Multiconfigurational Gaussian Wavepacket Dynamics: Interpolating between Accurate Quantum Dynamics and the Quantum-Classical Limit

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Topics

1. G-MCTDH
   - Preamble: MCTDH, G-MCTDH & vMCG
   - Quantum-Semiclassical MCTDH
   - Density Matrices & GWP/Langevin Dynamics

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2. Two-Layer/Multi-Layer G-MCTDH
   - Two-Layer Extension – Concept
   - Equations of Motion
   - Applications: Energy Transport in a Molecular Chain, Spin-Boson System

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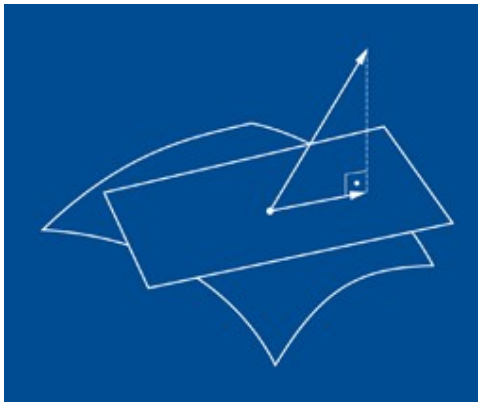
   - Two-Layer Extension – Concept
   - Equations of Motion
   - Applications: Energy Transport in a Molecular Chain, Spin-Boson System
3. Quantum-Classical Limit of G-MCTDH
   - Semiclassically Scaled G-MCTDH
   - Quantum-Classical Dynamics
   - Variational Multiconfigurational Ehrenfest Dynamics

Approximate Wavefunctions from the Dirac-Frenkel Variational Principle



C. Lubich, From Quantum to Classical Molecular Dynamics: Reduced Models and Numerical Analysis, Zürich (2008)

Dirac-Frenkel (DF) variational principle:

$\langle \delta\Psi | \hat{H} - i\frac{\partial}{\partial t} | \Psi \rangle = 0 \quad \longrightarrow$ dynamical equation for $\dot{\Psi}$

where $\delta\Psi \in \mathscr{T}_\Psi \mathscr{M}$ (tangent space wrt the approximate manifold $\mathscr{M}$ on which the wavefunction is defined)

Dirac 1930, Frenkel 1934, McLachlan 1964

- the time derivative is then given by
  $\dot{\Psi} = \mathscr{P}(\Psi)\frac{1}{i}\hat{H}\Psi$
  where $\mathscr{P}(\Psi)$ projects onto the tangent space
- the residual is minimized: $||\dot{\Psi} - \frac{1}{i}\hat{H}\Psi|| = \min$
- norm conservation, energy conservation
- symplectic flow

Unitary Dynamics in Many Dimensions: MCTDH

$$\Psi(r,t) = \sum_J A_J(t)\ \Phi_J(r,t) \equiv \sum_{j_1=1}^{n_1} \dots \sum_{j_N=1}^{n_N} A_{j_1 \dots j_N}(t)\, \varphi_{j_1}^{(1)}(r_1,t) \dots \varphi_{j_N}^{(N)}(r_N,t)$$

- Multi-Configuration Time-Dependent Hartree: tensor approximation scheme
  Meyer, Manthe, Cederbaum, Chem. Phys. Lett. **165**, 73 (1990), Beck et al., Phys. Rep. **324**, 1 (2000)
- EoM's from the Dirac-Frenkel variational principle: $\langle \delta\Psi | \hat{H} - i\frac{\partial}{\partial t} | \Psi \rangle = 0$
- MCTDH takes one to 50-100 modes; exponential scaling alleviated
- restriction on the form of the potential: sums over products

- related multi-layer variant (ML-MCTDH) goes up to 1000 modes
  Wang, Thoss, J. Chem. Phys. 119, 1289 (2003), Manthe, J. Chem. Phys. 128, 164116 (2008), Vendrell, Meyer, *ibid* 134, 044135 (2011)
- related MCTDH-F (fermion) and MCTDH-B (boson) methods
  Kato, Kono, Chem. Phys. Lett. 392, 533 (2004), Nest, Klamroth, Saalfrank, J. Chem. Phys. 122, 124102 (2005)
  Alon, Streltsov, Cederbaum, Phys. Lett. A 362, 453 (2007)
- density matrix variant
  Raab, Burghardt, Meyer, J. Chem. Phys. 111, 8759 (1999)
- hybrid approaches: e.g., Gaussian-based variant (G-MCTDH, vMCG)
  Burghardt, Meyer, Cederbaum, J. Chem. Phys. 111, 2927 (1999), Worth, Burghardt, Chem. Phys. Lett. 368, 502 (2003)

MCTDH – Equations of Motion

Coupled system of coefficient equations and low-dimensional non-linear equations for single-particle functions (SPFs) $\varphi^{(\kappa)}$:

coefficients: $$i\frac{dA_J}{dt} = \sum_L \langle \Phi_J | H | \Phi_L \rangle A_L$$

SPFs: $$i\frac{\partial \varphi^{(\kappa)}}{\partial t} = \left(\hat{1} - \hat{P}^{(\kappa)}\right)\left[\rho^{(\kappa)}\right]^{-1} \hat{H}^{(\kappa)} \varphi^{(\kappa)}$$

Meyer, Manthe, Cederbaum, CPL **165**, 73 (1990), Beck et al., Phys. Rep. **324**, 1 (2000)

- $\hat{P}^{(\kappa)} = \sum_j |\varphi_j^{(\kappa)}\rangle\langle\varphi_j^{(\kappa)}|$ is the time-dependent projector on the κth subspace
- $\hat{H}_{ij}^{(\kappa)} = \langle \psi_i^{(\kappa)} | \hat{H} | \psi_j^{(\kappa)} \rangle$ are mean-field Hamiltonian matrix elements
- $\rho_{ij}^{(\kappa)} = \langle \psi_i^{(\kappa)} | \psi_j^{(\kappa)} \rangle$ are reduced density matrix elements in the κth subspace
- here, we introduced the single-hole functions (SHFs): $\Psi = \sum_j \varphi_j^{(\kappa)} \psi_j^{(\kappa)}$
- recent approaches to "repair" singularity problem ($[\rho^{(\kappa)}]^{-1}$)

Manthe, J. Chem. Phys. **142**, 244109 (2015)
Lubich, Appl. Math. Res. Express 2, 311-328 (2015), Kloss, Burghardt, Lubich. J. Chem. Phys., 146, 174107 (2017)

Implementation of Projector Splitting Integrator for MCTDH

Lubich, Appl. Math. Res. eXpress 2015, 311 (2015), Kloss, Burghardt, Lubich, J. Chem. Phys. 146, 174107 (2017).

MCTDH equations in tensor notation:

$$i\dot{C} = \sum_q a_q C \times_{n=1}^{d} \mathbf{H}^q_{spf,n} \tag{1}$$

$$\dot{\mathbf{U}}_n = \sum_q a_q \left(\mathbf{I} - \mathbf{P}_n\right) \mathbf{H}^q_{prim,n} \mathbf{U}_n \mathscr{H}^q_n \rho_n^{-1} \tag{2}$$

To obtain Lubich's projector-splitting scheme, replace (2) with the following, where $\mathbf{K}_n = \mathbf{U}_n \mathbf{S}_n$ can be understood as modified SPFs that are *not* orthonormal – while the single-hole functions (SHFs) have been orthogonalized,

$$i\dot{\mathbf{K}}_n = \sum_q a_q \mathbf{H}^q_{prim,n} \mathbf{U}_n \mathbf{S}_n \mathscr{H}^q_n$$

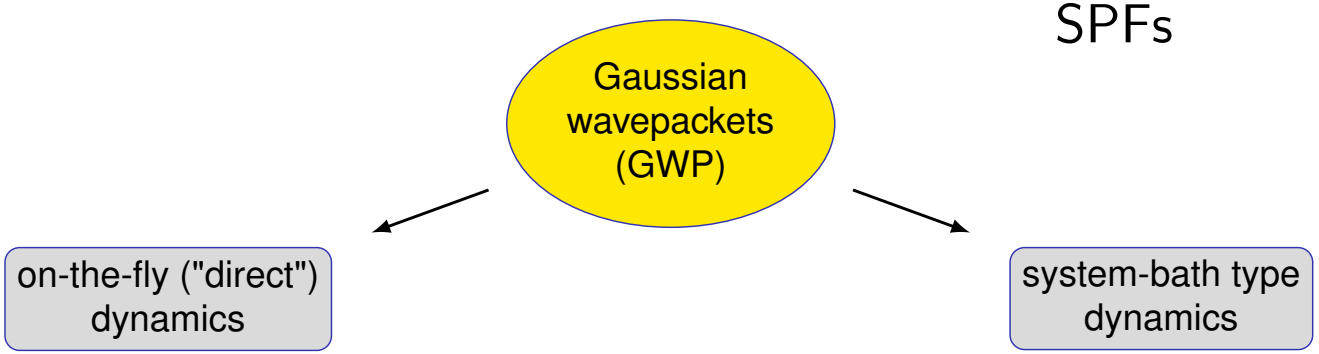
$$i\dot{\mathbf{S}}_n = \sum_q a_q \mathbf{H}^q_{SPF,n} \mathbf{S}_n \tilde{\mathscr{H}}^q_n$$

- The inverse of the density matrix no longer appears!

Gaussian-based MCTDH (G-MCTDH)

Burghardt, Meyer, Cederbaum, J. Chem. Phys. 111, 2927 (1999)

$$\Psi(r,t) = \sum_J A_J(t)\Phi_J(r,t) \quad ; \quad \Phi_J(r,t) = \underbrace{\prod_{\kappa=1}^{M} \varphi_{j_\kappa}^{(\kappa)}(r_\kappa,t)}_{\text{SPFs}} \underbrace{\prod_{\kappa=M+1}^{P} g_{j_\kappa}^{(\kappa)}(r_\kappa,t)}_{\text{GWPs}}$$



$\Psi(r,t) = \sum_j A_j(t) g_j(r,t)$ (vMCG)

Burghardt et al., JCP 119, 5364 (2003), 129, 174104 (2008)

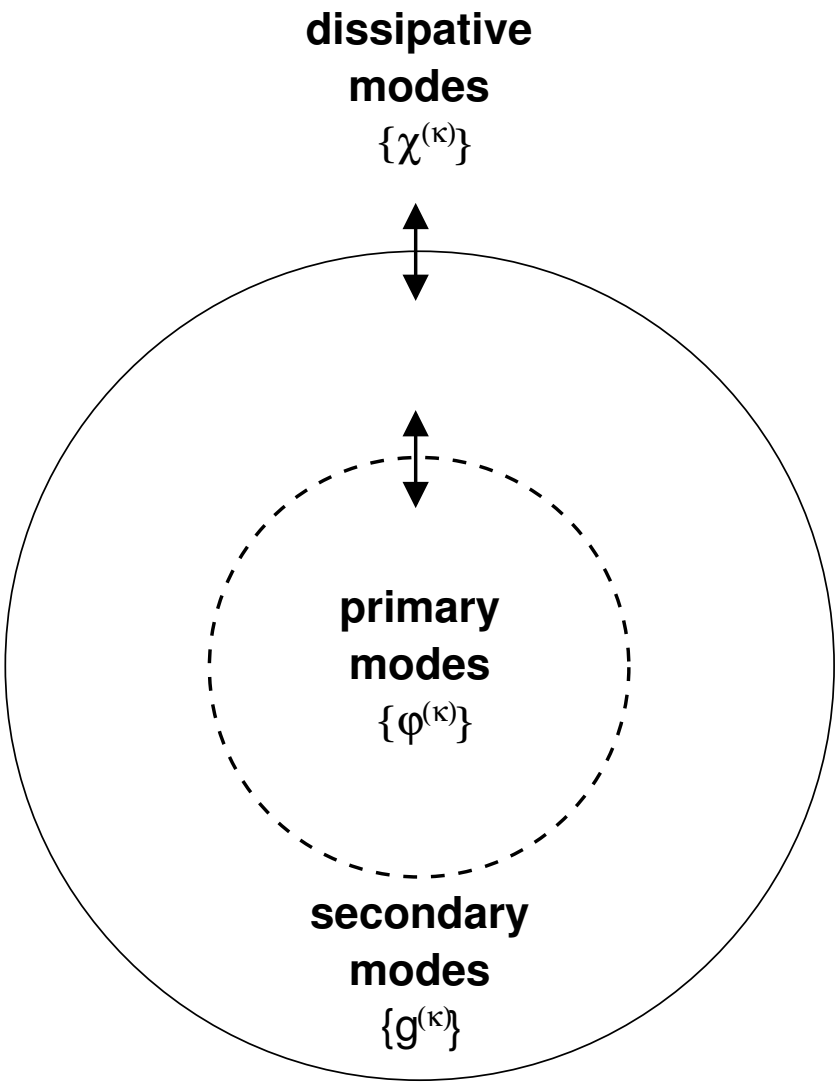
variational Multi-Configurational Gaussians

Worth, Burghardt, Chem. Phys. Lett. 368, 502 (2003), Richings et al., Int. Rev. Phys. Chem., 34, 265 (2015)

Related approaches:

- variational GWPs: Metiu & co (1985), Martinazzo & co (2007): LCSA (Local Coherent State Approximation)
- non-variational GWPs: Martínez & co (1996): FMS (Full Multiple Spawning); Shalashilin & co (2000): CCS (Coupled Coherent States); Batista & co (2003): MP/SOFT (Matching Pursuit)

G-MCTDH = Quantum-Semiclassical MCTDH



$$\Psi(r,t) = \sum_J A_J(t)\ \Phi_J(r,t)$$

$$\text{with } \Phi_J(r,t) = \prod_{\kappa=1}^{M} \varphi_{j_\kappa}^{(\kappa)}(r_\kappa,t)$$

Multi-Configuration Time-Dependent Hartree

Meyer et al., CPL **165**, 73 (1990), Beck et al., Phys. Rep. **324**, 1 (2000)

Gaussian-based hybrid method: G-MCTDH

$$\Phi_J(r,t) = \underbrace{\prod_{\kappa=1}^{M} \varphi_{j_\kappa}^{(\kappa)}(r_\kappa,t)}_{\text{primary nodes}} \quad \underbrace{\prod_{\kappa=M+1}^{P} g_{j_\kappa}^{(\kappa)}(r_\kappa,t)}_{\text{secondary modes}}$$

Burghardt, Meyer, Cederbaum, J. Chem. Phys. **111**, 2927 (1999)
Burghardt, Giri, Worth J. Chem. Phys. **129**, 174104 (2008)

Variational Dynamics

$$\Psi(r_1,\ldots,r_P,t) = \sum_{j_1}\cdots\sum_{j_P} A_{j_1\ldots j_P}(t) \prod_{\kappa=1}^{M} \varphi_{j_\kappa}^{(\kappa)}(r_\kappa,t) \prod_{\kappa=M+1}^{P} g_{j_\kappa}^{(\kappa)}(r_\kappa,t)$$

$$g_j^{(\kappa)}(r_\kappa,t) = \exp\left[r_\kappa \cdot a_j^{(\kappa)}(t) r_\kappa + \xi_j^{(\kappa)}(t)\cdot r_\kappa + \eta_j^{(\kappa)}(t)\right]$$

multidimensional Gaussian functions:

- "thawed" (TG) vs. "frozen" (FG)
- quasi-classical motion for $\xi_j = -2a_j q_j + i p_j$
- analytical integrals

Dirac-Frenkel variational principle:

$$\langle \delta\Psi | H - i\frac{\partial}{\partial t} | \Psi \rangle = 0 \quad \longrightarrow \quad \text{dynamical equations for } \Lambda_j^{(\kappa)} = (a_j^{(\kappa)}, \xi_j^{(\kappa)}, \eta_j^{(\kappa)})$$

- up to 50-100 modes – exponential scaling problem ($\sim f N^{f+1}$) is alleviated

Dynamical Equations

Burghardt, Meyer, Cederbaum, JCP 111, 2927 (1999)

coefficients: $$iS\dot{A} = \left[H - i\tau\right]A$$

SPFs (primary modes): $$i\dot{\varphi}^{(\kappa)} = \left(\hat{1} - \hat{P}^{(\kappa)}\right)\left[\rho^{(\kappa)}\right]^{-1}\hat{H}^{(\kappa)}\varphi^{(\kappa)}$$

GWPs (secondary modes): $$iC^{(\kappa)}\dot{\Lambda}^{(\kappa)} = Y^{(\kappa)}$$

$$S_{jl}^{(\kappa)} = \langle g_j^{(\kappa)} | g_l^{(\kappa)} \rangle \quad ; \quad \tau_{jl}^{(\kappa)} = \langle g_j^{(\kappa)} | \frac{\partial g_l^{(\kappa)}}{\partial t} \rangle$$

$$C_{j\alpha,l\beta}^{(\kappa)} = \rho_{jl}^{(\kappa)} \langle \frac{\partial g_j^{(\kappa)}}{\partial \lambda_{j\alpha}^{(\kappa)}} \Big| (\hat{1} - \hat{P}^{(\kappa)}) \Big| \frac{\partial g_l^{(\kappa)}}{\partial \lambda_{l\beta}^{(\kappa)}} \rangle \quad ; \quad Y_{j\alpha}^{(\kappa)} = \sum_l \langle \frac{\partial g_j^{(\kappa)}}{\partial \lambda_{j\alpha}^{(\kappa)}} \Big| (\hat{1} - \hat{P}^{(\kappa)}) \hat{H}_{jl}^{(\kappa)} \Big| g_l^{(\kappa)} \rangle$$

- evolution under multiconfigurational mean-field Hamiltonian
- coupled, variational equations for Gaussian parameters
- correlations between primary vs. secondary subspace
- analogous equations for density matrix evolution Burghardt, Meyer, Cederbaum, JCP 111, 2927 (1999)

Symplectic Structure of "VP Mechanics"

- variational formulation via action integral: $\delta\mathscr{S} = \delta\int dt\,\mathscr{L} = 0$

classical mechanics

$$\mathscr{L} = \sum_k p_k\dot{q}_k - H(q_k,p_k)$$

$$\dot{q}_k = \frac{\partial H}{\partial p_k}$$

$$\dot{p}_k = -\frac{\partial H}{\partial q_k}$$

VP mechanics

$$\mathscr{L} = \sum_{\alpha=1} S^{(0\alpha)}\dot{\lambda}_\alpha - \langle\Psi|H|\Psi\rangle$$

identify: $\tilde{p}_\alpha = S^{(0\alpha)} = i\langle\Psi|\frac{\partial\Psi}{\partial\lambda_\alpha}\rangle$

$$\dot{\lambda}_\alpha = \frac{\partial\langle H\rangle}{\partial\tilde{p}_\alpha}$$

$$= \sum_\beta \frac{\partial\langle H\rangle}{\partial\lambda_\beta}\frac{\partial\lambda_\beta}{\partial\tilde{p}_\alpha}$$

$$= \sum_\beta \frac{\partial\langle H\rangle}{\partial\lambda_\beta}\left(C^{-1}\right)_{\alpha\beta}$$

Kramer, Saraceno, Geometry of the time-dependent variational principle, Springer (1981), Shalashilin, Burghardt, JCP 129, 084104 (2008)

Classical Evolution as a Special Case

$\boxed{q_j, p_j}$ $\longleftrightarrow$ $g_j(r_\kappa) = N_j \exp\left[(r_\kappa - q_j) \cdot a_j (r_\kappa - q_j) + i p_j \cdot (r_\kappa - q_j)\right]$

where we used $\xi_j = -2 a_j q_j + i p_j$

We have classical motion of $(q_j(t), p_j(t))$ if

- single Gaussian (cf. Heller)
- superposition of TGs / single-surface + harmonic potential: "decoupling effect" (Metiu & co, JCP (1985))

or

- if the classical limit is reached ($\lambda_{dB} \ll L$), such that G-MCTDH becomes a true mixed quantum-classical method for $\psi^\varepsilon = \sum_{jl} A_{jl} e^{iS_l/\varepsilon} \varphi_j g_l^\varepsilon$, see below

Römer, Burghardt, Mol. Phys. 111, 3618 (2013)

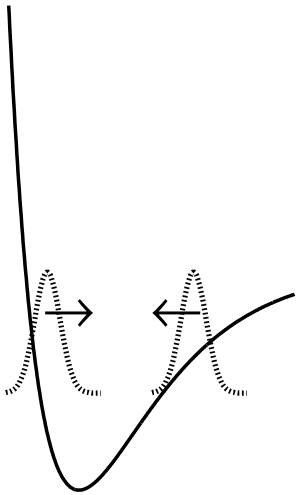
Implementation Details

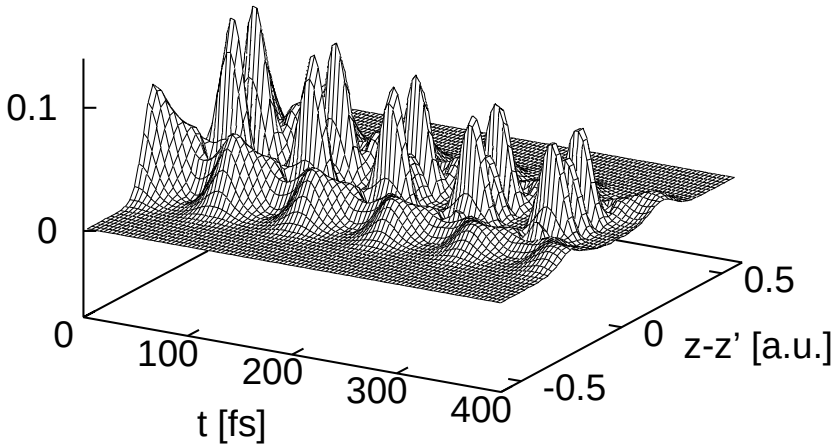
- frozen Gaussians (FGs) almost exclusively used due to numerical robustness
- however, thawed Gaussians (TGs) were successfully employed for system-bath problems
  [Burghardt, Nest, Worth (2003)]
- various conventions possible for complex GWP phase η_j: here, normalized GWPs, imaginary part of phase set to zero
- local harmonic approximation (LHA) or higher-order local expansion
- split off separable part of evolution: $i\dot{\Lambda}^{(\kappa)} = X_0^{(\kappa)} + (C^{(\kappa)})^{-1} Y_{\mathrm{corr}}^{(\kappa)}$
- Constant Mean Field (CMF) integrator used, by switching to an orthogonalized representation to match standard A coeff. propagation
- singularities of the $\boldsymbol{S}$ and $\boldsymbol{C}$ matrices (linear dependencies): standard regularization scheme
- Wigner sampling or single GWP as initial condition
- dynamic GWP allocation (G. Worth)

Example: System-Bath Correlations and Decoherence

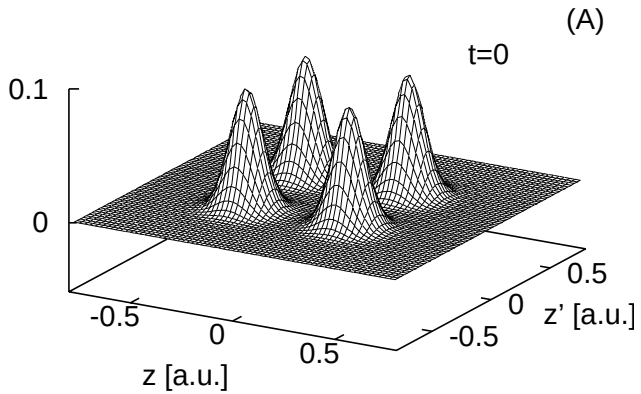
Thawed Gaussians (TGs)

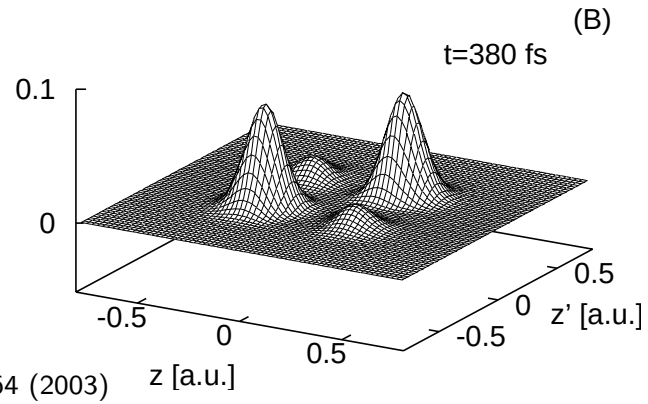
cat state + 60 HO-bath





coherence $\rho(z,z')$



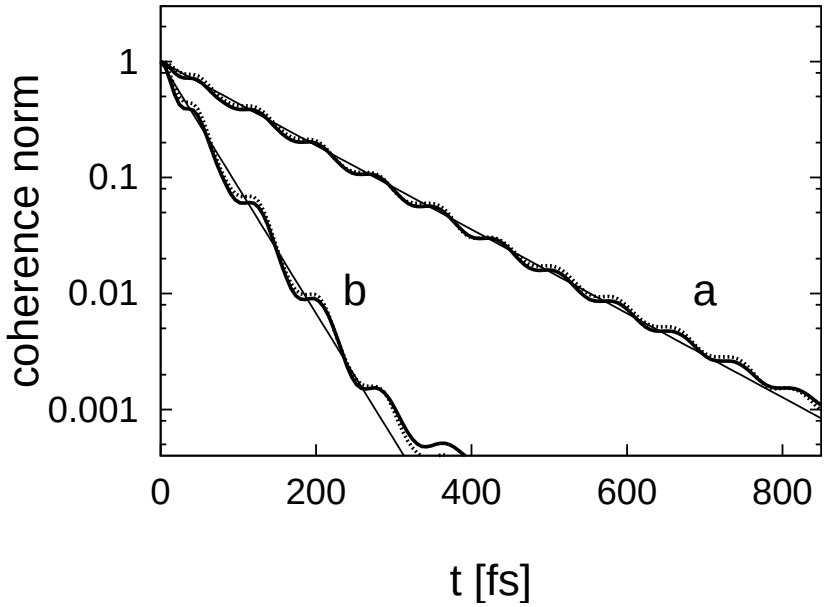


Burghardt, Nest, Worth, JCP 19, 5364 (2003)

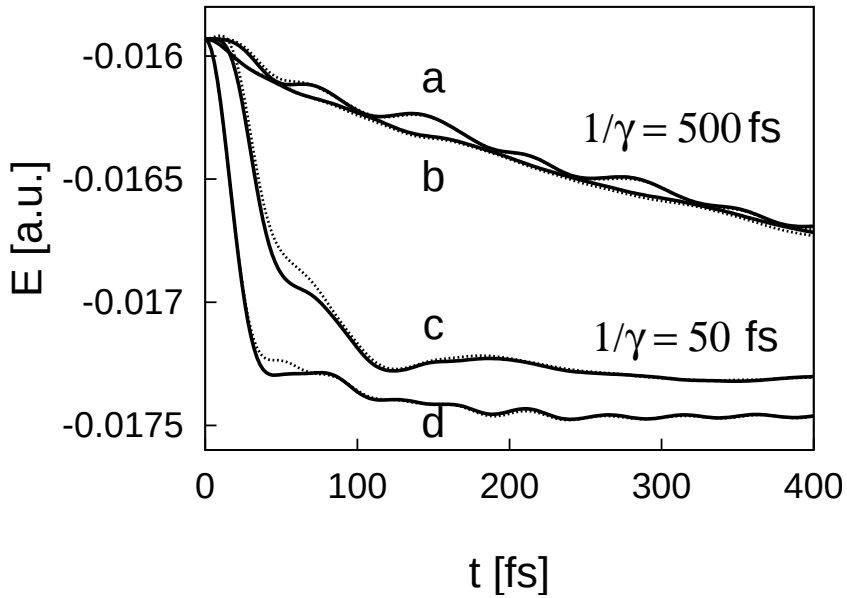
G-MCTDH: Morse Oscillator + 60-Mode Harmonic Bath

Thawed Gaussians (TGs)

decoherence



energy relaxation



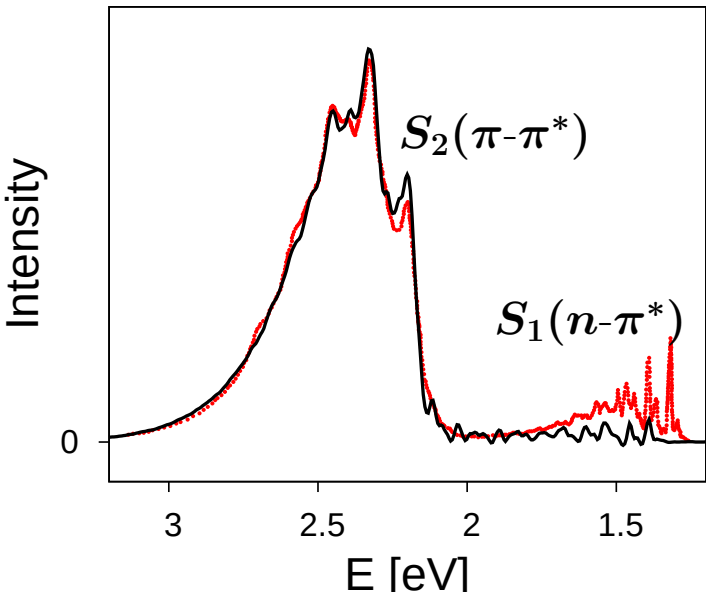
- typical configuration: $([5]_{\text{core}}, [3,3,3,4,4,3,3,3]_{\text{bath}})$

Burghardt, Nest, Worth, JCP 19, 5364 (2003)

G-MCTDH Calculation for S_2/S_1 CoIn in pyrazine

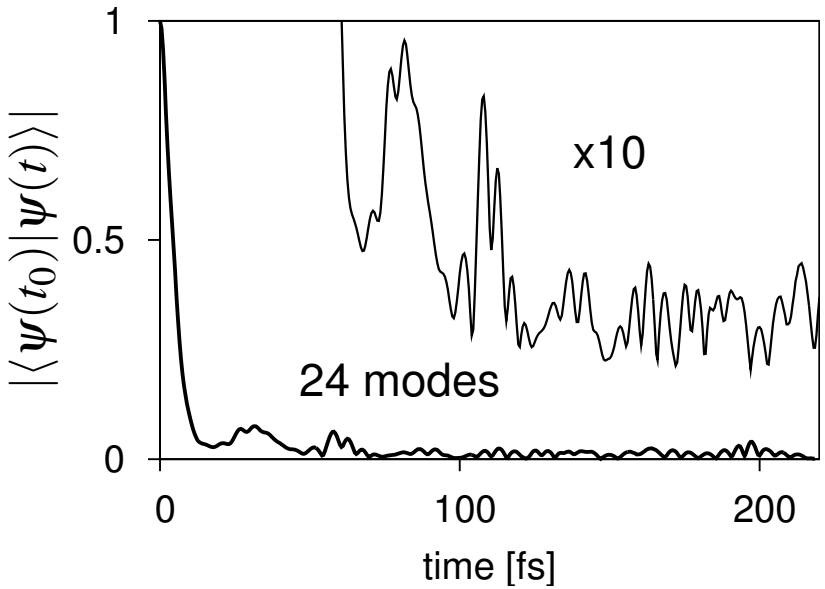
Hybrid calculation for 4+20 modes (FGs)

absorption spectrum



FT

autocorrelation function



dotted red line: experiment

Yamazaki et al., Faraday Discuss. **75**, 395 (1983)

full black line: G-MCTDH

Burghardt, Giri, Worth, JCP **129**, 174104 (2008)

state 1: $([19,10]_{\text{core}}, [18,10,18,10]_{\text{bath}})$

state 2: $([12,7]_{\text{core}}, [10,8,12,10]_{\text{bath}})$

150 fs / 1644 MB / 1250 hrs / 6962400 config's

MCTDH: 150 fs / 2614 MB / 279 hrs / 10966760 cf's

MCTDH & G-MCTDH for Density Operators

- multiconfigurational density operators of two types:
  - density operators of *type I*:

$$\rho(x_1,\ldots,x_N;x'_1,\ldots,x'_N) = \sum_{\tau_1}\ldots\sum_{\tau_N} B_{\tau_1\ldots\tau_N}(t)\prod_{\kappa=1}^{N}\sigma^{(\kappa)}_{\tau_\kappa}(x_\kappa,x'_\kappa,t)$$

  - density operators of *type II*:

$$\begin{aligned}\rho(x_1,\ldots,x_N;x'_1,\ldots,x'_N) \quad = \quad & \sum_{j_1}\ldots\sum_{j_N}\sum_{l_1}\ldots\sum_{l_N} B_{j_1,\ldots,j_N;l_1,\ldots,l_N}(t) \\ & \times\prod_{\kappa=1}^{N}\varphi^{(\kappa)}_{j_\kappa}(x_\kappa,t)\,\varphi^{(\kappa)*}_{l_\kappa}(x'_\kappa,t)\end{aligned}$$

Raab, Burghardt, Meyer, J. Chem. Phys. 111, 8759 (1999), Raab, Meyer, J. Chem. Phys. 112, 10718 (2000)

  - EOMs from variational principle for densities: $\langle\langle\delta\rho|\boldsymbol{L}-i\partial_t|\rho\rangle\rangle = 0$

- employ, e.g., in conjunction with Markovian MEs (Lindblad, Caldeira-Leggett)

G-MCTDH for Density Operators

Burghardt, Meyer, Cederbaum, J. Chem. Phys. 111, 2927 (1999)

- density operators of *type I*:

$$\rho(\boldsymbol{r};\boldsymbol{r}') = \sum_{\tau_1} \cdots \sum_{\tau_N} B_{\tau_1 \ldots \tau_N}(t) \prod_{\kappa=1}^{N} \mathscr{G}_{\tau_\kappa}^{(\kappa)}(\boldsymbol{r}_\kappa, \boldsymbol{r}'_\kappa, t)$$

$$\mathscr{G}_{\tau}^{(\kappa)}(\boldsymbol{r},\boldsymbol{r}',t) = \exp\left(\boldsymbol{r}\cdot\alpha_\tau(t)\cdot\boldsymbol{r} + \boldsymbol{r}'\cdot\alpha'_\tau(t)\cdot\boldsymbol{r}' + \beta_\tau(t)\cdot\boldsymbol{r} + \beta'_\tau(t)\cdot\boldsymbol{r}' + \boldsymbol{r}\cdot\nu'_\tau(t)\cdot\boldsymbol{r}' + \theta(t) \right)$$

- includes thermal GWPs, e.g., as initial condition:

$$\mathscr{G}_{\tau}^{(\kappa)}(r,r',t=0) = \exp\left(-\frac{m\omega}{2\sinh(\omega/kT)} \left[(r^2 + r'^2)\cosh(\omega/kT) - 2rr' \right] \right)$$

- density operators of *type II*: adjoint pairs of component densities

$$\mathscr{G}_{jl}^{(\kappa)}(\boldsymbol{r},\boldsymbol{r}',t) = g_j^{(\kappa)}(\boldsymbol{r}) g_l^{(\kappa)*}(\boldsymbol{r}') = \mathscr{G}_{lj}^{(\kappa)*}(\boldsymbol{r},\boldsymbol{r}',t)$$

Stochastic Schrödinger Equation in GWP/Mean-Field Setting

Burghardt, Meyer, Cederbaum, J. Chem. Phys. 111, 2927 (1999), see also: Peskin, Steinberg, J. Chem. Phys. 109, 704 (1999)

For example, consider a vMCG wavefunction + Hartree bath:

$$\psi(r_1,\ldots,r_N,\{q_n\},t) = \left[\sum_j A_j(t)\, g_j(r_1,\ldots,r_N,\Lambda(t))\right] \prod_{n=1}^{\infty} \chi^{(n)}(q_n,t)$$

Take a bath acting upon the kth DOF of the GWP particle: $\hat{H}_{SB} = -\sum_n c_{kn}\hat{r}_k\hat{q}_n$, resulting in the mean-field Hamiltonian

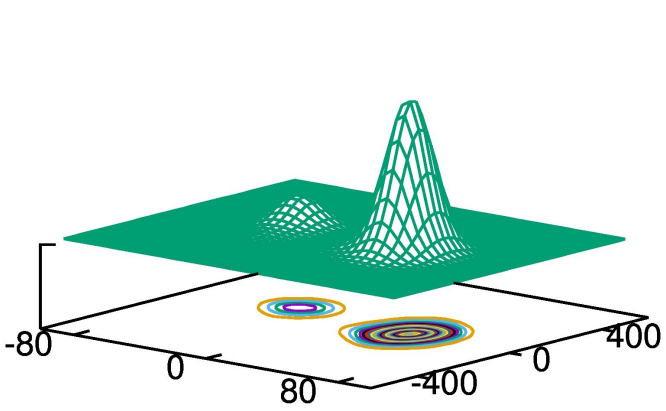
$$\langle H\rangle_{jl}(t) \quad = \quad -\rho_{jl}(t)\,\hat{r}_k \sum_n c_{kn}\langle\chi^{(n)}(t)|\hat{q}_n|\chi^{(n)}(t)\rangle = -\rho_{jl}(t)\,\hat{r}_k \sum_n c_{kn} Q_n(t)$$

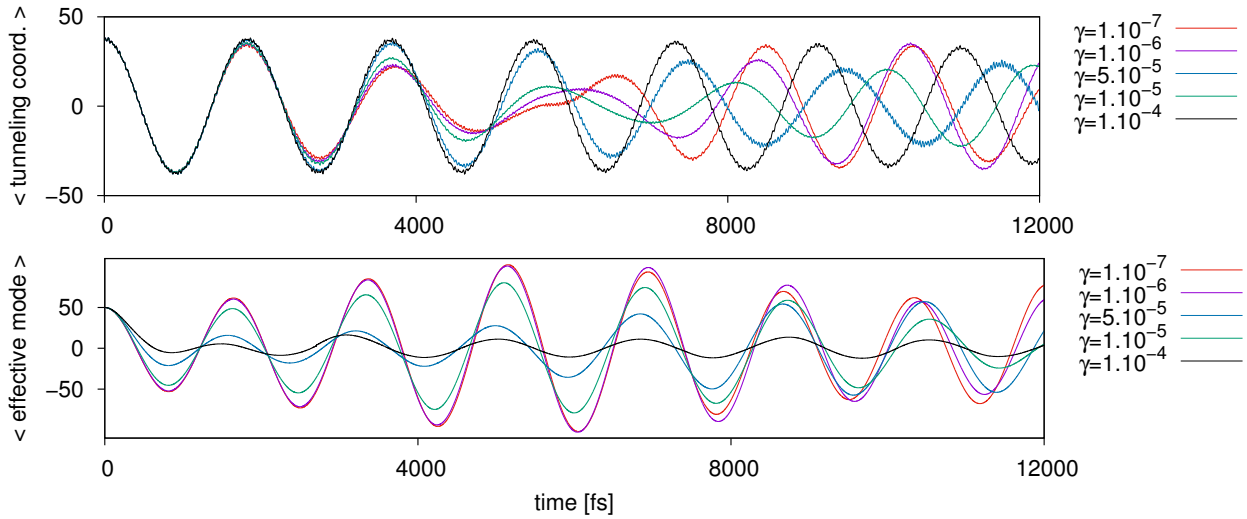
Now use: $\lim_{n\to\infty}(\sum_n c_n Q_n(t)) = f(t) - \int_0^t dt'\,\zeta(t-t')\dot{Q}_k(t') + \zeta(0)Q_k(t)$
In the simplest case, we obtain a Langevin type equation for the GWPs:

$$\dot{q}_{j,k} \quad = \quad \frac{p_{j,k}}{m}$$

$$\dot{p}_{j,k} \quad = \quad -\frac{\partial V_{\rm sys}}{\partial r_k}\bigg|_{r_k=q_k} + f(t) - \gamma\dot{Q}_k(t) + \zeta(0)\dot{Q}_k(0)$$

GWP/Langevin Dynamics: 2D Tunneling





- vMCG calculations with 20 two-dimensional GWPs (not entirely converged)
- Langevin dissipation acting on harmonic coordinate
- increasing friction destroys resonant dynamics between the two modes
- general scheme: Langevin closure of effective-mode chains
- cheap and physically intuitive way of implementing dissipation

GWP/Langevin Dynamics: 2D Tunneling

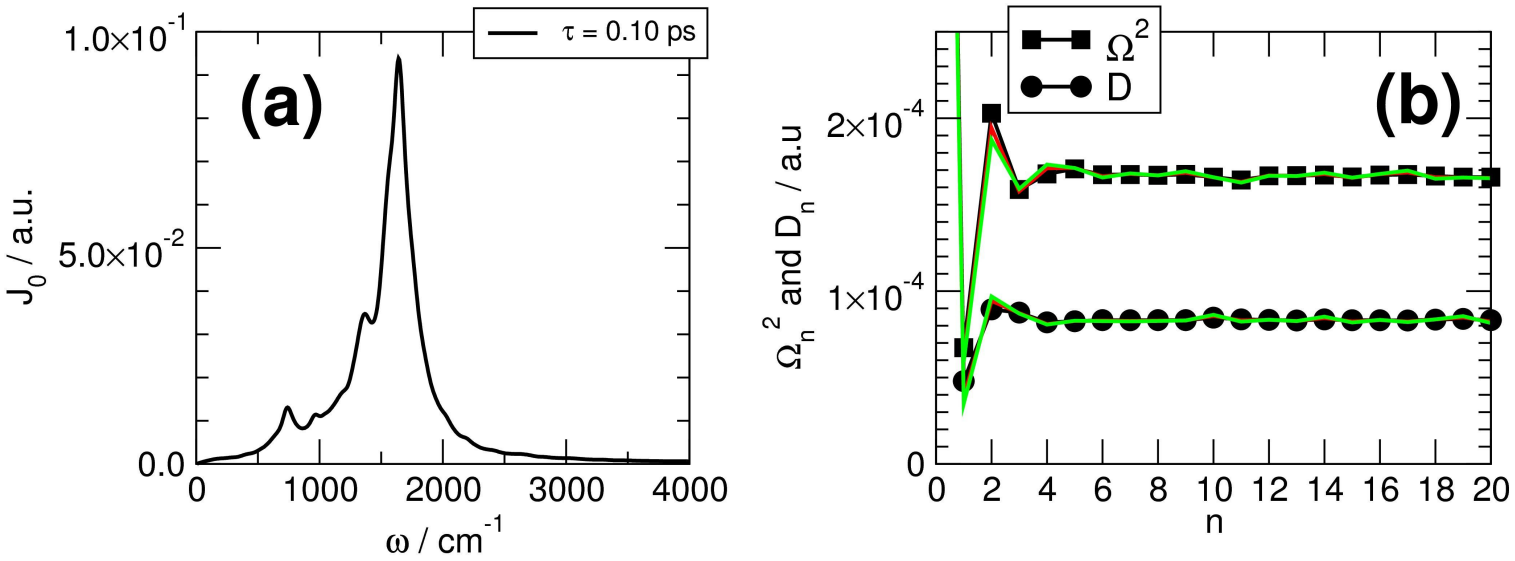
tunnel coordinate $\longleftrightarrow$ $J(\omega) = \sum_n \frac{c_n^2}{\omega_n}\delta(\omega-\omega_n) = \frac{2\gamma\omega D^2}{(\Omega^2-\omega^2)^2+4\gamma^2\omega^2}$

$\downarrow$

tunnel coordinate $\longleftrightarrow$ effective mode $\hat{X}_1$ $\longleftrightarrow$ $J^{\text{residual}}(\omega) = 2\gamma\omega$

- $\hat{H}_{SB}+\hat{H}_B = \hat{s}\sum_i c_n\hat{x}_n + \hat{H}_B \longrightarrow D\hat{s}\hat{X}_1$ – residual bath
- "Brownian oscillator" picture: 1 effective mode + Ohmic bath
- here, effective mode is chosen resonant with the tunneling frequency
- treat residual Ohmic bath by Langevin dynamics
- 2D system with damping of effective Brownian oscillator mode
- replaces discretized residual bath (or full discretization of SD)

G-MCTDH: System-Bath Models



- discretized bath spectral densities (SDs) represented by "GWP bath"
- hierarchical chain representations of SDs that are (partially) represented by GWPs including Langevin closure

$$\hat{H}_{SB}+\hat{H}_B=\hat{s}\sum_i c_n\hat{x}_n+\hat{H}_B \longrightarrow D\hat{s}\hat{X}_1+D_{12}\hat{X}_1\hat{X}_2+\ldots+\hat{X}_M\text{–residual bath}$$

Approximate SD's: Mth Order Truncation

$$J(\omega) = \frac{\pi}{2} \sum_n \frac{c_n^2}{\omega_n} \delta(\omega - \omega_n) \quad \longleftrightarrow \quad J^{(M)}(\omega) = \lim_{\varepsilon \to 0^+} \mathrm{Im}\, K_B^{(M)}(\omega - i\varepsilon)$$

Hughes, Christ, Burghardt, JCP 131, 124108 (2009), Garg, Onuchic, Ambegaokar, JCP 83, 4491 (1985), Leggett, Phys. Rev. B 30, 1208 (1984)

$$K_B^{(M)}(z) = -\cfrac{D_{0,1}^2}{\Omega_1^2 - z^2 - \cfrac{D_{1,2}^2}{\Omega_2^2 - z^2 - \cdots \cfrac{D_{M-2,M-1}^2}{\Omega_{M-1}^2 - z^2 - \cfrac{D_{M-1,M}^2}{\Omega_M^2 - z^2 - z^2 I^M(z)}}}}$$

Ohmic closure:

$$I^M_{\mathrm{ohm}}(z) = -i\frac{\gamma}{z}$$

Rubin (quasi-Ohmic) closure:

$$I^M_{\mathrm{Rubin}}(z) = \frac{1}{2z} \frac{{\Lambda_R}^2 - 2z^2 + 2iz\sqrt{{\Lambda_R}^2 - z^2}}{z + i\sqrt{{\Lambda_R}^2 - z^2}}$$

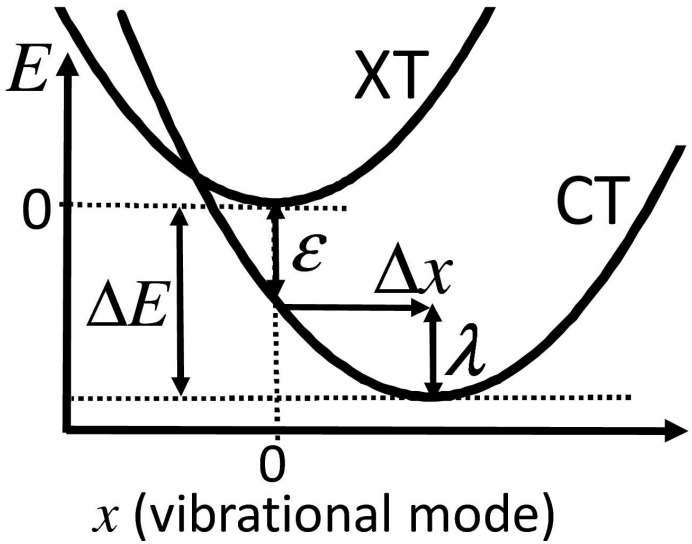
Hughes, Christ, Burghardt, J. Chem. Phys. 131, 024109 (2009), Martinazzo, Vacchini, Hughes, Burghardt, J. Chem. Phys. 134, 011101 (2011)

Topics

Two-Layer G-MCTDH – Motivation

- original G-MCTDH concept: combined, correlated TG modes (correlations through off-diagonal elements of the width matrix)
- in practice: G-MCTDH or vMCG using combined FG modes
  - factorizable, uncorrelated FG configurations
  - despite the separability, the C matrix is *not* block-diagonal
  - hence, expensive inversion step $\propto (\tilde{n}d)^3$
- alternative concept: replace high-dimensional FG's by superpositions of FG configurations $\longrightarrow$ two-layer approach

To Put Things in Perspective: Benchmarks for 2-State Model
(Donor-Acceptor Charge Transfer System)



$$\hat{H} = \hat{H}_0 + \hat{H}_R + \hat{H}_B$$

$\hat{H}_0$: electronic part
$\hat{H}_R$: inter-fragment coordinate part
$\hat{H}_B$: phonon bath part

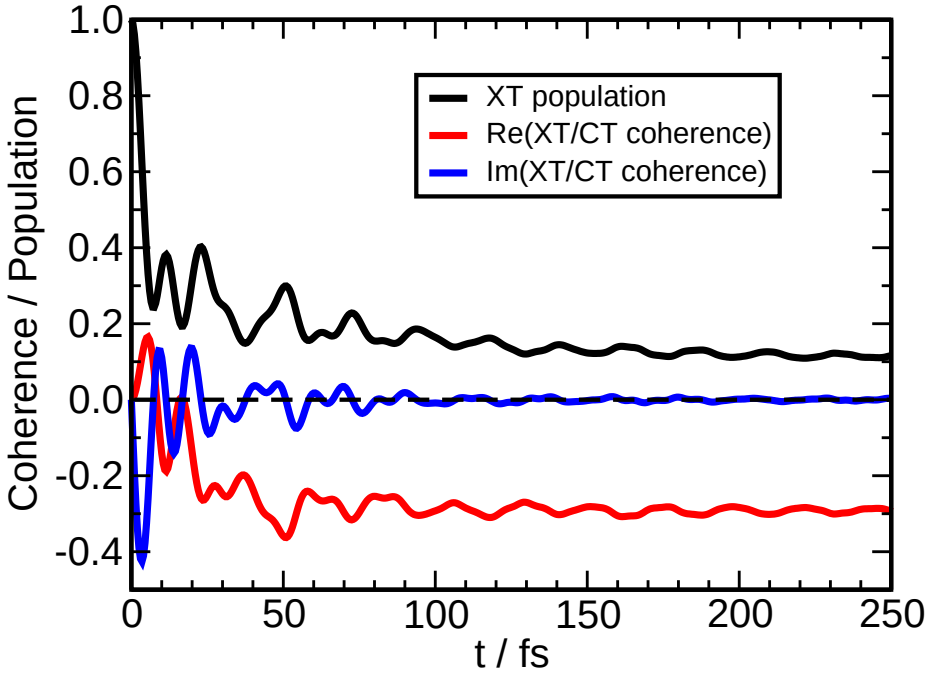
$$\hat{H}_0 = \Delta_{\mathrm{XT-CT}} |\mathrm{CT}\rangle\langle\mathrm{CT}| + \gamma\left(|\mathrm{XT}\rangle\langle\mathrm{CT}| + |\mathrm{CT}\rangle\langle\mathrm{XT}|\right)$$

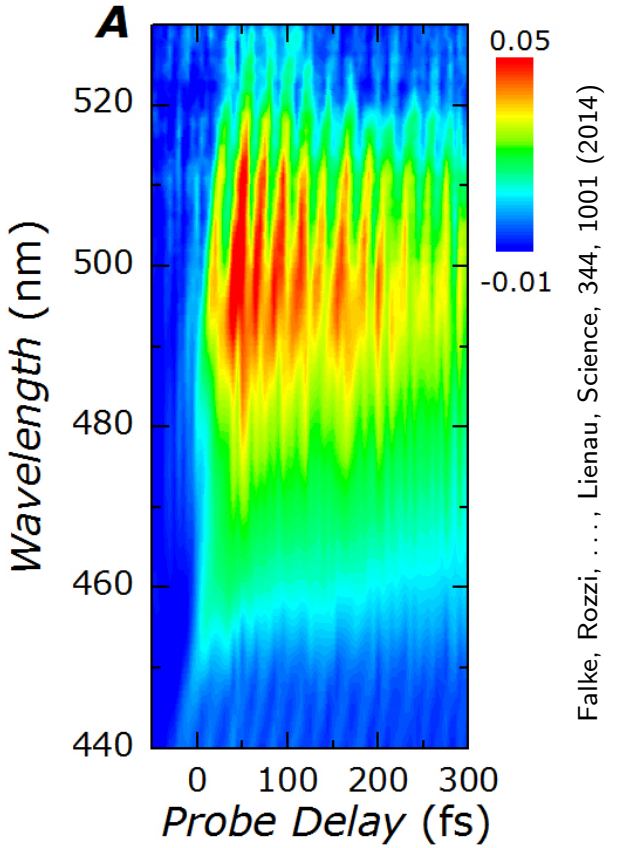
$$\begin{aligned}\hat{H}_R \quad = \quad & \frac{\omega_R}{2}(\hat{R}^2 + \hat{P}^2) + \kappa_R \hat{R}\,|\mathrm{CT}\rangle\langle\mathrm{CT}| \\ & + \gamma_R \hat{R}\left(|\mathrm{XT}\rangle\langle\mathrm{CT}| + |\mathrm{CT}\rangle\langle\mathrm{XT}|\right)\end{aligned}$$

$$\hat{H}_B = \sum_{i=1}^{N} \frac{\omega_i}{2}(\hat{x}_i^2 + \hat{p}_i^2) + \sum_{i=1}^{N} \kappa_i x_i\,|\mathrm{CT}\rangle\langle\mathrm{CT}| + \sum_{i=1}^{N} \frac{\kappa_i^2}{2\omega_i}$$

Tamura, Martinazzo, Ruckenbauer, Burghardt, J. Chem. Phys., 137, 22A540 (2012)

Ultrafast Coherent Transfer Dynamics (MCTDH/60 Modes)





el. coherence: $\rho_{XT,CT}(t) = \mathrm{Tr}\{|\mathrm{CT}\rangle\langle\mathrm{XT}|\hat{\rho}(t)\}$

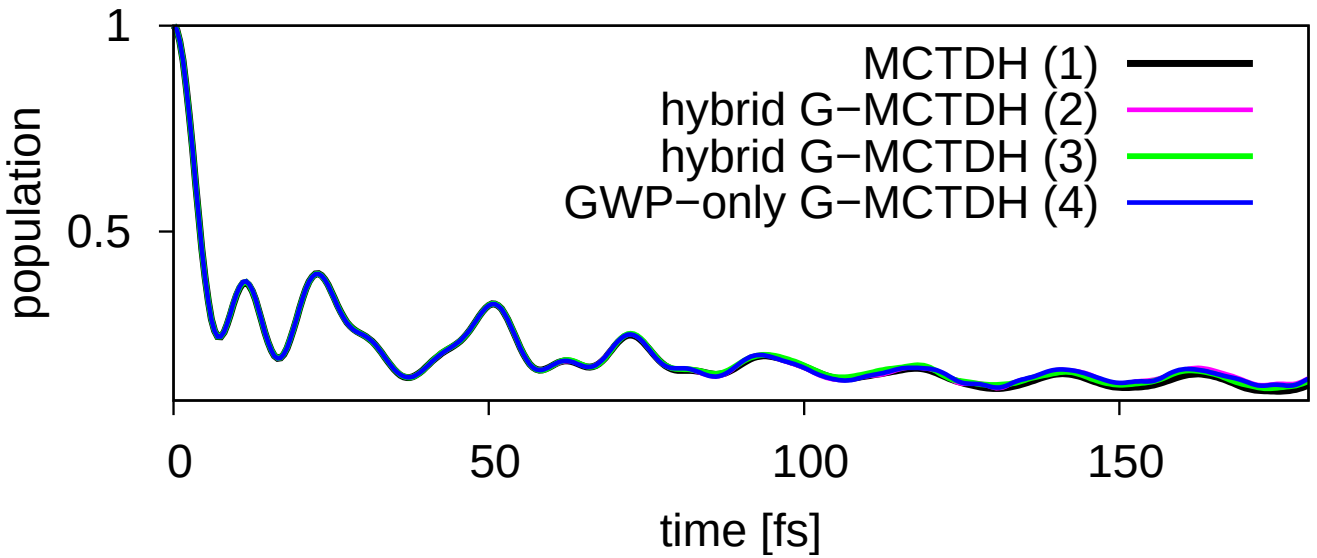
- imaginary part $(-2\gamma/\hbar)\mathrm{Im}\rho_{XT,CT}$ ⟷ population flux
- real part ⟷ stationary coherent superposition ($P_{\mathrm{XT}} \sim 0.1$, $P_{\mathrm{CT}} \sim 0.9$)
- experiment: ultrafast ET ($\sim$ 50 fs), oscillatory features [Brabec et al., CPL (2001)]) confirmed by recent pump-probe experiments by Lienau group [Science (2014)])

Benchmarks – 41D Spin-Boson System

Frozen Gaussians (FGs)

- different mode combinations and #'s of GWP config's
- C inversion in smaller subspaces
- all G-MCTDH calculations have reasonable timings
- memory requirements favorable

	calc. type	mode combination	# configs	memory [mb]	CPU time [hh:mm]	C inversion avg/tot time
1	MCTDH	[6,8],[6,8],[3,5],[2,3] [2,2],[2,2],[2,2],[2,2],[6,8]	143616	754	1:36	- -
2	G-MCTDH hybrid	[6,8],[6,8],[3,5],[2,3] [2,2],[2,2],[2,2],[2,2],[6,8]	143616	28	0:12	0.21 ms 0:01:48
3	G-MCTDH hybrid	[8,10],[8,10],[5,7],[4,5] [3,3],[3,3],[3,3],[3,3],[6,8]	2890080	521	3:56	7.65 ms 0:12:03
4	G-MCTDH all-GWP	[6,8],[6,8],[3,5],[2,3] [2,2],[2,2],[2,2],[2,2],[6,8]	143616	28	0:26	0.19 ms 0:06:13

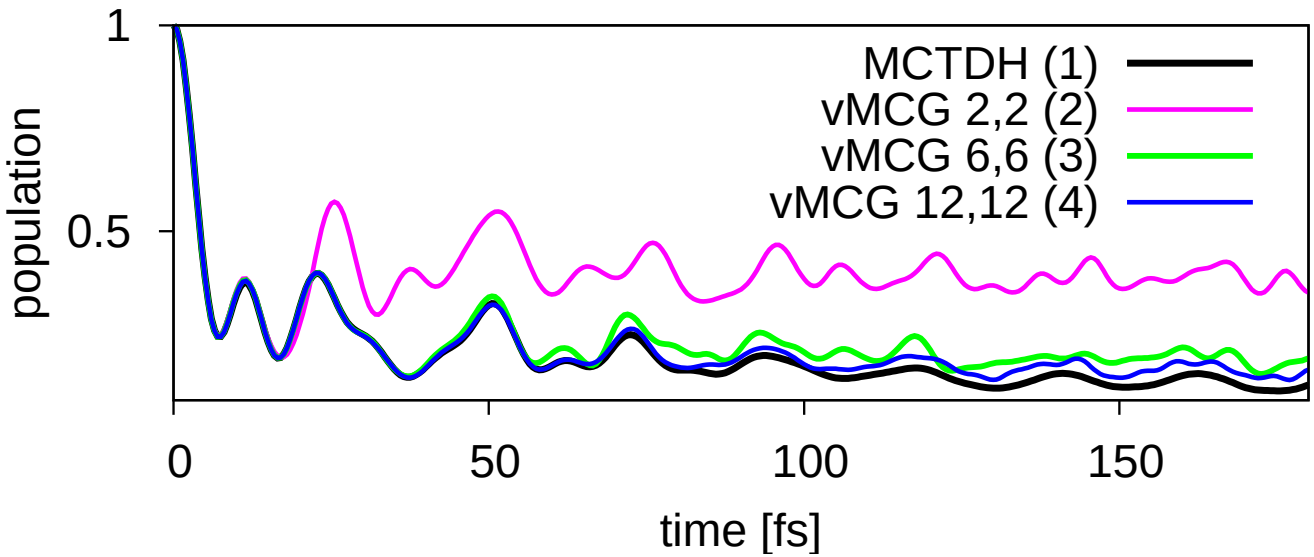


Benchmarks – 41D Spin-Boson System

Frozen Gaussians (FGs)

- 2 el. states, 1 subsystem mode, 40 bath modes
- qualitative agreement even of "cheap" calculations
- memory requirements favorable
- vMCG very expensive even for few config's

	calc. type	mode combination	# configs	memory [mb]	CPU time [hh:mm]	C inversion avg/tot time
1	MCTDH	[6,8],[6,8],[3,5],[2,3] [2,2],[2,2],[2,2],[2,2],[6,8]	143616	754	1:36	- -
2	vMCG 2,2	[2,2]	4	2	0:47	5.10 ms 0:03:60
3	vMCG 6,6	[6,6]	12	15	7:10	136.38 ms 1:29:18
4	vMCG 12,12	[12,12]	24	55	47:56	1758.71 ms 23:21:38



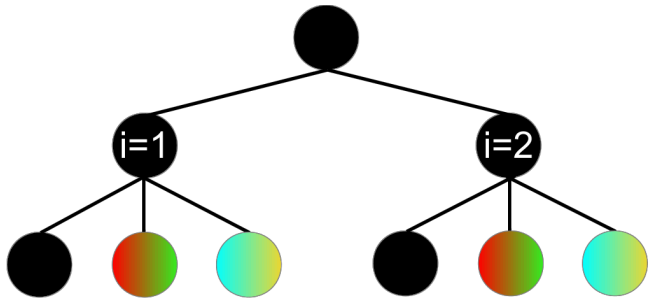
Two-Layer (2L)-G-MCTDH Scheme

Römer, Ruckenbauer, Burghardt, J. Chem. Phys. 138, 064106 (2013)

$$\Psi(r,t) = \sum_J A_J(t)\Phi_J(r,t) \;\; = \sum_J A_J(t) \prod_{\kappa=1}^{M} \varphi_{j_\kappa}^{(\kappa)}(r_\kappa,t)$$

where the single-particle functions (SPFs) $\varphi_{j_\kappa}^{(\kappa)}$ are now built as superpositions of Frozen Gaussian (FG) configurations,

$$\begin{aligned} \varphi_{j_\kappa}^{(\kappa)}(r_\kappa,t) &= \sum_L B_{j,L}^{(\kappa)}(t) G_L^{(\kappa)}(r_\kappa,t) \\ &= \sum_L B_{j,L}^{(\kappa)}(t) \prod_\mu g_{l_\mu}^{(\kappa,\mu)}(r_{\kappa_\mu},t) \end{aligned}$$



- hierarchical Tucker format
- intra-SPF correlations are carried by B coefficients
- GWP parameter dynamics in small (κ,μ) subspaces
- first-layer SPFs can be chosen to be orthogonal: $\langle \varphi_j^{(\kappa)}(t) | \varphi_{j'}^{(\kappa)}(t) \rangle = \delta_{jj'}$

Two-Layer G-MCTDH – Equations of Motion

1st layer coefficients: $$i\dot{A} = HA$$

2nd layer coefficients: $$iS^{(\kappa)}\dot{B}^{(\kappa)} = \left[\tilde{H}^{(\kappa)} - i\tilde{\tau}^{(\kappa)}\right] B^{(\kappa)}$$

GWPs (2nd layer): $$iC^{(\kappa,\mu)}\dot{\Lambda}^{(\kappa,\mu)} = Y^{(\kappa,\mu)}$$

where $\tilde{S}^{(\kappa)}_{jL,j'L'} = \delta_{jj'}\langle G^{(\kappa)}_L | G^{(\kappa)}_{L'}\rangle$, $\tilde{\tau}^{(\kappa)}_{jL,j'L'} = \delta_{jj'}\langle G^{(\kappa)}_L | \partial_t G^{(\kappa)}_{L'}\rangle$

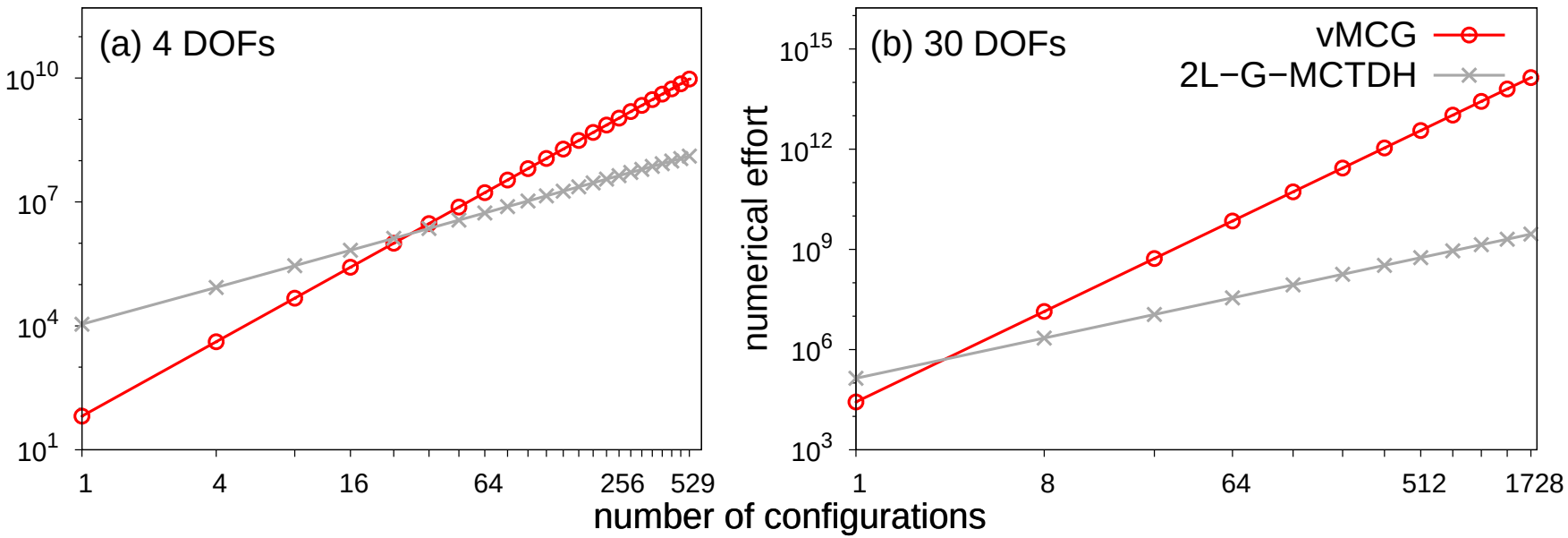
and the 1st layer mean field term: $\tilde{H}^{(\kappa)}_{jL,j'L'} = \langle G^{(\kappa)}_L | (1-\hat{P}^{(\kappa)}) \left[(\rho^{(\kappa)})^{-1}\hat{H}^{(\kappa)}\right]_{jj'} G^{(\kappa)}_{L'}\rangle$

and for the parameter equations: $C^{(\kappa,\mu)}_{j\alpha,l\beta} = \rho^{(\kappa,\mu)}_{jl}\langle \partial_\alpha g^{(\kappa,\mu)}_j | (\hat{1}-\hat{P}^{(\kappa,\mu)}) | \partial_\beta g^{(\kappa,\mu)}_l\rangle$

as well as $Y^{(\kappa,\mu)}_{j\alpha} = \sum_l \langle \partial_\alpha g^{(\kappa,\mu)}_j | (\hat{1}-\hat{P}^{(\kappa,\mu)})\hat{H}^{(\kappa,\mu)}_{jl} | g^{(\kappa,\mu)}_l\rangle$

Römer, Ruckenbauer, Burghardt, J. Chem. Phys. 138, 064106 (2013)

Two-Layer G-MCTDH – Scaling



$\text{effort}^{\text{G-MCTDH}} \sim m f^2 n^{f+1} + f(\tilde{d}n)^3$

calculation of mean fields + C matrix inversion

$\text{effort}^{\text{2L-G-MCTDH}} \sim m_1 f_1^2 n_1^{f_1+1} + m_1 m_2 f_1 f_2 n_1 n_2^{f_2+1}(f_2 + n_1) + f_1 f_2 (d_2 n_2)^3$

calculation of 1st and 2nd-layer mean fields + C matrix inversion

2L-G-MCTDH for Coupled Electronic States: Three Variants

— single-set: shared basis

$$\Psi_S(r,t) = \sum_{J,s} A_{Js}(t)\Phi_J(r,t)|s\rangle = \sum_{J,s} A_{Js}(t) \prod_{\kappa=1}^{N} \varphi_{j_\kappa}^{(\kappa)}(r_\kappa,t)|s\rangle$$

$$\varphi_{j_\kappa}^{(\kappa)}(r_\kappa,t) = \sum_L B_{j,L}^{(\kappa)}(t) G_L^{(\kappa)}(r_\kappa,t) = \sum_L B_{j,L}^{(\kappa)}(t) \prod_\mu g_{l_\mu}^{(\kappa,\mu)}(r_{\kappa_\mu},t)$$

— multi-set: state-specific basis

$$\Psi_M(r,t) = \sum_{J,s} A_J^{(s)}(t)\Phi_J^{(s)}(r,t)|s\rangle = \sum_{J,s} A_J^{(s)}(t) \prod_{\kappa=1}^{N} \varphi_{j_\kappa}^{(\kappa,s)}(r_\kappa,t)|s\rangle$$

$$\varphi_{j_\kappa}^{(\kappa,s)}(r_\kappa,t) = \sum_L B_{j,L}^{(\kappa,s)}(t) G_L^{(\kappa,s)}(r_\kappa,t) = \sum_L B_{j,L}^{(\kappa,s)}(t) \prod_\mu g_{l_\mu}^{(\kappa,\mu,s)}(r_{\kappa_\mu},t)$$

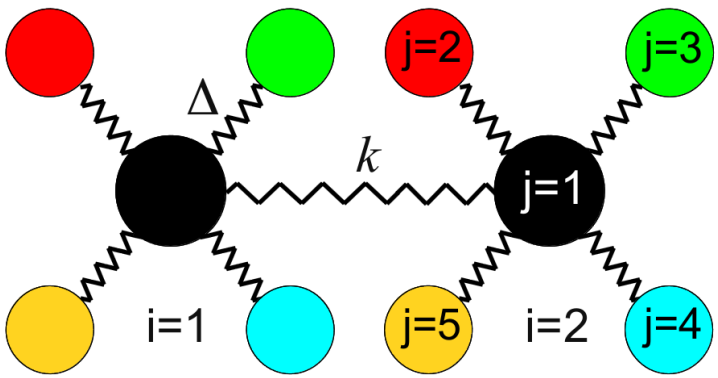
— hybrid-multi/single set ≡ hybrid-set: state-specific but shared 2nd-layer basis

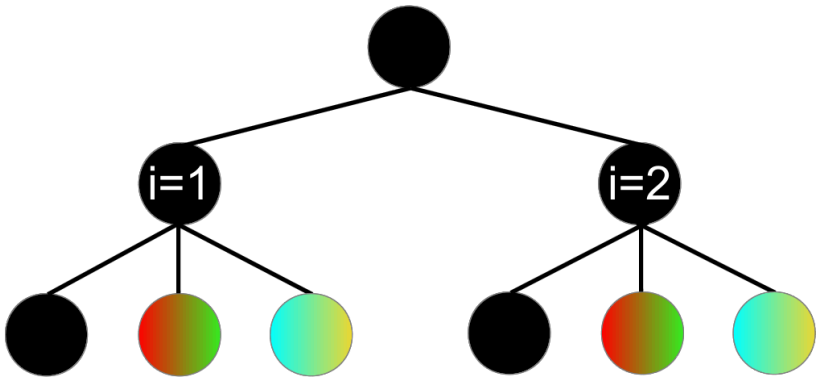
$$\Psi_H(r,t) = \sum_{J,s} A_J^{(s)}(t)\Phi_J^{(s)}(r,t)|s\rangle = \sum_{J,s} A_J^{(s)}(t) \prod_{\kappa=1}^{N} \varphi_{j_\kappa}^{(\kappa,s)}(r_\kappa,t)|s\rangle$$

$$\varphi_{j_\kappa}^{(\kappa,s)}(r_\kappa,t) = \sum_L B_{j,L}^{(\kappa,s)}(t) G_L^{(\kappa)}(r_\kappa,t) = \sum_L B_{j,L}^{(\kappa,s)}(t) \prod_\mu g_{l_\mu}^{(\kappa,\mu)}(r_{\kappa_\mu},t)$$

Model System: Intramolecular Vibrational Redistribution (IVR)

$$\hat{H} = \hat{T} + \frac{1}{2}\sum_{i=1}^{n}\sum_{j=1}^{m}\omega_i \hat{q}_{i,\,j}^2 + \frac{1}{2}\sum_{i=1}^{n-1} k\left(\hat{q}_{i,1} - \hat{q}_{i+1,1}\right)^2 + \Delta\sum_{i=1}^{n}\sum_{j=2}^{m}\hat{q}_{i,1}^2\hat{q}_{i,j}$$



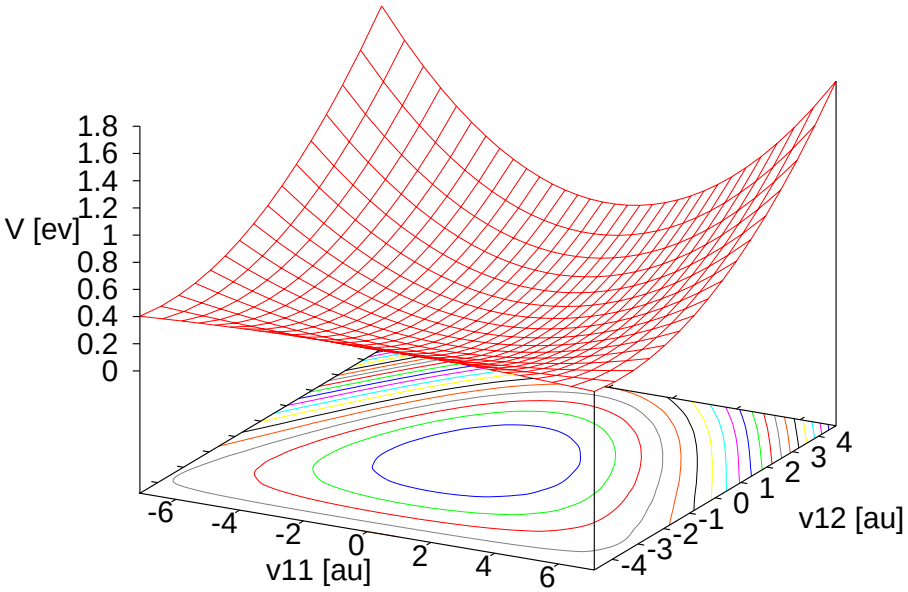


Schade, Hamm, J. Chem. Phys. **131**, 044511 (2009), Eisenbrandt, Ruckenbauer, Römer, Burghardt, in preparation (2017)

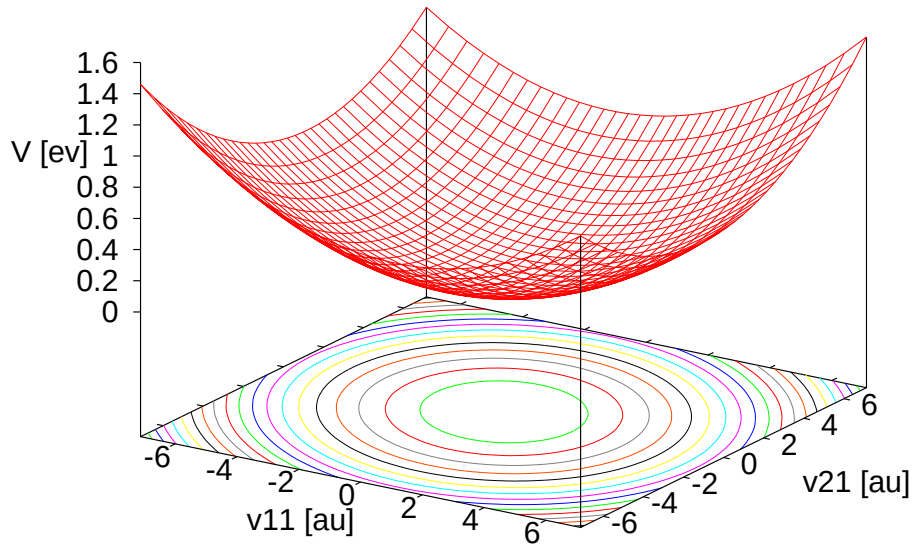
- low-frequency transporting modes + high-frequency local modes
- transporting/local modes communicate via Fermi resonances
- IVR efficiency is controlled by parameters k and Δ
- consider regime of "ballistic" transport along the chain
- $i = 1, \ldots f_1$ 1st-layer modes , $j = 1, \ldots f_2$ 2nd-layer modes/site

Model System: PES Cuts

$$\hat{H} = \hat{T} + \frac{1}{2}\sum_{i=1}^{n}\sum_{j=1}^{m}\omega_i \hat{q}_{i,\,j}^2 + \frac{1}{2}\sum_{i=1}^{n-1} k\left(\hat{q}_{i,1} - \hat{q}_{i+1,1}\right)^2 + \Delta\sum_{i=1}^{n}\sum_{j=2}^{m}\hat{q}_{i,1}^2\hat{q}_{i,j}$$



intra-site PES cut (q_{11}, q_{12})

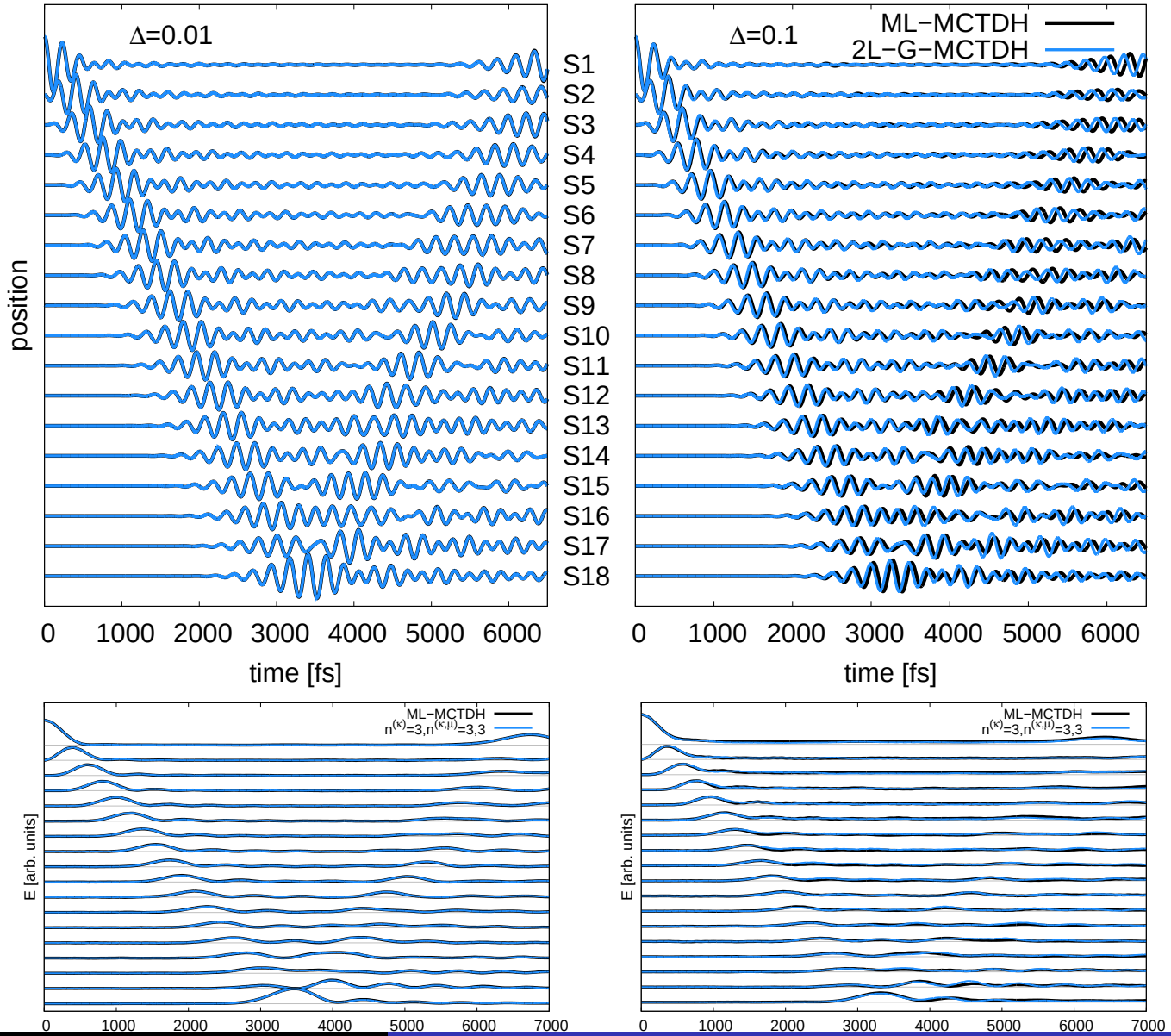


PES cut for transporting modes (q_{11}, q_{21})

Results & Benchmarks

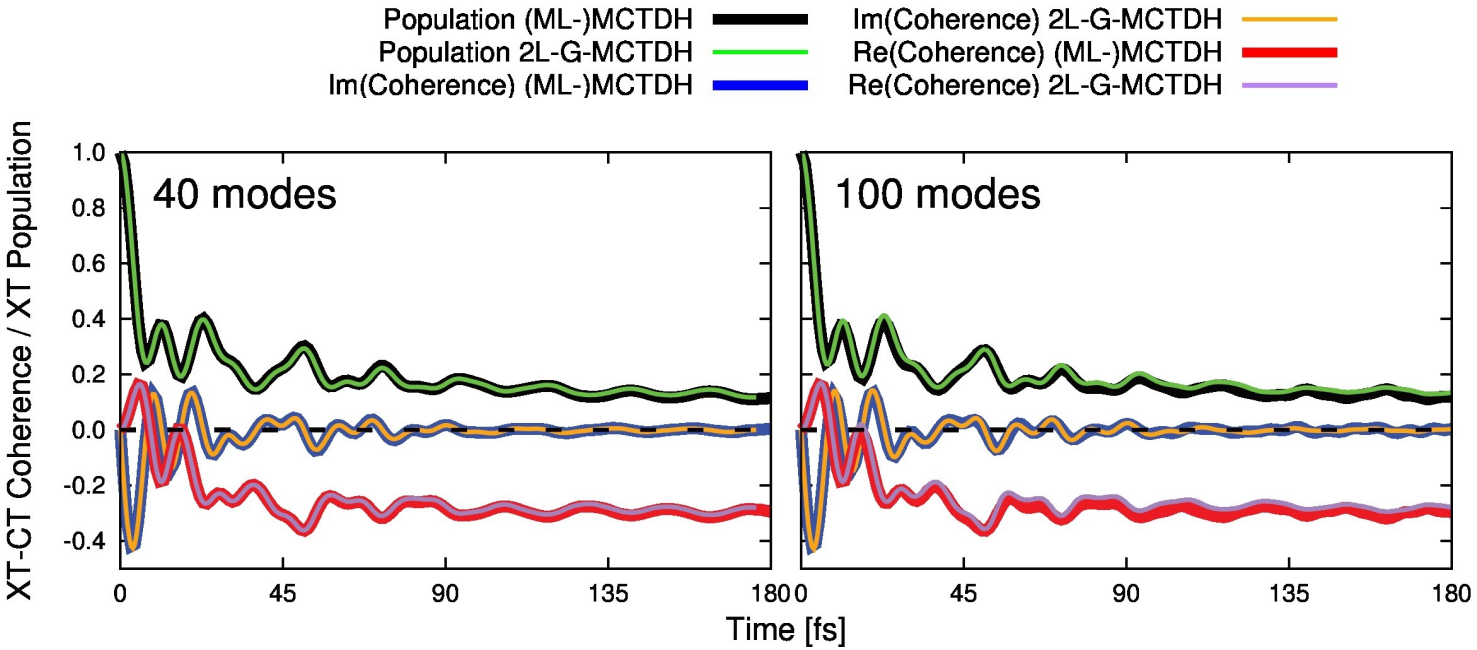
18 sites
90 DOFs
1st/2nd layer modes:
$f_1 = 6, f_2 = 6$
1st/2nd layer SPFs:
$n_1 = 3, n_2 = 3$

[140 hrs/36 MB]
in-house code
(vs. [136 hrs/215 MB]
2L-MCTDH
HD package)



Results & Benchmarks: Spin-Boson System

calc type	# L1 modes	# L1 SPFs	# L2 modes	# L2 SPFs	timing [s]
small	6	[4,4,4,4,4,7]	[4,4,4,4,4,1]	[3,3,3,3,3,7]	[8252]
medium	6	[6,6,5,5,5,7]	[4,4,4,4,4,1]	[5,5,5,5,5,8]	[122636]
large	6	[7,7,8,8,7,8]	[4,4,4,4,4,1]	[5,6,6,7,6,9]	[286980]



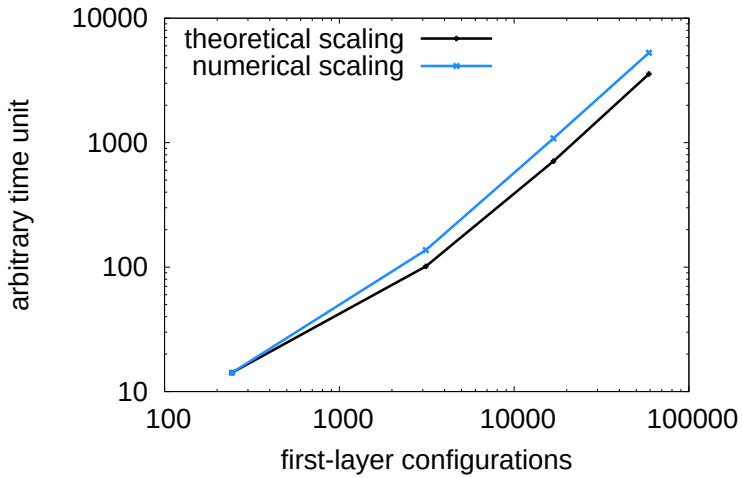
Eisenbrandt, Ruckenbauer, Römer, Burghardt, in preparation (2017)

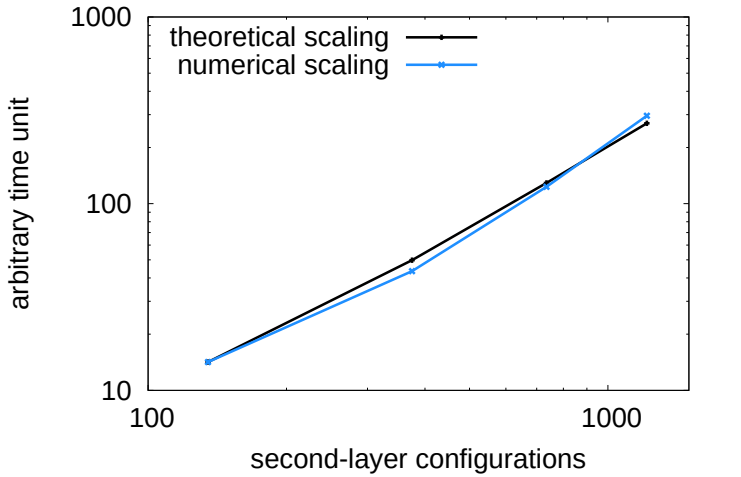
- single-set calculations for rediscretized SDs for 40 / 100 modes
- convergence properties are similar for single(S)/hybrid(H)/multi(M)-set
- on-the-fly implementation planned

Implementation & Scaling

- in-house code (M. Ruckenbauer, P. Eisenbrandt)
- general polynomial potentials
- Hamiltonian given as sum-over-products
- initial condition: shell-like spatial distribution (here, initially unoccupied GWPs narrower than central GWP)
- conventional regularization of $\boldsymbol{S}$ and $\boldsymbol{C}$ matrices
- ABM integrator (time step typically $\sim 10^{-2}$ fs)
- scaling in good agreement with theory

- NB: joint standard G-MCTDH/vMCG code with G. A. Worth now available within QUANTICS package at `http://ccpforge.cse.rl.ac.uk/`.





Multi-Layer Form

$$\Psi(t) = \sum_J A_J^{[1]}(t)\Phi_J^{[1]}(t) := \sum_J A_J^{[1]}(t) \prod_{\kappa_1=1}^{f^{[1]}} \chi_{j_{\kappa_1}}^{[1](\kappa_1)}(t)$$

with the spf's of the first $M-1$ layers ($m \in \{2,3,\ldots,M\}$),

$$\chi_j^{[m-1](\mu_m-1)}(t) \quad = \quad \sum_J A_{j,J}^{[m](\mu_m-1)}(t)\Phi_J^{[m](\mu_m-1)}(t) = \sum_J A_{j,J}^{[m](\mu_m-1)}(t) \prod_{\kappa_m=1}^{f_{\mu_{m-1}}^{[m]}} \chi_{j_{\kappa_m}}^{[m]}(t)$$

and the final (Mth) layer composed of FG's,

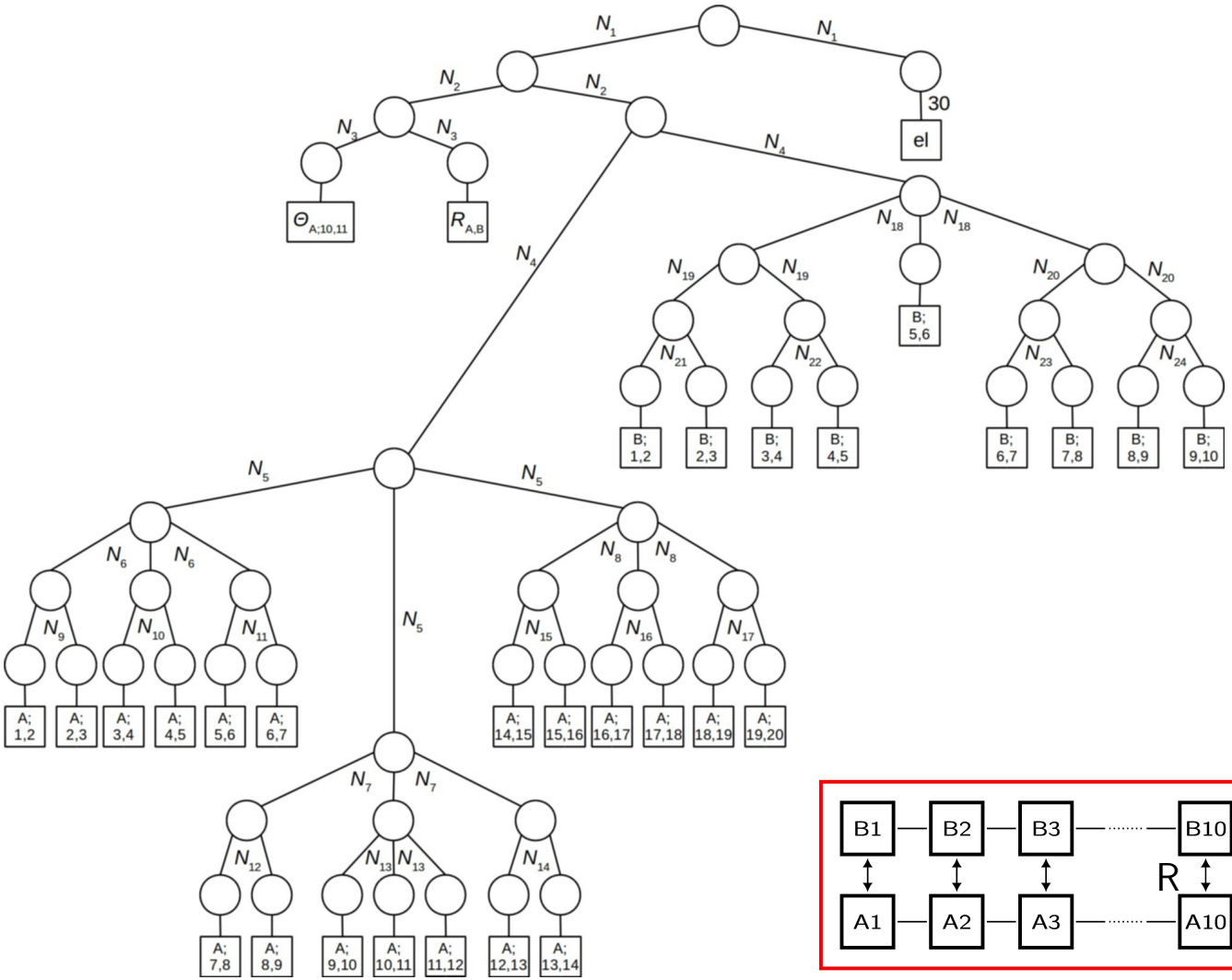
$$\chi_j^{[M](\mu_M)}(t) = g_j^{(\mu_M)}(\Lambda_j^{(\mu_M)}(t))$$

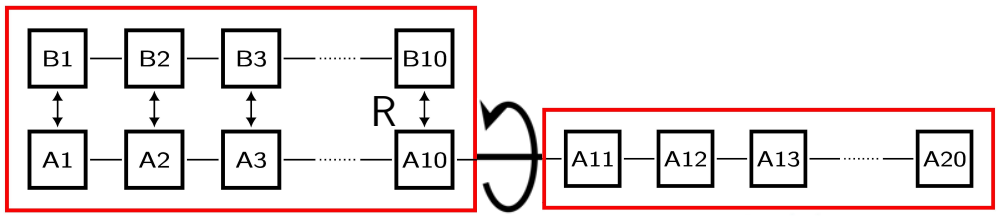
can be straightforwardly combined with existing ML-MCTDH approaches

Römer, Ruckenbauer, Burghardt, J. Chem. Phys. 138, 064106 (2013)

ML-MCTDH: Example

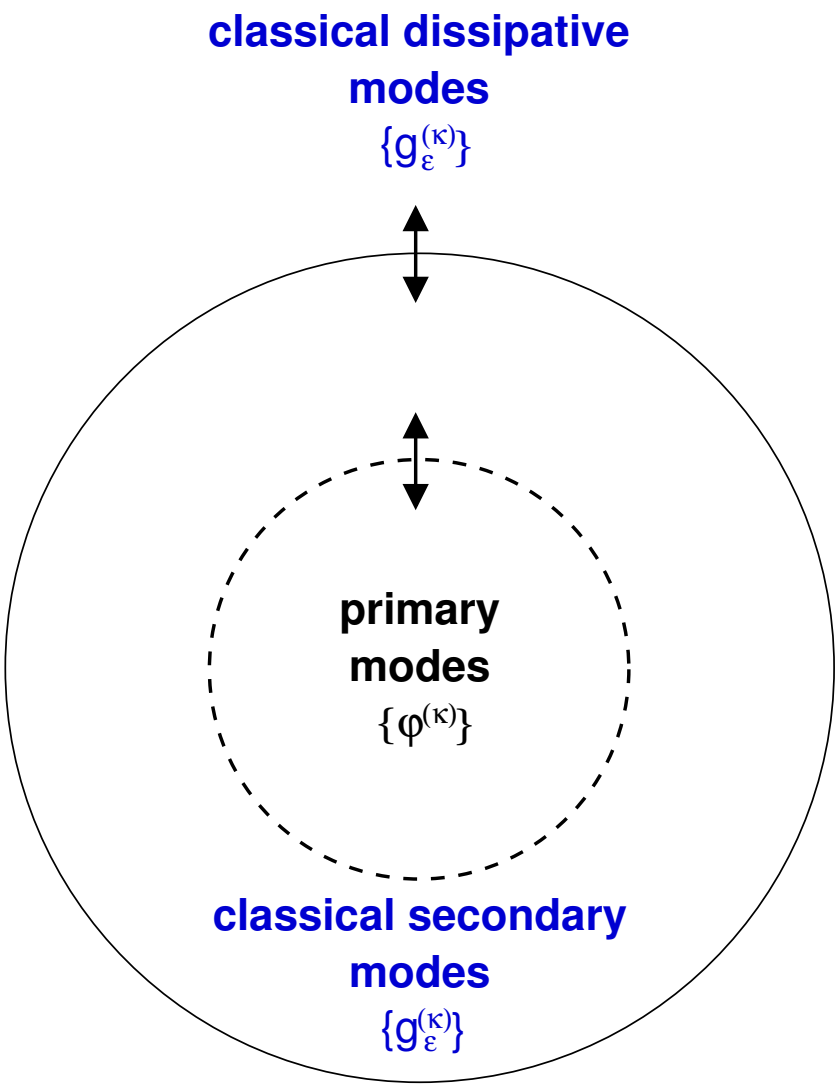
Binder, Polkehn, Ma, Burghardt, Chem. Phys. 482, 16 (2017)





Topics

Quantum-Classical Limit of G-MCTDH



take GWP subspace to classical limit:

$$\Psi^{\mathrm{qc}}(r,t) = \sum_J A_J(t)\ \Phi_J^{\mathrm{qc}}(r,t)$$

$$\Phi_J^{\mathrm{qc}}(r,t) = \underbrace{\prod_{\kappa=1}^{M} \varphi_{j_\kappa}^{(\kappa)}(r_\kappa,t)}_{\text{primary nodes}}\ \underbrace{\prod_{\kappa=M+1}^{P} g_{\varepsilon,j_\kappa}^{(\kappa)}(r_\kappa,t)}_{\text{secondary modes}}$$

Römer, Burghardt, Mol. Phys. 111, 3618 (2013)

use "narrow" semiclassical GWPs:

$$g_{\varepsilon,j_\kappa}^{(\kappa)}(r_\kappa) = N_\varepsilon \exp\left[-\frac{1}{2\varepsilon}(r_\kappa - q_{j_\kappa})\cdot a(r_\kappa - q_{j_\kappa}) + \frac{i}{\varepsilon} p_{j_\kappa}^{(\kappa)}(t)\cdot(r_\kappa - q_{j_\kappa})\right]$$

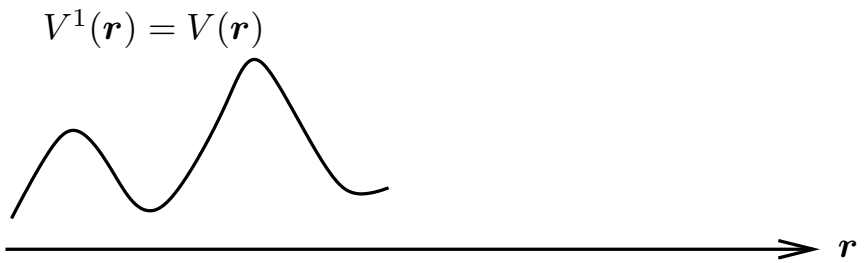
Classical Limit as Scaling Limit

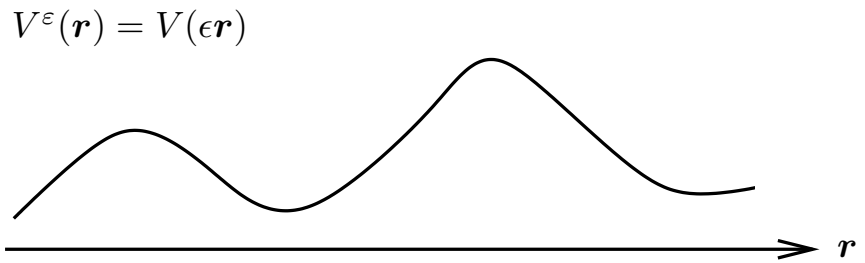
- condition for classicality:

  $\lambda_{dB} \ll L$

  λ_{dB} = de Broglie wave length; L = scale of variation of the potential V
- rescale potential: $V^{\varepsilon}(r) := V(\varepsilon r)$ such that $\varepsilon \to 0$ corresponds to the limit of slow variation of V^{ε}
- switch to macroscopic coordinates: $(\tilde{r}, \tilde{t}) = (\varepsilon r, \varepsilon t)$ such that the Schrödinger Equation reads ($\hbar = 1$, $m = 1$):

$$i\varepsilon \frac{\partial}{\partial \tilde{t}} \Psi(\tilde{r}, \tilde{t}) = \left[-\frac{\varepsilon^2}{2} \Delta_{\tilde{r}} + V(\tilde{r}) \right] \Psi(\tilde{r}, \tilde{t})$$





Classical-Limit Gaussian Wavepackets

$$g_{\varepsilon,j}(\tilde{r}) = N_\varepsilon \exp\left[-\frac{1}{2\varepsilon}(\tilde{r}-q_j)\cdot a(\tilde{r}-q_j) + \frac{i}{\varepsilon}p_j\cdot(\tilde{r}-q_j)\right]$$

- "narrow" wavepackets centered around position and momentum (q_j, p_j),
  $\|(\hat{r}-q_j)g_{\varepsilon,j}\| \sim \sqrt{\varepsilon} \qquad \|(\hat{p}-p_j)g_{\varepsilon,j}\| \sim \sqrt{\varepsilon}$
- move along classical trajectories (up to an error of order $\sqrt{\varepsilon}$)
  $g_{\varepsilon,j}(\tilde{r},\tilde{t}) \sim \exp\left(\frac{i}{\varepsilon}S^{\mathrm{cl}}(\tilde{t})\right) g_{\varepsilon,j}(\tilde{r}, q_j^{\mathrm{cl}}(\tilde{t}), p_j^{\mathrm{cl}}(\tilde{t}))$
- in this limit, the Gaussian wavepackets are decoupled from each other

G. Hagedorn, Ann. Inst. H. Poincaré Phys. Théor. **42** (1985), no. 4, 363, G. Hagedorn, Ann. Physics **269** (1998), 77

Mixed Quantum-Classically Evolved Wavefunction

$$\Psi^{\mathrm{qc}}(r,t) = \sum_{j_1} \cdots \sum_{j_M} \sum_{l} A^{\mathrm{qc}}_{j_1 \cdots j_M, l} \left(\prod_{\kappa=1}^{M} \varphi^{(\kappa)}_{j_\kappa}(r_\kappa, t) \right) \exp\left(\frac{i}{\varepsilon} S^{\mathrm{cl}}_l \right) g^{(f)}_{\varepsilon,l}(r_f; q^{(f)}_l, p^{(f)}_l)$$

coefficients:
$$i\dot{A}_l = H A_l$$

SPFs (primary modes):
$$i\dot{\varphi}^{(\kappa)} = \left(\hat{1} - \hat{P}^{(\kappa)} \right) \left[\rho^{(\kappa)} \right]^{-1} \hat{H}^{(\kappa)} \varphi^{(\kappa)}$$

classical secondary modes:
$$\dot{q}^{(f)}_l = p^{(f)}_l \qquad \dot{p}^{(f)}_l = -\nabla_{q_l} H^{(f)}_l$$

- the resulting quantum-classical dynamics corresponds to a multiconfigurational Ehrenfest (MCE) approach
- the trajectories are still coupled through the primary-mode mean fields

Römer, Burghardt, Mol. Phys. 111, 3618 (2013)

MCE Nonadiabatic Dynamics (Diabatic Representation)

$$\hat{H} = -\frac{\varepsilon^2}{2}\nabla_r^2 \hat{1} + \hat{V} \qquad \hat{V}(r) = \begin{pmatrix} V_{11}(r) & V_{12}(r) \\ V_{12}(r) & V_{22}(r) \end{pmatrix}$$

$$|\Psi^{\mathrm{qc}}(r,t)\rangle = \sum_{n=1}^{n_{\mathrm{states}}} \sum_{l=1}^{n_G} A_{nl}(t) \exp\left(\frac{i}{\varepsilon} S_l^{\mathrm{cl}}(t)\right) g_{\varepsilon,l}(r; q_l(t), p_l(t)) \, |n\rangle \qquad (\text{“single-set”})$$

coefficients: $i\dot{\boldsymbol{A}}_l = \boldsymbol{H}(q_l)\boldsymbol{A}_l$

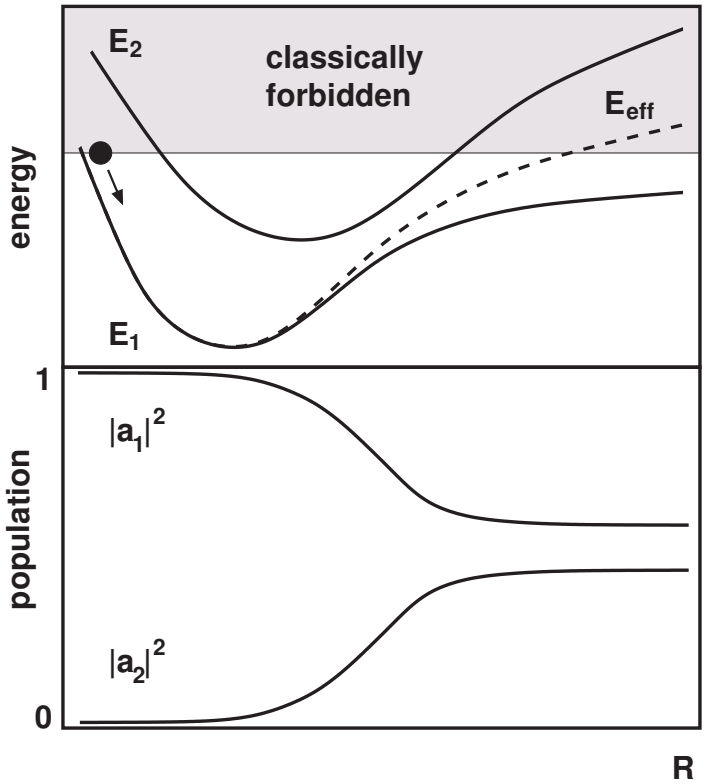
classical modes: $\dot{q}_l = p_l \qquad \dot{p}_l = -\nabla_{q_l} \bar{V}_l(q_l)$

with the mean-field potential $\bar{V}_l = \left[\sum_n |A_{nl}|^2\right]^{-1} \sum_n \sum_{n'} A_{nl}^* A_{n'l} \langle n|\hat{V}(r = q_l)|n'\rangle$

- Ψ^{qc} evolves along a superposition of Ehrenfest trajectories
- similarly for adiabatic representation (kinetic energy couplings)

see also Shalashilin, J. Chem. Phys. 130, 244101 (2009), 132, 244111 (2010)

Ehrenfest & Beyond



N. L. Doltsinis, in: Quantum Simulations of Complex Many-Body Systems: From Theory to Algorithms NIC Series, Jülich, 10, p. 377 (2002)

- single Ehrenfest trajectory: mean field
  $\bar{V}(q) = \sum_{n,n'} A_n A_{n'} \langle n|\hat{V}(q)|n'\rangle$

  Delos, Thorson, Knudson, Phys. Rev. A 6, 709 (1972)
  Billing, Chem. Phys. Lett. 100, 535 (1983)

- multiconfigurational Ehrenfest: coherent superposition of trajectories (q_l, p_l) with mean fields
  $\bar{V}_l(q_l) = [\sum_n |A_{nl}|^2]^{-1} \sum_{n,n'} A^*_{nl} A_{n'l} \langle n|\hat{V}(q_l)|n'\rangle$

  Shalashilin, J. Chem. Phys. 130, 244101 (2009), 132, 244111 (2010)
  Römer, Burghardt, Mol. Phys. 111, 3618 (2013)

- different from statistical Ehrenfest approach

  Alonso et al., J. Chem. Phys. 137, 054106 (2012)

MCE-like Dynamics for Non-Scaled GWPs

- important in practice, in view of GWP-based sampling of initial conditions and guaranteeing norm conservation
- two-layer ansatz required to restrict electronic coupling to lth subspace:

$$|\Psi^{\mathrm{qc}}(r,t)\rangle = \sum_{l=1}^{n_G} \tilde{A}_l(t)|\Phi_l^{\mathrm{qc}}(r,t)\rangle = \sum_{l=1}^{n_G} \tilde{A}_l(t)\exp\left(\frac{i}{\hbar}S_l^{\mathrm{cl}}(t)\right) g_l(r;q_l(t),p_l(t))\,|\chi_l^{(\mathrm{el})}(t)\rangle$$

$$|\chi_l^{(\mathrm{el})}(t)\rangle = \sum_{n=1}^{n_{\mathrm{states}}} B_{nl}(t)|n\rangle$$

$\tilde{\boldsymbol{A}}$ coefficients: $i\boldsymbol{S}\dot{\tilde{\boldsymbol{A}}} = (\boldsymbol{H} - i\tau)\tilde{\boldsymbol{A}}$

$\boldsymbol{B}$ coefficients: $i\dot{\boldsymbol{B}}_l = \boldsymbol{H}(q_l)\boldsymbol{B}_l$

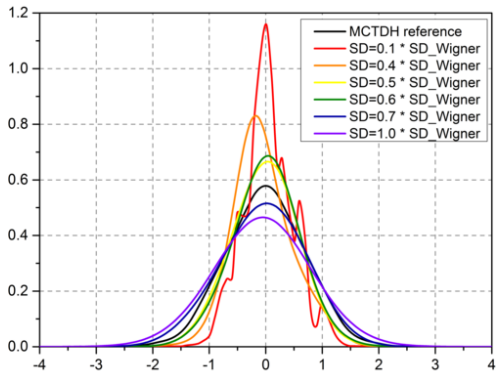
classical modes: $\dot{q}_l = p_l \quad \dot{p}_l = -\nabla_{q_l}\bar{V}_l(q_l)$

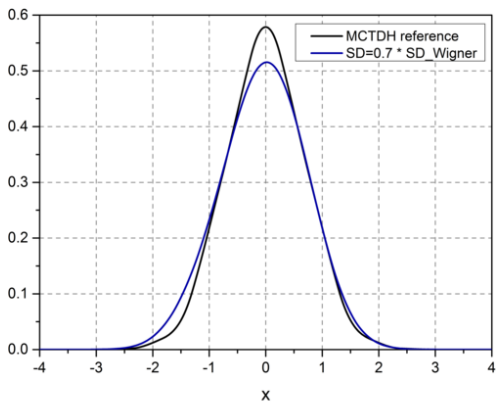
with the mean-field potential $\bar{V}_l = \left[\sum_n |B_{nl}|^2\right]^{-1} \sum_n \sum_{n'} B_{nl}^* B_{n'l} \langle n|\hat{V}(r=q_l)|n'\rangle$

see also Shalashilin, J. Chem. Phys. 132, 244111 (2010)

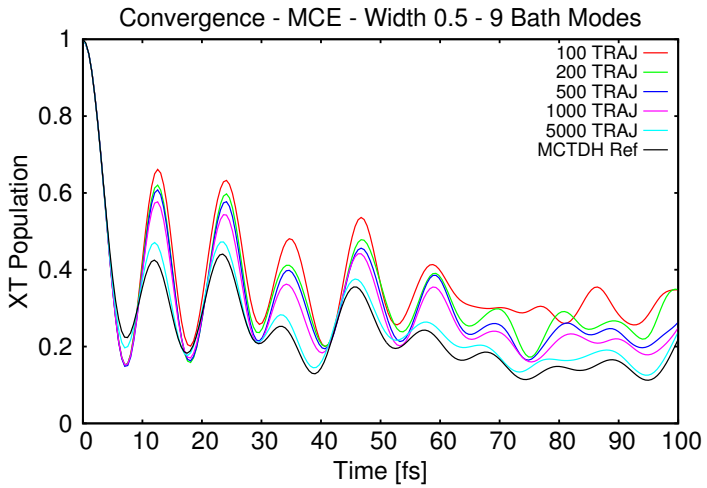
Multiconfigurational Ehrenfest Dynamics

- 4D – 40D spin-boson system
- several 1000 trajectories
- importance sampling over ρ_{Wigner}
- strong dependence on GWP width

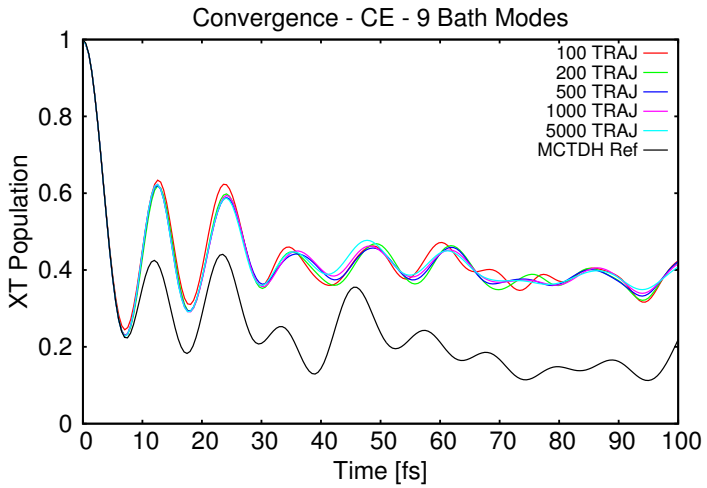




- Multiconfiguration Ehrenfest



- For Comparison: Statistical Ehrenfest



Multiconfigurational Ehrenfest System – Properties

- the quantum-classical wavefunction state carries correlations due to the multiconfigurational wavefunction form,

$$\Psi^{\mathrm{qc}}(r,t) = \sum_J \sum_l A^{\mathrm{qc}}_{J,l}(t)\Phi_J(r_\kappa,t)\exp\left(\frac{i}{\varepsilon}S^{\mathrm{cl}}_l\right) g^{(f)}_{\varepsilon,l}(r_f;q^{(f)}_l,p^{(f)}_l)$$

- the reduced density matrix of the quantum subsystem is in a mixed state,[1]

$$\rho^{sys}_{qc}(x,x',t) = \mathrm{Tr}_{cl}\left[\Psi^{\varepsilon}_{qc}(x,r,t)\Psi^{\varepsilon *}_{qc}(x',r',t)\right]$$

- statistical ensembles can be constructed as follows:

$$\rho^{\varepsilon}_{qc}(x,r,x',r',t) = \sum_n p_n \Psi^{\varepsilon}_{qc,n}(x,r,t)\Psi^{\varepsilon *}_{qc,n}(x',r',t)$$

[1] By contrast, single-trajectory Ehrenfest evolution always yields a pure subsystem state.

Is Multiconfigurational Ehrenfest Dynamics Consistent?

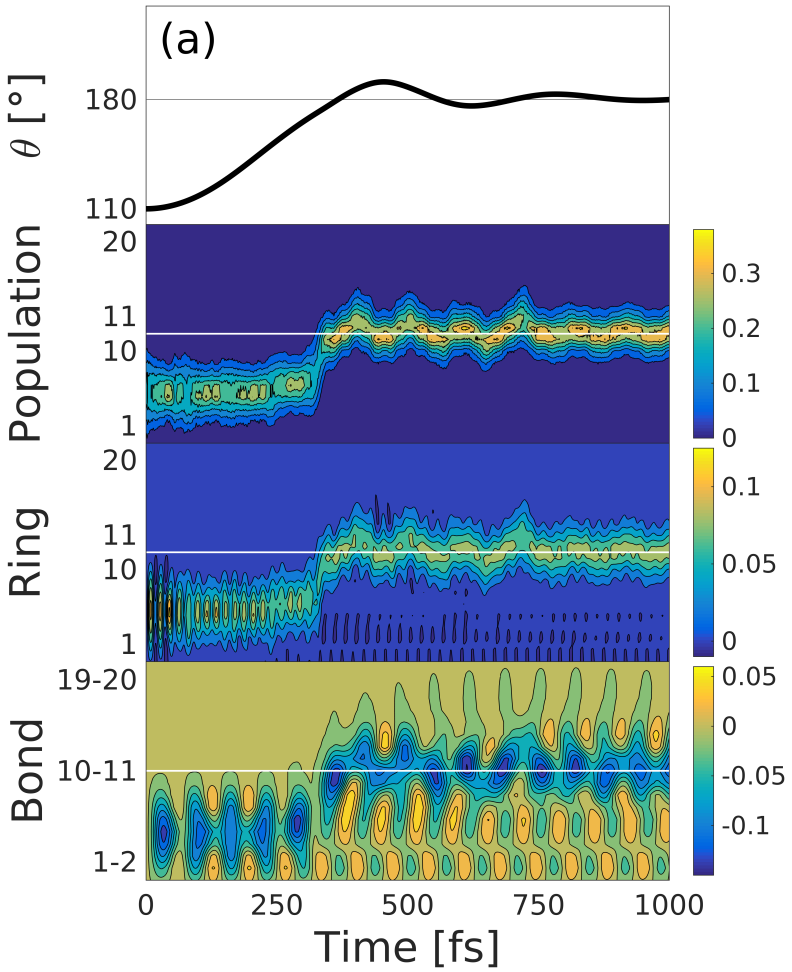
- the properties of the underlying wavefunction state Ψ_{qc} are preserved
- correlations between the quantum and classical subspaces are accounted for
- the dynamics is variational, hence a generalized Poisson bracket structure exists: $i\{\cdot,\cdot\}_{qc} = i\sum_n\{\langle H\rangle, A_n\} + i\sum_l\{\langle H\rangle, \xi_l\}$ where $\langle H\rangle = \langle\Psi_{qc}|\hat{H}|\Psi_{qc}\rangle$

However,

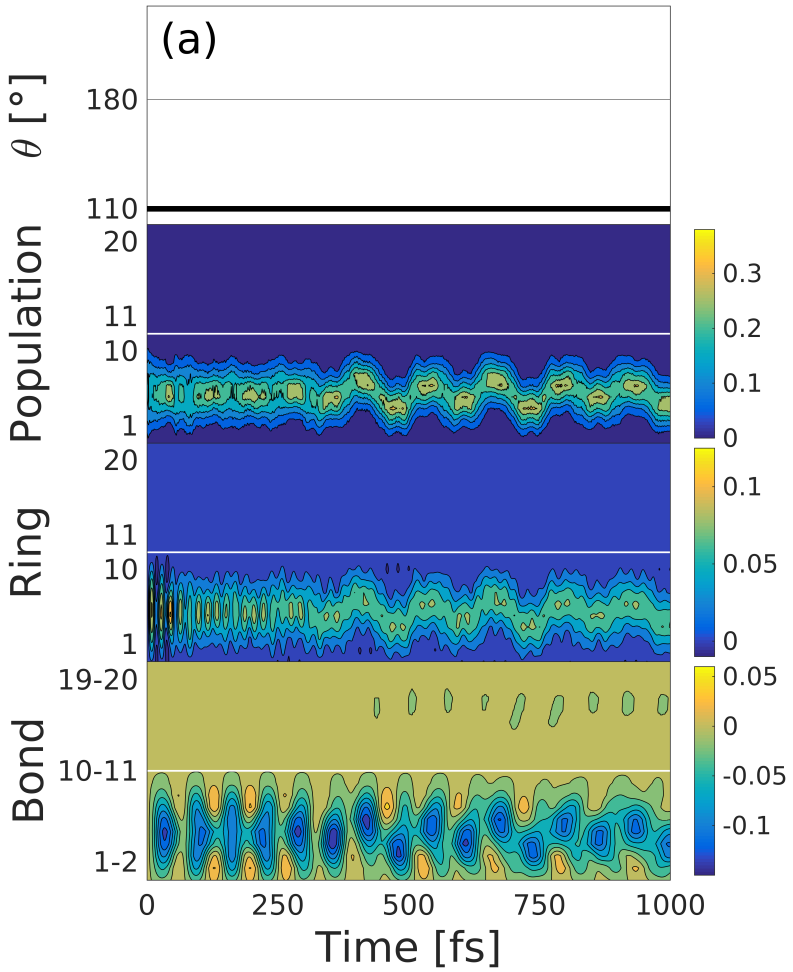
- the single-configurational (standard Ehrenfest) case is not a satisfactory quantum-classical description
- due to the non-linear structure of the equations, a direct comparison with other approaches (e.g., the QC Liouville Equation) is not straightforward

Where We're Heading: Exciton Dynamics

C-C inter-monomer mode + local C=C + torsion + bath

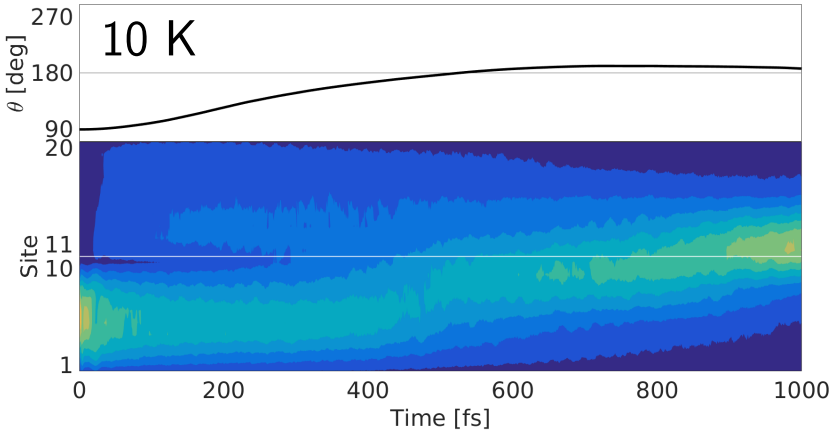


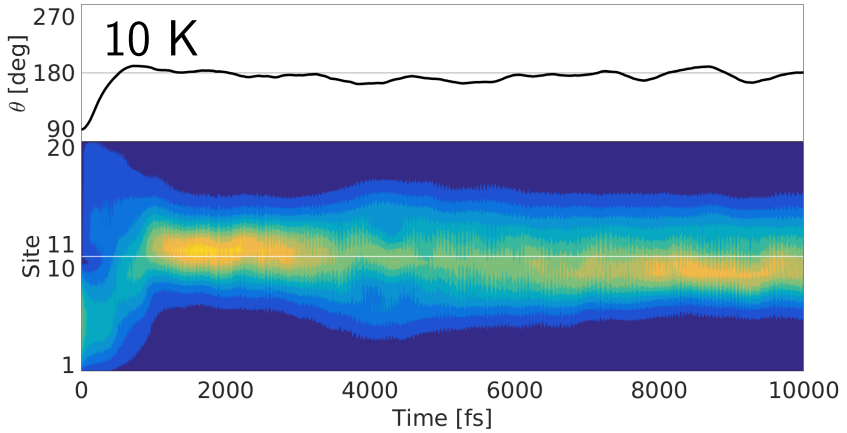
C-C inter-monomer + local C=C + fixed torsion

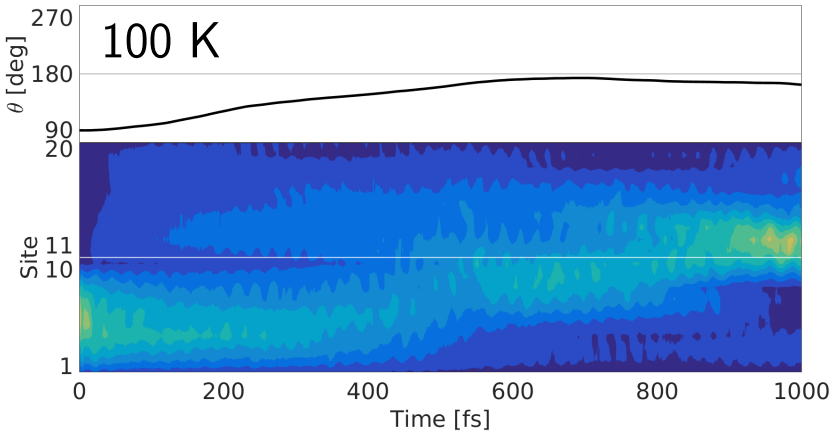


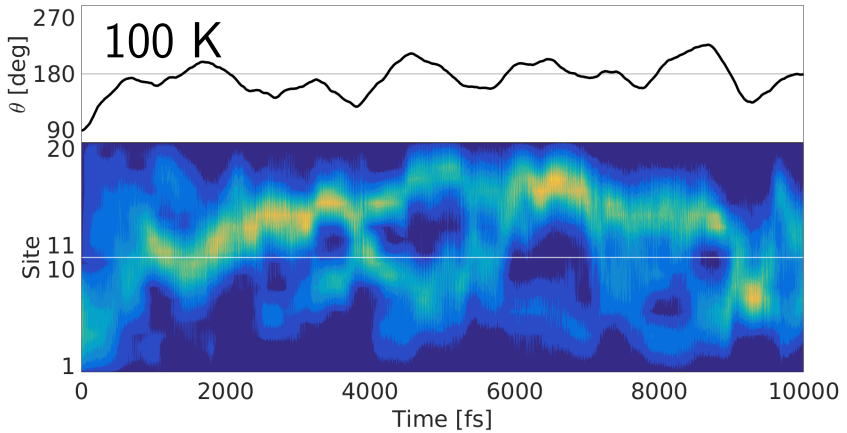
- ML-MCTDH: 20 Frenkel sites, up to 60 modes; w & w/o torsional relaxation

Temperature Effects: Ehrenfest/Langevin dynamics









- ultrafast transients not correctly reproduced by Ehrenfest dynamics
- at increasing temperatures, fluctuations start driving exciton migration

Summary

- G-MCTDH/ML-G-MCTDH/vMCG are useful due to their proximity to classical mechanics, while permitting full quantum convergence
- drawback: non-orthogonal functions – but various assets: analytical form of matrix elements, modest memory requirements, localized functions
- pure-GWP (vMCG) variant for on-the-fly applications (G. A. Worth): matching algorithm for 2L-vMCG phase-space points, PES database, ...
- two-layer (or multi-layer) variant employs correlated FG-based particles; need for sampling strategies when combining with on-the-fly applications
- natural quantum-classical limit of G-MCTDH: multiconfiguration Ehrenfest
- Langevin dynamics from a stochastic Schrödinger equation picture
- next steps: statistical sampling & extension to thermal GWPs; random-phase thermal wavepackets; GWP-based correlation functions (cf. Coughtrie & Tew, JCP 140, 194106 (2014)); GWP calculations for nonlinear optical signals, transport dynamics, multiscale microscopic/mesoscopic dynamics ...

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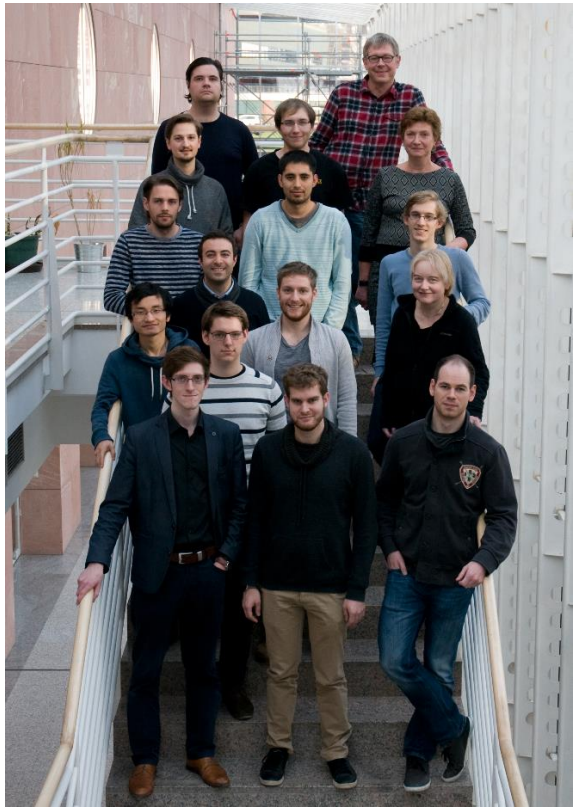

Theoretical Chemistry
of Complex Systems

AK Burghardt