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Exciton Transfer Near Donors and Acceptors

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Summary

Two new methods of calculation of memory functions, governing the exciton propagation, in linear finite chains and consequent calculation of the quantum yield of the exciton transfer, observable in e.g. experiments on monomer and excimer luminiscence, are reported. Illustrative numerical results are shown to discuss the effect of inhomogeinities, boundaries and relative magnitudes of relevant parameters on the result.

Introduction

The investigation of the excitation transfer is of great importance in diverse fields of study and much theoretical work has already been done in this area (KENKRE 1981).

The aim of this paper is the study of the exciton propagation, using our new general methods for finite systems, along the linear finite chain. We are interested in the time development of the occupation probabilities $P_m(t)$ of the sites m. They give us, at the end, the observable quantity, in such experiments as sensitized luminiscence or surface quenching, the quantum yield Q_g of a single trap at a guest place g.

Once the exciton is created at $t=0$ with the probability distribution $P_m(0)=P_{om}$, the further time development $P_m(t)$ is given by the generalized master equation (GME)

$$\frac{\partial P_m}{\partial t} = \sum_n \int_0^t w_{mn}(t-t') \, P_n(t') \, dt' \quad . \qquad (1)$$

It results from the universal Liouville equation for the density matrix (ZWANZIG 1964) taking in to account that $P_m(t)$ are

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given by diagonal elements of the density matrix. The kernels of the integral equation (1) are so called memory functions $w_{mn}(t)$, the crucial quantities in non-Markoffian treatments of the exciton transport.

Memory functions and a propagator for finite systems

For finite rigid systems without interaction with a bath, we arrived at the following matrix equation for the memory functions in a Fourier picture

$$i\ M(z)\ w(z) = z\ M(z) - 1 \tag{2}$$

where the matrix M is given as

$$M_{mn}(z) = \sum_{ab} (z - E_{ab})^{-1} \langle m|a\rangle\langle a|n\rangle\langle n|b\rangle\langle b|m\rangle\ . \tag{3}$$

Here $\{|m\rangle\}$ are Wannier - like states localized on sites,
$\{|a\rangle\}$ are eigenstates of the hamiltonian H and
E_{ab} are differences of the eigenenergies E_a and E_b.

As a function of time

$$i\ M_{mn}(t) = |\langle m|\ e^{-iHt}\ |n\rangle|^2 \tag{4}$$

describes the time evolution of the occupation probability $P_m(t)$, if the excitation initially resides at the site n. It means that $i\ M_{mn}(t)$ is the propagator.

The frequencies of the memory functions are given as solutions of the equation

$$\det M(z) = 0. \tag{5}$$

As an illustration, we used this formalism for a derivation of the MFś for the open chain of three molecules with the model hamiltonian

$$H = \begin{bmatrix} 0 & J & 0 \\ J & E_o & J \\ 0 & J & 0 \end{bmatrix} . \tag{6}$$

Here E_o is the difference in the exciton energy in absence of the intersite interaction between sites 2 and 1 or 3; J designates the transfer integral and is nonzero only between the neighbouring sites. Using (3) and (5), the final form of the independent MFś is

$$w_{12}(t) = 2\ J^2 \cos(tE_1)\ ; \qquad E_1 = (E_o^{\ 2} + 2J^2)^{1/2}$$

and

$$w_{13}(t) = 4\, J^4\, E_1^{-2}\, \sin^2(tE_1/2)\,. \tag{7}$$

This example shows us the following typical features:

1. the frequencies of memory functions $w_{mn}(t)$ do not generally coincide with eigenvalues of the hamiltonian or their differencies, though the latter do it in $P_m(t)$ in (1).
2. in case of dynamical uncoupling of some molecule in a chain ($|E_o| \gg J$ in our case), the MFś connected with this site vanish in sence of distribution.

Direct calculation of memory functions

To avoid lengthy numerical calculations of determinants (5) for large matrices with an indefiniteness in the condition (5) for the number of poles we suggested, for special cases , another method based on a direct inversion of the superoperator.

Let

$$S(I,K) = H_{i_1k_1}\,\delta_{i_2k_2} - H_{k_2i_2}\,\delta_{i_1k_1}\,, \tag{8}$$

where I denotes a pair (i_1i_2) for $i_1 \neq i_2$. We can choose the corespondence between (i_1i_2) and I in a such way, that the whole matrix may be written in the block diagonal form

$$S = \begin{bmatrix} S_p\,, & 0 \\ 0 & ,-S_p^{*} \end{bmatrix}\,. \tag{9}$$

In absence of external magnetic field, the elements of the matrix may be chosen real, i.e. we get real eigenvectors.

The final form of the MFś in the time domain reads

$$w_{mn}(t) = \sum_a A^a_{mn}\, \cos(f_a t) \tag{10}$$

with

$$A^a_{mn} = -2 \sum_{IK} (H_{mi_1}\,\delta_{mi_2} - H_{i_2m}\,\delta_{mi_1})\, \langle I|a\rangle$$

$$\langle a|K\rangle (H_{k_1n}\,\delta_{k_2n} - H_{nk_2}\,\delta_{nk_1})\,. \tag{11}$$

$\{f_a\}$ are eigenvalues and $\{|a\rangle\}$ eigenvectors of the matrix S_p.

Several important results can be revealed from our calculations:

a) the frequencies of MFś f_a can neither be generally deduced from E_{ab} by any simple algebraic manipulation, nor they are given by overlap (hopping) integrals only.
b) as long as the chain has a spatial symmetry (inversion), some of the frequencies f_a get zero, i.e. $w_{mn}(t)$ contain a constant term.
c) as long as a molecular atomic level on an acceptor (donor) differs appreciably from those in the host chain, the individual components of the memory functions $w_{mn}(t)$ connecting either this acceptor with its surroundings or two host sites separated by the acceptor turn to zero due to one of the following reasons:
I. A^a_{mn} tends to zero, uniform convergence.
II. f_a tends to infinite, but A^a_{mn} remain finite, disappearence as a distribution.
III. several f_a tend to zero, but the corresponding sum of A^a_{mn} turning to zero, nonuniform convergence. The memory functions in host part of the chain turn to those for an isolated part of the chain (dynamical splitting off the impurity sites).

These physical consequences may be deduced from this:
1) The knowledge of the energy spectrum is generally of no use for modelling the memory functions.
2) The Fourier or Laplace transform turn GME to an algebraic equation. Since the transform of a constant is singular as long as the Fourier frequency (Laplace parameter) gets zero, symmetry of the chain might be of a high importance for the exciton transfer. Similar effects cannot be derived from the Pauli equation in any finite order in hopping integrals.
3) Assuming from now on that the effect of the exciton-phonon coupling (bath) reduces to an exponentially damped prefactor e^{-Ft} of our memory functions, the dynamical splitting off the impurity means a big delay of the exciton before being trapped at an acceptor (or released at a donor). It means that deducing the diffusion constant (mobility) from the difference between the momenta of a creation of the exciton at a donor and its detection at an acceptor and ignoring this delay can lead to severe underestimations of the diffusivity in the host part of the chain. One should mention that this splitting off is

observed for $|E_0|>>J$ which is easily satisfied in realistic situations.

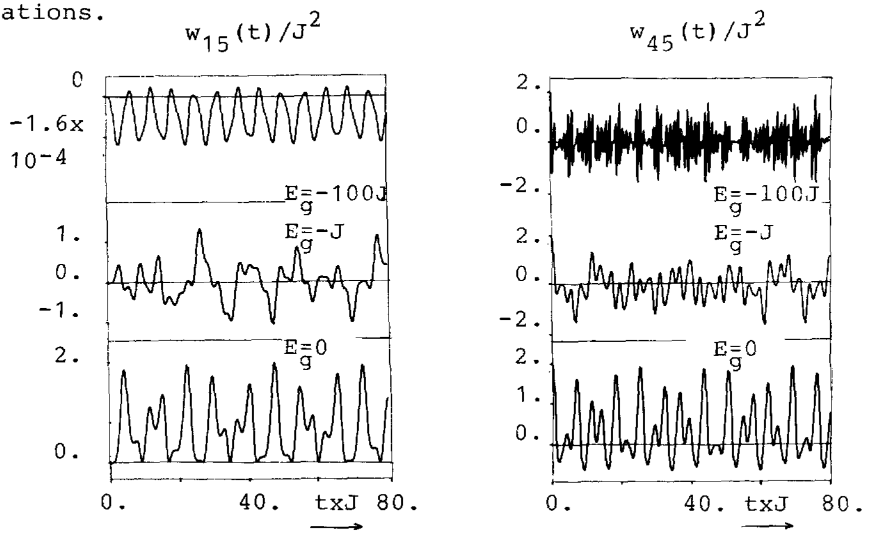


Fig. 1. The coherent memory functions $w_{15}(t)$ and $w_{45}(t)$ for a chain of five molecules. All site energies are equal to zero, E_g is the energy of the fifth molecule

Quantum yield of a single trap

To treat correctly results of the experimental investigation we have to add (phenomenologicaly) to (1) decay terms P_m/t_H and P_g/t_g with radiative life times t_H and t_g.

The experimental observable quantity, the quantum yield of a single trap at a site g

$$Q_g = \int_0^\infty P_g(t)\,dt \,/\, t_g \qquad (12)$$

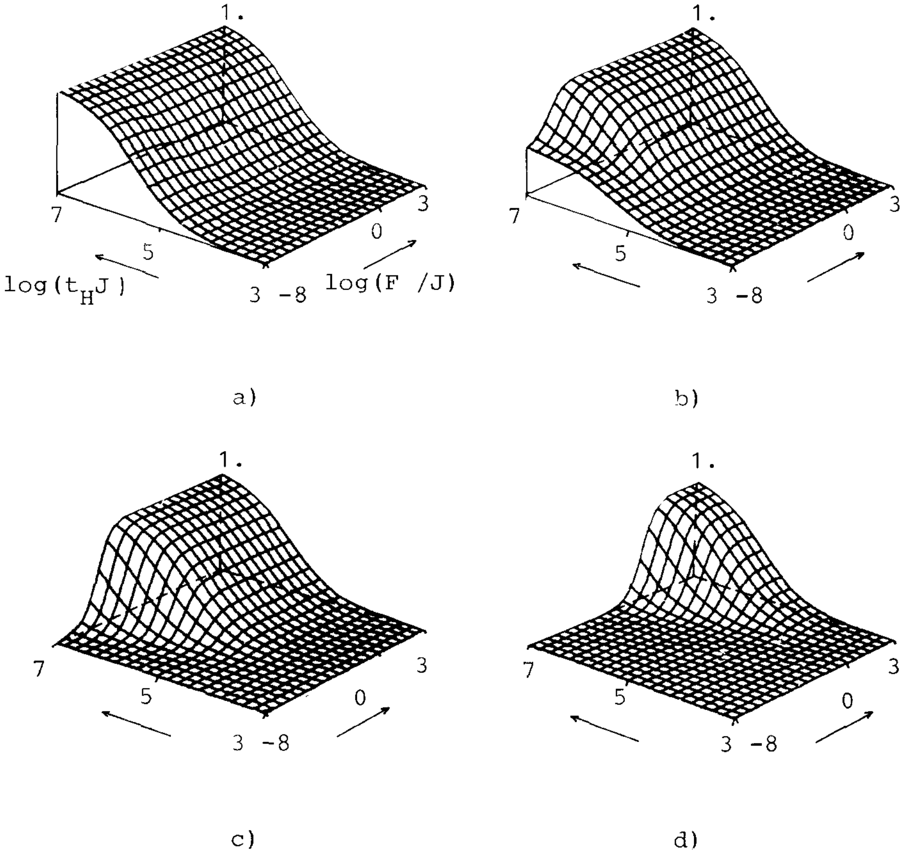
is then given by

$$Q_g = (\,1 + (t_H/t_g - 1)\,K_{gg}/t_H\,)^{-1}\,(1/t_H)\,\sum_l K_{gl}\,P_{ol} \qquad (13)$$

where

$$K = K(s,F) = (1-iFM(i(s+F)))^{-1}.\ iM(i(s+F)),\ s=1/t_H. \qquad (14)$$

The use of periodic boundary conditions in a calculation of memory functions leads to a pronounced underestimation of the quantum yield of a guest appended at one end of the linear chain (surface quenching) just in an area of low incoherence (F tends to zero). Incorporation of exact energies in the exact propagator iM leads to drastical changes in Q_g for high t_H



a) b) c) d)

Fig. 2. The quantum yield of a guest appended at one end of a chain with four host molecules. All host energies equal to zero. a) periodic, b) natural boundary conditions, E_g=0; c) natural boundary conditions, E_g=-5J; d) natural boundary conditions, E_g =-1000J

and low F. For larger differences between the energies of hosts and guest molecules, the changes in Q_g with F appear for larger F .

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