

# Commutator Matrix in Phase Space Mapping Models for Nonadiabatic Quantum Dynamics

Published as part of The Journal of Physical Chemistry virtual special issue "Yoshitaka Tanimura Festschrift".

Xin He, Baihua Wu, Zhihao Gong, and Jian Liu\*



Cite This: *J. Phys. Chem. A* 2021, 125, 6845–6863



Read Online

ACCESS |



Metrics & More

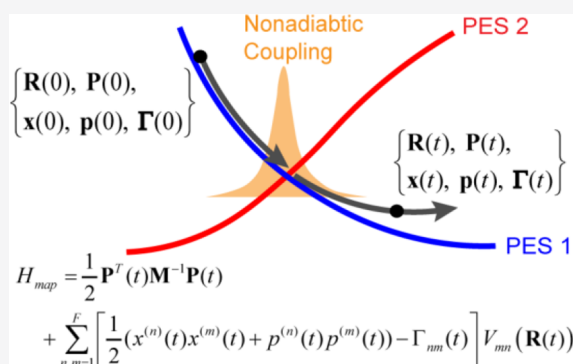


Article Recommendations



Supporting Information

**ABSTRACT:** We show that a novel, general phase space mapping Hamiltonian for nonadiabatic systems, which is reminiscent of the renowned Meyer–Miller mapping Hamiltonian, involves a commutator variable matrix rather than the conventional zero-point-energy parameter. In the exact mapping formulation on constraint space for phase space approaches for nonadiabatic dynamics, the general mapping Hamiltonian with commutator variables can be employed to generate approximate trajectory-based dynamics. Various benchmark model tests, which range from gas phase to condensed phase systems, suggest that the overall performance of the general mapping Hamiltonian is better than that of the conventional Meyer–Miller Hamiltonian.



## 1. INTRODUCTION

Many important processes from photochemistry to electron transfer in chemical, biological, and materials systems involve quantum mechanical behavior of both electrons and nuclei in the context of nonadiabatic dynamics.<sup>1–10</sup> The celebrated Meyer–Miller mapping model<sup>11–13</sup> is one of the important theoretical frameworks for developing practical nonadiabatic dynamics methods.<sup>14–56</sup> Consider a coupled  $F$ -electronic-state Hamiltonian operator

$$\begin{aligned}\hat{H} &= \sum_{n,m=1}^F H_{nm}(\hat{\mathbf{R}}, \hat{\mathbf{P}}) |n\rangle\langle m| \\ &= \sum_{n,m=1}^F \left[ \frac{1}{2} \hat{\mathbf{P}}^T \mathbf{M}^{-1} \hat{\mathbf{P}} \delta_{nm} + V_{nm}(\hat{\mathbf{R}}) \right] |n\rangle\langle m|\end{aligned}\quad (1)$$

in the diabatic representation (for simplicity), where the  $F$  electronic states consist of an orthogonal complete basis set, i.e.,

$$\begin{aligned}\langle m|n\rangle &= \delta_{mn} \\ \hat{I}_{ele} &= \sum_{n=1}^F |n\rangle\langle n|.\end{aligned}\quad (2)$$

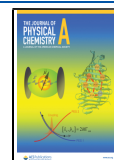
Here  $\hat{I}_{ele}$  is the identity operator in the electronic state space,  $\mathbf{M}$  is the diagonal “mass matrix” with elements  $\{m_j\}$ ,  $\{\mathbf{R}, \mathbf{P}\}$  are the coordinate and momentum variables for the nuclear DOFs (with  $N$  the total number of nuclear DOFs), and potential energy elements  $V_{nm}(\mathbf{R}) = V_{mn}(\mathbf{R})$  form a real symmetric matrix. The Meyer–Miller Hamiltonian reads

$$\begin{aligned}H_{MM}(\mathbf{R}, \mathbf{P}; \mathbf{x}, \mathbf{p}) &= \frac{1}{2} \mathbf{P}^T \mathbf{M}^{-1} \mathbf{P} \\ &+ \sum_{n,m=1}^F \left[ \frac{1}{2} (x^{(n)} x^{(m)} + p^{(n)} p^{(m)}) - \gamma \delta_{nm} \right] V_{nm}(\mathbf{R})\end{aligned}\quad (3)$$

where  $\{\mathbf{x}, \mathbf{p}\} = \{x^{(1)}, \dots, x^{(F)}, p^{(1)}, \dots, p^{(F)}\}$  are the mapping coordinate and momentum variables for the  $F$  electronic states.

There exist two alternative approaches that derive the Meyer–Miller mapping model in quantum mechanics.<sup>12,13</sup> The approach of Stock and Thoss<sup>12</sup> and of Sun et al.<sup>14</sup> suggests that parameter  $\gamma$  in the Meyer–Miller mapping Hamiltonian eq 3 is a parameter for the zero point energy of a singly excited oscillator for the underlying mapping DOFs for each electronic state,<sup>30–33</sup> which is in the similar spirit to that of the pioneering work of Meyer and Miller.<sup>11</sup> In comparison, the unified framework proposed in ref 13 offers a substantially different picture. It derives a mapping model reminiscent of the Meyer–Miller model,

**Received:** May 19, 2021  
**Revised:** July 3, 2021  
**Published:** August 2, 2021



$$H_{\text{MM}}(\hat{\mathbf{R}}, \hat{\mathbf{P}}; \mathbf{x}, \mathbf{p}) = \sum_{n,m=1}^F \left[ \frac{1}{2} (x^{(n)} x^{(m)} + p^{(n)} p^{(m)}) - \gamma \delta_{nm} \right] H_{mn}(\hat{\mathbf{R}}, \hat{\mathbf{P}}) \quad (4)$$

where parameter  $\gamma$  is interpreted as a parameter originated from a commutator of Pauli matrix  $-\frac{i}{4}[\hat{\sigma}_x^{(n)}, \hat{\sigma}_y^{(n)}] = -\frac{\hat{\sigma}_z^{(n)}}{2}$ , which allows both positive and negative values.<sup>13,42</sup> The one-to-one correspondence mapping formulation for the correlation function for nonadiabatic systems can rigorously be established.<sup>41,42</sup>

More interestingly, where the Meyer–Miller mapping Hamiltonian is rederived in the novel framework in ref 13, it is also indicated that there exists a more general mapping Hamiltonian

$$H_{\text{map}}(\mathbf{R}, \mathbf{P}; \mathbf{x}, \mathbf{p}; \mathbf{\Gamma}) = \sum_{n,m=1}^F \left[ \frac{1}{2} (x^{(n)} x^{(m)} + p^{(n)} p^{(m)}) - \Gamma_{nm} \right] H_{mn}(\mathbf{R}, \mathbf{P}) \quad (5)$$

where  $\mathbf{\Gamma}$  is a real symmetric matrix with the element  $\Gamma_{nm}$  in the  $n$ th row and  $m$ th column. Its element  $\Gamma_{nm}$  is a real variable for the corresponding commutator,  $-\frac{i}{8}([\hat{\sigma}_x^{(n)}, \hat{\sigma}_y^{(m)}] + [\hat{\sigma}_x^{(m)}, \hat{\sigma}_y^{(n)}])$ , as presented in ref 13.  $\mathbf{\Gamma}$  is denoted the commutator matrix. When off-diagonal elements of commutator matrix  $\mathbf{\Gamma}$  are set to zero and diagonal elements are the same, the general mapping Hamiltonian eq 5 is simplified to eq 4. Note that the commutator matrix  $\mathbf{\Gamma}$  can evolve with time when eq 5 is utilized to generate corresponding Hamilton's equations of motion. To the best of our knowledge, except as presented in ref 13, the general mapping Hamiltonian eq 5 with commutator matrix  $\mathbf{\Gamma}$  as a variable has *never* been proposed and used to generate the equations of motion for nonadiabatic dynamics. The purpose of the paper is to employ the general mapping Hamiltonian eq 5 for trajectory-based dynamics for nonadiabatic systems, in the exact mapping kernel formulation that we established in refs 41 and 42. The paper is organized as follows. Section 2 first reviews the one-to-one correspondence mapping formulation derived in refs 41 and 42 and then derives Hamilton's equations of motion from eq 5, where the frozen-nuclei limit as well as the Born–Oppenheimer limit are satisfied. Section 3 presents numerical results of various benchmark model tests for gas phase as well as condensed phase systems, which include the scattering models of Tully,<sup>57</sup> 3-state photodissociation models of Miller and co-workers,<sup>58</sup> 7-site model of the Fenna–Matthews–Olson (FMO) monomer,<sup>59</sup> and atom-in-cavity models.<sup>60–63</sup> Finally, conclusions are given in Section 4.

## 2. THEORY

**2.1. Phase Space Mapping Formulations for Nonadiabatic Systems.** Because it is convenient to obtain useful insight about the correspondence between quantum and classical concepts in phase space formulations of quantum mechanics,<sup>64–82</sup> they have been widely used in many areas of physics and chemistry since Wigner's pioneering work.<sup>64</sup> More recently, we have proposed a unified framework for the one-to-one correspondence mapping in phase space formulations of quantum mechanics,<sup>42</sup> which naturally includes and surpasses the classification scheme<sup>79,81,82</sup> for conventional approaches<sup>64–78,80</sup> for quantum systems represented in the

continuous coordinate space and is able to treat quantum systems described in the finite-dimensional Hilbert space.<sup>13,41</sup> Such a framework offers a useful tool for nonadiabatic systems where both continuous nuclear degrees of freedom (DOFs) and discretized electronic state DOFs are involved.

In the unified framework of phase space mapping models for the (coupled) multistate Hamiltonian (eq 1) in ref 13, eq 4 is the mapping model reminiscent of the Meyer–Miller model. When the mapping variables for the electronic state DOFs satisfy

$$\sum_{n=1}^F \left[ \frac{(x^{(n)})^2 + (p^{(n)})^2}{2} - \gamma \right] = 1 \quad (6)$$

the mapping Hamiltonian eq 4 is equal to the conventional Meyer–Miller Hamiltonian eq 3. This was first proposed in ref 41 for general  $F$ -state systems. The simplest way is to use the full constraint electronic space that eq 6 defines, i.e.,

$$S(\mathbf{x}, \mathbf{p}): \delta \left( \sum_{n=1}^F \left[ \frac{(x^{(n)})^2 + (p^{(n)})^2}{2} \right] - (1 + F\gamma) \right) \quad (7)$$

for constructing the formulation for physical properties in the mapping approach. The possible value of parameter  $\gamma$  for eq 6 or eq 7 implies  $\gamma \in (-\frac{1}{F}, \infty)$ .

The trace of a product of two operators is expressed in phase space as

$$\text{Tr}_{n,e}[\hat{A}\hat{B}] = \int (2\pi\hbar)^{-N} d\mathbf{R} d\mathbf{P} \int_{S(\mathbf{x},\mathbf{p})}^F d\mathbf{x} d\mathbf{p} \times A(\mathbf{R}, \mathbf{P}; \mathbf{x}, \mathbf{p}) \tilde{B}(\mathbf{R}, \mathbf{P}; \mathbf{x}, \mathbf{p}) \quad (8)$$

where

$$A(\mathbf{R}, \mathbf{P}; \mathbf{x}, \mathbf{p}) = \text{Tr}_{n,e}[\hat{A}\hat{K}_{\text{nuc}}(\mathbf{R}, \mathbf{P}) \otimes \hat{K}_{\text{ele}}(\mathbf{x}, \mathbf{p})] \quad (9)$$

$$\tilde{B}(\mathbf{R}, \mathbf{P}; \mathbf{x}, \mathbf{p}) = \text{Tr}_{n,e}[\hat{K}_{\text{nuc}}^{-1}(\mathbf{R}, \mathbf{P}) \otimes \hat{K}_{\text{ele}}^{-1}(\mathbf{x}, \mathbf{p})\hat{B}] \quad (10)$$

$(2\pi\hbar)^{-N} d\mathbf{R} d\mathbf{P} \otimes \int d\mathbf{x} d\mathbf{p}$  stands for the invariant measure on the mapping phase space for nuclear and electronic state DOFs, and  $\text{Tr}_n$  and  $\text{Tr}_e$  represent the trace over the nuclear DOFs and that over the  $F$  electronic states, respectively. The mapping kernel and its inverse satisfy the normalization

$$\begin{aligned} \text{Tr}_n[\hat{K}_{\text{nuc}}(\mathbf{R}, \mathbf{P})] &= \text{Tr}_n[\hat{K}_{\text{nuc}}^{-1}(\mathbf{R}, \mathbf{P})] = 1 \\ \text{Tr}_e[\hat{K}_{\text{ele}}(\mathbf{x}, \mathbf{p})] &= \text{Tr}_e[\hat{K}_{\text{ele}}^{-1}(\mathbf{x}, \mathbf{p})] = 1 \end{aligned} \quad (11)$$

and

$$\begin{aligned} (2\pi\hbar)^{-N} \int d\mathbf{R} d\mathbf{P} \hat{K}_{\text{nuc}}(\mathbf{R}, \mathbf{P}) &= \hat{I}_{\text{nuc}} \\ (2\pi\hbar)^{-N} \int d\mathbf{R} d\mathbf{P} \hat{K}_{\text{nuc}}^{-1}(\mathbf{R}, \mathbf{P}) &= \hat{I}_{\text{nuc}} \\ \int_{S(\mathbf{x},\mathbf{p})}^F d\mathbf{x} d\mathbf{p} \hat{K}_{\text{ele}}(\mathbf{x}, \mathbf{p}) &= \hat{I}_{\text{ele}} \\ \int_{S(\mathbf{x},\mathbf{p})}^F d\mathbf{x} d\mathbf{p} \hat{K}_{\text{ele}}^{-1}(\mathbf{x}, \mathbf{p}) &= \hat{I}_{\text{ele}} \end{aligned} \quad (12)$$

where  $\hat{I}_{\text{nuc}}$  is the identity operator in the nuclear space and the integral over constraint mapping space  $S(\mathbf{x}, \mathbf{p})$  is

$$\int_{S(\mathbf{x}, \mathbf{p})} F \, d\mathbf{x} \, d\mathbf{p} \, g(\mathbf{x}, \mathbf{p}) = \frac{\int F \, d\mathbf{x} \, d\mathbf{p} \, \delta\left(\sum_{n=1}^F \left[\frac{(x^{(n)})^2 + (p^{(n)})^2}{2}\right] - (1 + F\gamma)\right) g(\mathbf{x}, \mathbf{p})}{\int d\mathbf{x} \, d\mathbf{p} \, \delta\left(\sum_{n=1}^F \left[\frac{(x^{(n)})^2 + (p^{(n)})^2}{2}\right] - (1 + F\gamma)\right)} \quad (13)$$

The one-to-one correspondence mapping from  $A(\mathbf{R}, \mathbf{P}; \mathbf{x}, \mathbf{p})$  (or  $\tilde{B}(\mathbf{R}, \mathbf{P}; \mathbf{x}, \mathbf{p})$ ) of eq 9 back to operator  $\hat{A}$  (or  $\hat{B}$ ) is

$$\begin{aligned} \hat{A} &= \int (2\pi\hbar)^{-N} \, d\mathbf{R} \, d\mathbf{P} \int_{S(\mathbf{x}, \mathbf{p})} F \, d\mathbf{x} \, d\mathbf{p} \\ &\quad A(\mathbf{R}, \mathbf{P}; \mathbf{x}, \mathbf{p}) \hat{K}_{nuc}^{-1}(\mathbf{R}, \mathbf{P}) \otimes \hat{K}_{ele}^{-1}(\mathbf{x}, \mathbf{p}) \\ \hat{B} &= \int (2\pi\hbar)^{-N} \, d\mathbf{R} \, d\mathbf{P} \int_{S(\mathbf{x}, \mathbf{p})} F \, d\mathbf{x} \, d\mathbf{p} \\ &\quad \tilde{B}(\mathbf{R}, \mathbf{P}; \mathbf{x}, \mathbf{p}) \hat{K}_{nuc}(\mathbf{R}, \mathbf{P}) \otimes \hat{K}_{ele}(\mathbf{x}, \mathbf{p}). \end{aligned} \quad (14)$$

The mapping kernel for the nuclear DOFs (in eq 9) is

$$\hat{K}_{nuc}(\mathbf{R}, \mathbf{P}) = \left(\frac{\hbar}{2\pi}\right)^N \int d\boldsymbol{\zeta} \int d\boldsymbol{\eta} \, e^{i\boldsymbol{\zeta} \cdot (\hat{\mathbf{R}} - \mathbf{R}) + i\boldsymbol{\eta} \cdot (\hat{\mathbf{P}} - \mathbf{P})} f(\boldsymbol{\zeta}, \boldsymbol{\eta}) \quad (15)$$

and its inverse is

$$\begin{aligned} \hat{K}_{nuc}^{-1}(\mathbf{R}, \mathbf{P}) &= \left(\frac{\hbar}{2\pi}\right)^N \int d\boldsymbol{\zeta} \int d\boldsymbol{\eta} \, e^{-i\boldsymbol{\zeta} \cdot (\hat{\mathbf{R}} - \mathbf{R}) - i\boldsymbol{\eta} \cdot (\hat{\mathbf{P}} - \mathbf{P})} [f(-\boldsymbol{\zeta}, -\boldsymbol{\eta})]^{-1} \end{aligned} \quad (16)$$

where  $f(\boldsymbol{\zeta}, \boldsymbol{\eta})$  is a scalar function to determine the corresponding nuclear phase space. For instance, the Wigner function<sup>64,65</sup> has

$$f(\boldsymbol{\zeta}, \boldsymbol{\eta}) = 1 \quad (17)$$

and the Husimi function<sup>68</sup> has

$$f(\boldsymbol{\zeta}, \boldsymbol{\eta}) = \exp\left(-\frac{\boldsymbol{\zeta}^T \mathbf{G}^{-1} \boldsymbol{\zeta}}{4} - \frac{\hbar^2}{4} \boldsymbol{\eta}^T \mathbf{G} \boldsymbol{\eta}\right) \quad (18)$$

The mapping kernel for the  $F$  electronic states (in eq 9) is

$$\begin{aligned} \hat{K}_{ele}(\mathbf{x}, \mathbf{p}) &= \sum_{n,m=1}^F \left[ \frac{1}{2} (x^{(n)} + ip^{(n)}) (x^{(m)} - ip^{(m)}) \right. \\ &\quad \left. - \gamma \delta_{nm} \right] |n\rangle \langle m| \end{aligned} \quad (19)$$

and the inverse kernel

$$\begin{aligned} \hat{K}_{ele}^{-1}(\mathbf{x}, \mathbf{p}) &= \sum_{n,m=1}^F \left[ \frac{1+F}{2(1+F\gamma)} (x^{(n)} + ip^{(n)}) \right. \\ &\quad \left. \times (x^{(m)} - ip^{(m)}) - \frac{1-\gamma}{1+F\gamma} \delta_{nm} \right] |n\rangle \langle m| \end{aligned} \quad (20)$$

In eqs 8, 12, 14, 15, and 16, while the integrals for the nuclear DOFs are over the whole nuclear phase space when the Wigner or Husimi function is employed, those for the  $F$  electronic states are over the constraint electronic mapping space,  $S(\mathbf{x}, \mathbf{p})$ .

When the nuclear DOFs are described in Wigner phase space (eqs 15 and 16 with eq 17), the mapping kernel and its inverse are the same, i.e.,

$$\hat{K}_{nuc}(\mathbf{R}, \mathbf{P}) = \hat{K}_{nuc}^{-1}(\mathbf{R}, \mathbf{P}) \quad (21)$$

When the Wigner function (eqs 15 and 16 with eq 17) is used for the nuclear DOFs, it is easy to show that the real part of the mapping Hamiltonian  $H(\mathbf{R}, \mathbf{P}; \mathbf{x}, \mathbf{p}) = \text{Tr}_{n,e}[\hat{H} \hat{K}_{nuc}(\mathbf{R}, \mathbf{P}) \otimes \hat{K}_{ele}(\mathbf{x}, \mathbf{p})]$  with constraint eq 7 for the coupled multistate Hamiltonian operator eq 1 is the same as the conventional Meyer–Miller Hamiltonian eq 3. The equations of motion produced by the real part of  $H(\mathbf{R}, \mathbf{P}; \mathbf{x}, \mathbf{p}) = \text{Tr}_{n,e}[\hat{H} \hat{K}_{nuc}(\mathbf{R}, \mathbf{P}) \otimes \hat{K}_{ele}(\mathbf{x}, \mathbf{p})]$  are identical with those yielded by its imaginary part.

When the parameter

$$\gamma = \frac{\sqrt{F+1} - 1}{F} \quad (22)$$

is employed, the mapping kernel for the electronic DOFs is equal to the inverse kernel, i.e.,

$$\hat{K}_{ele}(\mathbf{x}, \mathbf{p}) = \hat{K}_{ele}^{-1}(\mathbf{x}, \mathbf{p}) \quad (23)$$

eq 22 offers the only physical value for parameter  $\gamma$  in the region  $(-\frac{1}{F}, \infty)$  to make eq 23 hold. We note that the so-called spin mapping model of refs 43 and 44 intrinsically based on the Meyer–Miller mapping Hamiltonian model (especially when  $F \geq 3$  electronic states are involved) is only a special case of the exact phase space mapping formulation that we established first in refs 13 and 41 and then in ref 42, i.e., parameter  $\gamma = 0$ ,  $(\sqrt{F+1} - 1)/F$ , or 1 in our exact phase space mapping formulation corresponds to the Q-version, W-version, or P-version of refs 43 and 44, respectively. Interestingly, the authors of ref 44 even failed to understand that the interpretation for general  $F$ -state systems constructed in Appendix A of ref 41 is simply an exact phase space mapping formulation for the parameter  $\gamma = 0$ . We also note that the exact phase space mapping formulation of the correlation function can be used to formalize various other methods based on the Meyer–Miller mapping Hamiltonian model in refs 14, 35, 45, 46, 49, and 83–86, as we will show in a forthcoming paper.

## 2.2. Expression of the Time Correlation Function.

Define the Heisenberg operator  $\hat{B}(t) = e^{i\hat{H}t/\hbar} \hat{B} e^{-i\hat{H}t/\hbar}$ . As a result of eq 8, an exact expression of the time correlation function of the nonadiabatic system

$$C_{AB}(t) = \text{Tr}_{n,e}[\hat{A}(0) \hat{B}(t)] \quad (24)$$

is

$$\begin{aligned} C_{AB}(t) &= \int (2\pi\hbar)^{-N} \, d\mathbf{R} \, d\mathbf{P} \int_{S(\mathbf{x}, \mathbf{p})} F \, d\mathbf{x} \, d\mathbf{p} \\ &\quad \times A(\mathbf{R}, \mathbf{P}; \mathbf{x}, \mathbf{p}) \tilde{B}(\mathbf{R}, \mathbf{P}; \mathbf{x}, \mathbf{p}; t) \end{aligned} \quad (25)$$

where

$$\tilde{B}(\mathbf{R}, \mathbf{P}; \mathbf{x}, \mathbf{p}; t) = \text{Tr}_{n,e}[\hat{K}_{nuc}^{-1}(\mathbf{R}, \mathbf{P}) \otimes \hat{K}_{ele}^{-1}(\mathbf{x}, \mathbf{p}) \hat{B}(t)] \quad (26)$$

When nuclear and electronic dynamics is exactly solved in eq 26, the correlation function formulation eq 25 is exact for nonadiabatic systems.<sup>41,42</sup>

When trajectory-based dynamics is introduced, eq 25 is recast into

$$\begin{aligned} C_{AB}(t) &= \int (2\pi\hbar)^{-N} \, d\mathbf{R} \, d\mathbf{P} \int_{S(\mathbf{x}, \mathbf{p})} F \, d\mathbf{x} \, d\mathbf{p} \\ &\quad \times A(\mathbf{R}, \mathbf{P}; \mathbf{x}, \mathbf{p}) \tilde{B}(\mathbf{R}, \mathbf{P}; \mathbf{x}_t, \mathbf{p}_t) \end{aligned} \quad (27)$$