STOCHASTIC LIOUVILLE EQUATIONS FOR INTERACTING QUASI-PARTICLES IN THE GENERALIZED HAKEN–STROBL MODEL

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A generalization of the one-particle Haken–Strobl model for the exciton–phonon interaction to the case of interacting excitons is proposed. In the framework of this model the exact set of stochastic Liouville equations for the exciton subsystem density matrix is obtained. In the case of strong transverse relaxation and weak resonance transfer of molecular excitations it is reduced to a chain of coupled equations describing random walks of incoherent excitons with allowance for their dynamic interaction (the main result of the work). These equations with a Lorentz-type jump probability dependence on the exciton–phonon and exciton–exciton interaction parameters and, moreover, those ones generalized in a way discussed in the paper are relevant to a number of applications including the description of exciton annihilation, recombination of point defects in crystals and many others. The connection of the obtained random-walk equations with classical diffusion equations for a system of interacting brownian particles is also discussed.

1. Introduction

Mathematical models for many real processes are based on the equations describing random-walk motion of particles (quasi-particles) in a given discrete space. The concept of random walks proved to be useful in the description of both one-particle and many-particle systems. In the case when only one particle effectively participates in a process (incoherent energy transfer in molecular crystals, energy trapping in the photosynthetic unit, ion transport through membrane channels) the corresponding equations are well known [1] and used in solid-state physics, physical chemistry and biophysics [2–10].

Less has been done so far as to the description of many-particle processes such as reactions between particles (exciton–exciton annihilation, annealing of point defects, recombination of solvated electrons with suitable reaction partners, etc.) when the interparticle interactions conserving the particle number (dynamic) and the non-conserving one (resulting in reactions) are important. In the theoretical study of these processes an adequate formalism is based on the chain of coupled equations for the density matrix [11–17]. But usually only the non-conserving part of the interaction is taken into account consistently. The role of the dynamic interaction which affects the reaction rate has been investigated at the stage of the two-particle correlation function [18–24]. In the framework of such an approach many-particle aspects of the problem are omitted and consequently the effect of high concentrations in the case of dynamic interactions cannot be considered. To avoid these difficulties in the theory of diffusion-influenced reactions one should start from a chain of equations describing random walks of particles with allowance for their dynamic interaction. The derivation of the corresponding equations is the aim of the present paper.

To take into account the mutual influence of particles on their motion resulting in a change of the jump probabilities it is necessary to consider both the interaction between particles and their interaction with the medium in which they move. Our discussion is concerned with a system of excitons interacting with each other and also with phonons. The generalized Haken–Strobl model [25] discussed in section 2 serves as the starting point. The above model introduced first to describe exciton dynamics [25–27] has been extensively

used in studying one-particle excitation properties [28]. Being generalized through the allowance for exciton–exciton dynamic interactions, it is used here to obtain the stochastic Liouville equations in the case of a many-particle system (section 3). In sections 4 and 5 the coupled chain of equations for a system of incoherent excitons is derived. To extend its range of applicability which is limited by the particular form of the exciton–phonon interaction, a generalization of the equations describing random walks of interacting quasi-particles is also discussed in section 5. Finally, in section 6 the connection of the equations obtained with the standard Bogoljubov hierarchy chain for brownian particles is outlined.

2. Description of the model

The hamiltonian operator of non-interacting Frenkel excitons reads

$$H_M = \sum_{n,m} M_{nm} B_n^+ B_m.$$ (1)

where M_{nm} with $n \neq m$ is the matrix element defining the rate of the excitation energy resonance transfer from the nth molecule to the mth. M_{nn} is the excitation energy of a molecule at the lattice site n, the latin index corresponds to the coordinates of a molecule in a crystal and the summation over such an index is carried out at the positions of all molecules of a crystal. B_n^- and B_n are the creation and annihilation operators of a localized excitation at the nth molecule.

In the Haken–Strobl model (see refs. [25–28]) the interaction between excitons and phonons is treated as a stochastic process described by the hamiltonian

$$H_{int} = \sum_{n,m} h_{nm}(t) B_n^+ B_m,$$ (2)

where the diagonal matrix element $h_{nn}(t)$ and the non-diagonal one $h_{nm}(t)$ represent the stochastic variations of the excitation energy at the lattice site n and of the coherent interaction matrix element M_{nm} of (1) respectively. The fluctuations of these quantities are assumed to be a gaussian stochastic process characterized by the following properties

$$\langle h_{nm}(t) \rangle = 0,$$

$$\langle h_{nm}(t_1) h_{n'm'}(t_2) \rangle = [\delta_{nn'}\delta_{mm'} + \delta_{nm'}\delta_{mn'}(1 - \delta_{nm})] 2\Gamma_{nm}\delta(t_1 - t_2),$$ (3)

where the angular brackets denote the averaging over fluctuations which, according to (3), are supposed to have a white spectrum. The averages of higher products of the $h_{nm}(t)$ can be expanded in terms of (3), i.e. the cumulant averages of a product of more than two $h_{nm}(t)$ are equal to zero [29]. The phenomenological quantities Γ_{nm} depend on the distance between lattice sites n and m and are commonly related to the local $\Gamma_{nn} \equiv \Gamma$ and non-local for $n \neq m$ scattering of excitons by phonons.

Eqs. (1)–(3) reflect the basic assumptions involved in the Haken–Strobl model describing one-particle excitation phenomena. To consider many-particle states with more than one molecule involved in excitation and related processes, one should take into account the exciton–exciton interaction. Since the non-conserving part of the interaction resulting in exciton annihilation has been considered in ref. [12], we include only the dynamic exciton–exciton interaction which can be written in the form

$$H_V = \frac{1}{2} \sum_{\substack{n,m \\ n \neq m}} V_{nm} B_n^+ B_n B_m^+ B_m.$$ (4)

where the matrix elements of the interaction energy V_{nm} as well as the M_{nm} are assumed to be functions of $|n - m|$.

We extend further the Haken–Strobl model by taking into account fluctuations of the interaction energy. These are also treated as a gaussian stochastic process described by the hamiltonian

$$H'_{int} = \sum_{\substack{n,m \\ n \neq m}} h'_{nm}(t) B_n^+ B_n B_m^+ B_m,$$ (5)

where the time-dependent matrix elements are supposed to be random quantities with the following properties

$$\langle h'_{nm}(t) \rangle = 0, \qquad \langle h'_{nm}(t) h_{n'm'}(t') \rangle = 0,$$

$$\langle h'_{nm}(t_1) h'_{n'm'}(t_2) \rangle = (\delta_{nn'}\delta_{mm'} + \delta_{nm'}\delta_{mn'}) \chi_{nm}\delta(t_1 - t_2).$$ (6)

The first of these relations means that the mean value of the interaction energy fluctuations is included in (4), the second one shows that the fluctuations described by $h_{nm}(t)$ and $h'_{nm}(t)$ are assumed to be statistically independent, the third relation implies the independence of the interaction energy fluctuations of different pairs of excitons. The parameters χ_{nm} represent the contribution to the non-local scattering rate of excitons arising from the fluctuations of the exciton–exciton interaction energy.

Thus, the total hamiltonian of the considered system reads

$$H = H_M + H_V + H_{int} + H'_{int}.$$ (7)

3. The stochastic Liouville equation for the exciton subsystem density matrix

We derive the stochastic Liouville equation (SLE) for the exciton density operator following the standard procedure described in ref. [28].

Averaging the formal solution of the equation of motion of the density operator with the hamiltonian (7) over the fluctuations we obtain ($\hbar = 1$)

$$\hat{\rho}(t) = \langle T \exp\left(-i \int_0^t [\hat{H}_{int}^\times(t') + \hat{H}_{int}'^\times(t')] dt' \right) \rangle \rho(0),$$ (8)

where $\rho(t)$ is the density operator of the exciton subsystem, the circumflex denotes the interaction representation $\hat{\rho}(t) = \exp[i(H_M + H_V)^\times t]\rho(t)$, $A^\times B = AB - BA$ for any two operators A and B, T is the time ordering operator, ordering operators in the expansion of the exponential from right to left with increasing time.

Rewriting (8) in terms of cumulant averages [29] and using the properties of the stochastically time-depending part of the hamiltonian (7) we get

$$\hat{\rho}(t) = T \exp\left(-\tfrac{1}{2} \int_0^t dt_1 \int_0^t dt_2 \langle [\hat{H}_{int}^\times(t_1) + \hat{H}_{int}'^\times(t_1)][\hat{H}_{int}^\times(t_2) + \hat{H}_{int}'^\times(t_2)] \rangle \right) \rho(0)$$

$$= \exp\left(-\int_0^t [\hat{Q}_M(t_1) + \hat{Q}_V(t_1)] dt_1 \right) \rho(0),$$ (9)

where

$$Q_M = \sum_{n,m} \left[\tfrac{1}{2} \Gamma \delta_{nm} + (1 - \delta_{nm}) \Gamma_{nm} \right] (B_n^+ B_m)^\times (B_n^+ B_m + B_m^+ B_n)^\times,$$ (10)

$$Q_V = \sum_{n,m} \chi_{nm} \left[(B_n^+ B_m^+ B_n B_m)^\times \right]^2.$$ (11)

Differentiating (9) with respect to time and transforming the resulting equation to the Schrödinger representation we arrive at the following equation of motion

$$\mathrm{d}\rho(t)/\mathrm{d}t = \left[-i(H_M + H_V)^\times - Q_M - Q_V \right]\rho(t),\tag{12}$$

with H_M, H_V, Q_M, and Q_V defined in (1), (4) (10), and (11). This equation reduces to that derived by Haken, Strobl and Reineker if we put H_V and Q_V equal to zero. Since we are interested in the exciton dynamics when more than one excitation is present H_V and Q_V cannot be ignored here.

The evolution of an exciton subsystem with S excitons is completely defined by the set of quantities

$$\rho^{(s)}_{n_1 n_2 \ldots n_s;n'_1 n'_2 \ldots n'_s} = \mathrm{Sp}\left\{ \rho(t) B^+_{n_1} B^+_{n_2} \ldots B^+_{n_s} B_{n'_1} B_{n'_2} \ldots B_{n'_s} \right\}, \qquad s = 1, 2, \ldots, S,\tag{13}$$

which will be called hereafter the matrix elements of the density matrix. The diagonal elements $\rho^{(1)}_{n_1;n_1}$ define the excitation distribution in molecules of a crystal, i.e. the exciton concentration; $\rho^{(2)}_{n_1 n_2,n_1 n_2}$ gives the probability of finding a pair of excitons at molecules n_1 and n_2, etc. Non-diagonal matrix elements $\rho^{(s)}_{n_1 \ldots n_s,n'_1 \ldots n'_s}$ define phase relations for one-particle, two-particle, ..., s-particle excitations in a crystal.

The equations of motion for these quantities follow directly from (12) and the commutation relations for the creation and annihilation operators which are supposed to be the Pauli ones

$$B_n B^+_m - B^+_m B_n = \delta_{nm}(1 - 2B^+_n B_n), \qquad B^2_n = B^{+2}_n = 0.\tag{14}$$

It is convenient to represent the time derivatives of the matrix elements of the density matrix symbolically

$$\frac{\mathrm{d}\rho^{(s)}}{\mathrm{d}t} = \left(\frac{\mathrm{d}\rho^{(s)}}{\mathrm{d}t}\right)_{H_M} + \left(\frac{\mathrm{d}\rho^{(s)}}{\mathrm{d}t}\right)_{H_t} + \left(\frac{\mathrm{d}\rho^{(s)}}{\mathrm{d}t}\right)_{Q_M} + \left(\frac{\mathrm{d}\rho^{(s)}}{\mathrm{d}t}\right)_{Q_t},\tag{15}$$

where indices of the derivatives denote the summand of the right-hand side of the eq. (12) due to which the change in the density matrix is produced. The corresponding expressions for these conventional derivatives are obtained using (12) and (14) in (13). They read

$$\left(\frac{\mathrm{d}\rho^{(1)}_{n_1 n'_1}}{\mathrm{d}t}\right)_{H_M} = i\mathrm{Sp}\left\{ \rho(t) H^\times_M B^+_{n_1} B_{n'_1} \right\} = i\sum_l \left[M_{n_1 l}\rho^{(1)}_{l n'_1} - M_{n'_1 l}\rho^{(1)}_{n_1 l} - 2\left(M_{n_1 l}\rho^{(2)}_{n_1 l,n_1 n'_1} - M_{n'_1 l}\rho^{(2)}_{n_1 n'_1;n'_1 l} \right) \right],\tag{16}$$

$$\left(\frac{\mathrm{d}\rho^{(2)}_{n_1 n_2\, n'_1 n'_2}}{\mathrm{d}t}\right)_{H_M} = i\sum_l \left[M_{n_1 l}\rho^{(2)}_{l n_2\cdot n'_1 n'_2} + M_{n_2 l}\rho^{(2)}_{n_1 l\, n'_1 n'_2} - M_{n'_1 l}\rho^{(2)}_{n_1 n_2,l n'_2} - M_{n'_2 l}\rho^{(2)}_{n_1 n_2\, n'_1 l} \right.$$
$$\left. -2\left(M_{n_1 l}\rho^{(3)}_{n_1 n_2 l,n'_1 n'_2 n_1} + M_{n_2 l}\rho^{(3)}_{n_1 n_2 l,n'_1 n'_2 n_2} - M_{n'_1 l}\rho^{(3)}_{n_1 n_2 n'_1,n'_1 n'_2 l} - M_{n'_2 l}\rho^{(3)}_{n_1 n_2 n'_2,n'_1 n'_2 l} \right) \right].\tag{17}$$

The expressions for $(\mathrm{d}\rho^{(s)}/\mathrm{d}t)_{H_M}$ for $s > 2$ can be easily written down in an analogous way.
We proceed with writing explicitly $(\mathrm{d}\rho^{(s)}/\mathrm{d}t)_{H_V}$

$$\left(\frac{\mathrm{d}\rho^{(1)}_{n_1,n'_1}}{\mathrm{d}t}\right)_{H_V} = i\,\mathrm{Sp}\left\{ \rho(t) H^\times_V B^+_{n_1} B_{n'_1} \right\} = i\sum_l (V_{l n_1} - V_{l n'_1})\rho^{(2)}_{n_1 l\, n'_1 l},\tag{18}$$

$$\left(\frac{\mathrm{d}\rho^{(2)}_{n_1 n_2;n'_1 n'_2}}{\mathrm{d}t}\right)_{H_V} = i\left((V_{n_1 n_2} - V_{n'_1 n'_2})\rho^{(2)}_{n_1 n_2,n'_1 n'_2} + \sum_l (V_{l n_1} + V_{l n_2} - V_{l n'_1} - V_{l n'_2})\rho^{(3)}_{n_1 n_2 l,n'_1 n'_2 l} \right),\tag{19}$$

and for any value of s

$$\left(\frac{\mathrm{d}\rho^{(s)}_{n_1\ldots n_s;n_1'\ldots n_s'}}{\mathrm{d}t}\right)_{H_V} = \mathrm{i}\left(\sum_{j<k=2}^{s}\left(V_{n_jn_k}-V_{n_j'n_k'}\right)\rho^{(s)}_{n_1\ldots n_s;n_1'\ldots n_s'}+\sum_l\sum_{j=1}^{s}\left(V_{ln_j}-V_{ln_j'}\right)\rho^{(s+1)}_{n_1\ldots n_s,l;n_1'\ldots n_s',l}\right). \quad (20)$$

The contribution to the change in the density matrix due to the interaction with phonons is represented by

$$\left(\frac{\mathrm{d}\rho^{(s)}_{n_1\ldots n_s;n_1'\ldots n_s'}}{\mathrm{d}t}\right)_{Q_M} = -\mathrm{Sp}\left\{\rho(t)Q_M B^+_{n_1}\ldots B^+_{n_s}B_{n_1'}\ldots B_{n_s'}\right\}$$

$$= -2\left\{s\left[\Gamma\left(1-s^{-1}\sum_{j,k=1}^{s}\delta_{n_jn_k'}\right)+\sum_{l\neq0}\Gamma_l\right]\rho^{(s)}_{n_1\ldots n_s,n_1'\ldots n_s'}\right.$$

$$-\sum_{l\neq n_j,\,j,k=1}^{s}\Gamma_{n_jl}\delta_{n_jn_k'}\rho^{(s)}_{n_1\ldots n_j=l\ldots n_s;n_1'\ldots n_k'=l\ldots n_s'}$$

$$\left.-\sum_{j,k=1}^{s}\Gamma_{n_jn_k'}\left(1-\delta_{n_jn_k'}\right)\rho^{(s)}_{n_1\ldots n_j=n_k'\ldots n_s,n_1'\ldots n_k'=n_j\ldots n_s'}\right\}. \quad (21)$$

where terms with $\rho^{(s+1)}$ are omitted, and

$$\left(\frac{\mathrm{d}\rho^{(s)}_{n_1\ldots n_s;n_1'\ldots n_s'}}{\mathrm{d}t}\right)_{Q_V} = -\mathrm{Sp}\left\{\rho(t)Q_V B^+_{n_1}\ldots B^+_{n_s}B_{n_1'}\ldots B_{n_s'}\right\}$$

$$= -2\left[\sum_{j<k=2}^{s}\left(\chi_{n_jn_k}+\chi_{n_j'n_k'}-2\chi_{n_jn_k}\sum_{j'\neq k'=2}^{s}\delta_{n_jn_{j'}}\delta_{n_kn_{k'}}\right)\rho^{(s)}_{n_1\ldots n_s,n_1'\ldots n_s'}\right.$$

$$\left.+\sum_l\sum_{j=1}^{s}\left(\chi_{n_jl}+\chi_{n_j'l}-2\chi_{n_jl}\sum_{j'=1}^{s}\delta_{n_jn_{j'}}\right)\rho^{(s+1)}_{n_1\ldots n_s,l;n_1'\ldots n_s',l}\right]. \quad (22)$$

The substitution of expressions (16)–(22) into the right-hand side of (15) leads to a coupled chain of equations for $\rho^{(s)}_{n_1\ldots n_s;n_1'\ldots n_s'}$, $s = 1, 2, \ldots, S$. The stochastic Liouville equations for the matrix elements of the exciton density matrix are exactly defined for the system with the hamiltonian (7) and can be used, in general, for the description of crystal properties at high levels of excitation. As in the case of the one-particle Haken–Strobl model, it is not necessary to make any a priori assumptions as to the character (coherent or incoherent) of the exciton motion.

In what follows we deal only with those crystal excited states which may be regarded as an ensemble of incoherent excitons. The corresponding equations can be derived from the above SLEs under certain conditions.

With this aim in mind we remind briefly the procedure of the derivation of the master equation describing the dynamics of an isolated incoherent exciton. Restricting ourselves to one-exciton states ($\rho^{(s)} = 0$, $s \geq 2$) we obtain from (15)–(22)

$$\frac{\mathrm{d}\rho^{(1)}_{n_1;n_1'}}{\mathrm{d}t} = \mathrm{i}\sum_l\left(M_{n_1l}\rho^{(1)}_{l;n_1'}-M_{n_1'l}\rho^{(1)}_{n_1;l}\right)-2\left(\sum_l\left(\Gamma_l\rho^{(1)}_{n_1;n_1'}-\delta_{n_1n_1'}\Gamma_{n_1l}\rho^{(1)}_{l;l}\right)-\left(1-\delta_{n_1n_1'}\right)\Gamma_{n_1n_1'}\rho^{(1)}_{n_1,n_1}\right). \quad (23)$$

This equation is equivalent to the one obtained by Haken and Strobl for the one-exciton density matrix, differing from the latter only by the sign of the first sum in (23) because of different definitions of the matrix elements of $\rho^{(1)}$.

When the rate of local and (or) non-local scattering is large in comparison with the coherent transfer rate,

$$|M_{nm}|/\left(\sum_l \Gamma_l + \Gamma_{nm}\right) \ll 1,$$ (24)

in other words, if the scattering length of excitons is smaller than the lattice constant, then, for times longer than the transverse relaxation time $(\Sigma_l \Gamma_l)^{-1}$ (scattering time), the number of variables needed to describe exciton dynamics is cut down and eq. (23) simplifies. It is easy to show [28,30] that on the time scale mentioned above the non-diagonal matrix elements $\rho^{(1)}_{n;n'}$ are negligibly small as compared to $\rho^{(1)}_{n;n} \equiv \rho_n^{(1)}$ and the latter satisfy the master equation describing a stochastic markovian process of random walks of an isolated quasi-particle

$$d\rho_n^{(1)}/dt = \sum_{n'} W_{nn'}^{(1)}\left(\rho_{n'}^{(1)} - \rho_n^{(1)}\right),$$ (25)

where

$$W_{nn'}^{(1)} = 2\Gamma_{nn'} + M_{nn'}^2/(\Sigma_l \Gamma_l + \Gamma_{nn'})$$ (26)

is the probability of a jump of an excitation from the nth molecule to the n'th.

To reduce the chain of SLEs to one containing only diagonal matrix elements $\rho^{(s)}_{n_1 \cdots n_1 \cdots n_s} = \rho^{(s)}_{n_1 \cdots n_s}$, the fulfilment of inequality (24) is not sufficient as is shown below. The approximations needed to exclude the non-diagonal matrix elements $\rho^{(s)}_{\text{non-diag}}$ and at the same time to take into account the interaction between excitons are clarified when a two-particle system is considered.

4. Master (random-walk) equation for the two-particle density matrix of an isolated pair of incoherent excitons

The stochastic Liouville equation for the two-particle density matrix following from (15), (17), (19), (21), and (22) with $\rho^{(3)} = 0$ is exact for a system with two excitons. It has the form

$$
\frac{d\rho^{(2)}_{n_1 n_2,n_1' n_2'}}{dt} = i\left(\sum_l \left(M_{n_1 l}\rho^{(2)}_{l n_2;n_1' n_2'} + M_{n_2 l}\rho^{(2)}_{n_1 l,n_1' n_2'} - M_{n_1' l}\rho^{(2)}_{n_1 n_2 \cdot l n_2'} - M_{n_2' l}\rho^{(2)}_{n_1 n_2,n_1' l}\right)\right.
$$

$$
+ \left(V_{n_1 n_2} - V_{n_1' n_2'}\right)\rho^{(2)}_{n_1 n_2,n_1' n_2'}\right) - 4\left(\Gamma\left[1 - \tfrac{1}{2}\left(\delta_{n_1 n_1'} + \delta_{n_1 n_2'} + \delta_{n_2 n_1'} + \delta_{n_2 n_2'}\right)\right] + \sum_{l \neq 0}\Gamma_l\right)\rho^{(2)}_{n_1 n_2 \cdot n_1' n_2'}
$$

$$
+ 2\sum_l \left[\Gamma_{n_1 l}\left(1 - \delta_{n_1 l}\right)\left(\delta_{n_1 n_1'}\rho^{(2)}_{l n_2,l n_2'} + \delta_{n_1 n_2'}\rho^{(2)}_{l n_2,n_1' l}\right)\right.
$$

$$
+ \Gamma_{n_2 l}\left(1 - \delta_{n_2 l}\right)\left(\delta_{n_2 n_1'}\rho^{(2)}_{n_1 l \cdot l n_2'} + \delta_{n_2 n_2'}\rho^{(2)}_{n_1 l \cdot n_1' l}\right)\right] + 2\left[\Gamma_{n_1 n_1'}\left(1 - \delta_{n_1 n_1'}\right)\rho^{(2)}_{n_1' n_2;n_1 n_2'}\right.
$$

$$
+ \Gamma_{n_1 n_2'}\left(1 - \delta_{n_1 n_2'}\right)\rho^{(2)}_{n_2' n_2;n_1' n_1} + \Gamma_{n_2 n_1'}\left(1 - \delta_{n_2 n_1'}\right)\rho^{(2)}_{n_1 n_1';n_2 n_2'} + \Gamma_{n_2 n_2'}\left(1 - \delta_{n_2 n_2'}\right)\rho^{(2)}_{n_1 n_2';n_1' n_2}\right]
$$

$$
- 2\left[\chi_{n_1 n_2} + \chi_{n_1' n_2'} - 2\chi_{n_1 n_2}\left(\delta_{n_1 n_1'}\delta_{n_2 n_2'} + \delta_{n_1 n_2'}\delta_{n_2 n_1'}\right)\right]\rho^{(2)}_{n_1 n_2;n_1' n_2'}.
$$ (27)

For diagonal matrix elements $\rho^{(2)}_{n_1 n_2}$ it follows from (27)

$$\frac{d\rho^{(2)}_{n_1 n_2}}{dt} = i \sum_l \left[M_{n_1 l} \left(\rho^{(2)}_{l n_2 : n_1 n_2} - \rho^{(2)}_{n_1 n_2 : l n_2} \right) + M_{n_2 l} \left(\rho^{(2)}_{n_1 l , n_1 n_2} - \rho^{(2)}_{n_1 n_2 : n_1 l} \right) \right]$$

$$- 2 \sum_l \left[\Gamma_{n_1 l} \left(\rho^{(2)}_{n_1 n_2} - \rho^{(2)}_{l n_2} \right) + \Gamma_{n_2 l} \left(\rho^{(2)}_{n_1 n_2} - \rho^{(2)}_{n_1 l} \right) \right]. \tag{28}$$

Calculating $\rho^{(2)}_{\text{non-diag}}$ the left-hand side of (27) can be ignored when the evolution of the system is sufficiently close to the steady-state limit, i.e. it is supposed that the rate of change in $\rho^{(2)}_{\text{non-diag}}$ is small compared to the rate of transverse relaxation at times $t \gg (\Sigma_l \Gamma_l)^{-1}$. Assuming also that inequality (24) is satisfied we neglect products such as $M\rho^{(2)}_{\text{non-diag}}$ in comparison with $\Gamma\rho^{(2)}_{\text{non-diag}}$. Then, to find the non-diagonal matrix elements occurring in (28) we obtain the following set of equations

$$\left[2 \left(\sum_l \Gamma_l + \chi_{n_2 n_1} + \chi_{n_2 n_1'} \right) - i \left(V_{n_2 n_1} - V_{n_2 n_1'} \right) \right] \rho^{(2)}_{n_1 n_2 : n_1' n_2} - 2 \Gamma_{n_1 n_1'} \rho^{(2)}_{n_1' n_2 : n_1 n_2}$$

$$= i M_{n_1 n_1'} \left(\rho^{(2)}_{n_1' n_2} - \rho^{(2)}_{n_1 n_2} \right) - 2 \sum_{l \neq n_2} \Gamma_{n_2 l} \left(\rho^{(2)}_{n_1 n_2 : n_1' n_2} - \rho^{(2)}_{n_1 l , n_1' l} \right), \tag{29}$$

$$\left[2 \left(\sum_l \Gamma_l + \chi_{n_2 n_1} + \chi_{n_2 n_1'} \right) + i \left(V_{n_2 n_1} - V_{n_2 n_1'} \right) \right] \rho^{(2)}_{n_1' n_2 : n_1 n_2} - 2 \Gamma_{n_1 n_1'} \rho^{(2)}_{n_1 n_2 . n_1' n_2}$$

$$= - i M_{n_1 n_1'} \left(\rho^{(2)}_{n_1' n_2} - \rho^{(2)}_{n_1 n_2} \right) - 2 \sum_{l \neq n_2} \Gamma_{n_2 l} \left(\rho^{(2)}_{n_1' n_2 : n_1 n_2} \rho^{(2)}_{n_1' l , n_1 l} \right), \tag{30}$$

where $n_1 \neq n_1'$. Introducing for convenience the quantities $\rho^{(2)-}_{n_1 n_2 : n_1' n_2} = \rho^{(2)}_{n_1 n_2 , n_1' n_2} - \rho^{(2)}_{n_1' n_2 , n_1 n_2}$, eqs. (29) and (30) can be transformed as follows

$$\left\{ 4 \left[\left(\sum_l \Gamma_l + \chi_{n_2 n_1} + \chi_{n_2 n_1'} \right)^2 - \Gamma^2_{n_1 n_1'} \right] + \left(V_{n_2 n_1} - V_{n_2 n_1'} \right)^2 \right\} \rho^{(2)-}_{n_1 n_2 : n_1' n_2}$$

$$= 4 i \left\{ M_{n_1 n_1'} \left(\sum_l \Gamma_l + \chi_{n_2 n_1} + \chi_{n_2 n_1'} - \Gamma_{n_1 n_1'} \right) \left(\rho^{(2)}_{n_1' n_2} - \rho^{(2)}_{n_1 n_2} \right) \right.$$

$$\left. - \sum_{l \neq n_2} \left[\frac{1}{2} \left(V_{n_2 n_1} - V_{n_2 n_1'} \right) - i \left(\sum_{l'} \Gamma_{l'} + \chi_{n_2 n_1} + \chi_{n_2 n_1'} - \Gamma_{n_1 n_1'} \right) \right] \Gamma_{n_2 l} \left(\rho^{(2)-}_{n_1 n_2 : n_1' n_2} - \rho^{(2)-}_{n_1 l : n_1' l} \right) \right\}. \tag{31}$$

First we consider the procedure of the elimination of $\rho^{(2)}_{\text{non-diag}}$ from (28) using (31) when $V = \chi = 0$. Applying the spatial Fourier transformation to the coordinates n_2 in (31)

$$\rho^{(2)-}_{n_1 n_2 , n_1' n_2} = \sum_q \rho^{(2)-}_{n_1 n_1'}(q) \exp(i q n_2), \tag{32}$$

where the summation is performed over the first Brillouin zone, one gets

$$\rho^{(2)-}_{n_1 n_2 : n_1' n_2} = \frac{i M_{n_1 n_1'}}{N} \sum_l \sum_q \frac{\exp[i q (n_2 - l)] \left(\rho^{(2)}_{n_1 l} - \rho^{(2)}_{n_1' l} \right)}{2 [\Gamma + \Gamma(0)] + \Gamma_{n_1 n_1'} - \Gamma(q)}, \tag{33}$$

where $\Gamma(q) = \Sigma_{l \neq 0} \Gamma_l \exp(i q l)$, N is the total number of molecules in a crystal.

The permutation of indices $n_1 \rightleftarrows n_2$ in (33) gives the expression of another combination of the non-diagonal matrix elements contained in the equation for $\rho^{(2)}_{n_1 n_2}$. Inserting $\rho^{(2)}_{\text{non-diag}}$ in the form of (33) into (28) we get

$$\frac{d\rho^{(2)}_{n_1 n_2}}{dt} = \sum_{l,l'} \left[\left(M^2_{n_1 l} G_{n_2 l'} + 2\Gamma_{n_1 l}\delta_{n_2 l'} \right)\left(\rho^{(2)}_{ll'} - \rho^{(2)}_{n_1 l'} \right) + \left(M^2_{n_2 l} G_{n_1 l'} + 2\Gamma_{n_2 l}\delta_{n_1 l'} \right)\left(\rho^{(2)}_{ll'} - \rho^{(2)}_{n_2 l'} \right) \right], \tag{34}$$

where the notation

$$G_{nl} = \frac{1}{N} \sum_q \frac{\exp[iq(n-1)]}{2[\Gamma + \Gamma(0)] + \Gamma_{nl} - \Gamma(q)} \tag{35}$$

is employed.

Eq. (34) takes the form of a random-walk equation if for all values of the wave vector q the condition

$$2\Gamma + \Gamma(0) + \Gamma_{nl} \gg |\Gamma(0) - \Gamma(q)| \tag{36}$$

is obeyed. In this case it follows from (34)

$$\frac{d\rho^{(2)}_{n_1 n_2}}{dt} = \sum_l \left[W^{(1)}_{n_1 l}\left(\rho^{(2)}_{l n_2} - \rho^{(2)}_{n_1 n_2} \right) + W^{(1)}_{n_2 l}\left(\rho^{(2)}_{l n_1} - \rho^{(2)}_{n_1 n_2} \right) \right], \tag{37}$$

where the probability $W^{(1)}_{nm}$ of a jump of an incoherent exciton is defined by eq. (26).

Inequality (36) holds for all q when the local scattering rate Γ is much greater than the non-local one. Under this condition the non-diagonal matrix elements can easily be excluded from (28) taking into account the quasi-particle interaction. Thus, we obtain an equation for $\rho^{(2)}_{n_1 n_2}$ coinciding in form with (37) but the jump probabilities, accounting for the interaction between excitons, take the form

$$W^{(1)}_{n_1 l} \Rightarrow W^{(2)}_{n_1 l}(n_2) = 2\Gamma_{n_1 l} + \frac{4M^2_{n_1 l}\left(\sum_{l'}\Gamma_{l'} + \chi_{n_2 n_1} + \chi_{n_2 l} - \Gamma_{n_1 l} \right)}{4\left[\left(\sum_{l'}\Gamma_{l'} + \chi_{n_2 n_1} + \chi_{n_2 l} \right)^2 - \Gamma^2_{n_1 l} \right] + \left(V_{n_2 n_1} - V_{n_2 l} \right)^2},$$

$$W^{(1)}_{n_2 l} \Rightarrow W^{(2)}_{n_2 l}(n_1). \tag{38}$$

Thus, the SLE for the two-particle density matrix reduces to the random-walk equation at times larger than the exciton scattering time when the conditions (24) and (36) are fulfilled.

We further use the recipe just discussed in the derivation of random-walk equations in the case of a many-particle system.

5. Random-walk equations for a system of interacting incoherent excitons

Now we turn to finding the chain of equations for the diagonal matrix elements of the density matrix with an arbitrary number of excitons in a system. It is assumed, as in section 4, that the rate of resonance energy transfer is small in comparison with the scattering rate and that the dominant mechanism of scattering is local. Under these conditions we can neglect the coupling in the SLEs via products such as $M\rho^{(s+1)}_{\text{non-diag}}$ in the equation for s-particle density matrix. However, we should take into account the terms containing $V\rho^{(s+1)}_{\text{non-diag}}$ and $\chi\rho^{(s+1)}_{\text{non-diag}}$. Since for the system under consideration the basic "survival" quantities are $\rho^{(s)}_{\text{diag}}$, and $\rho^{(s)}_{\text{non-diag}}$ in comparison with them are small, we can use, in determining the latter, the approximate expressions for $\rho^{(s+1)}_{\text{non-diag}}$ appearing in the equations for $\rho^{(s)}_{\text{diag}}$. It is just $\rho^{(s+1)}_{\text{non-diag}}$ that are

determined using the equations in which $\rho_{\text{non-diag}}^{(s+2)}$ are equated to zero.

In order to illustrate the chain decoupling procedure in terms of non-diagonal matrix elements, we consider in detail the derivation of the equations for $\rho_{\text{diag}}^{(s)}$ at $s = 1, 2$. For $\rho_{\text{diag}}^{(1)}$ it follows from (15), (16), (18), (21) and (22)

$$\frac{d\rho_{n_1}^{(1)}}{dt} = i\sum_l M_{n_1 l}\left(\rho_{l n_1}^{(1)} - \rho_{n_1 l}^{(1)}\right) + 2\sum_l \Gamma_{n_1 l}\left(\rho_l^{(1)} - \rho_{n_1}^{(1)}\right). \tag{39}$$

Taking into account the abovementioned conditions the needed non-diagonal matrix elements of $\rho^{(1)}$ at the late stage of the system's evolution are determined by

$$2\left(\sum_l \Gamma_l + \Gamma_{n_1 n_1'}\right)\left(\rho_{n_1 n_1'}^{(1)} - \rho_{n_1' n_1}^{(1)}\right) = 2i M_{n_1 n_1'}\left(\rho_{n_1'}^{(1)} - \rho_{n_1}^{(1)}\right) + \sum_l \left[i\left(V_{l n_1} - V_{l n_1'}\right)\rho_{n_1 l; n_1' l}^{(2)+} - 2\left(\chi_{l n_1} + \chi_{l n_1'}\right)\rho_{n_1 l; n_1' l}^{(2)-}\right], \tag{40}$$

where $n_1 \neq n_1'$ and $\rho_{n_1 l; n_1' l}^{(s)\pm} = \rho_{n_1 l, n_1' l}^{(s)} \pm \rho_{n_1' l; n_1 l}^{(s)}$. In the same approximation the equations for the two-particle density matrix take the form

$$\frac{d\rho_{n_1 n_2}^{(2)}}{dt} = i\sum_l \left(M_{n_1 l}\rho_{l n_2; n_1 n_2}^{(2)-} + M_{n_2 l}\rho_{n_1 l, n_1 n_2}^{(2)-}\right) + 2\sum_l \left[\Gamma_{n_1 l}\left(\rho_{l n_2}^{(2)} - \rho_{n_1 n_2}^{(2)}\right) + \Gamma_{n_2 l}\left(\rho_{n_1 l}^{(2)} - \rho_{n_1 n_2}^{(2)}\right)\right], \tag{41}$$

$$\left[2\left(\sum_l \Gamma_l + \chi_{n_2 n_1} + \chi_{n_2 n_1'}\right) - i\left(V_{n_2 n_1} - V_{n_2 n_1'}\right)\right]\rho_{n_1 n_2; n_1' n_2}^{(2)} - 2\Gamma_{n_1 n_1'}\rho_{n_1' n_2, n_1 n_2}^{(2)}$$

$$= i M_{n_1 n_1'}\left(\rho_{n_1' n_2}^{(2)} - \rho_{n_1 n_2}^{(2)}\right) + \sum_l \left[i\left(V_{n_1 l} - V_{n_1' l}\right) - 2\left(\chi_{n_1 l} + \chi_{n_1' l}\right)\right]\rho_{n_1 n_2 l; n_1' n_2 l}^{(3)}, \tag{42}$$

where $n_1 \neq n_1'$.

To eliminate $\rho_{\text{non-diag}}^{(2)}$ from (40) we find them from (42) omitting the terms with $\rho_{\text{non-diag}}^{(3)}$. In this approximation we have

$$\rho_{n_1 n_2; n_1' n_2}^{(2)+} = -\frac{2M_{n_1 n_1'}\left(V_{n_2 n_1} - V_{n_2 n_1'}\right)\left(\rho_{n_1' n_2}^{(2)} - \rho_{n_1 n_2}^{(2)}\right)}{4\left[\left(\sum_l \Gamma_l + \chi_{n_2 n_1} + \chi_{n_2 n_1'}\right)^2 - \Gamma_{n_1 n_1'}^2\right] + \left(V_{n_2 n_1} - V_{n_2 n_1'}\right)^2}, \tag{43}$$

and

$$\rho_{n_1 n_2\ n_1' n_2}^{(2)-} = \frac{4i\left(\sum_l \Gamma_l + \chi_{n_2 n_1} + \chi_{n_2 n_1'} - \Gamma_{n_1 n_1'}\right) M_{n_1 n_1'}\left(\rho_{n_1' n_2}^{(2)} - \rho_{n_1 n_2}^{(2)}\right)}{4\left[\left(\sum_l \Gamma_l + \chi_{n_2 n_1} + \chi_{n_2 n_1'}\right)^2 - \Gamma_{n_1 n_1'}^2\right] + \left(V_{n_2 n_1} - V_{n_2 n_1'}\right)^2}. \tag{44}$$

Using these expressions in (40) and the result obtained in (39) we arrive at the following equation

$$\frac{d\rho_{n_1}^{(1)}}{dt} = \sum_l W_{n_1 l}^{(1)}\left(\rho_l^{(1)} - \rho_{n_1}^{(1)}\right) + \sum_{l, l'} \left[W_{n_1 l}^{(2)}(l') - W_{n_1 l}^{(1)}\right]\left(\rho_{l l'}^{(2)} - \rho_{n_1 l'}^{(2)}\right), \tag{45}$$

where the jump probabilities $W_{n_1 l}^{(1)}$ and $W_{n_1 l}^{(2)}(l')$ are defined by (26) and (38), respectively.

Similarly when $\rho_{\text{non-diag}}^{(3)}$ are eliminated from (42) we use the solution of equations for $\rho_{\text{non-diag}}^{(3)}$ in terms of

$\rho_{\text{diag}}^{(3)}$ neglecting the terms which are proportional to $\rho_{\text{non-diag}}^{(4)}$. The corresponding expressions are

$$\rho_{n_1 n_2 n_3. n_1' n_2 n_3}^{(3)+} = -\frac{2M_{n_1 n_1'}\Sigma_{j=2,3}\left(V_{n_j n_1} - V_{n_j n_1'}\right)\left(\rho_{n_1' n_2 n_3}^{(3)} - \rho_{n_1 n_2 n_3}^{(3)}\right)}{4\left\{\left[\Sigma_l \Gamma_l + \Sigma_{j=2,3}\left(X_{n_j n_1} + X_{n_j n_1'}\right)\right]^2 - \Gamma_{n_1 n_1'}^2\right\} + \left[\Sigma_{j=2,3}\left(V_{n_j n_1} - V_{n_j n_1'}\right)\right]^2}, \qquad (46)$$

and

$$\rho_{n_1 n_2 n_3. n_1' n_2 n_3}^{(3)-} = \frac{4i\left[\Sigma_l \Gamma_l + \Sigma_{j=2,3}\left(X_{n_j n_1} + X_{n_j n_1'}\right) - \Gamma_{n_1 n_1'}\right] M_{n_1 n_1'}\left(\rho_{n_1' n_2 n_3}^{(3)} - \rho_{n_1 n_2 n_3}^{(3)}\right)}{4\left\{\left[\Sigma_l \Gamma_l + \Sigma_{j=2,3}\left(X_{n_j n_1} + X_{n_j n_1'}\right)\right]^2 - \Gamma_{n_1 n_1'}^2\right\} + \left[\Sigma_{j=2,3}\left(V_{n_j n_1} - V_{n_j n_1'}\right)\right]^2}. \qquad (47)$$

Eliminating the terms with $\rho_{\text{non-diag}}^{(3)}$ from (42) by means of (46) and (47) and inserting the result into (41) we obtain

$$\frac{d\rho_{n_1 n_2}^{(2)}}{dt} = \sum_l \left[W_{n_1 l}^{(2)}(n_2)\left(\rho_{l n_2}^{(2)} - \rho_{n_1 n_2}^{(2)}\right) + W_{n_2 l}^{(2)}(n_1)\left(\rho_{l n_1}^{(2)} - \rho_{n_1 n_2}^{(2)}\right)\right]$$

$$+ \sum_{l,l'}\left\{\left[W_{n_1 l}^{(3)}(n_2 l') - W_{n_1 l}^{(2)}(n_2)\right]\left(\rho_{l n_2 l'}^{(3)} - \rho_{n_1 n_2 l'}^{(3)}\right)\right.$$

$$\left. + \left[W_{n_2 l}^{(3)}(n_1 l') - W_{n_2 l}^{(2)}(n_1)\right]\left(\rho_{l n_1 l'}^{(3)} - \rho_{n_1 n_2 l'}^{(3)}\right)\right\}, \qquad (48)$$

where the jump probability $W_{n_1 n_1'}^{(3)}(n_2 n_3)$ of an incoherent exciton between molecules n_1 and n_1' in the presence of two other ones on the lattice sites n_2 and n_3 is equal to

$$W_{n_1 n_1'}^{(3)}(n_2 n_3) = 2\Gamma_{n_1 n_1'} + \frac{4\left[\Sigma_l \Gamma_l + \Sigma_{j=2,3}\left(X_{n_j n_1} + X_{n_j n_1'}\right) - \Gamma_{n_1 n_1'}\right] M_{n_1 n_1'}^2}{4\left\{\left[\Sigma_l \Gamma_l + \Sigma_{j=2,3}\left(X_{n_j n_1} + X_{n_j n_1'}\right)\right]^2 - \Gamma_{n_1 n_1'}^2\right\} + \left[\Sigma_{j=2,3}\left(V_{n_j n_1} - V_{n_j n_1'}\right)\right]^2}. \qquad (49)$$

The use of the above procedure in the equations for the s-particle density matrix yields

$$\frac{d\rho_{n_1 \ldots r_s}^{(s)}}{dt} = \sum_{j=1}^{s}\left(\sum_l W_{n_j l}^{(s)}\left(\{n_s\}_{n_j}'\right)\left(\rho_{n_1 \ldots n_j=l \ldots n_s}^{(s)} - \rho_{n_1 \ldots n_s}^{(s)}\right)\right.$$

$$\left. + \sum_{l,l'}\left[W_{n_j l}^{(s+1)}\left(\{n_s\}_{n_j=l'}'\right) - W_{n_j l}^{(s)}\left(\{n_s\}_{n_j}'\right)\right]\left(\rho_{n_1 \ldots n_j=l \ldots n_j l'}^{(s+1)} - \rho_{n_1 \ldots n_s l'}^{(s+1)}\right)\right), \qquad (50)$$

where $\{n_s\}_{n_j=l}$ denotes the coordinates of s incoherent excitons $n_1, n_2, \ldots, n_s$ with n_j replaced by l, $\{n_s\}_{n_j}'$ denotes the position of $s - 1$ excitons in a group of s excitons with the coordinates $n_1, n_2, \ldots, n_s$ without the one on the lattice site n_j. and

$$W_{n_j n_j'}^{(s)}\left(\{n_s\}_{n_j}'\right) = 2\Gamma_{n_j n_j'} + \frac{4\left[\Sigma_l \Gamma_l + \Sigma_{k=1(k\neq j)}^s\left(X_{n_j n_k} + X_{n_j' n_k}\right) - \Gamma_{n_j n_j'}\right] M_{n_j n_j'}^2}{4\left\{\left[\Sigma_l \Gamma_l + \Sigma_{k=1(k\neq j)}^s\left(X_{n_j n_k} + X_{n_j' n_k}\right)\right]^2 - \Gamma_{n_j n_j'}^2\right\} + \left[\Sigma_{k=1(k\neq j)}^s\left(V_{n_j n_k} - V_{n_j' n_k}\right)\right]^2}$$

$$(51)$$

is the exciton jump probability between molecules n_j and n_j' when there are $s - 1$ other excitons on molecules with coordinates $\{n_s\}_{n_j}' \neq n_j'$. It is implied in (50) that $\rho_{n_1 \ldots n_s}^{(s)} = 0$ if among the indices there are at least two coincident ones and that $l \neq \{n_s\}$.

The equations obtained determine the density matrix of the system under consideration at long times and have a transparent probability interpretation. Their derivation exemplifies a practical realization of Bogoljubov's idea [31] that the number of parameters needed to describe a system is reduced at the late stage of the system's evolution.

The structure of the chain (50) is analogous to the Bogoljubov chain of equations [32]. The coupling of the equation for the density matrix of the group of s excitons with that of the group of $s + 1$ excitons is due to the non-equivalence of the exciton jump over the same distance and in the same direction in groups of s and $s + 1$ quasi-particles, respectively. It is the direct consequence of the interparticle interaction. In contrast to classical systems, the exciton–exciton dynamic interaction does not enter the coupling terms of the chain linearly. It enters the jump probabilities as an interaction energy change in a group of s incoherent excitons when one of them changes its position jumping from one molecule to the other.

The probability expression (51) has the Lorentz form corresponding to the model of the exciton–phonon interaction and to the accepted relations between the microscopic parameters of the system. Note that (51) is analogous in form to the transition probability in a two-level system provided that the half-width of the levels is larger than the interaction stipulating the transition between them. The change in the interaction energy at a jump (see (51)) corresponds to the energy difference between the levels, and the local and non-local scattering rates are an analogue to the half-width of the levels.

Surely, the expression obtained for the jump probability is not general. Still the model discussed can be consistent with some real situations. For example, the random-walk equations (50), supplemented by adding certain terms accounting for the non-conserving part of the exciton interaction and the monomolecular excitation decay [12], are appropriate for the description of incoherent exciton annihilation with allowance for the dynamic interaction.

The range of applicability of (50) can be considerably extended by taking into account the non-equivalence of exciton jumps from one molecule to another and backward in the presence of one or several excitons at the other lattice sites. Owing to this the chain of equations describing random walks in a system of interacting quasi-particles reads

$$\frac{d\rho_{n_1}^{(1)}}{dt} = \sum_l \left[W_{n_1 \leftarrow l}^{(1)} \rho_l^{(1)} - W_{n_1 \rightarrow l}^{(1)} \rho_{n_1}^{(1)} \right] + \sum_{l,l'} \left\{ \left[W_{n_1 \leftarrow l}^{(2)}(l') - W_{n_1 \leftarrow l}^{(1)} \right] \rho_{l,l'}^{(2)} - \left[W_{n_1 \rightarrow l}^{(2)}(l') - W_{n_1 \rightarrow l}^{(1)} \right] \rho_{n_1 l'}^{(2)} \right\}, \quad (52)$$

for the one-particle density matrix, and for the s-particle one

$$\frac{d\rho_{n_1 \cdots n_s}^{(s)}}{dt} = \sum_{j=1}^{s} \left(\sum_l \left[W_{n_j \leftarrow l}^{(s)}\left(\{n_s\}_{n_j}'\right) \rho_{n_1 \cdots n_j = l \cdots n_s}^{(s)} - W_{n_j \rightarrow l}^{(s)}\left(\{n_s\}_{n_j}'\right) \rho_{n_1 \cdots n_s}^{(s)} \right] + \sum_{l,l'} \left[W_{n_j \leftarrow l}^{(s+1)}\left(\{n_s\}_{n_j = l'}\right) \right. \right.$$

$$\left. - W_{n_j \leftarrow l}^{(s)}\left(\{n_s\}_{n_j}'\right) \right] \rho_{n_1 \cdots n_j = l \cdots n_s, l'}^{(s+1)} - \sum_{l,l'} \left[W_{n_j \rightarrow l}^{(s+1)}\left(\{n_s\}_{n_j = l'}\right) - W_{n_j \rightarrow l}^{(s)}\left(\{n_s\}_{n_j}'\right) \right] \rho_{n_1 \cdots n_s, l'}^{(s+1)} \right), \quad (53)$$

where the probabilities $W_{n_j \rightleftarrows n_j'}^{(s)}(\{n_s\}_n')$ should be considered as phenomenological quantities. They have the same meaning as the ones defined by (51) but, in contrast to the latter, are supposed to be dependent on the direction of the exciton jump $W_{n_j \rightarrow n_j'}^{(s)}(\{n_s\}_{n_j}') \neq W_{n_j \leftarrow n_j'}^{(s)}(\{n_s\}_{n_j}')$.

Applications of random-walk equations in the form of (53) cover a wide range of problems mentioned in section 1, provided particles taking part in a process execute random walks. The dependence of jump probabilities on microscopic parameters of a system can be calculated for actual models of interaction of particles with a heat bath. An example of such a dependence, differing from that defined by (51), is given in section 6.

6. Bogoljubov's hierarchy chain for a system of interacting diffusing particles as a specific case of random-walk equations

The one-particle random-walk equation (25) is known to be transformed into a diffusion equation [1] when the change in $\rho_n^{(1)}$ at a distance of the order of the lattice constant is small. In this sense eq. (53) is connected with a chain of coupled diffusion equations for s-particle distribution functions. Such a chain can be derived by the method of Bogoljubov [32] under the assumption that the particle motion is subjected to the Smoluchovski–Debye equation

$$\frac{\mathrm{d}g^{(1)}(r, t)}{\mathrm{d}t} = \sum_{\nu, \mu} \nabla_\nu D_{\nu, \mu} \left[\nabla_\mu g^{(1)}(r, t) + \theta^{-1} g^{(1)}(r, t) \nabla_\mu U(r) \right], \quad \nu, \mu = x, y, z. \tag{54}$$

where $D_{\nu, \mu}$ are the components of the diffusion tensor, θ is the absolute temperature ($k_B = 1$), $U(r)$ is the potential energy of a particle at the point with coordinates r, $g^{(1)}(r, t)$ is the one-particle distribution function.

Here we show that the random-walk equations (53) can be reduced to a chain of coupled diffusion equations of the abovementioned type for a certain dependence of the jump probabilities on the interaction between excitons. For this purpose we use the expressions for $W_{n_j \rightleftharpoons n_j'}^{(s)}(\{n_s\}_{n_j}')$ which are obtained in the case of a strong exciton–phonon interaction [33]. These can be represented in the form [34]

$$W_{n_j \rightleftharpoons n_j'}^{(s)}\left(\{n_s\}_{n_j}'\right) = \left(\frac{\pi}{\theta\epsilon}\right)^{1/2} M_{n_j n_j'}^2 \exp\left(-\frac{\left[\epsilon \mp \sum_{k=1, k \neq j}^s \left(V_{n_k n_j} - V_{n_k n_j'}\right)\right]^2}{4\theta\epsilon}\right), \tag{55}$$

where ϵ is the jump activation energy of an isolated incoherent exciton.

Inserting (55) into (53) we expand the quantities depending on l in a series in $(l - n_j)$ restricting ourselves to powers not exceeding 2. In this approximation we can change the summation over l', a discrete index, by an integral in the continuous coordinates r': $\sum_{l'} \rightarrow \int \mathrm{d}^3 r'/v^3$. As a result, eq. (52) is transformed as follows

$$\frac{\mathrm{d}g^{(1)}(r, t)}{\mathrm{d}t} = \sum_{\nu, \mu} \nabla_\nu D_{\nu, \mu} \left(\nabla_\mu g^{(1)}(r, t) + \frac{c}{v^3\theta} \int g^{(2)}(r, r', t) \nabla_\mu V_{r, r'} \mathrm{d}^3 r' \right). \tag{56}$$

where

$$D_{\nu, \mu} = \tfrac{1}{2}(\pi/\theta\epsilon)^{1/2} \exp(-\epsilon/4\theta) \sum_l M_{n_j l}^2 (n_j - l)_\nu (n_j - l)_\mu, \tag{57}$$

$v^3 = a_x a_y a_z$, a_r are the lattice constants, $g^{(s)}(r_1 \ldots r_s, t) = c^{-s} \rho_{n_1 \ldots n_s}^{(s)}$, $c = S/N$.

Similarly, it can be shown that for any s eqs. (53) and (55) for small gradients reduce to diffusion equations of the form

$$\frac{\mathrm{d}g^{(s)}}{\mathrm{d}t}(r_1 \ldots r_s, t) = \sum_{\nu, \mu} \left[\sum_{j=1}^s (\nabla_j)_\nu D_{\nu, \mu} \left((\nabla_j)_\mu g^{(s)}(r_1 \ldots r_s, t) + \theta^{-1} g^{(s)}(r_1 \ldots r_s, t)(\nabla_j)_\mu \sum_{\substack{k=1 \\ k \neq j}}^s V_{r_j r_k} \right. \right.$$

$$\left. \left. + \frac{c}{v^3\theta} \int \left[g^{(s+1)}(r_1 \ldots r_s, r', t)(\nabla_j)_\mu V_{r_j r'} \mathrm{d}^3 r' \right] \right) \right], \tag{58}$$

which coincide with those obtained in ref. [32] by the method of Bogoljubov.

Note that in the general case the passage from (53) to (58), with $D_{\nu,\mu}$ independent of the interaction energy between quasi-particles, does not apply. Moreover, the assumption of small changes in the density matrix and the interaction energy on the length a_ν is not always justified, in particular, when particles nearly come into contact. Therefore, it seems more plausible to use (53) instead of (58) as has been done so far [11,15,17,24] (and references therein), for example in the case of short-range dynamic interactions. Such applications of the random-walk equations obtained here will be published elsewhere.

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