Excitation Transport on Substitutionally Disordered Lattices

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An exact diagrammatic analysis of transport of electronic excitations among chromophores distributed randomly on a lattice is presented. An approximate solution is obtained that allows calculation of transport properties for transfer rates of any range for any lattice type and any concentration. Simple cubic lattice results are presented for Förster transfer and nearest-neighbor transfer. The latter has a percolation threshold that is described in a qualitatively correct fashion by our approximation.

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The transport of electronic excitations in disordered materials has received considerable attention in recent years.[1] Most investigators have used continuum models which treat transport among randomly distributed chromophores. The continuum theory of Gochanour, Andersen, and Fayer[2] (hereafter referred to as GAF) yields results which are in excellent agreement with time-resolved experiments on transport[3] and trapping[4] of electronic excitations in dilute dye solutions. Sakun[5] has discussed the problem of energy transfer on a partially filled lattice, but his results are stated to be valid only at low concentration. Odagaki and Lax[6] have recently introduced a dynamical coherent medium approximation for hopping transport on a disordered lattice. Their results are limited to a nearest-neighbor transfer rate and to bond disorder rather than site disorder. In this Letter, we describe a theory of energy transfer among chromophores distributed randomly on a lattice that is analogous to the GAF treatment of the continuum problem and that is valid at all concentrations.

The probability that a particular chromophore is excited at a given time in a given configuration of chromophores is taken to satisfy a Pauli master equation in which the transfer rate from site i to site j, denoted $w(\vec{r}_{ij})$, depends only on the vector distance from one chromophore to another. As in the theory of GAF, the time dependence of the ensemble-averaged excitation density is described by a Green's function, $G(\vec{r}-\vec{r}',t)$, which for the present problem is a sum of $\delta_{\vec{r},\vec{r}'}G^s(t)$ and $G^m(\vec{r}-\vec{r}',t)$, where $\delta_{\vec{r},\vec{r}'}$ is the Kronecker delta function. $G^s(t)$ gives the probability that a chromophore initially excited at $t=0$ remains excited at time t. $G^m(\vec{r}-\vec{r}',t)$ is the probability that an excitation undergoes a displacement $\vec{r}-\vec{r}'$ in time t.

In the continuum problem, an ensemble average is carried out by averaging over the uncorrelated positions of all the chromophores. The lattice problem is complicated by the fact that a lattice site can be occupied by at most one chromophore. Therefore the chromophore positions are correlated, and ensemble averages must be taken only over allowed configurations.

Following GAF, we expand the Fourier-Laplace transforms of $G^s(\vec{r}-\vec{r}',t)$ and $G^m(\vec{r}-\vec{r}',t)$ in perturbation expansions in $1/\epsilon$, the inverse of the Laplace variable. Each term in these expansions is associated with a diagram. Just as in the GAF treatment, the diagrammatic formalism leads to the conclusion that the Fourier-Laplace transform of the Green's function $\hat{G}(\vec{k},\epsilon)$ can be expressed in terms of $\hat{G}^s(\epsilon)$, which is the Laplace transform of $G^s(t)$, and a self-energy $\tilde{\Sigma}[\vec{k},G^s(\epsilon)]$, which itself can be regarded as a functional of $\hat{G}^s(\epsilon)$. Evaluation of these two functions would permit calculation of the Green's function and hence of most measurable properties of interest, including the generalized diffusion coefficient $\hat{D}(\vec{k},\epsilon)$ and the time-dependent mean-squared displacement. $\hat{G}(\vec{k},\epsilon)$ can be shown to obey a generalized diffusion equation of the form given in Eq. (66) of GAF, with the generalized diffusion coefficient given by

$$\hat{D}(\vec{k},\epsilon)=c/k^2\{\tilde{\Sigma}[0,\hat{G}^s(\epsilon)]-\tilde{\Sigma}[\vec{k},\hat{G}^s(\epsilon)]\}. \quad (1)$$

If the $k\to 0$, $\epsilon\to 0$ limit of $\hat{D}(\vec{k},\epsilon)$ exists, then the mean-squared displacement of the excitation increases linearly at long time with a slope $2n\hat{D}(0,0)$, where n is the dimensionality of the system.

Two exact relationships between $\hat{G}^s(\epsilon)$ and $\tilde{\Sigma}[\vec{k},\hat{G}^s(\epsilon)]$ can be derived. The first,

$$\hat{G}^s(\epsilon)\{\epsilon+c\tilde{\Sigma}[0,\hat{G}^s(\epsilon)]\}-1=0, \quad (2)$$

is a consequence of the conservation of probability. The fraction of occupied sites is denoted by c. The second is an infinite diagrammatic series for $\tilde{\Sigma}[\vec{k},\hat{G}^s(\epsilon)]$.

$\tilde{\Sigma}[\vec{k},\hat{G}^s(\epsilon)]$ is equal to the sum of the values of

all topologically different graphs with the following characteristics. Each graph has two root circles (labeled 1 and 2), which may be connected by a wavy line, zero or more unlabeled field circles, vertices within the circles, solid arrows, and dashed arrows. A solid arrow starts at a vertex in the interior of one circle. It ends in the interior of another circle either at a vertex or at the start of a dashed arrow that leads back to a vertex in the circle at which the solid arrow started. Dashed arrows may only appear in this latter situation. There is a continuous path of solid and dashed arrows starting on a vertex in circle 1 and ending on a vertex in circle 2. With the exception of the vertices at the start and end of the path, each vertex is at the start of only one arrow and at the end of only one arrow. Each diagram satisfies the restriction that the removal of any one circle and its associated arrows and wavy lines must not make the diagram disconnected. If circles 1 and 2 are not connected by a solid arrow, then they must be connected by a wavy line.

With the exception of the possibility of a wavy line between the root circles, the topological specification of the diagrams for $\tilde{\Sigma}[\vec{k}, \hat{G}^s(\epsilon)]$ is the same as in the theory of GAF. See Eq. (56) of that paper, as well as Fig. 7, that has examples of the diagrams.

The value of a graph is obtained by assigning dummy labels to the field circles and performing a sum in which each of these labels extends over all possible positions in the lattice. The same type of summation for circle 2 (but not for 1) is also performed. The summand is a product of (1) a factor of c for each field circle; (2) $w(\vec{r}_{ij})$ for each solid arrow, where the subscripts are the labels on the circles at the start and end of the arrow; (3) $\hat{G}^s(\epsilon)$ for each vertex other than those at the start and end of the path; (4) -1 for each dashed arrow; (5) $\exp(i\vec{k}\cdot\vec{r}_{12})$; (6) a factor of $-\delta_{\vec{r}_1,\vec{r}_2}$ if there is a wavy line between the root circles; and (7) $Q_n(c)$ for each circle, if there is no wavy line. For circle 1, n is the number of solid arrows ending in the circle. For all other circles, n is one less than the number of solid arrows ending in the circle. If the two root circles are connected by a wavy line, they should be counted as a single circle and should be assigned one factor of $Q_n(c)$, where n is determined as for circle 2. The functions $Q_n(c)$ are polynomials related to the cumulant polynomials $P_n(c)$ discussed by Yonezawa and Matsubara,[7] Leath and Goodman,[8] and Sakun[5] as follows:

$$Q_n(c) = (1/c)P_{n+1}(c); \quad n \geq 0. \tag{3}$$

This prescription for the value of a diagram is similar to that of GAF except for the sixth and seventh types of factors and for the summation (rather than integration).

The $\tilde{\Sigma}[\vec{k}, \hat{G}^s(\epsilon)]$ diagrams can be divided into two classes. The values of diagrams in the first class contain only $Q_0(c)$ factors and are finite at $c=1$. These are the diagrams that would be present in an expansion of $\tilde{\Sigma}[\vec{k}, \hat{G}^s(\epsilon)]$ for an ordered lattice. The values of diagrams in the second class include one or more factors of $Q_n(c)$ with $n>0$ and vanish at $c=1$. These diagrams represent corrections that account for the correlated hopping characteristic of a disordered system.

We can classify the diagrams by the number of independent lattice positions that appear in the summand. A diagram with n circles and no wavy line or a diagram with $n+1$ circles and a wavy line is classified as an n body diagram. We shall approximate $\tilde{\Sigma}[\vec{k}, \hat{G}^s(\epsilon)]$ by the infinite series of all two-body diagrams. In the limit of small concentration this should be a good approximation because the neglected diagrams have more powers of c than those retained. For $c=1$, it can be shown that this approximation gives the exact result for $\hat{D}(0,0)$. Thus we expect that it will be a reasonable approximation at all concentrations.

The sum of all two-body diagrams in $\tilde{\Sigma}[\vec{k}, \hat{G}^s(\epsilon)]$ can be evaluated exactly to yield

$$\tilde{\Sigma}^{(2)}[\vec{k}, \hat{G}^s(\epsilon)] = \frac{1}{\hat{G}^s(\epsilon)} \sum_{\vec{r}} \int_0^1 d\alpha \left[\frac{\alpha^{1/z}}{1-c+c\alpha}\right]\left[\frac{\alpha \exp(i\vec{k}\cdot\vec{r})}{1-c+c\alpha} + \tfrac{1}{2}\ln(1-c+c\alpha^2)\right], \quad z = w(\vec{r})\hat{G}^s(\epsilon) \tag{4}$$

in which the sum is taken over all displacements in the lattice. The only assumption made about lattice type is that all sites in the lattice are symmetry equivalent. Equation (4) holds for the case of more than one site per unit cell, provided that the sites are related by symmetry operations. The integral in Eq. (4) must be done numerically.

The two-body $\hat{G}^s(\epsilon)$ is calculated by making the approximation $\tilde{\Sigma}[\vec{k}, \hat{G}^s(\epsilon)] = \tilde{\Sigma}^{(2)}[\vec{k}, \hat{G}^s(\epsilon)]$ and substituting Eq. (4) into Eq. (2). This yields an equation with $\hat{G}^s(\epsilon)$ as the only unknown. This equation can be solved numerically for $\hat{G}^s(\epsilon)$. A Laplace-transform inversion routine[9] can then

be used to obtain $G^s(t)$. The two-body $\hat{D}(0,0)$ is calculated by substituting Eq. (4) into Eq. (1) and taking the $\epsilon \to 0$, $k \to 0$ limit:

$$\hat{D}(0,0) = \frac{c}{2n\hat{G}^s(0)} \sum_{\vec{r}} r^2 \int_0^1 d\alpha \frac{\alpha^{(1+z_0)/z_0}}{(1-c+c\alpha)^2},$$

$$z_0 = w(r)\hat{G}^s(0). \quad (5)$$

n is the dimensionality of the system. The sum is again taken over all displacements in the lattice. The two-body $\hat{G}^s(0)$ for a given value of c is substituted into Eq. (5) which can then be evaluated numerically.

First we apply these results to the case in which the transfer rate is nonzero only between chromophores that are nearest neighbors on the lattice. This problem has a percolation threshold. Below some critical concentration, the chromophores exist only in clusters of finite size. The mean-squared displacement cannot grow linearly at long times and $\hat{D}(0,0)$ should be zero. Curve N in Fig. 1 illustrates the behavior of $\hat{D}(0,0)$ in the two-body approximation for a nearest-neighbor rate of magnitude w on a simple cubic lattice of spacing a. $\hat{D}(0,0)$ has the exactly correct value at $c=1$, approaches zero as c approaches 0.346 from above, and is zero below this concentration. The critical concentration for site percolation on a simple cubic lattice has been calculated by Monte Carlo methods to be 0.312 ± 0.001.[10] We have repeated this calculation for face-centered-cubic and body-centered-cubic lattices and find critical concentrations of 0.168 and 0.254, respectively. The best estimates of the site percolation threshold for these lattices are 0.198 ± 0.003 for the fcc lattice and 0.245 ± 0.004 for the bcc lattice.[11] Thus the two-body $\hat{D}(0,0)$ has a physically reasonable concentration dependence. We can test the two-body approximation further for a completely filled lattice by comparing $G^s(t)$ with the well-known exact result for nearest-neighbor hopping on a filled cubic lattice. The exact $G^s(t)$ is unity at $t=0$ and decreases monotonically to zero as t approaches infinity. For times at which $G^s > 0.1$, the two-body result differs by no more than 0.003; for later times it differs by no more than 0.008. For partially filled lattices, it can be shown that $G^s(t)$ decays to a finite nonzero value as t approaches infinity, whereas our two-body results decay to zero. This casts some doubt on the validity of the two-body approximation for this problem that has a percolation singularity, despite the reasonable behavior of $\hat{D}(0,0)$.

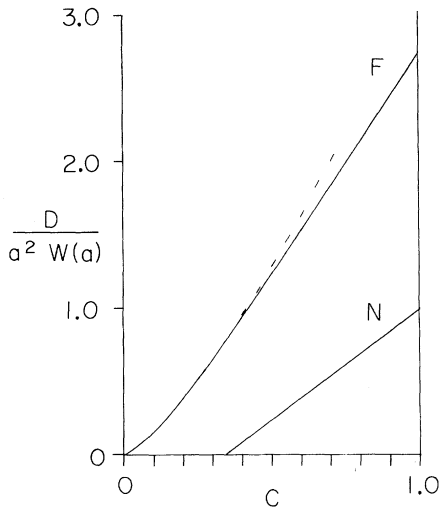

FIG. 1. The $\epsilon \to 0$ and $k \to 0$ limit of the generalized diffusion coefficient is plotted vs c, the fraction of occupied sites for a simple cubic lattice; a is the lattice spacing and $w(a)$ is the nearest-neighbor transfer rate. Curve F shows $\hat{D}(0,0)$ for a Förster dipole-dipole transfer rate. Curve N shows $\hat{D}(0,0)$ for a nearest-neighbor transfer rate. The dashed curve shows $\hat{D}(0,0)$ in the two-body approximation of GAF (Ref. 2) for a continuum with a chromophore number of density of c/a^3.

For any transfer rate of infinite range, however rapidly decaying with distance, such as that resulting from multipolar or exchange interactions, percolation effects will be absent. Curve F in Fig. 1 illustrates the concentration dependence of $\hat{D}(0,0)$ on a simple cubic lattice for the orientationally averaged Förster dipole-dipole transfer rate, $w(r) = (1/\tau)(R_0/r)^6$. As noted above, the result for $c=1$ is the exact result for an ordered lattice given by Förster[12]: $D = 2.76(R_0/a)^6(a^2/\tau)$. At low concentrations, the result approaches $D = 3.26(R_0^6/\tau)\rho^{4/3}$, where $\rho = c/a^3$ is the chromophore number density. The $\rho^{4/3}$ dependence is to be expected since in the limit of low concentration the lattice will cease to be important and transport should resemble that in a continuum, whose D must scale[1b] as $\rho^{4/3}$. The numerical coefficient is the same as that of the two-body continuum GAF $\hat{D}(0,0)$, which is believed to be a good approximation for a continuum. The only effect of the three-body corrections calculated by GAF on $\hat{D}(0,0)$ is to lower the multiplicative constant by 11%. The three-body results of GAF are in excellent agreement with experiments on dilute dye solutions.[3] Thus the two-body lattice $\hat{D}(0,0)$ shown in Fig. 1 has the exactly correct value at $c=1$, approaches an

accurate continuum approximation at low concentration, and hence is expected to be accurate for intermediate concentrations.

The approximation presented here allows one to calculate transport properties for any lattice type, any dimensionality, and any transfer rate. The results are expected to be good approximations over the full range of concentration, at least for transfer rates that will not give rise to a percolation problem. However, we expect the two-body approximation to be more accurate in three dimensions than in two dimensions. The agreement between our results at $c=1$ for $G^s(t)$ in the nearest-neighbor transfer problem becomes poorer with decreasing dimensionality. A detailed description of the model and calculations of time-dependent transport properties will be presented elsewhere.[13]

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