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Institute of Theoretical Physics, Academy of Sciences of the Ukrainian SSR, Kiev

Annihilation of Incoherent Excitons in Molecular Crystals with Allowance for Their Interaction

By

A. I. ONIPKO

The dependence of the exciton annihilation rate on the dynamic interaction between excitons in molecular crystals is studied. The equation of motion for the two-particle density matrix of incoherent excitons is used to obtain an expression for the annihilation rate constant in one-, two-, and three-dimensional crystals. It is shown that the interaction between excitons may considerably affect the annihilation rate and its temperature dependence, and that the contribution of exciton-exciton interaction to the annihilation process depends on the dimensionality of the system in which the excitons move.

В работе исследуется зависимость скорости экситонной аннигиляции в молекулярных кристаллах от величины динамического взаимодействия между экситонами. На основе уравнений для матрицы плотности некогерентных экситонов (прыжковая модель движения), найдено выражение для константы скорости аннигиляции в одно-, двух- и трехмерном кристалле. Показано, что взаимодействие между экситонами может существенно изменить скорость аннигиляции и ее температурную зависимость, а характер проявления экситон-экситонного взаимодействия в аннигиляции зависит от размерности системы, в которой происходит движение экситонов.

1. Introduction

The interaction between excitons can lead to the nonradiative disappearance of a pair of excitons — the exciton annihilation. Numerous theoretical and experimental investigations have been devoted to this process, because a number of interesting phenomena such as the photoconductivity [1 to 5], the delay and quenching of fluorescence [6 to 9], the weakness of the phosphorescence of pure molecular crystals [10], the nonlinear quenching induced by intense excitation [11 to 13] can be explained in terms of the annihilation.

Experimental data are generally analyzed on the basis of the well-known phenomenological diffusion equations (see, for example, [11]). Such an approach to the problem does not enable us to determine the mechanism of annihilation in detail and to associate the annihilation rate constant with microscopic characteristics of exciton excitations. Much theoretical effort [14 to 22] to calculate the annihilation rate constant has neither clarified completely the role of different exciton parameters in the annihilation process, so the possibilities to compare the theory with numerous experimental data are still limited. In particular, the question of how the so-called dynamic interaction between excitons affects the annihilation rate is of interest. This interaction manifests itself effectively as an attraction or repulsion of quasi-particles and can result in biexciton formation [23]. The attempt to study this question in the case of coherent excitons was made previously in [24]. In the present paper the exciton motion is assumed

to be completely incoherent (the hopping model). This assumption is relevant for the narrow band exciton excitation and a strong exciton-phonon coupling. This kind of the triplet exciton motion was verified experimentally at a temperature above 100 K in crystalline anthracene [25].

2. Theory

It is known [26, 27] that above the Debye temperature in the case of strong exciton-phonon interaction, the density matrix averaged over a phonon subsystem is diagonal in the spatial indices. We need to know only the reduced two-particle density matrix which describes the pairwise annihilation effect. For a system with uniform exciton density, the density matrix only depends on the vector difference of the position of two excitons, and for the quasi-particles of the same sort its equation of motion in steady-state conditions has the form [19]

$$\begin{aligned} \frac{dN_{\mathbf{R}}}{dt} = \sum_{\mathbf{R}'} (W_{\mathbf{R}' \rightarrow \mathbf{R}} N_{\mathbf{R}'} - W_{\mathbf{R} \rightarrow \mathbf{R}'} N_{\mathbf{R}}) (1 - \delta_{\mathbf{R}', 0}) (1 - \delta_{\mathbf{R}, 0}) - \\ - (\tau^{-1} + \omega_{\mathbf{R}}) N_{\mathbf{R}} + P(1 - \delta_{\mathbf{R}, 0}) = 0, \end{aligned} \quad (1)$$

where $N_{\mathbf{R}}$ gives the probability of finding a pair of excitons at the molecules with vector difference \mathbf{R} , $W_{\mathbf{R} \rightarrow \mathbf{R}'}$ is the per second probability of the vector difference to change from \mathbf{R} to \mathbf{R}' . If the dynamical interaction occurs, $W_{\mathbf{R} \rightarrow \mathbf{R}'}$ depends on the tendency of the exciton to change the distance ($W_{\mathbf{R} \rightarrow \mathbf{R}'} \neq W_{\mathbf{R}' \rightarrow \mathbf{R}}$). τ^{-1} is the doubled probability of the monomolecular decay of excitons, $\omega_{\mathbf{R}}$ the bimolecular annihilation probability for excitons separated by \mathbf{R} , P the creation rate of a pair of excitons at the distance \mathbf{R} . This term determines the change in the two-particle density matrix under the influence of an external source. The terms involving the δ -symbol take into account that two excitons cannot be at the same position simultaneously.

From (1) one can define the average rate of disappearance of a pair of excitons caused by the annihilation: $V = (P\tau)^{-1} \sum_{\mathbf{R}} \omega_{\mathbf{R}} N_{\mathbf{R}}$. As shown in [19] this quantity is related to the annihilation rate constant by $\gamma = v_0 V$ (v_0 is the average volume per molecule of a crystal) when certain conditions are satisfied.

Using the Green's function $G_{\mathbf{R}-\mathbf{R}'}$ satisfying

$$\left(\sum_{\mathbf{R}''} \tilde{W}_{\mathbf{R}-\mathbf{R}''} + \tau^{-1} \right) G_{\mathbf{R}-\mathbf{R}'} - \sum_{\mathbf{R}''} \tilde{W}_{\mathbf{R}-\mathbf{R}''} G_{\mathbf{R}''-\mathbf{R}'} = \delta_{\mathbf{R}, \mathbf{R}'}, \quad (2)$$

equation (1) can be formally solved,

$$\begin{aligned} N_{\mathbf{R}} = P\tau (1 - G_{\mathbf{R}} G_0^{-1}) + \delta_{\mathbf{R}, 0} \tau G_0^{-1} [P(\tau - G_0) - G_0 \sum_{\mathbf{R}'} \tilde{W}_{\mathbf{R}'} N_{\mathbf{R}'}] + \\ + \sum_{\mathbf{R}'} [(G_{\mathbf{R}-\mathbf{R}'} - G_{\mathbf{R}} G_{\mathbf{R}'} G_0^{-1}) + \delta_{\mathbf{R}, 0} \tau G_{\mathbf{R}'} G_0^{-1}] [(\tilde{W}_{\mathbf{R}'} - \omega_{\mathbf{R}'}) N_{\mathbf{R}'} + \\ + \sum_{\mathbf{R}''} (1 - \delta_{\mathbf{R}', 0}) (1 - \delta_{\mathbf{R}'', 0}) (\delta W_{\mathbf{R}'' \rightarrow \mathbf{R}'} N_{\mathbf{R}''} - \delta W_{\mathbf{R}' \rightarrow \mathbf{R}''} N_{\mathbf{R}''})], \end{aligned} \quad (3)$$

where $\delta W_{\mathbf{R} \rightarrow \mathbf{R}'} = W_{\mathbf{R} \rightarrow \mathbf{R}'} - \tilde{W}_{\mathbf{R}-\mathbf{R}'}$, $\tilde{W}_{\mathbf{R}}$ determines the probability of the change in mutual position of noninteracting excitons by the vector \mathbf{R} and is equal to the doubled incoherent jump rate for an exciton hopping by this vector.

In the case of localized excitons it is convenient to employ (3) instead of (1) because $\tilde{W}_{\mathbf{R}}$ and $\omega_{\mathbf{R}}$ decrease with the distance at least as R^{-6} . Assume also that the dynamical interaction between excitons is short range. Then (3) can be

solved in the nearest-neighbour approximation. Such a solution is obtained in the Appendix for one-, two- and three-dimensional crystals with one molecule per unit cell and with the following restrictions on the parameters of the system:

$$\left. \begin{aligned} \tilde{W}_R &= \begin{cases} W, & \mathbf{R} = \mathbf{a}, \\ 0, & \mathbf{R} \neq \mathbf{a}, \end{cases} & \omega_R &= \begin{cases} \omega, & \mathbf{R} = \mathbf{a}, \\ 0, & \mathbf{R} \neq \mathbf{a}, \end{cases} \\ \delta W_{R \neq R'} &= \delta W_{\mathbf{a} \neq 2\mathbf{a}}; & \text{when } \mathbf{R} \text{ or } \mathbf{R}' = \mathbf{a}, \\ \delta W_{R \neq R'} &= 0; & \mathbf{R}, \mathbf{R}' \neq \mathbf{a}, \end{aligned} \right\} \quad (4)$$

where \mathbf{a} is the lattice vector.

Using (A1), (A4) to (A6), one can calculate the annihilation rate constant for any values of the microscopic parameters which characterize the lifetime, the motion and the interaction of excitons. But the case when the probability of the exciton jump is much greater than the monomolecular decay probability (which is typical of molecular crystals) is of great interest. Let us find approximate expressions for the annihilation rate constant corresponding to $W\tau \gg 1$.

2.1 One-dimensional crystal

Taking into account that $G_0 \approx 0.5 \sqrt{\tau/W}$ and retaining in (A1), (A7) only the first terms of the expansion in powers of $(W\tau)^{-1/2}$ we obtain

$$\gamma = \frac{2a\omega \left(1 + \frac{1}{\sqrt{W_{2a \rightarrow a}\tau}}\right)}{\frac{\omega}{W} \sqrt{W\tau} \left(1 + \frac{1}{\omega\tau}\right) \left[1 + \frac{\sqrt{W\tau}}{\sqrt{W_{2a \rightarrow a}\tau}}\right] + \frac{W_{a \rightarrow 2a}}{W_{2a \rightarrow a}}}. \quad (5)$$

In the absence of the interaction the annihilation constant rate is equal to

$$\gamma_0 = \frac{2a\omega}{1 + \left(\frac{\omega}{W}\right) \sqrt{W\tau}}. \quad (6)$$

2.2 Two-dimensional crystal

Using the asymptotical expressions of the elliptic integrals in (A5), when k is close to 1 ($W\tau \gg 1$) we find to a first approximation

$$\gamma = \frac{4a^2\omega}{\frac{\omega}{W} \pi^{-1} \ln(32W\tau) + \frac{W_{a \rightarrow 2a}}{W_{2a \rightarrow a}}}, \quad (7)$$

$$\gamma_0 = \frac{4a^2\omega}{\left(\frac{\omega}{W}\right) \pi^{-1} \ln(32W\tau) + 1}. \quad (8)$$

2.3 Three-dimensional crystal

The Green's functions for a three-dimensional system have no singularities at $(W\tau)^{-1} = 0$ and near this point they can be replaced by their values for $(W\tau)^{-1} = 0$. Then the calculation of γ using the numerical data for the Green's

functions given by Koster and Slater [28] gives, with an accuracy to $(W\tau)^{-1/2}$,

$$\gamma = 6a^3\omega \left(\frac{\omega}{W} \frac{0.286 + 0.166W W_{2a \rightarrow a}^{-1} + 0.045W^{-1}W_{2a \rightarrow a}}{0.83 + 0.17W^{-1}W_{2a \rightarrow a}} + \frac{W_{a \rightarrow 2a}}{W_{2a \rightarrow a}} \right)^{-1}, \quad (9)$$

$$\gamma_0 = \frac{6a^3\omega}{0.497 \frac{\omega}{W} + 1}. \quad (10)$$

Equations (6), (8), (10) are similar to the corresponding results of [19] for noninteracting excitons. If the dynamic interaction between excitons is strong ($W W_{2a \rightarrow a}^{-1}$, $W_{a \rightarrow 2a} W_{2a \rightarrow a}^{-1}$ are essentially different from unity) a considerable deviation from the values and the temperature dependence predicted by the expressions for γ_0 is to be expected. This is so because the attraction or repulsion between the excitons affects the probability that they are sufficiently close to interact, and, consequently, their annihilation rate. The specific conditions when the interaction affects essentially the annihilation are given by the relations between the parameters τ , ω , W , $W_{2a \rightarrow a}$. Certain qualitative conclusions, however, can be derived from (5) to (10), without calculating the quantities just given above.

The dependence of the annihilation rate constant on the dynamic interaction between excitons is most important in a three-dimensional crystal and decreases with decreasing dimensionality of the system in which the excitons move. The weakening of the annihilation dependence upon exciton-exciton interaction occurs due to the decrease in the number of all possible ways of exciton separation. This result is in close relation with the following property of the random walk motion (see, for example, [29]): the probability that a particle returns, which has undergone a one- or two-dimensional motion, to the initial position is equal to unity; in three dimensions the probability that it ever returns is only about 0.34.

The contribution of the interaction to the annihilation also depends on the ratio between the magnitude of the annihilation probability and the exciton jump rate. If $\omega \ll W$, the annihilation rate constant is largely determined by the magnitude and the sign of the exciton-exciton interaction. For $\omega \gg W$ (the annihilation is governed by exciton diffusion), the interaction effect in one or two dimensions will be considerable for a very large repulsion between excitons $W_{a \rightarrow 2a} \gg W_{2a \rightarrow a}$, while in a three-dimensional crystal the interaction can come into play. For instance, if W is an order of magnitude higher than $W_{2a \rightarrow a}$, then $\gamma \approx 3a^3 W_{2a \rightarrow a} \ll \gamma_0 \approx 12a^3 W$.

To illustrate the results obtained above we calculate the temperature dependence of the annihilation rate constant. In this connection we have to know some information on the quantities ω , W , $W_{2a \rightarrow a}$. It can be shown [30] that in a certain approximation the probability $W_{2a \rightarrow a}$ is

$$W_{2a \rightarrow a} = 2 \frac{M^2}{\hbar} \sqrt{\frac{\pi}{kT\varepsilon}} \exp\left[-\frac{(\varepsilon + \Delta)^2}{4kT\varepsilon}\right], \quad W_{a \rightarrow 2a} = W_{2a \rightarrow a}(-\Delta), \quad (11)$$

where M is the matrix element of the energy of the resonance interaction between nearest neighbours, ε the energy of the thermal activation of the exciton jump, Δ the parameter determining the change in the energy of Coulomb interaction between excitons (with the lattice deformation taken into account) due to their approach. For free excitons $\Delta = 0$.

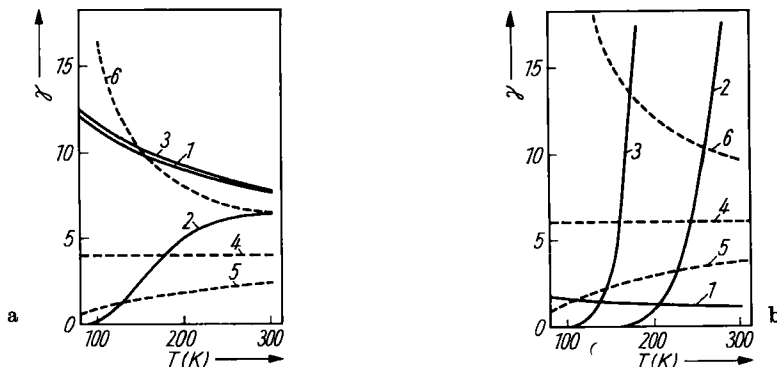


Fig. 1. The temperature dependence of annihilation rate constant in a) two-dimensional crystal (in units $a^2\omega$); b) three-dimensional crystal (in units $a^3\omega$). Curves 1, 2, 3 (Fig. 1 a, b) correspond to $\omega = 10^{11} \text{ s}^{-1}$, $\Delta = 0, +500 \text{ cm}^{-1}, -500 \text{ cm}^{-1}$, respectively; curves 4, 5, 6 to $\omega = 10^7 \text{ s}^{-1}$, $\Delta = 0, +100 \text{ cm}^{-1}, -100 \text{ cm}^{-1}$. The scale for curves 1, 2, 3 in Fig. 1 a is 10^2 and for the curves 2, 3 in Fig. 1 b is 10^4

Equation (11) was used to calculate the temperature dependence of the annihilation rate constant for various values of the exciton–exciton interaction parameter Δ (Fig. 1 a, b). The probability ω was supposed to be constant. This assumption is admissible when the density of final annihilation states is little varied in the interval of order of kT in the neighbourhood of the two-exciton state energy. To calculate γ we took the values of the parameters which are typical of triplet excitons in crystalline anthracene: $\omega = 10^{11} \text{ s}^{-1}$ [18, 19], $M = 2 \text{ cm}^{-1}$, $\tau = 10^{-3} \text{ s}$ [27], $\varepsilon = 50 \text{ cm}^{-1}$, so that the following relation holds: $\omega > W$.

The figures show that for the present values of Δ the interaction between excitons essentially changes the magnitude and the temperature behaviour of the annihilation rate, this change being more pronounced in three and less pronounced in two dimensions. In a one-dimensional system the effect of the interaction on the annihilation rate is negligible for the given Δ -values if the temperature is above 100 K. For $\omega \ll W$ (dashed lines) the exciton–exciton interaction is already appreciable at small values.

3. Conclusion

Let us summarize the main qualitative effects of dynamic interaction between excitons in the annihilation process:

1. The influence of the interaction on the annihilation rate depends on the dimensions of systems in which excitons execute a random walk. The effect is smallest in one, and largest in three dimensions.
2. The interaction effect is determined by the ratio between the annihilation probability and the jump rate of excitons.
3. If the attraction or repulsion between excitons is strong an exponential temperature dependence of the annihilation rate constant can be observed.

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Appendix

To calculate the annihilation rate constant we have to find the probability for observing two excitons at nearest-neighbour molecules $N_{R=a}$. The order of a set of non-uniform linear equations which determine N_a depends on the dimensions of the system and if the conditions (4) are valid N_a is equal to 4, 12, 24 for one, two and three dimensions, respectively. But as long as the quantity P in (3) is assumed to be independent of the coordinates, it follows from the symmetry of the system that N_R with equal R are equal. Taking this into account we find

$$N_a^{(i)} = \begin{vmatrix} Q_1^{(i)} & y_1^{(i)} & z_1^{(i)} \\ Q_2^{(i)} & y_2^{(i)} & z_2^{(i)} \\ Q_3^{(i)} & y_3^{(i)} & z_3^{(i)} \end{vmatrix} \begin{vmatrix} x_1^{(i)} & y_1^{(i)} & z_1^{(i)} \\ x_2^{(i)} & y_2^{(i)} & z_2^{(i)} \\ x_3^{(i)} & y_3^{(i)} & z_3^{(i)} \end{vmatrix}^{-1},$$

where $i = 1, 2, 3$ indicates the dimension of the system,

$$Q_1^{(i)} = P\tau \begin{cases} G_1 G_0^{-1} - 1; & i = 1, \\ G_{1,0} G_{0,0}^{-1} - 1; & i = 2, \\ G_{1,0,0} G_{0,0,0}^{-1} - 1; & i = 3, \end{cases} \quad Q_2^{(i)} = P\tau \begin{cases} 0; & i = 1, \\ G_{1,1} G_{0,0}^{-1} - 1; & i = 2, \\ G_{1,1,0} G_{0,0,0}^{-1} - 1; & i = 3, \end{cases}$$

$$Q_3^{(i)} = P\tau \begin{cases} G_2 G_0^{-1} - 1; & i = 1, \\ G_{2,0} G_{0,0}^{-1} - 1; & i = 2, \\ G_{2,0,0} G_{0,0,0}^{-1} - 1; & i = 3, \end{cases}$$

$$x_1^{(i)} = W^{-1} \begin{cases} (W - \omega) G_1 G_0^{-1} + \delta W_{a \rightarrow 2a} (G_2 - G_1) G_0^{-1} - W; & i = 1, \\ (W - \omega) G_{1,0} G_{0,0}^{-1} + \delta W_{a \rightarrow 2a} (2G_{1,1} + G_{2,0} - 3G_{1,0}) G_{0,0}^{-1} - W; & i = 2, \\ (W - \omega) G_{1,0,0} G_{0,0,0}^{-1} + \delta W_{a \rightarrow 2a} (4G_{1,1,0} + G_{2,0,0} - 5G_{1,0,0}) G_{0,0,0}^{-1} - W; & i = 3, \end{cases}$$

$$y_1^{(i)} = W^{-1} \begin{cases} 0; & i = 1, \\ 2\delta W_{2a \rightarrow a} (G_{1,0} - G_{1,1}) G_{0,0}^{-1}; & i = 2, \\ 4\delta W_{2a \rightarrow a} (G_{1,0,0} - G_{1,1,0}) G_{0,0,0}^{-1}; & i = 3, \end{cases}$$

$$z_1^{(i)} = W^{-1} \begin{cases} \delta W_{2a \rightarrow a} (G_1 - G_2) G_0^{-1}; & i = 1, \\ \delta W_{2a \rightarrow a} (G_{1,0} - G_{2,0}) G_{0,0}^{-1}; & i = 2, \\ \delta W_{2a \rightarrow a} (G_{1,0,0} - G_{2,0,0}) G_{0,0,0}^{-1}; & i = 3, \end{cases}$$

$$x_2^{(i)} = W^{-1} \begin{cases} 0; & i = 1, \\ (W - \omega) G_{1,1} G_{0,0}^{-1} + \delta W_{a \rightarrow 2a} [2W (G_{0,0} + G_{1,1} + 2G_{2,0} + G_{3,1} + G_{2,2} - 4G_{1,1}^2 G_{0,0}^{-1} - 2G_{1,1} G_{2,0} G_{0,0}^{-1}) - 3G_{1,1} G_{0,0}^{-1}]; & i = 2, \\ (W - \omega) G_{1,1,0} G_{0,0,0}^{-1} + \delta W_{a \rightarrow 2a} [2W (G_{0,0,0} + 5G_{1,1,0} + 2G_{2,0,0} + 5G_{2,1,1} + G_{3,1,0} + G_{2,2,0} - 3G_{1,1,0} G_{2,0,0} G_{0,0,0}^{-1} - 12G_{1,1,0}^2 G_{0,0,0}^{-1}) - 5G_{1,1,0} G_{0,0,0}^{-1}]; & i = 3, \end{cases}$$

$$y_2^{(i)} = W^{-1} \begin{cases} 0; & i = 1, \\ 2\delta W_{2a \rightarrow a} [G_{1,1} G_{0,0}^{-1} - W (G_{0,0} + 2G_{2,0} + G_{2,2} - 4G_{1,1}^2 G_{0,0}^{-1})] - W; & i = 2, \\ 2\delta W_{2a \rightarrow a} [2G_{1,1,0} G_{0,0,0}^{-1} - W (G_{0,0,0} + 4G_{1,1,0} + 2G_{2,0,0} + 4G_{2,1,1} + G_{2,2,0} - 12G_{1,1,0}^2 G_{0,0,0}^{-1})] - W; & i = 3, \end{cases}$$

$$\begin{aligned}
z_2^{(i)} &= W^{-1} \begin{cases} 0; & i=1, \\ \delta W_{2a \rightarrow a} [G_{1,1} G_{0,0}^{-1} - 2W (G_{1,1} + G_{3,1} - 2G_{1,1} G_{2,0} G_{0,0}^{-1})]; & i=2, \\ \delta W_{2a \rightarrow a} [G_{1,1,0} G_{0,0,0}^{-1} - 2W (G_{1,1,0} + G_{2,1,1} + G_{3,1,0} - \\ - 3G_{1,1,0} G_{2,0,0} G_{0,0,0}^{-1})]; & i=3, \end{cases} \\
x_3^{(i)} &= W^{-1} \begin{cases} (W - \omega) G_2 G_0^{-1} + \delta W_{a \rightarrow 2a} [W(G_0 + G_4 - 2G_2^2 G_0^{-1}) - G_2 G_0^{-1}]; & i=1, \\ (W - \omega) G_{2,0} G_{0,0}^{-1} + \delta W_{a \rightarrow 2a} [W(G_{0,0} + 4G_{1,1} + 4G_{3,1} + 2G_{2,2} + \\ + G_{4,0} - 8G_{1,1} G_{2,0} G_{0,0}^{-1} - 4G_{2,0}^2 G_{0,0}^{-1}) - 3G_{2,0} G_{0,0}^{-1}]; & i=2, \\ (W - \omega) G_{2,0,0} G_{0,0,0}^{-1} + \delta W_{a \rightarrow 2a} [W(G_{0,0,0} + 8G_{1,1,0} + 8G_{2,1,1} + \\ + 8G_{3,1,0} + 4G_{2,2,0} + G_{4,0,0} - 24G_{1,1,0} G_{2,0,0} G_{0,0,0}^{-1} - \\ - 6G_{2,0,0}^2 G_{0,0,0}^{-1}) - 5G_{2,0,0} G_{0,0,0}^{-1}]; & i=3, \end{cases} \\
y_3^{(i)} &= W^{-1} \begin{cases} 0; & i=1, \\ 2\delta W_{2a \rightarrow a} [G_{2,0} G_{0,0}^{-1} - 2W (G_{1,1} + G_{3,1} - 2G_{1,1} G_{2,0} G_{0,0}^{-1})]; & i=2, \\ 4\delta W_{2a \rightarrow a} [G_{2,0,0} G_{0,0,0}^{-1} - 2W (G_{1,1,0} + G_{2,1,1} + G_{3,1,0} - \\ - 3G_{1,1,0} G_{2,0,0} G_{0,0,0}^{-1})]; & i=3, \end{cases} \\
z_3^{(i)} &= W^{-1} \begin{cases} \delta W_{2a \rightarrow a} [G_2 G_0^{-1} - W(G_0 + G_4 - 2G_2^2 G_0^{-1})] - W; & i=1, \\ \delta W_{2a \rightarrow a} [G_{2,0} G_{0,0}^{-1} - W(G_{0,0} + 2G_{2,2} + G_{4,0} - 4G_{2,0}^2 G_{0,0}^{-1})] - W; & i=2, \\ \delta W_{2a \rightarrow a} [G_{2,0,0} G_{0,0,0}^{-1} - W(G_{0,0,0} + 4G_{2,2,0} + G_{4,0,0} - \\ - 6G_{2,0,0}^2 G_{0,0,0}^{-1})] - W; & i=3, \end{cases} \tag{A1}
\end{aligned}$$

where

$$G_{\mathbf{R}} = \begin{cases} G_n = \frac{1}{N_1} \sum_q \frac{\cos naq}{2W + \tau^{-1} - 2W \cos aq}; & i=1, \\ G_{m,n} = \frac{1}{N_2} \sum_{q_1, q_2} \frac{\cos maq_1 \cos naq_2}{4W + \tau^{-1} - 2W (\cos aq_1 + \cos aq_2)}; & i=2, \\ G_{l,m,n} = \frac{1}{N_3} \sum_{q_1, q_2, q_3} \frac{\cos laq_1 \cos maq_2 \cos naq_3}{6W + \tau^{-1} - 2W (\cos aq_1 + \cos aq_2 + \cos aq_3)}; & i=3. \end{cases} \tag{A2}$$

N_i is the number of molecules in the crystal.

In (A1) the equations,

$$\left. \begin{aligned} & [\alpha + (W\tau)^{-1}] G_0 - \alpha G_{\mathbf{a}} = W^{-1}, \\ & [\alpha + (W\tau)^{-1}] G_{\mathbf{a}} - \sum_{\mathbf{a}'} G_{\mathbf{a}-\mathbf{a}'} = 0, \end{aligned} \right\} \tag{A3}$$

following from (2) for $\mathbf{R} - \mathbf{R}' = 0$, \mathbf{a} are used. Here \mathbf{a}' are the values of \mathbf{R} for the nearest-neighbour molecules, $\alpha = 2, 4, 6$ for $i = 1, 2, 3$, respectively.

In order to find $N_{\mathbf{a}}$ we must calculate the Green's functions (A2). For one- and two-dimensional systems their dependence on the parameter $W\tau$ in units $(2W)^{-1}$ has the form

$$G_0 = \{[1 + (2W\tau)^{-1}]^2 - 1\}^{-1/2}, \tag{A4}$$

the other one-dimensional Green's functions are expressed in terms of G_0 by using (2),

$$\left. \begin{aligned} G_{0,0} &= \pi^{-1}kK, \quad G_{1,0} = (2\pi)^{-1}(2K - \pi), \\ G_{1,1} &= (\pi k)^{-1}[(2 - k^2)K + 2E], \quad G_{2,0} = (\pi k)^{-1}(k^2K + 4E - 2\pi), \\ G_{2,1} &= (2\pi k^2)^{-1}[(8 - 6k^2)K - 8E + \pi k^2], \\ G_{3,1} &= (\pi k^3)^{-1}[(8 - 6k^2 - k^4)K - (8 + 10k^2)E + 4\pi k^2] + 2k^{-1}F, \\ G_{2,2} &= (\pi k^3)^{-1}[(8 - 8k^2 + k^4)K - 8(1 - k^2)E] - 2k^{-1}F, \\ G_{4,0} &= (\pi k^3)^{-1}[(112 + 16k^2)E - (48 - 48k^2 - k^4)K - \\ &\quad - 8\pi(4 + k^2)] - 4k^{-1}F, \end{aligned} \right\} \text{(A5)}$$

where $K \equiv K(k)$, $E \equiv E(k)$ are complete elliptic integrals, $F \equiv F(\frac{3}{2}, -\frac{1}{2}; 2; k^2)$ is the hypergeometric Gauss function, and $k^{-1} = 1 + (4W\tau)^{-1}$.

The Green's functions of a three-dimensional crystal are tabulated in [28], where $G_{l,m,n}$ is represented as

$$G_{l,m,n} = \int_0^\infty \exp(-\chi t) I_l(t) I_m(t) I_n(t) dt; \quad \chi = 3 + (2W\tau)^{-1}. \quad \text{(A6)}$$

$I_n(t)$ is the Bessel function of imaginary argument. By using the table of integrals (A6) of [28], as well as the relation (2) between Green's functions with varying R , we can obtain numerical values for all Green's functions contained in (A1).

The solution of the set of equations (3) for crystals for which the dynamic interaction between excitons is negligible can be obtained from (A1) at $\delta W_{a\alpha 2a} = 0$. Taking (A3) into account we get

$$N_a = P\tau [\alpha\omega (G_0^{-1} - \tau^{-1})^{-1} + W^{-1}(W - \omega)^{-1}]. \quad \text{(A7)}$$

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