Exploring Phase Space Formulation for Nonadiabatic Problems and Trajectory-based Quantum Dynamics

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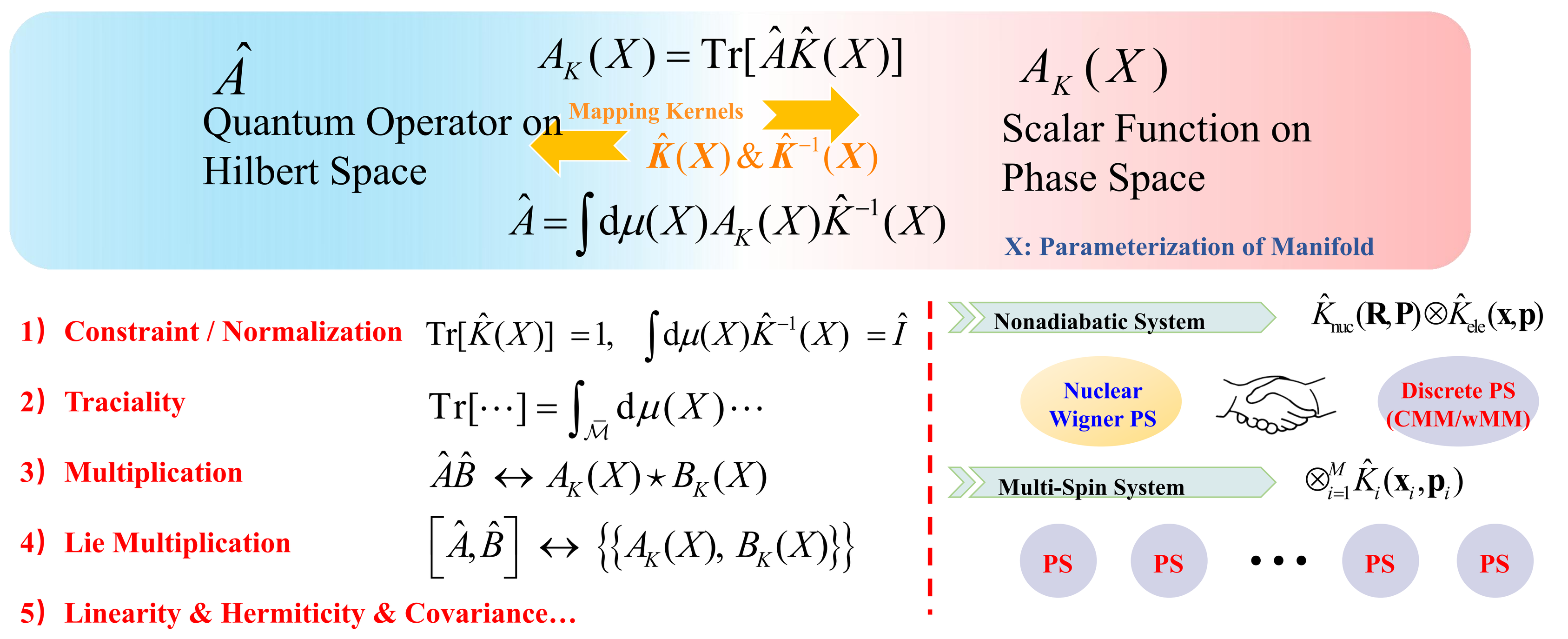
Introduction

We have developed the phase space formulation of quantum dynamics for nonadiabatic systems where both discrete and continuous degrees of freedom are involved. 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**[6].

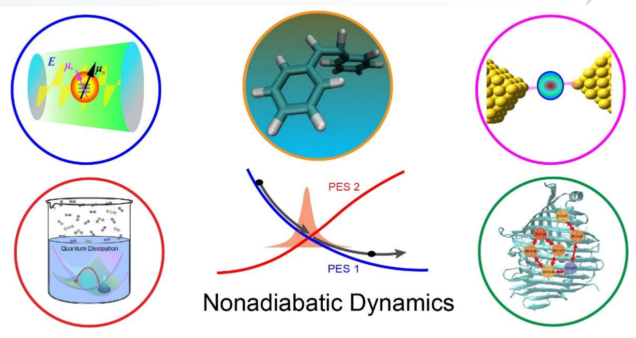


Our work first revealed the normalized constraint[2] for the discrete phase space (for electronic DOFs) and developed classical mapping models (CMM)[1-5], lying on the U(F)/U(F-1) manifold with Meyer-Miller variables, i.e., the constraint coordinated-momentum phase space (CPS). Combined with the continuous Wigner phase space for nuclear DOFs, the phase space formulation can be applied to nonadiabatic systems, as well as other composite systems. In addition, by employing characteristic function to depict a manifold and ensure the exact correspondence, we also develop weighted mapping model (wMM) based on weighted phase space (WPS).

Theory Framework

Three key elements in the phase space framework:

1. the initial condition of the trajectory (i.e., manifold),
2. the EOMs of the trajectory, and
3. the integral expression for the expectation/ensemble.



Initial Condition

Phase space $\leftrightarrow$ *manifold*

Sampling PS points

$$\int_{\mathcal{M}(\mathbf{x},\mathbf{p})} F d\mathbf{x}d\mathbf{p}\,(\cdot) = \frac{\int F d\mathbf{x}d\mathbf{p}\,\mathcal{M}(\mathbf{x},\mathbf{p})(\cdot)}{\int d\mathbf{x}d\mathbf{p}\,\mathcal{M}(\mathbf{x},\mathbf{p})}$$

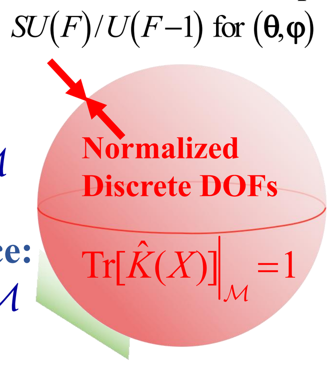
CMM Phase Space (CPS): $U(F)/U(F-1)$ for $(\mathbf{x},\mathbf{p})$

Stratonovich Phase Space: $SU(F)/U(F-1)$ for (θ,φ)

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

Manifold: $\mathcal{M}$

Tangent space: $T\mathcal{M}$



Equations of Motion

$$-\partial_t\rho = \{\{\rho(\mathbf{R},\mathbf{P},\mathbf{x},\mathbf{p},t), H(\mathbf{R},\mathbf{P},\mathbf{x},\mathbf{p})\}\}_{\mathrm{Moyal}}$$

$$\xrightarrow{o(\hbar)+\mathrm{MFA}} \{\rho(\mathbf{R},\mathbf{P},\mathbf{x},\mathbf{p},t), H(\mathbf{R},\mathbf{P},\mathbf{x},\mathbf{p})\}$$

EOMs based on symplectic structure

$$H = \mathbf{P}\mathbf{M}^{-1}\mathbf{P}/2 + \sum_{n,m=1}^{F}\mathrm{Tr}[\hat{K}_{\mathrm{ele}}(\mathbf{x},\mathbf{p})\hat{V}(\mathbf{R})]$$

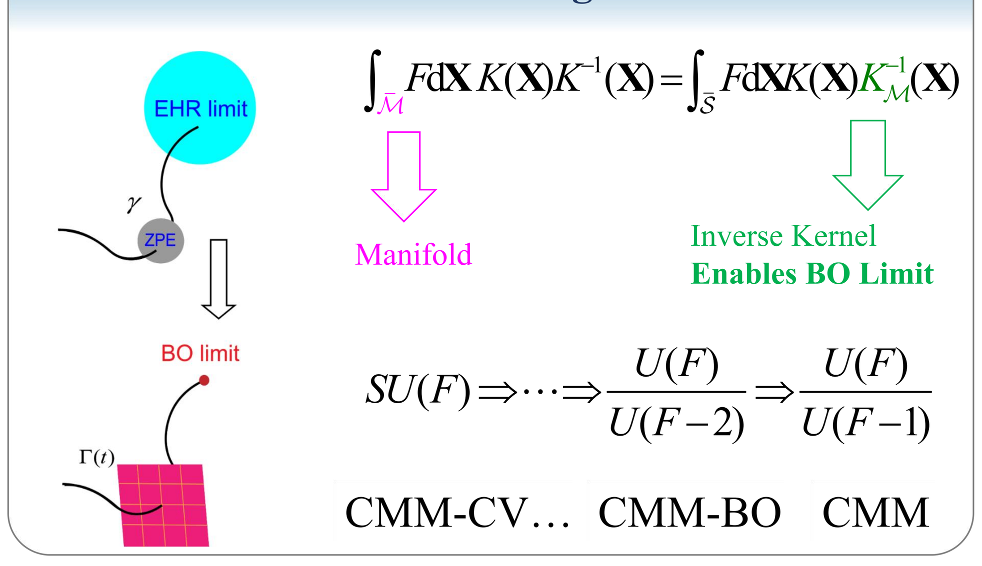
Time Correlation Function

$$\int_{\mathcal{S}} F d\mathbf{X} K_{nm}(\mathbf{X})[K^{-1}]_{kl}(\mathbf{X}) = \delta_{mk}\delta_{nl}$$

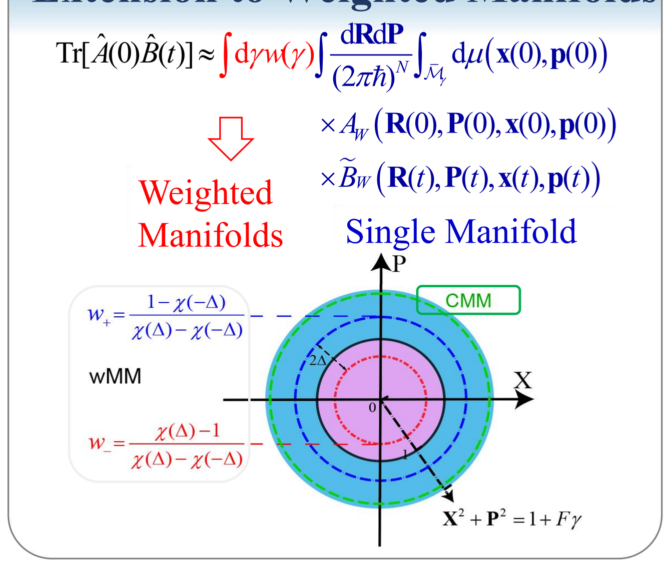
$$\int d\gamma\, w(\gamma)\chi(\gamma) = 1$$

Characteristic function shapes the manifold

Generalization of Single Manifold

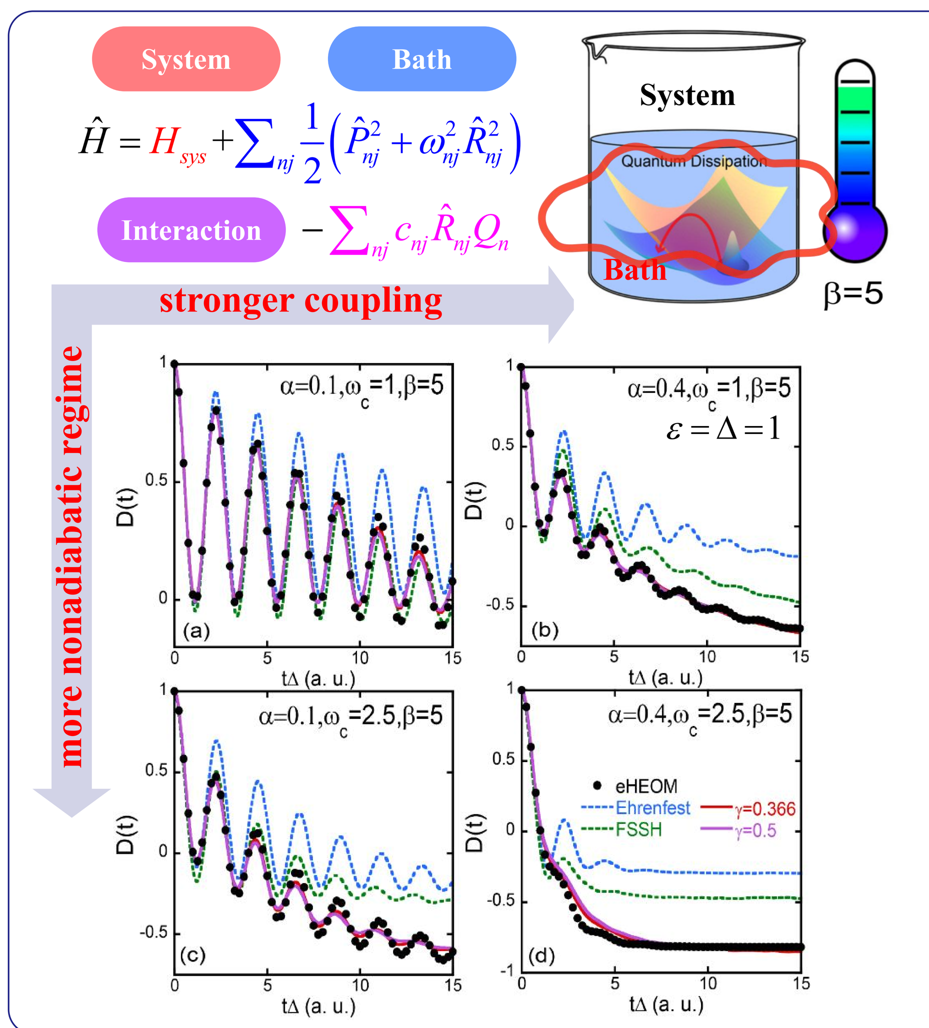


Extension to Weighted Manifolds



Numerical Results

1. Constraint Coordinate-Momentum Phase Space (CMM)



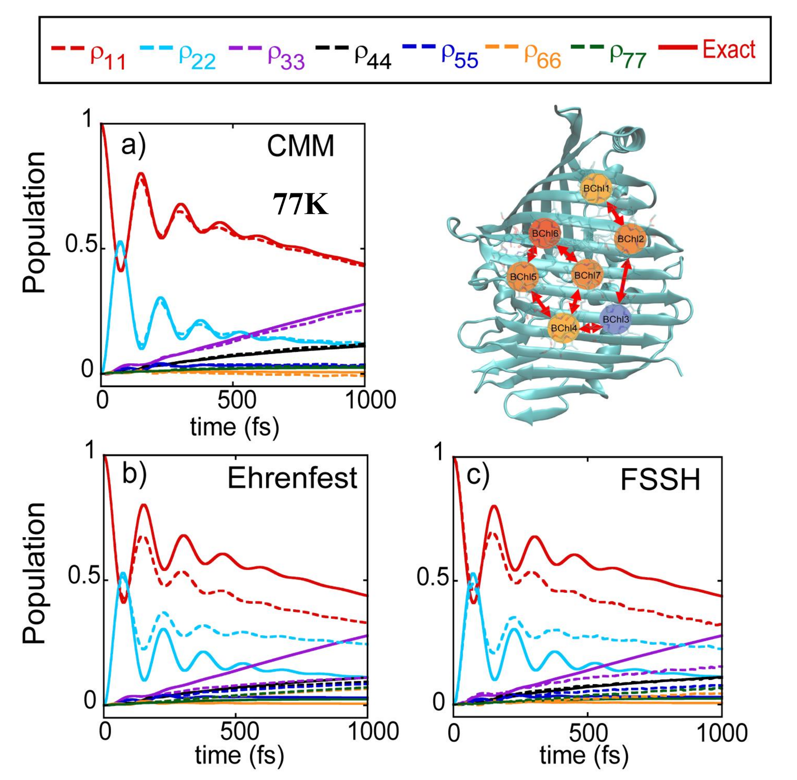
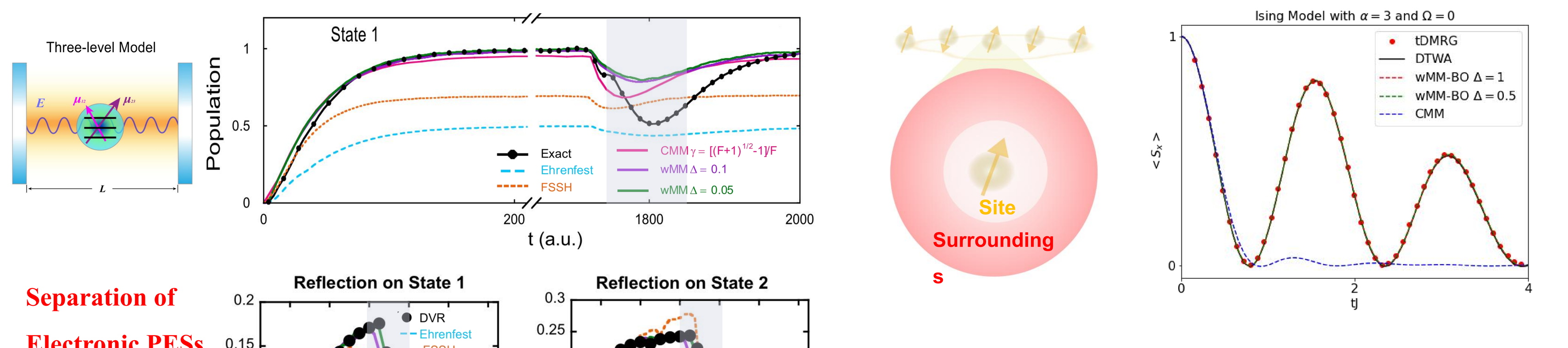


Figure 1. Quantum dissipation dynamics at low temperature with comparisons of three trajectory-based methods, including Ehrenfest dynamics, Surface Hopping and phase space mapping (CMM) approach for (left) spin-boson model and (right) FMO complex.

2. Weighted Phase Space (wMM)



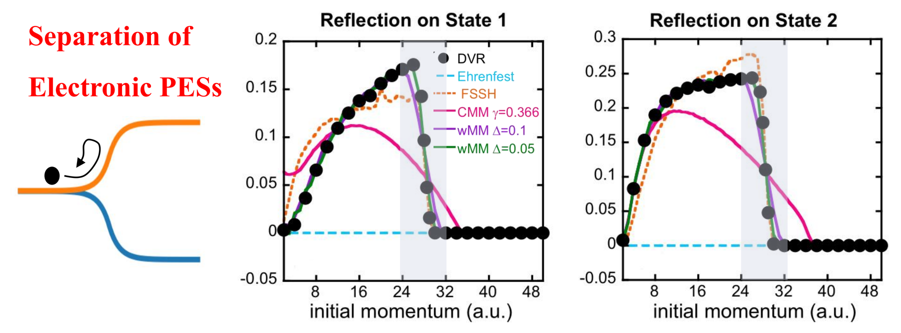


Figure 2. (upper-left) Cavity QED dynamics of trajectory dynamics, where CMM/wMM outperforms Ehrenfest/SH dynamics. (lower-left) Plateau of scattering probability of ECR model. (upper-right) Spin dynamics for Ising model with short range interaction.

3. Weighted U(F)/U(F-2) Rank=2 Manifold Scheme: wMM-BO

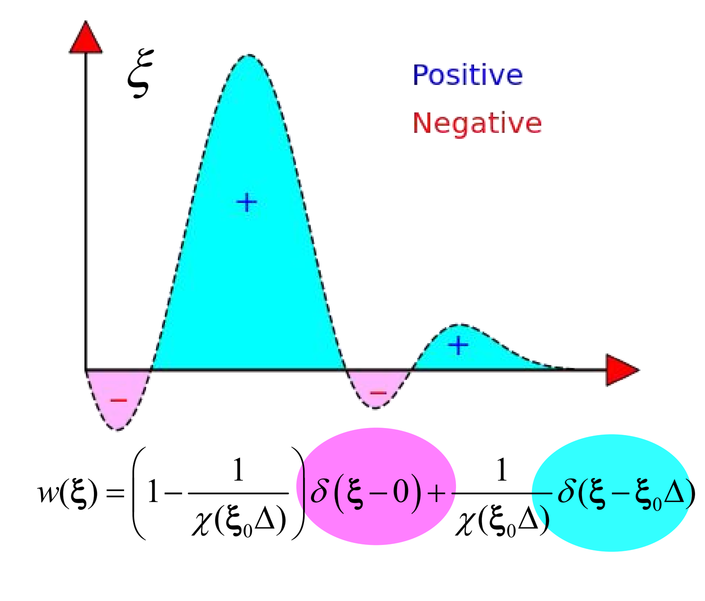
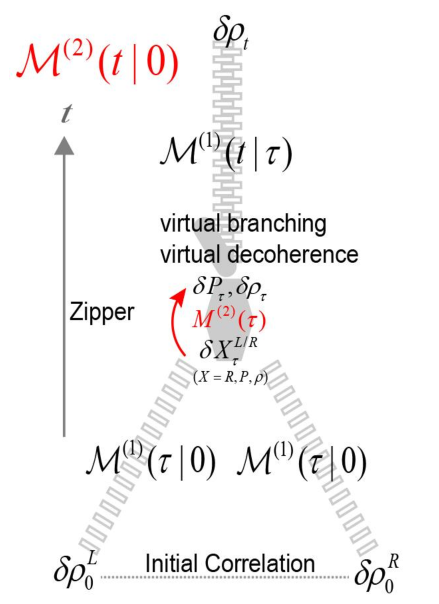


Figure 3. (left) Weighted scheme surrounding Ehrenfest trajectory given in wMM-BO. (right) A perturbative approach to include corrections for Ehrenfest dynamics.



Conclusions

It is suggested a phase space family with a constraint parameter that can be negative and continuous, interpreted as a manifold shape parameter other than the so-called "ZPE" factor[3]. We also develop generalization of single manifold and extend the mapping to weighted manifolds[6]. We have realized different kinds of efficient mapping manifolds and mapping kernels for better description of electronic coherence and decoherence, as well as of nuclear dynamics for nonadiabatic systems. Among trajectory-based methods, phase space mapping approach exhibits advantages for composite systems.

References

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