Validity of the Bilinear Rate Equation for Exciton Annihilation and Expressions for the Annihilation Constant

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The validity of the well-known bilinear rate equation, used for the interpretation of exciton annihilation observations in molecular crystals, is examined on the basis of a recently constructed exact theory of the annihilation process. Experimentally attainable situations, in which the traditional equation is not applicable, are pointed out and alternative equations are given for use in such cases. Explicit expressions for the annihilation constant $\gamma$ are given for situations in which the usual rate equation is applicable.

1. Introduction

Excitons, formed e.g. as a result of optical absorption by molecular crystals, can undergo the process of annihilation. This process has been studied experimentally [1–5] as well as theoretically [6–10]. The experimental observations have been usually based on a rate equation for the exciton density $n(x,t)$ containing an annihilation term proportional to the square of this density

$$\frac{\dot{n}(x,t)}{\tau} + n(x,t) = D\nabla^2 n(x,t) - \gamma n^2(x,t). \quad (1.1)$$

Here $D$ is the exciton diffusion constant, $\tau$ the radiative (or more generally the total) lifetime and the key quantity is the annihilation constant $\gamma$. Observations are reported in the form of values for $\gamma$ and most theories derive expressions for $\gamma$ in terms of microscopic parameters.

Clearly an important question in this context is whether (1.1) is even formally valid. In an earlier paper [10], hereafter referred to as I, an exact theory of annihilation has been constructed and various aspects of the phenomenon including the effect of dimensionality, of transport coherence, and of long-range annihilation, have been analyzed. The above mentioned validity question has also been raised. On the basis of that analysis, the present paper pursues the validity question further, presents new alternatives to (1.1) when the latter is not valid, and gives explicit expressions for $\gamma$ when it is valid. An earlier result of Jortner et al. [7], that $\gamma$ equals $8\pi RD$, where $R$ is a radius of influence, is obtained as a special case.

2. Basic Assumptions and Final Results of the General Theory

The reader is referred to I for derivation details of the general theory. The basic assumptions and the final results of I are described below.

The model considered is a dilute collection of $\rho N$ excitons which decay radiatively, move on the $N$ sites of a crystal of arbitrary dimensions obeying translational invariance, and annihilate on contact. The motion in the absence of the annihilation interaction may possess arbitrary complexity including coherent nature and is characterized by $P_m(t)$, the probability that the $m^{th}$ site is occupied by the exciton at time $t$

$$P_m(t) = \sum \psi_m(t) P(0). \quad (2.1)$$

The quantities $\psi_m(t)$ are the propagators for exciton motion in the absence of radiative decay and of
annihilation. An example of the evolution equation for $P_n(t)$ above is

$$\frac{dP_n(t)}{dt} = \sum_n \left[ F_{mn} P_n(t) - F_{nm} P_m(t) \right]$$  \hspace{1cm} (2.2)

where $F_{mn}$ are transition rates describing motion. However (2.1) could well refer to a more general evolution than (2.2), such as that corresponding to a generalized master equation.

By constructing a space of twice the number of dimensions as that of the actual crystal and considering the evolution equations for $P_{m,n}(t)$, the probability that the first exciton is at $m$ and the second at $n$, exact solutions are obtained [10] for a system of two annihilating excitons. The annihilation interaction causes the depletion of excitons at $m$ at a rate proportional to $2P_{m,n}(t)$, the probability that the $m$th site is occupied by two excitons.

Let us define the quantities

$$\eta^k(t) = \sum_m e^{ikm} [P_m(t)]^2$$  \hspace{1cm} (2.3)

$$\psi^k(t) = \sum_m e^{ikm} [\psi_m(t)]^2$$  \hspace{1cm} (2.4)

where the $m$'s and $k$'s are generally vectors, and $P_m(t)$ in the right hand side of (2.3) holds in the absence of annihilation as given by (2.1). We shall take [11] $2b$ as the basic rate of depletion of the probability $2P_{m,n}(t)$ through annihilation. The analysis of I then results in the following equation for the evolution of $f_m(t)$, the probable number of excitons at $m$ at time $t$:

$$\frac{df_m(t)}{dt} + \frac{f_m(t)}{\tau} = \sum_n \left[ F_{mn} f_n(t) - F_{nm} f_m(t) \right]$$

$$- \frac{4b}{N} e^{-2iv} \int \frac{e^{ikz}}{z} \sum_k [e^{ikm} \eta^k(z) [1 + 2b \psi^k(z)]^{-1}].$$  \hspace{1cm} (2.5)

As this is the primary starting point of this paper, several remarks are in order. The probable number $f_m$ is normalized to 2 i.e. $\sum_m f_m(t) = 2$ in the absence of decay and annihilation. Here and henceforth $\epsilon$ is the Laplace variable and tildes denote Laplace transforms. The integration is over the Bromwich contour and represents a Laplace inversion. Equation (2.5) contains both the effects of radiative decay and of annihilation, neither of which is contained in the quantities $\eta, \psi, \psi$ in (2.1) - (2.4). Equation (2.5) has not appeared in the above form in I but it is straightforward to derive it from the analysis in I (e.g. from (5.1)-(5.12) of I). The simplified form of (2.5), with no radiative decay and therefore with the second term on the left side and the factor $e^{-2iv}$ multiplying the integral missing, and with only nearest neighbor transition rates $F_{mn} = F_0 [\delta_{m,n+1} + \delta_{m,n-1}]$, is (3.3) of I. Although (2.5) above corresponds to (2.2) for the motion, coherence effects can be immediately incorporated in the former by replacing the first term in its right side by the corresponding generalized master equation term

$$\int_0^t \left[ \frac{dP}{dt} \sum_n [\eta^k_m(t-t')] P_n(t') - \eta^k_m(t-t') P_m(t') \right].$$

The form of the equation and all the following analysis up to an including (4.2) remain unchanged. Only the explicit details of the propagators $\psi$ and $\eta$ are changed. Those details may be found in I.

3. Alternatives to and Validity of (1.1)

The traditionally used bilinear rate Eq. (1.1) may first be written in discrete form as

$$\frac{df_m(t)}{dt} + \frac{f_m(t)}{\tau} = \sum_n \left[ F_{mn} f_n(t) - F_{nm} f_m(t) \right] - \frac{4b}{N} \left[ f_m(t) \right]^2.$$

Clearly (3.1) is more valid than (1.1), which merely involves imposing on the former the continuum approximation $a \to 0$, where $a$ is the lattice constant. The quantity $\gamma$ in (3.1) is connected to the annihilation constant $\gamma$ of (1.1) through

$$\gamma = v \gamma = a^3 \gamma$$

where $v$ is the unit cell volume. In (3.2) the first identity holds generally and the second for a simple cubic (three-dimensional) lattice.

One must now analyse (2.5) and test under what conditions its last term may be approximated by $-\gamma f_m^2$. These are the validity conditions we seek for (3.1) and therefore for (1.1).

The first approximation that will be made is a Markoffian approximation. This means that in the Laplace domain the $\epsilon$ is to be replaced by 0. In view of the decay factor $e^{-2iv}$ in the last term of (2.5), this gives

$$\frac{df_m(t)}{dt} + \frac{f_m(t)}{\tau} = \sum_n \left[ F_{mn} f_n(t) - F_{nm} f_m(t) \right]$$

$$- \sum_n A_{mn} \left[ P_n(t) \right]^2 e^{-2iv}$$

where

$$A_{mn} = b \sum_k e^{-ik(m-n)} [1 + 2b \psi^k(t)]^{-1}.$$  \hspace{1cm} (3.4)

The $P_n(t)$ appearing in (3.3) corresponds to the situation in the absence of decay and annihilation, i.e. to
(2.1). Therefore, in the presence of decay but absence of annihilation, one has

\[ t_{m}(t) = P_{m}(t)e^{-\gamma t}. \]  

(3.5)

To make (3.3) closed in the quantities \( f_{m} \) we shall make the further approximation that (3.5) holds in the last term of (3.3). We then get the result

\[ \frac{f_{m}(t)}{\tau} + \sum_{n} \left[ F_{mn} f_{n}(t) - F_{nm} f_{m}(t) \right] = \sum_{n} \lambda_{mn} \delta_{m}^{2}(t). \]  

(3.6)

This new result is an alternative to (3.1) and reduces it if the further, spatially local, approximation

\[ t(t) = \psi^{0}(t) \]  

(3.7)

is made. If it is made, we get an explicit expression \( \psi^{0} \) (and thus for \( \gamma \)). If it is not made, we get the new Eq. (3.6) with spatially non-local annihilation terms. It might be interesting to write down a continuum version of (3.6)

\[ \frac{D}{Dt} \left[ \frac{u(x,t)}{\tau} \right] + \left[ \int_{0}^{t} \Gamma(t')d't \right] \delta(t), \]  

(3.8)

and compare it to (1.1). The approximation (3.7) and its consequences will be explored in Sect. 4 below. Let us now return to the exact result (2.5), refrain from making the Markovian replacement used above and, instead, make the spatially local approximation (3.7). Under these conditions the alternative to (3.1) is

\[ \frac{DF_{m}(t)}{dt} + F_{m}(t) \]  

\[ = \sum_{n} \left[ F_{mn} f_{n}(t) - F_{nm} f_{m}(t) \right] - \frac{t}{\tau} \left[ \int_{0}^{t} \Gamma(t'-t')f_{m}^{2}(t') \right] \]  

(3.9)

where the replacement (3.5) is again made, and where

\[ \Gamma(t) = e^{-2\gamma t}\left[ d_{m}e^{\gamma t}b^{1+b\psi_{m}}(c) \right]^{-1}. \]  

(3.10)

In obtaining (3.10) we have used the chain condition

\[ \sum_{m} \psi_{m}(t) \psi_{m}(t) = \psi_{1}(2t) \]  

(3.11)

to obtain

\[ \psi^{0}(t) = \sum_{m} \psi_{m}(t) = \sum_{m} \psi_{2m}(t) = \psi_{1}(2t) \]  

(3.12)

in which the last two propagators are single exciton quantities. Equation (3.12) and (3.7) along the Laplace scale theorem give (3.10).

Equation (5.7) of I, which corresponds to (3.10) above differs from the latter through the fact that the single exciton propagator appears in (3.10), and that in the latter the factor \( e^{-2\gamma t} \) is present. This factor makes a further Markovian approximation in (3.9), i.e. the replacement of \( \Gamma(t) \) by

\[ \left[ \int_{0}^{t} \Gamma(t')d't' \right] \delta(t), \]  

perfectly allowable. It was impossible to do so in the context of I because in the corresponding equations radiative decay was absent, the integrals blow up at least in 1 and 2 dimensions and a cut-off had to be introduced. The above analysis shows that the cut-off procedure used on intuitive grounds in I is actually exact.

It is thus seen that, to arrive at the usual bilinear rate Eq. (1.1) from the exact result (2.5), four assumptions are necessary: (i) the replacement of \( \left[ P_{m}(t) \right]^{2} \) appearing in (2.5) through (3.5), by its value in the presence of annihilation, although its actual value in (2.5) is in the absence of annihilation, (ii) the local approximation (3.7) which substitutes \( \psi^{0} \) by \( \psi^{0} \), (iii) the Markovian approximation which replaces \( \Gamma(t) \) by \( \Gamma(0) \), and (iv) the continuum approximation \( a \to 0 \) which introduces the density \( n(x,t) \) instead of the probable number of excitons \( f_{m}(t) \).

The fourth approximation is straightforward and little needs to be said concerning it. The Markovian approximation is generally valid at times large compared to the characteristic time of the corresponding "memory function" such as \( \Gamma(t) \). If exciton motion is fast compared to probe times, the Markovian approximation will thus be sound. The "memory function" here is basically the Laplace-inverse of

\[ \left[ 1 + 2b \psi^{0} \left( \frac{2}{\tau} \right) \right]^{-1} \]  

and is thus controlled primarily by exciton motion. The local approximation (ii) may be rather objectionable in general, although its applicability is also decided by how fast the excitons move. The replacement of \( \psi^{0} \) by \( \psi^{0} \) corresponds to the assumption that the single exciton propagator \( \psi_{m} \) is strongly peaked in \( m \)-space. But this is true at short times and the assumption therefore becomes worse as time goes on and all \( \psi_{m} \)'s begin to get identical to one another. We thus conclude that approximation (ii) is better at short times while (iii) is better at long times with respect to a characteristic motion time. Because one generally believes the latter to be of the order of a tenths of a picosecond for singlets in aromatic crystals and the probe time in the best available spectroscopy is several picoseconds, one might conclude that the Markovian approximation is good but the local approximation should generally not be used.
Approximation (i) is the least transparent of the lot. The reason for making it is to obtain an equation that is closed in \( f_m(t) \) or in the density \( n(x,t) \). If it is not made, the latter quantities require the computation of \( P_m(t) \) in the absence of annihilation and its substitution in (2.5). It is thus clear that in the light of the exact theory of [1], or of (2.5), it is never necessary to make approximation (i) (or for that matter, any of the four approximations). The exact observable values are all given. However, in attempting to understand the validity of the commonly used starting points (1.1) and (3.1) we are, it appears, forced to invoke it.

If we do make approximation (i) but refrain from making the others, we get the following usable annihilation equation

\[
\frac{df_m(t)}{dt} + \frac{f_m(t)}{\tau} = \sum_n \left[ F_{mn} f_n(t) - F_{nm} f_m(t) \right] - \int_0^t dt' \sum_n \dot{\lambda}_{mn}(t-t') f_n(t') \tag{3.13}
\]

\[
\dot{\lambda}_{mn} = \int d\xi e^{i\xi b} \sum_k e^{-i(km-n)} \left[ 1 + 2b \phi_k \left( e^{-\frac{\xi}{\tau}} \right) \right]^{-1} \tag{3.14}
\]

Equation (3.13), its spatially local simplification (3.9), and its Markoffian simplification (3.3) are the alternatives to (1.1) or (3.1) that we present in this paper. It is trivial to write down the continuum versions of (3.13) or (3.9) in the same way that (3.8) follows from (3.3).

What is remarkable is that the range of validity of (3.9) is non-overlapping with that of (3.3) since the former holds for short times and the latter for long times w.r.t. a motion time. It would, therefore, appear that making both the spatial local and the Markoffian approximation at the same time is self-contradictory and that the traditional Eq. (1.1) or (3.1) can never be recovered from our exact analysis. This is a rather unsatisfactory state of affairs since much experimental data has been adequately explained in terms of a version of (1.1) in which \( n(x,t) = n(t) \) is homogeneous in space.

\[
\frac{dn}{dt} + \frac{n}{\tau} = -\gamma n^2. \tag{3.15}
\]

We shall now show that while the passage from (3.13) to (1.1) does involve the self-contradiction mentioned above, in the case of sufficiently fast motion the passage from (3.13) to (3.15) does not. The Markoffian approximation may be made to give (3.3) or its continuum version (3.8). If the initial conditions on \( n(x,t) \) are homogeneous in space, i.e. if \( n(x,0) \) is independent of \( x \), then \( n^2(x') \) in (3.8) may be taken out of the integration, and (3.15) is immediately obtained, since \( \Gamma^2 n(x,t) = 0 \) from homogeneity and

\[
\gamma = \int dx' A(x-x'). \tag{3.16}
\]

Initial homogeneity in \( n(x,t) \) cannot be disturbed by the nature of the annihilation interactions and makes a local approximation unnecessary for the purposes of recovering (3.15). Nevertheless there is a note of warning here. Our analysis shows that although (3.15) is valid for homogeneous situations, (1.1), with the \( \Delta \Gamma^2 n(x,t) \) term present, is inapplicable. Inhomogeneous situations can be easily attained experimentally. The traditional Eq. (1.1) should not be used for the analysis of such experiments but one should turn to (3.8) or (3.13).

4. Explicit Expressions for \( \gamma' \) and \( \gamma \)

When the various approximations (i)-(iii) analyzed in Sect. 3 are valid and we recover (3.15), it is useful to know how the annihilation constant \( \gamma \) in (3.15) depends on explicit microscopic parameters. From the above analysis one obtains

\[
\gamma = \frac{\int_0^\infty dt \sum_n \lambda_{mn}(t)}{\frac{1}{b} + \psi_0 \left( \frac{1}{\tau} \right)}. \tag{4.1}
\]

Equation (4.1), whose one-dimensional case had been displayed in I, is a remarkably simple result for the annihilation constant. If exciton motion is fast w.r.t. annihilation, i.e. if \( b \ll 1/\psi_0(1/\tau) \), the constant \( \gamma \) equals \( \tau b \) and is hardly affected by characteristics of exciton motion. In the opposite limit wherein exciton motion is slow w.r.t. annihilation, i.e. when \( b \gg 1/\psi_0(1/\tau) \), one obtains

\[
\gamma = \tau \left[ \psi_0(1/\tau) \right]^{-1}. \tag{4.2}
\]

It is generally believed [9] that this latter limit, represented by (4.2), applies to most, if not all, situations of experimental interest. This belief appears to be supported by the relative magnitudes of spectral overlaps corresponding to transitions associated with the relevant processes: overlaps associated with the annihilation process are considerably larger than those associated with the motion process. If the Förster-Dexter prescription can be applied to both processes, the reduction of (4.1) to (4.2) is therefore valid.

We shall now analyze the effect of crystal dimensionality on the annihilation constant, recover the re-
suit of Jortner et al. [7] in three dimensions, and give alternative expressions for $\gamma$ in other situations. It will be assumed below that exciton motion is incoherent, isotropic, proceeds via nearest-neighbour transition rates, and that the annihilation process is much faster than motion, allowing the use of (4.2). It is straightforward to relax these assumptions if required. One can return to (4.1) trivially if exciton motion is not slow, anisotropy and long-range transition rates can be handled via conceptually straightforward, if mathematically tedious, techniques, and effects of coherence have been analyzed in I.

The relevant propagators of exciton motion have been given in I. If $F$ is the nearest-neighbour transition rate, $\psi_0(t)$ is given by [10]

$$\dot{\psi}_0(t) = \left[ e^{-2Ft} I_0(2Ft) \right]^d$$

(4.3)

where $d$ is the number of dimensions, $I_0$ is the modified Bessel function and the lattices in 2 and 3 dimensions are respectively simple square and simple cubic. To calculate $\gamma$ we require

$$\dot{\psi}_0(t) = \frac{\tau}{\tau + 1} e^{-2Ft} I_0(2Ft).$$

(4.4)

In one and two dimensions the results are immediate [10]. Thus, in a one-dimensional crystal

$$\dot{\psi}_0(t) = \frac{\tau}{\tau + 1} e^{-2Ft} I_0(2Ft).$$

(4.5)

In the limit of fast exciton motion (relative to decay), i.e. when $F \tau \gg 1$, one obtains

$$\gamma = 2\tau (F \tau)^{1/2}.$$  

(4.6)

In the limit of slow exciton motion, i.e. when $F \tau \ll 1$, one has, on the other hand

$$\gamma = \tau \left[ 2F + (1/\tau) \right].$$

(4.7)

For a two-dimensional crystal (4.4) gives (with $d = 2$),

$$\dot{\psi}_0(t) = \frac{2\pi}{1 + 4F \tau} K \left( \frac{4F \tau}{1 + 4F \tau} \right)$$

(4.8)

where $K(x)$ is the complete elliptic integral of the first kind. In the limit of fast exciton motion ($F \tau \gg 1$) one gets

$$\gamma = \tau \frac{2\pi F}{\ln(4F \tau)}$$

(4.9)

whereas for $F \tau \ll 1$ i.e. for slow exciton motion, (4.8) gives

$$\gamma = \tau \left[ 4F + (1/\tau) \right].$$

(4.10)

To analyze the case of the three-dimensional crystal we rewrite (4.4), through trivial transformations, as

$$\dot{\psi}_0(t) = \frac{\tau}{\tau + 1} e^{-2Ft} I_0(2Ft)$$

(4.11)

and compare the expression thus obtained to (2.1) of Maradudin et al. [13].

$$I(a, b; c; \beta) = \frac{\pi}{\beta} \left[ 1 + \frac{1}{2} \beta \right]^{-1} e^{-\beta^2} I_0(I_0)$$

(4.12)

In terms of the $I$-function defined in [13], the annihilation constant $\gamma$ is then given by

$$\gamma = \tau (2F) \left[ I \left( 0, 0, 0, 1; 1 + \frac{1}{6F \tau} \right) \right]^{-1}.$$  

(4.13)

Equation (4.13) is the expression for $\gamma$ valid in 3-dimensions for arbitrary values of $F \tau$ and can be used practically with the help of the tables of the $I$-function. To evaluate (4.13) in the limits of slow and fast motion we use the asymptotic expressions given in [13]. In the slow exciton limit ($F \tau \ll 1$), from their (4.3), one obtains, for $\beta \ll 1$,

$$I(0, 0, 0, 1; \beta) = \frac{1}{3} \beta \left[ 1 + \frac{1}{6} + O \left( \frac{1}{\beta^2} \right) \right]$$

(4.14)

Since $\beta = 1 + (16F \tau) \gg 1$ in this limit, one gets

$$\gamma = \tau (1 + (1 + F \tau)^{-1} \approx \tau (1 + 1 - F \tau).$$

(4.15)

For the fast motion case ($F \tau \gg 1$), the asymptotic expression of Eq. (4.9) of [13], valid for $(\beta - 1) \ll 1$, may be used. The asymptotic expression is

$$I(0, 0, 0, 1; \beta) = 0.505462 - \frac{3(\beta - 1)^{1.2}}{2\pi^2} - 0.014625 [3(\beta - 1)] + \ldots$$

(4.16)

and it gives, for the annihilation constant,

$$\gamma = \tau (3.956776) F \left[ 1 + 0.314870 \frac{1}{F \tau} + \ldots \right].$$

(4.17)

It is interesting to notice that for this case when exciton motion is much faster than decay, (4.17) may be written approximately as

$$\gamma = 4F \tau.$$  

(4.18)

The factor 4, it should be remembered, is an approximation for 3.956776. The remarkably simple result (4.18) takes the form

$$\gamma = 8\pi RD.$$  

(4.19)
Table I. Values of $\gamma'$ in extreme limits

<table>
<thead>
<tr>
<th>Dimensionality</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slow: $F \ll 1/r$</td>
<td>$2F(1 - 2F)$</td>
<td>$(1 - 4F)$</td>
<td>$(1 - 4F)$</td>
</tr>
<tr>
<td>Fast: $F \gg 1/r$</td>
<td>$2F(1/r)^{-1}$</td>
<td>$2F[\ln(2) - 2F(1/r)]^{-1}$</td>
<td>$4F$</td>
</tr>
</tbody>
</table>

given by Jortner et al. [7] for the annihilation problem and earlier by Chandrashekhar and Smoluchowski [14] in other contexts, we identify $Fa^2$ as the diffusion constant $D$, $r$ as $a^2$, and take $a 2\pi$ as the radius of influence $R$. It is particularly satisfying that $R$ is essentially the lattice distance $a$ in this model with short-range annihilation. Alternatively one may use factors of order unity to connect $D$ and $Fa^2$ and absorb their reciprocals in $R$.

Table 1 shows the values of $\gamma'$ for the limits of slow and fast exciton motion in the $1-d$, $2-d$, and $3-d$ cases. Note that the annihilation constant $\gamma$ equals $\gamma'$ times a unit cell volume for the $3-d$ case, area for the $2-d$ case, and length (the lattice constant itself) for the $1-d$ case. We observe that proportionality of $\gamma'$ to $F$ (as is implicit in the traditional and frequently used result (4.19)) occurs only in the $3-d$ system for exciton motion which is fast with respect to decay. We have found that this conclusion has been arrived at in the earlier analysis of Suna [9], who has displayed a table like ours although only in the fast motion limit. Our results reduce in the continuum limit to those in [9] provided some numerical constants are rearranged or reinterpreted. The logarithmic behaviour in $2-d$ systems and square-root dependence in $1-d$ systems is clear in Suna’s results. The generality of our approach allows us to go beyond them, however, and to calculate the annihilation constant for arbitrary lattice structures, degree of coherence and extent of anisotropy.

5. Discussion

We have analyzed the validity of the bilinear rate equation used traditionally for exciton annihilation, provided alternatives to that equation, and given explicit expressions for the annihilation constant $\gamma$ from the general theory. The point of departure for our analysis is an exact calculation [10]. The frequently used bilinear Eq. (3.15) is found to be valid for long times but its generalization (1.1) which is also used often is found not to be valid under any conditions analyzed in this paper. Alternatives provided for long-time analysis are (3.8) in the continuum case and (3.6) more generally. For short times (3.9) and its obvious continuum counterpart may be used. For arbitrary times (3.13) is valid. Th e equation is non-local in time as well as space. It is curious that the conditions for the local approxima tion in time to be valid are non-overlapping with those required for the validity of the local approximation in space. It is this feature that raises serious objection to the use of (1.1).

For situations wherein the bilinear equation, e.g. (3.15), is valid, the annihilation constant $\gamma$ is given generally by (4.1) and, for the case of fast annihilation, by (4.2). Explicit expressions for motion which is slow with respect to decay are: (4.7), (4.10) and (4.15) for 1, 2 and 3 dimensional motion; for motion fast with respect to decay the respective expressions are (4.6), (4.9) and (4.17). Equation (4.17) has the simpler approximate form (4.18) and reduces simply to the oft-quoted result (4.19).

This analysis suggests that (4.19) should not be used for slow excitons in 3-dimensional crystals, and for any excitons in lower-dimensional crystals. It is clear from the table that fast excitons in $1-d$ and $2-d$ crystals exhibit expressions for $\gamma'$ which are quite different from the traditional result (4.19). It would appear that the slow-motion entries in the table are proportional to $F$. However it must be remembered that they correspond to $F$ being negligible with respect to $1/r$ and that $\gamma'$ is given essentially by $1/\tau$ in those cases. Since excitons are disappearing in our system both through decay and annihilation, one might be tempted to argue heuristically that one should subtract $1/\tau$ from the entries for $\gamma'$. While such a procedure would restore proportionality to $F$, the coefficient of the bilinear term in the annihilation equation such (3.1) would be the full entry in the table. Furthermore the slow $3-d$ case would give a negative result.

The general conclusion to be drawn from these considerations is that traditional results such as (4.19) should not be used without examination of the dimensionality and the relative value of $F$ with respect to $1/r$.

To avoid confusion we would also like to correct a few printing errors appearing in I. There should be no $N$ in (5.4), (5.5), (5.7) and (5.9) of I and the definition (3.5) of the elliptic integral $K(x)$ should have $x^2$ rather than $x$ in the integral. This same definition also applies to the present paper. It is important to stress this correction in meaning of $K(x)$ because two different usages exist in the literature. Also, the $M$-function in (3.9) of I is no other than the $I$-function in (4.12) of the present paper.

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References


11. The quantity 2b in this paper equals B in [10]. It is convenient to use the present notation: it leads to simpler forms for expressions used more frequently.

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