

# Forward and back photoinduced electron transfer in solid solutions: a comparison of theoretical methods

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Several methods for calculating the excited-state and radical-ion probabilities in systems undergoing photoinduced electron transfer are presented and compared. These calculations are for solid solution where there are donors present at low concentration surrounded by a random distribution of acceptors at any concentration. The transfer rate depends exponentially on distance and is time independent (no solvent relaxation). This problem forms the basis for more complex situations including molecular diffusion and solvent relaxation. For each method the range of applicability and the underlying assumptions are discussed.

## 1. Introduction

Photoinduced electron transfer from a donor molecule to an acceptor molecule is responsible for an important class of chemical reactions. Following the transfer of an electron from an excited donor to an acceptor or neutral donor to an excited acceptor, the highly reactive radical ions can go on to do useful chemistry. Electron back transfer, however, quenches the ions and prevents further chemistry from occurring [1–4].

In systems of randomly distributed donors and acceptors such as redox reactions in solid or liquid solution back transfer (geminate recombination) can be very rapid [5,6]. In a system of dilute donors and concentrated acceptors, the initial electron transfer is into a random distribution of acceptors. The back transfer problem, however, is more complex. The distribution of radical-ion pair separations formed by forward transfer is not random, but, rather, determined by the details of the forward transfer distance-dependent transfer rate. This leads to a complex averaging problem. In liquid solutions, back transfer competes with diffusional separation of the radical ions and may have a non-obvious influence on chemical reaction yields [6–9]. In both solid and liquid solutions, solvent relaxation also effects the dynamics of radical-ion formation and recombination [10–13]. In chemical reactions in solution all these factors are occurring at the same time and the combined effect is quite complex. To properly model forward and back transfer it is important that we understand the assumptions and approximations in the various mathematical treatments of the transfer problem in solid solution. This provides a necessary stepping stone [5,7,10,14] to more complex considerations. It is therefore important to discuss the available formulations of this problem and to discuss their validity and usefulness.

In this Letter, we present five different treatments of the problem of low concentration donors surrounded by a random distribution of acceptors in solid solution. The first method is the standard method for a formal solution. Although this is a correct formulation for the problem of point particles it is intractable [14]. The second method is the most simple. It assumes there is only one acceptor present [14]. It is accurate only at very low concentrations. The third formulation, presented here for the first time, is based on the nearest neighbor approximation [15–17]. In this treatment, a method of statistical averaging that considers transfer only to nearest neighbors is used. This averaging procedure was originally developed by Chandrasekhar [15]. It is significantly better than the one-acceptor approximation. In a fourth formulation we present work that was

developed by Mikhelashvili et al. [18]. We will show that this theory is equivalent to a power series of the one-acceptor approximation which provides a very small gain in accuracy. The last treatment considered is an exact solution of this problem which uses a novel averaging procedure [5,14]. Since the exact solution is available, it is possible to judge the realms of applicability of other methods.

## 2. The methods

In this section we will show five different methods for calculating the radical-ion probability for a donor surrounded by a random distribution of acceptors in solid solution. The methods are "the formal solution" (FS), the one-acceptor approximation (OA), the nearest neighbor approximation (NN), the one-acceptor series approximation (OAS), and the exact result (ER).

For each case, a three-level model is used (see fig. 1). At  $t=0$ , an ensemble of dilute donors is optically excited (in fig. 1 as  $D^*A$ ). In the absence of acceptors, the probability of finding the donor still excited is given by  $\langle P_{ex}(t) \rangle = \exp(-t/\tau)$ , where  $\tau$  is the donor's excited state life time. When acceptors are present the probability decays more rapidly due to the electron transfer pathway. Electron transfer creates a ground state radical-ion pair (represented in fig. 1 as  $D^+A^-$ ). Since the thermodynamically stable state of the system is the neutral ground state of the pair (in fig. 1 as  $DA$ ), electron back transfer will occur. Electron transfer from an anionic acceptor to a neutral acceptor is not likely because there is no driving force (in fact, it is energetically uphill because of solvent relaxation around the anion) and thermodynamically the lowest energy state of the system is composed of the neutral ground state donor and neutral acceptor. Therefore only direct back transfer is included [5]. This three-level process has the following rate constants:

$$K = 1/\tau, \quad K_f(R) = \tau^{-1} \exp[(R_0 - R)/a_f], \quad K_b(R) = \tau^{-1} \exp[(R_b - R)/a_b], \quad (1)$$

where  $R$  is the donor-acceptor separation.  $R_0$ ,  $a_f$ ,  $R_b$ , and  $a_b$  are molecular parameters that characterize the distance scales of the forward and back transfer rates [5,14].  $\tau$  is the donor's excited state life time.

There are three other parameters that will appear in some of the following treatments. There is the acceptor concentration,  $C$ , the center-to-center distance at contact of the donor and the acceptor,  $R_m$ , and the diameter of the acceptor,  $d$ . The latter two parameters are used to account for the finite size of real molecules. The effect of excluded volume is important and has been discussed elsewhere [5,14,19,20].

### 2.1. The formal solution

In the formal solution we have a single donor surrounded by  $N$  acceptors. The donors and acceptors are point particles. Excluded volume is not taken into account. For the forward transfer the excited state population can be calculated exactly [16,21],

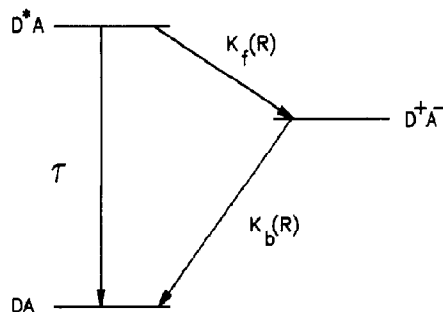


Fig. 1. The three-level system of the ground state ( $DA$ ), the excited state ( $D^*A$ ), and the radical-ion state ( $D^+A^-$ ). There are three rate processes:  $\tau$  is the excited state life time,  $K_f(R)$  is the forward electron transfer rate, and  $K_b(R)$  is the back electron transfer rate.

$$\langle P_{\text{ex}}(t) \rangle_{\text{FS}} = \exp(-t/\tau) \exp\left(-4\pi C \int_{R_m}^{\infty} \{1 - \exp[-K_f(R)t]\} R^2 dR\right). \quad (2)$$

$R_m$  is the sum of the donor and acceptor radii. For point particles  $R_m=0$ .

The radical-ion probability is much more complex. It is given by the following limit:

$$\langle P_{\text{ct}}(t) \rangle_{\text{FS}} = \lim_{N \rightarrow \infty} \left(\frac{4\pi C}{N}\right)^N \int_{R_m}^{R_v} \dots \int_{R_m}^{R_v} P_{\text{ct}}(R_1, \dots, R_N, t) R_1^2 \dots R_N^2 dR_1 \dots dR_N, \quad (3)$$

where  $R_v = (3N/4\pi C)^{1/3}$ . In practice this calculation is extremely tedious and time consuming, making it an essentially useless approach for all but the lowest concentrations. At moderate and high concentrations many acceptors are required for convergence and this leads to very high dimension integrals. Donor-acceptor excluded volume is included by using a nonzero value of  $R_m$ . Acceptor-acceptor excluded volume cannot be added easily into this formulation.

In the following treatments, the problem of high dimension integrals is avoided and some of the treatments include both types of excluded volume.

## 2.2. The one-acceptor solution

The one-acceptor solution is the first approximation to the formal solution above [14]. The difference is that there is only one acceptor; therefore there is no acceptor-acceptor excluded volume. Donor-acceptor excluded volume is included by a cutoff in the lower limit of the integral over the donor-acceptor separation. To take into account a particular concentration of acceptors the normalization factor is  $4\pi C$ . The upper limit of the integral is determined by the volume that one acceptor occupies at a concentration  $C$ . This volume is  $V=N/C$ . The expressions for the excited state and the radical-ion probabilities are

$$\langle P_{\text{ex}}(t) \rangle_{\text{OA}} = 4\pi C \exp(-t/\tau) \int_{R_m}^{(3/4\pi C)^{1/3}} \exp[-K_f(R)t] R^2 dR, \quad (4)$$

$$\langle P_{\text{ct}}(t) \rangle_{\text{OA}} = 4\pi C \int_{R_m}^{(3/4\pi C)^{1/3}} P_{\text{ct}}(R, t) R^2 dR, \quad (5)$$

where

$$P_{\text{ct}}(R, t) = \frac{K_f(R)}{K_b(R) - K_f(R) - 1/\tau} \{ \exp\{-[K_f(R) + 1/\tau]t\} - \exp[-K_b(R)t] \}.$$

This expression for the radical-ion probability only contains the effect of a single acceptor. Thus one would expect this to work only in the limit of very low concentration, where on average there is only one acceptor in a distance range for significant electron transfer probability. It is possible to improve this approximation by properly letting the upper limit of the integral go to infinity [14]. This is to allow the single particle to be located anywhere in space.

## 2.3. The nearest neighbor solution

In the one-particle solution, loss of excited state probability due to the presence of other acceptors is not included. The nearest neighbor approximation is similar to the one-particle solution except it uses a distribution function which takes into account the probability that an acceptor at a distance  $R$  is actually the nearest

neighbor [15–17]. There is only one acceptor, but it is the one closest to the donor. The nearest neighbor distribution function is [15–17]

$$w(R) = C \exp(-\frac{4}{3}\pi CR^3). \quad (6)$$

The excited state [16] and radical-ion probabilities are given by

$$\langle P_{\text{ex}}(t) \rangle_{\text{NN}} = 4\pi C \exp(-t/\tau) \int_{R_m}^{\infty} \exp[-tK_f(R)] \exp(-\frac{4}{3}\pi CR^3) R^2 dR, \quad (7)$$

$$\langle P_{\text{ct}}(t) \rangle_{\text{NN}} = 4\pi C \int_{R_m}^{\infty} \frac{K_f(R)}{K_b(R) - K_f(R) - 1/\tau} \{ \exp\{-[K_f(R) + 1/\tau]t\} - \exp[-K_b(R)t] \} \exp(-\frac{4}{3}\pi CR^3) R^2 dR. \quad (8)$$

This method has been used extensively in the analysis of trapped-electron scavenging reactions [16,17]. It neglects transfer to acceptors that are not the nearest neighbor. Thus at high concentrations where there are many acceptors near the donor we would expect this to be inaccurate. It will be shown below that this approximation is extremely good for forward transfer (excited state population) and is less accurate, but still very good, for back transfer (radical-ion population).

#### 2.4. The one-acceptor series solution

In a recent work by Mikhelashvili et al. [18] another method for calculating the radical-ion concentration was derived. For the excited state probability they used the result given by eq. (2), the exact result. The expression for the radical-ion population is

$$\langle P_{\text{ct}}(t) \rangle_{\text{OAS}} = 1 - \exp\left(-4\pi C \int_{R_m}^{\infty} \frac{K_f(R)}{K_b(R) - K_f(R) - 1/\tau} \{ \exp\{-[K_f(R) + 1/\tau]t\} - \exp[-K_b(R)t] \} R^2 dR\right). \quad (9)$$

If we examine eq. (9) (see appendix), it is a power series expansion in the one-acceptor result. It will be referred to as the one-acceptor series (OAS). Like the OA solution, it will be shown below that this formula is only good at very low concentrations. The main problem with the OAS result and the OA result is that they do not allow for more than one acceptor in the forward transfer process. Thus they miss the competition between the randomly distributed acceptors for the electron in setting up the distribution of cations for the back transfer process.

#### 2.5. The exact solution

In the exact solution [5,14], a novel averaging procedure is used to calculate the back transfer (radical-ion probability) average exactly. Donor-acceptor excluded volume and acceptor-acceptor excluded volume are included. The expression for the forward transfer (excited state population) is simply an extension of eq. (2), the exact result, and in the limit that molecular size goes to zero the equation goes to the point particle result. The excited state population is

$$\langle P_{\text{ex}}(t) \rangle_{\text{ER}} = \exp(-t/\tau) \exp\left(-\frac{4\pi}{d^3} \sum_{k=1}^{\infty} \frac{p^k}{k} \int_{R_m}^{\infty} \{1 - \exp[-K_f(R)t]\}^k R^2 dR\right), \quad (10)$$

where  $p = Cd^2$  and  $d$  is the diameter of the acceptor excluded volume. To derive this expression the donors and acceptors are first placed on a cubic lattice [14,19,20]. The spatial averages are performed and no two particles

are allowed to occupy the same lattice site. Then the continuum limit [19,20] is taken. This gives the desired result for random systems.

For the back transfer (radical-ion probability) a novel averaging procedure is used [14] to perform the averaging exactly. Instead of solving the differential equation for the radical-ion population then averaging over all configurations of the acceptors, the equation is first averaged over  $N-1$  acceptors, then solved. The solution is the pair distribution function for the radical-ion pairs that are formed upon forward electron transfer with the  $N-1$  other acceptors that do not receive the electron properly taken into account in the averaging. To get the total cation probability the pair distribution function is averaged over the final coordinate and the thermodynamic limit is taken [14]. The result is

$$\langle P_{\text{ct}}(t) \rangle_{\text{ER}} = 4\pi C \int_{R_m}^{\infty} K_f(R) \exp[-K_b(R)t] \int_0^t \exp\{-[K_f(R) - K_b(R)]t'\} \langle P_{\text{ex}}(t') \rangle_{\text{ER}} dt' R^2 dR. \quad (11)$$

Eq. (10) is used for  $\langle P_{\text{ex}}(t') \rangle$ . It takes into account both donor-acceptor and acceptor-acceptor excluded volume. For point particles,  $R_m$  is set equal to zero and eq. (2) is used for  $\langle P_{\text{ex}}(t') \rangle$ .

### 3. Discussion

In the following discussion we will compare the various formulations to the exact treatment eqs. (2) and (11) with (2). We will use high (1.0 M), medium (0.1 M), and low (0.01 M) concentrations of acceptors to find where each theory is applicable. For the purposes of comparison, we will use a set of reasonable forward and back transfer parameters. To simplify computations we will take the forward and back transfer parameters to be identical, i.e.  $K_f(R) = K_b(R)$ . The parameters used for the rates are  $\tau = 20$  ns,  $R_0 = R_b = 10.0$  Å,  $a_f = a_b = 0.5$  Å, and the excluded volumes are zero ( $R_m = d = 0$ ).

Fig. 2 shows the excited state population as a function of time for OA, NN, and ER for three different concentrations. At low concentration,  $C = 0.01$  M, all three methods are virtually the same. In this case, there is very little electron transfer and the signal is dominated by the excited state fluorescence life time. In fig. 2b the concentration has been increased to  $C = 0.1$  M (moderate concentration). At this concentration there is still no difference between ER and NN, but OA has dropped slightly. The OA has dropped because the particle that accepts the electron can be anywhere in space but the OA equation limits it to a finite volume. At the highest concentration,  $C = 1.0$  M, in fig. 2c we see that the OA result is very poor. The upper limit of integration has been greatly restricted resulting in too large probability of finding the acceptor close to the donor. The NN and ER results are slightly different. The ER result decays faster because acceptors other than the nearest neighbor can receive the electron, thus opening up other transfer pathways.

Fig. 3 shows the radical-ion state population as a function of time and concentration. In fig. 3a the concentration is  $C = 0.01$  M. The OA and OAS results are the same and lie above the NN and ER results. The OA result and the OAS results are virtually the same except for the upper limit of integration and the fact that the OAS result is a power series in the OA result. The OA and OAS results overcount the number of radical ions. Since the excited state probability was the same for all these curves then the differences between the methods at this low concentration only effects the recombination dynamics. The NN and ER results are the same.

At moderate concentration ( $C = 0.1$  M, fig. 3b) we see that all the curves are different. The OA and OAS results are above the NN and ER results and the differences are now large. At high concentration ( $C = 1.0$  M, fig. 3c) we see something different. The OA result rises and falls within 1 ns. At this high concentration the upper limit of integration is too small to catch all the possible electron transfer events and so undercounts the number of radical ions. As mentioned earlier it is possible to improve the OA result by letting the upper limit go to infinity. This is shown as a fifth curve labeled  $\text{OA}^\infty$ . The  $\text{OA}^\infty$  curve is similar to the OAS curve. Both

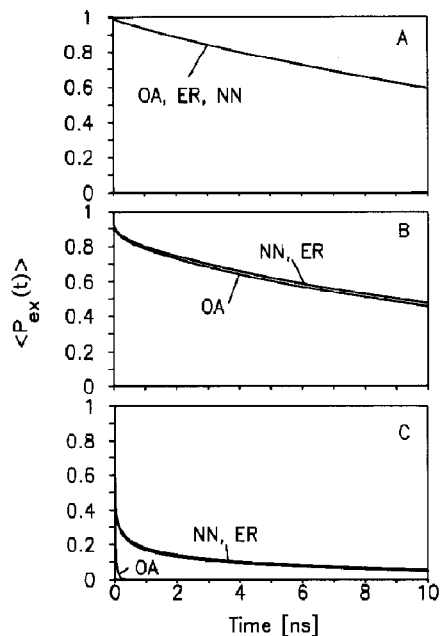


Fig. 2. The excited state population as a function of time,  $\langle P_{ex}(t) \rangle$ . The calculations were performed at three concentrations: (A) 0.01 M, (B) 0.1 M, and (C) 1.0 M. The electron transfer parameters used are  $R_0 = 10.0 \text{ \AA}$ ,  $a_f = 0.5 \text{ M}$ , and  $\tau = 20.0 \text{ ns}$ . OA is the one-acceptor approximation (eq. (4)), NN is the nearest neighbor result (eq. (7)), and ER is the exact result (eq. (2)).

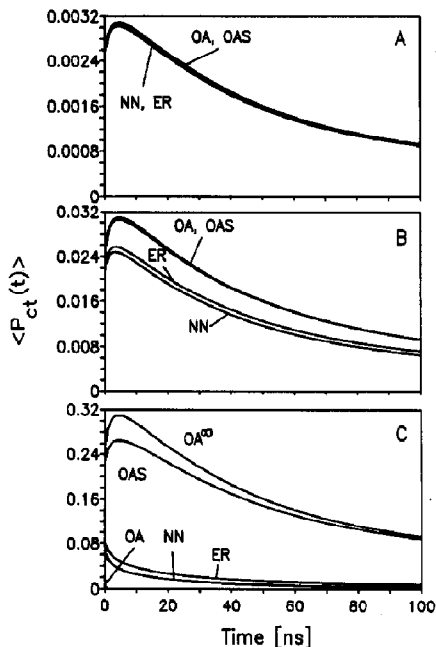


Fig. 3. The radical-ion state population as a function of time,  $\langle P_{ct}(t) \rangle$ . The calculations were performed at three concentrations: (A) 0.01 M, (B) 0.1 M, and (C) 1.0 M. The electron transfer parameters used are  $R_0 = R_b = 10.0 \text{ \AA}$ ,  $a_f = a_b = 0.5 \text{ M}$ , and  $\tau = 20.0 \text{ ns}$ . OA is the one-acceptor approximation (eq. (5)), OAS is the one-acceptor series result (eq. (9)), NN is the nearest neighbor result (eq. (8)), and ER is the exact result (eq. (11)). In C  $OA^\infty$  is the OA result with the upper limit of integration extended to infinity, see text.

of these curves are profoundly in error as can be seen by comparing them to the exact result, curve ER. On the other hand, the NN curve is a reasonable approximation to the exact result.

#### 4. Conclusion

We have shown three different methods for calculating the excited state population and four methods for calculating the radical-ion population for a system of low concentration donors surrounded by a random distribution of acceptors in solid solution. We have demonstrated that the NN result is virtually the same as the ER result, even up to high concentration, for the excited state population. The one-acceptor result is only good at low concentration for the excited state population. Only the NN result is close to the ER result for the radical-ion state population but shows much more deviation than in the excited state calculation. The OA and the OAS results are in some error even at low concentration and become highly inaccurate at higher concentration. In the calculations presented here only one set of parameters was used in all the calculations. Other sets of parameters will give radical-ion populations with similar relative accuracies for the methods discussed here. The OA and OAS methods should be avoided. However, the NN method can provide useful insights into trends and could be very helpful in initially fitting data. Comparison to the exact result gives a test for the NN method with a particular set of forward and back parameters.

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## Appendix

Here we will show that the OAS result given in eq. (9) is a power series in the OA result. The OAS result can be written in terms of the OA result where the upper limit of integration has been extended to infinity,

$$\langle P_{ct}(t) \rangle_{OAS} = 1 - \exp(-\langle P_{ct}(t) \rangle_{OA}^{\infty}), \quad (A.1)$$

where

$$\langle P_{ct}(t) \rangle_{OA}^{\infty} = 4\pi C \int_{R_m}^{\infty} \frac{K_f(R)}{K_b(R) - K_f(R) - 1/\tau} \{ \exp\{-[K_f(R) + 1/\tau]t\} - \exp[-K_b(R)t] \} R^2 dR. \quad (A.2)$$

Eq. (A.1) can be expanded into a Taylor series and has the following form in terms of the one-acceptor result:

$$\langle P_{ct}(t) \rangle_{OAS} = \sum_{n=1}^{\infty} \frac{(-1)^{n+1} (\langle P_{ct}(t) \rangle_{OA}^{\infty})^n}{n!}. \quad (A.3)$$

At low concentration, where the value of the radical-ion probability is small, the OA and the OAS results are the same. As can be seen in the series in eq. (A.3), terms higher than first order would be negligible at low concentration. At higher concentrations, the OA and OAS results are slightly different because of the addition of the higher order terms with alternating signs, but these terms do not correct for the fact that the problem is really many body in nature and so over estimates the radical-ion population.

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