Development of trajectory-based nonadiabatic dynamics under unified phase space formulation of both nucleus and electronic states

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

Abstract

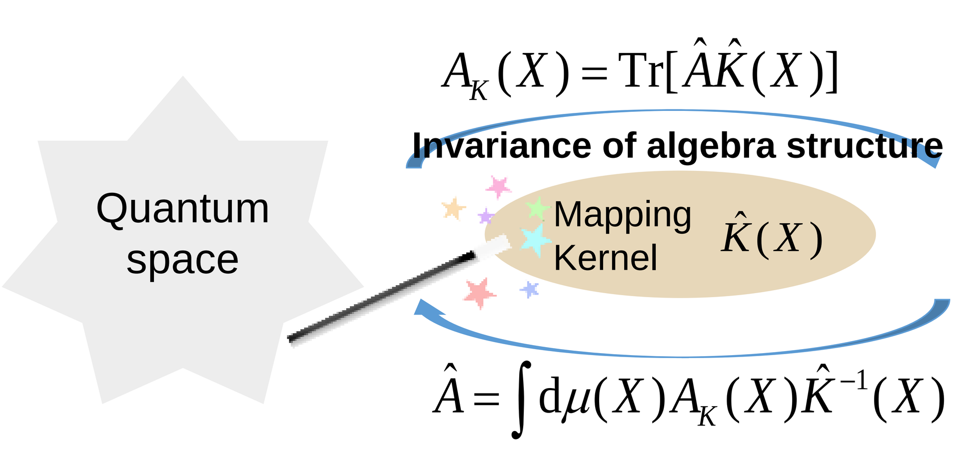
Inspired by Meyer-Miller mapping model (Ref. 1), we formulate a unified phase space for both nuclear and electronic DOFs to develop nonadiabatic dynamics. Rather than sampling from the traditional Winger (quasi-)distribution of mapped oscillators, we construct a novel phase space for discrete freedoms called CMM in a constrained space in Ref. 3, which differs and gives more satisfying approximation to describe so-called zero point energy (ZPE) effect. Our formulation unifies discrete mapping and continuous mapping in the same language via kernel transform, and point that ZPE factor can be even negative in Ref. 4. More recently, we also naturally extend traditional ZPE factor to commutator matrix in Ref. 5, whose dynamics can be described by introducing a set of auxiliary mapping variables. It promises Born-Oppenheimer limit when coupling terms are vanished before system crossing the coupling region. Our new scheme has been provided good validity in a wide range of systems including harmonic and anharmonic potential surface.

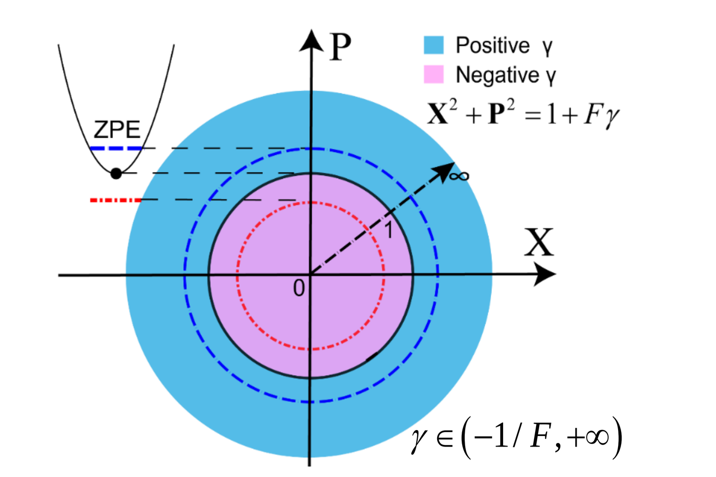
Theoretical Framework

Phase Space: Exact statistics formulation

Algebraic structure of rings under mapping

- **Identity Correspondence** $\mathrm{Tr}[\hat{K}(X)]=1,\quad \int d\mu(X)\hat{K}(X)=\hat{I}$
- **Ring's multiplication** $\hat{A}\hat{B} \leftrightarrow A_K(X)\star B_K(X)$
- **Lie multiplication** $[\hat{A},\hat{B}] \leftrightarrow \{A_K(X),B_K(X)\}_{possion}$
- **Trace Correspondence** $\mathrm{Tr}[\hat{A}\hat{B}]=\int d\mu(X)A_K(X)\tilde{B}_K(X)$





- Constraint phase space (eCMM)

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

- Wigner phase space

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

Hamiltonian trajectory: Approximate NA dynamics

Prcedure for simulation

Init. Cond.

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

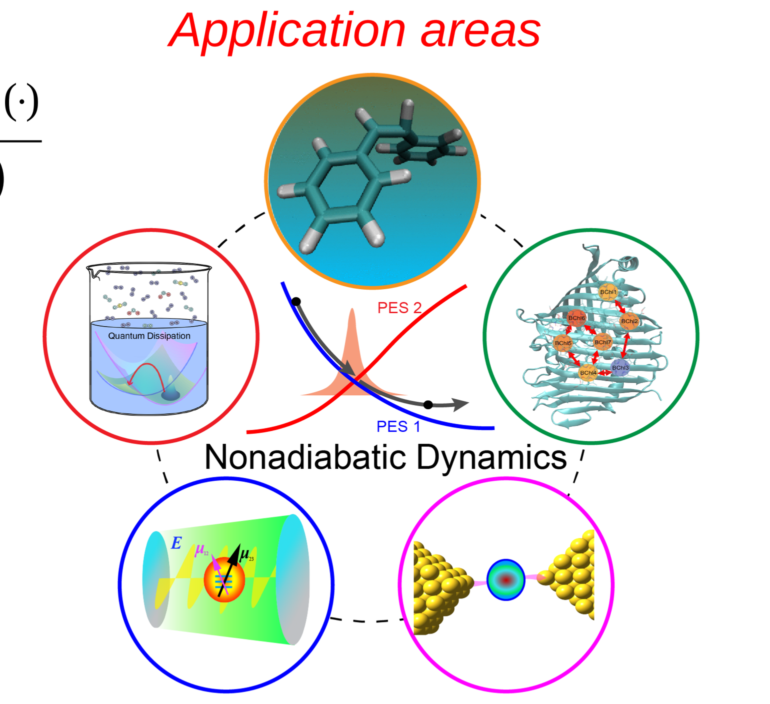
EOM

$$\begin{cases} d_t\mathbf{R}=\partial_{\mathbf{P}}H_{map}\\ d_t\mathbf{P}=-\partial_{\mathbf{R}}H_{map}\\ d_t\mathbf{x}=\partial_{\mathbf{p}}H_{map}\\ d_t\mathbf{p}=-\partial_{\mathbf{x}}H_{map}\end{cases}$$

TCF

$$Tr[\hat{A}(0)\hat{B}(t)]=\int d\mathbf{R}d\mathbf{P}\int_{\mathcal{S}}d\mu(\mathbf{x}(0),\mathbf{p}(0))\times A(\mathbf{R}(0),\mathbf{P}(0),\mathbf{x}(0),\mathbf{p}(0))B(\mathbf{R}(t),\mathbf{P}(t),\mathbf{x}(t),\mathbf{p}(t))$$

Application areas



Results

Harmonic Model Studies

■ Spin-boson model

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

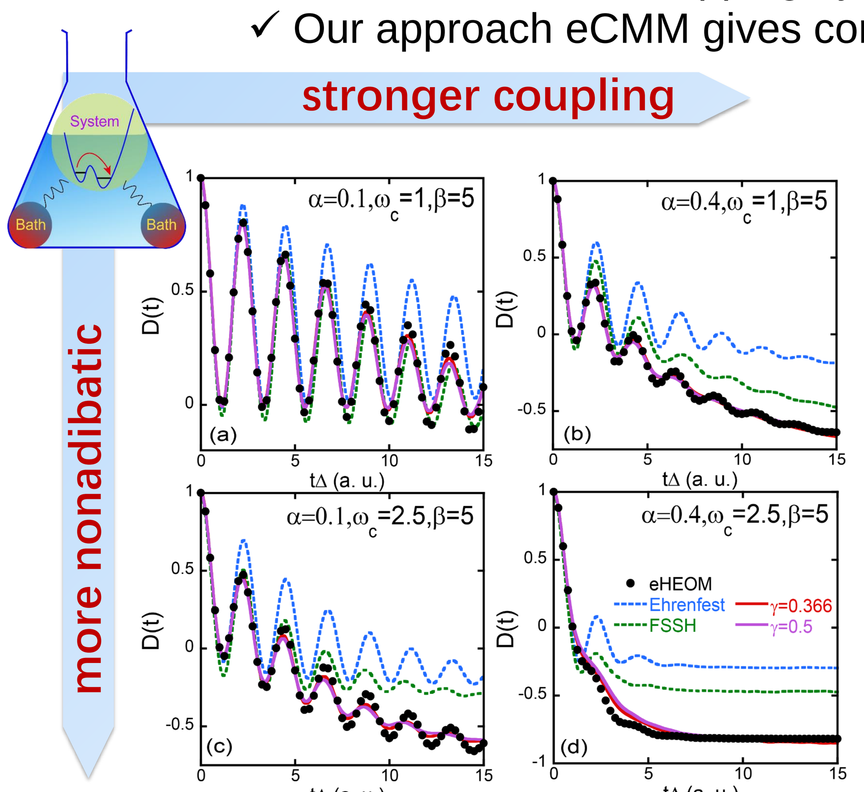


Figure 1: dissipative dynamics for spinboson models describe electron transfer process

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

■ Atom-in-Cavity model

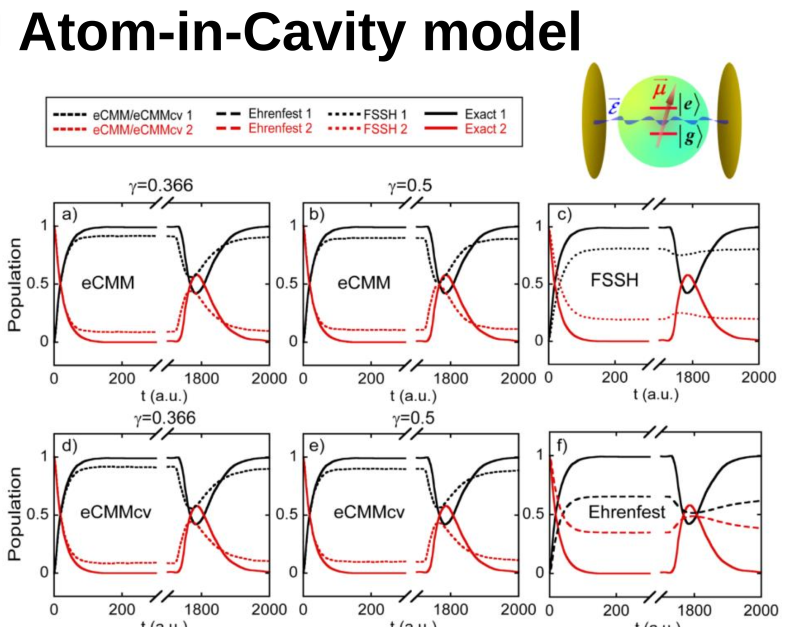

Figure 2: re-absorption and re-emission of photons after spontaneous emission of an atom in cavity

■ 7-site site-exciton FMO model

- Light harvest systems in green surfer bacteria
- eCMM outperforms EHR/FSSH in final equilibrium

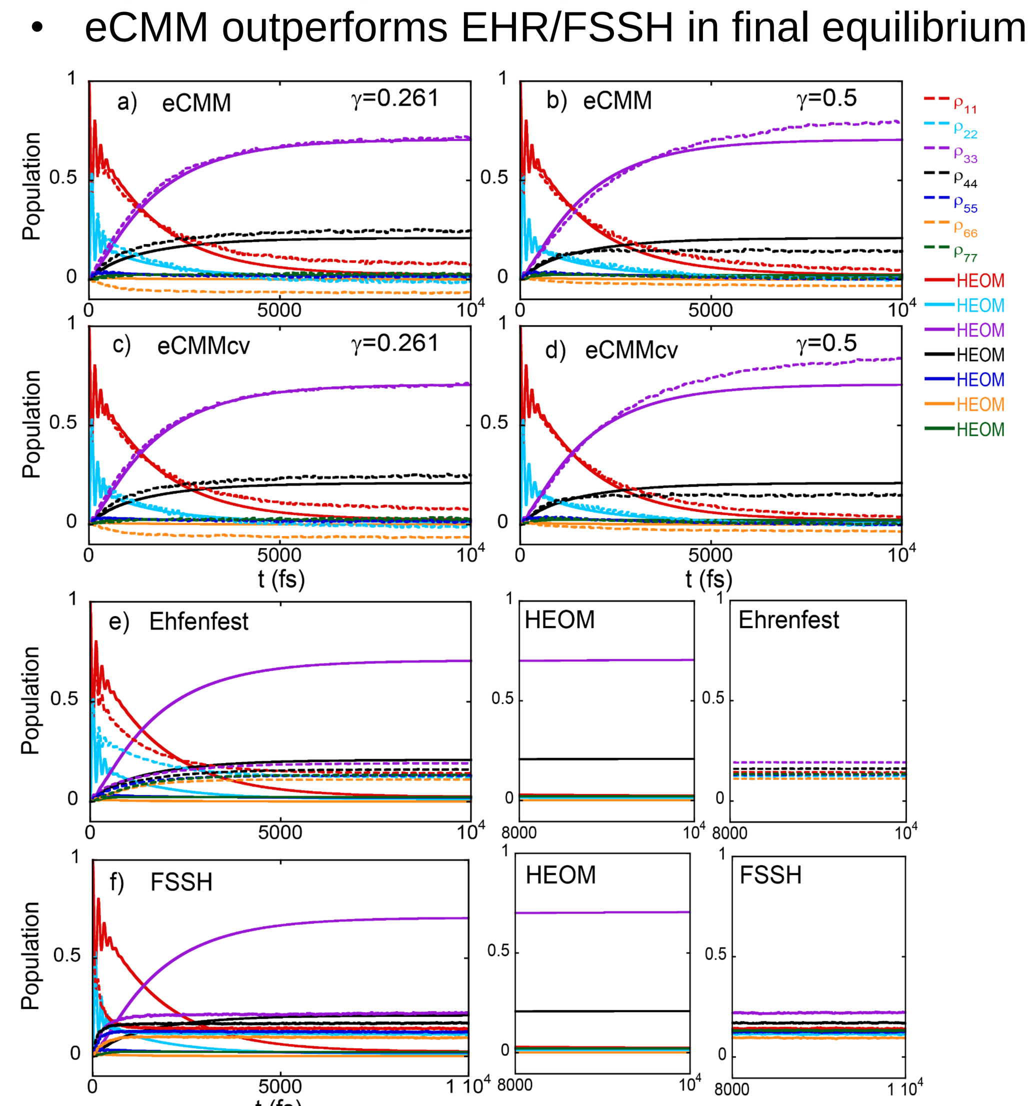

Figure 3: long time equilibrium for FMO exciton dynamics

Anharmonic Model Studies

■ Tully's scattering problem

✓ Better fitting with DAC's Stückelberg peak shape

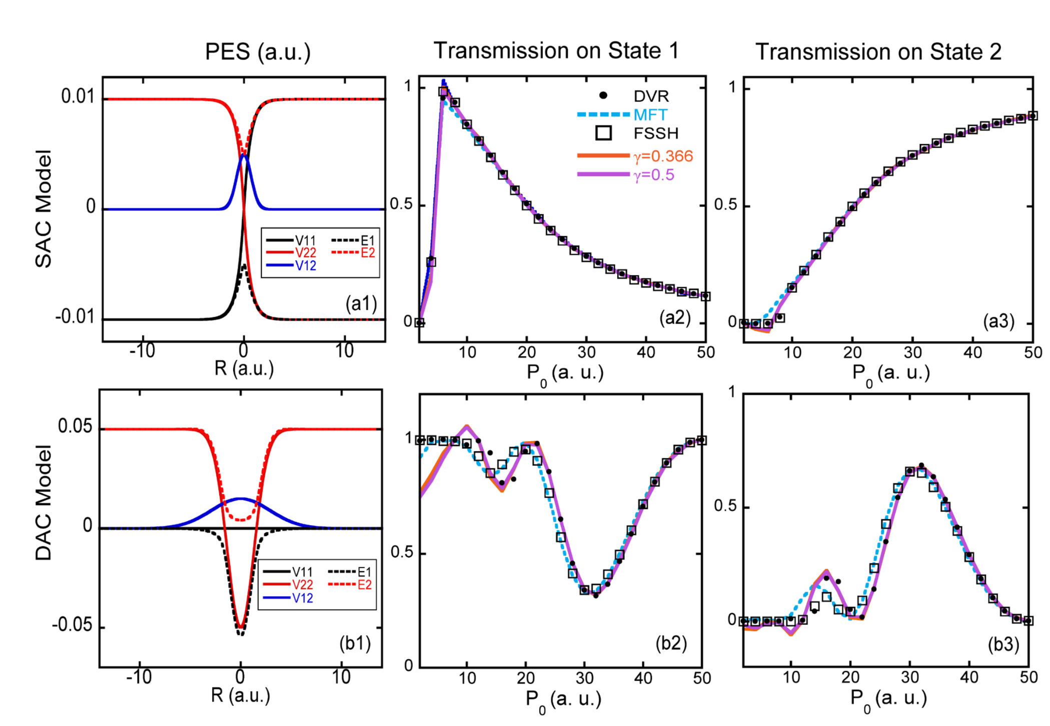

Figure 4: Transition probability on 1 or 2 surface with respect to initial momentum. Upper panel gives results of SAC (single avoid crossing) model, and the lower panel presents those of DAC (double avoid crossing) model.

■ Ultrafast photo-dissociation dynamics

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

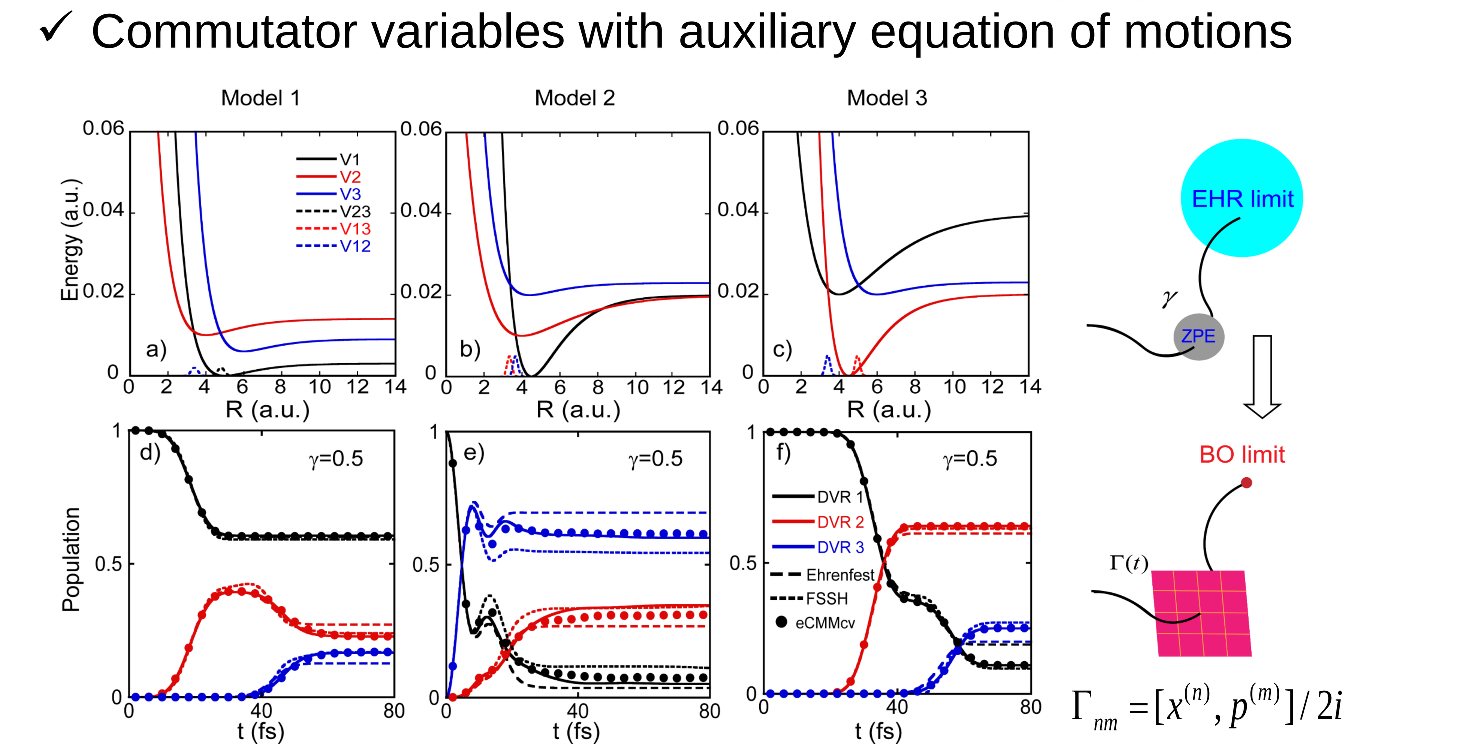

Figure 5: Population dynamics of eCMM with commutator variables

Summary

We develop a unified phase space dynamics framework for both nuclear and electronic DOFs. Constraint phase space for electronic with classical mapping trajectories captures better so-called "ZPE" effect in long time behavior. And as we introduced commutator variables, our scheme eCMMcv shows robust performance for either harmonic or anharmonic nonadiabatic systems.

References:

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