

Trapping of Excitation in the Average *T*-Matrix Approximation

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We investigate the trapping of excitation by a random array of acceptor ions embedded in an assembly of donors. The problem is formulated in terms of coupled rate equations. Exact results for the fraction of excited donors are obtained in the zero and rapid donor-donor transfer limits for arbitrary ratios of the donor to trap concentration. The average *T*-matrix approximation (ATA) is introduced to interpolate between these limits in situations where the concentration of traps is much less than the concentration of donor ions. In three-dimensional systems the ATA reproduces the results of earlier calculations in appropriate limits. The extension of the theory to higher trap concentration is discussed, as are problems connected with the application to one- and two-dimensional arrays.

KEY WORDS: trapping; donor-donor transfer; donor-acceptor transfer; average *T*-matrix approximation; diffusion; random walk.

1. INTRODUCTION

Excitation dynamics in the presence of a random array of trapping centers continues to be an important topic in condensed matter physics, with applications to optical spectroscopy, nuclear magnetic resonance, and particle transport. Broadly speaking, the problems can be divided into two categories depending on whether the transfer of excitation between individual atoms (or molecular units) takes place coherently, as in the case of a Frenkel or Wannier exciton, or incoherently (site-to-site hopping). In this paper we focus on the incoherent transfer problem.^(1,2)

We consider a situation where the donor atoms form a lattice, with the trapping centers or acceptor atoms distributed at random. We assume that

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at time $t = 0$ a small fraction of the donors are in the excited state. Our interest is in the fraction of donors still excited at some later time t . Because the transfer is assumed to be fully incoherent and the fraction of initially excited donors is small we can describe the dynamics by a set of occupation probabilities $\{P_n(t)\}$, where $P_n(t)$ is the probability that ion n is excited at time t , all other donor atoms being in the ground state. The time evolution of $P_n(t)$ is governed by the set of coupled rate equations

$$\frac{dP_n(t)}{dt} = -\left(X_n + \sum_{n'} W_{nn'}\right)P_n(t) + \sum_{n'} W_{n'n}P_{n'}(t) \quad (1)$$

Here $W_{nn'}$ is the transfer rate from donor n to donor n' , and X_n is the total transfer rate from donor n to all of the traps in the system. We assume that the donor-donor transfer is symmetric ($W_{nn'} = W_{n'n}$) and that there is no backtransfer from the traps.

The relative fraction of excited donors at time t , $f(t)$, is given by the configurational average of the sum of the $P_n(t)$ over the N donors, i.e.,⁽¹⁾

$$f(t) = \left\langle \sum_{n=1}^N P_n(t) \right\rangle_c \quad (2)$$

where $\langle \dots \rangle_c$ denotes an average over all trap distributions and $P_n(t)$ is a solution to (1) with initial condition $P_n(0) = \delta_{no}$.

Exact solutions of the problem are available in two limiting cases. The first of these corresponds to a situation where the donor-donor transfer is negligible on the time scale of interest. In this case we can set $W_{nn'}$ equal to zero. The function $f(t)$ is then given by^(2,3)

$$f(t) = \prod_l (1 - c + ce^{-X_{ol}t}) \quad (3)$$

Here c is the fraction of sites occupied by traps ($0 \leq c \leq 1$) and X_{ol} is the rate of transfer from a donor at site o (or l) to a trap at site l (or o). Equation (3) has a simple physical interpretation as the configurational average of $\exp(-X_{ol}t)$. If site l is occupied by a trap (which happens with probability c), it contributes a factor $\exp[-X_{ol}t]$ to $\exp[-X_{ol}t]$. If it is not occupied by a trap (probability $1 - c$), it contributes a factor of unity. Taking the configurational average leads directly to (3).

The second case pertains to the opposite limit where the transfer of excitation among donor ions is (infinitely) rapid in comparison with the rate of transfer to the traps. Under these conditions all of the $P_n(t)$ are identical for $t > 0$ so that we obtain^(1,4)

$$f(t) = \exp\left[-c \sum_l X_{ol}t\right] \quad (4)$$

It should be noted that both (3) and (4) have the same initial slope.

However, in the absence of donor–donor transfer the decay is strictly nonexponential for $c < 1$ whereas in the rapid transfer limit it is exponential at all times for all values of c .

The complexity of the trapping problem becomes evident in the intermediate regime where the donor–donor transfer rate is neither zero nor infinity. In this situation there are few exact results for $f(t)$ and recourse has to be made to approximations. These will be discussed in Sections 2 and 3.

2. INTERMEDIATE REGIME AND THE AVERAGE *T*-MATRIX APPROXIMATIONS

In this section we discuss the trapping of excitation in situations which lie between the limits of zero and infinitely rapid donor–donor transfer. In this regime it is convenient to introduce the laplace transform of the relative fraction of excited donors. Denoting the transform of $f(t)$ by $\hat{f}(s)$ we write it in the form

$$\hat{f}(s) = [s + M(s)]^{-1} \tag{5}$$

where $M(s)$ can be identified as a self-energy arising from the presence of the trapping centers.

As long as the traps are distributed at random there are no exact results for $M(s)$ which are valid for arbitrary values of the trap concentration and the ratio of the donor–donor to donor–trap transfer rates. For this reason attention has focused on developing approximations for $\hat{f}(s)$ which can be utilized in the analysis and interpretation of experimental data. One approach which has proven to be especially useful when there is a low concentration of traps is the average *T*-matrix approximation (ATA).⁽¹⁾ The ATA is equivalent to keeping the first term in the expansion of $M(s)$ in powers of c , i.e.,⁽⁵⁾

$$M(s) \rightarrow cm(s) \tag{6}$$

where $m(s)$ is written as the sum

$$m(s) = \sum_l T_l(s) \tag{7}$$

in which $T_l(s)$ is a solution to the equation

$$T_l(s) = X_{ol} - X_{ol} \sum_{l'} g_{ll'}(s) T_{l'}(s) \tag{8}$$

In (8) $g_{ol}(s)$ is a lattice Green's function defined by

$$g_{ol}(s) = \frac{1}{N} \sum_{\mathbf{k}} \frac{\exp[i\mathbf{k} \cdot (\mathbf{r}_0 - \mathbf{r}_l)]}{s + W(0) - W(\mathbf{k})} \tag{9}$$

where $W(\mathbf{k})$ is the Fourier transform of the donor-donor transfer rate

$$W(\mathbf{k}) = \sum_{l'} W_{ll'} \exp[i\mathbf{k} \cdot (\mathbf{r}_l - \mathbf{r}_{l'})] \quad (10)$$

and \mathbf{k} denotes a vector in the Brillouin zone of the donor lattice. The ATA can be looked upon as an approximation which treats the interaction with a single trap to all orders in the donor-trap transfer rate but which neglects interference effects between different traps.

In the absence of donor-donor transfer we have $g_{ol} = \delta_{ol}s^{-1}$. Under these conditions it can be shown that Eqs. (5)–(8) reproduce the exact result, (3), to first order in c .⁽¹⁾ In the opposite limit, $X_{ol} \ll W_{ol}$, we have $T_l(s) = X_{ol}$ (which corresponds to the first Born approximation for the t -matrix) and hence

$$f(s) = \left(s + c \sum_l X_{ol} \right)^{-1} \quad (11)$$

which is equivalent to (4). Like (3) and (4) $f(t)$ in the ATA has initial slope $f'(0) = c \sum_l X_{ol}$. The early-time quasiexponential behavior $\{f(t) \approx \exp[-f'(0)t]\}$ is followed by a period of nonexponential decay which in three dimensions (the behavior in lower dimensions is discussed in Section 3) evolves into the asymptotic exponential

$$f(t) \sim \exp\left\{-c \left[\sum_l T_l(0) \right] t\right\} \quad (12)$$

For a given value of c , $f(t)$ lies between the limiting curves associated with zero and infinitely rapid donor-donor transfer for all $t \geq 0$.

In many situations of experimental interest the donor-donor and donor-trap transfer rates are not limited to nearest neighbors but fall off exponentially or as an inverse power of the separation. Under these conditions the exact solution of the t -matrix equation is a formidable problem. Fortunately there exist reasonable approximations which apply to limiting cases.⁽¹⁾ To illustrate these we consider a system where $X_{ll'} = \alpha(r_{ll'})^{-6}$ and $W_{ll'} = \beta(r_{ll'})^{-6}$ (i.e., a dipole-dipole mechanism for both donor-trap and donor-donor transfer). When $\alpha \lesssim \beta$ there is only a small number of donor ions in the "sphere of influence" of a trap. Under these conditions a reasonable first approximation is to neglect the off-diagonal elements of the t matrix, which is equivalent to keeping only the terms with $l = l'$ on the right-hand side of (8). When this is done $\hat{f}(s)$ reduces to

$$\hat{f}(s) = \left\{ s + c \sum_l X_{ol} / [1 + X_{ol} g_{oo}(s)] \right\}^{-1} \quad (13)$$

If $g_{oo}(s)$ is approximated by $(s + 1/\tau)$, Eq. (13) becomes identical to the "hopping model" of Burshtein⁽⁶⁾ in which τ is a measure of the time the

excitation resides on a given donor ion in the absence of trapping. [Note the $g_{oo}(s)$ is the laplace transform of the conditional probability that an ion excited at $t = 0$ is still excited at a later time t .^(1,2)]

The second approximation pertains to the opposite limit, $\alpha \gg \beta$, where there is a large number of donors in the sphere of influence of a trap. Under these conditions it is appropriate to use a continuum formulation where

$$\hat{f}(s) = \left[s + n \int d\mathbf{r} T(\mathbf{r}, s) \right]^{-1} \tag{14}$$

Here n is the concentration of traps while $T(\mathbf{r}, s)$ satisfies the continuum equivalent of (8)

$$T(\mathbf{r}, s) = X(r) - X(r) \int d\mathbf{r}' g(\mathbf{r} - \mathbf{r}', s) T(\mathbf{r}', s) \tag{15}$$

where $X(r)$ is the donor-trap transfer rate at separation r . The continuum Green's function is given by

$$g(\mathbf{r}, s) = \frac{1}{(2\pi)^3} \int \frac{d\mathbf{k} e^{i\mathbf{k} \cdot \mathbf{r}}}{s + Dk^2} \tag{16}$$

in which the integral is over all of k space. The diffusion constant appearing in (16) is expressed as

$$D = \frac{1}{6} \sum_{l'} r_{ll'}^2 W_{ll'} \tag{17}$$

assuming cubic symmetry.²

Recently it has been shown that the integral equation (15) can be replaced by an equivalent differential equation.⁽⁹⁾ This is done by writing

$$T(\mathbf{r}, s) = X(r) - X(r) Q(\mathbf{r}, s) \tag{18}$$

where the auxilliary function $Q(\mathbf{r}, s)$ is the solution of the inhomogeneous equation

$$\left[-D \nabla^2 + s + X(r) \right] Q(\mathbf{r}, s) = X(r) \tag{19}$$

which is regular at the origin and vanishes at infinity.

² Trapping in the presence of anisotropic diffusion has been investigated by P. M. Richards (Ref. 7). We can recover his results by using an effective isotropic diffusion constant defined by

$$D_{\text{eff}} k^2 = \left(\frac{1}{4\pi} \int \frac{d\Omega_k}{D_x k_x^2 + D_y k_y^2 + D_z k_z^2} \right)^{-1}$$

in the ATA equations (Ref. 8).

In order to determine the evolution of $f(t)$ it is necessary to solve either (15) or (18)–(19) for $T(\mathbf{r}, s)$ and then invert the transform. However, in three dimensions the asymptotic behavior can be inferred from $T(\mathbf{r}, 0)$. We have

$$f(t) \sim \exp \left\{ -n \left[\int d\mathbf{r} T(\mathbf{r}, 0) \right] t \right\} \quad (20)$$

It can be shown that the integral of $T(\mathbf{r}, 0)$ can be expressed as⁽¹⁾

$$\int d\mathbf{r} T(\mathbf{r}, 0) = 4\pi D a_S \quad (21)$$

where a_S is the quantum mechanical scattering length of a particle of “mass” $\hbar^2/(2D)$ moving in the repulsive “potential” $X(r)$. From (20) and (21) we have $f(t) \sim \exp[-4\pi D n a_S t]$, a result first obtained by de Gennes⁽¹⁰⁾ in his study of the relaxation of the nuclear magnetization in the presence of paramagnetic impurities.

In concluding this section we emphasize that the results we have presented here pertain to a system where the donor atoms form a lattice. If the donor array is itself disordered then additional approximations are needed. Thus one would use the configurational average of $g_{oo}(s)$ in (13)³ and an average diffusion constant in (16) and (19).⁽¹²⁾

3. LOWER DIMENSIONS AND HIGHER CONCENTRATIONS

In this section we first discuss the trapping of excitation in lower-dimensional systems. This discussion is followed by brief comments on excitation dynamics at high trap concentration. In the interest of simplicity we consider the special case where each trap can receive excitation from a single donor at the rate X_{oo} . In this case Eq. (8) is readily solved for $T_l(s)$ with the result

$$T_l(s) = \frac{\delta_{ol} X_{oo}}{1 + X_{oo} g_{oo}(s)} \quad (22)$$

From (22) we obtain $\hat{f}(s)$ in the form

$$\hat{f}(s) = \left\{ s + c X_{oo} [1 + X_{oo} g_{oo}(s)]^{-1} \right\}^{-1} \quad (23)$$

In three dimensions, where $g_{oo}(0)$ is finite, we obtain $f(t) \sim \exp[-\Gamma t]$ as $t \rightarrow \infty$. The decay rate Γ is given by

$$\Gamma = \frac{c X_{oo}}{1 + X_{oo} g_{oo}(0)} \quad (24)$$

³ For an assessment of various approximations for $\langle g_{oo}(s) \rangle_c$ in dilute systems see Ref. 11.

In the limit $X_{oo}g_{oo}(0) \gg 1$, which is equivalent to the trap being a substitutional impurity with an effective donor-trap transfer rate equal to the rate for donor-donor transfer, Γ reduces to $cg_{oo}(0)^{-1}$, a result first obtained by Rosenstock.⁽¹³⁾ [Note that $g_{oo}(0)^{-1}t$ is the long-time limit for the mean number of lattice sites visited in time t .] As discussed by Weiss,⁽¹⁴⁾ the Rosenstock approximation gives reasonable results only for $c \lesssim 0.05$.

Although the ATA is a useful approximation at low trap concentration in three-dimensional systems, it gives rise to qualitatively incorrect results in one and two dimensions. In one dimension it yields the asymptotic behavior $f(t) \sim t^{-1/2}$ whereas in two dimensions one obtains $f(t) \sim t^{-1}$. In both cases the anomalous behavior in $f(t)$ reflects the divergence in $g_{oo}(s)$ as $s \rightarrow 0$.⁽¹⁵⁾ The asymptotic algebraic decay predicted by the ATA matches the exact results obtained for a *periodic* array of traps in lower dimensions.^(5,16) However, the decay in the presence of a *random* array of trapping centers is quite different.^(7,8) In particular in one dimension one has the asymptotic behavior⁽¹⁷⁾

$$f(t) \sim 8(4c^2Wt/3\pi)^{1/2} \exp\left[-3(\pi^2c^2Wt/4)^{1/3}\right] \quad (25)$$

where W is the nearest-neighbor donor-donor transfer rate.

As stressed above the ATA is appropriate only at low trap concentration. Useful results at higher trap concentration can be obtained by using the coherent potential approximation (CPA).^(19,20) In the CPA the self-energy, $M_{\text{CPA}}(s)$, is obtained from the equation

$$\int d\tilde{X}_{oo} \mathcal{P}(X_{oo}) \frac{[\tilde{X}_{oo} - M_{\text{CPA}}(s)]}{1 + [\tilde{X}_{oo} - M_{\text{CPA}}(s)]G_{oo}(s)} = 0 \quad (26)$$

where

$$\mathcal{P}(\tilde{X}_{oo}) = c\delta(\tilde{X}_{oo} - X_{oo}) + (1 - c)\delta(\tilde{X}_{oo}) \quad (27)$$

for the model under consideration while

$$G_{oo}(s) = g_{oo}(s + M_{\text{CPA}}(s)) \quad (28)$$

The CPA self-energy interpolates between the ATA result at low trap concentration and the exact result (for the model) at $c = 1$, $M(s) = X_{oo}$. Like the ATA it is most accurate in three dimensions. The CPA belongs to a class of theories known as effective medium approximations in which the excitation is assumed to propagate with a position-independent decay rate $M_{\text{CPA}}(s)$ which is determined self-consistently by requiring that the effect of a deviation of the decay rate from $M_{\text{CPA}}(s)$ vanishes on the average [cf. Eq. (26)].

4. RESPONSE AT FINITE WAVE VECTOR

Recently, attention has been drawn to the calculation of the spatial dependence of the density of excited donors.^(21,22) In the ATA the configurational average of the Fourier–Laplace transform of the density of excited donors evolving from a localized initial excitation takes the form⁽²¹⁾

$$\hat{f}(\mathbf{k}, s) = [s + Dk^2 + cm(\mathbf{k}, s)]^{-1} \quad (29)$$

where

$$m(\mathbf{k}, s) = \sum_l e^{i\mathbf{k} \cdot \mathbf{r}_l} T_l(\mathbf{k}, s) \quad (30)$$

The functions $T_l(\mathbf{k}, s)$ are solutions to the equations

$$T_l(\mathbf{k}, s) = X_{ol} e^{-i\mathbf{k} \cdot \mathbf{r}_l} - X_{ol} \sum_{l'} g_{ll'}(s) T_{l'}(s) \quad (31)$$

[Note that $\hat{f}(0, s)$, $m(0, s)$, and $T_l(0, s)$ correspond to the functions $\hat{f}(s)$, $m(s)$, and $T_l(s)$ introduced in Section 2.]

In the continuum limit it is convenient to make a partial wave expansion of T provided the donor–trap transfer rate is spherically symmetric. When this is done $m(k, s)$ is given by

$$cm(\mathbf{k}, s) = 4\pi n \left[\int_0^\infty X(r) r^2 dr - \sum_{l=0}^\infty \int_0^\infty X(r) j_l(kr) f_l^k(r, s) r^2 dr \right] \quad (32)$$

in which $j_l(kr)$ denotes a spherical bessel function. The function $f_l^k(r, s)$ is a solution to the inhomogeneous equation

$$\left[-D \frac{d^2}{dr^2} - \frac{2D}{r} \frac{d}{dr} + \frac{Dl(l+1)}{r^2} + sX(r) \right] f_l^k(r, s) = (2l+1)X(r)j_l(kr) \quad (33)$$

Equation (33) can be solved in closed form for the special case of a “square well” transfer rate, $X(r) = V_0$, $0 \leq r \leq R$; $X(r) = 0$, $r > R$. In the limit $V_0 \rightarrow \infty$ we recover the results of Bixon and Zwanzig, which were obtained by solving the diffusion equation in the presence of a trap with the boundary condition that the excitation density vanished for $r \leq R$ ⁽²²⁾

$$\hat{f}(\mathbf{k}, s) = \left\{ s(1 + \phi) + 3s^{1/2} \left(\frac{D}{R^2} \right)^{1/2} \phi + 3 \left(\frac{D}{R^2} \right) \phi + Dk^2 \left[1 + \phi \frac{(2 + \lambda R)}{1 + \lambda R} \right] \right\}^{-1} \quad (34)$$

where $\phi = (4\pi/3)nR^3$ and $\lambda = (s/D)^{1/2}$. Equation (34) can also be used to develop a self-consistent theory for $\hat{f}(\mathbf{k}, s)$ which goes beyond the ATA in

that it evolves higher-order terms in the density expansion of the self-energy.⁽²³⁾

5. DISCUSSION

The purpose of this paper has been to review a variety of theoretical studies of the trapping of excitation in systems with random arrays of trapping centers. We emphasize that we have considered only the incoherent transfer problem where the transfer of excitation among the donors and from the donors to the traps takes place incoherently. In such a situation it is appropriate to use rate equations to characterize the dynamics. The trapping of excitation in situations where the transfer of excitation takes place coherently is a much more complicated calculation since one has to work directly with the Hamiltonian (or equivalently the full density matrix).⁽²⁴⁾ An important aspect of the problem is the disorder introduced by the random positioning of the traps. This becomes especially significant when there is a high concentration of traps or when the donor array itself lacks translational symmetry. Finally we mention that the ATA formalism outlined here has found recent application in the analysis and interpretation of the time development of the 3P_o optical fluorescence of the Pr^{3+} ion in $\text{Pr}_{0.95}\text{Nd}_{0.05}\text{F}_3$, where the Nd^{3+} serves as a trap.^(25,26)

REFERENCES

1. D. L. Huber, *Phys. Rev. B* **20**:2307 (1979).
2. D. L. Huber, D. S. Hamilton, and B. Barnett, *Phys. Rev. B* **16**:4642 (1977); see also *Laser Spectroscopy of Solids*, W. M. Yen and P. M. Selzer, eds. (Springer-Verlag, Berlin, 1981), Chap. 3.
3. A. Blumen and J. Manz, *J. Chem. Phys.* **71**:4694 (1979); and references therein.
4. For a careful derivation of this result see D. Fay, *Phys. Rev. B* **25**:4245 (1982).
5. D. L. Huber, *J. Chem. Phys.* **75**:4749 (1981).
6. A. I. Burshtein, *Zh. Eksp. Teor. Fiz.* **62**:1695 (1972) [*Sov. Phys. JETP* **35**:882 (1972)].
7. P. M. Richards, *Phys. Rev. B* **25**:1514 (1982).
8. D. L. Huber, *Phys. Rev. B* **26**:3937 (1982).
9. K. K. Ghosh, D. L. Huber, and L.-H. Zhao, *Phys. Rev. B* **25**:3851 (1982).
10. P. G. de Gennes, *J. Phys. Chem. Solids* **7**:345 (1958). See also M. Yokota and O. Tanimoto, *J. Phys. Soc. Jpn.* **22**:779 (1967).
11. W. Y. Ching, D. L. Huber, and B. Barnett, *Phys. Rev. B* **17**:5025 (1978).
12. M. Trlifaj, *Czech. J. Phys.* **8**:510 (1958). See also C. R. Gochanour, H. C. Anderson, and M. D. Fayer, *J. Chem. Phys.* **70**:4254 (1979); K. Godzik and J. Jortner, *J. Chem. Phys.* **72**:4471 (1980).
13. H. B. Rosenstock, *Phys. Rev.* **187**:1166 (1974). See also Refs. 16 and 18 and R. D. Wieting, M. D. Fayer, and D. D. Dlott, *J. Chem. Phys.* **69**:1996 (1978).
14. G. H. Weiss, *Proc. Natl. Acad. Sci. USA* **77**:4391 (1980). See also G. Zumofen and A. Blumen, *Chem. Phys. Lett.* **83**:372 (1981).
15. K. K. Ghosh and D. L. Huber, *J. Lumin.* **21**:225 (1980).

16. J. Klafter and R. Silbey, *J. Chem. Phys.* **74**:3510 (1981).
17. B. Movaghar, G. W. Sauer, D. Würtz, and D. L. Huber, *Solid State Commun.* **39**:1179 (1981). See also B. Movaghar, G. W. Sauer, and D. Würtz, *J. Stat. Phys.* **27**:473 (1982).
18. G. Zumofen and A. Blumen, *J. Chem. Phys.* **76**:3713 (1982).
19. D. L. Huber, *Phys. Rev. B* **20**:5333 (1979).
20. K. K. Ghosh and D. L. Huber, *Phys. Rev. B* **23**:4441 (1981).
21. D. L. Huber and K. K. Ghosh *Phys. Rev. B* **26**:3453 (1982).
22. M. Bixon and R. Zwanzig, *J. Chem. Phys.* **75**:2354 (1981).
23. M. Muthukumar, *J. Chem. Phys.* **76**:2667 (1982).
24. D. L. Huber, *Phys. Rev. B* **22**:1714 (1980); **24**:1083 (1981).
25. K. K. Ghosh, J. Hegarty, and D. L. Huber, *Phys. Rev. B* **22**:2837 (1980).
26. J. Hegarty, D. L. Huber, and W. M. Yen, *Phys. Rev. B* **23**:6271 (1981).