SPATIALLY NONLOCAL TRANSFER RATES IN EXCITON TRANSPORT ARISING FROM LOCAL INTERSITE MATRIX ELEMENTS

V.M. KENKRE

Institute for Fundamental Studies, Department of Physics and Astronomy, University of Rochester, Rochester, New York 14627, USA

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Spatially non-local memory functions, and transfer rates are shown to result from local intersite interactions, through an explicit derivation for a simple model. Their effect on the exciton mean square displacement is discussed.

Much of the recent use [1] of generalized master equations in the description of exciton transport in molecular aggregates has been based on the weak coupling approximation wherein the relative weakness of the intersite transfer matrix element J justifies the retention of only the lowest order nonzero terms in a perturbation development of the memory functions. This approximation results in memory functions $\mathcal{W}(t)$ (and, when the Markoffian approximation is invoked, in transfer rates F) whose degree of spatial extent corresponds directly to that of the transfer matrix elements J. Thus, if J's have nearest-neighbour character, so do F's or $\mathcal{W}(t)$'s. However, if the matrix elements J are not too weak relative to a certain randomness parameter α (typically a quantity pertaining to the exciton-phonon interaction), the exact memory functions can be shown to develop a *spatially non-local* character. We have found no discussions of this conceptually interesting result in the literature with the exception of Goad's model calculation [2] wherein spatially exponentially decaying rates appear. In this note we give an explicit derivation of nonlocal memories for a simple system, report a general expression for them for more complicated systems, and mention their effect on expressions for the exciton mean square displacement and on effective transfer rates.

Consider an open one-dimensional "chain" consisting of only three sites 1, 2, and 3. Let the exciton energy in the absence of intersite interaction be site-independent and therefore considered zero without loss of generality. Let there be no phonons or other randomness in the system, and let site 2 be connected through an intersite transfer J to 1 as well as to 3 but let there be no Hamiltonian matrix element connecting 1 and 3. The equations obeyed by the amplitudes $c_m(t) \equiv \langle m|\psi(t)\rangle$, where $|\psi(t)\rangle$ is the system state and $|m\rangle$ represents a site-localized state (m = 1, 2, or 3), are therefore (with $\hbar = 1$)

$$\mathrm{i}\,\mathrm{d}c_{1,3}/\mathrm{d}t = Jc_2 \quad (1a)$$

$$\mathrm{i}\,\mathrm{d}c_2/\mathrm{d}t = J(c_1 + c_3) \quad (1b)$$

where $c_{1,3}$ denotes c_1 or c_3. Eqs. (1) are solved trivially and yield, for initial occupation of site 1 by the exciton,

$$P_1(t) = \cos^4(tJ/\sqrt{2}) \quad (2a)$$

$$P_2(t) = \tfrac{1}{2}\sin^2(tJ\sqrt{2}) \quad (2b)$$

$$P_3(t) = \sin^4(tJ/\sqrt{2}) \quad (2c)$$

where $P_m \equiv c_m^* c_m$ is the probability that the exciton is at site m. Inspection shows that eqs. (2) are equivalent to the generalized master equation

$$\frac{\mathrm{d}P_m(t)}{\mathrm{d}t} = \int_0^t \mathrm{d}t' \sum_n \left[\mathcal{W}_{mn}(t-t')P_n(t') - \mathcal{W}_{nm}(t-t')P_m(t')\right] \quad (3)$$

with $\mathcal{W}_{12} = \mathcal{W}_{21} = \mathcal{W}$ and $\mathcal{W}_{13} = \mathcal{W}_{31} = \eta$, provided

$$\mathcal{W}(t) = 2J^2\cos(tJ\sqrt{2}) \quad (4a)$$

$$\eta(t) = 2J^2\sin^2(tJ/\sqrt{2})\,. \quad (4b)$$

This is demonstrated by obtaining, from the Laplace-transform of (3),

$$\tilde{P}_1 - \tilde{P}_3 = (\epsilon + \tilde{\mathcal{W}} + 2\tilde{\eta})^{-1} \quad (5)$$

$$\tilde{P}_2 = \tfrac{1}{3}[\epsilon^{-1} - (\epsilon + 3\tilde{\mathcal{W}})^{-1}] \quad (6)$$

where tildes denote transforms and ϵ is the Laplace-variable. Comparison of (2b) with (6) gives (4a) and that of the difference of (2a) and (2c) with (5) gives $\mathcal{W}(t) + 2\eta(t) = 2J^2$, which in conjunction with (4a) yields (4b). Eqs. (4) can also be shown to follow directly from Zwanzig's expression [3] for the memory kernel containing projection operators.

In spite of its near-trivial simplicity the above calculation contains an interesting result: although no interaction matrix element exists between sites 1 and 3, a memory function (as given in eq. (4b)) does develop between them. The price one pays for a closed probability description is thus not only nonlocality in time but also nonlocality in space. At long times, the evolution in general will therefore be as given by a master equation with *long-range rates* in addition to the familiar short-range ones, the former being time-integrals of functions like $\eta(t)$ suitably modified by damping factors. One also notices that the spatially nonlocal memory function in (4b) is zero at $t = 0$ unlike the local memory function in (4a). It can be shown that this is a general characteristic and that it is directly responsible for the fact that the master equations (Markoffian or non-Markoffian) used in the part in the limit of small J, have no spatially nonlocal contributions. That analysis as well as a number of new results concerning these long-range memories and rates will be published elsewhere [4]. Here we shall (i) display the expression [4] for the local and nonlocal memories for a ring of N sites (arbitrary N) in the absence of exciton-phonon interactions, and (ii) present an equation for the mean square displacement of an exciton on an infinite chain in the light of the existence of the long range memories.

Defining $J^k \equiv (1/\sqrt{N})\, \Sigma_{(m-n)}\, J_{mn}\, \mathrm{e}^{\mathrm{i}k(m-n)}$, the memories are given by

$$\tilde{\mathcal{W}}_{mn}(\epsilon) = -\sum_k \mathrm{e}^{-\mathrm{i}k(m-n)}\left[\sum_q \{\epsilon + \mathrm{i}(J^{k+q} - J^q)\}^{-1}\right]^{-1} \tag{7}$$

where the k and q values, span over the N values "in the band". In the limit of infinite N, eq. (7) gives $\mathcal{W}(t)$'s that are combinations of squares of Bessel functions [4].

Considering an infinite linear chain on which an exciton moves with no bias, note that (3) may be rewritten as

$$\frac{\mathrm{d}P_m(t)}{\mathrm{d}t} = \sum_{r=1}^{\infty} \int_0^t \mathrm{d}t'\, \mathcal{W}_r(t-t') \times [P_{m+r}(t') + P_{m-r}(t') - 2P_m(t')] \tag{8}$$

which immediately gives, for $\overline{m^2} \equiv \Sigma_m\, m^2 P_m$,

$$\frac{\mathrm{d}\overline{m^2}}{\mathrm{d}t} = 2\int_0^t \mathrm{d}t'\, \langle m^2(t')\rangle \equiv 2\int_0^t \mathrm{d}t' \sum_{r=1}^{\infty} r^2\, \mathcal{W}_r(t') . \tag{9}$$

This constitutes a generalization of our earlier result [5], which corresponds to the first term in the r-summation. The other terms arise from nonlocal memories. Although eq. (9) and similar equations for higher moments predict diffusion constants and transfer rates that, in this large-J limit, differ from those given earlier [6] (which were based on the result in ref. [5]), the difference can be shown to be wholly in numerical factors. That is to say, the moment expressions always contain powers of (Jt) and the rates can thus be shown to go as $(1/J)$ in the large-J limit as stated earlier [6].

References

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