RAPID COMMUNICATIONS

PHYSICAL REVIEW A VOLUME 46, NUMBER 4 15 AUGUST 1992

Theory of electronic relaxation in solution: Exact solution for a δ-function sink in a parabolic potential

K. L. Sebastian

Department of Applied Chemistry, Cochin University of Science and Technology, Cochin 682 022, India

(Received 12 March 1992)

We give a general method for finding the exact solution for the problem of a particle undergoing diffusive motion in a potential in the presence of a δ-function sink of arbitrary position and strength. The solution requires knowledge of the Laplace transform of the Green's function for the motion in the absence of the sink. We find the exact solution for the case of the parabolic potential. This has long been an unsolved problem and is of considerable importance as a model for nonradiative electronic relaxation of a molecule in solution.

PACS number(s): 05.40.+j, 34.20.−b, 82.40.−g, 82.50.−m

The relaxation of an excited electronic state in solution has attracted considerable attention (see the recent excellent reviews by Bagchi and Fleming [1] and Lippert *et al.* [2]). A molecule in solution is put on an excited-state potential energy surface (PES) by absorption of light. It moves on the PES and if it reaches certain regions of the PES it may undergo nonradiative decay. It can also decay radiatively from anywhere on the surface. The problem is to calculate the survival probability, $P_e(t)$ that the molecule will still be found on the excited PES at time t.

Most currently available theoretical models assume motion on the excited PES to be one dimensional and diffusive, the relevant coordinate being denoted by x. In the discussion below, we shall refer to x as the position of a particle and to the deexcitation of the molecule as the decay of the particle. The probability $P(x,t)$, that the particle may be found at x at the time t obeys a modified Smoluchowski equation [3–5]

$$\frac{\partial P(x,t)}{\partial t} = \mathcal{L}P(x,t) - k_0 S(x) P(x,t) - k_r P(x,t) . \quad (1)$$

We have adopted the notation of Ref. [1]. In the above,

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

$V(x)$ is a potential causing the drift of the particle, $S(x)$ is a position-dependent sink function, taken to be normalized (for convenience), k_0 is the rate of nonradiative decay, and k_r is the rate of radiative decay. Initially, the particle's position is taken to have a probability distribution $P_0(x)$. Solutions to Eq. (1) have been obtained for the following cases.

(1) The instantaneous extinction models (see Bagchi [5]). This includes the Oster-Nishijima model [6], in which the particle is assumed to decay as soon as it goes out of the region $0 < x < a$, or a variant of this, referred to as the staircase model [6], in which the particle is reflected at $x=0$ and absorbed at $x=a$. These models put $V(x)=0$.

(2) The pinhole sink model. Here $V(x)$ is taken to be parabolic, which is much more reasonable than a flat potential and the sink is taken to be a δ function of infinite strength, located at the origin [7]. That is, $V(x)=Bx^2/2$, $S(x)=\delta(x)$, and $k_0 \to \infty$. However, a solution in the case where the δ function is located at x_s and its strength is finite [$S(x)=\delta(x-x_s)$ and $k_0 < \infty$] has been obtained numerically [6]. The numerical method was found to fail in the region of large k_0.

In the following, we give a general procedure for finding the exact solution of the problem with a δ-function sink. Solutions have been obtained for several different problems by this method and shall be reported separately [8]. The Laplace transform $\mathcal{P}(x,s)=\int_0^\infty P(x,t)e^{-st}dt$ obeys

$$[s - \mathcal{L} + k_0 S(x) + k_R]\mathcal{P}(x,s) = P_0(x) . \quad (3)$$

$P_0(x)=P(x,0)$ is the initial distribution. The solution of this equation may be written as

$$\mathcal{P}(x,s) = \int_{-\infty}^{\infty} dx_0 \mathcal{G}(x,s+k_r|x_0)P_0(x_0) , \quad (4)$$

$\mathcal{G}(x,s|x_0)$ is the Green's function, obeying

$$[s - \mathcal{L} + k_0 S(x)]\mathcal{G}(x,s|x_0) = \delta(x-x_0) . \quad (5)$$

$\mathcal{G}(x,s|x_0)$ describes motion in the case where there is no radiative decay. Using the operator notations of quantum mechanics, we write

$$\mathcal{G}(x,s|x_0) = \langle x|[s - \mathcal{L} + k_0 S]^{-1}|x_0\rangle . \quad (6)$$

Now we use the operator identity

$$[s - \mathcal{L} + k_0 S]^{-1} = [s-\mathcal{L}]^{-1} - [s-\mathcal{L}]^{-1} k_0 S [s - \mathcal{L} + k_0 S]^{-1}$$

and arrive at the Lippman-Schwinger-type equation

$$\mathcal{G}(x,s|x_0) = \mathcal{G}_0(x,s|x_0) - k_0 \int_{-\infty}^{\infty} dy\, \mathcal{G}_0(x,s|y)S(y)\mathcal{G}(y,s|x_0) . \quad (7)$$

$\mathcal{G}_0(x,s|x_0)=\langle x|[s-\mathcal{L}]^{-1}|x_0\rangle$ corresponds to propagation of the particle placed initially at x_0, in the absence of any sink. Note that it is the Laplace transform of $G_0(x,t|x_0)$, which is the probability that a particle starting at x_0 may be found at x at time t, given that there is no decay. Obviously, $\int_{-\infty}^{\infty} dx\, G_0(x,t|x_0)=1$, so that $\int_{-\infty}^{\infty} dx\, \mathcal{G}_0(x,s|x_0)=1/s$.

If $S(y)=\delta(y-y_s)$, then one can solve the Eq. (7) to obtain

$$\mathcal{G}(x,s|x_0)=\mathcal{G}_0(x,s|x_0)-k_0\mathcal{G}_0(x,s|x_s)\mathcal{G}_0(x_s,s|x_0)[1+k_0\mathcal{G}_0(x_s,s|x_s)]^{-1}. \tag{8}$$

Using the above equation in (4) gives us $\mathcal{P}(x,s)$ explicitly. Our interest is in the survival probability, $P_e(t)=\int_{-\infty}^{\infty}dx\,P(x,t)$ whose Laplace transform, $\mathcal{P}_e(s)$, is given by $\mathcal{P}_e(s)=\int_{-\infty}^{\infty}dx\,\mathcal{P}(x,s)$. From equations (4) and (8), we get

$$\mathcal{P}_e(s)=\frac{1}{s+k_r}\left[1-[1+k_0\mathcal{G}_0(x_1,s+k_r|x_1)]^{-1}k_0\int_{-\infty}^{\infty}dx_0\,\mathcal{G}_0(x_1,s+k_r|x_0)P_0(x_0)\right]. \tag{9}$$

An average- and a long-time rate constant may be used to characterize $P_e(t)$ [1]. They are defined by $k_I^{-1}=\int_0^{\infty}dt\,P_e(t)$ and $k_L=-\lim_{t\to\infty}(d/dt)\ln P_e(t)$. Clearly, $k_I^{-1}=\mathcal{P}_e(0)$ and k_L is the negative of the pole of $\mathcal{P}_e(s)$, closest to the origin. From Eq. (9),

$$k_I^{-1}=\frac{1}{k_r}\left[1-k_0[1+k_0\mathcal{G}_0(x_s,k_r|x_s)]^{-1}\int_{-\infty}^{\infty}dx_0\,\mathcal{G}_0(x_s,k_r|x_0)P_0(x_0)\right]. \tag{10}$$

Obviously, k_I is dependent on the initial probability distribution $P_0(x)$. On the other hand, k_L is the negative of the pole of $([1+k_0\mathcal{G}_0(x_s,s+k_r|x_s)][s+k_r])^{-1}$, closest to the origin, on the negative s axis, and is independent of the initial distribution.

In the following, we give results for the parabolic potential, where we take $V(x)=Bx^2/2$. In this case, one can solve the equation $[s-\mathcal{L}]\mathcal{G}_0(x,s|x_0)=\delta(x-x_0)$ using standard techniques for determination of Green's functions for ordinary differential equations [9] to obtain

$$\mathcal{G}_0(x,s|x_0)=F(z,s|z_0)/s\,, \tag{11}$$

with

$$F(z,s|z_0)=D_\nu(-z_<)D_\nu(z_>)\exp[(z_0^2-z^2)/4]\times\Gamma(1-\nu)[B/(2\pi A)]^{1/2}. \tag{12}$$

In the above, we have introduced a new variable z related to x by $z=x(A/B)^{1/2}$, $z_j=x_j(A/B)^{1/2}$ for any subscript j. $\nu=-s/B$ and Γ is the gamma function. $z_<=\min(z,z_0)$ and $z_>=\max(z,z_0)$. D_ν are parabolic cylinder functions. To get a qualitative idea of the behavior of the rate constants, we imagine the initial distribution P_0 to be sharply peaked at x_0, and to be well represented by $\delta(x-x_0)$. Then, we obtain

$$k_I^{-1}=k_r^{-1}\left[1-\frac{k_0F(z_s,k_r|z_0)}{k_r+k_0F(z_s,k_r|z_s)}\right]. \tag{13}$$

Further,

$$k_L=-[\text{value of } s \text{ for which } s+k_0F(z_s,s|z_s)=0]+k_r\,. \tag{14}$$

We note that k_I is dependent on the initial position x_0 (i.e., z_0) and k_r in a rather complex fashion. On the other hand, k_L is independent of x_0 and depends on k_r linearly. In the following, we let $k_r\to 0$, in which limit equations (13) and (14) simplify. By analyzing this limit, we arrive at conclusions, which we expect to be valid even when k_r is finite. Using the properties of $D_\nu(z)$ [10], we find that as $k_r\to 0$, $F(z_s,k_r|z_0)$ and $F(z_s,k_r|z_s)\to\exp(-z_s^2/2)[B/(2\pi A)]^{1/2}$ so that

$$k_0F(z_s,k_r|z_0)/[k_r+k_0F(z_s,k_r|z_s)]\to 1\,.$$

Hence

$$k_I^{-1}=-\left[\frac{\partial}{\partial k_r}\left(\frac{k_0F(z_s,k_r|z_0)}{k_r+k_0F(z_s,k_r|z_s)}\right)\right]_{k_r=0}. \tag{15}$$

We take, without loss of generality, $z_0<z_s$, so that the particle is initially placed to the left of the sink. Then

$$k_I^{-1}=\exp(z_s^2/2)/\{k_0[B/(2\pi A)]^{1/2}\}+\left[\frac{\partial}{\partial k_r}\left(\frac{\exp[(z_0^2-z_s^2)/4]D_\nu(-z_0)}{D_\nu(-z_s)}\right)\right]_{\nu=0}.$$

After somewhat lengthy algebra, we obtain

$$k_I^{-1}=\exp(z_s^2/2)/\{k_0[B/(2\pi A)]^{1/2}\}+\left[\int_{z_0}^{z_s}dz\exp(z^2/2)dz[1+\mathrm{erf}(z/\sqrt{2})]\right](\pi/2)^{1/2}/B. \tag{16}$$

In the limit of the pinhole sink, i.e., $k_0\to\infty$, this reduces to the expression of Poornimadevi and Bagchi [11], obtained by calculating the mean first passage time.

As in Ref. [1], the viscosity and temperature dependence of the rate constants k_I and k_L may be obtained by making the identifications $A=kT/\zeta$ and $B=\mu\omega^2/\zeta$, with ζ being proportional to the viscosity η. Note that A/B is independent of the viscosity. In the low viscosity or small k_0 limit, the dimensionless rate constant $\bar{k}_0=k_0/(2\pi AB)^{1/2}\ll 1$, only the first term on the right-hand side (RHS) of (16) is significant. k_I is then independent of η. If the sink is not at the origin, ($z_s\neq 0$) the rate exhibits Arrhenius-type activation. But if $z_s\simeq 0$, k_I would decrease with temperature, leading to an apparent negative activation energy. If the viscosity is high or k_0 is large, $\bar{k}_0\gg 1$, and k_I shows inverse dependence on η. Further, in this limit the k_I is determined by the rate of arrival of the particle at the sink position, which would increase with temperature. Therefore k_I increases with temperature.

The long-term rate constant k_L is determined by the value of s, which satisfy $s+k_0F(z_s,s|z_s)=0$. We write this equation as an equation for $\nu(=-s/B)$,

$$\nu/\bar{k}_0=D_\nu(-z_s)D_\nu(z_s)\Gamma(1-\nu)\,. \tag{17}$$

If $\nu=n$, where $n=0,1,2,\ldots$, then $D_\nu(z)=2^{-(n/2)}$

$\times\exp(-z^2/4)H_n(z/\sqrt{2})$, H_n being Hermite polynomials. $\Gamma(1-\nu)$ has simple poles at $\nu=1,2,\ldots$. A graphical analysis using the above information shows that there is one value of $\nu\in[n,n+1]$ which satisfies Eq. (17). Our interest is in $\nu\in[0,1]$, as $k_L=B\nu$. If $\bar{k}_0\ll 1$, or $z_s\gg 1$ then $\nu\ll 1$ and one gets $\nu\simeq\bar{k}_0 D_0(-z_s)D_0(z_s)$ and hence

$$k_L=\exp(-z_s^2/2)k_0[B/(2\pi A)]^{1/2}. \tag{18}$$

In this limit, the rate constant, k_L exhibits Arrhenius activation and is independent of η. If $\bar{k}_0\gg 1$, ν is determined by $D_\nu(-z_s)\,D_\nu(z_s)=0$. If $|\nu|<1$, $D_\nu(z)=0$ only for $z<0$, and hence we write this as $D_\nu(-|z_s|)=0$. If $\bar{k}_0=0$ and $z_s=0$, one gets $k_L=B$, the result for pinhole sink at origin [3,5]. However, for any other value of $\bar{k}_0$ and z_s, one has a solution of (17) for $\nu<1$. From the above analysis, one finds that both k_I and k_L are independent of η if $\bar{k}_0\ll 1$ and proportional to η^{-1} if $\bar{k}_0\gg 1$ as concluded by earlier authors [1,12]. At intermediate η, one expects fractional dependence on η.

Our Eq. (8) is quite general and we have used it to solve several related problems, involving δ-function sinks, for which $\mathcal{G}_0(x,s|x_0)$ is known. The same procedure is also applicable to the case where S is a nonlocal operator, and may be represented by $S\equiv|f\rangle k_0\langle g|$, where f and g are arbitrary acceptable functions. Choosing both of them to be Gaussian should be an improvement over the δ-function sink model. S may even be a linear combination of such operators. Results for these [8] and detailed numerical results for the parabolic potential shall be presented later [13].

This work was supported by the Department of Science and Technology, Government of India.

[1] B. Bagchi and G. R. Fleming, J. Phys. Chem. **94**, 9 (1990).

[2] E. Lippert, W. Rettig, V. Bonačič-Koutecky, F. Heisel, and J. A. Miehé, Adv. Chem. Phys. **68**, 1 (1987).

[3] B. Bagchi, G. R. Fleming, and D. W. Oxtoby, J. Chem. Phys. **78**, 7375 (1983).

[4] H. Sumi and R. A. Marcus, J. Chem. Phys. **84**, 4894 (1986).

[5] B. Bagchi, J. Chem. Phys. **87**, 5393 (1987).

[6] G. Oster and N. Nishijima, J. Am. Chem. Soc. **78**, 1581 (1956).

[7] K. Schulten, Z. Schulten, and A. Szabo, Physica A **100**, 599 (1980).

[8] N. Chakravarti and K. L. Sebastian (unpublished).

[9] R. Courant and D. Hilbert, *Methods of Mathematical Physics* (Wiley Eastern, New Delhi, 1975), Vol. 1, p. 351.

[10] *Higher Transcendental Functions*, edited by A. Erdélyi (McGraw-Hill, New York, 1953), Vol. II, p. 115.

[11] C. S. Poornimadevi and B. Bagchi, Chem. Phys. Lett. **149**, 411 (1988).

[12] B. Bachi, Chem. Phys. Lett. **138**, 315 (1987).

[13] K. L. Sebastian (unpublished).