Influence of exciton–exciton interaction on one-to-two exciton transitions in molecular aggregates with linear and circular geometries

Gediminas Juzeliūnas
Institute of Theoretical Physics and Astronomy, A. Goštauto 12, Vilnius 2600, Lithuania

Peter Reineker
Abteilung Theoretische Physik, Universität Ulm, 89069 Ulm, Germany

One- to two-exciton transitions have been examined in molecular aggregates with linear and circular geometries at various strengths of the exciton–exciton interaction. For the interaction parameter a sufficiently different from its critical value $a_{\mathrm{crit}} = 1$, the exciton–exciton interaction has been shown to have little influence on the transition dipole moments, as well as on the corresponding transition energies between the one-exciton states and the dissociated two-exciton states. The interaction between the excitons then may be represented in an effective manner by the replacement of the actual number N of molecules per aggregate by a nearby effective number N_{eff}, the latter being a-dependent. Hence, inclusion of the exciton–exciton coupling does not affect substantially the previous analysis of one- to two-exciton transitions based on the model of noninteracting one-dimensional excitons. That is, effects such as the blue shift of the excited-state absorption and the enhancement of nonlinear susceptibilities are not sensitive to the exciton–exciton interaction. These findings are relevant, *inter alia*, to J-aggregates in which there is no evidence for the coupling parameter a to be in the critical region or beyond. On the other hand, for the critical value of the exciton–exciton interaction ($a = a_{\mathrm{crit}}$), the blue shift is either totally absent in the excited-state absorption, or extremely small compared with the ordinary case. The above is in full agreement with earlier calculation of the pump–probe spectrum showing a weak dependence on the exciton–exciton interaction for $a < 1$, as well as a strong bleaching of the exciton band in the critical region. © *1997 American Institute of Physics.* [S0021-9606(97)03847-6]

I. INTRODUCTION

Recently there has been a great deal of interest in optical properties of molecular aggregates due to states with more than one exciton. The interest was motivated, to a considerable extent, by time resolved experiments performed on J-aggregates.[1–8] The J-aggregates are one-dimensional molecular structures exhibiting a narrow absorption band (the J-band) of excitonic origin shifted to the red from the monomer band.[9] The J-band is due to absorption to the bottom of the exciton band of one-dimensional J-aggregates,[10] the sharpness of the absorption line being due to motional narrowing.[10,11]

The two color pump–probe technique serves as a convenient means to study exciton states in J-aggregates. In the pump–probe experiments by Gadonas and co-authors,[1,2] a transient blue shift of the J-band has been observed. A similar effect has been reported in a number of recent experiments.[3–8] The blue shift of the J-band may be understood on the basis of the optical transitions between one- and two-exciton states,[12,13] invoking the concept of one-dimensional Fermi-excitons:[14] The analysis of such transitions[12,13] demonstrated an increase of energy of the excited-state absorption, as compared with the ground-state absorption. The influence of static disorder[15,16] and phonons[16] on the phenomenon has also been considered. It is noteworthy that the shiftlike optical changes have been observed in the transient absorption for other molecular complexes as well, including the bacteriochlorophyll (BChl)

molecules in the light harvesting antenna of the photosynthetic purple bacteria.[17] To explain the differential spectra, a circular structure has been proposed[18] for the BChl aggregates.

Recently, questions have been raised with respect to the influence of the exciton–exciton interaction on the (two color) pump–probe spectrum of molecular aggregates with linear geometries.[19–22] The analysis has been carried out in terms of two-particle Green functions adopting the continuum limit for the states forming the exciton band.[21,22] To take into account the finite size of the aggregates, numerical simulations have also been accomplished.[20–22] The calculations showed that the differential spectrum experiences significant changes if the strength of the exciton–exciton interaction is close to a critical value corresponding to the formation of biexcitonic states below the band of two dissociated excitons. It is noteworthy that the calculated pump–probe spectrum appeared to be almost independent of the magnitude of the exciton–exciton coupling[21,22] if the latter does not exceed the critical value.

In the present paper we shall examine further the effects of the exciton–exciton interaction on the one- to two-exciton transitions in molecular aggregates with linear geometries; the circular arrangement of the transition dipoles will also be considered. We shall explicitly derive and analyze the matrix elements for one- to two-exciton transitions in the presence of exciton–exciton coupling: These quantities, lacking a previous systematic treatment, are the key elements in studying

size-dependent quantities, such as the third-order suscepti-bilities due to exciton effects in molecular aggregates.[23,24] The investigation is carried out analytically and also without adopting the continuum limit in which size-dependent effects are lost. It will be demonstrated, *inter alia*, that the exciton–exciton interaction may be taken into account in an effective manner through the replacement of the actual number N of molecules forming the aggregate by an effective number N_{eff} (with $|N_{eff} - N| \ll N$) for a wide range of system parameters beyond the critical regime. This fact provides a natural explanation of the weak dependence of the pump–probe spectrum on the magnitude of the exciton–exciton coupling reported in Refs. 21 and 22. The brief outline of the paper is as follows. In the next section the system is defined. Section III A contains the general consideration of the two-exciton eigen-states and the matrix elements for the one- to two-exciton transitions. Section III B analyzes the specific cases at various strengths of the exciton–exciton coupling. The concluding Sec. IV summarizes the findings.

II. FORMULATION OF THE MODEL

Consider a molecular aggregate consisting of N two-level molecules. The dipole operator for the interaction of the aggregate with light is

$$\mathbf{M} = \sum_{n=1}^{N} (\boldsymbol{\mu}_n^* t_n^\dagger + \boldsymbol{\mu}_n t_n), \qquad (2.1)$$

where t_n ($t_n^\dagger$) is the Pauli operator for annihilation (creation) of an excitation at the molecule n, $\boldsymbol{\mu}_n$ being the corresponding transition dipole moment. For cyclic or linear geometries of interest, the latter $\boldsymbol{\mu}_n$ can be represented as

$$\boldsymbol{\mu}_n = \mu_\perp \mathbf{x} \cos(2\pi n/N) + \mu_\perp \mathbf{y} \sin(2\pi n/N) + \mu_\parallel \mathbf{z}, \quad (2.2)$$

($\mathbf{x}$, $\mathbf{y}$, and $\mathbf{z}$ being the unit Cartesian vectors), where the component $\mu_\perp$ rotates in the xy plane; another component $\mu_\parallel$ is parallel to the z axis for all the molecules n forming the aggregate. In the case where $\mu_\perp = 0$, the above arrangement of dipoles is relevant to aggregates with linear geometries as well. In that case we choose $\mathbf{z}$ to be parallel to $\boldsymbol{\mu}_n$. In what follows, we shall use the term ''linear aggregate'' to refer to such a situation. In passing we note that the size of the aggregate is supposed to be much smaller than the wavelength of light. Hence, the retardation factors have not been included in the operator (2.1): Incorporation of such factors is straightforward. Denoting

$$J_+(q) = \sum_{n=1}^{N} t_n^\dagger \exp(i2q\pi n/N), \qquad (2.3)$$

($q = 0, \pm 1$), the transition operator (2.1) takes the form

$$\mathbf{M} = \mu_\perp^* \frac{\mathbf{x} - i\mathbf{y}}{2} J_+(1) + \mu_\perp^* \frac{\mathbf{x} + i\mathbf{y}}{2} J_+(-1) + \mu_\parallel^* \mathbf{z} J_+(0)$$

$$+ h.c. \qquad (2.4)$$

We shall deal with interacting Frenkel excitons and consider nearest-neighbor interaction only. The Hamiltonian for such a system is

$$H = \sum_{n=1}^{N} [\varepsilon t_n^\dagger t_n - L(t_n^\dagger t_{n+1} + t_{n+1}^\dagger t_n) - \gamma t_n^\dagger t_n t_{n+1}^\dagger t_{n+1}], \qquad (2.5)$$

where $-L$ is the resonance coupling energy and $-\gamma$ is the (dynamical) interaction energy between the excitons.

In solving the Hamiltonian (2.5), we shall assume cyclic boundary conditions $t_{N+1} \equiv t_1$. In fact, it is quite common to exploit the periodic Hamiltonian in studies of the multiexciton states in linear geometries as well:[24-26] For finite aggregates, the cyclic boundary conditions alter to some extent the energies and transition matrix elements of excitons, as compared to excitons under free-end boundary conditions. Nevertheless, effects such as the blue shift of the excited-state absorption[13] persist also in the case of cyclic boundary conditions.[25,28]

For one-exciton states, the eigen-vectors and eigen-energies read[29]

$$|l_0\rangle = N^{-1/2} \sum_{n=1}^{N} |n\rangle \exp(i2\pi l_0 n/N), \qquad (2.6)$$

$$E(2\pi l_0/N) = \varepsilon - 2L \cos(2\pi l_0/N), \qquad (2.7)$$

($l_0 = 0, \pm 1, \ldots$ taking N integer values), where the state-vectors $|n\rangle \equiv t_n^\dagger |g\rangle$ form a basis for the one-exciton states, $|g\rangle$ denoting the ground electronic state. For transitions between the ground and the one-exciton states, the matrix elements for the operators (2.3) forming the dipole operator (2.4) are

$$\langle l_0 | J_+(q) | g \rangle = N^{1/2} \delta_{l_0, q}, \qquad (2.8)$$

so that the optically allowed transitions can take place to the one-exciton states $|q\rangle$ with $q = 0, \pm 1$.

In what follows we shall concentrate on the states with two excitons. Separating the motion of the ''center of mass'' from the relative motion in the usual way,[19,27,30] a basis set of the two-exciton states is

$$|l, s\rangle = \sum_{m=1}^{N} |m, m+s\rangle \exp[i\pi l(2m+s)/N], \qquad (2.9)$$

with $|m, m+s\rangle \equiv t_m^\dagger t_{m+s}^\dagger |g\rangle$, where the index l, characterising the motion of the center of mass, can take N integer values $0, \pm 1, \ldots$. Since

$$|l, s\rangle = |l, N-s\rangle (-1)^l, \qquad (2.10)$$

there are up to

$$s_{max} = \begin{cases} (N-1)/2, & \text{for odd } N \\ N/2, & \text{for even } N \end{cases}, \qquad (2.11)$$

different values of s describing physically different states. In the case where N is even and l is odd, one has $|l, s_{max}\rangle \equiv 0$. Accordingly, the total number of different basis states is $N(N-1)/2$ both for even and odd values of N, as required.

III. ANALYSIS OF TWO-EXCITON STATES AND TRANSITION DIPOLE MOMENTS

A. General

1. Two-exciton eigenstates

The eigenstates

$$H|l,k\rangle = E(l,k)|l,k\rangle , \qquad (3.1)$$

may be written in terms of the basic set (2.9), as

$$|l,k\rangle = (2N)^{-1/2} \sum_{s=1}^{N-1} |l,s\rangle U_s(l,k), \qquad (3.2)$$

where k is an index (to be specified later) characterizing the relative motion of the two excitons.

To avoid double counting of the basis states, the expansion coefficients for $s \geq s_{max}$ are to be related to those for $s \leq s_{max}$ through the following constraint:[31]

$$U_{N-s}(l,k) = U_s(l,k)(-1)^l. \qquad (3.3)$$

In addition, the normalization condition ($\langle l,k|l,k\rangle = 1$) yields

$$\sum_{s=1}^{N-1} |U_s(l,k)|^2 = 1. \qquad (3.4)$$

The eigenvalue Eq. (3.1) is equivalent to the following infinite set of difference equations:

$$U_{s-1}(l,k) + y U_s(l,k) + U_{s+1}(l,k) = 0, \qquad (3.5)$$

where the finiteness of the system and the exciton–exciton interaction are reflected via boundary conditions

$$U_0(l,k) = a U_1(l,k), \quad U_N(l,k) = a U_{N-1}(l,k), \qquad (3.6)$$

with

$$y = [E(l,k) - 2\varepsilon]/2L \cos(\pi l/N) \qquad (3.7)$$

and

$$a = \gamma/2L \cos(\pi l/N). \qquad (3.8)$$

The boundary conditions (3.6) incorporate effects of both the kinematical repulsion between the excitons (due to the Pauli exclusion principle) and also the dynamical exciton–exciton interaction, the latter acting at the separation distances $s=1$ and $s=N-1$. It is to be emphasized that for $s \geq N$ (or $s \leq 0$), the coefficients $U_s(l,k)$ are fictitious quantities that have been introduced for mathematical convenience only in order to convert the original finite set of difference equations for $U_s(l,k)$ $(s=1,2,...,N-1)$ into the infinite one (3.5).[32] In particular, the auxiliary coefficients $U_0(l,k)$ and $U_N(l,k)$, that are generally not equal to zero unless $a=0$, by no means represent the probability amplitudes for two excitons to reside at the same site.

Substituting

$$y = -2 \cos k, \qquad (3.9)$$

a solution to Eq. (3.5), subject to the constraint (3.3), is

$$U_s(l,k) = 2^{1/2} C \cos[(s - N/2)k + l\pi/2], \qquad (3.10)$$

the boundary conditions (3.6) leading to

$$\exp(ikN) = (-1)^l \frac{a \exp(ik) - 1}{1 - a \exp(-ik)}. \qquad (3.11)$$

Equation (3.11) determines the possible values of k. (Evidently, k and $-k$ describe the same physical state.) The corresponding eigen-energies of the two-exciton states are, through Eqs (3.7) and (3.9)

$$E_2(l,k) = E(\pi l/N + k) + E(\pi l/N - k), \qquad (3.12)$$

where $E(\cdots)$ are the one-exciton energies defined by Eq. (2.7). It is noteworthy that for $-1 < a < 1$, all the values of k are real. Under this condition, there can be no bound bi-exciton levels outside the band of the dissociated two-exciton states. For $a < -1$ $(a > 1)$ a bi-exciton level is formed below (above) the band. The bi-excitons have been analyzed in detail previously.[19,27,30] Hence the present paper will concentrate on the dissociated states characterized by real values of k. Exploiting the condition (3.4), the normalization constant reads for the dissociated states

$$C = \left[N - 1 + (-1)^l \frac{\sin(N-1)k}{\sin k} \right]^{-1/2}. \qquad (3.13)$$

2. Transitions between one- and two-exciton states

Consider the transition matrix elements between one- and two-exciton states. Using the state-vectors (2.6) and (3.2), the matrix elements of the operators $J_+(q)$, forming the dipole operator (2.4), become

$$\langle l,k|J_+(q)|l_0\rangle = (2)^{1/2} \delta_{l,l_0+q} \sum_{s=1}^{N-1} U_s^*(l,k)$$
$$\times \cos[\pi(l-2q)s/N], \qquad (3.14)$$

with $q = 0, \pm 1$. Calling on Eq. (3.10) for $U(l,k)$, one finds more explicitly

$$\langle l,k|J_+(q)|l_0\rangle = C \delta_{l,l_0+q}(\Pi_+ + \Pi_-) \qquad (3.15)$$

where

$$\Pi_\pm = \pm \frac{\sin(Nk/2 \mp d_\pm - l\pi/2)}{\sin(d_\pm)}, \qquad (3.16)$$

$$d_\pm = [\pi(l-2q)/N \pm k]/2, \qquad (3.17)$$

and k is again assumed to be real. Alternatively, Eq. (3.16) may be written as

$$\Pi_\pm = (-1)^{(q+l/2\pm l/2)} \frac{\sin[(N-1)d_\pm]}{\sin(d_\pm)}. \qquad (3.18)$$

In the case of linear geometry ($\mu_\perp = 0$) only the $q=0$ term contributes to the dipole operator (2.4), giving for the transitions originating from the lowest one-exciton level $l_0 = 0$

$$\langle l,k|\mathbf{M}|0\rangle = 2 C \mu_\parallel \mathbf{z} \delta_{l,0} \frac{\sin[(N-1)k/2]}{\sin(k/2)}. \qquad (3.19)$$

For such a geometry, the ground electronic state is optically connected to a single one-exciton state with $l_0 = 0$. Hence subsequent transitions to the two-exciton states do take place

from the state $|0\rangle$, unless other mechanism (phonons, etc.) cause population of higher one-exciton levels during the excited-state lifetime.

We conclude the general analysis by noticing that the above expressions hold for arbitrary strength of exciton–exciton coupling a, the a-dependence emerging implicitly via the eigenvalue equation (3.11) that gives us the spectrum for k.

B. Specific cases

Suppose first that $a=0$, i.e., the exciton–exciton interaction is ignored.

Then the general equations lead to

$$k=(2j+l+1)\pi/N \tag{3.20}$$

and

$$\langle l,k|J_+(q)|l_0\rangle=(-1)^j N^{-1/2}\delta_{l,l_0+q}[\cot(d_+)-\cot(d_-)], \tag{3.21}$$

where j can take integer values for which $k\neq 0$. The above is in agreement with the previous results for the one- to two-exciton transitions in the system of the noninteracting excitons in linear[25,28] and cyclic[18] geometries.

Consider next a specific, yet a very important case for the optical absorption where

$$|ka(1-a)^{-1}|\ll 1. \tag{3.22}$$

Equation (3.11) then reduces to

$$\exp(ikN)=-(-1)^l \exp[i2ka/(a-1)], \tag{3.23}$$

giving the following spectrum for k:

$$k=(2j+l+1)\pi/N_{\text{eff}}, \tag{3.24}$$

with

$$N_{\text{eff}}=N+2a/(1-a), \tag{3.25}$$

where j can take integer values subject to the condition (3.22). In passing we note that the condition (3.22) is always obeyed in the absence of the exciton–exciton coupling ($a=0$). In other words, the present case incorporates the previous case of the noninteracting excitons in the limit $a=0$.

Exploiting the condition (3.24), the solution (3.10) takes the form

$$U_s(l,k)=2^{1/2}C(-1)^j \sin\{[s+a/(1-a)]k\}, \tag{3.26}$$

with

$$C=\{N+[2ka/(1-a)]\cot(k)\}^{-1/2}, \tag{3.27}$$

($C=N_{\text{eff}}^{-1/2}$ for $k\ll 1$), so that the $k=0$ value is again to be excluded from the set (3.24). The transition matrix elements are now

$$\langle l,k|J_+(q)|l_0\rangle=(-1)^j N_{\text{eff}}^{-1/2}\delta_{l,l_0+q}[\cot d_+ - \cot d_-]. \tag{3.28}$$

Obviously, the above matrix elements have the same form as the previous relationship (3.21) for noninteracting excitons, subject to the replacement

$$N\rightarrow N_{\text{eff}}. \tag{3.29}$$

The replacement affects the quantization condition for k (3.24) as well. (However N is not to be altered in the expression (3.17) for $d_\pm$.)

For long aggregates ($N\gg 1$), the dominant contribution to the one- to two-exciton transitions is concentrated at $d_\pm\ll 1$. Thus, the assumption (3.22) implies that

$$|N_{\text{eff}}-N|/N\ll 1, \tag{3.30}$$

in the case of transitions from the lowest levels of the one-exciton band: $l_0\ll N$.[33] In this way, the exciton–exciton coupling has very little influence on the spectrum of k values (3.24), on the transition dipole moments (3.28), as well as on the transition energies $E_2(l,k)-E(2\pi l_0/N)$. The interaction between the excitons appears in an effective manner through the replacement of the actual number N of molecules per aggregate by a nearby effective number N_{eff}. Therefore, inclusion of the exciton–exciton coupling should not affect considerably the previous theories[12,13,18,23,24,28] based on the model of noninteracting one-dimensional excitons. Specifically, such effects as the blue shift of the excited-state absorption[12,13,18] and the enhancement of the nonlinear susceptibilities[23,24] persist in the present case of interacting excitons.

The assumptions (3.22) and (3.30) are relevant as long as the parameter a is not too close to its critical value $a_{\text{crit}}=1$

$$|a-1|\gg 1/N. \tag{3.31}$$

For $0<a<1$, the effective number N_{eff} is less than N; for $a>1$, one has the opposite: $N_{\text{eff}}>N$. In the latter situation, a biexcitonic level is formed below the band of the dissociated two-exciton levels: The biexciton "borrows" some oscillator strength from the optically active dissociated states at the bottom of the two-exciton band.[33] Note that our analysis does not cover the biexciton states (characterized by a purely imaginary wave number k) for which the localization length $|k|^{-1}$ is too small to comply with the assumption (3.22). Optical transitions due to biexcitons have been considered in detail recently;[19] the present paper concentrates on transitions to the dissociated two-exciton states.

For $a=a_{\text{crit}}=1$ one has

$$k=(2j+l)\pi/(N-1), \tag{3.32}$$

where j can take integer values. The solution (3.10) then reads

$$U_s(l,k)=2^{1/2}C(-1)^j \cos[(s-1/2)k], \tag{3.33}$$

with

$$C=\begin{cases}(N-1)^{-1/2}, & \text{for } 0<k<\pi \\ [2(N-1)]^{-1/2}, & \text{for } k=0\end{cases}. \tag{3.34}$$

Note that unlike in the previous cases, the $k=0$ value is now allowed provided l is even.

Consider first the one- to two-exciton transitions that take place from one-exciton states different from $|q\rangle$. The corresponding transition matrix elements are

$$\langle l,k|J_+(q)|l_0\rangle$$

$$= -(-1)^j \delta_{l,l_0+q}(N-1)^{-1/2}$$

$$\times \sum_{\pm} \frac{\sin[\pi(l-2q)/2N]}{\sin[\pi(l-2q)/2N \pm \pi(l+2j)/2(N-1)]},$$

$$(3.35)$$

$(l_0 \neq q)$. In the case of large aggregates ($N \gg 1$), the matrix elements with $j=-q$ are the dominant ones, the other ones are smaller by at least a factor of N. Neglecting the terms with $j \neq -q$, the formula (3.35) may then be approximated, by

$$\langle l,k|J_+(q)|q\rangle = (-1)^j \delta_{l,l_0+q}(N-7/2)^{1/2}\delta_{j,-q},$$

$$(l_0 \neq q). \quad (3.36)$$

At this point it is instructive to mention quite general sum rules that apply for transitions from the excited states of the aggregates.[12,13] For the ordered molecular aggregates in question, the following sum rule may be formulated for the operator $J_+(q)$:

$$\sum_{l,k} |\langle l,k|J_+(q)|l_0\rangle|^2 = N-2+N\delta_{l_0,q}. \quad (3.37)$$

Since now $l_0 \neq q$, the total strength of the one- to two-exciton transitions is $N-2$, the share of the dominant one- to two-exciton transitions (3.36) being $N-7/2$. The energies of the dominant transition ($j=-q$) read:

$$\Delta E \equiv E_2(l_0+q,k) - E(2\pi l_0/N)$$

$$= E(2\pi q/N) + 4L\pi^2(l_0-q)^2/N^3, \quad (3.38)$$

up to terms proportional to N^{-3}.

Consider next the transitions originating from the one-exciton state $|q\rangle$, i.e., the case where $l_0=q$. Then one has

$$\langle l,k|J_+(q)|q\rangle = (-1)^j \delta_{l,2q}(2N-2)^{1/2}\delta_{l,-j}, \quad (3.39)$$

i.e., transitions are strictly forbidden to two-exciton states with $j \neq -q$. The energy of the allowed one- to two-exciton transition ($j=-q$) is

$$\Delta E = E(2\pi q/N). \quad (3.40)$$

Note that the intensity of the one- to two-exciton transition is now proportional to $2N-2$, rather than to $N-2$. An extra N compensates a downward transition $|q\rangle \rightarrow |g\rangle$ described by the Hermitian conjugate operator $J(q)^\dagger$ that features in the transition operator (2.4) along with $J(q)$. It is also apparent that the transition moments (3.39) comply with the sum rule (3.37).

The transition energy (3.40) appears to be precisely equal to the energy of the allowed transition $|g\rangle \rightarrow |q\rangle$ from the ground state. Note that this fact has been already observed by Spano and Manas[22] who pointed out the absence of the frequency shift for the upward transitions from the lowest one-exciton level ($l_0=0$) in the case of linear geometries ($q=0$). On the other hand, for the first type of transitions ($l_0 \neq q$), there is some increase of the excitation energy (3.38). However, the energy shift (having an N^{-3} size-

dependence) is small compared with the usual N^{-2}-dependent increase of the excitation energy [12,13,23,24] characteristic for noninteracting excitons in one dimension, as well as for the previous case (3.22).

In this way, the present situation exhibits a number of unusual features for the optical transitions from the excited states. Nevertheless, this is a rather specific case that might be relevant only in a very small narrow critical region in which the assumption (3.31) breaks down.

IV. CONCLUSION

One- to two-exciton transitions have been examined in molecular aggregates with linear and circular geometries at various strengths of the exciton–exciton coupling. For the coupling parameter a sufficiently different from its critical value $a_{crit}=1$, the exciton–exciton interaction has been shown to influence only slightly both the transition dipole moments and the corresponding transitions energies between the one-exciton and the dissociated two-exciton states. The interaction between the excitons then may be represented in an effective manner through the replacement of the actual number N of molecules per aggregate by a closeby effective number N_{eff} which is a-dependent. Hence, inclusion of the exciton–exciton coupling does not affect substantially the previous analysis of one- to two-exciton transitions[12,13,18,23,24,28] based on the model of noninteracting one-dimensional excitons (some extra features might appear for $a > a_{crit}$ from the contribution due to a bound bi-exciton level[34]). That is, effects, such as the blue shift of the excited-state absorption[12,13,18] and the enhancement of nonlinear susceptibilities,[23,24] are not sensitive to the exciton–exciton interaction for $a < a_{crit}$. These findings are relevant, *inter alia*, to J-aggregates in which there is no evidence for the coupling parameter a to be in the critical region or beyond. On the other hand, for the critical value of the exciton–exciton coupling ($a=a_{crit}$), the blue shift is either totally supressed in the excited-state absorption of the aggregate, or extremely small compared with the ordinary case. These findings are in full agreement with the calculation of the pump-probe spectrum[21,22] showing a weak dependence of the spectrum on the exciton–exciton interaction for $a < a_{crit}$, as well as a strong bleaching of the exciton band in the critical region.

Note added in proof. After submitting the manuscript we became aware of recent work by Schulten and co-workers[35] demonstrating that the bacteriochlorophyll molecules form perfect cyclic aggregates in the photosynthetic units of purple bacteria.

[1] R. Gadonas, R. Danielius, A. Piskarskas, and S. Rentsch, Izv. Akad. Nauk SSSR, Ser. Fiz. **47**, 2445 (1983) [Eng. Transl.: Bull. Akad. Sci. USSR Phys. **47**(12), 151 (1983)].
[2] R. Gadonas, R. Danielius, A. Piskarskas, T. Gillbro, and V. Sundström, in, *Ultrafast Phenomena in Spectroscopy*, edited by Z. Rudzikas, A. Piskar-

skas, and R. Baltramiejūnas (World Scientific, Singapore, 1988), p. 411.

[3] H. Fidder, J. Knoester, and D. A. Wiersma, J. Chem. Phys. **98**, 6564 (1993).

[4] A. E. Johnson, S. Kumazaki, and K. Yoshihara, Chem. Phys. Lett. **211**, 511 (1993).

[5] K. Minoshima, M. Taiji, K. Misawa, and T. Kobayashi, Chem. Phys. Lett. **218**, 67 (1994).

[6] V. F. Kamalov, I. A. Struganova, Y. Koyama, and K. Yoshihara, Chem. Phys. Lett. **132**, 266 (1994).

[7] M. van Burgel, D. A. Wiersma, and K. Duppen, J. Chem. Phys. **102**, 20 (1995).

[8] J. Moll, S. Daehne, J. R. Durrant, and D. A. Wiersma, J. Chem. Phys. **102**, 6362 (1995).

[9] E. Daltrozzo, G. Scheibe, K. Gschwind, and F. Haimerl, Photograph. Sci. Eng. **18**, 441 (1974).

[10] J. S. Briggs and A. Herzenberg, Mol. Phys. **21**, 865 (1971); J. S. Briggs, Z. Phys. Chem. IN.F. (Frankfurt) **75**, 214 (1971).

[11] E. W. Knapp, Chem. Phys. **85**, 73 (1984).

[12] G. Juzeliūnas, Liet. Fiz. Rink. **27**(3), 261 (1987) [Eng. transl.: Sov. Phys.-Coll. **27**(3), 7 (1987)].

[13] G. Juzeliūnas, Z. Phys. D **8**, 379 (1988).

[14] D. B. Chesnut and A. Suna, J. Chem. Phys. **39**, 146 (1963).

[15] J. Knoester, J. Chem. Phys. **99**, 8466 (1993).

[16] S. Mukamel, P. Rott, and V. Chernyak, J. Chem. Phys. **104**, 5415 (1996).

[17] A. Yu. Borisov, R. V. Gadonas, R. V. Danielius, A. S. Piskarskas, and A. P. Razjivin, FEBS Lett. **138**, 25 (1982); A. P. Razjivin, R. V. Danielius, R. V. Gadonas, A. Yu. Borisov, and A. S. Piskarskas, *ibid.* **143**, 40 (1982); R. V. Danielius, A. P. Mineyev, and A. P. Razjivin, *ibid.* **250**, 183 (1989).

[18] V. I. Novoderezhkin and A. P. Razjivin, FEBS Lett. **330**, 5 (1993).

[19] G. Vektaris, J. Chem. Phys. **101**, 3031 (1994).

[20] H. Ezaki, T. Tokihiro, and E. Hanamura, Phys. Rev. B **50**, 10506 (1994).

[21] F. C. Spano, Chem. Phys. Lett. **234**, 29 (1995).

[22] F. C. Spano and E. S. Manas, J. Chem. Phys. **103**, 5939 (1995).

[23] F. C. Spano and S. Mukamel, Phys. Rev. A **40**, 5783 (1989).

[24] H. Ishihara and K. Cho, Phys. Rev. B **42**, 1724 (1990).

[25] G. Juzeliūnas, in *Proceedings of the Conference on Lasers and Optical Nonlinearity* (Institute of Physics, Vilnius, 1987), pp. 129–135.

[26] J. Knoester and F. C. Spano, Phys. Rev. Lett. **74**, 2780 (1995).

[27] V. M. Agranovich and M. D. Galanin, *Electronic Excitation Energy Transfer in Condensed Matter* (North-Holland, Amsterdam, 1982).

[28] F. C. Spano and J. Knoester, in *Advances in magnetic and optical resonance, Vol.18*, edited by W. S. Waren (Academic, New York, 1994), p. 117.

[29] A. S. Davydov, *Theory of Molecular Excitons* (Plenum, New York, 1971).

[30] R. E. Merrifield, J. Chem. Phys. **31**, 522 (1959).

[31] Note that the previous analysis of interacting excitons in one dimension by Merrifield (Ref. 30) was based on another constraint: $U_{N+s}(l,k)=U_s(l,k)(-1)^l$. Under such an approach, the boundary condition (3.6) can be applied only at one end site ($s=0$), the condition being not necessarily satisfied at another end side ($s=N$) unless $a=0$. This leads to somewhat different eigen-energies and eigen-states.

[32] Such an approach has been utilized in other areas as well, for instance analysing vibrational modes in the presence of surfaces, H. Puszkarski, Surf. Sci. **34**, 125 (1973).

[33] In this discussion, it is implicitly assumed that $L>0$, where $-L$ is the energy of the resonant coupling. In such a case, the optically allowed transitions take place to the levels situated at the bottom of the exciton band.

[34] One-exciton to bi-exciton transitions have been analyzed in detail recently (Refs. 19 and 22), the present paper concentrating on the transitions to the dissociated two-exciton states. Formation of bi-excitons at $a>1$ produce an extra peak at the red-side of the pump–probe spectrum.

[35] X. Hu and K. Schulten, Phys. Today **50** (No. 8), 28 (1997).