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On electronic energy transfer in disordered systems

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A generalized master equation (GME) describing the incoherent motion of an excitation in a disordered system is developed. The connection of the GME to the semi-Markovian theory of Scher and Lax, the generalized continuous random walk, and the self-energy approaches to the temporal properties of the transport is discussed. The theory is used in a model calculation to compute the mean square displacement and the probability of the excitation to remain at the origin as functions of time, and the results are compared to recent work on one dimensional systems, in which only nearest neighbor interactions are included.

INTRODUCTION

Recently, the phenomena of spectral and spatial diffusion of localized excitations have received attention both experimentally[1a,2-4] and theoretically.[1b,4-8] Most studies have been concerned with the motion of the excitation within an inhomogeneously broadened optical line,[2-7] although this is a special case of a much broader class of problems involving an incoherent, strong scattering process under the presence of disorder. Examples are electronic energy transfer (EET) in molecular crystals,[1] in ionic crystals,[2-4] EET in glasses,[9] and in solutions.[8] New insight may also be gained in problems like the primary process in photosynthesis,[10] electron transfer in solution and spin migration,[11] where the excitation obeys a master equation (ME) and the transfer rates are distributed according to a certain probability distribution function.

In what follows we shall be interested in EET (or the related phenomena) in *monomer* bands or in ordered (or almost ordered) systems; hence, no clusters are involved in the energy migration, except for those that provide a possible mechanism for randomizing the hopping rates, as will be discussed later. We will concentrate on two quantities: the mean square displacement $\langle \xi^2(t) \rangle$ and the probability of the excitation to remain at its origin at time t, $\langle p_0(t) \rangle$. Both quantities have been studied recently using a variety of methods:

(a) Solution of the ME for dilute systems in the short time limit, both for $\langle \xi^2(t) \rangle$[8] and $\langle p_0(t) \rangle$[4,12];

(b) Monte Carlo calculations of the ME in one dimension (1D) over the whole time regime[6] for $\langle p_0(t) \rangle$ only;

(c) 1D "exact" results for both $\langle \xi^2(t) \rangle$ and $\langle p_0(t) \rangle$ in the long time limit[13,14];

(d) Using the generalized continuous time random walk in *the pair approximation*[15] for calculating $\langle \xi^2(t) \rangle$;

(e) A diagrammatic approach for calculating $\langle \xi^2(t) \rangle$.[16]

In this paper, we show that the problem of the incoherent migration of an excitation in a disordered system can be described by a generalized master equation (GME) which provides the *connection* between the above-mentioned methods. Throughout this paper we shall be interested in the long time behavior of $\langle \xi^2(t) \rangle$ and $\langle p_0(t) \rangle$, which are still a matter of uncertainty.[7] We adopt the generalized continuous random walk approach[17] (GCTRW) and reduce it in the long time limit to a case equivalent to the multiple trapping model according to the Scher–Montrol theory.[18] The asymptotic behavior of $\langle \xi^2(t) \rangle$ and of $\langle p_0(t) \rangle$ exhibits the importance of the off-diagonal disorder which may result in a time dependent diffusion coefficient that represents quasitrapped excitations. A scaling argument based on the theory of Scher–Lax[17] is used to discuss probability distribution functions of the transfer rates, ω, which have singular behavior near $\omega = 0$. We assume that sinks and supertraps are not present; their effect on the long time behavior is discussed in another paper.[19]

II. GENERAL FORMALISM

Consider a lattice in which a certain fraction of sites, C, are occupied in a random manner by impurity molecules. An electronic excitation is supposed to migrate from one impurity to another. We assume that the equation governing the excitation migration is the ME:

$$\dot{p}_n(t) = \sum_{m \neq n} [W_{mn} p_m(t) - W_{nm} p_n(t)] , \tag{1}$$

where W_{mn} is the transition rate from site m to site n, and for convenience we will assume the high temperture limit so that $W_{mn} = W_{nm}$. We may write Eq. (1) as a matrix equation

$$\dot{\mathbf{p}}_n(t) = \sum_m (V)_{mn} \mathbf{p}_m(t) , \tag{2}$$

where

$$\mathbf{V}_{mn} = (1 - \delta_{nm}) W_{mn} - \delta_{mn} \sum_{q \neq n} W_{nq} . \tag{3}$$

The general properties of the solutions to Eq. (1) are well known and will not be considered further.

Equation (1) holds for every configuration of impurity molecules (at site fraction C), but with transition rates which depend on configuration. Each configuration gives rise to a set of interimpurity distances on the lattice, which in turn gives rise to a set of W_{mn}. For each configuration, we may solve for $p_n(t)$, assuming that the excitation was on site $n = 0$ at $t = 0$, and we find

$$p_n(t) = \{\exp(t\mathbf{V})\}_{no} . \tag{4}$$

Averaging over all configurations, we obtain

$$\langle p_n(t) \rangle = \langle \exp(t\mathbf{V}) \rangle_{no} . \tag{5}$$

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In the Laplace transform representation Eq. (5) is:

$$\langle \tilde{p}_n(u)\rangle = \langle (u - \mathbf{V})^{-1}\rangle_{no} \,. \tag{6}$$

Defining a projection operator as

$$\mathcal{P}\cdots = \langle \cdots\cdots\rangle \,, \tag{7}$$

we have (see Appendix for details) for the configurational average of $\tilde{p}_n(u)$

$$\begin{aligned}\langle \tilde{p}_n(u)\rangle &= \langle (u - \mathbf{V})^{-1}\rangle_{no} \\ &= [u - \langle \mathbf{V}\rangle - \langle \delta\mathbf{V}[u - (1-\mathcal{P})\mathbf{V}]^{-1}\delta\mathbf{V}\rangle]^{-1}_{no} \\ &= [u - \tilde{\boldsymbol{\Sigma}}(u)]^{-1}_{no} \,,\end{aligned} \tag{8}$$

where

$$\delta\mathbf{V} = \mathbf{V} - \langle \mathbf{V}\rangle \tag{9}$$

and $\tilde{\boldsymbol{\Sigma}}(u)$ is a self-energy matrix. Rewriting Eq. (8) we now have

$$\langle \tilde{p}_n(u)\rangle = [u^{-1} + u^{-1}\tilde{\boldsymbol{\Sigma}}(u)(u - \tilde{\boldsymbol{\Sigma}}(u))^{-1}]_{no} \tag{10}$$

and

$$\begin{aligned}u\langle \tilde{p}_n(u)\rangle &= \delta_{no} + \sum_l \tilde{\Sigma}_{nl}(u)\langle \tilde{p}_l(u)\rangle \\ &= \delta_{no} + \sum_{l\neq n} \tilde{\Sigma}_{nl}(u)\langle p_l(u)\rangle + \tilde{\Sigma}_{nn}(u)\langle \tilde{p}_n(u)\rangle \,;\end{aligned} \tag{11}$$

one then arrives at a GME for the $\langle p_n(t)\rangle$ with kernels (self-energy matrix elements) that contain the information about disorder:

$$\begin{aligned}\langle \dot{p}_n(t)\rangle = \int_0^t d\tau \Big\{ &\sum_{l\neq n} \Sigma_{nl}(\tau)\langle p_l(t-\tau)\rangle \\ &+ \Sigma_{nn}(\tau)\langle p_n(t-\tau)\rangle \Big\} \,,\end{aligned} \tag{12}$$

with the initial condition

$$\langle p_n(0)\rangle = \delta_{no} \,.$$

Upon averaging, the system is translationally invariant, representing an effective or averaged system; therefore,

$$\Sigma(\mathbf{k},\tau) = \sum_{n\neq l} \exp[-i\mathbf{k}\cdot(\mathbf{n}-\mathbf{l})]\Sigma_{nl}(\tau) \tag{13a}$$

$$\Sigma(\mathbf{k}=0,\tau) = \sum_{n\neq l} \Sigma_{nl}(\tau) = -\Sigma_{nn}(\tau) \tag{13b}$$

The GME can be rewritten as

$$\begin{aligned}\langle \dot{p}_n(t)\rangle = \sum_{l\neq n} \int_0^t d\tau \{&\Sigma_{nl}(t-\tau)\langle p_l(\tau)\rangle\} \\ &- \Sigma_{ln}(t-\tau)\langle p_n(\tau)\rangle \,.\end{aligned} \tag{14}$$

Laplace transforming this equation, one arrives at

$$u\langle \tilde{p}_n(u)\rangle - \delta_{no} = \sum_l \Sigma_{nl}(u)\langle \tilde{p}_l(u)\rangle - \tilde{\Sigma}_{ln}(u)\langle \tilde{p}_n(u)\rangle \,, \tag{15}$$

or, using the k representation,

$$u\langle \tilde{p}_{\mathbf{k}}(u)\rangle - 1 = [\tilde{\Sigma}(\mathbf{k},u) - \tilde{\Sigma}(\mathbf{0},u)]\langle \tilde{p}_{\mathbf{k}}(u)\rangle \,. \tag{16}$$

From Eq. (16) we derive the following relations:

$$\langle \tilde{p}_{\mathbf{k}}(u)\rangle = [u + \tilde{\Sigma}(\mathbf{0},u) - \tilde{\Sigma}(\mathbf{k},u)]^{-1} \equiv G(\mathbf{k},u) \,, \tag{17a}$$

and

$$\begin{aligned}\langle \tilde{p}_n(u)\rangle &= N^{-1}\sum_{\mathbf{k}} \frac{e^{i\mathbf{k}\cdot\mathbf{n}}}{u + \tilde{\Sigma}(\mathbf{0},u) - \tilde{\Sigma}(\mathbf{k},u)} \\ &= \frac{N^{-1}}{u + \tilde{\Sigma}(\mathbf{0},u)} \sum_{\mathbf{k}} \frac{e^{i\mathbf{k}\cdot\mathbf{n}}}{1 - [\tilde{\Sigma}(\mathbf{k},u)/(u + \tilde{\Sigma}(\mathbf{0},u))]} \,.\end{aligned} \tag{17b}$$

The two representations of the probability, Eqs. (17a) and (17b), can now easily be related to the methods mentioned in the introduction. Equation (17a) is the basic equation for the method which adopts a diagrammatric expansion by Gochanour *et al.*[16] This method is a generalization of the Haan–Zwanzig approach[8] to include also long time tails. Equation (17b) can be related to the GCTRW discussed by Scher and Lax,[17] which will be used in Secs. IV and V for a model system. Both approaches are closely related through the above equations, each providing a different starting point for approximations for summing up terms in the self-energy series expansions.

Gochanour *et al.*[16] define a generalized diffusion coefficient $D(\mathbf{k},u)$ by the identity

$$G(\mathbf{k},u) = [u + k^2 D(\mathbf{k},u)]^{-1} \,. \tag{18}$$

Using Eq. (17a) for $G(\mathbf{k},u)$, they obtain

$$D(\mathbf{k}=0,u) = \lim_{k\to 0} k^{-2}[\tilde{\Sigma}(\mathbf{0},u) - \Sigma(\mathbf{k},u)] \,. \tag{19}$$

Any function of u, say $H(u)$, can be added to $\tilde{\Sigma}(\mathbf{k},u)$ for all $\mathbf{k}$, and the form of Eqs. (17b) and (19) remains invariant.[16] The $k=0$ limit of the generalized diffusion coefficient determines migration of an excitation at large displacements and allows an exact definition of the $\langle \xi^2(t)\rangle$[8] for long times. The Laplace transform of the mean square displacement at small u is

$$\langle \tilde{\xi}^2(u)\rangle \sim \lim_{u\to 0} u^{-2} D(\mathbf{k}=0,u) \,. \tag{20}$$

If $D(\mathbf{k}=0,u)$ is independent of u, one gets the usual relation between $\langle \xi^2(t)\rangle$ and D.

In the following section we discuss the derivation of the GCTRW[17] equations starting from Eq. (17b).

III. THE GENERALIZED CONTINUOUS TIME RANDOM WALK

Equation (17b) provides a connection between the GME and the GCTRW theory. Defining a generalized structure function $\Lambda(\mathbf{k},u)$ by

$$\Lambda(\mathbf{k},u) \equiv \frac{\tilde{\Sigma}(\mathbf{k},u)}{u + \tilde{\Sigma}(\mathbf{0},u)} \,, \tag{21}$$

we rewrite Eq. (17b) as

$$\begin{aligned}\langle \tilde{p}_n(u)\rangle &= \frac{N^{-1}}{u + \tilde{\Sigma}(\mathbf{0},u)} \sum_{\mathbf{k}} \frac{e^{i\mathbf{k}\cdot\mathbf{n}}}{1 - \Lambda(\mathbf{k},u)} \\ &= \frac{1 - \Lambda(\mathbf{0},u)}{u} \cdot N^{-1} \sum_{\mathbf{k}} \frac{e^{i\mathbf{k}\cdot\mathbf{n}}}{1 - \Lambda(\mathbf{k},u)} \,.\end{aligned} \tag{22}$$

Let $\Psi(\mathbf{s},t)$ be the probability density for hopping a distance $\mathbf{s}$ with a hopping time t. $\tilde{\Psi}(\mathbf{s},u)$ is its Laplace transform; then by making the identification

$$\tilde{\Psi}(\mathbf{k},u) = \sum_{\mathbf{s}\neq 0} \tilde{\Psi}(\mathbf{s},u)\, e^{-i\mathbf{k}\cdot\mathbf{s}} \,, \tag{23}$$

an exact relationship between the GME and GCTRW is found. The following relationships are now easily verified:

$$\tilde{\Psi}(\mathbf{s},u) = \tilde{\Sigma}(\mathbf{s},u)[u + \tilde{\Sigma}(\mathbf{0},u)]^{-1} \,, \tag{24}$$

$$\tilde{\Psi}(u) \equiv \sum_{s\neq 0} \tilde{\Psi}(\mathbf{s},u) = \tilde{\Sigma}(\mathbf{0},u)\,[u+\tilde{\Sigma}(\mathbf{0},u)]^{-1}\ , \tag{25}$$

$$\tilde{\Sigma}(\mathbf{0},u) = u\tilde{\Psi}(u)/[1-\tilde{\Psi}(u)]\ . \tag{26}$$

These relations between the self-energies and the hopping time distribution function are *exact*. This is an extension of the conclusion by Butcher[20] that the GCTRW is equivalent to some modified pair approximation in solving the ME, Eq. (1). $\tilde{\Sigma}(0,u)$ can also be identified with the relaxation function in the work of Kenkre *et al.*[21] The above relations, equations (24)–(26) provide a clear connection among the various approaches to study the incoherent EET in disordered systems. In spite of the equivalence between the self-energy method and the GCTRW, the results for $\langle \xi^2(t)\rangle$ and $\langle p_0(t)\rangle$ may differ in the two frameworks owing to the use of different approximations.

From Eqs. (21) and (22) and from the relations between the self-energies and the hopping time distribution function, it turns out that

$$\langle \tilde{p}_n(u)\rangle = \frac{1-\tilde{\Psi}(u)}{u}\,R(n,u)\ , \tag{27}$$

where

$$R(n,u) = N^{-1}\sum_{\mathbf{k}} \frac{e^{i\mathbf{k}\cdot\mathbf{n}}}{1-\Lambda(\mathbf{k},u)} \tag{28}$$

is a generalized generating function.[17] $\langle \tilde{p}_n(u)\rangle$ has been derived here in the framework of a GME approach; it can also equivalently be derived from a generalization of the Montroll–Weiss CTRW.[17] $\langle p_0(t)\rangle$ is of course given by the inverse Laplace transform of $\langle \tilde{p}_0(u)\rangle$,

$$\langle p_0(t)\rangle = \mathcal{L}^{-1}\{\langle \tilde{p}_0(u)\rangle\}\ . \tag{29}$$

The mean square displacement at long times can be shown[17] to be the inverse Laplace transform of

$$\langle \tilde{\xi}^2(u)\rangle = \lim_{u\to 0} u^{-2}\sum_s \frac{s^2\,\tilde{\Psi}(s,u)u}{1-\tilde{\Psi}(u)}$$

$$= \lim_{u\to 0} u^{-2}\sum_s \tilde{\Sigma}(s,u)\,s^2\ . \tag{30}$$

A very useful limit of the GCTRW is the CTRW, or the Scher–Montroll limit,[18] which assumes a decoupling of the generalized structure factor $\Lambda(\mathbf{k},u)$, or of its Fourier transform $\tilde{\Psi}(\mathbf{s},u)$:

$$\Lambda(\mathbf{k},u) = \tilde{\Psi}(u)\sum_{s\neq 0} p(s)\,e^{-i\mathbf{k}\cdot\mathbf{s}}\ , \tag{31}$$

leading to

$$\langle \tilde{p}_n(u)\rangle = \frac{1-\tilde{\Psi}(u)}{u}\,R_0(n,\tilde{\Psi}(u))\ , \tag{32}$$

where

$$R_0(n,\tilde{\Psi}(u)) = N^{-1}\sum_{\mathbf{k}} \frac{e^{i\mathbf{k}\cdot\mathbf{u}}}{1-\tilde{\Psi}(u)\lambda(\mathbf{k})}\ ,$$

$$\lambda(\mathbf{k}) = \sum_{s\neq 0} p(s)\,e^{i\mathbf{k}\cdot\mathbf{s}}\ . \tag{33}$$

$R_0(n,u)$ is the lattice generating function, and $\lambda(\mathbf{k})$ is the usual structure factor.[21b,22]

Then,

$$\langle \tilde{\xi}^2(u)\rangle = \sum_s s^2 p(s)\,\frac{\tilde{\Psi}(u)}{[1-\tilde{\Psi}(u)]u}\ . \tag{34}$$

Note that the time dependence of $\langle \xi^2(t)\rangle$ in the CTRW scheme is given by

$$\frac{\tilde{\Psi}(u)}{u(1-\tilde{\Psi}(u))}\ ,$$

which depends on the disordered nature of the system and whose form does *not* depend on its dimensionality although the explicit function of u of course depends on the topology of the lattice. The form of $\langle p_0(t)\rangle$ on the other hand does depend on the system's dimensionality.

The different behavior of $\langle p_0(t)\rangle$ and of $\langle \xi^2(t)\rangle$ with respect to dimensionality generalizes in some sense the 1D results of Refs. 13 and 14, which point toward the interesting relation

$$\langle p_0(t)\rangle \sim \langle \xi^2(t)\rangle^{-d/2}\ , \tag{35}$$

where d is the dimensionality. We show later that this relation is typical only for the 1D problem in general, although it holds for all d in the diffusive limit.

In the present section, we have shown that the GCTRW is equivalent to the GME and is therefore exact. Thus an exact calculation can be done of *either* the $\Sigma_{nm}(t)$ for the GME or the $\Psi(s,t)$ for the GCTRW. In general, of course, exact calculations of either are impractical. However, an approximate calculation of $\Psi(t)$ can be done by connecting $\Psi(t)$, the distribution function of hopping times, to the distribution function of hopping rates. In the next section we will present a *plausible* but not exact relation between $\tilde{\Psi}(u)$ and the distribution function of hopping rates, $\rho(\omega)$ [where ω is a hopping rate related to the W_{mn}'s appearing in Eq. (1)] which will enable us to compute $\langle \xi^2(t)\rangle$ and $\langle p_0(t)\rangle$ *without calculating the kernels in the GME*. Since we are interested in the long time behavior of $\tilde{\Psi}(t)$, or equivalently the small u behavior of $\tilde{\Psi}(u)$, the important part of $\rho(\omega)$ will be near $\omega=0$. We also assume that the small ω part of the $\rho(\omega)$ is dominated by the distribution of nearest neighbor impurity W_{mn}'s appearing in the original master equation, Eq. (1).

IV. MODEL CALCULATIONS

The CTRW has been shown[23–25] to be equivalent to a multiple trapping model which provides a reasonable relation between $\tilde{\Psi}(u)$ and $\rho(\omega)$. The multiple trapping describes a situation where the excitation can choose to leave a site via a broad spectrum of relaxation rates, ω, with a reasonably smooth normalized $\rho(\omega)$, so that[23–25]

$$\Psi(t) = \int_0^\infty d\omega\,\omega\,e^{-\omega t}\,\rho(\omega)\ . \tag{36a}$$

$\tilde{\Psi}(u)$ is given by the Stieltjes transform of $\omega\rho(\omega)$

$$\tilde{\Psi}(u) = \int_0^\infty d\omega\,\frac{\omega\rho(\omega)}{\omega+u}\ , \tag{36b}$$

and

$$\frac{1-\tilde{\Psi}(u)}{u} = \int_0^\infty d\omega\,\frac{\rho(\omega)}{\omega+u}\ .$$

We now choose three typical distribution functions[13,14]:

(a) $\rho(\omega)$ such that $\langle\omega^{-1}\rangle$ exists ; (37a)

(b) $\rho(\omega) = \begin{cases} (1-\alpha)\omega^{-\alpha} & 1 \le \omega \le 0,\ 0 < \alpha < 1 \\ 0 & \text{otherwise;} \end{cases}$ (37b)

(c) $\rho(\omega)$ as in (b), but with $\alpha = 0$. (37c)

We will study each situation separately.

(a) $\rho(\omega)$ such that $\langle\omega^{-1}\rangle$ exists

According to Eq. (36),

$$\tilde{\Psi}(u) = 1 - \langle\omega^{-1}\rangle u + O(u^2) , \tag{38}$$

where

$$\langle\omega^{-m}\rangle = \int d\omega \frac{\rho(\omega)}{\omega^m} \tag{39}$$

and

$$\langle\omega^{-m}\rangle = m!\,\overline{t^m} ,$$

$$\overline{t^m} = \int t^m \Psi(t)\, dt . \tag{40}$$

In the framework of the CTRW, Eq. (34),

$$\langle\tilde{\xi}^2(u)\rangle \sim \frac{\tilde{\Psi}(u)}{u[1-\tilde{\Psi}(u)]} = \frac{1-\langle\omega^{-1}\rangle u}{u[\langle\omega^{-1}\rangle u]} . \tag{41}$$

It then follows that

$$\langle\xi^2(t)\rangle \sim \omega_{\text{eff}}\, t , \tag{42}$$

where

$$\omega_{\text{eff}}^{-1} = \langle 1/\omega\rangle^{-1} . \tag{43}$$

This result is *independent* of dimensionality. $\langle p_0(t)\rangle$ calculated according to Eqs. (32) yields

$$\langle p_0(t)\rangle = \frac{1-\tilde{\Psi}(u)}{u} R_0(0, \tilde{\Psi}(u))$$

$$\sim \langle\omega^{-1}\rangle R_0(0, \tilde{\Psi}(u)) \quad \text{as } u \to 0 . \tag{44}$$

$\langle p_0(t)\rangle$ strongly depends on dimensionality via $R_0(0,\tilde{\Psi}(u))$. $R_0(0,z)$ is found to be[22]

$$R_0(0,z) \sim \left\{ \begin{array}{ll} \text{1D } (1-z^2)^{-1/2} & \text{(45a)} \\ \text{2D } -\pi^{-1}\log(1-z) & \text{(45b)} \\ \text{3D const } + a(1-z)^{1/2} & \text{(45c)} \end{array} \right\} z \to 1 .$$

Therefore, the results for $\langle p_0(t)\rangle$ change drastically with dimensionality. One obtains in the case of a "well-behaved" $\rho(\omega)$ the usual asymptotic $\langle p_0(t)\rangle$ for ordered systems[26]; thus, a disordered system characterized by (37a) having first moment behaves at long time as an *ordered* system. An example of such a $\rho(\omega)$ is provided by multipolar interaction in all dimensions:

1D:

$$\langle\tilde{p}_0(u)\rangle \sim \omega_{\text{eff}}^{-1}[1-\tilde{\Psi}^2(u)]^{-1/2}$$

$$\sim \omega_{\text{eff}}^{-1/2} u^{-1/2}, \quad u \to 0 \tag{46}$$

and

$$\langle p_0(t)\rangle \sim \omega_{\text{eff}}^{-1/2} t^{-1/2}, \quad t \to \infty ; \tag{47}$$

2D:

$$\langle\tilde{p}_0(u)\rangle \sim \omega_{\text{eff}}^{-1}[-\pi^{-1}\log(1-\tilde{\Psi}(u))]$$

$$\sim \omega_{\text{eff}}^{-1}\log\left(\frac{1+Au}{Bu}\right) \quad \text{as } u \to 0 , \tag{48}$$

$$\langle p_0(t)\rangle \sim \omega_{\text{eff}}^{-1} t^{-1} \quad \text{as } t \to \infty ; \tag{49}$$

3D:

$$\langle\tilde{p}_0(u)\rangle \sim \omega_{\text{eff}}^{-1}[\text{const} + a(1-\tilde{\Psi}(u))^{1/2}]$$

$$\sim \omega_{\text{eff}}^{-1} \text{ const} + a\,\omega_{\text{eff}}^{-3/2} u^{1/2} \quad \text{as } u \to 0 , \tag{50}$$

$$\langle p_0(t)\rangle \sim \omega_{\text{eff}}^{-3/2} t^{-3/2} \quad \text{as } t \to \infty . \tag{51}$$

It is obvious that Relation (35) holds for the usual diffusive situation. We would like to emphasize here that Eqs. (42), (47), (49), and (51) can also be obtained by exactly solving the ME for ordered systems as $t \to \infty$[26] [the exact solution found by calculating the self-energy terms Eq. (17a)].

(b) $\rho(\omega) \sim \omega^{-\alpha}$; $0 \le \omega \le 1$

For this case $\langle 1/\omega\rangle$ does not exist. This interesting behavior is typical to dilute 1D systems dominated by exchange type interactions[19,27] or to systems where incoherent motion is induced by fluctuations of an Arrhenius activation law.[9,28,29] In the latter case α is temperature dependent and may change as a function of temperature to give all the three $\rho(\omega)$ given by Eqs. (37) ($\alpha < 0$, $\alpha = 0$, $\alpha > 0$). For $\alpha > 0$,

$$\tilde{\Psi}(u) = (1-\alpha)\int_0^1 \frac{\omega^{1-\alpha}}{\omega+u} d\omega \sim 1 - A u^{1-\alpha} , \quad u \to 0 \tag{52}$$

where A is independent of u,

$$\langle\tilde{\xi}^2(u)\rangle \sim u^{-(2-\alpha)}, \quad u \to 0 , \tag{53}$$

and

$$\langle\xi^2(t)\rangle \sim t^{1-\alpha} \quad \text{as } t \to \infty . \tag{54}$$

These results are again independent of dimension. Note that Alexander and Bernasconi[14] found $\langle\xi^2(t)\rangle^{1/2} \sim t^{(1-\alpha)/(2-\alpha)}$, which differs from (54). We shall comment on this later.

Calculating $\langle p_0(t)\rangle$ for 1D we obtain

$$\langle p_0(u)\rangle = \frac{A u^{1-\alpha}}{u}[1-(1-A u^{1-\alpha})^2]^{1/2} \tag{55}$$

$$\sim B u^{-(1+\alpha)/2}, \quad u \to 0 ,$$

$$\langle p_0(t)\rangle \sim t^{-[(1-\alpha)/2]}, \quad t \to \infty . \tag{56a}$$

Equations (54) and (56) clearly demonstrate that for 1D, Relation (35) holds.

Using Eqs. (32), (33), (45b), and (45c), we obtain for higher dimensionalities

$$\text{2D: } \langle p_0(t)\rangle \sim t^{\alpha-1} \lg t^{1-\alpha} \quad t \to \infty , \tag{56b}$$

$$\text{3D: } \langle p_0(t)\rangle \sim t^{\alpha-1} \quad t \to \infty , \tag{56c}$$

which show that Relation (35) does not hold for d higher than 1, *at least in the framework of our model calculation.* These interesting results are due to the singular $\rho(\omega)$, Eq. (37b), which is unlikely in 2D or 3D.

(c) $\rho(\omega) \sim$ const (i.e., $\alpha = 0$) $0 \le \omega \le 1$

In this case,

$$\tilde{\Psi}(u) = \int_0^1 \frac{\omega}{\omega+u} d\omega \to 1 + u\ln u - u, \quad u \to 0 . \tag{57}$$

It follows that

$$\langle \tilde{\xi}^2(u)\rangle \sim [-u^2 \ln u]^{-1}, \quad u \to 0 , \tag{58}$$

and therefore

$$\langle \xi^2(t)\rangle \sim t/\ln t, \quad t \to \infty . \tag{59}$$

$\langle p_0(t)\rangle$ calculated for 1D systems results in

$$\langle p_0(t)\rangle \sim (\ln t/t)^{1/2}, \quad t \to \infty , \tag{60}$$

which is again a manifestation of the special relation $\langle p_0(t)\rangle \sim \langle \xi^2(t)\rangle^{-1/2}$ in 1D.

V. ASYMPTOTIC BEHAVIOR FROM SCALING ARGUMENT

In this section, we present a scaling argument based on the Scher–Lax[17] formulation of theory, and which is also related to that suggested by Alexander and Bernasconi,[14] to calculate the mean square displacement. The results of this agree with those found in the last section and indicate *another way* to deal with distributions $\rho(\omega)$ with singular behavior in the Scher–Lax theory.

The argument proceeds in the following way: if $\rho(\omega)$ is such that $\langle 1/\omega\rangle (\equiv \omega_{\rm eff}^{-1})$ does not exist because of the $\omega \sim 0$ behavior, introduce a cutoff at ω_0, near zero, in $\rho(\omega)$. If ω_0 is small enough, then the distribution is largely unchanged; however, for the new distribution $\langle 1/\omega\rangle$ will exist and be a function of ω_0, leading to $\omega_{\rm eff}^{-1}(\omega_0)$. We then compute the mean square displacement for t on the order ω_0^{-1} with $\omega_{\rm eff}^{-1}(\omega_0)$, using a self-consistency argument then leads to forms for $\langle \xi^2(t)\rangle$ in agreement with the last section.

The distribution functions we will deal with are

(a) $\rho(\omega)$ as defined in Eq. (37b) having a singularity at $\omega = 0$, and

(b) $\rho(\omega)$ characterized by a finite value at $\omega = 0$. The example we choose is the most disordered case $\rho(\omega)$ in the family of disordered chains considered by Dyson[30]

$$\rho_n(\omega) = \left[\frac{n^n}{(n-1)!}\right] \omega^{n-1} e^{-n\omega} . \tag{61}$$

In order to compute the long time behavior of $\langle \xi^2(t)\rangle$ and $\Psi(t)$, we adopt the procedure used by Thomas *et al.*[31] to compute $\Psi(s,t)$ for dilute systems, obtaining for the Laplace transform of $\langle \xi^2(t)\rangle$, and using the $W_{mn} = W(m-n)$ appearing in the ME,

$$\begin{aligned}\langle \tilde{\xi}^2(u)\rangle &= C \sum_s s^2 W(s) \\ &\quad \times \int dt\, e^{-ut} e^{-W(s)t} \langle Q(t)\rangle [u(1-\tilde{\Psi}(u))]^{-1} \\ &= \left[C \sum_s s^2 W(s) \right. \\ &\quad \left. \times \int dt\, \frac{e^{-ut} e^{-W(s)t}}{\tilde{\Psi}(u)} \langle Q(t)\rangle \right] \left[\frac{\tilde{\Psi}(u)}{u(1-\tilde{\Psi}(u))}\right] ,\end{aligned} \tag{62}$$

where $\langle Q(t)\rangle$ is the probability of staying on site $n=0$ in the formulation of Thomas *et al.*[31] When the integrand in this expression is such that its first moment exists a requirement for which a sufficient condition is the existence of a second moment of $\Psi(t)$, $\bar{t}^2$, either in the original system or for the cutoff $\rho(\omega)$, then $\langle \xi^2(t)\rangle \sim t$ for $t > \bar{t}$. That is, for times longer than $\bar{t}$, the normal diffusion equation is valid. In our case, $\rho(\omega)$ *without* a cutoff leads to an infinite $\bar{t}$; however, introducing a cutoff ω_0 leads to the relation

$$\bar{t} = \bar{t}(\omega_0) = [\omega_{\rm eff}(\omega_0)]^{-1} . \tag{63}$$

In addition, by introducing the cutoff in $\rho(\omega)$ we find the long time form of $\Psi(t) (t > \omega_0^{-1})$ is given by[17]

$$\Psi(t) \to C \int_{\omega_0}^{\infty} d\omega\, \omega\, e^{-\omega t} \rho(\omega) . \tag{64}$$

This way of computing $\Psi(t)$ allows for hops to many impurities, not just nearest neighbors.[31]

We are now in a position to compute the mean square displacement. For our distribution with a cutoff, and for times $t \sim \omega_0^{-1} (> \omega_{\rm eff}^{-1} = \bar{t})$, we have

$$\langle \xi^2(t)\rangle \sim \omega_{\rm eff}\, t . \tag{65}$$

Consider the distribution function given in Eq. (37b), $\rho(\omega) \sim \omega^{-\alpha}$ for $0 < \alpha < 1$. We find when we introduce a cutoff at ω_0 that

$$\omega_{\rm eff}^{-1} = \langle 1/\omega\rangle^{-1} = \omega_0^{\alpha} \tag{66}$$

and

$$\langle \xi^2(t)\rangle = \omega_{\rm eff}(\omega_0)\, t , \tag{67}$$

But, since $t \sim \omega_0^{-1}$, we have $\langle \xi^2(t)\rangle \sim t^{1-\alpha}$, which agrees with the results in the previous section. Note that $\bar{t} = \omega_0^{-\alpha}$ and $t > \bar{t}$ (i.e., $\omega_0^{-1} > \omega_0^{-\alpha}$ for $0 < \alpha < 1$).

Now consider the distribution given in Eq. (61) for the disordered chain:

$$\rho_1(\omega) \sim e^{-\omega} . \tag{68}$$

Then

$$\omega_{\rm eff} = [-\ln \omega_0]^{-1} \tag{69}$$

and

$$\langle \xi^2(t)\rangle = \omega_{\rm eff}\, t = t/\ln t \tag{70}$$

for $t \sim \omega_0^{-1}$, which again agrees with our previous results for $\rho(\omega) \sim$ constant at $\omega = 0$. The other $\rho_n(\omega)$ $n > 1$ in the family given above in Eq. (61) have diffusive migration at long times.

It should be emphasized that the above conclusions apply to $\langle \xi^2(t)\rangle$ and not to $\langle p_0(t)\rangle$; although they may of course be calculated in the same framework of the Scher–Montroll theory as shown in Sec. IV.

The results of Secs. IV and V for $\rho(\omega) \sim \omega^{-\alpha}$ differ from those of Bernasconi, Alexander, and Orbach[13] and Alexander and Bernasconi.[14] *The latter papers deal with one-dimensional systems with nearest neighbor impurity interactions only.* Our method implicitly allows farther interactions [see Eq. (62) and Ref. 31]. We conjecture that this difference causes the difference in results found for $\rho(\omega) \sim \omega^{-\alpha}$. (Note that for less singular distributions, our results agree with Refs. 13 and 14.)

VI. CONCLUSIONS

In this paper, we have examined the incoherent migration of an electronic excitation in a disordered system. Starting with a Pauli master equation to describe the temporal behavior of the site probabilities in each configuration, an average over configurations was performed which results in a generalized master equation, i.e., time dependent transition rates. The exact connection of this formalism to the generalized continuous time random walk model was presented and discussed. This connection allows us to calculate the mean square displacement of the excitation, $\langle \xi^2(t) \rangle$ and the probability to remain on the initial site, $\langle p_0(t) \rangle$, in a variety of ways. The GME can be used, wherein a microscopic calculation of the self-energy, $\tilde{\Sigma}(\mathbf{k}, u)$, must be made. This is the route taken by Haan and Zwanzig[8] and Gochanour *et al.*[16] Alternatively, the CTRW can be used, either by calculating $\Psi(t)$ directly, or by calculating $\rho(\omega)$ from some microscopic model. The former method is similar to the approach taken by Godzik and Jortner.[15]

We have applied our results to EET in one dimension for exchange dominated transition rates using both a time scaling argument and the direct calculation of the long time behavior of $\langle \xi^2(t) \rangle$.

We believe that the powerful formalism of the GCTRW model allows a quick yet exact calculation of transfer probabilities in a number of physical situations. The difficult microscopic part of the calculation is in the computation of $\Psi(t)$ or $\rho(\omega)$; the solutions of the equations for $\langle \xi^2(t) \rangle$, etc., are straightforward consequences of this computation.

In related papers, we apply these results to excitation trapping in molecular crystals[19] and to the migration of atoms on disordered surfaces.[29]

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APPENDIX

There are a number of ways to derive the result given in Eq. (8). A straightforward procedure is to replace the W_{mn} where m and n are site indices) by

$$W_{mn}\,\xi_m\,\xi_n\ ,$$

where ξ_m is a random variable which takes the value $+1$ if site m is occupied by an impurity and 0 if site m is occupied by a host molecule. The configuration average $\langle \cdots \rangle$ is then the average over all possible values of the $\{\xi_n\}$ subject to $\langle \xi_n \rangle = c$. In order to compute $\langle \exp t\mathbf{V} \rangle$, note

$$\frac{d}{dt} P(\exp t\mathbf{V}) = P\mathbf{V}P\exp(t\mathbf{V}) + P\mathbf{V}(1-P)\exp t\mathbf{V}\ , \qquad \text{(A.1)}$$

$$\frac{d}{dt} P(1-P)(\exp t\mathbf{V}) = (1-P)\mathbf{V}P\exp(t\mathbf{V}) + (1-P)\mathbf{V}(1-P)\exp t\mathbf{V}\ . \qquad \text{(A.2)}$$

Solving (A2) with the condition $\lim_{t\to 0}(1-P)\exp(t\mathbf{V}) = 0$, we have

$$(1-P)\exp t\mathbf{V} = \int_0^t d\tau \exp[(1-P)\mathbf{V}(t-\tau)](1-P)\mathbf{V}P e^{\mathbf{V}\tau}\ ;$$

substituting into (A1), we find

$$\frac{d}{dt} P(\exp t\mathbf{V}) = P\mathbf{V}P\exp t\mathbf{V} + \int_0^t P\mathbf{V}(1-P) \times \exp[(1-P)\mathbf{V}(t-\tau)](1-P)\mathbf{V}P e^{\mathbf{V}\tau}$$

or

$$\frac{d}{dt}\langle e^{t\mathbf{V}} \rangle = \langle \mathbf{V} \rangle \langle e^{t\mathbf{V}} \rangle + \int_0^t d\tau \langle \delta\mathbf{V} \exp[(1-P)\mathbf{V}(t-\tau)]\delta\mathbf{V} \rangle \langle e^{\mathbf{V}\tau} \rangle\ ,$$

which upon Laplace transform yields Eq. (8).

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