

A THEORETICAL APPROACH TO EXCITON TRAPPING IN SYSTEMS WITH ARBITRARY TRAP CONCENTRATION *

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A simple approach to the trapping of moving quasiparticles in solids, valid for arbitrary concentration of traps, is developed. While the analysis is presented in the context of Frenkel excitons in molecular crystals, its applicability is general. A central result is that observable quantities such as the luminescence intensity, the quantum yield, and also the surviving number of quasiparticles can be obtained from exact expressions valid for a single trap by replacing the self-propagator by a sum over propagators in the trap-influenced region. Arbitrary concentrations and arbitrary nature of motion including arbitrary degree of coherence can thus be addressed within a unified framework of exciton dynamics.

1. Introduction and formalism

The motion and capture of Frenkel excitons in molecular crystals have been studied actively in recent times, both by experimentalists [1–5] and theorists [6–10]. The theoretical analysis of the problem runs into expected difficulties when the number of traps becomes large. Systems exist in which these difficulties are unimportant because solubility restrictions make high trap concentrations impossible to attain. This is the case for many aromatic hydrocarbon host crystals such as anthracene with traps such as tetracene wherein the relative trap concentration does not exceed 10^{-4} . The low-concentration theory [10] is then quite adequate and has been applied to study various effects including that of transport coherence in such systems. However, systems also exist [3–5] in which relative trap concentrations can be made to approach unity. For the analysis of exciton trapping in such systems it is necessary to develop new theoretical approaches. This note is an effort in that direction.

As in earlier work [10], we begin with the evolution of $P_m(t)$, the probability that the exciton occupies site m in the host crystal. If we employ the sim-

plest trapping model, called by us [10] the “sink model”, we may write

$$\begin{aligned} dP_m(t)/dt + P_m(t)/\tau \\ = \int_0^t dt' \sum [W_{mn}(t-t')P_n(t') \\ - W_{nm}(t-t')P_m(t')] - c \sum_r' \delta_{m,r} P_m(t). \end{aligned} \quad (1)$$

The use of the defect technique [11] allows us to write the “solution” of (1), with $\epsilon' = \epsilon + 1/\tau$, as

$$\tilde{P}_m(\epsilon) = \tilde{\eta}_m(\epsilon') - c \sum_r' \tilde{\psi}_{m-r}(\epsilon') \tilde{P}_r(\epsilon), \quad (2)$$

where tildes denote Laplace transforms, ϵ is the Laplace variable, and η is the solution of the homogeneous (trap-less) part of (1), i.e.

$$\eta_m(t) = \sum_n \psi_{m-n}(t) P_n(0). \quad (3)$$

The probabilities P_m in (2) are given, not explicitly but in terms of P_r . Thus we do not have a true solution. For systems with low trap concentrations one studies [10] the idealized one-trap problem, which allows (2) to be written as

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$$\tilde{P}_m(\epsilon) = \tilde{\eta}_m(\epsilon') - \frac{c\tilde{\psi}_{m-r}(\epsilon')\tilde{\eta}_r(\epsilon')}{1 + c\tilde{\psi}_0(\epsilon')}, \quad (4)$$

where r denotes the single trap-influenced host site. For n traps one must solve a set of n simultaneous equations for the respective probabilities before writing down an explicit solution such as (4). It is also possible to obtain [8,9] exact solutions for *periodic* traps, no matter what the concentration, by using discrete Fourier transforms in the trap super-lattice to solve the infinite number of simultaneous equations.

When the traps are not few in number, nor placed periodically, these methods fail. We suggest the following ν -function approach.

Our interest lies in the *total* excitation probability of the host or of the traps. The former is given by

$$n_H(t) = \sum_m P_m(t), \quad (5)$$

the summation being over all host sites. We now abandon pursuit of an exact solution of (2) and focus, instead, on solutions for n_H . Summing (2) over m we get

$$\tilde{n}_H(\epsilon) = \frac{1}{\epsilon'} \left[1 - c \sum_r \tilde{P}_r(\epsilon) \right], \quad (6)$$

where we have used the fact that the sum of the propagators $\psi_{m-r}(t)$ over m signifies the probability that the trap-less host remains excited in the absence of all decay, and is therefore exactly equal to 1.

Eq. (6) suggests we sum (2) over the trap-influenced sites, to attempt to evaluate the quantity $\sum_r P_r$, i.e. the probability that the trap-influence host region is excited. From (2) we obtain

$$\sum_r P_r(\epsilon) = \sum_r \tilde{\eta}_r(\epsilon') - c \sum_{r,s} \tilde{\psi}_{r-s}(\epsilon') \tilde{P}_s(\epsilon). \quad (7)$$

It is at this point that we define the ν -function:

$$\nu_s(t) = \sum_r \psi_{r-s}(t). \quad (8)$$

The definition obviously involves no assumption. But we now specifically assume that ν_s is independent of s . Note that ν_s is the sum of the trap-less decay-less host propagators from all trap-influenced sites r to the trap-influenced site s . Our assumption of the s inde-

pendence of this sum thus clearly involves an ensemble averaging of some sort in the general case. It is worth noting that the assumption is valid exactly for periodic trap placement as well as for the extreme dilute case, i.e. for a single trap. If we make the assumption, we find that (7) is solved as

$$\sum_r \tilde{P}_r(\epsilon) = \frac{\sum_r \tilde{\eta}_r(\epsilon')}{1 + c\tilde{\nu}(\epsilon')}. \quad (9)$$

The host excitation probability n_H is now

$$\tilde{n}_H(\epsilon) = \frac{1}{\epsilon'} \left[1 - \frac{c \sum_r \tilde{\eta}_r(\epsilon')}{1 + c\tilde{\nu}(\epsilon')} \right]. \quad (10)$$

In the frequently encountered case of uniform initial illumination, it is appropriate to take $P_n(0)$ to be $1/N$ for all n where N is the total number of host sites.

Then (10) reduces to

$$\tilde{n}_H(\epsilon) = \frac{1}{\epsilon'} \left[1 - \frac{\rho}{\epsilon' [c^{-1} + \tilde{\nu}(\epsilon')]} \right], \quad (11)$$

where ρ is the relative concentration, i.e. the ratio of trap-influenced host sites to the total number of host sites. Eq. (11) is the multi-trap analog of

$$\tilde{n}_H(\epsilon) = \frac{1}{\epsilon'} \left[1 - \frac{\rho}{\epsilon' [c^{-1} + \tilde{\psi}_0(\epsilon')]} \right] \quad (12)$$

showing clearly that our ν -function approach to the many-trap problem gives precisely the results of the single-trap problem with the single replacement of the self-propagator ψ_0 by ν , the sum over propagators in the trap-influenced host region. One can show that this result holds also when we employ not the simple sink model represented by (1) but more detailed substitutional models [10].

2. Evaluation of the ν -function

Since $\nu(t)$ is the sum of propagators from one trap-influenced host site to all trap-influenced host sites it contains $\psi_0(t)$ as the leading term. Thus, not only does $\nu(t)$ equal $\psi_0(t)$ exactly for the single-trap case but the equality holds approximately for small times for the multi-trap case. At large times $\nu(t)$ and $\psi_0(t)$ can deviate markedly, the latter tending to $1/N$ and thus to zero for an infinite system and the former to ρ which can be finite even for an infinite-size problem.

It is useful to calculate $\nu(t)$ exactly for the simple infinite one-dimensional host crystal wherein excitons move incoherently via nearest-neighbor transfer rates F and the traps are placed periodically. Several authors [6,7] have treated this system, exact solutions are available even for all the P_m , and it is therefore instructive to examine our ν -function for this case. Since the propagators are given by

$$\psi_m(t) = e^{-2Ft} I_m(2Ft), \quad (13)$$

where I_m is the modified Bessel function, the summation leading to ν is, in the Laplace domain,

$$\tilde{\nu}(\epsilon) = \sum_r \tilde{\psi}_{r-s}(\epsilon) = (\epsilon^2 + 4\epsilon F)^{-1/2} \times \sum_m \left[\frac{\epsilon + 2F - (\epsilon^2 + 4\epsilon F)^{1/2}}{2F} \right]^{m/\rho}, \quad (14)$$

where the m summation is over *all* integers from $-\infty$ to $+\infty$. The geometrical progression is summed trivially, with the result

$$\tilde{\nu}(\epsilon) = (\epsilon^2 + 4\epsilon F)^{-1/2} \times \left[\frac{(2F)^{1/\rho} + [\epsilon + 2F - (\epsilon^2 + 4\epsilon F)]^{1/\rho}}{(2F)^{1/\rho} - [\epsilon + 2F - (\epsilon^2 + 4\epsilon F)]^{1/\rho}} \right]. \quad (15)$$

It is convenient to reexpress (15) as

$$\epsilon \tilde{\nu}(\epsilon) = \frac{\tanh(\xi/2)}{\tanh(\xi/2\rho)} \quad (16)$$

with the definition of ξ as

$$\cosh \xi = 1 + \epsilon/2F. \quad (17)$$

The general behavior of $\nu(t)$ in an arbitrary system may be represented in a simplified fashion by approximating it through

$$\nu(t) = \rho + (1 - \rho)e^{-\Gamma t}. \quad (18)$$

This expression, which tends to ρ at long times, equals 1 at $t = 0$, and is controlled by a motion parameter Γ , can be used for rapid simplified calculations of the ρ dependence of exciton trapping. The expression is exact [11] in the above periodic trap-placement case when $\rho = 0.5$, i.e. when every other host site is trap-influenced.

Parris and the author have studied the behavior of $\nu(t)$ and its consequences for sensitized luminescence in a variety of systems. Those considerations will be reported elsewhere [11]. However, we mention here

without proof three interesting results from their analysis: (i) It is possible to reexpress $\nu(t)$ exactly as the sum of the product of a static quantity p_m and the dynamic quantity $\psi_m(t)$:

$$\nu(t) = \sum_m p_m \psi_m(t), \quad (19)$$

where ψ_m is the propagator describing exciton motion in the pure host and p_m is the probability that, given that the zeroth host site is trap-influenced, the m th host site is also trap-influenced. (ii) For periodic trap placement in arbitrary dimensions $\nu(t)$ equals the *self-propagator* for a smaller (finite and periodic) lattice of size $1/\rho$. (iii) If no correlations exist in the trap placement $\nu(t)$ and $\psi_0(t)$ are related via

$$\nu(t) = \rho + (1 - \rho) \psi_0(t). \quad (20)$$

3. Discussion

The generalized master equation approach to exciton trapping was formulated [10] specifically to study the effects of transport coherence on capture phenomena, i.e. on energy transfer. While it is adequate for low-concentration systems, it exhibits difficulties inherent in a single-trap analysis of a multi-trap situation. The ν -function approach advocated in the present note is a natural way to remove those difficulties. The disadvantage of the ν approach is that the assumed s independence of ν_s gives it a mean-field character, the treatment of fluctuations being absent from the analysis. The advantage of the approach is that it makes it possible to investigate sensitized luminescence for arbitrary trap concentration without using truncation or ρ -expansion procedures. The expressions [11] connecting ν to the trap-placement pair correlation function and to exciton propagators appear to be particularly useful in studying the wealth of experimental observations [3-5] that have been gathered in high-concentration systems in recent times. Some of those applications, a variety of further calculations and a comparison to other theories [6-9] will be reported separately.

It is interesting to mention in passing the $\nu(t)$ that corresponds to a recent exact calculation [9] of trapping in a one-dimensional host with nearest-neighbor transfer rates, no radiative decay, and infin-

itely fast capture. In the Laplace domain the relation (11) between ν and n_H when combined with the low-concentration expression given by Movaghar et al. [9]

$$\tilde{n}_H(\epsilon) = 1/\epsilon - (2y/\epsilon) \int_0^{\infty} e^{-s} \tanh(s/2y) ds, \quad (21)$$

where $y = \rho(F/\epsilon)^{1/2}$, immediately yields

$$\epsilon \tilde{\nu}(\epsilon) = \frac{\frac{1}{2}(\epsilon/F)^{1/2}}{\int_0^{\infty} e^{-s} \tanh[s(\epsilon/F)^{1/2}/2\rho] ds} \quad (22)$$

The similarity of (22) to the exact periodic trap expression (16) should be noted: in the light of (19) $\frac{1}{2}(\epsilon/F)^{1/2}$ equals $\sinh(\frac{1}{2}\xi)$ which would equal $\tanh(\frac{1}{2}\xi)$ for small ξ .

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