An Open System Dynamics Approach for Polyatomic Molecules: Excitons in Chromophore Complexes

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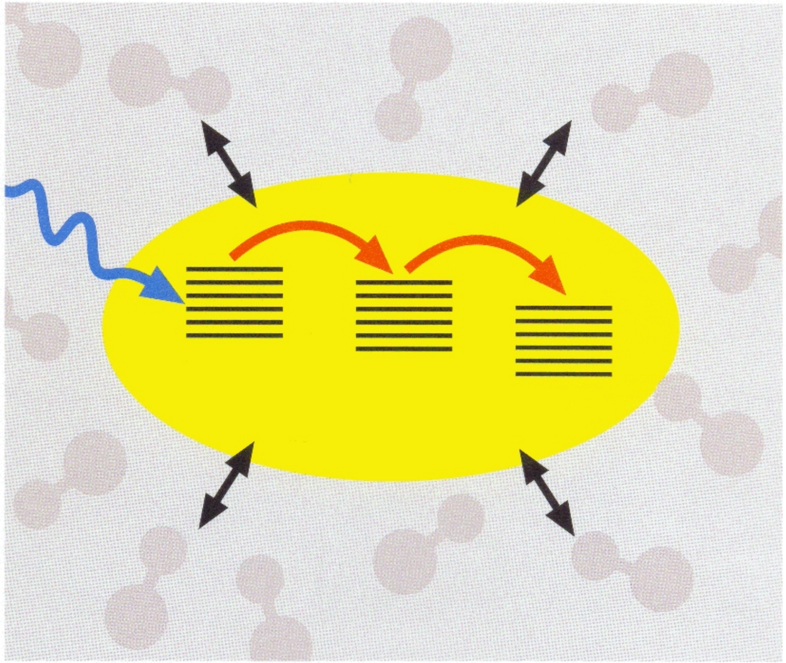
Charge and Energy Transfer Dynamics in Molecular Systems

Second, Revised and Enlarged Edition



This second edition is based on the successful concept of the first edition in presenting a unified perspective on molecular charge and energy transfer processes. The authors bridge the regimes of coherent and dissipative dynamics, thus establishing the connection between classic rate theories and modern treatments of ultrafast phenomena. The book serves as an introduction for graduate students and researchers.

Among the new topics of this second edition are:

- quasiclassical and quantum-classical hybrid formulations of molecular dynamics
- the basics of femtosecond nonlinear spectroscopy
- electron transfer through molecular bridges and proteins
- multidimensional tunneling in proton transfer reactions
- two-exciton states and exciton annihilation in biological and nonbiological chromophore complexes.

More illustrating examples as well as an enlarged reference list are added. A new chapter gives an introduction into the theory of laser pulse control of molecular transfer processes.

__Volkhard May__ studied Physics at the Humboldt-University Berlin, PhD in Theoretical Physics in 1981, Habilitation in Theoretical Physics at the College of Education, Güstrow in 1987, work at the Institute of Molecular Biology, Berlin, Department of Biophysics from 1987 to 1991, since 1992 senior researcher at the Institute of Physics of the Humboldt-University Berlin, research visits to Russia and USA, current research focussed on the theory of transfer phenomena in molecular nanostructures.

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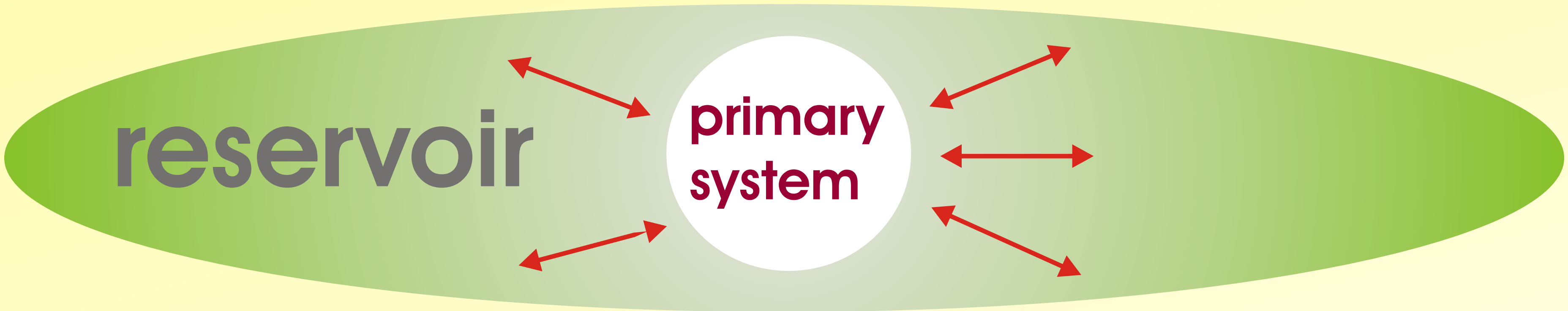
Content of the Talk

- the reduced density operator and the Quantum Master Equation
- some extensions
- laser pulse control of open system dynamics
- Frenkel-exciton dynamics in chromophore complexes

The Reduced Density Operator

complete description by the solution of the time-dependent Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\Psi(q_1,\ldots,q_N;t) = (H_{\mathrm{mol}} + H_{\mathrm{field}}(t))\Psi(q_1,\ldots,q_N;t)$$



reduced description by the determination of the density matrix of the primary system

$$\rho(q_1,\ldots,q_f,\bar{q}_1,\ldots,\bar{q}_f;t) = \int dq_{f+1}\ldots dq_N$$
$$\Psi(q_1,\ldots,q_f,q_{f+1},\ldots,q_N;t)\Psi^*(\bar{q}_1,\ldots,\bar{q}_f,q_{f+1},\ldots,q_N;t)$$

nonequilibrium density operator of the total system

$$\hat{W}(t) = \sum_{\alpha} w_{\alpha} |\psi_{\alpha}(t)\rangle\langle\psi_{\alpha}(t)|$$

observables determined by a selected set of coordinates

$$\hat{\rho}(t) = \sum_{r} \langle\phi_r|\hat{W}(t)|\phi_r\rangle \equiv \mathrm{tr}_{\mathrm{R}}\{\hat{W}(t)\}$$

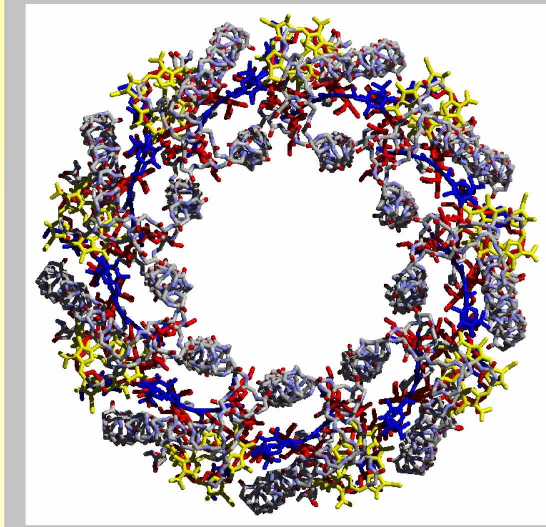
reduced density operator of the primary system

trace with respect to the secondary system (reservoir)

Computation of the reduced density operator ?

dissipative quantum dynamics -> introduction of a system-reservoir Hamiltonian

$$H(t) = H_{\mathrm{S}}(t) + H_{\mathrm{S-R}} + H_{\mathrm{R}}$$



Lh2 of purple bacteria

general structure of the density operator equation

$$\frac{\partial}{\partial t}\hat{\rho}(t) = \hat{I}(t,t_0) + -\frac{i}{\hbar}[H_{\mathrm{S}}(t) + H_{\mathrm{mf}}, \hat{\rho}(t)]_{-} + \hat{D}(t,t_0;\hat{\rho})$$

initial correlations

coherent dynamics

dissipative dynamics

The Quantum Master Equation

- second-order primary-system reservoir coupling
- if necessary neglect of memory effects

$$H_{\mathrm{S-R}} = \sum_u K_u \Phi_u$$

factorization of the system-reservoir coupling dissipative part of the quantum master equation

$$\hat{D}_{\mathrm{QME}}(t,t_0;\hat{\rho}) = -\sum_{u,v}\int_{t_0}^{t} d\bar{t}$$

$$(C_{uv}(t-\bar{t})[K_u,\ U_{\mathrm{S}}(t,\bar{t})K_v\hat{\rho}(\bar{t})U_{\mathrm{S}}^{+}(t,\bar{t})]_-$$

$$-C_{vu}(-t+\bar{t})[K_u,\ U_{\mathrm{S}}(t,\bar{t})\hat{\rho}(\bar{t})K_vU_{\mathrm{S}}^{+}(t,\bar{t})]_-)$$

memory effects versus Markovian approximation

$$\hat{D}_{\mathrm{QME}}(t,t_0;\hat{\rho}) = \mathcal{D}_{\mathrm{QME}}\ \hat{\rho}(t) = -\sum_{u,v}\int_{0}^{t-t_0} d\tau$$

$$(C_{uv}(\tau)[K_u,K_v(t-\tau,t)\hat{\rho}(t)]_- - C_{vu}(-\tau)[K_u,\hat{\rho}(t)K_v(t-\tau,t)]_-)$$

reservoir correlation function

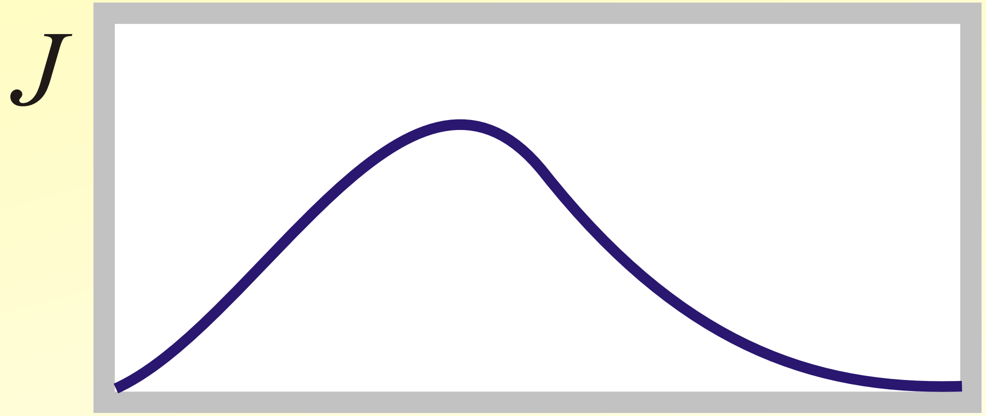
$$C_{uv}(t) = (< U_{\mathrm{R}}^{+}(t)\Phi_u U_{\mathrm{R}}(t)\Phi_v >_{\mathrm{R}} - < \Phi_u >_{\mathrm{R}} < \Phi_v >_{\mathrm{R}})/\hbar^2$$

$$\Phi_u = \hbar \sum_{\xi} \omega_\xi g_u(\xi) Z_\xi$$

linear coupling to normal mode reservoir oscillators

spectral density

$$J_{uv}(\omega) = \sum_{\xi} g_u(\xi) g_v(\xi) \delta(\omega - \omega_\xi)$$



spectral density representation of the reservoir correlation function

$$C_{uv}(t) = \int d\omega e^{-i\omega t} \omega^2 [1 - n(\omega)] (J_{uv}(\omega) - J_{uv}(-\omega))$$

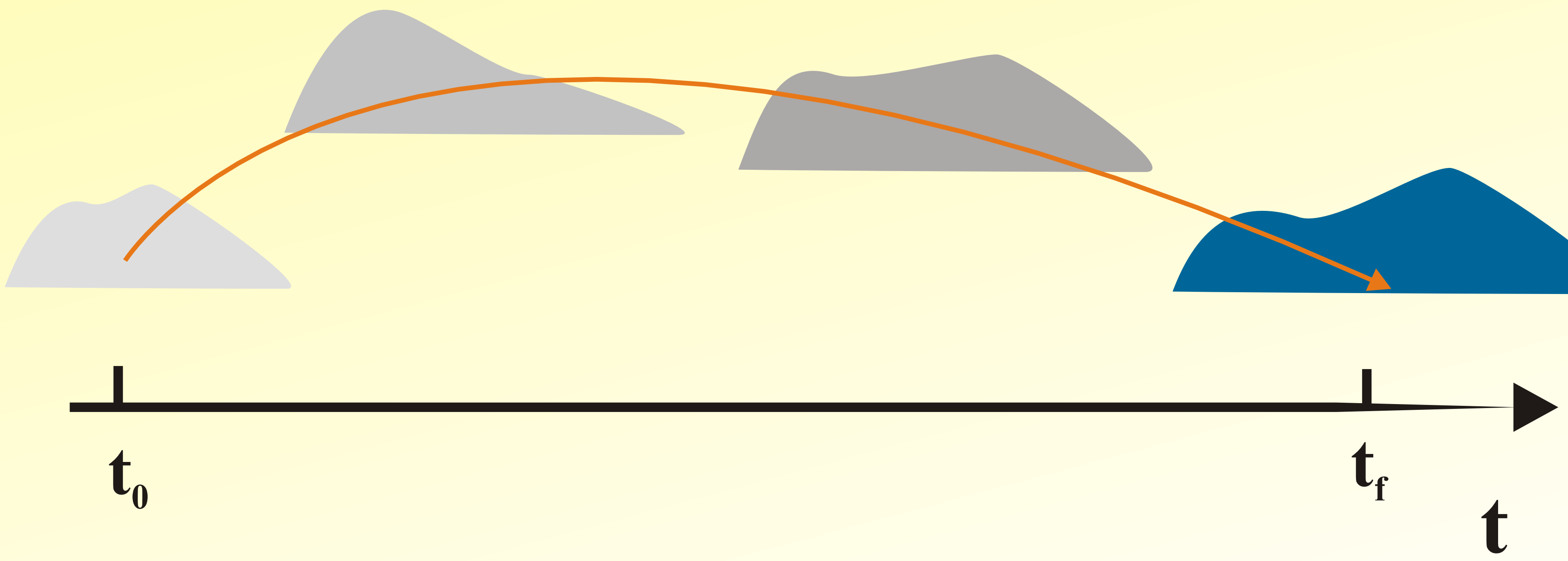
representation in the eigenstates of the molecular Hamiltonian

$$\rho_{ab}(t) = \langle \Psi_a | \hat{\rho}(t) | \Psi_b \rangle$$

multi-level Redfield-theory

$$\frac{\partial}{\partial t}\rho_{ab}(t) = -i\omega_{ab}\rho_{ab}(t) - \sum_{c,d} R_{ab,cd}\rho_{cd}(t)$$

Femtosecond Laser Pulse Control of Open System Dynamics



$$\mathcal{O}[\mathbf{E}_c] = \mathrm{tr_S}\{\hat{O}\hat{\rho}(t_f;\mathbf{E}_c)\}$$

optimization of an observable at a finite time (or in a time and parameter space interval)

control functional to be optimized

$$J[\mathbf{E_c}] = \mathcal{O}[\mathbf{E_c}] - \lambda\left(\frac{1}{2}\int_{t_0}^{t_f} dt\, \mathbf{E}_c^2(t) - I_0\right)$$

-> Optimal Control Theory

functional equation determining the optimal pulse

$$\mathbf{E}_c(t) = \frac{i}{\hbar\lambda}\mathrm{tr_S}\{\hat{O}\,\mathcal{U}(t_f,t;\mathbf{E}_c)[\hat{\mu},\hat{\rho}(t;\mathbf{E}_c)]\}$$

Overview

equation of motion methods

dissipation based on microscopic models

non-Markovian versus Markovian equations

Lindblad-type of dissipation

direct calculation

path-integral representation

two-level model of the reservoir

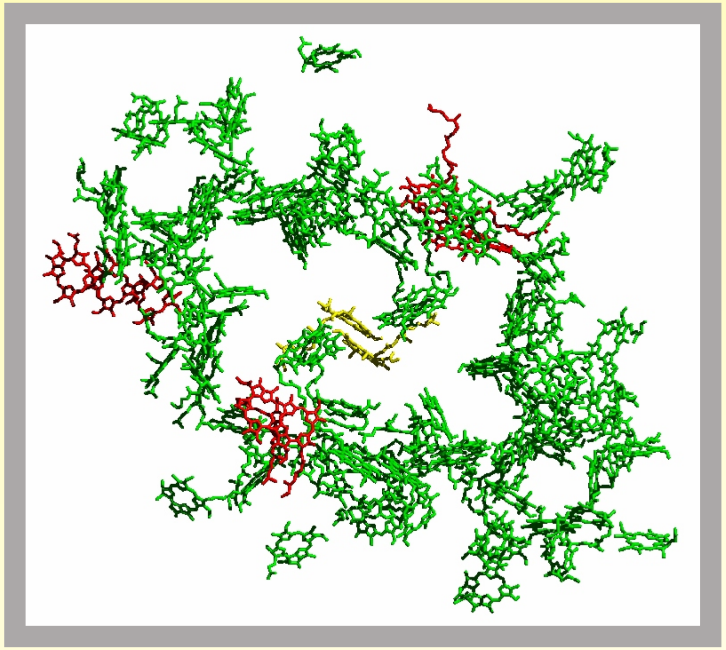
classical description of the reservoir

Application of the Density Operator Technique in Theoretical Chemical Physics and Theoretical Chemistry

- photoexcitation of molecules in a solvent (HF, betaine30, pyrazine)
- photoinduced ultrafast electron transfer in donor-acceptor complexes (mixed-valence compounds, reaction center)
- photodesorption (NO/Pt(111))
- hydrogen-bond dynamics (o-phthalic acid monomethylester)
- exciton transfer in chromophore complexes (Lh2, Lhc2, FMO, Ps1)

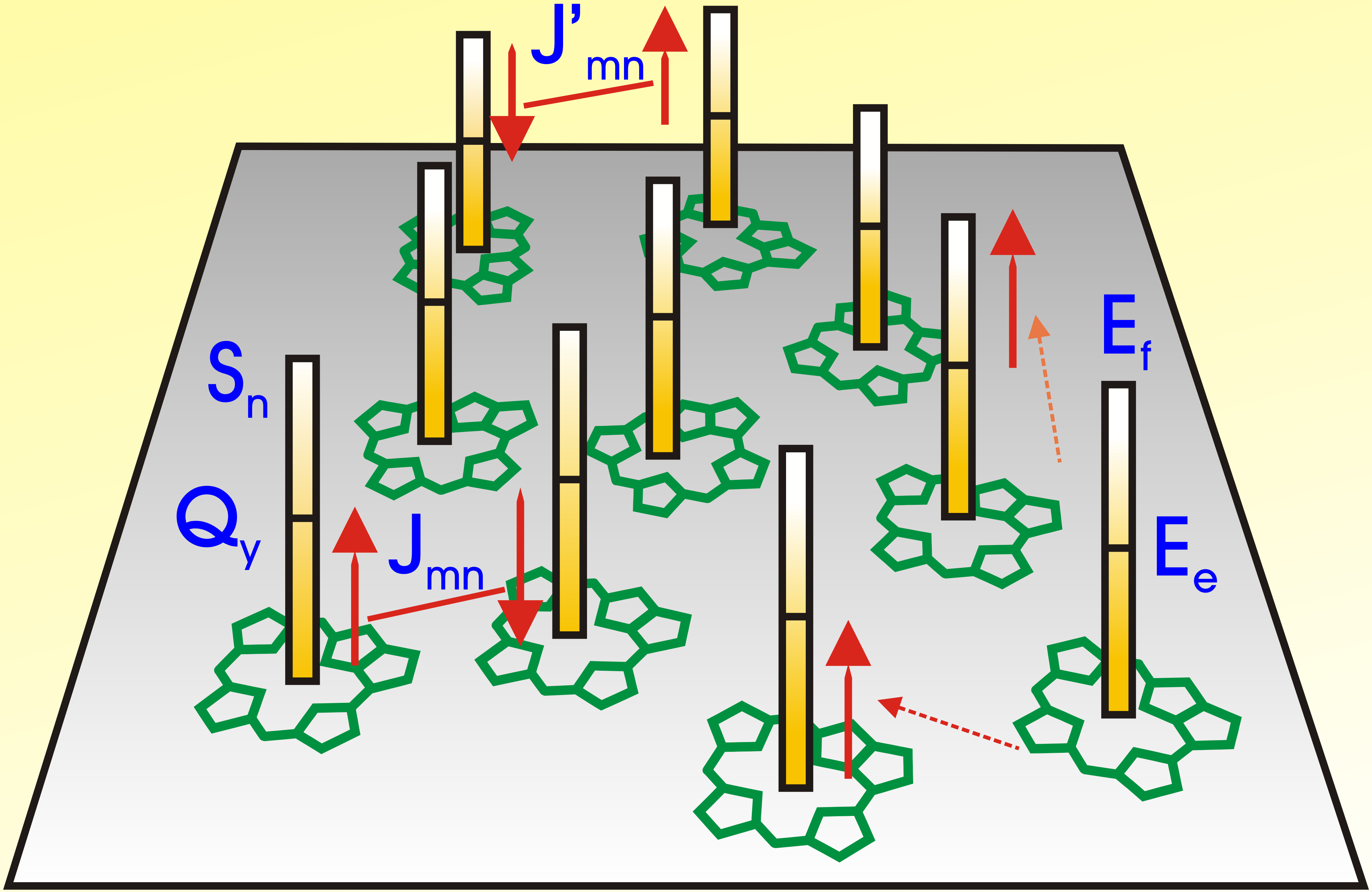
Reduced Density Matrix Description of Electronic Frenkel-Excitons

Excitation Energy Motion in Photosynthetic Antennae

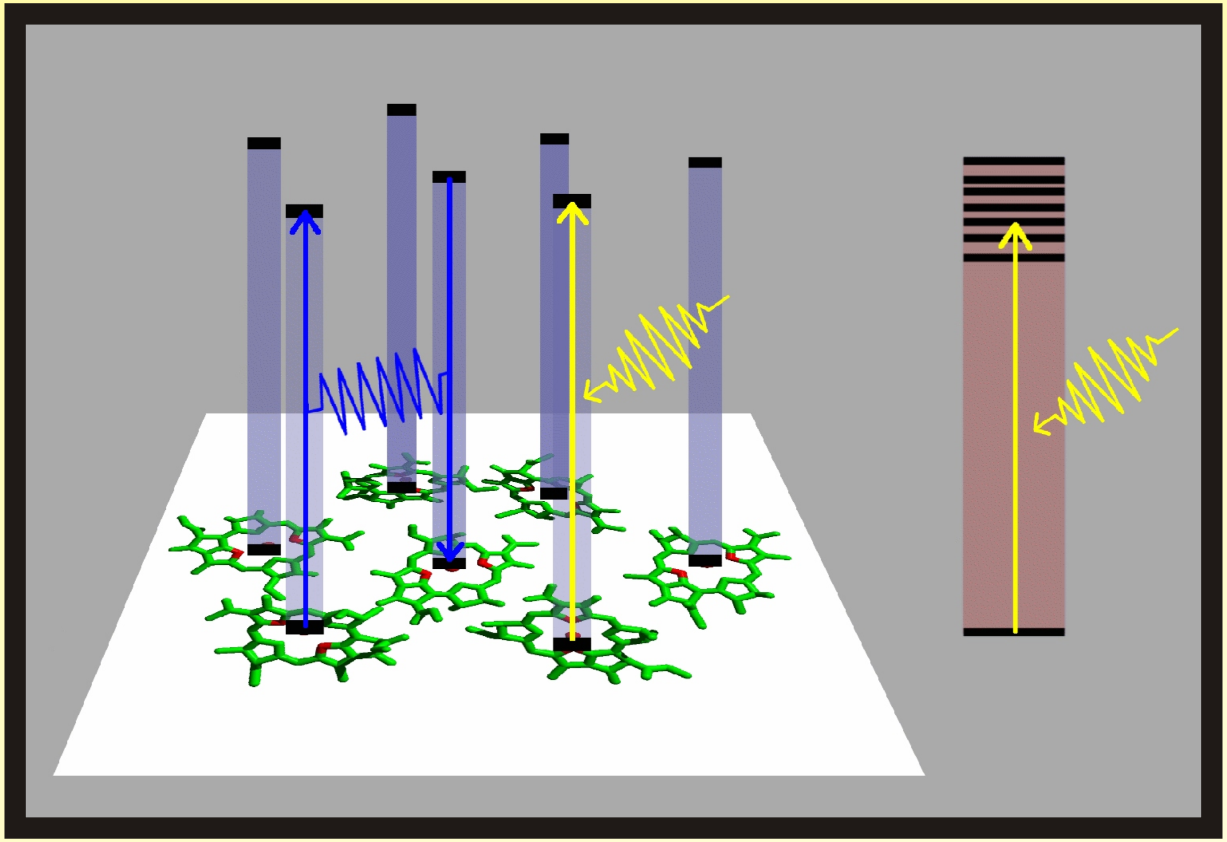


- primary system: excitons
- reservoir: vibrations (mainly intra molecular)
- moderate exciton-vibrational coupling

Electronic Level Scheme of the Chromophore Complex



Formation of Delocalized Single- and Two-Exciton States



ground-state

$$|\alpha_0\rangle = \prod_m |\varphi_{mg}\rangle$$

single exciton state

$$|\alpha_1\rangle = \sum_m C(\alpha_1; m)|\phi_m\rangle$$

two-exciton state

$$|\alpha_2\rangle = \sum_{m,n} C(\alpha_2; mn)|\phi_{mn}\rangle$$

Th. Renger, V. M., and O. Kühn,
Phys. Rep. 343, 137 (2001)

multiexciton density operator

$$\rho(\alpha_M, \beta_N; t) = \langle \alpha_M | \hat{\rho}(t) | \beta_N \rangle$$

multiexciton Quantum Master Equation

$$\frac{\partial}{\partial t}\hat{\rho}(t) = -\frac{i}{\hbar}[H_{\mathrm{mx}} + H_{\mathrm{field}}(t), \hat{\rho}(t)] - (\mathcal{R}_{\mathrm{mx-vib}} + \mathcal{R}_{\mathrm{eea}})\hat{\rho}(t)$$

external field induced coherent motion

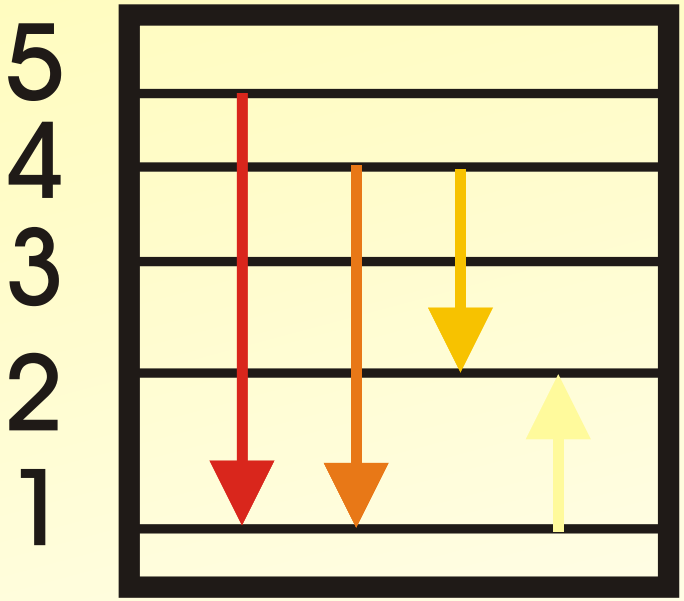
exciton relaxation

exciton-exciton annihilation

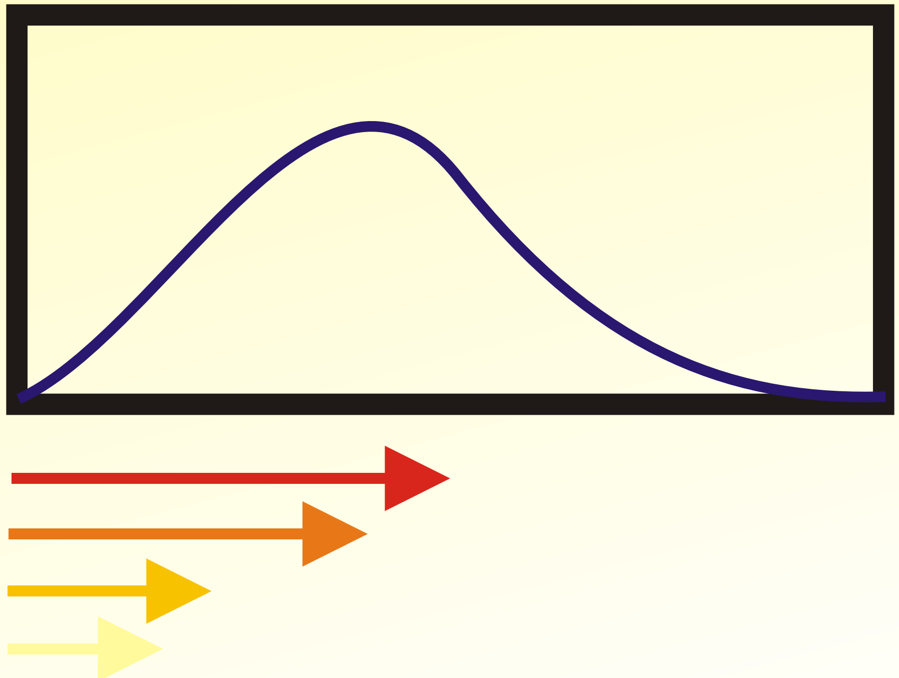
Exciton Relaxation and the Spectral Density

$$\mathcal{R}_{\mathrm{mx-vib}}\,\hat{\rho}(t) = \sum_{N=1,2}\sum_{\alpha_N,\beta_N} k^{(\mathrm{mx-vib})}_{\alpha_N\to\beta_N}$$
$$\times\{\frac{1}{2}[|\alpha_N\rangle\langle\alpha_N|,\hat{\rho}(t)]_+ - |\beta_N\rangle\langle\alpha_N|\hat{\rho}(t)|\alpha_N\rangle\langle\beta_N|\}$$

energy



spectral density

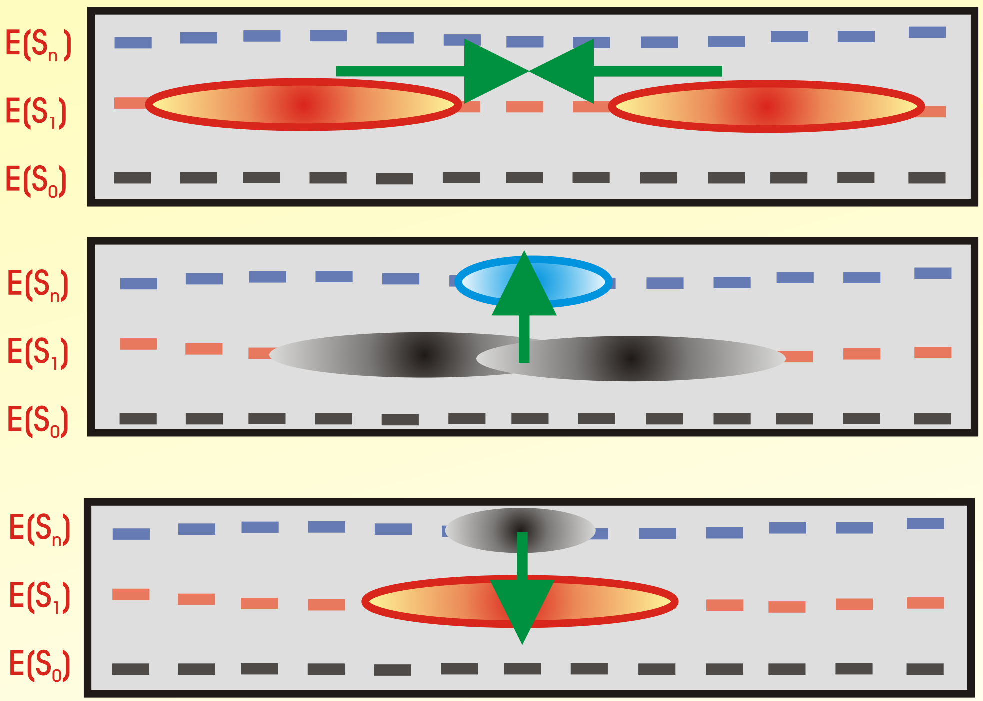


Exciton Exciton Annihilation

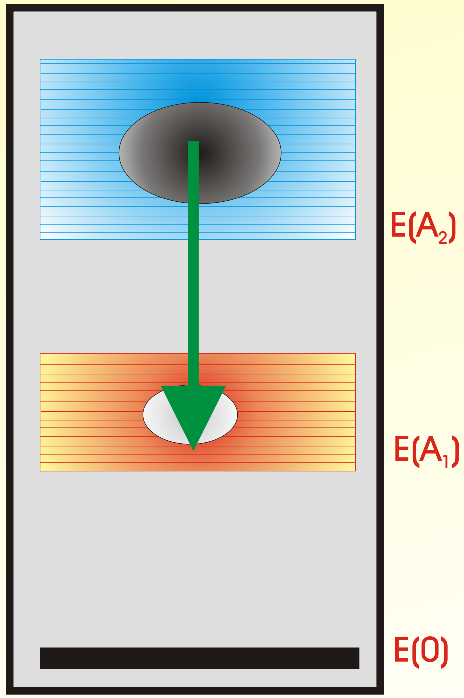
$$\mathcal{R}_{\mathrm{EEA}}\hat{\rho}(t) = \sum_{\alpha_2,\beta_1} k^{(\mathrm{EEA})}_{\alpha_2\to\beta_1}$$

$$\times\{\frac{1}{2}[|\alpha_2\rangle\langle\alpha_2|, \hat{\rho}(t)]_+ - |\beta_1\rangle\langle\alpha_2|\hat{\rho}(t)|\alpha_2\rangle\langle\beta_1|\}$$

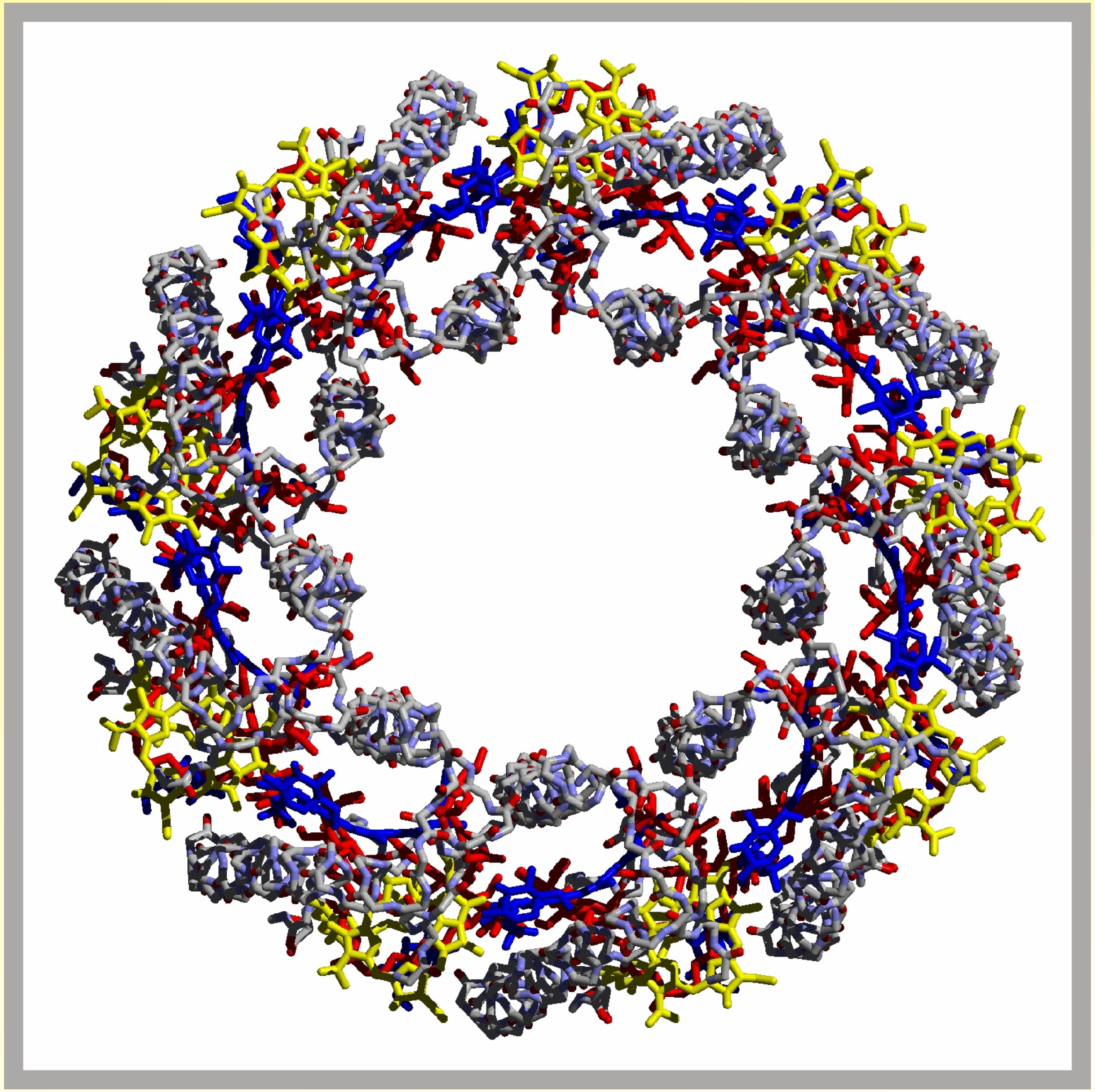
Chain of Three-Level Molecules



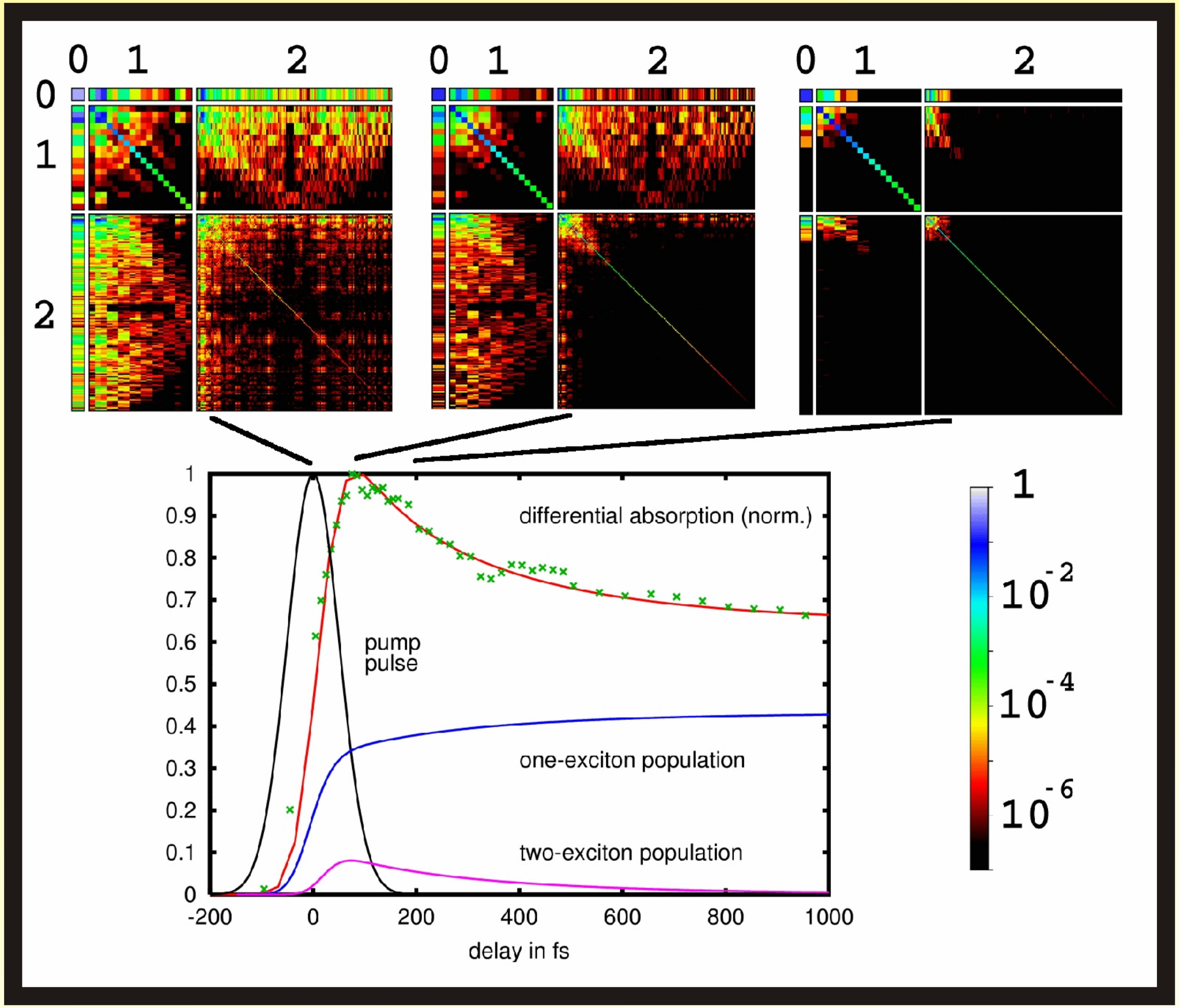
Transitions between Multiexciton States

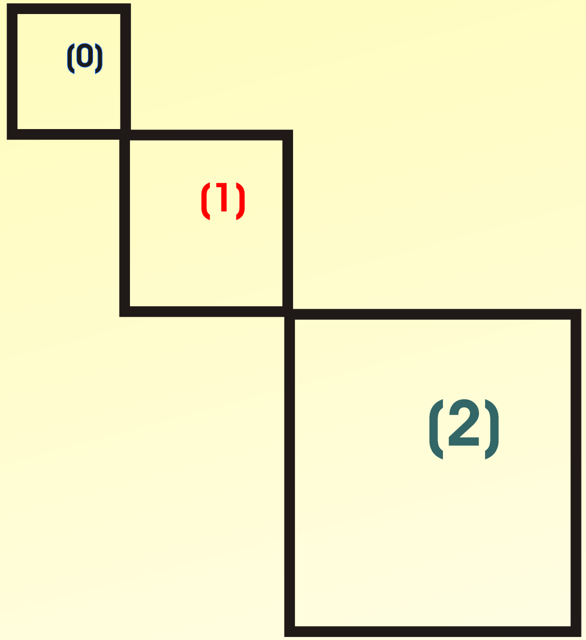


Lh2 of Purple Bacteria



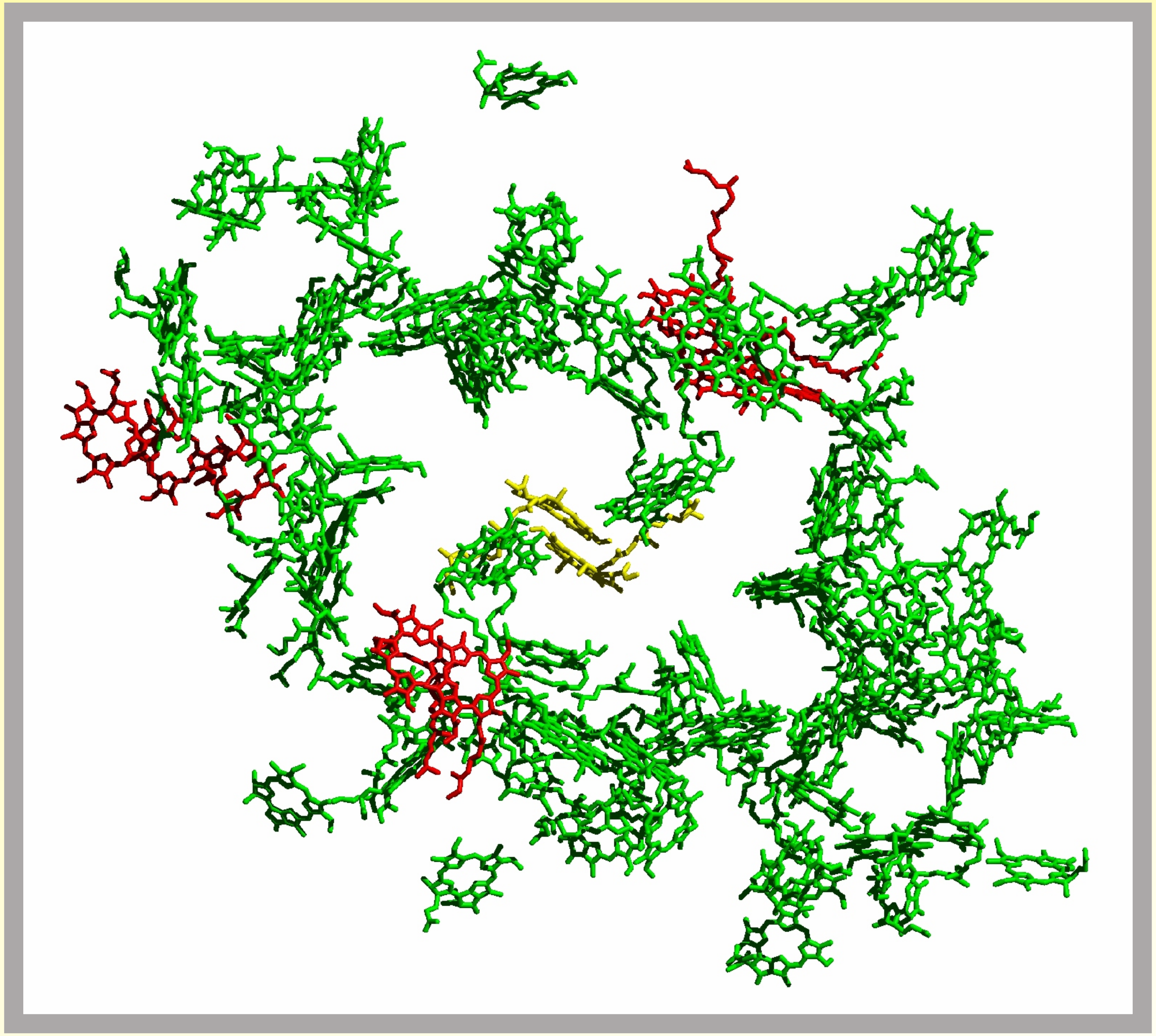
Multiexciton Dynamics and Transient Absorption of the Lh2



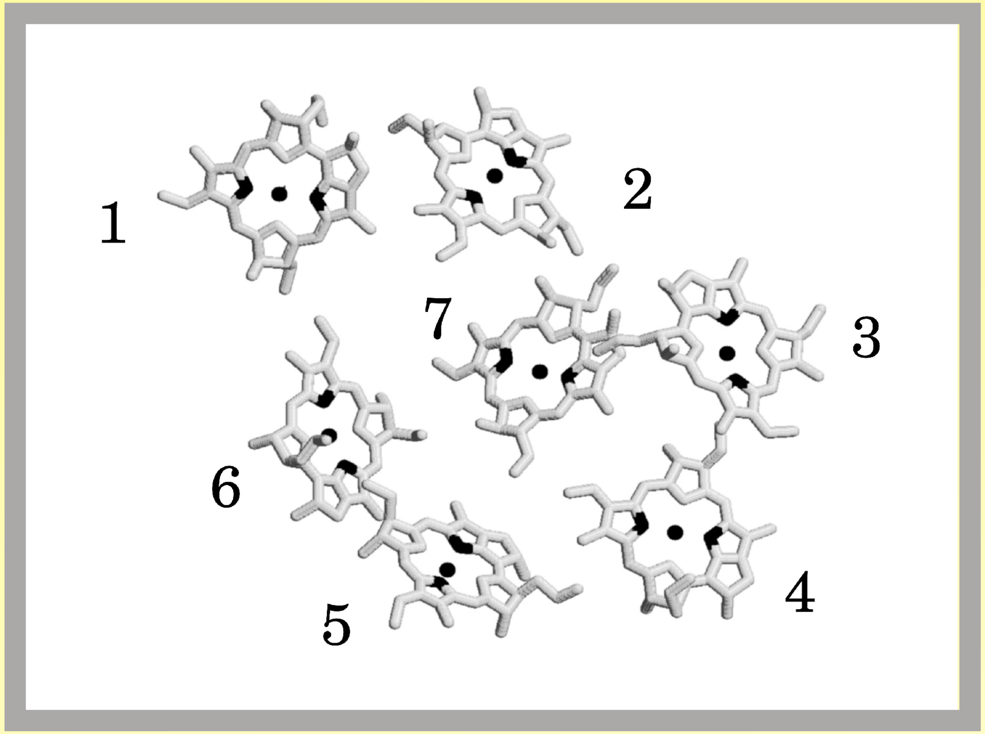


B. Brüggemann and V. M., JCP 120, 2325 (2004)

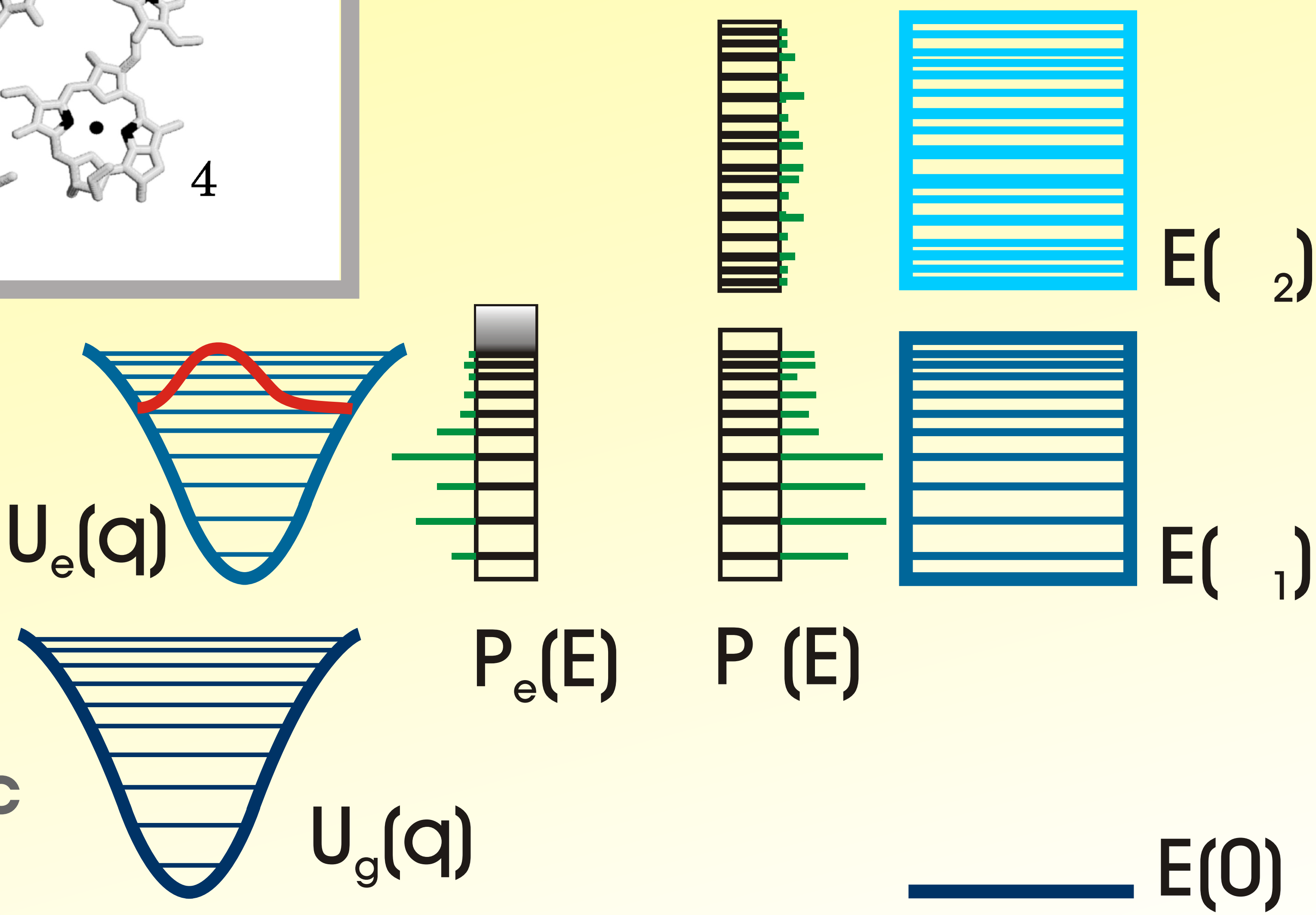
Ps1 complex of *Synechococcus elongatus*



Fs-Laser Pulse Control of Exciton Dynamics

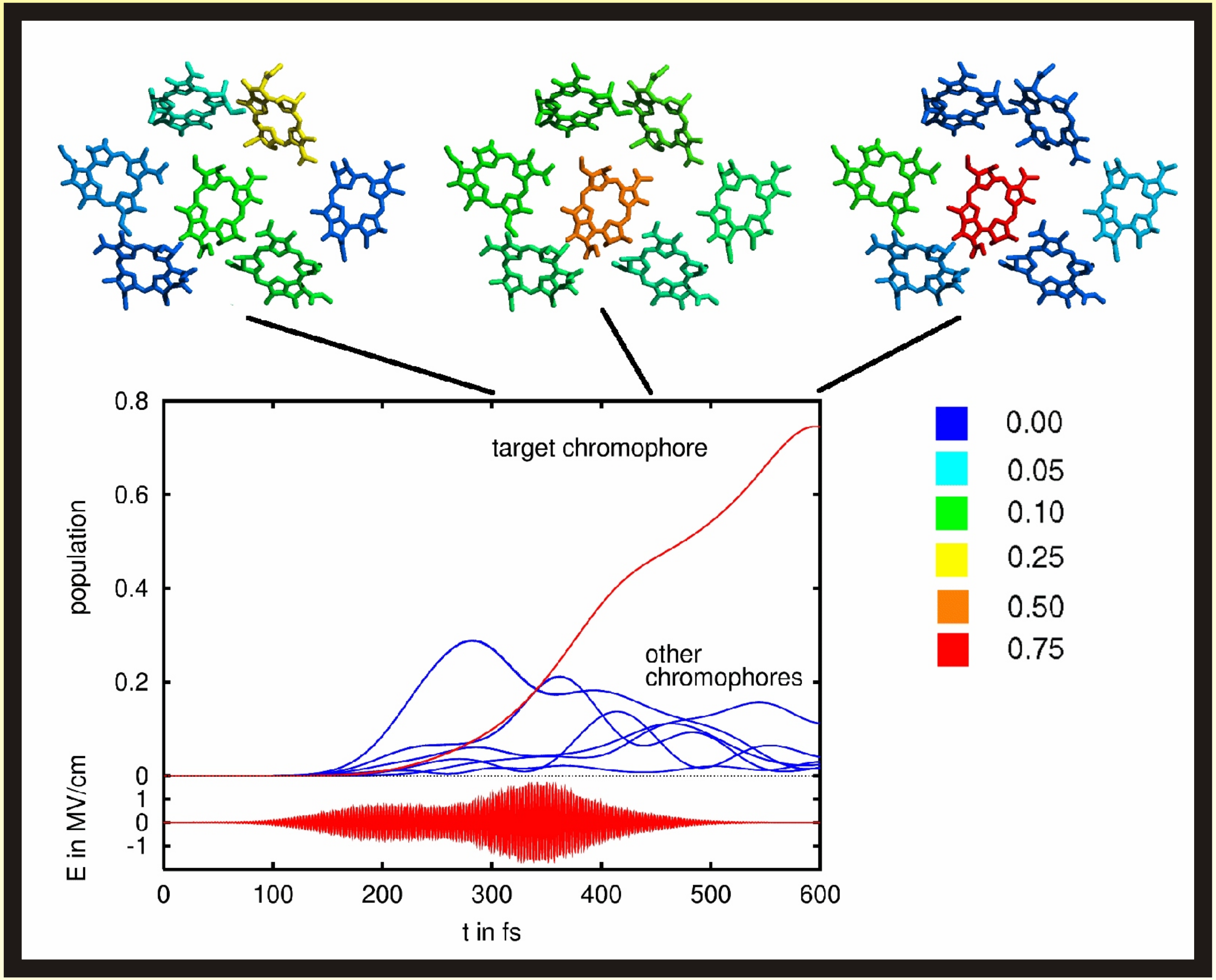


monomeric structure of the FMO complex



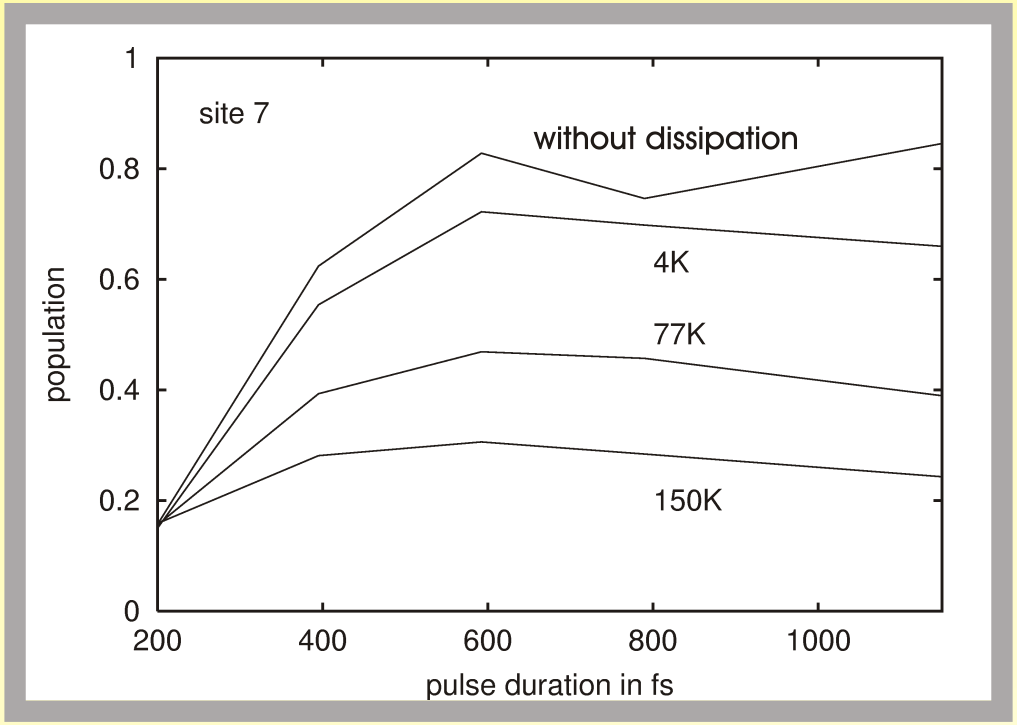
vibrational wavepackets versus excitonic wavepackets

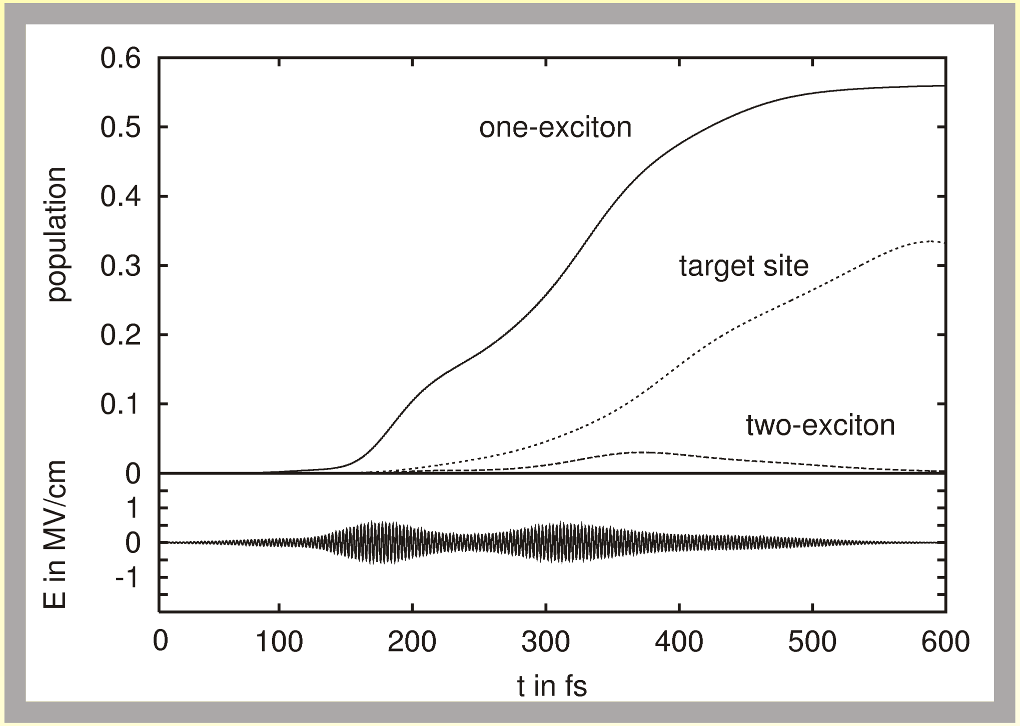
Laser Pulse Excitation Energy Localization in the FMO-Complex



B. Brüggemann, and V. M., JPC B 108, 10529 (2004)

Excitation Energy Localization at Chromophore m=7



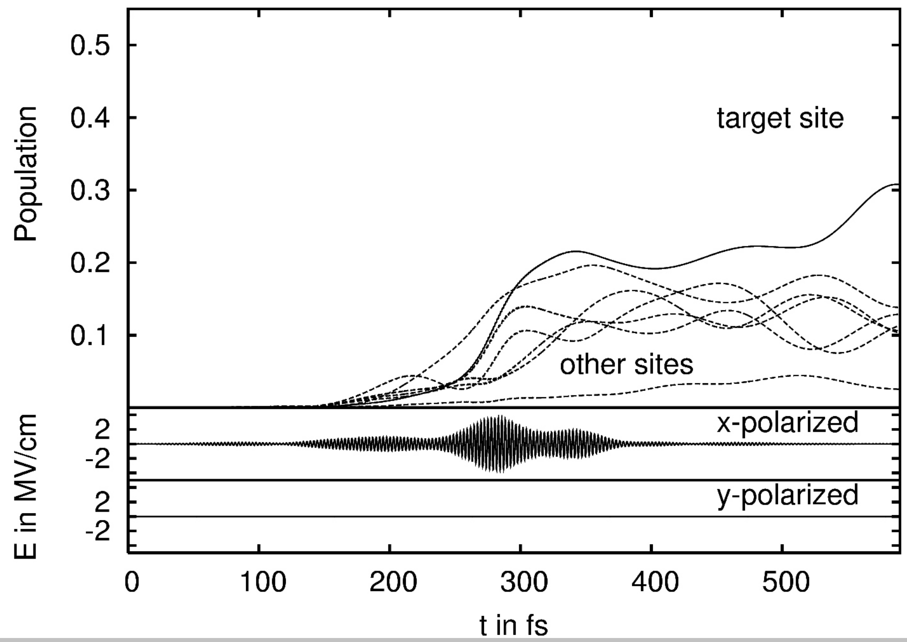


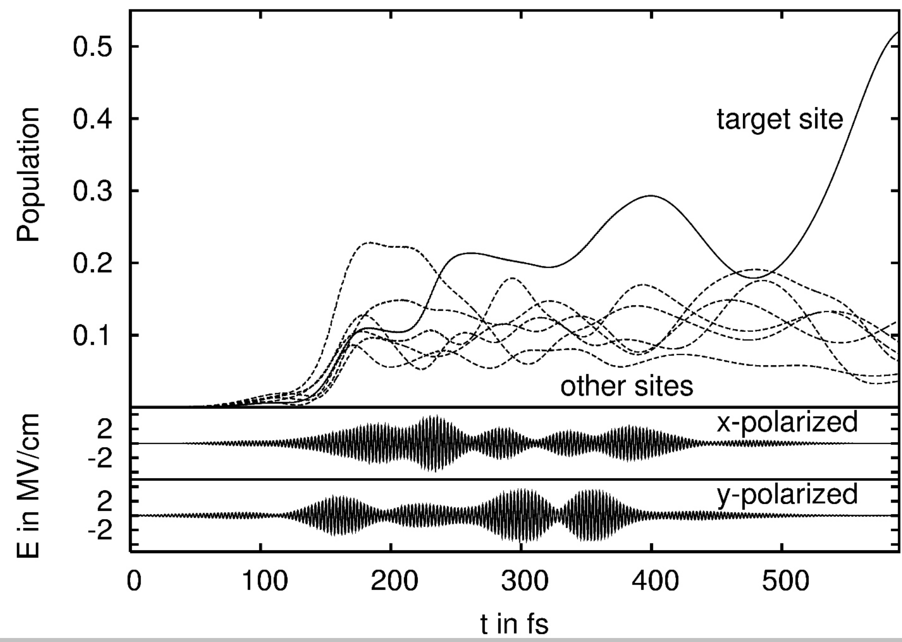
in dependence on:

- the control pulse length
- temperature
- including two-exciton states

Linear versus circular polarization of the control pulse

$$E_{j=x,y} = \frac{1}{N} \sum_p \frac{i}{\hbar\lambda} \mathrm{tr}\{\hat{\theta}^{(p)}(t; E_x, E_y)\, [\hat{\mu}_j^{(p)}, \hat{\rho}^{(p)}(t; E_x, E_y)]\}$$





B. Brüggemann, T. Pullerits, and V. M., (in press)

Conclusions

What are the applications the reduced density matrix theory is appropriate for ?

- the experiment suggests a system-reservoir separation
- weak coupling to the environment
- details of the equilibrium state of the environment are of less importance
- comprohensive description of an experiment (nonlinear action of ultrafast external fields)

Advertisement of a Vacancy

A PhD position is open at the Humboldt-University at Berlin, Institute of Physics in the field of Theoretical Chemical Physics.

The project is entitled:

Excitation Energy Transfer in Chromophore Complexes: Theoretical Investigations on Supramolecular Pheophorbide-a-Systems