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Theory of exciton annihilation in molecular crystals

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A theory of the kinematics of quasiparticle annihilation in lattices is developed on the basis of an exact calculation. Details relevant to its application to the annihilation of Frenkel excitons in molecular crystals are presented. Explicit expressions for observables such as the quantum yield and the time-dependent fluorescence intensity are obtained for one-, two-, and three-dimensional crystals. The range of validity of earlier theories is examined in the light of the exact solutions, and the limit of fast transport as well as that of fast annihilation is obtained. The effect of transport coherence is studied, and it is indicated how one might measure exciton coherence from the observables.

I. INTRODUCTION

This paper contains an analysis based on an exact calculation of the motion of particles on lattices accompanied by annihilation. As such, it is of general interest and should be applicable to a number of diverse phenomena. The physical system which motivated the present analysis and towards which some of the results are slanted is a collection of Frenkel excitons in molecular crystals. The annihilation of excitons in crystals such as anthracene has been studied for at least twenty years. Recent reviews are by Avakian and Merrifield and by Geacintov and Swenberg.[1] The best known theoretical description of the kinematics of of annihilating excitons is due to Suna.[2] Many experimental observations[3] have been made, some of which are time dependent and some of a steady-state nature. Others involve effects of the application of a magnetic field. The basic procedure consists in creating the excitons through optical absorption, observing the luminescence, and deducing aspects of the annihilation process from the observed light intensity and the quantum yield.

Most interpretations of the experimental observations have been based on the assumption that the exciton density is depleted through annihilation at a rate proportional to the square of the local density at that site, the constant of proportionality being termed the annihilation rate γ. Empirical values of γ have been deduced and presented for various systems.

One of the questions to be asked by a basic theory of annihilation is whether the above assumption is at all valid and what the range of validity is for a time-independent γ. Our present analysis contains an answer to this question. It also examines the effect of dimensionality of the lattice, the effect of coherence in exciton motion, and the effect of long-range annihilation. The observables computed in terms of the theory are the time-dependent emission light intensity and the quantum yield. In Sec. II we state the model and illustrate the technique by obtaining exact solutions for a one-dimensional lattice. In Sec. III we extend the results to two- and three-dimensional lattices. In Sec. IV we study the effect of nonlocal annihilation, in Sec. V we obtain Boltzmann-type equations and examine the validity and meaning of γ, and in Sec. VI we explore the effects of coherence (i.e., of wavelike or quantum-mechanical motion). A discussion and summary are given in Sec. VII.

II. TECHNIQUE OF SOLUTION AND ONE-DIMENSIONAL MODEL

We analyze a system of particles moving on a discrete lattice and being annihilated when they are close to one another. Throughout this paper we shall consider a system of two particles only but we shall analyze successively more complicated models. We begin with the simplest one consisting of two particles moving on a one-dimensional lattice of sites m, n, etc., through nearest-neighbor transfer rates F so that if the particles were not to interact, their occupation probabilities $P_m(t)$ would satisfy

$$\frac{dP_m}{dt}=F(P_{m+1}+P_{m-1}-2P_m)\,. \tag{2.1}$$

However, they do interact and indeed annihilate each other on contact. We describe this occurence by a depletion of their probability at rate B whenever they occupy the same site. The equation obeyed by $P_{m,n}(t)$, the probability that the first particle is at m and the second at n, is therefore

$$\frac{dP_{m,n}}{dt}=F(P_{m+1,n}+P_{m-1,n}+P_{m,n+1}+P_{m,n-1}-4P_{m,n})-\delta_{m,n}BP_{m,m}\,. \tag{2.2}$$

We shall solve this equation exactly by employing the Montroll defect technique.[4] It is straightforward to show that if the solution of (2.2) with

$B=0$ and $P_{m,n}(0)=\delta_{m,0}\delta_{n,0}$ is $\psi_{m,n}(t)$, the solution of (2.2) for arbitrary B and $P_{m,n}(0)$ is

$$\tilde{P}_{m,n}(\epsilon)=\sum_{r,s}\tilde{\psi}_{m-r,n-s}(\epsilon)P_{r,s}(0)-B\sum_{r,s}\delta_{r,s}\tilde{P}_{r,r}(\epsilon)\tilde{\psi}_{m-r,n-s}(\epsilon)\,. \qquad (2.3)$$

Here tildes denote Laplace transforms and ϵ is the Laplace variable. The first term on the right side of (2.3) is the solution of the problem without interparticle interactions and henceforth will be called $\tilde{\eta}_{m,n}(\epsilon)$. The second term is the result of the interaction but involves $\tilde{P}_{rr}(\epsilon)$ thus making the "solution" (2.3) useless from a practical point of view. The defect technique[4] however results in an exact solution of (2.3). We rewrite (2.3) as

$$\tilde{P}_{m,n}(\epsilon)=\tilde{\eta}_{m,n}(\epsilon)-B\sum_{r}\tilde{\psi}_{m-r,n-r}(\epsilon)\tilde{P}_{r,r}(\epsilon)\,. \quad (2.4)$$

Multiplying the case $m=n$ of (2.4) by e^{ikm}, summing over m, and calling

$$\sum_{m}\tilde{P}_{m,m}e^{ikm}=\tilde{P}^{k}\,, \qquad (2.5)$$

etc., we get

$$\tilde{P}^{k}(\epsilon)=\tilde{\eta}^{k}(\epsilon)/[1+B\tilde{\psi}^{k}(\epsilon)]\,. \qquad (2.6)$$

The right-hand side of (2.6) is known in principle in terms of the homogeneous solutions ψ and the initial conditions. Therefore, the inverse discrete Fourier transform of (2.6), when substituted in (2.4), provides the complete *practical* solution of (2.4).

The Montroll defect technique[4] which thus gives an *explicit* solution of (2.4) works when the "defect region" represented by the B terms is small. In this case that region is the line $m=n$ in the two-dimensional m,n space. The Fourier transform (2.5) may be said to convert the plane into a line and the defect line into a defect point, thus making the exact solution possible.

While the exact solution may thus be obtained for all $P_{m,n}$'s for arbitrary initial conditions, we shall be interested here only in the quantity

$$Q(t)=\sum_{m,n}P_{m,n}(t) \qquad (2.7)$$

for experimental reasons discussed in Sec. I. The Laplace transform of (2.7) is obtained from (2.4) and (2.6) as

$$\tilde{Q}(\epsilon)=\frac{1}{\epsilon}\left[1-B\left(\frac{\tilde{\eta}^{0}(\epsilon)}{1+B\tilde{\psi}^{0}(\epsilon)}\right)\right]. \qquad (2.8)$$

We have used the results that

$$\sum_{r,s}P_{r,s}(0)=1\,, \qquad (2.9)$$

$$\sum_{m,n}\psi_{m-r,n-s}(t)=1\,. \qquad (2.10)$$

The first of these is obvious. The second represents the fact that in the absence of B whatever sites they occupy initially the particles are at some place or the other in the lattice at any time t. We can rewrite (2.8) in the time domain in the suggestive form

$$\frac{dQ(t)}{dt}=-Bh(t)\,, \qquad (2.11)$$

$$\tilde{h}(\epsilon)=\tilde{\eta}^{0}(\epsilon)[1+B\tilde{\psi}^{0}(\epsilon)]^{-1}\,. \qquad (2.12)$$

The evaluation of $h(t)$ or of $Q(t)$ involves specifying the initial conditions. It is straightforward to carry through the analysis for any initial conditions. We shall however consider only the completely delocalized one,

$$P_{r,s}(0)=1/N^{2}\,, \qquad (2.13)$$

with N as the number of sites in the lattice, and the completely localized one

$$P_{r,s}(0)=\delta_{r,0}\delta_{s,l}\,. \qquad (2.14)$$

The former corresponds reasonably well to the experimental situation in the exciton problem. The latter represents the particles being placed a distance of l lattice sites apart (anywhere in the lattice) and can be made to give any $P_{r,s}(0)$ through the principle of superposition.

Equation (2.13) leads to

$$\eta^{0}(t)=1/N\,, \qquad (2.15)$$

whereas Eq. (2.14) gives

$$\eta^{0}(t)=\sum_{m}\psi_{m,m+l}(t)\,. \qquad (2.16)$$

These when Laplace transformed and substituted in (2.8) or (2.12) yield Q and h. Note that the right side of (2.16) is the primary quantity to be computed since its value at $l=0$ gives $\psi^{0}(t)$.

Equations (2.3) through (2.12) are valid for any transfer rates F_{mn} provided only that translational invariance applies on the lattice. We shall now evaluate h and Q for the specific nearest-neighbor F_{mn}'s of (2.2). We have for the propagator

$$\psi_{m,n}(t)=e^{-4Ft}I_{m}(2Ft)I_{n}(2Ft)\,, \qquad (2.17)$$

where I's are modified Bessel functions. This well-known result[5] may be established by Fourier transforming (2.2) with $B=0$ and using the integral representation of Bessel functions. This leads to the useful result

$$\sum_{m}\psi_{m,m+l}(t)=e^{-4Ft}I_{l}(4Ft)\,. \qquad (2.18)$$

We establish (2.18) through a simple manipulation of summation formulas[6] involving products of Bessel functions. A corollary of (2.18) is

$$\tilde{\psi}^0(\epsilon) = (\epsilon^2 + 8F\epsilon)^{-1/2} . \tag{2.19}$$

The key quantity $\tilde{Q}(\epsilon)$ is now obtained. For the delocalized initial condition (2.17) it is

$$\tilde{Q}(\epsilon) = \frac{1}{\epsilon}\left(1 - \frac{1}{N\epsilon}\,\frac{B}{1 + B/(\epsilon^2 + 8F\epsilon)^{1/2}}\right). \tag{2.20}$$

This expression is of experimental interest for excitons as it gives both the monitored intensity of light on Laplace transformation and the quantum yield on the substitution $\epsilon = 2/\tau$. For the localized initial condition (2.14) we have

$$\tilde{Q}(\epsilon) = \frac{1}{\epsilon}\left(1 - B\,\frac{\{(\epsilon/4F) + 1 - [(\epsilon/4F)^2 + (\epsilon/2F)]^{1/2}\}^l}{[(\epsilon^2 + 8F\epsilon)^{1/2} + B]}\right). \tag{2.21}$$

Note that for $l = 0$, i.e., if both excitons initially occupy the same site, (2.21) reduces to

$$\tilde{Q}(\epsilon) = \frac{1}{\epsilon}\left(\frac{1}{1 + \frac{B}{(\epsilon^2 + 8F\epsilon)^{1/2}}}\right). \tag{2.22}$$

III. TWO- AND THREE-DIMENSIONAL MODELS

It should be clear from the development in Sec. II that Eqs. (2.3) through (2.16) are independent of the dimensionality of the model or of the nature of the transfer rates F_{mn} provided that the latter depend only on the difference $(m - n)$. The results specific to the *one*-dimensional model are (2.17) and its consequences (2.18) through (2.22). In this section we analyze two- and three-dimensional models. We continue to consider only two particles as constituting the system. We now merely regard m, n of the previous sections as vectors of appropriate dimensions. Similarly k's form reciprocal lattices of the corresponding dimensions.

For a simple square lattice in two dimensions the propagator expression analogous to (2.17) is

$$\psi_{m_x m_y,\, n_x n_y}(t) = e^{-8Ft} I_{m_x}(2Ft) I_{m_y}(2Ft) I_{n_x}(2Ft) I_{n_y}(2Ft) , \tag{3.1}$$

and the result which corresponds to (2.18) is therefore

$$\sum_{m_x m_y} \psi_{m_x m_y,\, m_x + l_x\, m_y + l_y}(t) = e^{-8Ft} I_{l_x}(4Ft) I_{l_y}(4Ft) . \tag{3.2}$$

As seen in Sec. II the computation of the experimentally relevant quantity Q requires the Laplace transform of (3.2). The full expression is required for the initial condition (2.14) wherein the excitons are initially localized and separated by l_x lattice distances along the x axis and l_y lattice distances along the y axis. For this condition (2.16) then gives[7]

$$\tilde{\eta}^0(\epsilon) = \left(\frac{(4F)^{l_x + l_y}\Gamma((l_x + l_y + 1)/2)\Gamma((l_x + l_y + 2)/2)}{\sqrt{\pi}\,\Gamma(l_x + 1)\Gamma(l_y + 1)(\epsilon + 8F)^{l_x + l_y + 1}}\right) F_4\left(\frac{l_x + l_y + 1}{2}, \frac{l_x + l_y + 2}{2}; l_x + 1, l_y + 1; \left(\frac{4F}{\epsilon}\right)^2, \left(\frac{4F}{\epsilon}\right)^2\right), \tag{3.3}$$

where F_4 is the hypergeometric function of four variables. The particular case $l_x = l_y = 0$ of the above result gives $\tilde{\psi}^0(\epsilon)$:

$$\tilde{\psi}^0(\epsilon) = \frac{(2/\pi)}{\epsilon + 8F}\,\mathcal{K}\left(\frac{8F}{\epsilon + 8F}\right) , \tag{3.4}$$

where $\mathcal{K}$ is the elliptical integral of the first kind defined by

$$\mathcal{K}(x) = \int_0^{\pi/2} \frac{d\theta}{(1 - x \sin^2\theta)^{1/2}} . \tag{3.5}$$

Equation (3.4) is obviously the Laplace transform of $e^{-8Ft} I_0^2(4Ft)$. Finally a substitution of (3.3) and (3.4) into (2.8) gives the desired $\tilde{Q}(\epsilon)$ for the localized initial condition (2.14). Similarly the substitution of the result $\eta^0(t) = 1/N$ and (3.4) into (2.8) gives the desired $\tilde{Q}(\epsilon)$ for the delocalized initial condition $P_{r_x r_y,\, s_x s_y}(0) = 1/N^2$. Being both simpler and of greater experimental relevance, at least to the exciton problem, we display this result explicitly

$$\tilde{Q}(\epsilon) = \frac{1}{\epsilon}\left\{1 - \frac{B}{N\epsilon}\left[1 + \frac{(2/\pi)B}{\epsilon + 8F}\,\mathcal{K}\left(\frac{8F}{\epsilon + 8F}\right)\right]^{-1}\right\}. \tag{3.6}$$

For a simple cubic lattice in three dimensions the propagator is

$$\psi_{m_x m_y m_z,\, n_x n_y n_z}(t) = e^{-12Ft} I_{m_x}(2Ft) I_{m_y}(2Ft) I_{m_z}(2Ft) \times I_{n_x}(2Ft) I_{n_y}(2Ft) I_{n_z}(2Ft). \tag{3.7}$$

Equations analogous to (3.2) and (3.3) may be written down in a straightforward fashion. We show the explicit expressions only for the initially delocalized case $P_{r_x r_y r_z,\, s_x s_y s_z}(0) = 1/N^2$. One then requires only

$$\tilde{\psi}^0(\epsilon) = \int_0^\infty dt\, e^{-\epsilon t}\psi^0(t) = \int_0^\infty dt\, e^{-\epsilon t} e^{-12Ft} I_0^3(4Ft) . \tag{3.8}$$

The Laplace transform of I_0^3 has been tabulated by Maradudin *et al.*[8] in connection with problems of lattice dynamics. Calling that function $\tilde{\mathfrak{M}}(\epsilon)$ we find

$$\tilde{Q}(\epsilon)=\frac{1}{\epsilon}\left(1-\frac{B}{N\epsilon}\left[1+B\tilde{\mathfrak{M}}(\epsilon+12F)\right]^{-1}\right). \quad (3.9)$$

In obtaining the above expressions we have assumed that the particles have isotropic transfer rates. In case this is not true, or in case lattices other than the simple square and the simple cubic are to be considered, the above expressions may be modified in a straightforward fashion.

IV. EFFECT OF LONG-RANGE ANNIHILATION

The results of Secs. III and IV are based on the assumption that annihilation occurs only on contact, i.e., when the two particles occupy the same site. We shall now indicate how the analysis may be generalized to treat annihilation at finite distances.

What is required is clearly the replacement of the last term in (2.2) by $-\sum_l \delta_{m,m+l}B_l P_{m,n}$ where B_l is the annihilation rate at a separation of l lattice distances. Equation (2.4) is then generalized to

$$\tilde{P}_{m,m+l}=\tilde{\eta}_{m,m+l}-\sum_{r,l'} B_{l'}\tilde{\psi}_{m-r,m-r+l-l'}\tilde{P}_{r,r+l'}. \quad (4.1)$$

We now define $\tilde{P}_l^k$ through

$$\tilde{P}_l^k=\sum_m \tilde{P}_{m,m+l}e^{ikm} \quad (4.2)$$

and obtain

$$\tilde{P}_l^k=\tilde{\eta}_l^k-\sum_{l'} B_{l'}\tilde{\psi}_{l-l'}^k\tilde{P}_{l'}^k. \quad (4.3)$$

The summation in (4.3) extends over the range of the annihilation interaction. For $B_{l'}=B\delta_{l',0}$ the previous results such as (2.6) are recovered. The opposite limit of constant annihilation interaction (independent of interparticle distance) is represented by $B_{l'}=b$ and results in the trivial result that the total probability $Q(t)$ decays exponentially with the exponent b. For a general intermediate set of B_l's one cannot go further than (4.3) unless the structure of B_l is relatively simple. For instance, if B_l is zero for $l>l_0$, signifying that annihilation occurs only within a distance l_0, a determinant of l_0 rows and columns must be evaluated from (4.3). As an example, consider $B_l=0$ for $|l|>1$ and $B_1=B_{-1}$. This represents the particles annihilating each other at rate B_0 when they are in contact, and at rate B_1 when they are in nearest-neighbor positions. Equation (4.3) gives

$$\begin{aligned}(1+B_0\tilde{\psi}_0^k)\tilde{P}_0^k+B_1\tilde{\psi}_1^k\tilde{P}_1^k+B_1\tilde{\psi}_1^k\tilde{P}_{-1}^k&=\tilde{\eta}_0^k,\\ B_0\tilde{\psi}_1^k\tilde{P}_0^k+(1+B_1\tilde{\psi}_0^k)\tilde{P}_1^k+B_1\tilde{\psi}_2^k\tilde{P}_{-1}^k&=\tilde{\eta}_1^k,\\ B_0\tilde{\psi}_1^k\tilde{P}_0^k+B_1\tilde{\psi}_2^k\tilde{P}_1^k+(1+B_1\tilde{\psi}_0^k)\tilde{P}_{-1}^k&=\tilde{\eta}_{-1}^k,\end{aligned} \quad (4.4)$$

where we have set $\psi_1^k=\psi_{-1}^k$ but not $\eta_1^k=\eta_{-1}^k$ to allow total freedom in the initial condition. Note that a quantity such as ψ_1^0 is given by

$$\begin{aligned}\psi_1^0(t)&=\sum_m \psi_{m,m+1}(t)=\sum_m e^{-4Ft}I_m(2Ft)I_{m+1}(2Ft)\\&=e^{-4Ft}I_1(4Ft),\end{aligned} \quad (4.5)$$

where (2.18) has been used. Similarly $\psi_2^0(t)$ equals $e^{-4Ft}I_2(4Ft)$.

A solution of (4.4) for $k=0$ followed by a substitution of the solution in

$$\tilde{Q}(\epsilon)=\frac{1}{\epsilon}\{1-[B_0\tilde{P}_0(\epsilon)+B_1\tilde{P}_1(\epsilon)+B_1\tilde{P}_{-1}(\epsilon)]\} \quad (4.6)$$

gives the basic quantity of interest.

It is straightforward to solve for $\tilde{P}_0^0$, $\tilde{P}_1^0$, and $\tilde{P}_{-1}^0$ from (4.4) and evaluate (4.6). We do not exhibit the explicit expressions because they add little to the physics and are cumbersome. It is also only a matter of algebra to obtain similar expressions for two- and three-dimensional models. In the rest of the paper we shall return to the case $B_l=\delta_{l,0}$ for the sake of simplicity. It should be kept in mind, however, that if any particular application of the present theory makes it necessary to include the effects of long-range annihilation, they can be described by the methods shown in this section.

V. DERIVATION OF BOLTZMANN-TYPE EQUATIONS AND INCLUSION OF RADIATIVE DECAY

An interesting question that one might ask in the context of (2.2), the starting point of our analysis, is the following: What does it predict for the evolution of $f_m(t)$, the probable number of particles at m? The answer is immediate once one recognizes that

$$f_m(t)=\sum_n [P_{m,n}(t)+P_{n,m}(t)]. \quad (5.1)$$

Note that we use the normalization $\sum_m f_m(t)=2$ so that f_m measures the probable number of particles at m rather than the probability itself. Division by two gives the probability. We find for the evolution of $f_m(t)$

$$\frac{df_m}{dt}=F(f_{m+1}+f_{m-1}-2f_m)-2BP_{m,m}. \quad (5.2)$$

Compare (5.2) to (2.1) and observe the familiar connection of a lower member to a higher member in a hierachy of distribution functions.

Substitution of (2.6) in the inverse of (2.5) gives, with (5.2),

$$\frac{df_m}{dt}=F(f_{m+1}+f_{m-1}-2f_m) -\frac{2B}{N}\int d\epsilon\, e^{\epsilon t}\sum_k \{e^{-ikm}\tilde{\eta}^k(\epsilon)[1+B\tilde{\psi}^k(\epsilon)]^{-1}\}\ , \tag{5.3}$$

where the ϵ integration is on the Bromwich contour. This solution is explicit, although the last term in (5.3) contains the quantities η and ψ natural to a higher space. We shall now make it implicit in two steps. If $[1+B\tilde{\psi}^k(\epsilon)]^{-1}$ is expanded in B, and the lowest term is kept, (5.3) gives

$$\frac{df_m}{dt}=F(f_{m+1}+f_{m-1}-2f_m)-\left(\frac{2B}{N}\right)\eta_{m,m}(t)\ . \tag{5.4}$$

But $\eta_{mm}(t)$ is the probability that the two particles occupy the same site under the given initial conditions but with the provision $B=0$. For $B=0$ this probability is the square of the single-particle probability because the particles would be independent. The passage from (5.3) to (5.4) involved the assumption that the effect of B was small. Under the same assumption we shall replace $\eta_{mm}(t)$ by $\frac{1}{4}f_m^2(t)$ and obtain

$$\frac{df_m}{dt}=F(f_{m+1}+f_{m-1}-2f_m)-\left(\frac{B}{2N}\right)f_m^2 \tag{5.5}$$

as the familiar[2] equation with the bilinear "collision" annihilation term γ given by $(B/2N)$. An identical treatment of the quantity $Q(t)$ from Eq. (2.7) gives a similar approximation to the exact (2.11).

Approximate equations such as (5.5) have served as the basis of most analyses[1-3] of experimental observations relevant to excitons. It is thus important to understand their range of validity. Their derivation given above requires that the basic annihilation rate B be small. This is, however, in contradiction with the actual situation in most experiments where the annihilation rate is believed[2] to be much larger than the transfer rate. We shall now show that (5.5) may also result in such cases. Presumably this corresponds to the well-known fact that the usual Boltzmann equation for gases is known to be valid even for *strong* collisions provided the gas is dilute enough, and in the present context to the fact that the passage from (5.3) to (5.4) and that from (5.4) to (5.5) introduce errors in "opposite directions."

If we approximate (5.3) by replacing $\tilde{\psi}^k(\epsilon)$ by $\tilde{\psi}^0(\epsilon)$, we may write

$$\frac{df_m(t)}{dt}=F(f_{m+1}(t)+f_{m-1}(t)-2f_m(t)) -\int_0^t dt'\Gamma(t-t')f_m^2(t')\ , \tag{5.6}$$

where the further replacement of $\eta_{m,m}$ by $(\frac{1}{4})f_m^2$ has been made as in (5.5), and where the "annihilation memory function" $\Gamma(t)$ is given by

$$\Gamma(t)=\frac{1}{2N}\int d\epsilon\, e^{\epsilon t}B[1+B\tilde{\psi}^0(\epsilon)]^{-1}\ . \tag{5.7}$$

Basic to (5.6) is the replacement of $\tilde{\psi}^k(\epsilon)$ by $\tilde{\psi}^0(\epsilon)$. This replacement does not involve a small B approximation. It is similar to the replacement of nonlocal terms in time by local "Markoffian terms," the only difference being in that this approximation involves space rather than time. If we further make a Markoffian approximation in time, i.e., if we replace $\Gamma(t)$ by $\delta(t)$ times a suitable integral of $\Gamma(t)$ we recover (5.5). However it is easy to see that integration of $\Gamma(t)$ from $t=0$ to $t=\infty$ will not do because $\tilde{\psi}^0(0)$ is infinite. We therefore must introduce some cutoff in the integral. We shall call this cutoff time $\tau_0/2$. The existence of radiative decay in the exciton problem, which will be introduced explicitly below, makes it plausible to use that decay time as the cutoff time. In any case

$$\gamma=\int_0^\infty dt\, e^{-2t/\tau_0}\Gamma(t) \tag{5.8}$$

may be written independently of the identification of τ_0 with the radiative decay time τ. With such a prescription the one-dimensional model gives

$$\gamma=\left(\frac{1}{2N}\right)\left(\frac{B(1+4F\tau_0)^{1/2}/\tau_0}{B+(1+4F\tau_0)^{1/2}/\tau_0}\right)\ , \tag{5.9}$$

with B and $(1+4F\tau_0)^{1/2}/\tau_0$ being the respective limits of $(2N)\gamma$ as the annihilation rate B is small or large with respect to the "motion rate" $(1+4F\tau_0)^{1/2}/\tau_0$.

For the first time in our analysis we shall now introduce the radiative decay that excitons undergo. It is an important addition since the experimental observations rely on that decay itself to measure such quantities as $Q(t)$. In the absence of annihilation, i.e. of B, we would have had the term P_m/τ added to the left side of the probability Eq. (2.1). What should we add to (2.2)? A moment's consideration shows that one must replace (2.2) by

$$\frac{dP_{m,n}}{dt}+\frac{2P_{m,n}}{\tau}=F(P_{m+1,n}+P_{m-1,n}+P_{m,n+1} +P_{m,n-1}-4P_{m,n})-\delta_{m,n}BP_{m,m}\ . \tag{5.10}$$

The factor 2 arises *not* from the fact that there are two terms summed in (5.1) but from the fact that $P_{m,n}$ can be depleted through the decay of either particle. It is easy to check that for $B=0$ (5.10) would give (2.1) with P_m/τ added on the left side.

Our true starting point for the analysis of excitons undergoing radiative decay as well as annihilation and motion is therefore (5.10). However, is it enough as a starting point? Is the quantity obtained from (5.1) really the probable number of particles at m? The answer to the latter question is in the negative now that a τ has been introduced. The answer to the former question is also in the negative: An additional equation of motion is required for $p_m(t)$, the probability that there is *only a single particle* in the system and it is at m. This quantity is not included in $P_{m,n}(t)$ because underlying the latter is the tacit assumption that there are two particles in the system. Thus $\frac{1}{2}$ times the right side of (5.1) gives the probability that there is a particle at m *and there is a particle elsewhere*. As a result of the introduction of τ this probability must be added to $p_m(t)$ to give the total probability that there is a particle at m, irrespective of whether the other particle does or does not exist. To obtain the probable number of particles, which was denoted by f_m above, the right side of (5.1) should *not* be multiplied by $\frac{1}{2}$ before being added to p_m. Thus

$$f_m(t)=p_m(t)+\sum_n [P_{m,n}(t)+P_{n,m}(t)] \tag{5.11}$$

holds generally. It reduces to (5.1) if the possibility that a single particle exists is excluded.

Now we must seek an equation for $p_m(t)$ as well, since a complete description of the system requires p_m in addition to $P_{m,n}$. It is clear that this equation is

$$\frac{dp_m}{dt}+\frac{p_m}{\tau}=F(p_{m+1}+p_{m-1}-2p_m) + \frac{1}{\tau}\sum_n [P_{m,n}(t)+P_{n,m}(t)]. \tag{5.12}$$

If we also write an equation for $q(t)$, the probability that there is no particle in the system,

$$\frac{dq}{dt}=\frac{1}{\tau}\sum_m p_m+B\sum_m P_{m,m}, \tag{5.13}$$

we find that the probability,

$$\sum_m p_m+\tfrac{1}{2}\sum_{m,n}(P_{m,n}+P_{n,m})+q ,$$

is always equal to 1 as it should be. Note that the probable number of particles is given not by $1-q$ but by the sum over m of (5.11).

With the inclusion of radiative decay we must consider the system phase space to consist of three subspaces, the two-particle one with $P_{m,n}$, the one-particle one with p_m, and the zero-particle one with q for the description of the evolution.

The experimentally relevant quantity related to the monitored fluorescence intensity in the exciton case is the "differential photon count rate." Being the rate at which photons come out of the system as a result of the radiative decay of excitons, it is given by

$$\mathcal{I}(t)=\left(\frac{df_m}{dt}\right)_{\text{radiative}}=\frac{1}{\tau}\sum_m p_m(t)+\frac{2}{\tau}\sum_{m,n}P_{m,n}, \tag{5.14}$$

and the quantum yield, i.e., the ratio of the number of excitons that comes out radiatively as photons to the number put in, is

$$\phi=\tfrac{1}{2}\int_0^\infty dt\,\mathcal{I}(t)=\tfrac{1}{2}\lim_{\epsilon\to 0}\tilde{\mathcal{I}}(\epsilon). \tag{5.15}$$

However, if initially there are always two excitons in the system, $p_m(0)=0$ and (5.12) gives

$$\sum_m \tilde{p}_m(\epsilon)=\left(2\sum_{m,n}\tilde{P}_{m,n}(\epsilon)\right)\Big/(1+\epsilon\tau). \tag{5.16}$$

It is thus possible to express the differential photon count rate and the quantum yield ϕ arising from the conjunction of (5.10) and (5.12) in terms of the solution of $\sum_{m,n}P_{m,n}$ from (5.10) alone. Explicit use of (5.12) is no longer necessary. Recalling that $P_{m,n}$ in (5.10) is given by $e^{-2t/\tau}$ times the $P_{m,n}$ in (2.2) because of the absence of the radiative decay term in the latter, we finally write expressions for the observable quantities $\mathcal{I}(t)$ and ϕ in terms of the solutions of $Q(t)$ arising from (2.2)

$$\mathcal{I}(t)=(2/\tau)e^{-t/\tau}\left(e^{-t/\tau}Q(t)+\frac{1}{\tau}\int_0^t dt'\,e^{-t'/\tau}Q(t')\right), \tag{5.17}$$

$$\phi=(2/\tau)\tilde{Q}(2/\tau). \tag{5.18}$$

It is emphasized that these expressions are the result of Eqs. (5.10) and (5.12) which *do* incorporate radiative decay but that the Q appearing in (5.17) and (5.18) is the result of (2.2) or its generalizations without τ, and is thus given by (2.8), (2.20), (2.21), (3.6), or (3.9).

VI. EFFECT OF TRANSPORT COHERENCE

How should our analysis be modified if the basic transport equation is not (2.1) at all but describes "coherent" behavior, an extreme of which is described by the Schrödinger equation for amplitudes C_m? This question is of particular relevance to excitons because the issue of exciton coherence has been discussed a great deal[9,10] in recent times. By completely coherent transport is meant the wavelike transport characteristic of the equation

$$\frac{dC_m}{dt} = -iJ(C_{m+1} + C_{m-1}) \qquad (6.1)$$

(or of its non-nearest-neighbor counterpart involving J_{mn}'s) in obvious notation, the probabilities being given by $P_m = C_m^* C_m$. The completely incoherent limit is described by (2.1). Traditionally, quite different formalisms have been used in the two limits but we shall show here how a unified treatment can be given. Such a unified treatment may take as its starting point stochastic Liouville equations[9] or generalized master equations.[10] The former have been employed for other purposes such as the analysis of exciton trapping[11] and fluorescence depolarization[12] whereas the latter have been used for studying transient grating observations[13] and trapping.[14] They are essentially equivalent to each other[15] and we shall therefore begin with only the generalized master equation

$$\frac{dP_m(t)}{dt} = \int_0^t dt' \sum_n [\mathcal{W}_{mn}(t-t')P_n(t') - \mathcal{W}_{nm}(t-t')P_m(t')] \qquad (6.2)$$

to replace (2.1), a similar equation with B included being written in correspondence to (2.2). We stress that the completely incoherent case, i.e., (2.1), is recovered from (6.2) under

$$\mathcal{W}_{mn}(t) = F(\delta_{m,n+1} + \delta_{m,n-1})\delta(t) , \qquad (6.3)$$

whereas the completely incoherent case, i.e., (6.1), corresponds[13,15] to

$$\mathcal{W}_{mn}(t) = 2J^2[J^2_{m-n+1} + J^2_{m-n-1} + 2J_{m-n+1}J_{m-n-1} - 2J^2_{m-n} - J_{m-n}(J_{m-n+2} + J_{m-n-2})] , \qquad (6.4)$$

where J_m is the Bessel function of mth order of argument $2Jt$.

The entire further treatment of Sec. II remains unmodified except for the meaning of the ψ's. Thus, in particular, (2.3)–(2.7) and (2.8) hold exactly in the form given. However, the ψ's appearing therein must now be taken as products of propagators corresponding to (6.2) above rather than to (2.1). This is a remarkable result because it allows a unified description of the effect of transport coherence on annihilation, no matter how little or how large the amount of coherence. For instance, for the delocalized initial condition of (2.13), Eq. (2.8), written as

$$\tilde{Q}(\epsilon) = \frac{1}{\epsilon}\left(1 - \frac{1}{N\epsilon}\,\frac{B}{1 + B\tilde{\psi}^0(\epsilon)}\right) , \qquad (6.5)$$

shows clearly where transport coherence enters. It is in, and only in, $\tilde{\psi}^0(\epsilon)$. It has been shown in Eq. (5.18) that yield expressions are obtained by the replacement of ϵ by $2/\tau$. It follows therefore that substantial coherence effects will be observed in those cases when the actual $\tilde{\psi}^0(2/\tau)$ is substantially different from that [such as (2.19)] for the completely incoherent case. However, $\tilde{\psi}^0(\epsilon)$ is derived from Laplace transforms of $\mathcal{W}_{mn}(t)$, and the completely incoherent limit is given by the replacement [see Eq. (6.3)] of $\tilde{\mathcal{W}}_{mn}(\epsilon)$ by $\mathcal{W}_{mn}(0)$. Thus it follows that substantial differences in the actual yield and that predicted in the incoherent limit will occur when τ is comparable to or smaller than the decay time of the memory functions. This is completely in keeping with our physical understanding. The incoherent limit does in fact describe the situation wherein the memory functions decay very rapidly. The radiative decay time τ serves as a comparison time for the memory decay as far as yield observations are concerned.

To show the explicit effect of transport coherence on annihilation explicit expressions for $\mathcal{W}_{mn}$ must be written down. Such an expression has been obtained by the author earlier[13(a),15] and it is given by multiplying the right side of (6.4) by $e^{-\alpha t}$, where α is a randomizing or bath parameter.[16] The transform of the propagator, i.e., $\sum_m e^{ikm}\tilde{\psi}_m(\epsilon)$, has also been calculated[13(a)]:

$$\sum_m e^{ikm}\tilde{\psi}_m(\epsilon) = \{[(\epsilon+\alpha)^2 + 16J^2\sin^2\tfrac{1}{2}k]^{1/2} - \alpha\}^{-1} . \qquad (6.6)$$

We now point out that (2.18), which has made the exact calculations presented so far in this paper possible, is a particular case of the general chain condition[5] obeyed by probabilities. Thus for all propagators no matter what the detail of $\mathcal{W}_{mn}(t)$,

$$\psi_l(t_1 + t_2) = \sum_m \psi_{l-m}(t_1)\psi_m(t_2) , \qquad (6.7)$$

provided only that translational invariance applies. In fact a term such as the first one on the right of (2.3) is based on this chain result. Symmetry also gives $\psi_{l-m} = \psi_{m-l}$ for probabilities and (2.18) is thus seen to be indeed a particular case of (6.7).

As stated in Sec. II, the key quantity to be calculated is the right side of (2.16). With (6.7) we thus have

$$\sum_m \psi_{m,m+l}(at) = \psi_l(2at) , \qquad (6.8)$$

which for the propagator of (6.6), describing partial coherence, gives

$$\sum_m \tilde{\psi}_{m,m+l}(\epsilon) = \frac{1}{2N}\sum_k e^{-ikl}\{[(\tfrac{1}{2}\epsilon+\alpha)^2 + 16J^2\sin^2\tfrac{1}{2}k]^{1/2} - \alpha\}^{-1} \qquad (6.9)$$

with its particular case obtained by setting $l=0$ and taking the infinite size limit

$$\tilde{\psi}^0(\epsilon)=\frac{1}{4\pi}\int_0^{2\pi} dk\{[(\tfrac{1}{2}\epsilon+\alpha)^2+16J^2\sin^2\tfrac{1}{2}k]^{1/2}-\alpha\}^{-1}. \tag{6.10}$$

Equation (6.10) is valid for arbitrary degree of coherence and reduces to the completely incoherent case treated earlier [Eq. (2.19)] in the limit $J\to\infty, \alpha\to\infty, 2J^2/\alpha=F$. The integral in (6.10) has been evaluated exactly by Wong[17] in the context of the effect of exciton coherence on trapping observables and equals

$$\tilde{\psi}^0(\epsilon)=\frac{2\alpha}{[(\epsilon^2+4\epsilon\alpha)(\epsilon^2+4\epsilon\alpha+64J^2)]^{1/2}}+\frac{2/\pi}{[(\epsilon+2\alpha)^2+64J^2]^{1/2}}\mathcal{K}(x)+\frac{4\alpha^2}{[(\epsilon+2\alpha)^2+64J^2]^{1/2}}\,\frac{2/\pi}{\epsilon^2+4\epsilon\alpha+64J^2}\Pi(y^2,x), \tag{6.11}$$

where y^2 and x are given by $64J^2(\epsilon^2+4\epsilon\alpha+64J^2)^{-1}$, and $8J[(\epsilon+2\alpha)^2+64J^2]^{-1/2}$, respectively. Here $\mathcal{K}(x)$ is the elliptic integral of the first kind defined in (3.5) and $\pi(y^2,x)$ is the elliptical integral of the third kind defined by

$$\Pi(y^2,x)=\int_0^{\pi/2}\frac{d\theta}{(1-x^2\sin^2\theta)^{1/2}(1-y^2\sin^2\theta)}. \tag{6.12}$$

As stated above, (6.11) reduces to (2.19) in the incoherent limit and to

$$\tilde{\psi}^0(\epsilon)=\frac{2/\pi}{(\epsilon^2+64J^2)^{1/2}}\mathcal{K}\,\frac{8J}{(\epsilon^2+64J^2)^{1/2}} \tag{6.13}$$

in the coherent limit represented by (6.1). The observables $\mathcal{I}(t)$ and ϕ are now obtained from (5.17) and (5.18) after the substitution of (6.11) in (2.8). For instance, for purely coherent motion in one dimension with nearest-neighbor transfer elements J, the quantum yield for the initially delocalized condition is given by

$$\phi=1-(1/N)\left(\frac{B\tau/2}{1+(B\tau/2)(1+16J^2\tau^2)^{-1/2}(2/\pi)\mathcal{K}(4J\tau/(1+16J^2\tau^2)^{1/2})}\right). \tag{6.14}$$

We do not feel that it is necessary to repeat the analysis in higher dimensions or with long-range annihilation in the coherence context. The steps are all clearly given above and it is straightforward, although a little cumbersome, to combine the various elements into a single calculation.

We thus expect quite different expressions for the quantum yield for highly coherent transport [see (6.14)] and for highly incoherent transport [see (2.20)]. Values of J are often known from theoretical calculations. The use of (6.11) in (6.5) and of (5.17) and (5.18) will then allow one to measure the degree of coherence, described by the value of α or of J/α, from the observed quantum yield and fluorescence intensity. Another observation of use to the measurement of coherence would be the temperature variation of the quantum yield.

VII. DISCUSSION

We have presented above an analysis of particles that move on a lattice and annihilate one another, which is particularly relevant to excitons in molecular crystals. We begin this discussion by listing its advantages. The theory is based on an exact calculation and all observables are obtained in terms of analytic functions. It is applicable to two- and three-dimensional realistic crystals as well as for one-dimensional models. It gives exact expressions for the quantum yield and fluorescence intensity without going through the usual annihilation equation (5.5) whose validity is definitely not universal. It allows the incorporation of nonlocal annihilation. It describes in a unified manner the effect of transport coherence. It also gives expressions for the much-used quantity γ and sheds some light on the meaning of the assumption involving its use and the use of (5.5). The theory is not restricted to steady-state situations and the time dependence of fluorescence intensity is obtained analytically up to an inverse Laplace transform. The quantum yield expression on the other hand is totally explicit. The theory is also applicable for arbitrary initial conditions, not being restricted to symmetric situations.

The main shortcoming of the theory in the present form is its inapplicability for cases wherein there is a high concentration of particles. This refers in the exciton context to high intensities of exciting light. This inapplicability is reflected in the models considered above in the assumption that the system consists only of two particles. The actual system will initially contain ρN particles, where ρ is the initial concentration and N the number of lattice sites. If ρ is small compared to unity, the kinematics of each particle may be described by that of $\frac{1}{2}(\rho N-1)$ separate systems of two particles each of the kind analyzed in this paper. For small ρ, the factor $1/N$ appearing in the various expressions for the observables [such as (2.20), (3.6), (3.9), and (6.14) should be replaced by half the concentration ρ or, more accurately, by $(1/2N)(\rho N-1)$]. However, for high concentrations the analysis must be modified in a significant fashion. The other applicability question for the theory is connected with the suitability of the generalized master equation to describe the effects of coherence. The equation is exact for completely localized or completely delocalized initial conditions.[18] The latter represents fairly well the experimental situation for excitons. It is also expected that the generalized master equation is a good description for intermediate initial conditions provided that they do not involve severe departures from the complete localization or delocalization extreme. If they do, and if transport coherence is expected, a stochastic Liouville equation may be used. The present theory also needs to be generalized to treat effects of magnetic fields on annihilation.[2] It is intended to present these extensions of the theory in a future publication.

The specific results we have obtained are as follows. For a system of two particles annihilating each other on contact as in (2.2), but moving either as in (2.1) or more generally as in (6.2), the total probability $Q(t)$ that the two particles exist is given by (2.8). Particular cases of this result are (2.20) for a delocalized initial condition and (2.21) for a localized initial condition, both applicable for one-dimensional incoherent motion as in (2.2). Similar results for incoherent motion in the two-dimensional square lattice and the three-dimensional simple cubic lattice are, respectively, (3.6) and (3.9). Equation (6.5) with (6.11) gives the effect of transport coherence on exciton annihilation, the purely coherent limit being in (6.14). The effects of spatially nonlocal annihilation are in (4.6) and (4.4). The annihilation constant γ is given in (5.9) and a non-Markoffian generalization of it in (5.7). Most of the expressions presented in the various contexts are for $\tilde{Q}(\epsilon)$, the Laplace transform of the total probability $\sum_{m,n}\tilde{P}_{m,n}(\epsilon)$, and we therefore point out that (5.17) and (5.18) connect $\tilde{Q}(\epsilon)$ explicitly to the measurable quantities, viz., the fluorescence intensity $\mathcal{I}(t)$ and the quantum yield ϕ. Thus the general expression for ϕ for a delocalized initial condition is

$$\phi=1-(\rho/2)(\tau/2)\left(\frac{B[\tilde{\psi}^0(2/\tau)]^{-1}}{B+[\tilde{\psi}^0(2/\tau)]^{-1}}\right). \qquad (7.1)$$

The most general starting point for our analysis is the equation

$$\frac{dP_{m,n}(t)}{dt}+\frac{2P_{m,n}(t)}{\tau}=\int_0^t dt'\sum_n\left[\mathcal{W}_{mm',nn'}(t-t')P_{m',n'}(t')-\mathcal{W}_{nn',mm'}(t-t')P_{m,n}(t')\right]$$
$$-\sum_l\delta_{m,n+l}\int_0^t dt'\mathcal{B}_l(t-t')P_{m,n+l}(t'), \qquad (7.2)$$

and another equation for $p_m(t)$, whose details we do not show. Equations (2.2), (5.10), etc., are particular cases of (7.2). The $\mathcal{B}_l$'s decide the spatial range of the annihilation, the dimensionality of m, n, etc., corresponds to the dimensionality of the lattice, and the t dependence of $\mathcal{W}(t)$'s determines the coherence in transport. We have also included memory in the annihilation rates $\mathcal{B}_l$ for generality.

We stress that the replacement of $1/N$ in the various expressions such as (6.4) by $(\rho/2)$, where ρ is the particle concentration, is not an *ad hoc* approximation but can be shown to represent the first term in a series in ascending powers of the particle concentration. Our analysis is therefore by no means restricted to the trivial system of two particles in an infinite system but to one containing a finite, but not too large, concentration of annihilating particles. In the exciton context this means that the theory is applicable to cases wherein one has small intensities of exciting light since ρ is proportional to the light intensity.

The important question of whether the equation[1-3] for the exciton density

$$\frac{\partial n(\bar{r},t)}{\partial t}=-\gamma' n^2(\bar{r},t), \qquad (7.3)$$

which is the basis of most interpretations of experimental data, is universally valid has been answered in the negative in this paper. Furthermore, the discussion preceding (5.9) clarifies in what sense (7.3) is applicable and gives an expression for γ. Evidently that expression, which pertains to the evolution of the number of particles f_m and thus describes a rate, should be multiplied by the system volume (or area or length) to give the usual γ' in (7.3), which has the dimensions of $\mathrm{cm}^d\,\mathrm{sec}^{-1}$ where d is the dimensionality. The expression for γ given in (5.9) shows clearly the competing processes of annihilation and motion which contribute to it. It becomes identical to the basic annihilation rate or to the "motion rate" in the respective limits of slow or fast annihilation. Further elaboration on these matters will be given elsewhere.

We conclude by emphasizing that this paper contains a unified treatment of the *observable* effects of transport *coherence* on annihilation and is one of a series of papers[13(b),14] devoted to the question of how coherence may be actually measured from experiments.

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