Reviewer Report: Hempel, Analytical expressions for time evolution of spin systems affected by two or more interactions

Hempel introduces a method by which one can reduce the state space of exponentially-scaling spin systems and thereby derive analytical expressions for the time evolution. The method hinges on well known properties of Lie algebras, particularly that products of any two elements of a Lie group generate another member of that Lie group. This allows the author to generate the subspace of operators required to fully describe time evolution in specific cases given an initial starting state, thus permitting dimensionality reduction of the system. The author demonstrates for a variety of different cases how a mD space may be reduced to an nD space and derives analytical means for time evolution in those systems.

I would like to start by stating that the paper is generally laid out well and provides a thorough description of the development along with a diverse set of examples that support the theoretical tool being developed, and in general, I believe this is of worth to the Magnetic Resonance community.

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.

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.

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.

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 $\mathbf{L} \cdot \boldsymbol{\rho}$ 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 $\mathbf{U} \cdot \boldsymbol{\rho}$ (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 time-symmetry of quantum mechanics allows for this (up to a definition of a phase). As such, either I have misinterpreted how the evolution is calculated ($\mathbf{U} \cdot \boldsymbol{\rho}$), 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.

Specifically, I note the following points:

- *Page 2 line 31:* "dipol-dipol" is a typo.
- *Page 4 line 79:* Minor, but the author should use proper typesetting for dot products ($\mathbf{A}^{\dagger} \cdot \mathbf{B}$ instead of $\mathbf{A}^{\dagger} . \mathbf{B}$). This is a problem throughout page 4, but should be consistent in the entire article.
- *Page 5 line 122:* "on each operator A" missing the hat on the $\hat{A}$.
- *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 $\lambda_{nn} = 0$ by definition or drop them from the equations.
- *Page 7 line 77:* "The action of the Liouvillian on any $\hat{A}_i\,(i \in 1..N$ leads to a linear combination of the $\hat{A}_i$". Firstly, I believe there is a parentheses that is missing in after the N. 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.
- *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 $\mathbf{U} \cdot \begin{bmatrix} \hat{A}_1 & \hat{A}_2 & \cdots & \hat{A}_N \end{bmatrix}^{\mathrm{T}}$, 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.
- *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.
- *Page 9 line 227:* The author introduces in the case of a 2D subspace the operator basis

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

  which is a linear combination of the operators that one would typically encounter when exploring a 2-spin 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 non-intuitive basis to build. The author should discuss how, when this procedure is carried out in the native operator basis where the elements are instead

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

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.

- *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).
- *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.
- *Page 10 line 246:* It would be helpful if the author showed how this was calculated.
- *Page 12 line 292:* "In resonance" should be "on resonance".
- *Page 13 line 296:* "In resonance" should be "on resonance".
- *Page 14 line 321:* It would be helpful to explain what the LG condition is to the reader.
- *Page 15 line 341:* "the more the smaller the rf power" clumsy phrasing.