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

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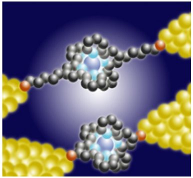
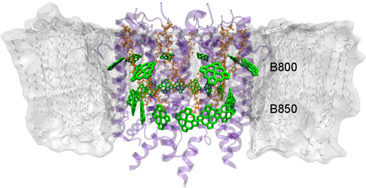
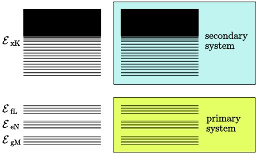
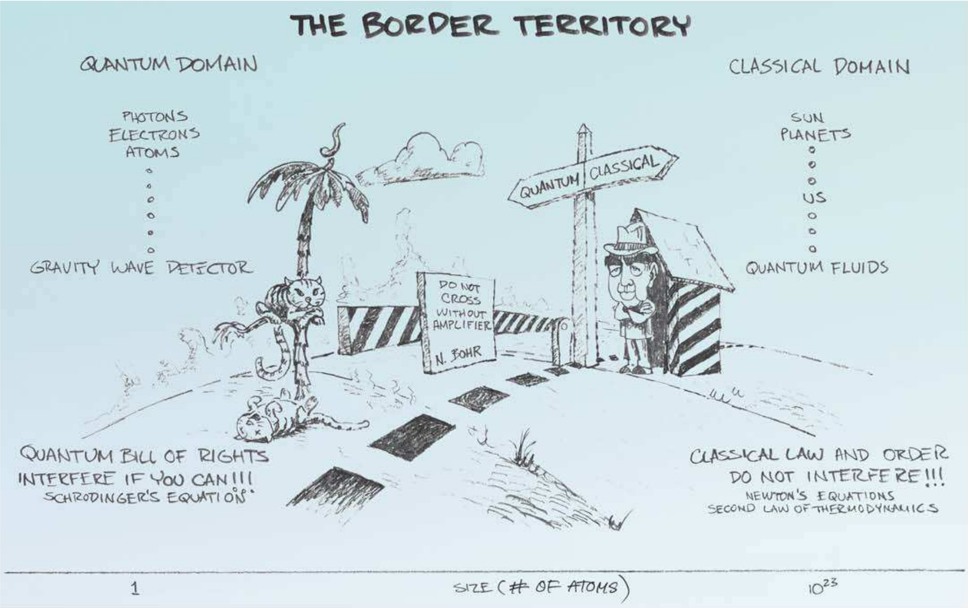
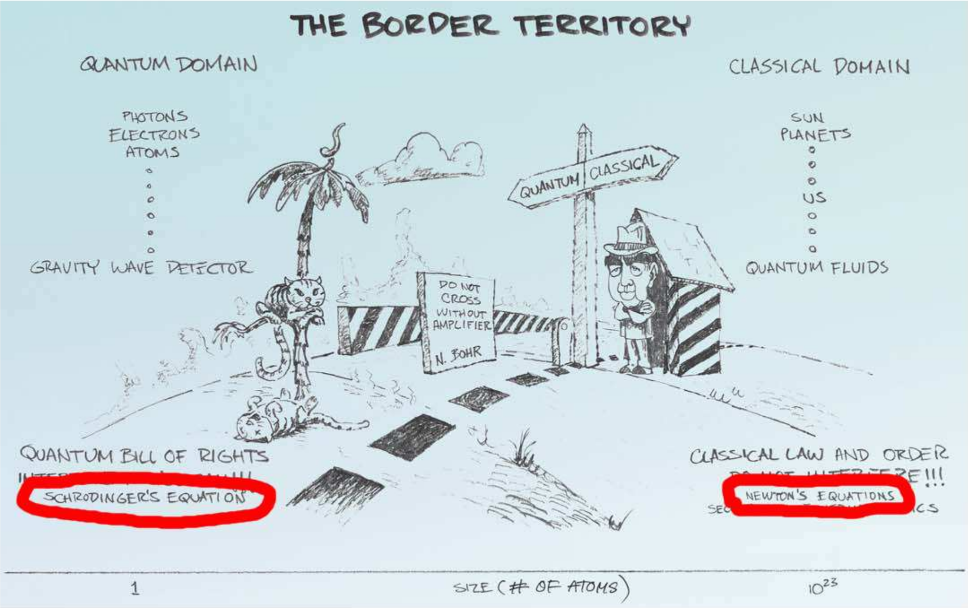








W.H. Zurek, Los Alamos Science **27**, 2 (2002). quant-ph/0306072



$$i\hbar \frac{d}{dt}|\Psi(x,t)\rangle = H(x,t)|\Psi(x,t)\rangle \qquad m_i \frac{d^2 \vec{R}_i(t)}{dt^2} = \vec{F}_i = -\vec{\nabla} V(\vec{R}_i(t))$$

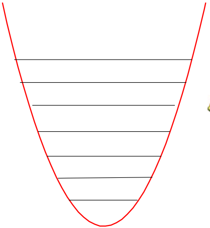
Outline

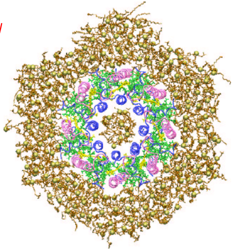
1. Density matrices and damped harmonic oscillators
2. Damped harmonic oscillator as accuracy test
3. Ultrafast Non–Resonant Multiphoton Transitions
4. Light-harvesting in purple bacteria
5. Transport through molecular wires
6. Hole Transfer in DNA Driven by Solvent Fluctuations

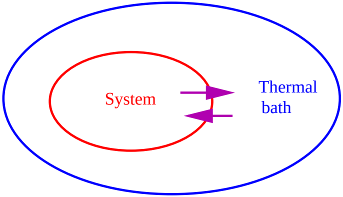
Outline

Different systems: one theory

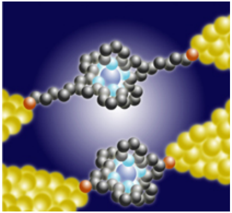
- harmonic oscillator or coupled two-level-systems coupled to bosonic thermal bath

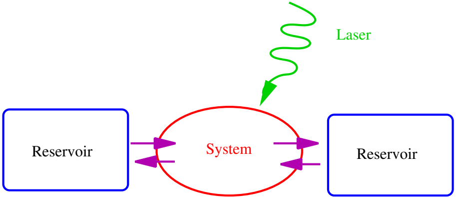






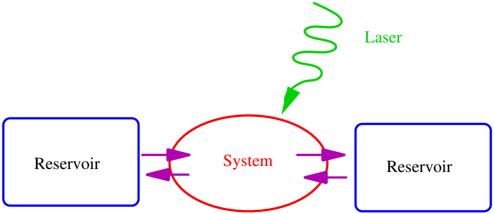
- tight-binding model coupled to two fermionic reservoirs





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



- σ - 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
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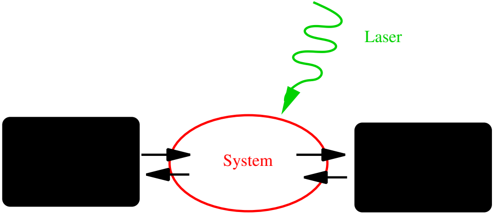


- reduced density-matrix:
  $\rho = tr_B(\sigma)$ - density matrix of the relevant system

$$i\hbar \frac{d\rho(t)}{dt} = [H_S(t), \rho(t)] + \mathcal{D}(t)\rho(t)$$

System-bath coupling

Hamiltonian

$H = H_S + H_B + H_{SB}$

- every environmental degree of freedom only slightly distorted
  $\Rightarrow$ modeled by harmonic oscillators
- how strongly does the environment absorb energy?
  $\Rightarrow$ spectral density $J(\omega)$
- perturbation theory in the system-bath coupling H_{SB}
- either time-nonlocal theory (time-convolution)

$$\frac{d\rho(t)}{dt} = \mathcal{L}_S\rho(t) + \int_0^t dt' K(t')\rho(t')$$

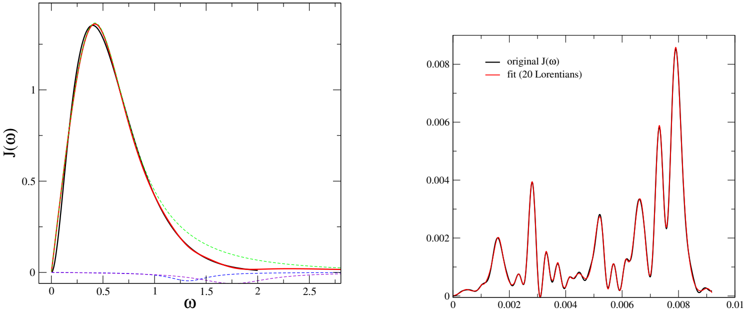
- or time-local theory (time-convolutionless)

$$\frac{d\rho(t)}{dt} = \mathcal{L}_S\rho(t) + \int_0^t dt' K(t')\rho(t)$$

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

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



C. Meier and D. J. Tannor, J. Chem. Phys. **111**, 3365 (1999)

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)

U. Kleinekathöfer, J. Chem. Phys. **121**, 2505 (2004).
S. Welack, M. Schreiber, U. Kleinekathöfer, J. Chem. Phys. **124**, 044712 (2006).

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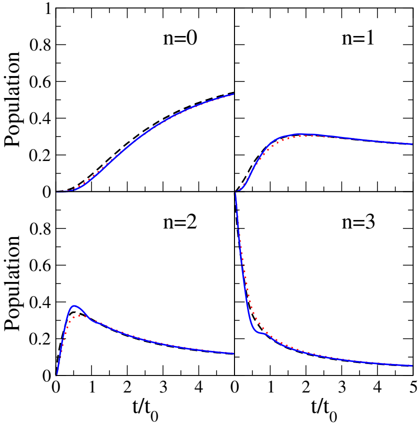
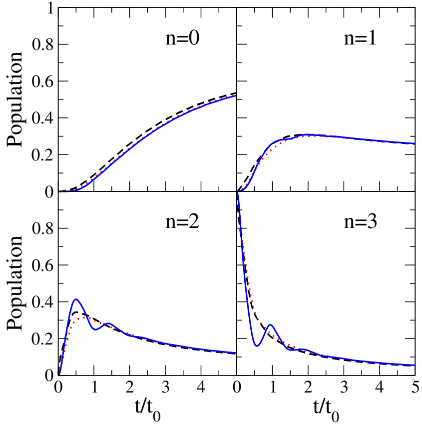
Population dynamics for harmonic oscillator

- initially all population in the 3rd excited level
- medium temperature: $\beta = 1/\omega_0$
- Drude form, cut-off: ω_D/ω_0=2, $\eta = 0.121$



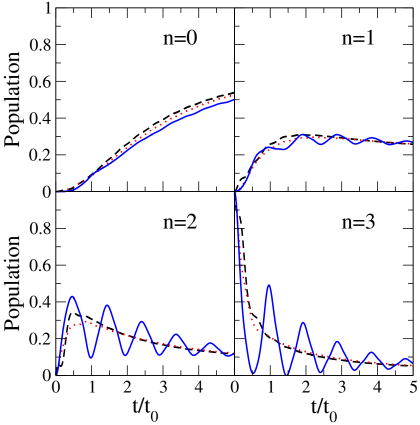
Population dynamics for harmonic oscillator

- initially all population in the 3rd excited level
- medium temperature: $\beta = 1/\omega_0$
- Drude form, cut-off: ω_D/ω_0=1, $\eta = 0.2$



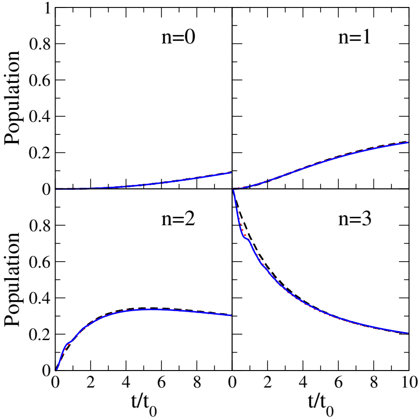
Population dynamics for harmonic oscillator

- initially all population in the 3rd excited level
- medium temperature: $\beta = 1/\omega_0$
- Drude form, cut-off: ω_D/ω_0=0.5, $\eta = 0.544$



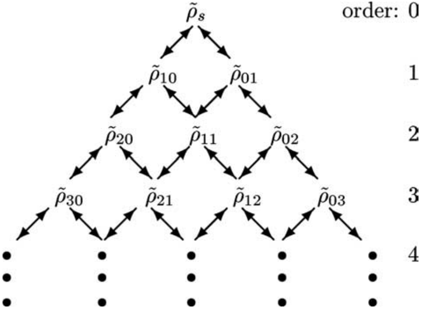
Population dynamics for harmonic oscillator

- initially all population in the 3rd excited level
- medium temperature: $\beta = 1/\omega_0$
- Drude form, cut-off: ω_D/ω_0=0.5, $\eta = 0.0544$



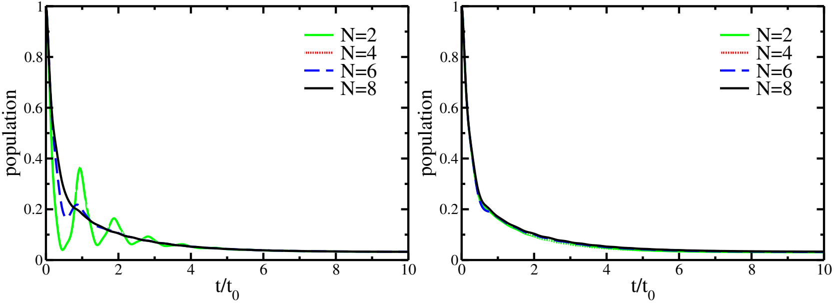
Hierachical scheme: Damped harmonic oscillator

- hierachical scheme for higher-order perturbation theory as proposed by Tanimura and Kubo (J. Phys. Soc. Jpn. 58, 101 1998) or Yan et al. (Chem. Phys. Lett. 395, 216 2004)
- for bath-correlation function $C(t) = a_1 e^{-\gamma_1 t}$



Hierachical scheme: Damped harmonic oscillator

- population dynamics of third excited state



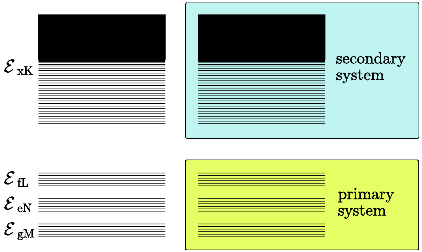
time-nonlocal

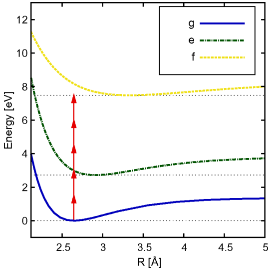
time-local

M. Schröder, M. Schreiber, U. Kleinekathöfer, J. Chem. Phys. **126**, 114102 (2007)

Outline

Three–Electronic Level Molecule





three electronic states, many vibrational states

J. Liebers, U. Kleinekathöfer, V. May, Chem. Phys. **347**, 229 (2008)

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)

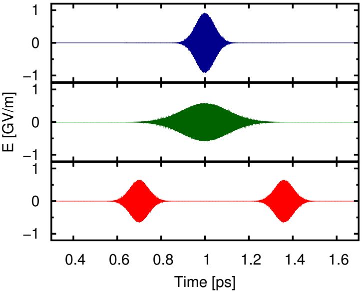
$$i\hbar\frac{\partial}{\partial t}|\Psi_1(t)\rangle = H_1(t)|\Psi_1(t)\rangle + \hat{P}H_{\text{field}}(t)\hat{Q}(1-\hat{\Sigma}(t))^{-1}\hat{\Sigma}(t)\hat{P}|\Psi_1(t)\rangle$$

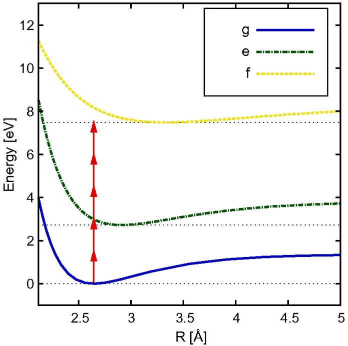
- using

$$\hat{\Sigma}(t) = -\frac{i}{\hbar}\int_{t_0}^{t} d\bar{t}\; U_2(t,\bar{t};\mathbf{E})\hat{Q}H_{\text{field}}(\bar{t})\hat{P}U(\bar{t},t;\mathbf{E})$$

- so far exact
- in the following: assumption of weak laser field

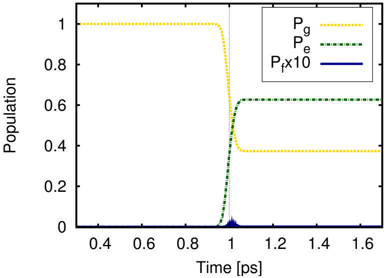
Different pulse scenarios



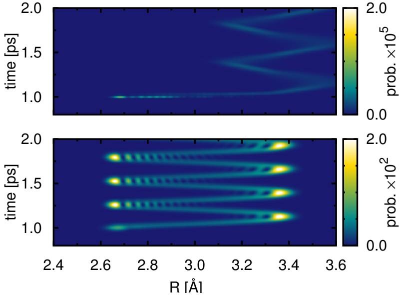


three different pulse scenarios

Short pulse

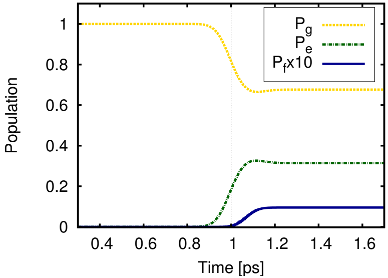


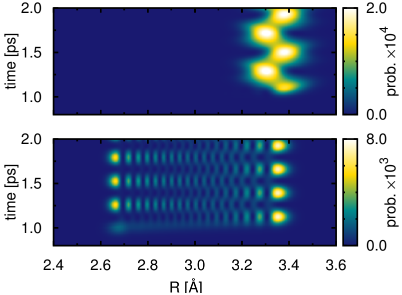
Population
Time [ps]
P_g
P_e
P_fx10
1
0.8
0.6
0.4
0.2
0
0.4
0.6
0.8
1
1.2
1.4
1.6



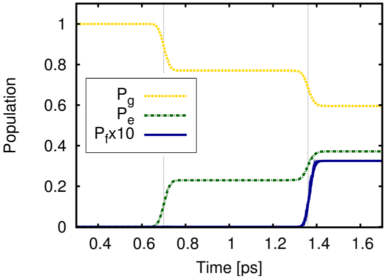
time [ps]
R [Å]
prob. $\times 10^5$
prob. $\times 10^2$
2.0
1.5
1.0
0.0
2.4
2.6
2.8
3.0
3.2
3.4
3.6

Longer pulse

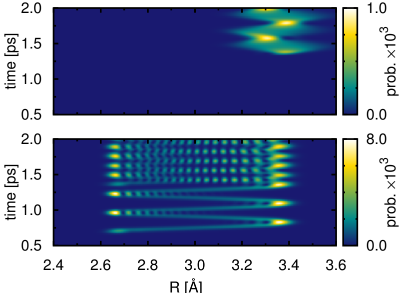




Two pulses



Population
Time [ps]
P_g
P_e
P_fx10
0
0.2
0.4
0.6
0.8
1
0.4
0.6
0.8
1
1.2
1.4
1.6

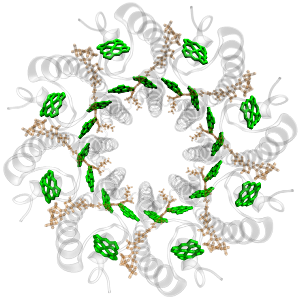


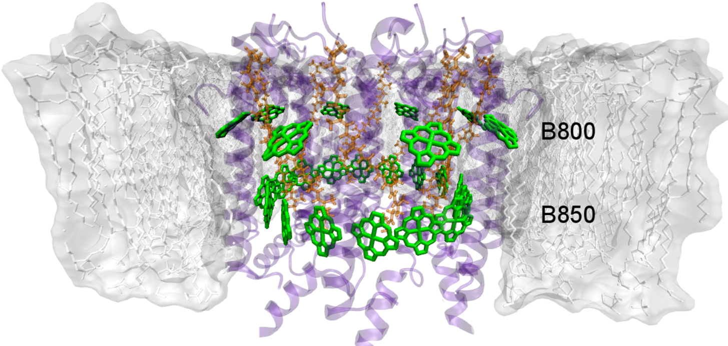
time [ps]
prob. ×10^3
R [Å]
2.0
1.5
1.0
0.5
1.0
0.0
8.0
0.0
2.4
2.6
2.8
3.0
3.2
3.4
3.6

Outline

Molecular dynamics simulation of LH-II

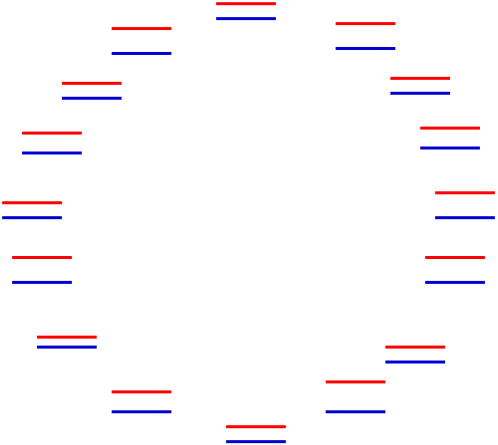
- LH-II complex of *Rhodospirillum molischianum*
- about 110 000 atoms
- using parallel MD code NAMD2
- 500-3000 snapshots every 2 fs

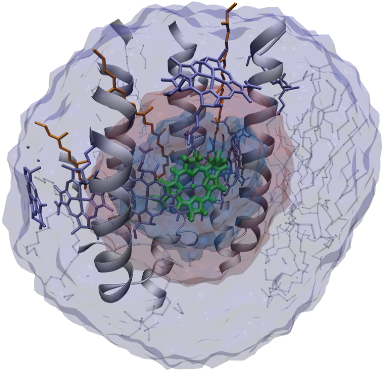




Energy gaps of single BChls

- Fast quantum chemical calculation for each snapshot configuration: ZINDO for each separate BChl incl. point charges using ORCA





ground states
excited states

Energy gaps of single BChls

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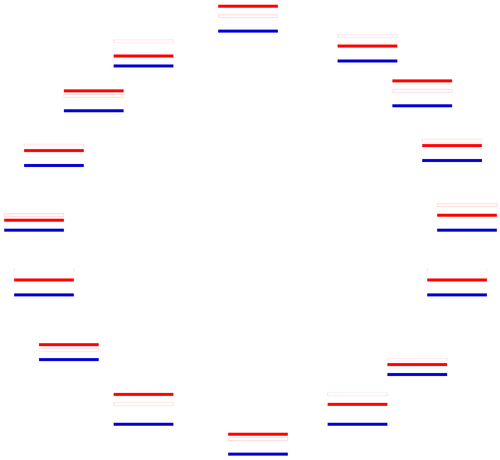
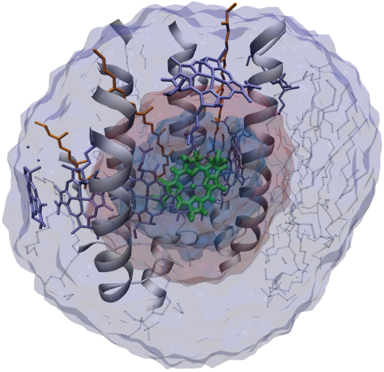




ground states
excited states

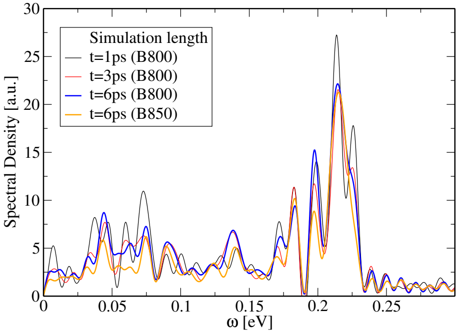
Spectral density of the protein environment

- Autocorrelation function of the energy gap ΔE_j

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

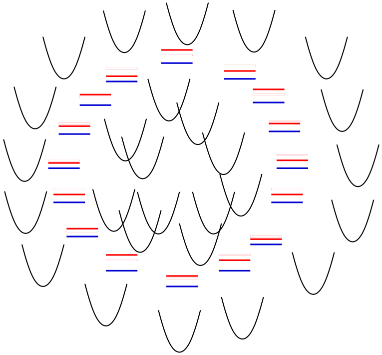
- Spectral density

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

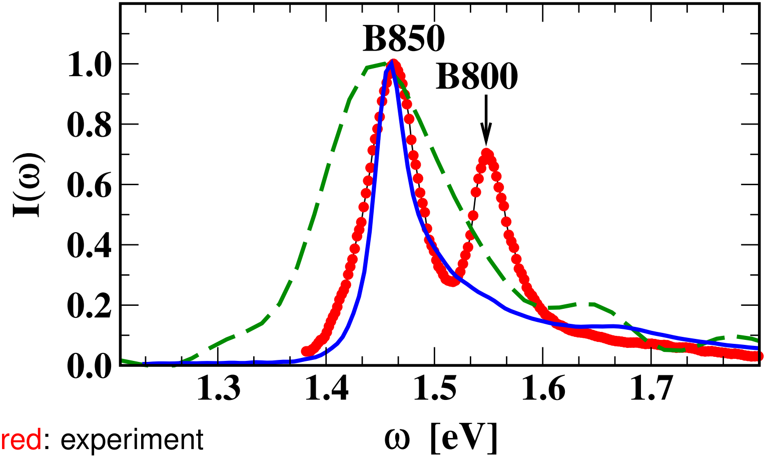


Quantum mechanical model for the B850 ring

- 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



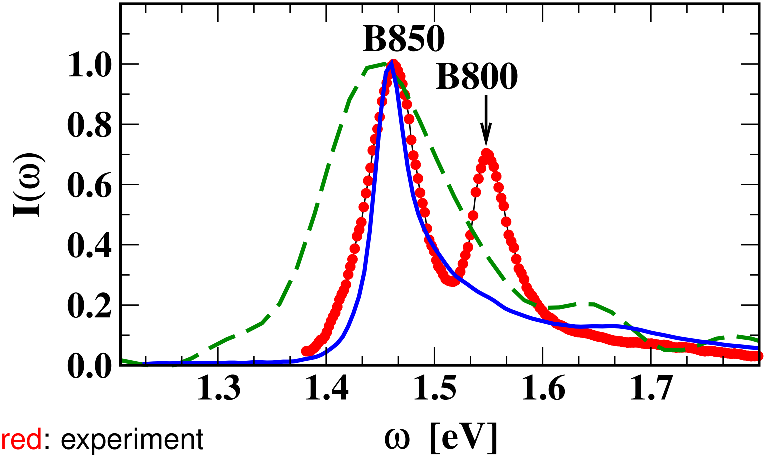
Absorption spectra for B850 ring



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

M. Schröder, U. Kleinekathöfer, M. Schreiber, J. Chem. Phys. **124**, 903 (2006)
A. Damjanović, I. Kosztin, U. Kleinekathöfer, K. Schulten, Phys. Rev. E **65**, 919 (2002)

Absorption spectra for B850 ring



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Quantum Biology

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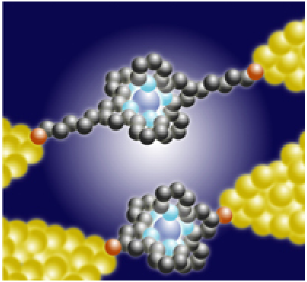
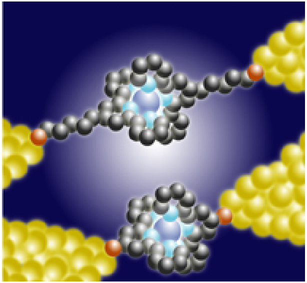
Outline

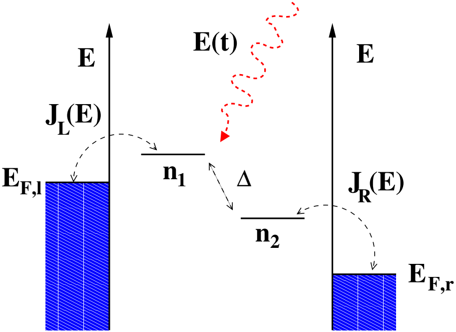
Molecular wires



- 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

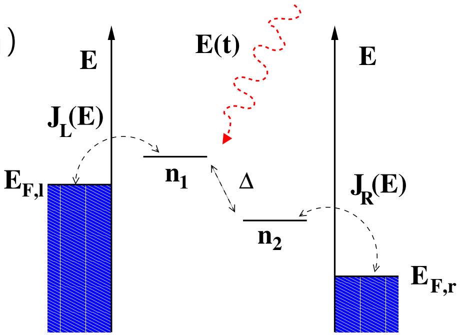
The model



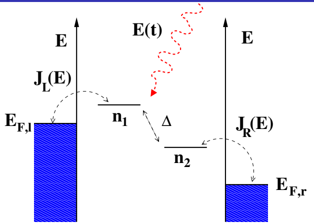


The model

$$
\begin{aligned}
H(t) &= H_S(t) + H_L + H_{SL} \\
H_S(t) &= \sum_n (E_n + U_n(t)) c_n^\dagger c_n - \Delta (c_n^\dagger c_{n-1} + c_{n-1}^\dagger c_n) \\
H_L &= \sum_q \omega_q c_q^\dagger c_q \\
H_{LS} &= \sum_q (V_q c_1^\dagger c_q + V_q^* c_q^\dagger c_1)
\end{aligned}
$$



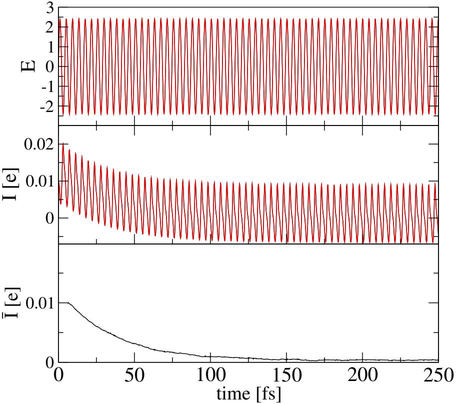
Coherent destruction of tunneling (CDT)



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

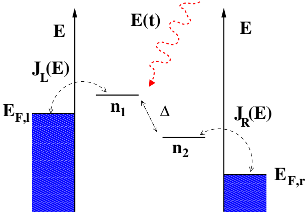
$\Delta = 0.1$ eV

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

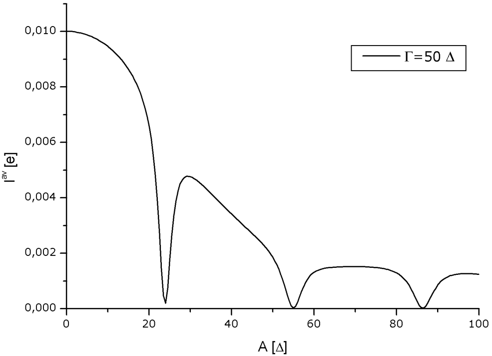


J. Lehmann, S. Camalet, S. Kohler, P. Hänggi, Chem. Phys. Lett. **368**, 282 (2003)

Coherent destruction of tunneling (CDT)

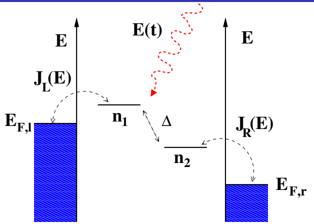


$$U_n(t) = A(t)\delta_{1n} - A(t)\delta_{2n}$$
$$A(t) = A_0 \sin(\omega t)$$

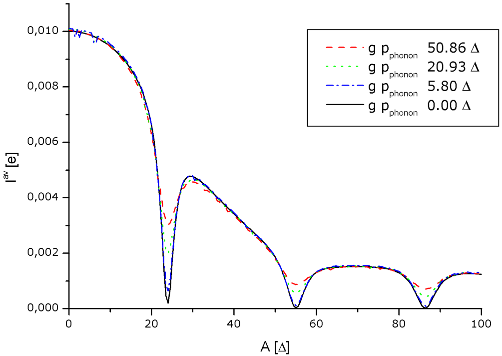


J. Lehmann, S. Camalet, S. Kohler, P. Hänggi, Chem. Phys. Lett. **368**, 282 (2003)

Coherent destruction of tunneling (CDT)

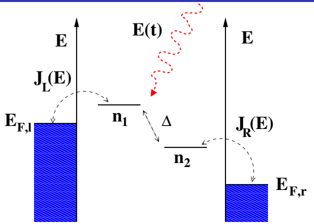


$$U_n(t) = A(t)\delta_{1n} - A(t)\delta_{2n}$$
$$A(t) = A_0 \sin(\omega t)$$



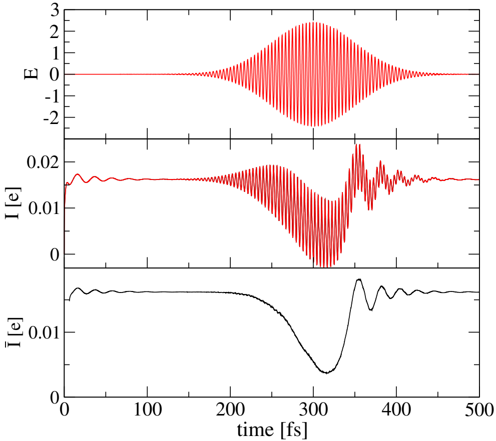
J. Lehmann, S. Kohler, V. May, P. Hänggi, J. Chem. Phys. **121**, 2278 (2003)

CDT: Short laser pulse



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

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



U. Kleinekathöfer, G.-Q. Li, S. Welack, M. Schreiber, Europhys. Lett. **75**, 139 (06).

Outline

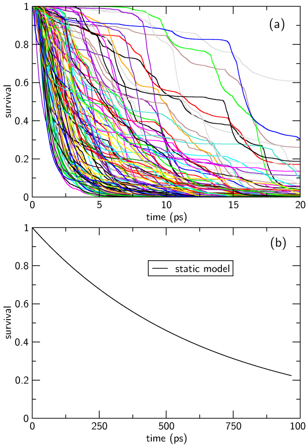
Computational Methodology

- 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

$$i\hbar\frac{\partial}{\partial t}\Psi = H\Psi$$

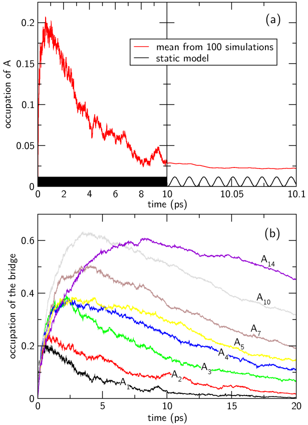
- initial state on one end and sink on the other end
- large fluctuations of site energies in the order of 0.4 eV, dramatically reduced barrier heights
- solvent fluctuations introduce a significant correlation between neighboring sites

Survival of hole $P(t)$ vs. time in GTGGG



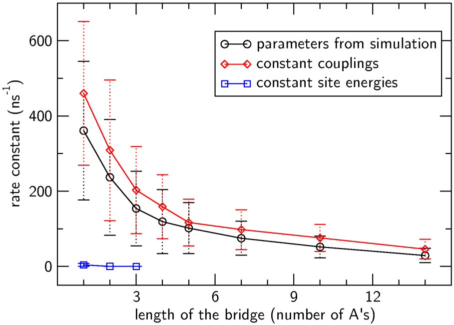
- a) 100 simulations, 20 ps each.
- b) survival with the static model (50 $\times$ longer time scale)

Occupation of bridge A by the hole in GTGGG



- a) averaged time dependence from dynamical simulations and the result with the completely static model
- b) occupation of A-bridge in all GT_nGGG sequences; the averaged time dependence from dynamical simulations

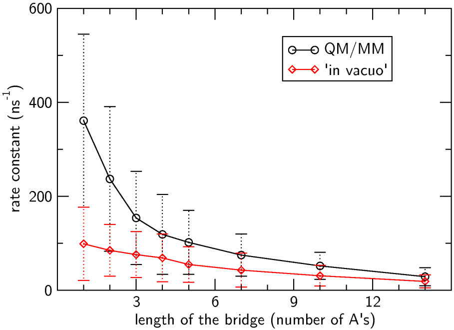
Rate constant of hole transfer in GT_nGGG



- data from full MD-based calculations as well as those based on constant site energies and on constant electronic couplings

T. Kubař, U. Kleinekathöfer, M. Elstner, J. Phys. Chem. B 113, 13107 (09).

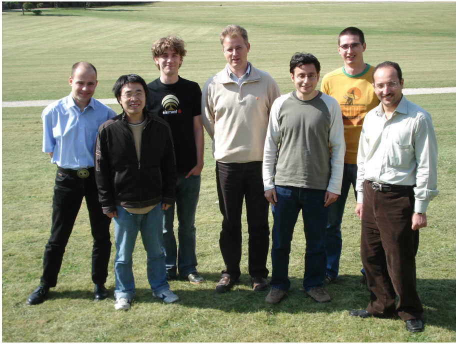
Rate constant of hole transfer in GT$_n$GGG



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

T. Kubař, U. Kleinekathöfer, M. Elstner, J. Phys. Chem. B 113, 13107 (09).

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 / Karlsruhe)