The influence of ultra-fast laser pulses on electron transfer in molecular wires studied by a non-Markovian density matrix approach

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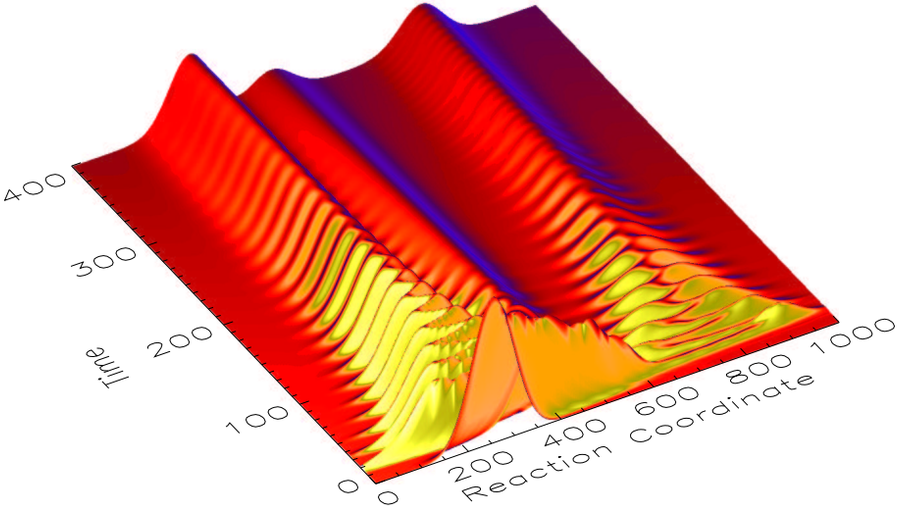
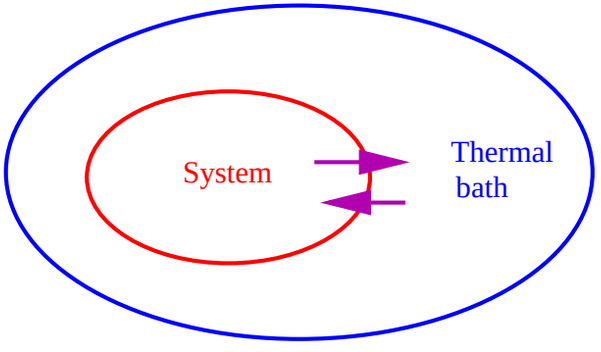
OF TECHNOLOGY

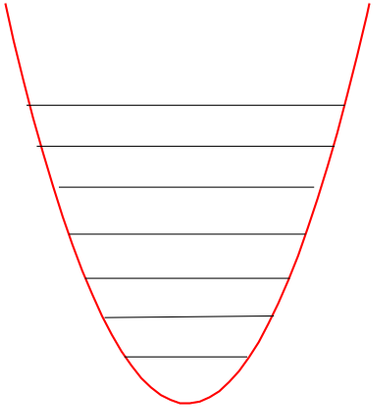


Outline

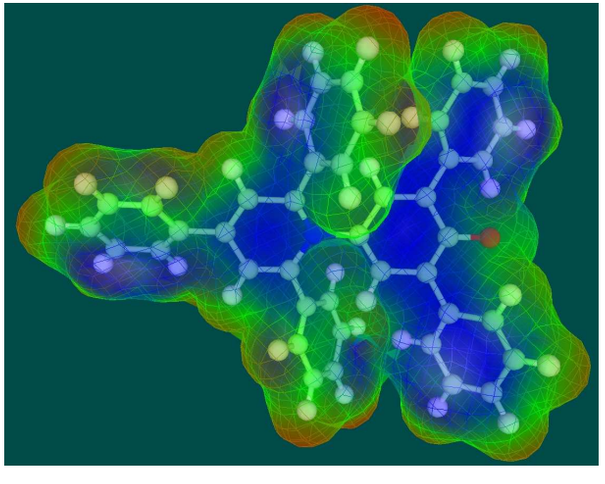
Non-Markovian theory



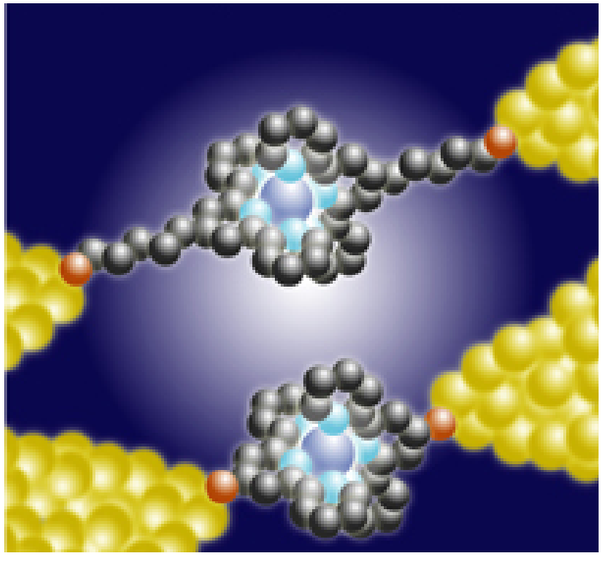
Damped harmonic oscillator



Control of electron transfer

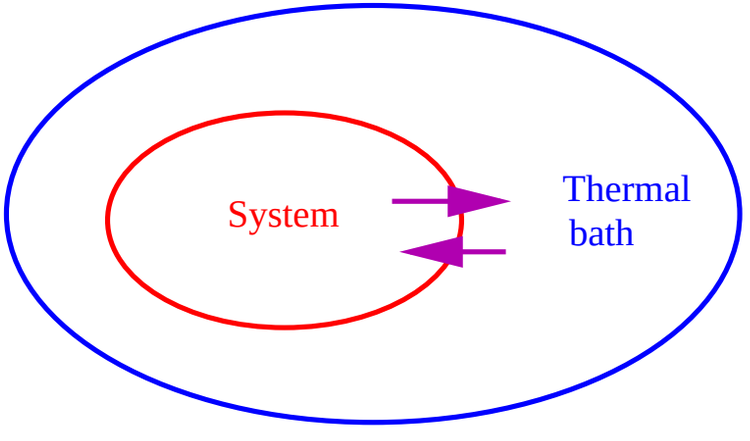


Molecular wires



Reduced density matrix formalism

- Goal: Description of ultra-fast (fs) processes in the condensed phase
- full quantum dynamics including dephasing, energy dissipation but also coherences, not only transfer rates, temperature dependence
- splitting in relevant system and thermal bath



- σ - density matrix of the full system
  (relevant system + bath)

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

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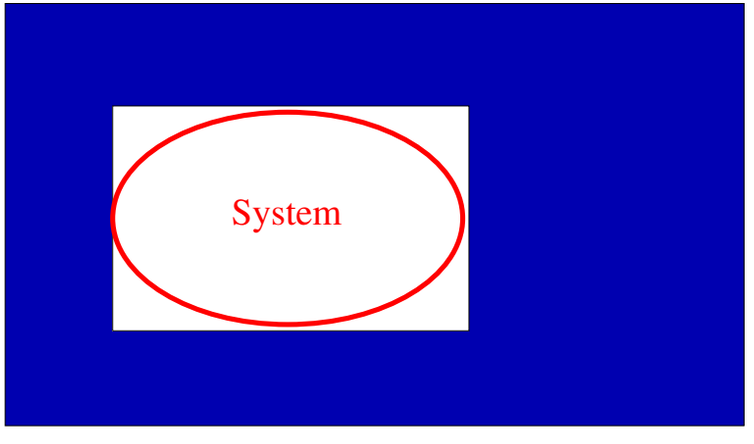

- reduced density-matrix:
  $\rho = tr_B(\sigma)$ - density matrix of the relevant system

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

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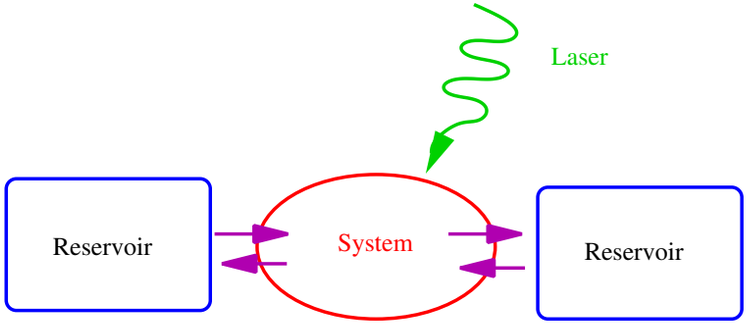

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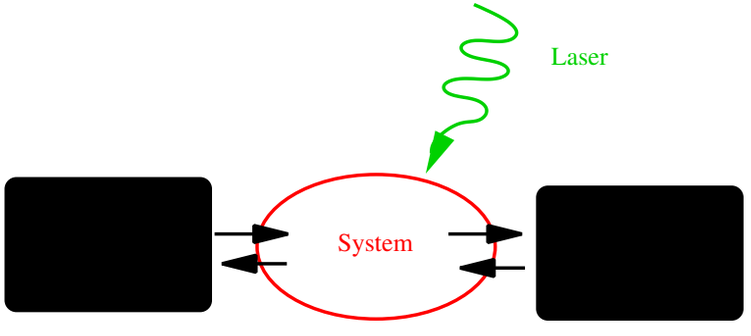

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Perturbative treatment

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

- 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}
  (2nd order or higher)
- in Redfield theory: Markov approximation (neglect of memory effects): bath correlation times $\tau_B << $ typical system times τ_S

Decomposition of the spectral density

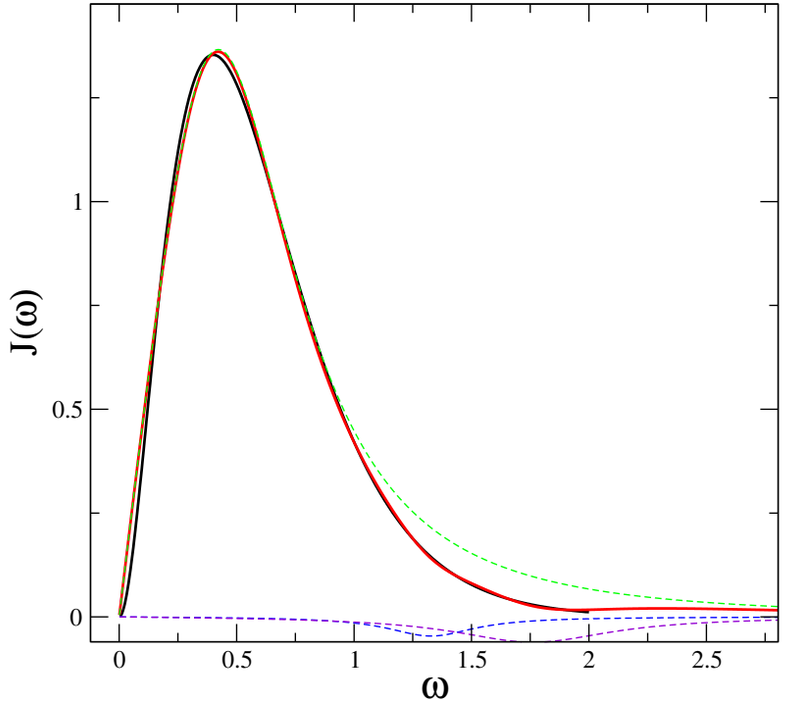
- information on the frequencies of the bath modes and their coupling to the system

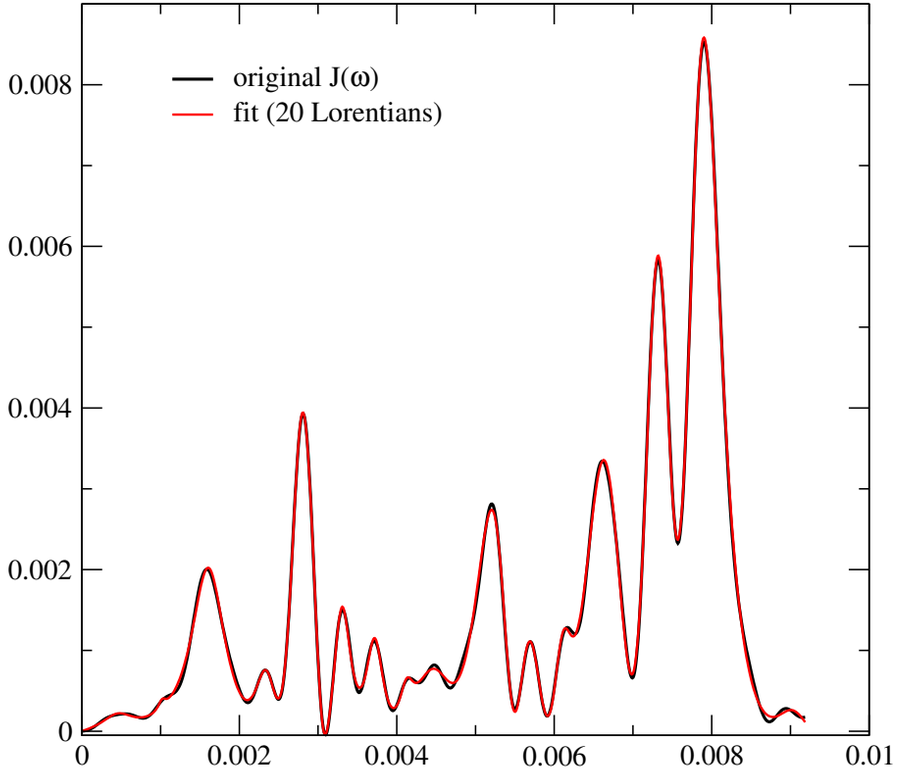
$$J(\omega) = \frac{\pi}{2} \sum_i \frac{c_i^2}{m_i \omega_i} \delta(\omega - \omega_i)$$

- property $J(-\omega) = -J(\omega)$
- numerical decomposition in Lorentzians (Meier and Tannor)

$$\begin{aligned} J(\omega) &= \sum_{k=1}^{n} \frac{p_k}{4\Omega_k} \left\{ \frac{1}{(\omega - \Omega_k)^2 + \Gamma_k^2} - \frac{1}{(\omega + \Omega_k)^2 + \Gamma_k^2} \right\} \\ &= \sum_{k=1}^{n} p_k \frac{\omega}{[(\omega + \Omega_k)^2 + \Gamma_k^2][(\omega - \Omega_k)^2 + \Gamma_k^2]} \end{aligned}$$

Decomposition of the spectral density





Environment correlation function

- using the theorem of residues

$$C(t) = a(t) - ib(t) = \int_{-\infty}^{\infty} \frac{d\omega}{\pi} J(\omega) \frac{e^{i\omega t}}{e^{\beta\omega} - 1} = \frac{2i}{\beta} \sum_{k=1}^{n'} J(i\nu_k) e^{-\nu_k t}$$

$$+ \sum_{k=1}^{n} \frac{p_k}{4\Omega_k \Gamma_k} \left\{ e^{i\Omega_k^+ t} n_B(\Omega_k^+) + e^{-i\Omega_k^- t} (n_B(\Omega_k^-) + 1) \right\}$$

- with $\Omega_k^+ = \Omega_k + i\Gamma_k$, $\Omega_k^- = \Omega_k - i\Gamma_k$, the Bose-Einstein distribution $n_B(\omega)$ and the Matsubara frequencies $\nu_k = 2\pi k/\beta$
- in principle, the sum over the Matsubara terms is an infinite one but in practice the sum can be truncated (temperature-dependent)
- time dependence in $C(t)$ is now fully exponential which enables further analytic treatment

Environment correlation function: Drude form

- Drude form

$$J(\omega) = \eta\,\omega/(1+(\omega/\omega_d)^2)$$

- poles at $\omega = \pm i\omega_d$
- using theorem of residues yields

$$a(t) = \frac{\eta}{2}\omega_d^2 \cot(\beta\omega_d/2)e^{-\omega_d t} - \frac{2\eta}{\beta}\sum_{k=1}^{n'} \frac{\nu_k e^{-\nu_k t}}{1-(\nu_k/\omega_d)^2}$$

and

$$b(t) = \frac{\eta}{2}\omega_d^2 e^{-\omega_d t}\ .$$

- singularities in $a(t)$ or $b(t)$ such as the singularities at $\nu_k = \omega_d$
- abbreviations
  - $a(t) = \sum_{k=1}^{n_r} \alpha_k^r e^{\gamma_k^r t}$ with $n_r = n' + 1$
  - $b(t) = \alpha_1^i e^{\gamma_1^i t}$ with $n_i = 1$

Nakajima-Zwanzig and Shibata identities

- Liouville equation $i\frac{d}{dt}\sigma(t) = \mathscr{L}\sigma(t)$ with $\mathscr{L}\ldots = \frac{1}{\hbar}[H,\ldots]$
- for simplicity here H time-independent
- use projector $\mathscr{P}$ onto relevant part of the whole system, $\mathscr{P}+\mathscr{Q}=1$, $\mathscr{P}=\mathscr{P}^2$, $\rho(t)=\mathscr{P}\sigma(t)$
- both identities exact, no approximation so far
- Nakajima-Zwanzig identity (time-nonlocal, TNL)

$$\begin{aligned}\frac{d}{dt}\mathscr{P}\sigma(t) &= -i\mathscr{P}\mathscr{L}\mathscr{P}\sigma(t) - \int_{t_0}^{t}\mathscr{P}\mathscr{L}\mathrm{e}^{-i(1-\mathscr{P})\mathscr{L}(t-\tau)}(1-\mathscr{P})\mathscr{L}\mathscr{P}\sigma(\tau)\,d\tau \\ &\quad -i\mathscr{P}\mathscr{L}\mathrm{e}^{-i(1-\mathscr{P})\mathscr{L}(t-t_0)}(1-\mathscr{P})\sigma(t_0)\end{aligned}$$

- Hashitsume-Shibata-Takahashi identity (time-local, TL)

$$\begin{aligned}\frac{d}{dt}\mathscr{P}\sigma(t) &= -i\mathscr{P}\mathscr{L}[1+i\int_0^t \mathrm{e}^{-i(1-\mathscr{P})\mathscr{L}\tau}(1-\mathscr{P})\mathscr{L}\mathscr{P}\mathrm{e}^{i\mathscr{L}\tau}\,d\tau]^{-1} \\ &\quad \cdot[\mathscr{P}\sigma(t)+\mathrm{e}^{-i(1-\mathscr{P})\mathscr{L}(t-t_0)}(1-\mathscr{P})\sigma(t_0)]\end{aligned}$$

Time-local approach

- factorized system-bath coupling $H_{S-B} = \sum_m K_m \Phi_m$
  - K_m system part, Φ_m bath part

$$\frac{d}{dt}\rho(t) \approx -\frac{i}{\hbar}[H_S, \rho(t)] - \sum_{m,n} \mathrm{Tr}_B \left([K_m \Phi_m, \int_0^t \mathrm{e}^{-i(\mathscr{L}_S + \mathscr{L}_B)\tau} [K_n \Phi_n, (\rho^B \otimes \mathrm{e}^{i\mathscr{L}_S \tau} \rho(t))]] d\tau \right)$$

- bath correlation functions (sum of exponentials)

$$C_{mn}(\tau) = \mathrm{Tr}_B \left(\mathrm{e}^{+iH_B\tau} \Phi_m \mathrm{e}^{-iH_B\tau} \Phi_n \right)$$

$$\begin{aligned} \frac{d}{dt}\rho(t) \approx -\frac{i}{\hbar}[H_S, \rho(t)] \quad - \quad & \sum_{m,n} \int_0^t d\tau \left\{ [K_m, \mathrm{e}^{-iH_S\tau} K_n \mathrm{e}^{iH_S\tau} \rho(t)] C_{mn}(\tau) \right. \\ & \left. + [\rho(t) \mathrm{e}^{-iH_S\tau} K_n \mathrm{e}^{iH_S\tau}, K_m] C^*_{mn}(\tau) \right\} \end{aligned}$$

- for simplicity: $H_{S-B} = K \sum_m \Phi_m$
- define operator

$$\Lambda(t) = \sum_n \int_0^t d\tau C_n(\tau) \mathrm{e}^{-iH_S\tau} K_n \mathrm{e}^{iH_S\tau}$$

Time-local approach: time-independent Hamiltonian

- define the non-Hermitian effective Hamiltonian

$$H_{\rm eff} = H_{\rm s} + H_{\rm ren} - iK\Lambda(t)$$

- the TL-QME is given by

$$\frac{\partial \rho(t)}{\partial t} = -i\left(H_{\rm eff}\rho(t) - \rho(t){H_{\rm eff}}^{\dagger}\right) + \left(K\rho(t)\Lambda^{\dagger}(t) + \Lambda(t)\rho(t)K\right) \ .$$

- in energy representation

$$\langle\mu|\Lambda(t)|\nu\rangle = \langle\mu|K|\nu\rangle \int_0^t dt' C(t') e^{-i\omega_{\mu\nu}t'} = \langle\mu|K|\nu\rangle \Theta^{+}(t,\omega_{\mu\nu})$$

with analytic expression for $\Theta^{+}(t,\omega_{\mu\nu})$ since $C(t)$ is sum of exponentials

Markov approximation and Redfield theory

- simple Markov limit: $\Theta^{+}(t \to \infty, \omega_{\mu\nu})$
- damping matrix $\Gamma_{\nu\mu,\kappa\lambda}$ for Redfield theory

$$\Gamma_{\nu\mu,\kappa\lambda} = \mathrm{Re}\langle\nu|K|\mu\rangle\langle\kappa|\Lambda(t=\infty)|\lambda\rangle \ .$$

- imaginary part (Lamb shift) is neglected
- at the same time (!) renormalization term is neglected
- neglect of only Lamb shift or only renormalization can cause severe problems
- in Redfield theory influence of time-dependent part of Hamiltonian (laser fields) is neglected (!)

Time-local approach: General formalism

- derived from a second-order cumulant expansion of the time-ordered exponential function

$$\frac{d\rho(t)}{dt} = -i\mathscr{L}_s^{\rm eff}\rho(t) + \int_0^t dt' \mathscr{K}(t')\rho(t)$$

using $C(t) = a(t) - ib(t)$ with

$$\mathscr{K}(t') = \mathscr{L}_- \mathscr{U}_s(t,t')[a(t-t')\mathscr{L}_- - b(t-t')\mathscr{L}_+]\mathscr{U}_s^\dagger(t,t') \ .$$

$$\mathscr{U}_s(t,t_0) = \mathscr{T}_+\left[e^{-i\int_{t_0}^t dt''\mathscr{L}_s(t'')}\right] \ , \ \mathscr{L}_- = -i[K,\cdot] \ , \ \mathscr{L}_+ = [K,\cdot]_+ \ ,$$

- this equation can be rewritten as

$$\frac{d\rho(t)}{dt} = -i\mathscr{L}_s^{\rm eff}\rho(t) + i\mathscr{L}_-\left([\rho(t),\Lambda^r(t)] + i[\rho(t),\Lambda^i(t)]_+\right) \ .$$

with

$$\Lambda^r(t) = \int_0^t dt' a(t-t')\mathscr{U}_s(t,t')K, \ \ \Lambda^i(t) = \int_0^t dt' b(t-t')\mathscr{U}_s(t,t')K$$

Time-local approach: time-dependent Hamiltonian

- define auxiliary operators

$$\Lambda_k^r(t) = \int_0^t dt' e^{\gamma_k^r t'} \mathscr{U}_s(t,t') K, \qquad \Lambda_k^i(t) = \int_0^t dt' e^{\gamma_k^r t'} \mathscr{U}_s(t,t') K \ .$$

- with these expressions the TL-QME can be written as

$$\frac{d\rho(t)}{dt} = -i\mathscr{L}_s^{\text{eff}}\rho(t) \quad + \quad \mathscr{L}_- \left(i \sum_{k=1}^{n_r} [\rho(t)\Lambda_k^r(t) - \Lambda_k^r(t)\rho(t)] \right.$$
$$\left. - \quad \sum_{k=1}^{n_i} [\rho(t)\Lambda_k^i(t) + \Lambda_k^i(t)\rho(t)] \right)$$

- auxiliary operators Λ_k^r and Λ_k^i can be determined via

$$\frac{d\Lambda_k^r}{dt} = (\gamma_k^r - i\mathscr{L}_s)\Lambda_k^r + K, \qquad \frac{d\Lambda_k^i}{dt} = (\gamma_k^i - i\mathscr{L}_s)\Lambda_k^r + K \ .$$

- no restriction concerning time-dependence in H_S

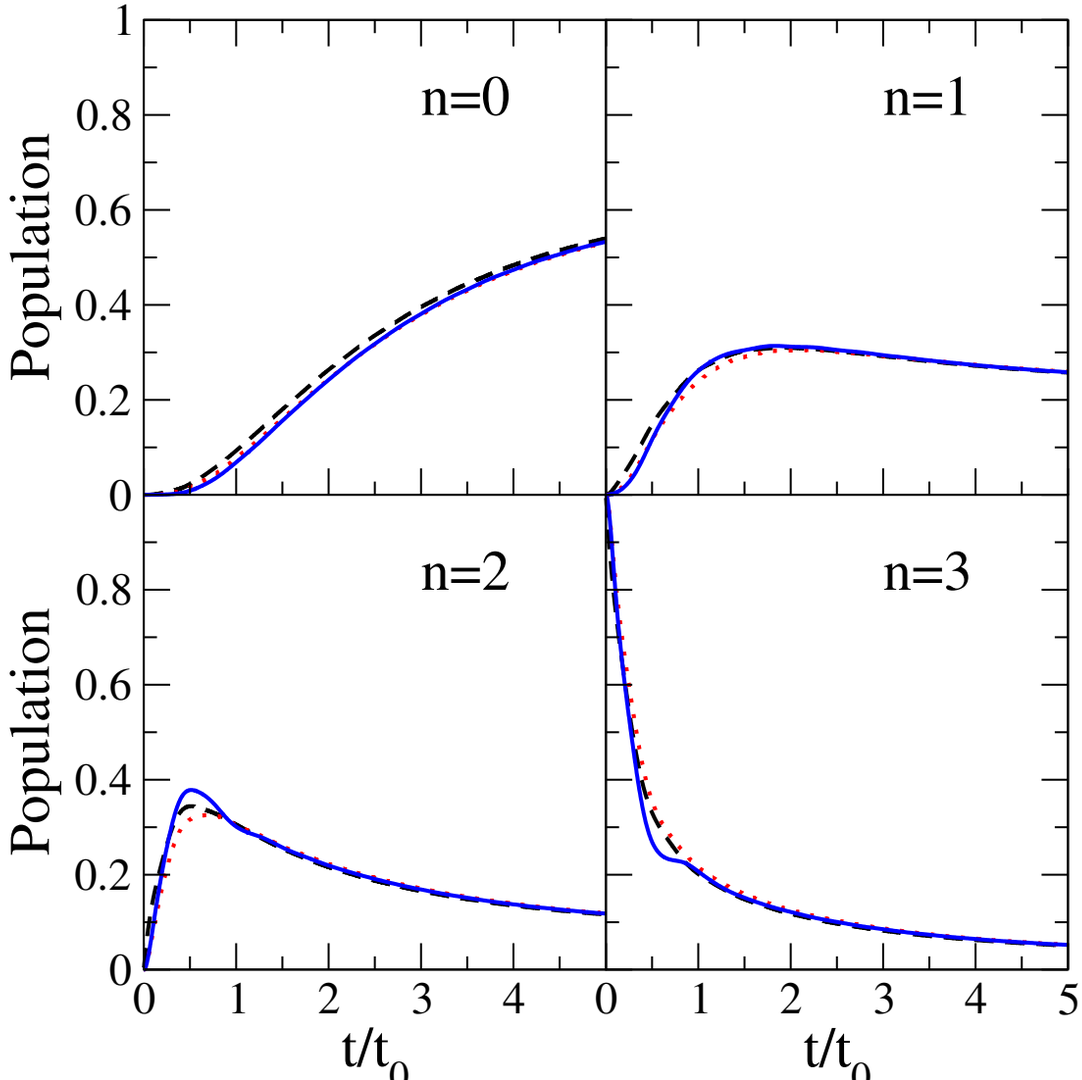
- time-nonlocal approach equivalent

Accuracy test:
Damped Harmonic Oscillator

Journal of Chemical Physics **121**, 2505 (2004).

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

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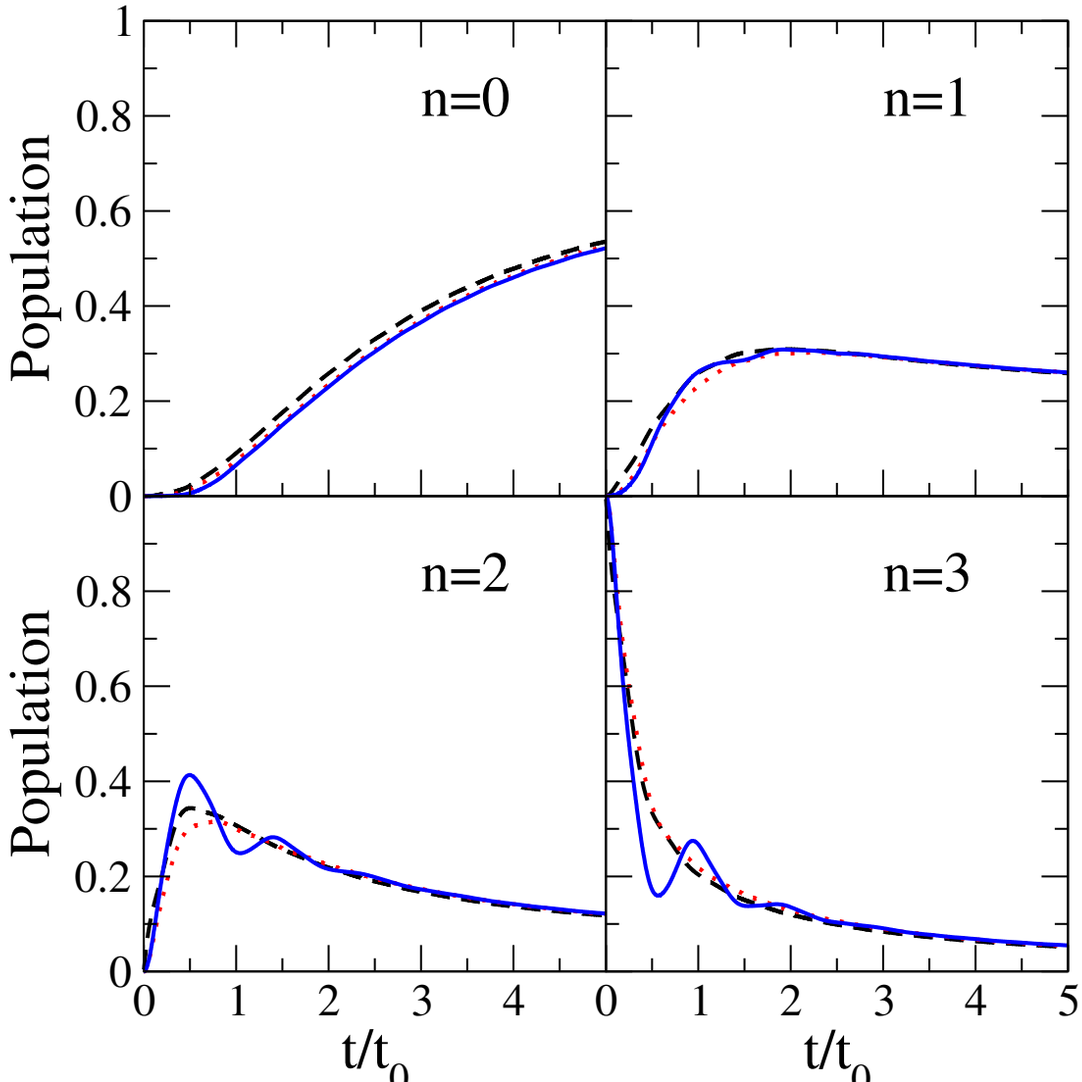

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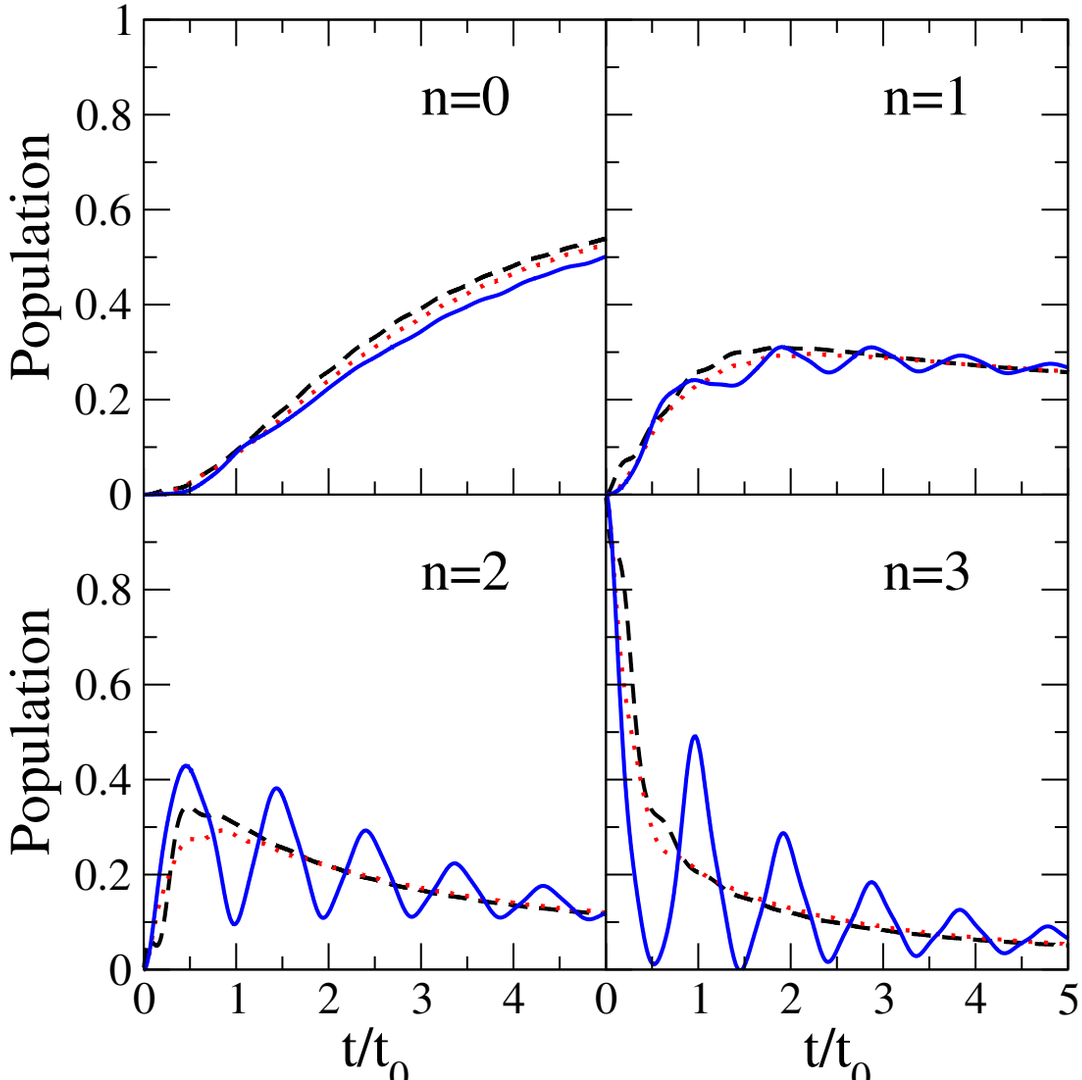
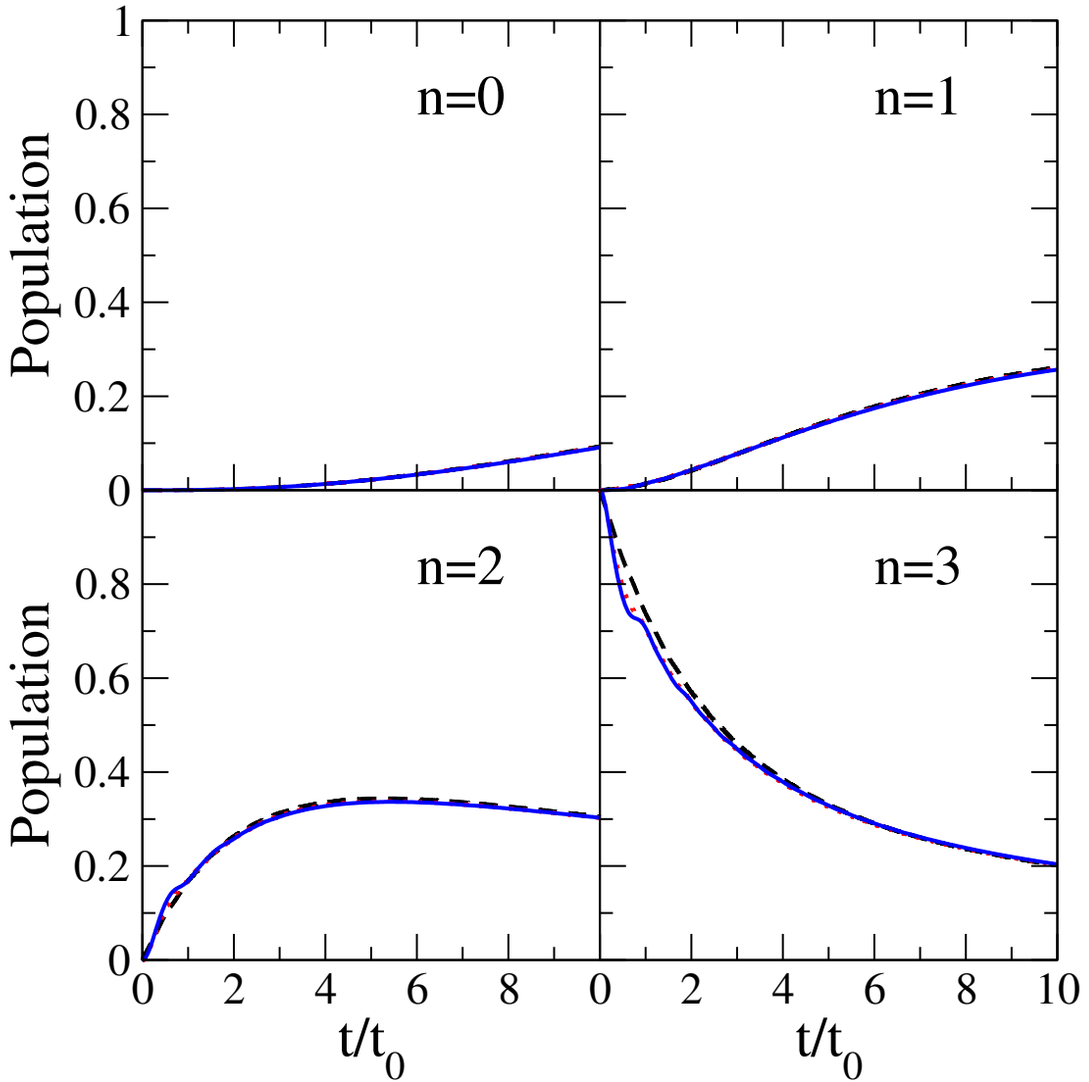


Population dynamics for harmonic oscillator

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



Results for harmonic oscillator: Variance of q

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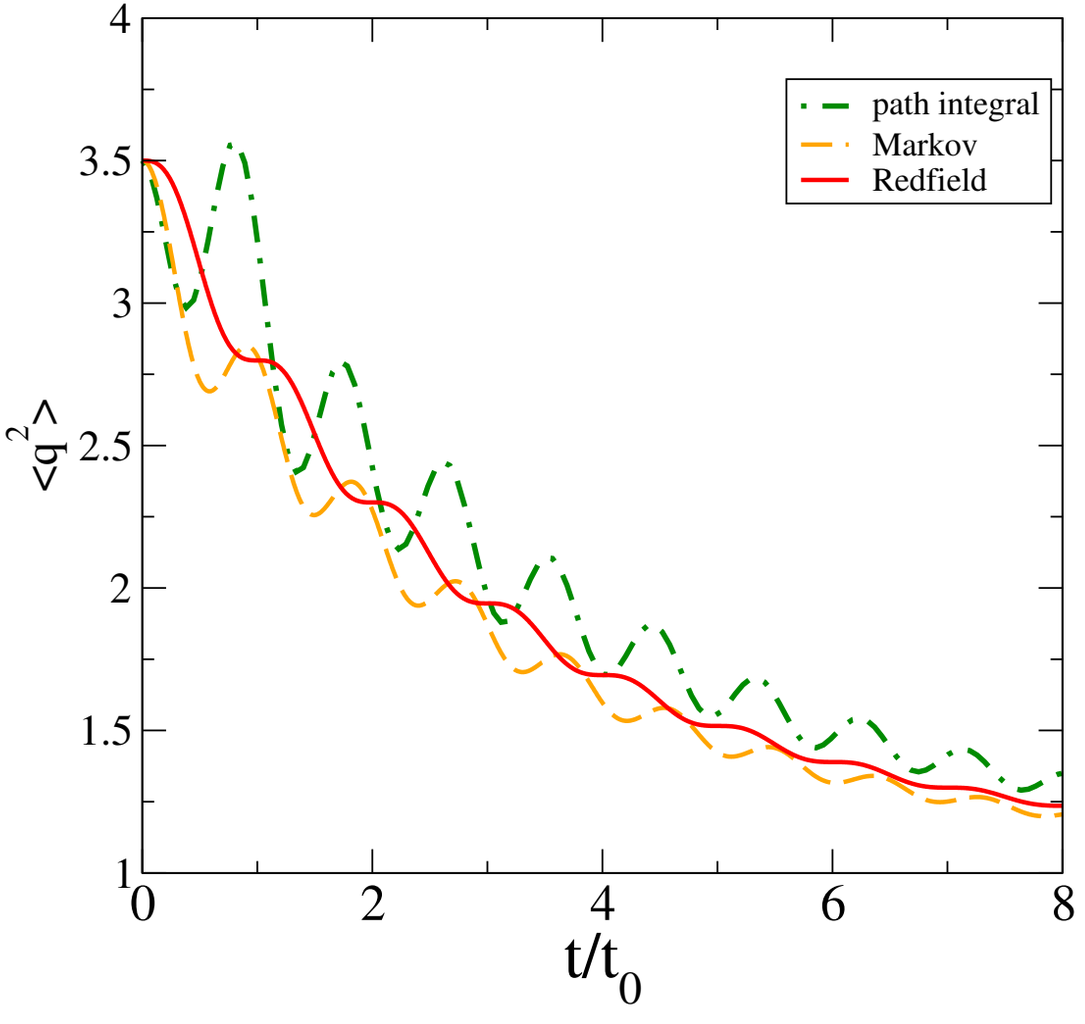

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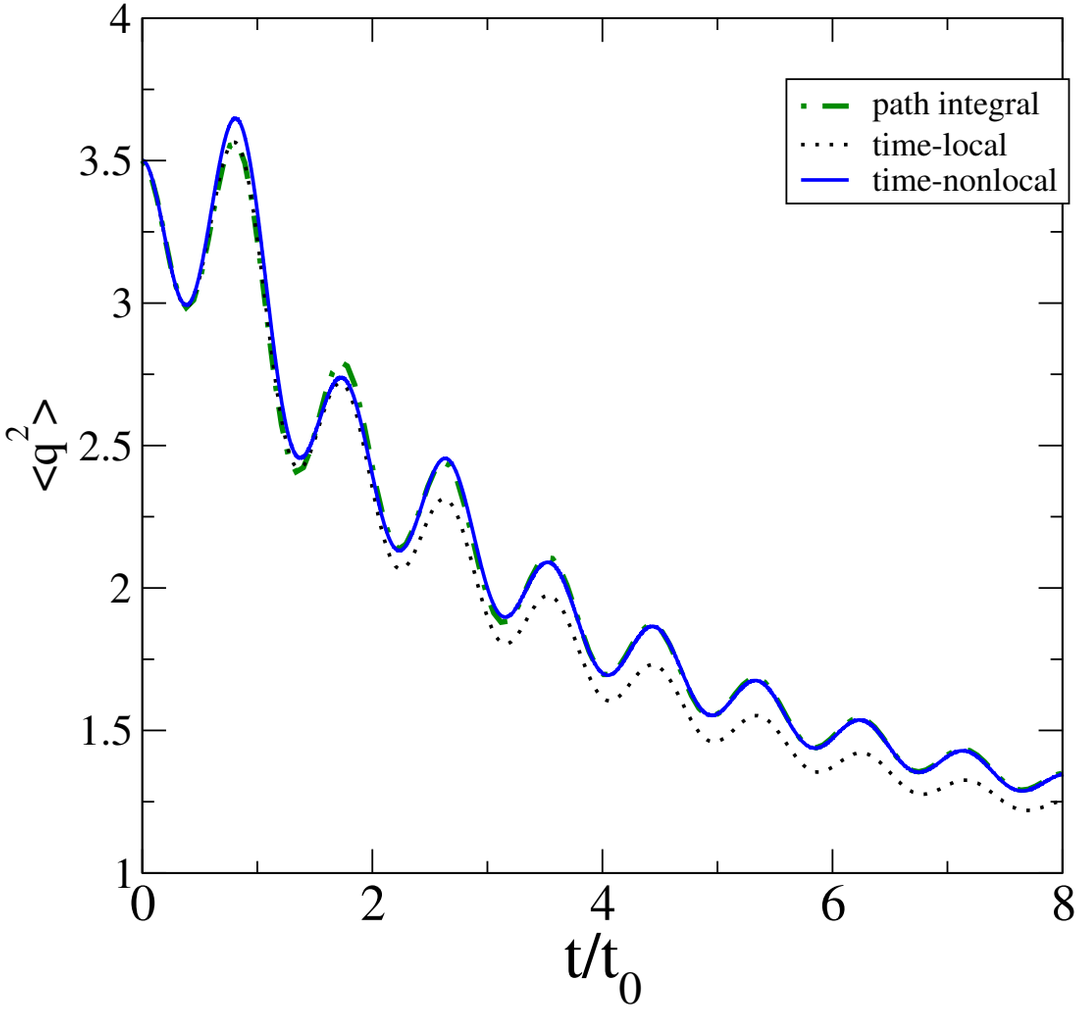
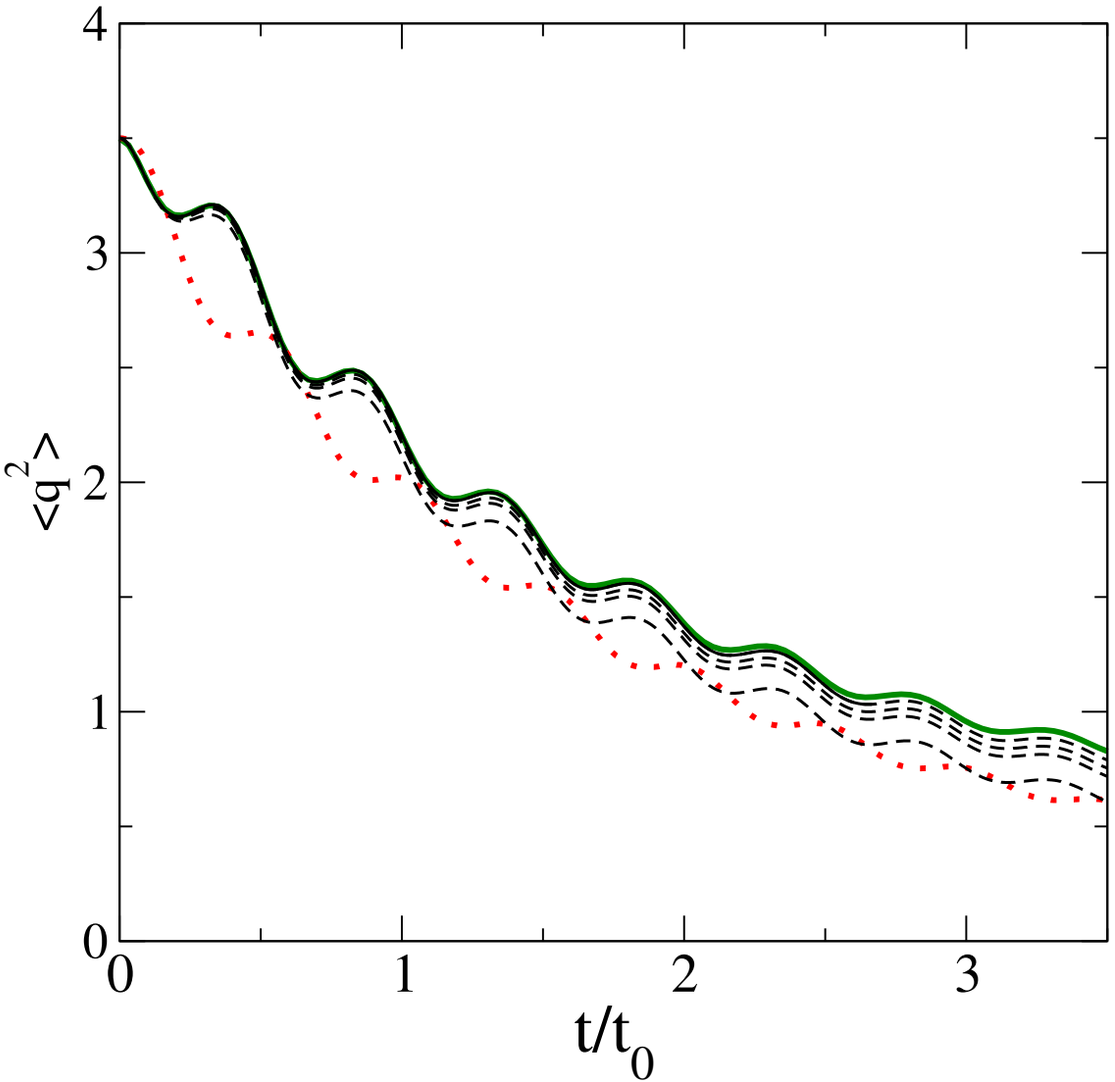


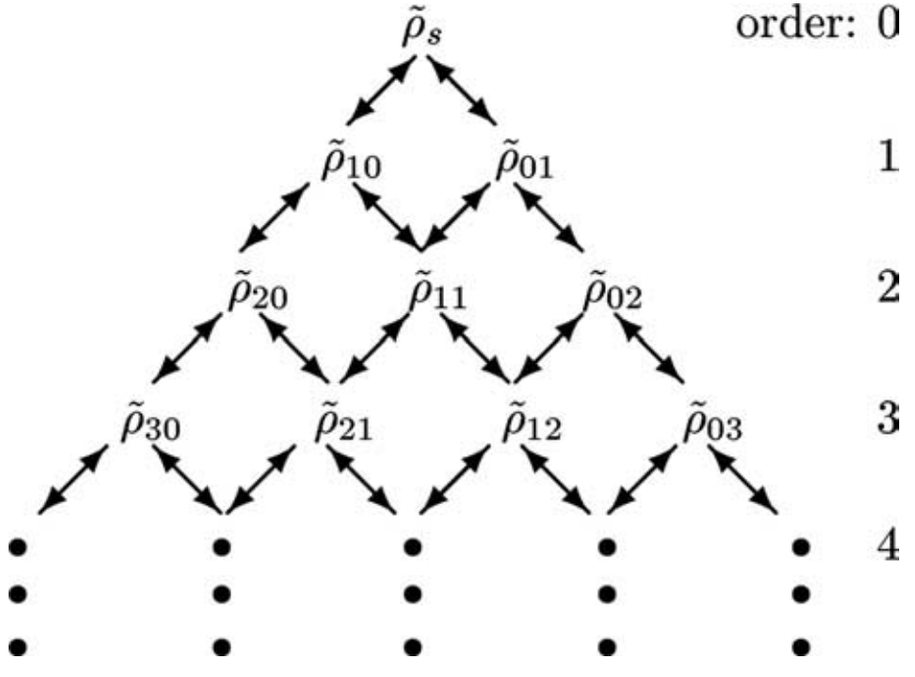
Results for harmonic oscillator: Low Temperature

- initially all population in the 3rd excited level
- low temperature: $\beta = 100/\omega_0$
- Drude form, cut-off: ω_D/ω_0=0.5, $\eta = 0.544$



Higher orders through hierarchical scheme

- above described non-Markovian schemes are lowest order of this scheme
- developed by groups of J. S. Shao (Chem. Phys. Lett. **395**, 216 (2004)) and J.-Y. Yan (J. Chem. Phys. **122**, 041103 (2004))
- for bath-correlation function $C(t) = a_1 e^{-\gamma_1 t}$



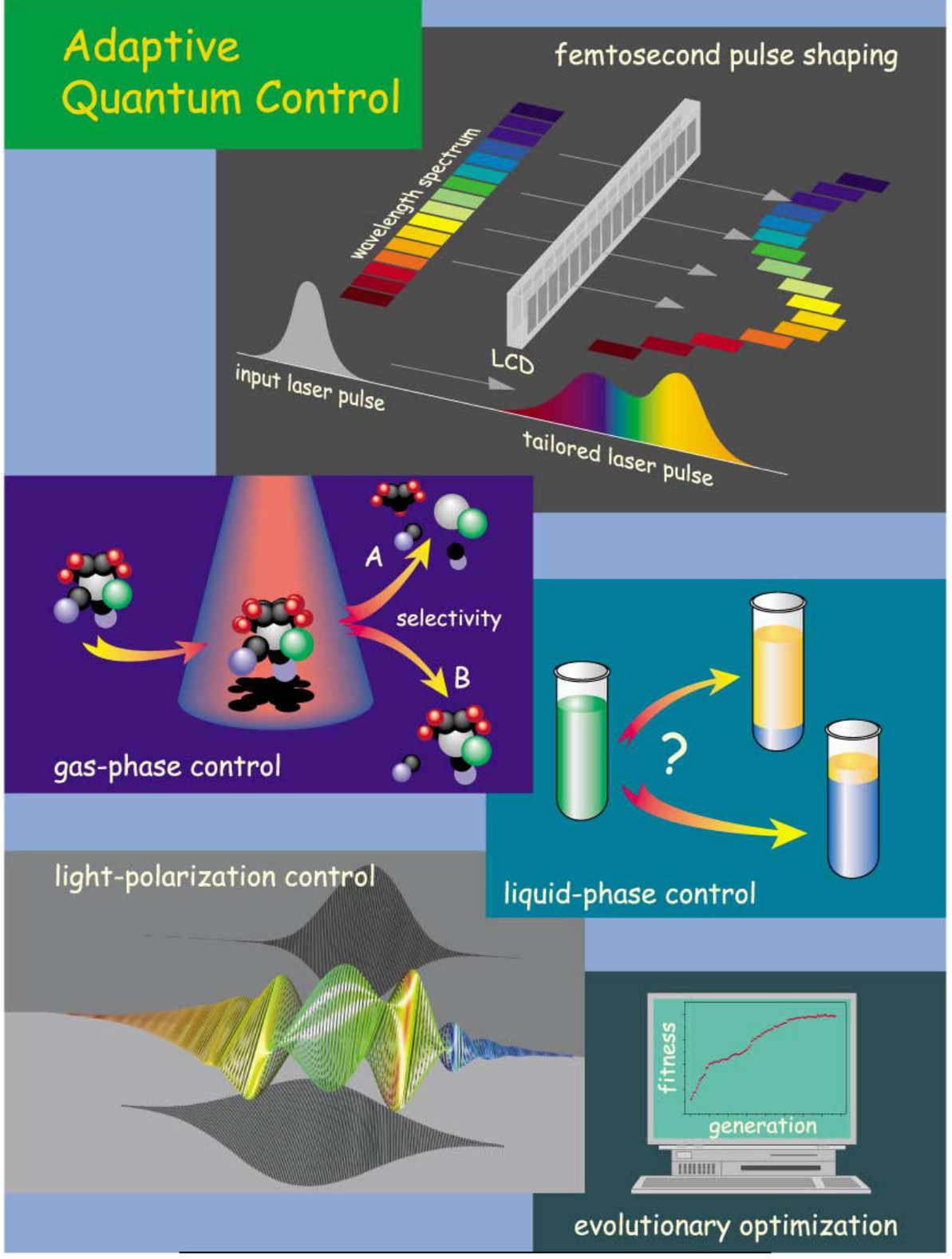
Coherent control of electron transfer

in collaboration with

Tomáš Mančal and Volkhard May

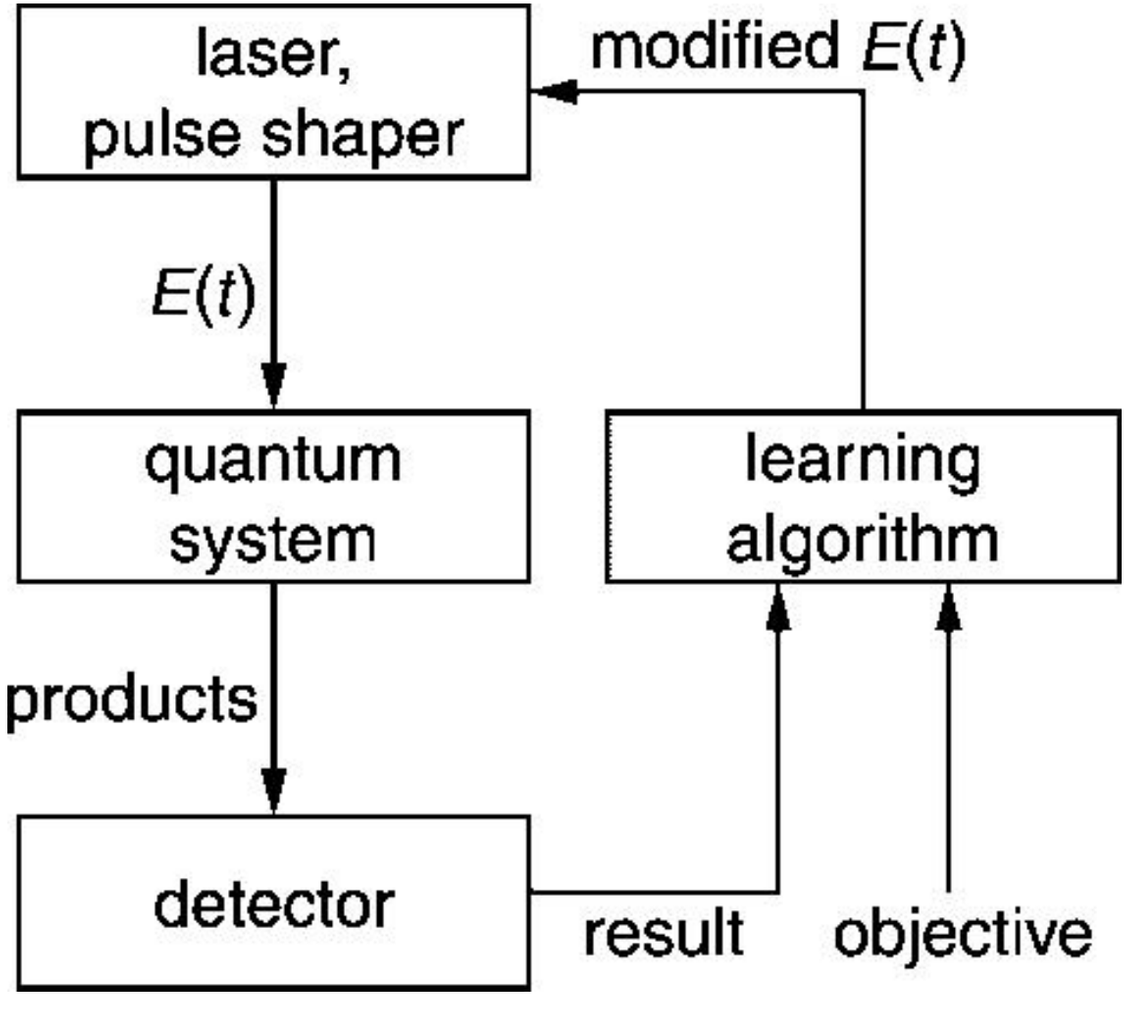
Humboldt–Universität zu Berlin

Journal of Chemical Physics **117**, 636–646 (2002).



T. Brixner and G. Gerber, ChemPhysChem **4**, 419 (2003). →

Adaptive coherent control



R.S. Judson and H. Rabitz **68**, 1500 (1992).

Coherent control in presence of dissipation

- optimal control theory of Rabitz et al.
- realization of an observable at a certain moment in time t_f

$$O(t_f) = \mathrm{tr_S}\{\hat{O}\hat{\rho}(t_f)\}$$

- the optimal pulse is defined as extremum of

$$J(t_f;\mathbf{E}) = O(t_f;\mathbf{E}) - \frac{1}{2}\int_{t_0}^{t_f} dt\ \lambda(t)\mathbf{E}^2(t)$$

- solution

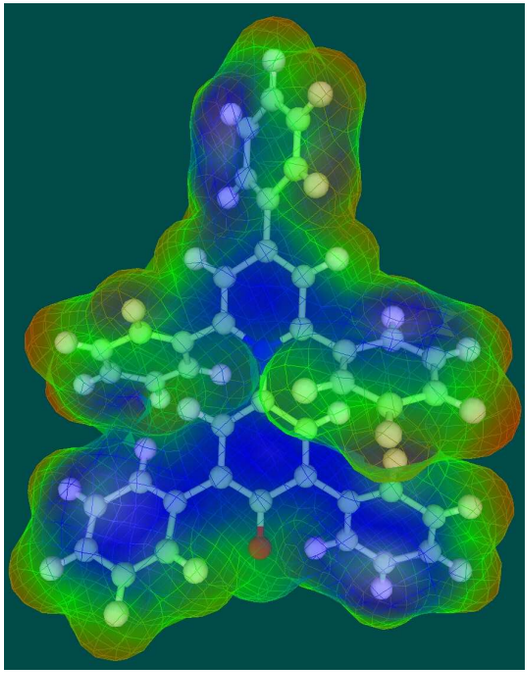
$$\mathbf{E}(t) = \frac{\mathbf{K}(t_f,t;\mathbf{E})}{\lambda(t)}$$

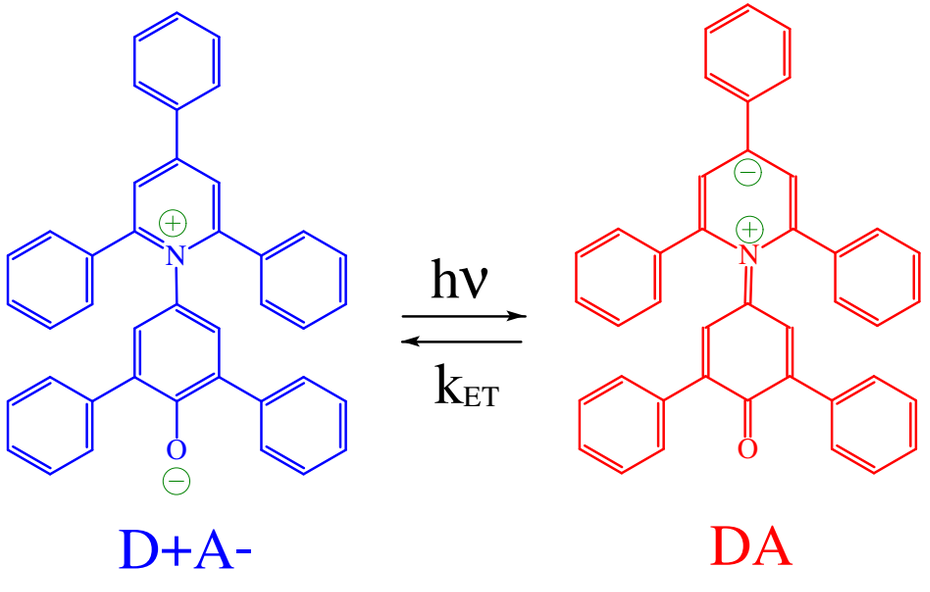
with

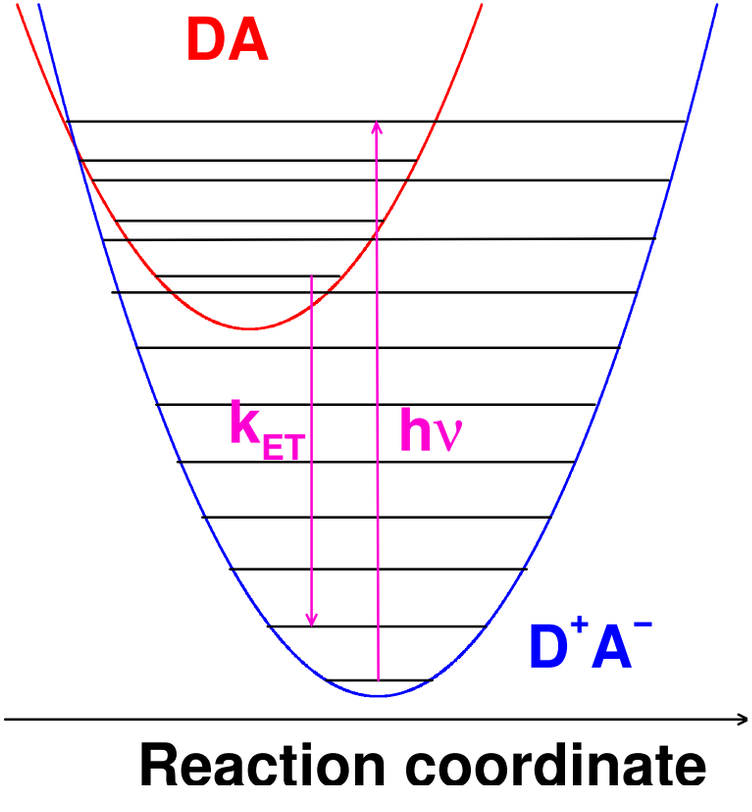
$$\mathbf{K}(t_f,t;\mathbf{E}) = \frac{i}{\hbar}\mathrm{tr_S}\{\hat{\eta}(t;\mathbf{E})\left[\hat{\mu},\hat{\rho}(t;\mathbf{E})\right]\}$$

Coherent control in betaine-30

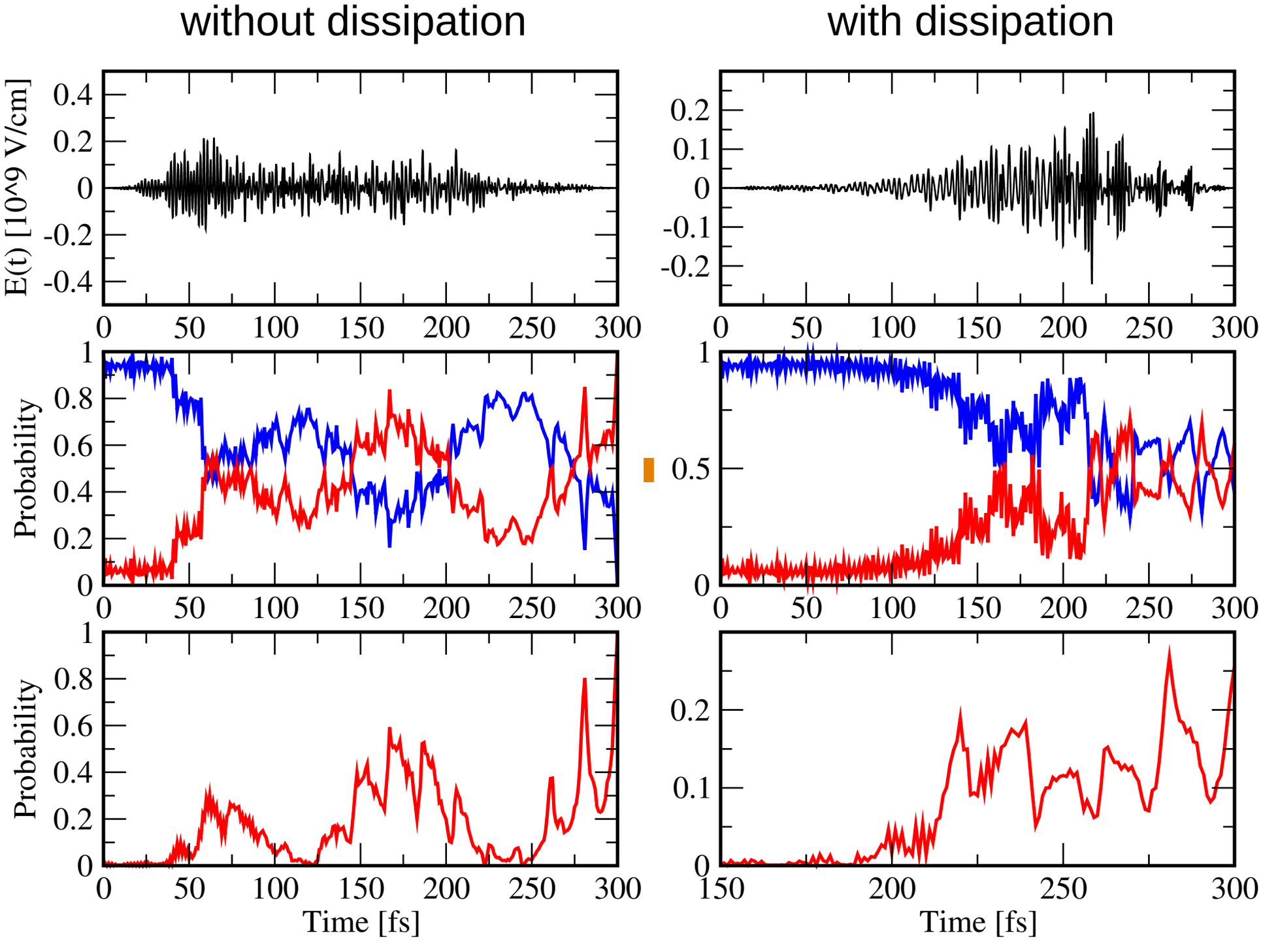
- goal: population of the 3rd vibrational state in the electronic excited state at time $t_f = 300$ fs







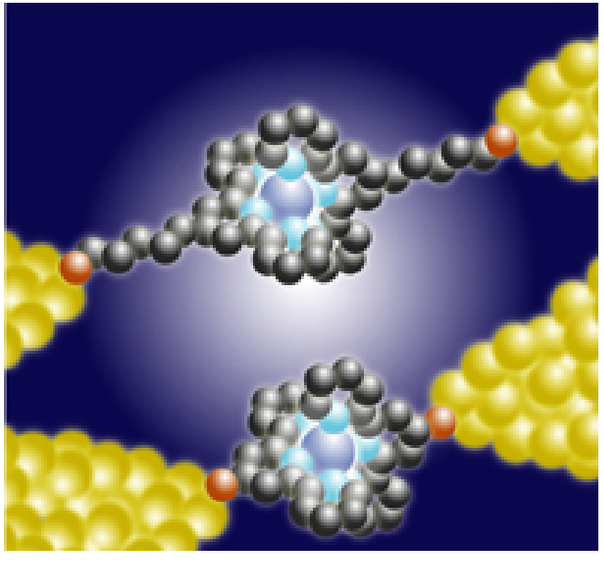
Laser pulse, electronic and vibronic populations

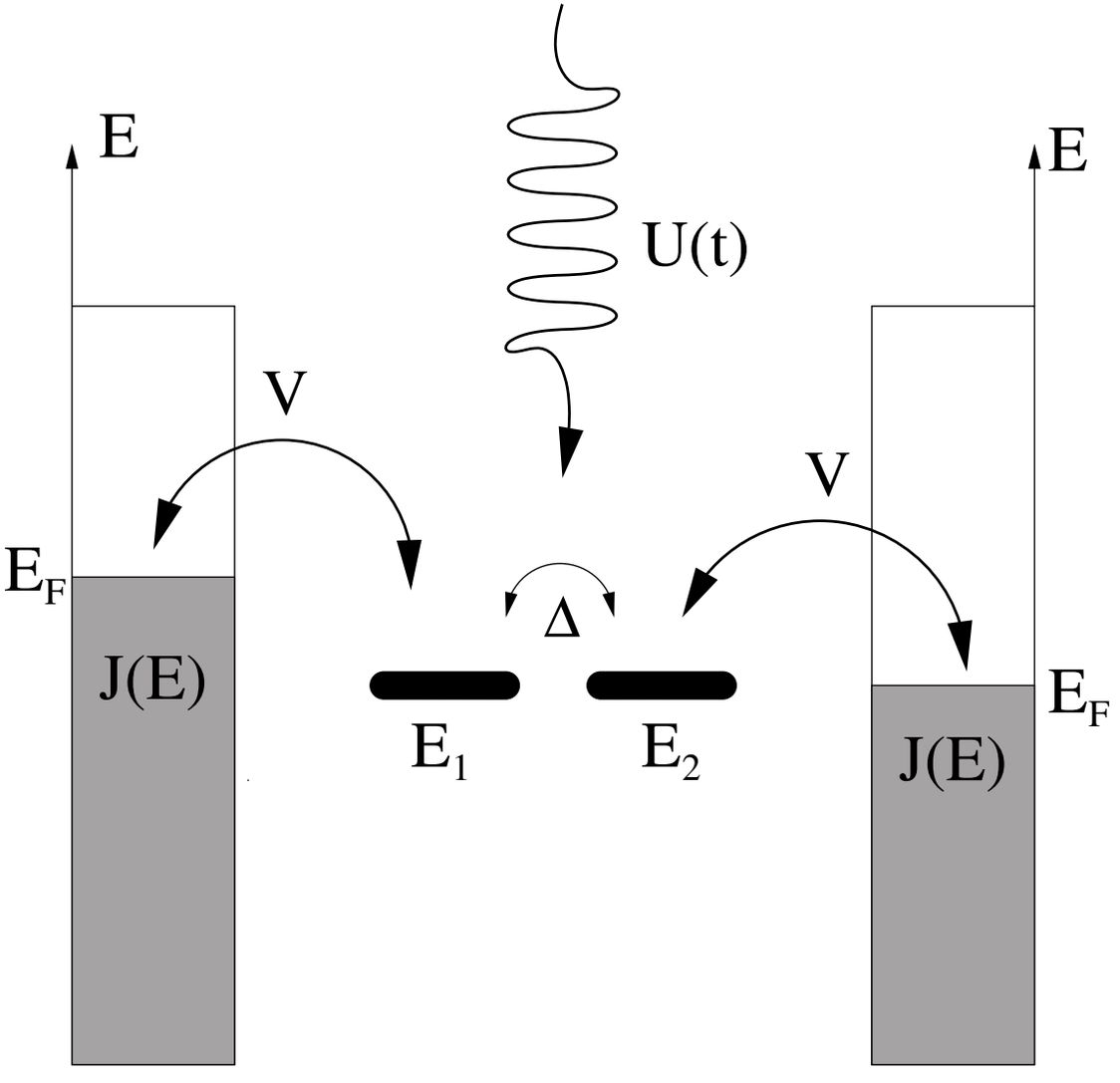


Molecular electronics: Influence of laser pulses on the electron transfer in molecular wires

Journal of Chemical Physics **124**, 044712 (2006).

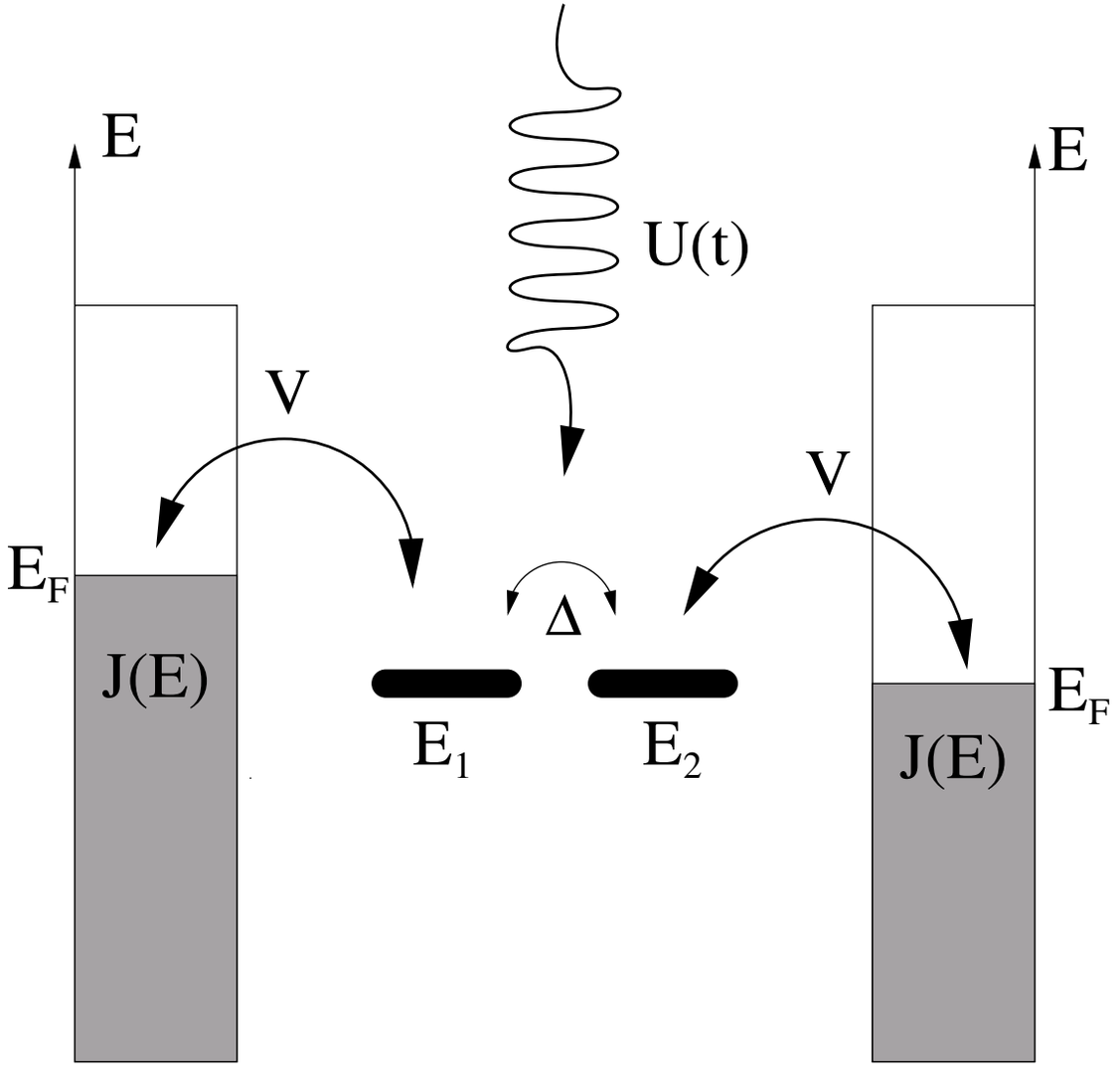
The model



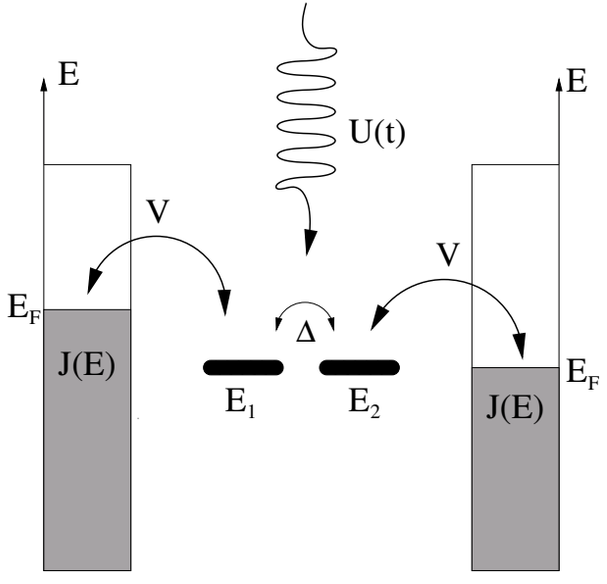


The model

$$
\begin{aligned}
H(t) &= H_S(t) + H_L + H_{SL} \\
H_S(t) &= \sum_{nn'} H_{nn'}(t) c_n^\dagger c_{n'} \qquad H_{nn'}(t) = -\Delta(\delta_{n+1,n'} + \delta_{n,n'+1}) + (E_n + U_n(t))\delta_{n,n'} \\
H_L &= \sum_q \omega_q c_q^\dagger c_q \\
H_{LS} &= \sum_q (V_q c_1^\dagger c_q + V_q^* c_q^\dagger c_1)
\end{aligned}
$$

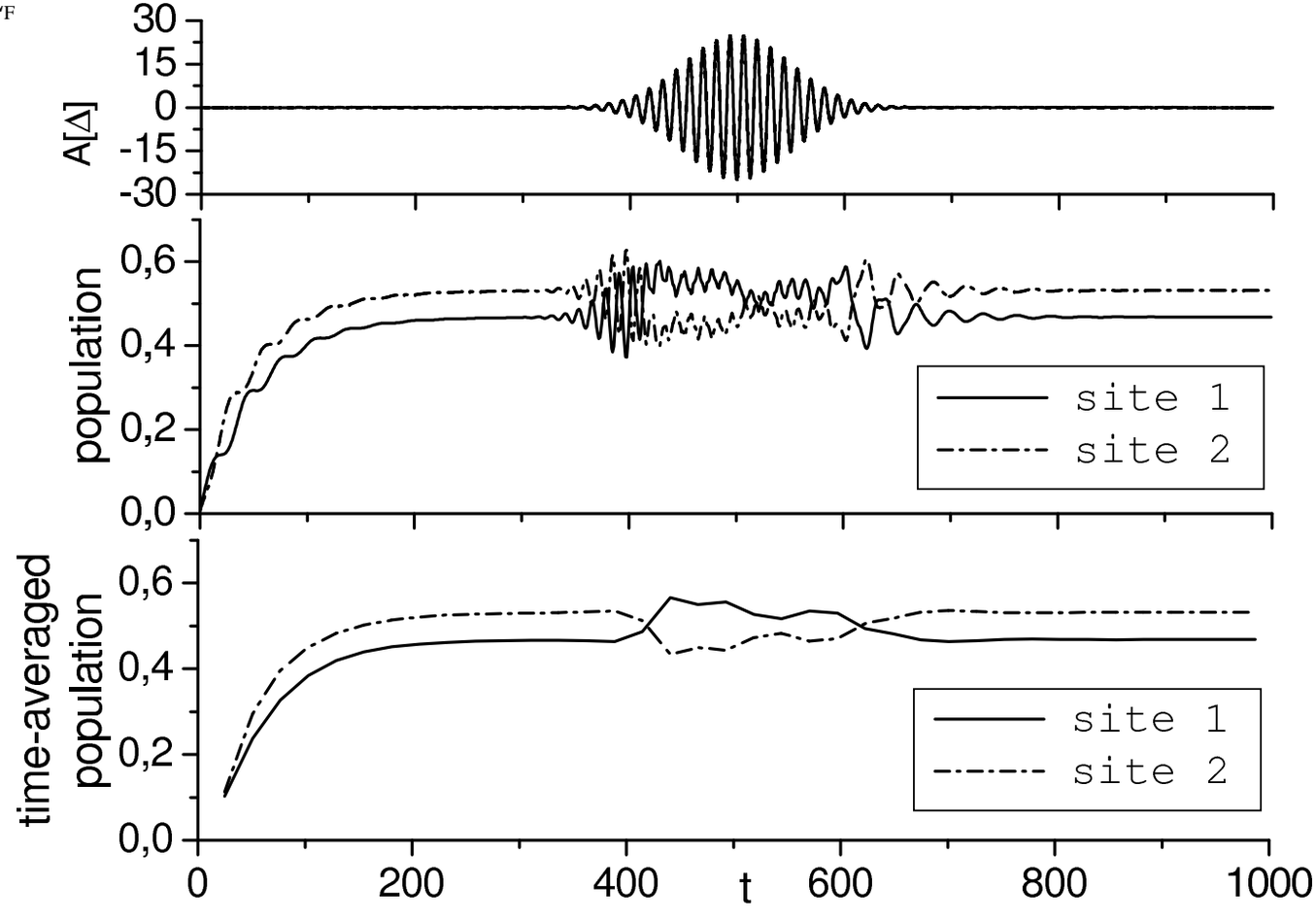


Population dynamics



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

$$E_1 = E_2 = E_{F,r} + 1\Delta = E_{F,l} - 1\Delta$$



Determination of the current

- using electron number operator $N_l = \sum_q c_q^\dagger c_q$

$$I_l(t) = e\frac{\mathrm{d}}{\mathrm{d}t}\mathrm{tr}\left\{N_l\sigma(t)\right\} = -ie\,\mathrm{tr}\{[N_l, H(t)]\sigma(t)\}$$

- defining auxiliary operators

$$\begin{aligned}
\Lambda_{12}(t) &= \int_{t_0}^{t} \mathrm{d}t'\, C_{12}(t-t')\, U_S(t,t')\, c_1\rho_S(t') = \sum_k^{m+m'} \Lambda_{12}^k(t) \\
\Lambda_{21}(t) &= \int_{t_0}^{t} \mathrm{d}t'\, C_{21}^*(t-t') U_S^\dagger(t,t')\, c_1^\dagger\rho_S(t') = \sum_k^{m+m'} \Lambda_{21}^k(t)
\end{aligned}$$

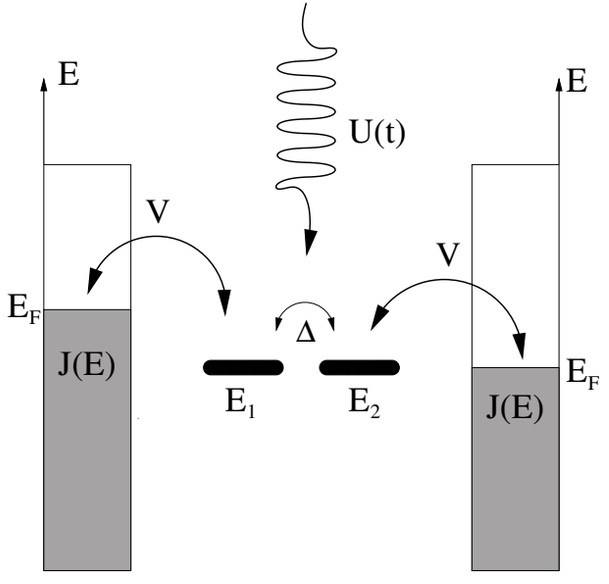
- equations of motion for auxiliary operators

$$\begin{aligned}
\dot{\Lambda}_{12}^k(t) &= \left(a_{12}^k\right) c_1\rho_S(t) - i[H_S(t), \Lambda_{12}^k(t)] + \left(\gamma_{12}^k\right)\Lambda_{12}^k(t) \\
\dot{\Lambda}_{21}^k(t) &= \left(a_{21}^k\right)^* c_1^\dagger\rho_S(t) - i[H_S(t), \widehat{\Lambda}_{21}^k(t)] + \left(\gamma_{21}^k\right)^*\Lambda_{21}^k(t)
\end{aligned}$$

- final current equation

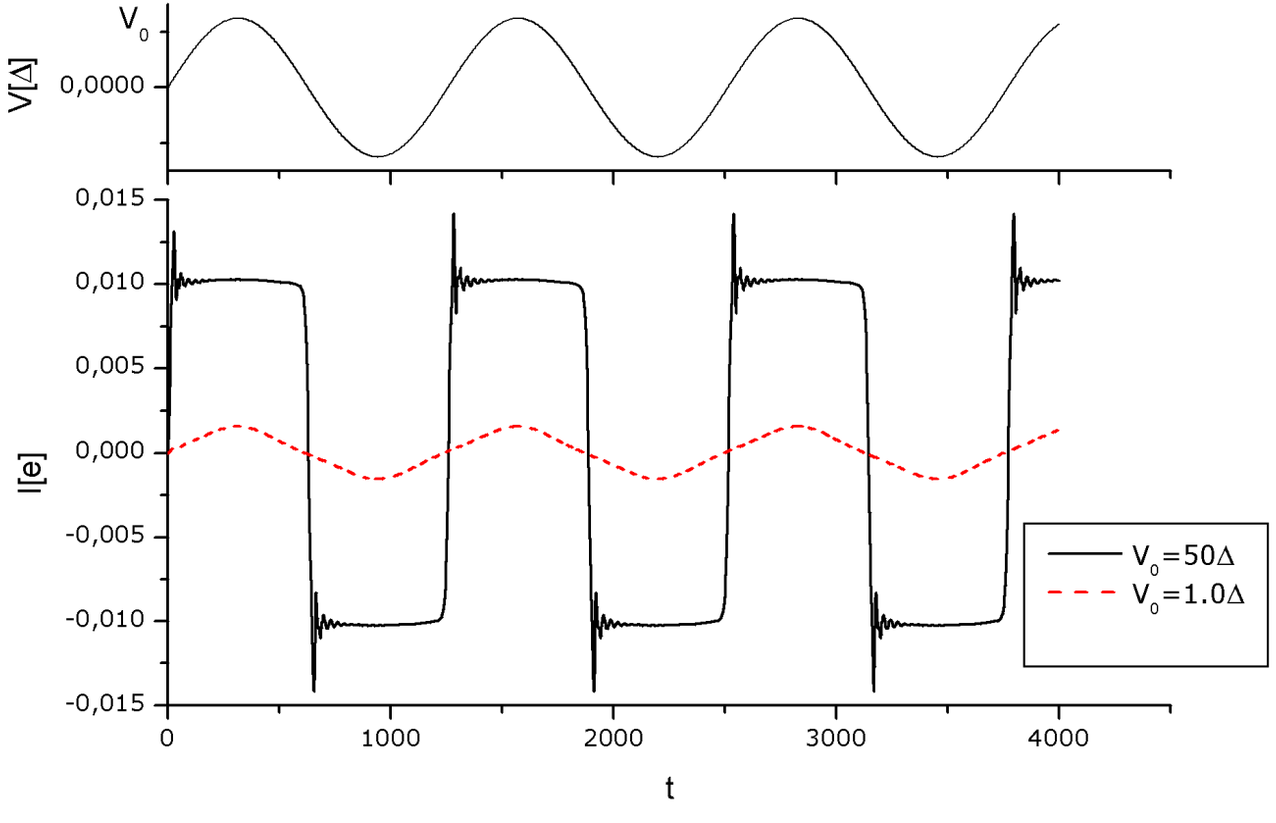
$$I_l(t) = 2e\,\mathrm{Re}\left(\mathrm{tr}_S\{c_1^\dagger\Lambda_{12}(t)\} - \mathrm{tr}_S\{c_1\Lambda_{21}(t)\}\right)$$

Periodic external potential

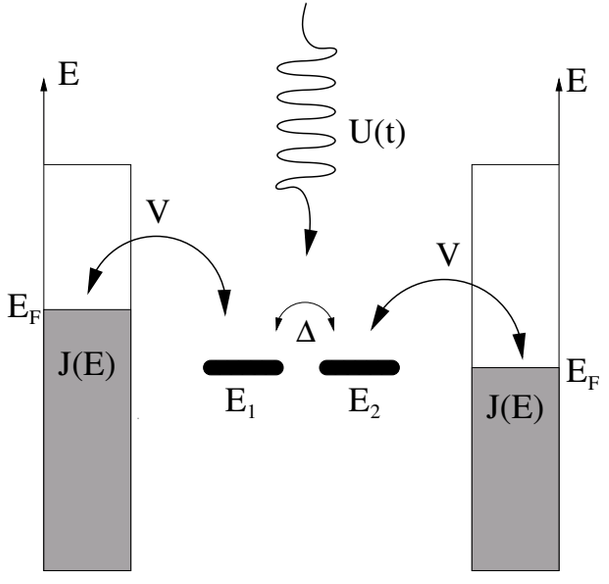


AC – Current

$$V(t) = E_{F,r} - E_{F,l} = V_0 \sin(\omega t)$$

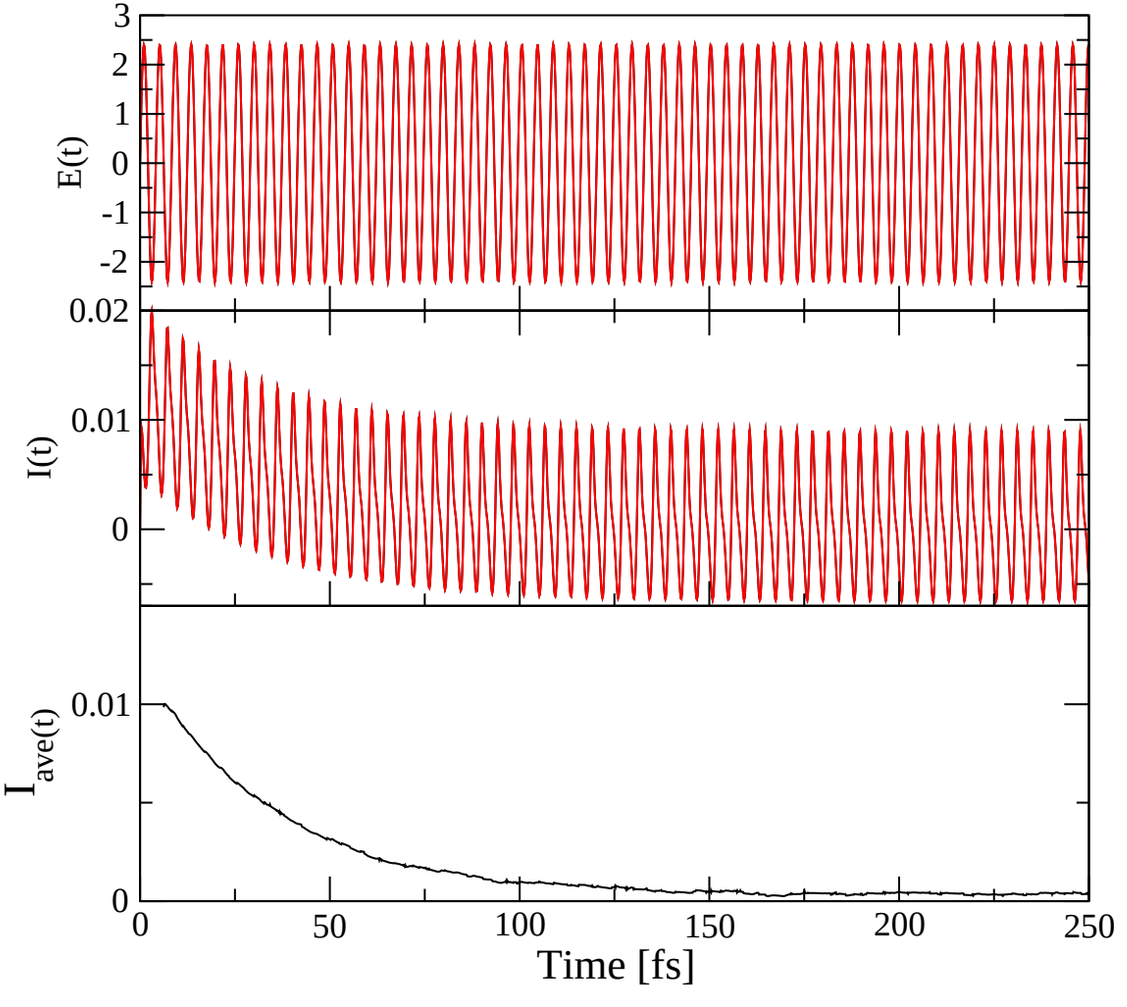


Coherent destruction of tunneling (CDT)

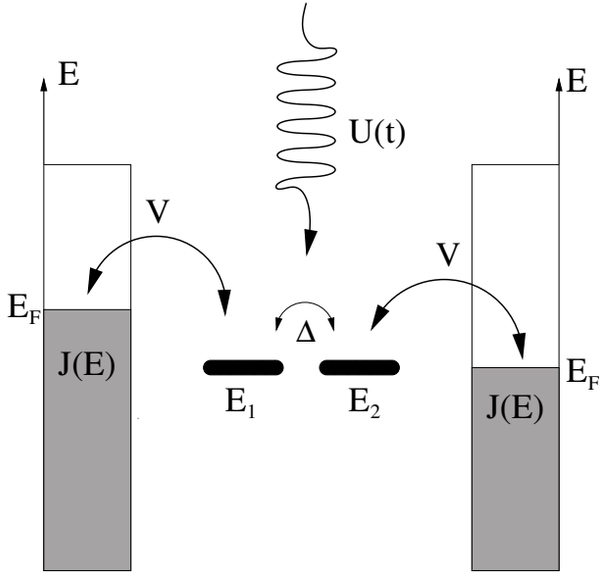


$$U_n(t) = A(t)\delta_{1n} - A(t)\delta_{2n}$$

$$A(t) = A_0 \sin(\omega t)$$

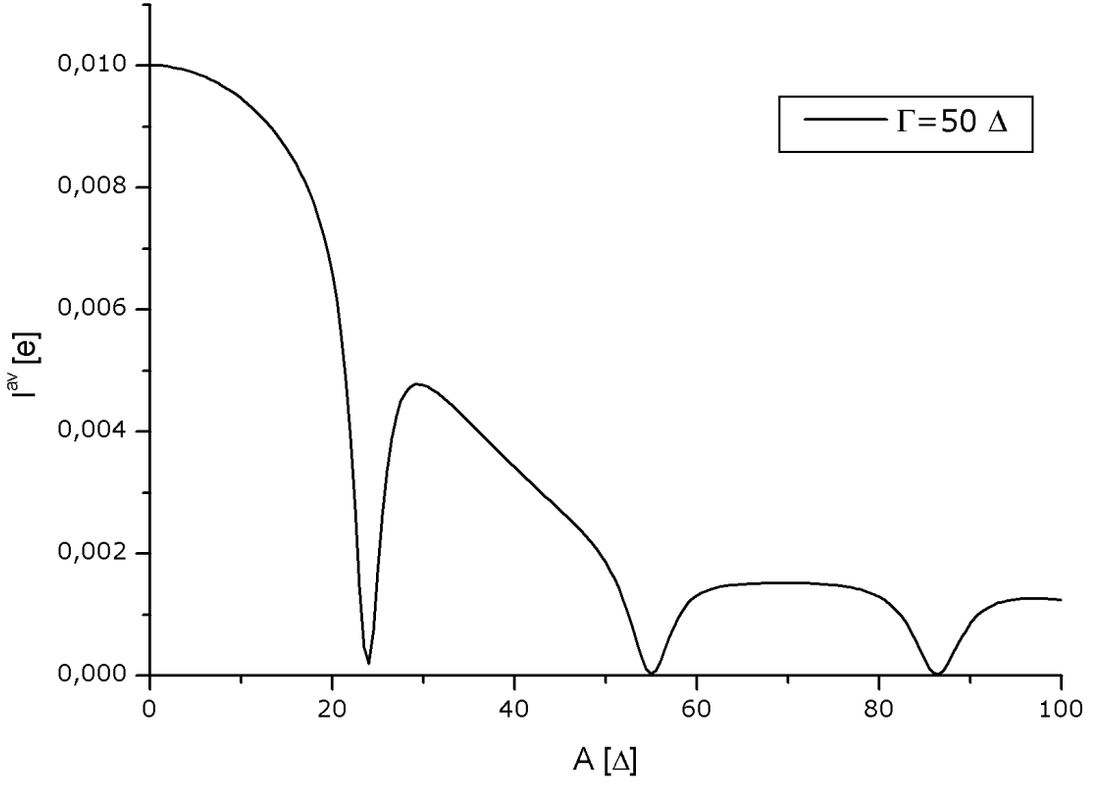


Coherent destruction of tunneling (CDT)



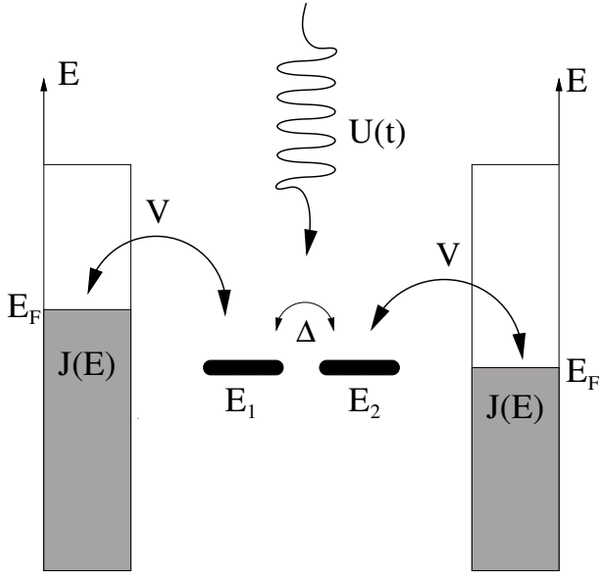
$$U_n(t) = A(t)\delta_{1n} - A(t)\delta_{2n}$$

$$A(t) = A_0 \sin(\omega t)$$



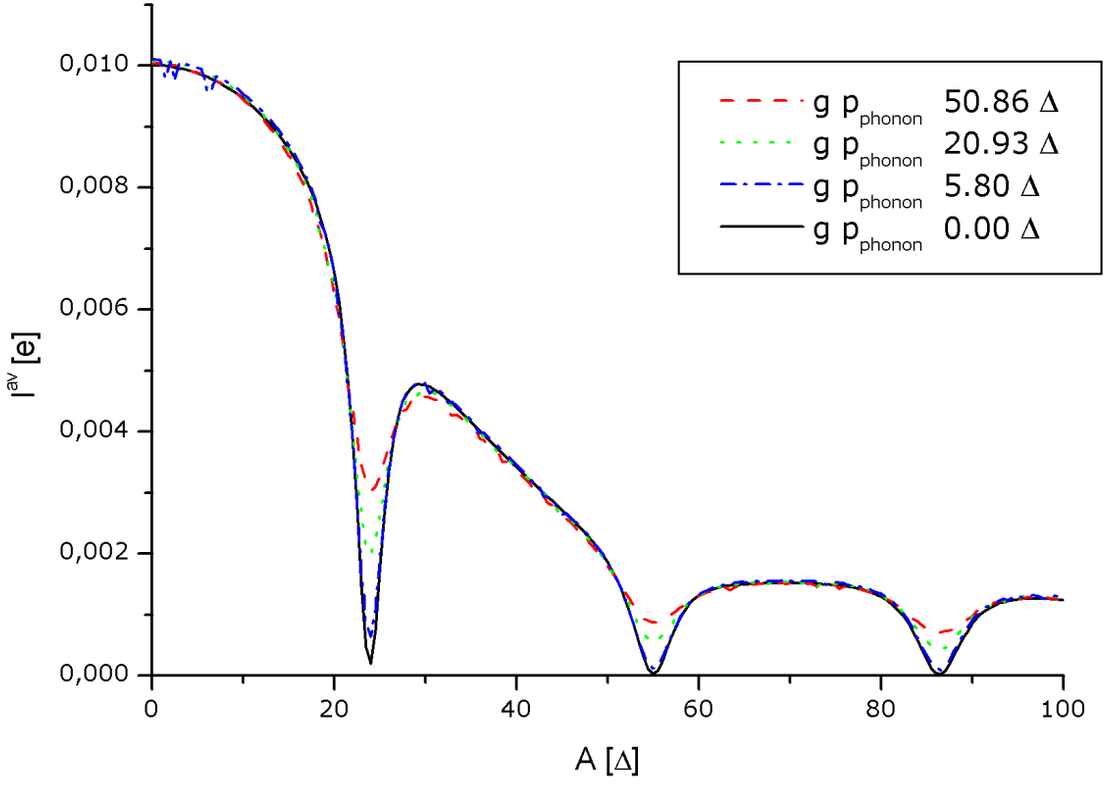
J. Lehmann, S. Camalet, S. Kohler and P. Hänggi, Chem. Phys. Lett. **368**, 282 (2003)

CDT: Coupling to phonon bath



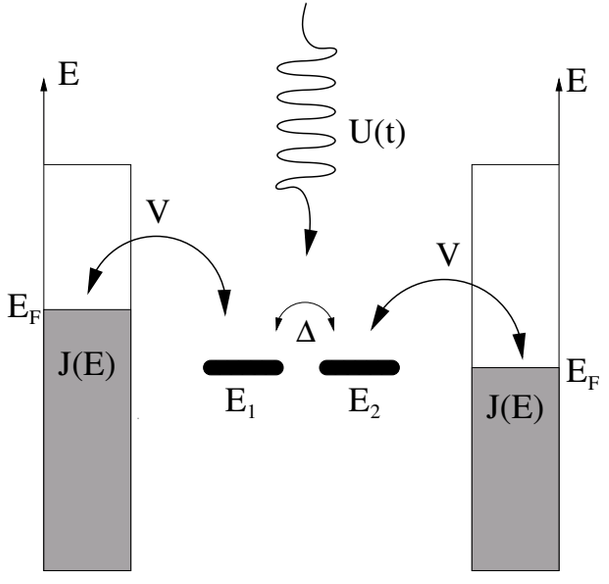
$$U_n(t) = A(t)\delta_{1n} - A(t)\delta_{2n}$$

$$A(t) = A_0 \sin(\omega t)$$



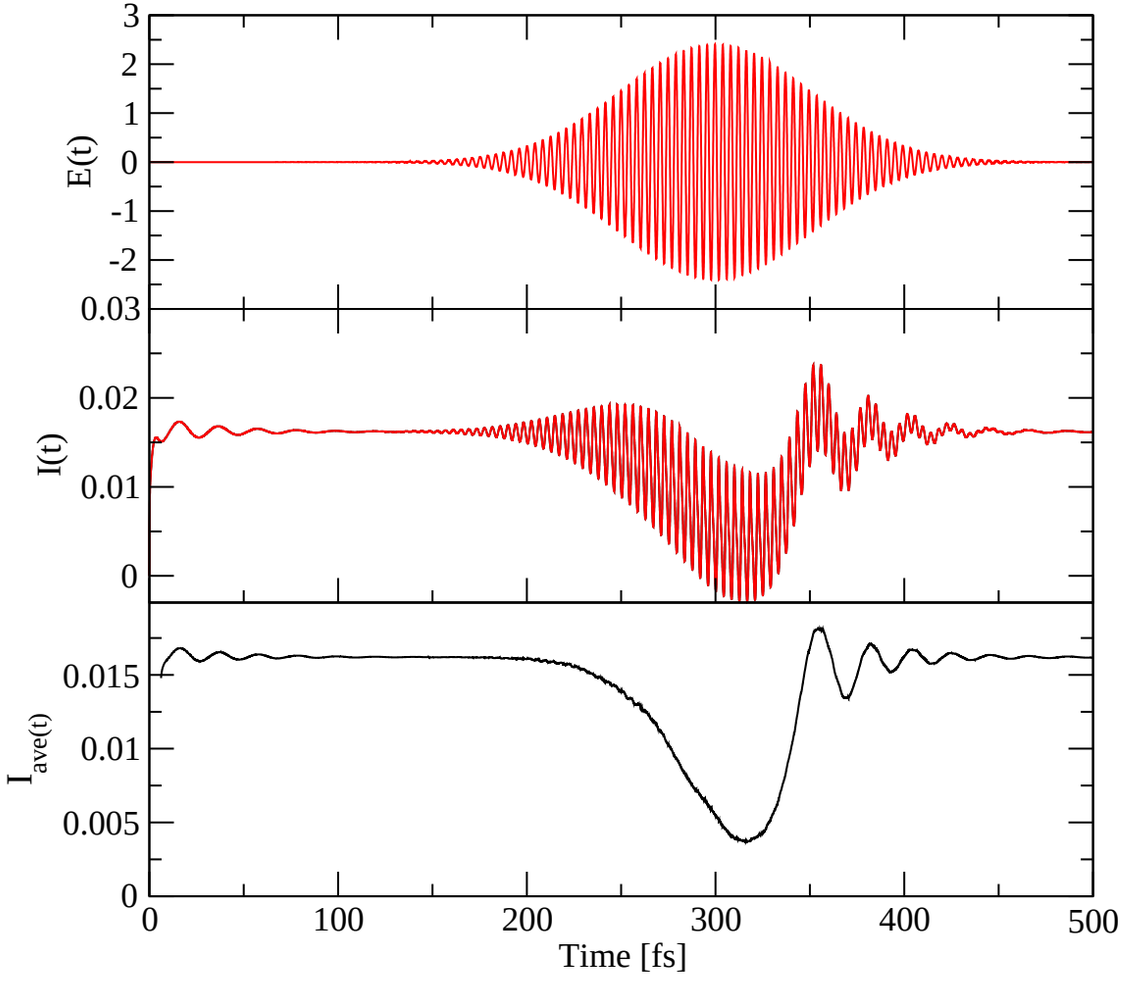
J. Lehmann, S. Kohler, V. May and P. Hänggi, J. Chem. Phys. **121**, 2278 (2003)

CDT: Short laser pulse

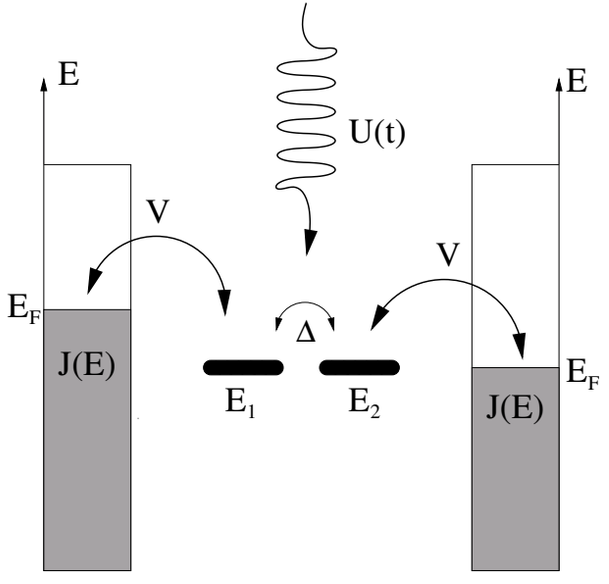


$$U_n(t) = A(t)\delta_{1n} - A(t)\delta_{2n}$$

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

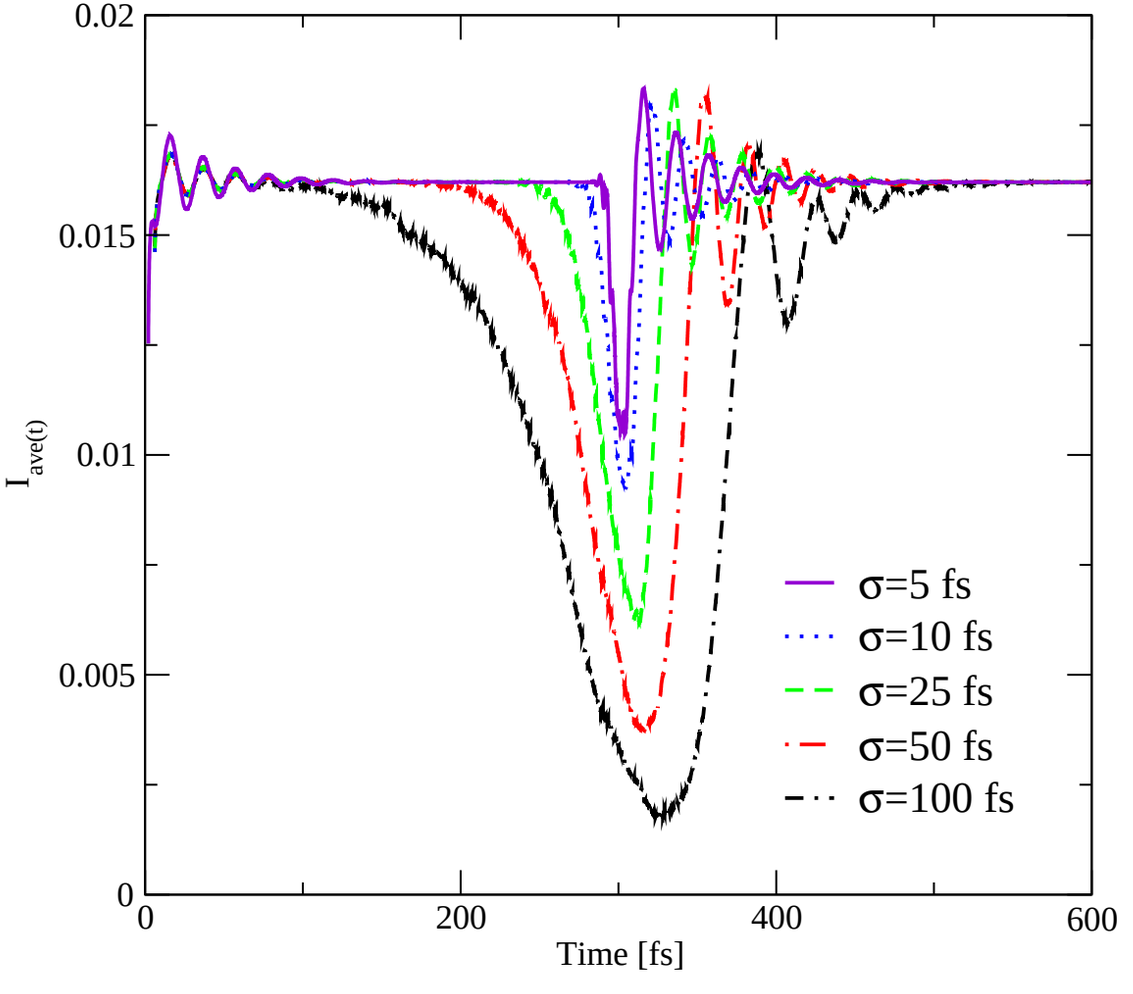


CDT: Pulse length

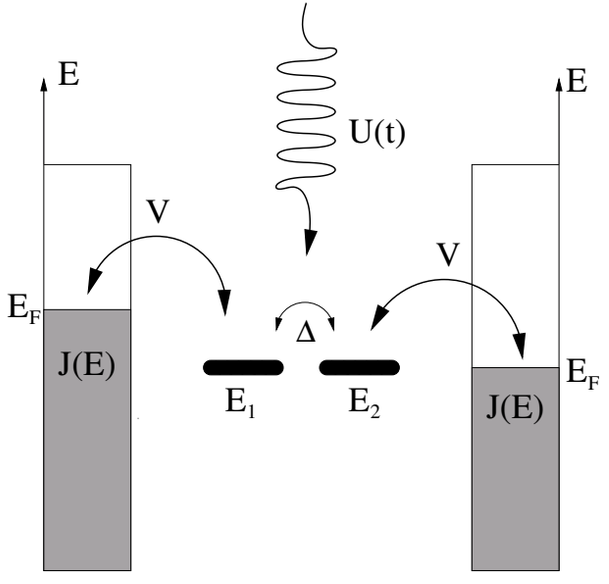


$$U_n(t) = A(t)\delta_{1n} - A(t)\delta_{2n}$$

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

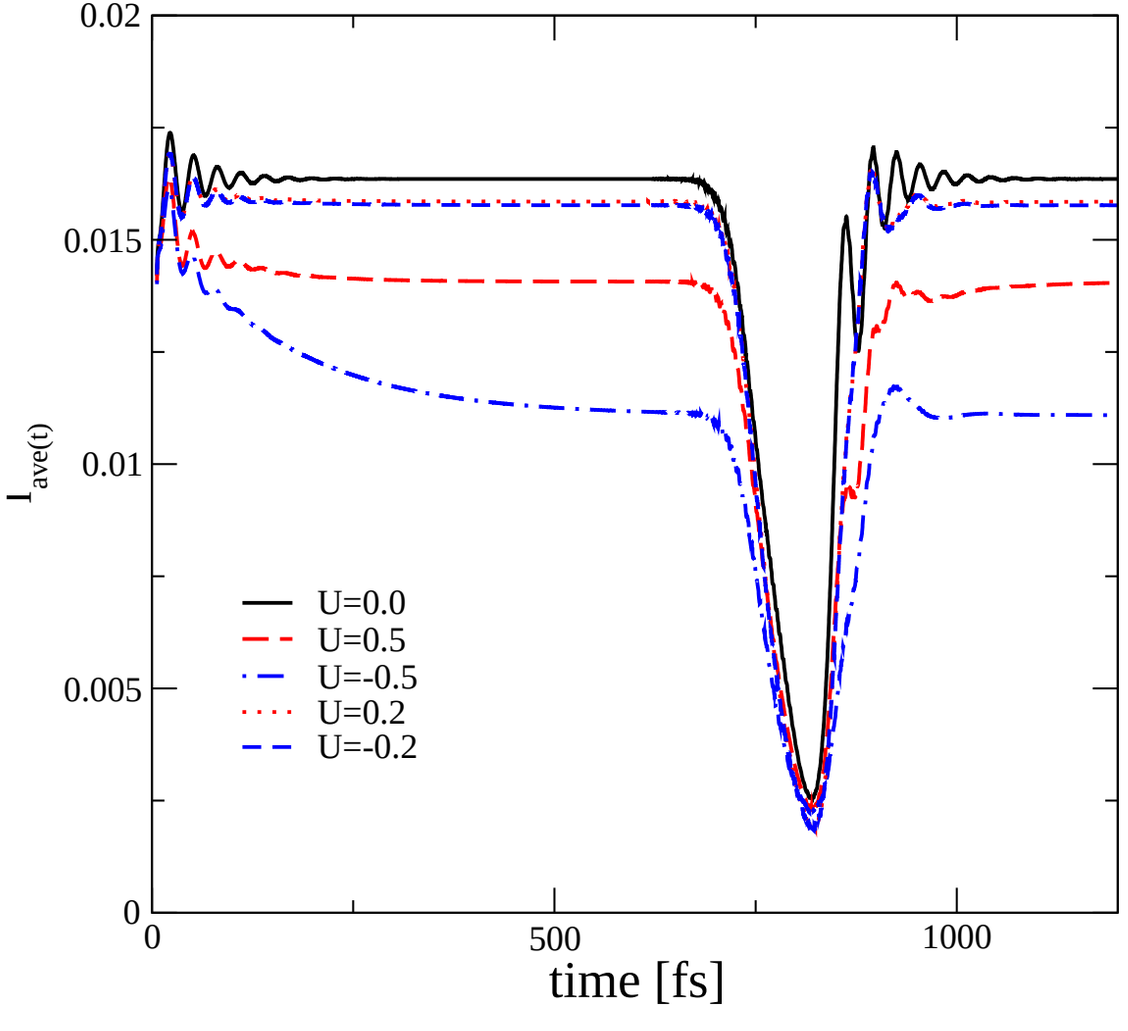


CDT: Electron correlation



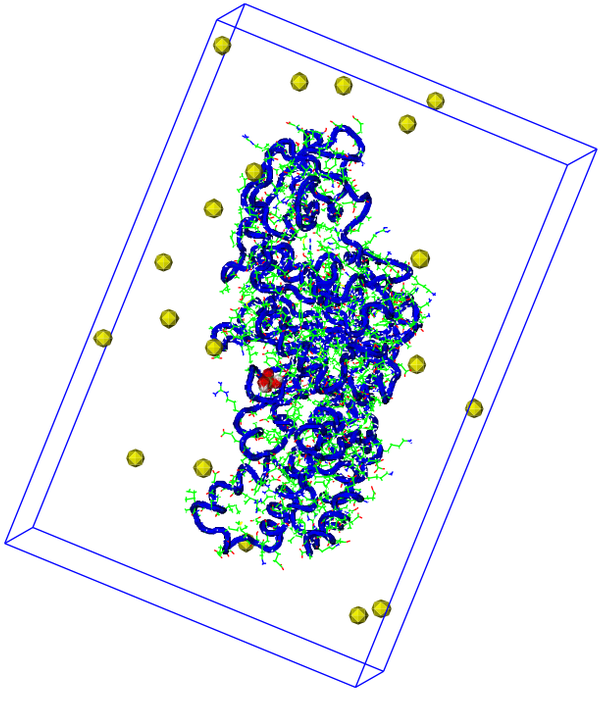
$$U_n(t) = A(t)\delta_{1n} - A(t)\delta_{2n}$$

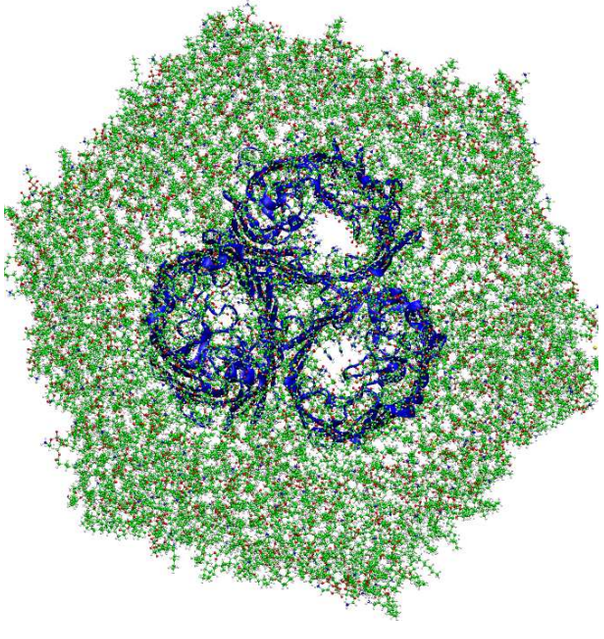
$$A(t) = A_0 \exp\left(\frac{-(t-T)^2}{\sigma^2}\right)$$



Other current projects in the group

- calculation of electron transfer in DNA
- time-dependent calculation and coherent control of CARS spectra (together with Arnulf Materny, IUB)
- MD simulations to understand the molecular motor F_1-ATPase

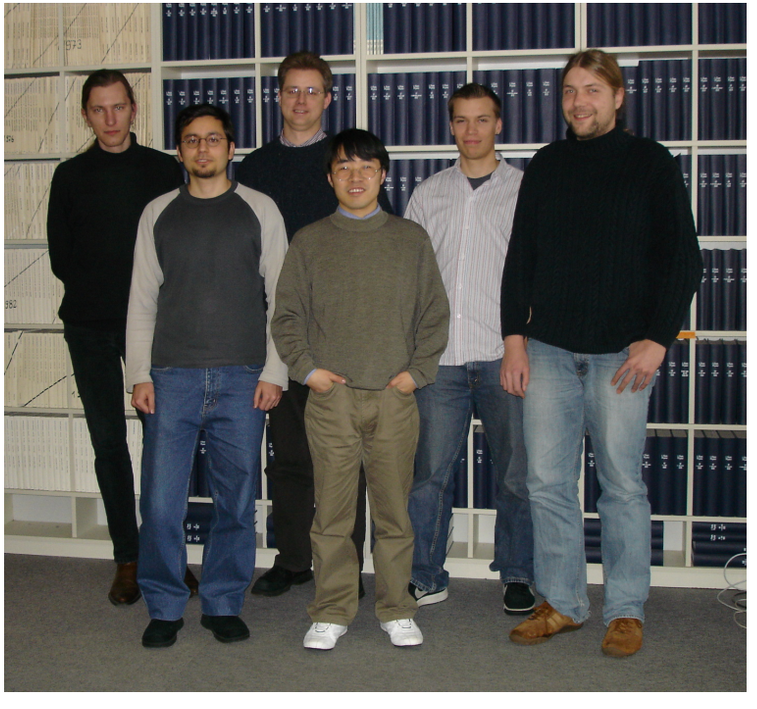




- MD simulations of antibiotics transport through channels of bacteria

Acknowledgments

- the group (as part of professorial chair „Theorie ungeordneter Systeme“ of Prof. Schreiber)



  - A. Novikov, S. Pezeshki, G.-Q. Li, S. Welack, M. Schröder

- David J. Tannor, Weizmann Institute of Science, Israel