On numerical simulations of equations of motion on Stratonovich phase space

Here we present some numerical comparisons of the equations of motion (EOMs) on Stratonovich phase space from Appendix 3 of Ref.[1], Huo's first version of manuscript [2] (denoted as Version 1, online on May 20, 2022) and Huo's second version of manuscript [3] (denoted as Version 2, online on May 27, 2022) . The EOMs of Meyer-Miller mapping model[4, 5] yield the exact results in frozen nuclei limit[4, 5] and are used as benchmarks. A three-state system used in Appendix C-2 of Ref. [4] is employed here, whose Hamiltonian matrix reads (in atomic unit here and below).

$$\mathbf{H}=\begin{pmatrix} 10 & \lambda & \lambda \\ \lambda & 7 & \lambda \\ \lambda & \lambda & 2 \end{pmatrix} \tag{1}$$

Both weak($\lambda = 0.02$) and strong($\lambda = 20$) coupling cases are considered here. At the initial moment, the amplitudes of wave function on each state are decided to be

$$\mathbf{c}=\left(\cos\left(0.01\right),\sin\left(0.01\right)\cos(1.56)e^{-0.78i},\sin(0.01)\sin(1.56)e^{0.78i}\right)^{T} \tag{2}$$

for $\lambda = 0.02$, and

$$\mathbf{c}=\left(\cos\left(0.78\right)e^{-0.01i},\sin\left(0.78\right)\cos(1.56)e^{0.79i},\sin(0.78)\sin(1.56)e^{-0.77i}\right)^{T} \tag{3}$$

for $\lambda = 20$, respectively. The time evolutions of the population (the modular square of quantum amplitude) as well as the real part of quantum amplitude of the first state (i.e., the highest one) will be investigated below.

- **Simulation I: EOMs in Huo's Version 1 v.s. Liu's EOMs**

Figure 1 shows the results of population dynamics yielded by Huo's EOMs in Version 1 [eq (105c-d)], EOMs in Appendix 3 of Ref. [1] [eq (S48)], and EOMs with Meyer-Miller mapping variables. It is shown obviously that the population dynamics yielded by EOMs in Appendix 3 of Ref. [1] (red solid lines in Figure 1) can reproduce the exact results as Meyer-Miller mapping model[4, 5] (black points in Figure 1), while the EOMs taken from Huo's manuscript[2] (blue solid lines in Figure 1) are *unable* to produce the exact dynamics even in frozen nuclei cases. Since there were three-state systems involved in Huo's Version 1 (e.g., Figure 4-5 in Version 1), it should be questioned if authors' simulations in Version 1 are loyalty to their formulations.

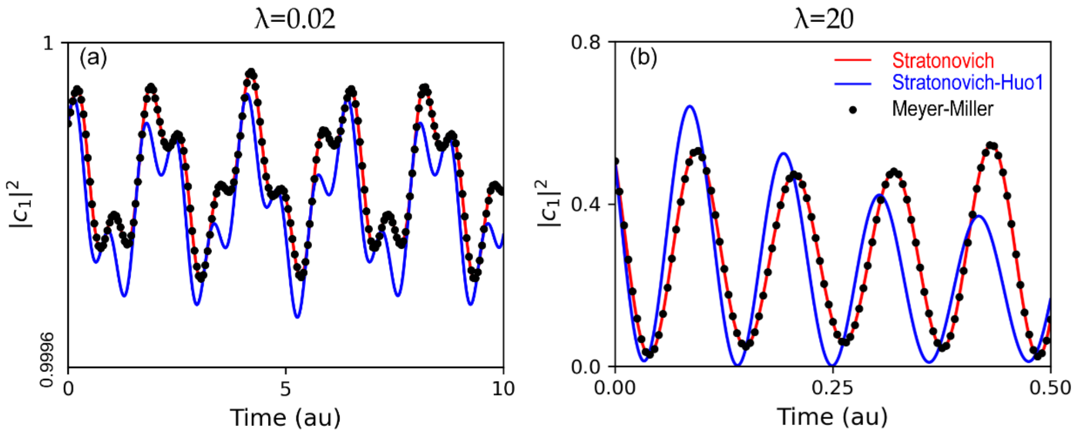

Figure 1. The population dynamics of the first state of three-state system with parameter $\lambda = 0.02$ [panel (a)] and $\lambda = 20$ [panel (b)]. In each panel, results yielded by EOMs of Stratonovich angle variables taken from eq(S48) in Appendix 3 of Ref. [1] are denoted in red solid lines, while those yielded by EOMs of Stratonovich angle variables taken from eq (105c-d) in Huo's Version 1[2] are shown in blue solid lines. The exact benchmarks calculated by Meyer-Miller mapping model[4, 5] are represented in black points.

- **Simulation II: EOMs in Huo's Version 2 v.s. Liu's EOMs**

Now we turn to Huo's Version 2. Figure 2 shows results of population dynamics yielded by Huo's EOMs in Version 2 [eq (113)], EOMs from eq (S48) in Appendix 3 of Ref. [1], and EOMs with Meyer-Miller mapping variables. Huo's EOMs from Version 2 can yield the exact population dynamics unlike those from their previous version. However, Huo and his coworkers did not clearly understand the role of global phase connected Stratonovich angle variables and Meyer-Miller mapping variables, which is also evolving in quantum dynamics. In Figure 3, we further compare the time evolution of the real part of the quantum amplitude. It is obviously that Huo's EOMs in Version 2 (green dashed-lines) are unable to produce the exact dynamics as Meyer-Miller mapping model (black points). Similarly, the EOMs from eq (S48) in Appendix 3 of Ref. [1] fail to capture the exact evolution either (red solid-lines). Once the evolving global phase is introduced, it can generate the exact dynamics of quantum amplitude with Stratonovich angle variables (violet solid lines). The simulations reveal that EOMs in Huo's Version 2 do not correspond the correct form of canonical

Hamilton's equation of motion with Meyer-Miller variables, and authors still did not understand this kind of relationship in current manuscript!

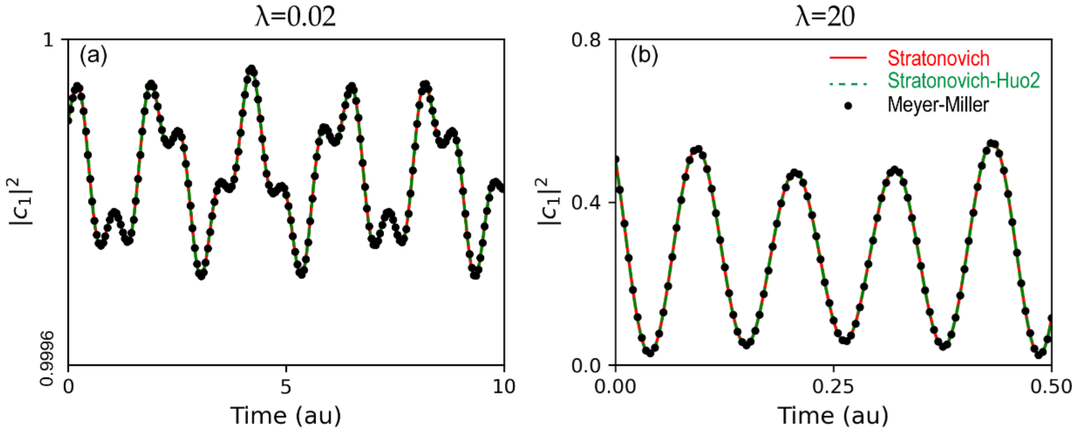

Figure 2. The population dynamics of the first state of three-state system with parameter $\lambda = 0.02$ [panel (a)] and $\lambda = 20$ [panel (b)]. In each panel, results yielded by EOMs of Stratonovich angle variables taken from eq (S48) in Appendix 3 of Ref. [1] are denoted in red solid lines, while those yielded by EOMs of Stratonovich angle variables taken from eq (113) in Huo's Version 2[3] are shown in green dashed lines. The exact benchmarks calculated by Meyer-Miller mapping model[4, 5] are represented in black points.

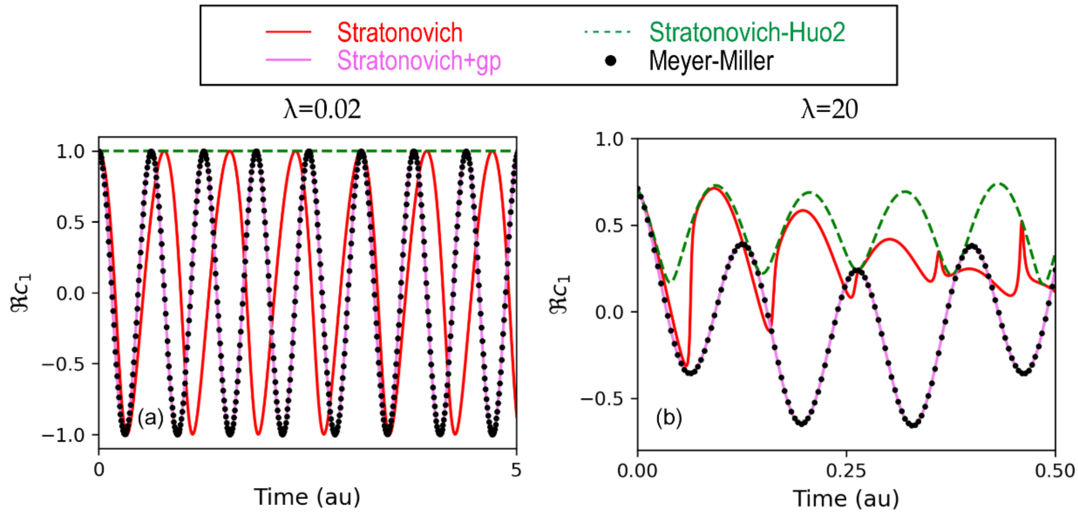

Figure 3. The real part of amplitude dynamics of the first state of three-state system with parameter $\lambda = 0.02$ [panel (a)] and $\lambda = 20$ [panel (b)]. In each panel, results yielded by EOMs of Stratonovich angle variables taken from eq (S48) and eq (S53) in Appendix 3 of Ref. [1] are denoted in red and violet solid lines respectively, while those yielded by EOMs of Stratonovich angle variables taken from eq (113) in Huo's Version 2[3] are shown in green dashed lines. The exact benchmarks calculated by Meyer-Miller mapping model[4, 5] are represented in black points.

Reference

[1] X. He, B. Wu, Y. Shang, B. Li, X. Cheng, and J. Liu, "New phase space formulations and quantum dynamics approaches", Wiley Interdiscip. Rev. Comput. Mol. Sci., e1619 (2022). http://dx.doi.org/10.1002/wcms.1619

[2] D. Bossion, S. Chowdhury, and P. Huo, "Non-adiabatic dynamics using the generators of the su(N) Lie algebra", ChemRxiv, (2022). http://dx.doi.org/10.26434/chemrxiv-2022-ntxcl

[3] D. Bossion, W. Ying, S. Chowdhury, and P. Huo, "Non-adiabatic mapping dynamics in the phase space of the SU(N) Lie group", ChemRxiv, (2022). http://dx.doi.org/10.26434/chemrxiv-2022-ntxcl-v2

[4] J. Liu, "A unified theoretical framework for mapping models for the multi-state Hamiltonian", J. Chem. Phys. **145**, 204105 (2016). http://dx.doi.org/10.1063/1.4967815

[5] H.-D. Meyer, and W. H. Miller, "A classical analog for electronic degrees of freedom in nonadiabatic collision processes", J. Chem. Phys. **70**, 3214 (1979). http://dx.doi.org/10.1063/1.437910