# Theory of exciton transport in the limit of strong intersite coupling. I. Emergence of long-range transfer rates

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A theory of exciton transport in molecular crystals is constructed by developing exact memory functions for pure systems and obtaining from them transfer rates for exciton motion which are particularly applicable in the limit of strong intersite coupling. This extension into the strong-coupling region is useful to stochastic-Liouville-equation theories as well as to the generalized-master-equation approach. Long-range transfer rates are shown to emerge from the analysis. They connect sites unconnected by matrix elements of the interaction and even the ordinary (Markoffian) rate equation used for the long-time description of exciton motion is thus shown to require modification for the strong-coupling case. Exact results are obtained for crystals of an arbitrary number of sites and particular cases of one-dimensional systems of a small number as well as an infinite number of sites are examined. Consequences of the new transport equations are obtained explicitly by analyzing the moments of the probability distribution as well as the probabilities themselves, and the former are used to extend an earlier theory of unified rates to strong-coupling situations in extended systems. Applications of the theory to experiment are discussed. The theory is directly applicable to the transport of other quasiparticles, in particular to that of small polarons.

## I. INTRODUCTION

The Frenkel description[1] of the motion of excitons in a molecular aggregate in the absence of phonons or other "bath" interactions is based on

$$\frac{dc_m}{dt} = -i\sum_n J_{mn} c_n , \tag{1.1}$$

where $m$, a vector of appropriate dimensions, labels the molecular site, $c_m(t) \equiv \langle m|\psi(t)\rangle$ is the amplitude at the $m$th site, $|m\rangle$ is a localized state, $|\psi(t)\rangle$ is the system state, and $J_{mn}$ is the Hamiltonian matrix element $\langle m|H|n\rangle$; here and throughout the paper $\hbar = 1$. If the molecular aggregate is a crystal, i.e., has translational invariance, bands and allied concepts become useful, being introduced into the description through a Fourier transform of (1.1).

This situation may be characterized by the limit $\alpha/J \to 0$, where $\alpha$ represents the exciton-phonon (more generally exciton-bath) interaction and $J$ typifies the $J_{mn}$'s. In the opposite limit $J/\alpha \to 0$ an appropriate description of the transport is generally believed to be[2]

$$\frac{dP_m}{dt} = \sum_n (F_{mn}P_n - F_{nm}P_m) , \tag{1.2}$$

wherein $P_m(t)$ is the probability of the exciton being at site $m$, and $F_{mn}$ are the transition rates, the symbolic connection between the latter and the $J_{mn}$'s being $F = J^2/\alpha$.

The intermediate situation, wherein $J$ and $\alpha$ do not have disparate values, is obviously difficult to describe and much recent effort has been directed at constructing theories capable of addressing this regime. In this paper we present an analysis of some questions that arise in the study of this intermediate region.

One of the recently developed formalisms for probing the intermediate region uses stochastic Liouville equations[3,4]

$$\frac{d\rho_{mn}}{dt} = -i\sum_s (\tilde{J}_{ms}\rho_{sn} - \tilde{J}_{sn}\rho_{ms}) + \delta_{mn}\sum_s (B_{ms}\rho_{ss} - B_{sm}\rho_{mm}) + \cdots , \tag{1.3}$$

whereas another uses generalized master equations[5,6]

$$\frac{dP_m(t)}{dt} = \int_0^t dt' \sum_n [W_{mn}(t-t')P_n(t') - W_{nm}(t-t')P_m(t')] . \tag{1.4}$$

In Eq. (1.3) only the terms of interest here have been displayed. The others may be found in Refs. 3 and 4. These descriptions [(1.3) and (1.4)] of the intermediate situation may be used either as phenomenological approaches or as theories whose parameters are obtained microscopically. If the former, they can be shown[7] to be essentially equivalent to each other at least when the stochastic Liouville equation is slightly generalized.[8] However, as microscopically obtainable descriptions they make predictions that are identical in several cases but conflicting in others. The conflicts arise from the difference in the particular truncation approximations invoked in the two theories. A discussion of these issues has been given earlier by the authors.[7(b)] In this paper we shall *not* be interested in these unresolved problems that arise in

 

the comparative study of the theories.

Whether (1.3) and (1.4) are taken to be in agreement or in conflict with each other, they are inadequate in certain limits of the physical parameters, when considered as microscopic theories. The inadequacy of the theories may be appreciated in the light of Silbey's objection[9] against the use of (1.4) with its particular approximate expressions[10] for the memories in extended systems in the absence of phonons. He has pointed out that the weak-coupling approximation used in the past[10] in (1.4) results in negative probabilities for such systems. This objection is certainly valid. However, we have shown explicitly elsehwere[11] that negative probabilities also arise out of the Grover-Silbey, or generally the stochastic-Liouville-equation, treatment when used with its approximate expressions. We shall not repeat the details here. Suffice it to say that such a demonstration should not come as a surprise. In most perturbation calculations it is the Schrödinger equation that is truncated and the approximate wave function thus obtained is multiplied by its complex conjugate to give the probabilities. The latter are therefore guaranteed to be positive no matter how hideous the truncation approximation. On the other hand, even a gentle truncation on the Liouville equation for the *density matrix* will generally give negative probabilities unless special care is taken to assure positivity. *All* the modern theories of exciton transport[3-7] truncate the density-matrix equation and none of them contains a procedure to ensure positivity of the diagonal elements of the density matrix. Of course the ranges of parameter values that make the theories inapplicable for the above reasons are different for the different theories. Thus the perturbation approximations used in the past along with (1.4) and with (1.3) will give unacceptable results for extended systems if the randomness parameter is small with respect to, respectively, the intersite matrix elements $J$ and that part of $J$ which does not conserve phonons.

Thus we see that Silbey's objection[9] applies to *all existing theories* of exciton transport in the intermediate region in one or the other limit of parameter values. It is therefore important to study the theories in those limits, and attempt to improve them. The present paper concentrates on (1.4) [although the results apply to (1.3) as well] and studies it in the limit in which it gives the least acceptable results,[9] i.e., the limit of very strong intersite coupling. It will be seen that this analysis leads naturally to a relatively new and highly interesting concept: that of long-range transfer rates and memories. With the exception of Goad's calculation[12] in which spatially exponential rates appear, we have uncovered no mention of this concept in the literature. Several of its consequences are worked out in this paper with a view towards extending the applicability of the existing theories of exciton transport in the limits outside the range of their validity in their present form.

The paper is outlined as follows. In Sec. II it is pointed out how long-range transfer rates appear in a calculation on a simple three-site model reported earlier.[13] In Sec. III exact expressions are obtained for the memory functions in the generalized master equation (1.4) as well as for simple transfer rates in a system of $N$ sites (arbitrary $N$) obeying translational invariance and periodic boundary conditions. Particular cases of the results of Sec. III are given in Sec. IV. These treat a small finite "crystal" of four molecules on one hand, and the infinite chain on the other. The new features of exciton motion predicted by these equations are studied in Sec. V by evaluating expressions for the mean-square displacement presented earlier,[13] by studying their effect on (and thereby extending) the unified definition of effective transfer rates given by Kenkre and Knox,[14] and by analyzing the full probabilities themselves, particularly in the long-time limit. That section also contains an illustrative application of the theory to a recently proposed experiment.[15] Concluding remarks appear in Sec. VI.

## II. APPEARANCE OF LONG-RANGE MEMORIES AND RATES

The concept of long-range memories and rates in the strong intersite-coupling limit may be immediately appreciated in the context of a simple model. The author has shown earlier[13] that in a system of three sites 1, 2, and 3, with Hamiltonian matrix elements $\langle m|H|m\rangle = 0 = \langle 1|H|3\rangle$ and $\langle 1|H|2\rangle = \langle 3|H|2\rangle = J$, initial localization on one of the sites leads to the generalized master equation (1.4) for the probability evolution where, in addition to the spatially local memories

$$\mathfrak{w}_{12}(t) = \mathfrak{w}_{23}(t) = 2J^2 \cos(tJ\sqrt{2}), \tag{2.1}$$

there arises the nonlocal memory

$$\mathfrak{w}_{13}(t) = 2J^2 \sin^2(tJ/\sqrt{2}). \tag{2.2}$$

A direct derivation of (2.1) and (2.2) from the Zwanzig formulas[16] is given in the Appendix. We term the memories in (2.1) *local* because their spatial extent is the same as that of the matrix elements of the Hamiltonian. On the other hand, (2.2) shows that a memory function connects sites 1 and 3 *despite the fact that no Hamiltonian matrix element exists between them*. We therefore call the memory *spatially nonlocal*.

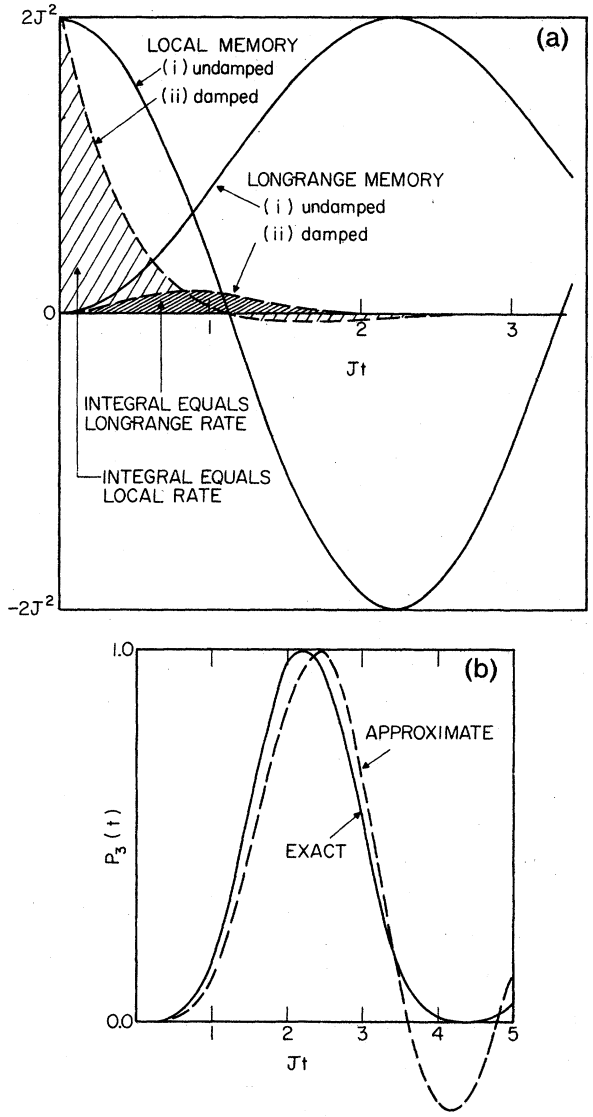


FIG. 1. (a) Local and long-range memory functions for the open three-site system of Sec. II for the pure (undamped) as well as the damped case: the disappearance of long-range transfer rates for weak $J$ is seen clearly from the nature of the long-range memory and its integral. (b) Probability $P_3(t)$ of one end of the open three-site "chain" in the absence of bath interactions and for the initial condition that the other end is occupied: the solid line is the exact solution and the dashed line is the "weak-coupling" approximation based on the truncated memory.

The exact results (2.1) and (2.2) should be compared to those given by the weak-coupling approximation used in earlier calculations of the memories. The approximate treatment would replace the right-hand sides of (2.1) and (2.2) by $2J^2$ and 0, respectively. It is easily shown that this would lead to the solution $P_3(t)=\frac{1}{3}+\frac{1}{6}(\cos tJ\sqrt{6})-\frac{1}{2}\cos(tJ\sqrt{2})$ if site 1 were initially occupied and therefore to negative probabilities [see Fig. 1(b)], whereas the exact solution as given by (2.1) and (2.2), $P_3(t)=\sin^4(tJ/\sqrt{2})$, obviously does not.

The significance of the nonlocal memory is made more apparent by comparing the Markoffian rate equations that would be ordinarily written for the three-site system[17]

$$\frac{dP_{1,3}}{dt}=\frac{2J^2}{\alpha}(P_2-P_{1,3}), \tag{2.3}$$

$$\frac{dP_2}{dt}=\frac{2J^2}{\alpha}(P_1+P_3-2P_2), \tag{2.4}$$

to the result that would be obtained by introducing damping into (2.1) and (2.2) in the usual manner and identifying rates with the time integrals of the memories:

$$\frac{dP_{1,3}}{dt}=\frac{\alpha^2}{\alpha^2+2J^2}\left(\frac{2J^2}{\alpha}\right)(P_2-P_{1,3}) + \frac{2J^2}{\alpha^2+2J^2}\left(\frac{J^2}{\alpha}\right)(P_{3,1}-P_{1,3}), \tag{2.5}$$

$$\frac{dP_2}{dt}=\frac{\alpha^2}{\alpha^2+2J^2}\left(\frac{2J^2}{\alpha}\right)(P_1+P_3-2P_2). \tag{2.6}$$

Here $\alpha$ represents the damping caused by the exciton-bath interaction. Equations (2.3) and (2.4), which are the consequence of the weak-coupling approximation valid for small $J/\alpha$, are seen to be modified by the introduction of the factors $\alpha^2/(\alpha^2+2J^2)$ and $2J^2/(\alpha^2+2J^2)$. These do indeed tend to 1 and 0, respectively, in the limit $J/\alpha\to 0$, reducing (2.5) and (2.6) to the weak-coupling results (2.3) and (2.4).

One should also observe that the nonlocal memory function (2.2) is zero at $t=0$ unlike the local memory function. [See also Fig. 1(a).] This is a general characteristic of nonlocal memory functions. Its consequence is that if the damping $\alpha$ is sufficiently strong, the nonlocal memories have no opportunity to rise to non-negligible values before they are forced to decay to zero by the damping agencies (viz., the bath interactions). Therefore, they make negligible contributions to transfer rates in the weak $J/\alpha$ limit. [See Fig. 1(a).] No nonlocal rates need thus be considered when the bath interactions are very strong. This corresponds to the $\lambda^2 t$ limit,[18] and the validity of rate equations used earlier[5] in the weak $J/\alpha$ situation is thus unaffected. This may be seen explicitly through the limits of the factor $2J^2/(\alpha^2+2J^2)$ multiplying the nonlocal terms in (2.5).

This simple illustrative example shows how nonlocal memories and rates arise and why they are unimportant in the *weak* $J/\alpha$ limit. In the following sections we obtain expressions valid in the strong $J/\alpha$ limit for more realistic systems.

## III. MEMORY FUNCTIONS AND TRANSFER RATES FOR THE $N$-SITE SYSTEM

Consider an exciton moving on a chain (linear, for simplicity) of $N$ molecular sites obeying periodic boundary conditions, the exciton energy in the absence of intersite interaction being site independent and therefore assumed zero without loss of generality, there being no randomness of any kind ($\alpha = 0$), and the interaction matrix elements between sites $m$ and $n$ being $J_{mn}$. In other words, the system obeys (1.1). We shall cast its evolution in the form of (1.4) and calculate the $\mathfrak{W}_{mn}(t)$'s exactly.

Define

$$c^k = \frac{1}{\sqrt{N}} \sum_m c_m e^{ikm} . \tag{3.1}$$

The Fourier transform of (1.1) has the solution

$$c^k(t) = (1/\sqrt{N}) e^{-itJ^k} , \tag{3.2}$$

where the initial localization on a single site has been used through (3.1) and, with $J_{m-n} = J_{mn}$,

$$J^k = \sum_m J_m e^{ikm} . \tag{3.3}$$

Inverting (3.2), the probability $P_m(t) = c_m^* c_m$ is obtained as

$$P_m(t) = \frac{1}{N^2} \sum_{q',q} e^{-it(J^{q'} - J^q)} e^{-im(q'-q)} . \tag{3.4}$$

However, it is also possible to obtain an expression for $P_m(t)$ directly from the generalized master equation (1.4). It involves the memories $\mathfrak{W}_{mn}$ and, when equated to (3.4), yields usable expressions for $\mathfrak{W}_{mn}$. Thus, the definition

$$\mathfrak{A}_{mm} = \sum_n \mathfrak{W}_{nm} , \tag{3.5a}$$

$$\mathfrak{A}_{mn} = -\mathfrak{W}_{mn} \quad \text{for } m \neq n , \tag{3.5b}$$

and the use of the system property of translational invariance ($\mathfrak{A}_{mn} = \mathfrak{A}_{m-n}$) allow (1.4) to be rewritten as

$$\frac{dP^k(t)}{dt} + \int_0^t dt' \mathfrak{A}^k(t-t') P^k(t') = 0 , \tag{3.6}$$

where $P^k$ and $\mathfrak{A}^k$ are Fourier transforms of $P_m$ and $\mathfrak{A}_m$ defined through equations completely analogous to Eqs. (3.1) and (3.3), respectively. Equating the expressions for the Laplace transform of the Fourier transform of $P_m(t)$ as computed from Eqs. (3.4) and (3.6), respectively, i.e.,

$$\tilde{P}^k(\epsilon) = \frac{1}{N^2\sqrt{N}} \sum_{q',q,m} \frac{e^{im(k+q-q')}}{\epsilon + i(J^{q'} - J^q)} = \frac{1}{\sqrt{N}} \frac{1}{\epsilon + \tilde{\mathfrak{A}}^k(\epsilon)} , \tag{3.7}$$

where tildes denote Laplace transforms and $\epsilon$ is the Laplace variable, one obtains

$$\tilde{\mathfrak{W}}_{mn}(\epsilon) = -\sum_k \left( e^{-ik(m-n)} \Big/ \sum_q (\epsilon + i\Lambda^{kq})^{-1} \right) , \tag{3.8}$$

where $\Lambda^{k\zeta} = J^{k+\zeta} - J^\zeta$. This is the required explicit result for the memory function. Note that

$$\Lambda^{kq} = -\Lambda^{kq+\zeta} \tag{3.9}$$

for $\zeta = 2\pi - (k+2q)$, since

$$\Lambda^{k2\pi-(k+q)} = J^{2\pi-q} - J^{2\pi-(k+q)} = J^q - J^{k+q} , \tag{3.10}$$

where the first identity follows from the definition of $\Lambda$ and the second from (3.3). If $k$ and $q$ have allowed values "in the band," i.e., if they are integral multiples of $2\pi/N$, $\zeta$ too has an allowed value. It follows therefore from (3.9) that for any $k$ the $q$ summation always has pairs of $\Lambda$'s which are equal in magnitude but opposite in sign.[19] This leads to a simplification of (3.8):

$$\tilde{\mathfrak{W}}_{mn}(\epsilon) = -\sum_k e^{-ik(m-n)} \left( \frac{d}{d\epsilon} [\ln \chi^k(\epsilon)] \right)^{-1} , \tag{3.11a}$$

$$\chi^k(\epsilon) = \prod_q [\epsilon^2 + (\Lambda^{kq})^2] , \tag{3.11b}$$

where the number of factors in the product in (3.11b) is $\frac{1}{2}N$ if $N$ is even and $\frac{1}{2}(N+1)$ if it is odd.[19] Calling this number $M$ and defining quantities $S^k$ through

$$S_1^k = \sum_q (\Lambda^{kq})^2 ,$$

$$S_2^k = \sum_{q<q'} (\Lambda^{kq})^2 (\Lambda^{kq'})^2 , \tag{3.12}$$

$$S_3^k = \sum_{q<q'<q''} (\Lambda^{kq})^2 (\Lambda^{kq'})^2 (\Lambda^{kq''})^2 ,$$

etc., the quantities $\mathfrak{A}^k(t)$ appearing in (3.6) can be shown to satisfy

$$\tilde{\mathfrak{A}}^k(\epsilon) = \epsilon \sum_{r=1}^{M} r S_r^k \epsilon^{2(M-r)} \Big/ \sum_{r=1}^{M} r S_{M-r}^k \epsilon^{2r} . \tag{3.13}$$

The system considered in this section so far is "pure," i.e., it does not interact with a bath. If bath interactions are now introduced phenomenologically through a damping $\alpha$, the memory functions are obtained by replacing $\epsilon$ by $(\epsilon + \alpha)$ in (3.8), (3.11), and (3.13). Thus, for instance

$$\tilde{\mathfrak{W}}_{mn}(\epsilon) = -\sum_k \left( e^{-ik(m-n)} \Big/ \sum_q (\epsilon + \alpha + i\Lambda^{kq})^{-1} \right) . \tag{3.14}$$

Unlike the "pure" memories, the damped memories have finite time integrals which are nothing but the transfer rates in the ordinary (markoffian) master equation (1.2). These rates $F_{mn}$ are immediately obtained by replacing $\epsilon$ by $\alpha$ in the above

undamped expressions for the Laplace transform of the memories or by 0 in the damped ones. Thus

$$F_{mn} = -\sum_k \left[ e^{-ik(m-n)} \Big/ \sum_q \left( \alpha + \frac{(\Lambda^{kq})^2}{\alpha} \right)^{-1} \right]. \qquad (3.15)$$

Notice the "two-term" nature of the rates, the terms being proportional to $\alpha$ and $1/\alpha$, respectively. Two-term transport quantities have appeared earlier in Refs. 3 and 4 and have been discussed in Ref. 7.

Equation (3.8) for the memories or more generally its "broadened" version obtained by replacing $\epsilon$ by $\epsilon + \alpha$, and Eq. (3.15) for the transfer rates constitute the main result of this paper, and should replace the "narrow-band"[20] expressions $2J^2/\epsilon$ and $2J^2/\alpha$, respectively, that would appear in the large $J/\alpha$ limit as a result of straightforward calculations[9] with the weak-coupling approximation. One should note that the molecular chain considered here need not be linear. All that needs to be done for a two- or three-dimensional crystal is to replace $m$, $n$, and $k$, $q$ by vectors in the direct and reciprocal lattices, respectively.

## IV. PARTICULAR CASES

The application of the results derived in Sec. III to particular situations is straightforward. Thus it may be easily shown that for a dimer (a molecule pair) Eq. (3.8) gives $\mathfrak{W}(t) = 2J^2$ and Eq. (3.15) gives $F = 2J^2/\alpha$, or that the memory for a *closed* trimer, i.e., $J = \langle 1|H|2\rangle = \langle 1|H|3\rangle = \langle 2|H|3\rangle$, is given by $2J^2\cos(tJ\sqrt{3})$. We present below explicit calculations for two specific cases: a ring of 4 and of an infinite number of molecules, respectively. The first case represents the smallest *closed* ring for which spatial nonlocality appears, while the second case shows the simplifications inherent in a large system. In both these cases we shall invoke tight binding, i.e., $J_{mn} = J(\delta_{m,n+1} + \delta_{m,n-1})$ which results from (3.3) in

$$J^k = 2J\cos k, \qquad (4.1a)$$

$$(\Lambda^{kq})^2 = 16J^2 \sin^2(\tfrac{1}{2}k)\sin^2(q + \tfrac{1}{2}k). \qquad (4.1b)$$

### A. Ring of four sites

From the relation $e^{ikm} = e^{ik(m+4)}$ demanded by periodic boundary conditions one obtains 0, $\frac{1}{2}\pi$, $\pi$, and $\frac{1}{2}3\pi$ as the allowed values of $k$. The respective values of $J^k$ are, from (4.1a), $2J$, 0, $-2J$, and 0. The quantities $(\Lambda^{kq})^2$ are given by

$$(\Lambda^{\pi/2\, q})^2 = 4J^2, 4J^2, \qquad (4.2a)$$

$$(\Lambda^{3\pi/2\, q})^2 = 4J^2, 4J^2, \qquad (4.2b)$$

$$(\Lambda^{\pi\, q})^2 = 0, 16J^2. \qquad (4.2c)$$

Therefore, the quantities $S^k$ are obtained from (3.12) as follows:

$$S_1^{\pi/2} = S_1^{3\pi/2} = 8J^2, \qquad (4.3a)$$

$$S_2^{\pi/2} = S_2^{3\pi/2} = 16J^4, \qquad (4.3b)$$

$$S_1^{\pi} = 16J^2, \qquad (4.3c)$$

$$S_2^{\pi} = 0. \qquad (4.3d)$$

Equation (3.16) gives

$$\tilde{\mathfrak{A}}^{\pi/2} = \tilde{\mathfrak{A}}^{3\pi/2} = \frac{\epsilon}{1}\,\frac{8J^2\epsilon^2 + 32J^4}{8J^2\epsilon^2 + 2\epsilon^4} = \frac{4J^2}{\epsilon}, \qquad (4.4a)$$

$$\tilde{\mathfrak{A}}^{\pi} = \frac{\epsilon}{1}\,\frac{16J^2\epsilon^2 + 0}{16J^2\epsilon^2 + 2\epsilon^4} = 8J^2\,\frac{\epsilon}{\epsilon^2 + 8J^2}, \qquad (4.4b)$$

$$\tilde{\mathfrak{A}}^{0} = 0. \qquad (4.4c)$$

Through (3.5) or directly through (3.8)

$$\tilde{\mathfrak{W}}_{12}(\epsilon) = 2J^2\,\frac{\epsilon}{\epsilon^2 + 8J^2}, \qquad (4.5a)$$

$$\tilde{\mathfrak{W}}_{13}(\epsilon) = 2J^2\left(\frac{1}{\epsilon} - \frac{\epsilon}{\epsilon^2 + 8J^2}\right), \qquad (4.5b)$$

which are inverted to yield the memories explicitly in the time domain:

$$\mathfrak{W}_{41}(t) = \mathfrak{W}_{23}(t) = \mathfrak{W}_{34}(t) = \mathfrak{W}_{12}(t) = 2J^2\cos(tJ2\sqrt{2}), \qquad (4.6a)$$

$$\mathfrak{W}_{13}(t) = \mathfrak{W}_{24}(t) = 2J^2[1 - \cos(tJ2\sqrt{2})] = 4J^2\sin^2(tJ\sqrt{2}). \qquad (4.6b)$$

In the presence of bath interactions, Eqs. (4.6) will be multipled by $e^{-\alpha t}$, and the *long time* evolution of the exciton will be as given by

$$\frac{dP_1}{dt} = \xi\left(\frac{2J^2}{\alpha}\right)(P_2 + P_4 - 2P_1) + (1-\xi)\left(\frac{2J^2}{\alpha}\right)(P_3 - P_1), \qquad (4.7)$$

and similar equations for $P_2$, $P_3$, and $P_4$. Note that although (4.7) is Markoffian, it contains nonlocal transfer rates. The first term on the right-hand side contains the local rate while the second contains the nonlocal rate, $\xi$ being the factor $\alpha^2/(\alpha^2 + 8J^2)$ which equals 1 in the weak-coupling limit $J/\alpha \to 0$.

### B. Ring (or chain) of an infinite number of sites

Rewriting (3.8) as

$$\tilde{\mathfrak{W}}_{mn}(\epsilon) = \frac{1}{N}\sum_k \tilde{\mathfrak{W}}^k(\epsilon)e^{-ik(m-n)}, \qquad (4.8)$$

one obtains in the limit $N \to \infty$,

$$\tilde{\mathfrak{W}}^k(\epsilon) = -2\pi \Big/ \epsilon \int_0^{2\pi} dq[\epsilon^2 + 8J^2(\sin^2\tfrac{1}{2}k)(1 - \cos 2q)]^{-1}. \qquad (4.9)$$

Using contour integration along the unit circle one finds

$$\tilde{\mathfrak{W}}^k(\epsilon) = -[\epsilon^2 + 4\mathfrak{J}^2 \sin^2 \tfrac{1}{2}k)]^{1/2} . \tag{4.10}$$

It is possible to invert the Fourier transform and obtain $\tilde{\mathfrak{W}}_{mn}(\epsilon)$ from (4.10). Thus the $N \to \infty$ limit of (4.8) gives

$$\tilde{\mathfrak{W}}_{mn}(\epsilon) = \frac{-(\epsilon^2 + 8\mathfrak{J}^2)^{1/2}}{2\pi} \int_0^{2\pi} dk\, e^{-ik(m-n)} \times \left(1 - \frac{8\mathfrak{J}^2}{\epsilon^2 + 8\mathfrak{J}^2} \cos k\right)^{1/2} , \tag{4.11}$$

which, with the substitution $\pi - k = k'$ can be reduced to a standard expression[21] involving Legendre functions $P^m_{1/2}$ of fractional order. The limit $\epsilon \to \alpha$ gives, as explained above, the transfer rates $F_{mn}$:

$$F_{mn} = [(-1)^{|m-n|+1}(\alpha^2 + 8\mathfrak{J}^2)^{1/2} P^{|m-n|}_{1/2}(\beta)\Gamma(\tfrac{3}{2})] \times [\beta^{1/2}\Gamma(|m-n| + \tfrac{3}{2})]^{-1} , \tag{4.12}$$

where $\beta = \alpha^{-1}(\alpha^2 + 16\mathfrak{J}^2)^{-1/2}(\alpha^2 + 8\mathfrak{J}^2)^{1/2}$. Obviously the memory functions $\tilde{\mathfrak{W}}_{mn}(\epsilon)$ are given by (4.12) with $\alpha$ replaced by the Laplace variable $\epsilon$. These can then be Laplace inverted to obtain expressions in the time domain. It is possible, however, to obtain the time domain expressions more conveniently by working directly from (4.10). Note that the functions $\mathfrak{W}^k(t)$ are generally unphysical [although $\mathfrak{W}_{mn}(t)$ are certainly well behaved] as they contain derivatives of $\delta$ functions. On the other hand, the functions $\mathfrak{A}^k(t)$ appearing, for instance, in (3.6) are always physical. They are generally related to $\mathfrak{W}^k(t)$ through

$$\tilde{\mathfrak{A}}^k(\epsilon) = \tilde{\mathfrak{W}}^0(\epsilon) - \tilde{\mathfrak{W}}^k(\epsilon) , \tag{4.13}$$

as is obvious from (3.5). Using (4.10) in (4.13), one gets

$$\tilde{\mathfrak{A}}^k(\epsilon) = (\epsilon^2 + 16\mathfrak{J}^2 \sin^2 \tfrac{1}{2}k)^{1/2} - \epsilon , \tag{4.14}$$

which is recognized as the Laplace transform of $(1/t)(4\mathfrak{J} \sin \tfrac{1}{2}k)[J_1(4\mathfrak{J}t \sin \tfrac{1}{2}k)]$ or what is the same, of $8\mathfrak{J}^2(\sin^2 \tfrac{1}{2}k)[J_0(4\mathfrak{J}t \sin \tfrac{1}{2}k) + J_2(4\mathfrak{J}t \sin \tfrac{1}{2}k)]$. Thus the inverse transform of (4.15) is

$$\mathfrak{W}^k(t) = (8\mathfrak{J}^2 \sin^2 \tfrac{1}{2}k)[J_0(4\mathfrak{J}t \sin \tfrac{1}{2}k) + J_2(4\mathfrak{J}t \sin \tfrac{1}{2}k)] + [L^{-1}(\epsilon)](16\mathfrak{J}^2 \sin^2 \tfrac{1}{2}k) , \tag{4.15}$$

where the last term is the derivative of the $\delta$ function and where $L^{-1}$ denotes the Laplace-inverse. To obtain the memory functions $\mathfrak{W}_{mn}(t)$ we use (4.15) in (4.8), recognize a particular case of the general result[22]:

$$\left(\frac{1 - e^{-ik}}{2 \sin \tfrac{1}{2}k}\right)^{\nu} J_\nu(4\mathfrak{J}t \sin \tfrac{1}{2}k) = \sum_{m=-\infty}^{+\infty} e^{imk} J_m(2\mathfrak{J}t) J_{m+\nu}(2\mathfrak{J}t) , \tag{4.16}$$

and use (3.5). We then obtain the required memories:

$$\mathfrak{W}_{mn}(t) = 2\mathfrak{J}^2 \{J^2_{m-n+1}(2\mathfrak{J}t) + J^2_{m-n-1}(2\mathfrak{J}t) + 2[J_{m-n+1}(2\mathfrak{J}t)][J_{m-n-1}(2\mathfrak{J}t)]\} - 2\mathfrak{J}^2 \{2J^2_{m-n}(2\mathfrak{J}t) + [J_{m-n}(2\mathfrak{J}t)] \times [J_{m-n+2}(2\mathfrak{J}t) + J_{m-n-2}(2\mathfrak{J}t)]\} . \tag{4.17}$$

These are exact expressions for the $\mathfrak{W}_{mn}(t)$'s in (1.4) for a pure ($\alpha = 0$) one-dimensional infinite crystal. The usual introduction of damping gives the "broadened" $\mathfrak{W}$'s applicable to the $\alpha \neq 0$ situation by multiplying the right-hand side of (4.17) by $e^{-\alpha t}$.[23] The correct transfer rates $F_{mn}$ in a Pauli-type master equation (1.2) are given *not by* $(2\mathfrak{J}^2/\alpha)(\delta_{m,n+1} + \delta_{m,n-1})$ *but by* time integrals of the broadened $\mathfrak{W}$'s, the explicit expression being (4.12).

## V. MOTION OF THE EXCITON

In the previous sections we have obtained new Markoffian as well as non-Markoffian transport equations for exciton motion in a crystal, and have examined some specific cases of those equations. In order to appreciate the new features of exciton motion predicted by them we shall now study their solutions by analyzing first the moments of the probability distribution and then the probabilities themselves.

### A. Moments and effective rates

The mean-square displacement $\langle\langle m^2(t)\rangle\rangle \equiv \sum_m m^2 P_m(t)$ contains useful information and can be obtained more easily than the entire probabilities of site occupation. It has thus been calculated by various authors[4,24,25] and has also been made the basis of a unified definition of "slow" and "fast" transfer rates for excitons.[14] Therefore, let us first ask what effect the long-range memories and rates discussed above have on $\langle\langle m^2(t)\rangle\rangle$. We have shown earlier[13] that, for the infinite chain, $\langle\langle m^2(t)\rangle\rangle$ is related to the second moment of the memory functions $\langle m^2(t)\rangle$ through

$$\frac{d\langle\langle m^2(t)\rangle\rangle}{dt} = 2\int_0^t dt' \langle m^2(t')\rangle \equiv 2\int_0^t dt' \sum_{m=1}^{\infty} m^2 \mathfrak{W}_m(t') . \tag{5.1}$$

The moments of $\mathfrak{W}_m(t)$ are obtained simply by Laplace inverse transforming derivatives of $\tilde{\mathfrak{W}}^k(\epsilon)$. Thus,

$$\sum_m m^2 \tilde{\mathfrak{W}}_m(\epsilon) = -\lim_{k \to 0} \frac{\partial^2 \tilde{\mathfrak{W}}^k(\epsilon)}{\partial k^2} . \tag{5.2}$$

A straightforward calculation using (5.2) and (3.8)

gives

$$\langle m^2(t)\rangle = 4J^2 e^{-\alpha t}, \tag{5.3}$$

in the general case and, of course,

$$\langle m^2(t)\rangle = 4J^2 \tag{5.4}$$

for the pure crystal. We emphasize that (5.4) is exact and does not involve weak-coupling or phenomenological assumptions. Since it leads through (5.1) to[26]

$$\langle\langle m^2(t)\rangle\rangle \equiv \sum_m m^2 P_m(t) = 4J^2 t^2 \tag{5.5}$$

for $\langle\langle m^2(0)\rangle\rangle = 0$, we have here the interesting result noted earlier by Silbey[9] that the weak-coupling approximation to (1.4) gives the *exact* value for the mean-square displacement although the predicted probabilities are quite different in the two cases. In other words the long-range character of the new memories leaves $\langle\langle m^2(t)\rangle\rangle$ entirely unaffected.

Recalling that the unified definition of coherent and incoherent transfer rates given by us earlier[14] is based on the evolution of $\langle\langle m^2(t)\rangle\rangle$, we conclude that those rates are in no way influenced by the modifications introduced into the transport equations in the previous sections. Although this is surprising, it obviously means that one must explore higher moments of the probability in order to see that influence. We therefore calculate $\langle m^4(t)\rangle$ or its Laplace transform

$$\sum_m m^4 \tilde{\mathfrak{W}}_m(\epsilon) = \lim_{k\to 0} \frac{\partial^4 \tilde{\mathfrak{W}}^k(\epsilon)}{\partial k^4}, \tag{5.6}$$

which is connected to $\langle\langle m^4(t)\rangle\rangle = \sum_m m^4 P_m(t)$ through

$$\frac{d\langle\langle m^4(t)\rangle\rangle}{dt} = 2\int_0^t dt' [\langle m^4(t')\rangle + 6\langle m^2(t-t')\rangle\langle\langle m^2(t')\rangle\rangle]. \tag{5.7}$$

Like Eq. (5.1), Eq. (5.7) is obtained immediately from Eq. (8) of Ref. 13. The evaluation of (5.6) yields

$$\langle m^4(t)\rangle = 4J^2 e^{-\alpha t}[1 - (\tfrac{1}{2})J^2 t^2], \tag{5.8}$$

which differs from the usual result that would arise in the weak-coupling situation as the latter would not have the second term in the parenthesis in (5.8). Equation (5.8), when combined with (5.7), produces

$$\frac{d\langle\langle m^4(t)\rangle\rangle}{dt} = 8J^2 \int_0^t dt' e^{-\alpha(t-t')}(1 + \tfrac{47}{2} J^2 t^2). \tag{5.9}$$

If one now relinquishes $\langle\langle m^2(t)\rangle\rangle$ in favor of $\langle\langle m^4(t)\rangle\rangle$ as the key quantity to be used in the definition of transfer rates, i.e., if instead of using the procedure given in Ref. 14 one defines the effective rate $w$ as the reciprocal of the time taken for $\langle\langle x^4(t)\rangle\rangle$ to build from the value 0 to the value $a^4$, where $x$ is the distance from the site occupied initially by the exciton and $a$ is the intersite distance, one obtains the implicit equation which should be compared to Eqs. (6) and (7) of Ref. 14:

$$\left(e^{-\alpha/w} - 1 + \frac{\alpha}{w}\right) + 47\left(\frac{J}{\alpha}\right)^2 \left[e^{-\alpha/w} - 1 + \frac{\alpha}{w} - \frac{1}{2!}\left(\frac{\alpha}{w}\right)^2 + \frac{1}{3!}\left(\frac{\alpha}{w}\right)^3\right] = \frac{\alpha^2}{8J^2}. \tag{5.10}$$

We make the following two observations: (a) The $J$ dependence of the rate $w$ is not changed in its essentials since in the coherent ($\alpha/J \to 0$) and incoherent ($J/\alpha \to 0$) limits the proportionality of $w$ to $J$ and $J^2$, respectively, continues to hold: thus there is no essential change brought about by the present theory in the unified description given earlier.[14] (b) The effect of the long-range memories and rates, although absent in the mean-square displacement, is strongly present from a numerical viewpoint already in the fourth moment and in the effective transfer rates derived from it.

Evidently a finite number of moments of the probability distribution contains only partial information about the exciton motion and these rate definitions based on them provide only indicators and not precise quantitative criteria.

### B. Evolution of the probabilities: Four-site ring

We now analyze the evolution of the entire probabilities first in the four-site system and then in the infinite chain. From the results of Sec. V we know that the *exact* evolution of the probabilities for the pure four-site system obeys the generalized master equation (1.4) with the memory functions given by (4.6) provided the exciton is initially localized or, more generally, provided an initial random phase or diagonality condition applies on the density matrix. Bath effects are introduced by multiplying the "pure" expressions (4.6) for the $\mathfrak{W}$'s by $\exp(-\alpha t)$ and their time integrals are the rates appearing in the rate equation of the Förster-Dexter form. This is explicitly displayed in (4.7).

We shall study the motion of the exciton under the condition that it is initially localized on site 1, i.e., $P_1(0) = 1$ and $P_2(0) = P_3(0) = P_4(0) = 0$. The standard way of calculating from the master equation involves the "modes" $P^k$. The initial condition may be written as $P^k(0) = \frac{1}{2}$ for all $k$ where we have an equation similar to (3.1). From (3.6) and (4.4),

$$P^0(t)=\tfrac{1}{2} \tag{5.11a}$$

$$P^{\pi/2}(t)=P^{3\pi/2}(t)$$
$$=\tfrac{1}{2}e^{-t\alpha/2}[\cos\Omega t+(\alpha/2\Omega)\sin\Omega t]\,, \tag{5.11b}$$

$$P^{\pi}(t)=[\tfrac{1}{2}e^{-t\alpha}]L^{-1}[(\epsilon^2+8J^2)(\epsilon^3-\alpha\epsilon^2$$
$$+\epsilon 16J^2-8J^2\alpha)^{-1}]\,, \tag{5.11c}$$

where $\Omega^2=J^2-\frac{1}{4}\alpha^2$. For any given values of $J$ and $\alpha$ the roots of the cubic equation relevant to (5.11c) can be found trivially and $P^{\pi}(t)$ obtained explicitly. The four probabilities $P_m(t)$ can then be written:

$$P_1=\tfrac{1}{2}(P^0+2P^{\pi/2}+P^{\pi})\,, \tag{5.12a}$$

$$P_2=P_4=\tfrac{1}{2}(P^0-P^{\pi})\,, \tag{5.12b}$$

$$P_3=\tfrac{1}{2}(P^0-2P^{\pi/2}+P^{\pi})\,, \tag{5.12c}$$

in terms of the expressions in (5.11). We shall not display any examples nor detail the system evolution as a function of the coherence parameter $J/\alpha$ as they would provide information which is basically identical to that contained, for instance, in Fig. 4 of Ref. 7(b). Of special interest in the present context is, however, the long-time motion of the exciton and, in particular, the effects on it of the long-range transfer rates discussed in this paper. Working from (4.7) we again obtain the "modes" $P^k$:

$$P^0(t)=\tfrac{1}{2}\,, \tag{5.13a}$$

$$P^{\pi/2}(t)=P^{3\pi/2}(t)=\tfrac{1}{2}e^{-t(J^2/\alpha)}\,, \tag{5.13b}$$

$$P^{\pi}(t)=\tfrac{1}{2}\exp\{-t(2J^2/\alpha)[\alpha^2/(\alpha^2+8J^2)]\}. \tag{5.13c}$$

The prediction of the usual rate equation[2] employing golden-rule rates would be identical to (5.13) except in that the exponent in (5.13c) would be merely $2J^2/\alpha$. At long times the probability $P_3(t)$ which describes the occupation of the site farthest from the initially occupied one is, explicitly,

$$P_3(t)=\tfrac{1}{4}(1+e^{-t\zeta(2J^2/\alpha)}-2e^{-t(J^2/\alpha)})\,, \tag{5.14}$$

from our present theory (which contains long-range rates from site 1 to site 3) but

$$P_3(t)=\tfrac{1}{4}(1+e^{-t(2J^2/\alpha)}-2e^{-t(J^2/\alpha)})\,, \tag{5.15}$$

from usual rate equations (containing only local rates). Here $\zeta$ equals $\alpha^2/(\alpha^2+8J^2)$ as in (4.7). Equations (5.14) and (5.15) are plotted[27] in Fig. 2. Note that the long-range rates result in faster transfer and that (5.15) is the weak-coupling limit $(J/\alpha\to 0)$ of (5.14).

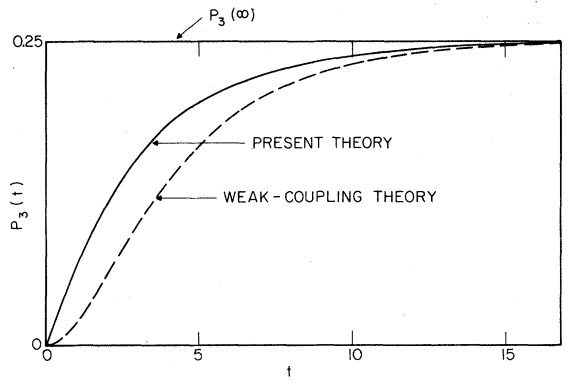


FIG. 2. Comparison of the predictions of ordinary (Markoffian) rate equations for exciton transport in a closed four-site "crystal": the solid line represents the present theory and incorporates long-range rates while the dashed line is the result of the conventional weak-coupling rate equation; the ordinate is the probability of the farthest site relative to the initially occupied one.

### C. Evolution of the probabilities: Infinite chain

The short-time evolution as given by the full memories in the generalized master equation and the detailed passage from wavelike to diffusive transport may also be studied explicitly from (4.10), (4.14), and (4.17) for motion on the infinite chain. However, since these issues have been discussed several times in the literature, we shall restrict our analysis again to the long-time evolution as given by the appropriate Markoffian rate equation.

The actual form of the transfer rates $F_{mn}$ as given in (4.12) is quite complex but we do not need to use them directly for calculations. Working in terms of $P^k(t)$, the important quantities are the $\mathfrak{A}^k$'s. Using the "broadened" versions of (4.14) and employing (3.6) leads to

$$P^k(t)=P^k(0)\exp\{-t\,[(\alpha^2+16J^2\sin^2\tfrac{1}{2}k)^{1/2}-\alpha]\}\,, \tag{5.16}$$

at long times. We point out at once that the usual (Förster-Dexter) rate equation

$$\frac{dP_m}{dt}=\frac{2J^2}{\alpha}(P_{m+1}+P_{m-1}-2P_m)\,, \tag{5.17}$$

leads, in place of (5.16), to

$$P^k(t)=P^k(0)\exp\{-t[(8J^2/\alpha)\sin^2\tfrac{1}{2}k]\}\,, \tag{5.18}$$

which is indeed the limit of (5.16) as $J/\alpha\to 0$. The relations

$$P_m(t)=\frac{1}{2\pi}\int_0^{2\pi}dk\,e^{-ikm}P^k(t)\,, \tag{5.19a}$$

$$P^k(t)=\sum_m P_m(t)e^{ikm}\,, \tag{5.19b}$$

and the result (5.16) allow the general solution to be written explicitly,

$$P_m(t)=\frac{1}{2\pi}\int_0^{2\pi} dk \sum_n P_n(0)\exp(-ikm) \times \exp\{-t[(\alpha^2+16J^2\sin^2\tfrac{1}{2}k)^{1/2}-\alpha]\}\,. \tag{5.20}$$

For initial localization on site 0,

$$P_m(t)=\frac{1}{2\pi}\int_0^{2\pi} dk \exp(-ikm) \times \exp\{-t[(\alpha^2+16J^2\sin^2\tfrac{1}{2}k)^{1/2}-\alpha]\}\,. \tag{5.21}$$

The explicit evolution of the probabilities is contained in (5.21) and its weak-coupling ($J/\alpha \to 0$) limit indeed yields the well-known result

$$P_m(t)=e^{-t(4J^2/\alpha)}I_m(t4J^2/\alpha)\,, \tag{5.22}$$

characteristic of (5.17). Here $I$ is the Bessel function of imaginary argument.

Another interesting prediction of the new rate equations occurs in the context of an experiment recently suggested by Fayer.[15] The idea is to create a spatially sinusoidal population of excitons:

$$P_m(0)=(1/N)(1+\text{const}\cos m\eta)\,, \tag{5.23}$$

where $2\pi a/\eta$ is the wavelength of the spatial variation of the exciton density and to monitor the decay of the spatial inhomogeneity in time, the observed signal being proportional to the square of the amplitude of the inhomogeneity. Our present theory may be immediately applied to this situation by using (5.19) and (5.16) and taking the limit $N\to\infty$ of (5.23).

$$P^k(t)=\delta_{k,0}+\tfrac{1}{2}\text{const}(\delta_{k,\eta}+\delta_{k,-\eta}) \times \exp\{-t[(\alpha^2+16J^2\sin^2\tfrac{1}{2}\eta)^{1/2}-\alpha]\}\,. \tag{5.24}$$

The rate of decay of the mode is directly given by the exponent in (5.24):

$$R=(\alpha^2+16J^2\sin^2\tfrac{1}{2}\eta)^{1/2}-\alpha\,, \tag{5.25}$$

and equals one half the decay rate of the signal because the latter is proportional to the square of the amplitude. This expression for the *mode decay rate* is quite interesting. It is completely different from the effective transfer rates defined in Ref. 14 or in (i) above, as it does *not* indicate directly the rate of site-to-site transfer. However it has limits similar to those of effective transfer rates. Thus, for $\eta=\pi$ it varies from $4J$ for small $\alpha/J$ (the "coherent" limit) to $4F$ for large $\alpha/J$ (the "incoherent" limit), where $F=2J^2/\alpha$. This dependence is displayed in Fig. 3. Notice the similarity to Fig. 1 of Ref. 14, although, as stated above, the rates plotted in the two figures are totally different from each other. The importance of $R$ in (5.25) stems from its being a directly observable quantity in contrast, for instance, to $w$.

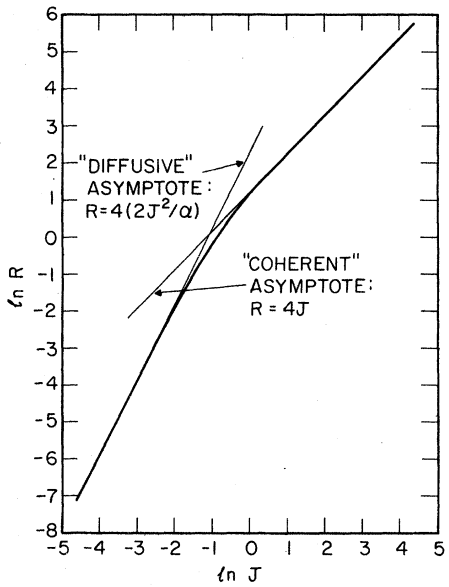


FIG. 3. Rate of decay of the signal in Fayer's transient grating experiment as given by the present theory under the assumption that the experimental time $(1/\tau)$ is larger that the coherence time $(1/\alpha)$: the coherent and diffusive asymptotes represent the $J>\alpha$ and the $\alpha>J$ situations, respectively; different points on the curve should be accessible through a variation in the temperature.

We emphasize in the light of these calculations that Fayer's proposed experiment, when carried out, could provide one of the most direct probes of exciton coherence available so far. Our present theory gives a simple prescription to assess the amount of coherence from the results of such an experiment. If the observations pertain to long times (long with respect to $1/\alpha$) the rate-equation result (5.25) is applicable. The observed decay rate will give $R$; the initial spatial variation of the exciton density (which can be measured directly),[15] will give $\eta$; and $J$ will be obtained from spectra or similar sources. Our equation (5.25) will then yield the value of $\alpha$. When compared to $J$, it will indicate the extent of coherence in the system which may be measured by the ratio $J/\alpha$. One might check the compatibility of such a derived value of $\alpha$ with values obtained[5] from optical spectra. Furthermore, useful information will be obtained by varying the temperature in the experiment. It should result not only in a variation of $\alpha$ but also of $J$ through the "polaron" or "dressing" effect.[4] This might provide an experimental test of the recent calculations of Yarkony and Silbey[28]

concerning the temperature variation of the effective intersite coupling.

The use of a Markoffian rate equation and of the particular result (5.25) are inapplicable, and the expectation of an exponentially decaying signal is incorrect, if the experiment possesses a characteristic time $\tau$ which is not much larger[29] than $1/\alpha$. In such cases the non-Markoffian equation with the memories (4.17) (but in the broadened form) is called for. We present here a result in the extreme coherent limit, i.e., if $1/\alpha$ is much larger than the experimental time. We are permitted then to neglect $\alpha$, use (4.17) in the unbroadened form and write instead of (5.24)

$$P^k(t) = \delta_{k,0} + \tfrac{1}{2}\,\mathrm{const}(\delta_{k,\eta} + \delta_{k,-\eta})\,J_0(4Jt\sin\tfrac{1}{2}\eta)\,. \tag{5.26}$$

Here we have used (4.14) in (3.6). Observe that (5.26) predicts a nonexponential decay of the signal in this extreme coherent limit. In fact the signal decays as the square of a zero-order $J$ Bessel function. Based on a different analysis, Fayer has earlier predicted[15] a signal decay in the coherent limit which is also nonexponential although it involves $I$ Bessel functions and is different from the square of (5.16). For the intermediate situation the present theory gives

$$\tilde{P}^k(\epsilon) = (\delta_{k,0}/\epsilon) + \tfrac{1}{2}\,\mathrm{const}(\delta_{k,\eta} + \delta_{k,-\eta}) \times \{[(\epsilon+\alpha)^2 + 16J^2\sin^2\tfrac{1}{2}\eta]^{1/2} - \alpha\}^{-1}\,. \tag{5.27}$$

The curly bracket in (5.27) describes the signal.

It is important to realize[29] that three different times are involved in the experiment: $\tau$, $1/J$, and $1/\alpha$. If $1/J \gg 1/\alpha$, a Markoffian rate equation may be used. Otherwise the generalized master equation must be used. In either case the Markoffian or non-Markoffian equation must have the long range rates or memories given by equations such as (4.17) if $J \ll \alpha$ is not satisfied.

## VI. CONCLUDING REMARKS

Much effort has been recently spent on attempts to understand the nature of exciton transport in molecular aggregates.[30] The questions asked concern mechanical issues such as whether the motion is wavelike or diffusive as well as the detailed mechanisms responsible for transport. On the experimental front, singlet motion has been studied through bulk and surface quenching experiments as well as through photoconductivity investigations and has been reviewed by Powell and Soos.[31] Triplet studies have been carried out on the basis of trap phosphorescence experiments by Fayer and Harris[32] and with the help of magnetic resonance techniques by Harris and Zewail.[33] Various other observations have also been reported.[34] On the theoretical side, in addition to the formalisms[3-7,10,14,24,25,28] discussed in Sec. I, there are the quenching studies of Hemenger *et al.*,[35] the analysis of magnetic resonance experiments by Davidovich and Knox,[36] the depolarization fluorescence theory of Rahman *et al.*,[37] and the studies of localization criteria by Aslangul and Kottis,[38] to name only a few. The fundamental questions asked in this active field are often similar to those asked in polaron transport.[39] To answer all these questions, whether they concern basics or detail, one requires a skeleton formalism describing the mechanics of the problem. The stochastic-Liouville equation and the generalized master equation mentioned in Sec. I provide two such basic skeletons capable of describing in a unified manner wavelike and diffusive motion. Both approaches have their advantages and disadvantages. The present paper makes a contribution primarily to the generalized master-equation formalism and secondarily to the stochastic-Liouville-equation approach; the former by extending it to large systems in the limit of strong intersite coupling (such as low-temperature crystals) and the latter by extending its master-equation part to cover the limit of strong phonon-assisted matrix elements.

The principal results of this paper are the memory expression (3.8), and its variants (3.11) and (3.13), and the rate expression (3.14). A resulting effective-rate expression is in (5.10). Other consequences are the generalized master equations (2.1), (2.2), (4.11), (4.14), and (4.17). Perhaps the most useful results are the ordinary (Markoffian) rate equations (2.5), (2.6), (4.7), and (4.12), the probability expressions (5.14) and (5.20), and the predicted experimental signals (5.24), (5.25), and (5.26). The last three provide a natural application of our theory as explained in Sec. V. Other applications to quenching situations which are related to the experiments in Ref. 32 and to the theory in Ref. 35 will be reported elsewhere.

In a modest manner this analysis perhaps answers[40] the question of what happens to a master equation when the Van Hove "$\lambda^2 t$ limit"[18] is not applicable as a result of large $\lambda$. In our context $\lambda$ is represented by $J$ and our answer is that the transition rates in the master equation are then given by new expressions such as (4.17) rather than the usual Fermi–golden-rule ones and that they develop spatially long-range character leading generally to faster transport. In a sense these expressions contain implicitly terms of higher orders than are present in the golden-rule expressions.

It might be of interest to remark here[23] that the phenomenological broadening introduced by replac-

ing $\epsilon$ by $\epsilon+\alpha$ in the Laplace transforms of memories or by multiplying the latter in the time domain by $e^{-\alpha t}$, is *exactly equivalent* to adding a decay term proportional to $-\alpha\rho_{mn}$ to the evolutions equations for all off-diagonal elements $\rho_{mn}$ of the density matrix:

$$\frac{\partial\rho_{mn}}{\partial t}=-i\sum_{s}(J_{ms}\rho_{sn}-J_{sn}\rho_{ms})-\alpha(1-\delta_{m,n})\rho_{mn}. \tag{6.1}$$

An explicit proof of this and related results has been given by the author elsewhere.[41] The significance of this result lies in the fact that (6.1) is nothing other than the "bare" or "undressed" equation that can be formally obtained *exactly* from the microscopic dynamics by projecting the exciton evolution out of an exciton-phonon or exciton-bath system *before using* a polaronlike transformation. This bare equation is also identical to the phenomenological equation introduced by Avakian *et al.*[42] and may also be obtained by omitting phonon-assisted terms from the Grover-Silbey or the Haken-Reineker-Strobl equation.

The transition from the generalized master equation (1.4) to the Markoffian master equation (1.2) that occurs for long times, requires comment in the case of the infinitely large system discussed in Sec. V. For that system there are two distinct ways of obtaining a Markoffian equation with sensible rates $F_{mn}$. One is the natural physical way of writing $F_{mn}$ as the integral of the "broadened" memories $\mathfrak{W}_{mn}(t)$ such as (3.14) which correspond to the transport equation (6.1). This way presumes that it is the bath interactions (symbolized by $\alpha$) that introduce irreversibility and make Markoffian equations (i.e., integrable $\mathfrak{W}$'s possible), and can be used for a finite as well as an infinite number of sites. Another way, applicable only to infinite systems, is based on the fact that the infinite size of the system (the thermodynamic limit) eliminates Poincaré cycles and makes the $\mathfrak{W}_{mn}$'s integrable without the addition of any bath interactions. Thus $F_{mn}$ may be given by integrating the pure memories (4.17) or equivalently taking the limit $\epsilon\to 0$ in (4.11). One then obtains instead of (4.12) and (5.20) the respective equations

$$F_{mn}=\frac{4J}{\pi}\sum_{m-n=1}^{\infty}[4(m-n)^2-1]^{-1}, \tag{6.2}$$

$$P_m(t)=\frac{1}{2\pi}\int_0^{2\pi}dk\sum_n P_n(0)e^{-ikm}e^{-t4J\sin(k/2)}. \tag{6.3}$$

We emphasize that this method of making the transition to the Markoffian rate equation is, in general, artificial as the usual source of irreversibility in the systems is bath interactions and not the size of the *exciton system*; this method would result in zero or infinite rates for a finite system as is evident by integrating equations such as (4.6). Note, however, that (6.2) and (6.3) represent approximations to (4.12) and (5.20) when $\alpha$ is small and lead in fact to (5.26) for the transient experiment[15] discussed in Sec. V.

One might wonder whether our theory supplies an answer to the question raised by Powell and Soos[31] regarding singlet motion in molecular crystals. This is, at the moment, no more than a speculation. The observation supporting the speculation is that transport faster than what is predicted by the conventional rate equations[2] of Förster and Dexter, which, in the opinion of the authors of Ref. 31 is necessary for explaining observed phenomena, is provided by our theory *without invoking* any change in the basic transport mechanism, i.e., in the interaction matrix elements $J_{mn}$.

It is obviously not necessary to use only spatially local matrix elements $J_{mn}$ as we have done in most of this paper. Expressions (3.3) for $J^k$ and (3.8) and its variations for $\mathfrak{W}_{mn}(t)$ do not require that the $J_{mn}$'s be local. Thus, for instance, if

$$J_{mn}=Je^{-\lambda|m-n|}, \tag{6.4}$$

one would still have (3.8) but (4.1b) would be replaced by

$$(\Lambda^{kq})^2=\lambda^2q^2(q+2k)^2(\lambda^2+k^2)^{-2}(\lambda^2+k^2+q^2+2kq)^{-2}. \tag{6.5}$$

In such cases the weak-coupling theory already predicts nonlocal rates because $J_{mn}$ is nonlocal. The present strong-coupling theory would predict additional long-range rates.

Our analysis was begun in Sec. I with the remark[9] that the older hybrid transport equations could lead to negative probabilities, where by the term "hybrid" we signify unified or combined equations such as (1.3) and (1.4). Needless to say, we have no guarantee that the new hybrid equations will never lead to negativities since a procedure to ensure positivity has still not been employed. The negativity remarks must be understood as expressing (particularly dramatically) objections to the approximation techniques used and *not* as the primary concern. Thus, the analysis presented in this paper is aimed not at removing negativity but at providing a better approximation to the actual motion of the exciton. In the latter it is indeed successful as should be clear from our discussion.

The modification that this development suggests in the stochastic-Liouville approach is the use of long-range rates in the second term on the right-hand side of (1.3). Whatever comments have been made concerning $F_{mn}$ and $\mathfrak{W}_{mn}(t)$ apply thus to $B_{mn}$

and $\mathfrak{G}_{mn}(t)$, respectively (see Ref. 8).

That the present theory would be applicable to the transport of other quasiparticles is obvious from the generality of the development. The field of small polaron transport[39] is particularly amenable to investigations within this framework.

We conclude this section by restating the main result of this paper: at sufficiently long times exciton transport in a crystal with nonzero bath interactions (i.e., in any real crystal) will be accurately described by a master equation such as (1.2); however, the rates in this master equation will be given by the familiar golden-rule expressions only if the intersite coupling $J$ is much smaller than the bath-interaction parameter $\alpha$. In situations where $J \ll \alpha$ does not apply, the rates, in general, have a long-range character and are given by (3.14). Master equations incorporating these rates, in contrast to those involving conventional golden-rule rates, are compatible with stochastic-Liouville equations such as (1.3) used earlier as in Refs. 3, 4, 9, and 35. At times shorter than those for which a master equation is valid (1.4) with (3.8) will describe the transport. The unification of coherent and incoherent motion through generalized master equations begun in Ref. 5 may thus be said to be completed through this explicit extension to large systems.[43]

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## APPENDIX

Very few exact evaluations of the Zwanzig memory kernel[16] exist in the literature. To show how general techniques for such computations may be developed, we exhibit here the direct derivation of (2.1) and (2.2) from

$$\frac{\partial \mathcal{P}\rho(t)}{\partial t} = -\int_0^t dt' \mathcal{P} L \exp[-i(t-t')(1-\mathcal{P})L] \times (1-\mathcal{P})L\mathcal{P}\rho(t'), \tag{A1}$$

which is the Zwanzig equation,[16] wherein $L$ is the Liouville operator denoting commutation with the Hamiltonian and $\mathcal{P}$ is the diagonalizing operator. For the open three-site "chain" of Sec. II

$$(LO)_{11} = J(O_{21} - O_{12}), \tag{A2}$$

$$(LO)_{22} = J[(O_{12} - O_{21}) + (O_{32} - O_{23})], \tag{A3}$$

$$(LO)_{13} = J(O_{23} - O_{12}), \tag{A4}$$

$$(LO)_{12} = J[(O_{22} - O_{11}) - O_{13}], \tag{A5}$$

and similar expressions for other corresponding elements. They yield

$$(1-\mathcal{P})LO = JO', \tag{A6}$$

$$[(1-\mathcal{P})L]^2 O = J^2(O + O''), \tag{A7}$$

$$[(1-\mathcal{P})L]^3 O = 2J^3 O' = 2J^2[(1-\mathcal{P})LO], \tag{A8}$$

where $O$ is any off-diagonal operator and the operators $O'$ and $O''$ are given in terms of the matrix elements of $O$ through

$$\begin{aligned} &-O'_{12} = O'_{23} = O_{13}; \quad -O'_{32} = O'_{21} = O_{31}, \\ &O'_{13} = O_{23} - O_{12}; \quad O'_{31} = O_{21} - O_{32}, \end{aligned} \tag{A9}$$

$$\begin{aligned} &-O''_{12} = O_{23}; \quad O''_{13} = O_{13}; \quad -O''_{21} = O_{32}, \\ &-O''_{23} = O_{12}; \quad O''_{31} = O_{31}; \quad -O''_{32} = O_{21}. \end{aligned} \tag{A10}$$

Equations (A6)–(A8) are the analog of Eq. (A2) of the first Ref. 5 and are immediately useful in obtaining

$$e^{-it(1-\mathcal{P})L} O = O\tfrac{1}{2}[1 + \cos(\sqrt{2}Jt)] - O'(i/\sqrt{2})\sin(\sqrt{2}Jt) - O''\tfrac{1}{2}[1 - \cos(\sqrt{2}Jt)] \tag{A11}$$

for any off-diagonal operator $O$. Taking $O$ to be $(1-\mathcal{P})L\mathcal{P}\rho$ so that $O_{mn} = P_n - P_m$, where $P$'s are the probabilities, it is shown in a straightforward way that $O'$ makes no contribution to (A1) and that (A1) gives (2.1) and (2.2).

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[8] The generalization consists in replacing "Markoffian" factors such as $B_{ms}$ in (1.3) by their "non-Markoffian

extensions", i.e., by convolutions such as $\int_0^t dt' \mathfrak{G}_{ms}(t-t')$. It is already implicit in the micropscopic developments such as Ref. 4.

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[17]Here and elsewhere $P_{1,3}$ means $P_1$ or $P_3$, respectively.

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[19]When $N$ is odd there is one $\Lambda$ which equals 0 and the others occur in pairs of equal and opposite number.

[20]By "narrow band " is meant the weak intersite coupling i.e., the small $J/\alpha$ situation.

[21]See, e.g., I. S. Gradshteyn and I. M. Ryzhik, *Table of Integrals, Series, and Products* (Academic, New York, 1965), p. 384.

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[23]As will be explained in Sec. VI, this apparently arbitrary introduction of damping is actually the result of a well-defined transport equation involving bath effects. See Eq. (6.1).

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[26]Equation (5.5) may be verified directly for the infinite crystal by using (4.21) and calculating from it $k$ derivatives of $J_0[4J\sin(\frac{1}{2}k)]$ or equivalently moments of $J_m^2(t)$.

[27]Note here that the fact that the slope of $P_3(t)$ at $t=0$ is zero for the curve corresponding to (5.15) but nonzero for the one corresponding to (5.14) does not have the same significance as a similar difference in curves appearing in Fig. 4 of Ref. 7(b) does. In the latter case the source of the zero slope is the underlying microscopic dynamics, whereas in the present case it is the absence of long-range rates in (5.15). Obviously, neither (5.14) nor (5.15) is to be used for an accurate description at short times for which the full Eqs. (5.11) and (5.12) must be used.

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[40]No claim is made here that this analysis clarifies the profound problems connected with the central problem of nonequilibrium statistical mechanics. In that context any progress made in this paper is essentially calculational.

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[43]An important element missing from our present analysis is a spectral prescription to extract the full rates and memories from absorption and emission experiments in a manner analogous to that given in Ref. 5. Such a prescription would be very useful from a practical standpoint and we hope that future work will make it available. Another direction which future work in this area should take is the study of the so-called initial-condition term in the generalized master equations. This term is zero for initial localized conditions. We have shown recently that it is also zero for fully delocalized initial conditions, i.e., whenever a single Bloch state of arbitrary wave vector is initially occupied. We have also obtained useable expressions for the initial-condition term which are similar to (3.8). These matters may be found in V. M. Kenkre, J. Stat. Phys. (to be published).