01 Oct 1989

Quantum Transport in the Presence of Random Traps

John Wm Edwards

Paul Ernest Parris
Missouri University of Science and Technology, parris@mst.edu

Recommended Citation

J. W. Edwards and P. E. Parris, "Quantum Transport in the Presence of Random Traps," *Physical Review B (Condensed Matter)*, vol. 40, no. 11, pp. 8045-8048, American Physical Society (APS), Oct 1989.
The definitive version is available at https://doi.org/10.1103/PhysRevB.40.8045

RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 40, NUMBER 11 15 OCTOBER 1989-I

Quantum transport in the presence of random traps

John Wm. Edwards and P. E. Parris
Department of Physics, University of Missouri-Rolla, Rolla, Missouri 65401
(Received 25 July 1989)

We calculate the asymptotic decay of a quantum particle moving in a d-dimensional medium doped with randomly placed trapping impurities, focusing on contributions from slowly decaying long-wavelength modes centered in large compact regions devoid of traps. By averaging the decay over the statistical distribution associated with these regions we find that the survival probability, $P(t) \sim \exp(-At^{d/(d+3)})$, decays more slowly in any dimension than for diffusive transport.

The dynamical behavior of a particle or excitation moving through a medium containing randomly placed traps or reaction centers is of central importance to numerous applications in chemistry and condensed-matter physics. Strong theoretical results have been obtained regarding this behavior in the limit in which the particle motion is diffusive.[1-4] In particular, it has been shown for diffusing particles that the asymptotic decay of the survival probability has a stretched-exponential form, resulting from anomalously long-lived particles that find themselves in large, rarely occurring, trap-free regions of the medium. It has also been observed that, due to the close relationship that exists between the diffusion equation and the Schrödinger equation, the tails of the distribution of decay rates associated with these long-lived diffusing particles are closely related to the tails that appear at low energies in the density of states of energetically disordered quantum-mechanical systems.[5,6]

At very low temperatures, however, the mean free path for phonon scattering becomes large, and so the survival probability associated with quasiparticle trapping in low-temperature condensed phases may be expected to exhibit significant deviations from behavior that obtains under the assumption of particle diffusion. It becomes desirable, therefore, to treat the trapping problem itself in quantum-mechanical terms.[7-9] It is this low-temperature, coherent limit of the trapping problem that forms the subject of the present study. Specifically, we calculate the asymptotic survival probability for a single quantum-mechanical particle moving at zero temperature in a d-dimensional medium containing randomly placed *irreversible* traps in fixed concentration q. The model is of considerable fundamental interest because it extends nonequilibrium studies involving trapping and reaction kinetics[3,4] into the quantum domain. At the same time it provides some rare insight into difficult problems associated with energy relaxation and redistribution in statically disordered quantum-mechanical systems. Indeed, while there exists an increasing body of literature on the behavior of a single quantum-mechanical particle moving in a static random potential,[10] the present calculation is one of the few which realistically takes into account dynamical effects associated with the presence of a zero-temperature phonon bath; one which can absorb energy from the particle and bring about its subsequent relaxation.

Our analysis is very similar in spirit to ones that have been used in the past to obtain exact results for the density-of-states problem,[5,6] and to study trapping in diffusive systems.[3] We emphasize, however, that important differences distinguish the current problem from those studied earlier. These differences manifest themselves most clearly in the fact that the tails which we find in the distribution of decay rates in the coherent trapping problem are different from those found in the diffusion studies or in the noninteracting density-of-states problem. They lead, moreover, to an asymptotic prediction for the survival probability, $P(t) \sim \exp(-At^{d/(d+3)})$, which is slower in any dimension than the diffusive result,[3] $P(t) \sim \exp(-At^{d/(d+2)})$, in spite of the fact that a particle at zero temperature does not suffer repeated scattering by phonons and so is able to move more rapidly in the region between the traps.

We begin by considering a single particle moving on an isotropic d-dimensional cubic lattice that is doped with a fractional concentration q of interstitial trapping impurities. These impurities are associated with energetically lower states which cause an irreversible decay of amplitude from neighboring host molecules of the lattice. Naturally, this localized decay is assumed to arise from the mutual interaction between the trap molecule, the host molecule next to which it resides, and the zero-temperature phonon bath which absorbs the excess energy lost in the trapping process. The dynamical effects associated with this decay can be treated in a number of ways.[7-9] For our purposes it is most easily accomplished through the use of an effective "Hamiltonian" which associates an imaginary potential energy $U=-i\gamma$ with each site located next to a trap.[9] In analogy to the usual Bethe-Lamb picture, the quantity 2γ is identified with the inverse lifetime of a particle on a host site located next to a trap, when all matrix elements J to the rest of the lattice are ignored. In what follows we will have no need to refer explicitly to states of the trap molecules themselves and will, for brevity, often refer to the host sites which are located next to the interstitial trap molecules as trap sites, or simply traps. We write for the effective Hamiltonian,

$$\mathcal{H}=-\sum_{n,m} J_{n,m}(|n\rangle\langle m|+|m\rangle\langle n|)-i\gamma\sum_i |n_i\rangle\langle n_i| , \quad (1)$$

in which $|n\rangle=|n_1,n_2,\ldots,n_d\rangle$ represents a state localized at the nth lattice site; $J_{n,m}=J$ is assumed to connect only nearest neighbors; and the sum over i includes all trap sites in the lattice. The (no longer unitary) evolution of the system is then governed by a Liouville–Von Neumann equation for the single-particle density matrix ρ. This evolution is most easily expressed in terms of the eigenstates and complex eigenvalues of the effective Hamiltonian of Eq. (1). In particular, the imaginary part of the eigenvalue for a given eigenvector gives the rate at which a particle in that particular state decays as a result of the presence of the trap molecules. Thus, to obtain the asymptotic decay of the survival probability we must ascertain the most slowly decaying eigenstates of the effective Hamiltonian.

In analogy to the corresponding diffusion problem, we expect the most important class of these states to be those which are centered on asymptotically large trap-free voids surrounded by regions of more typical trap density. We argue that in such voids a long-wavelength state with an energy near the band edge will be very strongly scattered by the disorder outside the trap-free region, and will therefore vanish exponentially into the region populated by traps. (Note that it is the traps themselves which are the source of the localizing disorder.) Thus, the larger the trap-free region associated with an eigenstate of this type, the smaller the fraction of the amplitude which will have any significant overlap with the traps, and the smaller will be the decay amplitude associated with that state. As a consequence, the asymptotic distribution of small decay amplitudes (or large lifetimes) will be effectively determined by the distribution of large, rarely occurring trap-free voids. While this is, of course, similar to the picture that obtains in the diffusive case[3] and in the density-of-states problem[5,6] there is a subtle difference. In the diffusive case it is possible to treat the area outside the trap-free region as being perfectly absorbing and thus identify the slowest decay rates with long-wavelength diffusive modes which vanish at the absorbing boundary of the trap-free region. Similarly, in the density-of-states problem one can treat the boundary as though it were an infinite potential barrier and identify the low-lying energy eigenstates in the region with long-wavelength modes which vanish at the boundary. In either case the extension of the corresponding mode into the defect region can, for asymptotically large voids, be ignored, because its effect on the eigenvalue is negligible in the asymptotic limit. This is not possible in the present case because the quantity of interest, namely the decay rate, is associated with the imaginary component of the energy, a quantity which is itself *entirely* determined by the degree of extension of the wave function into the trap-populated region. This necessitates a slightly more careful treatment of the boundary region.

The argument is further complicated by two other points which need to be addressed. The first arises from the fact that for low concentrations of traps in dimensions greater than two, the states of the disordered system will, in general, not all be localized. This will not affect the *asymptotic* decay of $P(t)$, however, because delocalized states will decay very quickly compared to localized states, having a substantial fraction (of order q) of their amplitude on trap sites. Localized states, on the other hand, tend to appear at the band edges,[10] so that for any finite concentration of traps there will exist long-wavelength low-energy states of the type identified, centered in asymptotically large trap-free voids. States of this type sufficiently near the bottom of the band (i.e., below the localization edge) will then be exponentially localized outside the trap-free region. It is precisely these states which will dominate the asymptotic decay in any dimension.

A different complication arises when one considers the decay from states centered in trap-free regions of different *shape*. Trap-free regions of the same number of sites (i.e., same d-dimensional volume V) occur with the same statistical weight $p_V \sim (1-q)^V$, but they can have very different decay characteristics depending on the shape of the void. By our previous argument, however, the decay rate for a state of this type is (roughly) proportional to the fraction of the wave function which extends into the trap-populated region. Thus, if λ is approximately the distance that the wave penetrates past the boundary, then the decay rate will be roughly proportional to the quantity $S\lambda/V$, where S is the $(d-1)$-dimensional measure of the boundary of the trap-free region. Hence those voids of a given volume which have the smallest boundary will minimize this fraction. We conclude, as in the diffusive case,[3-6] that of all voids with the same d-dimensional volume it is the ones which are most nearly rotationally symmetric (circles, spheres, etc.) that will possess the most slowly decaying states. Our approach to calculating the asymptotic properties of $P(t)$, then is as follows. First, we calculate the decay amplitude $\Gamma_R/2$ associated with long-wavelength excitations centered in rotationally symmetric trap-free voids of a given radius R. The survival probability for particles created in trap-free regions of the same volume will then be bounded by the exponential decay $P_R(t) \sim \exp(-\Gamma_R t)$. Then, assuming an initial condition in which there is a finite probability for populating a band-edge state of this type, we perform a statistical average of this decay over the volume of the trap-free region in which a particle may find itself.

The first step is to calculate the decay amplitude associated with a rotationally symmetric void in a region of more typical trap density. The fact that we are interested in long wavelengths allows us to work in the continuum. In the Bloch states $|k\rangle = |k_1, \ldots, k_d\rangle$ (the discrete Fourier transforms of the site states) the transport part of the Hamiltonian can be written $E(k) = H_{kk} = -2J \times \sum_j \cos(k_j)$, which for small k takes the form $H_{kk} = -2J + Jk^2$. Except for the constant term (which we now drop) this is the Hamiltonian for a free particle of effective mass $m = (2J)^{-1}$. We now focus on the states available to such a particle in a rotationally symmetric trap-free void surrounded by a region where trapping can occur. Because we are dealing with asymptotically long wavelengths, we now associate the region outside the void with a constant effective potential equal to the average value of the absorptive potential appearing in Eq. (1). This representation is based upon our belief that the tails of the wave function in the absorptive region, while small compared to the size of the void, will be long compared to the mean intertrap spacing, and hence will experience the imaginary potential of a significant number of sites. (We note in passing that "potential well" analogies of this type have also been used with significant success to study the standard quantum localization problem associated with elastic scattering from "real" energy defects.[11] In the localization problem, however, information is desired about the states well away from the band edge and so more sophisticated treatments of the potential outside the region of interest are usually required.) We are led, then, to consider the lowest mode of the continuum Hamiltonian

$$H = Jk^2 + V(r) = -J\nabla^2 + V(r) , \qquad (2)$$

associated with a particle in a trap-free void of radius R centered at the origin, where the potential term in Eq. (2) can be written

$$V(r) = -iq\gamma\Theta(r-R) , \qquad (3)$$

with $\Theta(x)$ the Heaviside step function. The lowest eigenstate of (2) is a rotationally symmetric solution to the "s-wave" equation[12]

$$\frac{1}{r^{d-1}}\frac{d}{dr}r^{d-1}\frac{d\psi(r)}{dr} + [\varepsilon - \mathcal{V}(r)]\psi(r) = 0 , \qquad (4)$$

where $\varepsilon = E/J$ and $\mathcal{V}(r) = V(r)/J$. For $r < R$ and $d > 1$ the solution to (4) which is regular at the origin can be written[13]

$$\phi_0(kr) = A\int_0^1 dt(1-t^2)^{(d-3)/2}\cos(krt) , \qquad (5)$$

where $k^2 = \varepsilon$, and A is a normalization constant. In the region $r > R$ we define $\kappa^2 = \varepsilon + iq\gamma/J$ (which becomes arbitrarily close to $iq\gamma/J$ for states sufficiently near the bottom of the band), and write the solution to (4) that is normalizable when $\mathrm{Im}\,\kappa > 0$ as[13]

$$\eta_0(\kappa r) = Be^{i\kappa r}\int_0^\infty dt(t^2-2it)^{(d-3)/2}\exp(-\kappa rt) . \qquad (6)$$

Now, for asymptotically large R the wave function will extend only a very short distance (compared to R) beyond the boundary at R. Thus, in the asymptotic limit the interior wave vector k will be only slightly smaller than the value k_0 which makes $\phi_0(kr)$ vanish at $r = R$, i.e., for which $\phi_0(k_0R) = 0$. Let us denote by x_{01} the first root of the function $\phi_0(x)$. By requiring continuity of $\psi(r)$ and its radial derivative at R we obtain two equations,[12] the ratio of which gives us an expression for determining the wave vector k. Expanding all quantities to lowest nontrivial order in $1/R$ and using the asymptotic properties of Eq. (6) we find $k = k_0[1-\exp(i\pi/4)(J/R^2q\gamma)^{1/2}]$. From this we obtain the eigenvalue $E = J\varepsilon = Jk^2$, and hence the decay rate

$$\Gamma_R = -2\,\mathrm{Im}[J\varepsilon(k)]$$
$$= -2J\,\mathrm{Im}[k^2] = x_{01}^2(2J^3/q\gamma)^{1/2}R^{-3} , \qquad (7)$$

for the lowest localized mode in this particular trap-free region.

Thus, a particle which is created at $t = 0$ in a trap-free region of volume $V(R) = C_dR^d$, where C_d is the volume of the unit sphere in d dimensions, will asymptotically have a decay which is bounded from below by

$$P_R(t) \sim f(R)\exp[-x_{01}^2t(2J^3/q\gamma)^{1/2}R^{-3}] , \qquad (8)$$

where the function $f(R)$ may depend upon the exact initial conditions, but is expected to vary, at most, algebraically with R, and is thus slowly varying compared to the statistical weight associated with the distribution of trap-free voids. Now, averaging Eq. (8) over the probability to find the particle created in a trap-free region of given volume, namely, $p_R \propto (1-q)^{V(R)}$, we obtain

$$P(t) \sim \int dR\,h(R)\exp(-aR^d - btR^{-3}) , \qquad (9)$$

where $a = -C_d\ln(1-q)$, $b = x_{01}^2(2J^3/q\gamma)^{1/2}$, and $h(R)$ is slowly varying with respect to the exponential terms. A change of variable, $R = yt^{1/(d+3)}$, puts the integral in a form which is amenable to saddlepoint methods. The leading behavior is

$$P(t) \sim C(t)\exp(-At^{d/(d+3)}) , \qquad (10)$$

where $A = [b(d+3)/d](ad/3b)^{3/(d+3)}$. Thus, in two dimensions we find $P(t) \sim \exp(-At^{2/5})$ where

$$A = (\tfrac{5}{2}[(2\pi/3)\ln(1/p)]^{3/5}(x_{01}^4J^3/2q\gamma)^{1/5} ,$$

$x_{01} \simeq 2.405$ is the first root of the Bessel function $J_0(x)$, and $p = 1-q$. In three dimensions the corresponding result is $P(t) \sim \exp(-At^{1/2})$ where the constant $A = [16\pi^3\ln(1/p)]^{1/2}(J/18q\gamma)^{1/4}$. [We note in passing that the prefactor $C(t)$ is slowly varying but nonuniversal since it depends upon initial conditions.] The decay is, therefore, slower in the asymptotic limit than is the case for diffusive motion, where an $\exp(-At^{d/(d+2)})$ decay law occurs. As anticipated in earlier analyses by Pearlstein, Hemenger, and Lakatos-Lindenberg,[7] this slower than diffusive decay can be traced to interference effects associated with the scattering of the coherent wave off of regions associated with a change of dispersion. It is, therefore, a distinctly quantum-mechanical effect which is unexplainable in terms of, e.g., a model based upon a free classical particle moving ballistically in the region between the traps.

In summary, we have calculated the asymptotic decay of particles which move coherently in a medium containing randomly placed traps of fixed concentration. We obtain in d dimensions an asymptotic decay of the form $P(t) \sim \exp(-At^{d/(d+3)})$ and have found explicit formulas for the constant in the exponent in terms of volumes of the unit sphere in d dimensions and the zeros of d-dimensional solutions to the radial Helmholtz equation. Our result points out the need for a unified theory which would allow a theoretical description of the crossover that must take place from a diffusive decay at high temperatures to a coherent decay as the temperature is lowered. The complexity of this latter problem can be inferred from the fact that the diffusive decay is expected to become *more rapid* as the diffusion constant increases (i.e., as the phonon scattering is reduced with decreasing temperature) but ultimately must change at zero temperature to a form that is always asymptotically slower than for any diffusion process.

[1]B. Movaghar, J. Phys. C **13**, 4915 (1980); B. Movaghar, G. W. Sauer, and D. Wurtz, J. Stat. Phys. **27**, 473 (1982); H. Scher and C. W. Wu, Proc. Natl. Acad. Sci. USA **78**, 22 (1980); P. E. Parris, Phys. Lett. **114A**, 250 (1986).

[2]J. Klafter, G. Zumofen, and A. Blumen, J. Phys. Lett. (Paris) **45**, L49 (1984); S. Havlin, B. Trus, G. H. Weiss, and D. J. Ben-Avraham, J. Phys. A **18**, L247 (1985).

[3]B. Ya Balagurov and V. G. Vaks, Zh. Exp. Teor. Fiz. **65**, 1939 (1973) [Sov. Phys. JETP **38**, 968 (1974)]; M. D. Donsker and S. R. S. Varadhan, Comm. Pure Appl. Math. **28**, 525 (1975); R. Grassberger and I. Procaccia, J. Chem. Phys. **77**, 6281 (1981); R. F. Kayser and J. B. Hubbard, Phys. Rev. Lett. **51**, 79 (1983).

[4]M. Bramson and J. L. Lebowitz, Phys. Rev. Lett. **61**, 2397 (1988).

[5]I. M. Lifshitz, Adv. Phys. **13**, 483 (1964).

[6]J. M. Luttinger and R. Tao, Ann. Phys. (N.Y.) **145**, 185 (1983); R. Freidberg and J. M. Luttinger, Phys. Rev. B **12**, 4460 (1975); Th. M. Nieuwenhuizen, Phys. Rev. Lett. **62**, 357 (1989).

[7]R. M. Pearlstein, J. Chem. Phys. **56**, 2431 (1972); R. P. Hemenger and R. M. Pearlstein, Chem. Phys. **2**, 424 (1973); R. P. Hemenger, K. Lakatos-Lindenberg, and R. M. Pearlstein, J. Chem. Phys. **60**, 3271 (1974).

[8]V. M. Kenkre, Phys. Status Solidi B **89**, 651 (1978); D. L. Huber, Phys. Rev. B **22**, 1714 (1980); *ibid.* **24**, 1083 (1981); V. M. Kenkre and Y. M. Wong, *ibid.* **22**, 5716 (1980); V. M. Kenkre and P. E. Parris, *ibid.* **27**, 3221 (1983).

[9]P. E. Parris, Phys. Rev. Lett. **62**, 1392 (1989); P. E. Parris, Phys. Rev. B **40**, 4928 (1989).

[10]See, e.g., P. A. Lee and T. V. Ramakrishnan, Rev. Mod. Phys. **57**, 287 (1985), and references therein.

[11]E. N. Economou and C. M. Soukoulis, Phys. Rev. B **28**, 1093 (1983); E. N. Economou, C. M. Soukoulis, and A. D. Zdetsis, *ibid.* **30**, 1686 (1984); E. N. Economou, *ibid.* **31**, 7710 (1985).

[12]See, e.g., A. Messiah, *Quantum Mechanics,* translated by G. M. Temmer (Wiley, New York, 1962), Vol. I, p. 355.

[13]See, e.g., W. Wasow, *Asymptotic Expansions for Ordinary Differential Equations* (Dover, New York, 1987), p. 123.