GENERALIZATION TO SPATIALLY EXTENDED SYSTEMS OF THE RELATION
BETWEEN STOCHASTIC LIOUVILLE EQUATIONS AND GENERALIZED MASTER EQUATIONS

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Through an exact calculation of the memory function in the generalized master equation (GME) which corresponds to a form of the stochastic Liouville equation (SLE) used in exciton transport, a relation is established between the GME and the SLE, which is useful in translating the parameters of one theory into the other, and which is valid for extended systems such as molecular crystals.

The coupled coherent and incoherent motion of excitons in molecular aggregates has been analysed in recent times in terms of stochastic Liouville equations (SLE) [1,2] on the one hand and generalized master equations (GME) [3] on the other. The relations that these two transport descriptions bear to each other are of obvious general interest whether or not one deals with excitons. These relations have been investigated from a formal view point [4] as well as in the context of the connection of spectral features to transport details [5]. The formal equivalence is useful in understanding the parameters of one kind of theory in terms of those of the other. However, as obtained earlier [4], it is valid only for motion on two sites, i.e., for a molecule pair. In this letter it is generalized to an extended system such as a crystal increasing thereby its usefulness in the context of real systems of experimental interest.

As in ref. [4] the connection between the two transport equations is found by expressing the SLE as a GME and calculating exactly the memory appearing in the latter. However the present calculation performs this operation systematically with the help of projection techniques. The SLE may be written as:

$$i\partial\rho/\partial t = S\rho = (S_J + S_A + S_\gamma)\rho , \tag{1}$$

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$$(S_J\rho)_{mn} = \sum_r (J_{mr}\rho_{rn} - J_{rn}\rho_{mr}) , \tag{2}$$

$$(S_A\rho)_{mn} = i\delta_{mn}\left[\sum_r (A_{mr}\rho_{rr} - A_{rm}\rho_{mm}) \right], \tag{3}$$

$$(S_\gamma\rho)_{mn} = -i(1 - \delta_{mn})\gamma\rho_{mn} , \tag{4}$$

where m, n, etc. denote sites in the molecular aggregate, ρ is the density matrix, S_J and S_A represent respectively the coherent and incoherent parts of the evolution and S_γ represents the well-known destruction of off-diagonal elements of the density matrix. Note that this form of the SLE is identical to that of Hemenger et al. [6] and is an approximation to the equation in refs. [1,2], the approximation consisting in dropping a ρ_{nn} term from the evolution of ρ_{mn}. The application of the Zwanzig diagonalizing projection operator to eq. (1) gives

$$\frac{\partial\mathcal{P}\rho(t)}{\partial t} = -i\mathcal{P}S\mathcal{P}\rho(t) - \int_0^t dt' \mathcal{P}S$$

$$\times \exp\left[-i(t - t')(1 - \mathcal{P})S\right](1 - \mathcal{P})S\mathcal{P}\rho(t') , \tag{5}$$

under the initial diagonality condition [7]. The problem of establishing the equivalence is thus the problem of evaluating the expressions in eq. (5). It is easily shown with the help of eqs. (2)–(4) that

$$\mathcal{P}S\mathcal{P}\rho = \mathcal{P}S_A\mathcal{P}\rho\,, \tag{6}$$

$$\mathcal{P}S\exp[-it''(1-\mathcal{P})S](1-\mathcal{P})S\mathcal{P}\rho(t') \tag{7}$$
$$= e^{-t''\gamma}[\mathcal{P}S_J\exp[-it''(1-\mathcal{P})S_J](1-\mathcal{P})S_J\mathcal{P}\rho(t')]\,.$$

The demonstration uses the following facts: (i) S_A drops out of the second term in eq. (5); (ii) S_A is the sole surviving term in the first term in eq. (5); (iii) $(1-\mathcal{P})S_\gamma$ "commutes" with $(1-\mathcal{P})S_J$ in the second term in eq. (5) and $\exp[-it''(1-\mathcal{P})S_\gamma]$ can be taken out as a multiplicative factor $e^{-t''\gamma}$. Eqs. (6) and (7) mean that the SLE (1), or its more familiar form

$$\frac{\partial\rho_{mn}}{\partial t} = -i\sum_r (J_{mr}\rho_{rn} - J_{rn}\rho_{mr})$$
$$+\delta_{mn}\sum_r (A_{mr}\rho_{rr} - A_{rm}\rho_{mm}) - (1-\delta_{mn})\gamma\rho_{mn}, \tag{8}$$

is equivalent to the GME

$$\frac{\partial P_m(t)}{\partial t} = \int_0^t dt' \sum_n [\mathcal{W}_{mn}(t-t')P_n(t')$$
$$-\mathcal{W}_{nm}(t-t')P_m(t')]\,, \tag{9}$$

where $P_m \equiv \rho_{mm}(t)$ is the probability that the site m is occupied and where the memory functions $\mathcal{W}_{mn}(t)$ are given by

$$\mathcal{W}_{mn}(t) = A_{mn}\delta(t) + e^{-\gamma t}\mathcal{W}^c_{mn}(t)\,. \tag{10}$$

Here $\mathcal{W}^c_{mn}(t)$ is the memory function relevant to the pure ($A = \gamma = 0$) crystal and has been calculated earlier [8,9]. Thus, for a finite (one-dimensional) crystal of N sites the Laplace transform of $\mathcal{W}^c_{mn}(t)$ is given [8] by

$$\tilde{\mathcal{W}}^c_{mn}(\epsilon) = -\sum_k e^{-ik(m-n)}$$
$$\times\left[\sum_q \{\epsilon + i(J^{k+q} - J^q)\}^{-1}\right]^{-1}\,, \tag{11}$$

where $J^k = \sum_m J_m e^{ikm}$. In terms of the reduction of eq. (11) in the case of an infinite crystal with nearest neighbour J_{mn}'s, which has been obtained recently [9], eq. (10) takes the form

$$\mathcal{W}_{mn}(t) = A_{mn}\delta(t) + e^{-\gamma t}[J^2_{m-n+1} + J^2_{m-n-1}$$
$$+ 2J_{m-n+1}J_{m-n-1} - 2J^2_{m-n}$$
$$- J_{m-n}J_{m-n+2} - J_{m-n}J_{m-n-2}]2J^2\,, \tag{12}$$

involving products of the J-Bessel functions (shown in parentheses) whose argument equals $2Jt$.

The new results of this letter are eq. (10) for the general case and eq. (12) for the infinite crystal with nearest-neighbour J_{mn}'s. It will be shown elsewhere how these results can be used for the computation of experimental observables. Note in passing that for a molecule pair $\mathcal{W}^c_{mn}(t)$ exactly equals $2J^2$ as has been proved earlier [10] and eq. (10) therefore shows that the SLE indeed corresponds to a GME with a memory that is the sum of a δ-function and an exponential. This is precisely the relations result of ref. [4] that we have thus generalized in eq. (10).

We have been informed by Kühne and Reineker that they have also obtained such a relation through the use of a procedure different from ours and starting from the SLE in refs. [1,2] rather than that in ref. [6].

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