

## Theoretical models of energy transfer in two-dimensional molecular assemblies

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An interesting class of Langmuir-Blodgett monolayers, which are called *J* aggregates or Scheibe aggregates, exhibit energy transfer that is activated through photon absorption and exhibits remarkable properties of fast and nearly lossless transmission. This paper presents theoretical models intended to address the question of energy transfer in two-dimensional molecular assemblies such as Scheibe aggregates. Second-quantized microscopic Hamiltonians are proposed and quantum-mechanical calculations are subsequently performed in several regimes. Numerical simulations illustrate the existence of long lifetime bound states on impurity ions with shallow energy levels. Due to their efficient energy capture these ions play the role of acceptors. A formulation of the problem in a strongly nonlinear regime leads to two other types of less probable but also possible behavior: soliton formation (the Davydov limit) and frequency selection (the Fröhlich limit).

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### I. INTRODUCTION

The phenomenon of a nearly lossless transfer of energy over distances of up to 100 nm was experimentally discovered by Kuhn [1,2] and Möbius [3] in a type of Langmuir-Blodgett monolayers [4] usually called *J* aggregates or Scheibe aggregates. Historically, Scheibe aggregates were first found in solutions of dye molecules and their characteristic feature was a narrow absorption band shifted to longer wavelengths relative to the monomer band with an associated fluorescence band. This has also been seen in various types of monolayers and the presence of the characteristic spectrum distinguishes them from other molecular assemblies. The techniques used in determining the structure of LB films of this type include (i) low-angle x-ray diffraction, (ii) electron diffraction, (iii) neutron diffraction, (iv) infrared spectroscopy; and (v) optical microscopy using polarized light [4].

The interstices between the carbon tails are filled with molecules (e.g., octadecane) which make the layer rigid and compact (see Fig. 1). Using LB techniques, Kuhn [1] has prepared *J* aggregates in which as little as 1 in 10 000 molecules of chromophore was an acceptor, the rest being donors. It appears that the monolayer acts as a cooperative molecular array which, after absorbing a photon, channels the energy laterally over exceptionally long distances to a particular energy-accepting molecule. The effect has not been observed in aggregates, where the molecular "filler" is absent and whose structure is less rigid and less ordered.

The energy migration in the layer of the host is facilitated by molecular interactions. To achieve fast exciton transfer the chromophores of the host must be in a compact arrangement which leads to the exciton hopping time on the order of  $10^{-13}$  s. For exciton traps exactly interlocked in the molecular structure and with appropri-

ate coupling present, it is expected that the host energy may be trapped by the guest molecule in concentrations as low as 1 per  $10^4$ . Thus, excited aggregates of the Scheibe type can be viewed as a large array of coupled quantum oscillators. A different (guest) molecule characterized by a resonance frequency slightly lower than the host molecule's would therefore act as an energy trap once it is incorporated into the lattice. In addition to energy trapping by the guest molecules in the *J* aggregate there exists the possibility of electron transfer from the excited host molecule to a guest molecule.

In the design of molecular photosensitive devices [5] and in the understanding of biological systems such as chlorophyll [6], the problem of efficient energy transfer is of primary importance. An investigation into molecular assemblies such as Scheibe aggregates, therefore, can resolve that difficulty by indicating the proper choice of molecular arrangements, which is essential for the development of photoresistors, photodiodes, photomemory, and photosensitive devices [7] based on the LB technique.

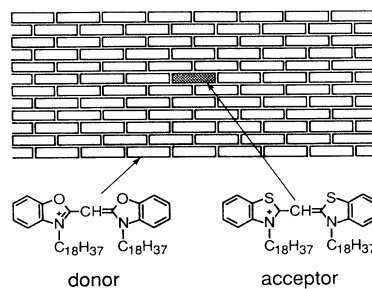


FIG. 1. A schematic illustration of the bricklayered structure of Scheibe aggregates with an oxycyanine and a thiacyanine groups labeled *A* and *B*, respectively.

Also, synthetic organizes are promising materials for solar energy conversion.

In this paper we investigate the question of efficient energy transfer in two-dimensional molecular assemblies on several levels of theoretical modeling. Section II is a review of recent theoretical approaches to the problem. First, the energy spectrum of a dimer is analyzed in order to provide realistic values of model parameters. Then, a one-dimensional chain is being simulated numerically in order to demonstrate the sensitivity of transport properties to energy parameters in an aggregate. This is followed by a brief review of the quantum-mechanical calculations carried out for a hexagonal lattice model with the inclusion of donor and acceptor molecules. This section is closed with a discussion of a spherically symmetric model involving self-focusing and soliton formation. In Sec. III a full-fledged quantum-mechanical theory of energy transfer processes is developed which accounts for electromagnetic energy capture and transmission along an aggregate. This is based on a perturbative approach to the problem. In order to include the possibility of a strongly nonlinear interaction under some circumstances Sec. IV deals with a solitonic regime. This paper is closed with a discussion and conclusions section where arguments are given for a special role of planar geometry in the remarkable efficiency of energy transfer.

## II. REVIEW OF THEORETICAL APPROACHES

### A. General considerations

There exists a vast body of literature concerned with the question of exciton transport and trapping in molecular crystals and biological molecular aggregates. Since these systems bear a relationship with  $J$  aggregates, we first give a brief overview of the most important results known to date which will serve as guidelines for the development of our models.

The main dividing line in the study of excitons is whether they are localized (incoherent) or delocalized (coherent). It is believed [8] that exciton migration in the absence of phonons occurs coherently at first with  $\langle x^2 \rangle \propto t^2$ , where  $x$  denotes position and  $t$  time, later in time becoming incoherent and satisfying the relationship  $\langle x^2 \rangle \sim t$  typical for diffusion. The two regimes leave their imprint on the absorption lines. Lorentzian character of the absorption lines is due to coherent behavior while Gaussian forms arise due to incoherent motion. The former is highly temperature dependent and occurs with weak exciton-phonon coupling, the latter takes place when exciton-phonon coupling is strong. In general, therefore, one should expect an intermediate regime where both localized and delocalized excitons participate in energy transfer [8–10]. The problem is rather complex and the presence of traps makes it even more complicated. Our approach should explore the many possible modes of behavior that exist and discuss the physical manifestations of each of them.

In fact, a recent paper [11] lists the following six pathways to energy relaxation in LB monolayers with dye molecules present: (i) monomer fluorescence, (ii) aggregate

fluorescence, (iii) energy trapping, (iv) energy migration between donors, (v) excimer formation, and (vi) energy migration to lower-energy sites and trapping there. The various processes are manifested by inhomogeneous broadening of phosphorescence spectra.

The first phenomenological attempt at modeling energy transfer in Scheibe aggregates was made by Möbius and Kuhn [12,13] using the so-called coherent exciton model involving a finite-size domain of exciton coherence. This attempt explained, in simple terms, the observed temperature dependence of the fluorescence quenching ratio (linear with  $T$ ). Below, we review other theoretical models proposed to describe energy capture and transfer processes in molecular assemblies such as Scheibe aggregates.

### B. The modeling of a dimer

The molecules that we are concerned with are chromophores, i.e., they have a delocalized electron which can be excited by light to a higher-energy level above the ground state with  $\Omega$  denoting the energy difference. Note that throughout this paper we have used units with  $\hbar=1$ . We model this system by an oscillator with an appropriate energy spacing. In addition, the close packing of chromophores induces a strong electron-electron interaction (of dipole-dipole type) with resonant energy  $J$ . We have then the following Hamiltonian typical for the molecular exciton model in a dimer [8]

$$H_2 = \Omega (A_1^\dagger A_1 + A_2^\dagger A_2) - J (A_1^\dagger A_2 + A_2^\dagger A_1), \quad (2.1)$$

where the operators  $A_\alpha^\dagger$  and  $A_\alpha$  ( $\alpha=1,2$ ) refer to a creation and destruction of a quantum of excitonic energy at site  $\alpha$ , respectively. The general eigenfunction for the Hamiltonian  $H_2$  of Eq. (2.1) can be written as

$$|\psi_2\rangle = (\alpha A_1^\dagger + \beta A_2^\dagger) |\Omega\rangle. \quad (2.2)$$

Consequently, the eigenmatrix takes the form

$$H_2 = \begin{bmatrix} \Omega & -J \\ -J & \Omega \end{bmatrix}, \quad (2.3)$$

which yields the following eigenvalue equation:

$$(\Omega - E)^2 - J^2 = 0. \quad (2.4)$$

Hence the eigenvalues  $E$  are found as

$$E = \Omega \pm J. \quad (2.5)$$

Using the data for oxycyanin yields  $\Omega=3.125$  eV for a monomer,  $E=3.44$  eV for a dimer, and, consequently, the coupling constant  $J$  is calculated as  $J=0.315$  eV. These data will be used in the following sections for modeling of monolayer assemblies composed of both donor and acceptor molecules. To properly simulate exciton kinetics we require lattice models. Hence, the next subsection provides an overview of recent numerical simulations for a one-dimensional chain.

### C. Numerical simulations in 1D

Since the bricklayer structure illustrated in Fig. 1 appears highly anisotropic with substantial elongation along

the  $x$  axis, it seems appropriate to study a one-dimensional (1D) approximation to the problem as a first step towards understanding cooperative behavior. First of all, neglecting the presence of acceptor molecules gives the Hamiltonian

$$H_0^{1D} = \sum_{n=-\infty}^{+\infty} \Omega A_n^\dagger A_n - J A_n^\dagger (A_{n-1} + A_{n+1}). \quad (2.6)$$

Taking the eigenfunction in the form of a linear superposition of excitations,

$$|\psi\rangle = \sum_{n=-\infty}^{+\infty} a_n A_n^\dagger |\Omega\rangle, \quad (2.7)$$

results in the following stationary Schrödinger equation:

$$E a_n = \Omega a_n - J(a_{n-1} + a_{n+1}). \quad (2.8)$$

Introducing an acceptor molecule at site  $n=0$  requires the use of a full Hamiltonian in the form

$$H^{1D} = H_0^{1D} + H_{acc}^{1D}, \quad (2.9)$$

where the acceptor contribution is

$$H_{acc}^{1D} = -V A_0^\dagger A_0 + (J_0 - J) \{ A_0^\dagger (A_1 + A_{-1}) + A_0 (A_1^\dagger + A_{-1}^\dagger) \}. \quad (2.10)$$

Using the wave function of Eq. (2.7) and writing the time-independent problem for the Hamiltonian  $H^{1D}$  of Eq. (2.9) as

$$H^{1D} |\psi\rangle = z |\psi\rangle \quad (2.11)$$

produces a system of recurrence relations for  $a_n$ :

$$(z - \Omega) a_n = -J(a_{n+1} + a_{n-1}) \quad (n \neq -1, 0, 1), \quad (2.12)$$

$$(z - \Omega + V) a_0 = -J_0(a_1 + a_{-1}), \quad (2.13)$$

$$(z - \Omega) a_1 = -J_0 a_0 - J a_2, \quad (2.14)$$

$$(z - \Omega) a_{-1} = -J_0 a_0 - J a_{-2}. \quad (2.15)$$

Only symmetric solutions exist for which  $a_n = a_{-n}$  and, for  $n > 1$ , they yield

$$a_n = \mu^n. \quad (2.16)$$

Equation (2.13) then gives

$$(z - \Omega) \mu^n = -J(\mu^{n+1} + \mu^{n-1}), \quad (2.17)$$

which yields a very important relation between the binding energy  $z$  and the decay rate of the wave function,

$$(z - \Omega) = -J(\mu + 1/\mu). \quad (2.18)$$

In order to have the wave function centered around the acceptor and extending over many sites it is required that  $\mu$  be close to 1. Next, considering Eq. (2.17) for  $n=2$ , i.e.,

$$(z - \Omega) \mu^2 = -J(\mu^3 + a_1), \quad (2.19)$$

it is found that  $a_1 = \mu$ , while from Eq. (2.14) it follows

that  $a_0 = J/J_0$ . It can be easily seen that in order to have  $a_0$  large,  $J_0$  has to be small. Finally, Eq. (2.15) gives an eigenvalue condition which is expressed in terms of  $\mu$  as

$$\mu^2(J^2 - 2J_0^2) - J_0 V \mu + J^2 = 0. \quad (2.20)$$

Dimensionless quantities  $w$  and  $\gamma$  are now introduced as

$$V = wJ, \quad J_0 = \gamma J, \quad (2.21)$$

so that Eq. (2.20) becomes

$$\mu^2(1 - 2\gamma^2) - w\mu + 1 = 0, \quad (2.22)$$

with its solutions

$$\mu_{1,2} = \frac{1}{2(1 - 2\gamma^2)} \{ w \pm (w^2 - 4 + 8\gamma^2)^{1/2} \}. \quad (2.23)$$

It is easily seen that with  $\gamma$  small we need  $w \simeq 2$ . Then, taking  $w=2$  an optimal case is found for  $\gamma \ll 1$  as  $\mu \simeq 1 - \sqrt{2}\gamma$ .

Numerical simulations of the time-dependent Schrödinger equation for the chain Hamiltonian of Eq. (2.9) were recently performed which involved solving coupled differential equations [14,15]. The numerical simulation was performed [14] for the chain of 1000 molecules. In these simulations the acceptor was placed in the middle of the string of molecules. The initial condition assumed the same probability of excitation for each particle. This situation corresponds to the irradiation of the molecular assembly by a short laser pulse. It can then be seen that the acceptor causes the probability distribution  $a_n(t)$  to evolve in time, especially at locations in its immediate vicinity. In general, the probability amplitude at a given site tends to oscillate with the exception of the acceptor site itself where the excitation probability increases. In general, no case led to the observation of a large probability of excitation at the acceptor site. However, for the optimal choice of parameters the situation changes dramatically (Fig. 2). The probability at the acceptor site attains very large values at the cost of the neighboring sites, whose excitation probabilities decrease. In other words, the acceptor absorbs the probability am-

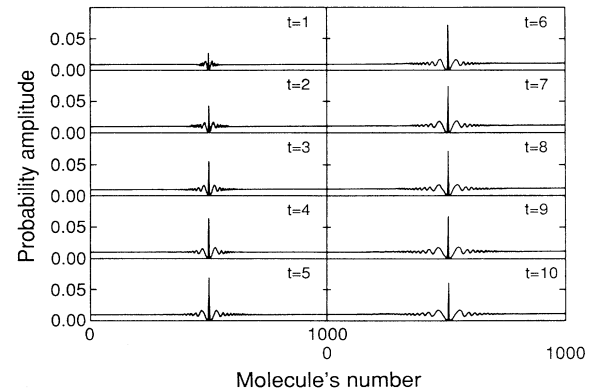


FIG. 2. The evolution of probability distribution [14] for the optimal choice of parameters:  $w=2$ ,  $\gamma=0.1$ . The time intervals are from  $t=1$  to 10. 1000 molecules have been used and the acceptor is located at molecule 500.

plitude from the neighboring sites. Furthermore, the probability of excitation at the acceptor site increased to large values before the disturbance has propagated over a long distance, i.e., the process is very fast. Although this type of behavior is very desirable it is not entirely clear whether the required fine tuning of the model parameters used is in agreement with experimental results. We tend to believe that this is an artifact of the one-dimensional character of the model used.

#### D. The hexagonal lattice calculation

The quantum-mechanical model of the energy transfer in  $J$  aggregates formulated by Bartnik and Blinowska [15] was developed using a time-dependent approach having much in common with the Davydov model [16] of energy transport in peptide chains. It was shown that, in a two-dimensional tight arrangement of molecules, a shallow bound state may exist. The spatial extent of such a shallow state is large and, therefore, an exciton capture is possible over considerable distances. The condition for the existence of such a shallow state was found by transforming the Hamiltonian into momentum space and solving the obtained Schrödinger equation numerically. It was found that the resonance interaction between acceptor and donor molecules should be slightly smaller than

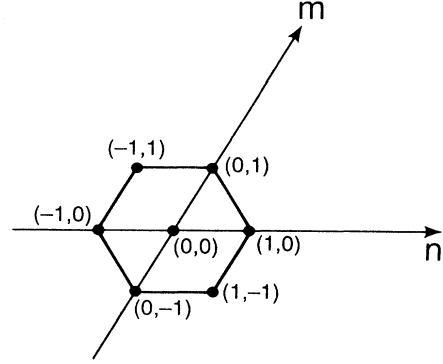


FIG. 3. A schematic representation of the hexagonal lattice structure used in Sec. II C.

the resonance interaction between donor molecules; exactly what would be expected from their chemical nature.

Before we actually study the role of acceptor sites (characterized by quantities with a subscript “0”) we wish to point out the properties of the donor part of the system. Placed on a hexagonal lattice (see Fig. 3) the appropriate Hamiltonian is

$$H_0^{2D} = \sum_{n,m} [\Omega A_{nm}^\dagger A_{nm} - J A_{nm}^\dagger (A_{n-1,m} + A_{n+1,m} + A_{n,m-1} + A_{n,m+1} + A_{n+1,m-1} + A_{n-1,m+1}) + \text{H.c.}] , \quad (2.24)$$

where subscripts  $n$  and  $m$  label the position of lattice sites on a hexagonal lattice (see Fig. 3). It should also be noted that due to lattice rigidity,  $\Omega = \epsilon - D$  where  $\epsilon$  is the exciton energy of an isolated donor molecule and  $D$  is the deformation energy of a donor molecule in the lattice.

The wave function for the donor system is in the form

$$|\psi\rangle = \sum_{n,m} a_{nm}(t) A_{nm}^\dagger |\Omega\rangle , \quad (2.25)$$

which yields the following time-dependent Schrödinger equation:

$$i \frac{\partial}{\partial t} |\psi\rangle = H_0^{2D} |\psi\rangle , \quad (2.26)$$

or explicitly

$$i \frac{\partial}{\partial t} a_{nm}(t) = \Omega a_{nm} - J (a_{n-1,m} + a_{n+1,m} + a_{n,m-1} + a_{n,m+1} + a_{n+1,m-1} + a_{n-1,m+1}) . \quad (2.27)$$

In order to account for the presence of an acceptor molecule consider the Hamiltonian

$$H^{2D} = H_0^{2D} + H_{\text{acc}}^{2D} , \quad (2.28)$$

where  $H_0^{2D}$  is that of Eq. (2.24) and  $H_{\text{acc}}$  defines the acceptor energy through

$$H_{\text{acc}}^{2D} = -V A_0^\dagger A_0 - (J_0 - J) \{ [A_{00}^\dagger (A_{-1,0} + A_{1,0} + A_{0,1} + A_{0,-1} + A_{-1,1} + A_{1,-1})] + \text{H.c.} \} . \quad (2.29)$$

The value of  $J_0$  is not readily available from experimental data but has been estimated theoretically for optimal energy capture over distances exceeding 50 nm as [15]  $0.81 < (J_0/J) < 0.9$ . Within this model, the probability of energy capture by an acceptor molecule is equal to the overlap of the wave functions

$$\langle \psi_0 | \psi_B \rangle = \psi_B(r_0) . \quad (2.30)$$

The asymptotic behavior of  $\Psi_B$  is

$$\Psi_B(r) \sim K_0(\alpha r) ,$$

where  $K_0$  is a Bessel function and  $\alpha = (2m_{\text{ex}} |\tilde{E}|)^{1/2}$ . The optimum value of  $\alpha$  for the energy capture probability is found to be inversely proportional to the average distance between the site of excitation and the acceptor molecule,

i.e.,  $\alpha \approx (2r_0)^{-1}$ . For the conditions used in experiments, where the acceptor concentration is 1:10 000, we have  $r_0 \approx 50$  nm. This results in the requirement on the exciton binding energy to be very small, i.e.,  $E \lesssim 5.5 \times 10^{-5}$  eV.

### E. Spherical (ring) soliton calculations

A completely different approach to the problem of energy transfer and trapping in Scheibe aggregates has been recently advocated in two papers [17,18]. The main idea put forward is to assume a strongly nonlinear regime of behavior on the basis of exciton-phonon coupling. The mathematical model developed as a consequence of this approximation starts from a Schrödinger equation for the molecular exciton's wave function [or more specifically, its amplitude  $a(r, t)$ ] as

$$\left[ i \frac{\partial}{\partial t} - \Lambda + J \nabla^2 + V(r) \right] a(r, t) = 0, \quad (2.31)$$

where  $\Lambda$  is the energy value at the bottom of the exciton band,  $J$  is the resonant interaction energy between two neighboring molecules, and  $V(r)$  is the local trapping potential due to a displacement of the molecules from their equilibrium positions. It is then argued that a Toda approximation is applicable to this anharmonic lattice dynamics. The related deformation  $\rho = |a|^2$  is given by

$$\rho_n(t) = \alpha^{-1} \sinh^2(ql) \operatorname{sech}^2[q(nl - vt)], \quad (2.32)$$

and the trapping potential then is found as  $V(r, t) = \sigma^2 \rho(r, t)$ . A self-consistent solution for  $a(r, t)$  is then found as

$$a(r, t) = \alpha^{-1/2} \sinh(ql) \operatorname{sech}[q(r - r_0 - vt)] \\ \times \exp[ik(r - r_0) - i\omega t], \quad (2.33)$$

which yields a nonlinear Schrödinger equation as the effective evolution equation for  $a(r, t)$ , i.e.,

$$\left[ i \frac{\partial}{\partial t} - \Lambda + J \nabla^2 \right] a = -\sigma^2 |a|^2 a. \quad (2.34)$$

Obviously, continuum limit is taken and a two-dimensional analysis is carried out which results in the formation of ring waves that exhibit expansion and collapse. The size of the obtained ring wave was estimated as 600 Å and the propagation velocity as 10–20 sound velocities, i.e., approximately  $10^4$  m/s. While numerical estimates demonstrate lifetimes of the ring waves compatible with experimental values (i.e., on the order of  $10^{-10}$  s), it is not entirely certain that the self-trapping limit is in fact appropriate in this problem. Indeed, based on experimental results of Inoue [5] it appears that the exciton-phonon coupling constant is less than the threshold value needed for self-trapping and hence this puts in question the validity of a nonlinear approach. However, since the experimental value is less than this threshold by only about 20% we cannot discount this possibility off hand. Therefore, in the following two sections we develop both a perturbative and a strongly nonlinear theoretical model of the aggregates.

III. QUANTUM FIELD THEORY APPROACH

### A. The total Hamiltonian

In this section we propose a more detailed approach to the problem of energy capture and transmission in Scheibe aggregates. We shall include the presence of donor molecules, an acceptor, and account for the presence of elastic modes of vibration of the lattice (phonons). Quanta of electromagnetic radiation will be explicitly incorporated in the Hamiltonian through a photon field designated by creation and annihilation operators  $c_p^\dagger$  and  $c_p$ , respectively.

The postulated Hamiltonian takes the form

$$H = H_{\text{donors}} + H_{\text{acceptor}} + H_{\text{phonons}} + H_{\text{photons}}, \quad (3.1)$$

where the Hamiltonian for the donor molecules is

$$H_{\text{donors}} = \sum_n [\Omega A_n^\dagger A_n - J A_n^\dagger (A_{n-1} + A_{n+1})], \quad (3.2)$$

and the acceptor term is

$$H_{\text{acceptor}} = \Omega_0 A_0^\dagger A_0 - J_0 [A_0^\dagger (A_{-1} + A_1)] + \text{H.c.} \quad (3.3)$$

The phonon part of the Hamiltonian is similar to the one postulated for peptide chains [16] but it is symmetric in chain positions

$$H_{\text{phonons}} = \sum_n \left\{ \frac{p_n^2}{2m} + k(x_n - x_{n\pm 1})^2 \right. \\ \left. + \chi_0 A_n^\dagger A_n (2x_n - x_{n-1} - x_{n+1}) \right\}, \quad (3.4)$$

and  $p_n$  denotes the linear momentum at site  $n$  with mass  $m$ ,  $k$  is the elastic constant, while  $\chi_0$  represents the exciton-phonon coupling coefficient. Finally, the Hamiltonian for the photon field is written as

$$H_{\text{photons}} = \int d^3p \left[ w_p c_p^\dagger c_p + \left[ g_p c_p \sum_n A_n^\dagger e^{in(\mathbf{p} \cdot \mathbf{d})} + \text{H.c.} \right] \right], \quad (3.5)$$

where  $\mathbf{p}$  is the momentum of a photon,  $c_p^\dagger$  and  $c_p$  create and annihilate a photon with momentum  $\mathbf{p}$ , respectively, and  $\mathbf{d}$  is the chain's displacement unit vector. In the dipole approximation  $g_p$ , the coupling parameter between photons and excitons, is a constant number independent of  $\mathbf{p}$ .

### B. Excitons in momentum space

The Hamiltonian for excitons can be rewritten as

$$H_{\text{exciton}} = \sum_{n=-\infty}^{+\infty} [\Omega A_n^\dagger A_n - J A_n^\dagger (A_{n+1} + A_{n-1}) - (\Omega - \Omega_0) A_0^\dagger A_0], \quad (3.6)$$

and the relative acceptor energy constant is defined as  $V = \Omega - \Omega_0 > 0$ . We now change the basis according to

$$A_n = \frac{1}{\sqrt{2\pi}} \int_{-\pi}^{\pi} dk e^{ink} A_k, \quad (3.7)$$

which results in the following separation of the exciton Hamiltonian

$$H_{\text{exciton}} = \int \Omega_k A_k^\dagger A_k dk - \frac{V}{2\pi} \int dk A_k^\dagger \int d\bar{k} A_{\bar{k}}, \quad (3.8)$$

where the dispersion relation is given by

$$\Omega_k = \Omega_0 - 2J \cos k. \quad (3.9)$$

Note that close to the bottom of the exciton band  $\Omega_k$  is parabolic unlike in the acoustic phonon (linear) case.

### C. Phonons in momentum space

Next, the phonon Hamiltonian, Eq. (3.4), is Fourier transformed to obtain

$$H_{\text{phonons}} = \frac{1}{2m} \int dq p(q)p(-q) + \frac{k}{2} \int dq 2(1 - \cos q)x(q)x(-q) + \chi_0 \int dk_1 dk_2 dq A_{k_1}^\dagger A_{k_2} x(q) \delta(k_1 - k_2 - q) 2(1 - \cos q). \quad (3.10)$$

Then, we second quantize the phonon dynamics in a standard way through

$$x(q) = \frac{1}{(2m\omega_q)^{1/2}} (a_q^\dagger + a_q) \quad (3.11)$$

and

$$p(q) = i \left[ \frac{m\omega_q}{2} \right]^{1/2} (a_q^\dagger - a_q). \quad (3.12)$$

As a result, the following form of the phonon Hamiltonian is obtained:

$$H_{\text{phonons}} = \int dq \omega_q a_q^\dagger a_q + \int dk_1 dk_2 2\chi_0 [1 - \cos(k_1 - k_2)] A_{k_1}^\dagger A_{k_2} (a_{k_1 - k_2}^\dagger + a_{k_2 - k_1}^\dagger), \quad (3.13)$$

where the dispersion relation for  $\omega(q)$  is given by

$$\omega(q) = [2\omega_0(1 - \cos q)]^{1/2}, \quad (3.14)$$

i.e., is that for acoustic phonons. Note that both  $\omega(q)$  and  $\chi(q) \equiv 2\chi_0(1 - \cos q)$  are slowly varying functions of momentum. This Hamiltonian is of the type derived earlier for molecular excitations [19]. The exciton-phonon interaction has been recognized as crucial in the phenomenon of self-trapping of molecular excitons [8]. The determining factor in the competition between localization and delocalization of excitons is the ratio of the lattice spacing to the extent of the exciton wave function. The possibility of these two extreme regimes will be discussed at length in Sec. IV. The intermediate regime of excitons ‘‘dressed’’ by phonons will be treated perturbatively in the remainder of this section.

### D. Coupling one oscillator and radiation

For simplicity we use scalar photons here, i.e., drop the polarization index. The relevant Hamiltonian for a single oscillator interacting with a photon field can be written as

$$H = \Omega A^\dagger A + \int d^3\mathbf{k} [\omega_k c_k^\dagger c_k + g_k (A c_k^\dagger + A^\dagger c_k)], \quad (3.15)$$

where the notation is the same as used in the previous calculations. Since the problem under consideration is of scattering type the wave function is in the form of the linear combination below

$$|\psi\rangle = c_0 A^\dagger |\Omega\rangle + \int d^3\mathbf{k} \psi_{k_0}^\dagger(k) c_k^\dagger |\Omega\rangle, \quad (3.16)$$

where

$$|\psi_{k_0}^\dagger\rangle = |\phi_{k_0}\rangle + |\psi_{\text{scattered}}^\dagger\rangle, \quad (3.17)$$

represents a combination of a plane wave and a scattered wave. Thus

$$\langle k | \psi_{k_0}^\dagger \rangle = \delta_3(\mathbf{k} - \mathbf{k}_0) + \langle \psi | \psi_{\text{scattered}}^\dagger \rangle. \quad (3.18)$$

The corresponding eigenvalue problem is

$$H|\psi\rangle = z|\psi\rangle, \quad (3.19)$$

where  $z = E + i\varepsilon$ . This gives

$$C_0 \Omega + \int d^3\mathbf{k} g_k \psi_{k_0}^\dagger(k) = z C_0 \quad (3.20)$$

and

$$\omega_k \psi_{k_0}^\dagger(k) + C_0 g(k) = z \psi_{k_0}^\dagger(k). \quad (3.21)$$

The first of the two equations above yields

$$C_0 = (z - \Omega)^{-1} \langle g | \psi_{k_0}^\dagger \rangle, \quad (3.22)$$

while the second yields

$$\omega_k |\psi_{k_0}^\dagger\rangle + |g\rangle (z - \Omega)^{-1} \langle g | \psi_{k_0}^\dagger \rangle = z |\psi_{k_0}^\dagger\rangle. \quad (3.23)$$

We then use the Lippman-Schwinger expansion for  $|\psi_{k_0}^\dagger\rangle$  as

$$|\psi_{k_0}^\dagger\rangle = |\phi_{k_0}\rangle + (z - \omega_k)^{-1} |g\rangle (z - \Omega)^{-1} \langle g | \psi_{k_0}^\dagger \rangle, \quad (3.24)$$

where  $|g\rangle (z - \Omega)^{-1} \langle g|$  appears as an energy-dependent effective potential. Equation (3.24) can be explicitly solved for  $|\psi_{k_0}^\dagger\rangle$  as

$$D \equiv z - \Omega - \langle g | G_0(z) | g \rangle = z - \Omega - \int d^3\mathbf{k} (z - \omega_k)^{-1} g^2(k) \simeq z - \Omega - i\pi g^2(k_0), \quad (3.26)$$

where the real part determines the frequency shift while the imaginary part determines the width of the spectral line.

### E. Excitons coupled to radiation

The appropriate Hamiltonian for a collection of excitons, photons, and coupling terms between them is

$$H = \int dk \Omega_k A_k^\dagger A_k + \int d^3\mathbf{p} \omega_p c_p^\dagger c_p + \int d^3\mathbf{p} g(p) [c_p A^\dagger(\mathbf{p}, \mathbf{d}) + \text{H.c.}] \quad (3.27)$$

The trial wave function for the problem is taken as

$$|\psi\rangle = \int d^3\mathbf{p} \psi_{p_0}^\dagger(p) c_p^\dagger |\Omega\rangle + \int dk \varphi(k) A_k^\dagger |\Omega\rangle. \quad (3.28)$$

Then, we rescale momentum according to  $\mathbf{p} \rightarrow \mathbf{p}/d$  and introduce the momentum components parallel and perpendicular to the molecular system as  $p_{\parallel}$  and  $p_{\perp}$ , respectively. Note that in the case of a molecular chain the space spanned by  $p_{\parallel}$  is two dimensional and that of  $p_{\perp}$  is one dimensional. For a molecular surface the opposite is

$$\psi_{p_0}^\dagger(p) = \delta(p_{\parallel}^0 - p_{\parallel}) \{ \delta_2(\mathbf{p}_{\perp} - \mathbf{p}_{\perp}^0) + (z - \omega_p)^{-1} [z - \Omega(p_{\parallel}^0)]^{-1} g_0^2 \}. \quad (3.34)$$

The latter equation means that the result of an incident electromagnetic wave being scattered off a collection of excitons is a plane wave in the direction normal to the surface and a scattered wave within the surface containing a chain of polarizable molecules. Thus, light is shown to induce a plane exciton wave.

Assuming that polarizable molecules form a two-dimensional lattice (rather than a one-dimensional chain, as done previously) results in a similar formula, namely,

$$\psi_{p_0}^\dagger(p) = \delta_2(p_{\perp} - p_{\perp}^0) \{ \delta(p_{\parallel} - p_{\parallel}^0) + g_0^2 (z - \omega_p)^{-1} [z - \Omega(p_{\perp}^0)]^{-1} \}. \quad (3.35)$$

Whereas in one-dimensional scattering there is only reflection and transmission of incident light, in two dimensions a genuine scattered wave emerges. Moreover, due to the momentum or energy mismatch between excitons and light,  $\mathbf{p}$  is very small in magnitude and hence  $\Omega(p_{\perp}^0) \simeq \Omega(0)$ .

Although this is not directly applicable to molecular aggregates, it is nevertheless instructive to see the difference between the previous two cases and a fully three-dimensional situation. Taking a Hamiltonian in the form of Eq. (3.27) and diagonalizing it yields the matrix

$$\begin{bmatrix} \Omega(p) & g(p) \\ g(p) & \omega(p) \end{bmatrix}, \quad (3.36)$$

$$|\psi_{k_0}^\dagger\rangle = |\phi_{k_0}\rangle + (z - \omega_k)^{-1} \frac{|g\rangle \langle g | \phi_{k_0}\rangle}{z - \Omega - \langle g | G_0(z) | g \rangle}, \quad (3.25)$$

where we have denoted the propagator as  $G_0(z) = (z - \omega_k)^{-1}$ . The denominator in Eq. (3.25) can be estimated as

true. We also set  $g(p) = g_0$  so that the interaction part of the Hamiltonian in Eq. (3.27) becomes

$$H_{\text{int}}^\gamma = g_0 \int dp_{\perp} dp_{\parallel} [c(p) A^\dagger(p_{\parallel}) + c^\dagger(p) A(p_{\parallel})]. \quad (3.29)$$

Consequently, the eigenequations take the form

$$(z - \Omega_k) \varphi(k) = g_0 \int d^2 p_{\perp} \psi_{p_0}^\dagger(p_{\perp}, k) \quad (3.30)$$

and

$$(z - \omega_p) \psi_{p_0}^\dagger(p) = g_0 \varphi(p_{\parallel}). \quad (3.31)$$

A perturbative approach is then carried out with a linear combination of a plane wave and a scattered wave for  $\psi_{p_0}^\dagger(p)$  as

$$\psi_{p_0}^\dagger(p) = \delta_3(\mathbf{p} - \mathbf{p}_0) + g_0^2 \psi_{\text{scattered}}(p). \quad (3.32)$$

This leads to the results

$$\varphi(k) = g_0 (z - \Omega_k)^{-1} \delta(p_{\parallel}^0 - k) \quad (3.33)$$

and

whose eigenvalues  $z$  satisfy the equation

$$(\Omega_p - z)(\omega_p - z) - g_p^2 = 0. \quad (3.37)$$

Hence

$$\Omega_{1,2} = \frac{1}{2} \{ \Omega_p + \omega_p \pm [(\Omega_p - \omega_p)^2 + 4g_p^2]^{1/2} \} \quad (3.38)$$

and, as a result, the energy spectrum develops two distinct branches separated by a gap which widens as  $p \rightarrow 0$ . This is illustrated in Fig. 4.

What we have demonstrated here is typical for photosensitive materials such as dye molecular assemblies [8] where *polaritons* form as a result of interactions of the radiation field with an exciton. Polaritons represent quasi-

particles of both photonic and excitonic character. The energy threshold depends on the crossover position of photon and exciton dispersion curves (see Fig. 4). In addition to the so-called extraordinary polaritons shown in Fig. 4, ordinary polaritons [20] exist with a linear dispersion relation:  $\omega = ck/n_{\perp}$  resulting from light polarization being perpendicular to the optical axis. For extraordinary polaritons, the upper branch of the dispersion curve describes longitudinal polaritons with exciton polarization parallel to the propagation direction. The lower branch refers to transverse polaritons where exciton po-

larization is perpendicular to the direction of propagation.

#### F. Inclusion of phonons

This part of the quantum-mechanical approach to the photon scattering problem off the molecular lattice supporting excitons is intended to incorporate lattice vibrations in the Hamiltonian. Designating  $a_q^{\dagger}$  and  $a_q$  for the creation and annihilation operator of a phonon with quasimomentum  $q$ , respectively, the total Hamiltonian of the system is

$$H = \int dk \Omega(k) A_k^{\dagger} A_k - V \left[ \int dk A_k^{\dagger} \right] \left[ \int dk A_k \right] + \int dq \varepsilon_q a_q^{\dagger} a_q + \int dk_1 dk_2 A_{k_1}^{\dagger} A_{k_2} \chi(k_1 - k_2) [a_{k_2 - k_1}^{\dagger} + a_{k_1 - k_2}] + \int d^3 p [\omega_p c_p^{\dagger} c_p + g_0 (c_p A_{p_{\parallel}}^{\dagger} + c_p^{\dagger} A_{p_{\parallel}})], \quad (3.39)$$

where  $p_{\parallel}$  represents the photon momentum component parallel to the molecular chain. This is consistent with earlier formulations of the molecular exciton problem [21]. Subsequently, we make an approximation which retains only single-phonon scattering processes which is called the Tamm-Dankov approximation [22,23]. Then, the trial wave function takes the form

$$|\psi\rangle = \int d^3 p \psi_{p_0}^{\dagger}(p) c_p^{\dagger} |\Omega\rangle + \int dk \varphi(k) A_k^{\dagger} |\Omega\rangle + \int dk dq \varphi_{\text{ph}}(k, q) A_k^{\dagger} a_q^{\dagger} |\Omega\rangle + \int d^3 p dq \varphi_{\gamma}(p, q) c_p^{\dagger} a_q^{\dagger} |\Omega\rangle, \quad (3.40)$$

where the subscript ph refers to the phonons while  $\gamma$  refers to photons. As a consequence, the eigenvalue problem reduces to the following set of four coupled equations:

$$(z - \omega_p) \psi_{p_0}^{\dagger}(p) = g_0 \varphi(p_{\parallel}), \quad (3.41)$$

$$(z - \Omega_k) \varphi(k) = -V f(k) \int dk' f(k') \varphi(k') + g_0 \int d_{p_{\perp}}^2 \psi_{p_0}^{\dagger}(p_{\perp}, k) + \int dk' \chi(k - k') \varphi_{\text{ph}}(k', k - k'), \quad (3.42)$$

$$(z - \Omega_k - \varepsilon_q) \varphi_{\text{ph}}(k, q) = \chi(q) \varphi(k + q) + g_0 \int d^2 p_{\perp} \varphi_{\gamma}(p_{\perp}, k; q) - V f(k) \int dk' f(k') \varphi_{\text{ph}}(k', q), \quad (3.43)$$

and

$$(z - \omega_p - \varepsilon_q) \varphi_{\gamma}(p, q) = g_0 \varphi_{\text{ph}}(p_{\parallel}, q). \quad (3.44)$$

Since the coupling to electromagnetic radiation is relatively weak, the first step towards solving this system is to expand the wave functions in powers of  $g_0$ . Thus,

$$\psi_{p_0}^{\dagger}(\mathbf{p}) = \delta_3(\mathbf{p} - \mathbf{p}_0) + (z - \omega_p)^{-1} g_0 \varphi(p_{\parallel}), \quad (3.45)$$

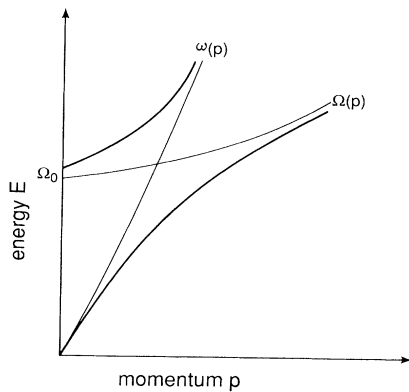


FIG. 4. A schematic illustration of the dispersion relation given by Eq. (3.38) for exciton-phonon coupling.

and, as a consequence,

$$\varphi_{\text{ph}}(k, q) = (z - \Omega_k - \varepsilon_q)^{-1} \chi(q) \varphi(k + q) \quad (3.46)$$

and

$$\begin{aligned} \varphi_{\gamma}(p, q) &= (z - \omega_p - \varepsilon_q)^{-1} g_0 \varphi_{\text{ph}}(p_{\parallel}, q) \\ &= (z - \omega_p - \varepsilon_q)^{-1} (z - \Omega_{p_{\parallel}} - \varepsilon_q)^{-1} \\ &\quad \times g_0 \chi(q) \varphi(p_{\parallel} + q). \end{aligned} \quad (3.48)$$

In Eq. (3.46) we have dropped the contribution due to the last term of Eq. (3.43). This term renormalizes the exciton-acceptor interaction and although it is simple to include it in the equations that follow, we have dropped it due to the smallness of the overlap between  $\chi(k)$  and  $f(k)$ . The only unknown part of the wave function is at this stage  $\varphi(k)$  which satisfies the following equation:

$$\begin{aligned} (z - \Omega_k) \varphi(k) &= g_0 \delta(k - p_{\parallel}^0) - V f(k) \int dk' f(k') \varphi(k') \\ &\quad + \varphi(k) \int dq \frac{\chi^2(q)}{z - \varepsilon_q - \Omega(k - q)}. \end{aligned} \quad (3.49)$$

The first term on the right-hand side represents an exciton plane wave induced by photon momentum transfer to the chain. The second describes scattering processes off the acceptor molecules while the last one arises due to scattering effects off phonons. It is worth commenting on



the form of the third term since it has both a real and an imaginary part, the latter giving rise to a *finite exciton lifetime*. Thus, we can renormalize the exciton dispersion relation according to

$$\tilde{\Omega}(k) = \Omega(k) - \int dq \frac{\chi^2(q)}{z - \varepsilon_q - \Omega(k-q)}. \quad (3.50)$$

From its form, it can be concluded that the exciton energy spectrum is shifted as a result of interactions with phonons. The imaginary part gives rise to a width of the spectrum.

In conclusion, this section provided a step-by-step development of the quantum-mechanical formalism for electromagnetic wave interaction processes off the molecular assemblies. The interaction with photons was shown to induce an excitonic plane wave which then interacts with acceptors and subsequently with phonons. In this derivation we have included the presence of acceptor and donor sites and studied the propagation of excitons resulting from photon absorption processes. The influence of phonons was shown to be twofold with an energy shift and the line broadening effect accompanying it. The technique of calculations proposed in this section was a perturbative one which corresponds to a relatively weak coupling regime. A schematic illustration of the physical situation analyzed here is shown in Fig. 5 where an exciton wave produced at a donor molecule is scattered off an acceptor.

We now give a brief overview of the thermal properties of both coherent and incoherent excitons in the presence of impurity molecules acting as energy traps. The results discussed below are relevant to the perturbative approach adopted in this section and much research has been done in the past on which we can draw. Capture of exciton energy by impurity molecules (traps) depends crucially on whether the excitons are coherent or incoherent. It was found [9] that *incoherent excitons*, with the inclusion of phonons, are characterized by an effective radius  $R_0$  for capture by a trap, which typically exceeds 10 lattice periods. The quenching rate is proportional to the square of the concentration of impurities. The transfer probability for exciton migration depends inversely on the sixth power of the distance between sites and, at low temperatures, is proportional to the absolute temperature, i.e., is thermally activated. This is consistent with experimental observations [24] for molecular crystals such as naphthalene, where the efficiency of energy transfer is *proportional to  $T$*  for low concentrations of acceptor molecules ( $10^{-7}$  to  $10^{-2}$ ). A possible explanation is that in a combined kinetic and diffusion model thermal fluctuations as well as phonons assist in hopping.

On the other hand, for shallow energy traps it was found [25] that *coherent excitons* are much more likely to

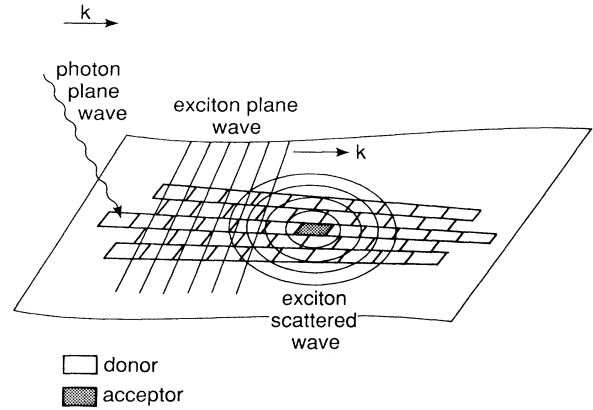


FIG. 5. A schematic illustration of the process of electromagnetic energy capture and transfer through exciton waves as discussed theoretically in Sec. III.

be captured. Quenching rate of coherent excitons by isolated impurities is proportional to the cubic power of their concentration [10]. If the trap depth is much less than the Debye energy, then one acoustic phonon is sufficient to capture an exciton on an impurity [9]. Otherwise, exciton capture is a multiphonon process. As a consequence, one finds that at low temperatures (compared to trap depth energy) the capture cross section is proportional to  $T^{-1/2}$  while at high temperatures it is proportional to  $T^{5/2}$ . Then the probability of capture shows a crossover from a nearly *constant value at low temperatures* to that *proportional to  $T^3$  at high temperatures*. For deep trap levels the probability of coherent exciton capture is largely temperature independent up to high temperatures where it is proportional to  $\exp(-\Delta E/kT)$  with  $\Delta E$  denoting activation energy [25]. The intermediate case of both coherent and incoherent excitons has also been studied [10,19] and the picture is rather complicated with several distinct kinetic regions of behavior.

Whereas this section focused on the perturbative effects of exciton behavior, nonlinear aspects of the model undoubtedly require the analysis of soliton formation and related effects. This will be studied in the next section.

#### IV. THE NONLINEAR REGIME

In this section the model Hamiltonian will be composed of only two main types of elementary excitations, i.e., excitons and phonons coupled together. The influence of photons is very simple and, as shown before, amounts to a creation of an excitonic plane wave. The approximate Hamiltonian studied here includes both donor and acceptor lattice sites and is given below

$$H = \sum_k \Omega(k) A_k^\dagger A_k + \sum_q \varepsilon(q) a_q^\dagger a_q + \sum_{k,q} \chi(k,q) A_{k+q}^\dagger A_k (a_q^\dagger + a_q) - \sum_{k,\Delta k} [V - J \cos(k + \Delta k)d] (A_k^\dagger A_{k+\Delta k} + A_{k+\Delta k}^\dagger A_k). \quad (4.1)$$

Note that the last term above is a  $k$ -space representation of the acceptor energy and interactions with the neighboring

donor sites. This term will be seen to be responsible for  $k$ -space dispersion and, under special conditions, self-focusing may take place. We have denoted lattice spacing by  $d$ . Then, Heisenberg equations of motion for the two types of operators  $a_k$  and  $A_k$  are obtained as

$$i\frac{\partial a_k}{\partial t} = \varepsilon(k)a_k + \sum_q \chi(k, q) A_{q-k}^\dagger A_q \quad (4.2)$$

and

$$i\frac{\partial A_k}{\partial t} = \Omega(k)A_k + \sum_q \chi(k-q, q) A_{k-q} (a_q^\dagger + a_q) - \sum_{\Delta k} [V - J \cos(k + \Delta k)d] (A_{k+\Delta k} + A_{k-\Delta k}). \quad (4.3)$$

Our objective will be to study the dynamics of exciton and phonon quantum fields under the assumption of their strong coupling. Moreover, on the basis of experimental data reviewed in Sec. I, a type of Born-Oppenheimer approximation will be adopted which assumes the phonon dynamics to be substantially faster than that of excitons [26]. This means that we seek solutions to Eq. (4.2) in the form

$$a_k \cong e^{i\omega_k t} a_k^0, \quad (4.4)$$

so that  $\partial a_k / \partial t = i\omega_k a_k$  and Eq. (4.2) can be solved for  $a_k$  to give

$$a_k = -[\omega_k + \varepsilon(k)]^{-1} \sum_q \chi(k, q) A_{q-k}^\dagger A_q, \quad (4.5)$$

which serves a dual purpose of formally solving for  $a_k$  and decoupling  $a_k$  from  $A_k$ . We then substitute Eq. (4.5) into Eq. (4.3) to obtain

$$i\frac{\partial A_k}{\partial t} = \Omega(k)A_k - \sum_q [\omega_q + \varepsilon(q)]^{-1} \chi(k-q, q) A_{k-q} \sum_{q'} \chi(q, q') A_{q'-q}^\dagger A_{q'} - \sum_{\Delta k} [V - J \cos(k + \Delta k)d] (A_{k+\Delta k} + A_{k-\Delta k}). \quad (4.6)$$

In order to solve the above equation, two distinct asymptotic regimes will be considered depending on the form of the coupling constant  $\chi(k, q)$ . Each of these regimes is exactly solvable.

#### A. Frequency selection (Fröhlich regime)

In this regime the following will be assumed.

(a) The sum over  $\Delta k$  is restricted to only three terms:  $\Delta k = 0, +\pi/d$ , and  $-\pi/d$ . The first term normalizes  $\Omega(k)$  while the last two are approximated by

$$\frac{1}{2}(V-J)(\Delta k)^2 \frac{\partial^2 A_k}{\partial k^2}.$$

(b) The coupling constant is truncated to involve only long phonon wavelengths ( $q \approx 0$ ) as having effects on scattering with excitons. Thus,

$$\chi(k, q) \cong \chi_0, \quad \text{for } q=0,$$

and is zero otherwise ( $q \neq 0$ ). As a result, Eq. (4.6) takes the following approximate form:

$$i\frac{\partial A_k}{\partial t} = \tilde{\Omega} A_k - \frac{|\chi(k, 0)d|^2}{\omega_0 + \varepsilon(0)} A_k A_k^\dagger A_k - \frac{(V-J)\pi^2}{d^2} \frac{\partial^2 A_k}{\partial k^2}, \quad (4.7)$$

where  $\tilde{\Omega} = \Omega - V + J$ . Therefore, the equation of motion

for  $A_k$  is of the *nonlinear Schrödinger* type in  $k$  space. Consequently, its solution is given by

$$A_k(t) = \exp(-iE_s t) A_k(0), \quad (4.8)$$

where  $A_k(0)$  is the classical envelope in the sech soliton form below

$$A_k(0) = \alpha_0 \operatorname{sech}(\lambda k), \quad (4.9)$$

with its amplitude

$$\alpha_0 = \pm \{-2(E_s - \tilde{\Omega})[\omega_0 + \varepsilon(0)] / |\chi(k, 0)|^2\}^{-1/2}, \quad (4.10)$$

and the inverse width

$$\lambda = [- (E_s - \tilde{\Omega}) / \tilde{J}]^{1/2}. \quad (4.11)$$

We have introduced the effective dispersion parameter

$$\tilde{J} = \frac{(V-J)\pi^2}{d^2}. \quad (4.12)$$

Note that the width of this  $k$ -space soliton increases with  $\sqrt{\tilde{J}}$  and its amplitude is proportional to the coupling constant  $\chi$ . The soliton energy  $E_s$  is given implicitly through the conservation of quasiparticles requirement, such that

$$N = \sum_k |A_k|^2. \quad (4.13)$$

We conclude this part by emphasizing that this particular regime, based on conditions (a) and (b), leads to self-

focusing in the frequency spectrum [27] which is narrowly peaked at the long-wavelength limit  $k=0$  and decreases virtually exponentially as  $k$  increases. An entirely opposite scenario is possible under different working conditions.

### B. Soliton formation (Davydov regime)

In this particular limit we make the following assumptions.

(a) Both  $\chi(k, q)$  and the energy dispersion formula for phonons  $\omega(q)$  and  $\varepsilon(q)$  are assumed constant parameters. This, of course, rules out acoustic phonons but allows for a coupling with optical phonons. The latter two quantities are, of course, slowly varying functions of  $q$  for optical phonons with  $q \approx 0$ . Thus, we take

$$\chi(k, q) \cong \chi_0 ,$$

$$\omega(q) \cong \omega_0 ,$$

$$\varepsilon(q) \cong \varepsilon_0 .$$

(b) The presence of acceptor sites is ignored so that the summation over  $\Delta k$  only includes the central value of  $\Delta k = 0$ .

(c) The dispersion relation for excitons is expanded to second order according to

$$\Omega(k) \cong \Omega_0 + \Omega_2 k^2 .$$

This set of conditions appears to be much more stringent than previously thought.

As a result, the following equation of motion is obtained for  $A_k$ :

$$i \dot{A}_k = \bar{\Omega}_0 A_k - \frac{\kappa}{N} \sum_{q, q'} A_{k-q} A_{q'-q}^\dagger A_{q'} + \Omega_2 k^2 A_k , \quad (4.14)$$

where we have introduced the following parameters:

$$\bar{\Omega}_0 = \Omega_0 - V + J ,$$

$$\bar{\Omega}_2 = \Omega_2 + \frac{J}{2} d^2 ,$$

$$\kappa = N \frac{|\chi_0|^2}{\omega_0 + \varepsilon_0} .$$

We then follow the recently developed method of coherent structures for strongly interacting quantum systems [28] and introduce a classical field corresponding to  $A_k$  as

$$\mathcal{A}(x, t) = N^{-1/2} \sum_k A_k(t) e^{ikx} . \quad (4.15)$$

Simultaneously, the equation of motion for the field  $\mathcal{A}(x, t)$  takes the form of the nonlinear Schrödinger equation in real space,

$$i \frac{\partial \mathcal{A}}{\partial t} = \bar{\Omega}_0 \mathcal{A} + \bar{\Omega}_2 \frac{\partial^2 \mathcal{A}}{\partial x^2} - \kappa |\mathcal{A}|^2 \mathcal{A} . \quad (4.16)$$

Its sech soliton solution is

$$\mathcal{A}(x, t) = \left[ \frac{\mathcal{N} \mu}{2} \right]^{1/2} \frac{\exp\{i[k_s(x-x_0) - \omega_s t]\}}{\cosh\left[\frac{\mu}{d}(x-x_0 - vt)\right]} , \quad (4.17)$$

where  $k_s$  is the wave number of the associated carrier wave,  $\mu$  is the inverse width,  $v$  is the velocity, and  $\omega_s$  the carrier wave frequency. The normalization condition

$$\int_{-\infty}^{+\infty} |\mathcal{A}(x, t)|^2 dx = \mathcal{N} , \quad (4.18)$$

relates  $\mathcal{N}$  and  $\mu$  in a linear relationship. Numerical details can be found in the literature on the nonlinear Schrödinger equation [16]. However, note that  $\mu$  is proportional to  $\kappa/\bar{\Omega}_2$ , hence the width of the soliton decreases with an increase of the nonlinear coupling parameter  $\kappa$ . Simultaneously with it the amplitude grows in proportion to  $\sqrt{\kappa}$ . A comparison of the two limiting regimes presented in this section is given in Fig. 6. It should be emphasized that strong coupling to phonons tends to enhance soliton formation. However, as was calculated earlier [19], self-trapping is destroyed with the increase of lattice spacing and the growth of temperature fluctuations. On the other hand, the self-trapping rate is proportional to the phonon frequency and the mean potential barrier transparency [29] (proportional to the appropriate Boltzmann factor).

It is known [29] that within a range of exciton and phonon coupling parameters self-trapped excitons (Davydov solitons) and free excitons may coexist. The two types of objects are manifested in the optical absorption spectra by (a) narrow peaks due to free excitons and (b) a structured wide-band background due to self-trapped states. Furthermore, the rate of production of solitons depends on the absolute temperature and is believed to be proportional to  $T$  in the low-temperature limit [30] and to  $\sqrt{T}$  in the high-temperature limit [31].

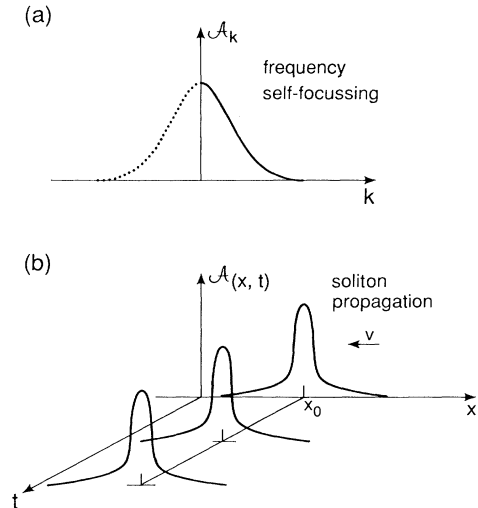


FIG. 6. A graphic comparison of the Fröhlich and Davydov regimes.

## V. SUMMARY AND CONCLUSIONS

In this paper we have given an overview of theoretical results concerning the very efficient electromagnetic energy capture and transport in two-dimensional molecular assemblies such as Scheibe aggregates. We first outlined a simple calculation of the eigenvalue problem for a dimer which gave values of model parameters for the theory. We have then numerically verified some of these results using a one-dimensional chain of molecules. It was shown that the one-dimensional model requires the presence of a fine-tuned acceptor level in order to generate a dramatic increase in the wave-function amplitude at the acceptor site. This wave function is substantially spread over the neighboring sites. This fine-tuning requirement does not appear supported by experimental findings. However, as we argue later in this section we believe that this is simply an artifact of the one-dimensional nature of the model. Calculations in two dimensions differ in this respect. A subsequent calculation for a hexagonal lattice with both donor and acceptor molecules present provided a criterion for efficient energy capture by acceptors. The main finding here was that acceptor levels should be sufficiently *shallow* to optimize exciton energy capture. A completely different approach was also discussed which relies on very strong exciton-phonon coupling and leads to a solitonic mechanism. While the current state of experimental data does not entirely preclude such a scenario, it does appear that it is less likely to expect soliton formation for  $J$  aggregates than in peptide chains.

In the next section, a field-theoretic Hamiltonian was postulated as a starting point for calculations involving excitons, photons, and phonons. A step-by-step development of fully quantum-mechanical calculations was provided in which donor and acceptor sites are accounted for. It was demonstrated that electromagnetic radiation induces an exciton plane wave on the surface of the aggregate which may be scattered off phonons and partially captured by the acceptor site. Most of the calculations were carried out in a two-dimensional space which has very special properties from the point of view of energy transfer.

The final section of the paper examined closely the possibility of two extremely nonlinear regimes. The first regime assumed the predominant role of long-wavelength phonons in scattering processes which led to self-focusing of exciton waves to a narrow range of  $k$  vectors (and correspondingly frequency values). This was quantitatively described by a nonlinear Schrödinger equation in  $k$  space with a soliton solution that models a condensation effect in reciprocal space. Due to its similarity to an earlier model of biological coherence we have referred to this limit as the Fröhlich regime. The other regime assumed a constant value of the coupling parameter irrespective of the phonon wave number. As a result, a real space nonlinear Schrödinger equation was found to model the exciton dynamics. This is analogous to Davydov soliton formation in peptide chains. This is why we refer to this limit as the Davydov regime.

A recent series of papers [32,33] investigated exciton

transport and trapping on spectrally *disordered* lattices. Several important conclusions were reached that are of relevance to our analysis. First of all, it was found that no simple relation exists between fluorescence excitation spectra and steady-state absorption spectra in structurally disordered systems. Indeed, it was observed that in some systems equilibrium may never be reached. Unlike the conclusion reached by Kuhn [1], these authors find the Förster hopping model adequate and include temperature dependence of the spectral overlap. This once again seems to indicate that several simultaneous energy transfer mechanisms may be at play.

Finally, we wish to once again draw the reader's attention to the fact that molecular assemblies such as Scheibe aggregates have a planar geometry, i.e., are two dimensional. We believe this is not accidental, but rather it is a specific property responsible (and designed) for long-range energy transfer. This can be seen when studying the Schrödinger equation for a quantum particle in a binding potential  $V(x,y)$ . It can be shown that shallow potentials giving quantum bound states are very difficult to find in both one- and three-dimensional geometries. That means, that a very low level of tolerance is present and small deviations, e.g., thermal fluctuations or coupling to other modes, would destroy the binding power of the local acceptor potential. Remarkably, however, two-dimensional calculations yield a result with a binding potential  $V$  determined through the relation:

$$\Delta_0 \geq \exp \left[ -\frac{1}{V} \right],$$

where  $\Delta_0$  is a specific constant. This indicates that decreasing potential strengths by simple factors lowers the binding energy by orders of magnitude, consequently retaining bound states. That is only true for two-dimensional systems. An interesting related experimental observation was made for photosynthetic and biological systems such as chlorophyll [6]. It was found that there exists a significant qualitative difference between one- and higher- (i.e., two and three) dimensional systems regarding exciton quenching on low-concentration traps. In the former case, quenching occurs much faster for periodic arrangements of traps than for random ones. This is *not* the case in higher-dimensional systems where there is very little change in exciton quenching times. In 2D systems the typical aggregate decay function has the form

$$P(t) \propto \exp \left[ -\kappa t^{1/3} - \frac{t}{\tau} \right],$$

where  $\tau$  is the exciton relaxation time with no quenching.

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- [1] H. Kuhn, *J. Photochem.* **10**, 111 (1979).
- [2] H. Büttcher and H. Kuhn, *Chem. Phys. Lett.* **6**, 183 (1970).
- [3] D. Möbius, *Ber. Bunsenges Phys. Chem.* **82**, 848 (1978).
- [4] R. H. Tredgold, *Rep. Prog. Phys.* **50**, 1609 (1987).
- [5] T. Inoue, *Thin Solid Films* **132**, 21 (1985).
- [6] R. M. Pearlstein, in *Excitons*, edited by E. I. Rashba and M. D. Sturge (North-Holland, Amsterdam, 1982).
- [7] M. Fujihira and H. Yamada, *Thin Solid Films* **160**, 125 (1988).
- [8] M. Pope and C. E. Swenberg, *Electronic Processes in Organic Crystals* (Clarendon Press, Oxford, 1982).
- [9] V. M. Agranovich and M. D. Galanin, *Electronic Excitation Energy Transfer in Condensed Matter* (North-Holland, Amsterdam, 1982).
- [10] R. P. Hemenger, K. Lakatos-Lindenberg, and R. M. Pearlstein, *J. Chem. Phys.* **60**, 3271 (1974).
- [11] N. Tamai, T. Yamazaki, and I. Yamazaki, *Can. J. Phys.* **68**, 1013 (1990).
- [12] D. Möbius and H. Kuhn, *J. Appl. Phys.* **64**, 5138 (1988).
- [13] D. Möbius and H. Kuhn, *Isr. J. Chem.* **18**, 375 (1979).
- [14] E. A. Bartnik, K. J. Blinowska, and J. A. Tuszynski, *Phys. Lett. A* **159**, 67 (1991).
- [15] E. A. Bartnik and K. J. Blinowska, *Phys. Lett. A* **134**, 448 (1989).
- [16] A. S. Davydov, *Solitons in Molecular Systems* (Reidel, Dordrecht, 1987).
- [17] G. C. Huth, F. Gutmann, and G. Vitiello, *Phys. Lett. A* **140**, 339 (1989).
- [18] P. L. Christiansen, S. Pagano, and G. Vitiello, *Phys. Lett. A* **154**, 381 (1991).
- [19] V. M. Agranovich and A. A. Zakhidov, *Chem. Phys. Lett.* **50**, 278 (1977).
- [20] H. J. Hesse, W. Fuchs, G. Weiser, and L. von Szentpaly, *Phys. Status Solidi B* **76**, 817 (1976).
- [21] *Spectroscopy and Excitation Dynamics of Condensed Molecular Systems*, edited by V. M. Agranovich and R. M. Hochstrasser (North-Holland, Amsterdam, 1983).
- [22] L. I. Schiff, *Quantum Mechanics* (McGraw-Hill, New York, 1968).
- [23] S. S. Schweber, *An Introduction to Relativistic Quantum Field Theory* (Harper and Row, New York, 1962).
- [24] R. Kopelman, in *Spectroscopy and Excitation Dynamics of Condensed Molecular Systems*, edited by V. M. Agranovich and A. A. Maradudin (North-Holland, Amsterdam, 1983), p. 139.
- [25] I. S. Osad'ko, in *Spectroscopy and Excitation Dynamics of Condensed Molecular Systems*, edited by V. M. Agranovich and A. A. Maradudin (North-Holland, Amsterdam, 1983), p. 437.
- [26] H. Bolterauer, J. A. Tuszynski, and M. V. Sataric, *Phys. Rev. A* **44**, 1366 (1991).
- [27] H. Fröhlich, *Adv. Electron. Electron Phys.* **53**, 85 (1980).
- [28] J. A. Tuszynski and J. M. Dixon, *Phys. Lett. A* **140**, 179 (1989).
- [29] E. I. Rashba, in *Excitons*, edited by E. I. Rashba and M. D. Sturge (North-Holland, Amsterdam, 1982).
- [30] F. G. Mertens and H. Büttner, *Phys. Lett.* **84A**, 335 (1981); *J. Phys. A* **15**, 1831 (1982).
- [31] Y. Muto, A. C. Scott, and P. L. Christiansen, *Phys. Lett. A* **136**, 33 (1989); *Physica D* **44**, 75 (1990).
- [32] J. M. Jean, C.-K. Chan, G. R. Fleming, and T. G. Owens, *Biophys. J.* **56**, 1203 (1989).
- [33] M. Werst, Y. Jia, L. Mets, and G. R. Fleming, *Biophys. J.* **61**, 1 (1992).