

Outline

1 Introduction

2 Local Coherent-State Approximation

- Basic idea
- Equations of motion

3 Application to model systems

- Small dimensional baths
- Large dimensional baths

4 Symplectic structure

- General considerations

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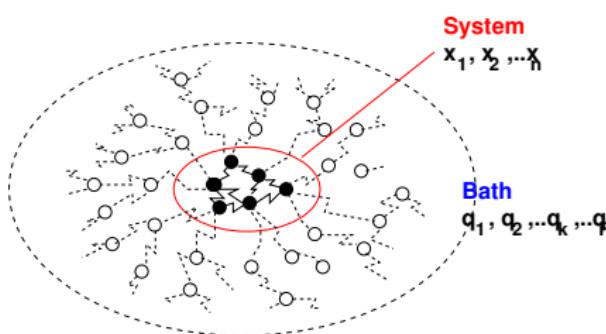
4 Symplectic structure

- General considerations



System-Bath dynamics

- **System:** relevant part, experimentally probed
⇒ Few, important DOFs
- **Bath:** irrelevant part, but responsible for energy transfer
⇒ Large number of DOFs of non-direct relevance



Quantum description is mandatory for inherently quantum systems and/or low-temperature baths..

System-Bath dynamics

..e.g. in surface science

- **sticking** of hydrogen atoms on cold surfaces
- **vibrational relaxation** of light adsorbates at surfaces
- surface **diffusion** of hydrogen atoms at low temperatures

System-Bath dynamics

Reduced equations of motion

First **project**, then **evolve**

- Density operator, $\rho^{sb} \rightarrow \rho^{sys}$
- (Approximate) equation of motion for $\rho_{\sim}^{sys}(t)$

..also REOM for system observables if Heisenberg picture is preferred

Unitary (approximate) evolution

First **evolve**, then **project**

- Approximate time-evolution of the whole system $\rho_{\sim}^{sb}(t)$
- Project whole state onto system space, $\rho^{sb} \rightarrow \rho^{sys}$

..also exact evolution if the bath is not too large

Reduced Equations of Motion

Reduced density operator:

$$\rho_S = \text{tr}_B[U(t, 0)\rho_0 U(t, 0)^\dagger]$$

Initial factorizing conditions

$$\rho(0) = \rho_S(0) \otimes \rho_B(0)$$

Dynamical map:

$$\rho_S(t) = V(t)\rho_S(0)$$

Markov Approximation, $\tau_B \ll \tau_R$

$$V(t_1)V(t_2) = V(t_1 + t_2), t_1, t_2 \geq 0$$

$V(t) = \exp(\mathcal{L}t)$ or equiv

$$\frac{d\rho_S(t)}{dt} = \mathcal{L}\rho_S$$

Lindblad's theorem

$$\mathcal{L} = \mathcal{L}_{\text{sys}} + \mathcal{L}_{\text{diss}}$$

- $\mathcal{L}_{\text{sys}}\rho_S = -i[H^S, \rho_S]$

- $\mathcal{L}_{\text{diss}}\rho_S = \sum_k \gamma_k (A_k \rho_S A_k^\dagger - \frac{1}{2}[A_k^\dagger A_k, \rho_S]_+)$

Approximate Unitary Evolution

Dissipative dynamics for $t < t_{rec} \propto \Delta\omega^{-1}$

$$H = H^{sys} + H^{coup} + H^{bath}$$

$$H^{bath} = \sum_{k=1}^F \left(\frac{p_k^2}{2m_k} + \frac{1}{2} m_k \omega_k^2 q_k^2 \right) \text{ and } H^{coup} = \sum_{k=1}^F f_k q_k$$

where $f_k = f_k(x)$ and eventually $\omega_k = \omega_k(x)$

- System-bath interactions are **local** in system coordinates
- Bath oscillators are (at least locally) **harmonic**

Approximate Unitary Evolution

Dissipative dynamics for $t < t_{rec} \propto \Delta\omega^{-1}$

$$H = H^{sys} + H^{env}$$

$$H^{sys} = H^{sys}(x, p)$$

$$H^{env} = H^{env}(q_1, p_1, \dots q_F, p_F; x)$$

- H^{env} is **local** in system coordinates
- H^{env} is approximately **harmonic** in bath coordinates

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Main ingredients

Local, approximately harmonic environment hamiltonian

$$H = H^{\text{sys}} + H^{\text{env}}$$

$$H^{\text{sys}} = H^{\text{sys}}(x, p)$$

$$H^{\text{env}} = H^{\text{env}}(q_1, p_1, \dots q_F, p_F; x)$$

- System **locality** \Rightarrow Discrete Variable Representation
- Bath **harmonicity** \Rightarrow Coherent-States



Basic idea

DVR and CSs

Main ingredients

Discrete Variable Representation (DVR)

- $P = P^\dagger, P = P^2$
- $\mathcal{E} = P\mathcal{H}$ interesting subspace
- $\mathcal{H} = L^2(\mathcal{M}), \mathcal{M} \supset \{x_\alpha\}$
e.g. for $\mathcal{M} = \mathbb{R}^N$

$$|\xi_\alpha\rangle = \frac{1}{\sqrt{N_\alpha}} P |x_\alpha\rangle$$

$$|\Delta_\alpha\rangle = P |x_\alpha\rangle$$

$$\langle \Delta_\alpha | \Delta_\beta \rangle = \Delta_\beta(x_\alpha) = N_\alpha \delta_{\alpha\beta}$$

$$V = V(x) \Rightarrow \langle \xi_\alpha | V | \xi_\beta \rangle \sim \delta_{\alpha\beta} V(x_\alpha)$$

Coherent-States (CSs)

$$\begin{aligned} H[\psi] &= \Delta p_\psi \Delta x_\psi \\ \delta H[\psi] = 0 &\Rightarrow (p - p_0) |\psi\rangle = \alpha(x - x_0) |\psi\rangle \\ \left\{ \frac{x}{2\Delta x} + i \frac{p}{2\Delta p} \right\} |\psi\rangle &= \left\{ \frac{x_0}{2\Delta x} + i \frac{p_0}{2\Delta p} \right\} |\psi\rangle \end{aligned}$$

$$(a - z) |\psi\rangle = 0 \rightarrow |z\rangle := |\psi\rangle$$

$$\Delta x = \sqrt{\hbar/2m\omega} \rightarrow H^{HO} = \hbar\omega(a^\dagger a + \frac{1}{2})$$

$$e^{-\frac{H^{HO}}{\hbar} t} |z_0\rangle = e^{-\frac{i}{2}\omega t} |z_t\rangle$$

$$z_t = e^{-i\omega t} z_0$$



LCSA *ansatz* for $T = 0$ K case

- DVR approximation **in system space**

$$|\Psi\rangle = \int dx |x\rangle \langle x| \Psi\rangle \approx \sum_{\alpha} |\xi_{\alpha}\rangle \langle \xi_{\alpha}| \Psi\rangle$$

$$\langle \xi_{\alpha} | \Psi\rangle_{sys} = C_{\alpha} |\Phi_{\alpha}\rangle_{bath}$$

- Hartree product approximation **to local bath states**

$$|\Phi_{\alpha}\rangle \approx |\phi_{\alpha}^1\rangle |\phi_{\alpha}^2\rangle \dots |\phi_{\alpha}^F\rangle$$

- Coherent-State approximation **to spfs**

$$|\phi_{\alpha}^k\rangle \approx |z_{\alpha}^k\rangle$$



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Basic idea

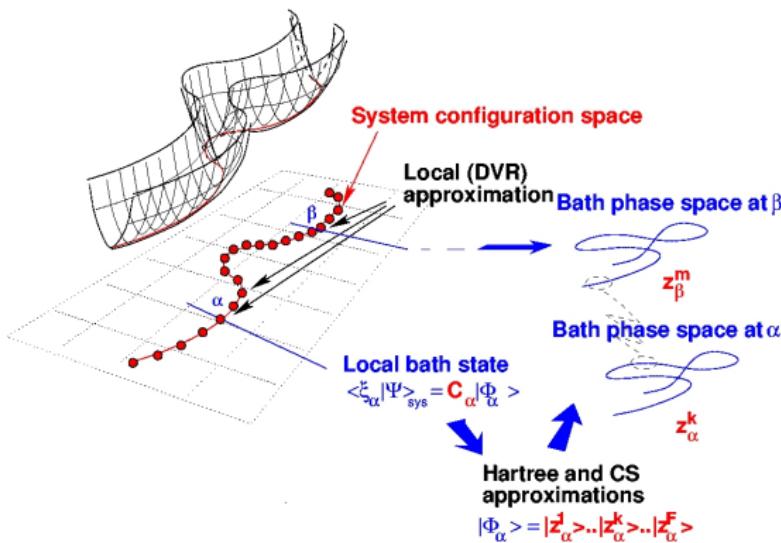
LCSA ansatz for $T = 0$ K case

Dynamical variables

- System: C_α
- Bath: z_α^k

$$|\Psi\rangle = \sum_\alpha C_\alpha |\xi_\alpha\rangle |Z_\alpha\rangle$$

$$|Z_\alpha\rangle = |z_\alpha^1\rangle |z_\alpha^2\rangle \dots |z_\alpha^F\rangle$$



Working equations

Dirac-Frenkel variational principle

$$\langle \delta \Psi | i\hbar \partial_t - H | \Psi \rangle = 0$$



$$i\hbar \dot{C}_\alpha = \sum_\beta H_{\alpha\beta}^{damp} C_\beta + v_\alpha^{\text{eff}} C_\alpha$$

$$i\hbar C_\alpha \dot{z}_\alpha^k = \sum_\beta H_{\alpha\beta}^{damp} (z_\beta^k - z_\alpha^k) C_\beta + C_\alpha \frac{\partial H_{\text{ord}}^{\text{env}}}{\partial a_k^\dagger} (\dots z_\alpha^{k*}, z_\alpha^k \dots; x_\alpha)$$



LCSA equations

Working equations: subsystem equations

- Damped hamiltonian:

$$H_{\alpha\beta}^{damp} = \langle \xi_\alpha | H^{sys} | \xi_\beta \rangle \langle Z_\alpha | Z_\beta \rangle = H_{\alpha\beta}^{sys} \langle Z_\alpha | Z_\beta \rangle$$

$$\langle Z_\alpha | Z_\beta \rangle = \exp \left(\Gamma_{\alpha\beta} - \frac{\Gamma_{\alpha\alpha}}{2} - \frac{\Gamma_{\beta\beta}}{2} \right) \text{ with } \Gamma_{\alpha\beta} = \sum_{k=1}^F z_\alpha^{k*} z_\beta^k$$

- Effective potential:

$$v_\alpha^{eff} = v_\alpha^{lmf} + v_\alpha^{gauge}$$

$$v_\alpha^{lmf} = \langle Z_\alpha | H^{env} | Z_\alpha \rangle = H_{ord}^{env} (..z_\alpha^{k*}, z_\alpha^k ..; x_\alpha)$$

$$v_\alpha^{gauge} = -i\hbar \sum_{k=1}^F \langle z_\alpha^k | \dot{z}_\alpha^k \rangle$$



LCSA equations

Working equations: bath equations

$$\dot{z}_{\alpha}^k = \dot{z}_{\alpha \text{ class}}^k + \dot{z}_{\alpha \text{ quant}}^k$$

- Classical ‘force’:

$$\dot{z}_{\alpha \text{ class}}^k = -\frac{i}{\hbar} \frac{\partial H_{\text{ord}}^{\text{env}}}{\partial a_k^\dagger} (\dots z_{\alpha}^{k*}, z_{\alpha}^k \dots; x_{\alpha})$$

e.g. for $H_{\text{ord}}^{\text{env}} = \sum_{k=1}^F \hbar \omega_k \left(a_k^\dagger a_k + \frac{1}{2} \right) - \sum_{k=1}^F \left(\lambda_k a_k^\dagger + \lambda_k^\dagger a_k \right)$

one gets $\frac{\partial H_{\text{ord}}^{\text{env}}}{\partial a_k^\dagger} = \hbar \omega_k z_{\alpha}^k - \lambda_k(x_{\alpha})$

- Quantum ‘force’:

$$\dot{z}_{\alpha \text{ quant}}^k = -\frac{i}{\hbar C_{\alpha}} \sum_{\beta} H_{\alpha \beta}^{\text{damp}} (z_{\beta}^k - z_{\alpha}^k) C_{\beta}$$





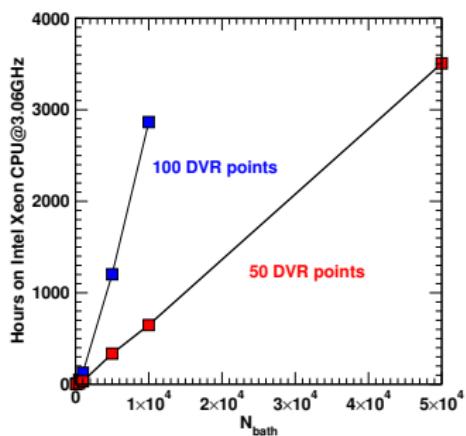
Working equations: properties

By using the Dirac-Frenkel variational principle, one gets for free

- Norm conservation
- Energy conservation
- ..and more generally a symplectic structure
- computational cost $\propto F^\alpha$

Working equations: properties

Power-law scaling



(No inter-mode coupling)

$T > 0$ case

$$\rho^{sb} = \sum_i p_i |\Psi_i^{LCSA}\rangle \langle \Psi_i^{LCSA}|$$

⇒ Independent wavepacket propagation

E.g. $\rho^{sb}(0) = \rho^{sys}(0) \otimes \rho_{\beta}^{bath}(0)$, harmonic bath in thermal equilibrium, $\rho_{\beta} = \Pi_k^{\otimes} \rho_{\beta}^k$

$$\rho_{\beta}^k = \int d^2 z w_{\beta}^k(|z|^2) |z_{\beta/2}\rangle \langle z_{\beta/2}| \quad w_{\beta}^k(s) = \frac{1-e^{-\beta \hbar \omega k}}{\pi} e^{-s(1-e^{-\beta \hbar \omega k})}$$

⇒ Monte Carlo sampling of $\int d^2 z^1 d^2 z^2 .. d^2 z^F$ for initial conditions

LCSA equations

Comparison with Gaussian-MCTDH

- $|\Psi\rangle = \sum_{\alpha} C_{\alpha} |\xi_{\alpha}\rangle |z_{\alpha}^1\rangle \dots |z_{\alpha}^F\rangle$
- System-states $|\xi_{\alpha}\rangle$ are time-independent
- For each α there is one CS product, $|z_{\alpha}^1\rangle \dots |z_{\alpha}^F\rangle$
- Different $\alpha \rightarrow$ different Z_{α}
- Orthogonal configurations
 $|\Psi_{\alpha}\rangle = |\xi_{\alpha}\rangle |z_{\alpha}^1\rangle \dots |z_{\alpha}^F\rangle$,
 $\langle \Psi_{\alpha} | \Psi_{\beta} \rangle = \delta_{\alpha\beta}$
- $|\Psi\rangle = \sum_{i_0, I} C_{i_0, I} |\phi_{i_0}\rangle |z_{i_1}^1\rangle \dots |z_{i_F}^F\rangle$
- System-states $|\phi_{i_0}\rangle$ are time-dependent
- For each i_0 there is a number of CS products, $\{|z_{i_1}^1\rangle \dots |z_{i_F}^F\rangle\}_I = \{Z_I\}_I$
- Different $i_0 \rightarrow$ same $\{Z_I\}_I$
- Non fully orthogonal configurations
 $|\Psi_{i_0, I}\rangle = |\phi_{i_0}\rangle |z_{i_1}^1\rangle \dots |z_{i_F}^F\rangle$,
 $\langle \Psi_{i_0, I} | \Psi_{j_0, J} \rangle = \delta_{i_0, j_0} \langle Z_I | Z_J \rangle$

LCSA is a selected-configuration G-MCTDH variant, with simpler eq.s of motion because it is tailored to system-bath problems

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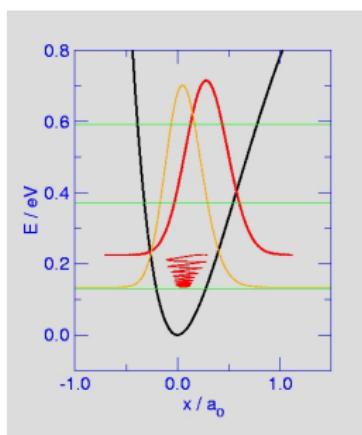
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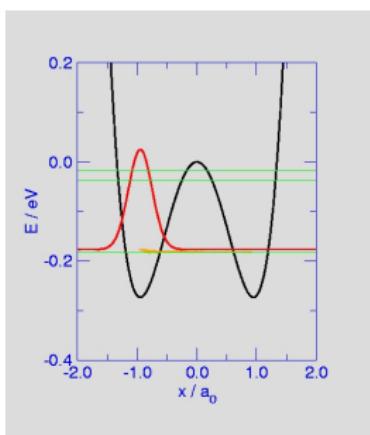


Model systems

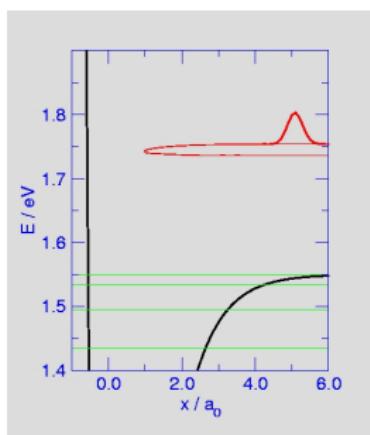
Subsystem: H atom



Vibrational
dynamics



Tunneling
dynamics



Sticking
dynamics

Model systems

Bath

Truncated, discretized Ohmic bath

$$H^{bc} = H^{HO} + H^{coup}$$

$$H^{coup} = - \sum_k (\lambda_k^\dagger a_k + \lambda_k a_k^\dagger) \quad \lambda_k = f(x) \Lambda_k$$

$$J(\omega) = \pi \sum_k \Lambda_k^2 \delta(\omega - \omega_k) = m\omega\gamma(\omega)$$

Ohm $\Rightarrow J(\omega) = m\omega\gamma$

$$\omega_k = k\Delta\omega = k\omega^{cutoff}/F \quad \omega^{cutoff} \gg \omega_{sys}$$

$$\Lambda_k = \sqrt{\frac{m\gamma\omega_k\Delta\omega}{\pi}}$$

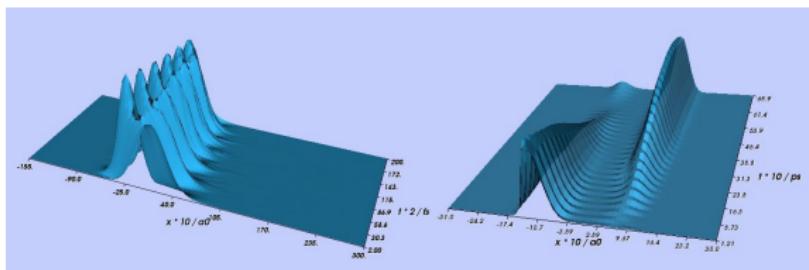
- ‘Shape function’ $f(x)$
- Relaxation time γ^{-1}

$$f(x) = \begin{cases} \frac{1-e^{\alpha x}}{\alpha} & \text{vibrational dyn} \\ x & \text{tunneling dyn} \end{cases}$$

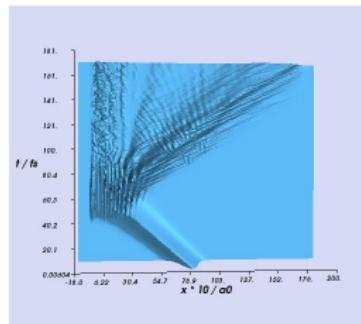
$$\gamma^{-1} = 10 - 1000 \text{ fs}$$

Model systems

Subsystem density matrix



Vibrational
dynamics



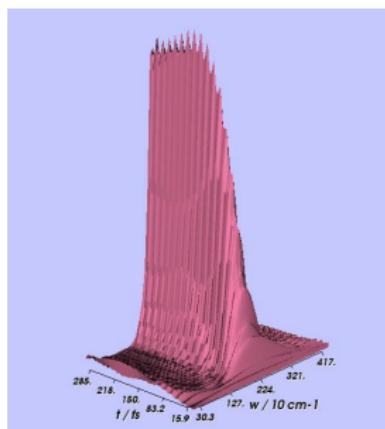
Tunneling
dynamics

Sticking
dynamics

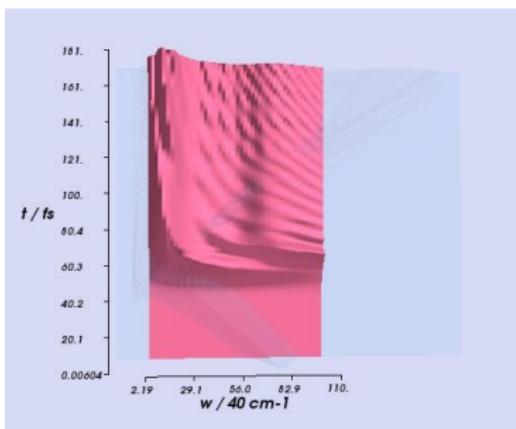


Model systems

Bath occupation numbers



Vibrational dynamics

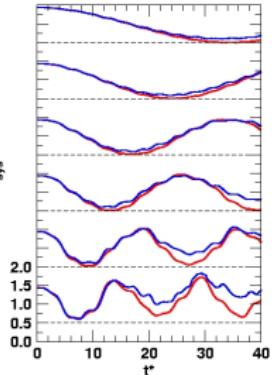
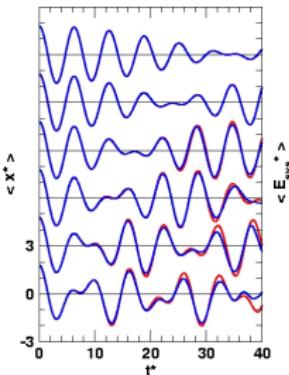


Sticking dynamics

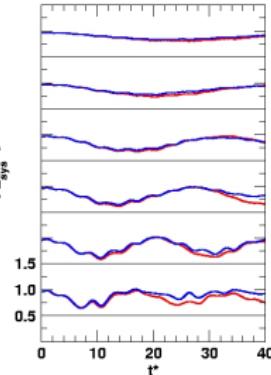
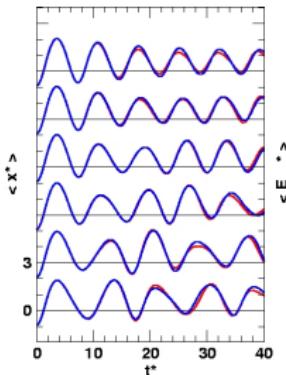
Small baths

Vibrational dynamics

1D bath



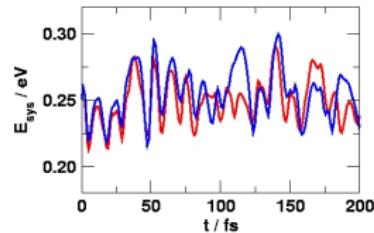
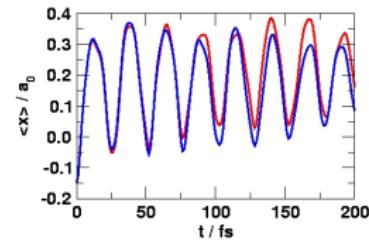
Harmonic oscillator



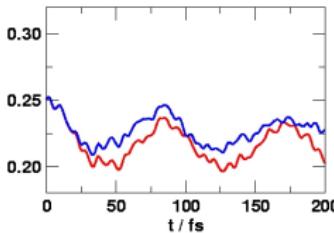
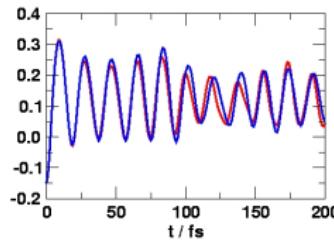
Morse oscillator



Vibrational dynamics



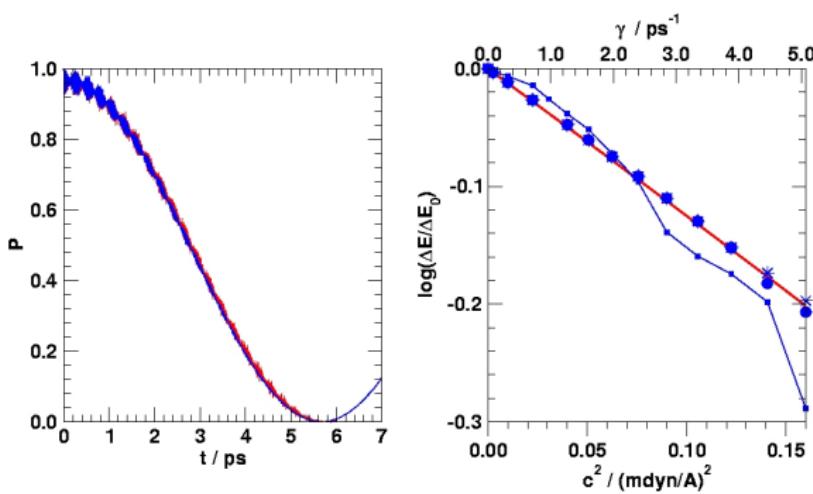
Morse + 2D bath, $\gamma^{-1} = 8 \text{ fs}$



Morse + 3D bath, $\gamma^{-1} = 32 \text{ fs}$

Tunneling dynamics

1D bath



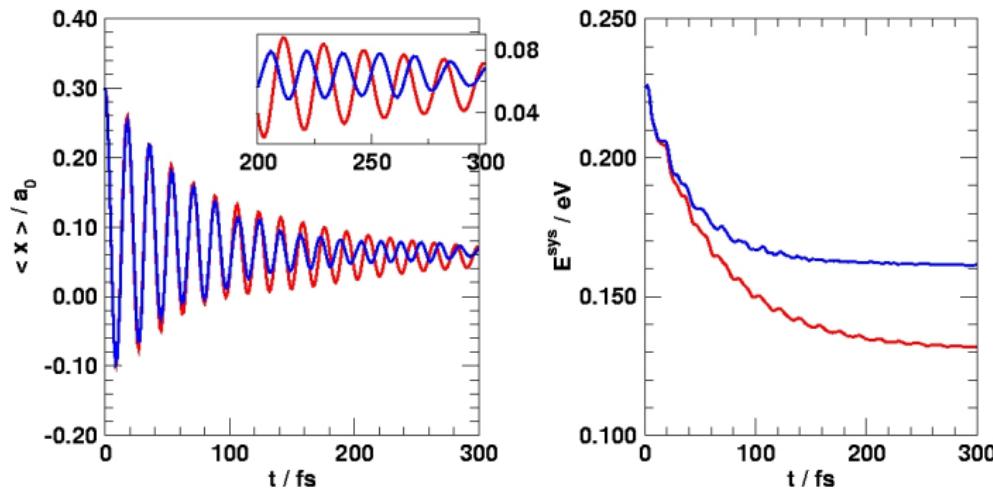
Double well, $E_b \sim 6 \text{ Kcal mol}^{-1}$, $\omega_{\text{sys}} = 1530 \text{ cm}^{-1}$



Large baths

Vibrational relaxation

Standard LCSA

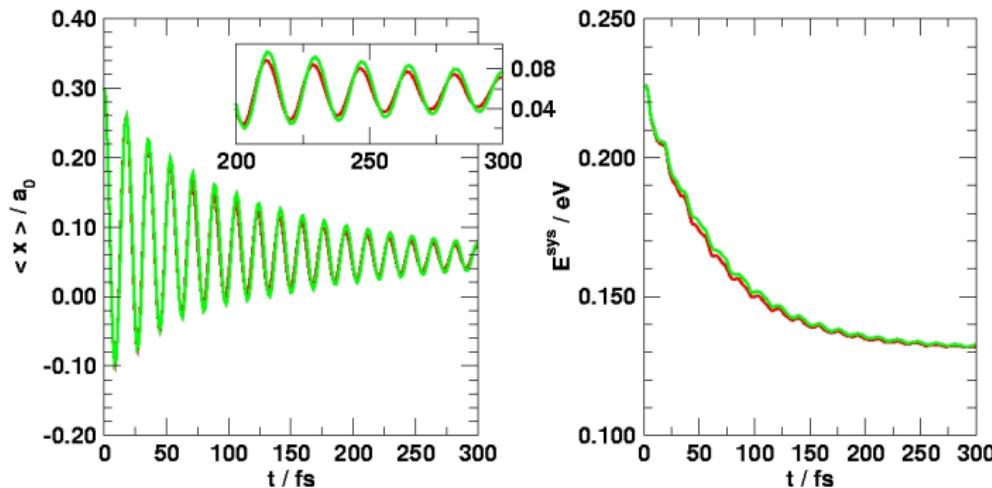


Morse + 50D bath, $\gamma^{-1} = 50$ fs

Large baths

Vibrational relaxation

Damped LCSA



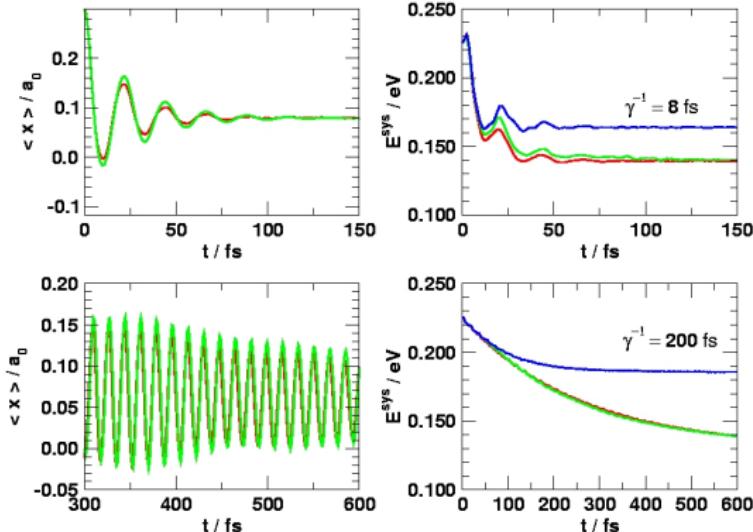
Morse + 50D bath, $\gamma^{-1} = 50 \text{ fs}$, $\eta^{-1} = 12.5 \text{ fs}$



Large baths

Vibrational relaxation

Damped LCSA



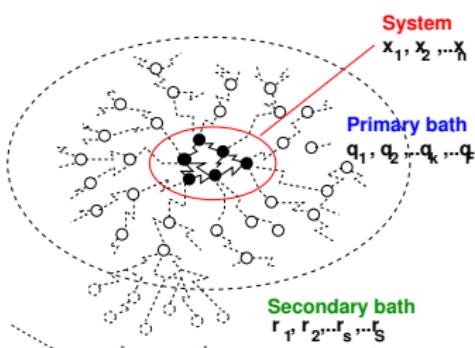
Morse + 50D bath, $\eta^{-1} = 12.5 \text{ fs}$



Large baths

“Damped” LCSA

- LCS approximation to system + p-bath + s-bath
- Classical approximation to s-bath, $z_\alpha^s \sim z_\beta^s$
- Continuum limit, Ohmic s-bath, $T=0$ K



$$\dot{z}_\alpha^k = iX_\alpha^k - \frac{\varsigma_k(t)}{2\Delta p_k} + \frac{\eta_k}{\omega_k} \operatorname{Re}(X_\alpha^k)$$

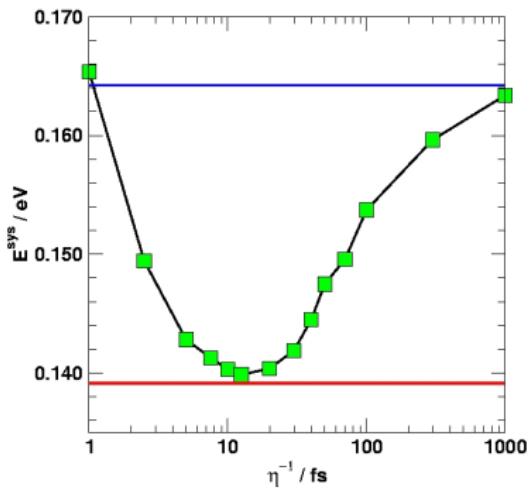
$$X_\alpha^k = \frac{1}{\hbar C_\alpha} \sum_\beta H_{\alpha\beta}^{damp}(z_\beta^k - z_\alpha^k) + \frac{1}{\hbar} \frac{\partial H_{ord}^{env}}{\partial a_k^\dagger} (\dots z_\alpha^{k*}, z_\alpha^k; x_\alpha)$$

$$\eta_k(t) = \frac{1}{m_k} \sum_s \frac{A_s^2}{m_k \omega_s^2} \cos(\omega_s t) \rightarrow \eta_k(t) = 2\eta_k \delta(t)$$

$$\varsigma_k(t) = \sum_s A_s [(q^s(0) - q_{eq}^s(0)) \cos(\omega_s t) + \frac{p^s(0)}{m_s \omega_s} \sin(\omega_s t)] \rightarrow 0$$

Large baths

“Damped” LCSA

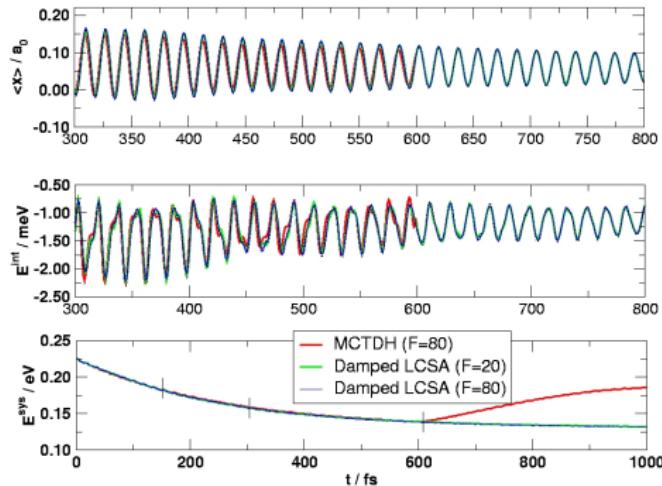


η Optimization: Morse + 50D bath, $\gamma^{-1} = 50$ fs, $t = 150.0$ fs

Large baths

“Damped” LCSA

True *dissipative* dynamics



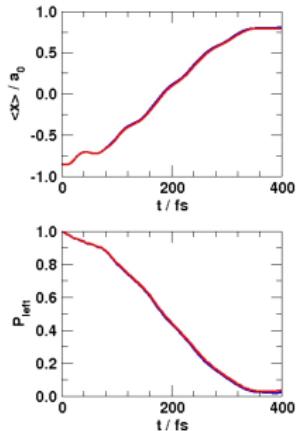
Recurrence problem removed

Morse + nD bath, $\omega^{\text{cutoff}} = 2\omega_{\text{sys}}$, $\gamma^{-1} = 200 \text{ fs}$, $\eta^{-1} = 12.5 \text{ fs}$

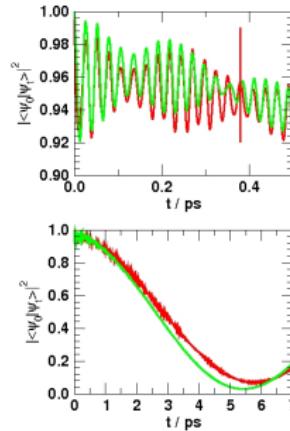
Large baths

Tunneling dynamics

Double well + 50D bath



$E_b \sim 2 \text{ Kcal mol}^{-1}$, $\omega_{\text{sys}} = 816 \text{ cm}^{-1}$
 $\omega^{\text{cutoff}} = 940 \text{ cm}^{-1}$, $\gamma^{-1} = 50 \text{ fs}$
 Standard LCSA, $\eta^{-1} = \infty \text{ fs}$

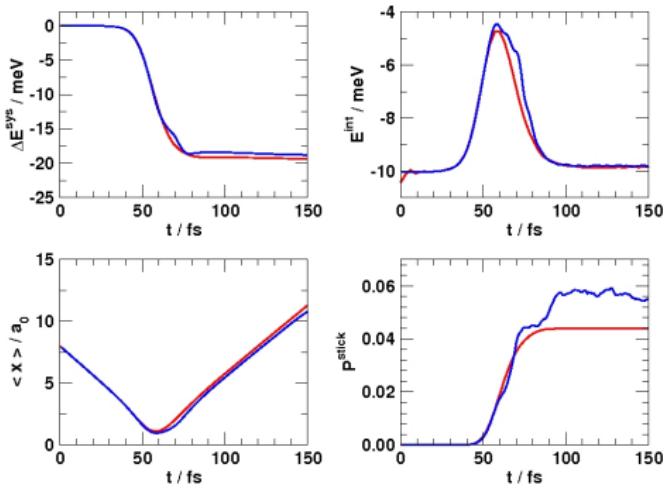


$E_b \sim 6 \text{ Kcal mol}^{-1}$, $\omega_{\text{sys}} = 1530 \text{ cm}^{-1}$
 $\omega^{\text{cutoff}} = 4390 \text{ cm}^{-1}$, $\gamma^{-1} = 50 \text{ fs}$
 Damped LCSA, $\eta^{-1} = 40 \text{ fs}$



Large baths

Sticking dynamics

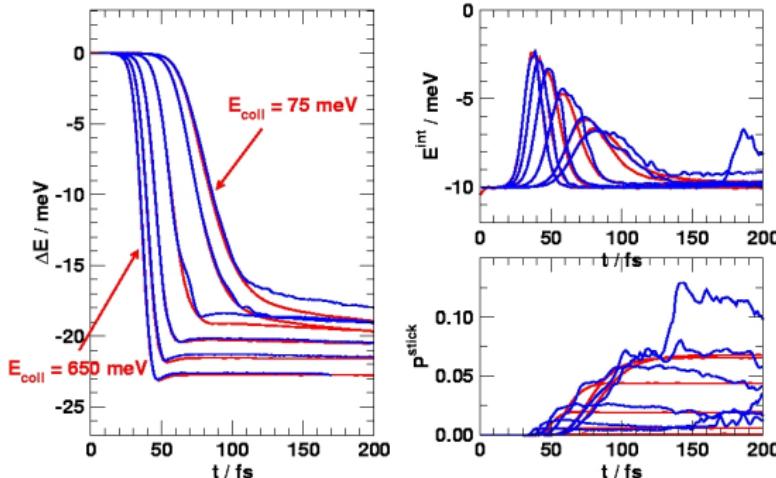
 $E_{coll} = 200 \text{ meV}$ 

Morse + 50D bath, $\gamma^{-1} = 1.0 \text{ ps}$

Large baths

Sticking dynamics

Overview

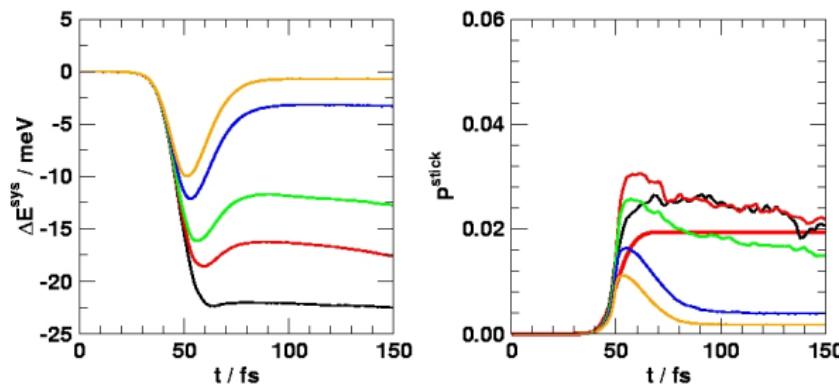


Morse + 50D bath, $\gamma^{-1} = 1.0 \text{ ps}$

Large baths

Sticking dynamics

Damped LCSA



Morse + 50D bath, $E_{\text{coll}} = 350 \text{ meV}, \gamma^{-1} = 1.0 \text{ ps}$

Outline

1 Introduction

2 Local Coherent-State Approximation

- Basic idea
- Equations of motion

3 Application to model systems

- Small dimensional baths
- Large dimensional baths

4 Symplectic structure

- General considerations

Generalities

Hamiltonian flows

Symplectic manifold (M, ω)

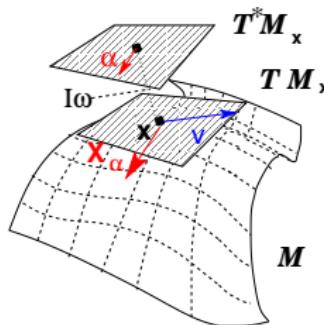
Manifold equipped with a *closed, non-degenerate* 2-form ω , $\omega = \sum \omega_{ij} dx^i dx^j$

- **Non-degeneracy** ($|\omega_{ij}| \neq 0$):
 $\alpha = \sum \alpha_i dx^i \leftrightarrow \mathbf{X}_\alpha$, $\omega(\mathbf{X}_\alpha, \mathbf{v}) = \alpha(\mathbf{v})$
 α has an associated *flow*, $\dot{x} = \mathbf{X}_\alpha$

In particular, $H \xrightarrow{\quad} dH \xleftarrow{\quad} \mathbf{X}_H$

\Rightarrow **Hamiltonian flow**, $\dot{\mathbf{x}} = \mathbf{X}_H$
 $dH(\mathbf{X}_H) = dH/dt = \omega(\mathbf{X}_H, \mathbf{X}_H) = 0$

- **Closedness** ($d\omega = 0$):
 $\mathcal{L}_{X_H}\omega = 0$



e.g. classical Phase-Space is a cotangent bundle $M = T^*(C)$

\Rightarrow natural, built-in symplectic form,
 $\omega = d\alpha, \alpha = \sum y_i dx^i$



Generalities

Hamiltonian flows in variational QD

Time-Dependent Variational Principle $\delta S = 0$

$$L = \frac{i\hbar}{2} \frac{\langle \Psi | \dot{\Psi} \rangle - \langle \dot{\Psi} | \Psi \rangle}{\langle \Psi | \Psi \rangle} - \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

Sample space $\Rightarrow M$ with coordinates x^i (**variational parameters**) $\rightarrow |\Psi(x)\rangle$,

$$L = \sum \dot{x}^i Z_i(\mathbf{x}) - \mathcal{H}(\mathbf{x})$$

- $\alpha = \sum Z_i dx^i \Rightarrow \omega = d\alpha$
If $\omega = \{\omega_{ij}\}$, $\omega_{ij} = \partial Z_i / \partial x^j - \partial Z_j / \partial x^i$ is non-singular $\Rightarrow (M, \omega)$ is symplectic
- Variational flow:

$$\sum \omega_{ij} \dot{x}^i = \frac{\partial \mathcal{H}}{\partial x^j}$$

\Rightarrow the **variational flow** is the **hamiltonian flow** of the hamiltonian $\mathcal{H}(\mathbf{x})$

$$\{f, g\} := \omega(\mathbf{X}_f, \mathbf{X}_g) = \sum \frac{\partial f}{\partial x^i} \frac{\partial g}{\partial x^i} \xi^{ij} \quad \xi = \omega^{-1}$$

Summary

The Local Coherent-State Approximation is reasonably accurate and computationally cheap to study

- vibrational relaxation
- tunneling
- sticking

..dynamics in the quantum regime.

It experiences numerical problems but they might be solved in the near future with robust, symplectic propagation schemes

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