Quantum information processing attributes of J-aggregates

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Abstract. We examine the unique spectroscopic features which give rise to quantum information processing attributes of one-dimensional J-aggregate systems, and as revealed by entanglement measures such as the von Neumann entropy, Wootters concurrence and Wei-Goldbart geometric measure of entanglement. The effect of dispersion and resonance terms in the exciton-phonon interaction are analyzed using Green function formalism and present J-aggregate systems as robust channels for large scale energy propagation for a select range of parameters. We show that scaling of the third order optical response $\chi^{(3)}$ with exciton delocalization size provides an experimentally demonstrable measure of quantifying multipartite entanglement in J-aggregates.

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1. Introduction

Quantum J-aggregates in organic dye molecular systems reveal an unusually sharp and intense red-shifted optical absorption band arising from molecular aggregation. This spectroscopic feature provides a spectacular example of nonlocal effects due to collective properties of the Frenkel exciton [1–4]. The narrow isolated band of J-aggregates usually formed in liquid or solid organic matrix, generally appears adjacent to a monomer based broad absorption band incorporating vibrational features. The absence of a similar vibrational structure in the polymer J-band is a striking phenomenon, almost equivalent to a decoherence-free subsystem, widely discussed in quantum information studies [5].

It is seen that subtle features of quantum J-aggregates cannot be adequately explained using conventional theory of exciton dynamics [6–8]. Recent technical advances in spectroscopic techniques such as two-dimensional (2D) coherent electronic spectroscopy with fast femtosecond time resolution [9] has made it possible to observe intricate dephasing processes of delocalized exciton states in the single J-band aggregate system [10]. Such detailed experimental probes of the entangled properties highlight the potential in utilizing opto-electronics properties of J-aggregate systems for quantum information processing. Optical-based applications have already been demonstrated in organic semiconductor microcavities [11]. The potential application to innovative “frontier technologies” based on new understanding of the puzzling effects of quantum sized structures therefore provide much impetus for further examination of J-aggregates, particularly from a quantum information perspective.

Narrow J-bands are generally studied using a model of identical monomers interacting with vibrations [12, 13] or an alternative model based on rigid monomers by just varying electronic site energies [14]. The $SP$ parameter, given by the ratio of inter-monomer interaction energy to the vibrational width of the monomer spectrum, was used by Simpson et al [12] to provide a measure of narrowness of the J-band. In the strong coupling region with high $SP$ values, excitation transfer between monomers occurs much faster than relaxation due to lattice vibrations. In Knapp’s Frenkel exciton model [14], specific details of the background medium was discarded with attention focussed on the the J-band. The time of propagation of the Frenkel exciton was considered faster than time variations in electronic site energies. The term “exchange narrowing” [14] was used to describe the decrease in linewidth by $1/\sqrt{N}$ in the absence of intersite correlation, $N$ being the number of monomers. The exchange narrowing process can be associated with $N$ monomers participating in a collective mode as a multipartite system, each monomer thus experiencing an effective disorder of magnitude $D/\sqrt{N}$ instead of $D$, the full disorder experienced by an isolated monomer.

It is well known that quantum non-locality is a collective property of quantum system of two or more subsystem (e.g monomers) in which the dynamics of constituent subsystems depend on spatially separated adjacent subsystems [5]. Pauli exclusion principle excludes the possibility of two excitons occupying the same molecular site, thus processes such as exciton-exciton scattering and excitation/de-excitation at a site invariably leads to entanglement in linear excitonic chains. The “spooky action at a distance” effect [15] ensures minimal participation of vibrational modes in quantum J-aggregates. The time taken for individual monomers to interact and form the collective J-band is far less than interaction time with lattice vibration as revealed experimentally [9, 10]. Recently the puzzling effects of entanglement was experimentally demonstrated [16] by joint weak measurement procedures using an...
entangled photon pair.

In this work, we examine the dynamics of J-aggregates using a quantum information approach in which the origin of its sharp J-band is attributed to entanglement and non-local effects associated with a system of excitonic monomers. We consider that decoherence effects [17–20] associated with a noisy environment invariably disrupts the delicate delocalized excitation which contributes to the narrowness of J-aggregate spectrum. In the extreme limit of an infinite chain with infinitely strong coupling, we assume that nonlocal effects is maximal with characteristics of an ideal J-band forming an infinitely narrow spike.

J-aggregates appear remarkably to be the first systems in which entanglement effects have been revealed so visibly during the 1930’s, understandably Scheibe [2] attributed the J-band as arising due to a collective state of electronic excitation. Despite the consistent observation of a collective excitonic mode by Scheibe [2], Simpson et al [12] and Knapp [14], attempts to bridge the gap between the well-known Frenkel exciton theory and the more recent field of quantum information theory has only been achieved recently in our work [21], where we have shown clear and explicit links between the quantum search process and actual physical processes taking place in the crystal. To simplify the numerical analysis in this work, we utilize the Markovian approximation scheme in which the time scales of lattice vibrations are considered to be short compared to other dynamical times present in the system. Hence we neglect the flow of information from phonons back to the excitonic system and assume that the reservoir system is disengaged from coherence effects between two or more molecular sites. In other words, we consider that the operating times associated with non local effects remain unaffected by “memory effects” present in a non-markovian reservoir system. We thus distinguish between propagation times of the excitation and times associated with entanglement effects of a delocalized exciton which determines the duration of coherence between different molecular sites.

In view of the importance of including entanglement effects in J-aggregates, we emphasise the general problem of quantifying the level of entanglement in any arbitrary multipartite system. Currently there is no satisfactory classification of genuine entanglement for a multipartite system of even pure states [22–27]. The manner of partitioning individual subsystems affects multipartite entanglement and introduces an element of subjectivity when using current classification of entanglement such as k-separability. For instance for a selected partition, one can obtain varying degrees of multipartite entanglement, changing from a fully separable to fully inseparable states with each member of the group sharing genuine multipartite entanglement. The possibility that such a change may be non-monotonic was recently shown in an earlier work where three members of a group which shared non-zero tangle entanglement displayed zero bipartite entanglement between two members [28]. We therefore expect investigations related to maximal entanglement of a fragile open systems such as excitonic chains with decoherence effects to remain unresolved for some time. In this regard, we point to the possibility that the scaling of the third order optical response $\chi^{(3)}$ with exciton delocalization size may provide an experimentally demonstrable means of categorizing genuine multipartite entanglement, at least in the case of J-aggregates.

This paper is organised as follows. In Sec. 2, we summarize salient features of the Frenkel exciton in molecular systems, including a brief description of the site basis representation appropriate to excitonic systems. In Sec. 3, we provide a brief description of the von Neumann entropy [24, 29], and in Sec. 4 we provide
mathematical details of derivations based on Green’s functions formalism. We also present results which show the usefulness of the entropy in capturing the transition from coherent to incoherent energy transfer in a finite one-dimensional J-aggregate system. In Sec. 5, we use the well-known Wootters concurrence [30] to interpret superradiance properties of one-dimensional excitonic systems. Finally, we analyze the intricate link between the third order optical response $\chi^{(3)}$ and the class of entanglement quantity known as the Wei-Goldbart geometric measure of entanglement [31] in Sec. 6.

2. J-aggregates and Frenkel Excitons

J-aggregates, also called “communal” states [2], are low dimensional molecular systems which display enhanced coherent interactions with light. For instance, a well known dye molecule pseudoisocyanine (PIC) forms a quasi-one dimensional arrangement of molecules under suitable conditions, displaying the characteristic feature of a sharp absorption spectrum red shifted from the broader monomer transition band. It is well known that many spectroscopic features of J-aggregates are interpreted via a model of one-dimensional Frenkel exciton system [6], with delocalised excitons considered the main reason behind the collective nature of such systems. There have been suggestions that the total number of molecules which form such collective states varies from ten to several hundreds [14].

The optical properties of J-aggregates are invariably linked to geometrical attributes of the molecular arrangement, however in this work we restrict our study to Frenkel excitons in a quasi one-dimensional system of finite $N$ molecular sites. We assume that the one-dimensional Frenkel excitonic model is applicable to one-dimensional aggregate systems as well. Excitons in molecular crystals are generally treated using the tight-binding model [6] due to the weak overlap of intermolecular wavefunctions and hence localization of excitation at individual molecular sites. The exact form of these functions are not needed to derive salient properties of Frenkel excitons, however every molecular site has an equal probability of being excited by an incident photon due translation symmetry, a salient feature which has important implications for quantum parallelism. Various mechanisms result in the loss of excitonic coherence, in this work we consider the effects due to coupling with lattice vibrations as well as the influence of finite temperature.

The absorption of a photon triggers an initialization process with creation of a delocalized exciton, representing an equal weighted superposed form of occupation probabilities at all lattice sites. While ideal crystal in vacuum state is equivalent to the null state $|0\rangle^{\otimes N}$ for $N$ sites, photon absorption process initiates a Hadamard-like transformation [5] at each site. In the absence of lattice vibrations, the exciton eigenvector can thus be written as

$$|K\rangle = N^{-1/2} \sum_l e^{iK.l} B_l^\dagger |0\rangle$$

where the reciprocal lattice vector $K = \frac{2\pi k}{N}$ within the Brillouin zone $k \in [-\frac{N}{2}, \frac{N}{2}]$, $|0\rangle$ is the vacuum state with all molecules in ground state and $B_l^\dagger$ is the creation operator of exciton at position coordinate $l$. $N$ is the number of unit cells in the crystal which increases with the number of molecules for each unit cell. In Eq.(1), we have dropped notations associated with the exciton spin for convenience reasons, and
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include notations in scalar form as we restrict the model considered here to a finite one-dimensional linear chain. It should be noted that we have considered that all molecular sites have an equal chance of absorbing a photon to raise it to an excited state $|0⟩$ which can be represented by the Hadamard-like transformation: $|0⟩ → |0⟩ + |1⟩$. It is important to note the vital difference between a photon absorption process and a true Hadamard gate conversion which can reset a state to its original form. For instance, other possible transformations inherent in a true Hadamard gate such as $|0⟩+|1⟩ → |0⟩$ and $|1⟩ → |0⟩ − |1⟩ → |1⟩$ are not present upon successive absorption of two or more photons at a molecular site.

The creator operator of a Frenkel exciton with wavevector $K$ can be easily obtained using the Fourier transform of Eq.(1)

$$B_{K}^\dagger = N^{-1/2} \sum_{l} e^{iK.l} B_{l}^\dagger \quad (2)$$

The exciton creation operator $B_{K}^\dagger$ localized in $K$-space is delocalized in real space [6]. The motion of the exciton in molecular systems is governed by an Hamiltonian derived using a tight-binding model [6–8]

$$\hat{H}_{ex} = \sum_{l} \left( \Delta E + \sum_{m \neq l} D_{l,m} \right) B_{l}^\dagger B_{l} + \sum_{m \neq l} M_{l,m} B_{l}^\dagger B_{m} \quad (3)$$

where $\Delta E$, the on-site (intra-site) excitation energy at equilibrium is the same at all sites due to translational symmetry. $D_{l,m}$ is the dispersive interaction matrix element which determines the energy difference between a pair of excited electron and hole at a molecular site and ground state electrons at neighboring sites [6,7]. $M_{l,m}$ the electron transfer matrix element between molecular sites at $l$ and $m$. Using Eq.(2), we obtain a Hamiltonian diagonal in $K$ space

$$\hat{H}_{ex} = \sum_{k} E_{0}(k) B_{k}^\dagger B_{k} \quad (4)$$

$$E_{0}(k) = \Delta E + \sum_{m \neq 0} D_{0,m} + M_{0,m} \exp(i k.m)$$

where $E(k)$ is energy of the exciton of wavevector $k$ and subscript 0 denotes the absence of lattice site fluctuations. For a simple one-dimensional lattice system, we approximate $M_{l,m} \sim V_{i,j}$ where $V_{i,j}$, the neighbor transfer energy is given by

$$V_{i,j} \propto \frac{\mu_{j} \mu_{i}}{d^{3}} \quad (5)$$

$\mu_{i}$ the molecular transition moment at site $i$ and $d$ is the separation between the two sites involved during the energy transfer.

2.1. Site basis representation

There are several ways to represent excitonic states as qubit states. For instance, Eq.(1) may be considered as the result of a single step of a naturally occurring process involving photon absorption, requiring the equivalent of $\log_{2}(N) + 1$ qubits to store the superposed state. On the other hand, each molecular site may be occupied by an exciton and thus considered a qubit depending on the presence (or absence) of an
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An exciton at a particular site and hence a two-level system. Eq.(3) can be formulated in terms of the terms of the exciton density matrix as:

$$\rho(t) = \sum_{n=1}^{N} \rho_{nn}(t) |n\rangle\langle n| + \sum_{n<m}^{N} \rho_{nm}(t) |n\rangle\langle m| + \rho_{nm}^*(t) |m\rangle\langle n|$$

where $|n\rangle$ represents a site basis state where the exciton is present at only the $n$th molecular site with all other sites unoccupied. The basis state $|n\rangle$ denotes $|0\rangle \otimes (n-1) \otimes |1\rangle \otimes |0\rangle \otimes (N-n)$, where $N \times N$ is the dimension of the global density matrix. $|0\rangle$ denotes the absence (presence) of an excitation at a given molecular site. The $N$ molecular sites occupied by the exciton correspond to the $2^N$ discrete states in the Hilbert space of dimension $N$. Transitions between the states in Hilbert states hence correlate with the transition amplitudes in the original Hamiltonian in Eq.(3).

A qubit state $\Psi$ associated with $N > 2$ subsystems can be written as a generalized Schmidt Decomposition belonging to the Hilbert space of $\hat{H}_{ex}$ in Eq.(3):

$$|\Psi\rangle = \sum_{n=1}^{N} c_n \left(|0\rangle \otimes (n-1) \otimes |1\rangle \otimes |0\rangle \otimes (N-n)\right)$$

with Schmidt coefficients $c_n$. The Schmidt Decomposition above is well known for the separability characterization of pure states. For the simpler case of just two molecular sites $N = 2$, the bipartite is separable only if there is one non-zero Schmidt coefficient. The state can be considered maximally entangled if all the Schmidt coefficients are non-zero and equal. The well known Dicke state $|W\rangle = \frac{1}{\sqrt{N}} (|100...0\rangle + |010...0\rangle + ... + |000...1\rangle)$ is symmetric under permutations of each basis state $|n\rangle$. The absorption of a single photon will give rise to a superposition of all possible states as shown in Eq.(1). These collection of states will also include the special subset of Dicke states which constitute an equal weighted superposed form of basis states.

3. Quantifying entanglement via the von Neumann entropy

We use the local density matrix $\rho_n = u_n|1\rangle\langle n| + (1 - u_n)|0\rangle\langle 0|$ to determine entanglement dynamics of the $n$th qubit associated with a basis which spans the two dimensional space ($|0\rangle$ and $|1\rangle$). The occupation probability at the $n$th molecular site is given by $u_n = \langle K|B_n|K\rangle$ where $B_n$ is the exciton creation operator localized at site $n$ and $|K\rangle$ is the exciton eigenvector in $K$-space (see Eq.(1)). The reduced density matrix has a simple form

$$\rho_n = \begin{pmatrix} 1 - u_n & 0 \\ 0 & u_n \end{pmatrix}.$$

A suitable entanglement measure for the Frenkel exciton described by the one-dimensional tight-binding model in Eq.(3) and corresponding to the density matrix in Eq.(8) is the widely used von Neumann entropy measure [24, 29]

$$S_n = -\text{Tr}_n \rho_n \ln \rho_n$$

where $S_n$ which is zero for pure states, is obtained by tracing over the degrees of freedom of the remaining $N-1$ molecular sites. The average von Neumann entropy measure is then given by

$$S = \frac{1}{N} \sum_{n=1}^{N} -\text{Tr}_n \rho_n \ln \rho_n$$
For the ideal delocalized state in Eq.(1), we obtain $S = \frac{K}{T} \ln N$ at very large $N$. The larger the entropy, greater is the entanglement between excitation at a given site with all other remaining sites. On the other hand, $S = 0$ for the localized state and hence is a useful measure in characterizing quantum phase transitions at the localization-delocalization borders. For the case of an extended state in a finite system of size $N$, we obtain $S = \frac{K}{T} \ln N - (1 - \frac{T}{k_B}) \ln(1 - \frac{T}{k_B})$. Using a time dependent density matrix (as will be considered in the next Section), we will show that the time evolution of the corresponding von Neumann entropy measure can reveal variations in entanglement properties as the exciton propagates in a noisy environment.

4. Green’s function formalism and probability propagator

We begin with the following crystal Hamiltonian [6]

$$
\hat{H}_T = \hat{H}_{ex} + \hat{H}_p + \hat{H}_{ep1} + \hat{H}_{ep2}
$$

(11)

$$
\hat{H}_p = \sum_q \hbar \omega(q) b_q^\dagger b_q
$$

(12)

$$
\hat{H}_{ep1} = N^{-1/2} \sum_{k,q} \{ F(k,q) + \chi(q) \} B_k^\dagger B_{k+q}(b_{-q}^\dagger + b_q)
$$

(13)

$$
\hat{H}_{ep2} = N^{-1/2} \sum_{k,q} \chi(q) B_k^\dagger B_k(b_{-q}^\dagger + b_q)
$$

(14)

where $\hat{H}_{ex}$ is given in Eq.(4), $\hat{H}_p$ denotes the phonon energies and $b_q^\dagger(b_q)$ is the creation (annihilation) phonon operator with frequency $\omega(q)$ and wavevector $q$. Explicit forms for the coupling functions $F(k,q)$ and $\chi(q)$ are given in Ref. [6]. It is important to note the difference in the two coupling functions, while $\chi(q)$ acts to localize an exciton at its original occupation site, $F(k,q)$ operates during dispersion of an exciton to neighboring sites. Thus $F(k,q)$ is influenced by the same factors which determine the exciton bandwidth. In situations where $\chi(q) >> F(k,q)$, self-trapped excitonic effects are expected to dominate while in the case of comparable coupling strengths $\chi(q) \sim F(k,q)$, coexistence of free and trapped excitons and localization effects are expected to prevail. Due to the finite time associated with lattice vibrations, nonlocal effects which govern entanglement properties of the delocalized exciton are likely to experience decoherence effects due to the first coupling term in Eq.(13). At very high neighbor transfer energies $J$, the second dispersive term in Eq.(14) acts as a small perturbation on exciton dynamics. We now investigate the effect of these different coupling terms using Green’s functions formalism introduced by Davydov [6].

The Green’s function for an exciton at time $t$ is given by [6,32]

$$
G(k,t) = -i\langle 0 : n_q | T \{ B_k(t)U(t,0)B_k^\dagger(0) \} | 0 : n_q \rangle
$$

(15)

$$
B_k(t) = B_k(0) \exp(iE(k)t)
$$

(16)

where $| 0 : n_q \rangle$ denotes a state with $n_q$ as the population of phonons with wavevector $q$ and zero exciton population. $T$ is the time ordering operator and $U(t,0)$ is the Dyson function

$$
U(t,0) = T \exp \left( -i \int_0^t \exp(i \hat{H}_T t') \left[ \hat{H}_{ep1} + \hat{H}_{ep2} \right] \exp(-i \hat{H}_T t') dt' \right)
$$

(17)

where $\hat{H}_T$, $\hat{H}_{ep1}$ and $\hat{H}_{ep2}$ are given in Eqs. (12), (13) and (14) respectively. A direct relation between the Green’s function $G(k,t)$ in Eq.(15) and exciton energy $E(k)$ has
been derived by Craig et al (see Eqs. 38 and 39 in Ref. [33]) at times larger than the inverse of phonon frequencies,

\[ G(E(k), t) = -i \exp \left[ -i \left( E(k) + \Delta(k) - N^{-1} \sum_q \frac{\chi(q)^2}{\omega(q)^2} \right) t \right] \] (18)

where

\[ \Delta(k) = N^{-1} \sum_q |F(k, q)|^2 \left[ \frac{\bar{n}_q}{\Omega_{k, q}} - \frac{\bar{n}_q + 1}{\Omega_{k, q}^+} \right] \] (20)

\[ \gamma(k) = N^{-1} \sum_q |F(k, q)|^2 \left[ \bar{n}_q \delta(\Omega_{k, q}^-) + (\bar{n}_q + 1) \delta(\Omega_{k, q}^+) \right] \] (21)

\[ \Omega_{k, q}^\pm = \hbar \omega(q) \pm (E(k + q) - E(k)) \] (22)

\[ \Lambda = N^{-1} \sum_q \frac{|\chi(q)|^2}{\omega(q)^2} (2\bar{n}_q + 1) \] (23)

where \( \Delta(k) \) yields the principal value of the term associated with it, and the mean phonon occupation number at temperature \( T \) is given by \( \bar{n}_q = \exp[\hbar \omega(q)/k_B T] - 1 \)^{-1}. We note that \( \Lambda \) is independent of time unlike the other terms, however this only applies in the Markovian approximation. A rigorous treatment in the non-Markovian range involves intense numerical computations and therefore will not be considered here. Nevertheless the Green’s function \( G(k, t) \) in Eq.(18) will suffice to reveal vital difference in the roles played by the two coupling functions, \( \chi(q) \) and \( F(k, q) \) in influencing the times of coherence between lattice sites.

The dynamics of a free particle in a one-dimensional system is determined entirely by the Green function \( G_{n, m}(t) = \langle n| G(t) |m \rangle \) [34], which yields the amplitude for an excitation to move from site \( m \) at \( t = 0 \) to site \( n \) at time \( t \). In a one-dimensional lattice with nearest-neighbor interaction energy \( 2V \cos(K) \) and zero lattice vibrations, \( G_{n, 0}(t) \) is given by

\[ G_{n, 0}(t) = N^{-1} \sum_k e^{ikn} \exp \left[ -i \frac{2Vt}{\hbar} \cos(K) \right] \] (24)

Accordingly, the probability \( P_{n0}(t) \) that an excitation which originates at site \( n \) at time \( t = 0 \) appears at site \( n \) at time \( t \) can be obtained using \( P_{n0}(t) = |G_{n, 0}(t)|^2 \).

To calculate the probability \( P_{n0}(t) \) for the exciton in the presence of dispersion and resonance terms \( \chi(q) \) and \( F(k, q) \) quantifying the exciton-phonon coupling, we use the Green’s function \( G(E(k), t) \) in Eq.(18). For very large \( N \to \infty \), we obtain

\[ P_{n0}(t) \approx N^{-1} J_n^2(\frac{2V}{\hbar} t) \exp(-\Lambda) \sum_k e^{-\gamma(k)t} \] (25)

where \( J_n(x) \) is Bessel function of the first kind and \( \gamma(k) \) is given in Eq.(21). In the absence of lattice vibrations, \( P_{n0}(t) \) reduces to the well-known form obtained by Merrifield [35] for an excitation propagating on infinite aggregate systems. We have assumed that the transfer interaction term \( V \) is independent of the environmental variables associated with lattice vibrations, also known as Condon approximation in Eq.(25). Recent experimental results [9] have shown that electron-phonon interactions between off-diagonal elements modulate the couplings between the dipoles, resulting in decoherence of the transfer interaction term \( V \). Here we assume that the transfer
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interaction term \( V \) remains intact, and Eq.(25) is a reasonably accurate description of the exciton propagation in the presence of lattice vibrations.

The subtle differences in influence of the coupling functions, \( \chi(q) \) and \( F(k,q) \) on the probability transfer function \( P_{n0}(t) \) is evident from Eq.(25). The dispersive coupling factor \( \chi(q) \) tends to localize the excitation at the original site of excitation rather than introduce decoherence during propagation. On the other hand, the resonance coupling term \( F(k,q) \) acts to retard the tendency for the exciton to move further away from the initial site of propagation by contributing to decoherence effect during propagation. Eq.(25) can be rewritten in terms of dimensionless arguments

\[
P_{n0}(t) \approx N^{-1}J^2_n(\alpha t) \exp(-\alpha^2) \sum_{k} e^{-b^2 t}
\]

where \( c = \frac{2V}{\hbar \omega(q)} \), \( a = \frac{\chi(q)}{\hbar \omega(q)} \) and \( b = \frac{F(k,q)}{\hbar \omega(q)} \). Time \( t \) is dimensionless as it is scaled by the factor \( \omega(q)^{-1} \). It is to be noted that \( t > 1 \) describes the Markovian limit reasonably well. At the Markovian limit, the flow of information from phonons back to the excitonic system can be neglected as the exciton hopping times are large compared to the phonon reservoir correlation times. This means that two propagating exciton states cannot be distinguished as they remain unaffected by correlations within the phonon reservoir at times larger than phonon correlation times.

In order to obtain an explicit result from based on Eq.(25), we make a few approximations, firstly we neglect the dispersion in phonon frequencies so that a single frequency, \( \omega(q) \sim 50 \text{cm}^{-1} \), representative of the lowest vibrational branch in common molecular crystals [33, 36] is considered. The band averages of the two coupling functions, \( \chi(q) \) and \( F(k,q) \) are then varied via parameters \( a \) and \( b \) (given below Eq.(26)), together with the electronic transfer energy, quantified by \( c \). As mentioned earlier, we consider a system of a finite number of molecular sites \( N \), and evaluate the von Neumann entropy measure of the system using

\[
S = \sum_{n=1}^{N} -\text{Tr}_n \rho_n \ln \rho_n
\]

The influence of the coupling functions obtained using Eq.(26) on the von Neumann entropy measure given in Eq.(27) can thus be easily evaluated.

In Fig. 1a, we show results of \( S \) versus time \( t \) obtained using Eq.(27) for various values of \( N \), and for an initial state, \( P_{n0}(0) = \delta_{n,0} \). At time \( t = 0 \), average entropy \( S = 0 \) due to presence of excitation at just one site, however the entropy rises rapidly reflecting the spread of excitation to more sites with constant velocity (determined by \( c \)). Instead \( S \) appears to display an approximate linear dependence on \( N \), as it should be as a system with large \( N \) results in the occupation of more lattice sites and greater chance of existing as an extended system. However as we are considering a finite system, the propagating exciton leaves the system under study after a critical time. Hence the entropy \( S \) can be seen to drop in all three cases of \( N \) considered in Fig. 1a. This drop is most pronounced at small \( N \) where there faster exit of the exciton. It is to be noted that both parameters \( a \) and \( b \) are set to zero in Fig. 1a so that phonon-coupling processes are absent, and this confirms that the noticeable drop in \( S \) is indeed due to the finite size effects of our chosen model.

It is important to note that at small time \( t \), there is a limit to the number of sites visited by the exciton and thus we expect an upper limit to \( S \) which is noticeable at \( t \sim 2 \). To illustrate this point, we show results of \( S \) versus number of sites \( N \) at
times \( t = 2 \) (solid), \( t = 5 \) (dashed) and \( t = 9 \) (dotted) in Fig. 1b. We note that at small \( t \), entropy \( S \) becomes flat after propagation to a finite number of sites. Thus the entropy \( S \) increases with \( N \) as more sites are visited before becoming independent of \( N > N^* \). The critical \( N^* \) is dependent on \( c \) and hence the transfer interaction term \( V \). At larger \( t \), more sites have a non-zero probability of occupation and therefore \( N^* \) increases with \( t \). The dependence of \( N^* \) on speed of excitation transfer (quantified by \( c \)) is illustrated in Fig. 1c where we note increase in \( S \) and \( N^* \) with increasing \( c \). The effect of the phonon coupling function \( b = F(k,q) \) on \( S \) is illustrated in Fig. 1d, which shows the gradual decrease of \( S \) due to increase coupling with phonons. Figs. 1a-d thus illustrate clearly the interplay of three competing effects: 1) the increase of \( S \) due to spreading; 2) subsequent decrease of \( S \) due to finite size effects (propagation out of the system) and, 3) decrease of \( S \) due to coupling with phonons.

In Fig. 1d, we have included a dotted-dashed line which corresponds to a fully extended state at which \( S = \frac{1}{N} \ln N - (1 - \frac{1}{N}) \ln(1 - \frac{1}{N}). \) The entropy \( S \) of the extended state is higher than other \( S \) values calculated for the case of the one-dimensional system considered in Figs. 1a to d. The results indicate that at large \( N \), the entanglement persist for longer times and \( S \) is almost comparable to that of a fully extended system. This suggests the large scale energy transport abilities of one-dimensional excitonic systems. We next examine in detail the mechanisms associated with varying coupling parameters \( a \) and \( b \) next (Fig. 2a,b,c).

Results obtained by varying \( a, b, c \) is illustrated in Fig. 2a,b,c and imply agreement with localization tendencies associated with coupling parameters, \( a \) and \( b \). The fall in \( S \) is noticeably steep for high values of \( b \sim 1 \) at intermediate \( N \sim 100 \). This shows the higher localization properties associated with the coupling function \( F(k,q) \) compared to \( \chi(q) \) (see Fig. 2b). Fig. 2c illustrates that high electronic transfer energies or \( c \) lead to fast rise in \( S \) in the time domain \( (0 < t < 6) \), which however is not sustained as excitation leaves the system as quickly as it spreads. For lower \( c \), the excitation remains extended for comparatively longer times with noticeable oscillations associated with “death and birth” type excitation and de-excitation process [37] at a monomer site. The results obtained in Figs. 1 and 2a,b,c highlight the prominence of the J-band in large systems and show the usefulness of the entropy in capturing the transition from coherent to incoherent energy transfer.

So far we have only considered the influence of two coupling terms on the von Neumann entropy measure using a simplified model, in which a single excitation is considered to propagate to neighboring sites. In reality, the electronic excitation is not confined to a single site but distributed over all \( N \) molecular sites of the crystal. The interaction between these sites then gives rise to \( N \) states, with each \( N \) state characterized by a wavevector \( k \) and associated energy level. The superposition of several such states give rise to an excitation which propagates from one site another. This highlights the inherent difficulties associated with a full computation of von Neumann entropy of a realistic system. One has to incorporate the possibility that each site becomes a source of excitation that propagates, while receiving an amplitude (of the form in Eq.(24)) from other sites. A full superposition of amplitudes from all possible sites have to be then taken into account with time as an added dimension to obtain an accurate picture of the excitation dynamics. In order to simplify analysis of the full model where all sites have equal probability of being excited, we consider the Wootters concurrence [30] which provides a convenient means to study bipartite entanglement in the next Section.
5. Molecular cooperativity as a paradigm of Collective entanglement

A notable optical response exhibited by one-dimensional excitonic systems is their enhanced rate of spontaneous emission compared to that of the monomer, an effect known as superradiance [38–40]. In a series of works [41–44], Mukamel and coworkers have shown a connection between cooperative emission mechanisms such as superradiance and “molecular cooperativity”, a term used to describe the effective coherent dynamics of a system of delocalized Frenkel excitons. The concept of a group of molecules acting in tandem to produce enhanced features in $\chi^{(3)}$, the third order optical response of one dimensional molecular systems was also shown in an earlier work by Hanamura and coworkers [39]. The oscillator strength of the $K = 0$ exciton state is directly proportional to the number of molecular sites in the absence of decoherence mechanisms, which implicates a scenario where all molecular dipoles act collectively in phase to produce giant oscillator strengths. These results highlight the potential in harnessing $\chi^{(3)}$ as a quantitative measure of multipartite entanglement if a quantum-information perspective is attached to the observed “cooperative” phenomena. This connection will be further examined in Sec. 6. In this section however, we utilize a popular entanglement measure, Wootters concurrence [30] to interpret superradiance of one-dimensional excitonic systems.
Quantum information processing attributes of J-aggregates

Figure 2. a) The von Neumann entropy $S$ versus time $t$ at $N = 150$, $b = 0$ and $c = 10$. The four curves correspond to (from top to bottom) $a = 0, 0.3, 0.7$ and $1.5$.

b) The von Neumann entropy $S$ versus time $t$ at $N = 100$, $a = 0$ and $c = 20$. The three curves correspond to (from top to bottom) $b = 0, 0.5$ and $1$.

c) The von Neumann entropy $S$ versus time $t$ at $N = 200$, $a = 0.5$ and $b = 0.3$. The three curves correspond to $c = 40$ (dotted), $20$ (dashed) and $5$ (solid line).
The well-known Wootters concurrence $C$ provides a measure of entanglement between a pair of qubits, it is zero for separable states and is equal to one for maximally entangled states such as the Bell states. $C$ has a simple form: The average pairwise concurrence $\langle C \rangle$ [45, 46] associated with a system of single-particle states is given by

$$\langle C \rangle = \frac{2}{N(N-1)} [\zeta - 1] \quad (28)$$

$\zeta$ is a measure of delocalization and is also known as inverse participation ratio (IPR) [47]. Small values of $\zeta$ correspond to localized states while larger values are linked with delocalization. At the extreme limit of localization at a single site $\zeta = 1$, $\langle C \rangle = 0$, while for states which are delocalized completely, $\zeta = N$ which yields the maximum entanglement of $2^N$. For extended excitonic system of J-aggregate structures, we consider $\zeta$ as playing similar role as $N_c$, the characteristic coherence size. $N_c$ has been formulated in terms of the density matrix as [44]

$$N_c = \left[ N \sum_{mn} |\rho_{mn}|^2 \right]^{-1} \left( \sum_{mn} |\rho_{mn}| \right)^2 \quad (29)$$

where $N$ is the total number of molecules or monomers and $\rho_{mn}$ is the reduced density matrix associated with sites $m$ and $n$. $N_c$ provides an approximate measure by which exciton at site $n$ is entangled with site $m$, and decays monotonically as a function of $(n-m)$. In the absence of any entanglement with extreme localization, $\rho_{mn} = N^{-1}\delta_{nm}$, $N_c = 1$ and the scaled concurrence obtained by dividing Eq.(28) with $\frac{2}{N}$, $\langle C \rangle_s = 0$. In the limit of complete delocalization, $\rho_{mn} = N^{-1}$, $N_c = N$ which yields the maximum $\langle C \rangle_s = 1$. Thus the inverse participation ratio $\zeta$ corresponds well with the characteristic coherence size $N_c$.

Using a coarse grained approximation (CGA) (described in Appendix B of Ref. [43]) to solve the exciton Green’s function (similar to Eq.(18)), Spano et al [43] determined the coherence size $N_c$ using a microscopic definition $G(0, t) \sim \exp(-N \gamma r t)$. The radiative rate is given by $N \gamma r$ in the superradiant limit at which excitation associated with individual sites act collectively on the molecular aggregate. In particular, Spano et al [43] obtained an empirical relation relating $N_c$ and the coupling function $F(k, q)$, temperature $T$, nearest neighbor transfer energy $V$ and phonon energy, $\hbar \omega(q)$. By rewriting the empirical relation obtained by Spano et al [43] in terms of the dimensionless constants $b$ and $c$ (given below Eq.(26)), we obtain

$$N_c \approx 2.16 \left( \frac{V^2 \hbar \omega(q)}{F^2(k, q) k_B T} \right)^\frac{1}{4} = 2.16 \left( \frac{c^2}{b t} \right)^\frac{1}{4} \quad (30)$$

where the dimensionless temperature term, $t_k = \frac{\hbar T}{\hbar \omega(q)}$. The molecular cooperativity due to the monomer’s dipoles lining up collectively in phase, results in a large net amplitude, giving rise to superradiant decay [41] and giant nonlinear optical properties [40]. The coherence size of the associated J-band is generally taken as the ratio of its radiative decay rate to that of a single monomer, however off-diagonal elements of the exciton density matrix in Eq.(6) can be also used as basis to compute the coherent size. Results obtained by Spano et al [43] showed pronounced decrease in $N_c$ at resonant points given by

$$N_c \approx 4\pi c \quad \text{resonance points} \quad (31)$$

when acoustic phonon frequencies match those between the $K$’th exciton level and $K = 0$ exciton level. The significance of these resonant points is attached to a transfer of oscillator strength away from the $K = 0$ state due to exciton-phonon scattering.
The results obtained using Eq. (30) in terms of the concurrence measure given in Eq. (28) is illustrated in Fig. 3. The figure shows gradual decrease in concurrence $C$ with aggregate size $N$ for various values of $b, c$ at constant $t_k = 2$. The temperature dependence of $N_c$ in Eq. (30) accounts for the sensitivity of lifetimes of the J-aggregate at increasing temperatures. Increasing the coupling term $F(k, q)$ (or $b$) leads to destruction of intermolecular cooperativity, hence there is associated decrease in concurrence $C$ as shown in Fig. 3. The superradiance phenomenon is thus less likely to occur at large $b$ values. We note that higher concurrence $C$ is obtained in systems with faster propagation of excitation (higher $c$ values) as also shown in Fig. 3. It is important to note that we have restricted consideration to only the pair-wise concurrence $C$ here, and not multipartite entanglement, which will be considered in the next section.

![Figure 3. Concurrence $C$ versus aggregate size $N$ at $t_k = 2$. Solid curves for $c = 15$, correspond to (from top to bottom) $b = 0.5, 0.1$. Dashed curves for $c = 5$, correspond to (from top to bottom) $b = 0.5, 0.1$.](image)

6. Theory of Two-exciton states

In this section, we examine the optical features of J-aggregates which present an experimentally quantifiable measure of multipartite entanglement, in the presence of dephasing mechanisms [20]. In this context, the class of entanglement quantity known as the Wei-Goldbart geometric measure of entanglement [31] may be convenient in analysing multipartite entanglement of J-aggregates based on properties of the third order optical susceptibility, $\chi^{(3)}$. An important feature related to non-linear optical properties of material systems is the existence of one- and two-exciton states. One-exciton states are easily identified as states in which an excitation is present at any one of the $N$ monomers while in a two-exciton state, any two of $N$ monomers are excited while the other monomers remain in the ground state. We emphasize that the two-exciton state here is vastly different from the biexciton state which consists of two coupled exciton pair system.

Two-exciton states may be identified with entangled states formed due to superposition of two spatially uncoupled excitons, such states having twice the bandwidth of the usually considered one-exciton states. This can be shown by writing the diagonal Hamiltonian of the two-exciton state in $K$ space (without involvement
The states in Eq. (34) are known to have an entanglement entropy measure \[31, 48\] transition between the one-exciton state and the two-exciton state. Using Eq. (34) as which are dependent on the number of ground states or 0’s \[31, 48\] basis, we consider that the two-exciton state are a manifestation of symmetric states, of phonon operators) as

\[\hat{H}_{ex} = \sum_k E_1(k)B_{1,k}^\dagger B_{1,k} + E_2(k)B_{2,k}^\dagger B_{2,k} + T_k(ij)\] (32)

\[T_k(ij) = \sum_{m\neq n} \exp[\imath k.(m_i - n_j)] V_{mn}\]

where $E_1(k)$ is energy of the exciton (labelled by subscript 1) with wavevector $k$ and $E_2(k)$ is energy of the second exciton (labelled by subscript 2) with wavevector $k$. The exciton operators $B_{1,k}^\dagger$, $B_{1,k}$ retain the same meaning as used in earlier sections. $V_{mn}$ denotes the interaction energy for coupling of transition moments for molecules at $m, n$. Eq. (32) can be diagonalized further in terms of the exciton operators

\[\chi_a(k) = \cos \beta(k)B_{1,k}^\dagger + \sin \beta(k)B_{2,k}^\dagger\]

\[\chi_b(k) = -\sin \beta(k)B_{1,k} + \cos \beta(k)B_{2,k}\]

we obtain

\[\hat{H}_{ex} = \sum_k E_a^*(k)\chi_a(k)\dagger \chi_a(k) + E_b^*(k)\chi_b(k)\dagger \chi_b(k)\] (34)

where $E_a^*(0)$ and $E_b^*(0)$ are exciton energies associated with Davydov branches at $k = 0$. The asterisk in the superscript denotes energies which are split due to the intermolecular interaction. Eq. (34) shows that two-exciton states are highly entangled with the degree of entanglement determined by $\cos \beta(k)$ and $\sin \beta(k)$. We next make a connection between two-exciton states and generalized symmetric states via the third order optical susceptibility, $\chi^{(3)}$.

6.1. Third order optical susceptibility, $\chi^{(3)}$ and entropy measure

The third order optical susceptibility, $\chi^{(3)}$ can be written as \[40\]

\[\chi^{(3)}(-\omega_s; \omega_1, \omega_2, \omega_3) = \sum \left[ \chi_c^{(3)}(-\omega_s; \omega_1, \omega_2, \omega_3) + \chi_b^{(3*)}(-\omega_s; \omega_1, \omega_2, \omega_3) \right] \] (35)

where the summation is performed over all possible permutations of frequencies of incident light, $\omega_1$, $\omega_2$, $\omega_3$ and $\omega_s = \sum_i \omega_i$. Expressions for $\chi_c^{(3)}(-\omega_s; \omega_1, \omega_2, \omega_3)$ and its conjugate are lengthy and given in an earlier work by Knoester \[40\], in terms of $\mu_{0,e1}$ and $\mu_{e2,e3}$. $\mu_{0,e1}$ is the dipole moment associated with transition between the ground state and one-exciton state in which an excitation is present at any one of the $N$ monomers, a generalization of the well known Dicke state $|W\rangle = \frac{1}{\sqrt{N}} (|000...0\rangle + |010...0\rangle + ... + |0...01\rangle)$. $\mu_{e2,e3}$ is the dipole moment associated with transition between the one-exciton state and the two-exciton state. Using Eq. (34) as basis, we consider that the two-exciton state are a manifestation of symmetric states, which are dependent on the number of ground states or 0’s \[31, 48\]

\[|S(N, M)\rangle \equiv \sqrt{\frac{M!(N-M)!}{N!}} \sum_{\text{permutations}} |0\rangle^\otimes M \otimes |1\rangle^\otimes (N-M)\] (36)

The states in Eq. (34) are known to have an entanglement entropy measure \[31, 48\]

\[E_A(N, M) = -\ln \Lambda(N, M)^2\]

\[\Lambda(N, M) = \sqrt{\frac{N!}{M!(N-M)!}} \left( \frac{M}{N} \right)^{\frac{M}{2}} \left( \frac{N-M}{N} \right)^{\frac{N-M}{2}}\] (38)
For fixed $N$, the minimum entanglement eigenvalue or geometric measure of entanglement [31] $\Lambda_{\text{max}}$ occurs for $M = N/2$ (even $N$) and $M = (N \pm 1)/2$ (odd $N$).

We consider that transitions involved in nonlinear optical effects occur via a simplified pathway represented as follows

$$\left| S(N, 0) \right> \rightarrow \left| S(N, 1) \right> \text{(one – exciton state)} \quad (39)$$

$$\rightarrow \left| S(N, 2) \right> \text{(two – exciton state)}$$

The terms of the form given in Eq.(36) are expected to give rise to the observed dependence of $\chi^{(3)}$ on non-local effects associated with energy transfer within various exciton site basis. Accordingly $\chi^{(3)}$ scales with the entanglement entropy $E_\Lambda$ in Eq.(37), however the explicit nature of relation between the two quantities is not immediately clear, this predicament also applies to a possible relation between $\chi^{(3)}$ and genuine multipartite entanglement involving all $N$ monomers. Here we keep the analysis tractable by examining the dependence of the intensity of third-harmonic generation (THG) $I_{\text{THG}} \propto |\chi^{(3)}(-3\omega; \omega, \omega, \omega)|^2$ on $N$ instead. We simplify the approach via the following proposed relations

$$\mu_{0,e1}^2 \approx N\mu^2 \zeta_1$$

$$\mu_{2,e2,e3}^2 \approx N\mu^2 \zeta_2$$

$$\zeta_1 = \frac{E_\Lambda(N, 1)}{E_\Lambda(N, N/2)}$$

$$\zeta_2 = \frac{E_\Lambda(N, 2)}{E_\Lambda(N, N/2)}$$

where $\mu$ is the transition dipole of individual monomers and the entanglement entropy measure $E_\Lambda(n, k)$ is given in Eq.(37). $\zeta_1$ and $\zeta_2$ are entropy measures associated with the transition efficiencies of one-exciton state and two-exciton state respectively.

Fig. 4 shows gradual decrease in these entropy measures with increasing aggregate size $N$, with $\zeta_2$ the entropy measure associated with two-exciton band seen as more resilient, which is expected as the associated entanglement persists for longer times due its wider bandwidth. In both cases, the entropy decreases with $N$ due to the faster increase of $E_\Lambda(N, N/2)$ with $N$. Using Eq.(40) and $\omega = \frac{1}{2} \Delta E$ where the excitation

![Figure 4. Entropy measures $\zeta_1$ (solid line) and $\zeta_2$ (dotted) versus aggregate size $N$.](image-url)
energy $\Delta E$ is defined in Eq.(3), we write the absolute value of the third order optical susceptibility with damping rate $\Gamma$ as

$$|\chi^{(3)}(-3\omega; \omega, \omega, \omega)| = N \frac{\mu^2 E_A(N,1)E_A(N,2)}{2\Gamma \hbar^3 (\omega^2 - \Delta E^2)}$$  \hspace{1cm} (41)

Fig. 5 shows gradual increase of $\frac{1}{N}|\chi^{(3)}(-3\omega; \omega, \omega, \omega)|$ (in which a constant term in Eq.(41) was factored out) with aggregate size $N$ before reaching an almost constant value which is independent of the size of system. The results of Fig. 5 illustrate the important fact that properties of the J-band is determined by a critical number of coherently coupled and entangled monomers rather than the total number $N$ of monomers present in the system.

The slope in Fig. 5 yields the degree of entanglement or multipartite entanglement measure. In this respect, the onset of zero slope during change of third order optical susceptibility with the system size $N$ can be viewed as the point of maximum entangled state. The results in Fig. 5 are consistent with earlier results [40] which showed the critical role played by the exciton delocalization length even Knoester [40] did not analyse his results from a quantum entanglement perspective.

The results obtained in Fig. 5 show that scaling of the third order optical response $\chi^{(3)}$ with exciton delocalization size may be used as basis in quantifying multipartite entanglement in J-aggregates or systems composed of excitonic spin chains. The result obtained here is significant considering that a rigorous definition of genuine multipartite entanglement is still lacking in the literature. Thus entanglement measures may be defined based on experimental observations and taking into account decoherence mechanisms [17, 18], exciton-photon interactions and laser detuning processes. In this regard, the results obtained so far has established some basic guidelines for an experimentally demonstrable measure of identifying multipartite entanglement in excitonic systems. In the table below, we list various quantum information processing attributes in J-aggregates systems.

| $N$ | $|\chi|/N$ |
|-----|--------|
| 20  | 1.4    |
| 40  | 1.6    |
| 60  | 1.8    |
| 80  | 2.0    |
| 100 | 2.2    |
| 200 | 2.4    |
| 300 | 2.6    |
| 400 | 2.8    |

\begin{center}
Figure 5. $\frac{1}{N}|\chi^{(3)}(-3\omega; \omega, \omega, \omega)|$ (see Eq.(41)) versus aggregate size $N$.
\end{center}

Table 1  \textit{Quantum information processing attributes in J-aggregates}
In conclusion, we have demonstrated the usefulness of the von Neumann entropy, Wootters concurrence and geometric measure of entanglement in characterizing the quantum information processing attributes quantum J-aggregates. We identify two-exciton states (entangled states of uncoupled excitons) and molecular cooperativity (manifestation of multipartite entanglement) as features which can be exploited for information processing. The entanglement and quantum correlations associated with a delocalized exciton over many monomer sites provides a clearer understanding of the processes behind observed behavior of J-aggregates. The delocalization of electronic states which give rise to narrowness of J-aggregate spectrum as expected is complicated by the fine interplay between excitation transfer mechanism and decoherence associated with a background of phonon bath. With control of the dispersive coupling ($\chi(q)$) and resonance coupling ($F(k, q)$) parameters via temperature and matrix characteristics, J-aggregate systems may be utilized as robust channels for large scale energy propagation.

We have also demonstrated that scaling of the third order optical response $\chi^{(3)}$ with exciton delocalization size provides an experimentally demonstrable measure of quantifying multipartite entanglement in Frenkel excitonic systems. $\chi^{(3)}$ may be used to distinguish between system with low and high fidelities. In future works, we seek to address the question of whether the J-band is a maximally entangled state or one that exhibits genuine multipartite. Lastly, the results of this work will be useful in understanding many-body correlated dynamics of excitonic systems, with impact on future experimental work involving measurement of multipartite entanglement. This is of considerable significance as a rigorous definition of genuine multipartite entanglement still remains an open question.

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