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Absence of bistable behavior in the optical response of a dimer

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The problem is examined whether a bistable behavior of optical response of a dimer really exists. We carry out an exact treatment of this problem based on the two-molecule density matrix, without its representation in the form of a product of the one-molecule density matrices of each molecule composing the dimer. Our conclusion is that the bistability discussed is an artifact originating from the splitting procedure. A condition for getting the bistable optical response from a linear chain of a large number of monomers is also formulated. [S1050-2947(98)07308-9]

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I. INTRODUCTION

In the last few years the problem of bistable behavior of a dimer composed of two molecules [1–3] as well as of a linear aggregate made up of many molecules [4,5] appeared to be extensively discussed. Much earlier, this problem was discussed in Refs. [6–9]. The effect consists of a sudden switching of the population (or number of excited units of an aggregate) when the external field amplitude exceeds some critical value. The model of dimer bistability has been already exploited for interpretation of the results of recent experiments on bistable behavior of both visible and near-infrared luminescence of a crystal $Cs_3Y_2Br_9:Yb^{3+}$ [10–12].

In order to treat the problem, the authors of all papers mentioned above used the one-molecule density matrix formalism, instead of considering the global density matrix of the system as a whole. The last approach, being of course the adequate one, has diminishing chances in treating aggregates of a large number of molecules. At the same time, optical response of a dimer can be entirely elaborated making use of the exact approach. Nevertheless, the authors of Refs. [1–3,9] restricted their studies to the approximate one-molecule density matrix formalism.

The aim of this paper is to show that the dimer bistability is an artifact that originates from splitting of the global (two-molecule) density matrix into a product of the density matrices (one-molecule) of each component of the dimer. We do not make use of such an approximation and solve the exact equations for the global density matrix written in the collective state representation. From our study, it follows that the optical response of the dimer (the intensity of luminescence, for instance) is a one-valued function of the driven field intensity and, hence, never manifests any bistable behavior. Thus, such behavior obtained in Refs. [1–3,9] is a result of the splitting procedure.

The paper is organized as follows. In Sec. II, we write down the system of equations for the density matrix of a dimer in the collective state representation. Section III deals with an analytical steady-state solution of this system of equations. In Sec. IV, we discuss, in some heuristic manner, the applicability of the splitting procedure in the case of aggregates composed of many molecules. Section V summarizes the paper.

II. EXCITONIC STATE REPRESENTATION FOR THE DENSITY MATRIX

For the sake of simplicity, we assume that the dimer is composed of two identical monomers separated by a distance much less than an emission wavelength with the transition dipole matrix elements $\boldsymbol{\mu}$ forming an angle θ with the dimer axis and with the static dipole moments equal to zero (these restrictions do not limit generality of our treatment). Let an external field $\mathcal{E}(t)=E_0(t)\cos(\omega_0 t)$ polarized parallel to $\boldsymbol{\mu}$ drive this system, with a slow varying envelope $E_0(t)$ and a frequency ω_0 in the vicinity of resonance with the dimer transitions (see Fig. 1). The behavior of the dimer treated as

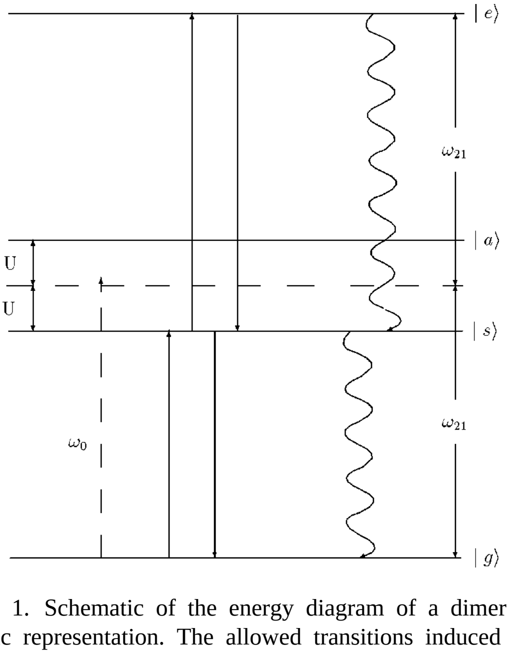

FIG. 1. Schematic of the energy diagram of a dimer in the excitonic representation. The allowed transitions induced by the external field are shown by solid arrows. Wavy arrows indicate the allowed spontaneous transitions. The dashed arrow shows the location of the external field frequency with respect to the dimer energy levels.

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a whole can be described in terms of the density operator $\rho(t)$. In the frame of the rotating-wave approximation, von Neuman's equation driving the evolution of this operator reads (see, for instance, [13])

$$\dot{\rho}(t)=-i[H_0^{\mathrm{RWA}}+V(t),\rho(t)] + \gamma[D\rho(t)D^\dagger-\tfrac{1}{2}D^\dagger D\rho(t)-\tfrac{1}{2}\rho(t)D^\dagger D], \quad (1a)$$

$$H_0^{\mathrm{RWA}}=\Delta\sum_{k=1,2} b_k^\dagger b_k+H_{dd}, \quad (1b)$$

$$V(t)=-\frac{1}{2}\mu E_0(t)(D^\dagger+D), \quad D=\sum_{k=1,2} b_k. \quad (1c)$$

Here, H_0^{RWA} is the Hamiltonian of the dimer in rotating frame in the absence of the field, $\Delta=\omega_{21}-\omega_0$ is the detuning of resonance for a monomer (ω_{21} is the monomer transition frequency), $b_k^\dagger$ and b_k are respectively creation and annihilation operators of an excitation of the kth monomer, H_{dd} is the Hamiltonian of the dipole-dipole interaction between monomers; $V(t)$ is the Hamiltonian of the dimer-external field interaction. The second term in square brackets in the right-hand side of Eq. (1) describes the interaction of monomers with the quantized electromagnetic field with γ being the spontaneous emission rate (hereafter $\hbar=1$). We do not include into our scheme any additional dephasing process. As can be seen further, it is of no importance.

In the problem at hand, it is natural to make use of a basis of collective (in fact, excitonic) states, which diagonalizes the Hamiltonian H_0^{RWA}. For a dimer system, it is represented by the well-known quartet of states

$$|g\rangle=|1g,2g\rangle, \quad (2a)$$

$$|s\rangle=\frac{1}{\sqrt{2}}(|1g,2e\rangle+|1e,2g\rangle), \quad (2b)$$

$$|a\rangle=\frac{1}{\sqrt{2}}(|1g,2e\rangle-|1e,2g\rangle), \quad (2c)$$

$$|e\rangle=|1e,2e\rangle. \quad (2d)$$

The first of them is the dimer ground state, with no excitons. The doublet of symmetric and antisymmetric states corresponds to the one-exciton states, with equal amplitudes on each monomer but with different relative phases of those. For the negative sign of the inter-monomer interaction (we choose hereafter $\langle 1g,2e|H_{dd}|1e,2g\rangle=-U,[U>0]$), the symmetric state is the lower state of the doublet. And finally, the last state of the quartet represents the two exciton state (both monomers are in the upper level). The eigenenergies of the quartet are 0, $\Delta-U$, $\Delta+U$, and 2Δ, respectively (see Fig. 1).

It is easy to check that the operator $D^\dagger+D$ has nonzero matrix elements only between the symmetric (with respect to a permutation of monomers) states of the dimer: $\langle g|(D^\dagger+D)|s\rangle=\langle s|(D^\dagger+D)|e\rangle=\sqrt{2}$. Thus, the interaction Hamiltonian $V(t)$ couples only ground, symmetric, and fully excited states. This, in particular, means that the frequency of the ground-to-one exciton transition, $\omega_{21}-U$, differs from that of the one-to-two exciton transition, $\omega_{21}+U$, by the magnitude of splitting $2U$ (see also Fig. 1). Note that the antisymmetric state has no contribution to the dimer optical response.

To account for the above, one can easily obtain the following system of equations for matrix elements of the density operator:

$$\dot{\rho}_{gg}=2\gamma\rho_{ss}+iF(t)(\rho_{sg}-\rho_{gs}), \quad (3a)$$

$$\dot{\rho}_{ss}=-2\gamma\rho_{ss}+2\gamma\rho_{ee}+iF(t)(\rho_{es}-\rho_{se}+\rho_{gs}-\rho_{sg}), \quad (3b)$$

$$\dot{\rho}_{ee}=-2\gamma\rho_{ee}+iF(t)(\rho_{se}-\rho_{es}), \quad (3c)$$

$$\dot{\rho}_{sg}=-(i\Delta'+\gamma)\rho_{sg}+2\gamma\rho_{es}+iF(t)(\rho_{gg}-\rho_{ss}+\rho_{eg}), \quad (3d)$$

$$\dot{\rho}_{es}=-[i(\Delta'+2U)+2\gamma]\rho_{es}+iF(t)(\rho_{ss}-\rho_{ee}-\rho_{eg}), \quad (3e)$$

$$\dot{\rho}_{eg}=-[2i(\Delta'+U)+\gamma]\rho_{eg}+iF(t)(\rho_{sg}-\rho_{es}), \quad (3f)$$

where $\Delta'=\Delta-U$ is the detuning of resonance with respect to the ground-to-one exciton transition renormalized by the intermonomer interaction as compared to its original value $\Delta=\omega_{21}-\omega_0$, and the notation is introduced: $F(t)=\mu E_0(t)/\sqrt{2}$.

As one of the possible quantities to characterize the optical response of the dimer, we choose the average number of excited molecules defined as

$$n=2\rho_{ee}+\rho_{ss}. \quad (4)$$

The fact should be especially mentioned that, when deriving Eqs. (3), no simplifications have been done except the standard rotating-wave approximation. This gives us a real tool to solve the problem we are interested in, whether the optical response of a dimer can manifest a bistable behavior.

III. STEADY-STATE ANALYSIS

Let us turn out to a steady-state solution of Eqs. (3). Then, assuming $F(t)=F=\mathrm{const}$ and substituting the time derivatives in Eqs. (3) by zero, one obtains

$$\rho_{gg}+\rho_{ss}+\rho_{ee}=1, \quad (5a)$$

$$2\gamma\rho_{ss}+iF(\rho_{sg}-\rho_{gs})=0, \quad (5b)$$

$$-2\gamma\rho_{ss}+2\gamma\rho_{ee}+iF(\rho_{es}-\rho_{se}+\rho_{gs}-\rho_{sg})=0, \quad (5c)$$

$$-2\gamma\rho_{ee}+iF(\rho_{se}-\rho_{es})=0, \quad (5d)$$

$$-(i\Delta'+\gamma)\rho_{sg}+2\gamma\rho_{es}+iF(\rho_{gg}-\rho_{ss}+\rho_{eg})=0, \quad (5e)$$

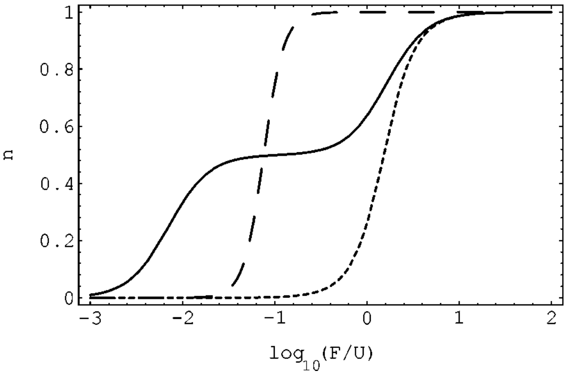

FIG. 2. A family of the field dependences of the averaged number of excited molecules of a dimer (n) obtained by numerical solution of Eq. (5) for three types of resonance conditions: the external field is in resonance with the ground-to-one exciton transition of the dimer, $\omega_0=\omega_{21}-U$ (solid line); the external field is in resonance with the transition of a monomer, $\omega_0=\omega_{21}$ (dashed line); the external field is in resonance with the one-to-two exciton transition of the dimer, $\omega_0=\omega_{21}+U$ (dotted line). $\gamma/U=0.01$.

$$-[i(\Delta'+2U)+2\gamma]\rho_{es}+iF(\rho_{ss}-\rho_{ee}-\rho_{eg})=0, \quad (5f)$$

$$-[2i(\Delta'+U)+\gamma]\rho_{eg}+iF(\rho_{sg}-\rho_{es})=0. \quad (5g)$$

Here, we have added the normalization condition, Eq. (5a).

Obviously, including the static dipole moments of monomers as well as additional dephasing constants, as was done in [1,3], is of no importance since it cannot disturb the structure of the resulting density matrix equations, causing only renormalization of both the relaxation constants and the energy shifts.

In order to demonstrate explicitly the character of the field dependence of the dimer optical response resulting from Eqs. (5), we carried out numerical calculations for different detunings of resonance Δ': (i) $\Delta'=0(\omega_0=\omega_{21}-U$, the exact resonance with the ground-to-one exciton transition); (ii) $\Delta'=-U(\omega_0=\omega_{21}$, the exact resonance with the monomer transition); (iii) $\Delta'=-2U(\omega_0=\omega_{21}+U$, the exact resonance with the one-to-two exciton transition). The results depicted in Fig. 2 do not manifest any bistability effect. Moreover, they can be easily explained in terms of saturation of the transitions as well as based on the fact that in order to saturate the system one should apply a field of strength F (in frequency units) exceeding the detuning of resonance (in our case, of the order of U).

We should only pay attention to the case (ii), where the saturating strength is noticeably less than the detuning magnitude U. This effect results from the fact that at $\omega_0=\omega_{21}$ one has the exact two-photon resonance with the ground-to-two exciton transition. The rate of this transition is given by the "golden rule" taken in the second order of the perturbation theory

$$w_{eg}=2\pi|\langle e|V(E_g-H_0^{\mathrm{RWA}})^{-1}V|g\rangle|^2\rho(E_e), \quad (6)$$

where V and H_0^{RWA} are determined by Eqs. (1b) and (1c), while the operator $V(E_g-H_0^{\mathrm{RWA}})^{-1}V$ represents an effective two-photon interaction operator initiating the transitions in both monomers. Substituting $E_g=0$ as well as the density of final states $\rho(E_e)$ by $(2\gamma)^{-1}$, one then obtains for the rate of two-photon transition:

$$w_{eg}=\frac{\pi}{\gamma}\left(\frac{F^2}{U}\right)^2. \quad (7)$$

In order to gain insight into the saturation peculiarities, one should compare the rate w_{eg} with the effective Rabi frequency of the two-photon transition, which in our case is given (analogously to the dipole transition) by $\langle e|V|s\rangle\langle s|(-H_0^{\mathrm{RWA}})^{-1}|s\rangle\langle s|V|g\rangle=F^2/U$. Equalizing these two magnitudes, we get the following estimation for the saturation magnitude of the external field strength

$$F^{\mathrm{sat}}=\left(\frac{\gamma U}{\pi}\right)^{1/2}. \quad (8)$$

For the value $\gamma/U=0.01$ used in the numerical calculation, it follows from Eq. (8) that $F^{\mathrm{sat}}/U=(1/100\pi)^{1/2}$, what is in full correspondence with the numerical result presented in Fig. 2 (dashed curve).

IV. DISCUSSION

A. Dimer

In this section, we discuss the origin of a discrepancy between the exact theory presented above and the one-molecule density matrix approximation used in Refs. [9,1,3] to treat the problem of dimer bistability. In the latter approach, a coupled system of equations for the density matrices of monomers is considered. We will write down this system of equation with no comments with respect to its derivation, forwarding the reader to Refs. [14–16] for details. Adopted to a dimer composed of two identical monomers, it has the form

$$\dot{Z}=-\frac{\gamma}{2}|R|^2+i\frac{\Omega(t)}{2}(R^{\star}-R)-\gamma(1+Z), \quad (9a)$$

$$\dot{R}=\left[-i(\Delta+UZ)+\frac{\gamma}{2}(Z-1)\right]R-i\Omega(t)Z. \quad (9b)$$

Here, the following notation is introduced: $\Omega(t)=\mu E_0(t)$ and $Z=\rho_{22}-\rho_{11}$, where ρ_{11} and ρ_{22} are diagonal elements of the density matrix of a dimer (no importance of which one, due to the system symmetry), while R is the amplitude of the off-diagonal element of that.

A great difference between Eqs. (9) and Eqs. (3)–(5) is that the former is *nonlinear*, on the contrary to the latter. The nonlinearity results from the coupling of monomers to each other. The basic sequence of this coupling, in fact, leading to a bistable effect, is the dependence of the resonance frequency on the population difference [4,5,16], which now ranges from $\omega_{21}-U$ in the ground dimer state to $\omega_{21}+U$ in the upper one [see Eq. (9b)]. Note that the limits of this change exactly correspond to the energy gap between the ground-to-one exciton and one-to-two exciton transitions in a dimer. In that sense, the one molecular density matrix approach mimics quite well these features. Nevertheless, it allows a continuous change of the resonance frequency not present in the frame of the exact description. In our opinion, this is a key discrepancy between the two approaches used in the literature. This finally causes a wrong description of the optical response of a dimer, in the frame of the one-molecular density matrix approach.

It seems to be very useful to get insight in the physical origin of the pseudobistability effect we are dealing with. In order to observe the effect, one should excite the system slightly above the renormalized resonance $\omega_{21}-U$. As the current detuning of resonance, $\Delta+UZ$, depends on the population difference Z, then the system, when exciting by an external field, ''wishes'' to reduce the detuning of resonance and, what is important, can do it continuously. The radiative damping, both incoherent and coherent represented in Eq. (9) by γ and R^2 terms, respectively, competes with this tendency, stabilizing the population at a certain level. However, at a certain threshold value of the incident field amplitude, the radiative damping cannot resist anymore the pumping, and the system experiences an abrupt jump to another level of population. We should notice once more that it happens at a fixed external field amplitude due to a *continuous* reduction of the detuning of resonance. When the latter changes stepwise (the case of a dimer), the upper level is excited monotonically as the Rabi frequency of the external field exceeds the energy gap. This is just what we demonstrated in the previous section.

B. *N*-molecule problem

Naturally, the question arises whether splitting of the global (N-molecule) density matrix of the system into a simple product of the one-molecule density matrices can be ever used for describing the optical response of a system built up of a large number of interacting monomers. As was already pointed out in Ref. [4], the one-molecule density matrix approach, tracing adequately the limits of the resonance frequency shift induced by the local field correction, totally fails nevertheless in describing quantization of the resonance frequency and, as a result, in a proper reflection of the spectral features of the third-order susceptibility [17]. From this it becomes clear that the problem we are going to discuss hardly has a universal solution. The one-molecule density matrix approach being appropriate for the description of some physical observables may not be adequate for doing that with respect to others.

We will try to get insight into the splitting problem in a heuristic manner, as applied to the problem of bistability of a regular linear Frenkel chain. Our treatment is based on the observation done above, namely, for getting bistability, the population-dependent resonance frequency of the system has to be changed continuously (and not stepwisely). From this it follows that one should compare the characteristic scale of changing the transition energies in the optically active spectral region, with the radiative damping constant γ_R attributed to this region (or maybe with the dephasing constant Γ, if it exceeds γ_R). If γ_R is large in that scale, quantization of the transition energies is not important. This is just a condition necessary (but not sufficient) for manifesting a bistable behavior.

In order to get some quantitative estimates let us turn to a regular linear Frenkel chain of N identical molecules accounting for the nearest-neighbor coupling only. By this approximation, one-dimensional Frenkel excitons become noninteracting fermions [18], so that the energy spectrum of the system can be easily built up by making use of the single-exciton energy spectrum and Pauli's exclusive principle. In addition, let all transition dipole moments of molecules be parallel and make an angle θ with the chain axis. Then, the interaction of nearest neighbors, U, can be written as follows: $-U=3\gamma(1-3\cos^2\theta)/4(k_0a)^3$, where $k_0=2\pi/\omega_{21}$. Further, we set $(1-3\cos^2\theta)=-1$ for definiteness, so that $U>0$. At the negative sign of the nearest-neighbor coupling, the states close to the bottom of multiexciton manifolds mostly contribute to the optical transitions [19–22]. The transition energy between manifolds of $n-1$ and n excitons is exactly equal to the energy of nth single exciton state $E_n=\hbar\omega_{21}-2U\cos[\pi n/(N+1)]$ [19]. Thus, the energy scale we are talking about is given by $E_2-E_1=3\pi^2U/N^2$ (at $N\gg1$). The radiative damping constant γ_R for a chain of size less than the emission wavelength λ is given by the expression $\gamma_R=\gamma N$ and does not exceed this interval [19]. In the opposite limit, $\gamma_R=3\pi\gamma\sin^2\theta/4k_0a=\pi\gamma/4k_0a(\sin^2\theta=1/3)$ [14,4], the necessary condition $\gamma_R\gg E_2-E_1$ can be definitely satisfied by raising the chain size. Equalizing γ_R to E_2-E_1, one finds a critical length $L^*=\lambda\sqrt{9/4\pi}$ for this condition to be valid.

The length L^* introduced above represents an exciton coherence length limited by the radiative damping. This means that any two molecules separated by a distance L exceeding L^* can be considered independent of one another. On the contrary, molecules inside a chain part of size less than L^* are strongly correlated. Clearly, applying the splitting procedure of the global density matrix into a product of the one-molecule density matrices seems to be a rather good approximation for the former and not for the latter. This observation provides a key for a heuristic answer to the question raised, namely, the one-molecule density matrix approach is expected to be a good approach for treating any attributive feature of the system as a whole (including bistability) as soon as the system length exceeds the correlation length L^*. More detailed analysis of this problem is in progress.

Concluding this subsection, we would like to comment on an attributive feature of the global density matrix ρ, which might result in a bistable behavior in systems of a larger number of monomers. Certainly, the rigorous treatment of this problem should be based on the von Neuman equation (1a), which obviously is always linear in ρ. At first sight, it is unclear how then bistability can appear if the latter normally results from a nonlinearity. The matter is that observable quantities showing bistability are not the elements of the global density matrix itself, but as averages are some functions of them. It is intuitively clear that for a mesoscopic or even macroscopic system, where the full set of quantum numbers is large, ρ represents a complex function, in principle, with several maxima over this set. Then, in calculating the averages, uniqueness of measuarable quantities versus the external parameters can be lost, resulting in a bistable and even multistable behavior.

V. SUMMARY

A rigorous analysis of the possibility to get a bistable optical response from a dimer composed of two identical monomers was carried out. Our treatment was based on the two-particle density matrix in the collective (excitonic) state representation without its splitting into a product of density matrices of monomers. The latter procedure leads to the appearance of a nonlinearity in the reduced equations for the one-particle density matrix which, in turn, results in the artifact of a bistable behavior of the dimer optical response.

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