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MATHEMATICAL METHODS FOR THE DESCRIPTION OF
ENERGY TRANSFER

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ABSTRACT

Some modern mathematical methods developed for the investigation of energy transfer are described. They are based primarily on master equations and are particularly useful for the description of coherent motion, capture, annihilation, and related phenomena involving quasiparticles such as Frenkel excitons.

I. INTRODUCTION

I.A. Preliminary Remarks

This article describes a unified framework of mathematical methods developed in recent years for the description of energy transfer in solids occurring via the motion of excitons. It is hoped that the article will fulfill two functions: the description of some modern theoretical approaches of transport theory of interest not only to exciton dynamics and energy transfer but to the broader area of quasiparticle transport, and the presentation of an overview, from the theoretical viewpoint, of Frenkel exciton motion in molecular crystals.

Although the applicability of these mathematical methods extends over a wide area, the systems of direct interest to these developments are molecular crystals. Examples are crystals of aromatic hydrocarbons such as anthracene, naphthalene, and tetrachlorobenzene. The special characteristics of these systems are that the entities occupying the lattice sites in the crystal, the molecules,

have complex internal structure and motion (whence intramolecular motions arise); that intermolecular interactions are weak relative to most inorganic solids; that anisotropy can prevail as a result of the non-spherical shape and orientation of the molecules; and that dynamic disorder is of paramount importance in transport phenomena. These characteristics force the transport theorist to abandon traditional methods of analysis that have been used with success for many years in fields such as that of electron transport in metals, and to look for fundamentally new formalisms. The traditional methods employ kinetic treatments in k -space. They are based on the theory of bands which are slightly perturbed by interactions with phonons or other sources of scattering which can therefore be treated as small corrections. However, in molecular crystals, the bandwidth of the moving quasiparticle, the thermal energy $k_B T$, phonon energies, and other interaction energies can all acquire magnitudes comparable to one another. The new methods that are described below are based on master equations, usually in real space. These master equations are of the so-called "generalized" kind as well as of the simple kind. The existence of disorder which is not a small perturbation on crystalline properties, and the fact that molecular crystals often retain the properties of the individual constituent molecules, lead to the use of real space transport equations. On the other hand, the fact that the disorder is dynamic rather than static (which would be the case for amorphous systems), the system being still perfectly crystalline at zero temperature, leads to translationally invariant master equations being used for the analysis.

The quasiparticle whose motion brings about the process of energy transfer in molecular crystals is the Frenkel exciton. Differences of opinion exist about the convenience of the terminology used around the phrase "Frenkel exciton." Some authors (see elsewhere in this book) prefer to mean by that phrase a Bloch state of the electronic excitation of the molecules in the crystal, following early usage [1]. Other authors [2-6] look upon the Frenkel exciton as a quasiparticle (in analogy with the electron) which may occupy a delocalized Bloch state, a localized Wannier state, or any other allowable state. We find the latter usage conceptually more natural and practically more convenient and therefore employ it in this article. Thus, excitation transfer is identical to Frenkel exciton transport in this article and, if one were to consider systems with sufficient static disorder to make quasimomentum a very poor quantum number, we would still describe excitation transfer as the motion of a Frenkel exciton albeit among the sites of a disordered array.

As is well known, the subject of energy transfer is of special importance because of its obvious connections to other disciplines such as biology [7]. Energy transfer in molecular crystals derives its particular importance both from the fact that it raises basic issues about transport as mentioned above, and from the well-known fact that a molecular crystal is a solid state physicist's

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The present article stresses mathematical methods for the transport description, although special effort has been made to relate the contents to experimental observations.

I.B. Processes and Questions of Interest

Optical absorption can produce electronic excitations in the crystal, i.e., it can create Frenkel excitons. These excitons lead a rather eventful life before they die their radiative or radiationless death. They may undergo vibrational relaxation which may be of a simple kind as when the excited molecule relaxes among its intramolecular modes, or of a relatively dramatic kind as when an excimer, involving a drastic interaction of two (or more) molecules, is formed. They may decay through luminescence, which may be fluorescence as in the case of singlets, or phosphorescence as in the case of triplets. They may undergo internal conversion, i.e., a transition from one singlet manifold to another, or intersystem crossing as when a singlet changes into a triplet. The excitons may move from molecular site to molecular site, i.e., bring about energy transfer from one spatial location to another. If during this motion they come under the influence of traps in the crystal, which may be there either inadvertently or precisely because they were put there to detect motion, the excitons may be captured. They may also come under the influence of one another during motion and undergo mutual annihilation. The latter process is particularly striking when the moving excitons are triplets because the product of the mutual annihilation is often the formation of singlets which luminesce differently - much faster and at higher frequencies producing blue rather than red light which is typical of triplets.

A variety of questions are of interest in this field. The extent and speed of energy transfer depends on the magnitude of the diffusion constant of the excitons. Measurements of this central quantity have been made by many experimentalists over the last three decades but serious problems of interpretation remain. The value of the diffusion constant of singlet excitons in a prototype crystal such as anthracene is therefore still unknown even at room temperature although opinions abound. There is thus a disparity of several orders of magnitude in the reported values of this quantity. The temperature dependence of the diffusion constant and the nature of the underlying processes are also under question. In particular, the coherence issue, concerning whether excitons move in a wave-like coherent manner or a diffusive incoherent manner, continues to be widely debated. The validity of the simple picture of an exciton thermalizing before each transfer event, i.e., the question of whether energy transfer occurs after, before, or during relaxation, also continues to be under study. So does the connection between

exciton motion and optical spectra. The validity of simple kinetic schemes for understanding exciton trapping and mutual annihilation, the role of the capture process (as differentiated from the motion process) in the former, and the existence of time-dependent versus time-independent rates of energy transfer constitute other important questions in this field.

I.C. Some Experiments

Of the large variety of experiments that have been carried out in the area of energy transfer in molecular crystals we depict schematically in Fig. 1, four kinds which use direct probes into

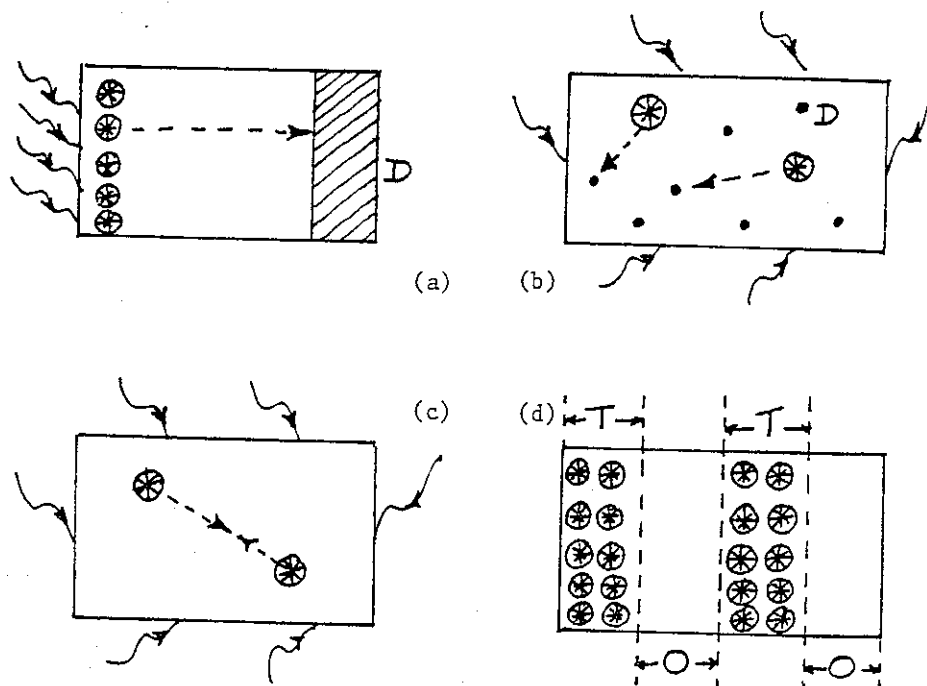


Fig. 1. Schematic depiction of four kinds of experiment for the measurement of energy transfer via exciton motion. Circled asterisks \otimes represent excitons, wavy lines with arrows show illumination and dotted lines with arrows represent the process which allows the measurement. In (a) and (b), D represents the detector material whose luminescence is monitored, and in (d), T and O respectively depict transparent and opaque regions of the gratings.

energy transfer in molecular crystals and serve as the basis for the experiments [8]. The experiment uses a detector material at the site end of the experiment. The illuminating molecules serve as the external source and employ the annihilation experiment of steady-state luminescence either to measure the rate of exciton creation in the crystal or by covering the parent structure to measure the delayed luminescence. In a second observation, the decay of the diffraction pattern is measured in a manner.

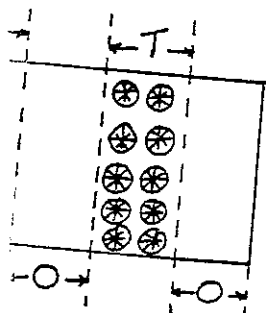
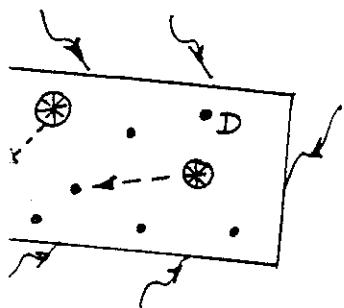
We have investigated the investigation closely related to the article. The experiments are described in the following.

I.D. Outline

The basic principle of the experiment is, viz, II. It consists of a crystal possessing a regular structure suitable for the measurement of these quantities. The procedures for the measurement of the results for the experiment are described in section III. Calculations are presented in section IV. The grating observation is appropriate to the experiment.

the validity of simple kinetic theory and mutual annihilation, differentiated from the motion of time-dependent versus time-independent excitons, constitute other important

that have been carried out in molecular crystals we depict use direct probes into



of experiment for the exciton motion. Circles with wavy lines with arrows represent the detector material whose diameter is T and O respectively. The wavy regions of the

energy transfer. Conceptually, the simplest experiment to measure energy transfer consists of starting excitons at one location in the crystal and detecting them at another. The two ends of a crystal serve as these well-defined locations in one of the oldest experiments [8] in this field. Shown in (a) in Fig. 1, the experiment uses a detector coating of a material which luminesces at a different frequency as the host crystal, illumination being at the opposite end of the crystal. Another, and more popular, kind of capture experiment is represented in Fig. 1(b) and involves homogeneous illumination of the entire crystal which is doped with other molecules serving as traps. Fig. 1(c) shows experiments which use no external agencies to probe into the motion of the excitons but employ the excitons themselves as the detectors. Their mutual annihilation is the probe process. In these capture and annihilation experiments, observables may be time-independent as in the case of steady-state quantum yields, or time-dependent as in the case of luminescence intensities. In capture observations they may refer either to the host or the guest, i.e., the traps. Fig. 1(d) represents the Ronchi grating experiments in which triplet excitons are created in the bulk of the crystal in spatially alternating regions by covering the crystal by an array of alternating opaque and transparent strips during illumination, and detecting their motion from the delayed fluorescence signal arising from their mutual annihilation. In a modern modification of this experiment which uses picosecond observations and studies singlet motion, laser beams are crossed to create a sinusoidal population of excitons, and the diffraction of a third laser beam off this population used to detect the decay of the amplitude of the inhomogeneity in a time-dependent manner.

We have not described many other important experiments used in the investigation of energy transfer simply because they are not as closely related to the mathematical methods to be developed in this article. Many excellent reviews exist on various aspects of the experiments [9-13] and should be consulted for further information.

I.D. Outline Of This Article

The basic transport equation to be used in most of the analysis, viz, the generalized master equation, is presented in section II. It contains the motivation for non-Markoffian, i.e, memory-possessing, transport equations and an explanation of their particular suitability for the systems and questions under study. Central to these transport equations are their "memory functions." Procedures for the calculation of these memory functions and explicit results for various models and interactions are exhibited in section III. Calculations of experimentally observable quantities are presented in section IV. They are directed specifically at capture and grating observations. Miscellaneous mathematical methods appropriate to energy transfer and concluding remarks form section V.

II. THE BASIC TRANSPORT INSTRUMENT: THE EVOLUTION EQUATION

II.A. Introduction and the Coherence-Incoherence Problem

Insight into the physics of the basic evolution equation to be used in the sequel can be gained by studying briefly some historical aspects of the subject. In 1932 Perrin attempted to use the Schrodinger equation among sharp molecular site states to describe excitation transfer in the context of experiments on fluorescence depolarization [14] and found clear disagreement with observations. That the problem lay in the evolution equation itself, and not in the specific transport mechanism assumed by Perrin - dipole-dipole interactions - was shown a number of years later by Foerster [15]. He recognized that the levels among which the motion transitions were occurring were not sharp but rather 'broadened' into groups of states as a result of bath (i.e., reservoir) interactions. By using a Master equation with transition rates given by the Fermi Golden Rule, with the same dipole-dipole interactions assumed by Perrin, Foerster was able to obtain excellent agreement with experiment. However, as further experiments were carried out at various temperatures with various environments and on various systems, departures from the Foerster theory were observed. The Schrodinger equation and the Master equation were clearly understood to be valid in the two extreme limits, called coherent and incoherent respectively. But one was faced with two non-trivial tasks: how to give a unified description which would reduce to the two limits and would furthermore be capable of treating the intermediate range, and how to ascertain practically which limit is applicable to a given experimental system.

The simplest way of appreciating the coherence-incoherence issue is to consider motion of the exciton in a system of just 2 sites, 0 and 1, which would have equal energies in the absence of the intersite interaction. If the latter is V , one solves a simple Schrodinger equation and shows that the probability $P_0(t)$ that the initially occupied site is occupied by the exciton at time t , is

$$P_0(t) = \cos^2(Vt) \quad (1)$$

Here and henceforth we put $\hbar=1$. Equation (1) shows oscillations, and a reversible or ringing character. However, if the 2 sites provide smeared-out (rather than sharp) levels, i.e., if each site represents a group of an extremely large number of states as a result of bath interactions, the familiar procedure is to take for the evolution equation the Master equation, the rates of transfer between the sites F being given by the Fermi Golden Rule

$$F = 2V^2/\alpha \quad (2)$$

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addition to other proportionality constants. The result for the probability of the initially occupied site is then

$$P_0(t) = (\frac{1}{2})[1 + \exp(-2Ft)] \tag{3}$$

and shows a non-oscillatory decay and an irreversible approach to equilibrium in contrast to (1). Equation (1) depicts coherent motion, while equation (3) describes incoherent motion. It is clear that these motions have entirely different character relative to each other.

A more realistic system is an infinite linear chain wherein the exciton moves via nearest-neighbour matrix elements V in the coherent case and nearest-neighbour transport rates F in the incoherent case. The evolution equation for coherent motion is the Schrödinger equation for the amplitude $c_m(t)$:

$$i\frac{dc_m}{dt} = V(c_{m+1} + c_{m-1}) \tag{4}$$

To solve (4) one multiplies it by $\exp(ikm)$ and sums over all sites m , i.e., performs a discrete Fourier transform. This is a standard mathematical procedure for the solution of translationally invariant equations such as (4). Denoting the discrete Fourier transforms by superscripts k as in

$$c^k = \sum_m c_m e^{ikm} \tag{5}$$

the interconnected equations (4) are transformed into N unconnected equations for the individual c^k 's, where N is the number of sites in the crystal (infinite in the present case). Thus,

$$i\frac{dc^k}{dt} = (2V\cos k)c^k \tag{6}$$

with the immediate solution $c^k(t) = c^k(0)\exp(-i2Vt\cos k)$. If, initially, the exciton occupies a single site which, without loss of generality we shall call 0, the $c^k(0)$'s are all equal to 1 from Eq. (5). The inversion of (5) through

$$c_m(t) = (1/N) \sum_k \exp(-i2Vt\cos k) e^{-ikm} \tag{7}$$

and multiplication by the complex conjugate of c_m then give $P_m(t)$, the probability of occupation of site m . In the limit $N \rightarrow \infty$ the right hand side of (7) equals $(1/2\pi)$ times an integral over a continuous k -variable from $-\pi$ to π . One immediately obtains for this infinite chain,

$$P_m(t) = J_m^2(2Vt) \quad (8)$$

where J is the ordinary Bessel function. The probabilities exhibit oscillations as in (1), although the infinite size of the system considered destroys Poincaré recurrences evident in the 2-site result (1).

The evolution equation in the incoherent case is the Master equation

$$\frac{dP_m}{dt} = F(P_{m+1} + P_{m-1} - 2P_m) \quad (9)$$

rather than (4). This probability equation can also be solved with the use of discrete Fourier transforms. Proceeding as above,

$$P_m = (1/N) \sum_k \exp[-4Ft \sin^2(k/2)] e^{-ikm} \quad (10)$$

which is analogous to (7) in the coherent case and results in

$$P_m(t) = [\exp(-2Ft)] I_m(2Ft) \quad (11)$$

where I_m is the modified Bessel function. Unlike (8), this incoherent result shows a non-oscillatory decay.

The profound difference in the nature of the motion depicted respectively by the coherent probability propagators (8) and their incoherent counterparts (11) is also reflected clearly in the mean-square-displacement $\langle x^2 \rangle$. With a as the lattice constant, i.e., the distance between nearest neighbour sites on the linear chain, one has the general result

$$\langle x^2 \rangle = a^2 \langle m^2 \rangle = a^2 \sum_m m^2 P_m = -a^2 \left[\frac{d^2 P^k}{dk^2} \right]_{k=0} \quad (12)$$

The discrete Fourier transform of (8) is

$$P^k = J_0[4Vt \sin(k/2)] \quad (13)$$

whereas that of (11), which occurs in the process of the derivation of (11), is

$$P^k = \exp[-4Ft \sin^2(k/2)] \quad (14)$$

On combining (13), (14) with (12), one sees that the mean-square-displacement is bilinear in t for the coherent case,

$$\langle x^2 \rangle = (\sqrt{2}Va)^2 t^2 \quad (15)$$

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but linear in t for the incoherent case,

$$\langle x^2 \rangle = 2(Fa^2)t \quad (16)$$

The quantities in parentheses in (15) and (16) should be familiar from standard treatments. In the incoherent case, it is the diffusion constant of the exciton, $D = Fa^2$. In the coherent case it is the square of the average over the band of the group velocity of the exciton. To recover the latter result, observe that the $c^k(t)$'s in (6) are nothing other than amplitudes in the Bloch representation, and the factor $2V\cos k$ in the exponent in the solution of (6) is but the band energy E_k in the tight-binding scheme. The group velocity, given by a times the k -derivative of E_k , therefore has the band average $\sqrt{2}Va$.

Fig. 2 shows the self-propagator, i.e., P_0 , the probability of occupation of the initially occupied site for the purely coherent case and the completely incoherent case obtained respectively from (8) and (11). These plots as well as the expression (15) and (16) for the mean-square-displacement $\langle x^2 \rangle$ given above make clear the strong differences between coherent and incoherent motion. While we have seen that it is trivial to describe these two extreme limits, the construction of a unified framework to treat them both as well as the intermediate range presents a challenging problem. A result of the solution of this problem is seen in Fig. 2, where the intermediate self-propagator is also plotted for two given arbitrary degrees of coherence. The corresponding expression and its derivation will be found in IV. For now the form of the problem and the relevant questions should be amply clear. What is the general expression for the probability propagator which has the general unifying behaviour shown in Fig. 2 and which reduces to (8) for a system wherein the exciton does not suffer any scattering but to (11) when the scattering is so strong that the exciton motion has the aspect of a random walker? What is the general evolution equation whose respective limits are (4) and (9)? What is a practical prescription to extract the degree of coherence, i.e., the degree of the departure from the two extreme limits, for a given realistic crystal? What are the observable effects of this departure in practical experiments?

It is worth commenting in passing that the discrete Fourier transform technique explained above can be used to obtain explicit solutions in the case of long-range interactions V_{mn} or F_{mn} as well as for higher-dimensional systems. To treat the former one merely forms the Fourier transforms of V_{mn} or F_{mn} since translational invariance demands that the V 's or F 's are functions of the differences $m-n$, and proceeds exactly as shown in the case of nearest-neighbour transfer. The generalization to higher-dimensional crystals is also straightforward. The indices m, k , etc. then represent vectors of appropriate dimensionality and expressions such as km in

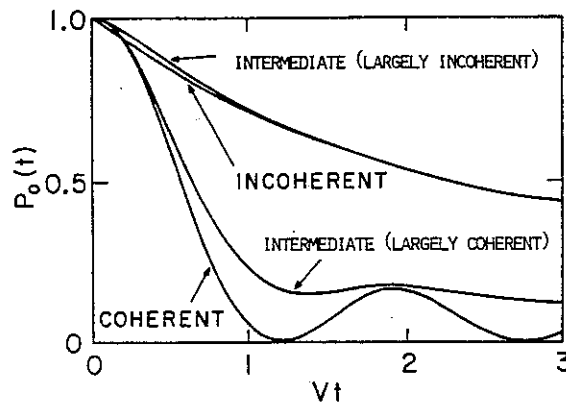


Fig. 2. The profound difference between coherent and incoherent motion shown through plots of the self-propagator, i.e., the probability of occupation of the initially occupied site, displayed as a function of (a dimensionless) time. Shown are the purely coherent case, the perfectly incoherent case and two intermediate cases, one being almost coherent and the other almost incoherent.

(5), (7), (10) represent dot products. Furthermore, for nearest-neighbour interactions in simple cubic lattices, allowing for arbitrary anisotropy, i.e., different V 's or F 's in different directions, the probability propagators P_m are simply products of the one-dimensional ones given in (8) and (11).

II. B. Motivation for the GME

The most natural and convenient solution of the unification problem posed in section II.A. is found in the method of the generalized master equation (GME). The essential characteristic of the GME is that it is non-Markoffian, i.e., an integro-differential equation with kernels which are non-local in time. These kernels, which are known as memory functions, give the GME its particular suitability for the analysis of the coherence-incoherence issue. In

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order to understand this suitability consider the two functions $y_c = \cos(wt)$ and $y_i = \exp(-Kt)$. The former oscillates and the latter decays. The single equation

$$\frac{dy(t)}{dt} + \int_0^t dt' z(t-t') y(t') = 0 \quad (17)$$

gives both y_c and y_i as solutions in the respective extreme limits $z(t) = w^2$ and $z(t) = K\delta(t)$ of the "memory kernel" $z(t)$. Furthermore, for an extremely large class of z 's the solution of (17) behaves like y_c and y_i at long times. To appreciate this quantitatively, take $z(t) = w^2 \exp(-\alpha t)$. One then has

$$\frac{d^2y}{dt^2} + \alpha \frac{dy}{dt} + w^2 y = 0 \quad (18)$$

which shows that one recovers from (17) y_c and y_i as extreme solutions for $\alpha \rightarrow 0$ and $\alpha \rightarrow \infty$, $w \rightarrow \infty$, $w^2/\alpha = K$ respectively. These correspond to the above two choices of the memory kernel z : a constant and a δ -function respectively. Also the solution of (17), i.e. of (18) behaves like y_c and y_i respectively for times which are much smaller than, and much larger than, $1/\alpha$. Equation (18) is only a special case of (17). Generally the time for comparison ($1/\alpha$ in the simple case of the exponential $z(t)$ corresponding to (17)) will be the characteristic time over which the kernel z decays. The initial value of z equals the square of the frequency of the oscillation of y_c while its time integral from $t=0$ to $t=\infty$ equals the decay constant of y_i . The unification of the oscillatory behaviour of the cosine and the decay behaviour of the exponential can thus be done with the help of (17).

We have seen the simplest possible example of the unification of oscillatory and decay behaviour via an evolution equation which is non-Markoffian. It should be immediately clear that such equations would be of value in the coherence-incoherence issue since oscillations and decay are indeed characteristic of coherent and incoherent motion respectively.

The above example corresponds to an actual physical system: the quantity y could be the amplitude of a damped harmonic oscillator with frequency w and damping constant α . Although this example does not contain site-to-site motion, one can easily include it by replacing $w^2 y$ in (18) by $-c^2 (\partial^2 y / \partial x^2)$. One now has the well-known wave equation and diffusion equation as the extreme (coherent and incoherent) limits which are unified by the single telegrapher's equation

$$\frac{\partial^2 y}{\partial t^2} + \alpha \frac{\partial y}{\partial t} = c^2 \frac{\partial^2 y}{\partial x^2} \quad (19)$$

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or what is the same, a memory-possessing diffusion equation with exponential memory. A perfect memory corresponds to wave-like behaviour with its oscillations and speed c , while a perfectly absent memory (a δ -function) to diffusive behaviour. The general solutions of (19) are well known to combine wave-like and diffusive behaviour. They exhibit transport coherence for times short with respect to the decay time of the memory and incoherence at large times.

All the power of evolution equations possessing memory functions would of course be useless to the issue under analysis if such equations were not natural to the exciton transport problem. In fact the telegrapher's equation (19) is of little direct use to excitons because the wave equation does not describe exciton motion in the coherent limit. The dispersion relation is quite different. However, memory-possessing evolution equations do turn out to be completely natural to exciton transport. Indeed they are actually unavoidable in the process of the derivation of the Master equation, the basis of Foerster's analysis of incoherent motion. We will therefore be able to harness their unification properties for the description of transport with arbitrary degree of coherence.

II.C. Derivation and Validity of the GME

Extensive details of the derivation and validity of the generalized master equation have been given in other reviews of the author [5,16] and will not be repeated here. Only a brief description follows.

The starting point for the evolution is the Von Neumann equation for ρ , the density matrix of the exciton along with whatever bath (phonons, imperfections, etc.) it is in interaction with. One defines projection operators P which diagonalize and coarsegrain the density matrix. The coarsegraining eliminates the bath coordinates and the diagonalization is in the representation of site-local states. Acting on the full density matrix ρ , the operator P thus yields a reduced probability vector which describes the probabilities of site occupation by the exciton. The procedure is exact, although it involves the elimination of the coordinates of a part of the total system - the bath - and although it involves only the diagonal part of the reduced density matrix. The Von Neumann equation is

$$i \frac{\partial \rho}{\partial t} = [H, \rho] = L\rho \quad (20)$$

where L is the Liouville operator which, acting on any operator, produces the commutator of the full Hamiltonian H with that operator. The respective application of the projection operator P and of its complement $(1-P)$ to (20), followed by the elimination of $(1-P)$ from the equation involving P through the simple substitution of the formal solution of $(1-P)$, gives

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$$\frac{dP\rho(t)}{dt} = - \int_0^t dt' PLe^{-i(t-t')(1-P)L}(1-P)L\rho(t') - iPLE^{-it(1-P)L}(1-P)\rho(0) \quad (21)$$

This equation is always exact. Furthermore, if the full density matrix at $t=0$ equals the projected density matrix, i.e., $\rho(0) = P\rho(0)$, the last term in (21) is zero at all times. One then has an evolution equation for $P\rho$, i.e., for the site-occupation probabilities of the exciton, which is closed in $P\rho$ (i.e., in the probabilities), and is non-Markoffian in nature. Since P has no off-diagonal elements in the site representation, the tetradics in (21) reduce to square matrices and one obtains the probability equation

$$\frac{dP_n(t)}{dt} = \int_0^t dt' \sum_n [w_{nm}(t-t')P_n(t') - w_{nm}(t-t')P_m(t')] \quad (22)$$

This is the generalized master equation.

The W 's are the memory functions. Their functional form depends on the extent of coarsegraining as well as on the interactions in the Hamiltonian. A detailed examination of how the memory functions vary on varying the level of coarsegraining may be found elsewhere [17]. What is important to realize is that, if the initial state is such that the last term in (21) vanishes, the GME is an exact consequence of microscopic dynamics. Even if the last term in (21) does not vanish at all times but does in some practical time range, the GME becomes exact in that time range. The GME is more general than the Master equation, the basis of traditional theories such as Foerster's, in that its W 's are not δ -functions. In fact the Master equation can be derived only when the approximation of replacing $W(t)$ by

$$\delta(t) \left[\int_0^\infty ds W(s) \right]$$

is made in the GME. To address the coherence issue, and to describe the exciton transport problem in a general way, one need merely refrain from making this approximation. The powers of non-Markoffian equations pointed out in section IIB are then at our disposal in an entirely natural manner.

The range of validity of the GME is decided by the validity of the passage from (21) to (22), i.e., the validity of neglecting the last term in the former. The condition $\rho(0) = P\rho(0)$ means, first, that the initial state is an outer product of an exciton state and a bath state and, second, that the exciton is initially site diagonal. The latter condition is extremely restrictive and would seldom apply

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in exciton physics since the creation of excitons usually involves optical absorption and, therefore, an initial state that is by no means localized. An initial Bloch state would be much more appropriate than an initial site-local state. Fortunately it can be shown [5,18] that a sufficient condition for the vanishing of the first term in (21) is that $L(1-P)\rho(0)=0$ rather than $(1-P)\rho(0)=0$. Initial Bloch state occupation or generally the initial occupation of a delocalized state does indeed result in $L(1-P)\rho(0)=0$ for crystals. The GME is thus valid for the practically occurring case of initially delocalized excitons as well as for initial localization.

To obtain the memory functions explicitly, it is necessary to evaluate the first term on the right hand side of (21). Some exact evaluations will be described in section III. Here we give the exact definition of the projection operator and a general approximate expression for the memory functions when the site-to-site interaction is small enough to be treated perturbatively.

The general definition of the projection operator P is

$$\langle \xi | P O | \mu \rangle = \left[\sum_{\xi \in m} \langle \xi | O | \xi \rangle \right] \left[\sum_{\xi \in m} 1 \right]^{-1} Q_{\xi} \delta_{\xi \mu} \quad (23)$$

where the ξ, μ are eigenstates of the full exciton-bath system, O is any operator, Q is arbitrary except for being subject to the condition

$$\sum_{\xi \in m} Q_{\xi} = \sum_{\xi \in m} 1$$

to ensure that P is idempotent. The summation of ξ in the "grain" m is the coarsegraining operation and involves the elimination of the bath coordinates. The Q 's do not affect the expressions for the memory functions in an exact calculation but do affect them in calculations involving approximations. If the Hamiltonian is $H_0 + V$, the part H_0 being site-diagonal, the memory functions are given perturbatively by

$$W_{mn}(t) = 2 \sum_{\xi \in m} \sum_{\mu \in n} [Q_{\mu} / g_n] |\langle \xi | V | \mu \rangle|^2 \cos[(E_{\xi} - E_{\mu})t] \quad (24)$$

$$W_{nm}(t) = 2 \sum_{\xi \in m} \sum_{\mu \in n} [Q_{\xi} / g_m] |\langle \xi | V | \mu \rangle|^2 \cos[(E_{\xi} - E_{\mu})t] \quad (25)$$

where $g_m = \sum_{\xi \in m} 1$ and $g_n = \sum_{\mu \in n} 1$.

Equations (24) and (25) are coarsegrained generalizations [16,17] of memory expressions given originally by Zwanzig [19].

II. D. Solut

If the dipole in n given by $1/R$ Rule is pro- tance deper- oscillations which is pr- often thoug- rates in the form of the rate versus was $1/R^6$ fo- theory in t- argue that- make the V- theory of tr- available [

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of excitons usually involves initial state that is by no means would be much more appropriate. Fortunately it can be done for the vanishing of the $\rho(0)=0$ rather than $(1-P)\rho(0)=0$. Usually the initial occupation is in $L(1-P)\rho(0)=0$ for crystal practically occurring case of sites for initial localization.

Explicitly, it is necessary to find side of (21). Some exact solution III. Here we give the generator and a general approximation when the site-to-site is perturbed.

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definition of ξ in the "grain" involves the elimination of the bath expressions for the exciton but do affect them in H_0 . If the Hamiltonian is $H_0 + H_{\mu}$ memory functions are given

$$[(E_{\xi} - E_{\mu})t] \quad (24)$$

$$[(E_{\xi} - E_{\mu})t] \quad (25)$$

regained generalizations usually by Zwanzig [19].

II. D. Solution of Foerster's Problem

If the interaction V responsible for exciton motion is dipole-dipole in nature, its dependence on the intersite distance R is given by $1/R^3$. The rate of transfer calculated through the Golden Rule is proportional to the square of V and has therefore the distance dependence $1/R^6$. However, if the motion is coherent, the oscillations of probability would be characterized by a frequency which is proportional to V at least for a two-site system. It was often thought, therefore, that the distance dependence of transfer rates in the coherent limit should be $1/R^3$. Foerster sharpened this form of the coherence question by presenting a plot of the transfer rate versus the intersite distance R . He stated that the dependence was $1/R^6$ for large R , i.e., for weak enough V for perturbation theory in terms of the Golden Rule to be valid, and that one might argue that the dependence was $1/R^3$ for small enough R which would make the V overwhelm the bath broadening. He further hoped that a theory of transfer rates which could bridge the two limits would be available [20].

The unification of transfer rates which Foerster had hoped for is possible in a natural way through the GME. No details of the memory functions are necessary. To stress the extreme simplicity of the argument, assume that the memory functions are of the separable form $W_{mn}(t) = F_{mn}\phi(t)$, the F 's being the transition rates in the corresponding Master equation, which one would arrive at on replacing $\phi(t)$ by a δ -function. One first realizes that it is necessary to define a transfer rate unambiguously and not merely take it to be a transition rate in one case and a frequency in the other. To that end one calculates the mean-square-displacement $\langle x^2 \rangle$ of the exciton for an initial localized condition, finds the time for which it becomes equal to the square of the lattice constant, and defines the reciprocal of that time as the rate of transfer w . Obviously this definition is sensitive to the time taken by the exciton to move one site irrespective of the degree of coherence. It is straightforward to see that this definition leads to

$$\frac{1}{w} = \frac{1}{t} \int_0^t dt \int_0^t dt' \phi(t') = \left[\sum_m m^2 F_m \right]^{-1} \equiv [\bar{m}^2]^{-1} \quad (26)$$

The unification is apparent from (26). For incoherent transfer is a δ -function, the first integration gives a constant and the rate w is proportional to \bar{m}^2 and for nearest neighbour F 's to R^{-6} . For coherent transfer ϕ is a constant, the first integration gives t , and w^2 is proportional to m^2 and thus the rate w is proportional to R^{-3} . To calculate an explicit expression for the R -dependence of the rate, assume a simple expression for $\phi(t)$ such as an exponential

$$\phi(t) = a e^{-at} \quad (27)$$

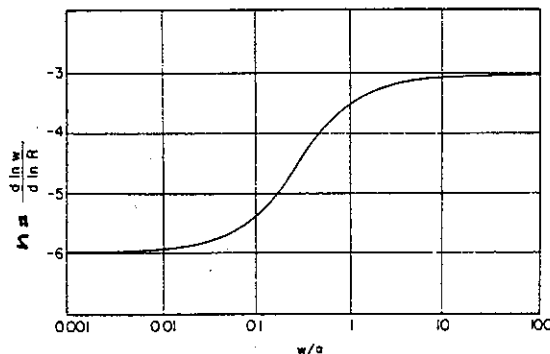


Fig. 3. The solution of Foerster's problem demonstrated through a plot of the exponent of R in the transfer rate for the case of dipolar interaction, as a function of the transfer rate in units of α . The inflection point is at $w/\alpha = 0.22$.

along with a simple expression such as $(2V^2/\alpha)(\delta_{m,n+1} + \delta_{m,n-1})$ for F_{mn} , representative of nearest-neighbour interactions on a linear chain. Substitution in (26) gives the implicit expression

$$(\alpha/w) + \exp[-(\alpha/w)] - 1 = (\alpha^2/2V^2) \tag{28}$$

With $V = \text{constant} \cdot R^{-3}$, a plot of the rate w versus the intersite distance R can be given from (28) and Foerster's problem solved explicitly [21]. In Fig. 3 is shown a plot of the exponent n in $w = \text{constant} \cdot R^n$, defined [21] as

$$n = \frac{d \ln w}{d \ln R} = 6 \left(\frac{w}{\alpha} - \frac{1}{1 - e^{-\alpha/w}} \right) \tag{29}$$

This plot has found use in analyzing excitation transfer in some biological systems [21,22].

II.E. General Remarks about the GME

The characteristic features of the GME are that it is an exact consequence of the microscopic dynamics for some initial conditions, that its memory functions may be obtained from knowledge of the microscopic interactions at least in principle, and that its non-Markoffian nature makes it especially adapted to the analysis of the coherence-incoherence issue. The structure of the GME approach is as follows. One calculates the memory functions of the GME from the microscopic interactions whenever possible. These calculations may be exact as is the case in a small number of model systems, or they may involve standard perturbation techniques. The memory functions may also be obtained in some cases directly from experimental

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observations which do not involve transport, an example being optical spectra. With the memory functions as an input, one calculates probability propagators. These appear directly in various experimental observables. A connection is thus established between memory functions and observables. Memory functions which are long-lived generally correspond to coherent motion and little or no bath interactions, although factors other than the latter also affect the decay. Rapidly decaying memory functions signal incoherent transport. The decay characteristics of the memories are reflected in the propagators and therefore in the observables. There are experiments such as the grating ones shown in Fig. 1d which probe directly the Fourier transforms of the propagators and are therefore highly sensitive to the degree of coherence in the system. While any realistic non-pathological system behaves coherently at short enough times and incoherently at long enough times, it is thus possible to measure the degree of coherence quantitatively by analyzing observations with the help of the GME framework outlined above.

III. MEMORY FUNCTIONS: EXPLICIT CALCULATIONS

III.A. Outline

Exact evaluation of the memory functions for a realistic system is obviously out of the question since such an evaluation would be tantamount to an exact solution of the dynamics of the full complex system. Model calculations are therefore undertaken as elsewhere in physics with the hope that in simplifying the mathematical problem the model does not sacrifice the essential features of the system under consideration. Such exact model calculations are to be found in III.B. and III.C. below. It is also necessary to perform approximate calculations of realistic systems which defy exact solution. Here the hope is that the approximation procedures employed do not destroy the essential features of the system. Section III.D. provides an example. An attractive result in the GME theory is that it is sometimes possible to obtain the memory functions for a real system directly from observations in a different realm. This is described in section III.E.

III.B. Exact Results for Pure Crystals

The general expression for the memory function $w_{mn}(t)$ for motion in a crystal of arbitrary dimensionality and size (but obeying periodic boundary conditions) is [5,23]:

$$w_{mn}(t) = -\int d\epsilon e^{\epsilon t} \sum_k \left\{ e^{-ik(m-n)} / \sum_q [\epsilon + i(\nu^k + q - \nu^q)]^{-1} \right\} \quad (30)$$

where the ϵ -integration is on the Bromwich contour, where m, n are direct lattice vectors, k, q are vectors in the first Brillouin zone

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of the reciprocal lattice of the crystal, km represents a dot product, the k and q summations are within the first Brillouin zone, and V is the discrete Fourier transform of the interaction matrix elements $V_{mn} = V_{m-n}$, the only peculiarity of the expressions relative to standard usage being that k, q, m, n are dimensionless in (30) as also elsewhere in this review.

Translational invariance, i.e., a true crystalline environment, is the only requirement to obtain (30). The proof is as follows. The Schroedinger equation for transport in the crystal is

$$\frac{dc_m(t)}{dt} = -i \sum_n V_{mn} c_n(t) \quad (31)$$

the site energies being taken to be zero without loss of generality. Equation (4) representing motion on a linear chain is a particular case of (31) and so is the 2-site equation whose solution leads to (1). Discrete Fourier transforms in the manner of section II.A. lead to the solution of $c^k(t)$ and thence through a Fourier inversion to $c_m(t)$. For the initial condition that the exciton occupies a single site, which we label zero, the solution gives, when multiplied by its complex conjugate,

$$P_m(t) = (1/N) \sum_{k,q} e^{-it(vk-vq)} e^{-im(k-q)} \quad (32)$$

If we define the quantities A_{mn} as equal to $-\omega_{mn}$ for $m \neq n$, with $A_{mm} = \sum_n \omega_{nm}$, the GME (22) takes on the form

$$\frac{dP_m(t)}{dt} + \int_0^t dt' \sum_n A_{mn}(t-t') P_n(t') = 0 \quad (33)$$

A discrete Fourier transform, a Laplace transform, and the initial condition stated above which leads to $P^k(0)=1$, yield from (33)

$$\tilde{A}^k(\epsilon) = [1/\tilde{P}^k(\epsilon)] - \epsilon \quad (34)$$

The calculation of the memory functions is now immediate on substituting the transform of (32) in (34) and using the relation

$$\tilde{\omega}^k(\epsilon) = -[\epsilon + \tilde{A}^k(\epsilon)] \quad (35)$$

which follows from the above definition of the A 's. The derivation of (32) is thus complete without the need to disentangle the projection operator expression (21).

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probability solutions which it is the function of the GME and of its
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it claims to obtain the $N(N-1)$ quantities w_{mn} from the N quantities
 P_m . The latter misconception is easily removed by observing that in
a translationally invariant system (which alone is under consider-
ation) the quantities w_{mn} are functions of $m-n$, there being thus
only N independent w 's or A 's. The other misconception will disap-
pear in section III.C. when this calculation will be put to use to
obtain results which are extremely hard to get without its help and
for which the probability solutions are certainly not known before-
hand.

Particular cases of the exact general result (30) are presented
in the table below. The interaction is characterized by the single
matrix element V in all cases and is of nearest-neighbour range in
all cases but the last one. In that last case the interaction is V
between any two sites. A system which can be said both to have such
a universal range in its interaction and to be of the nearest-
neighbour kind, as in the case of the others presented in the table,
is the trimer (3 sites). All the systems shown above obey periodic
boundary conditions, i.e., have no ends or surfaces. The crystals
being all pure (no bath interactions), the motion is perfectly
coherent in all cases.

The result for the dimer (2 sites) shows the constant memory
familiar from the pedagogical examples given in section II.A.
Introduction of bath interactions can indeed be shown to cause the
decay of this memory. In section III.C. we shall see that the

Table I

NO. OF SITES IN THE CRYSTAL	RANGE OF INTERACTION	MEMORY FUNCTIONS
2	-	$w_{12} = w_{21} = 2V^2$
3	-	$w_{12} = w_{23} = w_{31} = 2V^2 \cos(tV\sqrt{3})$
4	nearest-neighbour between sides 1 and 2, 2 and 3, 3 and 4, and 4 and 1.	$w_{12} = w_{23} = w_{34} = w_{41} =$ $2V^2 \cos(tV\sqrt{2})$ $w_{13} = w_{24} = 4V^2 \sin^2(tV\sqrt{2})$
linear chain)	nearest-neighbour	$w_{mn}(t) = \frac{1}{t} \frac{d}{dt} [J^2_{m-n}(2Vt)]$
N	equal among all sites	$w_{mn}(t) = 2V^2 \cos[tV\sqrt{N(N-2)}]$

exponential decay referred to in II.A. is quite physical in origin. However, it must not be concluded that coherent motion is always accompanied by constant memory functions. The result for the trimer already shows that the memory generally oscillates in the case of coherent motion. The frequency of this oscillation happens to be zero for a dimer. For crystals of finite size, true decay of memory functions does not occur unless some degree of incoherence is introduced. But the infinite chain result shows that the memories can decay even for purely coherent motion as a consequence of the destruction of Poincaré cycles brought about by the infinite size of the system. An alternative form of $w_{mn}(t)$ for the infinite linear chain is given below

$$w_{mn}(t) = 2V^2 [J^2_{m-n+1} + J^2_{m-n-1} + 2J_{m-n-1}J_{m-n+1} - 2J^2_{m-n} - J_{m-n}(J_{m-n+2} + J_{m-n-2})] \quad (36)$$

The J 's are all Bessel functions of argument $2Vt$.

III.C. Exact Results for an SLE

A transport equation that has often appeared [2,3,6,24] in the analysis of exciton motion as well as in other transport contexts is the stochastic Liouville equation (SLE). A form of the SLE is

$$\frac{\partial \rho_{mn}}{\partial t} = -i \sum_r (\tilde{V}_{mr} \rho_{rn} - \tilde{V}_{rn} \rho_{mr}) - (1 - \delta_{m,n}) \alpha \rho_{mn} + \delta_{m,n} \sum_r (\gamma_{mr} \rho_{rr} - \gamma_{rm} \rho_{mm}) \quad (37)$$

where ρ is the exciton density matrix; $m, n, \text{etc.}$, represent site-localized states as always in this review; \tilde{V} 's are the intersite interaction matrix elements; α represents scattering and is the rate at which the off-diagonal elements of ρ (in the m, n representation) decay; and the γ 's are additional rates of incoherent transfer. In microscopic derivations such as Silbey's [3], one naturally attaches the following meaning to these various quantities: \tilde{V} 's are proportional to the bandwidth of the exciton dressed with phonons, in other words to the bandwidth of the excitonic polaron; α arises from scattering of phonons and other sources; and the γ 's are phonon-assisted rates. An exact calculation of the memory functions appearing in the GME corresponding to (37) is possible [5,25] and leads to (22) with the w 's given by

$$w_{mn}(t) = w_{mn}^c(t) e^{-\alpha t} + \gamma_{mn} \delta(t) \quad (38)$$

In (38) the quantities w^c are the purely coherent memory functions corresponding to (37) in the absence of α and of the γ 's. The expression for them is given in (30) above.

The proof of operator manipulation rewrites the SLE as

$$i \frac{\partial \rho}{\partial t} = L_c \rho + \dots$$

where L_c represents coherent motion which describes the third term in the application of the application of the manner described in (21):

$$\frac{dP\rho(t)}{dt} = PL_a P$$

$$\times (1-P)$$

where we have dropped section II.C. With

$$0'' = (1-P)0$$

for any operator O

$$\{\exp[-it(1-P)]O\}$$

$$= [1 + (-it(1-P))O]$$

follows for any result is a consequence of off-diagonal operators when substituted in (38) follows complete contribution

This calculation is exact. It illustrates the usefulness of the operators about the usefulness of the solutions in the functions in the "assisted" transport such knowledge. and the γ 's do not appear and must (38) is obtained.

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ent memory functions and of the γ 's. The

The proof of (38) is facilitated by the introduction of some operator manipulations involving the projection operators P . One rewrites the SLE as

$$i\frac{\partial\rho}{\partial t} = L_c\rho + L_i\rho + L_a\rho \quad (39)$$

where L_c represents the first term in the right side of (37) which describes coherent motion, L_i represents the second term in (37) which describes the primary source of incoherence, and L_a represents the third term in (37) which describes the "assisted" transport. The application of the diagonalizing projection operator P to (39) in the manner described in section II.C. leads to a slightly modified form of (21):

$$\frac{dP\rho(t)}{dt} = PL_aP\rho(t) - \int_0^t dt' P(L_c+L_i)e^{-i(t-t')(1-P)(L_c+L_i)} \times (1-P)(L_c+L_i)P\rho(t') \quad (40)$$

where we have dropped the initial term involving $(1-P)\rho(0)$ as in section II.C. With the definition

$$O'' = (1-P)O \quad (41)$$

for any operator O , the identity

$$\{\exp[-it(1-P)(L_c+L_i)]\}O'' = [1+(-it)(L_c''-i\alpha) + \dots]O'' = e^{-\alpha t}\exp[-it(1-P)L_c] \quad (42)$$

follows for any off-diagonal operator O'' . This remarkably simple result is a consequence of the fact that $L_i'' = (1-P)L_i$, acting on any off-diagonal operator, merely multiplies it by $-i\alpha$. Equation (42) when substituted in (40), immediately produces the first term in the memory function result (38). The other part of the memory function in (38) follows directly from the term L_a in (40) and is the complete contribution of L_a .

This calculation of the memory functions for the SLE (37) is exact. It illustrates the method of direct computation with projection operators and clarifies the questions raised in section III.B. about the usefulness of the calculation of the coherent memories W^C . Although the latter are obtained from knowledge of the probability solutions in the coherent case, the result (38) for the full memory functions in the presence of the scattering α and of the "phonon-assisted" transport signified by the γ 's has been obtained without such knowledge. The probability solutions in the presence of the α and the γ 's do not bear a very simple relation to those in their absence and must be computed by solving the GME after the result (38) is obtained. On the other hand the memory functions in the two

cases are simply related. One merely multiplies the coherent memory functions by the exponential $e^{-\alpha t}$ and adds the δ -function terms $\gamma_{mn} \delta(t)$ to obtain the expression valid in the SLE case.

The physics underlying the SLE is that of the coexistence of two channels of transport: band or coherent transport represented by the V 's which is interrupted by scattering events controlled by α , and diffusion-type or incoherent transport represented by the γ 's. It is extremely satisfying that this coexistence is reflected so clearly in the expression for the memory function as a sum of two terms. The effect of scattering appears as a decay with time constant $1/\alpha$ superimposed on whatever time dependence the coherent memory function ω^c has. Such a clean separation of the contributions of the two scattering mechanisms also appears in transfer rates or diffusion constants obtained from the SLE [5,6] since they merely involve the integration of the memories from $t = 0$ to $t = \infty$.

III.D. Perturbative Evaluation for Linear Exciton-Phonon Coupling

The Hamiltonian H given by

$$H = E_0 \sum_m a_m^\dagger a_m + \sum_{m \neq n} V_{mn} a_m^\dagger a_n + \sum_q \omega_q b_q^\dagger b_q + \sum_{m,q} g_q \omega_q (b_q + b_{-q}^\dagger) a_m^\dagger a_m e^{iqm} \quad (43)$$

where a and b destroy respectively an exciton and a phonon, and where ω_q is the phonon frequency, is an important and useful model for the description of exciton transport in realistic systems. While the evaluation of memory functions is trivial when the exciton-phonon coupling term - the last term in (43) - is negligible or relatively small, the case when it dominates requires a transformation to be carried out prior to the application of a perturbative formula such as (24). The transformation [3,26] is designed to eliminate the coupling and it is said to dress the excitons with phonons, giving rise to excitonic polarons. The perturbative formula (24) is then applied to the residual interaction which is treated as a small quantity.

The transformation is given by the relation

$$Z = \left\{ \exp \left[\sum_{m,q} g_q (b_q - b_{-q}^\dagger) a_m^\dagger a_m e^{iqm} \right] \right\} z \left\{ \exp \left[- \sum_{m,q} g_q (b_q - b_{-q}^\dagger) a_m^\dagger a_m e^{iqm} \right] \right\} \quad (44)$$

where Z is the transformed operator corresponding to any operator z . It gives rise to the excitonic polaron operators A_m given by

$$A_m = a_m \exp \left[- \sum_q g_q (b_q - b_{-q}^\dagger) e^{iqm} \right] \quad (45)$$

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the coherent memory δ -function terms E case.

the coexistence of transport represented by excitons controlled by the presence is reflected in action as a sum of a decay with time of the coherent n of the contribution appears in transfer E [5,6] since they from $t = 0$ to $t = \infty$.

Exciton-Phonon Coupling

(43)

and a phonon, and t and useful model realistic systems. ideal when the excitation is negligible or requires a transformation of a perturbative [26] is designed to the excitons with perturbative form interaction which is

$$\sum_q (b_q - b_q^\dagger) a_m^\dagger a_m e^{iqm} \quad (44)$$

to any operator z_m given by

(45)

Their form obviously justifies the statement that the polaron consists of the bare particle surrounded by a cloud of phonons. The new (displaced) phonon operators B_q are given by

$$B_q = b_q + \sum_m g_q a_m^\dagger a_m e^{-iqm} \quad (46)$$

The Hamiltonian H is now expressed as

$$H = \sum_m [E_0 - \sum_q g_q^2 \omega_q] A_m^\dagger A_m + \sum_q \omega_q B_q^\dagger B_q + \sum_{m \neq n} V_{mn} A_m^\dagger A_n e^{i q m} e^{-i q n} \quad (47)$$

where

$$\alpha_m = \sum_q g_q (b_q - b_q^\dagger) e^{iqm}.$$

Application of the perturbative formula (24) with the last term of (47) as the perturbation leads [27] in the case of a dimer to the memory function expression

$$W_{mn}(t) = 2|V_{mn}|^2 \exp\left\{-\sum_{r,s} [h_{rs}(t) - h_{rs}(0)]\right\} \quad (48)$$

where r and s each take the values m and n, and h_{rs} is given by

$$h_{rs}(t) = -\sum_q 4g_q^2 \sin^2 q(r-s) [N_q e^{i\omega_q t} + (N_q + 1)e^{-i\omega_q t}] \quad (49)$$

N_q being the average number of phonons given by the Bose distribution $[\exp(\omega_q/k_B T) - 1]^{-1}$.

Equation (48) is the generalization of the pure dimer results displayed in the table of section III.B. to the case of exciton-phonon interactions as described in the Hamiltonian of (43) or (47).

III.E. Evaluation from Spectra

The rate of transfer F_{mn} for singlet exciton transport is given by the theories of Foerster [15] and Dexter [28] in a form which is extremely convenient from a practical point of view. In these theories the F's are proportional to the spectral overlap of the emission of the donor and the absorption of the acceptor. The great advantage of such a prescription is that, when valid, it allows one to bypass model calculations and assumptions and to connect exciton transport directly to another experimental realm, viz, optical spectra. In situations wherein the Foerster-Dexter mechanism of transport is valid but the Master equation formalism underlying the Foerster-Dexter theory is not, the memory functions can be obtained through a simple generalization [5,29] of their prescription. The generalization is based on the fact that an expression such as (24) for the memory function is a straightforward generalization of the

corresponding Golden Rule expression for the transfer rates F:

$$F_{mn} = 2\pi \sum_{\xi \in \mu} \sum_{\eta \in n} [Q_{\mu}/g_n] |\langle \xi | V | \eta \rangle|^2 \delta(E_{\xi} - E_{\mu}) \quad (50)$$

The only difference between (24) and (50) is that $\cos(E_{\xi} - E_{\mu})t$ appears in the former where $\pi\delta(E_{\xi} - E_{\mu})$ appears in the latter. Indeed the latter can be obtained from (24) by replacing each cosine by a δ -function in t , times the integral from $t=0$ to $t=\infty$ of the cosine. This is the Markoffian approximation necessary to convert the GME into the ordinary Master equation and is responsible for the fact that, while the GME is able to describe transport at short times, the Master equation is not. To gain the capability of providing a short-time (i.e. coherence) description while retaining the basic mechanism of transfer, one need therefore make only the necessary modifications in the Foerster-Dexter formula and obtain

$$W_{mn}(t) = \text{constant} \cdot \frac{1}{R_{mn}^6} \int_{z=-\infty}^{+\infty} dz \cos(zt) \int_{\omega=0}^{\infty} d\omega \frac{A(\omega-z)E(\omega+z)}{(\omega-z)^3(\omega+z)} \quad (51)$$

The constant factor in (51) is unimportant for the present discussion. The quantities A and E are the absorption and emission spectra respectively and R is the intersite distance, the sixth power being characteristic of the dipole-dipole interaction. The prescription implied by (51) is as follows. One obtains F_{mn} as given by the Foerster-Dexter prescription, renames it $f_{mn}(0)$, recalculates it after displacing the two spectra on the frequency axis by $z/2$ and

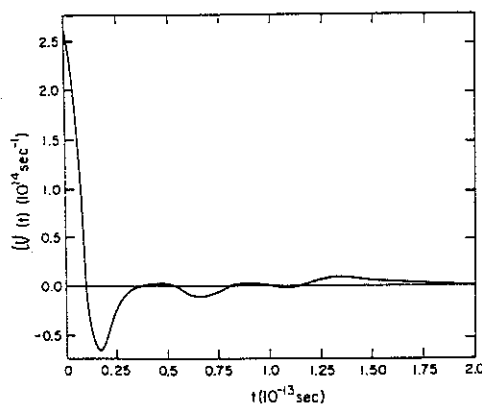


Fig. 4. The time dependence of the memory function for exciton transport among anthracene molecules in cyclohexane solution at room temperature obtained from the spectral prescription of (51). Ordinates are chosen in a way to normalize the memory function.

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$$-E_{\mu}) \quad (50)$$

is that $\cos(E_{\xi} - E_{\mu})t$ appears in the latter. Indeed the sine each cosine by a δ -function from $t=0$ to $t=\infty$ of the cosine. It is necessary to convert the GME into a form responsible for the fact that transport at short times, the capability of providing a reliable method of retaining the basic information to make only the necessary calculations and obtain

$$f_{mn}(z) = \int_{\omega=0}^{\infty} d\omega \frac{A(\omega-z)E(\omega+z)}{(\omega-z)^3(\omega+z)} \quad (51)$$

for the present discussion of absorption and emission at a site distance, the sixth order dipole interaction. The

One obtains F_{mn} as given in eq. (51) as it $f_{mn}(0)$, recalculates the frequency axis by $z/2$ and

$-z/2$ respectively, renames the results $f_{mn}(z)$ and repeats for all values of z . The Fourier cosine transform of the function $f_{mn}(z)$ thus obtained is the memory function $W_{mn}(t)$.

An intimate relation thus exists between spectra and memory functions. Narrow spectra generally correspond to long-lived memories and therefore to coherent behaviour in the transport whereas broad interactions cause incoherence as well as spectral broadening. Well-known restrictions exist on the applicability of the Foerster-Dexter theory, particularly when inhomogeneous broadening is important. These restrictions have been discussed elsewhere in this book and must certainly not be ignored in the use of the above procedure. However, when the restrictions do not apply, (51) provides a direct method of extracting memory functions from experiment. As an example of the application of (51), Fig. 4 shows the time-dependence of the memory function for exciton motion from one anthracene molecule to another in cyclohexane solution at room temperature.

IV. CALCULATION OF OBSERVABLES

IV.A. Prelude: Calculation of Propagators

The previous sections of this article have set up the basic evolution equation, the GME, and shown how its memory functions are obtained. Now we shall use that equation to address experiment. Of central relevance to the experimental quantities, particularly in the context of the experiments described schematically in Fig. 1, are the probability propagators ψ , which are nothing other than special solutions of the GME for initially localized conditions or, what is the same, the Green functions of the GME. Thus, by $\psi_m(t)$ is meant the probability that the exciton occupies the site m at time t , given that it occupied site 0 and time 0. Although for a disordered system with no translational invariance, the propagator would depend explicitly both on the site of initial occupation and that of later interest, the crystalline nature of our system makes the propagator a function of the single index m , the difference between the indices representing the two locations in question. Some of the observations require knowledge of $\psi_m(t)$, while others are related to its discrete Fourier transform $\psi^k(t)$ and yet others probe their respective Laplace transforms $\psi_m(\epsilon)$ and $\psi^k(\epsilon)$. Thus, the grating experiments depicted in Fig. 1d are directly sensitive to the time dependence of the propagator in the Fourier domain, i.e., to $\psi^k(t)$ and the capture experiments shown in Fig. 1b probe the self-propagator in the Laplace domain, i.e. $\psi_0(\epsilon)$. The GME itself is an integro-differential difference equation with a variable upper limit and a difference t -kernel in the time integration. The t -structure of the equation suggests the use of the Laplace transform for its solution while the crystalline nature, i.e., the properties in m,n -space, suggest the discrete Fourier transform.

memory function for exciton motion in cyclohexane solution from the spectral pre-chosen in a way to nor-



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Thus, purely calculational considerations focus one's attention on the propagator in the Laplace and Fourier domain. It is a delightful accident that some of the experiments probe the transformed propagators directly and thereby save the theorist the often troublesome - and always tedious - task of inverting the transforms.

One begins then with the GME (22) and uses the procedure already outlined in section III.A.: One calculates the $\tilde{A}_{mn}(t)$'s from the memory functions $W_{mn}(t)$'s, obtains the Fourier transform $\tilde{A}^k(t)$, and uses its Laplace transform in the following general relation between propagators and memory functions which is a trivial consequence of the GME itself:

$$\tilde{\psi}_m(\epsilon) = (1/2\pi)^d \int d^d k e^{-i k m} [\epsilon + \tilde{A}^k(\epsilon)]^{-1} \quad (52)$$

Here d is the number of dimensions of the crystal, taken to be infinite in extent, and the integration is in d -dimensional k -space. In arriving at (52) one also encounters the propagator in the Fourier domain:

$$\tilde{\psi}^k(\epsilon) = [\epsilon + \tilde{A}^k(\epsilon)]^{-1} \quad (53)$$

Equations (52) and (53) show how the various characteristics that memory functions possess enter into the behaviour of the propagators, i.e., the solutions of the GME, and therefore into that of observable quantities. Thus, if the memory functions are short-lived, the \tilde{A} 's are largely constant in ϵ -space, the $\tilde{\psi}^k$'s are exponential, and the behaviour of the ψ_m 's is the same as from a Master equation. It exhibits no coherence. For highly coherent systems on the other hand, \tilde{A} 's are far from constant in ϵ -space, the time dependence of the propagators is profoundly different from that of solutions of a simple Master equation and can indeed exhibit oscillations characteristic of coherence.

In order to study the effects of coherence on observables we shall choose the simplest possible evolution capable of describing exciton transport of arbitrary degree of coherence. It has the form

$$\frac{\partial \rho_{m n}}{\partial t} = -iV(\rho_{m+1 n} + \rho_{m-1 n} - \rho_{m n+1} - \rho_{m n-1}) - (1-\delta_{m,n})\alpha \rho_{m n} \quad (54)$$

It was first used for exciton transport by Avakian et al. [30] and can be considered to be a particular case of the SLE (37). In the absence of the scattering α , the off-diagonal elements of the density matrix do not decay and the motion of the exciton is purely coherent. The evolution is exactly the same as that of (4) if the system is taken to be a linear chain, and the propagators are given by (8). One can show that, if the scattering is very large and justifies the limit $\alpha \rightarrow \infty$, $V \rightarrow \infty$, $2V^2/\alpha = F$, (54) reduces to the Master equation (9) and the motion is perfectly incoherent. The

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underlying picture in (54) is "band motion" with a bandwidth proportional to V and scattering at the rate α . This can be made particularly clear by transforming (54) to k -space. The diagonal part of ρ in the k -representation follows the "Boltzmann" equation

$$\frac{\partial \rho^{kk}}{\partial t} = (\alpha/N) \sum_q (\rho^{qq} - \rho^{kk}) \quad (55)$$

which shows scattering with equal scattering rates (α/N) among all k -states, N being the number of sites in the crystal.

It is possible, in principle, to analyze the observables with any GME with any degree of complexity by following the procedure outlined earlier. However, to understand the coherence issue, it is important not to be distracted by other elements of the evolution which are not essential to the issue. All the calculations in this section will be made, therefore, from (54). The GME corresponding to (54) has the memory functions [5]

$$W_{mn}(t) = \left[\frac{1}{t} \frac{d}{dt} J_{m-n}^2(2Vt) \right] e^{-\alpha t} \quad (56)$$

as is clear from (36). The corresponding $\tilde{A}^k(\epsilon)$ is given by

$$\tilde{A}^k(\epsilon) = [(\epsilon + \alpha)^2 + 16V^2 \sin^2(k/2)]^{1/2} - \epsilon \quad (57)$$

The discrete Fourier transform of the square of the ordinary Bessel function with respect to the space index is given quite simply. Thus

$$\sum_{m=-\infty}^{+\infty} J_m^2(x) e^{ikm} = J_0(2x \sin |k/2|) \quad (58)$$

It is this simple result that allows the effortless passage from (56) to (57). Equation (53) yields, on Laplace inversion,

$$\psi^k(t) = e^{-\alpha t} J_0(bt) + \int_0^t du c e^{-\alpha(t-u)} J_0(b\sqrt{t^2-u^2}) \quad (59)$$

where $b = 4V \sin |k/2|$. The derivation of (59) uses a well-known theorem in Laplace-transform theory which allows inversion of transforms of the form $\tilde{f}[(\epsilon^2 + c^2)^{1/2}]$ in terms of known transforms of $f(\epsilon)$. Here f is any function and c is some ϵ -independent quantity. To obtain the real-space propagators one must evaluate the Fourier-inverse of (59). For this purpose one uses (58) in reverse. Then

$$\psi_m(t) = J_m^2(2Vt) e^{-\alpha t} + \int_0^t du e^{-\alpha(t-u)} J_m^2(2V\sqrt{t^2-u^2}) \quad (60)$$

Equations (59) and (60) constitute the solutions of the GME

corresponding to (54) and, with their counterparts in the Laplace domain, enter directly into the description of experimental observables. They exhibit oscillations when the degree of coherence is high, i.e., when α is small, and show incoherent behaviour when α is large. The former case is obtained trivially by taking the limit of small α in (59), (60); the latter is obtained by expressing the square root in (57) in the form of a Binomial expansion and retaining the lowest power of V/α . The cases (13) and (14) are thus recovered as extreme limits of (60). The solutions for intermediate degree of coherence displayed along with those extreme limits in Fig. 2 are given by (60).

IV.B. Application to Grating Experiments

The grating experiment of Fig. 1d consists of creating a periodic inhomogeneity in the spatial distribution of the excitons and measuring the time evolution of that inhomogeneity [31]. The spatial inhomogeneity is produced simply by covering the crystal with an array of alternating opaque and transparent strips during illumination. The excitons under study are triplets. The measurement of the time evolution can therefore be made by monitoring the delayed fluorescence which arises as a result of the formation of singlets through the mutual annihilation of the triplets. It is possible to make the illumination strength small enough to make the annihilation a negligible perturbation on the evolution of the exciton distribution and yet large enough to make the signal clearly discernible. The characteristics of the motion of the excitons is reflected in the time dependence of the delayed fluorescence. Exponential decay after illumination would be typical of incoherent motion. Oscillatory features would characterize a high degree of coherence.

The evolution equation is the GME (22) corresponding to (54) but with its right hand side augmented by two terms: a radiative term $-P_m(t)/\tau$ where τ is the exciton lifetime and a term $S_m(t)$ which describes the spatial and temporal dependence of the illumination. The former term merely multiplies the GME solutions by $\exp(-t/\tau)$, or replaces ϵ in the Laplace domain by $\epsilon' = \epsilon + 1/\tau$. The source term $S_m(t)$ introduces an additional driven contribution in the solution. Thus the solutions in the Laplace domain are now

$$\tilde{P}_m(\epsilon) = \sum_n \tilde{\psi}_{m-n}(\epsilon') P_n(0) + \sum_n \tilde{\psi}_{m-n}(\epsilon') \tilde{S}_n(\epsilon) \tag{61}$$

The Ronchi grating experiment consists of three parts. In the build-up part, in which the delayed fluorescence signal builds up to its saturation value, $P_n(0)$ is identically zero as there are no excitons initially, and (61) gives, through the Fourier transform,

$$\tilde{p}^k(\epsilon) = (1/\epsilon) i_0 g^k \tilde{\psi}^k(\epsilon') \tag{62}$$

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Here the illumination is switched on to a constant value which, when multiplied by the appropriate absorption coefficient, equals i_0 , and has a spatial dependence g_m characteristic of the ruling geometry. The second part of the experiment is concerned with the steady-state-value of the signal. The limit of $P^k(t)$ as $t \rightarrow \infty$ is given from (62) as

$$\lim_{t \rightarrow \infty} P^k(t) = i_0 g^k \tilde{\psi}^k(1/\tau) \quad (63)$$

The third part of the experiment consists of observing the time dependent decay of the signal from the steady state value. To calculate this decay, one returns to (61). There is no driving term S now, but the $P_n(0)$ are given by (63). Thus, for the decay

$$\tilde{P}^k(\epsilon) = [i_0 g^k \tilde{\psi}^k(1/\tau)] \tilde{\psi}^k(\epsilon') \quad (64)$$

It suffices for illustrative purposes to study only this decay stage (64). We see that, except for the time-independent quantity in the square brackets in (64), the probability solution is given in the time domain by $\exp(-t/\tau)$ times that given in (59) above.

The measured quantity is the delayed fluorescence signal which is proportional to

$$\sum_m [P_m(t)]^2$$

and therefore to

$$\sum_k P^k(t) P^{-k}(t)$$

following a standard Fourier result. It is therefore clear that, if the illumination were to excite a single Fourier component k , the delayed fluorescence signal would be given essentially by squaring the result (59) for $\psi^k(t)$. It is thus that the grating experiment contains a direct probe of the time dependence of the Fourier transform of the propagator.

The actual Ronchi grating experiment does not populate a single Fourier component but several ones with amplitudes given by the Fourier transform of the square wave, since a mask is employed. The expression for g_m and, therefore, for g^k in (62)-(64) is written down trivially. Straightforward calculations [32] lead then to explicit expressions for the normalized decay signal of delayed fluorescence. Careful experimentation requires that this signal be subtracted from one in the absence of the mask in order to eliminate spurious contributions. The difference signal thus obtained is given by $\Delta\phi(t)$ with

$$\Delta\phi(t) = e^{-2t/\tau} E(t) \tag{65}$$

$$E(t) = [1 + \sum_{\ell=1}^{\infty} A_{\ell}]^{-1} [\sum_{\ell=1}^{\infty} A_{\ell} [\psi^{k_{\ell}}(t)]^2 - 1] \tag{66}$$

$$A_{\ell} = 8[\pi^2(2\ell-1)^2]^{-1} [(1/\tau)\tilde{\psi}^{k_{\ell}}(1/\tau)]^2 \tag{67}$$

The quantity k_{ℓ} appearing in (61)-(63) is the dimensionless wave-vector given by

$$k_{\ell} = 2\pi(a/x_0)(2\ell-1) \tag{68}$$

with a as the lattice constant of the crystal and x_0 as the period of the ruling, i.e., of the mask. The dynamics of the exciton is reflected in the ψ 's appearing in (66) and (67). The grating period decides which Fourier components appear in the expression.

The time dependence of $E(t)$, equivalently that of the delayed fluorescence difference signal which differs from $E(t)$ only by the factor $\exp(-2t/\tau)$, is completely controlled by the time dependence of the Fourier transform of the propagator. For incoherent motion the latter is an exponential as given by (14) and $-E(t)$ rises from 0 to the value

$$[1 + \sum_{\ell} A_{\ell}]^{-1} [\sum_{\ell} A_{\ell}]$$

monotonically. For purely coherent motion, i.e., when the exciton suffers no scattering, $-E(t)$ rises in an oscillatory fashion. The

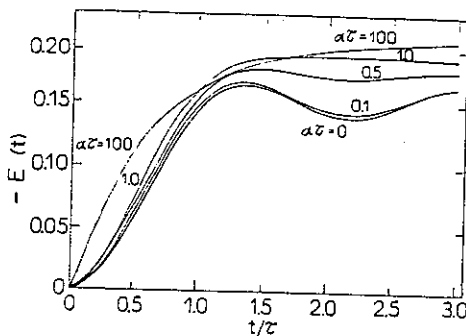


Fig. 5. The delayed fluorescence signal for the decay stage of the Ronchi ruling experiment times the factor $\exp(2t/\tau)$ plotted as a function of time for several degrees of exciton coherence. The effect of coherence is seen in the characteristic shape near the origin and in oscillations. See equation (66).

spatial incoherence but overshoot. Fig. 5 shows a typical example of the exciton

The measured oscillations exponential oscillations manifested a - of the thin crystals had discernible quantities extreme limit values exciton transport length l_T is the well-known by [32]

$$l_T = 2a$$

Fig. 6. De delayed fluorescence signal as a function of time for several degrees of exciton coherence. The effect of coherence is seen in the characteristic shape near the origin and in oscillations. See equation (66).

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spatial inhomogeneity disappears monotonically in the former case but overshooting with resultant oscillations occurs in the latter. Fig. 5 shows the evolution of $-E(t)$ for various degrees of coherence typified by several values of $\alpha\tau$. The latter parameter is the ratio of the exciton lifetime to the time between scattering events.

The measured quantity is $\Delta\phi(t)$ rather than $E(t)$. The clear oscillations seen in $E(t)$ are not always seen in $\Delta\phi(t)$ because the exponential factor in (65) generally suppresses them. However, oscillations are not the only characteristic of coherence. It is manifested also in the shape near the origin - concave versus convex - of the time dependence. Quantitative analysis for representative crystals has shown [32] that this latter effect would be quite discernible in realistic systems. Fig. 6 shows the actual measurable quantity $-\Delta\phi$, rather than the quantity $E(t)$, plotted for the extreme limits of pure coherence and complete incoherence for several values of the quantity, l_T/x_0 , which is the ratio of the exciton transport length l_T to the ruling period x_0 . The transport length l_T is a generalization, to arbitrary degree of coherence, of the well-known diffusion length. For the present system it is given by [32]

$$l_T = 2a (V/\alpha)(\alpha\tau - 1 + e^{-\alpha\tau})^{1/2} \tag{69}$$

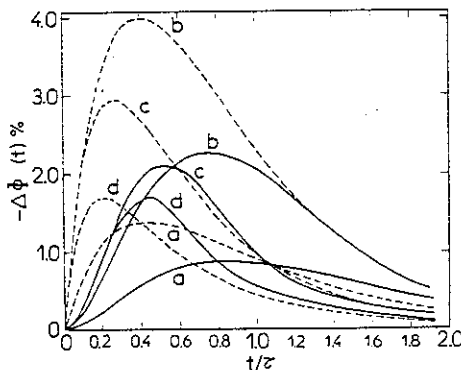


Fig. 6. Delayed fluorescence decay signal $-\Delta\phi(t)$ plotted as a function of the dimensionless time t/τ for the extreme cases of pure coherence and complete incoherence. Curves a, b, c, d, refer, respectively, to the values 0.05, 0.15, 0.35, 0.45 of l_T/x_0 , the ratio of the transport length to the ruling period. Solid lines represent the purely coherent case, and the dashed lines the completely incoherent case. Curves of the latter kind have been already observed experimentally [31].

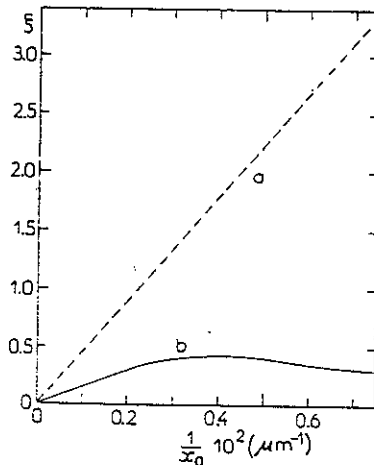


Fig. 7. Plot vs $(1/x_0)$, the spatial frequency of the rulings, of the dimensionless quantities $\xi_{coh} = 2\pi\sqrt{2}(\ell_T)_{coh}/x_0$ for the purely coherent case (curve a) and $\xi_{inc} = \pi\sqrt{2}(\ell_T)_{inc}/x_0$ for the completely incoherent case (curve b), as obtained by graphically inverting the relevant expressions for the same "observed" signal $-\Delta\phi(t)$. The latter is obtained by fitting curves such as those in Fig. 6. The straight-line behaviour a indicates that the correct theory has been used to interpret the measurements. The clear departure of curve b from straight-line behaviour shows that the theory used for b is incorrect. The straight line a corresponds to a transport length $\ell_T=50 \mu m$.

The measurable shown in Fig. 6 is quite different in the coherent and incoherent cases. Attempts to fit one with any of a family of curves of the other kind show [32] such poor results that experimental differentiation would be quite unambiguous. We exhibit this consequence graphically in Fig. 7.

The question of coherence has been debated for a long time in the literature. However, clear experimental methods for its measurement have not been developed. A careful study along the lines outlined in the present section has recently shown [32-34] that the Ronchi grating experiment is an excellent candidate for this task. This had not been realized earlier, although grating experiments have had a long history [31]. It is expected that such experiments will be carried out in the near future.

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IV.C. Capture Experiments

The capture experiment represented by Fig. 1b employs homogeneous bulk illumination of the host crystal under study which is doped with guest molecules. These capture the excitons moving in the host and luminesce at a frequency different from that of the host. Monitoring the luminescence from the host and/or guest allows one to measure exciton motion in the host. An enormous amount of information has been gathered over the years through the use of this technique [9,13,35,36].

The evolution equation is the GME (22) once again with two terms appended to its righthand side: $-P_m(t)/\tau$ to describe decay as in IV.B. and a term which represents capture by the guests or traps. The simplest form of the latter term is

$$-c \sum_r P_r \delta_{m,r}$$

and means that whenever the exciton is at one of the trap-influenced host sites r (over which the primed summation runs), its probability decays into the trap from the host at rate c . To solve the GME with these terms, a new mathematical technique needs to be introduced. This is the defect technique of Montroll [37]. The Laplace transform of the augmented GME gives an equation similar to but different from (61)

$$\tilde{P}_m(\epsilon) = \tilde{\eta}_m(\epsilon') - c \sum_r \tilde{\psi}_{m-r}(\epsilon') \tilde{P}_r(\epsilon) \quad (70)$$

Here, as in (61), $\epsilon' = \epsilon + 1/\tau$ and η is the homogeneous solution, i.e., the first term on the righthand side of (61).

The experimental observable is the total illumination intensity which is proportional to

$$n_H(t) = \sum_m P_m(t),$$

the probability that the host is excited. Summation of (70) over all host sites m gives

$$\tilde{n}_H(\epsilon) = \frac{1}{\epsilon'} [1 - c \sum_r \tilde{P}_r(\epsilon)] \quad (71)$$

and shows that n_H is simply related to the probability that the trap-influenced host region is excited. However, the latter cannot be generally evaluated since, from (70),

$$\sum_r \tilde{P}_r(\epsilon) = \frac{\rho}{\epsilon'} - c \sum_s \tilde{v}_s(\epsilon') \tilde{P}_s(\epsilon) \quad (72)$$

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where the initial illumination has been assumed explicitly homogeneous as in usual experiments, where ρ is the trap concentration, i.e., the ratio of the trap-influenced host sites to the total number of host sites, and ν is defined as

$$\nu_s(t) = \sum_r \psi_{r-s}(t) \quad (73)$$

An exact evaluation is possible for small ρ since then one can use the single-trap solution of (71)-(73). The ν -function is then equal to the self-propagator $\psi_0(t)$ and (71) is easily evaluated. An important observable is the steady-state yield ϕ_H defined as the ratio of the number of photons emerging radiatively from the host to that put initially through illumination and is given by

$$\phi_H = (1/\tau) \int_0^\infty dt n_H(t) = [\tilde{n}_H(\epsilon)]_{\epsilon=0} \quad (74)$$

for the simple case when the radiative lifetime equals the total lifetime. For the single-trap case one gets

$$\phi_H = 1 - \frac{\rho\tau}{(1/c\tau) + (1/\tau)\tilde{\psi}_0(1/\tau)} \quad (75)$$

Thus, in the capture experiment, characteristics of exciton motion influence the observable, in this case ϕ_H , through the self-propagator $\tilde{\psi}_0(1/\tau)$. To study the effect of coherence, (60) may be used as in IV.B. The propagator to be calculated is the $m=0$ case of (60) evaluated in the Laplace domain. The result is [38]

$$\begin{aligned} \tilde{\psi}_0(\epsilon) = & \frac{\alpha}{[\epsilon^2 + 2\epsilon\alpha](\epsilon^2 + 2\epsilon\alpha + 16V^2)^{1/2}} + \frac{(2/\pi)}{[(\epsilon + \alpha)^2 + 16V^2]^{1/2}} K(k) \\ & + \frac{1}{[(\epsilon + \alpha)^2 + 16V^2]^{1/2}} \cdot \frac{(2/\pi)}{(\epsilon^2 + 2\epsilon\alpha + 16V^2)^{1/2}} \Pi(a_1^2, k) \end{aligned} \quad (76)$$

where

$$a_1^2 = 16V^2(\epsilon^2 + 2\epsilon\alpha + 16V^2)^{-1}, \quad (77)$$

$$k = 4V[(\epsilon + \alpha)^2 + 16V^2]^{-1/2} \quad (78)$$

and K and Π are elliptic integrals of the first and third kinds respectively defined through

$$K(b) = \int_0^1 dx (1-x^2)^{-1/2} (1-b^2x^2)^{-1/2} \quad (79)$$

$$\Pi(a_1^2, b) = \int_0^1 \frac{dx}{(1-x^2)^{1/2} (1-b^2x^2)^{1/2}}$$

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$$\Pi(a_1^2, b) = \int_0^1 dx (1-x^2)^{-\frac{1}{2}} (1-b^2x^2)^{-\frac{1}{2}} (1-a_1^2x^2)^{-1} \quad (80)$$

In the coherent limit $\alpha \rightarrow 0$, (76) gives

$$(1/\tau)\Psi_0(1/\tau) = (2/\pi) (1+16V^2\tau^2)^{-\frac{1}{2}} K[(4V\tau(1+16V^2\tau^2)^{-\frac{1}{2}})] \quad (81)$$

(73)

whereas in the incoherent limit $\alpha \rightarrow \infty$, $V \rightarrow \infty$, $2V^2/\alpha = F$, one has

$$(1/\tau)\Psi_0(1/\tau) = (1+4F\tau)^{-\frac{1}{2}} \quad (82)$$

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For exciton transport $V\tau \gg 1$ and $F\tau \gg 1$ usually applies: the excitons cover a distance of many lattice constants before they die. It is then possible to express (81) and (82) more simply. The elliptic integral reduces to a logarithmic expression and (81) gives

$$(1/\tau)\Psi_0(1/\tau) \approx (1/4\pi V\tau) \ln(256V\tau) \quad (83)$$

(74)

as the key quantity in this experiment for coherent transport. On the other hand, for incoherence, (82) gives

$$(1/\tau)\Psi_0(1/\tau) \approx 1/(2\sqrt{F\tau}) \quad (84)$$

(75)

These results show that the quantity examined by these capture experiments is ℓ_T/a , the ratio of the transport length (see (69)) to the lattice constant. For higher concentration of traps the probed quantity can be shown to be ℓ_T/ℓ_θ where ℓ_θ is the distance between traps.

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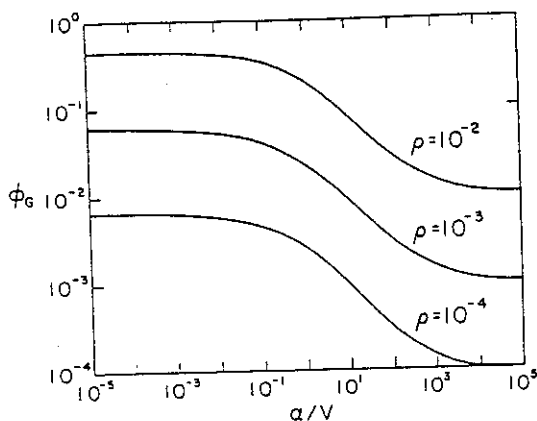


Fig. 8. Guest yield plotted as a function of the (in)coherence parameter α/V , i.e., the ratio of the lattice constant to the mean free path, for several values of the trap concentration.

To treat the multi-trap case one returns to (72) and by assuming s-independence of v_s writes an average form of (73):

$$v_s(t) = v(t) = \sum_m \psi_m(t) p_m \tag{85}$$

Here p_m is the probability that the m^{th} host-site is trap-influenced given that the 0^{th} is; it will be called the trap pair correlation function. The problem is now immediately solved, the generalization of (75) to the multi-trap case being

$$\phi_H = 1 - \frac{\rho\tau}{(1/c\tau) + (1/\tau)\sqrt{1/\tau}} \tag{86}$$

For random placement of traps, it follows that [39]

$$v(t) = \rho + (1-\rho)\psi_0(t) \tag{87}$$

Fig. 8 is the guest yield, i.e., $1-\phi_H$ obtained from (86) and (87), the exciton dynamics being given by (54), plotted to show the effect of coherence. The coherence parameter is V/α , which is proportional to the mean free path of the exciton in units of the lattice

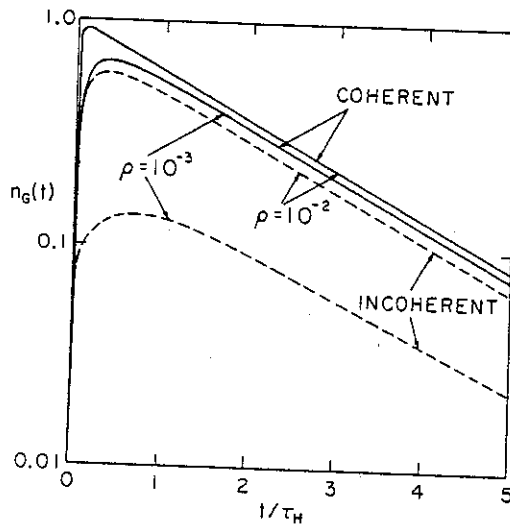


Fig. 9. Guest luminescence intensity plotted as a function of time for two values of the trap concentration to show the explicit effect of transport coherence. The extreme limits of completely coherent motion and completely incoherent motion are shown. The parameter values are $V\tau=1.8 \times 10^3$, $F\tau=1.8 \times 10^4$, and $c\tau=10^5$.

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defined from (86) and (87), plotted to show the effect of α , which is proportional to the number of units of the lattice



as a function of time concentration to show the difference. The extreme and completely incoherent parameter values are

constant. Higher degree of coherence is seen to result in more efficient trapping but no dramatic differences comparable to those in Figs. 5-7 in the grating context occur here. Fig. 9 shows the time dependence of guest luminescence obtained from the solution of (71) by using numerical inversion of the Laplace transform but again no striking difference occurs [39].

The fact that such a pronounced difference exists between the qualitative effects of coherence for capture experiments on the one hand and grating observations on the other suggests that one compare the two analyses. In both kinds of experiment one begins with

$$\frac{dP_m(t)}{dt} + \frac{P_m(t)}{\tau} + \int_0^t dt' \sum_n A_{mn}(t-t') P_n(t') = 0 \quad (88)$$

In the grating analysis one adds an annihilation term which gives rise to the delayed fluorescence signal but neglects it in finding solutions of (88). In the capture analysis one adds a capture term which, however, cannot be neglected. This difference is in keeping with the experimental situation. No information can be gathered about exciton motion if c in (70) is put equal to zero.

The initial condition on the exciton population is different for the two kinds of experiment. In the grating case it is inhomogeneous but periodic. In the capture case it is homogeneous. It is certainly possible to make it inhomogeneous in the latter case but the experiments carried out so far use homogeneous illumination or populations near one end. The latter case [5] is not treated in the present article.

The observed signal measures

$$\sum_k P_k P^{-k}, \text{ i.e., } \sum_k \psi^k \psi^{-k} g^k g^{-k}$$

in the grating experiment but is sensitive to $\sum_m \psi_m P_m$ in the capture observations. Here g_k is the Fourier transform of the spatial dependence - square wave - of the initial illumination and is controlled by the ruling period. The corresponding control in the capture case is exercised by the trap concentration ρ on the trap pair correlation function p_m . Thus, for random placement of traps,

$$p_m = \rho + (1-\rho)\delta_{m,0} \quad (89)$$

The control in the capture case is, however, much weaker than in the grating case because it is not as systematic. The rulings have a periodic arrangement. The doping by guest or trap molecules is random. This is the reason that dramatic manifestations of coherence are possible in the grating case but not in capture experiments. The quantity to measure in these experiments is the

diffusion length of excitons if the extent of transport is under study while it is the mean free path if the quality of transport (i.e., degree of coherence) is under study. The measuring unit employed in capture observations of the kind discussed is the inter-trap distance and is a random quantity. The measuring unit in grating observations is the ruling period which is a fixed quantity. In modern singlet grating experiments it appears possible to make the grating measurement unit even more systematic as it involves the selection of a single Fourier component of the P's by illuminating the crystal with crossed laser beams [5,40] instead of through a ruling.

V. MISCELLANEOUS METHODS AND CONCLUSIONS

V.A. Methods for Cooperative Trap Interactions

The mathematical technique of the GME and the issue of exciton transport coherence are well matched to each other, play a central role in the subject of energy transfer, and have been explained in sections II-IV. However, the subject poses other important issues and requires other useful mathematical methods. Although space considerations do not allow us to treat them all, an attempt is being made to describe one of them and briefly mention some of the others. The present section contains techniques used in capture situations with a high concentration of traps with particular reference to the difficult question, seldom discussed in the literature, of the effect of cooperative interactions among the traps, i.e., among the guest molecules in sensitized luminescence observations.

The interesting feature of this treatment is that it combines the methods of non-equilibrium statistical mechanics, i.e. transport theory, with techniques of equilibrium statistical mechanics, particularly Ising model arguments. Although time dependent observables can be analyzed as well as steady state quantities [39,41,42], attention will be restricted to the latter for simplicity. Central to this analysis are (86) which relate the observable, the yield, to the ν -function, and (85) which expresses the ν -function in terms of the p_m and the ψ_m . The powerful feature of (85) is that the observables can be calculated by combining two distinct parts of the system under study: (i) the dynamic part which involves the motion of the exciton in the pure host as described by the propagators ψ_m , and (ii) the static part which involves the placement of the traps in the doped crystal as described by the pair correlation function p_m . Calculation of the propagators has been illustrated in earlier sections. A procedure for obtaining the pair correlation function p_m follows.

If one represents the crystal under investigation by a lattice gas, one can exploit the well-known analogy between the latter and

the Ising model. The excitons in the gas sites, a and "unoccupied" sites are influenced by the ruling period l infinity if l is large, and z is the coordination number, Δ and $2\rho-1$, correspond to the Ising model. The yield p_m we

$$p_m = 1$$

We shall re-examine this model argument.

$$p_m = \delta_m$$

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Fig. 10 The static part of the pair correlation function p_m (E-trap)

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the Ising model, and use known results for spin correlation functions in the Ising model. The host sites are treated as the lattice gas sites, and are considered "occupied" if they are trap-influenced and "unoccupied" otherwise. The interaction between any two trap-influenced host sites is characterized by an energy which equals infinity if the two sites coincide, $-\Delta$ if they are nearest neighbours, and zero in all other cases. It follows that the quantities Δ and $2\rho-1$, where ρ is the trap concentration, respectively correspond to the magnetic interaction $4J$ and magnetization M of the Ising model. The spin-spin correlation function $\langle \sigma_0 \sigma_m \rangle$ is related to the p_m we seek, through

$$p_m = 1 - (1/4\rho)(1 - \langle \sigma_0 \sigma_m \rangle) \tag{90}$$

We shall restrict ourselves to a one-dimensional system. Ising model arguments and the above correspondence then give

$$p_m = \delta_{m,0} + (1 - \delta_{m,0})[\rho + (1 - \rho)x^{|m|}] \tag{91}$$

The details of the computation of $\langle \sigma_0 \sigma_m \rangle$ may be obtained from extensions of standard textbook calculations and therefore have not been

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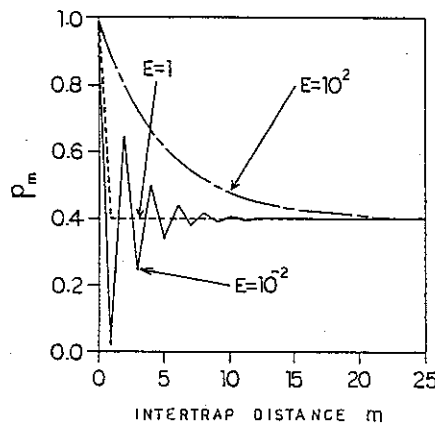


Fig. 10 The trap pair correlation function p_m plotted as a function of the dimensionless intertrap distance m for attractive, repulsive, and no interaction among the traps ($E=10^2, 10^{-2}, 1$ respectively). The value of the concentration has been arbitrarily made 0.4.

shown here. The quantity x in (91) is defined by

$$x = (y - 1)/(y + 1) \quad (92)$$

and can take values between -1 and 1 depending on the nature of the trap-trap interaction and the value of the concentration. Here y is given by

$$y = [1 - 4\rho(1-\rho)(1-E)]^{1/2} \quad (93)$$

and E , the trap-trap interaction parameter, equals $\exp(\Delta/k_B T)$ where T is a characteristic temperature. For no interactions Δ vanishes, E equals 1 , x vanishes since y equals 1 , and (91) reduces to the random placement result (87). Attractive interactions lead to the formation of clusters while repulsive ones generally cause desert regions to form. Fig. 10 shows the pair correlation function for three values of E showing typical spatial oscillations for repulsive interactions and slow decay for attractive ones.

The v -function is obtained by combining (91) with (85):

$$v(t) = \rho + (1-\rho) \sum_{m=-\infty}^{\infty} x^{|m|} \psi_m(t) \quad (94)$$

and reduces to (87) for random trap placement. The sum in (94) can be evaluated in simple cases. Thus, for incoherent motion with nearest-neighbour transfer rates F as in (9) or (11), the v -function gives, for the relevant quantity appearing in (86)

$$(1/\tau)\tilde{v}(1/\tau) = \rho + (1-\rho)[\tanh(\xi/2)][\tanh\{(\xi+\mu)/2\}]^{-\text{sgn}(x)} \quad (95)$$

The factors $\tanh(\mu/2)$ and $\tanh(\xi/2)$ respectively equal y and $(1/\tau)\tilde{\psi}_0(1/\tau)$ where $\tilde{\psi}_0$ is, as before, the self-propagator. The behaviour of v , and therefore that of the observables, is controlled by the interplay of the two quantities ξ and μ . They characterize the motion of the exciton and the interaction among the traps respectively and are given by

$$\xi = \cosh^{-1}[1 + (1/2F\tau)] \quad (96)$$

$$\mu = \ln(1/|x|) \quad (97)$$

Simple physical meaning can be ascribed to these two quantities in certain limits. Thus, for excitons in molecular crystals usually $F\tau \gg 1$ with the consequence that ξ equals $(4F\tau)^{-1/2}$ to an excellent approximation. Except for a factor of $\sqrt{2}$, ξ , therefore, equals the ratio of the lattice constant a to the diffusion length $\sqrt{2Fa^2\tau} = \sqrt{D\tau}$. It can be similarly shown [41] that, except for unimportant proportionality constants, μ equals the ratio of the lattice constant to the effective distance over which the trap-trap interaction extends. The effective distance is defined as one over which the

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$\exp(\Delta/k_B T)$ where Δ vanishes, μ reduces to the free diffusion coefficient. Attractive interactions lead to the formation of exciton pairs which usually cause desorption. Repulsive interactions lead to the formation of exciton pairs which usually cause desorption.

with (85):

(94)

The sum in (94) can be evaluated by substituting the free diffusion coefficient D in (86)

$$D = D_0 [1 - \text{sgn}(x)] \quad (95)$$

where D_0 is the free diffusion coefficient and $\text{sgn}(x)$ is the signum function. The parameter μ , which is controlled by the strength of the trap-trap interaction, is

(96)

(97)

Two quantities in (96) are usually taken to be an excellent approximation to the free diffusion coefficient. The first, D_0 , is the free diffusion coefficient, which is usually taken to be the free diffusion coefficient. The second, μ , is the trap-trap interaction energy, which is usually taken to be the trap-trap interaction energy.

pair correlation function p_m falls off by some characteristic amount. The reciprocal of μ therefore measures how far the effective trap-trap interaction extends, whereas the reciprocal of ξ measures how far the exciton can travel in its lifetime.

Fig. 11 shows the result of the application of this theory to compute the observable, the guest quantum yield ϕ_G which is obtained from (86). Specifically,

$$\phi_G = \rho \tau [(1/c\tau) + (1/\tau)\bar{v}(1/\tau)]^{-1} \quad (98)$$

with (95)-(97). One draws the conclusion that trapping is more efficient for repulsive interactions.

The present technique can be used for arbitrary degree of transport coherence (whose effect will be felt through the propagators appearing in (87)) and also for arbitrary strength of the capture rate. However, it involves the averaging approximation inherent in the use of the v -function theory [5,39]. An exact

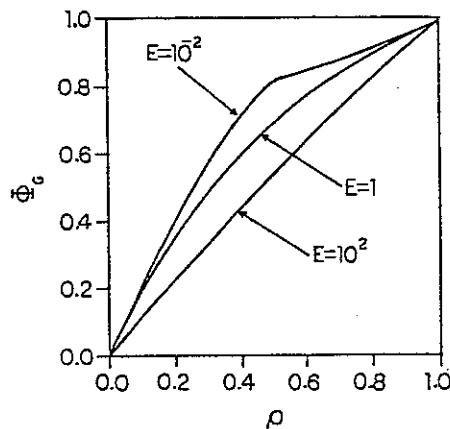


Fig. 11. The guest (trap) yield ϕ_G plotted as a function of the guest concentration ρ for the three values of trap-trap interactions corresponding to Fig. 10. Repulsive interactions are seen to lead to enhanced efficiency of capture, whereas attractive interactions inhibit capture.

solution which avoids all approximations is possible [42] if one is willing to sacrifice the ability to cover arbitrary degree of coherence and capture. For incoherent one-dimensional exciton motion with nearest-neighbour rates F and nearest-neighbour trap-trap interactions characterized by as above, the exact expression for the guest yield for the case of infinite capture rates is

$$\phi_G = \rho_e \sum_{N=1}^{\infty} \rho_e (1-\rho_e)^{N-1} [\tanh(\xi/2)]^{-1} \{ \tanh[(N+1)\xi/2] - \tanh(\xi/2) \} \quad (98)$$

where ρ_e is an "effective" trap concentration which equals $\rho(1-x)$, with x as in (92).

V.B. Conclusion

There is a large number of important questions and techniques which it has not been possible to describe in this review. One of those techniques addresses mutual annihilation of excitons. The procedure [5] is to consider the evolution of the system point representing two interacting (annihilating) excitons in a space of twice the number of dimensions as the real crystal. The annihilation problem reduces then to the capture problem explained in section IV. Another question concerns the applicability of traditional expressions for the so-called energy transfer rate and the time dependence of the latter. For many years sensitized luminescence observations had been interpreted in terms of a simple kinetic scheme involving an energy transfer rate which described the transfer of energy from the host to the guest [9]. Later experiments reported a time dependence of this rate [13] and various theoretical and experimental investigations of this time dependence began. The most recent developments on this question are as follows. The systems that were reported earlier [13] to exhibit time dependence in the energy transfer rate have been found [36] to have a time-independent rate. The earlier observations appear to have been an experimental artifact. However, time dependence in the rate is seen [43] for one-dimensional systems. The unified theoretical framework described in this article is able to reconcile quantitatively both of these observations (time-dependent rates in the experiments of ref. [43] and time-independent rates for the system of ref. [36]), as is clear from detailed fits carried out recently [44]. A related new development [45] is the concern that usual exciton capture experiments probe capture rather than motion parameters and a feeling is developing that a large amount of information gathered over the years may be of little relevance to exciton motion.

Another issue in this field is that of the interplay of energy transfer with vibrational relaxation. The natural mathematical technique to study it is to employ two interlocked master equations

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[5], one for the relaxation and the other for transfer. It is possible to investigate in this way the dependence of energy transfer on the wavelength of initial excitation which could be observable if relaxation occurs on a scale comparable to or slower than transfer.

A number of other techniques exist including those involving a return to k-space equations such as the Boltzmann equation. The interested reader is referred to several reviews by the author for detailed [5] as well as perspective [46-48] descriptions and also to other reviews cited in this article.

ACKNOWLEDGEMENTS

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As this article went to press, news arrived of the passing away of an esteemed friend and greatly renowned scientist who, in his active life, had made numerous pioneering contributions to the mathematics of energy transfer. Indeed, many of the techniques described in this article owe their origin to him. It is difficult to imagine the community of statistical mechanics without Elliott Montroll. This article is dedicated to his memory.

REFERENCES

1. D. L. Dexter and R. S. Knox, Excitons (Interscience, New York, 1965).
2. H. Haken and G. Strobl in The Triplet State, ed. by A. B. Zahlan (Cambridge University, Cambridge, 1967).
3. R. Silbey, Ann. Rev. Phys. Chem. 27, 203 (1976).
4. R. S. Knox in Collective Excitations in Solids, ed. by B. DiBartolo (Plenum, New York, 1981).
5. V. M. Kenkre in Exciton Dynamics in Molecular Crystals and Aggregates, ed. G. Hoehler (Springer-Verlag, Berlin, 1982).
6. P. Reineker in Exciton Dynamics in Molecular Crystals and Aggregates, ed. G. Hoehler (Springer-Verlag, Berlin, 1982).
7. R. S. Knox in Primary Processes of Photosynthesis, ed. by J. Barber (North-Holland, Amsterdam, 1977), p. 55.
8. O. Simpson, Proc. Royal Soc. London A, 238, 402 (1956).

9. H. C. Wolf in Adv. in Atomic and Molecular Physics, vol. 3, ed. by D. R. Bates, I. Esterman (Academic Press, New York, 1967).
10. D. Burland and A. Zewail, Adv. Chem. Phys., 50, 385 (1980).
11. C. B. Harris and D. A. Zwemer, Ann. Rev. Phys. Chem., 29, 473 (1978).
12. A. H. Francis and R. Kopelman in Excitation Dynamics in Molecular Solids, Topics in Applied Physics, ed. by W. M. Yen and P. M. Selzer (Springer, Berlin, Heidelberg, New York, 1981).
13. R. Powell and Z. Soos, J. Lumin., 11, 1 (1975).
14. F. Perrin, Ann. Physique, 17, 283 (1932).
15. Th. Foerster, Ann. Phys. (Leipzig) (b), 2, 55 (1948).
16. V. M. Kenkre in Statistical Mechanics and Statistical Methods in Theory and Application, ed. by U. Landman (Plenum, New York, 1977).
17. V. M. Kenkre, Phys. Rev. B, 11, 3406 (1975).
18. V. M. Kenkre, J. Stat. Phys., 19, 333 (1978).
19. R. W. Zwanzig in Lectures in Theor. Phys., ed. by W. Downs and J. Downs (Gordon and Breach, Boulder, Colorado, 1961).
20. Th. Foerster in Modern Quantum Chemistry, Part III, ed. by O. Sinanoglu (Academic Press, New York, 1965), p. 93.
21. V. M. Kenkre and R. S. Knox, Phys. Rev. Lett., 33, 803, 1974.
22. K. D. Philipson and K. Sauer, Biochem., 11, 1180 (1972).
23. V. M. Kenkre, Phys. Rev. B, 18, 4064 (1978).
24. R. P. Hemenger, K. Lakatos-Lindenberg, and R. M. Pearlstein, J. Chem. Phys., 60, 3271 (1974).
25. V. M. Kenkre, Phys. Lett., 65A, 391 (1978).
26. C. B. Duke and T. Soules, Phys. Lett. A, 29, 117 (1969).
27. V. M. Kenkre and T. S. Rahman, Phys. Lett., 50A, 170 (1974).
28. D. L. Dexter, J. Chem. Phys., 21, 836 (1953).
29. V. M. Kenkre and R. S. Knox, Phys. Rev. B, 9, 5279 (1974).
30. P. Avakian, B. Ern, R. E. Merrifield, and A. Suna, Phys. Rev., 165, 974 (1968).
31. V. Ern and M. Schott in Localization and Delocalization in Quantum Chemistry, ed. by O. Chalvet (D. Reidel Publishers, Dordrecht-Holland, 1976), vol. II, p. 249.
32. V. M. Kenkre, V. Ern, and A. Fort, Phys. Rev. B, 28, 598 (1983).
33. V. M. Kenkre, A. Fort, and V. Ern, Chem. Phys. Lett., 96, 658, (1983).
34. A. Fort, V. Ern, and V. M. Kenkre, Chem Phys., 80, 205 (1983).
35. H. Auweter, A. Braun, U. Mayer and D. Schmid, Z. Naturforsch., 34A, 761 (1979).
36. A. Braun, U. Mayer, H. Auweter, H. C. Wolf, and D. Schmid, Z. Naturforsch., 37a, 1013 (1982).
37. See e.g., E. W. Montroll and B. West, J. Stat. Phys., 13, 17 (1975).
38. V. M. Kenkre and Y. M. Wong, Phys. Rev. B, 23, 3748 (1981).
39. V. M. Kenkre and P. E. Parris, Phys. Rev. B, 27, 3221 (1983).

40.

41.

42.

43.

44.

45.

46.

47.

48.

Molecular Physics, vol. 3, ed. McGraw-Hill Press, New York, 1967).
 J. Chem. Phys., 50, 385 (1980).
 J. Chem. Phys. Chem., 29, 473

Excitation Dynamics in Molecular Physics, ed. by W. M. Yen and G. Heide, Heidelberg, New York,

1, 1 (1975).

(1932).

(b), 2, 55 (1948).

Excitations and Statistical Methods in Molecular Physics, ed. by Landman (Plenum, New York,

6 (1975).

3 (1978).

Excitation Dynamics in Molecular Physics, ed. by W. Downs and G. Heide, Colorado, 1961).

Excitation Dynamics in Molecular Physics, Part III, ed. by O. Schnecko, (1965), p. 93.

Rev. Lett. 33, 803, 1974.

Chem. Phys. Lett., 11, 1180 (1972).

4 (1978).

Phys. Rev. Lett., and R. M. Pearlstein, J.

(1978).

Phys. Rev. Lett., 29, 117 (1969).

Phys. Lett., 50A, 170 (1974).

(1953).

Rev. B, 9, 5279 (1974).

Phys. Rev. Lett., and A. Suna, Phys. Rev.

Excitations and Delocalization in Molecular Crystals, ed. by D. Reidel Publishers,

(1978), p. 249.

Phys. Rev. B, 28, 598

Chem. Phys. Lett. 96,

J. Chem. Phys., 80, 205 (1983).

D. Schmid, Z. Naturforsch.

C. Wolf, and D. Schmid, Z.

Phys. Lett., J. Stat. Phys. 13, 17

Rev. B 23, 3748 (1981).

Rev. B 27, 3221 (1983).

40. J. Salcedo, A. E. Siegman, D. D. Dlott, and M. D. Fayer, Phys. Rev. Lett. 41, 131 (1978).
41. V. M. Kenkre, P. E. Parris, and S. M. Phatak, Physica A, to be published (1984).
42. P. E. Parris, S. M. Phatak, and V. M. Kenkre, J. Stat. Phys., to be published (1984).
43. D. D. Dlott, M. D. Fayer, and R. D. Wieting, J. Chem. Phys. 69, 2753 (1978); 67, 3808 (1977).
44. P. E. Parris, Ph.D. Thesis, University of Rochester (1984).
45. V. M. Kenkre and D. Schmid, Chem. Phys. Lett. 94, 603 (1983).
46. V. M. Kenkre in Proceedings of the Fourth International Seminar on Energy Transfer, ed. J. Pantoflicek (Prague, 1981)p. 54.
47. V. M. Kenkre, J. Stat. Phys. 30, 293 (1983).
48. V. M. Kenkre in Electronic Excitations and Interaction Processes in Organic Molecular Aggregates, ed. P. Reineker, H. C. Wolf, and H. Haken (Spring-Verlag, Berlin, 1983).