\mathbf{U}^{\mathrm{T}}$ describe the same phenomenon in two different spaces where one is the dual space of the other.