ANALYTIC SOLUTION OF THE PAULI MASTER EQUATION FOR THE EXCITON MOTION IN THE INFINITE LINEAR CHAIN WITH A SINGLE TRAP

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An explicit analytic solution of the Pauli master equation for the incoherent exciton motion in the infinite linear chain with a single trap is presented. The total probability to find the exciton in the chain is also calculated.

1. Introduction

The motion of excitons in the condensed pase is actively investigated in recent time (see e.g. ref. [1]). The simplest one-dimensional trapping model corresponding to the sensitized luminescence experiments uses the Pauli master quation (PME) for the probability $P_n(t)$ to find the exciton at site n,

$$dP_n/dt = F(P_{n+1} + P_{n-1} - 2P_n) - c\delta_{n0}P_n\ , \quad n = ... -1, 0, 1, ..., \quad F, c > 0\ , \tag{1}$$

where F is the intermolecular rate constant and c is the trapping rate of the trap at site $n=0$. The solution of eq. (1) in the Laplace domain was obtained by means of the defect technique [1], however, an explicit analytic expression for $P_n(t)$ has not been known till now. The aim of this work is to provide the analytic solution of the problem (1).

2. Probability propagator

A general solution of eq. (1) for $c=0$ is known [1]. It has the form

$$P_n(t) = \sum_p P_p(0)\psi_{np}(t)\ , \tag{2}$$

where $P_p(0)$ are given initial values of the probabilities and

$$\psi_{np}(t) = \exp(-2Ft)I_{n-p}(2Ft) \tag{3}$$

is the so-called propagator i.e. the solution of the PME satisfying the localized initial condition

$$\psi_{np}(t) = P_n(t) \quad \text{for} \quad P_n(0) = \delta_{np} \tag{4}$$

and $I_n(t)$ is the modified Bessel function.

The most obvious but lengthy way of calculating the propagator of eq. (1) for $c \neq 0$ is analogous to the well-known approach to the problem of the electron states in a finite one-dimensional box. First, general solutions for $n<0$ and $n>0$ are found. In the second step, eq. (1) for $n=0$ is used to match the solutions in these two regions. The resulting expression for $\psi_{np}(t)$ contains coefficients which can be calculated from the initial condition (4). Instead of using this somewhat cumbersome approach we suggest a more straightforward method.

We search for the propagators of eq. (1) for $c \neq 0$. Similarly as above we require the fulfilment of the initial condition (4). First we note that except for the equation corresponding to $n=0$ all the equations are the same as in the case $c=0$. Therefore, it is advantageous to assume the propagator for $c \neq 0$ in the form of a linear combination of the propagators (3) corresponding to $c=0$ since any such linear combination satisfies all $n \neq 0$ equations and only one $n=0$ equation has to be solved. To be more concrete we assume the propagator of eq. (1) in the form of a linear combination of the propagators (3)

$$\psi_{np}(t) = \exp(-2Ft)\left[I_{n-p}(2Ft) + \sum_{l=1}^{\infty} a_{l|p|} I_{l+|n|}(2Ft) \right] . \quad (5)$$

This formula requires more detailed explanation. The first term in eq. (5) gives the propagator (3) corresponding to $c=0$ whilst the rest takes into account the effect of the trap. The first term is chosen in such a way that it guarantees the fulfilment of the correct initial condition (4) assuming the second term is zero at $t=0$. Taking into account the last condition and the property of the Bessel functions $I_n(0) = \delta_{n0}$ we get $l=1, 2, \ldots$ Further we note that except for the initial condition (4) the PME (1) is symmetric with respect to $n \to -n$. The initial condition is fulfilled by the first term so that we may assume that the sum in eq. (5) is a symmetric function of n and p. This leads to $|n|$ and $|p|$ in eq. (5). We note also that eq. (5) is a special case of the Neumann series [2]

$$\psi_n(t) = \exp(-2Ft) \sum_l a_l I_{l+n}(t) . \quad (6)$$

Now we substitute expression (5) into eq. (1) for $n=0$ and compare the coefficients before the Bessel functions of the same order. The resulting system of the reccurent relations for $a_{l|p|}$

$$a_{2|p|} = -(c/F)\delta_{0|p|} , \qquad a_{2|p|} = -(c/F)a_{1|p|} - (c/F)\delta_{1|p|} ,$$

$$a_{l+1,|p|} = -(c/F)a_{l,|p|} + a_{l-1,|p|} - (c/F)\delta_{l,|p|} , \quad l \geqslant 2 , \quad (7)$$

is easily solvable with the result

$$a_{l|p|} = -(c/F)(-\mathrm{i})^{l-|p|-1} U_{l-|p|-1}(\mathrm{i}c/2F) . \quad (8)$$

Here, the U's denote the analytic continuation of the Chebyshev polynomials of the second kind defined by therelations

$$U_0(x) = 1 , \qquad U_1(x) = 2x , \qquad U_{n+1}(x) = 2xU_n(x) - U_{n-1}(x) , \quad (9)$$

for an arbitrary complex argument. Using the relation (8) in eq. (5) we get the propagator of the PME (1) in the form

$$\psi_{np}(t) = \exp(-2Ft)\left(I_{n-p}(2Ft) - \frac{c}{F} \sum_{j=0}^{\infty} \mathrm{i}^j U_j(\mathrm{i}c/2F) I_{|n|+|p|+j+1}(2Ft) \right) . \quad (10)$$

Eq. (10) has a simple physical meaning. The first term on the right-hand side is the same as in the case of the chain without the trap ($c=0$). The second term results from the presence of the trap and, in contrast to the first one, it is not translationally invariant. It is a function of $|n| + |p|$ i.e. the total distance from the initial excitation site p to the trap and from the trap to site n where the probability to find the exciton is calculated.

The expression (10) is not suitable for the numerical calculations for $c/F > 1$. It has the following reason. Using the separation of variables

$$P_n(t) = \exp(\lambda t) c_n \quad (11)$$

the stationary problem corresponding to eq. (1) is

$$\lambda c_n = F(c_{n+1} + c_{n-1} - 2c_n) - c\delta_{n0} c_n . \quad (12)$$

The propagator corresponding to eq. (1) can be expressed in the form of a linear comination of the states (11)

$$\psi_{np}(t)=\sum_{\lambda} c_n(\lambda)c_p(\lambda)\,\exp(\lambda t)\ . \tag{13}$$

Here, $\sum_\lambda$ denotes the summation over all the states. Detailed analysis of the difference equation (12) (see also ref. [3]) gives the band of the extended states and one localized state existing for any $c\neq 0$. The extended states corresponding to

$$\lambda=2F(\cos\vartheta-1)\ ,\quad \vartheta\in(0,\pi) \tag{14}$$

are symmetric ($c^s_n=c^s_{-n}$)

$$c^s_n=\left[\pi\left(1+\frac{c^2}{4F^2\sin^2\vartheta}\right)\right]^{-1/2}\left(\cos n\vartheta+\frac{c}{2F\sin\vartheta}\sin(|n|\vartheta)\right) \tag{15}$$

or antisymmetric ($c_n=-c_{-n}$)

$$c_n=\pi^{-1/2}\sin(n\vartheta)\ . \tag{16}$$

The localized state equals

$$c_n=(\mathrm{tgh}\,\gamma)^{1/2}[\mathrm{sgn}(-c/F)\exp(-\gamma)]^{|n|}\ . \tag{17}$$

where

$$\gamma=\ln\{|c/2F|+[1+(c/2F)^2]^{1/2}\} \tag{18}$$

and

$$\lambda=-2F(1+\cosh\gamma)\ . \tag{19}$$

Substituting expressions (14)–(19) into eq. (13) we get another formula for the propagator. It is not necessary, however, to evaluate (13). We note only that the localized state contribution to the propagator is expanded in eq. (10) in terms of the delocalized Bessel functions. The highly localized state (γ large or $c/F\gg 1$) has to be expanded into a large number of Bessel functions yielding troubles with the numerical evaluation of the series. It is therefore desirable to write the localized and extended state contributions to eq. (10) separately. Adding and subtracting the localized state contribution to eq. (10) we get after some calculation an equivalent form of the propagator

$$\begin{aligned}\psi_{np}(t)&=\exp(-2Ft)\tanh(\gamma)[\mathrm{sgn}(-c/F)\exp(-\gamma)]^{|n|+|p|}\exp[2Ft\,\mathrm{sgn}(-c/F)\cosh\gamma]\\&\quad+\exp(-2Ft)\Big(I_{n-p}(2Ft)-\tanh(\gamma)[\mathrm{sgn}(-c/F)\exp(-\gamma)]^{|n|+|p|}\\&\quad\times\sum_{k=0}^{|n|+|p|}(2-\delta_{0,k})[\mathrm{sgn}(-c/F)]^k\cosh(k\gamma)I_k(2Ft)\Big)\ .\end{aligned} \tag{20}$$

Expression (20) is another decomposition of the propagator (10). The first term is the localized state contribution while the rest represents the delocalized state part. We see that the localized state contribution goes exponentially down with increasing $|n|$ and $|p|$. The numerical calculation of the propagator from eq. (20) for any c/F makes no difficulty.

Fig. 1 illustrates the effect of the trap at site $n=0$ on the probabilities to find the exciton at sites $n=0$, 1 and 2 assuming the initial excitation at the trap site ($p=0$). In the case of the existence of the trap ($c\neq 0$) the probabilities are lower than for $c=0$. Fig. 2 shows that the effect of the trap on the probabilities goes down wit the increasing distance of the trap and the initial excitation site p.

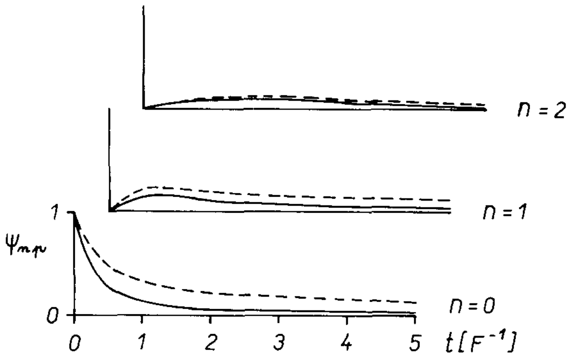

Fig. 1. The propagator $\psi_{np}(t)$ for $p=0$, $n=0, 1, 2$, $c=F$ as a function of time (full line). The dashed line corresponds to $c=0$ (no trap).

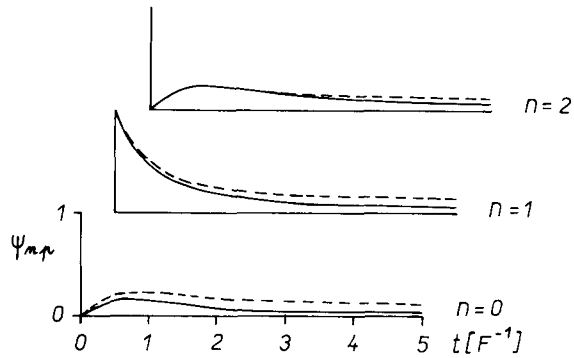

Fig. 2. The propagator $\psi_{np}(t)$ for $p=1$, $n=0, 1, 2$, $c=F$ as a function of time (full line). The dashed line corresponds to $c=0$ (no trap).

The effect of the trap on the total probability to find the exciton in the chain can be found from the equation

$$\frac{\mathrm{d}}{\mathrm{d}t}\sum_n P_n = -cP_0 \,, \tag{21}$$

showing that

$$\sum_n P_n \to 0 \quad \text{for} \quad t\to\infty \quad \text{for any } c>0 \,. \tag{22}$$

Eq. (22) can be reduced to the equation for the propagators

$$\frac{\mathrm{d}}{\mathrm{d}t}\sum_n \psi_{np}(t) = -c\psi_{0p}(t) \,. \tag{23}$$

Substituting the propagator (10) into eq. (23) and performing the integration we get

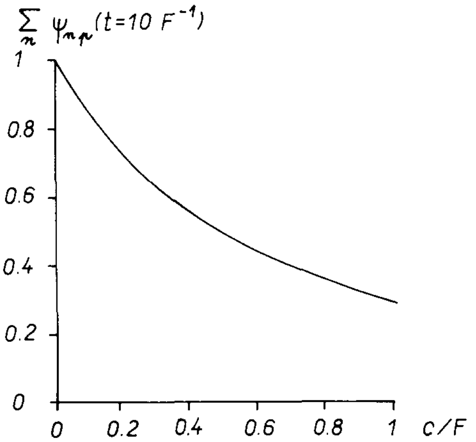

Fig. 3. The total probability $\sum_n \psi_{np}(t)$ to find the exciton in the chain for $t=10F^{-1}$, $p=0$ as a function of c/F.

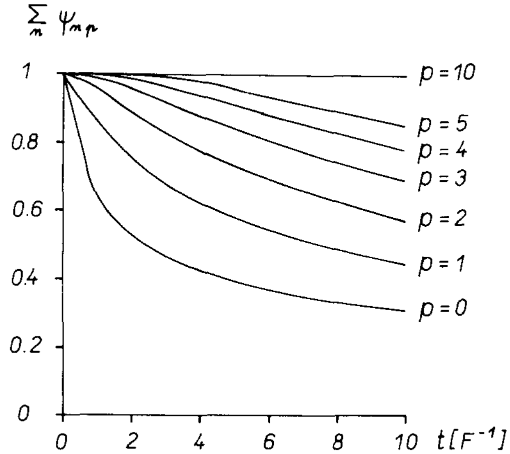

Fig. 4. The total probability $\sum_n \psi_{np}(t)$ to find the exction in the chain for $p=0, 1, 2, 3, 4, 5$ and 10 as a function of time. $c=F$.

$$\sum_n \psi_{np}(t) = 1 - \frac{c}{2F}\left(g_{|p|}(2Ft) - \frac{c}{F}\sum_{j=0}^{\infty} \mathrm{i}^j U_j(\mathrm{i}c/2F)\, g_{|p|+j+1}(2Ft) \right), \tag{24}$$

where

$$g_p(t) = t\mathrm{e}^{-t}[I_0(t)+I_1(t)] + p[\mathrm{e}^{-t}I_0(t)-1] + 2\mathrm{e}^{-t}\sum_{k=1}^{p-1}(p-k)I_k(t)\,. \tag{25}$$

Similarly to eq. (10) formula (24) is suitable for the numerical calculations for $c/F<1$. More complex expression applicable for any c/F can be derived from eq. (20).

Fig. 3 shows the total probability to find the exciton in the chain at time $t=10F^{-1}$ for the initial excitation at the trap site ($p=0$) as a function of c/F. Increasing the trap constant c the total probability goes quickly down. Fig. 4 shows the decreasing effect of the trap on the total probability with the increasing distance of the initial excitation site p from the trap. For $p=0$, the initial excitation is at the trap so that the total probability goes at first quickly down. Increasing time, the exciton becomes delocalized, the effect of the trap on the delocalized exciton is small and the decrease of the total probability is slower. For large p, the initially localized excitation needs some time to reach the trap so that the total probability is close to 1 at the beginning. Increasing time it goes slowly down.

3. Conclusion

The probability propagator for the incoherent exciton motion in the infinite linear chain with a single trap has been analytically calculated. Two analytic expressions for the propagator have been given. In the first case the propagator is written as the propagator for the chain without the trap plus the part resulting from the existence of the trap while in the second case the propagator is decomposed into the localized and extended states parts. The localized state contribution i.e. the effect of the trap goes exponentially down with the increasing distances $|n|$ and $|p|$ from the trap. The analytic expression for the total probability to find the exciton in the chain has also been given.

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