Referee Report on the paper « *Floquet Theory and Average Hamiltonian Theory Revisited : Equivalence, Convergence and Application to NMR* »
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This paper reviews two of the most important perturbative framework used to describe periodically driven spin systems in the solid-state NMR community : The Average Hamiltonian Theory (AHT) and the Floquet-Van Vleck (FVV) approach. One of the main point of the article is to show their equivalence using the Floquet-Magnus expansion (FME) which provides the most general expression of the evolution operator (Eq. (3)) $U_(t,t_0)= e^{-i\Lambda(t)} e{-i F (t-t_0)} e{-i\Lambda(t_0)} $, a unifying framework. The importance of the so-called kick-operator with a vanishing time-average ensures that the effective Hamiltonian (here F) is time-independent and independent of t_0 in the FME framework. Such an independence is lacking in the AHT (which derives from the Magnus expansion) which causes it to fail in some circumstances, as it have been discussed in several papers in the last decades (sometimes called the Magnus paradox). This one of the goal of the present paper to discuss this specific point with numerical simulations on relevant systems for solid-state NMR. I believe that the implicit choice of $t_0=0$ and other assumptions as discussed are also responsible for the common errors made by ignoring the role of the kick-operator. This point is also discussed but should be probably more emphasized.

One of the main results of the paper is the derivation of fourth-order terms is the various expansions investigated (AHT and FVV). To obtain them, the authors introduce an integration-free scheme based on the Fourier-transformation of the differential equation of $\Lambda(t)$ with the two main choices of gauges : (i) $\Lambda(t_0)=0$ (AHT), or (ii) $\int dt \Lambda(t) =0 $ (FVV). After numerical comparisons of truncated expansion for random periodic Hamiltonians, two NMR examples are treated :

- Bloch-Siegert shift for a spin 1/2 in linearly polarized RF field (this is a model that has been thoroughly investigated in the past, with an exact analytic solution; so the gain of the current approach is not that clear to me)
- MAS spectra of two and three dipolar-coupled spin systems under stroboscopic (again, the relevance of such a restriction is not clear to me for ssNMR spectroscopist) and non stroboscopic observation (more relevant for me, but there is an fundamental error in the present simulation I am discussing below)

The main conclusions are the following. If AHT and FVV are equivalent, they differs for truncated series (this point is also not that clear to me, abut as also outlined in the paper, the main error made in the common usage of AHT without accounting for the kick operator). FVV is found to be more accurate than AHT, but again FVV is simply the same as the FME but with a choice of the gauge (see (ii) above). The conclusion is that it is preferable to include the kick operator in any spin dynamics simulation.

The topic covered by the paper is highly relevant for the magnetic-resonance community and the paper is clearly written and – I am convinced - pedagogically useful. The integration-free derivation proposed is interesting, and the numerical comparison are well informative (but the dipolar-spin system ones needs some revisions). I would therefore recommend its publication but there are several points I would like to comment and ask for some revisions.

Prior Works (Major comment).

There are several references which are missing and they are highly relevant for this article. Because of the pedagogical usefulness, I believe they should be added and commented in the context of the paper.

First, there are two papers which overlap the current discussion :

1. A. Llor, *Equivalence between dynamical averaging methods for the Schrödinger equation : average Hamiltonian, secular averaging and Van Vleck transformation*, Chem. Phys. Lett. 2024, 217-218 (**1993**).
2. M. Goldman, P.J. Grandinetti, A. Llor, Z. Olejniczak, J.R. Sachleben, J.W. Zwanziger, *Theoretical aspects of higher-order truncation in solid-state nuclear magnetic resonance*, J. Chem. Phys 97, 8947-8960 (**1992**).

Paper 1 precisely addresses the equivalence discussed in the present paper, including the van Vleck transformation.
Paper 2 discusses the inconsistencies in high-order truncation using the Magnus expansion when neglecting the role kick operator. It contains a thorough discussion on the secular and non-secular separation of the AHT (such a separation is induced by the t0-dependence in the effective Hamiltonian) and in line with the recommendation made here in Section 5.

In addition, The *Russian School* (this naming is my choice) made significant contributions to the field in many papers which have been somehow forgotten. But once they are examined closely, despite the formal difficulty due to a different formalism in the derivation equations, it appears clearly that the same Theoretical framework as the FME was developed under different names (secular averaging or canonical transformation). I would highly encourage the authors to make a comparison of their framework with – for example - the following papers (in the field of Solid State NMR) :

1. L.L. Buishvili, M.G. Menadbe, Application of averaging to magnetic resonance problem in solids, Theor. Math. Phys. 44, 832-836 (**1980**).
2. L.L. Buishvili, E.B. Volzzhan, M.G. Menabde, Higher approximation in the theory of average Hamiltonian, Theor. Math. Phys. 46, 166-173 (**1981**)
3. L.L. Buishvili, M. E. Gumberidze, M.G. Menabde, O.V. Simenk, Dynamics of spin systems in rapidly oscillating external fields, Theor. Math. Phys. 64, 965-969 (**1985**).

This series of paper show how to built an effective Hamitonian for periodically driven spin systems, order by order, using the averaging method, and discuss higher-order approximations using near-identity canonical transformation (very close if not identical to representation defined by the kick-operator). It is the direct NMR antecedent of the FVV-type construction.

I believe the novelty of the present manuscript should be stated more precisely relative to them, I believe this would strengthen the current manuscript in giving more large view of the AHT, FVV and FME. I have the same comment regarding the positioning with respect to a last work that I consider as significant in the NMR field, which provided an earlier correspondence between AHT and Floquet Theory in NMR, M.M. Maricq, *Applications of average Hamiltonian theory to the NMR of solids*, Phys. Rev. B 25, 6622-6632 (**1982**)

About the Fourth order (minor comment).

High emphasis is put on the derivation of the fourth-order and the statement « no fourth-order effective Hamiltonian available in commutator form in AHT ». But fourth order Magnus term in nested-commutator form exist, see Eq. [46] in S. Blanes et al. , Phys. Rep. 470, 151-238 (**2009**). I believe there are other work with recursive scheme to build higher order Magnus expansion.

The Kick operator (minor comment)

The manuscript rightly stresses that the kick operator must be included to obtain the correct signals (Bloch Siegert shift, spinning sidebands – but in the latter case not properly, see comment below). I believe it should be better specified for the reader (and practitioners) the order to which Λ must be retained relative to F for reaching a better accuracy in the simulations. Is a partially truncated kick operator worse than no kick at all (a common practice in the NMR community, as written in the paper).

I have now several comments I give below as ordered they appears to me by reading the manuscript.

Page 2. lines 43-45. “repetitive pulse sequences” . Papers given above by Buishvili et al. are exactly covering this topic.

Page 2. line 54-55. “We demonstrate that both AHT and the Floquet-Van Vleck (FVV) …”. I believe that Ref. Mananga and Charpentier, 2011 was already addressing this specific point.

Page 3. line77. “a finite-dimensional truncation of the infinite-dimensional matrix”. Is there any formal correspondence between the order of such a truncation and the order on the expansion as presented here ?

Page 4. line 111. Eq. (3). This is the central Equation that should be always be preferred to any other representation of the evolution operator. I believe its crucial role should be really emphasized.

Page 4. line 115. Eq. (4). One the one drawback of the notation $\tilde F$ in that its implicit dependence on t_0 disappears. I would recommend to comment on it.

Page 5. line 134. “Eq.(8) is often rewritten as”. I believe the word “often” would require some references ?

Page 5. line 155. The two proposed choices of $\Lambda(t)$ were already proposed in Ref Mananga and Charpentier 2011. The Ref should be added.

Page 6. line 163. Eq. (14a). As written above, F_{AHT} is made t_0 dependent, in contrast to F_{FVV}. Should be stressed. Somehow, the AHT forces part of the micromotion to absorbed in the effective Hamiltonian (see Buishvili et al. with the concept of slow evolution).

Page 8. Lines 210-212. Here the ref Llor 1993, should be added.

Page 11. line 286. “All non-secular terms arise in the kick operator Λ” Somehow, I believe that F should have no non-secular terms (see Goldman et al. 1992) so the AHT choice is non-physical.

Page 14. line 339. “a) numerically exact integration” : how were these exact simulation performed ? Especially how discretized in time ?

Page 16. Eqs. (37). In the definition, t_0 is explicitly given whereas it disappears in Eqs. (38a). Why ? Shouldn't it be more apparent to capture its impact on the dynamics (and to show that is should be at lowest order have the role of a RF phase?)

Page 17. A general comment on the figures. Sometimes an enlarged view would be helpful for the reader to see the variations between the different orders. How does the numerical exact simulation compares to the exact result as derived in the work of Shirley ?

Section 4.2 . I have a problem with this section. Nothing is said about the formal equivalence between t_0 and the $\gamma" angle. So that in powder, the average on γ can be formally solved (for derivation See. Ref. http://dx.doi.org/10.1006/jmre.1998.1415 and also https://dx.doi.org/10.1016/j.chemphys.2015.02.006). It means that spinning sidebands in dipolar-coupled spins systems (for any number of spins) must be positive. This is not the case in Figure 12.