Exact Solution for the Diffusion of a Particle in a Medium with Site Diagonal and Off-Diagonal Dynamic Disorder

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Exact solutions for the motion of a particle in a medium with site diagonal and nearest-neighbor off-diagonal dynamic disorder are presented for the first time. Results obtained for the diffusion constant are of relevance to different areas of current interest, such as charge or exciton motion in molecular solids, and motion of light adsorbates on substrates with weak surface potentials.

Numerous studies[1-3] of the electronic properties of disordered systems have been conducted since the pioneering work[4] of Anderson showing the absence of diffusion in certain random lattices at absolute zero temperature almost two decades ago. Most of these studies have dealt with model systems, generally one dimensional, consisting of static site diagonal disorder and focused their attention on single-particle properties like the behavior of the single-particle density of states, the nature of the single-particle states, etc. Only recently, a few microscopic studies[5,6] of the quantum transport properties have been reported. An aspect of disordered systems which has received comparatively little attention[7-9] is the behavior of particle motion under the influence of dynamic (i.e., time-dependent) disorder. In this Letter we report the first exact solution for the motion of a particle in a system with site *diagonal and* nearest-neighbor *off-diagonal* dynamic disorder. This exact solution has relevance to many current areas of study which we briefly identify at the end.

The model Hamiltonian reads

$$H=\tfrac{1}{2}\sum_{m,n}\alpha_{mn}\{|m\rangle\langle n|+|n\rangle\langle m|\}+\tfrac{1}{2}\sum_{m,n}\beta_{mn}(t)\{|m\rangle\langle n|+|n\rangle\langle m|\}, \tag{1}$$

where α_{mm} and α_{mn} denote the site energy, and the tight-binding transfer integral between the mth and nth sites, respectively, for a one-dimensional periodic chain of lattice constant a (which we take as unity in the following). The $\beta_{mn}(t)$ define the time-dependent disorder introduced into the periodic chain by the action of a stochastic medium (say, e.g., phonons). We take the $\beta_{mn}(t)$ to be Gaussian random variables with a white-noise spectrum and specified by $\langle\beta_{mn}(t)\rangle=0$ and

$$\langle\beta_{mn}(t)\beta_{m'n'}(t')\rangle=g(m-n)\delta(t-t')(\delta_{mm'}\delta_{nn'}+\delta_{mn'}\delta_{m'n}-\delta_{mn}\delta_{m'n'}\delta_{nn'}), \tag{2}$$

where $\langle\;\rangle$ denotes the average over all realizations of the random configurations. $g(m-n)$ measures the strength of the disorder, which for thermally induced disorder (i.e., phonons) will be a function of the temperature and the appropriate carrier-phonon coupling strength. This explicit relation, as well as the δ-function behavior in time of the correlation function for phonons, will be shown later to be justifiable at temperatures high compared to characteristic phonon energies. Exact solutions for site diagonal disorder[9] [i.e., only $\beta_{mm}(t)$ nonzero] and the leading-order correction[10] due to nearest-neighbor off-diagonal disorder [i.e., $\beta_{m,n>m\pm1}(t)=0$] have been reported recently. However, in the following we present an exact, closed-form, analytic result for the diffusion constant in the presence of site diagonal and nearest-neighbor off-diagonal dynamic disorder.

We follow the Heisenberg equation of motion of the single-particle density matrix which provides the probability of finding the particle at site n at time t if it were at site m at $t=0$. We use functional-derivative techniques and exploit the following result[11] valid for any set of Gaussian random variables $\{X_i(t)\}$ and a functional of this set $F(\{X_i(t)\})$:

$$\langle X_i(t)F(\{X_i(t)\})\rangle=\sum_j\int dt'\langle X_i(t)X_j(t')\rangle\left\langle\frac{\delta F(\{X_i(t)\})}{\delta X_j(t')}\right\rangle. \tag{3}$$

The equation of motion for the density matrix averaged over the random configurations is easily obtained as

$$\frac{i\partial\rho(k,k';t)}{\partial t}=\int_{-\pi}^{\pi}dq\int_{-\pi}^{\pi}dq'\langle[K(k,q;t)\delta(k'-q')-K(q',k';t)\delta(k-q)]\rho(q,q';t)\rangle+(\epsilon_k-\epsilon_{k'})\langle\rho(k,k';t)\rangle, \tag{4}$$

where we have written the equation in the momentum representation by using the definitions

$$\epsilon_k=\sum_{m=-\infty}^{+\infty}\alpha_{n,n+m}e^{-ikm}, \tag{5a}$$

$$K(k,q;t)=\frac{1}{2\pi}\sum_{m=-\infty}^{+\infty}\beta_{nm}(t)e^{-ikn+iqm}. \tag{5b}$$

Utilizing Eq. (3) in evaluating terms of the type $\langle K(k,q;t)\rho(q,q';t)\rangle$ in Eq. (4) with the aid of (5b) and (2), we obtain a closed equation for the single-particle density matirx by virtue of the white-noise nature of (2). Equation (4) thus becomes

$$\frac{\partial\langle\rho(k,k';t)\rangle}{\partial t}=-[\Gamma+i(\epsilon_k-\epsilon_{k'})]\langle\rho(k,k';t)\rangle+\frac{1}{2\pi}\int_{-\pi}^{\pi}\Gamma\left(k+\frac{q}{2},k'+\frac{q}{2}\right)\langle\rho(k+q,k'+q;t)\rangle dq \tag{6}$$

where

$$\Gamma=2\sum_{m=-\infty}^{+\infty}g(m)$$

and

$$\Gamma(q,q')=2\left[\sum_{m=-\infty}^{+\infty}g(m)\{\cos[m(q+q')]+\cos[m(q-q')]\}-g(0)\right]. \tag{7}$$

We note that the loss of translational invariance due to the disordered nature of the system has led to a dependence of $\langle\rho\rangle$ on k and k' both, rather than simply on $k-k'$. Henceforth we restrict our analysis of Eq. (6) to site diagonal and nearest-neighbor off-diagonal disorder only [i.e., $\beta_{nm}(t)=0$ for all $|m|>|n+1|$]. Thus we retain only α_{mm} and $\alpha_{m,m\pm1}$ terms for the nonrandom part of (1). If we denote $\alpha_{m,m\pm1}$ by α and introduce the variables $s=(K+K')/2$ and $u=(K-K')/2$ and write $\langle\rho(K,K';t)\rangle\equiv e^{-\Gamma t}F(u,s;t)$, $\Gamma=2g_0+4g_1$, Eq. (6) gives

$$\frac{\partial F(u,s;t)}{\partial t}=X(u,s)F(u,s;t)+B(u)\int_{-\pi}^{\pi}F(u,q;t)dq+b\int_{-\pi}^{\pi}\cos(s+q)F(u,q;t)dq, \tag{8}$$

where we have used $g_1=g_{-1}$, $X(u,s)=4i\alpha\sin u\sin s$, $b=2g_1/\pi$, $B(u)=b\cos 2u+g_0/\pi$. Furthermore, with the initial condition, $F(u,s;t=0)=A$, a constant, Eq. (8) transforms into

$$F(u,s;t)=Ae^{X(u,s)t}+\int_0^t e^{X(u,s)(t-\tau)}[\varphi(u,\tau)+h(u,q;\tau)]d\tau, \tag{9}$$

where

$$\varphi(u,t)=B(u)\int_{-\pi}^{\pi}F(u,q;t)dq, \tag{10}$$

$$h(u,s;t)=b\int_{-\pi}^{\pi}\cos(s+q)F(u,q;t)dq. \tag{11}$$

Substituting the expression for $F(u,s;t)$ from Eq. (9) into (10) and (11), and taking the Laplace transform of the resulting equations for φ and h, we may write

$$\Phi(u,p)=l\left\{2\pi ABf(u,p)+B\int_{-\pi}^{\pi}dq\,fH\right\}, \tag{12}$$

$$H(u,s;p)=AbI+bIl\left\{2\pi ABf(u,p)+B\int_{-\pi}^{\pi}dq\,fH\right\}+b\int_{-\pi}^{\pi}\cos(s+q)fH\,dq, \tag{13}$$

where

$$I=I(s,p)=\int_{-\pi}^{\pi}\cos(s+q)f(u,q;p)dq,$$

and

$$l=l(u,p)=1/[1-2\pi Bf(u,p)],\quad f(u,p)=\mathfrak{L}(J_0(4\alpha t\sin u)),$$

$$f=f(u,q;p)=\mathfrak{L}(e^{X(u,q)t}),\quad H=H(u,q;p)=\mathfrak{L}(h(u,s;t)),\quad \Phi(u,p)=\mathfrak{L}(\varphi(u,t)).$$

Here J_0 is Bessel's function of order zero. Expanding the $\cos(s+q)$ factor in the last term of (13) reduces (12) and (13) to a set of three simultaneous algebraic equations for the functions

$$\Omega_1=\int_{-\pi}^{\pi}dq\,fH,\quad \Omega_2=\int_{-\pi}^{\pi}dq\cos q\,fH,\quad \Omega_3=\int_{-\pi}^{\pi}dq\sin q\,fH.$$

The resulting solutions for Ω_1, Ω_2, and Ω_3 are then substituted into (12) and (13) to get exact solutions for $\Phi(u,p)$ and $H(u,s;p)$. The inverse Laplace transforms of $\Phi(u,p)$ and $H(u,s;p)$ give $\varphi(u,t)$ and $h(u,s;t)$, which when substituted into Eq. (9) give the exact expression for $F(u,s;t)$, and thus the density matrix $\langle\rho(u,s;t)\rangle=e^{\Gamma t}F(u,s;t)$.

The main result of interest to us is the mean-square displacement of the particle, which is given by

$$\langle R^2\rangle=-\frac{1}{4}\int_{-\pi}^{\pi}\frac{\partial^2\langle\rho(u,s;t)\rangle}{\partial u^2}\bigg|_{u=0}ds=-\frac{1}{4}\frac{e^{-\Gamma t}}{2\pi i}\int_{-\pi}^{\pi}ds\int_{-i\infty+\delta}^{i\infty+\delta}e^{pt}\frac{\partial^2F(u,s;p)}{\partial u^2}\bigg|_{u=0}dp,\tag{14}$$

where $F(u,s;p)=\mathfrak{L}(F(u,s;t))$. We may thus circumvent a certain amount of tedious algebra by evaluating $\langle R^2\rangle$ directly, employing the expressions for $H(u,s;p)$ and $\Phi(u,s;p)$ in evaluating $(\partial^2F/\partial u^2)|_{u=0}$. The exact expression for the mean-square displacement is found to be

$$\begin{aligned}\langle R^2\rangle={}&\frac{4\alpha^2t}{\Gamma}-\frac{4\alpha^2}{\Gamma^2}(1-e^{-\Gamma t})+\left(4g_1-\frac{8g_1\alpha^2}{\Gamma^2}+\frac{16g_1{}^2\alpha^2}{\Gamma^2(\Gamma+2g_1)}\right)t+\left(\frac{16g_1\alpha^2}{\Gamma^3}-\frac{16g_1{}^2\alpha^2}{\Gamma^2(\Gamma+2g_1)^2}-\frac{32g_1{}^2\alpha^2}{\Gamma^3(\Gamma+2g_1)}\right)\\&+\left(-\frac{16g_1\alpha^2}{\Gamma^3}+\frac{16g_1{}^2\alpha^2}{\Gamma^2(\Gamma+2g_1)^2}+\frac{8g_1\alpha^2}{\Gamma(\Gamma+2g_1)^2}+\frac{16g_1\alpha^2}{\Gamma^2(\Gamma+2g_1)}-\frac{8\alpha^2}{\Gamma^2}+\frac{32g_1{}^2\alpha^2}{\Gamma^3(\Gamma+2g_1)}+\frac{4\alpha^2}{\Gamma(\Gamma+2g_1)}\right)e^{-\Gamma t}\\&+\left(\frac{8g_1\alpha^2}{\Gamma^2}-\frac{16\alpha^2g_1{}^2}{\Gamma^2(\Gamma+2g_1)}-\frac{8\alpha^2g_1}{\Gamma(\Gamma+2g_1)}\right)te^{-\Gamma t}\\&+\left(-\frac{8g_1\alpha^2}{\Gamma(\Gamma+2g_1)^2}-\frac{16g_1\alpha^2}{\Gamma^2(\Gamma+2g_1)}+\frac{8\alpha^2}{\Gamma^2}-\frac{4\alpha^2}{\Gamma(\Gamma+2g_1)}\right)\exp[-(\Gamma+2g_1)t]\ .\end{aligned}\tag{15}$$

The diffusion constant, defined as $D=t^{-1}\langle R^2\rangle$, may thus be obtained from (15).

It is easily checked that for $\alpha\gg g_0,g_1$ one obtains $D=2\alpha^2t$ reflecting free motion for $t<g_0{}^{-1}$, $g_1{}^{-1}$, as expected. For the interesting case $\alpha\ll g_0,g_1$, one also finds $D=2\alpha^2t$ for short times, i.e., for $t\ll g_0{}^{-1},g_1{}^{-1}$. For long times, i.e., $t\gg g_0{}^{-1}g_1{}^{-1}$ diffusive behavior sets in, with the diffusion constant given by

$$D=4g_1+\frac{\alpha^2}{\Gamma}\left[4-\frac{8g_1}{\Gamma}+\frac{16g_1{}^2}{\Gamma(\Gamma+2g_1)}\right],\tag{16}$$

where we recall that $\Gamma=2g_0+4g_1$. Setting g_1 or g_0 equal to zero, respectively, one obtains the results for site diagonal or off-diagonal disorder alone.

We now turn to a discussion of the relevance of the model and the significance of the exact result, Eq. (16), for the diffusion constant obtained by us. As an example, consider the site diagonal and off-diagonal disorder to arise from the random thermal motion of the atoms in the solid. For solids consisting of molecular species rather than single atoms (such as organic quasi one-dimensional conductors or molecular solids) one may consider the site diagonal disorder to arise from the intramolecular vibrational mode(s) and the off-diagonal disorder to arise from the random (thermal) modulation of the nearest-neighbor transfer integral of the carriers. The former corresponds to random modulation of the carrier site energy. In either case, it is a simple matter to show that at temperatures high compared to the relevant characteristic phonon energy, the correlation function for the displacement of the atoms goes like

$$\langle x_{mn}(t)x_{mn}(t')\rangle=(\pi^2T/12M\Omega_{\mathrm{D}}{}^3)\,\delta(t-t'),\tag{17}$$

where $x_{mn}(t)$ is the separation of the mth and nth atoms and we have, for explicitness, considered a Debye spectrum for phonons characterized by the Debye frequency Ω_{D}. M is the appropriate reduced mass of the ion. The δ-function behavior in time is a consequence of limiting ourselves to the regime $T\gg\Omega_{\mathrm{D}}$. Comparison of (17) and the defining equation (2) of our random variables shows that $g(m-n)=\gamma^2(m-n)(\pi^2T/12M\Omega_{\mathrm{D}}{}^3)$ where $\gamma(m-n)$ is the coupling strength of the carriers with the phonons. In particular, $\gamma(0)=(\partial\alpha_0/\partial x)|_{x=0}$ and $\gamma(1)=(\partial\alpha/\partial x)|_{x=0}$. Utilizing the linear temperature dependence of g_0 and g_1 we thus obtain from Eq. (16)

$$D=C\gamma_1{}^2T+\alpha^2V(CT)^{-1}\{4-8\gamma_1{}^2V+8\gamma_1{}^2VW\},\tag{18}$$

where $C=\pi^2/12M\Omega_{\mathrm{D}}{}^3$, $V=1/(2\gamma_0{}^2+4\gamma_1{}^2)$, $W=1/$

$(\gamma_0^2+3\gamma_1^2)$. Expression (18) is a remarkable new and exact result for thermally induced disorder. It shows that the contribution of the nearest-neighbor off-diagonal disorder gives rise to a leading-order term in the diffusion constant which is linearly proportional to the temperature in the high-temperature regime. An example of the significance of this result may be seen for nondegenerate carrier distribution, for which the mobility is readily obtained from the Einstein relation:

$$\mu = eD/k_B T = C_1 + C_2/T^2, \tag{19}$$

where C_1 and C_2 are constants. Thus for systems dominated by nearest-neighbor off-diagonal disorder and narrow band width (i.e., $C_1 \gg C_2$), we find that the carrier mobility will exhibit a very weak temperature dependence. We believe this to be an explanation of the observed weak temperature dependence of mobility in As_2S_3 which has hitherto remained unexplained.[12]

Finally, for organic molecular crystals, such as 1-4-dibromonaphthalene, it has been established[13,14] that the motion of the Frenkel exciton, which is crucial to the explanation of such properties as energy transfer without charge transfer, ESR, NMR, etc., shows a continuous change of the character of motion from purely coherent to purely diffusional with increasing temperature. For light adsorbates in weak surface potentials, such as helium on graphite or noble-gas solid surfaces, essentially coherent (i.e., free) motion has been found.[10] The behavior of both these systems has been discussed[10,14] for many years in terms of approximate solutions of the model Hamiltonian, Eq. (1). Our exact solution thus provides a rigorous basis for the understanding of these systems as well. Details of these comparisons will be published elsewhere.

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