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One-to-two-exciton transitions in molecular aggregates: Influence of the exciton–exciton interaction

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Abstract

One-to-two-exciton transitions have been examined in molecular aggregates with linear and circular geometries at various strengths of exciton–exciton coupling. For the case where the coupling parameter a does not fall into the critical region around $a_{\text{crit}} = 1$, the exciton–exciton interaction is shown to have little influence on the transition dipole moments, as well as on the corresponding transition energies. The interaction between the excitons may then be represented in an effective manner replacing an actual number N of molecules per aggregate by a close effective number N_{eff} , the latter being a -dependent. The analytical analysis is in agreement with earlier numerical calculation of the pump–probe spectrum showing a weak dependence on the exciton–exciton interaction beyond the critical region. © 1998 Elsevier Science B.V. All rights reserved.

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In recent years there has been a considerable 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 [1–7]. 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 [8]. The J-band is due to absorption to the bottom of exciton band of one-dimensional J-aggregates [9,10], the sharpness

of the absorption line being due to the motional narrowing [9–11].

The two colour pump–probe technique serves as a convenient means to study exciton states in J-aggregates. The pump–probe experiments show a transient blue shift of the J-band [1–7]. The shift may be understood on the basis of optical transitions between one- and two-exciton states [12,13], invoking the concept of one-dimensional Fermi-excitons [14]: Analysis of such transitions [12,13] demonstrates an increase of energy of the excited-state absorption, as compared with the ground-state absorption. The influence of the static disorder [15,16] and phonons [16] on the phenomenon has also been considered. It is noteworthy that the shift-like optical changes have been

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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 concerning the influence of the exciton–exciton interaction to the (two colour) pump–probe spectrum of molecular aggregates with linear geometries [19–21]. The analysis has been carried out in terms of two-particle Green functions adopting the continuum limit for the states forming the exciton band [20,21]. To take into account the finite size of the aggregates, the numerical simulations have also been accomplished [19–21].

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 and circular geometries. We shall explicitly derive and analyse 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 susceptibilities due to exciton effects in molecular aggregates [22,23]. The investigation is carried out analytically and also without adopting the continuum limit in which size-dependent effects are lost.

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

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

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

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

(\mathbf{x}, \mathbf{y} and \mathbf{z} being the unit Cartesian vectors), where the component μ_\perp rotates in the xy plane; another component μ_z 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 what follows, we shall use the term ‘linear aggregate’ to refer to such a situation. Denoting

$$J_+(q) = \sum_{n=1}^N t_n^\dagger \exp(i2q\pi n/N) \quad (3)$$

($q = 0, \pm 1$), the transition operator given by Eq. (1) takes the form

$$\begin{aligned} \mathbf{M} = & \mu_\perp^* \frac{\mathbf{x} - i\mathbf{y}}{2} J_+(1) + \mu_\perp^* \frac{\mathbf{x} + i\mathbf{y}}{2} J_+(-1) \\ & + \mu_z^* \mathbf{z} J_+(0) + \text{h.c.} \end{aligned} \quad (4)$$

We shall deal with interacting Frenkel excitons and consider nearest-neighbour interaction only. The Hamiltonian for such a system is, using the periodic boundary conditions

$$\begin{aligned} H = & \sum_{n=1}^N [et_n^\dagger t_n - L(t_n^\dagger t_{n+1} + t_{n+1}^\dagger t_n) \\ & - \gamma t_n^\dagger t_n t_{n+1}^\dagger t_{n+1}], \end{aligned} \quad (5)$$

where $-L > 0$ is the resonance coupling energy and $-\gamma$ is the energy of the (dynamical) interaction between the excitons.

In what follows, we shall concentrate on the states with two excitons. Separating the motion of the ‘centre of mass’ from the relative motion [24,25], a basis set of the two exciton states is

$$|l, s\rangle = \sum_{m=1}^N \left| m, m+s \right\rangle \exp[i\pi l(2m+s)/N], \quad (6)$$

with $|m, m+s\rangle \equiv t_m^\dagger t_{m+s}^\dagger |g\rangle$, where the index l , characterising the motion of the ‘centre of mass’, can take N integer values $0, \pm 1, \dots$. The eigenstates

$$H |l, k\rangle = E_2(l, k) |l, k\rangle, \quad (7)$$

may be written in terms of the basic set, Eq. (6), as

$$|l, k\rangle = (2N)^{-1/2} \sum_{s=1}^{N-1} |l, s\rangle U_s(l, k), \quad (8)$$

where k is the wave number (to be specified later) characterising the relative motion of the two excitons.

To avoid double counting of the basis states, the expansion coefficients for $s \geq N/2$ are to be related to those for $s \leq N/2$ through the following constraint:

$$U_{N-s}(l, k) = U_s(l, k)(-1)^l. \quad (9)$$

The eigenvalue equation, Eq. (7), is equivalent to the following infinite set of difference equations:

$$U_{s-1}(l, k) + \gamma U_s(l, k) + U_{s+1}(l, k) = 0, \quad (10)$$

where the finiteness of the system is reflected via boundary conditions:

$$U_0(l, k) = aU_1(l, k), \quad U_N(l, k) = aU_{N-1}(l, k), \quad (11)$$

with $\gamma = [E(l, k) - 2\varepsilon]/2L\cos(\pi l/N)$ and $a = \gamma/2L\cos(\pi l/N)$.

Substituting $\gamma = -2\cos k$, a solution to Eq. (10) is, subject to the constraint given by Eq. (9):

$$U_s(l, k) = 2^{1/2} C \cos[(s - N/2)k + l\pi/2], \quad (12)$$

the boundary conditions (11) providing a set of k values. The transition matrix elements between one- and two-exciton states are found, as:

$$\langle l, k | J_+(q) | l_0 \rangle = C \delta_{l, l_0 + q} (\Pi_+ + \Pi_-), \quad (13)$$

with

$$\Pi_{\pm} = \pm \frac{\sin(Nk/2 \mp d_{\pm} - l\pi/2)}{\sin(d_{\pm})}, \quad (14)$$

$$d_{\pm} = [\pi(l - 2q)/N \pm k]/2, \quad (15)$$

($q = 0, \pm 1$), where k is assumed to be real. 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 analysed in detail previously [21,24,25]. Hence, the present paper will concentrate on the dissociated states characterised by real values of k .

Consider next a specific, yet a very important case where

$$|ka(1 - a)^{-1}| \ll 1, \quad (16)$$

giving the following spectrum for k

$$k = (2j + l + 1)\pi/N_{\text{eff}} \quad (17)$$

with $N_{\text{eff}} = N + 2a/(1 - a)$, where j can take integer values subject to the condition given by Eq. (16). The transition matrix elements are now

$$\begin{aligned} \langle l, k | J_+(q) | l_0 \rangle &= (-1)^l N_{\text{eff}}^{-1/2} \delta_{l, l_0 + q} \\ &\times [\cot d_+ - \cot d_-]. \end{aligned} \quad (18)$$

The above matrix elements have the same form as the familiar relationship for the non-interacting excitons, subject to the replacement $N \rightarrow N_{\text{eff}}$. For large aggregates ($N \gg 1$), the dominant contribution to the one-to-two-exciton transitions is concentrated at $d_{\pm} \ll 1$. Thus, the assumption given by Eq. (16) implies that $|N_{\text{eff}} - N|/N \ll 1$ for transitions from the lowest levels of the one-exciton band: $l_0 \ll N$. It is noteworthy that the assumption given by Eq. (16) holds for a wide range of exciton-exciton coupling, as long as coupling parameter a is beyond the critical region around $a = a_{\text{crit}} = 1$.

In this way, the exciton-exciton coupling produces little influence on the spectrum of values of k , Eq. (17), on the transition dipole moments, Eq. (18), as well as on the transition energies $E_2(l, k) - E(2\pi l_0/N)$. The interaction between the excitons emerges 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 [12,13,18,22,23,26,27] based on the model of non-interacting one-dimensional excitons. Specifically, such effects as the blue shift of the excited-state absorption [12,13,18,27] and the enhancement of the non-linear susceptibilities [22,23,26] persist in the present case of interacting excitons. Finally, the present analysis is in agreement with the numerical calculations of the pump-probe spectrum [20,21] showing a weak dependence of the spectrum on the exciton-exciton interaction for $a < a_{\text{crit}}$.

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