SIMPLE CONNECTION BETWEEN SIGNALS IN TRANSIENT GRATING EXPERIMENTS AND MEMORIES IN GENERALIZED MASTER EQUATIONS FOR EXCITONS

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An exact, simple, and useful connection is shown to exist between transient grating signals and generalized master equations used in the analysis of exciton transport in molecular crystals. It is model independent and akin to the connection between the van Hove correlation function and scattering observables.

This note will show the intimate relationship that exists between observed signals in a certain type of experiment concerning the propagation of Frenkel excitons in molecular crystals [1] and memory functions that appear in a general theoretical formalism [2] used to describe exciton motion. The observations are transient grating signals [3] and the theoretical formalism is that of the generalized master equation [4].

The transient grating experiments [3] employ two time-coincident picosecond excitation pulses crossed in the bulk of the crystal at a definite but variable angle, to create, through optical absorption, a sinusoidal inhomogeneity in the exciton density. A third picosecond pulse is diffracted off, and is thus used to probe the amplitude of the transient grating of excitons. The signal is essentially the square of the amplitude of the inhomogeneity in the exciton density, and decays in time as a combined result of the motion of excitons and of their finite lifetime τ.

The generalized master equation [4] (GME) describes, in the exciton context, the probability $P_m(t)$ that the exciton occupies site m of the crystal at time t:

$$\frac{\mathrm{d}P_m(t)}{\mathrm{d}t} = \int_0^t \mathrm{d}t' \sum_n \left[\mathcal{W}_{mn}(t-t')P_n(t') - \mathcal{W}_{nm}(t-t')P_m(t') \right] , \tag{1}$$

the key quantities being the memory functions $\mathcal{W}_{mn}(t)$. These can be calculated [5–7] from microscopic models or obtained from optical spectra [5,8] and the GME is valid [9] under an extremely large class of conditions of experimental relevance.

The intimate relationship that exists between $\mathcal{W}_{mn}(t)$'s of eq. (1) and the signals in the grating experiments, is as follows. Let us, for convenience, call the square root of the actual signal the key experimental observable $S(t)$, define quantities $\mathcal{A}_{mn}(t) = -\mathcal{W}_{mn}(t)$ for $m \neq n$ and $\mathcal{A}_{mm}(t) = \Sigma_n \mathcal{W}_{nm}(t)$, and introduce the discrete Fourier transform $\mathcal{A}^k$:

$$\mathcal{A}^k(t) = \sum_{m-n} \mathcal{A}_{mn}(t) \mathrm{e}^{\mathrm{i}k(m-n)} . \tag{2}$$

If we now define the wavevector η through

$$\eta = (4\pi a/\lambda)\sin(\theta/2) , \tag{3}$$

where a is the lattice spacing, λ is the wavelength of excitation and θ is the angle of crossing of the exciting beams, the simple connection between the observable $S(t)$ and the memories $\mathcal{A}(t)$ is given by

$$\frac{\mathrm{d}S^\eta(t)}{\mathrm{d}t} + \frac{S^\eta(t)}{\tau} + \int_0^t \mathrm{d}t' \,\mathcal{A}^\eta(t-t')S^\eta(t') = 0 . \tag{4}$$

The connection has an even more direct appearance in the Laplace domain

$$\widetilde{S}^\eta(\epsilon)/S^\eta(0) = [\epsilon + \tau^{-1} + \widetilde{\mathcal{A}}^\eta(\epsilon)]^{-1} , \tag{5}$$

where tildes denote Laplace transforms and ϵ is the Laplace variable. The theory behind eqs. (4) and (5) was given by the author earlier [6]. We shall not repeat the details here. Suffice it to make the observation that

Table 1
Correspondence chart showing the connection between transient grating signals and meory functions. By "signal" is meant the quantity $e^{t/\tau}S^{\eta}(t)$ and by "memory" is meant $\mathcal{A}^{\eta}(t)$. See text for the explicit meaning of these quanties.

Memory function	Grating signal
$\mathcal{A}^{\eta}(t)$	$^{\eta}(t)\int d\epsilon\, e^{\epsilon t}[\epsilon+\int_0^{\infty} d\tau\, e^{-\epsilon\tau}\mathcal{A}^{\eta}(\tau)]^{-1}$
$R\delta(t)$	e^{-tR}
J^2	$\cos Jt$
$J^2 e^{-\alpha t}$	$e^{-\alpha t/2}[\cos\Omega t+(\alpha/2\Omega)\sin\Omega t]$ with $\Omega=[J^2-(\alpha^2/4)]^{1/2}$
$(2J^2e^{-\alpha t})(4\sin^2\frac{1}{2}\eta)[J_0(4Jt\sin\frac{1}{2}\eta)+J_2(4Jt\sin\frac{1}{2}\eta)]$	$1-e^{-\alpha t}b\int_0^t du\,\exp[\alpha(t^2-u^2)^{1/2}]\,J_1(b)$ with $b=4J\sin\frac{1}{2}\eta$

what makes the result (4) or (5) possible is that transient grating experiments directly measure the *Fourier coefficients* $P^k(t)$ of the exciton occupation probabilities.

The function of the present letter is to emphasize the generality and especially the practical usefulness of the above connection. Being only *model* calculations, our earlier treatments [6,10] have not clarified this point. The relations (4) and (5) are, however, completely general, i.e., independent of detailed model assumptions concerning the exciton dynamics. They allow one to build a simple correspondence chart (see table 1). One sees, for instance, that the signal equals $e^{-t/\tau}$ times (i) an exponential, (ii) a sinusoid and (iii) a damped sinusoid in the respective cases that the memory functions have a time dependence which is (i) a δ-function, (ii) a constant and (iii) an exponential. While the last two of these cases have only pedagogical significance, case (i) corresponds to totally incoherent motion and is thus experimentally relevant.

The practical usefulness of our result stems from the fact that it allows one to determine, at least in principle, the entire dynamics of excitions through transient grating experiments. It is clear from eq. (1) that knowing all the $\mathcal{W}_{mn}(t)$'s or $\mathcal{A}_{mn}(t)$'s is knowing the dynamics. But all these memories can be found through the inverse of (2) once all the Fourier components $\mathcal{A}^{\eta}$ are known! These components can be obtained through eq. (5) from the signal S^{η}. What is called for, is experiments that span the entire range of η by varying the angle of crossing θ, and/or the excitation wavelength λ. The resulting signals will then immediately yield the memory functions and therefore the details of the dynamics. The following is the combined explicit prescription to extract theoretical information from the signals:

$$\mathcal{A}_{mn}(t)=-(1/N)\sum_{\eta} e^{-i\eta(m-n)}\int d\epsilon\, e^{\epsilon t}$$
$$\times\left[\epsilon+\tau^{-1}-S^{\eta}(0)\left(\int_0^{\infty} dt'\, e^{-\epsilon t'}S^{\eta}(t')\right)^{-1}\right]. \quad (6)$$

Experimental signal data enter into the right-hand side and the left-hand side gives the exciton dynamics.

Signals obtained by Salcedo et al. [3] have been interpreted by them in terms of a diffusion for exciton motion. Such an interpretation gives only the value of the diffusion constant. It is obvious that considerably more detailed information can be extracted with the help of the present analysis. If the degree of exciton motion is coherent enough in comparison to the experimental probe time, i.e., if the latter is shorter than the coherence time (which is usually called $1/\alpha$ and signifies a randomizing time characteristic of bath interactions), non-exponential signals are expected. This is clear from eqs. (4) or (5). Such signals corresponding to a model memory (the last entry in table 1) have been given earlier [6,10]. If the probe time is longer than $1/\alpha$, the signals are purely exponential. But now there is another coherence question that should be asked: is $1/\alpha$ shorter or longer than $1/J$, a characteristic time for coherent motion? Here J is a characteristic site-to-site interaction matrix element (for instance, nearest-neighbour) expressed in inverse time units, and is therefore proportional to the exciton bandwidth. This second coherence question clearly concerns the lifetime of a k-state and has been analysed [6] in some detail in the grating context. It has been shown [6] that the exponential signal has considerably different features in the $J \gg \alpha$ (coherent) and $J \ll \alpha$ (incoherent) limits and that its variation with respect to J or α bears kinship to the variation [11] of a quite different quantity, viz. the Förster–Dexter transfer rate.

There is yet more that can be extracted from these experiments through the present analysis even when the degree of coherence is not of interest. Detailed information about the transfer rates, including their anisotropy and temperature dependence belong to this category. We have also obtained the effect that intramolecular relaxation processes such as vibrational relaxation, can have on transient grating signals when they compete with the motion process, and have shown that generally non-exponential signals result. These matters will be published elsewhere.

It is to be regretted that sufficient experimental information is not yet available on grating signals in pure crystals. The observations in ref. [3] concern mixed crystals and necessitate the inclusion of the additional complexity of transport in *random* systems in the above analysis. We hope that more transient grating observations will be made in the future on pure crystals and that the slight uncertainties about initial conditions that appear to exist will be removed experimentally. On the other hand we also hope that practical prescriptions to obtain GME's for random systems will be available from future theoretical work. These could be based on equivalences [4,12] such as those given by Klafter and Silbey and techniques [13] such as those of Scher and Montroll. In this context it might be useful to state that the exponential signals obtained in ref. [3] do not necessarily imply incoherent motion for the corresponding pure crystals because the spatial randomness gives rise to its own memory functions being superimposed [12] on the natural $\mathcal{W}_{mn}(t)$'s.

We conclude by stating that the present connection between grating signals and memory functions is similar in character to the connection between scattering observables and the van Hove self-correlation function [14]. Indeed the grating signal in the time domain and the well-known "scattering function" [14] in the frequency domain are Fourier transforms of each other.

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