Applying time-local quantum master equations to dissipative dynamics and transport

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THE BORDER TERRITORY

QUANTUM DOMAIN

PHOTONS
ELECTRON'S
ATOMS

GRAVITY WAVE DETECTOR

CLASSICAL DOMAIN

SUN
PLANETS

US

QUANTUM FLUIDS

QUANTUM BILL OF RIGHTS
INTERFERE IF YOU CAN!!!
SCHRÖDINGER'S EQUATION

DO NOT CROSS
WITHOUT AMPLIFIER
N. BOHR

CLASSICAL LAW AND ORDER
DO NOT INTERFERE!!!
NEWTON'S EQUATIONS
SECOND LAW OF THERMODYNAMICS

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INTERVENTION!!!

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DO NOT INTERFERE!!!

NEWTON'S EQUATIONS

\[ i\hbar \frac{d}{dt} |\psi(x, t)\rangle = H(x, t) |\psi(x, t)\rangle \]

\[ m_i \frac{d^2 \vec{R}_i(t)}{dt^2} = \vec{F}_i = -\vec{V}(\vec{R}_i(t)) \]
1. Density matrices and damped harmonic oscillators
2. Damped harmonic oscillator as accuracy test
3. Ultrafast Non–Resonant Multiphoton Transitions
4. Light-harvesting in purple bacteria
5. Transport through molecular wires
6. Hole Transfer in DNA Driven by Solvent Fluctuations
Outline

1. Density matrices and damped harmonic oscillators
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Different systems: one theory

- harmonic oscillator or coupled two-level-systems coupled to bosonic thermal bath
- tight-binding model coupled to two fermionic reservoirs
Reduced density matrix formalism

- Goal: description of **ultra-fast (fs) processes** in dissipative systems / molecular wires
- **Full quantum dynamics** including dephasing, energy dissipation but also coherences and accurate laser-matter interaction
- splitting in relevant system and bosonic / fermionic reservoirs

\[ i\hbar \frac{d\sigma(t)}{dt} = [H(t), \sigma(t)] \]

- \( \sigma \) - density matrix of the full system (relevant system + bath)
Goal: description of ultra-fast (fs) processes in dissipative systems / molecular wires

full quantum dynamics including dephasing, energy dissipation but also coherences and accurate laser-matter interaction

splitting in relevant system and bosonic / fermionic reservoirs

reduced density-matrix:
\[ \rho = \text{tr}_B(\sigma) \] - density matrix of the relevant system

\[ i\hbar \frac{d\rho(t)}{dt} = [H_S(t), \rho(t)] + D(t)\rho(t) \]
System-bath coupling

**Hamiltonian**

\[ H = H_S + H_B + H_{SB} \]

- every environmental degree of freedom only slightly distorted ⇒ modeled by harmonic oscillators
- how strongly does the environment absorb energy? ⇒ spectral density \( J(\omega) \)
- perturbation theory in the system-bath coupling \( H_{SB} \)
- either time-nonlocal theory (time-convolution)
  \[
  \frac{d\rho(t)}{dt} = \mathcal{L}_S \rho(t) + \int_0^t dt' K(t')\rho(t')
  \]
- or time-local theory (time-convolutionless)
  \[
  \frac{d\rho(t)}{dt} = \mathcal{L}_S \rho(t) + \int_0^t dt' K(t')\rho(t)
  \]
Decomposition of the spectral density

- information on the frequencies of the bath modes and their coupling to the system $J(\omega) = \frac{\pi}{2} \sum_i \frac{c_i^2}{m_i \omega_i} \delta(\omega - \omega_i)$
- numerical decomposition in Lorentzians

\[ J(\omega) = \sum_{k=1}^{n} \frac{p_k}{4 \Omega_k} \frac{1}{(\omega - \Omega_k)^2 + \Gamma_k^2} \]

Overview of the theory

- reservoir correlation function $C(t) = \int_{-\infty}^{\infty} \frac{d\omega}{\pi} J(\omega) \frac{e^{i\omega t}}{e^{\beta \omega} - 1}$
  $\Rightarrow$ sum of exponentials in $t$
- this allows further analytical treatment
- definition of auxiliary density matrices (time-nonlocal approach) or auxiliary operators $\Lambda_{12}^k(t)$ (time-local approach)
- instead of one quantum master equation one gets one master equation of the system and several auxiliary master equations
- Matsubara expansion $\Rightarrow$ many master equations for low temperatures
- no further approximation in the light-matter coupling (beyond semi-classical approximation)

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Population dynamics for harmonic oscillator

- initially all population in the 3rd excited level
- medium temperature: $\beta = 1/\omega_0$
- Drude form, cut-off: $\omega_D/\omega_0 = 2$, $\eta = 0.121$
initially all population in the 3rd excited level
medium temperature: $\beta = 1/\omega_0$
Drude form, cut-off: $\omega_D/\omega_0=1$, $\eta = 0.2$
Population dynamics for harmonic oscillator

- initially all population in the 3rd excited level
- medium temperature: $\beta = 1/\omega_0$
- Drude form, cut-off: $\omega_D/\omega_0 = 0.5$, $\eta = 0.544$
Population dynamics for harmonic oscillator

- Initially all population in the 3rd excited level
- Medium temperature: $\beta = 1/\omega_0$
- Drude form, cut-off: $\omega_D/\omega_0 = 0.5$, $\eta = 0.0544$

for bath-correlation function $C(t) = a_1 e^{-\gamma_1 t}$
Hierarchical scheme: Damped harmonic oscillator

- population dynamics of third excited state

![Graphs showing population dynamics for different N values: N=2, N=4, N=6, N=8.](image)

- time-nonlocal vs. time-local

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three electronic states, many vibrational states

Effective Schrödinger Equation for Non-resonant Processes

- projector into the space of primary states
  \[ \hat{P} = \sum_{a} |\varphi_a\rangle \langle \varphi_a| \]

- its orthogonal complement
  \[ 1 - \hat{P} \equiv \hat{Q} = \sum_{x} |\varphi_x\rangle \langle \varphi_x| \]

- leading to primary states
  \[ |\psi_1(t)\rangle = \hat{P} |\psi(t)\rangle \]

- and secondary states
  \[ |\psi_2(t)\rangle = \hat{Q} |\psi(t)\rangle \]
Effective Schrödinger Equation for Non-resonant Processes

- effective Schrödinger equation for primary states (in time-local form)

\[ i\hbar \frac{\partial}{\partial t} |\psi_1(t)\rangle = H_1(t) |\psi_1(t)\rangle + \hat{P}H_{\text{field}}(t)\hat{Q}(1 - \hat{\Sigma}(t))^{-1}\hat{\Sigma}(t)\hat{P} |\psi_1(t)\rangle \]

- using

\[ \hat{\Sigma}(t) = \frac{i}{\hbar} \int_{t_0}^{t} d\tilde{t} U_2(t, \tilde{t}; E) \hat{Q}H_{\text{field}}(\tilde{t})\hat{P}U(\tilde{t}, t; E) \]

- so far exact

- in the following: assumption of weak laser field
Different pulse scenarios

three different pulse scenarios
Short pulse

![Graphs depicting population and time in ps, with various parameters and probability scales.](image-url)
Longer pulse
Two pulses
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Molecular dynamics simulation of LH-II

- LH-II complex of *Rhodospirillum molischianum*
- about 110,000 atoms
- using parallel MD code NAMD2
- 500-3000 snapshots every 2 fs
Energy gaps of single BChls

- Fast quantum chemical calculation for each snapshot configuration: ZINDO for each separate BChl incl. point charges using ORCA
Energy gaps of single BChls

- Fast **quantum chemical calculation** for each snapshot configuration: ZINDO for each separate BChl incl. point charges using ORCA
**Spectral density of the protein environment**

- **Autocorrelation function** of the energy gap $\Delta E_j$

$$C(t_i) = \frac{1}{16} \sum_{j=1}^{16} \left[ \frac{1}{N-i} \sum_{k=1}^{N-i} \Delta E_j(t_i + t_k) \Delta E_j(t_k) \right]$$

- **Spectral density**

$$J(\omega) = \frac{2}{\pi} \tanh \left( \frac{\omega}{2k_bT} \right) \int_0^\infty dt \, C(t) \cos \omega t$$

![Graph showing spectral density with simulation lengths at t=1ps (B800), t=3ps (B800), t=6ps (B800), and t=6ps (B850).]
Quantum mechanical model for the B850 ring

- 16 coupled two-level systems
- coupled to a thermal bath, characterized by its spectral density $J(\omega)$
- only transfer between neighboring sites
- determination of spectra in perturbation theory
Absorption spectra for B850 ring

- red: experiment
- green: direct from MD simulation
- blue: quantum mechanical model

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Molecular wires

- first reproducible experiments on molecular wires
  - break junctions, STM setups, DNA wires, …

- influence of laser light on molecular wires gives an opto-electronic coupling

- with femtosecond laser pulses: high spatial as well as temporal resolution
The model
The model

\[ H(t) = H_S(t) + H_L + H_{SL} \]

\[ H_S(t) = \sum_n (E_n + U_n(t)) c_n^\dagger c_n - \Delta (c_n^\dagger c_{n-1} + c_{n-1}^\dagger c_n) \]

\[ H_L = \sum_q \omega_q c_q^\dagger c_q \]

\[ H_{LS} = \sum_q (V_q c_1^\dagger c_q + V_q^* c_q^\dagger c_1) \]
Coherent destruction of tunneling (CDT)

\[ U_n(t) = A(t)\delta_{1n} - A(t)\delta_{2n} \]
\[ A(t) = A_0 \sin(\omega t) \]

\[ \Delta = 0.1 \text{ eV} \]

\[ 1 \text{ [e]} \approx 2.4 \times 10^{-4} \text{ A} \]

Coherent destruction of tunneling (CDT)

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Coherent destruction of tunneling (CDT)

\[ U_n(t) = A(t)\delta_{1n} - A(t)\delta_{2n} \]

\[ A(t) = A_0 \sin(\omega t) \]

CDT: Short laser pulse

\[ U_n(t) = A(t)\delta_{1n} - A(t)\delta_{2n} \]

\[ A(t) = A_0 \exp \left( -\frac{(t - T)^2}{\sigma^2} \right) \]

Density matrices and damped harmonic oscillators

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Hole Transfer in DNA Driven by Solvent Fluctuations
Computational Methodology

- double-stranded DNA species of sequences GT\textsubscript{n}GGG with \( n = 1, 2, 3, 4, 5, 7, 10 \) and 14
- first, a classical MD simulation of the DNA
- CT parameters: TB Hamiltonian consisting of site energies and electronic couplings based on the SCC-DFTB method
- time-dependent Schrödinger equation

\[ i\hbar \frac{\partial}{\partial t} \psi = H\psi \]

- initial state on one end and sink on the other end
- large fluctuations of site energies in the order of 0.4 eV, dramatically reduced barrier heights
- solvent fluctuations introduce a significant correlation between neighboring sites
Survival of hole $P(t)$ vs. time in GTGGG

- a) 100 simulations, 20 ps each.
- b) survival with the static model (50 $\times$ longer time scale)
a) averaged time dependence from dynamical simulations and the result with the completely static model

b) occupation of A-bridge in all $\text{GT}_n\text{GGG}$ sequences; the averaged time dependence from dynamical simulations
data from full MD-based calculations as well as those based on constant site energies and on constant electronic couplings

Rate constant of hole transfer in $\text{GT}_n\text{GGG}$

- parameters calculated with the inclusion of environment (QM/MM) and without that (‘in vacuo’)

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