Stochastic Quantum Molecular Dynamics: a functional theory for electrons and nuclei dynamically coupled to an environment

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Outline

Open Quantum Systems

- Different approaches to deal with decoherence and dissipation
- Stochastic current density-functional theory
- Application: Stochastic simulation of (1,4)-phenylene-linked zincbacteriochlorin-bacteriochlorin complex
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Stochastic Quantum Molecular Dynamics: Theory and Applications
- Including nuclear motion: Stochastic Quantum Molecular Dynamics
- Application: Stochastic quantum MD of 4-(N,N-Dimethylamino)benzonitrile
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Outlook: future prospects of SQMD
Why Open Quantum Systems?

General aspects:

- Cannot have perfectly isolated quantum systems

Dissipation and Decoherence

Every measurement implies contact with an environment.

Research fields:

- Quantum computing/Quantum information theory
- (time-resolved) transport and optics
- Driven quantum phase transitions
- Quantum measurement
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Open Quantum System

\[ S + B : \hat{H}_S \otimes H_B, \Psi, \hat{\rho} \]

System
\[ S : \hat{H}_S, \Psi_S, \hat{\rho}_S \]

Environment
\[ B : \hat{H}_B, \Psi_B, \hat{\rho}_B \]

Hamiltonian of combined system

\[ \hat{H} = \hat{H}_S \otimes \hat{1}_B + \hat{1}_S \otimes \hat{H}_B + \hat{H}_{SB} \]
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Unitary time evolution
\[ i \partial_t \Psi(t) = \hat{H}(t) \Psi(t) \]
\[ \frac{d}{dt} \hat{\rho}(t) = -i \left[ \hat{H}(t), \hat{\rho}(t) \right] \]
Reduced system dynamics

\[ S + B : \hat{H}_S \otimes H_B, \Psi, \hat{\rho} \]

System

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Tracing over bath degrees of freedom

\[ \hat{\rho}_S = \text{Tr}_B \hat{\rho} \]

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\[ \hat{\rho}_S(t) \text{ represents in general no pure state.} \]
Nakajima-Zwanzig projection operator technique

Projection Operators

\[ \hat{P} \rho = \text{tr}_B \{ \rho \} \otimes \rho_B \equiv \rho_S \otimes \rho_B \]
\[ \hat{Q} \rho = \rho - \hat{P} \rho \]

Properties

\[ \hat{P} + \hat{Q} = I \]
\[ \hat{P}^2 = \hat{P} \]
\[ \hat{Q}^2 = \hat{Q} \]
\[ \hat{P} \hat{Q} = \hat{Q} \hat{P} = 0 \]

Nakajima-Zwanzig projection operator technique

Total Hamiltonian

\[ \hat{H} = \hat{H}_S + \hat{H}_B + \alpha \hat{H}_{SB} \]

Liouville von Neumann equation in interaction picture

\[ \frac{\partial}{\partial t} \hat{\rho}(t) = -i\alpha \left[ \hat{H}_{SB}, \hat{\rho}(t) \right] \equiv \alpha \hat{\mathcal{L}}_{SB}(t) \hat{\rho}(t) \]

Apply Projection Operators

\[ \frac{\partial}{\partial t} \hat{P} \hat{\rho}(t) = \alpha \hat{P} \hat{\mathcal{L}}_{SB}(t) \hat{P} \hat{\rho}(t) + \alpha \hat{P} \hat{\mathcal{L}}_{SB}(t) \hat{Q} \hat{\rho}(t) \]
\[ \frac{\partial}{\partial t} \hat{Q} \hat{\rho}(t) = \alpha \hat{Q} \hat{\mathcal{L}}_{SB}(t) \hat{P} \hat{\rho}(t) + \alpha \hat{Q} \hat{\mathcal{L}}_{SB}(t) \hat{Q} \hat{\rho}(t) \]

Nakajima-Zwanzig projection operator technique

Formally solve for $\hat{Q}\hat{\rho}(t)$

$$\hat{Q}\hat{\rho}(t) = G(t, t_0)\hat{Q}\hat{\rho}(t_0) + \alpha \int_{t_0}^{t} ds G(t, s)\hat{Q}\hat{L}_{SB}(s)\hat{Q}\hat{\rho}(s),$$

where

$$G(t, s) = T \exp \left[ \alpha \int_{s}^{t} \hat{Q}\hat{L}_{SB}(s')ds' \right], \quad G(s, s) = I$$

Nakajima-Zwanzig equation

$$\frac{\partial}{\partial t} \hat{P}\hat{\rho}(t) = \alpha \hat{P}\hat{L}_{SB}(t)\hat{P}\hat{\rho}(t) + \alpha \hat{P}\hat{L}_{SB}(t)G(t, t_0)\hat{Q}\hat{\rho}(t_0)$$

$$+ \alpha^2 \int_{t_0}^{t} \hat{P}\hat{L}_{SB}(t)G(t, s)\hat{Q}\hat{L}_{SB}(s)\hat{P}\hat{\rho}(s)ds$$

Source Term

Memory Term

Nakajima-Zwanzig projection operator technique

Typical approximations for the Nakajima-Zwanzig equation
▶ Perturbation theory in $\alpha$, e.g. Born approximation (up to $\alpha^2$).
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Typical approximations for the Nakajima-Zwanzig equation

- Perturbation theory in $\alpha$, e.g. Born approximation (up to $\alpha^2$).
- Linked cluster/cumulant expansions.

Problem: Approximations to the Nakajima-Zwanzig equation can lead to unphysical states (loss of positivity).

Similar problems: Redfield equations, Caldeira-Legget equation, ...
Nakajima-Zwanzig projection operator technique

Typical approximations for the Nakajima-Zwanzig equation

- Perturbation theory in $\alpha$, e.g. Born approximation (up to $\alpha^2$).
- Linked cluster/cumulant expansions.
- Markov approximation.

$$
\int_{t_0}^{t} \ldots \hat{\rho}(s) ds \quad \Rightarrow \quad \int_{t_0}^{t} \ldots \hat{\rho}(t) ds
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Redfield equations, Caldeira-Legget equation, ...
Lindblad theorem

Lindblad equation

\[ \frac{d}{dt} \hat{\rho}_S(t) = \mathcal{L} \hat{\rho}_S(t) \]

Most general form for the generator of a quantum dynamical semigroup

\[ \mathcal{L} \hat{\rho}_S(t) = -i \left[ \hat{H}, \hat{\rho}_S(t) \right] + \sum_k \gamma_k \left( \hat{V}_k \hat{\rho}_S(t) \hat{V}_k^\dagger - \frac{1}{2} \hat{V}_k^\dagger \hat{V}_k \rho_S(t) - \frac{1}{2} \hat{\rho}_S(t) \hat{V}_k^\dagger \hat{V}_k \right) \]

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Semigroup properties:

- \( \hat{Q}(t) \) is completely positive
- \( \hat{Q}(t) \hat{Q}(s) = \hat{Q}(t+s) \)
- \( \hat{Q}(0) = \hat{I} \)
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Semigroup preserves:
- Hermiticity (probabilities are real numbers)
- Trace (conservation of norm)
- Positivity (probabilities are positive)
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**Semigroup preserves:**

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Dynamical semigroup only for time-independent Hamiltonians

⇒ Problem for TDDFT formulation
Reduced system dynamics

\[ S + B : \hat{H}_S \otimes H_B, \Psi, \hat{\rho} \]

System
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Environment
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⇒ Use density operator \( \hat{\rho}_S \)
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\[ \Rightarrow \text{Use state vector } \Psi_S \]
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\[ \implies \text{Use state vector } \Psi_S \]

- No need to work with composite objects like density matrices
- Can trace out bath directly on the level of state vectors
\[
\hat{H} = \hat{H}_S + \hat{H}_B + \alpha\hat{H}_{SB}, \\
H_B \chi_n(x_B) = \varepsilon_n \chi_n(x_B)
\]
Feshbach Projection-Operator Method

\[ \hat{H} = \hat{H}_S + \hat{H}_B + \alpha \hat{H}_{SB}, \quad H_B \chi_n(x_B) = \varepsilon_n \chi_n(x_B) \]

Expand total wavefunction in arbitrary complete and orthonormal basis of the bath

\[ \Psi(x_S, x_B; t) = \sum_n \phi_n(x_S; t) \chi_n(x_B) \]

Projection Operators

\[ \hat{P} := \hat{I}_S \otimes | \chi_k \rangle \langle \chi_k | \quad \hat{Q} := \hat{I}_S \otimes \sum_{k \neq n} | \chi_k \rangle \langle \chi_k | \]
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Apply to TDSE

\[ i \partial_t \hat{P} \Psi(t) = \hat{P} \hat{H} \hat{P} \Psi(t) + \hat{P} \hat{H} \hat{Q} \Psi(t) \]
\[ i \partial_t \hat{Q} \Psi(t) = \hat{Q} \hat{H} \hat{Q} \Psi(t) + \hat{Q} \hat{H} \hat{P} \Psi(t) \]

Feshbach Projection-Operator Method

Effective equation for $\hat{P} \Psi$ (still fully coherent)

\[
    i\partial_t \hat{P}\Psi(t) = \hat{P}\hat{H}\hat{P}\hat{P}\Psi(t) + \hat{P}\hat{H}\hat{Q}e^{-i\hat{Q}\hat{H}\hat{Q}t}\hat{Q}\Psi(0) \\
    \quad - i \int_0^t d\tau \hat{P}\hat{H}\hat{Q}e^{i\hat{Q}\hat{H}\hat{Q}(t-\tau)}\hat{Q}\hat{H}\hat{P}\hat{P}\Psi(\tau)
\]

Source Term

Memory Term
**Feshbach Projection-Operator Method**

Effective equation for $\hat{P}\Psi$ (still fully coherent)

\[\begin{align*}
    i\partial_t \hat{P}\Psi(t) &= \hat{P}\hat{H}\hat{P}\hat{P}\Psi(t) + \hat{P}\hat{H}\hat{Q}e^{-i\hat{Q}\hat{H}\hat{Q}}\Psi(0) \\
    &\quad - i \int_0^t d\tau \hat{P}\hat{H}\hat{Q}e^{i\hat{Q}\hat{H}\hat{Q}}(t-\tau)\hat{Q}\hat{H}\hat{P}\hat{P}\Psi(\tau)
\end{align*}\]

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\[\Rightarrow\] Formal similarity to quantum transport formulation of Kurth and Stefanucci et. al.
Feshbach Projection-Operator Method

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    i\partial_t \hat{P}\Psi(t) &= \hat{P}\hat{H}\hat{P}\hat{P}\Psi(t) + \hat{P}\hat{H}\hat{Q}e^{-i\hat{Q}\hat{H}\hat{Q}t}\hat{Q}\Psi(0) \\
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\end{align*}$$

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$\implies$ Formal similarity to quantum transport formulation of Kurth and Stefanucci et. al.

Non-Markovian Stochastic Schrödinger equation

- perturbative expansion to second order in $\alpha H_{SB}$
- random phase approximation, dense bath spectrum, bath in statistical equilibrium

$$\begin{align*}
    i\partial_t \psi(t) &= \hat{H}_S\psi(t) + \alpha \sum_{\alpha} \eta_\alpha(t)\hat{V}_\alpha\psi(t) \\
    &\quad - i\alpha^2 \int_0^t d\tau \sum_{\alpha\beta} C_{\alpha\beta}(t-\tau) \hat{V}_\alpha^\dagger e^{-i\hat{H}_S(t-\tau)}\hat{V}_\beta\psi(\tau) + O(\alpha^3)
\end{align*}$$

Bath correlation functions

Markovian Stochastic Schrödinger equation

\( \delta \)-correlated bath

\[
C_{\alpha\beta}(t - \tau) = D_{\alpha\beta} \delta(t - \tau)
\]

Stochastic Schrödinger equation in Born-Markov approximation

\[
i\partial_t \psi(t) = \hat{H}_S \psi(t) + \alpha \sum_\alpha \eta_\alpha(t) \hat{V}_\alpha \psi(t) - i\alpha^2 \sum_{\alpha\beta} D_{\alpha\beta} \hat{V}_\alpha^\dagger \hat{V}_\beta \psi(t) + O(\alpha^3)
\]

Statistical average:

\[
\rho_S(t) = \frac{|\psi(t)\rangle\langle\psi(t)|}{\langle\psi(t)|\psi(t)\rangle}
\]

- Unravelling of Lindblad equation for static (linear) Hamiltonians
- Does not rely on semigroup property
- Valid for time-dependent Hamiltonians
- Gives always physical states
- Sound starting point to formulate stochastic TDDFT
TDDFT for Open Quantum Systems

- Approach in terms of density matrices
  - Density matrix evolution may not obey positivity during time-evolution
  - Scales as $O(N^2)$ due to usage of density matrix
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Approach in terms of stochastic Schrödinger equations

- Positivity is guaranteed by construction
- Scales as $O(N)$ since only state vectors are used
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Comparison to classical stochastic systems:

Fokker-Planck equation $\iff$ Langevin equation
Stochastic Time-Dependent Current-Density-Functional Theory

Can prove: For fixed bath operators $\hat{V}$ and initial state

$$\overline{j(r, t)} \overset{1:1}{\leftrightarrow} A(r, t)$$

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Can prove: For fixed bath operators $\hat{V}$ and initial state

$$j(r, t) \overset{1:1}{\leftrightarrow} A(r, t)$$


Mapping of fully interacting stochastic TDSE to stochastic TDKS equations

$$i\partial_t \psi_j(r, t) = \left[ \hat{H}_{KS}^{KS}(t) - \frac{1}{2} i\hat{V}^\dagger \hat{V} + \underbrace{l(t)\hat{V}}_{\text{fluctuations}} \underbrace{\text{damping}}_{\text{damping}} \right] \psi_j(r, t)$$
Stochastic Time-Dependent Current-Density-Functional Theory

Can prove: For fixed bath operators \( \hat{V} \) and initial state

\[
\begin{align*}
\overline{j(r, t)} & \quad \xleftrightarrow{1:1} \quad A(r, t)
\end{align*}
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Mapping of fully interacting stochastic TDSE to stochastic TDKS equations

\[
i\partial_t \psi_j(r, t) = \left[ \hat{H}^{KS}(t) - \frac{1}{2} i \hat{V} \hat{V}^\dagger + l(t) \hat{V} \right] \psi_j(r, t)
\]

\( l(t) \) : stochastic process

\[
\overline{l(t)} = 0, \quad \overline{l(t)l(t')} = \delta(t - t')
\]

Assumes

- Factorization at initial time: \( \psi(t_0) = \psi_S(t_0) \times \psi_B(t_0) \)
- Markovian approximation: no bath memory
- Weak coupling to the bath (second order in \( H_{SB} \))
Choice of bath operators: a simple model

Order-$N$ scheme and bath operators which obey Fermi statistics

$$V_{kk'}^j(r) = \delta_{kj}(1 - \delta_{kk'}) \sqrt{\gamma(r) f_D(\epsilon_k)} | \psi_j(r) \rangle \langle \psi_{k'}(r) |$$


Fermi-Dirac distribution

$$f_D(\epsilon_k) = \left[1 + \exp\left(\frac{\epsilon_k - \mu}{k_B T}\right)\right]^{-1}$$

Local relaxation rates

$$\gamma_{kk'}(r) = | \psi_k(r) \rangle \gamma_0 \langle \psi_{k'}(r) |$$
Choice of bath operators: a simple model

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V_{kk'}^j(r) = \delta_{kj}(1 - \delta_{kk'}) \sqrt{\gamma(r)f_D(\epsilon_k)} \langle \psi_j(r) | \langle \psi_k(r) | \langle \psi_k'(r) | 
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Local relaxation rates

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\gamma_{kk'}(r) = | \psi_k(r) \rangle \gamma_0 \langle \psi_{k'}(r) |
\]

- Operators ensure that Fermi statistics is obeyed.
- If a steady state is reached, it will be a thermal state.
Quantum jump algorithm

1) Draw uniform random number $\eta_j \in [0, 1]$

2) Propagate auxiliary wave function under non-Hermitian Hamiltonian

$$i \partial_t \Phi = \hat{H}_0 \Phi - i \hat{V}^\dagger \hat{V} \Phi$$

3) Propagate system wave function under norm-conserving Hamiltonian

$$i \partial_t \Psi = \hat{H}_0 \Psi - i \hat{V}^\dagger \hat{V} \Psi + i ||\hat{V} \Psi||^2 \Psi$$

4) If norm of auxiliary wave function drops below $\eta_j$, act with bath operator

$$||\Phi(t_j)|| \leq \eta_j, \quad \Psi(t_j) = \hat{V} \Psi(t_j), \quad \Phi(t_j) = \Psi(t_j)$$

5) Go to step 1)


$\implies$ Leads to piecewise deterministic evolution

Average over stochastic realizations:

$$\rho = |\Psi_j \rangle \langle \Psi_j |$$

guarantees always physical state!
Practical Implementation

Full-potential, all-electron code with local orbitals

http://www.fhi-berlin.mpg.de/aims/
Practical Implementation

Expansion of TD orbitals in non-orthogonal atom centered basis functions $\phi_k$

$$\psi_j(t) = \sum_k c_{jk}(t) \phi_k$$

Overlap matrix

$$S_{jk} = \langle \phi_j | \phi_k \rangle$$

TDKS equations

$$i \hat{S} \frac{\partial}{\partial t} c_j(t) = \hat{H}^{KS}(t) c_j(t)$$

Exponential midpoint approximation for short-time propagator

$$\hat{U}(t + \Delta t, t) = \exp \left[ -i \hat{S}^{-1} \hat{H}^{KS}(t + \Delta t/2) \Delta t + O(\Delta t^3) \right]$$

$$= \hat{S}^{-1/2} \exp \left[ -i \hat{S}^{-1/2} \hat{H}^{KS}(t + \Delta t/2) \Delta t \hat{S}^{-1/2} + O(\Delta t^3) \right] \hat{S}^{1/2}$$
Application

(1,4)-phenylene-linked zincbacteriochlorin-bacteriochlorin complex
Application: zincbacteriochlorin-bacteriochlorin complex

HOMO

LUMO
Free propagation of HOMO:

$$\psi_{\text{HOMO}}(t) = \psi_{\text{HOMO}}^{\text{GS}} \times e^{-i\varepsilon_{\text{HOMO}}t}$$

$$\text{Re}\{\psi_{\text{HOMO}}(t)\} = \psi_{\text{HOMO}}^{\text{GS}} \times \cos(\varepsilon_{\text{HOMO}}t)$$

(for real-valued orbitals)
Linear combination of HOMO and LUMO

Initial state

$$\psi_{\text{HOMO}}(t = 0) = \frac{1}{\sqrt{2}} \left[ \psi_{\text{HOMO}}^{\text{GS}} + e^{-i \frac{\pi}{2}} \psi_{\text{LUMO}}^{\text{GS}} \right]$$

Closed quantum system
Linear combination of HOMO and LUMO

Initial state

\[
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\]

Including coupling to environment
Outline

Open Quantum Systems
- Different approaches to deal with Decoherence and Dissipation
- Stochastic current density-functional theory
- Application: Stochastic simulation of (1,4)-phenylene-linked zincbacteriochlorin-bacteriochlorin complex

Stochastic Quantum Molecular Dynamics: Theory and Applications
- Including nuclear motion: Stochastic Quantum Molecular Dynamics
- Application: Stochastic quantum MD of 4-(N,N-Dimethylamino)benzonitrile

Outlook: future prospects of SQMD
Molecular Dynamics for Open Systems

Standard approaches like Car-Parinello MD, Born-Oppenheimer MD, Ehrenfest MD:
- Electronic degrees of freedom are treated with closed system approach

- Damping is added only to nuclear EOM (Langevin terms, velocity dep. forces)

However:
- Electrons are the first to experience energy transfer to a bath
- Nuclei feel bath directly but also through electron-ion interaction
  - ⇒ different forces on nuclei

Need open quantum theory for both electrons and nuclei
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Extension of stochastic TDCDFT to include nuclear degrees of freedom

\[ i\partial_t \Psi = \hat{H}(t)\Psi - \frac{1}{2}i\hat{V}^\dagger\hat{V}\Psi + l(t)\hat{V}\Psi \]

\[ \hat{H}(t) = \hat{T}_e(\mathbf{r}, t) + \hat{W}_{ee}(\mathbf{r}) + \hat{U}_{\text{ext},e}(\mathbf{r}, t) + \hat{T}_n(\mathbf{R}, t) + \hat{W}_{nn}(\mathbf{R}) + \hat{U}_{\text{ext},n}(\mathbf{R}, t) + \hat{W}_{en}(\mathbf{r}, \mathbf{R}) \]

Total current

\[ \langle J(x, t) \rangle = \langle j(r, t) \rangle + \langle J(R, t) \rangle, \quad x = (r, R) \]

For given initial state \( \Psi(x, t = 0) \) and bath operators \( V_\alpha(x, t) \)

\[ \langle J(x, t) \rangle \longleftrightarrow A(x, t) \]
Stochastic Quantum Molecular Dynamics: practical scheme

Extension of stochastic TDCDFT to include nuclear degrees of freedom

\[ i \partial_t \Psi(x, t) = \hat{H}(t) \Psi(x, t) - \frac{1}{2} i \hat{V}^\dagger \hat{V} \Psi(x, t) + l(t) \hat{V} \Psi(x, t) \]

In practice: resort as approximation to classical nuclei

Bath operators

\[ V^j_{kk'}(r, R(t); t) = \delta_{kj}(1 - \delta_{kk'}) \sqrt{\gamma(r, R(t); t) f_D(\epsilon_k)} | \psi_j(r, R(t); t) \rangle \langle \psi_{k'}(r, R(t); t) | \]

Ehrenfest forces as approximation for classical nuclei

\[ M_\alpha \ddot{R}_\alpha(t) = - \int \Psi^* \nabla_{R_\alpha} \hat{H}_e \Psi d\mathbf{r} \]

Note:

Wavefunctions are stochastic \( \Longrightarrow \) stochastic force on the nuclei

Vibronic excitation of Beryllium dimer, moving nuclei

closed quantum system
stretched initial condition
Vibronic excitation of Beryllium dimer, moving nuclei

closed quantum system
stretched initial condition

open quantum system
relaxation rate $\tau = 300$ fs

Maxwell-Boltzmann velocity distribution at jumps

$$f(\vec{v}) = \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-\frac{m\vec{v}^2}{2kT}\right)$$

Average over 15 stochastic realizations
Dual-Fluorescence in 4-(N,N-Dimethylamino)benzonitrile

Polar solvent: acetonitrile

Non-polar solvent: n-hexane

DMABN

Stochastic Quantum MD simulation for 4-(N,N-Dimethylamino)benzonitrile

Electron Localization Function

Rotated dimethyl group as initial condition
Stochastic Quantum MD simulation for 4-(N,N-Dimethylamino)benzonitrile

Conclusions

- SQMD allows to describe *ab-initio relaxation and dephasing* of electronic and nuclear degrees of freedom.
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Conclusions

- SQMD allows to describe ab-initio relaxation and dephasing of electronic and nuclear degrees of freedom
- In contrast to standard QMD, stochastic QMD allows also coupling of electrons to a heat bath
- Nuclei can feel the heat bath via electron-nuclear coupling

Within reach of Stochastic Quantum Molecular Dynamics

- Thermopower/Thermoelectric effects
- Excited state relaxation in solution
- Decoherence and dephasing in pump-probe experiments
- Driven quantum phase transitions
- ....
Future work

- Relaxation times from system-bath interaction Hamiltonian
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- Non-markovian dynamics: bath-correlation functions which are not delta correlated
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- Relaxation times from system-bath interaction Hamiltonian
- Non-markovian dynamics: bath-correlation functions which are not delta correlated
- Functionals: Dependence of XC-functional on bath operators
Thanks!

Massimiliano Di Ventra
Yonatan Dubi
Matt Krems
Jim Wilson
Roberto D’Agosta

Thank you for your attention!
Positivity

A density matrix which obeys positivity is a non-negative operator in Hilbert space

\[ \langle \Psi | \hat{\rho} | \Psi \rangle \geq 0, \quad \forall |\Psi\rangle \]

This guarantees that the expectation value of a positive operator \( \hat{A} \)

\[ \langle \hat{A} \rangle(t) = \sum_i p_i \langle \Psi(t) | \hat{A} | \Psi(t) \rangle = Tr\{\hat{\rho}(t)\hat{A}\} \geq 0 \]

and the variance of any operator \( \hat{B} \)

\[ \langle \hat{B}^2 \rangle(t) - \langle \hat{B} \rangle^2(t) \geq 0 \]