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# Optical properties of one-dimensional exciton systems: Beyond the Heitler-London approximation

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We study the properties of one-dimensional exciton systems in which the commonly made Heitler-London approximation (HLA) is relaxed. The nonresonant interaction terms which then exist, mix the multi-exciton bands of the HLA. Our approach is based on the exact diagonalization of the Hamiltonian, which is possible using the Jordan-Wigner and Bogoliubov transformations. Exact expressions for transition dipoles between multi-particle states are given. Results of our exact theory for the ground state and one-particle energies, the superradiant enhancement, the pump-probe spectrum, and the linear absorption to multi-particle states are compared quantitatively to the HLA, to the Bose approximation (where the excitons are treated as bosons), and to perturbation theory. In this comparative study, we use parameter values that are relevant to much studied quasi-one-dimensional J aggregates, such as PIC and TDBC. We find that for these systems the strongest effects of the HLA occur in the oscillator strengths of the various optical transitions. In particular, the exciton delocalization length derived from the experimentally observed superradiant enhancement is overestimated by roughly 10% due to the HLA. Also, the transition between the ground state and three-particle states, which is strictly forbidden in the HLA, does obtain a finite oscillator strength due to the non-resonant interactions. © *1997 American Institute of Physics.* [S0021-9606(97)51717-X]

## I. INTRODUCTION

Molecular assemblies, such as J aggregates and Langmuir-Blodgett films, have received much attention over the past decades, mainly because of their interesting collective optical properties. This collective behavior, examples of which are exciton superradiance,[1] motional narrowing,[2,3] and large optical nonlinearities,[4] arises from the interactions between the molecular transition dipoles, which give rise to delocalized Frenkel exciton states.[5,6] Over recent years, it has become clear that the salient linear as well as nonlinear optical properties of aggregates can be understood using the simplest possible Frenkel exciton Hamiltonian, which considers assemblies of nonpolar two-level molecules coupled by (dipolar) excitation transfer interactions.[7,8] This Hamiltonian conserves the number of molecular excitations on a single aggregate so that the eigenstates can be classified according to this number. In this picture, we have the ground state (all molecules in the ground state), one-excitons (the conventional Frenkel excitons), two-excitons, etc. Most recently, two-exciton states (two one-excitons that are scattered by the Pauli exclusion principle) have aroused particular interest. They have been observed in J aggregates by using pump-probe experiments under a variety of experimental conditions.[8,9] An interesting aspect of the pump-probe experiment is that, within certain limitations,[8] it may be used to obtain information about the exciton delocalization length.[10–13] Hole-burning experiments may yield such information in a similar way.[14] Extensions of the above ''mini-

mal'' Frenkel exciton model have also been studied recently, in particular, effects of exciton-exciton interactions[15] and higher molecular excited states.[16]

In this article, we will study the effect of the Heitler-London approximation (HLA),[5,6] which is commonly made in model studies of molecular assemblies, on various optical observables of quasi-one-dimensional exciton systems. In the HLA one neglects interaction terms that simultaneously create or annihilate excitations on two molecules. Such interaction terms naturally occur in the Frenkel exciton Hamiltonian.[5,6] Neglecting intermolecular electron transfer, these terms have exactly the same coupling constant ($J$) as the excitation transfer interaction, but, as they couple states that differ by two excitation energies ($2\omega_0$), while typically $|J| \ll \omega_0$, they are usually considered unimportant. Obviously, inclusion of these nonresonant interaction terms in principle mixes all multi-exciton bands defined above, and thus enormously complicates the calculation of the eigenstates. For the ground state, the strongest mixing occurs with the two-exciton band, which results in a lowering of the ground state energy that in a lowest-order (i.e., second order) treatment may be understood as the van der Waals interaction energy of the molecules in the aggregate.

The effects of relaxing the HLA have been studied for molecular crystals within the approximation that the excitons are treated as bosons.[5] In principle, an exact transformation from the exciton creation and annihilation operators to boson operators is possible, but this involves adding an extra (kinematic) interaction to the Hamiltonian.[6,17] This interaction, however, contains infinitely many terms, so that in practice it has to be truncated. In fact, in most theoretical treatments the

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kinematic interaction is totally neglected,[5,18] which is a level of treatment that we will refer to as the ''Bose approximation.'' One usually argues that the Bose approximation is good for linear optics where only few excitations exist in the system, although, as we will see, even in that case it is not exact. The Bose approximation cannot be used to describe nonlinear response. In spite of its approximate nature, we may use the Bose approximation to get a feeling for the size of effects of the HLA. It predicts, in particular, that the lowest-order correction of the transition frequencies of optically allowed exciton levels due to the nonresonant interaction terms is $2J^2/\omega_0$.[5] Well-studied examples of J aggregates are PIC (pseudo-isocyanine or 1,1′-diethyl-2,2′-cyanine) and TDBC (5,5′,6,6′-tetrachloro-1,1′-diethyl-3,3′-bis(4-sulfobutyl)-benzimidazolo carbocyanine), which have $J$ values of $-630$ cm$^{-1}$,[19] and -1230 cm$^{-1}$,[12] respectively, and both have $\omega_0$ in the order of 19 000 cm$^{-1}$. Thus, the shifts introduced by going beyond the HLA are in the order of 40 cm$^{-1}$ and 160 cm$^{-1}$, respectively. These shifts are very small compared to the transition frequency itself, and even compared to the exciton band width. However, they are not small compared to the observed energy differences between the induced-absorption and bleaching peaks in pump-probe spectra,[9,12] which may be used to determine the exciton delocalization length.

The above arguments demonstrate the importance of a proper quantitative study of the effects of the HLA on linear and nonlinear optical properties. In this article, we will conduct such a study for one-dimensional J aggregates and use the fact that, if we restrict ourselves to nearest-neighbor interactions, the complete Hamiltonian can be diagonalized exactly. This can be done using the Jordan-Wigner and Bogoliubov transformations.[20,21] To calculate exact transition dipole matrix elements, we closely follow the procedure of Lieb, Schultz, and Mattis to calculate spin-spin correlations in magnetic chains.[20] In our case, however, we are also interested in dipoles between multi-particle states, which involve higher-order correlations functions and are more difficult to evaluate. The emphasis of this article is not just to give formal methods to diagonalize the Hamiltonian, but rather to calculate quantitatively properties that are of experimental interest. Thus, our exact results allow us to evaluate the validity of the Heitler-London approximation, the Bose approximation, and perturbation theory for realistic parameter values.

The outline of this article is as follows. In Section II, we give the Hamiltonian and its exact diagonalization in terms of new multi-particle states that are mixtures of the old multi-excitons. This transformation is not new, but it is given to keep the article reasonably self-contained and to define the notation for later sections. In Section III.A, we present the general formalism to calculate transition dipole matrix elements between arbitrary multi-particle states. The results of this formalism for the dipoles between the ground state and the one-particle states, between the ground state and the three-particle states, and between the one- and the two-particle states are presented in Section III.B. The Bose approximation for J aggregates and the energy levels and tran-

sition dipoles that it predicts are discussed in Section IV. In Section V, we concentrate on homogeneous linear aggregates. We give explicit expressions for the various one-particle energies and the transformation coefficients needed to evaluate the dipole matrix elements. We also derive general optical selection rules that are imposed by the inversion symmetry in homogeneous chains. In Section VI, we compare the exact results obtained for typical parameter values to the Bose approximation and the HLA. Specific observables that will be considered are the one-particle energies, the superradiant enhancement factor, the pump-probe spectrum, and the linear absorption to three-particle states. Finally, we summarize our conclusions in Section VII.

## II. EXCITON HAMILTONIAN AND DIAGONALIZATION

We consider the standard Frenkel exciton model for molecular aggregates, which consists of a linear array of $N$ two-level molecules with transition frequencies and dipoles denoted by $\omega_n$ and $\boldsymbol{\mu}_n$, respectively ($n=1,\ldots,N$). In our general formalism, we will allow for arbitrary disorder in these quantities. We will assume the molecules to be nonpolar. The usual Pauli raising and lowering operators, $\hat{b}_n^\dagger$ and $\hat{b}_n$, describe transitions between the molecular ground and excited states.[5,6] They obey the commutation relations

$$[\hat{b}_n,\hat{b}_m^\dagger]=\delta_{nm}(1-2\hat{b}_n^\dagger\hat{b}_n), \quad [\hat{b}_n,\hat{b}_m]=0. \quad (1)$$

In terms of these operators, the Frenkel exciton Hamiltonian may be written[5,6]

$$\hat{H}=\sum_{n=1}^{N}\omega_n\hat{b}_n^\dagger\hat{b}_n+\sum_{n=1}^{N-1}J_n(\hat{b}_n^\dagger+\hat{b}_n)(\hat{b}_{n+1}^\dagger+\hat{b}_{n+1}), \quad (2)$$

where open boundary conditions are used and $\hbar$ has been set at unity. The first part of Eq. (2) accounts for the molecular excitation energy, while the second part describes the intermolecular interactions. We have restricted ourselves to nearest-neighbor interactions (see Section VII) and intermolecular charge transfer has been neglected.

The interaction terms separate into two types. The terms $\hat{b}_n^\dagger\hat{b}_{n+1}$ and $\hat{b}_n\hat{b}_{n+1}^\dagger$ are the transfer interactions, which are resonant. The terms $\hat{b}_n^\dagger\hat{b}_{n+1}^\dagger$ and $\hat{b}_n\hat{b}_{n+1}$, on the other hand, are nonresonant contributions, as they describe simultaneous (de-) excitation of two molecules. As discussed in Section I, one usually applies the HLA and neglects the nonresonant terms.

The first step in diagonalizing the Hamiltonian Eq. (2) (both in complete form and within the HLA), is to apply the Jordan-Wigner transformation[20,22]

$$\hat{c}_n=\exp\left(\pi i\sum_{j<n}\hat{b}_j^\dagger\hat{b}_j\right)\hat{b}_n=\prod_{j<n}(1-2\hat{b}_j^\dagger\hat{b}_j)\hat{b}_n, \quad (3)$$

to convert the Pauli operators $\hat{b}_n$ and $\hat{b}_n^\dagger$ to Fermi operators $\hat{c}_n$ and $\hat{c}_n^\dagger$ that satisfy the anticommutation relations $\{\hat{c}_n,\hat{c}_m^\dagger\}=\delta_{nm}$, $\{\hat{c}_n^\dagger,\hat{c}_m^\dagger\}=0$. The inverse Jordan-Wigner transformation may be represented in the following equivalent ways:

$$\hat{b}_n = \exp\left(\pi i \sum_{j<n} \hat{c}_j^\dagger \hat{c}_j\right)\hat{c}_n = \prod_{j<n}(1-2\hat{c}_j^\dagger \hat{c}_j)\hat{c}_n$$

$$= \prod_{j<n}(\hat{c}_j^\dagger + \hat{c}_j)(\hat{c}_j^\dagger - \hat{c}_j)\hat{c}_n. \tag{4}$$

After applying the Jordan-Wigner transformation, the Hamiltonian may be recognized as a generalization to the case of disorder of the Heisenberg-Ising Hamiltonian discussed by Lieb, Schultz, and Mattis (see Eq. (3.10) of Ref. 20). It is useful to write the Hamiltonian in the form

$$\hat{H} = \hat{H}_{HL} + \hat{H}_{nr}, \tag{5a}$$

$$\hat{H}_{HL} = \sum_{n,m} A_{nm}\hat{c}_n^\dagger \hat{c}_m, \tag{5b}$$

$$\hat{H}_{nr} = \frac{1}{2}\sum_{n,m} B_{nm}(\hat{c}_n^\dagger \hat{c}_m^\dagger + \hat{c}_m \hat{c}_n), \tag{5c}$$

where resonant (Heitler-London) and nonresonant contributions have been separated explicitly, and **A** and **B** are symmetric and antisymmetric tridiagonal matrices, respectively, given by

$$A_{nm} = \omega_n \delta_{nm} + J_n \delta_{m,n+1} + J_{n-1}\delta_{m,n-1}, \tag{6a}$$

$$B_{nm} = J_n \delta_{m,n+1} - J_{n-1}\delta_{m,n-1}. \tag{6b}$$

Before we discuss the diagonalization of the total Hamiltonian, we first briefly give the well-known results within the HLA.[23,24] In that case, the Hamiltonian ($\hat{H}_{HL}$) commutes with the operator for the total number of molecular excitations $\hat{\nu} = \sum_{n=1}^N \hat{b}_n^\dagger \hat{b}_n$, which is thus (in the absence of external fields) a conserved quantity. As a consequence, the eigenstates can be classified according to this number and are referred to as one-excitons, two-excitons, three-excitons, etc. The $\nu$-exciton band contains $N!/(\nu!(N-\nu)!)$ eigenstates. All multi-exciton states are easily generated by transforming $\hat{H}_{HL}$ to noninteracting fermions

$$\hat{H}_{HL} = \sum_{k=1}^N \Omega_k^{HL}\hat{\xi}_k^\dagger \hat{\xi}_k, \tag{7}$$

with

$$\hat{\xi}_k^\dagger = \sum_{n=1}^N \phi_{kn}\hat{c}_n^\dagger. \tag{8}$$

Here, $\Omega_k^{HL}$ and $\phi_{kn}$ $(k=1,\ldots,N)$ are the real eigenvalues and the components of the orthonormalized eigenvectors of the $N\times N$ matrix **A**, respectively. The eigenvectors will be chosen real, which is always possible.

If the typical interaction matrix element $J$ is small compared to the typical molecular transition frequency, the ground state $|0\rangle_{HL}$ is the state in which all molecules are in the ground state. This state has energy $\Omega_0^{HL}=0$.

An arbitrary $\nu$-exciton state can now be created by acting with $\nu$ different creation operators on the ground state:

$$|k_1,\ldots,k_\nu\rangle_{HL} = \hat{\xi}_{k_1}^\dagger \ldots \hat{\xi}_{k_\nu}^\dagger |0\rangle_{HL}, \tag{9}$$

where by convention $k_1 > k_2 > \cdots > k_\nu$. The energy of this state is the sum of the corresponding one-exciton energies

$$\Omega_{k_1 \ldots k_\nu}^{HL} = \sum_{i=1}^\nu \Omega_{k_i}^{HL}, \tag{10}$$

while its expansion in the site representation (i.e., on a basis spanned by the states $\hat{b}_{n_1}^\dagger \hat{b}_{n_2}^\dagger \ldots \hat{b}_{n_\nu}^\dagger |0\rangle_{HL}$) follows in a straightforward way by invoking the Jordan-Wigner transformation in the right-hand side of Eq. (9). This results in expansion coefficients that are given by Slater determinants of the one-exciton amplitudes $\phi_{kn}$.[23,24]

If we relax the HLA, the number of molecular excitations no longer is a conserved quantity. As a consequence of the nonresonant interactions, all $\nu$-exciton bands with $\nu$ even mix and similarly all those with $\nu$ odd mix. By using an additional Bogoliubov transform, it still is possible to diagonalize the Hamiltonian but it no longer is possible to expand the eigenstates in a simple way in the site representation, because the ground state no longer is the state that contains no molecular excitations.

For the derivation of the general diagonalization, we refer to Appendix A of Ref. 20. One then eventually finds that the Hamiltonian may be brought into the diagonal form

$$\hat{H} = \Omega_0 + \sum_{k=1}^N \Omega_k \hat{\eta}_k^\dagger \hat{\eta}_k. \tag{11}$$

Here, $\Omega_k$ $(k=1,\ldots,N)$ denote the new one-particle energies, $\Omega_0$ is the new ground state energy (*vide infra*), and $\hat{\eta}_k^\dagger$ and $\hat{\eta}_k$ denote the new one-particle creation and annihilation operators, which still obey Fermi commutation relations. These operators are given by

$$\hat{\eta}_k^\dagger = \frac{1}{2}\sum_{n=1}^N [(\varphi_{kn}+\psi_{kn})\hat{c}_n^\dagger + (\varphi_{kn}-\psi_{kn})\hat{c}_n]. \tag{12}$$

The one-particle energies $\Omega_k$ and the transformation coefficients $\varphi_{kn}$ follow from the $N\times N$ eigenvalue problem

$$\sum_{m=1}^N \varphi_{km}[(\mathbf{A}-\mathbf{B})(\mathbf{A}+\mathbf{B})]_{mn} = \Omega_k^2 \varphi_{kn}. \tag{13}$$

After this problem is solved, the $\psi_{kn}$ follow from

$$\sum_{m=1}^N \varphi_{km}(\mathbf{A}-\mathbf{B})_{mn} = \Omega_k \psi_{kn}. \tag{14}$$

As in the HLA, the one-particle energies are necessarily real $((\mathbf{A}-\mathbf{B})(\mathbf{A}+\mathbf{B})$ is real and symmetric), while the $\varphi$'s and $\psi$'s can always be chosen real and orthogonal. Requiring that the Bogoliubov transformation Eq. (12) is canonical, leads to the orthonormality relations

$$\sum_{n=1}^N \varphi_{kn}\varphi_{k'n} = \sum_{n=1}^N \psi_{kn}\psi_{k'n} = \delta_{kk'}, \tag{15a}$$

$$\sum_{k=1}^N \varphi_{kn}\varphi_{km} = \sum_{k=1}^N \psi_{kn}\psi_{km} = \delta_{nm}. \tag{15b}$$

We stress again that the new ground state $|0\rangle$ is *not* the state with all molecules in their ground state. In general, it is impossible to find the ground state in the site representation, as that involves diagonalizing a matrix of size $2^{N-1} \times 2^{N-1}$. Also, as a consequence of the nonresonant interaction terms, the ground state energy becomes strictly negative, i.e., the exact ground state energy is lower than that in the HLA. This follows from the relation[21]

$$\Omega_0 = -\sum_k \Omega_k \sum_n \frac{1}{4} (\varphi_{kn} - \psi_{kn})^2,  \tag{16}$$

which is found if one takes the ground state expectation value of the Hamiltonian in terms of $\hat{c}_n^\dagger$ and $\hat{c}_n$ operators (Eqs. (5b) and (5c)) and re-expresses these operators in $\hat{\eta}_k^\dagger$ and $\hat{\eta}_k$ operators using the inverse of the Bogoliubov transformation Eq. (12). Alternatively, using the invariance of the trace $\mathrm{tr}\hat{H}$ under canonical transformations, one may derive[20]

$$\Omega_0 = \frac{1}{2} \left( \sum_{n=1}^N \omega_n - \sum_{k=1}^N \Omega_k \right).  \tag{17}$$

We note finally that to lowest (second) order in $\hat{H}_{nr}$ the ground state energy corresponds to the ground state van der Waals interaction between the molecules.

As in the HLA, the excited states follow by operating with a string of one-particle creation operators on the ground state,

$$|k_1, \ldots, k_\nu\rangle = \hat{\eta}_{k_1}^\dagger \ldots \hat{\eta}_{k_\nu}^\dagger |0\rangle,  \tag{18}$$

($k_1 > k_2 > \cdots > k_\nu$ by convention) and have energies given by the sum of the corresponding one-particle energies (cf. Eq. (10)). Because the number of molecular excitations is no longer conserved, we cannot refer to these eigenstates as "$\nu$-exciton" states. Instead, a new type of fermions is conserved and we will simply refer to the new excited states as *$\nu$-particle* states. As in practice it is impossible to expand the ground state in the site representation, such an expansion also is impossible for the multi-particle states.

We also note that from this general diagonalization, the eigenstates and energies within the HLA are readily recovered. In that case, we set $\mathbf{B} = 0$, so that $\varphi_{km}$ and $\Omega_k^2$ are eigenvectors and eigenvalues of $\mathbf{A}^2$. Thus, the $\Omega_k$ reduce to $\Omega_k^{HL}$ and $\psi_{km}$ and $\varphi_{km}$ both can be chosen equal to $\phi_{km}$, so that $\hat{\eta}_k^\dagger$ reduces to $\hat{\xi}_k^\dagger$. Also, by using Eq. (17) and the fact that $\Sigma_k \Omega_k = \mathrm{tr}\mathbf{A} = \Sigma_n \omega_n$, the ground state energy is then indeed found to vanish.

## III. TRANSITION DIPOLES

### A. General formalism

We now address the general problem of how to calculate transition dipoles between arbitrary multi-particle states. Together with the particle energies that were discussed in Section II, this in principle suffices to calculate any optical observable.

If the aggregate is small compared to an optical wavelength, its interaction with external electromagnetic fields is determined by its total dipole operator, which reads

$$\hat{\mathbf{P}} = \sum_{n=1}^N \boldsymbol{\mu}_n (\hat{b}_n^\dagger + \hat{b}_n).  \tag{19}$$

We are interested in the general matrix elements

$$\langle k_1, \ldots, k_\nu | \hat{\mathbf{P}} | k_1', \ldots, k_{\nu'}' \rangle.  \tag{20}$$

The problem in calculating these matrix elements arises from the fact that $\hat{\mathbf{P}}$ is a many-particle operator in the basis of the eigenstates, which becomes clear when the inverse Jordan-Wigner transformation is substituted into Eq. (19).

We first briefly discuss the HLA. Then, the selection rule $\nu - \nu' = \pm 1$ is obvious: optical transitions are only allowed between states in two adjacent multi-exciton bands. As a result, only one-exciton states are visible in linear absorption, while one- and two-exciton states determine the third-order optical response. Apart from this selection rule, another simplifying circumstance in the HLA is that the multi-exciton states can be expanded in the site representation, on which $\hat{\mathbf{P}}$ in its representation Eq. (19) acts in a simple way. Using this, the dipole matrix elements in the HLA can be expressed in sums over products of two Slater determinants. For the detailed form of this expression, we refer to the literature.[23,24]

We next consider the general case, where the HLA is relaxed. First, as all exciton bands with $\nu$ even mutually mix and similarly for those with $\nu$ odd, the only selection that is left is $\nu - \nu' = $ odd. Thus, for example, not only one-particle states, but also three-particle states, five-particle states, etc. are now visible in linear absorption. A second and more important complication is that, as discussed above, the ground state $|0\rangle$ is not known in the site representation. This makes it impossible to work directly with the representation Eq. (19) for $\hat{\mathbf{P}}$. Instead, we will work in the basis of eigenstates, where the matrix elements can be expressed as the vacuum expectation value of a string of operators, which may be calculated by exploiting Wick's theorem. Our procedure is analogous to the one followed by Lieb *et al.* to calculate two-spin correlation functions.[20] It should be noted, however, that our general calculation is more involved, because the transition dipoles involving higher than one-particle bands are the analogues of correlators for four spins, six spins, etc.

The general procedure starts by using Eq. (4) to write

$$\hat{b}_n^\dagger + \hat{b}_n = \prod_{j<n} \hat{A}_j \hat{B}_j \hat{A}_n,  \tag{21}$$

where

$$\hat{A}_n \equiv \hat{c}_n^\dagger + \hat{c}_n = \sum_k \varphi_{kn} (\hat{\eta}_k^\dagger + \hat{\eta}_k),  \tag{22a}$$

$$\hat{B}_n \equiv \hat{c}_n^\dagger - \hat{c}_n = \sum_k \psi_{kn} (\hat{\eta}_k^\dagger - \hat{\eta}_k).  \tag{22b}$$

The operators $\hat{A}_n$ and $\hat{B}_n$ obey the anticommutation relations

$$\{\hat{A}_n, \hat{A}_m\} = -\{\hat{B}_n, \hat{B}_m\} = 2\delta_{nm}, \quad \{\hat{A}_n, \hat{B}_m\} = 0.  \tag{23}$$

Now the matrix element Eq. (20) can be written as

$$\langle k_1, \ldots, k_\nu | \hat{\mathbf{P}} | k_1', \ldots, k_{\nu'}' \rangle$$

$$= \sum_n \boldsymbol{\mu}_n \langle 0 | \hat{\eta}_{k_\nu} \hat{\eta}_{k_{\nu-1}} \cdots \hat{\eta}_{k_1} \left( \prod_{j<n} \hat{A}_j \hat{B}_j \right)$$

$$\times \hat{A}_n \hat{\eta}_{k_1'}^\dagger \cdots \hat{\eta}_{k_{\nu'}'}^\dagger | 0 \rangle. \tag{24}$$

Because all operators in this expression obey anticommutation relations, the vacuum expectation values $\langle 0 | \ldots | 0 \rangle$ can be evaluated using Wick's theorem.[25] Thus, the expectation value is broken down into products of vacuum expectation values of pairs of operators, where the sum over all pairings is taken.

The various relevant pair expectation values are easily obtained by rewriting the $\hat{A}_n, \hat{B}_n$ operators in terms of the $\hat{\eta}_k, \hat{\eta}_k^\dagger$ operators. We then find

$$\langle \hat{A}_n \hat{A}_m \rangle = -\langle \hat{B}_n \hat{B}_m \rangle = \delta_{nm}, \tag{25a}$$

$$\langle \hat{B}_n \hat{A}_m \rangle = -\sum_k \psi_{kn} \varphi_{km} \equiv G_{n,m}, \tag{25b}$$

$$\langle \hat{\eta}_k \hat{A}_n \rangle = \langle \hat{A}_n \hat{\eta}_k^\dagger \rangle = \varphi_{kn}, \tag{25c}$$

$$\langle \hat{\eta}_k \hat{B}_n \rangle = -\langle \hat{B}_n \hat{\eta}_k^\dagger \rangle = \psi_{kn}, \tag{25d}$$

$$\langle \hat{\eta}_k \hat{\eta}_{k'}^\dagger \rangle = \delta_{kk'}. \tag{25e}$$

Here $\langle \hat{\mathcal{O}}_1 \hat{\mathcal{O}}_2 \rangle$ is short for $\langle 0 | \hat{\mathcal{O}}_1 \hat{\mathcal{O}}_2 | 0 \rangle$, $\hat{\mathcal{O}}_i$ being an arbitrary operator. Finally, any pair expectation value with an $\hat{\eta}_k^\dagger$ as first operator or an $\hat{\eta}_k$ as second one vanishes.

To finish the general formalism, we consider sum rules. The total oscillator strength of *all* transitions between multiparticle states obeys the sum rule

$$\frac{1}{2} \sum_{i,f} |\langle i | \hat{\mathbf{P}} | f \rangle|^2 = \frac{1}{2} \operatorname{tr}(|\hat{\mathbf{P}}|^2) = 2^{N-1} \sum_{n=1}^N \boldsymbol{\mu}_n^2, \tag{26}$$

where $i$ and $f$ run over all eigenstates and the last step is made by calculating the trace in the site representation. This sum rule holds independent of the value of the molecular transition frequencies, the interaction matrix elements, and of the application of the HLA.

In the HLA, additional sum rules exist between pairs of adjacent exciton bands. For instance, the total oscillator strength between the ground state and all one-exciton states is given by

$$\sum_k |_{\text{HL}} \langle 0 | \hat{\mathbf{P}} | k \rangle_{\text{HL}}|^2 = \sum_n \boldsymbol{\mu}_n^2. \tag{27}$$

If the HLA is relaxed, a similar sum rule for the oscillator strength to the one-particle states does not hold, which implies that the total absorption strength in the energy region close to the single-molecule resonance in principle is not a conserved quantity. In Section VI, we will see that for J aggregates ($J < 0$), the oscillator strength to the one-particle states grows with the strength of the interaction.

## B. Examples

Here we will give explicit expressions for three types of transition dipoles that are of particular interest: those between (1) the ground state and the one-particle states, (2) the ground state and the three-particle states, and (3) the one-particle and the two-particle states. The use of Wick's theorem for these examples involves straightforward, though tedious, combinatorial algebra. For transition dipoles involving more particles the algebra gets very involved.

In all cases, it is useful to define the $(n-1) \times n$ matrix

$$\mathscr{G}(n) = \begin{pmatrix} G_{1,1} & \cdots & G_{n-1,1} \\ \vdots & & \vdots \\ G_{1,n} & \cdots & G_{n-1,n} \end{pmatrix}, \tag{28}$$

the $n$-dimensional column vector

$$\Phi_k(n) = \begin{pmatrix} \varphi_{k,1} \\ \vdots \\ \varphi_{k,n} \end{pmatrix}, \tag{29}$$

and the $(n-1)$-dimensional row vector

$$\Psi_k(n) = (\psi_{k,1} \ldots \psi_{k,n-1}). \tag{30}$$

Here, $G_{n,m}$ is as defined in Eq. (25b), and $\varphi_{kn}$ and $\psi_{kn}$ are the eigenvector components defined in Section II.

The transition dipole between the ground state and the one-particle state $|k\rangle$ may then be written as

$$\langle 0 | \hat{\mathbf{P}} | k \rangle = \sum_{n=1}^N \boldsymbol{\mu}_n | \Phi_k(n) \mathscr{G}(n) |, \tag{31}$$

where $|\Phi_k(n) \mathscr{G}(n)|$ denotes the determinant of the $n \times n$ matrix with $\Phi_k(n)$ as first column and the columns of $\mathscr{G}(n)$ as columns $2, 3, \ldots, n$. If $\hat{H}_{\text{nr}}$ is neglected, Eq. (31) properly reduces to the well-known expression

$$_{\text{HL}} \langle 0 | \hat{\mathbf{P}} | k \rangle_{\text{HL}} = \sum_{n=1}^N \boldsymbol{\mu}_n \phi_{kn}, \tag{32}$$

because in that case $\varphi_{kn} = \psi_{kn} = \phi_{kn}$, so that $|\Phi_k(n) \mathscr{G}(n)| = \phi_{kn}$.

We now turn to the transition dipole between the ground state and states in the three-particle band. Such transitions are not allowed in the HLA. In the presence of the nonresonant interaction $\hat{H}_{\text{nr}}$, however, they have finite oscillator strengths, which is most easily understood within a perturbative picture. To lowest order in $\hat{H}_{\text{nr}}$, the ground state in the HLA gets a small mixture with the two-exciton states and, similarly, the three-exciton states mix with the one-excitons. Thus, the allowed transitions from the ground state to the one excitons, the two-excitons to the three-excitons, and the one excitons to the two-excitons all lend oscillator strength to transitions between the ground state and three-particle states. It is not straightforward to actually calculate the dipole using this perturbative picture, as that turns out to require second-order degenerate perturbation theory for the wave functions.

Carrying out the combinatorial algebra generated by Wick's theorem, we eventually find the following exact expression for the transition dipole:

$$\langle 0|\hat{\mathbf{P}}|k_1 k_2 k_3\rangle = \sum_{n=2}^{N} \boldsymbol{\mu}_n \left\{ \begin{vmatrix} 0 & 0 & \Psi_{k_2}(n) \\ \Phi_{k_1}(n) & \Phi_{k_3}(n) & \mathscr{G}(n) \end{vmatrix} \right.$$

$$+ \begin{vmatrix} 0 & 0 & \Psi_{k_1}(n) \\ \Phi_{k_3}(n) & \Phi_{k_2}(n) & \mathscr{G}(n) \end{vmatrix}$$

$$+ \left. \begin{vmatrix} 0 & 0 & \Psi_{k_3}(n) \\ \Phi_{k_2}(n) & \Phi_{k_1}(n) & \mathscr{G}(n) \end{vmatrix} \right\}, \quad (33)$$

where $|\ldots|$ are the determinants of the $(n+1) \times (n+1)$ matrices built up from $\mathscr{G}(n), \Phi_{k_i}(n)$ and $\Psi_{k_j}(n)$ as indicated. If $\hat{H}_{\mathrm{nr}}$ is neglected, Eq. (33) can be re-expressed as the sum of six $n \times n$ determinants that cancel each other, thus showing proper reduction of the general expression to the HLA.

We finally discuss the dipoles between one- and two-particle states. These transitions are important in all third-order nonlinear optical experiments,[24] and are particularly crucial in weak-intensity pump-probe experiments.[8] Evaluating Eq. (24) for these transitions, we obtain the following general expression for their dipoles:

$$\langle k|\hat{\mathbf{P}}|k_1 k_2\rangle = \sum_{n=1}^{N} \boldsymbol{\mu}_n \left\{ \begin{vmatrix} -\delta_{k_1 k} & -\delta_{k_2 k} & \Psi_k(n) \\ \Phi_{k_1}(n) & \Phi_{k_2}(n) & \mathscr{G}(n) \end{vmatrix} \right.$$

$$+ \begin{vmatrix} 0 & 0 & \Psi_{k_2}(n) \\ \Phi_{k_1}(n) & \Phi_k(n) & \mathscr{G}(n) \end{vmatrix}$$

$$+ \left. \begin{vmatrix} 0 & 0 & \Psi_{k_1}(n) \\ \Phi_k(n) & \Phi_{k_2}(n) & \mathscr{G}(n) \end{vmatrix} \right\}. \quad (34)$$

When $\hat{H}_{\mathrm{nr}}$ is neglected, Eq. (34) properly reduces to

$$_{\mathrm{HL}}\langle k|\hat{\mathbf{P}}|k_1 k_2\rangle_{\mathrm{HL}} = \sum_{\substack{n,m=1 \\ m<n}}^{N} \boldsymbol{\mu}_n (\phi_{km} + \phi_{kn})$$

$$\times (\phi_{k_1 m} \phi_{k_2 n} - \phi_{k_1 n} \phi_{k_2 m}), \quad (35)$$

which is the well-known expression for this transition within the HLA.[26]

## IV. THE BOSE APPROXIMATION

As discussed in Section I, the effects of $\hat{H}_{\mathrm{nr}}$ have been investigated previously within the Bose approximation, where the paulions are replaced by bosons, i.e., the term $2\hat{b}_n^\dagger \hat{b}_n$ in Eq. (1) is neglected, and the kinematic interaction is also ignored. This approximation, which in fact allows for multiple excitations on each molecule, is usually argued to be good if the excitation density is low, particularly for the linear optical response.[5,6]

To avoid confusion, we will denote the Bose operators by $\hat{d}_n^\dagger$ and $\hat{d}_n$. The Hamiltonian Eq. (2) may then be written

$$\hat{H}^{\mathrm{B}} = \hat{H}_{\mathrm{HL}}^{\mathrm{B}} + \hat{H}_{\mathrm{nr}}^{\mathrm{B}}, \quad (36a)$$

$$\hat{H}_{\mathrm{HL}}^{\mathrm{B}} = \sum_{n,m} A_{nm} \hat{d}_n^\dagger \hat{d}_m, \quad (36b)$$

$$\hat{H}_{\mathrm{nr}}^{\mathrm{B}} = \frac{1}{2} \sum_{n,m} C_{nm} (\hat{d}_n^\dagger \hat{d}_m^\dagger + \hat{d}_m \hat{d}_n), \quad (36c)$$

with the matrix $\mathbf{A}$ as before (see Eq. (6a)) and $\mathbf{C}$ the real and symmetric matrix with components

$$C_{nm} = J_n \delta_{m,n+1} + J_{n-1} \delta_{m,n-1}. \quad (37)$$

In the HLA $\mathbf{C}$ is neglected and the same transformation that diagonalized the Hamiltonian in the HLA of the full paulion theory also now diagonalizes the problem (cf. Eqs. (7) and (8)). We thus have

$$\hat{H}_{\mathrm{HL}}^{\mathrm{B}} = \sum_{k=1}^{N} \Omega_k^{\mathrm{HL}} \hat{\chi}_k^\dagger \hat{\chi}_k, \quad (38)$$

with

$$\hat{\chi}_k^\dagger = \sum_{n=1}^{N} \phi_{kn} \hat{d}_n^\dagger, \quad (39)$$

where $\Omega_k^{\mathrm{HL}}$ and $\phi_{kn}$ are as defined in Section II. The difference from Section II is that now we have noninteracting *bosons* as collective excitations, i.e., $[\hat{\chi}_k, \hat{\chi}_{k'}^\dagger] = \delta_{kk'}$. Thus, multiple excitations of each $k$-mode are allowed and multi-exciton states may be constructed by operating with an arbitrary string of $\hat{\chi}^\dagger$ operators on $|0\rangle_{\mathrm{HL}}$. Clearly, the one-excitons are identical to those in Section II, which means that for the linear optics within the HLA the Bose approximation does not cause additional errors. The new multi-exciton states, however, do differ from the Pauli case, which implies that the nonlinear optical response is different. In fact, the nonlinear optical response vanishes identically within the Bose approximation (irrespective of the HLA), as the system has been reduced to a set of harmonic oscillators. We finally note that the transition dipoles in the Bose approximation are easy to evaluate, as the dipole operator is not a many-boson operator, but is simply given by

$$\hat{\mathbf{P}} = \sum_n \boldsymbol{\mu}_n (\hat{d}_n^\dagger + \hat{d}_n) = \sum_k \left( \sum_n \boldsymbol{\mu}_n \phi_{kn} \right) (\hat{\chi}_k^\dagger + \hat{\chi}_k). \quad (40)$$

If we do not make the HLA, but keep the nonresonant interaction Eq. (36c), the diagonalization of $\hat{H}^{\mathrm{B}}$ to noninteracting bosons can be performed by a Bogoliubov transformation in a way completely analogous to fermions.[20,21] This leads to

$$\hat{H}^{\mathrm{B}} = \Omega_0^{\mathrm{B}} + \sum_{k=1}^{N} \Omega_k^{\mathrm{B}} \hat{\zeta}_k^\dagger \hat{\zeta}_k, \quad (41)$$

where $\Omega_k^{\mathrm{B}}$ $(k=1,\ldots,N)$ denote the one-boson energies, $\Omega_0^{\mathrm{B}}$ is the energy of the ground state $|0\rangle_{\mathrm{B}}$, and $\hat{\zeta}_k^\dagger$ is the one-boson creation operator defined by

$$\hat{\zeta}_k^\dagger = \frac{1}{2} \sum_{n=1}^{N} [(\alpha_{kn} + \beta_{kn})\hat{d}_n^\dagger + (\alpha_{kn} - \beta_{kn})\hat{d}_n]. \quad (42)$$

Here $\beta_{kn}$ and $\Omega_k^{\mathrm{B}}$ follow from the generalized $N \times N$ eigenvalue problem

$$\sum_{m=1}^{N} \beta_{km}[(\mathbf{A}+\mathbf{C})]_{mn} = (\Omega_k^B)^2 \sum_{m=1}^{N} \beta_{km}[(\mathbf{A}-\mathbf{C})^{-1}]_{mn}, \tag{43}$$

and the $\alpha_{kn}$ follow from

$$\sum_{m=1}^{N} \alpha_{km}(\mathbf{A}-\mathbf{C})_{mn} = \Omega_k^B \beta_{kn}. \tag{44}$$

As $\mathbf{A}+\mathbf{C}$ is real and symmetric and $[(\mathbf{A}-\mathbf{C})^{-1}]_{mn} = \delta_{mn}/\omega_n$ is real, symmetric, and positive definite, Eq. (43) gives real eigenvalues and the $\alpha_{km}$ and $\beta_{km}$ can also be chosen real. In fact, from Eq. (44) it follows immediately that

$$\alpha_{km} = \frac{\Omega_k^B}{\omega_m} \beta_{km}. \tag{45}$$

Using this relation, the inverse Bogoliubov transformation reads

$$\hat{d}_n^\dagger = \frac{1}{2\omega_n} \sum_k \beta_{kn}[(\Omega_k^B+\omega_n)\hat{\zeta}_k^\dagger + (\Omega_k^B-\omega_n)\hat{\zeta}_k]. \tag{46}$$

Finally, the canonical nature of the Bogoliubov transformation now imposes the orthogonality relations

$$\sum_n \frac{1}{\omega_n} \beta_{kn}\beta_{k'n} = \frac{1}{\Omega_k^B} \delta_{kk'}, \tag{47a}$$

$$\sum_k \Omega_k^B \beta_{kn}\beta_{km} = \omega_m \delta_{nm}. \tag{47b}$$

The eigenvalues and eigenvectors differ in general from the exact treatment in Section II, which shows that if we go beyond the HLA, the Bose approximation is not even exact for the *linear* optical regime.

In analogy to Eq. (16), one finds for the ground state energy in the Bose approximation the negative value[21]

$$\Omega_0^B = -\sum_k \Omega_k^B \sum_n \frac{1}{4} \left(\frac{\Omega_k^B-\omega_n}{\omega_n}\right)^2 \beta_{kn}^2. \tag{48}$$

Finally, the transition dipoles in the Bose approximation can be evaluated much more easily than in the full theory of Sections II and III, as now the dipole operator is not a many-particle operator. The matrix elements are easily constructed from

$$\hat{\mathbf{P}} = \sum_n \boldsymbol{\mu}_n(\hat{d}_n^\dagger + \hat{d}_n) = \sum_k \left(\sum_n \boldsymbol{\mu}_n\beta_{kn}\right)(\hat{\zeta}_k^\dagger + \hat{\zeta}_k), \tag{49}$$

from which it is evident that, in contrast to Section III, now only transitions between adjacent multi-particle bands are allowed: $\hat{\mathbf{P}}$ can only induce transitions between states where the occupation of exactly one boson mode is increased or decreased by one quantum. The simplest example is the transition from the ground state to a one-particle state, which has a transition dipole

$$_B\langle 0|\hat{\mathbf{P}}|k\rangle_B = \sum_n \boldsymbol{\mu}_n\beta_{kn}. \tag{50}$$

Dipoles involving higher adjacent bands are equally straightforward to calculate, but they are not very interesting, since the Bose approximation is not suited to describe multi-particle states accurately.

## V. EXPLICIT EXPRESSIONS FOR HOMOGENEOUS CHAINS

We now consider the homogeneous chain, for which all molecular transition frequencies, transition dipoles, and interaction matrix elements are equal ($\omega_n = \omega_0$; $\boldsymbol{\mu}_n = \boldsymbol{\mu}; J_n = J$). For this case the various diagonalizations needed to evaluate the exact theory, the HLA, and the Bose approximation are known. The case of the HLA is particularly well-known: the transformation that diagonalizes the matrix $\mathbf{A}$ (identical for paulions and bosons) for homogeneous chains, has normalized coefficients

$$\phi_{kn} = \sqrt{\frac{2}{N+1}} \sin\frac{k\pi n}{N+1}, \tag{51}$$

and gives for the one-particle energies

$$\Omega_k^{HL} = \omega_0 + 2J \cos\frac{k\pi}{N+1}. \tag{52}$$

Here, as always, $k=1,2,\ldots,N$.

In the Bose approximation *with* nonresonant interactions ($\hat{H}_{nr}$), the transformation for the homogeneous case is very similar to that of the HLA. It has coefficients

$$\alpha_{kn} = \frac{\Omega_k^B}{\omega_0} \beta_{kn} = \sqrt{\frac{\Omega_k^B}{\omega_0}} \sqrt{\frac{2}{N+1}} \sin\frac{k\pi n}{N+1}, \tag{53}$$

and leads to one-particle energies given by

$$\Omega_k^B = \left(\omega_0^2 + 4\omega_0 J \cos\frac{k\pi}{N+1}\right)^{1/2}. \tag{54}$$

The ground state energy Eq. (48) reduces to

$$\Omega_0^B = \frac{1}{2} \left(\sum_k \Omega_k^B - N\omega_0\right), \tag{55}$$

which cannot be evaluated further in analytical form.

We discuss, finally, the exact case, where we use neither the HLA nor the Bose approximation. The diagonalization for the homogeneous chain can be found in Ref. 20. For $|2J|/\omega_0 < 1$, the transformation coefficients are given by

$$\varphi_{kn} = A_k \sin[(N+1-n)q(k)], \tag{56a}$$

$$\psi_{kn} = A_k\delta_k \sin[nq(k)], \tag{56b}$$

while the one-particle energies read

$$\Omega_k = (\omega_0^2 + 4\omega_0 J \cos[q(k)] + 4J^2)^{1/2}. \tag{57}$$

Here, $q(k)$ is the $k$th root ($k=1,2,\ldots,N$), in ascending order within the interval $0 < q(k) < \pi$, of the equation

$$\frac{\sin[(N+1)q(k)]}{\sin[Nq(k)]} = -\frac{2J}{\omega_0}, \tag{58}$$

and $\delta_k$ is the sign of $\sin q(k)/\sin[Nq(k)]$. From straightforward analysis it follows that $\delta_k=(-1)^{k+1}$. $A_k$ denotes the $k$-dependent normalization factor

$$A_k=2\{2N+1-\sin[(2N+1)q(k)]/\sin[q(k)]\}^{-1/2}. \tag{59}$$

Finally, the ground state energy Eq. (17) simplifies to

$$\Omega_0=\frac{1}{2}\left(N\omega_0-\sum_k\ \Omega_k\right), \tag{60}$$

whose form has a subtle difference from Eq. (55).

We note that for $J/\omega_0\to 0$, $q(k)\to k\pi/(N+1)$, so that the quantum numbers and the one-particle energies of the HLA are correctly recovered. In fact, for $|J/\omega_0|\ll 1$ and (or) $N\gg k$, it is easily shown that

$$q(k)-\frac{\pi k}{N+1}\approx\frac{2J}{\omega_0}\frac{\pi k}{(N+1)^2}. \tag{61}$$

We also note that in the case of J aggregates ($J<0$) the one-particle energies always increase monotonously with $k$, so that $k=1$ corresponds to the lowest energy. This is true in the HLA, the Bose approximation, and the exact theory. For H aggregates ($J>0$), the opposite holds.

To end this section, we discuss the optical selection rules that follow from the inversion symmetry with respect to the chain center for homogeneous chains. For the Bose approximation, the consequences of this symmetry are easiest to see. Combining Eq. (40) with Eq. (51) or Eq. (49) with Eq. (53) and using $\boldsymbol{\mu}_n=\boldsymbol{\mu}$, one finds immediately that only bosons with $k$ odd can be optically excited. Thus, in the Bose approximation any interaction between the homogeneous chain and a photon can only lead to the addition or loss of one boson with odd $k$ value. Within the field of linear optics, this selection rule is well known.

The selection rules for the exact case (paulions) are more complicated to derive due to the many-particle nature of the dipole operator. Below, we will treat the most general situation (including $\hat{H}_{\mathrm{nr}}$), from which the HLA follows directly.

We start by defining the inversion operator $\Pi$ with respect to the center of the chain. It transforms the Pauli operators as

$$\Pi\hat{b}_n^\dagger\Pi^\dagger=\hat{b}_{N+1-n}^\dagger. \tag{62}$$

For a homogeneous chain, the Hamiltonian is obviously invariant under inversion, which means that the eigenstates have definite parity with respect to it: $\Pi\Psi\Pi^\dagger=\pm\Psi$, with $\Psi$ the wave function for an arbitrary eigenstate. Furthermore, from Eq. (19) with $\boldsymbol{\mu}_n=\boldsymbol{\mu}$, it is obvious that $\Pi\hat{\mathbf{P}}\Pi^\dagger=\hat{\mathbf{P}}$, in other words, transition dipoles only exist between states of equal parity.

To evaluate the parity of an arbitrary multi-particle state, we consider

$$\Pi\hat{\eta}_{k_1}^\dagger\ldots\hat{\eta}_{k_\nu}^\dagger|0\rangle=\Pi\hat{\eta}_{k_1}^\dagger\Pi^\dagger\Pi\ldots\Pi\hat{\eta}_{k_\nu}^\dagger\Pi^\dagger\Pi|0\rangle. \tag{63}$$

By rewriting the $\hat{\eta}^\dagger$ operators in terms of Pauli operators ($\hat{b}_n^\dagger$ and $\hat{b}_n$) and using Eq. (62) and the symmetry properties for the pair of coefficients $\varphi_{kn}$ and $\psi_{kn}$ (Eqs. (56a) and (56b)), we find

$$\Pi\hat{\eta}_k^\dagger\Pi^\dagger=\hat{\eta}_k^\dagger(-1)^{k+1+\hat{\nu}}=(-1)^{k+\hat{\nu}}\hat{\eta}_k^\dagger, \tag{64}$$

where $\hat{\nu}$ is the operator for the number of molecular excitations, as defined in Section II. It must be noted that, even though in general the multi-particle states are not eigenstates of $\hat{\nu}$, they are eigenstates (with eigenvalues $\pm 1$) of the operator $(-1)^{\hat{\nu}}$, because $\hat{H}_{\mathrm{nr}}$ does not mix odd exciton bands with even ones. Also, $(-1)^{\hat{\nu}}$ anticommutes with the single-particle creation operators, as is clear from Eq. (64).

Combining Eqs. (63) and (64), we then finally find for the parity of the state $|k_1,k_2,\ldots,k_\nu\rangle$ the value

$$(-1)^{\sum_{i=1}^\nu k_i+\nu(\nu+1)/2}p_0\nu_0^\nu. \tag{65}$$

Here $p_0$ is the parity of the ground state and $\nu_0$ is the eigenvalue of the ground state under the operator $(-1)^{\hat{\nu}}$. It is obvious that, for all cases of practical interest, the ground state has a strong admixture from the state in which all molecules are in their ground state, which fixes both $p_0$ and $\nu_0$ at $+1$. Thus, we finally find that, for the homogeneous chain, the transition dipole Eq. (20) is only nonzero if

$$\sum_{i=1}^\nu k_i-\sum_{i=1}^{\nu'}k_i'+\frac{1}{2}[\nu(\nu+1)-\nu'(\nu'+1)]=\text{even}. \tag{66}$$

Otherwise, the transition is symmetry forbidden. This selection rule also holds if we restrict ourselves to the HLA. Furthermore, let us recall that on top of this the selection rule $\nu-\nu'=$ odd holds (general theory) or $\nu-\nu'=\pm 1$ (HLA).

An immediate consequence of the selection rule Eq. (66) is that starting from the ground state, only one-particle states with $k=$ odd can be excited optically. Similarly, the three-particle states that are dipole allowed from the ground state have $k_1+k_2+k_3=$ even, whereas the transition from the state $|k\rangle$ to the state $|k_1,k_2\rangle$ is allowed only if $k_1+k_2-k=$ even.

## VI. RESULTS AND DISCUSSION

Let us now analyze the formal results obtained above. First, we give a qualitative picture of the differences in the (multi-) particle energy level schemes for the four different approaches that we considered: the theory that recognizes the full paulion nature of the excitations, both in and beyond the HLA, and the Bose approximation, again both in and beyond the HLA. Figure 1 gives a schematic representation of the various energy level schemes for the simple case of a homogeneous dimer. First, we consider the full paulion theory, where four eigenstates occur. Within the HLA of this theory, the ground state has energy zero, two one-exciton states exist ($|k=1\rangle$ and $|k=2\rangle$) with energies $\omega_0\pm J$, and one two-exciton state exists ($|k_1=2, k_2=1\rangle$), with energy $2\omega_0$ (both molecules excited). If we include the nonresonant interactions (exact theory), the ground state shifts downward and the two-exciton state shifts upward. The one-excitons are not
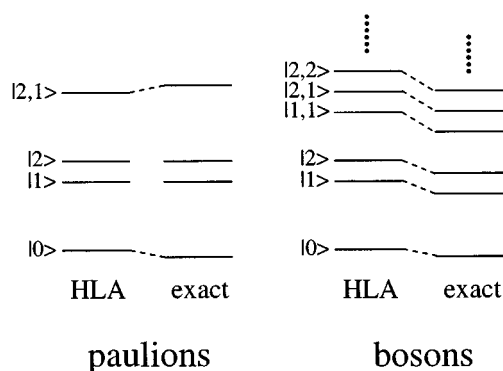
FIG. 1. Energy level diagrams of a homogeneous dimer for the four different approaches considered in this article (see the text). For clarity, the shifts due to the nonresonant interactions have been drawn unrealistically large.



FIG. 2. Deviation of the exact quantum number $q(k)$ from the HLA value $\pi k/(N+1)$ for $2J/\omega_0 = -0.13$ and $N=15$.

affected, as there are no three-excitons, five-excitons, etc. to which they couple. In the Bose approximation within the HLA, the ground state and the one-excitons are identical to the paulion theory. The new aspect is that, in addition to the two-exciton state $|k_1=2, k_2=1\rangle$, two (unphysical) states $|k_1=1, k_2=1\rangle$ and $|k_1=2, k_2=2\rangle$ also exist, because multiple excitations of the same exciton are allowed in the Bose approximation. In fact, infinitely many higher multiply excited states exist (indicated by the dots). If we relax the HLA in the Bose approximation, the ground state shifts downward, and so do the one-excitons (as now they do couple to triply excited states). The two-excitons also shift downward.

We now move to a quantitative analysis of our formal results. In order not to convolute effects of disorder with effects of the HLA, we will only consider homogeneous chains (some aspects of disorder will be addressed in Section VII). We will mostly work with two values of the parameter $2J/\omega_0$, which determines the relative importance of $\hat{H}_{\mathrm{nr}}$ (see Eq. (58)), namely $2J/\omega_0 = -0.07$ and $2J/\omega_0 = -0.13$. These values are appropriate for J aggregates of PIC and TDBC, respectively (see Section I). A third well-studied aggregate forming dye is BIC, which has a $2J/\omega_0$ value between those for PIC and TDBC.[27] Whenever a special value for the chain length is needed, we will choose $N=50$ for PIC (this is the exciton delocalization length for these aggregates in a low temperature glassy host[7,9]) and $N=15$ for TDBC (the delocalization in a room temperature solution[12]).

We first consider the quantum number $q(k)$, obtained by numerically solving Eq. (58). The deviation of $q(k)$ from the value $\pi k/(N+1)$ is partially responsible for the difference in the one-particle energies of the HLA and the exact theory, as is clear from Eqs. (52) and (57). Figure 2 presents this deviation for $2J/\omega_0 = -0.13$ and $N=15$ and clearly shows that the exact quantum numbers differ little from the ones in the HLA (cf. Eq. (61)).

Before showing how this translates into differences in the one-particle energies, we consider the ground state energy. Although this quantity is not observable in optical experiments, it is illustrative to present some results. Figure 3 presents the ground state energy as a function of the chain
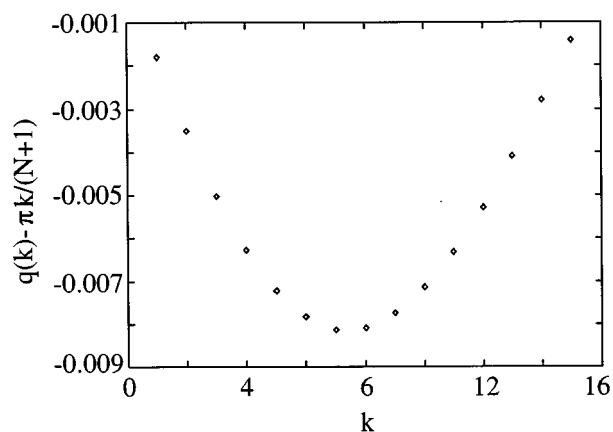
length for the two standard values of $2J/\omega_0$, according to the exact theory (Eq. (60)) and the Bose approximation (Eq. (55)). We recall that in the HLA the ground state energy vanishes. Figure 3 clearly demonstrates that the ground state energy is lowered appreciably if we account for $\hat{H}_{\mathrm{nr}}$; the typical corrections are of the order of 1%–10% of the molecular transition frequencies. Yet, the differences between the corrections in the exact treatment and within the Bose approximation are small ($\ll 1\%$). It is also seen that the ground state energy decreases linearly with the chain length. This may be understood from the following: for weak coupling, the total ground state energy is the sum of the Van der Waals interactions between neighboring molecules in the chain. This interaction is given by the second order (in $J/\omega_0$) correction to the ground state energy of a dimer, which in full form reads $\Omega_{0,\mathrm{dimer}} = \omega_0 - \sqrt{\omega_0^2 + J^2}$. Thus, one may expect the ground state energy to be well approximated by $(N-1)\Omega_{0,\mathrm{dimer}}$. Comparison shows that this approximation for the two values of $2J/\omega_0$ considered in Fig. 3, within
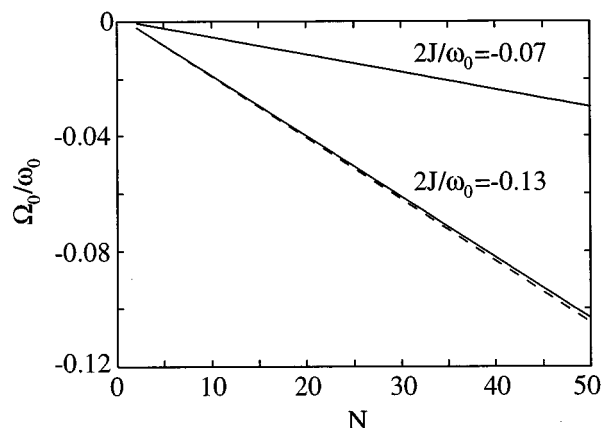


FIG. 3. The ground state energy $\Omega_0$ as a function of the chain length $N$ for two values of $2J/\omega_0$. Shown are the exact theory (solid line) and the Bose approximation (long dashed line). For $2J/\omega_0 = -0.07$ the two curves overlap. Within the HLA, $\Omega_0 = 0$.
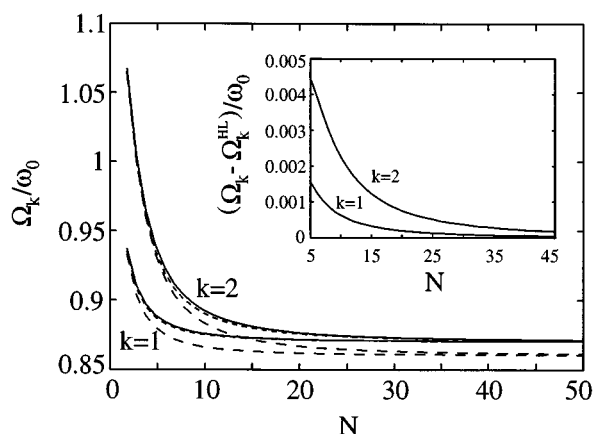
FIG. 4. The two lowest one-particle energies ($\Omega_{k=1}$ and $\Omega_{k=2}$), as a function of the chain length $N$, for a J aggregate with $2J/\omega_0 = -0.13$. Shown are the exact theory (solid line), the Bose approximation (long dashed line), and the HLA (short dashed line). The inset shows the difference between the exact theory and the HLA.
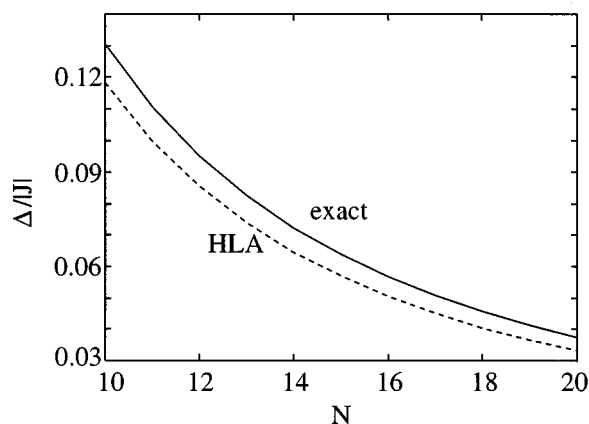


FIG. 5. Chain length dependence of the detuning $\Delta = \Omega_{k=2} - \Omega_{k=1}$ between the induced-absorption peak and the bleaching dip in the weak-intensity pump-probe spectrum of J aggregates with $2J/\omega_0 = -0.13$.

the accuracy of the plot, coincides with the exact theory for all $N$ values. In fact, this approximation holds to within 1% for interactions as strong as $2J/\omega_0 = -0.3$.

We next turn to the one-particle energies, which determine the positions of the peaks in linear and nonlinear optical spectra. These energies are easily observable as resonances in the linear absorption spectrum. Figure 4 gives $\Omega_k$ for $k=1$ and $k=2$ (the two lowest transitions for J aggregates) as a function of the chain length for $2J/\omega_0 = -0.13$. Given are the exact value (Eq. (57)), the Bose approximation (Eq. (54)), and the HLA (Eq. (52)). As is observed, the difference between the HLA and the exact theory (plotted separately in the inset) is small and vanishes for large $N$. From the asymptotic expression Eq. (61), the latter can easily be shown analytically for $N \gg k$. By contrast, the difference between the Bose approximation and the exact theory levels off at the finite value $-2J^2/\omega_0$ for large $N$. Although the relative size of this difference is not very large, its absolute value is in the order of 100 cm$^{-1}$, which is certainly not a small deviation. Figure 4 clearly demonstrates our earlier statement that even in the linear optical regime the Bose approximation does not yield exact results.

From the inset of Fig. 4, it is clearly seen that the deviation of the HLA from the exact value for the $k=2$ particle is larger than for the $k=1$ particle (this trend continues up to $k=N/2$, after which the difference decreases again). This affects the interpretation of the weak-intensity pump-probe spectrum in J aggregates. To lowest (third) order in the pulse intensities, this spectrum is dominated by a negative peak at $\Omega_{k=1}$ (bleaching of the ground state and stimulated emission of $|k=1\rangle$) and a positive feature at $\Omega_{k=2}$ (induced absorption from $|k=1\rangle$ to $|k_1=2, k_2=1\rangle$)[8,9]. The detuning $\Delta = \Omega_{k=2} - \Omega_{k=1}$ between these peaks drops with growing chain length (until a certain saturation size is reached, where other excited states become important as well) and the relation between $\Delta$ and $N$ may be used to estimate the exciton delocalization length (the effective chain length) from the

pump-probe spectrum.[8] Figure 5 shows the dependence of $\Delta$ on $N$ within the HLA ($\Delta \approx -3\pi^2 J/N^2$ for $N \gg 1$) and the exact theory for $2J/\omega_0 = -0.13$. The Bose approximation is not discussed here, as it really does not give rise to a pump-probe spectrum at all (it has a purely linear response). We observe that at the same value of $N$ and $J/\omega_0$, the exact theory predicts a larger value for $\Delta$ than does the HLA. Alternatively, we may conclude from Fig. 5 that, given an experimentally observed value for $\Delta$, the exciton delocalization length that corresponds to it in the HLA is smaller than its exact value. In particular, for the recent pump-probe experiment on TDBC, which, using the HLA, was interpreted in terms of a delocalization length of 15 molecules,[12] the exact theory would give 16 molecules. Given the many other sources for inaccuracy in these experiments and in their interpretation, this difference is hardly significant. For the case of PIC, a similar conclusion can be reached.

We now turn to an analysis of the oscillator strengths (defined as the absolute value squared of the transition dipoles) for various transitions. We first consider the transitions between the ground state and the one-particle manifold and concentrate mostly on the $k=1$ state. Within the HLA, this state is superradiant, i.e., it has an oscillator strength given by $0.81(N+1)\mu^2$ (for $N \gg 1$), where $\mu \equiv |\boldsymbol{\mu}|$.[2,26,28] As a result, this state dominates the linear absorption spectrum and has a size-enhanced spontaneous emission rate. These properties are maintained in the exact theory. Figure 6 gives $|\langle 0|\mathbf{P}|k=1\rangle|^2/[(N+1)\mu^2]$ (hereafter loosely denoted as the oscillator strength *per molecule*) as a function of the chain size for the two standard values of $2J/\omega_0$. Plotted are the HLA (which is independent of the interaction strength), the exact theory, the Bose approximation, and the results obtained by expanding the ground state and the one-particle states to first order in $\hat{H}_{\mathrm{nr}}$. We observe that inclusion of the nonresonant interaction terms even further increases the oscillator strength of this transition, with typical differences in the order of 10% for the interaction strengths considered here, independent of the chain length. This is easily under-
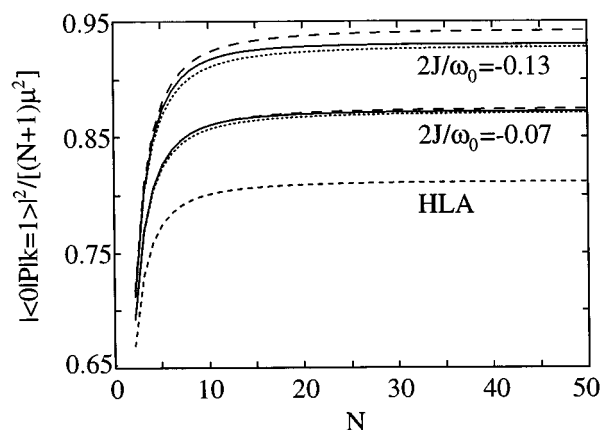
FIG. 6. Oscillator strength per molecule between the ground state and the $|k=1\rangle$ one-particle state for homogeneous aggregates, as a function of the chain length $N$. Shown are the HLA (short dashed line) and, for two values of $2J/\omega_0$, the exact theory (solid line), the Bose approximation (long dashed line), and perturbation theory (dots).
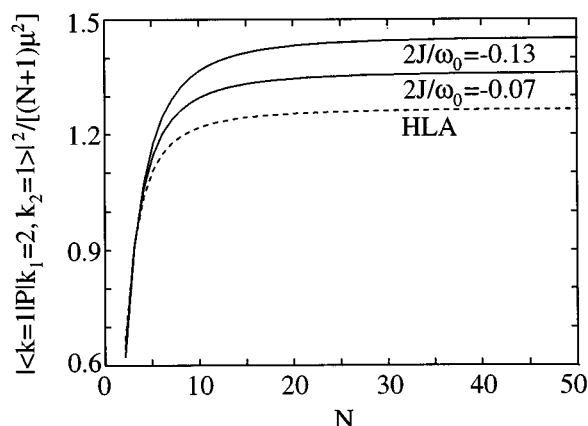


FIG. 7. Oscillator strength per molecule between the $|k=1\rangle$ one-particle state and $|k_1=2, k_2=1\rangle$ two-particle state, as a function of the chain length $N$. Shown are the HLA (dashed line) and, for two values of $2J/\omega_0$, the exact theory (solid line).

stood from the perturbation expansion in $\hat{H}_{nr}$, which yields,

$$|\langle 0|\hat{\mathbf{P}}|k\rangle|^2 = \left(1 - \frac{2J}{\omega_0}\right)|_{HL}\langle 0|\hat{\mathbf{P}}|k\rangle_{HL}|^2 + O\left(\frac{J}{\omega_0}\right)^2. \quad (67)$$

This expression shows that, for J aggregates ($J<0$), the nonresonant interaction terms increase the oscillator strength of the one-particle states by a relative amount $-2J/\omega_0$, independent of the chain length and also independent of $k$. In fact, this expression is even independent of the presence of diagonal disorder. This relative change is clearly confirmed by the plot. We also observe little difference between exact theory and perturbation theory, where it should be noted that the plotted perturbation curve is not just Eq. (67), but also contains second-order contributions from the cross products of the first-order wave functions. The Bose approximation gives a slightly larger deviation from the exact theory, but is still close to it.

From the above, it is also clear that the total oscillator strength between the ground state and the one-particle band approximately equals $(1-2J/\omega_0)N\mu^2$, which (for J aggregates) is larger than the usual sum rule in the HLA. In Section III.A, we already mentioned that if we go beyond the HLA, no exact sum rules exist between adjacent particle bands.

We comment finally on how our findings affect the interpretation of experiments. Comparing the superradiant emission rate to the single-molecule decay rate is a well-known means by which to estimate the exciton delocalization length.[1,7] From the above, we conclude that the usual HLA analysis of the experiments gives a relative error in the order of $2J/\omega_0$ in the thus estimated delocalization length.

We next turn to the transitions between the one- and the two-particle manifolds. The conclusions here are very similar to those for the ground state to the one-particle band. As an illustration, Fig. 7 gives the oscillator strength (per molecule) of the superradiant $|k=1\rangle$ to $|k_1=2, k_2=1\rangle$ transition

as a function of the chain length. Shown are the HLA and the exact theory for the two standard values of $2J/\omega_0$. It may again be derived that, to lowest order in $J/\omega_0$, the exact value differs by a relative amount $-2J/\omega_0$ from the HLA (cf. Eq. (67)), although now this result is only valid for $N \gg 1$.

Finally, we consider the oscillator strength of transitions between the ground state and the three-particle manifold. As discussed in Section III.B, such transitions become possible due to the nonresonant interaction $\hat{H}_{nr}$; within the HLA they are strictly forbidden. Using perturbative arguments, it is easily shown that the lowest-order contribution to the transition dipole of any ground state to three-particle state is of the order $(J/\omega_0)^2$ (various first-order contributions cancel), which means that the oscillator strength is of fourth order in the perturbation. Thus, for typical values of $J/\omega_0$ one should expect a very small effect only, which should be completely captured by using perturbation theory. Although in principle this is true, it turns out that practical implementation of perturbation theory is much more involved than working out the exact expression Eq. (33). The reason is that we would have to resort to second-order degenerate perturbation theory for the three-particle states, which is very cumbersome. We, therefore, only present exact results.

Figure 8 gives the total oscillator strength (per molecule) contained in all possible transitions between the ground state and the three-particle band. Apart from the two standard values of $2J/\omega_0$, we also give the results for two very large interaction values. It is clearly seen that, for typical parameter values, the oscillator strength is indeed exceedingly small and that little hope exists that this effect of the nonresonant interaction terms will be observable. This finding is reinforced by the fact that this small oscillator strength is spread over a large part of the three-particle band. As an example, Figs. 9(a) and 9(b) show the density of three-particle states and the density of their oscillator strength (from the ground state), respectively, for $2J/\omega_0 = -0.13$ and
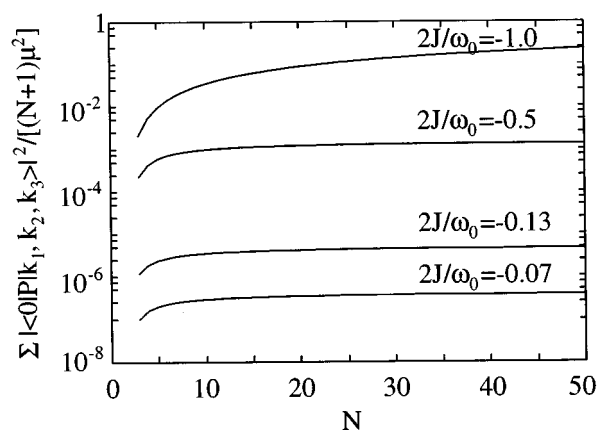
FIG. 8. Total oscillator strength per molecule between the ground state and all three-particle states, as a function of the chain length $N$ for various values of interaction strength. Only exact results are shown.

$N = 50$. In principle, the spectrum in Fig. 9(b) should be visible as a high-energy contribution to the linear absorption spectrum. In practice, the smallness of the oscillator strength compared to that of the ground state to one-particle transitions and compared to other (possibly even off-resonant and (or) counter-rotating) contributions from neglected higher excited molecular levels makes observation of this peak highly unlikely. We also note that, for very high values of the interaction (such as $2J/\omega_0 = -1$), the oscillator strength of the three-particle states does become appreciable (Fig. 8), but in that case, the three-particle band strongly overlaps with the one-particle band and a separation into low- and high-frequency contributions to the linear absorption spectrum becomes meaningless.

## VII. CONCLUDING REMARKS

In this article, we have studied the effects of going beyond the Heitler-London approximation (HLA) in one-dimensional exciton systems. Linear J aggregates of dye molecules, which have fairly large dipolar interactions, are examples of systems to which our theory is directly relevant.

Part of this article was devoted to defining the various transformations that diagonalize the one-dimensional exciton Hamiltonian either exactly, or within the Bose approximation or the HLA. These diagonalizations (using the Jordan-Wigner and Bogoliubov transformations) are not new, but need to be defined for proper understanding of the many-particle level scheme, the one-particle energies and, particularly, for the general expressions that we derived in Section III for the transition dipoles. The most important aspect of this article, however, lies in the fact that we have applied the formal theory to cases of practical interest, i.e., we have quantitatively worked out various observables for realistic parameter values.

As we have seen, the typical effects of the HLA are not very large. The largest effect is observed for the superradiant enhancement factor of the lowest exciton state. This factor is increased by a relative amount of about $-2J/\omega_0$, which is in the order of 10% for typical aggregates. As explained in Section VI, this leads to a 10% overestimation of the exciton delocalization length if that quantity is derived from the observed superradiant decay rate using the HLA in the analysis. As was shown, a similar effect (though smaller and with opposite sign) occurs if one derives the delocalization length from the pump-probe spectrum. An entirely new effect is that in principle three-particle states become visible in linear absorption due to the non-Heitler-London interaction terms. As we showed, however, the oscillator strength of these states scales as $(J/\omega_0)^4$, which in practice makes the effect too small to be observed. It may become an interesting direct indication for non-Heitler-London effects, however, if aggregates or other quasi-one-dimensional exciton systems with larger interactions are synthesized.

Our calculations also show that the deviation of the Bose approximation from the exact theory is not very large for typical parameter values. It should be stressed, however, that within this approximation, the optical response of the system is purely linear and that, even within the linear regime, the predictions of the Bose approximation are not exact.

Our results are exact within the model defined by the Hamiltonian Eq. (2). This model has several restrictions.
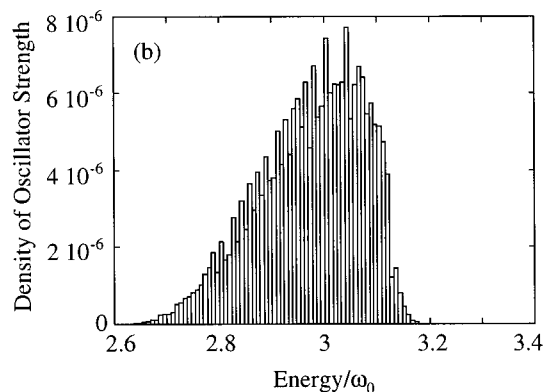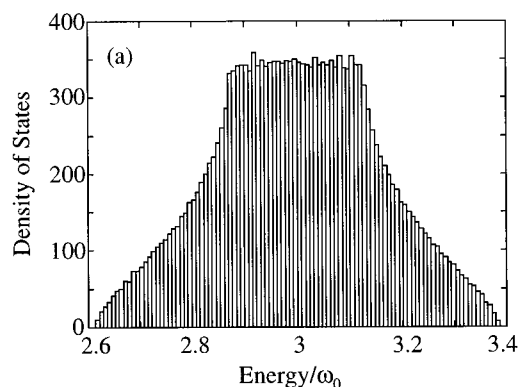


FIG. 9. (a) Density of three-particle states according to the exact theory for $2J/\omega_0 = -0.13$ and $N = 50$. The channel width used to make this histogram is $7.74 \times 10^{-3}\omega_0$. (b) Density of the oscillator strength between the ground state and the three-particle band. Parameters are the same as in (a).

First, it only accounts for one excited molecular state, which is, in fact, a resonance approximation. As going beyond the HLA implies including nonresonant interaction terms ($\hat{H}_{nr}$), it is not completely consistent to neglect higher excited molecular states in our theory.[16,18,29] The effects of this approximation are softened if the dipole of the molecular transition that we singled out is much larger than all other dipoles. A second approximation is that, in spite of the fact that the interactions are usually of a dipolar nature and drop off as $1/r^3$, we have restricted our treatment to nearest-neighbor interactions. This approximation was necessary in order to apply the Jordan-Wigner transformation, which ultimately allows us to solve the problem exactly.[30] We claim, however, that the qualitative as well as quantitative effects of the HLA in a model which does include long-range interactions are very similar to those observed in the presence of nearest-neighbor interactions only. To demonstrate this, we derived the analogue of Eq. (67) for the transition dipole between the ground state and the one-excitons in the presence of long-range interactions. The result shows that, for long chains ($N \gg 1$), the relative correction due to the nonresonant interaction terms is then given by $-2\Sigma_{r>0}J(r)/\omega_0$, where $J(r)$ is the interaction matrix element between two molecules that are $r$ lattice sites apart. For dipolar interactions, $J(r) = J/r^3$, this amounts to $-2J\zeta(3)/\omega_0 \approx -2.404J/\omega_0$. We thus see that the long-range interactions do not change the qualitative nature of the correction and only change the magnitude of the correction by 20%. For the ground state and one-particle energies and the oscillator strength to the three-particle states, the relative effect of long-range interactions is even smaller, as the effect of the nonresonant terms on these quantities involves powers of $J(r)$ (second for the energies and fourth for the oscillator strength).

We address finally the role of static disorder. While our general theory does account for disorder, we have restricted our quantitative analysis in Section VI to homogeneous chains. As is known, however, that diagonal disorder plays an important role in J aggregates, it is useful to comment on how this affects our conclusions. An important effect of disorder is to restrict the exciton delocalization length $N_{del}$. Therefore, a crude way to account for disorder is to consider a homogeneous chain with an effective length given by $N_{del}$.[8] This frequently applied level of modelling has led us to consider the particular effective aggregate lengths for PIC and TDBC quoted in Section VI. In this sense, disorder has already been accounted for in our analysis. We stress, however, that one of our most important results supersedes this crude approach: as noted already, Eq. (67) for the relative correction of the one-particle oscillator strength due to the nonresonant interaction terms is valid in the presence of arbitrary diagonal disorder. A further well-known disorder-related phenomenon is the motional narrowing of inhomogeneous spectral lines by a factor of the order $\sqrt{N_{del}}$.[2,3] A straightforward perturbative analysis in the disorder shows that relaxing the HLA increases the motional narrowing factor by a relative amount of $\frac{1}{2}(J/\omega_0)^2$, an effect that is too small to be observed. Finally, one may wonder whether

$N_{del}$ is affected by the nonresonant interactions. On the level of one-exciton states, these interactions give rise to effective next-nearest neighbor transfer interactions, which may help the exciton to pass a large diagonal disorder fluctuation on the chain and thus increase the delocalization. However, comparison of this effective interaction to next-nearest neighbor hopping mediated by the usual nearest-neighbor transfer interaction suggests that this effect only becomes important if the disorder fluctuation is in the order of an optical frequency, which is unrealistically large. A more detailed analysis of the role of disorder involves numerical simulations of our general expressions and lies outside the scope of this article.

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