

The Driven Anharmonic Oscillator

we consider the 1d–motion of an active system driven by a laser pulse and coupled to a reservoir; the latter is described as a huge number of harmonic oscillators in thermodynamic equilibrium; the system Hamiltonian takes the form

$$H_S(t) = \frac{p^2}{2m} + U(s) - \boldsymbol{\mu}\mathbf{E}(t)$$

s is the 1d–system coordinate; the potential shall have a minimum at $s = 0$; a possible application would be the OH–stretching vibration of a water molecule; the potential can be well approximated by a Morse–potential

$$U(s) = E_{\text{diss}} \left(1 - e^{-\alpha s}\right)^2 - E_{\text{diss}}$$

the laser pulse is linearly polarized

$$\mathbf{E}(t) = \mathbf{n}E(t)$$

oscillates with frequency ω_0 and has a duration of τ_p ; accordingly, we write

$$E(t) = E_0 \sin(\omega_0 t) \sin^2(\pi t / \tau_p)$$

we further note

$$\boldsymbol{\mu} = \mathbf{n}\boldsymbol{\mu} \sim e^{-\beta s}$$

the concrete s –dependence refers to the OH–stretching vibration of water;

we note the eigenvalue equation ($\chi_M(s) = \langle s|M \rangle$)

$$\left(\frac{p^2}{2m} + U(s)\right)\chi_M(s) = E_M\chi_M(s) \equiv \hbar\omega_M\chi_M(s)$$

the system–reservoir coupling is of the form

$$H_{S-R} = s \sum_{\xi} \hbar\omega_{\xi}g_{\xi}Q_{\xi}$$

according to the general notation we have $K_u = s$ and $\Phi_u = \sum_{\xi} \hbar\omega_{\xi}g_{\xi}Q_{\xi}$; the matrix elements of $K_u = K = s$ are

$$K_{MN} = \langle M|s|N \rangle = s_{MN}$$

the related reservoir correlation function has been already calculated

$$C(t) = 2\pi\omega^2[1 + n(\omega)](J(\omega) - J(-\omega))$$

we introduce the (reduced) density matrix

$$\rho_{MN}(t) = \langle M|\hat{\rho}(t)|N \rangle$$

and obtain the related equations of motion as

$$\frac{\partial}{\partial t}\rho_{MN}(t) = -i\omega_{MN}\rho_{MN}(t) + \frac{i}{\hbar}E(t) \sum_K (d_{MK}\rho_{KN}(t) - d_{KN}\rho_{MK}(t)) - \sum_{K,L} R_{MN,KL}\rho_{KL}(t)$$

the Redfield–tensor reads

$$R_{MN,KL} = \delta_{M,K} \sum_F \Gamma_{NF,FL}(\omega_{LF}) + \delta_{N,L} \sum_F \Gamma_{MF,FK}(\omega_{KF}) - \Gamma_{KM,NL}(\omega_{LN}) - \Gamma_{LN,MK}(\omega_{MK})$$

the relaxation matrix takes the form

$$\Gamma_{MN,KL}(\omega) = \text{Re} \sum_{u,v} K_{MN}^{(u)} K_{KL}^{(v)} \int_0^{\infty} d\tau e^{i\omega\tau} C_{uv}(\tau) = s_{MN} s_{KL} \text{Re} \hat{C}(\omega)$$

where we introduced the half–sided Fourier transformation

$$\hat{C}(\omega) = \int_0^{\infty} d\tau e^{i\omega\tau} C(\tau) = \int_0^{\infty} d\tau e^{i\omega\tau} \int \frac{d\omega'}{2\pi} e^{-i\omega'\tau} C(\omega') = - \int \frac{d\omega'}{2\pi i} \frac{C(\omega')}{\omega - \omega' + i\epsilon}$$

it follows $\text{Re} \hat{C}(\omega) = C(\omega)/2$ and we may write

$$\Gamma_{MN,KL}(\omega) = s_{MN} s_{KL} C(\omega)/2$$

in particular, the transition rates are

$$\begin{aligned} k_{M \rightarrow N} &= |s_{MN}|^2 C(\omega_{MN}) = 2\pi |s_{MN}|^2 \omega_{MN}^2 [1 + n(\omega_{MN})] (J(\omega_{MN}) - J(-\omega_{MN})) \\ &= \theta(M - N) 2\pi [1 + n(\omega_{MN})] |s_{MN} \omega_{MN}|^2 J(\omega_{MN}) + \theta(N - M) 2\pi n(\omega_{NM}) |s_{MN} \omega_{NM}|^2 J(\omega_{NM}) \end{aligned}$$

the unit step function θ regulates that the term $\sim 1 + n$ is valid for $M > N$ and the term $\sim n$ for $M < N$;

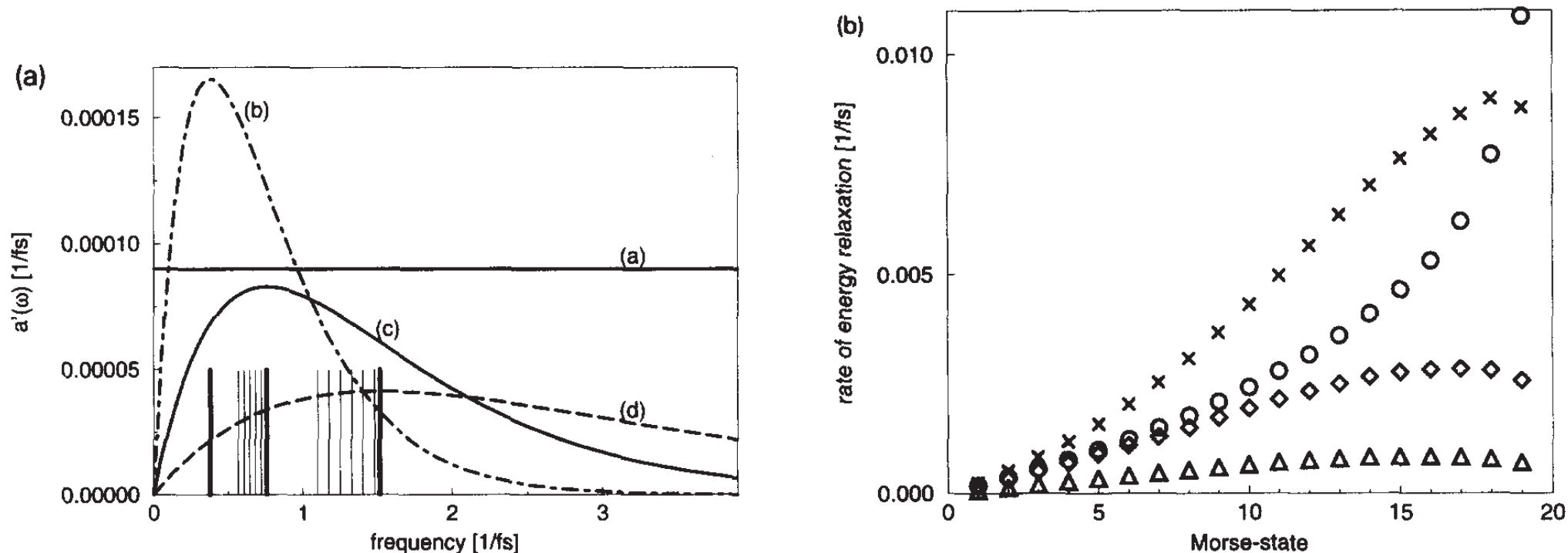


Fig. 7. Different forms of the spectral density and related vibrational energy relaxation rates. (a) Flat spectral density $\pi\hbar a(\omega)/(2\mu_{\text{red}}\omega_{10}) = 9.0 \times 10^{-5}/\text{fs}$ (curve a). Spectral densities according to Eq. (19) with $\epsilon = 2.5$ and with $\omega_c = \omega_{10}/2$ (curve b), $\omega_c = \omega_{10}$ (curve c), and $\omega_c = 2\omega_{10}$ (curve d). The position of the cut-off frequencies are marked separately by bold-face vertical lines. Furthermore, various transition frequencies are shown by the thin vertical lines. The first series starts at ω_{10} and extends to lower frequencies according to $\omega_{21}, \omega_{32}, \omega_{43}, \omega_{54}$ and ω_{65} . The second series starts from $2\omega_{10}$ and continues to lower frequencies with $\omega_{20}, \omega_{31}, \omega_{42}, \omega_{53}, \omega_{64}$ and ω_{75} . (b) Relaxation rates versus vibrational quantum numbers. Application of a flat spectral density $\pi\hbar a(\omega)/(2\mu_{\text{red}}\omega_{10}) = 9.0 \times 10^{-5}/\text{fs}$ (circles). Application of spectral densities according to Eq. (19) with $\epsilon = 2.5$ and with $\omega_c = \omega_{10}/2$ (crosses), $\omega_c = \omega_{10}$ (diamonds), and $\omega_c = 2\omega_{10}$ (triangles).

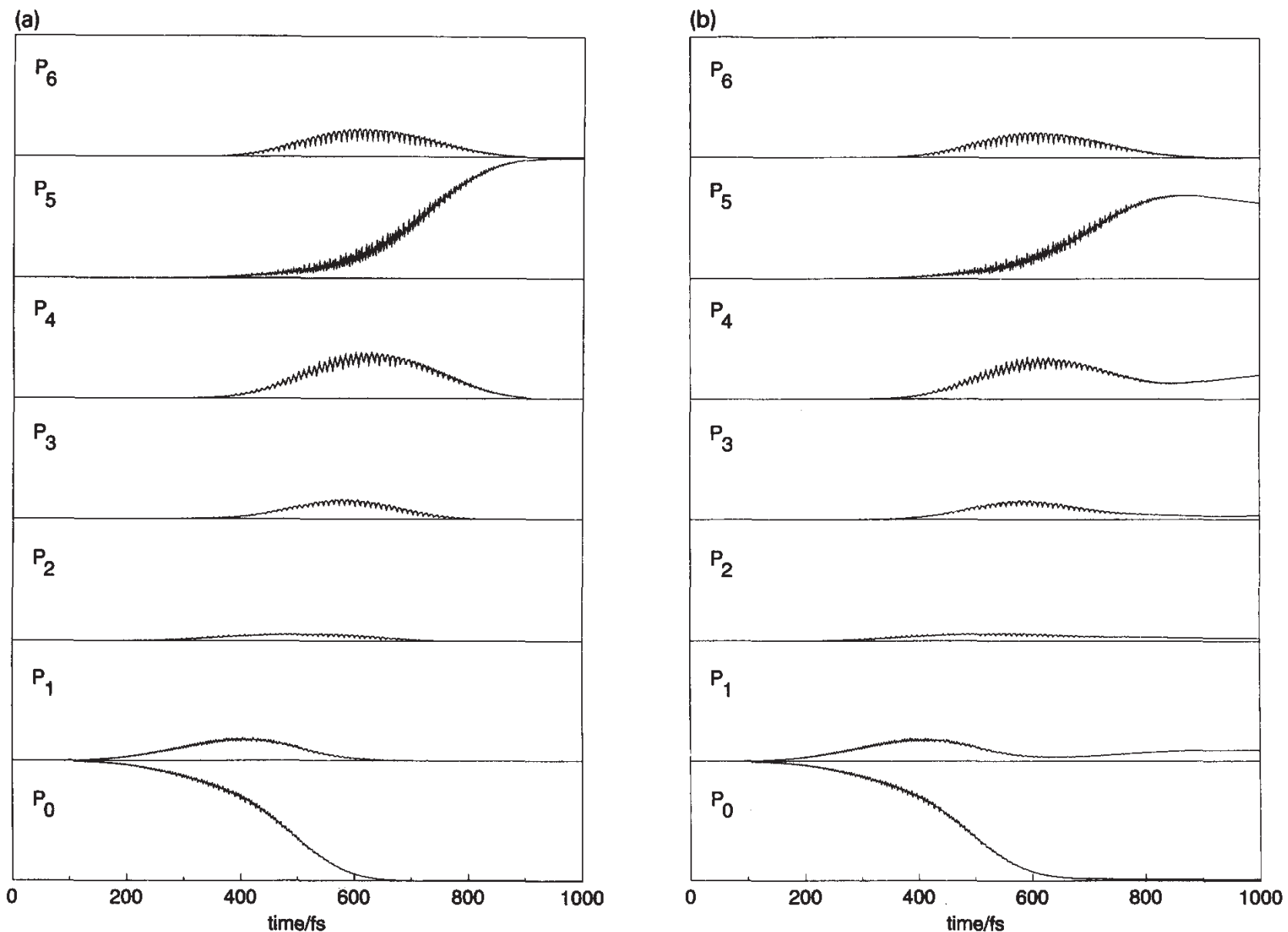


Fig. 2. Occupation probabilities $P_M(t)$ of the vibrational states versus time resulting from the action of a \sin^2 -pulse with frequency $\omega_0 = 0.6812/\text{fs} \approx (E_5 - E_0)/5\hbar$, pulse duration $\tau_p = 1$ ps and a field strength, corresponding to a Rabi frequency of $\omega_R = d_0\mathcal{E}_0/\hbar = 1.42/\text{fs}$. The results for the ground state and the first 6 excited states are shown from the lower to the upper panel. (a) Vanishing coupling to environmental degrees of freedom. (b) Coupling to an environment with a flat spectral density resulting in a life time of fifth state equal to the pulse duration $\tau_5 = \tau_p = 1$ ps.

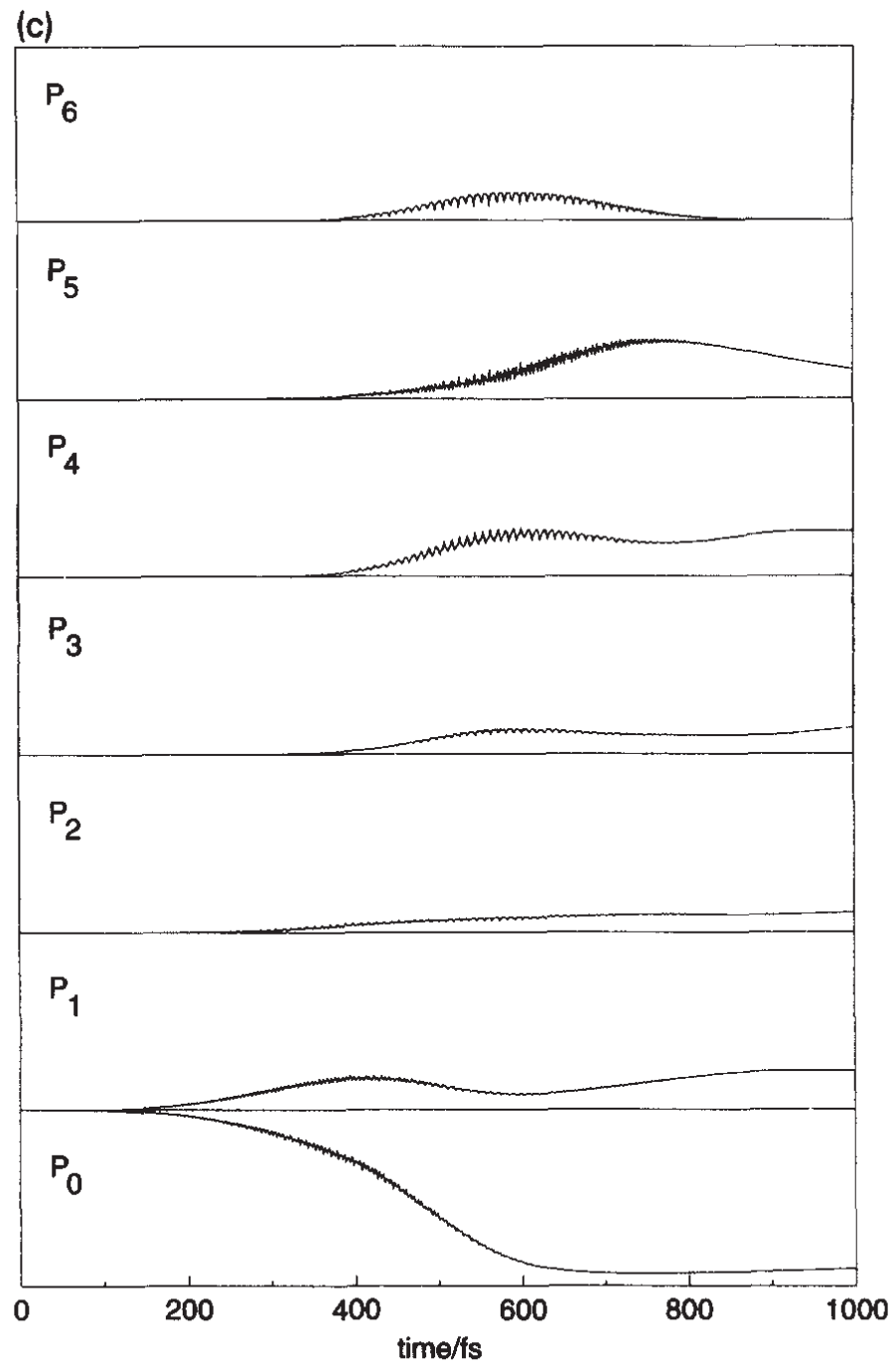


Fig. 2. (continued) (c) Coupling to an environment with a flat spectral density resulting in a life time of fifth state of $\tau_5 = \tau_p/4 = 250$ fs.

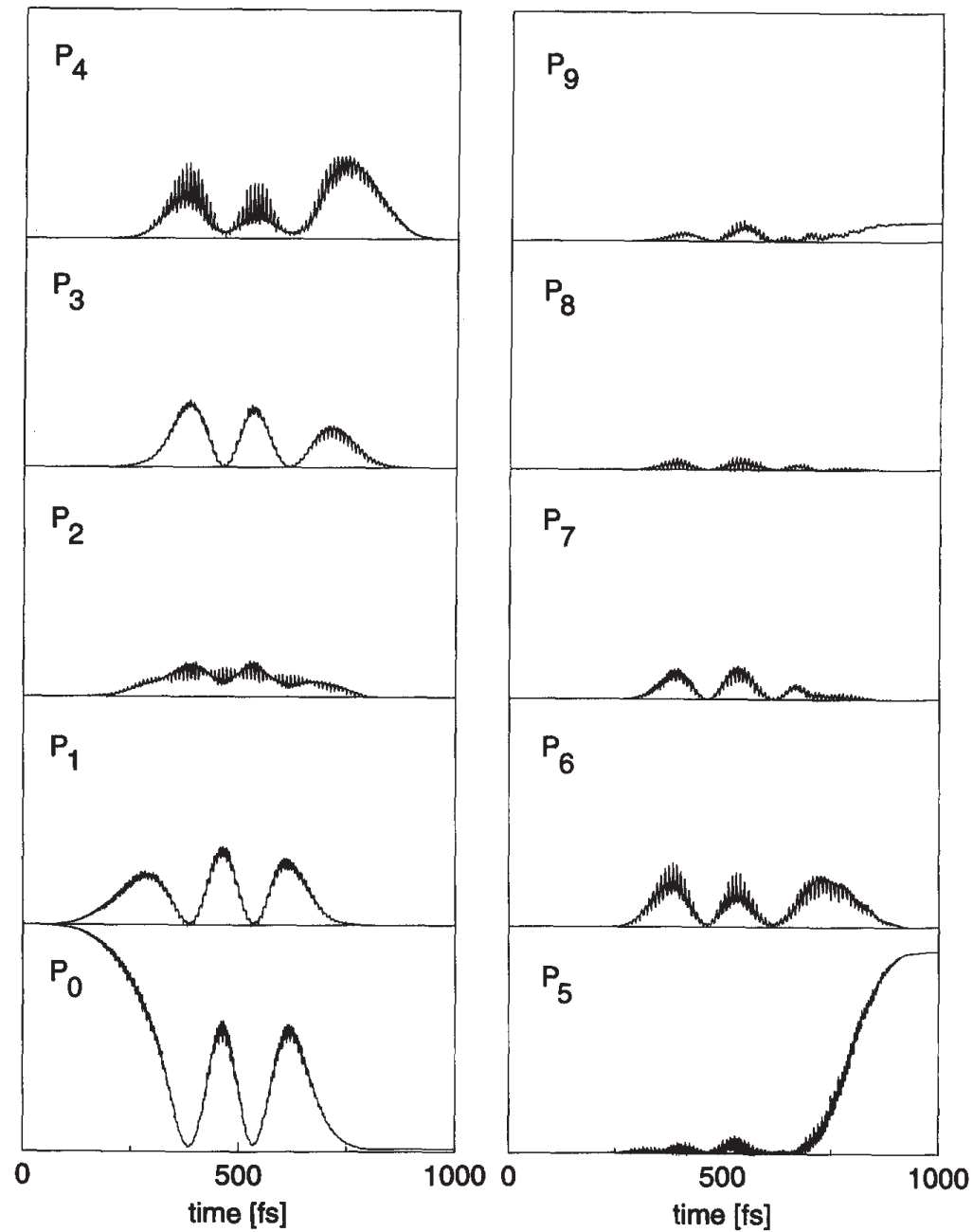


Fig. 5. Occupation probabilities $P_M(t)$ of the vibrational states versus time resulting from the action of a \sin^2 -pulse with frequency $\omega_0 = 0.6812/\text{fs} \approx (E_5 - E_0)/5\hbar$, pulse duration $\tau_p = 1$ ps and a field strength, corresponding to a Rabi frequency of $\omega_R = 2.49/\text{fs}$. The results for the ground state and the first 9 excited states are shown. (The pulse parameters correspond to the extreme in the middle of Fig. 3a. The competition between the fifth and ninth excited state results from a weak internal coupling due to the high field strength.)

7 Excitation Energy Transfer Dynamics

ensemble of N_{mol} molecules which can exchange intramolecular electronic excitation energy;
examples: dye aggregate, supramolecular complex, organic crystal; photosynthetic light harvesting systems; arrangement of semiconductor nanocrystals (quantum dots);
every molecule is labeled by m and described by its electronic ground-state φ_{mg} with energy E_{mg} and its first excited state φ_{me} with energy E_{me} ;
electronic excitation energy is moved from molecule m to molecule n via the Coulomb interaction J_{mn} ;
intermolecular wavefunction overlap is small and will be ignored;
product states of the various φ_{ma} ($a = g, e$) form an expansion basis;
intramolecular and intermolecular vibrations modulate the molecular energies and Coulomb coupling;
restriction to singly excited states results in the Frenkel-exciton Hamiltonian

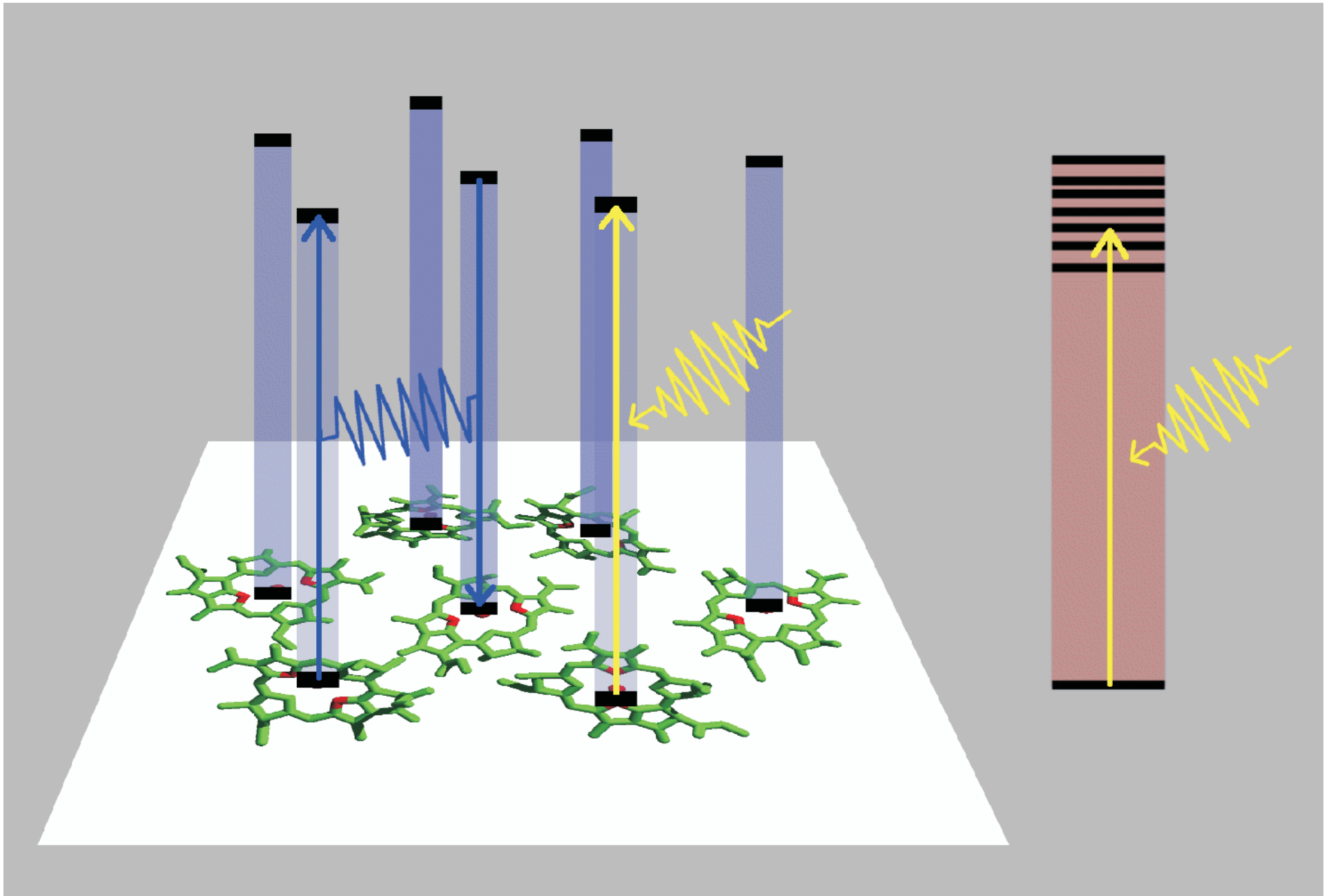
$$H_{\text{ex}} = \sum_{m,n} (\delta_{m,n} E_m + J_{mn}) |m\rangle \langle n|$$

singly excited state $|m\rangle = |\varphi_{me}\rangle \prod_{m \neq n} |\varphi_{ng}\rangle$

site energy $E_m = E_{me} - E_{mg}$

Coulomb coupling

$$J_{mn} = \int d^3\mathbf{x} d^3\mathbf{y} \frac{\rho_m(\mathbf{y}) \rho_n^*(\mathbf{y})}{|\mathbf{x} - \mathbf{y}|} \approx \frac{1}{X_{mn}} ([\mathbf{d}_m \mathbf{d}_n^*] - [\mathbf{d}_m \mathbf{n}][\mathbf{n} \mathbf{d}_n^*])$$



exciton states

$$|\alpha\rangle = \sum_m C_\alpha(m) |m\rangle$$

with energy \mathcal{E}_α diagonalize the exciton Hamiltonian

$$H_{\text{ex}} = \sum_\alpha \mathcal{E}_\alpha |\alpha\rangle \langle \alpha|$$

exciton vibrational coupling

$$H_{\text{ex-vib}} = \sum_{m,n} \sum_\xi \hbar\omega_\xi g_{mn}(\xi) Q_\xi |m\rangle \langle n| = \sum_{\alpha,\beta} \sum_\xi \hbar\omega_\xi \sum_{m,n} C_\alpha^*(m) g_{mn}(\xi) C_\beta(n) |\alpha\rangle \langle \beta|$$

vibrational Hamiltonian

$$H_{\text{vib}} = \sum_\xi \hbar\omega_\xi C_\xi^+ C_\xi$$

optical excitation

$$H_{\text{field}}(t) = -\mathbf{E}(t) \sum_m \mathbf{d}_m |m\rangle \langle 0| + \text{H.c.} = -\mathbf{E}(t) \sum_\alpha \mathbf{d}_\alpha |\alpha\rangle \langle 0| + \text{H.c.}$$

$$\mathbf{E}(t) = \mathbf{e}E(t)e^{-i\omega_0 t} + \text{c.c.}$$

the system part of the interaction Hamiltonian is

$$K_u = |\alpha\rangle \langle \beta|$$

and the bath part is

$$\Phi_u = \sum_\xi \hbar\omega_\xi g_{\alpha\beta}(\xi) (C_\xi^+ + C_\xi)$$

the reservoir correlation function takes the form

$$C_{\alpha\beta,\gamma\delta}(t) = \sum_{\xi} \omega_{\xi}^2 g_{\alpha\beta}(\xi) g_{\gamma\delta}(\xi) [[1 + n(\omega_{\xi})]e^{-i\omega_{\xi}t} + n(\omega_{\xi})e^{i\omega_{\xi}t}]$$

the spectral density has been defined in the general form:

$$j_{\alpha\beta,\gamma\delta}(\omega) = \sum_{\xi} g_{\alpha\beta}(\xi) g_{\gamma\delta}(\xi) \delta(\omega - \omega_{\xi})$$

transitions between different exciton states are accompanied by the absorption or emission of a single normal mode oscillator quantum; the spectral density $j_{\alpha\beta,\beta\alpha}$ taken at the exciton transition frequency regulates the strength of such a transitions;

let us use the most simple variant of the density matrix theory, which neglects all elements of the relaxation matrix that cannot be written in terms of energy relaxation and dephasing rates

$$\frac{\partial}{\partial t} \rho_{\alpha\beta} = -i\Omega_{\alpha\beta} \rho_{\alpha\beta} - \delta_{\alpha\beta} \sum_{\kappa} (k_{\alpha \rightarrow \kappa} \rho_{\alpha\alpha} - k_{\kappa \rightarrow \alpha} \rho_{\kappa\kappa}) - (1 - \delta_{\alpha\beta})(\gamma_{\alpha} + \gamma_{\beta}) \rho_{\alpha\beta}$$

since the basis $|\alpha\rangle$ diagonalizes the single-exciton Hamiltonian the coherent part on the right-hand side contains only the transition frequencies between exciton eigenstates, $\Omega_{\alpha\beta}$ the transition rates read

$$k_{\alpha \rightarrow \beta} = 2\pi \Omega_{\alpha\beta}^2 \left([1 + n(\Omega_{\alpha\beta})] j_{\alpha\beta,\beta\alpha}(\Omega_{\alpha\beta}) + n(\Omega_{\beta\alpha}) j_{\alpha\beta,\beta\alpha}(\Omega_{\beta\alpha}) \right)$$

respective dephasing rates are

$$\gamma_{\alpha} = \frac{1}{2} \sum_{\beta} k_{\alpha \rightarrow \beta}$$

the stationary limit of the equations of motion for the single-exciton reduced density matrix will be given by

$$\rho_{\alpha\beta}(\infty) = \delta_{\alpha\beta} \frac{e^{-\mathcal{E}_\alpha/k_B T}}{\sum_{\alpha'} e^{-E_{\alpha'}/k_B T}} ,$$

to illustrate the dynamics in the eigenstate representation we restrict ourselves to situations where a factorization of the exciton–vibrational coupling matrix is justified $g_{\alpha\beta}(\xi) = g_{\alpha\beta} \times g(\xi)$; the relaxation rates are given by

$$k_{\alpha \rightarrow \beta} = 2\pi |g_{\alpha\beta}|^2 \Omega_{\alpha\beta}^2 [1 + n(\Omega_{\alpha\beta})] [j(\Omega_{\alpha\beta}) - j(-\Omega_{\alpha\beta})]$$

in this case the dissipative influence of the aggregate's vibrational modes can be described by a single, exciton state independent, spectral density

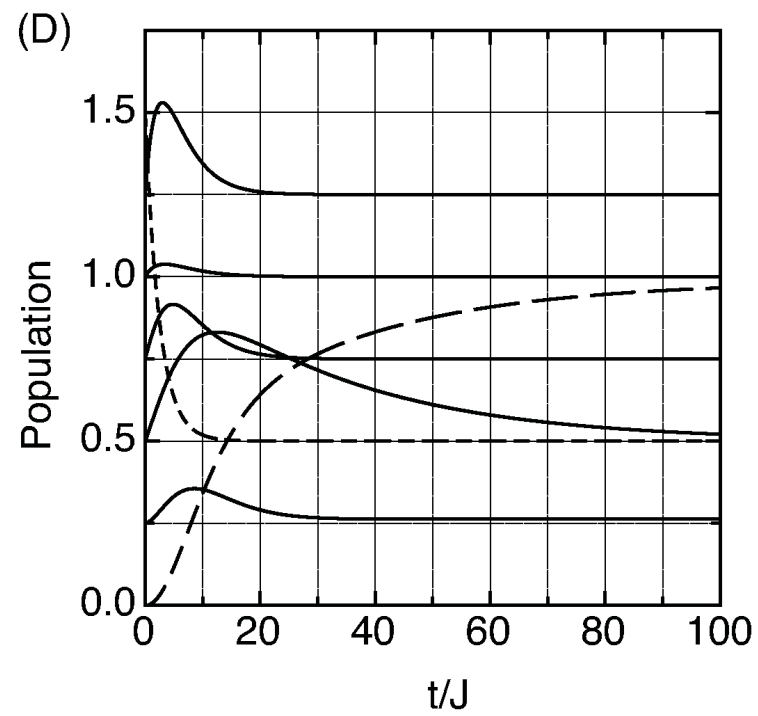
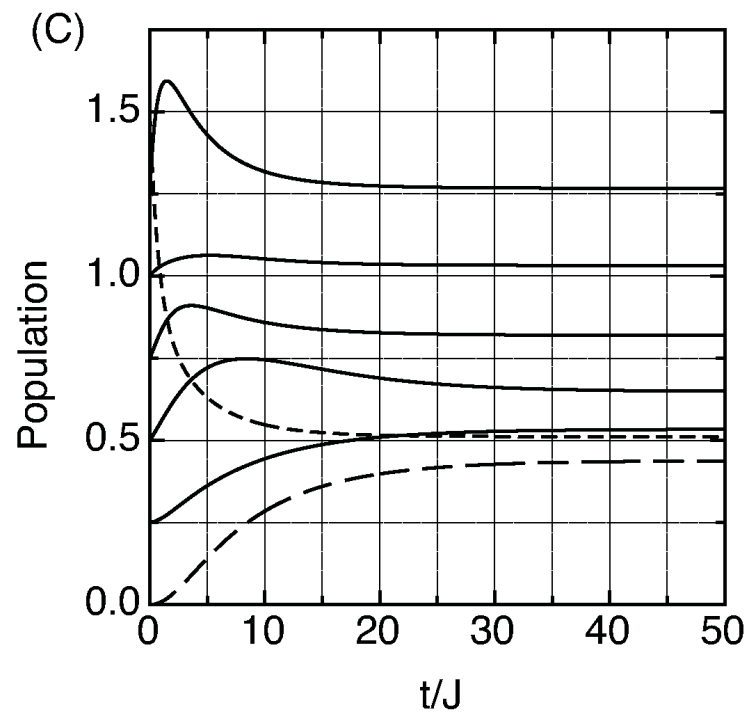
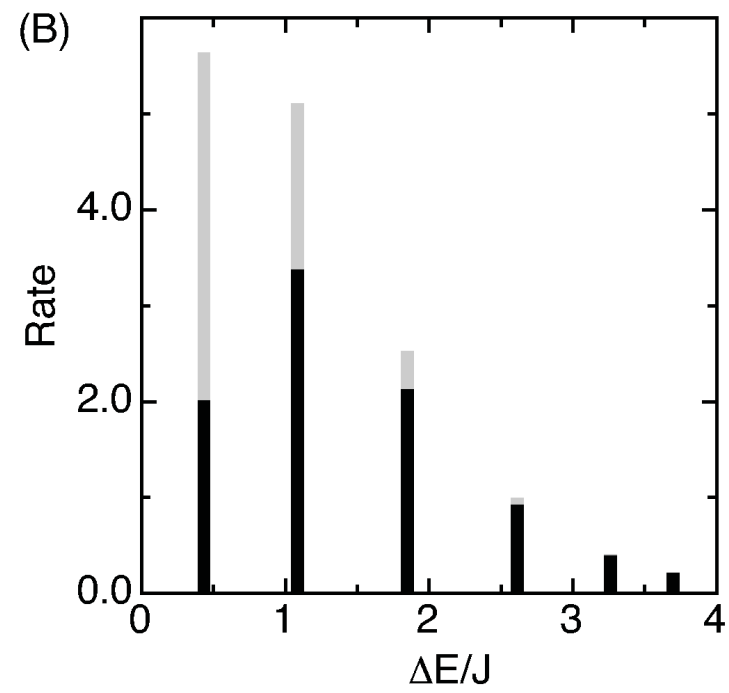
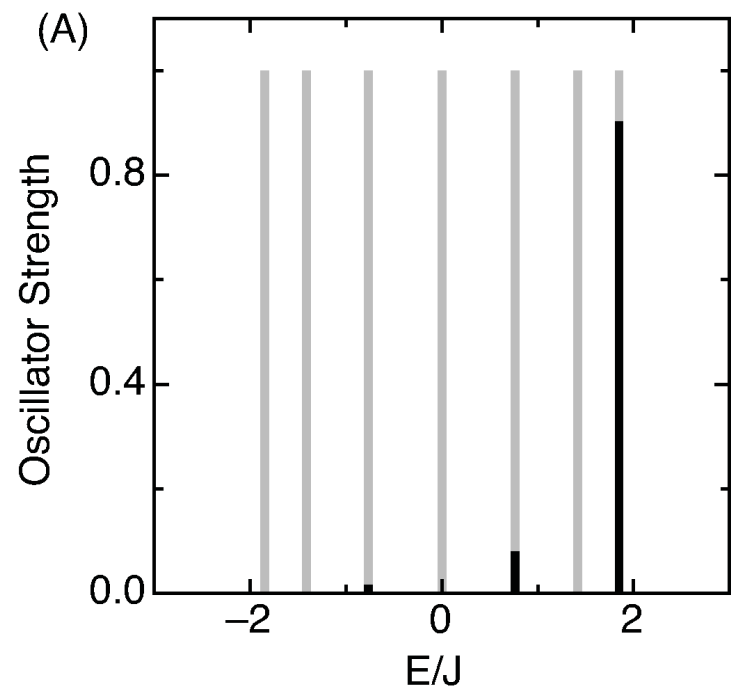
$$j(\omega) = \sum_{\xi} g^2(\xi) \delta(\omega - \omega_{\xi})$$

in the example we will use the model spectral density type

$$j(\omega) = \theta(\omega) \exp\{-\omega/\omega_c\} / 2\omega_c^3$$

being in H–aggregate configuration, the energetically highest exciton state has by far the largest transition amplitude;

this allows us to assume that an external field can prepare the system in this particular state; with the highest state being initially excited with probability one, the subsequent dynamics shows no oscillations but a relaxation towards the equilibrium distribution;



dissipative dynamics in a regular chain of seven molecules with nearest-neighbor coupling of strength J ($J_{mn}/J = \delta_{m,n+1} + \delta_{m,n-1}$):

(A) position of the energy levels (grey bars) as well as oscillator strengths (solid bars)

(B) transition rates from the state of highest energy to all states of lower energy (given at the respective energy gap) for $1/k_B T = J$ (grey) and $1/k_B T = 10J$ (solid);

the two lower panels show the population dynamics $\rho_{\alpha\alpha}(t) = P_\alpha(t)$ for $1/k_B T = J$ (C) and $1/k_B T = 10J$ (D);

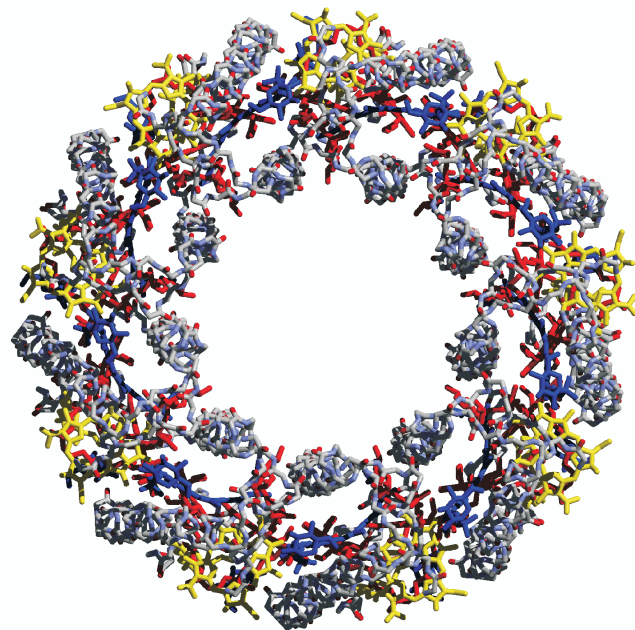
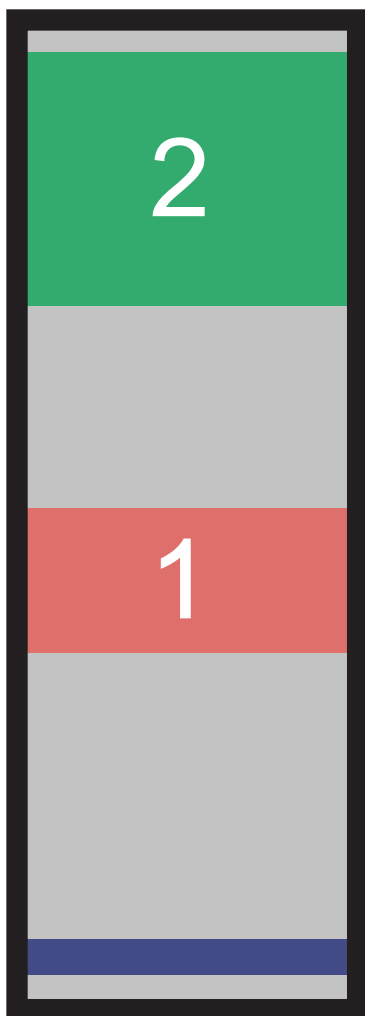
initially the state of highest energy has been populated;

the curves are offset with increasing energy (short dashes: highest state, long dashes: lowest state);

for the spectral density we have chosen $j(\omega) = \theta(\omega) \exp\{-\omega/\omega_c\} / 2\omega_c^3$ with the cut-off frequency $\hbar\omega_c = 0.5J$;

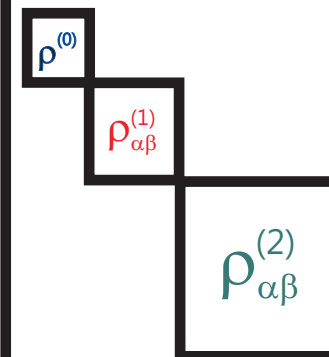
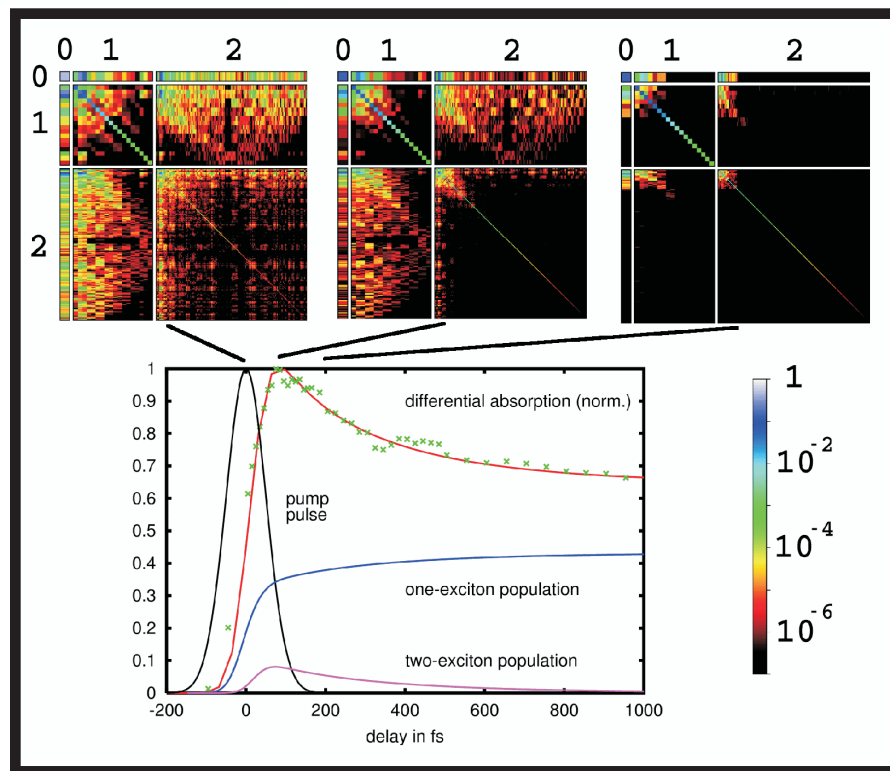
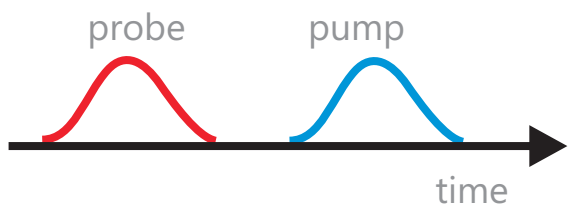
the coupling matrix has been set to $g_{mn} = 0.5J_{mn}$;

Ultrafast Spectroscopy of Photosynthetic Antenna Systems



single and two-exciton levels

Transient Absorption of the LH2



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