Effect of trapping on transport coherence. II. Continuous-time random-walk treatment

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Our recent investigation led to the conclusion that there is much agreement among theories of the excitation transfer: the generalized master equation (GME), the Haken-Strobl-Reineker stochastic-Liouville-equation theory, and the Grover-Silbey microscopic theory. Trapping effects influence memory functions entering the GME. Decoupling of the rest of the system from the sink in the nearly coherent regime for large trapping rates changes the form of the pausing-time-distribution functions and probability densities in the continuous-time random-walk method.

I. INTRODUCTION

In recent years, considerable interest has been concentrated on the theory of coupled coherent-incoherent excitation transfer and several different treatments have been developed: the generalized-master-equation (GME) method,[1–9] stochastic approaches by Haken, Strobl, and Reineker (HSR) based on the stochastic Liouville equations,[10–14] the continuous-time random-walk (CTRW) method,[15,16] and nonstochastic microscopic models of Silbey (GS) and co-workers.[17–25]

We have contributed to the development of excitation-transfer theory in several directions. We have thoroughly investigated the memory function (MF) $w_{mn}(t)$ which enters the generalized master equations in various regimes of the excitation transfer. We derived[26–29] the coherent memory functions for general finite systems, as well as their relationship to so-called propagators. Calculation of the memory functions from exact energies and eigenstates implies considerable changes in the quantum yield of the guest molecule. When the energy difference between the guest and host molecules increases, the exciton tries to avoid the trap and prefers to move within the unperturbed part of the system.

The interaction of the excitation with a bath has been modeled by the interaction with phonons. Our method of the calculation of $w_{mn}(t)$ was based[30–34] on a summation of special kinds of divergent (in the limit $t \rightarrow \infty$) terms in the perturbation expansion of $w_{mn}(t)$. The most divergent terms yield $w_{mn}(t)$ in the form of the rescaled coherent memory functions with rescaled transfer integrals J_{mn}. Further corrections are due to less divergent terms. We derived these corrections for arbitrary lattices composed of equivalent sites and for the nearest-neighbor transfer integral only. We obtain memory functions which have a two-channel form with two different decay times and different ranges of individual components in real space.

In the first channel the pronounced role of the long-range coherent memory functions is preserved, while the second channel corresponds in the long-time limit to phonon-assisted hops with a range given by $J_{mn} \neq 0$.

For general J_{mn} and arbitrary systems, we were able to reproduce (to second order) the lowest-order perturbation result by Kenkre and Rahman.[35] The correspondence is lost, however, with the semiphenomenological extension of the Kenkre- and Rahman theory to infinite order [formula (2.90) in Ref. 6], as well as the usual phenomenological inclusion of the influence of photons via a multiplicative exponential damping factor in front of the memory function [formula (2.71) in Ref. 6]. Our results also extend and modify the conclusion given by Sokolov and Hyznyakov in Refs. 36–38. It has been shown that the pure coherent memory functions also play a crucial role in the noncoherent regime of the excitation transfer.

These new results call for a revision of some of the conclusions given by Kenkre[6–8] about the relationship between the GME, GS, HSR, and CTRW methods which were based just on the lowest-order perturbation results[35] for a dimer. We have shown[39] that there is greater agreement between various theories considered than their diverse structures might lead us to believe and then this could have been guessed from the result of Kenkre[6–8] using only the lowest-order results for memory functions $w_{mn}(t)$ (Ref. 35) in the dimer.

The formal correspondence between the GME and HSR theories also led to the reconsideration of the problem of how to include a trap (here modeled as a sink) into the GME. Our results differ appreciably from those previously derived.

Pearlstein and co-workers[40–44] recognized that the consequences of the sink on the energy-transfer processes are different in the coherent and incoherent regimes. For a long time this fact has not properly been taken into account[6,45–47] in the GME treatment.

Čápek and Szöcs[48] pointed out the necessity of "transformation" of memory functions in the presence of the sink. They also gave a prescription for a proper inclusion of the sink into the HSR method. This led us to apply the HSR equations in the computer modeling of the exci-

tation transfer in photosynthetic systems.[49–53]

Recently, we succeeded[54–56] in deriving the form of the pure coherent memory functions in the presence of the trap (in the full sink model) and the consequences on the excitation transfer.[54] The case of the semi-infinite chain was considered in Ref. 57.

Kenkre, Montroll, and Shlesinger[15] concluded from their preliminary investigations that there is full equivalence between the GME and CTRW methods. Klafter and Silbey[58] tried to extend the CTRW method to all regimes of the exciton transfer. On the other hand, we have shown that correspondence between the GME and CTRW theories can be recovered from the mathematical point of view only for energetically homogeneous systems. The strange behavior of "probabilities," which enter the CTRW theory,[59–61] forces us to question the applicability of this method for computer modeling in this case of the quasicoherent regime, and disproves the usual physical interpretation of the formal CTRW equations in this case. On the other hand, because of the role of the pure coherent memory functions in the noncoherent regime of the excitation transfer, it is necessary to investigate the influence of the trap (sink) on the pausing-time-distribution functions and probability densities entering the CTRW.

The aim of this paper is to extend our recent investigations[61] in CTRW method. The relationship among various theories of the excitation transfer [GME, stochastic Liouville equation (SLE), and GS] is explained in Sec. II. The description of the trap in the full sink model, which is based on the correspondence of the GME and HSR theories, is presented in Sec. III. The CTRW treatment of the trap in the full sink model is given in Sec. IV.

II. RELATIONSHIP BETWEEN THEORIES OF EXCITON TRANSFER WITH EXCITON-PHONON INTERACTION

A. Generalized-master equation method

In general, the density operator ρ satisfies the Liouville–von Neumann equation

$$i\frac{\partial\rho}{\partial t}=\frac{1}{\hbar}[H,\rho]\equiv L\rho\ . \tag{2.1}$$

Here H is the Hamiltonian of the system and L is the Liouville superoperator.

One can use the Nakajima-Zwanzig equation[1–6] for projection on a relevant part of the density operator,

$$\frac{\partial\rho_D(t)}{\partial t}=-iDL\rho_D(t)-\int_0^t d\tau\, DLe^{-i\tau QL}QL\rho_D(t-\tau)\ , \tag{2.2}$$

$$Q=1-D\ .$$

The kernel of the integrals is the so-called (superoperator) memory function. The initial term [not shown in (2.2)] is omitted as a consequence of properly chosen initial conditions (see below).

Having chosen a proper diagonalizing form of D,[62] the term $-iDL\rho_D$ drops out (the presence of the trap is not yet considered), matrix elements of the operator $\rho_D=D\rho$ become proportional to site-occupation probabilities $P_m(t)$, and matrix elements of the superoperator MF are the memory functions $w_{mn}(t)$ in the usual sense. The formalism of the projection superoperator D employed in the derivation of (2.2) from (2.1) (Refs. 62 and 6) enables us to follow the site-occupation probability and thus the excitation migration. Generally, it is necessary to include the influence of phonons or another bath.

For a single exciton in a periodic linear chain interacting linearly and locally with phonons, the usual small-polaron Hamiltonian reads

$$H=H_e+H_{\rm ph}+H_{e\text{-ph}}\ , \tag{2.3}$$

where

$$H_e=\sum_r \varepsilon_r a_r^\dagger a_r+\sum_{r\neq s} J_{rs}a_r^\dagger a_s\ ,$$

$$H_{\rm ph}=\sum_{\mathbf{k}}\hbar\omega_{\mathbf{k}}b_{\mathbf{k}}^\dagger b_{\mathbf{k}}\ ,$$

$$H_{e\text{-ph}}=\frac{1}{\sqrt{N}}\sum_n g_{\mathbf{k}}\exp(i\mathbf{k}\cdot\mathbf{r}_n)\hbar\omega_{\mathbf{k}}a_n^\dagger a_n(b_{\mathbf{k}}+b_{-\mathbf{k}}^\dagger)\ .$$

We can rewrite the Hamiltonian as

$$H=H_0+\mathcal{H}\ , \tag{2.4}$$

with

$$H_0=\sum_r \varepsilon_r a_r^\dagger a_r+H_{\rm ph}+H_{e\text{-ph}}$$

and

$$\mathcal{H}=\sum_{r\neq s}J_{rs}a_r^\dagger a_s\ .$$

H_0 can be directly diagonalized, and the corresponding eigenstates and eigenenergies are

$$|m\mu\rangle=\prod_k\left[\frac{1}{\sqrt{\mu_{\mathbf{k}}!}}\left[b_{\mathbf{k}}^\dagger+\frac{1}{\sqrt{N}}g_{\mathbf{k}}\exp(i\mathbf{k}\cdot\mathbf{r}_m)\right]^{\mu_{\mathbf{k}}}\right]\exp\left[\frac{1}{\sqrt{N}}\sum_{\mathbf{k}}g_{\mathbf{k}}\exp(i\mathbf{k}\cdot\mathbf{r}_m)(b_{\mathbf{k}}-b_{-\mathbf{k}}^\dagger)\right]a_m^\dagger|\mathrm{vac}\rangle\ ,\quad \mu_{\mathbf{k}}=0,1,2\ldots\ , \tag{2.5}$$

$$E_{m\mu}=\varepsilon_m+\sum_{\mathbf{k}}\hbar\omega_{\mathbf{k}\mu_{\mathbf{k}}}-\frac{1}{N}\sum_{\mathbf{k}}\hbar\omega_{\mathbf{k}}|g_{\mathbf{k}}|^2\ . \tag{2.6}$$

Let us assume that the excitation is initially localized at a specific site and that the lattice is relaxed around it with the initial lattice density matrix $\rho^R_{\mu\nu}$. Then (as mentioned above) the initial condition term [already dropped in (2.4)] really disappears.[31]

We derived[30–34] the following form for the memory functions [just for equivalent sites ($\varepsilon_m=0$) with nearest-neighbor hopping integral J]:

$$w_{mn}(t)=w^{\mathrm{qcoh}}_{mn}(t)+w^{\mathrm{incoh}}_{mn}(t)\ , \tag{2.7}$$

where

$$w^{\mathrm{qcoh}}_{mn}(t)=\exp(-2\Gamma t)w^{\mathrm{coh}}_{mn}(t)|_{J_{mn}\to\tilde{J}_{mn}}\ ,$$

$$w^{\mathrm{incoh}}_{mn}(t)=2\frac{\tilde{J}^2_{mn}}{\hbar^2}\{\mathrm{Re}\exp[h_{mn}(t)]-1\}\ .$$

Here

$$h_{mn}(t)=\frac{2}{N}\sum_{\mathbf{k}}|g_{\mathbf{k}}|^2\{1-\cos[\mathbf{k}\cdot(\mathbf{r}_m-\mathbf{r}_n)]\}\times[n_B(\hbar\omega_{\mathbf{k}})\exp(i\omega_{\mathbf{k}}t)]+[1+n_B(\hbar\omega_{\mathbf{k}})\exp(-i\omega_{\mathbf{k}}t)]\ ,$$

$$n_B(z)=[\exp(\beta z)-1]^{-1}\ ,$$

$$\tilde{J}_{mn}=\begin{cases}\tilde{J}=J\exp[-h_{mn}(0)/2] & \text{for nearest neighbors}\ ,\\ 0 & \text{otherwise}\ ,\end{cases}$$

$$2\Gamma=z2(\tilde{J}/\hbar)^2\int_0^{+\infty}\{\mathrm{Re}\exp[h_{mn}(t)]-1\}\ ,\qquad m,n \text{ nearest neighbors} \tag{2.8}$$

(z is the coordination number, i.e., the number of the nearest neighbors to a given site).

Thus the structure of the memory function is two channel; the first term $w^{\mathrm{qcoh}}_{mn}(t)$ corresponds to a quasicoherent long-range propagation with a small exponential damping of the rescaled pure coherent memory function, while the second one is (in our approximation) short ranged and results from phonon-assisted processes. The decay constants of the two channels are entirely different.

We calculated[33] the coherence time $\tau_c=(2\Gamma)^{-1}$ of the excitation and contributions of each of the two channels to the excitation transfer and coherence time of the excitation for a broad range of input parameters, e.g., temperature T, bare bandwidth $\sim J$, excitation-phonon coupling g, and optical-phonon frequency $\hbar\omega$, and in the Markovian approximation applied to the second channel of the MF.

We showed the mutual connection of two channels in the memory functions $w_{mn}(t)$ in different regimes of the excitation transfer (coherent, quasicoherent, and incoherent).

The connection between the integral of the second term in (2.7) and the damping constant 2Γ of the first term [see (2.8)] has a physical meaning in relation to the stochastic-Liouville-equation method, as can be seen in the next section.

B. Stochastic-Liouville-equation method

In the stochastic-Liouville-equation method, the influence of vibrations (forming a genuine thermodynamic bath or reservoir) is substituted by an external stochastic potential field $V(t)$ with prescribed statistical properties.

It is assumed that $V(t)$ is a Gaussian stochastic process, i.e.,

$$\langle V(t_1)\cdots V(t_{2k-1})\rangle=0\ ,$$
$$\langle V(t_1)\cdots V(t_{2k})\rangle=\sum_{l=2}^{2k}\langle V(t_1)V(t_l)\rangle\langle V(t_2)\cdots V(t_{l-1})V(t_{l+1})\cdots V(t_{2k})\rangle\ ,\quad k=1,2,\ldots, \tag{2.9}$$

which means that any correlation function is either zero or is determined by the pair correlation function $\langle V(t)V(t')\rangle$. Further, it is supposed that $V(t)$ is a δ-correlated (white-noise) Markov process, i.e.,

$$\langle V_{mn}(t_1)V_{pq}(t_2)\rangle=\delta(t_1-t_2)2\Lambda_{mnpq}\ . \tag{2.10}$$

With the Haken-Strobl-Reineker[12] parametrization

$$\Lambda_{mnpq}=\gamma_{mn}\delta_{mq}\delta_{np}+\bar{\gamma}_{mn}\delta_{mp}\delta_{nq}(1-\delta_{mn})\ ,\qquad \gamma_{mn}=\gamma_{nm}\ ,\ \bar{\gamma}_{mn}=\bar{\gamma}_{nm}\ , \tag{2.11}$$

the HSR stochastic Liouville equations for the single-exciton density matrix $\rho^e_{mn}(t)$ has the following form (taking $\bar{\gamma}_{mn}=0$);

$$\frac{\partial}{\partial t}\rho^e_{mn}(t)=-\frac{i}{\hbar}([H_e,\rho^e(t)])_{mn}+\delta_{mn}\sum_p[2\gamma_{mp}\rho^e_{pp}(t)-2\gamma_{pm}\rho^e_{mm}(t)]-(1-\delta_{mn})\Gamma_{mn}\rho^e_{mn}(t)\ ,$$
$$2\Gamma_{mn}=\sum_r[\gamma_{rm}+\gamma_{rn}]=2\Gamma_{nm}\ . \tag{2.12}$$

In periodic systems, Γ_{mn} becomes independent of m and n ($\Gamma_{mn}=\Gamma$). In nonperiodic systems (finite chains, etc.), this m,n dependence survives.

Reineker and Kühne[12–14] thoroughly discussed various regimes (pure coherent, pure incoherent, quasicoherent, incoherent) of the excitation transfer governed by different parts of the HSR equations.

Čàpek and Szöcz[63,64] generalized this treatment by introducing the generalized stochastic Liouville equation model (GSLEM) by replacing the classical field $V(t)$ (leading just to induced transitions) by a quantum field (yielding both induced and spontaneous transitions). Thus the symmetry relations $\gamma_{mn}=\gamma_{nm}$ become invalid and are (in the lowest order in J_{mn}) replaced by detailed balance conditions. In the Haken-Strobl-Reineker parametrization, however, (2.12) remains valid.

C. Grover-Silbey microscopical theory

The theory (GS) developed in the 1970's by Silbey and co-workers[17–25] is one of the earlier microscopic and, simultaneously, most advanced theories of exciton migration in molecular crystals.

Grover and Silbey[18] were looking for

$$\mathcal{G}_{mn}(t)=\langle 0|A_0\langle A_n^\dagger(t)A_m(t)\rangle A_0^\dagger|0\rangle \ . \tag{2.13}$$

Here $|0\rangle$ denotes the electronic as well as vibrational ground state and $A_n^\dagger$ creates the exciton (carrier) polaron at the nth molecule, while $\langle\cdots\rangle$ denotes as thermal phonon average.

The equations at which Grover and Silbey arrived (after some manipulations and approximations; see Ref. 18) have for a perfect infinite molecular crystal in the narrow phonon band limit (Einstein model of dispersionless phonons) with just the nearest-neighbor resonance integral J in one dimension the form

$$\frac{\partial}{\partial t}\mathcal{G}_{nm}(t)\approx\frac{i}{\hbar}\tilde{J}[\mathcal{G}_{n+1,m}(t)+\mathcal{G}_{n-1,m}(t)-\mathcal{G}_{n,m+1}(t)-\mathcal{G}_{n,m-1}(t)]$$
$$-2\frac{\tilde{J}^2}{\hbar^2}\gamma_1(t)\{2\mathcal{G}_{nm}(t)-[\mathcal{G}_{n+1,m+1}(t)+\mathcal{G}_{n-1,m-1}(t)]\delta_{nm}-(\delta_{n,m+1}+\delta_{n,m-1})\mathcal{G}_{mn}(t)\} \ . \tag{2.14}$$

D. Conclusions

Kenkre[8] and also Hemenger, Lakatos-Lindenberg, and Pearlstein[42] recognized that the structure of the GS equations (2.14), if a Markovian approximation takes place, corresponds to that of the HSR (2.12), with

$$\gamma_{n,n\pm1}\approx\tilde{J}^2\gamma_1(+\infty)/\hbar^2 \ ,$$

and other γ_{mn} being zero, including, in particular,

$$\gamma_{n,n}(\equiv\gamma_0)=0 \ . \tag{2.15}$$

The coincidence in this form cannot hide some physical differences such as lack of local scattering in the GS theory, the presence of the rescaled transfer integral $\tilde{J}$ in the GS equations in contrast to the bare J in the HSR counterpart (2.12), and so on. They are certainly a result of the different schemes used; the HSR theory (2.12) (and a similar equation for the GSLEM) is based on expansion in terms of the exciton-phonon coupling; i.e., if one resorts to some approximations, the HSR theory is good just when this coupling is weak enough. On the contrary, (2.14) is based on expansion in powers of the rescaled (i.e., renormalized owing to the exciton-phonon coupling) exciton resonance integrals (or exciton bandwidth) so that the Grover-Silbey approach should be good when this coupling is rather strong.

The parameters γ_{mn} in the stochastic Liouville equations are phenomenological parameters, while the Grover-Silbey theory[18] gives for $\gamma_1(t)$ a microscopic explanation which is exactly the same as obtained by us from the microscopic definition of the memory functions. One can say that GS and HSR theories, although almost formally equivalent, are two complementary approaches with different areas of applicability.

Let us point out that Reineker and Kühne succeeded[12–14] in the derivation of the memory functions which should correspond to HSR (GS) equations. They derived their form with an exponentially damped quasicoherent channel and incoherent (hopping) one. They also showed that the inverse coherence time of the excitation (damping of the first channel of the memory function) is given by $\Gamma=z\gamma_1+\gamma_0$.

We see a direct correspondence to our result (2.7) and (2.8). The coherence time entering the quasicoherent part of the memory function is given by the integral of the second (incoherent, hopping) part. The main difference is that in our theory, as in the theory of Grover and Silbey, $\gamma_0=0$ for the Hamiltonian with a linear local excitation-phonon interaction.

We concluded[39] that in the case of a linear local excitation-phonon interaction there is only one form of the memory functions (from many principal possibilities discussed by Kenkre [(3.4a), (3.9), and (4.4)–(4.6) of Ref. 8]) which can be derived microscopically and correspond exactly to the GS theory after making the Markovian approximation. All further discussions[5–8] concerning how to connect the Kenkre lowest-order result for memory functions with the GS theory[8] are completely unnecessary.

Recently, we tried to explain the differences between the HSR and GS theories (the lack of the parameter γ_0 in the GS theory, the presence of the bare J in the HSR treatment, etc.) from the microscopic viewpoint and we suggested a way for the unification of these theories.[65,66]

III. EXCITON TRANSFER AND TRAPPING

In many applications it is necessary to describe not only the exciton transfer but also the exciton trapping. It has been very popular[6] to work just with the original system (as if there were no finite-lifetime or trapping effects) and to include these effects by additional terms to the unchanged GME. for example, Eq. (2.2) then reads

$$\frac{\partial}{\partial t}P_m(t)=\sum_{n(\neq m)}\int_{t_0}^{t}[w_{mn}(t-\tau)P_n(\tau) - w_{nm}(t-\tau)P_m(\tau)]d\tau-2\gamma P_0(t)\delta_{m0}\ , \tag{3.1}$$

assuming that site zero is either connected with, e.g., a trap to which the exciton (carrier) located at this site can escape from the system with the escape rate 2γ. The channel via which the exciton or carrier may thus escape from the system may be called a sink and (3.1) is then the so-called sink model. It is very easy to generalize (3.1) to a greater number of sinks which may be connected with any site (molecule) in the system, with possibly different sink parameters. One should realize that, in accordance with the physics of such processes, (3.1) implies

$$\frac{\partial}{\partial t}\sum_m P_m(t)=-2\gamma P_0(t)\leq 0\ , \tag{3.2}$$

probabilities $P_m(t)=\rho_{mm}(t)$ of finding the exciton (carrier) at individual sites then remain non-negative. The results of Čápek and Szöcz indicated that inclusion of the sink effect to the GME equation for probabilities should consist of two steps: (1) inclusion of the additional sink term as in (3.1) and (2) changing the memory functions in the vicinity of the sink.

Numerical modeling[49–53] in the framework of the stochastic Liouville equations indicated that this second effect (suppression of the memory functions) leads to an interesting behavior of the quasiparticle (exciton, carrier). The quasiparticle tends to avoid (at least partly) the sites (molecules) connected to the sink (i.e., places where it could be canceled or captured) as far as the sink parameter 2γ exceeds a certain critical value. Increasing the sink parameter 2γ to infinity then dynamically splits off completely those molecules which are connected to the sink. On the other hand, any change of the memory functions in the vicinity of the sink is very undesirable from the technical point view (e.g., the periodicity is lost).

To clarify the influence of the trap (sink) on the behavior of the MF's, we generalized[54] our direct method[28] for the calculation of the coherent memory functions and investigated several simple sink models.[52,53] Again, these works confirmed the significant modifications of all the memory functions as a consequence of the presence of the sink. The unperturbed memory functions for these finite systems are periodic in time.[28] Once the sink is introduced, the memory functions lose their periodicity. In the trimer with the sink appended at one end ($s=3$), an increase of the trapping rate leads to an effective decoupling of the rest of the system (dimer) from the sink site. The decoupling manifests itself not only in the fact that as far as $2\gamma>0$ and $P_m(t)\geq 0$. So the total probability of finding the exciton (carrier) in the system is not only nonconserving, but it should always monotonically decrease. This should be the basic property of the sink model which might be well accepted in many situations. Let us mention that in calculating experimental integral quantities such as, e.g., the quantum yield, the sink model has been found to be very useful (see, e.g., Ref. 5 and the literature quoted therein).

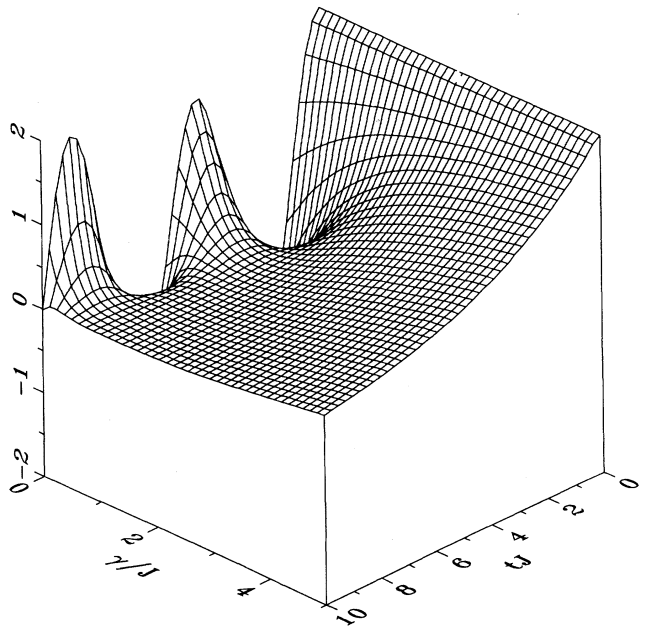

FIG. 1. Memory function $w_{12}(t)$ for a trimer with the sink $[-2\gamma P_3(t)]$.

Pearlstein and co-workers showed[40–44] the different consequences of the presence of the trap (sink) on the experimental quantities in different excitation-transfer regimes (coherent, quasicoherent, and incoherent). This fact has not been for a long time taken properly into account[6,45–47] in the excitation-transfer treatment by the GME method. Čápek and Szöcz[48] pointed out the necessity of a "transformation" of the MF's. The absence of such a transformation could lead to completely erroneous

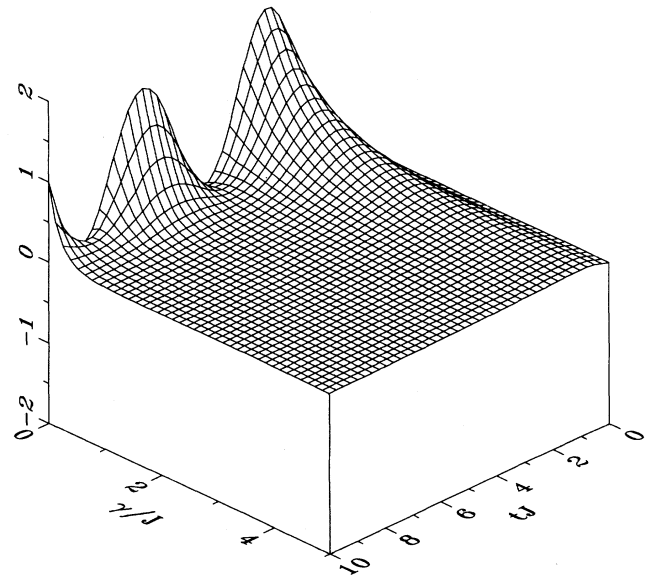

FIG. 2. Memory function $w_{13}(t)$ for a trimer with the sink $[-2\gamma P_3(t)]$.

results. The serious problem is that the sink model in the Kenkre-Wong-Paris treatment (we call it the restricted sink model) yields probabilities which are, in the vicinity of the coherent regime, not necessarily non-negative for any t. [Thus the inequality (3.2) may be also disturbed.]

Čápek and Szöcz[63] showed that proper inclusion of the sink effect should be connected, at least, with adding the term

$$-\frac{1}{2\tau_0}[\delta_{m0}+\delta_{n0}]\rho_{mn} \tag{3.3}$$

to the right-hand side of (2.17). (Here we mean the situation when the sink is connected just with site 0; a possible and the most direct generalization to any greater number of sites connected with such sinks means just to take a sum of analogous terms.) Numerical studies[49–53] then confirmed that the exciton moves entirely in the dimer and avoids the sink site. This could be understood if the memory functions $w_{13}(t)$ and $w_{23}(t)$ were exponentially damped as suggested by Čápek and Szöcz.[48] The result, however, is that the memory function in the rest of the system (here a dimer) is transformed to that for the isolated dimer. Thus our paper[54] questioned the results of Kenkre and Wong[46] (in which no modification of the memory functions due to the sink are introduced) mainly for large trapping rates and for finite systems at least. Recently, we demonstrated the sink avoidance effect also in the excitation transfer along a semifinite chain.[57] The influence of two different (host and guest) lifetimes on the excitation transfer was investigated in Ref. 55.

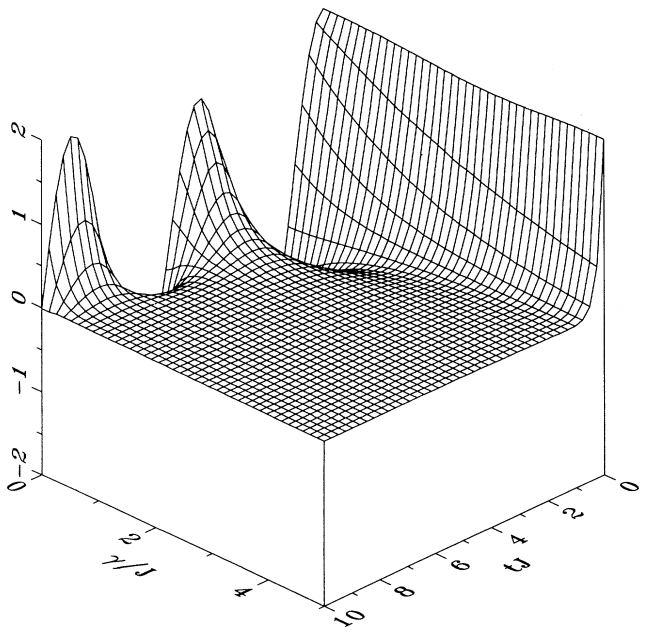

FIG. 3. Memory function $w_{23}(t)$ for a trimer with the sink $[-2\gamma P_3(t)]$.

IV. CTRW TREATMENT

A. GME and CTRW methods

The equivalence of the GME and CTRW methods was suggested by Montroll and co-workers.[15,16] We have looked at it in more detail.[60]

Using the retarded Fourier-Laplace transformation

$$f(t)\Theta(t)=\int_{-\infty}^{+\infty} f^{\omega+i\delta}\exp[-i(\omega+i\delta)t]\frac{d\omega}{2\pi}\ , \tag{4.1a}$$

$$f^{\omega+i\delta}=\int_{0}^{+\infty} f(t)\exp[i(\omega+i\delta)t]dt \tag{4.1b}$$

[$\Theta(t)$ being the Heaviside step function $=0$, $\frac{1}{2}$, or 1 for $t<0$, $t=0$, or $t>0$, respectively], one can easily turn (2.2) to

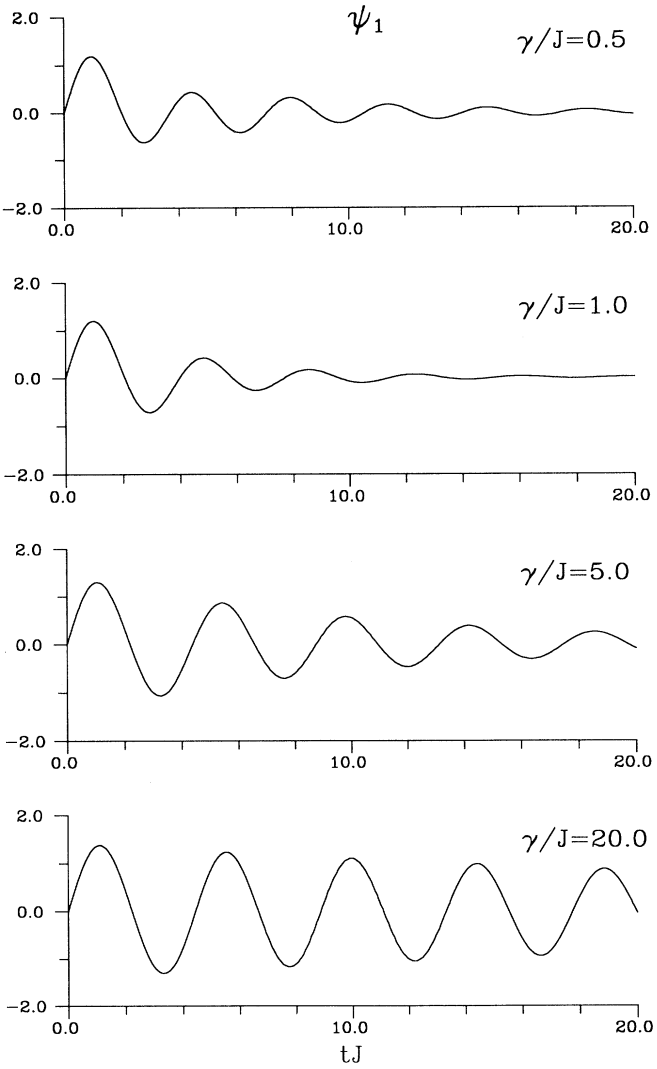

FIG. 4. Pausing-time-distribution function $\psi_1(t)$ for a trimer with the sink $[-2\gamma P_3(t)]$.

$$P_m^z = \frac{i}{z}\left[1-\frac{\sum_{r(\neq m)} w_{rm}^z}{-iz+\sum_{r(\neq m)} w_{rm}^z}\right] P_m(t_0)\exp(izt_0) + \sum_{n(\neq m)} \frac{w_{mn}^z}{-iz+\sum_{r(\neq m)} w_{rm}^z} P_n^z , \quad z=\omega+i\delta , \tag{4.2}$$

with w_{mn}^z and P_m^z bing the transformations of $w_{mn}(t)$ and $P_m(t)$. Denoting

$$\psi_m^z = 1+\frac{iz}{-iz+\sum_{r(\neq m)} w_{rm}^z} , \tag{4.3}$$

$$Q_{mn}^z = \frac{w_{mn}^z}{-iz+\sum_{r(\neq m)} w_{rm}^z} , \tag{4.4}$$

and using the reciprocal transformation (4.1a), one turns (4.2) to

$$P_m(t) = \left[1-\int_0^{t-t_0}\psi_m(\tau)d\tau\right]P_m(t_0) + \sum_{n(\neq m)}\int_0^{t-t_0} Q_{mn}(\tau)P_n(t-\tau)d\tau . \tag{4.5}$$

Let us as usual interpret $\psi_m(\tau)d\tau$ as a probability [i.e., $\psi_m(\tau)$ is the probability density] that there has been a hop from site m to anywhere else in the time interval $(\tau,\tau+d\tau)$ after the time at which the quasiparticle (exciton, charge carrier) has certainly been found at m; let $Q_{mn}(\tau)$ be the same quantity for the hop $n\rightarrow m$. Then (4.5) is the total balance condition serving as a basis for the continuous-time random-walk method. It is clear that if (4.5) were (in the above way) properly interpreted, this would be an indispensable basis for modeling the exciton or carrier dynamics.

Though formally correct, (4.5) cannot be in general well interpreted as above. Objections against this interpretation are as follows.

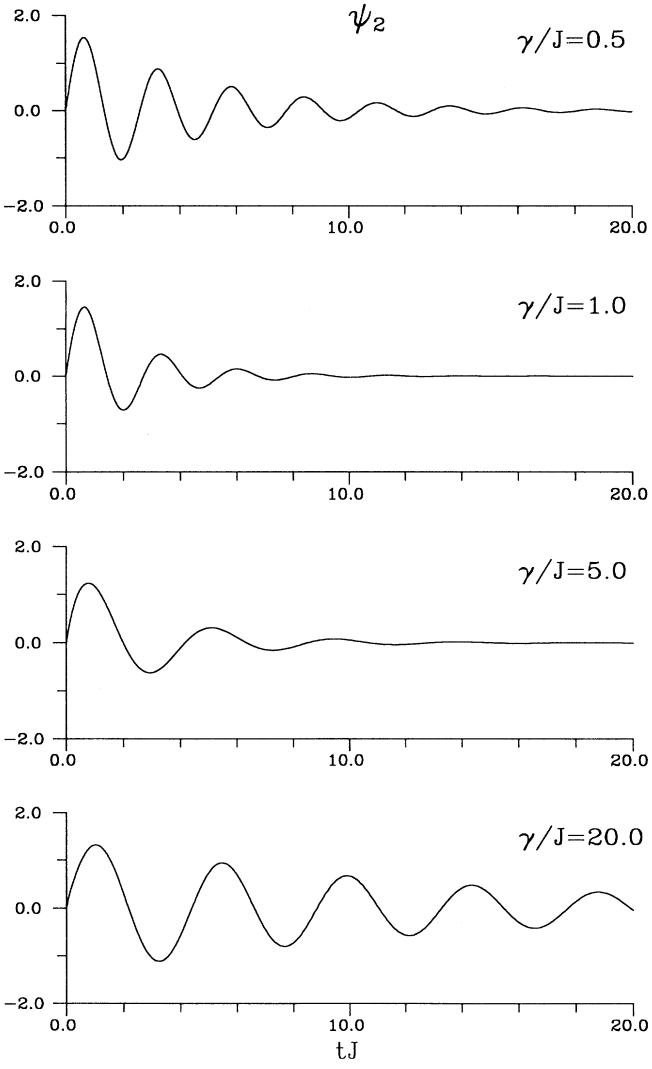

FIG. 5. Pausing-time-distribution function $\psi_2(t)$ for a trimer with the sink $[-2\gamma P_3(t)]$.

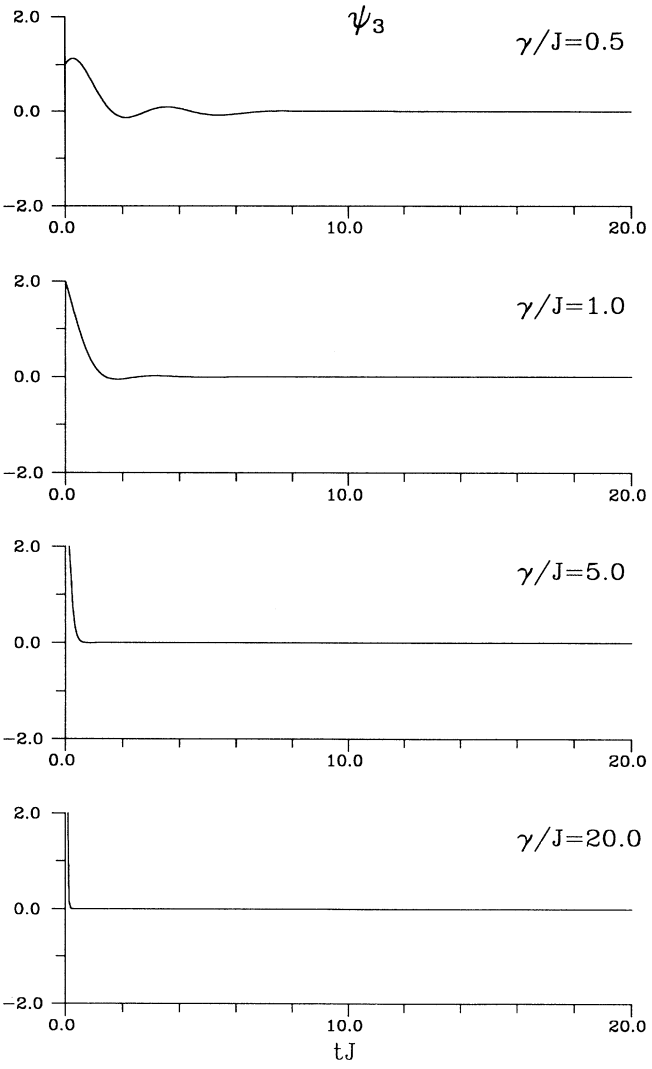

FIG. 6. Pausing-time-distribution function $\psi_3(t)$ for a trimer with the sink $[-2\gamma P_3(t)]$.

From the above interpretation, one easily deduces that

$$\sum_{m(\neq n)} Q_{mn}(\tau)=\psi_n(\tau) , \tag{4.6a}$$

i.e.,

$$\sum_{m(\neq n)} Q^z_{mn}=\psi^z_n . \tag{4.6b}$$

From (4.3) and (4.4) we see that (4.6b) is true just when $\sum_{r(\neq m)} w^z_{rm}$ [i.e., also $\sum_{r(\neq m)} w_{rm}(t)$] is independent of m. Unfortunately, this is in general not true; it applies only for systems of equivalent sites (e.g., perfect molecular crystals made of identical molecules in physically equivalent positions). In this case (but not in general), both sides of (4.6a) become independent of n so that, from (4.5), we obtain

$$\sum_m P_m(t)=1 , \tag{4.7}$$

as far as $\sum_m P_m(t')=1$ or any $t'\in(t_0,t)$ (number-of-quasiparticles conservation law). So, if at all, CTRW methods cased on (4.5) are justified just for systems of equivalent sites.

The second objection against the above interpretation [i.e., CTRW methods based on (4.5)] is that both $\psi_m(t)$ and $Q_{mn}(t)$ must be non-negative. Namely, this is the point which excludes any applicability of CTRW methods based on (4.5) (owing to its improper interpretation) for the coherent (or quasicoherent) regime, in accordance with the introductory discussion. The problem is that the inequalities

$$\psi_m(t)\geq 0 , \quad Q_{mn}(t)\geq 0 \tag{4.8}$$

do not apply for every t in the coherent or quasicoherent regimes.

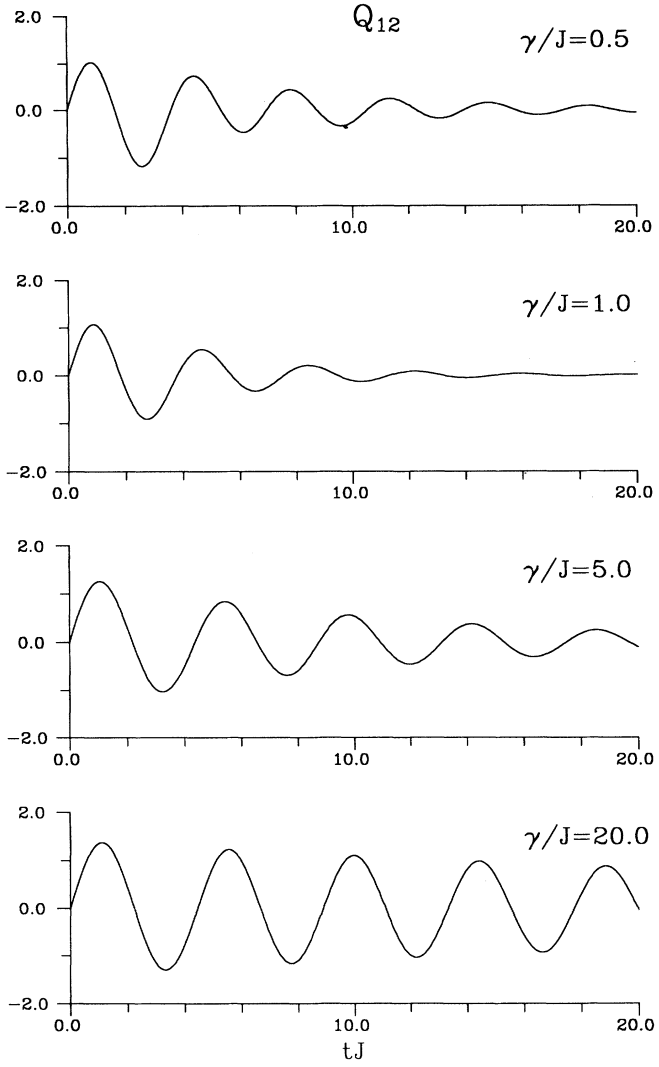

FIG. 7. Probability density $Q_{12}(t)$ for a trimer with the sink $[-2\gamma P_3(t)]$.

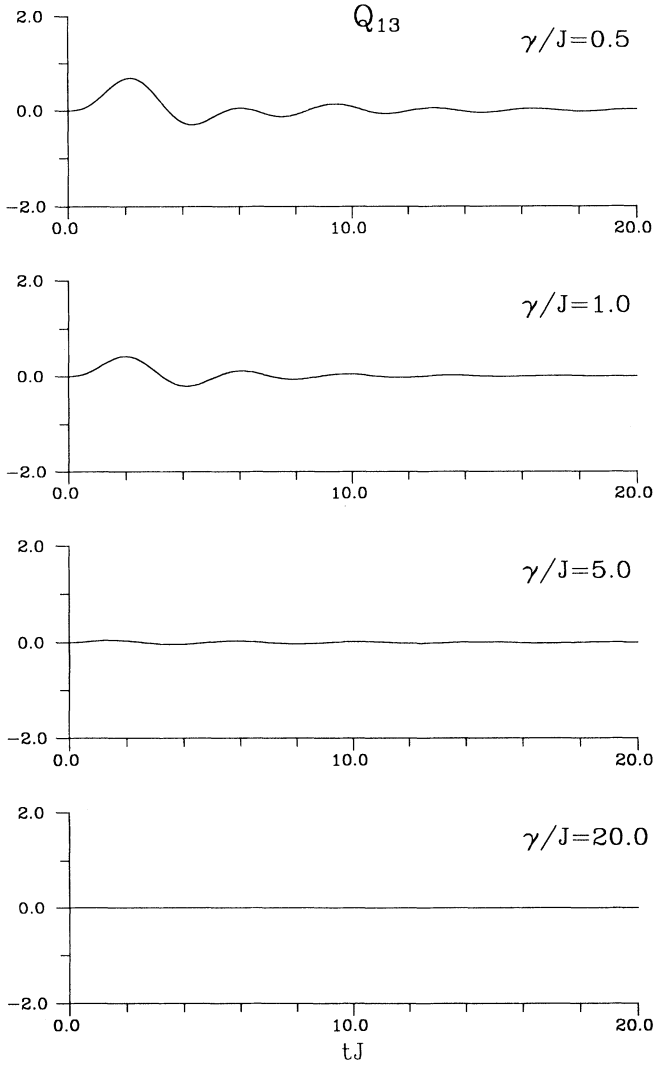

FIG. 8. Probability density $Q_{13}(t)$ for a trimer with the sink $[-2\gamma P_3(t)]$.

We illustrated[60] this shortcoming for a symmetric dimer and trimer.

Thus, in contrast to standard opinion, CTRW methods are not in general equivalent to the GME and they are well applicable in computer modeling [as far as being based on (4.5) with the above interpretation] for systems of equivalent sites and, simultaneously, sufficiently incoherent transfer only.[54,39]

B. Trapping in the CTRW treatment

Recently, we started to investigate[61] the influence of the sink in finite systems on the time dependence of $\psi_m(t)$ and $Q_{mn}(t)$. We used exact forms of the coherent memory functions given in Ref. 61.

The Hamiltonian H of the finite system which includes an effect of the sink reads

$$H_{ii}=\varepsilon_i-i\gamma\delta_{is}\ , \qquad H_{ik}=H_{ki}^{*}=J_{ik}\quad \text{for } i\neq k\ . \tag{4.9}$$

The coherent memory functions for finite system with the sink have the form[61]

$$w_{mn}(t)=-\sum_{\alpha=1}^{2I_0} r_\alpha(m,n)e^{i\sigma_\alpha t}\ , \tag{4.10}$$

where σ_α, r_α, and I_0 are given by the Hamiltonian H.

We restricted[59] ourselves to the simple example, namely a trimer, to keep the problem also analytically solvable. In a symmetric trimer there are two possibilities to place a sink: in the center ($s=2$) or at the end ($s=3$).

The first case was investigated thoroughly in Ref. 61 using the memory functions given in Ref. 54.

The memory functions $w_{12}(t)$, $w_{13}(t)$, and $w_{23}(t)$ obtained analytically for the case that the sink is placed at the end of timer in Ref. 54 are presented in Figs. 1–3.

Fourier transformation of (3.1) may be rearranged as

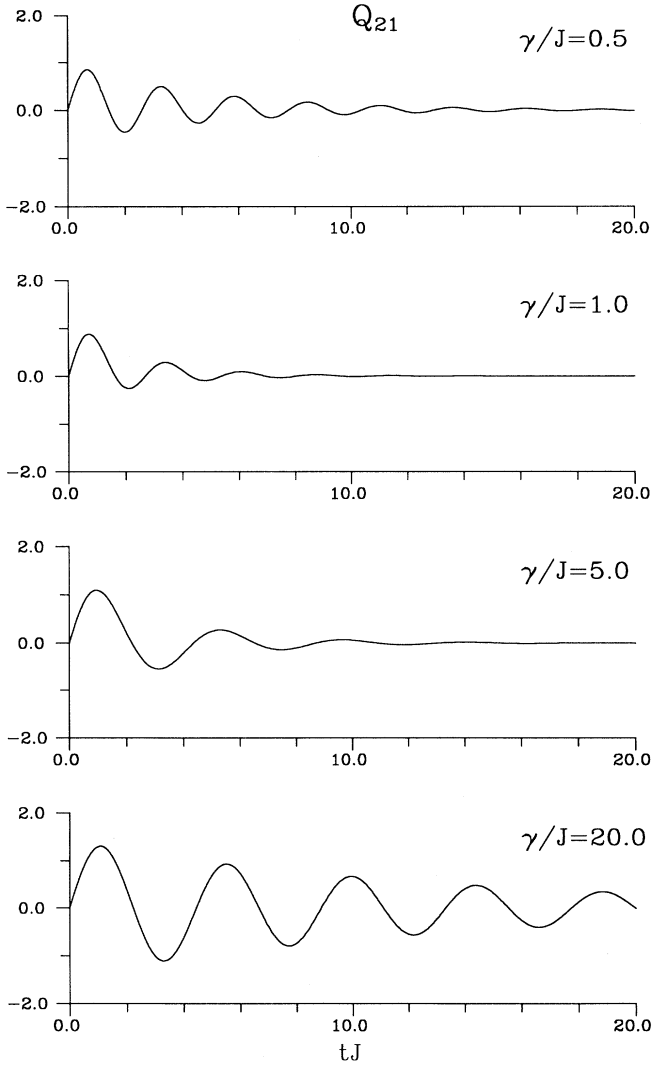

FIG. 9. Probability density $Q_{21}(t)$ for a trimer with the sink $[-2\gamma P_3(t)]$.

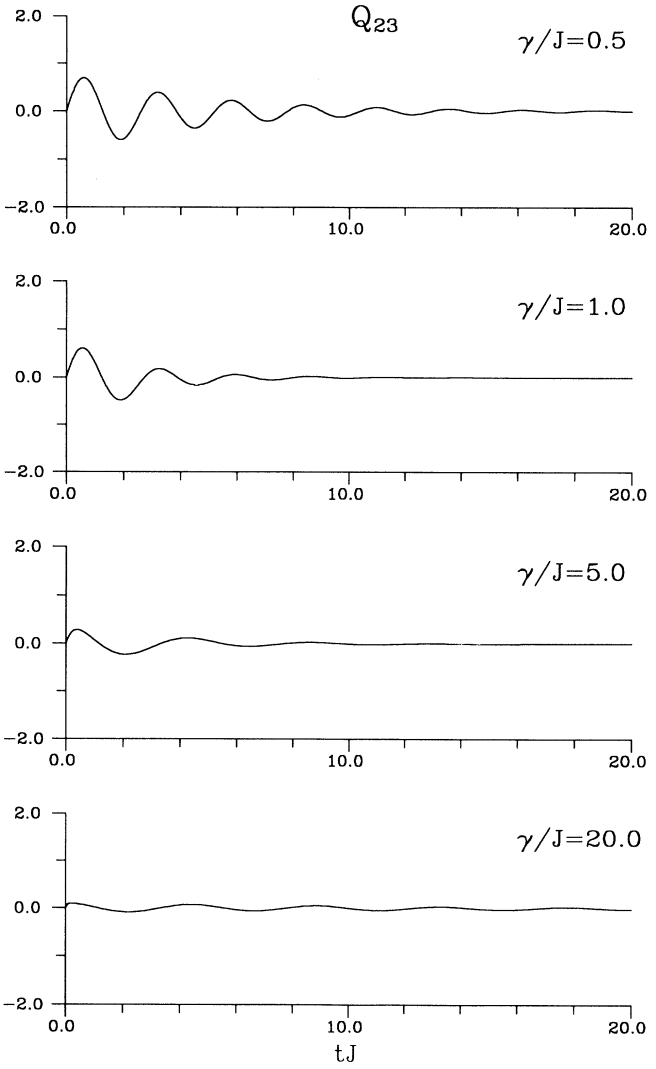

FIG. 10. Probability density $Q_{23}(t)$ for a trimer with the sink $[-2\gamma P_3(t)]$.

$$P_m(z)=\frac{i}{z}\left[1-\frac{2\gamma\delta_{ms}+\sum_{r(\neq m)}w_{rm}(z)}{-iz+2\gamma\delta_{ms}+\sum_{r(\neq m)}w_{rm}(z)}\right]\times P_m(t_0)e^{izt_0}+\sum_{n(\neq m)}\frac{w_{mn}(z)}{-iz+2\gamma\delta_{ms}+\sum_{r(\neq m)}w_{rm}(z)}P_n(z)\ , \tag{4.11}$$

with

$$\psi_m(z)=\frac{2\gamma\delta_{ms}+\sum_{r(\neq m)}w_{rm}(z)}{-iz+2\gamma\delta_{ms}+\sum_{r(\neq m)}w_{rm}(z)} \tag{4.12}$$

and

$$Q_{mn}(z)=+\frac{w_{mn}(z)}{-iz+2\gamma\delta_{ms}+\sum_{r(\neq m)}w_{rm}(z)}\ . \tag{4.13}$$

Contrary to the results of Ref. 61, we did not succeed for a trimer with the sink at the end in the analytical treatment of the functions $\psi_m(t)$ and $Q_{nm}(t)$. We found them only numerically.

The time dependences of the pausing-time-distribution functions $\psi_m(t)$ and probability densities $Q_{mn}(t)$ are presented in Figs. 4–12.

V. CONCLUSIONS

As stated in the Introduction, this paper addresses a specific problem in the exciton transfer in molecular aggregates, namely, the influence of the trap (here modeled according to Kenkre's suggestion as a sink[6]) on the pausing-time-distribution functions $\psi_m(t)$ and the probability densities $Q_{nm}(t)$ of the continuous-time random-walk theory.

Investigation of the relationships among different theories of the excitation transfer pointed out the crucial

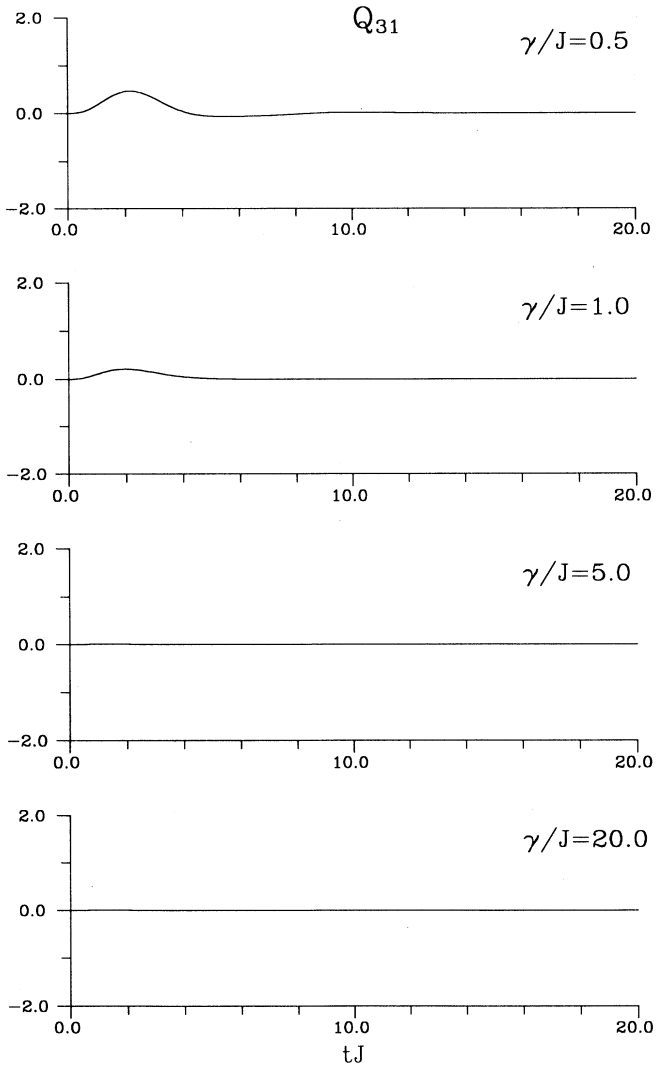

FIG. 11. Probability density $Q_{31}(t)$ for a trimer with the sink $[-2\gamma P_3(t)]$.

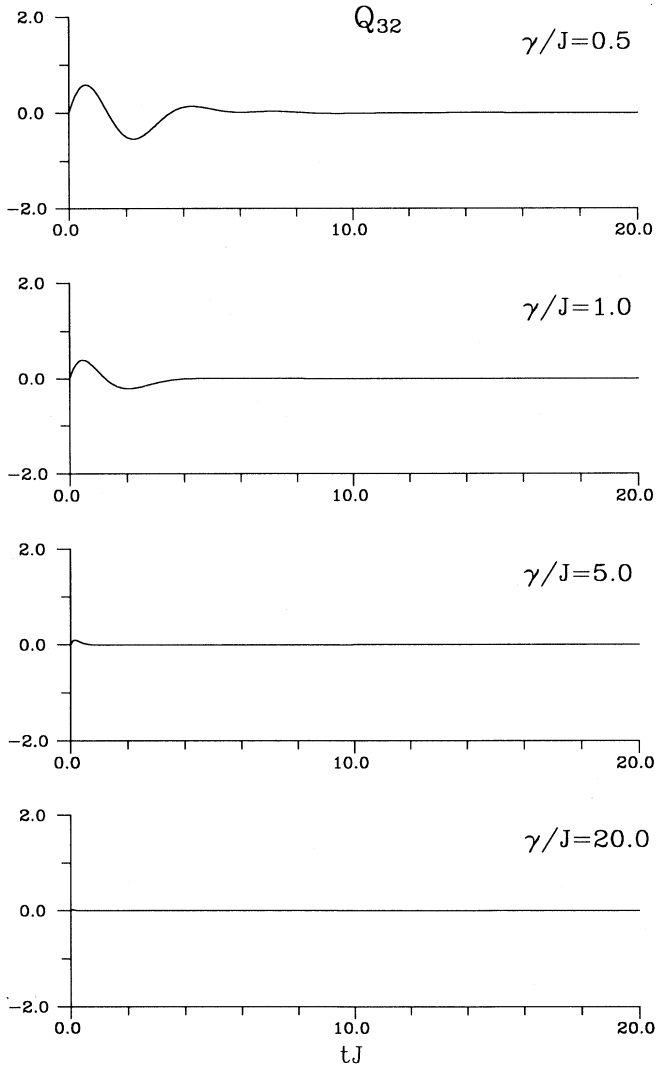

FIG. 12. Probability density $Q_{32}(t)$ for a trimer with the sink $[-2\gamma P_3(t)]$.

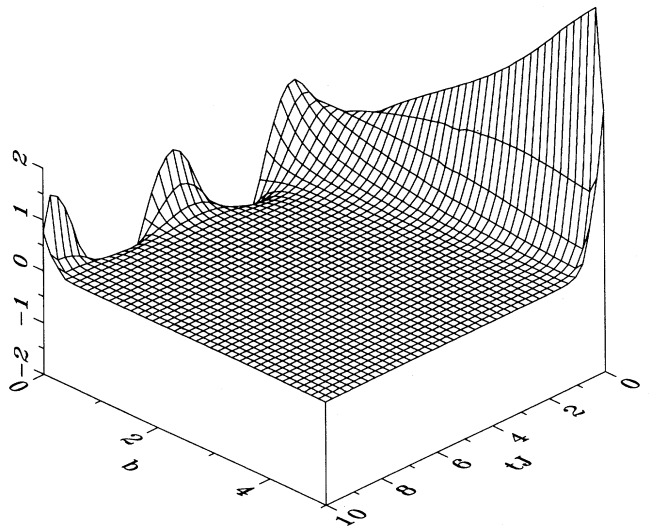

FIG. 13. Pausing-time-distribution function $\psi_1(t)$ for a dimer.

role of the pure coherent memory functions also in the noncoherent regime of the excitation transfer.

We used the pure coherent memory functions $w_{mn}(t)$ connecting different sites of the system in the derivation of the CTRW counterpart of the GME formalism. Our generalized method which we used Ref. 61 for obtaining the pure coherent memory functions $w_{mn}(t)$ entering as kernel in the Nakajima-Zwanzig equations is based on a direct inversion of the superoperator expression. This allowed us to investigate thoroughly the memory functions in the general finite system in the presence of a trap modeled as a sink.

A description of the exciton transfer in the presence of a trap requires[61] for a sufficiently large trapping rate 2γ more pronounced modification of the generalized master equation (2.2) than suggested by Kenkre.[6] One has not only to append the sink term to the GME but also to use the proper form of the memory functions $w_{mn}(t)$, in calculation of which the influence of the sink was taken into account. This results also in a form of the causing-time-distribution functions $\psi_m(t)$ and the probability densities $Q_{mn}(t)$.

We presented dramatic changes of the analytical form of the pausing-time-distribution functions $\psi_m(t)$ and probability densities $Q_{mn}(t)$ which take into account the influence of the sink. We showed[61] that the presence of the sink leads to a transformation of not only those memory functions which connect the sink with other places. The decoupling of the rest of the system from the very strong sink is not only owing to a diminishing of the memory functions connecting the sink with the rest of the system.

In Figs. 1–3 is shown that in a trimer in which the sink influences (γ) one end (site 3) the memory function $w_{12}(t)$ transforms to that of the rest (dimer) of the system.

Our calculation (Figs. 4–12) shows that in the time dependence of $\psi_m(t)$ it is reflected that the coherent memory function are generally losing their periodic character with increasing of the trapping rate 2γ and memory effects are preserved for shorter times.

We conclude that in some regimes the pausing-time-distribution functions and the probability densities are negative for some times so that their usual interpretation as probabilities becomes dubious.

Hence we repeat here our former conclusion[60,61] that though the mathematical form of (4.5) as the CTRW counterpart of the GME is doubtless, its physical interpretation and consequently its practical use in, e.g., the Monte Carlo modeling of the excitation transfer may get into trouble in the near-coherent regime.

Our conclusions are based on results for finite systems. To close the investigation of the connection between the CTRW and GME (and other methods), it would be desirable to obtain the pausing-time-distribution functions $\psi_m(t)$ and probability densities $Q_{mn}(t)$ for infinite systems taking into account the two-channel form of memory functions.

Preliminary results for the time dependence of the pausing-time-distribution function $\psi_m(t)$ in symmetric dimer during the transition from the pure coherent to incoherent regime of the excitation transfer is shown on Fig. 13. We have used the two-channel form of the dimer memory function[8,33]

$$w_{12}(t)=a\exp(-2bt)+b\,\delta(t)\ .$$

The microscopic meaning of the parameters a and b was discussed in Ref. 33.

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