01 Feb 1988

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(Received 21 May 1987)

We report results of a theoretical investigation into the mutual annihilation of tight-binding excitons. The results are in apparent contradiction with intuitive expectations and provide corrections to expressions given by one of the present authors (V.M.K.) in an earlier analysis. A part of that analysis was based on a mapping of the dynamics of two mobile, mutually annihilating excitons onto the dynamics of a single exciton migrating in the presence of a fixed trap. We find that while this equivalence is valid for incoherent, randomly walking particles in an ordered system, it does not hold for an arbitrary degree of transport coherence. Any nonvanishing coherence makes a "moving trap," i.e., a second exciton, less effective than the corresponding stationary trap. For realistic intersite interactions, the quantum yield for annihilation passes through a maximum, i.e., the fluorescence yield passes through a minimum, as the exciton motion becomes less coherent. The earlier predictions are recovered in the incoherent limit.

I. INTRODUCTION

Luminescence observations of exciton annihilation have served as a probe of Frenkel exciton dynamics in molecular crystals and aggregates for a long time. In an earlier paper Kenkre[1] gave a comprehensive theory of the dynamics of the annihilation process with the help of a generalized-master-equation (GME) approach. One of the features of that theory was that, on the basis of the memory functions in the GME, it addressed an arbitrary degree of exciton-transport coherence and analyzed the effects that such coherence would have on annihilation observables such as the fluorescence quantum yield. We have discovered that, while the general development and most of the results of that theory are valid, one of the procedures used[1] in conjunction with those results, viz., the so-called chain rule, is valid only in the incoherent limit. The chain rule is thus useful only for systems with exciton lifetimes much larger than exciton scattering times. One of the two purposes of the present study is to point out the difficulties associated with that procedure and to provide prescriptions for correcting the corresponding expressions given in Ref. 1. The other purpose is to reinvestigate the effects of exciton coherence on the quantum yield in annihilation experiments without the use of the chain rule. Surprising results about the annihilation efficiency as a function of transport coherence are reported, along with suggested applications of the theory.

II. BREAKDOWN OF THE CHAIN RULE

The theory of Ref. 1 exploited the similarity between the problem of two particles moving on a lattice and undergoing mutual annihilation and that of a single particle moving on a higher-dimensional lattice and undergoing capture at a fixed trap.[2] An exact solution was presented for the two-particle problem on an ordered lattice and was used to obtain the following expression for the fluorescence yield in the presence of annihilation:

$$\Phi = 1 - \frac{\gamma^* \tau}{2N} \frac{1}{1+\gamma^* \tilde{\Psi}^0(1/\tau)} , \tag{1}$$

where τ is the radiative lifetime, γ^* is the rate at which annihilation proceeds for two particles located at the same site, N is the number of sites or chromophores in the system, and $\tilde{\Psi}^0(\epsilon)$ is the Laplace transform of a two-particle propagator $\Psi^0(t)$ giving the probability (in the absence of annihilation) for two particles to be found at the same site in the system at time t given that they were both at the origin at time $t=0$. Because of the independence of the particles in the absence of annihilation, one obtains

$$\Psi^0(t) = \sum_n \psi_{n[0]}(t)\psi_{n[0]}(t) , \tag{2}$$

where $\psi_{n[m]}(t)$ are the unperturbed *single-particle* propagators, assumed to obey an appropriate GME, each giving the probability for a single particle to be at site n at

time t if it was at site m at $t=0$. In a translationally invariant system these are functions only of the distance $m-n$, and hence often written with a single subscript, i.e., $\psi_{n[m]}=\psi_{m-n}$. Details of the derivation of (1) can be found in Ref. 1. It is important to realize that for the yield and many other observables, all information regarding exciton transport is contained in the propagator $\Psi^0(t)$. Equation (1) is indeed an exact consequence of the starting equations for arbitrary coherence.

For incoherent motion, the evaluation of the yield is facilitated by use of the so-called chain rule,[3] which expresses the evolution of one-particle probabilities through the relation

$$\psi_{n[0]}(t_1+t_2)=\sum_m \psi_{m[0]}(t_1)\psi_{n[m]}(t_2) . \tag{3}$$

Use of this relation with $t_1=t_2$ allows the evaluation of the propagator appearing in (1) as $\Psi^0(t)=\psi_{0[0]}(2t)$. Thus, through the use of the chain rule the two-particle propagator is expressed as a single-particle propagator moving at twice the rate. Indeed, as was pointed out in Ref. 1, when (2) and (3) are substituted into (1) the results are formally identical to those for a single particle moving in the presence of a fixed trap[2] of capture rate γ^*. This result is appealing from a physical point of view since it seems to agree with the intuitive idea of transforming to center-of-mass coordinates and thus working only with the separation distance of the particles (clearly the relevant variable for the annihilation problem). It was partially on the basis of this picture that an extension of the analysis to coherent transport was presented in Ref. 1. However, as we shall show below, the chain rule, Eq. (3), is strictly valid only when the memory functions which appear in the GME are proportional to δ functions, i.e., when the probabilities obey a (Markovian) Pauli master equation (PME). We find that, although the general results of Kenkre's theory, such as Eq. (1), as well as their consequences for *incoherent* motion are exact, that part of the analysis in Ref. 1 which addresses *highly coherent* motion must be viewed as an approximation whose validity must be determined.

That the probability propagators corresponding to solutions of a PME obey the chain rule is well known[3] and easily demonstrated. To show that the only solutions of the GME which obey the chain rule are those corresponding to δ-function kernels is slightly more complicated but still straightforward. Let $g_{m,n}(t)$ be the propagator solutions to a GME, which we may write in the general form

$$\dot{g}_{m,n}(t)=\int_0^t dt' \sum_{s,p} A_{m,s,n,p}(t-t')g_{s,p}(t') , \tag{4}$$

where, in the interest of generality, we have not assumed translational invariance, where $A_{m,s,n,p}(t)$ are memory functions, and where $g_{m,n}(0)=\delta_{m,n}$. Introducing matrix notation we may write the Laplace transform of a matrix G, whose (m,n)th element is $g_{m,n}$, in the form

$$\tilde{G}(\epsilon)=[\epsilon+\tilde{A}(\epsilon)]^{-1} , \tag{5}$$

where ϵ is the Laplace variable conjugate to time and the matrix $A(t)$ has elements $A_{m,s,n,p}(t)$ as in Eq. (4). Assume that the propagators $g_{m,n}(t)$ obey the chain rule, which in matrix notation may be expressed as

$$G(t)=G(t-t')G(t') . \tag{6}$$

Let us now ask: What form can the memory functions $A(t)$ have, subject to the chain-rule condition (6)? To find out, we integrate Eq. (6) over t' from 0 to t, obtaining

$$tG(t)=\int_0^t dt'G(t-t')G(t') , \tag{7}$$

and then Laplace transform over t to find the following differential equation in the Laplace variable ϵ:

$$\frac{d\tilde{G}(\epsilon)}{d\epsilon}=-\tilde{G}(\epsilon)^2 . \tag{8}$$

On the left-hand side we have used the fact that $\mathcal{L}[tf(t)]=-d\tilde{f}(\epsilon)/d\epsilon$, in which $\mathcal{L}[\cdots]$ denotes the Laplace transform of $[\cdots]$, and on the right-hand side the convolution theorem of Laplace-transform theory. Substituting from (5) into (8) yields a trivial differential equation for $\tilde{A}(\epsilon)$, viz., $d\tilde{A}(\epsilon)/d\epsilon=0$, or $\tilde{A}(\epsilon)=A_0$, independent of ϵ. Hence, $A(t)=A_0\delta(t)$, the GME (4) reduces to a PME, and the matrix $G(t)$ can be written in the form $G(t)=\exp(-A_0t)$.

The results of the preceding paragraph are rather general. They clearly indicate that the chain rule holds in the incoherent limit but breaks down for an arbitrary degree of transport coherence.

We conclude this section by exhibiting explicitly the breakdown of the chain rule for translationally invariant systems through an expression which also facilitates the computation of correction factors. The crux of the matter lies in (3), whose left-hand side (for $n=0$) can be written as

$$\psi_0(t_1+t_2)=(1/N)\sum_k \psi^k(t_1+t_2) , \tag{9}$$

where ψ^k denotes the discrete Fourier transform of the single-particle propagator and N is the number of sites in the lattice. The reciprocal-lattice vector k has the dimensions of the lattice. The right-hand side of (3), on the other hand, can be written as

$$\sum_m \psi_m(t_1)\psi_m(t_2)=(1/N)^2\sum_{k,q,m}\psi^k(t_1)\psi^q(t_2)e^{-i(k+q)m} , \tag{10}$$

where $(k+q)m$ represents a dot product of the (dimensionless) direct-lattice vector m and the (dimensionless) reciprocal-lattice vector $k+q$. In (10) we have written $\psi_{-m}=\psi_m$ as a consequence of translational invariance. A simplification of (10) leads to

$$\sum_m \psi_m(t_1)\psi_m(t_2)=(1/N)\sum_k \psi^k(t_1)\psi^{-k}(t_2) . \tag{11}$$

We will call the difference between the left- and the right-hand sides of (3) the correction Δ. By using (9) and (11) in (3), along with the inversion symmetry im-

plied by $\psi^k=\psi^{-k}$, we obtain the explicit correction prescription

$$\Delta\equiv(1/N)\sum_k \Delta_k \ , \tag{12a}$$

$$\Delta_k=\psi^k(t_1+t_2)-\psi^k(t_1)\psi^k(t_2) \ . \tag{12b}$$

It is trivial to show[4] that, for incoherent motion, $\psi^k(t)$ is always an exponential: Δ_k in (12b) is thus always zero and the chain rule holds. It is also straightforward to see from (12b) explicitly how the chain rule breaks down for coherent motion, for instance, on a one-dimensional infinite chain with nearest-neighbor transfer interactions J. For such a system, $\psi^k(t)$ is given by $J_0(4Jt\sin(k/2))$,where J_0 is the usual Bessel function and the departure from the results of the chain rule are the direct consequence of the difference in the values of $J_0(x_1)J_0(x_2)$ from $J_0(x_1+x_2)$. Coincidentally, this difference has been examined graphically, and in detail, by Fort, Ern, and Kenkre[5] in their analysis of Ronchi ruling signals in two- and three-dimensional systems. From that discussion we can conclude here that the chain rule will be accurate to a reasonable degree for small enough values of t. More precisely, the argument of the Bessel function must be smaller than, or of the order of, its first zero. Since the radiative lifetime τ serves as a natural cutoff on the time t, in the calculation of annihilation observables such as the yield for purely coherent motion, the chain-rule results will break down when the radiative lifetime of the excitons is of the order of, or larger than, the motion time, i.e., for $J\tau>1$. An explicit demonstration of this result follows from a comparison of the quantity

$$\int_0^\infty dt[\exp(-2t/\tau)]J_0^2(bt)$$

to the quantity

$$\int_0^\infty dt[\exp(-t/\tau)]J_0(2bt) \ ,$$

with $b=4J\sin(k/2)$. The difference between these quantities is $\int dt\,\Delta_k(t)$ in the presence of radiative decay. The two quantities have been calculated earlier[4] and are in the ratio

$$(2/\pi)K(2b\tau/(1+4b^2\tau^2)^{1/2}) \ ,$$

where K is the complete elliptic integral of the first kind. Since for $b\tau\to 0$, K equals $\pi/2$, the chain-rule results are acceptable for slow motion; however, since K diverges logarithmically for $b\tau\to\infty$, severe departures from the chain-rule approximation can occur for motion which is fast enough with respect to radiative decay.

III. EFFECTS OF EXCITON COHERENCE ON THE QUANTUM YIELD

We now return to the problem of analyzing the effects of coherence on the annihilation observables. We emphasize that the expression (1) for the fluorescence yield remains valid for any GME, as long as the two-particle propagator $\Psi^0(t)$ and its Laplace transform are correctly evaluated. It is obvious from Sec. II that for coherent or partially coherent motion that task is complicated by the lack of a rule such as (3).

A. Evaluation of two-particle propagators

It is known that $\phi^k(t)$, the coherent one-exciton propagator for an N-site translationally symmetric system with an energy dispersion relationship $E(k)$, where k is the wave vector, is given by[6]

$$\phi^k(t)=\mathcal{L}^{-1}[\tilde{\phi}^k(\epsilon)]$$
$$=\mathcal{L}^{-1}\left\{\sum_{k'}\left[\frac{1}{N}\left[\epsilon+\frac{i}{h}[E(k-k')-E(k')]\right]^{-1}\right]\right\} , \tag{13}$$

where $\mathcal{L}^{-1}$ is the inverse Laplace transform. $\phi^k(t)$ is related to $\phi_l(t)$ by the usual discrete Fourier transform

$$\phi_l(t)=\frac{1}{N}\sum_k e^{-ikl}\phi^k(t) \ . \tag{14}$$

There is a well-known prescription[7,4] for constructing the Laplace transform of $\psi^k(t)$ for an arbitrary coherence parameter if the corresponding coherent propagator $\phi^k(t)$ is known. This prescription is

$$\tilde{\psi}^k(\epsilon)=\tilde{\phi}^k(\epsilon+\alpha)/[1-\tilde{\phi}^k(\epsilon+\alpha)] \ . \tag{15}$$

Equations (2) and (13)–(15) can be used to construct the two-particle propagators for specific systems. Examples are given in the following for systems in compact- and ring-interaction geometries. Here, "compact" refers to a case in which there are equal interactions among all the sites of an N-site system. By "ring" we mean equal nearest-neighbor interactions of an N-site translationally symmetric system of coordination number 2 and with periodic boundary conditions.

1. Dimer

As a meeting place for ring- and compact-interaction geometries, the simplest system, the dimer, is discussed first. Since we consider small "compact" systems in Sec. III A 2 in detail, in order not to repeat ourselves we simply refer to Eqs. (17) and (18). From these two equations, the correct and chain-rule approximation dimer ($N=2$) propagators are, respectively,

$$\tilde{\Psi}^0(\epsilon)=\tfrac{1}{2}\left[\frac{1}{\epsilon}+\frac{\epsilon^2+3\alpha\epsilon+2\alpha^2+8J^2}{(\epsilon+\alpha)(\epsilon^2+2\epsilon\alpha+16J^2)}\right] \tag{16a}$$

and

$$\tilde{\Psi}^0(\epsilon)=\tfrac{1}{2}\tilde{\psi}^0(\epsilon/2)=\tfrac{1}{2}\left[\frac{1}{\epsilon}+\frac{\epsilon+2\alpha}{\epsilon^2+2\alpha\epsilon+16J^2}\right] , \tag{16b}$$

where J is the intersite interaction in units such that $\hbar=1$.

The difference between (16a) and (16b) is

$$\tilde{\Delta}(\epsilon)=4J^2/[(\epsilon+\alpha)(\epsilon^2+2\alpha\epsilon+16J^2)] \ . \tag{16c}$$

Under the chain-rule assumption, the dimer two-particle propagator always decreases [Eq. (16b)] and

$\tilde{\Delta}(\epsilon)$ always increases as the motion becomes more coherent ($\alpha \to 0$). On the other hand, the correct propagator [Eq. (16a)] always has a minimum at $\alpha/J = 2-(1/J)\tau$; that is, as long as $J\tau > 1/2$. In other words, there is a minimum when the scattering equals the bandwidth ($\alpha = 2J$) if $\tau \to \infty$. The plots for the quantities given in Eqs. (16a)–(16c) are given in Fig. 1.

2. *Small systems in compact interaction geometry*

Although compact-interaction geometry cannot represent large systems realistically since the intersite interaction does not die down with distance, it is a reasonable model for systems consisting of only a few chromophores. Using the dispersion relation $E(k) = J(N\delta_{k,0} - 1)$ in Eq. (13), one finds

$$\tilde{\phi}^{0}(\epsilon) = 1/\epsilon$$

and (17)

$$\tilde{\phi}^{k\neq 0}(\epsilon) = \tilde{\phi}(\epsilon) = \frac{N-2}{N\epsilon} + \frac{1}{N}\frac{2\epsilon}{\epsilon^2 + (NJ)^2} .$$

From Eqs. (17) and (15), one obtains

$$\psi^{0}(t) = 1 \tag{18a}$$

and

$$\psi^{k\neq 0}(t) = \psi(t)$$

$$= \mathcal{L}^{-1}\left[\frac{(\epsilon+\alpha)^2 + V^2}{(\epsilon+\alpha)^3 - \alpha(\epsilon+\alpha)^2 + (V')^2(\epsilon+\alpha) - \alpha V^2}\right], \tag{18b}$$

where $V^2 = N(N-2)J^2$ and $(V')^2 = N^2J^2$.

An explicit expression for $\tilde{\Psi}^{0}(\epsilon)$ is found by using the fact that $\tilde{\phi}^{k}(\epsilon)$ is independent of k [see Eq. (17)],

$$\tilde{\Psi}^{0}(\epsilon) = \frac{1}{N}\left[\frac{1}{\epsilon} + (N-1)\mathcal{L}\,|\,\psi(t)\,|^2\right], \tag{19}$$

where $\psi(t)$ is given by Eq. (18b). Performing the Laplace inversion of equation (18b), we have

$$\psi(t) = \sum_{i=1}^{3} C_i e^{-r_i t},$$

where

$$C_i = \frac{r_i^2 - 2\alpha r_i + \alpha^2 + V^2}{(r_i - r_j)(r_i - r_k)} \quad (i,j,k = 1,2,3)$$

and $r_i = \alpha - z_i$. The z_i's are the roots of the cubic equation in the denominator of Eq. (18b). The fluorescence yield is evaluated using Eq. (19) in Eq. (1). The results for several small systems are shown in Fig. 2. It is interesting to note that no minimum occurs if α is held constant and J is varied. However, this has less physical applicability, since it really is the scattering rate that is likely to change with temperature and thus decide the degree of coherence in transport.

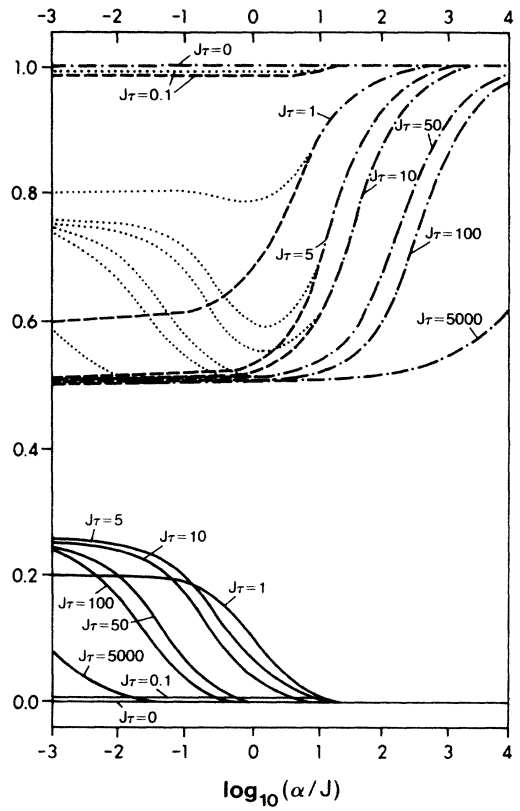

FIG. 1. The dimeric two-particle propagator [Eq. (16a)] (· · · ·), the chain-rule approximation two-particle propagator [Eq. 16(b)] (— — —), and the correction [Eq. 16(c)] (——) as a function of the coherence parameter (α/J) for a wide variety of intersite interaction strengths ($J\tau$) ranging from 0 to 5×10^3 ($J \sim 3.5$ meV if $\tau = 1$ ns). Where the two propagators overlap, the curves are combined (—·—·—·).

3. *Infinitely large systems of ring-interaction geometry*

The evaluation of the fluorescence yield Φ from Eq. (1) is straightforward also for systems possessing ring-interaction geometry, i.e., $E(k) = 2J\cos k$. As a practical example we consider the infinite linear chain with nearest-neighbor interactions J, as in the discussion at the end of Sec. II, as a useful approximation to molecular crystals. We shall show here some of the explicit expressions for the two-particle propagator $\Psi^{0}(t)$, particularly in the presence of arbitrary degree of coherence.

Equations (2) and (11) and the explicit expression[9,10] for the single-particle propagator for the infinite linear chain allow us to write the two-particle propagator as

$$\Psi^{0}(t) = (1/2\pi)\int dk\, e^{-2\alpha t}\left[J_0(b_k t) + \int_0^t du\, \alpha e^{\alpha u} J_0[b_k(t^2-u^2)^{1/2}]\right]^2, \tag{20}$$

where $b_k = 4J \mid \sin(k/2) \mid$. Here and below, the k integration is over the first Brillouin zone. The use of the chain rule would have led us to write the expression

$$e^{-2\alpha t} J_0(2b_k t) + \int_0^t du\, \alpha e^{2\alpha u} J_0[2b_k (t^2 - u^2)^{1/2}]$$

as the integrand on the right-hand side of (20).

For highly coherent motion, the u integral may be neglected in comparison to the other term in large parentheses, with the result that

$$\Psi^0(t) = (1/2\pi) \int dk\, e^{-2\alpha t} J_0^2(b_k t) \ . \tag{21}$$

This time-domain expression leads to the following result for the Laplace transform $\tilde{\Psi}^0(2/\tau) \equiv \int dt\, e^{-2t/\tau} \Psi^0(t)$:

$$\tilde{\Psi}^0(2/\tau) = (1/2\pi) \int dk (2/b_k \tau_1) x_k K(x_k) \quad \text{(exact)} \ , \tag{22}$$

where $1/\tau_1 = \alpha +$ and x_k is given by

$$2b_k \tau_1 (1 + 4b_k^2 \tau_1^2)^{-1/2} \ .$$

By contrast, the use of the chain rule would have given us

$$\Psi^0(t) = (1/2\pi) \int dk\, e^{-2\alpha t} J_0(2b_k t) \tag{23}$$

instead of (21) and, since the two integrals can be evaluated exactly in this case,

$$\tilde{\Psi}^0(2/\tau) = (1/J\tau_1) x K(x) \quad \text{(chain rule)} \ , \tag{24}$$

where $x = 4J\tau_1 (1 + 16J^2 \tau_1^2)^{-1/2}$.

It is interesting to compare (22) and (24). The exact expression, i.e., (22), involves an integral over the Brillouin zone of the chain-rule expression, i.e., (24), with the replacement of J by $2J \mid \sin(k/2) \mid$. The chain-rule expression *is* the value of the integrand of the exact expression at $k = \pi/3$. The Laplace transform of the two-particle propagator,

$$\tilde{\Psi}^0(2/\tau) \equiv \int_0^\infty dt\, e^{-2t/\tau} \Psi^0(t) \ ,$$

can thus be written as the product of two factors. The first factor is $(1 + \alpha\tau)^{-1}$ and decreases as α is increased from 0, i.e., from the purely coherent limit. The second factor is the Laplace transform of the *purely coherent* two-particle propagator but with the replacement of $1/\tau$ by $1/\tau + \alpha$. The exact and chain-rule expressions for this factor both imply an increase of this second factor as α is increased from 0. Whenever there is a minimum in $\tilde{\Psi}^0(2/\tau)$, this increase must be slower than the decrease of the first factor in the exact expression and, therefore, produce a minimum. It would be interesting to learn whether this is a general property of the exact result. Such behavior is absent in the chain-rule expression.

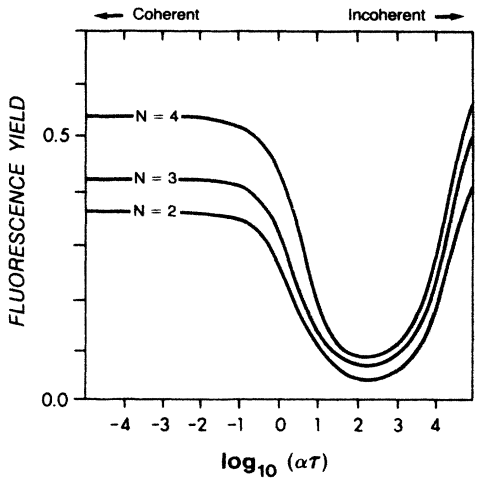

FIG. 2. Fluorescence yield Φ [Eq. (1)] of several small compact-interaction geometry complexes vs degree of coherence ($\alpha\tau$) at a fixed value of the annihilation (γ^*) and the motion (J) rates. Here, $J\tau = \gamma^* = 10^2$, which corresponds to $J \sim 0.1$ meV if $\tau = 1$ ns. $\gamma^* = 10^{11}$ s^{-1} is a reasonable value of the pairwise rate of annihilation for some systems, as discussed in Ref. 8.

B. Results

The results given in Figs. 1 and 2 show clearly that the dynamics of two mutually annihilating excitons can be correlated with trapping predictions[2] only for the range of α values exceeding a critical value, α_c, which corresponds to the regime in which the scattering rate is greater than the bandwidth. For values smaller than α_c, a totally opposite character is exhibited. Below we will refer to the nature of dynamics as "bi-excitonic" and "single excitonic," respectively, for $\alpha < \alpha_c$ and $\alpha > \alpha_c$.

Note again that the fluorescence yield is proportional to the two-particle propagator, $\tilde{\Psi}^0(\epsilon)$, which contains all information regarding coherence and other transport properties. $1/\tilde{\Psi}^0(\epsilon)$ is proportional to the probability of finding two excitons on the same site at any time given that they were both at the origin at $t = 0$. For every nonzero value of J and any value of α, the correct probability is always lower than the one obtained under the validity of the chain-rule assumption (see Figs. 1 and 2). We can therefore say that a moving trap is less effective than the corresponding stationary trap and its ineffectiveness increases with increasing coherence.

The competition between the two effects associated with the opposite α dependences of $\tilde{\psi}^0(\epsilon/2)$ and $\tilde{\Delta}(\epsilon)$ gives rise to single- and bi-excitonic dynamics, although both effects coexist for any degree of coherence. In the bi-excitonic regime, $\tilde{\Delta}$ increases more quickly than $\frac{1}{2}\tilde{\psi}^0(\epsilon/2)$ decreases with decreasing α as shown in Fig. 1. Therefore, the probability of the two excitons being on the same site decreases as α increases; i.e., the fluorescence yield increases with increasing degree of coherence. In the single-excitonic regime, $\tilde{\Delta}$ decreases and quickly approaches zero while $\frac{1}{2}\tilde{\psi}^0(\epsilon/2)$ increases more rapidly with increasing degree of incoherence, as shown in Fig. 1. Therefore, the probability that the excitons visit the same site decreases as α increases, i.e., the yield increases with increasing degree of coherence.

For a critical value of interaction (e.g., $J\tau < \frac{1}{2}$ for a dimer), the overall nature of the dynamics always looks single excitonic since the increase in $\tilde{\Delta}(\epsilon)$ never overcomes the decrease in $\frac{1}{2}\tilde{\psi}^0(\epsilon/2)$. Although we have not explicitly shown $\tilde{\Delta}(\epsilon)$ for $N>2$, it can be concluded from a comparison of Figs. 1 and 2 and by considering the results of Ref. 2 and the discussion of Sec. III A 3 that the same behavior is implied for any other size.

Incidentally, a breakdown of the chain rule also occurs for the configurationally averaged propagators of a disordered system—even in the limit of incoherent transport—because such propagators are known to obey a non-Markovian GME. This observation allows one to understand in a simple way the results of a recent continuous time–random-walk study of one- and two-particle kinetics in disordered systems.[11] (For any fixed realization of incoherent transport on an ordered or disordered lattice, however, the chain rule is, of course, valid.)

IV. APPLICATIONS AND CONCLUSION

Applications of a direct method of extracting the degree of coherence from optical spectra[12] indicate coherence to be lost within 10 fs to 50 ps for several systems at room temperature. A first clear demonstration of coherence in singlet-exciton motion has recently been available through a careful interpretation[13] of pure transport observations on anthracene crystals[14] where the transport is shown to be quite coherent at low temperatures (up to 280 intersite distances at 1.8 K and 20 intersite distances at 20 K).

In essence, our prediction here can also be used to assess the degree of coherence in singlet-exciton motion. For this purpose, a series of quantum yield measurements from complexes subjected to high excitation intensities would be necessary. At low temperatures where substantially coherent motion can be expected, one may be able to detect a drop in the yield by increasing the temperature. Conversely, starting from the high-temperature side where incoherent exciton motion is expected, first an enhancement and then a decrease of quenching by decreasing the temperature may be detected. Good independent estimates of the several parameters (such as γ^*, J and τ) may even lead to a quantitative deduction of coherence times. It has been pointed out earlier[15] that, in annihilation experiments, a certain competition exists between γ^* and a quantity[16] $M=[\int_0^\infty e^{-t/\tau}\Psi^0(t)dt]^{-1}$ called the "motion rate." Measurements of the overall rate constant $\gamma=[(1/\gamma^*)+(1/M)]^{-1}$ may not always be helpful to reveal the transport characteristics, since for the cases where $M \gg \gamma^*$ the behavior of γ will essentially be independent of the motion characteristics buried in the propagator $\Psi^0(t)$. The temperature independence of γ in naphthalene and anthracene have been interpreted along this line.[15] We would like to point out that the fact of γ being independent of temperature changes in anthracene may be attributed in part to a very strong intersite interaction [$J\tau=10^5$ (Ref. 13)]. Our numerical experiments point out that no matter how effective the pairwise annihilation is, if the interaction is very strong (e.g., $J\tau=5\times10^3$ of Fig. 1) there is a flat region of the propagator (or the yield) persisting for almost five decades of incoherence parameter (α/J).

In the past, there have been reports on the decreasing rates of annihilation (γ) with increasing temperature (T).[17,18] These usually have been correlated with the $T^{-1/2}$ dependence of the diffusion constant (D) of coherent excitons[19] through a commonly used linear relationship between D and γ.[20] The inconsistency of using $\gamma \propto D$ in this fashion has been indicated earlier.[4,15] In addition, our prediction of the difference of one- and two-exciton dynamics shows that, even in a system in which annihilation is motion limited (so that $\gamma \propto D$) and the diffusion constant is limited by scattering with acoustic phonons ($D \propto T^{-1/2}$), the dependence of the annihilation constant on temperature could be substantially different. From the time dependence of benzophenone triplet-exciton phosphorescence, Delyukov, Klimusheva, and Turchin[21] infer a decrease of annihilation efficiency with a decrease in temperature (15–4.2 K). This is consistent with our results for small values of α as displayed in Figs. 1 and 2. Delyukov, Klimusheva, and Turchin believe that a physical interaction is effecting a lower diffusion constant at lower temperatures. Thus, while both their explanation and ours involve two-exciton effects, the mechanisms are quite different and a diffusion experiment may resolve the issue.

In summary, the central result of this paper is a predicted reduction in the efficiency of annihilation or a hindering of exciton motion arising from coherence in the two-particle transport. The results are both surprising and interesting because they are contrary to what one would expect in the coherent limit on the basis of the chain rule. One can see from the form of Eq. (3) that the chain-rule assumption is tantamount to assuming that the exciton density matrix is diagonal at arbitrary times, rather than only at $t=0$, as is required for a derivation of the GME from the Liouville–von Neumann equations of motion for the density matrix (see Ref. 4 for details). The chain rule is quite unrelated, therefore, to the intuitive picture we mentioned earlier regarding a transformation to center of mass and relative coordinates. An analysis based on such a transformation, which would express the two-particle propagator $\Psi^0(t)$ in terms of *some* single-particle propagator describing just the relative motion of the two particles, would provide, we believe, a complete conceptual understanding of the problem.

ACKNOWLEDGMENTS

Two of us (D.G. and R.S.K.) acknowledge the support of the National Science Foundation (NSF) under Grant No. PCM-83-03004, and V.M.K. acknowledges NSF support under Grant No. DMR-85-06438. A preliminary report of this work has appeared [D. Gülen, Bull. Am. Phys. Soc. 31, 549 (1986)]. It is based in part on a thesis submitted in partial fulfillment of the requirements for the Ph.D. in physics (D.G.).

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