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Relations among theories of excitation transfer. II. Influence of spectral features on exciton motion*

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The generalized-master-equation (GME) theory of excitation transfer is applied to the standard model of linearly interacting excitons and phonons, the spectral prescription for memory functions given by Kenkre and Knox is verified for the model, peculiarities of memory functions pertinent to isolated versus open systems are analyzed, and exciton transport relevant to representative memory functions is studied. Physical relations are established between the GME theory and the stochastic-Liouville-equation theories, thus completing the author's earlier formal study of these relations. The influence of spectral features on exciton motion is analyzed in detail and it is shown that the presence of zero-phonon peaks in optical spectra is an indication of long-time coherence in exciton motion. Criteria for the validity of theories in the context of a given real system are developed on the basis of the spectral analysis.

I. INTRODUCTION

In view of the diversity of formalisms used in some recent theories of excitation transfer in molecular aggregates and of possible conflicts among their results, a thorough examination of the relationships among these theories is necessary. The beginnings of such an examination were presented in an earlier publication[1] (hereafter referred to as I). That study is continued in the present paper with the help of specific model calculations and physical considerations, and criteria for the applicability of the theories are developed on the basis of features of optical spectra.

Of the many attempts at the description of excitation transfer the following four were chosen in I for comparative study: (i) the traditional (Förster-Dexter) theory,[2] (ii) the semistochastic development of Haken-Reineker-Strobl[3] (HRS), (iii) the formalism of Grover and Silbey[4] (GS), and (iv) the generalized-master-equation (GME) theory of Kenkre and Knox[5] (KK). It was shown in I that a formal equivalence exists between HRS (without the local fluctuation terms) and GS under rather general conditions, the specific equation containing the equivalence between GS–HRS and KK was displayed for a two-molecule system, and a discussion of the validities of the various theories for various values of time was given, a distinction being made between the GS–HRS *formalism* and the GS–HRS *equation* (the forms of the theory before and after the partial Markoffian approximation, respectively).

The content of the theories considered may be generally divided into (a) their basic formalisms and (b) the specifics of the system analyzed with the formalisms. The study in I was concerned entirely with (a) and the formal remarks made therein require further clarification and elaboration in the context of (b). Having decided upon a particular formal structure, a theory must choose for its analysis between a real system, with its direct relevance but with its complexities that make exact analysis practically impossible, and a model system which, in spite of being only a highly simplified and therefore a distant approximation to the real system, has the attractive property of being largely tractable and sometimes even exactly soluble. In the study of real many-body systems, where an exact solution definitely lies beyond one's wildest hopes, these two kinds of theories complement each other and are equally important. Like the Förster-Dexter theory,[2] the KK theory[5b] addresses itself to real systems. The GS–HRS treatment and particularly the GS analysis[4] deal with a specific model system. This model system has been studied by a number of authors,[6] and the comparative study of theories of excitation transfer would therefore be helped by an analysis of that system with the GME formalism underlying the KK theory. Such a model calculation was undertaken recently,[7] and it will be seen in the following that it aids the comparative understanding of exciton motion as envisaged by the various theories.

The direct verification (for the above model) of the prescription given in KK[5(b)] for obtaining memory functions from optical spectra is given in Sec. III. The memory computed for the model exhibits some curious features, and their meaning is discussed in Sec. IV. In Sec. V simplified versions of typical spectra and the implied memory functions are discussed, and exciton motion is studied by analyzing the probability evolution for representative memory functions. These are obtained from the model calculation as well as from the other theories through the results of I. This analysis brings out the differences and agreements of the predictions of the various theories for the model system and allows one to develop validity conditions for the theories in the context of a given real system. This discussion is given in Secs. VI and VII.

The model calculation discussed in Sec. III is facilitated by the definition of a modified projection operator, given in Sec. II.

II. PROJECTION OPERATOR

The projection operator $\mathcal{P}$ defined in Ref. 5(b) satisfies

$$\langle \xi' | \mathcal{P} \mathcal{O} | \mu' \rangle = \left(\sum_{\xi' \subset \xi} \langle \xi' | \mathcal{O} | \xi' \rangle \Big/ \sum_{\xi' \subset \xi} 1 \right) \delta_{\xi', \mu'} \qquad (2.1)$$

for any operator $\mathcal{O}$ and thus involves a coarse graining over the microscopic states ξ' of the system-bath aggregate into "grains" or macroscopic states ξ. It was remarked in Ref. 5(b) that this equal-weight summation, accompanied by the infinite size (thermodynamic) limit of the system-bath aggregate, led to the onset of irreversibility on one hand and to the thermalization factors, in the space of the phonons, on the other. While that definition of $\mathcal{P}$ was constructed particularly with the irreversibility question in mind, it is possible (and, in the particular context of the comparison of the theories, advisable) to obtain the subsequent results of the KK theory with another definition of $\mathcal{P}$, when one wishes *merely to calculate* the relevant memory expressions.[8] This definition,[9] given by

$$\langle M, m | \mathcal{P} \mathcal{O} | N, n \rangle = e^{-\beta E_m} \left(\sum_m e^{-\beta E_m} \right)^{-1} \left(\sum_m \langle M, m | \mathcal{O} | M, m \rangle \right) \delta_{m,n} \delta_{M,N} , \qquad (2.2)$$

involves a trace over the phonon variables, a diagonalization, and a multiplication by the normalized equilibrium (thermal) phonon density matrix, and it will be used in the subsequent analysis. The bath is not alluded to at all in this definition and appears only indirectly at a later stage when assumptions of line broadening are made.[8] As in Ref. 5(b), here M, N and m, n refer, respectively, to exciton states and phonon states, E_m is the energy of the vibrational state m, and $\beta = 1/kT$. It is a straightforward exercise to show that Eqs. (23), (24), (28), and (29) of Ref. 5(b) do indeed result when Eq. (2.2) is used to evaluate the expression

$$\langle M, m | \left(- \int_0^t ds\, \mathcal{P} L e^{-i(t-s)(1-\mathcal{P})L} (1 - \mathcal{P}) L \mathcal{P} \rho(s) \right) | M, m \rangle$$

appearing in the GME, when the assumption and approximations discussed in I are made. It then follows that the probabilities of site occupation by the exciton, given by

$$P_M = \sum_m \langle M, m | \rho | M, m \rangle , \qquad (2.3)$$

obey[5] the GME

$$\frac{\partial P_M(t)}{\partial t} = \int_0^t ds \sum_N [\mathcal{W}_{MN}(t-s) P_N(s) - \mathcal{W}_{NM}(t-s) P_M(s)] , \qquad (2.4)$$

where the "memory-possessing transition probabilities" $\mathcal{W}_{MN}$ are given by

$$\mathcal{W}_{MN}(t) = 2 \left(\sum_m e^{-\beta E_m} \right)^{-1} \sum_{m,n} e^{-\beta E_n} | \langle M, m | V | N, n \rangle |^2 \times \cos(\Omega_{MN} + \omega_{mn}) t . \qquad (2.5)$$

Ω_{MN} and ω_{mn} being the exciton and vibrational energy differences $\epsilon_M - \epsilon_N$ and $E_m - E_n$, respectively, and V the interaction. One observes that the thermal factors appear naturally in the expression for $\mathcal{W}$. An analysis of excitation transfer in unlike molecules can be made with the help of Eq. (2.5), but it is of no relevance here. However, it is interesting to note, in passing, that detailed balance follows as an immediate consequence of Eq. (2.5).

III. MODEL CALCULATIONS AND CONNECTION WITH SPECTRA

The standard model of linearly interacting excitons and phonons, investigated earlier by various authors[4,6] will now be studied with the GME technique. The model has the Hamiltonian

$$H = \epsilon \sum_M a_M^\dagger a_M + \sum_{M \neq N} J_{MN} a_M^\dagger a_N + \sum_q \omega_q b_q^\dagger b_q + \sum_{M,q} \omega_q X_q^M (b_q + b_{-q}^\dagger) a_M^\dagger a_M \qquad (3.1)$$

which, with the help of a well-known transformation,[10] may be rewritten

$$H = \sum_M \left(\epsilon - \sum_q |X_q^M|^2 \omega_q \right) A_M^\dagger A_M + \sum_{M \neq N} J_{MN} e^{\alpha_M^\dagger} e^{\alpha_N} A_M^\dagger A_N + \sum_q \omega_q b_q^\dagger b_q \qquad (3.2)$$

on dropping a term involving exciton-exciton interactions, with $A_M = a_M e^{\alpha_M^\dagger}$ and $\alpha_M = \sum_q X_q^M (b_q - b_{-q}^\dagger)$. Our interest lies in the evolution of the probabilities of occupation of localized exciton states which are the eigenstates of H without the second term in Eq. (3.2), coarse grained over the phonon states as depicted in Eq. (2.3). They satisfy the GME (2.4), and a trivial generalization of the results of Kenkre and Rahman[7] shows[11] that Eq. (2.5) gives, for the above model

$$\mathcal{W}_{MN}(t) = 2 |J_{MN}|^2 \exp\left(- \sum_{R,S} [h_{RS}(t) - h_{RS}(0)] \right) , \qquad (3.3a)$$

$$h_{RS}(t) = (\mathrm{Tr}\, e^{-\beta H_{\mathrm{ph}}})^{-1} \mathrm{Tr} (e^{-(\beta - it) H_{\mathrm{ph}}} \alpha_R e^{-it H_{\mathrm{ph}}} \alpha_S) . \qquad (3.3b)$$

In Eq. (3.3a) each of R and S takes values M and N. The mathematical exercise required to obtain Eqs. (3.3) exploits the fact that H_{ph} contains only harmonic terms. The explicit form of $\mathcal{W}_{MN}$ may further be written [as in Eq. (6) of Ref. 7] as

$$\mathcal{W}_{MN}(t) = 2 |J_{MN}|^2 \exp\Bigl(- \sum_q (|X_q^M|^2 + |X_q^N|^2$$

$$-X_q^M X_{-q}^N - X_q^N X_{-q}^M)\{\coth(\tfrac{1}{2}\beta\omega_q) - [N_q e^{i\omega_q t} + (N_q+1)e^{-i\omega_q t}]\}\Big) , \qquad (3.4a)$$

$$N_q = (e^{\beta\omega_q} - 1)^{-1} . \qquad (3.4b)$$

Consider now the absorption and emission spectra of a single molecule at M. Transitions involving, respectively, the creation and the destruction of an exciton, caused by an electromagnetic field among the states of the Hamiltonian

$$H_M = \epsilon a_M^\dagger a_M + \sum_q \omega_q b_q^\dagger b_q + \sum_q \omega_q X_q^M (b_q^\dagger + b_{-q}) a_M^\dagger a_M , \qquad (3.5)$$

are therefore of interest. A number of authors[12] have dealt with the problem of the calculation of optical spectra of molecules. For our present purpose Lax's analysis[12(a)] and the expressions calculated by Maradudin[12(c)] and Soules and Duke[6(b)] are immediately applicable in the present context. The "modified spectra" (the spectral coefficients divided by the appropriate powers of the frequency[5(b)]), are obtained from Eq. (13.9) of Ref. 12(c) or Eqs. (3.9) of Ref. 6(b). Thus the "modified absorption coefficient" for the molecule at site M may be written in our notation (except for constant factors) as

$$I_M^a(\omega) = \{|\mathfrak{M}|^2 \exp[h_{MM}(0)]\} \times \int_{-\infty}^{+\infty} dt \exp[-h_{MM}(t) + i(\omega - \epsilon)t] , \qquad (3.6)$$

where $\mathfrak{M}$ is the dipole matrix element between the electronic ground and excited states. A similar expression, relevant to emission by the molecule at N, will be denoted by $I_N^e(\omega)$.

The prescription given in Eq. (28) of Ref. 5(b) for obtaining the memory function from optical spectra states that

$$\mathcal{W}_{MN}(t) = \text{const} \int_{z=-\infty}^{z=+\infty} dz \cos zt \int_{\omega=0}^{\infty} d\omega\, I_M^a(\omega - \tfrac{1}{2}z) \times I_N^e(\omega + \tfrac{1}{2}z) . \qquad (3.7)$$

It can be easily shown that Eq. (3.7) implies

$$\mathcal{W}_{MN}(t) = \text{const}\, \text{Re}\{[\mathcal{G}_M^a(t)][\mathcal{G}_N^e(t)]^*\} , \qquad (3.8)$$

where $\mathcal{G}_M^a(t)$ and $\mathcal{G}_N^e(t)$ (the "characteristic functions" of Lax[12(a)]) are the Fourier transforms of $I_M^a(\omega)$ and $I_N^e(\omega)$, respectively. Equations (3.8) and (3.6) immediately yield

$$\mathcal{W}_{MN}(t) = \text{const} \exp\Big(-\sum_{R=M,N} [h_{RR}(t) - h_{RR}(0)]\Big) , \qquad (3.9)$$

where $R = M, N$. Equation (3.9) is identical to Eq. (3.3a) when the terms in the exponential wherein $R \neq S$ are dropped from the latter. This confirms the spectral prescription of Ref. 5(b) and gives the smallness of $h_{MN}(t) - h_{MN}(0)$ for $M \neq N$ as the condition for its validity. This is precisely the condition obtained by Soules and Duke[6(b)] for the validity of the Förster-Dexter theory.

IV. MEANING OF THE MODEL MEMORY

In real systems the correlation functions $h(t) = \langle \alpha(t)\alpha \rangle$ are expected to tend to zero for large t's. The thermodynamic limit will ensure this decay for the model considered. Equation (3.3a) then predicts that the memory functions pertinent to excitation transfer in this model start off with the value $2|J_{MN}|^2$ at $t=0$ and drop off to a *nonzero* value $2|J_{MN}|^2 \exp[\sum_{R,S} h_{RS}(0)]$ at $t = \infty$. Comparison of Eqs. (3.4a) and (28) of Ref. 4 shows that the memory functions go from $2|J_{MN}|^2$ to $2|\tilde{J}_{MN}|^2$ where, as in Ref. 4,

$$|\tilde{J}_{MN}|^2 = |J_{MN}|^2 \exp\Big(-\sum_q (|X_q^M|^2 + |X_q^N|^2 - X_q^M X_{-q}^N - X_q^N X_{-q}^M) \coth(\tfrac{1}{2}\beta\omega_q)\Big) . \qquad (4.1)$$

At first sight this behavior of $\mathcal{W}_{MN}(t)$ appears rather strange, particularly in view of Fig. 2 of Ref. 5(b), where the memory calculated for transfer between anthracene molecules in cyclohexane solution exhibits a complete decay. However, closer inspection shows this to be the natural behavior of an isolated system. For note from Eq. (2.5) that $\mathcal{W}_{MN}(t)$ has the form $\sum_{z_i} F(z_i) \cos z_i t$. The trivial observation that cosines of all nonzero arguments oscillate around the value zero, but one of zero argument is constant at unity for all time, leads to the conclusion that this expression has two components, one of which is steady at $F(0)$. It then follows that for times which are sufficiently long, but not of the order of the recurrence times, the above function goes from $\sum_{z_i} F(z_i)$ at short times to $F(0)$ at long times. Every memory function therefore seems to have this general behavior, and Eq. (2.5) with $\Omega_{MN} = 0$ indeed predicts that $\mathcal{W}_{MN}(t)$ varies from

$$2\Big(\sum_m e^{-\beta E_m}\Big)^{-1} \sum_{m,n} e^{-\beta E_m} |\langle M, m | V | N, n\rangle|^2 ,$$

which equals $2|J_{MN}|^2$ for the above model, to

$$2\Big(\sum_m e^{-\beta E_m}\Big)^{-1} \sum_{m,n;E_m=E_n} e^{-\beta E_m} |\langle M, m | V | N, n\rangle|^2 ,$$

which equals $2|\tilde{J}_{MN}|^2$.

Having understood the "strange" behavior of $\mathcal{W}_{MN}$ as a natural property of our memory functions, one must reconcile this with the general expectation of completely decaying memories for normal systems and particularly with Fig. 2 of Ref. 5(b). Consider again the expression $\sum_{z_i} F(z_i) \cos z_i t$, and note that in the thermodynamic limit the discrete z_i's pass into a continuous z and the above sum into the integral $\int dz\, \rho(z) F(z) \cos zt$, where $\rho(z)$ is a density of states. This integral goes from $\int dz\, \rho(z)F(z)$ to $dz\, \rho(0)F(0)$, i.e., always to zero unless $\rho(0)F(0)$ is singular. Since $\sum_{z_i} F(z_i)\cos z_i t$ may be written as the above integral with $\rho(z) = \sum_{z_i} \delta(z - z_i)$, one observes that the limit that turns the sum into the integral can remove the singularity in $\rho(0)$ by making the strength of the δ function at $z = 0$ (smaller and smaller and eventually) zero.

The above discussion may also be given in the context of optical spectra. The $f(t)$ of Eq. (8.13) of Lax,[12(a)] the $g(t)$ of Eq. (13.14) of Maradudin,[12(c)] or the $\phi(T, t)$ in Eq. (3.9a) of Soules and Duke[6(b)] does not tend to $-\infty$ as $t \to \infty$. Since these functions appear in the exponential in the expression for the "characteristic function," this must result in a singularity in the optical spectra at the exciton energy. This singularity or δ function in the frequency domain is connected with the eventual nonzero value of our memory in the time domain. And precisely those mechanisms (interaction with the bath) that broaden the δ function in the spectrum to a nonsingular value, force the memory to decay to a zero value. It is thus seen that, while memory functions with a constant component at $t = \infty$ and optical spectra with a δ function at zero (phonon) energy are natural properties of *isolated* systems, the existence of interactions with the bath will lead to the decay of the memory component and the broadening of the spectral one. Furthermore, the existence of sharp (but not truly singular) zero-phonon lines will lead to memories with multiple time constants like the one depicted in Fig. 2 of I. This will be made clearer in Sec. V.

V. REPRESENTATIVE SPECTRA, MEMORIES, AND MOTION

Before undertaking a comparative analysis (Sec. VI) of exciton transfer it is useful to study representative spectra, the memory functions they imply through the KK prescription, and the probability evolution that follows from these memory functions.

Consider the expression

$$I_M^a(\omega) = C_0 l_{\alpha_0}(\omega) + C_s l_{\alpha_s}(\omega - \omega_s) \tag{5.1}$$

as typifying a "modified absorption spectrum" possessing both a zero-phonon line and a sideband. Here $l_\alpha(\omega) = \alpha/(\omega^2 + \alpha^2)$ is the Lorentzian with width 2α, the zero of ω being taken at the zero-phonon line. If mirror symmetry applies, the "modified emission spectrum" is given by

$$I_N^e(\omega) = C_0 l_{\alpha_0}(\omega) + C_s l_{\alpha_s}(\omega + \omega_s) \ , \tag{5.2}$$

and Eqs. (3.8), (5.1), and (5.2) give

$$\mathcal{W}_{MN}(t) = \text{const}(C_0^2 e^{-2\alpha_0 t} + 2C_0 C_s e^{-(\alpha_0+\alpha_s)t}\cos\omega_s t + C_s^2 e^{-2\alpha_s t}\cos 2\omega_s t) \ . \tag{5.3}$$

The spectra given by Eqs. (5.1) and (5.2) have been

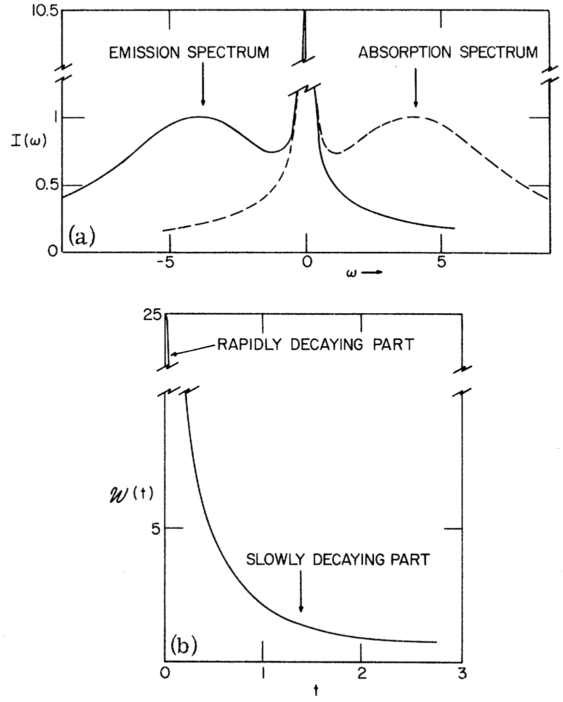

FIG. 1. (a) "Modified" absorption (dashed line) and emission (solid line) spectra as typified by Eqs. (5.1) and (5.2), plotted for exaggerated relative values of C_0, C_s, α_0, α_s, ω_s, showing the zero-phonon peaks and the sidebands. The zero of ω is taken at the zero-phonon energy. The areas of the Lorentzians at 0 and ω_s are C_0 and C_s, and their widths are $2\alpha_0$ and $2\alpha_s$, respectively. (b) The memory function corresponding to the spectra in (a), exhibiting multiple time constants. Oscillations arising from the Stokes shift have been suppressed to make clearer the multiple-time-constant nature of $\mathcal{W}(t)$ Units in (a) and (b) are arbitrary.

plotted in Fig. 1(a). In order to bring out the multiple-time-constant nature of $\mathcal{W}_{MN}$ resulting from zero-phonon peaks, exaggerated relative values of C_0, C_s, α_0, α_s, and ω_s have been used for Fig. 1(a), and the oscillations in $\mathcal{W}_{MN}$ caused by the Stokes shift ($\omega_s \neq 0$) have been suppressed in Fig. 1(b). The slowly decaying component of $\mathcal{W}_{MN}$ would be absent in the absence of the zero-phonon peak.

Equation (5.3) reduces to

$$\mathcal{W}_{MN}(t) = \text{const}\, C_s^2 e^{-2\alpha_s t}\cos 2\omega_s t \tag{5.4}$$

in the limit $\alpha_0 \to \infty$ (or $C_0 \to 0$), which represents the absence of a zero-phonon line, and in the opposite limit of a δ-function zero-phonon line, i.e., when $\alpha_0 \to 0$, exhibits the constant component C_0^2 at $t = \infty$:

$$\mathcal{W}_{MN}(t) = \text{const}(C_0^2 + 2C_0 C_s e^{-\alpha_s t}\cos\omega_s t + C_s^2 e^{-2\alpha_s t}\cos 2\omega_s t) \ . \tag{5.5}$$

Equation (5.5) is a crude representation of the memory [Eq. (3.4a) or (3.9)] obtained for the model of Sec. III, whereas the situation, wherein the model is put in interaction with a bath, is described by Eq. (5.3) with $\alpha_0 \neq 0$ and by Fig. 2 of I. Note in Eq. (5.5) that, except for constant factors, $\mathcal{W}_{MN}(t)$ has the value $(C_0 + C_s)^2$ at $t=0$ and decays to C_0^2 at $t=\infty$. A comparison with Eqs. (3.4a) or (3.9) immediately establishes that $C_0 + C_s$, the strength of the entire spectrum, and C_0, the strength of the zero-phonon peak [see Eq. (5.1)], play the respective roles of J and $\tilde{J}$. It should be clear from these examples (as well as from a direct analysis) that in the absence of a zero-phonon line the quantity $\tilde{J}$ must equal zero.

Several different forms of the memory function $\mathcal{W}_{MN}(t)$ [see Eqs. (3.4a), (3.9), and (4.4)–(4.6) above in addition to Eqs. (5) and (8)–(10) of I, Eq. (9) of Ref. 5(a), and Fig. 2 of Ref. 5(b)] have appeared in the description of excitation transfer. We shall now study their consequences in connection with the evolution of exciton probabilities. For the sake of simplicity, consider, as in I, a system of two identical molecules. Equation (2.4) gives, for this system,

$$\tilde{P}_M(\epsilon) = 1/2\epsilon + [P_M(0) - \tfrac{1}{2}]/(\epsilon + 2\tilde{\mathcal{W}}) , \tag{5.6}$$

where tildes denote Laplace transforms, ϵ is the Laplace variable in keeping with the notation in I and Ref. 5(b) (and should not be confused with the energy which it represents in Sec. III), $\tilde{\mathcal{W}} = \tilde{\mathcal{W}}_{12} = \tilde{\mathcal{W}}_{21}$, and $M=1,2$. The first term represents the final equilibrated value $\frac{1}{2}$ of the probability on either molecule and the second the "decay" of the difference of the initial value from this final value. One could substitute Eq. (3.4a) into Eq. (5.6) and, in principle, obtain the probabilities as functions of time. However, this being a rather complicated exercise, we shall consider the effect of simplified $\mathcal{W}$'s in which we attempt to retain the basic qualitative features of the actual $\mathcal{W}$'s.

Consider the memory function

$$\mathcal{W}(t) = A\gamma e^{-\gamma t} + 2\tilde{J}^2 e^{-\alpha_1 t} . \tag{5.7}$$

This has some of the essential characteristics of the memory functions discussed above and, when substituted into Eq. (5.6), gives

$$\begin{aligned}\tilde{P}_M(\epsilon) = 1/2\epsilon + [P_M(0) - \tfrac{1}{2}]&[\epsilon^2 + (\gamma+\alpha_1)\epsilon + \gamma\alpha_1] \\ &\times [\epsilon^3 + (\gamma+\alpha_1)\epsilon^2 + (\gamma\alpha_1 + 2A\gamma + A\tilde{J}^2)\epsilon \\ &+ (2A\gamma\alpha_1 + A\tilde{J}^2\gamma)]^{-1} .\end{aligned} \tag{5.8}$$

The two terms on the right-hand side of Eq. (5.7) represent contributions from the sidebands and the zero-phonon line, respectively (oscillating factors arising from the Stokes shift have been neglected). The limits $\gamma \to \infty$, $\tilde{J} \to 0$, and $A=F$ give $\mathcal{W}(t) = F\delta(t)$ and represent the Förster-Dexter theory,[2] and Eq. (5.8) then reduces to the familiar form

$$P_M(t) = \tfrac{1}{2} + [P_M(0) - \tfrac{1}{2}]e^{-2Ft} . \tag{5.9}$$

The Perrin oscillations[13] are recovered for $\gamma \to 0$, $A\gamma \to 2J^2$, $\tilde{J}=0$, (or, equivalently, for $\alpha_1 \to 0$, $\tilde{J}=J$, $A=0$) and correspond to no exciton-phonon interaction and no spectrum broadening:

$$P_M(t) = \tfrac{1}{2} + [P_M(0) - \tfrac{1}{2}]\cos 2Jt . \tag{5.10}$$

Here $\mathcal{W}(t) = 2J^2$. These two cases may be unified[5(c)] in a simple manner by taking $\mathcal{W}(t) = 2J^2 \exp[(-2J^2/F)t]$, which is Eq. (5.7) with $A=F$, $\gamma = 2J^2/F$, and $\tilde{J}=0$. This takes into account the noninfinite nature of the spectral widths but allows for no zero-phonon lines. The resulting probability is given by

$$\begin{aligned}P_M(t) = \tfrac{1}{2} + [P_M(0) - \tfrac{1}{2}]e^{-(J^2/F)t}\{&\cos 2J[1-(J/2F)^2]^{1/2}t \\ &+ (J/2F)[1-(J/2F)^2]^{-1/2}\sin 2J[1-(J/2F)^2]^{1/2}t\} .\end{aligned} \tag{5.11}$$

The basic feature of the memory function computed[7] for the model in Sec. III is that, on taking the thermodynamic limit, it drops off from $2J^2$ to a steady value $2\tilde{J}^2$. If the partial Markoffian approximation is made on the decaying part (as in the GS–HRS *equation*) one might represent the memory in Eq. (3.4a) by the crude form $\mathcal{W}(t) = A\delta(t) + 2\tilde{J}^2$, which arises from (5.7) when $\gamma \to \infty$ and $\alpha_1 \to 0$ and corresponds to the presence of an unbroadened (singular) zero-phonon line. It leads to

$$\begin{aligned}P_M(t) = \tfrac{1}{2} + [P_M(0) - \tfrac{1}{2}]e^{-At}\{&\cos 2\tilde{J}[1-(A/2\tilde{J})^2]^{1/2}t \\ &- (A/2\tilde{J})[1-(A/2\tilde{J})^2]^{-1/2}\sin 2\tilde{J}[1-(A/2\tilde{J})^2]^{1/2}t\}.\end{aligned} \tag{5.12}$$

As shown earlier[1,5(a),5(b)] the GS–HRS *equation* corresponds to a memory consisting of the sum of an exponential and a δ function. Such a form also results from the case discussed immediately above, when the constant component of strength $2\tilde{J}^2$ is allowed to decay, i.e., when the broadening of the zero-phonon line is taken into account. This is the $\gamma \to \infty$ limit of (5.7) and gives

$$\begin{aligned}P_M(t) = \tfrac{1}{2} + [P_M(0) - \tfrac{1}{2}]&e^{-(A+\alpha_1/2)t} \\ &\times \left\{\cos 2\tilde{J}\left[1 - \left(\frac{A-\alpha_1/2}{2\tilde{J}}\right)^2\right]^{1/2} t\right. \\ &- \left(\frac{A-\alpha_1/2}{2\tilde{J}}\right)\left[1 - \left(\frac{A-\alpha_1/2}{2\tilde{J}}\right)^2\right]^{-1/2} \\ &\left.\times \sin 2\tilde{J}\left[1 - \left(\frac{A-\alpha_1/2}{2J}\right)^2\right]^{1/2} t\right\} .\end{aligned} \tag{5.13}$$

Note that, except in the exponential, A and α_1 have opposite effects in Eq. (5.13). This has the interesting effect that for the case of the GS–HRS equation which has [see Eq. (5) of I] $\alpha_1 = 2A$, the equation reduces to

$$P_M(t) = \tfrac{1}{2} + [P_M(0) - \tfrac{1}{2}]e^{-2At}\cos 2\tilde{J}t . \tag{5.14}$$

Equations (5.9)–(5.14) have been plotted in Figs. 2 and 4 and discussed in Secs. VI and VII.

VI. COMPARATIVE ANALYSIS OF EXCITON MOTION

In order to gain a comparative understanding of the predictions of the various theories let us first consider a highly simplified system, enrich it by successive steps so that its parameters evolve towards those of real systems found in nature, and at each step attempt to apply the theories and compare their results. Begin then with the model system whose Hamiltonian is obtained from that given in Eq. (3.1) by dropping the last two terms and writing $M, N = 1, 2$ and $J_{MN} = J$ for simplicity. The GS–HRS theory predicts [see Eqs. (6) and (7) of I] that the evolution of exciton density matrix elements obeys

$$\frac{d\rho_{11}}{dt} = -iJ(\rho_{21} - \rho_{12}) , \tag{6.1a}$$

$$\frac{d\rho_{12}}{dt} = -iJ(\rho_{22} - \rho_{11}) , \tag{6.1b}$$

while, for the initial condition $\rho_{12}(0) = \rho_{21}(0) = 0$, the KK theory gives

$$\frac{d\rho_{11}(t)}{dt} = 2J^2 \int_0^t ds\,[\rho_{22}(s) - \rho_{11}(s)] , \tag{6.2}$$

which is equivalent to Eqs. (6.1). The analysis of Ref. 12 [see Eq. (3.6) of this paper] shows that the "modified" spectra $I^a(\omega)$ and $I^e(\omega)$, relevant to absorption and emission by a single molecule with the Hamiltonian $H = \epsilon a^\dagger a$, are δ functions at energy ϵ (zero-phonon lines). These correspond to "characteristic functions" $g^a(t)$ and $g^e(t)$, which are exponentials of imaginary argument and which lead, through Eq. (3.8), to

$$\mathcal{W}(t) = 2J^2 , \tag{6.3}$$

a result in complete agreement with Eq. (6.2). The Förster-Dexter theory cannot analyze this system since it is based on the golden rule, which is not applicable to this situation. Equations (6.1) and (6.2) predict that probability evolution follows Eq. (5.5) and exhibits the Perrin oscillations.[13]

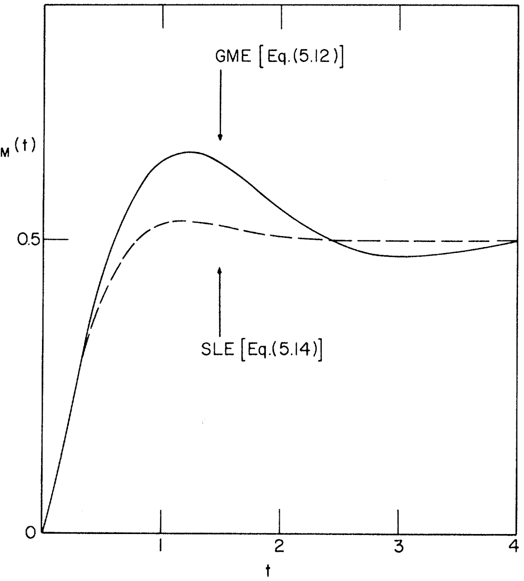

FIG. 2. Probability evolution of the exciton in a dimer, for the initial condition $P_M(0) = 0$ as described by the generalized-master-equation (GME) and the stochastic-Liouville-equation (SLE) approaches for the model of Sec. III, under the partial Markoffian approximation.

Consider now the system described by adding the third term of Eq. (3.1) to the Hamiltonian considered above. The exciton density matrix may be defined through a thermal coarse graining, as shown in Eq. (2.3). Since the phonons here do not interact with the excitons, the GS–HRS and KK predictions are again given by Eqs. (6.1) and (6.2), respectively; the spectrum calculations are unchanged, and so is the probability evolution.

If one now turns on the exciton-phonon interaction, returning to the model of Sec. III [Eqs. (3.1) or (3.2)], the GS–HRS formalism predicts

$$\frac{d\rho_{11}(t)}{dt} = -i\tilde{J}(\rho_{21} - \rho_{12}) + \int_0^t ds\,\mathcal{A}(t-s)[\rho_{22}(s) - \rho_{11}(s)] , \tag{6.4a}$$

$$\frac{d\rho_{12}(t)}{dt} = -i\tilde{J}(\rho_{22} - \rho_{11}) + \int_0^t ds\,\mathcal{B}(t-s)[\rho_{21}(s) - \rho_{12}(s)] . \tag{6.4b}$$

The functions $\mathcal{A}(t)$ and $\mathcal{B}(t)$ are not calculated by HRS, but assumed to be δ functions, and, as discussed in I, this results in the GS–HRS *equation*. The GS treatment, however, calculates them explicitly. The calculation involves a single approximation: the perturbation of the "kernel" or "propagator" appearing in the integro-differential equation [Eq. (3.21) of Ref. 6(c)], and the result is

$$\begin{aligned}\mathcal{A}(t) &= \mathcal{B}(t)\\ &= 2J^2 \exp\Big(\sum_{R,S} h_{RS}(0)\Big)\Big[\exp\Big(-\sum_{R,S} h_{RS}(t)\Big) - 1\Big]\\ &\equiv 2\tilde{J}^2\Big[\exp\Big(-\sum_{R,S} h_{RS}(t)\Big) - 1\Big]\end{aligned} \tag{6.5}$$

in the notation of Eq. (3.3) above.[14] The results of Sec. III show that the KK theory predicts

$$\frac{d\rho_{11}(t)}{dt} = \int_0^t ds\,\mathcal{W}(t-s)[\rho_{22}(s) - \rho_{11}(s)] , \tag{6.6}$$

where

$$\mathcal{W}(t) = 2J^2 \exp\Big(\sum_{R,S} [h_{RS}(0) - h_{RS}(t)]\Big)$$

$$\equiv 2\tilde{J}^2 \exp\left(-\sum_{R,S} h_{RS}(t)\right) , \qquad (6.7)$$

provided the correlations h_{MN} with $M \neq N$, neglected by the spectral prescription, are put back into the memory. The derivation of Eq. (6.7) also involves a single (perturbation) approximation, which is formally similar to, but different in content from, its GS counterpart. Equations (6.5) and (6.7) show that

$$\mathcal{W}(t) = \mathcal{A}(t) + 2\tilde{J}^2 \ . \qquad (6.8)$$

The spectral expressions for this system are obtained from Eq. (3.6). From an Abelian theorem connecting the behavior of $e^{-h(t)}$ as $t \rightarrow \infty$ to that of $I^a(\omega)$ or $I^e(\omega)$ as $\omega \rightarrow \epsilon$, one sees that, since the correlations drop to zero[12] at large times (on taking the thermodynamic limit), the spectra have singularities at $\omega = \epsilon$. Observing that $|\mathcal{M}|^2$ in Eq. (3.6) is proportional to J, one concludes therefore that the spectra possess zero-phonon lines of strength $J e^{h_{11}(0)}$ in addition to sidebands.[15] When $h_{12}(0) = h_{21}(0) = 0$, the strength of the zero-phonon line is $\tilde{J}$ (see also Sec. V).

This parameter $\tilde{J}$, introduced by GS, is thus of significance in several places. We have shown above that it is proportional to the relative strength of the zero-phonon singularity in the optical spectrum of the isolated molecule. It is also the key coherent parameter in Eqs. (6.4) as it controls the basic oscillations of the density matrix elements as predicted by GS [see also Eq. (5.14)]. Furthermore, Eq. (6.7) shows that $2\tilde{J}^2$ denotes the constant component of the KK memory $\mathcal{W}(t)$ and (in the thermodynamic limit) equals $\mathcal{W}(\infty)$.[16] These conclusions are quite general and are not restricted to the particular model considered. The discussion in Sec. IV has shown that the memory $\mathcal{W}(t)$ always has a constant component which equals

$$2\left(\sum_m e^{-\beta E_m}\right)^{-1}\left(\sum_{m,\,E_m=E_n} e^{-\beta E_m}\,|V_{mn}|^2\right)$$

or

$$2\left(\sum_m e^{-\beta E_m}\right)^{-1}\left(\sum_m e^{-\beta E_m}\,|V_{mm}|^2\right)$$

if degeneracy is absent, or $2|V_{00}|^2$ if the temperature is zero, where $|0\rangle$ denotes the lowest vibrational state. Furthermore this quantity $|V_{00}|$ (or its more complex forms shown above) *must* figure in a GS-like treatment, as can be shown in detail, and must also appear in the spectra.

In view of the importance of the parameter $\tilde{J}$ we shall now study its evolution as the system is enriched from a highly simple form to a real molecular aggregate. For the noninteracting system considered at the beginning of this section, the spectrum is an unbroadened zero-phonon line with strength J, the function $F(z)$ of Fig. 1 of Ref. 5(b) is a δ function (at $z = 0$) of strength proportional to J^2, the memory $\mathcal{W}(t)$ is a constant [see Eq. (6.3)] of value $2J^2$, and the exciton motion consists of oscillations with frequency proportional to J. When the exciton-phonon interaction is switched on, as in the system of Eqs. (3.1) or (3.2), the strength of the zero-phonon line is reduced (borrowed to form the sideband), $F(z)$ too forms a sideband with a consequent weakening of the δ function at zero, the memory $\mathcal{W}(t)$ drops at large times to $2\tilde{J}^2$ (although at $t = 0$ it still equals $2J^2$ corresponding to the value of $\tilde{J}$ for the case of no interactions), and the exciton motion has oscillations which are controlled initially by J and then by $\tilde{J}$, and eventually attains a diffusive nature for times small compared to recurrence times [see Eqs. (5.11)–(5.14)].[17] This system is, however, still an isolated model system. If a real system is represented by this system in interaction with a bath, the latter can bring about further broadening, reducing the value of $\tilde{J}$, i.e., the strength of the spectral δ function, the frequency of oscillations, the value of the constant component of $\mathcal{W}(t)$, in short, the coherence of the system. This $\tilde{J}$ thus crucially depends on the presence or absence of the bath and its nature, and great care must therefore be taken when estimating its value.

Before applying a model theory to describe a situation in real nature, its parameters must be evaluated in the context of the given real system. Since model systems can only caricature real systems, the safest manner of evaluating these parameters is to connect them (with the help of the theory) to properties of the system in the context of a different phenomenon, and then to measure these properties experimentally. The Förster-Dexter and the KK theories operate in this spirit. In systems wherein the condition $h_{MN}(t) - h_{MN}(0) \approx 0$ for $M \neq N$ is valid, the crucial parameter of the GS–HRS theory, viz., $\tilde{J}$, can be estimated in this manner from the results obtained above by examining the optical spectra of single molecules in the given environment. For systems such as F-aggregate color centers,[18] zero-phonon peaks are indeed observed in the spectra. Such systems have been typified by Fig. 1 above and Fig. 2 of I. On the other hand, an examination of the spectra of several aromatic molecules[19] in solution at ordinary temperatures shows no zero-phonon lines, which means that $\tilde{J} \approx 0$ for these systems at those temperatures. The absence of significantly differentiated peaks in the spectra lead to a memory with essentially a single time constant. The $\mathcal{W}(t)$'s like those displayed in Fig. 2 of Ref. 5(b) result. The GS–HRS formalism [see Eq. (6.4a)] gives

$$\frac{d\rho_{11}(t)}{dt} = \int_0^t ds\ \mathcal{A}(t-s)[\rho_{22}(s) - \rho_{11}(s)] , \qquad (6.9)$$

which, in view of the result $\mathcal{W}(t) = \mathcal{A}(t)$ from Eq. (6.7), is *identical to the KK equation* (6.6). For such systems, the GS–HRS diffusion constant

$$D = 2a^2\tilde{J}^2/3\alpha + a^2\alpha \tag{6.10}$$

loses its two-term nature,[1,3,4] since the "coherent" part equals zero,[20] and the GS–HRS *equation* becomes identical to the Pauli master equation, the basis of the Förster-Dexter theory.

One of the conclusions to be drawn from this analysis is that there is greater agreement between the various theories considered than their diverse structures might lead one to believe. Systems that one encounters in the course of an analysis of excitation transfer must fall in one of the following three categories: (i) real systems whose optical spectra exhibit no zero-phonon peaks at all; (ii) isolated hypothetical systems with true δ functions at the zero-phonon energy; and (iii) real systems with distinguishable zero-phonon peaks in their spectra. Assume that the validity conditions for the spectral prescriptions for transport parameters hold in these systems. We have shown above that for systems (i) an *exact* (not merely formal) equivalence exists between the GS–HRS and KK theories and that the additional coherence implied by the parameter $\tilde{J}$ is absent in these systems since $\tilde{J} = 0$. For systems (ii) there *is* a disagreement between the theories. This is apparent in Eqs. (5.12) and (5.14) (see Fig. 2), which give the probability evolution as predicted for the model of Sec. III (under the partial Markoffian approximation valid for times that are not too small) by our analysis[7] and the GS–HRS theory, respectively. Unlike the former, the latter does not exhibit "overdamping" for any value of the ratio $A/2\tilde{J}$ of the incoherent and coherent parameters. Agreement occurs only in the extreme limits $A/2\tilde{J} \gg 1$ and $A/2\tilde{J} \ll 1$. In view of the result established in I that the GS–HRS formalism corresponds to a memory with the Laplace transform

$$\tilde{\mathcal{W}}(\epsilon) = 2\tilde{J}^2/[\epsilon + 2\tilde{\mathcal{B}}(\epsilon)] + \tilde{\mathcal{A}}(\epsilon) \;, \tag{6.11}$$

one reencounters the disagreement in the results $\tilde{\mathcal{B}} = \tilde{\mathcal{A}}$ and $\tilde{\mathcal{B}} = 0$ of the GS analysis and our Eq. (6.8), respectively. The analysis of the present paper assigns, to the $2\tilde{J}^2$ memory component, a decay constant controlled by the width of the zero-phonon line (zero in the present case). The GS–HRS theory, on the other hand, assigns to it a value equal to twice the *integral of the other part of the memory*. The source of this conflict may be traced to the difference in the perturbation approximations made in the two theories. Although formally similar, these approximations differ in actual content (except when $\tilde{J} = 0$). In the analysis of Ref. 7 the perturbation expansion is in powers of the second term of Eq. (3.26), while in the GS treatment it is in powers of the "fluctuation" of that term from its "thermalized" value. One might argue that the expansion parameter is smaller in the latter and that therefore the GS approximation is preferable. This may well be true. However, in the absence of any proof or indication of the convergence of the expansion in either case, such an argument is not too meaningful. An *exact* solution, which would provide the only way of deciding between the two approximations, is unavailable at the present moment.

Systems of type (iii) may be considered similar both to those types (i) and (ii). They are like (ii) in that they do possess structure at the zero-phonon energy and like (i) in that, being real open systems, they do not exhibit *true* δ functions in their spectra. In the latter view, $\tilde{J} = 0$ again, and once again complete agreement is obtained between the theories and the extra coherence contributed by $\tilde{J}$ is absent.[21] However, the $\mathcal{A}(t)$ of Eq. (6.4a), or equivalently the $\mathcal{W}(t)$ of KK, develops multiple time constants and in this manner handles the additional coherence [see Eq. (5.3) and Fig. 1]. The results of the KK theory are particularly important for these systems since, for spectral lines which are narrow enough, its predictions differ substantially from the traditional theory.[2] Viewed as "broadened" versions of isolated systems, systems (iii) might also be examined by the stochastic-Liouville-equation approach of Refs. 3 and 4 since, for times small with respect to the reciprocal of the zero-phonon-peak width, they might indeed be approximated by systems (ii).[22]

It is worth emphasizing that true disagreement between the theories considered exists only for the isolated model system. Even in this hypothetical system the disagreement disappears if the ratio of the coherent and incoherent parameters is either too large or too small. A study of the spectra of several real systems has shown that even in cases wherein zero-phonon peaks are present, their strengths *relative to those of the sidebands* are often such as to produce negligible amounts of $\tilde{J}$ coherence. For instance, for the color centers studied in Ref. 18 the ratio $2\tilde{J}^2/2J^2$ of the initial value of the slow component of the memory to that of the entire memory ranges from 10^{-4} to 10^{-34} for all cases except one, in which it equals 1.4×10^{-1}.

In situations wherein $h_{MN}(t) - h_{MN}(0) \neq 0$ for $M \neq N$ [see Ref. 6(b) for a discussion] the above considerations do not appear to require significant changes, although correction factors will have to be applied to the quantities obtained from the spectral prescription. Thus note that the $\mathcal{W}(t)$ in Eq. (3.3a) can be written

$$\mathcal{W}(t) = \mathcal{W}_s(t)\,\mathcal{W}_c(t) \;, \tag{6.12}$$

where $\mathcal{W}_c(t)$, the correction factor due to the neglected correlations, to be applied to the spectrally obtained [Eq. (3.9)] $\mathcal{W}_s(t)$, is given by

$$\mathcal{W}_c(t)=\exp\{-[h_{MN}(t)+h_{NM}(t)-h_{MN}(0)-h_{NM}(0)]\}. \tag{6.13}$$

Note that since $\mathcal{W}_c(0)=1$, and $\mathcal{W}_c(\infty)$ is not expected to be infinite, $\mathcal{W}(t)$ varies from $\mathcal{W}_s(0)$ to zero for real systems. These considerations therefore do not need to be changed qualitatively when these correlations are not neglected.

VII. CONCLUDING REMARKS

Figure 3(a) represents the model of Eq. (3.1) with a constant (involving no phonons) intermolecular interaction J and an "intramolecular" exciton-phonon interaction. (The latter is not strictly intramolecular, but an interaction between phonons and *localized* excitons.) The states are those of the bare exciton. The states of the "dressed" exciton[23] obtained after the transformation are shown by wavy lines in Fig. 3(b). They diagonalize (3.2a) without the second term of (3.2b). There is no "intramolecular" interaction among them, but the intermolecular interaction $\mathcal{J}\equiv J e^{\alpha_1^\dagger} e^{\alpha_2} A_1^\dagger A_2$ does connect states with unequal phonon numbers. Figure 3(b) shows the separation of $\mathcal{J}$ into a constant part $\tilde{J}$, which, like J, involves no phonons, and the "fluctuating part" $\mathcal{J}-\tilde{J}$. Before the transformation the intermolecular interaction J connected any one state on molecule 1 to only the corresponding state on molecule 2, but after the transformation (and due to the exciton-phonon interaction) the intermolecular interaction is "spread over" all states of molecule 2. The interaction strength is conserved in this "spreading over" and the constant no-phonon part $\tilde{J}$ is therefore smaller than J. It is thus that $\tilde{J}$ is reduced as the number of states increases (thermodynamic limit, interaction with bath) and in the continuum limit can tend to zero. The GS theory treats $\tilde{J}$ exactly and $\mathcal{J}-\tilde{J}$ approximately through $\alpha(t)$. The same kind of approximation is used by the KK theory to treat the entire $\mathcal{J}$. There is thus a difference for $\tilde{J}\neq 0$, but none for $\tilde{J}=0$. All theories considered above analyze the evolution of the coarse-grained density matrix. Evolution among intramolecular states does not therefore enter into the description, and the $\tilde{J}$ considered is truly a (thermal) average over all phonon states. The relation with spectra is also based on this fact. The $F(z)$ of Ref. 5(b) is sketched in Fig. 3(c) (the Stokes shift is neglected), and the memory $\mathcal{W}(t)$, which is its Fourier transform, is shown in Fig. 3(d).

In addition to the *unification* of coherence and incoherence, the concept of the *coexistence* of these two characters of exciton motion emerges from the discussion in this paper. The use of the generalized master equation brings about a unification, as has been shown explicitly in Ref. 5(c). This explains the transition from an R^{-3} to an R^{-6} transfer rate, and combines wavelike behavior at short times [any finite $\mathcal{W}(t)$ can be approximated by the constant $\mathcal{W}(0)$ near $t=0$] with diffusive behavior at long times [after $\mathcal{W}(t)$ has decayed, its integral equals that of a δ function of value $[\int_0^\infty dt'\,\mathcal{W}(t')]$ placed at $t=0$]. The coexistence concept is apparent in stochastic-Liouville equations and is relevant to a memory with multiple time constants.[1] The model calculations[7] discussed in Sec. III show

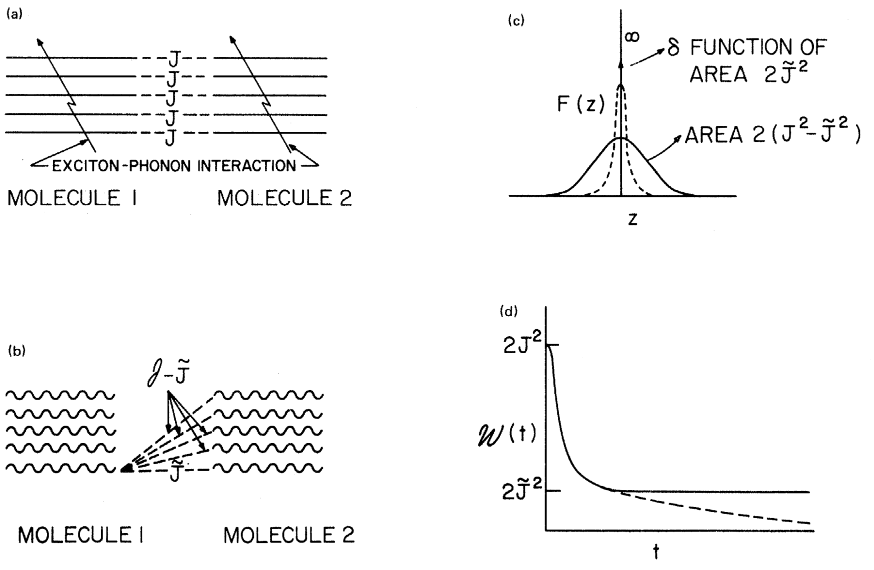

FIG. 3. Model of Sec. III. (a) The intermolecular interaction J and the phonon–localized-exciton interaction (symbolized by the arrow) among "bare" states; (b) no phonon–localized-exciton interaction exists among "dressed" states. The intermolecular interaction consists of a part $\tilde{J}$ and a part $\mathcal{J}-\tilde{J}$. Only the interaction with one of the states of molecule 1 is shown. (c) The $F(z)$ defined in Ref. 5(b) is plotted for this model, suppressing the effects of the Stokes shift. (d) The memory $\mathcal{W}(t)$, which is the transform of $F(z)$. The dashed lines in (c) and (d) show the effects of broadening.

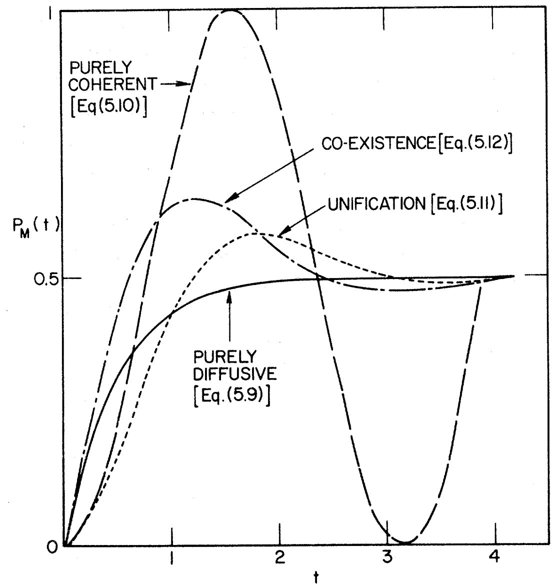

FIG. 4. Probability evolution of the exciton in a dimer, for the initial condition $P_A(0)=0$, plotted for different cases, showing motion which is, respectively, purely diffusive, purely coherent, exhibits unification of these two characters, and their coexistence.

[see Eq. (6.5)] that initially there is wavelike behavior[24] controlled by $\mathcal{W}(0)=\mathfrak{a}(0)+2\tilde{J}^2=2J^2$, but after $\mathfrak{a}(t)$ has decayed it contributes only diffusive motion. There is, however, a coexistence of this diffusive (hopping) motion with the additional wavelike (coherent) motion controlled by $2\tilde{J}^2$. Equations (5.11) and (5.12) with $J=\tilde{J}$ describe, respectively, the *unification* and the *coexistence* of purely coherent [Eq. (5.10)] and purely diffusive [Eq. (5.9)] motion. The results of these four equations have been shown in Fig. 4. Note that for $J=\tilde{J}$, $2J^2/F=A$, Eqs. (5.11) and (5.12) differ only in the sign of the last term and agree in the limit that the coherent parameter is large. The unification concept always occurs in real systems since real spectra display neither infinite widths nor infinite heights. However, coexistence occurs only when significantly differentiated peaks exist in the spectra.

While the radiative lifetime of the excitons has been considered to be infinite in the foregoing analysis, it is an assumption made in all the theories considered above. It is justifiable when the transport characteristic times are much smaller than the radiative decay times. The finite lifetime may be taken into account by appending a real decay to the treatment, as done by Förster.[2] It should also be mentioned that the assumption of homogeneous broadening, which also underlies the traditional theory,[2] has been made in this treatment.

Note added in proof. It was stated in Sec. VI that *exact* solutions, capable of deciding between the perturbation approximations inherent in the SLE and the GME theories, were unavailable. We have now obtained them for some highly simplified models. Comparison of the exact, the GME, and the SLE results shows that, in spite of the expansion parameter being larger in the GME calculation, the latter provides a decidely better approximation than the SLE. It must be emphasized, however, that these results are known to be true only for the models considered and a *general* statement is not yet possible.

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[8] This definition of $\mathcal{P}$ has the advantage that it facilitates comparison with other theories but the drawback that it cannot make any contribution toward the understanding of irreversibility. The latter appears in the problem

only when additional (direct) assumptions of line broadening are made (just as in other approaches to the present problem, for instance Ref. 4).

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[13] F. Perrin, Ann. Chim. Phys. 17, 283 (1932).

[14] To obtain Eq. (6.5) it is also necessary to assume $J = J^*$, which we do for simplicity.

[15] In a finite isolated system the side bands also consist of δ functions. The proximity of neighboring δ functions increases with the size of the system, and they broaden into real bands in the thermodynamic limit or when a bath is attached to the system.

[16] This also means that $2\tilde{J}^2$ is the strength of the δ function at $z=0$ in the quantity $F(z)$ [plotted in Fig. 1 of Ref. 5(b)], whose Fourier transform is the memory $\mathcal{W}(t)$.

[17] The partial Markoffian approximation made in Eqs. (5.12)–5.14) obscures the initial oscillations with frequency J.

[18] See, e.g., D. B. Fitchen, in *Physics of Color Centers*, edited by W. Beall Fowler (Academic, New York, 1968).

[19] Unpublished results concerning room-temperature solutions of anthracene, naphthalene, tetracene, and pyrene in cyclohexane; also bacteriochlorophyll *a* in ether and adenoisine monophosphate (AMP) in a 1 : 1 mixture of water and ethylene glycol at 77 °C.

[20] The two terms of this diffusion constant are thus understood as arising essentially from the interplay of the zero-phonon line and the sideband. Expressions (6,12) should be compared with the three term

$$D = \text{const} \times \left(\frac{C_0^2}{2\alpha_0} + \frac{2C_0C_s(\alpha_0+\alpha_s)}{(\alpha_0+\alpha_s)^2+\omega_s^2} + \frac{C_s^2\alpha_s}{2(\alpha_s^2+\omega_s^2)} \right),$$

which is a consequence of Förster-Dexter or KK theory and is obtained by integrating Eq. (5.3).

[21] The interaction represented by the function $F(z)$ consists of δ functions for the isolated model of Sec. III. The GS analysis effectively extracts the δ function at $z=0$, and treats it differently from the other δ functions. When this model is considered to be in contact with a bath, it is easy to overlook the broadening of the separated zero-z δ function (of the strength $2\tilde{J}^2$) and to allow only the other δ functions to be broadened. Such a misuse of the GS formalism would result in an incorrect description of exciton motion.

[22] However, it is not immediately apparent how one might include the effects of broadening in this approach unambiguously without putting $\tilde{J}=0$.

[23] In our analysis the words "bare" and "dressed" refer, respectively, to the eigenstates of the appropriate Hamiltonian excluding and including the exciton-phonon term of Eq. (3.1d).

[24] The initial wavelike behavior, which is idenpendent of the presence or absence of zero-phonon lines, has not been emphasized in this paper (although it is apparent in two of the curves of Fig. 3). It has been analyzed in Ref. 5, particularly in 5(a) and 5(c). In the specific context of the model of Sec. III, of this paper, it has also been studied recently with the GS technique by R. W. Munn [Chem. Phys. 6, 469 (1974)].