EXACT PROPAGATOR FOR COHERENT MOTION OF EXCITONS IN A LINEAR CHAIN WITH ONE IMPURITY

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An explicit analytic expression for the propagator for the coherent motion of excitons in a one-dimensional crystal with one impurity is presented and the probability of capturing the exciton by the localized state is calculated.

The propagation of excitons in molecular crystals has been actively investigated in recent times (see e.g. refs. [1,2]). One interesting basic issue is that of the effect of the degree of transport coherence on the character of the motion (see refs. [1–4]). Another important step in the direction of more realistic models is the investigation of the effect of impurities. Some important results in this respect are known [1], however, the so-called propagator describing the time and spatial development of the motion has not been known till now. For this reason we decided to investigate this problem for a simple model represented by an infinite linear chain with a single impurity. The purpose of this work is to provide an analytic expression for the propagator for the coherent motion in the chain. The expression is analytic, has a simple physical interpretation and can be exploited in further calculations (the mean square displacement, quantum yields, and others). We show also that because of the existence of the localized state in the chain the exciton does not spread out in the crystal for $t\to\infty$, however, it remains partly localized in the neighbourhood of the impurity.

We assume that the coherent motion of the exciton in the chain with the impurity at the origin is described by the time-dependent Schrödinger equation for the site amplitudes $c_n(t)$ in the form

$$\mathrm{i}\,\mathrm{d}c_n/\mathrm{d}t=c_{n-1}+c_{n+1}\,,\quad n\neq 0;\quad ,\ \mathrm{i}\,\mathrm{d}c_0/\mathrm{d}t=c_{-1}+\epsilon c_0+c_1\,,\quad n=0\,. \tag{1}$$

We assume $\hbar=1$, the nearest-neighbour hopping integral equal to 1 and zero diagonal matrix element of the hamiltonian everywhere except for the impurity (ϵ). The key quantity giving the solutions of eqs. (1) is the amplitude propagator $\psi_{np}(t)$, i.e. the solution $c_n(t)$ corresponding to the initial excitation at site $p=...,-1,0,1,...$

$$\psi_{np}(t)=c_n(t)\quad\text{for}\quad c_n(0)=\delta_{np}\,. \tag{2}$$

The probability to find the exciton at site n is $|\psi_{np}(t)|^2$.

We first exhibit the result and then show its derivation. The propagator equals

$$\psi_{np}(t)=(-\mathrm{i})^{n-p}J_{n-p}(2t)+\tanh(\gamma)[\mathrm{sgn}(\epsilon)\mathrm{e}^{-\gamma}]^{|n|+|p|}$$
$$\times\left(\exp[-2\mathrm{i}t\,\mathrm{sgn}(\epsilon)\cosh\gamma]-\sum_{k=0}^{|n|+|p|}\epsilon(k)[\mathrm{sgn}(\epsilon)]^k\cosh(k\gamma)(-\mathrm{i})^kJ_k(2t)\right)$$

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$$+2\tanh\gamma\,(-\mathrm{i})^{|n|+|p|+1}\{\mathrm{sgn}(\epsilon)\sinh[(|n|+|p|)\gamma]U_{|n|+|p|+1}(2t\mathrm{e}^{-\gamma},2t)$$
$$-\mathrm{i}\cosh[(|n|+|p|)\gamma]U_{|n|+|p|+2}(2t\mathrm{e}^{-\gamma},2t)\}\,. \quad (3)$$

Here, $U_n(x,y)$ denotes the Lommel function [5]:

$$U_n(x,y)=\sum_{j=0}^{\infty}(-1)^j(x/y)^{2j+n}J_{2j+n}(y)\,, \quad (4)$$

γ is defined by

$$\mathrm{e}^{\gamma}=|\epsilon|/2+(1+\epsilon^2/4)^{1/2}\,, \quad (5)$$

$\epsilon(k)=1$ for $k=0$ and 2 otherwise, $\mathrm{sgn}(\epsilon)=1$ for $\epsilon>0$ and -1 for $\epsilon<0$ and J is the Bessel function. Another form of eq. (3) which is not, however, suitable for the numerical calculations for large ϵ is

$$\psi_{np}(t)=(-\mathrm{i})^{n-p}J_{n-p}(2t)+\epsilon(-\mathrm{i})^{|n|+|p|+1}\sum_{j=0}^{\infty}(-1)^jU_j(\mathrm{i}\epsilon/2)J_{|n|+|p|+j+1}(2t)\,, \quad (6)$$

where the U_j of one argument denote the analytic continuation of the Chebyshev polynomials of the second kind defined by the recurrence relations

$$U_0(x)=1\,,\quad U_1(x)=2x\,,\quad U_{n+1}(x)=2xU_n(x)-U_{n-1}(x)\,, \quad (7)$$

for arbitrary complex argument.

Eqs. (3) and (6) have a simple physical meaning. The first term on the right-hand side of eq. (3) or (6) is the same as in case of a perfect chain without the impurity [1] and represents the motion of the exciton without scattering. The second term results from the scattering on the impurity 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 impurity and from the impurity to site n where the probability to find the exciton is calculated. It can be shown that the structure of eq. (6) corresponds to the perturbation expansions of the Dyson equation

$$G=G_0+G_0VG_0+G_0VG_0VG_0+\ldots\,, \quad (8)$$

where the role of G, G_0 and V in the site representation is played by $\psi_{np}(t)$, $(-\mathrm{i})^{n-p}J_{n-p}(2t)$ and $\delta_{n0}\delta_{p0}\epsilon\delta(t-t')$, respectively. For example, the Born approximation to $\psi_{np}(t)$ exact to the first power of ϵ equals

$$\psi_{np}^{\mathrm{B.a.}}(t)=(-\mathrm{i})^{np}J_{n-p}(2t)+\epsilon(-\mathrm{i})^{|n|+|p|+1}U_{|n|+|p|+1}(2t,2t)\,. \quad (9)$$

We see that the Lommel function U in eq. (9) describes the scattered wave in the Born approximation.

In a periodic crystal without the impurity the exciton spreads out with increasing time in the whole volume of the crystal. We show that the motion in the presence of the impurity has a different character. For $t\to\infty$ the propagator in the neighbourhood of the impurity is given by the localized state contribution (see below and eq. (3))

$$\psi_{np}(t\to\infty)=\tanh\gamma\,[\mathrm{sgn}(\epsilon)\mathrm{e}^{-\gamma}]^{|n|+|p|}\exp[2\mathrm{i}t\,\mathrm{sgn}(\epsilon)\cosh\gamma]\,, \quad (10)$$

n, p finite, $t\to\infty$, and the probability to find the exciton at site n equals

$$|\psi_{np}(t\to\infty)|^2=[\tanh\gamma\,\mathrm{e}^{-\gamma(|n|+|p|)}]^2\,. \quad (11)$$

The total probability of the exciton to be captured by the localized state

$$\sum_n|\psi_{np}(t\to\infty)|^2=\tanh\gamma\,\mathrm{e}^{-2\gamma|p|} \quad (12)$$

is less than 1 and approaches 1 for $|\epsilon|\gg1$ and $p=0$. The effect of the impurity goes down exponentially with

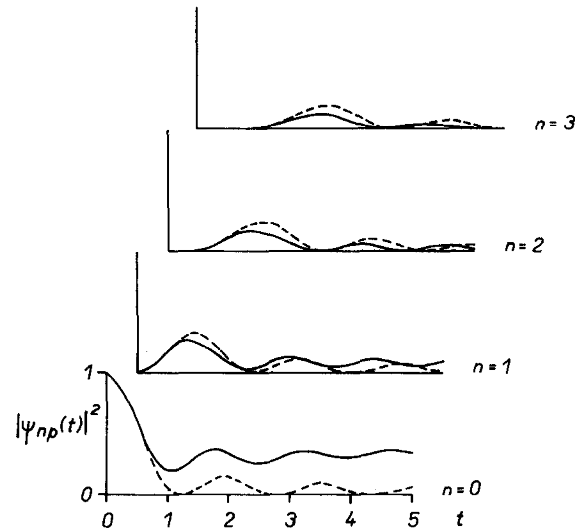

Fig. 1. The probability propagator $|\psi_{np}(t)|^2$ for $p=0$, $n=0, 1, 2, 3$ and $\epsilon=1.5$ (full line) in comparison with the propagator for $\epsilon=0$ (dashed line) showing the capturing of the exciton by the localized state.

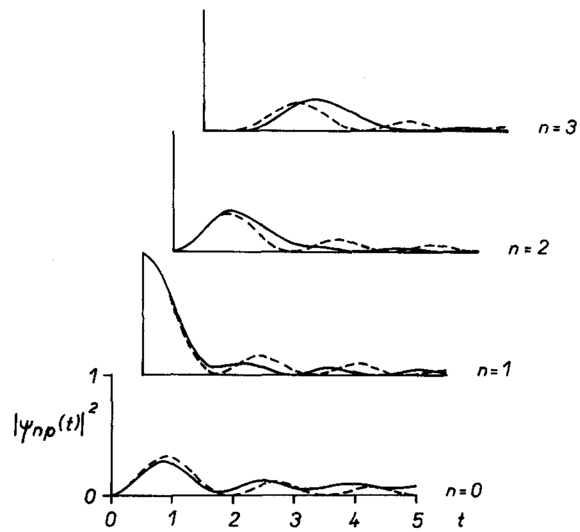

Fig. 2. The probability propagator $|\psi_{np}(t)|^2$ for $p=1$, $n=0, 1, 2, 3$ and $\epsilon=1.5$ (full line) in comparison with the propagator for $\epsilon=0$ (dashed line) showing the decreasing effect of the impurity with increasing p.

increasing $|n|$ and $|p|$.

The probability propagator $|\psi_{np}(t)|^2$ is shown for $\epsilon=0$ and 1.5, $p=0$ and 1 in figs. 1 and 2. We see from fig. 1 for $\epsilon=1.5$ that the exciton localized at $n=0$ for $t=0$ only partly spreads out in the crystal with increasing time. We see also (see namely $n=0$ and 1) that the probability to find the exciton in the neighbourhood of the impurity does not go to zero for large t. The propagators for $\epsilon=1.5$ and $\epsilon=0$ have similar wave-like character. The oscillations are a little bit quicker for $\epsilon=1.5$. Fig. 2 shows that the effect of the impurity goes down with increasing $|p|$. The probability propagators are functions of $|\epsilon|$.

The derivation of eq. (3) is based on the solution of the stationary Schrödinger equation corresponding to eqs. (1)

$$Ec_n = c_{n-1} + c_{n+1}\ , \quad n \neq 0; \qquad Ec_0 = c_{-1} + \epsilon c_0 + c_1\ , \quad n=0\ . \tag{13a,b}$$

Solving this problem the propagator $\psi_{np}(t)$ can be calculated from

$$\psi_{np}(t) = \sum_E c_n^*(E) c_p(E) \mathrm{e}^{-\mathrm{i}Et}\ , \tag{14}$$

where $\sum_E$ denotes the summation over all states. The fulfilment of eq. (2) follows from the completeness relation

$$\psi_{np}(0) = \sum_E c_n^*(E) c_p(E) = \delta_{np}\ . \tag{15}$$

The Green function method usually applied to eqs. (13) yields the transcendent equation for the energies and cannot be used to evaluate (14). For this reason we find the explicit analytic solution given below.

A general solution of the difference equation (13a) can be derived in a standard way [6]. It has the form

$$c_n = A\mathrm{e}^{\mathrm{i}n\vartheta} + B\mathrm{e}^{-n\vartheta}\ , \tag{16}$$

where ϑ is given by

$$E=2\cos\vartheta \tag{17}$$

and A and B are constants. Using eq. (13b) we get the symmetric ($c_n=c_{-n}$)

$$c_n^{(+)}=\left[\pi\left(1+\frac{\epsilon^2}{4\sin^2\vartheta}\right)\right]^{-1/2}\left(\cos n\vartheta-\frac{\epsilon}{2\sin\vartheta}\sin|n|\vartheta\right) \tag{18}$$

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

$$c_n^{(-)}=\pi^{-1/2}\sin n\vartheta \tag{19}$$

solutions. These extended states have the energies in the band of the states

$$E=2\cos\vartheta\,,\quad \vartheta\in(0,\pi)\,. \tag{20}$$

The localized state existing for any $\epsilon\neq 0$ can be obtained by assuming the imaginary "k-vector" ϑ in eq. (16) and equals

$$c_n=(\tanh\gamma)^{1/2}[\mathrm{sgn}(\epsilon)\mathrm{e}^{-\gamma}]^{|n|}\,. \tag{21}$$

It has the energy

$$E=2\,\mathrm{sgn}(\epsilon)\cosh\gamma \tag{22}$$

and is symmetric.

The derivation of eq. (3) from

$$\psi_{np}(t)=\int_0^\pi (c_n^{(+)}c_p^{(+)}+c_n^{(-)}c_p^{(-)})\exp(-2it\cosh\vartheta)\,\mathrm{d}\vartheta+c_nc_p\exp[-2it\,\mathrm{sgn}(\epsilon)\cosh\gamma] \tag{23}$$

is straightforward but time consuming and we do not give it here.

We have discussed the one-dimensional case here. As far as the capturing of the exciton by the localized state is concerned this assumption is not substantial and can be relaxed. Concluding we point out that the time-dependent scattering on impurities arises in a number of contexts so that the analytic solution of the problem is of interest not only in the theory of the exciton transport.

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References

[1] V.M. Kenkre and P. Reineker, in: Exciton dynamics in molecular crystals and aggregates, ed. G. Hoehler (Springer, Berlin, 1982).
[2] V.M. Kenkre, in: Energy transfer processes in condensed matter, ed. B. Di Bartolo (Plenum, New York, 1984).
[3] L. Skála and V.M. Kenkre, Phys. Lett. A 114 (1986) 395.
[4] V.M. Kenkre and S.M. Phatak, Phys. Lett. A 100 (1984) 101.
[5] H. Bateman and A. Erdelyi, Higher transcendental functions, Vol. 2 (McGraw-Hill, New York, 1953).
[6] S. Goldberg, Introduction to difference equations (Wiley, New York, 1958).