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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 analytic solution of the Volterra type integral equation. To demonstrate the effect of the trap for the exciton motion clearly, the numerical calculation has been made. It is found that the role of the trap is only to accelerate the escape of the exciton towards infinity. This is completely different from the situation of the coherent exciton motion under the influence of impurities.

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 the understanding of 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

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

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

In the present Letter, we address the analytic solution of this problem for the incoherent exciton motion with the help of explicit solution of the Volterra type integral equation. The exact results for the probability propagator and the total probability to find 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.

2. Probability propagator

In solving Eq. (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 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 the simplicity, we consider the situation of the exciton being located at site 0 in the initial time, i.e., $P_n(0) = \delta_{n0}$. This makes $f_k(0)$ become 1. Thus, substituting Eq. (4) into Eq. (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 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. After some calculations, we have

$$L[P_0(t)] = \frac{1}{\sqrt{s}\sqrt{s+4F}}\left(1 + \frac{c^2}{(s-a)(s+b)}\right) - \frac{c}{(s-a)(s+b)} \ , \tag{9}$$

where

$$a = \sqrt{4F^2+c^2} - 2F, \qquad b = \sqrt{4F^2+c^2} + 2F \ . \tag{10}$$

This gives the solution for the self-propagator

$$\begin{aligned} P_0(t) &= e^{-2Ft}\Big\{I_0(2Ft) - \frac{c}{\sqrt{4F^2+c^2}}\sinh(t\sqrt{4F^2+c^2})\Big\} \\ &+ \frac{c^2}{\sqrt{4F^2+c^2}} e^{-2Ft}\int_0^t dt' I_0(2F(t-t'))\sinh(t'\sqrt{4F^2+c^2}) \ . \end{aligned} \tag{11}$$

Substituting Eq. (11) into Eq. (6), to get the explicit expression for the probability propagator is straightforward.

Another equivalent expression for the self-propagator can be derived directly from Eq. (11) by completing the integral. The result is

$$\begin{aligned} P_0(t) &= e^{-2Ft}\Big\{I_0(2Ft) + \frac{c}{\sqrt{4F^2+c^2}} e^{-t\sqrt{4F^2+c^2}}\Big\} \\ &- \frac{c}{\sqrt{4F^2+c^2}} e^{-2Ft}\Big\{I_0(2Ft) + 2\sum_{k=1}^{\infty} I_{2k}(2Ft)\Big(\frac{c-\sqrt{4F^2+c^2}}{2F}\Big)^{2k}\Big\} \ . \end{aligned} \tag{12}$$

Comparing this result with Eq. (20) of Ref. [4] one will find that Skala and Bilek's result missed the last term of Eq. (12).

3. Total probability

The total probability to find the exciton in the crystal under the influence of the trap can be obtained by summing the both sides of Eq. (6)

$$\sum_n P_n(t) = e^{-2Ft}\sum_n I_n(2Ft) - c\int_0^t dt' P_0(t') e^{-2F(t-t')}\sum_n I_n(2F(t-t')) \ . \tag{13}$$

Using the identity [6]

$$e^z = \sum_n I_n(z) \ , \tag{14}$$

Eq. (13) reads

$$\sum_n P_n(t) = 1 - c\int_0^t dt' P_0(t') \ . \tag{15}$$

By substituting Eq. (12) into Eq. (15), and by using the identity [6]

$$\begin{aligned} \int_0^z dt e^{-t} I_n(t) &= z e^{-z}[I_0(z) + I_1(z)] + n\left[e^{-z} I_0(z) - 1\right] \\ &+ 2e^{-z}\sum_{k=1}^{n-1}(n-k) I_k(z) \ , \end{aligned} \tag{16}$$

one finds that

$$\begin{aligned} \sum_n P_n(\tau) &= 1 + \frac{\alpha^2}{\sqrt{1+\alpha^2}(1+\sqrt{1+\alpha^2})}\Big(e^{-(1+\sqrt{1+\alpha^2})\tau} - 1\Big) \\ &+ \frac{1}{\sqrt{1+\alpha^2}}\Big(e^{-\tau} I_0(\tau) - 1\Big) \\ &+ \frac{4\alpha^2}{\sqrt{1+\alpha^2}}\sum_{k=1}^{\infty}(\sqrt{1+\alpha^2} - \alpha)^{2k}\sum_{l=1}^{2k-1}(2k-l) e^{-\tau} I_l(\tau) \ , \end{aligned} \tag{17}$$

where $\tau = 2Ft$, $\alpha = c/2F$. This result is completely different from that of Ref. [4] (see Eqs. (24) and (25) in Ref. [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 behavior for the total probability. By taking the limit $t \to \infty$ in Eqs. (24) and (25) of Ref. [4], we find that the total probability becomes infinity since Eqs. (24) and (25) of Ref. [4] contain the factor $te^{-t}[I_0(t)+I_1(t)]$ which will be large enough with increasing time to infinity. Obviously, such a result is unreasonable.

4. Discussion and summary

In contrast to Eq. (10) of Ref. [4], our expressions for the propagator $P_n(t)$ presented by Eqs. (6) and (11) (or (12)) and the total probability $\sum_n P_n(t)$ presented by Eq. (17) 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), (11) and (17) 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 Figs. 1-3.

In Figs. 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 seen clearly that (1), the probabilities to find the exciton at sites $n = 0$, 1, and 2 with the trap ($c/2F \neq 0$) are lower than the case without the trap ($c/2F = 0$); (2), there is a maximum probability to find the exciton at the site $n(\neq 0)$ in some instant, however, such instant for the appearance of the maximum probability does not dependent on the trap. These properties mean that the role of the trap is only to *accelerate* the escape of the exciton towards infinity, which can also be seen from the fact that the total probability to find the exciton in the crystal drops rapidly with increasing the reduced trap $c/2F$ as shown in Fig. 3. Such findings are completely different from the situation of the coherent exciton motion under the influence of impurities [8] where, just the opposite, the role of the impurity is to *decelerate* the escape of the exciton towards infinity.

In Fig. 3, another evident property is shown definitely that the total probability to find the exciton in the crystal 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 Eq. (17) straightforwardly that the total probability will reach its limit value $\sum_n P_n(t \to \infty) = 0$, as expected.

Comparing our Figs. 1 and 2 with Fig. 1 of Ref. [4], one can find that the propagators $P_n(t)$ $(n = 1, 2)$ have obvious maximums in different instants and $P_n(t)$ show sensible variation with the dimensionless time $2Ft$, while these features are obscure in Fig. 1 of Ref. [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 analytic solution of the Volterra type integral equation, from which the effect of the trap can be seen clearly. Our analytic results in this Letter will provide the basis for further investigation on the theory of the exciton transport since such topics arise in a number of contexts.

Acknowledgments

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Figure Captions

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

Fig. 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 $c/2F = 0$ (Fig. a), 0.5 (Fig. b), and 1 (Fig. c) for $n = 0$ (dashed line), 1 (dotted line), and 2(solid line), respectively.

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

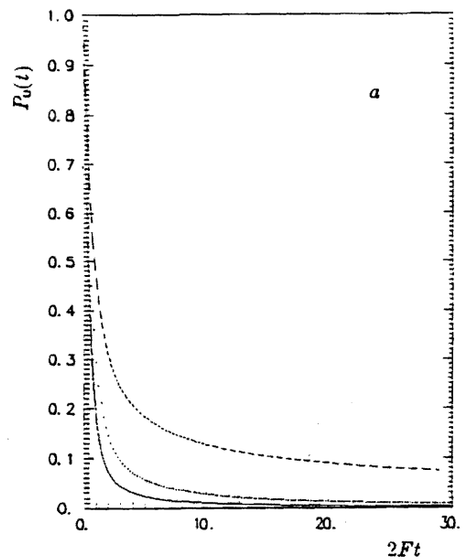
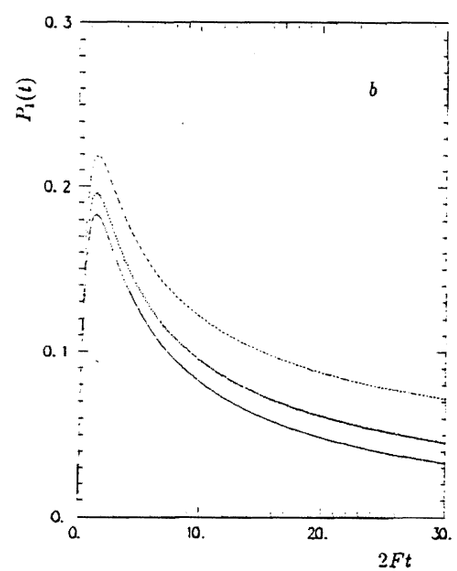


Fig. 1



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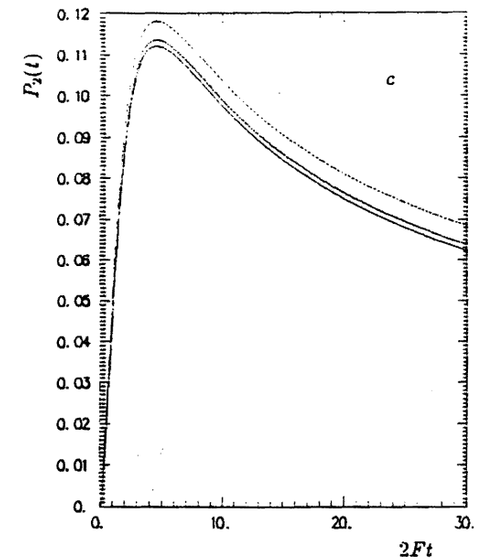

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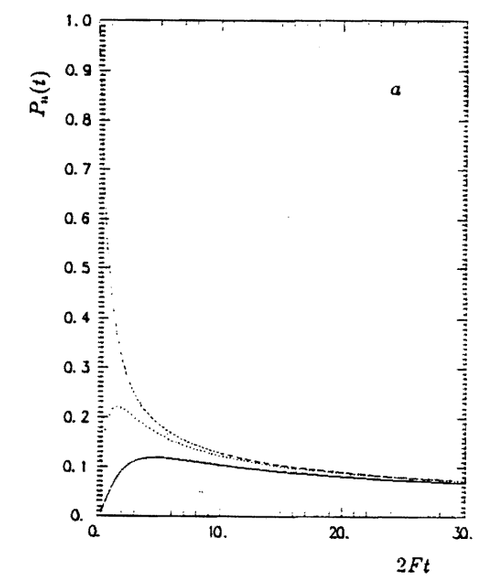
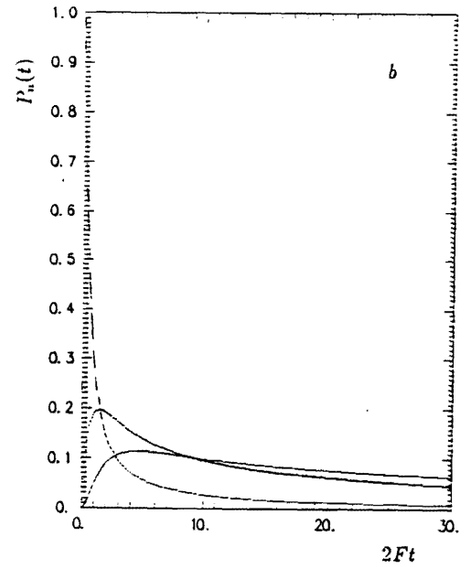


Fig. 2



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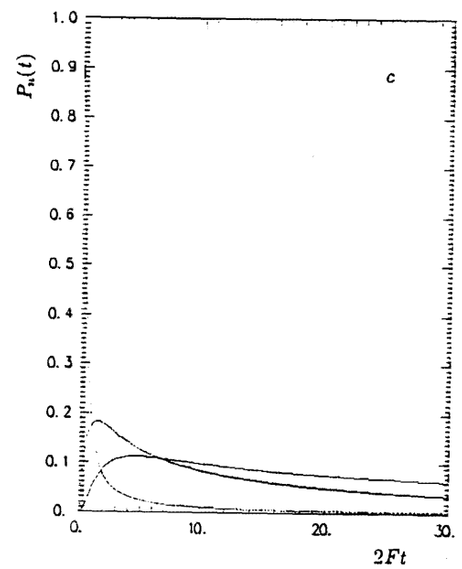

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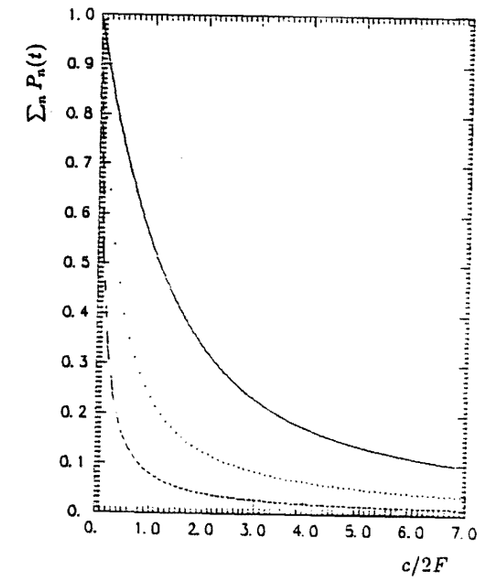

Fig. 3.