PHYSICAL REVIEW B VOLUME 22, NUMBER 6 15 SEPTEMBER 1980

Extension of exciton-transport theory for transient grating experiments into the intermediate coherence domain

Y. M. Wong*
Institute for Fundamental Studies, Department of Physics and Astronomy, University of Rochester, Rochester, New York 14627

V. M. Kenkre†
Institute for Fundamental Studies, Department of Physics and Astronomy, University of Rochester, Rochester, New York 14627 and Abteilung für Theoretische Physik I, Universität Ulm, Oberer Eselsberg, Ulm, Germany

(Received 27 March 1980)

Transient grating experiments provide a powerful new probe for exciton motion in molecular systems. An earlier theory of exciton transport directed at these experiments is extended into the intermediate coherence domain. Diffusion-equation results existing in the literature are shown to emerge as particular cases of this theory. Practically usable expressions for observed signals are given for an arbitrary degree of exciton coherence, and it is shown how coherence may be measured from the observations in experiments.

I. INTRODUCTION

Transient grating experiments[1,2] constitute a novel technique for probing into the details of exciton motion in molecular systems. In contrast to the usual direct measurements of exciton dynamics, which employ material detectors such as guest molecules introduced into the host in sensitized luminescence experiments,[3] or surface layers of a different substance placed at the end of the sample,[4] or other excitons whose collisions and consequent annihilation can be monitored,[5] transient grating experiments detect exciton motion by following the evolution in time of a transient grating created by two crossed time-coincident picosecond excitation pulses. The two pulses are crossed at a definite but variable angle. Optical absorption then results in a spatially varying exciton density following the optical interference pattern and thus creates the diffraction grating. A third picosecond pulse is used to probe the strength of this grating by studying its Bragg diffraction from the grating. The grating, or equivalently, the spatial inhomogeneity, disappears in time not only through radiative decay but through exciton motion in space. The observed signal is the time-dependent diffracted probe intensity and is, therefore, essentially proportional to the square of the amplitude of the inhomogeneity. The characteristics of exciton motion are thus reflected in the time dependence of the signal. The experimental variables are the angle of crossing, the wavelength of excitation, the temperature of the crystal, and the concentration of the solute if the system is a solid solution, i.e., a mixed crystal, (the solute molecules being the ones excited to form the grating). The diffusion constant, the nature of coherence in the exciton motion, and other such transport characteristics may then be deduced from the signal. Results that have been reported so far concern single crystals of p-terphenyl doped with pentacene.[2]

The directness of these transient grating experiments, i.e., the fact that they are sensitive to the transport itself rather than to magnetic properties[6] or the effects of defects,[3,4] makes them particularly interesting to the theorist. This paper studies the effects of exciton coherence on the output of these experiments and makes specific predictions for the signal obtained. The issue of coherence in exciton motion has received immense attention[7,8] in recent times, and one of the present authors has constructed a generalized-master-equation (GME) theory[8] especially directed at these transient grating experiments incorporating the effects of coherence. Usable expressions for the observables have however been given only in the extreme limits of completely coherent and completely incoherent motion. In this paper we obtain practically useful expressions for the observed signals for arbitrary degree of coherence, thus making possible the description of the results of these experiments in the intermediate coherence domain. We also give an explicit demonstration of how the general results of Ref. 8 reduce to those in Ref. 2 as a special case.

The paper is set out as follows. In Sec. II the essential aspects of the experiment are stated from a theoretician's point of view. The notation and presentation of Salcedo *et al.*,[2] who performed the experiment, are followed. In Sec. III the theoretical description given by Kenkre,[8] which includes the effects of coherence as well as discreteness (in space), is introduced and shown to give the results of Ref. 2 as a particular case. In Sec. IV the predicted signal is evaluated

explicitly for an arbitrary degree of exciton coherence. A discussion is presented in Sec. V. The present analysis, as well as that in Ref. 8, assumes the incoherent initial condition for the problem suggested by Fayer *et al.* in Refs. 1 and 2.

II. THE DIFFUSION EQUATION TREATMENT

We refer the reader to Ref. 2 for details and state that it follows from the discussion therein or from the description of the experiment given in Sec. I above that, if θ is the angle of crossing between the laser beams which produce the grating through optical absorption and λ is their wavelength, the fringe spacing of the grating is $d = [\lambda/2\sin(\theta/2)]$ and the initial condition, imposed on the excitation population $p(x,t)$ at the instant the grating is formed, is

$$p(x,0) = \tfrac{1}{2}[1+\cos(\Delta x)], \tag{2.1}$$

where $\Delta = 2\pi/d$. If one assumes,[2] for the sake of simplicity, that the excitation population evolves in time through the continuum diffusion equation, i.e., D is the exciton diffusion constant and τ the radiative lifetime, then

$$\frac{\partial p(x,t)}{\partial t} = D\frac{\partial^2 p(x,t)}{\partial x^2} - \frac{p(x,t)}{\tau}. \tag{2.2}$$

In conjunction with (2.1), Eq. (2.2) immediately gives

$$p(x,t) = \tfrac{1}{2}e^{-t/\tau}[1+e^{-\Delta^2 Dt}\cos(\Delta x)]. \tag{2.3}$$

The observed signal in these experiments is essentially proportional to the square of the grating depth, i.e., to

$$[p(0,t) - p(d/2,t)]^2.$$

From (2.3) one sees that this is a simple exponential with the exponent given by

$$K = 2(\Delta^2 D + 1/\tau). \tag{2.4}$$

Independent measurement of τ and knowledge of λ and θ (and therefore of Δ) thus allow one to deduce D from the above exponent of the observed signal. We mention in passing (and refer the reader to Ref. 2 for details) that, although the observed signal generally involves convolutions with the pulse-excitation functions, it equals the square of the grating depth as stated above for a short optical pulse condition. Such a condition is indeed met in the experiment. Furthermore, in situations wherein it does not hold, it is straightforward to carry out the various convolutions required. We do not exhibit them here because they would add little to the physics of the problem.

III. THE GENERALIZED-MASTER-EQUATION TREATMENT

The discussion[2] in the previous section neglects at least two characteristics of exciton motion: (i) the molecular crystal is not actually a continuum: exciton motion takes place in a discrete space, and (ii) it is not known *a priori* that the incoherence in the motion is high enough to allow the use of (2.2). We shall first show that an analysis incorporating the former, but not the latter, characteristic does introduce changes but continues to predict an exponential signal. After that we shall discuss the significant modifications brought about by coherence in exciton motion.

We therefore start with the discrete-space equation

$$\frac{dP_m}{dt} = F(P_{m+1} + P_{m-1} - 2P_m) - \frac{P_m}{\tau}, \tag{3.1}$$

which describes the evolution of $P_m(t)$, the number of excitons at site m (alternatively, the probability of a single exciton), in terms of transfer rates F and is more general and corresponds more closely to the actual (discrete) situation in the molecular solid. Note, however, that (3.1) reduces to (2.2) in the continuum limit

$$a \to 0,\ (1/a)P_m(t) \to p(x,t),\ F \to \infty,\ Fa^2 \to D.$$

The solution of (3.1) for $P_n(0) = \delta_{n,0}$ is the well-known expression[9]

$$P_m(t) = e^{-t/\tau}e^{-2Ft}I_m(2Ft), \tag{3.2}$$

which, in the continuum limit stated above, goes over to the familiar solution of the diffusion equation

$$p(x,t) = \frac{1}{(4\pi Dt)^{1/2}}e^{-t/\tau}e^{-x^2/4Dt}. \tag{3.3}$$

It therefore follows that for the initial condition (2.1) characteristic of transient grating experiments, written in the discrete form

$$P_m(0) = \tfrac{1}{2}[1+\cos(\eta m)], \tag{3.4}$$

where $\eta = \Delta a$, one has

$$P_m(t) = \tfrac{1}{2}e^{-t/\tau}[1+e^{-4Ft\sin^2(\eta/2)}\cos(\eta m)]. \tag{3.5}$$

The observed signal $S(t)$ continues to have an exponential time dependence

$$S(t) = S(0)\exp\{-2t[4F\sin^2(\eta/2) + 1/\tau]\}. \tag{3.6}$$

The exponent is, however, different from that given[2] in the previous section [Eq. (2.4)] in that it involves $4\sin^2(\eta/2)$ rather than η^2. The result of Salcedo *et al.*[2] is, of course, recovered from (3.6) in the limit $a \to 0$ because then $\eta \to 0$ and $4\sin^2(\eta/2)$ may be replaced by η^2.

A much greater change occurs in the predicted signal when allowance is made for exciton motion to be at least partially coherent. Equations (2.2) or (3.1) cannot be used to describe this situation. A unified theory of this experiment incorporating coherence effects had already been constructed[8] before the experiment in Ref. 2 was performed. It takes the generalized master equation (GME)

$$\frac{dP_m}{dt} = \int_0^t dt' \left(\sum_n \mathcal{W}_{mn}(t-t') P_n(t') - \mathcal{W}_{nm}(t-t') P_m(t') \right) - \frac{P_m}{\tau} . \quad (3.7)$$

to describe the exciton motion and is, therefore, capable of handling *any* degree of coherence. One begins with

The memory functions are derived analytically from a simple model for the motion and are found[8] to have the form

$$\mathcal{W}_{mn}(t) = 2J^2 e^{-\alpha t} \{ [J^2_{m-n+1}(2Jt) + J^2_{m-n-1}(2Jt) + 2J_{m-n+1}(2Jt) J_{m-n-1}(2Jt)] - \{ 2J^2_{m-n}(2Jt) + J_{m-n}(2Jt) [J_{m-n+2}(2Jt) + J_{m-n-2}(2Jt)] \} \} , \quad (3.8)$$

where J is the intersite matrix element, taken to have nearest-neighbor character for simplicity, and α is the randomization parameter arising from exciton-bath interactions. In the limit $\alpha \to 0$ signifying no bath interactions, (3.7) and (3.8) are equivalent to results obtained from the Schrödinger equation, and in the limit $\alpha \to \infty$, $J \to \infty$, $2J^2/\alpha = F$, signifying extreme incoherence, (3.1) and therefore (2.2) are recovered. The details of the derivation of (3.8) will be found in Ref. 8 where the following four results have been obtained in the specific context of transient grating experiments:

(*a*) *Purely incoherent motion with small intersite interaction.* The signal is exponential in time and is given exactly by (3.6). As stated earlier, the results of Salcedo *et al.*[2] follow in the limit $a \to 0$.

(*b*) *Purely incoherent motion with large intersite interaction.* An unexpected result of Ref. 8 involved spatially long-range transfer rates arising from spatially local J's. It shows that even when the assumption of purely incoherent motion is made, large J's (with respect to α) would generally invalidate (3.1) and, consequently, the diffusion equation (2.2) in the continuum limit. One would have, in place of (3.5),

$$P_m(t) = \tfrac{1}{2} e^{-t/\tau} \left[1 - \exp\left(-t \{ [\alpha^2 + 16J^2 \sin^2(\eta/2)]^{1/2} - \alpha \} \right) \right] . \quad (3.9)$$

Equation (3.9) reduces to (3.5) and therefore yields (3.6) in the limit of small J/α, specifically, $\alpha \to \infty$, $J \to \infty$, $J^2/\alpha = \text{const}$. Note, however, that for arbitrary J/α the signal is

$$S(t) = S(0) e^{-2t/\tau} \exp\left(-2t \{ [\alpha^2 + 16J^2 \sin^2(\eta/2)]^{1/2} - \alpha \} \right) , \quad (3.10)$$

and that, in the continuum limit unaccompanied by the limit $J/\alpha \to 0$, one gets results *which are not those of the diffusion equation*. The decay rate of (3.10) has been plotted in Ref. 8, and an explicit method is given to ascertain the degree of coherence with its use.

(*c*) *Purely coherent motion.* This case involves $\alpha = 0$ and results in a highly nonexponential signal

$$S(t) = S(0) e^{-2t/\tau} J_0^2(4Jt \sin \tfrac{1}{2} \Delta a) \quad (3.11)$$

which has little resemblance to (3.6) or (3.10).

(*d*) *Partial coherence: intermediate domain.* For arbitrary relative values of J and α, the signal was predicted in Ref. 8 only up to a Laplace transform

$$S(t) = S(0) e^{-2t/\tau} \left(\int_c d\epsilon \, e^{\epsilon t} \{ [\epsilon^2 + 16J^2 \sin^2(\Delta a/2)]^{1/2} - \alpha \}^{-1} \right)^2 , \quad (3.12)$$

where the ϵ integration is on the Bromwich contour. In the next section we shall give an explicit evaluation of (3.12) in the time domain and exhibit the plots of the predicted signal in the intermediate domain.

IV. EXPLICIT CALCULATION OF THE SIGNAL IN THE INTERMEDIATE COHERENCE DOMAIN

We now evaluate explicitly the Laplace transform in (3.12) by making use of the identity

$$\tilde{f}(\{(\epsilon^2 + b^2)^{1/2}\}) = \mathcal{L} \left(f(t) - b \int_0^t du \, J_1(bu) f(\{(t^2 - u^2)^{1/2}\}) \right) , \quad (4.1)$$

where $\mathcal{L}$ denotes the Laplace transform, J_1 is the

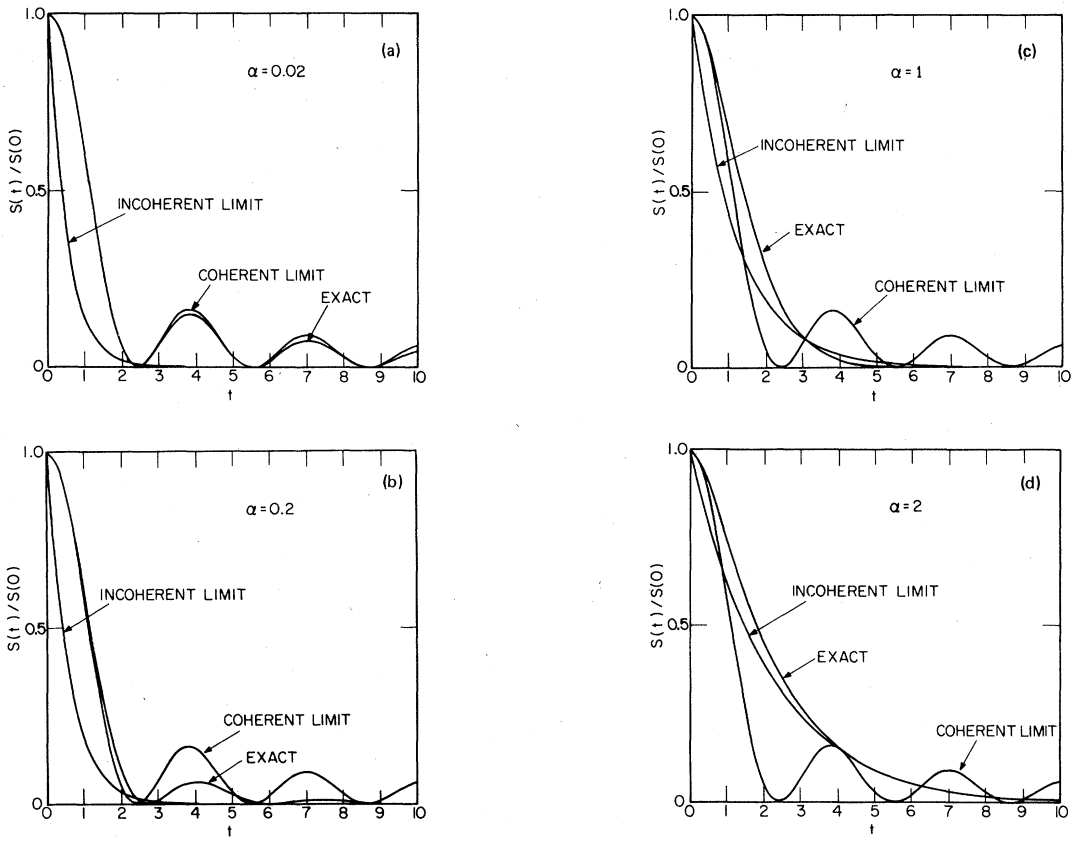

FIG. 1. Effect of coherence on the transient grating signal as a function of time. Curves respectively denote the signal in the incoherent limit given by (3.9), the coherent limit given by (3.10), and the intermediate exact expression given by (4.3). Parameters are arbitrary: $4J\sin(\Delta a/2)=1$. The four cases correspond respectively to (a) $\alpha=0.02$, (b) $\alpha=0.2$, (c) $\alpha=1.0$, and (d) $\alpha=2.0$.

J Bessel function, and $f(t)$ is any function with Laplace transform $\tilde{f}(\epsilon)$. Identifying $f(t)$ with $e^{\alpha t}$ we get

$$\int_0^\infty dt\, e^{-\epsilon t}[(\epsilon^2+b^2)^{1/2}-\alpha]^{-1}=\mathcal{L}\left(e^{\alpha t}-b\int_0^t du\, J_1(bu)e^{\alpha(t^2-u^2)^{1/2}}\right), \tag{4.2}$$

with which (3.12) yields, after one puts $b=4J\sin(\Delta a/2)$,

$$S(t)=S(0)\,e^{-2t/\tau}\left[1-e^{-\alpha t}\left(4J\sin\frac{\Delta a}{2}\right)\int_0^t du\, J_1\left(4Ju\sin\frac{\Delta a}{2}\right)e^{\alpha(t^2-u^2)^{1/2}}\right]^2. \tag{4.3}$$

Equation (4.3) is the primary result of this paper. It gives the transient grating signal for an arbitrary degree of coherence. It reduces to the various purely coherent and purely incoherent limits given earlier. For instance, when $\alpha=0$ the square bracket in (4.3) is

$$1-[4J\sin(\Delta a/2)]\int_0^t du\, J_1(4J\sin(\Delta a/2)t),$$

which is $J_0(4J\sin(\Delta a/2)t)$ and leads to the reduction of (4.3) to (3.11). Equation (4.3) has been plotted in Figs. 1(a)–1(d) for various relative values of the parameter J/α. For convenience we have held J constant and set $4J\sin^2(\Delta a/2)$ equal to one. In particular in Fig. 1(a), with $\alpha=0.02$, the three curves denote, respectively, the signals in the incoherent limit given by (3.6), the coherent limit given by (3.10), and the intermediate regime given by (4.3). This is repeated for three other values of α, i.e., $\alpha=0.2$, 1.0, and 2.0, to demonstrate the change in the nature of the signal as one passes from the coherent regime (small

α) to the incoherent regime. To make this change clearer we have suppressed the factor $e^{-2t/\tau}$ that multiplies the curves shown.

V. DISCUSSION

The main contribution of this paper is the explicit evaluation of (3.12). Although (3.12) was given in Kenkre's unified analysis,[8] only the purely coherent and purely incoherent limits had been calculated in the time domain. Equation (4.3) derived here, and the plots in Figs. 1(a) through 1(d), extend the theory of Ref. 8 and make it usable for an arbitrary degree of exciton coherence. The qualitative as well as quantitative features of the predicted signal are seen to be dependent on the degree of coherence. Measurement of coherence is therefore possible by comparing these figures with observations.

Another result reported in this paper is the explicit demonstration of how the GME expression (4.3) for the predicted signal reduces to the expression of Salcedo *et al.*[2] under the Markoffian and the continuum limits. We stress that (4.3) is the general result for an arbitrary degree of coherence and for discrete space. It is therefore applicable whatever the values of the intermolecular distance a, the intersite matrix element J, and the bath-interaction parameter α. A few numerical estimates might be of some help in appreciating the extent of validity of the various treatments. The values $\alpha = 10^{12}$ sec^{-1}, $J = 10^{12}$ sec^{-1}, and $\tau = 10^{-8}$ sec allow (3.10) to be used because $\alpha\tau \gg 1$. Furthermore, because $(4J/\alpha)$ is not a small quantity, the validity of the further reduction to (3.5) and (3.6) depends on the value of the lattice distance a and the wavelength λ, since $\eta = (4\pi a/\lambda)\sin(\theta/2)$. For a concentration of about 1.6×10^{-3} mol/mol as in Ref. 2, $a \approx 50$ Å and $\lambda = 5\times10^{4}$ Å, we see that $16J^2\sin^2(\eta/2) \ll \alpha^2$, and thus we are indeed in the domain of validity not only of (3.6) but also of the diffusion equation treatment of Ref. 2. However, in the case of $\alpha = 10^{10}$ sec^{-1}, which might correspond to low temperatures, a suitably large value of (a/λ) could make α^2 much smaller than $16J^2\sin^2(\eta/2)$ for appropriate values of the crossing angle θ. In such a situation, if α could be neglected with respect to $4J\sin(\eta/2)$, one could even have, from (2.10),

$$S(t) = S(0)\, e^{-2t/\tau} \exp\{-t[4J\sin(\eta/2)]\}, \qquad (5.1)$$

which shows a dependence of the decay constant K of the signal on the concentration, which is completely different from that expected from earlier expressions such as (3.6). The dependence of K on the crossing angle θ would also be linear rather than quadratic (for small θ's). Finally, for such low relative values of α the experimental observations could exhibit nonexponential behavior, as a result of a high degree of coherence, and warrant interpretation in terms of the full intermediate expression (4.3).

We now comment on the limitations of our analysis. It is based on the one-dimensional periodic lattice model with nearest-neighbor interactions J for exciton motion and with a single bath parameter α. The one-dimensional character is hardly a limitation since the inhomogeneity created in the crystal is, in fact, one dimensional. The nearest-neighbor character of the intersite matrix element is an assumption made universally in exact calculations for such problems and is reasonable for short-range interactions. While it is an excellent assumption thus for triplet excitons, the excitons created in the experiment of Ref. 2 are singlets. Even here, however, the next-nearest-neighbor matrix element is $2^6 = 64$ times smaller than the nearest-neighbor one. The quantitative corrections would therefore not be significant. The assumption of the single bath parameter α is, we believe, adequate at this stage, although use of the actual contribution made to the memory functions by the exciton-phonon interactions, computed along the lines of the analysis of Kenkre and Knox,[10] would be preferable. In that case, however, exact calculation of the predicted signal as given in (4.3) is not possible, and numerical methods have to be used. The assumption that the underlying structure along which the exciton moves is periodic is the most restrictive of the lot, from the point of view of the experiments already performed.[2] This is so because although the p-terphenyl forms a crystal, the exciton moves along the pentacene molecules which form a noncrystalline array. There is, in fact, a great deal of analysis[11-13] that is being directed at the problem of motion in disordered structures. Thus it has been shown by Haan and Zwanzig[11] that for a slightly disordered system, e.g., a low-concentration solution, the average mean-square displacement clearly exhibits nondiffusive behavior at short times. This has been extended by Gochanour *et al.*[13] to the case of highly disordered systems and arbitrary times. In these approaches, the master equation with Förster transfer rates has been employed in the very beginning to describe the motion. Consequently, they can study the effect of randomness only on *incoherent* motion. Gochanour *et al.*[13] have mentioned that coherent transport can be important at low temperatures. Such situations necessitate a general approach using generalized master equations as in the present paper. However, we have not treated the effect of randomness. We

believe that the most efficient way to analyze coherence and randomness is to convert[14] the randomness into a pausing time distribution,[15] the latter into memory functions,[16] and thus to use a combined $\mathscr{W}_{mn}(t)$ within the framework presented in Ref. 8 and this paper. In closing we point out that while the analysis presented here corresponds to exciton transport according to

$$\frac{d\rho_{mn}}{dt} = -iJ(\rho_{m+1,n} + \rho_{m-1,n} - \rho_{m,n+1} - \rho_{m,n-1}) - (1 - \delta_{m,n})\alpha\rho_{mn}, \tag{5.2}$$

it is a straightforward matter to generalize these results either by using long-range J_{mn}'s or more complicated versions of the stochastic Liouville equation, such as Eq. (8) of Ref. 17.

ACKNOWLEDGMENTS

One of us (V. M.K.) wishes to thank Professor R. Reineker for his invitation to, and hospitality at, the Universität Ulm, and the Deutsches Forschungsgmeinshaft for financial support. Y.M.W. wishes to thank J. Yeh for numerical assistance. This work was supported in part by NSF Grant No. DMR-7919539.

---

*Present address: Physics Department, Catholic University of America, Washington, D. C. 20064.

†Permanent address.

[1] M. D. Fayer, in Proceedings of the VIII International Symposium on Molecular Crystals, Santa Barbara, 1977 (unpublished).

[2] J. R. Salcedo, A. E. Siegman, D. D. Dlott, and M. D. Fayer, Phys. Rev. Lett. 41, 131 (1978).

[3] H. C. Wolf, in *Advances in Atomic and Molecular Physics*, edited by D. R. Bates and I. Estermann (Academic, New York, 1967), Vol. 3; R. Powell and Z. Soos, J. Lumin. 11, 1 (1975); A. Braun, H. Pfisterer, and D. Schmidt, *ibid.* 17, 15 (1978).

[4] O. Simpson, Proc. R. Soc. London A238, 402 (1956).

[5] N. E. Geacintov and C. E. Swenberg, in *Organic Molecular Photophysics*, edited by J. B. Birks (Wiley, New York, 1973), Vol. I; S. Fujiwara, T. Nakayama, and N. Itoh, Phys. Status Solidi B 78, 519 (1976); F. Heisel, J. A. Miehe, B. Sipp, and M. Schott, Chem. Phys. Lett. 56, 178 (1978).

[6] C. B. Harris and D. A. Zwemer, Annu. Rev. Phys. Chem. 29, 473 (1978); D. M. Burland and A. H. Zewail, Adv. Chem. Phys. (in press).

[7] H. Haken and P. Reineker, Z. Phys. 249, 153 (1972); R. Silbey, Annu. Rev. Phys. Chem. 27, 203 (1976); V. M. Kenkre and R. S. Knox, J. Lumin. 12/13, 187 (1976).

[8] V. M. Kenkre, Phys. Rev. 18, 4064 (1978).

[9] See, e.g., E. W. Montroll, *Energies in Mettallurgical Phenomena* (Gordon and Breach, New York, 1963), Vol. 3.

[10] V. M. Kenkre and R. S. Knox, Phys. Rev. B 9, 5279 (1974).

[11] S. Haan and R. Zwanzig, J. Chem. Phys. 68, 1874 (1978).

[12] R. Kopelman, J. Chem. Phys. 80, 2191 (1976).

[13] C. R. Gochanour, H. C. Andersen, and M. D. Fayer, J. Chem. Phys. 70, 4254 (1979).

[14] J. Klafter and R. Silbey, Phys. Rev. Lett. 44, 55 (1980).

[15] H. Scher and M. Lax, Phys. Rev. B 7, 4491 (1973).

[16] V. M. Kenkre, E. W. Montroll, and M. F. Shlesinger, J. Stat. Phys. 9, 45 (1973); V. M. Kenkre, in *Statistical Mechanics and Statistical Methods in Theory and Application*, edited by U. Landman (Plenum, New York, 1977).

[17] V. M. Kenkre, Phys. Lett. 65A, 391 (1978); see also P. Reineker, Phys. Rev. B 19, 1999 (1979).