COHERENCE IN EXCITON TRANSPORT IN MOLECULAR CRYSTALS AND BIOLOGICAL SYSTEMS

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One of the most fundamental questions in the physics of excitation dynamics in complex entities such as biological systems and molecular crystals is that of coherence in the transport of excitation. Its study has occupied experimentalists and theorists over many years [1-6]. The major theoretical problems appear to have been solved but a clear experimental demonstration of coherence is still lacking. Spin-based experiments are plagued by the possible mixture of spin coherence and transport coherence in their interpretation. Experiments which attempt to probe into coherence on the basis of the temperature dependence of characteristic observables are often inconclusive because many different factors having little to do with coherence can affect such temperature dependence. The present lecture consists of three parts. In the first the primary questions regarding the transport coherence of excitons are addressed via the unifying framework of generalized master questions [4,6]. In the second part existing observations [7] on the motion of singlet excitons in pure crystals of anthracene are analyzed to deduce information regarding their transport coherence [8]. In the third part the technique of Ronchi rulings [9] is described and shown to be ideally suited to measure the coherence of triplet excitons [10]. The three parts thus consist, respectively, of the theoretical framework, an application to existing

experiments (on singlets), and a proposal for future experiments (on triplets), all directed at exciton coherence.

The question of coherence has to do with whether excitation moves in a wave-like fashion or in the diffusive manner of a random walker. These two modes of transport are profoundly different. It is obvious that in a perfect crystal, i.e. one with no defects and no vibrations, the motion of excitation is perfectly coherent. No scattering occurs, the mean free path of the propagating excitation is infinite, and phase relations are maintained forever and at infinite distances. However, imperfections such as molecular vibrations, lattice phonons, and defects, destroy these relations in a real crystal or aggregate. A simple manner of addressing motion with arbitrary degree of coherence is the generalized master equation [4,11]

$$dP_m(t)/dt = \int_0^t dt' \sum_n [\, \mathcal{W}_{mn}(t-t')\ P_n(t') - \mathcal{W}_{nm}(t-t')\ P_m(t') \,]$$

which describes the time evolution of $P_m(t)$, the probabilities of occupation of sites - or molecules - m by the excitation. A detailed description of the origin, characteristics and uses of this equation may be found elsewhere [4]. Suffice it to state here that the degree of coherence of the transport corresponds directly to the time dependence of the "memory functions" $\mathcal{W}_{mn}$, which describe the transfer of excitation from sites n to sites m. It is possible to derive these memory functions from the microscopics of the particular biological system or molecular crystal and to analyze coherence from them. A collection of such results for the memory functions is available [4,12]. From them, the solutions of the generalized master equation may be obtained and used to address experiment. This has been

done for sensitized luminescence observations, transient grating observations and Ronchi ruling experiments. The results for sensitized luminescence experiments are inconclusive for reasons that fall beyond the scope of this lecture (see /13–15/). We discuss the results for the singlet grating and triplet ruling experiments in the rest of this lecture.

Rose et. al. [7] have recently reported an investigation of exciton transport in anthracene crystals at low temperatures using the method of picosecond transient gratings. The method consists of splitting a picosecond laser pulse into two parts and causing the two parts to arrive simultaneously at a variable angle in the crystal. Optical absorption creates an exciton population which varies sinusoidally in space as a result of the interference of the two pulses.By studying the subsequent time evolution of the (transient) exciton grating thus produced, Rose et. al.[7] report that the diffusion constant varies from (10 ± 2) cm^2/s at 1.8 K, through (1.3 ± 0.4) cm^2/s at 10 K, to (0.8 ± 0.2) cm^2/s at 20 K. By using the theory of transient gratings [5,16] detailed coherence parameters can be determined for this system. The resulting table [8] is reproduced below.

TABLE 1: SCATTERING RATES α AND MEAN FREE PATHS Λ FOR SINGLET EXCITONS IN ANTHRACENE AS OBTAINED FROM THE TRANSIENT GRATING EXPERIMENTS OF REF. /7/

T[K]	τ[ns]	d[μm]	K[$10^8 s^{-1}$]	α[$10^9 s^{-1}$]	Λ/a	Λ[nm]
20	10	3.2	7.6	17	125	63
		4.6	4.2	21	101	53
10	10	4.1	10	7.4	286	150
		9.6	3.1	8.7	243	128
1.8				≤ 1.2	≥ 1770	≥ 930

The first 4 columns of Table 1 contain experimental information from /7/, d and K being, as stated above, the fringe spacing and the signal decay rate respectively. The last 3 columns contain deductions concerning the coherence parameters of the system. These are α, the reciprocal of the time between scattering events; Λ/a, the number of nearest-neighbour distances over which the exciton moves coherently, i.e. without being scattered; and Λ, the mean free path. The value of V used in constructing Table 1 is 50 cm^{-1} and corresponds to 1.5×10^{12} s^{-1}. We believe that the experiments of Rose et. al. [7] provide the first clear indication of the coherence of singlet excitons in molecular crystals.

The precursor of the transient grating technique is the Ronchi ruling technique which was developed by Ern et. al. [9] to study the diffusion constant of triplet excitons. We have recently shown [10,12] that it is ideally suited to the investigation of triplet transport coherence. Triplets are created in the crystal by illumination through a ruling, i.e. an alternating series of opaque and transparent strips. The evolution of the spatially periodic inhomogeneity thus created is measured by observing the total delayed fluorescence from the crystal. The delayed fluorescence arises from singlets produced by the mutual annihilation of the migrating triplets. The observed signal is sensitive to $\Sigma_k \psi^k \psi^{-k} g_k g_{-k}$ where k spans the relevant Fourier space, ψ^k is the Fourier transform of the exciton probability propagator, and g^k is the transform of the square wave corresponding to the mask placed over the crystal during illumination. The quantity ψ^k contains coherence information which can be reflected in oscillations or other shape effects in the delayed fluorescence signal if

sufficient coherence exists, and g^k provides the systematic experimental probe varied by changing the spatial periodicity of the mask. These experiments have been carried out extensively [9] but only at high temperatures so far. The detailed theory which has been constructed recently [10] with particular attention to coherence is complete and awaiting experiments. It is hoped that direct coherence information will be available for triplets through this method in the near future.

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