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# Polarons, localization, and excitonic coherence in superradiance of biological antenna complexes

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A real-space formulation of time-resolved fluorescence of molecular aggregates is developed using the one-exciton density matrix  $\rho(t)$  of the optically driven system. A direct relationship is established between the superradiance enhancement factor  $L_s$  and the exciton coherence size  $L_p$  associated with the off-diagonal density matrix elements in the molecular representation. Various factors which affect the latter, including finite temperature, energetic disorder, coupling with phonons, and polaron formation are explored. The theory is applied for the interpretation of recent measurements in the B850 system of the LH2 photosynthetic complexes. © 1997 American Institute of Physics. [S0021-9606(97)50634-9]

## I. INTRODUCTION

Optical properties of photosynthetic antenna complexes have become an object of intensive experimental and theoretical studies over the last years.<sup>1,2</sup> Time and frequency resolved measurements including fluorescence depolarization,<sup>3,4</sup> hole burning,<sup>5-8</sup> pump-probe,<sup>9-12</sup> and photon echoes<sup>13,14</sup> provide direct information regarding the dynamics of excitons, energy transfer, and electronic and nuclear relaxation in these systems. In this paper we focus on time-resolved fluorescence and cooperative spontaneous emission (superradiance) which is one of the most interesting elementary signatures of intermolecular coherence. Molecular aggregates are often characterized by ultrafast radiative decays. This effect has a simple classical interpretation: When a collection of dipoles oscillate in phase, their amplitudes add up coherently to form a large effective dipole. The oscillator-strength and consequently the radiative decay rate is then proportional to the number of dipoles. The superradiance coherence size  $L_s$  of a molecular aggregate is defined as the ratio of its radiative decay rate to that of a single molecule. (For simplicity we assume in this definition that all molecules are identical and have the same radiative decay rate. This definition can be generalized to aggregates made of different molecules.) The concept of a coherence size was invoked by Mobius and Kuhn<sup>15</sup> in analyzing the dependence of fluorescence quenching on the acceptor surface density for a system consisting of an acceptor monolayer on top of a J-aggregate monolayer. Molecules separated by more than the optical wavelength  $\lambda$  may not emit coherently.  $(\lambda/a)^d$  is therefore the fundamental upper bound for  $L_s$ ,<sup>16,17</sup>  $a$  being the lattice constant, and  $d$  the dimensionality (see Ref. 18 for  $d=1$  and Ref. 19 for  $d=2$ ). In practice, however, the coherence size is usually determined by other dephasing mechanisms such as exciton-phonon interactions and static disorder<sup>18,20-26</sup> and is typically much smaller than both the aggregate physical size and the optical wavelength.<sup>20,27</sup> Similar types of aggregates can have very different coherence sizes in different environments.<sup>28</sup>

Recent work on photosynthetic antenna complexes

showed coherence sizes of 2-3 at room temperature, whereas at low temperatures  $L_s=3$  for LH2 antenna complexes and  $L_s=9$  for LH1.<sup>22</sup> Significant decrease of fluorescence lifetimes in J-aggregates of pseudisocyanine (PIC) dyes compared to single chromophores has been observed<sup>29</sup> with the fluorescence lifetime varying between 70 ps at 1.5 K to 450 ps at 200 K. PIC J-aggregates are one-dimensional clusters of dye molecules with collective superradiant emission and optical nonlinearities. For example, in PIC-Br J-band, a Strickler-Berg analysis gives the monomer radiative lifetime 3700 ps<sup>30</sup> and 70 ps for the aggregate. This implies a superradiance coherence size  $L_s=50$  which is much smaller than the number of molecules in the aggregate:  $\approx 5 \times 10^4$  obtained from a study of exciton-exciton annihilation.<sup>21</sup> Coherence sizes of 2-3 were found in mixtures of isocyanine dyes adsorbed on silver halide substrates at room temperature,<sup>28</sup> whereas  $L_s=70$  has been reported for PIC aggregates in a low temperature glass.<sup>27</sup>

The finite coherence size  $L_s$  in large aggregates is related to the breakdown of translational symmetry of excitons due to static disorder<sup>18,20,24,25</sup> or to exciton-phonon interactions.<sup>23</sup> In the former case, the coherence size  $L_s$  has been attributed to exciton localization length<sup>18,20,24,25</sup> which exists in one-dimensional systems even for infinitely weak disorder.<sup>31</sup> Effects of weak disorder on emission of two-dimensional aggregates have been studied using perturbative methods.<sup>32</sup> Phonon-induced exciton dephasing has been shown to destroy excitonic coherence and control the superradiance.<sup>23</sup>

In this paper we show how the time-resolved fluorescence from aggregates may be calculated and analyzed by exploring exciton dynamics in real-space using the single-exciton density matrix. The superradiance size  $L_s$  is shown to be primarily determined by the exciton coherence size  $L_p$ . A precise definition of the latter in term of the "anti-diagonal" section of the density matrix is given. We study the effects of static disorder and strong exciton-phonon-coupling on  $L_p$ . The density matrix approach further allows us to express the time-resolved fluorescence signal as an overlap of a doorway and a window excitonic wave packets.

The doorway represents the reduced density matrix of the exciton driven by the external pump whereas the window accounts for the system's geometry.

In Sec. II we develop the doorway-window (DW) picture and define the density matrix coherence size  $L_\rho$ . The influence of temperature and static disorder on  $L_\rho$  in cyclic aggregates is then explored in Sec. III. An additional mechanism for  $L_\rho$  resulting from strong exciton-phonon coupling and the formation of polarons is discussed in Sec. IV. A variational calculation of the polaron wave function using Toyozawa's Ansatz allows us to compute the reduced exciton density matrix by tracing the joint (exciton plus phonon) density matrix over the phonon variables. When nuclear motions are slow, we may adopt the simplified adiabatic polaron model commonly used in the description of exciton self-trapping in low-dimensional systems.<sup>33,34</sup> The DW approach is utilized in Sec. V to calculate the dependence of the superradiance enhancement factor  $L_s$  on static disorder, diagonal and off-diagonal exciton-phonon-coupling using the models of Secs. III and IV. Finally in Sec. VI we discuss and summarize our results.

## II. REAL-SPACE PICTURE OF TIME-RESOLVED FLUORESCENCE

In this section we develop a real-space description of time-resolved polarized and depolarized fluorescence from molecular aggregates. We show how this signal may be recast in terms of a doorway function which contains all relevant information about the electronic state of the system (expressed through the exciton density matrix), and a window function related to the system's geometry. To set the stage, we introduce a Frenkel-exciton model Hamiltonian which represents an aggregate made out of two-level molecules interacting with a bath consisting of nuclear (intramolecular, intermolecular, and solvent) degrees of freedom:

$$\hat{H} = \sum_n \Omega_n(\mathbf{q}) B_n^\dagger B_n + \sum_{m,n}^{m \neq n} J_{mn}(\mathbf{q}) B_m^\dagger B_n + \hat{H}^{ph}. \quad (1)$$

Here  $B_n$  ( $B_n^\dagger$ ) are exciton annihilation (creation) operators for the  $n$ th molecule,  $\hat{H}^{ph}$  is the bath (phonon) Hamiltonian, and  $\mathbf{q}$  represents the complete set of nuclear coordinates. Exciton-phonon interactions and static disorder are described through the dependence of molecular frequencies  $\Omega_n$  and the intermolecular couplings  $J_{mn}$  on nuclear coordinates  $\mathbf{q}$ .

The dipole interaction with the optical field is

$$\hat{H}_{\text{int}} = -\mathbf{E}(t) \cdot \mathbf{P}, \quad (2)$$

where the polarization operator is given by

$$\mathbf{P} = \mu \sum_n U_n(\mathbf{q}) \mathbf{d}_n (B_n + B_n^\dagger). \quad (3)$$

Here  $\mu \mathbf{d}_n$  is the transition dipole of the  $n$ -th molecule,  $\mu$  is an average transition dipole and  $\mathbf{d}_n$  a dimensionless vector. When all molecular dipole moments are the same,  $\mathbf{d}_n$  will be

a unit vector. Otherwise its magnitude will vary with  $n$ .  $U_n(\mathbf{q})$  are  $3 \times 3$  orthogonal rotation matrices describing molecular orientations.

The time- and frequency-resolved fluorescence can be related to the dipole-dipole tensor  $S^{ij}(\omega, \tau)$ :

$$S^{ij}(\omega, \tau) \equiv \frac{\gamma}{\mu^2} \int_{-\infty}^{\infty} dt e^{i\omega t} \left\langle P^i \left( \tau + \frac{t}{2} \right) P^j \left( \tau - \frac{t}{2} \right) \right\rangle, \quad (4)$$

where  $\gamma = 4\mu^2 \bar{\omega}^3 / 3\hbar c^3$  is the radiative decay rate of a single molecule with optical frequency  $\bar{\omega}$ , and the time evolution of  $B_n(\tau)$  is given by the molecular Hamiltonian with the external driving field included ( $\hat{H} + \hat{H}_{\text{int}}$ ). Here  $i, j = x, y, z$  denote the tensor components of  $S$  in a molecular frame. To eliminate propagation and polariton effects which are not essential for the present discussion, we assume that the aggregate's size is much smaller than the optical wavelength.<sup>35</sup>

The model introduced by Eq. (1) conserves the number of excitons  $\mathcal{N} \equiv \sum_n \langle B_n^\dagger B_n \rangle$ . If exciton annihilation processes (radiative or nonradiative) are taken into account,  $\mathcal{N}$  becomes time-dependent; however, the timescale of  $\mathcal{N}$  is typically long compared with exciton equilibration. In either case it is convenient to represent the time-resolved signals as  $\mathcal{N}$  times the signal per exciton.

The time-resolved polarized signal  $S_n(\tau)$  is given by

$$S_n(\tau) = \gamma \mathcal{N}(\tau) \sum_{i,j=1}^3 \mathcal{P}^{ij}(\tau) n^i n^j, \quad (5)$$

or using operator notation

$$S_n(\tau) = \gamma \mathcal{N}(\tau) \mathbf{n} \cdot \mathcal{P}(\tau) \cdot \mathbf{n}. \quad (6)$$

Here  $\mathbf{n}$  is a unit vector denoting the polarization direction of the emitted light, and

$$\begin{aligned} \mathcal{P}^{ij}(\tau) &= [\gamma \mathcal{N}(\tau)]^{-1} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} S^{ij}(\omega, \tau) \\ &= \frac{1}{\mu^2 \mathcal{N}(\tau)} \langle P^i(\tau) P^j(\tau) \rangle \end{aligned} \quad (7)$$

is the polarization tensor.

The total time- and frequency-resolved fluorescence signal  $S(\omega, \tau)$  (summed over directions of polarizations) can be represented in a form

$$\begin{aligned} S(\omega, \tau) &= \frac{\gamma}{\mu^2} \int_{-\infty}^{\infty} dt e^{i\omega t} \left\langle \mathbf{P} \left( \tau + \frac{t}{2} \right) \cdot \mathbf{P} \left( \tau - \frac{t}{2} \right) \right\rangle \\ &= \sum_i S^{ii}(\omega, \tau). \end{aligned} \quad (8)$$

The corresponding time-resolved signal is

$$S(\tau) \equiv \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} S(\omega, \tau) = \gamma \mathcal{N}(\tau) L_s(\tau), \quad (9)$$

where  $L_s(\tau)$  is given by the trace of the polarization matrix

$$L_s(\tau) = Tr[\mathcal{A}(\tau)] = \sum_{i=1}^3 \mathcal{P}^{ii}(\tau). \quad (10)$$

We shall now introduce the DW representation for the time-resolved signal  $S(\tau)$  by relating  $L_s(\tau)$  to the time-dependent doorway ( $N$ ) and window ( $M$ ) functions

$$L_s(\tau) \equiv Tr[MN(\tau)] = \sum_{mni} M_{mn}^{ij} N_{mn}^{ij}(\tau), \quad (11)$$

where we use the tensor notation of Eq. (8).  $M$  and  $N(\tau)$  are thus direct products of  $L_0 \times L_0$  matrices in the exciton space ( $L_0$  is the number of molecules) and  $3 \times 3$  matrices in real space. Hereafter we invoke the rotating-wave approximation for the signal by omitting the terms  $\langle B_m B_n \rangle$ ,  $\langle B_m^\dagger B_n^\dagger \rangle$ , and  $\langle B_m B_n^\dagger \rangle$  occurring in correlation functions of polarization operators in Eqs. (4), (7), and (8). The doorway function  $N(\tau)$  is then given by:

$$N_{mn}^{ij}(\tau) \equiv \mathcal{N}^{-1}(\tau) \langle [U_m^\dagger(q) U_n(q)]^{ij} B_m^\dagger B_n \rangle, \quad (12)$$

where the expectation value in the right hand side (r.h.s.) of Eq. (12) is taken with respect to the full density matrix of the system at time  $\tau$ . The window function is defined by:

$$M_{mn}^{ij} \equiv d_m^i d_n^j. \quad (13)$$

Equations (11), (12), and (13) constitute the DW representation of time-resolved spontaneous light emission. Assuming that the averaging in the r.h.s. of Eq. (12) can be factorized, we obtain

$$N_{mn}^{ij}(\tau) \equiv \mathcal{N}^{-1}(\tau) \langle [U_m^\dagger(q) U_n(q)]^{ij} \rangle \langle B_m^\dagger B_n \rangle. \quad (14)$$

Equation (14) holds in three typical situations: (i) static disorder, when orientational disorder is not correlated with energetic disorder; (ii) weak exciton-phonon-coupling, whereby the full density matrix can be factorized into a product of electronic and equilibrated nuclear parts, which makes the first factor in the r.h.s. of Eq. (14) time independent; (iii) when nuclear motions do not affect dipole orientations.

Neglecting orientational disorder and assuming that all molecules have fixed directions in space, the doorway and window functions become scalars in real space:

$$L_s(\tau) \equiv Tr[MN(\tau)] = \sum_{mn} M_{mn} \rho_{mn}(\tau), \quad (15)$$

with

$$M_{mn} \equiv \mathbf{d}_n \cdot \mathbf{d}_m. \quad (16)$$

The doorway function now coincides with the reduced exciton density matrix:

$$N_{mn}(\tau) = \rho_{mn}(\tau) \equiv \mathcal{N}^{-1}(\tau) \langle B_m^\dagger(\tau) B_n(\tau) \rangle, \quad (17)$$

normalized to a unit trace  $Tr[\rho] = \sum_n \rho_{nn} = 1$ .

These results can be readily extended to the polarized signal [cf. Eq. (11)]. The DW representation for the polarization matrix becomes

$$\mathcal{P}^{ij}(\tau) = \sum_{mn} \sum_{lk} M_{mn}^{lk} \bar{N}_{mn}^{ij,kl}(\tau), \quad (18)$$

with the window given by Eq. (13), and the doorway

$$\bar{N}_{mn}^{ij,kl}(\tau) \equiv \mathcal{N}^{-1}(\tau) \langle U_m^{il}(q) U_n^{jk}(q) B_m^\dagger B_n \rangle. \quad (19)$$

The doorway function of Eq. (14) is related to the doorway function of Eq. (19) by

$$N_{mn}^{ij}(\tau) = \sum_{k=1}^3 \bar{N}_{mn}^{kk,ij}(\tau). \quad (20)$$

Assuming fixed molecular orientations and neglecting reorientational disorder, the DW representation adopts the form

$$\mathcal{P}^{ij}(\tau) = \sum_{mn} M_{mn}^{ij} \rho_{mn}(\tau), \quad (21)$$

where  $M_{mn}^{ij}$  is given by Eq. (13) and  $\rho_{mn}$  is the reduced exciton density matrix defined by Eq. (17).

The window function  $M_{mn}$  introduced in this section carries all the information regarding dipole orientations necessary for calculating the fluorescence. We note that both  $M$  and  $\rho$  are  $L_0 \times L_0$  Hermitian matrices,  $L_0$  being the number of one-exciton states. They satisfy

$$Tr[\rho] = 1, \quad Tr[M] = f, \quad (22)$$

where  $f$  is the total aggregate oscillator strength

$$f \equiv \sum_n f_n, \quad f_n \equiv |\mathbf{d}_n|^2, \quad (23)$$

$f_n$  being the oscillator strength of the  $n$ th molecule.

The matrices  $M_{mn}$  and  $\rho_{mn}$  can be diagonalized using basis sets denoted  $\phi_\alpha$  and  $\Psi_\alpha$ , respectively, with  $\alpha = 0, 1, \dots, L_0 - 1$ . These basis sets are generally different. However, if the aggregate has some symmetry, they may coincide. It is shown in Appendix A that  $M$  has no more than three nonzero eigenvalues (superradiant states) denoted by  $\bar{f}_\alpha$ ,  $\alpha = 1, 2, 3$ ; the corresponding three eigenstates  $\phi_\alpha$  will be hereafter referred to as the superradiant states. We further introduce three orthogonal vectors  $\mathbf{d}_\alpha$  which represent the transition dipoles between the ground state and the superradiant states:

$$\mathbf{d}_m = \sum_{\alpha=1}^3 \mathbf{d}_\alpha \phi_\alpha(m), \quad (24)$$

and  $\bar{f}_\alpha = |\mathbf{d}_\alpha|^2$ . Equation (24) implies that each superradiant state is responsible for the components of all molecular dipoles along one of the orthogonal directions in the laboratory frame; these directions are uniquely determined by the aggregate geometry and are not arbitrary. When all molecular dipoles are in the plane determined by  $\mathbf{d}_\alpha$  with  $\alpha = 1, 2$  we have  $\bar{f}_3 = 0$ , while  $\bar{f}_2 = \bar{f}_3 = 0$  when all dipoles are oriented along  $\mathbf{d}_1$ . Denoting  $\bar{\rho}_\alpha \equiv \langle \phi_\alpha | \rho | \phi_\alpha \rangle$ , we obtain for the superradiance factor

$$L_s = \sum_{\alpha=1}^3 \bar{f}_\alpha \bar{\rho}_\alpha, \quad (25)$$

and since  $\sum_{\alpha=0}^{L_0-1} \bar{\rho}_\alpha = 1$  we have  $L_s \leq \max_\alpha(\bar{f}_\alpha)$ , with  $\sum_{\alpha=1}^3 \bar{f}_\alpha = f$ , which gives an upper bound for the superradiance factor for a given geometry.

The polarization matrix can be also represented in terms of the superradiant states  $\phi_\alpha (\alpha=1,2,3)$ :

$$\mathcal{P}^{ij} = \sum_{\alpha=1}^3 d_\alpha^i d_\alpha^j \bar{\rho}_\alpha, \quad (26)$$

where  $d_\alpha^i$  are components of the superradiant dipole  $\mathbf{d}_\alpha$ .

The DW representation of time-resolved spontaneous emission given by Eqs. (15)–(17) will be applied in the coming sections to explore the roles of temperature, disorder and exciton-phonon coupling on the time-resolved fluorescence and superradiance of aggregates. To that end we shall introduce the coherence size  $L_\rho$  which characterizes the size of a domain where the molecules emit coherently. Within the approximations adopted here, all information about the state of the system relevant for superradiance is given by the reduced exciton density matrix  $\rho_{mn}(\tau)$  whose time dependence reflects the role of relaxation processes on the superradiance factor  $L_s(\tau)$ . This allows us to introduce a formal definition of the characteristic coherence size  $L_\rho$  in terms of the density matrix. By applying the inverse participation ratio concept commonly used in the theory of quantum localization<sup>36</sup>

$$L_\rho \equiv \left[ L_0 \sum_{mn} \left| \rho_{mn} \right|^2 \right]^{-1} \left[ \left( \sum_{mn} \left| \rho_{mn} \right| \right)^2 \right]. \quad (27)$$

This quantity gives the length-scale on which the density matrix decays along the ‘‘anti-diagonal’’ direction, i.e., as a function of  $n - m$ . Similar measures have been successfully used in the analysis of off resonant polarizabilities of aggregates,<sup>37,38</sup> conjugated polymers,<sup>39</sup> and semiconductor nanocrystals.<sup>40</sup> In the absence of any coherence  $\rho_{nm} = L_0^{-1} \delta_{nm}$  and we have  $L_\rho = 1$ . For a completely coherent distribution  $\rho_{nm} = L_0^{-1}$ , and  $L_\rho = L_0$ . If the molecular dipoles are oriented in the same direction, then the superradiance factor is related to the number of molecules in this domain and loss of coherence which leads to the decrease of  $L_\rho$  reduces the superradiance. The picture is very different in the opposite situation when the total dipole of an aggregate (i.e., the vector sum of the molecular dipoles) vanishes due to cancellation of contributions from individual molecules. In this case the emission is induced by the loss of coherence, and should increase with the decrease of  $L_\rho$ . It is important to note that the size  $L_\rho$  depends on the state of the aggregate and is changed when exciton relaxation takes places. This length has only an implicit dependence on the dipole orientation, which comes from the process of preparation of the initially excited state by the exciting optical field. These arguments show that superradiance is a combined effect of aggregate geometry (dipole orientations) and its state, and at least qualitatively all information about the aggregate state relevant for superradiance is contained in the coherence size  $L_\rho$ , irrespective of the underlying physical dephasing mechanisms. Superradiance can then be analyzed by first studying the role of different physical mechanisms in affect-

ing the coherence length  $L_\rho$  and then relating the superradiance factor  $L_s$  to  $L_\rho$  and to geometry through the window function.

In the following sections we study various mechanisms which determine the coherence size  $L_\rho$ : finite temperatures, disorder-induced localization of excitons, and exciton self-trapping induced by exciton-phonon-coupling. Characteristic sizes associated with these mechanisms will be introduced, and their relations to  $L_s$  will be discussed in Sec. V. We shall restrict the following analysis to the case where the exciton equilibration timescale in the excited state manifold is short compared with the radiative decay, and the fluorescence comes from the fully-relaxed exciton density matrix. This case, which always represents the fluorescence at long times, allows us to introduce all the relevant coherence sizes and dephasing mechanisms.

### III. TEMPERATURE- AND DISORDER-CONTROL OF EXCITONIC COHERENCE IN CYCLIC AGGREGATES

The  $\approx 2.5$  Å resolution structure of the LH2 antenna complex of purple bacteria shows two rings: an inner ring (the B850 system) made of 18 chlorophyll molecules and an outer ring (the B800 system) with 9 chlorophylls.<sup>41</sup> Cyclic complexes appear also in other systems such as LH1 which has 32 chlorophylls. All calculations in this article were performed on the B850 system. This aggregate is slightly dimerized and in Appendix B we present the window functions for circular aggregates with two molecules in a unit cell. The values of the coupling  $J$  between adjacent chlorophyll molecules in the B850 band used in Ref. 42 are  $-273$  cm<sup>-1</sup> and  $-291$  cm<sup>-1</sup>. However, we do not expect this dimerization to significantly affect the superradiance and for simplicity we have used an average nearest neighbor coupling parameter of  $J = -280$  cm<sup>-1</sup>.

In the absence of disorder, the exciton eigenstates of a ring  $\Psi_\alpha$  and their energies  $\epsilon_\alpha$  are determined by the momenta  $k_\alpha = 2\pi\alpha/L_0$ ,  $\alpha = 0, 1, \dots, L_0 - 1$

$$\Psi_\alpha = \frac{1}{\sqrt{L_0}} e^{ik_\alpha m}; \quad \epsilon_\alpha = 2J \cos(k_\alpha). \quad (28)$$

Since  $J$  is negative, the  $k_0 = 0$  state has the lowest energy.

In this section we shall consider two mechanisms for the loss of excitonic coherence (dephasing): finite temperature, and diagonal energetic disorder. A third mechanism: strong exciton-phonon-coupling resulting in polaron formation will be discussed in the next section.

For weak exciton-phonon-coupling, electronic and nuclear degrees of freedom are decoupled in the equilibrium density matrix (the only role of phonons is then to equilibrate the electronic degrees of freedom), and the reduced exciton density matrix  $\rho$  assumes the canonical form:

$$\rho_{\alpha\beta} = \delta_{\alpha\beta} Z^{-1} \exp(-\epsilon_\alpha/T), \quad (29)$$

where we set Boltzmann’s constant to 1 and  $Z \equiv \sum_\alpha \exp(-\epsilon_\alpha/T)$ ,  $\epsilon_\alpha$  were introduced in Eq. (28) and  $T$  is

the temperature. In Eq. (29) Greek indices label one-exciton eigenstates  $\Psi_\alpha$  with energies  $\epsilon_\alpha$ . In real-space we have

$$\rho_{mn} = Z^{-1} \sum_{\alpha} \Psi_{\alpha}^{*}(m) \Psi_{\alpha}(n) \exp(-\epsilon_{\alpha}/T). \quad (30)$$

At temperatures lower than the spacing between exciton levels, the aggregate is in the lowest, completely delocalized, exciton state,  $\rho_{mn} = L_0^{-1}$  and  $L_{\rho} \approx L_0$ . As the temperature is raised, higher-momentum excitons become occupied, which decreases  $L_{\rho}$ . We define the characteristic thermal size  $l_T$  as the size of a cyclic J-aggregate with nearest-neighbor interaction  $J$  in which the splitting between the lowest exciton levels is equal to the temperature  $T$

$$l_T^2 = 4\pi^2 |J| T^{-1}. \quad (31)$$

In a translationally-invariant system the density matrix coherence length  $L_{\rho}$  is related to  $l_T$ . This relation contains a numerical factor which can be calculated using Eq. (30). For example, when the temperature is much smaller than the exciton bandwidth, but much larger than the splitting between the exciton levels at the bottom of the band:  $4\pi^2 J/L_0^2 \ll T \ll 4J$ , the numerical factor can be evaluated analytically using Eq. (30) and turns out to be close to 1:  $L_{\rho} = \sqrt{2/\pi} l_T$ .

Disorder can be easily incorporated by averaging Eq. (30) over realizations of disorder using Monte Carlo sampling, resulting in  $\langle \rho \rangle$ . Static disorder breaks translational symmetry. However, this symmetry is restored upon averaging over disorder, which implies that  $\langle \rho \rangle$  becomes diagonal in the momentum representation. The coherence size  $L_{\rho}$  is determined by the population of higher-momentum excitons even at low temperatures. Since in one-dimensional systems static disorder leads to localization of exciton states,  $L_{\rho}$  can be related to the exciton Anderson localization length  $l_{\psi}$ , as can be seen from Eq. (30).

Using these definitions we now discuss the influence of temperature and disorder on the density matrix  $\rho_{mn}$ . Figures 1(a)–1(c) show the “anti-diagonal” sections of the density matrices  $\rho_{mn}$  calculated using Eq. (30) for different temperatures and disorder strengths. Neglecting disorder and assuming a temperature lower than the splitting between the lowest excitons, only the lowest exciton is populated in thermal equilibrium. Due to the symmetry, the corresponding density matrix will be delocalized over the entire ring, and  $L_{\rho}$  will be equal to the system size  $L_0 = 18$ .

With increasing temperature, higher exciton states are populated and  $\rho$  becomes more localized. This effect is shown in Fig. 1(a), where the canonical density matrices for temperatures 50 K (solid), 100 K (dashed), and 300 K (dotted) are displayed. The temperature-induced localization can be clearly seen. The corresponding values of  $L_{\rho}$  are 14.6, 10.5, and 5.95, respectively. In the high temperature limit all exciton states are equally populated and the density matrix becomes completely localized (diagonal) resulting in  $L_{\rho} = 1$ .

Figure 1(b) illustrates how disorder leads to localization of the density matrix at low temperatures. Energetic diagonal disorder has been included by assuming that  $\Omega_n$  have inde-

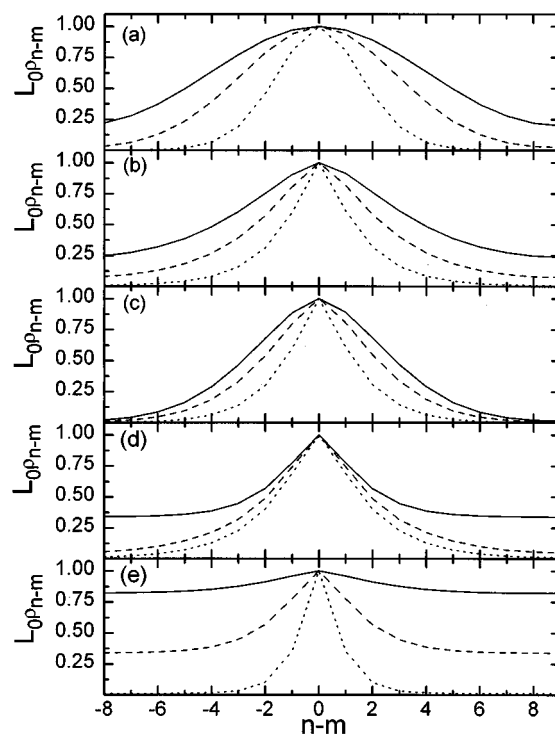


FIG. 1. Thermally relaxed density matrices. (a) Purely exciton systems (no disorder and phonons), for different temperatures, solid: 50 K,  $L_{\rho} = 14.55$ ; dashed: 100 K,  $L_{\rho} = 10.47$ ; dotted: 300 K,  $L_{\rho} = 5.95$ . (b) For different disorder strengths at 4 K, solid:  $330 \text{ cm}^{-1}$ ,  $L_{\rho} = 14.55$ ; dashed:  $565 \text{ cm}^{-1}$ ,  $L_{\rho} = 10.64$ ; dotted:  $1130 \text{ cm}^{-1}$ ,  $L_{\rho} = 6.16$ . (c) For different disorder strengths at 100 K, solid:  $330 \text{ cm}^{-1}$ ,  $L_{\rho} = 9.40$ ; dashed:  $565 \text{ cm}^{-1}$ ,  $L_{\rho} = 8.044$ ; dotted:  $1130 \text{ cm}^{-1}$ ,  $L_{\rho} = 5.53$ . (d) Diagonal exciton-phonon coupling,  $J_R = 8$ ,  $\kappa = 0.5$  and three reduced temperatures, solid:  $T_R = 10^{-3}$ ,  $L_{\rho} = 15.5$ ; dashed:  $T_R = 0.1$ ,  $L_{\rho} = 9.58$ ; dotted:  $T_R = 0.2$ ,  $L_{\rho} = 7.26$ . (e) Diagonal exciton-phonon coupling,  $T_R = 10^{-3}$ ,  $J_R = 8$  and three values of  $\kappa$ , solid:  $\kappa = 0.125$ ,  $L_{\rho} = 17.9$ ; dashed:  $\kappa = 0.5$ ,  $L_{\rho} = 15.5$ ; dotted:  $\kappa = 0.781$ ,  $L_{\rho} = 3.52$ .

pendent Gaussian distributions with the same mean  $\bar{\Omega}$  (independent of  $n$ ) and FWHM  $\sigma$ . Calculations were made using a Monte Carlo sampling over different realizations. As shown in Fig. 1(b), this localization becomes stronger with increasing  $\sigma$ . The corresponding values of  $L_{\rho}$  at 4 K are 14.6, 10.6, and 6.16 for  $\sigma = 330 \text{ cm}^{-1}$ ,  $565 \text{ cm}^{-1}$ , and  $1130 \text{ cm}^{-1}$ , respectively. In the limit of very strong disorder the density matrix becomes completely localized (diagonal) and we have  $L_{\rho} = 1$ . The combined influence of disorder and temperature is illustrated in Fig. 1(c) where equilibrium density matrices are shown at  $T = 100 \text{ K}$  for different values of  $\sigma$ . The values of  $L_{\rho}$  at 100 K are 9.40, 8.04, and 5.53 for  $\sigma = 330 \text{ cm}^{-1}$ ,  $565 \text{ cm}^{-1}$ , and  $1130 \text{ cm}^{-1}$ , respectively. The density matrices become more localized with increasing disorder and temperature, as is evident by comparing Fig. 1(c) with Fig. 1(b).

#### IV. POLARON CONTROL OF EXCITONIC COHERENCE

When exciton-phonon-coupling is weak, the phonon degrees of freedom may be eliminated and their effects incorporated through relaxation superoperators calculated perturbatively in the exciton-phonon-coupling strength.<sup>43,44</sup> The

detailed-balance condition satisfied by the relaxation super-operator guarantees that at long times the system evolves into a thermal distribution of bare excitons. The corresponding coherence size  $L_\rho$  then does not depend on the nature of the phonons and their coupling with excitons. The analysis of equilibrated excitons in Sec. III therefore implicitly assumes weak exciton-phonon coupling. This state of affairs changes drastically as the coupling strength is increased. In this section we consider the effects of strong exciton-phonon-coupling on the coherence size. It is shown in Appendix C how higher order effects of exciton-phonon coupling on the reduced exciton density matrix  $\rho_{mn}$  can be taken into account perturbatively. The following analysis is non-perturbative and is based on the polaron model.<sup>33</sup>

We adopt the Hamiltonian Eq. (1) with the Einstein phonon Hamiltonian  $\hat{H}^{ph}$ ,

$$\hat{H}^{ph} = \sum_n \hbar \omega_0 b_n^\dagger b_n, \quad (32)$$

where  $b_n^\dagger$  creates a phonon of frequency  $\omega_0$  on site  $n$ , and we have one Einstein oscillator per molecule. Exciton-phonon interactions enter through the nuclear coordinate influence on both molecular frequencies (diagonal coupling) and intermolecular interactions (off-diagonal coupling). Expanding  $\Omega_n(\mathbf{q})$  to first order in phonon coordinate  $\mathbf{q}$ , the first term of Eq. (1) reads

$$\sum_n \Omega_n(\mathbf{q}) B_n^\dagger B_n = \sum_n \Omega_n(\mathbf{q}=0) B_n^\dagger B_n + \hat{H}^{diag}, \quad (33)$$

with the diagonal exciton-phonon-coupling term

$$\hat{H}^{diag} = g \hbar \omega_0 \sum_n B_n^\dagger B_n (b_n^\dagger + b_n), \quad (34)$$

and  $g$  is a dimensionless diagonal coupling constant.

Expanding  $J_{mn}(\mathbf{q})$  to first order in phonon coordinates, we write the second term of Eq. (1) as

$$\sum_{m,n}^{m \neq n} J_{mn}(\mathbf{q}) B_m^\dagger B_n = \sum_{m,n}^{m \neq n} J_{mn}(\mathbf{q}=0) B_m^\dagger B_n + \hat{H}^{o.d.} \quad (35)$$

with the off-diagonal coupling term<sup>45,46</sup>

$$\begin{aligned} \hat{H}^{o.d.} = & \frac{\phi}{2} \hbar \omega_0 \sum_{nl} [B_n^\dagger B_{n+1} (b_l^\dagger + b_l) (\delta_{n+1,l} - \delta_{nl}) \\ & + B_n^\dagger B_{n-1} (b_l^\dagger + b_l) (\delta_{nl} - \delta_{n-1,l})]. \end{aligned} \quad (36)$$

The second term of (36) is the Hermitian conjugate of the first. Here we have assumed nearest-neighbor coupling, and  $\phi$  is a dimensionless parameter controlling the off-diagonal coupling strength. Equation (34) and Eq. (36), together with  $\hat{H}^{ph}$  and the zeroth-order intermolecular coupling term, result in the generalized Holstein Hamiltonian  $\hat{H}^{GH}$  (the original Holstein Hamiltonian contains diagonal coupling only).<sup>34</sup>

$$\begin{aligned} \hat{H}^{GH} = & \sum_n \Omega_n(\mathbf{q}=0) B_n^\dagger B_n + \sum_{mn}^{m \neq n} J_{mn}(\mathbf{q}=0) B_m^\dagger B_n + \hat{H}^{ph} \\ & + \hat{H}^{diag} + \hat{H}^{o.d.} \end{aligned} \quad (37)$$

There are two competing energy scales in the Holstein Hamiltonian, namely, the lattice relaxation energy  $g^2 \omega_0$  and the bare exciton bandwidth  $4J$ . Their ratio will be denoted the coupling strength

$$\kappa = g^2 \omega_0 / 4J \quad (38)$$

which determines the size of the polaron as well as exciton-phonon correlations. In typical molecular crystals,  $g^2 \lesssim 1$ , in ionic crystals  $g^2$  is large compared to unity, and in semiconductors  $g^2$  is between the former two. In anthracene, for example,  $\kappa$  is about 0.4, and in pyrene, about 0.8~1.6.<sup>47</sup> The other two important parameters of the model are the reduced bandwidth (the ratio between the bare exciton bandwidth  $4J$  and the characteristic phonon frequency  $\omega_0$ )

$$J_R = 4J / \omega_0, \quad (39)$$

and the reduced temperature

$$T_R = T / \omega_0. \quad (40)$$

For strong exciton-phonon-coupling ( $\kappa \gg 1$ ), solutions of the Holstein Hamiltonian are known as small polarons because the exciton-induced lattice distortion is confined to essentially a single exciton site.<sup>48</sup> For weak exciton-phonon coupling ( $\kappa \ll 1$ ), the spatial extent of the lattice distortion is significantly increased and the resulting phonon-dressed exciton is called a large polaron. The crossover from a large polaron to a small polaron with increasing exciton-phonon coupling (often called the self-trapping transition) is rather abrupt for large intermolecular coupling  $J$ . In the limit of slow lattice motions ( $J_R \gg 1$ ), adiabatic polaron theories admit approximate solutions in the form of solitons.

The off-diagonal coupling in Eq. (36) has positive (negative) signs for electronic transfer to the left (right) of the distorted lattice site. While exact solutions exist for diagonal coupling in the  $J_R \rightarrow 0$  limit (the small polaron), the Hamiltonian with off-diagonal coupling has not been diagonalized analytically. Adding intermolecular interactions and diagonal coupling complicates the problem even further. Due to difficulties in obtaining simple solutions,<sup>49</sup> off-diagonal coupling is less frequently used compared with its diagonal counterpart.

To calculate  $\rho_{mn}$  we assume that exciton-phonon coupling leads to the formation of bands of collective exciton-phonon states, and the many-body polaron wave function is given by the Toyozawa Ansatz<sup>50</sup> (see Appendix D):

$$|K\rangle = L_0^{-1} \sum_n e^{iKn} |\Lambda_n^K\rangle \sum_m \psi_{m-n}^K B_m^\dagger |0\rangle_{ex}. \quad (41)$$

Here  $|K\rangle$  is the lowest polaron state with momentum  $K$ ,  $|0\rangle_{ex}$  is the exciton vacuum state, and  $|\Lambda_n^K\rangle$  are phonon wave functions centered at site  $n$  containing a coherent state on each site  $l$  with a displacement  $\lambda_l^K$  [cf. Eq. (D6)].  $|\Lambda_n^K\rangle$  is different from  $|\Lambda_{n'}^K\rangle$  only by a shift of  $n - n'$  lattice con-

stants. The parameters  $\lambda_l^K$ ,  $\psi_l^K$ , and the polaron energy band  $E_K$ , are obtained variationally. The phonon wave functions  $|\Lambda_n^K\rangle$  represent a lattice distortion forming a potential well centered at  $n$  and trapping the exciton with an amplitude distribution of  $\psi_l^K$ .

At sufficiently low temperatures ( $T_R \ll 1$ ), only the lowest polaron band is populated, and the many-body exciton-phonon density matrix  $\rho_M$  is given by

$$\rho_M = Z^{-1} \sum_K \langle K|K\rangle^{-1} |K\rangle e^{-E_K/T} \langle K|, \quad (42)$$

where  $E_K$  are the polaron energies and  $Z \equiv \sum_K \exp(-E_K/T)$  is the partition function.

It should be emphasized that the polaron state is delocalized over the entire aggregate even though both exciton amplitudes  $\psi_l^K$  and phonon displacements  $\lambda_l^K$  are localized. We shall demonstrate that the size of  $\psi_l^K$ , hereafter referred to as the polaron size  $l_p$ , which can be formally defined by  $l_p \equiv 1/|\sum_l \psi_l^K|^4$ , shows up as the localization length of  $\rho_{mn}$  (i.e., as the coherence size  $L_\rho$ ).  $l_p$  can therefore be directly observed in superradiance measurements. To that end we substitute Eqs. (42) and (41) into  $\rho_{mm'} = \text{Tr}(\rho_M B_m^\dagger B_{m'})$  yielding

$$\rho_{mm'} = L_0^{-2} \sum_K \langle K|K\rangle^{-1} e^{-E_K/T} \times \sum_{nn'} e^{iK(n'-n)} \psi_{m-n}^K \psi_{m'-n'}^{K*} F_{n'n}^K, \quad (43)$$

with the Debye-Waller factor

$$F_{n'n}^K \equiv \langle \Lambda_{n'}^K | \Lambda_n^K \rangle = \exp \left[ L_0^{-1} \sum_q |\lambda_q^K|^2 (e^{iq(n-n')} - 1) \right], \quad (44)$$

and  $\lambda_q^K$  is the Fourier transform of  $\lambda_n^K$  (see Appendix D):

$$\lambda_q^K = \sum_n e^{-iqn} \lambda_n^K. \quad (45)$$

Localization of  $\rho_{mm'}$  is determined by the combined effect of electronic confinement (that of  $\psi_{m-n}^K$ ) and the nuclear factor  $F_{n'n}^K$  which represents the overlap (scalar product)  $\langle \Lambda_{n'}^K | \Lambda_n^K \rangle$  of two coherent states.

The reduced density matrix  $\rho_{m-n}$  is shown in Fig. 1(d) for  $J_R=8$ ,  $\kappa=0.5$  and three reduced temperatures  $T_R=10^{-3}$ , 0.1, 0.2.  $L_\rho$  for the three reduced temperatures are 15.5, 9.58, and 7.26, respectively. Comparison with the other panels shows that at finite temperatures, polaron-induced and disorder-induced localization of  $\rho_{m-n}$  are very similar. At zero temperature, only the  $K=0$  polaron state is populated, and the reduced density matrix becomes

$$\rho_{mm'} \propto \sum_{nn'} \psi_{m-n}^{K=0} \psi_{m'-n'}^{K=0*} \langle \Lambda_{n'}^{K=0} | \Lambda_n^{K=0} \rangle. \quad (46)$$

In Fig. 1(e), we display the reduced density matrix  $\rho_{m-n}$  for  $T_R=10^{-3}$ ,  $J_R=8$ , and  $\kappa=0.125$ , 0.5 and 0.78. The corresponding  $L_\rho$  are 17.9, 15.5, and 3.52, respectively.  $\rho_{m-n}$  has a constant finite component at large  $|m-n|$  in addition to the

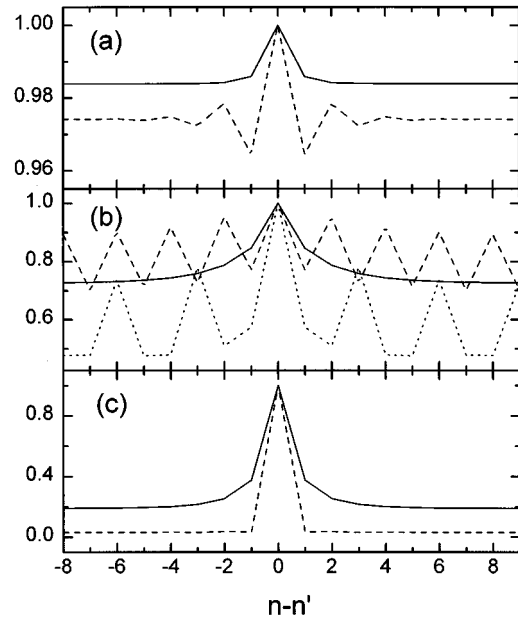


FIG. 2. The Debye-Waller factor  $F_{n'n}^K$ . (a) Weak coupling,  $\kappa=0.0125$ , narrow band,  $J_R=0.8$ , two crystal momenta are shown:  $K=0$  (solid) and  $K=\pi$  (dashed); (b) weak coupling,  $\kappa=0.125$ , broad band,  $J_R=8$ , three crystal momenta are shown:  $K=0$  (solid),  $K=\pi$  (dashed) and  $K=2/3\pi$  (dotted); (c) intermediate coupling,  $\kappa=0.5$ ,  $J_R=8$ , two crystal momenta are selected:  $K=0$  (solid) and  $K=\pi$  (dashed).

polaron-induced localized structure at small  $|m-n|$ . To trace the origin of this behavior, let us examine more carefully the Debye-Waller factor.  $F_{n'n}^K$  decreases from 1 at  $n=n'$  to a constant at large  $|n-n'|$  over a characteristic lengthscale which will be denoted by  $l_{DW}$ . A formal definition of  $l_{DW}$  can be obtained by subtracting its value  $\bar{F}$  for large  $|n-n'|$  and substituting  $F_{n'n}^K - \bar{F}$  into Eq. (27) instead of  $\rho_{mn}$ . The Debye-Waller factor can be recast in the form

$$F_{n'n}^K = \exp(\sigma_{n-n'}^K - \sigma_0^K), \quad (47)$$

where  $\sigma_{n-n'}^K$  is the Fourier transform of  $|\lambda_q^K|^2$ . Because  $\sigma_{n-n'}^K$  decays rapidly to zero with increasing  $|n-n'|$ , the Debye-Waller factor  $\langle \Lambda_{n'}^K | \Lambda_n^K \rangle$  at large  $|n-n'|$  equals  $\exp(-\sigma_0^K)$  which becomes  $\exp(-g^2)$  in the  $J_R \rightarrow 0$  limit.

In Fig. 2, the Debye-Waller factor  $\langle \Lambda_{n'}^K | \Lambda_n^K \rangle$  is displayed as a function of  $n-n'$  for different polaron momenta  $K$ . Two weak-coupling cases are shown,  $\kappa=0.0125$ ,  $J_R=0.8$  ( $J_R < 1$ , narrow band) and  $\kappa=0.125$ ,  $J_R=8$  ( $J_R > 1$ , broad-band). For the first case,  $F_{n'n}^K$  hardly deviates from 1 for both  $K=0$  and  $K=\pi$ , as shown in Fig. 2(a). For the second case, the Debye-Waller factor reflects the one-phonon plane-wave of high momentum states. For  $J_R=8$ ,  $\kappa=0.5$ , the Debye-Waller factor has a constant component  $\exp(-\sigma_0^K)$  which decreases with increasing crystal momentum as is evident from comparing the two crystal momenta,  $K=\pi$  and  $K=2/3\pi$ , displayed in Fig. 2(c). For intermediate to strong couplings, it is safe to assume that the Debye-Waller factor size  $l_{DW}$  is much smaller than  $l_p$ . This implies that only those terms with  $|n-n'| \leq l_p$  contributes to Eq. (43), and since  $\psi_l^K$  has a size of  $l_p$  the reduced density matrix is localized on the  $l_p$



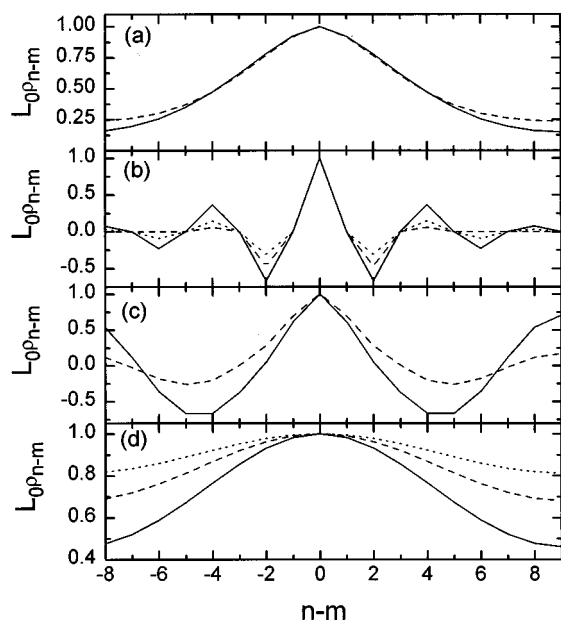


FIG. 3. Reduced exciton density matrices for the polaron model. (a) For two reduced temperatures  $T_R=0.27$  (solid,  $L_\rho=13.24$ ), and  $T_R=0.49$  (dashed,  $L_\rho=14.27$ ),  $J_R=8, \kappa=0.125$ . The corresponding polaron band is shown in Fig. 4(a). (b) For two temperatures  $T_R=0$  (solid,  $L_\rho=5.95$ ) and  $T_R=0.2$  (dotted,  $L_\rho=2.93$ ),  $\phi=1, J_R=g=0$ . Also shown for comparison is the reduced density matrix for  $\phi=g=1, J_R=T_R=0$  (dashed,  $L_\rho=3.71$ ). The corresponding polaron band is shown in Fig. 4(b). (c)  $\phi=1, J_R=2$  and  $T_R=10^{-3}$  (solid,  $L_\rho=13.9$ ),  $T_R=10^{-2}$  (dashed,  $L_\rho=8.9$ ). The corresponding polaron band is shown in Fig. 4(c). (d) For soliton profiles [Eqs. (48) and (50)] for three strengths of nonlinearity:  $a_0=3$  (solid),  $a_0=4$  (dashed) and  $a_0=5$  (dotted).  $L_\rho=17.9, 17.7$ , and  $16.8$ , respectively.

lengthscale as a function of  $|n-n'|$ . The constant component of the reduced density matrix  $\rho_{m-n}$  for large  $n-m$  shown in Fig. 1(d) reflects the similar behavior of the Debye-Waller factor.

In the weak coupling ( $\kappa \ll 1$ ) limit of the broadband ( $J_R > 1$ ) case, the Debye-Waller factor Eq. (44) for high crystal momentum states has a one-phonon plane-wave component due to strong interactions with the one-phonon scattering continuum, as shown in Fig. 2(b). As a result, for some temperature range,  $\rho_{mm'}$  may become more delocalized at higher temperatures. This counterintuitive behavior is related to the increase in population of higher-momentum states which have the one-phonon plane-wave as the phonon wave function, as the temperature is raised. As shown in Fig. 3(a),  $\rho_{mm'}$  at  $T_R=0.49$  has a longer off-diagonal tail than  $\rho_{mm'}$  at  $T_R=0.27$ . For small  $|m-m'|$ , though,  $\rho_{mm'}$  at  $T_R=0.49$  remains slightly more localized than  $\rho_{mm'}$  at  $T_R=0.27$ .  $L_\rho$  for the two cases are 14.27 and 13.24, respectively. Figure 4(a) shows the corresponding polaron band. The flat regions of the polaron band at higher crystal momenta are responsible for the counterintuitive behavior of the reduced exciton density matrix shown in Fig. 3(a).

In summary, we have shown that in the absence of static disorder and at low temperatures, the coherence size  $L_\rho$  is related to the characteristic sizes  $l_p$  and  $l_{DW}$ , even though the excitons are not localized, in contrast to the case of static disorder. The polaron size  $l_p$  reflects the size of the trapped

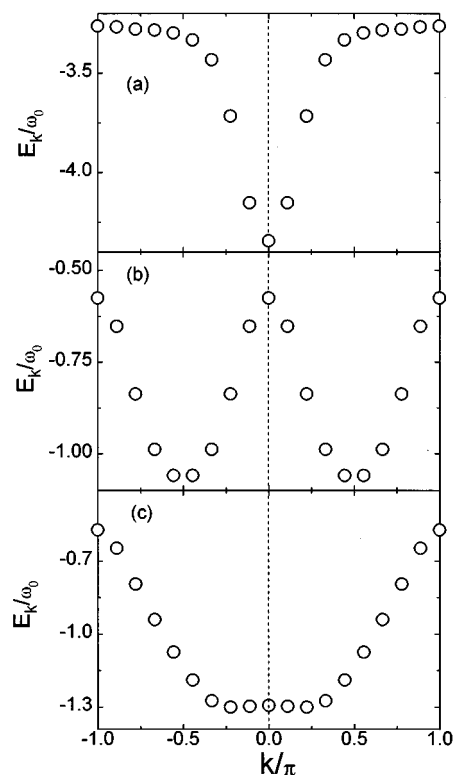


FIG. 4. Dispersion curves ( $E_K$  vs  $K$ ) for the lowest polaron band. (a) Diagonal coupling only,  $J_R=8, \kappa=0.125$ . (b) Diagonal and off-diagonal coupling,  $J_R=0, \phi=g=1$ . (c) Off-diagonal coupling only,  $\phi=1, J_R=2$ .

exciton wave function, whereas  $l_{DW}$  shows a typical separation between the traps related to the left (bra) and right (ket) components of the density matrix. The coherence size depends on both  $l_p$  and  $l_{DW}$ , however when  $l_{DW} \ll l_p$  the length  $l_{DW}$  is irrelevant. The constant tail  $\bar{F}$  of  $F_{nn'}$ , which does not vanish at large values of  $|n-n'|$  may be important in large aggregates and at low temperatures. Representing the Debye-Waller factor as  $F_{mn} = (F_{mn} - \bar{F}) + \bar{F}$  in Eq. (43) we recast the density matrix  $\rho_{mm'}$  in a form  $\rho_{mm'} = \rho_{mm'}^{(0)} + \rho_{mm'}^{(1)}$ . By substituting  $\rho_{mm'}^{(0)}$  and  $\rho_{mm'}^{(1)}$  into Eq. (27) we obtain  $L_\rho$  which saturates and scales like  $L_0$ , respectively, for large  $L_0$ . Since in the case of strong and intermediate coupling  $\bar{F}$  is usually small at intermediate sizes  $L_0$ ,  $L_\rho$  does not depend on  $L_0$  while at large  $L_0$  we have  $L_\rho \propto L_0$ . The size  $l_c$  which determines the crossover region can be defined as the value of  $L_0$  when contributions of  $\rho_{mm'}^{(0)}$  and  $\rho_{mm'}^{(1)}$  are equal. The smaller  $\bar{F}$ , the larger is  $l_c$ .

We now turn to off-diagonal coupling. LH2 has significant dipole-dipole interactions up to the third neighbor.<sup>42</sup> It is reasonable to assume that these interactions are affected by various phonon modes. The two sets of variational parameters  $\psi_l$  and  $\lambda_l$  of the Toyozawa Ansatz provide an adequate description of off-diagonal coupling as well, and the resulting exciton-phonon correlations and polaron energy bands compare favorably with the Munn-Silbey approach at zero temperature.<sup>45,46</sup>

In Fig. 3(b) we show the influence of off-diagonal cou-

pling on the reduced density matrix  $\rho_{mn}$ . For  $J_R = g = 0$  (off-diagonal coupling only), the polaron band is symmetric with respect to  $K = \pm \pi/2$  as demonstrated in Fig. 4(b). As a result,  $\rho_{m-n}$  vanishes for odd  $m-n$ . For even  $m-n$ ,  $\rho_{m-n}$  has alternating signs reflecting the dynamic dimerization introduced by off-diagonal coupling. Increase in temperature reduces the amplitudes of  $\rho_{m-n}$  at nonzero even  $m-n$ . Diagonal coupling has a similar effect on  $\rho_{m-n}$  as the temperature, i.e., it suppresses  $\rho_{m-n}$  for nonzero even  $m-n$ . However, as is evident from Fig. 3(b), diagonal coupling reduces equally  $\rho_{m-n}$  for all nonzero even  $m-n$ . This is clearly reflected in the sizes of  $L_\rho$  for the three cases displayed in Fig. 3(b): 5.95 ( $T_R = 0, \phi = 1, J_R = g = 0$ ), 2.93 ( $T_R = 0.2, \phi = 1, J_R = g = 0$ ) and 3.71 ( $T_R = 0, g = \phi = 1, J_R = 0$ ). With increasing temperature,  $\rho_{m-n}$  for  $m-n = \pm 4, \pm 6, \pm 8$  vanishes much faster than  $m-n = \pm 2$ . For diagonal coupling only,  $\rho_{m-n}$  is completely localized on  $m-n=0$ . Off-diagonal coupling thus induces localization as well as assists transport of electronic excitations.

Addition of the transfer integral  $J$  destroys the folded polaron band structure by lowering the zone center energy  $E_{K=0}$  [cf. Fig. 4(b)]. Consequently, the structure of  $\rho_{m-n}$  is expanded while retaining the oscillatory feature in Fig. 3(b). As the zone center energy  $E_{K=0}$  is lowered to the level of  $E_{K=\pm\pi/2}$ , the polaron band has a rather flat structure at the zone center, as illustrated in Fig. 4(c) for the case of  $\phi = 1, J_R = 2$ , causing the reduced density matrix to change abruptly as the temperature is raised from zero. In Fig. 3(c) we compare  $\rho_{m-n}$  for two low temperatures  $T_R = 10^{-3}$  and  $10^{-2}$  for  $J_R = 8, \phi = 1$ . A temperature increase of one hundredth of the phonon frequency drastically affects the profile of  $\rho_{m-n}$  due to a flat band bottom at the zone center, and  $L_\rho$  also drops from 13.9 ( $T_R = 10^{-3}$ ) to 8.94 ( $T_R = 10^{-2}$ ). For sufficiently large transfer integrals, the polaron band acquires a similar shape as the weak coupling band of diagonal exciton-phonon-coupling, and so does the reduced density matrix  $\rho_{mn}$ .

So far our calculations were based on the assumption that the temperature is much lower than the phonon frequency  $T_R \ll 1$ , which is typically the case for optical phonons even at room temperature. Aggregates may have strong coupling to low-frequency solvent modes. Nuclear spectral densities representing coupling to low-frequency modes have been used to fit photon-echo measurements in light-harvesting complexes.<sup>14</sup> This corresponds to the opposite limit  $T_R \equiv T/\omega_0 \gg 1$  (here  $\omega_0$  denotes a typical frequency of low-energy solvent modes) and the adiabatic polaron theory can be applied. The calculation of the polaron wave functions is greatly simplified when nuclear motions are much slower than the electronic ones. In this case we can adopt the Born-Oppenheimer (adiabatic) approximation. The adiabatic polaron theory was first developed by Pekar<sup>51</sup> for an analogous continuum Hamiltonian—the Fröhlich Hamiltonian—describing a slow electron moving in an ionic crystal.<sup>52</sup> Later the Pekar-type adiabatic solution was generalized to the Holstein Hamiltonian for molecular crystals.<sup>33,34</sup> Both the large and small adiabatic polaron can be captured

by the Holstein Hamiltonian, while in the Fröhlich Hamiltonian only the large polaron is physically meaningful. If the characteristic phonon frequency is small compared to the splitting between exciton levels the lattice kinetic energy can be neglected in the zero-order adiabatic approximation.<sup>53</sup>

For the diagonal coupling we get (see Appendix E for the derivation)

$$\rho_{mn} = \frac{1}{L_0} \sum_s \Psi^*(m+s) \Psi(n+s), \quad (48)$$

where the exciton wave function satisfies the discrete nonlinear Schrödinger equation<sup>33,34,54</sup>

$$-J[\Psi(n+1) + \Psi(n-1)] - 4\lambda |\Psi(n)|^2 \Psi(n) = E\Psi(n), \quad (49)$$

where  $2\lambda$  is the Stokes shift of a single molecule ( $2\lambda = g^2\omega_0$  for the Holstein model) and  $E$  is the polaron energy. For large polarons (i.e., when the polaron size  $l_p$  is much larger than the lattice constant but still smaller than the system's size), one can apply the one-dimensional infinite-size continuum model, which yields the following (soliton) solution of Eq. (49).<sup>33,34</sup>

$$\Psi(n) = \sqrt{\frac{1}{2a_0}} \operatorname{sech}\left(\frac{n}{a_0}\right), \quad (50)$$

with  $a_0 \equiv J/\lambda$ . Solutions of the continuum version of Eq. (49) on a ring, which generalize Eq. (50) to finite systems have been obtained recently in Ref. 55. The connection between the soliton solutions and the Toyozawa Ansatz is discussed in Appendix D. In Fig. 3(d), we show the reduced density matrices calculated using Eqs. (48) and (50). For the three strengths of nonlinearity shown  $a_0 = 3, 4, 5$ , the corresponding values of  $L_\rho$  are 17.9, 17.7 and 16.8, respectively.

Equation (48) allows us to treat effects of disorder and phonon coupling on exciton coherence size in the same fashion. In the case of static disorder  $\Psi(m)$  is a localized exciton wave function, whereas in the polaron picture represented by the Toyozawa Ansatz,  $\Psi(m)$  is the self-trapped exciton wave function represented by  $\psi_m^K$  in Eq. (41). In the case of static disorder, Eq. (48) should be averaged over disorder realizations with the canonical distribution [see Eq. (30)]. For strong or intermediate exciton-phonon-coupling the averaging of Eq. (48) is given by Eq. (43) by setting  $\langle \Lambda_n^K | \Lambda_n^K \rangle = \delta_{n'n}$ . In the adiabatic polaron approach  $\Psi(m)$  is the solution of Eq. (49).

## V. SUPERRADIANCE IN CYCLIC AGGREGATES

It was shown in Sec. II that the superradiance enhancement factor depends on two ingredients: the exciton density matrix and the window function  $M_{ij}$  which carries information regarding the aggregate geometry. In this section we consider various models for dipole orientations and combine them with the calculation of the density matrix presented in the last two sections to explore the superradiant behavior of the LH2 complexes.

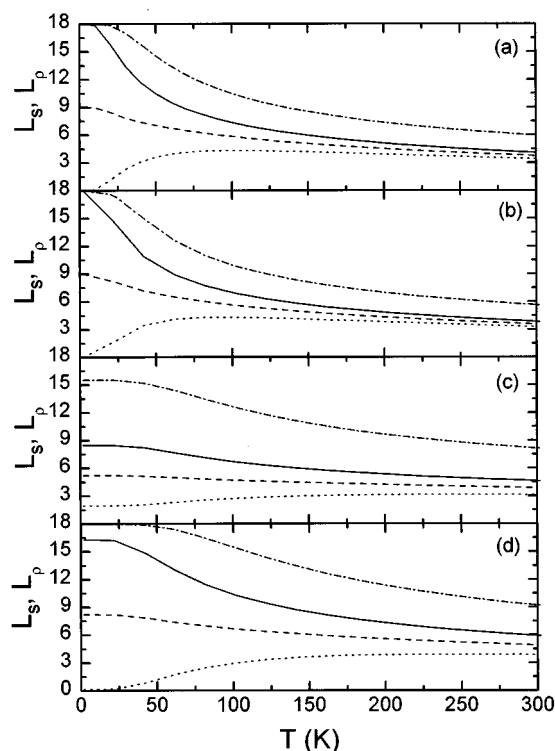


FIG. 5. Variation of  $L_s$  with temperature. Solid: model III; dashed: model II; dotted: model I; dashed-dotted:  $L_\rho$ . (a) Without disorder and exciton-phonon-coupling. (b) Diagonal coupling, the weak coupling limit  $\kappa \rightarrow 0$  and  $J_R = 0.8$ . (c) Diagonal coupling,  $J_R = 8$ ,  $\kappa = 0.5$ .  $\omega_0 = 1253 \text{ cm}^{-1}$ . (d) Off-diagonal coupling,  $\phi = 1$  and  $J_R = 5$ .  $\omega_0 = 1253 \text{ cm}^{-1}$ .

The window function for a cyclic aggregate can be readily calculated. Denoting the angle between the molecular dipole and the aggregate plane by  $\Theta$  we obtain:

$$M_{mn} = d^2 \left[ \sin^2 \Theta + \cos^2 \Theta \cos \left( \frac{2\pi(m-n)}{L_0} \right) \right]. \quad (51)$$

It follows from the circular symmetry, that  $\rho$  and  $M$  are diagonal in the same basis set and the superradiant states are

$$\phi_{1,2}(m) = \frac{1}{\sqrt{L_0}} e^{\pm i2\pi m/L_0}, \quad \phi_3(m) = \frac{1}{\sqrt{L_0}}, \quad (52)$$

with the corresponding oscillator strengths

$$\bar{f}_1 = \bar{f}_2 = \frac{1}{2} d^2 L_0 \cos^2 \Theta, \quad \bar{f}_3 = d^2 L_0 \sin^2 \Theta. \quad (53)$$

The state  $\phi_3$  has a transition dipole orthogonal to the aggregate's plane, whereas  $\phi_1$  and  $\phi_2$  have an in-plane dipole. Combining Eqs. (15) and (51)–(53) we have for the superradiance factor:

$$L_s = \left( \cos^2 \Theta \frac{\rho_1 + \rho_2}{2} + \sin^2 \Theta \rho_3 \right) L_0, \quad (54)$$

with  $\rho_1 + \rho_2 + \rho_3 \leq 1$ .

We first examine the effect of finite temperature. Figure 5(a) shows the variation of  $L_s$  with temperature for three orientations of the dipoles with respect to the ring: model I ( $\Theta = 0^\circ$ ), model II ( $\Theta = 45^\circ$ ), and model III ( $\Theta = 90^\circ$ ).  $L_\rho$

displayed for comparison decreases with increasing temperature [see Fig. 1(a)]. For model III the temperature dependence of  $L_s$  is close to that of  $L_\rho$ : both decrease from 18 for low temperatures to 1 in the high temperature limit. However, for model I,  $L_s$  shows a very different temperature dependence: at low temperatures the density matrix is completely delocalized, and the summation over all the inner products of the dipole vectors in the calculation of  $L_s$  yields  $L_s = 0$ . With increasing temperature the coherence size  $L_\rho$  decreases and  $L_s$  becomes finite and eventually reaches a maximum when  $L_\rho$  is somewhat larger than half the system size. At high temperatures, all three models have similar superradiance factors which eventually approach 1. It follows from Eq. (54) that the superradiance factor for model II is simply the average of models I and III. It is therefore easy to calculate  $L_s$  for all angles  $\Theta$ , using the curves for models I and III.

Figures 5(b)–5(d) display the temperature-dependence of  $L_s$  and  $L_\rho$  due to diagonal and off-diagonal exciton-phonon-coupling. Within the polaron model as outlined Sec. IV, localization of  $\rho_{mm'}$  may have several origins. Increased temperature results in smaller  $L_\rho$ . This is clearly shown when the bandwidth  $4J$  is less than the Einstein phonon frequency  $\omega_0$  ( $J_R < 1$ ) so that the bare exciton band does not cross into the one-phonon scattering continuum. For  $J_R > 1$ , the weak coupling limit is nonperturbative in the sense that the  $\kappa \rightarrow 0^+$  polaron band is different from the bare exciton band due to level repulsion from the phonon continuum.<sup>56–59</sup>

In Fig. 5(b), we display  $L_\rho$  and the superradiance length  $L_s$  for our three models and for  $J_R = 0.8$  in the weak coupling limit ( $\kappa \rightarrow 0$ ). At zero temperature, both  $L_\rho$  and the superradiance length  $L_s$  for parallel dipoles (model III) are equal to the size of the system, 18. Due to the momentum selection rule,  $L_s$  for the in-plane dipole configuration (model I) reaches a maximum at a temperature whereby the  $K = 2\pi/18$  state is most populated.  $L_\rho$  and the superradiance length  $L_s$  for  $\Theta = 0^\circ, 45^\circ, 90^\circ$  are shown in Fig. 5(c) for intermediate exciton-phonon coupling  $\kappa = 0.5$ ,  $J_R = 8$ . At zero temperature the superradiance length  $L_s$  for parallel dipoles is only half the size of the ring, and  $L_\rho$  is also less than 18. For strong exciton-phonon coupling, the superradiance size  $L_s$  is independent of temperature. In Fig. 5(d) we show  $L_\rho$  and the superradiance length  $L_s$  for models I, II and III as a function of the temperature for  $J_R = 4$ ,  $\phi = 1$  and  $g = 0$ . The dependence of the superradiance length  $L_s$  on temperature is very similar to the diagonal coupling case.

In Fig. 6(a) we display  $L_s$  and  $L_\rho$  versus the static disorder parameter  $\sigma$  at 4 K. The curves are slightly different, but their general appearance and limits are similar to Fig. 5(a). Figure 6(b) repeats the calculations of Fig. 6(a) for a higher temperature (100 K). Due to the temperature-induced loss of coherence,  $L_\rho$  and  $L_s$  for model III are smaller than the system size for weak disorder, and  $L_s$  for model I no longer vanishes. Analogous to Fig. 6(a), with increasing disorder  $L_s$  becomes similar for all models. For very strong disorder,  $L_\rho$  as well as  $L_s$  approach 1.

The correlations between  $L_s$  and  $L_\rho$  are clearly shown in Fig. 7(a), where we display them for the different localiza-

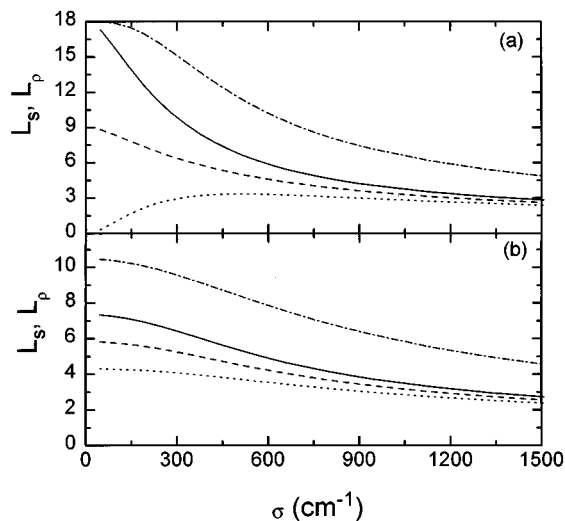


FIG. 6. Variation  $L_s$  with disorder strength, in the absence of exciton-phonon coupling. (a)  $T=4$  K and (b)  $T=100$  K. Solid: model III; dashed: model II; dotted: model I; dashed-dotted:  $L_\rho$ .

tion mechanisms and dipole orientations. For the two localization mechanisms considered in Fig. 7(a) (temperature- and disorder-induced dephasing) we find a very similar correlation between  $L_s$  and  $L_\rho$  in models I and III, which demonstrates that the superradiance enhancement factor is in both cases primarily determined by the off-diagonal spread of the density matrix  $L_\rho$ , and that both mechanisms influence the superradiative enhancement factor in a similar fashion. In Fig. 7(b),  $L_s$  from model III is plotted vs  $L_\rho$  within the polaron approach for different temperatures, intermolecular couplings and diagonal exciton-phonon couplings. This again shows the strong correlation between  $L_s$  and  $L_\rho$  is not sensitive to the underlying mechanisms.

We have identified the density matrix size  $L_\rho$  as the primary factor in determining the superradiance size  $L_s$ . This allows us to predict  $L_s$  using  $L_\rho$ , regardless of the specific microscopic mechanism that determines  $L_\rho$ . A commonly used measure of the exciton localization length is provided by the inverse participation ratio of a wave function  $\Psi_\alpha(m)$ <sup>36</sup>

$$l_\alpha \equiv \frac{1}{\sum_m |\Psi_\alpha(m)|^4}. \quad (55)$$

The thermally averaged size associated with the wave function is defined by:

$$l_\psi \equiv Z^{-1} \sum_\alpha l_\alpha \exp(-\epsilon_\alpha/T). \quad (56)$$

We shall now discuss the connection between  $l_\psi$  and  $L_\rho$ . At low temperatures  $L_\rho$  depends on exciton localization and is related to  $l_\psi$ . The numerical factor which relates the two depends on the form of the wave function and the system size  $L_0$ . To illustrate this point we plot in Fig. 8(a) the dependence of  $L_\rho$  on  $l_\psi$  for different models. Assuming a uniform wave function  $\Psi(m) = \theta(m) \theta(l_\psi - m) / \sqrt{l_\psi}$  where  $\theta(m)$  is the Heaviside function, we obtain

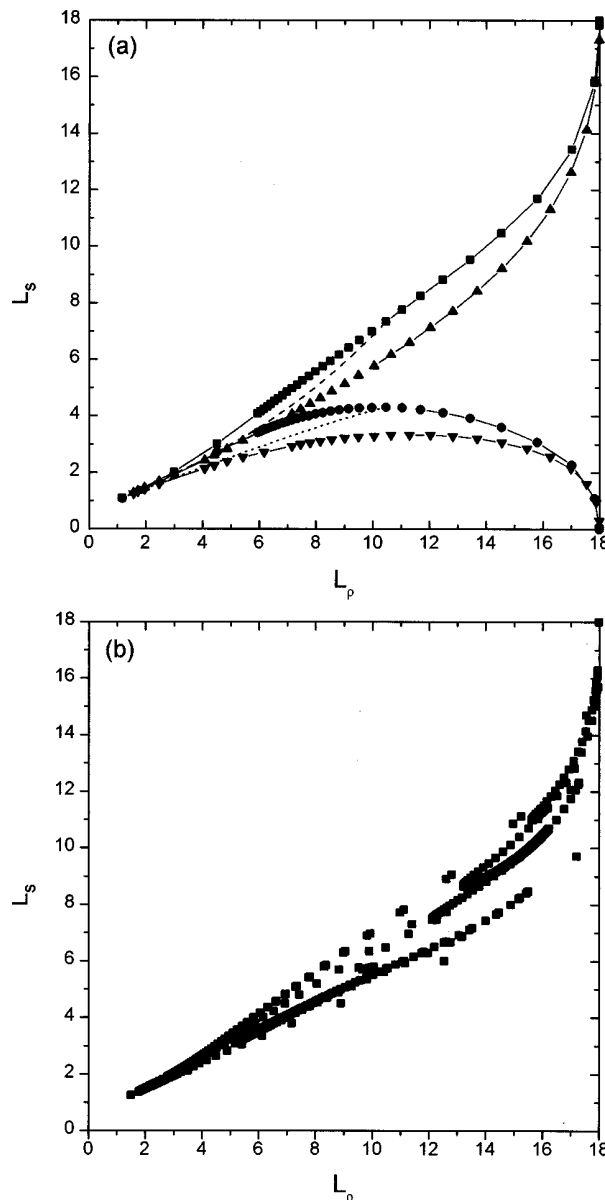


FIG. 7. Correlation between the superradiance enhancement factor  $L_s$  and the density matrix size  $L_\rho$ . (a) Squares: model III for different temperatures, triangles up: model III for different disorder strengths at  $T=4$  K; dashed line: model III for different disorder strengths at  $T=100$  K, circles: model I for different temperatures; triangles down: model I for different disorder strengths at  $T=4$  K; dotted line: model I for different disorder strengths at  $T=100$  K; (b) model III for different temperatures  $T$ , intermolecular couplings  $J$  and diagonal exciton-phonon coupling strength  $g$ .

$$L_\rho = \frac{3l_\psi^3}{2l_\psi^2 + 1}, \quad \text{for } l_\psi \leq \frac{L_0}{2}; \quad (57)$$

$$L_\rho = \frac{3l_\psi^4}{l_\psi(2l_\psi^2 + 1) + (2l_\psi - L_0)^3 - (2l_\psi - L_0)}, \quad \text{for } l_\psi > \frac{L_0}{2}.$$

In particular  $L_\rho = l_\psi$  when  $l_\psi = L_0$ . Therefore in the absence of disorder and at low temperatures ( $T=4$  K) both measures give  $L_\rho = l_\psi = L_0 = 18$ , since the lowest exciton is completely delocalized. With increasing disorder however, they start to

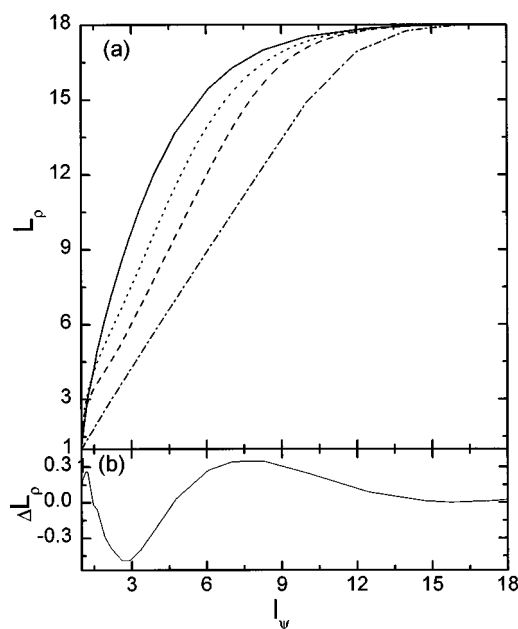


FIG. 8. (a)  $L_\rho$  versus  $l_\psi$  of the lowest exciton wave function for different models. Dashed-dotted: uniform wave function; dashed: Gaussian wave function; dotted: sech wave function [Eq. (50)]; solid:  $T=4$  K with varying disorder. (b) Difference between the solid curve of (a) and the Padé approximant Eq. (58).

differ, since the exciton wave function is no longer uniform. For  $L_0 \gg l_\psi \gg 1$ , we have  $L_\rho \approx 1.5l_\psi$  as shown in Fig. 8(a). For the Gaussian wave function  $\Psi(m)$ , we have  $L_\rho = 2l_\psi$  if  $L_0 \gg l_\psi \gg 1$ . The soliton wave functions Eq. (50) show a similar behavior. Monte Carlo averaging over diagonal disorders yields the solid curve in Fig. 8(a). An excellent fit is obtained using the Padé approximant [see Fig. 8(b)]

$$L_\rho = \frac{1 + 7.88(l_\psi - 1)}{1 + 0.316(l_\psi - 1) + 0.00393(l_\psi - 1)^2}. \quad (58)$$

These examples illustrate that the coherence length  $L_\rho$  representing the number of coherently coupled molecules is closely related to the size of the corresponding wave functions which is usually defined through the inverse participation ratio  $l$  given by Eq. (55) where  $l = l_\psi$  for the model of static disorder and  $l = l_p$  for the case of exciton-phonon coupling. However, the relations between these quantities contain important numerical factors representing the wave function shape<sup>60</sup> and the system size. All models show a very similar behavior with the numerical ratio of  $l_\psi$  and  $L_\rho$  varying from 1.0 to 3.3 depending on the model and the value of  $l_\psi$ . This has a very important implication for analyzing experimental data on the superradiance enhancement factor  $L_s$  in light-harvesting complexes.<sup>22</sup>

In all four cases shown in Fig. 8(a), the wave functions are nonoscillatory and  $l_\psi$  is the only factor which determines  $L_\rho$ . This situation is changed as the temperature is increased. It follows from Eq. (30) that both the amplitude and the phase of thermally populated exciton wave functions affect  $L_\rho$ . At low temperatures only excitons at the bottom of the band with nonoscillatory wave functions are populated.

Therefore  $L_\rho$  is determined by localization of the amplitude and is related to  $l_\psi$ . In the absence of disorder exciton states are delocalized over the entire aggregate and  $L_\rho$  is determined by oscillations of wave functions corresponding to higher-energy excitons which are populated when the temperature is raised. This implies that the characteristic length  $l_T$  reflects the phase oscillations of the exciton wave functions. In a disordered aggregate at low temperatures when  $l_\psi \ll l_T$ , phase oscillations are negligible and  $L_\rho$  is related to  $l_\psi$ . As the temperature is raised and higher-energy excitons become populated,  $l_\psi$  increases since localization is weaker at higher energies whereas phase oscillations become more important, as reflected in the decrease of  $l_T$ .  $L_\rho$  then decreases while  $l_\psi$  increases. In this intermediate region  $l_\psi \sim l_T$ ,  $L_\rho$  is influenced by the competition of the amplitude and the phase-induced mechanisms. At higher temperatures  $l_T \ll l_\psi$ , exciton localization becomes irrelevant and  $L_\rho$  is determined by the thermal size  $l_T$ . This can be illustrated as follows: our numerical simulations of the thermal- and disorder-averaged density matrix  $\langle \rho \rangle$ , with  $\sigma = 377 \text{ cm}^{-1}$  gives  $L_\rho = 13.7$ . Using Eq. (56) we then obtain  $l_\psi = 4.8$ , so that  $L_\rho/l_\psi \approx 3$ . We recall that for these parameters we find a superradiance enhancement factor of  $L_s = 3.2$  for model I. With increasing disorder both measures become more localized. For  $\sigma = 754 \text{ cm}^{-1}$  and  $T = 4 \text{ K}$  we obtain  $L_\rho = 8.6$  and  $l_\psi = 2.6$ , and their ratio is 3.3. With increasing temperature, due to the contribution of energetically higher exciton states which are more delocalized,  $l_\psi$  increases, while  $L_\rho$  decreases. For  $T = 300 \text{ K}$  we have  $L_\rho = 5.8$  and  $l_\psi = 6.6$ . These examples illustrate an interplay of the characteristic sizes  $l_\psi$  and  $l_T$  in determining the coherence size  $L_\rho$ . We reiterate that superradiance is strongly affected by geometry and  $L_s$  is not necessarily proportional to  $l_\psi$ , i.e., for weak disorder  $L_s$  is determined by the loss of coherence  $L_0 - L_\rho$  rather than  $l_\psi$ . Usually one can divide the aggregate into domains  $L_g$  ( $g$  stands for geometry) within which molecular dipoles are oriented in more or less the same direction. These directions are different for different domains and the total dipole of the aggregate vanishes due to cancellation of contributions from different domains. At long times, when excitons are equilibrated,  $L_\rho$  is independent on the system's geometry. In contrast, the size  $L_g$  depends only on the dipole orientations (and the system's symmetry) and is independent on the state of the aggregate. It is easy to see that for a given geometry (and  $L_g$ ) there is an optimal value of the coherence size  $L_\rho$ , which maximizes the superradiance, namely  $L_\rho \approx L_g$ .

The dipole orientations in LH1 and LH2 imply that the fluorescence should vanish if all monomers emit coherently (i.e.,  $L_\rho = L_0$ ).<sup>61</sup> The factor  $L_s$  can then be small in two cases: either  $L_\rho \ll L_0$  where we have  $L_s \approx L_\rho$  (since the dipoles emitting coherently are almost parallel) or  $L_0 - L_\rho \ll L_0$  where we have  $L_s \approx L_0 - L_\rho$  and the signal is proportional to the measure of coherence destruction. This means that  $L_s$  is not necessarily proportional to  $l_\psi$ . For example, in calculations performed for LH2<sup>61</sup>  $l_\psi \approx 6$ ,  $L_\rho \approx 15$  and  $L_s \approx 3$  which satisfies  $L_s \approx L_0 - L_\rho$ . This could explain the difference between low-temperature superradiance of LH1 ( $L_s \approx 9$ ) and LH2 ( $L_s \approx 3$ ) observed in Ref. 22 despite close values of

parameters for both complexes. The differences in  $L_s$  could be attributed to different geometric factors (and window functions) resulting from the different number of pigments ( $L_0 = 32$  versus  $L_0 = 18$ ) in these complexes.

## VI. DISCUSSION

Spectroscopic properties of J-aggregates<sup>24,25,27,62,63</sup> and light-harvesting complexes<sup>3,4,9,14,22,64</sup> are often related to a coherence size known as the exciton delocalization length [cf. Eq. (56)]. In the absence of disorder and exciton-phonon interaction, the exciton states are delocalized over the entire aggregate, and the exciton delocalization length is equal to the aggregate size. Since in infinite one-dimensional disordered systems all exciton states become localized,<sup>31</sup> static disorder induces a finite (Anderson-type) exciton delocalization length. Effects of exciton localization on optical signals of disordered aggregates can be rationalized by examining properties of individual states and their contributions to  $l_\psi$ .

Effects of nuclear motions on the exciton localization length have been denoted dynamical localization.<sup>14,62</sup> Dynamical localization is much more complex than its static counterpart, since excitons are coupled to a large (often macroscopic) number of nuclear degrees of freedom. The only practical way to introduce an exciton delocalization length in this case is through observables which involve exciton variables. Such observables can always be represented in terms of Green functions of exciton operators<sup>36,49,65</sup> and in some cases in terms of reduced exciton density matrices (which constitute a particular case of Green functions). Despite this formal difficulty which can be overcome by applying the Green function formalism, it is clear that there is a substantial physical difference between static and dynamical localization: in aggregates with exciton-phonon coupling but without static disorder excitons are self-trapped<sup>33,34</sup> rather than localized. This implies that a natural measure for the exciton dynamical delocalization will be the polaron size  $l_p$  defined in Sec. IV as the size of the self-trapped exciton wave function  $\Psi_{m-n}^K$  which enters the expression for the polaron wave function [Eq. (41)]. The main difference between static localization and dynamic (self-trapping) localization is that a localized exciton is confined in a certain region in space whereas the exciton density in the polaron wave function is spread over the entire aggregate. However, since the wave function of the self-trapped exciton  $\psi_{m-n}^K$  is localized, self-trapping and localization have common features and similar effects on some spectroscopic measurements.

In the remainder of this section we discuss how static and dynamical localization show up in various spectroscopic techniques. Exciton localization naturally leads to a decrease of the superradiance factor in the time-resolved emission<sup>20,22,24,61</sup> and affects energy transfer which affects in depolarization measurements.<sup>3,4,64</sup> In particular, in the absence of nuclear motions no transport should take place in a system with localized excitons, and the fluorescence will retain its initial polarization at all times. In the presence of nuclear

motions exciton localization affects transport properties by increasing the depolarization timescale.

Static localization of excitons also affects the temperature dependence of fluorescence decay<sup>24,63</sup> and pump-probe signals<sup>9,25,27,61,62</sup> in a more delicate way. The effect may be rationalized using the Mott picture of Anderson localization which implies that localized states with close energies must be spatially separated.<sup>66</sup> This leads to a qualitative picture whereby the aggregate can be divided into noninteracting segments whose sizes are equal to the localization length. The signals from a large disordered aggregate can therefore be related to the signal from a homogeneous aggregate whose physical size is given by the localization length.

It has been shown in Ref. 61 that polaron formation (self-trapping) and static localization lead to similar features in the pump-probe signal for long time delays. In both cases the shift between positive (induced-absorption) and negative (bleaching) peaks in the differential absorption reflects the energy difference between the lowest and the next lowest excitons. This is in turn related to the polaron binding energy  $E_p$  (i.e., the binding energy of the self-trapped exciton) in the dynamical case, and is given by the minimal energy splitting between exciton states located in the same region in space.<sup>67</sup> For weak exciton-phonon coupling<sup>61</sup> the pump-probe signal was related to the one-exciton Green function, and the shift in the pump-probe signal was related to the exciton mean-free path which plays the role of the coherence size for the pump-probe signal.

The exciton delocalization length can show up directly in transport processes. Although aggregate sizes are usually smaller than the optical wavelength, nonuniform population distributions are obtained by optical excitation of light-harvesting complexes with polarized light due to dipole orientations. Population relaxation can be observed by depolarization measurements.<sup>3,4</sup> A model in which an excitation is localized on a dimer due to static disorder has been used<sup>3,4</sup> to fit energy transfer experiments. The possibility of dynamical contributions to exciton localization in the context of transport phenomena has been discussed.<sup>14</sup> A theory of energy transfer in molecular aggregates with strong exciton-phonon coupling using canonical transformations in the joint exciton-phonon space has been developed.<sup>45,68</sup> The role of polaron effects on the energy transfer has been discussed for the cases of small and large polarons.<sup>45,69</sup> An application of transport theories will be to connect the exciton delocalization size due to coupling to nuclear motions with the depolarization timescale observed in Refs. 3 and 4. An interesting attempt to introduce a coherence size related to transport by means of the Green function techniques in Ref. 64 for a system with static disorder and exciton-phonon coupling has been treated within the Redfield theory<sup>44,70</sup> with the Redfield relaxation operator taken in the Haken-Strobl form.<sup>71,72</sup> However, the Green function  $G_{ii,ii}^{(0)}$  used in Eq. (39) of Ref. 64 to define the participation ratio is related to a model with a finite lifetime rather than homogeneous dephasing, for which most calculations have been made. This can be clearly seen from Eq. (40) of Ref. 64 which shows the same rate  $\Gamma$  for the decay of populations and coherences. Thus the coher-

ence size defined in Ref. 64 is related to exciton lifetime and not to pure dephasing processes due to exciton-phonon coupling.

In this paper, utilizing the DW representation we have related the time-resolved fluorescence signal to the reduced exciton density matrix. Superradiance is usually attributed to coherent emission of a set of electronic dipoles confined within a region of a size much smaller than the wavelength of the emitted light. This coherence can be partially or completely eroded by interactions with additional degrees of freedom such as nuclear motions and static disorder. The density matrix further allows us to visualize various mechanisms by staying in the exciton phase space (as opposed to the joint exciton-phonon space). This is impossible using a wave function description. The calculations presented here clearly show that the coherence size of the density matrix is the natural lengthscale which controls cooperativity in spontaneous emission. Calculations based on eigenstates are numerically expensive and often do not lead to a clear insight. Since properties of individual eigenstates are usually highly averaged and lost in observables. For example, the thermal density matrix at high temperatures is localized, although the individual exciton states are fully delocalized! The destruction of superradiance is determined by the density matrix. It is hard to envision this effect in a unified fashion for various models by examining individual eigenstates. Our calculations demonstrate that the exciton localization length  $l_\psi$  due to static disorder and the size of self-trapped exciton  $l_p$  in the case of strong exciton-phonon-coupling have similar signatures in the reduced exciton density matrix and superradiance.

## ACKNOWLEDGMENTS

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## APPENDIX A: THE SUPERRADIANT STATES

In this Appendix we prove the statements in Sec. III made with regard to the eigenstates of the window function  $M$ . To that end we define a linear map  $\mathbf{D}: V \rightarrow \mathcal{R}^3$  from the  $L_0$  dimensional space of real one-exciton functions to the space of real 3-dimensional vectors by

$$\mathbf{D}\phi = \sum_m \mathbf{d}_m \phi(m). \quad (\text{A1})$$

The matrix  $M$  viewed as a bilinear form of  $V$  can be written in a form:

$$M(\phi, \Psi) = \mathbf{D}(\phi) \cdot \mathbf{D}(\Psi). \quad (\text{A2})$$

Since  $\mathcal{R}^3$  is 3-dimensional and  $V$  is  $L_0$ -dimensional there is a  $(L_0 - 3)$  dimensional subspace  $V_1 \subset V$  with  $\mathbf{D}(V_1) = 0$ . Let  $V_0$  be the 3-dimensional orthogonal component to  $V_1$ , then  $M(\phi, \Psi) \neq 0$  only if both  $\phi, \Psi \in V_0$ , which means that  $M$

can be viewed as a bilinear form on  $V_0$  and all eigenstates of  $M$  viewed as a linear operator  $M: V \rightarrow V$  with nonzero eigenvalues belong to  $V_0$ .  $M$  can be diagonalized on  $V_0$  in an orthogonal basis set represented by  $\phi_\alpha$ ,  $\alpha = 1, 2, 3$ . We then denote for  $\alpha = 1, 2, 3$

$$\mathbf{d}_\alpha = \sum_m \mathbf{d}_m \phi_\alpha(m). \quad (\text{A3})$$

In the notation of Sec. II,  $\phi_\alpha$  are the superradiant states with transition dipoles  $\mathbf{d}_\alpha$ . The relations  $\mathbf{d}_\alpha \cdot \mathbf{d}_\beta = 0$  for  $\alpha \neq \beta$  and  $f_\alpha = |\mathbf{d}_\alpha|^2$  follows from the fact that  $M$  is diagonal in the basis set of superradiant states and using Eqs. (A1) and (A2).

## APPENDIX B: WINDOW FUNCTION FOR DIMERIZED CIRCULAR AGGREGATES

In this Appendix we present expressions for the window functions for a circular aggregate with two molecules in a unit cell. Let  $\Theta_j$ ,  $j = 0, 1$  be the angles which molecular dipoles in a unit cell form with the aggregate plane and  $\phi_j$  are the angles between their projections into the plane and the circle. A simple calculation yields:

$$\begin{aligned} M_{2m+j, 2n+k} &= d^2 \left\{ \sin \Theta_j \sin \Theta_k + \cos \Theta_j \cos \Theta_k \right. \\ &\quad \left. \times \cos \left[ \frac{2\pi}{L_0} (2m - 2n + j - k + \phi_j - \phi_k) \right] \right\}, \quad (\text{B1}) \end{aligned}$$

with  $m, n = 0, 1, \dots, (L_0 - 2)/2$  and  $j, k = 0, 1$ .

The superradiant states can be evaluated using the approach of Appendix A and have the following form:

$$\begin{aligned} \Phi_3(2m+j) &= \left[ \frac{L_0}{2} (\sin^2 \Theta_0 + \sin^2 \Theta_1) \right]^{-1/2} \sin \Theta_j, \\ \Phi_{1,2}(2m+j) &= \left[ \frac{L_0}{2} (\cos^2 \Theta_0 + \cos^2 \Theta_1) \right]^{-1/2} \\ &\quad \times \cos \Theta_j \exp \left\{ \pm i \left[ \frac{2\pi}{L_0} (2m+j) + \phi_j \right] \right\}, \quad (\text{B2}) \end{aligned}$$

with the corresponding oscillator-strengths

$$\begin{aligned} \bar{f}_3 &= d^2 \frac{L_0}{2} (\sin^2 \Theta_0 + \sin^2 \Theta_1), \\ \bar{f}_1 = \bar{f}_2 &= d^2 \frac{L_0}{4} (\cos^2 \Theta_0 + \cos^2 \Theta_1). \quad (\text{B3}) \end{aligned}$$

## APPENDIX C: DENSITY MATRIX OF EXCITONS COUPLED TO PHONONS

In this Appendix we discuss perturbative treatments of exciton-phonon coupling on the reduced exciton density matrix. For weak exciton-phonon-coupling the reduced exciton density matrix adopts the Boltzmann form in the exciton basis set [cf. Eqs. (29) and (30)] at long time. This is no longer the case as the exciton-phonon coupling is increased. This can be shown using perturbative arguments. We con-

sider the generalized master equation (GME) for the evolution of the reduced exciton density matrix  $\rho_{mn}$  which can be derived using the projection operator techniques.<sup>38,43</sup> The kernel of the GME can be explicitly calculated perturbatively in the exciton-phonon-coupling. The long-time value of  $\rho_{mn}$  is then the stationary point of the GME

$$-i[h, \rho]_{mn} - \sum_{kl} R_{mn,kl} \rho_{kl} = 0, \quad (C1)$$

where the matrix  $h_{ij} = \Omega_i \delta_{ij} + J_{ij}(1 - \delta_{ij})$  represents one-exciton Hamiltonian and  $R_{mn,kl}$  is the Redfield tensor,<sup>44,70</sup> given by the zero-frequency value of the GME kernel. When the Redfield tensor is calculated to lowest (second) order in exciton-phonon coupling, Eq. (C1) yields the Boltzmann distribution of bare excitons<sup>70</sup> given by Eqs. (29) and (30) for  $\rho_{mn}$ . Finding  $\rho_{mn}$  from Eq. (C1) with the Redfield tensor  $R_{mn,kl}$  calculated in the next (fourth) order in coupling strength will show a deviation of  $\rho_{mn}$  from the Boltzmann distribution.

Another perturbative argument can be made as follows: assuming that at long times the full density matrix  $\rho_M$  of the joint exciton-phonon system adopts the canonical form, the reduced exciton density matrix  $\rho_{mn}$  can be represented as

$$\rho_{mn} = \text{Tr}(B_m^\dagger B_n \rho_M). \quad (C2)$$

The r.h.s. of Eq. (C2) can be evaluated perturbatively in the exciton-phonon coupling strength, e.g., by applying the Matsubara Green's function techniques.<sup>65</sup> The zero-order result yields Eq. (30) whereas the second-order contribution results in deviations of  $\rho_{mn}$  from the bare Boltzmann distribution. Deviation from the Boltzmann distribution of bare exciton at long times for weak exciton-phonon-coupling has been demonstrated in Ref. 23. However, the non-Boltzmann asymptotic behavior of the exciton distribution originates from neglecting environmental (e.g., solvent) nuclear modes in the model: The system does not have enough phonons to equilibrate. Adding solvent modes with a continuous spectrum to that model will lead to a Boltzmann distribution of bare excitons at long times within the formalism of Ref. 23, which is based on perturbative in exciton-phonon coupling calculation of the GME<sup>43,73</sup> with memory. This implies that the results of Ref. 23 describe a situation with weak coupling to solvent modes for intermediate timescales when coupling to solvent modes is unimportant and exciton dephasing is induced by the aggregate intermolecular and intramolecular modes.

#### APPENDIX D: TOYOZAWA'S ANSATZ FOR THE POLARON WAVE FUNCTION

In this Appendix we present the details of the Toyozawa Ansatz for polaron wave functions. We start with generalizing the Holstein Hamiltonian, also known as the molecular crystal model, by adding the linear off-diagonal exciton-phonon coupling:

$$\hat{H} = \hat{H}^{ex} + \hat{H}^{ph} + \hat{H}^{ex-ph}, \quad (D1)$$

$$\hat{H}^{ex} = -J \sum_n B_n^\dagger (B_{n+1} + B_{n-1}), \quad (D2)$$

$$\hat{H}^{ph} = \hbar \omega_0 \sum_n b_n^\dagger b_n, \quad (D3)$$

$$\begin{aligned} \hat{H}^{ex-ph} = & g \hbar \omega_0 \sum_n B_n^\dagger B_n (b_n^\dagger + b_n) \\ & + \frac{\phi}{2} \hbar \omega_0 \sum_{nl} [B_n^\dagger B_{n+1} (b_l^\dagger + b_l) (\delta_{n+1,l} - \delta_{nl}) \\ & + B_n^\dagger B_{n-1} (b_l^\dagger + b_l) (\delta_{nl} - \delta_{n-1,l})]. \end{aligned} \quad (D4)$$

Here  $|0\rangle$  is the vacuum state for both the exciton and the phonon degrees of freedom, and  $B_n^\dagger$  ( $b_n^\dagger$ ) creates an exciton (phonon) on site  $n$ .  $\omega_0$  is the Einstein phonon frequency,  $J$  is the exciton transfer integral between nearest-neighbor sites, and  $g$  ( $\phi$ ) is the diagonal (off-diagonal) exciton-phonon coupling strength. The original Holstein model contains only diagonal exciton-phonon-coupling. The Hamiltonian Eq. (D1) can be obtained from Eq. (1) by expanding molecular frequencies  $\Omega_n(\mathbf{q})$  and intermolecular couplings  $J_{mn}(\mathbf{q})$  up to first order in nuclear coordinates  $\mathbf{q}$ . We also assume the nearest neighbor form of intermolecular couplings  $J_{mn}(\mathbf{q})$  and Einstein phonons.

Following Toyozawa,<sup>50</sup> we construct the one-exciton wave function

$$\begin{aligned} |K\rangle = & \sum_n e^{iKn} \sum_{n_1} \psi_{n_1-n}^K B_{n_1}^\dagger \exp \left[ - \sum_{n_2} (\lambda_{n_2-n}^K b_{n_2}^\dagger \right. \\ & \left. - \lambda_{n_2-n}^{K*} b_{n_2}) \right] |0\rangle. \end{aligned} \quad (D5)$$

The variationally optimized parameters  $\lambda_n^K$  describe the phonon distortion of site  $n$ , and  $\psi_n^K$  are the corresponding exciton amplitudes. Equation (D5) is equivalent to Eq. (41) where the phonon wave functions  $|\Lambda_n^K\rangle$  are explicitly written in terms of phonon coherent states

$$|\Lambda_n^K\rangle = \exp \left[ - \sum_{n_2} (\lambda_{n_2-n}^K b_{n_2}^\dagger - \lambda_{n_2-n}^{K*} b_{n_2}) \right] |0\rangle_{ph}. \quad (D6)$$

Equation (D5) can be alternatively represented in momentum-space as

$$\begin{aligned} |K\rangle = & L_0^{-1/2} \sum_{nk} e^{i(K-k)n} \psi_k^K B_k^\dagger \\ & \times \exp \left[ - L_0^{-1/2} \sum_q (\lambda_q^K e^{-iqn} b_q^\dagger - \lambda_q^{K*} e^{iqn} b_q) \right] |0\rangle, \end{aligned} \quad (D7)$$

where  $B_k^\dagger$ ,  $b_q^\dagger$ ,  $\psi_k^K$  and  $\lambda_q^K$  are Fourier transforms of  $B_n^\dagger$ ,  $b_n^\dagger$ ,  $\psi_n^K$  and  $\lambda_n^K$ :

$$B_k^\dagger = L_0^{-1/2} \sum_n e^{-ikn} B_n^\dagger, \quad (D8)$$



$$b_q^\dagger = L_0^{-1/2} \sum_n e^{-iqn} b_n^\dagger, \quad (\text{D9})$$

$$\psi_k^K = \sum_n e^{ikn} \psi_n^K, \quad (\text{D10})$$

$$\lambda_q^K = \sum_n e^{iqn} \lambda_n^K. \quad (\text{D11})$$

The exciton amplitudes  $\psi_n^K$  serve as weights in a linear superposition of phonon coherent states if Toyozawa's Ansatz (D5) is viewed in a different form:<sup>74</sup>

$$|K\rangle = L_0^{-1/2} \sum_n e^{iKn} B_n^\dagger \sum_{n_1} e^{-iKn_1} \psi_{n_1}^K \times \exp \left[ - \sum_{n_2} (\lambda_{n_2+n_1-n}^K b_{n_2}^\dagger - \lambda_{n_2+n_1-n}^{K*} b_{n_2}) \right] |0\rangle. \quad (\text{D12})$$

Equation (D12) can be obtained from Eq. (D5) by relabeling  $n$  as  $n-n_1$ , and  $n_1$  as  $n$ . Defining the phonon part of the wave function as  $|\Phi_n^K\rangle$  [the summation over  $n_1$  in Eq. (D12)],

$$|\Phi_n^K\rangle = \sum_{n_1} e^{-iKn_1} \psi_{n_1}^K |\Lambda_{n-n_1}^K\rangle, \quad (\text{D13})$$

$|K\rangle$  is written in the compact form

$$|K\rangle = L_0^{-1/2} \sum_n e^{iKn} |\Phi_n^K\rangle B_n^\dagger |0\rangle_{ex}. \quad (\text{D14})$$

We approximate the density matrix by Eq. (42), which is well-justified in the low temperature regime (especially for intermediate and strong exciton-phonon-couplings a finite gap is formed between the one-exciton ground state and the high-lying phonon continuum). Carrying out the trace over the phonon bath, one arrives at

$$\rho_{mn} = \sum_K \langle K|K\rangle^{-1} e^{-\beta E_K} e^{iK(m-n)} \langle \Phi_n^K | \Phi_m^K \rangle, \quad (\text{D15})$$

where

$$\langle \Phi_n^K | \Phi_m^K \rangle = \sum_{n_1, n_2} e^{iK(n_1-n_2)} \psi_{n_1}^{K*} \psi_{n_2}^K \times \exp \left[ L_0^{-1} \sum_q |\lambda_q^K|^2 (e^{iq(n_2-n_1)+iq(n-m)} - 1) \right]. \quad (\text{D16})$$

Noting that

$$\langle \Phi_n^K | \Phi_n^K \rangle = L_0^{-1} \langle K|K\rangle, \quad (\text{D17})$$

we have

$$\rho_{nn} = L_0^{-1}. \quad (\text{D18})$$

Also  $\rho_{mn}$  is found to be real so that

$$\rho_{mn} = \rho_{nm}. \quad (\text{D19})$$

Taking into account the translational symmetry, we may label  $\rho_{mn}$  with one index, i.e.,  $\rho_{m-n} = \rho_{mn}$ .

We now discuss the connection between adiabatic polaron theory and variational Ansätze. Equation (49) can also be deduced using a time-dependent variational principle as soliton theory is usually implemented. Localized polaron Ansätze, such as the Davydov Ansatz,

$$\sum_n \psi_n(t) B_n^\dagger |0\rangle_{ex} \otimes \exp \left[ - \sum_n (\lambda_n(t) b_n^\dagger - \lambda_n^*(t) b_n) \right] |0\rangle_{ph} \quad (\text{D20})$$

are often employed, and equations of motion are derived for the time-dependent parameters characterizing the exciton wave function and the phonon fields. Neglecting the time-derivative of the phonon fields  $\lambda_n$  as the adiabatic condition requires, Eq. (E8) is recovered, and the exciton wave function is found to follow Eq. (49). For large polarons where the continuum approximation is justified, the static solution for the exciton wave function again assumes the soliton profile (50). The physical picture is that the exciton creates a static lattice deformation  $\lambda_n$  and then become self-trapped in the potential well that is established by the deformation.

The delocalized Toyozawa Ansatz employed in this work can be obtained by applying a delocalization projection operator

$$\hat{P} = L_0^{-1} \sum_n \exp \left[ in \left( K - \sum_k k B_k^\dagger B_k - \sum_q q b_q^\dagger b_q \right) \right] \quad (\text{D21})$$

to the Davydov Ansatz (D20). Within the Toyozawa Ansatz, a ‘‘locking’’ relation similar to (E8) is found for  $\lambda_n^K$  and  $\psi_n^K$  in the adiabatic regimes of the phase diagram for both small and large polarons,<sup>46</sup> although for weak exciton-phonon-coupling nonadiabaticity emerges as the one-phonon plane-wave from the background of the large adiabatic polaron as the coupling is decreased. It is worth noting that extended states yield lower energies than the localized parent states.<sup>75</sup> Ansatz (D5) with optimized  $\lambda_n^K$  and  $\psi_n^K$ , and its generalization with the replacement of  $\lambda_{n_2-n}^K$  in (D5) by a two-parameter sum  $\alpha_{n_2-n}^K + \beta_{n_2-n_1}^K$ , constitute the most sophisticated variational wave functions applied to the Holstein Hamiltonian. We note that the delocalization procedure which transforms (D20) into (D5) preserves the locality of exciton-phonon correlations.

## APPENDIX E: ADIABATIC POLARONS

In this Appendix we evaluate the reduced exciton density matrix  $\rho_{mn}$  using the adiabatic polaron model. To that end we represent the phonon Hamiltonian which enters Eq. (1) in a form:

$$H_{ph} = T_{ph} + V(\mathbf{q}), \quad (\text{E1})$$

where  $T_{ph}$  is the nuclear kinetic energy and  $V(\mathbf{q})$  is the potential energy. We adopt the Born-Oppenheimer approach to the polaron problem<sup>60,76,77</sup> by representing the eigenfunctions of the joint system in a form

$$\Phi = \sum_n \Psi_\alpha(n; \mathbf{q}) B_n^\dagger |0\rangle \Lambda_\alpha(\mathbf{q}), \quad (\text{E2})$$

where  $\Psi_\alpha(n; \mathbf{q})$  is the  $\alpha$ th exciton wave function with energy  $E_\alpha(\mathbf{q})$ .  $\Lambda_\alpha(\mathbf{q})$  is an eigenfunction of the phonon effective adiabatic Hamiltonian  $H_\alpha^{eff}$  defined as

$$H_\alpha^{eff} \equiv T_{ph} + V_\alpha^{eff}(\mathbf{q}), \quad (\text{E3})$$

with

$$V_\alpha^{eff}(\mathbf{q}) \equiv V(\mathbf{q}) + E_\alpha(\mathbf{q}). \quad (\text{E4})$$

The adiabatic ansatz for the wave functions represented by Eqs. (E2)–(E4) allows to represent the reduced exciton density matrix in a form

$$\rho_{mn} = \sum_\alpha \int d\mathbf{q} \Psi_\alpha^*(m; \mathbf{q}) \Psi_\alpha(n; \mathbf{q}) \langle \mathbf{q} | \exp(-H_\alpha^{eff}/T) | \mathbf{q} \rangle. \quad (\text{E5})$$

If the energy splitting between trapped excitons is larger than the temperature, only the  $\alpha=0$  term related to the lowest exciton needs to be retained in Eq. (E5) which yields

$$\rho_{mn} = \int d\mathbf{q} \Psi^*(m; \mathbf{q}) \Psi(n; \mathbf{q}) \langle \mathbf{q} | \exp(-H^{eff}/T) | \mathbf{q} \rangle, \quad (\text{E6})$$

where the  $\alpha=0$  subscript has been omitted.

If temperature is higher than the phonon frequency the phonon density matrix  $\exp(-H^{eff}/T)$  can be represented in form

$$\rho_{mn} = Z^{-1} \sum_\alpha \int d\mathbf{q} \Psi_\alpha^*(m; \mathbf{q}) \Psi_\alpha(n; \mathbf{q}) \times \exp(-V_\alpha^{eff}(\mathbf{q})/T), \quad (\text{E7})$$

with the partition function  $Z \equiv \int d\mathbf{q} \exp(-V^{eff}(\mathbf{q})/T)$ . Equation (E7) is valid for any number of low-frequency modes coupled to molecules;  $q_n$  should then be treated as the collective bath coordinate coupled to the  $n$ th molecule<sup>78,79</sup> rather than a single-mode (microscopic) coordinate.

The integral on the r.h.s. of Eq. (E7) can be computed using Monte Carlo techniques. Here to get a qualitative picture we consider a simple case when the temperature is higher than the frequencies of low-energy nuclear modes, but is still lower than the energy scale of the variation of  $V^{eff}$  itself. In this case the most important contributions to the integral in Eq. (E7) come from the vicinity of the minimum of  $V^{eff}(\mathbf{q})$ . The existence of a nontrivial minimum of  $V^{eff}$  in low-dimensional systems has been outlined by Rashba.<sup>33</sup> At the minimum of  $V^{eff}$  we have

$$q_n = g |\Psi(n)|^2 \quad (\text{E8})$$

and the exciton wave function satisfies the discrete nonlinear Schrödinger equation<sup>33,34,54</sup> given by Eq. (49). When each molecule is coupled to a distribution of solvent modes, the parameter  $\lambda$  can be expressed in terms of the bath spectral density  $C(\omega)$ :<sup>78</sup>

$$\lambda = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \frac{C(\omega)}{\omega}. \quad (\text{E9})$$

Solutions of Eq. (49) are commonly referred to as solitons. The nonlinearity induced by the exciton-phonon coupling is the mechanism supporting the soliton excitations. For the continuum model with the solution given by Eq. (50) the energy splitting between the lowest trapped exciton and the next one is given by  $\lambda^2/|J|$ .<sup>34</sup> This implies that Eq. (E5) which is valid in the adiabatic limit is derived under the condition  $\omega_0 \ll \lambda^2/|J|$ . This equation leads to Eq. (E6) in the  $T \ll \lambda^2/|J|$  limit. Equation (E7) which follows from Eq. (E6) when  $T \gg \omega_0$  is hence valid when  $\omega_0 \ll T \ll \lambda^2/|J|$ .

Neglecting fluctuations of collective bath coordinates in the vicinity of the minimum of  $V^{eff}(\mathbf{q})$  we obtain a simple expression for  $\rho_{mn}$  given by Eq. 48. Equation. (48) can also be obtained using the Toyozawa ansatz and setting the Debye-Waller factor  $\langle \Lambda_n^K | \Lambda_n^K \rangle = \delta_{nn'}$ , which means that in the adiabatic polaron theory  $l_{DW} = 0$  (this reflects the fact that the traps related to left and right components of the density matrix have the same positions) and  $l_p$  is the only lengthscale which determines  $L_p$ .

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