INITIAL CONDITION EFFECTS ON THE TIME DEPENDENCE OF THE SIGNAL IN TRANSIENT GRATING EXPERIMENTS *

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Transient grating and Ronchi ruling experiments, which constitute a powerful observational tool for the investigation of the motion of excitons in molecular crystals, are usually interpreted in terms of an analysis which assumes the initial density matrix of the exciton to be random. This assumption cannot be verified clearly on the basis of currently available experimental data. Recent work has shown that if the assumption is relaxed or changed, significant deviations can occur in the evolution of the signal. Interpretation of the experiments and extraction of exciton motion parameters could therefore be in serious error at least in principle. We carry out a detailed analysis of this initial condition effect on the theoretically predicted signal, present specific time dependences for the signal, and conclude that, at the present state of technology and experimentation, initial condition effects are negligible for most systems studied so far including pure anthracene crystals at 20 K and 10 K for which the motion is known to be quite coherent. The usual theory is therefore quite adequate in such situations. For pure anthracene at 1.8 K, we find that the effects of the deviations from a random initial density matrix are on the borderline of being discernible and, with improved experimentation, might be measurable in the future.

1. Introduction

Luminescence in molecular crystals and aggregates is influenced by a variety of excitonic phenomena such as spatial transport, energy relaxation, and dephasing. Many ingenious experimental techniques and theoretical methods have been developed to investigate these phenomena. One of the outstanding techniques for the experimental determination of the motion parameters of Frenkel excitons in molecular crystals is based on the initial creation of a spatial inhomogeneity in the density of excitons in the crystal and the subsequent monitoring of the time evolution of the inhomogeneity. In the triplet realm the technique is called the Ronchi ruling method [1–3]. Triplets are created in the crystal by illuminating the crystal through a series of alternating transparent and opaque strips - the Ronchi ruling. Triplet motion results in their mutual annihilation and the consequent formation of singlets. The time dependence of the (delayed) fluorescence of these singlets contains information concerning triplet motion. Through careful experimentation along these lines, Ern et al. [1–3] have compiled tables of triplet diffusion constants in several aromatic hydrocarbon crystals. In the singlet realm the technique goes under the name of the transient grating method [4–10] and it has been developed recently as a result of dramatic improvements in picosecond methods. A picosecond laser pulse is split into two parts and the two parts are caused to arrive simultaneously at a variable angle in the crystal. Optical absorption creates a (singlet) excitation population which varies sinusoidally in space as a result of the interference of the two pulses. The subsequent time evolution of the transient exciton grating thus produced is monitored through the diffraction of a third laser pulse which is delayed appropriately. The method was pioneered by Fayer [1] for molecular crystals, and has been recently used actively by Powell and others in inorganic solids [8–10].

The notable advantage that this method of following the time evolution of an inhomogeneity in

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the density has over standard methods that employ trapping or similar phenomena [11–13] is that no external detectors are employed. Questions of interpretation that have to do with the role of the detectors are thereby avoided. Furthermore, the length characteristic of the experiment is not a random quantity as in trapping experiments (e.g., sensitized luminescence) – wherein it is the distance between detector molecules. Instead, it is one that can be controlled in a systematic manner: the ruling period or fringe spacing is well-defined and easily varied. Partly as a result of this non-random nature of the experimental probe length [14,15], the technique lends itself ideally to coherence investigations. The basic theory for such coherence studies has been given [16–20], applied to experiments on singlets [21], and is awaiting low temperature observations on triplets. The application to observations on singlets [6] has resulted in what, to our knowledge, is the first direct demonstration of transport coherence for singlets in a molecular crystal [21].

In the construction of an appropriate theory for these grating or ruling experiments, there remains, however, an open question. It concerns the nature of the initial conditions involved in the experiment. The present paper addresses that question. The usual theory of transient grating and Ronchi ruling observations assumes [16–20] that the excitation density matrix is initially random, i.e., diagonal in the site representation. It appears plausible that the actual physical manner of illumination might result in such a random initial density matrix, since, at least for the singlet transient grating experiment, the excitation occurs well above the exciton band and is followed by numerous transitions which are well expected to destroy any phase relations present in the original state. It is, however, important to investigate the effects of non-random initial density matrices, because the nature of the processes leading from the initially excited state to the exciton state is not known in detail, and also because profound modifications in the time evolution of the signal can occur as a result of non-random initial density matrices. This question has been discussed by Kenkre et al. [22] who showed that it is possible to obtain a signal which is completely independent of time for a coherent system if the exciton initially occupies two \( k \)-states of equal and opposite wavevectors, each of one-half the magnitude of the wavevector of the probability distribution. The probability distribution is then forever the initial sinusoid in contrast to one with a Bessel-function temporal variation which is predicted by the usual theory [16–20]. This was subsequently noted also by Garrity and Skinner [23] who calculated the signal for various degrees of transport coherence for the initial condition given in ref. [22] and showed that its time dependence could show considerable variation in its decay. Since little is known about the precise nature of the initial state, what should be of immediate experimental interest is the effect of varying the initial condition itself, rather than, or in addition to, the degree of coherence. Such an analysis is given below.

We describe briefly our results here. We first find that the sinusoidal variation in the probability with the wavevector dictated by the wavelength and the crossing angle of the exciting laser beams can be made compatible with a variety of density matrices including the two extreme limits discussed above. All situations in which the excitation resides in two \( k \)-states which differ by the wavevector \( \eta \), say in the states with \( k = \kappa - \eta / 2 \) and \( k = \kappa + \eta / 2 \), correspond to a probability distribution which varies sinusoidally with the wavevector \( \eta \). However, they evolve in drastically different ways. Thus, for the case of no exciton scattering, i.e. in the perfectly coherent limit, the square of the amplitude of the probability distribution, equivalently the transient grating signal, shows strong oscillations whose frequency is larger, the larger the value of \( \kappa \). The case when the exciton occupies all such pairs with \( \kappa \)-values ranging all over the band, is nothing other than the standard one with a density matrix which is initially completely diagonal in the site representation. We study the evolution of physically significant states in the intermediate region by considering the superposition of these pairs all over the band symmetrically with appropriate weights. When such “wavepackets” have zero width around the value 0 for \( \kappa \) we return to one of the above limits, viz. the one in refs. [22,23], whereas for infinite width we recover the limit in refs. [16–21].
As a result of the detailed study of the time evolution, we conclude that initial condition effects are negligible for parameter values corresponding to most of the existing experimental data. In agreement with the results of ref. [23] we find that the effects may be discernible for highly coherent motion and very small fringe spacings. The former condition drives us to 1.8 K or lower in pure anthracene crystals and the latter to fringe spacings of 1 μm or smaller. These conditions bring us truly to the absolute limit of effective coherence in existing experiments: data for 1.8 K is not available in sufficient detail in the literature and the lowest fringe spacings reported so far are 4.1 μm. The conclusion is, therefore, that we need have no concern about the applicability of the usual theory involving the initial random condition for most data. On the other hand, pushing the experimentation limits even a little further might well result in our being able to probe into the initial condition effects.

The rest of the paper is as follows. We discuss the initial conditions in section 2, present in section 3 the analysis leading to the effects under investigation, and conclude in section 4.

2. Initial conditions

The initial density matrix assumed in the usual theory of the grating and ruling experiments is given by
\[
\rho_{mn}(0) = \frac{2}{N} \cos^2(m\eta/2) \delta_{mn},
\]  
where \(N\) is the number of sites in the crystal, \(m\) and \(n\) are site indices and \(\eta\) is the grating wavevector given, for transient grating experiments, by
\[
\eta/2 = (2\pi/\lambda) \sin(\theta/2),
\]  
\(\lambda\) and \(\theta\) being the wavelength of excitation and the crossing angle of the exciting beams respectively. We shall present the rest of our discussion of this paper in the language appropriate to the manner in which the singlet transient grating experiments are carried out. All considerations apply with trivial modifications to the Ronchi ruling observations.

In (2.1) the factor \(\delta_{mn}\) ensures that the density matrix is random. Needless to say, for the given probability distribution, this vanishing of off-diagonal elements is possible only for a mixed state, i.e., for one involving many members of a statistical ensemble. If, however, a pure state is considered in which the exciton occupies the two Bloch states of equal and opposite momenta, \(k = \eta/2\) and \(k = -\eta/2\), the initial density matrix is given by
\[
\rho_{mn}(0) = \left(\frac{2}{N}\right) \left[ \cos(m\eta/2) \right] \left[ \cos(n\eta/2) \right].
\]  
This result is obtained simply by writing \(\rho(0)\) in the representation of Bloch states and carrying out a double Fourier transform. The probability distribution in (2.3) is the same as in (2.1) but the off-diagonal elements are by no means zero. This is the initial condition considered in refs. [22,23].

It is however possible to get the same probability distribution as in (2.1) and (2.3) — i.e., varying sinusoidally with wavevector \(\eta\) as in the experiment — and yet have a variety of different physically meaningful distributions of off-diagonal elements. Indeed, if we consider the exciton to occupy two Bloch states as above but with \(k = \kappa - \eta/2\) and \(k = \kappa + \eta/2\), we get a generalization of (2.3) with the same sinusoidal probability distribution as before. The generalization is
\[
\rho_{mn}(0) = \left(\frac{2}{N}\right) \left[ \cos(m\eta/2) \right] \left[ \cos(n\eta/2) \right] \times \exp\left[i\kappa(m-n)\right].
\]  
Figure 1 depicts the pair state represented by (2.4).

The \(k\)-interval between the two states is equal to \(\eta\), the wavevector of the probability distribution. The center of the pair is at \(\kappa\) which may be anywhere in the Brillouin zone. If \(\kappa = 0\) then (2.4) reduces to (2.3) and leads to the pathological time evolution of the signal discussed in refs. [22,23]. If \(\kappa \neq 0\), our results from fig. 2 will show that oscillations will occur in the signal with frequencies which are large whenever the difference in the exciton energies of the two states in the pair is large. Furthermore, it we take equal superpositions of all pair states represented in (2.4), i.e. if we sum (2.4) with equal weight over all \(\kappa\)'s throughout the Brillouin zone, we recover the random initial density matrix of (2.1)! This is a highly convenient result. Not only can the pathological case of refs.
Fig. 1. Energy band of the exciton (k is the dimensionless quasimomentum) and the two states (depicted by circles) occupied initially by the exciton as in eq. (2.4). The exciton probability distribution is sinusoidal with wavevector $\eta$ as in the experiment and is independent of $\kappa$. A realistic initial state can be made up by a wave-packet superposition of such pair states by integrating $\kappa$ over the Brillouin zone with suitable weights.

\[ g(k) = (2\pi\sigma^2)^{-1/2} \exp\left(-k^2/2\sigma^2\right). \]  

(2.5)

In the subsequent analysis we shall obtain the time evolution of the signal from (2.4) and we shall sum the result over values of $\kappa$ in the Brillouin zone with the weighting factor $g(k)$ to obtain the signal corresponding to the general state. This will give us the complete evolution of the signal for a large class of initial conditions which contain the earlier discussed cases as special cases and will allow us to study the effect of the initial conditions by varying the value of the width $\sigma$ of the weighting factor.

We conclude this section with a brief discussion of the physics behind the general wave-packet state that has been presented above and will be used below. In the actual process of illumination in the transient grating experiment in molecular crystals [1], the initial population is in an electronic state energetically higher than the exciton band under consideration. The passage of the exciton into the band is bound to be accompanied by various relaxation and dephasing processes which lead to a rearrangement and randomizing of the phase relations in the original state. Processes of this kind, which mix the $k$-states of the exciton as a result of scattering but leave the spatial distribution of the exciton probability unchanged, can be imagined easily. For instance, as a result of defect or phonon scattering, the exciton, originally restricted to $k = \eta/2$ and $k = -\eta/2$ as a consequence of crossed beam laser excitation, could be scattered into the four additional states $k = \pm(\eta/2 + \kappa)$ and $k = \pm(-\eta/2 + \kappa)$. The standing wave pattern in the spatial probability distribution, which was originally made up of two waves
travelling in opposite directions, would now be (unchanged but) made up of six travelling waves with three pairs of equal and opposite quasi-momenta. Further scattering events of the same kind could place the exciton into another set of four additional states with \( \kappa \) replaced by \( \kappa' \), and so on. Under this kind of scattering, the probability distribution in real space would remain invariant (sinusoidal with the dimensionless wavevector \( \eta \)) but the distribution in \( \kappa \)-space would undergo a smearing characteristic of bath processes. Writing down a model for these bath processes is trivial but unilluminating for the purposes of the present paper. The important points to note are that such processes are expected to be present in any real crystal, that they do not change the spatial distribution of the exciton by assumption, and they do lead to a smearing of the distribution in the exciton band. The nature of the distribution of the smearing produced in \( \kappa \)-space will depend on the nature of the processes. We have taken it to be Gaussian in the present paper and denoted its width by \( \sigma \). It is possible to do the computations with several other distributions, including one that represents a thermalization of the exciton within the band and another which corresponds to a pseudo-thermalization and allows one to recover some previous results [4] (see section 4). It is important to realize that, even if the illumination process were to place the excitation in the exciton band directly and thereby initially produce the pair state (with zero \( \kappa \)) of eq. (2.3), the numerous scattering processes which exist in any real crystal would cause a scattering into other states. We make no assumptions about the extent of this scattering or smearing. In particular, we do not assume that the smearing is large. Instead, we examine the dependence of observables on the extent of the smearing, and our analysis contains both the extreme case of no smearing at all and that of complete smearing over the band, as well as the entire intermediate range. For the purposes of this paper we have taken the scattering to occur to nearby states in the Brillouin zone, to leave the spatial probability distribution unchanged initially, and to have a Gaussian width. The consequences of relaxing these assumptions will be reported elsewhere.

3. The SLE and its solution

As in past analyses [16–23] we shall take the excitons to obey the simple stochastic Liouville equation (SLE) which describes the evolution of the elements of the density matrix \( \rho \) in the site representation in terms of a "coherent" Hamiltonian \( H \) and a randomizing parameter \( \alpha \) which is the rate of decay of the off-diagonal elements of \( \rho \):

\[
\frac{d\rho_{mn}}{dt} = -i[H, \rho]_{mn} - \alpha(1 - \delta_{mn})\rho_{mn}.
\]  

(3.1)

In \( \kappa \)-space, the parameter \( \alpha \) is nothing other than the (constant) scattering rate among the band states of the exciton. We have recently developed a convenient method of solution of this equation which is based on a formal application of the defect technique [24] used by Montroll and collaborators in the unrelaxed context of trapping. This method is closely associated with one we have developed for annihilation problems [25] and has also been applied for the calculation of neutron scattering functions [26]. We rewrite (3.1) as

\[
\frac{d\rho_{mn}}{dt} + i\rho_{mn} = -i[H, \rho]_{mn} + \alpha\delta_{mn}\rho_{mn}.
\]  

(3.2)

and denote by \( \psi_{mn} \) the density matrix propagator for the coherent case, i.e. the solution of (3.1) or (3.2) with \( \alpha = 0 \), the initial condition being \( \rho_{mn}(0) = \delta_{mn}\delta_{m0} \). It is obvious then that the coherent solution \( \eta_{mn} \) for arbitrary initial conditions is

\[
\eta_{mn}(t) = \sum_{m'n'}\psi_{m'n'n}(t)\rho_{m'n'}(0).
\]  

(3.3)

Since the second term in the left-hand side of (3.2) is a simple decay and the second term in the right-hand side can be considered to be a formal trap along the "line" \( m = n \), the full solution of (3.1) or (3.2) can be written at once as

\[
\tilde{\rho}_{mn}(\epsilon) = \tilde{\eta}_{mn}(\epsilon + \alpha)
\]

\[
+ \alpha\sum_{m'}\tilde{\psi}_{m'n'n'}(\epsilon + \alpha)\tilde{\rho}_{m'n'}(\epsilon)
\]  

(3.4)

in the Laplace domain. Here \( \epsilon \) is the Laplace variable and tildes denote Laplace transforms. By taking the case \( m = n \) of (3.4) and by introducing discrete Fourier transforms through relations such as

\[
\rho^k = \sum_m \rho_{mm} \exp(ikm)
\]  

(3.5)

we obtain the main result [26] of interest to us.
here, viz.,
\[ \tilde{\rho}^k(\epsilon) = \left[ \tilde{\eta}^k(\epsilon + \alpha) \right] / \left[ 1 - \alpha \tilde{\eta}^k(\epsilon + \alpha) \right]. \tag{3.6} \]

The transient grating signal is nothing other than \( \rho^k(t) \) with \( k \) equal to the grating wavevector \( \eta \). Our procedure therefore consists of determining the density matrix propagators \( \psi \) for the coherent case, using the initial conditions discussed in section 2 in (3.3), substituting the result in (3.6), and evaluating the inverse Laplace transform to obtain the signal in the time domain.

The simple Hamiltonian used in past analyses [16–23] of the problem is
\[ H_{mn} = V(\delta_{m,n+1} + \delta_{m,n-1}). \tag{3.7} \]
and represents exciton transfer interactions \( V \) which are nearest neighbour in character. The coherent propagators for this Hamiltonian are well known [18] in terms of Bessel functions \( J_m \):
\[ \psi_{mn}(t) = i^{m-n}J_m(2Vt)J_n(2Vt), \tag{3.8} \]
and they lead to
\[ \psi^k(t) = J_0(4Vt \sin(k/2)), \tag{3.9} \]
\[ \eta^k(t) = \sum_{m,n}J_{m-n} \left[ 2Vt \sin(k/2) \right] \eta_m \eta_n(0) \times \exp[i(k/2)(m' + n')]. \tag{3.10} \]
The transient grating signal \( S(t) \), which, except for constants of proportionality and instrument function convolutions, is the square of \( \rho^k(t) \) evaluated at \( k = \eta \), is obtained by substituting the initial condition (2.4) in (3.10), and the Laplace transform of (3.9), (3.10) in (3.6). The result is
\[ S(t) = \left[ \rho^0(t) \right]^2, \tag{3.11} \]
\[ \tilde{\rho}^0(\epsilon) = \left[ \tilde{f}_\epsilon(\epsilon) \right] \left[ \tilde{\rho}_{\text{rand}}^0(\epsilon) \right]. \tag{3.12} \]
In this paper we take the exciton lifetime to be infinite, for simplicity. In (3.12) the quantity \( \rho_{\text{rand}}^0(\epsilon) \) is the solution for the random initial condition of the usual theory, is given by [16–22]
\[ \rho_{\text{rand}}^0(\epsilon) = \left\{ \left[ (\epsilon + \alpha)^2 + b^2 \right]^{1/2} - \alpha \right\}^{-1}, \tag{3.13} \]
where \( b = 4V \sin(\eta/2) \), and gives rise to the Bessel function temporal variation [16–22] of the signal. The factor \( \tilde{f}_\epsilon(\epsilon) \) contains information about the location of the pair state (i.e., of its center \( \kappa \)) in the Brillouin zone, and is given by
\[ \tilde{f}_\epsilon(\epsilon) = \left[ (\epsilon + \alpha)^2 + b^2 \right]^{1/2}/\left[ (\epsilon + \alpha)^2 + b^2 \sin^2\kappa \right]. \tag{3.14} \]
It is trivial to see that \( (1/2\pi) \) times the integral of \( \tilde{f}_\epsilon(\epsilon) \) over \( \kappa \) from \( -\pi \) to \( +\pi \) equals 1. The usual signal for the initial random condition is therefore obtained by summing the pair states all over the Brillouin zone as expected. The other extreme of refs. [22,23] is recovered by putting \( \kappa \) equal to 0. The signal in this extreme may then be obtained as
\[ S(t) = e^{-2\sigma t} \left\{ 1 + \alpha \int_0^t dt' J_0(bt') \right. \]
\[ + \alpha^2 \int_0^t dt'' \int_0^{t''} dt''' e^{\sigma(t'' - t''')} J_0 \left( b(t'' - t''')^{1/2} \right)^2 \right\} \tag{3.15} \]
in the time domain and is the basis of the treatment of ref. [23].

Our interest lies in the intermediate regime and in the effect of intermediative wave-packet widths on the signal. We therefore sum (3.12) or (3.13) with the weighting factor \( g(k) \) of width \( \sigma \) as in (2.5). Laplace-invert the resulting expressions, and square to obtain the signal in the time domain. While it is possible to display the result explicitly in the time domain, the expression is in the form of multiple integrals and the numerical inversion procedure is at least equally adequate to perform the computations.

The signals obtained in this fashion are displayed in figs. 2–4. In fig. 2 we consider the pair state as in (2.4) or fig. 1 along with the symmetric pair (about \( k = 0 \)) and show the signal for a variety of values of \( \kappa \) in the band. As seen in fig. 2A, the signal displays oscillations whose frequency is dependent on the location of the pair state (or of \( \kappa \) in the band. Of importance in these figures is the coherence parameter \( \xi = b/\alpha = (4V/\alpha) \sin(\eta/2) = (4\pi/\sqrt{2}) \Lambda/d \). In the last expression we have written \( \xi \) in terms of the mean free path \( \Lambda \) (the length over which the exciton moves coherently, i.e. between scattering events) and the fringe spacing \( d \) of the transient grating. In fig. 2A the coherence parameter \( \xi \) equals 10 and the curves (a) through (e) are for various values of
\( \kappa \) as shown. It is to be noted that in fig. 2B, in which the motion is incoherent over the length characteristic of the experiment, \( \xi \) being equal to 0.1, the signal is practically insensitive to where the pair state lies in the band and the signal is exponential.

In figs. 3 and 4 we display the signals for the physically reasonable initial conditions involving wavepackets of width \( \sigma \). The largely coherent case is shown in fig. 3, \( \xi \) being equal to 100 in 3A and 10 in 3B, and the relatively incoherent case is in fig. 4, \( \xi \) being 1 in 4A and 0.1 in 4B. In each case curves (a) through (e) represent, not the location in the band as in fig. 2 - since symmetrical pair states all over the band go to make the wavepacket, but the values of the width \( \sigma \) of the wavepacket: 1, 0.7, 0.3, 0.1 and 0, respectively. We see again that differences in the signal due to differences in the initial condition are discernible for coherent motion, hardly so for motion with \( \xi = 1 \), and completely negligible for the largely incoherent case. The experimentally important question is whether these differences would be observable. Available data in the molecular crystal literature concerns (i) mixed crystals (transient grating experiments) [5], (ii) pure crystals at temperatures higher than 100 K (Ronchi ruling experiments) [3], and (iii) anthracene pure crystals at temperatures as low as 1.8 K (transient grating experiments) [6]. Case (ii) corresponds to highly incoherent motion [21] and case (i) is effectively so. Detailed extraction of the coherence parameters for case (iii) has been carried out by Kenkre and Schmid recently [21] and the motion has been found to be remarka-
bly coherent: the mean-free-path has been estimated to be larger than 1700 intersite distances for anthracene at 1.8 K. The analysis above shows that, if any initial condition effects are to be experimentally discernible, it is in coherent systems such as those studied by Rose et al. [6] that they should be sought. We evaluate the coherence parameter $\xi$ for the observations of ref. [6]. For temperatures of 20 K and 10 K, exciton motion is quite coherent (the mean-free-path is more than 100 and 200 intersite distances respectively [21]) but with the fringe spacings that have been used, $\xi$ equals about 0.1 in all cases except one in which it is 0.3. We are thus in the realm of fig. 4B and we see that initial condition effects are completely negligible. For 1.8 K, the data is not available in sufficient detail [6] to draw unambiguous conclusions. However, using a fringe spacing of 4.1 $\mu$m and the parameters extracted in ref. [21] from the reported diffusion constant [6], a value of 2 may be deduced for $\xi$. Figure 4A shows that, for $\xi = 1$, some quantitative difference in the signals does exist but no qualitative changes in signal shape appear. A clear indication of initial condition effects does not therefore emerge (of the kind apparent in figs. 3A and 3B where $\xi \gg 10$). If $\xi$ is made a little larger, by producing fringe spacings which are smaller, or by examining systems in which the mean-free-path is larger, these effects may turn out to be discernible. It is quite difficult to do both in molecular crystals but 0.2 $\mu$m fringe spacings have been hoped for recently [6]. If they become practical one may indeed be able to observe these initial condition effects. We note in passing that fig. 4A shows that, when the effects are non-negligible, the use of the random initial condition underestimates the diffusion constant of the excitons for the relevant parameter range.

4. Concluding remarks

Initial conditions during electronic excitation are known poorly from the observational viewpoint and also studied inadequately from the theoretical viewpoint. Among the few efforts of the latter kind are refs. [22,23] and the present paper. The transient grating — or Ronchi ruling — technique is an experimental method of considerable potential and it is therefore important to understand the limits of applicability of theories that are used to interpret observations based on it. Our purpose in presenting this investigation is to test whether initial condition effects, which certainly exist in principle [22], are experimentally observable. Our conclusion is that, for most of the existing grating/ruling data in molecular crystals [1–6], they are not observable. On the other hand, we find that they would be observable in highly coherent systems such as those of ref. [6] at 1.8 K provided improved experimentation is used which would produce fringe spacings smaller than 1 $\mu$m.

We comment on the relationship of the results presented in this paper to those of two earlier similar investigations [22,23]. That initial condition effects can exist in principle and can modify the signal profoundly from that corresponding to the random initial condition was shown by Kenkre et al. [22] who treated coherent evolution (to show maximum deviation) from one initial state. The evolution for arbitrary coherence from this state was treated by Garrity and Skinner [23]. Both these references address a single initial state, viz. the pair state with $\kappa = 0$. This state can be considered to be a member of one of two infinite classes. Both these classes are treated in their entirety in the present paper and our prime interest lies in the variation of the initial condition within these classes. The first class is of pair states with $\kappa$ at arbitrary locations within the band. This class is represented in fig. 2 and is of some theoretical interest. Of greater relevance to experiment is the second class we treat which is that of “wavepackets”, i.e., states consisting of weighted sums of the pair states with arbitrary width. Figure 3 and 4 represent this class. In addition to being experimentally more relevant, this class also has the random initial condition as another extreme member. Previous work, such as that of Garrity and Skinner [23] thus corresponds to the one curve labelled (e) in figs. 3A, 3B and 4A. The random initial condition [16–21] lies at the other extreme and essentially corresponds to the curve labelled (a) in those figures. A state prepared in the laboratory will generally lie in the intermediate range and the main concern of this paper is in all those intermediate situations.
We have not considered wave-packet states which would not be symmetrical in the band only because there is no reason to believe that the experiment corresponds to them. Evolution from such more general conditions can also be determined with the use of our methods, if desirable.

It is interesting to note that, if we replace the Gaussian weight function \( g(\kappa) \) of \((2.5)\) by the pseudo-thermalization weight function
\[
g(\kappa) = \left[ 2 \pi I_0(2\beta V) \right]^{-1} \exp(-2\beta V \cos \kappa),
\]
where \( I_0 \) is the modified Bessel function of zero order and \( \beta \) is the reciprocal of the product of the Boltzmann constant and the temperature \( T \), the integrals over \( \kappa \) can be performed exactly and the transient grating signal \( S(t) \) can be evaluated analytically:
\[
S(t) = e^{-2\alpha t} \left[ \int_0^t dt' S_1(t-t')S_2(t') \right]^2,
\]
\[
S_1(t) = \delta(t) + \alpha J_0(bt)
+ \alpha^2 \int_0^t dt'' e^{a t''} J_0 \left[ b(t''^2 - u^2)^{1/2} \right],
\]
\[
S_2(t) = \left[ 2 \pi I_0(2\beta V) \right]^{-1} \int_{-\pi}^{\pi} d\kappa e^{-2\beta V \cos \kappa}
\times \cos(bt \sin \kappa),
\]
where \( b \) equals \( 4V \sin(\eta/2) \) as before. It is remarkable that this expression reduces to all three limits discussed previously: in the limit \( T \to \infty \), equivalently \( \beta \to 0 \), the random initial condition result \([16–20]\) is obtained; in the limit \( T \to 0 \), the pair state result \([22,23]\) is recovered; and, what is quite surprising, under the coherent limit \( \alpha \to 0 \), we obtain the expressions given by Fayer \([4]\) on the basis of trajectory arguments. In the latter case, \((4.3)\) shows that \( S_1(t) \) is simply the delta-function and the signal is the square of \( S_2(t) \). The recovery of the pair state result \([22,23]\) \((3.15)\) is immediate because, for \( \beta \to \infty \), \( S_2(t) \) equals 1 and a single integration of \((4.3)\) yields \((3.15)\), while for \( \beta \to 0 \), \( S_2(t) \) equals \( J_0(bt) \). It is perhaps surprising that the result which Fayer derived \([4]\) on the basis of arguments which associate a grating wavevector spatial variation with each \( k \)-state exciton, actually contains (although only for the perfectly coherent case) both the pair-state result \([22,23]\) and the random condition result \([16–20]\) as the respective special cases of 0 and \( \infty \) temperature. We have called the distribution \((4.1)\) used above a pseudo-thermalization distribution because it does not correspond to a true thermalization of the exciton. These issues, as well as the detailed relations among all the treatments of the initial condition existing in the literature and the analysis of temperature effects, will be reported in a separate publication.

The other new feature of our work is the mathematical method we employ for solving the SLE \((3.1)\). It produces simple expressions \((3.11)–(3.15)\) which are highly convenient and usable for numerical computations. The convenience is easily appreciated on comparing our results such as \((3.15)\) for the signal for the pair state studied in ref. \([23]\), to the equivalent result, viz., eqs. \((61)\), \((54)\) of ref. \([23]\), obtained with alternative methods.

Of the assumptions used in our analysis, that of nearest-neighbour transfer interactions \((3.7)\) is the most serious one for singlet excitons since they move via dipole–dipole interactions which are long-range. The \( V \) we use is to be taken in an effective sense \([21]\). As a result of the uncertainty in the effective value of this parameter, the conclusions we draw possess some quantitative uncertainty.

We hope that the present analysis, as also the work of Garrity and Skinner \([23]\), will motivate further experimental investigations into initial condition effects.

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References


[22] Ref. [20], footnote 34.


