Stochastic Unraveling and Exciton Transfer

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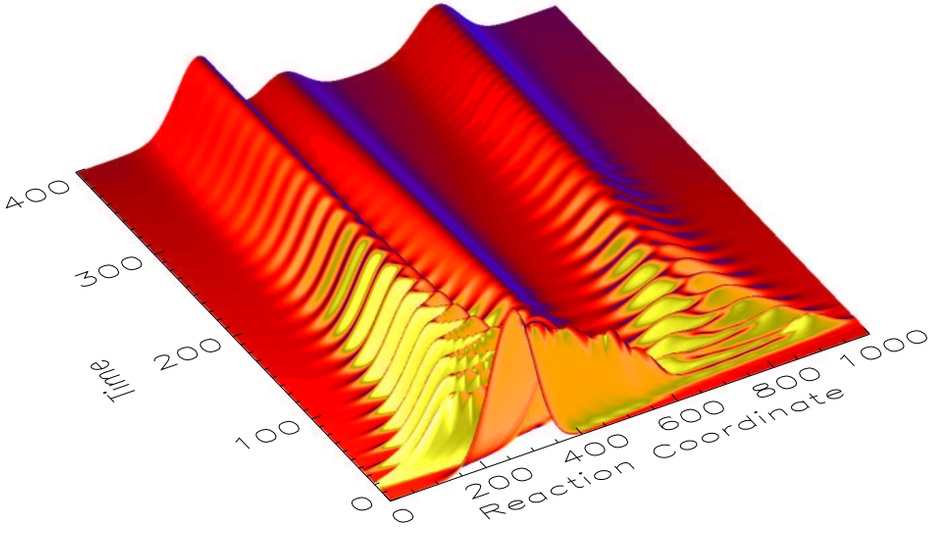


Overview

- Performance of different numerical propagators
- Stochastic unraveling incl. derivation and examples
- Introduction to light-harvesting
- Calculation of a spectral density
- Anisotropy in fluorescence

Redfield Theory

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

ρ - density matrix of the full system

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

- thermal bath consisting of harmonic oscillators, described by its the spectral density
- 2nd-order perturbation theory in system bath coupling H_{SB}
- Markov approximation
  (bath correlation times $\tau_B << $ typical system times τ_S)
- using eigenstate basis
- no secular approximation
- no rotating wave approximation

Redfield theory

equations $\propto N^5$

$$\frac{\partial \sigma_{ij}}{\partial t} = -i\omega_{ij}\sigma_{ij} + \sum_{kl} R_{ijkl}\sigma_{kl}$$

assumption of factorized system-bath coupling:

$$V = \sum_a G_a F_a$$

simplified equations $\propto N^3$:

$$\frac{\partial \sigma(t)}{\partial t} = -i\Omega\sigma(t) + \sum_a \{[G_a^+ \sigma(t), G_a] + H.\ c.\}$$

Diabatic-Damping Approximation:
equations $\propto N^{2.3}$

Quantum Trajectories:
equations $\propto N^2$

Efficiency of numerical propagators

- test system: two coupled diabatic surfaces

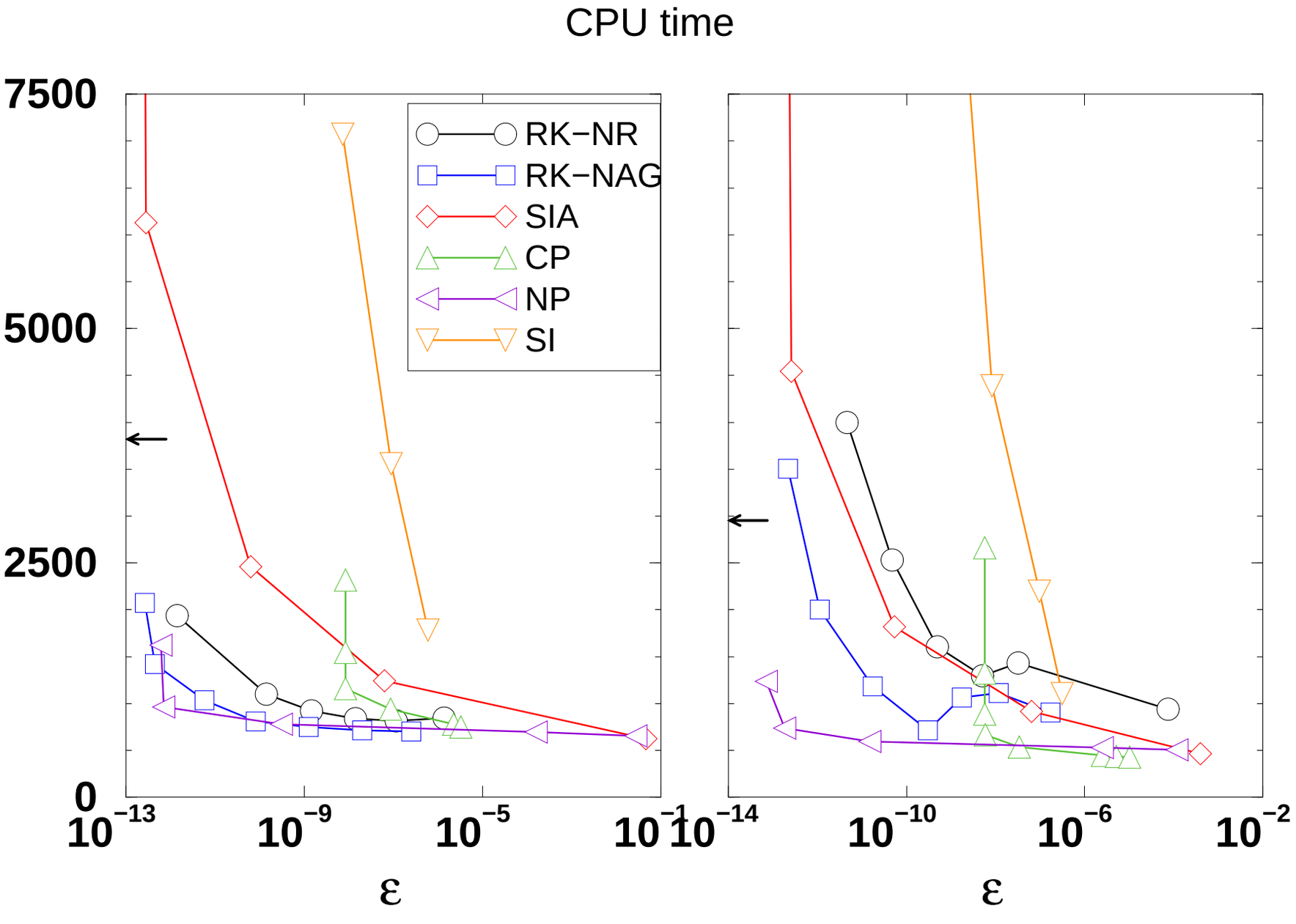
Propagators

- Runge-Kutta from *Numerical Recipes* (RK-NR)
- Runge-Kutta from *Numerical Algorithms Group* (RK-NAG)
- Short-Iterative-Arnoldi (SIA)
- short-time Chebyshev polynomial (CP)
- Newtonian polynomial (NP)
- symplectic integrator (SI)

I. Kondov, U. Kleinekathöfer, M. Schreiber, J. Chem. Phys. **114**, 1497-1504 (2001)

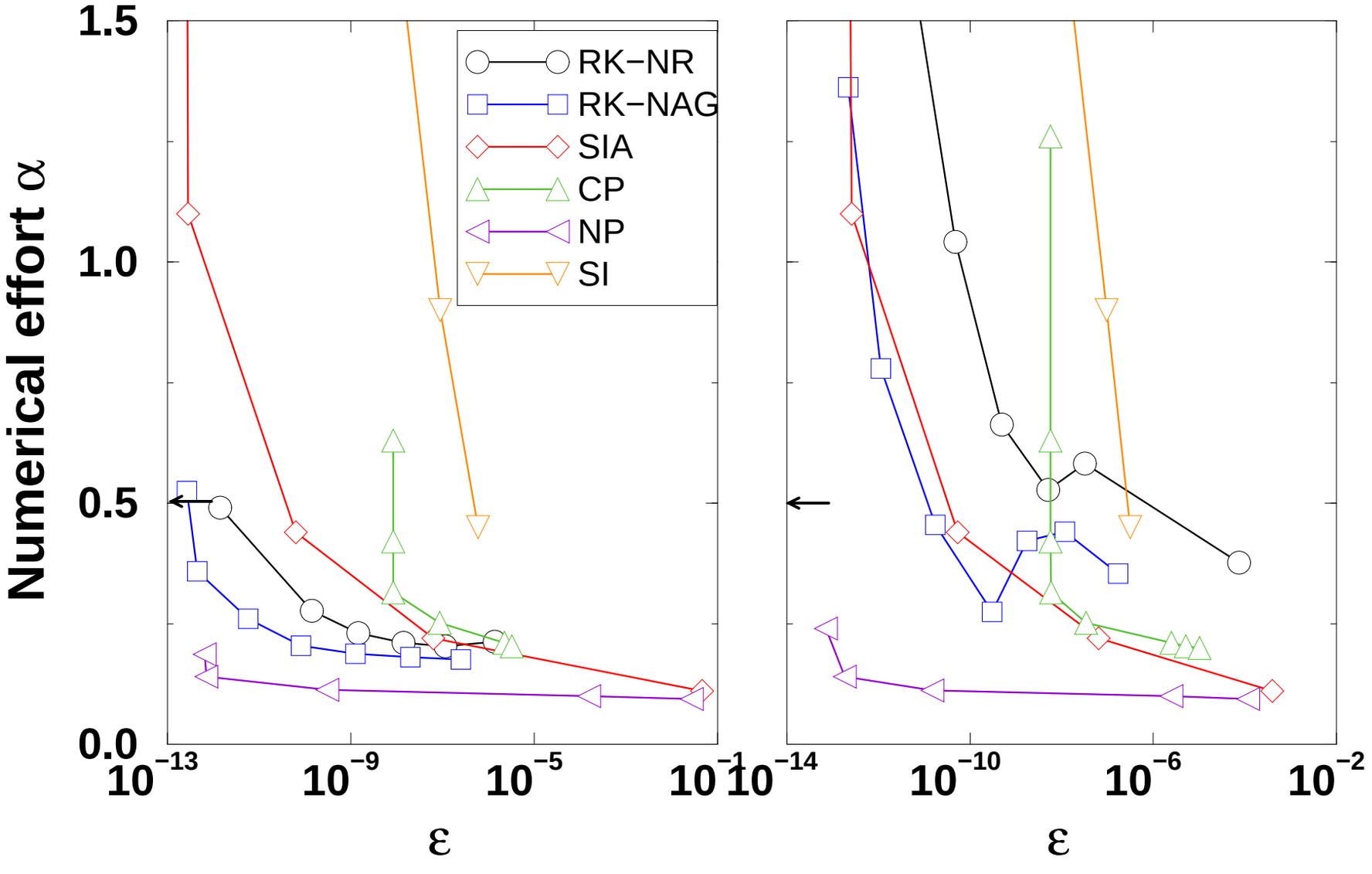
M. Schreiber, I. Kondov, U. Kleinekathöfer, J. Mol. Liq. **86**, 77 (2000)

Efficiency of numerical propagators



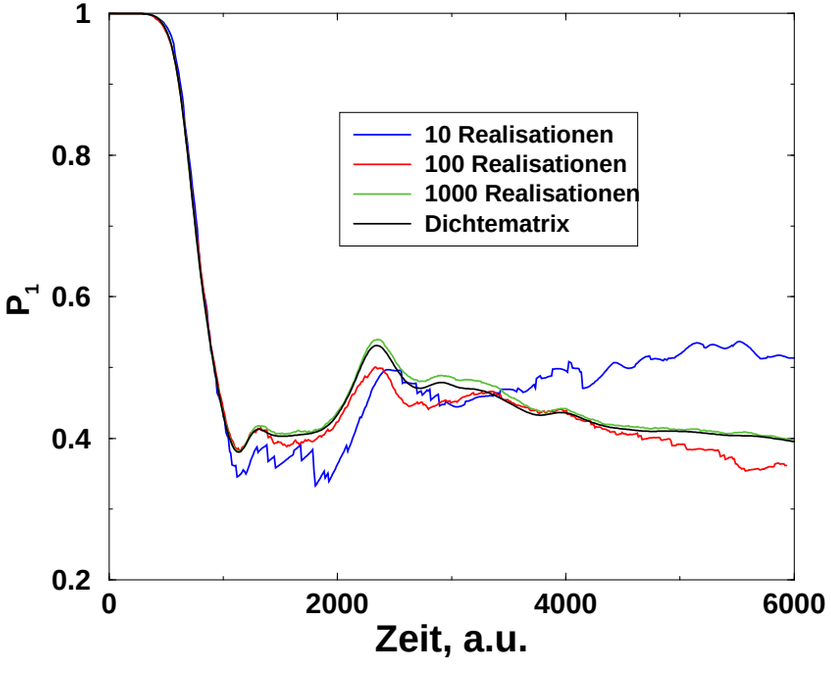
Efficiency of numerical propagators

Calls to $\mathscr{L}\rho$ divided by total propagation time



Monte Carlo wave function method

- no density matrices, but wave packets (using non-Hermitian operators)
- quantum jumps allowed, exchange of one vibrational quantum with the bath
- at each point in time random decision, if propagation by Δt or quantum jumps
- advantage scaling $\propto N^2$, disadvantage: many realizations needed



Why Monte Carlo wave function methods?

- able to propagate density matrices of large multi-dimensional systems
  - including more of the strongly coupled modes into the system
  - perturbation theory more reasonable
- stochastic methods for arbitrary system-bath coupling strength yield QME with stochastic element
  - Stockburger, Mak, Phys. Rev. Lett. **80**, 2657 (1998)
  - Breuer, Phys. Rev. A **39**, 022115 (2004)
  - Jiushu Shao, Chem. Phys. Lett. **395**, 216 (2004)

Density matrices

- pure state: $\sigma = |\Psi\rangle\langle\Psi|$
- mixed state: $\sigma = \sum_n W_n |\Psi_n\rangle\langle\Psi_n|$
- evolution

$$\begin{aligned} i\hbar\frac{d\sigma(t)}{dt} &= i\hbar\frac{d|\Psi\rangle\langle\Psi|}{dt} = i\hbar\left(\frac{|d\Psi\rangle}{dt}\langle\Psi| + |\Psi\rangle\frac{\langle d\Psi|}{dt}\right) \\ &= [H(t), \sigma(t)] \end{aligned}$$

- observables:

$$\begin{aligned} \langle Q\rangle = \langle\Psi|Q|\Psi\rangle &= \sum_n \langle\Psi|n\rangle\langle n|Q|\Psi\rangle \\ &= \sum_n \langle n|Q|\Psi\rangle\langle\Psi|n\rangle = tr(Q\sigma) \end{aligned}$$

- some global phase information lost

Monte Carlo wave function method

- standard Monte Carlo wave function method only valid for Lindblad form

$$\frac{\partial \sigma}{\partial t} = i[H_s, \sigma] - \frac{1}{2}\sum_n (L_m^\dagger L_m \sigma + \sigma L_m^\dagger L_m - 2 L_m \sigma L_m^\dagger)$$

- Redfield equation has only Lindblad form if the secular approximation is invoked

- Monte Carlo wave function version in a doubled Hilbert space for general master equation

$$\frac{\partial \sigma}{\partial t} = i[H_s, \sigma] + A(t)\sigma + \sigma B^\dagger(t) + \sum_i C_i(t) \sigma E_i^\dagger(t)$$

- density matrix in doubled Hilbert space does not need to be normalized

- this schemes works for Redfield equations

- implementation is numerically very inefficient

Breuer, Kappler, Petruccione, Phys. Rev. A **59**, 1633 (1999)

New Monte Carlo wave function method

- generalized time-local Hermiticity-conserving QME

$$\frac{d\rho(t)}{dt} = A(t)\rho(t) + \rho(t)A^{\dagger}(t) + \sum_{k=1}^{M} \left\{ C_k(t)\rho(t)E_k^{\dagger}(t) + E_k(t)\rho(t)C_k^{\dagger}(t) \right\}$$

- arbitrary operators $A(t)$, $C_k(t)$, and $E_k(t)$
- restriction to norm conservation
- doubled Hilbert space with state vector $(|\psi\rangle, |\phi\rangle)^T$
- density matrix reconstructed as ensemble average $\rho = \overline{|\psi\rangle\langle\phi|} + \overline{|\phi\rangle\langle\psi|}$
- stochastic differentials $d\xi_k^i(t)$ are assumed to have zero mean, to be normalized and uncorrelated

$$\overline{d\xi_k^i} = 0, \ \overline{d\xi_k^{i*} d\xi_l^j} = \delta_{ij}\delta_{kl}dt,$$

Kleinekathöfer, Kondov, Schreiber, Phys. Rev. E **66**, 037701 (2002); J. Chem. Phys. **119**, 6635 (2003).

New Monte Carlo wave function method

- an *ansatz*

$$d|\psi\rangle = D_1|\psi\rangle dt + \sum_{k=1}^{M}\sum_{i=1}^{2} S_{1k}^{i}|\psi\rangle d\xi_k^i\,, \qquad d|\phi\rangle = D_2|\phi\rangle dt + \sum_{k=1}^{M}\sum_{i=1}^{2} S_{2k}^{i}|\phi\rangle d\xi_k^i\,.$$

- operators D_1 and D_2 govern the deterministic and S_{jk}^{i} the stochastic part of the evolution

- differentiate $\rho = \overline{|\psi\rangle\langle\phi|} + \overline{|\phi\rangle\langle\psi|}$, neglecte all terms higher than first order in dt, assume that ensemble averages always factorize

- doing ensemble average

$$d\rho = \left[D_1\overline{|\psi\rangle\langle\phi|} + D_2\overline{|\phi\rangle\langle\psi|}\right] dt + \sum_{k=1}^{M}\left[S_{1k}^{1}\overline{|\psi\rangle\langle\phi|}S_{2k}^{1\dagger} + S_{2k}^{2}\overline{|\phi\rangle\langle\psi|}S_{1k}^{2\dagger}\right] dt + \; h.c.$$

- compare with QME: $S_{1k}^{1} = S_{2k}^{2}$ and $S_{2k}^{1} = S_{1k}^{2}$

- $S_{2k}^{1} = C_k + \alpha_k^1$ and $S_{2k}^{2} = E_k + \alpha_k^2$

- α_k^1 and α_k^2 being arbitrary scalar functions of $(|\psi\rangle, |\phi\rangle)^T$ and possibly of time

New Monte Carlo wave function method

- constraint

$$D_1 = D_2 = A - \sum_{k=1}^{M} \left(\alpha_k^{2*} C_k + \alpha_k^{1*} E_k + \alpha_k^1 \alpha_k^{2*} \right) \ .$$

- stochastic differential ($dn_k^i = 0, 1$)

$$d\xi_k^i = \frac{dn_k^i - p_k^i dt}{\sqrt{p_k^i}} e^{i\varphi}, \qquad \overline{dn_k^i} = \overline{(dn_k^i)^2} = p_k^i dt$$

- phase factor $e^{i\varphi}$ irrelevant

- substituting $d\xi_k^i$ one gets $\alpha_k^i = -\sqrt{p_k^i}$ for a jump process

$$|\psi\rangle \quad \rightarrow \quad \frac{E_k}{\sqrt{p_k^1}} |\psi\rangle$$

$$|\phi\rangle \quad \rightarrow \quad \frac{C_k}{\sqrt{p_k^1}} |\phi\rangle$$

New Monte Carlo wave function method

- SSEs for our quantum jump method read

$$
\begin{aligned}
d|\psi\rangle &= \left(A+\sum_{k=1}^{M}\frac{p_k^1+p_k^2}{2}\right)|\psi\rangle dt+\sum_{k=1}^{M}\left[\left(\frac{E_k}{\sqrt{p_k^1}}-1\right)dn_k^1+\left(\frac{C_k}{\sqrt{p_k^2}}-1\right)dn_k^2\right]|\psi\rangle,\\
d|\phi\rangle &= \left(A+\sum_{k=1}^{M}\frac{p_k^1+p_k^2}{2}\right)|\phi\rangle dt+\sum_{k=1}^{M}\left[\left(\frac{C_k}{\sqrt{p_k^1}}-1\right)dn_k^1+\left(\frac{E_k}{\sqrt{p_k^2}}-1\right)dn_k^2\right]|\phi\rangle.
\end{aligned}
$$

Optimization of the stochastic process

- jump rates p_k^1 and p_k^2 still remain free parameters
- Condition for norm conservation of every single sample (!)

$$\mathrm{Tr}\left\{\frac{d}{dt}\left[|\psi\rangle\langle\phi| + |\phi\rangle\langle\psi|\right]\right\} = 0$$

- the norm conservation of the QME

$$A + A^\dagger = -\sum_{k=1}^{M}\left(E_k^\dagger C_k + C_k^\dagger E_k\right)$$

- if applied to the deterministic part of the corresponding SSE yields the total jump rate

$$p = -\frac{\langle\phi|A + A^\dagger|\psi\rangle + \langle\psi|A + A^\dagger|\phi\rangle}{\langle\phi|\psi\rangle + \langle\psi|\phi\rangle}.$$

Optimization of the stochastic process

- jump rates for different jumps, their sum gives the total jump rate p

$$p_k^1 = \frac{\langle\phi|C_k^\dagger E_k|\psi\rangle + \langle\psi|E_k^\dagger C_k|\phi\rangle}{\langle\phi|\psi\rangle + \langle\psi|\phi\rangle}$$

$$p_k^2 = \frac{\langle\phi|E_k^\dagger C_k|\psi\rangle + \langle\psi|C_k^\dagger E_k|\phi\rangle}{\langle\phi|\psi\rangle + \langle\psi|\phi\rangle}$$

- jump propabilities p_k^2 not always positive, take absolute values
- slight deviations from the norm
- allow for a "'negative"'weight

The stochastic wave function algorithm

- Lindblad equation $\dot{\rho} = -i\,[H_{\rm S}, \rho] + \frac{1}{2}\sum_k \{2L_k \rho L_k^\dagger - L_k^\dagger L_k \rho - \rho L_k^\dagger L_k\}$

- The solution is obtained as follows

1. define a set $\{\psi_n(t=0)\}_{n=1}^{N_S}$
2. define $H_{\rm eff} = H_{\rm S} + \frac{i}{2}\sum_k L_k^\dagger L_k$
3. normalize $|\psi_n(t)\rangle$
4. send $\rho_n(t) = |\psi_n(t)\rangle\langle\psi_n(t)|$ for averaging
5. calculate $p_k = \langle\psi_n(t)|L_k^\dagger L_k|\psi_n(t)\rangle$
6. draw a random number $\varepsilon \in (0,1)$
7. if $\varepsilon > dt\sum_k p_k$ then
   - find $|\psi_n(t+dt)\rangle$ solving $|\dot{\psi}_n(t)\rangle = -iH_{\rm eff}|\psi_n(t)\rangle$
   - let $t = t + dt$ and go to item 3

   else
   - perform a single jump using the probabilities $p_k dt$ $|\psi_n(t)\rangle \rightarrow L_k|\psi_n(t)\rangle/\sqrt{p_k}$
   - go to item 5

Quantum Brownian motion

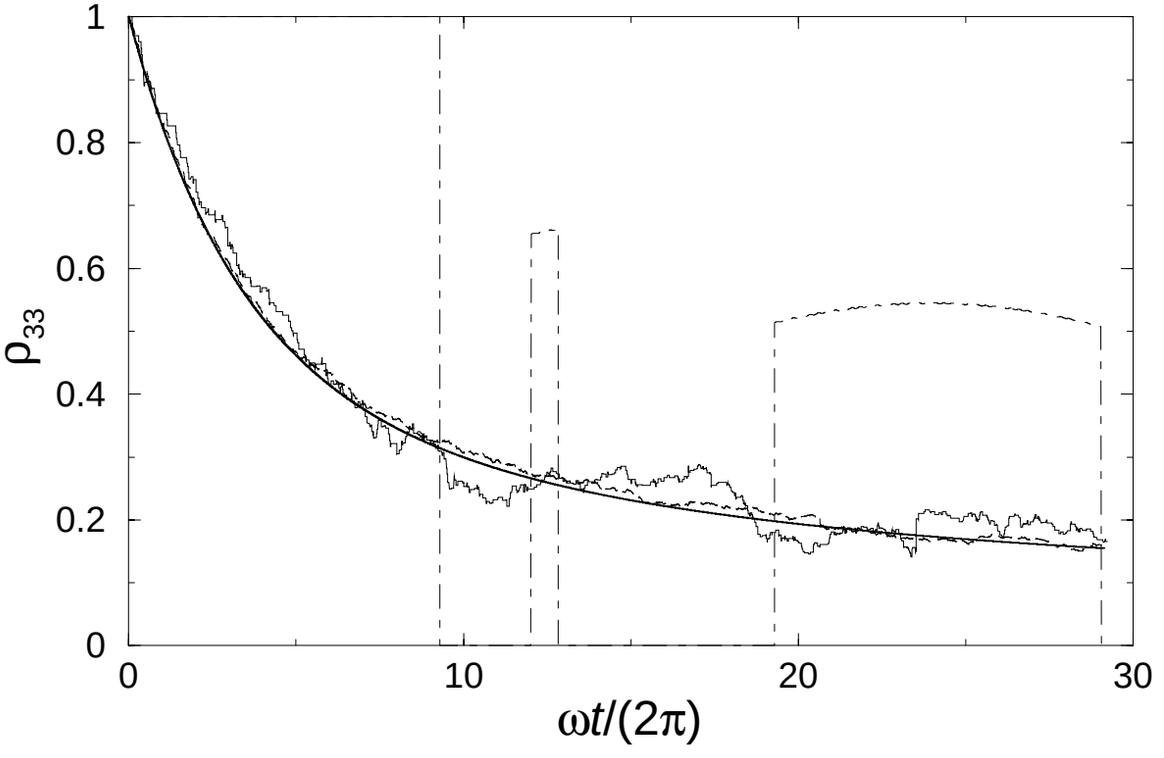
- quantum master equation

$$\frac{d\rho}{dt} = -\frac{i}{\hbar}[H_S, \rho] - \frac{i\gamma}{2\hbar}[q, \{p, \rho\}] - \frac{m\gamma kT}{\hbar^2}[q, [q, \rho]]$$

- harmonic oscillator ($M = 2$)

$$\begin{aligned} E_1 &= \sqrt{\frac{\gamma}{2\hbar}} q,\ C_1 = -i\sqrt{\frac{\gamma}{2\hbar}} p, \\ E_2 &= \sqrt{\frac{m\gamma kT}{\hbar^2}} q,\ C_2 = E_2, \\ A &= -\frac{i}{\hbar} H_S + \frac{i\gamma}{2\hbar} qp - \frac{m\gamma kT}{\hbar^2} qq. \end{aligned}$$

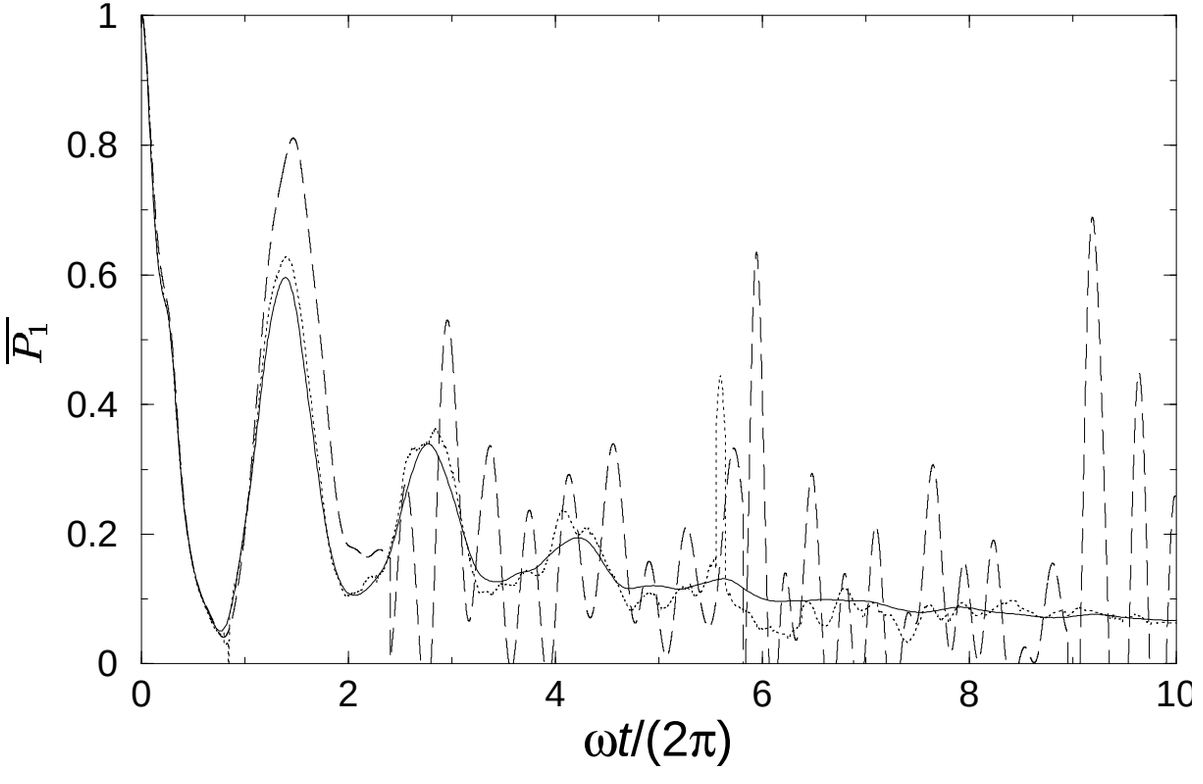
Quantum Brownian motion



Electron transfer systems

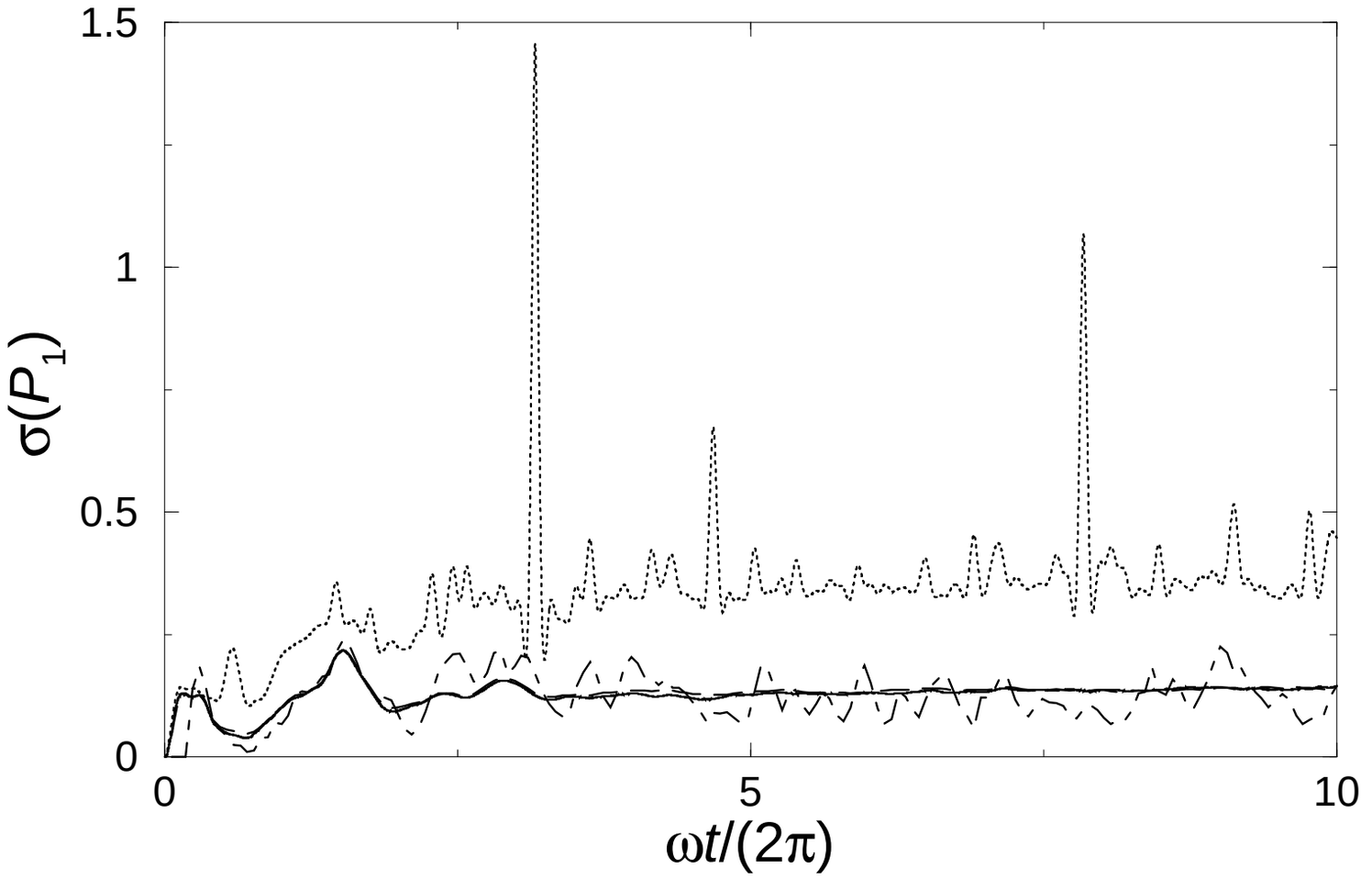
- electron transfer in Redfield theory

$$\frac{d\rho}{dt} = -\frac{i}{\hbar}[H_{\mathrm{S}}, \rho] + \frac{1}{\hbar^2}\Big\{ \left[\Lambda\rho, K\right] + \left[K, \rho\Lambda^{\dagger}\right] \Big\}$$



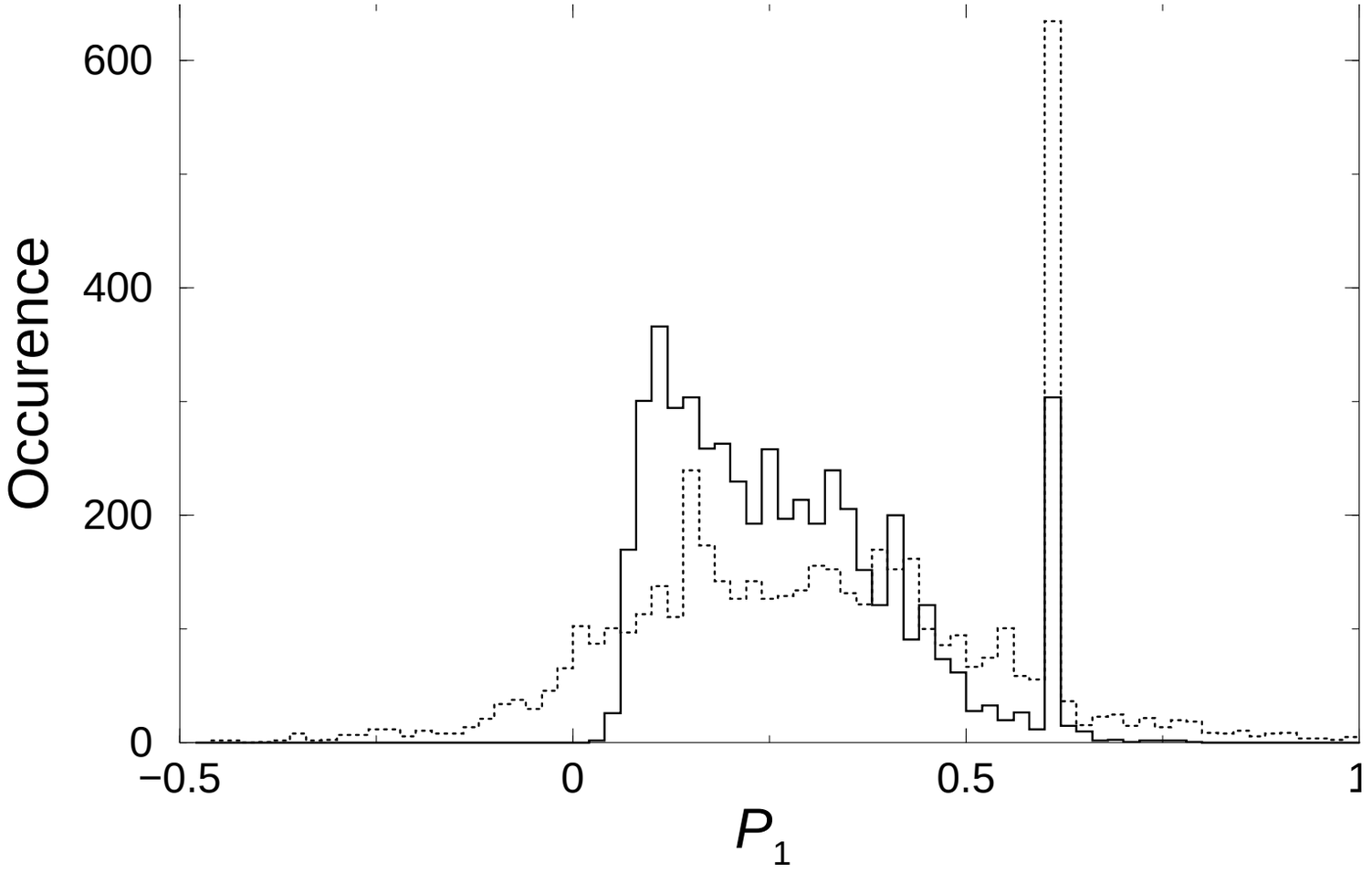
Statistics

- Dispersion

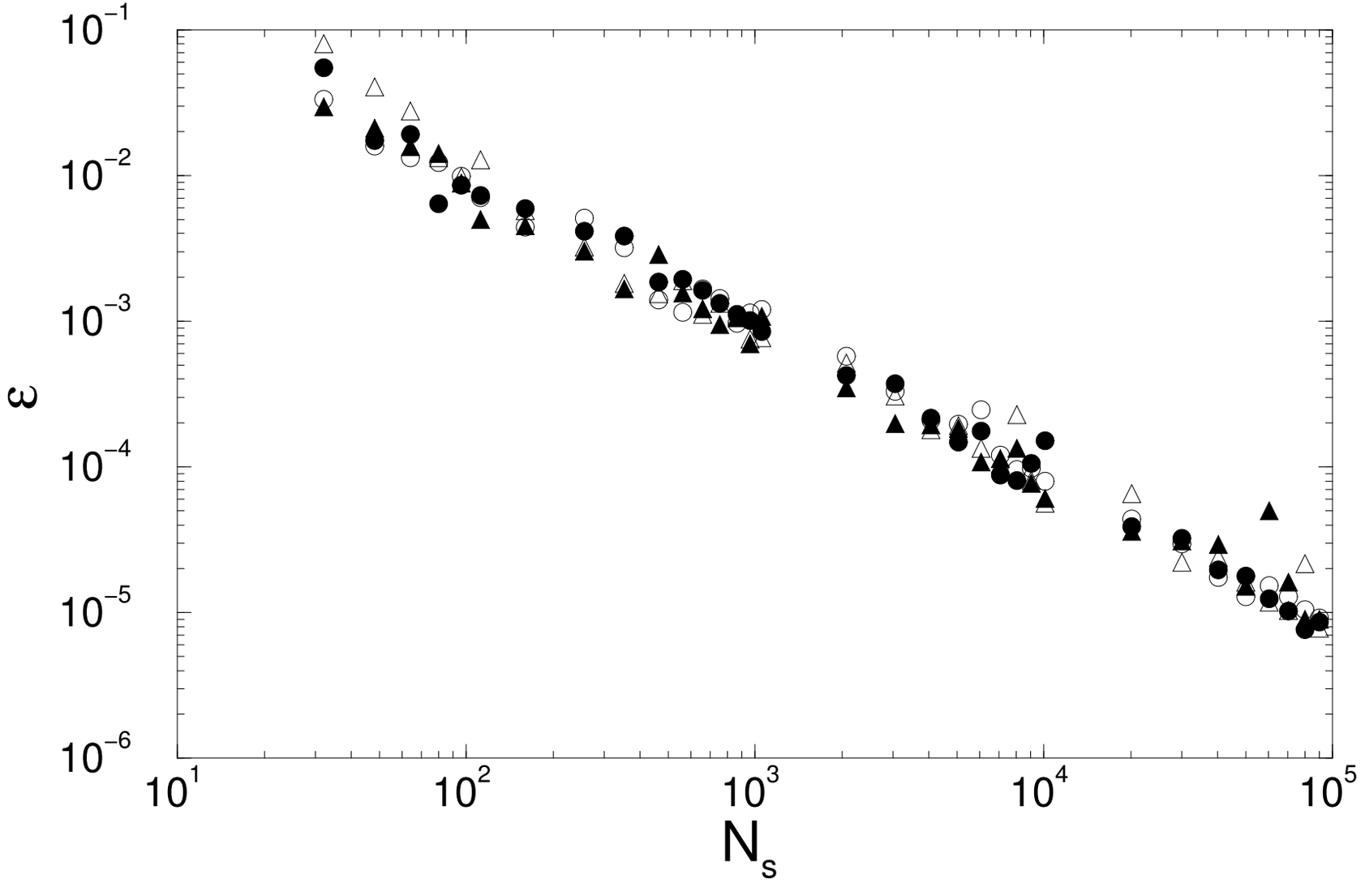


Statistics

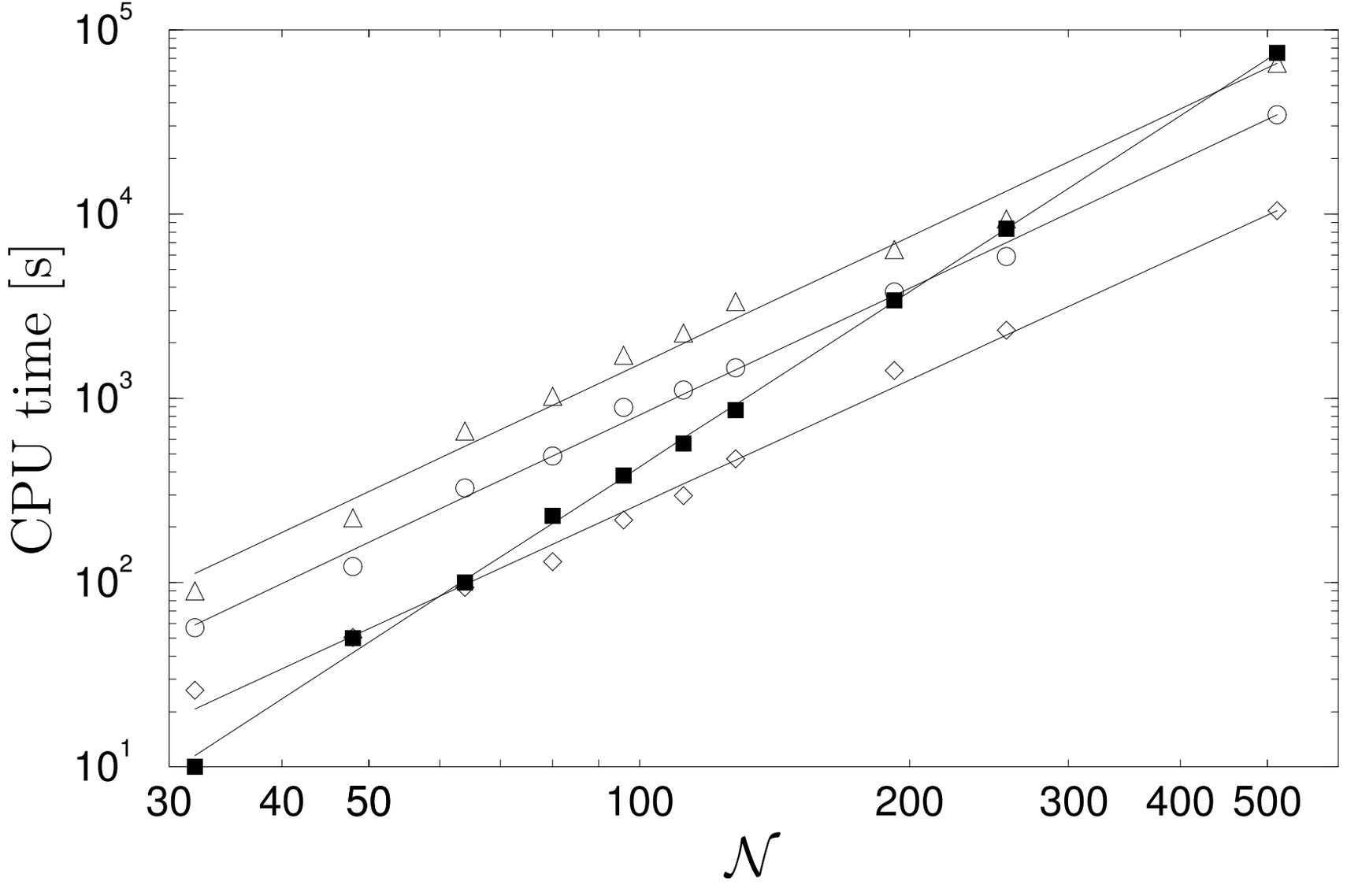
- Distribution of populations



Logarithmic convergence

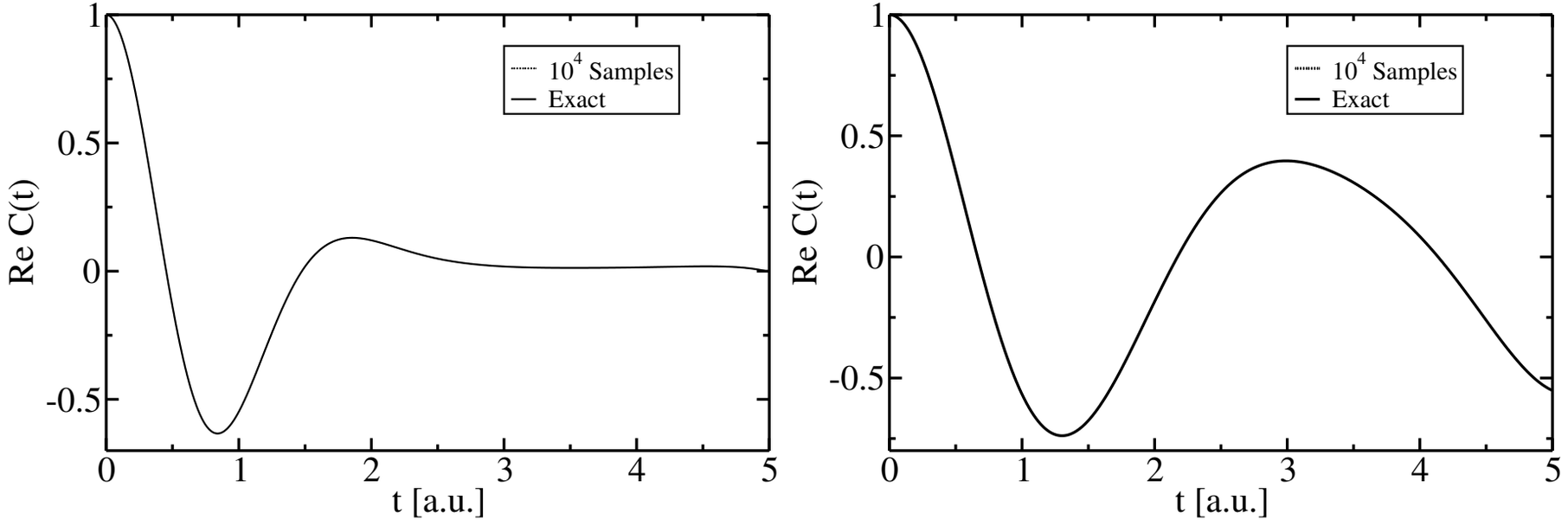


Performance



Monte Carlo method for propagating multi-dimensional wave packets

- TDH plus recovering the correlations by stochastic process



M. Schröder and U. Kleinekathöfer, phys. stat. sol. (b) **241**, 2157–2167 (2004).

Exciton transfer:

Combination of molecular dynamics, quantum chemistry and a quantum mechanical model

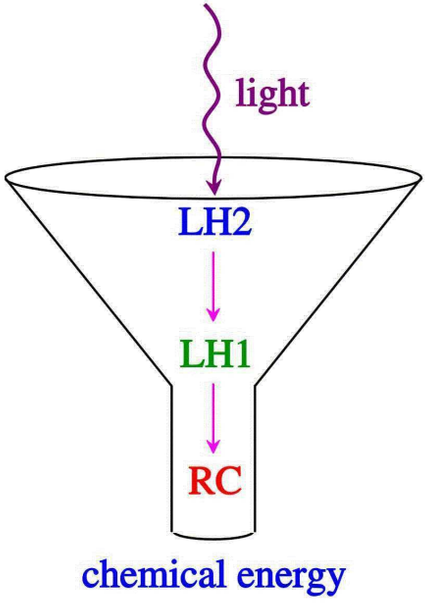
in collaboration with

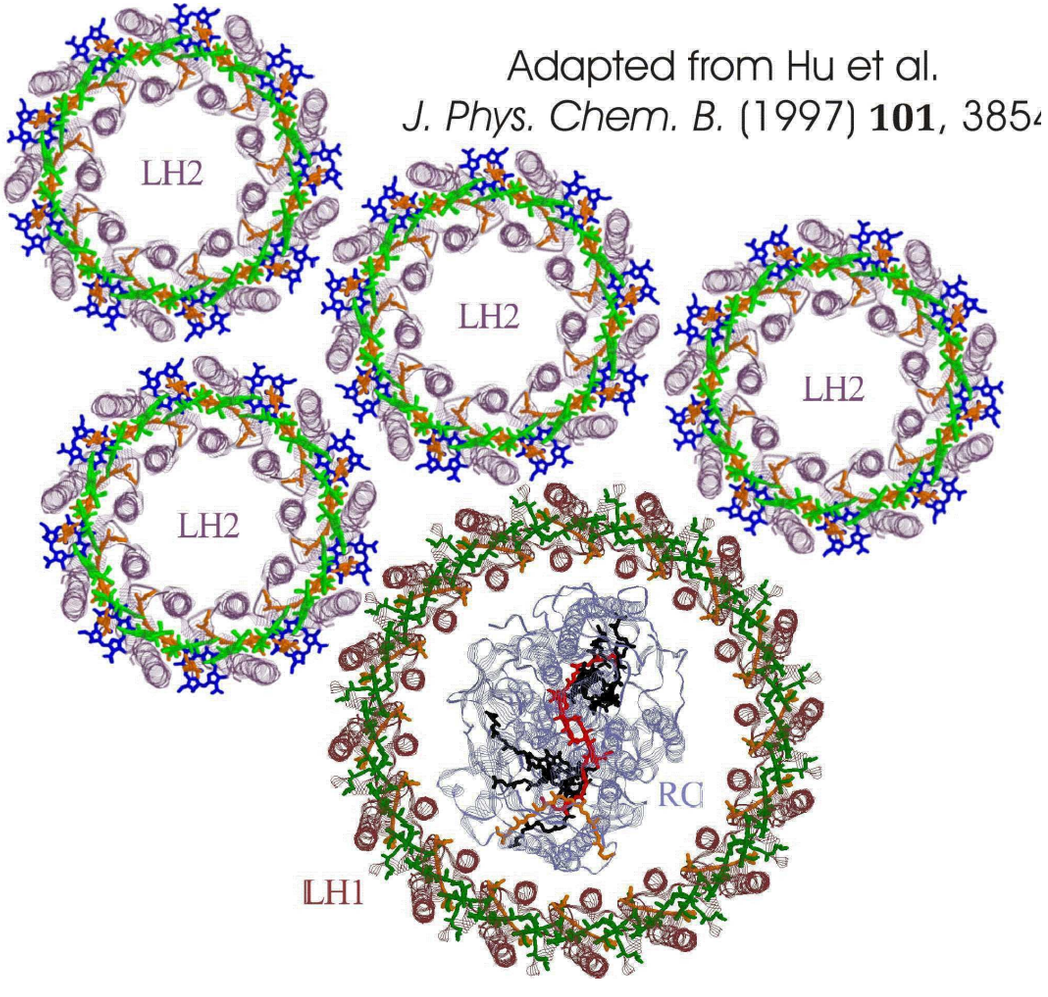
Ana Damjanović, Ioan Kosztin, Klaus Schulten

University of Illinois, Urbana-Champaign

Physical Review E **65**, 031919/1-24 (2002).

Harvesting of light





- exciton: coherent, delocalized electronic excitation

Idea of Combining MD, QC and QM modeling

- as input one uses X-ray data of *Rhodospirillum molischianum*

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- do a molecular dynamics simulation

  - add hydrogen atoms
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- develop a quantum mechanical model to determine experimental values
  - time-independent absorption, circular dichroism, etc
  - transient phenomena (not done yet)

Molecular Dynamics Calculations

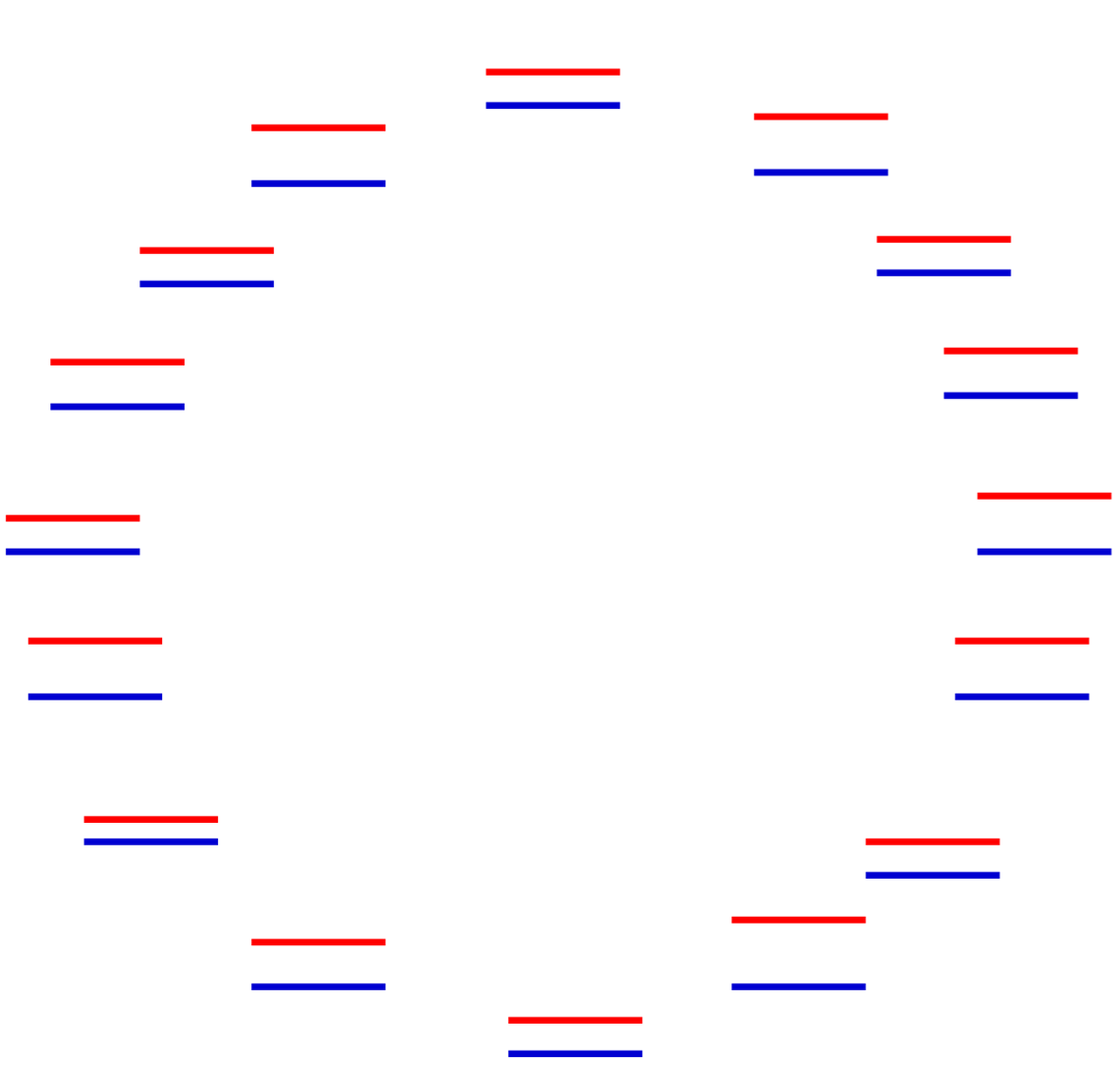
- macroscopic properties often determined by molecular level behavior
- quantitative and/or qualitative information can be obtained from simulation at atomistic level
- motion of the atoms using Newtonian dynamics
- each point i at position r_i is treated as a point with a mass m_i and a fixed charge q_i

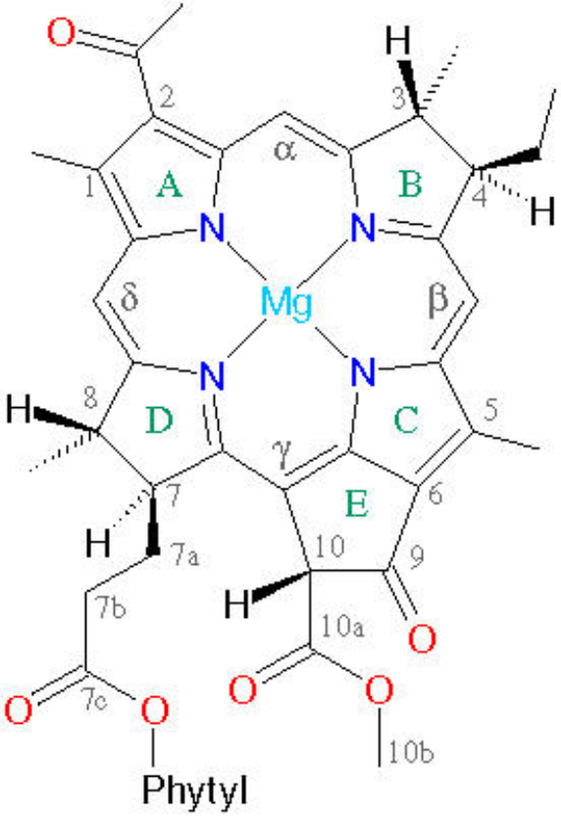
MD simulation of LH-II

- LH-II complex of *Rhodospirillum molischianum* (8-fold symmetry)
- 87 055 atoms included
- using the program NAMD2 (Schulten's group)
- 400 snapshots every 2 fs

Energy gaps of single BChls

- Quantum chemical calculation per snapshot configuration:
  (CI-S with GAUSSIAN98) for each separate BChl





ground states

excited states

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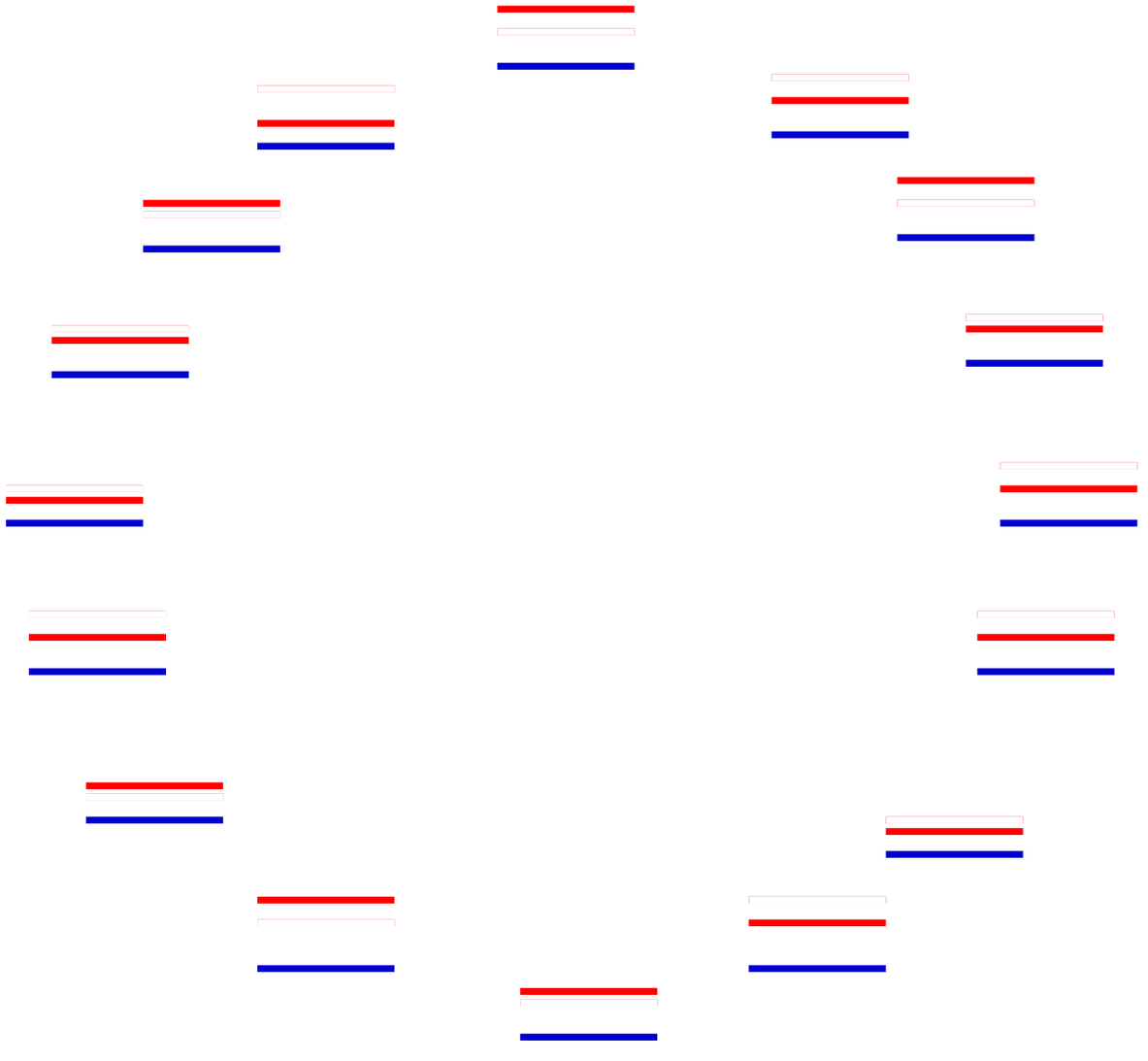

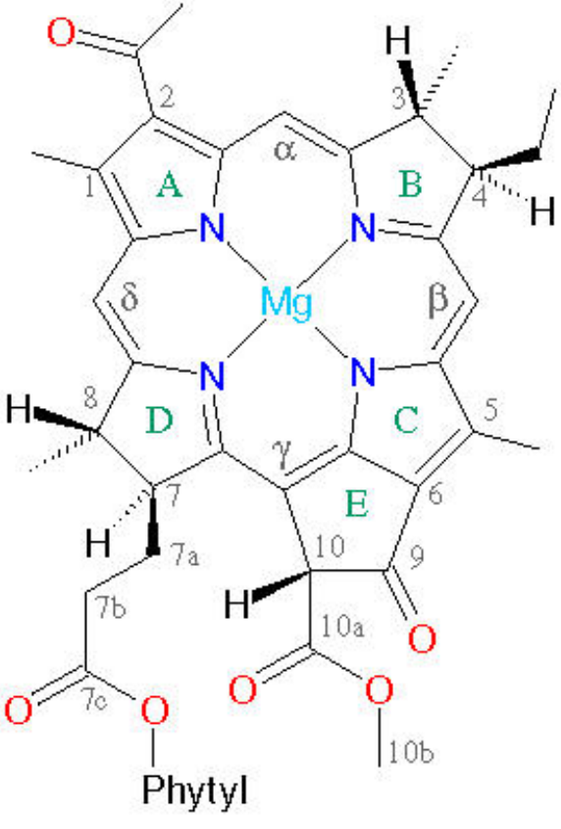

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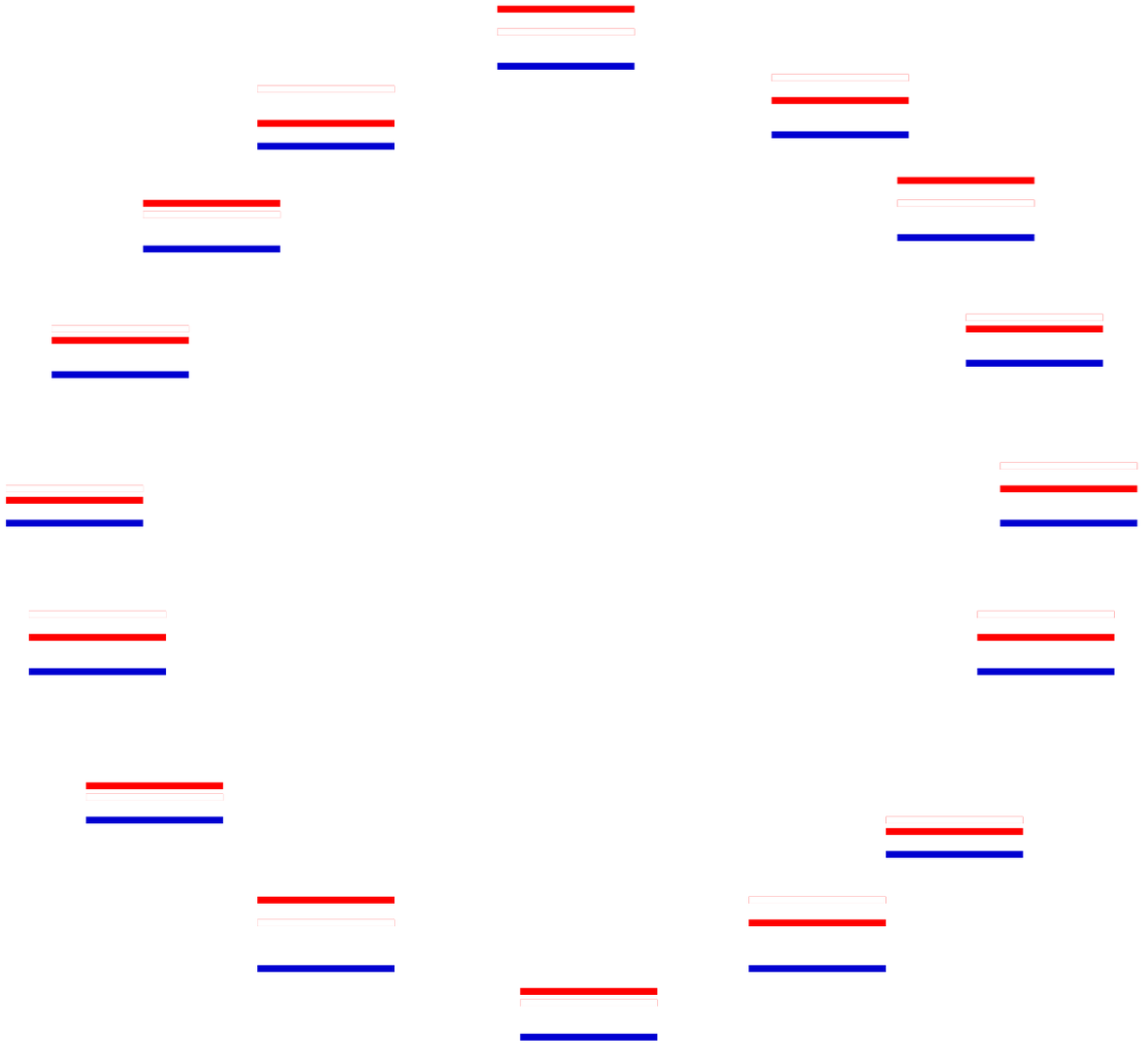
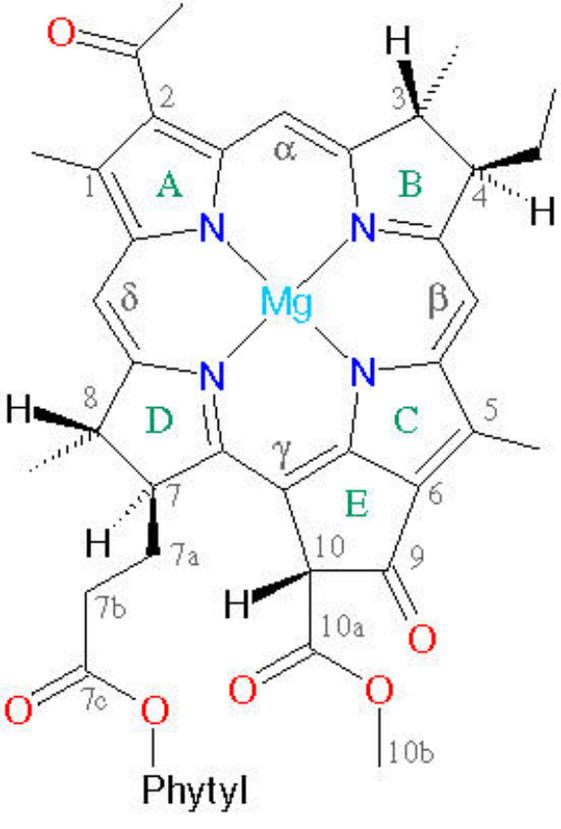


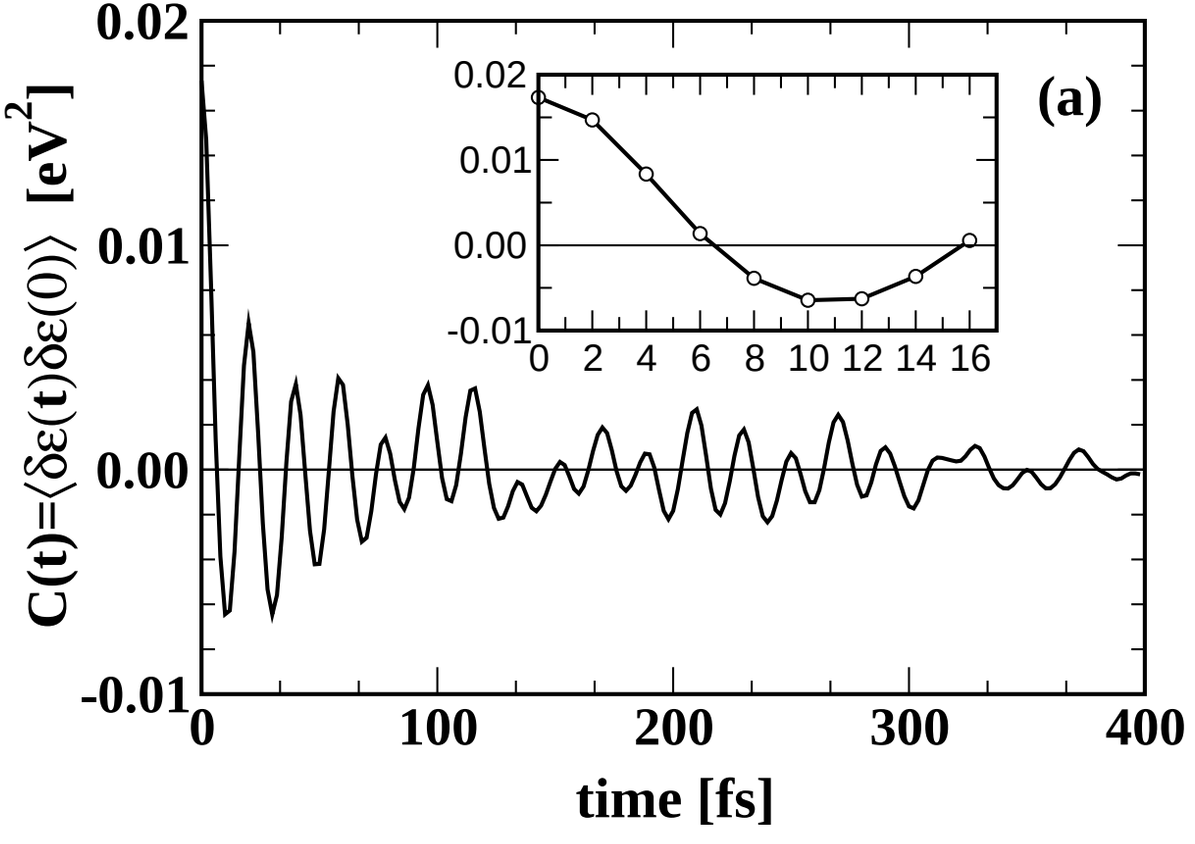


ground states

excited states

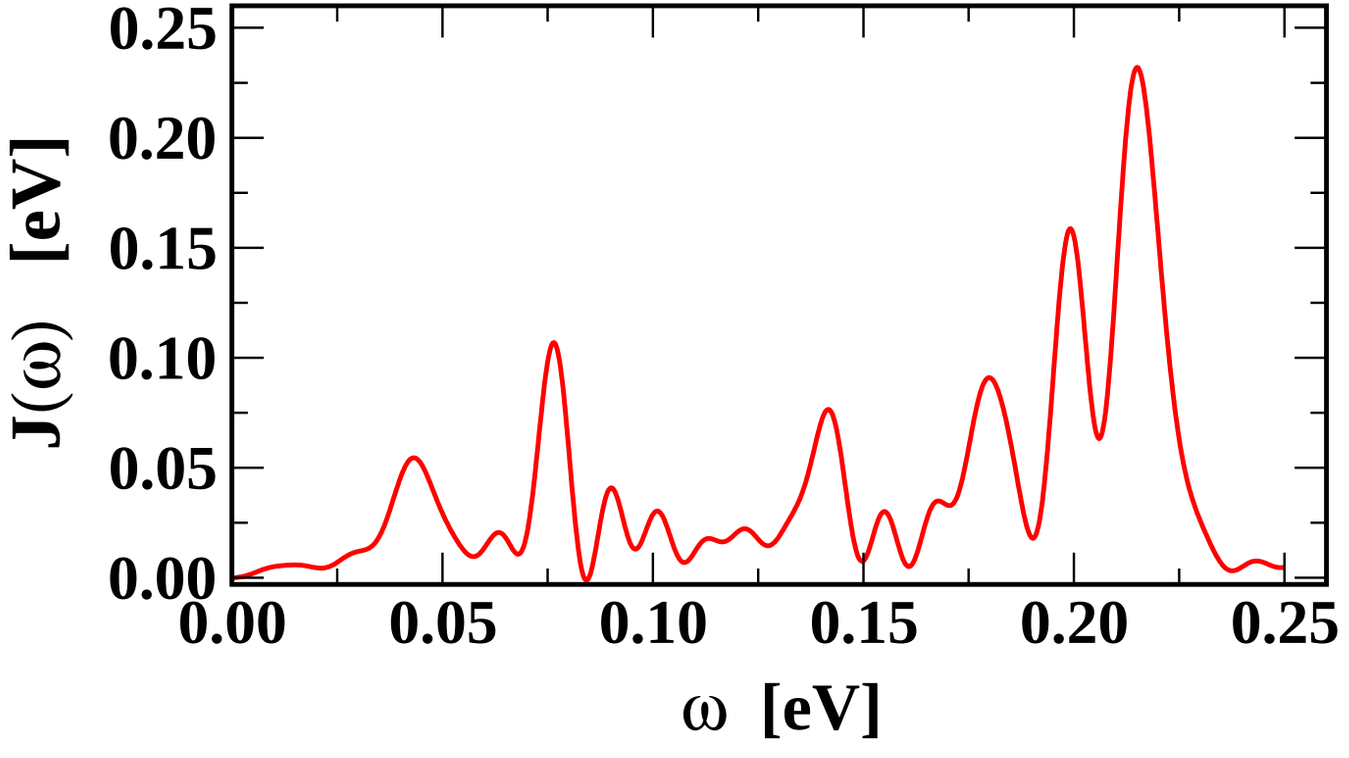
Energy gap correlation function

$$\mathscr{C}(t_i) = \frac{1}{M}\sum_{j=1}^{M}\left[\frac{1}{N-i}\sum_{k=1}^{N-i}\delta\varepsilon_j(t_i+t_k)\delta\varepsilon_j(t_k)\right]$$



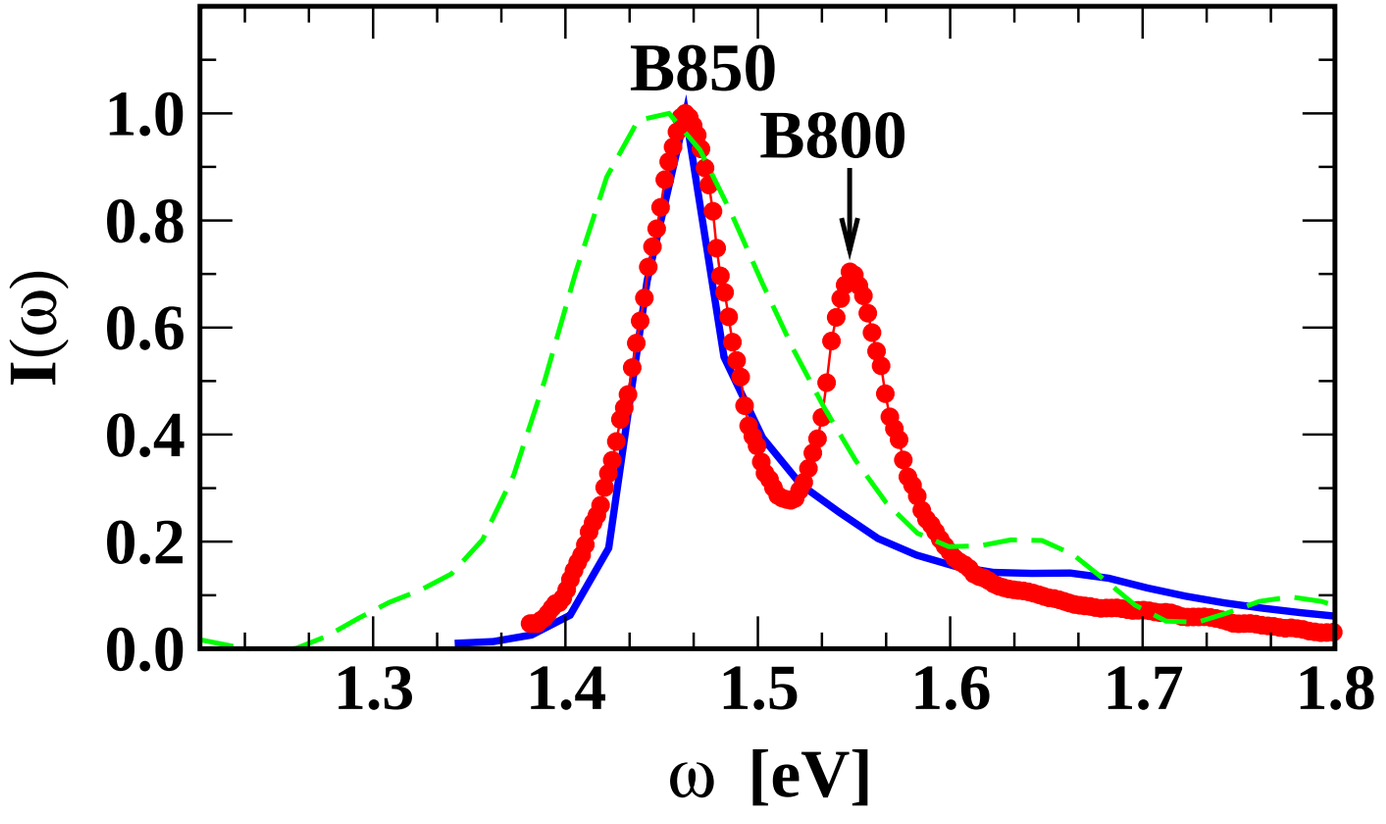
Spectral density

$$J(\omega) = \frac{2}{\pi} \tanh(\beta\omega/2) \int_0^\infty dt\, \mathscr{C}(t) \cos \omega t$$



Absorption spectra for ring

Quantum biology



- red: experiment
- green: direct from MD simulation
- blue: polaron model

Fluorescence depolarization dynamics in the B850 ring of purple bacteria

in collaboration with

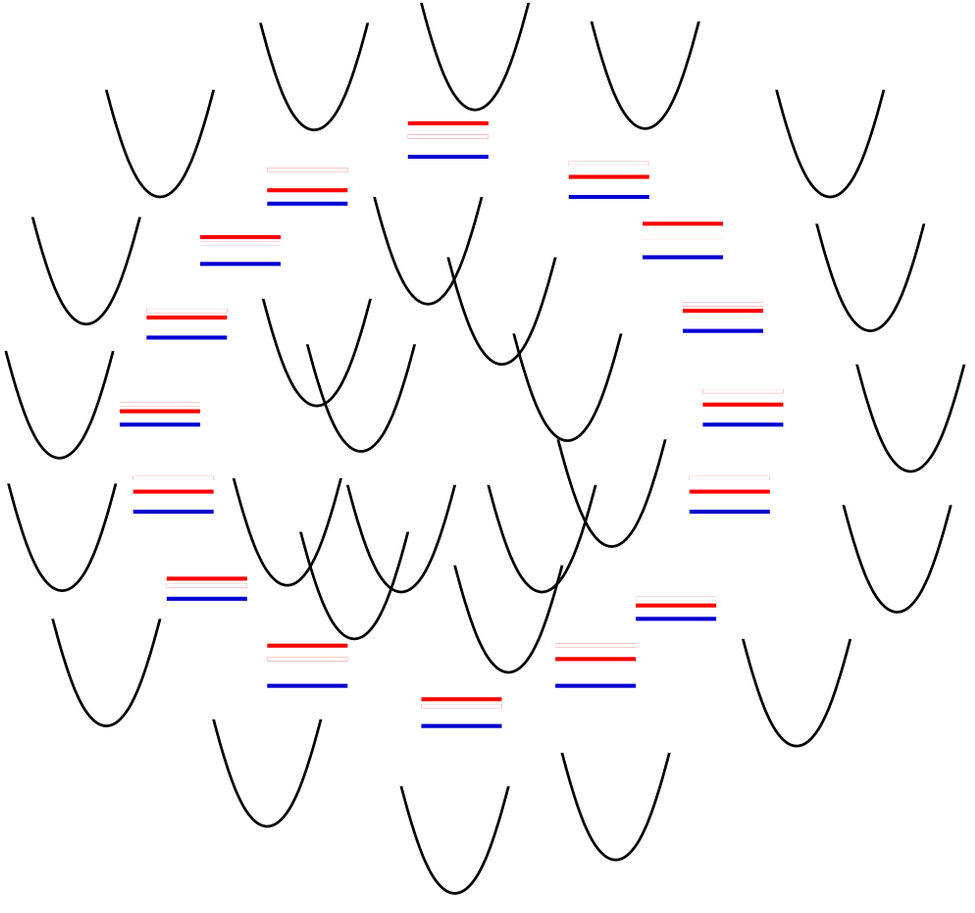
I. Barvík, P. Heřman, I. Kondov, M. Schreiber

Prag, Hradec Králové, Chemnitz, Chemnitz

Chem. Phys. **275**, 1–13 (2002)
J. Phys. Chem. B. **107**, 14094–14102 (2003)

Modeling

- 18 coupled two-level systems
- coupled to a thermal bath, which is characterized by its spectral density $J(\omega)$



- only transfer between neighboring sites
- $H_{\mathrm{sb}} = -\sum_M a_M^\dagger a_M \sum_{i=1}^{N} c_i^M x_i$

Model of LH-II (B850 ring)

- tight-binding model for ring with 18 sites
- only transfer between neighboring sites
- two different transfer strengths: $J_2 = 0.7J$
- dissipation in Redfield approximation
- static site disorder with Gaussian distribution
  (standard deviation Δ)
- dipole-allowed transitions from the ground state populate only the degenerate $k = \pm 1$ levels
- orientational averaging
- time scale: $\tau = 1$ corresponds to 13 fs
  (for $J = 400\mathrm{cm}^{-1}$)

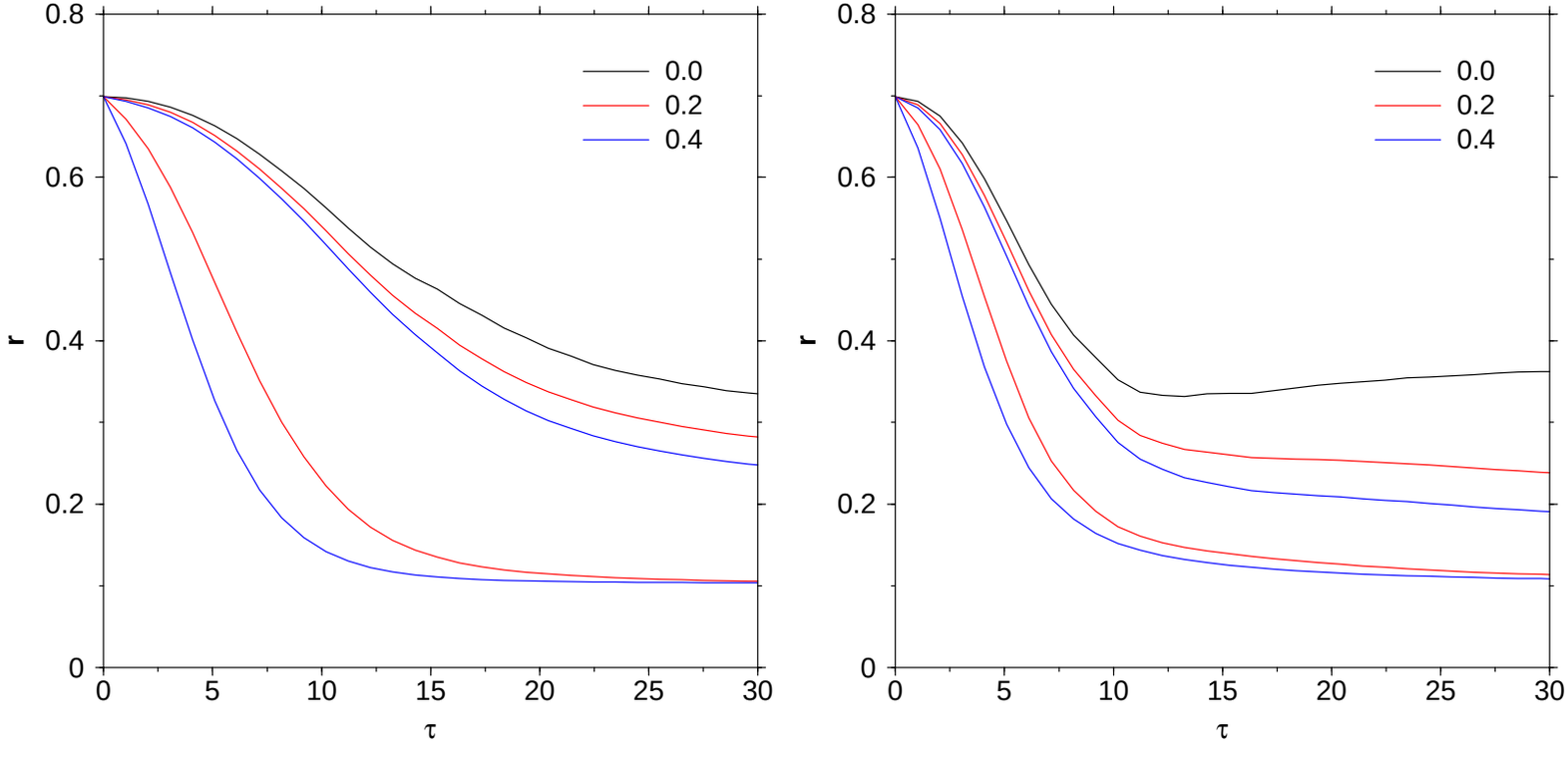
Anisotropy of Fluorescence

$$r(t) = \frac{\langle S_{xx}(t)\rangle - \langle S_{xy}(t)\rangle}{\langle S_{xx}(t)\rangle + 2\langle S_{xy}(t)\rangle}$$

Transient Gain Signal

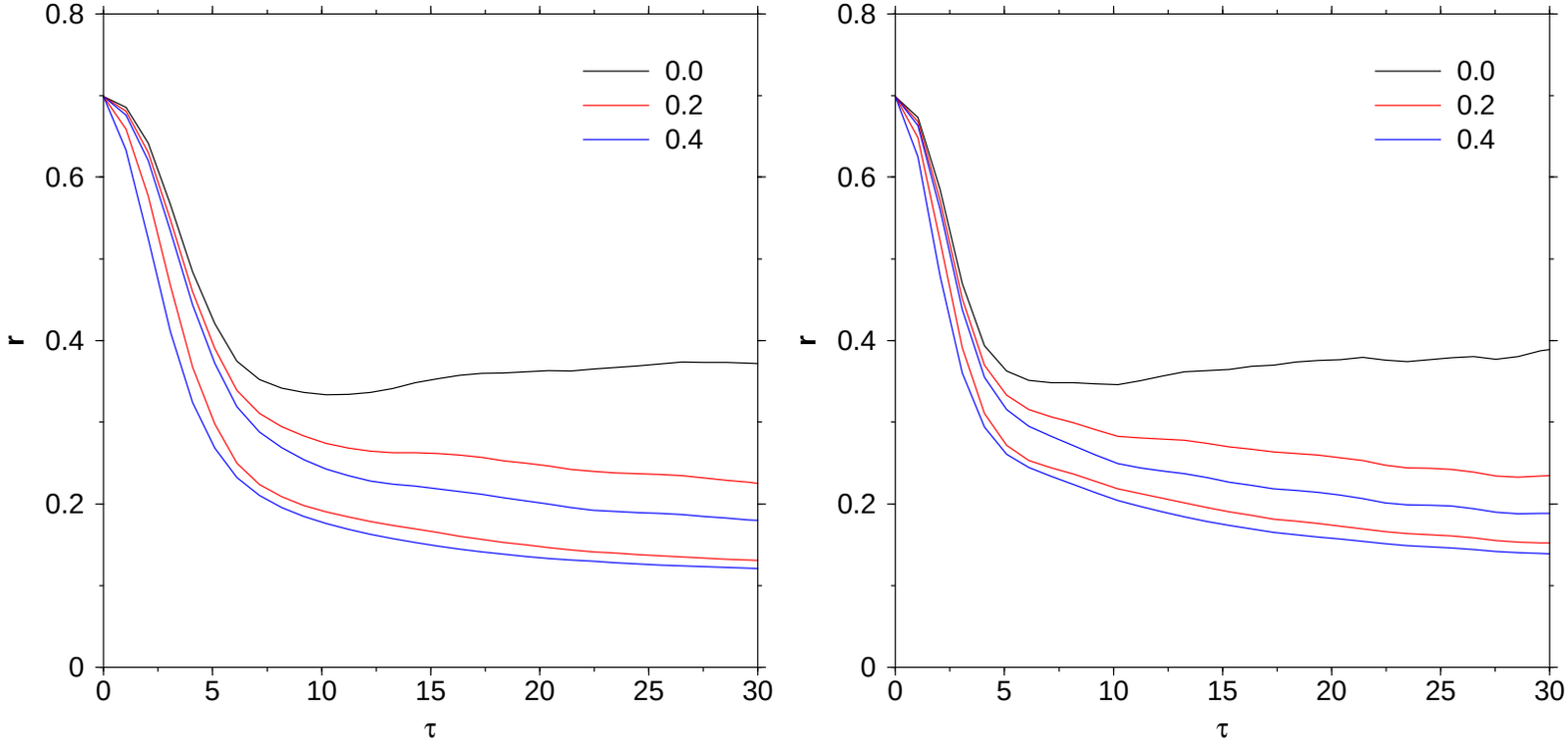
$$\langle S_{xy}(t)\rangle = \langle | \sum_{\alpha,l,n} (\vec{e}_x \cdot \vec{\mu}_\alpha)(\vec{e}_y \cdot \vec{\mu}_l) c_n^{\alpha *} c_n^l \mathrm{e}^{-i\omega_l t} |^2 \rangle$$

Static Disorder: $\Delta = 0.2J$ and $\Delta = 0.4J$



Anisotropy of Fluorescence

Static Disorder: $\Delta = 0.6J$ and $\Delta = 0.8J$



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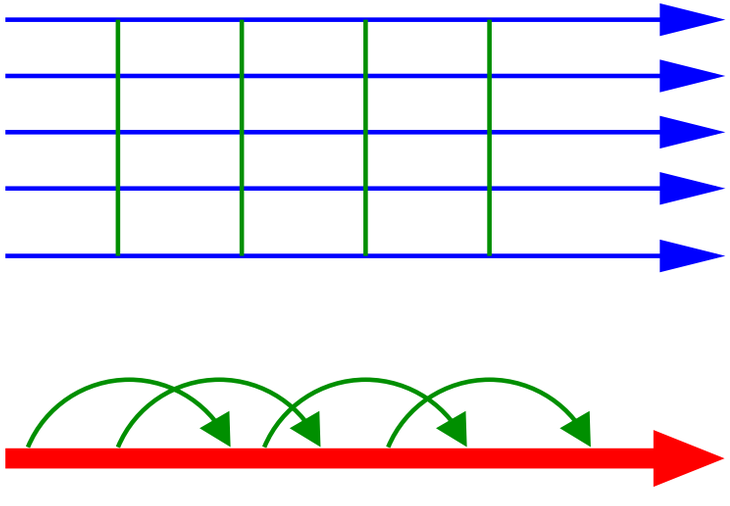
R. Kumble and R. Hochstrasser, J. Chem. Phys. **109**, 855 (1998)

Redfield theory

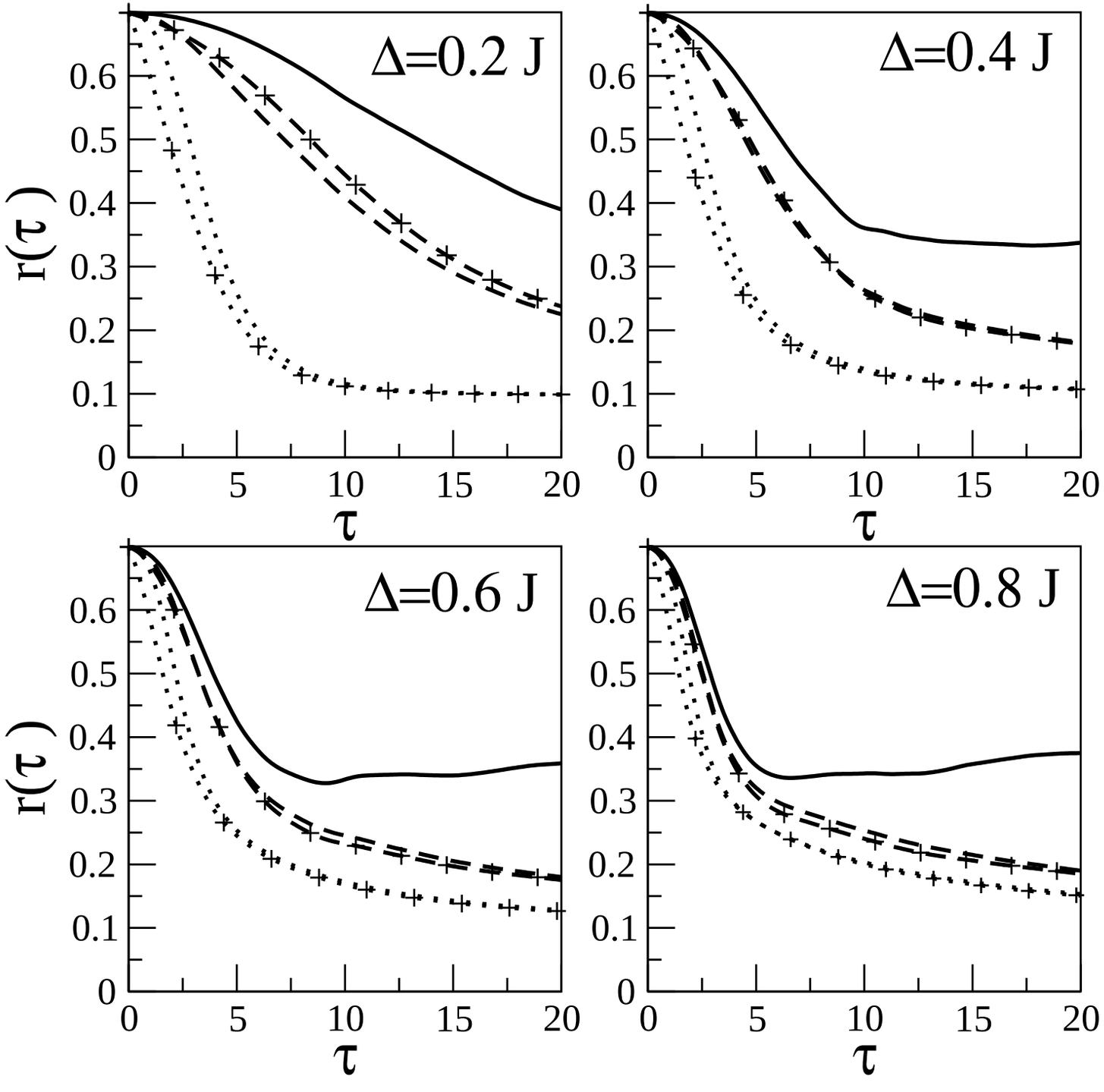
$$H = H_S + H_B + H_{SB}$$

- every environmental degree of freedom only slightly distorted
  $\Rightarrow$ modeled by harmonic oscillators
- how strongly does the environment absorb energy?
  $\Rightarrow$ spectral density $J(\omega)$
- 2nd order perturbation theory in the system-bath coupling H_{SB}
- Markov approximation (neglect of memory effects)
  (bath correlation times τ_B << typical system times τ_S)

$$\rho = tr_B(\sigma)$$



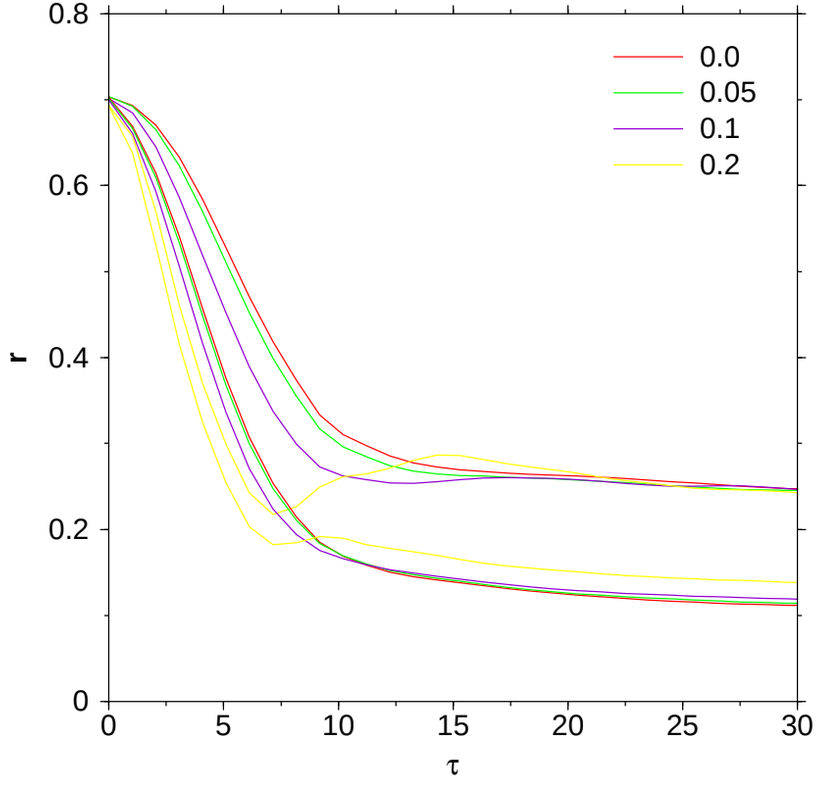
Memory effects



Elliptical Deformation of the Ring

- recent single molecule spectroscopy experiments show C_2 distortion of the LH2 ring

- not clear if also present *in vivo*



M. Matsushita, et al. Biophys. J. **80** 1604 (2001)

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