The 17th National Conference on Chemical Dynamics

Phase Space Mapping Formulation of Quantum Dynamics for Nonadiabatic Systems

Xin He, Baihua Wu, Jian Liu*
College of Chemistry and Molecular Engineering, Peking University, Beijing, 100871
Email: jianliupku@pku.edu.cn

Abstract

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[1]. In particular, the phase space for discrete variables (e.g., electronic DOFs) is consistent with the normalized population constraint[2], which can be parameterized onto the U(F)/U(F-1) manifold with Meyer-Miller variables, called classical mapping models (CMM)[1-3], while the phase space for continuous variables (e.g., nuclear DOFs) adopts Wigner quasi-distribution. It presents three important keys in phase space framework[1]: 1) the EOMs of the trajectory (generated by Hamiltonian dynamics), 2) the initial condition of the trajectory (sampled from specific manifold), and 3) the integral expression for the expectation/ensemble (held for one-to-one mapping).

Theoretical Framework

Phase Space Representation

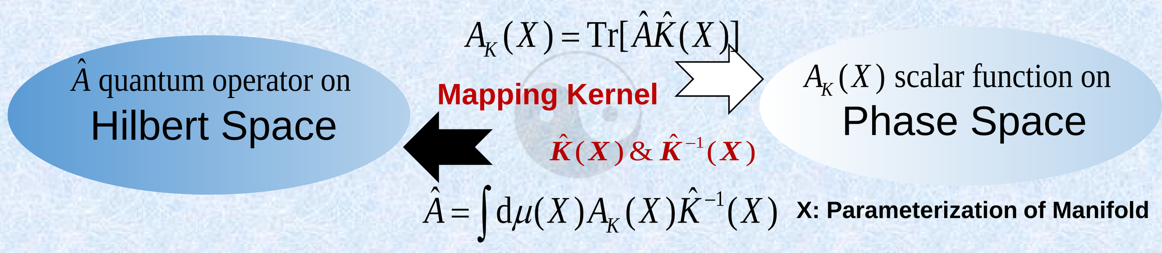
1) Normalization $\mathrm{Tr}[\hat{K}(X)]=1, \quad \int \mathrm{d}\mu(X)\hat{K}(X)=\hat{I}$

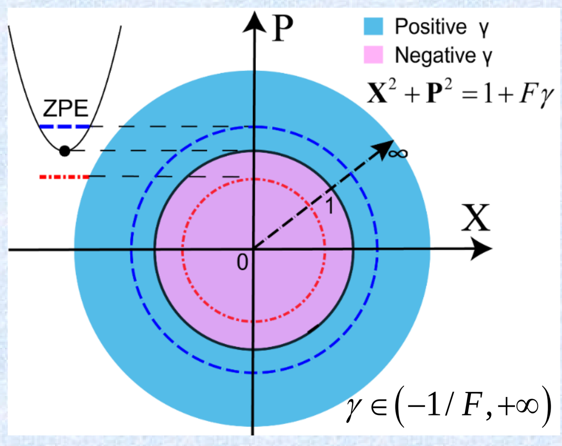
2) Traciality $\mathrm{Tr}[\hat{A}\hat{B}]=\int \mathrm{d}\mu(X)A_K(X)\tilde{B}_K(X)$

3) Multiplication $\hat{A}\hat{B} \leftrightarrow A_K(X)\star B_K(X)$

4) Lie Multiplication $[\hat{A},\hat{B}] \leftrightarrow \{\{A_K(X), B_K(X)\}\}$

5) Linearity & Hermiticity & Covariance...





- Constraint Phase Space (CMM)

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

- Wigner phase space

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

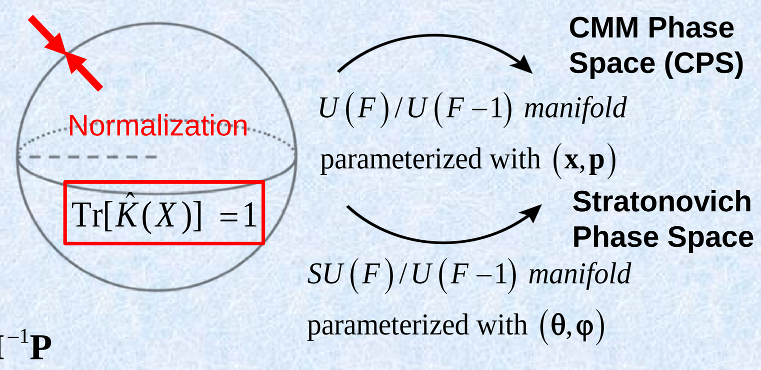
Hamiltonian Trajectory Approximation

3 key elements

Init. Cond.

Phase space ↔ *manifold*

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



EOMs

Governed by Hamiltonian:

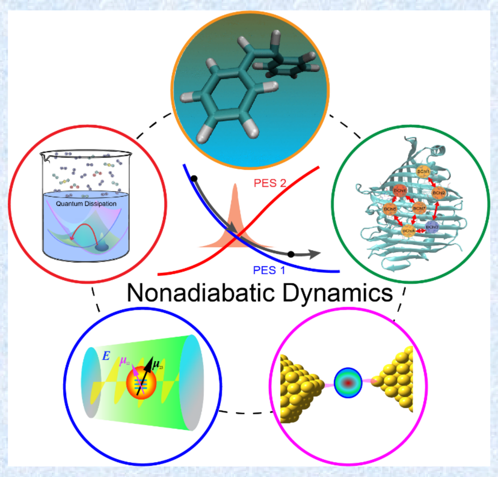
$$H_{map}(\mathbf{R},\mathbf{P},\mathbf{x},\mathbf{p})=\frac{1}{2}\mathbf{P}^T\mathbf{M}^{-1}\mathbf{P}+\sum_{n,m=1}^{F}\left[\frac{1}{2}(x^{(n)}+ip^{(n)})(x^{(m)}-ip^{(m)})-\gamma\delta_{nm}\right]V_{nm}(\mathbf{R})$$

TCF

$$\mathrm{Tr}[\hat{A}(0)\hat{B}(t)]\approx\int d\gamma w(\gamma)\int\frac{\mathrm{d}\mathbf{R}\mathrm{d}\mathbf{P}}{(2\pi\hbar)^N}\int_{\mathcal{S}_\gamma}\mathrm{d}\mu(\mathbf{x}(0),\mathbf{p}(0))\times A_W(\mathbf{R}(0),\mathbf{P}(0),\mathbf{x}(0),\mathbf{p}(0))\times B_W(\mathbf{R}(t),\mathbf{P}(t),\mathbf{x}(t),\mathbf{p}(t))$$

Weighted Manifolds

Single Manifold



Results

Harmonic Model Studies

■ Spin-boson model

× Ehrenfest/Surface hopping dynamics fails in long time limit
✓ Our approach CMM gives correct asymptotic behavior which insensitive to γ

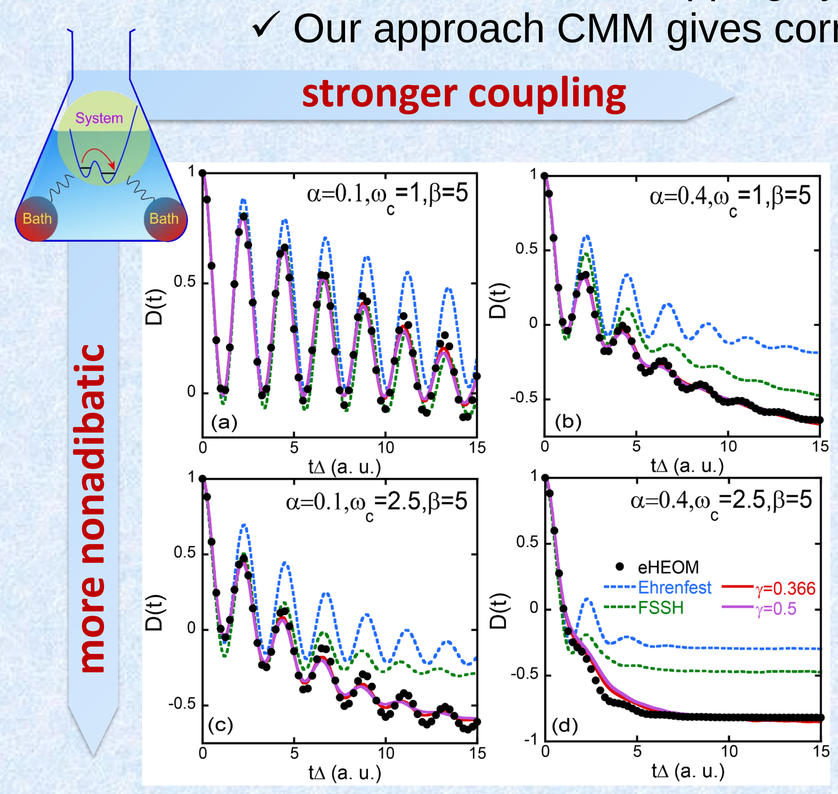


Figure 1: dissipative dynamics for spinboson models describe electron transfer process

System | Bath | Interaction

$$\hat{H}=H_{sys}+\sum_{nj}\frac{1}{2}\left(\hat{P}_{nj}^2+\omega_{nj}^2\hat{R}_{nj}^2\right)-\sum_{nj}c_{nj}\hat{R}_{nj}Q_n$$

■ Atom-in-Cavity model

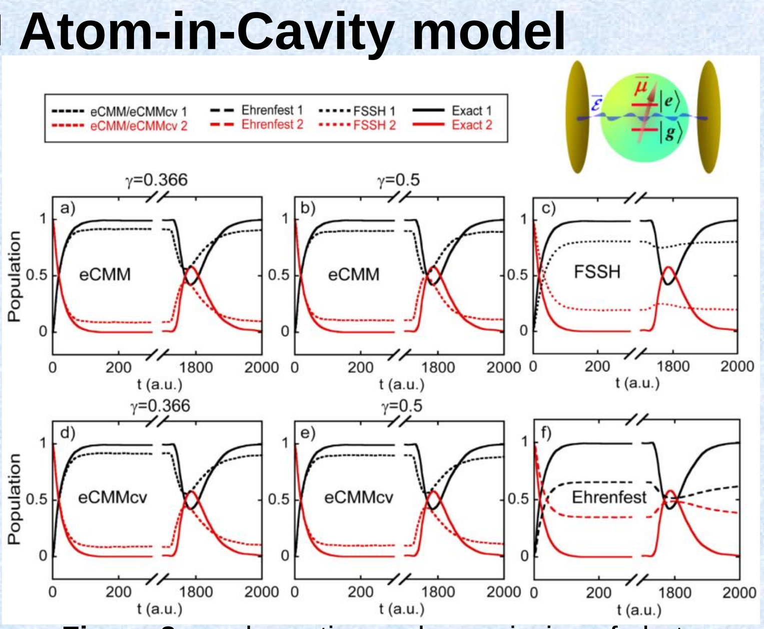


Figure 2: re-absorption and re-emission of photons after spontaneous emission of an atom in cavity

■ 7-site site-exciton FMO model

- Light harvest systems in green surfer bacteria
- (e)CMM outperforms EHR/FSSH in final equilibrium

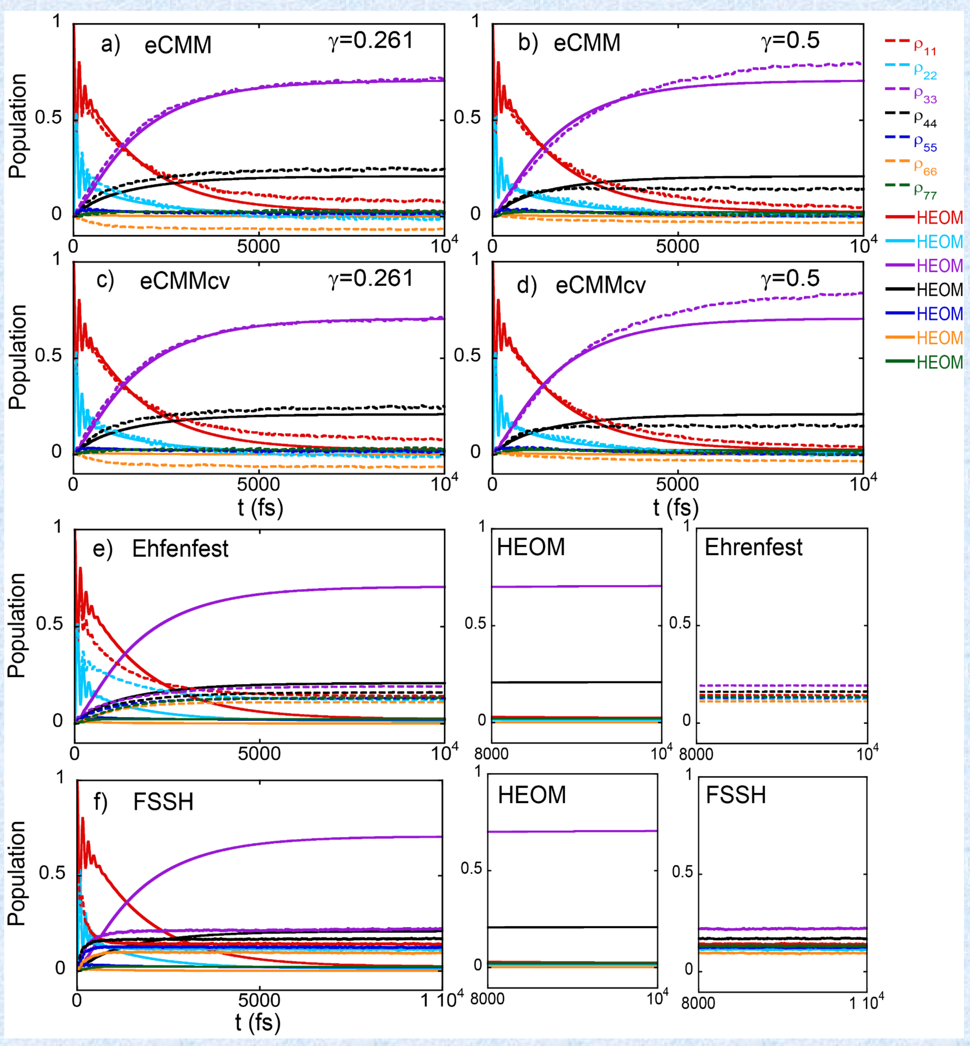


Figure 3: long time equilibrium for FMO exciton dynamics

Anharmonic Model Studies

■ Ultrafast photo-dissociation dynamics

✓ Satisfy BO dynamics before entering coupling region
✓ Commutator variables with auxiliary equation of motions

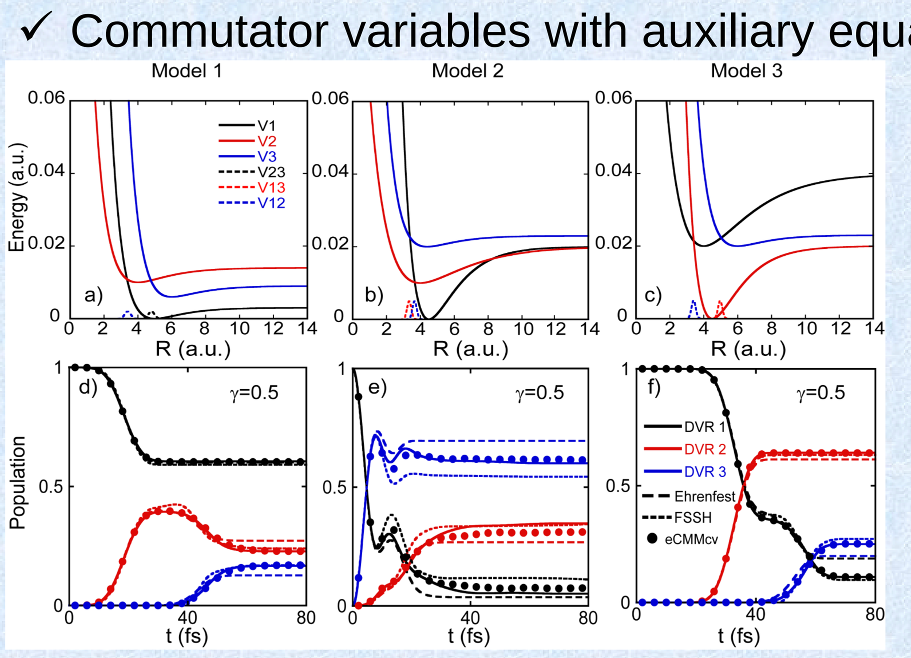
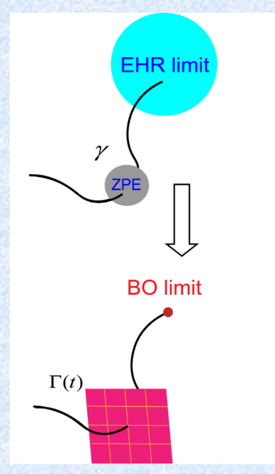


Figure 4: Population dynamics with commutator variables



$\Gamma_{nm}=[x^{(n)},p^{(m)}]/2i$

■ Tully's scattering problem

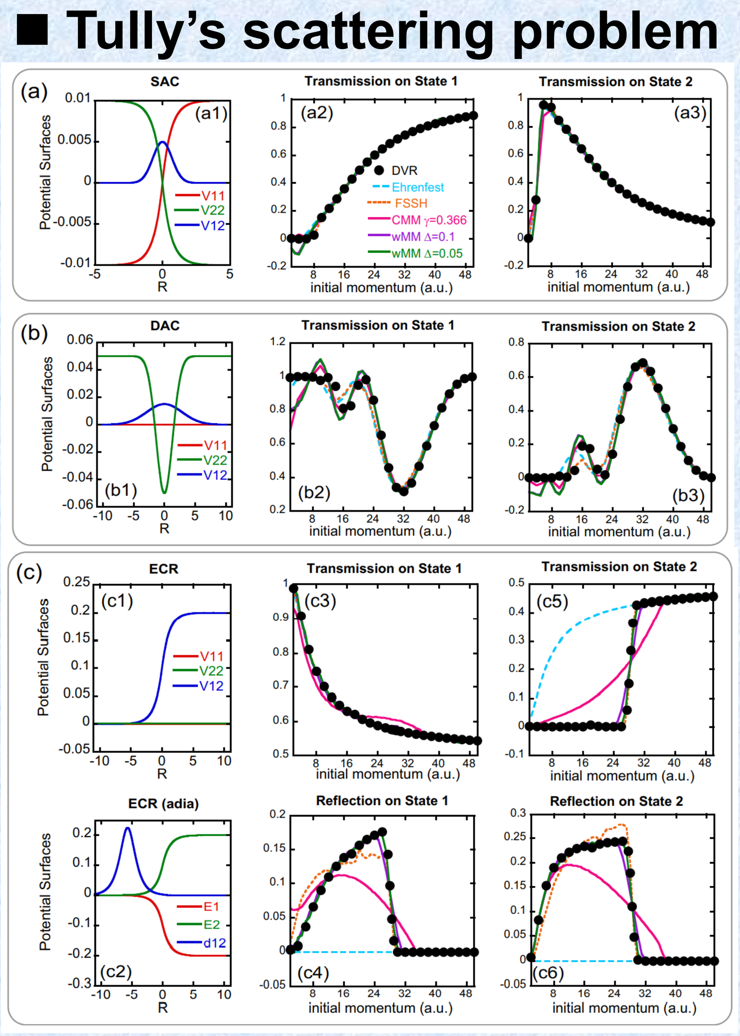


Figure 6: Transition probability on 1 or 2 surface with respect to initial momentum. Panel a) gives results of SAC model, panel b) presents those of DAC model, and panel c) shows those of ECR model.

- Weighted manifolds

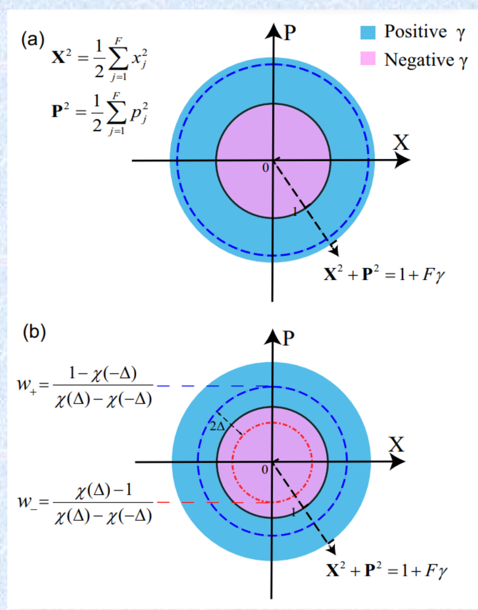


Figure 5: (a) CMM vs (b) wMM.

Summary

It is suggested that the constraint parameter can be negative, more than a so-called "ZPE" factor[3]. We also naturally extend a scalar "ZPE" factor to commutator variables to improve nuclear dynamics[4], and weighted constraint manifolds (denoted as wMM) for better description of electronic coherence and decoherence[1]. The unified phase space framework has provided the solid base for developing more accurate mixed quantum-classical methods for various nonadiabatic systems[1-5].

References:
[1] X. He, B. Wu, Y. Shang, B. Li, X. Cheng, J. Liu, *Wiley Interdiscip. Rev. Comput. Mol. Sci.*, e1619 (2022).
[2] X. He, J. Liu, *J. Chem. Phys.* 151, 024105 (2019).
[3] X. He, Z. Gong, B. Wu, J. Liu, *J. Phys. Chem. Lett.* 12, 2496 (2021).
[4] X. He, B. Wu, Z. Gong, J. Liu, *J. Phys. Chem. A.* 125, 6845-6863 (2021).
[5] J. Liu, X. He, B. Wu, *Acc. Chem. Res.*, 54, 4215-4228 (2021).

Acknowledgement: 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.