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Unified Formulation of Phase Space Mapping Approaches for Nonadiabatic Quantum Dynamics

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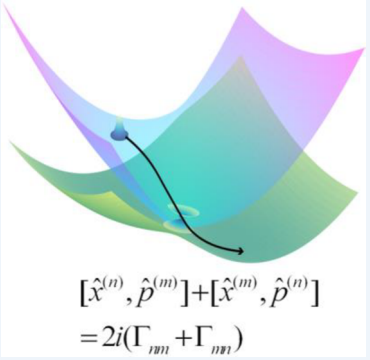
CONSPECTUS: Nonadiabatic dynamical processes are one of the most important quantum mechanical phenomena in chemical, materials, biological, and environmental molecular systems, where the coupling between different electronic states is either inherent in the molecular structure or induced by the (intense) external field. The curse of dimensionality indicates the intractable exponential scaling of calculation effort with system size and restricts the implementation of "numerically exact" approaches for realistic large systems. The phase space formulation of quantum mechanics offers an important theoretical framework for constructing practical approximate trajectory-based methods for quantum dynamics. This Account reviews our recent progress in phase space mapping theory: a unified framework for constructing the mapping Hamiltonian on phase space for coupled F-state systems where the renowned Meyer−Miller Hamiltonian model is a special case, a general phase space formulation of quantum mechanics for nonadiabatic systems where the electronic degrees of freedom are mapped onto constraint space and the nuclear degrees of freedom are mapped onto infinite space, and an isomorphism between the mapping phase space approach for nonadiabatic systems and that for nonequilibrium electron transport processes. While the zero-point-energy parameter is conventionally assumed to be positive, we show that the constraint implied in the conventional Meyer−Miller mapping Hamiltonian requires that such a parameter can be negative as well and lies in $(-1/F, +\infty)$ for each electronic degree of freedom. More importantly, the zero-point-energy parameter should be interpreted as a special case of a commutator matrix in the comprehensive phase space mapping Hamiltonian for nonadiabatic systems. From the rigorous formulation of mapping phase space, we propose approximate but practical trajectory-based nonadiabatic dynamics methods. The applications to both gas phase and condensed phase problems include the spin-boson model for condensed phase dissipative two-state systems, the three-state photodissociation models, the seven-site model of the Fenna−Matthews−Olson monomer in photosynthesis of green sulfur bacteria, the strongly coupled molecular/atomic matter−optical cavity systems designed for controlling and manipulating chemical dynamical processes, and the Landauer model for a quantum dot state coupled with two electrodes. In these applications the overall performance of our phase space mapping dynamics approach is superior to two prevailing trajectory-based methods, Ehrenfest dynamics and fewest switches surface hopping.



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- Liu, J. Isomorphism between the Multi-State Hamiltonian and the Second-Quantized Many-Electron Hamiltonian with Only 1-Electron Interactions. *J. Chem. Phys.* **2017**, *146*, 024110.[2] The paper shows that there exists an isomorphism between the mapping phase space approach for nonadiabatic systems and that for nonequilibrium electron transport processes.
- He, X.; Liu, J. A New Perspective for Nonadiabatic Dynamics with Phase Space Mapping Models. *J. Chem. Phys.* **2019**, *151*, 024105.[3] In this article, mapping approaches on constraint phase space have first been proposed for nonadiabatic dynamics.
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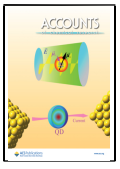

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for Nonadiabatic Dynamics. *J. Phys. Chem. Lett.* **2021**, *12*, 2496−2501.[4] This work presents a new general formulation for constructing exact mapping approaches on constraint phase space for a finite number of discrete electronic states of nonadiabatic systems.

1. INTRODUCTION

Because the difference between the mass of an electron and that of a nucleus is at least 3 orders of magnitude, the celebrated Born−Oppenheimer (BO) approximation makes the assumption that the electronic and nuclear motions are separated.[5] In the BO scheme, the adiabatic electronic states are obtained when the coordinates of nuclei are fixed. The potential energy surface (PES) for the relevant adiabatic electronic state is then produced either in advance or on-the-fly as nuclear dynamics is considered.

The BO approximation is, however, not valid in nonadiabatic dynamics that occur in many important quantum mechanical phenomena, such as photochemistry, electron transport or transfer, and cavity-modified transition processes in chemical, materials, biological, and environmental molecular systems.[6−9] Nonadiabatic dynamics includes quantum mechanical behavior of both electrons and nuclei. In such processes, nuclear dynamics involves two or more coupled electronic states, where the state−state coupling is either inherent in the molecular structure or induced by the (intense) external field. As it is often intractable to use "numerically exact" methods for realistic multidimensional anharmonic systems, considerable effort has been focus on developing practical (trajectory-based) methodologies[10−14] to address the fundamental nature of nonadiabatic dynamic processes in complex (large) molecular systems.

The phase space formulation of quantum mechanics[15−17] that employs both coordinate and momentum variables offers a widely useful tool to gain insight on bridging quantum and classical counterpart concepts. Since the renowned work of Meyer and Miller[13] and its successful applications to describing the electronic-to-rotational or electronic-to-vibrational resonance energy transfer in nonadiabatic collision reactions,[18,19] the Meyer−Miller mapping model has offered an important theoretical framework for developing practical trajectory-based nonadiabatic dynamics methods.[14,20−41] A recent review[28] has briefly summarized the important developments and applications of the Meyer−Miller mapping model.

In this Account, we will report our more recent progress in phase space mapping theory since 2016, which is focused on a novel unified framework for mapping Hamiltonian models[1] and offers a novel way to derive the Meyer−Miller model, a new comprehensive formulation for the one-to-one correspondence mapping onto phase space,[1,3,4,42] and an isomorphism between the mapping phase space approach for the coupled multistate system and that for the second-quantized many-electron Hamiltonian system.[2] In the applications to nonadiabatic transition processes, we will discuss the comparison of the phase space mapping approaches to two prevailing trajectory-based methods, Ehrenfest dynamics[10] and Tully's fewest switches surface hopping (FSSH).[11]

2. MEYER−MILLER MAPPING HAMILTONIAN MODEL

In 1927, Dirac demonstrated that the time-dependent Schrödinger equation for an F-state quantum system is identical to Hamilton's equations of motion (EOMs) for the action-angle variables.[43] In 1979, Meyer and Miller suggested a heuristic mapping Hamiltonian model with the "Langer correction" for a finite set of electronic states of a molecular system such that both nuclear and electronic degrees of freedom (DOFs) are treated on the same footing for dynamics.[13] Use the diabatic representation for simplicity. The Meyer−Miller Hamiltonian is

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

Here, $\{\mathbf{R}, \mathbf{P}\}$ are the nuclear coordinate and momentum variables (the total number of nuclear DOFs is N), $\mathbf{M}$ is the diagonal "mass matrix" with elements $\{m_j\}$,$\{\mathbf{x}, \mathbf{p}\} = \{x^{(1)}, ..., x^{(F)}, p^{(1)}, ..., p^{(F)}\}$ are the mapping coordinate and momentum variables for the finite set of electronic states (with F being the total number of states), and parameter $\gamma = 1/2$ in Meyer and Miller's original version where the Langer correction [for the zero-point-energy (ZPE)] is employed.[13] Equation 1 is the mapping Hamiltonian for the coupled F-electronic-state Hamiltonian in quantum mechanics

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

where the F electronic states form an orthogonal complete basis set, that is,

$$\langle m|n\rangle = \delta_{mn}, \qquad \hat{I}_{\mathrm{ele}} = \sum_{n=1}^{F}|n\rangle\langle n| \tag{3}$$

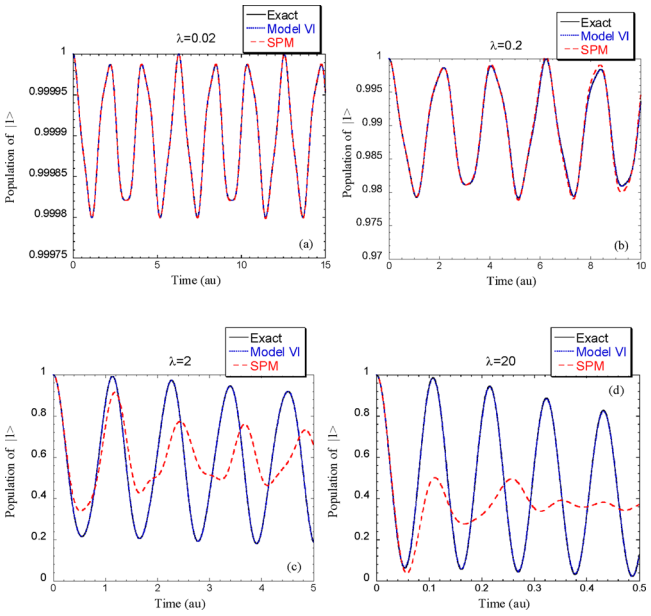

Figure 1. Comparison between the exact mapping model of ref 1 and the SPM of ref 26 for population dynamics of state $|1\rangle$ for a 3-state Hamiltonian system.[1] As the state−state coupling, λ, increases, the performance of the SPM becomes worse. Reproduced with permission from ref 1. Copyright 2016 American Institute of Physics.

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Here $\hat{I}_{ele}$ is the identity operator of the electronic state space, and $\{V_{nm}(\mathbf{R}) = V_{mn}(\mathbf{R})\}$ are the elements of the real symmetric matrix for the potential energy operator.

In ref 20, Stock and Thoss used the oscillator model of angular momentum proposed by Schwinger and suggested the mapping relations

$$|n\rangle \rightarrow \underbrace{|0_1 \ldots 1_n \ldots 0_F\rangle}_{F\text{-states}} \tag{4}$$

and

$$|n\rangle\langle m| \rightarrow \hat{a}_n^+ \hat{a}_m \tag{5}$$

where conventional commutation relations of the harmonic-oscillator creation and annihilation operators $\{\hat{a}_n^+, \hat{a}_n\}$ are

$$[\hat{a}_m, \hat{a}_n^+] = \delta_{mn} \quad (\forall\, m, n) \tag{6}$$

The Hamiltonian operator of eq 2 is then equivalent to

$$\hat{H} = \sum_{n,m=1}^{F} H_{nm}(\hat{\mathbf{R}}, \hat{\mathbf{P}}) \hat{a}_n^+ \hat{a}_m \tag{7}$$

After the creation/annihilation operators are transformed into pairs of operators

$$\hat{x}_n = \frac{\hat{a}_n + \hat{a}_n^+}{\sqrt{2}} \qquad \hat{p}_n = \frac{\hat{a}_n - \hat{a}_n^+}{\sqrt{2}\, i} \tag{8}$$

the coupled F-electronic-state Hamiltonian operator eq 7 becomes the Meyer−Miller mapping Hamiltonian eq 1. Equation 6 yields

$$[\hat{x}_m, \hat{p}_n] = i\delta_{mn} \quad (\forall\, m, n) \tag{9}$$

where δ_{mn} is the Kronecker delta. Substitution of eqs 8 and 9 into eq 7 leads to eq 1, which demonstrates that parameter $\gamma = 1/2$ comes from the commutation relation eq 9 and is the ZPE of the harmonic oscillator for each underlying electronic DOF.[20] It is then evident that eq 1 is an exact mapping Hamiltonian model for eq 2, the coupled F-electronic-state Hamiltonian in quantum mechanics. In practice, the ZPE parameter is chosen to be $1/3$, $(\sqrt{3} - 1)/2$, $(\sqrt{F+1} - 1)/F$, and other non-negative values in its semiclassical or quasiclassical applications.[20,21,25−32,37,44]

Because there exist an infinite number of energy eigenstates of a harmonic oscillator, the mapping of eqs 4 and 5 is then restricted onto the oscillator subspace with a single excitation, that is, only ground and first excited levels are employed. Evaluation of physical properties or time correlation functions invokes a space of singly excited oscillators (SEOs).[14,20−23,31,32,34,37,38,45,46] Appendix A of ref 1 evidently shows that eq 6 or eq 9 holds only when an infinite number of eigenstates of a harmonic oscillator are involved. In ref 26, Cotton and Miller pointed out that the Meyer−Miller mapping model "is not the most natural one". They suggested a spin mapping model (SPM),[26] but SPM is not exact for general multi-electronic-state systems even in the frozen nuclei limit (i.e., variables of nuclear DOFs are fixed)[1] (see Figure 1). This explains why SPM performs worse than the Meyer−Miller model. It is evidently nontrivial to obtain exact mapping Hamiltonian models on phase space for the coupled multistate Hamiltonian. To the best of our knowledge, except the Meyer−Miller model,[13,20] no exact phase space mapping Hamiltonian models for nonadiabatic systems were explicitly proposed before 2016.

3. UNIFIED FORMULATION FOR PHASE SPACE MAPPING APPROACHES

3.1. Unified Framework for Mapping Hamiltonian Models

In ref 1, we proposed a unified framework for constructing exact phase space mapping Hamiltonian models. The three key elements are

(1) We first introduce a vacuum (or reference) state $|\overline{0}\rangle \rightarrow \underbrace{|0_1 \cdots 0_n \cdots 0_F\rangle}_{F\text{-states}}$ such that state n of eq 4 is represented by a single excitation from the vacuum state, that is,

$$|n\rangle = \hat{a}_n^+ |\overline{0}\rangle \tag{10}$$

Here, an excitation stands for the occupation of the corresponding state, and the vacuum state, $|\overline{0}\rangle$, is orthogonal to any occupied state $|n\rangle$.

(2) Because only a single excitation is invoked, we can define the creation and annihilation operators as

$$\hat{a}_n^+ = |n\rangle\langle\overline{0}| \qquad \hat{a}_n = |\overline{0}\rangle\langle n| \tag{11}$$

Equation 11 leads to eq 5 as well as eq 7. It is straightforward to derive the commutation and anti-commutation relations from eq 11, which demonstrate that the underlying DOFs are neither bosons nor Fermions.[1] Define

$$\hat{\sigma}_x^{(n)} = \hat{a}_n + \hat{a}_n^+ \qquad \hat{\sigma}_y^{(n)} = \frac{\hat{a}_n - \hat{a}_n^+}{i} \tag{12}$$

$\{\hat{\sigma}_x^{(n)}, \hat{\sigma}_y^{(n)}\}$ stand for the Pauli matrices (for a spin 1/2 particle) in the x and y directions, respectively.

(3) We then obtain equivalent expressions of the coupled multistate Hamiltonian operator of eq 7 in terms of only $\{\hat{\sigma}_x^{(n)}, \hat{\sigma}_y^{(n)}\}$ and develop the criteria for obtaining exact phase space mapping models.

The novel framework involves *only* quantum operators for constructing exact mapping Hamiltonian models. In contrast, the conventional way in the literature always involves a space of SEOs for implementing the Meyer−Miller mapping model.[20,21]

An equivalent representation of the Hamiltonian operator of eq 7 reads

$$\hat{H} = \sum_{n,m=1}^{F} H_{nm}(\hat{\mathbf{R}}, \hat{\mathbf{P}}) \left\{ \frac{1}{4}(\hat{\sigma}_x^{(n)} \hat{\sigma}_x^{(m)} + \hat{\sigma}_y^{(n)} \hat{\sigma}_y^{(m)}) - \frac{i}{4}(\hat{\sigma}_y^{(n)} \hat{\sigma}_x^{(m)} - \hat{\sigma}_x^{(n)} \hat{\sigma}_y^{(m)}) \right\} \tag{13}$$

A change of variables

$$x^{(n)} = \frac{\sigma_x^{(n)}}{\sqrt{2}} \qquad p^{(n)} = \frac{\sigma_y^{(n)}}{\sqrt{2}} \tag{14}$$

in eq 13 yields

$$H(\mathbf{x}, \mathbf{p}; \boldsymbol{\Gamma}; \mathbf{R}, \mathbf{P}) = \sum_{n,m=1}^{F} \left[\frac{1}{2}(x^{(n)} x^{(m)} + p^{(n)} p^{(m)}) - \Gamma_{nm} \right] \times H_{nm}(\mathbf{R}, \mathbf{P}) \tag{15}$$

Here

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$$\Gamma_{nm} = \frac{i}{4}(\hat{\sigma}_y^{(n)}\hat{\sigma}_x^{(m)} - \hat{\sigma}_x^{(n)}\hat{\sigma}_y^{(m)}) \tag{16}$$

is the element in the nth row and mth column of commutator matrix $\mathbf{\Gamma}$. eq 16 implies

$$\hat{x}^{(n)}\hat{p}^{(m)} - \hat{p}^{(n)}\hat{x}^{(m)} = 2i\Gamma_{nm} \tag{17}$$

or the commutation relation

$$[\hat{x}^{(n)}, \hat{p}^{(m)}] + [\hat{x}^{(m)}, \hat{p}^{(n)}] = 2i(\Gamma_{nm} + \Gamma_{mn}) \tag{18}$$

Equation 18 is the commutation relation between the position and momentum operators of the quasi-particles of the electronic mapping DOFs. It is evident that the conventional canonical commutation relation eq 9 is only a special case of eq 18.

When the equality

$$\sum_{n=1}^{F}\left[\frac{(x^{(n)})^2 + (p^{(n)})^2}{2} - \Gamma_{nn}\right] = 1 \tag{19}$$

holds for the mapping phase variables of the electronic DOFs, the mapping Hamiltonian becomes

$$H(\mathbf{x}, \mathbf{p}; \mathbf{\Gamma}; \mathbf{R}, \mathbf{P}) = \frac{1}{2}\mathbf{P}^{\mathrm{T}}\mathbf{M}^{-1}\mathbf{P} + \sum_{n,m=1}^{F}\left[\frac{1}{2}(x^{(n)}x^{(m)} + p^{(n)}p^{(m)}) - \Gamma_{nm}\right]V_{mn}(\mathbf{R}) \tag{20}$$

The conventional Meyer−Miller mapping Hamiltonian eq 1 is intrinsically a special case with $\Gamma_{nm} = \gamma\delta_{nm}$ for eq 20, the general and comprehensive mapping Hamiltonian[1,3,42] (i.e., model II of ref 1).

The unified framework of ref 1 provides the scene for obtaining more equivalent representations of the F-state quantum system and their corresponding exact phase space mapping Hamiltonian models. As shown in ref 1, the mapping in analogy to angular momentum leads to model I,

$$H(\mathbf{x}, \mathbf{p}_x, \mathbf{y}, \mathbf{p}_y; \mathbf{\Gamma}; \mathbf{R}, \mathbf{P}) = \sum_{n,m=1}^{F}[(x^{(n)}p_y^{(m)} - y^{(n)}p_x^{(m)}) - \Gamma_{nm}]H_{nm}(\mathbf{R}, \mathbf{P}) \tag{21}$$

Models III, IV, V, and VI for the coupled multistate Hamiltonian operator (proposed in ref 1) are

$$H = \sum_{n=1}^{F}\left(\frac{(x^{(n)} + p_y^{(n)})^2 + (y^{(n)} - p_x^{(n)})^2}{4} - \Gamma_{nn}\right)H_{nn}(\mathbf{R}, \mathbf{P}) + \sum_{n\neq m}(x^{(n)}p_y^{(m)} - y^{(m)}p_x^{(n)} - \Gamma_{nm})H_{nm}(\mathbf{R}, \mathbf{P}) \tag{22}$$

$$H = \sum_{n=1}^{F}\left(\frac{(x^{(n)} + p_y^{(n)})^2 + (y^{(n)} - p_x^{(n)})^2}{4} - \Gamma_{nn}\right)H_{nn}(\mathbf{R}, \mathbf{P}) + \sum_{n<m}((x^{(n)}x^{(m)} + p_x^{(n)}p_x^{(m)}) + (y^{(n)}y^{(m)} + p_y^{(n)}p_y^{(m)}) - \Gamma_{nm} - \Gamma_{mn})H_{nm}(\mathbf{R}, \mathbf{P}) \tag{23}$$

$$H = \sum_{n=1}^{F}\left(\frac{(x^{(n)} + p_y^{(n)})^2 + (y^{(n)} - p_x^{(n)})^2}{4} - \Gamma_{nn}\right)H_{nn}(\mathbf{R}, \mathbf{P}) + \sum_{n<m}\left(\frac{(x^{(n)} + p_y^{(n)})(x^{(m)} + p_y^{(m)}) + (y^{(n)} - p_x^{(n)})(y^{(m)} - p_x^{(m)})}{2} - \Gamma_{nm} - \Gamma_{mn}\right)H_{nm}(\mathbf{R}, \mathbf{P}) \tag{24}$$

and

$$H = \sum_{n=1}^{F}(x^{(n)}p_y^{(n)} - y^{(n)}p_x^{(n)} - \Gamma_{nn})H_{nn}(\mathbf{R}, \mathbf{P}) + \sum_{n<m}((x^{(n)}x^{(m)} + p_x^{(n)}p_x^{(m)}) + (y^{(n)}y^{(m)} + p_y^{(n)}p_y^{(m)}) - \Gamma_{nm} - \Gamma_{mn})H_{nm}(\mathbf{R}, \mathbf{P}) \tag{25}$$

respectively. Similar to eq 19, when we have the equality for the mapping phase variables of the electronic DOFs

$$\sum_{n=1}^{F}(x^{(n)}p_y^{(n)} - y^{(n)}p_x^{(n)} - \Gamma_{nn}) = 1 \tag{26}$$

for eq 21 or eq 25, or

$$\sum_{n=1}^{F}\frac{(x^{(n)} + p_y^{(n)})^2 + (y^{(n)} - p_x^{(n)})^2}{4} - \Gamma_{nn} = 1 \tag{27}$$

for eq 22, 23, or 24, the term related to kinetic energy, $\mathbf{P}^{\mathrm{T}}\mathbf{M}^{-1}\mathbf{P}/2$, of the mapping Hamiltonian does not include any electronic state mapping variables.[3] For example, the mapping Hamiltonian eq 21 becomes

$$H(\mathbf{x}, \mathbf{p}_x, \mathbf{y}, \mathbf{p}_y; \mathbf{\Gamma}; \mathbf{R}, \mathbf{P}) = \frac{1}{2}\mathbf{P}^{\mathrm{T}}\mathbf{M}^{-1}\mathbf{P} + \sum_{n,m=1}^{F}[(x^{(n)}p_y^{(m)} - y^{(n)}p_x^{(m)}) - \Gamma_{nm}]V_{mn}(\mathbf{R}) \tag{28}$$

Here we demonstrate two more mapping Hamiltonian models. Consider an equivalent representation of the Hamiltonian operator of eq 7,

$$\hat{H} = \sum_{n}\frac{1}{4}([\hat{\sigma}_x^{(n)}, \hat{\sigma}_x^{(n)}]_+ + [\hat{\sigma}_y^{(n)}, \hat{\sigma}_y^{(n)}]_+)H_{nn}(\hat{\mathbf{R}}, \hat{\mathbf{P}}) + \sum_{n<m}\frac{1}{2}([\hat{\sigma}_x^{(n)}, \hat{\sigma}_x^{(m)}]_+ + [\hat{\sigma}_y^{(n)}, \hat{\sigma}_y^{(m)}]_+)H_{nm}(\hat{\mathbf{R}}, \hat{\mathbf{P}}) \tag{29}$$

Employing the mapping strategy by analogy with the classical vector as described in section III-C of ref 1 leads to

$$H(\mathbf{x}, \mathbf{p}_x, \mathbf{y}, \mathbf{p}_y; \mathbf{\Gamma}; \mathbf{R}, \mathbf{P}) = \sum_{n,m=1}^{F}\left[\frac{(x^{(n)}x^{(m)} + p_x^{(n)}p_x^{(m)}) + (y^{(n)}y^{(m)} + p_y^{(n)}p_y^{(m)})}{2} - \Gamma_{nm}\right] \times H_{nm}(\mathbf{R}, \mathbf{P}) \tag{30}$$

Making the transformation of variables[1]

$$\mathbf{x} = \mathbf{q}, \quad \mathbf{y} = -\mathbf{p}_\mathbf{q}, \quad \mathbf{p}_\mathbf{x} = \mathbf{p}_\mathbf{r}, \quad \mathbf{p}_\mathbf{y} = \mathbf{r} \tag{31}$$

in eq 21 yields

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$$H(\mathbf{q}, \mathbf{p}_q, \mathbf{r}, \mathbf{p}_r; \mathbf{\Gamma}; \mathbf{R}, \mathbf{P}) = \sum_{n,m=1}^{F} [(q^{(n)}r^{(m)} + p_q^{(n)}p_r^{(m)}) - \Gamma_{nm}]H_{nm}(\mathbf{R}, \mathbf{P}) \quad (32)$$

Switching between $\mathbf{q}$ and $\mathbf{r}$ and that between $\mathbf{p}_q$ and $\mathbf{p}_r$ make no difference. It is then trivial to obtain from eq 32

$$H(\mathbf{q}, \mathbf{p}_q, \mathbf{r}, \mathbf{p}_r; \mathbf{\Gamma}; \mathbf{R}, \mathbf{P}) = \sum_{n,m=1}^{F} \left[\frac{(q^{(n)}r^{(m)} + p_q^{(n)}p_r^{(m)}) + (r^{(n)}q^{(m)} + p_r^{(n)}p_q^{(m)})}{2} - \Gamma_{nm} \right] \times H_{nm}(\mathbf{R}, \mathbf{P}) \quad (33)$$

It is evident that the two mapping Hamiltonian models proposed in ref 47 are simply a special case of eq 30 and of eq 33, which are yielded in the unified framework for mapping Hamiltonian models for coupled multistate systems.[1] The Clifford algebra can be used for the mapping Hamiltonian models (eqs 21−25 and eqs 32 and 33) that involve $4F$ mapping phase variables for the electronic DOFs. When different mapping Hamiltonian models in the unified framework are treated in the same fashion, they in principle produce the same results, regardless of different convergence performance.

3.2. General Formulation of the One-to-One Correspondence Mapping on Phase Space for Systems Involving Both Continuous and Discrete DOFs

In addition to the mapping Hamiltonian, evaluation of physical properties lies in the center of the phase space formulation of quantum mechanics. As first pointed out for general coupled multistate systems in ref 3, eq 19, 26, or 27 suggests the constraint phase space for the mapping variables. This is very different from the classification scheme[16,17] of the conventional mapping onto full phase space with infinite boundaries[15,16] for quantum systems that involve the continuous coordinate space. In refs 3 and 4, we have first proposed a unified formulation for the one-to-one correspondence mapping on phase space, which is capable of treating quantum systems represented in the finite-dimensional, as well as infinite-dimensional, Hilbert space.[1,3,4,42] The general phase space formulation provides a useful tool for studying nonadiabatic dynamics, where a finite set of electronic states as well as continuous nuclear DOFs is involved.

For demonstration, we use the mapping approach eq 20 that is reminiscent of the Meyer−Miller model. Consider the simplest case $\Gamma_{nm} = \delta_{nm}\gamma$ $(\forall n,m)$ for commutator matrix $\mathbf{\Gamma}$. Because the electronic state mapping variables should satisfy eq 19, a simple strategy is to employ the constraint space,

$$\mathcal{S}(\mathbf{x}, \mathbf{p}): \delta\left(\sum_{n=1}^{F} \frac{(x^{(n)})^2 + (p^{(n)})^2}{2} - (1 + F\gamma) \right) \quad (34)$$

for developing the formulation for evaluation of physical observables. In eq 34, the possible value of parameter γ lies in $(-\frac{1}{F}, \infty)$. The trace of a product of two operators is expressed on phase space as

$$\mathrm{Tr}_{n,e}[\hat{A}\hat{B}] = \int (2\pi\hbar)^{-N} \, d\mathbf{R} \, d\mathbf{P} \int_{\mathcal{S}(\mathbf{x},\mathbf{p})} F \, d\mathbf{x} \, d\mathbf{p} \times A(\mathbf{R}, \mathbf{P}; \mathbf{x}, \mathbf{p})\tilde{B}(\mathbf{R}, \mathbf{P}; \mathbf{x}, \mathbf{p}) \quad (35)$$

where

$$A(\mathbf{R}, \mathbf{P}; \mathbf{x}, \mathbf{p}) = \mathrm{Tr}_{n,e}[\hat{A}\hat{K}_{nuc}(\mathbf{R}, \mathbf{P}) \otimes \hat{K}_{ele}(\mathbf{x}, \mathbf{p})] \quad (36)$$

$$\tilde{B}(\mathbf{R}, \mathbf{P}; \mathbf{x}, \mathbf{p}) = \mathrm{Tr}_{n,e}[\hat{K}_{nuc}^{-1}(\mathbf{R}, \mathbf{P}) \otimes \hat{K}_{ele}^{-1}(\mathbf{x}, \mathbf{p})\hat{B}] \quad (37)$$

$(2\pi\hbar)^{-N} \, d\mathbf{R} \, d\mathbf{P} \otimes F \, d\mathbf{x} \, d\mathbf{p}$ represents the invariant measure on the mapping phase space for the nuclear and electronic DOFs, Tr_n stands for the trace over the nuclear DOFs, and Tr_e is the trace over the F electronic states. The inverse one-to-one correspondence mapping from phase space function $A(\mathbf{R},\mathbf{P};\mathbf{x},\mathbf{p})$ (or $\tilde{B}(\mathbf{R},\mathbf{P};\mathbf{x},\mathbf{p})$) of eq 36 to operator $\hat{A}$ (or $\hat{B}$) is

$$\hat{A} = \int (2\pi\hbar)^{-N} \, d\mathbf{R} \, d\mathbf{P} \int_{\mathcal{S}(\mathbf{x},\mathbf{p})} F \, d\mathbf{x} \, d\mathbf{p} \, A(\mathbf{R}, \mathbf{P}; \mathbf{x}, \mathbf{p})\hat{K}_{nuc}^{-1}(\mathbf{R}, \mathbf{P}) \otimes \hat{K}_{ele}^{-1}(\mathbf{x}, \mathbf{p})$$
$$\hat{B} = \int (2\pi\hbar)^{-N} \, d\mathbf{R} \, d\mathbf{P} \int_{\mathcal{S}(\mathbf{x},\mathbf{p})} F \, d\mathbf{x} \, d\mathbf{p} \, \tilde{B}(\mathbf{R}, \mathbf{P}; \mathbf{x}, \mathbf{p})\hat{K}_{nuc}(\mathbf{R}, \mathbf{P}) \otimes \hat{K}_{ele}(\mathbf{x}, \mathbf{p}) \quad (38)$$

The integral over constraint space $\mathcal{S}(\mathbf{x}, \mathbf{p})$ reads

$$\int_{\mathcal{S}(\mathbf{x},\mathbf{p})} F d\mathbf{x} d\mathbf{p} g(\mathbf{x}, \mathbf{p}) = \frac{\int F \, d\mathbf{x} \, d\mathbf{p} \, \delta\left(\sum_{n=1}^{F} \left[\frac{(x^{(n)})^2 + (p^{(n)})^2}{2} \right] - (1 + \sum_{n=1}^{F} \Gamma_{nn}) \right) g(\mathbf{x}, \mathbf{p})}{\int d\mathbf{x} \, d\mathbf{p} \, \delta\left(\sum_{n=1}^{F} \left[\frac{(x^{(n)})^2 + (p^{(n)})^2}{2} \right] - (1 + \sum_{n=1}^{F} \Gamma_{nn}) \right)} \quad (39)$$

Because the nuclear DOFs involve infinite energy levels, their integrals are over the mapping nuclear phase space with infinite boundaries. The classification scheme[16,17] can be recast into the definition of the mapping kernel for the nuclear DOFs (in eq 36)

$$\hat{K}_{nuc}(\mathbf{R}, \mathbf{P}) = \left(\frac{\hbar}{2\pi} \right)^N \int d\boldsymbol{\zeta} \int d\boldsymbol{\eta} \, e^{i\boldsymbol{\zeta}\cdot(\hat{\mathbf{R}}-\mathbf{R})+i\boldsymbol{\eta}\cdot(\hat{\mathbf{P}}-\mathbf{P})} f(\boldsymbol{\zeta}, \boldsymbol{\eta}) \quad (40)$$

and that of the inverse kernel (in eq 37)

$$\hat{K}_{nuc}^{-1}(\mathbf{R}, \mathbf{P}) = \left(\frac{\hbar}{2\pi} \right)^N \int d\boldsymbol{\zeta} \int d\boldsymbol{\eta} \, e^{-i\boldsymbol{\zeta}\cdot(\hat{\mathbf{R}}-\mathbf{R})-i\boldsymbol{\eta}\cdot(\hat{\mathbf{P}}-\mathbf{P})} \times [f(-\boldsymbol{\zeta}, -\boldsymbol{\eta})]^{-1} \quad (41)$$

In eq 40 and eq 41, $f(\boldsymbol{\zeta},\boldsymbol{\eta})$ is a scalar function that defines the mapping nuclear phase space of choice. For example, the Wigner function[15] takes

$$f(\boldsymbol{\zeta}, \boldsymbol{\eta}) = 1 \quad (42)$$

In eqs 35, 38, 40, and 41, the integrals for the mapping phase variables for the finite set of electronic states are over constraint space $\mathcal{S}(\mathbf{x}, \mathbf{p})$. As derived first in Appendix A of ref 3 and then in the Supporting Information of ref 4, the mapping kernel for the F electronic states (in eq 36) is

$$\hat{K}_{ele}(\mathbf{x}, \mathbf{p}) = \sum_{n,m=1}^{F} \left[\frac{1}{2}(x^{(n)} + ip^{(n)})(x^{(m)} - ip^{(m)}) - \gamma\delta_{nm} \right] |n\rangle\langle m| \quad (43)$$

and the corresponding inverse kernel (in eq 37) is

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$$\hat{K}_{\text{ele}}{}^{-1}(\mathbf{x},\mathbf{p}) = \sum_{n,m=1}^{F}\left[\frac{1+F}{2(1+F\gamma)^2}(x^{(n)}+ip^{(n)})\times(x^{(m)}-ip^{(m)}) - \frac{1-\gamma}{1+F\gamma}\delta_{nm}\right]|n\rangle\langle m| \tag{44}$$

As pointed out in ref 42, it is trivial to show that the Q-version, W-version, or P-version of ref 36 corresponds to parameter $\gamma = 0$, $(\sqrt{F+1}-1)/F$, or 1 of the exact phase space mapping formulation that we *first* proposed in refs 1 and 3 and then in ref 4, respectively. It will be interesting to use our general phase space mapping formulation to include or reformulate other approaches that use the Meyer−Miller mapping model.[21,25,28−30,34,37,41,45,48]

Equation 35 also sets the scene for expressing real time dynamics in the phase space formulation of quantum mechanics. An exact expression of the time correlation function of nonadiabatic systems

$$C_{AB}(t) = \text{Tr}_{\text{n,e}}[\hat{A}(0)\hat{B}(t)] \tag{45}$$

is

$$C_{AB}(t) = \int(2\pi\hbar)^{-N}\,\mathrm{d}\mathbf{R}\,\mathrm{d}\mathbf{P}\int_{S(\mathbf{x},\mathbf{p})}F\,\mathrm{d}\mathbf{x}\,\mathrm{d}\mathbf{p}\times A(\mathbf{R},\mathbf{P};\mathbf{x},\mathbf{p})\tilde{B}(\mathbf{R},\mathbf{P};\mathbf{x},\mathbf{p};t) \tag{46}$$

where

$$\tilde{B}(\mathbf{R},\mathbf{P};\mathbf{x},\mathbf{p};t) = \text{Tr}_{\text{n,e}}[\hat{K}_{\text{nuc}}{}^{-1}(\mathbf{R},\mathbf{P})\otimes\hat{K}_{\text{ele}}{}^{-1}(\mathbf{x},\mathbf{p})\hat{B}(t)] \tag{47}$$

In eq 45, the Heisenberg operator $\hat{B}(t) = \mathrm{e}^{i\hat{H}t/\hbar}\,\hat{B}\,\mathrm{e}^{-i\hat{H}t/\hbar}$ is used. It is straightforward to express the quantum Liouville equation for $\tilde{B}(\mathbf{R},\mathbf{P};\mathbf{x},\mathbf{p};t)$ of eq 47 in the general phase space formulation. As long as we exactly solve the EOMs (for nuclear and electronic DOFs) in eq 47, the formulation of the correlation function eq 46 is exact for describing nonadiabatic systems.[3,4]

It is, however, often challenging if not at all impossible to exactly solve the EOMs when both nuclear and electronic DOFs are coupled. When we make the trajectory-based dynamics approximation, eq 46 is then recast into

$$C_{AB}(t) = \int(2\pi\hbar)^{-N}\,\mathrm{d}\mathbf{R}\,\mathrm{d}\mathbf{P}\int_{S(\mathbf{x},\mathbf{p})}F\,\mathrm{d}\mathbf{x}\,\mathrm{d}\mathbf{p}\times A(\mathbf{R},\mathbf{P};\mathbf{x},\mathbf{p})\tilde{B}(\mathbf{R}_t,\mathbf{P}_t;\mathbf{x}_t,\mathbf{p}_t) \tag{48}$$

When only the electronic state variables evolve with time, that is, in the frozen nuclei limit, trajectory-based dynamics governed by Hamilton's EOMs of the mapping Hamiltonian (eq 1, eq 15, and other exact mapping Hamiltonian models) produce exact results, that is, eq 48 is equivalent to eq 46. When both nuclear and electronic DOFs are involved, the independent trajectory generated by the mapping Hamiltonian of section 3.1 is an approximation to the quantum Liouville equation of the corresponding phase space, that is, eq 48 is an approximation to eq 46. The formulation of the correlation function eq 48 is often expressed on constraint space $\mathcal{S}(\mathbf{x},\mathbf{p})$ and Wigner phase space for electronic and nuclear DOFs, respectively. The extended classical mapping model (eCMM) approach[3,4] utilizes the Meyer−Miller Hamiltonian eq 1 to yield the EOMs of the trajectory. In contrast, the eCMM with commutator variables (eCMMcv) employs the comprehensive mapping Hamiltonian eq 20 to produce trajectory-based dynamics, where initial values for commutator variables are given by

$$\tilde{\mathcal{S}}(\mathbf{x},\mathbf{p};\mathbf{\Gamma}): \delta\left(\sum_{n=1}^{F}\frac{(x^{(n)})^2+(p^{(n)})^2}{2}-(1+F\gamma)\right)\times\prod_{n=1}^{F}\left(\delta\left(\Gamma_{nn}+\delta_{n,j_{\text{occ}}}-\frac{(x^{(n)})^2+(p^{(n)})^2}{2}\right)\prod_{k\neq n}^{F}\delta(\Gamma_{nk})\right) \tag{49}$$

Here j_{occ} denotes the index of the initially occupied state. Both the frozen-nuclei limit and Born−Oppenheimer limit are satisfied in the eCMMcv approach. Our general phase space formulation is not limited to the mapping of a finite set of states onto constraint phase space eq 34 or eq 49. Other options that satisfy eq 19, eq 26, or eq 27 are possible for the constraint space, upon which the one-to-one correspondence mapping can be established. More discussion on this will be available in a forthcoming paper.

Finally, we note that it is easy to extend the phase space mapping approach to the adiabatic representation or other representations. As shown in the Supporting Information of ref 42, we can directly apply the strategy of ref 29 to the comprehensive mapping Hamiltonian model (of section 3.1) in the adiabatic representation. The EOMs of the trajectory in the phase space mapping approach are then independent of the electronic representation of choice.

4. APPLICATIONS TO NONADIABATIC SYSTEMS

The preceding discussion has reviewed the unified framework of phase space mapping approaches for nonadiabatic quantum dynamics. Below we highlight a few illustrative applications of the eCMM and eCMMcv approaches. Ehrenfest dynamics[10] or

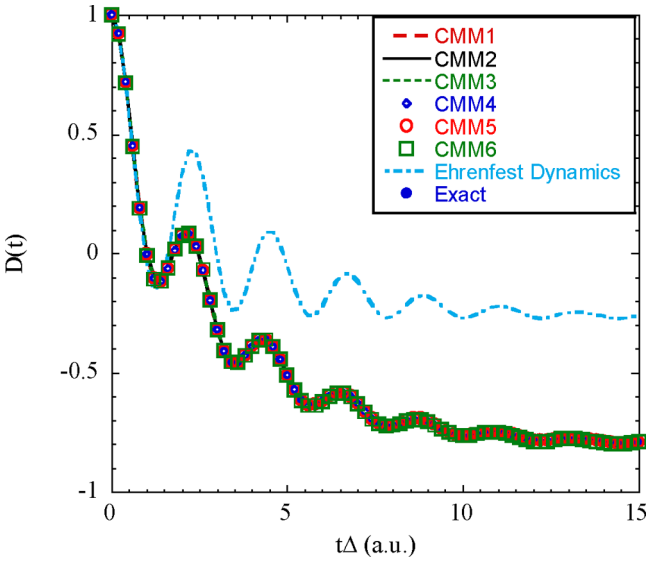

Figure 2. Population difference $D(t) = P_{1\leftarrow1}(t) - P_{2\leftarrow1}(t)$ of the spin-boson Hamiltonian with the Debye bath at finite temperature. The six mapping Hamiltonian models of ref 1 are used in CMM1−CMM6 (i.e., for eCMM approaches with $\gamma = 0$). Ehrenfest dynamics results as well as exact results are demonstrated for comparison. Reproduced with permission from ref 3. Copyright 2019 American Institute of Physics.

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