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Two-exciton excited states of *J*-aggregates in the presence of exciton–exciton annihilation

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ABSTRACT

We study decay of two-exciton states of a *J*-aggregate that is collective in nature. We use mathematical formalism based on effective non-Hermitian Hamiltonian suggested in nuclear theory. We show that decay of two-exciton states is strongly affected by the interference processes in the exciton–exciton annihilation. Our evaluations of the imaginary part of the effective Hamiltonian show that it exceeds the spacing between real energies of the two-exciton states that gives rise to the transition to the regime of overlapping resonances supplying the system by the new collectivity – the possibility of coherent decay in the annihilation channel. The decay of two-exciton states varies from twice bimolecular decay rate to the much smaller values that is associated with population trapping. We have also considered the corresponding experiment in the framework of our approach, the picture of which appears to be more complex and richer than it was reasoned before.

1. Introduction

Collective mechanism of excitation of linear molecular *J*-aggregates determines their unique nonlinear optical properties [1]. Among them the *N*-fold enhancement of the spontaneous emission rate and the N^2 scaling of the cubic hyperpolarizability, where N is the number of molecules in the aggregate. The reason is the collective (excitonic) character of aggregate eigenfunctions. The collective mechanism also results in a bistable behavior of molecular *J*-aggregates [2,3], and dissipative solitons [4,5] that arise in these structures under resonant laser excitation. These solitons are nanosized structures, which are localized almost within the region of a single molecule, which opens up possibilities for creating subminiature memory cells.

The bistability and dissipative solitons predicted are strongly affected by the process of excitonic annihilation, which plays a role with increasing pump intensity [6–9]. Exciton annihilation in molecular crystals was studied in Refs. [6,7], and in dye *J*-aggregates in Refs. [10–12] experimentally and [13,14] theoretically. In Ref. [15] the anharmonic oscillator approach was developed to model exciton annihilation in pigment-protein complexes. Consider two-exciton excitation of a molecular aggregate. The scheme of the exciton–exciton annihilation process through a third molecular level [13,14] includes two steps. In the first step, one excited molecule goes to the ground state $|g\rangle$ while another excited molecule passes to the third level $|f\rangle$ (due to the energy conservation). The second step is the radiationless relaxation of the third level $|f\rangle$ to the ground $|g\rangle$ and excited $|e\rangle$ states of the transition of interest. It is assumed that the third level $|f\rangle$ is vibronic in its nature and decays very rapidly transferring its energy to the excited $|e\rangle$ and ground $|g\rangle$ levels with the rates Γ_{fe} and Γ_{fg}, respectively.

In Ref. [3] an ensemble of molecular aggregates in a thin film was considered using an effective four-level scheme, and in Refs. [2,4,5] *J*-aggregates were described using a local field approximation [16], in which a chain of molecules is described by a system of Bloch equations for one-particle density matrices. In this case, the interaction between molecules is derived using the classical expression for the retarding interaction between a system of dipoles by which molecules are modeled. In addition, the above mentioned interaction that leads to exciton–exciton annihilation is also introduced into the system (usually phenomenologically). As a rule, in the system of equations obtained in this way, only two particle interactions are taken into account, which are

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presented in the factorized form, i.e., without taking into account correlations between molecules.

However, the system of equations for *J*-aggregates can also be derived from first principles. In this case, a hierarchy of mutually coupled equations for the expectation values of products of operators that refer to different molecules of the chain arises [16]. This system contains expectation values beginning from one particle and ending with N particle expectation values (N is the number of molecules in the chain, and $N \gg 1$). An important aspect of this problem is that the third level of molecules is a system of a large number of vibrational sublevels, interaction with which leads to dissipation of energy and to irreversibility of the exciton–exciton annihilation process. If this interaction is correctly taken into account from the first principles, the equations of motion will acquire a number of multiparticle contributions that describe the relaxation of the system related to the exciton–exciton annihilation [17] but that, however, are absent in the purely phenomenological picture. In Ref. [17] we took the two-particle expectation values into account directly in the hierarchical system of equations. In general, taking the interaction with a third level of molecules into account leads to the appearance not only of three-particle but also of four-particle relaxation terms in equations of motion. As a consequence, the exciton–exciton annihilation processes also result in mixing the optical transitions in *J* -aggregates.

Furthermore, equations of Ref. [17] were written in the site representation. However, the applicability of the bimolecular theory, which implies the approach of two excitons before they annihilate, is questionable [13,14]. Authors of earlier pioneering work [13] obtained an insight into the possible channels of excitonic annihilation at low temperatures, when one-dimensional excitons become localized in the part of the aggregate due to a weak static disorder. They proposed an alternative channel of excitonic annihilation that was inversely proportional to the cube of the localization length. In the present work following Ref. [13] we also take the localization of one-dimensional excitons in the part of the aggregate into consideration. However, in contrast to Ref. [13], we consider rather eigenstates of the effective non–Hermitian Hamiltonian [18] including the decay due to the exciton–exciton annihilation, than eigenstates obtained by diagonalization of the Hamiltonian of a *J*-aggregate with respect to the dipole–dipole interaction between its molecules, Eq. (6) below. This is an important generalization of the theory when the value of the dipole–dipole interaction between molecules of a *J*-aggregate (see Eq. (6) below) $|J|$ is not much larger than the probability of bimolecular decay w_a (see below). By this means the spectrum of the problem under consideration should be found with taking the decay due to the exciton–exciton annihilation into account. In addition, the exciton–exciton annihilation is described by non-diagonal relaxation matrix due to both the relaxation of two-particle variables associated with that of three- and four-particles variables, and using basis $|\mu\nu\rangle$ in which even the relaxation of two-particle variables becomes non-diagonal. The appropriate mathematical formalism for the description of this physics is provided by the effective non–Hermitian Hamiltonian [18] suggested in nuclear theory that will be used in the present work. This formalism is highly efficient for the study of collective states demonstrating various behaviors, the two extreme cases of which are super-radiance by Dicke [19,20] and the population trapping [21,18]. At the end of the 20th century it was understood that the physics underlying super-radiance is much more general and can find broad applications in various regions of the quantum world [18].

For our goal, the main lesson is that the quantum states can be coupled also through the continuum of open decay channels. Since the continuum coupling determines the width 2α, or the lifetime $\tau \sim \hbar/(2\alpha)$, the states become quasi-stationary and can be characterized by a complex energy, $\widetilde{E} = E - i\alpha$. Similar to standard perturbation theory, the efficiency of coupling is determined by the ratio of the coupling strength to the energy spacing between the coupled states. If the width 2α is of the order of, or exceeds, the spacing between real energies E, coupling through the continuum turns out to be effectively strong. This transition to the regime of overlapping resonances supplies the system by the new collectivity - the possibility of coherent decay [18].

The paper is organized as follows. We start with the model in Section 2. In Section 3 we consider the evolution of the two-exciton excited states and specify the effective non–Hermitian Hamiltonian. Then we present the results of the numerical diagonalization of the effective Hamiltonian and discuss them, Section 4. In Section 5 we compare our results with previous calculations and experiment. In Section 6, we briefly conclude.

2. Model and Hamiltonian

Consider a linear chain that consists of N three-level molecules. Assume that the lowest state of each molecule is determined by the state vector $|g\rangle$, and the energy of this state is E_g. Correspondingly, the excited state will be determined by the state vector $|e\rangle$ with energy E_e. State vectors $|mg\rangle$ and $|me\rangle$ correspond to a molecule that is located at site m of the chain. Using these vectors, we can construct the following operators of creation and annihilation for each molecule: $B_m = |mg\rangle\langle me|$ is the operator that describes the annihilation of an excitation in molecule m at level e, and $B^\dagger_m = |me\rangle\langle mg|$ is the operator that describes the creation of an excitation in molecule m to level e. Furthermore, the upper level f of a molecule in the system of three-level molecules is a vibronic, and, to correctly perform calculations, we should take into account its structure. We will assume that upper level f consists of a series of sublevels v, which correspond to different vibrational states and which are characterized by the density of states $\rho(E) = \sum_v \delta(E - E_{fv})$ necessary for the calculation of the transition probabilities. As a result, the third state will be determined by state vectors $|fv\rangle$ with energies E_{fv} where $E_{fv} > E_e > E_g$. In a similar manner, we shall also define the following operators: $D_{mv} = |me\rangle\langle mfv|$, and $D^\dagger_{mv} = |mfv\rangle\langle me|$. In Ref. [17] the processes of exciton–exciton annihilation were described by the following Hamiltonian

$$H_{annih} = \sum_{\substack{k\neq l\\ v}} \left(V_{kl} B_k D^+_{lv} + V_{lk} D_{lv} B^+_k\right) \tag{1}$$

The two-exciton state corresponding to the excitation of sites m and n can be written as $|mene\rangle = B^\dagger_m B^\dagger_n |mg\rangle|ng\rangle$. The energy of this state will be close to the energy $|kfv\rangle$ of any site k. Therefore, we shall seek the two-exciton wave function in the form

$$\Psi = \sum_{m>n} C_{mn} |mene\rangle \prod_{k\neq m,n} |kg\rangle + \sum_{m,v} d_{mv} |mfv\rangle \prod_{k\neq m} |kg\rangle \tag{2}$$

where C_{mn} and d_{mv} are the amplitudes of the corresponding states. The evolution of two-exciton wave function Ψ

$$i\hbar \frac{d\Psi}{dt} = H\Psi \tag{3}$$

is determined by the Hamiltonian

$$H = H_0 + H_{int} + H_{annih} \tag{4}$$

Here

$$H_0 = \sum_m \hbar\omega_{me,g} B^+_m B_m + \sum_{m,v} \hbar\omega_{mfv,g} D^+_{mv} D_{mv} \tag{5}$$

is the Hamiltonian of free molecules of a *J*-aggregate,