Barrierless Electronic Relaxation in Solution: An Analytically Solvable Model

Aniruddha Chakraborty
School of Basic Sciences, Indian Institute of Technology Mandi,
Mandi, Himachal Pradesh, 175001, India

(Dated: May 11, 2014)

We propose an analytical method for understanding the problem of electronic relaxation in solution, modelled by a particle undergoing diffusive motion under the influence of two potentials. The coupling between the two potentials is assumed to be represented by a Dirac Delta function. The diffusive motion in this paper is described by the Smoluchowski equation. Our solution requires the knowledge of the Laplace transform of the Green’s function for the motion in both the uncoupled potentials. Our model is more general than all the earlier models, because we are the first one to consider the effect of ground state potential energy surface explicitly.

Relaxation of an excited electronic potential energy surface of a molecule which is in a polar solvent is an interesting problem both theoretically and experimentally [1-4]. A molecule immersed in a polar solvent can be put on an electronically excited potential energy surface by the absorption of radiation. The molecule executes a walk on that potential energy surface, 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 surface and also undergoes radiative decay from anywhere on that surface. So the problem is to calculate the probability that the molecule will still be in the electronically excited potential energy surface after a finite time $t$. We denote the probability that the molecule would survive on the electronically excited potential energy surface by $P_e(x,t)$. We also use $P_g(x,t)$ to denote the probability that the molecule would be found in the ground state potential energy surface. It is very common to assume the motion on both the potential energy surface to be one dimensional and diffusive, the relevant coordinate being denoted by $x$. It is also usual to assume that the motion on both the potential energy surface is overdamped. Thus both the probability $P_e(x,t)$ and $P_g(x,t)$ may be found at $x$ at the time $t$ obeys a modified Smoluchowski equation.

$$\frac{\partial P_e(x,t)}{\partial t} = \mathcal{L}_e P_e(x,t) - k_r P_e(x,t) - k_0 S(x) P_g(x,t)$$

(1)

$$\frac{\partial P_g(x,t)}{\partial t} = \mathcal{L}_g P_g(x,t) - k_r P_g(x,t) - k_0 S(x) P_e(x,t).$$

In the above

$$\mathcal{L}_i = A \frac{\partial^2}{\partial x^2} + \frac{\partial}{\partial x} \frac{dV_i(x)}{dx}.$$  

(2)

$V_i(x)$ is the potential causing the drift of the particle, $S(x)$ is a position dependent sink function, $k_0$ is the rate of non-radiative decay and $k_r$ is the rate of radiative decay. We have taken $k_r$ to be independent of position. $A$ is the diffusion coefficient. Our model is more general than the model proposed by Sebastian et. al., [3, 4], in the sense that our model considers the motion on the ground state potential energy surface explicitly. It is quite unlikely that the shape of the ground state potential energy surface do not play any role in the electronic relaxation process, but unfortunately this fact was not considered in any of the earlier studies [3, 11]. Before we excite, the molecule is in the ground state potential energy surface, 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 energy surface. So, $x_0$ the initial position of the particle, on the excited state potential energy surface is random. We assume it to be given by the probability density $P^0_e(x_0)$. 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

$$[s - \mathcal{L}_e + k_r] \mathcal{P}_e(x, s) + k_0 S(x) \mathcal{P}_g(x, s) = P^0_e(x_0)$$

$$[s - \mathcal{L}_g + k_r] \mathcal{P}_g(x, s) + k_0 S(x) \mathcal{P}_e(x, s) = 0,$$

(3)

where $P^0_e(x_0) = P_e(x,0)$ is the initial distribution at the electronically excited state and $P_g(x,0) = 0$ is the initial distribution at the electronically ground state.

$$\begin{pmatrix} \mathcal{P}_e(x, s) \\ \mathcal{P}_g(x, s) \end{pmatrix} = \begin{pmatrix} s - \mathcal{L}_e + k_r & k_0 S(x) \\ k_0 S(x) & s - \mathcal{L}_g + k_r \end{pmatrix}^{-1} \begin{pmatrix} P^0_e(x) \\ 0 \end{pmatrix},$$

(4)
Using the partition technique, solution of this equation can be expressed as
\[ \mathcal{P}_e(x, s) = \int_{-\infty}^{\infty} dx_0 G(x, s; x_0) P^0_e(x_0), \tag{5} \]
where \( G(x, s; x_0) \) is the Green’s function defined by
\[ G(x, s; x_0) = \exp \left( \int_{x_0}^{x} ds \left[ s - L_s(x) + k_s \right] - \int_{x_0}^{s} ds \left[ s - L_s(x) + k_s \right]^{-1} \right), \tag{6} \]
The above equation is true for any general \( S \). This expressions simplify considerably if \( S \) is a Dirac Delta function located at \( x_c \). In operator notation \( S \) may be written as \( S = | x_c \rangle \langle x_c | \). Then
\[ G(x, s; x_0) = \langle x | s - L_s(x) + k_s \rangle^{-1} | x_0 \rangle, \tag{7} \]
where
\[ G^0_g(x, s; x_0) = \langle x | s - L_s(x) + k_s \rangle^{-1} | x_0 \rangle \tag{8} \]
and corresponds to propagation of the particle starting from \( x_0 \) on the ground state potential energy surface in the absence of coupling. \( G(x, s; x_0) \) can be found at \( x, s \), and corresponds to propagation of the particle put initially at \( x_0 \), in the absence of coupling, it is actually the Laplace Transform of \( G_0(x, t; x_0) \), which is the probability that a particle starting at \( x_0 \) can be found at \( x \) at time \( t \). We now put \( x = x_c \) in the above equation and solve for \( G(x_c, s; x_0) \) to get
\[ G(x, s; x_0) = \frac{G^0_g(x, s; x_0)}{1 - k^2 G^0_g(x, s; x_0) G^0_g(x, s; x_0)}. \tag{11} \]

This when substituted back into Eq. (10) gives
\[ G(x, s; x_0) = G^0_g(x, s; x_0) + \frac{k^2 G^0_g(x, s; x_0) G^0_g(x, s; x_0) G^0_g(x, s; x_0)}{1 - k^2 G^0_g(x, s; x_0) G^0_g(x, s; x_0)}. \tag{12} \]

Using this Green’s function in Eq. (5) one can calculate \( \mathcal{P}_e(x, s) \) explicitly. Here we are interested to know the survival probability at the electronically excited state potential energy surface \( P_e(t) = \int_{-\infty}^{\infty} dx \mathcal{P}_e(x, s) \). It is possible to evaluate Laplace Transform \( \mathcal{P}_e(s) \) of \( P_e(t) \) directly. \( \mathcal{P}_e(s) \) is defined in terms of \( \mathcal{P}_e(x, s) \) by the following equation,
\[ \mathcal{P}_e(s) = \left( 1 + \left[ 1 - k^2 G^0_g(x, s; x_0) G^0_g(x, s; x_0) \right]^{-1} k^2 G^0_g(x, s; x_0) \int_{-\infty}^{\infty} dx_0 G^0_g(x, s; x_0) P^0_e(x_0) \right) / (s + k_c). \tag{13} \]

From the above equation we see that \( \mathcal{P}_e(s) \) depends on \( G^0_g(x, s; x_0) \) which is different from the results of all earlier studies \cite{1, 2}. The average and long time rate constants can be found from \( \mathcal{P}_e(s) \) \cite{3}. Thus, \( k^{-1}_I = \mathcal{P}_e(0) \) and \( k_L = -\left( \text{pole of \left[ 1 - k^2 G^0_g(x, s; x_0) G^0_g(x, s; x_0) (s + k_c) \right]^{-1} \right) \), closest to the origin, on the negative \( s \)-axis, and is independent of the initial distribution but depends on \( G^0_g(x, s; x_0) \). The expression that we have obtained for \( \mathcal{P}_e(s) \), \( k_I \) and \( k_L \) are quite general and are valid for any set of potentials.

[1] D. Ben-Amotz and C. B. Harris, J. Chem. Phys. 86, 4856 (1987).
[2] D. Ben-Amotz and C. B. Harris, J. Chem. Phys. 86, 5433 (1987).
[3] D. Ben-Amotz, R. Jeanloz and C. B. Harris, J. Chem. Phys. 86, 6119 (1987).
[4] B. Bagchi and G. R. Fleming, J. Phys. Chem. 94, 9 (1990).
[5] K. L. Sebastian, Phys. Rev. A 46, R1732 (1992).
[6] N. Chakravarti and K. L. Sebastian, Chem. Phys. Lett. 204, 496 (1993).
[7] B. Bagchi and G. R. Fleming and D. W. Oxtoby, J. Chem. Phys. 78, 7375 (1983).
[8] H. Sumi and R. A. Marcus, J. Chem. Phys. 84, 4894 (1986).
[9] B. Bagchi, J. Chem. Phys. 87, 5393 (1987).
[10] G. Oster and N. Nishijima, J. Am. Chem. Soc. 78, 1581 (1956).
[11] K. Schulten, Z. Schulten and A. Szabo, Physica A 100, 599 (1980).
[12] P. Lowdin, J. Math. Phys. 3, 969 (1962).