



# Long range electron transfer reactions in solution: An analytically solvable model



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## ABSTRACT

We propose an analytical method for understanding the problem of long range electron transfer reaction in solution, modeled by a particle undergoing diffusive motion under the influence of large number of potentials which are involved (donor – long bridge – acceptor) in the process. The coupling between these potentials are assumed to be represented by Dirac delta functions. The diffusive motion in this paper is represented by the Smoluchowski equation. Our solution requires the knowledge of the Laplace transform of the Green's function for the motion in all the uncoupled potentials. For the case where all potentials are parabolic, we have derived a very simple expression for the Green's function of the whole process under the semi-infinite limit.

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## 1. Introduction

Understanding of electron transfer processes in condensed phase is very important in chemistry, physics, and biological sciences, for the experimentalists as well as theoreticians [1–20]. A large amount of research in this area has been dedicated in the understanding of the behavior of electron transfer reactions exhibited by donor–acceptor pairs in solutions. Long range electron transfer in condensed phase may occur over long distances (up to several tens of angstroms), plays a key role in many physical, chemical and biological processes [21]. Since the pioneering work of Zusman [22] there are a large number of studies devoted to solvent effects on outer sphere ET reactions with backward reactions however a complete picture is given by Nadler and Marcus [23] to include the effect of diffusion and reaction in both directions which is also considered by Ghosh and coworkers. There are a large number of citations in the literature in the area of electron transfer reactions, like Ghosh and coworkers [24] derived an exact analytical expression averaged forward of a reversible electron transfer reaction. In this work a reaction coordinate is undergoing diffusive motion in arbitrary potential wells of reactant and the product. Localized sink has arbitrary position and strength. The model given by them can explain the non-Marcus free energy gap dependence of the rate of electron transfer reactions. Similarly, an exact solution of the Smoluchowski equation for a Brownian particle moving in an arbitrary potential well with a sink are also provided by same authors [25] in which they

considered the case of diffusion in a harmonic potential well. In the following we propose a simple analytical method for understanding the problem of long range electron transfer reaction in solution, modeled by a particle undergoing diffusive motion under the influence of many (donor – bridge – acceptor) potentials explicitly. A molecule (donor – bridge – acceptor) immersed in a polar solvent can be put on an electronically excited potential (represents the free energy of the donor surface) by the absorption of radiation. The molecule executes a walk on that potential, which may be taken to be random as it is immersed in the polar solvent. As the molecule moves it may undergo non-radiative decay from certain regions of that potential to another potential (represents the free energy of one, among many which constitutes bridge potentials). So the problem is to calculate the probability that the molecule will still be on the electronically excited donor potential after a finite time  $t$ .

## 2. Our model

We denote the probability that the molecule would survive on the donor potential by  $P_d(x, t)$ . We also use  $P_a(x, t)$  to denote the probability that the molecule would be found in the acceptor potential and  $P_i(x, t)$  to denote the probability that the molecule would be found on the  $i$ th bridge potential. It is very usual to assume the motion on all the potentials to be one dimensional and diffusive, the relevant coordinate being denoted by  $x$ . It is also common to assume that the motion on all the potential energy surface is over damped. Thus all the probability  $P_d(x, t)$ ,  $P_i(x, t)$  and  $P_a(x, t)$  may be found at  $x$  at the time  $t$  obeys a modified Smoluchowski equation.

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$$\begin{aligned} \frac{\partial P_d(x,t)}{\partial t} &= \mathcal{L}_d P_d(x,t) - k_r P_d(x,t) + k_0 S(x) P_1(x,t) - k_0 S(x) P_d(x,t) \\ \frac{\partial P_1(x,t)}{\partial t} &= \mathcal{L}_1 P_1(x,t) - k_r P_1(x,t) + k_0 S(x) P_2(x,t) \\ &\quad + k_0 S(x) P_d(x,t) - k_0 S(x) P_1(x,t) \\ \frac{\partial P_2(x,t)}{\partial t} &= \mathcal{L}_2 P_2(x,t) - k_r P_2(x,t) + k_0 S(x) P_3(x,t) \\ &\quad + k_0 S(x) P_1(x,t) - k_0 S(x) P_2(x,t) \\ &\dots\dots\dots \\ \frac{\partial P_a(x,t)}{\partial t} &= \mathcal{L}_a P_a(x,t) - k_r P_a(x,t) + k_0 S(x) P_N(x,t) - k_0 S(x) P_a(x,t). \quad (1) \end{aligned}$$

In the above

$$\mathcal{L}_i = D \left[ \frac{\partial^2}{\partial x^2} + \beta \frac{\partial}{\partial x} \frac{dV_i(x)}{dx} \right]. \quad (2)$$

$V_i(x)$  is the potential causing the drift of the particle,  $S(x)$  is a position dependent sink function,  $k_r$  is the rate of radiative decay and  $k_0$  is the rate of electron transfer. We have taken  $k_r$  to be independent of position.  $D$  is the diffusion coefficient. Before we excite, the molecule is in the ground state, and as the solvent is at a finite temperature, its distribution over the coordinate  $x$  is random. From this it undergoes Franck–Condon excitation to the excited state potential (donor). So,  $x_0$  the initial position of the particle, on the excited state potential is random. We assume it to be given by the probability density  $P_1^0(x_0)$ .

### 3. Analytical solution

In the following we provide a general procedure for finding the exact analytical solution of Eq. (1). The Laplace transform  $\mathcal{P}_i(x,s) = \int_0^\infty P_i(x,t) e^{-st} dt$  obeys

$$\begin{aligned} [s - \mathcal{L}_d + k_r + k_0 S(x)] \mathcal{P}_d(x,s) - k_0 S(x) \mathcal{P}_1(x,s) &= P_d^0(x_0) \\ [s - \mathcal{L}_1 + k_r + k_0 S(x)] \mathcal{P}_1(x,s) - k_0 S(x) \mathcal{P}_2(x,s) - k_0 S(x) \mathcal{P}_d(x,s) &= 0, \\ [s - \mathcal{L}_2 + k_r + k_0 S(x)] \mathcal{P}_2(x,s) - k_0 S(x) \mathcal{P}_3(x,s) - k_0 S(x) \mathcal{P}_1(x,s) &= 0, \\ &\dots\dots\dots \\ [s - \mathcal{L}_a + k_r + k_0 S(x)] \mathcal{P}_a(x,s) - k_0 S(x) \mathcal{P}_N(x,s) &= 0, \quad (3) \end{aligned}$$

as  $k(r)$  is a constant, so the solution of above equation can be written as [26]

$$[s - \mathcal{L} + k_r + k_0 S(x)] G(s, s|x_0) = \delta(x - x_0) \quad (4)$$

where

$$G(x, s|x_0) = \langle x | [s - \mathcal{L} + k_r + k_0 S(x)]^{-1} | x_0 \rangle$$

with

$$G^0(x, s|x_0) = G_0(x, s|x_0) - k_0 G_0(x, s|x_0) G_0(x_s, s|x_0) [1 + k_0 G_0(x_s, s|x_0)]^{-1}. \quad (5)$$

In the above Eq.  $P_d^0(x_0) = P_d(x, 0)$  is the initial distribution at the electronically excited state (donor potential),  $P_i(x, 0) = 0$  and  $P_a(x, 0) = 0$  is the initial distribution at the acceptor potential, hence in matrix notation we can write it as

$$\begin{aligned} &\begin{pmatrix} \mathcal{P}_d(x,s) \\ \mathcal{P}_1(x,s) \\ \mathcal{P}_2(x,s) \\ \dots\dots\dots \\ \mathcal{P}_a(x,s) \end{pmatrix} \\ &= \begin{pmatrix} s - \mathcal{L}_d + k_r + k_0 S(x) & k_0 S(x) & 0 & \dots & \dots \\ k_0 S(x) & s - \mathcal{L}_1 + k_r + k_0 S(x) & k_0 S(x) & 0 & \dots \\ 0 & k_0 S(x) & s - \mathcal{L}_2 + k_r + k_0 S(x) & k_0 S(x) & \dots \\ 0 & 0 & k_0 S(x) & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots \end{pmatrix}^{-1} \\ &\begin{pmatrix} P_d^0(x_0) \\ 0 \\ 0 \\ \dots \\ 0 \end{pmatrix}, \quad (6) \end{aligned}$$

The solution of the above equation can be written as

$$\mathcal{P}_{d-a}(x, s) = \int_{-\infty}^{\infty} dx_0 G_{d-a}^0(x, s; x_0) P_d^0(x_0), \quad (7)$$

where  $G_{d-a}(x, s; x_0)$  is the corresponding Green's function. In the following we will derive an analytical expression for the Greens function for this long range electron transfer process. We start with the simplest version of the problem i.e., we are dealing with the case which involved only two potentials, as given below

$$\begin{pmatrix} \mathcal{P}_d(x,s) \\ \mathcal{P}_1(x,s) \end{pmatrix} = \begin{pmatrix} s - \mathcal{L}_d + k_r + k_0 S(x) & k_0 S(x) \\ k_0 S(x) & s - \mathcal{L}_1 + k_r + k_0 S(x) \end{pmatrix}^{-1} \begin{pmatrix} P_d^0(x) \\ 0 \end{pmatrix}, \quad (8)$$

Using the partition technique [27], solution of this equation can be written as

$$\mathcal{P}_{d-1}(x, s) = \int_{-\infty}^{\infty} dx_0 G_{d-1}^0(x, s; x_0) P_d^0(x_0), \quad (9)$$

where  $G(x, s; x_0)$  is the Green's function defined by the following equation

$$G_{d-1}^0(x, s; x_0) = \langle x | [s - \mathcal{L}_d + k_r + k_0 S(x) + k_0^2 S [s - \mathcal{L}_1 + k_r]^{-1} S]^{-1} | x_0 \rangle \quad (10)$$

The above equation is true for any general sink  $S$ . But this expressions simplify considerably if  $S$  is a Dirac delta function located at  $x_1$ . In the operator notation  $S$  can be written as  $S = |x_1\rangle\langle x_1|$ . So

$$G_{d-1}^0(x, s; x_0) = \langle x | [s - \mathcal{L}_d + k_r + k_0 S(x) + k_0^2 G_1^0(x_1, s; x_1) S]^{-1} | x_0 \rangle, \quad (11)$$

where

$$G_1^0(x, s; x_0) = \langle x | [s - \mathcal{L}_1 + k_r + k_0 S(x)]^{-1} | x_0 \rangle \quad (12)$$

and corresponds to propagation of the particle starting from  $x_0$  on the first bridge potential in the absence of any coupling. Now we use the operator identity

$$\begin{aligned} [s - \mathcal{L}_d + k_r + k_0^2 G_1^0(x_1, s; x_1) S]^{-1} &= [s - \mathcal{L}_d + k_r]^{-1} - [s - \mathcal{L}_d + k_r]^{-1} \\ &\quad \times k_0^2 G_1^0(x_1, s; x_1) S [s - \mathcal{L}_d + k_r - k_0^2 G_1^0(x_1, s; x_1) S]^{-1} \quad (13) \end{aligned}$$

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