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CONDENSED-MATTER SPECTROSCOPY

Derivation of the Equation of Motion for Resonantly Excited Molecular J Aggregates Taking into Account Multiparticle Effects

B. N. Levinsky[a], L. A. Nesterov[b], B. D. Fainberg[a], and N. N. Rosanov[b, c, d]

[a] *Holon Institute of Technology, 58102 Holon, Israel*

[b] *St. Petersburg National Research University of Information Technologies, Mechanics, and Optics, St. Petersburg, 197101 Russia*

[c] *Vavilov State Optical Institute, St. Petersburg, 199034 Russia*

[d] *Ioffe Physical-Technical Institute, Russian Academy of Sciences, St. Petersburg, 194021 Russia*

e-mail: nrosanov@yahoo.com, fainberg@hit.ac.il

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Abstract—We have analyzed a model of molecular J aggregates in the form of a chain of three-level molecules. Equations of motion for these chains with taking into account multiparticle contributions caused by different mechanisms by which molecules interact with each other (dipole–dipole interactions, exciton–exciton annihilation, etc.) are presented. These contributions describe not only the interaction of any pair of molecules with each other, but also the interaction of a given molecule simultaneously with two, three, or more number of molecules. In the general case, it is necessary to take into account effects related to correlations between such molecules. To take into account these correlation effects, it is necessary to derive equations of motion from the first principles. As a result, a hierarchy of mutually coupled equations for the expectation values of the products of operators that refer to different molecules of the chain. In this work, we take into account only two-particle correlations between molecules. This, in turn, has led us to the necessity of taking into account equations for the two-particle expectation values with subsequent factorization of higher-order averages to obtain a closed system of equations. Correct taking into account of the mechanism of exciton–exciton annihilation from first principles has made it necessary to introduce multiparticle contributions into equations of motion that describe the relaxation of the system due to this mechanism and that are absent in a purely phenomenological consideration. By this means, we have obtained a set of equations that makes it possible to successively and rigorously take into account two-particle correlations between molecules of J aggregates.

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1. INTRODUCTION

The objective of this work is to derive the equations of motion for J aggregates with taking into account multiparticle contributions caused by different mechanisms by which molecules interact with each other (dipole–dipole interactions, exciton–exciton annihilation, etc.). These contributions describe not only the interaction of any pair of molecules between each other, but also the interaction of a given molecule simultaneously with two, three, and greater number of molecules. In general case, it is necessary to take into account correlation effects between such molecules. In this work, we restrict our consideration by two-particle correlations related to above-indicated interactions of molecules and, in particular, to two-exciton excitations of the system. A set of equations refined in this way will be further used to study the hysteresis and to calculate and analyze characteristics of dissipative solitons that arise in these structures under resonant laser excitation. Previously, such solitons have been revealed in [1] (see also [2]) upon modeling of J aggregates by a chain of N three-level molecules [3], however, without taking into account multiparticle effects.

In this work, we will also use the model of the J aggregate in the form of a chain of three-level molecules. This model assumes that, upon interaction with an external radiation field, a transition from the ground to the second level of the molecule prevails. As a rule, the remaining radiative transitions can be neglected. It is also assumed that frequencies of transitions from the ground level of the molecule to the second level and from the second to the third level are rather close between each other.

If there are no radiative transitions from the first and second levels to the third one, this latter level is pumped as a result of direct transfer of excitation from one molecule to another that is located in the neighboring site of the chain. In this process, one of the molecules that resides on the second excited level interacts with another molecule in the same state, gives its energy to this molecule, and returns to the ground state, whereas the molecule that received the energy passes to the third level. It is assumed that the

third level is vibronic in its nature and decays very rapidly transferring its energy to the second and first levels.

It is a distinctive feature of J aggregates that they possess a collective (exciton) mechanism of excitation by external radiation. This manifests itself in the fact that the chain molecules under consideration have one-exciton states with energies close to the energy of the second excited level and two-exciton states with energies that are close to the energy of the third level. As a result, the mechanism by which the excitation is transferred between neighboring molecules leads to annihilation of the two-exciton state, which interacts with a vibronic level of the molecule of a close energy that decays very rapidly. In terms of one-particle description, the decay of the two-exciton state is represented as annihilation of two one-exciton excitations (one of them is the excitation to the ground state, while another is the deexcitation to a higher-lying molecular state with a short lifetime) [3–5].

The existence of the collective mechanism of excitation of J aggregates leads to large values of their linear and nonlinear responses with subpicosecond transient times. Therefore, these structures can be very promising for use in information processing [6], as well as in laser technologies [7]. In [8, 3], the effect of bistability in an individual J aggregate upon its resonant excitation by laser radiation has been predicted and studied theoretically. This effect indicates that this structure can be used in schemes of molecular memory. In [9], the possibility of formation of dispersive optical solitons in linear molecular aggregates based on two-level molecules was demonstrated for the first time. 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.

Usually, J aggregates are described using a semiclassical approach, 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 based on 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 presented in the factorized form, i.e., without taking into account correlations between molecules.

However, as we will show below, 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. 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 but that, however, are absent in terms of the purely phenomenological approach.

In this case, if we restrict ourselves to consideration of the set of equations for only one-particle averages and discard all the remaining ones, then taking into account the interaction mentioned above leads to the appearance in equations not only of already known two-particle contributions, but also of three-particle ones. By representing the expectation values that correspond to these latter contributions in the form of a product of one-particle averages, we arrive at a refined system of Bloch equations, in which the three-particle relaxation is also taken into account. Analysis showed that, by virtue of particular features of the considered system of molecules, among obtained three-particle contributions, there are contributions of the same order of magnitude as that of the known two-particle contributions.

Finally, if in the initial hierarchical system of equations, we also take into account equations for two-particle averages, and all the remaining multiparticle averages, we express via combinations of products of one-particle and corresponding two-particle averages, then we can take into account two-particle correlations between molecules of the chain, which, among other things, can also be related to two-exciton excitations in this chain. This is precisely the final goal of our derivation of the system of equations for the description of J aggregates.

In general case, taking into account the interaction with a third level of molecules leads to the appearance in equations of motion not only of three-particle but also of four-particle relaxation terms. In general, all these multiparticle relaxation terms have the interference nature, which reflects the fact that a transition to a given state can, as a rule, be realized not by only one pathway, but, rather, by a combination of different pathways. A correct calculation of all the multiparticle contributions mentioned above is the most complicated and the most important part of this work.

As was noted above, our work is devoted to the derivation of equations of motion taking into account two-particle correlations between molecules. In this case, it is most difficult to calculate the above-mentioned multiparticle contributions caused by the exci-

ton–exciton annihilation mechanism. Since calculation and the analysis of these contributions are a rather complicated and independent problem, the derivation of equations of motion is naturally divided into two stages. At the first stage (Section 2), we investigate the evolution of the system without taking into account the exciton–exciton annihilation mechanism; as a consequence, we do not take into consideration the interaction with a third level of molecules. Therefore, at this stage, the system is considered to be quasi-two-level. At the next stage (Section 3), we take into account only the mechanism of exciton–exciton annihilation and calculate relaxation terms that describe the evolution of the system under the influence of this mechanism alone. In other words, we assume that, in Section 3, relaxation terms can be calculated irrespective of the influence of all the other processes [10]. Clearly, the total system of equations is the sum of contributions from the second and third sections of this work.

2. DERIVATION OF EQUATIONS OF MOTION WITHOUT TAKING INTO ACCOUNT THE MECHANISM OF EXCITON–EXCITON ANNIHILATION

2.1. Definitions for States of Molecules and Operators

Consider a linear chain that consists of N three-level molecules. As was mentioned above, this chain can be used to model J aggregates. We will assume that the lowest state of each molecule is determined by the state vector $|g\rangle$ or $|1\rangle$, and the energy of this state is E_1. Correspondingly, the second state will be determined by the state vector $|e\rangle$ or $|2\rangle$ with energy E_2. Finally, the third state will be determined by the state vector $|f\rangle$ or $|3\rangle$ with energy E_3. It is clear that $E_3 > E_2 > E_1$.

For the energy levels, there is also another set of designations, which will be used in the text—namely, $E_1 = E_g$, $E_2 = E_e$, and $E_3 = E_f$. State vectors $|mg\rangle$, $|me\rangle$, and $|mf\rangle$ will 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, which are projection operators onto the corresponding states of the molecule: $B_m = |mg\rangle\langle me|$ is the operator that describes the annihilation of an excitation in molecule m at the level "e" and its transition to the ground state $|mg\rangle$, and, also, $B_m^+ = |me\rangle\langle mg|$ is the operator that describes the creation of an excitation in molecule m to the level "e."

According to the same principle, we will also define the following operators: $C_m = |mg\rangle\langle mf|$, $C_m^+ = |mf\rangle\langle mg|$, $D_m = |me\rangle\langle mf|$, and $D_m^+ = |mf\rangle\langle me|$.

Let us also define the operators of the number of molecules N_{mg}, N_{me}, and N_{mf} in states $|mg\rangle$, $|me\rangle$, and $|mf\rangle$, respectively:

$$\begin{aligned} N_{mg} &= B_m B_m^+ = |mg\rangle\langle me|me\rangle\langle mg| = |mg\rangle\langle mg|, \\ N_{me} &= B_m^+ B_m = |me\rangle\langle mg|mg\rangle\langle me| = |me\rangle\langle me|, \\ N_{mf} &= C_m^+ C_m = |mf\rangle\langle mg|mg\rangle\langle mf| = |mf\rangle\langle mf|, \\ N_{mg} &+ N_{me} + N_{mf} = 1. \end{aligned} \quad (1)$$

It is clear that all operators that refer to different molecules commute with each other. Concerning definitions and notation, see also [11, 12].

2.2. The Total Hamiltonian of the System

The total Hamiltonian of the system is combined from the Hamiltonian of free molecules and the Hamiltonians of the interaction of molecules with an external field and with each other. In particular, this Hamiltonian also involves the interaction that leads to the exciton–exciton annihilation.

The Hamiltonian of free molecules has the form

$$H_{\text{free}} = \frac{1}{2}\left\{\sum_m \Big[E_{mg}(B_m B_m^+ + C_m C_m^+) + E_{me}(B_m^+ B_m + D_m D_m^+) + E_{mf}(C_m^+ C_m + D_m^+ D_m)\Big]\right\}. \quad (2)$$

The Hamiltonian of the interaction with an external electromagnetic field with frequency ν_{12} can be represented as

$$H_{\text{el}}(t) = -\frac{1}{2}\sum_m (\boldsymbol{\mu}^{12}\mathbf{e}_1)[B_m^+ E_1 \exp(-i\nu_{12}t) + \text{H.c.}]. \quad (3)$$

Here, the external field is defined by the formula $\mathbf{E} = [\mathbf{e}_1 E_1 \exp(-i\nu_{12}t) + \text{c.c.}]/2$, while Hamiltonian (3) itself represents the interaction of this field with the polarization vector $\mathbf{P}$ of the system of molecules: $H_{\text{el}}(t) = -\mathbf{PE}$. This interaction is taken into account in the rotation field approximation. In this case, $\boldsymbol{\mu}^{12}$ is the dipole moment of the molecule for transition $1 \to 2$.

The interaction between molecules includes the dipole–dipole interaction and the interaction via a transverse radiation field of molecules. For the Hamiltonian that describes the former of these interactions (dipole–dipole), the following expression can be obtained [8, 11–14]:

$$H_{\text{int}} = \frac{1}{2}\sum_{m\neq n}(J_{mn}^{gege} B_m^+ B_n + J_{mn}^{gege*} B_n^+ B_m). \quad (4)$$

The first term in (4) describes the annihilation of the state $|e\rangle$ of molecule n and the creation of the state $|e\rangle$ for molecule m, and the second term describes a similar effect but with the replacement of n by m and vice versa.

The interaction between molecules via the transverse radiation field will be taken into account later directly in equations of motion. Finally, concerning the interaction Hamiltonian that leads to the exciton–exciton annihilation, we will denote it as H_{annih}. The explicit form of this Hamiltonian and taking into account its contribution to equations of motion will be considered in the third section of the work.

Based on the aforesaid, the complete Hamiltonian of the system can be represented as a sum of two Hamiltonians $H(t) + H_{\text{annih}}$, where $H(t)$ has the form

$$H(t) = H_{\text{free}} + H_{\text{el}}(t) + H_{\text{int}}. \quad (5)$$

In fact, Hamiltonian (5) describes transitions only between the first and second levels of molecules, since the interaction with the third level arises only upon taking into account H_{annih}. For particular calculations, it is convenient to replace H_{free} in (5) with its truncated form if we set $E_{m1} \equiv E_{mg} = 0$ and take into account that all the interaction Hamiltonians, including H_{annih}, do not depend on the operators C_m and C_m^+. Then, H_{free} can be represented as

$$H_{\text{free}} = \sum_m (\hbar\omega_{m12} B_m^+ B_m + \hbar\omega_{m13} D_m^+ D_m), \quad (6)$$

where $\hbar\omega_{m12} = E_{m2} - E_{m1}$ and $\hbar\omega_{m13} = E_{m3} - E_{m1}$. In this part of the work, upon the derivation of equations of motion, we will use only Hamiltonian $H(t)$, or, more exactly, its stationary version H, which will be obtained in the next section.

2.3. Equations of Motion for Operators of the System

Having known the Hamiltonian of the system, one can derive equations of motion for an arbitrary operator A of the system. Such an equation of motion has the form

$$dA/dt = i[H(t), A]/\hbar. \quad (7)$$

Let us eliminate the explicit dependence on time from $H(t)$. For this purpose, instead of the operators B_m, we should introduce new operators $b_m = B_m \exp(i\nu_{12} t)$ (see Eq. (3)). In this case, in order to preserve the independence on time of the Hamiltonian H_{annih}, we should also introduce the operator $d_m = D_m \exp(i\nu_{12} t)$ instead of D_m. Based on (7), we can obtain the following equations of motion for operators b_m and d_m:

$$\begin{aligned} db_m/dt &= i\nu_{12} b_m + i[H(t), b_m]/\hbar, \\ dd_m/dt &= \nu_{12} d_m + i[H(t), d_m]/\hbar. \end{aligned} \quad (8)$$

It can be shown that frequency shifts in these equations are a result of the application of the following operation to the operators b_m and d_m:

$$\begin{aligned} i\nu_{12} b_m &= -i[H_{12}, b_m]/\hbar, \\ i\nu_{12} d_m &= -i[H_{12}, d_m]/\hbar, \end{aligned} \quad (9)$$

where

$$H_{12} = \hbar\nu_{12} \sum_m (b_m^+ b_m + 2 d_m^+ d_m). \quad (10)$$

By substituting (9) into (8) and replacing the operators B_m and D_m (and, correspondingly, B_m^+ and D_m^+) in $H(t)$ by $b_m (b_m^+)$ and $d_m (d_m^+)$, we finally obtain the following equations of motion:

$$\begin{aligned} db_m/dt &= i[H, b_m]/\hbar, \\ dd_m/dt &= i[H, d_m]/\hbar. \end{aligned} \quad (11)$$

Here, H denotes the stationary operator of the following form:

$$H = [H(t) - H_{12}]\Big|_{\substack{B_m = b_m \exp(-i\nu_{12} t) \\ D_m = d_m \exp(-i\nu_{12} t)}}. \quad (12)$$

As a result of the replacement of operators performed above, the Hamiltonian $H_{\text{el}}(t)$ ceases to explicitly depend on time and will be further denoted as H_{el}, while operator H_{free} (6) is transformed into a new operator, which we will denote as H_0:

$$\begin{aligned} H_0 &= (H_{\text{free}} - H_{12}) \\ &= \sum_m \left[\hbar(\omega_{m12} - \nu_{12}) b_m^+ b_m + \hbar(\omega_{m13} - 2\nu_{12}) d_m^+ d_m \right]. \end{aligned} \quad (13)$$

In this case, the designations for the operators H_{int} and H_{annih} remain unchanged.

It is rather evident that the passage from the operators B_m, D_m, and C_m to the operators b_m, d_m, and c_m is equivalent to a certain unitary transformation $a = UAU^+$. From the aforesaid, we can easily verify that

$$U = \exp(-iH_{12} t/\hbar). \quad (14)$$

According to the accepted notations, we finally obtain the following expression for operator H:

$$H = H_0 + H_{\text{el}} + H_{\text{int}}. \quad (15)$$

Precisely this stationary operator will determine the evolution of the system in this section.

For a quasi-two-level system, which is described by operator (15), the most important one-particle operators that determine the behavior of the system are b_m, N_{me}, and N_{mg} ($m = 1, 2, \ldots, N$). Using (15), one can

show that the system of equations for these operators can be represented in the following form (see (11)):

$$\frac{db_m}{dt} = i\left[-\Delta_{12}b_m - \frac{1}{2\hbar}(\boldsymbol{\mu}^{12}\mathbf{e}_1)E_1(N_{me} - N_{mg}) + \frac{1}{\hbar}\sum_{n\neq m} J_{mn}^{gege}(N_{me} - N_{mg})b_n\right], \quad (16)$$

$$\frac{dN_{me}}{dt} = i\left[-\frac{1}{2\hbar}(\boldsymbol{\mu}^{12}\mathbf{e}_1)E_1(b_m - b_m^+) + \frac{1}{\hbar}\sum_{n\neq m}(J_{mn}^{gege*}b_n^+ b_m - J_{mn}^{gege}b_m^+ b_n)\right], \quad (17)$$

$$\frac{dN_{mg}}{dt} = i\left[\frac{1}{2\hbar}(\boldsymbol{\mu}^{12}\mathbf{e}_1)E_1(b_m - b_m^+) + \frac{1}{\hbar}\sum_{n\neq m}(J_{mn}^{gege}b_m^+ b_n - J_{mn}^{gege*}b_n^+ b_m)\right]. \quad (18)$$

Here, we assume that, in equations, $\omega_{m12} = \omega_{12}$, and $\Delta_{12} = \omega_{12} - \nu_{12}$. It should also be noted that

$$J_{mn}^{gege*} = J_{nm}^{gege}. \quad (19)$$

This relation follows from the hermiticity of the operator H_{int} (see (4)).

2.4. Equations of Motion for Averages of Operators

In what follows, we will be mainly interested in equations for the expectation values of operators, which are obtained by averaging of the latter over the time-independent density matrix of the system ρ_0. Then, the expectation value $\langle A\rangle$ of the operator A will be defined by the expression $\langle A\rangle = \mathrm{Tr}(A\rho_0)$. By averaging Eqs. (16) and (17) in this way, we obtain the following system of equations for $\langle b_m\rangle$ and $\langle N_{me}\rangle$:

$$\frac{d\langle b_m\rangle}{dt} = i\left[-\Delta_{12}\langle b_m\rangle - \frac{1}{2\hbar}(\boldsymbol{\mu}^{12}\mathbf{e}_1)E_1\langle 2N_{me} - 1 + N_{mf}\rangle + \frac{1}{\hbar}\sum_{n\neq m} J_{mn}^{gege}(2\langle N_{me}b_n\rangle - \langle b_n\rangle + \langle N_{mf}b_n\rangle)\right], \quad (20)$$

$$\frac{d\langle N_{me}\rangle}{dt} = i\left[-\frac{1}{2\hbar}(\boldsymbol{\mu}^{12}\mathbf{e}_1)E_1\left(\langle b_m\rangle - \langle b_m^+\rangle\right) + \frac{1}{\hbar}\sum_{n\neq m}\left(J_{mn}^{gege*}\langle b_n^+ b_m\rangle - J_{mn}^{gege}\langle b_m^+ b_n\rangle\right)\right]. \quad (21)$$

In this case, using relation $N_{mg} + N_{me} + N_{mf} = 1$, we eliminate N_{mg} from consideration here and below by expressing it in terms of N_{me} and N_{mf}. Since the equation for $\langle N_{mf}\rangle$ will be obtained only in the third section of this work, the system of equations for one-particle averages in this section is reduced to merely equations for $\langle b_m\rangle$ and $\langle N_{me}\rangle$.

It can be easily verified that these equations contain expressions for two-particle averages, such as $\langle N_{me}b_n\rangle$, $\langle b_m^+ b_n\rangle$, etc. It is clear that equations of motion for these expressions should also be derived. Thus, e.g., for $\langle N_{me}b_n\rangle$, the following equation can be obtained:

$$\frac{d\langle N_{me}b_n\rangle}{dt} = i\left\{-\frac{1}{2\hbar}(\boldsymbol{\mu}^{12}\mathbf{e}_1)E_1\left(\langle b_m b_n\rangle - \langle b_m^+ b_n\rangle\right) + \frac{1}{\hbar}\sum_{l\neq m}\left[\left(J_{mn}^{gege*}\langle b_l^+ b_m b_n\rangle - J_{ml}^{gege}\langle b_m^+ b_l b_n\rangle\right)\right] - \Delta_{12}\langle N_{me}b_n\rangle - \frac{1}{2\hbar}(\boldsymbol{\mu}^{12}\mathbf{e}_1)E_1(2\langle N_{me}N_{ne}\rangle - \langle N_{me}\rangle + \langle N_{me}N_{nf}\rangle) + \frac{1}{\hbar}\sum_{l\neq n}\left[J_{nl}^{gege}\left(2\langle N_{me}N_{ne}b_l\rangle - \langle N_{me}b_l\rangle + \langle N_{me}N_{nf}b_l\rangle\right)\right]\right\}. \quad (22)$$

In turn, this equation contains expressions for two-particle averages, such as $\langle b_m b_n\rangle$, $\langle N_{me}N_{ne}\rangle$, $\langle N_{me}N_{nf}\rangle$, etc., as well as expressions for three-particle averages. It is also necessary to derive equations for them. This procedure could be continued further.

In order to close this system and to operate on a finite number of equations, the factorization method can be applied. A simplest case of the use of factorization is that two-particle averages in equations for one-particle averages are replaced by a product of one-particle averages. As a result, we obtain a closed system of equations, in terms of which a soliton was previously revealed in [1].

Taking into account two-particle correlations requires preserving equations for two-particle averages. In this case, there arises the problem choosing the basis system of averages, which determine the behavior of the system. This system contains both one- and two-particle averages. As soon as this system is defined, all remaining multiparticle averages in equations of motion are factorized into different products of basis averages. As a result, we can obtain a closed system of equations for one- and two-particle averages. In this work, we used the quantities $\langle b_m\rangle$, $\langle N_{me}\rangle$, and $\langle N_{mf}\rangle$, as well as the quantities $\langle N_{me}N_{ne}\rangle$, $\langle N_{me}b_n\rangle$, and $\langle b_m b_n\rangle$ ($m \neq n$), which, in particular, can be related with two-exciton excitations of the system. Corresponding complex conjugate quantities should also be included in this set. In this case, the quantity $\langle b_m\rangle$ is proportional to the dipole moment of the molecule upon transition $1 \to 2$; the quantities $\langle N_{me}\rangle$ and $\langle N_{mf}\rangle$ determine the populations of the second and

third levels of the molecule; $\langle N_{me}N_{ne}\rangle$ can be associated with the population of two-exciton states, and so on.

It follows from the aforesaid that, it is also necessary to add equations for $\langle b_m b_n\rangle$ and $\langle N_{me}N_{ne}\rangle$ to Eqs. (20), (21), and (22). It can be shown that the equations for these two-particle averages have the following form:

$$\frac{d\langle b_m b_n\rangle}{dt} = i\Big\{-\Delta_{12}\langle b_m b_n\rangle - \frac{1}{2\hbar}(\boldsymbol{\mu}^{12}\mathbf{e}_1)E_1[2\langle N_{me}b_n\rangle - \langle b_n(1-N_{mf})\rangle] + \frac{1}{\hbar}\sum_{l\neq m,l\neq n} J_{ml}^{gege}[2\langle N_{me}b_n b_l\rangle - \langle b_l b_n(1-N_{mf})\rangle] \quad (23)$$

$$- \Delta_{12}\langle b_m b_n\rangle - \frac{1}{2\hbar}(\boldsymbol{\mu}^{12}\mathbf{e}_1)E_1[2\langle b_m N_{ne}\rangle - \langle b_m(1-N_{nf})\rangle] + \frac{1}{\hbar}\sum_{l\neq n,l\neq m} J_{nl}^{gege}[2\langle b_m N_{ne}b_l\rangle - \langle b_m b_l(1-N_{nf})\rangle]\Big\},$$

$$\frac{d\langle N_{me}N_{ne}\rangle}{dt} = i\Big\{-\frac{1}{2\hbar}(\boldsymbol{\mu}^{12}\mathbf{e}_1)E_1\left(\langle N_{ne}b_m\rangle - \langle b_m^+ N_{ne}\rangle\right) + \frac{1}{\hbar}\sum_{l\neq m,l\neq n}\left(J_{ml}^{gege*}\langle b_l^+ N_{ne}b_m\rangle - J_{ml}^{gege}\langle b_m^+ N_{ne}b_l\rangle\right) - \frac{1}{2\hbar}(\boldsymbol{\mu}^{12}\mathbf{e}_1)E_1\left(\langle N_{me}b_n\rangle - \langle b_n^+ N_{me}\rangle\right) + \frac{1}{\hbar}\sum_{l\neq n,l\neq m}\left(J_{nl}^{gege*}\langle N_{me}b_n b_l^+\rangle - J_{nl}^{gege}\langle N_{me}b_n^+ b_l\rangle\right)\Big\}. \quad (24)$$

Equations (20)–(24) take into account the interaction of molecules with an external radiation field, as well as the dipole–dipole interaction between molecules.

Expectation values like $\langle b_m^+ b_n\rangle$, $m \neq n$ have not been included into the basis system of averages considered above. These averages describe intermolecular interactions, which can be associated with the excitation of one-exciton states. Following [14], we describe these averages as products of one-particle averages (see also [11, 15]).

Concerning correlations related to three-particle processes, they are corrections of higher orders of smallness and are not taken into account in this study.

The next stage of the derivation of equations of motion deals with taking into account the interaction of molecules via the transverse radiation field and with the factorization of these equations.

2.5. Taking into Account the Interaction of Molecules via a Transverse Field of Their Radiation and Factorization of Equations of Motion

In order to further generalize the obtained system of equations, we take into account interactions of molecules via the transverse field of their radiation. It can be shown that, for an arbitrary operator Q of the system under consideration, an equation that takes into account this interaction has the form [16]

$$\frac{\partial\hat{Q}}{\partial t} \sim 2\sum_{l,k}\gamma_{l,k}\left[b_l^+\hat{Q}b_k - \frac{1}{2}(b_l^+ b_k\hat{Q} + \hat{Q}b_l^+ b_k)\right]. \quad (25)$$

By successively substituting operators b_m, N_m, $N_m b_n$, $b_m b_n$, and $N_{me}N_{ne}$ into (25), we obtain a system of equations, the right-hand sides of which describe the evolution of these operators due to the interaction of molecules with the field of their radiation. After the averaging the obtained equations, their right-hand sides should be added to the corresponding right-hand sides of Eqs. (20)–(24).

The matrix γ_{mn} in (25) is the imaginary part of the complex matrix $\Delta_{mn} - i\gamma_{mn}$, which has previously been obtained in [8]. This latter matrix can be interpreted as a matrix that describes the intermolecular retarding interaction in a chain of molecules, with the matrix γ_{mn} describing the interaction via the transverse field. Explicit expressions for the matrices γ_{mn} and Δ_{mn} have been obtained in [8], and this expression for γ_{mn} has the form

$$\gamma_{mn} = \frac{\mu^2}{\hbar a^3}\left\{\left[k_0 a\frac{\cos(k_0 a|m-n|)}{|m-n|^2} - \frac{\sin(k_0 a|m-n|)}{|m-n|^3}\right]\times\left(1-3\cos^2\theta\right) + (k_0 a)^2\frac{\sin(k_0 a|m-n|)}{|m-n|}\sin^2\theta\right\}. \quad (26)$$

Here, a is the distance between neighboring molecules of the chain of N molecules, θ is the angle between the dipole moment $\boldsymbol{\mu}^{12}$ and the axis of the chain, and $k_0 = \nu_{21}/c$. In the particular case of aggregates with the chain length $L = Na \ll \lambda$ (λ is the wavelength of the radiation), γ_{mn} has the form

$$\gamma_{mn} = 2\mu^2 k_0^3/3\hbar = \gamma_0/2, \quad (27)$$

where γ_0 is the radiation damping constant of an isolated molecule. In turn, the real part Δ_{mn} of the complex matrix can be related to constants of the dipole–dipole interaction between molecules. This relation can be represented in the following form [3, 8, 14]:

$$J_{mn}^{gege}/\hbar = \Delta_{mn}. \quad (28)$$

If the chain length is much shorter than the wavelength, Δ_{mn} is reduced to the expression

$$\Delta_{mn} = \left(\mu^2/\hbar r_{mn}^3\right)\left(1-3\cos^2\theta\right), \quad (29)$$

where $r_{mn} = a(m - n)$. It can be seen from (29) that Δ_{mn} describes the ordinary dipole–dipole interaction. Taking into account the interaction via the transverse field in equations for averages leads to taking into account the radiation damping of molecules. Analysis shows that, in the right-hand side of the equation for $\langle b_m \rangle$, a term $-\gamma_{mm}$ arises, while, in the right-hand side of the equation for $\langle N_{me} \rangle$, a term $-2\gamma_{mm}$ appears. These terms can be interpreted as the transverse and longitudinal relaxation constants, respectively, which are obliged for their origin to the interaction with the radiation field. It follows from (29) that these constants do not depend on the number m. In reality, longitudinal and transverse relaxations are caused not only by the radiation field, but also by intramolecular processes. Therefore, it is reasonable to generalize the expressions for the constants considered above by introducing effective quantities that take into account these processes. We will do this phenomenologically by introducing into the equation for $\langle b_m \rangle$ the quantity $\gamma_\perp$ instead of γ_{mm} and by introducing into the equation for $\langle N_{me} \rangle$ the quantity γ_2 instead of $2\gamma_{mm}$. We will also do the same with the constants in the equations for two-particle averages. These constants will also be expressed in terms of $\gamma_\perp$ and γ_2. Implementation of all the transformations that were referred to in this section yields a system of equations, which, along with one-particle averages, also contains averages of products of two and three operators that refer to different particles. In order to close the obtained system, it is necessary to express these averages in terms of the basis quantities listed in the preceding section by means of the factorization operation. Upon performing the factorization, it is necessary first of all to take into account a fast decay of the third level. This immediately makes it possible to factorize averages that contain the operators N_{mf}, c_m, and d_m. Therefore, averages, e.g., of the form $\langle AN_{mf} \rangle$, can be represented as a product $\langle A \rangle \langle N_{mf} \rangle$. We also noted that two-particle averages of the form $\langle b_m^+ b_n \rangle$ should also be factorized, since they are not included in the list of basis averages (see above). The situation regarding factorization of three-particle averages is more complicated, since, generally speaking, this operation is not unambiguous. In this work, we used a standard expression for representation of arbitrary three-particle averages in the factorized form. This expression is as follows (see also [15]):

$$\begin{aligned}\langle P_l Q_m R_n \rangle \cong \langle P_l \rangle \langle Q_m R_n \rangle + \langle Q_m \rangle \langle P_l R_n \rangle \\ + \langle R_n \rangle \langle P_l Q_m \rangle - 2\langle P_l \rangle \langle Q_m \rangle \langle R_n \rangle.\end{aligned} \tag{30}$$

It can be easily seen that, if the distance between any pair of particles in this average is fixed and the remainder is moved to a considerably longer distance, we will always obtain a correct asymptotic expression for the factorized average. If all the particles are separated to a long distance, then (30) also yields a correct asymptotic expression in the form of a product of one-particle averages. The meaning of representation (30) becomes evident if the expression $\langle P_l \rangle \langle Q_m \rangle \langle R_n \rangle$ is added to and subtracted from its right-hand side. Then, (30) can be represented as

$$\begin{aligned}\langle P_l Q_m R_n \rangle \cong \langle P_l \rangle \langle Q_m \rangle \langle R_n \rangle + \langle P_l \rangle \Delta(Q_m, R_n) \\ + \langle Q_m \rangle \Delta(P_l, R_n) + \langle R_n \rangle \Delta(P_l, Q_m),\end{aligned} \tag{31}$$

where

$$\begin{aligned}\Delta(Q_m, R_n) = \langle Q_m R_n \rangle - \langle Q_m \rangle \langle R_n \rangle, \\ \Delta(P_l, R_n) = \langle P_l R_n \rangle - \langle P_l \rangle \langle R_n \rangle, \\ \Delta(P_l, Q_m) = \langle P_l Q_m \rangle - \langle P_l \rangle \langle Q_m \rangle.\end{aligned} \tag{32}$$

Therefore, expression (30) is a sum of a completely factorized average and three terms that take into account all the possible two-particle correlation corrections. Physically and mathematically, this representation is quite justified. However, the use of (30) requires taking into account certain peculiarities that are related to the choice of initial basis averages. As an example, we consider the expectation value $\langle N_l b_m^+ b_n \rangle$. If we factorize it according to (30), then the term $\langle b_m^+ b_n \rangle$ arises, which is not contained in the set of basis two-particle averages and which, therefore, should be factorized. Then, however, this term will be automatically cancelled and, as a result, we obtain the following representation for $\langle N_l b_m^+ b_n \rangle$:

$$\begin{aligned}\langle N_l b_m^+ b_n \rangle = \langle b_m^+ \rangle \langle N_l b_n \rangle \\ + \langle b_n \rangle \langle N_l b_m^+ \rangle - \langle N_l \rangle \langle b_m^+ \rangle \langle b_n \rangle.\end{aligned} \tag{33}$$

Reasoning in the same way upon factorization of the expectation value of the form $\langle b_l b_m^+ b_n \rangle$, we obtain

$$\langle b_l b_m^+ b_n \rangle \cong \langle b_m^+ \rangle \langle b_l b_n \rangle. \tag{34}$$

Upon derivation of equations of motion, along with three-particle expectation values, four-particle expectation values also arise (in the third section of the work), which should also be represented in the factorized form. In this case, among these averages of the product of four operators, there are averages in which one of the operators is the operator N_{mg}. According to the aforesaid (see Sect. 2.4), N_{mg} should be replaced by $1 - N_{me} - N_{mf}$ and only averages with N_{me} and N_{mf} should be considered as four-particle expectation values that are subjected to factorization. Taking into account, as before, only two-particle correlations, we can easily show that, in turn, there is a factorized expression for four-particle expectation values, which is an analog of expression (30):

$$\begin{aligned}\langle P_l Q_m R_n S_p \rangle \cong \langle P_l Q_m \rangle \langle R_n S_p \rangle + \langle P_l R_n \rangle \langle Q_m S_p \rangle \\ + \langle P_l S_p \rangle \langle Q_m R_n \rangle - 2\langle P_l \rangle \langle Q_m \rangle \langle R_n \rangle \langle S_p \rangle.\end{aligned} \tag{35}$$

Here, $l \neq m \neq n \neq p$. In this case, it can be easily verified that (35) has the proper asymptotic behavior with increasing distance between individual molecules. Similarly to (32), formula (35) can be expressed via correlations,

$$\begin{aligned}\langle P_l Q_m R_n S_p\rangle &\cong \langle P_l\rangle\langle Q_m\rangle\langle R_n\rangle\langle S_p\rangle \\ &+ \langle P_l\rangle\langle Q_m\rangle\Delta(R_n,S_p) + \langle P_l\rangle\langle R_n\rangle\langle Q_m S_p\rangle \\ &+ \langle P_l\rangle\langle S_p\rangle\Delta(Q_m,R_n) + \Delta(P_l,Q_m)\langle R_n\rangle\langle S_p\rangle \\ &+ \langle P_l R_n\rangle\langle Q_m\rangle\langle S_p\rangle + \Delta(P_l,S_p)\langle Q_m\rangle\langle R_n\rangle \\ &+ \Delta(P_l,Q_m)\Delta(R_n,S_p) + \Delta(P_l,R_n)\Delta(Q_m,S_p) \\ &+ \Delta(P_l,S_p)\Delta(Q_m,R_n).\end{aligned} \tag{36}$$

Here, expressions of the type $\Delta(P_l,Q_m)$ have the same meaning as in (32). It is seen from (36) that this expression is a sum of the completely factorized average and all the possible two-particle correlation corrections of the first and second orders in these corrections. It should be noted that, similarly to cases (33) and (34), expressions (35) and (36) also have their peculiarities that are related to the choice of basis averages. These peculiarities will be taken into account upon uncoupling particular four-particle expectation values. All that has been said above makes it possible to completely unambiguously factorize averages and obtain a closed set of equations of motion.

Completing the derivation of equations of motion in this part of the work, let us formulate them in terms of a local field. The local field $E_{\text{loc}}^{(m)}$ is the field that acts on a molecule with the number m from the side of the external field and from the side of all the remaining molecules. We will define this field by the following expression:

$$(\boldsymbol{\mu}^{12}\mathbf{E}_{\text{loc}}^{(m)}) = (\boldsymbol{\mu}^{12}\mathbf{e}_1)E_1 - 2\hbar\sum_{l\neq m}(\Delta_{ml} - i\gamma_{ml})\langle b_l\rangle. \tag{37}$$

Introduction of local fields makes it possible to single out in the explicit form principal terms and correlation corrections that arise upon uncoupling multiparticle averages.

Taking into account all the aforesaid, we obtain a factorized system of equations that was derived with allowance for interaction with the external radiation field and the dipole–dipole interaction, as well as the interaction with the transverse radiation field of molecules,

$$\begin{aligned}\frac{d\langle b_m\rangle}{dt} &= -\left(\gamma_\perp + i\Delta_{12}^{\nu}\right)\langle b_m\rangle \\ &+ \frac{i}{2\hbar}(\boldsymbol{\mu}^{12}\mathbf{E}_{\text{loc}}^{(m)})\left(1 - \langle N_{mf}\rangle - 2\langle N_{me}\rangle\right) \\ &+ 2i\sum_{l\neq m}(\Delta_{ml} - i\gamma_{ml})\left(\langle N_{me}b_l\rangle - \langle N_{me}\rangle\langle b_l\rangle\right),\end{aligned} \tag{38}$$

$$\begin{aligned}\frac{d\langle N_{me}\rangle}{dt} &= -\gamma_2\langle N_{me}\rangle \\ &+ \frac{i}{2\hbar}\left[\left(\boldsymbol{\mu}^{12}\mathbf{E}_{\text{loc}}^{(m)}\right)\left\langle b_m^+\right\rangle - \left(\boldsymbol{\mu}^{12}\mathbf{E}_{\text{loc}}^{(m)*}\right)\langle b_m\rangle\right],\end{aligned} \tag{39}$$

$$\begin{aligned}\frac{d\langle N_{me}b_n\rangle}{dt} &= -\left[i\Delta_{12}^{\nu} + (\gamma_2 + \gamma_\perp)\right]\langle N_{me}b_n\rangle \\ &+ (i\Delta_{mn} - \gamma_{mn})\langle N_{ne}b_m\rangle \\ &- \frac{i}{2\hbar}\left[\left(\boldsymbol{\mu}^{12}\mathbf{E}_{\text{loc}}^{(m)*}\right) + 2\hbar(\Delta_{mn} - i\gamma_{mn})^*\left\langle b_n^+\right\rangle\right]\langle b_m b_n\rangle \\ &+ \frac{i}{2\hbar}\left[\left(\boldsymbol{\mu}^{12}\mathbf{E}_{\text{loc}}^{(m)}\right) + 2\hbar(\Delta_{mn} - i\gamma_{mn})\langle b_n\rangle\right]\left\langle b_m^+\right\rangle\langle b_n\rangle \\ &+ \frac{i}{2\hbar}\left[\left(\boldsymbol{\mu}^{12}\mathbf{E}_{\text{loc}}^{(n)}\right) + 2\hbar(\Delta_{mn} - i\gamma_{mn})\langle b_m\rangle\right] \\ &\times\left[\langle N_{me}\rangle\left(1 - \langle N_{nf}\rangle\right) - 2\langle N_{me}N_{ne}\rangle\right] \\ &- i\sum_{l\neq m,n}(\Delta_{ml} - i\gamma_{ml})\left\langle b_m^+\right\rangle\left(\langle b_n b_l\rangle - \langle b_n\rangle\langle b_l\rangle\right) \\ &+ i\sum_{l\neq m,n}(\Delta_{nl} - i\gamma_{nl})\left[2\left(\langle N_{ne}b_l\rangle - \langle N_{ne}\rangle\langle b_l\rangle\right)\langle N_{me}\rangle\right. \\ &\left.- \left(\langle N_{me}b_l\rangle - \langle N_{me}\rangle\langle b_l\rangle\right)\left(1 - \langle N_{nf}\rangle - 2\langle N_{ne}\rangle\right)\right],\end{aligned} \tag{40}$$

$$\begin{aligned}\frac{d\langle b_m b_n\rangle}{dt} &= \left\{-\left(i\Delta_{12}^{\nu} + \gamma_\perp\right)\langle b_m b_n\rangle\right. \\ &+ \frac{i}{2\hbar}\left[\left(\boldsymbol{\mu}^{12}\mathbf{E}_{\text{loc}}^{(m)}\right) + 2\hbar(\Delta_{mn} - i\gamma_{mn})\langle b_n\rangle\right] \\ &\times\left[\langle b_n\rangle\left(1 - \langle N_{mf}\rangle\right) - 2\langle N_{me}b_n\rangle\right] \\ &+ i\sum_{l\neq m,n}(\Delta_{ml} - i\gamma_{ml})\left[2\left(\langle N_{me}b_l\rangle - \langle N_{me}\rangle\langle b_l\rangle\right)\langle b_n\rangle\right. \\ &\left.\left.- \left(\langle b_n b_l\rangle - \langle b_n\rangle\langle b_l\rangle\right)\left(1 - \langle N_{mf}\rangle - 2\langle N_{me}\rangle\right)\right]\right\} + \{m \Leftrightarrow n\},\end{aligned} \tag{41}$$

$$\begin{aligned}\frac{d\langle N_{me}N_{ne}\rangle}{dt} &= \left\{-\gamma_2\langle N_{me}N_{ne}\rangle\right. \\ &+ \left[\frac{i}{2\hbar}\left(\left(\boldsymbol{\mu}^{12}\mathbf{E}_{\text{loc}}^{(m)}\right) + 2\hbar(\Delta_{mn} - i\gamma_{mn})\langle b_n\rangle\right)\left\langle N_{ne}b_m^+\right\rangle\right. \\ &\left.\left.- i\sum_{l\neq m,n}(\Delta_{ml} - i\gamma_{ml})\left(\langle N_{ne}b_l\rangle - \langle N_{ne}\rangle\langle b_l\rangle\right)\left\langle b_m^+\right\rangle + \text{c.c.}\right]\right\} \\ &+ \{m \Leftrightarrow n\}.\end{aligned} \tag{42}$$

Here, $\Delta_{12} \equiv \Delta_{12}^{\nu}$ (to distinguish from Δ_{mn}), and $\{m \Leftrightarrow n\}$ denotes the replacement of m by n and vice versa. The contribution to the equations related to taking into account the exciton–exciton interaction will be obtained in the next part of the work.

3. TAKING INTO ACCOUNT THE EXCITON–EXCITON ANNIHILATION

3.1. Formulation of the Problem

In this section, we take into account the mechanism of exciton–exciton annihilation, which ensures the interaction with a third level of molecules, and obtain an equation for the population of this level, which is described by the quantity $\langle N_{mf} \rangle$. In this equation, we also phenomenologically take into account the decay of the third level due to transitions to the first and second levels, which will be done by introducing the relaxation constants Γ_{31} and Γ_{32}, respectively. The sum of these constants will be denoted as $\Gamma = \Gamma_{31} + \Gamma_{32}$. Taking into account the exciton–exciton annihilation leads to the appearance of contributions of this process to all the previously derived equations of motion of the system. The calculation of these contributions and final formulation of equations is the main task of this part of our work. These calculations are rather cumbersome; therefore, here, we restrict ourselves mainly to the consideration of the approach to solve this problem.

Previously, upper level f of the molecule in the system of three-level molecules was considered as a single level. However, this level is vibronic, and, to correctly perform calculations at this stage of the work, we should take into account its structure. We will assume that upper level f consists of a series of sublevels ν, which correspond to different vibrational states and which are characterized by density of states $\rho(E) = \sum_{\nu} \delta(E - E_{f\nu})$ necessary for calculations of the probability of transitions. As a result, the operators C_m and D_m (see Section 2.1), which describe transitions between the first and third levels and between the second and third levels, respectively, will now also depend on ν and will be defined

$$\begin{aligned} C_{m\nu} &= |mg\rangle\langle mf\nu|, \\ D_{m\nu} &= |me\rangle\langle mf\nu|. \end{aligned} \tag{43}$$

The contribution of the process of exciton–exciton annihilation to the total Hamiltonian will be described by the Hamiltonian H_{annih}, which has the form

$$H_{\text{annih}} = \sum_{\substack{\nu \\ k \neq l}} (V_{kl} b_k d_{l\nu}^{+} + V_{lk} d_{l\nu} b_k^{+}). \tag{44}$$

Here, we assume that matrix elements $V_{kl\nu}$ depend weakly on ν and, therefore, this dependence is neglected in (44); however, for detunings $\Delta_{23\nu}$ and $\Delta_{13\nu}$, it certainly should be taken into account. Therefore, operator H_0 (13) should also be revised, which will be now written in a more general form

$$\begin{aligned} H_0 = \sum_m \Bigg[& \hbar(\omega_{m12} - \nu_{12}) b_m^{+} b_m \\ & + \sum_{\nu} \hbar(\omega_{m13\nu} - 2\nu_{12}) d_{m\nu}^{+} d_{m\nu} \Bigg]. \end{aligned} \tag{45}$$

3.2. Calculation of Contributions to Equations of Motion Caused by Exciton–Exciton Annihilation

In the general form, the contribution to the equation of motion that is related to exciton–exciton annihilation is described by the equation

$$dA/dt = i[H_{\text{annih}}, A]/\hbar, \tag{46}$$

where A is an arbitrary operator of the system. In order to clarify the essence of the approach that is used in calculations of these contributions, let us consider very briefly the simplest example of calculation of the contribution from the exciton–exciton annihilation to the equation for $\langle N_{me} \rangle$. To this end, let us consider the commutator $[H_{\text{annih}}, N_{me}]$ in formula (46),

$$\begin{aligned} & \sum_{\substack{\nu \\ p \neq l}} [(V_{pl} b_p d_{l\nu}^{+} + V_{lp} d_{l\nu} b_p^{+}) N_{me} \\ & - N_{me} (V_{pl} b_p d_{l\nu}^{+} + V_{lp} d_{l\nu} b_p^{+})]. \end{aligned} \tag{47}$$

For terms in (47) for which all the indices are different, the commutator is obviously zero. Therefore, only terms for which some indices coincide can make nonzero contributions to the sum. It can be easily verified that there are only two such combinations: $l = m$, $p \neq m$ and $p = m$, $l \neq m$. Taking these indices and substituting explicit expressions for operators that were determined in Section 2.1, the equation for N_{me} can be reduced to the following form:

$$\frac{dN_{me}}{dt} = \frac{i}{\hbar} \sum_{\substack{\nu \\ p \neq m}} [(V_{pm} b_p d_{m\nu}^{+} - \text{H.c.}) + (V_{mp} b_m d_{p\nu}^{+} - \text{H.c.})]. \tag{48}$$

Now, let us consider the equation for the operator $b_p d_{m\nu}^{+}$, which appears in the right-hand side of (48),

$$d(b_p d_{m\nu}^{+})/dt = i\left[(H_0 + H_{\text{annih}}), b_p d_{m\nu}^{+}\right]/\hbar. \tag{49}$$

We will analyze the commutator with H_{annih}, writing it in the explicit form

$$\begin{aligned} & \frac{i}{\hbar} \sum_{\substack{\nu \\ k \neq l}} \{(V_{kl} b_k d_{l\nu}^{+} + V_{lk} d_{l\nu} b_k^{+}) b_p d_{m\nu}^{+} \\ & - b_p d_{m\nu}^{+} (V_{kl} b_k d_{l\nu}^{+} + V_{lk} d_{l\nu} b_k^{+})\}. \end{aligned} \tag{50}$$

As above, commutator (50) is nonzero only if some indices coincide. It can be shown that there are six combinations with coinciding indices,

$$\begin{gathered} k = m; \quad l = p; \quad p \neq m, \\ k = p; \quad l = m; \quad p \neq m, \\ k \neq m, p; \quad l = m; \quad p \neq m, \\ k = m; \quad l \neq m, p; \quad p \neq m, \\ k \neq m, p; \quad l = p; \quad p \neq m, \\ k = p; \quad l \neq m, p; \quad p \neq m. \end{gathered} \tag{51}$$

Calculating these combinations by substituting the explicit expressions for operators, we arrive at the expression for the commutator into the sum in (50),

$$[(H_{\text{annih}})_{klv}, b_p d_{mv}^+] = V_{mk} N_{me} b_k^+ b_p \delta_{lm}(1 + \delta_{kp}). \tag{52}$$

Because the third level rapidly decays, we neglect the terms that contain the operators $c_{mv}(c_{mv}^+)$, $d_{mv}(d_{mv}^+)$, and, naturally, N_{mfv}.

Based on the explicit form of operators, we can also calculate the commutator $i[H_0, b_p d_{mv}^+]/\hbar$. As a result, we obtain

$$i[H_0, b_p d_{mv}^+]/\hbar = i(\omega_{mfv} - \omega_{pe} - \omega_{me}) b_p d_{mv}^+, \tag{53}$$

where $\omega_{mfv} = \omega_{ml3v}$, $\omega_{pe} = \omega_{p12}$, $\omega_{me} = \omega_{ml2}$. The calculations performed lead to the following equation for the average of the operator $b_p d_{mv}^+$:

$$\begin{aligned} \frac{d\left\langle b_p d_{mv}^+ \right\rangle}{dt} &= i(\omega_{mfv} - \omega_{pe} - \omega_{me}) \left\langle b_p d_{mv}^+ \right\rangle \\ &+ \frac{i}{\hbar} \left[V_{mp} \left\langle N_{me} N_{pe} \right\rangle + \sum_{\substack{k \neq p \\ k \neq m}} V_{mk} \left\langle N_{me} b_k^+ b_p \right\rangle \right]. \end{aligned} \tag{54}$$

Formal integration of this equation makes it possible to obtain the following solution:

$$\begin{aligned} \left\langle b_p d_{mv}^+ \right\rangle &= \frac{i}{\hbar} \int_{-\infty}^{t} dt' \exp[i(\omega_{mfv} - \omega_{pe} - \omega_{me})(t - t')] \\ &\times \left[V_{mp} \left\langle N_{me} N_{pe} \right\rangle(t') + \sum_{\substack{k \neq p \\ k \neq m}} V_{mk} \left\langle N_{me} b_k^+ b_p \right\rangle(t') \right]. \end{aligned} \tag{55}$$

We will use the approach of the Markovian process and assume that $\left\langle N_{me} N_{pe} \right\rangle(t')$ and $\left\langle N_{me} b_k^+ b_p \right\rangle(t')$ are slowly varying functions of time and can be taken outside the integral at $t' = t$. Then,

$$\begin{aligned} \left\langle b_p d_{mv}^+ \right\rangle &= \frac{i}{\hbar} \left[V_{mp} \left\langle N_{me} N_{pe} \right\rangle(t) + \sum_{\substack{k \neq p \\ k \neq m}} V_{mk} \left\langle N_{me} b_k^+ b_p \right\rangle(t) \right] \\ &\times \left[\frac{iP}{\omega_{fv} - 2\omega_e} + \pi \delta(\omega_{fv} - 2\omega_e) \right], \end{aligned} \tag{56}$$

where $\omega_{mfv} = \omega_{fv}$, $\omega_{pe} = \omega_{me} = \omega_e$, and P denotes the principal value of the integral, which arises further upon replacement of the summation over v by the integration. Averaging (48), we can easily find that all the remaining expectation values in this equation can be simply calculated merely by permutating subscripts in expression (56) and taking the complex conjugate of it. Having done this and substituting the obtained expressions into (48), we finally arrive at the following equation for $\left\langle N_{me} \right\rangle$:

$$\begin{aligned} \frac{d\left\langle N_{me} \right\rangle}{dt} &= -\sum_{p \neq m} \left\{ w_{mp} \left\langle N_{me} N_{pe} \right\rangle \right. \\ &+ \operatorname{Re} \sum_{\substack{k \neq p \\ k \neq m}} \left[(\Gamma_{pmmk} + i2\Delta_{pmmk}) \left\langle N_{me} b_k^+ b_p \right\rangle \right. \\ &\left. \left. + (\Gamma_{mppk} + i2\Delta_{mppk}) \left\langle N_{pe} b_k^+ b_m \right\rangle \right] \right\}, \end{aligned} \tag{57}$$

where the constants Δ_{pmmk}, Γ_{pmmk}, and w_{mp} have the following form:

$$\begin{aligned} \Delta_{pmmk} &= \frac{1}{\hbar^2} P \sum_v \frac{V_{pm} V_{mk}}{\omega_{fv} - 2\omega_e}, \\ \Gamma_{pmmk} &= \frac{2\pi}{\hbar^2} \sum_v V_{pm} V_{mk} \delta(\omega_{fv} - 2\omega_e), \end{aligned} \tag{58}$$

$$w_{mp} = 2\Gamma_{mppm}. \tag{59}$$

The constant w_{mp} coincides with the same constant that, in particular, appears in [4].

A procedure that is similar to that described above is also applied for the calculation of contributions from the exciton–exciton annihilation to all the remaining equations of the system under consideration. It should be noted that the calculation of contributions to the equations for two-particle expectation values become even more bulky. The calculations performed yielded the following system of equations, in which we also took into account the decay of the third level:

$$\begin{aligned} \frac{d\langle N_{mf} \rangle}{dt} &= \frac{1}{2} \sum_{l \neq m} w_{ml} \langle N_{me} N_{le} \rangle \\ &+ \operatorname{Re} \sum_{k \neq m, l \neq m} (\Gamma_{lmmk} + 2i\Delta_{lmmk}) \langle N_{me} b_k^+ b_l \rangle - \Gamma \langle N_{mf} \rangle, \end{aligned} \tag{60}$$

$$\frac{d\langle N_{me}\rangle}{dt} = -\sum_{l\neq m}\Bigg\{w_{ml}\langle N_{me}N_{le}\rangle + \mathrm{Re}\sum_{\substack{k\neq l\\ k\neq m}}\Big[(\Gamma_{lmmk}+i2\Delta_{lmmk})\langle N_{me}b_k^+b_l\rangle + (\Gamma_{mllk}+i2\Delta_{mllk})\langle N_{le}b_k^+b_m\rangle\Big]\Bigg\} + \Gamma_{32}\langle N_{mf}\rangle, \tag{61}$$

$$\frac{d\langle b_m\rangle}{dt} = \sum_{l\neq m}\Bigg\{\sum_{\substack{k\neq l\\ k\neq m}}(-i2\Delta_{kllm}+\Gamma_{kllm})\langle N_{le}N_{me}b_k\rangle + \sum_{\substack{n\neq l\\ n\neq m}}\left(i\Delta_{nllm}-\frac{1}{2}\Gamma_{nllm}\right)\langle b_nN_{le}\rangle + \left(i2\Delta_{mllm}-\frac{1}{2}w_{ml}\right)\langle N_{le}b_m\rangle + \sum_{\substack{k\neq m\\ k\neq l}}\left(i\Delta_{kmml}-\frac{1}{2}\Gamma_{kmml}\right)\langle b_l^+b_kb_m\rangle\Bigg\}, \tag{62}$$

$$\begin{aligned}\frac{d\langle N_{me}N_{ne}\rangle}{dt} \sim{}& -w_{mn}\langle N_{me}N_{ne}\rangle - \sum_{k\neq n,k\neq m}(w_{mk}+w_{nk})\langle N_{ke}N_{ne}N_{me}\rangle \\ &- \mathrm{Re}\sum_{k\neq n,k\neq m}[(\Gamma_{mnnk}+i2\Delta_{mnnk})\langle N_{ne}b_k^+b_m\rangle + (\Gamma_{nmmk}+i2\Delta_{nmmk})\langle N_{me}b_k^+b_n\rangle] \\ &- \sum_{\substack{k\neq n,k\neq m,k\neq l\\ l\neq n,l\neq m}}(\Gamma_{lmmk}+\Gamma_{l\,nnk})\langle b_k^+b_lN_{me}N_{ne}\rangle \\ &- \mathrm{Re}\sum_{\substack{k\neq n,k\neq m,k\neq l\\ l\neq n,l\neq m}}[(\Gamma_{mllk}+i2\Delta_{mllk})\langle b_k^+b_mN_{le}N_{ne}\rangle + (\Gamma_{nllk}+i2\Delta_{nllk})\langle b_k^+b_nN_{le}N_{me}\rangle] \\ &+ \Gamma_{32}(\langle N_{me}N_{nf}\rangle + \langle N_{ne}N_{mf}\rangle),\end{aligned} \tag{63}$$

$$\begin{aligned}\frac{d\langle b_mb_n\rangle}{dt} \sim{}& -\left(\frac{1}{2}w_{mn}-2i\Delta_{mnnm}\right)\langle b_mb_n\rangle - \frac{1}{2}\sum_{\substack{k\neq n,\\ k\neq m}}(\Gamma_{kmmn}-2i\Delta_{kmmn})\langle b_mb_k\rangle - \frac{1}{2}\sum_{\substack{k\neq n,\\ k\neq m}}(\Gamma_{knnm}-2i\Delta_{knnm})\langle b_nb_k\rangle \\ &- \sum_{\substack{k\neq n,\\ k\neq m}}\left[\frac{1}{2}(w_{mk}+w_{nk})-2i(\Delta_{mkkm}+\Delta_{nkkn})\right]\langle b_mb_nN_{ke}\rangle \\ &+ \frac{1}{2}\sum_{\substack{k\neq n,\\ k\neq m}}(\Gamma_{kmmn}-2i\Delta_{kmmn})\langle b_mb_kN_{ne}\rangle + \frac{1}{2}\sum_{\substack{k\neq n,\\ k\neq m}}(\Gamma_{knnm}-2i\Delta_{knnm})\langle b_nb_kN_{me}\rangle \\ &- \frac{1}{2}\sum_{\substack{k\neq n,k\neq m\\ l\neq m,l\neq n\\ k\neq l}}[(\Gamma_{lmmk}+\Gamma_{lnnk})-2i(\Delta_{lmmk}+\Delta_{lnnk})]\langle b_nb_mb_k^+b_l\rangle \\ &- \frac{1}{2}\sum_{\substack{k\neq n,k\neq m\\ l\neq m,l\neq n\\ k\neq l}}(\Gamma_{lkkm}-2i\Delta_{lkkm})\langle b_nN_{ke}b_l\rangle + \sum_{\substack{k\neq n,k\neq m\\ l\neq m,l\neq n\\ k\neq l}}(\Gamma_{lkkm}-2i\Delta_{lkkm})\langle b_nN_{me}N_{ke}b_l\rangle \\ &- \frac{1}{2}\sum_{\substack{k\neq n,k\neq m\\ l\neq m,l\neq n\\ k\neq l}}(\Gamma_{lkkn}-2i\Delta_{lkkn})\langle b_mN_{ke}b_l\rangle + \sum_{\substack{k\neq n,k\neq m\\ l\neq m,l\neq n\\ k\neq l}}(\Gamma_{lkkn}-2i\Delta_{lkkn})\langle b_mN_{ne}N_{ke}b_l\rangle,\end{aligned} \tag{64}$$

$$\begin{aligned}\frac{d\langle b_nN_{me}\rangle}{dt} \sim{}& -\left(\frac{1}{2}w_{mn}-2i\Delta_{mnnm}\right)\langle b_nN_{me}\rangle - \frac{1}{2}\sum_{\substack{k\neq m,\\ k\neq n}}(\Gamma_{knnm}-2i\Delta_{knnm})\langle b_kb_nb_m^+\rangle - \frac{1}{2}\sum_{\substack{k\neq m,\\ k\neq n}}(\Gamma_{kmmn}-2i\Delta_{kmmn})\langle b_kN_{me}\rangle \\ &- i2\sum_{\substack{k\neq m,\\ k\neq n}}\Delta_{kmmn}\langle b_kN_{me}N_{ne}\rangle - \sum_{\substack{k\neq m,\\ k\neq n}}\left(\frac{1}{2}w_{nk}+w_{mk}-2i\Delta_{nkkn}\right)\langle b_nN_{me}N_{ke}\rangle \\ &- \frac{1}{2}\sum_{\substack{k\neq n,\\ k\neq m}}(\Gamma_{mkkn}+2i\Delta_{mkkn})\langle b_mN_{ke}N_{ne}\rangle - \frac{1}{2}\sum_{\substack{l\neq m,l\neq n\\ k\neq m,k\neq n\\ l\neq k}}(\Gamma_{lkkn}-2i\Delta_{lkkn})\langle N_{me}N_{ke}b_l\rangle \\ &- \frac{1}{2}\sum_{\substack{l\neq m,l\neq n\\ k\neq m,k\neq n\\ l\neq k}}[(\Gamma_{lmmk}+\Gamma_{lnnk})-2i(\Delta_{lmmk}+\Delta_{lnnk})]\end{aligned} \tag{65}$$

$$\times \left\langle b_n N_{me} b_k^+ b_l \right\rangle - \frac{1}{2} \sum_{\substack{l\neq m, l\neq n \\ k\neq m, k\neq n \\ l\neq k}} (\Gamma_{lkkm} - 2i\Delta_{lkkm}) \left\langle b_n N_{ke} b_m^+ b_l \right\rangle$$

$$- \frac{1}{2} \sum_{\substack{l\neq m, l\neq n \\ k\neq m, k\neq n \\ l\neq k}} (\Gamma_{mkkl} + 2i\Delta_{mkkl}) \left\langle b_l^+ N_{ke} b_m b_n \right\rangle$$

$$- \frac{1}{2} \sum_{\substack{l\neq m, l\neq n \\ k\neq m, k\neq n \\ l\neq k}} (\Gamma_{kmml} + 2i\Delta_{kmml}) \left\langle b_l^+ N_{me} b_k b_n \right\rangle$$

$$+ \sum_{\substack{l\neq m, l\neq n \\ k\neq m, k\neq n \\ l\neq k}} (\Gamma_{lkkn} - 2i\Delta_{lkkn}) \left\langle N_{ne} N_{me} N_{ke} b_l \right\rangle + \Gamma_{32} \left\langle b_n N_{mf} \right\rangle.$$

3.3. Equations of Motion in Factorized Form

In the preceding section, we obtained the system of equations that describes the contribution to the total system of equations of motion that is caused by the exciton–exciton annihilation. This system contains multiparticle expectation values, which should be represented in a factorized form in order to obtain a closed system of equations of motion. Clearly, as a result of this factorization, the multiparticle expectation values mentioned above should be in the form of combinations of products of one- and two-particle expectation values that belong to the basic system of the expectation values, which was constructed previously in the second section of this work. Following the rules of factorization that we introduced in this section, we finally obtain the following system of equations of motion:

$$\frac{d\langle N_{mf}\rangle}{dt} = \sum_{l\neq m} \left\{ \frac{1}{2} w_{ml} \langle N_{me} N_{le} \rangle \right.$$

$$+ \mathrm{Re} \sum_{\substack{k\neq l \\ k\neq m}} (\Gamma_{lmmk} + i2\Delta_{lmmk}) \left(\left\langle b_k^+ \right\rangle \langle N_{me} b_l \rangle + \langle b_l \rangle \left\langle b_k^+ N_{me} \right\rangle \right.$$

$$\left. \left. - \left\langle b_k^+ \right\rangle \langle b_l \rangle \langle N_{me} \rangle \right) \right\} - \Gamma \langle N_{mf} \rangle, \tag{66}$$

$$\frac{d\langle N_{me}\rangle}{dt} = -\sum_{l\neq m} \left\{ w_{ml} \langle N_{me} N_{le} \rangle \right.$$

$$+ \mathrm{Re} \sum_{\substack{k\neq l \\ k\neq m}} \left[(\Gamma_{lmmk} + i2\Delta_{lmmk}) \left(\left\langle b_k^+ \right\rangle \langle N_{me} b_l \rangle \right.\right.$$

$$\left. + \langle b_l \rangle \left\langle N_{me} b_k^+ \right\rangle - \left\langle b_k^+ \right\rangle \langle b_l \rangle \langle N_{me} \rangle \right) \tag{67}$$

$$+ (\Gamma_{mllk} + i2\Delta_{mllk}) \left(\left\langle b_k^+ \right\rangle \langle N_{le} b_m \rangle \right.$$

$$\left. \left. \left. + \langle b_m \rangle \left\langle N_{le} b_k^+ \right\rangle - \left\langle b_k^+ \right\rangle \langle b_m \rangle \langle N_{le} \rangle \right) \right] \right\} + \Gamma_{32} \langle N_{mf} \rangle,$$

$$\frac{d\langle b_m\rangle}{dt} = \sum_{l\neq m} \left\{ \sum_{\substack{k\neq l \\ k\neq m}} (\Gamma_{kllm} - i2\Delta_{kllm}) (\langle N_{le} \rangle \langle N_{me} b_k \rangle \right.$$

$$+ \langle N_{me} \rangle \langle N_{le} b_k \rangle + \langle b_k \rangle \langle N_{le} N_{me} \rangle - 2 \langle N_{le} \rangle \langle N_{me} \rangle \langle b_k \rangle)$$

$$- \sum_{\substack{n\neq l \\ n\neq m}} \left(\frac{1}{2} \Gamma_{nllm} - i\Delta_{nllm} \right) \langle b_n N_{le} \rangle \tag{68}$$

$$\left. - \left(\frac{1}{2} w_{ml} - i2\Delta_{mllm} \right) \langle N_{le} b_m \rangle \right.$$

$$\left. - \sum_{\substack{k\neq m \\ k\neq l}} \left(\frac{1}{2} \Gamma_{kmml} - i\Delta_{kmml} \right) \left\langle b_l^+ \right\rangle \langle b_k b_m \rangle \right\},$$

$$\frac{d\langle N_{me} N_{ne}\rangle}{dt} \sim -w_{mn} \langle N_{me} N_{ne} \rangle$$

$$- \sum_{\substack{k\neq m, \\ k\neq n}} (w_{mk} + w_{nk}) (\langle N_{ke} \rangle \langle N_{ne} N_{me} \rangle + \langle N_{ne} \rangle \langle N_{ke} N_{me} \rangle$$

$$+ \langle N_{me} \rangle \langle N_{ke} N_{ne} \rangle - 2 \langle N_{ke} \rangle \langle N_{ne} \rangle \langle N_{me} \rangle)$$

$$- \mathrm{Re} \sum_{\substack{k\neq m, \\ k\neq n}} (\Gamma_{mnnk} + 2i\Delta_{mnnk}) (\langle b_m \rangle \left\langle b_k^+ N_{ne} \right\rangle$$

$$+ \left\langle b_k^+ \right\rangle \langle b_m N_{ne} \rangle - \langle b_m \rangle \left\langle b_k^+ \right\rangle \langle N_{ne} \rangle)$$

$$- \mathrm{Re} \sum_{\substack{k\neq m, \\ k\neq n}} (\Gamma_{nmmk} + 2i\Delta_{nmmk}) (\langle b_n \rangle \left\langle b_k^+ N_{me} \right\rangle$$

$$+ \left\langle b_k^+ \right\rangle \langle b_n N_{me} \rangle - \langle b_n \rangle \left\langle b_k^+ \right\rangle \langle N_{me} \rangle)$$

$$- \sum_{\substack{l\neq m, l\neq n, \\ k\neq m, k\neq n, \\ l\neq k}} (\Gamma_{kmml} + \Gamma_{knnl}) (\langle b_k \rangle \left\langle b_l^+ \right\rangle \langle N_{me} N_{ne} \rangle$$

$$+ \langle b_k N_{me} \rangle \left\langle b_l^+ N_{ne} \right\rangle + \langle b_k N_{ne} \rangle \left\langle b_l^+ N_{me} \right\rangle \tag{69}$$

$$- 2 \langle b_k \rangle \left\langle b_l^+ \right\rangle \langle N_{me} \rangle \langle N_{ne} \rangle)$$

$$- \mathrm{Re} \sum_{\substack{l\neq m, l\neq n, \\ k\neq m, k\neq n, \\ l\neq k}} (\Gamma_{mkkl} + 2i\Delta_{mkkl}) (\langle b_m \rangle \left\langle b_l^+ \right\rangle \langle N_{ke} N_{ne} \rangle$$

$$+ \langle b_m N_{ke} \rangle \left\langle b_l^+ N_{ne} \right\rangle + \langle b_m N_{ne} \rangle \left\langle b_l^+ N_{ke} \right\rangle$$

$$- 2 \langle b_m \rangle \left\langle b_l^+ \right\rangle \langle N_{ke} \rangle \langle N_{ne} \rangle)$$

$$- \mathrm{Re} \sum_{\substack{l\neq m, l\neq n, \\ k\neq m, k\neq n, \\ l\neq k}} (\Gamma_{nkkl} + 2i\Delta_{nkkl}) (\langle b_n \rangle \left\langle b_l^+ \right\rangle \langle N_{me} N_{ke} \rangle$$

$$+\langle b_n N_{me}\rangle\langle b_l^+ N_{ke}\rangle+\langle b_n N_{ke}\rangle\langle b_l^+ N_{me}\rangle$$
$$-2\langle b_n\rangle\langle b_l^+\rangle\langle N_{me}\rangle\langle N_{ke}\rangle)$$
$$+\Gamma_{32}(\langle N_{me}\rangle\langle N_{nf}\rangle+\langle N_{ne}\rangle\langle N_{mf}\rangle),$$
$$\frac{d\langle b_m b_n\rangle}{dt}\sim-\left(\frac{1}{2}w_{mn}-2i\Delta_{mnnm}\right)\langle b_m b_n\rangle$$
$$-\frac{1}{2}\sum_{\substack{k\neq n,\\ k\neq m}}(\Gamma_{kmmn}-2i\Delta_{kmmn})\langle b_m b_k\rangle$$
$$-\frac{1}{2}\sum_{\substack{k\neq n,\\ k\neq m}}(\Gamma_{knnm}-2i\Delta_{knnm})\langle b_n b_k\rangle$$
$$-\sum_{\substack{k\neq n,\\ k\neq m}}\left(\frac{1}{2}(w_{mk}+w_{nk})-2i(\Delta_{mkkm}+\Delta_{nkkn})\right)$$
$$\times(\langle b_m\rangle\langle b_n N_{ke}\rangle+\langle b_n\rangle\langle b_m N_{ke}\rangle+\langle N_{ke}\rangle\langle b_m b_n\rangle$$
$$-2\langle b_m\rangle\langle b_n\rangle\langle N_{ke}\rangle)+\frac{1}{2}\sum_{\substack{k\neq n,\\ k\neq m}}(\Gamma_{kmmn}-2i\Delta_{kmmn})$$
$$\times(\langle b_m\rangle\langle b_k N_{ne}\rangle+\langle b_k\rangle\langle b_m N_{ne}\rangle+\langle N_{ne}\rangle\langle b_m b_k\rangle$$
$$-2\langle b_m\rangle\langle b_k\rangle\langle N_{ne}\rangle)+\frac{1}{2}\sum_{\substack{k\neq n,\\ k\neq m}}(\Gamma_{knnm}-2i\Delta_{knnm})$$
$$\times(\langle b_k\rangle\langle b_n N_{me}\rangle+\langle b_n\rangle\langle b_k N_{me}\rangle+\langle N_{me}\rangle\langle b_k b_n\rangle$$
$$-2\langle b_k\rangle\langle b_n\rangle\langle N_{me}\rangle)-\frac{1}{2}\sum_{\substack{k\neq n,k\neq m\\ l\neq m,l\neq n\\ k\neq l}}(\Gamma_{lmmk}+\Gamma_{lnnk})$$
$$-2i(\Delta_{lmmk}+\Delta_{lnnk})\langle b_k^+\rangle(\langle b_l\rangle\langle b_m b_n\rangle \qquad (70)$$
$$+\langle b_m\rangle\langle b_l b_n\rangle+\langle b_n\rangle\langle b_l b_m\rangle-2\langle b_l\rangle\langle b_m\rangle\langle b_n\rangle)$$
$$-\frac{1}{2}\sum_{\substack{k\neq n,k\neq m\\ l\neq m,l\neq n\\ k\neq l}}(\Gamma_{lkkm}-2i\Delta_{lkkm})(\langle b_l\rangle\langle b_n N_{ke}\rangle+\langle b_n\rangle\langle b_l N_{ke}\rangle$$
$$+\langle N_{ke}\rangle\langle b_l b_n\rangle-2\langle b_l\rangle\langle b_n\rangle\langle N_{ke}\rangle)$$
$$+\sum_{\substack{k\neq n,k\neq m\\ l\neq m,l\neq n\\ k\neq l}}(\Gamma_{lkkm}-2i\Delta_{lkkm})(\langle N_{ke}b_l\rangle\langle N_{me}b_n\rangle$$
$$+\langle N_{ke}N_{me}\rangle\langle b_l b_n\rangle+\langle N_{ke}b_n\rangle\langle b_l N_{me}\rangle$$
$$-2\langle N_{ke}\rangle\langle b_l\rangle\langle N_{me}\rangle\langle b_n\rangle)-\frac{1}{2}\sum_{\substack{k\neq n,k\neq m\\ l\neq m,l\neq n\\ k\neq l}}(\Gamma_{lkkn}-2i\Delta_{lkkn})$$
$$\times(\langle b_l\rangle\langle b_m N_{ke}\rangle+\langle b_m\rangle\langle b_l N_{ke}\rangle+\langle N_{ke}\rangle\langle b_l b_m\rangle$$
$$-2\langle b_l\rangle\langle b_m\rangle\langle N_{ke}\rangle)+\sum_{\substack{k\neq n,k\neq m\\ l\neq m,l\neq n\\ k\neq l}}(\Gamma_{lkkn}-2i\Delta_{lkkn})$$
$$\times(\langle N_{ke}b_l\rangle\langle N_{ne}b_m\rangle+\langle N_{ke}N_{ne}\rangle\langle b_l b_m\rangle$$
$$+\langle N_{ke}b_m\rangle\langle b_l N_{ne}\rangle-2\langle N_{ke}\rangle\langle b_l\rangle\langle N_{ne}\rangle\langle b_m\rangle),$$
$$\frac{d\langle b_n N_{me}\rangle}{dt}\sim-\left(\frac{1}{2}w_{mn}-2i\Delta_{mnnm}\right)\langle b_n N_{me}\rangle$$
$$-\frac{1}{2}\sum_{\substack{k\neq m,\\ k\neq n}}(\Gamma_{knnm}-2i\Delta_{knnm})\langle b_m^+\rangle\langle b_k b_n\rangle$$
$$-\frac{1}{2}\sum_{\substack{k\neq m,\\ k\neq n}}(\Gamma_{kmmn}-2i\Delta_{kmmn})\langle b_k N_{me}\rangle$$
$$-i2\sum_{\substack{k\neq m,\\ k\neq n}}\Delta_{kmmn}(\langle b_k\rangle\langle N_{me}N_{ne}\rangle+\langle N_{me}\rangle\langle b_k N_{ne}\rangle$$
$$+\langle N_{ne}\rangle\langle b_k N_{me}\rangle-2\langle b_k\rangle\langle N_{me}\rangle\langle N_{ne}\rangle)$$
$$-\sum_{\substack{k\neq m,\\ k\neq n}}\left(\frac{1}{2}w_{nk}+w_{mk}-2i\Delta_{nkkn}\right)(\langle b_n\rangle\langle N_{me}N_{ke}\rangle$$
$$+\langle N_{me}\rangle\langle b_n N_{ke}\rangle+\langle N_{ke}\rangle\langle b_n N_{me}\rangle-2\langle b_n\rangle\langle N_{me}\rangle\langle N_{ke}\rangle)$$
$$-\frac{1}{2}\sum_{\substack{k\neq n,\\ k\neq m}}(\Gamma_{mkkn}+2i\Delta_{mkkn})(\langle b_m\rangle\langle N_{ne}N_{ke}\rangle$$
$$+\langle N_{ne}\rangle\langle b_m N_{ke}\rangle+\langle N_{ke}\rangle\langle b_m N_{ne}\rangle-2\langle b_m\rangle\langle N_{ne}\rangle\langle N_{ke}\rangle)$$
$$-\frac{1}{2}\sum_{\substack{l\neq m,l\neq n\\ k\neq m,k\neq n\\ l\neq k}}(\Gamma_{lkkn}-2i\Delta_{lkkn})(\langle b_l\rangle\langle N_{me}N_{ke}\rangle$$
$$+\langle N_{me}\rangle\langle b_l N_{ke}\rangle+\langle N_{ke}\rangle\langle b_l N_{me}\rangle-2\langle b_l\rangle\langle N_{me}\rangle\langle N_{ke}\rangle)$$
$$-\frac{1}{2}\sum_{\substack{l\neq m,l\neq n\\ k\neq m,k\neq n\\ l\neq k}}[(\Gamma_{lmmk}+\Gamma_{lnnk})-2i(\Delta_{lmmk}+\Delta_{lnnk})] \qquad (71)$$
$$\times\left(\langle b_k^+ N_{me}\rangle\langle b_l b_n\rangle+\langle b_k^+\rangle[\langle b_l\rangle\Delta(N_{me},b_n)\right.$$
$$\left.+\langle b_n\rangle\Delta(b_l,N_{me})]\right)-\frac{1}{2}\sum_{\substack{l\neq m,l\neq n\\ k\neq m,k\neq n\\ l\neq k}}(\Gamma_{lkkm}-2i\Delta_{lkkm})$$
$$\times\left(\langle b_m^+ N_{ke}\rangle\langle b_l b_n\rangle+\langle b_m^+\rangle[\langle b_l\rangle\Delta(N_{ke},b_n)+\langle b_n\rangle\Delta(b_l,N_{ke})]\right)$$
$$-\frac{1}{2}\sum_{\substack{l\neq m,l\neq n\\ k\neq m,k\neq n\\ l\neq k}}(\Gamma_{mkkl}+2i\Delta_{mkkl})\left(\langle b_l^+ N_{ke}\rangle\langle b_m b_n\rangle\right.$$
$$\left.+\langle b_l^+\rangle[\langle b_m\rangle\Delta(N_{ke},b_n)+\langle b_n\rangle\Delta(b_m,N_{ke})]\right)$$

$$-\frac{1}{2}\sum_{\substack{l\neq m,l\neq n\\ k\neq m,k\neq n\\ l\neq k}}(\Gamma_{kmml}+2i\Delta_{kmml})\sum_{\substack{l\neq m,l\neq n\\ k\neq m,k\neq n\\ l\neq k}}(\Gamma_{mkkl}+2i\Delta_{mkkl})$$
$$\times\Big(\big\langle b_l^+ N_{me}\big\rangle\langle b_k b_n\rangle+\big\langle b_l^+\big\rangle[\langle b_k\rangle\Delta(N_{me},b_n)+\langle b_n\rangle\Delta(b_k,N_{me})]\Big)\cdot$$
$$+\sum_{\substack{l\neq m,l\neq n\\ k\neq m,k\neq n\\ l\neq k}}(\Gamma_{lkkn}-2i\Delta_{lkkn})\big(\langle N_{ke}b_l\rangle\langle N_{me}N_{ne}\rangle$$
$$+\langle N_{ke}N_{me}\rangle\langle b_l N_{ne}\rangle+\langle N_{ke}N_{ne}\rangle\langle b_l N_{me}\rangle$$
$$-2\langle N_{ke}\rangle\langle b_l\rangle\langle N_{me}\rangle\langle N_{ne}\rangle\big)+\Gamma_{32}\langle b_n\rangle\langle N_{mf}\rangle.$$

Upon numerical solution of the above-presented system of equations, we will approximately assume that all the quantities of form Δ_{pqqs} are zero. We also assume that quantities Γ_{pqqs}, which are expressed in terms of matrix elements of the exciton–exciton interaction, are nonzero only for the interaction with nearest neighbors, when $|p-q|=|q-s|=1$ $(p\neq q\neq s)$, and the quantities $\Gamma_{pqqp}=w_{pq}/2$ are nonzero when $|p-q|=1$. We will also assume that all the quantities Γ_{pqqs} are real-valued. By virtue of what has been, expressions for Γ_{pqqs} used in equations have the following form:

$$\text{(i)}\ \Gamma_{mkkm}=\Gamma_{kmmk}=w_{mk}/2,$$
$$w_{mk}=w\big(\delta_{k(m-1)}+\delta_{k(m+1)}\big),\quad k\neq m,$$
$$w_{nk}=w_{mk}\big|_{m\to n},\quad k\neq n.$$

Here, $m\to n$ denotes the replacement of m by n and δ_{pq} is the Kronecker symbol.

$$\text{(ii)}\ w_{mn}=w\big(\delta_{n(m-1)}+\delta_{n(m+1)}\big),\quad m\neq n,$$
$$w_{mk}=w\big(\delta_{k(m-1)}+\delta_{k(m+1)}\big)\big(1-\delta_{kn}\big),\quad k\neq m,n,$$
$$w_{nk}=w_{mk}\big|_{m\Leftrightarrow n},\quad k\neq m,n,\quad m\neq n.$$

The expression $m\Leftrightarrow n$ denotes the replacement of m by n and vice versa.

$$\text{(iii)}\ \Gamma_{mnnk}=\Gamma_{knnm}=w\big(\delta_{k(n+1)}\delta_{n(m+1)}+\delta_{k(n-1)}\delta_{n(m-1)}\big)/2,$$
$$k\neq m,n,\quad m\neq n.$$
$$\text{(iv)}\ \Gamma_{nmmk}=\Gamma_{kmmn}=w\big(\delta_{n(m+1)}\delta_{k(m-1)}+\delta_{n(m-1)}\delta_{k(m+1)}\big)/2,$$
$$k\neq m,n,\quad m\neq n.$$
$$\text{(v)}\ \Gamma_{mkkn}=\Gamma_{nkkm}=w\big(\delta_{k(m-1)}\delta_{n(m-2)}+\delta_{k(m+1)}\delta_{n(m+2)}\big)/2,$$
$$k\neq m,n,\quad m\neq n.$$
$$\text{(vi)}\ \Gamma_{kmml}=\Gamma_{lmmk}=w(\delta_{k(m-1)}\delta_{l(m+1)}$$
$$+\delta_{k(m+1)}\delta_{l(m-1)})\big(1-\delta_{kn}\big)\big(1-\delta_{ln}\big)/2,$$
$$k\neq m,n,\quad l\neq m,n,\quad k\neq l.$$
$$\text{(vii)}\ \Gamma_{knnl}=\Gamma_{lnnk}=\Gamma_{kmml}\big|_{m\Leftrightarrow n}.$$
$$\text{(viii)}\ \Gamma_{mkkl}=\Gamma_{lkkm}=w(\delta_{k(m-1)}\delta_{l(m-2)}$$
$$+\delta_{k(m+1)}\delta_{l(m+2)})\big(1-\delta_{kn}\big)\big(1-\delta_{ln}\big)/2,$$
$$k\neq m,n,\quad l\neq m,n,\quad k\neq l.$$
$$\text{(ix)}\ \Gamma_{nkkl}=\Gamma_{lkkn}=\Gamma_{mkkl}\big|_{m\Leftrightarrow n}.$$

Clearly, the total system of equations is obtained by combining Eqs. (38)–(42) from the second section and Eqs. (66)–(71) presented above. Because this total system is extremely cumbersome, we omit the combined version.

Therefore, in this work, we have obtained from first principles a closed system of equations of motion for molecular J aggregates in the form of a chain of three-level molecules, in which we took into account two-particle correlations between molecules of the chain. The system of equations refined in this way can be used to study the hysteresis and various nonlinear effects, as well as for calculation and analysis of characteristics of dissipative molecular solitons.

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