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### A Kinetic Theory of Incoherent Exciton Annihilation

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# A Kinetic Theory of Incoherent Exciton Annihilation†

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The properties of an exciton system with the high concentration are investigated on the basis of microscopical equations for the density matrix of the type of BBGKY hierarchy. A new recipe for decoupling a chain of equations is proposed, which takes into account the effect of three-particle collisions on the definition of a two-particle distribution function of an exciton subsystem. Using this decoupling procedure and making no assumption about the smallness of the quadratic concentration effects the set of equations for density matrix reduced to the known phenomenological equation describing exciton annihilation under steady-state excitation.

The kinetic equations applicable to an essentially larger concentration region are also derived taking into account high concentration effects. There use for the case of excitons with a great diffusion length permits us to predict a new effect of additional luminescence quenching at high excitation levels. This effect turns to be very appreciable in two-, and particularly, in one-dimensional systems and may manifest itself in the kinetics of nonlinear luminescence quenching. A qualitatively new-behaviour of the quantum yield dependence on excitation intensity is predicted, which gives reasonable explanation of recent experimental results.

The limits on concentration and intensity values where the present theory is good are pointed out.

The results of the paper may be applied to other quantum many-particle systems where the coordinates of a quasi-particle are good quantum numbers, and also to chemical reaction theory, to coagulation and the related problems.

## I INTRODUCTION

Experimental and theoretical research concerning the exciton annihilation and the related problems is central in the field of organic compound physics. It is enhanced by numerous possibilities to get original information about the characteristics of exciton motion and interaction. Thus, it is possible to predict many properties of molecular crystals in the excited state which are primarily concerned with the excitons.

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† This work was firstly reported at the school on the spectroscopy of molecules and crystals held in Chernovtsy (USSR) May, 1979. The results close to this paper were obtained in a slightly

The annihilation (or fusion) is a nonradiative disappearance of a pair of excitons caused by their interaction. The well-known equation implying that this reaction proceeds pair-wise

$$\frac{\partial c}{\partial t} = -\beta c - \gamma c^2 + I \quad (1)$$

is usually used in the phenomenological description of phenomena explained in terms of the annihilation. In Eq. (1)  $c$  is the relative exciton concentration,  $I$  is the external excitation intensity relative to the total molecular number in a system,  $\beta$  is the inverse life time of an exciton noninteracting with the others,  $\gamma$  is the constant determining the rate of exciton decay due to annihilation.<sup>†</sup>

In the case of coherent excitons  $\gamma$  is calculated as the transition probability from a two-exciton state to another excited state without initial excitons.<sup>1-4</sup> For an incoherent and intermediate type of excitons the definition of  $\gamma$  is based on the solution of a diffusion equation<sup>6,7</sup> or more specifically, an equation describing the random walk motion of quasi-particles.<sup>8-10</sup>

In the papers mentioned it was supposed that each of the pairs is annihilated independently. As a result the many-particle aspect of the problem was omitted. Moreover, in the framework of the above approach it is impossible to determine concentration limits where Eq. (1) gives a satisfactory annihilation description. At the same time it appears to be really an important problem, because the fast motion and strong interaction of excitons may result in a dominant annihilation effect already at relatively small concentrations. The possibility of this situation in many molecular crystals immediately follows from the great values of  $\gamma$  measured in experiment. In this case the usual condition of low concentration,  $c \ll 1$ , is not enough and the question arises as to the importance of multiple collisions, i.e. whether it is necessary to include into (1) additional terms proportional to higher powers of  $c$  or not.

The many-particle approach to describe exciton annihilation was first discussed by Suna.<sup>8</sup> In particular, he has shown that the exact set of exciton density matrix equations in steady-state conditions reduces to Eq. (1) if the annihilation term is small compared to the monomolecular decay term

$$\gamma c \ll \beta \quad (2)$$

Here to calculate  $\gamma$ , the equation for a binary distribution function may be used and the interaction of an exciton pair with other excitons may be neglected.

<sup>†</sup> The present definition of  $\gamma$  differs from the experimentally measured annihilation rate constant  $\gamma_{\text{exp}}$  by the dimensional factor:  $\gamma_{\text{exp}} = v\gamma$ , where  $v$  is the average volume per molecule.

So far Suna's theory is the only microscopically substantiated approach to the problem under consideration,<sup>11</sup> but its application is essentially restricted by (2). This condition assumes the nonlinear concentration effects to be small perturbations. The inequality (2) may, in fact, be satisfied, for example, when the delay fluorescence<sup>12</sup> or the magnetic field effect on prompt and delay fluorescence is studied.<sup>13-15</sup> But in experiments on nonlinear fluorescence quenching<sup>16-18</sup> where the main effect is caused by the annihilation process Suna's condition is violated and the validity of (1) (still widely used) is very much doubtful.

An attempt to clarify the problem is made in the present paper. An exciton annihilation theory applicable to high concentrations is developed. It may be constructed only on the basis of many-particle approach. Keeping this in mind the model Hamiltonian and the set of interacting exciton density matrix equations that follows from it are accepted as a starting point of our consideration (Section II). In Section III a new recipe for the equation chain decoupling procedure is proposed, leading to (1), but the condition (2) was not used, as distinct from Ref. 8. The aim of Section IV is to extend the theory to the case of high exciton concentrations. This is done for excitons with large diffusion length. We obtained an equation analogous to (1), but with the annihilation rate constant replaced by a certain function  $\tilde{\gamma}(I)$ . This implies an inclusion into (1) of high concentration effects. In Section V we apply our approach to the theory of nonlinear luminescence quenching under a stationary high-intensity excitation in one-, two- and three-dimensional molecular systems. The model numerical calculations of Section VI illustrate the qualitative results of the previous sections. At last Section VII summarises the main conclusions of our investigation stressing the possibilities of its application.

For the sake of simplicity our discussion is for crystals with simple cubic lattice. The theory may be straightforwardly extended on any crystal structure.

## II MICROSCOPIC DESCRIPTION OF AN EXCITON SUBSYSTEM

Let us write the molecular crystal Hamiltonian in the form

$$H = H_{ex} + H_T + V_c + V_{nc}, \quad (3)$$

where the first term represents the Hamiltonian of an exciton excitation branch

$$H_{ex} = \sum_{\mathbf{n}, \mathbf{m}} (\varepsilon \delta_{\mathbf{nm}} + M_{\mathbf{nm}}) B_{\mathbf{n}}^+ B_{\mathbf{m}}. \quad (4)$$

$\varepsilon$  is the molecular excitation energy,  $M_{nm}$  are the matrix elements of the energy of the resonance excitation transfer between molecules with coordinates  $\mathbf{n}$  and  $\mathbf{m}$ ,  $B_n^+, B_n$  are Pauli operators which create and destroy an excitation on the  $n$ th molecule.

The second term corresponds to the thermostat Hamiltonian operator describing all other crystal excitation branches (electron excitation, phonon excitation, etc.) which are not included into (4).

The interaction operator conserving the exciton number is

$$V_c = \sum_{\mathbf{n}, \sigma, \mathbf{q}} \chi_{\sigma, \mathbf{q}} \exp(i\mathbf{q}\mathbf{n}) B_n^+ B_n (b_{\sigma, \mathbf{q}}^+ + b_{\sigma, -\mathbf{q}}), \quad (5)$$

where  $b_{\sigma, \mathbf{q}}^+, b_{\sigma, \mathbf{q}}$  are the Bose creation and annihilation operators of phonons of  $\sigma$ -branch with a wave vector  $\mathbf{q}$ ,  $\chi_{\sigma, \mathbf{q}}$  is the exciton-phonon coupling constant determining the motion character of excitons which would be established as a result of their interaction with the thermostat.

The operator not conserving the total number of excitons

$$V_{nc} = \sum_{\mathbf{n}} A_n^+ B_n^+ + \sum_{\mathbf{n}, \mathbf{m}} K_{nm}^+ B_n B_m + h.c., \quad (6)$$

describes transitions between the states of subsystems with the Hamiltonian  $H_{ex}$  and  $H_T$ . The exciton-external field interaction is also defined by (4) in the linear approximation (it is supposed that the Hamiltonian of a noninteracting electromagnetic field is included in  $H_T$ ). The  $A_n^+, K_{nm}^+$  operators commute with  $B_n^+, B_n$  and do not commute with the operators of  $H_T$ .

The exciton subsystem evolution in a time-scale exceeding thermostat correlation time  $\tau_T$  ( $\tau_T$  is of order  $10^{-14}$  s for molecular crystals) is described by

$$\begin{aligned} \rho_1(\mathbf{n}_1, \mathbf{n}_2, t) &\equiv Sp\{\rho(t) B_{n_1}^+ B_{n_2}\}, \\ \rho_2(\mathbf{n}_1, \mathbf{n}_2, \mathbf{n}_3, \mathbf{n}_4, t) &\equiv Sp\{\rho(t) B_{n_1}^+ B_{n_2}^+ B_{n_3} B_{n_4}\}, \dots, \end{aligned} \quad (7)$$

where  $\rho(t)$  is the nonequilibrium density matrix of the system with the Hamiltonian (3).

In the second order of the perturbation theory in the interaction operators (5), (6) one can find equations defining the density matrix of an exciton subsystem using the methods of nonequilibrium statistical operator theory.<sup>19</sup> For the diagonal matrix elements we have

$$\begin{aligned} \frac{\partial \rho_1(\mathbf{n}_1, t)}{\partial t} &= I_{x_1} - (\beta + 2I_{x_1})\rho_1(\mathbf{n}_1, t) \\ &- \sum_{\mathbf{n}} W_{nn_1} [\rho_1(\mathbf{n}_1, t) - \rho_1(\mathbf{n}, t)] - \sum_{\mathbf{n}} \omega_{nn_1} \rho_2(\mathbf{n}, \mathbf{n}_1, t), \end{aligned} \quad (8)$$

$$\begin{aligned}
\frac{\partial \rho_2(\mathbf{n}_1, \mathbf{n}_2, t)}{\partial t} = & I_{\mathbf{n}_1} \rho_1(\mathbf{n}_2, t) + I_{\mathbf{n}_2} \rho_1(\mathbf{n}_1, t) - 2(\beta + I_{\mathbf{n}_1} + I_{\mathbf{n}_2}) \rho_2(\mathbf{n}_1, \mathbf{n}_2, t) \\
& - \sum_{\mathbf{n}} \left\{ W_{\mathbf{n}\mathbf{n}_1} [\rho_2(\mathbf{n}_1, \mathbf{n}_2, t) - \rho_2(\mathbf{n}, \mathbf{n}_2, t)] (1 - \delta_{\mathbf{n}\mathbf{n}_2}) \right. \\
& + W_{\mathbf{n}\mathbf{n}_2} [\rho_2(\mathbf{n}_1, \mathbf{n}_2, t) - \rho_2(\mathbf{n}, \mathbf{n}_1, t)] (1 - \delta_{\mathbf{n}\mathbf{n}_1}) \left. \right\} - \omega_{\mathbf{n}_1\mathbf{n}_2} \rho_2(\mathbf{n}_1, \mathbf{n}_2, t) \\
& - \sum_{\mathbf{n}} (\omega_{\mathbf{n}\mathbf{n}_1} + \omega_{\mathbf{n}\mathbf{n}_2}) \rho_3(\mathbf{n}, \mathbf{n}_1, \mathbf{n}_2), \dots, \quad (9)
\end{aligned}$$

where

$$\rho_1(\mathbf{n}_1, t) \equiv \rho_1(\mathbf{n}_1, \mathbf{n}_1, t), \rho_2(\mathbf{n}_1, \mathbf{n}_2, t) \equiv \rho_2(\mathbf{n}_1, \mathbf{n}_2, \mathbf{n}_1, \mathbf{n}_2, t),$$

In deriving these equations† we suppose that the transverse relaxation time  $\tau$  is much shorter than the other characteristic times of an exciton subsystem. In the model under consideration  $\tau^{-1} \sim \tau_T^{-1} \times \sum_{\sigma, q} (|\chi_{\sigma, q}|^2 / \hbar^2 \omega_{\sigma, q}^2)$ , where  $\omega_{\sigma, q}$  is the phonon frequency. This time defines the decay of non-diagonal parts of the exciton density matrix. Consequently, our consideration is restricted to the case of a completely incoherent exciton motion which is relevant for narrow exciton bands and a strong exciton-phonon interaction.

In Eqs. (8), (9)  $I_{\mathbf{n}}$  is the per second probability of an excitation of  $n$ th molecule (this quantity corresponds to  $I$  in (1)).  $W_{\mathbf{n}\mathbf{n}_2}$  is the exciton hopping rate at the distance  $|\mathbf{n}_1 - \mathbf{n}_2|$ ,  $\omega_{\mathbf{n}\mathbf{n}_2}$  is the bimolecular annihilation probability of excitons occupying molecules  $\mathbf{n}_1$  and  $\mathbf{n}_2$ .

The generation of excitons by the two-particle mechanism is supposed to be negligible. The terms connected with the dynamical exciton-exciton interaction are also omitted. The effects caused by this interaction were discussed previously.<sup>10</sup>

The chain of Eqs. (8), (9), ..., is a quantum mechanical analog to the BBGKY hierarchy for standard many-particle systems.  $\rho_1(\mathbf{n}, t)$  gives the probability of finding an exciton on the  $n$ th molecule at time  $t$ ,  $\rho_2(\mathbf{n}_1, \mathbf{n}_2, t)$  defines the same probability for a pair of excitons, etc. These equations as in the case of classical systems have very clear physical meaning and can be easily derived by the probability arguments, the only exception being terms  $2I_{\mathbf{n}}\rho_1(\mathbf{n}, t)$ ,  $2(I_{\mathbf{n}_1} + I_{\mathbf{n}_2})\rho_2(\mathbf{n}_1, \mathbf{n}_2, t)$  and the terms proportional to the  $\delta$ -symbol. They result from the fact that the initial exciton operators are Pauli. The inclusion of these terms is important sometimes. For example, in the case of noninteracting excitons in steady-state conditions we have  $\rho_1(\mathbf{n}) = 0.5$  when  $I_{\mathbf{n}}$  goes to infinity. This result means that only half molecules may be excited. Thus, it is necessary to take into consideration the above terms in the case of a very intense pumping or long-lived excitations.

† A detailed derivation of equations analogous to (8), (9) is given in Ref.<sup>8</sup>.

### III DECOUPLING PROCEDURE WITHOUT SUNA'S RESTRICTION. THE STATIONARY AND UNIFORM SOLUTION

The set of equations (8), (9), ..., is valid for any exciton concentration in the general case of a nonstationary and nonuniform excitation. But the problem of finding exact solutions to this set of equations, however, is unrealizable. Therefore, we wish to find a simpler approach to describe an interacting exciton system similar to (1) and formulate criteria for the validity of our approximation.

To simplify comparison with the previous theory,<sup>8</sup> let us consider the case of uniform and stationary pumping:  $I_n = I$ ,  $\rho_1(\mathbf{n}, t) = c$ ,  $\rho_2(\mathbf{n}_1, \mathbf{n}_2, t) = \rho_2(\mathbf{n}_1 - \mathbf{n}_2) \equiv \rho_r$ . The terms  $2Ic$  in (8) and  $4I\rho_r$  in (9) were not taken into account in<sup>8</sup> and we put them equal to zero (the role of these terms will be discussed later on). Neglecting terms with  $\rho_3$  we get a set of equations completely coinciding with that used by Suna

$$\beta c + \sum_{\mathbf{r}} \omega_{\mathbf{r}} \rho_{\mathbf{r}} = I, \quad (10)$$

$$2\beta \rho_{\mathbf{r}} + 2 \sum_{\mathbf{r}'} W_{\mathbf{r}\mathbf{r}'} (\rho_{\mathbf{r}} - \rho_{\mathbf{r}'}) + (\omega_{\mathbf{r}} - 2W_{\mathbf{r}}) \rho_{\mathbf{r}} = 2Ic. \quad (11)$$

This decoupling procedure is correct only in the case when steady-state conditions are achieved mainly due to the monomolecular decay of excitons and when the exciton collision effects are small

$$\sum_{\mathbf{r}} \omega_{\mathbf{r}} \rho_{\mathbf{r}} \ll \beta c. \quad (12)$$

Then, following,<sup>8</sup> in zeroth approximation we have

$$c = I\beta^{-1}, \quad (13)$$

and the equation for the two-particle density matrix reduces to

$$\beta \rho_{\mathbf{r}} + \sum_{\mathbf{r}'} W_{\mathbf{r}\mathbf{r}'} (\rho_{\mathbf{r}} - \rho_{\mathbf{r}'}) + (\frac{1}{2}\omega_{\mathbf{r}} - W_{\mathbf{r}}) \rho_{\mathbf{r}} = \beta c^2. \quad (14)$$

In the nearest-neighbour approximation justified in the case of incoherent excitons one can write its solution in the form

$$\rho_{\mathbf{r}} = c^2 \left\{ 1 - \frac{G_{\mathbf{r},0}}{G_{0,0}} + \frac{2W - \omega}{2W} g_a \left( \frac{G_{\mathbf{r},0}}{G_{0,0}} - \delta_{\mathbf{r}0} \right) \right\}, \quad (15)$$

$$g_a \equiv c^{-2} \rho_{|\mathbf{r}|=a} = \left[ d\omega (G_{0,0}^{-1} - \beta)^{-1} + \frac{2W - \omega}{2W} \right]^{-1}, \quad (16)$$



where

$$\omega = \omega_{|\mathbf{r}|=a}, \quad W = W_{|\mathbf{r}-\mathbf{r}'|=a},$$

$$G_{\mathbf{r},\mathbf{r}'} = N^{-d} \sum_{\mathbf{K}} \frac{\exp[i\mathbf{K}(\mathbf{r} - \mathbf{r}')] }{\beta + 2dW - 2W\varepsilon_{\mathbf{K}}}, \quad \varepsilon_{\mathbf{K}} = \frac{1}{2} \sum_{\Delta} \cos(\mathbf{K}\Delta), \quad (17)$$

$$\mathbf{K} = \{K_1, K_2, K_3\}, \quad K_d = \frac{\pi}{Na} l, \quad l = 0, \pm 1, \dots, \pm N, \quad d = 1, 2, 3,$$

$2d$  is the number of nearest neighbours,  $N^d$  is the total number of molecules,  $a$  is the lattice constant, the summation over  $\Delta$  henceforward covers only distances between neighbours.

The correction to (13) calculated with the help of (15) is equal to

$$\sum_{\mathbf{r}} \omega_{\mathbf{r}} \rho_{\mathbf{r}} = \gamma c^2, \quad (18)$$

where the annihilation rate constant is defined by

$$\gamma = 2d\omega \left[ d\omega(G_{0,0}^{-1} - \beta)^{-1} + \frac{2W - \omega}{2W} \right]^{-1}. \quad (19)$$

The substitution of (18) into (10) leads to (1) rewritten for steady-state conditions.

It is obvious that (12) (or equivalently (2)) used in this approach imposes a rigid enough restriction on the exciton concentration. It is also to be noted that the correct asymptotic behaviour of the two-particle density matrix:  $\lim_{\mathbf{r} \rightarrow \infty} \rho_{\mathbf{r}} = c^2$  which results from (15), may be obtained only in a zeroth approximation in concentration.

To avoid the difficulties of the theory presented it is necessary to take into account the terms in (9) describing three-particle exciton collisions. We will make it approximately putting in (9)

$$\sum_{\mathbf{n}} (\omega_{\mathbf{n}\mathbf{n}_1} + \omega_{\mathbf{n}\mathbf{n}_2}) \rho_3(\mathbf{n}, \mathbf{n}_1, \mathbf{n}_2) = 2c \sum_{\mathbf{r}} \omega_{\mathbf{r}} \rho_{\mathbf{r}}. \quad (20)$$

Substituting this relation into (9) and excluding in it  $\sum_{\mathbf{r}} \omega_{\mathbf{r}} \rho_{\mathbf{r}}$  with the help of (10) we again get (14). Thus the decoupling procedure used conserves the above equations for  $c$  and  $\gamma$ , but their validity is now determined by (20). In this case three- (and more) particle collisions are approximately included into the definition of a two-particle density matrix. We can therefore hope that Eq. (1) will find a wider range of application than it is implied by (12), at least in some special cases. To prove this we shall continue our discussion using a more correct form for  $\rho_3$  in the next section. But to conclude the present one we briefly discuss the case of small values of  $\beta$ .

It was not considered in Ref. 8, because the inequality (12) does not permit us to use (1) for long-lived excitations. For example, in the case of one-dimensional excitons the expression for  $\gamma$  takes the form

$$\gamma = 2\omega \left[ \frac{\omega}{2W} (W\beta^{-1})^{1/2} + 1 \right]^{-1}, \quad (21)$$

if  $W\beta^{-1} \gg 1$ . Consequently, when  $\beta \rightarrow 0$  we have a meaningless result  $\gamma = 0$ . The above passage to the limit, however, cannot be made neglecting the terms in (8), (9) which involve the occupation of a molecule by an excitation. They can easily be formally introduced in all formulas by changing  $\beta$  to  $\beta + 2I$ . The resulting dependence of  $\gamma$  on  $I$  may seem to be surprising, but it will be shown in the next section that the dependence of  $\gamma(I)$  in (1) is quite natural and it manifests itself in some cases even at  $\beta \ll I$  (the last inequality is henceforward supposed to be met).

#### IV KIRKWOOD'S SUPERPOSITION APPROXIMATION FOR THE THREE PARTICLE DENSITY MATRIX

We have taken advantage of the fact that the three-particle density matrix should satisfy certain asymptotic requirements. At great distances between quasi-particles their motion is not correlated. Therefore, in this case  $\rho_3$  has to be equal to  $c^3$ . Accordingly, if the distance between only two of these particles is small, for example, between molecules on sites  $n$  and  $n_1$ , then the behaviour has to follow that of the function  $c\rho_2(\mathbf{n}, \mathbf{n}_1)$ , etc. The decoupling used in (13) is exact only in the sense of the first of the demands on the asymptotic behaviour. To improve it let us take the three-particle density matrix in the form

$$\rho_3(\mathbf{n}, \mathbf{n}_1, \mathbf{n}_2) = c^3 g(\mathbf{n}, \mathbf{n}_1) g(\mathbf{n}, \mathbf{n}_2) g(\mathbf{n}_1, \mathbf{n}_2), \quad (22)$$

where

$$g(\mathbf{n}_1, \mathbf{n}_2) = c^{-2} \rho_2(\mathbf{n}_1, \mathbf{n}_2). \quad (23)$$

As is known, the approximation (22) is good in the statistical theory of dense gases in a wide range of concentrations.<sup>21</sup>

Using (22), (23) for (9) we get a set of nonlinear integral equations. Passing then to dimensionless parameters we have

$$1 + c \sum_{\mathbf{r}} \Omega_{\mathbf{r}} g_{\mathbf{r}} = \alpha, \quad (24)$$

$$g_{\mathbf{r}} + \sum_{\mathbf{r}'} M_{\mathbf{r}\mathbf{r}'} (g_{\mathbf{r}} - g_{\mathbf{r}'}) + (\frac{1}{2}\Omega_{\mathbf{r}} - M_{\mathbf{r}}) g_{\mathbf{r}} + c g_{\mathbf{r}} \sum_{\mathbf{r}'} \Omega_{\mathbf{r}'} g_{\mathbf{r}'} g_{\mathbf{r}-\mathbf{r}'} = \alpha, \quad (25)$$

where

$$g_r \equiv g(\mathbf{n}_1 - \mathbf{n}_2), \alpha = jc^{-1}, j = I\beta^{-1},$$

$$\Omega_r = \omega_r \beta^{-1}, M_r = W_r \beta^{-1}.$$

In the nearest-neighbour approximation the set of equations for  $g_r$  may be considerably simplified. With the help of (24) it is reduced to a set quadratic in  $g_r$ . For the sake of convenience we also introduce a new quantity  $v_r = 1 - g_r$  ( $v_r \rightarrow 0$ , when  $\mathbf{r} \rightarrow \infty$ ). As a result we get,

$$(\alpha + 2dM)v_r - \tilde{M} \sum_{\Delta} v_{r-\Delta} = (\frac{1}{2}\Omega - M_r)(1 - v_r) + \frac{\alpha - 1}{2d} \sum_{\Delta} v_r v_{r-\Delta}, \quad (26)$$

where

$$\tilde{M} = M \left( 1 - \frac{\alpha - 1}{2dM} \right).$$

Using the Green's function satisfying equations

$$(\alpha + 2dM)\tilde{G}_{r,r'} - \tilde{M} \sum_{\Delta} \tilde{G}_{r-\Delta,r'} = \delta_{rr'},$$

we may write the formal solution of (26)

$$v_r = \sum_{r'} \tilde{G}_{r,r'} \left[ (\frac{1}{2}\Omega_{r'} - M_{r'})(1 - v_{r'}) + \frac{\alpha - 1}{2d} \sum_{\Delta} v_{r'} v_{r'-\Delta} \right], \quad (27)$$

where

$$\tilde{G}_{r,r'} = N^{-d} \sum_{\mathbf{K}} \frac{\exp[i\mathbf{K}(\mathbf{r} - \mathbf{r}')] }{\alpha + 2dM - \tilde{M}\epsilon_{\mathbf{K}}}. \quad (28)$$

It is implicit in (27) that  $v_{r=0} = 1$ , i.e.  $\rho_{r=0} = 0$ . This condition implies that two excitations may not happen to be on the same molecule simultaneously. Taking into account the kinematic repulsion through the use of a known formal procedure<sup>20</sup> we may write instead of (27)

$$v_r = \frac{\tilde{G}_{r,0}}{\tilde{G}_{0,0}} + \sum_{r'} \left( \tilde{G}_{r,r'} - \frac{\tilde{G}_{r,0}\tilde{G}_{0,r'}}{\tilde{G}_{0,0}} \right) \times \left[ (\frac{1}{2}\Omega_{r'} - M_{r'})(1 - v_{r'}) \right. \\ \left. + \frac{\alpha - 1}{2d} \sum_{\Delta} v_{r'} v_{r'-\Delta} \right], \quad (29)$$

where the condition  $v_{r=0} = 1$  is met automatically.

One can see from Eqs. (28), (29) that the last of them becomes linear and equivalent to (14) when  $\alpha = 1$ . It is just the case treated by Suna. When  $\alpha \neq 1$  we solve (29) by the successive approximation method using the solution of

a linearized equation as a zeroth approximation

$$v_r^{(0)} = \frac{\tilde{G}_{r,0}}{\tilde{G}_{0,0}} \left[ 1 + \frac{\Omega - 2M}{2\tilde{M}} (1 - v_a^{(0)}) \right] - \delta_{r0} \frac{\Omega - 2M}{2\tilde{M}} (1 - v_a^{(0)}), \quad (30)$$

where the quantity

$$1 - v_a^{(0)} = \tilde{M} \left( M - \frac{1}{2}\Omega + \tilde{M} \frac{d\Omega + 1 - \alpha}{\tilde{G}_{0,0}^{-1} + 1 - 2\alpha} \right)^{-1} \quad (31)$$

defines the probability of finding a pair of excitons at neighbouring molecules.

In the first approximation we find the correction to  $v_a^{(0)}$  by substituting (30) into the quadratic terms of (29)

$$v_a^{(1)} = \left[ 1 + \frac{\Omega - 2M}{2\tilde{M}} (1 - v_a^{(0)}) \right]^2 \times \frac{(1 - \alpha)(\alpha + 2dM)}{2d\tilde{M}^2} \sum_{r=0} \frac{\tilde{G}_{r,0}^3}{\tilde{G}_{0,0}^3}. \quad (32)$$

It may be shown that the solution  $v_a = v_a^{(0)} + v_a^{(1)}$  is valid ( $v_a^{(1)} \ll v_a^{(0)}$ ) whenever, the condition  $\alpha \ll M$  holds. Then the expression for the quantity analogous to the annihilation rate constant in Section III:  $\bar{\gamma} = 2d\omega(1 - v_a)$ ,† turns to be dependent on  $I$ , and instead of (1) we have

$$\beta c + \bar{\gamma}(I)c^2 = I. \quad (33)$$

Thus, the linearized equations (29) already involve high-concentration corrections. Within the phenomenological approach to a description of interacting excitons this corresponds to taking into account collisions whose frequency is proportional to concentration degrees higher than  $c^2$ .

## V INTENSE NONLINEAR LUMINESCENCE QUENCHING FOR EXCITONS WITH A GREAT DIFFUSION LENGTH

Let us now consider the special but practically important case of strong nonlinear quenching when the monomolecular decay term in (33) is negligible compared to the nonlinear decay term,  $\alpha \gg 1$ . (This is just the opposite condition to that treated by Suna.) In addition, the inequality  $\alpha \ll M$  must hold when the solution of the problem found in the previous section is correct. Both of them may be satisfied for excitons with a great diffusion length and under a sufficiently intense excitation.

† It seems more appropriate henceforward to call  $\bar{\gamma}$  the annihilation rate. The annihilation rate constant is now its limiting value:  $\lim_{I \rightarrow 0} \bar{\gamma}(I) = \gamma$ .

Under conditions mentioned above the solution of (29) for nearest neighbours may be approximately written in the form

$$v_a^{(0)} = \begin{cases} 1 - \left( \frac{\Omega}{4M} + 1 \right)^{-1}, & d = 3, \\ 1 - \left\{ \frac{\Omega}{2M} \left[ \pi^{-1} \ln \left( \frac{16M}{\alpha} \right) - 1 \right] + 1 \right\}^{-1}, & d = 2, \\ 1 - \left[ \frac{\Omega}{2M} \left( \frac{1}{2} M \alpha^{-1} \right)^{1/2} + 1 \right]^{-1}, & d = 1. \end{cases} \quad (34)$$

Corrections to the solution defined by

$$v_a^{(1)} \approx \frac{\alpha}{M} \begin{cases} \ln \left( \frac{M}{\alpha} \right), & d = 3, \\ \left( \frac{M}{\alpha} \right)^{1/2d}, & d = 2, 1 \end{cases} \quad (35)$$

are small and may be neglected.

From the analysis of formulas given it follows that an upper limit on the exciton concentration when the use of the solutions (34) is justified depends on the dimensionality of the system and the ratio between characteristic exciton parameters. This limit turns out to be most rigorous for three-dimensional excitons and corresponds to the inequality  $c \ll [6 \ln(M/6c\Omega)]^{-1}$  if  $\Omega \ll M$ . In realistic situations this concentration will be much greater than that satisfying (2). In all other cases the validity of (34) is guaranteed by the conditions

$$1 \ll \alpha \ll M, c \ll 1. \quad (36)$$

Supposing the above conditions to be met we get the following expressions for the annihilation rate in three-, two- and one-dimensional systems

$$\frac{\omega}{\tilde{\gamma}(I)} = \begin{cases} \frac{1}{6} \left( \frac{\omega}{4W} + 1 \right), & d = 3, \\ \frac{1}{4} \left\{ \frac{\omega}{2W} \left[ \pi^{-1} \ln \left( \frac{16Wc}{I} \right) - 1 \right] + 1 \right\}, & d = 2, \\ \frac{1}{2} \left[ \frac{\omega}{2W} \left( \frac{Wc}{2I} \right)^{1/2} + 1 \right], & d = 1, \end{cases} \quad (37)$$

and the dependence of the concentration on the exciton intensity is given by the equation

$$\tilde{\gamma}(I)c^2 = I. \quad (38)$$

In the following we discuss separately the case of a diffusion-controlled annihilation and the case when the annihilation process practically does not depend on the exciton motion (kinetic regime). Note that only for three-dimensional motion the annihilation is controlled by diffusion when  $\omega/W \ll 1$  (this is usually implied). But this condition reduces to  $\omega/W \gtrsim 1$  in two-, and to  $\omega/W \gg (\beta/W)^{1/2}$  in one-dimensional cases. The latter may be satisfied even at  $\omega/W \ll 1$  when the exciton diffusion length is sufficiently large. At high concentrations the first two conditions are not considerably violated but the third one is to be changed to  $\omega/W \gg (I/Wc)^{1/2}$ .

In the case of a diffusion-controlled annihilation the steady-state conditions for the exciton concentration are achieved mainly due to the annihilation process if

$$c \gg (32W\beta^{-1})^{-1/2}, c \gg \frac{\ln(16W\beta^{-1})}{8\pi W\beta^{-1}}, c \gg (6W\beta^{-1})^{-1}, \quad (39)$$

for one-, two-, and three-dimensional excitons, respectively.

As it follows from (39), for the annihilation effect to be dominant it is necessary to create the densest exciton gas in the case of one-dimensional excitons. The same effect of nonlinear quenching in a three-dimensional exciton gas may be observed at essentially lower concentrations at the same values of all the other parameters. In this sense a two-dimensional exciton gas belongs to an intermediate case.

The quantitative difference in conditions under which an intense nonlinear quenching effect occurs for excitons executing a random walk in three, two and one dimensions arises from the fact that this type of motion has quite different properties in various dimensions (see, for example,<sup>22</sup> and also Ref. 8).

The dependence of the stationary concentration value on the excitation intensity is also different for excitons moving in various dimensions. From (37), (38) we have

$$I = 24Wc^2, \quad d = 3, \quad (40)$$

$$I = 8\pi W \left[ \ln \left( \frac{16Wc}{I} \right) - \pi^{-1} \right]^{-1} c^2, \quad d = 2, \quad (41)$$

$$I = 32Wc^3, \quad d = 1. \quad (42)$$

Thus, it varies from  $c \sim I^{1/2}$  (what is usually expected) to  $c \sim I^{1/3}$  if the exciton motion is close to one dimension.

It is worth mentioning that in addition to the deviation from a root-like dependence of the quantum yield, which is not described by (33) involving the standard definition of the annihilation rate constant, application of (33) with  $\gamma$  instead of  $\tilde{\gamma}(I)$  as a tool for studying the exciton diffusivity under

intense excitation would lead to an under-estimated diffusion coefficient for excitons undergoing nearly two-, and especially, one-dimensional motion.

From the comparison of formulas (41), (42) and (38) one can see that an increase in the excitation intensity manifests itself as an increase in the annihilation rate measured experimentally. This is equivalent to a stronger nonlinear quenching effect at higher  $I$  than at low  $I$ , which is not connected with the concentration difference. An effect of this kind has recently been observed in anthracene.<sup>17</sup> To explain it the occurrence of new annihilation centers was supposed. A quite different explanation of the strengthening of the fluorescence quenching at high excitation intensities may be given within our approach if two-dimensional exciton motion is relevant to the case. In the framework of this hypothesis an additional quenching effect may be connected with an increase in the annihilation probability of each excitation as a result of its interaction with many others while it travels. Thus, the annihilation process becomes not a pairwise, but many-particle reaction at high concentrations. This is effectively manifested in increasing  $\tilde{\gamma}(I)$ .

Now we turn to the case of the kinetic regime of the annihilation process. Because of fast diffusion the peculiarities of incoherent exciton motion in different dimensions are no longer important (the binary exciton distribution function slightly deviates from  $c^2$  at any distances between excitons). Instead of (39), we now have a single condition  $c \gg \beta\omega^{-1}$  guaranteeing that the exciton annihilation channel is dominant irrespective of the dimensionality of exciton motion. The concentration dependence on the pumping intensity is also the same,  $c \sim I^{1/2}$ , for one-, two- and three-dimensional excitons.

Thus in the case of intense nonlinear quenching the root-like dependence of  $c$  on  $I$  may be observed when the exciton band is almost isotropic, but when the exciton motion is nearly two- or one-dimensional  $c \sim I^{1/2}$  only in the kinetic regime of annihilation.

Let us now estimate the singlet exciton concentration region where our consideration may be applied to nonlinear fluorescence quenching in anthracene and naphthalene crystals. The basic inequalities (36) of the present theory expressed in terms of experimentally measured quantities may be written in the form

$$v\beta \ll c\gamma_{\text{exp}} \ll aD, \quad (43)$$

where  $D$  is the average exciton diffusion coefficient.

Using experimental data,<sup>18</sup> we put  $a = 5 \text{ \AA}$ ,  $\beta = 10^9 \text{ s}^{-1}$ ,  $D_c = 10^{-2} \text{ cm}^2/\text{s}$ ,  $\gamma_{\text{exp}} = 10^{-8} \text{ cm}^3/\text{s}$  for singlet excitons in crystalline anthracene and  $\beta = 10^7 \text{ s}^{-1}$ ,  $D_c = 10^{-5} \text{ cm}^2/\text{s}$ ,  $\gamma_{\text{exp}} = 10^{-11} \text{ cm}^3/\text{s}$  in naphthalene. Taking into account that the diffusivity in the  $ab$  crystal plane must be at least an

order of magnitude higher than the value of  $D_c$ , we get, according to (43),  $10^{-4} \ll c \ll 10^{-1}$  for naphthalene and  $10^{-5} \ll c \ll 10^{-1}$  for anthracene crystals.

The upper allowed concentration limit is considerably higher than that defined by Suna's condition (2). Its attainment in experiment is unlikely.

Inequalities analogous to (43) for the excitation intensity reduce to

$$v\beta^2 \ll I\gamma_{\text{exp}} \ll D^2 a^{-1}. \quad (44)$$

Substituting into it the experimental values from<sup>18</sup> we get the following intensity limits  $10^3 \text{ s}^{-1} \ll I \ll 10^{10} \text{ s}^{-1}$  and  $10^4 \text{ s}^{-1} \ll I \ll 10^{13} \text{ s}^{-1}$  for naphthalene and anthracene crystals respectively. They give us the intensity region where the results of this section are valid.

## VI NUMERICAL RESULTS

The discussion made in the previous section was concerned with the case of intense nonlinear quenching. The opposite case is described by Suna's theory. When both channels of exciton decay are comparable the concentration dependence on the intensity is defined by (33) involving the annihilation rate

$$\tilde{\gamma}(I) = 2d\omega \left[ \frac{d\Omega - \alpha + 1}{\tilde{G}_{0,0}^{-1} - 2\alpha + 1} + \frac{2W - \omega}{2W} \right]^{-1}, \quad (45)$$

where

$$\begin{aligned} \tilde{G}_{0,0} &= [4M(2\alpha - 1)]^{-1/2}, \quad d = 1; \\ \tilde{G}_{0,0} &= (4\pi M)^{-1} \ln\left(\frac{16M}{\alpha}\right), \quad d = 2; \\ \tilde{G}_{0,0} &= (2M)^{-1} \left[ 0.5 - \pi^{-1} \left( \frac{2\alpha - 1}{2M} \right)^{1/2} \right], \quad d = 3, \end{aligned} \quad (46)$$

with the condition  $\alpha \ll M$  taken into account.

To clarify this result the model calculations of quantities  $\tilde{\gamma}(j)$ ,  $c(j)$ ,  $\varphi(j) = j^{-1}c(j)$ , were performed. The last of these quantities corresponds to the luminescence quantum yield in steady-state conditions.

In our calculations some of the typical exciton parameter values for triplet and singlet excitons in molecular crystals have been used. The calculated results may therefore be employed as guide-lines of observing the effects predicted in various crystals.

To decrease the number of the unknown parameters the dimensional quantities are given in units  $\beta$ . Thus, there are only two free parameters  $M$



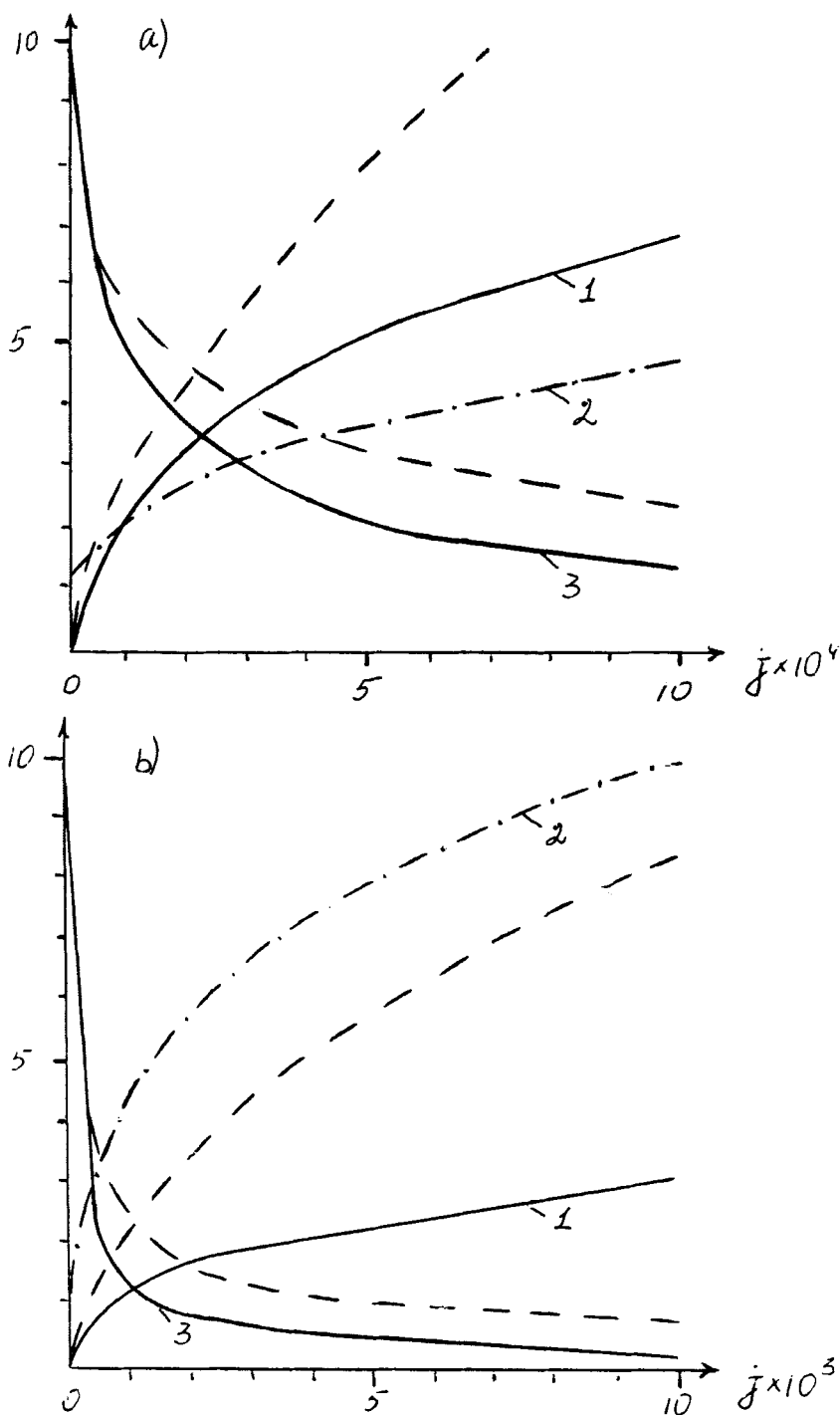


FIGURE 1 One-dimensional excitons.  $M = 10^7$ ,  $\omega/W = 10$ . a) curves 1, 2, 3 correspond to  $c \cdot 10^4$ ;  $\bar{\gamma} \cdot \beta^{-1} \cdot 10^{-4}$ ;  $\phi \cdot 10$ , respectively; b) curves 1, 2, 3 correspond to  $c \cdot 10^4$ ;  $\bar{\gamma} \cdot \beta^{-1} \cdot 10^{-4}$ ;  $\phi \cdot 10$ , respectively. Dashed lines correspond to  $c$  and  $\phi$  calculated for  $\bar{\gamma}(0) = \gamma = 1.26 \cdot 10^4 \cdot \beta$ .

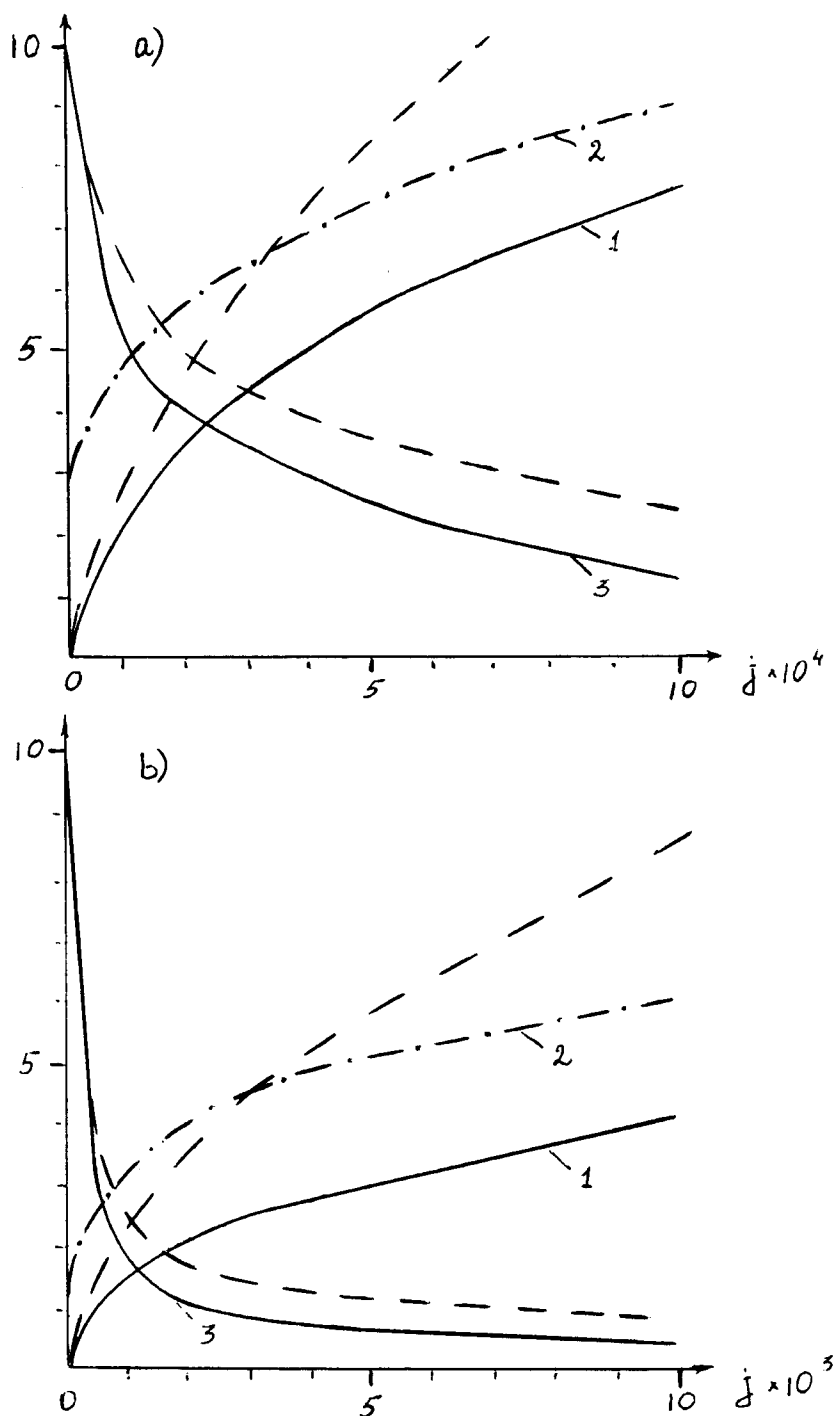


FIGURE 2 One-dimensional excitons.  $M = 10^7$ ,  $\omega/W = 10^{-2}$ . a) curves 1, 2, 3 correspond to  $c \cdot 5 \cdot 10^4$ ;  $\bar{y} \cdot \beta^{-1} \cdot 2.5 \cdot 10^{-4}$ ;  $\phi \cdot 10$ , respectively; b) curves 1, 2, 3, correspond to  $c \cdot 10^4$ ;  $\bar{y} \cdot \beta^{-1} \cdot 10^{-4}$ ;  $\phi \cdot 10$ , respectively. Dashed lines correspond to  $c$  and  $\phi$  calculated for  $\bar{y}(0) = \gamma = 1.12 \cdot 10^4 \cdot \beta$ .

and  $\omega/W$ . Calculations were carried out for  $j \ll 1$  which corresponds to  $j = I/\beta$ .

Figures from 1 to 3 correspond to one-dimensional case. The curves for the same of the parameter values, but in different intensity regions: (a)  $0 \leq j \leq 10^{-3}$  ( $1 \leq \alpha \lesssim 7$ ) and (b)  $0 \leq j \leq 10^{-2}$  ( $1 \leq \alpha \lesssim 30$ ) are presented in Figure 1. The equality  $M = 10^7$ , for example, corresponds to the hopping rate  $10^{10} \text{ s}^{-1}$  and to the decay time  $10^{-3} \text{ s}$  which are typical for triplet excitons. For the ratio  $\omega/W = 10$  taken the dimensionless annihilation rate  $\tilde{\gamma}(0) = \gamma$  is equal to  $1.26 \cdot 10^4$ . For this value of  $\gamma$  the concentration and quantum yield dependence correspond to dashed lines. It is easily seen that the high concentration effects influence appreciably these dependencies (solid lines) even at relatively small values of  $\alpha$ . When  $\alpha$  changes from 1 to 7 the  $\tilde{\gamma}$  (dashed-dotted line) increases approximately 4 times. This is reflected in a considerable decrease in the corresponding values of the concentration and the quantum yield. When the excitation intensity starting from those values of  $j$  where the nonlinear quenching effect is noticeable, increases

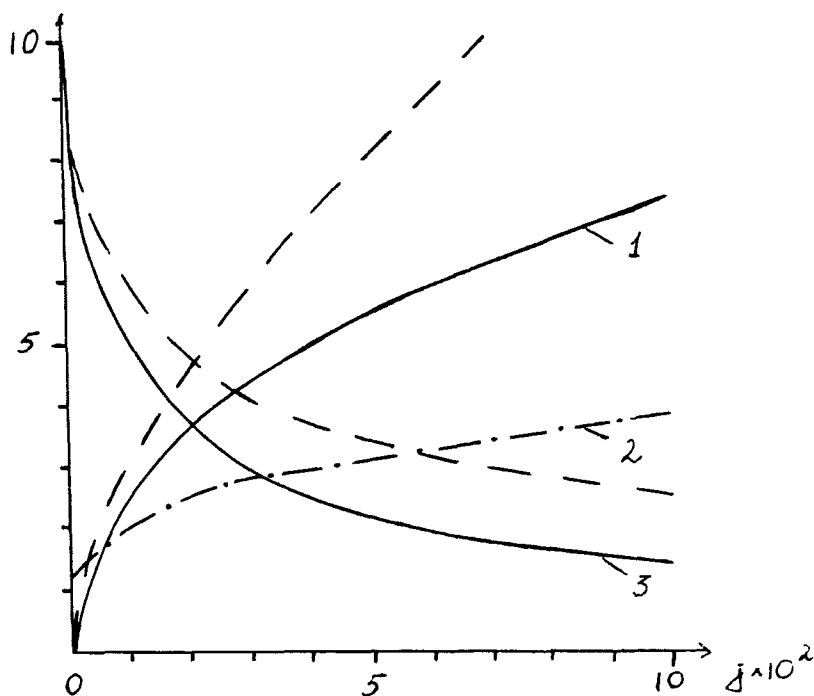


FIGURE 3 One-dimensional excitons.  $M = 10^3$ ,  $\omega/W = 1$ . Curves 1, 2, 3 correspond to  $c \cdot 5 \cdot 10^2$ ;  $\tilde{\gamma} \cdot \beta^{-1} \cdot 10^{-2}$ ;  $\phi \cdot 10$ , respectively. Dashed lines correspond to  $\tilde{\gamma}$  and  $\phi$  calculated for  $\tilde{\gamma}(0) = \gamma = 1.21 \cdot 10^2 \cdot \beta$ .

about two orders of magnitude, the quenching is enhanced 3 times (quenching enhancement is proportional to  $(\tilde{\gamma}(j)/\tilde{\gamma}(0))^{1/2}$  for  $\alpha \gg 1$ ).

It is interesting to note that for the given  $M$  the deviation of the  $c(j)$  and  $\varphi(j)$  dependences from the values when  $\tilde{\gamma}(0) = \gamma$  is used is essential in a wide range of the values of the parameter  $\omega/W$ . For example, at  $\omega/W = 10^{-2}$  (Figures 2(a), (b)) the quenching effect is enhanced approximately 2.4 times when  $\alpha$  changes from 1 to 25. This is caused by the fact that the annihilation process is strongly dependent on the exciton diffusion even at those ratios between the annihilation probability and the hopping rate when in two- and three-dimensional cases this dependence is negligible. This may be considered as an argument that the dependence  $\tilde{\gamma}(I)$  arises, because the increase in concentration influences the exciton motion.

The dependences just considered above are represented in Figure 3 for a much lower value of  $M$ ,  $M = 10^3$ , ( $\omega/W = 1$ ). As it is readily seen from (45), (46) the dependence  $\tilde{\gamma}(I)$  is less pronounced and will manifest itself at

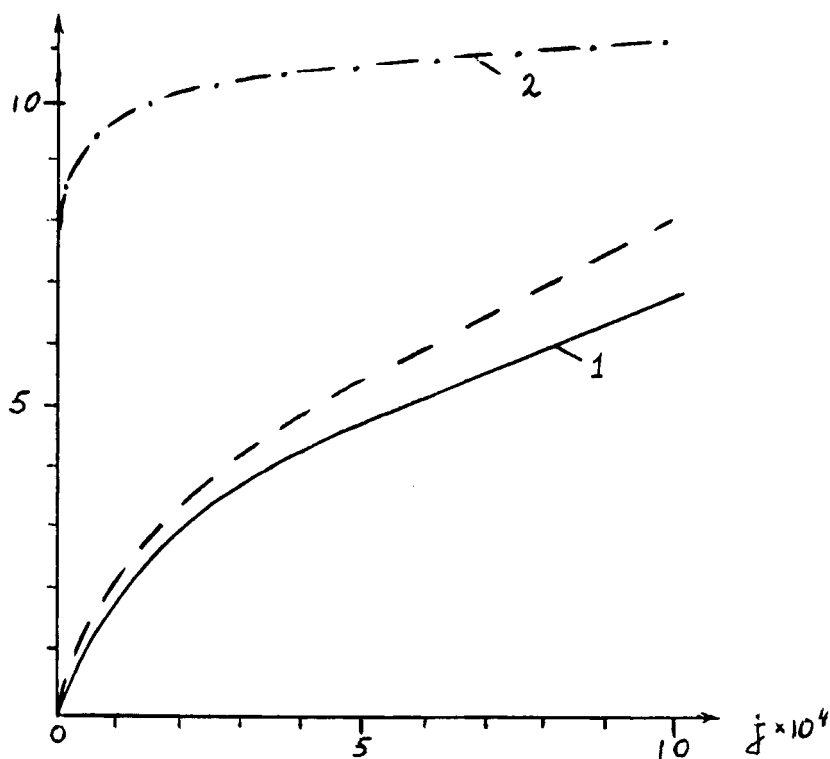


FIGURE 4 Two-dimensional excitons.  $M = 10^7$ ,  $\omega/W = 10$ . Curves 1, 2 correspond to  $c \cdot 10^6$ ;  $\tilde{\gamma} \cdot \beta^{-1} \cdot 5 \cdot 10^{-7}$ , respectively. The dashed line corresponds to  $c$  calculated for  $\tilde{\gamma}(0) = \gamma = 1.53 \cdot 10^7 \cdot \beta$ .

much higher concentration values. This is connected with the smallness of the value  $\tilde{\gamma}(0)$ .

We choose the last example for the calculation keeping in mind the properties of the 1,4-dibromonaphthalene crystal (DBN) known to be a quasi-one-dimensional crystal for triplet excitons.<sup>23-25</sup> It is made of stacks of molecules piled up along the  $c$ -axis. Interstack ( $W_{\text{inter}}$ ) and intrastack ( $W_{\text{intra}}$ ) hopping rates differ by several orders of magnitude.<sup>23-24</sup> If we make an assumption that only intrastack annihilation is important, then to take into account the interstack exciton motion it is enough to replace  $\beta$  by  $W_{\text{inter}}$  when the condition  $W_{\text{intra}} \gg W_{\text{inter}}$  holds.<sup>8</sup> Putting  $W_{\text{intra}}/W_{\text{inter}} = 10^3$  and  $\omega = W_{\text{intra}}$  we get the results represented in Figure 3. Thus the presented calculations are the simplest model for a real quasi-one-dimensional system. But it is still too rough to compare with experiment. In particular, recent investigations<sup>14</sup> show that there is an appreciable interstack annihilation between triplets belonging to different, neighbouring, molecular stacks. Therefore to predict correctly the  $\tilde{\gamma}(j)$ ,  $c(j)$ ,  $\varphi(j)$  dependences for DBN crystals a more realistic model is to be considered.

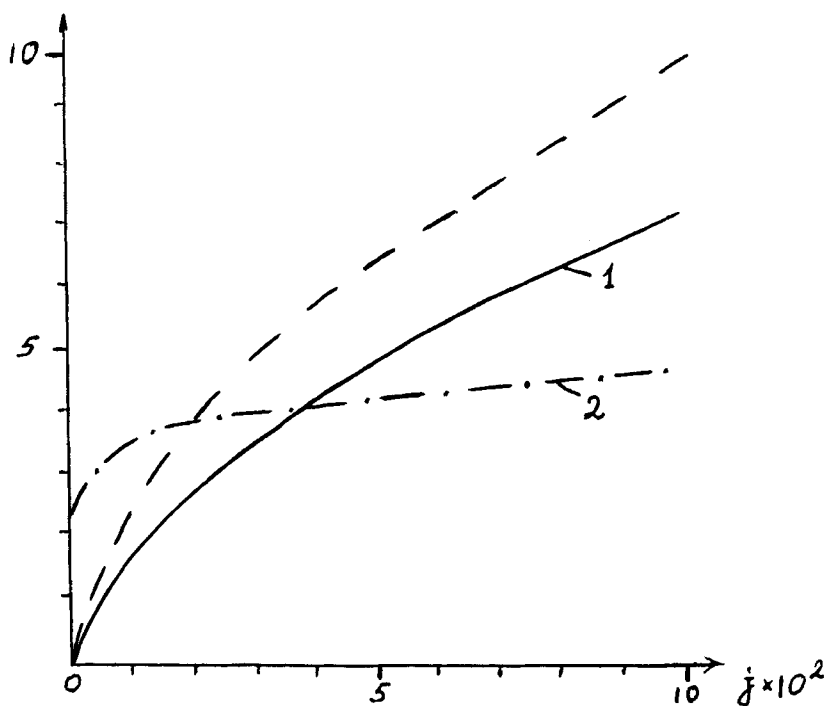


FIGURE 5 Two-dimensional excitons.  $M = 10^4$ ,  $\omega/W = 10$ . Curves 1, 2 correspond to  $c \cdot 5 \cdot 10^3$ ;  $\tilde{\gamma} \cdot \beta^{-1} \cdot 10^{-4}$ , respectively. The dashed line corresponds to  $c$  calculated for  $\tilde{\gamma}(0) = \gamma = 2.65 \cdot 10^4 \cdot \beta$ .

All calculations performed show that the additional quenching effect (increasing  $\tilde{\gamma}$  with  $I$ ) rises monotonously with increasing excitation intensity. The behaviour of  $\tilde{\gamma}(I)$  is qualitatively the same in two- and three-dimensional cases, but is much less pronounced. The curves of Figure 4 representing two-dimensional motion were calculated for the same exciton parameter values as those for the curves in Figure 1. It may be seen that the increase of  $\alpha$  up to 150 is reflected in the increase  $\tilde{\gamma}$  by about 1.5 times. Correspondingly, the quenching effect enhances only 1.2 times. In the case of three-dimensional excitons  $\tilde{\gamma}$  is practically constant for this parameter values.

In Figure 5 the calculated results for lower values of  $M$  equal to  $10^4$  corresponding to singlet excitons in naphthalene and anthracene crystals are given. As distinct from one-dimensional excitons, the effect of quenching enhancement increases for smaller  $M$ . Namely,  $\tilde{\gamma}$  increases approximately two times (and accordingly, the quenching effect grows 1.5 times) when  $\alpha$  changes from 1 to 70.

Figure 6 illustrates the  $\tilde{\gamma}(j)$  dependence and the related effects for three-dimensional excitons. This dependence though existing, in principle, is very small when  $c \ll 1$ .

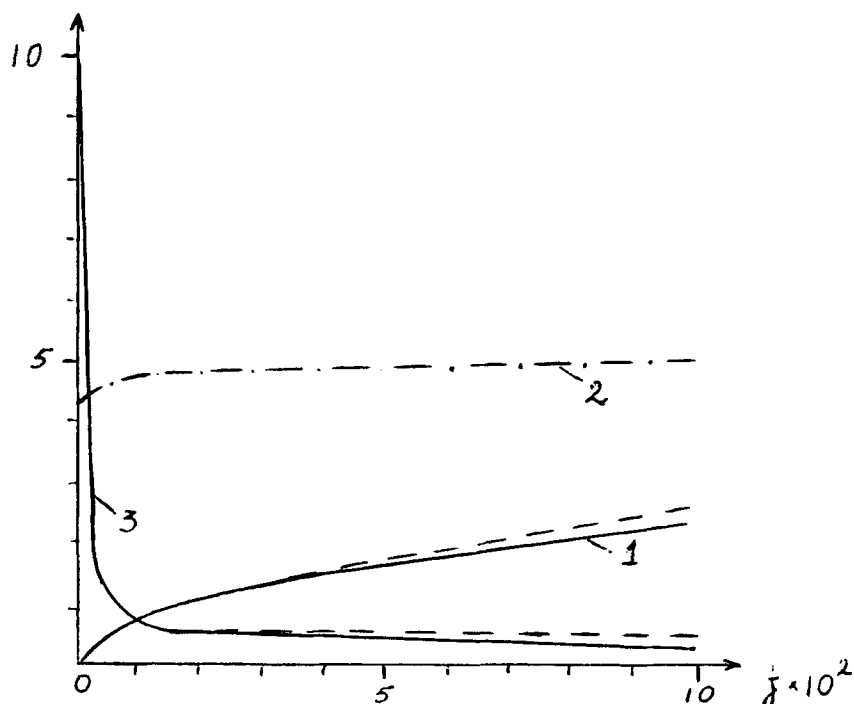


FIGURE 6 Three-dimensional excitons.  $M = 10^3$ ,  $\omega/W = 10$ . Curves 1, 2, 3 correspond to  $C \cdot 10^3$ ;  $\tilde{\gamma} \cdot \beta^{-1} 2$ ,  $5 \cdot 10^{-4}$ ;  $\varphi \cdot 10$ , respectively. Dashed lines correspond to  $C$  and  $\varphi$  calculated for  $\tilde{\gamma}(0) = \gamma = 1.75 \cdot 10^4 \cdot \beta$ .

Our calculations show that in the case of one-dimensional exciton motion it is necessary to take into account the annihilation rate dependence on the excitation intensity even at comparable values of rates of monomolecular and annihilation decay.

At the same time it is possible to neglect the deviation of the solution of (33) with  $\tilde{\gamma}(I)$  replaced by  $\gamma$  from its exact solution when the annihilation of excitons with three-dimensional isotropic motion is described. Thus, Suna's theory is relevant to this case even at high concentrations including the case of strong nonlinear quenching.

The deviations from Suna's theory predictions may also turn out to be negligible when nearly two-dimensional exciton annihilation takes place. But for certain ratios between exciton parameters the additional luminescence quenching effect predicted by our theory may be important.

## VII CONCLUSION

The procedure for decoupling a set of exciton density matrix equations based on the superposition approximation for a three-particle density matrix proves to be very useful in describing the dense incoherent exciton gas kinetics. Even a linearized theory of such an approach permits us to include into a discussion of the annihilation process higher concentration effects which has not been done in previous papers on the same problem. As a result, the annihilation theory in the case of steady-state conditions is extended to the high concentration region where the phenomenological equation (1) or microscopic Suna's theory may be irrelevant. In particular, the present approach applied to nonlinear luminescence quenching in molecular crystals is reasonable up to the concentration

$$c \ll (6 \ln(W/6c\omega))^{-1}$$

which is considerably higher than that permitted by Suna's theory,

$$c \ll \frac{\beta}{\gamma} = \frac{1}{6} \left( \frac{\beta}{\omega} \right) \left( 0.5 \frac{\omega}{W} + 1 \right).$$

High exciton concentration effects are mostly important for two- and one-dimensional excitons. For one-dimensional exciton motion in the case of diffusion-controlled annihilation the cubic root-like dependence of the concentration on the excitation intensity is to be expected. Therefore, it seems extremely interesting to perform experimental investigations of the triplet-triplet exciton annihilation in DBN, analogous to those in Refs. 12, 14, but at higher intensities. Measuring the annihilation rate in a wide region of excitation intensities may be used as a productive tool for studying kinetic

exciton properties, particularly for testing the exciton hopping rate parameters.

Although a system of interacting excitons has been discussed the theory developed may be applied to systems consisting of other sorts of quasi-particles with coordinates as good quantum numbers, and to classical systems where the interaction does not conserve the particle number. An interesting example of this application is given in Ref. 26, where the many-particle aspects of diffusion-controlled reactions were investigated on the basis of equations analogous to (8), (9).

The existence of a small parameter connected with a great exciton diffusion length was supposed when the present theory was applied to nonlinear luminescence quenching. This is a quite real situation for molecular crystal excitons. But for the type of small mobility excitations and at high excitation intensities our approximation fails and other solutions of nonlinear equations (24), (25) must be found and used. In this connection we mention the theoretical and experimental investigation of nonlinear quenching in the system of nearly immovable eximer excitations.<sup>16</sup> It was shown that the description of the annihilation process by a term quadratic in concentration is not relevant at high intensities, which is in agreement with our theory.

In conclusion we emphasize that the results presented are only concerned with the case of a stationary and uniform excitation. Therefore, application of microscopic equations (8), (9) to describe a dense elementary excitation gas in nonsteady-state and nonuniform conditions is an urgent problem in annihilation theory.

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