# Nondiffusive Quantum Transport in a Dynamically Disordered Medium

A. M. Jayannavar and N. Kumar
*Department of Physics, Indian Institute of Science, Bangalore 560012, India*
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For a dynamically disordered continuum it is found that the exact quantum mechanical mean square displacement $\langle x^2(t)\rangle \sim t^3$, for $t \to \infty$. A Gaussian white-noise spectrum is assumed for the random potential. The result differs qualitatively from the diffusive behavior well known for the one-band lattice Hamiltonian, and is understandable in terms of the momentum cutoff inherent in the lattice, simulating a "momentum bath."

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In recent years there has been growing interest in the study of quantum diffusion in a randomly fluctuating medium.[1-4] The existing theoretical treatments are based almost entirely on the lattice ($L$) Hamiltonian, namely the tight-binding one-band Hamiltonian[1]

$$H_L = \sum_i \epsilon_i(t)\,|i\rangle\langle i| + \sum_{i\neq j} V_{ij}(t)\,|i\rangle\langle j|, \qquad (1)$$

in obvious notation. The dynamical disorder is introduced by treating the potentials, i.e., the site-diagonal and the off-diagonal matrix elements, as random $c$-number variables, evolving stochastically in time. Such a time dependence is known to arise from the random modulation of the potential by the incoherent lattice vibrations of thermal origin. It must be emphasized here that in all the treatments referred to above, as also in the treatment to follow, this time dependence is taken to be parametric in that the potential is supposed to introduce no additional dynamical degrees of freedom in the problem. For the Gaussian choice of randomness having a white-noise spectrum, i.e., $\delta$ correlated in time but arbitrarily correlated in space, the problem has been solved exactly by several workers.[1,2] In all cases one obtains a classical diffusive behavior in that the mean square displacement $\langle x^2(t)\rangle \sim t$, for $t \to \infty$, implying a well-defined diffusion constant and hence mobility. This common result, however plausible and expected from the physical point of view, is surprising when analyzed more carefully. Indeed, as the following exact treatment reveals, for the corresponding continuum problem we have $\langle x^2(t)\rangle \sim t^3$ asymptotically, implying nondiffusive motion. Thus, the diffusive behavior obtained by the other workers is due presumably to the specific nature of the one-band lattice Hamiltonian. To the best of our knowledge this rather fundamental point has not been noticed so far. This has prompted us to report our findings.

In order to appreciate this point fully it is expedient to consider first the related problem of classical diffusion *à la* Langevin equation in a spatial one-dimensional continuum:

$$m\,du/dt = -\Gamma u + f(t), \qquad (2)$$

where the fluctuating random force $f(t)$ and the concomitant dissipation represented by the frictional coefficient $\Gamma$ are related by the fluctuation-dissipation theorem, i.e.,

$$\langle f(t)f(t')\rangle = 2k_B T\Gamma\,\delta(t-t') \equiv \Delta^2\delta(t-t').$$

As is well known this gives a mean square displacement $\langle x^2(t)\rangle \sim 2Dt$, for $t \to \infty$, defining the diffusion constant $D = k_B T/\Gamma$. If, however, we omit the dissipative term $(-\Gamma u)$ from Eq. (2), i.e., we set

$$m\,du/dt = f(t), \qquad (3)$$

we can readily show that

$$\langle x^2(t)\rangle \sim (\Delta^2/4m^2)t^3, \quad \text{for } t \to \infty. \qquad (4)$$

This implies a nondiffusive random motion. Here the particle continues to absorb energy from the fluctuating force and accelerates indefinitely. In short the particle "heats up" to an infinite temperature. Now, the quantum mechanical treatment based on the Hamiltonian $H_L$ in Eq. (1) corresponds precisely to this nondissipative classical system in that no dissipation is incorporated explicitly in $H_L$. And yet the mean square displacement calculated exactly from Eq. (1) shows a diffusive behavior as noted above.[1,2] In the following, we address ourselves to this paradoxical situation. More specifically, we will first show that the exactly solvable continuum analog of Eq. (1) also reproduces $t^3$ behavior as in Eq. (4). We then argue that the diffusive behavior obtained by other workers referred to above is entirely due to the one-band lattice nature of the Hamiltonian given in Eq. (1).

To this end we will now obtain an exact solution

of the quantum problem in a continuum. For simplicity we shall treat the case of one space dimension. Generalization to arbitrary dimension is straightforward. The quantum evolution is now given by the time-dependent Schrödinger equation,

$$i\hbar \frac{\partial \psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \psi(x,t)}{\partial x^2} + V(x,t)\psi(x,t), \quad (5)$$

where $V(x,t)$ is the stochastic potential assumed to be Gaussian, with space-time correlation

$$\langle V(x,t)V(x',t')\rangle = V_0^2 \delta(t-t')g(x-x'). \quad (6)$$

The physical quantities of interest can be conveniently expressed in terms of the reduced density matrix $\langle \rho(x',x,t)\rangle$, where

$$\rho(x',x,t) = \psi^*(x't)\psi(x,t). \quad (7)$$

and the angular brackets denote the average over the stochastic potential. Clearly $\rho(x',x,t)$ is a functional of the Gaussian random variable $V(x,t)$ and hence the Novikov theorem[5] applies. Following essentially the earlier treatments,[1,2] we get the equation of motion

$$\frac{\partial}{\partial t}\langle \rho(x',x,t)\rangle = -\frac{i\hbar}{2m}\left(\frac{\partial^2}{\partial x^2} - \frac{\partial^2}{\partial x'^2}\right)\langle \rho(x',x,t)\rangle - \frac{V_0^2}{\hbar^2}[g(0) - g(x-x')]\langle \rho(x',x,t)\rangle. \quad (8)$$

This has to be solved subject to the initial condition that the particle was prepared initially in a wave packet centered at the origin, $x=0$. We shall take conveniently

$$\rho(x',x,t=0) = \psi^*(x',t=0)\psi(x,t=0),$$

where

$$\psi(x,t=0) = [(2\pi)^{1/4}\sigma^{1/2}]^{-1}\exp(-x^2/4\sigma^2). \quad (9)$$

This ensures correct normalization, $\int_{-\infty}^{+\infty}\rho(x,x,t=0)dx = 1$. Here $\sigma$ denotes the spatial spread of the initial wave packet. Because of the unbounded nature of the kinetic energy operator in the continuum limit, it is necessary to choose a wave packet with $\sigma > 0$. The asymptotic ($t \to \infty$) behavior is, of course, independent of the precise form of the wave packet. This problem does not arise in the case of the lattice Hamiltonian $H_L$ which is bounded. Equation (8) can be solved by first taking the time Laplace transform and then considering the resulting hyperbolic equation in the two independent variables $x$ and $x'$. We get

$$\frac{2i\hbar}{m}\frac{\partial^2}{\partial X\,\partial Y}\tilde{R}(X,Y,s) + \left(s + \frac{V_0^2}{\hbar^2}g(0) - \frac{V_0^2}{\hbar^2}g(Y)\right)\tilde{R}(X,Y,s) = R(X,Y,t=0), \quad (10)$$

where we have introduced the characteristic coordinates $X = x + x'$, $Y = x - x'$. Here $s$ is the Laplace transform variable. We have defined

$$R(X,Y,t) \equiv \rho(x',x,t); \quad \tilde{R}(X,Y,s) = \int_0^\infty R(X,Y,t)e^{-st}dt. \quad (11)$$

The mean square displacement can be expressed as

$$\langle x^2(t)\rangle = -\frac{1}{8}\frac{\partial^2}{\partial K^2}\bar{R}(K,Y=0,t)\Big|_{K=0}, \quad (12)$$

with

$$\bar{R}(K,Y,t) = \int_{-\infty}^{+\infty} R(X,Y,t)e^{iKX}dX. \quad (13)$$

Here an overbar denotes the spatial Fourier transform while a tilde denotes the time Laplace transform. Equation (12) holds provided $\bar{R}(K,Y=0,t)$ is analytic in $K$ at $K=0$.

Equation (10) can be converted into an ordinary differential equation in $Y$ by taking Fourier transform with respect to $X$, which can then be solved readily subject to the initial condition to give

$$\bar{\tilde{R}}(K,Y=0,s) = \int_0^\infty 2\exp\left[-\left(2\sigma^2 + \frac{\hbar^2Y^2}{2m^2\sigma^2}\right)K^2\right]e^{-sY}\exp\left\{-\frac{V_0^2}{\hbar^2}\left[g(0)Y - \int_0^Y g\left(\frac{2\hbar|K|Y'}{m}\right)dY'\right]\right\}dY. \quad (14)$$

The right-hand side of this equation is already in the form of a Laplace transform. Hence we get at

once on inversion

$$\bar{R}(K, Y=0, t) = 2\exp\left[-\left(2\sigma^2+\frac{\hbar^2 t^2}{2m^2\sigma^2}\right)\right] K^2 \exp\left\{-\frac{V_0^2}{\hbar^2}\left[g(0)t - \int_0^t g\left(\frac{2\hbar|K|Y'}{m}\right)dY'\right]\right\}. \quad (15)$$

One can confirm that Eq. (15) fulfills the normalization and the initial condition. We now choose an explicit form for the function $g(Y)$. For simplicity we take it to be Gaussian, i.e.,

$$g(Y) = [(2\pi)^{1/2}\alpha]^{-1} \exp(-Y^2/2\alpha^2). \quad (16)$$

With this choice, $\bar{R}(K, Y=0, t)$ can be seen to be analytic in $K$ at $K=0$. Thus, from Eqs. (12) and (15) we get for the mean square displacement

$$\langle x^2(t)\rangle = \sigma^2 + \frac{\hbar^2}{4m^2\sigma^2} t^2 + \frac{1}{3\sqrt{2}\pi} \frac{V_0^2}{m^2\alpha^3} t^3. \quad (17)$$

This is an exact result. It shows clearly that the particle motion is nondiffusive on any time scale. In fact, the above result is quite general and depends only on the fact that $g(Y)$ is an even function of $Y$ and is analytic in $Y$ at $Y=0$. The special case $g(Y) \sim e^{-\alpha|Y|}$ which is not analytic at $Y=0$ calls for a somewhat more detailed evaluation by quadrature. Thus, we confirm that the quantum motion in a fluctuating continuum gives nondiffusive motion. The result is essentially identical to that for the classical motion in a fluctuating medium as in Eqs. (3) and (4). In point of fact one may choose $V(x, t) = xf(t)$ such that the random force obtained as the gradient of potential $V(x, t)$ is actually $f(t)$ as in Eq. (3). One can readily verify that the asymptotic time behavior remains cubic as obtained above.

The fact that the exact quantum treatment on the lattice gives diffusive behavior has, therefore, to do with the specific nature of the lattice Hamiltonian $H_L$. The question is how to understand this difference. The point is that a one-band lattice Hamiltonian has a momentum cutoff inherent in it. This limiting momentum is related to the Bragg reflection at the Brillouin zone boundary or, what is essentially the same, one has the umklapp process. The lattice acts as an infinite momentum sink and prevents indefinite acceleration of the particle. More transparently, as the particle quasimomentum increases towards the limiting value, the group velocity decreases and even reverses sign.[6] Since it is the group velocity that leads to physical displacement the above results are understandable.

In order to see more clearly how such a limiting momentum can lead to diffusive motion, it is very revealing to consider again the classical motion in a fluctuating medium described by Eq. (3), with the proviso that the physical velocity $u$ be defined modulo some limiting velocity $u_0$, say. This mathematically simulates the umklapp process. For instance, we could redefine physical velocity $u$ as

$$u = u_0 \sin(2\pi u/u_0), \quad (18)$$

and calculate the mean square displacement, with $u$ as the physical velocity. We get

$$\langle x^2(t)\rangle = \langle\{\int_0^t u_0 \sin[2\pi\int_0^{t'} f(t'')dt'']dt'\}^2\rangle,$$

$$= u_0^2 a(t + 2ae^{-t/a} - \tfrac{1}{2}ae^{-2t/a} - \tfrac{3}{2}a), \quad (19)$$

where $a = u_0^2/2\pi^2\Delta^2 m^2$. It is clear that

$$\langle x^2(t)\rangle \sim u_0^2 a\, t \quad \text{as } t \to \infty, \quad (20)$$

which is again diffusive. In deriving this we have used the well-known result $\langle\exp[i\int_0^t f(t')dt']\rangle = \exp[-(\frac{1}{2}\Delta^2)t]$. It seems clear, therefore, that the quantum treatment based on the lattice Hamiltonian is *per se* not a quantum analog of the Brownian motion. The diffusive behavior with $H_L$ results entirely from the momentum absorption by the lattice via Bragg reflections. The latter is absent in the case of the continuum, and hence the nondiffusive behavior.

Finally, we must clarify that for a quantum particle in a *real* fluctuating continuum we do expect a diffusive behavior. Here the effect of the interaction of the test particle with the dynamical degrees of freedom of the background fluctuating medium, however, cannot be represented entirely by a stochastic potential $V(x, t)$ having a parametric time dependence. We must necessarily incorporate the analog of a dissipative term as well. Such a decomposition, if at all possible, will lead to the quantum Langevin equation. This problem is still not completely solved.[7] We would also like to point out that the one-band lattice Hamiltonian has no continuum limit. As is well known, for the latter one has to have an infinite-band lattice Hamiltonian.

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# Exciton and Pair Recombination at Intimate Valence-Alternation Pairs in $a$-$As_2S_3$

S. P. Depinna and B. C. Cavenett
*Physics Department, The University of Hull, Hull HU6 7RX, United Kingdom*
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Optically detected magnetic resonance in $a$-$As_2S_3$ has shown that the emission consists of a high-energy triplet exciton recombination overlapping a low-energy pair process. The results are consistent with recombination at axial defects such as $(D^+, D^-)$ intimate valence-alternation pairs.

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The observation of light-induced EPR signals in $a$-$As_2S_3$ by Bishop, Strom, and Taylor[1,2] was an important step forward to the understanding of the defects which occur in this and related materials since the measurements were consistent with the Mott-Davis-Street model[3] which postulated the existence of $D^+$ and $D^-$ diamagnetic centers in the dark. The EPR results showed that if a hole is localized near a sulphur atom, then a narrow EPR signal is observed, whereas an electron localized at an arsenic atom is characterized by a much broader resonance due to the arsenic nuclear spin ($I = \frac{3}{2}$). These signals were assigned to the isolated defects $D^+$ and $D^-$ capturing holes and electrons, respectively, and it has been generally assumed that these centers are the native defects in $a$-$As_2S_3$. More recently Biegelsen and Street[4] reexamined the photoinduced EPR in the light of measurements by Mollot, Cernogora, and Benoît à la Guillaume[5] on $Ge_xSe_{1-x}$ glasses and showed that spin densities of $\sim 10^{20}$ cm$^{-3}$ can be induced by light in $As_2S_3$. These new measurements suggested that there are two sets of defects, the isolated "native" defects and the photoinduced defects, which Biegelsen and Street[4] suggested were due to $(D^+, D^-)$ pairs that can capture either an electron or a hole, inducing paramagnetism and midgap absorption. Luminescence in $a$-$As_2S_3$ was first reported by Kolomiets, Mamontova, and Babaev[6] and the generally accepted recombination model proposed by Street[7] suggests that the luminescence observed at $\sim 1.2$ eV involves hole capture at a $D^-$ center followed by electron-hole recombination involving a tail-state electron, i.e. $(D^0, e^-) \rightarrow D^-$. However, recent time-resolved spectroscopy (TRS) measurements by Street,[8] Bosch and Shah,[9] and Higashi and Kastner[10] are far from agreement. The only consistent pattern in these studies is that at longer delay times there is a shift of the emission to lower energies. In fact, Bosch and Shah[9] have observed two emission components, one at high energy, with short lifetime, and a second longer-lived band at lower energy. In analogy with recent TRS[11] and optically detected magnetic resonance[12] measurements in amorphous phosphorus ($a$-P), this suggests that the high-energy emission is excitonic, and that the low-energy emission is a pair process (contrary to $a$-P, where triplet exciton recombination occurs at low energies). We have explored the link between the luminescence and the identity of the defects by optically detected magnetic resonance, and report in this paper triplet and pair optically detected magnetic resonance signals which confirm that the luminescence in $a$-$As_2S_3$ is due to exciton and pair recombination, where the high-energy region is principally exciton emission. We propose that the magnetic and optical properties of $a$-$As_2S_3$ can be attributed to $(D^+, D^-)$ pairs alone.

The photoluminescence (PL) at 2 K induced by excitation above the band gap is a broad, featureless band centered at $\sim 1.2$ eV, and we show a typical PL spectrum, measured with a Ge detector, in Fig. 1(a). The effect of exciting below