New phase space formulations and quantum dynamics approaches

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Funding information
Ministry of Science and Technology of the People’s Republic of China, Grant/Award Number: 2017YFA0204901; National Natural Science Foundation of China, Grant/Award Number: 21961142017

Edited by: Jinlong Yang, Associate Editor and Peter R. Schreiner, Editor-in-Chief

Abstract
We report recent progress on the phase space formulation of quantum mechanics with coordinate-momentum variables, focusing more on new theory of (weighted) constraint coordinate-momentum phase space for discrete-variable quantum systems. This leads to a general coordinate-momentum phase space formulation of composite quantum systems, where conventional representations on infinite phase space are employed for continuous variables. It is convenient to utilize (weighted) constraint coordinate-momentum phase space for representing the quantum state and describing nonclassical features. Various numerical tests demonstrate that new trajectory-based quantum dynamics approaches derived from the (weighted) constraint phase space representation are useful and practical for describing dynamical processes of composite quantum systems in the gas phase as well as in the condensed phase.

This article is categorized under:
Molecular and Statistical Mechanics > Molecular Dynamics and Monte-Carlo Methods
Theoretical and Physical Chemistry > Reaction Dynamics and Kinetics
Theoretical and Physical Chemistry > Statistical Mechanics

KEYWORDS
composite quantum systems, constraint phase space, nonadiabatic dynamics, phase space formulation, quantum dynamics

1 | INTRODUCTION

Phase space with coordinate-momentum variables is a fundamental concept and offers a convenient tool to describe statistics as well as dynamics in classical mechanics. In comparison to other equivalent interpretations of quantum mechanics, phase space formulations offer more insight and understanding between quantum and classical counterpart concepts, which are widely used in chemical and biological dynamics and spectroscopy, quantum optics, cryogenic physics/chemistry, quantum information and computation, and so forth.

Phase space formulations of quantum mechanics have been developed since two important pioneering works, the Weyl transform in 1927, of which the original formulation converted a Hamiltonian on classical phase space into a quantum mechanical operator, and the Wigner function in 1932 that in principle depicts the inverse transform although a pure state was used for demonstration. The most essential element is the one-to-one correspondence...
mapping between quantum operators and classical functions often defined on a smooth manifold, namely, phase space. Because of the commutation relation of conjugate operators, the mapping is not unique in quantum mechanics.\(^{90,91}\)

When infinite phase space is employed for a continuous-variable quantum system, most phase space formulations can be described by Cohen’s generalized form\(^ {92}\) in 1966. Quantum dynamics with phase space variables is expressed by the Moyal or Moyal-like bracket as first proposed by Groenewold\(^ {93}\) in 1946 and Moyal\(^ {94}\) in 1949. The Wigner and Husimi representations are most often used for the continuous-variable system. When the Moyal bracket is approximated by the Poisson bracket in the Wigner phase space expression of the quantum Liouville theorem, which was also derived as the linearized semiclassical initial value representation (LSC-IVR) or classical Wigner model\(^ {4\text{–}8,11,20,23}\) for the quantum correlation function, it reproduces exact quantum correlation functions even of nonlinear operators (i.e., nonlinear functions of the coordinate or momentum operator) in the harmonic or classical limit. The truncated Wigner approximation\(^ {74}\) with the time-dependent generalization of the Bopp representation\(^ {90,95}\) is similar to the LSC-IVR, but the former requests more demanding evaluation of the stability matrix elements along the trajectory when nonlinear operators are involved in the correlation function. Liu and Miller\(^ {15}\) suggest a practical way to implement the imaginary time path integral treatment of the Boltzmann density operator in the LSC-IVR for general molecular systems that often contain imaginary frequencies. Its recent application illustrates that quantum dynamical effects play a critical role in reproducing the peaks in the intermediate region between the librational and bending bands, those between the bending and stretching bands, and the double-peak in the stretching band in the experimental isotropic Raman spectrum of liquid water\(^ {19}\) (as shown in Figure 1). In addition that more advanced versions of SC-IVR\(^ {96\text{–}99}\) are capable of improving over the LSC-IVR, in Reference\(^ {11}\), we first employed the quantum Liouville theorem in the phase space formulation to develop trajectory-based approaches to satisfy the two fundamental criteria: conservation of the quantum Boltzmann distribution for the thermal equilibrium system and being exact for any quantum thermal correlation functions in the classical and harmonic limits. Such trajectory-based approaches can in principle be further improved by higher order corrections of the exact series expansion of the phase space propagator as demonstrated in Reference\(^ {44}\). More progress along this line can be found in References\(^ {37\text{–}47}\). (Figure 2 shows molecular vibrational spectra produced by the new phase space quantum dynamics methods.)

Phase space representations of a finite discrete F-state quantum system were first independently described by Stratonovich\(^ {100}\) in 1956, Feynman\(^ {101}\) in 1987, and Wootters\(^ {102}\) in 1987. Further developments of Stratonovich’s formulation have focused on an SU(2) or SU(F) structure of phase space,\(^ {103\text{–}117}\) while those on the construction of a discrete phase space are described in References\(^ {78,118\text{–}126}\). Other than the 2-state (or spin 1/2) system, the exact equations of motion

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**FIGURE 1** Quantum dynamical effects are decisive in reproducing the experimental isotropic Raman spectrum of liquid water at room temperature, as illustrated by the LSC-IVR simulation where infinite (Wigner) phase space for nuclear DOFs is used. Converged results were obtained with 216 water molecules in a box with periodic boundary conditions. (Reprinted with permission from Reference\(^ {19}\), Copyright 2018, Taylor & Francis).
(EOMs) of phase variables (expressed by the Moyal-like bracket) involved in these approaches for the finite discrete multi-state system are often tedious and numerically unfavourable.\textsuperscript{109,127–130,299,302} (See Appendix 3 of the Supporting Information for more discussion.) Recent theoretical progress on exactly mapping the finite discrete $F$-state quantum system onto constraint coordinate-momentum phase space suggests that there exists a novel unified framework to derive comprehensive exact mapping Hamiltonians,\textsuperscript{44,57,131,132} of which the quantum EOMs of mapping coordinate-momentum variables are simply linear.\textsuperscript{44,57,131–134}

**FIGURE 2** Molecular vibrational spectra produced by more advanced trajectory-based dynamics methods with infinite (Wigner) phase space used for nuclear DOFs, which satisfy the two fundamental criteria: Conservation of the quantum Boltzmann distribution for the thermal equilibrium system and being exact for any quantum thermal correlation functions in the classical and harmonic limits. (a) Vibrational spectrum of the H$_2$O molecule at 100 K and that at 300 K. Reprinted with permission from Reference 41, Copyright 2016 American Institute of Physics publishing. (b) Vibrational spectrum of the H$_2$O$_2$ molecule at 100 K. Reprinted with permission from Reference 44, Copyright 2021, American Institute of Physics publishing.
The unified formulation on coordinate-momentum phase space\textsuperscript{44,57,131–134} then offers a useful tool to treat dynamics of a composite quantum system, in which both continuous and finite discrete degrees of freedom (DOFs) are involved and coupled with one another. Because a typical molecular system has vibrational, rotational, and translational motion, it is often much more convenient to employ continuous coordinate space rather than Hilbert space with dense states to describe the nuclear DOFs. On the other hand, the energy gap between different electronic states of interest is often significantly larger such that the (adiabatic or diabatic) state representation is more useful to depict the electronic DOFs. It is evident that a general description of the molecular system leads to a composite quantum system, especially in the nonadiabatic region\textsuperscript{135–152} A comprehensive version of the Meyer–Miller mapping Hamiltonian model\textsuperscript{153,154} can rigorously be formulated in the general coordinate-momentum phase space formulation.\textsuperscript{44,57,131–134}

In the Focus Article, we focus on novel developments on the phase space formulation of quantum mechanics with coordinate-momentum variables for discrete-variable systems as well as for composite systems.\textsuperscript{44,57,131–134} In Section 2, we first review the general coordinate-momentum phase space formulation, where infinite space is used for describing continuous variables and constraint space is employed for mapping discrete variables. We then propose a weighted constraint phase space representation that is also an exact formulation for mapping discrete-variable quantum systems. Section 3 demonstrates several examples and discusses implications of the (weighted) constraint coordinate-momentum phase space for studying and illustrating discrete-variable or composite quantum systems. When we use the weighted constraint phase space representation for mapping composite quantum systems, the mapping Hamiltonian (we use the Meyer–Miller mapping Hamiltonian for demonstration throughout the article, albeit that other mapping Hamiltonians are also available\textsuperscript{57,58,131,132}) yields a novel trajectory-based approximate approach for composite systems. Such a new method satisfies the frozen nuclei limit [i.e., the dynamics reproduces the exact evolution when only finite discrete (electronic) DOFs are involved]. In Section 4, the performance of new trajectory-based quantum dynamics approaches on (weighted) constraint phase space is extensively tested for a few typical benchmark composite systems in the gas phase as well as in the condensed phase. Finally, conclusion remarks are presented in Section 5.

2 | GENERAL COORDINATE-MOMENTUM PHASE SPACE FORMULATION OF QUANTUM MECHANICS

Consider a (molecular) system with $N$ continuous (nuclear) DOFs and $F$ discrete (electronic) states, of which the Hamiltonian reads

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

where $\mathbf{R}$ and $\mathbf{P}$ are the nuclear coordinate and momentum variables, respectively, $\mathbf{M}$ is the diagonal mass matrix, and the $F$ states form an orthonormal complete basis set, that is,

$$\langle m|n\rangle = \delta_{mn} \hat{I}_{\text{ele}} = \sum_{n=1}^{F} |n\rangle \langle n|.$$

$\hat{I}_{\text{ele}}$ and $\hat{I}_{\text{nuc}}$ stand for the identity operator of the discrete (electronic) DOFs and that of the continuous (nuclear) DOFs. For simplicity, Equation (1) employs the (electronically) diabatic representation, where the Hermitian potential matrix $\mathbf{V}(\mathbf{R})$ is a function of only the coordinate vector. (In applications $\mathbf{V}(\mathbf{R})$ is often a real symmetric matrix.) More discussion on the adiabatic representation of discrete (electronic) DOFs is available in Section 4.1.

The unified formulation of mapping phase space with coordinate-momentum variables offers a useful exact approach to describe the composite system. The trace of a product of two quantum operators is expressed as an integral of two functions on mapping phase space, that is,

$$\text{Tr}_{n,e} \left[ AB \right] = \int \mathcal{D}(\mathbf{x}, \mathbf{p}) \int \mathcal{D}(\mathbf{R}, \mathbf{P}) \text{d} \mu_{\text{nuc}}(\mathbf{R}, \mathbf{P}) \text{d} \mu_{\text{ele}}(\mathbf{x}, \mathbf{p}) A_{C}(\mathbf{R}, \mathbf{P}; \mathbf{x}, \mathbf{p}) B_{C}(\mathbf{R}, \mathbf{P}; \mathbf{x}, \mathbf{p})$$
with

\[ A_C(R, P; x, p) = \text{Tr}_{\text{nuc}} \left[ \hat{\mathbb{A}} \hat{\mathbb{K}}_{\text{nuc}}(R, P) \otimes \hat{\mathbb{K}}_{\text{ele}}(x, p) \right] \tag{4} \]

\[ \tilde{B}_C(R, P; x, p) = \text{Tr}_{\text{nuc}} \left[ \hat{\mathbb{K}}_{\text{nuc}}^{-1}(R, P) \otimes \hat{\mathbb{K}}_{\text{ele}}^{-1}(x, p) \hat{\mathbb{B}} \right] \tag{5} \]

\[ d\mu_{\text{nuc}}(R, P) = (2\pi\hbar)^{-N} dR dP \] and \[ d\mu_{\text{ele}}(x, p) = F dxdp \] as the integration measure on nuclear phase space and that on electronic phase space, respectively, and \( \text{Tr}_{\text{nuc}} \) represents the trace over the corresponding nuclear and electronic Hilbert space. The integral over the mapping phase space variables for the finite discrete (electronic) DOFs in Equation (3) is performed as

\[ \int_{S(x,p)} F dxdp g(x, p) = \int F dxdp \frac{1}{\Omega} S(x, p) g(x, p) = \int F dxdp \bar{S}(x, p) g(x, p), \tag{6} \]

where the area of constraint space \( S(x, p) \)

\[ \Omega = \int dxdp S(x, p) \tag{7} \]

is the normalization constant, and \( \bar{S}(x, p) \) is the normalized constraint space.

The normalization of the (inverse) mapping kernel reads

\[ \text{Tr}_{\text{nuc}} \left[ \hat{\mathbb{K}}_{\text{nuc}}(R, P) \right] = \text{Tr}_{\text{nuc}} \left[ \hat{\mathbb{K}}_{\text{nuc}}^{-1}(R, P) \right] = 1 \tag{8} \]

\[ \text{Tr}_{\text{ele}} \left[ \hat{\mathbb{K}}_{\text{ele}}(x, p) \right] = \text{Tr}_{\text{ele}} \left[ \hat{\mathbb{K}}_{\text{ele}}^{-1}(x, p) \right] = 1 \tag{9} \]

and

\[ \int d\mu_{\text{nuc}}(R, P) \hat{\mathbb{K}}_{\text{nuc}}(R, P) = \int d\mu_{\text{nuc}}(R, P) \hat{\mathbb{K}}_{\text{nuc}}^{-1}(R, P) = \hat{I}_{\text{nuc}} \tag{10} \]

\[ \int_{S(x,p)} d\mu_{\text{ele}}(x, p) \hat{\mathbb{K}}_{\text{ele}}(x, p) = \int_{S(x,p)} d\mu_{\text{ele}}(x, p) \hat{\mathbb{K}}_{\text{ele}}^{-1}(x, p) = \hat{I}_{\text{ele}}. \tag{11} \]

The one-to-one correspondence mapping from phase space function \( A_C(R, P; x, p) \) or \( \tilde{B}_C(R, P; x, p) \) of Equation (4) back to operator \( \hat{A} \) or \( \hat{B} \) is

\[ \hat{A} = \int d\mu_{\text{nuc}}(R, P) \int_{S(x,p)} d\mu_{\text{ele}}(x, p) A_C(R, P; x, p) \hat{\mathbb{K}}_{\text{nuc}}^{-1}(R, P) \otimes \hat{\mathbb{K}}_{\text{ele}}^{-1}(x, p) \]

\[ \hat{B} = \int d\mu_{\text{nuc}}(R, P) \int_{S(x,p)} d\mu_{\text{ele}}(x, p) \tilde{B}_C(R, P; x, p) \hat{\mathbb{K}}_{\text{nuc}}^{-1}(R, P) \otimes \hat{\mathbb{K}}_{\text{ele}}(x, p). \tag{12} \]

The nuclear or electronic kernel should satisfy five criteria, namely, linearity, reality, standardization (normalization), traciality, and covariance.\(^{93,94,100,115}\)
2.1 Mapping kernel for continuous (nuclear) degrees of freedom

The integrals for \( \mathbf{R}, \mathbf{P} \) in Equations (3), (10), and (12) are over infinite (nuclear) phase space. The mapping kernel and its inverse for the nuclear DOFs are

\[
\hat{K}_{\text{nuc}}(\mathbf{R}, \mathbf{P}) = \left( \frac{\hbar}{2\pi} \right)^N \int d\zeta d\eta e^{\frac{\zeta}{\hbar}} (\mathbf{R} - \mathbf{r}) + i n (\mathbf{P} - \mathbf{p}) f(\zeta, \eta)
\]

and

\[
\hat{K}_{\text{nuc}}^{-1}(\mathbf{R}, \mathbf{P}) = \left( \frac{\hbar}{2\pi} \right)^N \int d\zeta d\eta e^{\frac{\zeta}{\hbar}} (\mathbf{R} - \mathbf{r}) + i n (\mathbf{P} - \mathbf{p}) \left[ f(-\zeta, -\eta) \right]^{-1}
\]

(13)

where \( f(\zeta, \eta) \) is a scalar function. For example, we have the Wigner function\(^{89,155} \)

\[
f(\zeta, \eta) = 1,
\]

the Husimi function\(^{156} \)

\[
f(\zeta, \eta) = \exp \left( -\frac{\zeta^T \Gamma^{-1} \zeta}{4} - \frac{\hbar^2}{4} \eta^T \Gamma \eta \right),
\]

(15)

the anti-Husimi function

\[
f(\zeta, \eta) = \exp \left( \frac{\zeta^T \Gamma^{-1} \zeta}{4} + \frac{\hbar^2}{4} \eta^T \Gamma \eta \right),
\]

(16)

the Glauber–Sudarshan P function\(^{61,62,66} \) (with the characteristic frequency matrix \( \mathbf{\omega} \) of the system)

\[
f(\zeta, \eta) = \exp \left[ \frac{\hbar}{4} \zeta^T \mathbf{M}^{-1/2} \mathbf{\omega}^{-1} \mathbf{M}^{-1/2} \zeta + \frac{\hbar^2}{4} \eta^T \mathbf{M}^{1/2} \mathbf{\omega} \mathbf{M}^{1/2} \eta \right],
\]

(17)

and its generalized versions,\(^{66} \) the Glauber Q function\(^{157} \)

\[
f(\zeta, \eta) = \exp \left[ -\frac{\hbar}{4} \zeta^T \mathbf{M}^{-1/2} \mathbf{\omega}^{-1} \mathbf{M}^{-1/2} \zeta - \frac{\hbar}{4} \eta^T \mathbf{M}^{1/2} \mathbf{\omega} \mathbf{M}^{1/2} \eta \right],
\]

(18)

the normal–antinormal ordered function\(^{91} \)

\[
f(\zeta, \eta) = \cosh \left[ \frac{\hbar}{4} \zeta^T \mathbf{M}^{-1/2} \mathbf{\omega}^{-1} \mathbf{M}^{-1/2} \zeta + \frac{\hbar}{4} \eta^T \mathbf{M}^{1/2} \mathbf{\omega} \mathbf{M}^{1/2} \eta \right],
\]

(19)

the Kirkwood antistandard-ordered function\(^{158,159} \)

\[
f(\zeta, \eta) = e^{i\hbar \zeta^T \eta^{1/2}},
\]

(20)

the Mehta standard-ordered function\(^{160} \)

\[
f(\zeta, \eta) = e^{-i\hbar \zeta^T \eta^{1/2}},
\]

(21)

the Rivier function\(^{161,162} \)
\[ f(\zeta, \eta) = \cos \left( \frac{1}{2} \hbar \zeta^T \eta \right) , \]  

(22)

and the distribution function of Born and Jordan\(^{163}\)

\[ f(\zeta, \eta) = \frac{\sin \left( \frac{1}{2} \hbar \zeta^T \eta \right)}{\frac{1}{2} \hbar \zeta^T \eta} , \]  

(23)

and so forth.

When operator \( \hat{A} \) is a function of only the nuclear DOFs, its phase space function from Equation (4) and the dual function from Equation (5) become

\[ A_{nuc}(\mathbf{R}, \mathbf{P}) = \text{Tr}_n \left[ \hat{A} \hat{K}_{nuc}(\mathbf{R}, \mathbf{P}) \right] \]  

(24)

and

\[ \tilde{A}_{nuc}(\mathbf{R}, \mathbf{P}) = \text{Tr}_n \left[ \hat{K}^{-1}_{nuc}(\mathbf{R}, \mathbf{P}) \hat{A} \right] . \]  

(25)

When the Wigner function Equation (14) is used, the mapping kernel and its inverse are the same, that is, \( \hat{K}_{nuc}(\mathbf{x}, \mathbf{p}) = \hat{K}^{-1}_{nuc}(\mathbf{x}, \mathbf{p}) \). The Wigner phase space function of operator \( \hat{A} \) (from Equation (24)) is identical to its dual (from Equation (25)),

\[ A^W_{nuc}(\mathbf{R}, \mathbf{P}) = \tilde{A}^W_{nuc}(\mathbf{R}, \mathbf{P}) . \]  

(26)

When the Husimi phase space (Equation (15)) is employed, it is straightforward to show the relationship between the Wigner and Husimi phase space functions (obtained from Equation (24))

\[ A^H_{nuc}(\mathbf{R}, \mathbf{P}) = \exp \left[ -\frac{1}{4} \left( \frac{d}{d \mathbf{R}} \right)^T \Gamma^{-1} \left( \frac{d}{d \mathbf{R}} \right) + \frac{\hbar}{4} \left( \frac{d}{d \mathbf{P}} \right)^T \Gamma \left( \frac{d}{d \mathbf{P}} \right) \right] A^W_{nuc}(\mathbf{R}, \mathbf{P}) , \]  

(27)

and the relationship between the dual function of Husimi phase space \( \tilde{A}^H_{nuc}(\mathbf{R}, \mathbf{P}) \) and the Wigner phase space function \( A^W_{nuc}(\mathbf{R}, \mathbf{P}) \)

\[ \tilde{A}^H_{nuc}(\mathbf{R}, \mathbf{P}) = \exp \left[ -\frac{1}{4} \left( \frac{d}{d \mathbf{R}} \right)^T \Gamma^{-1} \left( \frac{d}{d \mathbf{R}} \right) - \frac{\hbar}{4} \left( \frac{d}{d \mathbf{P}} \right)^T \Gamma \left( \frac{d}{d \mathbf{P}} \right) \right] A^W_{nuc}(\mathbf{R}, \mathbf{P}) . \]  

(28)

Because any choice of \( f(\zeta, \eta) \) in Equation (13) leads to an informationally complete representation of the continuous-variable quantum system, it is not difficult to establish the relationship between different (dual) phase space functions in addition to Equations (27) and (28).

### 2.2 Mapping kernel on constraint space for discrete (electronic) degrees of freedom

As derived first in appendix A of Reference 132 in the spirit of Reference 131 and then in the Supporting Information of Reference 134, the kernel that maps a set of \( F \) states onto constraint phase space \( S(\mathbf{x}, \mathbf{p}) \) reads...
\[
\tilde{K}_{\text{slc}}(\mathbf{x}, \mathbf{p}) = \sum_{n,m=1}^{F} \left[ \frac{1}{2} (\chi^{(n)} + ip^{(n)}) (\chi^{(m)} - ip^{(m)}) - \gamma \delta_{nm} \right] |n\rangle \langle m|, \tag{29}
\]

and the corresponding inverse kernel is
\[
\tilde{K}_{\text{slc}}^{-1}(\mathbf{x}, \mathbf{p}) = \sum_{n,m=1}^{F} \left[ \frac{1 + F}{2(1 + F\gamma)} (\chi^{(n)} + ip^{(n)}) (\chi^{(m)} - ip^{(m)}) - \frac{1 - \gamma}{1 + F\gamma} \delta_{nm} \right] |n\rangle \langle m|. \tag{30}
\]

As naturally required by Equation (9), constraint phase space \(\delta(\mathbf{x}, \mathbf{p})\) is defined by
\[
\delta \left( \sum_{n=1}^{F} \left( \frac{\chi^{(n)}}{2} + \frac{(p^{(n)})^2}{2} \right) - (1 + F\gamma) \right), \tag{31}
\]

of which the area is
\[
\Omega(\gamma) = \int dx dp \delta \left( \sum_{n=1}^{F} \left( \frac{\chi^{(n)}}{2} + \frac{(p^{(n)})^2}{2} \right) - (1 + F\gamma) \right). \tag{32}
\]

The normalized constraint phase space is \(\overline{\delta}(\mathbf{x}, \mathbf{p}) = \delta(\mathbf{x}, \mathbf{p}) / \Omega(\gamma)\).

Equations (29)–(32) define the mapping kernel and inverse kernel as well as constraint phase space, which are the key elements of the coordinate-momentum phase space formulation of the discrete-variable quantum system that we first established in References 131,132 and further developed in References 57,58,134. As yielded from Equation (4), when the Wigner function Equation (14) is used for the nuclear DOFs, the mapping Hamiltonian for the quantum Hamiltonian operator Equation (1) reads
\[
H_C(\mathbf{R}, \mathbf{P}; \mathbf{x}; \mathbf{p}; \gamma) = \frac{1}{2} \mathbf{P}^T \mathbf{M}^{-1} \mathbf{P} + \sum_{n,m=1}^{F} V_{mn}(\mathbf{R}) \left[ \frac{1}{2} (\chi^{(n)} + ip^{(n)}) (\chi^{(m)} - ip^{(m)}) - \gamma \delta_{nm} \right]. \tag{33}
\]

Because \(V(\mathbf{R})\) is Hermitian, the mapping Hamiltonian is real. As \(V(\mathbf{R})\) is often a real symmetric matrix, Equation (33) becomes
\[
H_C(\mathbf{R}, \mathbf{P}; \mathbf{x}; \mathbf{p}; \gamma) = \frac{1}{2} \mathbf{P}^T \mathbf{M}^{-1} \mathbf{P} + \sum_{n,m=1}^{F} V_{mn}(\mathbf{R}) \left[ \frac{1}{2} (\chi^{(n)} \chi^{(m)} + p^{(n)} p^{(m)}) - \gamma \delta_{nm} \right], \tag{34}
\]

which is the seminal Meyer–Miller Hamiltonian\(^{153}\) that has extensively been implemented for nonadiabatic dynamics in the literature.\(^{5,6,60,138,154,164–218}\) In References 58,131,132, it is shown that there also exist other comprehensive mapping Hamiltonian models in the general coordinate-momentum phase space formulation of quantum mechanics. When the mapping Hamiltonian is employed to generate trajectory-based dynamics in the phase space formulation for a composite quantum system, we denote it as the classical mapping model (CMM) approach. It satisfies the frozen nuclei limit. We use the Meyer–Miller Hamiltonian for demonstration throughout the Focus Article.

When Meyer and Miller proposed the conventional Meyer–Miller mapping Hamiltonian model for the nonadiabatic system in 1979, they did not invoke the phase space formulation. In 1997, Stock and Thoss\(^{154}\) utilized the Schwinger oscillator theory of angular momentum\(^{219,220}\) to derive the Meyer–Miller mapping Hamiltonian.\(^{153}\) Its LSC-IVR approximation\(^4\) in principle includes infinite Wigner phase space for the finite set of (electronic) states. The applications, however, suggest that the LSC-IVR approximation in the framework of References \(4,154,170\) is not good.\(^{172,177,181,187,195,200,202}\) More advanced semiclassical approaches\(^{96,97}\) improve the performance but request more
computational effort.\textsuperscript{172,173} The symmetric-window function and other techniques have been introduced to practically overcome the drawbacks.\textsuperscript{177,181,187,195,200,202} Recent progress along this line is briefly summarized in Reference 138.

Equation (31) indicates that parameter $\gamma$ lies in region $(-1/F, \infty)$. It is shown that parameter $\gamma$ can be either positive or negative\textsuperscript{131,134} and should be interpreted as a special case of the commutator matrix\textsuperscript{57,58,131,134} rather than the conventional zero-point-energy parameter.\textsuperscript{153,154} There exist three key elements for a trajectory-based quantum dynamics method to evaluate the evolution of the expectation/ensemble average of physical property, namely,

1. the EOMs of the trajectory,
2. the initial condition of the trajectory, and
3. the integral expression for the expectation/ensemble average of the physical property of interest.

In the frozen-nuclei limit, Hamilton’s EOMs governed by the Meyer–Miller mapping Hamiltonian is isomorphic to exact dynamics. While it is reasonable to employ the mapping Hamiltonian to define the EOMs of the trajectory, the left two elements are also important to consider such that the trajectory-based dynamics method is consistent. The constraint coordinate-momentum phase space formulation then offers a more advanced platform to consider all the three key elements.

It is evident that Equation (31) is a special choice of constraint phase space $S(x, p)$. The interpretation of parameter $\gamma$ in References 57,58,131,134 hints that a more comprehensive choice of normalized constraint phase space $\tilde{S}(x, p)$ is

$$\int_{-1/F}^{\infty} d\gamma w(\gamma) \frac{1}{\Omega(\gamma)} \delta \left( \sum_{n=1}^{F} \left( \frac{\langle n \rangle^2}{2} + \langle p(n) \rangle^2 - (1 + F_\gamma) \right) \right),$$  \hspace{1cm} (35)

with the quasi-probability distribution function

$$\int_{-1/F}^{\infty} d\gamma w(\gamma) = 1. \hspace{1cm} (36)$$

Equation (6), the integral over the mapping phase space variables for the finite discrete (electronic) DOFs then becomes

$$\int_{S(x, p)} Fdx dp g(x, p)$$

$$= \int_{-1/F}^{\infty} d\gamma w(\gamma) \sum_{n=1}^{F} \int_{-1/F}^{\infty} dx dp \frac{1}{\Omega(\gamma)} \delta \left( \sum_{n=1}^{F} \left( \frac{\langle n \rangle^2}{2} + \langle p(n) \rangle^2 - (1 + F_\gamma) \right) \right) g(x, p).$$  \hspace{1cm} (37)

If we require that the kernel is the same as its inverse, that is,

$$\tilde{K}_{ele}(x, p) = \tilde{K}_{ele}^{-1}(x, p) = \sum_{n,m=1}^{F} \left[ \frac{1}{2} \langle n \rangle \left( \langle n \rangle + i \langle p(n) \rangle \right) \left( \langle m \rangle - i \langle p(m) \rangle \right) - \gamma \delta_{nm} \right] |n,m\rangle \langle n,m|,$$  \hspace{1cm} (38)

it is then not difficult to obtain

$$\int_{-1/F}^{\infty} d\gamma w(\gamma) \chi(\gamma) = 1$$  \hspace{1cm} (39)
with

$$\chi(\gamma) = F\gamma^2 + 2\gamma. \quad (40)$$

(See Appendix 1 of the Supporting Information for more discussion.) Equations (35–40) define normalized constraint phase space $\mathcal{S}(x,p)$, the mapping kernel and inverse kernel, and the quasi-probability distribution function $w(\gamma)$ of parameter $\gamma$. The weighted constraint phase space formulation for the discrete-variable quantum system is the key new theoretical result of the Focus Article. When the Wigner function Equation (14) is used for the nuclear DOFs, where $\hat{K}_{\text{nuc}}(x,p) = \hat{K}_{\text{nuc}}^{-1}(x,p)$, Equation (4) is then identical to Equation (5) when $\hat{A} = \hat{B}$. The mapping Hamiltonian for the quantum Hamiltonian operator Equation (1) produced by either of Equations (4) and (5) leads to the same expression as Equation (34). When the mapping Hamiltonian is utilized to produce the trajectory-based dynamics for a composite system, it is denoted as the weighted mapping model (wMM) approach. The frozen nuclei limit is satisfied in wMM.

Many choices are possible for the discrete or continuous version of the normalized quasi-probability distribution function $w(\gamma)$ in the weighted constraint phase space mapping theory. In the Focus Article, we consider only the simplest cases of the discrete version. When but a single value of parameter $\gamma$ is chosen in Equation (39), that is, $w(\gamma) = \delta(\gamma - \gamma_1)$, we obtain

$$F\gamma^2 + 2\gamma = 1, \quad (41)$$

of which the physical solution is

$$\gamma = \frac{\sqrt{1+F} - 1}{F}. \quad (42)$$

Equation (42) is a trivial result that was used in References.\textsuperscript{57,114,115,117,197} In this case, the weighted constraint phase space formulation is identical to the constraint phase space formulation, and wMM becomes CMM with Equation (42) when trajectory-based dynamics is considered. When only two values of parameter are selected, that is,

$$w(\gamma) = \sum_{j=1}^{2} \delta(\gamma - \gamma_j), \quad (43)$$

Equations (36) and (39) lead to

$$w(\gamma_1) = \frac{1 - \chi(\gamma_1)}{\chi(\gamma_1) - \chi(\gamma_2)} \chi(\gamma_2),$$

$$w(\gamma_2) = \frac{\chi(\gamma_1) - 1}{\chi(\gamma_1) - \chi(\gamma_2)}. \quad (44)$$

When the values of parameter $\gamma$ are close to zero or smaller than zero in region $(-1/F, \infty)$, trajectories produced by the Meyer–Miller mapping Hamiltonian Equation (34) for nonadiabatic molecular dynamics are stable. For demonstration in the paper, we choose

$$\gamma_1 = -\gamma_2 = \Delta \quad (45)$$

with $\Delta$ a reasonably small positive real number in region $(0, 1/F)$. Figure 3 presents the constraint coordinate-momentum phase space formulation when a single value of parameter $\gamma$ is used (Figure 3a) as well as the weighted formulation when two values of parameter $\gamma$ suggested by Equation (45) are used (Figure 3b).
Recent advances in quantum technologies make it possible to control and manipulate quantum states in experiments. Because the phase space formulation offers an informationally complete description of the density matrix, direct measurements of phase space of the quantum system with continuous DOFs, those of the quantum system with discrete DOFs, and those of the composite quantum system have been realized in experiments.\textsuperscript{70,85,221–234} While the celebrated Wigner phase space has long been used for illustration of the negative quasi-probability for continuous-variable systems,\textsuperscript{225,235} Stratonovich phase space has recently been proposed for visualization and tomography of discrete-variable systems.\textsuperscript{85,113,227–229,231,236,237} A combination of these two spaces has been used for illustration of nonclassical correlations or entanglement between the discrete DOF and the continuous DOF of the composite system.\textsuperscript{238,239} (In Appendix 3 of the Supporting Information, we briefly review Stratonovich phase space with an either SU(2) or SU($F$) structure,\textsuperscript{114,300,301} as well as the relationship between Stratonovich phase space and constraint coordinate-momentum phase space as already pointed out in References 57,58.)

As coordinate-momentum phase space is well-established in classical mechanics, the formulation of (weighted) constraint coordinate-momentum phase space described in Section 2 offers a potentially useful approach for describing correlations and dynamics in the discrete-variable system as well as the composite system in quantum mechanics. When (weighted) constraint coordinate-momentum phase space is used for mapping an $F$-state system, the phase space distribution is

\begin{align*}
X^2 &= \frac{1}{2} \sum_{j=1}^{F} x_j^2 \\
P^2 &= \frac{1}{2} \sum_{j=1}^{F} p_j^2 \\
X^2 + P^2 &= 1 + F \gamma
\end{align*}

\begin{align*}
w_+ &= \frac{1 - \chi(-\Delta)}{\chi(\Delta) - \chi(-\Delta)} \\
w_- &= \frac{\chi(\Delta) - 1}{\chi(\Delta) - \chi(-\Delta)}
\end{align*}

FIGURE 3 Illustration of the exact mapping formulation with constraint coordinate-momentum phase space. Panel (a) presents constraint phase space with only a single value of parameter $\gamma$. Panel (b) demonstrates weighted constraint phase space with two values of parameter $\gamma$, where the quasi-probability distribution function is $w(\gamma) = w_+ \delta(\gamma - \Delta) + w_- \delta(\gamma + \Delta)$. Constraint phase space with the positive weight is blue-dashed, while that with the negative weight is red dot-dashed. (Panel (a) is reprinted with permission from Reference 134, Copyright 2021, American Chemical Society.)

3 | PHASE SPACE REPRESENTATION OF THE NONCLASSICAL FEATURE OF QUANTUM SYSTEMS

Recent advances in quantum technologies make it possible to control and manipulate quantum states in experiment. Because the phase space formulation offers an informationally complete description of the density matrix, direct measurements of phase space of the quantum system with continuous DOFs, those of the quantum system with discrete DOFs, and those of the composite quantum system have been realized in experiments.\textsuperscript{70,85,221–234} While the celebrated Wigner phase space has long been used for illustration of the negative quasi-probability for continuous-variable systems,\textsuperscript{225,235} Stratonovich phase space has recently been proposed for visualization and tomography of discrete-variable systems.\textsuperscript{85,113,227–229,231,236,237} A combination of these two spaces has been used for illustration of nonclassical correlations or entanglement between the discrete DOF and the continuous DOF of the composite system.\textsuperscript{238,239} (In Appendix 3 of the Supporting Information, we briefly review Stratonovich phase space with an either SU(2) or SU($F$) structure,\textsuperscript{114,300,301} as well as the relationship between Stratonovich phase space and constraint coordinate-momentum phase space as already pointed out in References 57,58.)

As coordinate-momentum phase space is well-established in classical mechanics, the formulation of (weighted) constraint coordinate-momentum phase space described in Section 2 offers a potentially useful approach for describing correlations and dynamics in the discrete-variable system as well as the composite system in quantum mechanics. When (weighted) constraint coordinate-momentum phase space is used for mapping an $F$-state system, the phase space distribution is
\[
\rho_C(x, p) = \sum_{m,n=1}^{F} \rho_{mn} K_{mn}(x, p),
\]

where \(\rho_{mn} = \langle m | \hat{\rho} | n \rangle\) and \(K_{mn}(x, p) = \langle n | \hat{K}_{\text{ele}}(x, p) | m \rangle\) defined in Equation (38). For the sake of visualization, it is convenient to further reduce constraint phase space variables \((x, p)\) to two relevant variables, \((x^{(n)}, x^{(m)})\) or \((x^{(n)}, p^{(m)})\) for describing the correlation on arbitrary two states \(|n\rangle\) and \(|m\rangle\). We define the marginal function, \(\mathcal{K}_{(n,m)}(x^{(n)}, x^{(m)})\), on constraint coordinate-momentum phase space (Figure 4),

\[
\mathcal{K}_{(n,m)}(x^{(n)}, x^{(m)}) = \int Fdx_\perp \, dp_\perp \frac{1}{\Omega(\gamma)} \delta \left( \sum_{j=1}^{F} \left( x^{(j)} \right)^2 + \left( p^{(j)} \right)^2 - (1 + F \gamma) \right) K_{mn}(x, p; \gamma),
\]

where \(x_\perp\) represents all \(x^{(i)}\) other than \(|x^{(n)}, x^{(m)}\rangle\), and that on weighted constraint phase space,

\[
\mathcal{K}_{(n,m)}(x^{(n)}, x^{(m)}) = \int_{-1/F}^{\infty} d\gamma w(\gamma) \frac{1}{\Omega(\gamma)} \int Fdx_\perp \, dp_\perp \delta \left( \sum_{j=1}^{F} \left( x^{(j)} \right)^2 + \left( p^{(j)} \right)^2 - (1 + F \gamma) \right) K_{mn}(x, p; \gamma).
\]

Figure 5 demonstrates the case of Equation (48) when the quasi-probability distribution function \(w(\gamma)\) is defined by Equations (43)–(45) where two symmetrical values of parameter \(\gamma\) are used. Similar definitions are also applied for \(\mathcal{K}_{(n,m)}(x^{(n)}, p^{(m)})\). The explicit formula of these marginal functions can be derived by using the integral techniques (where we use Wick’s theorem) \cite{297,298} in Appendix 1 of the Supporting Information.

Figures 4 and 5 demonstrate a composite system that consists of a discrete DOF for spin-1/2 and a continuous DOF for a harmonic oscillator. The marginal joint distribution function of the composite system reads

\[
\rho_{C,m}^{(n,m)}(R, P; x^{(n)}, x^{(m)}) = \text{Tr}_{n,e} \left[ \hat{\rho}_{\text{nucl}}(R, P) \otimes |n\rangle \langle m| \mathcal{K}_{(n,m)}(x^{(n)}, x^{(m)}) \right].
\]

The marginal quasi-probability distribution functions of the continuous variable for both the pure state and the mixed state are presented in Figure 4a, where infinite Wigner phase space is employed. The marginal functions of the discrete variables (based on Equation (47)) of the spin-1/2 system read

\[
\begin{pmatrix}
\mathcal{K}_{11}(x^{(1)}, x^{(2)}) & \mathcal{K}_{11}(x^{(1)}, x^{(2)}) \\
\mathcal{K}_{11}(x^{(1)}, x^{(2)}) & \mathcal{K}_{11}(x^{(1)}, x^{(2)})
\end{pmatrix}
= \frac{1}{2\pi(1 + 2\gamma)}
\begin{pmatrix}
\left( 1 + \frac{1}{2} x^{(1)} \right)^2 & -\frac{1}{2} \left( x^{(2)} \right)^2 \\
-\frac{1}{2} \left( x^{(2)} \right)^2 & \left( 1 - \frac{1}{2} x^{(1)} \right)^2 + \frac{1}{2} \left( x^{(2)} \right)^2
\end{pmatrix},
\]

where notations \(\uparrow, \downarrow\) are used to represent the two discrete states.

The marginal functions for the discrete variable are demonstrated on constraint coordinate-momentum phase space in Figure 4b and on weighted constraint space in Figure 5b. More interestingly, the identical angular behavior and the radial cancellation behavior of two weighted components lead to a hollow ring structure on weighted constraint phase space (Figure 5a, also see Appendix 4 of the Supporting Information). The difference between the Schrödinger cat state and the mixed state is distinct in either Figure 4b on constraint space or Figure 5b on weighted constraint space.

The marginal joint function of a pure Bell entangled state, \(|0\rangle |\uparrow\rangle + |1\rangle |\downarrow\rangle /\sqrt{2}\), of the composite system is demonstrated in Figure 4c (by adopting the similar strategy of References \cite{238,239}), where constraint coordinate-momentum phase space is used for the discrete DOF at each grid, as well as in Figure 5c where weighted constraint space is employed for the discrete DOF at each grid. The two-dimensional grids represent variables \((R, P)\) of infinite Wigner phase space for the continuous DOF in either of Figures 4c and 5c. When the pure Bell entangled state is studied, both Figures 4c and 5c clearly demonstrate a Gaussian decay of the joint marginal function against Wigner phase space.
FIGURE 4  Legend on next page.
variables \((R,P)\) of the continuous DOF. Either Figures 4c or 5c also shows the pattern of the correlation between the continuous DOF and the discrete DOF. It is convenient to distinguish the pure Bell entangled state, \(\langle 0\rangle\langle 1\rangle + \langle 1\rangle\langle 0\rangle\)/2, from the direct product of the Schrödinger cat states, \(\langle 0\rangle\langle 1\rangle \otimes \langle 1\rangle\langle 1\rangle\)/2, when the hybrid representation of the general coordinate-momentum phase space is used.

4  DYNAMICS OF COMPOSITE QUANTUM SYSTEMS

The quantum Liouville equation can be expressed as a generalized Moyal bracket on hybrid coordinate-momentum phase space. When the Poisson bracket for classical Hamilton’s EOMs governed by the mapping Hamiltonian, Equation (34), is used to approximate the generalized Moyal bracket on phase space, we have CMM when constraint space is used, and wMM when weighted constraint space is employed. (Please see Appendices 2, 3, and 5 of the Supporting Information for more discussion.) We compare the new wMM and CMM approaches to Ehrenfest dynamics as well as the fewest-switches surface hopping (FSSH) method, two prevailing trajectory-based dynamics methods for a few typical composite quantum systems. (In this section we set \(\hbar = 1\) for simplicity if it is not specifically stated).

4.1  Equations of motion governed by the mapping Hamiltonian

In Equation (1), the “complete” set of diabatic states \(\{|n\rangle\}\) is independent of nuclear coordinate/configuration \(R\). The mapping variables for discrete (electronic) DOFs, \((x,p)\), are independent of \(R\). Define \(g = x + ip\). The EOMs governed by Equation (33), the mapping Hamiltonian of Equation (1), then read,

\[
\begin{align*}
g &= -iV(R)g \\
R &= M^{-1}P \\
\dot{P} &= -\sum_{n,m=1}^{F} (\nabla_R V_{mn}(R)) \left( \frac{1}{2} (x^{(n)} + ip^{(n)}) (x^{(m)} - ip^{(m)}) - \gamma \delta_{nm} \right).
\end{align*}
\]

Diabatic potential matrix \(V(R)\) is Hermitian, so is the force matrix, \(\nabla_R V_{mn}(R)\). It is trivial to verify that the mean force of the right-hand side (RHS) of Equation (53) is always real. When \(V(R)\) is a real symmetric matrix, the EOMs become

\[
\begin{align*}
\dot{x} &= V(R)p \\
\dot{p} &= -V(R)x \\
\dot{R} &= M^{-1}P \\
\dot{P} &= -\sum_{n,m=1}^{F} (\nabla_R V_{mn}(R)) \left[ \frac{1}{2} (x^{(n)}x^{(m)} + p^{(n)}p^{(m)}) - \gamma \delta_{nm} \right].
\end{align*}
\]

**FIGURE 4** Illustrations of (a) Wigner representation of a continuous-variable system, (b) constraint phase space representation of a discrete-variable system, and (c) hybrid coordinate-momentum phase space representation of a composite system with both discrete and continuous DOFs. (a) Wigner distribution for \(|0\rangle\langle 0|\) (Panel a1), for \(|1\rangle\langle 1|\) (Panel a4), real part (Panel a2) and imaginary part (Panel a3) of the Wigner distribution for \(|0\rangle\langle 1|\), Wigner distribution for mixed state \(|0\rangle\langle 0| + |1\rangle\langle 1|\)/2 (Panel a5), and that for Schrödinger cat state \(|0\rangle\langle 1| + |1\rangle\langle 0|\)/2 (Panel a6). Here, \(|0\rangle\) and \(|1\rangle\) are two energy levels of a continuous-variable system. (b) Marginal distribution of constraint phase space coordinates \((x^{(1)},x^{(2)})\) for \(|\rangle\langle 1|\) (Panel b1), \(|\rangle\langle 1|\) (Panel b4), that for \(|\rangle\langle 1|\) (Panel b2), that for \(|\rangle\langle 1|\) (Panel b3), that for mixed state \(|\rangle\langle 1|\) (Panel b5), and that for Schrödinger cat state \(|\rangle\langle 1|\) (Panel b6). Here, \(|\rangle\rangle\) and \(|\rangle\rangle\rangle\) represent two discrete states of a discrete-variable system. (c) Panel c1: Schematic representation of the composite system and the pure entangled state \(|0\rangle\langle 1| + |1\rangle\langle 0|\)/2; Panel c2: hybrid coordinate-momentum phase space representation of the entangled state. The grid is on the Wigner phase space \((R,P)\) for the continuous DOF, and each circle of a grid stands for the local marginal distribution function of constraint phase space variables \((x^{(1)},x^{(2)})\). The notations are identical to those in Panels (a) and (b).
FIGURE 5  Legend on next page.
Consider the full Hamiltonian of nuclei and electrons of the molecular system,

$$\hat{H} = \frac{1}{2} \vec{P}^T \mathbf{M}^{-1} \vec{P} + \hat{H}_d(\vec{R}),$$  \hspace{1cm} (55)$$

where $\hat{H}_d(\vec{R})$ is the electronic Hamiltonian. Its representation in the diabatic basis reads

$$\hat{H}_d(\vec{R}) = \sum_{n,m} V_{nm}(\vec{R}) |n\rangle \langle m|,$$  \hspace{1cm} (56)$$

and that in the adiabatic basis is

$$\hat{H}_d(\vec{R}) = \sum_k E_k(\vec{R}) |\phi_k(\vec{R})\rangle \langle \phi_k(\vec{R})|,$$  \hspace{1cm} (57)$$

where $E_k(\vec{R})$ denotes the adiabatic potential energy surface of the $k$-th adiabatic electronic state. Assume that the unitary transformation between a set of diabatic basis states, $\{|m\rangle\}$, and a set of adiabatic basis states, $\{|\phi_k(\vec{R})\rangle\}$, is

$$|\phi_k(\vec{R})\rangle = \sum_m U_{mk}(\vec{R}) |m\rangle$$

$$|n\rangle = \sum_k U_{nk}^*(\vec{R}) |\phi_k(\vec{R})\rangle,$$  \hspace{1cm} (58)$$

where $U_{mk}(\vec{R}) = \langle m|\phi_k(\vec{R})\rangle$. This states the diagonalization of the diabatic potential matrix,

$$\sum_{n,m} U_{nj}^*(\vec{R}) V_{nm}(\vec{R}) U_{mk}(\vec{R}) = E_k(\vec{R}) \delta_{kj},$$  \hspace{1cm} (59)$$

or equivalently,

$$V_{nm}(\vec{R}) = \sum_k U_{mk}(\vec{R}) E_k(\vec{R}) U_{nk}^*(\vec{R}).$$  \hspace{1cm} (60)$$

Define the nonadiabatic coupling vector,

$$d_{mn}(\vec{R}) = \langle \phi_m(\vec{R}) | \frac{\partial \phi_n(\vec{R})}{\partial \vec{R}} \rangle.$$  \hspace{1cm} (61)$$

It is trivial to show

$$d_{mn}(\vec{R}) = -d_{nm}^*(\vec{R}),$$  \hspace{1cm} (62)$$

because of the orthonormality of the basis set, that is, $\langle \phi_m(\vec{R}) | \phi_n(\vec{R}) \rangle = \delta_{mn}$. We then obtain

**Figure 5** Illustrations of (a) components and (b) marginal distribution functions of the weighted constraint phase space representation of a discrete-variable system, and (c) weighted hybrid representation of the same composite system as that of Figure 4c. (a) Marginal distribution of constraint phase space coordinates ($x^{(1)},x^{(2)}$) for Schrödinger cat state ($|\rangle + |\rangle)/\sqrt{2}$ with $\gamma = \Delta$ weighted by $w$, (Panel a1), with $\gamma = -\Delta$ weighted by $w$. (Panel a2). The sum of the two components yields the marginal distribution of constraint phase space coordinates ($x_1,x_2$) of the weighted representation with two values of parameter $\gamma$ for the Schrödinger cat state (Panel a3). Coordinates are scaled by the larger radius $\sqrt{2(1+2\Delta)}$. (b) Weighted marginal distribution of constraint phase space coordinates ($x^{(1)},x^{(2)}$) for the same properties as those in Figure 4b. (c) Same as Figure 4c, but using weighted marginal distribution for the discrete DOF.
\[
\n\nabla_R \mathcal{U}^*_{mk}(R) = \langle \mathcal{U}^*_{mk}(R) | m \rangle - \sum_n \langle \mathcal{U}^*_{mk}(R) | \phi_n \rangle \langle \phi_n | m \rangle = \sum_n \mathbf{d}^*_n(R) \mathcal{U}^*_{mn}(R) = \sum_n \mathcal{U}_{mn}(R) \mathbf{d}_n(R).
\]

(63)

and

\[
\nabla_R \mathcal{U}_{mk}(R) = -\sum_n \mathbf{d}^*_n(R) \mathcal{U}_{mn}(R) = \sum_n \mathcal{U}_{mn}(R) \mathbf{d}_n(R).
\]

(64)

Below we show the explicit form of the EOMs, Equations (51)–(53), under the diabatic-to-adiabatic transformation, Equation (58).

The covariant transformation for mapping variables corresponding to the diabatic-to-adiabatic transformation, Equation (58), reads

\[
\mathbf{x}^{(n)}(R) + i\mathbf{p}^{(n)}(R) = \sum_m \mathcal{U}^*_{mn}(R) \left( \mathbf{x}^{(m)} + i \mathbf{p}^{(m)} \right)
\]

(65)

or

\[
\mathbf{x}^{(n)} + i\mathbf{p}^{(n)} = \sum_m \mathcal{U}_{mn}(R) \left( \mathbf{x}^{(m)} + i \mathbf{p}^{(m)} \right).
\]

(66)

Denote \( \tilde{\mathbf{g}}(R) = \mathbf{x}(R) + i\tilde{\mathbf{p}}(R) \). Equations (65)–(66) become

\[
\tilde{\mathbf{g}}(R) = \mathbf{U}^\dagger(R) \mathbf{g}
\]

\[
\mathbf{g} = \mathbf{U}(R) \tilde{\mathbf{g}}(R).
\]

(67)

The electronic mapping kernel, Equation (29), is

\[
\tilde{K}_{ele} = \sum_{n,m} \left[ \frac{1}{2} \left( \mathbf{x}^{(n)} + i\mathbf{p}^{(n)} \right) \left( \mathbf{x}^{(m)} - i\mathbf{p}^{(m)} \right) - \gamma \delta_{nm} \right] |\phi_n \rangle \langle \phi_m|,
\]

(68)

under the transformation for a specific nuclear configuration, \( R \). Substitution of Equation (63) into Equation (65) yields

\[
\nabla_R \left( \mathbf{x}^{(n)}(R) + i\mathbf{p}^{(n)}(R) \right) = -\sum_k \mathbf{d}_{nk}(R) \left( \mathbf{x}^{(k)}(R) + i\mathbf{p}^{(k)}(R) \right).
\]

(69)

The total time derivative of \( \mathbf{x}^{(n)} + i\mathbf{p}^{(n)} \) reads

\[
\frac{d}{dt} \left( \mathbf{x}^{(n)} + i\mathbf{p}^{(n)} \right) = \sum_m \mathcal{U}^*_{mn}(R) \left( \frac{d}{dt} \left( \mathbf{x}^{(m)} + i\mathbf{p}^{(m)} \right) \right) + \sum_m \left( \frac{d}{dt} \mathcal{U}^*_{mn}(R) \right) \left( \mathbf{x}^{(m)} + i\mathbf{p}^{(m)} \right) = -i \sum_k \mathbf{R} \cdot \mathbf{d}_{nk}(R) \left( \mathbf{x}^{(k)} + i\mathbf{p}^{(k)} \right)
\]

(70)

Equation (70) is the EOMs for mapping variables of electronic DOFs in the adiabatic representation.
We then consider the EOMs of nuclear mapping variables under the transformation Equation (58). Equation (52) remains invariant under the transformation. Substitution of Equations (60), (63), (64), and (69) into Equation (53) produces

\[
\ddot{P} = - \sum_{n,m=1}^{F} (\nabla_R V_{mn}(R)) \left[ \frac{1}{2} (\dot{x}^{(n)} + ip^{(n)}) (\dot{x}^{(m)} - ip^{(m)}) - \gamma \delta_{nm} \right]
\]

\[
= - \sum_{n,m} \nabla_R \left( \sum_k U_{mk}(R) E_k(R) U^{*}_{nk}(R) \right) \left[ \frac{1}{2} (\dot{x}^{(n)} + ip^{(n)}) (\dot{x}^{(m)} - ip^{(m)}) - \gamma \delta_{nm} \right]
\]

\[
= \sum_{k,l} d_{lk}(R) (E_l(R) - E_k(R)) \left[ \frac{1}{2} (\dot{x}^{(k)} + ip^{(k)}) (\dot{x}^{(l)} - ip^{(l)}) - \gamma \delta_{kl} \right] - \sum_{k,l} \nabla_R E_k(R) \delta_{kl} \left[ \frac{1}{2} (\dot{x}^{(k)} + ip^{(k)}) (\dot{x}^{(l)} - ip^{(l)}) - \gamma \delta_{kl} \right].
\]

(71)

Since force matrix \( \{ F_{kl} = \nabla_R E_k(R) \delta_{kl} + (E_k(R) - E_l(R)) d_{lk}(R) \} \) is Hermitian, the mean force of the RHS of Equation (71) stays real. Under the diabatic-to-adiabatic transformation, Equation (58), the EOMs of nuclear phase variables (Equations (52) and (53)) are then recast into

\[
\ddot{R} = M^{-1} P
\]

\[
\ddot{P} = - \sum_{k,l} [\nabla_R E_k(R) \delta_{kl} + (E_k(R) - E_l(R)) d_{lk}(R)] \left[ \frac{1}{2} (\dot{x}^{(k)} + ip^{(k)}) (\dot{x}^{(l)} - ip^{(l)}) - \gamma \delta_{kl} \right].
\]

(72)

Define the effective potential matrix, \( V^{(\text{eff})}_{nk}(R, P) = E_n(R) \delta_{nk} - i \dot{R} \cdot d_{nk}(R) = E_n(R) \delta_{nk} - i M^{-1} P \cdot d_{nk}(R) \).

(73)

A more compact form of Equation (70) for the electronic phase variables becomes

\[
\ddot{\bar{g}} = - V^{(\text{eff})}(R, P) \bar{g}.
\]

(74)

Equations (72) and (74) are the final EOMs under the covariant transformation Equation (65).

When the electronic wavefunction of the basis set is always real, that is, \( \langle r | \phi_n(R) \rangle \) is real for any \( n \), which is often the case for molecular systems, Equation (62) leads to

\[
d_{mn}(R) = -d_{nm}(R).
\]

(75)

Equation (72) is simplified to

\[
\ddot{R} = M^{-1} P
\]

\[
\ddot{P} = - \sum_{k,l} [\nabla_R E_k(R) \delta_{kl} + (E_k(R) - E_l(R)) d_{lk}(R)] \left[ \frac{1}{2} (\dot{x}^{(k)} + ip^{(k)}) (\dot{x}^{(l)} - ip^{(l)}) - \gamma \delta_{kl} \right].
\]

(76)

Note that the mapping Hamiltonian of Equation (33) (obtained in the diabatic representation) becomes

\[
H_c(R, P, \bar{x}, \bar{p}, \bar{x}, \bar{p}) = \frac{1}{2} P^T M^{-1} P + \sum_{n=1}^{F} E_n(R) \left( \frac{1}{2} (\dot{x}^{(n)}(R))^2 + (\dot{p}^{(n)}(R))^2 \right) - \gamma
\]

(77)
under the transformation defined by Equations (60) and (65). The new EOMs, Equations (72) and (74), conserve the mapping Hamiltonian of Equation (77). The diabatic-to-adiabatic transformation depends on nuclear coordinate \( \mathbf{R} \), which is also a time-dependent variable of the evolution. The time-dependent canonical transformation for the Hamiltonian system yields a new set of EOMs by the chain rule.245

In Equations (71)–(74) and (76)–(77) \( \mathbf{P} \) correspond to the mapping momentum in the diabatic representation, but not the canonical momentum in the adiabatic representation because Equation (71) is not generated from Hamilton’s equations of motion. Equations (74) and (76) share a similar form to the EOMs proposed by Cotton et al.184 and discussed in the Supporting Information of Reference 57. Define the covariant transformation for nuclear phase variables,

\[
\mathbf{\tilde{P}} = \mathbf{P} + i \sum_{m,n} \left[ \frac{1}{2} \left( \chi^{(n)} + i \mathbf{\tilde{p}}^{(n)} \right) \left( \chi^{(m)} - i \mathbf{\tilde{p}}^{(m)} \right) - \gamma \delta_{nm} \right] \mathbf{d}_{mn}(\mathbf{R}).
\]

(78)

The Hamiltonian of Equation (77) becomes

\[
H_C(\mathbf{\tilde{R}}, \mathbf{\tilde{P}}, \chi, \mathbf{\tilde{p}}) = \frac{1}{2} \mathbf{P} (\mathbf{\tilde{P}} \cdot \mathbf{\tilde{P}} - \mathbf{\tilde{R}}) M^{-1} \mathbf{P} (\mathbf{\tilde{P}} \cdot \mathbf{\tilde{P}} + \mathbf{\tilde{R}}) - \gamma,
\]

(79)

of which the canonical variables are \( \{ \mathbf{\tilde{R}}, \mathbf{\tilde{P}}, \chi, \mathbf{\tilde{p}} \} \) instead of \( \{ \mathbf{R}, \mathbf{P}, \chi, \mathbf{p} \} \). (See more discussion in Appendix 2 of the Supporting Information). The mapping diabatic momentum, \( \mathbf{P} \), is related to the kinematic momentum of the adiabatic representation. Although we can directly use Hamilton’s EOMs for \( \{ \mathbf{R}, \mathbf{P}, \chi, \mathbf{p} \} \), it is more convenient to employ the EOMs for \( \{ \mathbf{\tilde{R}}, \mathbf{\tilde{P}}, \chi, \mathbf{\tilde{p}} \} \) instead to avoid the derivative of nonadiabatic coupling terms. This is indeed the strategy suggested by Cotton et al.184 When the initial condition does not involve nonadiabatic coupling terms, the sampling of \( \mathbf{P} \) in the diabatic representation is the same for that of \( \mathbf{\tilde{P}} \) in the adiabatic representation. This is the case in the following applications, where FSSH has to be used in the adiabatic representation. By applying the covariance relation under the diabatic-to-adiabatic transformation, the EOMs on mapping phase space are independent of the representation of the (electronic) basis set, which is also the merit of Ehrenfest dynamics.

We note that either Equation (51) or Equation (74) can analytically be solved by a symplectic approach that employs an exact propagator on electronic phase space at each nuclear phase point. For example, for Equation (74), we use

\[
\tilde{U}(\mathbf{R}, \mathbf{P}; \Delta t) = \exp\left[ -i \Delta t V^{(\text{eff})} \right],
\]

(80)

such that the evolution of electronic phase variables follows \( \tilde{\mathbf{g}}(t + \Delta t) = \tilde{U}(\mathbf{R}, \mathbf{P}; \Delta t) \tilde{\mathbf{g}}(t) \).

We then test a range of benchmark systems, including two-site dissipative models, Tully’s scattering models, atomic systems in cavity interacted with a number of field modes, and linear vibronic coupling model systems that involve the conical intersection.135,246–248 They are typical composite quantum systems in chemistry, physics, condensed matter science, quantum optics, and quantum information.

### 4.2 Spin-boson models at low-temperature in condensed phase

The first model illustrated is the spin-boson model, which describes a two-site system interacted with an environmental bath in the condensed phase. It is also a simplified model for electron transfer and energy transfer in chemical and biological reactions. Several numerically exact benchmark methods for solving the spin-boson model include quasiadiabatic propagator path integral (QuAPI)249–252 and more efficient small matrix PI (SMatPI),304,305 hierarchy equations of motion (HEOM),253–261 and (multi-layer) multi-configuration time-dependent Hartree [(ML-)MCTDH].262–268 Quantum dynamics of the spin-boson model exhibits interesting dissipative characters, of which the asymptotic behaviors are
often missed by either of Ehrenfest dynamics and FSSH in the low-temperature regime.\textsuperscript{58} Spin-boson models with strong coupling in the low-temperature regime present challenging tests for trajectory-based dynamics methods.

The Hamiltonian of the spin-boson model is divided to three parts, \( \hat{H} = \hat{H}_x + \hat{H}_b + \hat{H}_{\text{int}} \). Here \( \hat{H}_x = \epsilon \hat{\sigma}_x + \Delta \hat{\sigma}_z \) describes a two-site system with the bias, \( \epsilon \), and tunneling \( \Delta \), while the bath part of the Hamiltonian is discretized into a combination of a number of quantum harmonic oscillators \( \hat{H}_b = \sum_{j=1}^{N_b} \left( \frac{\hat{p}_j^2}{2m} + \frac{\alpha_j^2 \hat{q}_j^2}{2} \right) / 2 \). The system-bath coupling adopts a bilinear interaction, \( \hat{H}_{\text{int}} = -\sum_{j=1}^{N_b} \alpha_j \hat{c}_j \hat{\sigma}_z \). Here, we use an Ohmic bath spectral density \( J(\omega) = (\pi/2) \omega \alpha e^{-\omega/\omega_c} \), where \( \alpha \) is the Kondo parameter and \( \omega_c \) is the cut-off frequency. Its discrete frequencies and coupling strengths \( \{\omega_j, \alpha_j\} \) are sampled\textsuperscript{269,270,306} from

\[
\begin{align*}
\omega_j &= -\omega_c \ln \left[ 1 - \frac{1}{j + N_b} \right], \\
\alpha_j &= \omega_j \sqrt{\omega_c / \left( 1 + N_b \right)}, \quad j = 1, \ldots, N_b.
\end{align*}
\]

The initial density is set as \( |1\rangle_s \otimes |\rho_b \rangle \), where the system is in excited state \( |1\rangle_s \) while all bath modes are at thermal equilibrium with \( \hat{\rho}_b = e^{-\beta \hat{H}_b} / Z_b \). Initial nuclear DOFs are sampled from the Wigner distribution of \( \hat{\rho}_b \), while initial electronic DOFs are sampled from (weighted) constraint coordinate-momentum phase space \( S(x, p) \). The continuous spectral density is discretized into \( N_b = 300 \) effective bath modes to guarantee numerical convergence in simulations.

In Figure 6, we demonstrate results produced by wMM with parameter \( \Delta = 0.05 \), by wMM with \( \Delta = 0.1 \), and by CMM with \( \gamma = (\sqrt{F + 1} - 1) / F = 0.366 \) that is a special case of CMM of Reference 134. Numerically exact results, as well as results yielded by Ehrenfest dynamics and FSSH, are also shown for comparison. Figure 6 indicates that wMM, as well as CMM, outperforms both Ehrenfest dynamics and FSSH dynamics, either for short-time coherences or for long-time dissipations.

### 4.3 Tully’s gas phase scattering models

Tully’s scattering models\textsuperscript{242} mimic different intersection types of molecular systems, which have widely been tested for various nonadiabatic dynamics methods. They describe a two-state Hamiltonian with a central coupling area and asymptotic plateau regions where diabatic potential function \( V_{\text{ap}}(R \to \pm \infty) \) is flat. All the three models, including the single avoided crossing (SAC), dual avoided crossing (DAC), and extended coupling region (ECR) problems, are used in our numerical tests.

Atomic units are used in the simulations of the Tully models. The SAC model (Panel a1 of Figure 7) describes the simplest but essential surface crossing in molecular systems. In the diabatic representation, its diagonal potential energy surfaces (PESes) are \( V_{11} = -V_{22} = A(1 - e^{-BR}) \text{sgn}(R) \) and off-diagonal coupling terms are \( V_{12} = V_{21} = Ce^{-DR^2} \). Here, the parameters are \( A = 0.01 \), \( B = 1.6 \), \( C = 0.005 \), and \( D = 1.0 \). The DAC model (Panel b1 of Figure 7) includes two crossing points, thus different (electronic) paths are interfered with the dependence on the initial momentum. Its diagonal PESes are \( V_{11} = 0 \) and \( V_{22} = -Ae^{-BR} + E_0 \), and off-diagonal coupling terms are \( V_{12} = V_{21} = Ce^{-DR^2} \) in the diabatic representation with parameters \( A = 0.10 \), \( B = 0.28 \), \( E_0 = 0.05 \), \( C = 0.015 \), and \( D = 0.06 \). The ECR model in the diabatic representation (Panel c1 of Figure 7) has diagonal PESes \( V_{11} = -V_{22} = E_0 \) and coupling terms \( V_{12} = V_{21} = C[e^{BR} \Theta(-R) + (2 - e^{-BR}) \Theta(R)] \), with \( E_0 = -0.0006 \), \( B = 0.9 \), and \( C = 0.1 \). Here, \( \Theta(R) \) is the Heaviside function of coordinate \( R \). The adiabatic PESes and nonadiabatic coupling vector of the ECR model are also illustrated in Panel c2 of Figure 7.

We investigate the transmission and reflection coefficients of each state. In the simulations, the initial condition is a nuclear wavepacket, \( \Psi(R; t = 0) \propto e^{i \alpha(R - R_0)^2 / 2 + i(R - R_0)P_0} \) (here we adopt \( \hbar = 1 \)), occupied in state 1, where \( \alpha = 1 \) is the Gaussian width parameter, and \( R_0 \) and \( P_0 \) are the initial average coordinate and momentum. The initial average coordinate is set at \( R_0 = -3.8, -10, \) and \(-13\) for the SAC, DAC, and ECR models, respectively. The initial Wigner distribution for the nuclear DOF is then \( \rho^{\text{Wig}}(R, P) \propto e^{-\alpha(R - R_0)^2 - (P - P_0)^2 / \alpha} \).

Figure 7a shows that all methods are capable of quantitatively describing transmission coefficients in (diabatic) state 1 and state 2 of the SAC model. Figure 7b demonstrates that either wMM or CMM outperforms Ehrenfest dynamics and FSSH in predicting the peak shape when the initial momentum is relatively high, for example, \( P_0 \geq 15 \text{ au} \). This indicates that the trajectory-based approximate dynamics approaches in the mapping phase space formulation are good for fast processes in the gas phase composite/nonadiabatic system. However, the performance of either wMM or CMM in the low initial momentum region should be improved. It is important to note that the EOMs of wMM/CMM are
invariant with the representation of the electronic state, as described in the Supporting Information of Reference 57. (More discussion is also available in Appendix 2 of the Supporting Information.) That is, both the diabatic and adiabatic representations produce the same results for wMM or CMM, which is often not satisfied in FSSH and other nonadiabatic dynamics approaches.

For the ECR model of Figure 7c, the numerically exact DVR solution indicates an energy threshold for a bifurcation. Ehrenfest dynamics totally misses the step-like behaviors for the transmission coefficient in state 1, and for the reflection coefficient in either state 1 or state 2. CMM greatly improves over Ehrenfest dynamics. It is more encouraging that wMM is capable of faithfully describing such step-like behaviors. Tully’s original FSSH algorithm is not able to well describe the ECR model, but a modified version for treating frustrated hopping of FSSH (e.g., see Reference 244) is capable of qualitatively capturing the step-like behaviors. As shown in Figure 7c, in comparison to the traditional FSSH approach, the overall performance of wMM for the ECR model is better.

4.4 Atom/molecule-in-cavity models of quantum electrodynamic light-matter systems

The cavity quantum electrodynamics (cQED) focuses on studying the interaction between light and a multi-level system (e.g., an atom or a molecule) in an optical cavity, which has many applications in the field of quantum information and quantum computation. There exist many interesting and important phenomena in cQED, for example, the Purcell effect when the coupling is weak and the vacuum Rabi splitting when the coupling becomes strong. When the general atomic/molecular system is coupled to multi-cavity modes, it is often intractable to solve the exact evolution in real time due to the curse of dimensionality. We test wMM for two typical models that describe an imprisoned multi-level atom coupled with a series of optical modes in a one-dimensional lossless cavity.
FIGURE 7  Legend on next page.
The total Hamiltonian consists of three parts. The optical field is depicted by \( N \) effective modes

\[
\hat{H}_\text{p} = \sum_{j=1}^{N} \frac{1}{2} \left( \hat{p}_j^2 + \omega_j^2 \hat{R}_j^2 \right),
\]

(82)

where \( \{ \hat{R}_j, \hat{P}_j \} \) denote the canonical coordinate-momentum variables of \( j \)-th optical field mode with the corresponding photonic frequency \( \omega_j \). The atomic system is described by \( \hat{H}_\text{a} = \sum e_n |n\rangle \langle n| \) with \( e_n \) representing the \( n \)-th atomic energy level. Employing the dipole approximation, one can formulate the interaction between atom and optical field as

\[
\hat{H}_\text{c} = \sum_{n \neq m}^{F} \left( \sum_{j=1}^{N} \omega_j \lambda_j(r_0) \hat{R}_j \right) \mu_{nm} |n\rangle \langle m|.
\]

(83)

Here \( \mu_{nm} \) denotes the transitional dipole moment between the \( n \)-th and \( m \)-th atomic levels, and the coupling between the \( j \)-th mode and the atom is

\[
\lambda_j(r_0) = \sqrt{\frac{2}{\varepsilon_0 L}} \sin \left( \frac{j \pi r_0}{L} \right),
\]

(84)

where \( L \) is the volume length of cavity, \( \varepsilon_0 \) denotes the vacuum permittivity, and \( r_0 \) represents the location of the atom. In the simulation, the volume length of the cavity is set to 236,200 au, and the atom is frozen at the central location, that is, \( r_0 = L/2 \). The optical field is depicted by 400 standing-wave modes in cavity, of which the \( j \)-th frequency is \( \omega_j = j \pi c / L \) with \( c \) the light speed in vacuum. We use two benchmark models for studying cQED processes, a three-level model with \( \varepsilon_1 = -0.6738, \varepsilon_2 = -0.2798, \varepsilon_3 = -0.1547, \mu_{12} = -1.034, \mu_{23} = -2.536 \) (all in atomic units), and a reduced two-level model where only the two lowest atomic levels are employed.

The highest atomic level of each model is initially occupied with no photon in cavity, that is, all cavity modes are in the corresponding vacuum state. The spontaneous emission occurs at the beginning, the released photon evolves in the cavity, and the re-absorption and re-emission happen later when the photon is reflected to meet the atom. Figure 8 shows the population transfer of each atomic level of the two models. The wMM results are compared with CMM, Ehrenfest dynamics, FSSH, and exact results. Results of Ehrenfest dynamics and of FSSH significantly deviate from exact results even since very short time, while CMM and wMM yield much more reasonable descriptions for all energy levels, including the transfer behavior at short time and the revival at around \( t = 1800 \) au. The wMM approach shows overall better performance than CMM in most of the cases. Figure 8 implies that the trajectory-based methods in the general coordinate-momentum phase space formulation will be useful for studying cQED phenomena in the field of quantum optics and quantum information.

4.5 Linear vibronic coupling model for the molecular system involving the conical intersection

The conical intersection widely exists in molecular systems and plays a central role in many photophysical and photochemical phenomena. The linear vibronic coupling model (LVCM) is the simplest but effective...
model widely used to describe dynamic properties around the conical intersection region, of which Hamiltonian in the diabatic representation is

\[ \hat{H} = \hat{H}_0 + \hat{H}_I + \hat{H}_c. \]

FIGURE 8  Results of population dynamics for the atom-in-cavity models. Panels (a) and (b) represent data of the first and second states of the two-level model, respectively. Panels (c–e) denote data of the first, second, and third states of the three-level model, respectively. Magenta solid lines: CMM with \( \gamma = (\sqrt{F + 1} - 1)/F \); purple solid lines: wMM with \( \Delta = 0.1 \); green solid lines: wMM with \( \Delta = 0.05 \); cyan long-dashed lines: Ehrenfest dynamics; Orange short-dashed lines: FSSH; black solid-dotted lines: Exact results from References 287,288. In each model, 400 continuous DOFs (i.e., standing-wave modes) are involved.
Here, $\hat{H}_0 = \sum_{k=1}^{N} \omega_k \left( \hat{p}_k^2 + \hat{r}_k^2 \right)/2$ is the zeroth-order harmonic oscillator Hamiltonian in normal-mode space of the electronic ground state, where $\hat{p}_k, \hat{r}_k (k = 1, \ldots, N)$ denote the $k$-th effective weighted normal-mode variables with frequency $\omega_k$ (i.e., $p_k = p_k/\sqrt{\omega_k}$, $r_k = \sqrt{\omega_k} r_k$, where $p_k, r_k$ are the canonical momentum, and canonical coordinate of $k$-th normal-mode). In Equation (85), $\hat{H}_1 = \sum_{n=1}^{F} \left( E_n + \sum_{k=1}^{N} \kappa_k^{(n)} \hat{r}_k \right) |n\rangle \langle n|$ contains the vertical excitation energy, $E_n (n = 1, \ldots, F)$ of $F$ electronic states, and the linear coupling term $\kappa_k^{(n)}$ of each nuclear DOF for diagonal Hamiltonian elements, while $\hat{H}_c = \sum_{n \neq m} \left( \sum_{k=1}^{N} \kappa_k^{(nm)} \hat{r}_k \right) |n\rangle \langle m|$ includes linear coupling $\kappa_k^{(nm)}$ for each normal-mode between two different electronic states, $|n\rangle$ and $|m\rangle$.

A typical two-level 3-mode LVCM describes the S1/S2 conical intersection of the pyrazine molecule. The parameters of this model are fitted from semi-empirical electronic structure calculations by Schneiders and Domcke in Reference 294. The excitation energies for the two electronic states are $E_1 = 3.94$ eV and $E_2 = 4.84$ eV. The diagonal linear coupling terms of the first two modes $\{ \hat{R}_1, \hat{R}_2 \}$ are $\kappa_1^{(1)} = 0.037$ eV, $\kappa_1^{(2)} = -0.105$ eV for the first electronic state, and $\kappa_1^{(3)} = -0.254$ eV, $\kappa_2^{(2)} = 0.149$ eV for the second electronic state, respectively. The off-diagonal linear coupling of third mode $\hat{R}_3$ is $\kappa_3^{(12)} = \kappa_3^{(21)} = 0.262$ eV. The normal-mode vibronic frequency of each mode is $\omega_1 = 0.126$ eV, $\omega_2 = 0.074$ eV, and $\omega_3 = 0.118$ eV, respectively. Initial conditions of nuclear DOFs are sampled from the corresponding Wigner function of the vibronic ground state while the second electronic state is occupied. All simulations employ $\sim 10^5$ trajectories and time stepsize $\Delta t = 0.01$ fs for fully converged results. Numerically exact result of this model calculated by ML-MCTDH are available in Reference 212.

Figure 9 shows population dynamics of state 2 yielded by wMM, CMM, Ehrenfest dynamics, FSSH and ML-MCTDH. It is evident that Ehrenfest dynamics performs poorly even for the short-time behavior (before 100 fs). In comparison, wMM, CMM, and FSSH more reasonably describe the radiationless energy transfer process at short time. Interestingly, wMM describes the oscillating behaviors in the long-time region (after 300 fs) better than other approximate methods. Such oscillating behavior in population dynamics indicates the molecular system passes through the “slopped” conical intersection region.

Figures 6–9 demonstrate that the overall performance of wMM is better than CMM, especially in the gas phase scattering case of Figure 7c and the quantum electrodynamic light-matter systems of Figure 8. Both wMM and CMM approaches are able to outperform Ehrenfest dynamics as well as FSSH for condensed phase systems (e.g., in Figures 6 and 8).
5 | CONCLUSION REMARKS

The phase space formulation of quantum mechanics not only presents a type of convenient interpretation to describe quantum-classical correspondences as well as nonclassical correlations/entanglement, but also sets the insightful scene for developing practical and useful trajectory-based quantum dynamics approaches.

In the Focus Article, we show that the constraint coordinate-momentum phase space formulation for the discrete-variable system which we have recently developed, and the weighted representation that we propose in the Focus Article are useful approaches for illustration of nonclassical features of quantum systems. The novel formulation is expected to have potential use for the illustration of nonclassical features of quantum states, as well as for future phase point measurement experiment.\textsuperscript{70,85,221–234}

It is straightforward to show the relationship between the SU(F)/U(F-1) Stratonovich phase space\textsuperscript{114} and constraint coordinate-momentum phase space, which is diffeomorphic to U(F)/U(F-1). When $F > 2$, it is inevitable to meet singularities in dynamics for discrete-variable systems when Stratonovich phase space is used (based on the symplectic structure of the phase space).\textsuperscript{303} In comparison, (weighted) constraint coordinate-momentum phase space does not cause any singularities in trajectory-based exact dynamics, which is much more numerically favorable. (See more discussion in Appendix 3 of the Supporting Information).

When the general Moyal bracket of the quantum Liouville theorem is approximated by the corresponding Poisson bracket\textsuperscript{57,58} on (weighted) constraint phase space, it reproduces the correct frozen-nuclei limit of composite/nonadiabatic systems. Such trajectory-based EOMs on (weighted) constraint coordinate-momentum phase space does not rely on the choice of representation of electronic states and are straightforward to obtain the form under covariant transformations. Because second-order nonadiabatic coupling terms are avoided in the EOMs of the adiabatic representation, it is especially useful for applications to realistic molecular systems. (In addition to Section 4.1, more discussion on the EOMs is presented in Appendices 2 and 5 of the Supporting Information.) Various benchmark model tests from gas phase to condensed phase quantum systems (as shown in Figures 6–9) indicate that wMM, the new trajectory-based approximate approach with the weighted constraint coordinate-momentum phase space representation, demonstrates overall better performance than FSSH as well as Ehrenfest dynamics. It is expected that more investigations on the (weighted) constraint phase space formulation will shed light on more numerically favorable dynamics approaches with the Meyer–Miller mapping Hamiltonian or other mapping Hamiltonians (e.g., those of Reference 131 and discussed in Reference 58).

We note that the (weighted) constraint coordinate-momentum phase space formulation is established for any systems with a finite set of states, not only limited to discrete electronic states, but also for finite discrete nuclear states. The weighted phase space strategy that we propose can also be applied to other types of phase space formulations of the discrete-variable system, such as Stratonovich phase space, and Wootters phase space, albeit the general coordinate-momentum phase space formulation presented in the Focus Article will be more convenient, for experimental measurements, tomography, or characterizations of fidelity, coherence, inequalities, displaced parity, atomic/molecular/optical Schrodinger cat states, and entanglement in quantum information and computation\textsuperscript{70,85,221–234,295,296} as well as for studying dynamic processes of composite systems in physics, chemistry, materials, biology, and environmental science.

AUTHOR CONTRIBUTIONS

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ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (NSFC) Grant No. 21961142017, and by the Ministry of Science and Technology of China (MOST) Grant No. 2017YFA0204901. We acknowledge the High-
performance Computing Platform of Peking University, Beijing PARATERA Tech CO., Ltd., and Guangzhou supercomputer center for providing computational resources.

CONFLICT OF INTEREST
The authors have declared no conflicts of interest for this article.

DATA AVAILABILITY STATEMENT
Data sharing is not applicable to this article as no new data were created or analyzed in this study.

RESEARCH RESOURCES
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