Subject:	JCP: Review instructions, manuscript JCP22-AR-01244
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Cc:	liujian@gmail.com

Dear Prof. Dr. Liu,

Thank you for agreeing to review the below manuscript for The Journal of Chemical Physics. Please return your comments by 22-Apr-2022.

Title: "Non-adiabatic Dynamics using the Generators of the $\mathfrak{su}(N)$ Lie Algebra"
Manuscript No.: JCP22-AR-01244
Authors: Duncan Bossion, Sutirtha Chowdhury, and Pengfei Huo
Section: Article

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Sincerely,

Professor Qiang Shi
Associate Editor
The Journal of Chemical Physics
Institute of Chemistry
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22-Apr-2022

Manuscript Number: JCP22-AR-01244

Title: "Non-adiabatic Dynamics using the Generators of the $\mathfrak{su}(N)$ Lie Algebra"

Author: Duncan Bossion, Sutirtha Chowdhury, and Pengfei Huo

Prof. Dr. Jian Liu
Peking University
College of Chemistry and Molecular Engineering
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China

Dear Prof. Dr. Liu,

Thank you for your review of the above manuscript. We sincerely appreciate your time, expertise, and support of The Journal of Chemical Physics.

A copy of your review is below for your reference.

If you would like to have a record of this review sent to your ORCID account, click on the link below:
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Sincerely yours,

Professor Qiang Shi
Associate Editor
The Journal of Chemical Physics
Institute of Chemistry
Chinese Academy of Sciences

Manuscript Number JCP22-AR-01244:

Overall Rating (required): Bottom 25% - major deficiencies in scientific reasoning

Comments to the Author:
The manuscript, "Nonadiabatic dynamics using the generators of the SU(N) Lie algebra", by Bossion et al. does not present anything new or creative beyond what were already known. In various places, the authors present what have already been proposed or discussed in the literature in such a way as if they first propose the ideas. The current manuscript also include various sloppy statements, which suggest that the authors may have to digest the key papers. I am afraid that the current manuscript should not be published in JCP.
Here I list only a few of them.
1. If the authors indeed grasped the Lie algebra, they would have understood the accurate description of the key concept is manifold, or namely phase space, rather than generators, in Ref. 29, Ref. 52, and Ref. 55 that provide the majority of the key elements for nonadiabatic dynamics in the current manuscript.
2. The Stock-Thoss derivation (Ref. 8) of the Meyer-Miller mapping model invoked the Schwinger oscillator theory of angular momentum. It was first discussed in theory in JCP 145, 204105 (2016) that there exists inconsistency in using the Schwinger oscillator theory in mapping multi-state systems and that the commutation relation between mapping variables (x and p) is questionable for a finite set of states. It was then first suggested in J. Chem. Phys. 151, 024105 (2019) that the physical condition 1/N * Tr[Sum_over_n |n><n|] = 1 should be used in constructing nonadiabatic dynamics methods for general N-state systems. When parameter gamma is zero, the derivation for population dynamics has been clearly given in Appendix A. It was published much earlier than Ref. 29 and even earlier than Ref. 24 where only two-states were considered. In the same paper, it is clearly stated that "The new viewpoint in CMMs can also have implication for nonadiabatic dynamics with semiclassical/quasiclassical mapping models in the Cartesian phase space ...", which means the value of parameter gamma plays a role. In January 2020, the authors of Ref. 29 were even informed by those of J. Chem. Phys. 151, 024105 (2019) that the arXiv preprint of Ref. 29 was in practice an extension of the earlier work [J. Chem. Phys. 151,

024105 (2019)]. Ironically, the authors of Ref. 29 still failed to understand J. Chem. Phys. 151, 024105 (2019) presents an exact mapping approach when gamma is zero. This is indicated by the related discussion on Page 8 of Ref. 29.

3. When such approaches of J. Chem. Phys. 151, 024105 (2019) were expanded for non-zero values for parameter gamma in J. Phys. Chem. Lett. 12, 2496 (2021), it is evident that the W, P, Q versions of Ref. 29 are only three special cases of eCMM originated from J. Chem. Phys. 151, 024105 (2019). This has also been clearly pointed out in J. Phys. Chem. A 125, 31, 6845-6863 (2021) as well as in Acc. Chem. Res. 54, 23, 4215-4228 (2021). In viewpoint of the Lie algebra (if one indeed understands it!), the U(N)/U(N-1) phase space was employed to directly derive the Meyer-Miller mapping model (as an example) in [J. Chem. Phys. 151, 024105 (2019); J. Phys. Chem. Lett. 12, 2496 (2021)]. When Stratanovich phase space with an SU(2) or SU(N) structure was used for quantum dynamics in the literature, most scholars were limited to only the W, P, Q versions, for instance, check what the authors of Phys. Rev. A 101, 033803 (2020) and those of Ref. 29 did even in 2020. More examples can be found. The authors of Ref. 29 even claimed that their approach is parameter-free, with no understanding that three specific values of the parameter are assigned to the W, P, Q versions and that the value can be continuously changed in a certain regime as long as the mapping kernel and its inverse change consistently. It was clear from J. Phys. Chem. Lett. 12, 2496 (2021) that dynamics on Stratanovich phase space should not be limited to the W, P, Q versions and there exists a continuous region of the parameter. Quite interestingly, the authors of the current manuscript presents in Section III-D in such a way as if they come up with the idea and the corresponding relation.

4. It was presented in J. Phys. Chem. Lett. 12, 2496 (2021) and its Supporting Information that the mapping Hamiltonian (with the Meyer-Miller mapping Hamiltonian as an example) as well as the formulation of the time correlation function can be naturally derived from the phase space formulation of quantum mechanics when Wigner phase space is used for nuclear DOFs and constraint phase space that rigorously satisfy 1/N * Tr[Sum_over_n |n><n|] = 1 is employed for discrete electronic state DOFs. When the trajectory-based equations of motion derived from the mapping Hamiltonian is used to approximate exact dynamics of the quantum Liouville equation of corresponding phase space, it leads to approximate trajectory-based nonadiabatic dynamics methods. The viewpoint has also been stated over again in J. Phys. Chem. A 125, 31, 6845-6863 (2021) as well as Acc. Chem. Res. 54, 23, 4215-4228 (2021). The same viewpoint has been used by Lang et. al in Ref. 52 where the mapping Hamiltonian with N^2-1 variables on the SU(N) phase space. The authors only follow the same idea in Section IV and Section V, of which typos and sloppy statements are in quite a few places. For instance, in eqs (83), (84), (85), (87), (91), and (93), it should be mentioned whether Einstein summation is used or not. When the authors expressed the N^2-1 variables (\Omega_i) in terms of the 2N-2 variables of the SU(N)/U(N-1) Stratanovich phase space as done in Ref. 29, the partial differential equation of eq (91) are coupled with N^2-1 variables. It is sloppy to "derive" eq (93) from eq (91).

5. It is clearly mentioned in in J. Phys. Chem. A 125, 31, 6845-6863 (2021) as well as Acc. Chem. Res. 54, 23, 4215-4228 (2021) that it is straightforward to show the relation between constraint coordinate-momentum phase space [J. Chem. Phys. 151, 024105 (2019); J. Phys. Chem. Lett. 12, 2496 (2021)] and the SU(N) Stratonovich phase space employed in Ref. 29. When the authors state "the work in Ref. 55 can be viewed as a reformulation of the SW kernel that leads to an equivalent transformation of the quantum phase space into a classical phase space", it only indicates that the authors fail to digest the literature and to understand the subtlety. The constraint coordinate-momentum phase space of [J. Chem. Phys. 151, 024105 (2019); J. Phys. Chem. Lett. 12, 2496 (2021)] is diffeomorphic to U(N)/U(N-1), which naturally yields the Meyer-Miller mapping Hamiltonian that produces linear equations of motion that are isomorphic to exact quantum dynamics. By contrast, the authors of the current manuscript simply follow Ref. 29 to use the coherent state variables of the SU(N) Stratonovich phase space of Tilma et al, which is inherently diffeomorphic to SU(N)/U(N-1) without the global phase. It is trivial to see the relation between SU(N)/U(N-1) and CP(N-1). The mapping Hamiltonian on the SU(N)/U(N-1) Stratonovich phase space leads to Hamilton's equations of motion that are nonlinear and where singularities are inevitable. In fact, Stratonovich phase space with an SU(2), SU(3), SU(1,1), or SU(N)/U(N-1) structure in the literature only yields nonlinear exact equations of motion that are not numerically useful because of their singularities for general N-state systems (especially when N is not small).

Not less importantly, the mapping Hamiltonian on the SU(N)/U(N-1) Stratonovich phase space is not intrinsically the same as the Meyer-Miller mapping Hamiltonian. In order to honestly derive from the equations of motion governed by the mapping Hamiltonian on the SU(N)/U(N-1) Stratonovich phase space without (in a cheating way) invoking the fact the Meyer-Miller mapping Hamiltonian leads to exact dynamics, we have to work out the equation of motion of the global phase on Stratonovich phase space to recover the linear equations of motion of the Meyer-Miller Hamiltonian. The global phase is, however, not constant during the evolution. The authors of Ref. 29 as well as the authors of the current manuscript simply fail to capture the critical point. Neither of them are capable of indeed deriving the Meyer-Miller mapping Hamiltonian from the SU(N) Stratonovich phase space. The spin mapping model from SU(N)/U(N-1) of Ref. 29 intrinsically uses the Meyer-Miller mapping Hamiltonian for equations of motion. The authors of the current manuscript used Eq. (113) that was earlier employed by the authors of Ref. 29 to show the same hand-waving argument, without offering insight in understanding the problem. On the other hand, if the authors were able to digest the derivations presented in eCMM [J. Chem. Phys. 151, 024105 (2019); J. Phys. Chem. Lett. 12, 2496 (2021)], it would have been much more convenient to understand the relation to as well as the limitation of Stratonovich phase space.

6. In Ref. 52 Lang et al has already done their original work in directly using N^2-1 variables (based on the Generalized Gell-Mann matrices for SU(N)) to study nonadiabatic dynamics, where 1/N * Tr[Sum_over_n |n><n|] = 1 is also satisfied. Eq. (14) was already used in Ref. 52. the so-called generalized truncated Wigner approximation (TWA) to the quantum Liouville equation. All content of Section II has been presented earlier in Ref. 52 and Ref. 29.

7. 1/N * Tr[Sum_over_n |n><n|] = 1 is a physical condition for representing general N-state systems. One can use U(N)/U(N-1) with 2*N variables (with the constraint of the physical condition) to construct constraint coordinate-momentum phase space where exact equations of motion are linear and simple, or employ the SU(N)/U(N-1) Stratanovich phase space with (2*N-2) variables but the exact EOMs are nonlinear and include singularities, or take SU(N) with N^2-1 variables. Quantum dynamics of a finite set of N states on SU(N)/U(N-1), SU(N), SU(2), SU(3), or SU(1,1) phase space had already been well studied by applied mathematicians and physicists in the literature. That is, the phase space formulation with either SU(N)/U(N-1) or SU(N) had been already available before Ref. 29 and Ref. 52. In comparison, constraint coordinate-momentum phase space formulation with U(N)/U(N-1) has not been proposed until [J. Chem. Phys. 151, 024105 (2019); J. Phys. Chem. Lett. 12, 2496 (2021)].

In fact, all the points listed above have been reported or hinted in the literature.

Finally, while the authors express in their own way what have already been developed or used by others, I hardly see in the manuscript that the authors have contributed anything new or useful beyond the literature. For instance, does it lead to any new method or idea

better than or more efficient than the mapping approaches that have been proposed? This is the major problem.

Confidential Comments to the Editor:
Qiang, the manuscript is more like a report for doing the literature study. In various places, the authors present the content in such a way as if they come up with the ideas that have already been proposed by others. The content on SU(N) and SU(N)/U(N-1) has extensively presented by physicists and applied mathematicians in the literature and even used by the authors of Ref. 52 and those of Ref. 29 on nonadiabatic dynamics. Section V-B is full of typos and sloppy statements when they try to "derive" the equations of motion. From the whole manuscript, I hardly learn anything that I don't know.

It is difficult to understand why the authors submit a manuscript in this way. The authors probably think few theoretical chemists understand the Lie algebra. This is the longest review that I have ever made. The purpose is to help the authors better understand the related papers. The authors should present new information in the manuscript.

Recommendation: Reject

Willing to Review Again (Confidential): Yes

New Potential Energy Surface: No
