Interplay of creation, propagation, and relaxation of an excitation in a dimer

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Interplay of simultaneous creation, annihilation, propagation, and relaxation of an excitation in molecular condensates interacting with an ultrashort quantum optical pulse is studied in general and specialized to a dimer. A microscopic model appropriate for such systems (with a strong exciton–phonon coupling) is presented. It also incorporates effects of (quantum) noise in the optical field.

A variety of new features in the initial stage of excitation dynamics (when it is being created) is revealed; a strong influence of the coherent excitation propagation on the processes of excitation creation and annihilation in a molecule strongly interacting with phonons is the most remarkable one.

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1. Introduction

Over the last decades, a great deal of attention has been devoted to the study of dynamics of excitations in systems with strong exciton– or electron–phonon interactions like in molecular condensates (see, Refs. [1,2,3,4,5,6,7]; for review, see, Ref. [8,9,10,11,12]). A strong exciton–phonon interaction leads to polaron formation which results in quasicoherent propagation of excitations. Quasicoherent propagation has been extensively studied for various models of the exciton–phonon interaction based on the (generalized) master equation approach (see, e.g., Ref. [8]). However, all previously developed models assumed that an excitation already exists at the beginning of the interaction with phonons (e.g., as a result of the interaction with an ultrashort pulse).

An alternative approach to quasicoherent propagation in molecular condensates is based on the Green functions technique [13,14]. But it has in general a different range of validity in comparison with the master equation approach.

On the other hand, the optical Bloch equations provide the description of a two-level system with relaxation interacting with a classical optical field [15]. This approach is appropriate in many experimental situations (see, e.g., Refs. [16,17]). However, it fails in systems interacting strongly with phonons. A generalization of the Bloch equations in case of a two-level system interacting strongly with phonons and a classical monochromatic optical field has been found in Ref. [18]. It has been also shown in Ref. [18] that field dependent relaxation rates emerge for strong optical fields. Also intermolecular coherent transfer influences substantially excitation dynamics in systems interacting with optical fields [19,20,21,22,23]. Influence of statistical properties of optical fields in interaction with simple matter systems (free and interacting atoms in resonant cavities, atoms in traps, etc.) has been developed in quantum optics (see, e.g., Refs. [15,24,25,26,27,28,29]).

However, the above mentioned theories are not appropriate for the description of excitation dynamics in molecular condensates interacting with pulsed optical fields. The paper provides such a theory, i.e. the theory applicable to the description of excitation dynamics in systems i) with coherent transfer of excitations, ii) with a strong exciton–phonon interaction, and iii) being under the influence of optical fields (e.g., in the form of an ultrashort pulse). It thus provides a tool for the investigation of the initial stage of excitation dynamics, i.e. when an excitation is being created. Understanding of the excitation dynamics in the initial stage is the main goal of the paper. Moreover, the theory encompasses also the influence of (quantum) noise in an optical field.

The theory is based on projection operator formalism [30,31,32,33,34,35]. The formalism of the theory is more complex in comparison with the previously developed theories, but it is much more general. In fact, it generalizes the theories of quasicoherent transfer [8] which did not take into account interaction with an optical field and thus were not able to describe at least the initial stage of excitation dynamics. However, when the optical field is gone, the formalism provides the same excitation dynamics as the older theories.

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The general theory is specialized to a dimer interacting with an ultrashort optical pulse. The initial stage of excitation dynamics is then studied in cases in which processes of excitation creation, transfer, relaxation, and annihilation occur at the same timescale, i.e., they mutually compete. In such cases, the previously derived theories cannot be applied. Influence of the coherent excitation transfer on the processes of excitation creation and annihilation in a molecule strongly interacting with a phonon system is the most important effect. Influence of noise in the optical field is also investigated. It is shown, that the theory provides the long-time excitation dynamics in agreement with equilibrium statistical physics.

The theory is primarily developed for the description of excitation dynamics in various molecular condensates. However, it can also be applied to other physical systems, e.g., to the dynamics of an excitation in an impurity in a crystal.

Section 2 provides a general theory valid for an arbitrary exciton system. It is specialized to a dimer in Section 3. The initial stage of excitation dynamics is investigated in Section 4. Influence of an optical noise is studied in Section 5. Section 6 is devoted to the long-time behavior of an excitation. Section 7 summarizes obtained results. Appendix contains definitions of coefficients entering equations for the dimer.

2. Description of a general model

A system under consideration appropriate for the description of excitation dynamics in molecular condensates consists of the exciton (or electron), photon, and phonon subsystems with the exciton–photon and exciton–phonon interactions (for details, see Refs. [36,37]). Hamiltonians of the free exciton ($\hat{H}_e$), photon ($\hat{H}_f$), and phonon ($\hat{H}_{ph}$) subsystems are given as follows

\[
\begin{align*}
\hat{H}_e & = \sum_{m,n} J_{mn} c_m^\dagger c_n, \\
\hat{H}_f & = \sum_K \hbar \omega_K \hat{a}_K^\dagger \hat{a}_K, \\
\hat{H}_{ph} & = \sum_k \hbar \Omega_k \hat{b}_k^\dagger \hat{b}_k,
\end{align*}
\]

(1)

where $c_m^\dagger$ ($c_m$) means the exciton creation (annihilation) operator at the $m$th site of the lattice (Frenkel excitons are considered), $\hat{a}_K^\dagger$ ($\hat{a}_K$) represents the creation (annihilation) operator of the $K$th photon mode and $\hat{b}_k^\dagger$ ($\hat{b}_k$) is the creation (annihilation) operator of the $k$th phonon mode. The exciton operators $c_m^\dagger$ and $c_m$ obey the Pauli commutation relations, i.e., the operator $c_m^\dagger$ can be expressed as $c_m^\dagger = d_m^\dagger c_m$, where $d_m^\dagger$ is the creation operator of an electron in the excited state and $c_m$ means the annihilation operator of an electron in the ground state at the $m$th site. The photon and phonon operators $\hat{a}_K$, $\hat{a}_K^\dagger$, $\hat{b}_k^\dagger$, and $\hat{b}_k$ obey the boson commutation relations. The coefficients $J_{mn}$ describe energies of the free exciton subsystem for $m = n$ and coherent transfer in the exciton subsystem given by overlaps of wave functions for $m \neq n$. The excitonless state $|0\rangle$ is assumed to have zero energy. The symbol $\omega_K$ ($\Omega_k$) stands for the frequency of the $K$th ($k$th) mode of the photon (phonon) field. The symbol $\sum_K$ ($\sum_k$) means summation over all photon (phonon) modes and $\sum_m$ denotes summation over all exciton states; $\hbar$ is the reduced Planck constant.

The exciton–photon interaction Hamiltonian $\hat{H}_{e-f}$ in the rotating wave approximation reads

\[
\hat{H}_{e-f} = \sum_{m,K} \hbar \omega_{K_0} F^m_K \left( \hat{a}_K c_m^\dagger + \hat{a}_K^\dagger c_m \right),
\]

(2)

where $\omega_{K_0}$ is a typical photon frequency. The exciton–photon coupling constants $F^m_K$ are given in the dipole approximation by

\[
F^m_K = -\frac{1}{\hbar \omega_{K_0}} \sqrt{\frac{\hbar e}{2\epsilon_0 V \omega_K m_e}} \epsilon_K \cdot \langle m|\hat{p}|0\rangle \exp (i \mathbf{K} \cdot \mathbf{r}_m).
\]

(3)

Here $e$ ($e < 0$) is the charge of electron, $m_e$ the mass of electron, $\mathbf{p}$ the momentum operator of electron, $\mathbf{r}_m$ the mean position of the $m$th molecule in a lattice, $|0\rangle$ describes the excitonless state, $|m\rangle$ the state with one exciton localized at the $m$th site of the lattice and the dot means the scalar product; $\epsilon_K$ is the polarization vector of the $K$th mode of the photon field, $\epsilon_0$ permittivity of vacuum, and $V$ the quantization volume of the electromagnetic field.

The exciton–phonon interaction is described by the interaction Hamiltonian $\hat{H}_{e-ph}$ in the form

2
\[ \hat{H}_{c-ph} = \frac{1}{\sqrt{N}} \sum_{m,k} \hbar \Omega_k G_n^m c_m^\dagger c_m \left( \hat{b}_k + \hat{b}_k^\dagger \right) \]  

(4)

with only the site-diagonal exciton–phonon coupling constants \( G_n^m \) on the site index \( m \) and the mode index \( k \) is determined according to the type of phonons (optical or acoustic) and according to the model of the exciton–phonon interaction; \( N \) means the number of phonon modes. Hamiltonian (4) describes a deformation of the lattice around a given site \( m \) after it was occupied by the exciton (polaron effect).

The excitation dynamics in such a complex system can be conveniently described by the generalized master equations for the exciton reduced density matrix \( \hat{\rho}(t) \). The application of the time-convolutionless formalism \[39\] in connection with a time-dependent projector \[40\] and the assumption that \( \hat{\rho}(t) \) lies within the space corresponding to the Hilbert space spanned by the excitonless state \( |0\rangle \) and by states \(|m\rangle \) with one exciton at a given site \( m \) (“single-excitation approximation”) result in the following set of equations for the matrix elements of the exciton reduced density matrix \( \hat{\rho}(t) \) (for details, see Refs. \[33, 37\]):

\[
\frac{d}{dt} \rho_{mn}(t) = -\frac{i}{\hbar} \sum_p J_{mn,p} \rho_{pn}(t) - \sum_p G_{mn,p}(t) \rho_{pn}(t) - \sum_p G_{nm,p}^*(t) \rho_{mp}(t) \\
- \sum_p I_{m,p}(t) \rho_{pn}(t) - \sum_p I_{n,p}(t) \rho_{mp}(t) \\
- i F_m(t) \rho_{0n}(t) + i F_n^*(t) \rho_{0m}(t) + \left[ I_{m,n}(t) + I_{n,m}^*(t) \right] \rho_{00}(t), 
\]

(5)

\[
\frac{d}{dt} \rho_{00}(t) = -\sum_l \left[ I_{l,l}(t) + I_{l,l}(t) \right] \rho_{00}(t) \\
- i \sum_p F_p(t) \rho_{0p}(t) + i \sum_p F_p^*(t) \rho_{0p}(t) + \sum_{s,p} \left[ I_{s,p}(t) + I_{s,p}^*(t) \right] \rho_{sp}(t), 
\]

(6)

\[
\frac{d}{dt} \rho_{0m}(t) = \frac{i}{\hbar} \sum_p J_{mn,p} \rho_{0p}(t) - \sum_p G_{mn,p}(t) \rho_{0p}(t) - \sum_p I_{n,p}(t) \rho_{0p}(t) - \sum_l I_{l,l}(t) \rho_{0m}(t) \\
+ \sum_p \left[ I_{m,p}(t) + I_{m,p}^*(t) \right] \rho_{0p}(t) - i \sum_p F_p(t) \rho_{0p}(t) + i F_n^*(t) \rho_{00}(t). 
\]

(7)

The matrix element \( \rho_{mn} \) describes the probability that an exciton is in a state localized at the site \( m \) and \( \rho_{00} \) determines the probability of the system to be in the excitonless state. The non-diagonal elements \( \rho_{mn} (m \neq n) \) containing information about the mutual coherence between states localized at sites \( m \) and \( n \) play the dominant role in the description of quasicoherent excitation propagation. The elements \( \rho_{0m} \) reflecting a mutual coherence between the excitonless state and excited states are important for the description of excitation creation and annihilation.

The coefficients \( J_{mn} \) describe the inner dynamics of the exciton subsystem (coherent transfer). The time-dependent coefficients \( G_{mn,p}(t) \) and \( G_{n,p}(t) \) originating in the exciton–phonon interaction describe effects of polaron formation. They renormalize the coefficients \( J_{mn} \) (see Section 6 later). This results in quasicoherent excitation propagation. The time-dependent coefficients \( F_{mn}(t) \) are responsible for excitation creation and annihilation caused by the coherent part of the optical field, whereas the coefficients \( I_{m,n}(t), I_{m,p}(t), \) and \( I_{m,p}(t) \) reflect effects of the incoherent part of the optical field (noise).

The time-dependent coefficients in Eqs. (5—7) are correct to the second power of the exciton–photon or exciton–phonon coupling constants. However, this does not mean that the solution of Eqs. (5—7) is also restricted to the second order.

The time-dependent coefficients \( G_{mn,p}(t) \) and \( G_{n,p}(t) \) are given as follows

\[
G_{mn,p}(t) = \int_{t_{-0}}^{t_0} dt \frac{1}{N} \sum_k \Omega_k^2 (G_n^m G_k^p - G_k^m G_n^p) \left\{ [n_B(\hbar \Omega_k) + 1] \exp(-i\Omega_k \tau) + n_B(\hbar \Omega_{-k}) \exp(i\Omega_{-k} \tau) \right\} \\
\times \sum_s G_{-k,s}^m \langle m|s\rangle(\tau) \langle p|s\rangle^*(\tau), 
\]

\[
G_{n,p}(t) = \int_{t_{-0}}^{t_0} dt \frac{1}{N} \sum_k \Omega_k^2 G_k^p \left\{ [n_B(\hbar \Omega_k) + 1] \exp(-i\Omega_k \tau) + n_B(\hbar \Omega_{-k}) \exp(i\Omega_{-k} \tau) \right\} \\
\times \sum_s G_{s}^n \langle n|s\rangle(\tau) \langle p|s\rangle^*(\tau), 
\]

(8)
where the symbol

\[ n_{B}(\hbar \Omega_{k}) = \frac{1}{\exp(\beta \hbar \Omega_{k}) - 1} \]  

(9)
denotes the mean value of the number of phonons in the mode \( K \) being in the equilibrium state and the correlation function \( \langle p|s \rangle(t) \) of the noninteracting exciton subsystem is defined by

\[ \langle p|s \rangle(t) = \langle p|\exp \left( -\frac{i}{\hbar} \hat{H}_{e}t \right) |s \rangle. \]  

(10)

The time-dependent coefficients \( F_{m}(t) \), \( I_{m,p}(t) \), \( \tilde{I}_{m,p}(t) \), and \( \tilde{I}_{m,p}(t) \) are expressed in the form

\[ F_{m}(t) = \omega_{K_{0}} \tilde{F}_{K_{0}}^{m} A(t), \]
\[ I_{m,p}(t) = \int_{t_{0}}^{t} d\tau \omega_{K_{0}}^{2} \tilde{F}_{K_{0}}^{m} \sum_{s} \tilde{F}_{K_{0}}^{s} \delta N(t,\tau)\langle p|s \rangle^{*}(t-\tau), \]
\[ \tilde{I}_{m,p}(t) = \int_{t_{0}}^{t} d\tau \omega_{K_{0}}^{2} \tilde{F}_{K_{0}}^{m} \sum_{s} \tilde{F}_{K_{0}}^{s} \delta N_{e}(t,\tau)\langle p|s \rangle^{*}(t-\tau), \]
\[ \tilde{I}_{m,p}(t) = \int_{t_{0}}^{t} d\tau \omega_{K_{0}}^{2} \tilde{F}_{K_{0}}^{m} \sum_{s} \tilde{F}_{K_{0}}^{s} \delta N_{a}(t,\tau)\langle p|s \rangle^{*}(t-\tau), \]

(11)

where

\[ \tilde{F}_{K_{0}}^{m} = -\frac{1}{\hbar \omega_{K_{0}}} e^{-\epsilon_{K_{0}} \cdot \langle m|\hat{p}|0 \rangle} \exp(i\mathbf{K}_{0} \cdot \mathbf{r}_{m}). \]

(12)
The optical field is assumed to be polarized in the direction \( \epsilon_{K_{0}}. \) The function

\[ A(t) = \sum_{K} \sqrt{\frac{\hbar}{2\epsilon_{0}V\omega_{K}}} (\alpha_{K}(t))_{f} \]  

(13)
describes a classical amplitude of the field. Second moments of the optical field are characterized by the functions

\[ \delta N(t,\tau) = \sum_{K,K'} \frac{\hbar}{2\epsilon_{0}V\sqrt{\omega_{K}\omega_{K'}}} (\delta \alpha_{K}(t)\delta \alpha_{K'}^{*}(\tau))_{f}, \]
\[ \delta N_{e}(t,\tau) = \delta N(t,\tau) + \sum_{K} \frac{\hbar}{2\epsilon_{0}V\omega_{K}} \exp \left[ -i\omega_{K}(t-\tau) \right], \]
\[ \delta N_{a}(t,\tau) = \sum_{K,K'} \frac{\hbar}{2\epsilon_{0}V\sqrt{\omega_{K}\omega_{K'}}} (\delta \alpha_{K}^{*}(t)\delta \alpha_{K'}^{*}(\tau))_{f}. \]  

(14)

The above introduced correlation functions of the photon field operators are defined as follows:

\[ \langle \alpha_{K}(t) \rangle_{f} = \text{Tr}_{f} \{ \hat{\rho}_{f}(t_{0}) \hat{a}_{K}(t - t_{0}) \}, \]
\[ \langle \alpha_{K}(t)\alpha_{K'}^{*}(\tau) \rangle_{f} = \text{Tr}_{f} \{ \hat{\rho}_{f}(t_{0}) \hat{a}_{K'}^{*}(\tau - t_{0}) \hat{a}_{K}(t - t_{0}) \}, \]
\[ \langle \alpha_{K}^{*}(t)\alpha_{K'}^{*}(\tau) \rangle_{f} = \text{Tr}_{f} \{ \hat{\rho}_{f}(t_{0}) \hat{a}_{K'}^{*}(\tau - t_{0}) \hat{a}_{K}^{*}(t - t_{0}) \}, \]
\[ \delta \alpha_{K}(t) = \alpha_{K}(t) - \langle \alpha_{K}(t) \rangle_{f}. \]  

(15)

A detailed analysis of the above general equations is contained in Refs. \[36,37\].

3. Asymmetric dimer

The model developed in the previous section is now specialized to a dimer consisting in general of two different molecules. We assume that the first (second) molecule has the energy \( E + 2\varepsilon \) \((E)\) and that coherent exciton transfer between molecules is described by a real constant \( J \). Hence
\[ J_{11} = E + 2\varepsilon, \quad J_{22} = E, \quad J_{12} = J_{21} = J. \]  

The exciton Hamiltonian (16) can be easily diagonalized by the eigenvectors

\[ |+\rangle = \frac{1}{\sqrt{2\Delta(\Delta - \varepsilon)}} [J|1\rangle + (-\varepsilon + \Delta)|2\rangle], \]
\[ |-\rangle = \frac{1}{\sqrt{2\Delta(\Delta + \varepsilon)}} [J|1\rangle + (-\varepsilon - \Delta)|2\rangle] \]

with the corresponding eigenenergies

\[ E_+ = E + \varepsilon + \Delta, \]
\[ E_- = E + \varepsilon - \Delta, \]

where

\[ \Delta = \frac{1}{2}(E_+ - E_-) = \sqrt{\varepsilon^2 + J^2}. \]

This enables us to calculate the correlation functions \( \langle ps(t) \rangle \) in Eq. (10) and then to determine the time-dependent coefficients entering Eqs. (5—7). The resulting equations represent a set of nine coupled differential equations with a special structure. They can be conveniently written in the matrix form:

\[
\frac{d}{dt} \begin{bmatrix} R_1(t) \\ R_2(t) \end{bmatrix} = \begin{bmatrix} \mathcal{F}_1(t) & \mathcal{F}_2(t) \\ \mathcal{F}_3(t) & \mathcal{F}_4(t) \end{bmatrix} \begin{bmatrix} R_1(t) \\ R_2(t) \end{bmatrix} - \begin{bmatrix} G_1(t) & 0 \\ 0 & G_2(t) \end{bmatrix} \begin{bmatrix} R_1(t) \\ R_2(t) \end{bmatrix}.
\]

The vectors \( R_1(t) \) and \( R_2(t) \) are defined as follows:

\[ R_1(t) = \begin{bmatrix} \rho_{11}(t) \\ \rho_{22}(t) \\ \rho_{r1}(t) \\ \rho_{i1}(t) \\ \rho_{00}(t) \end{bmatrix}, \]
\[ R_2(t) = \begin{bmatrix} \rho_{r2}(t) \\ \rho_{i2}(t) \end{bmatrix}. \]

The exciton matrix elements in Eqs. (21) and (22) are expressed as follows:

\[ \rho_r(t) = \frac{1}{2} \{ \rho_{12}(t) + \text{c.c.} \}, \]
\[ \rho_i(t) = \frac{1}{2i} \{ \rho_{12}(t) - \text{c.c.} \}, \]
\[ \rho_{jr}(t) = \frac{1}{2} \left\{ \rho_{0j}(t) \exp \left[ -\frac{i}{\hbar}(E + \varepsilon)t \right] + \text{c.c.} \right\}, \]
\[ \rho_{ji}(t) = \frac{1}{2i} \left\{ \rho_{0j}(t) \exp \left[ -\frac{i}{\hbar}(E + \varepsilon)t \right] - \text{c.c.} \right\}, \quad j = 1, 2, \]

where c.c. means complex conjugate.

The matrices \( \mathcal{F}_1 \) and \( \mathcal{F}_2 \) describe coherent transfer in the free exciton subsystem. Effects of polaron formation as a result of the exciton–phonon interaction are contained in the matrices \( \mathcal{G}_1(t) \) and \( \mathcal{G}_2(t) \). Excitation creation and annihilation caused by the coherent part of a photon field is described in the matrices \( \mathcal{F}_3(t) \) and \( \mathcal{F}_4(t) \). Finally, the matrices \( \mathcal{F}_1(t) \) and \( \mathcal{F}_4(t) \) contain the influence of noise in the photon field. Definitions of these matrices as well as the description of their role in excitation dynamics are contained in Appendix. We limit ourselves only to the discussion of main characteristic features here.

The matrices on the right-hand side of Eq. (20) have a remarkable block structure. The dynamics of the free exciton subsystem is governed by the mutually independent vectors \( R_1(t) \) and \( R_2(t) \) as a result of the special type of
the exciton Hamiltonian in Eq. (1). Owing to the number of excitation conservation as a consequence of our special form of the exciton–phonon coupling (4), the latter interaction changes the dynamics of \( R_1(t) \) and \( R_2(t) \), but it does not change their mutual independence. Noise in the photon field acts similarly. The coherent part of an optical field introduces mutual coupling between the vectors \( R_1(t) \) and \( R_2(t) \) and thus leads to an effective exciton generation. We note that exciton generation can also be caused by noise in the optical field (for details, see Appendix).

Interaction with the coherent component of the photon field creates two different kinds of paths leading to excitation generation. In the first kind, for molecule 1, an excitation (nonzero \( \rho_{11}(t) \)) emerges along the path \( \rho_{00} \rightarrow \rho_{10} \rightarrow \rho_{01} \rightarrow \rho_{12} \rightarrow \rho_{11} \) including double interaction of the photon field at this molecule. Terms corresponding to such a path are the same as those in the exact equations for a two-level system interacting with a classical deterministic time-dependent field [37]. In this case, the solution of our equations is nonperturbative with respect to the exciton–photon coupling constants. For the second kind of excitation paths, the existence of a surrounding molecule is necessary. An excitation can emerge along the paths \( \rho_{00} \rightarrow \rho_{10} \rightarrow \rho_{11} \rightarrow \rho_{12} \rightarrow \rho_{21} \rightarrow \rho_{11} \) including double interaction with the photon field at molecules 1 and 2 and transfer through \( J \).

The statistics of an optical field is not limited to a classical noise. Quantum description of the optical field provides a tool for investigations of the influence of nonclassical properties of light (e.g. squeezing of vacuum fluctuations).

Time development of the coefficients originating in exciton–phonon coupling reflects a polaron cloud formation around the exciton. The coefficients are practically zero for short times and start to act significantly for longer times when they renormalize coefficients in the matrices \( J_1 \) and \( J_2 \). Their time development ceases for times comparable with the phonon relaxation time \( \tau_R \) when they reach asymptotic values. The magnitude of renormalization is proportional to the strength of exciton–phonon coupling. Asymptotic values of the renormalization are given by the Debye-Waller factor as will be shown in Section 6. That means that our model, although perturbative in exciton–phonon coupling, is able to describe correctly effects of a strong exciton–phonon coupling (small polaron formation).

The above presented equations for a dimer (20) extend Bloch equations in three respects: i) they include transfer of an excitation from and to a given molecule, ii) they describe interaction with a phonon reservoir on a “microscopic level” (polaron formation), and finally iii) they incorporate effects of (quantum) noise in the optical field.

4. Initial stage of excitation dynamics

Based on the above introduced model of the dimer, excitation dynamics is investigated under the conditions when time characterizing pulse duration, propagation, and relaxation are comparable. In this case, the model provides new interesting results. Firstly, excitation dynamics is studied in a two-level system strongly interacting with phonons (Subsection 4.1). In comparison with Ref. [13] the model is valid also for pulsed light and provides a more accurate description of effects stemming from the exciton–phonon interaction. Effects of excitation transfer are studied in a dimer in which either one molecule interacts with a pulse (Subsection 4.2) or both molecules interact with a pulse simultaneously (Subsection 4.3). Such models are appropriate for a variety of physical situations (e.g. two interacting molecules of the same or different kind, a molecule surrounded by an environment with which it can exchange energy, etc.).

Investigation of the excitation dynamics is based on the numerical solution of Eq. (20) for the model of the exciton–phonon interaction discussed in Appendix (for details, see Ref. [37]). The real envelope of the optical field \( \tilde{A}(t) \) (for definition, see (A9) in Appendix) is assumed in the form \( \tilde{A}(t) = A\tilde{A}_n(t) \), where \( A \) determines the strength of the optical field and the function \( \tilde{A}_n(t) \) has the form

\[
\tilde{A}_n(t) = \begin{cases} 1, & \text{for } t \leq \tau_1 \\ \exp \left( -\frac{t - \tau_1}{\tau_2} \right), & \text{for } t > \tau_1. \end{cases}
\]

(25)

Pulse duration is characterized by the constant \( \tau_1 + \tau_2 \). The constants \( F_1 = \hbar \omega_{K_0} \tilde{F}_{K_0}^{1} A \) and \( F_2 = \hbar \omega_{K_0} \tilde{F}_{K_0}^{2} A \) are used in the further discussion.

We introduce the following simplified notation: \( p_0(t), p_1(t), p_2(t) \) denote the probabilities that the exciton system is in the excitonless state \( \rho_0(t) = \rho_{00}(t) \), in the state localized at molecule 1 \( \rho_1(t) = \rho_{11}(t) \), and in the state localized at molecule 2 \( \rho_2(t) = \rho_{22}(t) \); \( \bar{p}_1(t) \) and \( \bar{p}_2(t) \) mean the real and imaginary parts of \( p_2(t) \). Meaning of parameters of the system under consideration is schematically shown in Fig. 1. The energy and time scales are introduced so that quantities in energy units are in eV and time is in femtoseconds.
4.1. Two-level system

A two-level system interacting with an optical field shows Rabi oscillations (the stronger the field the higher the frequency is). Detuning (\(\delta'\)) between the carrying frequency of the pulse and the frequency of the two-level system means faster oscillations (with the generalized Rabi frequency) and a lower excitation level (smaller \(p_1(t)\)). When the strength of the optical field is constant the system can return to the excitonless state, but the excitonless state cannot be reached in the period of the pulse quenching.

Interaction with phonons leads to polaron formation around the exciton. This causes a successive diminishing of the effective strength of exciton–photon coupling and thus smaller values of the probability \(p_1(t)\) (it cannot take on value 1 for a nonzero exciton–photon coupling constant \(G\)) (see Fig. 2). This diminishing originates in lower effective values of the electric dipole moment \(-e\langle\hat{x}\rangle\) caused by a successive formation of the polaron state from a bare excited state and in renormalization of the two-level system energy leading to a greater effective detuning \(\delta'\). Strong exciton–phonon coupling suppresses deexcitation of the two-level system (see curves B, C, and D in Fig. 2). Effects of polaron formation are more pronounced for higher temperatures, i.e. for greater mean numbers of equilibrium phonons \(n_B\).

FIG. 2. The influence of the exciton–phonon coupling constant \(G\) on the probability \(p_1(t); G = 0\) [A], \(G = 0.004\) [B], \(G = 0.01\) [C], \(G = 0.02\) [D]; \(J = 10^{-8}\), \(h\delta' = 0\), \(F_1 = 0.01, F_2 = 0, \varepsilon = 0, \tau_1 = 100, \tau_2 = 100\), \(G_1/G = 1 + 0.25i, G_2/G = 1 - 0.25i\), \(n_B = 0, h\Omega_{ph} = 0.01, h\gamma_{ph} = 0.001\).

The magnitude of exciton–photon coupling constants in energy units can be estimated from the mean value of the exciton–photon interaction Hamiltonian \(\hat{H}_{e-f}\) as follows: \(\langle H_{e-f} \rangle \approx \frac{\hbar}{m_0} \langle \hat{p} \rangle A \approx \frac{\hbar}{m_0} \langle [\hat{x}, \hat{\epsilon}_{e, \lambda}] \rangle \approx \frac{\hbar}{m_0} \langle \epsilon_{e} - \epsilon_{g} \rangle \langle \hat{x} \rangle \approx \frac{\hbar}{m_0} \langle \epsilon_{e} - \epsilon_{g} \rangle a_{B} \frac{\hbar}{m_0}\), where \(A\) is the vector potential of a classical field, \(E\) the intensity of the field, \(\omega_{0}\) the mean frequency of the field, \(\hat{p}\) (\(\hat{x}\)) means the momentum (position) operator of electron, \(\epsilon_{e}\) (\(\epsilon_{g}\)) denotes the energy of the excited (ground) state, and \(a_{B}\) is the Bohr radius; \(E = 10^{7} \text{ Vm}^{-1}\), \(\lambda_{0} = 600 \text{ nm}\), and \(\epsilon_{e} - \epsilon_{g} = 2 \text{ eV}\) implies \(\langle H_{e-f} \rangle \approx 5.10^{-4} \text{ eV}\).
4.2. Dimer with one molecule interacting with a pulse

Only molecule 1 is assumed to interact with the pulse as, e.g., a consequence of a special orientation of the transition dipole momentum of molecule 2. In case of exciton dynamics, the “single-excitation” approximation requires that values of the whole excitation probability of the dimer $p_1(t) + p_2(t)$ are approximately less than 0.6 (for details, see Subsection 4.3). The obtained results are appropriate also for electron transfer as a result of the “single-excitation” approximation which rules out differences originating in Fermi and Pauli commutation relations. In this case, the above limitation does not apply.

4.2.1. Energetically balanced dimer

The effect of coherent transfer (described by $J$) on the dynamics of the dimer noninteracting with phonons is shown in Figs. 3a,b. The increase of $J$ leads to a faster exchange of excitation between molecules 1 ($p_1(t)$) and 2 ($p_2(t)$) (its frequency is given by $J$). The transfer strongly affects the processes of excitation creation and annihilation at molecule 1. Fig. 3a shows that the value of $J$ affects the time in which the excitation of molecule 1 is replaced by its deexcitation; especially greater values of $J$ mean an earlier time of deexcitation. This results in smaller values of the whole excitation probability $p_1(t) + p_2(t)$ for greater values of $J$.

FIG. 3. Increasing values of the transfer integral $J$ influence values of the probabilities $p_1(t)$ (a) and $p_2(t)$ (b); $J = 10^{-8}$ [A], $J = 0.0005$ [B], $J = 0.001$ [C], $J = 0.002$ [D]; $F_1 = 0.0005$, $F_2 = 0$, $\varepsilon = 0$, $\hbar\delta' = 0$, $\tau_1 = 1000$, $\tau_2 = 200$, $G = 0$.

Molecule 2 can be excited ($p_2 \neq 0$) even in the time when molecule 1 is not excited ($p_1 = 0$) (see Fig. 4 for $t \approx 300$). In this time molecule 2 is completely decoupled because $\rho_r = \rho_i = 0$. Such an effect has already been observed in Ref. [45]. The exciton subsystem can also return to the excitonless state ($p_0 = 1$, see Fig. 4 for $t \approx 600$). However, when the pulse becomes weak the exciton subsystem cannot reach the state with $p_0 = 1$ (see Figs. 3a,b).

Interaction with phonons influences the dynamics as follows. In case of small $J$ a decrease of the whole excitation probability $p_1(t) + p_2(t)$ (see Figs. 5a,b) with the increase of $G$ occurs as a consequence of the prevailing effect of polaron formation at molecule 1. An increase of the whole excitation probability $p_1(t) + p_2(t)$ with the increase of $G$ for greater $J$ is observed, because $J$ is renormalized by the interaction to its smaller values which suppresses the destructive effect of $J$ on the excitation creation. But when $G$ is great enough (according to the value of $J$) the effect of polaron formation at molecule 1 decreases the whole excitation probability. The magnitude of $G$ also influences the time when the excitation creation is replaced by its annihilation. Especially, annihilation occurs earlier when the polaron formation at molecule 1 prevails for smaller $J$ (compare curves A, B, and C in Figs. 5a,b).
FIG. 5. Increasing values of the exciton–phonon coupling constant $G$ mean the decrease of the probabilities $p_1(t)$ (a) and $p_2(t)$ (b): $G = 0$ [A], $G = 0.003$ [B], $G = 0.005$ [C]; $F_1 = 0.0005$, $F_2 = 0$, $J = 0.0005$, $\varepsilon = 0$, $\hbar\delta' = 0$, $\tau_1 = 1000$, $\tau_2 = 200$, $G_1/G = 1 + 0.25i$, $G_2/G = 1 - 0.25i$, $\omega_{\text{ph}} = 0.01$, $\gamma_{\text{ph}} = 0.001$, $n_B = 0$.

After the pulse is gone, the frequency of excitation exchange between molecules 1 and 2 decreases with increasing $G$. This manifests the renormalization of $J$. Also a complete deexcitation of molecules ($p_1 = 0$, $p_2 = 0$) cannot be reached owing to the polaron effect.

4.2.2. Energetically unbalanced dimer

The energy difference $2\varepsilon$ between the excited states of molecules 1 and 2 affects the phononless system as follows. Greater values of the probabilities $p_1(t)$ (see Fig. 6a) and $p_1(t) + p_2(t)$ for greater values of $|\varepsilon|$ have their origin in decoupling of molecule 2 from molecule 1 which partially suppresses the effect of coherent transfer ($J$). Decoupling of molecule 2 then causes smaller values of $p_2(t)$ (see Fig. 6b). The case when molecule 2 has a lower energy than molecule 1 ($\varepsilon > 0$, $\delta' < 0$) cannot be distinguished from the case in which molecule 2 has a higher energy than molecule 1 ($\varepsilon < 0$, $\delta' > 0$); time development of $p_0(t)$, $p_1(t)$, and $p_2(t)$ is the same.

FIG. 6. The increase of the energy difference $2\varepsilon$ suppresses the effect of $J$, this is demonstrated in the time development of the probabilities $p_1(t)$ (a) and $p_2(t)$ (b): $\varepsilon = 0$, $\hbar\delta' = 0$ [A], $\varepsilon = 0.0005$, $\hbar\delta' = -0.0005$ [B], $\varepsilon = 0.001$, $\hbar\delta' = -0.001$ [C], $\varepsilon = 0.002$, $\hbar\delta' = -0.002$ [D]; $F_1 = 0.0005$, $F_2 = 0$, $J = 0.002$, $\tau_1 = 1000$, $\tau_2 = 200$, $G = 0$.

The increase of $\varepsilon$ may result in the decrease of the probability $p_1(t) + p_2(t)$ when exciton–phonon coupling is nonzero. Also the above mentioned indistinguishability is lost.

If molecule 2 has a lower energy than molecule 1 (positive $\varepsilon$), values of the probabilities $p_1(t)$ (see Fig. 7a) and $p_1(t) + p_2(t)$ (compare Figs. 7a,b) increase with the increase of $G$. This indicates the increasing renormalization of $J$. However, when values of $G$ are too great, then polaron formation at molecule 1 enters into play and the lowering of values of $p_1(t)$ and $p_1(t) + p_2(t)$ is observed.

Increasing positive $\varepsilon$ leads to greater values of $p_1(t) + p_2(t)$ in cases when the polaron formation at molecule 1 does not play an important role (for smaller values of $G$). This is caused by the decrease of the destructive effect of transfer on the excitation creation. However, the increase of positive $\varepsilon$ means the decrease of $p_1(t) + p_2(t)$ if the polaron formation at molecule 1 plays a dominant role. In this case, the destructive effect of transfer on the polaron formation at molecule 1 becomes weaker with increasing $\varepsilon$. 
Increasing values of the exciton–phonon coupling constant $G$ suppress the effect of $J$ and that means the increase of the probabilities $p_1(t)$ (a) and $p_2(t)$ (b); $G = 0$ [A], $G = 0.003$ [B], $G = 0.005$ [C]; $F_1 = 0.0005$, $F_2 = 0$, $J = 0.005$, $\varepsilon = 0.004$, $\hbar\delta' = -0.004$, $\tau_1 = 1000$, $\tau_2 = 200$, $G_1/G = 1 + 0.25i$, $G_2/G = 1 - 0.25i$, $\hbar\Omega_{ph} = 0.01$, $\hbar\gamma_{ph} = 0.001$, $n_B = 0$.

If molecule 2 has a higher energy than molecule 1 (negative $\varepsilon$), the increase of $G$ results in the decrease of the probabilities $p_1(t)$ and $p_1(t) + p_2(t)$ in all cases. Thus the interaction with phonons supports the destructive effect of $J$ on the excitation creation.

The increase of $J$ need not mean only smaller values of $p_1(t)$ caused by the destructive effect of $J$ on the excitation creation. Especially, when a strong interaction with phonons forms a polaron at molecule 1 suppressing its excitation, greater values of $J$ can partially break the polaron formation and admit greater values of $p_1(t)$ (this effect is well pronounced for greater positive $\varepsilon$).

An exciton moving on the dimer can be “partially localized” by the interaction with phonons (see Fig. 8). A complete localization of the exciton cannot be reached because coherent transfer cannot be completely suppressed (see asymptotic expressions in Section 6).

4.3. Dimer with both molecules interacting with a pulse

We first address the validity of “single-excitation” approximation considering a two-level system and a symmetric dimer with $J$ being practically zero and comparing their levels of excitation. Omission of the two-exciton state in the dimer manifests itself in lower values of the excitation probability $p_1(t)$ (or $p_2(t)$) in comparison with that for a two-level system. The deviations can be estimated for a given value of the excitation probability from curves in Fig. 9. In general, the “single-excitation” approximation is very well accepted for values of the whole excitation probability $p_1(t) + p_2(t)$ up to $\approx 0.2$. The deviations in $p_1(t) + p_2(t)$ are less than about 10 % for values of $p_1(t) + p_2(t)$ up to $\approx 0.6$, which is also well acceptable.

Results of this section are not applicable to the electron dynamics because only one excitationless state for the whole system has been considered.
4.3.1. Energetically balanced dimer

Coherent transfer ($J$) affects the excitation dynamics similarly as it is discussed in Subsection 4.2; i.e. the increase of $J$ in the phononless system means the decrease of the whole excitation probability $p_1(t) + p_2(t)$. The exciton subsystem can return to the excitonless state ($p_0 = 1$).

The increasing interaction with phonons ($G$) decreases $p_1(t) + p_2(t)$ for small $J$ as a result of the polaron formation at both molecules. However, the increase of $G$ leads to the increase of $p_1(t) + p_2(t)$ for greater values of $J$ because the destructive effect of transfer on the excitation creation is partially suppressed.

4.3.2. Energetically unbalanced dimer

We assume that molecule 1 is pumped resonantly and molecule 2 nonresonantly in the further discussion. Despite the effect of coherent transfer, small values of $\varepsilon$ lead to a strong asymmetry in the time development of the probabilities $p_1(t)$ and $p_2(t)$ (see Fig. 10) having its origin in the nonresonant interaction of molecule 2 with the pulse.
Interaction with phonons modifies the excitation dynamics as follows. For molecule 2 having a lower energy than molecule 1 ($\varepsilon < 0$), the probability $p_1(t) + p_2(t)$ increases with increasing $G$ until the range of values of $G$ is reached in which the polaron formation at molecule 1 causes the decrease of $p_1(t) + p_2(t)$. The higher the $\varepsilon$ is the less the destructive effect of $J$ on the polaron formation at molecule 1 is. The excitation dynamics is then influenced for weaker $G$.

When the energy of molecule 2 is slightly higher than that of molecule 1 ($\varepsilon > 0$), the increase of $G$ leads to the decrease of $p_1(t)$ (effects of transfer and polaron formation support each other). But an increase of $p_2(t)$ occurs because interaction with phonons tunes molecule 2 to the resonance with the field. The probability $p_1(t) + p_2(t)$ also increases with increasing $G$. For greater values of $|\varepsilon|$, the probability $p_1(t) + p_2(t)$ decreases with increasing $G$.

After the pulse is gone the excitation dynamics is the same as that discussed in Subsection 4.2.

The obtained numerical results elucidate the validity of perturbation approximation. We consider the perturbation approximation in the exciton–photon coupling constants to be reliable for arbitrary times at least for classical deterministic fields. The positive semidefiniteness of the exciton reduced density matrix has been slightly broken for interaction approximation in the exciton–photon coupling constants to be reliable for arbitrary times at least for classical deterministic fields. The positive semidefiniteness of the exciton reduced density matrix has been slightly broken for classical deterministic fields. The positive semidefiniteness of the exciton reduced density matrix has been slightly broken for classical deterministic fields. The positive semidefiniteness of the exciton reduced density matrix has been slightly broken for classical deterministic fields. The positive semidefiniteness of the exciton reduced density matrix has been slightly broken for classical deterministic fields. The positive semidefiniteness of the exciton reduced density matrix has been slightly broken for classical deterministic fields. The positive semidefiniteness of the exciton reduced density matrix has been slightly broken for classical deterministic fields.

5. Influence of optical field fluctuations

Effects originating both in the amplitude and phase fluctuations of a pulsed optical field on the excitation dynamics are studied.

We assume that the noisy part of the photon field amplitude is proportional to the strength of its coherent part. The normalized photon field correlation function $\delta N_\alpha(t, \tau)$ has then the form (the strength of the field is absorbed into $F_1$ and $F_2$):

$$\delta N_\alpha(t, \tau) = \bar{A}_\alpha(t)\bar{A}_\alpha^*(\tau)\langle \delta A_\alpha(t)\delta A_\alpha^*(\tau) \rangle_f,$$

where the normalized envelope of the pulse is given in Eq. (25). The optical field fluctuations are described by the amplitude deviation $\delta A_\alpha(t)$,

$$\delta A_\alpha(t) = \frac{1}{A(t)} \sum_K \sqrt{\frac{\hbar}{2\kappa_0 V}} \delta \alpha_K(t),$$

normalized with respect to the envelope $\bar{A}(t)$ defined in (A9) in Appendix. A stochastic model (29, p. 137) for both the amplitude and phase fluctuations of $\delta A_\alpha(t)$ provides the relation

$$\langle \delta A_\alpha(t)\delta A_\alpha^*(\tau) \rangle_f = \langle |\delta A_\alpha(t)|^2 \rangle_f \exp\left[-i(\omega_{K_0} + \omega_s)(t-\tau)\right]\langle \exp[\phi(t) - i\phi(\tau)] \rangle_f.$$

The moment $\langle |\delta A_\alpha|^2 \rangle_f$ involves averaging over amplitude fluctuations, $\omega_s$ denotes the frequency shift of amplitude fluctuations and the factor $\langle \exp[\phi(t) - i\phi(\tau)] \rangle_f$ involves averaging over the phase $\phi(t)$. If $\phi(t) - \phi(\tau) = \int_t^\tau d\tau' \Delta \omega(\tau')$, where $\Delta \omega(\tau)$ represents the Gaussian Markovian process, then Eq. (28) can be rewritten into the form

$$\langle \delta A_\alpha(t)\delta A_\alpha^*(\tau) \rangle_f = n_s \exp[-i(\omega_{K_0} + \omega_s)(t-\tau)] \exp[-\gamma_s|t-\tau|].$$

The quantity $n_s = \langle |\delta A_\alpha|^2 \rangle_f$ characterizes the strength of noise, whereas $\gamma_s$ describes the strength of phase correlations ($\langle \Delta \omega(t)\Delta \omega(t') \rangle = 2\gamma_s \delta(t-t')$).

The correlation function $\delta N_\alpha(t, \tau)$ in (26) then gets the form:

$$\delta N_\alpha(t, \tau) = \bar{A}_\alpha(t)\bar{A}_\alpha^*(\tau) n_s \exp[-i(\omega_{K_0} + \omega_s)(t-\tau)] \exp[-\gamma_s|t-\tau|].$$

We further omit vacuum fluctuations in the photon field and thus $\delta N_\nu(t, \tau) = \delta N(t, \tau)$ (see Eq. (14)). We also assume $\delta N_\alpha(t, \tau) = 0$ as a consequence of averaging over the phases of $\delta \alpha_K^*(t)$ and $\delta \alpha_K^*(\tau)$ in $\langle \delta A_\alpha^*(t)\delta A_\alpha^*(\tau) \rangle_f$ in Eq. (14).

The influence of noise on the excitation dynamics is described by the matrices $\mathcal{F}_1(t)$ and $\mathcal{F}_2(t)$ given in Eq. (A7) in Appendix. The time-dependent coefficients $M_1(t) = M_1(t)$, . . . , $P_2(t) = P_2(t)$ defined in Eqs. (A10—A12) contain the normalized correlation function $\delta N_\alpha(t, \tau)$ given in Eq. (30) instead of $\delta N(t, \tau)$.

Optical noise influences the dynamics of a two-level system in such a way that it forces the system to evolve in the direction to the state with $p_0 = p_1 = 1/2$, $\rho_{10} = 0$ (see Fig. 12). The increase of $n_s$ leads to the increased influence
of noise. The decrease of $\gamma_s$ means the increase of the correlation time of noise $\tau_s = 1/\gamma_s$ and results in the increased effect of noise.

For values of the exciton-photon coupling constants $F_1$ and $F_2$ and pulse durations ($\tau_1 + \tau_2$) used in Section 4, the influence of noise with reasonable values of parameters ($\tau_s \leq 0.1$, $\gamma_s \geq 0.01$) is negligible.

These results show that noise in ultrashort pulsed optical fields does not influence substantially experimental results under standard conditions. Effects originating in nonclassical properties of photon fields are the matter of further investigations.

6. Long-time behaviour

Eq. (20) is analyzed for times when the photon field (the pulse) does not act on the exciton subsystem and for times longer than the relaxation time $\tau_R$ of the phonon reservoir. Vacuum fluctuations of the photon field are also omitted and hence, e.g., the exciton decay processes are not taken into account. Then the third matrix in Eq. (20) is analyzed for times when the photon field (the pulse) does not act on the exciton subsystem and for standard conditions. Effects originating in nonclassical properties of photon fields are the matter of further investigations.

FIG. 12. A typical excitation dynamics in the two-level system interacting with a noisy pulse described by the probabilities $p_0(t)$ [A] and $p_1(t)$ [B]; $F_1 = 0.01$, $F_2 = 0$, $J = 10^{-8}$, $\varepsilon = 0$, $\hbar \delta' = 0$, $\tau_1 = 1000$, $\tau_2 = 200$, $G = 0$, $n_s = 0.1$, $\gamma_s = 0.01$, $\omega_s = 0$.

The excitation dynamics is then driven by the following equations:

$$
\begin{align*}
\frac{d}{dt} & \begin{bmatrix} \rho_{11}(t) \\ \rho_{22}(t) \\ \rho_r(t) \\ \rho_s(t) \end{bmatrix} = \frac{1}{\hbar} \begin{bmatrix} 0 & 0 & 0 & -2J \\ 0 & 0 & 2J & 0 \\ J & -J & -2\varepsilon & 0 \\ -2\varepsilon & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} \rho_{11}(t) \\ \rho_{22}(t) \\ \rho_r(t) \\ \rho_s(t) \end{bmatrix} \\
&- \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ A_{as} & C_{as} & E_{as} & -F_{as} \\ B_{as} - D_{as} & F_{as} & E_{as} & \rho_l(t) \end{bmatrix} \begin{bmatrix} \rho_{11}(t) \\ \rho_{22}(t) \\ \rho_r(t) \\ \rho_s(t) \end{bmatrix}.
\end{align*}
$$

(31)

The coefficients $A_{as}, \ldots, F_{as}$ express asymptotic values of the time-dependent coefficients $A(t), \ldots, F(t)$ given in (A3) in Appendix for $t \rightarrow \infty$;

$$
\begin{align*}
A_{as} &= \frac{\pi J}{\hbar N} \sum_k |G_k^1 - G_k^2|^2 \{ \varepsilon [2n_B(h\Omega_k) + 1] + \Delta \} \delta(h\Omega_k - 2\Delta), \\
B_{as} &= \frac{J}{\hbar N} \sum_k |G_k^1 - G_k^2|^2 \varepsilon' \frac{\Omega_k^2}{\Omega_k^2 - 4\Delta^2} \left\{ [2n_B(h\Omega_k) + 1] + \frac{2\varepsilon}{h\Omega_k} \right\}, \\
C_{as} &= \frac{\pi J}{\hbar N} \sum_k |G_k^1 - G_k^2|^2 \{ -\varepsilon [2n_B(h\Omega_k) + 1] + \Delta \} \delta(h\Omega_k - 2\Delta), \\
D_{as} &= \frac{J}{\hbar N} \sum_k |G_k^1 - G_k^2|^2 \varepsilon' \frac{\Omega_k^2}{\Omega_k^2 - 4\Delta^2} \left\{ [2n_B(h\Omega_k) + 1] - \frac{2\varepsilon}{h\Omega_k} \right\}, \\
E_{as} &= \frac{2\pi J^2}{\hbar N} \sum_k |G_k^1 - G_k^2|^2 [2n_B(h\Omega_k) + 1] \delta(h\Omega_k - 2\Delta), \\
F_{as} &= \frac{1}{N} \sum_k (G_k^1 - G_k^2) (G_k^1 + G_k^2) \Omega_k, \\
\end{align*}
$$

(32)

$\varepsilon'$ denotes principal value.

For $\varepsilon = 0$ (it implies that $B_{as} = D_{as}$) and $J \ll \Delta W_{ph}$ ($\Delta W_{ph}$ being the width of phonon spectrum) the transfer integral $J$ at the positions (4,1) and (4,2) in Eq. (31) is renormalized to a new value

\[J' = \frac{J}{\sqrt{1 - \varepsilon^2}}\]
\[ J_{\text{ren}} = J - \hbar B_{\text{as}} = J \exp(-2W) + o(G^2), \]
\[ W = \frac{1}{2N} \sum_k \left[ |G_k^1 - G_k^2|^2 [2n_B(\hbar \Omega_k) + 1] \right], \tag{33} \]
where \( W \) denotes the Debye-Waller factor describing the small polaron formation \[43,44\].

The transfer integral \( J \) at the positions (4,1) and (4,2) is renormalized twice and \( J \) at the positions (1,4) and (2,4) is not renormalized. But the effect of renormalization on the matrix elements \( \rho_{11}(t) \) and \( \rho_{22}(t) \) with the nondiagonal matrix elements \( \rho_{12}(t) \) and \( \rho_{21}(t) \) excluded \[44\].

The asymptotic state of the dimer (i.e. the state reached for \( t - t_0 \to \infty \)) has the form correct up to \( G^2 \) as follows,
\[ (\rho_{11}^{\text{as}}, \rho_{22}^{\text{as}}, \rho^{\text{as}_{\text{r}}}, \rho^{\text{as}_{\text{i}}}) \approx (-\gamma_1 \Delta + \gamma_2 \epsilon, -\gamma_1 \Delta - \gamma_2 \epsilon, J \gamma_2, 0), \tag{34} \]
where
\[ \gamma_1 = \frac{1}{N} \sum_k \left[ |G_k^1 - G_k^2|^2 [2n_B(\hbar \Omega_k) + 1] \delta(\hbar \Omega_k - 2\Delta) \right], \]
\[ \gamma_2 = \frac{1}{N} \sum_k \left[ |G_k^1 - G_k^2|^2 \delta(\hbar \Omega_k - 2\Delta) \right]. \tag{35} \]

Its form written in the basis of the eigenstates \( |+\rangle \) and \( |--\rangle \) (17),
\[ \frac{\rho^{\text{as}_{++}}}{\rho^{\text{as}_{--}}} = \frac{\Delta - \epsilon}{\Delta + \epsilon} \exp(-2\beta \Delta), \quad \rho^{\text{as}_{+-}} = \rho^{\text{as}_{-+}} = 0, \tag{36} \]
is in agreement with the result of equilibrium statistical physics for an already created excitation. This indicates that the theory is valid also for longer times despite the perturbation approximation applied in the derivation.

7. Conclusions

A microscopic theory of the excitation dynamics in molecular condensates interacting with optical fields (with ultrashort pulses) has been developed. It has provided a tool for the investigation of the initial stage of excitation dynamics, i.e. when an excitation is being created.

The theory has been applied to a dimer under the conditions when times characterizing pulse duration and propagation and relaxation of an excitation are comparable. The following results have been obtained. In this case, coherent transfer strongly influences the processes of excitation creation and annihilation. The stronger the coherent transfer is, the lower the excitation level is. The influence of coherent transfer is suppressed by the increase of energy difference between excited states. Interaction with phonons leads in general to polaron formation. This leads to lower excitation levels on one side, but on the other side it partially preserves the excitation from being annihilated. Interesting behaviour occurs when effects of coherent transfer and polaron formation compete. Interaction with phonons can partially suppress the destructive effect of coherent transfer on the excitation creation; this leads to higher excitation levels. This occurs when the energy of a molecule being excited is higher than that of surrounding molecules. On the other hand, interaction with phonons can support the effect of coherent transfer on the excitation creation and thus can lead to the further lowering of the excitation level. This is the case when the energy of a molecule being excited is lower than that of surrounding molecules. The theory also provides a long-time dynamics being in agreement with equilibrium statistical physics.

It has been shown that noise in an ultrashort pulse does not influence substantially the initial stage of excitation dynamics under standard conditions. However, the theory is also suitable for the description of effects originating in nonclassical properties of interacting optical fields (e.g., those with squeezed vacuum fluctuations).

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APPENDIX A

Definitions of matrices in Eq. (20)

Appendix contains the definitions of the matrices $J_1$, $J_2$, $G_1(t)$, $G_2(t)$, $F_1(t)$, $F_2(t)$, $F_3(t)$, and $F_4(t)$ in Eq. (20). The influence of their elements on the excitation dynamics is also discussed.

The matrices $J_1$ and $J_2$ describe the dynamics of the free exciton system:

$$J_1 = \frac{1}{\hbar} \begin{bmatrix} 0 & 0 & 0 & -2J & 0 \\ 0 & 0 & 0 & 2J & 0 \\ 0 & 0 & 0 & 2\varepsilon & 0 \\ J & -J & -2\varepsilon & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{bmatrix}, \quad J_2 = \frac{1}{\hbar} \begin{bmatrix} 0 & -\varepsilon & 0 & -J & 0 \\ \varepsilon & 0 & J & 0 & 0 \\ 0 & -J & 0 & \varepsilon & 0 \\ J & 0 & -\varepsilon & 0 \end{bmatrix}. \quad (A1)$$

The matrices $G_1(t)$ and $G_2(t)$ stem from the exciton-phonon interaction:

$$G_1(t) = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ A & C & E & -F & 0 \\ B & -D & F & E & 0 \\ 0 & 0 & 0 & 0 & 0 \end{bmatrix}, \quad G_2(t) = \begin{bmatrix} A_1 & -B_1 & C_1 & -D_1 \\ B_1 & A_1 & D_1 & C_1 \\ C_2 & -D_2 & A_2 & -B_2 \\ D_2 & C_2 & B_2 & A_2 \end{bmatrix}. \quad (A2)$$

The time-dependent coefficients $A(t), \ldots, D_2(t)$ are given as follows

$$A(t) = \frac{J^2}{\Delta^2} G^2 \bar{g}_{2,1} + \frac{J}{2\Delta} G^2 \bar{g}_{3,2},$$

$$B(t) = \frac{J^2}{\Delta^2} G^2 \bar{g}_{2,2} - \frac{J}{2\Delta} G^2 \bar{g}_{3,1},$$

$$C(t) = \frac{J^2}{\Delta^2} G^2 \bar{g}_{2,1} + \frac{J}{2\Delta} G^2 \bar{g}_{3,2},$$

$$D(t) = \frac{J^2}{\Delta^2} G^2 \bar{g}_{2,2} - \frac{J}{2\Delta} G^2 \bar{g}_{3,1},$$

$$E(t) = G^2 \bar{g}_{1,1} - \frac{2J^2}{\Delta^2} G^2 \bar{g}_{2,1},$$

$$F(t) = -G^2 \bar{g}_{1,3}, \quad (A3)$$

$$A_1(t) = G^2 \bar{g}_{1,4} + \frac{J^2}{\Delta^2} G^2 [\bar{g}_{2,4} + \bar{g}_{2,5} + \bar{g}_{2,10}],$$

$$B_1(t) = G^2 \bar{g}_{1,8} + \frac{J^2}{\Delta^2} G^2 [\bar{g}_{2,6} - \bar{g}_{2,8} + \bar{g}_{2,9}],$$

$$A_2(t) = G^2 \bar{g}_{1,7} + \frac{J^2}{\Delta^2} G^2 [\bar{g}_{2,5} - \bar{g}_{2,7} - \bar{g}_{2,10}],$$

$$B_2(t) = G^2 \bar{g}_{1,11} + \frac{J^2}{\Delta^2} G^2 [\bar{g}_{2,6} + \bar{g}_{2,9} - \bar{g}_{2,11}],$$

$$C_1(t) = \frac{J^2}{\Delta^2} G^2 [\bar{g}_{2,4} - \bar{g}_{2,5} - \bar{g}_{2,10}] + \frac{J}{2\Delta} G^2 [\bar{g}_{3,6} + \bar{g}_{3,8} - \bar{g}_{3,9}],$$

$$D_1(t) = \frac{J^2}{\Delta^2} G^2 [\bar{g}_{2,6} + \bar{g}_{2,8} - \bar{g}_{2,9}] + \frac{J}{2\Delta} G^2 [\bar{g}_{3,4} + \bar{g}_{3,5} + \bar{g}_{3,10}],$$

$$C_2(t) = \frac{J^2}{\Delta^2} G^2 [\bar{g}_{2,5} - \bar{g}_{2,7} - \bar{g}_{2,10}] + \frac{J}{2\Delta} G^2 [\bar{g}_{3,6} - \bar{g}_{3,9} + \bar{g}_{3,11}],$$

$$D_2(t) = \frac{J^2}{\Delta^2} G^2 [\bar{g}_{2,6} + \bar{g}_{2,9} - \bar{g}_{2,11}] + \frac{J}{2\Delta} G^2 [\bar{g}_{3,5} - \bar{g}_{3,7} - \bar{g}_{3,10}]. \quad (A4)$$

The functions

$$\bar{g}_{1,3}(t) = \int_{t_0}^{t} d\tau \, g_{1,3}(\tau),$$

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\[ g_{2,j}(t, \Delta') = \int_{0}^{t-t_0} d\tau g_j(\tau) \sin^2(\Delta' \tau), \]
\[ g_{3,j}(t, \Delta') = \int_{0}^{t-t_0} d\tau g_j(\tau) \sin(2\Delta' \tau), \quad j = 1, \ldots, 11 \]  

(A5)
describe the response of the exciton subsystem to the phonon one. The phonon subsystem is characterized by the functions \( \bar{g}_{2,j} \) and \( \bar{g}_{3,j} \) of the dispersion of coupling constants. The symbols \( \text{Re} \) and \( \text{Im} \) denote real and imaginary parts. The new symbol \( \bar{h} \) follows from Eq. (A6) in order to get \( g_1(\tau), \ldots, g_{11}(\tau) \) dependent only on the dispersion of coupling constants. The symbols \( \text{Re} \) and \( \text{Im} \) denote real and imaginary parts. The new symbol \( \Delta' = \Delta / \hbar \) has been introduced here.

The constant \( G \) having the meaning of the mean exciton–phonon interaction constant has been introduced into Eqs. (A3) and (A4) as well as into the definitions given in Eq. (A6) in order to get \( g_1(\tau), \ldots, g_{11}(\tau) \) dependent only on the dispersion of coupling constants. The symbols \( \text{Re} \) and \( \text{Im} \) denote real and imaginary parts. The new symbol \( \Delta' = \Delta / \hbar \) has been introduced here.

The time-dependent coefficients \( B(t) \) and \( D(t) \) given in Eq. (A3) renormalize the transfer integral \( J \). The coefficients \( A(t) \) and \( C(t) \) are important for relaxation to equilibrium state (see, e.g., Refs. [14,24,25]).

The matrices \( \mathcal{F}_1(t), \mathcal{F}_2(t), \mathcal{F}_3(t), \) and \( \mathcal{F}_4(t) \) originate in the interaction with an optical field:

\[
\mathcal{F}_1(t) = \begin{bmatrix}
2\bar{M}_1 & \bar{O}_1 & 2\bar{O}_2 & -2\bar{M}_1 \\
2\bar{N}_1 & 2\bar{P}_1 & -2\bar{P}_1 & -2\bar{N}_1 \\
\bar{P}_1 & \bar{O}_1 & \bar{M}_1 + \bar{N}_1 & -\bar{M}_2 + \bar{N}_2 & -\bar{O}_1 - \bar{P}_1 \\
-\bar{P}_2 & \bar{O}_2 & \bar{M}_2 - \bar{N}_2 & \bar{M}_1 + \bar{N}_1 & \bar{P}_2 - \bar{O}_2 \\
-2\bar{M}_1 & -2\bar{N}_1 & -2\bar{P}_1 - 2\bar{O}_1 & 2\bar{P}_2 - 2\bar{O}_2 & 2\bar{M}_1 + 2\bar{N}_1
\end{bmatrix}.
\]

(A6)

2In numerical calculations, we assume that \( \hbar \Omega_k G^+_k = G_k \) in one half of the \( \k \)-space and \( \hbar \Omega_k G^+_k = G^+_k \) in the remaining half of the \( \k \)-space \( (i = 1, 2) \) (for details, see, Ref. [23]). This assumption is in agreement with hermiticity of \( H_{e-ph} \). Further, the mean numbers of phonons \( n_B(\hbar \Omega_k) \) are assumed to be \( k \)-independent \( (n_{B_k}(\hbar \Omega_{k_0}) = n_B) \). The remaining summations \( \sum_k \text{cos}(\Omega_k \tau) \) and \( \sum_k \text{cos}(\Omega_k \tau) \) in Eqs. (A6) are replaced by the expressions \( \text{sin}(\Omega_{ph} \tau) \exp(-\gamma_{ph} \tau) \) and \( \text{cos}(\Omega_{ph} \tau) \exp(-\gamma_{ph} \tau) \), respectively. The frequency \( \Omega_{ph} \) then characterizes a mean phonon oscillation frequency and \( \gamma_{ph} \) describes damping originating in dephasing.
The symbol \( \delta \) characterizes the response of the exciton subsystem to the photon field:

\[
\tilde{\mathcal{F}}_2(t) = \begin{bmatrix}
2K_1 & -2K_2 & 0 & 0 \\
0 & 0 & 2L_1 & -2L_2 \\
L_1 & -L_2 & K_1 & -K_2 \\
-2K_1 & 2K_2 & -2L_1 & 2L_2 \\
\end{bmatrix},
\]

\[
\tilde{\mathcal{F}}_3(t) = \begin{bmatrix}
-K_1 & 0 & -L_1 & L_2 \\
K_2 & 0 & L_2 & K_1 \\
0 & -L_1 & K_1 & -K_2 \\
0 & L_2 & K_2 & -K_1 & -L_2 \\
\end{bmatrix},
\]

\[
\tilde{\mathcal{F}}_4(t) = \begin{bmatrix}
2M_1 + N_1 - 2\bar{M}_1 & 2M_2 + N_2 - 2\bar{M}_2 & O_1 - \bar{O}_1 & \bar{P}_2 & O_2 - \bar{O}_2 - \bar{P}_2 \\
-2M_2 - N_2 - 2\bar{M}_2 & 2M_1 + N_1 + 2\bar{M}_1 & -O_2 - \bar{O}_2 - \bar{P}_2 & O_1 + \bar{O}_1 + \bar{P}_1 \\
-\bar{P}_1 - \bar{O}_1 - \bar{P}_2 & \bar{P}_2 - \bar{O}_2 - \bar{P}_2 & 2N_1 + M_1 - 2\bar{N}_1 & 2N_2 + M_2 - 2\bar{N}_2 \\
-\bar{P}_2 - \bar{O}_2 - \bar{P}_2 & \bar{P}_1 + \bar{O}_1 + \bar{P}_1 & -2N_2 - M_2 - 2\bar{N}_2 & 2N_1 + M_1 + 2\bar{N}_1 \\
\end{bmatrix}.
\]

(A7)

The coefficients \( K_1(t), K_2(t), L_1(t), \) and \( L_2(t) \) describing the influence of the coherent part of an optical field have the form (the constants \( \tilde{F}_{K_0}^1 \) and \( \tilde{F}_{K_0}^2 \) are assumed to be real):

\[
K_1(t) = -\omega_K \tilde{F}_{K_0}^1 \text{Im} \left[ \tilde{A}(t) \exp(i\delta't) \right],
\]

\[
K_2(t) = \omega_K \tilde{F}_{K_0}^1 \text{Re} \left[ \tilde{A}(t) \exp(i\delta't) \right],
\]

\[
L_1(t) = -\omega_K \tilde{F}_{K_0}^2 \text{Im} \left[ \tilde{A}(t) \exp(i\delta't) \right],
\]

\[
L_2(t) = \omega_K \tilde{F}_{K_0}^2 \text{Re} \left[ \tilde{A}(t) \exp(i\delta't) \right].
\]

(A8)

The symbol \( \delta' \) denotes the frequency mismatch \((\delta' = (E + \varepsilon)/\hbar - \omega_K)\) and the envelope \( \tilde{A}(t) \) of the field is defined as follows,

\[
\tilde{A}(t) = A(t) \exp(i\omega_K t).
\]

(A9)

The coefficients \( M_1(t), \ldots, P_2(t) \) reflect statistical properties of the optical field (noise) and can be expressed in the form

\[
M_1(t) = (\tilde{F}_{K_0}^1)^2 i_1 - (\tilde{F}_{K_0}^1)^2 \frac{\varepsilon}{\Delta} i_4 - \tilde{F}_{K_0}^1 \tilde{F}_{K_0}^2 \frac{J}{\Delta} i_4,
\]

\[
M_2(t) = (\tilde{F}_{K_0}^1)^2 i_3 + (\tilde{F}_{K_0}^1)^2 \frac{\varepsilon}{\Delta} i_2 + \tilde{F}_{K_0}^1 \tilde{F}_{K_0}^2 \frac{J}{\Delta} i_2,
\]

\[
N_1(t) = (\tilde{F}_{K_0}^2)^2 i_1 + (\tilde{F}_{K_0}^2)^2 \frac{\varepsilon}{\Delta} i_4 - \tilde{F}_{K_0}^1 \tilde{F}_{K_0}^2 \frac{J}{\Delta} i_4,
\]

\[
N_2(t) = (\tilde{F}_{K_0}^2)^2 i_3 - (\tilde{F}_{K_0}^2)^2 \frac{\varepsilon}{\Delta} i_2 + \tilde{F}_{K_0}^1 \tilde{F}_{K_0}^2 \frac{J}{\Delta} i_2,
\]

\[
O_1(t) = -(\tilde{F}_{K_0}^1)^2 \frac{J}{\Delta} i_4 + \tilde{F}_{K_0}^1 \tilde{F}_{K_0}^2 i_1 + \tilde{F}_{K_0}^1 \tilde{F}_{K_0}^2 \frac{\varepsilon}{\Delta} i_4,
\]

\[
O_2(t) = (\tilde{F}_{K_0}^1)^2 \frac{J}{\Delta} i_2 + \tilde{F}_{K_0}^1 \tilde{F}_{K_0}^2 i_3 - \tilde{F}_{K_0}^1 \tilde{F}_{K_0}^2 \frac{\varepsilon}{\Delta} i_2,
\]

\[
P_1(t) = -(\tilde{F}_{K_0}^2)^2 \frac{J}{\Delta} i_4 + \tilde{F}_{K_0}^1 \tilde{F}_{K_0}^2 i_1 - \tilde{F}_{K_0}^1 \tilde{F}_{K_0}^2 \frac{\varepsilon}{\Delta} i_4,
\]

\[
P_2(t) = (\tilde{F}_{K_0}^2)^2 \frac{J}{\Delta} i_2 + \tilde{F}_{K_0}^1 \tilde{F}_{K_0}^2 i_3 + \tilde{F}_{K_0}^1 \tilde{F}_{K_0}^2 \frac{\varepsilon}{\Delta} i_2.
\]

(A10)

The functions \( i_1(t, \Delta', \delta'), i_2(t, \Delta', \delta') \) characterize the response of the exciton subsystem to the photon field:

\[
i_1(t, \Delta', \delta') = \omega_K \int_0^t d\tau \cos[\Delta'(t - \tau)] \text{Re} \left[ \delta\tilde{N}(t, \tau) \exp[i\delta'(t - \tau)] \right],
\]

\[
i_2(t, \Delta', \delta') = \omega_K \int_0^t d\tau \sin[\Delta'(t - \tau)] \text{Re} \left[ \delta\tilde{N}(t, \tau) \exp[i\delta'(t - \tau)] \right],
\]

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\[
i_3(t, \Delta', \delta') = \omega_{K_0}^2 \int_0^t d\tau \cos [\Delta'(t - \tau)] \Im \left[ \delta \tilde{N}(t, \tau) \exp [i\delta'(t - \tau)] \right],
\]
\[
i_4(t, \Delta', \delta') = \omega_{K_0}^2 \int_0^t d\tau \sin [\Delta'(t - \tau)] \Im \left[ \delta \tilde{N}(t, \tau) \exp [i\delta'(t - \tau)] \right].
\] (A11)

The photon field correlation function \(\delta \tilde{N}(t, \tau)\) is of the form:
\[
\delta \tilde{N}(t, \tau) = \delta N(t, \tau) \exp [i\omega_{K_0}(t - \tau)].
\] (A12)

The coefficients \(\tilde{M}_1(t), \ldots, \tilde{P}_2(t)\) are defined similarly as the coefficients \(M_1(t), \ldots, P_2(t)\) in Eqs. (A10) and (A11); only the photon field correlation function
\[
\delta \tilde{N}_\nu(t, \tau) = \delta N_\nu(t, \tau) \exp [i\omega_{K_0}(t - \tau)]
\] (A13)
occur in Eq. (A11) instead of \(\delta \tilde{N}(t, \tau)\). Thus, the coefficients with bars include in addition effects of vacuum fluctuations.

Also the coefficients \(\tilde{M}_1(t), \ldots, \tilde{P}_2(t)\) are defined similarly as the coefficients \(M_1(t), \ldots, P_2(t)\) in Eqs. (A10) and (A11): only the expression \(\delta \tilde{N}(t, \tau) \exp [i\delta'(t - \tau)]\) in Eq. (A11) must be replaced by the expression \(\delta \tilde{N}_\nu(t, \tau) \exp [-i\delta'(t + \tau)]\), where
\[
\delta \tilde{N}_\nu(t, \tau) = \delta N_\nu(t, \tau) \exp [-i\omega_{K_0}(t + \tau)].
\] (A14)

The coefficients \(\tilde{O}_2(t)\) and \(\tilde{P}_2(t)\) renormalize the transfer integral \(J\) both at the positions (4,1), (1,4) and (4,2), (2,4) in the matrix \(\tilde{J}_1\), in contrast to the coefficients originating in the exciton–phonon interaction.

The influence of the coefficient \(\tilde{M}_1(t)\) (\(\tilde{N}_1(t)\)) in the equations for \(\rho_{1r}(t)\) and \(\rho_{1s}(t)\) (\(\rho_{2r}(t)\) and \(\rho_{2s}(t)\)) is remarkable. When, e.g., \(\tilde{M}_1(t)\) (\(\tilde{N}_1(t)\)) is negative, it represents damping of \(\rho_{1r}(t)\) (\(\rho_{2r}(t)\)), but at the same time amplification of \(\rho_{1s}(t)\) (\(\rho_{2s}(t)\)). This property is connected with phase relations in the photon field reflected by \(\delta \tilde{N}_\nu(t, \tau)\) given in Eq. (A14).

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