Optical control of transport through molecular junctions

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Warwick, August 2009
\[ \frac{i\hbar}{\hbar} \frac{d}{dt} |\psi(x, t)\rangle = H(x, t) |\psi(x, t)\rangle \]

\[ m_i \frac{d^2 \vec{R}_i(t)}{dt^2} = \vec{F}_i = -\vec{\nabla} V(\vec{R}_i(t)) \]
Outline

1. Density matrices and damped harmonic oscillators
2. Light-harvesting in purple bacteria
3. Transport through molecular wires
4. Hole Transfer in DNA Driven by Solvent Fluctuations
Density matrices and damped harmonic oscillators

Light-harvesting in purple bacteria

Transport through molecular wires

Hole Transfer in DNA Driven by Solvent Fluctuations
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

$\sigma$ - density matrix of the full system
(relevant system + bath)

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

- 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)
  \[
  \frac{d\rho(t)}{dt} = \mathcal{L}_S \rho(t) + \int_0^t dt' K(t') \rho(t)
  \]
Hierachical scheme: Damped harmonic oscillator

population dynamics of third excited state

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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
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

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

Simulation length:
- $t=1\text{ps (B800)}$
- $t=3\text{ps (B800)}$
- $t=6\text{ps (B800)}$
- $t=6\text{ps (B850)}$
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

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

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

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

\[ H_{LS} = \sum_q (V_q c_1^\dagger c_q + V_q^* c_q^\dagger c_1) \]
Population dynamics

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

\[ E_1 = E_2 = E_{F,r} + 1\Delta = E_{F,l} - 1\Delta \]
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)

\[ U_n(t) = A(t)\delta_1 n - A(t)\delta_2 n \]

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

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

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

Predefined current pattern

- goal: determine laser field which creates predefined current (target is non-local in time)

\[ J_0(E) = \int dt \left \{ P(t) - \text{tr} \{ I(t) \rho_S(t) \} \right \}^2 \]

\[ J(t, E) = J_0(E) + \frac{\lambda}{2} \int_{t_0}^{t_f} dt \frac{(E(t) - \tilde{E}(t))^2}{s(t)} \]

- \( P(t) \) - predefined current pattern
- \( \tilde{E}(t) \) - laser field of the previous iteration
- functional derivative of \( J \) with respect to \( E(t) \)

\[ E(t) = \tilde{E}(t) - \frac{s(t)}{\lambda} \int d\tau \left \{ 2 \text{tr} \{ I(\tau) \rho_S(\tau) \} - 2P(\tau) \right \} \text{tr} \left \{ I(\tau) \frac{\delta \rho_S(\tau)}{\delta E(\tau)} \right \} \]

\[ - \frac{s(t)}{\lambda} \int d\tau \left \{ 2 \text{tr} \{ I(\tau) \rho_S(\tau) \} - 2P(\tau) \right \} \text{tr} \left \{ \frac{\delta I(\tau)}{\delta E(\tau)} \rho_S(\tau) \right \} \]
Optimal control with Gaussian target

\[ E_L(E) \quad n_1 \quad \Delta \quad n_2 \quad E_R(E) \]

\[ E_F, L \quad E_F, R \]

\[ I \ [\text{nA}] \]

\[ E \ [\text{eV}] \]

\[ \text{Time} \ [\text{fs}] \]

Optimal control with step function target

Optimal control with oscillatory target

Spin current through quantum dot: CDT

\[ E \]

\[ J_L(E) \]

\[ E_{F,l} \]

\[ J_R(E) \]

\[ E_{F,r} \]

\[ \epsilon \]

\[ \epsilon \]

\( I \, [\text{nA}] \)

\( \text{Time} \, [\text{fs}] \)

Spin current through quantum dot: CDT

\[ J_{L}(E) \]  
\[ J_{R}(E) \]

\[ E_{F,l} \]  
\[ E_{F,r} \]

\[ \varepsilon_{\uparrow} \]  
\[ \varepsilon_{\downarrow} \]

\[ J(E)_{L} \]  
\[ J(E)_{R} \]

Spin current through quantum dot: Optimal control

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**Computational Methodology**

- double-stranded DNA species of sequences $GT_nGGG$ 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 GT\textsubscript{n}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’)

Comparison of dynamical and statistical models

parameter set generated in dynamical simulation (a) and the statistical model (b)
Acknowledgments: The Group

- R. Schulz, G.-Q. Li, J. Liebers, S. Pezeshki, C. Olbrich, A. Amin, (L. Moevius, S. Welack, M. Schröder)
- K. Schulten and his team (Urbana-Champaign)
- T. Kubar and M. Elstner (TU Braunschweig)