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# Master Equation Techniques for Exciton Motion, Relaxation, Capture, and Annihilation

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Techniques developed recently for the study of exciton dynamics in molecular solids are discussed. They include master equation methods for the analysis of prerelaxation energy transfer, the generalized master equation approach to coherence in exciton motion, and the defect technique as applied to exciton trapping and annihilation.

**KEY WORDS:** Master equations; trapping; annihilation; relaxation; exciton dynamics; memory functions.

## 1. INTRODUCTION: GMEs AND MEMORY FUNCTIONS

Frenkel excitons, produced in molecular crystals as a result of optical absorption, lead a rather eventful life. They move, undergo vibrational relaxation, are captured by traps, participate in mutual annihilation when in pairs, and die, radiatively or otherwise. A number of master equation techniques have been found to be naturally applicable to the study of these excitons, and we present here a brief description of some of them, in the form of an overview.

Details of the characteristics of Frenkel excitons or of molecular crystals may be found elsewhere.(1,2) Suffice it to state that the physics of the system makes it appropriate and practical to use the (real) space of the sites of a (crystalline) lattice for the description of the motion. The central quantity is most often the probability $P_m(t)$ that the exciton occupies site $m$ at time $t$. A natural evolution equation describing decay with lifetime $\tau$ and

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motion with transition rates $F_{mn}$ is

$$\frac{dP_m(t)}{dt} + \frac{P_m(t)}{\tau} = \sum_n \left[ F_{mn} P_n(t) - F_{nm} P_m(t) \right] \tag{1}$$

Equation (1) is, however, restricted to incoherent motion. A fundamental concern in this field being the degree of coherence in exciton transport, we employ the generalized master equation (GME)

$$\frac{dP_m(t)}{dt} + \frac{P_m(t)}{\tau} = \int_0^t dt' \sum_n \left[ \mathscr{W}_{mn}(t-t') P_n(t') - \mathscr{W}_{nm}(t-t') P_m(t') \right] \tag{2}$$

rather than (1) as our starting point. The GME (2) reduces to the ordinary Master equation (1) for large times (except in special cases) and is capable of describing motion with arbitrary degree of coherence. It is thus particularly useful for studies of exciton motion at low temperatures and/or at short times as in picosecond observations. As is well known, the GME is an exact consequence of microscopic dynamics(3,4) for certain initial conditions. These may be either completely localized(3) or completely delocalized.(5) The latter result (5) is relatively new and is nontrivial because selection rules for optical absorption naturally result in largely delocalized initial placement of the exciton. A driving term is appended to the GME in the intermediate case as when exciton wavepackets of finite size and dispersion are formed.

Equations like (2) are generally used with phenomenological memory functions $\mathscr{W}_{mn}(t)$. Our own emphasis has been, instead, on deriving them from the microscopic dynamics of the exciton. Exact expressions for them have been presented(6) for crystals of arbitrary dimensionality and structure as also for systems including phenomenological baths and for those whose evolution is governed by various stochastic Liouville equations. Direct connections of $\mathscr{W}_{mn}(t)$ to optical spectra have been established(7) and used to extract the former from measurements of the latter without the use of model assumptions. The interplay of spectral features such as zero-phonon lines and sidebands with multiple-time-constant memories has been studied(8) and correction factors(9) neglected in the traditional analysis(10) have been obtained explicitly. To dispel the notion that $\mathscr{W}(t)$'s are phenomenological constructs and to stress the availability of these microscopically calculated memory functions, we display a composite of some of these treatments:

$$\mathscr{W}_{mn}(t) = \left[ \mathscr{W}^{c}_{mn}(t) \right] \left[ \phi^{b}_{mn}(t) \right] e^{-\alpha t} \tag{3}$$

In (3) the coherent memory function $\mathscr{W}^{c}_{mn}(t)$ is given by its Laplace and (discrete) Fourier transform $\tilde{\mathscr{W}}_k^c(\epsilon)$ as(6,11)

$$\tilde{\mathscr{W}}_k^c(\epsilon) = -\left\{(1/N)\sum_q \left[\epsilon + i(V^{k+q} - V^q)\right]^{-1}\right\}^{-1} \tag{4}$$

where $V^k$ is the Fourier transform of the intersite matrix element $V_{mn}$, the dimensionality is arbitrary ($k, q, m, n$ are vectors) but translational periodicity has been assumed, $\epsilon$ is the Laplace variable, and tildes denote Laplace transforms. The bath contribution $\phi^b_{mn}(t)$ in (3) has been assumed multiplicative for simplicity. It can be proved to be so in simple cases. For the linearly interacting standard exciton–phonon model it can be shown to be closely related to the characteristic functions given by Lax in his treatment of spectra of impurities.(12) The dependence of the memory on temperature, phonon frequencies, and exciton–phonon coupling constants can be calculated explicitly. Another useful and nontrivial example of $\mathscr{W}(t)$'s is

$$\mathscr{W}_{mn}(t) = 2V^2 e^{-\alpha t}\big(J^2_{m-n+1} + J^2_{m-n-1} + 2J_{m-n-1}J_{m-n+1} - 2J^2_{m-n} - J_{m-n}J_{m-n+2} - J_{m-n}J_{m-n-2}\big) + \delta(t)\Gamma_{mn} \tag{5}$$

wherein the $J$'s are Bessel functions of argument $2Vt$. This memory function corresponds exactly(11,13) to a simplified form of the so-called stochastic Liouville equation (SLE).(13,14) The motion described in (5) has a coherent part controlled by nearest-neighbor Hamiltonian matrix elements $V$ and influenced by a randomizing or scattering bath parameter $\alpha$, and an incoherent part associated with transfer rates $\Gamma_{mn}$. The simplest way(15,16) of describing motion with an intermediate degree of coherence is through memory functions (5) without the last term. The corresponding density matrix elements $\rho_{mn}$ obey the simplified SLE

$$\frac{d\rho_{mn}}{dt} = -iV(\rho_{m+1n} + \rho_{m-1n} - \rho_{mn+1} - \rho_{mn-1}) - (1 - \delta_{m,n})\alpha\rho_{mn} \tag{6}$$

and the degree of coherence is measured by the ratio $V/\alpha$ which is essentially the ratio of the mean free path to the lattice constant. We shall use (6), and the $\mathscr{W}(t)$ of (5) corresponding to it, in some of the sequel to give a quick-and-ready description of coherence effects.

## 2. MOTION IN PURE LATTICES: GRATING OBSERVATIONS

One way to study the motion of particles in a lattice is to observe the time evolution of an initially created inhomogeneity in the particle population. Transient grating observations provide an ingenuous example.(17,18) Two laser beams crossed at an angle interfere and thereby produce, through optical absorption, a *sinusoidal* initial population of excitons in the crystal. The time evolution of the amplitude of the population sinusoid is measured by using another laser beam as a diffraction probe. The amplitude suffers loss in time as a result of the exciton motion as well as of its decay. Motion characteristics, such as the degree of coherence and the magnitude of the relevant transport parameters, may thus be deduced from the time evolution of the diffraction signal.

If we define $\mathscr{A}_{mn}(t) = -\mathscr{W}_{mn}(t)$ for $m \neq n$ and $\mathscr{A}_{mm}(t) = \sum_n \mathscr{W}_{nm}(t)$, the GME (2) gives

$$\frac{dP^k(t)}{dt} + \frac{P^k(t)}{\tau} + \int_0^t dt'\, \mathscr{A}^k(t-t')P^k(t') = 0 \tag{7}$$

where $P^k$ and $\mathscr{A}^k$'s are discrete-Fourier transforms of $P_m$ and $\mathscr{A}_m$. Whereas most situations require a Fourier inversion of the solution of (7) in order to extract the physics, it is not necessary in the grating context. The Fourier transform $P^k$ (more precisely, the square of $P^k$) is itself the grating signal! A universal model-independent relation between the observed signal $P^k(t)$ and the memory functions is thus provided by (7). Explicitly,

$$\tilde{P}^\eta(\epsilon)/P^\eta(0) = \left[\epsilon + \frac{1}{\tau} + \tilde{\mathscr{A}}^\eta(\epsilon)\right]^{-1} \tag{8}$$

where we have replaced $k$ by $\eta$, the grating wave vector. As the latter is given by

$$\eta = (4\pi a/\lambda)\sin(\theta/2) \tag{9}$$

where $a$ is the lattice spacing, $\lambda$ the wavelength of excitation, and $\theta$ the angle of crossing, it is possible, at least in principle, to span the full $\eta$ space experimentally and thereby to deduce the $\mathscr{A}_{mn}(t)$'s or $\mathscr{W}_{mn}(t)$'s and thus the *entire* dynamics of the exciton. Charts of memory functions and the corresponding transient grating signals have been constructed(11,18) on the basis of this relationship between $P^k$'s and $\mathscr{A}^k$'s and an explicit practical prescription to obtain the memories from the observed signals has been given.

To appreciate the effects of transport coherence on grating signals one may calculate the latter for the simple exciton system governed by (6). The signal is found(19) to be generally

$$P^\eta(t)/P^\eta(0) = e^{-t/\tau}\left[1 - e^{-\alpha t} y \int_0^t du\, e^{\alpha(t^2-u^2)^{1/2}} J_1(yu)\right] \tag{10}$$

where $y = 4V\sin(\eta/2)$, but reduces to a simple $J_0$ form

$$P^\eta(t)/P^\eta(0) = e^{-t/\tau} J_0\left[4Vt\sin(\eta/2)\right] \tag{11}$$

in the purely coherent limit when $\alpha = 0$, signifying no scattering or bath interactions. Its oscillations are damped out as $\alpha$ is increased, and in the completely incoherent limit $\alpha \to \infty$, $V \to \infty$, $V^2/\alpha = F$ with $F$ finite, it becomes the familiar exponential with the exponent $[1/\tau + 4F\sin^2(\eta/2)]$. The oscillations of $J_0$ in (11) can be immediately understood as arising from overshooting tendencies of the sinusoidal inhomogeneity in the coherent limit. These tendencies are damped out as scattering is increased.

## 3. MOTION IN DEFECTIVE LATTICES: CAPTURE BY TRAPS

An obvious way of studying exciton motion is to start them at one end of a crystal by illumination and to capture and detect them at the other end.(11) This kind of capture experiment, although interesting and useful, will not be reviewed here for reasons of space limitation. Consider, instead, the bulk-quenching system consisting of a crystal doped in the bulk with traps, i.e., guest molecules. Excitons moving in the host crystal are trapped when they wander near, or within the influence of, the traps. The latter decay radiatively in a frequency range different from that of the host molecules, making detection possible. An appropriate evolution equation is (2) with the term $-c\sum_r' \delta_{m,r} P_m(t)$ appended to its right side. The $r$'s denote host sites which are trap-influenced. When the exciton reaches one of them its probability decays at rate $c$ into the traps. It is possible, and sometimes important, to study a variety of more sophisticated trapping models(20) but here we shall restrict ourselves to the above simple one. The "solution" of (2) with the trapping term may be written in the Laplace domain as

$$\tilde{P}_m(\epsilon) = \tilde{\eta}_m(\epsilon') - c\sum_r{}' \tilde{\psi}_{m-r}(\epsilon')\tilde{P}_r(\epsilon) \tag{12}$$

where $\epsilon' = \epsilon + 1/\tau$, the homogeneous solution $\sum_n \psi_{m-n}(t)P_n(0)$ in the absence of traps is denoted by $\eta_m(t)$, and $\psi_m(t)$ is the propagator for the trapless decayless host.

We first study the effect of coherence by considering the dilute case, specifically the case of a single trap.(20) The summation in (12) is restricted then to a single term. The case $m = r$ of (12) yields an explicit solution of $\tilde{P}_r(\epsilon)$ and its substitution in (12) gives all $P_m$'s. The host luminescence intensity is proportional to $n_H(t) \equiv \sum_m P_m(t)$, the probability that the host is excited at time $t$. It is given from (12), for uniform initial illumination, by

$$\tilde{n}_k(\epsilon) = \frac{1}{\epsilon'}\left\{1 - \frac{\rho}{\epsilon'[(1/c) + \tilde{\psi}_0(\epsilon')]}\right\} \tag{13}$$

Here $\rho$ is the relative concentration, i.e., the ratio of the number of trap-influenced host sites to $N$ the total number of host sites, and thus equals $1/N$.

The observable $n_H(t)$ requires the inversion of the Laplace transform in (13). This, however, is not the case for the observable $\phi_H$, which is known as the quantum yield of the host, and is defined as the ratio of the total number of excitons emerging radiatively from the host as photons to the number initially put into the host through illumination:

$$\phi_H = 1 - \left[\frac{\rho\tau}{(1/c) + \tilde{\psi}_0(1/\tau)}\right] \tag{14}$$

The effect of transport characteristics on the luminescence intensity and on the yield is felt through $\psi_0$ in the above expressions. An evaluation of $\tilde{\psi}_0(\epsilon)$ or $\tilde{\psi}_0(1/\tau)$ may always be carried out from the memory functions, through the relation, with $d$ as the number of dimensions,

$$\tilde{\psi}_0(\epsilon) = (1/2\pi)^d \int dk \left[\epsilon + \tilde{\mathscr{A}}^k(\epsilon)\right]^{-1} \tag{15}$$

For the simple SLE model of (6), $\tilde{\psi}_0$ is found explicitly$^{(20)}$ to be a combination of elliptic integrals and the corresponding plots of the yield are available showing dependence on the coherence parameter $V/\alpha$.

Having explored the coherence theme in exciton capture phenomena by studying the exact single trap solutions, we now turn to the multitrap case. Obviously, an exact solution of (12) is out of the question except when the number of traps is small or when they are systematically arranged, e.g., periodically. It is, however, possible to make considerable headway into the problem by using the fact that the observables, viz., $n_H(t)$ and $\phi_H$, require for their solution the quantity $\sum_r' P_r(t)$ rather than the individual occupation probabilities $P_m(t)$. Thus, summing (12) over all sites $m$,

$$\tilde{n}_k(\epsilon) = \frac{1}{\epsilon'}\left[1 - c\sum_r{}' P_r(\epsilon')\right] \tag{16}$$

The quantity $\sum_r' P_r(t)$, which is the probability that the trap-influenced sites are excited, is obtained by summing (12) over those sites.

$$\sum_r{}' \tilde{P}_r(\epsilon) = \sum_r{}' \tilde{\eta}_r(\epsilon') - c\sum_s{}' \tilde{\nu}_s(\epsilon')\tilde{P}_s(\epsilon) \tag{17}$$

where we introduce the function $\nu_s \equiv \sum_r' \psi_{r-s}$, which is the sum of propagators from the trap-influenced site $s$ to all the trap-influenced sites. If we now make the assumption that $\nu_s$ is independent of $s$, (17) is immediately solved in terms of $\nu$. Indeed, all the single-trap expressions such as (13) and (14) now apply exactly to the multitrap case with the simple replacement of the self-propagator $\psi_0$ by the propagator sum $\nu$.

The function $\nu(t)$ is equal to $\psi_0(t)$ for short times but at large times tends to $\rho$ rather than to $1/N$ as does $\psi_0(t)$. In an infinite system with finite $\rho$, we see that $\psi_0$ tends to zero as $t \to \infty$ but $\nu$ tends to the finite value $\rho$. It is possible to show[21] that $\nu(t)$ may be rewritten as

$$\nu(t) = \sum_m p_m \psi_m(t) \tag{18}$$

which is a sum over *all* host sites of the product of the dynamic host quantity $\psi_m(t)$ which describes exciton motion in the host and the static trap quantity $P_m$ which describes trap placement within the host. The former is the propagator and the latter is the probability that the $m$th site is trap-influenced given that the zeroth site is trap-influenced. If no correlation exists in trap placement, (18) reduces to

$$\nu(t) = \rho + (1 - \rho)\psi_0(t) \tag{19}$$

If the other extreme applies, i.e., if the traps are placed periodically, $\nu(t)$ equals the self-propagator for a smaller lattice of sites $1/\rho$. As an explicit example, the case of periodic traps in one dimension can be shown to lead to, where $\cosh\xi$ equals $1 + \epsilon/2F$,

$$\epsilon\tilde{\nu}(\epsilon) = \frac{\tanh(\xi/2)}{\tanh(\xi/2\rho)} \tag{20}$$

Although it possesses a certain kind of mean-field character, the $\nu$-function approach to exciton capture appears to be quite powerful. Further consequences and its relations to other existing approaches[22-25] are being worked out.

## 4. MOTION IN THE PRESENCE OF MUTUAL ANNIHILATION

Two excitons approaching each other may undergo mutual annihilation as a result of their interaction. The basic observables are, as in the capture case, the quantum yield $\phi$ and the luminescence intensity which is proportional to the excitation probability $n(t)$. The natural way to analyze this phenomenon is by considering the many-particle system and studying the evolution of the system-point in the corresponding higher-dimensional space. An exact solution can be obtained[27] for the two-exciton system. The annihilation problem is transformed into a trapping problem in the space of twice the number of dimensions as the actual system. Thus the quantity $P_{m,n}(t)$, the probability that the first exciton occupies site $m$ and the second exciton occupies site $n$, would obey, in the simple case of incoherent motion with nearest-neighbor rates $F$ and of destruction rate $2b$,

$$\frac{dP_{m,n}}{dt} = F(P_{m+1,n} + P_{m-1,n} + P_{m,n+1} + P_{m,n-1} - 4P_{m,n}) - \delta_{m,n}2bP_{m,n} \tag{21}$$

It is assumed for simplicity that annihilation occurs at rate $2b$ when the two excitons occupy the same site. The region $m = n$ is thus a trapping region in the higher space. Space limitation does not allow us to show even the full starting equations(27) for the problem. Suffice it to say that two other equations, one for the probability that there is only a single exciton and it is at site $m$, and the other for the probability that there is no exciton left in the system are written down and solved along with the generalization of (21) for arbitrary degree of coherence (and also for longer annihilation range, if required). The solution is exact and results in expressions for the experimentally accessible quantities of $\phi$ and $n(t)$. Furthermore, it is possible to study, with its help, the range of validity of the traditional bilinear equation which describes annihilation through a term $-\gamma n^2(t)$, and also to derive expressions for the proportionality constant $\gamma$ (the annihilation constant) in terms of microscopic parameters. The general result is

$$\gamma = v\left[\frac{1}{b} + \tilde{\psi}_0(1/\tau)\right]^{-1} \tag{22}$$

where $v$ is the volume of the unit cell. Once again we see how the memory functions of (2), which enter into the propagator through (15), influence the physical measurable, in this case the annihilation constant. On the basis of (22) explicit calculations of $\gamma$ showing the effects of dimensionality, of lattice structure, and of the degree of coherence have been performed.(11,26,27)

While the annihilation theory outlined here is exact for arbitrary magnitude and kind of exciton motion, it is not directly applicable to very high exciton densities. Since the latter present a true many-body problem, radically new approaches must be introduced. A problem which is related to the exciton context only in a distant way will now be described briefly along with its solution. One hopes that insights into exciton annihilation at high densities will be gained by its study.

The problem concerns pycnonuclear reactions in the interior of stars. Every one of the $N$ sites of a lattice is initially occupied by a particle. The particles do not move but may undergo mutual pairwise annihilation if the participating particles occupy neighboring sites. The problem can be approached by studying the system evolution in configuration space. An exact solution is possible for one dimension. One gets(28)

$$f_1(t) = \exp\left[-2(1 - e^{-Rt})\right] \tag{23}$$

as the surviving fraction of particles at time $t$, $R$ being the rate of annihilation. An approximate method of solution has been applied to study the problem in dimensions other than 1 and results in

$$f_1(\infty) = (2d - 1)^{-(d/d-1)} \tag{24}$$

for the eventual ($t \to \infty$) limit of the surviving fraction in $d$ dimensions. Equation (24) gives $f_1(\infty)$ as $5^{-3/2} = 0.0894$ in three dimensions, $1/9 = 0.1111$ in two dimensions, and reduces to the exact result $e^{-2} = 0.1353$ (see 23) in one dimension. Efforts are under way to combine this problem which has no motion but has high particle densities with the true exciton problem described earlier which has a complete description of motion but is valid only for low densities.

## 5. MOTION ACCOMPANIED BY VIBRATIONAL RELAXATION

One of the important questions in exciton transport is whether exciton motion occurs before, during, or after vibrational relaxation. The master equation approach to this problem(29) addresses $P_{m,\mu}(t)$, the probability that the exciton is at the $m$th site, *and* the system is in the vibrational state $\mu$. Combined transition rates describing relaxation and motion are written down. The motion rates have the same site dependence as the tradition rates but depend on the system vibrational state. The vibrational rates are assumed to correspond to the representation of the molecule as a harmonic oscillator and to a bath interaction which is linear in the oscillator displacement. By using techniques originally developed(30) for the pure relaxation problem and extended(31) for the luminescence-relaxation situation, explicit solutions can be obtained(29) for various initial conditions in the vibrational manifold. They include $\delta$ functions, Poisson distributions, and Laguerre polynomials, corresponding, respectively, to laser excitation, broad band excitation at zero temperatures, and broad band excitation at nonzero temperatures.

The concept of time-dependent motion rates emerges from this analysis. Thus the counterpart of the master equation (1) in the presence of vibrational relaxation is

$$\frac{dP_m(t)}{dt} + \frac{P_m(t)}{\tau} = \sum_n \left[ F_{mn}(t)P_n(t) - F_{nm}(t)P_m(t) \right] \tag{25}$$

The transition rates show a time dependence and a curious effect at long times. Their initial values are determined by the excitation condition and they change in time as the relaxation or thermalization process proceeds during motion. As $t \to \infty$, they do *not* tend to their thermalized values but are usually smaller. This rate-depression phenomenon is a general result of the interplay of relaxation and exciton motion. This theory has been applied to study the dependence of transfer efficiency on initial excitation wavelength and the effect of vibrational relaxation on transient grating signals. In simple cases $F_{mn}(t)$ is of the form $F_{mn}\phi(t)$, the temporal behavior of the rates being independent of the spatial character. The propagators of

(25) are then trivially seen to be the same as those of (1) with the substitution $t \rightarrow \int_0^t dt' \, \phi(t')$.

Explicit forms for $\phi(t)$ have been calculated.$^{(29)}$ The resulting propagators are being used to study exciton phenomena such as capture, grating observations, and annihilation, in the presence of the interplay of vibrational relaxation and motion.

## 6. REMARKS

We have seen how generalized master equations find natural application in the study of exciton motion (Section 2), capture (Section 3), and annihilation (Section 4), a common theme in that treatment being the effect of transport coherence. We have attempted a unification of wavelike or ringing (coherent) behavior on one hand and of diffusive or hopping (incoherent) behavior on the other. We have emphasized the calculation of memory functions from microscopic interactions as well as their direct connection to experimentally observable quantities. We have also briefly reviewed an approach to exciton capture by many traps, a static annihilation problem and shown how the interplay of relaxation and motion can be investigated.

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