

# Random walk in disordered systems with dipole–dipole interactions: diffusion coefficient

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A new method is proposed for calculating diffusion coefficients. The method involves a restructuring of the series expansion of the propagator in powers of the concentration. This series converges only poorly at long times. The leading approximation for  $D$  and the first correction to it are calculated. The result agrees well with the exciton diffusion coefficient which has been measured previously by optical four-wave mixing.

1. One of the most fundamental random-walk processes in disordered systems is the delocalization of excitations described by the kinetic equation

$$\dot{p}_{i0} = - \sum_j (\nu_{ji} p_{i0} - \nu_{ij} p_{j0}) \quad , \quad p_{i0}(t=0) = \delta_{i0} \quad . \quad (1)$$

The indices  $i$  and  $j$  here specify the impurity centers (donors), which are distributed at random among the sites  $\vec{r}_i$  of the regular  $d$ -dimensional lattice and which form the

disordered system. The quantity  $p_{i0}(t)$  is the probability for observing the excitation at donor  $i$  at time  $t$  under the condition that the excitation was initially at donor 0. If the transport is a consequence of dipole-dipole interactions, the transition rate in many cases is

$$\nu_{ij} = \nu_0 (r_0/r_{ij})^s, \quad (2)$$

where  $s = 6$ . Within the orientation factor in (2), which has not yet been taken into account, this is the way in which problems of the incoherent delocalization of excitons,<sup>1-5</sup> electron spin diffusion,<sup>6</sup> and nuclear spin diffusion<sup>7-9</sup> (among others) are formulated. As a rule, it is more convenient to work with the propagator  $\tilde{P}_{xy}(t)$ , which has the meaning that the excitation is observed at lattice site  $\vec{x}$  if the excitation was initially at site  $\vec{y}$ . The propagator satisfies the equation<sup>7-10</sup>

$$\frac{\partial}{\partial t} \tilde{P}_{xy} = - \sum_{\vec{z}} (n_x \nu_{xz} n_x \tilde{P}_{zy} - n_x \nu_{zx} n_x \tilde{P}_{xy}) \quad , \quad \tilde{P}_{xy}(t=0) = \frac{n_y}{c} \delta_{xy} \quad . \quad (3)$$

Here  $n_x$  is an occupation number:  $n_x = 1$  (0) if site  $\vec{x}$  is occupied (not occupied) by a donor;  $\nu_{xz} = \nu_{ij}$  ( $\vec{r}_i = \vec{x}$ ,  $\vec{r}_j = \vec{z}$ ). We will restrict the discussion below to the case in which the concentration satisfies  $c = \langle n_x \rangle \ll 1$ . Theoretically, the problem of a random walk in a disordered system is one of calculating  $P_{xy}(t) = \langle \tilde{P}_{xy}(t) \rangle$ , i.e., the propagator averaged over the random distribution of donors in the crystal. Experimentally, one measures either the autocorrelation function<sup>3,4,9</sup>  $P_{yy}(t) = P_{00}(t)$  or the Fourier transform of the propagator,<sup>5</sup>  $P(\vec{k}, t)$ . The time scale in the system is set by the so-called Förster constant  $\beta$ , which is defined by  $\langle \exp(-\sum_z n_z \nu_{zx} t) \rangle = \exp(-(\beta t)^{d/s})$ . With  $d = 3$  and  $s = 6$  we would have  $\beta = (16\pi^3/9)\rho^2 \nu_0 r_0^6$ , where  $\rho = c/\Omega = 1/\bar{r}^3$  is the donor density,  $\bar{r}$  is the mean distance between donors, and  $\Omega$  is the volume of the unit cell.

A general regular basis for calculating propagators under the condition  $\beta t \lesssim 1$  is the cumulant form of the concentration expansion<sup>10,9</sup> (see also the review in Ref. 11). Among the numerous methods which have been offered for determining the long-time asymptotic behavior, we will mention those of Refs. 2 and 12. It was shown in Ref. 12 (see also Refs. 4 and 9-11) that the hypothesis that the asymptotic behavior  $P_{xy}(\beta t \rightarrow \infty)$  is of a diffusion nature should be formulated in the following way:

$$P_{yy}(\beta t \rightarrow \infty) = (\Omega/c)(4\pi Dt)^{-d/2} \quad , \quad (4)$$

$$P_{x \neq y}(\beta t \rightarrow \infty) = \Omega(4\pi Dt)^{-d/2} \exp\left(-\frac{(x-y)^2}{4Dt}\right) \quad . \quad (5)$$

Furthermore, in the case of a dipole transport there should be a characteristic onset of asymptotic expression (4) for  $P_{yy}$ ; this conclusion found experimental support in Ref. 4. Gochanour *et al.*<sup>2</sup> have proposed a method for calculating the diffusion coefficient  $D$ . In their method, one calculates not only the leading approximation  $D_{OGAF}$  but also, and in contrast with other approaches (some of which were offered more recently), the first correction  $\Delta D_{OGAF}$ , which has proved to be small:  $|\Delta D_{OGAF}|/D_{OGAF} = 0.11$ .

The method used in Ref. 2 is based on a calculation of the autocorrelation function  $P_{00}$ , but relation (4) did not hold in the method used there. For one-dimensional and two-dimensional systems, the method of Ref. 2 incorrectly predicts both  $P_{00}(t \rightarrow \infty)$  and the Laplace transform  $P_{00}(\lambda \rightarrow 0)$ , in terms of which  $D$  is expressed [here and below,  $f(\lambda) = \int_0^\infty dt \exp(-\lambda t)f(t)$ ]. A direct measurement of the diffusion coefficient  $D$ , which was carried out in Ref. 5 for  $\beta t \sim 10^3$ , led to a value differing from the prediction of Ref. 2 by a much greater extent than would have been expected on the basis of a comparison of  $D_{OGAF}$  and  $\Delta D_{OGAF}$ . These shortcomings of Ref. 2 persisted in a subsequent analysis.<sup>13</sup> Accordingly, in the present study we have developed a new method for calculating the diffusion coefficient. This new method is free of the flaws listed above, and it leads to a satisfactory agreement with experiment.

2. Noting that we have  $n_x \tilde{P}_{xy} = \tilde{P}_{xy}$ , and replacing the initial condition in (3) by  $\tilde{P}_{xy}(t=0) = \delta_{xy}$ , we find the equation<sup>14,11</sup>

$$\frac{\partial}{\partial t} \tilde{G}_{xy} = - \sum_z (n_x \nu_{zx} \tilde{G}_{xy} - n_x \nu_{zx} \tilde{G}_{zy}) \quad , \quad \tilde{G}_{xy}(t=0) = \delta_{xy} \quad . \quad (6)$$

This equation describes a process in which the excitation is initially not at a donor, as in (3), but at an arbitrary lattice site, and the excitation subsequently moves to the nearest donors and thereafter migrates only from donor to donor. Consequently, the diffusion coefficients of the propagators  $G = \langle \tilde{G} \rangle$  and  $P$  are identical. Going over to the Laplace representation, introducing a memory operator, and using the conservation law  $\sum_x G_{xy}(t) = 1$ , we have

$$G(\lambda) = [\lambda + \bar{D}(\lambda) - N(\lambda)]^{-1} \quad , \quad \bar{D}_{xx} = \delta_{xx} \bar{D}_0 \quad , \quad \bar{D}_0 = \sum_x N_{xx} \quad . \quad (7)$$

We obviously have  $G_{yy}(t) \sim c^0$  and  $G_{x \neq y}(t) \leq c$ . At small values of  $c$  we thus have<sup>11</sup>

$$G_{yy}(\lambda) = [\lambda + \bar{D}_0(\lambda)]^{-1} \quad . \quad (8)$$

The diffusion coefficient is  $D = \lim_{\lambda \rightarrow 0} D(\lambda)$ , where

$$D(\lambda) = \frac{1}{2d} \sum_x x^2 N_{x0}(\lambda) = \frac{\lambda^2}{2d} \sum_x x^2 G_{x0}(\lambda) \quad . \quad (9)$$

Let us examine the concentration expansions for  $G_{00}(\lambda)$  and  $D(\lambda)$ . Within terms on the order of  $c^3$  inclusively, with  $d = 3$  and  $s = 6$ , we have

$$G_{00} = \frac{1}{\lambda} \left( 1 - \frac{1}{2} \pi^{1/2} \xi + \frac{1}{2} \xi^2 - \frac{1}{8} \pi^{1/2} \xi^3 \right) \quad , \quad (10)$$

$$D(\lambda) = \frac{\lambda}{6} \left( \frac{\beta}{\lambda} \right)^{5/6} d_0 \pi^2 (1 + d_1 \xi + d_2 \xi^2) \quad , \quad (11)$$

where  $\xi = (\beta/\lambda)^{1/2}$ ,  $d_0 = 6^{2/3}/(4\pi^{1/2}) = 0.46573$ ,  $d_1 = 0.01521$ , and  $d_2 = -0.2036(8)$ . In deriving expression (10) we made use of the equality<sup>14</sup>  $G_{00}(t) = \exp(-(\beta t)^{1/2})$ ; expression (11) was derived by the method of Ref. 10. The error in  $d_2$  reflects the error in the calculation of the corresponding sextuple integral.

From expansion (10) we find an expansion for  $\bar{D}_0(\lambda)$ , using (8):

$$\bar{D}_0(\lambda) = \lambda(b_1\xi + b_2\xi^2 + b_3\xi^3) , \quad (12)$$

where  $b_1 = \frac{1}{2}\pi^{1/2}$ ,  $b_2 = \frac{\pi}{4} - \frac{1}{2}$ , and  $b_3 = \frac{1}{8}\pi^{1/2}(\pi - 3)$ . If we expand Eq. (10) in  $\lambda$ , and if we also find the relation  $\lambda = \lambda_0(G_{00})$  as an expansion in  $c$  [i.e., in  $(\beta G_{00})^{1/2}$ ] and substitute it into (12), we find, using (8), the equation

$$G_{00} = [\lambda + \bar{D}_0(\lambda_0(G_{00}))]^{-1} \quad (13)$$

for the function  $G_{00}(\lambda)$ . Solving Eq. (13), we find that  $\beta G_{00}(\lambda = 0)$  has the values 1.273, 1.819, and 1.918 when one, two, and three terms, respectively, are retained in the expansion of  $\bar{D}_0$  in  $(\beta G_{00})^{1/2}$ . The exact value is 2. A corresponding calculation for  $G_{00}(t) = \exp(-(\beta t)^\alpha)$  with  $\alpha = 3/10$  (this value corresponds to quadrupole-quadrupole transport) leads to values of 1.434, 3.821, and 8.467 for  $\beta G_{00}(\lambda = 0)$ . The exact value is 9.261. In this case, however, it was necessary to carry out an additional restructuring of the expansion of  $\bar{D}_0$  as a chain fraction in  $(\beta G_{00})^\alpha$ . Otherwise,  $G_{00}$  would be complex in the second step. These examples demonstrate the efficiency of the self-consistency method proposed in Ref. 2. The primary distinction is that the derivation of expansions (10)–(12) used (in accordance with the suggestions of Refs. 15, 16, and 13) a concentration expansion instead of a diagram technique, and the method was applied not to  $P_{00}$ , as in Ref. 2, but to  $G_{00}$ , which is known accurately.

3. In the *GAF* method,<sup>2</sup> to calculate  $D$ , it is now necessary to replace  $\lambda$  by  $\lambda_0(G_{00})$  in (11) and to thereby obtain an expansion of  $D(\lambda)$  in  $[\beta G_{00}(\lambda)]^{1/2}$ . The result can be put in the form

$$D = \kappa D_0 \quad , \quad D_0 = \frac{1}{6}\beta\bar{r}^2 . \quad (14)$$

When terms of order up to  $c$ ,  $c^2$ , and  $c^3$  are retained, one finds the values  $\kappa'_1 = 0.447$ ,  $\kappa'_2 = 0.346$ , and  $\kappa'_3 = 0.152(1)$ , respectively, for  $\kappa$ . The second correction turns out to be considerably larger than the first:  $|\kappa'_3 - \kappa'_2|/\kappa'_3 = 1.28 \gg |\kappa'_1 - \kappa'_2|/\kappa'_2 = 0.29$ . We recall that Gochanour *et al.*<sup>2</sup> used an equation equivalent to our equation (3) and terms on the order of  $c$  and  $c^2$  to find the values  $\kappa_{1GAF} = 0.355$  and  $\kappa_{2GAF} = 0.315$  for  $\kappa$ . The difference here,  $|\kappa_{2GAF} - \kappa_{1GAF}|/\kappa_{2GAF} = 0.13$ , is small, but  $\kappa_{2GAF}$  turned out to be larger by a factor of nearly two than the number corresponding to the experiments of Ref. 5 (§4).

The fact that the first correction to  $D$  is small in the *GAF* method thus does not lead to a rapid convergence of the results based on the first terms of the concentration expansion, either in the original version of the method<sup>2</sup> or after a switch to Eq. (3), which eliminates some of the shortcomings of the method which were pointed out in §1.

The essential reason here is that the functions  $\bar{D}_0(\lambda)$  and  $D(\lambda)$  are extremely different. It is thus natural to attempt to calculate  $D$  by the same method which has been used successfully to calculate  $G_{00}$ . That method cannot be applied directly to expansion (11), since the latter is not of the standard form in (10), beginning with a  $1/\lambda$  term. Comparing (11) with the expansion for  $D(\lambda)$  in the Sher-Lax theory,<sup>12,17</sup>

$$D_{SL} = \frac{1}{6} \sum_x x^2 \nu_{x0} G_{00}(\lambda + \nu_{x0}) / G_{00}(\lambda), \quad (15)$$

and the corresponding representation for  $D$  in the lowest order of the  $GAF$  theory, we might suggest that the common factor of  $\lambda$  in (11) is the starting point for an expansion in  $c$  for  $1/G_{00}(\lambda)$ , so we could rewrite  $D(\lambda)$  in the form

$$D(\lambda) = \frac{d_0 \bar{r}^2}{6G_{00}(\lambda)} \Phi(\lambda) \quad ,$$

$$\Phi(\lambda) = \lambda G_{00}(\lambda) (1 + d_1 \xi + d_2 \xi^2) (\beta/\lambda)^{5/6} = (\beta F)^{5/6} \quad (16)$$

The expansion in  $c$ , i.e., in  $\xi = (\beta/\lambda)^{1/2}$ , for  $F$  is

$$F = \frac{1}{\lambda} (1 - f_1 \xi + f_2 \xi^2 + \dots) \quad . \quad (17)$$

The method described above can be applied to this expansion. As a result, we find  $\kappa_2 = 0.216$  and  $\kappa_3 = 0.186(1)$  when the first two terms and the first three terms, respectively, from (17) are considered. When the same method is used to calculate  $D_{SL}(\lambda = 0)$ , values larger by factors of 1.318, 1.077, and 1.046 than the exact value  $\kappa_{SL} = 0.3725$  are found when terms up to  $c^2$ ,  $c^3$ , and  $c^4$ , respectively, are retained. These results indicate that the method converges well again in this case. This comparison makes it possible to estimate the methodological error of the calculation of  $\kappa_3$  to be 10%.

4. In order to compare these numbers with the experimental data of Ref. 5, we need to allow for the anisotropy of the transition probability. This anisotropy was dealt with in Refs. 2, 5, and 18 by means of the substitution  $c \rightarrow c \langle |\chi_{ij}| \rangle_d = 0.845c$ , where  $\chi_{ij} = \sqrt{\frac{3}{2}} [\vec{d}_i \vec{d}_j - 3(\vec{n}_{ij} \vec{d}_i)(\vec{n}_{ij} \vec{d}_j)]$ ,  $\vec{d}_i$  are unit vectors along the directions of the transition dipole moments,  $\vec{n}_{ij} = \vec{r}_{ij}/r_{ij}$ , and the average  $\langle \dots \rangle_d$  is taken over the isotropic random distribution of the vectors  $\vec{d}_k$  (Refs. 1 and 18). This method leads to the substitution<sup>5</sup>  $D \rightarrow RD = 0.845^{4/3} D = 0.799D$ . An analysis of expression (15) and the leading approximation for  $D$  in the  $GAF$  theory shows, however, that the renormalization factor is  $R = \langle |\chi| \rangle^{1/6} \langle |\chi|^{5/3} \rangle = 0.899$  in these cases. When we take it into account, the value  $\kappa_3 = 0.186$  listed above becomes  $\kappa_{\text{theor}} = 0.167$ . At large values of  $\beta t$  we find  $P(\vec{k}, t) = \exp(-M(\vec{k})t)$ , where  $M(\vec{k} \rightarrow 0) = Dk^2 - \sigma k^3 + O(k^4)$  and  $\sigma = (3/(64\pi))\beta \bar{r}^3$ . This expansion was used previously in Refs. 12, 4, and 11. Gomez-Jahn *et al.*<sup>5</sup> assumed  $\sigma = 0$  and found the value  $\kappa_{\text{exp}} = 0.147(15)$ . When the correct value of  $\sigma$  is used, we find  $\kappa_{\text{exp}} = 0.168(17) = \kappa_{\text{theor}}$ .

The results presented above apparently mean that this study has yielded the first regular method for calculating the diffusion coefficient  $D$  in a multipole transport, and it has yielded a value of  $D$  which agrees with the experimental value within the experimental error and within the methodological error of the calculations.

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