

Relations among theories of excitation transfer

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A study of the formal relations existing among three recent theories of excitation transfer is made and exact results concerning the two-molecule system are presented. An equivalence is established between the Haken-Reineker-Strobl (HRS) and the Grover-Silbey (GS) formalisms (before the partial Markoffian approximation) on one hand and the Kenkre-Knox (KK) formalism on the other. This equivalence takes the form of a simple relation between the KK memory $\mathcal{W}(t)$ and a function $[g(t) - 1]$ appearing in the GS theory. It is shown that the two-term nature of the GSHRS diffusion constant can be understood clearly in terms of this relation, and the ranges of validity of the various theories, including that of the "GSHRS equation," are discussed.

I. INTRODUCTION

Excitation transfer in molecular aggregates and in particular its coupled wavelike (coherent) and diffusive (incoherent) nature have recently been the subject of considerable theoretical analysis. In the context of extended systems the problem of the coupled behavior is popularly known as the issue of the Förster-Dexter motion¹ versus the Frenkel motion² of excitons. Formalisms capable of providing a unified description of such hybrid motion have been constructed³⁻⁵ by (i) Haken and Strobl, and Haken and Reineker (HRS), (ii) Grover and Silbey (GS), and (iii) Kenkre and Knox (KK), among others. The various assumptions and approximations used in these formalisms as well as the conclusions reached appear to differ (sometimes significantly) and it is therefore important to examine the relation that these approaches bear to one another. The beginnings of such an examination are the content of this paper.

The three formalisms³⁻⁵ mentioned above provide evolution equations for a coarse-grained density matrix in the space of the molecular sites, the starting point for these analyses being the Liouville equation for the microscopic density matrix. The HRS theory³ splits the intersite interaction into a coherent and an incoherent part, treats the former through the Liouville equation and the latter through stochastic analysis, and arrives at an equation describing the coupled wavelike and diffusive motion of excitons. An important transformation resulting in a "clothing" of excitons is used in the GS theory but in view of the fact that we are here concerned only with the *formalisms* for the evolution of the density matrix, no comments will be made here on the transformation. Similarly, differences like the presence of the local scattering term in the analysis of Ref. 3 but not in that of Ref. 4 are of no relevance to the present discussion of the *formal* structure of the theories. The GS theory may then be described as proceeding

through phonon-averaging projections (or equivalent methods) to an evolution equation for the density matrix which has a coherent part as in the HRS equation and an "incoherent" part which is non-Markoffian in nature. If the Markoffian assumption is made on this part, the GS theory provides an equation which is formally identical to its HRS counterpart. This agreement should not be surprising. Although the two theories do differ widely in their initial approach, the Markoffian assumption, when made for the "incoherent" term in the GS theory takes the place of the stochastic assumption in the HRS theory. There is thus a formal identity which causes both theories to result in the same equation. We shall term this the GSHRS equation.

The KK theory differs both in the technique of its derivation and the formal nature of the resulting equation. The Zwanzig derivation of the generalized master equation and its further developments⁶ form the basis of this theory. Using projections which diagonalize and coarse grain simultaneously a closed equation is derived for the *diagonal* part of the coarse-grained density matrix. This is a non-Markoffian equation which leads to the Förster theory in the Markoffian limit. Unlike the GSHRS treatment, the KK analysis does not involve a separation of the coherent and the incoherent parts in the evolution equation. Rather the two are combined into the memory and the "coherent part of the evolution" is reflected in the non- δ nature of this memory.

As a first step in the understanding of the relation between the GSHRS and the KK theories, the mean-square displacement $\langle x^2(t) \rangle$ was analyzed⁷ in the context of the two theories. It was shown that the $\langle x^2 \rangle$ predicted by the GSHRS equation corresponds to the one arrived at through the KK theory when the memory in the KK equation is taken as the sum of an exponential and a δ function and it was remarked that this is an approximation to the much more complex memory obtained in the KK

theory from optical spectra. The above form of the memory corresponding to the GSHRS equation is however valid only for the calculation of $\langle x^2 \rangle$ and the computation of the actual memory occurring in the *probability* equation is still necessary. Such a computation is given below.

II. RELATION

A formal equivalence has been stated above to exist between the HRS and the GS theories. An explicit demonstration is straightforward. Equation (3.31) of Ref. 3a is

$$\begin{aligned} \frac{d\langle \rho_{mm'} \rangle}{dt} &= -i[\bar{H}, \langle \rho \rangle]_{mm'} - 2\Gamma \langle \rho_{mm'} \rangle \\ &+ 2\delta_{m'} \sum_r \gamma_{n-r} \langle \rho_{rr} \rangle + 2(1 - \delta_{mm'}) \gamma_{n-n'} \langle \rho_{n'n} \rangle, \\ \Gamma &= \sum_m \gamma_m. \end{aligned} \quad (1a)$$

In keeping with the nearest-neighbor approximation made in Ref. 4 and the absence therein of the local scattering, we write $\bar{H}_{mm'} = \bar{J}(\delta_{n,n'+1} + \delta_{n,n'-1})$, $\gamma_0 = 0$, and $\gamma_{n-n'} = \gamma_1(\delta_{n,n'+1} + \delta_{n,n'-1})$, which reduces the above equations (1) to

$$\begin{aligned} \frac{d\langle \rho_{nn'} \rangle}{dt} &= -i\bar{J}(\langle \rho_{n+1,n'} \rangle + \langle \rho_{n-1,n'} \rangle \\ &- \langle \rho_{n,n+1} \rangle - \langle \rho_{n,n-1} \rangle) \\ &- \Gamma[2\langle \rho_{mm'} \rangle - \delta_{nn'}(\langle \rho_{n+1,n'+1} \rangle + \langle \rho_{n-1,n'-1} \rangle) \\ &- (\delta_{n,n'+1} + \delta_{n,n'-1}) \langle \rho_{n'n} \rangle], \\ \Gamma &= 2\gamma_1. \end{aligned} \quad (1a')$$

With the identification of the GS symbols $m, g_{nm}^*(t)$ and $2\bar{J}^2\gamma_1(t)$, with the respective HRS symbols $n, \langle \rho_{mm'} \rangle$, and Γ , Eqs. (1) are exactly equivalent to Eq. (34) of Ref. 4. [This involves the approximation $\gamma_1(t) = \gamma_1(\infty)$ mentioned above.]

It therefore suffices to investigate the relationship existing between the KK theory and the combined GSHRS theory. This is particularly simple in the context of a two-molecule system. Labelling the two equal-energy molecules 1 and 2, the GSHRS equation takes the form

$$\frac{d\rho_{11}}{dt} = -i\bar{J}(\rho_{21} - \rho_{12}) + A(\rho_{22} - \rho_{11}), \quad (2a)$$

$$\frac{d\rho_{12}}{dt} = -i\bar{J}(\rho_{22} - \rho_{11}) + B(\rho_{21} - \rho_{12}), \quad (2b)$$

etc., where ρ_{11}, ρ_{22} are the probabilities that the excitation resides on the two molecules and ρ_{12}, ρ_{21} are the off-diagonal elements of the coarse-grained density matrix. Equations (2) may be obtained either from the GS formalism in Ref. 4 or from Eq. (3.35) of Ref. 8. The quantities $A(0)$ and $\hat{\gamma}(0)$ in the latter correspond, respectively, to $2A$ and $2B$ above. The coherent parameter \bar{J} is pres-

ent in the Liouville-equation-like term and the incoherent parameters A and B are factors in the Master-equation-like terms. The absence of the \bar{J} terms would give incoherent hopping and that of the A, B terms would result in purely coherent oscillations. The GSHRS theory thus describes the coupled motion by the "addition" of coherent and incoherent terms.

In almost all applications of the GSHRS theory it is assumed that at $t = 0$ the excitation resides totally on one molecule, although this (important) initial condition is not always stated explicitly. This assumption will also be made in the subsequent analysis in this paper. Equation (2b) and a similar equation for ρ_{21} , when Laplace transformed, give

$$\epsilon(\tilde{\rho}_{21} - \tilde{\rho}_{12}) = -2i\bar{J}(\tilde{\rho}_{11} - \tilde{\rho}_{22}) - 2B(\tilde{\rho}_{21} - \tilde{\rho}_{12}), \quad (3)$$

where the tilde denotes the transform (except in \bar{J} , which is in keeping with the notation of Ref. 4) and ϵ is the Laplace variable. With (3) in the transform of (2a) and a Laplace inversion, one immediately recasts (2a) as a closed probability equation in the KK form

$$\frac{d\rho_{11}(t)}{dt} = \int_0^t ds \mathfrak{W}(t-s)[\rho_{22}(s) - \rho_{11}(s)], \quad (4)$$

where the memory $\mathfrak{W}(t)$ is given by

$$\mathfrak{W}(t) = 2\bar{J}^2 e^{-2Bt} + A\delta(t). \quad (5)$$

The functional form of the memory in the actual probability equation for the two-molecule system is therefore identical to the form obtained earlier⁷ for the particular purpose of the calculation of the mean-square displacement. This should be compared with a curve like the one shown in Fig. 2 of Ref. 5b, which has been obtained from the KK theory for the system of two anthracene molecules in cyclohexane solution. The exponential part can be understood as corresponding to a Lorentzian approximation to the $F(z)$ curve of Fig. 1 in Ref. 5b, which would be exact if the modified absorption and emission spectra were Lorentzians without a Stokes shift. Attempts at understanding the origin of the $A\delta(t)$ term in (5) in terms of the KK theory lead one to the requirement that $F(z)$ must have a nonzero part at $z = \infty$, which could result only from the catastrophic requirement that the modified absorption and emission spectra possess nonzero values at infinite frequency. It should be trivially obvious, however, that this unphysical conclusion is the result of stretching the GSHRS equation beyond its range of validity. As has surely been recognized by the authors of Refs. 3 and 4, the equation is not valid at times which are too small and the singular term in Eq. (5) must not therefore be used at very small t 's or its corresponding $F(z)$ at very large z 's. This restriction

on the GSHRS *equation* concerning the time scale of description is not shared by the KK theory. The latter should therefore be compared with the formalism of Refs. 3 and 4 *without* the Markoffian approximation.

Consider then

$$\frac{d\rho_{11}(t)}{dt} = -i\tilde{J}(\rho_{21} - \rho_{12}) + \int_0^t ds \alpha(t-s)[\rho_{22}(s) - \rho_{11}(s)], \quad (6)$$

$$\frac{d\rho_{12}(t)}{dt} = -i\tilde{J}(\rho_{22} - \rho_{11}) + \int_0^t ds \beta(t-s)[\rho_{21}(s) - \rho_{12}(s)] \quad (7)$$

from which Eqs. (1) and (2) were derived via the approximation $\alpha(t) = A\delta(t)$; $\beta(t) = B\delta(t)$. These equations correspond to Eq. (3.23) of Ref. 8 and may be said to appear implicitly in Refs. 3 and 4, e.g., before the approximation imposed by Eq. (3.17) of Ref. 3b. In Ref. 8 the time dependence of $\alpha(t)$ is identical to that of $\beta(t)$. Writing these terms as $A\eta(t)$ and $B\eta(t)$, respectively, where $\eta(t)$ is identical, except for constant factors, to the $[g(t) - 1]$ of Ref. 4, one can prove the following relation between the Laplace transforms of these quantities and of the memory $\mathfrak{w}(t)$ appearing in Eq. (4):

$$\tilde{\mathfrak{w}}(\epsilon) = 2\tilde{J}^2/[\epsilon + 2B\tilde{\eta}(\epsilon)] + A\tilde{\eta}(\epsilon). \quad (8)$$

This exact relation between the GSHRS formalism in its general form (without the Markoffian approximation) and the KK formalism, established for the two-molecule system, is the primary result of this paper. Equation (5) is recovered under the approximation $\eta(t) = \delta(t)$, consistent with the GSHRS *equation*. The memory in the KK equation is seen to be a sum of two exponentials with different time constants if in Eqs. (6) and (7) the Markoffian approximation is made on the $\beta(t)$ term and if $\alpha(t)$ is assumed to be an exponential. It is instructive to calculate the form of $\mathfrak{w}(t)$ when $\eta(t)$ is the normalized exponential $\gamma e^{-\gamma t}$. Equation (8) predicts

$$\mathfrak{w}(t) = 2J^2 e^{-\gamma t/2} \left[\cos\left(\frac{\gamma at}{2}\right) + \frac{1}{a} \sin\left(\frac{\gamma at}{2}\right) \right] + A\gamma e^{-\gamma t} \quad (9)$$

if $\gamma a^2 \equiv 8B - \gamma \geq 0$ and

$$\mathfrak{w}(t) = (J^2/b)[(1+b)e^{-\gamma(1-b)t/2} - (1-b)e^{-\gamma(1+b)t/2}] + A\gamma e^{-\gamma t} \quad (10)$$

if $\gamma b^2 \equiv \gamma - 8B \geq 0$. Equation (9) shows decay with oscillations, a behavior often observed in $\mathfrak{w}(t)$'s computed from the spectra of real substances⁹ and

Eq. (10) corresponds to an $F(z)$ built from three Lorentzians.

III. DISCUSSION

Formal relations existing among three recent theories of excitation transfer have been investigated above. An equivalence has been established under quite general conditions between two of them (HRS and GS) and the relation between these and the third theory (KK) has been exhibited in the particular context of a two-molecule system. This relation takes the form of an explicit expression [Eq. (8)] connecting the memory $\mathfrak{w}(t)$ and the function $\eta(t)$ {or, in the terminology of Ref. 4, $[g(t) - 1]$ } appearing, respectively, in the KK and GSHRS theories. Within the present restricted context, Eq. (8) may be said to establish a bridge not only between these theories of excitation transfer but between two general approaches to transport analysis: the formalism of non-Markoffian equations^{6,10} and that of generalized "stochastic-Liouville" equations.¹¹ The latter describe coupled coherent and incoherent motion essentially by an addition of terms as in Eqs. (2), (6), and (7), whereas the former do not resort to such a separation but utilize the non- δ nature of the memory.

One of the primary results of the GS and the HRS theories has been the diffusion constant D pertaining to the eventual incoherent motion of the excitons. Both these theories predict D to have a two-term nature. Equation (8) above yields an immediate formal understanding of this two-term nature. The author has shown elsewhere⁷ that $d\langle x^2 \rangle/dt$ is proportional to the integral of the memory $\mathfrak{w}(t)$. Using Munn's result¹² concerning the identity of D and $\frac{1}{2}(d\langle x^2 \rangle/dt)_{t=\infty}$, one obtains

$$2D = \int_0^\infty dt \mathfrak{w}(t) = \tilde{\mathfrak{w}}(0) = \frac{\tilde{J}^2}{B\tilde{\eta}(0)} + A\tilde{\eta}(0). \quad (11)$$

Viewed thus, it is clear that the two-term nature of GSHR diffusion constant is merely a consequence of expressing the actual memory $\mathfrak{w}(t)$, or more generally the evolution, as the sum of two terms. This is the result of the particular formal structure of "stochastic-Liouville" equations. One sees that the characterization of one of the terms in D as purely coherent and the other as totally incoherent is not necessarily appropriate under arbitrary conditions.

For purposes of comparison we identify three entities: (i) the KK formalism, (ii) the GSHRS *formalism*, and (iii) the GSHRS *equation*. Their essential formal contents are, respectively, (i) the generalized master equation, e.g., Eq. (4), (ii) the generalized "stochastic-Liouville" equation which is also partly non-Markoffian, e.g., Eqs. (6) and (7), and (iii) the "stochastic-Liouville" equation which has no memory, e.g., Eqs. (2).

Entity (ii) appears explicitly in the GS treatment^{4,8} but only implicitly in the HRS analysis.³ Entity (iii) has *not* been displayed or used by GS except for calculating $\langle x^2 \rangle$ for long times. It has, however, been used by other authors¹³ as the starting point of their analyses and it also appears explicitly in the HRS theory.³

As we have shown above, entities (i) and (ii) are formally equivalent to each other and entity (iii) is an approximate form of entity (ii) under the partial Markoffian assumption. In the context of the two-molecule system, the relation between (i) and (iii) is given by Eq. (5) and that between (i) and (ii) by Eq. (8). The latter equation makes particularly clear the various ranges of validity on the time axis. Using the complete memory $\mathfrak{w}(t)$ gives the maximum domain of validity (next to that of the Liouville equation itself) and this corresponds to entity (i) or equivalently to (ii). Entity (iii) has a smaller range of validity (is valid only at larger times) due to its Markoffian approximation on a part [viz., $A\eta(t)$] of the memory $\mathfrak{w}(t)$. Finally, the traditional theory¹ based on the Pauli master equation has the smallest range of validity due to its Markoffian assumption on the entire $\mathfrak{w}(t)$. Obviously, a completely correct description of the reversible nature of the excitation transfer can be provided only by the Liouville equation itself. The thermodynamic limit or the assumption of line broadening (the elimination of Poincaré cycles), whether taken explicitly or implicitly, already introduces a change in the description. Further approximations, whether like the Markoffian assumption on the "incoherent" part resulting in the GSHRS equation or like the Markoffian assumption on the entire part resulting in the Pauli Master equation can provide only approximate descriptions of the actual (reversible) nature of excitation transfer.

Although an equivalence exists between the formalisms underlying the KK and GSHRS theories, the latter is used primarily under the partial Markoffian approximation and the validity of the GSHRS

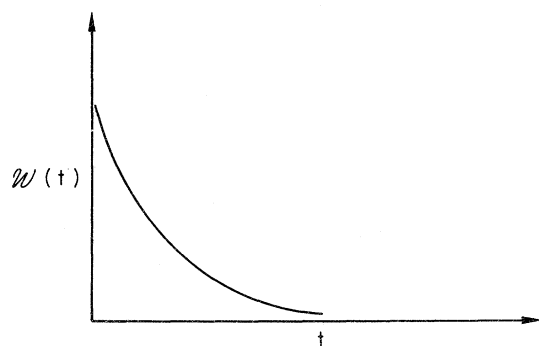


FIG. 1. Memory with a single time constant.

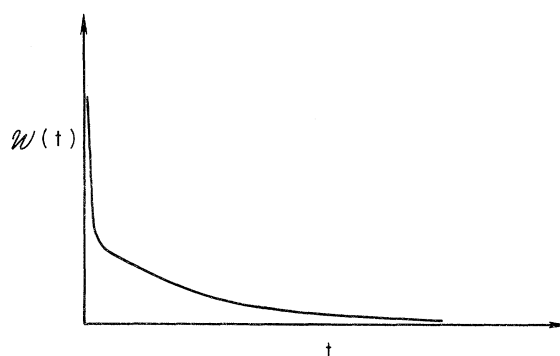


FIG. 2. Memory with two time constants.

equation must therefore be examined more carefully. It is obvious that in all nonpathological cases evolution at sufficiently long times will be correctly described by the GSHRS equation. However a description of the motion for short times and analyses like coherence criteria, which are based on the short-time behavior, could well be in error. To appreciate this fact examine Eq. (8) and observe that the approximation leading to the GSHRS equation has two effects on the memory $\mathfrak{w}(t)$: (a) a part of $\mathfrak{w}(t)$ is approximated by a δ function, and (b) the other part is approximated by an exponential, leading thus to a form for $\mathfrak{w}(t)$ which has two parts possessing widely differing time constants. While effect (a) above involves an approximation, it is relatively unimportant particularly if interest is focused on evolution for times large compared to the decay of the part approximated.¹⁴ Effect (b) is serious and it forces $\mathfrak{w}(t)$ into a particular form independent of its actual form. Given a Hamiltonian, a representation, a level of coarse graining, and a certain class of initial conditions, there always exists a definite memory $\mathfrak{w}(t)$. It may or may not have the two-time-constant form which the GSHRS equation must impose. It should be clear therefore that while for systems with memories like that in Fig. 2 the GSHRS equation can provide a good description, serious errors in analyses like coherence criteria (often predicting more coherence than actually exists) would result if the equation is used for systems with memories like that in Fig. 1.

We must hasten to add that the comparison in the present paper is only between the formal frameworks of the various theories and that their detailed physical content (as well as the validity of the perturbation approximations used in them) has not been discussed here. These are important issues, we have analyzed them recently and they will be reported elsewhere. In view of the conclusion that the approach of the stochastic-Liouville equations is particularly useful for the description of

systems typified by Fig. 2 but not of systems typified by Fig. 1, one must ask what systems possess such memories and what criteria can help one decide the applicability of the approach for a given system. Answers to these questions have been provided in terms of spectral properties and have

been confirmed by model calculations.¹⁵

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¹⁴Through a simple extension of a result proved by R. W. Zwanzig [in *Quantum Statistical Mechanics*, edited by P. H. E. Meijer (Gordon and Breach, New York, 1966), p. 142], it is possible [on account of effect (a)] to show that the GSHRS equation predicts incorrect values of the probability derivative at $t=0$ and therefore of $(d\langle x^2 \rangle / dt)_{t=0}$, that this is responsible for its incorrect description of $\langle x^2 \rangle$ at short times [compare Eqs. (42) and (46) of Ref. 4] and that this can lead to inconsistencies and even wrong values of D if blind use is made of the GSHRS equation. These, however, are minor points and can be guarded against by employing care when using the equation.

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