Simulation of quantum dynamics and transport using multiconfiguration wave-function methods

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Outline

- **Methodology**

  Basis-set methods for quantum dynamics

  Multilayer Multiconfiguration Time-Dependent Hartree method (ML-MCTDH)

  Extension of ML-MCTDH to treat indistinguishable particles and transport problems

  Combination with reduced density matrix schemes

- **Applications**

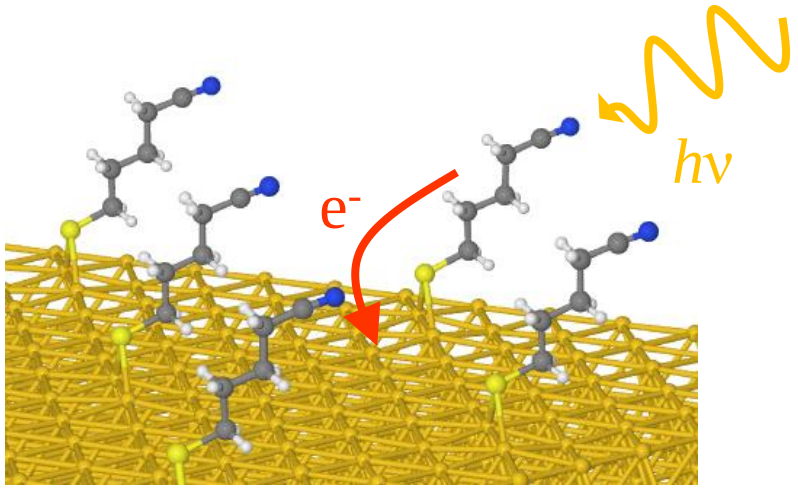
  Spin-Boson model for charge and energy transport

  Photoinduced electron transfer processes

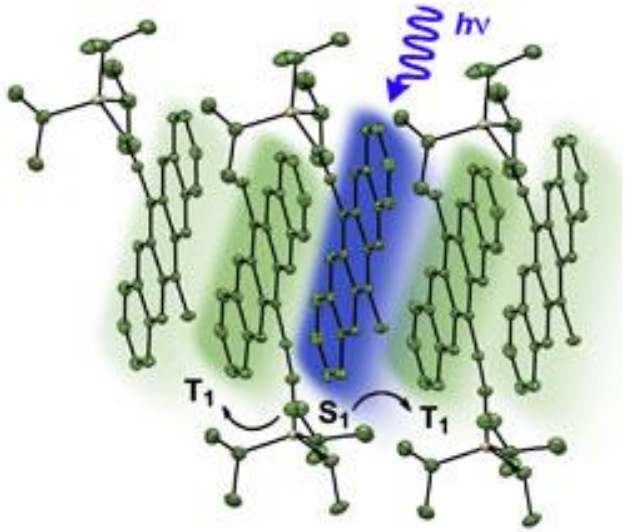
  Charge transport in single-molecule junctions

Quantum dynamical processes

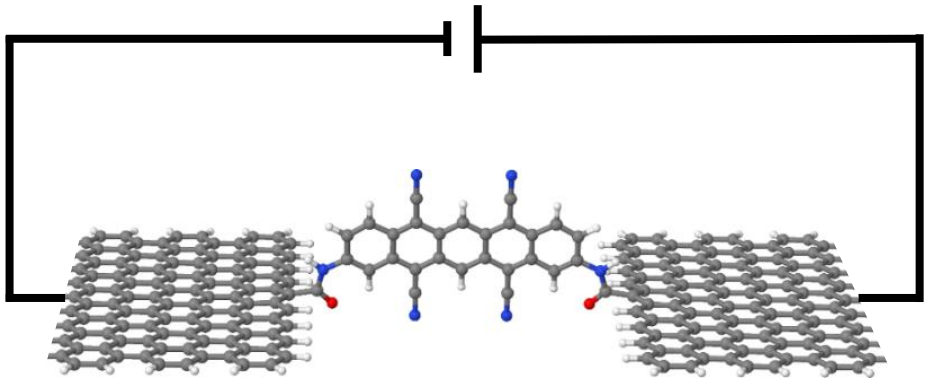
Electron transfer in molecules, at surfaces, and in solution



Energy transfer in molecular materials



Quantum transport in nanostructures



Quantum dynamics: Methods

$$i\frac{\partial}{\partial t}|\Psi(t)\rangle = H|\Psi(t)\rangle$$

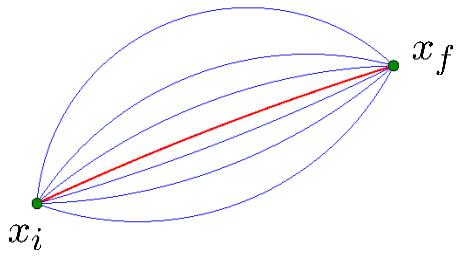
$$C(t) = \mathrm{tr}(e^{-\beta H}Ae^{iHt}Be^{-iHt})$$

- **Quantum dynamical basis-set methods**

$$|\Psi(t)\rangle = \sum_J A_J(t)|\Phi_J\rangle$$

- **Trajectory-based semiclassical methods**

$$\langle x_f|e^{-iHt}|x_i\rangle \approx \sum_{\text{class.paths}} \left[2\pi i \left|\frac{\partial x_f}{\partial p_i}\right|\right]^{-1/2} e^{iS}$$



- **System-bath methods: Path integral, reduced density matrix, …**

$$\frac{\partial}{\partial t}\rho(t) = -i[H_s,\rho(t)] - \int_0^t d\tau\kappa(\tau)\rho(t-\tau)$$

Conventional quantum dynamical basis-set methods

$$i\frac{\partial}{\partial t}|\Psi(t)\rangle = H|\Psi(t)\rangle \qquad H = \sum_j \frac{1}{2m_j}p_j^2 + V(x_1,\ldots,x_f)$$

- Expansion of the wave function in a fixed time-independent basis set

$$|\Psi(t)\rangle = \sum_J A_J(t)|\Phi_J\rangle = \sum_{j_1=1}^{N}\cdots\sum_{j_f=1}^{N} A_{j_1\ldots j_f}(t)\prod_{k=1}^{f}|\phi_{j_k}^k\rangle$$

- Dirac-Frenkel variational principle $\langle\delta\Psi|i\frac{\partial}{\partial t} - H|\Psi\rangle = 0$

- Equations of motion $i\dot{A}_J(t) = \sum_L \langle\Phi_J|H|\Phi_L\rangle A_L(t)$

- Scaling of numerical effort for f degrees of freedom: $\sim N^f$

  for $N = 10$ basis states:
  3 atoms ($f = 3$): 10^3 equations
  6 atoms ($f = 12$): 10^{12} equations

Multiconfiguration Time-Dependent Hartree (MCTDH) Method

- Multiconfiguration expansion of the wavefunction

$$|\Psi(t)\rangle = \sum_J A_J(t)|\Phi_J(t)\rangle = \sum_{j_1}\cdots\sum_{j_f} A_{j_1\ldots j_N}(t)\prod_{k=1}^{f}|\phi_{j_k}^k(t)\rangle$$

with time-dependent configurations $|\Phi_J(t)\rangle$ and 'single-particle' functions $|\phi_{j_k}^k(t)\rangle$

- Variations $\left\langle \delta\Psi(t)\left| i\frac{\partial}{\partial t} - H\right|\Psi(t)\right\rangle_{\text{coefficients}} = 0 \qquad \left\langle \delta\Psi(t)\left| i\frac{\partial}{\partial t} - H\right|\Psi(t)\right\rangle_{\text{orbitals}} = 0$

- MCTDH equations of motion

$$i\dot{A}_J(t) = \sum_L \langle\Phi_J(t)|H|\Phi_L(t)\rangle A_L(t)$$

$$i|\dot{\underline{\phi}}^k(t)\rangle = \left[1-P^k(t)\right]\left[\rho^k(t)\right]^{-1}\langle H(t)\rangle^k|\underline{\phi}^k(t)\rangle$$

Meyer, Manthe, Cederbaum, CPL **165**, 73 (1990); Beck, Jäckle, Worth, Meyer, Phys. Rep. **324**, 1 (2000)

Multiconfiguration Time-Dependent Hartree (MCTDH) Method

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– projector on single particle space $P^k(t) = \sum_n |\phi_n^k(t)\rangle\langle\phi_n^k(t)|$

– reduced density matrix $\rho_{nm}^k(t) = \langle G_n^k(t)|G_m^k(t)\rangle$

– single-hole function $|G_n^k(t)\rangle = \langle\phi_n^k(t)|\Psi(t)\rangle$

– mean-field operator $\langle H(t)\rangle_{nm}^k = \langle G_n^k(t)|H|G_m^k(t)\rangle$

Meyer, et al. Phys. Rep. **324**, 1 (2000); Meyer, Gatti, Worth, *Multidimensional Quantum Dynamics* (Wiley, 2009)

Multiconfiguration Time-Dependent Hartree (MCTDH) Method

- Multiconfiguration expansion of the wavefunction

$$|\Psi(t)\rangle = \sum_{j_1,\ldots,j_f=1}^{n} A_{j_1\ldots j_f}(t) \prod_{k=1}^{f} |\phi_{j_k}^k(t)\rangle$$

- MCTDH equations of motion

$$i\dot{A}_J(t) = \sum_L \langle \Phi_J(t)|H|\Phi_L(t)\rangle A_L(t)$$

$$i|\dot{\underline{\phi}}^k(t)\rangle = \left[1 - P^k(t)\right]\left[\rho^k(t)\right]^{-1} \langle H(t)\rangle^k |\underline{\phi}^k(t)\rangle$$

- Accuracy: depends on number of single particle functions n

$n = 1$: $|\Psi(t)\rangle = A(t)\,|\phi^1(t)\rangle \cdots |\phi^f(t)\rangle$ time-dependent Hartree (poor approximation for interacting systems)

$n > 1$: converges variationally towards solution of time-dependent Schrödinger equation

MCTDH – Scaling of numerical effort

Consider a system with f degrees of freedom, each of which is described by a basis of N states

method	wavefunction	memory
standard	$\|\Psi(t)\rangle = \sum_J C_J(t) \prod_{k=1}^{f} \|\chi_{j_k}^k\rangle$ $j_k = 1,\ldots,N$	~ N^f
MCTDH	$\|\Psi(t)\rangle = \sum_J A_J(t) \prod_{k=1}^{f} \|\phi_{j_k}^k(t)\rangle$ $j_k = 1,\ldots,n$ $\|\phi_j^k(t)\rangle = \sum_{i=1}^{N} B_i^{k,j}(t)\|\chi_i^k\rangle$	~ $n^f + f\ n\ N$

typically $n \ll N$

Multiconfiguration Time-Dependent Hartree (MCTDH) Method

- MCTDH wavefunction

$$|\Psi(t)\rangle = \sum_{j_1,\ldots,j_f=1}^{n} A_{j_1\ldots j_f}(t) \prod_{k=1}^{f} |\phi_{j_k}^k(t)\rangle$$

$$|\phi_j^k(t)\rangle = \sum_{i=1}^{N} B_i^{k,j}(t)|\chi_i^k\rangle$$

- Tensor decomposition: Tucker format

$$|\Psi(t)\rangle = \sum_{i_1,\ldots,i_f=1}^{N} C_{i_1\ldots i_f}(t) \prod_{k=1}^{f} |\chi_{i_k}^k\rangle$$

$$C_{i_1\ldots i_f}(t) = \sum_{j_1,\ldots,j_f=1}^{n} A_{j_1\ldots j_f}(t) B_{i_1}^{1,j_1}(t)\cdots B_{i_f}^{f,j_f}(t)$$

Applied Mathematics: Grasedyck, SIAM J. Matrix Anal. Appl. **31**, 2029 (2010)

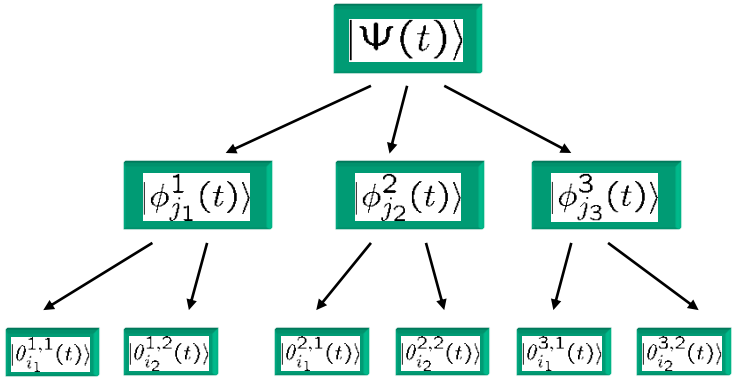
Multilayer Multiconfiguration Time-Dependent Hartree (ML-MCTDH) Method

- MCTDH $$|\Psi(t)\rangle = \sum_{j_1} \cdots \sum_{j_M} A_{j_1 \ldots j_M}(t) \prod_{k=1}^{M} |\phi_{j_k}^{k}(t)\rangle$$

- Multiconfiguration expansion of multidimensional single-particle functions

$$|\phi_{j}^{k}(t)\rangle = \sum_{i_1} \cdots \sum_{i_Q} B_{i_1 \ldots i_Q}^{k,j}(t) \prod_{q=1}^{Q} |\theta_{i_q}^{k,q}(t)\rangle$$

- Multilayer representation of wavefunction



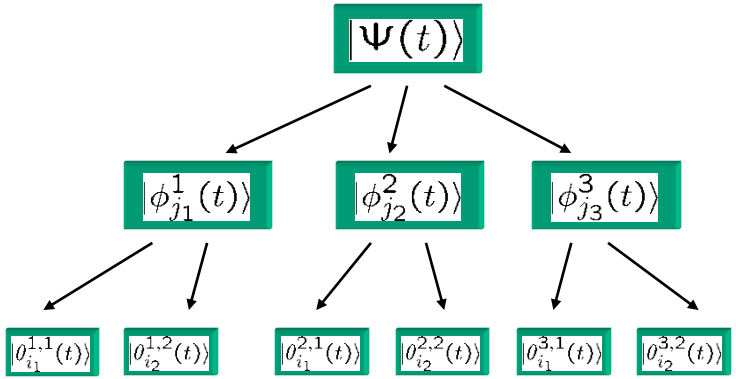
$$|\Psi(t)\rangle = \sum_{j_1} \cdots \sum_{j_M} A_{j_1 \ldots j_M}(t) \prod_{k=1}^{M} |\phi_{j_k}^{k}(t)\rangle$$

$$|\phi_{j}^{k}(t)\rangle = \sum_{i_1} \cdots \sum_{i_Q} B_{i_1 \ldots i_Q}^{k,j}(t) \prod_{q=1}^{Q} |\theta_{i_q}^{k,q}(t)\rangle$$

Wang, MT, J. Chem. Phys. **119**, 1289 (2003); Manthe, J. Chem. Phys. **128**, 164116 (2008)

Multi-Layer MCTDH Method

- Multilayer representation of wavefunction



$$|\Psi(t)\rangle = \sum_{j_1}\cdots\sum_{j_M} A_{j_1\ldots j_M}(t) \prod_{k=1}^{M} |\phi^k_{j_k}(t)\rangle$$

$$|\phi^k_j(t)\rangle = \sum_{i_1}\cdots\sum_{i_Q} B^{k,j}_{i_1\ldots i_Q}(t) \prod_{q=1}^{Q} |\theta^{k,q}_{i_q}(t)\rangle$$

- ML-MCTDH equations of motion (two-layer version) $\langle \delta\Psi | i\frac{\partial}{\partial t} - H|\Psi\rangle = 0$

$$i\dot{A}_J(t) = \sum_L \langle \Phi_J(t)|H|\Phi_L(t)\rangle A_L(t)$$

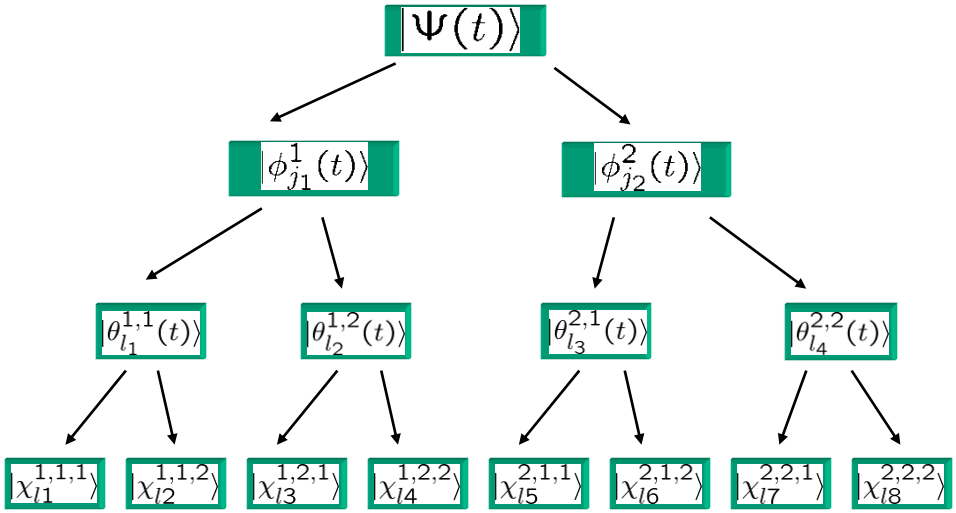
$$i|\dot{\underline{\phi}}^k(t)\rangle = \left[1 - P^k_{\mathsf{L}1}(t)\right]\left[\rho^k_{\mathsf{L}1}(t)\right]^{-1} \langle H(t)\rangle^k_{\mathsf{L}1} |\underline{\phi}^k(t)\rangle$$

$$i|\dot{\underline{\theta}}^{k,q}(t)\rangle = \left[1 - P^{k,q}_{\mathsf{L}2}(t)\right]\left[\rho^{k,q}_{\mathsf{L}2}(t)\right]^{-1} \langle H(t)\rangle^{k,q}_{\mathsf{L}2} |\underline{\theta}^{k,q}(t)\rangle$$

Wang, MT, J. Chem. Phys. **119**, 1289 (2003); Wang, J. Phys. Chem. A **119**, 7951 (2015)

Multi-Layer MCTDH Method

- Multilayer representation of wavefunction



$$|\Psi(t)\rangle = \sum_{j_1}\cdots\sum_{j_M} A_{j_1\ldots j_M}(t)\prod_{k=1}^{M}|\phi^k_{j_k}(t)\rangle$$

$$|\phi^k_j(t)\rangle = \sum_{l_1}\cdots\sum_{l_Q} B^{k,j}_{l_1\ldots l_Q}(t)\prod_{q=1}^{Q}|\theta^{k,q}_{l_q}(t)\rangle$$

$$|\theta^{k,q}_l(t)\rangle = \sum_{i_1}\cdots\sum_{i_R} C^{k,q,l}_{i_1\ldots i_R}(t)\prod_{r=1}^{R}|\chi^{k,q,r}_{i_r}\rangle$$

- Tensor decomposition: Hierarchical Tucker format

$$|\Psi(t)\rangle = \sum_{i_1,\ldots,i_f=1}^{N} D_{i_1\ldots i_f}(t)\prod_{k=1}^{f}|\chi^k_{i_k}\rangle$$

$$D_{i_1\ldots i_f}(t) = \sum_{j_1\ldots j_M=1}^{n} A_{j_1\ldots j_M}(t)\prod_{k=1}^{M}\sum_{l_1\ldots l_{Q_k}=1}^{n} B^{k,j_k}_{l_1\ldots l_{Q_k}}(t)\prod_{q=1}^{Q_k} C^{k,q,l_q}_{i_1\ldots i_{R_q}}(t)$$

Wang, MT, J. Chem. Phys. **119**, 1289 (2003); Wang, J. Phys. Chem. A **119**, 7951 (2015)

Applied Mathematics: Grasedyck, SIAM J. Matrix Anal. Appl. **31**, 2029 (2010)

ML-MCTDH – Scaling of numerical effort

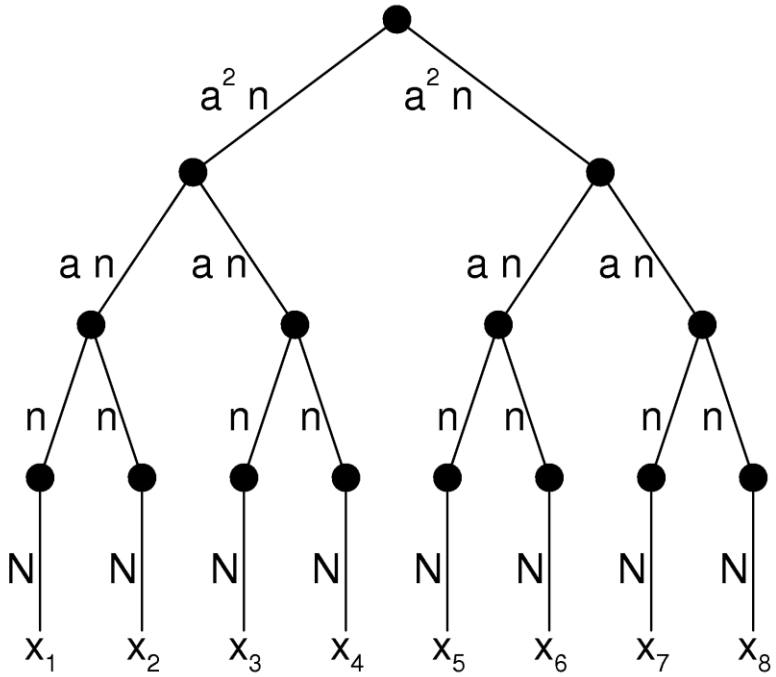
- f number of degrees of freedom ($f=2^L$)
- L number of layers
- n number of single-particle functions (SPF)
- N number of static basis functions
- a increase factor of SPFs in higher layers

number of coefficients (A,B,C, …)

$$\frac{a}{2}\cdot\frac{\frac{a^3}{2}f^{3\log_2 a}-f}{\frac{a^3}{2}-1}\cdot n^3+\ldots$$

$$a=1: \quad \sim f\cdot n^3$$

$$a=2: \quad \sim f^3\cdot n^3$$



$$|\Psi(t)\rangle = \sum_{j_1=1}^{a^2 n}\sum_{j_2=1}^{a^2 n} A_{j_1 j_2}(t)|\phi^1_{j_1}(t)\rangle|\phi^2_{j_2}(t)\rangle$$

$$|\phi^k_n(t)\rangle = \sum_{i_1=1}^{an}\sum_{i_2=1}^{an} B^{k,n}_{i_1 i_2}(t)|\theta^{k,1}_{i_1}(t)\rangle|\theta^{k,2}_{i_2}(t)\rangle$$

$$|\theta^{k,m}_n(t)\rangle = \sum_{l_1=1}^{n}\sum_{l_2=1}^{n} C^{k,m,n}_{l_1 l_2}(t)|\chi^{k,m,1}_{l_1}(t)\rangle|\chi^{k,m,2}_{l_2}(t)\rangle$$

$$|\chi^{k,m,r}_n(t)\rangle = \sum_{p=1}^{N} D^{k,m,r,n}_p(t)|\zeta^{k,m,r}_p\rangle$$

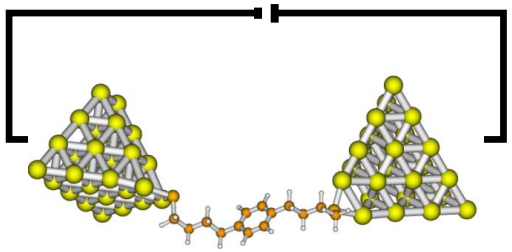
Manthe, J. Chem. Phys. **128**, 164116 (2008)

Multi-Layer MCTDH Method

- Simulation of time-correlation functions at finite temperature

$$C(t) \;=\; \mathrm{tr}(e^{-\beta H} A e^{iHt} B e^{-iHt}) \qquad\qquad \beta = \frac{1}{k_B T}$$

- Evaluation of Boltzmann operator $e^{-\beta H}$ via imaginary time propagation and Monte Carlo sampling
- Extension to describe correlated dynamics of indistinguishable particles, in particular many-electron problems
- Simulation of laser-driven dynamics and transport phenomena



- Heidelberg MCTDH program package (Meyer et al.): www.pci.uni-heidelberg.de/cms/mctdh.html

Wang, MT, et al., JCP **124**, 034114 (2006); **131**, 024114 (2009); PRB **89**, 205129 (2014)

Meyer, Gatti, Worth (Eds.) *Multidimensional Quantum Dynamics* (Wiley, 2009)

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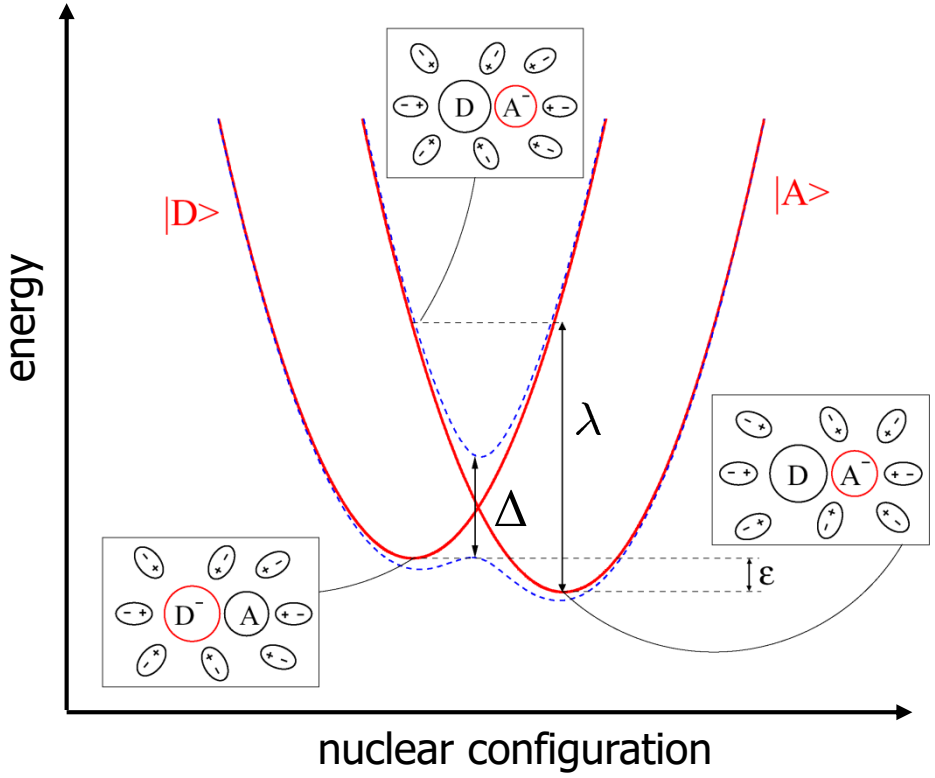
  Spin-Boson model

  Photoinduced electron transfer processes

  Charge transport in single-molecule junctions

Spin-Boson model

$$H = \frac{\varepsilon}{2}\sigma_z + \Delta\sigma_x + \frac{1}{2}\sum_j (p_j^2 + \omega_j^2 q_j^2) + \sigma_z \sum_j c_j q_j$$



Electron transfer in the condensed phase

bath spectral density

$$J(\omega) = \frac{\pi}{2}\sum_j \frac{c_j^2}{\omega_j}\delta(\omega - \omega_j) = \frac{\pi}{2}\alpha\omega e^{-\omega/\omega_c}$$

Δ electronic coupling

ε energy gap

λ reorganization energy

$$\lambda = 2\pi\alpha\omega_c$$

$$\sigma_z = |D\rangle\langle D| - |A\rangle\langle A|$$

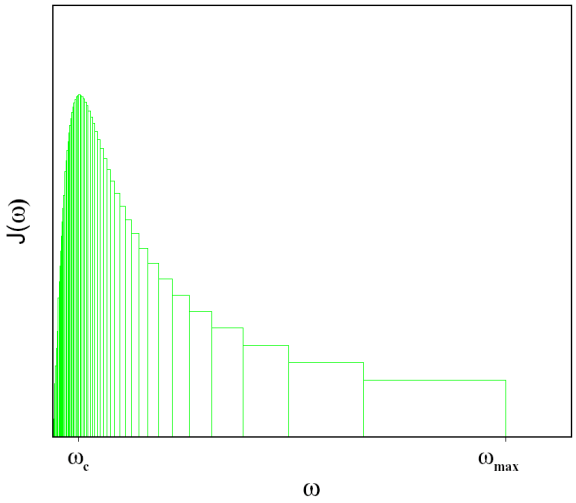
$$\sigma_x = |D\rangle\langle A| + |A\rangle\langle D|$$

Spin-Boson model

$$P(t) = \mathrm{tr}\left\{\rho_0\, e^{iHt}|D\rangle\langle D|\, e^{-iHt}\right\} \qquad \rho_0 = \frac{e^{-\beta H_0}}{Q}|D\rangle\langle D|$$

- Discretization of the continuous distribution of bath modes, J(ω), with a finite number of modes

$$J(\omega) = \frac{\pi}{2}\sum_l \frac{c_l^2}{\omega_l}\delta(\omega-\omega_l) \qquad c_j = \frac{2}{\pi}\omega_j \frac{J(\omega_j)}{g(\omega)}$$



density of frequencies $g(\omega)$

$$\int_0^{\omega_j} d\omega\, g(\omega) = j \qquad j = 1, \ldots, N_b$$

$$g(\omega) = \frac{4}{\pi}\frac{N_b}{E_r}\frac{J(\omega)}{\omega}\frac{1}{1-e^{-\omega/\omega_{\max}}}$$

Spin-Boson model

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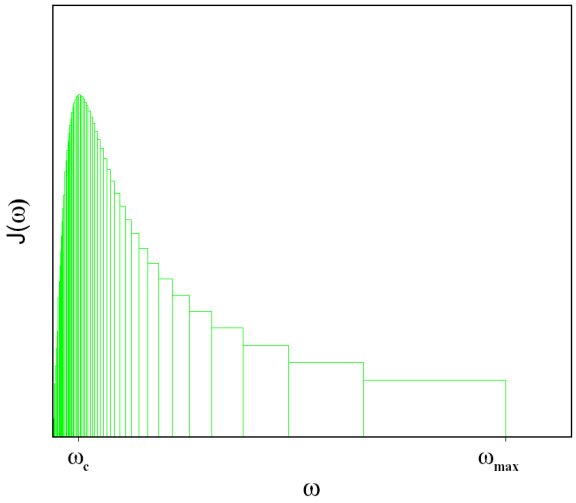

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- Discretization of the continuous distribution of bath modes, $J(\omega)$, with a finite number of modes

- Sampling of thermal distribution of initial state $e^{-\beta H_0} = \sum_n e^{-\beta E_n}|n\rangle\langle n|$

$$P_d(t) = \sum_n \rho_n \langle n|\, e^{iHt}\, |\phi_d\rangle\langle\phi_d|\, \underbrace{e^{-iHt}\, |n\rangle}_{|\Psi_n(t)\rangle} \qquad \rho_n = \frac{e^{-\beta E_n}}{Q}$$

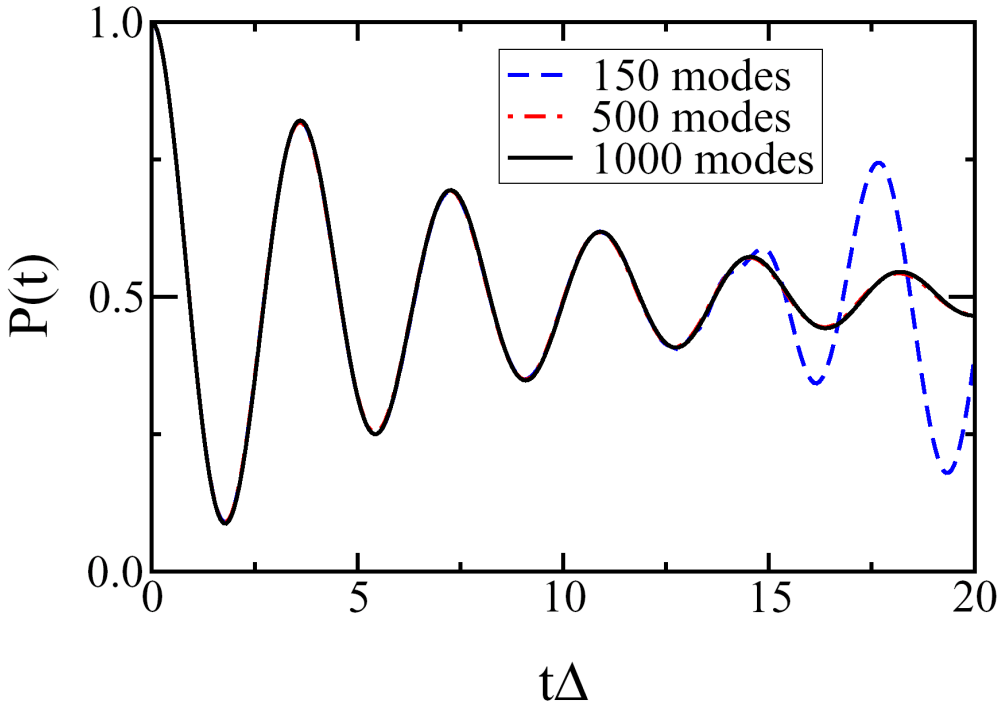
$$\rightarrow \quad i\frac{\partial}{\partial t}|\Psi_n(t)\rangle = H|\Psi_n(t)\rangle$$

ML-MCTDH

Spin-Boson model

Discretization of bath

$$H = \varepsilon\sigma_z + \Delta\sigma_x + \frac{1}{2}\sum_j (p_j^2 + \omega_j^2 q_j^2) + \sigma_z \sum_j c_j q_j$$



$$P(t) = \mathrm{tr}\left\{\rho_0\, e^{iHt}|D\rangle\langle D|\, e^{-iHt}\right\}$$

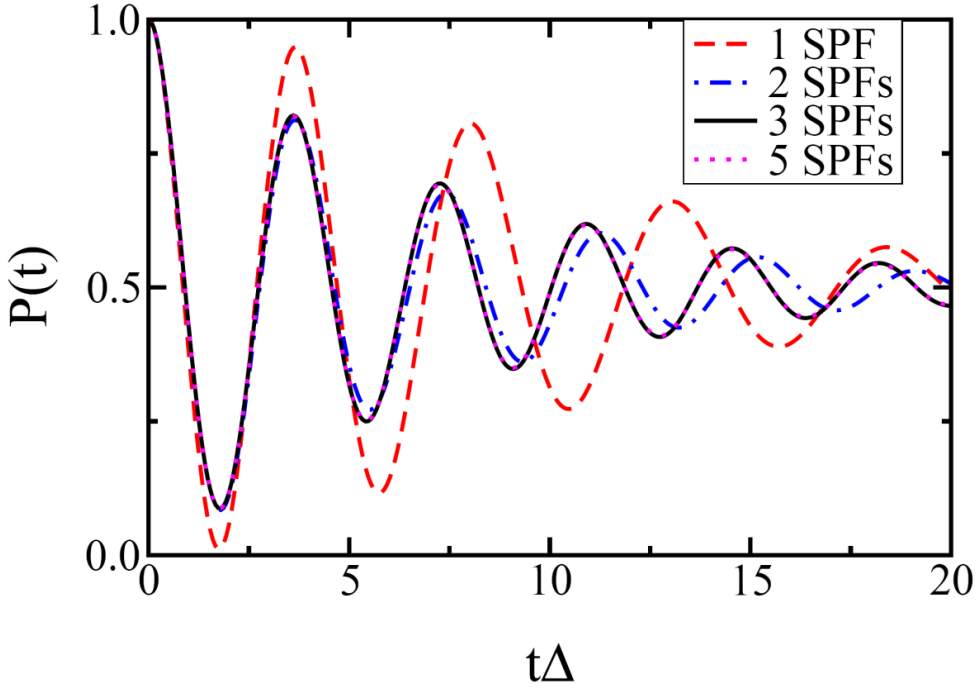
$$\rho_0 = \frac{e^{-\beta H_0}}{Q}|D\rangle\langle D|$$

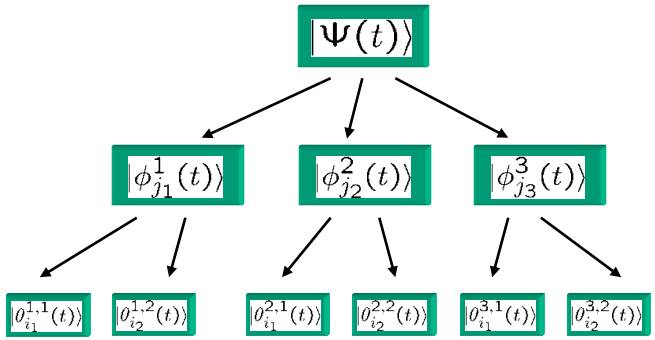
$$J(\omega) = \frac{\pi}{2}\sum_j \frac{c_j^2}{\omega_j}\delta(\omega-\omega_j) = \frac{\pi}{2}\alpha\omega e^{-\omega/\omega_c}$$

$\varepsilon = 0$ $\quad k_BT/\Delta = 0.1$ $\quad \alpha = 0.05$ $\quad \omega_c/\Delta = 60$

Spin-Boson model

Convergence with respect to number of basis functions (SPFs)



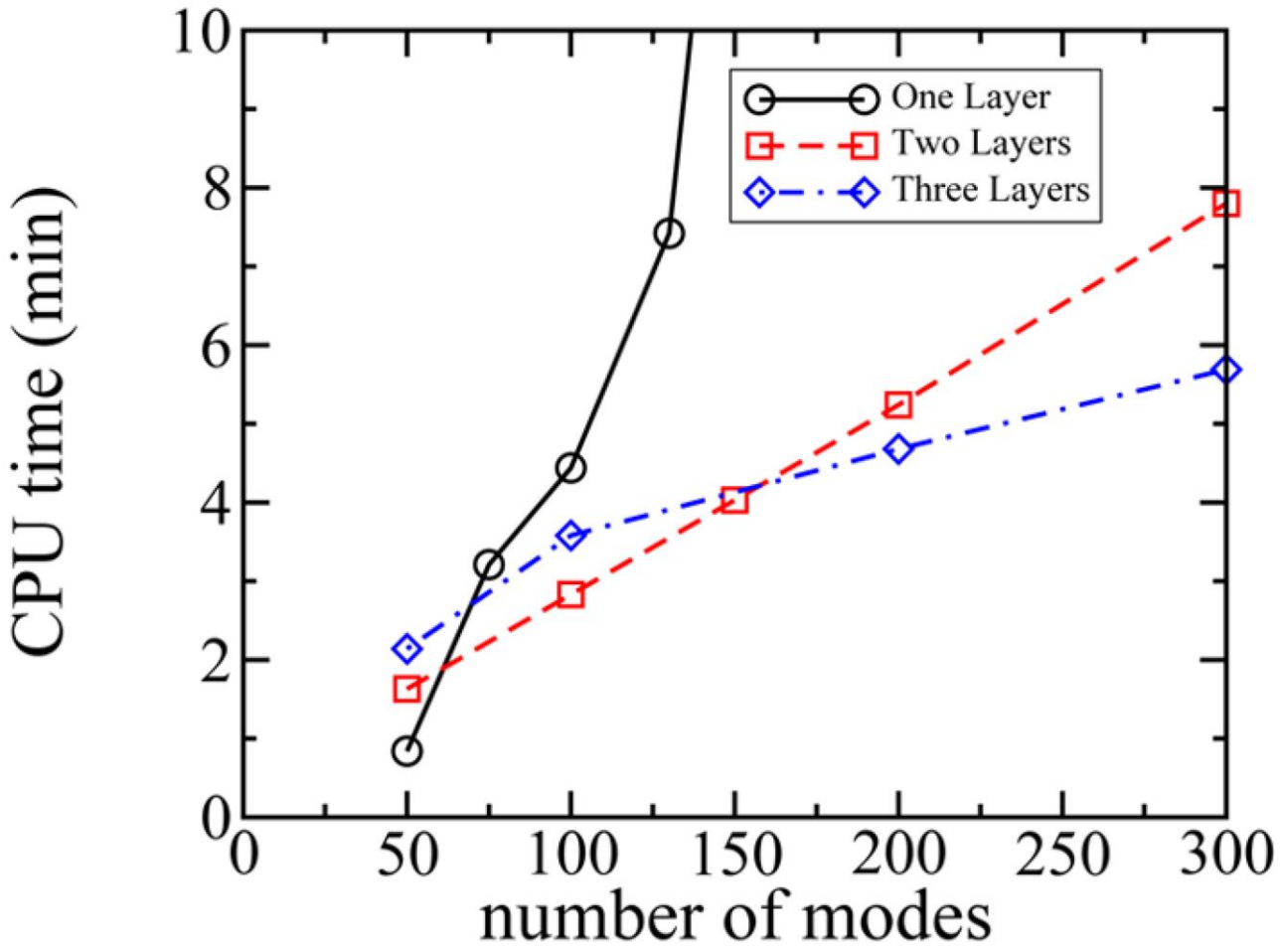


$$|\Psi(t)\rangle = \sum_{j_1=1}^{n} \cdots \sum_{j_M=1}^{n} A_{j_1 \ldots j_M}(t) \prod_{k=1}^{M} |\phi^k_{j_k}(t)\rangle$$

$$|\phi^k_j(t)\rangle = \sum_{i_1=1}^{n} \cdots \sum_{i_Q=1}^{n} B^{k,j}_{i_1 \ldots i_Q}(t) \prod_{q=1}^{Q} |\theta^{k,q}_{i_q}(t)\rangle$$

Spin-Boson Model

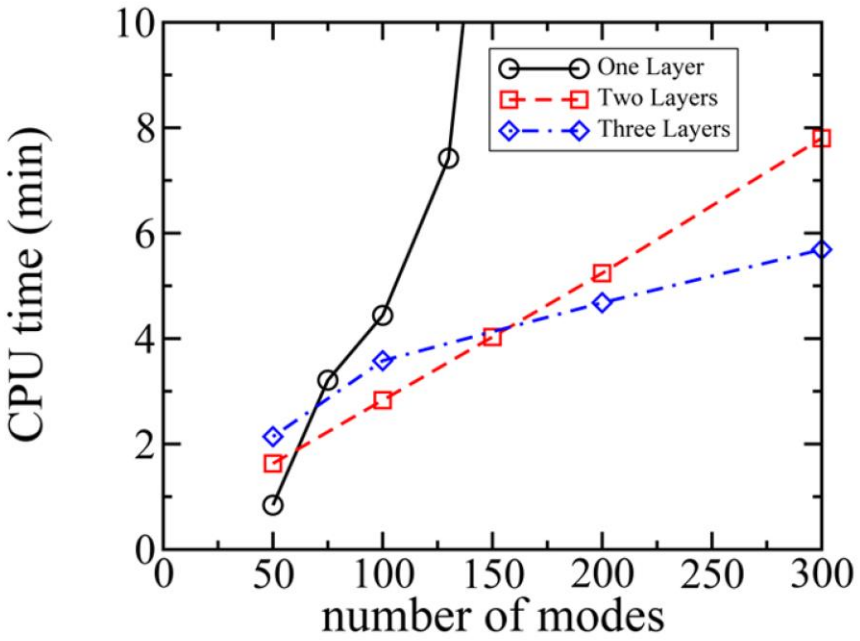
Scaling of ML-MCTDH method

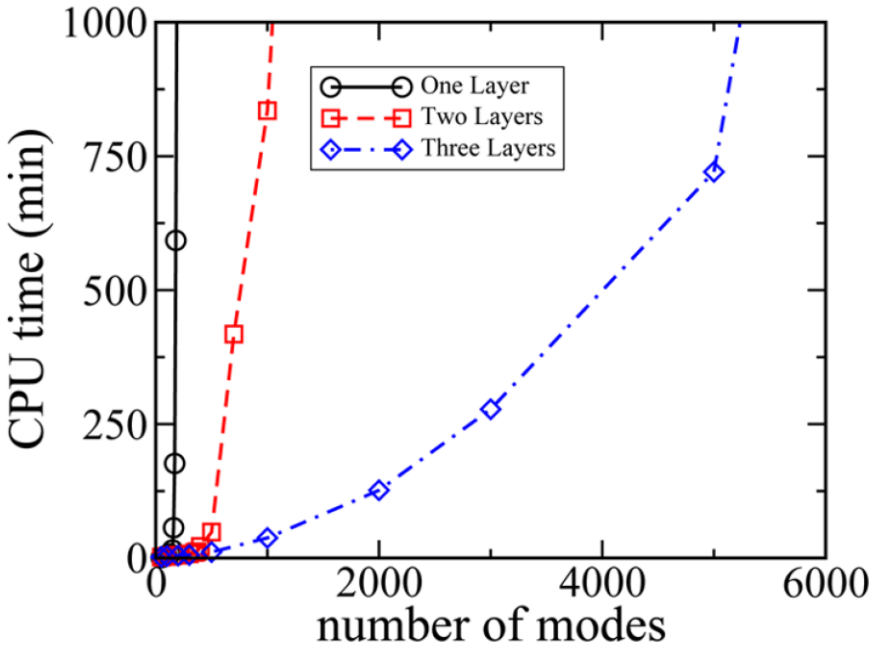


Wang, J. Phys. Chem. A **119**, 7951 (2015)

Spin-Boson Model

Scaling of ML-MCTDH method

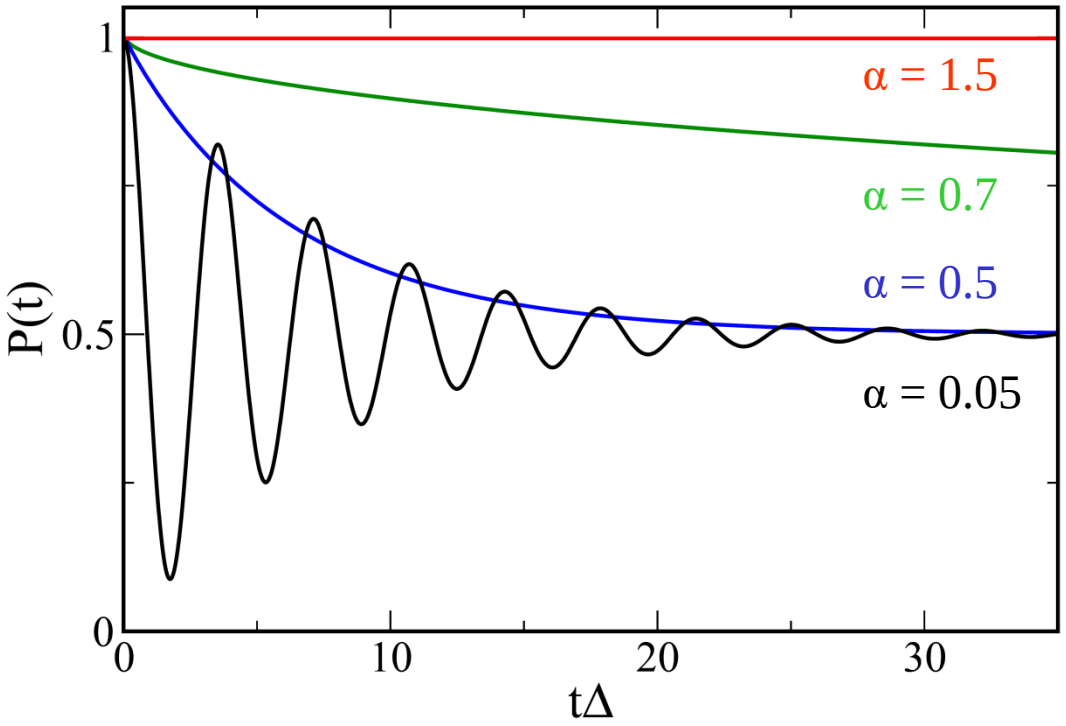




Wang, J. Phys. Chem. A **119**, 7951 (2015)

Spin-Boson model

Ohmic spectral density, T = 0 K



$$J(\omega) = \frac{\pi}{2}\alpha\omega e^{-\omega/\omega_c}$$

$$\varepsilon = 0$$

$$\omega_c/\Delta = 40$$

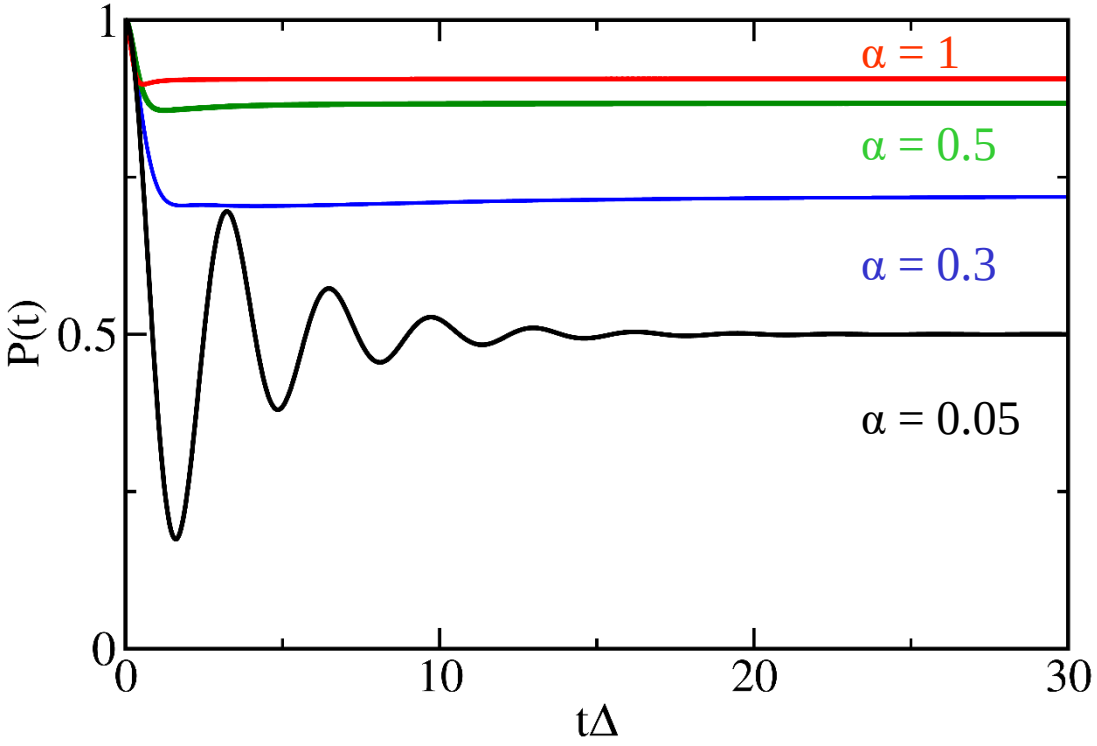
For increasing electron-phonon coupling α, the dynamics undergoes a transition

coherent → incoherent → localization

Wang, Thoss, J. Chem. Phys. **119**, 1289 (2003); New J. Phys. 10, 115005 (2008)

Spin-Boson model

Sub-Ohmic spectral density, T = 0 K



$$J(\omega) = \frac{\pi}{2}\alpha\frac{\omega^s}{w_c^{s-1}}e^{-\omega/\omega_c}$$

$$s = \frac{1}{2}$$

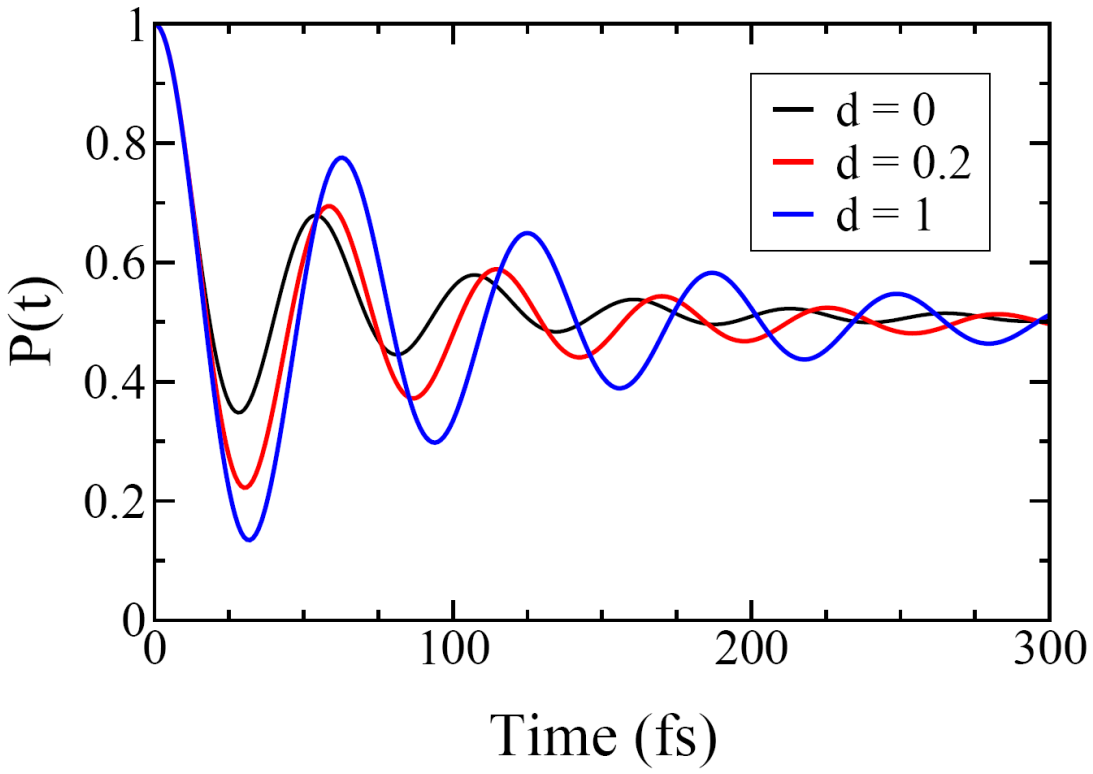
$$\varepsilon = 0$$

$$\omega_c/\Delta = 10$$

Wang, Thoss, Chem. Phys. 370, 78 (2010)

Spin-Boson model with anharmonic bath

$$H = \varepsilon\sigma_z + \Delta\sigma_x + \frac{1}{2}\sum_j (p_j^2 + \omega_j^2 q_j^2) + \sum_j d_j q_j^4 + \sigma_z \sum_j c_j q_j$$



$$d = 2d_j/\omega_j^3$$

$$\varepsilon = 0$$

$$\Delta = 250 \text{ cm}^{-1}$$

$$T = 300 \text{ K}$$

$$J(\omega) = \frac{\pi}{2}\sum_j \frac{c_j^2}{\omega_j}\delta(\omega - \omega_j) = \sqrt{\pi}\frac{\lambda_G \omega}{4\omega_G} e^{-[\omega/(2\omega_G)]^2} + \frac{\lambda_D}{2}\frac{\omega\omega_D}{\omega^2 + \omega_D^2}$$

$$\omega_D = 20 \text{ cm}^{-1}$$

$$\omega_G = 200 \text{ cm}^{-1}$$

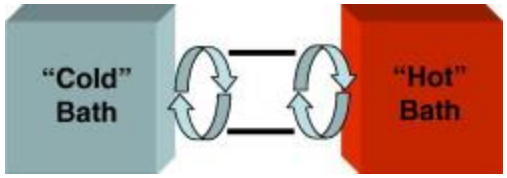
$$\lambda_D = \lambda_G = 250 \text{ cm}^{-1}$$

Wang, Thoss, J. Phys. Chem. A **111**, 10369 (2007)

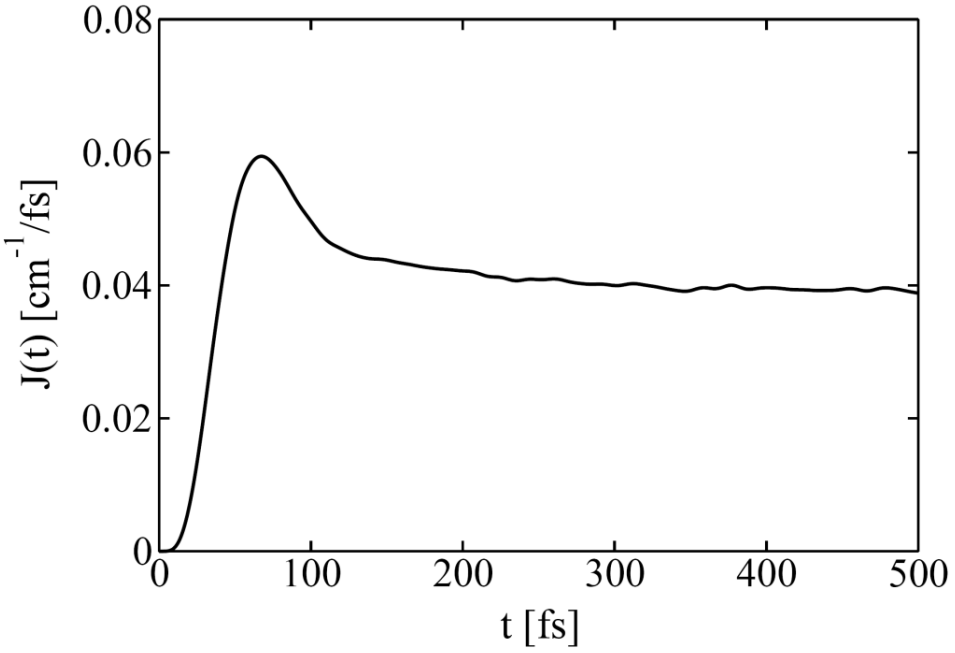
Energy transport in a spin-boson model

$$H = \varepsilon\sigma_z + \frac{1}{2}\sum_{j,\alpha\in L,R}(p_{j\alpha}^2 + \omega_{j\alpha}^2 q_{j\alpha}^2) + \sigma_x \sum_{j,\alpha\in L,R} c_{j\alpha}q_{j\alpha}$$

T = 60 K T = 120 K



energy current



energy current

$$J_L(t) = \frac{d}{dt}\{\rho_0 e^{iHt} H_{BL} e^{-iHt}\}$$

$$J(t) = (J_L(t) - J_R(t))/2$$

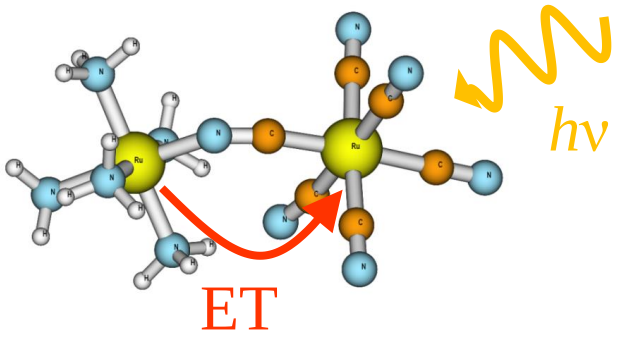
$$J(\omega) = \frac{E_r}{4\omega_c}\omega e^{-\omega/\omega_c}$$

$E_r = 100\ \mathrm{cm}^{-1}$ $\omega_c = 400\ \mathrm{cm}^{-1}$ $\varepsilon = 300\ \mathrm{cm}^{-1}$

Velizhanin, Wang, Thoss,
Chem. Phys. Lett. **460**, 325 (2008)

Segal, Nitzan, Phys. Rev. Lett. **94**, 034301 (2005);
J. Chem. Phys. **122** , 194704 (2005)

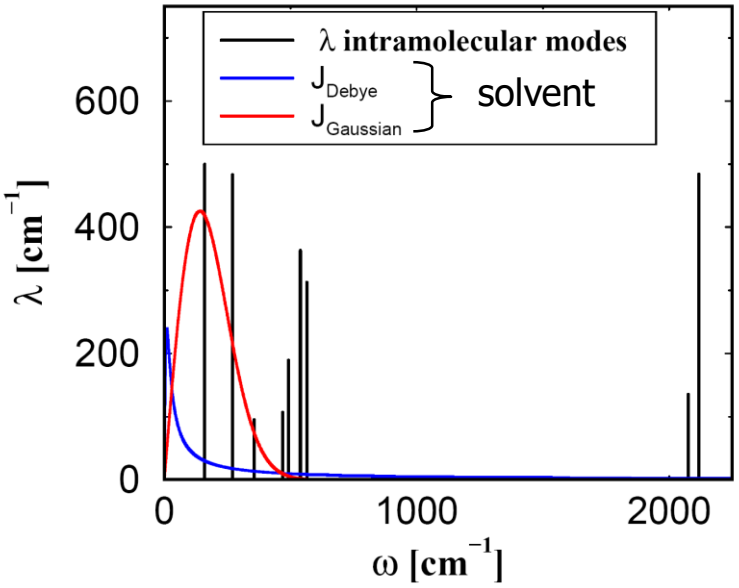
Photoinduced electron transfer in mixed-valence compounds



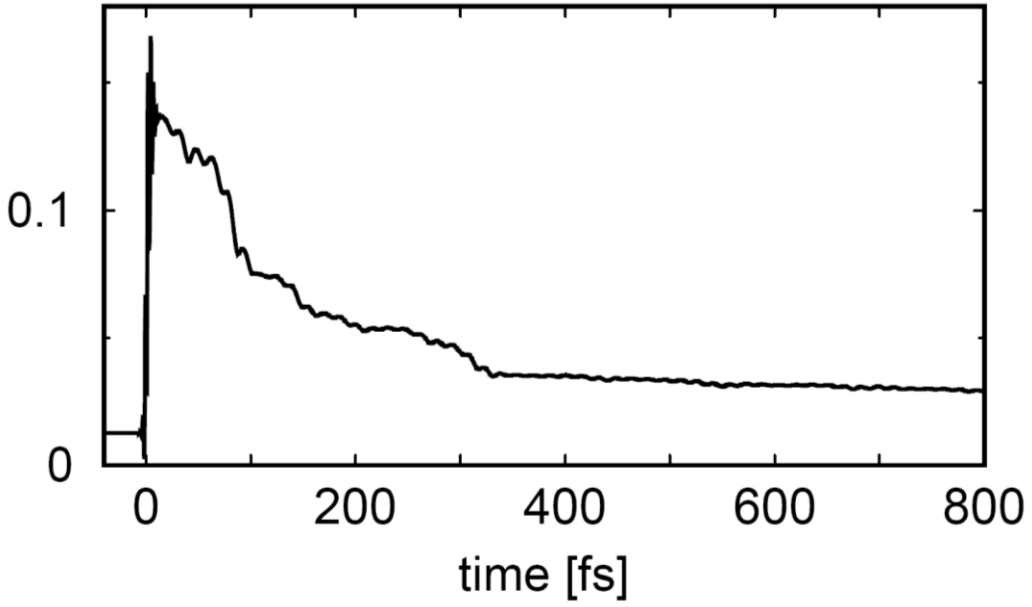
$$P_d(t) = Q^{-1}\mathrm{tr}\left\{e^{-\beta H_M}U^\dagger\,|\phi_d\rangle\langle\phi_d|\,U\right\}$$

$$i\hbar\frac{\partial}{\partial t}U = H(t)U \qquad H(t) = H_M - \mu E(t)$$

electronic-vibrational coupling



population of the excited electronic state

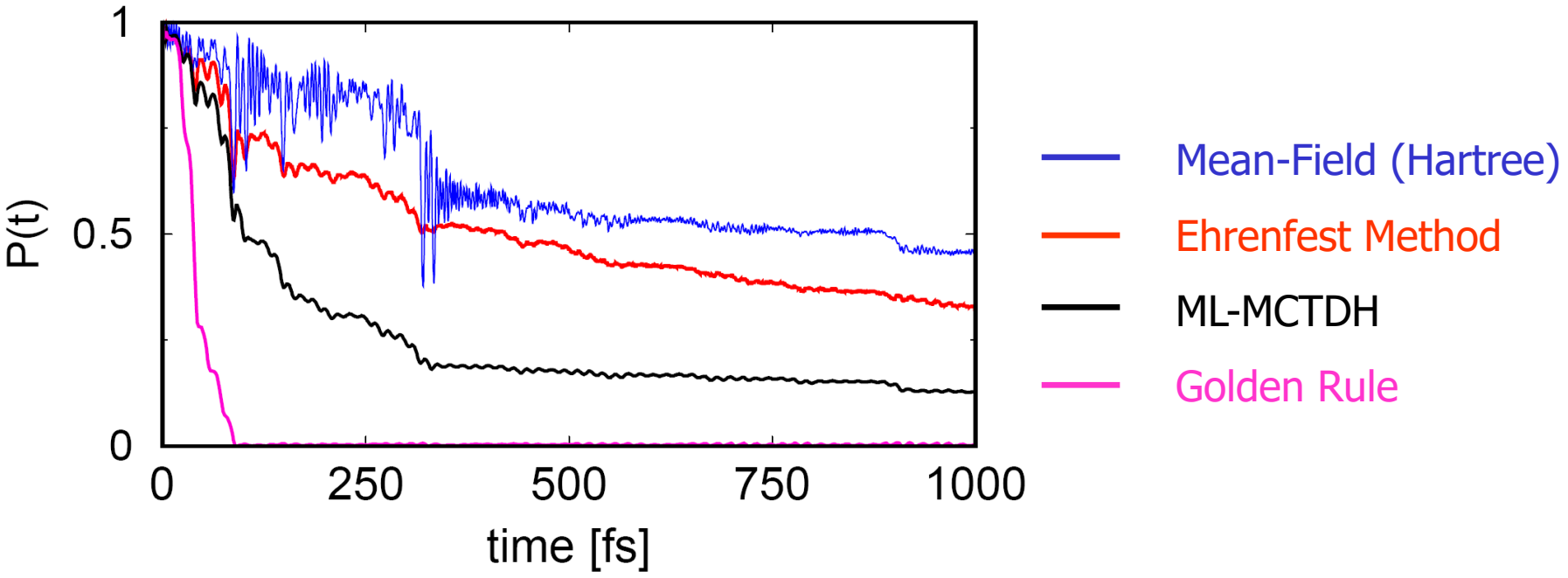


Wang, MT, et al., J. Chem. Phys. **124**, 034114 (2006)

Photoinduced electron transfer in mixed-valence compounds

$$(NH_3)_5Ru^{III}NCRu^{II}(CN)_5^- \underset{ET}{\overset{h\nu}{\rightleftharpoons}} (NH_3)_5Ru^{II}NCRu^{III}(CN)_5^-$$

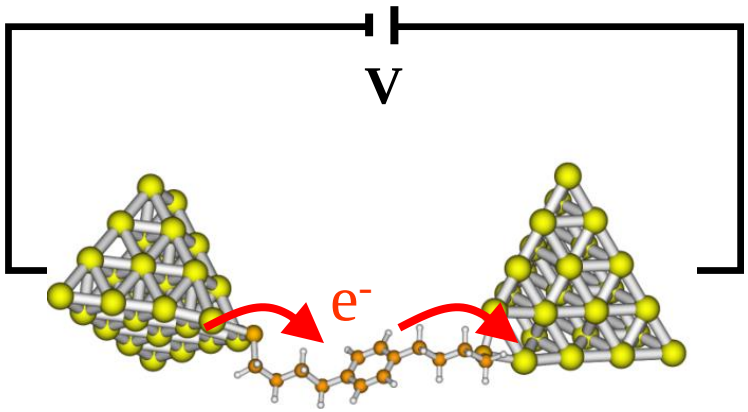
Dynamics after photoexcitation - comparison of different methods



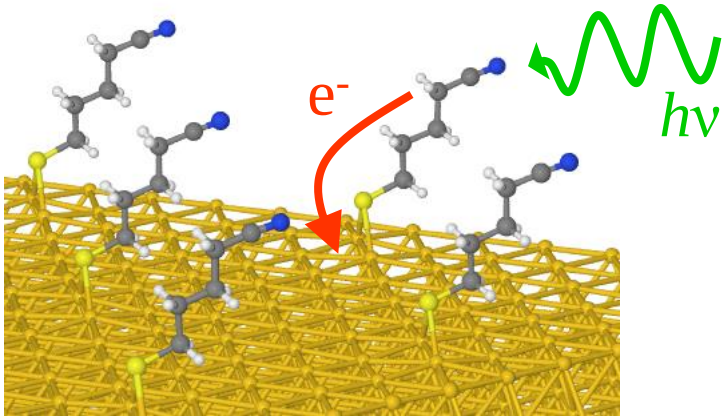
- dynamical correlations and quantum effects are important
- perturbation theory is not valid

Extension of the ML-MCTDH method to treat many-electron problems

Electron transport in molecular junctions



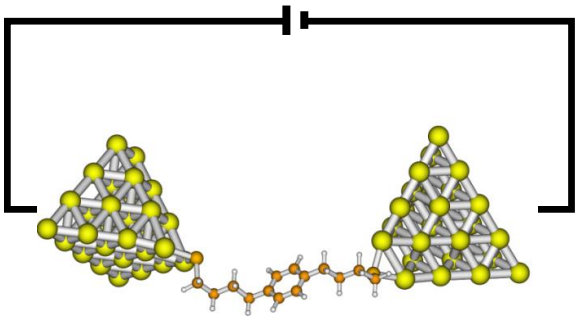
Electron transfer in molecular systems at metal surfaces



ML-MCTDH method for indistinguishable particles

Electron transport in single molecule junctions

Model



$$H = \sum_{k_L} \epsilon_{k_L} c^\dagger_{k_L} c_{k_L} + \sum_j \epsilon_j d^\dagger_j d_j + \sum_{k_R} \epsilon_{k_R} c^\dagger_{k_R} c_{k_R}$$ metal – molecule – metal

$$+ \sum_k (V_{jk} d^\dagger_j c_k + V_{kj} c^\dagger_k d_j)$$ molecule-metal interaction

$$+ \sum_l \omega_l a^\dagger_l a_l$$ vibrations

$$+ \sum_{l,j} \lambda^{(j)}_l (a_l + a^\dagger_l) d^\dagger_j d_j$$ electronic-vibrational coupling

$$+ \sum_{i,j} U_{ij} d^\dagger_i d_i d^\dagger_j d_j$$ electron-electron interaction

Härtle, MT, et al., PRL **107**, 046802 (2011); Ullmann, Leitherer, MT, Weber, et al., Nano Lett. **15**, 3512 (2015)

Simulation of electron transport using wavefunction methods

- **Expression for current in terms of wavefunctions**

$$I(t) = -e\frac{d}{dt}\left\langle \sum_{l\in L} c_l^\dagger c_l(t) \right\rangle = -e\,\mathrm{tr}\Big\{\rho_0\, e^{iHt}\, \underbrace{i[H, \sum_{l\in L} c_l^\dagger c_l]}_{\hat{I}}\, e^{-iHt}\Big\}$$

$$= -e\sum_{\mathbf{nv}} \rho_{0\mathbf{n}} \langle \Psi_{\mathbf{nv}}|\, e^{iHt}\, \hat{I}\, \underbrace{e^{-iHt}|\Psi_{\mathbf{nv}}\rangle}_{|\Psi_{\mathbf{nv}}(t)\rangle}$$

initial state: $\rho_0 = \dfrac{e^{-\beta(H_0-\mu_L N_L-\mu_R N_R)}}{Q} = \sum_{\mathbf{nv}} |\Psi_{\mathbf{nv}}\rangle \rho_{0\mathbf{nv}} \langle \Psi_{\mathbf{nv}}|$

bias voltage: $V = \mu_L - \mu_R$

$$|\Psi_{\mathbf{nv}}\rangle = |\mathbf{n}\rangle|\mathbf{v}\rangle$$

electrons: $|\mathbf{n}\rangle = |n_1, n_2, \ldots\rangle = \prod_l (c_l^\dagger)^{n_l}|\mathbf{0}\rangle$

vibrations: $|\mathbf{v}\rangle$

$$H_0 = \sum_j \epsilon_{dj} d_j^\dagger d_j + \sum_k \epsilon_k c_k^\dagger c_k + \sum_l \omega_l a_l^\dagger a_l$$

$$H = H_0 + \sum_{k,j}(V_{kj} d_j^\dagger c_k + V_{jk} c_k^\dagger d_j) + \sum_{l,j} \kappa_l^{(j)} (a_l + a_l^\dagger) d_j^\dagger d_j + \sum_{i,j} U_{ij} d_i^\dagger d_i d_j^\dagger d_j$$

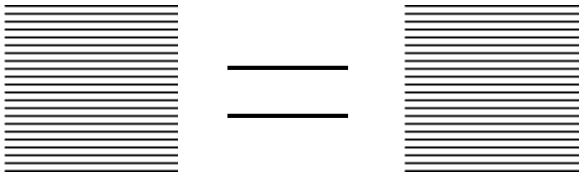
Simulation of electron transport using wavefunction methods

- **Expression for current in terms of wavefunctions**

$$I(t) = -e\frac{d}{dt}\left\langle \sum_{l\in L} c_l^\dagger c_l(t) \right\rangle = -e\,\mathrm{tr}\Big\{\rho_0\, e^{iHt}\, \underbrace{i[H, \sum_{l\in L} c_l^\dagger c_l]}_{\hat{I}}\, e^{-iHt}\Big\}$$

$$= -e\sum_{\mathbf{nv}} \rho_{0\mathbf{n}} \langle \Psi_{\mathbf{nv}}|\, e^{iHt}\, \hat{I}\, \underbrace{e^{-iHt}|\Psi_{\mathbf{nv}}\rangle}_{|\Psi_{\mathbf{nv}}(t)\rangle}$$

- **Finite representation of the infinite leads employing a discretization of the electronic continuum**



- **Quantum dynamics:** $|\Psi_{\mathbf{nv}}(t)\rangle = e^{-iHt}|\Psi_{\mathbf{nv}}\rangle$

Multilayer Multiconfiguration Time-Dependent Hartree Method ?

But: $|\Psi_{\mathbf{nv}}(t)\rangle$ involves indistinguishable particles (electrons) !

Wang, Thoss, et al., J. Chem. Phys. **131**, 024114 (2009); **138**, 134704 (2013)

ML-MCTDH method for indistinguishable particles

Concept: Employ second quantization representation of Fock space

$$c_i c_j^\dagger + c_j^\dagger c_i = \delta_{ij} \qquad |\mathbf{n}\rangle = |n_1, \ldots, n_M\rangle = \prod_l (c_l^\dagger)^{n_l} |\mathbf{0}\rangle \qquad n_i = 0, 1$$

$$|n_1, \ldots, n_M\rangle = " |n_1\rangle |n_2\rangle \ldots |n_M\rangle "$$

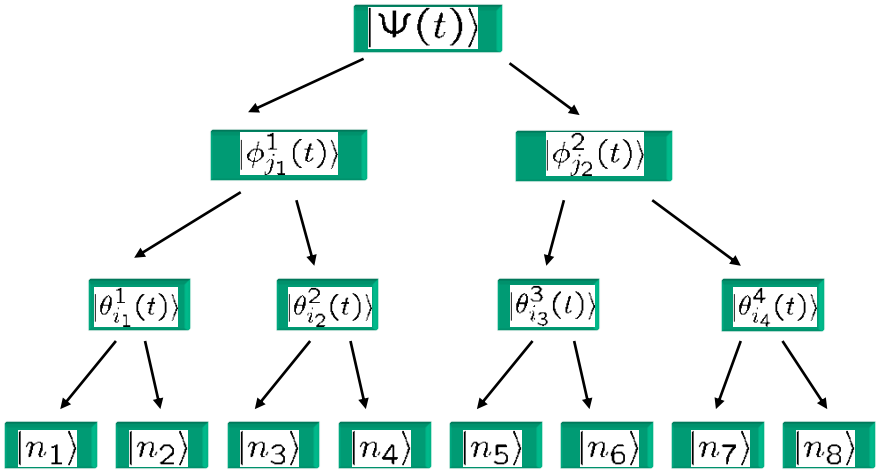
occupation number states can be formally represented as products

Example: Two-layer MCTDH with 8 orbitals

$$|\Psi(t)\rangle = \sum_{j_1} \sum_{j_2} A_{j_1 j_2}(t) \, |\phi_{j_1}^1(t)\rangle \, |\phi_{j_2}^2(t)\rangle$$

$$|\phi_j^1(t)\rangle = \sum_{i_1} \sum_{i_2} B_{i_1,i_2}^{1,j}(t) \, |\theta_{i_1}^{1,1}(t)\rangle \, |\theta_{i_2}^{1,2}(t)\rangle$$

$$|\theta_l^{1,1}(t)\rangle = \sum_{n_1} \sum_{n_2} C_{n_1 n_2}^{1,1,l}(t) |n_1 \, n_2\rangle$$



Wang, Thoss, J. Chem. Phys. **131**, 024114 (2009)

cf. also: Multiconfiguration Time-Dependent Hartree Fock (MCTDHF): Koto, Nest, Scrinzi, McCurdy, …

Bosons (MCTDHB): Schmelcher, Streltsov, Alon, Cederbaum, …

ML-MCTDH method for indistinguishable particles

Implementation: Sign operator

$$c_i c_j^\dagger + c_j^\dagger c_i = \delta_{ij} \qquad c_\nu^\dagger \,|n_1,\ldots,n_M\rangle = \prod_{q=1}^{\nu-1} (-1)^{n_q}\, \delta_{n_\nu,0}\, |n_1,\ldots,n_\nu+1,\ldots,n_M\rangle$$

$$(c_\nu^{(\kappa)})^\dagger = \left(\prod_{\mu=1}^{\kappa-1} \widehat{S}_\mu\right) (\tilde{c}_\nu^{(\kappa)})^\dagger$$

cf. Jordan-Wigner transformation:

$$c_\nu^\dagger = e^{i\frac{\pi}{2}\sum_{\mu=1}^{\nu-1}(\sigma_{\nu z}+1)}\sigma_\nu^\dagger$$

$$|\Psi(t)\rangle = \sum_{j_1}\sum_{j_2}\ldots\sum_{j_L} A_{j_1 j_2 \ldots j_L}(t) \prod_{\kappa=1}^{L} |\varphi_{j_\kappa}^{(\kappa)}(t)\rangle$$

$$|\varphi_{j_\kappa}^{(\kappa)}(t)\rangle = \sum_{n_1=0}^{1}\sum_{n_2=0}^{1}\ldots\sum_{n_{m_\kappa}=0}^{1} B^{\kappa,j_\kappa}_{n_1 n_2 \ldots n_{m_\kappa}}(t)\; |n_1\rangle|n_2\rangle\ldots|n_{m_\kappa}\rangle$$

$$\widehat{S}_\mu|\varphi_{j_\mu}^{(\mu)}(t)\rangle = \sum_{n_1=0}^{1}\sum_{n_2=0}^{1}\ldots\sum_{n_{m_\mu}=0}^{1}\left[\prod_{q=1}^{m_\mu}(-1)^{n_q}\right] B^{\mu,j_\mu}_{n_1 n_2 \ldots n_{m_\mu}}(t)\; |n_1\rangle|n_2\rangle\ldots|n_{m_\mu}\rangle$$

$$(\tilde{c}_\nu^{(\kappa)})^\dagger|\varphi_{j_\kappa}^{(\kappa)}(t)\rangle = \sum_{n_1=0}^{1}\sum_{n_2=0}^{1}\ldots\sum_{n_{m_\kappa}=0}^{1}\delta_{n_\nu,0}\left[\prod_{q=1}^{\nu-1}(-1)^{n_q}\right] B^{\kappa,j_\kappa}_{n_1 n_2 \ldots n_{m_\kappa}}(t)\; |n_1\rangle|n_2\rangle\ldots|1_\nu\rangle\ldots|n_{m_\kappa}\rangle$$

Wang, Thoss, J. Chem. Phys. **131**, 024114 (2009)

ML-MCTDH method for indistinguishable particles

- **Multiconfiguration expansion of wavefunction in terms of single-particle functions for electrons and nuclei**

$$|\Psi(t)\rangle \;=\; \sum_J A_J(t)|\Phi_J(t)\rangle = \sum_{j_1}\cdots\sum_{j_M} A_{j_1\ldots j_M}(t) \prod_{k=1}^{M_{\mathsf{el}}} |\phi^k_{j_k}(t)\rangle_{\mathsf{el}} \prod_{k=M_{\mathsf{el}}+1}^{M_{\mathsf{nucl}}} |\phi^k_{j_k}(t)\rangle_{\mathsf{nucl}}$$

$$M = M_{\mathsf{el}} + M_{\mathsf{nucl}}$$

- **Multilayer representation of wavefunction**

$$|\phi^k_l(t)\rangle \;=\; \sum_I B^{k,l}_I(t)|\Theta^k_I(t)\rangle = \sum_{i_1}\cdots\sum_{i_Q} B^{k,l}_{i_1\ldots i_Q}(t) \prod_{q=1}^{Q} |\theta^{k,q}_{i_q}(t)\rangle$$

- **Representation of single-particle functions of deepest layer by time-independent basis functions (fermionic Fock space)**

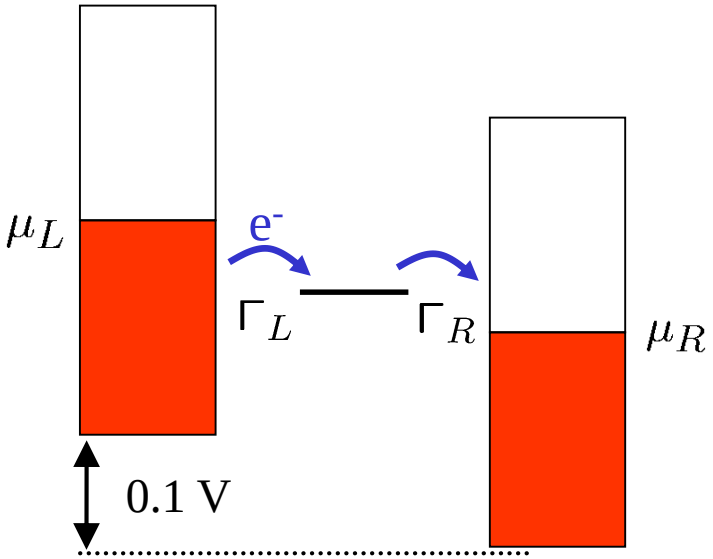
$$|\theta^{k,q}_i(t)\rangle_{\mathsf{el}} \;=\; \sum_{\mathbf{n}} C^{i,k,q}_{\mathbf{n}}(t)|\mathbf{n}^{k,q}\rangle_{\mathsf{el}} \qquad |\theta^{k,q}_i(t)\rangle_{\mathsf{nucl}} \;=\; \sum_{\mathbf{v}} C^{i,k,q}_{\mathbf{v}}(t)|\mathbf{v}^{k,q}\rangle_{\mathsf{nucl}}$$

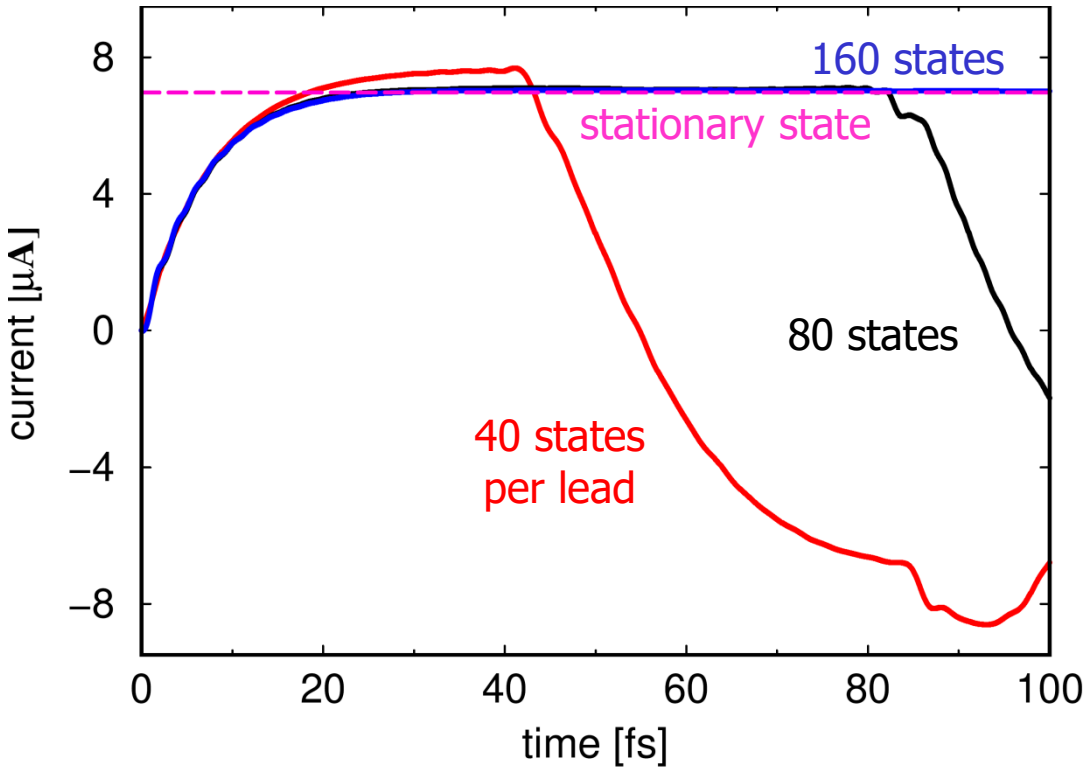
$$|\mathbf{n}^{k,q}\rangle_{\mathbf{el}} \;=\; |n_1,\ldots,n_{R(k,q)}\rangle = \prod_l (c^\dagger_l)^{n_l}|\mathbf{0}\rangle$$

$$n_l \;=\; 0,1 \qquad\qquad c_l c^\dagger_m + c^\dagger_m c_l \;=\; \delta_{ml}$$

Simulation of electron transport

Test: 'Noninteracting' problem





$$\epsilon_d = 0$$

$$\Gamma_L(E) = \frac{v_0^2}{v^2}\sqrt{4v^2 - (E-\mu_L)^2}$$

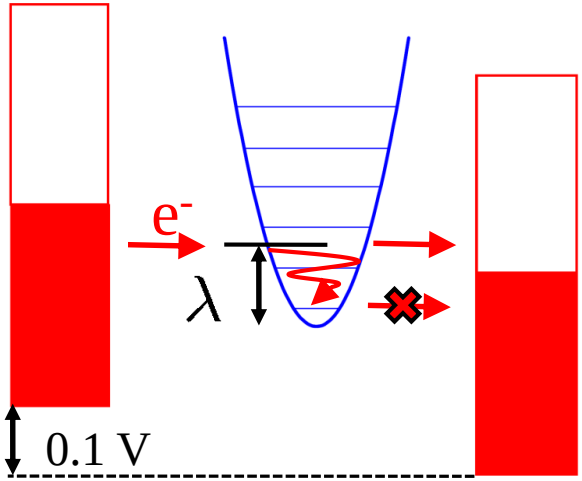
$v_0 = 0.2\,\text{eV}$ $\qquad$ $v = 1\,\text{eV}$

$$I(t) = (I_L(t) - I_R(t))/2$$

$$H = \sum_{k_l} \epsilon_{k_l} c_{k_l}^\dagger c_{k_l} + \epsilon_d d^\dagger d + \sum_{k_r} \epsilon_{k_r} c_{k_r}^\dagger c_{k_r} + \sum_k (V_k d^\dagger c_k + V_k c_k^\dagger d)$$

Simulation of electron transport

Transient and stationary current in a molecular junction with electron-vibrational interaction

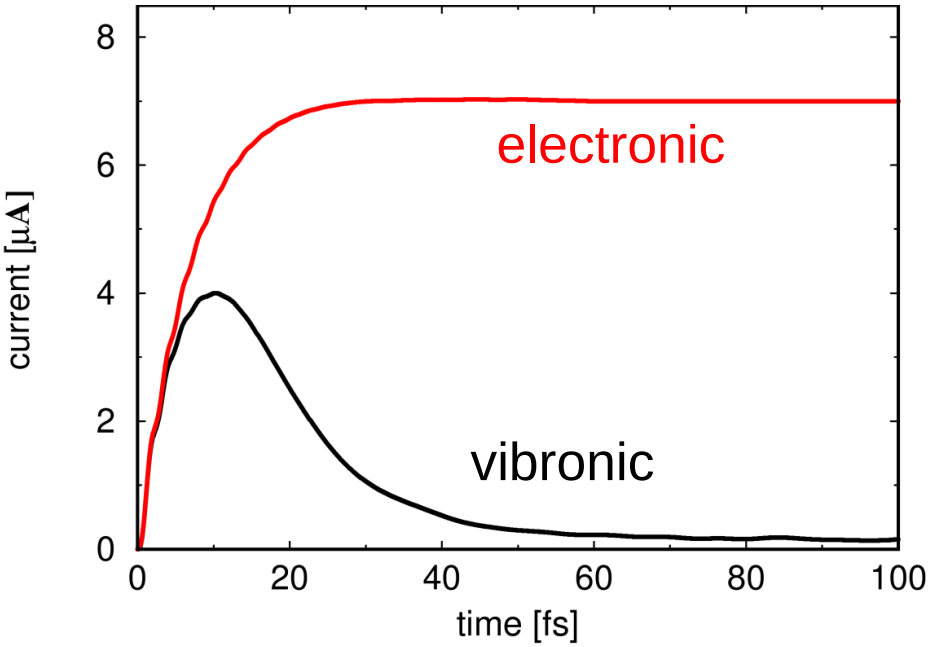


$$H = \epsilon_d d^\dagger d + \sum_k \epsilon_k c_k^\dagger c_k + \sum_k (V_k d^\dagger c_k + V_k c_k^\dagger d) + \sum_l \omega_l a_l^\dagger a_l + \sum_l \kappa_l (a_l + a_l^\dagger) d^\dagger d$$

$$\epsilon_d = 0 \qquad \Gamma_L = 0.08\,\text{eV} = \Gamma_R$$

$$J(\omega) \sim \lambda \frac{\omega}{\omega_c} e^{-\omega/\omega_c} \qquad \omega_c = 0.06\,\text{eV}$$

$$\lambda = \sum_l \kappa_l^2/\omega_l = 0.25\,\text{eV}$$

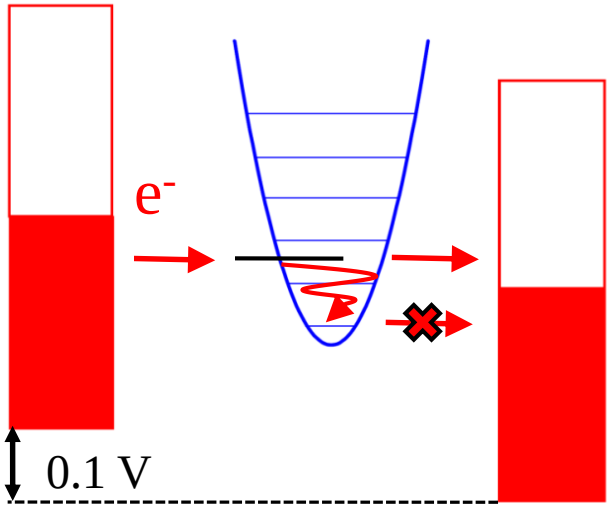


Correlated electronic-vibrational dynamics results in suppression of current (phonon blockade)

Wang, MT et al., J. Chem. Phys. **131**, 024114 (2009); **135**, 244506 (2011)

Simulation of electron transport

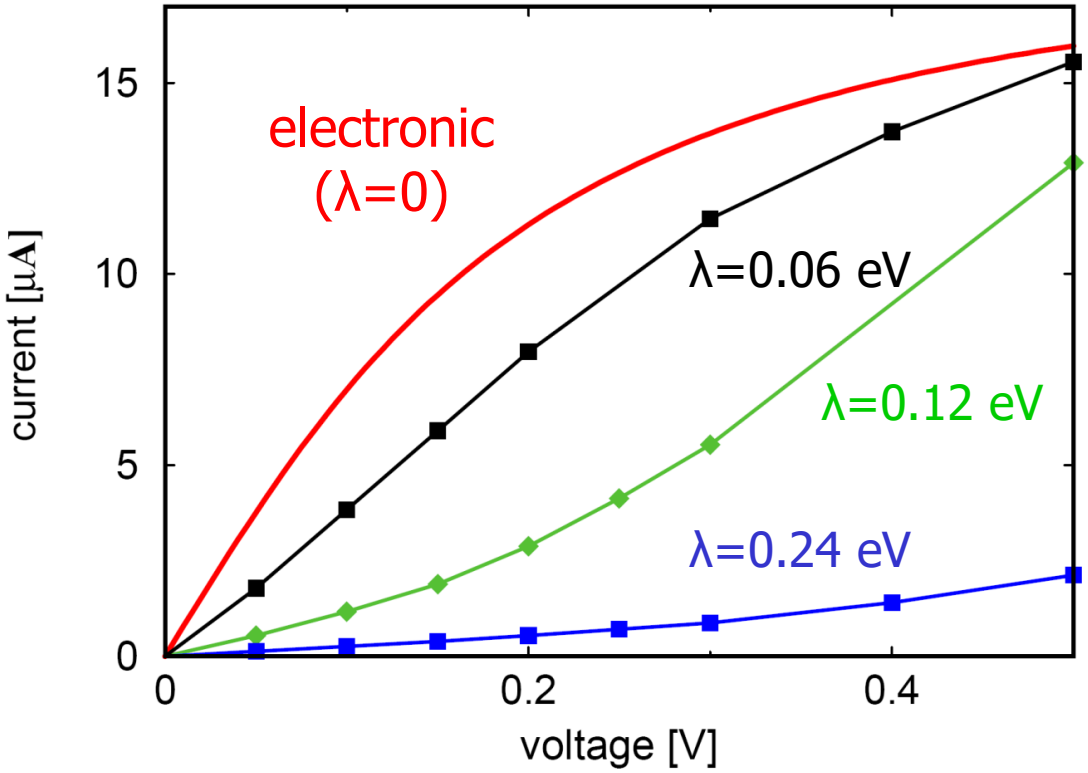
Effect of electron-vibrational interaction: Phonon blockade



$$\epsilon_d = 0 \qquad \Gamma_L = 0.08\,\text{eV} = \Gamma_R$$

$$J(\omega) \sim \lambda \frac{\omega}{\omega_c} e^{-\omega/\omega_c}$$

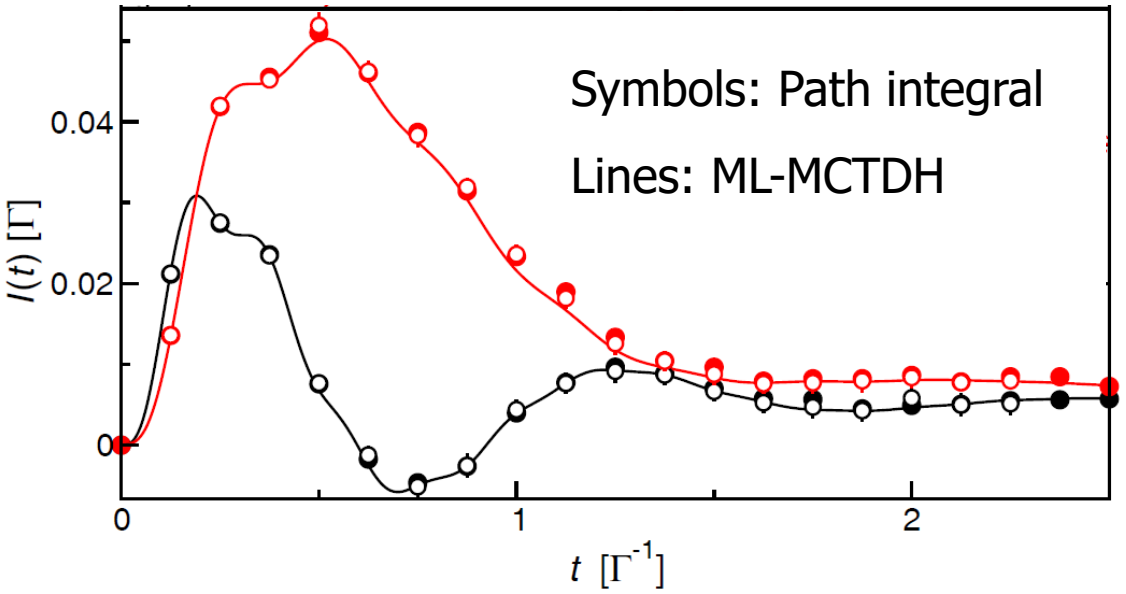
$$\omega_c = 0.06\,\text{eV}$$



Wang, Pshenichnyuk, Härtle, Thoss, J. Chem. Phys. **135**, 244506 (2011)

Simulation of electron transport

Comparison: Path integral – ML-MCTDH



$$J(\omega) \sim \lambda \frac{\omega}{\omega_c} e^{-\omega/\omega_c}$$

$\omega_c = 0.774\Gamma$

$\epsilon_d = 4.7\Gamma$

$V = 1.25\Gamma$

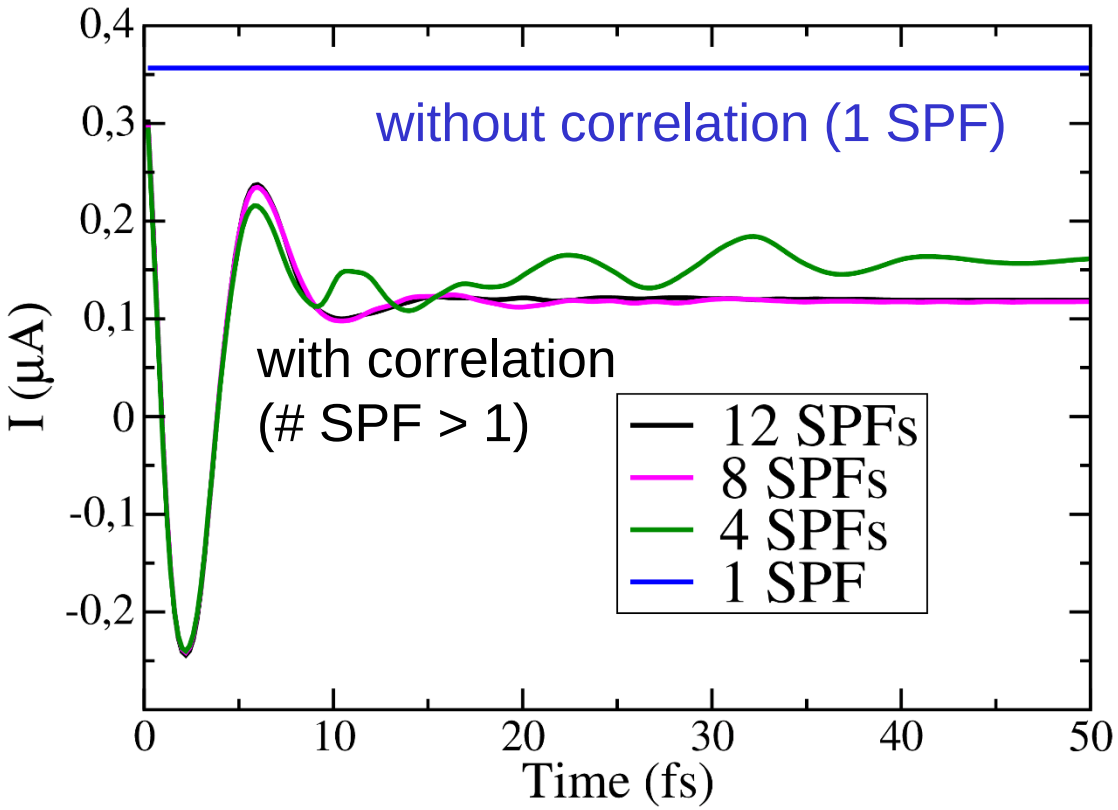
$$H = \sum_{k_L} \epsilon_{k_L} c_{k_L}^\dagger c_{k_L} + \epsilon_d d^\dagger d + \sum_{k_R} \epsilon_{k_R} c_{k_R}^\dagger c_{k_R} + \sum_k (V_k d^\dagger c_k + V_k c_k^\dagger d) + \sum_l \omega_l a_l^\dagger a_l + \sum_l \kappa_l (a_l + a_l^\dagger) d^\dagger d$$

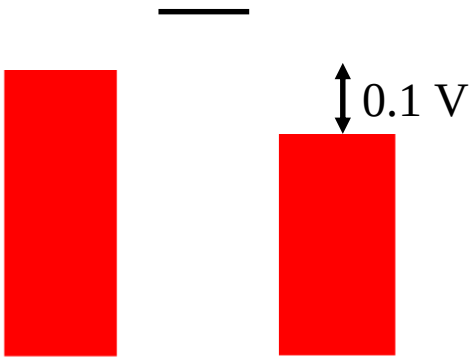
Albrecht, Wang, Mühlbacher, Thoss, Komnik, Phys. Rev. B **86**, 081412(R) (2012)

Mühlbacher, Rabani, PRL **100**, 176403 (2008)

Simulation of electron transport

Influence of electronic-vibrational correlation





$\epsilon_d = 0.5\text{eV}$ $\omega_c = 0.06\,\text{eV}$

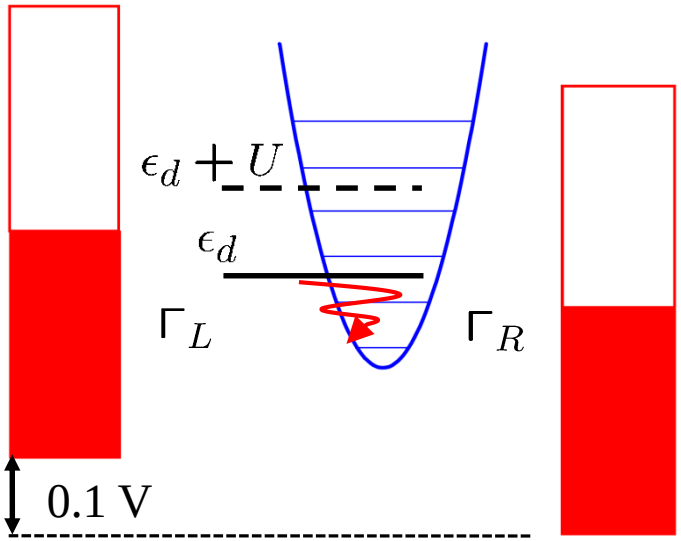
$$\lambda = \sum_l \kappa_l^2/\omega_l = 0.25\,\text{eV}$$

Wang, Thoss, J. Chem. Phys. **138**, 134704 (2013)

Simulation of electron transport

Electron-electron (U) and electron-vibrational (λ) interaction

$$H = H_0 + U d_\uparrow^\dagger d_\uparrow d_\downarrow^\dagger d_\downarrow + \sum_j \lambda_j q_j (d_\uparrow^\dagger d_\uparrow + d_\downarrow^\dagger d_\downarrow)$$



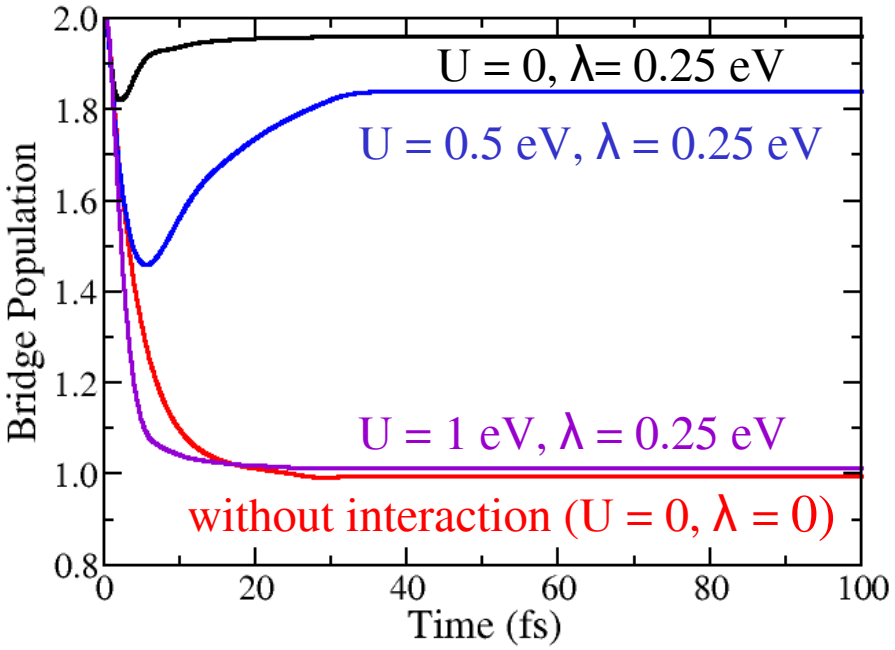
$$\epsilon_d = 0$$

$$J(\omega) \sim \lambda \frac{\omega}{\omega_c} e^{-\omega/\omega_c}$$

$$\omega_c = 0.06\,\text{eV}$$

$$\Gamma_{L/R} = 0.08\,\text{eV}$$

population of bridge state $\langle d_\uparrow^\dagger d_\uparrow + d_\downarrow^\dagger d_\downarrow \rangle$



Wang, Thoss, J. Chem. Phys. **138**, 134704 (2013)

cf. recent application as impurity solver: Balzer, Li, Vendrell, Eckstein, PRB **91**, 045136 (2015)

Simulation of electron transport

Dynamics on longer time scales: Combination of reduced density matrix theory and ML-MCTDH

Nakajima-Zwanzig equation for reduced density matrix ρ of electronic degrees of freedom of molecular bridge

$$i\frac{\partial}{\partial t}\rho(t) = L_S\rho(t) - i\int_0^t d\tau\, \kappa(\tau)\rho(t-\tau)$$

Kernel $\kappa(t)$ decays typically on significantly shorter time scale than the reduced density matrix ρ

Strategy: Calculate kernel $\kappa(t)$ using the ML-MCTDH method

Wilner, Wang, Cohen, Thoss, Rabani, PRB **88**, 045137 (2013); **92**, 195143 (2015)

Zhang, Ka, Geva, JCP **125**, 044106 (2006); Cohen, Rabani, PRB **84**, 075150 (2011), Cohen, Gull, Reichman, Millis, Rabani, PRB **87**, 195108 (2013)

Simulation of electron transport

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$$i\frac{\partial}{\partial t}\rho(t) = L_S\rho(t) - i\int_0^t d\tau\, \kappa(\tau)\rho(t-\tau) \qquad L_S\rho = [H_S, \rho]$$

$$\kappa(t) = tr_B\{L_{SB}e^{-iQLQt}QL\rho_B\} \qquad P = \rho_B tr_B \qquad Q = 1 - P$$

$$\kappa(t) = i\frac{\partial}{\partial t}\Phi(\mathrm{t}) - \Phi(t)L_S + i\int_0^t d\tau\, \Phi(t-\tau)\,\kappa(\tau)$$

$$\Phi(t) = tr_B\{L_{SB}e^{-iLt}\rho_B\}$$

Wilner, Wang, Cohen, Thoss, Rabani, PRB **88**, 045137 (2013); **92**, 195143 (2015)

Zhang, Ka, Geva, JCP **125**, 044106 (2006); Cohen, Rabani, PRB **84**, 075150 (2011), Cohen, Gull, Reichman, Millis, Rabani, PRB **87**, 195108 (2013)

Simulation of electron transport

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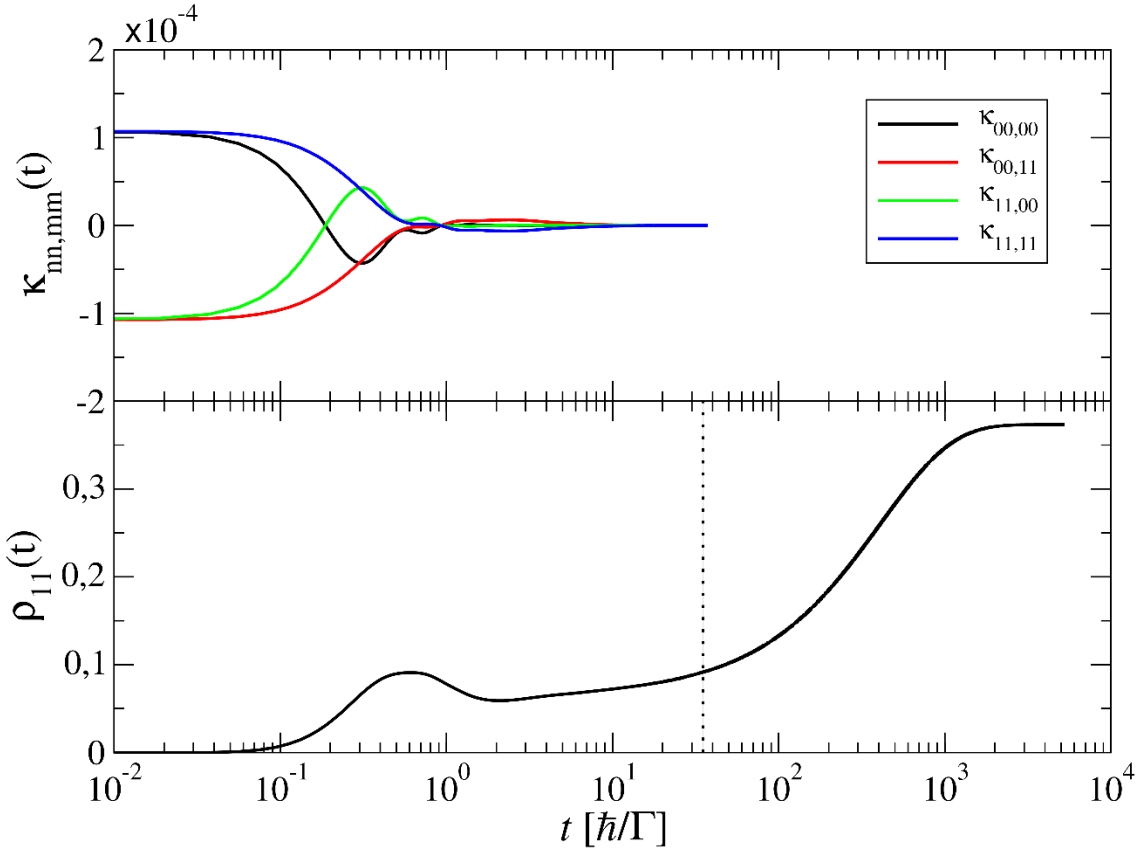


$\epsilon_d = 0.5$ eV

$\omega_c = 0.06$ eV

$\lambda = 0.48$ eV

$\Gamma = 0.16$ eV

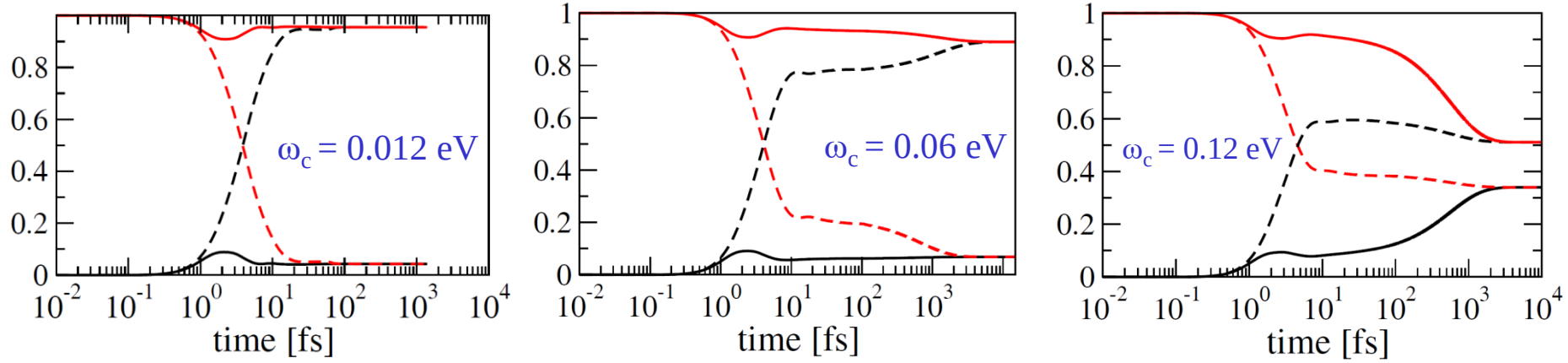
$T = 0$ K

Wilner, Wang, Thoss, Rabani, PRB **90**, 115145 (2014)

Simulation of electron transport

Combination of reduced density matrix theory and ML-MCTDH

population of bridge state $\langle d^\dagger d \rangle$

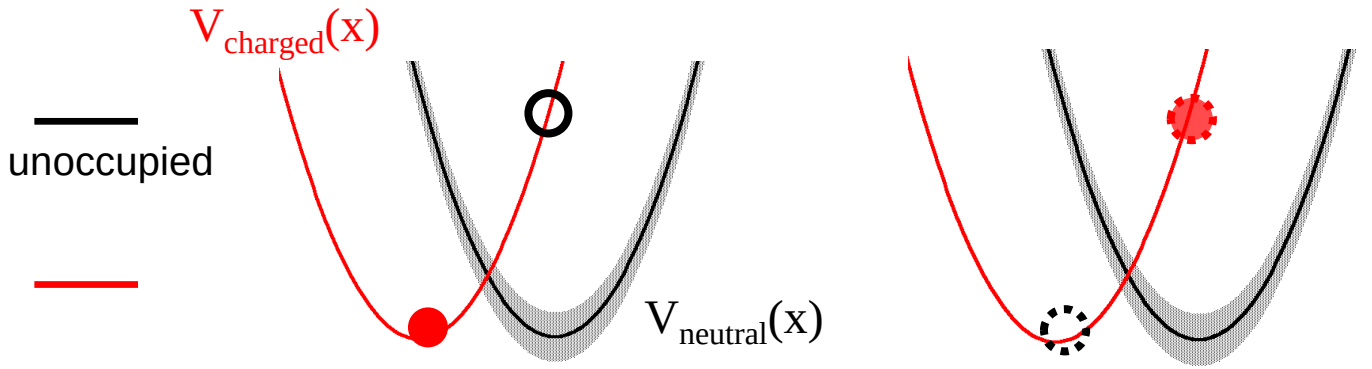


Preparation at t=0:

‘equilibrium’

‘nonequilibrium’

$\Gamma_{\mathrm{eff}} = \Gamma e^{-\frac{\lambda}{\omega_c}}$



occupied, vibrations equilibrated with unoccupied state

unoccupied, vibrations equilibrated with occupied state

Summary

- Multiconfiguration wave function methods are efficient approaches to describe quantum dynamics
- ML-MCTDH method allows accurate quantum dynamical simulations of systems with many degrees of freedom, including indistinguishable particles and condensed phase models at finite temperature
- Combination with density matrix theory extends accessible time scale

Current limitations of ML-MCTDH:

- Applications to large systems are limited to restricted form of the Hamiltonian
- Propagation for long times in systems with strong correlation

Wang, J. Phys. Chem. A **119**, 7951 (2015)

Wilner, Wang, Thoss, Rabani, Phys. Rev. B **92**, 195143 (2015)

Meyer, Gatti, Worth (Eds.) *Multidimensional Quantum Dynamics* (Wiley, 2009)

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