

## EXACT PROBABILITY PROPAGATORS FOR MOTION WITH ARBITRARY DEGREE OF TRANSPORT COHERENCE<sup>☆</sup>

V.M. KENKRE and S.M. PHATAK

*Department of Physics and Astronomy, University of Rochester, Rochester, NY 14627, USA*

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We present an explicit expression for probability propagators for the motion of a quasiparticle in a one-dimensional crystal with arbitrary degree of transport coherence. The expression is exact, simple, and convenient for practical computations, analytical as well as numerical.

The motion of quasiparticles such as Frenkel excitons, in periodic lattices as in molecular crystals, has come under active investigation in recent times [1–3]. A particularly interesting basic issue is that of the degree of transport coherence. Various models have been studied to this end. It is thus well known that in a one-dimensional crystal of equivalent sites in which the quasiparticle moves through nearest-neighbor transfer rates  $F$ , the probability that the  $m$ th site will be occupied at time  $t$ , counting from the initially occupied site as the 0th site, is given by

$$P_m(t) = e^{-2Ft} I_m(2Ft), \quad (1)$$

where  $I$  is a modified Bessel function. This probability is called the propagator, the quasiparticle motion is said to be completely incoherent, the underlying picture is that of a hopping one from site to site in the manner of the random walker, and the equation of motion is

$$dP_m(t)/dt = F [P_{m+1}(t) + P_{m-1}(t) - 2P_m(t)]. \quad (2)$$

On the other hand, if the quasiparticle moves through nearest-neighbor interaction matrix elements  $V$ , relevant to a (tight-binding) band with energy  $2V \cos k$ , the probability propagator is

$$P_m(t) = J_m^2(2Vt), \quad (3)$$

where  $J$  is the ordinary Bessel function. The motion is said to be purely coherent in this case, the underlying picture being that of motion through band states with no scattering among them. The corresponding evolution for the amplitudes  $C_m$ , whose squares are the probabilities,  $P_m$ , is

$$dC_m(t)/dt = -iV[C_{m+1}(t) + C_{m-1}(t)]. \quad (4)$$

Of importance is the intermediate situation wherein scattering occurs at a finite rate  $\alpha$ . It yields the above two cases as extreme limits and is generally represented by the evolution equation

$$d\rho_{mn}/dt = -iV(\rho_{m+1n} + \rho_{m-1n} - \rho_{mn+1} - \rho_{mn-1}) - \alpha(1 - \delta_{m,n})\rho_{mn} \quad (5)$$

for the quasiparticle density matrix  $\rho$ . The coherent limit is  $\alpha \rightarrow 0$  which gives eq. (4) and the incoherent one is  $V \rightarrow \infty$ ,  $\alpha \rightarrow \infty$ ,  $2V^2/\alpha = \text{const} = F$ , which gives eq. (2).

Although eq. (5) has been used in a variety of ways [2,3], as for calculating mean-square displacements, velocity auto-correlation functions, quantum yields, etc., its solution, e.g. the probability propagator, has not been given in a convenient form. The purpose of the present note is to provide such a convenient, simple, and practically usable expression for the propagator.

We first exhibit that result and then show its derivation. The result is

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$$P_m(t) = J_m^2(2Vt)e^{-\alpha t} + \int_0^t du \alpha e^{-\alpha(t-u)} J_m^2(2V(t^2 - u^2)^{1/2}). \quad (6)$$

One immediately sees the simplicity of eq. (6) and its connection to the coherent result eq. (3). The *practical* usefulness of eq. (6) arises from that connection and the fact that numerical calculation from eq. (6) is trivial. It involves nothing more complicated than a single integration which is, furthermore, unimportant at short times, the propagator being given then simply by the product of the coherent expression eq. (3) and the exponential  $\exp(-\alpha t)$ :

$$P_m(t) \approx J_m^2(2Vt)e^{-\alpha t}. \quad (7)$$

The two limits of eq. (6) viz. eqs. (1) and (3), can be obtained easily by Laplace transforming eq. (6), as will be evident below. We have plotted the self-propa-

gator  $P_0(t)$  and the propagator for the nearest neighbor,  $P_1(t)$  for several values of the coherence parameter  $V/\alpha$  in figs. 1a and 1b respectively. The coherence parameter is essentially the mean free path in units of the lattice constant since the average group velocity of the coherent quasiparticle is proportional to  $V$  and the time between scattering events to  $1/\alpha$ . We have also displayed the coherent limit, i.e. eq. (3) and the incoherent limit, i.e. eq. (1). Already for  $V/\alpha = 0.1$  we see that the exact result coincides with the incoherent limit except for the shape difference at small times. As has been explained several times in the literature [2,4,5], this shape difference can signal the presence or absence of coherence.

Another expression for the propagator exists [3] in the literature and has been used for numerical calculations. It is given by

$$P_m(t) = \frac{\alpha}{2\pi} \int_{-\bar{\kappa}}^{\bar{\kappa}} dk e^{ikm} [\alpha^2 - 16V^2 \sin^2(k/2)]^{-1/2} \times \exp\{t[-\alpha + [\alpha^2 - 16V^2 \sin^2(k/2)]^{1/2}]\} + \frac{1}{8\pi^2} \int_{-\pi}^{\pi} dk \int_0^{\pi} dl e^{ikm} [8V \sin l \sin(k/2)]^2 \times [16V^2 \sin^2(k/2) \sin^2 l - \alpha^2]^{-1} \times \exp\{t[-\alpha + i4V \sin(k/2) \cos l]\}, \quad (8)$$

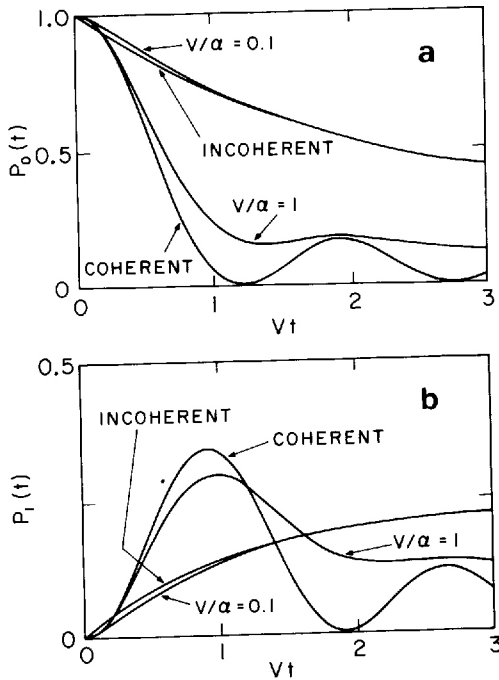


Fig. 1. Probability propagators plotted as a function of the dimensionless time  $Vt$  for several values of the coherence parameter  $V/\alpha$ , which is proportional to the mean free path in units of the lattice constant. The probability of the initially occupied site is plotted in fig. 1a and that of its nearest neighbor in fig. 1b. The extreme limits of pure coherence and complete incoherence are also shown.

where the first term is present if  $\alpha > |4V \sin(\kappa/2)|$ , in which case  $\bar{\kappa} = 2 \sin^{-1}|\alpha/4V|$ . This expression involves two integrations and its connection with the extreme limits is by no means transparent. The considerable advantages that eq. (6) possesses over eq. (8) for analytical as well as numerical calculations are obvious from a comparison. Indeed we have already utilized the simplicity of our central results eq. (6) in various calculations, analytical as well as numerical, including those for Ronchi grating signals [4,5] and for trapping observables in the presence of cooperative trap interactions [6].

The derivation of eq. (6) from eq. (5) proceeds through the conversion of eq. (5) into a generalized master equation with the memory functions  $\mathcal{W}_{mn}(t)$

$$\mathcal{W}_{mn}(t) = e^{-\alpha t} t^{-1} (d/dt) J_{m-n}^2(2Vt), \quad (9)$$

as shown elsewhere [2], followed by the calculation

of the propagator in the Fourier and Laplace domain as

$$\tilde{P}^k(\epsilon) = [\epsilon + \tilde{\mathcal{W}}^0(\epsilon) - \tilde{\mathcal{W}}^k(\epsilon)]^{-1} \\ = \{[(\epsilon + \alpha)^2 + 16V^2 \sin^2(k/2)]^{1/2} - \alpha\}^{-1}. \quad (10)$$

Tildes denote Laplace transforms,  $\epsilon$  is the Laplace variable, and the discrete Fourier transforms are defined through expressions such as

$$P^k = \sum_m P_m e^{ikm}. \quad (11)$$

The inversion of the Laplace transform into the form

$$P^k(t) = 1 - e^{-\alpha t} [4V \sin(k/2)] \\ \times \int_0^t du \exp[\alpha(t^2 - u^2)^{1/2}] J_1 [4Vu \sin(k/2)] \quad (12)$$

is straightforward [2,7] and uses well-known results from Laplace transform theory [8]. We now integrate eq. (12) by parts and use the fact that  $J_1$  equals the negative derivative of  $J_0$  to obtain

$$P^k(t) = J_0 [4Vt \sin^2(k/2)] e^{-\alpha t} \\ + \int_0^t du \alpha e^{-\alpha(t-u)} J_0 [4V(t^2 - u^2)^{1/2} \sin^2(k/2)]. \quad (13)$$

For grating signal calculations [4,5,7] eq. (13) is directly useful. To obtain the propagator form eq. (6) explicitly, we merely Fourier invert eq. (13) recognizing that the inverse of  $J_0 [Z \sin^2(k/2)]$  is  $J_m^2(Z/2)$ . The derivation is thus complete.

The extreme limits of eq. (6) are seen clearly through those of eq. (10). The coherent limit is trivial as it involves  $\alpha \rightarrow 0$ . The incoherent limit of eq. (10) gives, through a binomial expansion,

$$\tilde{P}^k(\epsilon) = [\epsilon + (8V^2/\alpha) \sin^2(k/2)]^{-1}, \quad (14)$$

which is the transform of the incoherent propagator eq. (1), with  $F = 2V^2/\alpha$ .

For the sake of completeness we also present the propagator corresponding to a richer form of the stochastic Liouville equation (5) viz.

$$d\rho_{mn}/dt = -iV(\rho_{m+1n} + \rho_{m-1n} - \rho_{mn+1} - \rho_{mn-1}) \\ - \alpha(1 - \delta_{m,n})\rho_{mn} + \delta_{m,n}\gamma \\ \times (\rho_{m+1m+1} + \rho_{m-1m-1} - 2\rho_{mm}), \quad (15)$$

where  $\gamma$  denotes the rate at which the quasiparticle moves via an additional channel of motion such as through the assistance of phonons. The propagator expression is

$$P_m(t) = J_m^2(2Vt) e^{-\alpha t} + \int_0^t du \alpha \exp[-\alpha(t-u)] \\ \times \sum_n H_{m-n}(u) J_n^2(2V(t^2 - u^2)^{1/2}), \quad (16)$$

$$H_{m-n}(u) = e^{-2\gamma u} [I_{m-n} \\ + (\gamma/\alpha)(I_{m-n+1} + I_{m-n-1} - 2I_{m-n})]. \quad (17)$$

The  $I$ 's are, as before, modified Bessel functions and have the argument  $2\gamma t$ . The Laplace and Fourier transform of eq. (16) can be used directly in work on Ronchi gratings [4,5]. However, the practical usefulness of eq. (16) in the time domain is less apparent than that of eq. (6).

Finally, we would like to comment that the basic equation of motion, eq. (5), has appeared in a variety of places [1-3,9-11] and is perhaps the simplest possible way of describing motion with arbitrary degree of coherence. Its solution presented in the simple and practical form in this note should be of interest not only in exciton transport where its use is already being demonstrated, but in quite general contexts.

It is interesting to observe the connection between our central result eq. (6) and

$$\tilde{P}^k(\epsilon) = [\tilde{P}_{\text{coh}}^k(\epsilon + \alpha)] [1 + \alpha \tilde{P}^k(\epsilon)], \quad (18)$$

which was given under general conditions as eq. (3.36) in ref. [2]. Here  $\tilde{P}_{\text{coh}}^k$  refers to the coherent propagator. The first term of eq. (6) is immediately identified with its counterpart in eq. (18) and exactly forms the right-hand side of eq. (7). The remaining part in eq. (18), if iterated and summed exactly, produces the second term in eq. (6) above for our one-dimensional crystal. Such a simplification is particular to the one-dimensional system considered here and does not appear possible in higher dimensions.

### References

- [1] R. Silbey, *Annu. Rev. Phys. Chem.* 27 (1976) 203.
- [2] V.M. Kenkre, in: *Exciton dynamics in molecular crystals and aggregates*, ed. G. Höhler (Springer, Berlin, 1982).

- [3] P. Reineker, in: Exciton dynamics in molecular crystals and aggregates, ed. G. Höhler (Springer, Berlin, 1982) p. 134.
- [4] V.M. Kenkre, A. Fort and V. Ern, Chem. Phys. Lett. 96 (1983) 658.
- [5] V.M. Kenkre, V. Ern and A. Fort, Phys. Rev. B28 (1983) 598.
- [6] V.M. Kenkre, P.E. Parris and S.M. Phatak, Motion and capture of quasiparticles in solids in the presence of cooperative trap interactions, University of Rochester preprint.
- [7] Y.M. Wong and V.M. Kenkre, Phys. Rev. B22 (1980) 3072.
- [8] M.G. Smith, Laplace transform theory (Van Nostrand, New York, 1966).
- [9] P. Avakian, V. Ern, R.E. Merrifield and A. Suna, Phys. Rev. 165 (1968) 974.
- [10] G.H. Wannier, Solid state theory (Cambridge Univ. Press, London, 1959).
- [11] D. Brown and V.M. Kenkre, in: Electron structure and properties of hydrogen in metals, eds. P. Jena and C. Satterthwaite (Plenum, New York, 1983) p. 177.