

Generalized Master Equations Under Delocalized Initial Conditions¹

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The initial condition term that must be appended to the generalized master equation (GME) when the density matrix is not initially diagonal in the representation chosen is studied and explicit expressions are obtained for several cases. The term is shown to vanish for initial occupation of a Bloch state of arbitrary wave vector if the system is a crystal and the representation is that of site states, despite the violation of the initial diagonality condition. It is pointed out how one is to use the expressions for the initial term in transport calculations.

KEY WORDS: Generalized master equations ; initial diagonality, localized and delocalized conditions, exciton transport in molecular crystals.

1. INTRODUCTION

Most macroscopic observations in the field of nonequilibrium statistical mechanics are conventionally approached in terms of the (Markovian) master equation⁽¹⁻³⁾ obeyed by $P_m(t)$, the probabilities of occupation of states m of the system. The generalized master equation (GME) is a by-product of attempts⁽⁴⁻¹¹⁾ to derive this master equation from microscopic dynamics. It has the form

$$\partial P_m(t)/\partial t = \int_0^t dt' \sum_n [\mathcal{W}_{mn}(t-t')P_n(t') - \mathcal{W}_{nm}(t-t')P_m(t')] \quad (1)$$

and is formally connected to the master equation (sometimes termed the Pauli master equation) through the fact that the replacement $\mathcal{W}_{mn}(t) = F_{mn} \delta(t)$, where the F_{mn} are the transition rates in the master equation, reduce Eq. (1) to the latter. In the last few years the GME has ceased to be a mere intermediate step in the derivation of the master equation and has been put

¹ This article is dedicated to Prof. Max Dresden on the occasion of his sixtieth birthday.

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to use in practical transport calculations. Some of this work has been reviewed recently.⁽¹²⁾

The GME can be shown⁽⁴⁻¹¹⁾ to be an exact consequence of the microscopic dynamics, represented by the Liouville-von Neumann equation for the density matrix ρ , under a special initial condition, viz. that $\rho(0)$ is initially diagonal in the states m . The fact that Eq. (1) (and consequently the master equation) cannot be derived for initially nondiagonal ρ 's, at least by the methods of Refs. 4-11, is generally understood as representing the well-known fact that not all initial conditions³ in a dynamic system result in approach to equilibrium and irreversible behavior. (The latter are characteristic of the master equation.) Unfortunately, this disregard of the effect of the initial condition is not always permissible in situations where the GME has been put to practical use. Some of these situations specifically involve nondiagonal ρ 's at $t = 0$. An example is provided by exciton transport.⁽¹²⁻¹⁴⁾ There $P_m(t)$ is the probability that the m th site in a crystal or a molecular aggregate is electronically excited. The creation of such an excitation (termed an exciton) involves definite phase relations over many sites: light, whose absorption creates the exciton, has a wavelength which is at least several hundreds of times as large as the intersite distance, and localized excitation in the absence of impurities is experimentally not attainable. Unless the description is changed from site space to k space, one must therefore contend with initial nondiagonal ρ 's.

In such situations one must examine the validity of transport theories employing the GME and, if possible, one must extend Eq. (1) to cover situations where the initial diagonality condition does not apply. This paper attempts to make some headway toward these two goals.

2. EXTENSION OF THE RANGE OF VALIDITY OF THE GME

Following Zwanzig,⁽⁸⁾ one obtains

$$\begin{aligned} \frac{\partial \mathcal{P}\rho(t)}{\partial t} = & - \int_0^t dt' \mathcal{P}Le^{-it'(1-\mathcal{P})L}(1-\mathcal{P})L\mathcal{P}\rho(t') \\ & - i\mathcal{P}Le^{-it(1-\mathcal{P})L}(1-\mathcal{P})\rho(0) \end{aligned} \quad (2)$$

as an *exact* consequence of the microscopic dynamics under *arbitrary* initial conditions. Here L is the Liouville operator denoting commutation with the Hamiltonian H , \mathcal{P} is the diagonalizing operator, which may or may not involve an additional coarse-graining operation,^(11-13,15) and \hbar has been put

³ Consider, for instance, the initial state of a gas of atoms that interact only through collisions, placed in a container such that all atoms have velocities parallel to one another and perpendicular to a pair of opposite walls, and in such a way that the ensuing motion never results in atom-atom collisions.

equal to 1. If the last term in Eq. (2) is neglected, the m th element of Eq. (2) is the GME Eq. (1). The two goals of this paper are therefore most naturally attempted by (i) examining the conditions under which the last term in Eq. (2) is zero, and (ii) evaluating it when it is nonzero. We thus investigate

$$\mathcal{J}_m(t) = -i \langle m | \mathcal{P} L e^{-it(1-\mathcal{P})L} (1-\mathcal{P})\rho(0) | m \rangle \quad (3)$$

We shall take \mathcal{P} not to contain the coarse-graining operation.^(11-13,15) This term $\mathcal{J}_m(t)$, whose addition to Eq. (1) results in a universally valid equation, is known⁽⁶⁾ to be zero for initially localized conditions since $(1-\mathcal{P})\rho(0)$ is then zero. Here and henceforth we picture the states m as localized on the sites of a crystal, because our primary motivation for this study comes from exciton transport. Obviously, the results are not restricted to this meaning of the representation of states m .

Consider now the other extreme for the initial condition. Let the system be initially totally delocalized: in fact, let it occupy a single Bloch state of the crystal with an arbitrary wave vector η . Consider a one-dimensional crystal of N sites for simplicity. Then

$$\rho_{mn}(0) \equiv \langle m | \rho(0) | n \rangle = (1/N) e^{i\eta(m-n)} \quad (4)$$

This represents equal initial probability at every site and $(1-\mathcal{P})\rho(0) = 0$ is definitely *not* satisfied. Writing the matrix elements of the crystal Hamiltonian specifically as $\langle m | H | n \rangle = J_{mn} = J_{m-n}$, where the last identity represents translational invariance in the crystal, leads to

$$[L\rho(0)]_{mn} = \frac{1}{N} \sum_s [J_{m-s} e^{i\eta(s-n)} - J_{s-n} e^{i\eta(m-s)}] = 0 \quad (5)$$

Needless to say, single-indexed quantities such as J_m do *not* represent diagonal elements. Equations (4) and (5) and the fact that the diagonal part of $\rho(0)$, being a multiple of the identity, commutes with any operator, result in $L(1-\mathcal{P})\rho(0) = 0$. Expanding the exponential operator in Eq. (3), rearranging the terms, and using the result just obtained, leads to

$$\mathcal{J}_m(t) = -i \langle m | \mathcal{P} e^{-itL(1-\mathcal{P})L} (1-\mathcal{P})\rho(0) | m \rangle = 0 \quad (6)$$

The GME (1) is thus accurate not only for localized initial conditions, but *also for fully delocalized ones* (in the sense of the occupation of a Bloch state), despite the fact that the latter correspond to a nondiagonal $\rho(0)$.

3. EXPRESSIONS FOR THE INITIAL TERM

We shall attempt to derive useable expressions for $\mathcal{J}_m(t)$ in intermediate situations which are neither localized nor fully delocalized. The Schrödinger equation

$$i \partial c_m / \partial t = \sum_n J_{m-n} c_n \quad (7)$$

for the amplitude c_m that the system occupies the site m , gives

$$c_m(t) = (1/N) \sum_{n,q} \{ \exp(-itJ^q) \exp[-iq(m-n)] \} c_m(0) \quad (8)$$

for arbitrary initial conditions. Here $J^q = \sum_m J_m e^{iqm}$. Define $\mathcal{A}_{mn} = -\mathcal{W}_{mn}$ for $m \neq n$ and $\mathcal{A}_{mn} = \sum_n \mathcal{W}_{nm}$ and the discrete Fourier transforms $\mathcal{A}^q, \mathcal{J}^q, P^q$ of the quantities $\mathcal{A}_m, \mathcal{J}_m, P_m$, respectively, in a manner analogous to the definition of J^q . Here $P_m \equiv c_m^* c_m$ is the probability of site occupation as in Eq. (1). Adding the term $\mathcal{J}_m(t)$ to Eq. (1) and performing Fourier and Laplace transforms on it, one obtains

$$\tilde{P}^k(\epsilon) = \frac{1}{\epsilon + \tilde{\mathcal{J}}^k(\epsilon)} [P^k(0) + \tilde{\mathcal{J}}^k(\epsilon)] \quad (9)$$

where tildes denote Laplace transforms and ϵ is the Laplace variable. On the other hand, Eq. (8) gives

$$\tilde{P}^k(\epsilon) = \frac{1}{N} \sum_q \frac{\rho^{k+q,q}(0)}{\epsilon + i(J^{k+q} - J^q)} \quad (10)$$

where

$$\rho^{k,q}(0) = \sum_{n,l} e^{ikn} e^{-iql} c_n(0) c_l^*(0) \quad (11)$$

Equating the right-hand-sides of Eqs. (9) and (10) leads to expressions for $\mathcal{W}_{mn}(t)$ and $\mathcal{J}_m(t)$ as follows. For the initially localized condition, $\mathcal{J}_m(t)$ [and consequently $\tilde{\mathcal{J}}^k(\epsilon)$] is zero and $\rho^{k+q,q}(0)$ equals 1. Comparison of Eqs. (9) and (10), with the reverse use of the definition of the \mathcal{A}_{mn} , gives

$$\tilde{\mathcal{W}}_{mn}(\epsilon) = - \sum_k \frac{e^{-ik(m-n)}}{\sum_q [\epsilon + i(J^{k+q} - J^q)]^{-1}} \quad (12)$$

which has been obtained, evaluated, and used by the author recently.⁽¹⁸⁾ The Zwanzig treatment⁽⁸⁾ of Eq. (2) shows explicitly that the memory kernel is independent of $\rho(t)$ or of initial conditions. We are assured therefore that Eq. (12) also holds when $\tilde{\mathcal{J}}^k(\epsilon) \neq 0$ and we can thus use it to obtain an expression for $\tilde{\mathcal{J}}^k(\epsilon)$ or for $\mathcal{J}_m(t)$. Thus

$$\tilde{\mathcal{J}}^k(\epsilon) = \frac{\sum_q [\rho^{k+q,q}(0) - P^k(0)] [\epsilon + i(J^{k+q} - J^q)]^{-1}}{\sum_q [\epsilon + i(J^{k+q} - J^q)]^{-1}} \quad (13)$$

$$\tilde{\mathcal{J}}_m(\epsilon) = (1/N) \sum_k \tilde{\mathcal{J}}^k(\epsilon) e^{-ikm} \quad (14)$$

Using Eq. (12) and the definition $\tilde{\mathcal{W}}^k(\epsilon) = \sum_m \tilde{\mathcal{W}}_m(\epsilon) e^{ikm}$, one may rewrite Eq. (13) as

$$\tilde{\mathcal{J}}^k(\epsilon) = (-N) [\tilde{\mathcal{W}}^k(\epsilon)] \sum_q \frac{\sum_n \sum_{l(l \neq n)} e^{i(k+q)n} c_n(0) e^{-iql} c_l^*(0)}{\epsilon + i(J^{k+q} - J^q)} \quad (15)$$

It is a straightforward exercise to show from Eqs. (15) and (14) that $\mathcal{J}_m(t)$ equals zero for localized and fully delocalized initial conditions. We shall give here results for two slightly more complex initial situations: (i) equal occupation of two distinct sites r and s , and (ii) equal occupation of two distinct Bloch states η and μ . In these respective cases

$$\rho^{k+a,q}(0) - P^k(0) = \frac{1}{2}[e^{ikr}e^{iq(r-s)} + e^{iks}e^{iq(s-r)}] \tag{16}$$

$$\rho^{k+a,q}(0) - P^k(0) = \frac{1}{2}[\delta_{k,0}\{N(\delta_{a,\mu} + \delta_{a,\eta}) - 2\} + \delta_{k,\mu-\eta}\{N\delta_{a,\eta} - 1\} + \delta_{k,\eta-\mu}\{N\delta_{a,\mu} - 1\}] \tag{17}$$

For variety we shall exhibit $\tilde{\mathcal{J}}^k(\epsilon)$ for case (i) and $\mathcal{J}_m(t)$ for case (ii). Equation (16) yields after using Eqs. (15) and (12)

$$\tilde{\mathcal{J}}^k(\epsilon) = \frac{1}{2}[e^{tkr}\tilde{Q}_{r-s}^k(\epsilon) + e^{tks}\tilde{Q}_{s-r}^k(\epsilon)] \tag{18}$$

with

$$\tilde{Q}_m^k(\epsilon) = \left[\sum_q \frac{e^{iqm}}{\epsilon + i(J^{k+q} - J^q)} \right] \left[\sum_q \frac{1}{\epsilon + i(J^{k+q} - J^q)} \right]^{-1} \tag{19}$$

For initial equal occupation of the Bloch states η and μ , Eqs. (17), (15), (14), and (12) give

$$\mathcal{J}_m(t) = (1/N)[\mathcal{C}(t) \cos\{(\mu - \eta)m\} + \mathcal{S}(t) \sin\{(\mu - \eta)m\}] \tag{20}$$

$$\mathcal{C}(t) = \int_0^t dt' \mathcal{W}^{(\mu-\eta)}(t-t') \cos\{(J^\eta - J^\mu)t'\} \tag{21}$$

$$\mathcal{S}(t) = -\int_0^t dt' \mathcal{W}^{(\mu-\eta)}(t-t') \sin\{(J^\eta - J^\mu)t'\} \tag{22}$$

where $\mathcal{W}^{\mu-\eta}$ is given by the replacement $k = \mu - \eta$ in the expression $\mathcal{W}^k = \sum_m e^{ikm}\mathcal{W}_m$, where \mathcal{W}_m is given by Eq. (12).

For the infinitely long chain with nearest neighbor interactions J , it can be shown that

$$\tilde{\mathcal{W}}^k(\epsilon) = -[\epsilon^2 + 16J^2 \sin^2(k/2)]^{1/2} \tag{23}$$

$$\mathcal{C}(\epsilon) = \frac{\epsilon\{\epsilon^2 + 16J^2 \sin^2[\frac{1}{2}(\mu - \eta)]\}^{1/2}}{\epsilon^2 + 16J^2 \sin^2[\frac{1}{2}(\mu - \eta)] \sin^2[\frac{1}{2}(\mu + \eta)]} \tag{24}$$

$$\tilde{\mathcal{S}}(\epsilon) = \{4J \sin[\frac{1}{2}(\mu - \eta)] \sin[\frac{1}{2}(\mu + \eta)]\} \{\epsilon^2 + 16J^2 \sin^2[\frac{1}{2}(\mu - \eta)]\}^{1/2} \times \{\epsilon^2 + 16J^2 \sin^2[\frac{1}{2}(\mu - \eta)] \sin^2[\frac{1}{2}(\mu + \eta)]\}^{-1} \tag{25}$$

For instance, for the case where $\mu + \eta = \pi$, Eq. (25) gives

$$\mathcal{S}(t) = \{4J \sin[\frac{1}{2}(\mu - \eta)]\} J_0 \{4Jt \sin[\frac{1}{2}(\mu - \eta)]\} \tag{26}$$

where J_0 is the Bessel function of zeroth order.

Equation (9) shows the precise manner in which one should put to use

the various terms obtained in this section. They act as source terms in the GME Eq. (1) and are known from the initial condition. The well-known technique of obtaining solutions of a linear inhomogeneous equation from those of the homogeneous counterpart, which is, in fact, embodied in Eq. (9), goes on then to yield the probabilities.

4. DISCUSSION

Of what practical use are the expressions for \mathcal{J}^k and \mathcal{J}_m obtained in the previous section if for the perfect crystals for which they apply, direct solutions of Eq. (7) can be written down as easily? This is evidently a relevant question. The answer is that they are useful in the analysis of not-so-perfect crystals in which there are "bath interactions," such as the exciton-phonon interaction, which introduce irreversibility into the problem and bring about approach to equilibrium. In such situations it is not known clearly how to augment the Schrödinger equation (7), but a physical extension of the Liouville-von Neumann equation exists:

$$\partial\rho_{mn}/\partial t = -i \sum_s [J_{ms}\rho_{sn} - J_{sn}\rho_{ms}] - \alpha(1 - \delta_{m,n})\rho_{mn} \quad (27)$$

The last term in Eq. (27) causes the destruction of off-diagonal elements of the density matrix, and α represents the "bath interactions." This equation has been used widely⁽¹⁷⁾ and can be considered a particular case of the stochastic Liouville equation.⁽¹⁸⁻²⁰⁾ The author has shown recently⁽²¹⁾ that the $\mathcal{W}_{m-n}(t)$ and $\mathcal{J}_m(t)$ corresponding to Eq. (27) are obtained from those corresponding to Eq. (27) in the absence of the α term by multiplying the latter quantities by $e^{-\alpha t}$. It is for these situations (corresponding to *real* systems, since bath interactions always exist in the real world) that the present analysis and that in Ref. 16 are useful, although they derive from the pure (α -less) situation, which is as easily analyzable from Eq. (10).

Thus, for real systems one replaces ϵ by $\epsilon + \alpha$ in the right-hand sides of Eqs. (12), (13), and (15), (18) and multiplies that of Eq. (20) by $e^{-\alpha t}$. This is no doubt an essentially phenomenological way of introducing irreversibility into the system and it presupposes that the characteristic times of $\mathcal{J}(t)$ and $\mathcal{W}(t)$'s are exactly the same. This presupposition leads, however, to the comfortable result that the time range for which the Markovian approximation is applicable is also the time range for which the $\mathcal{J}(t)$ terms can be neglected. The Markovian master equation does not therefore require to be supplemented by driving terms arising from $\mathcal{J}(t)$. Needless to say, there is no reason to believe that this situation is universally valid.

Being motivated by exciton transport in crystals, we have attempted to examine the $\mathcal{J}(t)$ term for a system characterized by translational invariance. Equations (13) and (15) provide the explicit useable expressions for the $\mathcal{J}(t)$

terms in the general case, Eq. (9) shows how to use them, Eqs. (18) and (20) constitute particular cases, and the striking result is in Eq. (9), that the $\mathcal{J}(t)$ term is zero for an initial Bloch state despite the violation of the initial diagonality condition. This result is significant for exciton transport, as it answers objections to the GME theory that one might have raised on the basis of the nature of light absorption, i.e., of exciton creation.⁽¹⁴⁾

The result is also expected on symmetry grounds: occupation of a single Bloch state ensures equal probabilities at all sites and consequently no further change in them. Thus the left-hand side of Eq. (1) is zero for all times and so is the right-hand side by symmetry in the crystal. The $\mathcal{J}_m(t)$ term appended to Eq. (1) must therefore be also zero for all times. This comment raises the question of the usefulness of the result proved in Section 2. If initial occupation of a Bloch state leads to constant probabilities for all times, of what interest can a result relevant to this situation be? Once again the answer lies in the possibility of an approximate extension: the most common use of transport equations, of which Eq. (1) is an example, lies in situations where an additional term involving a trap, physical or formal, is appended to the equations. The trap term may represent an absorber which collects and removes excitation, as in photosynthesis^{(22,23),4} or in other experimental situations.⁽²⁴⁾ In this case the creation of the exciton may be considered to a good approximation to lead to the initial occupation of a single Bloch state. Although the probabilities are initially uniform over the system, the trap effect will lead to changes in them. Whether it is the GME or the master equation that controls the dynamics will certainly make a difference in the time dependence of the "excitation function,"⁽²⁰⁾ which is the total probability that the system is excited. One should thus certainly apply the GME theory to this situation if any nonnegligible coherence is suspected to be present in the dynamics. To apply the GME theory in the form of Eq. (1) one must be assured that $\mathcal{J}_m(t)$ is zero. The result of Section 2 provides this assurance. The general message of that result is thus to use Eq. (1) whenever a wave packet of very narrow or very wide spread in wave vector values is created initially (by light absorption in the exciton case). In the more complex situation of an intermediate spread, $\mathcal{J}_m(t)$ terms such as those in Eqs. (18) and (20) must be evaluated and used as explained above. It is planned to present in a future publication details of such calculations in several practical cases.

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⁴ Reference 23 is a recent review.

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