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Incoherent motion of excitons in one-dimensional crystals with one trap

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Abstract. The Pauli master equation for the incoherent exciton motion in one-dimensional crystals with a single trap is solved analytically. Exact results for the probability propagator and the total probability are addressed with the help of an analytic solution of the Volterra type integral equation. To demonstrate the effect of the trap for the exciton motion clearly, a numerical calculation has been made.

1. Introduction

In recent years much attention has been paid to the set of problems deeply connected with the coherence and incoherence effects for the exciton transfer in molecular aggregates. Considerable progress in understanding these problems has been achieved by Silbey [1], Kenkre [2] and Reineker [3]. On the other hand, to get the explicit and analytic solution of the probability propagator for the exciton motion, some simple models have been favoured. Of special interest is the one-dimensional trapping model corresponding to the sensitized luminescence experiments described by the Pauli master equation for the probability $P_n(t)$ to find the exciton at site n

$$\frac{\mathrm{d}}{\mathrm{d}t}P_n = F(P_{n+1} + P_{n-1} - 2P_n) - cP_n\delta_{n0} \qquad n = 0, \pm 1, \pm 2, \ldots \qquad F, c > 0 \tag{1}$$

where F is the intermolecular rate constant and c is the trapping rate of the trap at site $n = 0$. This model was first investigated by Skala and Bilek several years ago [4]. However, as we indicated more recently [5] and as we will show in the following, the centre results for the probability propagator and the total probability they obtained are incorrect, which definitely affects the correctness of their numerical calculation. Therefore, it is necessary to study this problem further.

In the present paper, we address the analytic solution of this problem for the incoherent exciton motion with the help of an explicit solution of the Volterra type integral equation. The exact results for the probability propagator and the total probability of finding the exciton in the one-dimensional system are presented, which provide the possibility of making the numerical analysis for any value of the reduced trap c/F. Finally, we illustrate the effect of the trap for the exciton motion numerically.

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2. Probability propagator

In solving (1), we first perform the Fourier transform

$$f_k(t) = \sum_n e^{-ink} P_n(t) \tag{2}$$

where $P_n(t)$ is given by the inverse Fourier transform

$$P_n(t) = \frac{1}{2\pi} \int_0^{2\pi} dk e^{ink} f_k(t). \tag{3}$$

The amplitude propagator $f_k(t)$ in k space satisfies the following integral equation:

$$f_k(t) = e^{2F(\cos k-1)t} f_k(0) - \frac{c}{2\pi} \int_0^t dt' e^{2F(\cos k-1)(t-t')} \int_0^{2\pi} dk' f_{k'}(t'). \tag{4}$$

For simplicity, we consider the situation of the exciton being located at site 0 at the initial time, i.e., $P_n(0) = \delta_{n0}$. This makes $f_k(0)$ become 1. Thus, substituting (4) into (3), and by using the identity [6]

$$e^{x\cos k} = \sum_m I_m(x) e^{imk} \tag{5}$$

where I_m is the modified Bessel function, we get the following integral equation for the probability propagator $P_n(t)$ in real space

$$P_n(t) = e^{-2Ft} I_n(2Ft) - c \int_0^t dt' P_0(t') e^{-2F(t-t')} I_n(2F(t-t')). \tag{6}$$

The self-propagator $P_0(t)$, i.e., the probability propagator of the initially excited site, satisfies the well known Volterra integral equation of the second kind [7]

$$P_0(t) = e^{-2Ft} I_0(2Ft) - c \int_0^t dt' P_0(t') e^{-2F(t-t')} I_0(2F(t-t')). \tag{7}$$

This equation can be solved analytically by performing the Laplace transform

$$L[P_0(t)] = \frac{L[e^{-2Ft} I_0(2Ft)]}{1 + cL[e^{-2Ft} I_0(2Ft)]} \tag{8}$$

where $L[\ ]$ is the Laplace operator. By using the table of Laplace transforms [8], we have

$$L[e^{-2Ft} I_0(2Ft)] = \frac{1}{\sqrt{s}\sqrt{s+4F}} \tag{9}$$

which leads to (8) being

$$L[P_0(t)] = L[P_{01}(t)] + L[P_{02}(t)] + L[P_{03}(t)] \tag{10}$$

with

$$L[P_{01}(t)] = \frac{1}{\sqrt{s}\sqrt{s+4F}} \tag{11}$$

$$L[P_{02}(t)] = \frac{1}{\sqrt{s}\sqrt{s+4F}} \frac{c^2}{((s-a)(s+b)} \tag{12}$$

$$L[P_{03}(t)] = -\frac{c}{((s-a)(s+b)} \tag{13}$$

where

$$a = \sqrt{4F^2+c^2} - 2F \qquad b = \sqrt{4F^2+c^2} + 2F. \tag{14}$$

Employing the convolution (Faltung) theorem and the table of Laplace transforms [8] to (11)–(13) yields

$$P_{01}(t) = \mathrm{e}^{-2Ft} I_0(2Ft) \tag{15}$$

$$P_{02}(t) = \frac{c^2}{\sqrt{4F^2+c^2}} \mathrm{e}^{-2Ft} \int_0^t \mathrm{d}t' I_0(2F(t-t')) \sinh(t'\sqrt{4F^2+c^2}) \tag{16}$$

$$P_{03}(t) = -\frac{c}{\sqrt{4F^2+c^2}} \sinh(t\sqrt{4F^2+c^2}) \mathrm{e}^{-2Ft}. \tag{17}$$

This gives the solution for the self-propagator

$$\begin{aligned} P_0(t) = \mathrm{e}^{-2Ft}\{I_0(2Ft) - \frac{c}{\sqrt{4F^2+c^2}} \sinh(t\sqrt{4F^2+c^2})\} \\ + \frac{c^2}{\sqrt{4F^2+c^2}} \mathrm{e}^{-2Ft} \int_0^t \mathrm{d}t' I_0(2F(t-t')) \sinh(t'\sqrt{4F^2+c^2}). \end{aligned} \tag{18}$$

Substituting (18) into (6), to get the explicit expression for the probability propagator is straightforward.

Another equivalent expression for the self-propagator can be derived directly from (18) by completing the integral. The result is

$$\begin{aligned} P_0(t) = \mathrm{e}^{-2Ft}\left\{ I_0(2Ft) + \frac{c}{\sqrt{4F^2+c^2}} \mathrm{e}^{-t\sqrt{4F^2+c^2}} \right\} \\ - \frac{c}{\sqrt{4F^2+c^2}} \mathrm{e}^{-2Ft} \left\{ I_0(2Ft) + 2\sum_{k=1}^{\infty} I_{2k}(2Ft) \left(\frac{c - \sqrt{4F^2+c^2}}{2F} \right)^{2k} \right\}. \end{aligned} \tag{19}$$

Comparing this result with equation (20) of [4] one will find that Skala and Bilek's result missed the last term of (19).

3. Total probability

The total probability of finding the exciton in the crystal under the influence of the trap can be obtained by summing both sides of (6):

$$\sum_n P_n(t) = \mathrm{e}^{-2Ft} \sum_n I_n(2Ft) - c \int_0^t \mathrm{d}t' P_0(t') \mathrm{e}^{-2F(t-t')} \sum_n I_n(2F(t-t')). \tag{20}$$

Using the identity [6]

$$\mathrm{e}^z = \sum_n I_n(z) \tag{21}$$

equation (20) reads

$$\sum_n P_n(t) = 1 - c \int_0^t \mathrm{d}t' P_0(t'). \tag{22}$$

By substituting (19) into (22), and by using the identity [6]

$$\int_0^z \mathrm{d}t \mathrm{e}^{-t} I_n(t) = z\mathrm{e}^{-z} [I_0(z) + I_1(z)] + n \left[\mathrm{e}^{-z} I_0(z) - 1\right] + 2\mathrm{e}^{-z} \sum_{k=1}^{n-1} (n-k) I_k(z) \tag{23}$$

one finds that

$$\sum_n P_n(\tau) = 1 + \frac{\alpha^2}{\sqrt{1+\alpha^2}(1+\sqrt{1+\alpha^2})} (\mathrm{e}^{-(1+\sqrt{1+\alpha^2})\tau} - 1) + \frac{1}{\sqrt{1+\alpha^2}} (\mathrm{e}^{-\tau} I_0(\tau) - 1)$$
$$+ \frac{4\alpha^2}{\sqrt{1+\alpha^2}} \sum_{k=1}^{\infty} (\sqrt{1+\alpha^2} - \alpha)^{2k} \sum_{l=1}^{2k-1} (2k-l) \mathrm{e}^{-\tau} I_l(\tau) \tag{24}$$

where $\tau = 2Ft$, $\alpha = c/2F$. This result is completely different from that of [4] (see equations (24) and (25) in [4]). In fact, it is easy to show that Skala and Bilek's result for the total probability is unacceptable in physics. To see this point, we consider the long time behaviour for the total probability. By taking the limit $t \to \infty$ in (24) and (25) of [4], we find that the total probability becomes infinity since (24) and (25) of [4] contain the factor $t\mathrm{e}^{-t}[I_0(t) + I_1(t)]$ which will be large enough with increasing time to infinity. Obviously, such a result is unreasonable.

4. Discussion and summary

In contrast to equation (10) of [4], our expressions for the propagator $P_n(t)$ presented by (6) and (18) (or (19)) and the total probability $\sum_n P_n(t)$ presented by (24) provide the possibility of carrying out the numerical analysis for any value of the reduced trap c/F. To demonstrate the effect of the trap for the exciton motion clearly, based on the expressions (6), (18) and (24) we calculated the propagators $P_n(t)$ ($n = 0, 1, 2$) as functions of the dimensionless time $2Ft$ for different values of the reduced trap $c/2F$ and the total probability $\sum_n P_n(t)$ as a function of the reduced trap $c/2F$ for different instants which were presented in figures 1–3.

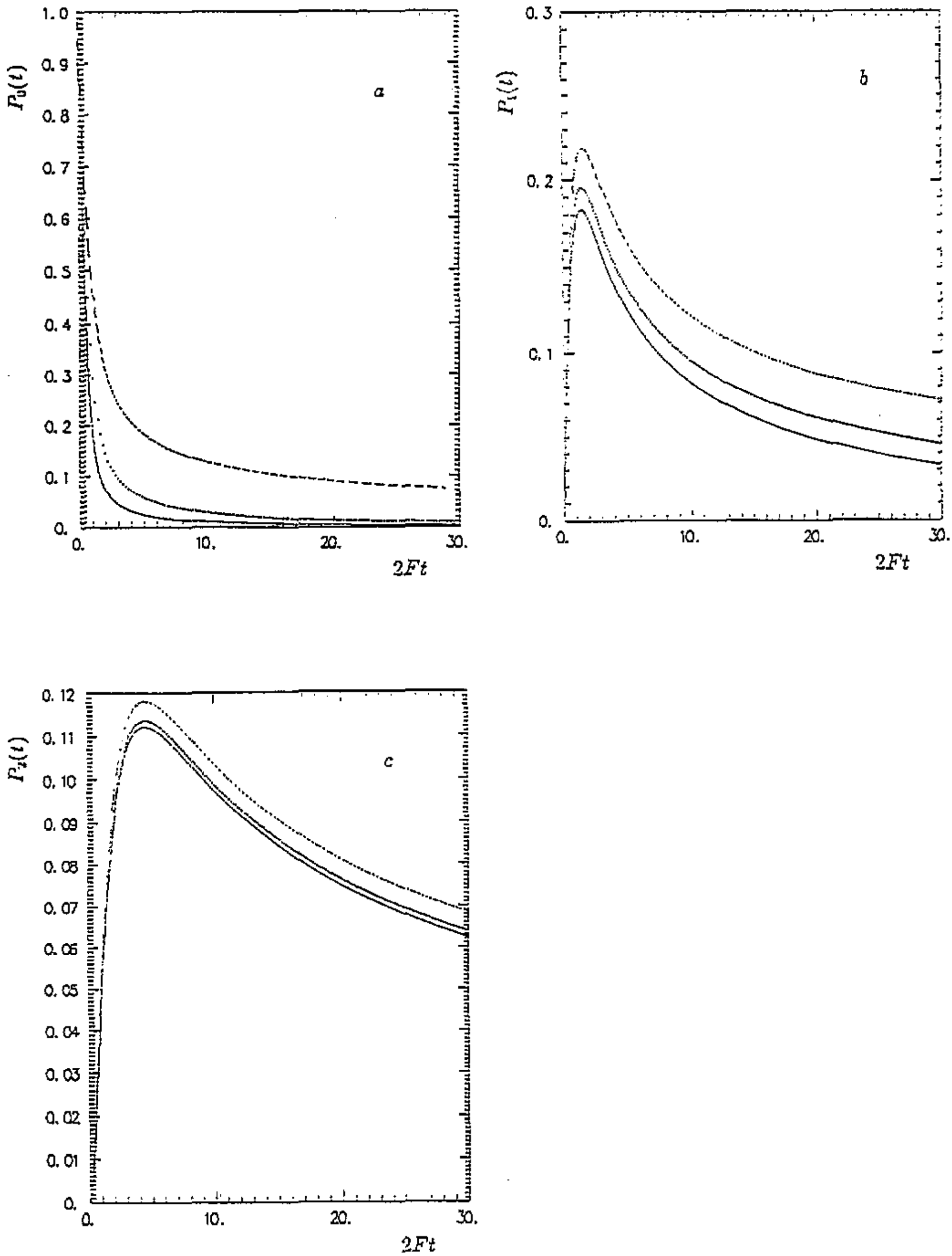

Figure 1. The propagators (*a*) $P_0(t)$, (*b*) $P_1(t)$ and (*c*) $P_2(t)$ plotted as functions of the dimensionless time $2Ft$ for different values of the reduced trap $c/2F$. The dotted ($c/2F = 0.5$) and full ($c/2F = 1$) curves show the effect of the trap in comparison with the case of the perfect lattice ($c/2F = 0$, broken curve).

In figures 1 and 2, the effect of the trap for the exciton motion has been exhibited through a plot of the propagator $P_n(t)$ versus the dimensionless time $2Ft$ for different values of the reduced trap $c/2F$. From these curves it can be clearly seen that the probabilities of

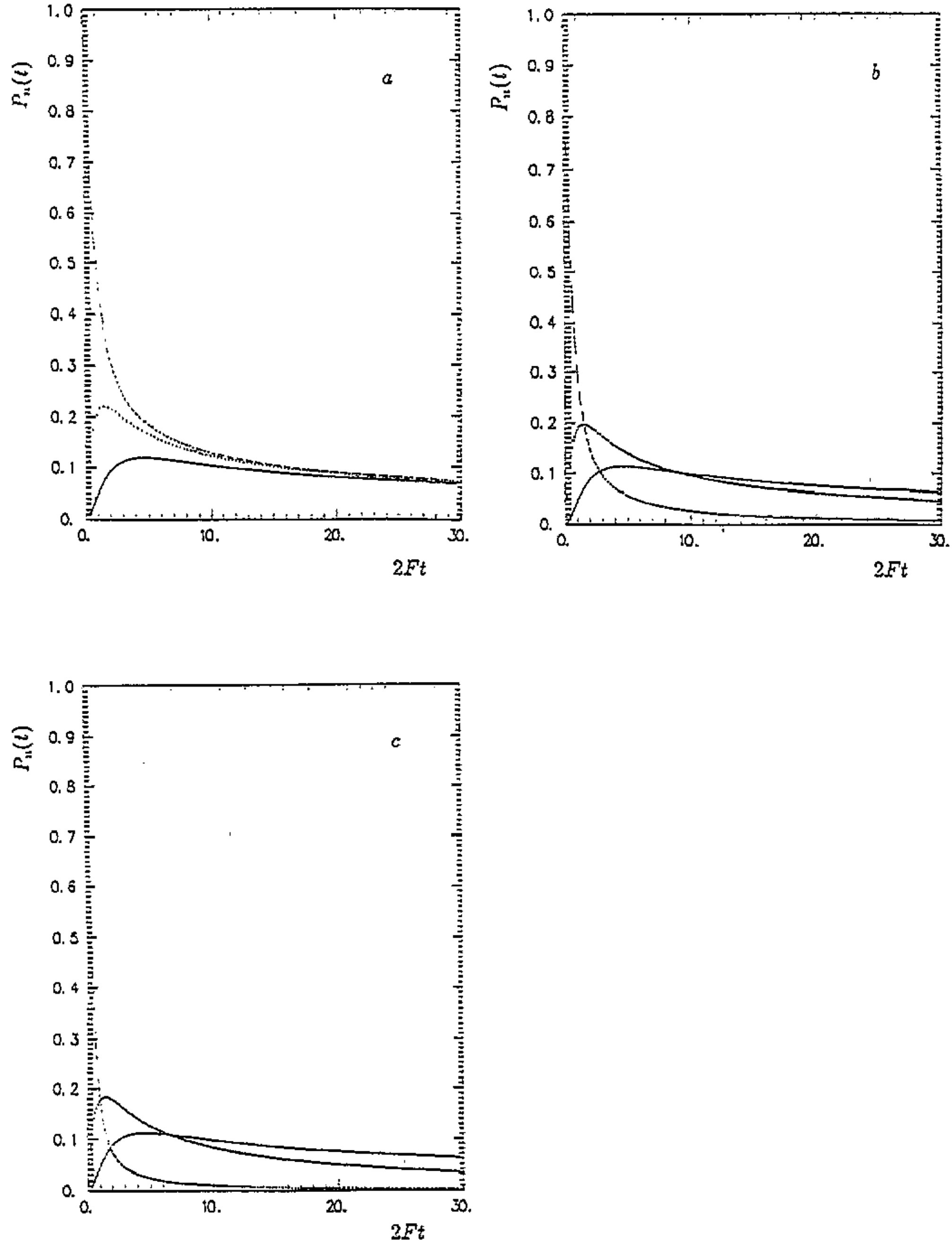

Figure 2. The propagator $P_n(t)$ plotted as a function of the dimensionless time $2Ft$ for different values of the reduced trap $c/2F$. The curves show the cases $c/2F = 0$ (*a*), 0.5 (*b*), and 1 (*c*) for $n = 0$ (broken curve), 1 (dotted curve), and 2 (full curve), respectively.

finding the exciton at sites $n = 0$, 1, and 2 with the trap ($c/2F \neq 0$) are lower than the case without the trap ($c/2F = 0$). This means that the presence of the trap annihilates the excitons, which can also be seen from the fact that the total probability of finding the exciton

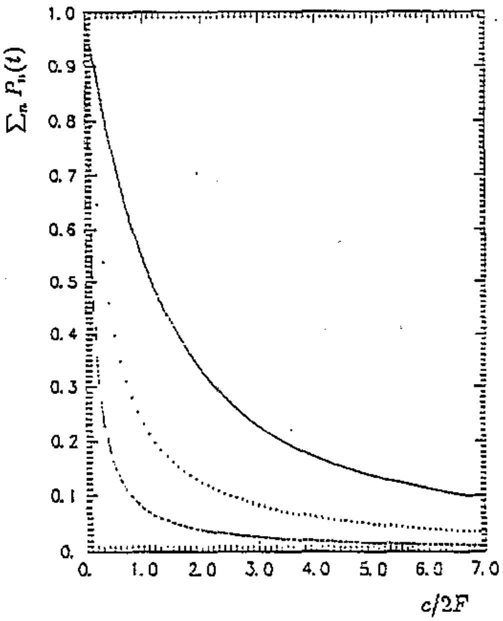

Figure 3. The total probability $\sum_n P_n(t)$ plotted as a function of the reduced trap $c/2F$ for different instants. The full curve shows the case $2Ft = 1$ while the dotted and broken curves show the cases $2Ft = 10$ and $2Ft = 100$ respectively.

in the crystal drops rapidly with increasing the reduced trap $c/2F$ as shown in figure 3.

In figure 3, another evident property is shown definitely that the total probability to find the exciton in the crystal, which represents the total number of excitons, tends towards vanishing with increasing time as long as the trap is present. In the limit case of $t \to \infty$, it can be proved by (24) straightforwardly that the total probability will reach its limit value $\sum_n P_n(t \to \infty) = 0$, as expected.

Comparing our figures 1 and 2 with figure 1 of [4], one can find that the propagators $P_n(t)$ $(n = 1, 2)$ have obvious maxima in different instants and $P_n(t)$ show sensible variation with the dimensionless time $2Ft$, while these features are obscure in figure 1 of [4].

In summary, we have solved analytically the Pauli master equation for the incoherent exciton motion in one-dimensional crystals with one trap. The exact and explicit solutions for the probability propagator and the total probability have been obtained with the help of an analytic solution of the Volterra type integral equation, from which the effect of the trap can be seen clearly. Our analytic results in this paper will provide the basis for further investigation on the theory of the exciton transport since such topics arise in a number of contexts.

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